

October 2013 Mineral of the Month

REALGAR-ORPIMENT

For October we are featuring brightly colored, composite specimens of red realgar and yellow-orange orpiment. Both are uncommon, closely related arsenic sulfides from an 11,800-foot-high mine in the Peruvian Andes. Our write-up focuses on realgar, explaining its mineralogy and history, and providing an overview of the element arsenic.

Because of their arsenic content, realgar and orpiment are toxic. Exercise care when handling specimens, such as washing hands after handling. (See “Composition”).

OVERVIEW:

PHYSICAL PROPERTIES:

Chemistry: As_4S_4 Arsenic Sulfide

Class: Sulfides

Subclass: Anhydrous Sulfides

Group: Realgar

Crystal System: Monoclinic

Crystal Habits: Crystals are rare and occur as short, striated prisms terminated with wedge-shaped domes; usually granular, massive, earthy, powdery, and encrusting.

Color: Deep-red to orange-red, becomes yellow upon prolonged exposure to light.

Luster: Resinous to adamantine; occasionally sub-metallic.

Transparency: Transparent to translucent

Streak: Orange to orange-yellow

Cleavage: Good in one direction

Fracture: Conchoidal, brittle.

Hardness: 1.5-2.0

Specific Gravity: 3.5-3.6

Luminescence: None

Refractive Index: 2.538-2.704

Distinctive Features and Tests: Best field marks are softness, deep-red to orange-red color, occurrence in epithermal-vein environments and association with orpiment [arsenic sulfide, As_2S_3]. Can be confused with cinnabar [mercury sulfide, HgS], which is harder and more dense.

Dana Classification Number: 2.8.22.1

NAME: The name “realgar,” pronounced ree-AHL-gur, stems from the Arabic *rahj al ghār*, meaning “powder of the mine,” referring to its often-powdery occurrence in vein-type, metal-ore deposits. Alternate names are “ruby sulfur,” “ruby arsenic,” “red orpiment,” “realgarite,” “eolite,” “risigallum,” “sandaracha,” “risigallo,” “arsenic rouge,” and “red arsenic.” In European mineralogical literature, realgar appears as *realgarita*, *rejaigar*, and *realgaar*. The name “orpiment” stems from the Latin *auripigmentum*, meaning “gold pigment,” an allusion to its yellow-orange color.

October 2013 Mineral of the Month

COMPOSITION: Realgar is one of the approximately 350 members of the sulfide class of minerals, in which sulfur is combined with one or more metals or semimetals. Realgar's molecular weight is made up of 70.03 percent arsenic (As) and 29.97 percent sulfur (S). It occurs primarily in low-temperature (epithermal) veins in association with orpiment, cinnabar, and various metal-sulfide ore minerals. Because of its unusual, arsenic-arsenic bonding arrangements, realgar is very soft (Mohs 1.5-2.0). As an idiochromatic or "self-colored" mineral, realgar's deep-red to orange-red colors are due to the nature of its crystal structure, which absorbs the blue, green, and yellow wavelengths of visible light, transmitting or reflecting only the red wavelengths. Our specimens consist of bright-red realgar and yellow-orange orpiment, the latter a closely related arsenic sulfide. Realgar is chemically unstable; with prolonged exposure to intense light, it will eventually alter into yellowish pararealgar [arsenic sulfide, AsS]. Collectors are advised to store realgar specimens in closed, lightproof containers, removing them only for brief periods of viewing, display, and study.

COLLECTING LOCALITIES: Realgar specimens are found in Peru, Chile, Mexico, the Czech Republic, Hungary, Romania, Greece, Macedonia, Switzerland, France, Germany, Italy, Canada, China, Iran, Japan, Namibia, and Turkey. In the United States, realgar is collected in California, Utah, Washington, Wyoming, and Nevada.

HISTORY, LORE & USES: Realgar has been known for at least 5,000 years and was used in medicinal preparations and as a red pigment in paints and cosmetics in Mesopotamia and Egypt. Ancient physicians recognized both the toxicity of realgar and its therapeutic value when administered in proper dosages. During the Bronze Age, realgar was added to molten bronze to provide the arsenic necessary to harden the alloy. Realgar has played a prominent role in Chinese medicine since 1400 B.C. It was an important trade commodity in ancient Rome; medieval alchemists would later attempt to transform realgar crystals into ruby [corundum, aluminum oxide, Al₂O₃]. When the word "realgar" entered the English language in the early 1400s, realgar was the primary pigment in orange-red paints used by artists. Although too soft and chemically unstable for jewelry use, realgar crystals are occasionally faceted into beautiful collectors' gems with a distinctive, deep-red color and brilliant "fire," the latter due to a refractive index even higher than that of diamond. Until the 1960s, realgar was an important ore of arsenic. Realgar continues to have limited use in medicine and pyrotechnics. According to modern metaphysical practitioners, realgar energizes the body, heightens sexuality, increases fertility, opens subconscious areas of the mind, aids in retrieving forgotten thoughts and memories, stimulates physical growth and health, and unlocks suppressed dreams and desires.

ABOUT OUR SPECIMENS: Our realgar-orpiment specimens are from the Quiruvilca Mine in the Quiruvilca District, Santiago de Chuco Province, La Libertad Department, Peru. Quiruvilca is 60 miles east of the coastal city of Trujillo and 250 air miles north-northwest of the national capital of Lima. Spanish prospectors discovered mineralized outcrops in what is now the Quiruvilca District in 1677, but because of its remoteness, limited mining did not begin until the 1780s. Systematic mining began after 1900, when foreign mine ownership was legalized and mining boomed throughout Peru. The underground Quiruvilca Mine, which produces copper, lead, zinc, and small amounts of silver and gold, has operated continuously since 1940. In 1995, Pan American Silver acquired the mine and increased production to 1,700 tons per day. In 2012,

October 2013 Mineral of the Month

Southern Peaks Mining purchased the mine. Quiruvilca now has ore reserves for at least five more years of mining, but core-drill exploration is expected to locate additional ore reserves to significantly extend its operating life. Over the years, Quiruvilca has yielded many fine specimens of realgar, orpiment, pyrite, enargite, and hutchinsonite. Miners are permitted to gather specimens as long as production of ore is not compromised. Both the town of Quiruvilca and the Quiruvilca Mine are situated above timberline at an elevation of 11,800 feet. The town of Quiruvilca, population 8,000, is one of the highest communities of its size in the world. As the trading center for Quiruvilca Mine specimens, or *laques*, as they are known in the native Quechuan language, the town attracts many mineral dealers from Lima who pay top prices for fine specimens.

COMPREHENSIVE WRITE-UP:

COMPOSITION:

This month's featured mineral is a composite of realgar on a matrix of orpiment. Both minerals are colorful; realgar is a distinctive red, orpiment a yellow-orange. Realgar and orpiment are closely related chemically and structurally, and also occur in close association within the same mineralogical environments. **While realgar and orpiment are toxic because of their arsenic content, specimens do not constitute a health hazard under normal conditions of storage and display. Never ingest realgar-orpiment particles or inhale realgar-orpiment dust. Always wash hands thoroughly after handling realgar-orpiment specimens. Never heat realgar-orpiment specimens, as this may release arsenic fumes.**

As shown by its chemical formula As_4S_4 , realgar contains the elements arsenic (As) and sulfur (S). Its molecular weight is made up of 70.03 percent arsenic and 29.97 percent sulfur. Like all molecules, those of realgar consist of cations (positively charged ions) and anions (negatively charged ions). The realgar cation is made up of four trivalent arsenic ions 4As^{3+} with an *effective* combined charge of +8. Realgar's anion consists of four divalent sulfur ions 4S^{2-} with a combined -8 charge. These balanced cationic and anionic charges provide the realgar molecule with electrical stability.

The realgar cation 4As^{3+} would appear to have a +12 charge ($4 \times +3 = +12$), rather than the +8 charge that is needed to balance the molecule. The reason for this is that three of the four As^{3+} ions are covalently bonded together in a chain. In this configuration, the two end ions each retain two valence charges, while the double-bonded center ion retains only one valence charge. This gives the three bonded arsenic ions an effective collective +5 charge, while the single unbonded arsenic ion retains its normal +3 charge. This arrangement produces a total cationic charge of +8 and explains why the realgar formula is expressed as As_4S_4 rather than as AsS (now the formula assigned to pararealgar).

Realgar is one of about 350 sulfide minerals, in which sulfur is combined with one or more metals or semimetals. In realgar, sulfur is combined with arsenic, which is a semimetal or metalloid (see "Arsenic: The King of Poisons"). Most sulfides are opaque, generally dull in

October 2013 Mineral of the Month

color, and have a distinct metallic luster. Realgar is one of the few exceptions: it is bright red, transparent to translucent, and only occasionally exhibits a subtle, sub-metallic luster.

The structure of realgar is analogous to that of sulfur, which crystallizes in the orthorhombic system with eight sulfur ions linked together in a ring. In realgar's structure, arsenic ions and sulfur ions alternate to produce rings of As_4S_4 , which join together to form the crystal lattice. Very little covalent bonding exists between these rings. They are instead joined primarily by van der Waals' forces, a very weak bond that is created by the attraction of electron-poor sections of electrically neutral molecules to the electron-rich sections of adjacent, electrically neutral molecules. This is the same weak force that accounts for the coherence, surface tension, and capillary action of liquids.

Although sulfur crystallizes in the orthorhombic system, the presence of arsenic in realgar distorts the lattice to a monoclinic symmetry. The monoclinic system is characterized by three axes of different lengths, two of which are perpendicular. Monoclinic crystals tend to have one elongated axis that produces prismatic crystals. Many minerals that are chemically complex or have complex bonding arrangements crystallize in the monoclinic system. Although realgar is chemically simple, its arsenic-arsenic and arsenic-sulfur bonding arrangements are complex.

Because of the predominance of the weak van der Waals' forces, together with very weak arsenic-arsenic covalent bonding, realgar is quite soft at Mohs 1.5-2.0. The stacking of flat, arsenic-sulfur ring structures within its crystal lattice explains its one-directional cleavage. In most metal sulfides, metallic bonding produces opacity and a distinct metallic luster. But because the semimetal arsenic participates only minimally in metallic bonding, realgar has good transparency and only occasionally exhibits a sub-metallic luster. Despite arsenic's relatively high atomic weight of 74.91, realgar's loose atomic packing makes it considerably less dense (specific gravity 3.5-3.6) than most sulfide minerals.

As an idiochromatic or "self-colored" mineral, realgar's bright-red color is due to the nature of its crystal structure, which absorbs the blue, green, and yellow wavelengths of visible light, while transmitting or reflecting only the red wavelengths. Realgar crystals are also strongly pleochroic and exhibit color shifts from deep-red to orange-red with changes in the viewing angle. Pleochroism occurs when different sections of the crystal absorb different wavelengths of white light.

The Dana mineral classification number 2.8.22.1 first identifies realgar as a sulfide, selenide, or telluride (2). The sub classification (8) defines it by the general formula AmBnXp , in which "A" and "B" can be arsenic or other chemically related elements, "X" is sulfur, selenium, or tellurium, and "m," "n," and "p" are quantifiers. Realgar is then assigned to the realgar group (22) as the first (1) of four members. The other three realgar-group members, all chemically and structurally related, are:

pararealgar	arsenic sulfide	AsS	monoclinic
uzonite	arsenic sulfide	As_4S_5	monoclinic
alacránite	arsenic sulfide	As_8S_9	monoclinic

October 2013 Mineral of the Month

Realgar is also very closely related to orpiment [arsenic sulfide, As_2S_3] and is almost identical in hardness, specific gravity, and cleavage. Both minerals crystallize in the monoclinic system and occur in the same mineralogical environments. Realgar is bright-red in color, while orpiment is yellow-orange. Whether arsenic and sulfur ions will combine into realgar or orpiment depends upon the temperature at the time of crystallization. Because the arsenic-arsenic bonds in realgar are inherently weak and heat-labile, realgar crystallizes at a lower temperature than orpiment. Orpiment, which has stronger, more heat-tolerant, arsenic-sulfur bonding, crystallizes at higher temperatures.

Realgar occurs primarily in low-temperature (epithermal) veins in association with orpiment, stibnite [antimony trisulfide, Sb_2S_3], and cinnabar [mercury sulfide, HgS]. It is a fairly common gangue mineral in certain vein-type deposits of metal-sulfide ores, especially those of lead, copper, zinc, silver, gold, and antimony. Because of its bright-red color, it serves as an “indicator” mineral that can infer the nearby presence of valuable ore minerals. Small amounts of realgar also occur as sublimation products in volcanic fumaroles.

Realgar is chemically unstable and with exposure to light will eventually alter into yellowish pararealgar [arsenic sulfide, AsS]. The pararealgar prefix stems from the Greek *para* meaning, in this usage, “closely related to.” Prolonged exposure to intense light, especially direct sunlight, will accelerate this alteration process. Although alteration begins immediately upon exposure to light, it proceeds very slowly. The energy of incident light breaks realgar’s weak arsenic-arsenic bonds to produce free arsenic ions that disrupt the crystal lattice and part the weak van der Waals’ bonding. This frees both arsenic and sulfur ions, which then bond together to become stable as pararealgar.

Realgar’s chemical instability in prolonged exposure to strong light does not mean that significant alteration is imminent. However, collectors should store realgar specimens in closed, lightproof containers, removing them only for short periods of viewing, display, and study.

COLLECTING LOCALITIES:

Our realgar specimens are from the Quiruvilca Mine in the Quiruvilca District, Santiago de Chuco Province, La Libertad Department, Peru. Peruvian realgar specimens are also collected at the Siglo Veinte Mine at Llalagua, Bustillos Province, Potosí Department; and the Atacocha district at Cerro de Pasco, Pasco Province, Pasco Department. Latin America’s other sources include the Alacrán Mine at Alacrán, Pampa Larga District, Tierra Amarilla, Copiapó Province, Chile; and the Santa Eulalia mines at Aquiles Serdán, Chihuahua, Mexico.

In Europe, realgar occurs at Sokolov in the Karlovy Vary Region, Bohemia, Czech Republic; Hercegköves Hill, Rátka, Tokaj Mountains, Borsod-Abaúj-Zemplén County, Hungary; the Crven Dol Mine, Allchar, Roszdan, Macedonia; the Cavnice mines at Baia Sprie, Maramureș County, Romania; the Plaka mines at Laurion, Attiki Prefecture, Greece; and the Lengenbach Quarry at Imfeld in the Binn Valley, Valais, Switzerland. It also occurs in France at the Matra

October 2013 Mineral of the Month

Mine at Corte, Haute-Corse, Corsica; and the L'Eguisse Mine at Duranus, Alpes-Maritimes, Alpes-Côte d'Azur Province. German specimens are collected at the Hilfe Gottes Mine, Schiltach, Baden-Württemberg; and the Beust and Segen Gottes mines in the Schneeberg district, Erzgebirge, Saxony. Italian localities include the Somma-Vesuvius Complex, Naples Province, Campania; and the Bicchieri and Ravaccione quarries at Carrara in the Apuan Alps, Massa-Carrara Province, Tuscany.

Other localities include the Golden Giant and David Bell mines at the Hemlo gold deposit at Marathon, Ontario, Canada; the Ningshan arsenic-gold deposit in Ningshan County, Arkang Prefecture, Shaanxi Province, China; the Sary Gunay gold deposit, Qorveh, Kordestan Province, Iran; the Teine Mine at Sapporo, Hokkaido, Japan; the Tsumeb Mine at Tsumeb, Otjikoto Region, Namibia; and the Hisarcik and Killik mines at the Emet borate deposit, Kütahya Province, Turkey.

Localities in the United States include the Baker Mine at the Kramer Borate Deposit at Boron, Kern County, California; the Mercur district mines in the Oquirrh Mountains, Tooele County, Utah; the Green River Canyon prospects near Palmer, King County, Washington; the Yellowstone National Park geyser deposits in Wyoming; and the Getschell Mine in the Potosi District in Humboldt County, and the Black Mammoth and White Caps mines in the Manhattan District in Nye County, both in Nevada.

JEWELRY & DECORATIVE USES:

Although realgar is too soft and chemically unstable for use in jewelry, it is occasionally cut into beautiful collectors' gems. Realgar's great softness makes it difficult to facet, while cutting can release toxic arsenic fumes and arsenic-containing dust. Despite the faceting problems, realgar collectors' gems have a distinctive, deep-red color and brilliant "fire," the latter due to realgar's very high refractive index of 2.538-2.704, which is even higher than that of diamond.

As a former decorative stone, realgar was carved into figurines, most notably in China. Virtually all Chinese realgar carvings, many of which are hundreds of years old, have undergone extensive chemical alteration; their surfaces have deteriorated into a powder and their color has changed from bright-red to the yellowish color of pararealgar.

Realgar is collected for its rarity, deep-red color, and associations with such minerals as red cinnabar, yellow-orange orpiment, and silvery-gray stibnite. Large, well-developed realgar crystals, which are rare, are especially valuable.

HISTORY & LORE:

Realgar, which has been known for at least 5,000 years, was first used in medicinal preparations and as a red pigment in paints and cosmetics in Mesopotamia and Egypt. Ancient physicians recognized both the toxicity of realgar, as well as its therapeutic value when administered in

October 2013 Mineral of the Month

proper dosages. During the Bronze Age, realgar was added to molten mixtures of copper and tin to provide the arsenic needed to harden the resulting bronze.

Realgar has played a prominent role in Chinese medicine since 1400 B.C. The Chinese also believed that carved realgar amulets could ward off evil and that ingesting realgar-based potions would prevent many diseases. Rice wine with finely powdered realgar was a prominent part of China's Dragon Boat festivals that evolved some 2,000 years ago as national holidays and feast days. When the wine had been consumed in ceremonial toasting, the remaining wine-realgar paste remaining in cups was used to decorate the foreheads and arms of children. This practice continues today in some rural areas of China.

Realgar was an important trade commodity throughout the Roman Empire and had many medical uses. Medieval alchemists later attempted to transform realgar crystals into ruby [corundum, aluminum oxide, Al_2O_3]. When the word "realgar" entered the English language in the early 1400s, realgar was the primary pigment in orange-red paints used by artists. Unfortunately, the realgar-based paints that were used in many celebrated examples of Renaissance art have faded to orange or yellow as the realgar altered into pararealgar (see "Composition"). For centuries, realgar mixed with flour was the standard rat poison throughout Europe. By the mid-1700s, realgar and other arsenic compounds had become the preferred drugs for treating such diseases as syphilis and remained in use until the early 20th century.

X-ray diffraction analysis revealed realgar's atomic structure in 1928. Nevertheless, mineralogists were unable to fully define its complex, arsenic-arsenic bonding arrangements until the 1980s, when realgar's formula was formally changed from "AsS" to As_4S_4 . The "AsS" is now assigned to pararealgar.

Realgar appeared on the 2000-franc stamp of the Central African Republic in 1968. According to modern metaphysical practitioners, realgar energizes the body, heightens sexuality, increases fertility, opens subconscious areas of the mind, aids in retrieving forgotten thoughts and memories, stimulates physical growth and health, and unlocks suppressed dreams, desires, and memories.

TECHNOLOGICAL USES:

Realgar and orpiment served as ores of arsenic until the early 1960s (see "Arsenic: The King of Poisons"). Small amounts of realgar are still mined in China today for specialty uses. Until powdered aluminum and magnesium became available after World War II, realgar was used in pyrotechnics to produce white flame. In an instantaneous reduction-oxidation reaction, the realgar burned in a reduction reaction to produce elemental arsenic, which then instantly oxidized into arsenic trioxide (As_2O_3) and emitted a dazzling white light. Realgar still has minor uses in pyrotechnics. Realgar served extensively in medicine for thousands of years and continues to have limited use, especially in China, where the current *Pharmacopoeia of the Peoples Republic of China* lists more than two dozen realgar-based, medicinal compounds. In the 1990s, Chinese researchers refocused their attention on realgar as an agent to treat leukemia

October 2013 Mineral of the Month

and related cancers. Powdered realgar is also still available as a red-orange pigment for specialty artists' paints.

ARSENIC: THE “KING OF POISONS”:

The toxicity of arsenic is legendary. For thousands of years, the element has been synonymous with poisoning and death, and for good reason: Arsenic and its compounds are highly toxic to virtually all multicellular animal and plant life. For centuries, arsenic compounds were the poison of choice for countless assassinations. Because of their potency and hard-to-define symptoms, arsenic compounds were the poisons of choice that the ruling classes of Europe used to surreptitiously eliminate the opposition—the reason that arsenic became known as the “king of poisons” and the “poison of kings.” Even today, arsenic remains synonymous with certain health hazards and forms of environmental degradation. Yet arsenic and its compounds do have positive uses in everything from metallurgy and medicine to glassmaking and wood preservation.

The word “arsenic” is rooted in the Persian *zarnikh*, meaning “yellowish” or “golden,” alluding to its occurrence in orpiment. The Greeks adopted this word as *arsenikon*, meaning “masculine” or “potent” and referring to the powerful toxicity of arsenic compounds. The German philosopher, theologian, and saint Albertus Magnus (Albert the Great, Albert von Boll-städt, circa 1200-1280) first isolated elemental arsenic in 1250 A.D.

Elemental arsenic is trimorphic, meaning it exists in three structural forms. The most abundant is arsenic itself, which crystallizes in the monoclinic system. The other two forms, which crystallize in the orthorhombic system, are arsenolamprite and para-arsenolamprite. Arsenic exists in three allotropic forms. The most common is “gray arsenic,” a dense, extremely brittle, metallic-gray semimetal with a specific gravity of 5.73 and poor electrical and heat conductivity. “Black metallic arsenic” also has high density and an unusual, layered crystal structure. The “yellow arsenic” allotrope has a much lower specific gravity of 2.0. All three allotropes occasionally occur free in nature. Arsenic ranks 52nd among the elements in crustal abundance and is about as common as tin.

On the periodic table of elements, arsenic joins nitrogen, phosphorus, antimony, and bismuth in column 15. Of these elements, arsenic, antimony, and bismuth (some researchers also include selenium and tellurium) are classified as semimetals or metalloids, elements that share the properties of both metals and nonmetals. Elemental arsenic has an atomic number of 33, an atomic weight of 74.92 (somewhat higher than that of zinc), and commonly occurs in the -3, +3, and +5 oxidation states. Unlike most elements, the boiling point of arsenic (1137° F., 614° C.) is lower than its melting temperature (1503° F., 817° C.). When heated, arsenic will therefore sublime directly to a gas, then condense directly to a solid.

Although traces of arsenic occur naturally in the human body and in many foods, ingesting as little as one-tenth of a gram can be fatal. Arsenic's toxicity is due to its chemical similarity to phosphorus. Phosphorus is vital to the cellular chemistry of all animals and plants, because it is needed for the production of adenosine triphosphate (ATP), a compound that provides the energy

October 2013 Mineral of the Month

required for all metabolic processes. Because of its chemical similarity, arsenic can partially substitute for phosphorus in ATP and other cellular compounds. Even tiny amounts of arsenic can thus disrupt normal cellular functions and metabolism. Arsenic was long considered the “perfect” poison because of its toxicity and the difficulty in detecting its presence in the tissues of its victims. In 1836, English chemist James Marsh (1794-1846) developed a procedure that enabled forensic investigators to detect excessive amounts of arsenic in human tissue. After the Marsh Test became a standard forensic procedure, the incidence of criminal arsenic poisonings dropped sharply.

Despite their toxicity, arsenic compounds have many high-volume, industrial applications. Each year, industries in the United States use some 6,900 tons of arsenic (as contained in compounds), mostly as arsenic trioxide (As_2O_3). About 4,000 tons are used in wood preservatives to protect against fungi and boring insects. Another 1,500 tons go into agricultural herbicides, fungicides, and pesticides. Smaller amounts of arsenic compounds are used to manufacture chemical-warfare agents, decolorize glass, and formulate drugs to treat psoriasis and certain forms of cancer. Elemental arsenic is alloyed with lead to strengthen terminal posts and grids in automotive batteries, while gallium arsenide (GaAs) semiconductors are standard components in lasers, solar cells, light-emitting diodes, and electronic-circuit boards.

Until 1960, the world’s supply of arsenic came from mining, milling, and smelting realgar, orpiment, and Arsenopyrite ores. Since then, efforts to reduce the air pollution associated with base- and precious-metal smelting and refining have resulted in the recovery of large amounts of arsenic-rich “smelter dust,” which is processed to satisfy industrial demand for arsenic.

Arsenic is a key component in chromated copper arsenate (CCA), the standard preservative in most pressure-treated wood products. Since 2003, CCA has been banned from use in residential wood products. However, its continued use in industrial and marine wood products and telephone poles still accounts for half of all arsenic demand. Arsenic also serves as an alloying agent to harden copper, bronze, and lead; as an antifriction agent in Babbitt-metal alloys for bearings; and as a semiconductor material in computers and other electronic devices.

Arsenic production is measured in tonnage of arsenic trioxide (As_2O_3), the feedstock for the manufacture of elemental arsenic and all arsenic compounds. China accounts for half of the world’s annual production of 52,000 metric tons of arsenic trioxide. Chile and Morocco are also major producers. Arsenic trioxide sells for 30 cents per pound, elemental arsenic for 50 cents per pound. Because of heightened environmental and health awareness and the phasing out of many arsenic-containing wood preservatives, arsenic use is steadily declining.

ABOUT OUR SPECIMENS:

Our realgar specimens are from the Quiruvilca Mine in the Quiruvilca District, Santiago de Chuco Province, La Libertad Department, Peru. La Libertad, one of Peru’s 21 departments (political divisions comparable to American states), is in northern Peru. It borders the Pacific Ocean and extends eastward into the high Andes. Covering 9,845 square miles, La Libertad is

October 2013 Mineral of the Month

roughly equal in area to the state of Maryland. Its capital is the coastal city of Trujillo which, with 700,000 residents, is Peru's third largest city. La Libertad Department is administratively divided into 12 provinces (comparable to American counties). Located in southeastern La Libertad, Santiago de Chuco Province is in the Cordillera Blanca, a major Andean sub-range that has a rugged, mountain topography. Santiago de Chuco is subdivided into eight administrative districts (comparable to American townships). The Quiruvilca District covers 1,026 square miles and has 57,000 residents and an average elevation of 9,000 feet. It is 60 miles east of Trujillo and 250 air miles north-northwest of the national capital of Lima. The general map coordinates of the Quiruvilca District are 7°59' south latitude and 78°21' west longitude.

The Andes were uplifted during the Andean Orogeny (mountain-building episode) some 60 million years ago. This uplifting of massive amounts of granitic basement rock was accompanied by extensive volcanic activity and the emplacement of necks and plugs of the low-silica, volcanic rocks andesite and dacite. Associated mineral-rich, hydrothermal solutions surged through the fractured, granitic country rock where they precipitated an array of metallic and semimetallic minerals in erratic vein systems. Gases accompanying the epithermal (low-temperature) deposition phases sometimes created cavities within the veins that provided space for unrestricted crystal growth. Erosion later exposed sections of these veins as mineralized outcrops.

Spanish prospectors discovered these outcrops in what is now the Quiruvilca District in 1677. But because of the area's remoteness, mining did not begin until the 1780s. Spanish, and later Peruvian, miners conducted sporadic, small-scale silver mining for the next century. Systematic mining began after 1900, when foreign mine ownership became legal and mining boomed throughout Peru. Of several Quiruvilca mines, the largest was operated by the Northern Peru Mining & Smelting Company, a subsidiary of the United States-based American Smelting & Refining Company (now ASARCO, Inc.) In the 1920s, ASARCO consolidated all the Quiruvilca mines and constructed a modern flotation-concentration mill. This underground mine shut down in 1930, but resumed full production a decade later at the rate of 300 tons of ore per day.

In 1978, when production had been increased to 1,100 tons per day, the company's name was changed to Corporación Minera Nor Peru, S.A. Annual production at that time reached 350,000 tons of ore yielding 2,400 tons of copper, 3,500 tons of lead, 10,000 tons of zinc, 1.8 million troy ounces of silver, and 2,600 troy ounces of gold. Although the small, erratic veins made mining difficult, the high grade of the ore also made it quite profitable. Soaring metal prices in the 1980s spurred drilling-exploration programs that delineated large reserves of remaining ore. In 1995, Pan American Silver acquired the mine and increased production to 1,700 tons per day. In 2012, the mine was acquired by Southern Peaks Mining. Today, Quiruvilca's ore reserves are sufficient for at least five more years of mining, but the results of recent core-drilling exploration indicates that the operating life of the mine will be extended significantly.

The primary ore minerals at Quiruvilca are chalcopyrite [copper iron sulfide, CuFeS_2], enargite [copper arsenic sulfide, Cu_3AsS_4], galena [lead sulfide, PbS], sphalerite [zinc sulfide, ZnS], pyrite [iron disulfide, FeS_2], and wurtzite [zinc iron sulfide, $(\text{Zn,Fe})\text{S}$], all of which contain

October 2013 Mineral of the Month

economic amounts of silver and gold. Quiruvilca's diverse mineralization also includes quartz [silicon dioxide, SiO_2], calcite [calcium carbonate, CaCO_3], bournotite [lead copper antimony sulfide, PbCuSbS_3], barite [barium sulfate, BaSO_4] and rhodochrosite [manganese carbonate, MnCO_3]. Quiruvilca's mineralization is quite rich in arsenic, which is apparent in the occurrence of realgar, orpiment, elemental arsenic, tennantite [copper iron zinc arsenic antimony sulfide, $\text{Cu}_6\text{Cu}_4(\text{Fe,Zn})_2(\text{As,Sb})_4\text{S}_{13}$], arsenopyrite [iron arsenic sulfide, FeAsS], and hutchinsonite [lead thallium arsenic sulfide, $(\text{Pb,Tl})_2\text{As}_5\text{S}_9$].

Quiruvilca has yielded fine specimens of realgar, orpiment, enargite, pyrite, and hutchinsonite. Since international specimen markets began to boom in the 1960s, Quiruvilca miners have collected and sold specimens as a source of secondary income. Unlike many mines, Quiruvilca does not have an organized, specimen-collection system. Miners are permitted to collect specimens as long as the practice does not interfere with production. Many miners therefore collect before and after their shifts, or during their meal and rest breaks. Cooperating shift bosses share in the profits.

Both the town of Quiruvilca and the Quiruvilca Mine are situated just above timberline at an elevation of 11,800 feet. Quiruvilca, population 8,000, is one of the highest communities of its size in the world. As the trading center for Quiruvilca Mine specimens, or *laques*, as they are known in the native Quechuan language, the town attracts mineral dealers from Lima who purchase specimens. Because Quiruvilca *laques* of realgar, orpiment, pyrite, enargite, and hutchinsonite are always in demand on international markets, their collection and sale is important to the local economy.

As you examine your specimen, note first that it consists both of realgar and orpiment. The realgar is present as small, deep-red to orange-red prisms. The orpiment, which forms the matrix of the specimen, is present as yellow-orange, radial, botryoidal masses with coatings of tiny, drusy crystals. In some specimens, the orpiment has formed on a base of colorless or white barite; on other specimens the orpiment rests on a base of fine-grained, light-colored, altered granite, which is a section of the vein wall. Specks and "hairline" veins of glittering, golden pyrite can be seen in the altered granite. Some specimens also have well-developed, sharp-edged crystals of colorless barite on the orpiment. Notice also that your specimen has a faint, yet distinctive odor of sulfur, which indicates the presence of free sulfur produced by the breaking down of arsenic-sulfur bonds. Your specimen is a fine example of realgar-orpiment as it occurs in hydrothermal-vein environments in the high, multimetal mines of the Peruvian Andes. And as a reminder, when you have finished studying your realgar-orpiment specimen, replace it in a lidded box and be sure to wash your hands.

October 2013 Mineral of the Month

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