

November 2004 Mineral of the Month: Vivianite

“The goal of collectors in respect to vivianite specimens, is to obtain single crystals from the Bolivian localities.”— John Sinkankas, *Mineralogy*, 1964

PHYSICAL PROPERTIES

Chemistry: $\text{Fe}^{2+}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ Hydrous Iron Phosphate (Iron Phosphate Hydrate)

Class: Phosphates, Arsenates, and Vanadates

Subclass: Hydrous Phosphates, Arsenates, and Vanadates

Group: Vivianite

Crystal System: Monoclinic

Crystal Habits: Short to long, parallel, flattened, prismatic crystals, sometimes with micaceous appearance; also as globular masses, radial crystals and fibers, earthy masses, crusts, and coatings

Color: Fresh specimens not exposed to light are colorless or pale yellow; most other specimens are usually pale-to-dark shades of blue, greenish-blue, or bluish-green; becoming a dark indigo blue on prolonged exposure to light

Luster: Dull to vitreous, pearly on cleavage surfaces

Transparency: Transparent to translucent

Streak: Pale blue

Cleavage: Perfect in one direction.

Fracture: Splintery, earthy, fibrous; sectile; thin flakes flexible

Hardness: Mohs 1.5-2.0

Specific Gravity: 2.6-2.7

Luminescence: None

Distinctive Features and Tests: Blue color and pale-blue streak, softness, highly perfect, easily developed cleavage, and flexibility of thin crystals

Dana Classification Number: 40.3.6.1



Figure 1. Vivianite crystal

NAME

The name “vivianite,” which is correctly pronounced “VIV-ee-an-ite,” honors John Henry Vivian, the English mineralogist who identified the mineral in 1817. Vivianite has also been known as “glaucoisiderite” and “mullicite” and, in reference to its characteristic blue color, as “native Prussian blue,” “blau eisemerz,” “blue iron ore,” “blue iron earth,” “azure ochre,” and “blue ochre.”

COMPOSITION

What a pleasure it is to feature a mineral of such beautiful color! And while the appeal of its color is hard to describe in words, we enhance our appreciation for it by learning what causes it, and that of course is directly related to its atomic make-up and resulting crystal structure.

Vivianite’s chemical formula, $\text{Fe}^{2+}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, identifies this mineral as a hydrous iron phosphate (or iron phosphate hydrate) containing the elements iron (Fe), phosphorus (P), oxygen (O), and hydrogen (H). In terms of atomic weight, each molecule of vivianite contains 33.40 percent iron, 12.35 percent phosphorus, 3.22 percent hydrogen, and 51.03 percent oxygen. Notice that oxygen is present in both the phosphate anion $(\text{PO}_4)^{-3}$ and in the attached water molecules. Water (H_2O) accounts for 28.73 percent of vivianite’s atomic weight. Within the vivianite molecule, the +6 charge of the cation, which consists of ferrous iron (Fe^{++}), balances the anionic -6 charge of the phosphate ion $(\text{PO}_4)^{-3}$.

November 2004 Mineral of the Month: Vivianite

Vivianite's chemical formula also shows that eight water molecules ($\cdot 8\text{H}_2\text{O}$) are bound to each molecule of iron phosphate. Because vivianite contains water as a specific number of water molecules, it is classified as a hydrous mineral, or hydrate. Vivianite's water, which is referred to as "water of hydration," is not merely absorbed, but actually chemically bonded into the atomic structure of the iron-phosphate lattice. This water is not bonded as separate oxygen and hydrogen ions, but as integral water molecules that retain their characteristic composition and structure. The chemical formulas of all hydrous minerals end with $\cdot n\text{H}_2\text{O}$ ("n" is variable). In the chemical formulas of hydrous minerals, a chemical period (·) separates the parent mineral from its bonded water.

Vivianite is a member of the Phosphates, Arsenates, and Vanadates class of minerals. This class contains more than 240 recognized species, most of which are rare. The basic building blocks of these minerals-- the phosphate ion $(\text{PO}_4)^{-3}$, the arsenate ion $(\text{AsO}_4)^{-3}$, and the vanadate ion $(\text{VO}_4)^{-3}$ -- are tetrahedra in which the metal or semi-metal (vanadium is a metal, phosphorus and arsenic are semi-metals) ions are surrounded by four oxygen ions. The three negative charges on each ion are distributed evenly over its four oxygen ions, enabling the phosphate, arsenate, or vanadate anions to bond readily with certain positively charged metal cations.

Vivianite is also a member of the Vivianite Group, which has a general formula of $\text{X}_3(\text{AO}_4)_2 \cdot 8\text{H}_2\text{O}$, in which "X" represents a divalent metal ion, such as iron, zinc, cobalt, magnesium, manganese, or nickel. The "A" represents either phosphorus or arsenic combined in a phosphate $(\text{PO}_4)^{-3}$ or arsenate $(\text{AsO}_4)^{-3}$ radical. In vivianite, the divalent metal ion is ferrous iron (Fe^{++}), while the cation is the phosphate radical. The more common minerals of the Vivianite Group show how the different divalent metal cations combine with the phosphate or arsenate anionic radicals. These minerals include annabergite, hydrous nickel arsenate, $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$; baričite, hydrous magnesium iron phosphate, $(\text{Mg}, \text{Fe}^{2+})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$; erythrite, hydrous cobalt arsenate, $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$; and kottigitite, hydrous zinc arsenate, $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$. Rounding out the group are arupite [$\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$], hörnesite [$\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$], and parasympleite [$\text{Fe}^{2+}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$]. Bobierite [$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] and manganese-hörnesite [$(\text{Mn}^{2+}, \text{Mg})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$] are also related to the vivianite group, though having b-axes ("b" signifies the lateral axis) twice those of vivianite group minerals. More research is needed!

The vivianite molecule is bound together by a complex combination of strong covalent atomic bonds, intermediate-strength ionic bonds, and weak hydrogen bonds. In the phosphate anion $(\text{PO}_4)^{-3}$, the phosphorus atom is covalently bonded to four oxygen atoms that form the corners of a tetrahedron. In turn, these negatively charged phosphate anions are weakly bound to the positively charged ferrous iron (Fe^{++}) cations by ionic bonds. Vivianite's basic crystal lattice therefore consists of repeating, ionically bonded iron and phosphate ions.

The water of hydration is attached by even weaker hydrogen bonds. In a water molecule, a large oxygen atom is covalently bound to two hydrogen atoms. The two hydrogen atoms are not symmetrically opposed, but rather are grouped together on one side of the oxygen atom. Although water molecules are technically neutral, their two closely grouped hydrogen atoms retain a weak positive charge, while the opposite side of the molecule, which is dominated by the large oxygen atom, retains a small negative charge. Because of these positively and negatively charged ends, or poles, each individual water molecule behaves as a tiny dipole magnet. Hydrogen bonding, also called polar bonding, forms when the faintly positive poles of the water molecules attract the electrons of other atoms. In vivianite, this attraction is toward the slight negative charge of the oxygen atoms of the phosphate anions. Within the vivianite lattice, iron-phosphate molecules form layers which "sandwich" the attached water molecules. This arrangement explains vivianite's perfect, one-directional cleavage in which the cleavage planes are those that contain the weakly bound water molecules. These weak hydrogen bonds, and to a lesser extent the weak ionic iron-phosphate bonds, explain both vivianite's softness and the flexibility of its thin crystals.

November 2004 Mineral of the Month: Vivianite

Vivianite is a secondary mineral resulting from the alteration of shallow deposits of primary phosphate minerals. In general, it forms where oxidation alters iron-rich minerals in the presence of phosphate ions. Vivianite occurs as a minor constituent in such varied mineralogical environments as sedimentary deposits, oxidized metal-mineral veins, and oxidized pegmatites. It is especially common in disseminated hydrothermal replacement deposits where it is associated with muscovite, quartz, and sphalerite, and in the gossan (rust-colored oxidized zones) of iron-rich, metal ore deposits. Vivianite is found in certain clays and glauconitic sediments (sediments rich in potassium iron silicate), and in peat bogs and bog-iron ore deposits in which the phosphate is usually derived from organic sources. Thin coatings of vivianite create the blue tinge seen in many fossils, and distinctive, blue clusters of tiny vivianite crystals are also found inside fossilized clam shells or attached to fossilized animal bone.

One of vivianite's most interesting characteristics— a photosensitivity that causes it to shift from colorless to blue with exposure to light— is due to oxidation of the iron within its crystal lattice. When vivianite is formed, its iron is all of the ferrous (Fe^{2+}) variety. When first exposed to light, fresh vivianite specimens reflect all light wavelengths more or less equally and thus appear colorless or a very pale yellow. But after continued exposure to light, the ferrous ions absorb some of the light energy. This energizes and oxidizes the ferrous ions, converting them to ferric (Fe^{3+}) ions which distort the crystal lattice and alter its light-reflecting and light-absorbing characteristics. As more ferrous ions convert to ferric ions, vivianite absorbs more of the red end of the visible spectrum, thus making the mineral appear blue. Prolonged exposure to light converts most of the ferrous ions to ferric ions, turning the specimen an intense blue or blue-green and eventually to a deep indigo blue. Because of this color shift, many collectors store their vivianite specimens in the dark.

Due to the oxidation of ferrous ions, even fresh specimens of colorless vivianite show a pale blue streak. To prepare a streak, a mineral is drawn against an abrasive surface, which finely powders a tiny portion of the mineral to create the streak. This immediately exposes an enormous surface area to light. In vivianite, this greatly accelerates ferrous oxidation to almost immediately produce a pale blue color. Also, the ferrous ions absorb part of the mechanical energy expended in the abrasion process to further accelerate the oxidation process which produces the blue shift.

COLLECTING LOCALITIES

Although widely distributed, vivianite usually occurs only in small quantities. Bladed specimens up to two inches in length have come from the Blackbird Mine near Cobalt in Lemhi County, Idaho, and from the Ibex Mine in the Leadville Mining District in Lake County, Colorado. In Maryland, vivianite nodules with radiating, crystalline interiors have been collected at Oxon Hill near Washington D.C., and at the bog-iron-ore deposits at Nassawango Creek in Worcester County. Masses of radiating vivianite blades are common in the bog-iron ore deposits at Mullica Hill in Gloucester County, New Jersey.

In Canada, radiating nodules of vivianite occur along the Big Fish River in the northern Yukon Territory, and bladed crystals up to two inches in length are found at Vaudreuil, not far from Montreal, Quebec. In Russia, many vivianite specimens have come from the Kudinovskoye bog-iron-ore deposits near Moscow. The Caroline Mine at Eberbächle in Baden-Württemberg, Germany, has yielded long and well-formed vivianite blades. And after nearly two centuries, vivianite's type locality, the bog deposits at St. Agnes, Cornwall, England, continue to produce nice specimens. Transparent blue crystal aggregates are found at Santa Eulalia, Chihuahua, Mexico; at Anloua, Adamaoua, Cameroon; and at Trepça, Serbia. A recent find at the Tomokoni Mine in the Savendra Province of Bolivia's Potosí Department yields well-formed vivianite crystals in a red sandstone matrix, as explained in *About Our Specimens*.

November 2004 Mineral of the Month: Vivianite



Figure 1. Location map showing some important localities in Bolivia.

Figure 2. From "A Guide to Mineral Localities in Bolivia," Nov-Dec 2001 Mineralogical Record, used with permission.

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November 2004 Mineral of the Month: Vivianite

JEWELRY & DECORATIVE USES

Because of its great softness (Mohs 1.5-2.0), easily developed cleavage, heat sensitivity and tendency to splinter, vivianite is extremely difficult to fashion into gemstones, and is rarely used in jewelry. Inch-long, dark blue blades of vivianite are occasionally mounted for wear in pendants. Cheryl set one in wire a few months ago, with great difficulty, and can testify to its propensity for splintering. However, these weaknesses have not prevented rare gemstone collectors and mineral collectors from loving its color. Vivianite is also appreciated as the natural coloring agent in organic material found in sedimentary deposits, such as the blue dendrites (mineral crystallizing in another mineral in a branching or treelike form) in mammoth ivory, or the turquoise color of some fossil bone.

HISTORY & LORE

Vivianite has been known since antiquity and served as a blue pigment for the artists of classical Greece. During the 13th and 14th centuries A.D., English artists obtained vivianite from the bogs at Cornwall, using it as a pigment in wall paintings. At the same time, artists in what is now Cologne, Germany, were using vivianite as the pigment for sky-tone paints. By the 15th century, however, vivianite had only limited use as a pigment after artists began noting that older vivianite-pigment paints sometimes altered to a pale yellow. The cause of this color shift remains uncertain, although it may have been due to a chemical reaction between the finely powdered vivianite and the other paint components.

English mineralogist John Henry Vivian (1785-1855) identified vivianite as a mineral in 1817 after studying specimens obtained from the type locality at St. Agnes, Cornwall, England. That same year, German geologist and mineralogist Abraham Gottlob Werner (1749-1817), Vivian's mentor, named the mineral in his student's honor.

According to modern metaphysicists, the energy of vivianite conveys love and inspiration, clears negative thought patterns, aids in establishing goals, and helps to discover and understand aspects of the inner consciousness. Metaphysicists also believe that wearing or carrying vivianite can alleviate the symptoms of stress and depression.

TECHNOLOGICAL USES

Vivianite served as a minor ore of iron when it was mined from bog-iron ore deposits together with much larger quantities of limonite (an indefinite mixture of hydrous iron oxides with the general formula $[\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}]$). Vivianite is still used today as a natural mineral pigment that provides a stable, intense, dark-blue color with subtle reddish undertones. For use as a pigment, soft, friable vivianite concretions are collected from peat bogs or bog-iron ore deposits, carefully washed to remove clay and organic matter, dried, then ground to a very fine powder.

ABOUT OUR SPECIMENS

Elaborating on our opening quote concerning the desirability of Bolivian vivianites, John Sinkankas continues: "Most are sharp, smooth-faced, and uncommonly perfect in addition to being very large. Furthermore, most are transparent, and many, flawless." The Mineralogical Record has reported on the exceptional color and form of new vivianite finds from mines in Bolivia a number of times since the magazine's inception in 1970, with accompanying photos of the most outstanding ones, including a cover photo adorning the September-October 1994 issue. Peter Bancroft, in his 1984 book *Gem & Crystal Treasures* highlights two localities in Bolivia, one for phosphophyllite and other rare phosphate

November 2004 Mineral of the Month: Vivianite

group minerals, and one for rare phosphates like vauxite and “extraordinary crystals of transparent, beautifully-formed vivianite to 15 centimeters in length.” This latter locality is the now-closed Siglo XX mine (Spanish for twentieth century), at Lllaqua, as seen on the map in Figure 2. Other localities producing outstanding vivianites are Morocococala and Huanuni, both found on the map.

Our pieces come from a new find about 40 miles northeast of Potosí, in the Colavi-Machacamarca mining district, a group of silver and tin mines dating to the Spanish colonial period. Potosí can be seen on the map in Figure 2, and this district would be just northeast of it. In June of last year, a trio of brothers, miners from Colavi, were hiking and discovered a blue streak in the red sandstone on the nearby Tomokoni claim. Within hours, they had uncovered fractures and cavities containing wonderful green vivianite specimens, and within days, the local Bolivian mineral dealers were buying them up and sending them overseas. Soon, miners from two nearby mines, Colavi and Canutillos, were fighting over the right to collect there, and the Corporacion Minera de Bolivia (COMIBOL) stepped in and stopped all collecting there. In August 2003, American visitors found three small adits had been dug at Tomokoni, and local miners were sneaking in to collect. By December of last year, about the same time we first set eyes on some of these gorgeous specimens, an agreement had been negotiated, and collecting was ongoing. One author speculated that several thousand specimens might be unearthed this year alone, but said that accumulation of groundwater would eventually halt production.

The matrix found on many of our pieces has been described as argillaceous sandstone, a term applied to rocks composed of clay minerals, or having a notable proportion of clay in their composition, especially sedimentary materials like marl or shale. Argillaceous rocks can be distinguished by an earthy odor when breathed on— try this if you have a piece with larger matrix. We noticed a strange odor this way! The only other minerals occasionally found with the vivianite are rosettes of thin white barite and druses of siderite.

The argillaceous sandstone matrix is very crumbly, and we have had a couple of crystals come off their matrix under normal handling here, so you might handle your piece as little as possible. Also, since light causes the color to change, as previously explained, you might like to store your specimen in a dark place. How fortunate we are to be able to add such an extraordinary mineral to our collections— with mesmerizing color and a lovely, sharp crystal form, to boot! Not to mention its unique characteristics and uses. We have been blessed!

References: *Dana's New Mineralogy*, Eighth Edition, John Wiley & Sons, Inc.; *Encyclopedia of Minerals*, Second Edition, Roberts, et al, Van Nostrand Reinhold Company; *1999 Glossary of Mineralogical Species*, J. A. Mandarino; *Mineralogy*, John Sinkankas, Van Nostrand Reinhold Company; *Gem & Lapidary Materials*, June Culp Zeitner, Geoscience Press; *Gem & Crystal Treasures*, Peter Bancroft, Western Enterprises/Mineralogical Record; *Gemstone and Mineral Data Book*, John Sinkankas, Geoscience Press; “A Vivianite Occurrence in Contra Costa County, California,” C. B. DeWitt, *The Mineralogical Record*, September-October 1989; An Occurrence of Vivianite in North Carolina,” P. Tien, *The Mineralogical Record*, May-June 1974; “Connoisseur's Choice: Vivianite from the Morocococala Area, Oruru, Bolivia,” Robert Cook, *Rocks & Minerals*, March-April 1994; “From Minerals to Art,” Susan Robinson, *Rocks & Minerals*, September-October 1999; “The Bolivian Death Switch,” Rock H. Currier, *Mineralogical Record*, May-June 1995; “A Guide to Mineral Localities in Bolivia,” Alfredo Petrov and Bill & Carol Smith, *Mineralogical Record*, November-December 2001; “Abundant New Vivianites,” Alfredo Petrov, *Mineral News*, March 2004. Special thanks to Alfredo Petrov and Rock Currier.