

January 2014 Mineral of the Month

FLUORITE

This month's mineral is fluorite from the Huanggang Mine, one of China's newest and most modern underground mines. Our write-up discusses the properties of fluorite, the origin of the Huanggang skarn deposit, and the properties, uses, and nature of the element fluorine.

OVERVIEW

PHYSICAL PROPERTIES

Chemistry: Calcium Fluoride CaF_2

Class: Halides

Group: Fluorite

Crystal System: Isometric (Cubic)

Crystal Habits: Usually cubic, often as penetration twins; less frequently octahedral; rarely dodecahedral; also occurs in botryoidal, granular, massive, columnar, and earthy forms, and as cleavage masses.

Color: White, colorless, violet, purple, lilac, blue, green, yellow, brown, amber, bluish-black, pink, and rose-red.

Luster: Vitreous

Transparency: Transparent and translucent to nearly opaque

Streak: White

Cleavage: Perfect in four directions to form octahedrons

Fracture: Uneven, brittle.

Hardness: 4.0

Specific Gravity: 3.0-3.2

Luminescence: Often fluorescent and phosphorescent, sometimes thermoluminescent and triboluminescent.

Refractive Index: 1.433

Distinctive Features and Tests: Best field indicators are cubic or octahedral crystal form and excellent crystal development; perfect, four-directional cleavage; relative softness; and occurrence in fluorine-rich mineral environments.

Dana Classification Number: 9.2.1.1

NAME: The name "fluorite," pronounced FLOR-ite, stems from the Latin *fluere*, meaning "to flow" and alluding to fluorite's ability to reduce the melting temperatures of metals in smelting processes. Fluorite's many alternative names include "androdamant," "bruiachite," "Derbyshire spar," "fluor," "fluores," "fluoride of calcium," "fluoride of lime," "fluorspar," "fluorspath," "flusse," "flusspat," "liparite," "murrhina," and "spath vitreux." In European mineralogical literature, fluorite appears as *fluorit*, *fluorita*, and *fluorin*. Color-variety names include "false emerald," "false amethyst," "false ruby," and "fluorite rose." "Chlorophane" refers to a thermoluminescent variety. The "blue john" variety, found only in England, has alternating yellow, blue, and purple bands; "rainbow fluorite" is multicolored.

COMPOSITION: The chemical formula CaF_2 shows that fluorite contains calcium (Ca) and fluorine (F). Calcium accounts for 51.33 percent of fluorite's molecular weight, fluorine for 48.67 percent. The fluorite molecule and crystal lattice are held together almost entirely by ionic bonding. Because of ionic bonding's inherent weakness, fluorite has perfect, four-directional cleavage to form octahedrons and is relatively soft at Mohs 4.0. Fluorite has the broadest color range of all minerals. Its colors are caused by traces of nonessential elements called chromophores, or by lattice defects called "color centers" that result from abnormal crystal growth, exposure to natural geophysical radiation, or the displacement of free fluorine ions. Fluorite is relatively abundant and forms in several mineralogical environments. In epithermal (low-temperature) veins, it is associated with calcite, rhodochrosite, and chalcedony. Fluorite occurs with albite and pyrite in carbonatites, with calcite and spinel in the hornfels of contact metamorphic rocks, and occasionally with albite in granite pegmatites. In hydrothermal replacement deposits, it occurs with galena, pyrite, sphalerite, and barite and is a common gangue mineral with many lead, zinc, and silver ores. It is also found in fluorine-rich skarn environments in association with diopside, wollastonite, tremolite, and andradite.

COLLECTING LOCALITIES: Fluorite is collected in China, England, Russia, Pakistan, Namibia, Morocco, South Africa, Zimbabwe, Norway, Sweden, Spain, Germany, Italy, Peru, Bolivia, Australia, Hungary, Canada, and Mexico. In the United States, specimens are collected in Illinois, Kentucky, Oklahoma, Ohio, New Hampshire, Colorado, New Mexico, and Tennessee.

HISTORY, LORE & USES: Used as a decorative stone since ancient times, fluorite is fashioned into spheres, dishes, figurines, vases, and other utilitarian and ornamental objects. Although its softness limits its use in jewelry, fluorite is often faceted into collectors' gems. Fluorite has been used as a smelting flux since about 600 B.C. and continues to serve in metallurgical processes today. Fluorite is mined extensively as the primary source of fluorine for the manufacture of hydrofluoric acid, an important feedstock for the chemical and pharmaceutical industries. It is also converted into uranium hexafluoride (UF_6) for use in the gas-diffusion concentration of the uranium-235 isotope for nuclear fuel rods and nuclear weapons. Considerable amounts of fluorite are processed into aluminum fluoride (AlF_3) and synthetic cryolite [sodium aluminum fluoride, Na_3AlF_6] for use as a flux in aluminum-smelting processes. According to metaphysical beliefs, fluorite calms the spirit and mind when preparing for meditation, clarifies the decision-making process, and enhances objectivity and concentration.

ABOUT OUR SPECIMENS: Our fluorite specimens were collected at the Huanggang Mine in Hexigten Banner (County) near the city of Chifeng, Chifeng Prefecture, Autonomous Region of Inner Mongolia, China. Huanggang, one of China's newest mines, is actually a mining complex that consists of seven shaft-accessed, underground mines. The shafts are approximately 2,000 feet deep. Construction of the complex began in 2002 and was completed in 2008 when limited production began. The main economic products are tin and iron. The Huanggang ores are part of a large skarn deposit that formed when magma intruded strata of limestone and dolomite rock. The heat and pressure associated with magmatic intrusions initially caused contact metamorphism where the magma contacted the host rock. Hot, acidic solutions associated with the magma then circulated through the altered rocks, reacting with the carbonates in the

limestone and dolomite rock to create new minerals. Many skarns host economic mineral deposits. Huanggang yielded its first mineral specimens in 2010 and has since gained international recognition as a source of fine and unusual specimens.

COMPREHENSIVE WRITE-UP

COMPOSITION

This is the fifth time we have featured fluorite as our Mineral of the Month. Because of fluorite's unusually wide range of colors, varied distinctive crystal habits, large number of collecting localities, and many mineralogical associations, our specimens have all differed greatly in appearance. Our specimens this month are from a recently opened locality that contributes to the remarkable diversity of fluorite specimens.

The chemical formula CaF_2 shows that fluorite contains the elements calcium (Ca) and fluorine (F). Fluorite's molecular weight consists of 51.33 percent calcium and 48.67 percent fluorine. The chemically simple fluorite molecule has a single cation (positively charged ion) and a single anion (negatively charged ion). This molecule is joined together almost entirely by ionic bonding. Ionic bonding is the attractive force between the positively charged ions of metallic elements and the negatively charged ions of nonmetallic elements. In fluorite, the calcium ion Ca^{2+} with its +2 charge is attracted to, and ionically bonds with, two fluorine ions 2F^{1-} with their collective -2 charge. Electrical stability within the molecule is provided by the balance of the anionic and cationic charges.

Within the fluorite crystal lattice, eight fluorine ions surround each calcium ion, while four calcium ions surround each fluorine ion. This arrangement creates alternating rows of calcium ions and fluorine ions that create a cubic structure with the calcium ions at the eight corners of each cube and at the centers of its six faces. Because of the weakness of ionic bonding, fluorite is relatively soft at Mohs 4.0 and exhibits perfect, four-directional cleavage to cleave easily into octahedrons. Although the atomic weights of its essential elements calcium (40.08) and fluorine (19.00) would indicate a specific gravity of about 2.8, fluorite actually has a substantially higher specific gravity 3.0-3.2 because of the close atomic packing of its calcium and fluorine ions within a rigid, well-organized cubic structure. While the ionic bonding within the crystal lattice is weak enough to produce relative softness and perfect cleavage planes, the ionic bonding within the molecule is much stronger and provides fluorite with a high degree of chemical stability.

Fluorite has the widest color range of all minerals because of elemental impurities, defects in the crystal lattice, and unbound fluorine ions. As an allochromatic or "other-colored" mineral, fluorite's colors are most often caused by traces of nonessential elements called chromophores (color-causing agents). When pure, fluorite is colorless or white, but traces of iron and the rare-earth elements yttrium and cerium can substitute for calcium, altering the light-absorption and light-reflection properties of the lattice. Iron imparts green and yellow colors to fluorite, traces of yttrium and cerium impart pink and rose colors, and lanthanum imparts green colors. Purple, blue, and violet colors are usually due to lattice defects called "color centers," which result from

abnormal crystal growth or exposure to natural geophysical radiation. In fluorite, color centers form when fluorine ions are displaced from their normal lattice positions to create voids which then trap electrons. White light boosts these trapped electrons to higher energy levels; as the electrons return to normal levels, they release this excess energy as purple, blue, or violet light. Fluorite is often color-zoned, color-banded, or multicolored, depending upon conditions at the time of crystallization. Fluorite that formed through single-phase precipitation is usually monocolored with minimal color-zoning. But changes in the chemistry of hydrothermal solutions during slow or multiple-phase precipitation often create multicolored or banding effects.

Fluorite is often luminescent and can exhibit fluorescence, phosphorescence, thermoluminescence, and triboluminescence. Luminescence occurs when some minerals absorb electromagnetic, mechanical, thermal, and or radiation energy. This energy excites certain electrons, boosting them from normal-energy, inner orbits to high-energy, outer orbits. To return to their normal orbits, they release excess energy as visible light. In fluorescence, electromagnetic energy in the form of ultraviolet light energizes certain electrons, which then release excess energy by emitting visible light, usually in the blue wavelengths. The term “fluorescence” is actually derived from the word “fluorite,” which was the first mineral used to study this phenomenon. In phosphorescence, minerals continue to emit visible light even after the input energy source, such as ultraviolet light, has been removed. Triboluminescent minerals emit light when subjected to mechanical stress; thermoluminescent minerals emit light when heated.

Fluorite is relatively abundant and forms in several mineralogical environments. In epithermal (low-temperature) veins, it is associated with calcite [calcium carbonate, CaCO_3], rhodochrosite [manganese carbonate, MnCO_3], and chalcedony [microcrystalline quartz, silicon dioxide, SiO_2]. In hydrothermal replacement deposits, it occurs with galena [lead sulfide, PbS], pyrite [iron disulfide, FeS_2], sphalerite [zinc sulfide, ZnS], and barite [barium sulfate, BaSO_4]. Fluorite is a common gangue mineral associated with many lead, zinc, and silver ores. It occurs with albite [sodium aluminum silicate, $\text{NaAlSi}_3\text{O}_8$] and pyrite in carbonatites (calcium-rich igneous rocks); with calcite and spinel [magnesium aluminum oxide, MgAl_2O_4] in the hornfels (fine-grained, altered silicate rocks) of contact metamorphic zones; and occasionally with albite in granite pegmatites. Fluorite is also found in fluorine-rich skarn deposits in association with andradite [garnet group, calcium iron silicate, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$], wollastonite [calcium silicate, CaSiO_3], diopside [calcium magnesium silicate, $\text{CaMgSi}_2\text{O}_6$], and tremolite [basic calcium magnesium silicate, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$].

The Dana classification number 9.2.1.1 first identifies fluorite as a halide mineral (9). It is subclassified (2) as an anhydrous halide with the general formula AX_2 , in which “A” can be calcium, barium, or the rare-earth element yttrium, and “X” is any halogen element. Fluorite is then assigned to the fluorite group (1) as the first (1) of three members, which include the physically similar minerals frankdicksonite [barium fluoride, BaF_2] and tveitite-Y [calcium yttrium fluoride, $\text{Ca}_{14}\text{Y}_3\text{F}_{43}$].

COLLECTING LOCALITIES

As a relatively abundant and widely distributed mineral, fluorite has many collecting localities. Our specimens are from the Huanggang Mine in Hexigten Banner (County) near the city of Chifeng in Chifeng Prefecture in the Autonomous Region of Inner Mongolia, China. Other Chinese sources are the Tongbai fluorite mine in Tongbai County, Gaoxin District, Nanyang Prefecture, Henan Province; and the Huangshaping, Yaogangxian, Dongpo, Xianghualing, Chashan, and Xianghuapu lead-zinc mines in Chenzou Prefecture, Hunan Province.

In the Pakistan's Northern Areas, specimens come from the Nagir and Chumar Bakhoor areas of the Hunga Valley in the Gilgit District, and the Baha and Apo Ali Gun areas near Baltistan. Russian sources include the Pouvyia and Dodo mines at Tyumenskaya Oblast' in the Polar Urals of the Western-Siberian Region, and the Aunik rare-metals deposit at Buriatia in Transbaikalia in the Eastern-Siberian Region. In Peru, fluorite is collected in the Huaron Mining District at Cerro del Pasco in Pasco Department, and the Pasto Buena Mining District in Ancash Department. In Australia, fluorite occurs at the Sandy Creek fluorite deposit at Walwa in Victoria, the Cannington silver-lead-zinc deposit in the Mt. Isa-Cloncurry area of Queensland, and the Gulf Fluorite Mine at The Gulf in New South Wales. Other localities include the El Hammam Mine at Meknès, Meknès-Tafilalet Region, Morocco; the Okoruso Mine in the Otjiwarongo District and the Kombat Mine in the Grootfontein District, both in Namibia's Otjozondjupa Region; the Hwange lead-zinc district in Matabeleland, North District, Zimbabwe; the Mururata and Chojilla mines in Sud Yungas Province, La Paz Department, Bolivia; the Aladdin Fluorite Mine at Sinkwazi in KwaZulu-Natal Province, and the Marico Fluorspar Mine in the Marico district in Northwest Province, both in South Africa.

In Mexico, fluorite occurs in the Navidad Mine near El Rodeo, and the China, Ojuela, and Reina mines at Mapimí, all in Durango; and the Cantera and Asturiana mines, Mun. de Zacatecas, Zacatecas. Canadian sources include the Rogers Fluorspar Mine at Madoc in Huntingdon Township, Hastings County, Ontario; the Poudrett, Uni-Mix, and Desourdy quarries at Mont Saint-Hilaire, Rouville County, Québec; and the Penobsquis potash mines, Kings County, New Brunswick. In England, fluorite sources include the Rogerley Mine in the Weardale district near Frosterly, North Pennines County, Durham; and the Blue John and Old Tor mines and Treak Cliff Cavern at Castleton, Derbyshire, Cornwall. Other localities are the Lassedalen fluorite deposit and the Kongsberg silver mines near Kongsberg, Buskerud, Norway; the Manhem, Kåravet, and Finnbo mines at Falun, Dalarna, Sweden; the La Florina and Gloria mines at Hornachuelos near Córdoba, Andalusia, Spain; the Bella Mine at Pákozd in the Velencei Mountains of Fejér County, Hungary; the Badenweiler lead-mining district in the Black Forest region of Baden-Württemberg, Germany; and the Carrara marble quarries in the Apuan Alps of Massa-Carrara Province, Tuscany, Italy.

In the United States, fluorite occurs throughout the Illinois-Kentucky Fluorspar District, notably in the Cave-in-Rock and Ozark-Mahoning subdistricts of Hardin County, Illinois; and the Babb, Commodore, Tabb, and Dike-Eaton subdistricts of Crittenden and Caldwell counties, Kentucky. The Elmwood Mine at Carthage in Smith County, Tennessee, has yielded exceptional specimens. Colorado's localities include the Sweet Home Mine at Alma, Park County; the Barstow Mine near Ouray, Ouray County; and the Browns Canyon Fluorspar District, Chaffee County. In New Mexico, fluorite occurs at Fluorite Ridge, Luna County; the Hansonburg district near Bingham in Socorro County; and Pine Canyon near Tyrone in Grant County. Fluorite is also collected at the

Capital and Ten Acre quarries, Johnston County, Oklahoma; the William Wise Mine in Westmoreland, Cheshire County, New Hampshire; and the Kelly Island Stone Quarry at Clay Center, Ottawa County, Ohio.

JEWELRY & DECORATIVE USES

Fluorite, usually cleaved into octahedrons, has long served as a gemstone. Faceted fluorite gems were popular in Europe in the 1600s, when color varieties called “false emerald,” “false ruby,” and “false amethyst” were popular imitations of more valuable gems. As a gem, fluorite has good transparency, many attractive colors, a vitreous luster, and sizeable crystals that can be cut into large gems. But its gemological drawbacks include a low refractive index of 1.433 that limits brilliance, four-directional cleavage that complicates cutting, and a softness that makes it unsuitable for everyday jewelry wear. Nevertheless, fluorite cabochons and faceted gems are occasionally mounted in pendants and brooches. Collectors’ gems are often cut into sizes exceeding 100 carats. The National Museum of Natural History (Smithsonian Institution) in Washington D.C. displays a remarkable collection of fluorite gems, the largest weighing 492.1 carats. Massive fluorite is also carved into such decorative objects as spheres, dishes, vases, and figurines.

Fluorite mineral specimens are widely collected because of their large crystal size, excellent crystal development, availability, affordability, and broad range of colors.

HISTORY & LORE

Amulets and decorative objects have been carved from massive fluorite for thousands of years. Greek metalworkers began using fluorite around 600 B.C. as a smelting flux to remove impurities from, and lower the melting temperature of, silver. The Romans later mined fluorite in Spain and England as a smelting flux for lead, silver, and copper ores. The distinctive, blue-purple-and-yellow-banded “Blue John” fluorite mined in England was a favorite Roman carving medium. By 1500 A.D., European metallurgists were using fluorite, which they called *flusse* or *flussspat*, as a standard smelting flux. In his classic *De re Metallica*, German scholar Georgius Agricola (Georg Bauer, 1494-1555) described the use of *flussspat*, which he called “*lapides igni liquiscentes*,” literally “stones that become liquid in fire.” Agricola also renamed *flussspat* using the Latin word *fluere*, meaning “to flow,” a word later anglicized to “fluor” and “fluorspar.” By 1670, German glassworkers were treating *flussspat* with sulfuric acid to produce another acid called *flussspatäure* (“acid of *flussspat*”) that could etch glass and greatly advanced the art of glassmaking. Fluorite was formally named in 1868.

Medieval physicians prescribed powdered fluorite to treat kidney disease and fluorite crystals to alleviate arthritic pain. Modern metaphysical practitioners believe that fluorite calms the spirit and mind when preparing for meditation, enhances objectivity and concentration, and clarifies the decision-making process. Metaphysical healers assign specific powers to individual fluorite colors: White is thought to help access the spiritual world, green to energize the heart and mind,

blue to provide inner peace, purple to focus the mind, and yellow to facilitate group communication.

Fluorite is the official state mineral of Illinois. Fluorite specimens have been featured on Switzerland's 10-centime stamp of 1961, Namibia's 2-cent stamp of 1991, Kyrgyzstan's 80-tyiyn stamp of 1994, Kenya's 80-cent stamp of 1977, Algeria's 2.40-dinar stamp of 1983, and France's 5-franc stamp of 1986.

THE FACTS ABOUT FLUORINE

Fluorine, one of fluorite's two essential elements, is the most abundant of the halogens, a group of five closely related, chemically active elements—fluorine, chlorine, bromine, iodine, and astatine. The name “halogen” stems from the Greek *hals*, meaning “salt,” and *genēs*, or “born,” and literally means “salt former,” alluding to the halogens' ability to combine with sodium to form salts similar to common salt or halite [sodium chloride, NaCl].

Fluorine is a pale-yellow gas with a pungent, penetrating somewhat metallic odor. It has an atomic weight of 18.998; its specific gravity of 1.51 makes it slightly denser than air. Ranking 17th in crustal abundance, it is about as common as sulfur. The fluorine atom has nine electrons: two in the inner orbit and seven in the outer orbit. Because atoms achieve stability when their outer rings contain eight electrons, fluorine requires just one additional electron for stability and will accept electrons from most other atoms. As the most electronegative element, no other element attracts electrons as strongly as fluorine. This extraordinary electronegativity gives fluorine a level of chemical reactivity that is the highest of all the elements. Fluorine is so reactive that it bonds explosively with hydrogen and such chemically reactive metals as sodium. When subjected to jets of fluorine gas, wood and even water will ignite without a spark.

Fluorine occurs in more than 60 minerals, usually in very small amounts. Only three minerals are sufficiently abundant and contain enough fluorine to serve as commercial sources of fluorine:

Fluorite [calcium fluoride, CaF_2] is the main commercial source of fluorine and fluorine compounds. Fluorite contains 48.67 percent fluorine (see “Composition” and “Technological Uses”).

Apatite-(CaF) [calcium fluorophosphate, $\text{Ca}_5(\text{PO}_4)_3\text{F}$], formerly known as “fluorapatite,” is by far the most abundant of all fluorine-containing minerals, although it contains only 3.77 percent fluorine. Most of the fluorine in the Earth's crust is present as apatite-(CaF). Apatite-(CaF), as phosphate rock, is mined worldwide as a source of phosphorus compounds. In the United States, phosphate-rock waste is reprocessed to recover fluorosilicates as a source of fluorine.

Cryolite [sodium aluminum fluoride, Na_3AlF_6] is the least abundant of the three major fluorine-containing minerals. Consisting of 54.30 percent fluorine, it is also the most concentrated natural source of fluorine. It was formerly mined for use as a metallurgical flux for aluminum smelting, a purpose now served by synthetic cryolite.

By 1800, chemists realized that fluorite and the powerful acid derived from it contained an extraordinarily reactive, but unknown element. In 1813, French physicist André Marie Ampère (1775-1836) named this mysterious element *phlor* (Greek for “destructive”). The influential English chemist Sir Humphry Davy (1778-1829), however, preferred the word “fluorine,” a derivative of the traditional “fluorspar.”

Progress in isolating this strange element was slowed by the exceptional dangers involved. At least six chemists and other researchers lost their health or their lives by inhaling or contacting fluorine-based acids and vapors and became known as the “fluorine martyrs.” All attempts to isolate the element were hindered by the extreme reactivity and corrosiveness of hydrogen fluoride and of fluorine itself. In many experiments, fluorine either combined explosively with other elements or hydrofluoric acid destroyed the laboratory glassware.

Finally in 1886, French chemist Ferdinand Frederick Henri Moissan (1852-1907) isolated pure fluorine by electrolytically reducing hydrofluoric acid and potassium fluoride (KF). In his experiments, Moissan used corrosion-resistant laboratory equipment made of platinum-iridium alloys, with stoppers carved from fluorite. Moissan’s work to reveal the chemical nature of fluorine earned him the 1906 Nobel Prize for chemistry, but also caused his death just months later at age 55. Moissan’s Nobel citation read: . . . *in recognition of the great services rendered by him in his investigation and isolation of the element fluorine. . . . The whole world has admired the experimental skill with which you have studied that savage beast among the elements.*

The element that Moissan had isolated would later have enormous scientific and industrial uses. In the early 1930s, the DuPont de Nemours Company began producing chlorofluorocarbons (CFCs), the most notable of which was Freon-12™, a non-toxic refrigerant that revolutionized refrigeration technology. In 1938, a DuPont researcher accidentally discovered Teflon™, a fluorine-containing polymer that is among the most corrosion-resistant and thermally stable polymers ever developed. During World War II, one of the biggest challenges facing the Manhattan Project, the American effort to develop an atomic bomb, was separating the fissionable U-235 isotope of uranium. Uranium hexafluoride (UF₆) was the only material suited for the gas-diffusion concentration of U-235. It is still used today to prepare enriched uranium for nuclear fuel rods and fission components for nuclear weapons. Large quantities of fluorite are also converted to synthetic cryolite [sodium aluminum fluoride, Na₃AlF₆] for use in aluminum smelting.

Today, fluorochemical manufacturing is a \$15 billion global industry. Fluorine is a component of most modern refrigerant gases. After most CFCs were banned for environmental reasons in the 1980s, they were replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) that are standard today in refrigerants, water repellants, anti-reflection optical coatings, aerosol propellants, and solvents. Fluoropolymers, specifically polytetrafluoroethylenes (PTFEs), are core components in such products as Teflon™, many electrical insulating compounds, and such textile fibers as Gore-Tex™.

One-quarter of all modern pharmaceuticals contain fluorine, including such widely used drugs as cholesterol-reducing Lipitor™ and the asthma medication Advair™. Adding traces of fluorine

to drugs greatly changes their chemical properties and the manner in which they interact with the body. In other medical uses, a fluorine isotope is vital in positron emission tomography (PET) scanning.

Since the 1960s, drinking water has been fluorinated to reduce tooth decay. Fluorine is present in apatite-(CaF), apatite-(CaCl), and apatite-(CaOH), which are the primary components of bones and especially of teeth in vertebrate animals. Of these three minerals, apatite-(CaF) is by far the hardest and most durable. When added to drinking water and toothpaste, fluorides displace chlorine and hydroxyl ions, thus converting apatite-(CaCl) and apatite-(CaOH) into much more decay-resistant fluorapatite-(CaF) that increases the hardness and durability of teeth.

For more than 200 years, researchers have debated whether fluorine could occur naturally in its elemental state. Because of its extreme reactivity, most chemists traditionally believed that elemental fluorine did not exist in nature. But fluorite specimens from the Maria Mine at Woelsendorf, Upper Palatinate, Germany, had long created scientific uncertainty. When crushed, these fluorite specimens emitted a pungent, penetrating odor that chemists attributed to everything from iodine, ozone, and sulfur to selenium and phosphorus compounds. This particular variety of fluorite, which has an unusual, dark color, became known as “fetid fluorite,” “antozonite,” and various German names that alluded to its unpleasant odor when crushed.

Finally, in 2012, a German research team proved that elemental fluorine did indeed cause the odor in those dark fluorite specimens from the Maria Mine. Those specimens were found to contain inclusions of uranium that emitted nuclear or ionizing radiation. Researchers learned that this radiation breaks some of the calcium-fluorine bonds in the fluorite and prevents these bonds from reestablishing. The result is tiny pockets filled with elemental, gaseous fluorine, the source of the pungent odor, and elemental calcium, the cause of the dark color in the fluorite specimens. This unlikely existence of elemental fluorine in nature is just another of the many fascinating aspects of fluorine.

TECHNOLOGICAL USES

Fluorite is the primary component of fluorspar ore, which is the main commercial source of fluorine and fluorine compounds. Fluorite mining is a billion-dollar-per year industry, with five million metric tons of fluorspar worth \$225 per metric ton mined worldwide each year. China is the leading producer, followed by Mexico, Mongolia, South Africa, and Russia. Fluorspar is concentrated by flotation separation into two basic grades: “metspar” and “acidspar.”

Metspar (metallurgical-grade fluorspar) contains 60-85-percent fluorite and is used exclusively in steelmaking. Fluorine’s extreme chemical reactivity enables it to combine readily with impurities to form volatile fluorides, which are removed as vapors, while fluorite’s calcium component combines with silicate impurities to produce easily removable slag. Six pounds of metspar are needed to produce one metric ton of steel.

Acidspar is fluorspar that has been refined to a purity of 97 percent or higher. Small amounts are added to ceramics, glass, fiberglass, and welding-rod coatings. Most is converted to hydrogen

fluoride, the primary fluorine-containing feedstock for the chemical and pharmaceutical industries. Large quantities of acid spar are also converted to uranium hexafluoride (UF₆) for use in enriching uranium.

Flawless, transparent fluorite crystals were once cut into apochromatic lenses free from chromatic and spherical aberrations for infrared and ultraviolet optical uses. Today, synthetic fluorite serves this purpose. Synthetic fluorite that has been “doped” or mixed with small amounts of with uranium and rare-earth elements is also used in certain lasers.

ABOUT OUR SPECIMENS

Our fluorite specimens are from the Huanggang Mine in Hexigten Banner (County) near the city of Chifeng, Chifeng Prefecture, Autonomous Region of Inner Mongolia, China. The Autonomous Region of Inner Mongolia is one of the provincial-level, administrative divisions of China. It occupies north-central China and borders mostly on the independent nation of Mongolia to the north. The Autonomous Region of Inner Mongolia (which appears on many maps as *Nei Mongol Zizhiqu*) is roughly twice the size of the state of Texas and has a population of 24 million.

The Huanggang Mine is among China’s newest mines. It is located approximately at 43° 40’ north latitude and 117° 30’ east longitude in the Huanggangliang National Forest Park, an area of low, forested mountains. The mine is 350 miles north of the Chinese capital of Beijing, from which it is reached by an eight-hour drive over a good highway. The Huanggang Mine is actually a mining complex that consists of seven shaft-accessed, underground mines. The shafts are approximately 2,000 feet deep. Construction of the mining complex began in 2002, with limited production commencing in 2008. Huanggang’s main products are tin and iron, and its production capacity is a substantial 15,000 tons of ore per day.

The Huanggang ores are part of a large skarn deposit. Skarns are created when magma intrudes formations of limestone or dolomite rock. Limestone is a sedimentary rock consisting mainly of calcite [calcium carbonate, CaCO₃]; dolomite rock is a sedimentary rock consisting mainly of the mineral dolomite [calcium magnesium carbonate, CaMg(CO₃)₂]. The heat and pressure associated with magmatic intrusions initially caused contact metamorphism where the magma contacted the host rock. Hot, acidic solutions associated with the magma then circulated through the altered rocks, reacting with the carbonates in the limestone and dolomite rock to create new and unusual minerals. The host rocks supplied calcium, magnesium, and carbon dioxide, while the magma provided silicon, aluminum, iron, and other elements. Skarns are characterized by such silicate minerals as vesuvianite, wollastonite [calcium silicate, CaSiO₃], diopside [calcium magnesium silicate, CaMgSi₂O₆], and tremolite [basic calcium magnesium silicate, Ca₂Mg₅Si₈O₂₂(OH)₂]. Skarns often host economic mineral deposits.

The Huanggang skarn formed about 100 million years ago during the mid-Cretaceous Period when orthoclase-rich, granitic magma penetrated the 260-million-year-old limestone and dolomite rock of the Dashizai and Huanggangliang formations. The resulting highly mineralized, and now largely oxidized, skarn is one mile wide and twelve miles long. The

important ore minerals are magnetite [ferrous-ferric iron oxide, $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$] and cassiterite [tin oxide, SnO_2], which generally occur along the igneous-sedimentary contact zones in complex systems of brecciated masses, veins, and disseminated bodies. Huanggang geologists have identified 185 individual ore bodies. Mineralization is very complex and includes low grades of molybdenum, lead, zinc, copper, and gold, which may later prove to be of economic consequence. Accessory minerals include andradite [garnet group, calcium iron silicate, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$], grossular [garnet group, calcium aluminum silicate, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$], diopside [calcium magnesium silicate, $\text{CaMgSi}_2\text{O}_6$], quartz [silicon dioxide, SiO_2], calcite, fluorite, pyrite [iron disulfide, FeS_2], and arsenopyrite [iron arsenic sulfide, FeAsS].

The Huanggang Mine began yielding mineral specimens in 2010 and has already gained recognition as a classic locality for certain minerals. Among these are reddish-purple fluorite in the cubic habit, greenish-black ilvaite [basic calcium iron oxysilicate, $\text{CaFe}(\text{Fe})_2\text{O}(\text{Si}_2\text{O}_7)(\text{OH})$], pink manganoan calcite, green andradite, hedenbergite [calcium iron silicate, $\text{CaFeSi}_2\text{O}_6$], löllingite [iron arsenide, FeAs_2], and chorite-included green quartz. Huanggang has even yielded specimens of the aquamarine variety of beryl [beryllium aluminum silicate, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$], a mineral that is unusual in skarn deposits. The variety and quality of Huanggang mineral specimens has been favorably compared with those coming from the classic skarn locality at Dal'negorsk, Russia.

As you examine your fluorite specimen, note its intense, reddish-purple color, which has been variously described as “wine purple” and “electric purple.” The color intensity of these specimens is unusual for fluorite. This basic reddish-purple color is caused by color centers (see “Composition”), with the reddish highlights due to traces of rare-earth elements. The high degree of transparency in these crystals enhances their color intensity. Also notice the prominent color zoning that is characteristic of fluorite. Under ultraviolet light, your specimen will exhibit a purplish-white fluorescence. Almost all the crystals in your specimen are cubic in habit with only slight dimensional modification. Study your specimen closely under an intense light source to observe the countless penetration combinations and intergrowths of the basic cubic forms. The noticeable “heft” of your specimen in the hand is due to its specific gravity of 3.0-3.2, which indicates a 15 percent greater density than a similar volume of quartz. The fluorite crystals rest atop a matrix of colorless or white massive fluorite, which is actually a section of the vein wall. Your specimen is a fine example of intensely colored, cubic fluorite from the Huanggang Mine, one of China’s newest and most modern mines.

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