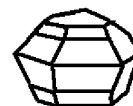


May 2004 Mineral of the Month: Sulfur

One of the most versatile elements, sulfur is absolutely necessary for life, yet some of its compounds are positively lethal. Neither we nor modern civilization can exist without it. We invite you to consider this beautiful element in all its forms and with all its fascinating properties.

PHYSICAL PROPERTIES

Chemistry: S Native sulfur, usually pure. Selenium and tellurium may be present in small amounts.
Class: Native elements Group: Sulfur
Crystal System: Orthorhombic. Dimorphous with rhombic sulfur (S), which is γ -sulfur and is monoclinic
Crystal Habits: Usually as small crystals or irregular masses imperfectly crystallized. Also, granular massive, reniform, stalactic, as incrustations, earthy
Color: Bright yellow; with impurities to shades of green, gray, and red
Luster: Resinous to greasy in larger crystals, but vitreous in small, well-formed crystals
Transparency: Transparent to translucent
Streak: Colorless
Cleavage: Imperfect
Fracture: Uneven to conchoidal; brittle
Hardness: 1.5-2.5
Specific Gravity: 2.05-2.09
Refractive Index: 1.958-2.245
Luminescence: None
Distinctive Features and Tests: Unmistakable transparent yellow crystals; softness; low melting point; extremely strong sulfur dioxide (rotten egg) smell and blue flame when burnt
Dana Classification Number: 1.3.5.1



NAME

The name derives from the Middle English *sulfre* or *sulphre*, from the Latin word *sulphur*, and can be spelled sulfur or sulphur, though for the sake of uniformity, the first spelling is preferred. The ancient Greeks called it "thios," from a root word meaning "God" (found in such modern words as theology and theocracy) because they believed sulfur was God-given. In former times, it was known as "brimstone," meaning "the stone that burns."

COMPOSITION

In our 99th month, we are featuring this essential element for the second time, the first time being August of 1997. This is the fourth native element we have featured, the others being gold, copper, and carbon in one of its minerals forms as diamond, and this is now the fourth mineral we have featured twice, after fluorite, aragonite, and apatite.

Not counting the free gases in the atmosphere, sulfur is one of only about thirty elements that can be found in the native state, that is, uncombined with any other elements, and is the most abundant native element, accounting for about 0.05% (1/10,000) of the earth's crust. Specimens of most native elements are rare, however, as most elements combine with others to form minerals. This is especially true of sulfur, whose atomic structure is such that it is highly reactive and readily combines with a number of other elements, as we will see.

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Scientists divide the native elements into three groups: metals, semi-metals, and nonmetals. Metals, such as gold, silver, copper, platinum, and iron, tend to be heavy, soft, and malleable. The semi-metals, such as arsenic, antimony, and bismuth, are also heavy and soft, but are brittle rather than malleable. The nonmetals, such as sulfur, diamond, and graphite (the last two of which are native carbon), have little in common with the metals or semi-metals or each other.

Sulfur is a highly active element, so-called because it readily combines with other elements to form compounds. Its atomic structure allows it to share several of its electrons in different circumstances. For example, like oxygen, (listed in Group VI of the Periodic Table along with sulfur, selenium, tellurium, and polonium,) its outer ring is two electrons short of being complete (see Atoms, Elements, Crystals and Everything Else in Our Universe), and as a result, sulfur easily combines with other elements, particularly metallic ones. Hundreds and hundreds of minerals contain sulfur as an integral part, so many that they make up several of the mineral classes:

The **sulfides class** consists of minerals containing sulfur bonded to a metallic cation, the most abundant being iron, copper, and zinc. The majority of ore minerals (pyrite, galena, sphalerite, chalcopyrite, marcasite, cinnabar, realgar, orpiment, stibnite and many others) belong to this class. Most sulfide minerals are opaque with distinctive colors, metallic lusters, high specific gravities, and tend to form in hydrothermal ore veins. The rarer sulfarsenides, arsenides, and tellurides are also included in this class.

The **sulfosalts** are also part of the sulfides class. These contain sulfur ions bonded to a metallic element as above along with a semi-metallic element, usually antimony, arsenic, or bismuth. The sulfosalts are found as minor minerals associated with the more common sulfides in hydrothermal veins.

In the **sulfates class** are minerals containing $(\text{SO}_4)^{2-}$ as the anion. There are hundreds of minerals in this class, further divided according to the presence of water, hydroxyl, or one of the halogen elements such as chlorine. Minerals in this class tend to be soft, fragile, and lightly tinged with color, except those that contain copper. Many are not stable. The chromates, molybdates, and tungstates are included in this class. The best known and most stable sulfate minerals are gypsum, barite, celestite, and anhydrite.

Native sulfur exists in two forms, or allotropes, with different properties. When it forms as orthorhombic crystals, it is classified as sulfur, but when it forms as monoclinic crystals, as a mineral it is called rosickýite, named for Vojtech Rosický, former Director of the Mineralogical and Petrological Institute of Masaryk University, Brno, Czechoslovakia. (A third form is plastic sulfur, made by pouring molten sulfur into cold water, but being man-made it is not recognized as an approved mineral.) Orthorhombic sulfur is also called alpha sulfur, and is generally stable below 205°, while monoclinic sulfur (rosickýite) is also called beta-sulfur, and is generally stable between 205° and sulfur's melting point, 246°.

Native sulfur forms in groups of eight atoms that form a ring by sharing electrons to complete their outermost shells. At times, selenium, a semi-metallic element rarely found as a native element, can be incorporated into the sulfur crystal structure, in which case the mineral is called selenian, or selen-sulfur, and has a more orange-yellow color and higher specific gravity. The mineral selenian is quite rare.

Native sulfur forms chiefly in two very distinct ways. The first is when sulfur-containing gases such as hydrogen sulfide or sulfur dioxide escape from the mantle of the earth through volcanoes and fumaroles, vents in the earth's surfaces that emit hot gases, usually found in volcanic areas. Upon contact with the much cooler atmosphere, some of the gaseous sulfur alters from a gas to a solid and is deposited in cracks and openings, a process known as sublimation.

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The other method of sulfur formation is more complex. It starts with huge underground beds of the sulfate minerals gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4), which contain calcium, sulfur, and oxygen. A bacterium called anaerobe, which can live and grow in an environment where there is no air, decomposes these minerals and live off the extracted oxygen, leaving behind the calcium and sulfur as calcium sulfide (CaS). Underground water then comes into contact with the calcium sulfide, and the calcium combines with the H_2O to form calcium carbonate (CaCO_3) in the form of calcite and aragonite, freeing the sulfur to crystallize in a native, uncombined state.

COLLECTING LOCALITIES

The world's finest sulfur crystals come from large deposits on the island of Sicily. Although there are volcanoes nearby, the grand sulfur deposits on Sicily were formed by the second method mentioned above. There the sulfur crystals are found in association with calcite, celestite, aragonite, halite, and selenite in extraordinarily attractive combinations. We rarely see Sicilian sulfur specimens for sale, so you might consider adding one from this classic locality to your collection if you find some at a fair price.

Other outstanding localities include salt domes in Louisiana and Texas; fumaroles in Yellowstone Park, Wyoming; in California at Sulphur Bank, Lake County, the Leviathan Mine, Alpine County, and Mt. Shasta, Siskiyou County; Mauna Loa and Kilauea, Hawaii; San Felipe, Baja California, Mexico, where our August 1997 featured specimens were dug; Conil near Cadiz, Spain; Shor Su, Fergana, Uzbekistan; localities in Japan's volcanic regions; the White Islands of New Zealand; and Bolivia, as we will see.

JEWELRY & DECORATIVE USES

Native sulfur's unique properties make it unsuitable for gem use. It is too brittle and weak, and large crystals, when placed near the ear, can even be heard to crack from the warmth of our fingers! Most minerals containing sulfur are not suitable for jewelry, either.

However, as a display mineral, it is a completely different story. One would be hard pressed to find an excellent mineral collection that does not contain numerous fine specimens of native sulfur and sulfur-containing minerals.

HISTORY & LORE

Historians believe that the ancient cultures centered on the Mediterranean Sea were familiar with nine of the elements, namely, gold, silver, copper, lead, iron, tin, mercury, carbon, and this month's featured mineral. They were cognizant of sulfur's low burning temperature and its acrid odor and put these properties to good use.

Sulfur was used as a pigment for paint and as a medicine, and its fumes, which are deadly in high concentrations, were used to fumigate their homes and to bleach their cloth. The earliest known gas warfare took place during an attack on a Greek city in 424 B.C., when attackers sent a pungent cloud of sulfur dioxide on the wings of the wind toward the enemy city. The Romans used sulfur in making the first matches. South and North American Indians used sulfur in ceremonial healings and offerings.

The earliest Scriptural reference to sulfur is in connection with the destruction of Sodom and Gomorrah. Here fire and sulfur rained down, perhaps from a volcanic eruption in the area, as suggested by the prevalence of sulfur in the region today. Many believe that the high-temperature incinerator in the Valley

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of Hinnom (Greek, *Gehenna*) just outside ancient Jerusalem was kept burning by the addition of sulfur.

Alchemists of the Dark and Middle Ages believed that all metals were made of sulfur and mercury and performed countless experiments mixing the two with other compounds in a futile effort to create gold. With the arrival of gunpowder from the Orient, the demand for sulfur, a key ingredient, took off, and sulfur mining was undertaken in Sicily at least a thousand years ago.

Modern-day metaphysicists attribute to sulfur the ability to remove negative willfulness, eliminate distracting intellectual thoughts and emotions, attract non-caustic attributes and attitudes, and promote an abundance of energy, flashes of inspiration, and melt the barriers-blocking process.

TECHNOLOGICAL USES

Our modern technological world would not exist without sulfur. In the form of sulfuric acid (H_2SO_4), it is used in nearly every industry, not just in the creation of sulfur-containing products, but as a chemical agent in the manufacturing of many chemical products. Sulfur is used in the making of matches, gunpowder, fireworks, medicines including insulin, dyes, car batteries, detergents, insecticides, fertilizers, steel, aluminum, paper, textiles, skin ointments, in processing photographs, and in fumigation.

In 1839, American inventor Charles Goodyear (1800-1860), who had been trying unsuccessfully for many years to find some means to improve the quality of sticky, runny natural rubber, dropped on a hot stove a piece of rubber he had treated with sulfur, thus accidentally discovering that rubber heated with sulfur at a high temperature had greatly improved strength. This process became known as vulcanization and is the basis for all current uses for rubber.

Sulfur was used in the past in the manufacturing of paper, and still is today for cheap paper, and is the reason such paper yellows. When used as a solvent (in the form of sodium sulfate or magnesium sulfate) to remove lignin, the organic substance forming the essential part of woody fiber, some sulfur would remain in the paper and with the passing of time, turn the paper yellow and then create sulfuric acid, which makes the paper become brittle and fall apart.

Sulfur is mined for all these activities from the world's largest known sulfur deposit, beneath the waters of the Gulf Mexico along the Gulf Coast of Texas, Louisiana, and Mexico. No sulfur specimens will ever be recovered from this huge deposit, however, because of the destructive mining process used there, known as the Frasch process, after its inventor, German-born American chemist Herman Frasch. This process, invented in 1890 after four men were asphyxiated by hydrogen sulfide gas while trying to remove the sulfur by normal mining methods in Louisiana, involves forcing superheated water down a well into the sulfur bed, melting the sulfur, then pumping it to the surface, to cool and recrystallize in massive blocks, some 40 feet high and covering about 5 acres each!

Sulfur is also an essential part of life. It is present as a component of amino acids in our hair, fingernails, and skin, and in breast milk. The disagreeable odor resulting from flatulence is caused by compounds of sulfur. Many organic compounds containing sulfur have a foul stench, particularly a group of compounds called thiols, or mercaptans, where sulfur substitutes for oxygen in the form of the OH (hydroxyl) radical. Thiols can be sensed in very low concentrations, and are responsible for the awful stench emitted by skunks. Foul-smelling thiols in small concentrations are added to odorless natural gas to help detect leaks. Other thiols have a pleasant (to some) aroma, such as those found in garlic.

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Important Sulfur Compounds

Sulfuric acid (H_2SO_4) is a clear, dense, oily, highly reactive liquid, formerly known as vitriol. Water added to sulfuric acid boils immediately, a very dangerous reaction. Sulfuric acid dissolves many metals, and is a strong dehydrating agent. Protective care must be used in handling it, for it immediately reacts with human skin, removing water from skin molecules and forming an acid burn. Sulfuric acid is used to convert phosphate-containing rock into fertilizer, as the electrolyte in lead-acid batteries, to remove impurities from gasoline and kerosene, to clean the surface of steel, and in the making of artificial fibers, explosives, paints, paper, and textiles.

Hydrogen sulfide (H_2S) is a highly poisonous gas with a choking odor, found in fossil fuels and produced by decaying matter.

Sulfur dioxide (SO_2) is a dense, colorless, foul-smelling, poisonous gas. It is used as a bleaching agent and food preservative. When released into the atmosphere by petrochemical or other refineries, it causes severe environmental problems.

Sulfites (SO_3^{-2}) are widely used to preserve food and wine. These work by removing oxygen from air, denying fungi, insects, and other undesirables needed air to breathe. Similar sulfur compounds create mildly acidic environments that organisms cannot survive.

Dichlorodiethyl sulfide ($\text{Cl-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-Cl}$), commonly called Mustard gas, is a horrible weapon of war first used during World War I. When breathed in, it damages the cells of the lung lining, causing fluid to leave the blood and fill the lungs, drowning the victim. Even small amounts damage the skin and permanently damage the lungs.

Many other sulfur compounds are an essential part of everyday life.

At shows, many people instinctively pick up and sniff at our sulfur specimens, not realizing that pure sulfur has no taste or odor. They wonder why some sulfur compounds smell like rotten eggs. Actually, it should be phrased the other way around. When an egg rots, hydrogen sulfide is produced, with its characteristic obnoxious smell. Sulfur is also present in the oils of mustard, garlic, and onion. When we slice an onion, a sulfur-containing enzyme causes a mild chemical reaction, releasing sulfenic acids. When this mild acid reacts to the moisture protecting our eyes, a mild sulfuric acid is produced, irritating the eyes, and our tear ducts produce more water to dilute the acid and protect our eyes.

On the negative side, sulfur dioxide is released into the atmosphere through the burning of fossil fuels such as gas, coal, and oil, and is one of the worst air pollutants. When sulfur dioxide combines with moisture in the air, sulfuric acid is produced and carried long distances to fall to the earth as a primary constituent of acid rain, snow, and fog.

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ABOUT OUR SPECIMENS

Our excellent specimens come from El Desierto Mine, a sulfur mine near the border of Bolivia and Chile, about 200 miles west and slightly south of Potosí, Bolivia. The mine is just south of the Salar de Empexa, one of several enormous salt flats in southwestern Bolivia, including the Salar de Unuyi, which at three millions acres of blinding white salt is the world's largest salt flat. The July-August 2003 *Mineralogical Record* provides an excellent firsthand account by Alfredo Petrov of the arduous (to say the least) trip to reach the mine.

To say conditions are harsh here in the high-altitude plain called Altiplano is an understatement. As Mr. Petrov writes: "The miners . . . were being paid about eight times more per week than the average Bolivian miner, but they were earning every penny of it the hard way. Their eyes were burned bright red by the acidic sulfate dust. Their clothes and shoes were also being destroyed by the acid. No one had had a bath in six weeks. One miner had arrived at the work site with his wife and two small children, and everyone in the family was infested with lice. After two days at the mine, the lice were dropping off dead. (A visit to this mine would probably also be a rapid cure for stubborn fungal infections of the skin!)"

El Desierto is one of many sulfur mines in this part of western Bolivia, and has been worked since the early 20th century, producing almost pure sulfur, with some containing only small amounts of arsenic and selenium. Other minerals found here include potassium alum $[\text{KAl}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}]$, coquimbite $[\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}]$, kalinite $[\text{KAl}(\text{SO}_4)_2 \cdot 11\text{H}_2\text{O}]$, mirabilite $[\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}]$, melanterite $[\text{Fe}^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O}]$, alunogen $[\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}]$, and pickeringite $[\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}]$. As you notice from the formulae, all are sulfate minerals and contain water. These final two are present in the matrix, which must be treated to prevent it combining with atmospheric hydrogen to form sulfuric acid, which destroys the paper the specimens are wrapped in at the mine, and would destroy our boxes if not treated. Other minerals found in the matrix are clay minerals, hyalite, alunite, gypsum, and minor films of manganese oxides.

Most Bolivian sulfur mines are located at high altitudes in volcanic craters of the Western Andes Mountains. El Desierto and the other local mines are seated in an old debris avalanche, a Pliocene (from two to thirteen million years ago) volcanic ash bed. There is still some fumarolic activity at the mine, and parts of the sulfur deposit occasionally catch on fire, as sulfur burns so easily. Such fires can only be extinguished with water, a very scarce resource in this high desert! The mines are owned by Empresa Minera Clavijo, which estimates reserves at millions of tons, so mining should continue here for quite a while. Specimen collecting is allowed with permission from the mine manager.

In this write-up, we have noted in detail some of sulfur's beneficial and destructive properties. Care must be exercised in handling and storing sulfur specimens, to avoid activating any of these properties. Some recommend not washing sulfur specimens, so it cannot react with water. Others recommend storing sulfur specimens away from other minerals, so sulfur compounds do not affect other specimens in the collection. Probably the best idea is to keep an eye on our collections to watch for damage at all times. We hope we have piqued your interest in this diverse element and enhanced your appreciation for your specimen!

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