May 2005 Mineral of the Month: Orpiment

> "The Elbrusskiy mine . . . has for a while now produced brilliant red-orange microcrystal crusts of orpiment." –Tom Moore, What's New in Minerals–Tucson Show 2002, *Mineralogical Record*

PHYSICAL PROPERTIES

Chemistry: As_2S_3 Arsenic Trisulfide (Diarsenic Trisulfide)
Class: Sulfides
Group: Orpiment
Crystal System: Monoclinic
Crystal Habits: Crystals, which occur as short, small prisms, are uncommon and poorly developed; often foliated, columnar, or fibrous; also as micaceous flakes, reniform and botryoidal masses, granular and powdery aggregates, and earthy incrustations.

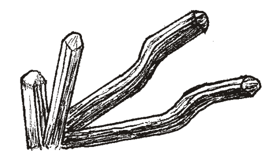

Figure 1. Orpiment crystals from Elbrusskiy

Color: Lemon-yellow and gold-yellow to orange, appears golden in thin sections or flakes
Luster: Resinous, pearly on cleavage surfaces
Transparency: Translucent to transparent
Streak: Lemon-yellow
Refractive Index: 2.4
Cleavage: Perfect in one direction
Fracture: Flaky; cleavage fragments flexible; sectile, scraping with knife blade produces curved shavings.
Hardness: 1.5-2.0
Specific Gravity: 3.4-3.5
Luminescence: None
Distinctive Features and Tests: Sometimes confused with sulfur, orpiment is the only other yellow mineral found in the same mineralogical environments, but sulfur lacks orpiment's perfect, one-directional cleavage. The best field identification features for orpiment are color, perfect cleavage, and frequent association with realgar (red-orange arsenic sulfide, As_4S_4).
Dana Classification Number: 2.11.1.1

NAME

The name "orpiment," pronounced ORE-puh-ment, derives from the Latin *auripigmentum*, literally "gold-colored," in reference to its distinctive yellow-gold color. Because of its wide distribution and long use as a pigment, orpiment has many alternative names, including "king's yellow," "yellow orpiment," "yellow arsenic," "yellow arsenic sulfide," "auripigment," "orpimento," "jaune royal," "rauschgelb," "arsenblende," "yellow arsenic ore," "arrhenicum," and "arsenikon." "Arsenic" derives from the Greek term *arsenikos*, meaning "strong, masculine."

COMPOSITION

The chemical formula of orpiment, As_2S_3, shows that it contains the elements arsenic (As) and sulfur (S). The molecular weight of orpiment is made up of 60.90 percent arsenic and 39.10 percent sulfur. Arsenic is a semimetal (an element with both metallic and nonmetallic properties) with three oxidation, or valence, states: +5, +3, and -3. Sulfur, a nonmetal, has four oxidation states: +6, +4, 0, and -2. Because of their positive and negative oxidation states, both arsenic and sulfur can act as cations (positively charged ions) or anions (negatively charged ions) in chemical compounds. Because orpiment contains trivalent arsenic (As^{3+}) and divalent sulfur (S^{2-}), the collective +6 charge of the diarsenic cation [$(As_2)^{3+}$] balances the -6 charge of the trisulfur anion [$(S_2)^{3-}$].

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Orpiment's Dana mineral-classification number, 2.11.1.1, places it in the sulfide class (2), which includes selenides and tellurides. It is subclassified (11) by the general formula $A_mB_nX_p$ in which the ratio of m+n to p is 2:3. A and B represent cations, while X represents an anion. This 2:3 ionic ratio is clearly apparent in orpiment's chemical formula As_2S_3. Orpiment is assigned to the orpiment group (1), in which it is the first member (1). The only other member of the orpiment group is getchellite (2.11.1.2), an arsenic antimony trisulfide with the chemical formula $AsSbS_3$. Notice how the getchellite formula, even with its double cation, meets the 2:3 ionic-ratio requirement of the orpiment group.

Arsenic, the semimetallic component of orpiment, occurs occasionally as a native element in combination with small amounts of antimony, nickel, silver, iron, or sulfur. It is brittle with little malleability, has poor electrical conductivity, and its fresh fracture surfaces tarnish quickly from tin-white to dull gray. Arsenic has a hardness of Mohs 3.5 and a specific gravity of 5.7. Elemental arsenic will sublime (turn directly from a solid to a gas) at about 600 degrees C. Even moderate heating will slowly volatilize arsenic, creating poisonous fumes with a diagnostic, garlic-like odor.

Arsenic has a great chemical affinity for sulfur, because both elements have numerous oxidation states and readily share electrons to form strong covalent bonds. Arsenic's affinity for sulfur is reflected in the large number of simple arsenic-sulfide minerals. Along with orpiment [As_2S_3], these include duranusite [As_4S], dimorphite [As_4S_3], realgar [As_4S_4], pararealgar [AsS, a paramorph of realgar], alacranite [As_8S_9], and uzonite [As_4S_5]. Arsenic's affinity for sulfur also explains its notorious toxicity. When arsenic or its compounds are ingested or inhaled, the arsenic ionizes and immediately begins bonding to any available sulfur ions which, unfortunately, include those that help make up the body's protein molecules. Arsenic-sulfur bonding destroys these protein molecules, disrupting normal physiological processes and causing chronic illness or death.

Orpiment molecules join together to form corrugated, polymeric, sheet-like structures, with two arsenic ions covalently bound to three sulfur ions, which are in turn bound to two arsenic ions. These sheets are layered but, because they are electrically neutral, cannot form strong covalent or ionic bonds with adjacent sheets. Instead, they are joined only by "van der Waals forces," which act much like static-electrical charges. These weak attractive forces between neutral atoms and molecules are generated by electrical polarization induced by the proximity of other particles. Because van der Waals forces are very weak compared to the strong covalent bonding within the layers, orpiment exhibits a perfect, one-directional cleavage. Scratching with a knife blade is enough to part the van der Waals forces, causing the individual molecular sheets to slip, thus making orpiment appear soft and accounting for its low Mohs hardness rating of 1.5-2.0. (See the February 2005 molybdenite write-up for more details on van der Waals forces.)

Orpiment is an idiochromatic, or "self-colored," mineral, meaning that its color is created by essential elemental components or by the nature of its atomic structure. Orpiment's bright yellow-orange color is explained by the "band-gap theory" of how its outer electrons absorb light energy. In semiconductors such as arsenic, some electrons are bound to specific ions while others, called "free" electrons, belong to the entire molecule. Exposure to light energizes some of the free outer electrons, thus stretching the outer energy levels into two separate "bands." The "valance band" represents the normal energy level of the electrons, while the "conduction band" is a higher energy level in which electrons have greater mobility. The energy difference between these two levels is called the "band gap." When white-light energy strikes orpiment, some electrons are boosted from the valance band into the conduction band. The gap between these two energy bands determines which part of the visible spectrum will be absorbed and which will be reflected. In orpiment, the band gap is such that absorption occurs only at the high-energy, blue-violet end of the spectrum. The remaining light energy is reflected and includes only the low-energy spectral wavelengths which we perceive as yellow and orange—the characteristic colors of orpiment.

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Orpiment is hydrothermally emplaced in epithermal (low-temperature), vein-type metal deposits. It most often occurs near hot springs, areas of volcanic activity, and fumaroles, where it is a product of sublimation (vaporization and subsequent condensation). Minerals associated with orpiment include cinnabar (mercury sulfide, HgS); calcite (calcium carbonate, $CaCO_3$); stibnite (antimony trisulfide, Sb_2S_3), barite (barium sulfate, $BaSO_4$), gypsum (calcium sulfate, $CaSO_4 \cdot 2H_2O$), and, most notably, realgar (arsenic sulfide, As_4S_4). Orpiment also forms from the alteration of realgar, native arsenic, and occasionally arsenopyrite (iron arsenic sulfide, FeAsS). The close association of realgar and orpiment is a diagnostic feature for the identification of both minerals, in fact, composite specimens of orange-red realgar and yellow-orange orpiment are common.

COLLECTING LOCALITIES

Orpiment has many collecting localities worldwide. In Japan, orpiment is collected at the Nyu Mine in Mie Prefecture and at the Nishinomaki mine in Gumma Prefecture. Fine specimens have come from the realgar deposit at Shimen (Chujiang), Hunan Province, China. Australia's orpiment sources include the Taliskere Mine at Cape Jervis and the Preamimma Mine in the Mt. Lofty Ranges, both in South Australia. In Italy, orpiment has long been collected at Monte Somma in the Vesuvius-Somma Complex in Naples Province, Campania; at the Molinello Mine near Ne in Genova Province, Liguria; and more recently at the marble quarries at Seravezza, Lucca Province, Tuscany. Russia's orpiment sources include the Elbrusskiy Mine in the Northern Causcasus Region, as we will see; the Lenskoye molybdenum-uranium deposit at Amurskaya Oblast' in the Far-Eastern Region; and the Senduchen area in the Lena River Basin in the Eastern-Siberian Region.

Most of South America's orpiment localities are in Peru and include the Atacocha district, Cerro el Pasco, Alcides Carrión Province, Pasco Department; the Casapalca Mine, Casapalca, Huarachiri Province, Lima Department; and the Julcani District, Angaraes Province, Huancavelica Department. In Mexico, fine specimens have come from the Soledad Mine at Guadalcázar in San Luis Potosí and the San Juan Nepomuceno Mine at Cadereyta in Querétaro. In Canada, the Taylor Pit in Huntingdon Township, Hastings County, Ontario, has yielded nice orpiment specimens.

Orpiment localities in the United States are largely concentrated in Utah and Nevada, due to the many, shallow, base- and precious-metal deposits and associated geothermal systems of the Basin-and-Range geological province. In Utah, an abundance of specimens have come from numerous mines in the Mercur district in the Oquirrh Mountains of Tooele County; at Butterfield Canyon in the Bingham District, Salt Lake County; and at the Fumarole No.2 and Camp Bird No. 7 mines in the San Rafael District of Emery County. In Nevada, orpiment is frequently associated with gold mineralization and occurs at the Meikle, Rain, and Jerritt Canyon gold mines in Elko County; the Carlin, Goldstrike, Gold Bar, and Gold Quarry mines in Eureka County; the Getchell, Turquoise Ridge, Pinson, and Twin Creeks mines in Humboldt County; the Copper Canyon Mine in Lander County; the Lucky Boy, White Caps, Manhattan Consolidated, Paradise Peak, and Florida Canyon mines in Nye County; and at Steamboat Hot Springs in Washoe County.

JEWELRY & DECORATIVE USES

While orpiment is far too soft (Mohs 1.5-2.0) to serve as a gemstone, it is highly valued by collectors for its mineralogical interest and color. Orpiment crystals are uncommon, but occur in sizes up to three inches. Two precautions are advised for the storage of orpiment specimens. Orpiment is light-sensitive; prolonged exposure to bright, white light can cause both chemical and physical deterioration, the latter apparent as a very slow breakdown of the crystalline structure into a powder. Also heat, such as that produced by bright lights in enclosed display cabinets, can cause orpiment to sublime into potentially harmful vapors. While displaying orpiment specimens under normal conditions is not a problem, many collectors store their specimens in cool, dark places. Remember that arsenic and its compounds are toxic, so never heat orpiment for any reason, and be sure to wash your hands after handling orpiment or any other arsenic compound.

HISTORY & LORE

Orpiment has been known since antiquity. Egyptian artists used it as a pigment as early as 3100 B.C. Because of its golden color, the Roman emperor Caligula (*Gaius Caesar*, 12-41 A.D.) instructed his alchemists to concentrate on orpiment in their efforts to create gold. Even in medieval times, European alchemists were still trying to convert orpiment to gold. Although orpiment was the only available, natural yellow-gold pigment, it was difficult to prepare because grinding broke it down into rough cleavage fragments, rather than into a more desirable fine powder. Nevertheless, orpiment was a very popular pigment among Europe's Renaissance artists. But its use declined after 1550, when artists realized that it was not stable and that it chemically darkened certain other mineral-based pigments that it contacted. Orpiment pigments regained popularity after 1750 in Asia and the Middle East, where it remained in use until finally being replaced by synthetic yellow-orange pigments in the early 1900s.

Historians believe that the German philosopher, theologian, and naturalist Albertus Magnus (1193-1280) first isolated elemental arsenic in the year 1230 by chemically reducing orpiment. Despite its toxicity, arsenic and its compounds were long employed in medicine, usually as purgatives and to treat infections. Its medicinal use persisted until the development of sulfa drugs and antibiotics in the 20th century.

Orpiment was an important ore of arsenic until the 1970s, when new air-quality regulations mandated the "scrubbing" of smokestack emissions at metal smelters. Because arsenic often substitutes for zinc, lead, and silver in sulfide-ore minerals, stack emissions contained large quantities of arsenic. "Stack scrubbers" now recover enough arsenic to satisfy worldwide industrial demand, eliminating the need to mine orpiment and other arsenic-bearing minerals.

Orpiment has appeared in 1982 on the 4-fen stamp of the People's Republic of China and in 1994 on the 120-tyiyn stamp of Kyrgyzstan. According to current metaphysical belief, orpiment speeds recovery from disease and aids in the understanding and elimination of mental blocks by imparting direction and a sense of purpose.

TECHNOLOGICAL USES

Arsenic and its compounds have many industrial applications. About 35,000 tons of arsenic are recovered worldwide at metal-smelting and -refining operations annually. Some 21,000 tons, worth about $18 million, are used in the United States each year, most for manufacturing wood preservatives which are toxic to fungi and wood-boring insects and worms. Smaller amounts are added to glass mixtures to eliminate the greenish tinge caused by difficult-to-remove iron impurities. Elemental arsenic is alloyed with lead to make harder, stronger posts and grids for automotive batteries. Synthetic arsenic disulfide, brightly colored like its natural-sulfide counterparts orpiment and realgar, is known as "red orpiment" or "ruby arsenic" and is a commercial red pigment for specialty paints and pyrotechnics. Because arsenic is a semimetal, it is used to manufacture gallium arsenide and other synthetic semiconducting materials needed for solid-state components of high-speed computers. Because of public health concerns related to arsenic's toxicity, many nations are steadily reducing the industrial use of arsenic.

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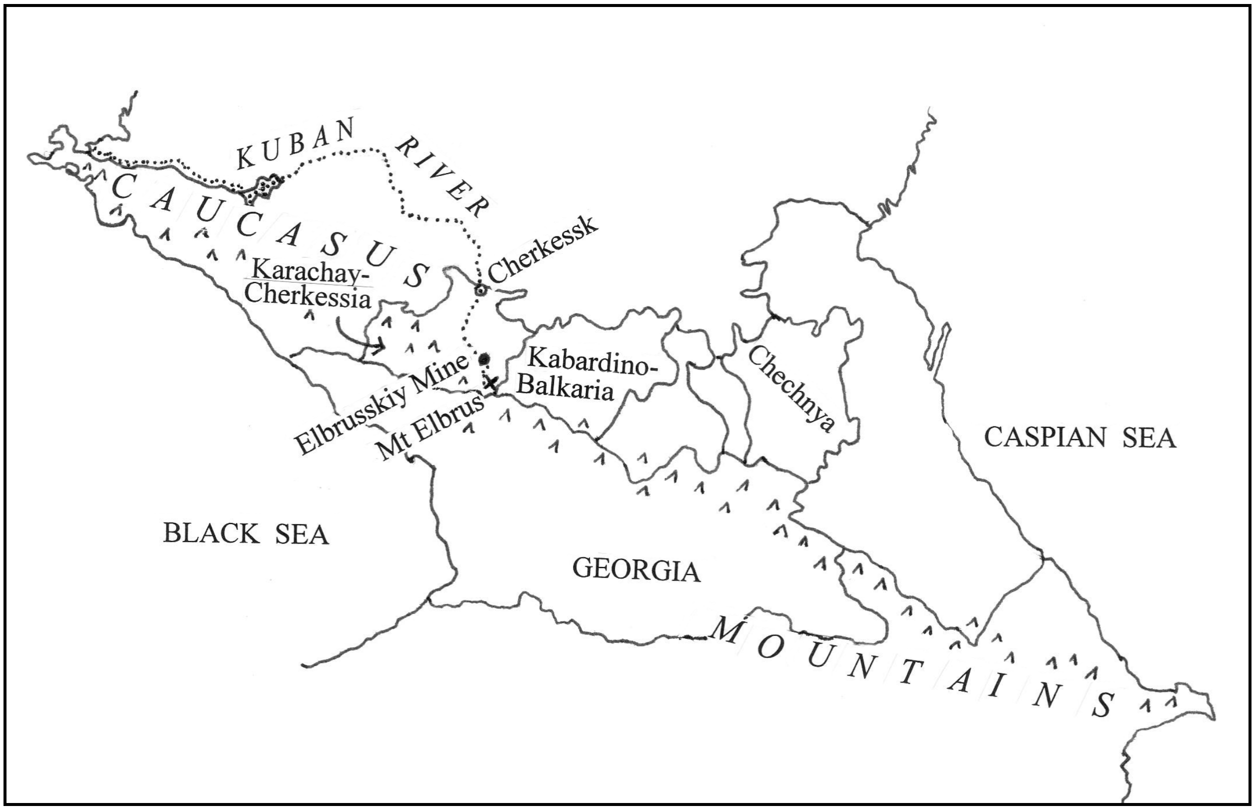

Figure 2. Caucasia region

ABOUT OUR SPECIMENS

To find the locality of our fine orpiment pieces, let's gradually zero in on it, and get a little history as we go. First, find the Caucasia (or Caucasus) region, a mountainous area on an isthmus, with the Black Sea to the west, and the Caspian Sea to the east. The Caucasus Mountains traverse from the northwestern shores of the Black Sea to the to the southeastern Caspian, and are considered the border between Europe and Asia. The region includes the countries of Armenia, Azerbaijan, and Georgia, and several of the 21 Russian autonomous republics, which are the administrative units with the greatest amount of independence in the Russian Federation.

This region was one of mankind's first settled area, with farming and mining dating back to earliest recorded history. Nestled between the two large seas, Caucasia was seen by ancient empires as a militarily vital transit corridor. Around 1800 AD, a European anthropologist erroneously postulated that Caucasia was the original home of the hypothetical Indo-European people, and used the term "Caucausian" to designate the "race" of "white" people, centered on the Mediterranean. This was during a time when anthropologists proposed various systems of racial classifications based on such observable characteristics as skin color, hair type, body proportions, and skull measurements. Modern anthropogists reject such attempts at classification, and the designation "Caucasian" is no longer used by scientists. Aren't we all just members of the human race?

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Now we'll focus on Mount Elbrus (El'brus), which, at 18,510 feet is the highest peak in Europe, although it is barely in Europe. This peak sits in the Karachay-Cherkessia autonomous republic (AR), near where it meets the country of Georgia, and another AR, Kabardino-Balkaria. Karachay-Cherkessia covers about 5,400 square miles and has a population of 436,000. Cherkessk is its administrative center. The republic lies on the northern slopes of the Caucasus Mountains, a land of farmers, livestock herders, miners (coal, zinc, lead, and copper,) and manufacturers (rubber, chemicals, furniture, and building materials.)

About 35 miles north of Mt. Elbrus lies Elbrusskiy (also spelled El'brusskiy), evidently the name of both the local mine and the local town, on the Kuban (or Kuban′) River. Elbrusskiy Mine is an old lead/arsenic mine, which produces, not surprisingly, fine, colorful specimens of orpiment like ours, and rarely, crystals of barite, On one occasion, barite crystals up to 4" long literally dropped off the walls, falling at the feet of surprised collectors! We obtained our specimens from a group of Russian collectors who made a large find at Elbrusskiy a few years ago. A second trip was made, and virtually nothing like our specimens was found! We'll try to keep you informed on further attempts there.

Orpiment now joins the ranks of the minerals we have featured twice in the Club from different localities. In November 1997 we sent Club members chunks of massive yellow orpiment from the Getchell Mine, Humboldt County, in northern Nevada. Getchell is a gold mine that has been worked off and on since 1934, and for the last few years, gold has been recovered from large veins of orpiment, up to 100 feet across, filling cracks and fractures in the host rock there. In an effort to recover as much gold as possible, the gold-bearing orpiment ore was crushed, and chemicals used to leach out even submicroscopic particles! In 1996, 171,286 ounces of gold were recovered by these methods!

Those of you with a magnifier glass or jeweler's loupe will enjoy a close look at the thin prismatic crystals on your specimen, looking rather like our drawing in Figure 1. What color and transparency-- and look at those amazing terminations! These are excellent examples of prismatic crystals (when used to describe crystals, "prism" means a solid figure whose bases or ends have the same size and shape and are parallel to one another). According to one source, the crystals are flexible, but bending them causes them to change to an opaque yellow crystal form, which we would hate to do. Fortunately, many of our specimens have such yellow crystals around the edges, perhaps from crystals being bent during removal from the mine. According to another source, the orpiment forms on a bed of white barite crystals, and we did get a few specimens where small barite crystals can be seen. As mentioned earlier, be careful where you store or display your specimen, so no damage is done by light or proximity to heat. And be sure to wash your hands after each time you handle it!

References: Dana's New Mineralogy, Eighth Edition; *Encyclopedia of Minerals*, Second Edition, Roberts, et al, Van Nostrand Reinhold Company; *2004 Fleischer's Glossary of Mineral Species*, J. A. Mandarino, The Mineralogical Record, Inc.; *Mineralogy*, John Sinkankas, Van Nostrand Reinhold Company; *Minerals of Nevada*, Stephen B. Castor and Gregory C. Ferdock, University of Nevada Press; "Arsenic," *2003 Minerals Yearbook*, United States Geological Survey; *Artists' Pigments: A Handbook of Their History and Characteristics*, Volume 3, E. W. Fitzhugh (editor), Oxford University Press; "Connoisseurs' Choice: Orpiment, Twin Creeks Mine, Humboldt County, Nevada," Robert B. Cook, *Rocks & Minerals*, March-April 2000; "Orpiment From Hunan, China: A Crystallographic Note," R. Peter Richards, *Rocks & Minerals*, July-August 1998; "Mineralogy of the Seravezza Marble," P. Orlandi, L. Del Chiaro, and R. Pegrano, *The Mineralogical Record*, January-February 1996; "Mines and Minerals of Peru," Jack Crowley, Rock Currier, and Terry Szenics, *The Mineralogical Record*, July-August 1997; "What's New in Minerals: Denver Show 2004," Tom Moore, *The Mineralogical Record*, January-February 2005; "A Guide to Mineral Localities in the Former Soviet Union," Bill & Carol Smith, *The Mineralogical Record*, November-December 1995; "The Gold Quarry Mine, Carlin Trend, Eureka County, Nevada," M. C. Jensen, J. C. Rota, and E. E. Foord, *The Mineralogical Record*, September-October 1995; "Another Specimen-Recovery Project," Bryan Lees, *Rocks & Minerals*, November-December 1999.