Mineralogy

A Reference Guide

a Wikipedia Book

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A Reference Guide

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0.1 Mineral

For other uses, see Mineral (disambiguation).

A **mineral** is a naturally occurring substance that is solid and inorganic representable by a chemical formula, usually abiogenic, and has an ordered atomic structure. It is different from a rock, which can be an aggregate of minerals or non-minerals and does not have a specific chemical composition. The exact definition of a mineral is under debate, especially with respect to the requirement a valid species be abiogenic, and to a lesser extent with regard to it having an ordered atomic structure. The study of minerals is called mineralogy.

Amethyst, a variety of quartz

There are over 4,900 known mineral species; over 4,660 of these have been approved by the International Mineralogical Association (IMA). The silicate minerals compose over 90% of the Earth's crust. The diversity and abundance of mineral species is controlled by the Earth's chemistry. Silicon and oxygen constitute approximately 75% of the Earth's crust, which translates directly into the predominance of silicate minerals. Minerals are distinguished by various chemical and physical properties. Differences in chemical composition and crystal structure distinguish various species, and these properties in turn are influenced by the mineral's geological environment of formation. Changes in the temperature, pressure, and bulk composition of a rock mass cause changes in its mineralogy; however, a rock can maintain its bulk composition, but as long as temperature and pressure change, its mineralogy can change as well.

Minerals can be described by various physical properties which relate to their chemical structure and composition. Common distinguishing characteristics include crystal structure and habit, hardness, lustre, diaphaneity, colour, streak, tenacity, cleavage, fracture, parting, and specific gravity. More specific tests for minerals include reaction to acid, magnetism, taste or smell, and radioactivity.

Minerals are classified by key chemical constituents; the two dominant systems are the Dana classification and the Strunz classification. The silicate class of minerals is subdivided into six subclasses by the degree of polymerization in the chemical structure. All silicate minerals have a base unit of a $[SiO_4]^{4-}$ silica tetrahedra—that is, a silicon cation coordinated by four oxygen anions, which gives the shape of a tetrahedron. These tetrahedra can be polymerized to give the subclasses: orthosilicates (no polymerization, thus single tetrahedra), disilicates (two tetrahedra bonded together), cyclosilicates (rings of tetrahedra), inosilicates (chains of tetrahedra), phyllosilicates (sheets of tetrahedra), and tectosilicates (three-dimensional network of tetrahedra). Other important mineral groups include the native elements, sulfides, oxides, halides, carbonates, sulfates, and phosphates.

0.1.1 Definition

Basic definition

The general definition of a mineral encompasses the following criteria:[1]

1. Naturally occurring
2. Stable at room temperature
3. Represented by a chemical formula
4. Usually abiogenic (not resulting from the activity of living organisms)
5. Ordered atomic arrangement

The first three general characteristics are less debated than the last two.[1] The first criterion means that a mineral has to form by a natural process, which excludes anthropogenic compounds. Stability at room temperature, in the simplest sense, is synonymous to the mineral being solid. More specifically, a compound has to be stable or metastable at 25 °C. Classical examples of exceptions to this rule include native mercury, which crystallizes at −39 °C, and water ice, which is solid only below 0 °C; as these two minerals were described prior to 1959, they were grandfathered by the International Mineralogical Association (IMA).[2][3] Modern advances have included extensive study of liquid crystals, which also extensively involve mineralogy. Minerals are chemical compounds, and as such they can be described by fixed or a variable formula. Many mineral groups and species are composed of a solid solution; pure substances are not usually found because of contamination or chemical substitution. For example, the olivine group is described by the variable formula (Mg, Fe)$_2$SiO$_4$, which is a solid solution of two end-member species, magnesium-rich forsterite and iron-rich fayalite, which are described by a fixed chemical formula. Mineral species themselves could have a variable compositions, such as the sulfide mackinawite, (Fe, Ni)$_9$S$_8$, which is mostly a ferrous sulfide, but has a very significant nickel impurity that is reflected in its formula.[1][4]

The requirement of a valid mineral species to be abiogenic has also been described as similar to have to be inorganic; however, this criterion is imprecise and organic compounds have been assigned a separate classification branch. Finally, the requirement of an ordered atomic arrangement is usually synonymous to being crystalline; however, crystals are periodic in addition to being ordered, so the broader criterion is used instead.[1] The presence of an ordered atomic arrangement translates to a variety of macroscopic physical properties, such as crystal form, hardness, and cleavage.[5] There have been several recent proposals to amend the definition to consider biogenic or amorphous substances as minerals. The formal definition of a mineral approved by the IMA in 1995:

> “A mineral is an element or chemical compound that is normally crystalline and that has been formed as a result of geological processes.”[6]

In addition, biogenic substances were explicitly excluded:

> “Biogenic substances are chemical compounds produced entirely by biological processes without a geological component (e.g., urinary calculi, oxalate crystals in plant tissues, shells of marine molluscs, etc.) and are not regarded as minerals. However, if geological processes were involved in the genesis of the compound, then the product can be accepted as a mineral.”[6]

Recent advances

Mineral classification schemes and their definitions are evolving to match recent advances in mineral science. Recent changes have included the addition of an organic class, in both the new Dana and the Strunz classification schemes.[7][8] The organic class includes a very rare group of minerals with hydrocarbons. The IMA Commission on New Minerals and Mineral Names adopted in 2009 a hierarchical scheme for the naming and classification of mineral groups and group names[9] and established seven commissions and four working groups to review and classify minerals into an official listing of their published names.[10] According to these new rules, “mineral species can be grouped in a number of different ways, on the basis of chemistry, crystal structure, occurrence, association, genetic history, or resource, for example, depending on the purpose to be served by the classification.”[9]

The Nickel (1995) exclusion of biogenic substances was not universally adhered to. For example, Lowenstam (1981) stated that “organisms are capable of forming a diverse array of minerals, some of which cannot be formed inorganically in the biosphere.”[11] The distinction is a matter of classification and less to do with the constituents of the minerals themselves. Skinner (2005) views all solids as potential minerals and includes biominerals in the mineral kingdom, which are those that are created by the metabolic activities of organisms. Skinner expanded the previous definition of a mineral to classify “element or compound, amorphous or crystalline, formed through *biogeochemical* processes,” as a mineral.[12]

Recent advances in high-resolution genetic and x-ray absorption spectroscopy is opening new revelations on the biogeochemical relations between microorganisms and minerals that may make Nickel’s (1995)[6] biogenic mineral exclusion obsolete and Skinner’s (2005) biogenic mineral inclusion a necessity.[12] For example, the IMA commissioned 'Environmental Mineralogy and Geochemistry Working Group'[13] deals with minerals in the hydrosphere, atmosphere, and biosphere. Mineral forming microorganisms inhabit the areas that this working group deals with. These organisms exist on nearly every rock, soil, and particle surface spanning the globe reaching depths at 1600 metres below the sea floor (possibly further) and 70 kilometres into the stratosphere (possibly entering the mesosphere).[14][15][16] Biologists and geologists have started to research and appreciate the magnitude of mineral geoengineering that these creatures are capable of. Bacteria have contributed to the formation of minerals for billions of years and critically define the biogeochemical cycles on this planet. Microorganisms can precipitate metals from solution contributing to the formation of ore deposits in addition to their ability to catalyze mineral dissolution, to respire, precipitate, and form minerals.[17][18][19]

Prior to the International Mineralogical Association’s listing, over 60 biominerals had been discovered, named, and published.[20] These minerals (a sub-set tabulated in Lowenstam (1981)[11]) are considered minerals proper according to the Skinner (2005) definition.[12] These biominerals are not listed in the International Mineral Association official list of mineral names,[21] however, many of these biomineral representatives are distributed amongst the 78 mineral classes listed in the Dana classification scheme.[12] Another rare class of minerals (primarily biological in origin) include the mineral liquid crystals that are crystalline and liquid at the same time. To date over 80,000 liquid crystalline compounds have been identified.[22][23]

> Concerning the use of the term “mineral” to name this family of liquid crystals, one can

> argue that the term inorganic would be more appropriate. However, inorganic liquid crystals have long been used for organometallic liquid crystals. Therefore, in order to avoid any confusion between these fairly chemically different families, and taking into account that a large number of these liquid crystals occur naturally in nature, we think that the use of the old fashioned but adequate "mineral" adjective taken sensus largo is more specific that an alternative such as "purely inorganic", to name this subclass of the inorganic liquid crystals family.[23]

The Skinner (2005) definition[12] of a mineral takes this matter into account by stating that a mineral can be crystalline or amorphous. Liquid mineral crystals are amorphous. Biominerals and liquid mineral crystals, however, are not the primary form of minerals, most are geological in origin,[24] but these groups do help to identify at the margins of what constitutes a mineral proper. The formal Nickel (1995) definition explicitly mentioned crystalline nature as a key to defining a substance as a mineral. A 2011 article defined icosahedrite, an aluminium-iron-copper alloy as mineral; named for its unique natural icosahedral symmetry, it is also a quasicrystal. Unlike a true crystal, quasicrystals are ordered but not periodic.[25][26]

Rocks, ores, and gems

Minerals are not equivalent to rocks. Whereas a mineral is a naturally occurring usually solid substance, stable at room temperature, representable by a chemical formula, usually abiogenic, and has an ordered atomic structure, a rock is either an aggregate of one or more minerals, or not composed of minerals at all.[27] Rocks like limestone or quartzite are composed primarily of one mineral—calcite or aragonite in the case of limestone, and quartz in the latter case.[28][29] Other rocks can be defined by relative abundances of key (essential) minerals; a granite is defined by proportions of quartz, alkali feldspar, and plagioclase feldspar.[30] The other minerals in the rock are termed accessory, and do not greatly affect the bulk composition of the rock. Rocks can also be composed entirely of non-mineral material; coal is a sedimentary rock composed primarily of organically derived carbon.[27][31]

In rocks, some mineral species and groups are much more abundant than others; these are termed the rock-forming minerals. The major examples of these are quartz, the feldspars, the micas, the amphiboles, the pyroxenes, the olivines, and calcite; except the last one, all of the minerals are silicates.[32] Overall, around 150 minerals are considered particularly important, whether in terms of their abundance or aesthetic value in terms of collecting.[33]

Schist is a metamorphic rock characterized by an abundance of platy minerals. In this example, the rock has prominent sillimanite porphyroblasts as large as 3 cm (1.2 in).

Commercially valuable minerals and rocks are referred to as industrial minerals. For example, muscovite, a white mica, can be used for windows (sometimes referred to as isinglass), as a filler, or as an insulator.[34] Ores are minerals that have a high concentration of a certain element, typically a metal. Examples are cinnabar (HgS), an ore of mercury, sphalerite (ZnS), an ore of zinc, or cassiterite (SnO_2), an ore of tin. Gems are minerals with an ornamental value, and are distinguished from non-gems by their beauty, durability, and usually, rarity. There are about 20 mineral species that qualify as gem minerals, which constitute about 35 of the most common gemstones. Gem minerals are often present in several varieties, and so one mineral can account for several different gemstones; for example, ruby and sapphire are both corundum, Al_2O_3.[35]

Nomenclature and classification

In general, a mineral is defined as naturally occurring solid, that is stable at room temperature, representable by a chemical formula, usually abiogenic, and has an ordered atomic structure. However, a mineral can be also narrowed down in terms of a mineral group, series, species, or variety, in order from most broad to least broad. The basic level of definition is that of mineral species, which is distinguished from other species by specific and unique chemical and physical properties. For example, quartz is defined by its formula, SiO_2, and a specific crystalline structure that distinguishes it from other minerals with the same chemical formula (termed polymorphs). When there exists a range of composition between two minerals species, a mineral series is defined. For example, the biotite series is represented by variable amounts of the endmembers phlogopite, siderophyllite, annite, and eastonite. In contrast, a mineral group is a grouping of mineral species with some common chemical properties that share a crystal structure. The pyroxene group has a common formula of $XY(Si,Al)_2O_6$, where X and Y are both cations, with X typically bigger than Y; the pyroxenes are single-chain silicates that crystallize in either the orthorhombic or monoclinic crystal systems. Finally, a mineral variety is a specific type of mineral species that differs by some physical characteristic, such as colour or crystal habit. An example is amethyst, which is a purple variety of quartz.[36]

Two common classifications are used for minerals; both the Dana and Strunz classifications rely on the composition of the mineral, specifically with regards to important chemical groups, and its structure. The Dana *System of Mineralogy* was first published in 1837 by James Dwight Dana, a leading geologist of his time; it is in its eighth edition (1997 ed.). The Dana classification, assigns a four-part number to a mineral species. First is its class, based on important compositional groups; next, the type gives the ratio of cations to anions in the mineral; finally, the last two numbers group minerals by structural similarity with a given type or class. The less commonly used Strunz classification, named for German mineralogist Karl Hugo Strunz, is based on the Dana system, but combines both chemical and structural criteria, the latter with regards to distribution of chemical bonds.[37]

There are over 4,660 approved mineral species.[38] They are most commonly named after a person (45%), followed by discovery location (23%); names based on chemical composition (14%) and physical properties (8%) are the two other major groups of mineral name etymologies.[36][39] The common suffix *-ite* of mineral names descends from the ancient Greek suffix -ίτης (-ites), meaning “connected with or belonging to”.[40]

0.1.2 Mineral chemistry

The abundance and diversity of minerals is controlled directly by their chemistry, in turn dependent on elemental abundances in the Earth. The majority of minerals observed are derived from the Earth’s crust. Eight elements account for most of the key components of minerals, due to their abundance in the crust. These eight elements, summing to over 98% of the crust by weight, are, in order of decreasing abundance: oxygen, silicon, aluminium, iron, magnesium, calcium, sodium and potassium. Oxygen and silicon are by far the two most important — oxygen composes 46.6% of the crust by weight, and silicon accounts for 27.7%.[41]

Hübnerite, the manganese-rich end-member of the wolframite series, with minor quartz in the background

The minerals that form are directly controlled by the bulk chemistry of the parent body. For example, a magma rich in iron and magnesium will form mafic minerals, such as olivine and the pyroxenes; in contrast, a more silica-rich magma will crystallize to form minerals than incorporate more SiO_2, such as the feldspars and quartz. In a limestone, calcite or aragonite (both $CaCO_3$) form because the rock is rich in calcium and carbonate. A corollary is that a mineral will not be found in a rock whose bulk chemistry does not resemble the bulk chemistry of a given mineral with the exception of trace minerals. For example, kyanite, Al_2SiO_5 forms from the metamorphism of aluminium-rich shales; it would not likely occur in aluminium-poor rock, such quartzite.

The chemical composition may vary between end member species of a mineral series. For example, the plagioclase feldspars comprise a continuous series from sodium-rich end member albite ($NaAlSi_3O_8$) to calcium-rich anorthite ($CaAl_2Si_2O_8$) with four recognized intermediate varieties between them (given in order from sodium- to calcium-rich): oligoclase, andesine, labradorite, and bytownite.[42] Other examples of series include the olivine series of magnesium-rich forsterite and iron-rich fayalite, and the wolframite series of manganese-rich hübnerite and iron-rich ferberite.

Chemical substitution and coordination polyhedra explain this common feature of minerals. In nature, minerals are not pure substances, and are contaminated by whatever other elements are present in the given chemical system. As a result, it is possible for one element to be substituted for another.[43] Chemical substitution will occur between ions of a similar size and charge; for example, K^+ will not substitute for Si^{4+} because of chemical and structural incompatibilities caused by a big difference in size and charge. A common example of chemical substitution is that of Si^{4+} by Al^{3+}, which are close in charge, size, and abundance in the crust. In the example of plagioclase, there are three cases of substitution. Feldspars are all framework silicates, which have a silicon-oxygen ratio of 2:1, and the space for other elements is given by the substitution of Si^{4+} by Al^{3+} to give a base unit of $[AlSi_3O_8]^-$; without the substitution, the formula would be charge-balanced as SiO_2, giving quartz.[44] The significance of this structural property will be explained further by coordination polyhedra. The second substitution occurs between Na^+ and Ca^{2+}; however, the difference in charge has to accounted for by making a second substitution of Si^{4+} by Al^{3+}.[45]

Coordination polyhedra are geometric representation of how a cation is surrounded by an anion. In mineralogy, due its abundance in the crust, coordination polyhedra are usually considered in terms of oxygen. The base unit of silicate minerals is the silica tetrahedron — one Si^{4+} surrounded by four O^{2-}. An alternate way of describing the coordination of the silicate is by a number: in the case of the silica tetrahedron, the silicon is said to have a coordination number of 4. Various cations have a specific range of possible coordination numbers; for silicon, it is almost always 4, except for very high-pressure minerals where compound is compressed such that silicon is in six-fold (octahedral) coordination by oxygen. Bigger cations have a bigger coordination number because of the increase in relative size as compared to oxygen (the last orbital subshell of heavier atoms is different too). Changes in coordination numbers between leads to physical and mineralogical differences; for example, at high pressure such as in the mantle, many minerals, especially silicates such as olivine and garnet will change to a perovskite structure, where silicon is in octahedral coordination. Another example are the aluminosilicates kyanite, andalusite, and sillimanite (polymorphs, as they share the formula Al_2SiO_5), which differ by the coordination number of the Al^{3+}; these minerals transition from one another as a response to changes in pressure and temperature.[41] In the case of silicate materials, the substitution of Si^{4+} by Al^{3+} allows for a variety of minerals because of the need to balance charges.[46]

Changes in temperature and pressure, and composition alter the mineralogy of a rock sample. Changes in composition can be caused by processes such as weathering or metasomatism (hydrothermal alteration). Changes in temperature and pressure occur when the host rock undergoes tectonic or magmatic movement into differing physical regimes. Changes in thermodynamic conditions make it favourable for mineral assemblages to react with each other to produce new minerals; as such, it is possible for two rocks to have an identical or a very similar bulk rock chemistry without having a similar mineralogy. This process of mineralogical alteration is related to the rock cycle. An example of a series of mineral reactions is illustrated as follows.[47]

When minerals react, the products will sometimes assume the shape of the reagent; the product mineral is termed to be a pseudomorph of (or after) the reagent. Illustrated here is a pseudomorph of kaolinite after orthoclase. Here, the pseudomorph preserved the Carlsbad twinning common in orthoclase.

Orthoclase feldspar ($KAlSi_3O_8$) is a mineral commonly found in granite, a plutonic igneous rock. When exposed to weathering, it reacts to form kaolinite ($Al_2Si_2O_5(OH)_4$, a sedimentary mineral, and silicic acid):

$$2\ KAlSi_3O_8 + 5\ H_2O + 2\ H^+ \rightarrow Al_2Si_2O_5(OH)_4 + 4\ H_2SiO_3 + 2\ K^+$$

Under low-grade metamorphic conditions, kaolinite reacts with quartz to form pyrophyllite ($Al_2Si_4O_{10}(OH)_2$):

$$Al_2Si_2O_5(OH)_4 + SiO_2 \rightarrow Al_2Si_4O_{10}(OH)_2 + H_2O$$

As metamorphic grade increases, the pyrophyllite reacts to form kyanite and quartz:

$$Al_2Si_4O_{10}(OH)_2 \rightarrow Al_2SiO_5 + 3\ SiO_2 + H_2O$$

Alternatively, a mineral may change its crystal structure as a consequence of changes in temperature and pressure without reacting. For example, quartz will change into a variety of its SiO_2 polymorphs, such as tridymite and cristobalite at high temperatures, and coesite at high pressures.[48]

0.1.3 Physical properties of minerals

Classifying minerals ranges from simple to difficult. A mineral can be identified by several physical properties, some of them being sufficient for full identification without equivocation. In other cases, minerals can only be classified by more complex optical, chemical or X-ray diffraction analysis; these methods, however, can be costly and time-consuming. Physical properties applied for classification include crystal structure and habit, hardness, lustre, diaphaneity, colour, streak, cleavage and fracture, and specific gravity. Other less general tests include fluorescence, phosphorescence, magnetism, radioactivity, tenacity (response to mechanical induced changes of shape or form), piezoelectricity and reactivity to dilute acids.[49]

Crystal structure and habit

Main articles: Crystal system and Crystal habit
See also: Crystal twinning

Crystal structure results from the orderly geometric spatial arrangement of atoms in the internal structure of a mineral. This crystal structure is based on regular internal atomic or ionic arrangement that is often expressed in the geometric form that the crystal takes. Even when the mineral grains are too small to see or are irregularly shaped, the underlying crystal structure is always periodic and can be determined by X-ray diffraction.[1] Minerals are typically described by their symmetry content. Crystals are restricted to 32 point groups, which differ by their symmetry. These groups are classified in turn into more broad categories, the most encompassing of these being the six crystal families.[50]

Topaz has a characteristic orthorhombic elongated crystal shape.

These families can be described by the relative lengths of the three crystallographic axes, and the angles between them; these relationships correspond to the symmetry operations that define the narrower point groups. They are summarized below; a, b, and c represent the axes, and α, β, γ represent the angle opposite the respective crystallographic axis (e.g. α is the angle opposite the a-axis, viz. the angle between the b and c axes):[50]

The hexagonal crystal family is also split into two crystal *systems* — the trigonal, which has a three-fold axis of symmetry, and the hexagonal, which has a six-fold axis of symmetry.

Chemistry and crystal structure together define a mineral. With a restriction to 32 point groups, minerals of different chemistry may have identical crystal structure. For example, halite (NaCl), galena (PbS), and periclase (MgO) all belong to the hexaoctahedral point group (isometric family), as they have a similar stoichiometry between their different constituent elements. In contrast, polymorphs are groupings of minerals that share a chemical formula but have a different structure. For example, pyrite and marcasite, both iron sulfides, have the formula FeS_2; however, the former is isometric while the latter is orthorhombic. This polymorphism extends to other sulfides with the generic AX_2 formula; these two groups are collectively known as the pyrite and marcasite groups.[51]

Polymorphism can extend beyond pure symmetry content. The aluminosilicates are a group of three minerals — kyanite, andalusite, and sillimanite — which share the chemical formula Al_2SiO_5. Kyanite is triclinic, while andalusite and sillimanite are both orthorhombic and belong to the dipyramidal point group. These difference arise correspond to how aluminium is coordinated within the crystal structure. In all minerals, one aluminium ion is always in six-fold coordination by oxygen; the silicon, as a general rule is in four-fold coordination in all minerals; an exception is a case like stishovite (SiO_2, an ultra-high pressure quartz polymorph with rutile structure).[52] In kyanite, the second aluminium is in six-fold coordination; its chemical formula can be expressed as $Al^{[6]}Al^{[6]}SiO_5$, to reflect its crystal structure. Andalusite has the second aluminium in five-fold coordination ($Al^{[6]}Al^{[5]}SiO_5$) and sillimanite has it in four-fold coordination ($Al^{[6]}Al^{[4]}SiO_5$).[53]

Differences in crystal structure and chemistry greatly influence other physical properties of the mineral. The carbon allotropes diamond and graphite have vastly different properties; diamond is the hardest natural substance, has an adamantine lustre, and belongs to the isometric crystal family, whereas as graphite is very soft, has a greasy lustre, and crystallises in the hexagonal family. This difference is accounted by differences in bonding. In diamond, the carbons are in sp^3 hybrid orbitals, which means they form a framework where each carbon is covalently bonded to three neighbours in a tetrahedral fashion; on the other hand, graphite is composed of sheets of carbons in sp^2 hybrid orbitals, where each carbon is bonded covalently to only two others. These sheets are held together by much weaker van der Waals forces, and this discrepancy translates to big macroscopic differences.[54]

Twinning is the intergrowth of two or more crystal of a

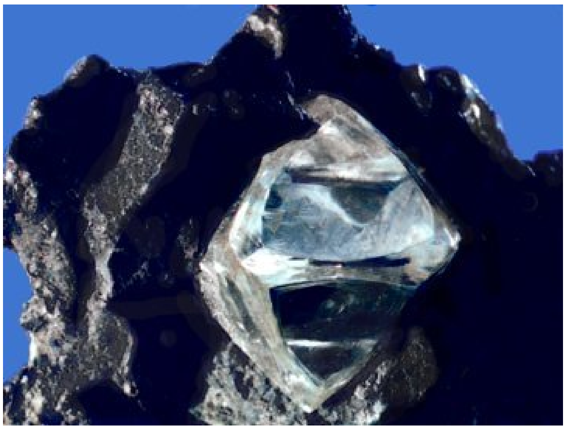
Contact twins, as seen in spinel

single mineral species. The geometry of the twinning is controlled by the mineral's symmetry. As a result, there are several types of twins, including contact twins, reticulated twins, geniculated twins, penetration twins, cyclic twins, and polysynthetic twins. Contact, or simple twins, consist of two crystals joined at a plane; this type of twinning is common in spinel. Reticulated twins, common in rutile, are interlocking crystals resembling netting. Geniculated twins have a bend in the middle that is caused by start of the twin. Penetration twins consist of two single crystals that have grown into each other; examples of this twinning include cross-shaped staurolite twins and Carlsbad twinning in orthoclase. Cyclic twins are caused by repeated twinning around a rotation axis. It occurs around three, four, five, six, or eight-fold axes, and the corresponding patterns are called threelings, fourlings, fivelings, sixlings, and eightlings. Sixlings are common in aragonite. Polysynthetic twins are similar to cyclic twinning by the presence of repetitive twinning; however, instead of occurring around a rotational axis, it occurs along parallel planes, usually on a microscopic scale.[55][56]

Crystal habit refers to the overall shape of crystal. Several terms are used to describe this property. Common habits include acicular, which described needlelike crystals like in natrolite, bladed, dendritic (tree-pattern, common in native copper), equant, which is typical of garnet, prismatic (elongated in one direction), and tabular, which differs from bladed habit in that the former is platy whereas the latter has a defined elongation. Related to crystal form, the quality of crystal faces is diagnostic of some minerals, especially with a petrographic microscope. Euhedral crystals have a defined external shape, while anhedral crystals do not; those intermediate forms are termed subhedral.[57][58]

Hardness

Main article: Mohs scale of mineral hardness



Diamond is the hardest natural material, and has a Mohs hardness of 10.

The hardness of a mineral defines how much it can resist scratching. This physical property is controlled by the chemical composition and crystalline structure of a mineral. A mineral's hardness is not necessarily constant for all sides, which is a function of its structure; crystallographic weakness renders some directions softer than others.[59] An example of this property exists in kyanite, which has a Mohs hardness of 5½ parallel to [001] but 7 parallel to [100].[60]

The most common scale of measurement is the ordinal Mohs hardness scale. Defined by ten indicators, a mineral with a higher index scratches those below it. The scale ranges from talc, a phyllosilicate, to diamond, a carbon polymorph that is the hardest natural material. The scale is provided below:[59]

Lustre and diaphaneity

Main article: Lustre (mineralogy)

Pyrite has a metallic lustre.

Lustre indicates how light reflects from the mineral's surface, with regards to its quality and intensity. There are numerous qualitative terms used to describe this property, which are split into metallic and non-metallic categories. Metallic and sub-metallic minerals have high reflectivity like metal; examples of minerals with this lustre are galena and pyrite. Non-metallic lustres include: adamantine, such as in diamond; vitreous, which is a glassy lustre very common in silicate minerals; pearly, such as in talc and apophyllite, resinous, such as members of the garnet group, silky which common in fibrous minerals such as asbestiform chrysotile.[61]

The diaphaneity of a mineral describes the ability of light to pass through it. Transparent minerals do not diminish the intensity of light passing through it. An example of such a mineral is muscovite (potassium mica); some varieties are sufficiently clear to have been used for windows. Translucent minerals allow some light to pass, but less than those that are transparent. Jadeite and nephrite (mineral forms of jade are examples of minerals with this property). Minerals that do not allow light to pass are called opaque.[62][63]

The diaphaneity of a mineral depends on thickness of the sample. When a mineral is sufficiently thin (e.g., in a thin section for petrography), it may become transparent even if that property is not seen in hand sample. In contrast, some minerals, such as hematite or pyrite are opaque even in thin-section.[63]

Colour and streak

Main article: Streak (mineralogy)

Colour is the most obvious property of a mineral, but it is often non-diagnostic.[64] It is caused by electromagnetic radiation interacting with electrons (except in the case of incandescence, which does not apply to minerals).[65] Two broad classes of elements are defined with regards to their contribution to a mineral's colour. Idiochromatic elements are essential to a mineral's composition; their contribution to a mineral's colour is diagnostic.[62][66] Examples of such minerals are malachite (green) and azurite (blue). In contrast, allochromatic elements in minerals are present in trace amounts as impurities. An example of such a mineral would be the ruby and sapphire varieties of the mineral corundum.[66] The colours of pseudochromatic minerals are the result of interference of light waves. Examples include opal, labradorite, ammolite and bornite.

In addition to simple body colour, minerals can have various other distinctive optical properties, such as play of colours, asterism, chatoyancy, iridescence, tarnish, and pleochroism. Several of these properties involve variability in colour. Play of colour, such as in opal, results in the sample reflecting different colours as it is turned, while pleochroism describes the change in colour as light passes through a mineral in a different orientation. Iridescence is a variety of the play of colours where light scatters off a coating on the surface of crystal, cleavage planes, or off layers having minor gradations in chemistry.[67] In contrast, the play of colours in opal is caused by light refracting from ordered microscopic silica spheres within its physical structure.[68] Chatoyancy ("cat's eye") is the wavy banding of colour that is observed as the sample is rotated; asterism, a variety of chatoyancy, gives the appearance of a star on the mineral grain. The latter property is particularly common in gem-quality corundum.[67][68]

The streak of a mineral refers to the colour of a mineral in powdered form, which may or may not be identical to its body colour.[66] The most common way of testing this property is done with a streak plate, which is made out of porcelain and coloured either white or black. The streak of a mineral is independent of trace elements[62] or any weathering surface.[66] A common example of this property is illustrated with hematite, which is coloured black, silver, or red in hand sample, but has a cherry-red[62] to reddish-brown streak.[66] Streak is more often distinctive for metallic minerals, in contrast to non-metallic minerals whose body colour is created by allochromatic elements.[62] Streak testing is constrained by the hardness of the mineral, as those harder than 7 powder the *streak plate* instead.[66]

Cleavage, parting, fracture, and tenacity

Main articles: Cleavage (crystal) and Fracture (mineralogy)

By definition, minerals have a characteristic atomic arrangement. Weakness in this crystalline structure causes planes of weakness, and the breakage of a mineral along such planes is termed cleavage. The quality of cleavage can be described based on how cleanly and easily the mineral breaks; common descriptors, in order of decreasing quality, are "perfect", "good", "distinct", and "poor". In particularly transparent mineral, or in thin-section, cleavage can be seen a series of parallel lines marking the planar surfaces when viewed at a side. Cleavage is not a universal property among minerals; for example, quartz, consisting of extensively interconnected silica tetrahedra, does not have a crystallographic weakness which would allow it to cleave. In contrast, micas, which have perfect basal cleavage, consist of sheets of silica tetrahedra which are very weakly held together.[69][70]

As cleavage is a function of crystallography, there are a variety of cleavage types. Cleavage occurs typically in either one, two, three, four, or six directions. Basal cleavage in one direction is a distinctive property of the micas. Two-directional cleavage is described as prismatic, and occurs in minerals such as the amphiboles and pyroxenes. Minerals such as galena or halite have cubic (or isometric) cleavage in three directions, at 90°; when three directions of cleavage are present, but not at 90°, such as in calcite or rhodochrosite, it is termed rhombohedral cleavage. Octahedral cleavage (four directions) is present in fluorite and

Perfect basal cleavage as seen in biotite (black), and good cleavage seen in the matrix (pink orthoclase).

diamond, and sphalerite has six-directional dodecahedral cleavage.[69][70]

Minerals with many cleavages might not break equally well in all of the directions; for example, calcite has good cleavage in three direction, but gypsum has perfect cleavage in one direction, and poor cleavage in two other directions. Angles between cleavage planes vary between minerals. For example, as the amphiboles are double-chain silicates and the pyroxenes are single-chain silicates, the angle between their cleavage planes is different. The pyroxenes cleave in two directions at approximately 90°, whereas the amphiboles distinctively cleave in two directions separated by approximately 120° and 60°. The cleavage angles can be measured with a contact goniometer, which is similar to a protractor.[69][70]

Parting, sometimes called "false cleavage", is similar in appearance to cleavage but is instead produced by structural defects in the mineral as opposed to systematic weakness. Parting varies from crystal to crystal of a mineral, whereas all crystals of a given mineral will cleave if the atomic structure allows for that property. In general, parting is caused by some stress applied to a crystal. The sources of the stresses include deformation (e.g. an increase in pressure), exsolution, or twinning. Minerals that often display parting include the pyroxenes, hematite, magnetite, and corundum.[69][71]

When a mineral is broken in a direction that does not correspond to a plane of cleavage, it is termed to have been fractured. There are several types of uneven fracture. The classic example is conchoidal fracture, like that of quartz; rounded surfaces are created, which are marked by smooth curved lines. This type of fracture occurs only in very homogeneous minerals. Other types of fracture are fibrous, splintery, and hackly. The latter describes a break along a rough, jagged surface; an example of this property is found in native copper.[72]

Tenacity is related to both cleavage and fracture. Whereas fracture and cleavage describes the surfaces that are created when a mineral is broken, tenacity describes how resistant a mineral is to such breaking. Minerals can be described as brittle, ductile, malleable, sectile, flexible, or elastic.[73]

Specific gravity

Galena, PbS, is a mineral with a high specific gravity.

Specific gravity numerically describes the density of a mineral. The dimensions of density are mass divided by volume with units: kg/m^3 or g/cm^3. Specific gravity measures how much water a mineral sample displaces. Defined as the quotient of the mass of the sample and difference between the weight of the sample in air and its corresponding weight in water, specific gravity is a unitless ratio. Among most minerals, this property is not diagnostic. Rock forming minerals — typically silicates or occasionally carbonates — have a specific gravity of 2.5–3.5.[74]

High specific gravity is a diagnostic property of a mineral. A variation in chemistry (and consequently, mineral class) correlates to a change in specific gravity. Among more common minerals, oxides and sulfides tend to have a higher specific gravity as they include elements with higher atomic mass. A generalization is that minerals with metallic or adamantine lustre tend to have higher specific gravities than those having a non-metallic to dull lustre. For example, hematite, Fe_2O_3, has a specific gravity of 5.26[75] while galena, PbS, has a specific gravity of 7.2–7.6,[76] which is a result of their high iron and lead content, respectively. A very high specific gravity becomes very pronounced in native metals; kamacite, an iron-nickel alloy common in iron meteorites has a specific gravity of 7.9,[77] and gold has an observed specific gravity between 15 and 19.3.[74][78]

Other properties

Carnotite (yellow) is a radioactive uranium-bearing mineral.

Other properties can be used to diagnose minerals. These are less general, and apply to specific minerals.

Dropping dilute acid (often 10% HCl) aids in distinguishing carbonates from other mineral classes. The acid reacts with the carbonate ($[CO_3]^{2-}$) group, which causes the affected area to effervesce, giving off carbon dioxide gas. This test can be further expanded to test the mineral in its original crystal form or powdered. An example of this test is done when distinguish calcite from dolomite, especially within rocks (limestone and dolostone respectively). Calcite immediately effervesces in acid, whereas acid must be applied to powdered dolomite (often to a scratched surface in a rock), for it to effervesce.[79] Zeolite minerals will not effervesce in acid; instead, they become frosted after 5–10 minutes, and if left in acid for a day, they dissolve or become a silica gel.[80]

When tested, magnetism is a very conspicuous property of minerals. Among common minerals, magnetite exhibits this property strongly, and it is also present, albeit not as strongly, in pyrrhotite and ilmenite.[79]

Minerals can also be tested for taste or smell. Halite, NaCl, is table salt; its potassium-bearing counterpart, sylvite, has a pronounced bitter taste. Sulfides have a characteristic smell, especially as samples are fractured, reacting, or powdered.[79]

Radioactivity is a rare property; minerals may be composed of radioactive elements. They could be a defining constituent, such as uranium in uraninite, autunite, and carnotite, or as trace impurities. In the latter case, the decay of a radioactive element damages the mineral crystal; the result, termed a *radioactive halo* or *pleochroic halo*, is observable by various techniques, such as thin-section petrography.[79]

0.1.4 Mineral classes

As the composition of the Earth's crust is dominated by silicon and oxygen, silicate elements are by far the most important class of minerals in terms of rock formation and diversity. However, non-silicate minerals are of great economic importance, especially as ores.[81][82]

Non-silicate minerals are subdivided into several other classes by their dominant chemistry, which included native elements, sulfides, halides, oxides and hydroxides, carbonates and nitrates, borates, sulfates, phosphates, and organic compounds. The majority of non-silicate mineral species are extremely rare (constituting in total 8% of the Earth's crust), although some are relative common, such as calcite, pyrite, magnetite, and hematite. There are two major structural styles observed in non-silicates: close-packing and silicate-like linked tetrahedra. The close-packed structures, which is a way to densely pack atoms while minimizing interstitial space. Hexagonal close-packing involves stacking layers where every other layer is the same ("ababab"), whereas cubic close-packing involves stacking groups of three layers ("abcabcabc"). Analogues to linked silica tetrahedra include SO_4 (sulfate), PO_4 (phosphate), AsO_4 (arsenate), and VO_4 (vanadate). The non-silicates have great economic importance, as they concentrate elements more than the silicate minerals do.[83]

The largest grouping of minerals by far are the silicates; most rocks are composed of greater than 95% silicate minerals, and over 90% of the Earth's crust is composed of these minerals.[84] The two main constituents of silicates are silicon and oxygen, which are the two most abundant elements in the Earth's crust. Other common elements in silicate minerals correspond to other common elements in the Earth's crust, such aluminium, magnesium, iron, calcium, sodium, and potassium.[85] Some important rock-forming silicates include the feldspars, quartz, olivines, pyroxenes, amphiboles, garnets, and micas.

Silicates

Main article: Silicate minerals

The base of unit of a silicate mineral is the $[SiO_4]^{4-}$ tetrahedron. In the vast majority of cases, silicon is in four-fold or tetrahedral coordination with oxygen. In very high-pressure situations, silicon will be six-fold or octahedral coordination, such as in the perovskite structure or the quartz polymorph stishovite (SiO_2). In the lat-

Aegirine, an iron-sodium clinopyroxene, is part of the inosilicate subclass.

ter case, the mineral no longer has a silicate structure, but that of rutile (TiO_2), and its associated group, which are simple oxides. These silica tetrahedra are then polymerized to some degree to create various structures, such as one-dimensional chains, two-dimensional sheets, and three-dimensional frameworks. The basic silicate mineral where no polymerization of the tetrahedra has occurred requires other elements to balance out the base 4- charge. In other silicate structures, different combinations of elements are required to balance out the resultant negative charge. It is common for the Si^{4+} to be substituted by Al^{3+} because of similarity in ionic radius and charge; in those case, the $[AlO_4]^{5-}$ tetrahedra form the same structures as do the unsubstituted tetrahedra, but their charge-balancing requirements are different.[86]

The degree of polymerization can be described by both the structure formed and how many tetrahedral corners (or coordinating oxygens) are shared (for aluminium and silicon in tetrahedral sites).[87] Orthosilicates (or nesosilicates) have no linking of polyhedra, thus tetrahedra share no corners. Disilicates (or sorosilicates) have two tetrahedra sharing one oxygen atom. Inosilicates are chain silicates; single-chain silicates have two shared corners, whereas double-chain silicates have two or three shared corners. In phyllosilicates, a sheet structure is formed which requires three shared oxygens; in the case of double-chain silicates, some tetrahedra must share two corners instead of three as otherwise a sheet structure would result. Framework silicates, or tectosilicates, have tetrahedra that share all four corners. The ring silicates, or cyclosilicates, only need tetrahedra to share two corners to form the cyclical structure.[88]

The silicate subclasses are described below in order of decreasing polymerization.

Tectosilicates Main category: Tectosilicates
Tectosilicates, also known as framework silicates, have the highest degree of polymerization. With all corners of a tetrahedra shared, the silicon:oxygen ratio becomes 1:2. Examples are quartz, the feldspars, feldspathoids, and the zeolites. Framework silicates tend to be particularly chemically stable as a result of strong covalent bonds.[89]

Natrolite is a mineral series in the zeolite group; this sample has a very prominent acicular crystal habit.

Forming 12% of the Earth's crust, quartz (SiO_2) is the most abundant mineral species. It is characterized by its high chemical and physical resistivity. Quartz has several polymorphs, including tridymite and cristobalite at high temperatures, high-pressure coesite, and ultra-high pressure stishovite. The latter mineral can only be formed on Earth by meteorite impacts, and its structure has been composed so much that it had changed from a silicate structure to that of rutile (TiO_2). The silica polymorph that is most stable at the Earth's surface is α-quartz. Its counterpart, β-quartz, is present only at high temperatures and pressures (changes to α-quartz below 573 °C at 1 bar). These two polymorphs differ by a "kinking" of bonds; this change in structure gives β-quartz greater symmetry than α-quartz, and they are thus also called high quartz (β) and low quartz (α).[84][90]

Feldspars are the most abundant group in the Earth's crust, at about 50%. In the feldspars, Al^{3+} substitutes for Si^{4+}, which creates a charge imbalance that must be accounted for by the addition of cations. The base structure becomes either $[AlSi_3O_8]^-$ or $[Al_2Si_2O_8]^{2-}$ There are 22 mineral species of feldspars, subdivided into two major subgroups—alkali and plagioclase—and two less common groups—celsian and banalsite. The alkali feldspars are most commonly in a series between potassium-rich orthoclase and sodium-rich albite; in the case of plagioclase, the most common series ranges from albite to calcium-rich anorthite. Crystal twinning is common in feldspars, especially polysynthetic twins in plagioclase and Carlsbad twins in alkali feldspars. If the latter subgroup cools slowly from a melt, it forms exsolution lamellae because the two components—orthoclase and albite—are unstable in solid solution. Exsolution can be on a scale from microscopic to readily observable in hand-sample; perthitic texture forms when Na-rich feldspar exsolve in a K-rich host. The opposite texture (antiperthitic), where K-rich feldspar exsolves in a Na-rich host, is very rare.[91]

Feldsapthoids are structurally similar to feldspar, but differ in that they form in Si-deficient conditions which allows for further substitution by Al^{3+}. As a result, feldsapthoids cannot be associated with quartz. A common example of a feldsapthoid is nepheline ((Na, K)$AlSiO_4$); compared to alkali feldspar, nepheline has an Al_2O_3:SiO_2 ratio of 1:2, as opposed to 1:6 in the feldspar.[92] Zeolites often have distinctive crystal habits, occurring in needles, plates, or blocky masses. They form in the presence of water at low temperatures and pressures, and have channels and voids in their structure. Zeolites have several industrial applications, especially in waste water treatment.[93]

Phyllosilicates Main category: Phyllosilicates

Phyllosilicates consist of sheets of polymerized tetrahedra. They are bound at three oxygen sites, which gives a characteristic silicon:oxygen ratio of 2:5. Important examples include the mica, chlorite, and the kaolinite-serpentine groups. The sheets are weakly bound by van der Waals forces or hydrogen bonds, which causes a crystallographic weakness, in turn leading to a prominent basal cleavage among the phyllosilicates.[94] In addition to the tetrahedra, phyllosilicates have a sheet of octahedra (elements in six-fold coordination by oxygen) that balanced out the basic tetrahedra, which have a negative charge (e.g. $[Si_4O_{10}]^{4-}$) These tetrahedra (T) and octahedra (O) sheets are stacked in a variety of combinations to create phyllosilicate groups. Within an octahedral sheet, there are three octahedral sites in a unit structure; however, not all of the sites may be occupied. In that case, the mineral is termed dioctahedral, whereas in other case it is termed trioctahedral.[95]

Muscovite, a mineral species in the mica group, within the phyllosilicate subclass

The kaolinite-serpentine group consists of T-O stacks (the 1:1 clay minerals); their hardness ranges from 2 to 4, as the sheets are held by hydrogen bonds. The 2:1 clay minerals (pyrophyllite-talc) consist of T-O-T stacks, but they are softer (hardness from 1 to 2), as they are instead held together by van der Waals forces. These two groups of minerals are subgrouped by octahedral occupation; specifically, kaolinite and pyrophyllite are dioctahedral whereas serpentine and talc trioctahedral.[96]

Micas are also T-O-T-stacked phyllosilicates, but differ from the other T-O-T and T-O-stacked subclass members in that they incorporate aluminium into the tetrahedral sheets (clay minerals have Al^{3+} in octahedral sites). Common examples of micas are muscovite, and the biotite series. The chlorite group is related to mica group, but a brucite-like ($Mg(OH)_2$) layer between the T-O-T stacks.[97]

Because of their chemical structure, phyllosilicates typically have flexible, elastic, transparent layers that are electrical insulators and can be split into very thin flakes. Micas can be used in electronics as insulators, in construction, as optical filler, or even cosmetics. Chrysotile, a species of serpentine, is the most common mineral species in industrial asbestos, as it is less dangerous in terms of health than the amphibole asbestos.[98]

Inosilicates Main category: Inosilicates

Inosilicates consist of tetrahedra repeatedly bonded in chains. These chains can be single, where a tetrahedron is bound to two others to form a continuous chain; alternatively, two chains can be merged to create double-chain silicates. Single-chain silicates have a silicon:oxygen ratio of 1:3 (e.g. $[Si_2O_6]^{4-}$), whereas the double-chain variety has a ratio of 4:11, e.g. $[Si_8O_{22}]^{12-}$. Inosilicates contain two important rock-forming mineral groups; single-chain silicates are most commonly pyroxenes, while double-chain silicates are often amphiboles.[99] Higher-order chains exist (e.g. three-member, four-member, five-member chains, etc.) but they are rare.[100]

The pyroxene group consists of 21 mineral species.[101] Pyroxenes have a general structure formula of $XY(Si_2O_6)$, where X is an octahedral site, while Y can vary in coordination number from six to eight. Most varieties of pyroxene consist of permutations of Ca^{2+}, Fe^{2+} and Mg^{2+} to balance the negative charge on the backbone. Pyroxenes are common in the Earth's crust

Asbestiform tremolite, part of the amphibole group in the inosilicate subclass

(about 10%) and are a key constituent of mafic igneous rocks.[102]

Amphiboles have great variability in chemistry, described variously as a "mineralogical garbage can" or a "mineralogical shark swimming a sea of elements". The backbone of the amphiboles is the $[Si_8O_{22}]^{12-}$; it is balanced by cations in three possible positions, although the third position is not always used, and one element can occupy both remaining ones. Finally, the amphiboles are usually hydrated, that is, they have a hydroxyl group ($[OH]^-$), although it can be replaced by a fluoride, a chloride, or an oxide ion.[103] Because of the variable chemistry, there are over 80 species of amphibole, although variations, as in the pyroxenes, most commonly involve mixtures of Ca^{2+}, Fe^{2+} and Mg^{2+}.[101] Several amphibole mineral species can have an asbestiform crystal habit. These asbestos minerals form long, thin, flexible, and strong fibres, which are electrical insulators, chemically inert and heat-resistant; as such, they have several applications, especially in construction materials. However, asbestos are known carcinogens, and cause various other illnesses, such as asbestosis; amphibole asbestos (anthophyllite, tremolite, actinolite, grunerite, and riebeckite) are considered more dangerous than chrysotile serpentine asbestos.[104]

Cyclosilicates Main category: Cyclosilicates
Cyclosilicates, or ring silicates, have a ratio of silicon to oxygen of 1:3. Six-member rings are most common, with a base structure of $[Si_6O_{18}]^{12-}$; examples include the tourmaline group and beryl. Other ring structures exist, with 3, 4, 8, 9, 12 having been described.[105] Cyclosilicates tend to be strong, with elongated, striated crystals.[106]

An example of elbaite, a species of tourmaline, with distinctive colour banding.

Tourmalines have a very complex chemistry that can be described by a general formula $XY_3Z_6(BO_3)_3T_6O_{18}V_3W$. The T_6O_{18} is the basic ring structure, where T is usually Si^{4+}, but substitutable by Al_{3+} or B^{3+}. Tourmalines can be subgrouped by the occupancy of the X site, and from there further subdivided by the chemistry of the W site. The Y and Z sites can accommodate a variety of cations, especially various transition metals; this variability in structural transition metal content gives the tourmaline group greater variability in colour. Other cyclosilicates include beryl, $Al_2Be_3Si_6O_{18}$, whose varieties include the gemstones emerald (green) and aquamarine (bluish). Cordierite is structurally similar to beryl, and is a common metamorphic mineral.[107]

Sorosilicates Main category: Sorosilicates
Sorosilicates, also termed disilicates, have tetrahedron-tetrahedron bonding at one oxygen, which results in a 2:7 ratio of silicon to oxygen. The resultant common structural element is the $[Si_2O_7]^{6-}$ group. The most common disilicates by far are members of the epidote group. Epidotes are found in variety of geologic settings, ranging from mid-ocean ridge to granites to metapelites. Epidotes are built around the structure $[(SiO_4)(Si_2O_7)]^{10-}$ structure; for example, the mineral *species* epidote has calcium, aluminium, and ferric iron to charge balance: $Ca_2Al_2(Fe^{3+}, Al)(SiO_4)(Si_2O_7)O(OH)$. The presence of iron as Fe^{3+} and Fe^{2+} helps understand oxygen fugacity,

Epidote often has a distinctive pistachio-green colour.

which in turn is a significant factor in petrogenesis.[108]

Other examples of sorosilicates include lawsonite, a metamorphic mineral forming in the blueschist facies (subduction zone setting with low temperature and high pressure), vesuvianite, which takes up a significant amount of calcium in its chemical structure.[108][109]

Orthosilicates Main category: Nesosilicates

Orthosilicates consist of isolated tetrahedra that are charge-balanced by other cations.[110] Also termed nesosilicates, this type of silicate has a silicon:oxygen ratio of 1:4 (e.g. SiO_4). Typical orthosilicates tend to form blocky equant crystals, and are fairly hard.[111] Several rock-forming minerals are part of this subclass, such as the aluminosilicates, the olivine group, and the garnet group.

Black andradite, an end-member of the orthosilicate garnet group.

The aluminosilicates—kyanite, andalusite, and sillimanite, all Al_2SiO_5—are structurally composed of one $[SiO_4]^{4-}$ tetrahedron, and one Al^{3+} in octahedral coordination. The remaining Al^{3+} can be in six-fold coordination (kyanite), five-fold (andalusite) or four-fold (sillimanite); which mineral forms in a given environment is depend on pressure and temperature conditions. In the olivine structure, the main olivine series of $(Mg, Fe)_2SiO_4$ consist of magnesium-rich forsterite and iron-rich fayalite. Both iron and magnesium are in octahedral by oxygen. Other mineral species having this structure exist, such as tephroite, Mn_2SiO_4.[112] The garnet group has a general formula of $X_3Y_2(SiO_4)_3$, where X is a large eight-fold coordinated cation, and Y is a smaller six-fold coordinated cation. There are six ideal endmembers of garnet, split into two group. The pyralspite garnets have Al^{3+} in the Y position: pyrope ($Mg_3Al_2(SiO_4)_3$), almandine ($Fe_3Al_2(SiO_4)_3$), and spessartine ($Mn_3Al_2(SiO_4)_3$). The ugrandite garnets have Ca^{2+} in the X position: uvarovite ($Ca_3Cr_2(SiO_4)_3$), grossular ($Ca_3Al_2(SiO_4)_3$) and andradite ($Ca_3Fe_2(SiO_4)_3$). While there are two subgroups of garnet, solid solutions exist between all six endmembers.[110]

Other orthosilicates include zircon, staurolite, and topaz. Zircon ($ZrSiO_4$) is useful in geochronology as the Zr^{4+} can be substituted by U^{6+}; furthermore, because of its very resistant structure, it is difficult to reset it as a chronometer. Staurolite is a common metamorphic intermediate-grade index mineral. It has a particularly complicated crystal structure that was only fully described in 1986. Topaz ($Al_2SiO_4(F, OH)_2$, often found in granitic pegmatites associated with tourmaline, is a common gemstone mineral.[113]

Non-silicates

Native elements Main article: Native element minerals

Native elements are those that are not chemically bonded to other elements. This mineral group includes native metals, semi-metals, and non-metals, and various alloys and solid solutions. The metals are held together by metallic bonding, which confers distinctive physical properties such as their shiny metallic lustre, ductility and malleability, and electrical conductivity. Native elements are subdivided into groups by their structure or chemical attributes.

The gold group, with a cubic close-packed structure, includes metals such as gold, silver, and copper. The platinum group is similar in structure to the gold group. The iron-nickel group is characterized by several iron-nickel alloy species. Two examples are kamacite and taenite, which are found in iron meteorites; these species differ by the amount of Ni in the alloy; kamacite has less than 5–7% nickel and is a variety of native iron, whereas the nickel content of taenite ranges from 7–37%. Arsenic

Native gold. Rare specimen of stout crystals growing off of a central stalk, size 3.7 x 1.1 x 0.4 cm, from Venezuela.

group minerals consist of semi-metals, which have only some metallic; for example, they lack the malleability of metals. Native carbon occurs in two allotropes, graphite and diamond; the latter forms at very high pressure in the mantle, which gives it a much stronger structure than graphite.[114]

Sulfides Main article: Sulfide minerals

The sulfide minerals are chemical compounds of one or more metals or semimetals with a sulfur; tellurium, arsenic, or selenium can substitute for the sulfur. Sulfides tend to be soft, brittle minerals with a high specific gravity. Many powdered sulfides, such as pyrite, have a sulfurous smell when powdered. Sulfides are susceptible to weathering, and many readily dissolve in water; these dissolved minerals can be later redeposited, which creates enriched secondary ore deposits.[115] Sulfides are classified by the ratio of the metal or semimetal to the sulfur, such as M:S equal to 2:1, or 1:1.[116] Many sulfide minerals are economically important as metal ores; examples include sphalerite (ZnS), an ore of zinc, galena (PbS), an ore of lead, cinnabar (HgS), an ore of mercury, and molybdenite (MoS_2, an ore of molybdenum.[117] Pyrite (FeS_2), is the most commonly occurring sulfide, and can be found in most geological environments. It is not, however, an ore of iron, but can be instead oxidized to produce sulfuric acid.[118] Related to the sulfides are the rare sulfosalts, in which a metallic element is bonded to sulfur and a semimetal such as antimony, arsenic, or bismuth. Like the sulfides, sulfosalts are typically soft, heavy, and brittle minerals.[119]

Red cinnabar (HgS), a mercury ore, on dolomite

Oxides Main article: Oxide minerals

Oxide minerals are divided into three categories: simple oxides, hydroxides, and multiple oxides. Simple oxides are characterized by O^{2-} as the main anion and primarily ionic bonding. They can be further subdivided by the ratio of oxygen to the cations. The periclase group consists of minerals with a 1:1 ratio. Oxides with a 2:1 ratio include cuprite (Cu_2O) and water ice. Corundum group minerals have a 2:3 ratio, and includes minerals such as corundum (Al_2O_3), and hematite (Fe_2O_3). Rutile group minerals have a ratio of 1:2; the eponymous species, rutile (TiO_2) is the chief ore of titanium; other examples include cassiterite (SnO_2; ore of tin), and pyrolusite (MnO_2; ore of manganese).[120][121] In hydroxides, the dominant anion is the hydroxyl ion, OH^-. Bauxites are the chief aluminium ore, and are a heterogeneous mixture of the hydroxide minerals diaspore, gibbsite, and bohmite; they form in areas with a very high rate of chemical weathering (mainly tropical conditions).[122] Finally, multiple oxides are compounds of two metals with oxygen. A major group within this class are the spinels, with a general formula of $X^{2+}Y^{3+}{}_2O_4$. Examples of species include spinel ($MgAl_2O_4$), chromite ($FeCr_2O_4$), and magnetite (Fe_3O_4). The latter is readily distinguishable by its strong magnetism, which occurs as it has iron in two oxidation states ($Fe^{2+}Fe^{3+}{}_2O_4$), which makes it a multiple oxide instead of a single oxide.[123]

Halides Main article: Halide minerals

The halide minerals are compounds where a halogen (fluorine, chlorine, iodine, and bromine) is the main anion. These minerals tend to be soft, weak, brittle, and water-soluble. Common examples of halides include halite ($NaCl$, table salt), sylvite (KCl), fluorite (CaF_2). Halite and sylvite commonly form as evaporites, and can be dominant minerals in chemical sedimentary rocks. Cryolite, Na_3AlF_6, is a key mineral in the extraction of aluminium from bauxites; however, as the only significant occurrence at Ivittuut, Greenland, in a granitic pegmatite, was depleted, synthetic cryolite can be made from fluorite.[124]

Pink cubic halite (NaCl; halide class) crystals on a nahcolite matrix (NaHCO$_3$; a carbonate, and mineral form of sodium bicarbonate, used as baking soda).

Carbonates Main article: Carbonate minerals

The carbonate minerals are those were the main anionic group is carbonate, $[CO_3]^{2-}$. Carbonates tend to be brittle, many have rhombohedral cleavage, and all react with acid.[125] Due to the last characteristic, field geologists often carry dilute hydrochloric acid to distinguish carbonates from non-carbonates. The reaction of acid with carbonates, most commonly found as the polymorph calcite and aragonite ($CaCO_3$), relates to the dissolution and precipitation of the mineral, which is a key in the formation of limestone caves, features within them such as stalactite and stalagmites, and karst landforms. Carbonates are most often formed as biogenic or chemical sediments in marine environments. The carbonate group is structurally a triangle, where a central C^{4+} cation is surrounded by three O^{2-} anions; different groups of minerals form from different arrangements of these triangles.[126] The most common carbonate mineral is calcite, and is the primary constituent of sedimentary limestone and metamorphic marble. Calcite, $CaCO_3$, can have a high magnesium impurity; under high-Mg conditions, its polymorph aragonite will form instead; the marine geochemistry in this regard can be described as an aragonite or calcite sea, depending on which mineral preferentially forms. Dolomite is a double carbonate, with the formula $CaMg(CO_3)_2$. Secondary dolomitization of limestone is common, where calcite or aragonite are converted to dolomite; this reaction increases pore space (the unit cell volume of dolomite is 88% that of calcite), which can create a reservoir for oil and gas. These two minerals species are members of eponymous mineral groups: the calcite group includes carbonates with the general formula XCO_3, and the dolomite group constitutes minerals with general formula $XY(CO_3)_2$.[127]

Sulfates Main article: Sulfate minerals

Gypsum desert rose

The sulfate minerals all contain the sulfate anion, $[SO_4]^{2-}$. They tend to be transparent to translucent, soft, and many are fragile.[128] Sulfate minerals commonly form as evaporites, where they precipitate out of evaporating saline waters; alternative, sulfates can also be found in hydrothermal vein systems associated with sulfides,[129] or as oxidation products of sulfides.[130] Sulfates can be subdivded into anhydrous and hydrous minerals. The most common hydrous sulfate by far is gypsum, $CaSO_4{\cdot}2H_2O$. It forms as an evaporite, and is associated other evaporites such as calcite and halite; if it incorporates sand grains as it crystallizes, gypsum can form desert roses. Gypsum has very low thermal conductivity and maintains a low temperature when heated as it loses that heat by dehydrating; as such, gypsum is used as an insulator in materials such as plaster and drywall. The anhydrous equivalent of gypsum is anhydrite; it can form directly from seawater in highly arid conditions. The barite group has the general formula XSO_4, where the X is a large 12-coordinated cation. Examples include barite ($BaSO_4$), celestine ($SrSO_4$), and anglesite ($PbSO_4$); anhydrite is not part of the barite group, as the smaller Ca^{2+} is only in eight-fold coordination.[131]

Phosphates Main article: Phosphate minerals

The phosphate minerals are characterized by the tetrahedral $[PO_4]^{3-}$ unit, although the structure can be generalized, and phosphorus is replaced by antimony, arsenic, or vanadium. The most common phosphate is the apatite group; common species within this group are fluorapatite ($Ca_5(PO_4)_3F$), chlorapatite ($Ca_5(PO_4)_3Cl$) and hydroxylapatite ($Ca_5(PO_4)_3(OH)$). Minerals in this group are the main crystalline constituents of teeth and bones in vertebrates. The relatively abundant monazite group has a general structure of ATO_4, where T is phosphorus or arsenic, and A is often a rare-earth element (REE). Monazite is important in two ways: first, as a REE “sink”, it can sufficiently concentrate these elements to become an ore; secondly, monazite group elements can incorporate relatively large amounts of uranium and thorium, which can be used to date the rock based on the decay of the U and Th to lead.[132]

Organic minerals Main article: Organic minerals

The Strunz classification includes a class for organic minerals. These rare compounds contain organic carbon, but can be formed by a geologic process. For example, whewellite, $CaC_2O_4 \cdot H_2O$ is an oxalate that can be deposited in hydrothermal ore veins. While hydrated calcium oxalate can be found in coal seams and other sedimentary deposits involving organic matter, the hydrothermal occurrence is not considered to be related to biological activity.[82]

0.1.5 Astrobiology

It has been suggested that biominerals could be important indicators of extraterrestrial life and thus could play an important role in the search for past or present life on the planet Mars. Furthermore, organic components (biosignatures) that are often associated with biominerals are believed to play crucial roles in both pre-biotic and biotic reactions.[133]

On January 24, 2014, NASA reported that current studies by the *Curiosity* and *Opportunity* rovers on Mars will now be searching for evidence of ancient life, including a biosphere based on autotrophic, chemotrophic and/or chemolithoautotrophic microorganisms, as well as ancient water, including fluvio-lacustrine environments (plains related to ancient rivers or lakes) that may have been habitable.[134][135][136][137] The search for evidence of habitability, taphonomy (related to fossils), and organic carbon on the planet Mars is now a primary NASA objective.[134][135]

0.1.6 See also

- Dietary mineral
- List of minerals
- List of minerals (complete)
- Mineral collecting

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0.1.9 External links

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- “Mineral Identification Key II” Mineralogical Society of America
- “American Mineralogist Crystal Structure Database”
- Minerals and the Origins of Life (Robert Hazen, NASA) (video, 60m, April 2014).

Chapter 1

Native Elements

1.1 Native copper

Native copper is an uncombined form of copper which occurs as a natural mineral. Copper is one of the few metallic elements to occur in native form, although it most commonly occurs in oxidized states and mixed with other elements. Native copper was an important ore of copper in historic times and was used by pre-historic peoples.

Native copper occurs rarely as isometric cubic and octahedral crystals, but more typically as irregular masses and fracture fillings. It has a reddish, orangish, and/or brownish color on fresh surfaces, but typically is weathered and coated with a green tarnish of copper(II) carbonate (also known as patina or verdigris). Its specific gravity is 8.9 and its hardness is 2.5–3.[5]

The mines of the Keweenaw native copper deposits of Upper Michigan were major copper producers in the 19th and early 20th centuries, and are the largest deposits of native copper in the world.[6] Native Americans mined copper on a small scale at this and several other locations,[7] and evidence exists of copper trading routes throughout North America among native peoples, proven by isotopic analysis. The first commercial mines in the Keweenaw Peninsula (which is nicknamed the "Copper Country" and "Copper Island"), opened in the 1840s. Isle Royale in western Lake Superior was also a site of many tons of native copper. Some of it was extracted by native peoples, but only one of several commercial attempts at mining turned a profit there.[6]

Another major native copper deposit is in Coro Coro, Bolivia.

The name copper comes from the Greek *kyprios*, of Cyprus, the location of copper mines since pre-historic times.[3]

1.1.1 Gallery

- Specimens from notable native copper localities worldwide
- Broken Hill, New South Wales, Australia.
- Native copper cementing host rock, Ray Mine, Arizona. Click & scroll down for a detail photo.
- Itauz Mine, Kazakhstan.
- Tsumeb, Namibia.
- Dendritic native copper encased in transparent gypsum, Mission Mine, Pima County, Arizona, USA.
- “Halfbreed” copper-silver nugget, Keweenaw County, Michigan, USA.
- Native Copper, Keweenaw Peninsula, Michigan,USA

1.1.2 See also

- Copper Inuit

1.1.3 References

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1.1.5 External links

1.2 Diamond

This article is about the mineral. For the gemstone, see Diamond (gemstone). For other uses, including the shape ◊, see Diamond (disambiguation).

In mineralogy, **diamond** (/daɪ(ə)mənd/; from the ancient Greek ἀδάμας – *adámas* “unbreakable”) is a metastable allotrope of carbon, where the carbon atoms are arranged in a variation of the face-centered cubic crystal structure called a diamond lattice. Diamond is less stable than graphite, but the conversion rate from diamond to graphite is negligible at standard conditions. Diamond is renowned as a material with superlative physical qualities, most of which originate from the strong covalent bonding between its atoms. In particular, diamond has the highest hardness and thermal conductivity of any bulk material. Those properties determine the major industrial application of diamond in cutting and polishing tools and the scientific applications in diamond knives and diamond anvil cells.

Because of its extremely rigid lattice, it can be contaminated by very few types of impurities, such as boron and nitrogen. Small amounts of defects or impurities (about one per million of lattice atoms) color diamond blue (boron), yellow (nitrogen), brown (lattice defects), green (radiation exposure), purple, pink, orange or red. Diamond also has relatively high optical dispersion (ability to disperse light of different colors).

Most natural diamonds are formed at high temperature and pressure at depths of 140 to 190 kilometers (87 to 118 mi) in the Earth's mantle. Carbon-containing minerals provide the carbon source, and the growth occurs over periods from 1 billion to 3.3 billion years (25% to 75% of the age of the Earth). Diamonds are brought close to the Earth's surface through deep volcanic eruptions by a magma, which cools into igneous rocks known as kimberlites and lamproites. Diamonds can also be produced synthetically in a HPHT method which approximately simulates the conditions in the Earth's mantle. An alternative, and completely different growth technique is chemical vapor deposition (CVD). Several non-diamond materials, which include cubic zirconia and silicon carbide and are often called diamond simulants, resemble diamond in appearance and many properties. Special gemological techniques have been developed to distinguish natural, synthetic diamonds and diamond simulants.

1.2.1 History

See also: Diamond (gemstone)

The name *diamond* is derived from the ancient Greek *αδάμας (adámas)*, “proper”, “unalterable”, “unbreakable”, “untamed”, from ἀ- (a-), “un-" + *δαμάω* (*damáō*), “I overpower”, “I tame”.[3] Diamonds are thought to have been first recognized and mined in India, where significant alluvial deposits of the stone could be found many centuries ago along the rivers Penner, Krishna and Godavari. Diamonds have been known in India for at least 3,000 years but most likely 6,000 years.[4]

Diamonds have been treasured as gemstones since their use as religious icons in ancient India. Their usage in engraving tools also dates to early human history.[5][6] The popularity of diamonds has risen since the 19th century because of increased supply, improved cutting and polishing techniques, growth in the world economy, and innovative and successful advertising campaigns.[7]

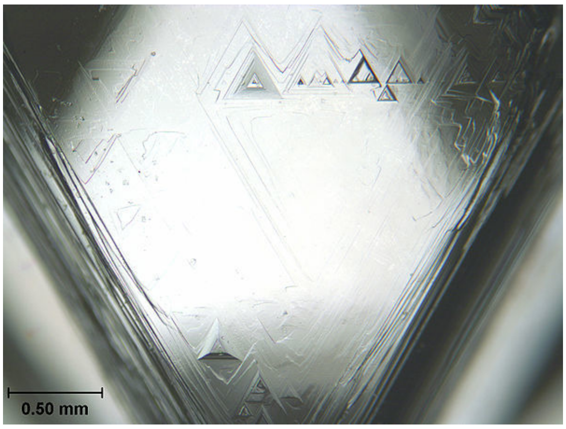
In 1772, Antoine Lavoisier used a lens to concentrate the rays of the sun on a diamond in an atmosphere of oxygen, and showed that the only product of the combustion was carbon dioxide, proving that diamond is composed of carbon.[8] Later in 1797, Smithson Tennant repeated and expanded that experiment.[9] By demonstrating that burning diamond and graphite releases the same amount of gas he established the chemical equivalence of these substances.[10]

The most familiar use of diamonds today is as gemstones used for adornment, a use which dates back into antiquity. The dispersion of white light into spectral colors is the primary gemological characteristic of gem diamonds. In the 20th century, experts in gemology have developed methods of grading diamonds and other gemstones based on the characteristics most important to their value as a gem. Four characteristics, known informally as the *four Cs*, are now commonly used as the basic descriptors of diamonds: these are *carat* (its weight), *cut* (quality of the cut is graded according to proportions, symmetry and polish), *color* (how close to white or colorless; For fancy diamonds how intense is its hue), and *clarity* (how free is it from inclusions).[11] A large, flawless diamond is known as a paragon.

Natural history

The formation of natural diamond requires very specific conditions—exposure of carbon-bearing materials to high pressure, ranging approximately between 45 and

60 kilobars (4.5 and 6 GPa), but at a comparatively low temperature range between approximately 900 and 1,300 °C (1,650 and 2,370 °F). These conditions are met in two places on Earth; in the lithospheric mantle below relatively stable continental plates, and at the site of a meteorite strike.[12]



One face of an uncut octahedral diamond, showing trigons (of positive and negative relief) formed by natural chemical etching

Formation in cratons The conditions for diamond formation to happen in the lithospheric mantle occur at considerable depth corresponding to the requirements of temperature and pressure. These depths are estimated between 140 and 190 kilometers (87 and 118 mi) though occasionally diamonds have crystallized at depths about 300 kilometers (190 mi).[13] The rate at which temperature changes with increasing depth into the Earth varies greatly in different parts of the Earth. In particular, under oceanic plates the temperature rises more quickly with depth, beyond the range required for diamond formation at the depth required. The correct combination of temperature and pressure is only found in the thick, ancient, and stable parts of continental plates where regions of lithosphere known as *cratons* exist. Long residence in the cratonic lithosphere allows diamond crystals to grow larger.[13]

Through studies of carbon isotope ratios (similar to the methodology used in carbon dating, except with the stable isotopes C-12 and C-13), it has been shown that the carbon found in diamonds comes from both inorganic and organic sources. Some diamonds, known as *harzburgitic*, are formed from inorganic carbon originally found deep in the Earth's mantle. In contrast, *eclogitic* diamonds contain organic carbon from organic detritus that has been pushed down from the surface of the Earth's crust through subduction (see plate tectonics) before transforming into diamond. These two different source of carbon have measurably different ^{13}C:^{12}C ratios. Diamonds that have come to the Earth's surface are generally quite old, ranging from under 1 billion to 3.3 billion years old. This is 22% to 73% of the age of the Earth.[13]

Diamonds occur most often as euhedral or rounded octahedra and twinned octahedra known as *macles*. As diamond's crystal structure has a cubic arrangement of the atoms, they have many facets that belong to a cube, octahedron, rhombicosidodecahedron, tetrakis hexahedron or disdyakis dodecahedron. The crystals can have rounded off and unexpressive edges and can be elongated. Sometimes they are found grown together or form double "twinned" crystals at the surfaces of the octahedron. These different shapes and habits of some diamonds result from differing external circumstances. Diamonds (especially those with rounded crystal faces) are commonly found coated in *nyf*, an opaque gum-like skin.[14]

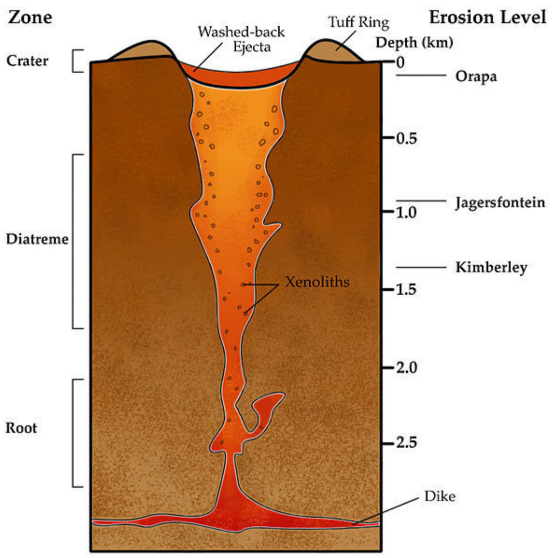
Space diamonds See also: Aggregated diamond nanorod

Primitive interstellar meteorites were found to contain carbon possibly in the form of diamond (Lewis et al. 1987).[15] Not all diamonds found on Earth originated here. A type of diamond called carbonado that is found in South America and Africa may have been deposited there via an asteroid impact (not formed from the impact) about 3 billion years ago. These diamonds may have formed in the intrastellar environment, but as of 2008, there was no scientific consensus on how carbonado diamonds originated.[16][17]

Diamonds can also form under other naturally occurring high-pressure conditions. Very small diamonds of micrometer and nanometer sizes, known as *microdiamonds* or *nanodiamonds* respectively, have been found in meteorite impact craters. Such impact events create shock zones of high pressure and temperature suitable for diamond formation. Impact-type microdiamonds can be used as an indicator of ancient impact craters.[12] Popigai crater in Russia may have the world's largest diamond deposit, estimated at trillions of carats, and formed by an asteroid impact.[18]

Scientific evidence indicates that white dwarf stars have a core of crystallized carbon and oxygen nuclei. The largest of these found in the universe so far, BPM 37093, is located 50 light-years (4.7×10^{14} km) away in the constellation Centaurus. A news release from the Harvard-Smithsonian Center for Astrophysics described the 2,500-mile (4,000 km)-wide stellar core as a *diamond*.[19] It was referred to as *Lucy*, after the Beatles' song "Lucy in the Sky With Diamonds".[20][21]

Transport from mantle Diamond-bearing rock is carried from the mantle to the Earth's surface by deep-origin volcanic eruptions. The magma for such a volcano must originate at a depth where diamonds can be formed[13]—150 km (93 mi) or more (three times or more the depth of source magma for most volcanoes). This is a relatively rare occurrence. These typically small surface volcanic craters extend downward in formations known as volcanic



Schematic diagram of a volcanic pipe

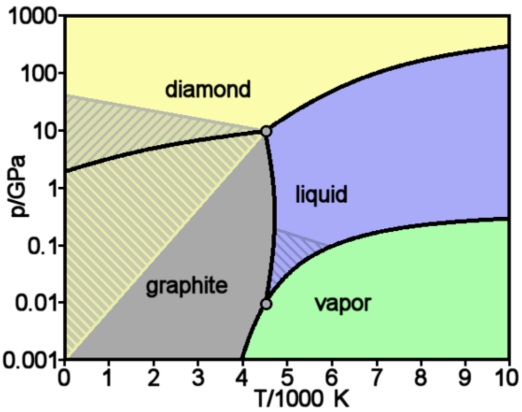
pipes.[13] The pipes contain material that was transported toward the surface by volcanic action, but was not ejected before the volcanic activity ceased. During eruption these pipes are open to the surface, resulting in open circulation; many xenoliths of surface rock and even wood and fossils are found in volcanic pipes. Diamond-bearing volcanic pipes are closely related to the oldest, coolest regions of continental crust (cratons). This is because cratons are very thick, and their lithospheric mantle extends to great enough depth that diamonds are stable. Not all pipes contain diamonds, and even fewer contain enough diamonds to make mining economically viable.[13] Diamonds are very rare[22] because most of the crust is too thin to permit diamond crystallization, whereas most of the mantle has relatively little carbon.

The magma in volcanic pipes is usually one of two characteristic types, which cool into igneous rock known as either kimberlite or lamproite.[13] The magma itself does not contain diamond; instead, it acts as an elevator that carries deep-formed rocks (xenoliths), minerals (xenocrysts), and fluids upward. These rocks are characteristically rich in magnesium-bearing olivine, pyroxene, and amphibole minerals[13] which are often altered to serpentine by heat and fluids during and after eruption. Certain *indicator minerals* typically occur within diamantiferous kimberlites and are used as mineralogical tracers by prospectors, who follow the indicator trail back to the volcanic pipe which may contain diamonds. These minerals are rich in chromium (Cr) or titanium (Ti), elements which impart bright colors to the minerals. The most common indicator minerals are chromium garnets (usually bright red chromium-pyrope, and occasionally green ugrandite-series garnets), eclogitic garnets, orange titanium-pyrope, red high-chromium spinels, dark chromite, bright green chromium-diopside, glassy green olivine, black picroilmenite, and magnetite. Kimberlite deposits are known as *blue ground* for the deeper serpentinized part of the deposits, or as *yellow ground* for the near surface smectite clay and carbonate weathered and oxidized portion.[13]

Once diamonds have been transported to the surface by magma in a volcanic pipe, they may erode out and be distributed over a large area. A volcanic pipe containing diamonds is known as a *primary source* of diamonds. *Secondary sources* of diamonds include all areas where a significant number of diamonds have been eroded out of their kimberlite or lamproite matrix, and accumulated because of water or wind action. These include alluvial deposits and deposits along existing and ancient shorelines, where loose diamonds tend to accumulate because of their size and density. Diamonds have also rarely been found in deposits left behind by glaciers (notably in Wisconsin and Indiana); in contrast to alluvial deposits, glacial deposits are minor and are therefore not viable commercial sources of diamond.[13]

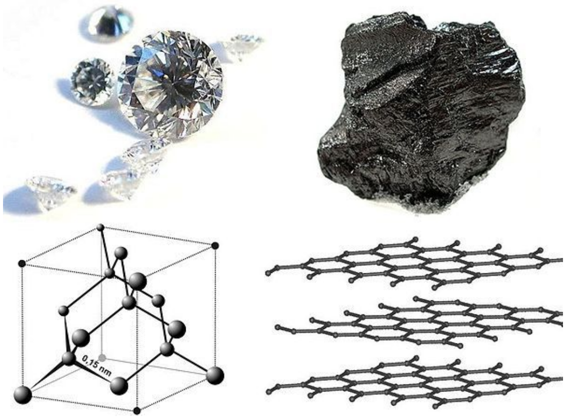
1.2.2 Material properties

Main articles: Material properties of diamond and Crystallographic defects in diamond



Theoretically predicted phase diagram of carbon

A diamond is a transparent crystal of tetrahedrally bonded carbon atoms in a covalent network lattice (sp^3) that crystallizes into the diamond lattice which is a variation of the face centered cubic structure. Diamonds have been adapted for many uses because of the material's exceptional physical characteristics. Most notable are its extreme hardness and thermal conductivity (900–2,320 $W{\cdot}m^{-1}{\cdot}K^{-1}$),[23] as well as wide bandgap and high optical dispersion.[24] Above 1,700 °C (1,973 K / 3,583 °F) in vacuum or oxygen-free atmosphere, diamond converts to graphite; in air, transformation starts at ~700 °C.[25] Diamond's ignition point is 720 – 800 °C in oxygen and 850 – 1,000 °C in air.[26] Naturally occurring diamonds have a density ranging from 3.15–3.53 g/cm^3, with pure diamond close to 3.52 g/cm^3.[1] The chemical bonds that hold the carbon atoms in diamonds to-



Diamond and graphite are two allotropes of carbon: pure forms of the same element that differ in structure.

The extreme hardness of diamond in certain orientations makes it useful in materials science, as in this pyramidal diamond embedded in the working surface of a Vickers hardness tester.

gether are weaker than those in graphite. In diamonds, the bonds form an inflexible three-dimensional lattice, whereas in graphite, the atoms are tightly bonded into sheets, which can slide easily over one another, making the overall structure weaker.[27]

Hardness

Diamond is the hardest known natural material on the Mohs scale of mineral hardness, where hardness is defined as resistance to scratching and is graded between 1 (softest) and 10 (hardest). Diamond has a hardness of 10 (hardest) on this scale and is four times harder than corundum, 9 Mohs.[28] Diamond's hardness has been known since antiquity, and is the source of its name.

Diamond hardness depends on its purity, crystalline perfection and orientation: hardness is higher for flawless, pure crystals oriented to the <111> direction (along the longest diagonal of the cubic diamond lattice).[29] Therefore, whereas it might be possible to scratch some diamonds with other materials, such as boron nitride, the hardest diamonds can only be scratched by other diamonds and nanocrystalline diamond aggregates.

The hardness of diamond contributes to its suitability as a gemstone. Because it can only be scratched by other diamonds, it maintains its polish extremely well. Unlike many other gems, it is well-suited to daily wear because of its resistance to scratching—perhaps contributing to its popularity as the preferred gem in engagement or wedding rings, which are often worn every day.

The hardest natural diamonds mostly originate from the Copeton and Bingara fields located in the New England area in New South Wales, Australia. These diamonds are generally small, perfect to semiperfect octahedra, and are used to polish other diamonds. Their hardness is associated with the crystal growth form, which is single-stage crystal growth. Most other diamonds show more evidence of multiple growth stages, which produce inclusions, flaws, and defect planes in the crystal lattice, all of which affect their hardness. It is possible to treat regular diamonds under a combination of high pressure and high temperature to produce diamonds that are harder than the diamonds used in hardness gauges.[20]

Somewhat related to hardness is another mechanical property *toughness*, which is a material's ability to resist breakage from forceful impact. The toughness of natural diamond has been measured as 7.5–10 MPa·m$^{1/2}$.[30][31] This value is good compared to other gemstones, but poor compared to most engineering materials. As with any material, the macroscopic geometry of a diamond contributes to its resistance to breakage. Diamond has a cleavage plane and is therefore more fragile in some orientations than others. Diamond cutters use this attribute to cleave some stones, prior to faceting.[32] “Impact toughness” is one of the main indexes to measure the quality of synthetic industrial diamonds.[26]

Electrical conductivity

Other specialized applications also exist or are being developed, including use as semiconductors: some blue diamonds are natural semiconductors, in contrast to most diamonds, which are excellent electrical insulators.[33] The conductivity and blue color originate from boron impurity. Boron substitutes for carbon atoms in the diamond lattice, donating a hole into the valence band.[33]

Substantial conductivity is commonly observed in nominally undoped diamond grown by chemical vapor deposition. This conductivity is associated with hydrogen-related species adsorbed at the surface, and it can be removed by annealing or other surface treatments.[34][35]

Surface property

Diamonds are naturally lipophilic and hydrophobic, which means the diamonds' surface cannot be wet by water but can be easily wet and stuck by oil. This property can be utilized to extract diamonds using oil when making synthetic diamonds.[26] However, when diamond surfaces are chemically modified with certain ions, they are expected to become so hydrophilic that they can stabilize multiple layers of water ice at human body temperature.[36]

Chemical stability

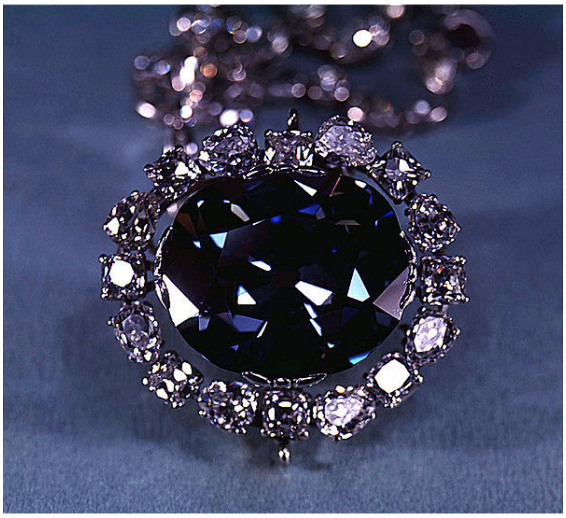
Diamonds are not very reactive. Under room temperature diamonds do not react with any chemical reagents including strong acids and bases. A diamond's surface can only be oxidized at higher temperatures.[26]

Color

Main article: Diamond color

Diamond has a wide bandgap of 5.5 eV corresponding to the deep ultraviolet wavelength of 225 nanometers. This means pure diamond should transmit visible light and appear as a clear colorless crystal. Colors in diamond originate from lattice defects and impurities. The diamond crystal lattice is exceptionally strong and only atoms of nitrogen, boron and hydrogen can be introduced into diamond during the growth at significant concentrations (up to atomic percents). Transition metals Ni and Co, which are commonly used for growth of synthetic diamond by high-pressure high-temperature techniques, have been detected in diamond as individual atoms; the maximum concentration is 0.01% for Ni[37] and even less for Co. Virtually any element can be introduced to diamond by ion implantation.[38]

Brown diamonds at the National Museum of Natural History in Washington, D.C.



The most famous colored diamond, Hope Diamond in 1974.

Nitrogen is by far the most common impurity found in gem diamonds and is responsible for the yellow and brown color in diamonds. Boron is responsible for the blue color.[24] Color in diamond has two additional sources: irradiation (usually by alpha particles), that causes the color in green diamonds; and plastic deformation of the diamond crystal lattice. Plastic deformation is the cause of color in some brown[39] and perhaps pink and red diamonds.[40] In order of rarity, yellow diamond is followed by brown, colorless, then by blue, green, black, pink, orange, purple, and red.[32] "Black", or Carbonado, diamonds are not truly black, but rather contain numerous dark inclusions that give the gems their dark appearance. Colored diamonds contain impurities or structural defects that cause the coloration, while pure or nearly pure diamonds are transparent and colorless. Most diamond impurities replace a carbon atom in the crystal lattice, known as a carbon flaw. The most common impurity, nitrogen, causes a slight to intense yellow coloration depending upon the type and concentration of nitrogen present.[32] The Gemological Institute of America (GIA) classifies low saturation yellow and brown diamonds as diamonds in the *normal color range*, and applies a grading scale from "D" (colorless) to "Z" (light yellow). Diamonds of a different color, such as blue, are called *fancy colored* diamonds, and fall under a different grading scale.[32]

In 2008, the Wittelsbach Diamond, a 35.56-carat (7.112 g) blue diamond once belonging to the King of Spain, fetched over US$24 million at a Christie's auction.[41] In May 2009, a 7.03-carat (1.406 g) blue diamond fetched the highest price per carat ever paid for a diamond when it was sold at auction for 10.5 million Swiss francs (6.97 million euro or US$9.5 million at the time).[42] That record was however beaten the same year: a 5-carat (1.0 g) vivid pink diamond was sold for $10.8 million in Hong Kong on December 1, 2009.[43]

Identification

Diamonds can be identified by their high thermal conductivity. Their high refractive index is also indicative, but other materials have similar refractivity. Diamonds cut glass, but this does not positively identify a diamond because other materials, such as quartz, also lie above glass on the Mohs scale and can also cut it. Diamonds can scratch other diamonds, but this can result in damage to one or both stones. Hardness tests are infrequently used in practical gemology because of their potentially destructive nature.[28] The extreme hardness and high value of diamond means that gems are typically polished slowly using painstaking traditional techniques and greater attention to detail than is the case with most other gemstones;[10] these tend to result in extremely flat, highly polished facets with exceptionally sharp facet edges. Diamonds also possess an extremely high refractive index and fairly high dispersion. Taken together, these factors affect the overall appearance of a polished diamond and most diamantaires still rely upon skilled use of a loupe (magnifying glass) to identify diamonds 'by eye'.[44]

1.2.3 Industry

A round brilliant cut diamond set in a ring

See also: Diamonds as an investment

The diamond industry can be separated into two distinct categories: one dealing with gem-grade diamonds and another for industrial-grade diamonds. Both markets value diamonds differently.

Gem-grade diamonds

Main article: Diamond (gemstone)

A large trade in gem-grade diamonds exists. Unlike other commodities, such as most precious metals, there is a substantial mark-up in the retail sale of gem diamonds.[45] There is a well-established market for resale of polished diamonds (e.g. pawnbroking, auctions, second-hand jewelry stores, diamantaires, bourses, etc.). One hallmark of the trade in gem-quality diamonds is its remarkable concentration: wholesale trade and diamond cutting is limited to just a few locations; in 2003, 92% of the world's diamonds were cut and polished in Surat, India.[46] Other important centers of diamond cutting and trading are the Antwerp diamond district in Belgium, where the International Gemological Institute is based, London, the Diamond District in New York City, Tel Aviv, and Amsterdam. A single company – De Beers – controls a significant proportion of the trade in diamonds.[47] They are based in Johannesburg, South Africa and London, England. One contributory factor is the geological nature of diamond deposits: several large primary kimberlite-pipe mines each account for significant portions of market share (such as the Jwaneng mine in Botswana, which is a single large pit operated by De Beers that can produce between 12,500,000 carats (2,500 kg) to 15,000,000 carats (3,000 kg) of diamonds per year,[48]) whereas secondary alluvial diamond deposits tend to be fragmented amongst many different operators because they can be dispersed over many hundreds of square kilometers (e.g., alluvial deposits in Brazil).

The production and distribution of diamonds is largely consolidated in the hands of a few key players, and concentrated in traditional diamond trading centers, the most important being Antwerp, where 80% of all rough diamonds, 50% of all cut diamonds and more than 50% of all rough, cut and industrial diamonds combined are handled.[49] This makes Antwerp a de facto "world diamond capital".[50] Another important diamond center is New York City, where almost 80% of the world's diamonds are sold, including auction sales.[49] The DeBeers company, as the world's largest diamond miner holds a dominant position in the industry, and has done so since soon after its founding in 1888 by the British imperialist Cecil Rhodes. De Beers owns or controls a significant portion of the world's rough diamond production facilities (mines) and distribution channels for gem-quality diamonds. The Diamond Trading Company (DTC) is a subsidiary of De Beers and markets rough diamonds from De Beers-operated mines. De Beers and its subsidiaries own mines that produce some 40% of annual world diamond production. For most of the 20th century over 80% of the world's rough diamonds passed through De Beers,[51] but by 2001–2009 the figure had decreased to around 45%,[52] and by 2013 the company's market share had further decreased to around 38% in value terms and even less by volume.[53] De Beers sold off the vast majority of its diamond stockpile in the late 1990s – early 2000s[54] and the remainder largely represents working stock (diamonds that are being sorted before sale).[55] This was well documented in the press[56] but remains little known to the general public.

As a part of reducing its influence, De Beers withdrew from purchasing diamonds on the open market in 1999 and ceased, at the end of 2008, purchasing Russian diamonds mined by the largest Russian diamond company Alrosa.[57] As of January 2011, De Beers states that it only sells diamonds from the following four countries: Botswana, Namibia, South Africa and Canada.[58] Alrosa had to suspend their sales in October 2008 due to the global energy crisis,[59] but the company reported that it had resumed selling rough diamonds on the open market by October 2009.[60] Apart from Alrosa, other important diamond mining companies include BHP Billiton, which is the world's largest mining company;[61] Rio Tinto Group, the owner of Argyle (100%), Diavik (60%), and Murowa (78%) diamond mines;[62] and Petra Diamonds, the owner of several major diamond mines in Africa.

Diamond polisher in Amsterdam

Further down the supply chain, members of The World Federation of Diamond Bourses (WFDB) act as a medium for wholesale diamond exchange, trading both polished and rough diamonds. The WFDB consists of independent diamond bourses in major cutting centers such as Tel Aviv, Antwerp, Johannesburg and other cities across the USA, Europe and Asia.[32] In 2000, the WFDB and The International Diamond Manufacturers Association established the World Diamond Council to prevent the trading of diamonds used to fund war and inhumane acts. WFDB's additional activities include sponsoring the World Diamond Congress every two years, as well as the establishment of the *International Diamond Council* (IDC) to oversee diamond grading.

Once purchased by Sightholders (which is a trademark term referring to the companies that have a three-year supply contract with DTC), diamonds are cut and polished in preparation for sale as gemstones ('industrial' stones are regarded as a by-product of the gemstone market; they are used for abrasives).[63] The cutting and polishing of rough diamonds is a specialized skill that is concentrated in a limited number of locations worldwide.[63] Traditional diamond cutting centers are Antwerp, Amsterdam, Johannesburg, New York City, and Tel Aviv. Recently, diamond cutting centers have been established in China, India, Thailand, Namibia and Botswana.[63] Cutting centers with lower cost of labor, notably Surat in Gujarat, India, handle a larger number of smaller carat diamonds, while smaller quantities of larger or more valuable diamonds are more likely to be handled in Europe or North America. The recent expansion of this industry in India, employing low cost labor, has allowed smaller diamonds to be prepared as gems in greater quantities than was previously economically feasible.[49]

Diamonds which have been prepared as gemstones are sold on diamond exchanges called *bourses*. There are 28 registered diamond bourses in the world.[64] Bourses are the final tightly controlled step in the diamond supply chain; wholesalers and even retailers are able to buy relatively small lots of diamonds at the bourses, after which they are prepared for final sale to the consumer. Diamonds can be sold already set in jewelry, or sold unset ("loose"). According to the Rio Tinto Group, in 2002 the diamonds produced and released to the market were valued at US$9 billion as rough diamonds, US$14 billion after being cut and polished, US$28 billion in wholesale diamond jewelry, and US$57 billion in retail sales.[65]

Cutting Main articles: Diamond cutting and Diamond cut

Mined rough diamonds are converted into gems through a multi-step process called "cutting". Diamonds are extremely hard, but also brittle and can be split up by a single blow. Therefore, diamond cutting is traditionally considered as a delicate procedure requiring skills, scientific knowledge, tools and experience. Its final goal is to produce a faceted jewel where the specific angles between the facets would optimize the diamond luster, that is dispersion of white light, whereas the number and area of facets would determine the weight of the final product. The weight reduction upon cutting is significant and can

The Darya-I-Nur Diamond—an example of unusual diamond cut and jewelry arrangement be of the order of 50%.[66] Several possible shapes are considered, but the final decision is often determined not only by scientific, but also practical considerations. For example the diamond might be intended for display or for wear, in a ring or a necklace, singled or surrounded by other gems of certain color and shape.[67]

The most time-consuming part of the cutting is the preliminary analysis of the rough stone. It needs to address a large number of issues, bears much responsibility, and therefore can last years in case of unique diamonds. The following issues are considered:

- The hardness of diamond and its ability to cleave strongly depend on the crystal orientation. Therefore, the crystallographic structure of the diamond to be cut is analyzed using X-ray diffraction to choose the optimal cutting directions.
- Most diamonds contain visible non-diamond inclusions and crystal flaws. The cutter has to decide which flaws are to be removed by the cutting and which could be kept.
- The diamond can be split by a single, well calculated blow of a hammer to a pointed tool, which is quick, but risky. Alternatively, it can be cut with a diamond saw, which is a more reliable but tedious procedure.[67][68]

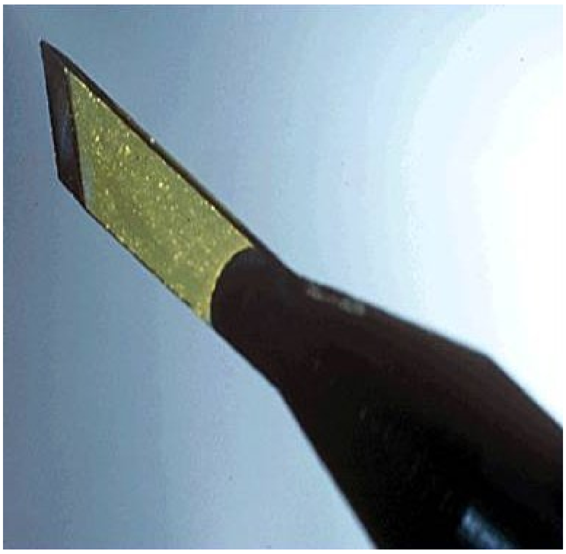
After initial cutting, the diamond is shaped in numerous stages of polishing. Unlike cutting, which is a responsible but quick operation, polishing removes material by gradual erosion and is extremely time consuming. The associated technique is well developed; it is considered as a routine and can be performed by technicians.[69] After polishing, the diamond is reexamined for possible flaws, either remaining or induced by the process. Those flaws are concealed through various diamond enhancement techniques, such as repolishing, crack filling, or clever arrangement of the stone in the jewelry. Remaining non-diamond inclusions are removed through laser drilling and filling of the voids produced.[28]

Marketing Marketing has significantly affected the image of diamond as a valuable commodity.

N. W. Ayer & Son, the advertising firm retained by De Beers in the mid-20th century, succeeded in reviving the American diamond market. And the firm created new markets in countries where no diamond tradition had existed before. N. W. Ayer's marketing included product placement, advertising focused on the diamond product itself rather than the De Beers brand, and associations with celebrities and royalty. Without advertising the De Beers brand, De Beers was also advertising its competitors' diamond products as well.[70] De Beers' market share dipped temporarily to 2nd place in the global market below Alrosa in the aftermath of the global economic crisis of 2008, down to less than 29% in terms of carats mined, rather than sold.[71] The campaign lasted for decades but was effectively discontinued by early 2011. De Beers still advertises diamonds, but the advertising now mostly promotes its own brands, or licensed product lines, rather than completely "generic" diamond products.[71] The campaign was perhaps best captured by the slogan "a diamond is forever".[7] This slogan is now being used by De Beers Diamond Jewelers,[72] a jewelry firm which is a 50%/50% joint venture between the De Beers mining company and LVMH, the luxury goods conglomerate.

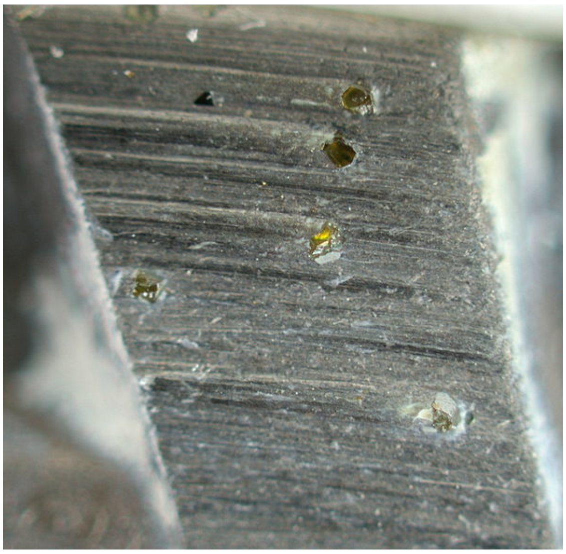
Brown-colored diamonds constituted a significant part of the diamond production, and were predominantly used for industrial purposes. They were seen as worthless for jewelry (not even being assessed on the diamond color scale). After the development of Argyle diamond mine in Australia in 1986, and marketing, brown diamonds have become acceptable gems.[73][74] The change was mostly due to the numbers: the Argyle mine, with its 35,000,000 carats (7,000 kg) of diamonds per year, makes about one-third of global production of natural diamonds;[75] 80% of Argyle diamonds are brown.[76]

Industrial-grade diamonds

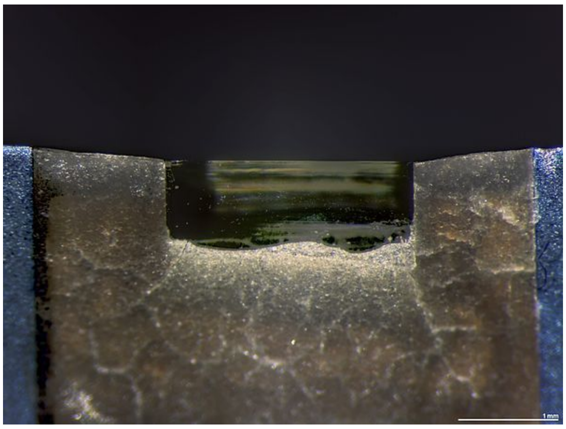


A scalpel with synthetic diamond blade

Industrial diamonds are valued mostly for their hardness and thermal conductivity, making many of the gemological characteristics of diamonds, such as the 4 Cs, irrelevant for most applications. 80% of mined diamonds (equal to about 135,000,000 carats (27,000 kg) annually), are unsuitable for use as gemstones, and used industrially.[77] In addition to mined diamonds, synthetic diamonds found industrial applications almost immediately after their invention in the 1950s; another 570,000,000 carats (114,000 kg) of synthetic diamond is produced annually for industrial use (in 2004; in 2014



Close-up photograph of an angle grinder blade with tiny diamonds shown embedded in the metal



A diamond knife blade used for cutting ultrathin sections (typically 70 to 350 nm for transmission electron microscopy.

it's 4,500,000,000 carats (900,000 kg), 90% by produced in China). Approximately 90% of diamond grinding grit is currently of synthetic origin.[78]

The boundary between gem-quality diamonds and industrial diamonds is poorly defined and partly depends on market conditions (for example, if demand for polished diamonds is high, some lower-grade stones will be polished into low-quality or small gemstones rather than being sold for industrial use). Within the category of industrial diamonds, there is a sub-category comprising the lowest-quality, mostly opaque stones, which are known as bort.[79]

Industrial use of diamonds has historically been associated with their hardness, which makes diamond the ideal material for cutting and grinding tools. As the hardest known naturally occurring material, diamond can be used to polish, cut, or wear away any material, including other diamonds. Common industrial applications of this property include diamond-tipped drill bits and saws, and the use of diamond powder as an abrasive. Less expensive industrial-grade diamonds, known as bort, with more flaws and poorer color than gems, are used for such purposes.[80] Diamond is not suitable for machining ferrous alloys at high speeds, as carbon is soluble in iron at the high temperatures created by high-speed machining, leading to greatly increased wear on diamond tools compared to alternatives.[81]

Specialized applications include use in laboratories as containment for high pressure experiments (see diamond anvil cell), high-performance bearings, and limited use in specialized windows.[79] With the continuing advances being made in the production of synthetic diamonds, future applications are becoming feasible. The high thermal conductivity of diamond makes it suitable as a heat sink for integrated circuits in electronics.[82]

Mining

See also: List of diamond mines and Exploration diamond drilling

Approximately 130,000,000 carats (26,000 kg) of diamonds are mined annually, with a total value of nearly US$9 billion, and about 100,000 kg (220,000 lb) are synthesized annually.[83]

Roughly 49% of diamonds originate from Central and Southern Africa, although significant sources of the mineral have been discovered in Canada, India, Russia, Brazil, and Australia.[78] They are mined from kimberlite and lamproite volcanic pipes, which can bring diamond crystals, originating from deep within the Earth where high pressures and temperatures enable them to form, to the surface. The mining and distribution of natural diamonds are subjects of frequent controversy such as concerns over the sale of *blood diamonds* or *conflict diamonds* by African paramilitary groups.[84] The diamond supply chain is controlled by a limited number of powerful businesses, and is also highly concentrated in a small number of locations around the world.

Only a very small fraction of the diamond ore consists of actual diamonds. The ore is crushed, during which care is required not to destroy larger diamonds, and then sorted by density. Today, diamonds are located in the diamond-rich density fraction with the help of X-ray fluorescence, after which the final sorting steps are done by hand. Before the use of X-rays became commonplace,[66] the separation was done with grease belts; diamonds have a stronger tendency to stick to grease than the other minerals in the ore.[32]

Historically, diamonds were found only in alluvial deposits in Guntur and Krishna district of the Krishna River delta in Southern India.[85] India led the world in diamond production from the time of their discovery in approximately the 9th century BC[4][86] to the mid-18th century

Siberia's Udachnaya diamond mine

AD, but the commercial potential of these sources had been exhausted by the late 18th century and at that time India was eclipsed by Brazil where the first non-Indian diamonds were found in 1725.[4] Currently, one of the most prominent Indian mines is located at Panna.[87]

Diamond extraction from primary deposits (kimberlites and lamproites) started in the 1870s after the discovery of the Diamond Fields in South Africa.[88] Production has increased over time and now an accumulated total of 4,500,000,000 carats (900,000 kg) have been mined since that date.[89] Twenty percent of that amount has been mined in the last five years, and during the last 10 years, nine new mines have started production; four more are waiting to be opened soon. Most of these mines are located in Canada, Zimbabwe, Angola, and one in Russia.[89]

In the U.S., diamonds have been found in Arkansas, Colorado, Wyoming, and Montana.[90][91] In 2004, the discovery of a microscopic diamond in the U.S. led to the January 2008 bulk-sampling of kimberlite pipes in a remote part of Montana.[91]

Today, most commercially viable diamond deposits are in Russia (mostly in Sakha Republic, for example Mir pipe and Udachnaya pipe), Botswana, Australia (Northern and Western Australia) and the Democratic Republic of Congo.[92] In 2005, Russia produced almost one-fifth of the global diamond output, reports the British Geological Survey. Australia boasts the richest diamantiferous pipe, with production from the Argyle diamond mine reaching peak levels of 42 metric tons per year in the 1990s.[90][93] There are also commercial deposits being actively mined in the Northwest Territories of Canada and Brazil.[78] Diamond prospectors continue to search the globe for diamond-bearing kimberlite and lamproite pipes.

Political issues

Main articles: Kimberley Process, Blood diamond and Child labour in the diamond industry

Unsustainable diamond mining in Sierra Leone

In some of the more politically unstable central African and west African countries, revolutionary groups have taken control of diamond mines, using proceeds from diamond sales to finance their operations. Diamonds sold through this process are known as *conflict diamonds* or *blood diamonds*.[84] Major diamond trading corporations continue to fund and fuel these conflicts by doing business with armed groups. In response to public concerns that their diamond purchases were contributing to war and human rights abuses in central and western Africa, the United Nations, the diamond industry and diamond-trading nations introduced the Kimberley Process in 2002.[94] The Kimberley Process aims to ensure that conflict diamonds do not become intermixed with the diamonds not controlled by such rebel groups. This is done by requiring diamond-producing countries to provide proof that the money they make from selling the diamonds is not used to fund criminal or revolutionary activities. Although the Kimberley Process has been moderately successful in limiting the number of conflict diamonds entering the market, some still find their way in. Conflict diamonds constitute 2–3% of all diamonds traded.[95] Two major flaws still hinder the effectiveness of the Kimberley Process: (1) the relative ease of smuggling diamonds across African borders, and (2) the violent nature of diamond mining in nations that are not in a technical state of war and whose diamonds are therefore considered “clean”.[94]

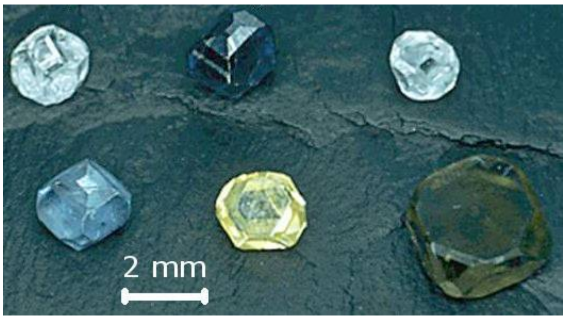
The Canadian Government has set up a body known as Canadian Diamond Code of Conduct[96] to help authenticate Canadian diamonds. This is a stringent tracking system of diamonds and helps protect the “conflict free” label of Canadian diamonds.[97]

1.2.4 Synthetics, simulants, and enhancements

Synthetics

Main article: Synthetic diamond

Synthetic diamonds are diamonds manufactured in a laboratory, as opposed to diamonds mined from the Earth. The gemological and industrial uses of diamond have



Synthetic diamonds of various colors grown by the high-pressure high-temperature technique

created a large demand for rough stones. This demand has been satisfied in large part by synthetic diamonds, which have been manufactured by various processes for more than half a century. However, in recent years it has become possible to produce gem-quality synthetic diamonds of significant size.[13] It is possible to make colorless synthetic gemstones that, on a molecular level, are identical to natural stones and so visually similar that only a gemologist with special equipment can tell the difference.[98]

The majority of commercially available synthetic diamonds are yellow and are produced by so-called High Pressure High Temperature (HPHT) processes.[99] The yellow color is caused by nitrogen impurities. Other colors may also be reproduced such as blue, green or pink, which are a result of the addition of boron or from irradiation after synthesis.[100]

Colorless gem cut from diamond grown by chemical vapor deposition

Another popular method of growing synthetic diamond is chemical vapor deposition (CVD). The growth occurs under low pressure (below atmospheric pressure). It involves feeding a mixture of gases (typically 1 to 99 methane to hydrogen) into a chamber and splitting them to chemically active radicals in a plasma ignited by microwaves, hot filament, arc discharge, welding torch or laser.[101] This method is mostly used for coatings, but can also produce single crystals several millimeters in size (see picture).[83]

As of 2010, nearly all 5,000 million carats (1,000 tonnes) of synthetic diamonds produced per year are for industrial use. Around 50% of the 133 million carats of natural diamonds mined per year end up in industrial use.[98][102] The cost of mining a natural colorless diamond runs about $40 to $60 per carat, and the cost to produce a synthetic, gem-quality colorless diamond is about $2,500 per carat.[98] However, a purchaser is more likely to encounter a synthetic when looking for a fancy-colored diamond because nearly all synthetic diamonds are fancy-colored, while only 0.01% of natural diamonds are.[103]

Simulants

Main article: Diamond simulant

A diamond simulant is a non-diamond material that is used to simulate the appearance of a diamond, and may be referred to as diamante. Cubic zirconia is the most common. The gemstone Moissanite (silicon carbide) can be treated as a diamond simulant, though more costly to produce than cubic zirconia. Both are produced synthetically.[104]

Gem-cut synthetic silicon carbide set in a ring

Enhancements

Main article: Diamond enhancement

Diamond enhancements are specific treatments performed on natural or synthetic diamonds (usually those already cut and polished into a gem), which are designed to better the gemological characteristics of the stone in one or more ways. These include laser drilling to remove inclusions, application of sealants to fill cracks, treatments to improve a white diamond's color grade, and treatments to give fancy color to a white diamond.[105]

Coatings are increasingly used to give a diamond simulant such as cubic zirconia a more “diamond-like” appearance. One such substance is diamond-like carbon—an amorphous carbonaceous material that has some physical properties similar to those of the diamond. Advertising suggests that such a coating would transfer some of these diamond-like properties to the coated stone, hence enhancing the diamond simulant. Techniques such as Raman spectroscopy should easily identify such a treatment.[106]

Identification

Early diamond identification tests included a scratch test relying on the superior hardness of diamond. This test is destructive, as a diamond can scratch another diamond, and is rarely used nowadays. Instead, diamond identification relies on its superior thermal conductivity. Electronic thermal probes are widely used in the gemological centers to separate diamonds from their imitations. These probes consist of a pair of battery-powered thermistors mounted in a fine copper tip. One thermistor functions as a heating device while the other measures the temperature of the copper tip: if the stone being tested is a diamond, it will conduct the tip's thermal energy rapidly enough to produce a measurable temperature drop. This test takes about 2–3 seconds.[107]

Whereas the thermal probe can separate diamonds from most of their simulants, distinguishing between various types of diamond, for example synthetic or natural, irradiated or non-irradiated, etc., requires more advanced, optical techniques. Those techniques are also used for some diamonds simulants, such as silicon carbide, which pass the thermal conductivity test. Optical techniques can distinguish between natural diamonds and synthetic diamonds. They can also identify the vast majority of treated natural diamonds.[108] "Perfect" crystals (at the atomic lattice level) have never been found, so both natural and synthetic diamonds always possess characteristic imperfections, arising from the circumstances of their crystal growth, that allow them to be distinguished from each other.[109]

Laboratories use techniques such as spectroscopy, microscopy and luminescence under shortwave ultraviolet light to determine a diamond's origin.[108] They also use specially made instruments to aid them in the identification process. Two screening instruments are the *DiamondSure* and the *DiamondView*, both produced by the DTC and marketed by the GIA.[110]

Several methods for identifying synthetic diamonds can be performed, depending on the method of production and the color of the diamond. CVD diamonds can usually be identified by an orange fluorescence. D-J colored diamonds can be screened through the Swiss Gemmological Institute's[111] Diamond Spotter. Stones in the D-Z color range can be examined through the DiamondSure UV/visible spectrometer, a tool developed by De Beers.[109] Similarly, natural diamonds usually have minor imperfections and flaws, such as inclusions of foreign material, that are not seen in synthetic diamonds.

Screening devices based on diamond type detection can be used to make a distinction between diamonds that are certainly natural and diamonds that are potentially synthetic. Those potentially synthetic diamonds require more investigation in a specialized lab. Examples of commercial screening devices are D-Screen (WTOCD / HRD Antwerp) and Alpha Diamond Analyzer (Bruker / HRD Antwerp).

1.2.5 Stolen diamonds

Occasionally large thefts of diamonds take place. In February 2013 armed robbers carried out a raid at Brussels Airport and escaped with gems estimated to be worth \$50m (£32m; 37m euros). The gang broke through a perimeter fence and raided the cargo hold of a Swiss-bound plane. The gang have since been arrested and large amounts of cash and diamonds recovered.[112]

The identification of stolen diamonds presents a set of difficult problems. Rough diamonds will have a distinctive shape depending on whether their source is a mine or from an alluvial environment such as a beach or river - alluvial diamonds have smoother surfaces than those that have been mined. Determining the provenance of cut and polished stones is much more complex.

The Kimberley Process was developed to monitor the trade in rough diamonds and prevent their being used to fund violence. Before exporting, rough diamonds are certificated by the government of the country of origin. Some countries, such as Venezuela, are not party to the agreement. The Kimberley Process does not apply to local sales of rough diamonds within a country.

Diamonds may be etched by laser with marks invisible to the naked eye. Lazare Kaplan, a US-based company, developed this method. However, whatever is marked on a diamond can readily be removed.[113][114]

1.2.6 See also

- List of diamonds
- List of minerals

1.2.7 References

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1.2.9 External links

- Properties of diamond: Ioffe database
- “A Contribution to the Understanding of Blue Fluorescence on the Appearance of Diamonds”. (2007) Gemological Institute of America (GIA)
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- Have You Ever Tried to Sell a Diamond?

1.3 Gold

“Element 79” redirects here. For the short story and anthology by Fred Hoyle, see Element 79 (anthology). This article is about the metal. For the color, see Gold (color). For other uses, see Gold (disambiguation).

Gold is a chemical element with symbol **Au** and atomic number 79. It is a bright yellow dense, soft, malleable and ductile metal. The properties remain when exposed to air or water. Chemically, gold is a transition metal and a group 11 element. It is one of the least reactive chemical elements, and is solid under standard conditions. The metal therefore occurs often in free elemental (native) form, as nuggets or grains, in rocks, in veins and in alluvial deposits. It occurs in a solid solution series with the native element silver (as electrum) and also naturally alloyed with copper and palladium. Less commonly, it occurs in minerals as gold compounds, often with tellurium (gold tellurides).

Gold's atomic number of 79 makes it one of the higher atomic number elements that occur naturally in the universe, and is traditionally thought to have been produced in supernova nucleosynthesis to seed the dust from which the Solar System formed. Because the Earth was molten when it was just formed, almost all of the gold present in the Earth sank into the planetary core. Therefore most of the gold that is present today in the Earth's crust and mantle is thought to have been delivered to Earth later, by asteroid impacts during the late heavy bombardment, about 4 billion years ago.

Gold resists attacks by individual acids, but it can be dissolved by aqua regia (nitro-hydrochloric acid), so named because it dissolves gold into a soluble gold tetrachloride cation. Gold compounds also dissolve in alkaline solutions of cyanide, which have been used in mining. It dissolves in mercury, forming amalgam alloys; it is insoluble in nitric acid, which dissolves silver and base metals, a property that has long been used to confirm the presence of gold in items, giving rise to the term *acid test*.

This metal has been a valuable and highly sought-after precious metal for coinage, jewelry, and other arts since long before the beginning of recorded history. In the past, a gold standard was often implemented as a monetary policy within and between nations, but gold coins ceased to be minted as a circulating currency in the 1930s, and the world gold standard (see article for details) was finally abandoned for a fiat currency system after 1976. The historical value of gold was rooted in its medium rarity, easy handling and minting, easy smelting, non-corrosiveness, distinct color, and non-reactivity to other elements.

A total of 174,100 tonnes of gold have been mined in human history, according to GFMS as of 2012.[3] This is roughly equivalent to 5.6 billion troy ounces or, in terms of volume, about 9200 m^3, or a cube 21 m on a side. The world consumption of new gold produced is about 50% in jewelry, 40% in investments, and 10% in industry.[4]

Gold's high malleability, ductility, resistance to corrosion and most other chemical reactions, and conductivity of electricity have led to its continued use in corrosion resistant electrical connectors in all types of computerized devices (its chief industrial use). Gold is also used in infrared shielding, colored-glass production, and gold leafing. Certain gold salts are still used as anti-inflammatories in medicine.

1.3.1 Etymology

"Gold" is cognate with similar words in many Germanic languages, deriving via Proto-Germanic _*gulþą_ from Proto-Indo-European _*ǵ^{h}elh$_3$-_ ("to shine, to gleam; to be yellow or green").[5][6]

The symbol **Au** is from the Latin: *aurum*, the Latin word for "gold".[7] The Proto-Indo-European ancestor of *aurum* was _*h_2é-$h_2$us-o-_, meaning "glow". This word is derived from the same root (Proto-Indo-European _*h_2u̯es-_ "to dawn") as _*$h_2$éu̯sōs_, the ancestor of the Latin word Aurora, "dawn".[8] This etymological relationship is presumably behind the frequent claim in scientific publications that *aurum* meant "shining dawn".[9][10]

1.3.2 Characteristics

Gold is the most malleable of all metals; a single gram can be beaten into a sheet of 1 square meter, or an ounce into 300 square feet. Gold leaf can be beaten thin enough to become transparent. The transmitted light appears greenish blue, because gold strongly reflects yellow and red.[11] Such semi-transparent sheets also strongly reflect infrared light, making them useful as infrared (radiant heat) shields in visors of heat-resistant suits, and in sun-visors for spacesuits.[12]

Gold readily dissolves in mercury at room temperature to form an amalgam, and forms alloys with many other metals at higher temperatures. These alloys can be produced to modify the hardness and other metallurgical properties, to control melting point or to create exotic colors.[13] Gold is a good conductor of heat and electricity and reflects infrared radiation strongly. Chemically, it is unaffected by air, moisture and most corrosive reagents, and is therefore well suited for use in coins and jewelry and as a protective coating on other, more reactive metals. However, it is not chemically inert. Gold is almost insoluble, but can be dissolved in aqua regia or solutions of sodium or potassium cyanide, for example.

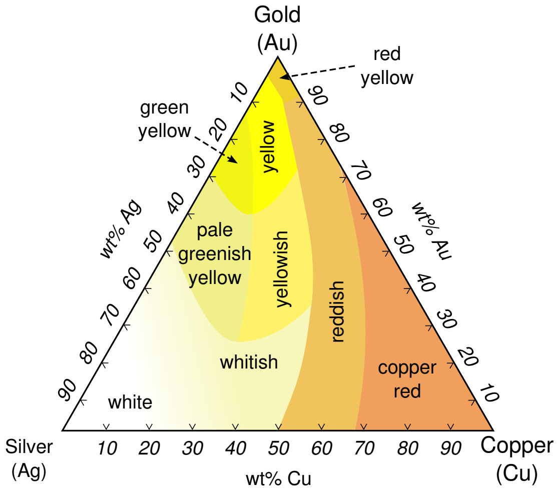
Common oxidation states of gold include +1 (gold(I) or aurous compounds) and +3 (gold(III) or auric compounds). Gold ions in solution are readily reduced and precipitated as metal by adding any other metal as the reducing agent. The added metal is oxidized and dissolves, allowing the gold to be displaced from solution and be recovered as a solid precipitate.

In addition, gold is very dense, a cubic meter has a mass of 19,300 kg. By comparison, the density of lead is 11,340 kg/m^3, and that of the densest element, osmium, is 22,588 ± 15 kg/m^3.[14]

Color

Whereas most other pure metals are gray or silvery white, gold is yellow. This color is determined by the density of loosely bound (valence) electrons; those electrons oscillate as a collective "plasma" medium described in terms of a quasiparticle called plasmon. The frequency of these oscillations lies in the ultraviolet range for most metals, but it falls into the visible range for gold due to subtle relativistic effects that affect the orbitals around gold atoms.[15][16] Similar effects impart a golden hue to metallic caesium.

Common colored gold alloys such as rose gold can be created by the addition of various amounts of copper and silver, as indicated in the triangular diagram to the left. Alloys containing palladium or nickel are also important in commercial jewelry as these produce white



Different colors of Ag-Au-Cu alloys

gold alloys. Less commonly, addition of manganese, aluminium, iron, indium and other elements can produce more unusual colors of gold for various applications.[13]

Isotopes

Main article: Isotopes of gold

Gold has only one stable isotope, ^{197}Au, which is also its only naturally occurring isotope. Thirty-six radioisotopes have been synthesized ranging in atomic mass from 169 to 205. The most stable of these is ^{195}Au with a half-life of 186.1 days. The least stable is ^{171}Au, which decays by proton emission with a half-life of 30 µs. Most of gold's radioisotopes with atomic masses below 197 decay by some combination of proton emission, α decay, and β^+ decay. The exceptions are ^{195}Au, which decays by electron capture, and ^{196}Au, which decays most often by electron capture (93%) with a minor β^- decay path (7%).[17] All of gold's radioisotopes with atomic masses above 197 decay by β^- decay.[18]

At least 32 nuclear isomers have also been characterized, ranging in atomic mass from 170 to 200. Within that range, only ^{178}Au, ^{180}Au, ^{181}Au, ^{182}Au, and ^{188}Au do not have isomers. Gold's most stable isomer is ^{198m2}Au with a half-life of 2.27 days. Gold's least stable isomer is ^{177m2}Au with a half-life of only 7 ns. ^{184m1}Au has three decay paths: β^+ decay, isomeric transition, and alpha decay. No other isomer or isotope of gold has three decay paths.[18]

1.3.3 Modern applications

The world consumption of new gold produced is about 50% in jewelry, 40% in investments, and 10% in industry.[4]

Jewelry

Main article: Jewelry

Moche gold necklace depicting feline heads. Larco Museum Collection. Lima-Peru

Because of the softness of pure (24k) gold, it is usually alloyed with base metals for use in jewelry, altering its hardness and ductility, melting point, color and other properties. Alloys with lower carat rating, typically 22k, 18k, 14k or 10k, contain higher percentages of copper or other base metals or silver or palladium in the alloy. Copper is the most commonly used base metal, yielding a redder color.[19]

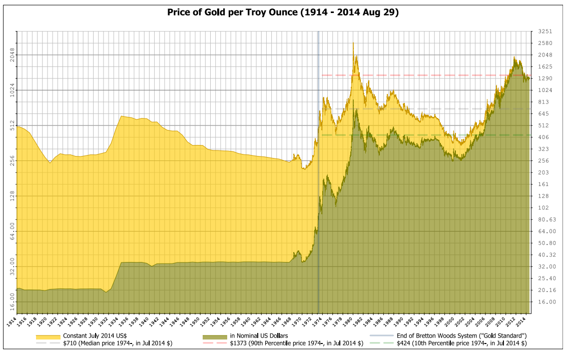
Eighteen-carat gold containing 25% copper is found in antique and Russian jewelry and has a distinct, though not dominant, copper cast, creating rose gold. Fourteen-carat gold-copper alloy is nearly identical in color to certain bronze alloys, and both may be used to produce police and other badges. Blue gold can be made by alloying with iron and purple gold can be made by alloying with aluminium, although rarely done except in specialized jewelry. Blue gold is more brittle and therefore more difficult to work with when making jewelry.[19]

Fourteen- and eighteen-carat gold alloys with silver alone appear greenish-yellow and are referred to as green gold. White gold alloys can be made with palladium or nickel. White 18-carat gold containing 17.3% nickel, 5.5% zinc and 2.2% copper is silvery in appearance. Nickel is toxic, however, and its release from nickel white gold is controlled by legislation in Europe.[19]

Alternative white gold alloys are available based on palladium, silver and other white metals,[19] but the palladium alloys are more expensive than those using nickel. High-carat white gold alloys are far more resistant to corrosion than are either pure silver or sterling silver. The Japanese craft of Mokume-gane exploits the color contrasts between laminated colored gold alloys to produce decorative wood-grain effects.

By 2014 the gold jewelry industry was escalating despite a dip in gold prices. Demand in the first quarter of 2014 pushed turnover to $23.7 billion according to a World Gold Council report.

Investment



Gold prices (US$ per troy ounce), in nominal US$ and inflation adjusted US$.

Main article: Gold as an investment

Many holders of gold store it in form of bullion coins or bars as a hedge against inflation or other economic disruptions. However, economist Martin Feldstein does not believe gold serves as a hedge against inflation or currency depreciation.[20]

The ISO 4217 currency code of gold is XAU.

Modern bullion coins for investment or collector purposes do not require good mechanical wear properties; they are typically fine gold at 24k, although the American Gold Eagle and the British gold sovereign continue to be minted in 22k (0.92) metal in historical tradition, and the South African Krugerand, first released in 1967, is also 22k (0.92).[21] The *special issue* Canadian Gold Maple Leaf coin contains the highest purity gold of any bullion coin, at 99.999% or 0.99999, while the *popular issue* Canadian Gold Maple Leaf coin has a purity of 99.99%.

Several other 99.99% pure gold coins are available. In 2006, the United States Mint began producing the American Buffalo gold bullion coin with a purity of 99.99%. The Australian Gold Kangaroos were first coined in 1986 as the Australian Gold Nugget but changed the reverse design in 1989. Other modern coins include the Austrian Vienna Philharmonic bullion coin and the Chinese Gold Panda.

Electronics connectors

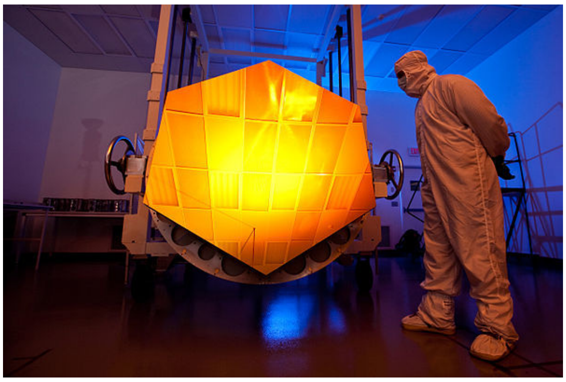
Only 10% of the world consumption of new gold produced goes to industry,[4] but by far the most important industrial use for new gold is in fabrication of corrosion-free electrical connectors in computers and other electrical devices. For example, according to the World Gold council, a typical cell phone may contain 50 mg of gold, worth about 50 cents. But since nearly one billion cell phones are produced each year, a gold value of 50 cents in each phone adds to $500 million in gold from just this application.[22]

Though gold is attacked by free chlorine, its good conductivity and general resistance to oxidation and corrosion in other environments (including resistance to non-chlorinated acids) has led to its widespread industrial use in the electronic era as a thin layer coating electrical connectors, thereby ensuring good connection. For example, gold is used in the connectors of the more expensive electronics cables, such as audio, video and USB cables. The benefit of using gold over other connector metals such as tin in these applications has been debated; gold connectors are often criticized by audio-visual experts as unnecessary for most consumers and seen as simply a marketing ploy. However, the use of gold in other applications in electronic sliding contacts in highly humid or corrosive atmospheres, and in use for contacts with a very high failure cost (certain computers, communications equipment, spacecraft, jet aircraft engines) remains very common.[23]

Besides sliding electrical contacts, gold is also used in electrical contacts because of its resistance to corrosion, electrical conductivity, ductility and lack of toxicity.[24] Switch contacts are generally subjected to more intense corrosion stress than are sliding contacts. Fine gold wires are used to connect semiconductor devices to their packages through a process known as wire bonding.

The concentration of free electrons in gold metal is 5.90×10^{22} cm^{-3}. Gold is highly conductive to electricity, and has been used for electrical wiring in some high-energy applications (only silver and copper are more conductive per volume, but gold has the advantage of corrosion resistance). For example, gold electrical wires were used during some of the Manhattan Project's atomic experiments, but large high current silver wires were used in the calutron isotope separator magnets in the project.

Non-electronic industry



Mirror for the future James Webb Space Telescope coated in gold to reflect infrared light

- Gold solder is used for joining the components of gold jewelry by high-temperature hard soldering or brazing. If the work is to be of hallmarking quality, gold solder must match the carat weight of the

The world's largest gold bar has a mass of 250 kg. Toi museum, Japan.

A gold nugget of 5 mm in diameter (bottom) can be expanded through hammering into a gold foil of about 0.5 square meters. Toi museum, Japan.

work, and alloy formulas are manufactured in most industry-standard carat weights to color match yellow and white gold. Gold solder is usually made in at least three melting-point ranges referred to as Easy, Medium and Hard. By using the hard, high-melting point solder first, followed by solders with progressively lower melting points, goldsmiths can assemble complex items with several separate soldered joints.

- Gold can be made into thread and used in embroidery.
- Gold produces a deep, intense red color when used as a coloring agent in cranberry glass.
- In photography, gold toners are used to shift the color of silver bromide black-and-white prints towards brown or blue tones, or to increase their stability. Used on sepia-toned prints, gold toners produce red tones. Kodak published formulas for several types of gold toners, which use gold as the chloride.[25]
- Gold is a good reflector of electromagnetic radiation such as infrared and visible light as well as radio waves. It is used for the protective coatings on many artificial satellites, in infrared protective faceplates in thermal protection suits and astronauts' helmets and in electronic warfare planes like the EA-6B Prowler.
- Gold is used as the reflective layer on some high-end CDs.
- Automobiles may use gold for heat shielding. McLaren uses gold foil in the engine compartment of its F1 model.[26]
- Gold can be manufactured so thin that it appears transparent. It is used in some aircraft cockpit windows for de-icing or anti-icing by passing electricity through it. The heat produced by the resistance of the gold is enough to deter ice from forming.[27]

Commercial chemistry

Gold is attacked by and dissolves in alkaline solutions of potassium or sodium cyanide, to form the salt gold cyanide—a technique that has been used in extracting metallic gold from ores in the cyanide process. Gold cyanide is the electrolyte used in commercial electroplating of gold onto base metals and electroforming.

Gold chloride (chloroauric acid) solutions are used to make colloidal gold by reduction with citrate or ascorbate ions. Gold chloride and gold oxide are used to make cranberry or red-colored glass, which, like colloidal gold suspensions, contains evenly sized spherical gold nanoparticles.[28]

Medicine

Gold (usually as the metal) is perhaps the most anciently administered medicine (apparently by shamanic practitioners)[29] and known to Dioscorides,[30][31] apparent paradoxes of the actual toxicology of the substance nevertheless suggests the possibility still of serious gaps in understanding of action on physiology.[32]

In medieval times, gold was often seen as beneficial for the health, in the belief that something so rare and beautiful could not be anything but healthy. Even some modern esotericists and forms of alternative medicine assign metallic gold a healing power.[33]

Only salts and radioisotopes of gold are of use in standard pharmacological value, since elemental (metallic) gold is inert to all chemicals it encounters inside the body (i.e., ingested gold cannot be attacked by stomach acid). Some gold salts do have anti-inflammatory properties and at present two are still used as pharmaceuticals in the treatment of arthritis and other similar conditions in the US (sodium aurothiomalate and auranofin). These drugs have been explored as a means to help to reduce the pain and swelling of rheumatoid arthritis, and also (historically) against tuberculosis and some parasites.[34]

Gold alloys are used in restorative dentistry, especially in tooth restorations, such as crowns and permanent bridges. The gold alloys' slight malleability facilitates the creation of a superior molar mating surface with other teeth and produces results that are generally more satisfactory than those produced by the creation of porcelain crowns. The use of gold crowns in more prominent teeth such as incisors is favored in some cultures and discouraged in others.

Colloidal gold preparations (suspensions of gold nanoparticles) in water are intensely red-colored, and can be made with tightly controlled particle sizes up to a few tens of nanometers across by reduction of gold chloride with citrate or ascorbate ions. Colloidal gold is used in research applications in medicine, biology and materials science. The technique of immunogold labeling exploits the ability of the gold particles to adsorb protein molecules onto their surfaces. Colloidal gold particles coated with specific antibodies can be used as probes for the presence and position of antigens on the surfaces of cells.[35] In ultrathin sections of tissues viewed by electron microscopy, the immunogold labels appear as extremely dense round spots at the position of the antigen.[36]

Gold, or alloys of gold and palladium, are applied as conductive coating to biological specimens and other non-conducting materials such as plastics and glass to be viewed in a scanning electron microscope. The coating, which is usually applied by sputtering with an argon plasma, has a triple role in this application. Gold's very high electrical conductivity drains electrical charge to earth, and its very high density provides stopping power for electrons in the electron beam, helping to limit the depth to which the electron beam penetrates the specimen. This improves definition of the position and topography of the specimen surface and increases the spatial resolution of the image. Gold also produces a high output of secondary electrons when irradiated by an electron beam, and these low-energy electrons are the most commonly used signal source used in the scanning electron microscope.[37]

The isotope gold-198 (half-life 2.7 days) is used, in nuclear medicine, in some cancer treatments and for treating other diseases.[38][39]

Food and drink

- Gold can be used in food and has the E number 175.[40]
- Gold leaf, flake or dust is used on and in some gourmet foods, notably sweets and drinks as decorative ingredient.[41] Gold flake was used by the nobility in medieval Europe as a decoration in food and drinks, in the form of leaf, flakes or dust, either to demonstrate the host's wealth or in the belief that something that valuable and rare must be beneficial for one's health.
- Danziger Goldwasser (German: Gold water of Danzig) or Goldwasser (English: Goldwater) is a traditional German herbal liqueur[42] produced in what is today Gdańsk, Poland, and Schwabach, Germany, and contains flakes of gold leaf. There are also some expensive (~$1000) cocktails which contain flakes of gold leaf.[43] However, since metallic gold is inert to all body chemistry, it has no taste, it provides no nutrition, and it leaves the body unaltered.[44]

1.3.4 Monetary exchange (historical)

Gold is commonly formed into bars for use in monetary exchange.

Gold has been widely used throughout the world as money, for efficient indirect exchange (versus barter), and to store wealth in hoards. For exchange purposes,

Two golden 20 kr coins from the Scandinavian Monetary Union, which was based on a gold standard. The coin to the left is Swedish and the right one is Danish.

mints produce standardized gold bullion coins, bars and other units of fixed weight and purity.

The first coins containing gold were struck in Lydia, Asia Minor, around 600 BC.[45] The *talent* coin of gold in use during the periods of Grecian history both before and during the time of the life of Homer weighed between 8.42 and 8.75 grams.[46] From an earlier preference in using silver, European economies re-established the minting of gold as coinage during the thirteenth and fourteenth centuries.[47]

Bills (that mature into gold coin) and gold certificates (convertible into gold coin at the issuing bank) added to the circulating stock of gold standard money in most 19th century industrial economies. In preparation for World War I the warring nations moved to fractional gold standards, inflating their currencies to finance the war effort. Post-war, the victorious countries, most notably Britain, gradually restored gold-convertibility, but international flows of gold via bills of exchange remained embargoed; international shipments were made exclusively for bilateral trades or to pay war reparations.

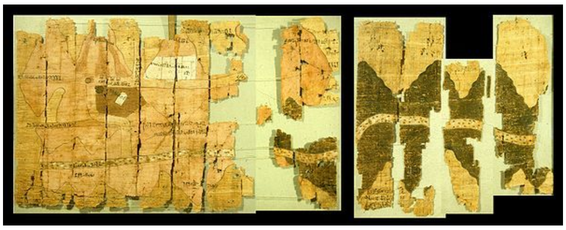
After World War II gold was replaced by a system of nominally convertible currencies related by fixed exchange rates following the Bretton Woods system. Gold standards and the direct convertibility of currencies to gold have been abandoned by world governments, led in 1971 by the United States' refusal to redeem its dollars in gold. Fiat currency now fills most monetary roles. Switzerland was the last country to tie its currency to gold; it backed 40% of its value until the Swiss joined the International Monetary Fund in 1999.[48]

Central banks continue to keep a portion of their liquid reserves as gold in some form, and metals exchanges such as the London Bullion Market Association still clear transactions denominated in gold, including future delivery contracts. Today, gold mining output is declining.[49] With the sharp growth of economies in the 20th century, and increasing foreign exchange, the world's gold reserves and their trading market have become a small fraction of all markets and fixed exchange rates of currencies to gold have been replaced by floating prices for gold and gold future contract. Though the gold stock grows by only 1 or 2% per year, very little metal is irretrievably consumed. Inventory above ground would satisfy many decades of industrial and even artisan uses at current prices.

The gold content of alloys is measured in carats (k). Pure gold is designated as 24k. English gold coins intended for circulation from 1526 into the 1930s were typically a standard 22k alloy called crown gold,[50] for hardness (American gold coins for circulation after 1837 contained the slightly lower amount of 0.900 fine gold, or 21.6 kt).[51]

Although the prices of some platinum group metals can be much higher, gold has long been considered the most desirable of precious metals, and its value has been used as the standard for many currencies. Gold has been used as a symbol for purity, value, royalty, and particularly roles that combine these properties. Gold as a sign of wealth and prestige was ridiculed by Thomas More in his treatise *Utopia*. On that imaginary island, gold is so abundant that it is used to make chains for slaves, tableware, and lavatory seats. When ambassadors from other countries arrive, dressed in ostentatious gold jewels and badges, the Utopians mistake them for menial servants, paying homage instead to the most modestly dressed of their party.

1.3.5 Cultural history



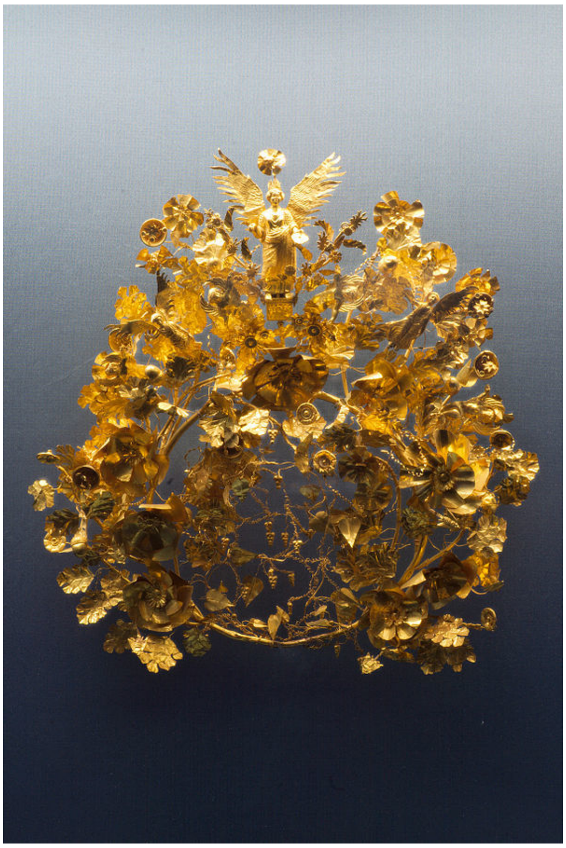
The Turin Papyrus Map

Gold artifacts found at the Nahal Kana cave cemetery dated during the 1980s, showed these to be from within the Chalcolithic, and considered the earliest find from the Levant (Gopher *et al.* 1990).[52] Gold artifacts in the Balkans also appear from the 4th millennium BC, such as those found in the Varna Necropolis near Lake Varna in Bulgaria, thought by one source (La Niece 2009) to be the earliest "well-dated" find of gold artifacts.[53] Gold artifacts such as the golden hats and the Nebra disk appeared in Central Europe from the 2nd millennium BC Bronze Age.

Egyptian hieroglyphs from as early as 2600 BC describe gold, which king Tushratta of the Mitanni claimed was "more plentiful than dirt" in Egypt.[54] Egypt and especially Nubia had the resources to make them major gold-producing areas for much of history. The earliest known

Funerary mask of Tutankhamun

Jason returns with the golden fleece on an Apulian red-figure calyx krater, ca. 340–330 BC.



Ancient Greek golden decorated crown, funerary or marriage material, 370–360 BC. From a grave in Armento, Campania

map is known as the Turin Papyrus Map and shows the plan of a gold mine in Nubia together with indications of the local geology. The primitive working methods are described by both Strabo and Diodorus Siculus, and included fire-setting. Large mines were also present across the Red Sea in what is now Saudi Arabia.

The legend of the golden fleece may refer to the use of fleeces to trap gold dust from placer deposits in the ancient world. Gold is mentioned frequently in the Old Testament, starting with Genesis 2:11 (at Havilah), the story of The Golden Calf and many parts of the temple including the Menorah and the golden altar. In the New Testament, it is included with the gifts of the magi in the first chapters of Matthew. The Book of Revelation 21:21 describes the city of New Jerusalem as having streets "made of pure gold, clear as crystal". Exploitation of gold in the south-east corner of the Black Sea is said to date from the time of Midas, and this gold was important in the establishment of what is probably the world's earliest coinage in Lydia around 610 BC.[55] From the 6th or 5th century BC, the Chu (state) circulated the Ying Yuan, one kind of square gold coin.

In Roman metallurgy, new methods for extracting gold on a large scale were developed by introducing hydraulic mining methods, especially in Hispania from 25 BC onwards and in Dacia from 106 AD onwards. One of their largest mines was at Las Medulas in León (Spain), where seven long aqueducts enabled them to sluice most of a large alluvial deposit. The mines at Roşia Montană in Transylvania were also very large, and until very recently, still mined by opencast methods. They also exploited smaller deposits in Britain, such as placer and hard-rock deposits at Dolaucothi. The various methods they used are well described by Pliny the Elder in his encyclopedia Naturalis Historia written towards the end of the first century AD.

During Mansa Musa's (ruler of the Mali Empire from 1312 to 1337) hajj to Mecca in 1324, he passed through Cairo in July 1324, and was reportedly accompanied by a camel train that included thousands of people and nearly a hundred camels where he gave away so much gold that it depressed the price in Egypt for over a decade.[56] A contemporary Arab historian remarked:

> Gold was at a high price in Egypt until they came in that year. The mithqal did not go below 25 dirhams and was generally above, but from that time its value fell and it cheapened in price and has remained cheap till now. The mithqal does not exceed 22 dirhams or less. This has been the state of affairs for about twelve years until this day by reason of the large amount of gold which they brought into Egypt and spent there [...].
> —Chihab Al-Umari, Kingdom of Mali[57]

The Portuguese overseas expansion started in 1415 with the taking of Ceuta, to control the gold trade coming across the desert. Although the caravan trade routes were then diverted, the Portuguese continued expansing southwards along the coast and eventually buying the gold directly (or less indirectly) from the Africans in the Gulf of Guinea.

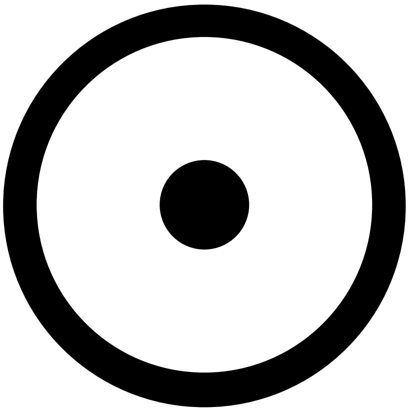
The European exploration of the Americas was fueled in no small part by reports of the gold ornaments displayed in great profusion by Native American peoples, especially in Mesoamerica, Peru, Ecuador and Colombia. The Aztecs regarded gold as literally the product of the gods, calling it "god excrement" (*teocuitlatl* in Nahuatl), and after Moctezuma II was killed, most of this gold was shipped to Spain.[58] However, for the indigenous peoples of North America gold was considered useless and they saw much greater value in other minerals which were directly related to their utility, such as obsidian, flint, and slate.[59] Rumors of cities filled with gold fueled legends of El Dorado.

Gold played a role in western culture, as a cause for desire and of corruption, as told in children's fables like Rumplestiltskin, where the peasant's daughter turns hay into gold, in return for giving up her child when she becomes a princess, and stealing the hen that lays golden eggs in Jack and the beanstalk.

The top prize at the Olympic games is the gold medal.

There is an age-old tradition of biting gold to test its authenticity. Although this is certainly not a professional way of examining gold, the *bite test* was not to check if the coin was gold (90% gold coins are fairly strong) but to see if the coin was gold plated lead. A lead coin would be very soft and thus teeth marks would result. Fake gold coins were a common problem before 1932 so weighing a coin and also sliding a coin through a "counterfeit detector" slot was common (making a lead coin thicker would add weight thus why slide it through a measured slot). Most establishments (especially US Western saloons) would never accept a gold (or silver) coin of high value before weighing such an item.

75% of all gold ever produced has been extracted since 1910.[60] It has been estimated that all gold ever refined would form a single cube 20 m (66 ft) on a side (equivalent to 8,000 m^3).[60]



Circled dot, the alchemical symbol for gold

One main goal of the alchemists was to produce gold from other substances, such as lead — presumably by the interaction with a mythical substance called the philosopher's stone. Although they never succeeded in this attempt, the alchemists promoted an interest in what can be done with substances, and this laid a foundation for today's chemistry. Their symbol for gold was the circle with a point at its center (☉), which was also the astrological symbol and the ancient Chinese character for the Sun.

Golden treasures have been rumored to be found at various locations, following tragedies such as the Jewish temple treasures in the Vatican, following the temple's destruction in 70 AD, a gold stash on the Titanic, the Nazi gold train – following World War II.

The Dome of the Rock on the Jerusalem temple site is covered with an ultra-thin golden glasure. The Sikh Golden temple, the Harmandir Sahib, is a building covered with gold. Similarly the Wat Phra Kaew emerald Budha temple in Thailand has ornamental gold statues walls and roofs. Some European king and queen's crowns were made of gold, and gold was used for the bridal crown since antiquity. An ancient Talmudic text circa 100 AD describes Rachel, Rabbi Akiba's wife asking for a "Jerusalem of Gold" (crown). A Greek burial crown made of gold was found in a grave circa 370 BC.

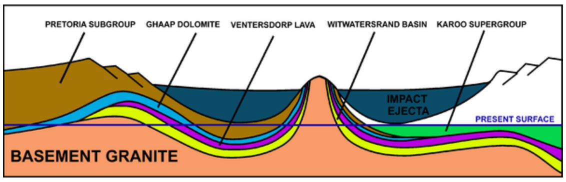
1.3.6 Occurrence

This 156-troy-ounce (4.9 kg) nugget, known as the Mojave Nugget, was found by an individual prospector in the Southern California Desert using a metal detector.

Gold's atomic number of 79 makes it one of the higher atomic number elements that occur naturally. Although traditionally, gold is thought to have formed by supernova nucleosynthesis.,[61] a new theory suggests that gold and other elements heavier than iron are made by the collision of neutron stars instead.[62][63] Either way, satellite spectrometers in theory detect the resulting gold, "but we have no spectroscopic evidence that [such] elements have truly been produced."[64]

These gold nucleogenesis theories hold that the resulting explosions scattered metal-containing dusts (including heavy elements like gold) into the region of space in which they later condensed into our solar system and the Earth.[65] Because the Earth was molten when it was just formed, almost all of the gold present on Earth sank into the core. Most of the gold that is present today in the Earth's crust and mantle is thought to have been delivered to Earth later, by asteroid impacts during the late heavy bombardment.[66][66][67][68][69][70]

The asteroid that formed Vredefort crater 2.020 billion years ago is often credited with seeding the Witwatersrand basin in South Africa with the richest gold deposits on earth.[71][72][73][74] However, the gold bearing Witwatersrand rocks were laid down between 700 and 950 million years before the Vredefort impact.[75][76] These gold bearing rocks had furthermore been covered by a thick layer of Ventersdorp lavas, and the Transvaal Supergroup of rocks before the meteor struck. What the Vredefort impact achieved, however, was to distort the Witwatersrand basin in such a way that the gold bearing rocks were brought to the present erosion surface in Johannesburg, on the Witwatersrand, just inside the rim of the original 300 km diameter crater caused by the meteor strike. The discovery of the deposit in 1886 launched the Witwatersrand Gold Rush. Nearly 50% of all the gold ever mined on earth has been extracted from these Witwatersrand rocks.[76]



A schematic diagram of a NE (left) to SW (right) cross-section through the 2.020 billion year old Vredefort impact crater in South Africa and how it distorted the contemporary geological structures. The present erosion level is shown. Johannesburg is located where the Witwatersrand Basin (the yellow layer) is exposed at the "present surface" line, just inside the crater rim, on the left. Not to scale.

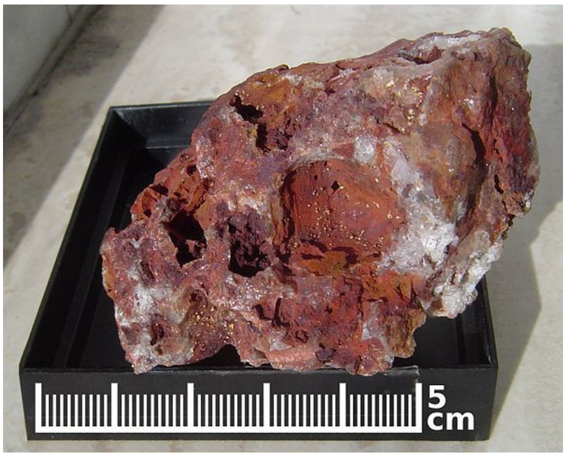
On Earth, gold is found in ores in rock formed from the Precambrian time onward.[53] It most often occurs as a native metal, typically in a metal solid solution with silver (i.e. as a gold silver alloy). Such alloys usually have a silver content of 8–10%. Electrum is elemental gold with more than 20% silver. Electrum's color runs from golden-silvery to silvery, dependent upon the silver content. The more silver, the lower the specific gravity.

Native gold occurs as very small to microscopic particles embedded in rock, often together with quartz or sulfide minerals such as "Fool's Gold", which is a pyrite.[77] These are called lode deposits. The metal in a native state is also found in the form of free flakes, grains or larger nuggets[53] that have been eroded from rocks and end up in alluvial deposits called placer deposits. Such free gold is always richer at the surface of gold-bearing veins owing to the oxidation of accompanying minerals followed by weathering, and washing of the dust into streams and rivers, where it collects and can be welded by water action to form nuggets.

Gold sometimes occurs combined with tellurium as the minerals calaverite, krennerite, nagyagite, petzite and sylvanite (see telluride minerals), and as the rare bismuthide maldonite (Au_2Bi) and antimonide aurostibite ($AuSb_2$). Gold also occurs in rare alloys with copper, lead, and mercury: the minerals auricupride (Cu_3Au), novodneprite ($AuPb_3$) and weishanite ($(Au, Ag)_3Hg_2$).

Recent research suggests that microbes can sometimes play an important role in forming gold deposits, transporting and precipitating gold to form grains and nuggets that collect in alluvial deposits.[78]

Relative sizes of an 860 kg block of gold ore, and the 30 g of gold that can be extracted from it. Toi gold mine, Japan.



Gold left behind after a pyrite cube was oxidized to hematite. Note cubic shape of cavity.

Another recent study has claimed water in faults vaporizes during an earthquake, depositing gold. When an earthquake strikes, it moves along a fault. Water often lubricates faults, filling in fractures and jogs. About 6 miles (10 kilometers) below the surface, under incredible temperatures and pressures, the water carries high concentrations of carbon dioxide, silica, and gold. During an earthquake, the fault jog suddenly opens wider. The water inside the void instantly vaporizes, flashing to steam and forcing silica, which forms the mineral quartz, and gold out of the fluids and onto nearby surfaces.[79]

Seawater

The world's oceans contain gold. Measured concentrations of gold in the Atlantic and Northeast Pacific are 50–150 fmol/L or 10–30 parts per 1,000,000,000,000,000 quadrillion (about 10–30 g/km^3). In general, gold concentrations for south Atlantic and central Pacific samples are the same (~50 fmol/L) but less certain. Mediterranean deep waters contain slightly higher concentrations of gold (100–150 fmol/L) attributed to wind-blown dust and/or rivers. At 10 parts per quadrillion the Earth's oceans would hold 15,000 tonnes of gold.[80] These figures are three orders of magnitude less than reported in the literature prior to 1988, indicating contamination problems with the earlier data.

A number of people have claimed to be able to economically recover gold from sea water, but so far they have all been either mistaken or acted in an intentional deception. Prescott Jernegan ran a gold-from-seawater swindle in the United States in the 1890s. A British fraudster ran the same scam in England in the early 1900s.[81] Fritz Haber (the German inventor of the Haber process) did research on the extraction of gold from sea water in an effort to help pay Germany's reparations following World War I.[82] Based on the published values of 2 to 64 ppb of gold in seawater a commercially successful extraction seemed possible. After analysis of 4,000 water samples yielding an average of 0.004 ppb it became clear that the extraction would not be possible and he stopped the project.[83] No commercially viable mechanism for performing gold extraction from sea water has yet been identified. Gold synthesis is not economically viable and is unlikely to become so in the foreseeable future.

Specimens of crystalline native gold

- Native gold nuggets
- "Rope gold" from Lena River, Sakha Republic, Russia. Size: 2.5×1.2×0.7 cm.
- Crystalline gold from Mina Zapata, Santa Elena de Uairen, Venezuela. Size: 3.7×1.1×0.4 cm.
- Gold leaf from Harvard Mine, Jamestown, California, USA. Size 9.3×3.2× >0.1 cm.

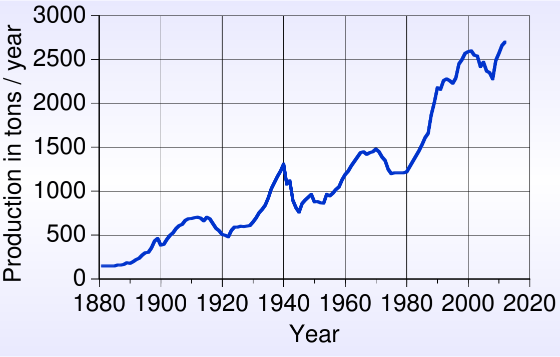
1.3.7 Production

Main article: List of countries by gold production

At the end of 2009, it was estimated that all the gold

The entrance to an underground gold mine in Victoria, Australia

Pure gold precipitate produced by the aqua regia refining process



Time trend of gold production

ever mined totaled 165,000 tonnes.[3] This can be represented by a cube with an edge length of about 20.28 meters. At $1,600 per troy ounce, 165,000 metric tonnes of gold would have a value of $8.5 trillion.

World production for 2011 was at 2,700 tonnes, compared to 2,260 tonnes for 2008.

Since the 1880s, South Africa has been the source for a large proportion of the world's gold supply, with about 50% of all gold ever produced having come from South Africa. Production in 1970 accounted for 79% of the world supply, producing about 1,480 tonnes. In 2007 China (with 276 tonnes) overtook South Africa as the world's largest gold producer, the first time since 1905 that South Africa has not been the largest.[84]

1.3.8 Mining

Main article: Gold mining

As of 2013, China was the world's leading gold-mining country, followed in order by Australia, the United States, Russia, and Peru. South Africa, which had dominated world gold production for most of the 20th Century, had declined to sixth place.[85] Other major producers are the Ghana, Burkina Faso, Mali, Indonesia and Uzbekistan.

In South America, the controversial project Pascua Lama aims at exploitation of rich fields in the high mountains of Atacama Desert, at the border between Chile and Argentina.

Today about one-quarter of the world gold output is estimated to originate from artisanal or small scale mining.[86]

The city of Johannesburg located in South Africa was founded as a result of the Witwatersrand Gold Rush which resulted in the discovery of some of the largest gold deposits the world has ever seen. The gold fields are confined to the northern and north-western edges of the Witwatersrand basin, which is a 5–7 km thick layer of archean rocks located, in most places, deep under the Free State, Gauteng and surrounding provinces.[87] These Witwatersrand rocks are exposed at the surface on the Witwatersrand, in and around Johannesburg, but also in isolated patches to the south-east and south-west of Johannesburg, as well as in an arc around the Vredefort Dome which lies close to the center of the Witwatersrand basin.[75][87] From these surface exposures the basin dips extensively, requiring some of the mining to occur at depths of nearly 4000 m, making them, especially the Savuka and TauTona mines to the south-west of Johannesburg, the deepest mines on earth. The gold is found only in six areas where archean rivers from the north and north-west formed extensive pebbly braided river deltas before draining into the "Witwatersrand sea" where the rest of the Witwatersrand sediments were deposited.[87]

The Second Boer War of 1899–1901 between the British Empire and the Afrikaner Boers was at least partly over the rights of miners and possession of the gold wealth in South Africa.

Prospecting

Main article: Gold prospecting

During the 19th century, gold rushes occurred whenever large gold deposits were discovered. The first documented discovery of gold in the United States was at the Reed Gold Mine near Georgeville, North Carolina in 1803.[88] The first major gold strike in the United States occurred in a small north Georgia town called Dahlonega.[89] Further gold rushes occurred in California, Colorado, the Black Hills, Otago in New Zealand, Australia, Witwatersrand in South Africa, and the Klondike in Canada.

1.3.9 Bioremediation

A sample of the fungus *Aspergillus niger* was found growing from gold mining solution; and was found to contain cyano metal complexes; such as gold, silver, copper iron and zinc. The fungus also plays a role in the solubilization of heavy metal sulfides.[90]

1.3.10 Extraction

Main article: Gold extraction

Gold extraction is most economical in large, easily mined deposits. Ore grades as little as 0.5 mg/kg (0.5 parts per million, ppm) can be economical. Typical ore grades in open-pit mines are 1–5 mg/kg (1–5 ppm); ore grades in underground or hard rock mines are usually at least 3 mg/kg (3 ppm). Because ore grades of 30 mg/kg (30 ppm) are usually needed before gold is visible to the naked eye, in most gold mines the gold is invisible.

The average gold mining and extraction costs were about US$317/oz in 2007, but these can vary widely depending on mining type and ore quality; global mine production amounted to 2,471.1 tonnes.[91]

Refining

After initial production, gold is often subsequently refined industrially by the Wohlwill process which is based on electrolysis or by the Miller process, that is chlorination in the melt. The Wohlwill process results in higher purity, but is more complex and is only applied in small-scale installations.[92][93] Other methods of assaying and purifying smaller amounts of gold include parting and inquartation as well as cupellation, or refining methods based on the dissolution of gold in aqua regia.[94]

1.3.11 Synthesis from other elements

Gold was synthesized from mercury by neutron bombardment in 1941, but the isotopes of gold produced were all radioactive.[95] In 1924, a Japanese physicist, Hantaro Nagaoka, accomplished the same feat.[96]

Gold can currently be manufactured in a nuclear reactor by irradiation either of platinum or mercury.

Only the mercury isotope ^{196}Hg, which occurs with a frequency of 0.15% in natural mercury, can be converted to gold by neutron capture, and following electron capture-decay into ^{197}Au with slow neutrons. Other mercury isotopes are converted when irradiated with slow neutrons into one another, or formed mercury isotopes which beta decay into thallium.

Using fast neutrons, the mercury isotope ^{198}Hg, which composes 9.97% of natural mercury, can be converted by splitting off a neutron and becoming ^{197}Hg, which then disintegrates to stable gold. This reaction, however, possesses a smaller activation cross-section and is feasible only with un-moderated reactors.

It is also possible to eject several neutrons with very high energy into the other mercury isotopes in order to form ^{197}Hg. However such high-energy neutrons can be produced only by particle accelerators.

1.3.12 Consumption

The consumption of gold produced in the world is about 50% in jewelry, 40% in investments, and 10% in industry.[4]

According to World Gold Council, China is the world's largest single consumer of gold in 2013 and toppled India for the first time with Chinese consumption increasing by 32 percent in a year, while that of India only rose by 13 percent and world consumption rose by 21 percent. Unlike India where gold is used for mainly for jewellery, China uses gold for manufacturing and retail.[97]

1.3.13 Pollution

Further information: Mercury cycle

Gold production is associated with contribution to hazardous pollution.[101][102] The ore, generally containing less than one ppm gold metal, is ground and mixed with sodium cyanide or mercury to react with gold in the ore for gold separation. Cyanide is a highly poisonous chemical, which can kill living creatures when exposed in minute quantities. Many cyanide spills[103] from gold mines have occurred in both developed and developing countries which killed marine life in long stretches of affected rivers. Environmentalists consider these events major environmental disasters.[104][105] When mercury is used in gold production, minute quantity of mercury compounds reach water bodies, causing heavy metal contamination. Mercury can then enter into the human food chain in the form of methylmercury. Mercury poisoning in humans causes incurable brain function damage and severe retardation.

Thirty tons of used ore is dumped as waste for producing one troy ounce of gold.[106] Gold ore dumps are the source of many heavy elements such as cadmium, lead, zinc, copper, arsenic, selenium and mercury. When sulfide bearing minerals in these ore dumps are exposed to air and water, the sulfide transforms into sulfuric acid which in turn dissolves these heavy metals facilitating their passage into surface water and ground water. This process is called acid mine drainage. These gold ore dumps are long term, highly hazardous wastes second only to nuclear waste dumps.[106]

Gold extraction is also a highly energy intensive industry, extracting ore from deep mines and grinding the large quantity of ore for further chemical extraction requires with 25 kW·h of electricity required per gram of gold produced.[107]

1.3.14 Chemistry

Gold (III) chloride solution in water

Although gold is the most noble of the noble metals,[108][109] it still forms many diverse compounds. The oxidation state of gold in its compounds ranges from −1 to +5, but Au(I) and Au(III) dominate its chemistry. Au(I), referred to as the aurous ion, is the most common oxidation state with soft ligands such as thioethers, thiolates, and tertiary phosphines. Au(I) compounds are typically linear. A good example is $Au(CN)_2^-$, which is the soluble form of gold encountered in mining. Curiously, aurous complexes of water are rare. The binary gold halides, such as AuCl, form zigzag polymeric chains, again featuring linear coordination at Au. Most drugs based on gold are Au(I) derivatives.[110]

Au(III) (auric) is a common oxidation state, and is illustrated by gold(III) chloride, Au_2Cl_6. The gold atom centers in Au(III) complexes, like other d^8 compounds, are typically square planar, with chemical bonds that have both covalent and ionic character.

Aqua regia, a 1:3 mixture of nitric acid and hydrochloric acid, dissolves gold. Nitric acid oxidizes the metal to +3 ions, but only in minute amounts, typically undetectable in the pure acid because of the chemical equilibrium of the reaction. However, the ions are removed from the equilibrium by hydrochloric acid, forming $AuCl_4^-$ ions, or chloroauric acid, thereby enabling further oxidation.

Some free halogens react with gold.[111] Gold also reacts in alkaline solutions of potassium cyanide. With mercury, it forms an amalgam.

Less common oxidation states

Less common oxidation states of gold include −1, +2, and +5.

The −1 oxidation state occurs in compounds containing the Au^- anion, called aurides. Caesium auride (CsAu), for example, crystallizes in the caesium chloride motif.[112] Other aurides include those of Rb^+, K^+, and tetramethylammonium $(CH_3)_4N^+$.[113] Gold has the highest Pauling electronegativity of any metal, with a value of 2.54, making the auride anion relatively stable.

Gold(II) compounds are usually diamagnetic with Au–Au bonds such as $[Au(CH_2)_2P(C_6H_5)_2]_2Cl_2$. The evaporation of a solution of Au(OH)
3 in concentrated H
2SO
4 produces red crystals of gold(II) sulfate, $Au_2(SO_4)_2$. Originally thought to be a mixed-valence compound, it has been shown to contain Au4+
2 cations.[114][115] A noteworthy, legitimate gold(II) complex is the tetraxenonogold(II) cation, which contains xenon as a ligand, found in $[AuXe_4](Sb_2F_{11})_2$.[116]

Gold pentafluoride, along with its derivative anion, AuF−6, and its difluorine complex, gold heptafluoride, is the sole example of gold(V), the highest verified oxidation state.[117]

Some gold compounds exhibit *aurophilic bonding*, which describes the tendency of gold ions to interact at distances that are too long to be a conventional Au–Au bond but shorter than van der Waals bonding. The interaction is estimated to be comparable in strength to that of a hydrogen bond.

Mixed valence compounds

Well-defined cluster compounds are numerous.[113] In such cases, gold has a fractional oxidation state. A representative example is the octahedral species $\{Au(P(C_6H_5)_3)\}_6^{2+}$. Gold chalcogenides, such as gold sulfide, feature equal amounts of Au(I) and Au(III).

1.3.15 Toxicity

Pure metallic (elemental) gold is non-toxic and non-irritating when ingested[118] and is sometimes used as a food decoration in the form of gold leaf. Metallic gold is also a component of the alcoholic drinks Goldschläger, Gold Strike, and Goldwasser. Metallic gold is approved as a food additive in the EU (E175 in the Codex Alimentarius). Although the gold ion is toxic, the acceptance of metallic gold as a food additive is due to its relative chemical inertness, and resistance to being corroded or transformed into soluble salts (gold compounds) by any known chemical process which would be encountered in the human body.

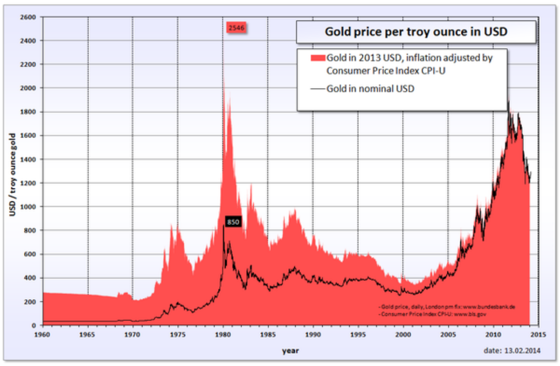
Soluble compounds (gold salts) such as gold chloride are toxic to the liver and kidneys. Common cyanide salts of gold such as potassium gold cyanide, used in gold electroplating, are toxic by virtue of both their cyanide and gold content. There are rare cases of lethal gold poisoning from potassium gold cyanide.[119][120] Gold toxicity can be ameliorated with chelation therapy with an agent such as dimercaprol.

Gold metal was voted Allergen of the Year in 2001 by the American Contact Dermatitis Society. Gold contact allergies affect mostly women.[121] Despite this, gold is a relatively non-potent contact allergen, in comparison with metals like nickel.[122]

1.3.16 Price

Further information: Gold as an investment

Gold is currently valued at around US$62,000 per kilogram.



Gold price history in 1960–2011

Like other precious metals, gold is measured by troy weight and by grams. When it is alloyed with other metals the term *carat* or *karat* is used to indicate the purity of gold present, with 24 carats being pure gold and lower ratings proportionally less. The purity of a gold bar or coin can also be expressed as a decimal figure ranging from 0 to 1, known as the millesimal fineness, such as 0.995 being very pure.

History

The price of gold is determined through trading in the gold and derivatives markets, but a procedure known as the Gold Fixing in London, originating in September 1919, provides a daily benchmark price to the industry. The afternoon fixing was introduced in 1968 to provide a price when US markets are open.[123]

Historically gold coinage was widely used as currency; when paper money was introduced, it typically was a receipt redeemable for gold coin or bullion. In a monetary system known as the gold standard, a certain weight of gold was given the name of a unit of currency. For a long period, the United States government set the value of the US dollar so that one troy ounce was equal to $20.67 ($664.56/kg), but in 1934 the dollar was devalued to $35.00 per troy ounce ($1125.27/kg). By 1961, it was becoming hard to maintain this price, and a pool of US and European banks agreed to manipulate the market to prevent further currency devaluation against increased gold demand.[124]

On 17 March 1968, economic circumstances caused the collapse of the gold pool, and a two-tiered pricing scheme was established whereby gold was still used to settle international accounts at the old $35.00 per troy ounce ($1.13/g) but the price of gold on the private market was allowed to fluctuate; this two-tiered pricing system was abandoned in 1975 when the price of gold was left to find its free-market level. Central banks still hold historical gold reserves as a store of value although the level has generally been declining. The largest gold depository in the world is that of the U.S. Federal Reserve Bank in New York, which holds about 3%[125] of the gold ever mined, as does the similarly laden U.S. Bullion Depository at Fort Knox. In 2005 the World Gold Council estimated total global gold supply to be 3,859 tonnes and demand to be 3,754 tonnes, giving a surplus of 105 tonnes.[126]

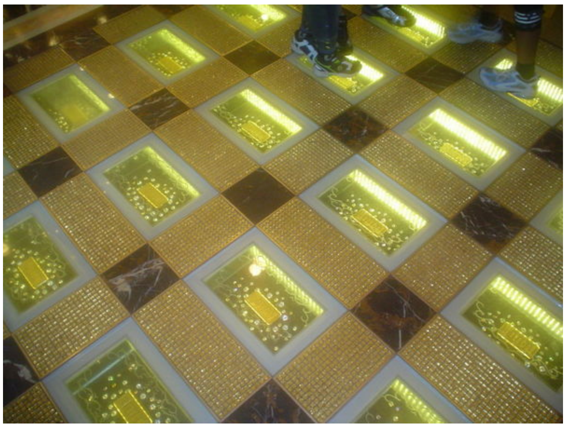
Sometime around 1970 the price began in trend to greatly increase,[127] and since 1968 the price of gold has ranged widely, from a high of $850/oz ($27,300/kg) on 21 January 1980, to a low of $252.90/oz ($8,131/kg) on 21 June 1999 (London Gold Fixing).[128] The period from 1999 to 2001 marked the "Brown Bottom" after a 20-year bear market.[129] Prices increased rapidly from 2001, but the 1980 high was not exceeded until 3 January 2008 when a new maximum of $865.35 per troy ounce was set.[130] Another record price was set on 17 March 2008 at $1023.50/oz ($32,900/kg).[130]

In late 2009, gold markets experienced renewed momentum upwards due to increased demand and a weakening US dollar. On 2 December 2009, Gold reached a new high closing at $1,217.23.[131] Gold further rallied hitting new highs in May 2010 after the European Union debt crisis prompted further purchase of gold as a safe asset.[132][133] On 1 March 2011, gold hit a new all-time high of $1432.57, based on investor concerns regarding ongoing unrest in North Africa as well as in the Middle East.[134]

Since April 2001 the gold price has more than quintupled in value against the US dollar, hitting a new all-time high of $1,913.50 on 23 August 2011,[135] prompting speculation that this long secular bear market has ended and a bull market has returned.[136]

1.3.17 Symbolism

Great human achievements are frequently rewarded with gold, in the form of gold medals, golden trophies and



Gold bars at the Emperor Casino in Macau

other decorations. Winners of athletic events and other graded competitions are usually awarded a gold medal. Many awards such as the Nobel Prize are made from gold as well. Other award statues and prizes are depicted in gold or are gold plated (such as the Academy Awards, the Golden Globe Awards, the Emmy Awards, the Palme d'Or, and the British Academy Film Awards).

Aristotle in his ethics used gold symbolism when referring to what is now commonly known as the golden mean. Similarly, gold is associated with perfect or divine principles, such as in the case of the golden ratio and the golden rule.

Gold is further associated with the wisdom of aging and fruition. The fiftieth wedding anniversary is golden. Our most valued or most successful latter years are sometimes considered “golden years”. The height of a civilization is referred to as a "golden age".

In some forms of Christianity and Judaism, gold has been associated both with holiness and evil. In the Book of Exodus, the Golden Calf is a symbol of idolatry, while in the Book of Genesis, Abraham was said to be rich in gold and silver, and Moses was instructed to cover the Mercy Seat of the Ark of the Covenant with pure gold. In Byzantine iconography the halos of Christ, Mary and the Christian saints are often golden.

Medieval kings were inaugurated under the signs of sacred oil and a golden crown, the latter symbolizing the eternal shining light of heaven and thus a Christian king’s divinely inspired authority.

According to Christopher Columbus, those who had something of gold were in possession of something of great value on Earth and a substance to even help souls to paradise.[137]

Wedding rings have long been made of gold. It is long lasting and unaffected by the passage of time and may aid in the ring symbolism of eternal vows before God and/or the sun and moon and the perfection the marriage signifies. In Orthodox Christian wedding ceremonies, the wedded couple is adorned with a golden crown (though some opt for wreaths, instead) during the ceremony, an amalgamation of symbolic rites.

In popular culture gold has many connotations but is most generally connected to terms such as good or great, such as in the phrases: “has a heart of gold”, “that’s golden!", “golden moment”, “then you're golden!" and “golden boy”. It remains a cultural symbol of wealth and through that, in many societies, success.

1.3.18 State emblem

In 1965, the California Legislature designated gold “the State Mineral and mineralogical emblem”.[138]

In 1968, the Alaska Legislature named gold “the official state mineral”.[139]

1.3.19 See also

- Bulk leach extractable gold
- Chrysiasis (dermatological condition)
- Commodity fetishism (Marxist economic theory)
- Digital gold currency
- Gold Anti-Trust Action Committee
- Gold fingerprinting
- Gold phosphine complex
- Gold Prospectors Association of America
- Mining in Roman Britain
- Prospecting
- Tumbaga

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1.3.21 Further reading

- Hart, Matthew, *Gold : the race for the world’s most seductive metal”*, New York : Simon & Schuster, 2013. ISBN 9781451650020

1.3.22 External links

- Chemistry in its element podcast (MP3) from the Royal Society of Chemistry's Chemistry World: Gold www.rsc.org
- Gold at *The Periodic Table of Videos* (University of Nottingham)
- *Getting Gold* 1898 book, www.lateralscience.co.uk

- Technical Document on Extraction and Mining of Gold at the Wayback Machine (archived March 7, 2008), www.epa.gov
- Picture in the Element collection from Heinrich Pniok, www.pniok.de
- The Art of Precolumbian Gold: The Jan Mitchell Collection, an exhibition catalog from The Metropolitan Museum of Art (fully available online as PDF)

1.4 Graphite

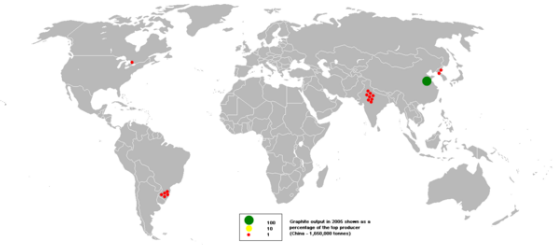
For other uses, see Graphite (disambiguation).

Graphite /ˈɡræfaɪt/ is made almost entirely of carbon atoms, and as with diamond, is a semimetal native element mineral, and an allotrope of carbon. Graphite is the most stable form of carbon under standard conditions. Therefore, it is used in thermochemistry as the standard state for defining the heat of formation of carbon compounds. Graphite may be considered the highest grade of coal, just above anthracite and alternatively called meta-anthracite, although it is not normally used as fuel because it is difficult to ignite.

1.4.1 Types or varieties

There are three principal types of natural graphite, each occurring in different types of ore deposit:

- Crystalline flake graphite (or flake graphite for short) occurs as isolated, flat, plate-like particles with hexagonal edges if unbroken and when broken the edges can be irregular or angular;
- *Amorphous graphite*: very fine flake graphite is sometimes called amorphous in the trade;[4]
- Lump graphite (also called vein graphite) occurs in fissure veins or fractures and appears as massive platy intergrowths of fibrous or acicular crystalline aggregates, and is probably hydrothermal in origin.[5]
- Highly *ordered* pyrolytic graphite or highly *oriented* pyrolytic graphite (HOPG) refers to graphite with an angular spread between the graphite sheets of less than 1°.[6]
- The name “graphite fiber” is also sometimes used to refer to carbon fiber or carbon fiber-reinforced polymer.



Graphite output in 2005

1.4.2 Occurrence

Graphite occurs in metamorphic rocks as a result of the reduction of sedimentary carbon compounds during metamorphism. It also occurs in igneous rocks and in meteorites.[3] Minerals associated with graphite include quartz, calcite, micas and tourmaline. In meteorites it occurs with troilite and silicate minerals.[3] Small graphitic crystals in meteoritic iron are called cliftonite.[5]

According to the United States Geological Survey (USGS), world production of natural graphite in 2012 was 1,100,000 tonnes, of which the following major exporters are: China (750 kt), India (150 kt), Brazil (75 kt), North Korea (30 kt) and Canada (26 kt). Graphite is not mined in the United States, but U.S. production of synthetic graphite in 2010 was 134 kt valued at $1.07 billion.[7]

1.4.3 Properties

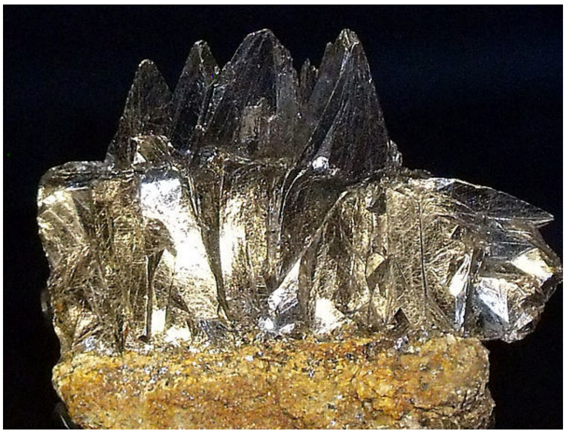
Structure

Graphite has a layered, planar structure. In each layer, the carbon atoms are arranged in a honeycomb lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm.[8] The two known forms of graphite, *alpha* (hexagonal) and *beta* (rhombohedral), have very similar physical properties, except the graphene layers stack slightly differently.[9] The hexagonal graphite may be either flat or buckled.[10] The alpha form can be converted to the beta form through mechanical treatment and the beta form reverts to the alpha form when it is heated above 1300 °C.[11]

- Scanning tunneling microscope image of graphite surface atoms
- Graphite’s unit cell
- Animated view of the unit cell in three layers of graphene (note that this is a slightly different unit cell from the one to the left)
- Ball-and-stick model of graphite (two graphene layers)
- Side view of layer stacking

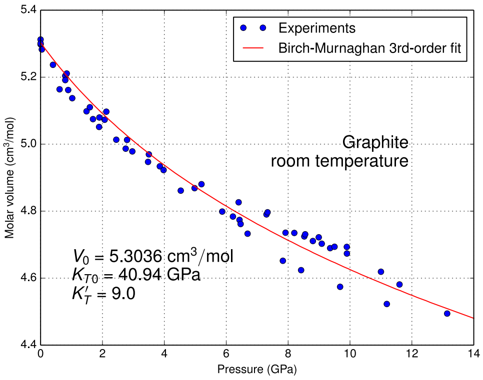
- Plane view of layer stacking
- Rotating graphite stereogram

Other properties



Graphite plates and sheets, 10-15 cm high, Mineral specimen from Kimmirut, Baffin Island.

The acoustic and thermal properties of graphite are highly anisotropic, since phonons propagate quickly along the tightly-bound planes, but are slower to travel from one plane to another.



Molar volume vs. pressure at room temperature.

Graphite is an electric conductor, consequently, useful in such applications as arc lamp electrodes. It can conduct electricity due to the vast electron delocalization within the carbon layers (a phenomenon called aromaticity). These valence electrons are free to move, so are able to conduct electricity. However, the electricity is primarily conducted within the plane of the layers. The conductive properties of powdered graphite[12] allows its use as pressure sensor in carbon microphones.

Graphite and graphite powder are valued in industrial applications for their self-lubricating and dry lubricating properties. There is a common belief that graphite's lubricating properties are solely due to the loose interlamellar coupling between sheets in the structure.[13] However, it has been shown that in a vacuum environment (such as in technologies for use in space), graphite is a very poor lubricant. This observation led to the hypothesis that the lubrication is due to the presence of fluids between the layers, such as air and water, which are naturally adsorbed from the environment. This hypothesis has been refuted by studies showing that air and water are not absorbed.[14] Recent studies suggest that an effect called superlubricity can also account for graphite's lubricating properties. The use of graphite is limited by its tendency to facilitate pitting corrosion in some stainless steel,[15][16] and to promote galvanic corrosion between dissimilar metals (due to its electrical conductivity). It is also corrosive to aluminium in the presence of moisture. For this reason, the US Air Force banned its use as a lubricant in aluminium aircraft,[17] and discouraged its use in aluminium-containing automatic weapons.[18] Even graphite pencil marks on aluminium parts may facilitate corrosion.[19] Another high-temperature lubricant, hexagonal boron nitride, has the same molecular structure as graphite. It is sometimes called *white graphite*, due to its similar properties.

When a large number of crystallographic defects bind these planes together, graphite loses its lubrication properties and becomes what is known as pyrolytic graphite. It is also highly anisotropic, and diamagnetic, thus it will float in mid-air above a strong magnet. If it is made in a fluidized bed at 1000–1300 °C then it is isotropic turbostratic, and is used in blood contacting devices like mechanical heart valves and is called (pyrolytic carbon), and is not diamagnetic. Pyrolytic graphite, and pyrolytic carbon are often confused but are very different materials.

Natural and crystalline graphites are not often used in pure form as structural materials, due to their shear-planes, brittleness and inconsistent mechanical properties.

1.4.4 History of natural graphite use

In the 4th millennium B.C., during the Neolithic Age in southeastern Europe, the Mariţa culture used graphite in a ceramic paint for decorating pottery.[20]

Some time before 1565 (some sources say as early as 1500), an enormous deposit of graphite was discovered on the approach to Grey Knotts from the hamlet of Seathwaite in Borrowdale parish, Cumbria, England, which the locals found very useful for marking sheep.[21][22] During the reign of Elizabeth 1 (1533–1603), Borrowdale graphite was used as a refractory material to line moulds for cannonballs, resulting in rounder, smoother balls that could be fired farther, contributing to the strength of the English navy. This particular deposit of graphite was extremely pure and soft, and could easily be broken into sticks. Because of its military importance, this unique mine and its production were strictly controlled by the Crown.[23]

Other names

Historically, graphite was called **black lead** or **plumbago**.[5][24]

Plumbago was commonly used in its massive mineral form. Both of these names arise from confusion with the similar-appearing lead ores, particularly galena. The Latin word for lead is *plumbum*, which gave its name to both the English term for this grey metallic-sheened mineral and even the leadworts or plumbagos, plants with flowers that resemble this colour.

The term *black lead* usually refers to a powdered or processed graphite, which is matte black in color.

The name *graphite* ("writing stone") was coined by Abraham Gottlob Werner in 1789. He attempted to clear the confusion of what molybdena, plumbago and blacklead actually are after Carl Wilhelm Scheele in 1778 proved that there are at least three different minerals. Scheele's analysis showed that the chemical compounds molybdenum sulfide (molybdenite), lead(II) sulfide (galena) and graphite were three different soft black minerals.[25][26][27]

1.4.5 Uses of natural graphite

Natural graphite is mostly consumed for refractories, batteries, steelmaking, expanded graphite, brake linings, foundry facings and lubricants.[7] Graphene, which occurs naturally in graphite, has unique physical properties and might be one of the strongest substances known; however, the process of separating it from graphite will require some technological development before it is economically feasible to use it in industrial processes.

Refractories

This end-use begins before 1900 with the graphite crucible used to hold molten metal; this is now a minor part of refractories. In the mid-1980s, the carbon-magnesite brick became important, and a bit later the alumina-graphite shape. Currently the order of importance is alumina-graphite shapes, carbon-magnesite brick, monolithics (gunning and ramming mixes), and then crucibles.

Crucibles began using very large flake graphite, and carbon-magnesite brick requiring not quite so large flake graphite; for these and others there is now much more flexibility in size of flake required, and amorphous graphite is no longer restricted to low-end refractories. Alumina-graphite shapes are used as continuous casting ware, such as nozzles and troughs, to convey the molten steel from ladle to mold, and carbon magnesite bricks line steel converters and electric arc furnaces to withstand extreme temperatures. Graphite Blocks are also used in parts of blast furnace linings where the high thermal conductivity of the graphite is critical. High-purity monolithics are often used as a continuous furnace lining instead of the carbon-magnesite bricks.

The US and European refractories industry had a crisis in 2000–2003, with an indifferent market for steel and a declining refractory consumption per tonne of steel underlying firm buyouts and many plant closings. Many of the plant closings resulted from the acquisition of Harbison-Walker Refractories by RHI AG and some plants had their equipment auctioned off. Since much of the lost capacity was for carbon-magnesite brick, graphite consumption within refractories area moved towards alumina-graphite shapes and monolithics, and away from the brick.The major source of carbon-magnesite brick is now imports from China. Almost all of the above refractories are used to make steel and account for 75% of refractory consumption; the rest is used by a variety of industries, such as cement.

According to the USGS, US natural graphite consumption in refractories was 12,500 tonnes in 2010.[7]

Batteries

The use of graphite in batteries has been increasing in the last 30 years. Natural and synthetic graphite are used to construct the anode of all major battery technologies.[7] The lithium-ion battery utilizes roughly twice the amount of graphite than lithium carbonate.[28]

The demand for batteries, primarily nickel-metal-hydride and lithium-ion batteries, has caused a growth in graphite demand in the late 1980s and early 1990s. This growth was driven by portable electronics, such as portable CD players and power tools. Laptops, mobile phones, tablet, and smartphone products have increased the demand for batteries. Electric vehicle batteries are anticipated to increase graphite demand. As an example, a lithium-ion battery in a fully electric Nissan Leaf contains nearly 40 kg of graphite.

Steelmaking

Natural graphite in this end use mostly goes into carbon raising in molten steel, although it can be used to lubricate the dies used to extrude hot steel. Supplying carbon raisers is very competitive, therefore subject to cut-throat pricing from alternatives such as synthetic graphite powder, petroleum coke, and other forms of carbon. A carbon raiser is added to increase the carbon content of the steel to the specified level. An estimate based on USGS US graphite consumption statistics indicates that 10,500 tonnes were used in this fashion in 2005.[7]

Brake linings

Natural amorphous and fine flake graphite are used in brake linings or brake shoes for heavier (nonautomotive) vehicles, and became important with the need to substitute for asbestos. This use has been important for quite some time, but nonasbestos organic (NAO) compositions are beginning to cost graphite market share. A brake-lining industry shake-out with some plant closings has not helped either, nor has an indifferent automotive market. According to the USGS, US natural graphite consumption in brake linings was 6,510 tonnes in 2005.[7]

Foundry facings and lubricants

A foundry facing mold wash is a water-based paint of amorphous or fine flake graphite. Painting the inside of a mold with it and letting it dry leaves a fine graphite coat that will ease separation of the object cast after the hot metal has cooled. Graphite lubricants are specialty items for use at very high or very low temperatures, as forging die lubricant, an antiseize agent, a gear lubricant for mining machinery, and to lubricate locks. Having low-grit graphite, or even better no-grit graphite (ultra high purity), is highly desirable. It can be used as a dry powder, in water or oil, or as colloidal graphite (a permanent suspension in a liquid). An estimate based on USGS graphite consumption statistics indicates that 2,200 tonnes was used in this fashion in 2005.[7]

Pencils

Graphite pencils

The ability to leave marks on paper and other objects gave graphite its name, given in 1789 by German mineralogist Abraham Gottlob Werner. It stems from *graphein*, meaning *to write/draw* in Ancient Greek.[5][29]

Pencil lead is most commonly a mix of powdered graphite and clay; it was invented by Nicolas-Jacques Conté in 1795.[30][31] It is chemically unrelated to the metal lead, whose ores had a similar appearance, hence the continuation of the name. **Plumbago** is another older term for natural graphite used for drawing, typically as a lump of the mineral without a wood casing. The term plumbago drawing is normally restricted to 17th and 18th century works, mostly portraits.

Today, pencils are still a small but significant market for natural graphite. Around 7% of the 1.1 million tonnes produced in 2011 was used to make pencils.[28] Low-quality amorphous graphite is used and sourced mainly from China.[7]

Other uses

Natural graphite has found uses in zinc-carbon batteries, in electric motor brushes, and various specialized applications. Graphite is also commonly used in the form of powders, and sticks for the purpose of writing or drawing. Graphite of various hardness or softness results in different qualities and tones when used as an artistic medium.[32] Railroads would often mix powdered graphite with waste oil or linseed oil to create a heat resistant protective coating for the exposed portions of a steam locomotive's boiler, such as the smokebox or lower part of the firebox.[33]

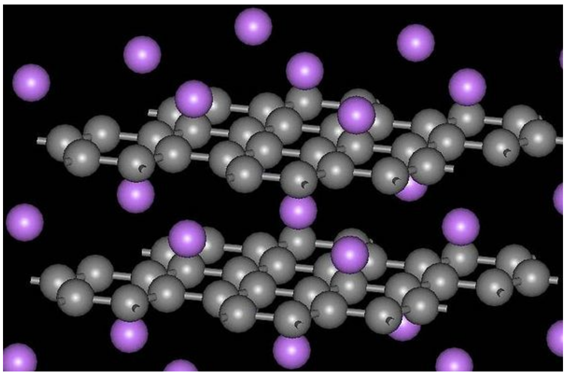
Expanded graphite

Expanded graphite is made by immersing natural flake graphite in a bath of chromic acid, then concentrated sulfuric acid, which forces the crystal lattice planes apart, thus expanding the graphite. The expanded graphite can be used to make graphite foil or used directly as "hot top" compound to insulate molten metal in a ladle or red-hot steel ingots and decrease heat loss, or as firestops fitted around a fire door or in sheet metal collars surrounding plastic pipe (during a fire, the graphite expands and chars to resist fire penetration and spread), or to make high-performance gasket material for high-temperature use. After being made into graphite foil, the foil is machined and assembled into the bipolar plates in fuel cells. The foil is made into heat sinks for laptop computers which keeps them cool while saving weight, and is made into a foil laminate that can be used in valve packings or made into gaskets. Old-style packings are now a minor member of this grouping: fine flake graphite in oils or greases for uses requiring heat resistance. A GAN estimate of current US natural graphite consumption in this end use is 7,500 tonnes.[7]

Intercalated graphite

Main article: Graphite intercalation compound

Graphite forms intercalation compounds with some metals and small molecules. In these compounds, the host molecule or atom gets "sandwiched" between the graphite layers, resulting in a type of compounds with variable stoichiometry. A prominent example of an intercalation compound is potassium graphite, denoted by the



Structure of CaC_6

formula KC_8. Graphite intercalation compounds are superconductors. The highest transition temperature (by June 2009) $T_c = 11.5$ K is achieved in CaC_6, and it further increases under applied pressure (15.1 K at 8 GPa).[34]

1.4.6 Uses of synthetic graphite

Invention of a process to produce synthetic graphite

A process to make synthetic graphite was invented by Edward Goodrich Acheson (1856–1931). In the mid-1890s, Acheson discovered that overheating carborundum, which he is also credited with discovering, produced almost pure graphite. While studying the effects of high temperature on carborundum, he had found that silicon vaporizes at about 4,150 °C (7,500 °F), leaving behind graphitic carbon. This graphite was another major discovery for him, and it became extremely valuable and helpful as a lubricant.[5]

In 1896 Acheson received a patent for his method of synthesizing graphite,[35] and in 1897 started commercial production.[5] The Acheson Graphite Co. was formed in 1899. In 1928 this company was merged with National Carbon Company (now GrafTech International). Acheson also developed a variety of colloidal graphite products including Oildag and Aquadag. These were later manufactured by the Acheson Colloids Co. (now Acheson Industries, a unit of Henkel AG).

Scientific research

Highly oriented pyrolytic graphite (HOPG) is the highest-quality synthetic form of graphite. It is used in scientific research, in particular, as a length standard for scanner calibration of scanning probe microscope.[36]

Electrodes

Graphite electrodes carry the electricity that melts scrap iron and steel (and sometimes direct-reduced iron: DRI) in electric arc furnaces, which are the vast majority of steel furnaces. They are made from petroleum coke after it is mixed with coal tar pitch. They are then extruded and shaped, baked to carbonize the binder (pitch), and finally graphitized by heating it to temperatures approaching 3000 °C, at which the carbon atoms arrange into graphite. They can vary in size up to 11 ft. long and 30 in. in diameter. An increasing proportion of global steel is made using electric arc furnaces, and the electric arc furnace itself is getting more efficient, making more steel per tonne of electrode. An estimate based on USGS data indicates that graphite electrode consumption was 197,000 tonnes in 2005.[7]

On a much smaller scale, graphite is also used for making electrodes for electrical discharge machining (EDM), commonly used to make plastic injection molds.

Powder and scrap

The powder is made by heating powdered petroleum coke above the temperature of graphitization, sometimes with minor modifications. The graphite scrap comes from pieces of unusable electrode material (in the manufacturing stage or after use) and lathe turnings, usually after crushing and sizing. Most synthetic graphite powder goes to carbon raising in steel (competing with natural graphite), with some used in batteries and brake linings. According to the USGS, US synthetic graphite powder and scrap production was 95,000 tonnes in 2001 (latest data).[7]

Neutron moderator

Main article: Nuclear graphite

Special grades of synthetic graphite also find use as a matrix and neutron moderator within nuclear reactors. Its low neutron cross-section also recommends it for use in proposed fusion reactors. Care must be taken that reactor-grade graphite is free of neutron absorbing materials such as boron, widely used as the seed electrode in commercial graphite deposition systems—this caused the failure of the Germans' World War II graphite-based nuclear reactors. Since they could not isolate the difficulty they were forced to use far more expensive heavy water moderators. Graphite used for nuclear reactors is often referred to as nuclear graphite.

Other uses

Graphite (carbon) fiber and carbon nanotubes are also used in carbon fiber reinforced plastics, and in heat-resistant composites such as reinforced carbon-carbon (RCC). Commercial structures made from carbon fiber graphite composites include fishing rods, golf club shafts, bicycle frames, sports car body panels, the fuselage of the Boeing 787 Dreamliner and pool cue sticks and have been successfully employed in reinforced concrete, The mechanical properties of carbon fiber graphite-reinforced plastic composites and grey cast iron are strongly influenced by the role of graphite in these materials. In this context, the term "(100%) graphite” is often loosely used to refer to a pure mixture of carbon reinforcement and resin, while the term “composite” is used for composite materials with additional ingredients.[37]

Modern smokeless powder is coated in graphite to prevent the buildup of static charge.

Graphite has been used in at least three radar absorbent materials. It was mixed with rubber in Sumpf and Schornsteinfeger, which were used on U-boat snorkels to reduce their radar cross section. It was also used in tiles on early F-117 Nighthawk (1983)s.

1.4.7 Graphite mining, beneficiation, and milling

Graphite is mined by both open pit and underground methods. Graphite usually needs beneficiation. This may be carried out by hand-picking the pieces of gangue (rock) and hand-screening the product or by crushing the rock and floating out the graphite. Beneficiation by flotation encounters the difficulty that graphite is very soft and “marks” (coats) the particles of gangue. This makes the “marked” gangue particles float off with the graphite, yielding impure concentrate. There are two ways of obtaining a commercial concentrate or product: repeated regrinding and floating (up to seven times) to purify the concentrate, or by acid leaching (dissolving) the gangue with hydrofluoric acid (for a silicate gangue) or hydrochloric acid (for a carbonate gangue).

In milling, the incoming graphite products and concentrates can be ground before being classified (sized or screened), with the coarser flake size fractions (below 8 mesh, 8–20 mesh, 20–50 mesh) carefully preserved, and then the carbon contents are determined. Some standard blends can be prepared from the different fractions, each with a certain flake size distribution and carbon content. Custom blends can also be made for individual customers who want a certain flake size distribution and carbon content. If flake size is unimportant, the concentrate can be ground more freely. Typical end products include a fine powder for use as a slurry in oil drilling and coatings for foundry molds, carbon raiser in the steel industry (Synthetic graphite powder and powdered petroleum coke can also be used as carbon raiser). Environmental impacts from graphite mills consist of air pollution including fine particulate exposure of workers and also soil contamination from powder spillages leading to heavy metals contaminations of soil.

1.4.8 Graphite recycling

The most common way of recycling graphite occurs when synthetic graphite electrodes are either manufactured and pieces are cut off or lathe turnings are discarded, or the electrode (or other) are used all the way down to the electrode holder. A new electrode replaces the old one, but a sizeable piece of the old electrode remains. This is crushed and sized, and the resulting graphite powder is mostly used to raise the carbon content of molten steel. Graphite-containing refractories are sometimes also recycled, but often not because of their graphite: the largest-volume items, such as carbon-magnesite bricks that contain only 15–25% graphite, usually contain too little graphite. However, some recycled carbon-magnesite brick is used as the basis for furnace-repair materials, and also crushed carbon-magnesite brick is used in slag conditioners. While crucibles have a high graphite content, the volume of crucibles used and then recycled is very small.

A high-quality flake graphite product that closely resembles natural flake graphite can be made from steelmaking kish. Kish is a large-volume near-molten waste skimmed from the molten iron feed to a basic oxygen furnace, and consists of a mix of graphite (precipitated out of the supersaturated iron), lime-rich slag, and some iron. The iron is recycled on site, leaving a mixture of graphite and slag. The best recovery process uses hydraulic classification (which utilizes a flow of water to separate minerals by specific gravity: graphite is light and settles nearly last) to get a 70% graphite rough concentrate. Leaching this concentrate with hydrochloric acid gives a 95% graphite product with a flake size ranging from 10 mesh down.

1.4.9 See also

- Acheson process
- Carbon fiber
- Carbon nanotube
- Diamond
- Exfoliated graphite nano-platelets
- Fullerene
- Graphene
- Graphite intercalation compound
- Intumescent
- Lonsdaleite
- Passive fire protection
- Plumbago drawing
- Pyrolytic carbon

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1.4.11 Further reading

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1.4.12 External links

- Battery Grade Graphite
- Graphite at Minerals.net
- Mineral galleries
- Mineral & Exploration – Map of World Graphite Mines and Producers 2012
- Mindat w/ locations
- giant covalent structures
- The Graphite Page
- Video lecture on the properties of graphite by Prof. M. Heggie, University of Sussex
- CDC – NIOSH Pocket Guide to Chemical Hazards

1.5 Kamacite

Kamacite is an alloy of iron and nickel, which is found on earth only in meteorites. The proportion iron:nickel is between 90:10 to 95:5; small quantities of other elements, such as cobalt or carbon may also be present. The mineral has a metallic luster, is gray and has no clear cleavage although the structure is isometric-hexoctahedral. Its density is around 8 g/cm^3 and its hardness is 4 on the Mohs scale. It is also sometimes called balkeneisen.

The name was coined in 1861 and is derived from the Greek *kamask* (lath or beam). It is a major constituent of iron meteorites (octahedrite and hexahedrite types). In the octahedrites it is found in bands interleaving with taenite forming Widmanstätten patterns. In hexahedrites, fine parallel lines called Neumann lines are often seen, which are evidence for structural deformation of adjacent kamacite plates due to shock from impacts.

At times kamacite can be found so closely intermixed with taenite that it is difficult to distinguish them visually, forming plessite. The largest documented kamacite crystal measured 92×54×23 centimetres (36.2×21.3×9.1 in).[2]

See also: list of minerals

1.5.1 See also

- Glossary of meteoritics

1.5.2 References

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1.6 Silver

This article is about the chemical element. For the color, see Silver (color). For other uses, see Silver (disambiguation).

Silver is a chemical element with symbol **Ag** (Greek: ἄργυρος *árguros*, Latin: *argentum*, both from the Indo-European root **arg-* for "grey" or "shining") and atomic number 47. A soft, white, lustrous transition metal, it possesses the highest electrical conductivity of any element, the highest thermal conductivity of any metal and is the most reflective metal on the planet. The metal occurs naturally in its pure, free form (native silver), as an alloy with gold and other metals, and in minerals such as argentite and chlorargyrite. Most silver is produced as a byproduct of copper, gold, lead, and zinc refining.

While silver has long been valued as a precious metal it is also used in currency coins, solar panels, water filtration, jewelry and ornaments, high-value tableware and utensils (hence the term silverware) and as an investment in the forms of coins and bullion. Silver is used industrially in electrical contacts and conductors, in specialized

Kamacite and taenite after taenite, exhibiting the octahedral structure of taenite, Nantan (Nandan) iron meteorite, Nandan County, Guangxi Zhuang Autonomous Region, China. Size: 4.8×3.0×2.8 cm. The Nantan irons, a witnessed fall in 1516, have a composition of 92.35% iron and 6.96% nickel.

mirrors, window coatings and in catalysis of chemical reactions. Its compounds are used in photographic film and X-rays. Dilute silver nitrate solutions and other silver compounds are used as disinfectants and microbiocides (oligodynamic effect), added to bandages and wound-dressings, catheters and other medical instruments.

1.6.1 Characteristics

Silver 1000 oz t (~31 kg) bullion bar

Silver is produced during certain types of supernova explosions by nucleosynthesis from lighter elements through the r-process, a form of nuclear fusion that produces many elements heavier than iron, of which silver is one.[2]

Silver is a very ductile, malleable (slightly harder than gold), univalent coinage metal, with a brilliant white metallic luster that can take a high degree of polish. It is the most reflective metal on Earth.[3] It has the highest electrical conductivity of all metals, even higher than copper, but its greater cost has prevented it from being widely used in place of copper for electrical purposes. An exception to this is in radio-frequency engineering, particularly at VHF and higher frequencies, where silver plating to improve electrical conductivity of parts, including wires, is widely employed. During World War II in the US, 13,540 tons were used in the electromagnets used for enriching uranium, mainly because of the wartime shortage of copper.[4][5][6]

Among metals, pure silver has the highest thermal conductivity (the nonmetal carbon in the form of diamond and superfluid helium II are higher) and the highest optical reflectivity[7] (protected silver has higher reflectance than aluminium at all wavelengths longer than ~450 nm; below 450 nm, silver is inferior to aluminium and its reflectance drops to zero near 310 nm).[8] Silver is the best conductor of heat and electricity of any metal in the periodic table. Silver also has the lowest contact resistance of any metal. Silver halides are photosensitive and are remarkable for their ability to record a latent image that can later be developed chemically. Silver is stable in pure air and water, but tarnishes when it is exposed to air or water containing ozone or hydrogen sulfide, the latter forming a black layer of silver sulfide which can be cleaned off with dilute hydrochloric acid.[9] The most common oxidation state of silver is +1 (for example, silver nitrate, $AgNO_3$); the less common +2 compounds (for example, silver(II) fluoride, AgF_2), and the even less common +3 (for example, potassium tetrafluoroargentate(III), $KAgF_4$) and even +4 compounds (for example, potassium hexafluoroargentate(IV), K_2AgF_6)[10] are also known.

1.6.2 Isotopes

Main article: Isotopes of silver

Naturally occurring silver is composed of two stable isotopes, ^{107}Ag and ^{109}Ag, with ^{107}Ag being slightly more abundant (51.839% natural abundance). Silver's isotopes are almost equal in abundance, something which is rare in the periodic table. Silver's atomic weight is 107.8682(2) g/mol.[11][12]

Twenty-eight radioisotopes have been characterized, the most stable being ^{105}Ag with a half-life of 41.29 days, ^{111}Ag with a half-life of 7.45 days, and ^{112}Ag with a half-life of 3.13 hours. This element has numerous meta states, the most stable being ^{108m}Ag ($t_{1/2} = 418$ years), ^{110m}Ag ($t_{1/2} = 249.79$ days) and ^{106m}Ag ($t_{1/2} = 8.28$ days). All of the remaining radioactive isotopes have half-lives of less than an hour, and the majority of these have half-lives of less than three minutes.

Isotopes of silver range in relative atomic mass from 93.943 (^{94}Ag) to 126.936 (^{127}Ag);[13] the primary decay mode before the most abundant stable isotope, ^{107}Ag, is electron capture and the primary mode after is beta decay. The primary decay products before ^{107}Ag are palladium (element 46) isotopes, and the primary products after are cadmium (element 48) isotopes.

The palladium isotope ^{107}Pd decays by beta emission to ^{107}Ag with a half-life of 6.5 million years. Iron meteorites are the only objects with a high-enough palladium-to-silver ratio to yield measurable variations in ^{107}Ag abundance. Radiogenic ^{107}Ag was first discovered in the Santa Clara meteorite in 1978.[14] The discoverers suggest the coalescence and differentiation of iron-cored small planets may have occurred 10 million years after a nucleosynthetic event. ^{107}Pd–^{107}Ag correlations observed in bodies that have clearly been melted since the accretion of the solar system must reflect the presence of unstable nuclides in the early solar system.[15]

1.6.3 Compounds

Silver metal dissolves readily in nitric acid (HNO
3) to produce silver nitrate (AgNO
3), a transparent crystalline solid that is photosensitive and readily soluble in water. Silver nitrate is used as the starting point for the synthesis of many other silver compounds, as an antiseptic, and as a yellow stain for glass in stained glass. Silver metal does not react with sulfuric acid, which is used in jewelry-making to clean and remove copper oxide firescale from silver articles after silver soldering or annealing. Silver reacts readily with sulfur or hydrogen sulfide H
2S to produce silver sulfide, a dark-colored compound familiar as the tarnish on silver coins and other objects. Silver sulfide Ag
2S also forms silver whiskers when silver electrical contacts are used in an atmosphere rich in hydrogen sulfide.

$$4\ \mathrm{Ag} + \mathrm{O_2} + 2\ \mathrm{H_2S} \rightarrow 2\ \mathrm{Ag_2S} + 2\ \mathrm{H_2O}$$

Silver chloride (AgCl) is precipitated from solutions of silver nitrate in the presence of chloride ions, and the other silver halides used in the manufacture of photographic emulsions are made in the same way, using bromide or iodide salts. Silver chloride is used in glass electrodes for pH testing and potentiometric measurement, and as a transparent cement for glass. Silver iodide has been used in attempts to seed clouds to produce rain.[9] Silver halides are highly insoluble in aqueous solutions and are used in gravimetric analytical methods.

Silver oxide (Ag
2O), produced when silver nitrate solutions are treated with a base, is used as a positive electrode (anode) in watch batteries. Silver carbonate (Ag

Cessna 210 equipped with a silver iodide generator for cloud seeding

2CO
3) is precipitated when silver nitrate is treated with sodium carbonate (Na
2CO
3).[16]

$$2\ \mathrm{AgNO_3} + 2\ \mathrm{OH^-} \rightarrow \mathrm{Ag_2O} + \mathrm{H_2O} + 2\ \mathrm{NO_3^-}$$

$$2\ \mathrm{AgNO_3} + \mathrm{Na_2CO_3} \rightarrow \mathrm{Ag_2CO_3} + 2\ \mathrm{NaNO_3}$$

Silver fulminate (AgONC), a powerful, touch-sensitive explosive used in percussion caps, is made by reaction of silver metal with nitric acid in the presence of ethanol (C
2H
5OH). Other dangerously explosive silver compounds are silver azide (AgN
3), formed by reaction of silver nitrate with sodium azide (NaN
3),[17] and silver acetylide, formed when silver reacts with acetylene gas.

Latent images formed in silver halide crystals are developed by treatment with alkaline solutions of reducing agents such as hydroquinone, metol (4-(methylamino)phenol sulfate) or ascorbate, which reduce the exposed halide to silver metal. Alkaline solutions of silver nitrate can be reduced to silver metal by reducing sugars such as glucose, and this reaction is used to silver glass mirrors and the interior of glass Christmas ornaments. Silver halides are soluble in solutions of sodium thiosulfate (Na
2S
2O
3) which is used as a photographic fixer, to remove excess silver halide from photographic emulsions after image development.[16]

Silver metal is attacked by strong oxidizers such as potassium permanganate (KMnO
4) and potassium dichromate (K
2Cr

2O 7), and in the presence of potassium bromide (KBr); these compounds are used in photography to bleach silver images, converting them to silver halides that can either be fixed with thiosulfate or redeveloped to intensify the original image. Silver forms cyanide complexes (silver cyanide) that are soluble in water in the presence of an excess of cyanide ions. Silver cyanide solutions are used in electroplating of silver.[16]

Although silver normally has oxidation state +1 in compounds, other oxidation states are known, such as +3 in AgF 3, produced by the reaction of elemental silver or silver fluoride with krypton difluoride.[18]

Silver artifacts primarily under go three forms of deterioration. Silver sulfide is the most common form of silver degradation. Fresh silver chloride is pale yellow colored, becoming purplish on exposure to light and projects slightly from the surface of the artifact or coin. The precipitation of copper in ancient silver can be used to date artifacts.[19]

1.6.4 Applications

Many well-known uses of silver involve its precious metal properties, including currency, decorative items, and mirrors. The contrast between its bright white color and other media makes it very useful to the visual arts. By contrast, fine silver particles form the dense black in photographs and in silverpoint drawings. It has also long been used to confer high monetary value as objects (such as silver coins and investment bars) or make objects symbolic of high social or political rank. Silver salts have been used since the Middle Ages to produce a yellow or orange colors to stained glass, and more complex decorative color reactions can be produced by incorporating silver metal in blown, kilnformed or torchworked glass.[20]

Currency

Main articles: Silver coin and Silver standard

Silver, in the form of electrum (a gold–silver alloy), was coined to produce money around 700 BC by the Lydians. Later, silver was refined and coined in its pure form. Many nations used silver as the basic unit of monetary value. In the modern world, silver bullion has the ISO currency code XAG. The name of the pound sterling (£) reflects the fact it originally represented the value of one pound Tower weight of sterling silver; other historical currencies, such as the French livre, have similar etymologies. During the 19th century, the bimetallism that prevailed in most countries was undermined by the discovery of large deposits of silver in the Americas; fearing a sharp decrease in the value of silver and thus the currency, most states switched to a gold standard by 1900. In some languages, such as Sanskrit, Spanish, French, and Hebrew, the same word means both silver and money.

The 20th century saw a gradual movement to fiat currency, with most of the world monetary system losing its link to precious metals after Richard Nixon took the United States dollar off the gold standard in 1971; the last currency backed by gold was the Swiss franc, which became a pure fiat currency on 1 May 2000. During this same period, silver gradually ceased to be used in circulating coins. In 1964, the United States stopped minting their silver dime and quarter. They minted their last circulating silver coin in 1970 in its 40% half-dollar.[21]

In 1968, Canada minted their last circulating silver coins which were the 50% dime and the 50% quarter. The Royal Canadian Mint still makes many collectible silver coins with various dollar denominations. In addition to Canada, the United States and many other countries continue to mint silver coins that are collected for their bullion and numismatic value. The U.S. coin is known as the “Silver Eagle”.

Silver is used as a currency by many individuals, and is legal tender in the US state of Utah.[22] Silver coins and bullion are also used as an investment to guard against inflation and devaluation.

Jewelry and silverware

Shallow silver bowl, Persian, 6th century BC (Achaemenid). The deeper depressions reperesent lotus buds, an Egyptian motif. Walters Art Museum collections.

Main articles: jewelry and silversmith

Jewelry and silverware are traditionally made from sterling silver (standard silver), an alloy of 92.5% silver with 7.5% copper. In the US, only an alloy consisting of at least 90.0% fine silver can be marketed as “silver” (thus frequently stamped 900). Sterling silver (stamped 925) is harder than pure silver, and has a lower melting point (893 °C) than either pure silver or pure copper.[9] Britannia silver is an alternative, hallmark-quality standard containing 95.8% silver, often used to make silver tableware and wrought plate. With the addition of germanium, the patented modified alloy Argentium Sterling silver is formed, with improved properties, including resistance to firescale.

Sterling silver jewelry is often plated with a thin coat of .999 fine silver to give the item a shiny finish. This process is called “flashing”. Silver jewelry can also be plated with rhodium (for a bright, shiny look) or gold (to produce silver gilt).

Silver is a constituent of almost all colored carat gold alloys and carat gold solders, giving the alloys paler color and greater hardness.[23] White 9 carat gold contains 62.5% silver and 37.5% gold, while 22 carat gold contains a minimum of 91.7% gold and 8.3% silver or copper or other metals.[23]

Historically, the training and guild organization of goldsmiths included silversmiths, as well, and the two crafts remain largely overlapping. Unlike blacksmiths, silversmiths do not shape the metal while it is red-hot, but instead, work it at room temperature with gentle and carefully placed hammer blows. The essence of silversmithing is to take a flat piece of metal and to transform it into a useful object using different hammers, stakes and other simple tools.[24]

While silversmiths specialize in, and principally work silver, they also work with other metals, such as gold, copper, steel, and brass. They make jewelry, silverware, armor, vases, and other artistic items. Because silver is such a malleable metal, silversmiths have a large range of choices with how they prefer to work the metal. Historically, silversmiths are mostly referred to as goldsmiths, which was usually the same guild. In the western Canadian silversmith tradition, guilds do not exist; however, mentoring through colleagues becomes a method of professional learning within a community of craftspeople.[25]

Traditionally, silversmiths mostly made "silverware" (cutlery, tableware, bowls, candlesticks and such). Only in more recent times has silversmithing become mainly work in jewelry, as much less solid silver tableware is now handmade.

Solar energy

About 20g of silver is used in every crystalline solar photovoltaic panel made.[26] Silver is also used in plasmonic solar cells. 100 million ounces of silver are projected for use by solar energy in 2015.[27]

Silver is the reflective coating of choice for concentrated solar power reflectors.[28] In 2009, scientists at the National Renewable Energy Laboratory (NREL) and SkyFuel teamed to develop large curved sheets of metal that have the potential to be 30% less expensive than today’s best collectors of concentrated solar power by replacing glass-based models with a silver polymer sheet that has the same performance as the heavy glass mirrors, but at much lower cost and weight. It also is much easier to deploy and install. The glossy film uses several layers of polymers, with an inner layer of pure silver.

Solar modules mounted on solar trackers

Water purification

Silver is used in water purifiers. It prevents bacteria and algae from building up in filters. The catalytic action of silver, in concert with oxygen, sanitizes water and eliminates the need for chlorine. Silver ions are also added to water purification systems in hospitals, community water systems, pools and spas, displacing chlorine.[27]

Dentistry

Silver can be alloyed with mercury at room temperature to make amalgams that are widely used for dental fillings. To make dental amalgam, a mixture of powdered silver and other metals such as tin and gold is mixed with mercury to make a stiff paste that can be adapted to the shape of a cavity. The dental amalgam achieves initial hardness within minutes, and sets hard in a few hours.

Photography and electronics

The use of silver in photography, in the form of silver nitrate and silver halides, has rapidly declined due to the lower demand for consumer color film from the advent of digital technology. From the peak global demand for photographic silver in 1999 (267,000,000 troy ounces or 8304.6 metric tonnes) the market had contracted almost 70% by 2013.[29]

Some electrical and electronic products use silver for its superior conductivity, even when tarnished. The primary example of this is in high quality RF connectors. The increase in conductivity is also taken advantage of in RF engineering at VHF and higher frequencies, where conductors often cannot be scaled by 6%, due to tuning requirements, e.g. cavity filters. As an additional example, printed circuits and RFID antennas can be made using silver paints,[9][30] and computer keyboards use silver electrical contacts. Silver cadmium oxide is used in high-voltage contacts because it can withstand arcing.

Some manufacturers produce audio connector cables, speaker wires, and power cables using silver conductors, which have a 6% higher conductivity than ordinary copper ones of identical dimensions, but cost much more. Though debatable, many hi-fi enthusiasts believe silver wires improve sound quality.

Small devices, such as hearing aids and watches, commonly use silver oxide batteries due to their long life and high energy-to-weight ratio. Another usage is high-capacity silver-zinc and silver-cadmium batteries.

In World War II, there was a shortage of copper and silver borrowed from the United States Treasury for electrical windings for several production facilities including those of the Manhattan Project; see below under History, WWII.

Glass coatings

Telescopic mirrors

Mirrors in almost all reflective telescopes use vacuum aluminum coatings.[31] However thermal or infrared telescopes use silver coated mirrors because of silver's ability to reflect some types of infrared radiation more effectively than aluminum, as well as silver's ability to reduce the amount of radiation actually emitted from the mirror (its thermal emissivity).[32]

Silver, in protected or enhanced coatings, is seen as the next generation metal coating for reflective telescope mirrors.[33]

Windows

Using a process called sputtering, silver, along with other optically transparent layers, is applied to glass, creating low emissivity coatings used in high-performance insulated glazing. The amount of silver used per window is small because the silver layer is only 10–15 nanometers thick.[34] However, the amount of silver-coated glass worldwide is hundreds of millions of square meters per year, leading to silver consumption on the order of 10 cubic meters or 100 metric tons/year. Silver color seen in architectural glass and tinted windows on vehicles is produced by sputtered chrome, stainless steel or other alloys.

Silver-coated polyester sheets, used to retrofit windows, are another popular method for reducing light transmission.[27]

Other industrial and commercial applications

This Yanagisawa A9932J alto saxophone has a solid silver bell and neck with a solid phosphor bronze body. The bell, neck, and key-cups are extensively engraved. It was manufactured in 2008.

Silver and silver alloys are used in the construction of high-quality musical wind instruments of many types.[35] Flutes, in particular, are commonly constructed of silver alloy or silver plated, both for appearance and for the frictional surface properties of silver.[36]

Silver's catalytic properties make it ideal for use as a catalyst in oxidation reactions, for example, the production of formaldehyde from methanol and air by means of silver screens or crystallites containing a minimum 99.95 weight-percent silver. Silver (upon some suitable support) is probably the only catalyst available today to convert ethylene to ethylene oxide (later hydrolyzed to ethylene glycol, used for making polyesters)— an important industrial reaction. It is also used in the Oddy test to detect reduced sulfur compounds and carbonyl sulfides.

Because silver readily absorbs free neutrons, it is commonly used to make control rods to regulate the fission chain reaction in pressurized water nuclear reactors, generally in the form of an alloy containing 80% silver, 15% indium, and 5% cadmium.

Silver is used to make solder and brazing alloys, and as a thin layer on bearing surfaces can provide a significant increase in galling resistance and reduce wear under heavy load, particularly against steel.

Biology

Silver stains are used in biology to increase the contrast and visibility of cells and organelles in microscopy. Camillo Golgi used silver stains to study cells of the nervous system and the Golgi apparatus.[37] Silver stains are used to stain proteins in gel electrophoresis and polyacrylamide gels, either as primary stains or to enhance the visibility and contrast of colloidal gold stain.[38] Different yeasts from Brazilian gold mines, bioaccumulate free and complexed silver ions.[39] A sample of the fungus Aspergillus niger was found growing from gold mining solution; and was found to contain cyano metal complexes; such as gold, silver, copper iron and zinc. The fungus also plays a role in the solubilization of heavy metal sulfides.[40]

Medicine

Main article: Medical uses of silver

The **medical uses of silver** include its incorporation into wound dressings, and its use as an antibiotic coating in medical devices. Wound dressings containing silver sulfadiazine or silver nanomaterials may be used to treat external infections. Silver is also used in some medical applications, such as urinary catheters and endotracheal breathing tubes, where there is tentative evidence that it is effective in reducing catheter-related urinary tract infections and ventilator-associated pneumonia respectively.[41][42] The silver ion (Ag+
) is bioactive and in sufficient concentration readily kills bacteria *in vitro*. Silver and silver nanoparticles are used as an antimicrobial in a variety of industrial, healthcare and domestic applications.[43]

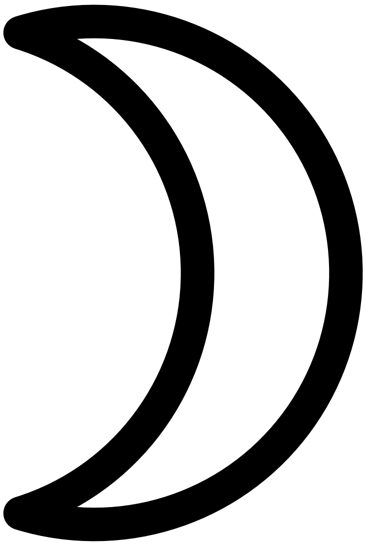
Investing

Silver coins and bullion are used for investing. Mints sell a wide variety of silver products for investors and collectors. Various institutions provide safe storage for large physical silver investments, and various types of silver investments can be made on the stock markets, including mining stocks. Silver bullion bars are sold in a wide range of ounces, provided by various mints and mines around the world. Silver coins and bullion bars are generally 99.9% pure, and labeled with ".999”.

Clothing

Silver inhibits the growth of bacteria and fungi on clothing, such as socks, so is sometimes added to reduce odors and the risk of bacterial and fungal infections. It is incorporated into clothing or shoes either by integrating silver nanoparticles into the polymer from which yarns are made or by coating yarns with silver.[44][45] The loss of silver during washing varies between textile technologies, and the resultant effect on the environment is not yet fully known.[46][47]

1.6.5 History



The crescent moon has been used since ancient times to represent silver.

Silver has been used for thousands of years for ornaments and utensils, trade, and as the basis for many monetary systems. Its value as a precious metal was long considered second only to gold. The word “silver” appears in Anglo-Saxon in various spellings, such as *seolfor* and *siolfor*. A similar form is seen throughout the Germanic languages (compare Old High German *silabar* and *silbir*). The chemical symbol Ag is from the Latin word for “silver”, *argentum* (compare Greek άργυρος, *árgyros*), from the Indo-European root **arg-*, meaning “white” or “shining”. Silver has been known since ancient times. Mentioned in the Book of Genesis, slag heaps found in Asia Minor and on the islands of the Aegean Sea indicate silver was being separated from lead as early as the 4th millennium BC using surface mining.[9]

The stability of the Roman currency relied to a high degree on the supply of silver bullion, which Roman miners produced on a scale unparalleled before the discovery of the New World. Reaching a peak production of 200 t per year, an estimated silver stock of 10,000 t circulated in the Roman economy in the middle of the second century AD, five to ten times larger than the combined amount of silver available to medieval Europe and the Caliphate around 800 AD.[48][49] Financial officials of the Roman Empire worried about the loss of silver to pay for highly demanded silk from Sinica (China).

Mines were made in Laureion during 483 BC.[50]

In the Gospels, Jesus’ disciple Judas Iscariot is infamous for having taken a bribe of 30 coins of silver from religious leaders in Jerusalem to turn Jesus of Nazareth over to soldiers of the High Priest Caiaphas.[51]

The Chinese Empire during most of its history primarily used silver as a means of exchange. In the 19th century, the threat to the balance of payments of the United Kingdom from Chinese merchants demanding payment in silver in exchange for tea, silk, and porcelain led to the Opium War because Britain had to find a way to address the imbalance in payments, and they decided to do so by selling opium produced in their colony of British India to China.[52]

Silver mining and processing in Kutná Hora, Central Europe, 1490s

Islam permits Muslim men to wear silver rings on the little finger of either hand.[53] Muhammad himself wore a silver signet ring.[54]

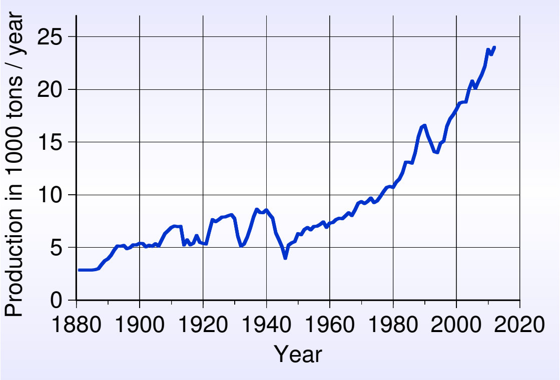
In the Americas, high temperature silver-lead cupellation technology was developed by pre-Inca civilizations as early as AD 60–120.[55]

World War II

During World War II, the shortage of copper led to the substitution of silver in many industrial applications. The United States government loaned out silver from its massive reserve located in the West Point vaults to a wide range of industrial users. One very important use was for bus bars for new aluminum plants needed to make aircraft. During the war, many electrical connectors and switches were silver plated. Another use was aircraft master rod bearings and other types of bearings. Since silver can replace tin in solder at a lower volume, a large amount of tin was freed up for other uses by substituting government silver. Silver was also used as the reflector in searchlights and other types of lights. Silver was used in nickels during the war to save that metal for use in steel alloys.[56]

The Manhattan Project to develop the atomic bomb used about 14,700 tons of silver borrowed from the United States Treasury for calutron windings for the electromagnetic separation process in the Y-12 National Security Complex at the Oak Ridge National Laboratory. After the war ended, the silver was returned to the vaults.)[57]

1.6.6 Occurrence and extraction



Time trend of silver production

Native silver

Main article: Silver mining

Silver is found in native form, as an alloy with gold (electrum), and in ores containing sulfur, arsenic, antimony or chlorine. Ores include argentite (Ag_2S), chlorargyrite ($AgCl$) which includes horn silver, and pyrargyrite (Ag_3SbS_3). The principal sources of silver are the ores of copper, copper-nickel, lead, and lead-zinc obtained from Peru, Bolivia, Mexico, China, Australia, Chile, Poland and Serbia.[9] Peru, Bolivia and Mexico have been mining silver since 1546, and are still major world producers. Top silver-producing mines are Cannington (Australia), Fresnillo (Mexico), San Cristobal (Bolivia), Antamina (Peru), Rudna (Poland), and Penasquito (Mexico).[58] Top near-term mine development projects through 2015 are Pascua Lama (Chile), Navidad (Argentina), Jaunicipio (Mexico), Malku Khota (Bolivia),[59] and Hackett River (Canada).[58] In Central

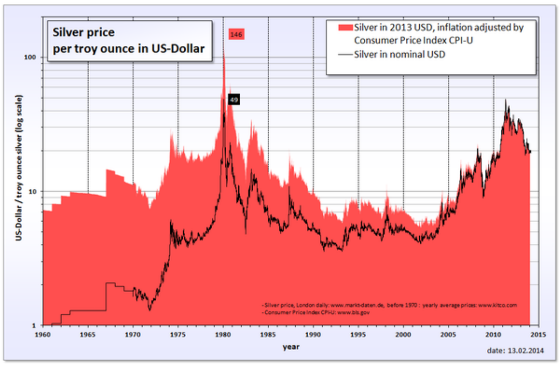
Asia, Tajikistan is known to have some of the largest silver deposits in the world.[60]

The metal is primarily produced as a byproduct of electrolytic copper refining, gold, nickel, and zinc refining, and by application of the Parkes process on lead metal obtained from lead ores that contain small amounts of silver. Commercial-grade fine silver is at least 99.9% pure, and purities greater than 99.999% are available. In 2011, Mexico was the top producer of silver (4,500 tonnes or 19% of the world's total), closely followed by Peru (4,000 t) and China (4,000 t).[61]

1.6.7 Price

Main articles: Silver as an investment and Silver standard

As of 5 August 2014, the price of silver is US$649.28 per kilogram (US$20.1950 per troy ounce[62]). This equates to approximately 1/64 the price of gold. The ratio has varied from 1/15 to 1/100 in the past 100 years. Physical silver bullion prices are higher than the paper prices, with premiums increasing when demand is high and local shortages occur.[63]



Silver price history in 1960–2011

In 1980, the silver price rose to a peak for modern times of US$49.45 per troy ounce (ozt) due to market manipulation of Nelson Bunker Hunt and Herbert Hunt. Inflation-adjusted to 2012, this is approximately US$138 per troy ounce. Some time after Silver Thursday, the price was back to $10/ozt.[64] From 2001 to 2010, the price moved from $4.37 to $20.19 (average London US$/oz).[65] According to the Silver Institute, silver's recent gains have greatly stemmed from a rise in investor interest and an increase in fabrication demand.[65] In late April 2011, silver reached an all-time high of $49.76/ozt.

In earlier times, silver has commanded much higher prices. In the early 15th century, the price of silver is estimated to have surpassed $1,200 per ounce, based on 2011 dollars.[66] The discovery of massive silver deposits in the New World during the succeeding centuries has been stated as a cause for its price to have diminished greatly.

The price of silver is important in Judaic law. The lowest fiscal amount a Jewish court, or Beth Din, can convene to adjudicate a case over is a *shova pruta* (value of a Babylonian *pruta* coin). This is fixed at .025 grams (0.00088 oz) of pure, unrefined silver, at market price. In a Jewish tradition, still continuing today, on the first birthday of a first-born son, the parents pay the price of five pure-silver coins to a *Kohen* (priest). Today, the Israel mint fixes the coins at 117 grams (4.1 oz) of silver. The *Kohen* will often give those silver coins back as a gift for the child to inherit.[67]

1.6.8 Human exposure and consumption

Silver plays no known natural biological role in humans, and possible health effects of silver are a disputed subject. Silver itself is not toxic to humans, but most silver salts are. In large doses, silver and compounds containing it can be absorbed into the circulatory system and become deposited in various body tissues, leading to argyria, which results in a blue-grayish pigmentation of the skin, eyes, and mucous membranes. Argyria is rare, and although, so far as known, this condition does not otherwise harm a person's health, it is disfiguring and usually permanent. Mild forms of argyria are sometimes mistaken for cyanosis.[9]

Monitoring exposure

Overexposure to silver can occur in workers in the metallurgical industry, persons taking silver-containing dietary supplements, patients who have received silver sulfadiazine treatment, and individuals who accidentally or intentionally ingest silver salts. Silver concentrations in whole blood, plasma, serum, or urine may be measured to monitor for safety in exposed workers, to confirm the diagnosis in potential poisoning victims, or to assist in the forensic investigation in a case of fatal overdosage.[68]

Use in food

Silver is used in food coloring; it has the E174 designation and is approved in the European Union.

The safety of silver for use in food is disputed.[69] Traditional Indian dishes sometimes include the use of decorative silver foil known as *vark*,[70] and in various cultures, silver *dragée* are used to decorate cakes, cookies, and other dessert items.[69] The use of silver as a food additive is not approved in the United States.

1.6.9 See also

- List of silver compounds
- Silverpoint drawing
- Free silver

- List of elements
- Hardnesses of the elements (data page)

1.6.10 References

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1.6.11 External links

- Chemistry in its element podcast (MP3) from the Royal Society of Chemistry's Chemistry World: Silver
- Silver at *The Periodic Table of Videos* (University of Nottingham)
- Society of American Silversmiths
- The Silver Institute A silver industry website
- A collection of silver items Samples of silver
- Transport, Fate and Effects of Silver in the Environment
- CDC – NIOSH Pocket Guide to Chemical Hazards – Silver
- Picture in the Element collection from Heinrich Pniok

1.7 Sulfur

This article is about the chemical element. For other uses, see Sulfur (disambiguation).

Sulfur or **sulphur** (see spelling differences) is a chemical element with symbol **S** and atomic number 16. It is an abundant, multivalent non-metal. Under normal conditions, sulfur atoms form cyclic octatomic molecules with chemical formula S_8. Elemental sulfur is a bright yellow crystalline solid when at room temperature. Chemically, sulfur can react as either an oxidant or a reducing agent. It oxidizes most metals and several nonmetals, including carbon, which leads to its negative charge in most organosulfur compounds, but it reduces several strong oxidants, such as oxygen and fluorine.

Sulfur occurs naturally as the pure element (native sulfur) and as sulfide and sulfate minerals. Elemental sulfur crystals are commonly sought after by mineral collectors for their distinct, brightly colored polyhedron shapes. Being abundant in native form, sulfur was known in ancient times, mentioned for its uses in ancient India, ancient Greece, China and Egypt. Fumes from burning sulfur were used as fumigants, and sulfur-containing medicinal mixtures were used as balms and antiparasitics. Sulfur is referred to in the Bible as *brimstone* (burn stone) in English, with this name still used in several nonscientific tomes.[3] It was needed to make the best quality of black gunpowder. In 1777, Antoine Lavoisier helped convince the scientific community that sulfur was a basic element rather than a compound.

Elemental sulfur was once extracted from salt domes where it sometimes occurs in nearly pure form, but this method has been obsolete since the late 20th century. Today, almost all elemental sulfur is produced as a byproduct of removing sulfur-containing contaminants from natural gas and petroleum. The element's largest commercial use (after mostly being converted to sulfuric acid) is to produce sulfate and phosphate fertilizers, because of the relatively high requirement of plants for sulfur and phosphorus. Sulfuric acid is also a primary industrial chemical outside fertilizer manufacture. Other well-known uses for the element are in matches, insecticides and fungicides. Many sulfur compounds are odoriferous, and the smell of odorized natural gas, skunk scent, grapefruit, and garlic is due to sulfur compounds. Hydrogen sulfide produced by living organisms imparts the characteristic odor to rotting eggs and other biological processes.

Sulfur is an essential element for all life, and is widely used in biochemical processes. In metabolic reactions, sulfur compounds serve as both fuels (electron donors) and respiratory (oxygen-alternative) materials (electron acceptors). Sulfur in organic form is present in the vitamins biotin and thiamine, the latter being named for the Greek word for sulfur. Sulfur is an important part of many enzymes and in antioxidant molecules like glutathione and thioredoxin. Organically bonded sulfur is a component of all proteins, as the amino acids cysteine and methionine. Disulfide bonds are largely responsible for the mechanical strength and insolubility of the protein keratin, found in outer skin, hair, and feathers, and the element contributes to their pungent odor when burned.

1.7.1 Spelling and etymology

Sulfur is historically a Latin word. The original Latin spelling was *sulpur*, but this was Hellenized to *sulphur*; the form *sulfur* appears toward the end of the Classical period. (The true Greek word for sulfur, *θεῖον*, is the source of the international chemical prefix *thio-*.) In 12th-century Anglo-French, it was *sulfre*; in the 14th century the Latin *ph* was restored, for *sulphre*; and by the 15th century the full Latin spelling was restored, for *sulfur, sulphur*. The parallel *f~ph* spellings continued in Britain until the 19th century, when the word was standardized as *sulphur*.[4] *Sulfur* was the form chosen in the United States, while Canada uses both. However, the IUPAC adopted the spelling *sulfur* in 1990, as did the Nomenclature Committee of the Royal Society of Chemistry in 1992, restoring the spelling *sulfur* to Britain.[5] The Oxford Dictionaries note that "in chemistry ... the -f- spelling is now the standard form in all related words in the field in both British and US contexts."[6]

The Latin word also continues in the Romance languages: French *soufre*, Italian *zolfo* (from *solfo*), Spanish *azufre* (from *açufre*, from earlier *çufre*), Portuguese *enxofre* (from *xofre*). The Spanish and Portuguese forms are prefixed with the Arabic article, despite not being Arabic words.[4] The root has been traced back to reconstructed proto-Indo-European *swépl̥ (genitive *sulplós), a nominal derivative of *swelp 'to burn', a lineage also preserved in the Germanic languages, where it is found for example as modern German *Schwefel*, Dutch *zwavel*, and Swedish *svavel*, and as Old English *swefl*.[7]

1.7.2 Characteristics

When burned, sulfur melts to a blood-red liquid and emits a blue flame that is best observed in the dark.

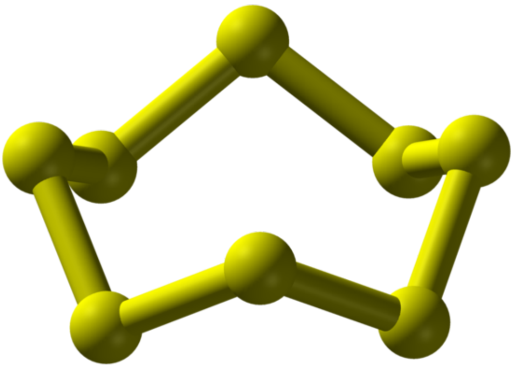
Physical properties

Sulfur forms polyatomic molecules with different chemical formulas, with the best-known allotrope being octasulfur, cyclo-S_8. Octasulfur is a soft, bright-yellow solid with only a faint odor, similar to that of matches.[8] It melts at 115.21 °C, boils at 444.6 °C and sublimes easily.[3] At 95.2 °C, below its melting temperature, cyclo-octasulfur changes from α-octasulfur to the β-polymorph.[9] The structure of the S_8 ring is virtually unchanged by this phase change, which affects the intermolecular interactions. Between its melting and boiling temperatures, octasulfur changes its allotrope again, turning from β-octasulfur to γ-sulfur, again accompanied by a lower density but increased viscosity due to the formation of polymers.[9] At even higher temperatures, however, the viscosity decreases as depolymerization occurs. Molten sulfur assumes a dark red color above 200 °C. The density of sulfur is about 2 $g{\cdot}cm^{-3}$, depending on the allotrope; all of its stable allotropes are excellent electrical insulators.

Chemical properties

Sulfur burns with a blue flame concomitant with formation of sulfur dioxide, notable for its peculiar suffocating odor. Sulfur is insoluble in water but soluble in carbon disulfide and, to a lesser extent, in other nonpolar organic solvents, such as benzene and toluene. The first and the second ionization energies of sulfur are 999.6 and 2252 $kJ{\cdot}mol^{-1}$, respectively. Despite such figures, the +2 oxidation state is rare, with +4 and +6 being more common. The fourth and sixth ionization energies are 4556 and 8495.8 $kJ{\cdot}mol^{-1}$, the magnitude of the figures caused by electron transfer between orbitals; these states are only stable with strong oxidants as fluorine, oxygen, and chlorine.

Allotropes



The structure of the cyclooctasulfur molecule, S_8.

Main article: Allotropes of sulfur

Sulfur forms over 30 solid allotropes, more than any other element.[10] Besides S_8, several other rings are known.[11] Removing one atom from the crown gives S_7, which is more deeply yellow than S_8. HPLC analysis of “elemental sulfur” reveals an equilibrium mixture of mainly S_8, but with S_7 and small amounts of S_6.[12] Larger rings have been prepared, including S_{12} and S_{18}.[13][14]

Amorphous or “plastic” sulfur is produced by rapid cooling of molten sulfur—for example, by pouring it into cold water. X-ray crystallography studies show that the amorphous form may have a helical structure with eight atoms per turn. The long coiled polymeric molecules make the brownish substance elastic, and in bulk this form has the feel of crude rubber. This form is metastable at room temperature and gradually reverts to crystalline molecular allotrope, which is no longer elastic. This process happens within a matter of hours to days, but can be rapidly catalyzed.

Isotopes

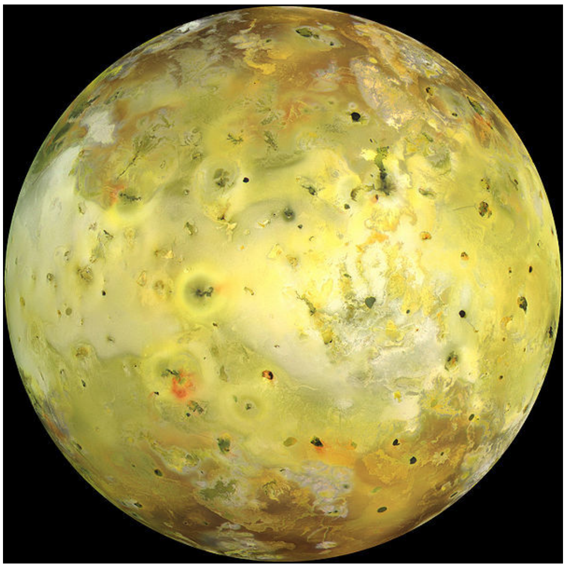
Main article: Isotopes of sulfur

Sulfur has 25 known isotopes, four of which are stable: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%). Other than ^{35}S, with a half-life of 87 days and formed in cosmic ray spallation of ^{40}Ar, the radioactive isotopes of sulfur have half-lives less than 3 hours.

When sulfide minerals are precipitated, isotopic equilibration among solids and liquid may cause small differences in the δS-34 values of co-genetic minerals. The differences between minerals can be used to estimate the temperature of equilibration. The δC−13 and δS-34 of coexisting carbonate minerals and sulfides can be used to determine the pH and oxygen fugacity of the ore-bearing fluid during ore formation.

In most forest ecosystems, sulfate is derived mostly from the atmosphere; weathering of ore minerals and evaporites contribute some sulfur. Sulfur with a distinctive isotopic composition has been used to identify pollution sources, and enriched sulfur has been added as a tracer in hydrologic studies. Differences in the natural abundances can be used in systems where there is sufficient variation in the ^{34}S of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have different δ^{34}S values from lakes believed to be dominated by watershed sources of sulfate.

Natural occurrence



Most of the yellow and orange hues of Io are due to elemental sulfur and sulfur compounds, produced by active volcanoes.

Native sulfur crystals

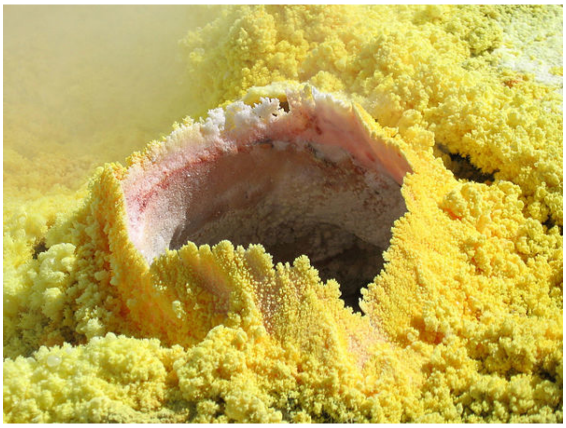
A man carrying sulfur blocks from Kawah Ijen, a volcano in East Java, Indonesia, 2009

^{32}S is created inside massive stars, at a depth where the temperature exceeds 2.5×10^{9} K, by the fusion of one nucleus of silicon plus one nucleus of helium.[15] As this is part of the alpha process that produces elements in abundance, sulfur is the 10th most common element in the universe.

Sulfur, usually as sulfide, is present in many types of meteorites. Ordinary chondrites contain on average 2.1% sulfur, and carbonaceous chondrites may contain as much as 6.6%. It is normally present as troilite (FeS), but there are exceptions, with carbonaceous chondrites containing free sulfur, sulfates and other sulfur compounds.[16] The distinctive colors of Jupiter's volcanic moon Io are attributed to various forms of molten, solid and gaseous sulfur.[17]

On Earth, elemental sulfur can be found near hot springs and volcanic regions in many parts of the world, especially along the Pacific Ring of Fire; such volcanic deposits are currently mined in Indonesia, Chile, and Japan. Such deposits are polycrystalline, with the largest documented single crystal measuring 22×16×11 cm.[18] Historically, Sicily was a large source of sulfur in the Industrial Revolution.[19]

Native sulfur is synthesised by anaerobic bacteria acting on sulfate minerals such as gypsum in salt domes.[20][21] Significant deposits in salt domes occur along the coast



Sulfur could be found in fumaroles such as this one in Vulcano, Italy

of the Gulf of Mexico, and in evaporites in eastern Europe and western Asia. Native sulfur may be produced by geological processes alone. Fossil-based sulfur deposits from salt domes have until recently been the basis for commercial production in the United States, Russia, Turkmenistan, and Ukraine.[22] Currently, commercial production is still carried out in the Osiek mine in Poland. Such sources are now of secondary commercial importance, and most are no longer worked.

Common naturally occurring sulfur compounds include the sulfide minerals, such as pyrite (iron sulfide), cinnabar (mercury sulfide), galena (lead sulfide), sphalerite (zinc sulfide) and stibnite (antimony sulfide); and the sulfates, such as gypsum (calcium sulfate), alunite (potassium aluminium sulfate), and barite (barium sulfate). On Earth, just as upon Jupiter's moon Io, elemental sulfur occurs naturally in volcanic emissions, including emissions from hydrothermal vents.

1.7.3 Production

Sulfur may be found by itself and historically was usually obtained in this way, while pyrite has been a source of sulfur via sulfuric acid.[23] In volcanic regions in Sicily, in ancient times, it was found on the surface of the Earth, and the *"Sicilian process"* was used: sulfur deposits were piled and stacked in brick kilns built on sloping hillsides, with airspaces between them. Then, some sulfur was pulverized, spread over the stacked ore and ignited, causing the free sulfur to melt down the hills. Eventually the surface-borne deposits played out, and miners excavated veins that ultimately dotted the Sicilian landscape with labyrinthine mines. Mining was unmechanized and labor-intensive, with pickmen freeing the ore from the rock, and mine-boys or *carusi* carrying baskets of ore to the surface, often through a mile or more of tunnels. Once the ore was at the surface, it was reduced and extracted in smelting ovens. The conditions in Sicilian sulfur mines were horrific, prompting Booker T. Washington to write *"I am not prepared just now to say to what extent I believe in a physical hell in the next world, but a sulphur mine in Sicily is about the nearest thing to hell that I expect to see in this life."*.[24]

Today's sulfur production is as a side product of other industrial processes such as oil refining; in these processes, sulfur often occurs as undesired or detrimental compounds that are extracted and converted to elemental sulfur. As a mineral, native sulfur under salt domes is thought to be a fossil mineral resource, produced by the action of ancient bacteria on sulfate deposits. It was removed from such salt-dome mines mainly by the Frasch process.[22] In this method, superheated water was pumped into a native sulfur deposit to melt the sulfur, and then compressed air returned the 99.5% pure melted product to the surface. Throughout the 20th century this procedure produced elemental sulfur that required no further purification. However, due to a limited number of such sulfur deposits and the high cost of working them, this process for mining sulfur has not been employed in a major way anywhere in the world since 2002.[25][26]

Sulfur recovered from hydrocarbons in Alberta, stockpiled for shipment in North Vancouver, B.C.

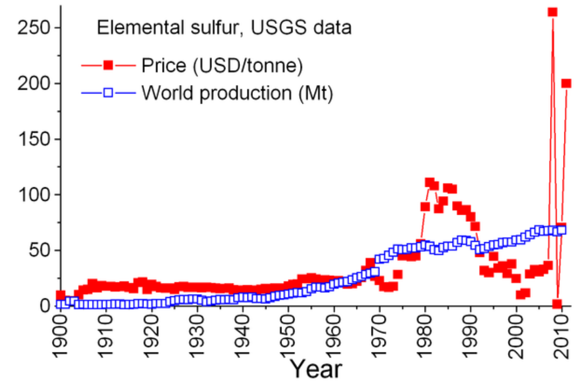
Today, sulfur is produced from petroleum, natural gas, and related fossil resources, from which it is obtained mainly as hydrogen sulfide. Organosulfur compounds, undesirable impurities in petroleum, may be upgraded by subjecting them to hydrodesulfurization, which cleaves the C–S bonds:[25][26]

$$\mathrm{R\text{-}S\text{-}R + 2\,H_2 \rightarrow 2\,RH + H_2S}$$

The resulting hydrogen sulfide from this process, and also as it occurs in natural gas, is converted into elemental sulfur by the Claus process. This process entails oxidation of some hydrogen sulfide to sulfur dioxide and then the comproportionation of the two:[25][26]

$$\mathrm{3\,O_2 + 2\,H_2S \rightarrow 2\,SO_2 + 2\,H_2O}$$
$$\mathrm{SO_2 + 2\,H_2S \rightarrow 3\,S + 2\,H_2O}$$

Owing to the high sulfur content of the Athabasca Oil Sands, stockpiles of elemental sulfur from this process now exist throughout Alberta, Canada.[27] Another way



Production and price (US market) of elemental sulfur

of storing sulfur is as a binder for concrete, the resulting product having many desirable properties (see sulfur concrete).[28]

The world production of sulfur in 2011 amounted to 69 million tonnes (Mt), with more than 15 countries contributing more than 1 Mt each. Countries producing more than 5 Mt are China (9.6), US (8.8), Canada (7.1) and Russia (7.1).[29] While the production has been slowly increasing from 1900 to 2010, the price was much less stable, especially in the 1980s and around 2010.[30]

1.7.4 Compounds

Common oxidation states of sulfur range from −2 to +6. Sulfur forms stable compounds with all elements except the noble gases.

Sulfur polycations

Sulfur polycations, S_8^{2+}, S_4^{2+} and S_{19}^{2+} are produced when sulfur is reacted with mild oxidising agents in a strongly acidic solution.[31] The colored solutions produced by dissolving sulfur in oleum were first reported as early as 1804 by C.F Bucholz, but the cause of the color and the structure of the polycations involved was only determined in the late 1960s. S_8^{2+} is deep blue, S_4^{2+} is yellow and S_{19}^{2+} is red.[9]

Sulfides

Treatment of sulfur with hydrogen gives hydrogen sulfide. When dissolved in water, hydrogen sulfide is mildly acidic:[3]

$$H_2S \rightleftarrows HS^- + H^+$$

Hydrogen sulfide gas and the hydrosulfide anion are extremely toxic to mammals, due to their inhibition of the oxygen-carrying capacity of hemoglobin and certain cytochromes in a manner analogous to cyanide and azide (see below, under *precautions*).

Reduction of elemental sulfur gives polysulfides, which consist of chains of sulfur atoms terminated with S^- centers:

$$2\ Na + S_8 \rightarrow Na_2S_8$$

This reaction highlights arguably the single most distinctive property of sulfur: its ability to catenate (bind to itself by formation of chains). Protonation of these polysulfide anions gives the polysulfanes, H_2S_x where x = 2, 3, and 4.[32] Ultimately reduction of sulfur gives sulfide salts:

$$16\ Na + S_8 \rightarrow 8\ Na_2S$$

The interconversion of these species is exploited in the sodium-sulfur battery. The radical anion S_3^- gives the blue color of the mineral lapis lazuli.

Lapis lazuli owes its blue color to a sulfur radical.

Oxides, oxoacids and oxoanions

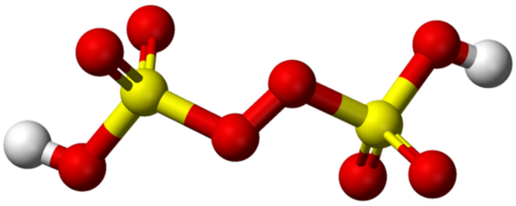
The principal sulfur oxides are obtained by burning sulfur:

$$S + O_2 \rightarrow SO_2$$

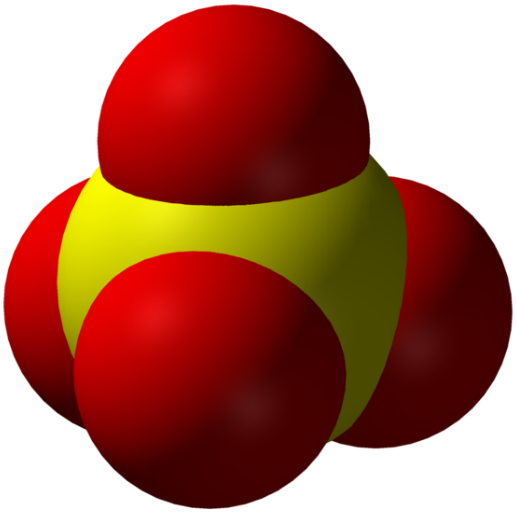
$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

Other oxides are known, sulfur rich oxides e.g. sulfur monoxide and disulfur mono- and dioxides and higher oxides containing peroxo groups.

Sulfur forms a number of sulfur oxoacids, some of which cannot be isolated and are only known through their salts. Sulfur dioxide and sulfites (SO2−
3) are related to the unstable sulfurous acid (H_2SO_3). Sulfur trioxide and sulfates (SO2−
4) are related to sulfuric acid. Sulfuric acid and SO_3 combine to give oleum, a solution of pyrosulfuric acid ($H_2S_2O_7$) in sulfuric acid.



Peroxydisulfuric acid



*The sulfate anion, SO2−
4*

Thiosulfate salts (S
2O2−
3), sometimes referred as "hyposulfites", used in photographic fixing (HYPO) and as reducing agents, feature sulfur in two oxidation states. Sodium dithionite (Na
2S
2O
4), contains the more highly reducing dithionite anion (S
2O2−
4).

Halides and oxyhalides

The two main sulfur fluorides are sulfur hexafluoride, a dense gas used as nonreactive and nontoxic propellant, and sulfur tetrafluoride, a rarely used organic reagent that is highly toxic.[33] Sulfur dichloride and disulfur dichloride are important industrial chemicals. Sulfuryl chloride and chlorosulfuric acid are derivatives of sulfuric acid; thionyl chloride ($SOCl_2$) is a common reagent in organic synthesis.[34]

Pnictides

An important S–N compound is the cage tetrasulfur tetranitride (S_4N_4). Heating this compound gives polymeric sulfur nitride ($(SN)_x$), which has metallic properties even though it does not contain any metal atoms. Thiocyanates contain the SCN^- group. Oxidation of thiocyanate gives thiocyanogen, $(SCN)_2$ with the connectivity NCS-SCN. Phosphorus sulfides are numerous, the most important commercially being the cages P_4S_{10} and P_4S_3.[35][36]

Metal sulfides

Main article: Sulfide mineral

The principal ores of copper, zinc, nickel, cobalt, molybdenum, and other metals are sulfides. These materials tend to be dark-colored semiconductors that are not readily attacked by water or even many acids. They are formed, both geochemically and in the laboratory, by the reaction of hydrogen sulfide with metal salts. The mineral galena (PbS) was the first demonstrated semiconductor and found a use as a signal rectifier in the cat's whiskers of early crystal radios. The iron sulfide called pyrite, the so-called "fool's gold," has the formula FeS_2.[37] The upgrading of these ores, usually by roasting, is costly and environmentally hazardous. Sulfur corrodes many metals via the process called tarnishing.

Organic compounds

Main article: Organosulfur compounds

- Illustrative organosulfur compounds
- Allicin, the active ingredient in garlic

- R-cysteine, an amino acid containing a thiol group
- Methionine, an amino acid containing a thioether
- Diphenyl disulfide, a representative disulfide
- Perfluorooctanesulfonic acid, a controversial surfactant
- Dibenzothiophene, a component of crude oil
- Penicillin

Some of the main classes of sulfur-containing organic compounds include the following:[38]

- Thiols or mercaptans (as they are **mer**cury **capt**urers as chelators) are the sulfur analogs of alcohols; treatment of thiols with base gives thiolate ions.
- Thioethers are the sulfur analogs of ethers.
- Sulfonium ions have three groups attached to a cationic sulfur center. Dimethylsulfoniopropionate (DMSP) is one such compound, important in the marine organic sulfur cycle.
- Sulfoxides and sulfones are thioethers with one and two oxygen atoms attached to the sulfur atom, respectively. The simplest sulfoxide, dimethyl sulfoxide, is a common solvent; a common sulfone is sulfolane.
- Sulfonic acids are used in many detergents.

Compounds with carbon–sulfur bonds are uncommon with the notable exception of carbon disulfide, a volatile colorless liquid that is structurally similar to carbon dioxide. It is used as a reagent to make the polymer rayon and many organosulfur compounds. Unlike carbon monoxide, carbon monosulfide is only stable as a dilute gas, as in the interstellar medium.[39]

Organosulfur compounds are responsible for some of the unpleasant odors of decaying organic matter. They are used in the odoration of natural gas and cause the odor of garlic and skunk spray. Not all organic sulfur compounds smell unpleasant at all concentrations: the sulfur-containing monoterpenoid grapefruit mercaptan in small concentrations is responsible for the characteristic scent of grapefruit, but has a generic thiol odor at larger concentrations. Sulfur mustard, a potent vesicant, was used in World War I as a disabling agent.[40]

Sulfur-sulfur bonds are a structural component to stiffen rubber, in a way similar to the biological role of disulfide bridges to rigidify proteins (see biological below). In the most common type of industrial “curing” or hardening and strengthening of natural rubber, elemental sulfur is heated with the rubber to the point that chemical reactions form disulfide bridges between isoprene units of the polymer. This process, patented in 1843, allowed rubber to become a major industrial product, especially automobile tires. Because of the heat and sulfur, the process was named vulcanization, after the Roman god of the forge and volcanism.

1.7.5 History

Antiquity

Pharmaceutical container for sulfur from the first half of the 20th century. From the Museo del Objeto del Objeto collection

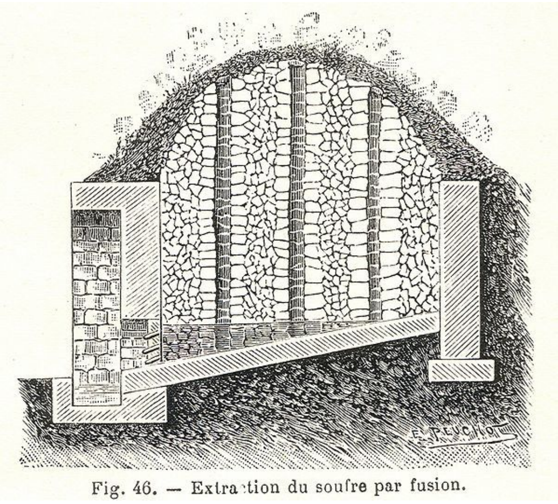
Being abundantly available in native form, sulfur (Latin *sulphur*) was known in ancient times and is referred to in the Torah (Genesis). English translations of the Bible commonly referred to burning sulfur as “brimstone”, giving rise to the name of 'fire-and-brimstone' sermons, in which listeners are reminded of the fate of eternal damnation that await the unbelieving and unrepentant. It is from this part of the Bible that Hell is implied to “smell of sulfur” (likely due to its association with volcanic activity). According to the Ebers Papyrus, a sulfur ointment was used in ancient Egypt to treat granular eyelids. Sulfur was used for fumigation in preclassical Greece;[41] this is mentioned in the *Odyssey*.[42] Pliny the Elder discusses sulfur in book 35 of his *Natural History*, saying that its best-known source is the island of Melos. He mentions its use for fumigation, medicine, and bleaching cloth.[43]

A natural form of sulfur known as *shiliuhuang* was known in China since the 6th century BC and found in Hanzhong.[44] By the 3rd century, the Chinese discovered that sulfur could be extracted from pyrite.[44] Chinese Daoists were interested in sulfur’s flammability and its reactivity with certain metals, yet its earliest practical uses were found in traditional Chinese medicine.[44] A Song Dynasty military treatise of 1044 AD described different formulas for Chinese black powder, which is a mixture of potassium nitrate (KNO
3), charcoal, and sulfur.

Indian alchemists, practitioners of “the science of mercury” (sanskrit rasaśāstra, रसशास्त्र), wrote extensively about the use of sulfur in alchemical operations with mercury, from the eighth century AD onwards.[45] In the rasaśāstra tradition, sulfur is called “the smelly” (sanskrit gandhaka, गन्धक).

Early European alchemists gave sulfur its own alchemical symbol, a triangle at the top of a cross. In traditional skin treatment before the modern era of scientific medicine, elemental sulfur was used, mainly in creams, to alleviate conditions such as scabies, ringworm, psoriasis, eczema, and acne. The mechanism of action is unknown—though elemental sulfur does oxidize slowly to sulfurous acid, which in turn (through the action of sulfite) acts as a mild reducing and antibacterial agent.[46][47][48]

Modern times



Sicilian kiln used to obtain sulfur from volcanic rock.

In 1777, Antoine Lavoisier helped convince the scientific community that sulfur was an element, not a compound. Sulfur deposits in Sicily were the dominant supply source for over half a century. Approximately 2000 tons per year of sulfur were imported into Marseilles, France for the production of sulfuric acid via the Leblanc process by the late 18th century. In industrializing Britain, with the repeal of tariffs on salt in 1824, demand for sulfur from Sicily surged upward. The increasing British control and exploitation of the mining, refining and transportation of the sulfur, coupled with the failure of this lucrative export to transform Sicily’s backward and impoverished economy led to the 'Sulfur Crisis’ of 1840, when King Ferdinand II gave a monopoly of the sulfur industry to a French firm, violating an earlier 1816 trade agreement with Britain. A peaceful negotiated solution was eventually mediated by France.[49][50]

In 1867, sulfur was discovered in underground deposits in Louisiana and Texas. The highly successful Frasch process was developed to extract this resource.[51]

In the late 18th century, furniture makers used molten sulfur to produce decorative inlays in their craft. Because of the sulfur dioxide produced during the process of melting sulfur, the craft of sulfur inlays was soon abandoned. Molten sulfur is sometimes still used for setting steel bolts into drilled concrete holes where high shock resistance is desired for floor-mounted equipment attachment points. Pure powdered sulfur was used as a medicinal tonic and laxative.[22] With the advent of the contact process, the majority of sulfur today is used to make sulfuric acid for a wide range of uses, particularly fertilizer.[52]

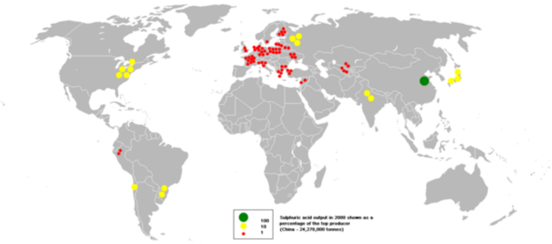
1.7.6 Applications

See also: Sulfur (pharmacy)

Sulfuric acid

Elemental sulfur is mainly used as a precursor to other chemicals. Approximately 85% (1989) is converted to sulfuric acid (H_2SO_4):

$$2\,S + 3\,O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4$$



Sulfuric acid production in 2000

Because of its importance, sulfuric acid was considered an excellent indicator of a country’s industrial well-being.[53] For example with 32.5 million tonnes in 2010, the United States produces more sulfuric acid every year than any other inorganic industrial chemical.[30] The principal use for the acid is the extraction of phosphate ores for the production of fertilizer manufacturing. Other applications of sulfuric acid include oil refining, wastewater processing, and mineral extraction.[22]

Other large-scale sulfur chemicals

Sulfur reacts directly with methane to give carbon disulfide, which is used to manufacture cellophane and rayon.[22] One of the direct uses of sulfur is in vulcanization of rubber, where polysulfide chains crosslink organic polymers. Sulfites are heavily used to bleach paper and as preservatives in dried fruit. Many surfactants and detergents, e.g. sodium lauryl sulfate, are produced are sulfate derivatives. Calcium sulfate, gypsum, ($CaSO_4 \cdot 2H_2O$) is mined on the scale of 100 million tons each year for use in Portland cement and fertilizers.

When silver-based photography was widespread, sodium and ammonium thiosulfate were widely used as “fixing agents.” Sulfur is a component of gunpowder.

Fertilizer

Sulfur is increasingly used as a component of fertilizers. The most important form of sulfur for fertilizer is the mineral calcium sulfate. Elemental sulfur is hydrophobic (that is, it is not soluble in water) and, therefore, cannot be directly utilized by plants. Over time, soil bacteria can convert it to soluble derivatives, which can then be utilized by plants. Sulfur improves the use efficiency of other essential plant nutrients, particularly nitrogen and phosphorus.[54] Biologically produced sulfur particles are naturally hydrophilic due to a biopolymer coating. This sulfur is, therefore, easier to disperse over the land (via spraying as a diluted slurry), and results in a faster release.

Plant requirements for sulfur are equal to or exceed those for phosphorus. It is one of the major nutrients essential for plant growth, root nodule formation of legumes and plants protection mechanisms. Sulfur deficiency has become widespread in many countries in Europe.[55][56][57] Because atmospheric inputs of sulfur continue to decrease, the deficit in the sulfur input/output is likely to increase, unless sulfur fertilizers are used.

Fine chemicals

A molecular model of the pesticide malathion.

Organosulfur compounds are used in pharmaceuticals, dyestuffs, and agrochemicals. Many drugs contain sulfur, early examples being antibacterial sulfonamides, known as *sulfa drugs*. Sulfur is a part of many bacterial defense molecules. Most β-lactam antibiotics, including the penicillins, cephalosporins and monolactams contain sulfur.[38]

Magnesium sulfate, known as Epsom salts when in hydrated crystal form, can be used as a laxative, a bath additive, an exfoliant, magnesium supplement for plants, or (when in dehydrated form) as a desiccant.

Fungicide and pesticide

Sulfur candle originally sold for home fumigation

Elemental sulfur is one of the oldest fungicides and pesticides. “Dusting sulfur,” elemental sulfur in powdered form, is a common fungicide for grapes, strawberry, many vegetables and several other crops. It has a good efficacy against a wide range of powdery mildew diseases as well as black spot. In organic production, sulfur is the most important fungicide. It is the only fungicide used in organically farmed apple production against the main disease apple scab under colder conditions. Biosulfur (biologically produced elemental sulfur with hydrophilic characteristics) can be used well for these applications.

Standard-formulation dusting sulfur is applied to crops with a sulfur duster or from a dusting plane. Wettable sulfur is the commercial name for dusting sulfur formulated with additional ingredients to make it water miscible.[58][59] It has similar applications and is used as a fungicide against mildew and other mold-related problems with plants and soil.

Elemental sulfur powder is used as an "organic" (i.e. “green”) insecticide (actually an acaricide) against ticks and mites. A common method of use is to dust clothing or limbs with sulfur powder.

Diluted solutions of lime sulfur (made by combinding calcium hydroxide with elemental sulfur in water), are used as a dip for pets to destroy ringworm (fungus), mange and other dermatoses and parasites. Sulfur candles consist of almost pure sulfur in blocks or pellets that are burned to fumigate structures. It is no longer used in the home due to the toxicity of the products of combustion.

Bactericide in winemaking and food preservation

Small amounts of sulfur dioxide gas addition (or equivalent potassium metabisulfite addition) to fermented wine to produce traces of sulfurous acid (produced when SO_2 reacts with water) and its sulfite salts in the mixture, has been called "the most powerful tool in winemaking."[60] After the yeast-fermentation stage in winemaking, sulfites absorb oxygen and inhibit aerobic bacterial growth that otherwise would turn ethanol into acetic acid, souring the wine. Without this preservative step, indefinite refrigeration of the product before consumption is usually required. Similar methods go back into antiquity but modern historical mentions of the practice go to the fifteenth century. The practice is used by large industrial wine producers and small organic wine producers alike.

Sulfur dioxide and various sulfites have been used for their antioxidant antibacterial preservative properties in many other parts of the food industry also. The practice has declined since reports of an allergy-like reaction of some persons to sulfites in foods.

1.7.7 Biological role

Protein and organic cofactors

Sulfur is an essential component of all living cells. It is the seventh or eighth most abundant element in the human body by weight, being about as common as potassium, and a little more common than sodium or chlorine. A 70 kg human body contains about 140 grams of sulfur.

In plants and animals, the amino acids cysteine and methionine contain most of the sulfur. The element is thus present in all polypeptides, proteins, and enzymes that contain these amino acids. In humans, methionine is an essential amino acid that must be ingested. However, save for the vitamins biotin and thiamine, cysteine and all sulfur-containing compounds in the human body can be synthesized from methionine. The enzyme sulfite oxidase is needed for the metabolism of methionine and cysteine in humans and animals.

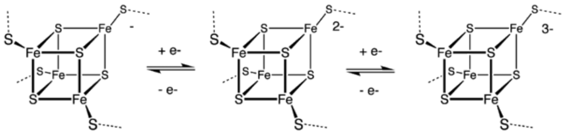
Disulfide bonds (S-S bonds) formed between cysteine residues in peptide chains are very important in protein assembly and structure. These covalent bonds between peptide chains confer extra toughness and rigidity.[61] For example, the high strength of feathers and hair is in part due to their high content of S-S bonds and their high content of cysteine and sulfur. Eggs are high in sulfur because large amounts of the element are necessary for feather formation, and the characteristic odor of rotting eggs is due to hydrogen sulfide. The high disulfide bond content of hair and feathers contributes to their indigestibility and to their characteristic disagreeable odor when burned.

Homocysteine and taurine are other sulfur-containing acids that are similar in structure, but not coded by DNA, and are not part of the primary structure of proteins. Many important cellular enzymes use prosthetic groups ending with -SH moieties to handle reactions involving acyl-containing biochemicals: two common examples from basic metabolism are coenzyme A and alpha-lipoic acid.[61] Two of the 13 classical vitamins, biotin and thiamine contain sulfur, with the latter being named for its sulfur content. Sulfur plays an important part, as a carrier of reducing hydrogen and its electrons, for cellular repair of oxidation. Reduced glutathione, a sulfur-containing tripeptide, is a reducing agent through its sulfhydryl (-SH) moiety derived from cysteine. The thioredoxins, a class of small protein essential to all known life, using neighboring pairs of reduced cysteines to act as general protein reducing agents, to similar effect.

Methanogenesis, the route to most of the world's methane, is a multistep biochemical transformation of carbon dioxide. This conversion requires several organosulfur cofactors. These include coenzyme M, $CH_3SCH_2CH_2SO_3^-$, the immediate precursor to methane.[62]

Metalloproteins and inorganic cofactors

Inorganic sulfur forms a part of iron-sulfur clusters as well as many copper, nickel, and iron proteins. Most pervasive are the ferrodoxins, which serve as electron shuttles in cells. In bacteria, the important nitrogenase enzymes contains an Fe-Mo-S cluster, is a catalyst that performs the important function of nitrogen fixation, converting atmospheric nitrogen to ammonia that can be used by microorganisms and plants to make proteins, DNA, RNA, alkaloids, and the other organic nitrogen compounds necessary for life.[63]



Sulfur metabolism and the sulfur cycle

Main articles: Sulfur metabolism and Sulfur cycle

The sulfur cycle was the first of the biogeochemical cycles to be discovered. In the 1880s, while studying Beggiatoa (a bacterium living in a sulfur rich environment), Sergei Winogradsky found that it oxidized hydrogen sulfide (H_2S) as an energy source, forming intracellular sulfur droplets. Winogradsky referred to this form of metabolism as inorgoxidation (oxidation of inorganic compounds). He continued to study it together with Selman Waksman until the 1950s.

Sulfur oxidizers can use as energy sources reduced sulfur compounds, including hydrogen sulfide, elemental sulfur, sulfite, thiosulfate, and various polythionates (e.g., tetrathionate).[64] They depend on enzymes such as sulfur oxygenase and sulfite oxidase to oxidize sulfur to sulfate. Some lithotrophs can even use the energy contained in sulfur compounds to produce sugars, a process known as chemosynthesis. Some bacteria and archaea use hydrogen sulfide in place of water as the electron donor in chemosynthesis, a process similar to photosynthesis that produces sugars and utilizes oxygen as the electron acceptor. The photosynthetic green sulfur bacteria and purple sulfur bacteria and some lithotrophs use elemental oxygen to carry out such oxidization of hydrogen sulfide to produce elemental sulfur (S^0), oxidation state = 0. Primitive bacteria that live around deep ocean volcanic vents oxidize hydrogen sulfide in this way with oxygen; see giant tube worm for an example of large organisms that use hydrogen sulfide (via bacteria) as food to be oxidized.

The so-called sulfate-reducing bacteria, by contrast, “breathe sulfate” instead of oxygen. They use organic compounds or molecular hydrogen as the energy source. They use sulfur as the electron acceptor, and reduce various oxidized sulfur compounds back into sulfide, often into hydrogen sulfide. They can grow on a number of other partially oxidized sulfur compounds (e.g. thiosulfates, thionates, polysulfides, sulfites). The hydrogen sulfide produced by these bacteria is responsible for some of the smell of intestinal gases (flatus) and decomposition products.

Sulfur is absorbed by plants via the roots from soil as the sulfate and transported as a phosphate ester. Sulfate is reduced to sulfide via sulfite before it is incorporated into cysteine and other organosulfur compounds.[65]

$SO_4^{2-} \rightarrow SO_3^{2-} \rightarrow H_2S \rightarrow$ cysteine $\rightarrow$ methionine

1.7.8 Precautions

Effect of acid rain on a forest, Jizera Mountains, Czech Republic

Elemental sulfur is non-toxic, as generally are the soluble sulfate salts, such as Epsom salts. Soluble sulfate salts are poorly absorbed and laxative. However, when injected parenterally, they are freely filtered by the kidneys and eliminated with very little toxicity in multi-gram amounts.

When sulfur burns in air, it produces sulfur dioxide. In water, this gas produces sulfurous acid and sulfites, which are antioxidants that inhibit growth of aerobic bacteria and allow its use as a food additive in small amounts. However, at high concentrations these acids harm the lungs, eyes or other tissues. In organisms without lungs such as insects or plants, it otherwise prevents respiration in high concentrations. Sulfur trioxide (made by catalysis from sulfur dioxide) and sulfuric acid are similarly highly corrosive, due to the strong acids that form on contact with water.

The burning of coal and/or petroleum by industry and power plants generates sulfur dioxide (SO_2), which reacts with atmospheric water and oxygen to produce sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3). These acids are components of acid rain, which lower the pH of soil and freshwater bodies, sometimes resulting in substantial damage to the environment and chemical weathering of statues and structures. Fuel standards increasingly require that fuel producers extract sulfur from fossil fuels to prevent acid rain formation. This extracted and refined sulfur represents a large portion of sulfur production. In coal-fired power plants, flue gases are sometimes purified. More modern power plants that use synthesis gas extract the sulfur before they burn the gas.

Hydrogen sulfide is as toxic as hydrogen cyanide, and kills by the same mechanism, though hydrogen sulfide is less likely to cause surprise poisonings from small inhaled amounts, because of its disagreeable warning odor. Though pungent at first, however, hydrogen sulfide quickly deadens the sense of smell—so a victim may breathe increasing quantities and be unaware of its presence until severe symptoms occur, which can quickly lead to death. Dissolved sulfide and hydrosulfide salts are also toxic by the same mechanism.

1.7.9 See also

- Cysteine
- Disulfide bond
- Methionine
- Stratospheric sulfur aerosols
- Sulfur assimilation
- Sulfur cycle
- Sulfur metabolism
- Ultra-low sulfur diesel

1.7.10 References

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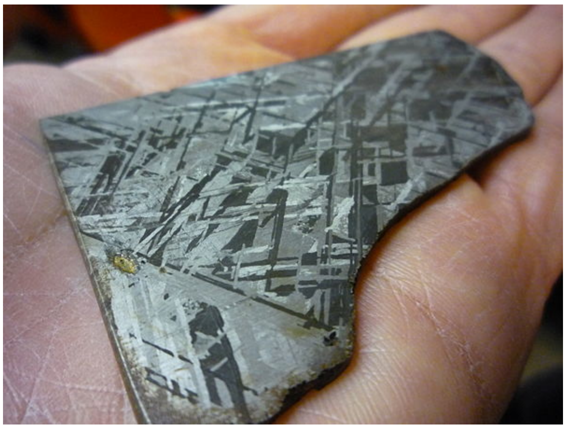
1.7.11 External links

- Sulfur at *The Periodic Table of Videos* (University of Nottingham)
- Atomic Data for Sulfur, NIST Physical Measurement Laboratory
- Sulfur phase diagram, Introduction to Chemistry For Ages 13–17

- Crystalline, liquid and polymerization of sulfur on Vulcano Island, Italy
- Sulfur and its use as a pesticide
- The Sulphur Institute
- Nutrient Stewardship and The Sulphur Institute

1.8 Taenite



Widmanstätten pattern showing the two forms of Nickel-Iron, Kamacite and Taenite, in an octahedrite meteorite

Taenite (Fe,Ni) is a mineral found naturally on Earth mostly in iron meteorites. It is an alloy of iron and nickel, with nickel proportions of 20% up to 65%.

The name is derived from the Greek ταινία for "band, ribbon". Taenite is a major constituent of iron meteorites. In octahedrites it is found in bands interleaving with kamacite forming Widmanstätten patterns, whereas in ataxites it is the dominant constituent. In octahedrites a fine intermixture with kamacite can occur, which is called plessite.

Taenite is one of four known Fe-Ni meteorite minerals: The others are kamacite, tetrataenite, and antitaenite.

1.8.1 Properties

It is opaque with a metallic grayish to white color. The structure is isometric-hexoctahedral. Its density is around 8 g/cm^3 and hardness is 5 to 5.5 on the Mohs scale. Taenite is magnetic. The crystal lattice has the $c \approx a = 3.582Å \pm 0.002Å$.[3] The Strunz classification is I/A.08-20, while the Dana classification is 1.1.11.2 . It is a Hexoctahedral (cubic) in structure.

1.8.2 Meteorite Localities with this Mineral

- Campo del Cielo crater in Argentina.
- Henbury Meteorites Conservation Reserve in Australia.
- Canyon Diablo in Arizona.

1.8.3 See also

- Glossary of meteoritics
- list of minerals

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Chapter 2

Sulfides

2.1 Acanthite

Acanthite, Ag_2S, crystallizes in the monoclinic system and is the stable form of silver sulfide below 173 °C. Argentite is the stable form above that temperature. As argentite cools below that temperature its cubic form is distorted to the monoclinic form of acanthite. Below 173 °C acanthite forms directly.[1][4] Acanthite is the only stable form in normal air temperature.

2.1.1 Occurrence

Acanthite is a common silver mineral in moderately low-temperature hydrothermal veins and in zones of supergene enrichment. It occurs in association with native silver, pyrargyrite, proustite, polybasite, stephanite, aguilarite, galena, chalcopyrite, sphalerite, calcite and quartz.[1]

Acanthite was first described in 1855 for an occurrence in the Jáchymov (St Joachimsthal) District, Krušné Hory Mts (Erzgebirge), Karlovy Vary Region, Bohemia, Czech Republic. The name is from the Greek “akantha” meaning thorn or arrow, in reference to its crystal shape.[2][3][4]

2.1.2 Gallery

- Acanthite - Locality: Chispas Mine, Arizpe, Sonora, Mexico. Scale is one inch with a ruled line at one cm.
- Classic acanthite specimen from the Rayas Mine at Guanajuato, Mexico.Size: 2.4 x 1.1 x 1.1 cm.

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2.2 Arsenopyrite

Arsenopyrite is an iron arsenic sulfide (FeAsS). It is a hard (Mohs 5.5-6) metallic, opaque, steel grey to silver white mineral with a relatively high specific gravity of 6.1.[1] When dissolved in nitric acid, it releases elemental sulfur. When arsenopyrite is heated, it becomes magnetic and gives off toxic fumes. With 46% arsenic content, arsenopyrite, along with orpiment, is a principal ore of arsenic. When deposits of arsenopyrite become exposed to the atmosphere, usually due to mining, the mineral will slowly oxidize, converting the arsenic into oxides that are more soluble in water, leading to acid mine drainage.

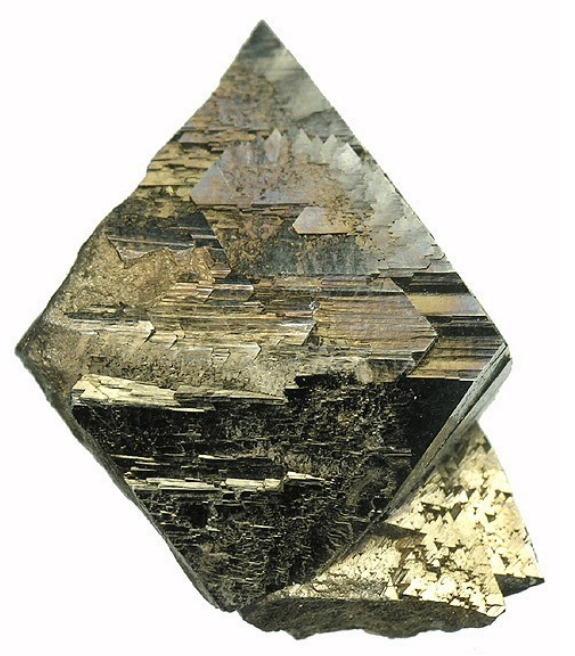
The crystal habit, hardness, density, and garlic odor when struck are diagnostic. Arsenopyrite in older literature may be referred to as *mispickel*, a name of German origin.[4]

Arsenopyrite also can be associated with significant amounts of gold. Consequently it serves as an indicator of gold bearing reefs. Many arsenopyrite gold ores are refractory, i.e. the gold is not easily liberated from the mineral matrix.

Arsenopyrite is found in high temperature hydrothermal veins, in pegmatites, and in areas of contact metamorphism or metasomatism.

2.2.1 Crystallography

Arsenopyrite crystallizes in the monoclinic crystal system and often shows prismatic crystal or columnar forms with striations and twinning common. Arsenopyrite may be referred to in older references as orthorhombic, but it has been shown to be monoclinic. In terms of its atomic structure, each Fe center is linked to three As atoms and three S atoms. The material can be described as Fe^{3+} with the diatomic trianion AsS^{3-}. The connectivity of the atoms is more similar to that in marcasite than pyrite. The ion description is imperfect because the material is



Arsenopyrite crystal from the Yaogangxian Mine, Hunan, China (size: 2.7 x 2.0 x 1.7 cm)

semiconducting and the Fe-As and Fe-S bonds are highly covalent.[5]

2.2.2 Related minerals

Various transition group metals can substitute for iron in arsenopyrite. The arsenopyrite group includes the following rare minerals:

- Clinosafflorite: (Co,Fe,Ni)AsS
- Gudmundite: FeSbS
- Glaucodot or alloclasite: (Fe,Co)AsS or (Co,Fe)AsS
- Iridarsenite: (Ir,Ru)AsS
- Osarsite or ruarsite: (Os,Ru)AsS or (Ru,Os)AsS

2.2.3 See also

- Classification of minerals
- List of minerals

2.2.4 References

[1] Hurlbut, C. S.; Klein, C., 1985, Manual of Mineralogy, 20th ed., ISBN 0-471-80580-7

[2] http://rruff.geo.arizona.edu/doclib/hom/arsenopyrite.pdf Handbook of Mineralogy

[3] Mindat.org

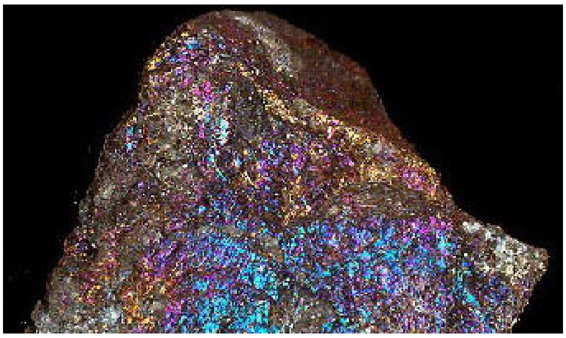
[4] Mindat Mispickel

[5] Vaugn, D. J.; Craig, J. R. Mineral Chemistry of Metal Sulfides" Cambridge University Press, Cambridge: 1978. ISBN 0-521-21489-0.

2.3 Bornite

Bornite, also known as **peacock ore**, is a sulfide mineral with chemical composition Cu_5FeS_4 that crystallizes in the orthorhombic system (pseudo-cubic).

2.3.1 Appearance



Tarnish of bornite

Bornite has a brown to copper-red color on fresh surfaces that tarnishes to various iridescent shades of blue to purple in places. Its striking iridescence gives it the nickname *peacock copper* or *peacock ore*.

2.3.2 Mineralogy

Bornite is an important copper ore mineral and occurs widely in porphyry copper deposits along with the more common chalcopyrite. Chalcopyrite and bornite are both typically replaced by chalcocite and covellite in the supergene enrichment zone of copper deposits. Bornite is also found as disseminations in mafic igneous rocks, in contact metamorphic skarn deposits, in pegmatites and in sedimentary cupriferous shales.[2] It is important as an ore for its copper content of about 63 percent by mass.[1]

Structure

At temperatures above 228 °C, the structure is isometric with a unit cell that is about 5.50 Å on an edge. This structure is based on cubic close-packed sulfur atoms, with copper and iron atoms randomly distributed into six of the eight tetrahedral sites located in the octants of the cube. With cooling, the Fe and Cu become ordered, so that 5.5 Å subcells in which all eight tetrahedral sites are filled alternate with subcells in which only four of the tetrahedral sites are filled; symmetry is reduced to orthorhombic.[4]

Composition

Substantial variation in the relative amounts of copper and iron is possible and solid solution extends towards chalcopyrite ($CuFeS_2$) and digenite (Cu_9S_5). Exsolution of blebs and lamellae of chalcopyrite, digenite, and chalcocite is common.[4]

Form and twinning

Rare crystals are approximately cubic, dodecahedral, or octahedral. Usually massive. Penetration twinning on the crystallographic direction, {111}.[4]

2.3.3 Occurrence

Bornite with silver from Zacatecas, Mexico (size: 7.5 x 4.3 x 3.4 cm)

It occurs globally in copper ores with notable crystal localities in Butte, Montana and at Bristol, Connecticut in the U. S. It is also collected from the Carn Brea mine, Illogan, and elsewhere in Cornwall, England. Large crystals are found from the Frossnitz Alps, eastern Tirol, Austria; the Mangula mine, Lomagundi district, Zimbabwe; from the N'ouva mine, Talate, Morocco, the West Coast of Tasmania and in Dzhezkazgan, Kazakhstan.[2] There are also traces of it found amongst the hematite in the Pilbara region of Western Australia.

2.3.4 History and etymology

It was first described in 1725 for an occurrence in the Krušné Hory Mountains (Erzgebirge), Karlovy Vary Region, Bohemia in what is now the Czech Republic. It was named in 1845 for Austrian mineralogist Ignaz von Born (1742–1791).[3]

2.3.5 See also

- Cuprite
- Tennantite
- Tetrahedrite
- List of minerals named after people

2.3.6 References

[1] Webmineral

[2] Handbook of Mineralogy

[3] Mindat.org

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- Palache, C., H. Berman, and C. Frondel (1944) *Dana's system of mineralogy*, (7th edition), v. I, 195–197.
- Manning, P.G. (1966) *A study of the bonding Properties of Sulphur in Bornite,* The Canadian Mineralogist, 9, 85-94

2.4 Carrollite

Carrollite, $CuCo_2S_4$, is a sulfide of copper and cobalt, often with substantial substitution of nickel for the metal ions, and a member of the linnaeite group. It is named after the type locality in Carroll County, Maryland, USA, at the Patapsco mine, Finksburg, Sykesville.[4]

2.4.1 Unit cell

Space group: Fd3m. Unit cell parameters = a = 9.48 Å, Z = 8. Unit cell volume: V = 851.97 Å^3 (calculated from unit cell parameters).[6]

Carrollite from Katanga, specimen 11 × 6 cm

2.4.2 Linnaeite group

The linnaeite group is a group of sulfides and selenides with the general formula AB_2X_4 in which X is sulfur or selenium, A is divalent Fe, Ni, Co or Cu and B is trivalent Co, Ni or, for daubréelite, Cr. The minerals are isometric, space group Fd3m and isostructural with each other and with minerals of the spinel group.

The structure of the linnaeite group consists of a cubic close packed array of X (X is oxygen in the spinels and sulfur or selenium in the linnaeite group). Within the array of Xs there are two types of interstices, one type tetrahedrally co-ordinated and one type octahedrally co-ordinated. One eighth of the tetrahedal sites A are typically occupied by 2^+ cations, and half of the octahedral sites B by 3^+ cations.[7] Charnock et al. confirmed that carrollite contains Cu wholly within the tetrahedral sites.[8] Thus, the ideal formula one would expect for a spinel like carrollite is $Cu^{2+}Co^{3+}{}_2S^{2-}{}_4$, but as in the case of copper sulfides in general the oxidation state of the copper atom is 1+, not 2+. An assignment of valences as $Cu^{+}Co^{3+}{}_2S^{1.75-}{}_4$ is more appropriate; this was confirmed in a study of 2009.[9] The one missing electron per four sulfur atoms is delocalized, leading to metallic conductivity and even superconductivity at very low temperatures, combined with a complicated magnetic behavior.[10]

2.4.3 Solid solutions

A solid solution results when one cation can substitute for another across an appreciable composition range. In carrollite Co^{2+} can substitute for Cu^+ at the A sites, and when the substitution is complete the mineral formed is called linnaeite, $Co^{2+}Co^{3+}{}_2S_4$. This means that there is a solid solution series between carrollite and linnaeite. Also, Ni substitutes for both Co and Cu in the carrollite structure,[11] giving a solid solution from carrollite to cuprian siegenite. Siegenite, $Co^{2+}Ni^{3+}{}_2S_4$, is itself a member of the solid solution series between linnaeite and polydymite, $Ni^{2+}Ni^{3+}{}_2S_4$. (Wagner and Cook found no evidence for solid solution between carrollite and fletcherite, $CuNi_2S_4$).

2.4.4 Environment

Carrollite occurs in hydrothermal vein deposits[12] associated with tetrahedrite, chalcopyrite, bornite, digenite, djurleite, chalcocite, pyrrhotite, pyrite, sphalerite, millerite, gersdorffite, ullmannite, cobaltoan calcite, and with linnaeite group members linnaeite, siegenite and polydymite.

Phase relations in the Cu-Co-S system have been investigated.[13] At temperatures around 900 °C a chalcocite-digenite solid solution coexists with cobalt sulfides. With decreasing temperature, at 880 °C a carrollite-linnaeite solid solution develops, becoming more copper-rich on coling, with the carrollite composition at about 500 °C. Below 507 °C covellite is stable and coexists with copper-bearing cattierite. Low chalcocite appears at 103 °C, djurleite appears at 93 °C, and digenite disappears and anilite appears around 70 °C. There is some evidence for supergene replacement of an intermediate member of the linnaeite-carrollite series by djurleite.[13]

2.4.5 Distribution

Carollite and native copper on calcite

Carrollite is found world-wide; reported in Australia, Austria, Azerbaijan, Brazil, Bulgaria, Canada, Chile, China, the Czech Republic, the Democratic Republic of Congo,[14] France, Germany, Japan, Morocco, Namibia, North Korea, Norway, Oman, Poland, Romania, Russia, Slovakia, Sweden, Switzerland, USA and Zambia.[4]

2.4.6 References

[1] Ramdohr, R (1980) The Ore Minerals and their Intergrowths. Pergamom.

[2] Criddle, A J and Stanley, C J (1993) Quantitative data file for ore minerals. Chapman & Hall page 74

[3] http://www.webmineral.com/data/Carrollite.shtml

[4] http://www.mindat.org/min-911.html Mindat.org

[5] http://rruff.geo.arizona.edu/doclib/hom/carrollite.pdf Handbook of Mineralogy

[6] Gaines et al (1997) Dana's New Mineralogy Eighth Edition. Wiley

[7] Klein and Hurlbut (1993) *Manual of Mineralogy*, 21st edition

[8] Charnock, Garner, Pattrick and Vaughan (1990) American Mineralogist 75: 247-255

[9] Electronic environments in carrollite, CuCo2S4, determined by soft X-ray photoelectron and absorption spectroscopy.
Buckley AN, Skinner WM, Harmer SL, Pring A, Fan LJ GEOCHIMICA ET COSMOCHIMICA ACTA Volume: 73 Issue: 15 Pages: 4452–4467

[10] Magnetism and Superconductivity in Copper Spinels
Kazuo Miyatani, Toshiro Tanaka, Shigenobu Sakita1, Masayasu Ishikawa and Naoki Snirakawa, Jpn. J. Appl. Phys. 32 (1993) Supplement 32-3 pp. 448–450

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[14] Currier, R H (2002) Mineralogical Record 33: 473-487

2.5 Chalcocite

Chalcocite, copper(I) sulfide (Cu_2S), is an important copper ore mineral. It is opaque, being colored dark-gray to black with a metallic luster. It has a hardness of 2½ - 3 on the Mohs scale. It is a sulfide with an orthorhombic crystal system.

The term chalcocite comes from the alteration of the obsolete name *chalcosine*, from the Greek *khalkos*, meaning copper. It is also known as redruthite, vitreous copper and copper-glance.

2.5.1 Occurrence

Chalcocite is sometimes found as a primary vein mineral in hydrothermal veins. However, most chalcocite occurs in the supergene enriched environment below the oxidation zone of copper deposits as a result of the leaching of copper from the oxidized minerals. It is also often found in sedimentary rocks.

It has been mined for centuries and is one of the most profitable copper ores. The reasons for this is its high copper content (66.6% atomic ratio and nearly 80% by weight) and the ease at which copper can be separated from sulfur.

Chalcocite crystals from the Mammoth Mine, Mount Isa - Cloncurry area, Queensland, Australia (size: 3.0 x 2.9 x 2.4 cm)

Since chalcocite is a secondary mineral that forms from the alteration of other minerals, it has been known to form pseudomorphs of many different minerals. A pseudomorph is a mineral that has replaced another mineral atom by atom, but it leaves the original mineral's crystal shape intact. Chalcocite has been known to form pseudomorphs of the minerals bornite, covellite, chalcopyrite, pyrite, enargite, millerite, galena and sphalerite.

2.5.2 See also

- Copper(I) sulfide
- Copper monosulfide

2.5.3 References

[1] Mindat.org

[2] Webmineral.com

[3] Handbook of Mineralogy

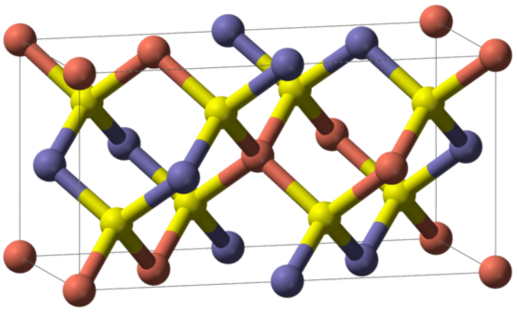
- Dana's Manual of Mineralogy ISBN 0-471-03288-3
- Mineral Galleries

2.6 Chalcopyrite

Chalcopyrite (/ˌkælkəˈpaɪraɪt/ ***KAL**-ko-**PY**-ryt*) is a copper iron sulfide mineral that crystallizes in the tetragonal system. It has the chemical formula $CuFeS_2$. It has a brassy to golden yellow color and a hardness of 3.5 to 4 on the Mohs scale. Its streak is diagnostic as green tinged black.

On exposure to air, chalcopyrite oxidises to a variety of oxides, hydroxides and sulfates. Associated copper minerals include the sulfides bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), digenite (Cu_9S_5); carbonates such as malachite and azurite, and rarely oxides such as cuprite (Cu_2O). Chalcopyrite is rarely found in association with native copper.

2.6.1 Chemistry



The unit cell of chalcopyrite. Copper is shown in pink, iron in blue and sulfur in yellow.

Natural chalcopyrite has no solid solution series with any other sulfide minerals. There is limited substitution of Zn with Cu despite chalcopyrite having the same crystal structure as sphalerite.

Minor amounts of elements such as Ag, Au, Cd, Co, Ni, Pb, Sn, and Zn can be measured (at part per million levels), likely substituting for Cu and Fe. Selenium, Bi, Te, and As may substitute for sulfur in minor amounts.[6]

2.6.2 Paragenesis

Chalcopyrite is present with many ore-bearing environments via a variety of ore forming processes.

Chalcopyrite is present in volcanogenic massive sulfide ore deposits and sedimentary exhalative deposits, formed by deposition of copper during hydrothermal circulation. Chalcopyrite is concentrated in this environment via fluid transport.

Porphyry copper ore deposits are formed by concentration of copper within a granite stock during the ascent and crystallisation of a magma. Chalcopyrite in this environment is produced by concentration within a magmatic system.

Chalcopyrite is an accessory mineral in Kambalda type komatiitic nickel ore deposits, formed from an immiscible sulfide liquid in sulfide-saturated ultramafic lavas. In this environment chalcopyrite is formed by a sulfide liquid stripping copper from an immiscible silicate liquid.

2.6.3 Occurrence

Chalcopyrite is the most important copper ore. Chalcopyrite ore occurs in a variety of ore types, from huge masses as at Timmins, Ontario, to irregular veins and disseminations associated with granitic to dioritic intrusives as in the porphyry copper deposits of Broken Hill, the American cordillera and the Andes. The largest deposit of nearly pure chalcopyrite ever discovered in Canada was at the southern end of the Temagami greenstone belt where Copperfields Mine extracted the high-grade copper.[7]

Chalcopyrite is present in the supergiant Olympic Dam Cu-Au-U deposit in South Australia.

Chalcopyrite may also be found in coal seams associated with pyrite nodules, and as disseminations in carbonate sedimentary rocks.

2.6.4 Structure

Crystallographically the structure of chalcopyrite is closely related to that of zinc blende ZnS (sphalerite). The unit cell is twice as large, reflecting an alternation of Cu^+ and Fe^{3+} ions replacing Zn^{2+} ions in adjacent cells. In contrast to the pyrite structure chalcopyrite has single S^{2-} sulfide anions rather than disulfide pairs. Another difference is that the iron cation is not diamagnetic low spin Fe(II) as in pyrite.

- Brass-yellow Chalcopyrite crystals below large striated pyrite cubes
- Botryoidal chalcopyrtite, locally called “Blister Copper”, Redruth Cornwall England

2.6.5 See also

- Classification of minerals
- List of minerals
- Kesterite

2.6.6 References

[1] Klein, Cornelis and Cornelius S. Hurlbut, Jr., *Manual of Mineralogy,* Wiley, 20th ed., 1985, pp. 277 – 278 ISBN 0-471-80580-7

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[3] http://www.mindat.org/min-955.html mindat.org

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2.7 Cinnabar

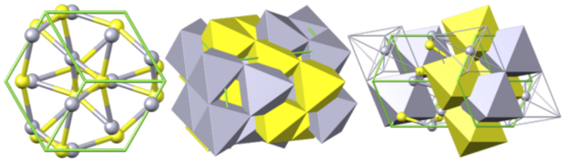
This article is about the mineral. For the plant resin, see Dragon's blood. For the moth, see Cinnabar moth.

Cinnabar (pronounced /ˈsɪnəbɑr/) or **cinnabarite** /sɪnəˈbɑraɪt/ (red mercury(II) sulfide (HgS), native vermilion), is the common ore of mercury.

2.7.1 Etymology

The name comes from κινναβαρι (*kinnabari*),[5] a Greek word most likely applied by Theophrastus to several distinct substances. Other sources say the word comes from the Persian شنگرف *shangarf* (Arabicized as زنجفرة *zinjifrah*), a word of uncertain origin (also compare, Sanskrit सुगर *sugara*). In Latin it was sometimes known as *minium*, meaning also "red cinnamon", though both of these terms now refer specifically to lead tetroxide.[6]

2.7.2 Structure



Crystal structure of cinnabar

HgS adopts two structures, i.e. it is dimorphous.[7] The more stable form is cinnabar, which has a structure akin to that for HgO: each Hg center has two short Hg-S bonds (2.36 Å), and four longer Hg---S contacts (3.10, 3.10, 3.30, 3.30 Å). The black form of HgS has the zincblende structure.

2.7.3 Properties

Cinnabar is generally found in a massive, granular or earthy form and is bright scarlet to brick-red in color.[8] It occasionally occurs in crystals with a non-metallic adamantine luster. Cinnabar has a rhombohedral bravais lattice, and belongs to the hexagonal crystal system, trigonal division. Its crystals grow usually in a massive habit, though they are sometimes twinned. The twinning in cinnabar is distinctive, and it forms a penetration twin that is ridged with six ridges surrounding the point of a pyramid. It could be thought of as two scalahedral crystals grown together, with one crystal going the opposite way of the other crystal. The hardness of cinnabar is 2–2.5, and its specific gravity 8.1.

Cinnabar

Cinnabar resembles quartz in its symmetry and certain of its optical characteristics. Like quartz, it exhibits birefringence. It has the highest refractive power of any mineral. Its mean index for sodium light is 3.08,[9] whereas the index for diamond is 2.42 and that for gallium(III) arsenide (GaAs) is 3.93.

2.7.4 Occurrence

Cinnabar mercury ore from Nevada, USA

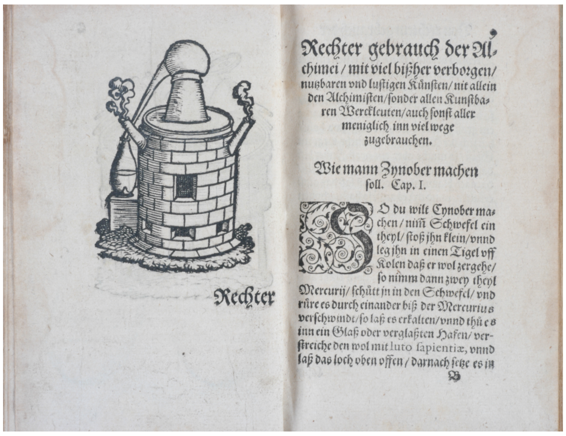
Generally cinnabar occurs as a vein-filling mineral associated with recent volcanic activity and alkaline hot springs. Cinnabar is deposited by epithermal ascending aqueous solutions (those near surface and not too hot) far removed from their igneous source.

It is associated with native mercury, stibnite, realgar, pyrite, marcasite, opal, quartz, chalcedony, dolomite, calcite and barite.[2]

Cinnabar is found in all localities that yield mercury, notably Puerto Princesa (Philippines); Almadén (Spain); New Almaden (California); Hastings Mine and St. John's Mine, Vallejo, California;[10] Idrija (Slovenia); New Idria (California); Giza, Egypt; Landsberg, near Obermoschel in the Palatinate; Ripa, at the foot of the Apuan Alps and in the Mount Amiata (Tuscany); the mountain Avala (Serbia); Huancavelica (Peru); Murfreesboro, Arkansas; Terlingua (Texas); and the province of Guizhou in China, where fine crystals have been obtained. It was also mined near Red Devil, Alaska on the middle Kuskokwim River. Red Devil was named after the Red Devil cinnabar mine, a primary source of mercury.

Cinnabar is still being deposited at the present day from the hot waters of Sulphur Bank Mine in California and Steamboat Springs, Nevada.

2.7.5 Mining and extraction of mercury



Rechter

Rechter gebrauch der Alchimei / mit viel bißher verborgen/ nutzbaren vnd luſtigen Künſten/ nit allein den Alchimiſten/ſonder allen Kunſtbaren Werckleuten/auch ſonſt aller meniglich inn viel wege zugebrauchen.

Wie mann Zynober machen ſoll. Cap. I.

SO du wilt Cynober machen / nim̃ Schwefel ein theyl/ ſtoß jhn klein/vnnd leg jhn in einen Tigel vff Kolen daß er wol zergehe/ ſo nimm dann zwey theyl Mercurij/ ſchütt jn in den Schwefel/ vnd rüre es durch einander biß der Mercurius verſchwindt/ſo laß es erkalten/vnnd thů es inn ein Glaß oder verglaßten Hafen/ verſtreiche den wol mit luto ſapientiæ, vnnd laß das loch oben offen / darnach ſetze es in

B

Apparatus for the distillation of cinnabar, Alchimia*, 1570*

Cinnabar has been mined since the Neolithic Age.[11] During the Roman Empire it was mined both as a pigment (Vitruvius, DA VII; IV-V) (Pliny, HN; XXXIII, XXXVI-XLII) and for its mercury content (Pliny HN; XXXIII, XLI), and it has been the main source of mercury throughout the centuries.

To produce liquid mercury (quicksilver), crushed cinnabar ore is roasted in rotary furnaces. Pure mercury separates from sulfur in this process and easily evaporates. A condensing column is used to collect the liquid metal, which is most often shipped in iron flasks.

2.7.6 Toxicity

See also: Mercury poisoning

Because of its mercury content, cinnabar can be toxic to human beings. Though peoples in ancient South America often used cinnabar for art, or processed it into refined mercury (as a means to gild silver and gold to objects) "the toxic properties of mercury were well known. It was dangerous to those who mined and processed cinnabar, it caused shaking, loss of sense, and death. Data suggests that mercury was retorted from cinnabar and the workers were exposed to the toxic mercury fumes."[12] Overexposure to mercury, mercurialism, was seen as an occupational disease to the ancient Romans, "Mining in the Spanish cinnabar mines of Almadén, 225 km southwest of Madrid, was regarded as being akin to a death sentence due to the shortened life expectancy of the miners, who were slaves or convicts."[13]

2.7.7 Decorative use

Cinnabar has been used for its color in the New World since the Olmec culture.[14] Cinnabar was used in royal burial chambers during the peak of Maya civilization, most dramatically in the Tomb of the Red Queen in Palenque (600–700 AD), where the remains of a noble woman and objects belonging to her in her sarcophagus were completely covered with bright red powder made from cinnabar.[15]

The most popularly known use of cinnabar is in Chinese carved lacquerware, a technique that apparently originated in the Song Dynasty. The danger of mercury poisoning may be reduced in ancient lacquerware by entraining the powdered pigment in lacquer,[16] but could still pose an environmental hazard if the pieces were accidentally destroyed. In the modern jewelry industry, the toxic pigment is replaced by a resin-based polymer that approximates the appearance of pigmented lacquer.

2.7.8 Other forms

- **Hepatic cinnabar** is an impure variety from the mines of Idrija in the Carniola region of Slovenia, in which the cinnabar is mixed with bituminous and earthy matter.
- **Metacinnabarite** is a black-colored form of HgS, which crystallizes in the cubic form.
- **Synthetic cinnabar** is produced by treatment of Hg(II) salts with hydrogen sulfide to precipitate black, synthetic metacinnabarite, which is then heated in water. This conversion is promoted by the presence of sodium sulfide.[17]
- **Hypercinnabar**, crystallised in the hexagonal form.

2.7.9 See also

- China red
- Classification of minerals
- List of minerals

2.7.10 References

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[2] Mineral Handbook

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[17] Holleman, A. F.; Wiberg, E. (2001). *Inorganic Chemistry*. San Diego, CA, USA: Academic Press. ISBN 0-12-352651-5.

2.7.11 External links

- MSDS for cinnabar
- Dartmouth Toxic Metals Research Program – Mercury
- Cinnabar visual reference

2.8 Cobaltite

Cobaltite is a sulfide mineral composed of cobalt, arsenic and sulfur, CoAsS. It contains up to 10 percent iron and variable amounts of nickel.[3] Structurally it resembles pyrite (FeS_2) with one of the sulfur atoms replaced by an arsenic atom.

Although rare it is mined as a significant source of the strategically important metal cobalt. Secondary weathering incrustations of erythrite, hydrated cobalt arsenate, are common.

The name is from the German, *Kobold*, "underground spirit" in allusion to the "refusal" of cobaltiferous ores to smelt as they are expected to.[4]

It occurs in high temperature hydrothermal deposits and contact metamorphic rocks. It occurs in association with magnetite, sphalerite, chalcopyrite, skutterudite, allanite, zoisite, scapolite, titanite, calcite along with numerous other Co–Ni sulfides and arsenides.[1] It was described as early as 1832.[2]

It is found chiefly in Sweden, Norway, Germany, Cornwall, England, Canada, Australia, Democratic Republic of the Congo and Morocco.[1][3]

2.8.1 References

[1] http://rruff.geo.arizona.edu/doclib/hom/cobaltite.pdf Mineral Handbook

[2] http://webmineral.com/data/Cobaltite.shtml Webmineral data

[3] Klein, Cornelus and Cornrlius Hurlbut, 1996, *Manual of Mineralogy*, 20th ed., Wiley, p.288, ISBN 0-471-80580-7

[4] http://www.mindat.org/min-1093.html Mindat

- Mineral galleries

2.8.2 External links

- Spencer, Leonard James (1911). "Cobaltite". In Chisholm, Hugh. *Encyclopædia Britannica* **6** (11th ed.). Cambridge University Press. p. 605.

Cubic Cobaltite, 1.6 x 1.4 x 1.1 cm, Brazil Lake Occurrence (Elizabeth Lake Mine), Sudbury District, Ontario, Canada

2.9 Dimorphite

Dimorphite (chemical name tetraarsenic trisulfide) is a very rare orange-yellow chalcogenide mineral. In nature, dimorphite forms primarily by deposition in volcanic fumaroles at temperatures of 70–80 °C (158–176 °F). Dimorphite was first discovered in a such a fumarole near Naples, Italy in 1849 by the mineralogist Arcangelo Scacchi (1810–1893). Since its discovery, dimorphite has been found in the Alacrán silver mine near Copiapó, Chile.[2] It has also been reported from Cerro de Pasco, Peru, and the Lavrion District Mines in Attica, Greece.[1]

2.9.1 Properties and applications

Dimorphite has two crystal forms, A- and B−. This property gives rise to its name, which comes from the Greek for “two” and “form.” Dimorphite transitions between its α- and β- forms at around 130 °C (266 °F).[4]

Dimorphite can be synthesized by melting arsenic and sulfur together in the proper molar ratios in vacuum.[4]

Initial research indicates the possibility of using synthetic dimorphite in the development of gas sensors,[5][6] due to the semiconductive properties of dimorphite.

2.9.2 References

[1] Dimorphite mineral information and data Mindat.org

[2] Handbook of Mineralogy

[3] Webmineral data

[4] Wiberg, Egon, Nils Wiberg, and Arnold Frederick Holleman. *Inorganic Chemistry.* San Diego: Academic Press, 2001.

[5] Tsiulyanu, D.; Golbam, G.; Kolomeyho, E.; Melnic, O. (1996). “Photoconductivity and optical absorption of dimorphite thin films”. *Physica Status Solidi (b)* **197** (1): 61–64. Bibcode:1996PSSBR.197...61T. doi:10.1002/pssb.2221970110.

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2.10 Enargite

Enargite is a copper arsenic sulfosalt mineral with formula: Cu_3AsS_4. It takes its name from the Greek word enarge, “distinct.” Enargite is a steel gray, blackish gray, to violet black mineral with metallic luster. It forms slender orthorhombic prisms as well as massive aggregates. It has a hardness of 3 and a specific gravity of 4.45.

Enargite is dimorph of the tetragonal luzonite.[1]

2.10.1 Occurrence

It is a medium to low temperature hydrothermal mineral occurring with quartz, pyrite, sphalerite, galena, bornite, tetrahedrite–tennantite, chalcocite, covellite and baryte.[3] It occurs in the mineral deposits at Butte, Montana, San Juan Mountains, Colorado and at both Bingham Canyon and Tintic, Utah. It is also found in the copper mines of Canada, Mexico, Argentina, Chile, Peru, and the Philippines.

Enargite was originally described as a new species from the copper mines of the San Francisco vein, Junin Department, Peru. The name is from Greek ἐναργής for *distinct,* in reference to its distinct cleavage.[1][3]

Enargite is related to *lazarevicite* (named after M. Lazarevic), which has the same chemical formula, but cubic crystalline structure.[4]

2.10.2 References

[1] http://www.mindat.org/min-1380.html Mindat

[2] http://webmineral.com/data/Enargite.shtml Webmineral

[3] Handbook of Mineralogy

[4] “Lazarevicite on Mindat”. Retrieved 2009-06-06.

2.10.3 External links

Media related to Enargite at Wikimedia Commons

- Crystal structure of enargite

2.11 Galena

For other uses, see Galena (disambiguation).

Galena, also called lead glance, is the natural mineral form of lead(II) sulfide. It is the most important ore of lead and an important source of silver.[4]

Galena is one of the most abundant and widely distributed sulfide minerals. It crystallizes in the cubic crystal system often showing octahedral forms. It is often associated with the minerals sphalerite, calcite and fluorite.

2.11.1 Lead ore deposits

Galena with druzy calcite

Galena is the main ore of lead, used since ancient times. Because of its somewhat low melting point, it was easy to liberate by smelting.

In some areas galena contains about 1-2 percent silver. In these areas the silver byproduct far outweighs the main lead ore in revenue. Galena deposits often also contain significant amounts of silver as included silver sulfide mineral phases or as limited solid solution within the galena structure. These argentiferous galenas have long been the most important ore of silver.

Galena deposits are found worldwide in various environments.[3] Noted deposits include those at Freiberg, Saxony;[1] Cornwall, The Mendips, Somerset, Derbyshire, and Cumberland, England; the Madan, Smolyan Province, Rhodope Mountains, Bulgaria; the Sullivan Mine of British Columbia; Broken Hill, Australia and the ancient mines of Sardinia. Galena also occurs in North African countries and at Mount Hermon in Northern Israel. In the United States, it occurs most notably in the Mississippi Valley type deposits of the Lead Belt in southeastern Missouri,[1] and in the Driftless Area of Illinois, Iowa and Wisconsin. The economic importance of galena to the early history of the Driftless Area was so great that one of the towns in the region was named Galena, Illinois.

Cubic galena with calcite from Jasper County, Missouri, USA (size: 5.1×3.2×2.8 cm)

Galena also was a major mineral of the zinc-lead mines of the tri-state district around Joplin in southwestern Missouri and the adjoining areas of Kansas and Oklahoma.[1] Galena is also an important ore mineral in the silver mining regions of Colorado, Idaho, Utah and Montana. Of the latter, the Coeur d'Alene district of northern Idaho was most prominent.[1]

Galena is the official state mineral of the U.S. states of Missouri and Wisconsin; the former mining town of Galena, Kansas takes its name from deposits of this mineral.

Derbyshire in the UK was one of the main areas where galena was mined.

The largest documented crystal of galena is composite cubo-octahedra from Great Laxey Mine, Isle of Man, U.K. measuring 25×25×25 cm.[5]

2.11.2 Crystal structure

Galena belongs to the octahedral sulfide group of minerals with metal ions in octahedral positions, like members pyrrhotite and niccolite. The galena group is named after its most common member, with other isometric members that include manganese bearing alabandite and niningerite.[3]

Divalent lead (Pb) cations and sulfur (S) anions form a close packed cubic unit cell much like the mineral halite of the halide mineral group. Zinc, cadmium, iron, copper, antimony, arsenic, bismuth, and selenium also occur in variable amounts in galena. Selenium substitutes for sulfur in the structure constituting a solid solution series. The lead telluride mineral altaite has the same crystal structure as galena.

2.11.3 Geochemistry

Within the weathering or oxidation zone galena alters to anglesite (lead sulfate) or cerussite (lead carbonate). Galena exposed to acid mine drainage can be oxidized to anglesite by naturally occurring bacteria and archaea, in a process similar to bioleaching.[6]

2.11.4 Galena uses

One of the oldest uses of galena was as kohl, which, in Ancient Egypt, was applied around the eyes to reduce the glare of the desert sun and to repel flies, which were a potential source of disease.[7]

Galena is the primary ore of lead which is mainly used in making lead-acid batteries; however, significant amounts are also used to make lead sheets and shot. Galena is often mined for its silver content (e.g. the Galena Mine in northern Idaho).

Also known as "potters ore", galena is used in a green glaze applied to pottery.

Galena is a semiconductor with a small bandgap of about 0.4 eV which found use in early wireless communication systems. It was used as the crystal in crystal radio sets, in which it was used as a point-contact diode to detect the radio signals. The galena crystal was used with a sharp wire, known as a "cat's whisker". The operation of the radio required that the point of contact on the galena be shifted about to find a part of the crystal that acted as a diode. Making such wireless sets was a popular home hobby in Britain and other European countries during the 1930s. Scientists associated with the investigation of the diode effect are Karl Ferdinand Braun and Sir Jagdish Bose. In modern wireless communication systems, galena detectors have been replaced by more reliable semiconductor devices.

2.11.5 Health issues

Galena contains lead, a toxic element. While bound to crystal structure, the lead content of galena is of minor concern and the mineral is safe to handle. However, prolonged exposure to the pulverized dust in the form of inhalation or ingestion is hazardous to one's health.

2.11.6 See also

- List of minerals
- Lead smelter

2.11.7 Notes

[1] Anthony, John W.; Bideaux, Richard A.; Bladh, Kenneth W. and Nichols, Monte C., ed. (1990). "Galena" (PDF). *Handbook of Mineralogy*. I (Elements, Sulfides, Sulfosalts). Chantilly, VA, US: Mineralogical Society of America. ISBN 0962209708.

[2] Galena. Webmineral

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2.11.8 References

- Klein, Cornelis and Cornelius S. Hurlbut, Jr. (1985) *Manual of Mineralogy*, Wiley, 2nd ed., pp. 274–276, ISBN 0-471-80580-7.
- Franklin and Sterling Hill mineral deposits.

2.11.9 External links

- Case Studies in Environmental Medicine (CSEM): Lead Toxicity.
- ToxFAQs: Lead.
- Mineral information institute entry for lead.

2.12 Marcasite

This article is about the mineral. For the jewellery, see Marcasite jewellery.

The mineral **marcasite**, sometimes called **white iron pyrite**, is iron sulfide (FeS_2) with orthorhombic crystal structure. It is physically and crystallographically distinct from pyrite, which is iron sulfide with cubic crystal structure. Both structures do have in common that they contain the disulfide ${S_2}^{2-}$ ion having a short bonding distance between the sulfur atoms. The structures differ in how these di-anions are arranged around the Fe^{2+} cations. Marcasite is lighter and more brittle than pyrite. Specimens of marcasite often crumble and break up due to the unstable crystal structure.

On fresh surfaces it is pale yellow to almost white and has a bright metallic luster. It tarnishes to a yellowish or brownish color and gives a black streak. It is a brittle material that cannot be scratched with a knife. The thin, flat, tabular crystals, when joined in groups, are called "cockscombs."

In marcasite jewellery, pyrite used as a gemstone is termed "marcasite". That is, marcasite jewellery is made from pyrite not from marcasite. In the late medieval and early modern eras the word "marcasite" meant both pyrite and marcasite (and iron sulfides in general).[4] The narrower, modern scientific definition for marcasite as orthorhombic iron sulfide dates from 1845.[2] The jewellery sense for the word pre-dates this 1845 scientific redefinition. Marcasite in the scientific sense is not used as a gem due to its brittleness.

2.12.1 Occurrence

Marcasite can be formed as both a primary or a secondary mineral. It typically forms under low-temperature highly acidic conditions. It occurs in sedimentary rocks (shales, limestones and low grade coals) as well as in low temperature hydrothermal veins. Commonly associated minerals include pyrite, pyrrhotite, galena, sphalerite, fluorite, dolomite and calcite.[1]

As a primary mineral it forms nodules, concretions and crystals in a variety of sedimentary rock, such as at Dover, Kent, England, where it forms as sharp individual crystals and crystal groups, and nodules (similar to those shown here) in chalk.

As a secondary mineral it forms by chemical alteration of a primary mineral such as pyrrhotite or chalcopyrite.

2.12.2 Alteration

Marcasite reacts more readily than pyrite under conditions of high humidity. The product of this disintegration is iron(II) sulfate and sulfuric acid. The hydrous iron sulfate forms a white powder consisting of the mineral melanterite, $FeSO_4 \cdot 7H_2O$.[5]

This disintegration of marcasite in mineral collections is known as "pyrite decay". When a specimen goes through pyrite decay, the marcasite reacts with moisture and oxygen in the air, the sulfur oxidizing and combining with water to produce sulfuric acid that attacks other sulfide minerals and mineral labels. Low humidity (less than 60%) storage conditions prevents or slows the reaction.[6]

Iridescent cluster of marcasite crystals (3.3 x 2.1 x 1.4 cm)

Two halves of a ball of radiating marcasite from France.

2.12.3 References

[1] Handbook of Mineralogy

[2] Mindat.org

[3] Webmineral data

[4] CNRTL (in French)

[5] Klein, Cornelis and Cornelius S. Hurlbut, *Manual of Mineralogy,* Wiley, 20th ed. 1985, p.286 ISBN 0-471-80580-7

[6] http://www.nps.gov/history/museum/publications/conserveogram/11-02.pdf NPS *Storage Concerns For Geological Collections,* Conserv-O-Gram, April 1998

2.12.4 External links

- How Minerals Form and Change "Pyrite oxidation under room conditions".

2.13 Millerite

For the religious movement, see Millerism.
For the neighborhood in Gary, see Miller Beach.

Millerite is a nickel sulfide mineral, NiS. It is brassy in colour and has an acicular habit, often forming radiating masses and furry aggregates. It can be distinguished from pentlandite by crystal habit, its duller colour, and general lack of association with pyrite or pyrrhotite.

2.13.1 Paragenesis

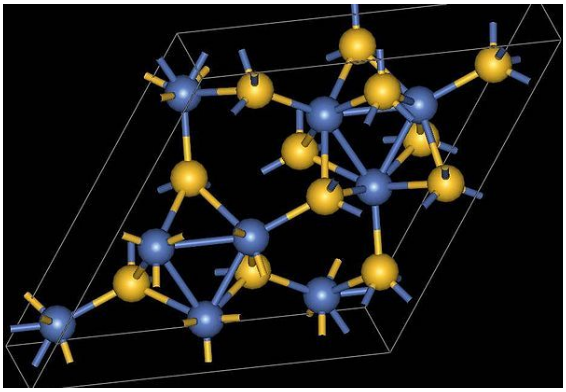
Millerite is a common metamorphic mineral replacing pentlandite within serpentinite ultramafics. It is formed in this way by removal of sulfur from pentlandite or other nickeliferous sulfide minerals during metamorphism or metasomatism.

Millerite is also formed from sulfur poor olivine cumulates by nucleation. Millerite is thought to form from sulfur and nickel which exist in pristine olivine in trace amounts, and which are driven out of the olivine during metamorphic processes. Magmatic olivine generally has up to ~4000 ppm Ni and up to 2500 ppm S within the crystal lattice, as contaminants and substituting for other transition metals with similar ionic radii (Fe^{2+} and Mn^{2+}).

During metamorphism, sulfur and nickel within the olivine lattice are reconsitituted into metamorphic sulfide minerals, chiefly millerite, during serpentinization and talc carbonate alteration. When metamorphic olivine is produced, the propensity for this mineral to resorb sulfur, and for the sulfur to be removed via the concomittant loss of volatiles from the serpentinite, tends to lower sulfur fugacity.

This forms disseminated needle like millerite crystals dispersed throughout the rock mass.

Millerite may be associated with heazlewoodite and is considered a transitional stage in the metamorphic production of heazlewoodite via the above process.



Millerite structure

2.13.2 Economic importance

Millerite, when found in enough concentration, is a very important ore of nickel because, for its mass as a sulfide mineral, it contains a higher percentage of nickel than pentlandite. This means that, for every percent of millerite, an ore contains more nickel than an equivalent percentage of pentlandite sulfide.

Millerite forms an important ore constituent of the Silver Swan, Wannaway, Cliffs, Honeymoon Well, Yakabindie and Mt Keith (MKD5) orebodies. It is an accessory mineral associated with nickel laterite deposits in New Caledonia.

2.13.3 Occurrence

Lustrous mass of intergrown millerite needles from Kalgoorlie, Western Australia. (size: 3.9 x 3.5 x 2.2 cm)

Millerite is found as a metamorphic replacement of pentlandite within the Silver Swan nickel deposit, Western Australia, and throughout the many ultramafic serpentinite bodies of the Yilgarn Craton, Western Australia, generally as a replacement of metamorphosed pentlandite.

It is commonly found as radiating clusters of acicular needle-like crystals in cavities in sulfide rich limestone and dolomite or in geodes. It is also found in nickel-iron meteorites, such as CK carbonaceous chondrites.[5]

Millerite was discovered by Wilhelm Haidinger in 1845 in the coal mines of Wales. It was named for British mineralogist William Hallowes Miller. The mineral is quite rare in specimen form, and the most common source of the mineral is the in Halls Gap area of Lincoln County, Kentucky in the United States.

2.13.4 See also

- List of minerals
- List of minerals named after people

2.13.5 References

[1] http://rruff.geo.arizona.edu/doclib/hom/millerite.pdf Handbook of Mineralogy

[2] http://www.mindat.org/min-2711.html Mindat

[3] http://webmineral.com/data/Millerite.shtml Webmineral

[4] Hurlbut, Cornelius S.; Klein, Cornelis, 1985, Manual of Mineralogy, 20th ed., pp. 279-280, ISBN 0-471-80580-7

[5] Geiger, T.; Bischoff, A. (1995). "Formation of opaque minerals in CK chondrites". *Planetary and Space Science* **43** (3–4): 485–498. Bibcode:1995P&SS...43..485G. doi:10.1016/0032-0633(94)00173-O.

2.13.6 External links

- Mineral galleries
- Wisconsin minerals
- University of Kentucky, Kentucky Geological Survey, Sulfide Minerals

2.14 Molybdenite

Molybdenite is a mineral of molybdenum disulfide, MoS_2. Similar in appearance and feel to graphite, molybdenite has a lubricating effect that is a consequence of its layered structure. The atomic structure consists of a sheet of molybdenum atoms sandwiched between sheets of sulfur atoms. The Mo-S bonds are strong, but the interaction between the sulfur atoms at the top and bottom of separate sandwich-like tri-layers is weak, resulting in easy slippage as well as cleavage planes. Molybdenite crystallizes in the hexagonal crystal system as the common polytype 2H and also in the trigonal system as the 3R polytype.[1][2][5]

2.14.1 Description

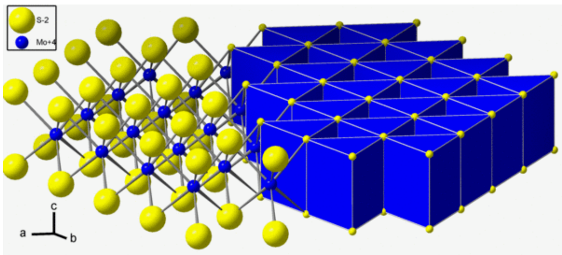
Occurrence

A sample of molybdenite mineral less pure than the single-crystal specimen at right.

Molybdenite occurs in high temperature hydrothermal ore deposits. Its associated minerals include pyrite, chalcopyrite, quartz, anhydrite, fluorite, and scheelite. Important deposits include the disseminated porphyry molybdenum deposits at Questa, New Mexico and the Henderson and Climax mines in Colorado. Molybdenite also occurs in porphyry copper deposits of Arizona, Utah, and Mexico.

The element rhenium is always present in molybdenite as a substitute for molybdenum, usually in the parts per million (ppm) range, but often up to 1–2%. High rhenium content results in a structural variety detectable by X-ray diffraction techniques. Molybdenite ores are essentially the only source for rhenium. The presence of the radioactive isotope rhenium-187 and its daughter isotope osmium−187 provides a useful geochronologic dating technique.

Features



Crystal structure of molybdenite

Molybdenite is extremely soft with a metallic luster, and is superficially almost identical to graphite. It marks paper in much the same way as graphite. Its distinguishing feature from graphite is its higher specific gravity, as well as its tendency to occur in a matrix.

2.14.2 Uses

Molybdenite is an important ore of molybdenum, and is the most common source of the metal.[2] While molybdenum is rare in the Earth's crust, molybdenite is relatively common and easy to process, and accounts for much of the metal's economic viability. Molybdenite is purified by froth floatation, and then oxidized to form soluble molybdate. Reduction of ammonium molybdate yields pure molybdenum metal, which is used for fertilizer, as a catalyst, and in battery electrodes. By far the most common use of molybdenum is as an alloy with iron. Ferromolybdenum is an important component of high strength and corrosion-resistant steel.

Semiconductor

Multilayer molybdenite flakes are semiconductors with an indirect bandgap. In contrast, monolayer flakes have a direct gap.[6] In the early years of the 20th century, molybdenite was used in some of the first crude semiconductor diodes, called cat's whisker detectors, which served as a demodulator in early crystal radios. Monolayer molybdenite shows good charge carrier mobility and can be used to create small or low-voltage transistors.[7] The transistors can detect and emit light and may have future use in optoelectronics.[8]

2.14.3 See also

- Powellite (calcium molybdate : $CaMoO_4$)
- Rheniite
- Wulfenite (lead molybdate : $PbMoO_4$)

2.14.4 References

[1] Handbook of Mineralogy

[2] Mindat.org

[3] Webmineral data for Molybdenite

[4] Dana's Manual of Mineralogy ISBN 0-471-03288-3

[5] Molybdenite 3R on Mindat

[6] "Atomically Thin MoS2: A New Direct-Gap Semiconductor". 24 Sep 2010.

[7] "Molybdenite transistor is a first". 8 Feb 2011.

[8] First light from molybdenite transistors. 19 Apr 2013

2.15 Nickeline

Nickeline or **niccolite** is a mineral consisting of nickel arsenide, NiAs, containing 43.9% nickel and 56.1% arsenic.

Small quantities of sulfur, iron and cobalt are usually present, and sometimes the arsenic is largely replaced by antimony. This last forms an isomorphous series with breithauptite (nickel antimonide).

2.15.1 Etymology and history

When, in the medieval German Erzgebirge, or Ore Mountains, a red mineral resembling copper-ore was found, the miners looking for copper could extract none from it, as it contains none; worse yet, the ore also sickened them. They blamed a mischievous sprite of German mythology, Nickel (similar to *Old Nick*) for besetting the copper (German: Kupfer): the mischievous *Kupfernickel*.[4] This German equivalent of "copper-nickel" was used as early as 1694 (other old German synonyms are *Rotnickelkies* and *Arsennickel*).

In 1751, Baron Axel Fredrik Cronstedt was attempting to extract copper from kupfernickel mineral, and obtained instead a white metal that he called after the spirit, nickel.[5] In modern German, Kupfernickel and Kupfer-Nickel designates the alloy Cupronickel.

The names subsequently given to the ore, *nickeline* from F. S. Beudant, 1832, and *niccolite,* from J. D. Dana, 1868, refer to the presence of nickel; in Latin, *niccolum.*

2.15.2 Preparation of NiAs

The main compound within nickeline, nickel arsenide (NiAs), can be prepared by direct combination of the elements:

$Ni(s) + As(s) \rightarrow NiAs(s)$[6]

2.15.3 Occurrence

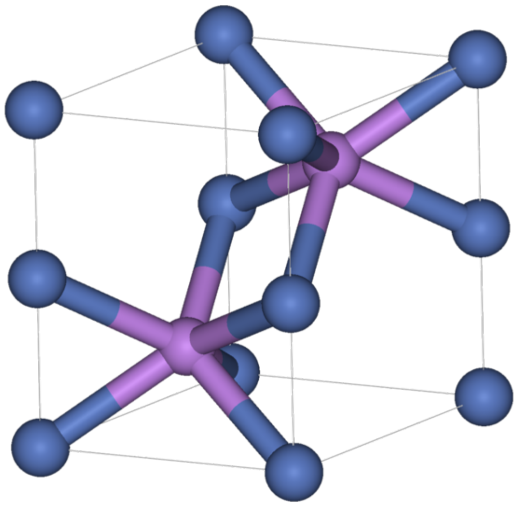
Nickeline is formed by hydrothermal modification of ultramafic rocks and associated ore deposits, and may be formed by replacement of nickel-copper bearing sulfides (replacing pentlandite, and in association with copper arsenic sulfides), or via metasomatism of sulfide-free ultramafic rocks, where metasomatic fluids introduce sulfur, carbonate, and arsenic. This typically results in mineral assemblaged including millerite, heazelwoodite and metamorphic pentlandite-pyrite via sulfidation and associated arsenopyrite-nickeline-breithauptite.

Associated minerals include: arsenopyrite, barite, silver, cobaltite, pyrrhotite, pentlandite, chalcopyrite, breithauptite and maucherite. Nickeline alters to annabergite (a coating of green nickel arsenate) on exposure to moist air.

Most of these minerals can be found in the areas surrounding Sudbury and Cobalt, Ontario. Other localities include the eastern flank of the Widgiemooltha Dome, Western Australia, from altered pentlndite-pyrite-pyrrhotite assemblages within the Mariners, Redross and Miitel nickel mines where nickeline is produced by regional Au-As-Ag-bearing alteration and carbonate metasomatism. Other occurrences include within similarly modified nickel mines of the Kambalda area.

2.15.4 Crystal structure

The unit cell of nickeline is used the prototype of a class of solids with similar crystal structures. Compounds adopting the NiAs structure are generally the chalcogenides, arsenides, antimonides and bismuthides of transition metals. Members of this group include cobalt(II) sulfide and iron(II) sulfide.



*The unit cell of **nickel arsenide***

The following are the members of the nickeline group:[7]

- Achavalite: iron selenide, FeSe
- Breithauptite: nickel antimonide, NiSb
- Freboldite: cobalt selenide, CoSe
- Imgreite: nickel telluride, NiTe
- Langistite: cobalt nickel arsenide, (Co,Ni)As
- Nickeline: nickel arsenide, NiAs
- Pyrrhotite: iron sulfide $Fe_{1-x}S$
- Sederholmite: nickel selenide, NiSe
- Stumpflite: platinum antimonide bismuthide, Pt(Sb,Bi)
- Sudburyite: palladium nickel antimonide, (Pd,Ni)Sb
- Troilite: iron sulfide, FeS

2.15.5 Economic Importance

Nickeline is rarely used as a source of nickel due to the presence of arsenic, which is deleterious to most smelting and milling techniques. When nickel sulfide ore deposits have been altered to produce nickeline, often the presence of arsenic renders the ore uneconomic when concentrations of As reach several hundred parts per million. However, arsenic bearing nickel ore may be treated by blending with 'clean' ore sources, to produce a blended feedstock which the mill and smelter can handle with acceptable recovery.

The primary problem for treating nickeline in conventionally constructed nickel mills is the specific gravity of nickeline versus that of pentlandite. This renders the ore difficult to treat via the froth flotation technique. Within the smelter itself, the nickeline contributes to high arsenic contents which require additional reagents and fluxes to strip from the nickel metal.

2.15.6 References

[1] http://rruff.geo.arizona.edu/doclib/hom/nickeline.pdf Handbook of Mineralogy

[2] http://www.mindat.org/min-2901.html Mindat.org

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2.16 Orpiment

Orpiment is a deep orange-yellow colored arsenic sulfide mineral with formula As_2S_3. It is found in volcanic fumaroles, low temperature hydrothermal veins, and hot springs and is formed both by sublimation and as a byproduct of the decay of another arsenic mineral, realgar. It takes its name from the Latin *auripigmentum* (*aurum* – gold + *pigmentum* – pigment) because of its deep-yellow color.

2.16.1 Historical uses

Orpiment was traded in the Roman Empire and was used as a medicine in China even though it is very toxic. It has been used as a fly poison and to tip arrows with poison. Because of its striking color, it was of interest to alchemists, both in China and the West, searching for a way to make gold.

For centuries, orpiment was ground down and used as a pigment in painting and for sealing wax. It was one of the few clear, bright-yellow pigments available to artists until the 19th Century. However, its extreme toxicity and incompatibility with other common pigments, including lead and copper-based substances such as verdigris and azurite, meant that its use as a pigment ended when cadmium yellows and dye-based colors were introduced during the 19th Century.

Orpiment, as the Latin *Auripigmentum*, is mentioned by Robert Hooke in *Micrographia* for the manufacture of small shot in the 17th century.[4]

2.16.2 Contemporary uses

Orpiment is used in the production of infrared-transmitting glass, oil cloth, linoleum, semiconductors, photoconductors, pigments, and fireworks. Mixed with two parts of slaked lime, orpiment is still commonly used in rural India as a depilatory. It is used in the tanning industry to remove hair from hides.

2.16.3 Physical and optical properties

Orpiment is a common monoclinic arsenic sulfide mineral. It has a Mohs hardness of 1.5 to 2 and a specific gravity of 3.49. It melts at 300 °C to 325 °C. Optically it is biaxial (–) with refractive indices of a=2.4, b=2.81, g=3.02.

2.16.4 Crystal structure

- Orpiment's unit cell

- Orpiment's crystal structure consists of sheets

- The sheets are stacked into layers

2.16.5 Gallery of orpiment specimens

- Orpiment and realgar on a vuggy, quartz matrix, Nishinomaki Mine, Gunma Prefecture, Japan. Size: 5.5 x 4.0 x 3.8 cm.

- El'brusskiy arsenic mine, Kabardino-Balkarian Republic, Northern Caucasus Region, Russia. Size 5.8 x 3.5 x 1.7 cm.

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2.16.7 External links

- Webexhibits "Pigments Through the Ages: Orpiment"

- Babylonian Talmud Tractate Chullin see Rashi 'haZarnich' (Hebrew)

2.17 Proustite

Proustite is a sulfosalt mineral consisting of; silver sulfarsenide, Ag_3AsS_3, known also as **light red silver** or **ruby silver ore**, and an important source of the metal. It is closely allied to the corresponding sulfantimonide, pyrargyrite, from which it was distinguished by the chemical analyses of Joseph L. Proust (1754-1826) in 1804, after whom the mineral received its name.

The prismatic crystals are often terminated by the scalenohedron and the obtuse rhombohedron, thus resembling calcite (dog-tooth-spar) in habit. The color is scarlet-vermilion and the lustre adamantine; crystals are transparent and very brilliant, but on exposure to light they soon become dull black and opaque. The streak is scarlet, the hardness 2.5, and the specific gravity 5.57.

Proustite occurs in hydrothermal deposits as a phase in the oxidized and supergene zone. I is associated with other silver minerals and sulfides such as native silver, native arsenic, xanthoconite, stephanite, acanthite, tetrahedrite and chlorargyrite.[1]

Magnificent groups of large crystals have been found at Chañarcillo in Chile; other localities which have yielded fine specimens are Freiberg and Marienberg in Saxony, Joachimsthal in Bohemia and Markirch in Alsace.

- **Proustite** (long prismatic crystal) - Chañarcillo, Copiapo Province, Chile. Specimen height is 4 cm.

2.17.1 See also

- List of minerals
- List of minerals named after people

2.17.2 References

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2.18 Pyrargyrite

Pyrargyrite is a sulfosalt mineral consisting of silver sulfantimonide, Ag_3SbS_3. Known also as **dark red silver ore** or **ruby silver**, it is an important source of the metal.

It is closely allied to, and isomorphous with, the corresponding sulfarsenide known as proustite or light red silver ore. Ruby silver or red silver ore (German *Rotgiiltigerz*) was mentioned by Georg Agricola in 1546, but the two species so closely resemble one another that they were not completely distinguished until chemical analyses of both were made.

Both crystallize in the ditrigonal pyramidal (hemimorphic-hemihedral) class of the rhombohedral system, possessing the same degree of symmetry as tourmaline. Crystals are perfectly developed and are usually prismatic in habit; they are frequently attached at one end, the hemimorphic character being then evident by the fact that the oblique striations on the prism faces are directed towards one end only of the crystal. Twinning according to several laws is not uncommon. The hexagonal prisms of pyrargyrite are usually terminated by a low hexagonal pyramid or by a drusy basal plane.

The color of pyrargyrite is usually greyish-black and the lustre metallic-adamantine; large crystals are opaque, but small ones and thin splinters are deep ruby-red by transmitted light, hence the name, from the Greek *pyr* and *argyros*, “fire-silver” in allusion to color and silver content, given by E. F. Glocker in 1831. The streak is purplish-red, thus differing markedly from the scarlet streak of proustite and affording a ready means of distinguishing the two minerals. The Mohs hardness is 2.75, and the specific gravity 5.85. The refractive indices ($n\omega$=3.084 $n\varepsilon$=2.881) and birefringence (δ=0.203) are very high. There is no very distinct cleavage and the fracture is conchoidal. The mineral occurs in metalliferous veins with calcite, argentiferous galena, native silver, native arsenic, &c. The best crystallized specimens are from Sankt Andreasberg in the Harz, Freiberg in Saxony, and Guanajuato in Mexico. It is not uncommon in many silver mines in the United States, but rarely as distinct crystals; and it has been found in some Cornish mines.

Pyrargyrite silver ore from the Comstock Lode, Storey Co., Nevada, USA

Although the red silver ores afford a good example of isomorphism, they rarely form mixtures; pyrargyrite rarely contains as much as 3% of arsenic replacing antimony, and the same is true of antimony in proustite. Dimorphous with pyrargyrite and proustite respectively are the rare monoclinic species pyrostilpnite or fireblende (Ag_3SbS_3) and xanthoconite (Ag_3AsS_3): these four minerals thus form an isodimorphous group.

2.18.1 External links

2.18.2 References

- Mindat
- Webmineral data
- Amethyst Galleries’ Mineral Gallery

This article incorporates text from a publication now in the public domain: Chisholm, Hugh, ed. (1911).

Encyclopædia Britannica (11th ed.). Cambridge University Press.

2.19 Pyrite

"Fool's Gold" redirects here. For other uses, see Fool's Gold (disambiguation).
This article is about iron pyrite. For other pyrite minerals, see Pyrite group.

The mineral **pyrite**, or **iron pyrite**, also known as **fool's gold**, is an iron sulfide with the chemical formula FeS_2. This mineral's metallic luster and pale brass-yellow hue give it a superficial resemblance to gold, hence the well-known nickname of *fool's gold*. The color has also led to the nicknames *brass*, *brazzle*, and *Brazil*, primarily used to refer to pyrite found in coal.[5][6]

Pyrite is the most common of the sulfide minerals. The name pyrite is derived from the Greek πυρίτης (*pyritēs*), "of fire" or "in fire",[7] in turn from πύρ (*pyr*), "fire".[8] In ancient Roman times, this name was applied to several types of stone that would create sparks when struck against steel; Pliny the Elder described one of them as being brassy, almost certainly a reference to what we now call pyrite.[9] By Georgius Agricola's time, the term had become a generic term for all of the sulfide minerals.[10]

Pyrite is usually found associated with other sulfides or oxides in quartz veins, sedimentary rock, and metamorphic rock, as well as in coal beds and as a replacement mineral in fossils. Despite being nicknamed fool's gold, pyrite is sometimes found in association with small quantities of gold. Gold and arsenic occur as a coupled substitution in the pyrite structure. In the Carlin–type gold deposits, arsenian pyrite contains up to 0.37 wt% gold.[11]

2.19.1 Uses

Pyrite enjoyed brief popularity in the 16th and 17th centuries as a source of ignition in early firearms, most notably the wheellock, where the cock held a lump of pyrite against a circular file to strike the sparks needed to fire the gun.

Pyrite has been used since classical times to manufacture *copperas*, that is, iron(II) sulfate. Iron pyrite was heaped up and allowed to weather (an example of an early form of heap leaching). The acidic runoff from the heap was then boiled with iron to produce iron sulfate. In the 15th century, such leaching began to replace the burning of sulfur as a source of sulfuric acid. By the 19th century, it had become the dominant method.[12]

Pyrite remains in commercial use for the production of sulfur dioxide, for use in such applications as the paper industry, and in the manufacture of sulfuric acid. Thermal decomposition of pyrite into FeS (iron(II) sulfide) and elemental sulfur starts at 550 °C; at around 700 °C pS_2 is about 1 atm.[13]

Pyrite from Ampliación a Victoria Mine, Navajún, La Rioja, Spain.

A newer commercial use for pyrite is as the cathode material in Energizer brand non-rechargeable lithium batteries.[14]

Pyrite is a semiconductor material with a band gap of 0.95 eV.[15]

During the early years of the 20th century, pyrite was used as a mineral detector in radio receivers, and is still used by 'crystal radio' hobbyists. Until the vacuum tube matured, the crystal detector was the most sensitive and dependable detector available – with considerable variation between mineral types and even individual samples within a particular type of mineral. Pyrite detectors occupied a midway point between galena detectors and the more mechanically complicated perikon mineral pairs. Pyrite detectors can be as sensitive as a modern 1N34A germanium diode detector.[16][17]

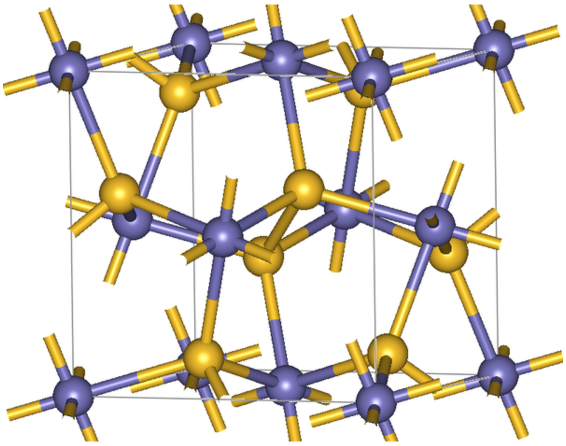
Pyrite has been proposed as an abundant, inexpensive material in low cost photovoltaic solar panels.[18] Synthetic iron sulfide was used with copper sulfide to create the photovoltaic material.[19]

Pyrite is used to make marcasite jewelry. Marcasite jewelry, made from small faceted pieces of pyrite, often set in silver, was known since ancient times and was popular in the Victorian era.[20] At the time when the term became common in jewelry making, "marcasite" referred to all iron sulfides including pyrite, and not to the orthorhombic FeS_2 mineral marcasite which is lighter in color, brittle and chemically unstable, and thus not suitable for jewelry making. Marcasite jewelry does not actually contain the mineral marcasite.

2.19.2 Formal oxidation states for pyrite, marcasite, and arsenopyrite

From the perspective of classical inorganic chemistry, which assigns formal oxidation states to each atom, pyrite is probably best described as $Fe^{2+}S_2{}^{2-}$. This formalism recognizes that the sulfur atoms in pyrite occur in pairs with clear S–S bonds. These **persulfide** units can be viewed as derived from hydrogen disulfide, H_2S_2. Thus pyrite would be more descriptively called iron persulfide, not iron disulfide. In contrast, molybdenite, MoS_2, features isolated sulfide (S^{2-}) centers and the oxidation state of molybdenum is Mo^{4+}. The mineral arsenopyrite has the formula FeAsS. Whereas pyrite has S_2 subunits, arsenopyrite has [AsS] units, formally derived from deprotonation of H_2AsSH. Analysis of classical oxidation states would recommend the description of arsenopyrite as $Fe^{3+}[AsS]^{3-}$.[21]

2.19.3 Crystallography



Crystal structure of pyrite. In the center of the cell a $S_2{}^{2-}$ pair is seen in yellow.

Iron-pyrite FeS_2 represents the prototype compound of the crystallographic pyrite structure. The structure is simple cubic and was among the first crystal structures solved by X-ray diffraction.[22] It belongs to the crystallographic space group *Pa*3 and is denoted by the Strukturbericht notation C2. Under thermodynamic standard conditions the lattice constant a of stoichiometric iron pyrite FeS_2 amounts to 541.87 pm.[23] The unit cell is composed of a Fe face-centered cubic sublattice into which the S ions are embedded. The pyrite structure is also used by other compounds MX_2 of transition metals M and chalcogens X = O, S, Se and Te. Also certain dipnictides with X standing for P, As and Sb etc. are known to adopt the pyrite structure.[24]

In the first bonding sphere, the Fe atoms are surrounded by six S nearest neighbours, in a distorted octahedral arrangement. The material is a diamagnetic semiconductor and the Fe ions should be considered to be in a *low spin* divalent state (as shown by Mössbauer spectroscopy as well as XPS), rather than a tetravalent state as the stoichiometry would suggest.

The positions of X ions in the pyrite structure may be derived from the fluorite structure, starting from a hypothetical $Fe^{2+}(S^{-})_2$ structure. Whereas F^{-} ions in CaF_2 occupy the centre positions of the eight subcubes of the cubic unit cell (¼ ¼ ¼) etc., the S^{-} ions in FeS_2 are shifted from these high symmetry positions along <111> axes to reside on (*uuu*) and symmetry-equivalent positions. Here, the parameter u should be regarded as a free atomic parameter that takes different values in different pyrite-structure compounds (iron pyrite FeS_2: u(S) = 0.385 [25]). The shift from fluorite u = 0.25 to pyrite u = 0.385 is rather large and creates a S-S distance that is clearly a binding one. This is not surprising as in contrast to F^{-} an ion S^{-} is not a closed shell species. It is isoelectronic with a chlorine *atom*, also undergoing pairing to form Cl_2 molecules. Both low spin Fe^{2+} and the disulfide $S_2{}^{2-}$ moeties are closed shell entities, explaining the diamagnetic and semiconducting properties.

The S atoms have bonds with three Fe and one other S atom. The site symmetry at Fe and S positions is accounted for by point symmetry groups $C_{3}i$ and C_3, respectively. The missing center of inversion at S lattice sites has important consequences for the crystallographic and physical properties of iron pyrite. These consequences derive from the crystal electric field active at the sulfur lattice site, which causes a polarisation of S ions in the pyrite lattice.[26] The polarisation can be calculated on the basis of higher-order Madelung constants and has to be included in the calculation of the lattice energy by using a generalised Born–Haber cycle. This reflects the fact that the covalent bond in the sulfur pair is inadequately accounted for by a strictly ionic treatment.

Arsenopyrite has a related structure with heteroatomic As-S pairs rather than homoatomic ones. Marcasite also possesses homoatomic anion pairs, but the arrangement of the metal and diatomic anions is different from that of pyrite. Despite its name a chalcopyrite does not contain dianion pairs, but single S^{2-} sulfide anions.

2.19.4 Crystal habit

Pyrite usually forms cuboid crystals, sometimes forming in close association to form raspberry-like framboids. However, under certain circumstances, it can form anastamozing filaments or T-shaped crystals.[27] Pyrite can also form dodecahedral crystals and this suggests an explanation for the artificial geometrical models found in Europe as early as the 5th century BC.[28]

Dodecahedron- shaped crystals from Italy.

2.19.5 Varieties

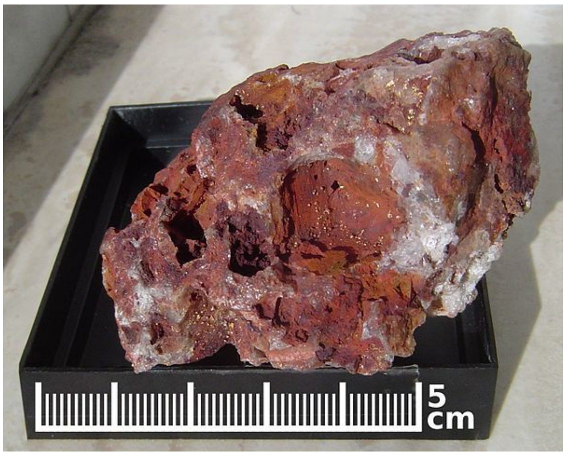
Cattierite (CoS_2) and vaesite (NiS_2) are similar in their structure and belong also to the pyrite group.

Bravoite is a nickel-cobalt bearing variety of pyrite, with > 50% substitution of Ni^{2+} for Fe^{2+} within pyrite. Bravoite is not a formally recognised mineral, and is named after Peruvian scientist Jose J. Bravo (1874–1928).[29]

2.19.6 Distinguishing similar minerals

It is distinguishable from native gold by its hardness, brittleness and crystal form. Natural gold tends to be anhedral (irregularly shaped), whereas pyrite comes as either cubes or multifaceted crystals. Chalcopyrite is brighter yellow with a greenish hue when wet and is softer (3.5–4 on Mohs' scale).[30] Arsenopyrite is silver white and does not become more yellow when wet.

2.19.7 Hazards



A pyrite cube (center) has dissolved away from a host rock, leaving behind trace gold.

Iron pyrite is unstable in the natural environment: in nature it is always being created or being destroyed. Iron pyrite exposed to air and water decomposes into iron oxides and sulfate. This process is hastened by the action of *Acidithiobacillus* bacteria which oxidize the pyrite to produce ferrous iron and sulfate. These reactions occur more rapidly when the pyrite is in fine crystals and dust, which is the form it takes in most mining operations.

Acid drainage

Sulfate released from decomposing pyrite combines with water, producing sulfuric acid, leading to acid rock drainage and potentially acid rain.

Dust explosions

Pyrite oxidation is sufficiently exothermic that underground coal mines in high-sulfur coal seams have occasionally had serious problems with spontaneous combustion in the mined-out areas of the mine. The solution is to hermetically seal the mined-out areas to exclude oxygen.[31]

In modern coal mines, limestone dust is sprayed onto the exposed coal surfaces to reduce the hazard of dust explosions. This has the secondary benefit of neutralizing the acid released by pyrite oxidation and therefore slowing the oxidation cycle described above, thus reducing the likelihood of spontaneous combustion. In the long term, however, oxidation continues, and the hydrated sulfates formed may exert crystallization pressure that can expand cracks in the rock and lead eventually to roof fall.[32]

Weakened building materials

Building stone containing pyrite tends to stain brown as the pyrite oxidizes. This problem appears to be significantly worse if any marcasite is present.[33] The presence of pyrite in the aggregate used to make concrete can lead to severe deterioration as the pyrite oxidizes.[34] In early 2009, problems with Chinese drywall imported into the United States after Hurricane Katrina were attributed to oxidation of pyrite.[35] In the United States, in Canada,[36] and more recently in Ireland,[37][38] where it was used as underfloor infill, pyrite contamination has caused major structural damage. Modern tests for aggregate materials[39] certify such materials as free of pyrite.

2.19.8 Pyritised fossils

Pyrite and marcasite commonly occur as replacement pseudomorphs after fossils in black shale and other sedimentary rocks formed under reducing environmental conditions.

However, *pyrite dollars* or *pyrite suns* which have an appearance similar to sand dollars are pseudofossils and

As a replacement mineral in an ammonite from France.

Disc or "pyrite dollar" from south of Tucson, United States; diameter 10 cm

lack the pentagonal symmetry of the animal.

2.19.9 References

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2.19.10 Further reading

- American Geological Institute, 2003, *Dictionary of Mining, Mineral, and Related Terms*, 2nd ed., Springer, New York, ISBN 978-3-540-01271-9
- Mineral galleries

2.19.11 External links

- Educational article about the famous pyrite crystals from the Navajun Mine
- How Minerals Form and Change "Pyrite oxidation under room conditions".
- Poliakoff, Martyn (2009). "Fool's Gold". *The Periodic Table of Videos*. University of Nottingham.

2.20 Pyrrhotite

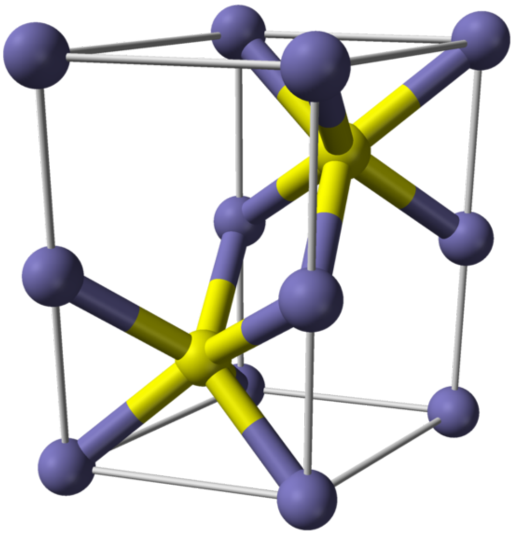
Pyrrhotite is an unusual iron sulfide mineral with a variable iron content: $Fe_{(1-x)}S$ (x = 0 to 0.2). The FeS endmember is known as troilite. Pyrrhotite is also called magnetic pyrite because the color is similar to pyrite and it is weakly magnetic. The magnetism decreases as the iron content decreases, and troilite is non-magnetic.

2.20.1 Etymology and history

The name pyrrhotite is derived from Greek *pyrrhos*, flame-colored.[1]

2.20.2 Crystal structure

Pyrrhotite has a number of polytypes of hexagonal or monoclinic crystal symmetry; several polytypes often occur within the same specimen. Their crystalline structure is based on the NiAs unit cell, where metal occurs in octahedral coordination and anions in trigonal prismatic arrangement. An important feature of this structure is an ability to omit metal atoms with the total fraction up to 1/8, thereby creating iron vacancies. One of such structures is pyrrhotite-4C (Fe_7S_8). Here "4" indicates that iron vacancies form a superlattice which is 4 times larger than the unit cell in the "C" direction. The C direction is conventionally chosen parallel to the main symmetry axis of the crystal; this direction usually corresponds



NiAs structure of basic pyrrhotite-1C

to the largest lattice spacing. Other polytypes include: pyrrhotite-5C (Fe_9S_{10}), 6C ($Fec_{11}S_{12}$), 7C (Fe_9S_{10}) and 11C ($Fe_{10}S_{11}$). Every polytype can have monoclinic (M) or hexagonal (H) symmetry, and therefore some sources label them, for example, not as 6C, but 6H or 6M depending on the symmetry.[1][4] The monoclinic forms are stable at temperatures below 254 °C, whereas the hexagonal forms are stable above that temperature. The exception is for those with high iron content, close to the troilite composition (47 to 50% atomic percent iron) which exhibit hexagonal symmetry.[5]

2.20.3 Magnetic properties

The ideal FeS lattice, such as that of troilite, is non-magnetic. Magnetic properties vary with Fe content. More Fe-rich, hexagonal pyrrhotites are antiferromagnetic. However, the Fe-deficient, monoclinic Fe_7S_8 is ferrimagnetic[6] The ferromagnetism which is widely observed in pyrrhotite is therefore attributed to the presence of relatively large concentrations of iron vacancies (up to 20%) in the crystal structure. Vacancies lower the crystal symmetry. Therefore, monoclinic forms of pyrrhotite are in general more defect-rich than the more symmetrical hexagonal forms, and thus are more magnetic.[7] Upon heating to 320 °C, pyrrhotite loses its magnetism, but also starts decomposing to magnetite. The saturation magnetization of pyrrhotite is 0.12 tesla.[8]

2.20.4 Occurrence

Pyrrhotite is a rather common trace constituent of mafic igneous rocks especially norites. It occurs as segregation deposits in layered intrusions associated with pentlandite, chalcopyrite and other sulfides. It is an important constituent of the Sudbury intrusion where it occurs in masses associated with copper and nickel mineralisation.[5] It also occurs in pegmatites and in contact metamorphic zones. Pyrrhotite is often accompanied by pyrite, marcasite and magnetite. Pyrrhotite does not have specific applications. It is mined primarily because it is associated with pentlandite, sulfide mineral that can contain significant amounts of nickel and cobalt.[1]

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2.20.6 External links

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2.21 Realgar

Realgar, α-As_4S_4, is an arsenic sulfide mineral, also known as “ruby sulphur” or “ruby of arsenic”. It is a soft, sectile mineral occurring in monoclinic crystals, or in granular, compact, or powdery form, often in association with the related mineral, orpiment (As_2S_3). It is orange-red in colour, melts at 320 °C, and burns with a bluish flame releasing fumes of arsenic and sulfur. Realgar is soft with a Mohs hardness of 1.5 to 2 and has a specific gravity of 3.5. Its streak is orange colored. It is trimorphous with alacranite and pararealgar.[1] Its name comes from the Arabic *rahj al-ġār* (رهج الغار, “powder of the mine”), via Catalan and Medieval Latin, and its earliest record in English is in the 1390s.[5]

2.21.1 Occurrence

Realgar most commonly occurs as a low-temperature hydrothermal vein mineral associated with other arsenic and antimony minerals. It also occurs as volcanic sublimations and in hot spring deposits. It occurs in association with orpiment, arsenolite, calcite and barite.[1]

It is found with lead, silver and gold ores in Hungary, Bohemia and Saxony. In the US it occurs notably in Mercur, Utah; Manhattan, Nevada and in the geyser deposits of Yellowstone National Park.[4]

It is commonly held that after a long period of exposure to light realgar changes form to a yellow powder known as pararealgar (β-As_4S_4). It was once thought that this powder was the yellow sulfide orpiment, but has been recently shown to be a distinct chemical compound.

2.21.2 Uses

Realgar, orpiment, and arsenopyrite provide nearly all the world's supply of arsenic as a byproduct of smelting concentrates derived from these ores.

Realgar was used by firework manufacturers to create the color white in fireworks prior to the availability of powdered metals such as aluminium, magnesium and titanium. It is still used in combination with potassium chlorate to make a contact explosive known as "red explosive" for some types of torpedoes and other novelty exploding fireworks branded as 'cracker balls', as well in the cores of some types of crackling stars.

Realgar is toxic. The ancient Greeks, who called it *"sandaracha"*, understood it is poisonous. It was used to poison rats in medieval Spain and in 16th century England.[6] It is still sometimes used to kill weeds, insects, and rodents,[7] even though more effective arsenic-based agents are available.

The Chinese name for realgar is *xionghuang* ⍰⍰, literally 'masculine yellow', as opposed to orpiment which was 'feminine yellow'. Its toxicity was also well known to them, and it was frequently sprinkled around houses to repel snakes and insects, as well as being used in Chinese medicine.[8] Realgar is mixed with rice liquor to make realgar wine, which is consumed during the Dragon Boat Festival in order to ward off evil, alluding to its repellent properties. (This practice has become rarer in modern times, with the awareness that realgar is a toxic arsenic compound.)

Realgar was commonly applied in leather manufacturing to remove the hair from animal pelts. Because realgar is a known carcinogen, and an arsenic poison, and because competitive substitutes are available, it is rarely used today for this purpose.

Realgar was, along with orpiment, a significant item of trade in the ancient Roman Empire and was used as a red paint pigment. Early occurrences of realgar as a red painting pigment are known for works of art from China, India, Central Asia, and Egypt. It was used in European fine-art painting during the Renaissance era, a use which died out by the 18th century.[9] It was also used as medicine.

Other traditional uses include manufacturing lead shot, printing and dyeing calico cloth.

2.21.3 Realgar gallery

- Realgar, gemmy crystals on calcite, 8.9 x 6.9 x 3.6 cm. From Shimen County, Hunan Province, China
- Realgar with tetrahedrite, Palomo Mine, Huancavelica Department, Perù
- Realgar from Nagyag, Hungary (now Romania). Hand-colored copper-plate engraving by James Sowerby (1813)
- On long exposure to light, realgar disintegrates into a reddish-yellow powder. Specimens should be protected from bright light.
- The unit cell of realgar, showing clearly the As_4S_4 molecules it contains

2.21.4 See also

- Classification of minerals
- List of minerals

2.21.5 References

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2.21.6 Further reading

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- American Mineralogist Vol 20, pp 1266–1274, 1992

2.21.7 External links

- Mindat.org: Pararealgar

2.22 Sphalerite

"Zincblende" redirects here. For crystal structure, see Zincblende (crystal structure).

Sphalerite ((Zn,Fe)S) is a mineral that is the chief ore of zinc. It consists largely of zinc sulfide in crystalline form but almost always contains variable iron. When iron content is high it is an opaque black variety, **marmatite**. It is usually found in association with galena, pyrite, and other sulfides along with calcite, dolomite, and fluorite. Miners have also been known to refer to sphalerite as **zinc blende**, **black-jack**, and ruby jack.

2.22.1 Chemistry

The mineral crystallizes in the cubic crystal system. In the crystal structure, zinc and sulfur atoms are tetrahedrally coordinated. The structure is closely related to the structure of diamond. The hexagonal analog is known as the wurtzite structure. The lattice constant for zinc sulfide in the zinc blende crystal structure is 0.541 nm,[4] calculated from geometry and ionic radii of 0.074 nm (zinc) and 0.184 nm (sulfide). It forms ABCABC layers.

2.22.2 Varieties

Its color is usually yellow, brown, or gray to gray-black, and it may be shiny or dull. Its luster is adamantine, resinous to submetallic for high iron varieties. It has a yellow or light brown streak, a Mohs hardness of 3.5–4, and a specific gravity of 3.9–4.1. Some specimens have a red iridescence within the gray-black crystals; these are called "ruby sphalerite." The pale yellow and red varieties have very little iron and are translucent. The darker, more opaque varieties contain more iron. Some specimens are also fluorescent in ultraviolet light. The refractive index of sphalerite (as measured via sodium light, 589.3 nm) is 2.37. Sphalerite crystallizes in the isometric crystal system and possesses perfect dodecahedral cleavage. Gemmy, pale specimens from Franklin, New Jersey (see Franklin Furnace), are highly fluorescent orange and/or blue under longwave ultraviolet light and are known as *cleiophane*, an almost pure ZnS variety.

Sharp, tetrahedral sphalerite crystals with minor associated chalcopyrite from the Idarado Mine, Telluride, Ouray District, Colorado, USA (size: 2.3×2.3×1.2 cm)

2.22.3 Occurrence

Sphalerite is the major ore of zinc and is found in thousands of locations worldwide.[2]

Sources of high quality crystals include:[3]

- Freiberg, Saxony, and Neudorf, Harz Mountains of Germany
- The Lengenbach Quarry, Binntal, Valais, Switzerland, has produced colorless crystals.
- Horni Slavkov (Schlaggenwald) and Pribram, Czech Republic
- From Rodna, Romania
- Transparent green to opaque black Madan, Smolyan Province, Rhodope Mountains, Bulgaria;
- Transparent crystals in the Aliva mine, Picos de Europa Mountains, Cantabria [Santander] Province, Spain
- In England, from Alston Moor, Cumbria
- At Dalnegorsk, Primorskiy Kray, Russia

- In Canada
    - Watson Lake, Yukon Territory
    - Gord Cowie at Hudson Bay Mining and Smelting processes Sphalerite in Flin Flon, Manitoba
- In the USA
    - the Tri-State district including deposits near Baxter Springs, Cherokee County, Kansas; Joplin, Jasper County, Missouri and Picher, Ottawa County, Oklahoma
    - From the Elmwood mine, near Carthage, Smith County, Tennessee
    - the Eagle mine, Gilman district, Eagle County, Colorado
- In Mexico, from Santa Eulalia and Naica, Chihuahua, and Cananea, Sonora
- Huaron, Casapalca, and Huancavelica, Peru
- In Zinkgruvan, Sweden.

2.22.4 Gemstone use

Gem quality twinned cherry-red sphalerite crystal (1.8 cm) from Hunan Province, China

Crystals of suitable size and transparency have been fashioned into gemstones, usually featuring the brilliant cut to best display sphalerite's high dispersion of 0.156 (B-G interval)—over three times that of diamond. Freshly cut gems have an adamantine luster. Owing to the softness and fragility the gems are often left unset as collector's or museum pieces (although some have been set into pendants). Gem-quality material is usually a yellowish to honey brown, red to orange, or green.

2.22.5 See also

- List of minerals

2.22.6 References

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- Minerals.net
- Minerals of Franklin, NJ

2.22.7 External links

- The sphalerite structure
- Possible relation of Sphalerite to origins of life and precursor chemicals in 'Primordial Soup'

2.23 Stibnite

Stibnite, sometimes called **antimonite**, is a sulfide mineral with the formula Sb_2S_3. This soft grey material crystallizes in an orthorhombic space group. It is the most important source for the metalloid antimony.[4] The name is from the Greek *stibi* through the Latin *stibium* as the old name for the mineral and the element antimony.[1][2] As an antimony sulfide, it is potentially toxic and should be handled with care.

2.23.1 Structure

Stibnite has a structure similar to that of arsenic trisulfide, As_2S_3. The Sb(III) centers, which are pyramidal and three-coordinate, are linked via bent two-coordinate sulfide ions. It is grey when fresh, but can turn superficially black due to oxidation in air.

- Crystal from Henan Province, China (size: 16.8×5.4×5.4 cm)
- Needles of stibnite within a transparent crystal of calcite (size: 4.5×3.5×1.8 cm)

2.23.2 Uses

Pastes of Sb_2S_3 powder in fat[5] or in other materials have been used since ca. 3000 BC as eye cosmetics in the Middle East and farther afield; in this use, Sb_2S_3 is called kohl. It was used to darken the brows and lashes, or to draw a line around the perimeter of the eye.

Antimony trisulfide finds use in pyrotechnic compositions, namely in the glitter and fountain mixtures. Needle-like crystals, "Chinese Needle", are used in glitter compositions and white pyrotechnic stars. The "Dark Pyro" version is used in flash powders to increase their sensitivity and sharpen their report. It is also a component of modern safety matches. It was formerly used in flash compositions, but its use was abandoned due to toxicity and sensitivity to static electricity.[6]

The natural sulfide of antimony, stibnite, was known and used ever since protodynastic Ancient Egypt as a medication and a cosmetic. The *Sunan Abi Dawood* reports, "prophet Muhammad said: 'Among the best types of collyrium is antimony (*ithmid*) for it clears the vision and makes the hair sprout.'"[7]

The 17th century alchemist Eirenaeus Philalethes, also known as George Starkey, describes stibnite in his alchemical commentary *An Exposition upon Sir George Ripley's Epistle*. Starkey used stibnite as a precursor to philosophical mercury, which was itself a hypothetical precursor to the Philosopher's stone.[8]

2.23.3 Occurrence

Stibnite occurs in hydrothermal deposits and is associated with realgar, orpiment, cinnabar, galena, pyrite, marcasite, arsenopyrite, cervantite, stibiconite, calcite, ankerite, barite and chalcedony.[1]

Small deposits of stibnite are common, but large deposits are rare. It occurs in Canada, Mexico, Peru, Japan, China, Germany, Romania, Italy, France, England, Algeria, and Kalimantan, Borneo. In the United States it is found in Arkansas, Idaho, Nevada, California, and Alaska.

As of May 2007, the largest specimen on public display (1000 pounds) is at the American Museum of Natural History.[9][10] The largest documented single crystals of stibnite measured ~60×5×5 cm and originated from different locations including Japan, France and Germany.[11]

2.23.4 See also

- List of minerals

2.23.5 References

[1] Stibnite. Handbook of Mineralogy

[2] Stibnite. Mindat.org

[3] Stibnite. Webmineral

[4] Sabina C. Grund, K. Hanusch, H. J. Breunig, H. U. Wolf, "Antimony and Antimony Compounds" in Ullmann's Encyclopedia of Industrial Chemistry 2006, Wiley-VCH, Weinheim. doi:10.1002/14356007.a03 055.pub2

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[10] "Chinese stibnite crystal on display in US". Retrieved 2009-06-06.

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2.23.6 External links

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2.24 Tetrahedrite

Tetrahedrite is a copper antimony sulfosalt mineral with formula: (Cu,Fe)
12Sb
4S
13. It is the antimony endmember of the continuous solid solution series with arsenic-bearing tennantite. Pure endmembers of the series are seldom if ever seen in nature. Of the two, the antimony rich phase is more common. Other elements also substitute in the structure, most notably iron and zinc, along with less common silver, mercury and lead. Bismuth also substitutes for the antimony site and *bismuthian tetrahedrite* or *annivite* is a recognized variety. The related, silver dominant, mineral species freibergite, although rare, is notable in that it can contain up to 18% silver.

Tetrahedrite gets its name from the distinctive tetrahedron shaped cubic crystals. The mineral usually occurs in massive form, it is a steel grey to black metallic mineral with Mohs hardness of 3.5 to 4 and specific gravity of 4.6 to 5.2.

Tetrahedrite crystals with chalcopyrite and sphalerite from the Casapalca Mine, Peru (size: 8.2 x 6.4 x 4.7 cm)

It occurs in low to moderate temperature hydrothermal veins and in some contact metamorphic deposits. It is a minor ore of copper and associated metals. It was first described in 1845 for occurrences in Freiberg, Saxony, Germany.

2.24.1 Applications

California-based Alphabet Energy announced plans to offer a thermoelectric device based on tetrahedrite to turn heat into electricity. The company claimed that other thermoelectrics typically produce about 2.5 percent efficiency, while tetrahedrite could achieve 5 to 10 percent.[3]

Other thermoelectrics are either scarce, expensive ($24-146/kg vs $4 for tetrahedrite) and/or toxic. Working with a natural material also reduces manufacturing costs, which otherwise chemically process pure materials.[3]

2.24.2 See also

- Bornite
- Cuprite
- List of Minerals

2.24.3 References

[1] Handbook of Mineralogy

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2.24.4 External links

Media related to Tetrahedrite at Wikimedia Commons

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- Mineral galleries
- Webmineral data

2.25 Skutterudite

Skutterudite is a cobalt arsenide mineral that has variable amounts of nickel and iron substituting for cobalt with a general formula: (Co,Ni,Fe)As_3. Some references give the arsenic a variable formula subscript of 2-3. High nickel varieties are referred to as nickel-skutterudite, previously chloanthite. It is a hydrothermal ore mineral found in moderate to high temperature veins with other Ni-Co minerals. Associated minerals are arsenopyrite, native silver, erythrite, annabergite, nickeline, cobaltite, silver sulfosalts, native bismuth, calcite, siderite, barite and quartz.[1] It is mined as an ore of cobalt and nickel with a by-product of arsenic.

The crystal structure of this mineral has been found to have important technological uses for several compounds isostructural with the mineral.

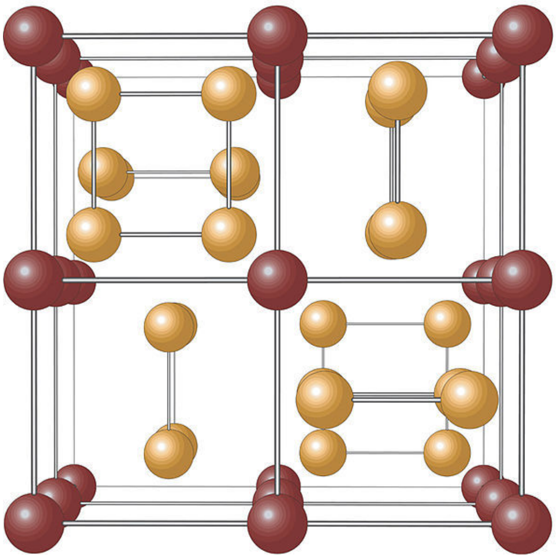
The mineral has a bright metallic luster, and is tin white or light steel gray in color with a black streak. The specific gravity is 6.5 and the hardness is 5.5-6. Its crystal structure is isometric with cube and octahedron forms similar to that of pyrite. The arsenic content gives a garlic odor when heated or crushed.

It was discovered in Skuterud Mines, Modum, Buskerud, Norway, in 1845.[2] Smaltite is a synonym for the mineral. Notable occurrences include Cobalt, Ontario, Skuterud, Norway, and Franklin, New Jersey in the United States. The rare arsenide minerals are classified in Dana’s sulfide mineral group, even though it contains no sulfur.

2.25.1 The skutterudite crystal structure

The crystal structure of the skutterudite mineral was determined in 1928 by Oftedahl to be cubic, belonging to space group Im-3 (number 204). The unit cell can be considered to consist of eight smaller cubes made up of the Co atoms. Six of these cubes are filled with (almost) square planar rings of As, each of which is oriented parallel to one of the unit cell edges, see image on the right. The As atoms then form octahedra with Co in the centre.

In crystallographic terms, the Co atoms occupy the 8c sites, while the As atoms occupy the 24g sites. The position of the Co atoms within the unit cell is fixed, while the positions of the As atoms are determined by the parameters x and y. It has been shown that for the As-rings to be fully square, these parameters must satisfy the Oftedahl relation x+y=1/2. Any deviation from this relation yields



The skutterudite unit cell.

a rectangular configuration of the As atoms. Indeed, this is the case for all known compounds with this structure, and the As atoms then do not form perfect octahedra.

Together with the unit cell size and the assigned space group, these two parameters fully describe the crystal structure of the material which is often referred to as *the skutterudite structure*.

2.25.2 Applications

Skutterite has found use as a low cost thermoelectric material [5] with low thermal conductivity.[6]

2.25.3 References

[1] http://rruff.geo.arizona.edu/doclib/hom/skutterudite.pdf Handbook of Mineralogy

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2.26 Sylvanite

This article is about the mineral. For the place, see Sylvanite, Montana.

Sylvanite or **silver gold telluride**, $(Ag,Au)Te_2$, is the most common telluride of gold.

2.26.1 Properties

The gold:silver ratio varies from 3:1 to 1:1. It is a metallic mineral with a color that ranges from a steely gray to almost white. It is closely related to calaverite, which is more purely gold telluride with 3% silver. Sylvanite crystallizes in the monoclinic 2/m system. Crystals are rare and it is usually bladed or granular. It is very soft with a hardness of 1.5 - 2. It has a high relative density of 8 - 8.2. Sylvanite is photosensitive and can accumulate a dark tarnish if it is exposed to bright light for too long.

2.26.2 Occurrence

Sylvanite is found in Transylvania, from which its name is partially derived.[4] It is also found and mined in Australia in the East Kalgoorlie district. In Canada it is found in the Kirkland Lake Gold District, Ontario and the Rouyn District, Quebec. In the United States it occurs in California and in Colorado where it was mined as part of the Cripple Creek ore deposit. Sylvanite is associated with native gold, quartz, fluorite, rhodochrosite, pyrite, acanthite, nagyagite, calaverite, krennerite, and other rare telluride minerals. It is found most commonly in low temperature hydrothermal vein deposits.

2.26.3 Use

Sylvanite represents a minor ore of gold and tellurium.

2.26.4 References

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2.26.5 External links

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Chapter 3

Oxides

3.1 Cassiterite

Cassiterite is a tin oxide mineral, SnO_2. It is generally opaque, but it is translucent in thin crystals. Its luster and multiple crystal faces produce a desirable gem. Cassiterite has been the chief tin ore throughout ancient history and remains the most important source of tin today.[1]

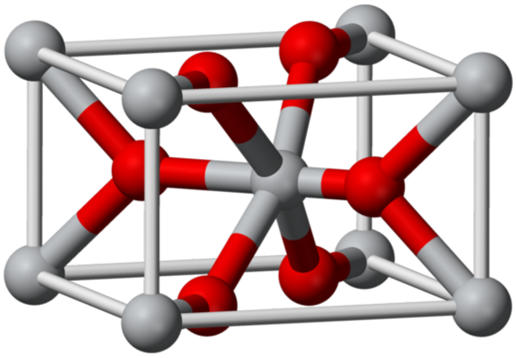
3.1.1 Occurrence

Cassiterite bipyramids, edge length ca. 30 mm, Sichuan, China

Most sources of cassiterite today are found in alluvial or placer deposits containing the resistant weathered grains. The best sources of primary cassiterite are found in the tin mines of Bolivia, where it is found in hydrothermal veins. Rwanda has a nascent cassiterite mining industry. Fighting over cassiterite deposits (particularly in Walikale) is a major cause of the conflict waged in eastern parts of the Democratic Republic of the Congo.[5][6] This has led to cassiterite being considered a conflict mineral.

Cassiterite is a widespread minor constituent of igneous rocks. The Bolivian veins and the old exhausted workings of Cornwall, England, are concentrated in high temperature quartz veins and pegmatites associated with granitic intrusives. The veins commonly contain tourmaline, topaz, fluorite, apatite, wolframite, molybdenite, and arsenopyrite. The mineral occurs extensively in Cornwall as surface deposits on Bodmin Moor, for example, where there are extensive traces of an hydraulic mining method known as *streaming*. The current major tin production comes from placer or alluvial deposits in Malaysia, Thailand, Indonesia, the Maakhir region of Somalia, and Russia. Hydraulic mining methods are used to concentrate mined ore, a process which relies on the high specific gravity of the SnO_2 ore, of about 7.0.

3.1.2 Crystallography



Crystal structure of cassiterite

Crystal twinning is common in cassiterite and most aggregate specimens show crystal twins. The typical twin is bent at a near-60-degree angle, forming an "elbow twin". Botryoidal or reniform cassiterite is called *wood tin*.

Cassiterite is also used as a gemstone and collector specimens when quality crystals are found.

3.1.3 Etymology

The name derives from the Greek *kassiteros* for "tin"—or from the Phoenician word *Cassiterid* referring to the islands of Ireland and Britain, the ancient sources of tin—or, as Roman Ghirshman (1954) suggests, from the region of the Kassites, an ancient people in west and central Iran.

3.1.4 References

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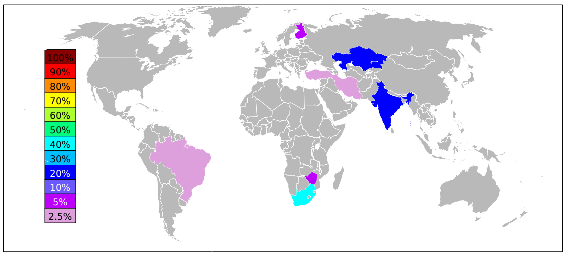
Stalactitic-botryoidal, banded, "wood tin" ***cassiterite****, 5.0 x 4.9 x 3.3 cm, Durango, Mexico*

3.2 Chromite

This article is about the mineral. For the chromium(III) anion and its salts, see Chromite (compound).

Chromite is an iron chromium oxide: $FeCr_2O_4$. It is an oxide mineral belonging to the spinel group. Magnesium can substitute for iron in variable amounts as it forms a solid solution with magnesiochromite ($MgCr_2O_4$);[5] substitution of aluminium occurs leading to hercynite ($FeAl_2O_4$).[6]

Close up of cassiterite crystals, Blue Tier tinfield, Tasmania, Australia



Chromium ore output in 2002

It is an industrially important mineral for the production of metallic chromium, used as an alloying ingredient in stainless and tool steels.

3.2.1 Occurrence

A chromite prospect in Yukon. The black bands are ***chromite****, which also carries platinum group metals. Gray rock is bleached ultramafics.*

Chromite is found as orthocumulate lenses of chromitite in peridotite from the Earth's mantle. It also occurs in layered ultramafic intrusive rocks.[7] In addition, it is found in metamorphic rocks such as some serpentinites. Ore deposits of chromite form as early magmatic differentiates. It is commonly associated with olivine, magnetite, serpentine, and corundum. The vast Bushveld igneous complex of South Africa is a large layered mafic to ultramafic igneous body with some layers consisting of 90% chromite making the rare rock type, chromitite.[8] The Stillwater igneous complex in Montana also contains significant chromite.[2]

3.2.2 Usage

The only ores of chromium are the minerals chromite and magnesiochromite. Most of the time, economic geology names chromite the whole chromite-magnesiochromite series: $FeCr_2O_4$, $(Fe,Mg)Cr_2O_4$, $(Mg,Fe)Cr_2O_4$ and $MgCr_2O_4$.[4] The two main products of chromite refining are ferrochromium and metallic chromium; for those products the ore smelter process differs considerably. For the production of ferrochromium the chromite ore ($FeCr_2O_4$) is reduced with either aluminium or silicon in an aluminothermic reaction and for the production of pure chromium the iron has to be separated from the chromium in a two step roasting and leaching process.[9] Chromite is also used as a refractory material, because it has a high heat stability.[10]

As a major source of the metal chromium, the extracted chromium from chromite is used in chrome plating and alloying for production of corrosion resistant superalloys, nichrome, and stainless steel. Chromium is used as a pigment for glass, glazes, and paint, and as an oxidizing agent for tanning leather.[11]

3.2.3 Mining

In 2002 14,600,000 metric tons of chromite were mined. The largest producers were South Africa (44%) India (18%),[12] Kazakhstan (16%) Zimbabwe (5%), Finland (4%) Iran (4%) and Brazil (2%) with several other countries producing the rest of less than 10% of the world production.[13][14]

Minor production

Afghanistan has significant deposits of high grade chromite ore, which is mined illegally in Khost Province and then smuggled out of the country.[15]

In Pakistan, chromite is mined from the ultramafic rocks in mainly the khanozai area of Pishine District of Balochistan. Most of the chromite is of metallurgical grade with Cr_2O_3 averaging 54% and a chrome to iron ratio of 2.6:1.

Recently, the biggest user of chromite ore has been China, importing large quantities from South Africa, Pakistan and other countries. The concentrate is used to make ferrochromium, which is in turn used to make stainless steel and some other alloys.[16]

In April 2010 the Government of Ontario announced[17] that they would be opening up a large chromite deposit to development in the northern part of Ontario known as the Ring of Fire. This plan has since been suspended.[18]

Australia has a single working chromite mine in the Pilbara region of Western Australia, near the Indigenous community of Jigalong. The mine produces high grade lump chromite in the region of 300,000 tonnes per year.

3.2.4 References

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3.2.5 External links

- Minerals.net
- USGS info.

3.3 Chrysoberyl

The mineral or gemstone **chrysoberyl** is an aluminate of beryllium with the formula $BeAl_2O_4$.[3] The name chrysoberyl is derived from the Greek words χρυσός *chrysos* and βήρυλλος *beryllos*, meaning "a gold-white spar". Despite the similarity of their names, chrysoberyl and beryl are two completely different gemstones, although they both contain beryllium. Chrysoberyl is the third-hardest frequently encountered natural gemstone and lies at 8.5 on the hardness scale, between corundum (9) and topaz (8).[4]

An interesting feature of its crystals are the cyclic twins called *trillings*. These twinned crystals have a hexagonal appearance, but are the result of a triplet of twins with each "twin" oriented at 120° to its neighbors and taking up 120° of the cyclic trilling. If only two of the three possible twin orientations are present, a "V"-shaped twin results.

Ordinary chrysoberyl is yellowish-green and transparent to translucent. When the mineral exhibits good pale green to yellow color and is transparent, then it is used as a gemstone. The three main varieties of chrysoberyl are: ordinary yellow-to-green chrysoberyl, cat's eye or **cymophane**, and **alexandrite**. Yellow-green chrysoberyl was referred to as "chrysolite" during the Victorian and Edwardian eras, which caused confusion since that name has also been used for the mineral olivine ("peridot" as a gemstone); that name is no longer used in the gemological nomenclature.

Alexandrite, a strongly pleochroic (trichroic) gem, will exhibit emerald green, red and orange-yellow colors depending on viewing direction in partially polarised light. However, its most distinctive property is that it also changes color in artificial (tungsten/halogen) light compared to daylight. The color change from red to green is due to strong absorption of light in a narrow yellow portion of the spectrum, while allowing large bands of blue-greener and red wavelengths to be transmitted. Which of these prevails to give the perceived hue depends on the spectral balance of the illumination. Fine-quality alexandrite has a green to bluish-green color in daylight (relatively blue illumination of high color temperature), changing to a red to purplish-red color in incandescent light (relatively yellow illumination).[5] However, fine-color material is extremely rare. Less-desirable stones may have daylight colors of yellowish-green and incandescent colors of brownish red.[6]

Cymophane is popularly known as "cat's eye". This variety exhibits pleasing chatoyancy or opalescence that reminds one of an eye of a cat. When cut to produce a cabochon, the mineral forms a light-green specimen with a silky band of light extending across the surface of the stone.

3.3.1 Occurrence

Chrysoberyl forms as a result of pegmatitic processes. Melting in the Earth's crust produces relatively low-density molten magma which can rise upwards towards the surface. As the main magma body cools, water originally present in low concentrations became more concentrated in the molten rock because it could not be incorporated into the crystallization of solid minerals. The remnant magma thus becomes richer in water, and also in rare elements that similarly do not fit in the crystal structures of major rock-forming minerals. The water extends the temperature range downwards before the magma becomes completely solid, allowing concentration of rare elements to proceed so far that they produce their own distinctive minerals. The resulting rock, igneous in appearance but formed at a low temperature from a water-rich melt, with large crystals of the common minerals such as quartz and feldspar, but also with elevated concentrations of rare elements such as beryllium, lithium, or niobium, often forming their own minerals, is called a pegmatite. The high water content of the magma made it possible for the crystals to grow quickly, so pegmatite crystals are often quite large, which increases the likelihood of gem specimens forming.

Chrysoberyl can also grow in the country rocks near to pegmatites, when Be- and Al-rich fluids from the pegmatite react with surrounding minerals. Hence, it can be found in mica schists and in contact with metamorphic deposits of dolomitic marble. Because it is a hard, dense mineral that is resistant to chemical alteration, it can be weathered out of rocks and deposited in river sands and gravels in alluvial deposits with other gem minerals such as diamond, corundum, topaz, spinel, garnet, and tourmaline. When found in such placers, it will have rounded edges instead of sharp, wedge-shape forms. Much of the chrysoberyl mined in Brazil and Sri Lanka is recovered from placers, as the host rocks have been intensely weathered and eroded.

If the pegmatite fluid is rich in beryllium, crystals of beryl or chrysoberyl could form. Beryl has a high ratio of beryllium to aluminium, while the opposite is true for chrysoberyl. Both are stable with the common mineral quartz. For alexandrite to form, some chromium would also have had to be present. However, beryllium and chromium do not tend to occur in the same types of rock. Chromium is commonest in mafic and ultramafic rocks in which beryllium is extremely rare. Beryllium becomes concentrated in felsic pegmatites in which chromium is almost absent. Therefore, the only situation where an alexandrite can grow is when Be-rich pegmatitic fluids react with Cr-rich country rock. This unusual requirement explains the rarity of this chrysoberyl variety.

3.3.2 Alexandrite

The alexandrite variety displays a color change (alexandrite effect) dependent upon the nature of ambient lighting. Alexandrite effect is the phenomenon of an observed color change from greenish to reddish with a change in source illumination.[7] Alexandrite results from small scale replacement of aluminium by chromium ions in the crystal structure, which causes intense absorption of light over a narrow range of wavelengths in the yellow region (580 nm) of the visible light spectrum.[7] Because human vision is more sensitive to light in the green spectrum and the red spectrum, alexandrite appears greenish in daylight where a full spectrum of visible light is present and reddish in incandescent light which emits less green and blue spectrum.[7] This color change is independent of any change of hue with viewing direction through the crystal that would arise from pleochroism.[7]

Alexandrite from the Ural Mountains in Russia can be green by daylight and red by incandescent light. Other varieties of alexandrite may be yellowish or pink in daylight and a columbine or raspberry red by incandescent light.

Alexandrite step cut cushion, 26.75 cts.

Stones that show a dramatic color change and strong colors (e.g. red-to-green) are rare and sought-after,[8] but stones that show less distinct colors (e.g. yellowish green changing to brownish yellow) may also be considered alexandrite by gem labs.[9]

According to a popular but controversial story, alexandrite was discovered by the Finnish mineralogist Nils Gustaf Nordenskiöld (1792–1866), and named alexandrite in honor of the future Tsar Alexander II of Russia. Nordenskiöld's initial discovery occurred as a result of an examination of a newly found mineral sample he had received from Perovskii, which he identified as emerald at first. [10] The first emerald mine had been opened in 1831.

Alexandrite 5 carats (1,000 mg) and larger were traditionally thought to be found only in the Ural Mountains, but have since been found in larger sizes in Brazil. Other deposits are located in India (Andhra Pradesh), Madagascar, Tanzania and Sri Lanka. Alexandrite in sizes over three carats are very rare.

Today, several labs can produce synthetic lab-grown stones with the same chemical and physical properties as natural alexandrite. One of these methods produces what is called flux-grown alexandrite, which produces gems that are fairly difficult to distinguish from natural alexandrite as they contain inclusions that can look natural. Another method produces the Czochralski or pulled alexandrite, which is easier to identify because it is very clean and contains curved striations visible under magnification. Although the color change in pulled stones can be from blue to red, the colour change does not truly resemble that of natural alexandrite from any deposit. However, some gemstones falsely described as lab-grown synthetic alexandrite are actually corundum laced with trace elements (e.g., vanadium) or color-change spinel and are not actually chrysoberyl. As a result, they would be more accurately described as simulated alexandrite rather than synthetic. This alexandrite-like sapphire material has been around for almost 100 years and shows a characteristic purple-mauve colour change, which does not really look like alexandrite because there is never any green. [11]

3.3.3 Cymophane

Fine-color cymophane with a sharp and centered eye

Translucent yellowish chatoyant chrysoberyl is called **cymophane** or *cat's eye*. Cymophane has its derivation also from the Greek words meaning 'wave' and 'appearance', in reference to the haziness that visually distorts what would normally be viewed as a well defined surface of a cabochon. This effect may be combined with a cat eye effect. In this variety, microscopic tubelike cavities or needle-like inclusions [12] of rutile occur in an orientation parallel to the c-axis, producing a chatoyant effect visible as a single ray of light passing across the crystal. This effect is best seen in gemstones cut in cabochon form perpendicular to the c-axis. The color in yellow chrysoberyl is due to Fe^{3+} impurities.

Although other minerals such as tourmaline, scapolite, corundum, spinel and quartz can form "cat's eye" stones similar in appearance to cymophane, the jewelry industry designates these stones as “quartz cat’s eyes”, or “ruby cat’s eyes” and only chrysoberyl can be referred to as “cat’s eye” with no other designation.

Gems lacking the silky inclusions required to produce the cat’s eye effect are usually faceted. An alexandrite cat’s eye is a chrysoberyl cat’s eye that changes color. “Milk and honey” is a term commonly used to describe the color of the best cat’s eyes. The effect refers to the sharp milky ray of white light normally crossing the cabochon as a center line along its length and overlying the honey-colored background. The honey color is considered to be top-grade by many gemologists but the lemon yellow colors are also popular and attractive. Cat’s eye material is found as a small percentage of the overall chrysoberyl production wherever chrysoberyl is found.

Cat’s eye really became popular by the end of the 19th century when the Duke of Connaught gave a ring with a cat’s eye as an engagement token; this was sufficient to make the stone more popular and increase its value greatly. Until that time, cat’s eye had predominantly been present in gem and mineral collections. The increased demand in turn created an intensified search for it in Sri Lanka.[13]

3.3.4 See also

- List of minerals

3.3.5 References

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3.4 Corundum

Not to be confused with Carborundum.

Corundum is a crystalline form of aluminium oxide (Al
2O
3) with traces of iron, titanium and chromium.[2] It is a rock-forming mineral. It is one of the naturally transparent materials, but can have different colors when impurities are present. Transparent specimens are used as gems, called ruby if red and padparadscha if pink-orange. All other colors are called sapphire, e.g., “green sapphire” for a green specimen.

The name “corundum” is derived from Tamil word *Kuruvindam* or Sanskrit word *Kuruvinda* meaning *ruby*.[6]

Because of corundum’s hardness (pure corundum is defined to have 9.0 Mohs), it can scratch almost every other mineral. It is commonly used as an abrasive on everything from sandpaper to large machines used in machining metals, plastics, and wood. Some emery is a mix of corundum and other substances, and the mix is less abrasive, with an average Mohs hardness of 8.0.

In addition to its hardness, corundum is unusual for its density of 4.02 g/cm^3, which is very high for a transparent mineral composed of the low atomic mass elements aluminium and oxygen.[7]

3.4.1 Geology and occurrence

Corundum from Brazil, size about 2 cm × 3 cm (0.8 in × 1 in).

Corundum occurs as a mineral in mica schist, gneiss, and some marbles in metamorphic terranes. It also occurs in low silica igneous syenite and nepheline syenite intrusives. Other occurrences are as masses adjacent to ultramafic intrusives, associated with lamprophyre dikes and as large crystals in pegmatites.[5] It commonly occurs as a detrital mineral in stream and beach sands because of its hardness and resistance to weathering.[5] The largest documented single crystal of corundum measured about 65×40×40 cm (26×16×16 in), and weighed 152 kg (335 lb).[8] The record has since been surpassed by certain synthetic boules.[9]

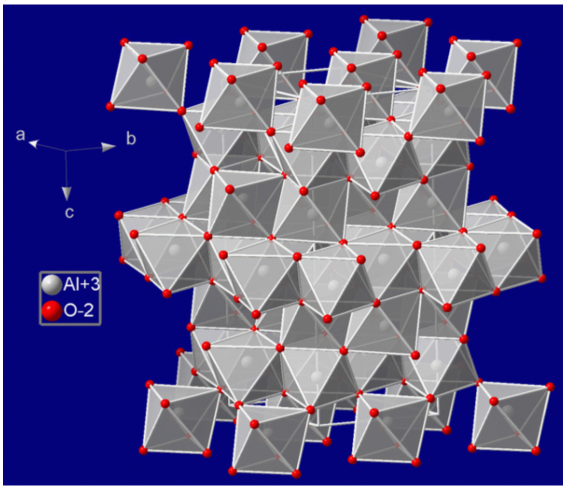
Corundum for abrasives is mined in Zimbabwe, Russia, Sri Lanka and India. Historically it was mined from deposits associated with dunites in North Carolina, USA and from a nepheline syenite in Craigmont, Ontario.[5] Emery grade corundum is found on the Greek island of Naxos and near Peekskill, New York, USA. Abrasive corundum is synthetically manufactured from bauxite.[5] Four corundum axes dating back to 2500 BCE from the Liangzhou culture have been discovered in China. The surfaces of the axes are remarkably smoothly polished.[10]

3.4.2 Synthetic corundum

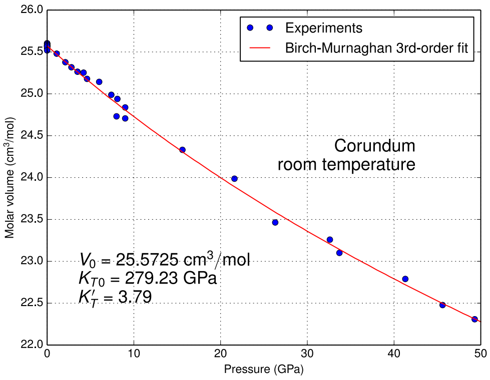
In 1837, Marc Antoine Gaudin made the first synthetic rubies by fusing alumina at a high temperature with a small amount of chromium as a pigment.[11] In 1847, Ebelmen made white synthetic sapphires by fusing alumina in boric acid. In 1877 Frenic and Freil made crystal corundum from which small stones could be cut. Frimy and Auguste Verneuil manufactured artificial ruby by fusing BaF
2 and Al
2O
3 with a little chromium at temperatures above 2,000 °C (3,632 °F). In 1903, Verneuil announced he could produce synthetic rubies on a commercial scale using this flame fusion process.[12]

The Verneuil process allows the production of flawless single-crystal sapphires, rubies and other corundum gems of much larger size than normally found in nature. It is also possible to grow gem-quality synthetic corundum by flux-growth and hydrothermal synthesis. Because of the simplicity of the methods involved in corundum synthesis, large quantities of these crystals have become available on the market causing a significant reduction of price in recent years. Apart from ornamental uses, synthetic corundum is also used to produce mechanical parts (tubes, rods, bearings, and other machined parts), scratch-resistant optics, scratch-resistant watch crystals, instrument windows for satellites and spacecraft (because of its transparency in the ultraviolet to infrared range), and laser components.

3.4.3 Structure and physical properties



Crystal structure of corundum



Molar volume vs. pressure at room temperature.

Corundum crystallizes with trigonal symmetry in the space group $R3c$ and has the lattice parameters a = 4.75 Å and c = 12.982 Å at standard conditions. The unit cell contains six formula units.

In the lattice of corundum, the oxygen atoms form a slightly distorted hexagonal close packing in which two thirds of the gaps between the octahedra are occupied by aluminum ions.

3.4.4 References

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3.5 Cuprite

Cuprite is an oxide mineral composed of copper(I) oxide Cu_2O, and is a minor ore of copper.

Cuprite from Tsumeb Mine (size:2.3 x 2.1 x 1.2 cm

Its dark crystals with red internal reflections are in the isometric system hexoctahedral class, appearing as cubic, octahedral, or dodecahedral forms, or in combinations. Penetration twins frequently occur. In spite of its nice color it is rarely used for jewelry because of its low Mohs hardness of 3.5 to 4. It has a relatively high specific gravity of 6.1, imperfect cleavage and a brittle to conchoidal fracture. The luster is sub-metallic to brilliant adamantine. The “chalcotrichite” variety typically shows greatly elongated (parallel to [001]) capillary or needle like crystals forms.

Chalcotrichite from Ray, Arizona

It is a secondary mineral which forms in the oxidized zone of copper sulfide deposits. It frequently occurs in association with native copper, azurite, chrysocolla, malachite, tenorite and a variety of iron oxide minerals.[4] It is known as *ruby copper* due to its distinctive red color.

Cuprite was first described in 1845 and the name derives from the Latin *cuprum* for its copper content.[2]

Cuprite is found in the Ural Mountains, Altai Mountains, and Sardinia, and in more isolated locations in Cornwall, France, Arizona, Chile, Bolivia, and Namibia.

[5] **Cuprite as a gemstone**

Though almost all crystals of cuprite are far too small to yield faceted gemstones, one unique deposit from Onganja, Southwest Africa, which was discovered in the 1970s, has produced crystals which were both large and gem quality. Virtually every faceted stone over one carat (0.2 gm) in weight is from this single deposit, which has long been mined out. The number of faceted gems over two carats (0.4 gm) is difficult to estimate, but according to Joel Arem, one-time curator for the Smithsonian National Gem and Mineral Collection in Washington DC, faceted cuprite of any size is considered one of the most collectible and spectacular gems in existence, with its deep garnet coloring and higher brilliance than a diamond. Only the gem’s soft nature prevents it from being among the most valuable jewelry stones.

3.5.1 See also

- Bornite
- Tennantite
- Tetrahedrite

3.5.2 References

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3.6 Franklinite

Franklinite is an oxide mineral belonging to the normal spinel subgroup's iron (Fe) series, with the formula $ZnFe^{3+}{}_2O_4$.

As with another spinel member magnetite, both ferrous (2+) and ferric (3+) iron may be present in Franklinite samples. Divalent iron and/or manganese (Mn) may commonly accompany zinc (Zn) and trivalent manganese may substitute for some ferric iron.

At its type locality, Franklinite can be found with a wide array of minerals, many of which are fluorescent. More commonly, it occurs with willemite, calcite, and red zincite. In these rocks, it forms as disseminated small black crystals with their octahedral faces visible at times. It may rarely be found as a single large euhedral crystal.

Franklinite was a minor ore of zinc, manganese, and iron. It is named after its local discovery at the Franklin Mine and Sterling Hill Mines in New Jersey.

3.6.1 See also

- Spinel
- Classification of minerals
- List of minerals

3.6.2 References

- Mindat page for franklinite

3.6.3 External links

Media related to Franklinite at Wikimedia Commons

3.7 Hematite

For other uses, see Hematite (disambiguation).

Hematite, also spelled as **haematite**, is the mineral form of iron(III) oxide (Fe_2O_3), one of several iron oxides. Hematite crystallizes in the rhombohedral lattice system, and it has the same crystal structure as ilmenite and corundum. Hematite and ilmenite form a complete solid solution at temperatures above 950 °C (1,740 °F).

Hematite is a mineral, colored black to steel or silver-gray, brown to reddish brown, or red. It is mined as the main ore of iron. Varieties include *kidney ore*, *martite* (pseudomorphs after magnetite), *iron rose* and *specularite* (specular hematite). While the forms of hematite vary, they all have a rust-red streak. Hematite is harder than pure iron, but much more brittle. Maghemite is a hematite- and magnetite-related oxide mineral.

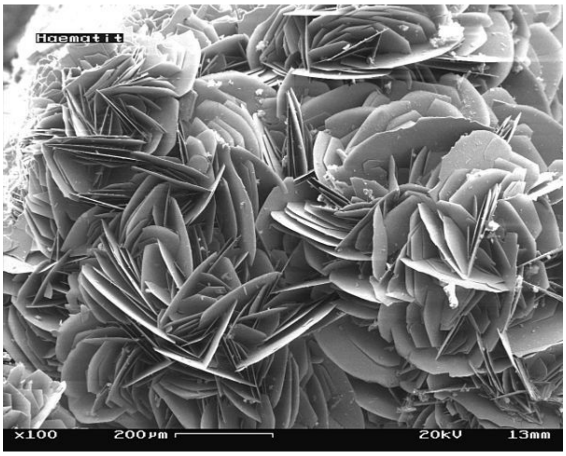
Huge deposits of hematite are found in banded iron formations. Gray hematite is typically found in places where there has been standing water or mineral hot springs, such as those in Yellowstone National Park in North America. The mineral can precipitate out of water and collect in layers at the bottom of a lake, spring, or other standing water. Hematite can also occur without water, however, usually as the result of volcanic activity.

Clay-sized hematite crystals can also occur as a secondary mineral formed by weathering processes in soil, and along with other iron oxides or oxyhydroxides such as goethite, is responsible for the red color of many tropical, ancient, or otherwise highly weathered soils.

3.7.1 Etymology and history

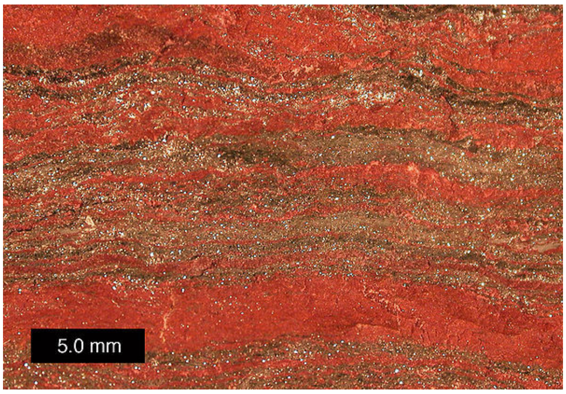
Main article: Ochre

The name hematite is derived from the Greek word for blood αἷμα *haima* because hematite can be red, as in rouge, a powdered form of hematite. The color of hematite lends itself to use as a pigment. The English name of the stone is derived from Middle French: Hématite Pierre, which was imported from Latin: Lapis Hæmatites, which originated from Ancient



Hematite in a scanning electron microscope, magnification 100x

Hematite (blood ore) from Michigan



Close-up of hematitic banded iron formation specimen from Upper Michigan. Scale bar is 5.0 mm.

Cypro-Minoan cylinder seal (left) made from hematite with corresponding impression (right), approximately 14th century BC

Greek: αἱματίτης λίθος (haimatitēs lithos, "blood-red stone").

Ochre is a clay that is colored by varying amounts of hematite, varying between 20% and 70%.[4] Red ochre contains unhydrated hematite, whereas yellow ochre contains hydrated hematite ($Fe_2O_3 \bullet H_2O$). The principal use of ochre is for tinting with a permanent color.[4]

The red chalk writing of this mineral was one of the earliest in the history of humans. The powdery mineral was first used 164,000 years ago by the Pinnacle-Point man possibly for social purposes.[5] Hematite residues are also found in old graveyards from 80,000 years ago. Near Rydno in Poland and Lovas in Hungary, palaeolitic red chalk mines have been found that are from 5000 BC, belonging to the Linear Pottery culture at the Upper Rhine.

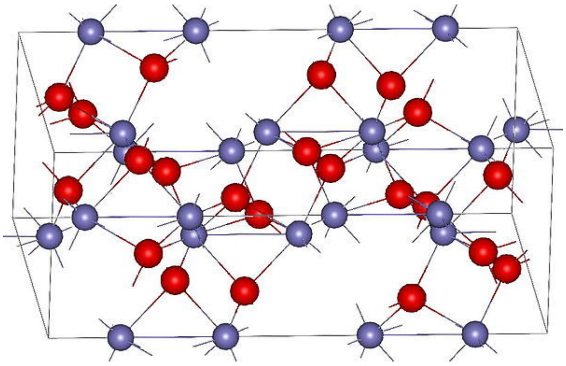
Rich deposits of hematite have been found on the island of Elba that have been mined since the time of the Etruscans.

Jewelry

Hematite carving, 5 cm (2 in) long.

Hematite's popularity in jewelry was at its highest in Europe during the Victorian era. Certain types of hematite or iron oxide-rich clay, especially Armenian bole, have been used in gilding. Hematite is also used in art such as in the creation of intaglio engraved gems. Hematine is a synthetic material sold as *magnetic hematite*.[6]

3.7.2 Magnetism



Crystal structure of hematite

Hematite is an antiferromagnetic material below the Morin transition at 250 kelvin (K) or −9.7 degrees Fahrenheit (°F), and a canted antiferromagnet or weakly ferromagnetic above the Morin transition and below its Néel temperature at 948 K, above which it is paramagnetic.

The magnetic structure of a-hematite was the subject of considerable discussion and debate in the 1950s because it appeared to be ferromagnetic with a Curie temperature of around 1000 K, but with an extremely tiny moment (0.002 µB). Adding to the surprise was a transition with a decrease in temperature at around 260 K to a phase with no net magnetic moment. It was shown that the system is essentially antiferromagnetic, but that the low symmetry of the cation sites allows spin–orbit coupling to cause canting of the moments when they are in the plane perpendicular to the c axis. The disappearance of the moment with a decrease in temperature at 260 K is caused by a change in the anisotropy which causes the moments to align along the c axis. In this configuration, spin canting does not reduce the energy.[7][8] The magnetic properties of bulk hematite differ from their nanoscale counterparts. For example, the Morin transition temperature of hematite decreases with a decrease in the particle size. The suppression of this transition has also been observed in some of the hematite nanoparticles, and the presence of impurities, water molecules and defects in the crystals were attributed to the absence of a Morin transition. Hematite is part of a complex solid solution oxyhydroxide system having various contents of water, hydroxyl groups and vacancy substitutions that affect the mineral's magnetic and crystal chemical properties.[9] Two other endmembers are referred to as protohematite and hydrohematite.

Iron from mine tailings

Hematite is present in the waste tailings of iron mines. A recently developed process, magnetation, uses magnets to glean waste hematite from old mine tailings in Minnesota's vast Mesabi Range iron district.[10]

Falu red is a pigment used in traditional Swedish house paints. Originally, it was made from tailings of the Falu mine.[11]

3.7.3 Discovery on Mars

The spectral signature of hematite was seen on the planet Mars by the infrared spectrometer on the NASA Mars Global Surveyor ("MGS") and 2001 Mars Odyssey spacecraft in orbit around Mars.[12] The mineral was seen in abundance at two sites[13] on the planet, the Terra Meridiani site, near the Martian equator at 0° longitude, and the Aram Chaos site near the Valles Marineris.[14] Several other sites also showed hematite, e.g., Aureum Chaos.[15] Because terrestrial hematite is typically a mineral formed in aqueous environments or by aqueous alteration, this detection was scientifically interesting enough that the second of the two Mars Exploration Rovers was sent to a site in the Terra Meridiani region designated Meridiani Planum. In-situ investigations by the Opportunity rover showed a significant amount of hematite, much of it in the form of small spherules that were informally named "blueberries" by the science team. Analysis indicates that these spherules are apparently concretions formed from a water solution. "Knowing just how the hematite on Mars was formed will help us characterize the past environment and determine whether that environment was favorable for life". [16]

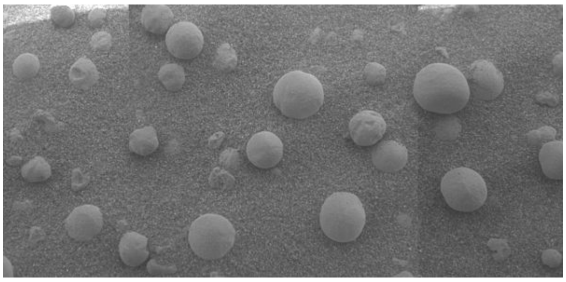


Image mosaic from the Mars Exploration Rover Microscopic Imager shows Hematite spherules partly embedded in rock at the Opportunity landing site. Image is ca. 5 cm (2 in) across.

3.7.4 See also

- Mill scale
- Mineral redox buffer
- Wüstite

3.7.5 References

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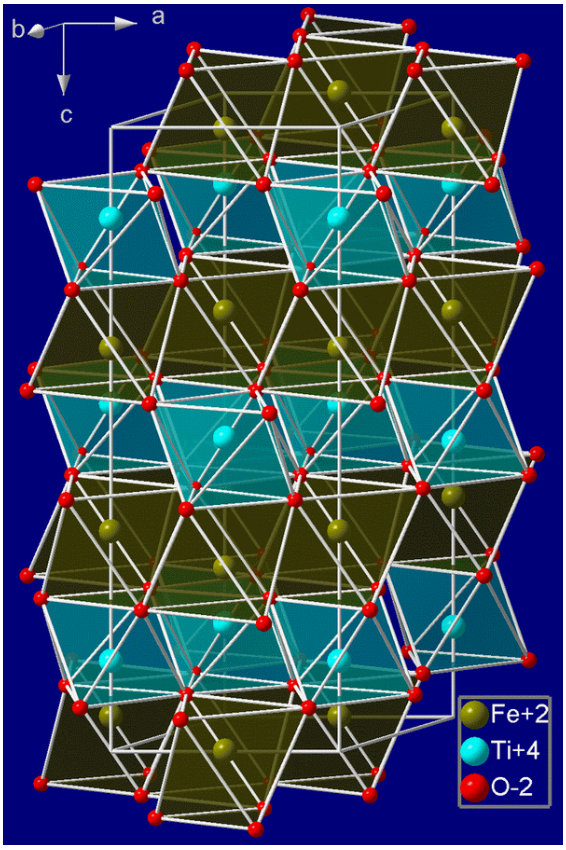
[16] Hematite. NASA. Last Updated: 12 Jul 2007

3.7.6 External links

- Martite – Mindat w/ location data
- Iron rose – Mindat w/ locations
- Abandoned Mine Research.
- Mars spheres image.
- Mars trench image showing a shiny texture of half-buried spheres (dark line is equipment shadow)
- Florence Mine, Cumbria, UK.
- MineralData.org



Crystal structure of ilmenite

3.8 Ilmenite

Ilmenite is the titanium-iron oxide mineral with the idealized formula FeTiO
3. It is a weakly magnetic black or steel-gray solid. From the commercial perspective, ilmenite is the most important ore of titanium.[4]

3.8.1 Structure and properties

Ilmenite crystallizes in the trigonal system. The ilmenite crystal structure consists of an ordered derivative of the corundum structure; in corundum all cations are identical but in ilmenite Fe^{2+} and Ti^{4+} ions occupy alternating layers perpendicular to the trigonal c axis. Containing high spin ferrous centers, ilmenite is paramagnetic.

Ilmenite is commonly recognized in altered igneous rocks by the presence of a white alteration product, the pseudo-mineral leucoxene. Often ilmenites are rimmed with leucoxene, which allows ilmenite to be distinguished from magnetite and other iron-titanium oxides. The example shown in the image at right is typical of leucoxene-rimmed ilmenite.

In reflected light it may be distinguished from magnetite by more pronounced reflection pleochroism and a brown-pink tinge.

Samples of ilmenite exhibit a weak response to a hand magnet.

3.8.2 Mineral chemistry

Ilmenite from Froland, Aust-Agder, Norway; 4.1 x 4.1 x 3.8 cm

Ilmenite most often contains appreciable quantities of magnesium and manganese and the full chemical formula can be expressed as (Fe,Mg,Mn,Ti)O_3. Ilmenite forms a solid solution with geikielite (MgTiO
3) and pyrophanite (MnTiO
3) which are magnesian and manganiferous end-members of the solid solution series.

Although there appears evidence of the complete range of mineral chemistries in the (Fe,Mg,Mn,Ti)O_3 system naturally occurring on Earth, the vast bulk of ilmenites are restricted to close to the ideal FeTiO
3 composition, with minor mole percentages of Mn and Mg. A key exception is in the ilmenites of kimberlites where the mineral usually contains major amounts of geikielite molecules, and in some highly differentiated felsic rocks ilmenites may contain significant amounts of pyrophanite molecules.

At higher temperatures it has been demonstrated there is a complete solid solution between ilmenite and hematite. There is a miscibility gap at lower temperatures, resulting in a coexistence of these two minerals in rocks but no solid solution. This coexistence may result in exsolution lamellae in cooled ilmenites with more iron in the system than can be homogeneously accommodated in the crystal lattice.

Altered ilmenite forms the mineral leucoxene, an important source of titanium in heavy mineral sands ore deposits. Leucoxene is a typical component of altered gabbro and diorite and is generally indicative of ilmenite in the unaltered rock.

3.8.3 Paragenesis

Tellnes opencast ilmenite mine, Sokndal, Norway

Ilmenite is a common accessory mineral found in metamorphic and igneous rocks. It is found in large concentrations in layered intrusions where it forms as part of a cumulate layer within the silicate stratigraphy of the intrusion. Ilmenite generally occurs within the pyroxenitic portion of such intrusions (the 'pyroxene-in' level).

Magnesian ilmenite is indicative of kimberlitic paragenesis and forms part of the MARID association of minerals (mica-amphibole-rutile-ilmenite-diopside) assemblage of glimmerite xenoliths. Manganiferous ilmenite is found in granitic rocks and also in carbonatite intrusions where it may also contain anomalous niobium.

Many mafic igneous rocks contain grains of intergrown magnetite and ilmenite, formed by the oxidation of ulvospinel. Ilmenite also occurs as discrete grains, typically with some hematite in solid solution, and complete solid solution exists between the two minerals at temperatures above about 950 °C.

Titanium was identified for the first time by William Gregor in 1791 in ilmenite from the Manaccan valley in Cornwall, southwest England.

Ilmenite is named after the locality of its discovery in the Il'menski Mountains, near Miass, Russia.

3.8.4 Processing and consumption

Most ilmenite is mined for titanium dioxide production. In 2011, about 47% of the titanium dioxide produced worldwide were based on this material.[5] Finely ground titanium dioxide is a bright white powder widely used as a base pigment in paint, paper and plastics.

North America and Europe together consume about 50% of the world's titanium dioxide production. Demand by India and China is growing rapidly and may eventually surpass Western consumption.

Ilmenite is ultimately converted into pigment grade titanium dioxide via either the sulfate process or the chloride process. Sulfate process plants must utilise low-vanadium ilmenite, as vanadium is a penalty element. Titanium dioxide pigment can also be produced from higher titanium content feedstocks such as upgraded slag, rutile and leucoxene via a chloride acid process. Sulfate and chloride process pigment tends to be used for lower and higher quality applications respectively, users more and more preferring the chloride process. The five largest TiO_2 pigment processors are Dupont, Cristal Global, Huntsman, Kronos and Tronox, Dupont having pioneered the chloride process in the 1960s and having converted to the use of the chloride process for all its applications.[7] Major paint and coating company end users for pigment grade titanium dioxide include Akzo Nobel, PPG Industries, Sherwin Williams, BASF, Kansai Paints and Valspar.[8] Global TiO_2 pigment demand for 2010 was 5.3 Mt with annual growth expected to be about 3-4%.[9]

Most ilmenite ore production from Canada, South Africa and Norway is destined for titaniferous slag application.[10] Carbon (anthracite) and energy are added in large electric arc smelting furnaces to convert the ilmenite into molten iron bath and slag rich in titanium dioxide. The iron can be further processed as pig iron, as continuous cast steel billets, or as iron or steel powders. A related chemically process technology is termed the Becher process.

Ilmenite ore is used as a flux by steelmakers to line blast furnace hearth refractory.[11]

Ilmenite sand is also used as a sandblasting agent in the cleaning of diecasting dies.

3.8.5 Feedstock Production

Australia was the world's largest ilmenite ore producer in 2011, with about 1.3 million tonnes of production, followed by South Africa, Canada, Mozambique, India, China, Vietnam, Ukraine, Norway, Madagascar and United States.

Although most ilmenite is recovered from heavy mineral sands ore deposits, ilmenite can also be recovered from layered intrusive sources or "hard rock" titanium ore sources.

The top four ilmenite and rutile feedstock producers in 2010 were Rio Tinto Group, Iluka Resources, Exxaro and Kenmare Resources, which collectively accounted for more than 60% of world's supplies.[8]

The world's two largest open cast ilmenite mines are:

- The Tellnes mine located in Sokndal, Norway, and run by Titania AS (owned by Kronos Worldwide Inc.) with 0.55 Mtpa capacity and 57 Mt contained TiO_2 reserves.
- The Rio Tinto Group's Lac Tio mine located near Havre Saint-Pierre, Quebec in Canada with a 3 Mtpa capacity and 52 Mt reserves.[13]

Major mineral sands based ilmenite mining operations include:

- Richards Bay Minerals in South Africa, majority-owned by the Rio Tinto Group.
- Kenmare Resources' Moma mine in Mozambique.
- Iluka Resources' mining operations in Australia including Murray Basin, Eneabba and Capel.
- The Kerala Minerals & Metals Ltd (KMML), Indian Rare Earths (IRE), VV Mineral mines in India.
- TiZir Ltd.'s Grande Cote mine in Senegal[14]
- QIT Madagascar Minerals mine, majority-owned by the Rio Tinto Group, which began production in 2009 and is expected to produce 0.75 Mtpa of ilmenite, potentially expanding to 2 Mtpa in future phases.

Attractive major potential ilmenite deposits include:

- The Karhujupukka magnetite-ilmenite deposit in Kolari, northern Finland with around 5 Mt reserves and ore containing about 6.2% titanium.
- The Balla Balla magnetite-iron-titanium-vanadium ore deposit in the Pilbara of Western Australia, which contains 456 million tonnes of cumulate ore horizon grading 45% Fe, 13.7% TiO_2 and 0.64% V_2O_5, one of the richest magnetite-ilmenite ore bodies in Australia[15]
- The Coburn, WIM 50, Douglas, Pooncarrie mineral sands deposits in Australia.

3.8.6 Lunar ilmenite

Ilmenite has been found in Moon rocks, and is typically highly enriched in magnesium similar to the kimberlitic association. In 2005[16] NASA used the Hubble Space Telescope to locate potentially ilmenite-rich locations. This mineral could be essential to an eventual Moon base, as ilmenite would provide a source of iron and titanium for the building of structures and essential oxygen extraction.

3.8.7 References

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3.9 Magnetite

Not to be confused with Magnesite, Maghemite, or Magnemite.

Magnetite is a mineral, one of the three common naturally occurring iron oxides (chemical formula Fe_3O_4) and a member of the spinel group. Magnetite is the most magnetic of all the naturally occurring minerals on Earth.[5] Naturally magnetized pieces of magnetite, called lodestone, will attract small pieces of iron, and this was how ancient people first noticed the property of magnetism.

Small grains of magnetite occur in almost all igneous and metamorphic rocks. Magnetite is black or brownish-black with a metallic luster, has a Mohs hardness of 5–6 and a black streak.

The chemical IUPAC name is iron(II,III) oxide and the common chemical name is **ferrous-ferric oxide**.

3.9.1 Properties

Lodestones were used as an early form of magnetic compass. Magnetite typically carries the dominant magnetic signature in rocks, and so it has been a critical tool in paleomagnetism, a science important in understanding plate tectonics and as historic data for magnetohydrodynamics and other scientific fields. The relationships between magnetite and other iron-rich oxide minerals such as ilmenite, hematite, and ulvospinel have been much studied; the reactions between these minerals and oxygen influence how and when magnetite preserves a record of the Earth's magnetic field.

Magnetite has been very important in understanding the conditions under which rocks form. Magnetite reacts with oxygen to produce hematite, and the mineral pair forms a buffer that can control oxygen fugacity. Commonly, igneous rocks contain grains of two solid solutions, one of magnetite and ulvospinel and the other of ilmenite and hematite. Compositions of the mineral pairs are used to calculate how oxidizing was the magma (i.e., the oxygen fugacity of the magma): a range of oxidizing conditions are found in magmas and the oxidation state helps to determine how the magmas might evolve by fractional crystallization.

Magnetite also occurs in many sedimentary rocks, including banded iron formations. In many igneous rocks, magnetite-rich and ilmenite-rich grains occur that precipitated together in magma. Magnetite also is produced from peridotites and dunites by serpentinization.

The Curie temperature of magnetite is 858 K (585 °C; 1,085 °F).

3.9.2 Distribution of deposits

A fine textured sample, ~5cm across

Magnetite and other heavy minerals (dark) in a quartz beach sand (Chennai, India).

Magnetite is sometimes found in large quantities in beach sand. Such black sands (mineral sands or iron sands) are found in various places, such as California and the west coast of the North Island of New Zealand.[6] The magnetite is carried to the beach via rivers from erosion and is concentrated via wave action and currents.

Huge deposits have been found in banded iron formations. These sedimentary rocks have been used to infer changes in the oxygen content of the atmosphere of the Earth.

Large deposits of magnetite are also found in the Atacama region of Chile, Valentines region of Uruguay, Kiruna, Sweden, the Pilbara, Midwest and Northern Goldfields regions in Western Australia, New South Wales in the Tallawang Region, and in the Adirondack region of New York in the United States. Kediet ej Jill, the highest mountain of Mauritania, is made entirely of the mineral.[7] Deposits are also found in Norway, Germany, Italy, Switzerland, South Africa, India, Indonesia, Mexico, and in Oregon, New Jersey, Pennsylvania, North Carolina, Virginia, New Mexico, Utah, and Colorado in the United States. In 2005, an exploration company, Cardero Resources, discovered a vast deposit of magnetite-bearing sand dunes in Peru. The dune field covers 250 square kilometers (100 sq mi), with the highest dune at over 2,000 meters (6,560 ft) above the desert floor. The sand contains 10% magnetite.[8]

Transformation of ferrous hydroxide into magnetite

Under anaerobic conditions, the ferrous hydroxide ($Fe(OH)_2$) can be oxidized by the protons of water to form magnetite and molecular hydrogen. This process is described by the Schikorr reaction:

$$3\ Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2\ H_2O$$

ferrous hydroxide → magnetite + hydrogen + water

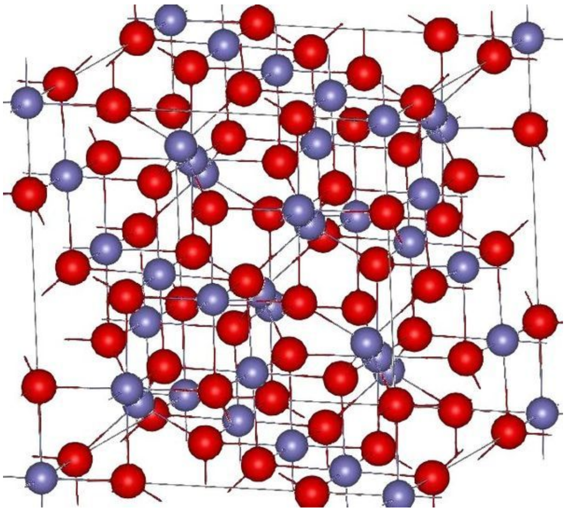
The well-crystallized magnetite (Fe_3O_4) is thermodynamically more stable than the ferrous hydroxide ($Fe(OH)_2$).[9]

3.9.3 Biological occurrences

Biomagnetism is usually related to the presence of biogenic[10] crystals of magnetite, which occur widely in organisms.[11] These organisms range from bacteria (e.g., *Magnetospirillum magnetotacticum*) to animals, where these crystals are found in the brain.[12] These crystals are involved in magnetoreception, the ability to sense the polarity or the inclination of the Earth's magnetic field, and aid in navigation. [10]

Chitons have teeth made of magnetite on their radula.[10]

3.9.4 Synthetic magnetite



Crystal structure of magnetite. Red atoms are oxygens.

Magnetite can be prepared in the laboratory as a ferrofluid in the Massart method by mixing iron(II) chloride and iron(III) chloride in the presence of sodium hydroxide.[13] Magnetite can also be prepared by the chemical co-precipitation in presence of ammonia, which consist in a mixture of a solution 0.1 M of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ with mechanic agitation of about 2000 rpm. The molar ratio of $FeCl_3$:$FeCl_2$ can be 2:1; heating this solution at 70 °C, and immediately the speed is elevated to 7500 rpm and adding quickly a solution of NH_4OH (10 volume %), immediately a dark precipitate will be formed, which consists of nanoparticles of magnetite.[14] In both cases, the precipitation reaction rely on a quick transformation of acidic hydrolyzed iron ions into the spinel iron oxide structure, by hydrolysis at elevated pH values (above ca. 10).

Considerable efforts has been devoted towards controlling the particle formation process of magnetite nanoparticles due to the challenging and complex chemistry reactions involved in the phase transformations prior to the formation of the magnetite spinel structure.[15] Magnetite particles are of interests in bioscience applications such as in magnetic resonance imaging (MRI) since iron oxide magnetite nanoparticles represent a non-toxic alternative to currently employed gadolinium-based contrast agents. However, due to lack of control over the specific transformations involved in the formation of the particles, truly superparamagnetic particles have not yet been prepared from magnetite, i.e. magnetite nanoparticles that completely lose their permanent magnetic characteristic in the absence of an external magnetic field (which by definition show a coercivity of 0 A/m). The smallest values currently reported for nanosized magnetite particles is Hc = 8.5 A m^{-1},[16] whereas the largest reported magnetization value is 87 Am^2 kg^{-1} for synthetic magnetite.[17][18]

3.9.5 Applications

Magnetic recording

Magnetic iron oxides are often used in magnetic storage,[19] for example in the magnetic layer of hard disks, floppy disks and cassette tapes. These consist of a thin sheet of plastic material, with embedded magnetic particles. The particles can be magnetized to represent binary or analog data. Magnetic ink character recognition (MICR) also uses magnetic particles suspended in an ink which can be read by special scanning hardware.

Most newly generated information, such as text, photographs, and audiovisual recordings, is now stored in magnetic media, and much of the world's legacy of information in other media has been transcribed to magnetic form, because it is cheap, compact, and computer-accessible.

Catalysis

Magnetite is the catalyst for the industrial synthesis of ammonia.[20]

As a sorbent

Magnetite powder efficiently removes arsenic(III) and arsenic(V) from water, the efficiency of which increases ~200 times when the magnetite particle size decreases from 300 to 12 nm.[21] Arsenic-contaminated drinking water is a major problem around the world, which can be solved using magnetite as a sorbent.

Other

Because of its stability at high temperatures, it is used for coating industrial watertube steam boilers. The magnetite layer is formed after a chemical treatment (e.g. by using hydrazine).

3.9.6 Gallery of magnetite mineral specimens

- Octahedral crystals of magnetite up to 1.8 cm across, on cream colored Feldspar crystals. Locality: Cerro Huañaquino, Potosí Department, Bolivia. Size: 8.4 x 5.2 x 3.2 cm.
- Unusual octahedral magnetite & chalcopyrite association, Aggeneys, Northern Cape Province, South Africa. Size 7 x 6 x 4 cm.
- Red gem-like crystals of Chondrodite with magnetite, Tilly Foster mine, Brewster, New York USA. Size 2.8 x 2.6 x 2.1 cm.
- Unusual specular hematite pseudomorph after magnetite, from Payun Matru volcano, Reserva Provincial La Payunia, Argentina. Size: 11.8 x 5.6 x 4.4 cm.
- Metallic, jet black, complex cubes of magnetite, from ZCA Mine No. 4, Balmat-Edwards district, St. Lawrence County, New York USA. Field of view, about 4 cm.

3.9.7 See also

- Bluing (steel), a process in which steel is partially protected against rust by a layer of magnetite
- Buena Vista Iron Ore District
- Corrosion product
- Ferrite
- Greigite
- Maghemite
- Magnesia (in natural mixtures with magnetite)
- Magnetotactic bacteria
- Mill scale
- Mineral redox buffer

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3.9.10 External links

- Mineral galleries
- Bio-magnetics
- History of Magnetite Mining in the NJ Highlands
- Magnetite mining in New Zealand Accessed 25-Mar-09
- Mineral Survey of Santa Cruz County - Black Sand
- Peruvian sand dunes

3.10 Pyrolusite

Pyrolusite is a mineral consisting essentially of manganese dioxide (MnO_2) and is important as an ore of manganese. It is a black, amorphous appearing mineral, often with a granular, fibrous or columnar structure, sometimes forming reniform crusts. It has a metallic luster, a black or bluish-black streak, and readily soils the fingers. The specific gravity is about 4.8. Its name is from the Greek for *fire* and to *wash*, in reference to its use as a way to remove tints from glass.[3]

3.10.1 Occurrence

Pyrolusite and romanechite are among the most common manganese minerals. Pyrolusite occurs associated with manganite, hollandite, hausmannite, braunite, chalcophanite, goethite and hematite under oxidizing conditions in hydrothermal deposits. It also occurs in bogs and often results from alteration of manganite.[3]

3.10.2 Use

The metal is obtained by reduction of the oxide with sodium, magnesium, aluminium, or by electrolysis. Pyrolusite is extensively used for the manufacture of spiegeleisen and ferromanganese and of various alloys such as manganese-bronze. As an oxidizing agent it is used in the preparation of chlorine; indeed, chlorine gas itself was first described by Karl Scheele in 1774 from the reaction products of pyrolusite and hydrochloric acid. Natural pyrolusite has been used in batteries, but high-quality batteries require synthetic products. Pyrolusite is also used to prepare disinfectants (permanganates) and for decolorizing glass. When mixed with molten glass it oxidizes the ferrous iron to ferric iron, and so discharges the green and brown tints (making it classically useful to glassmakers as a decolorizer). As a coloring material, it is used in calico printing and dyeing; for imparting violet, amber, and black colors to glass, pottery, and bricks; and in the manufacture of green and violet paints.

3.10.3 Variations in crystal habit

- Botryoidal
- Dendritic
- Acicular radiating
- crystal structure of pyrolusite

3.10.4 See also

Other manganese oxides:

- Birnessite
- Psilomelane

3.10.5 References

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3.11 Rutile

Rutile is a mineral composed primarily of titanium dioxide, TiO_2.

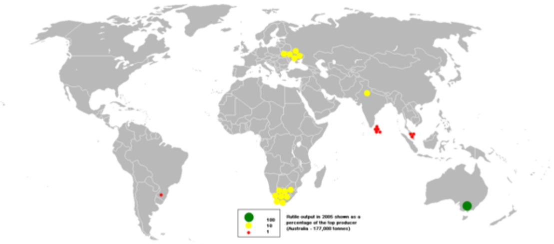
Rutile is the most common natural form of TiO_2. Two rarer polymorphs of TiO_2 are known:

- Anatase (sometimes known by the obsolete name “octahedrite”), a tetragonal mineral of pseudo-octahedral habit
- Brookite, an orthorhombic mineral

Rutile has among the highest refractive indices at visible wavelengths of any known crystal, and also exhibits a particularly large birefringence and high dispersion. Owing to these properties, it is useful for the manufacture of certain optical elements, especially polarization optics, for longer visible and infrared wavelengths up to about 4.5μm.

Natural rutile may contain up to 10% iron and significant amounts of niobium and tantalum. Rutile derives its name from the Latin *rutilus*, red, in reference to the deep red color observed in some specimens when viewed by transmitted light.

3.11.1 Occurrence



Rutile output in 2005

Rutile is a common accessory mineral in high-temperature and high-pressure metamorphic rocks and in igneous rocks.

Thermodynamically, rutile is the most stable polymorph of TiO_2 at all temperatures, exhibiting lower total free energy than metastable phases of anatase or brookite.[5] Consequently, the transformation of the metastable TiO_2 polymorphs to rutile is irreversible. As it has the lowest molecular volume of the three main polymorphs; it is generally the primary titanium bearing phase in most high-pressure metamorphic rocks, chiefly eclogites.

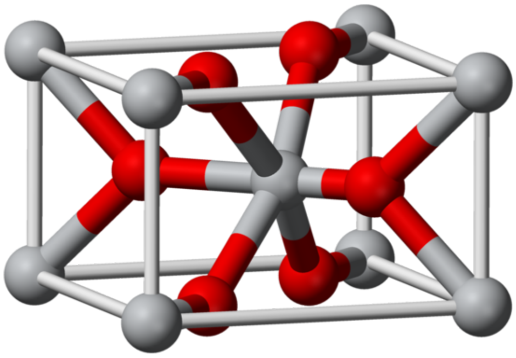
Rutile in quartz

Within the igneous environment, rutile is a common accessory mineral in plutonic igneous rocks, though it is also found occasionally in extrusive igneous rocks, particularly those that have deep mantle sources such as kimberlites and lamproites. Anatase and brookite are found in the igneous environment particularly as products of autogenic alteration during the cooling of plutonic rocks; anatase is also found in placer deposits sourced from primary rutile.

The occurrence of large specimen crystals is most common in pegmatites, skarns, and granite greisens. Rutile is found as an accessory mineral in some altered igneous rocks, and in certain gneisses and schists. In groups of acicular crystals it is frequently seen penetrating quartz as in the *fléches d'amour* from Graubünden, Switzerland. In 2005 the Republic of Sierra Leone in West Africa had a production capacity of 23% of the world's annual rutile supply, which rose to approximately 30% in 2008. The reserves, lasting for about 19 years, are estimated at 259,000,000 metric tons (285,000,000 short tons).[6]

3.11.2 Crystal structure

Rutile has a body-centred tetragonal unit cell, with unit cell parameters a=b=4.584 Å, and c=2.953 Å.[7] The titanium cations have a coordination number of 6 meaning they are surrounded by an octahedron of 6 oxygen atoms. The oxygen anions have a co-ordination number of 3 resulting in a trigonal planar co-ordination. Rutile also shows a screw axis when its octahedra are viewed sequentially.[8]



The unit cell of rutile. Ti atoms are gray; O atoms are red.

Acicular crystals of rutile protruding from a quartz crystal

3.11.3 Uses and economic importance

In large enough quantities in beach sands, rutile forms an important constituent of heavy minerals and ore deposits. Miners extract and separate the valuable minerals—e.g., rutile, zircon, and ilmenite. The main uses for rutile are the manufacture of refractory ceramic, as a pigment, and for the production of titanium metal.

Finely powdered rutile is a brilliant white pigment and is used in paints, plastics, paper, foods, and other applications that call for a bright white color. Titanium dioxide pigment is the single greatest use of titanium worldwide. Nanoscale particles of rutile are transparent to visible light but are highly effective in the absorption of ultraviolet radiation. The UV absorption of nano-sized rutile particles is blue-shifted compared to bulk rutile, so that higher-energy UV light is absorbed by the nanoparticles. Hence, they are used in sunscreens to protect against UV-induced skin damage.

Small rutile needles present in gems are responsible for an optical phenomenon known as asterism. Asteriated gems are known as "star" gems. Star sapphires, star rubies, and other "star" gems are highly sought after and are generally more valuable than their normal counterparts.

Rutile is widely used as a welding electrode covering. It is also used as a part of the ZTR index, which classifies highly weathered sediments.

3.11.4 Synthetic rutile

Synthetic rutile was first produced in 1948 and is sold under a variety of names. Very pure synthetic rutile is transparent and almost colorless (slightly yellow) in large pieces. Synthetic rutile can be made in a variety of colors by doping. The high refractive index gives an adamantine luster and strong refraction that leads to a diamond-like appearance. The near-colorless diamond substitute is sold as “Titania”, which is the old-fashioned chemical name for this oxide. However, rutile is seldom used in jewellery because it is not very hard (scratch-resistant), measuring only about 6 on the Mohs hardness scale.

3.11.5 See also

- List of minerals

3.11.6 References

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3.11.7 External links

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3.12 Spinel

See also: Spinel group

Spinel /ˈspɪnɛl/ is the magnesium aluminium member of the larger spinel group of minerals. It has the formula $MgAl_2O_4$.[1] **Balas ruby** is an old name for a rose-tinted variety.

3.12.1 Properties of true spinel

Cut spinel

Spinel crystallizes in the isometric system; common crystal forms are octahedra, usually twinned. It has an imperfect octahedral cleavage and a conchoidal fracture. Its hardness is 8, its specific gravity is 3.5–4.1 and it is transparent to opaque with a vitreous to dull luster. It may be colorless, but is usually various shades of red, blue, green, yellow, brown, or black. There is a unique natural white spinel, now lost, that surfaced briefly in what is now Sri Lanka. Some spinels are among the most famous gemstones: Among them are the Black Prince’s Ruby and the "Timur ruby" in the British Crown Jewels, and the “Côte de Bretagne”, formerly from the French Crown jewels. The Samarian Spinel is the largest known spinel in the world, weighing 500 carats (100 g).

The transparent red spinels were called spinel-rubies or balas rubies. In the past, before the arrival of modern science, spinels and rubies were equally known as rubies. After the 18th century the word ruby was only used for the red gem variety of the mineral corundum and the word spinel became used. “Balas” is derived from Balascia, the ancient name for Badakhshan, a region in central Asia situated in the upper valley of the Kokcha River, one of the principal tributaries of the Oxus River. The Badakshan Province was for centuries the main source for red and pink spinels.

3.12.2 Occurrence

Spinel has long been found in the gemstone-bearing gravel of Sri Lanka and in limestones of the Badakshan Province in modern day Afghanistan and of Mogok in Burma. Recently gem quality spinels were also found in the marbles of Luc Yen (Vietnam), Mahenge and Matombo (Tanzania), Tsavo (Kenya) and in the gravels of Tunduru (Tanzania) and Ilakaka (Madagascar). Spinel is found as a metamorphic mineral, and also as a primary mineral in rare mafic igneous rocks; in these igneous rocks, the magmas are relatively deficient in alkalis relative to aluminium, and aluminium oxide may form as the mineral corundum or may combine with magnesia to form spinel. This is why spinel and ruby are often found together.

Spinel, $(Mg,Fe)(Al,Cr)_2O_4$, is common in peridotite in the uppermost Earth's mantle, between approximately 20 km to approximately 120 km, possibly to lower depths depending on the chromium content.[3] At significantly shallower depths, above the Moho, calcic plagioclase is the more stable aluminous mineral in peridotite, while garnet is the stable phase deeper in the mantle below the spinel stability region.

Spinel, $(Mg,Fe)Al_2O_4$, is a common mineral in the Ca-Al-rich inclusions (CAIs) in some chondritic meteorites.

3.12.3 Synthetic spinel

Synthetic spinel was accidentally produced in the middle of the 18th century, and has been more recently described in scientific publications in 2000 and 2004.[4]

3.12.4 See also

- Ceylonite
- The Samarian Spinel: the largest known spinel in the world, part of the Iranian Crown Jewels
- Black Prince's Ruby

3.12.5 References

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3.12.7 External links

- Spinel structure at the University of Wisconsin - Green Bay
- Spinel structure at the Institut for materials science of the University of Kiel

3.13 Uraninite

"Pitchblende" redirects here. For other uses, see Pitchblende (disambiguation).

Uraninite is a radioactive, uranium-rich mineral and ore with a chemical composition that is largely UO_2, but due to oxidation the mineral typically contains variable proportions of U_3O_8. Additionally, due to radioactive decay, the ore also contains oxides of lead and trace amounts of helium. It may also contain thorium, and rare earth elements.[1][3] It used to be known as **pitchblende** (from *pitch*, because of its black color, and *blende*, a term used by German miners to denote minerals whose density suggested metal content, but whose exploitation, at the time they were named, was either unknown, impossible or not economically feasible). The mineral has been known at least since the 15th century from silver mines in the Ore Mountains, on the German/Czech border. The type locality is the town of Jáchymov, on the Czech side of the mountains, where F.E. Brückmann described the mineral in 1772.[3][5] Pitchblende from the Johanngeorgenstadt deposit in Germany was used by M. Klaproth in 1789 to discover the element uranium.[6]

All uraninite minerals contain a small amount of radium as a radioactive decay product of uranium. Uraninite also always contains small amounts of the lead isotopes ^{206}Pb and ^{207}Pb, the end products of the decay series of the uranium isotopes ^{238}U and ^{235}U respectively. Small amounts of helium are also present in uraninite as a result of alpha decay. Helium was first found on Earth in uraninite after having been discovered spectroscopically in the Sun's atmosphere. The extremely rare elements technetium and promethium can be found in uraninite in very small quantities (about 200 pg/kg and 4 fg/kg respectively), produced by the spontaneous fission of uranium-238.

3.13.1 Occurrence

Uraninite crystals from Topsham, Maine (size: 2.7×2.4×1.4 cm)

Uraninite is a major ore of uranium. Some of the highest grade uranium ores in the world were found in the Shinkolobwe mine in the Democratic Republic of the Congo (the initial source for the Manhattan Project) and in the Athabasca Basin in northern Saskatchewan, Canada. Another important source of pitchblende is at Great Bear Lake in the Northwest Territories of Canada, where it is found in large quantities associated with silver. It also occurs in Australia, the Czech Republic, Germany, England, and South Africa. In the United States it can be found in the states of Arizona, Colorado, Connecticut, Maine, New Hampshire, New Mexico, North Carolina and Wyoming. The geologist Charles Steen made a fortune on the production of Uraninite in his Mi Vida mine in Moab, Utah.

Uranium ore is generally processed close to the mine into yellowcake, which is an intermediate step in the processing of uranium.

3.13.2 See also

- Thorianite
- Uranium ore deposits
- List of minerals
- List of uranium mines

3.13.3 References

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3.13.4 External links

Media related to Uraninite at Wikimedia Commons

3.14 Zincite

Not to be confused with Zincate.

Zincite is the mineral form of zinc oxide (ZnO). Its crystal form is rare in nature; a notable exception to this is at the Franklin and Sterling Hill Mines in New Jersey, an area also famed for its many fluorescent minerals. It has a hexagonal crystal structure and a color that depends on the presence of impurities. The zincite found at Franklin Furnace is red-colored (mostly due to iron and manganese) and associated with willemite and franklinite.

Zincite crystals can be grown artificially, and synthetic zincite crystals are available as a by-product of zinc smelting. Synthetic crystals can be colorless or can range in color from dark red, orange, or yellow to light green.

Synthetic zincite crystals

Both natural and synthetic zincite crystals are significant for their early use as semiconductor crystal detectors in the early development of crystal radios before the advent of vacuum tubes. As an early radio detector it was used in conjunction with another mineral, galena, and this combination was known as the cat’s-whisker detector.

3.14.1 See also

- List of minerals
- Oleg Losev

3.14.2 References

[1] Zincite. Handbook of Mineralogy

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3.14.3 External links

- Mineral galleries

Chapter 4

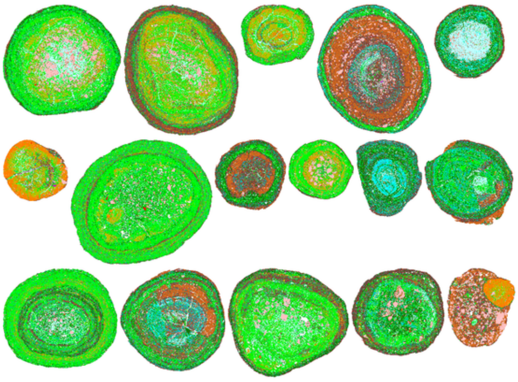
Hydroxides

4.1 Bauxite

This article is about the ore. For the town in Arkansas, see Bauxite, Arkansas.

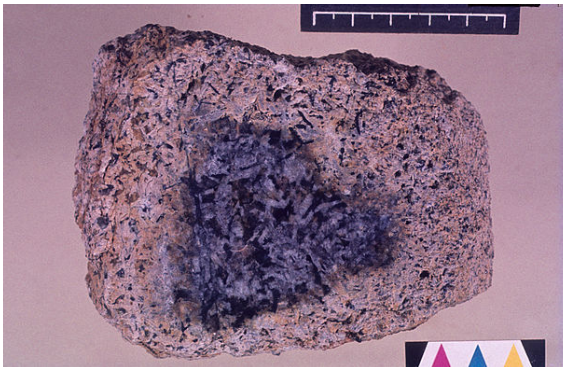
Bauxite, an aluminium ore, is the world's main source of aluminium. It consists mostly of the minerals gibbsite $Al(OH)_3$, boehmite γ-AlO(OH) and diaspore α-AlO(OH), mixed with the two iron oxides goethite and haematite, the clay mineral kaolinite and small amounts of anatase TiO_2. Bauxite was named by the French geologist Pierre Berthier in 1821 after the village of Les Baux in Provence, southern France, where he discovered

Bauxite with US penny for comparison



QEMSCAN mineral maps of bauxite ore-forming pisoliths

Bauxite in Les Baux-de-Provence, France



Bauxite with core of unweathered rock

One of the world's largest bauxite mines in Weipa, Australia it and was the first to recognize that it contained aluminium.

4.1.1 Formation

Lateritic bauxites (silicate bauxites) are distinguished from karst bauxite ores (carbonate bauxites). The carbonate bauxites occur predominantly in Europe and Jamaica above carbonate rocks (limestone and dolomite), where they were formed by lateritic weathering and residual accumulation of intercalated clay layers – dispersed clays which were concentrated as the enclosing limestones gradually dissolved during chemical weathering.

The lateritic bauxites are found mostly in the countries of the tropics. They were formed by lateritization of various silicate rocks such as granite, gneiss, basalt, syenite, and shale. In comparison with the iron-rich laterites, the formation of bauxites depends even more on intense weathering conditions in a location with very good drainage. This enables the dissolution of the kaolinite and the precipitation of the gibbsite. Zones with highest aluminium content are frequently located below a ferruginous surface layer. The aluminium hydroxide in the lateritic bauxite deposits is almost exclusively gibbsite.

India's bauxite deposits are mainly found in the Amarkantak plateau, Maikal hills and the plateau region of Bilaspur - Katni. Orrissa is the largest bauxite producing state in India with 45% of the country's total production in 2000- 01. Panchpatmali deposits in Koraput district are the most important bauxite deposits in the state. In the case of Jamaica, recent analysis of the soils showed elevated levels of cadmium, suggesting that the bauxite originates from recent Miocene ash deposits from episodes of significant volcanism in Central America.

4.1.2 Production trends

In 2009, Australia was the top producer of bauxite with almost one-third of the world's production, followed by China, Brazil, India, and Guinea. Although aluminium demand is rapidly increasing, known reserves of its bauxite ore are sufficient to meet the worldwide demands for aluminium for many centuries.[1] Increased aluminium recycling, which has the advantage of lowering the cost in electric power in producing aluminium, will considerably extend the world's bauxite reserves.

In November 2010, Nguyen Tan Dung, the prime minister of Vietnam, announced that Vietnam's bauxite reserves might total 11000 Mt; this would be the largest in the world.[4]

4.1.3 Processing

Bauxite is usually strip mined because it is almost always found near the surface of the terrain, with little or no overburden. Approximately 70% to 80% of the world's dry bauxite production is processed first into alumina, and then into aluminium by electrolysis as of 2010. Bauxite rocks are typically classified according to their intended commercial application: metallurgical, abrasive, cement, chemical, and refractory.

Bauxite being loaded at Cabo Rojo, Dominican Republic, to be shipped elsewhere for processing; 2007

Usually, bauxite ore is heated in a pressure vessel along with a sodium hydroxide solution at a temperature of 150 to 200 °C. At these temperatures, the aluminium is dissolved as an aluminate (the Bayer process). After separation of ferruginous residue (red mud) by filtering, pure gibbsite is precipitated when the liquid is cooled, and then seeded with fine-grained aluminium hydroxide. The gibbsite is usually converted into aluminium oxide, Al_2O_3, by heating. This mineral is dissolved at a temperature of about 960 °C in molten cryolite. Next, this molten substance can yield metallic aluminium by passing an electric current through it in the process of electrolysis, which is called the Hall–Héroult process, named after its American and French discoverers.

Prior to the invention of this process in 1886, elemental aluminium was made by heating ore along with elemental sodium or potassium in a vacuum. The method was complicated and consumed materials that were themselves expensive at that time. This made early elemental aluminium more expensive than gold.[5]

4.1.4 See also

- Alcoa
- Bauxite, Arkansas
- Rio Tinto Alcan
- United Company RUSAL

4.1.5 References

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4.1.7 External links

- USGS Minerals Information: Bauxite
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4.2 Brucite

Brucite is the mineral form of magnesium hydroxide, with the chemical formula $Mg(OH)_2$. It is a common alteration product of periclase in marble; a low-temperature hydrothermal vein mineral in metamorphosed limestones and chlorite schists; and formed during serpentinization of dunites. Brucite is often found in association with serpentine, calcite, aragonite, dolomite, magnesite, hydromagnesite, artinite, talc and chrysotile.

Notable locations include Wood's Chrome Mine, Cedar Hill Quarry, Lancaster County, Pennsylvania, USA.

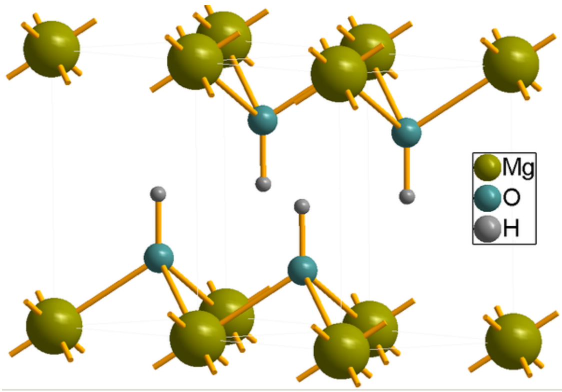
4.2.1 Discovery

Brucite was first described in 1824 and named for the discoverer, American mineralogist, Archibald Bruce (1777–1818). A fibrous variety of Brucite is called **Nemalite**. It occurs in fibers or laths, usually elongated along [1010], but sometimes [1120] crystalline directions.

Nemalite

Brucite crystals from the Sverdlovsk Region, Urals, Russia (size: 10.5 x 7.8 x 7.4 cm

4.2.2 Industrial applications



Crystal structure

Brucite is used as a flame retardant because it thermally decomposes to release water in a similar way to aluminium hydroxide and mixtures of huntite and hydromagnesite.[4][5] It also constitutes a significant source of magnesium for industry.

4.2.3 Magnesian attack of cement and concrete

When cement or concrete are exposed to non negligible concentration of Mg^{2+}, e.g. when these materials are left in prolonged contact with sea water or brines, $Mg(OH)_2$ precipitates under the high pH conditions prevailing in the cement porewater. The neoformation of brucite, an expansive material, induces mechanical stress in the hardened cement paste and is responsible for the formation of cracks and fissures in concrete.

The use of dolomite as aggregate in concrete can also cause the magnesian attack and should be avoided.

4.2.4 See also

- List of minerals
- List of minerals named after people
- Portlandite, $Ca(OH)_2$

4.2.5 References

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[3] Brucite on Webmineral

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4.3 Boehmite

Boehmite or **böhmite** is an aluminium oxide hydroxide (γ-AlO(OH)) mineral, a component of the aluminium ore bauxite. It is dimorphous with diaspore. It crystallizes in the orthorhombic dipyramidal system and is typically massive in habit. It is white with tints of yellow, green, brown or red due to impurities. It has a vitreous to pearly luster, a Mohs hardness of 3 to 3.5 and a specific gravity of 3.00 to 3.07. It is colorless in thin section, optically biaxial positive with refractive indices of $n\alpha = 1.644$ - 1.648, $n\beta = 1.654$ - 1.657 and $n\gamma = 1.661$ - 1.668.

Boehmite occurs in tropical laterites and bauxites developed on alumino-silicate bedrock. It also occurs as a hydrothermal alteration product of corundum and nepheline. It occurs with kaolinite, gibbsite and diaspore in bauxite deposits; and with nepheline, gibbsite, diaspore, natrolite and analcime in nepheline pegmatites.[3]

It was first described by J. de Lapparent in 1927 for an occurrence in the bauxites of Mas Rouge, Les Baux-de-Provence, France, and named[5] for the Bohemian-German chemist Johann Böhm (1895–1952) who carried out X-ray studies of aluminium oxide hydroxides in 1925[6] (and not for the German geologist Johannes Böhm (1857–1938) as often stated).[1][2]

4.3.1 References

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[2] "Boehmite". Mindat with location data. Retrieved 2010-07-10.

[3] Mineral Data Pub. Handbook of Mineralogy

[4] "The Mineral Boehmite". minerals.net. Retrieved June 10, 2014.

[5] http://www.springerlink.com/content/u2005q723h61km44/

[6] http://onlinelibrary.wiley.com/doi/10.1002/zaac.19251490114/abstract

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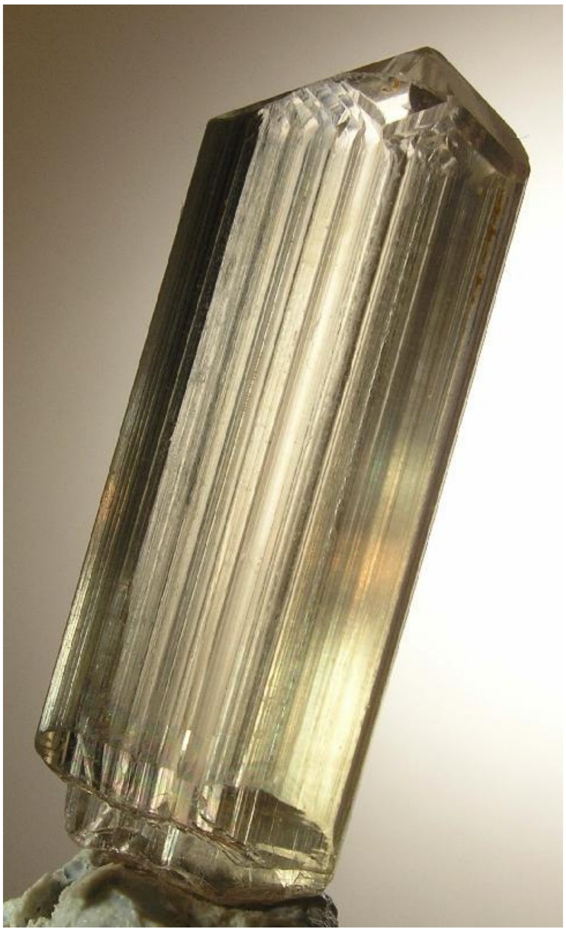
4.4 Diaspore

Not to be confused with diaspora.
For the plant seed structure, see diaspore (botany).

Diaspore /ˈdaɪəspɔːr/, also known as **empholite**, **kayserite**, or **tanatarite**, is an *aluminium oxide hydroxide* mineral, α-AlO(OH), crystallizing in the orthorhombic system and isomorphous with goethite. It occurs sometimes as flattened crystals, but usually as lamellar or scaly masses, the flattened surface being a direction of perfect cleavage on which the lustre is markedly pearly in character. It is colorless or greyish-white, yellowish, sometimes violet in color, and varies from translucent to transparent.[3] It may be readily distinguished from other colorless transparent minerals with a perfect cleavage and pearly luster—like mica, talc, brucite, and gypsum— by its greater hardness of 6.5 - 7. The specific gravity is 3.4. When heated before the blowpipe it decrepitates violently, breaking up into white pearly scales.



Twinned crystal of Turkish diaspore from Mugla Province, Aegean Region, Turkey (1.8 x .6 x .4 cm)

The mineral occurs as an alteration product of corundum or emery and is found in granular limestone and other crystalline rocks. Well-developed crystals are found in the emery deposits of the Urals and at Chester, Massachusetts, and in kaolin at Schemnitz in Hungary. If obtainable in large quantity, it would be of economic importance as a source of aluminium.

Diaspore, along with gibbsite and boehmite, is a major component of the aluminium ore bauxite.[2]

It was first described in 1801 for an occurrence in Mramorsk Zavod, Sverdlovskaya Oblast, Middle Urals, Russia. The name is from the Greek for διασπείρειν, *to scatter,* in allusion to its decrepitation on heating.[1]

Csarite, *ottomanite*, and *zultanite* are trade names for gem-quality diaspore (also known as Turkish diaspore) from the İlbir Mountains of southwest Turkey.[4]

4.4.1 See also

- aluminium oxide
- aluminium hydroxide

4.4.2 References

[1] Handbook of Mineralogy

[2] Klein, Cornelis and Cornelius S. Hurlbut, *Manual of Mineralogy,* Wiley, 1985, 20th ed. p.318 ISBN 0-471-80580-7

[3] "The Mineral diaspore". minerals.net. Retrieved June 10, 2014.

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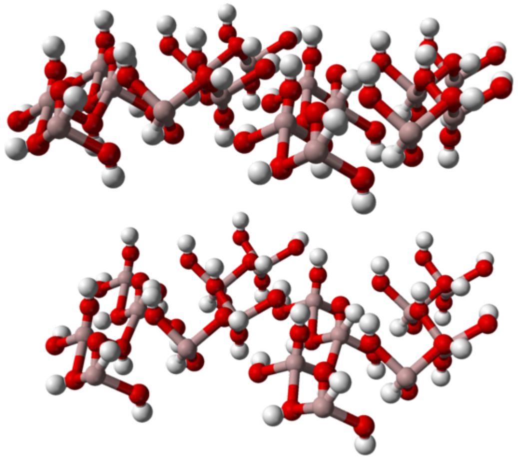
Chisholm, Hugh, ed. (1911). "Diaspore". *Encyclopædia Britannica* (11th ed.). Cambridge University Press. This article incorporates text from a publication now in the public domain: Chisholm, Hugh, ed. (1911). *Encyclopædia Britannica* (11th ed.). Cambridge University Press.

4.5 Gibbsite

Gibbsite, Al(OH)$_3$, is one of the mineral forms of aluminium hydroxide. It is often designated as γ-Al(OH)$_3$ (but sometimes as α-Al(OH)$_3$.[1]). It is also sometimes called hydrargillite (or hydrargyllite).

Gibbsite is an important ore of aluminium in that it is one of three main phases that make up the rock bauxite. Bauxite is often thought of as a mineral but it is really a rock composed of hydroxide and oxyhydroxide minerals such as gibbsite, boehmite (γ-AlO(OH)), and diaspore



Ball-and-stick model of the part of the crystal structure of gibbsite

(α-AlO(OH)), as well as clays, silt, and iron oxides and hydroxides.

Gibbsite has three named structural polymorphs or polytypes: **bayerite** (designated often as α-$Al(OH)_3$, but sometimes as β-$Al(OH)_3$), **doyleite**, and **nordstrandite**. Gibbsite and bayerite are monoclinic, whereas doyleite and nordstrandite are triclinic forms.

4.5.1 Structure

The structure of gibbsite is interesting and analogous to the basic structure of the micas. The basic structure forms stacked sheets of linked octahedrons of aluminium hydroxide. The octahedrons are composed of aluminium ions with a +3 charge bonded to six octahedrally coordinated hydroxides with a −1 charge. Each of the hydroxides is bonded to only two aluminium atoms because one third of the octahedrons are vacant a central aluminium. The result is a neutral sheet since +3/6 = +1/2 (+3 charge on the aluminiums divided by six hydroxide bonds times the number of aluminiums) and −1/2 = −1/2 (−1 charge on the hydroxides divided between only two aluminiums); thus the charges cancel. The lack of a charge on the gibbsite sheets means that there is no charge to retain ions between the sheets and act as a “glue” to keep the sheets together. The sheets are only held together by weak residual bonds and this results in a very soft easily cleaved mineral.

Gibbsite’s structure is closely related to the structure of brucite, $Mg(OH)_2$. However the lower charge in brucite’s magnesium (+2) as opposed to gibbsite’s aluminium (+3) does not require that one third of the octahedrons be vacant of a central ion in order to maintain a neutral sheet. The different symmetry of gibbsite and brucite is due to the different way that the layers are stacked.

It is the gibbsite layer that in a way forms the “floor plan” for the mineral corundum, Al_2O_3. The basic structure of corundum is identical to gibbsite except the hydroxides are replaced by oxygen. Since oxygen has a charge of −2 the layers are not neutral and require that they must be bonded to other aluminiums above and below the initial layer producing the framework structure that is the structure of corundum.

Gibbsite is interesting for another reason because it is often found as a part of the structure of other minerals. The neutral aluminium hydroxide sheets are found sandwiched between silicate sheets in important clay groups: the illite, kaolinite, and montmorillonite/smectite groups. The individual aluminium hydroxide layers are identical to the individual layers of gibbsite and are referred to as the *gibbsite layers*.[2]

4.5.2 Etymology

Gibbsite is named after George Gibbs (1776–1833), an American mineral collector.[3] G. Gibbs’ collection was acquired by Yale University early in the nineteenth century.[4]

4.5.3 References

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[2] GIBBSITE (Aluminum Hydroxide)

[3] Gibbsite Mineral Data

[4] Gibbsite: Gibbsite mineral information and data

4.5.4 Further reading

- Hurlbut, Cornelius S.; Klein, Cornelis, 1985, *Manual of Mineralogy*, 20th ed., ISBN 0-471-80580-7

4.5.5 External links

- Webmineral Gibbsite

4.6 Goethite

Goethite (FeO(OH)), (/ˈɡɜrtaɪt/ ***GUR**-tite*) named after the German polymath and poet Johann Wolfgang von Goethe (1749–1832), an iron bearing hydroxide mineral of the diaspore group, is found in soil and other low-temperature environments. Goethite has been well known since ancient times for its use as a pigment (ochre). Evidence has been found of its use in paint pigment samples taken from the caves of Lascaux in France. It was first described in 1806 for occurrences in the Hollertszug Mine, Dermbach, Herdorf, Siegerland, Rhineland-Palatinate, Germany.[3]

Unusual specimen of Goethite replacing a gypsum stalactite; the center is hollow. From Santa Eulalia, Chihuahua, Mexico.

In 2003, nanoparticulate authigenic goethite was shown to be the most common diagenetic iron oxyhydroxide in both marine and lake sediments.[5]

4.6.1 Composition

Goethite is an iron oxyhydroxide with ferric iron. It is the main component of rust and bog iron ore. Goethite's hardness ranges from 5.0 to 5.5 on the Mohs Scale, and its specific gravity varies from 3.3 to 4.3. The mineral forms prismatic needle-like crystals ("needle iron ore"), but is more typically massive.

Feroxyhyte and lepidocrocite are both polymorphs of the iron oxyhydroxide FeO(OH). Although they have the same chemical formula as goethite they each have different crystalline structures making them distinct minerals.

4.6.2 Usage

Its main modern use is as an iron ore, being referred to as *brown iron ore*. It does have some use as a clay earth pigment. Iron rich lateritic soils developed over serpentinite rocks in tropical climates are mined for their iron content as well as other metals.

Fine goethite specimens are rare and therefore are valued collectibles. Banded or iridescent varieties are cut and polished into cabochons for jewelry making.

4.6.3 Formation

Goethite often forms through the weathering of other iron-rich minerals, and thus is a common component of soils, concentrated in laterite soils. The formation of goethite is marked from the oxidation state change of Fe^{2+} to Fe^{3+}, which allows for goethite to exist at surface conditions. Because of this oxidation state change, goethite is commonly seen as a pseudomorph. As iron-bearing minerals are brought to the zone of oxidation within the soil, the iron turns from iron(II) to iron(III), however, the original shape of the parent mineral is maintained in this process. Examples of common goethite pseudomorphs are: goethites after pyrite, goethite, siderite, and marcasite, though any iron(II) bearing mineral could become a goethite pseudomorph if proper conditions are met. It may also be precipitated by groundwater or in other sedimentary conditions, or form as a primary mineral in hydrothermal deposits. Goethite has also been found to be produced by the excreation processes of certain bacteria types.

4.6.4 Prevalence

Goethite is found all over the planet, usually in the form of concretions, stalactitic formations, oolites (a form consisting of tiny round grains cemented together), reniform (kidney shapes) or botryoidal (globular, like bunches of grapes) accumulations. It is also a very common pseudomorph. It is frequently encountered in the swampy areas at the head of spring waters ('bog iron'), on cave floors, and on the bottom of lakes and small creeks. The *boxworks* or gossan resulting from the oxidation of sulfide ore deposits is formed of goethite along with other iron oxides and quartz.

Significant deposits of goethite are found in England, Australia, Cuba, and Michigan, Minnesota, Missouri, Colorado, Alabama, Georgia, Virginia, and Tennessee in the United States.

Deposits significant in location, if not in abundance, have been found in Gusev by NASA's Spirit rover, providing strong evidence for the presence of liquid water on the planet Mars in an earlier stage of its evolution.

4.6.5 Gallery

- Goethite from Minas Gerais, Brazil.
- Goethite coating/replacing rusted pyrite cubes.
- Goethite--Leadville mining district, Colorado

4.6.6 See also

- Ochre
- List of minerals

4.6.7 References

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[3] http://www.mindat.org/min-1719.html Mindat data with locations

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[5] van der Zee, C.; Roberts, D.; Rancourt, D. G.; Slomp, C. P. (2003). "Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments". *Geology* **31** (11): 993–996. Bibcode:2003Geo....31..993V. doi:10.1130/G19924.1.

4.6.8 External links

- Leonard James Spencer (1911). "Göthite". *Encyclopædia Britannica* (11th ed.).

Bog ore

Limonite deposited from mine runoff

Galena and Limonite

4.7 Limonite

Limonite is an iron ore consisting of a mixture of hydrated iron(III) oxide-hydroxides in varying composition. The generic formula is frequently written as $FeO(OH)\cdot nH_2O$, although this is not entirely accurate as the ratio of oxide to hydroxide can vary quite widely. Limonite is one of the two principal iron ores, the other being hematite, and has been mined for the production of iron since at least 2500 BCE.[4][5]

Limonite pseudomorphs after Garnet

4.7.1 Names

Limonite is named from the Greek word for meadow (λειμών), in allusion to its occurrence as **bog iron ore** in meadows and marshes. In its brown form it is sometimes called **brown hematite** or **brown iron ore**. In its bright yellow form it sometimes called **lemon rock** or **yellow iron ore**.

4.7.2 Characteristics

Limonite is relatively dense with a specific gravity varying from 2.7 to 4.3.[6] It varies in colour from a bright lemony yellow to a drab greyish brown. The streak of limonite on an unglazed porcelain plate is always brownish, a character which distinguishes it from hematite with a red streak, or from magnetite with a black streak. The hardness is variable, but generally in the 4 - 5.5 range.[6]

Although originally defined as a single mineral, limonite is now recognized as a mixture of related hydrated iron oxide minerals, among them goethite, akaganeite, lepidocrocite, and jarosite. Individual minerals in limonite may form crystals, but limonite does not, although specimens may show a fibrous or microcrystalline structure,[7] and limonite often occurs in concretionary forms or in compact and earthy masses; sometimes mammillary, botryoidal, reniform or stalactitic. Because of its amorphous nature, and occurrence in hydrated areas limonite often presents as a clay or mudstone. However there are limonite pseudomorphs after other minerals such as pyrite.[6] This means that chemical weathering transforms the crystals of pyrite into limonite by hydrating the molecules, but the external shape of the pyrite crystal remains. Limonite pseudomorphs have also been formed from other iron oxides, hematite and magnetite; from the carbonate siderite and from iron rich silicates such as almandine garnets.

4.7.3 Formation

Limonite usually forms from the hydration of hematite and magnetite, from the oxidation and hydration of iron rich sulfide minerals, and chemical weathering of other iron rich minerals such as olivine, pyroxene, amphibole, and biotite. It is often the major iron component in lateritic soils. It is often deposited in run-off streams from mining operations.

4.7.4 Uses of limonite

One of the first uses was as a pigment. The yellow form produced yellow ochre for which Cyprus was famous,[8] while the darker forms produced more earthy tones. Roasting the limonite changed it partially to hematite, producing red ochres, burnt umbers and siennas.[9]

Bog iron ore and limonite mudstones are mined as a source of iron, although commercial mining of them has ceased in the United States.

Iron caps or gossans of siliceous iron oxide typically form as the result of intensive oxidation of sulfide ore deposits.[10] These gossans were used by prospectors as guides to buried ore. In addition the oxidation of those sulfide deposits which contained gold, often resulted in the concentration of gold in the iron oxide and quartz of the gossans. Goldbearing limonite gossans were productively mined in the Shasta County, California mining district.[10] Similar deposits were mined near Rio Tinto in Spain and Mount Morgan in Australia. In the Dahlonega gold belt in Lumpkin County, Georgia gold was mined from limonite-rich lateritic or saprolite soil. The gold of the primary veins was concentrated into the limonites of the deeply weathered rocks. In another example the deeply weathered iron formations of Brazil served to concentrate gold with the limonite of the resulting soils.

4.7.5 History

Main article: History of ferrous metallurgy

While the first iron ore was likely Meteoric iron, and hematite was far easier to smelt, in Africa, where the first evidence of iron metallurgy occurs, limonite is the most prevalent iron ore. Before smelting, as the ore was heated and the water driven off, more and more of the limonite was converted to hematite. The ore was then pounded as it was heated above 1250°C,[11] at which temperature the metallic iron begins sticking together and non-metallic impurities are thrown off as sparks. Complex systems developed, notably in Tanzania, to process limonite.[12] Nonetheless, hematite and magnetite remained the ores of choice when smelting was by bloomeries, and it was only with the development of blast furnaces in 1st century BCE in China[13] and about 1150 CE in Europe,[14] that the brown iron ore of limonite could be used to best advantage.

Main article: Ochre § History

As regards to the use of limonite for pigments, it was one of the earliest man-used materials and can be seen in Neolithic cave paintings and pictographs.[15]

4.7.6 Notes

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[7] Boswell, P. F. and Blanchard, Roland (1929) "Cellular structure in limonite" *Economic Geology* 24(8): pp. 791–796

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[9] Heckel, George B. (1910) "Iron Oxide Paints" *Paint, oil and drug review* 50(4): pp. 14–21, page 14

[10] Brown, G. Chester (1915) *Mines and mineral resources of Shasta county, Siskiyou county, Trinity county* California State Mining Bureau, California State Printing Office, Sacramento, California, pages 15–16, OCLC 5458708

[11] Iron oxide becomes metallic iron at roughly 1250°C, almost 300 degrees below iron's melting point of 1538°C.

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4.7.7 See also

- Bog iron
- Iron ore
- Ore genesis

4.7.8 External links

- Mineral galleries
- Mindat
- Gold and limonite

4.8 Manganite

This article is about the mineral of formula MnO(OH), for other uses of the term manganite see Manganite (disambiguation)

Manganite is a mineral. Its composition is manganese oxide-hydroxide, MnO(OH), crystallizing in the monoclinic system (pseudo-orthorhombic).[1] Crystals of manganite are prismatic and deeply striated parallel to their length; they are often grouped together in bundles. The color is dark steel-grey to iron-black, and the luster brilliant and submetallic. The streak is dark reddish-brown. The hardness is 4, and the specific gravity is 4.3. There is a perfect cleavage parallel to the brachypinacoid, and less-perfect cleavage parallel to the prism faces. Twinned crystals are not infrequent.

The mineral contains 89.7% manganese sesquioxide; it dissolves in hydrochloric acid with evolution of chlorine.

4.8.1 Occurrence

Manganite crystal group

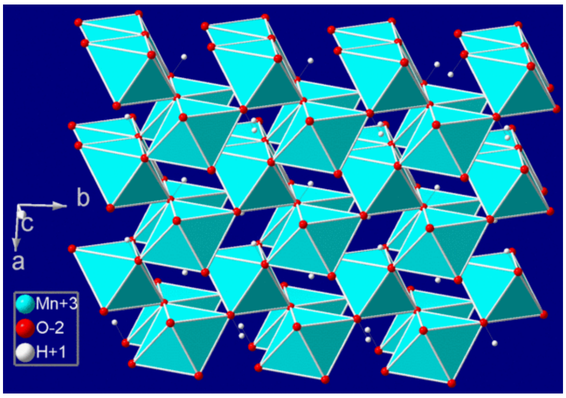
Manganite occurs with other manganese oxides in deposits formed by circulating meteoric water in the weathering environment in clay deposits and laterites. It forms by low temperature hydrothermal action in veins in association with calcite, barite, and siderite. Often associated with pyrolusite, braunite, hausmannite and goethite.[1][4]

Manganite occurs in specimens exhibiting good crystal form at Ilfeld in the Harz Mountains of Germany,[5] where the mineral occurs with calcite and barite in veins traversing porphyry. Crystals have also been found at Ilmenau in Thuringia, Neukirch near Sélestat in Alsace (newkirkite), Granam near Towie in Aberdeenshire, and in Upton Pyne near Exeter, UK and Negaunee, Michigan, United States, and in the Pilbarra of Western Australia. Good crystals have also been found at Atikokan, Ontario and Nova Scotia, Canada. As an ore of manganese it is much less abundant than pyrolusite or psilomelane.

Although described with various other names as early as 1772, the name *manganite* was first applied in a publication by W. Haidinger in 1827.[6]

4.8.2 See also

- Manganese oxide



Crystal structure of manganite

4.8.3 References

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[5] T. P. Moore, *Famous Mineral Localities: Ilfeld, Harz Mountains, Thuringia, Germany*, The Mineralogical Record, vol. 41, no. 6, 2010.

[6] Palache, Charles, Harry Berman and Clifford Frondel, *The System of Mineralogy* V.1, p. 646, Wiley, 7th ed., 1944

- This article incorporates text from a publication now in the public domain: Chisholm, Hugh, ed. (1911). *Encyclopædia Britannica* (11th ed.). Cambridge University Press.

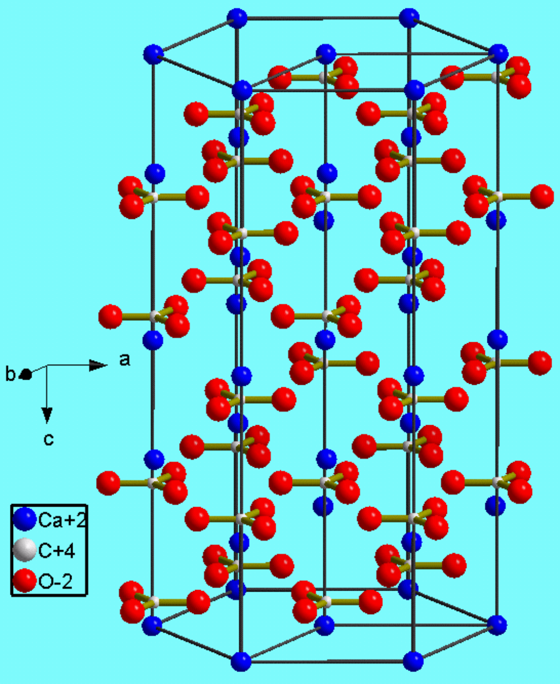
Chapter 5

Halides

Chapter 6

Carbonates

6.1 Calcite



Crystal structure of calcite

Calcite is a carbonate mineral and the most stable polymorph of calcium carbonate ($CaCO_3$). The other polymorphs are the minerals aragonite and vaterite. Aragonite will change to calcite at 380–470 °C,[5] and vaterite is even less stable.

6.1.1 Properties

Calcite crystals are trigonal-rhombohedral, though actual calcite rhombohedra are rare as natural crystals. However, they show a remarkable variety of habits including acute to obtuse rhombohedra, tabular forms, prisms, or various scalenohedra. Calcite exhibits several twinning types adding to the variety of observed forms. It may occur as fibrous, granular, lamellar, or compact. Cleavage is usually in three directions parallel to the rhombohedron form. Its fracture is conchoidal, but difficult to obtain.

It has a defining Mohs hardness of 3, a specific gravity of 2.71, and its luster is vitreous in crystallized varieties. Color is white or none, though shades of gray, red, orange, yellow, green, blue, violet, brown, or even black can occur when the mineral is charged with impurities.

Calcite is transparent to opaque and may occasionally show phosphorescence or fluorescence. A transparent variety called *Iceland spar* is used for optical purposes. Acute scalenohedral crystals are sometimes referred to as “dogtooth spar” while the rhombohedral form is sometimes referred to as “nailhead spar”.

Single calcite crystals display an optical property called birefringence (double refraction). This strong birefringence causes objects viewed through a clear piece of calcite to appear doubled. The birefringent effect (using calcite) was first described by the Danish scientist Rasmus Bartholin in 1669. At a wavelength of ~590 nm calcite has ordinary and extraordinary refractive indices of 1.658 and 1.486, respectively.[6] Between 190 and 1700 nm, the ordinary refractive index varies roughly between 1.9 and 1.5, while the extraordinary refractive index varies between 1.6 and 1.4.[7]

Calcite, like most carbonates, will dissolve with most forms of acid. Calcite can be either dissolved by groundwater or precipitated by groundwater, depending on several factors including the water temperature, pH, and dissolved ion concentrations. Although calcite is fairly insoluble in cold water, acidity can cause dissolution of calcite and release of carbon dioxide gas. Ambient carbon dioxide, due to its acidity, has a slight solubilizing effect on calcite. Calcite exhibits an unusual characteristic called retrograde solubility in which it becomes less soluble in water as the temperature increases. When conditions are right for precipitation, calcite forms mineral coatings that cement the existing rock grains together or it can fill fractures. When conditions are right for dissolution, the removal of calcite can dramatically increase the porosity and permeability of the rock, and if it continues for a long period of time may result in the formation of caves. On a landscape scale, continued dissolution of calcium carbonate-rich rocks can lead to the expansion and eventual collapse of cave systems, resulting in various forms of karst topography.

6.1.2 Use and applications

High-grade optical calcite was used in World War II for gun sights, specifically in bomb sights and anti-aircraft weaponry.[8] Also, experiments have been conducted to use calcite for a cloak of invisibility.[9] Microbiologically precipitated calcite has a wide range of applications, such as soil remediation, soil stabilization and concrete repair.

6.1.3 Natural occurrence

The largest documented single crystals of calcite originated from Iceland, measured 7×7×2 m and 6×6×3 m and weighed about 250 tons.[10][11]

Calcite is a common constituent of sedimentary rocks, limestone in particular, much of which is formed from the shells of dead marine organisms. Approximately 10% of sedimentary rock is limestone.

Calcite is the primary mineral in metamorphic marble. It also occurs as a vein mineral in deposits from hot springs, and it occurs in caverns as stalactites and stalagmites.

Lublinite is a fibrous, efflorescent form of calcite.[12]

Calcite may also be found in volcanic or mantle-derived rocks such as carbonatites, kimberlites, or rarely in peridotites.

Calcite is often the primary constituent of the shells of marine organisms, e.g., plankton (such as coccoliths and planktic foraminifera), the hard parts of red algae, some sponges, brachiopods, echinoderms, some serpulids, most bryozoa, and parts of the shells of some bivalves (such as oysters and rudists). Calcite is found in spectacular form in the Snowy River Cave of New Mexico as mentioned above, where microorganisms are credited with natural formations. Trilobites, which became extinct a quarter billion years ago, had unique compound eyes that used clear calcite crystals to form the lenses.[13]

6.1.4 Formation processes

Calcite forms from a poorly ordered precursor (amorphous calcium carbonate, ACC).[14] The crystallization process occurs in two stages; firstly, the ACC nanoparticles rapidly dehydrate and crystallize to form individual particles of vaterite; secondly, the vaterite transforms to calcite via a dissolution and reprecipitation mechanism with the reaction rate controlled by the surface area of calcite.[15] The second stage of the reaction is approximately 10 times slower than the first. However, the crystallization of calcite has been observed to be dependent on the starting pH and presence of Mg in solution.[16] A neutral starting pH during mixing promotes the direct transformation of ACC into calcite. Conversely, when ACC forms in a solution that starts with a basic initial pH, the transformation to calcite occurs via metastable vaterite, which forms via a spherulitic growth mechanism.[17] In a second stage this vaterite transforms to calcite via a surface-controlled dissolution and recrystallization mechanism. Mg has a noteworthy effect on both the stability of ACC and its transformation to crystalline $CaCO_3$, resulting in the formation of calcite directly from ACC, as this ion unstabilizes the structure of vaterite.

6.1.5 In Earth history

Calcite seas existed in Earth history when the primary inorganic precipitate of calcium carbonate in marine waters was low-magnesium calcite (lmc), as opposed to the aragonite and high-magnesium calcite (hmc) precipitated today. Calcite seas alternated with aragonite seas over the Phanerozoic, being most prominent in the Ordovician and Jurassic. Lineages evolved to use whichever morph of calcium carbonate was favourable in the ocean at the time they became mineralised, and retained this mineralogy for the remainder of their evolutionary history.[18] Petrographic evidence for these calcite sea conditions consists of calcitic ooids, lmc cements, hardgrounds, and rapid early seafloor aragonite dissolution.[19] The evolution of marine organisms with calcium carbonate shells may have been affected by the calcite and aragonite sea cycle.[20]

6.1.6 Gallery

- Doubly terminated calcite crystal.
- Trilobite eyes employed calcite.
- Calcite crystals inside a test of the cystoid *Echinosphaerites aurantium* (Middle Ordovician, northeastern Estonia).
- Calcite rhomb from Iceberg claim, Dixon, New Mexico showing double refraction.
- Mississippian marble (made of calcite) in Big Cottonwood Canyon, Wasatch Mountains, Utah.
- Thin section view of calcite crystals inside a recrystallized bivalve shell in a biopelsparite.
- Calcite containing niobium (giving it distinctive bluish color), from Medford Quarry, Maryland.
- Nailhead spar calcite.
- Reddish rhombohedral calcite crystals from China. Its red color is due to the presence of iron.
- Calcite fluoresces pink under long wave ultraviolet light.
- Calcite fluoresces blue under short wave ultraviolet light.

6.1.7 See also

- Iceland Spar
- Ikaite, $CaCO_3 \cdot 6H_2O$
- List of minerals
- Lysocline
- Manganoan Calcite, $(Ca,Mn)CO_3$
- Monohydrocalcite, $CaCO_3 \cdot H_2O$
- Ocean acidification
- Ulexite aka “TV rock”, another mineral with an optical property often illustrated in the same way.
- Yule Marble

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6.1.9 Further reading

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6.1.10 External links

- Calcite information and images

Chapter 7

Phosphates

7.1 Hureaulite

Hureaulite is a manganese phosphate with the formula $Mn^{2+}{}_5(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$. It was discovered in 1825 and named in 1826 for the type locality, Les Hureaux, Saint-Sylvestre, Haute-Vienne, Limousin, France. It is sometimes written as huréaulite, but the IMA does not recommend this for English language text.[6]

A complete series exists from lithiophilite, $LiMn^{2+}PO_4$ to triphylite, $LiFe^{2+}PO_4$, including hureaulite, strengite, $FePO_4 \cdot 2H_2O$, stewartite, $Mn^{2+}Fe^{3+}{}_2(OH,PO_4)_2 \cdot 8H_2O$, and sicklerite, $(LiMn^{2+},Fe^{3+})PO_4$.[7]

7.1.1 Environment

Hureaulite is a secondary mineral occurring in granite pegmatites.[5] At the type locality it occurs in a zone of altered triphylite, $LiMn^{2+}PO_4$, in pegmatite. Typically occurs very late in the sequence of formation of secondary phosphate minerals.[8] Associated at the type locality with vivianite, $Fe^{2+}{}_3(PO_4)_2 \cdot 8H_2O$; rockbridgeite, $Fe^{2+}Fe^{3+}{}_4(PO_4)_3(OH)_5$; heterosite, $(Fe^{3+},Mn^{3+})PO_4$ and cacoxenite, $Fe^{3+}{}_{24}AlO_6(PO_4)_{17}(OH)_{12} \cdot 17H_2O$. It can be synthesised;[9] most natural hureaulites are Mn-rich compounds but extensive (Mn,Fe) solution is known for synthetic material.[8]

7.1.2 Localities

The type locality is Les Hureaux, Saint-Sylvestre, Haute-Vienne, Limousin, France. Hureaulite is also found in a granite pegmatite known for its phosphates in the Aimorés pegmatite district, at the Cigana claim in Galiléia, Doce valley, Minas Gerais, Brazil, formerly known as the Jocão Mine.[3]

7.1.3 References

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7.2 Pseudomalachite

Pseudomalachite is a phosphate of copper with hydroxyl, named from the Greek for "false" and "malachite", because of its similarity in appearance to the carbonate mineral malachite, $Cu_2(CO_3)(OH)_2$. Both are green coloured secondary minerals found in oxidised zones of copper deposits, often associated with each other. Pseudomalachite is polymorphous with reichenbachite and ludjibaite. It was discovered in 1813. Prior to 1950 it was thought that dihydrite, lunnite, ehlite, tagilite and prasin were separate mineral species, but Berry analysed specimens labelled with these names from several museums, and found that they were in fact pseudomalachite. The old names are no longer recognised by the IMA.[5]

7.2.1 Type Locality

The type locality is the Virneberg Mine, Rheinbreitbach, Westerwald, Rhineland-Palatinate, Germany. This is an area of ancient copper mining dating back to Roman times, and worked intermittently up until 1872.[1] The type material is held at the Mining Academy, Freiberg, Germany.[3]

7.2.2 Structure

The copper ions are co-ordinated by six oxygen ions to form distorted octahedra.[6] These octahedra are linked by sharing edges to form two distinct types of infinite chains, parallel to b. The chains are linked alternately, again by sharing octahedral edges, to form sheets parallel to the bc plane. Distorted phosphate tetrahedra link the sheets, and there is some doubt about the exact position of the hydrogen ions in the structure.[7]

7.2.3 Environment

It is a secondary mineral found in the oxidised zones of copper ore deposits. Associated with libethenite at several localities in New South Wales, Australia,[8] and at the Chino Mine, New Mexico, USA.[9] Other associated minerals are apatite, azurite, chalcedony, chrysocolla, cornetite, cuprite, malachite, pyromorphite, tenorite, and iron oxyhydroxides.

7.2.4 Distribution

Pseudomalachite has been reported from Argentina, Australia, Austria, Belgium, Brazil, Canada, Chile, Czech Republic, Democratic Republic of Congo, France, Germany, Ireland, Israel, Italy, Japan, Kazakhstan, Madagascar, Mexico, Namibia, Norway, Poland, Portugal, Republic of Congo, Romania, Russia, Slovakia, South Africa, Spain, UK, USA and Zambia.

7.2.5 References

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[9] Rocks & Minerals (2009) 84:6 page 498

7.3 Woodhouseite

Woodhouseite belongs to the beudantite group $AB_3(XO_4)(SO_4)(OH)_6$ where A = Ba, Ca, Pb or Sr, B = Al or Fe and X = S, As or P. Minerals in this group are isostructural with each other and also with minerals in the crandallite and alunite groups. They crystallise in the rhombohedral system with space group R3m and crystals are usually either tabular {0001} or pseudo-cubic to pseudo-cuboctahedral. Woodhouseite was named after Professor Charles Douglas Woodhouse[4] (1888–1975), an American mineralogist and mineral collector from the University of California, Santa Barbara, USA, and one-time General Manager of Champion Sillimanite, Inc.

7.3.1 Environment

Woodhouseite is a secondary mineral found where wall rock alteration occurred in hydrothermal and disseminated ore deposits; rare in cave deposits, formed from guano. At the type locality it occurs in vugs in quartz veins in an andalusite, Al_2OSiO_4, deposit. This is in pre-Cambrian meta-quartzite that has been intruded by late Jurassic granitic rocks. Woodhouseite is found only near masses of lazulite, $MgAl_2(PO_4)_2(OH)_2$. Associated Minerals at the type locality include topaz, $Al_2SiO_4F_2$, quartz, SiO_2, augelite, $Al_2PO_4(OH)_3$, lazulite, $MgAl_2(PO_4)_2(OH)_2$, tourmaline, baryte, $BaSO_4$, muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$, and pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, all of which formed before the woodhouseite, which is a late-forming mineral.[5]

7.3.2 Localities

The type locality is the Champion Mine (White Mountain Mine), White Mountain, Laws, White Mountains, Mono County, California, USA. This is a former sillimanite mine located near Laws; mineralisation is a metamorphic sillimanite deposit hosted in quartzite.

7.3.3 Structure

Space Group: R3 2/m
Unit Cell Parameters: a = 6.993 Å, c = 16.386 Å, Z: 3

7.3.4 References

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Chapter 8

Sulfates

Chapter 9

Silicates

9.1 Ashburtonite

Ashburtonite is a rare lead copper silicate-bicarbonate mineral with formula: $HPb_4Cu^{2+}{}_4Si_4O_{12}(HCO_3)_4(OH)_4Cl$.[4]

9.1.1 Geological occurrence

Ashburtonite was first described as a secondary mineral in a shear zone in a series of shales and graywackes. It is an alteration product of galena and chalcopyrite.[3] The secondary minerals within the shear consist of carbonates, arsenates, and sulfates of lead and copper, and to a much lesser extent of zinc and iron.[4] Ashburtonite is associated with beudantite, brochantite, caledonite, cerussite, diaboleite, duftite, malachite, plattnerite, adamite, antlerite, bayldonite, bindheimite, carminite, chenevixite, chlorargyrite, chrysocolla, cinnabar, hemimorphite, hydrozincite, jarosite, lavendulan, linarite, mimetite, olivenite, paratacamite, and rosasite.

Ashburtonite was first described in 1991 for an occurrence in the Anticline prospects 11 km southwest of Ashburton Downs in the Capricorn Range of Western Australia.[3] It has also been reported from the Tonopah–Belmont Mine in the Big Horn Mountains of Maricopa County, Arizona.[2]

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9.2 Bustamite

Bustamite is a calcium manganese inosilicate (chain silicate) and a member of the wollastonite group. Magnesium, zinc and iron are common impurities substituting for manganese. It is a polymorph of johannsenite, with bustamite as the high-temperature form of $CaMnSi_2O_6$ and johannsenite as the low temperature form. The inversion takes place at 830 °C, but may be very slow.[2] Bustamite could be confused with light-colored rhodonite or pyroxmangite, but both these minerals are biaxial (+) whereas bustamite is biaxial (-).

9.2.1 Cell parameters

There is considerable variety in the literature about the size and type of the unit cell, the formula to be used, and the value of Z, the number of formula units per unit cell.

Bustamite is a triclinic mineral, which could be described by a primitive unit cell, but the larger A-centered cell is often preferred, in order to facilitate comparison with the similar mineral wollastonite.[7]

The formula for bustamite is $CaMn(SiO_3)_2$[1] but it is sometimes written $(Ca,Mn)SiO_3$, and changing the formula in this way will change the value of Z. The structure is chains of SiO_4 tetraheda with repeat unit of three tetrahedra, unlike the pyroxenes where the repeat unit is two.[8] Ca^{++} and Mn^{++} are positioned between the chains. There are 12 tetrahedra in the A-centered unit cell.[7]

The unit cell, the formula and Z cannot be taken separately; they are interlinked and form a consistent set of values. In this article we adopt the A-centred unit cell (space group A1) with a = 7.736 Å, b = 7.157 Å and c = 13.824 Å, the formula $CaMn(SO_3)_2$ and Z = 6. Deer et al.[2] take the formula as $(Mn,Ca,Fe)[SiO_3]$ so their value of Z is doubled to 12. Mindat[5] apparently gives the lattice parameters for a face-centred cell,[7] although they give the space group as P1.

9.2.2 Type locality

The type locality was originally taken as Tetela de Jonotla, Puebla, Mexico, and the mineral was named for General Anastasio Bustamante (1780–1853), three times President of Mexico. The material from Puebla, however, was later found to be a mixture of johannsenite and rhodonite,[8] so the type locality is now the Franklin Mine, Franklin, Sussex County, New Jersey, USA.[5]

Both bustamite and johansennite are found at Franklin.[3] Bustamite is moderately common there and occurs in a variety of assemblages, associated with rhodonite and tephroite, calcite and tephroite or glaucochroite and tephroite. Vesuvianite, wollastonite, garnet, diopside, willemite, johannsenite, margarosanite and clinohedrite also may be present.

9.2.3 Environment

Bustamite typically results from metamorphism of manganese-bearing sediments, with attendant metasomatism. At the (new) type locality, Franklin, the oldest rocks are Precambrian gneisses of mixed sedimentary and volcanic origin. Franklin Marble was deposited within these rocks, along with sediments containing zinc, manganese and iron minerals. These sediments were metamorphosed later in the Precambrian, then the rocks were uplifted from the late Precambrian into the Cambrian and quartzite was deposited on the eroded surface. In Cambrian-Ordovician time the quartzite was in turn overlain by limestone, and the rocks have been subject to uplift and erosion up to the present time.[9]

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9.2.5 External links

9.3 Hsianghualite

Hsianghualite is a tectosilicate (framework silicate) of lithium, calcium and beryllium, with fluorine, a member of the zeolite group. It was discovered in 1958 and named for the type locality, Hsiang Hua, □□, meaning fragrant flower.

9.3.1 Structure

Structure is analogous to that of analcime with Be and Si in tetrahedral co-ordination forming a three-dimensional framework.[2] Its space group is $I2_13$[2] (Previously reported as $I4_132$[1]). Unit cell parameters are a = 12.879 or 12.897,[1][4] and Z = 8.

9.3.2 Environment

It occurs within phlogopite veins in the light-coloured band of green and white banded metamorphosed Devonian limestone which has been intruded by beryllium-bearing granite.[5] Associated mineral include fluorite, liberite, chrysoberyl, taaffeite and nigerite.[2]

9.3.3 Localities

Hsianghualite has been found only at the type locality, the Xianghualing Mine in Linwu County, Hunan Province, China.

9.3.4 References

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[5] Roberts, Campbell and Rapp (1990) Encyclopedia of Minerals, 2nd edition

9.3.5 External links

- Mindat
- Webmineral data

9.4 Quartz

This article is about the mineral. For other uses, see Quartz (disambiguation).

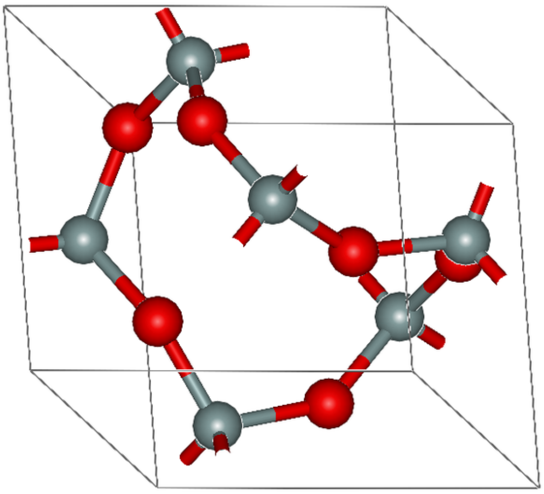
Quartz is the second most abundant mineral in the Earth's continental crust, after feldspar. It is made up of a continuous framework of SiO_4 silicon–oxygen tetrahedra, with each oxygen being shared between two tetrahedra, giving an overall formula SiO_2.

There are many different varieties of quartz, several of which are semi-precious gemstones. Especially in Europe and the Middle East, varieties of quartz have been since antiquity the most commonly used minerals in the making of jewelry and hardstone carvings.

9.4.1 Etymology

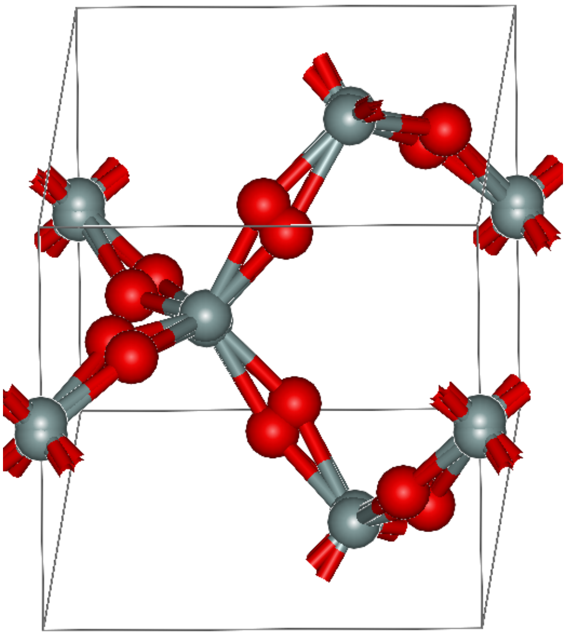
The word “quartz” is derived from the German word “Quarz” and its Middle High German ancestor “twarc”, which probably originated in Slavic (cf. Czech *tvrdý* (“hard”), Polish *twardy* (“hard”)).[6]

9.4.2 Crystal habit and structure



Crystal structure of α-quartz

Quartz belongs to the trigonal crystal system. The ideal crystal shape is a six-sided prism terminating with six-sided pyramids at each end. In nature quartz crystals are often twinned, distorted, or so intergrown with adjacent crystals of quartz or other minerals as to only show part of this shape, or to lack obvious crystal faces altogether and appear massive. Well-formed crystals typically form in a 'bed' that has unconstrained growth into a void; usually the crystals are attached at the other end to a matrix and only one termination pyramid is present. However doubly-terminated crystals do occur where they develop freely without attachment, for instance within gypsum. A quartz geode is such a situation where the void is approximately spherical in shape, lined with a bed of crystals pointing inward.



β-quartz

α-quartz crystallizes in the trigonal crystal system, space group $P3_121$ and $P3_221$ respectively. β-quartz belongs to the hexagonal system, space group $P6_222$ and $P6_422$, respectively.[7] These spacegroups are truly chiral (they each belong to the 11 enantiomorphous pairs). Both α-quartz and β-quartz are examples of chiral crystal structures composed of achiral building blocks (SiO_4 tetrahedra in the present case). The transformation between α- and β-quartz only involves a comparatively minor rotation of the tetrahedra with respect to one another, without change in the way they are linked.

9.4.3 Varieties (according to color)

Pure quartz, traditionally called **rock crystal** (sometimes called **clear quartz**), is colorless and transparent (clear) or translucent, and has often been used for hardstone carvings, such as the Lothair Crystal. Common colored varieties include citrine, rose quartz, amethyst, smoky quartz, milky quartz, and others. Quartz goes by an array of different names. The most important distinction between types of quartz is that of *macrocrystalline* (individual crystals visible to the unaided eye) and the microcrystalline or cryptocrystalline varieties (aggregates of crystals visible only under high magnification). The cryptocrystalline varieties are either translucent or mostly opaque, while the transparent varieties tend to be macrocrystalline. Chalcedony is a cryptocrystalline form of silica consisting of fine intergrowths of both quartz, and its

Figurine of a child carved in rock crystal, hittite, between 1500 and 1200 BC

monoclinic polymorph moganite.[8] Other opaque gemstone varieties of quartz, or mixed rocks including quartz, often including contrasting bands or patterns of color, are agate, sard, onyx, carnelian, heliotrope, and jasper.

Citrine

Citrine

"Citrine" redirects here. For other uses, see Citrine (disambiguation).

Citrine is a variety of quartz whose color ranges from a pale yellow to brown due to ferric impurities. Natural citrines are rare; most commercial citrines are heat-treated amethysts or smoky quartzes. However, a heat-treated amethyst will have small lines in the crystal, as opposed to a natural citrine's cloudy or smokey appearance. It is nearly impossible to tell cut citrine from yellow topaz visually, but they differ in hardness.Brazil is the leading producer of citrine, with much of its production coming from the state of Rio Grande do Sul. The name is derived from Latin citrina which means "yellow" and is also the origin of the word "citron." Sometimes citrine and amethyst can be found together in the same crystal, which is then referred to as ametrine.[9]

Rose quartz

An elephant carved in rose quartz, 10 cm (4 inches) long

Rose quartz is a type of quartz which exhibits a pale pink to rose red hue. The color is usually considered as due to trace amounts of titanium, iron, or manganese, in the massive material. Some rose quartz contains microscopic rutile needles which produces an asterism in transmitted light. Recent X-ray diffraction studies suggest that the color is due to thin microscopic fibers of possibly dumortierite within the massive quartz.[10]

Additionally, there is a rare type of pink quartz (also frequently called crystalline rose quartz) with color that is thought to be caused by trace amounts of phosphate or aluminium. The color in crystals is apparently photosensitive and subject to fading. The first crystals were found in a pegmatite found near Rumford, Maine, USA, but most crystals on the market come from Minas Gerais, Brazil.[11]

Rose quartz is not popular as a gem – it is generally too clouded by impurities to be suitable for that purpose. Rose quartz is more often carved into figures such as people or hearts. Hearts are commonly found because rose quartz is pink and an affordable mineral.

Amethyst

Amethyst Guerrero, Mexico

Main article: Amethyst

Amethyst is a popular form of quartz that ranges from a bright to dark or dull purple color. The world's largest deposits of amethysts can be found in Brazil, Mexico, Uruguay, Russia, France, Namibia and Morocco. Sometimes amethyst and citrine are found growing in the same crystal. It is then referred to as ametrine. An amethyst is formed when there is iron in the area where it was formed.

Smoky quartz

Main article: Smoky quartz

Smoky quartz is a gray, translucent version of quartz. It ranges in clarity from almost complete transparency to a brownish-gray crystal that is almost opaque. Some can also be black.

Smoky quartz.

Milky quartz

Milk quartz or **milky quartz** may be the most common variety of crystalline quartz and can be found almost anywhere. The white color may be caused by minute fluid inclusions of gas, liquid, or both, trapped during the crystal formation. The cloudiness caused by the inclusions effectively bars its use in most optical and quality gemstone applications.[12]

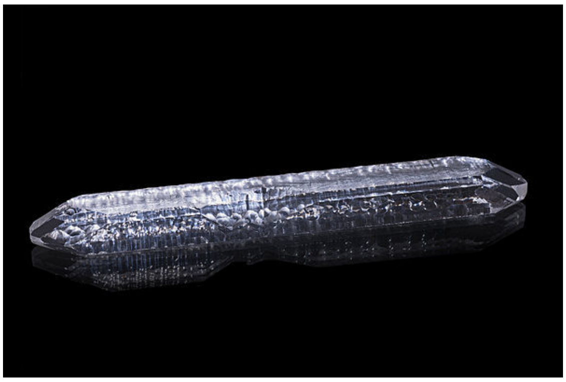
Milky quartz sample

Ancient Roman cameo onyx engraved gem of Augustus

9.4.4 Varieties (according to microstructure)

Although many of the varietal names historically arose from the color of the mineral, current scientific naming schemes refer primarily to the microstructure of the mineral. Color is a secondary identifier for the cryptocrystalline minerals, although it is a primary identifier for the macrocrystalline varieties. This does not always hold true.

9.4.5 Synthetic and artificial treatments



A synthetic quartz crystal grown by the hydrothermal method, about 19 cm long and weighing about 127 grams

Not all varieties of quartz are naturally occurring. Prasiolite, an olive colored material, is produced by heat treatment; natural prasiolite has also been observed in Lower Silesia in Poland. Although citrine occurs naturally, the majority is the result of heat-treated amethyst. Carnelian is widely heat-treated to deepen its color.

Because natural quartz is often twinned, synthetic quartz is produced for use in industry. Large, flawless, single crystals are synthesized in an autoclave via the hydrothermal process; emeralds are also synthesized in this fashion.

9.4.6 Occurrence

Quartz is an essential constituent of granite and other felsic igneous rocks. It is very common in sedimentary rocks such as sandstone and shale and is also present in variable amounts as an accessory mineral in most carbonate rocks. It is also a common constituent of schist, gneiss, quartzite and other metamorphic rocks. Because of its resistance to weathering it is very common in stream sediments and in residual soils. Quartz, therefore, occupies the lowest potential to weather in the Goldich dissolution series.

While the majority of quartz crystallizes from molten magma, much quartz also chemically precipitates from hot hydrothermal veins as gangue, sometimes with ore minerals like gold, silver and copper. Large crystals of quartz are found in magmatic pegmatites. Well-formed crystals may reach several meters in length and weigh hundreds of kilograms.

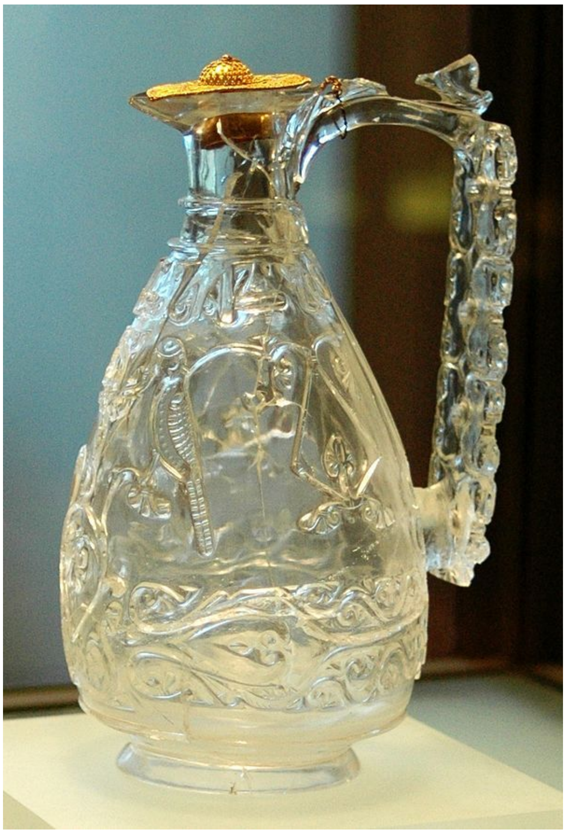
Naturally occurring quartz crystals of extremely high purity, necessary for the crucibles and other equipment used for growing silicon wafers in the semiconductor industry, are expensive and rare. A major mining location for high purity quartz is the Spruce Pine Gem Mine in Spruce Pine, North Carolina, United States.[13]

The largest documented single crystal of quartz was found near Itapore, Goiaz, Brazil; it measured approximately 6.1×1.5×1.5 m and weighed more than 44 tonnes.[14]

9.4.7 Related silica minerals

Tridymite and cristobalite are high-temperature polymorphs of SiO_2 that occur in high-silica volcanic rocks. Coesite is a denser polymorph of quartz found in some meteorite impact sites and in metamorphic rocks formed at pressures greater than those typical of the Earth's crust. Stishovite is a yet denser and higher-pressure polymorph of quartz found in some meteorite impact sites. Lechatelierite is an amorphous silica glass SiO_2 which is formed by lightning strikes in quartz sand.

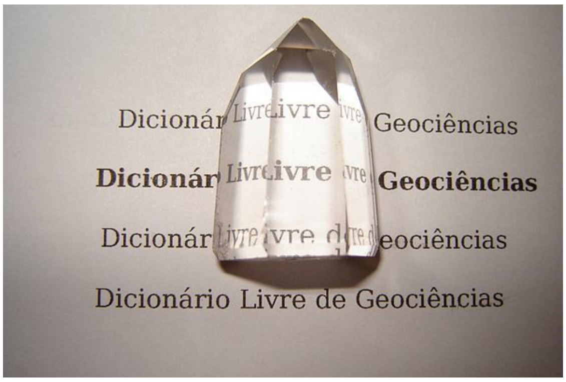
9.4.8 History



Fatimid carved rock crystal (clear quartz) vase, c. 1000

The word "quartz" comes from the German 🔊 *Quarz* ,[15] which is of Slavic origin (Czech miners called it *křemen*). Other sources attribute the word's origin to the Saxon word *Querkluftertz*, meaning *cross-vein ore*.[16]

Quartz is the most common material identified as the mystical substance maban in Australian Aboriginal mythology. It is found regularly in passage tomb cemeteries in Europe in a burial context, such as Newgrange or Carrowmore in Ireland. The Irish word for quartz is



Quartz crystal demonstrating transparency

grian cloch, which means 'stone of the sun'. Quartz was also used in Prehistoric Ireland, as well as many other countries, for stone tools; both vein quartz and rock crystal were knapped as part of the lithic technology of the prehistoric peoples.[17]

While jade has been since earliest times the most prized semi-precious stone for carving in East Asia and Pre-Columbian America, in Europe and the Middle East the different varieties of quartz were the most commonly used for the various types of jewelry and hardstone carving, including engraved gems and cameo gems, rock crystal vases, and extravagant vessels. The tradition continued to produce objects that were very highly valued until the mid-19th century, when it largely fell from fashion except in jewelry. Cameo technique exploits the bands of color in onyx and other varieties.

Roman naturalist Pliny the Elder believed quartz to be water ice, permanently frozen after great lengths of time.[18] (The word “crystal” comes from the Greek word $\kappa\varrho\acute{\upsilon}\sigma\tau\alpha\lambda\lambda o\varsigma$, “ice”.) He supported this idea by saying that quartz is found near glaciers in the Alps, but not on volcanic mountains, and that large quartz crystals were fashioned into spheres to cool the hands. He also knew of the ability of quartz to split light into a spectrum. This idea persisted until at least the 17th century.

In the 17th century, Nicolas Steno's study of quartz paved the way for modern crystallography. He discovered that regardless of a quartz crystal’s size or shape, its long prism faces always joined at a perfect 60° angle.[19]

Quartz’s piezoelectric properties were discovered by Jacques and Pierre Curie in 1880.[20] The quartz oscillator or resonator was first developed by Walter Guyton Cady in 1921.[21][22] George Washington Pierce designed and patented quartz crystal oscillators in 1923.[23][24] Warren Marrison created the first quartz oscillator clock based on the work of Cady and Pierce in 1927.[25]

Efforts to synthesize quartz began in the mid nineteenth century as scientists attempted to create minerals under laboratory conditions that mimicked the conditions in which the minerals formed in nature: German geologist Karl Emil von Schafhäutl (1803-1890)[26] was the first person to synthesize quartz when in 1845 he created microscopic quartz crystals in a pressure cooker.[27] However, the quality and size of the crystals that were produced by these early efforts were poor.[28] By the 1930s, the electronics industry had become dependent on quartz crystals. The only source of suitable crystals was Brazil; however, World War II disrupted the supplies from Brazil, so nations attempted to synthesize quartz on a commercial scale. German mineralogist Richard Nacken (1884-1971) achieved some success during the 1930s and 1940s.[29] After the war, many laboratories attempted to grow large quartz crystals. In the United States, the U.S. Army Signal Corps contracted with Bell Laboratories and with the Brush Development Company of Cleveland, Ohio to synthesize crystals following Nacken’s lead.[30][31] (Prior to World War II, Brush Development produced piezoelectric crystals for record players.) By 1948, Brush Development had grown crystals that were 1.5 inches (3.8 cm) in diameter, the largest to date.[32][33] By the 1950s, hydrothermal synthesis techniques were producing synthetic quartz crystals on an industrial scale, and today virtually all the quartz crystal used in the modern electronic industry is synthetic.

9.4.9 Piezoelectricity

Quartz crystals have piezoelectric properties; they develop an electric potential upon the application of mechanical stress. An early use of this property of quartz crystals was in phonograph pickups. One of the most common piezoelectric uses of quartz today is as a crystal oscillator. The quartz clock is a familiar device using the mineral. The resonant frequency of a quartz crystal oscillator is changed by mechanically loading it, and this principle is used for very accurate measurements of very small mass changes in the quartz crystal microbalance and in thin-film thickness monitors.

9.4.10 Gallery of quartz mineral specimens

- Quartz scepters
- Locality: Slovakia. Size: 3×2.1×0.7 cm.
- A very unusual scepter: translucent, pastel-amethystine quartz atop a terminated shaft of translucent, green, hedenbergite-included quartz. Locality: Mega Horio, Serifos, Cyclades, Greece. Size: 15.3×3.8×3.7 cm.
- An unusual scepter, from Pennoyer Amethyst Mine, Red Feather Lakes, Colorado, USA. Size: 4.5×2.3×1.9 cm.
- Amethystine quartz

- Slice of amethyst from an unusual stalactite, Jalgaon district, Maharashtra, India. Size: 8.2×7.5×0.3 cm.
- Slice through a star-shaped stalactite from Artigas, Uruguay. Size: 7.1×6.6×0.5 cm.
- An unusual tabular amethyst crystal, from Brandberg District, Erongo Region, Namibia. Detail, overall size: 5.7×1.8×1.6 cm.

- Citrines
- Citrine, Boekenhoutshoek area, Mpumalanga Province, South Africa. Size Size: 9.1×4.8×4.2 cm.
- Cluster of citrine crystals from a geode
- “Citrine” made by heating amethyst

9.4.11 See also

- Fused quartz
- List of minerals
- Shocked quartz
- Quartz reef mining

9.4.12 References

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[18] Pliny the Elder, *The Natural History*, Book 37, Chapter 9. Available on-line at: Perseus.Tufts.edu.

[19] Nicolaus Steno (Latinized name of Niels Steensen) with John Garrett Winter, trans., *The Prodromus of Nicolaus Steno’s Dissertation Concerning a Solid Body Enclosed by Process of Nature Within a Solid* (New York, New York: Macmillan Co., 1916). On page 272, Steno states his law of constancy of interfacial angles: “Figures 5 and 6 belong to the class of those which I could present in countless numbers to prove that in the plane of the axis both the number and the length of the sides are changed in various ways without changing the angles; … "

[20] See:

- Jacques and Pierre Curie (1880) “Développement par compression de l’électricité polaire dans les cristaux hémièdres à faces inclinées” (Development, via compression, of electric polarization in hemihedral crystals with inclined faces), *Bulletin de la Société minérologique de France*, vol. 3, pages 90 - 93.
- Reprinted in: Jacques and Pierre Curie (1880) Développement, par pression, de l’électricité polaire dans les cristaux hémièdres à faces inclinées,” *Comptes rendus ...* , vol. 91, pages 294 - 295.
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[24] "The Quartz Watch – George Washington Pierce". *The Lemelson Center, National Museum of American History*. Smithsonian Institution.

[25] "The Quartz Watch – Warren Marrison". *The Lemelson Center, National Museum of American History*. Smithsonian Institution.

[26] For biographical information about Karl von Schafhäutl, see German Wikipedia's article: Karl Emil von Schafhäutl (in German).

[27] von Schafhäutl, Karl Emil (10 April 1845). "Die neuesten geologischen Hypothesen und ihr Verhältniß zur Naturwissenschaft überhaupt (Fortsetzung)" [The latest geological hypotheses and their relation to science in general (continuation)]. *Gelehrte Anzeigen* (München: im Verlage der königlichen Akademie der Wissenschaften, in Commission der Franz'schen Buchhandlung) **20** (72): 577–584. OCLC 1478717. From page 578: 5) *Bildeten sich aus Wasser, in welchen ich im Papinianischen Topfe frisch gefällte Kieselsäure aufgelöst hatte, beym Verdampfen schon nach 8 Tagen Krystalle, die zwar mikroscopisch, aber sehr wohl erkenntlich aus sechseitigen Prismen mit derselben gewöhnlichen Pyramide bestanden.* (5) There formed from water in which I had dissolved freshly precipitated silicic acid in a Papin pot [i.e., pressure cooker], after just 8 days of evaporating, crystals, which albeit were microscopic but consisted of very easily recognizable six-sided prisms with their usual pyramids.)

[28] K. Byrappa and Masahiro Yoshimura, *Handbook of Hydrothermal Technology* (Norwich, New York: Noyes Publications, 2001), Chapter 2: History of Hydrothermal Technology.

[29] Nacken, R. (1950) "Hydrothermal Synthese als Grundlage für Züchtung von Quarz-Kristallen" (Hydrothermal synthesis as a basis for the production of quartz crystals), *Chemiker Zeitung*, **74** : 745–749.

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[31] Michael Lombardi (October 2011) "The evolution of time measurement, part 2: Quartz clocks," *IEEE Instrumentation & Measurement Magazine*, **14** (5) : 41-48; see page 45. Available on-line at: NIST.gov.

[32] "Record crystal," *Popular Science*, **154** (2) : 148 (February 1949).

[33] Brush Development's team of scientists included: Danforth R. Hale, Andrew R. Sobek, and Charles Baldwin Sawyer (1895-1964). The company's U.S. patents included:

  - Andrew R. Sobek, "Apparatus for growing sigle crystals of quartz," U.S. Patent no. 2674520 (filed: April 11, 1950 ; issued: April 6, 1954).
  - Andrew R. Sobek and Danforth R. Hale, "Method and apparatus for growing single crystals of quartz," U.S. Patent no. 2,675,303 (filed: April 11, 1950 ; issued: April 13, 1954).
  - Charles B. Sawyer, "Production of artificial crystals," U.S. Patent no. 3,013,867 (filed: March 27, 1959 ; issued: December 19, 1961). (Note: This patent was assigned to Sawyer Research Products of Eastlake, Ohio.)

9.4.13 External links

- Quartz varieties, properties, crystal morphology. Photos and illustrations
- *Arkansas quartz*, Rockhounding Arkansas
- Gilbert Hart *Nomenclature of Silica*, American Mineralogist, Volume 12, pages 383–395, 1927
- Queensland University of Technology Origin of the word quartz.
- PDF of Charles Sawyer's cultured quartz process description
- "The Quartz Watch – Inventors". *The Lemelson Center, National Museum of American History*. Smithsonian Institution.
- Terminology used to describe the characteristics of Quartz Crystals when used as oscillators

Chapter 10

Organic

10.1 Hoelite

Hoelite is a mineral, discovered in 1922 at Mt. Pyramide, Spitsbergen, Norway and named after Norwegian geologist Adolf Hoel (1879–1964). Its chemical formula is $C_{14}H_8O_2$ (9,10-anthraquinone).[3][1]

It is a very rare organic mineral which occurs in coal fire environments in association with sal ammoniac and native sulfur.[1]

10.1.1 References

[1] Handbook of Mineralogy

[2] Webmineral data

[3] Mindat.org

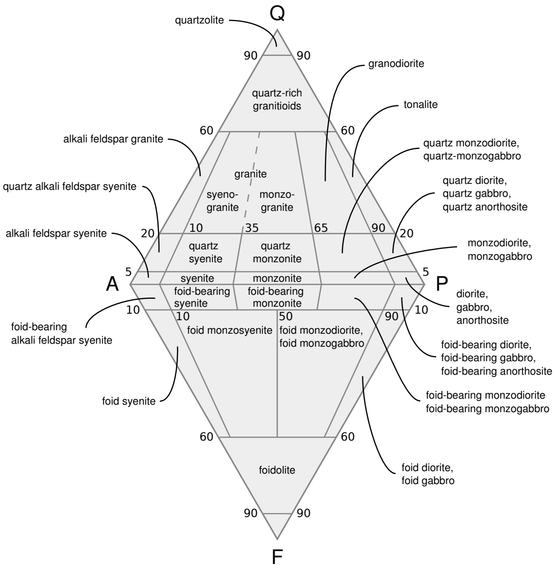
Chapter 11

Igneous Rocks

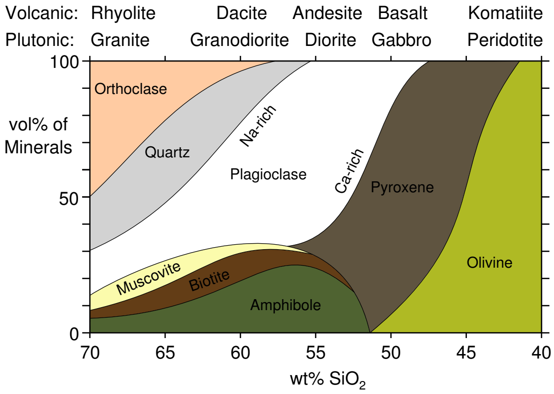
11.1 Granite

For other uses, see Granite (disambiguation).

Granite /ˈgrænɨt/ is a common type of felsic intrusive igneous rock which is granular and phaneritic in texture. The word “granite” comes from the Latin *granum*, a grain, in reference to the coarse-grained structure of such a holocrystalline rock. The term 'granite' also applies to a group of intrusive igneous rocks with similar textures and slight variations on composition and origin. These rocks mainly consist of feldspar, quartz, mica, and amphibole minerals. These form interlocking somewhat equigranular matrix of feldspar and quartz with scattered darker biotite mica and amphibole (often hornblende) peppering the lighter color minerals. Occasionally some individual crystals (phenocrysts) are larger than the groundmass, in which case the texture is known as porphyritic. A granitic rock with a porphyritic texture is known as a granite porphyry. Granites can be predominantly white, pink, or gray in color, depending on their mineralogy. By definition, granite is an igneous rock with at least 20% quartz and up to 65% alkali feldspar by volume. Granite differs from granodiorite in that at least 35% of the feldspar in granite is alkali feldspar as opposed to plagioclase; it is the potassium feldspar that gives many granites a distinctive pink color. The extrusive igneous rock equivalent of granite is rhyolite.



QAPF diagram for classification of plutonic rocks



Mineral assemblage of igneous rocks

Granite is nearly always massive (lacking any internal structures), hard and tough, and therefore it has gained widespread use throughout humanity, and more recently as a construction stone. The average density of granite is between 2.65[1] and 2.75 g/cm^3, its compressive strength usually lies above 200 MPa, and its viscosity near STP is 3–6 • 10^{19} Pa·s.[2] Melting temperature is 1215–1260 °C.[3]

Granite has poor primary permeability but strong secondary permeability.

Granitoid is a general, descriptive field term for lighter-colored, coarse-grained igneous rocks. Petrographic examination is required for identification of specific types of granitoids.[4]

The term 'granitic' means granite-like and is applied to granite and rocks of similar composition or texture.

The rock known as *black granite* is usually gabbro.[5]

Orbicular granite, an unusual type of granite, near the town of Caldera, northern Chile

The Stawamus Chief is a granite monolith in British Columbia

Close-up of granite exposed in Chennai, India

Various granites (cut and polished surfaces)

Close-up of granite from Yosemite National Park, valley of the Merced River

Roche Rock, Cornwall

The Cheesewring, a granite tor on the southern edge of Bodmin Moor, Cornwall

11.1.1 Mineralogy

Granite is classified according to the QAPF diagram for coarse grained plutonic rocks and is named according to the percentage of quartz, alkali feldspar (orthoclase, sanidine, or microcline) and plagioclase feldspar on the A-Q-P half of the diagram. True granite according to modern petrologic convention contains both plagioclase and alkali feldspars. When a granitoid is devoid or nearly devoid of plagioclase, the rock is referred to as alkali feldspar granite. When a granitoid contains less than 10% orthoclase, it is called tonalite; pyroxene and amphibole are common in tonalite. A granite containing both muscovite and biotite micas is called a binary or *two-mica* granite. Two-mica granites are typically high in potassium and low in plagioclase, and are usually S-type granites or A-type granites.

Chemical composition

A worldwide average of the chemical composition of granite, by weight percent, based on 2485 analyses:[6]

11.1.2 Occurrence

Outcrops of granite tend to form tors and rounded massifs. Granites sometimes occur in circular depressions surrounded by a range of hills, formed by the metamorphic aureole or hornfels. Granite is usually found in the continental plates of the Earth's crust.

Granite is currently known only on Earth, where it forms a major part of continental crust. Granite often occurs as relatively small, less than 100 km^2 stock masses (stocks) and in batholiths that are often associated with orogenic mountain ranges. Small dikes of granitic composition called aplites are often associated with the margins of granitic intrusions. In some locations, very coarse-grained pegmatite masses occur with granite.

Granite has been intruded into the crust of the Earth during all geologic periods, although much of it is of Precambrian age. Granitic rock is widely distributed throughout the continental crust and is the most abundant basement rock that underlies the relatively thin sedimentary veneer of the continents.

11.1.3 Origin

Granite has felsic composition and is more common in recent geologic time in contrast to Earth's ultramafic ancient igneous history. Felsic rocks are less dense than mafic and ultramafic rocks, and thus they tend to escape subduction, whereas basaltic or gabbroic rocks tend to sink into the mantle beneath granitic rocks of the continental cratons. Therefore, granitic rocks form the basement of all land continents.

Geochemical origins

Granitoids are a ubiquitous component of the crust. They have crystallized from magmas that have compositions at or near a eutectic point (or a temperature minimum on a cotectic curve). Magmas will evolve to the eutectic because of igneous differentiation, or because they represent low degrees of partial melting. Fractional crystallisation serves to reduce a melt in iron, magnesium, titanium, calcium and sodium, and enrich the melt in potassium and silicon - alkali feldspar (rich in potassium) and quartz (SiO_2), are two of the defining constituents of granite.

This process operates regardless of the origin of the parental magma to the granite, and regardless of its chemistry. However, the composition and origin of the magma which differentiates into granite, leaves certain geochemical and mineral evidence as to what the granite's parental rock was. The final mineralogy, texture and chemical composition of a granite is often distinctive as to its origin. For instance, a granite which is formed from melted sediments may have more alkali feldspar, whereas a granite derived from melted basalt may be richer in plagioclase feldspar. It is on this basis that the modern "alphabet" classification schemes are based. Granite has a slow cooling process which forms larger crystals.

Chappell & White classification system

The letter-based Chappell & White classification system was proposed initially to divide granites into *I-type* granite (or igneous protolith) granite and *S-type* or sedimentary protolith granite.[7] Both of these types of granite are formed by melting of high grade metamorphic rocks, either other granite or intrusive mafic rocks, or buried sediment, respectively.

M-type or mantle derived granite was proposed later, to cover those granites which were clearly sourced from crystallized mafic magmas, generally sourced from the mantle. These are rare, because it is difficult to turn basalt into granite via fractional crystallisation.

A-type or *anorogenic* granites are formed above volcanic "hot spot" activity and have peculiar mineralogy and geochemistry. These granites are formed by melting of the lower crust under conditions that are usually extremely dry. The rhyolites of the Yellowstone caldera are examples of volcanic equivalents of A-type granite.[8][9]

H-type or *hybrid* granites are formed following a mixing of two granitic magmas from different sources, e.g. M-type and S-type.

Granitization

An old, and largely discounted theory, *granitization* states that granite is formed in place by extreme metasomatism by fluids bringing in elements e.g. potassium and removing others e.g. calcium to transform the metamorphic rock into a granite. This was supposed to occur across a migrating front. The production of granite by metamorphic heat is difficult, but is observed to occur in certain amphibolite and granulite terrains. In-situ granitisation or melting by metamorphism is difficult to recognise except where leucosome and melanosome textures are present in migmatites. Once a metamorphic rock is melted it is no longer a metamorphic rock and is a magma, so these rocks are seen as a transitional between the two, but are not technically granite as they do not actually intrude into other rocks. In all cases, melting of solid rock requires high temperature, and also water or other volatiles which act as a catalyst by lowering the solidus temperature of the rock.

11.1.4 Ascent and emplacement

The ascent and emplacement of large volumes of granite within the upper continental crust is a source of much debate amongst geologists. There is a lack of field evidence for any proposed mechanisms, so hypotheses are predominantly based upon experimental data. There are two major hypotheses for the ascent of magma through the crust:

- Stokes diapir
- Fracture propagation

Of these two mechanisms, Stokes diapir was favoured for many years in the absence of a reasonable alternative. The basic idea is that magma will rise through the crust as a single mass through buoyancy. As it rises it heats the wall rocks, causing them to behave as a power-law fluid and thus flow around the pluton allowing it to pass rapidly and without major heat loss.[10] This is entirely feasible in the warm, ductile lower crust where rocks are easily deformed, but runs into problems in the upper crust which is far colder and more brittle. Rocks there do not deform so easily: for magma to rise as a pluton it would expend far too much energy in heating wall rocks, thus cooling and solidifying before reaching higher levels within the crust.

Fracture propagation is the mechanism preferred by many geologists as it largely eliminates the major problems of moving a huge mass of magma through cold brittle crust. Magma rises instead in small channels along self-propagating dykes which form along new or pre-existing fracture or fault systems and networks of active shear zones.[11] As these narrow conduits open, the first magma to enter solidifies and provides a form of insulation for later magma.

Granitic magma must make room for itself or be intruded into other rocks in order to form an intrusion, and several mechanisms have been proposed to explain how large batholiths have been emplaced:

- Stoping, where the granite cracks the wall rocks and pushes upwards as it removes blocks of the overlying crust
- Assimilation, where the granite melts its way up into the crust and removes overlying material in this way
- Inflation, where the granite body inflates under pressure and is injected into position

Most geologists today accept that a combination of these phenomena can be used to explain granite intrusions, and that not all granites can be explained entirely by one or another mechanism.

11.1.5 Weathering

Further information: Weathering

Physical weathering occurs on a large scale in the form of exfoliation joints, which are the result of granite expanding and fracturing as pressure is relieved when overlying material is removed by erosion or other processes.

Grus sand and granitoid it derived from

Chemical weathering of granite occurs when dilute carbonic acid, and other acids present in rain and soil waters, readily alter feldspar in a process called hydrolysis.[12][13] As demonstrated in the following reaction, this causes potassium feldspar to form kaolinite, with potassium ions, bicarbonate and silica in solution as byproducts. An endproduct of granite weathering is grus, which is often made up of coarse-grained fragments of disintegrated granite.

$$2\ KAlSi_3O_8 + 2\ H_2CO_3 + 9\ H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 4\ H_4SiO_4 + 2\ K^+ + 2\ HCO_3^-$$

Cleopatra's Needle, London

Climatic variations also influence the weathering rate of granites. For about two thousand years, the relief engravings on Cleopatra's Needle obelisk had survived the arid conditions of its origin prior to its transfer to London. Within two hundred years, the red granite has drastically deteriorated in the damp and polluted air.[14]

11.1.6 Natural radiation

Granite is a natural source of radiation, like most natural stones. However, some granites have been reported to have higher radioactivity thereby raising some concerns about their safety.

Potassium-40 is a radioactive isotope of weak emission, and a constituent of alkali feldspar, which in turn is a common component of granitic rocks, more abundant in alkali feldspar granite and syenites. Naturally, a geiger counter should register this low effect.

Some granites contain around 10 to 20 parts per million (ppm) of uranium. By contrast, more mafic rocks such as tonalite, gabbro or diorite have 1 to 5 ppm uranium, and limestones and sedimentary rocks usually have equally low amounts. Many large granite plutons are the sources for palaeochannel-hosted or roll front uranium ore deposits, where the uranium washes into the sediments from the granite uplands and associated, often highly radioactive, pegmatites. Cellars and basements sunk into soils over granite can become a trap for radon gas, which is formed by the decay of uranium.[15] Radon gas poses significant health concerns, and is the number two cause of lung cancer in the US behind smoking.[16]

Thorium occurs in all granites as well.[17] Conway granite has been noted for its relatively high thorium concentration of 56 (±6) PPM.[18]

There is some concern that materials sold as granite countertops or as building material may be hazardous to health. Dan Steck of St. Johns University, has stated[19] that approximately 5% of all granite will be of concern, with the caveat that only a tiny percentage of the tens of thousands of granite slab types have been tested. Various resources from national geological survey organizations are accessible online to assist in assessing the risk factors in granite country and design rules relating, in particular, to preventing accumulation of radon gas in enclosed basements and dwellings.

A study of granite countertops was done (initiated and paid for by the Marble Institute of America) in November 2008 by National Health and Engineering Inc of USA. In this test, all of the 39 full size granite slabs that were measured for the study showed radiation levels well below the European Union safety standards (section 4.1.1.1 of the National Health and Engineering study) and radon emission levels well below the average outdoor radon concentrations in the US.[20]

11.1.7 Uses

World's First temple built entirely of granite by the Emperor RajaRaja Chozha I, 10th century A.D.; Tanjore, India.

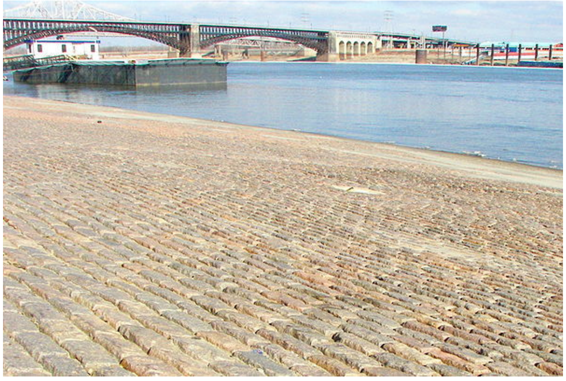
Antiquity

The Red Pyramid of Egypt (c.26th century BC), named for the light crimson hue of its exposed granite surfaces, is the third largest of Egyptian pyramids. Menkaure's Pyramid, likely dating to the same era, was constructed of limestone and granite blocks. The Great Pyramid of Giza (c.2580 BC) contains a huge granite sarcophagus fashioned of "Red Aswan Granite." The mostly ruined

Life-size elephant and other creatures carved in granite, 7-9th century A.D.; Mahabalipuram, India.

Polished red granite tombstone

Black Pyramid dating from the reign of Amenemhat III once had a polished granite pyramidion or capstone, now on display in the main hall of the Egyptian Museum in Cairo (see Dahshur). Other uses in Ancient Egypt include columns, door lintels, sills, jambs, and wall and floor veneer.[21] How the Egyptians worked the solid granite is still a matter of debate. Dr. Patrick Hunt[22] has postulated that the Egyptians used emery shown to have higher hardness on the Mohs scale.



Granite was used for setts on the St. Louis riverfront and for the piers of the Eads Bridge (background)

The granite peaks of the Torres del Paine in the Chilean Patagonia

Half Dome, Yosemite, a classic granite dome and popular rock climbing destination

Rajaraja Chola I of the Chola Dynasty in South India built the world's first temple entirely of granite in the 11th century AD in Tanjore, India. The Brihadeeswarar temple Brihadeeswarar Temple dedicated to Lord Shiva was built in 1010. The massive Gopuram (ornate, upper section of shrine) is believed to have a mass of around 81 tonnes. It was the tallest temple in south India.[23]

Modern

Sculpture and memorials In some areas granite is used for gravestones and memorials. Granite is a hard stone and requires skill to carve by hand. Until the early 18th century, in the Western world, granite could only be carved by hand tools with generally poor results.

A key breakthrough was the invention of steam-powered cutting and dressing tools by Alexander MacDonald of Aberdeen, inspired by seeing ancient Egyptian granite carvings. In 1832 the first polished tombstone of Aberdeen granite to be erected in an English cemetery was installed at Kensal Green cemetery. It caused a sensation in the London monumental trade and for some years all polished granite ordered came from MacDonalds.[24] Working with the sculptor William Leslie, and later Sidney Field, granite memorials became a major status symbol in Victorian Britain. The royal sarcophagus at Frogmore was probably the pinnacle of its work, and at 30 tons one of the largest. It was not until the 1880s that rival machinery and works could compete with the MacDonald works.

Modern methods of carving include using computer-controlled rotary bits and sandblasting over a rubber stencil. Leaving the letters, numbers and emblems exposed on the stone, the blaster can create virtually any kind of artwork or epitaph.

The rock known as *black granite* is usually gabbro, which has a completely different chemical composition.[5][25]

Buildings Granite has been extensively used as a dimension stone and as flooring tiles in public and commercial buildings and monuments. Aberdeen in Scotland, which is constructed principally from local granite, is known as “The Granite City”. Because of its abundance, granite was commonly used to build foundations for homes in New England. The Granite Railway, America’s first railroad, was built to haul granite from the quarries in Quincy, Massachusetts, to the Neponset River in the 1820s. With increasing amounts of acid rain in parts of the world, granite has begun to supplant marble as a monument material, since it is much more durable. Polished granite is also a popular choice for kitchen countertops due to its high durability and aesthetic qualities. In building and for countertops, the term “granite” is often applied to all igneous rocks with large crystals, and not specifically to those with a granitic composition.

Engineering Engineers have traditionally used polished granite surface plates to establish a plane of reference, since they are relatively impervious and inflexible. Sandblasted concrete with a heavy aggregate content has an appearance similar to rough granite, and is often used as a substitute when use of real granite is impractical. A most unusual use of granite was in the construction of the rails for the Haytor Granite Tramway, Devon, England, in 1820. Granite block is usually processed into slabs and after can be cut and shaped by a cutting center. Granite tables are used extensively as a base for optical instruments due to granite’s rigidity, high dimensional stability and excellent vibration characteristics.

Other uses Curling stones are traditionally fashioned of Ailsa Craig granite. The first stones were made in the 1750s, the original source being Ailsa Craig in Scotland. Because of the particular rarity of the granite, the best stones can cost as much as US$1,500. Between 60–70 percent of the stones used today are made from Ailsa Craig granite, although the island is now a wildlife reserve and is still used for quarrying under license for Ailsa granite by Kays of Mauchline for Curling stones.[26]

11.1.8 Rock climbing

Granite is one of the rocks most prized by climbers, for its steepness, soundness, crack systems, and friction. Well-known venues for granite climbing include Yosemite, the Bugaboos, the Mont Blanc massif (and peaks such as the Aiguille du Dru, the Mountains of Mourne, the Adamello-Presanella Alps, the Aiguille du Midi and the Grandes Jorasses), the Bregaglia, Corsica, parts of the Karakoram (especially the Trango Towers), the Fitzroy Massif, Patagonia, Baffin Island, Ogawayama, the Cornish coast, the Cairngorms, Sugarloaf Mountain in Rio de Janeiro, Brazil, and the Stawamus Chief, British Columbia, Canada.

Granite rock climbing is so popular that many of the artificial rock climbing walls found in gyms and theme parks are made to look and feel like granite.

11.1.9 See also

11.1.10 References

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11.1.12 External links

- The Emplacement and Origin of Granite

Chapter 12

Sedimentary Rocks

12.1 Flint

This article is about the sedimentary rock. For the city in Michigan, see Flint, Michigan. For other uses, see Flint (disambiguation).

Flint is a hard, sedimentary cryptocrystalline form of the mineral quartz,[1][2] categorized as a variety of chert. It occurs chiefly as nodules and masses in sedimentary rocks, such as chalks and limestones.[3][4] Inside the nodule, flint is usually dark grey, black, green, white, or brown in colour, and often has a glassy or waxy appearance. A thin layer on the outside of the nodules is usually different in colour, typically white and rough in texture. From a petrological point of view, "flint" refers specifically to the form of chert which occurs in chalk or marly limestone. Similarly, "common chert" (sometimes referred to simply as "chert") occurs in limestone.

A sample of Miorcani flint from the Cenomanian chalky marl layer of the Moldavian Plateau. (ca. 7.5 cm wide)

Pebble beach made up of flint nodules eroded out of the nearby chalk cliffs, Cape Arkona, Rügen

Neolithic flint axe, about 31 cm long

12.1.1 Origin

The exact mode of formation of flint is not yet clear but it is thought that it occurs as a result of chemical changes in compressed sedimentary rock formations, during the process of diagenesis. One hypothesis is that a gelatinous ma-

Detail of flint used in a building in Wiltshire, England.

Striped flint

terial fills cavities in the sediment, such as holes bored by crustaceans or molluscs and that this becomes silicified. This hypothesis certainly explains the complex shapes of flint nodules that are found. The source of dissolved silica in the porous media could be the spicules of silicious sponges.[3] Certain types of flint, such as that from the south coast of England, contain trapped fossilised marine flora. Pieces of coral and vegetation have been found preserved like amber inside the flint. Thin slices of the stone often reveal this effect.

Puzzling giant flint formations known as paramoudra and flint circles are found around Europe but especially in Norfolk, England on the beaches at Beeston Bump and West Runton.[5]

Flint sometimes occurs in large flint fields in Jurassic or Cretaceous beds, for example in Europe.

12.1.2 Uses

Tools or cutting edges

Flint was used in the manufacture of tools during the Stone Age as it splits into thin, sharp splinters called flakes or blades (depending on the shape) when struck by another hard object (such as a hammerstone made of another material). This process is referred to as knapping.

In Europe, some of the best toolmaking flint has come from Belgium (Obourg, flint mines of Spiennes),[6] the coastal chalks of the English Channel, the Paris Basin, Thy in Jutland (flint mine at Hov), the Sennonian deposits of Rügen, Grimes Graves in England, the Upper Cretaceous chalk formation of Dobruja and the lower Danube (Balkan flint), the Cenomanian chalky marl formation of the Moldavian Plateau (Miorcani flint) and the Jurassic deposits of the Kraków area and Krzemionki in Poland. Flint mining is attested since the Palaeolithic, but became more common since the Neolithic (Michelsberg culture, Funnelbeaker culture).

To ignite fire or gunpowder

Assorted reproduction firesteels typical of Roman to Medieval period.

When struck against steel, a flint edge will produce sparks. The hard flint edge shaves off a particle of the steel that exposes iron which reacts with oxygen from the atmosphere and can ignite the proper tinder. Prior to the wide availability of steel, rocks of iron pyrite would be used along with the flint, in a similar (but more time-consuming) way. These methods are popular in woodcraft, bushcraft, and among those who wish to use traditional skills.

Flintlocks A later, major use of flint and steel was in the flintlock mechanism, used primarily in flintlock firearms, but also used on dedicated fire-starting tools. A piece of flint held in the jaws of a spring-loaded hammer, when released by a trigger, strikes a hinged piece of steel ("frizzen") at an angle, creating a shower of sparks and exposing a charge of priming powder. The sparks ignite the priming powder and that flame, in turn, ignites the main charge, propelling the ball, bullet, or shot through the barrel. While the military use of the flintlock declined after the adoption of the percussion cap from the 1840s onward, flintlock rifles and shotguns remain in use amongst recreational shooters.

Comparison with ferrocerium Flint and steel used to strike sparks were superseded by ferrocerium (sometimes referred to as “flint”, although not true flint, "mischmetal", “hot spark”, “metal match”, or “fire steel”). This man-made material, when scraped with any hard, sharp edge, produces sparks that are much hotter than obtained with natural flint and steel, allowing use of a wider range of tinders. Because it can produce sparks when wet and can start hundreds or thousands of fires when used correctly, ferrocerium is commonly included in survival kits. Ferrocerium is used in many cigarette lighters, where it is referred to as “flint”.

As a building material

Flint, knapped or unknapped, has been used since antiquity (for example at the Late Roman fort of Burgh Castle in Norfolk) up to the present day as a material for building stone walls, using lime mortar, and often combined with other available stone or brick rubble. It was most common in parts of southern England, where no good building stone was available locally, and brick-making not widespread until the later Middle Ages. It is especially associated with East Anglia, but also used in chalky areas stretching through Hampshire, Sussex, Surrey and Kent to Somerset. Flint was used in the construction of many churches, houses, and other buildings, for example the large stronghold of Framlingham Castle. Many different decorative effects have been achieved by using different types of knapping or arrangement and combinations with stone (flushwork), especially in the 15th and early 16th centuries.

- Close-up of the wall of the Roman shore fort at Burgh Castle, Norfolk, showing alternating courses of flint and brick
- Elaborate 15th century flint and limestone flushwork at Long Melford
- A typical medieval wall (with modern memorial) at Canterbury Cathedral - knapped and unknapped (“cobble”) flints are mixed with pieces of brick and other stones
- Ruins of Thetford Priory show flints and mortar through the whole depth of the wall
- Elaborate patterned flushwork at top (restored in the 19th century) and flint and limestone chequers below. Norwich Cathedral

A flint church - the Parish Church of Saint Thomas, in Cricket Saint Thomas, Somerset, England. The height of the very neatly knapped flints varies between 3 and 5 inches (7.6 and 12.7 cm).

Ceramics

Flint pebbles are used as the media in ball mills to grind glazes and other raw materials for the ceramics industry.[7] The pebbles are hand-selected based on colour; those having a tint of red, indicating high iron content, are discarded. The remaining blue-grey stones have a low content of chromophoric oxides and so are less deleterious to the colour of the ceramic composition after firing.[8]

Until recently flint was also an important raw material in clay-based ceramic bodies produced in the UK.[9][10] In preparation for use flint pebbles, frequently sourced from the coasts of South-East England or Western France, were calcined to around 1,000 °C. This heat process both removed organic impurities and induced certain physical reactions, including converting some of the silica to cristobalite. After calcination the flint pebbles were milled to a fine particle size.[11][12][13][14] However, the use of flint has now been superseded by quartz.[15] Because of the historical use of flint, the word "flint" is used by some potters, especially in the US, to refer to siliceous materials that are not flint.[16][17][18]

Jewellery

Flint bracelets were known in Ancient Egypt and several examples have been found.[19] Striped flint is today in use as a gemstone as well.

Fragmentation

While flint may be used in fire-lighting, it should not be exposed to excessive heat, as from a fire. Due to the stone's molecular makeup, flint may fracture, sometimes violently, when different parts of the stone expand to different degrees. This tendency, to fracture, is enhanced by the fact that most samples of flint contain impurities that may expand to a greater or lesser degree than the surrounding stone. This tendency to fracture is similar, but not identical, to the tendency of glass to shatter when exposed to heat. [20]

To combat fragmentation, flint/chert may be heat-treated, being slowly brought up to a temperature of 150 to 260 °C (300 to 500 °F) for 24 hours, then slowly cooled to room temperature. This makes the material more homogenous and thus more "knappable" and produces tools with a cleaner, sharper cutting edge.

12.1.3 See also

- **Mineralogy**
  - Agate
  - Chalcedony
  - Chert
  - Eolith
  - Jasper
  - Nodule (geology) not to be confused with Concretion
  - Obsidian
  - Onyx
  - Opal
  - Whinstone
- **Archaeology**
  - Ancient Egyptian flint jewellery
  - Clovis Points, archaeological artefacts of the Clovis culture in New Mexico
  - Grimes Graves, a prehistoric flint mine in Norfolk, England
  - Flint Ridge State Memorial, a Native American flint quarry in Hopewell Township, Licking County, Ohio
  - Flint mine

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12.1.5 External links

- Flint Architecture of East Anglia Book by Stephen Hart
- Flintsource.net European Artefacts - detailed site
- Flint circles and paramoudra - Beeston Bump
- Paramoudras and flint circles photograph collection
- Winchester Cathedral Close
- Flint and the Conservation of Flint Buildings Introduction to the historical use of flint in construction and the repair and conservation of historic flint buildings

12.2 Limestone

For other uses, see Limestone (disambiguation).

Limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate ($CaCO_3$). Most limestone is composed of skeletal fragments of marine organisms such as coral or foraminifera.

Limestone makes up about 10% of the total volume of all sedimentary rocks. The solubility of limestone in water and weak acid solutions leads to karst landscapes, in which water erodes the limestone over thousands to millions of years. Most cave systems are through limestone bedrock.

Limestone has numerous uses: as a building material, as aggregate for the base of roads, as white pigment or filler in products such as toothpaste or paints, and as a chemical feedstock.

The first geologist to distinguish limestone from dolomite was Belsazar Hacquet in 1778.[1]

12.2.1 Description

Like most other sedimentary rocks, most limestone is composed of grains. Most grains in limestone are skeletal fragments of marine organisms such as coral or foraminifera. Other carbonate grains comprising limestones are ooids, peloids, intraclasts, and extraclasts. These organisms secrete shells made of aragonite or calcite, and leave these shells behind after the organisms die.

Limestone quarry at Cedar Creek, Virginia, USA

Cutting the limestone blocks at a quarry in Gozo, Malta

La Zaplaz formations in the Piatra Craiului Mountains, Romania.

Limestone often contains variable amounts of silica in the form of chert (chalcedony, flint, jasper, etc.) or siliceous skeletal fragment (sponge spicules, diatoms, radiolarians), and varying amounts of clay, silt and sand (terrestrial detritus) carried in by rivers.

Some limestones do not consist of grains at all, and are formed completely by the chemical precipitation of calcite or aragonite, i.e. travertine. Secondary calcite may be deposited by supersaturated meteoric waters (groundwater that precipitates the material in caves). This produces speleothems, such as stalagmites and stalactites. Another form taken by calcite is oolitic limestone, which can be recognized by its granular (oolite) appearance.

The primary source of the calcite in limestone is most commonly marine organisms. Some of these organisms can construct mounds of rock known as reefs, building upon past generations. Below about 3,000 meters, water pressure and temperature conditions cause the dissolution of calcite to increase nonlinearly, so limestone typically does not form in deeper waters (see lysocline). Limestones may also form in lacustrine and evaporite depositional environments.[2][3]

Calcite can be dissolved or precipitated by groundwater, depending on several factors, including the water temperature, pH, and dissolved ion concentrations. Calcite exhibits an unusual characteristic called retrograde solubility, in which it becomes less soluble in water as the temperature increases.

Impurities (such as clay, sand, organic remains, iron oxide, and other materials) will cause limestones to exhibit different colors, especially with weathered surfaces.

Limestone may be crystalline, clastic, granular, or massive, depending on the method of formation. Crystals of calcite, quartz, dolomite or barite may line small cavities in the rock. When conditions are right for precipitation, calcite forms mineral coatings that cement the existing rock grains together, or it can fill fractures.

Travertine is a banded, compact variety of limestone formed along streams, particularly where there are waterfalls, and around hot or cold springs. Calcium carbonate is deposited where evaporation of the water leaves a solution supersaturated with the chemical constituents of calcite. Tufa, a porous or cellular variety of travertine, is found near waterfalls. Coquina is a poorly consolidated limestone composed of pieces of coral or shells.

During regional metamorphism that occurs during the mountain building process (orogeny), limestone recrystallizes into marble.

Limestone is a parent material of Mollisol soil group.

12.2.2 Classification

Two major classification schemes, the Folk and the Dunham, are used for identifying limestone and carbonate rocks.

Folk classification

Main article: Folk classification

Robert L. Folk developed a classification system that places primary emphasis on the detailed composition of grains and interstitial material in carbonate rocks. Based on composition, there are three main components: allochems (grains), matrix (mostly micrite), and cement (sparite). The Folk system uses two-part names; the first refers to the grains and the second is the root. It is helpful to have a petrographic microscope when using the Folk scheme, because it is easier to determine the components present in each sample.[4]

Dunham classification

Main article: Dunham classification

The Dunham scheme focuses on depositional textures. Each name is based upon the texture of the grains that make up the limestone. Robert J. Dunham published his system for limestone in 1962; it focuses on the depositional fabric of carbonate rocks. Dunham divides the rocks into four main groups based on relative proportions of coarser clastic particles. Dunham names are essentially for rock families. His efforts deal with the question of whether or not the grains were originally in mutual contact, and therefore self-supporting, or whether the rock is characterized by the presence of frame builders and algal mats. Unlike the Folk scheme, Dunham deals with the original porosity of the rock. The Dunham scheme is more useful for hand samples because it is based on texture, not the grains in the sample.[5]

12.2.3 Limestone landscape

Main article: Karst topography

Limestone makes up about 10% of the total volume of all sedimentary rocks.[6][7]

Limestone is partially soluble, especially in acid, and therefore forms many erosional landforms. These include limestone pavements, pot holes, cenotes, caves and gorges. Such erosion landscapes are known as karsts. Limestone is less resistant than most igneous rocks, but more resistant than most other sedimentary rocks. It is therefore usually associated with hills and downland, and occurs in regions with other sedimentary rocks, typically clays.

Karst topography and caves develop in limestone rocks due to their solubility in dilute acidic groundwater. The solubility of limestone in water and weak acid solutions leads to karst landscapes. Regions overlying limestone

The Cudgel of Hercules*, a tall limestone rock (*Pieskowa Skała Castle *in the background)*

bedrock tend to have fewer visible above-ground sources (ponds and streams), as surface water easily drains downward through joints in the limestone. While draining, water and organic acid from the soil slowly (over thousands or millions of years) enlarges these cracks, dissolving the calcium carbonate and carrying it away in solution. Most cave systems are through limestone bedrock. Cooling groundwater or mixing of different groundwaters will also create conditions suitable for cave formation.

Coastal limestones are often eroded by organisms which bore into the rock by various means. This process is known as bioerosion. It is most common in the tropics, and it is known throughout the fossil record (see Taylor and Wilson, 2003).

Bands of limestone emerge from the Earth's surface in often spectacular rocky outcrops and islands. Examples include the Burren in Co. Clare, Ireland; the Verdon Gorge in France; Malham Cove in North Yorkshire and the Isle of Wight,[8] England; on Fårö near the Swedish island of Gotland, the Niagara Escarpment in Canada/United States, Notch Peak in Utah, the Ha Long Bay National Park in Vietnam and the hills around the Lijiang River and Guilin city in China.

The Florida Keys, islands off the south coast of Florida, are composed mainly of oolitic limestone (the Lower Keys) and the carbonate skeletons of coral reefs (the Upper Keys), which thrived in the area during interglacial periods when sea level was higher than at present.

Unique habitats are found on alvars, extremely level expanses of limestone with thin soil mantles. The largest such expanse in Europe is the Stora Alvaret on the island of Öland, Sweden. Another area with large quantities of limestone is the island of Gotland, Sweden. Huge quarries in northwestern Europe, such as those of Mount Saint Peter (Belgium/Netherlands), extend for more than a hundred kilometers.

The world's largest limestone quarry is at Michigan Limestone and Chemical Company in Rogers City, Michigan.[9]

12.2.4 Uses

The Megalithic Temples of Malta *such as* Ħaġar Qim *are built entirely of limestone. They are among the oldest free-standing structures in existence.*

Limestone is very common in architecture, especially in Europe and North America. Many landmarks across the world, including the Great Pyramid and its associated complex in Giza, Egypt, are made of limestone. So many buildings in Kingston, Ontario, Canada were constructed from it that it is nicknamed the 'Limestone City'.[10] On the island of Malta, a variety of limestone called Globigerina limestone was, for a long time, the only building material available, and is still very frequently used on all types of buildings and sculptures. Limestone is readily available and relatively easy to cut into blocks or more elaborate carving. It is also long-lasting and stands up well to exposure. However, it is a very heavy material, making it impractical for tall buildings, and relatively expensive as a building material.

Limestone was most popular in the late 19th and early 20th centuries. Train stations, banks and other structures from that era are normally made of limestone. It is used as a facade on some skyscrapers, but only in thin plates for covering, rather than solid blocks. In the United States, Indiana, most notably the Bloomington area, has long been a source of high quality quarried limestone, called Indiana limestone. Many famous buildings in London are built from Portland limestone.

Limestone was also a very popular building block in the Middle Ages in the areas where it occurred, since it is hard, durable, and commonly occurs in easily accessible

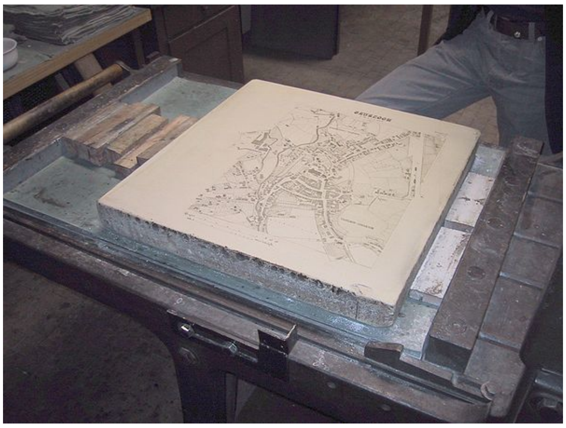
The Great Pyramid of Giza, one of the Seven Wonders of the Ancient World has an outside cover made entirely from limestone.

Courthouse built of limestone in Manhattan, Kansas

surface exposures. Many medieval churches and castles in Europe are made of limestone. Beer stone was a popular kind of limestone for medieval buildings in southern England.

Limestone and (to a lesser extent) marble are reactive to acid solutions, making acid rain a significant problem to the preservation of artifacts made from this stone. Many limestone statues and building surfaces have suffered severe damage due to acid rain. Acid-based cleaning chemicals can also etch limestone, which should only be cleaned with a neutral or mild alkaline-based cleaner.

Other uses include:



A limestone plate with a negative map of Moosburg in Bavaria is prepared for a lithography print.

- It is the raw material for the manufacture of quicklime (calcium oxide), slaked lime (calcium hydroxide), cement and mortar.
- Pulverized limestone is used as a soil conditioner to neutralize acidic soils.
- It is crushed for use as aggregate—the solid base for many roads as well as in asphalt concrete.
- Geological formations of limestone are among the best petroleum reservoirs;
- As a reagent in flue-gas desulfurization, it reacts with sulfur dioxide for air pollution control.
- Glass making, in some circumstances, uses limestone.
- It is added to toothpaste, paper, plastics, paint, tiles, and other materials as both white pigment and a cheap filler.
- It can suppress methane explosions in underground coal mines.
- Purified, it is added to bread and cereals as a source of calcium.
- Calcium levels in livestock feed are supplemented with it, such as for poultry (when ground up).[11]
- It can be used for remineralizing and increasing the alkalinity of purified water to prevent pipe corrosion and to restore essential nutrient levels.[12]
- Used in blast furnaces, limestone binds with silica and other impurities to remove them from the iron.
- It is often found in medicines and cosmetics.
- It is used in sculptures because of its suitability for carving.

12.2.5 Degradation by organisms

The cyanobacterium *Hyella balani* can bore through limestone; as can the green algae *Eugamantia sacculata* and the fungus *Ostracolaba implexa*.[13]

12.2.6 Gallery

- A stratigraphic section of Ordovician limestone exposed in central Tennessee, U.S. The less-resistant and thinner beds are composed of shale. The vertical lines are drill holes for explosives used during road construction.
- Thin-section view of a Middle Jurassic limestone in southern Utah. The round grains are ooids; the largest is 1.2 mm in diameter. This limestone is an oosparite.
- Photo and etched section of a sample of fossiliferous limestone from the Kope Formation (Upper Ordovician) near Cincinnati, Ohio.
- Biosparite limestone of the Brassfield Formation (Lower Silurian) near Fairborn, Ohio, showing grains mainly composed of crinoid fragments.

12.2.7 See also

- Alvar
- Calcium carbonate
- Chalk
- Coral sand
- Dolomite
- Kurkar
- In Praise of Limestone
- List of types of limestone by location
- Sandstone

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Chapter 13

Metamorphic Rocks

Chapter 14

Non classified minerals

14.1 Coloradoite

Coloradoite, also known as mercury telluride (HgTe), is a rare telluride ore associated with metallic deposit (especially gold and silver). Gold usually occurs within tellurides (e.g. Coloradoite) as a high finess native-metal (Fadda et al., 2005).[4]

The quest for mining led to the discovery of telluride ores which were found to be associated with metals. Tellurides are ingrown into ores containing these precious metals and are also responsible for a significant amount these metals being produced. Coloradoite is a member of the coordination subclass of tellurides is a covalent compound that is isostructural with sphalerite (ZnS) (Povarennykh, 1972).[5] Its chemical properties are highly instrumental in distinguishing it from other tellurides. First discovered in Colorado in 1877, other deposits containing coloradoite have been discovered since then. Although it plays an important role in the geology of minerals, it can also be used for other purposes.

14.1.1 Introduction

Telluride ores occur mainly with metal deposits. In 1848, C.T. Jackson was the first to discover an American mineral containing the element tellurium in the Whitehall mine, in Spotsylvania County, near Frederickson, VA. (Kemp, 1898).[6] Tellurides of gold were first discovered in 1782 in Transylvania and subsequently other telluride ores were found in other parts of the world (Mark and Scibird, 1908). The first discovery and description of coloradoite was by Frederick Augustus Genth in the Boulder veins of Colorado in 1877 (Kelly and Goddard, 1969)[7] and so named after the place of discovery. Other studies have reported its occurrence in other mines of the region and also in mines of the world's significant telluride locations. First classified in the 02 class of minerals by James Dana (Dana, 1904),[8] its classification number is 02.08.02.05. It is also has a Strunz classification of 02.CB.05a, as a metal sulfide with gold, silver, iron, copper and other metals (Strunz and Nickel, 2001).[9]

14.1.2 Composition

The chemical formula for coloradoite is HgTe. Theoretically the composition (%) of HgTe is Hg 61.14, Te 38.86 (Vlasov, 1966);[10] Table 1 shows results from a chemical analyses reported by Vlasov on samples collected from two different locations. Because it is found with other telluride ores, it carries some other metals like gold and silver (Wallace, 1908).[11] In its pure form, it has the composition mentioned above. A little hard to identify, petzite which is hazardous could be mistaken for coloradoite, on the other hand, petzite is anisotropic as opposed to coloradoite being an isotropic mineral (Ramdohr, 1980).[12] It is a binary compound with the general formula AX.

14.1.3 Structure

Coloradoite has a sphalerite structure also known as the "diamond" or "blende" structure; a face centered cubic array in which Hg^{2+} are in tetrahedral coordination with Te^{2-}, with a stacking sequence of ABCABC (Klein and Dutrow, 2007).[13] The tetrahedral in the sphalerite group a joined together through their apices and rotated through 60° with respect to each other (Stanton, 1972).[14] Figure 1 shows the atomic structure of coloradoite. The structure is a unit cube with the Te^{2-} ions at the corners and face centers. The four mercury atoms are coordinated so that each mercury atom lies at the center of a regular tetrahedron of tellurium atoms and each tellurium lies at the center of a regular tetrahedron of mercury atoms. Its crystal point group of *43m and space group is F*43m (Anthony et al., 1990).[15] It is a covalent compound with a high proportion of metallic bonding, due to its low valencies and even lower interatomic distances (Povarennykh). It is also isotropic, meaning it has just one refractive index.

14.1.4 Physical properties

Coloradoite is a brittle, massively granular mineral, with a hardness of 2.5. (Vlasov, 1966)[10] It has a metallic luster, which could be explained by the presence of metallic bonding in the crystal. Its specific gravity is 8.10 and is an opaque mineral with colors iron-black inclining to gray; in polished sections, and white with slight grayish brown tint, tarnishing to dull purple. Its fracture is uneven to subconchordial with a cell length of 6.44 angstroms (Anthony et al., 1990).[15] For ease of identification, its etching tests are as follows; With HNO_3 it slowly produces a weak brown variegated deposit that acts as a protector to the surface and can be removed completely; with Aqua regia it effervesces and produces a weak deposit that can be rubbed off and white, radiating spherules are formed, reaction with $FeCl_3$ yields a browning of the surface at different rates and produces black rims of droplet (Ramdohr, 1980).[12] Reactions with HCl, KCN, KOH and $HgCl_2$ yield no precipitates or residue as opposed to petzite which turns dark brown with HNO_3 (Ramdohr, 1980).[12]

14.1.5 Geologic occurrence

Coloradoite was first discovered in 1877 by F. A. Genth, from the Smuggler mine at Balarat and the Keystone and Mountain Lion mines of the Magnolia district in Colorado (Kelly and Goddard, 1969);[7] it was named after the state it was found in. Later studies showed its existence in other mines of the region as well as Kalgoorlie, Australia and Kirkland Lake District, Canada (Bateman, 1956). It is found in large quantities in ores made up of intergrown tellurium, calverite or sylvanite, melonite and altaite, as anhedral grains either enclosed in single crystals of tellurium or localized along grain boundaries in tellurium aggregates, among others (Kelly and Goddard, 1969).[7] The tectonic settings for ore deposits are; (a) Magmatic deposits (Waarkraal, South Africa) (b) Contact metasomatic (Nickel Plate mine, British Columbia, (c) Lode and Massive replacement deposits (Kirkland Lake, Ontario and South Dakota respectively), and (d) Cavity filling (Cripple Creek, Colorado, Kalgoorlie, Australia) (Bateman, 1956). Tellurides are accountable for just about 20% of gold production and gold mineralization is hosted chiefly by Archean-aged dolerites and basalts that have been metamorphosed to the greenschist facies. This mineralization occurs in hundreds of auriferous and telluride-bearing lodes (Shackleton et al., 2003).[16]

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14.1.7 External links

- Coloradoite at WebElements.com

14.2 Duftite

Duftite is a relatively common arsenate mineral with the formula $CuPb(AsO_4)(OH)$, related to conichalcite. It is green and often forms botryoidal aggregates. It is a member of the Adelite-Descloizite Group, Conichalcite-Duftite Series. Duftite and conichalcite specimens from Tsumeb are commonly zoned in colour and composition. Microprobe analyses and X-ray powder-diffraction studies indicate extensive substitution of Zn for Cu, and Ca for Pb in the duftite structure. This indicates a solid solution among conichalcite, $CaCu(AsO_4)(OH)$, austinite, $CaZn(AsO_4)(OH)$ and duftite $PbCu(AsO_4)(OH)$, all of them belonging to the adelite group of arsenates.[4] It was named after Mining Councilor G Duft, Director of the Otavi Mine and Railroad Company, Tsumeb, Namibia.[5] The type locality is the Tsumeb Mine, Tsumeb, Otjikoto Region, Namibia.

14.2.1 Structure

The structure[6] is composed of chains of edge-sharing CuO_6 distorted octahedra parallel to the c axis. The chains are linked by AsO_4 tetrahedra and Pb atoms.

14.2.2 Environment

Duftite is an uncommon product of weathered sulfide ore deposits. It is associated with azurite at the type locality,[5] and with bayldonite, segnitite, agardite and gartrellite at the Central Cobar Mines, New South Wales, Australia, where some pseudomorphs of duftite after mimetite have also found.[7] It occurs in association with olivenite, mottramite, azurite, malachite, wulfenite and calcite in the Tsumeb, Namibia deposit. It occurs with bayldonite, beudantite, mimetite and cerussite in the Cap Garonne mine, France.[3]

Duftite on cerussite, Tsumeb mine, Namibia. Size: 6×5×3 cm.

14.2.3 Distribution

Reported from Argentina, Australia, Austria, Chile, the Czech Republic, France, Germany, Greece, Italy, Japan, Mexico, Namibia, Poland, Portugal, Russia, South Africa, Spain, Switzerland, the UK, the USA and Zimbabwe.[2]

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14.3 Moissanite

Moissanite /ˈmɔɪsənaɪt/,[4] a form of silicon carbide, is a rare mineral discovered by Henri Moissan,and having the chemical formula SiC, and to various crystalline polymorphs. Earlier, this material had been synthesized in laboratories.

14.3.1 Background

Mineral moissanite was discovered by Henri Moissan while examining rock samples from a meteor crater located in Canyon Diablo, Arizona, in 1893. At first, he mistakenly identified the crystals as diamonds, but in 1904 he identified the crystals as silicon carbide.[5][6] The mineral form of silicon carbide was named moissanite in honor of Moissan later on in his life. The discovery in the Canyon Diablo meteorite and other places was challenged for a long time as carborundum contamination from human abrasive tools.[7]

14.3.2 Geological occurrence

Until the 1950s no other source, apart from meteorites, had been encountered. Later moissanite was found as inclusions in kimberlite from a diamond mine in Yakutia in 1959, and in the Green River Formation in Wyoming in 1958.[8] The existence of moissanite in nature was questioned even in 1986 by Charles Milton, an American geologist.[9]

Moissanite, in its natural form, is very rare. It has only been discovered in a small variety of places from upper mantle rock to meteorites. Discoveries have shown that moissanite occurs naturally as inclusions in diamonds, xenoliths, and ultramafic rocks such as kimberlite and lamproite.[7] They have also been identified in carbonaceous chondrite meteorites as presolar grains.[10]

14.3.3 Meteorites

Analysis of SiC grains found in the Murchison carbonaceous chondrite meteorite has revealed anomalous isotopic ratios of carbon and silicon, indicating an origin from outside the solar system.[11] 99% of these SiC grains originate around carbon-rich Asymptotic giant branch stars. SiC is commonly found around these stars as deduced from their infrared spectra.

14.3.4 Sources

All applications of silicon carbide today use synthetic material, as the natural material is very scarce.

Silicon carbide was first synthesized by Jöns Jacob Berzelius, who is best known for his discovery of silicon.[12] Years later, Edward Goodrich Acheson produced viable minerals that could substitute diamond as an abrasive and cutting material. This was possible as moissanite is one of the hardest substances known, with a hardness below that of diamond and comparable with those of cubic boron nitride and boron.

Pure synthetic moissanite can be made from thermal decomposition of the preceramic polymer poly(methylsilyne), requiring no binding matrix (e.g. cobalt metal powder).

14.3.5 Physical properties

Main article: Silicon carbide

The crystalline structure is held together with strong covalent bonding similar to diamonds,[5] that allows moissanite to withstand high pressures up to 52.1 gigapascals.[5][13] Colours vary widely and are graded in the I-J-K range on the diamond color grading scale.[14]

14.3.6 Applications

Main article: Silicon carbide § Uses

Gem-cut synthetic moissanite set in a ring

Moissanite was introduced to the jewelry market in 1998.[15] It is regarded as a diamond alternative, with some optical properties exceeding those of diamond. Its lower price, and less exploitative mining practices necessary to obtain it, makes it a popular alternative to diamonds. Due in part to the similar thermal conductivity of moissanite and diamond, it is a popular target for scams; however, higher electrical conductivity and birefringence of moissanite may alert a buyer to fraud. On the Mohs scale it is a 9.5, with a diamond being a 10.[3] Moissanite is stronger than sapphire or ruby. In many developed countries, the use of moissanite in jewelry has been patented; these patents expire in 2015 for the US, and 2016 in other countries.[16][17][18] Moissanite gemstones are sometimes marketed under the trademark *Berzelian*, a reference to the work of Berzelius on SiC.

Because of its hardness, it can be used in high-pressure experiments, as a replacement for diamond (see diamond anvil cell).[5] Since large diamonds are usually too expensive to be used as anvils, synthetic moissanite is more often used in large-volume experiments. Synthetic moissanite is also interesting for electronic and thermal applications because its thermal conductivity is similar to that of diamonds.[13] High power SiC electronic devices are expected to find use in the design of protection circuits used for motors, actuators, and energy storage or pulse power systems.[19]

14.3.7 See also

- Glossary of meteoritics
- Engagement ring
- Fair trade

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Annoyomous, Testing times, PlanetStar, Hallpriest9, Patriot62371, Swliv, ToePeu.bot, SheepNotGoats, Texcoco, Krawi, Winchelsea, Dawn Bard, Viskonsas, Caltas, This, that and the other, Chloh, Purbo T, Keilana, Happysailor, Tiptoety, Emilfarb, Oda Mari, Nopetro, Hdotnet, Chirag155, Ifish4cats, Skipsievert, Oxymoron83, Faradayplank, Nathanfrank, Bagatelle, AlaskaMining, Lightmouse, Tombomp, Boromir123, Grunkhead, Hatster301, Rum130, MadmanBot, StaticGull, Msrasnw, Chillum, Mygerardromance, Sapeli, Wiki-BT, Superbeecat, Florentino floro, Nergaal, Bananabean, C0nanPayne, FlyLikeAMouse, Addd wiki, Rombethor, Explicit, Squash Racket, Lolroflmao, Dlrohrer2003, Gubernatoria, Twinsday, Martarius, Sfan00 IMG, Thewriter23, De728631, Ecjmartin, Elassint, ClueBot, PipepBot, Fyyer, The Thing That Should Not Be, Johnnyboi54, Kane gibbons, Shniken1, ImperfectlyInformed, Arakunem, Kaktookee, JHiesey, Mild Bill Hiccup, Denna Haldane, Seed 90, California123123, Yamakiri, Regibox, Chiko2154, 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jougler, PranksterTurtle, Glane23, AndersBot, Partykid33, Debresser, Kyle1278, LinkFA-Bot, Jasper Deng, Lemonade100, Alchemist-hp, Tkeller28, 84user, Numbo3-bot, Ehrenkater, Erutuon, Tide rolls, Alan16, Lightbot, Luckas Blade, Сергей Олегович, MissAlyx, Legobot, Luckas-bot, Yobot, WikiDan61, OrgasGirl, Fraggle81, Gambori, Donfbreed, II MusLiM HyBRiD II, Цуканов Кирилл, PMLawrence, Mmxx, THEN WHO WAS PHONE?, Brougham96, KamikazeBot, Wonderfl, Tempodivalse, Useagev2, Synchronism, Tonyrex, AnomieBOT, Jameson.lee, 1exec1, ThaddeusB, Mike928, Daniele Pugliesi, Killiondude, Jim1138, Linden.940, Becky-and-annalise, John.Longanecker, THEN WHOSE WAS PHONE??, Ipatrol, AdjustShift, Yotcmdr, Henry Godric, Kingpin13, Yachtsman1, Theseeker4, Пика Пика, Ulric1313, Jude45, Powerzilla, Chris Scuglia, Materialscientist, Dgg2, Pepo13, Hillnainai, Jamesmoyse, Citation bot, Miami1canes, Charm993, ReedGoldMine, Abdclmop, Neurolysis, ArthurBot, Balatung, Quebec99, LilHelpa, Alster1, Xqbot, Ywaz, Capricorn42, 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Tea with toast, FoxBot, Double sharp, TobeBot, Ticklewickleukulele, Yunshui, Animalparty, Jonkerz, Herberq, Lotje, Extra999, Begoon, Kylepetz, Koko2363, Ngstevens2, TWST48, Bcai388, Kenari109a, WikiKing1234, Vera.tetrix, IRISZOOM, Tbhotch, Rahuloof, Difu Wu, Mean as custard, RjwilmsiBot, Codehydro, CerberusAlpha, Teravolt, Realissimo, S12400, Ottomachin, CalicoCatLover, Grondemar, Sotongdj, Strickja, EmausBot, WikitanvirBot, Yca.zuback, Gfoley4, Pete Hobbs, Haon 2.0, Boundarylayer, Dewritech, Sumsum2010, Solarra, Timbow191, Djembayz, Entanio, ZéroBot, Brothernight, Josve05a, Thewhyman, StringTheory11, Oncenawhile, Baedudu, Mahlulu22, Emily Jensen, The Bizniss, Lamellama, H3llBot, Asimov123, Dennis Kwaria, Rcsprinter123, Brandmeister, Sahimrobot, L Kensington, Alborzagros, Gsarwa, MDChaara, Anonimski, Yasharelliin, Puffin, Dansalignatious, Hellrazer025, Targaryen, Indian1985, Whoop whoop pull up, Mjbmrbot, ClueBot NG, Ypnypn, Theober555, Gilderien, Piast93, Osterluzei, Twillisjr, 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Tang, NawlinWiki, Mal7798, Wiki alf, Bachrach44, Nirvana2013, Janke, Grafen, Badagnani, Trovatore, The Thadman, Dureo, Matticus78, Zwobot, Dbfirs, Lockesdonkey, Mieciu K, Bota47, Jhinman, Moncubus, Alpha 4615, Tetracube, FF2010, Donbert, Orchid Righteous, 21655, Zzuuzz, Lt-wiki-bot, Pb30, KGasso, Jmackaerospace, Steventrouble, Wikiwawawa, BorgQueen, Vicarious, Diddims, Jaranda, Markvs88, RunOrDie, Darren Lee, Katieh5584, Kungfuadam, Junglecat, Appleseed, Tyrhinis, DearPrudence, Paul Erik, GrinBot, Asterion, Bibliomaniac15, Quadpus, Crusty007, Sycthos, Itub, Alextrevelian 006, Crystallina, Larrylarr, SmackBot, Amcbride, Haza-w, KnowledgeOfSelf, Melchoir, Pgk, Od Mishehu, Vald, Grigzie, Yuyudevil, Thunderboltz, Jrockley, Eskimbot, Chych, Jab843, Dpwkbw, Josephprymak, Edgar181, Alsandro, Commander Keane bot, Yamaguchi⍰⍰, Pathless, Mastcell, Magicalsaumy, Gilliam, Ohnoitsjamie, Hmains, Skizzik, Anwar saadat, TheDarkArchon, Kurykh, Skookum1, Geneb1955, Persian Poet Gal, DroEsperanto, Ankurjain, Tree Biting Conspiracy, MalafayaBot, GraemeS, Deli nk, Jerome Charles Potts, Baa, Baronnet, Darth Panda, Brinerustle, 56, Gracenotes, Can't sleep, clown will eat me, Shalom Yechiel, Kelvin Case, Chlewbot, Bisected8, Gurps npc, Yidisheryid, Rrburke, DGerman, Juan andrés, Stevenmitchell, Amazon10x, COMPFUNK2, Krich, Korda, CanDo, Ratel, Nakon, B jonas, SunShun32, Jake Lancaster, WookMuff, Rjp0i, Sokolesq, DMacks, Diasimon2003, Kalathalan, Bejnar, Pilotguy, SashatoBot, Lama21, Rory096, Archimerged, Vanished user 9i39j3, Kuru, Akendall, John, Scientizzle, Koft, ML5, KarlM, Geeteshgadkari, Goodnightmush, Mr. Lefty, Ckatz, Beetstra, Kyoko, Waggers, Geologyguy, Ryulong, Citicat, Pseudoanonymous, Jose77, Andoru, NinjaCharlie, Sifaka, ShakingSpirit, Ginkgo100, Emx, Iridescent, Michaelbusch, Joseph Solis in Australia, T.O. Rainy Day, Blakegripling ph, J Di, Igoldste, Shoshonna, Esurnir, MottyGlix, Ketchupkid713, Courcelles, Gilabrand, PaddyM, Chovain, Hossenfeffer, Thricecube, Tawkerbot2, Daniel5127, Pithecanthropus, Poolkris, LessHeard vanU, Lahiru k, Slippyd, JForget, Stifynsemons, Rgriga1, Ale jrb, Sir Vicious, SkyScrapers, Iuio, Scohoust, SupaStarGirl, Rawling, JohnCD, 0zymandias, Casper2k3, Dragon guy, Kribbeh, Icek, Cydebot, Future Perfect at Sunrise, MichaelZX, DrunkenSmurf, Rifleman 82, Gogo Dodo, Cristian Cappiello, Tonymora, Tawkerbot4, Roberta F., DumbBOT, Ameliorate!, Nabokov, Optimist on the run, Robowurmz, Kozuch, Omicronpersei8, Victoriaedwards, WIKIPEDIAVI, Casliber, Click23, Thijs!bot, Epbr123, Bloger, Pstanton, Drewerd, Keraunos, Gamer007, Headbomb, Marek69, John254, Keelm, Dcouprie, Big Bird, Dawnseeker2000, Es-

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J.delanoy, Pharaoh of the Wizards, Trusilver, AltiusBimm, Gem-fanat, Ginsengbomb, Extransit, Amckeen, Vizio, Gzkn, Acalamari, Rod57, NBFNBFF, IdLoveOne, Katalaveno, Gman124, McSly, AndPud, Troutsneeze, Janus Shadowsong, Jeepday, Skier Dude, AntiSpamBot, Spinach Dip, Linuxmatt, Xvedejas, Warut, TomasBat, NewEnglandYankee, SJP, Shoessss, DARKFLIGHTER100, Evil lemming, Jamesontai, Vanished user 39948282, DorganBot, Inter16, V. berus, Squids and Chips, Aescwyn, CardinalDan, Idioma-bot, Spellcast, Rossnorman, Timmduffy, Jgump95, Gogobera, Lights, Hugo999, Rodolph, Deor, 28bytes, VolkovBot, ABF, Macedonian, Christophenstein, Jennavecia, Netito777, AlnoktaBOT, Katydidit, Ryan032, Dougie monty, Philip Trueman, BSMet94, TXiKiBoT, Oshwah, Athiril, Java7837, Sl smith00, Reibot, Mathwhiz 29, Chchan1995, Qxz, Vanished user ikijeirw34iuaeolaseriffic, Piperh, Davelapo555, Martin451, Axiosaurus, Smb1138, Jackfork, LeaveSleaves, Superruss, Wikifreeknturd, Psyche825, Seb az86556, Jessejj89, Kaenneth, 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Bookworm9999, DragonBot, Wthubble, Excirial, Gwguffey, Vivio Testarossa, JoelHuang, Cenarium, Thegreat161, Jotterbot, New4325, Nvvchar, Morel, Enigmatic2k3, Dekisugi, ChrisHodgesUK, BOTarate, Thehelpfulone, Thingg, Aitias, Wuzur, Atder, Versus22, Laurelin17, Wewwjon, SoxBot III, Martim33, 20percent, InternetMeme, Nick in syd, BarretB, XLinkBot, Pichpich, Rror, Holycow1313, SilvonenBot, Mifter, Jasynnash2, WikiDao, SkyLined, HexaChord, 23Burnsie, JBsupreme, Roentgenium111, Denali134, Blackphobia, Landon1980, Dontforgetneeb, Eduardo1111111111, Fieldday-sunday, J619, Ggttthhheeeeswsss, Fluffernutter, Ronkonkaman, 1axvn, Lon of Oakdale, NjardarBot, John Chamberlain, Download, Silverbackmarlin, CarsracBot, BepBot, Glass Sword, AndersBot, Debresser, FCSundae, Baffle gab1978, Jasper Deng, Naidevinci, Alchemist-hp, Numbo3-bot, Modabombrocks, VASANTH S.N., Tide rolls, Tressor, BrianKnez, Verbal, Avono, Teles, A10t2, Ronschmidtling, Drpickem, Luckas-bot, TheSuave, Yobot, Ptbotgourou, II MusLiM HyBRiD II, THEN WHO WAS PHONE?, Nallimbot, Lauren 218, KamikazeBot, IW.HG, Lightenoughtotravel, Tempodivalse, Dmarquard, AnomieBOT, Jim1138, Piano non troppo, Becky-and-annalise, AdjustShift, Law, Theseeker4, Equaaldoors, Alechopkins, Crystal whacker, Flewis, Materialscientist, The High Fin Sperm Whale, Citation bot, Maxis ftw, Comec, PowerUserPCDude, ArthurBot, Quebec99, Parthian Scribe, Xqbot, Tc.bongers, Ywaz, TinucherianBot II, Nxtid, JimVC3, Capricorn42, Gigemag76, RishiKrishnan, Br77rino, Mrdarkside423, Inferno, Lord of Penguins, Srich32977, WingedSkiCap, Qulix rules, Ashsama, GigidyMan123, GrouchoBot, Corruptcopper, Ute in DC, Mvpolis, Omnipaedista, Cjtconner, Coolalchemist001, RibotBOT, SassoBot, Chris.urs-o, Basharh, Doulos Christos, Moxy, Calz22123, Dfcerkoney, Brandon silvis02, Alina1234567890, Heng Da, Dougofborg, Djcam, LucienBOT, Tobby72, Bookworm123454321, Lmxdoomguyx, Arlen22, Danielson183, Saehrimnir, TurningWork, Alxeedo, BamboQ5, Finalius, Cannolis, HamburgerRadio, Citation bot 1, Rethyudis, Diwas, Nirmos, BertQ5, Firenze Light, Pinethicket, I dream of horses, HRoestBot, Bailhound13, Rameshngbot, Skyerise, Bryancpark, Mikespedia, Xeworlebi, Jauhienij, Logical Gentleman, ActivExpression, C messier, Pretin, Tim1357, Gryllida, Guganovic, Double sharp, TobeBot, Themegakornfan, Vrenator, Neelpandey, Pollytc, Yoiloper, Seahorseruler, Ivanvector, Mttcmbs, Tbhotch, DARTH SIDIOUS 2, Farij, MornMore, Cromulant, Sargdub, Silverhands925, Elvis thein, Teravolt, Androstachys, EmausBot, Santamoly, Rbaselt, Pete Hobbs, RA0808, Minimac's Clone, NotAnonymous0, Illogicalpie, Solarra, Slightsmile, Timbow191, Wikipelli, Thewikiman2255, Zabigetsu321, Evanh2008, Comesturnruler, ZéroBot, John Cline, Zincman, Edwardbrian11, Tylercino, StringTheory11, Kiwi128, Chemicalinterest, H3llBot, Netknowle, Gniniv, Osiris384, Wayne Slam, Wagino 20100516, Brandmeister, Donner60, Honesty First, Milestone flyzone, ChuispastonBot, Matthewrbowker, Gibbo10, JohnLloydScharf, Sven Manguard, DASHBotAV, Whoop whoop pull up, Tpronquillo, Michael Bailes, Petrb, Gwen-chan, ClueBot NG, This lousy T-shirt, Satellizer, Real.sim.phony, Vader119, Bped1985, Movses-bot, Twillisjr, Monsoon Waves, Braincricket, Steve85260, Lefty michael, Hurricanes30, XJRZ2U, Something1234567, Alentia, Eli706, RafikiSykes, Vanadium123, Helpful Pixie Bot, Fexlom, Icallitvera, Fallonista, Curb Chain, Titodutta, Gob Lofa, Bibcode Bot, Maggothair, Lowercase sigmabot, Barkerchangesstuff, Jerryjackson42, Finn1234, Minimike171, Brettrimmer, Biggorrilla, Dvbyrne, MusikAnimal, Lucario808, Mark Arsten, Zakoria333, 2bellaisa, Snow Blizzard, TomeHale, Cormac596, Ἑρμῆς, Glacialfox, Loriendrew, Klilidiplomus, Shisha-Tom, Veggie1o1, Miskandar E. 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B., Narco, Gyrobo, Hgrosser, Zsinj, Xchbla423, Yaf, Can't sleep, clown will eat me, Shalom Yechiel, OrphanBot, Snowmanradio, Gurps npc, PyroTom, VMS Mosaic, Hairouna, RedHillian, DGerman, SundarBot, Phaedriel, Stevenmitchell, Huon, HeteroZellous, Cybercobra, Makemi, Nakon, SuperDude511, Jiddisch, Eran of Arcadia, Smokefoot, Gschadow, Xen 1986, DMacks, FelisLeo, Kukini, Ohconfucius, Serein (renamed because of SUL), Swatjester, NotMuchToSay, Attys, Archimerged, Srikeit, Kuru, John, AmiDaniel, Microchip08, Demicx, Buchanan-Hermit, Gm1121983, Disavian, Sir Nicholas de Mimsy-Porpington, Mbeychok, Minna Sora no Shita, NongBot, Aleenf1, Ckatz, The Man in Question, Slakr, Beetstra, Waggers, Tuspm, Magere Hein, Novangelis, H, Jose77, Ubiquitousintelligence, Hu12, BranStark, Sfgagnon, Iridescent, JayZ, Dreftymac, StephenBuxton, Igoldste, FelisSchrödingeris, Jamesy, Thricecube, Tawkerbot2, Pi, Dlohcierekim, Poolkris, Hammer Raccoon, Ccroberts, Owen214, MightyWarrior, SkyWalker, JForget, InvisibleK, Porterjoh, Ale jrb, Earthlyreason, Funion987, KyraVixen, Im.a.lumberjack, Dgw, OMGsplosion, Pyrope, DonCalo, Infodek, Halofan101, MC10, Steel, Vanished user vjhsduheuiui4t5hjri, Rifleman 82, Michaelas10, Gogo Dodo, Difluoroethene, Benjiboi, Odie5533, Tawkerbot4, Dynaflow, DumbBOT, RWG, Briantw, Cherubfish, Omicronpersei8, Gimmetrow, FrancoGG, Rjm656s, Thijs!bot, Epbr123, Bezking, Wikid77, Tsogo3, N5iln, Gamer007, Headbomb, Marek69, John254, Tapir Terrific, A3RO, NorwegianBlue, Sweetgirl20099, Ufwuct, Rhrad, Sinn, CharlotteWebb, Nokhc, Sikkema, MichaelMaggs, Dawnseeker2000, Vernie, Escarbot, Mentifisto, AntiVandalBot, Luna Santin, Opelio, N1ywb, Diched, Jj137, RESURGAM, Chill doubt, Gdo01, Zedla, V----l Sch----l, Myanw, Res2216firestar, JAnDbot, Dan D. Ric, Deflective, Leuko, MER-C, Plantsurfer, Dududuh, Duh duh duh, Nthep, Sheitan, Seddon, Not the duke of Devonshire, Hut 8.5, At the speed of light, PhilKnight, Savant13, Helge Skjeveland, Joshua, Acroterion, Jragon, Mikemill, Karlhahn, Bongwarrior, VoABot II, Jarekt, Confiteordeo, Xnobjafnyy, Avicennasis, Animum, Master of the prick, DINGGGGG!, TICK TOCK, Causesobad, 28421u2232nfenfcenc, Allstarecho, Wikipedia is immoral, Porud!!!, Spellmaster, Vssun, DerHexer, InvertRect, Robdonkey, AliaGemma, Xenonite, Greenguy1090, Riccardobot, S3000, Sire22, MartinBot, Lazybozo, BetBot, A suyash, Arjun01, ChemNerd, Rettetast, Jmac2k6, R'n'B, AlexiusHoratius, Nono64, Pekaje, Smokizzy, EdBever, Tgeairn, Watch37264, J.delanoy, Trusilver, Dansmith01, Bogey97, Davep1987, Sirtrebuchet, Extransit, WarthogDemon, GeoWriter, Davidprior, Ijustam, Gzkn, BrokenSphere, Katalaveno, DarkFalls, McSly, Eric in SF, JayFout, Devils angel10, Coppertwig, (jarbarf), Warut, Krasniy, NewEnglandYankee, Rominandreu, SmilesALot, Chasw0405, Minesweeper.007, Juliancolton, Cometstyles, WJBscribe, RB972, Moondoll, U.S.A.U.S.A.U.S.A., Vanished user 39948282, DorganBot, Jarry1250, Useight, Adamankin, Ads85, Hogahasfa, Cjh57, Squids and Chips, CardinalDan, Idioma-bot, My Core Competency is Competency, Farley666, VolkovBot, CWii, ABF, Thisisborin9, DSRH, Wiseman75, Jeff G., Jennavecia, Chris Dybala, AlnoktaBOT, Soliloquial, Pparazorback, Philip Trueman, TXiKiBoT, JohnSRoberts1, Toll booth, Hqb, GDonato, Rei-bot, AWP1012933, Qxz, Piperh, Oxfordwang, Anna Lincoln, Una Smith, Melsaran, Corvus cornix, Axiosaurus, Leafyplant, Jackfork, LeaveSleaves, From-cary, Psyche825, Seb az86556, Soniiic, Cremepuff222, Bevanhouston, FuddRucker, Kfholmesattivor2, LPFixIt, Axlenz, Lamro, Hintersatz, Tomaxer, Enviroboy, Turgan, Vector Potential, Ssryry2, RaseaC, Insanity Incarnate, Wavehunter, AlleborgoBot, LuigiManiac, Sfmammamia, Dodo von den Bergen, PericlesofAthens, Kbrose, Gaelen S., SieBot, You knnow who, You knnow what, Ttony21, Tresiden, PlanetStar, Jrm2007, Dawn Bard, Caltas, Calabraxthis, Andrewjlockley, France3470, Aillema, Flyer22, Snshady, Joseph 098, Clan Lord, Afroman rmb, Oda Mari, Profesorytatori, DaBler, Misbahkhaninuk, Courtss, Oxymoron83, Antonio Lopez, AngelOfSadness, Panicitsnore, Grunkhead, Alex.muller, Macy, Andrij Kursetsky, C'est moi, Pemmy, StaticGull, Thelmadatter, Anchor Link Bot, Latics, Spazure, Mygerardromance, Indmin, Pinkadelica, Nergaal, Precious Roy, Troy 07, Solidus469, WikipedianMarlith, Hpdl, ClueBot, Reza kalani, Identification01, Bleedingshoes, The Thing That Should Not Be, Nnemo, Pi zero, Tanglewood4, NPIC, Dwitow, Cp111, Uncle Milty, DanielDeibler, Boing! 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Wilson, Mikkelskov, Bobthebigmanwhite, Lboscher, ClueBot NG, Satellizer, Rezabot, Widr, Hans Frörum, Mogism, CarlesMillan and Anonymous: 40

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Kingofkings450, Blacklabpuppy, Thehelpfulbot, Gemstonesmarket, FrescoBot, Dogposter, Pepper, Archaeodontosaurus, Clehane1, A little insignificant, HamburgerRadio, Kfong13, AstaBOTh15, Snazzra, Pinethicket, Merlind, A8UDI, Bryancpark, Hantzen, Tretertret, ContinueWithCaution, Jahahn, Jauhienij, SkyMachine, TobeBot, ItsZippy, SeoMac, Tobias1984, Defender of torch, Antipastor, Reaper Eternal, Fastilysock, Jhenry922, Minimac, VernoWhitney, Beyond My Ken, CalicoCatLover, DASHBot, John of Reading, Ozric14, Yeahitsmenick, ScottyBerg, Super48paul, Good888, Princess Lirin, Wikipelli, John Cline, Daonguyen95, Josve05a, CapeMayDiamonds, Access Denied, Goraghosh, EWikist, Surya Prakash.S.A., Wayne Slam, Tolly4bolly, Jsayre64, Aidarzver, Fpr155, Donner60, Aemartz, ClueBot NG, MelbourneStar, GallaghersGreek, Feedintm, Fatdog23, Basti cz, The High Fin Sock Whale, Widr, Mollberg, PrincessWortheverything, Iste Praetor, KD888, Thelegendarysauron, Curb Chain, Arnavchaudhary, GeodeFinder, Kangaroopower, Cyberpower678, MusikAnimal, Dan653, Raven Sees The Ages, Eric198739, Rutebega, Alopor, Justincheng12345-bot, Cyberbot II, Ziggley1696, Shyncat, BuzyBody, Dexbot, Vanquisher.UA, Lugia2453, Samlivesinnovascotia, Telfordbuck, Eyesnore, Alphaceo, Rochefoucauld, Nanapanners, Awesomeness1311, Storeadr000, Rachelcal1231, Karla776, Happy Attack Dog, Therizinosaurian, Trackteur, GenuineGemGeek, Oliverhanson, Adambob, Aurelienreys, Bebekidz3, ModestOhaio, Aluracein82, AngryZinogre, SugarQuartz, Nicogutlol and Anonymous: 715

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Gustafson, Camw, LOL, Uncle G, Robwingfield, Benbest, KaurJmeb, Cbdorsett, SDC, CharlesC, Wdanwatts, Christopher Thomas, Mandarax, Magister Mathematicae, Sjö, Saperaud, Sjakkalle, Rjwilmsi, Guyd, Jake Wartenberg, Panoptical, Soakologist, ScottJ, DoubleBlue, Titoxd, FlaBot, Crazycomputers, EronMain, Chobot, DVdm, Gwernol, YurikBot, SatuSuro, RussBot, Rxnd, Limulus, Stephenb, Rsrikanth05, Bovineone, Ugur Basak, NawlinWiki, Wiki alf, Arichnad, Dake, Coderzombie, Iancarter, Bota47, Nick123, Rwxrwxrwx, Lt-wiki-bot, Ninly, Closedmouth, Josh3580, BorgQueen, Spliffy, Ethan Mitchell, ArielGold, Katieh5584, Kungfuadam, JDspeeder1, Samuel Blanning, Cmglee, DVD R W, That Guy, From That Show!, Akrabbim, Bluesun geo, SmackBot, Hobbes2k, Selfworm, Zerida, Kimon, Bomac, Finavon, Lsommerer, PJM, Josephprymak, Canthusus, HalfShadow, Xaosflux, Pzavon, Gilliam, Skizzik, Enno, JMiall, Chris the speller, Thumperward, Qasdzxc, SchfiftyThree, TheFeds, DHN-bot, Darth Panda, Audriusa, Can't sleep, clown will eat me, OrphanBot, TheKMan, Rrburke, Addshore, SundarBot, Alanf777, -xfi-, Rolinator, Dreadstar, RandomP, DMacks, Maelnuneb, Trackerball, Bejnar, Dogears, Rory096, Fremte, Dreslough, Kipala, Xornok, Coredesat, Minna Sora no Shita, Tlesher, Aleenf1, IronGargoyle, Slakr, TFNorman, Rickert, Waggers, Geologyguy, Jose77, ShakingSpirit, Hu12, DabMachine, Olivierd, BranStark, Wizard191, BananaFiend, Iridescent, Igoldste, Tony Fox, Octane, Mulder416sBot, Courcelles, Tawkerbot2, Poolkris, Le savoir et le savoir-faire, Ale jrb, Glennlowney, GeorgeLouis, Dgw, Geekers, ArgentTurquoise, Barbarianbug, Clayoquot, Gogo Dodo, Christian75, Nabokov, Viridae, Pinky sl, Jstuby, Aldis90, הסרפד, Rosser1954, Thijs!bot, Epbr123, Samuel sogunle, Marek69, SouthernMan, Neil916, Electron9, Kulveer, Snoop0x7b, AntiVandalBot, Omphacite, Voyaging, Mountolive, Jj137, Mikenorton, Volcanoguy, JAnDbot, Deflective, Leuko, Husond, Barek, Plantsurfer, Ericoides, Instinct, Armagion, Carlos Botelho, Andonic, Coolhandscot, 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