OHIO FLUORITE

Amber, Cubic Crystals from the Classic Clay Center Locality

The combination of excellent crystal structure, varied colors, and interesting mineralogical associations make fluorite one the most collectible of all minerals. All collectors admire the nearly perfect symmetry of fluorite's cubic crystals, and no other mineral can match its remarkably wide range of colors. And with its many mineralogical associations, fluorite often occurs in interesting and attractive composite specimens.

As a relatively common mineral, fluorite has many collecting localities. Few, however, provide specimens that combine the best attributes of crystal form, color, and mineralogical associations. One source that does it all is the classic locality at Clay Center in Ottawa County, Ohio.

Clay Center specimens are best known for colors that are rare in fluorite. These colors, which range from honey-brown to amber and golden-yellow, are caused by inclusions of bituminous matter derived from crude petroleum. The geological and mineralogical origins behind Clay Center fluorite are as fascinating as the specimens themselves.

Clay Center fluorite has been collected for more than a century, but in recent years their supply has become erratic, and both collector demand and prices have reached all-time highs.

Fluorite, the mineral form of calcium fluoride (CaF_2), consists of the elements calcium (Ca) and fluorine (F), which respectively make up 51.33 percent and 48.67 percent of its molecular weight. In the fluorite crystal lattice, eight fluorine ions surround each calcium ion, while four calcium ions surround each fluorine ion. The resulting three-dimensional lattice with four axial directions creates a cubic structure in which calcium ions occupy the eight corners of each cube and the centers of its six faces.

Te fluorite molecule and lattice are entirely held together by ionic bonding. Because of the inherent weakness of ionic bonds, fluorite exhibits perfect, four-directional cleavage, cleaves easily into octahedrons, and is relatively soft at Mohs 4.0. Despite the light atomic weights of its elemental components, close atomic packing within its well-organized cubic structure gives fluorite a surprisingly high specific gravity of 3.0-3.2.

Although fluorite is chemically and structurally simple, fluorite colors have complex chromophoric origins. Fluorite is generally categorized as an allochromatic mineral, meaning that its colors are usually caused by traces of nonessential elements called chromophores. When pure or nearly pure, fluorite is most often colorless. But traces of iron and the rare-earth elements yttrium and cerium that substitute for calcium can alter the manner in which the crystal lattice absorbs, reflects, and transmits the wavelengths of white light. Iron imparts greens and yellows to fluorite, while traces of yttrium and cerium impart pink hues.

The purple, blue, and violet colors common in fluorite are not caused by chromophores, but by lattice defects called "color centers" or "Frenkel defects." These color centers develop when fluorine ions are displaced from their normal lattice positions. The resulting vacant lattice sites trap electrons, which white light then boosts to higher energy levels. To return to normal levels, these electrons release excess energy in the form of purple, blue, or violet light.

Fluorite colors can also result from other types of lattice defects caused by abnormal crystal growth or the effects of exposure to natural geophysical radiation.

The colors in Clay Center fluorite, however, have an entirely different origin. These distinctive honey-brown-to-amber and golden-yellow colors are due to microscopic inclusions of particulate bituminous matter that both reflect incident light and alter the lattice structure.

Fluorite is often color-zoned or multicolored because of variations in the chemistry of the crystallizing solutions during the crystallization process. Fluorite can crystallize in either single or multiple phases. Fluorite that formed in rapid, single-phase crystallization tends to exhibit a single color with minimal color-zoning. But when the chemistry of the crystallizing solutions varies during slow or multiple-phase crystallization, fluorite crystals can exhibit bands of two or more colors or color intensities.

Fluorite is one of the most luminescent of all minerals. Under ultraviolet light, nearly pure fluorite emits soft, glowing hues of white, blue, and green, while the trace presence of accessory elements and foreign materials can create a yellow or pink fluorescence. Fluorite can also be phosphorescent.

Fluorite forms in several mineralogical environments. In epithermal (low-temperature) veins, it is associated with calcite, rhodochrosite, and chalcedony; in hydrothermal replacement deposits, it occurs with galena, pyrite, sphalerite, barite, and celestine. Fluorite frequently occurs with lead, zinc, and silver ores. It also is found with albite and pyrite in carbonatites (calcium-rich igneous rocks); with calcite and spinel in the hornfels (fine-grained, altered silicate rocks) of contact metamorphic zones; and with albite in granite pegmatites. Fluorite can occur as distinct crystals, and in botryoidal and massive forms.

Although fluorite has many collecting localities, fine specimens are uncommon. England, China, Russia, Pakistan, Namibia, Spain, Peru, Bolivia, Australia, and Mexico all have notable collecting localities. In the United States, fine specimens are found in Ohio, Illinois, Kentucky, Oklahoma, and Tennessee.

Amulets carved from massive fluorite have been recovered from 4,000-year-old Egyptian tombs. By 600 B.C., the ancient Greeks were using fluorite as a smelting flux to remove impurities from, and lower the melting temperature of, silver ores. The Romans later mined fluorite in Spain and England for use in lead, silver, and copper smelting.

By 1500 A.D., the Chinese were carving beautiful, jade-like figurines from massive green fluorite, while European metallurgists were using it as their standard smelting flux. The word "fluorite" actually stems from the Latin *fluere*, meaning "to flow" and alluding to its ability to reduce the melting temperatures of metal ores in smelting processes.

By the mid-1800s, chemists realized that fluorite contained an unidentified, but extraordinarily reactive and hazardous element. In 1886, French chemist Ferdinand Frederick Henri Moissan isolated this element—fluorine—by electrolytically reducing hydrofluoric acid and potassium fluoride. His experiments demonstrated that fluorine was the most chemically reactive of all elements. Although Moissan's fluorine research won the 1906 Nobel Prize for chemistry, it also caused his premature death. Moissan is remembered as one of the "fluorine martyrs"—the chemists who lost their health or their lives by inhaling or contacting fluorine-based acids and vapors in laboratory experiments.

Medieval physicians prescribed the ingestion of powdered fluorite to treat kidney disease and also placed fluorite crystals against joints to alleviate arthritic pain. In today's metaphysical uses, fluorite is believed to calm the mind in preparation for meditation, enhance objectivity and concentration, and clarify the decision-making process. Metaphysical healers assign specific powers to individual fluorite colors: white helps to access the spiritual world, green energizes the heart and mind, blue provides inner peace, purple focuses the mind, and yellow facilitates communication.

Fluorspar, the massive, impure form of fluorite, is mined in large quantities. Because of its extreme chemical reactivity, fluorite is an excellent metallurgical flux that combines readily with metal impurities. Fluorite is a feedstock for the manufacture of hydrofluoric acid, a major industrial chemical. It is also converted to aluminum fluoride (AlF_3) for use in smelting aluminum, and to uranium hexafluoride (UF_6) for use in the gas-diffusion concentration of the uranium-235 isotope needed for nuclear fuel rods and nuclear weapons. Until the recent synthesis of optical-grade fluorite, flawless, transparent crystals of natural fluorite were cut into apochromatic lenses for infrared and ultraviolet optical applications.

Fluorite's gemological qualities include good transparency, many pleasing colors, a vitreous luster, and crystals suitable for cutting into large gems. But, unfortunately, fluorite also has a low refractive index of 1.433 that compromises gem brilliance, a softness unsuitable for everyday jewelry use, and perfect, four-directional cleavage that makes cutting difficult. Nevertheless, fluorite cabochons and faceted gems are occasionally mounted in pendants and brooches.

Fluorite collectors' gems of 100 carats or more are popular and affordable for both display and study purposes. The Smithsonian Institution in Washington D.C. displays a 492.1-carat fluorite gem. As a decorative stone, large quantities of massive fluorite are carved into spheres, dishes, figurines, and vases.

Fluorite is widely collected as both individual and composite specimens. Colorful, well-developed, cubic or octahedral fluorite crystals can greatly enhance the value and visual appeal of composite mineral specimens.

For more than a century, superb fluorite specimens have made Clay Center the foremost mineral-collecting locality in Ohio. Clay Center, population 250, is a small village located 12 miles southeast of downtown Toledo and the same distance south of the shore of Lake Erie.

Geologically, Clay Center is located on the Findlay Arch, a branch of the Cincinnati Arch, a major uplift that stretches from Tennessee north to the Canadian border. The Findlay Arch consists of sediments that were deposited during the early Paleozoic Era and later acted as a stratigraphic trap to accumulate quantities of petroleum derived from the compression and destructive distillation of buried organic matter.

At Clay Center, erosion has exposed certain strata of the Findlay Arch, notably the Lockport Formation. The Lockport Formation consists of 440-million-year-old dolomite rock, a marine sedimentary rock that is similar chemically and physically to limestone and consists primarily of the mineral dolomite, or calcium magnesium carbonate. Lockport dolomite is a buff-to-brownish-yellow, granular rock. It is porous and contains vugs that were created when groundwater dissolved portions of the dolomite. This groundwater also filled many vugs with such minerals as fluorite and celestine, along with smaller quantities of pyrite, marcasite, calcite, gypsum, galena, and sphalerite.

During the 1880s, the rapid development of nearby Toledo created a demand for crushed stone and gravel for paving and construction uses. The durable dolomite rock of the Lockport Formation was conveniently exposed as bedrock near Clay Center, where a number of quarries opened. Quarrying revealed that the dolomite rock sometimes contained vugs filled with attractive crystals of fluorite and celestine. Clay Center quickly became a popular mineral-collecting locality that was well-known as a source of fine and distinctly colored fluorite crystals.

During the 1930s, Clay Center fluorite specimens attracted mineralogists who were intrigued by their unusual honey-brown-to-amber and golden-yellow colors. Analysis revealed that these rare fluorite colors were caused by both microscopic and macroscopic particles of bituminous matter that originated with crude petroleum and other hydrocarbon materials that had become trapped beneath the Cincinnati Arch and its Findlay Arch branch. These bituminous particles had been transported by groundwater through the porous Lockport dolomite and were present in the mineralizing solutions when the fluorite precipitated. Mineralogists also identified the source of the fluorine in the crystallizing solutions as the bones and teeth of fossilized marine life within the Lockport dolomite.

The distinctive colors, particularly the brownish hues, of the Clay Center fluorite are caused by light reflecting directly from included bituminous particles. Some lighter, yellowish hues may be caused in part by the manner in which the included bituminous particles have distorted the fluorite crystal lattice.

Color zoning is common and most apparent in the more intensely colored crystals, with the crystal centers tending to be darker than the outer portions. The crystals are generally transparent, but visible inclusions of bituminous material sometimes impart a slight cloudiness or sub-transparency.

The Clay Center fluorite crystals, which are well-formed with sharp edges, usually measure between one-quarter inch and one-half inch in size. Exceptional crystals measure an inch or more. The fluorite sometimes occurs in association with milky-white celestine crystals.

Clay Center fluorite crystals are highly luminescent. Unlike most forms of fluorite, Clay Center specimens emit a light-yellow to deep, yellow-orange fluorescence, the intensity of which depends upon the density of the included bituminous material. Many specimens also exhibit phosphorescence, continuing to glow even after the ultraviolet light has been removed.

The source of the Clay Center fluorite specimens, the White Rock Quarry, is an active dolomite-rock mining operation. Because fluorite occurs only in certain sections of the quarry, specimen availability is uncertain and depends upon exactly where quarrying operations are being conducted. Quarry operators occasionally approve visits by rockhounding-club members and commercial collectors who search for specimens of what many consider to be the world's most unusual fluorite.