

Feature

Element of the Month

Sulfur

Produced inside massive stars by fusion of one nucleus of silicon with a nucleus of helium through the *alpha process*, sulfur, a Group XVI polyatomic nonmetal with 16 protons in its nucleus, is the 10th most abundant element in the Universe!

Described as an element in 1777 by Antoine Lavoisier, sulfur, derived from the Sanskrit word *sulvere*, comprises about 0.05% of the Earth's crust. It is a multivalent "p-block" nonmetal element that is often found in its native form, but more commonly occurs combined directly with metals to form primary sulfides, or in oxidized compounds as sulfate salts. In fact, sulfur reacts with all elements except gold, platinum, iridium, tellurium, and the noble gases (helium, argon, et al).

The principal ores of copper, zinc, nickel, cobalt, molybdenum, and other metals are sulfides. These minerals tend to be dark-colored, and 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.

Common sulfur-bearing minerals include the sulfides *pyrite* (iron sulfide, FeS), *chalcopyrite* (copper iron sulfide, CuFeS_2), *galena* (lead sulfide, PbS), and *sphalerite* (zinc sulfide, ZnS);

and the sulfates *gypsum* (hydrous calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), *epsomite* (hydrous magnesium sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), *barite* (BaSO_4), and *celestite* (SrSO_4).

Sulfur also occurs abundantly in its native form. The atoms combine in crown-shaped, cyclic octatomic molecules that form a bright yellow orthorhombic crystalline solid at ordinary temperatures. Thus, the mineral that is formed, α -sulfur, has a chemical formula of S_8 . At higher temperatures the molecules rearrange into the monoclinic polymorphs β -sulfur and γ -sulfur (*rosickyite*) that differ only in how the rings are packed. However, β -sulfur will revert to the orthorhombic form when the temperature drops below 95.3°C . Sulfur



melts at 115.21°C (239.38°F), boils at 444.6°C (832.3°F) and sublimates easily at 95.2°C (203.4°F). Its density is about 2 g/cm^3 , depending on the allotrope; all of the stable allotropes are excellent electrical insulators.

Since elemental sulfur is so common in nature, it was known in prehistoric and ancient times, finding various uses in Greece, Egypt, China, and India. Early humans presumably employed sulfur's characteristic yellow coloring for cave paintings, and the mineral was referred to in Genesis as *brimstone*. Burning sulfur produces a blue flame, thus it was widely used by priests in temple rites for *purification*. In traditional skin treatment, elemental sulfur was used (mainly in creams) to alleviate such conditions as scabies, ringworm, psoriasis, eczema, and acne.

According to the Ebers Papyrus, a sulfur ointment was used in ancient Egypt to treat granular eyelids. Additionally, it was used first by Egyptians, then Greeks and Romans, to bleach cottons and linens, and burned in homes as a fumigant. In this vane, Homeric writings (particularly in the *Odyssey*) mention sulfur as “pest averting.”

Alchemists attempted to incorporate sulfur's “yellowness” into other substances in the pursuit of producing gold. Indian alchemists, practitioners of “the science of mercury,” wrote extensively about the use of sulfur in alchemical operations with mercury from the eighth century AD onwards.

Nevertheless, probably the best-known use for sulfur dating from historical times is as the main ingredient in gunpowder (a mixture of potassium nitrate, charcoal, and sulfur), ostensibly discovered by the Chinese circa the 12th century.

Sulfur is present in many types of meteorites, usually in sulfide form. Ordinary chondrites (stony, non-metallic, and non-magnetic) contain on average 2.1% sulfur, although carbonaceous varieties contain as much as 6.6%, normally as the mineral troilite (hexagonal FeS). The distinctive colors of Jupiter's moon, Io, are attributed to various types of sulfur products in molten, solid, and gaseous states.

On Earth, elemental sulfur is ubiquitously found near hot springs and volcanic regions in many parts of the world. Such sources are currently mined in Indonesia, Chile, and Japan. Historically, Sicily was the major source of sulfur during the Industrial Revolution.

However, deposits of native



sulfur synthesized by anaerobic bacteria acting on sulfate minerals, primarily gypsum, have also been found in geologic formations called salt domes (thick beds of evaporate minerals, primarily halite, that have intruded vertically into overlying rock strata). The first such dome was surreptitiously discovered in 1890 during exploratory drilling in Beaumont, Texas.

In 1894, Herman Frasche (1851-1914) invented the mining process by which superheated water was pumped down into the deposit, thereby melting the sulfur, which could then be forced to the surface by compressed air. Six years later, the Frasche process allowed extensive sulfur deposits in Texas and Louisiana to be profitably mined, thus providing a new source of high-purity (99.5%) elemental sulfur, and harkening the golden age of the US sulfur industry, which ranked first as world producer by 1914, well above Sicily.

Due to economic pressures exerted by the cheap recovery of hydrogen sulfide as a byproduct from petroleum refining, the Frasche process was discontinued in the US in 2002, but is still used in Mexico and Poland. Such sources are now of secondary commercial importance, and most are no longer worked.

A Collection of Sulfur Minerals

I 20 C



I 02 D



α -Sulfur

*Bladed crystals filling
pockets in Geyserite.*

Specimen about 2.5 x 2 inches
Yellowstone National Park

Sulfur

*Crystalline aggregate embedded
in weathered, impure mass.*

Specimen 3.75 x 2.25 inches
Goldfield, NV

I 06 D

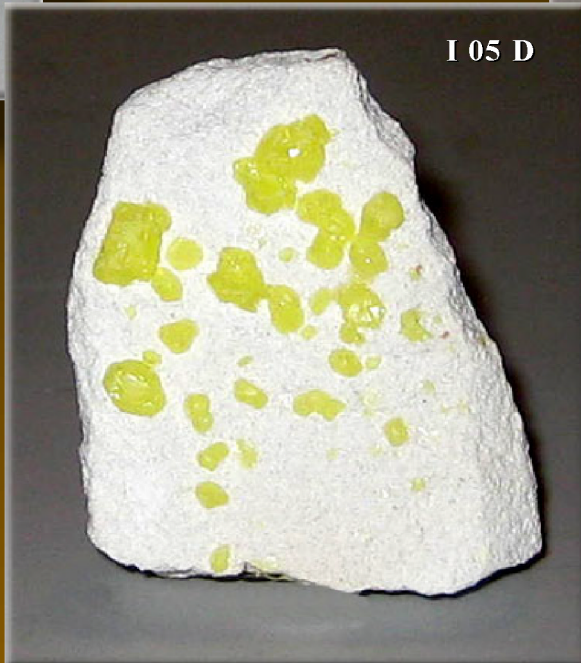


Frasche Sulfur

*Block of re-crystallized native
element from salt dome.*

Specimen about 2 x 2.25 inches
Texas

I 05 D



α -Sulfur

*Blocky and tabular crystals
on volcanic ash.*

Specimen about 1.5 x 1.75 inches
Baja, Mexico

All specimens from the G. Miles Lehman Collection

A Collection of Sulfur Minerals



Enargite

*Massive aggregate of crystals
altering to
unknown green arsenate.*
Specimen 4 x 3.5 inches
Mexico



Gypsum

Prismatic aggregate on clay matrix.
Specimen 4.5 x 2.5 x 2.5 inches
Mt Gunson; SA, Australia



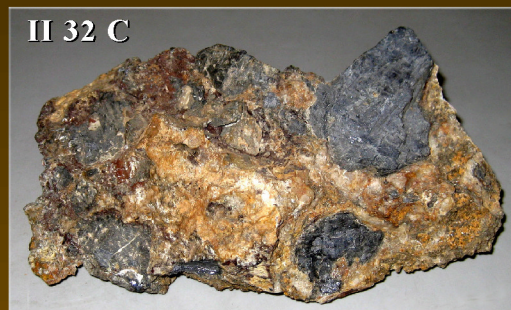
Copiapite

*Non-matrix xl aggregate with
Halotrichite and Chalcantithite.*
Specimen 3.25 x 2.75 inches
Antler Mine
Kingman, AZ



Realgar

Bladed crystals in Ulexite
Specimen 1.75 x 1.5 inches
Boron Open Pit Mine
Boron, Kern Co., CA



Galena

*Massive sulfide in hydrothermal
replacement deposit in limestone.*
Specimen approx. 7 x 4 inches
Lookout Mine; Goodsprings, NV



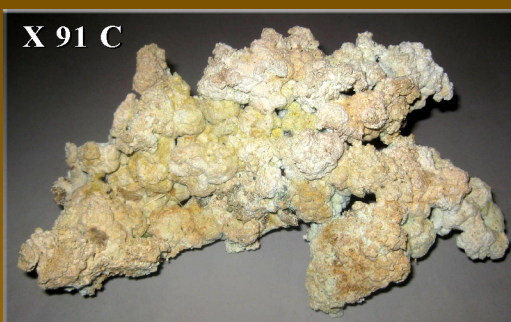
Coquimbite

*Purple crystals with Alunogen,
Halotrichite, and Romerite.*
Specimen 5 x 3.6 cm
Javier Mine
Huachuas, Peru



Sphalerite

*Granular aggregate of
crystals in limestone.*
Specimen 2.5 x 2.25 inches
Potosi Mine
Goodsprings, NV



Halotrichite

*Radial acicular crystals
with Copiapite and Pisanite.*
Specimen 7.75 x 4.58 inches
Antler Mine; Kingman, AZ



Chalcopyrite

*Massive sulfide fragment
without matrix.*
Specimen 1.38 x 1.25 inches
Allured Mine
Ivanpah Mountains, CA

All specimens from the G. Miles Lehman Collection

Sulfur remains one of the basic materials of industrial manufacturing. World production in 2011 amounted to about 69 million tons (Mt). More than 15 countries contributed over 1 Mt each, led by China (9.6 Mt), USA (8.8 Mt), Canada (7.1 Mt) and Russia (7.1 Mt).

Mainly converted to sulfuric acid, this workhorse of chemistry is a major component in the manufacture of fertilizer and hundreds of other applications, including agriculture, chemicals, detergents, feed additives, synthetic resins, carbon bisulfide, iron and steel, pulp, pigments, leather extraction, matches, insecticides, etc.

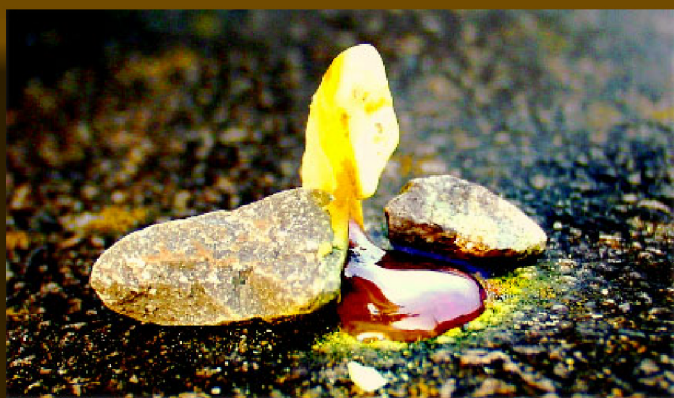
Disulfides (characterized by S—S bonds) confer mechanical strength and insolubility to the protein *keratin* found in skin, hair, fingernails, feathers, etc. These same bonds are a structural component used to stiffen rubber. In the most common type of industrial curing (i.e. hardening and strengthening) of natural rubber, elemental sulfur is heated with the rubber to the point that the chemical reactions form disulfide bridges between isoprene (*2-methyl-1,3 butadiene*) units of the polymer. Patented in 1844 by Charles Goodyear, this process, called *vulcanization*, eventually made rubber a major industrial product, especially for automobile tires.

Many sulfur compounds are odoriferous, and the smells of odorized natural gas (methanethiol; CH_3SH), skunk scent (*(E)*-2-butene-1-thiol and *3-methyl-1-butanethiol*), grapefruit (grapefruit mercaptan; *(R)*-2-(4-methylcyclohex-3-enyl) propane-2-thiol; pleasant in low concentration), and garlic (allicin; *2-propene-1-sulfinothioic acid S*-2-propenyl ester) are due to organosulfur compounds. Hydrogen sulfide (H_2S) gives the characteristic odor to rotting eggs and other biological processes.

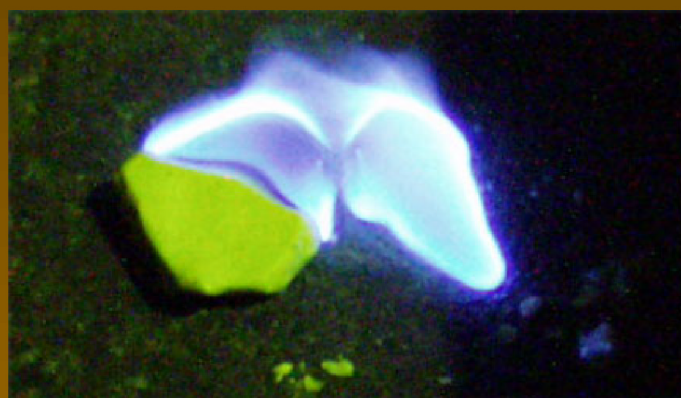
Sulfur is an essential element for all life, almost always in the form of metal sulfides and organosulfur compounds, including amino acids such as *cysteine*, *cystine*, and *methionine*, and the vitamins *biotin* (B7) and *thiamine* (B1). Many cofactors also contain sulfur, including *glutathione*, *thioredoxin*, and iron-sulfur proteins.

Elemental sulfur is non-toxic, as are most of the soluble sulfatesalts, such as Epsom salt. Soluble sulfate salts are poorly absorbed and serve as effective laxatives. When injected parenterally, they are freely filtered by the kidneys and eliminated with very little toxicity in multi-gram amounts.

On the other hand, hydrogen sulfide is as toxic as hydrogen cyanide, and kills by the same mechanism (inhibition of the respiratory enzyme *cytochrome oxidase*), though hydrogen sulfide is less likely to cause surprise poisonings from small inhaled amounts, because of its disagreeable odor. Hydrogen sulfide quickly deadens the sense of smell and a victim may breathe increasing quantities without noticing the increase until severe symptoms cause death. Dissolved sulfide and hydrosulfide salts are toxic by the same mechanism.



Sulfur melts to a thick red liquid . . .



and burns with a blue noxious flame

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. Being multivalent, the +4 and +6 valences are most common, while the +2 oxidation state is rare. Sulfur burns with a blue flame, forming sulfur dioxide, a suffocating and irritating gas.

Sulfur has over 30 solid allotropes (different forms of an element within the same phase, i.e. solid, liquid, gas), more than any other element. Besides S₈, several other molecular rings are known. Removing one atom from the crown gives S₇, which is more deeply yellow than S₈. Larger rings have been prepared, including S₁₂ and S₁₈. At 444°C sulfur boils to a vapor containing S₈, S₆, S₄, and S₂ molecules.

There are more than 20 known isotopes (variants of an element that differ only in the number of neutrons in the nucleus of the atom) of sulfur, only four of which are stable, the most common being sulfur-32. Other than sulfur-35 that is formed by *cosmic ray spallation* of argon-40 and has a half-life of 87 days, the radioactive isotopes of sulfur have half-lives of less than 3 hours.

Amorphous, or *plastic*, sulfur is produced by rapid cooling of molten sulfur (for example, by pouring it into cold water). This brownish substance is elastic, and in bulk has the feel of crude rubber, but gradually reverts to the crystalline non-elastic allotrope.

The burning of coal and petroleum generates sulfur dioxide (SO₂) that reacts with atmospheric water and oxygen to produce sulfuric acid (H₂SO₄) and sulfurous acid (H₂SO₃). These chemicals react with atmospheric water to produce acid rain, which lowers the pH of soil and freshwater bodies, sometimes resulting in substantial damage to the environment and chemical weathering of statues and structures.

Protective environmental standards increasingly require fuel producers to extract sulfur from fossil fuels, thereby reducing acid rain formation. It is this extracted and refined sulfur that currently represents the major source of commercially available sulfur.

Since sulfur combines with so many elements, sulfur-bearing minerals—sulfides, sulfasalts, sulfates, and native specimens—comprise a significant portion of minerals in the mineral kingdom. While many are common and relatively unimpressive ore minerals, many others rank among the most impressive minerals in the mineral kingdom, and deserve their rightful place in any mineral collection.

Tests for Sulfur

Hepar Reaction: Minerals containing sulfur (in oxidized or unoxidized states), fused on charcoal with sodium carbonate, produce a brown mass of soluble sodium sulfide. When the mass is placed on a silver surface and moistened with water, a dark brown stain of silver sulfide forms, proving the presence of sulfur in the test sample.

Open Tube Test: Sulfides heated in an open tube produce noxious fumes of sulfur dioxide. The fumes turn blue litmus paper red due to the formation of sulfurous acid.

Closed Tube Test: Sulfides that contain a large percentage of sulfur (e.g. pyrite) when heated in a closed test tube produce sulfur that is deep red when hot, then yellow when cool.

Charcoal Test: The noxious odor of sulfur dioxide may be obtained when a sulfide is roasted on charcoal.

Soluble Sulfate Test: Soluble sulfates dissolved in HCl will form a heavy white precipitate of barium sulfate when barium chloride is added to the solution.