

# Feature

## Element of the Month

# Copper

One of the first metals utilized by ancient civilizations, copper, a Group IB (11) transition metal with 29 protons in its nucleus, is the 25th most abundant element in the Earth's crust.

Few metallic elements occur in nature in their native state. Of those that do, copper has played a significant role in shaping human civilization since ancient times. Although its mere .0068% abundance in the Earth's crust (about 50 parts per million) ranks it just below zinc and above cerium among elements found on the planet, natural processes concentrate the disseminated element into economically viable deposits. Thus, copper's propensity for occurring in both native form and the combined state places it among the premier elements that have enjoyed widespread use for millennia.

### History

Ancestral humans lacked the knowledge and ability to extract elements from the minerals containing them. Therefore, early civilizations had to rely on metals found in the native state, such as gold and meteoric iron (the only metals used before copper), precluding the need for any refining techniques. Since copper can occur in its native form, making it directly usable for such things as ornaments, artifacts, and bartering, this led to extensive exploitation dating back at least 10,000 years—the beginning of a time now referred to as the **Copper Age**.

Several thousands of years passed before the discovery of separating the element from copper-bearing minerals. Thereby, copper became the first such metal smelted from its sulfide ores sometime around 5000 BC. The

metal was also the first to be cast into a mold about a thousand years later, and about 500 years more to be the first metal *purposefully* alloyed with another metal, tin, to herald the so-called **Bronze Age**, about 3500 BC. Before this, a natural “bronze” containing small amounts of tin, silicon, and arsenic had been in use for a couple thousand years.

Knowledge gained by smelting copper eventually led to the smelting of iron ores, which ultimately led to a time now called the **Iron Age**, beginning in Asia circa 2000 BC and spreading to northern Europe by about 600 BC.

During Roman times the element was known as *aes Cyprium*, Latin for “copper alloys from Cyprus,” where much copper was mined. As time passed, the name was simplified to *cuprum*, and eventually to the English *copper*.

In Roman mythology, Cyprus was sacred to the goddess Venus (Aphrodite in Greek mythology). Since the seven heavenly bodies known to the ancients were associated with the seven metals known in antiquity, copper was assigned to Venus, because of the element's unique and beautiful luster.

The Romans originally used copper nuggets for currency, but eventually the shape and look played a more important role. Coins were fashioned from an alloy of copper, lead, and tin during Octavianus Augustus Caesar's rule; Julius Caesar preferred brass (an alloy of



copper and zinc), which became an important supplement to bronze.

While the scale of Roman copper mining was unsurpassed until the beginning of the 20th century, the metal did not reach its commercial potential until modern times, ushering in the **Industrial Revolution!**

### Chemistry

Copper (symbol **Cu** from the Latin *cuprum*) is a *d*-block transition metal in Group 11 of the Periodic Table, the group that also includes gold and silver. These three metals share the commonality of being soft, malleable, and ductile.

They all possess one *s*-orbital electron above a fully filled *d*-electron shell, accounting for such qualities as high ductility and conduciveness. The softness of pure copper, arising from a weak resistivity to electron transport at room temperature, partly explains its high electrical and thermal conductivity (second only to silver). Moreover, in contrast to metals with incomplete *d*-shells, characterized by covalent bonds between atoms with opposing charges, copper's *d*-shells are filled with a full compliment of electrons. Thus, it is the very active electrons in the *s*-shell that account for the bulk of interactions between copper atoms through *metallic bonds*, which are relatively weak compared to covalent bonds.

While most metallic elements have a distinctive gray or silver color, copper presents a pinkish-orange color on fresh surfaces (that darkens to a more red tarnish when exposed to air). This characteristic color results from the energy difference between the filled 3*d* and partly filled 4*s*

atomic shells, which is emitted as orange light.

Copper is unaffected by water, but does react slowly with atmospheric oxygen to form a protective brown-black oxide coating that prevents further corrosion to the underlying metal, a process called *passivation*. Additionally, with continued exposure to atmospheric carbon dioxide, a green patina (also called *verdigris*) of copper carbonate forms, as seen on older structures, such as the Statue of Liberty.

Copper occurs in two stable isotopes (Cu-63 and Cu-65) and 27 radioactive isotopes. Of the latter, Cu-67 is the most stable with a half-life of 61.83 hours; the rest have half-lives ranging from just a few minutes up to about 13 hours. Those with a mass number (total number of protons and neutrons in the nucleus) above 64 decay by the *b<sup>-</sup>-decay* process, whereas those with a mass number below 64 will decompose by the *b<sup>+</sup>-decay* process. Cu-64 decays both ways. About 70% of all copper found in nature is Cu-63.

Copper atoms primarily occur in one of two oxidation states, 1+ (cuprous) and 2+ (cupric), forming a rich variety of simple to complex (and often colorful) minerals. The simplest are binary compounds (containing only two elements), mainly oxides, sulfides, and halides. However, 3+ (cuprate) is also known, most often as an oxide, such as potassium cuprate (KCuO<sub>2</sub>).

Cupric ions bind with *ligands* (ions or molecules that bind to a central metal atom) to form *coordination complexes*. This affords an easy test of

copper(II) ions for mineral enthusiasts to perform. In an aqueous solution, the copper exists as [Cu(H<sub>2</sub>O)<sub>6</sub>] (the ligands in this case being water molecules). Adding an aqueous solution of sodium hydroxide (NaOH)—commonly known as lye—yields a light blue precipitate of copper(II) hydroxide, proving the presence of copper in a mineral specimen.

In fact, many wet-chemical tests for copper exist. Another example involves using potassium ferrocyanide (K<sub>4</sub>[Fe(CN)<sub>6</sub>]<sup>2-</sup>·3H<sub>2</sub>O) as a reagent; adding it to the test solution yields a brown precipitate if ferric copper is present (see page 25, Tests for Copper).

### Occurrence

Forged in exploding massive stars, the total quantity of copper in Earth's crust is actually vast, amounting to an estimate of over 5 million years worth. However, only a very small fraction of that is considered to be economically viable, enough for perhaps the next 25 to 60 years relative to today's rate of consumption.

Even though humans have been using copper for some 10,000 years, over 95% *ever mined* has occurred only since about the beginning of last century due mainly to the demand for it attributed to the rise of electrical power usage!

Starting in 1844, one of the world's premier copper locations was the Keweenaw District on the Keweenaw Peninsula in northern Michigan. Known as **Michigan Copper Country**, this region exploited copper mainly in its native form. The largest



mass of native copper was discovered in 1857; it weighed over 500 tons! As those deposits began to deplete, the immense sulfide deposits found near Butte, Montana supplanted them.

Prospectors and miners in the late 1800s to early 1900s obtained copper primarily from secondary minerals formed in hydrothermal veins by *meteoric* water (surface water working its way down into crust) weathering and oxidizing the primary minerals. During this period, the United States produced up to about half of the world's newly mined copper.

The list of secondary minerals found in the hydrothermal veins is quite extensive, including such examples as the sulfosalts tetrahedrite ((Cu,Fe)<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>), tennantite ((Cu,Fe)<sub>12</sub>As<sub>4</sub>S<sub>13</sub>), and enargite (Cu<sub>3</sub>AsS<sub>4</sub>); the carbonates azurite (Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>) and malachite (Cu<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>); the oxides cuprite (Cu<sub>2</sub>O) and tenorite (CuO); and to a minor extent the sulfate chalcantite (CuSO<sub>4</sub>·5H<sub>2</sub>O). Such minerals can be so exquisite in form, color, rarity, etc., that they have become highly sought after by mineral collectors.

Today, copper is obtained mostly from highly disseminated, minute grains of chalcopyrite (CuFeS<sub>2</sub>) in low-grade ore bodies known as *porphyry copper deposits*. Bornite (Cu<sub>5</sub>FeS<sub>4</sub>), covellite (CuS), and chalcocite (Cu<sub>2</sub>S) are also included to a lesser extent. Such deposits are emplaced by hydrothermal fluids originating from deep-seated magmas intruded into the crust by subduction zone tectonic activity that occurred anywhere from about 500 to 20 millions years ago. Large porphyry copper deposits are found in Chile, the U.S., Zambia, Zaire, Peru, and Zimbabwe.

### Extraction and Refining

Although these ores average only about 2% copper, they are so extensive, mining and refining techniques are sufficiently effective and efficient, and other valuable metals (gold, silver, molybdenum, etc.) are often also recovered to offset costs, that such deposits are economically viable.

Rather than employing underground mining methods, which are typically difficult, dangerous, and expensive, these deposits are accessed by open-pit mining. Such mines can be huge! Famous sites include Chuquicamata in Chile, Bingham Canyon in Utah, and the El Chino Mine in New Mexico.

The low-grade ore is crushed to a powder (a process called *comminution*) to liberate the various valuable minerals into separate grains dispersed throughout the gangue, then concentrated by *froth flotation* to 10-15% copper.

Any iron in the concentrate is removed by *flash smelting* with silica to produce a silicate slag. The resulting mass is called *copper matte*, consisting of 80-95% copper sulfide (Cu<sub>2</sub>S); the remainder includes various amounts of sulfides, arsenides, and alloys containing Fe, Co, Ni, Mo, Pb, Ag, Au, As, etc.

The matte is then roasted to drive off sulfur (collected as valuable sulfur dioxide) and convert all the sulfides into their corresponding oxides. Ultimately, copper oxide is then easily refined to the pure metal by *electrolysis* and *electrorefining*. While known reserves are being depleted, demand continues to increase dramatically. In fact, copper is so widely used that it is becoming very scarce. The U.S. Bureau of Mines estimates that the currently known worldwide reserves of copper ore will be exhausted sometime in the first half of this century!

Fortunately, because copper is reusable without any loss of quality, it is the third most recycled metal, after iron and aluminum. Recycling reduces the pressure on mining companies to discover and extract new sources of the metal, and still provide for the world's needs. It is estimated that about 80% of all copper ever mined is still in use today for numerous applications!

### Applications

Alloys find extensive employment. The addition of zinc produces brass, while primarily tin produces bronze. Other elements (e.g. aluminum, iron, silicon, manganese, nickel, silver, etc.) may also be substituted or included to various proportions in order to produce desired qualities for specific purposes, such as statuary, jewelry, solders, decorations, plumbing, and coinage.

*Muntz metal* (copper, tin, trace iron) is particularly valued for its anti-microbial and anti-biofouling functions, since copper has biostatic qualities (bacteria and other life forms will not grow on it). Thus, it is utilized in hospitals (doorknobs, bedrails, sinks, faucets, toilet hardware, etc.) to reduce transfer of diseases (e.g. E.coli, Staphylococcus, and Clostridium),



and in marine environments for corrosion resistance and to protect against the growth of such organisms as barnacles and mussels.

Copper salts that impart blue or green colors have been used historically as pigments in decorative art and painting, though today these have been mostly replaced by synthetic substitutes. Various other copper-bearing compounds are used as anti-bacterial agents, fungicides, and wood preservatives.

Nevertheless, native copper is still in greatest demand. The major consumer is the electrical industry for wire (power transmission and generation, telecommunications, electronic circuitry, electrical equipment, etc.). About half of all the copper mined is applied to producing electrical wire and cable conductors.

Other significant applications of the metal include roofing and architecture (e.g. cladding, flashings, gutters), machinery (e.g. appliances), transportation (e.g. electric cars), and home decorative products (e.g. bathroom fixtures, countertops, handrails) to name just a few.

### Biology

Copper is essential to living organisms as a trace dietary mineral, owing to its being a key constituent in such critical biochemicals as the enzyme *cytochrome c oxidase* (a respiratory protein found in mitochondria) and *ceruloplasmin* (a copper-carrying ferroxidase enzyme in blood that plays a role in iron metabolism). The human body contains up to about 2 mg of copper per kg of body mass, found mainly in the liver, muscles, and bones.

Interestingly, whereas all vertebrates except icefish utilize the iron-bearing protein *hemoglobin* for oxygen transport in blood, many invertebrates, namely mollusks and arthropods, employ the copper-bearing *hemocyanin* for the same purpose. Thus, their blood is blue!

According to the U.S. Institute of Medicine, the **Adequate Intake** (AI) for humans ranges from 200  $\mu\text{g}$  of copper for newborns to 900  $\mu\text{g}$  for adults, although slightly higher limits are accepted for expectant mothers. The **Tolerable Upper Intake Level** (UL) is set at 10 mg/day for adults. Half that amount is recommended by European standards.

According to the Occupational Safety and Health Administration (OSHA), the **Permissible Exposure Limit** (PEL), measured in *time-weighted average* (TWA), for copper dust and fumes in the workplace is a mere 1 mg/m<sup>3</sup>! The amount considered to be imminently dangerous to life and health is 100 mg/m<sup>3</sup>.

For food and dietary supplement labeling purposes, the acceptable level of copper in a serving is expressed by **Daily Value** (%DV). 100% of the DV is set at 0.9 mg. Copper deficiency can lead to various maladies, including anemia-like symptoms, impaired growth and bone abnormalities, hypopigmentation, osteoporosis, and more.

Conversely, accumulation of copper in body tissues can also cause numerous afflictions. The most common is Wilson's disease, resulting from the mutation of a gene that produces a protein responsible for carrying excess copper to the liver to be incorporated in bile for eventual elimination. Complications include liver failure, liver cancer, and kidney issues. Elevated copper levels have also been linked to worsening symptoms of Alzheimer's disease. However chronic copper toxicity is unusual in humans, because of the body's ability to regulate absorption and excretion of the metal.

Copper and its compounds in mineral collections is a reminder of, and tribute to, the element's unique and versatile properties that have played a pivotal role in helping to shape and advance human civilization for thousands of years, and no doubt will continue to do so well into the future.



**Horseshoe Crab**  
(*Limulus polyphemus*)

Tracing their origins to about 450 mya, these relatives of spiders (not crabs) are considered living fossils. The copper-bearing protein hemocyanin colors their blood blue, unlike the red of mammals from hemoglobin. This blood is harvested by the medical industry for its bacterial-detecting properties.



# A Collection of Copper Minerals



**Copper**

dendritic xls on basalt matrix

3 x 2.25 inches

Unknown Site

Keweenaw Peninsula; MI



**Chalcopyrite**

minute xls on gossan matrix

2 x 1 inches

Mohawk Mine

Mountain Pass; CA



**Bornite**

iridescent "Peacock Ore"

1.5 x 1.2 inches

Unknown Site

Unknown Location



**Cuprite**

in calcite on gossan matrix

2.38 x 1.58 x 1.75 inches

Unknown Site

Arizona



**Malachite**

feathery aggregates on matrix

2.9 x 2.125 x 1.38 inches

Unknown Site

Shaba, Congo



**Azurite**

aggregate of rosette xls

4 x 2.5 inches

Unknown Site

Bisbee, AZ



**Aurichalcite**

feathery xl sprays on gossan

2 x 1.25 inches

Ojuela Mine

Mapimi, Mexico



**Adacamite**

bladed xls on clay matrix

2.5 x 1.5 inches

Unknown Site

Atacama Desert; Chile



**Brochantite**

drusy aggregates on gossan

1.25 x .75 inches

Douglas Hill Copper Mine

Ludwig, Nevada



**Glaukosphaerite**

botry. crust on hornblende

2.75 x 2 x 1.25 inches

Key West Mine

Bunkerville, NV



**Callaghanite**

blue xls on magnesite

1.5 x 1.5 inches

Premier Chemicals Mine

Gabbs, NV



**Devilline**

silky green xls on ankerite

1.88 x 1.5 inches

Bou Bekker

Touissit, Morocco

*All specimens from the G. Miles Lehman Collection*





### Tennantite

xl aggregate w/o matrix

1.75 x 1.5 x .88 inches

Jucani Mine

Huancavelica, Peru



### Diaboleite

crystalline grains on barite

1.5 x .6 x .75 inches

Rowley Mine

Maricopa Co., AZ



### Cuprite

dendritic xls altering to Cu

.75 x 1.25 inches

Unknown Site

Pinal Co., AZ



### Conichalcite

aggregates on gossan

2.5 x 1.5 x 1.38 inches

Mohawk Mine

Mountain Pass; CA



### Linarite

bladed xls on hematite

3 x 2.25 inches

Blue Bell Mine

Soda Mtns; Baker, CA



### Antlerite

radial xl sprays on gossan

Specimen 3 x 2.25 inches

Chuquicamata Mine

2.5 x 2 x 1.25

# Tests for Copper

**Flame Test:** an oxidized compound of copper when introduced to the flame yields a vivid green color (due to the copper oxide volatilized). When moistened with HCl, and then heated, the flame is an intense blue tinged with green (due to CuCl). Note: if the mineral is a sulfide, it must be roasted in the oxidizing flame before moistening with HCl.

**Solution with Ammonium Hydroxide:** if an acid solution containing copper is made alkaline with ammonium hydroxide, it will assume a deep blue color.

**Reduction to Metal on Charcoal:** a small amount of a copper compound mixed with the reducing mixture (equal parts sodium carbonate and charcoal), then heated intensely in the reducing flame on a charcoal block, will produce malleable metal globules with typical copper color. Sulfides must first be roasted before testing.

**Solution with Potassium Ferrocyanide:** if potassium ferrocyanide is added to a slightly acidic solution, a reddish to reddish brown precipitate indicates the presence of copper(II) ions; ppt insoluble in dilute acid, but soluble in ammonium hydroxide; test is extremely sensitive.

**Bead Test:** copper imparts characteristic colors when fused in borax/sodium carbonate beads, then heated in both the oxidizing (o) and reducing (r) flames.

#### Borax

o, hot/cold: pale green/blue-green  
r, hot/cold: colorless/opaque red

#### Sodium Carbonate

o, hot/cold: NA/yellow to orange  
r, hot/cold: NA/opaque (spongy mass of Cu)