

September 2003 Mineral of the Month: Ikaite

Ikaite is one mineral we will likely never have in our collections, unless we have some well-connected friends and a super-cooled environment to store it in. Although this month's mineral falls apart at temperatures above freezing, still we can see its crystal forms and habits, as they have been painstakingly and accurately preserved by the calcite crystals that replaced them.

PHYSICAL PROPERTIES (Because ikaite is unstable at ambient temperatures, some of the mineral's physical properties have not been accurately determined.)

Chemistry: $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ Hydrated Calcium Carbonate or Calcium Carbonate Hexahydrate

Class: Hydrated Carbonates Subclass: Hydrated Carbonates without foreign cations

Crystal System: Monoclinic

Crystal Habits: Usually tabular, thin in one dimension; stalactitic in pendant growths; stalagmitic as columns; also encrustations

Color: Chalky white

Luster: Earthy, dull

Transparency: Translucent to opaque

Streak: White

Refractive Index: 1.45-1.54

Cleavage: None

Fracture: Uncertain

Hardness: Uncertain, believed to be softer than calcite (Mohs 3.0)

Specific Gravity: 1.8

Luminescence: Uncertain

Distinctive Features and Tests: Unstable at room temperature, quickly decomposes to water and calcite

Dana Classification Number: 15.1.4.1

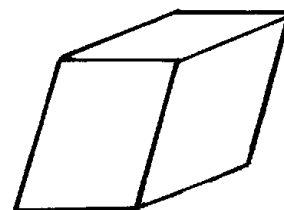


Figure 1 Monoclinic crystal.

NAME

The name "ikaite" (correct pronunciation IKE-a-ite) derives from the mineral's type locality at Ikka (formerly spelled "Ika") Fjord, Inuvit, Greenland. Ikaite pseudomorphs in nodule or rosette forms are also known as "glendonite," a name derived from their discovery locality off the southern coast of New South Wales, Australia. Other names for pseudomorphs of calcite after ikaite are derived from locality names and include "fundylite," "jarrowite," "gennoishi," "gersternkörner," and "White Sea hornlets."

COMPOSITION

Before delving into ikaite's composition, you may enjoy reading the information on pseudomorphs in the box on the next page.

Ikaite's chemical formula, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, indicates that it consists of the elements calcium (Ca^{+2}), carbon (C^{+2}), and oxygen (O^{-2}). The +2 charge of the calcium cation is drawn to the combined -2 charge of the carbonate (CO_3) anion. Six water (H_2O) molecules are bound to each calcium carbonate molecule. In terms of atomic weight, each ikaite molecule consists of 19.25 percent calcium, 5.77 percent carbon, 69.17 percent oxygen, and 5.81 percent hydrogen. Water makes up 51.92 percent of the weight of the ikaite molecule, and explains ikaite's low density (specific gravity 1.8).

Hydrated minerals, those with chemical formulas ending in " H_2O ," are called hydrates and contain water in the form of a definite number of water molecules. This water, referred to as "water of hydration," is not

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September 2003 Mineral of the Month: Ikaite

PSEUDOMORPHS

While discussing the composition and other aspects of ikaite, let's look at mineral pseudomorphs, which include our September specimen in which calcite has replaced ikaite.

A pseudomorph is a mineral that has replaced a previously deposited mineral, but that retains the crystalline form of the original mineral. Derived from the Greek words *pseudēs* and *morphe*, the term "pseudomorph" literally means "false form." Pseudomorphic relationships are conventionally expressed in two ways. With "A" representing the original mineral and "B" the replacement mineral, pseudomorphic relationships are expressed as "A > B," or as "B after A." Our September mineral may therefore be described as "ikaite > calcite" or "calcite after ikaite."

Pseudomorphs are classified according to their formation. First are pseudomorphs in which both the original and the replacing mineral have the same chemistry. Most often, the original mineral has formed under high temperatures or pressures. Later, as temperatures and pressures decrease, the atoms and molecules within the crystal rearrange themselves to form a new mineral. An example is calcite after aragonite. Although both minerals are calcium carbonate (CaCO_3), calcite crystallizes in the hexagonal system, while aragonite crystallizes in the orthorhombic system. In the pseudomorph, calcite exhibits the orthorhombic form of the original aragonite. Such pseudomorphs are also called paramorphs, or "closely related forms."

In the second pseudomorph classification, the original mineral gains or loses one or several elemental components, but the replacing pseudomorph retains at least one component of the original mineral. An example is copper (Cu) after cuprite (Cu_2O). The original cuprite loses oxygen and is replaced by elemental copper, which assumes cuprite's isometric crystal form. Our September mineral, calcite after ikaite, is another example.

In other pseudomorphs, the replacement mineral has no chemical commonality with the original mineral. These pseudomorphs are usually casts formed from molds. Consider a calcite crystal that is encased in dolomite [calcium magnesium carbonate, $\text{CaMg}(\text{CO}_3)_2$]. The calcite may dissolve to leave a hollow dolomite shell in the shape of the original calcite crystal. Should that void fill with another mineral, such as halite (sodium chloride, or NaCl), the halite, an isometric crystal, will assume the hexagonal shape of the original calcite even though it has none of the elemental components of the original calcite. Such pseudomorphs are called epimorphs, or "outer forms."

merely absorbed, but is chemically bonded into the parent mineral's atomic structure. This water does not link with the parent mineral as separate oxygen and hydrogen ions, but as integral water molecules that retain their characteristic composition and structure. For this reason, the chemical formula of ikaite is not written as, for example, $\text{H}_{12}\text{CaCO}_9$, but as $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$. The chemical period (·) is a notational device that both represents and symbolizes a chemical bond between two separate components of a mineral. In the case of ikaite, the chemical period indicates that calcium carbonate, the parent mineral, is bonded to six molecules of water.

Because heat can drive off water of hydration, hydrous minerals vary broadly in their chemical stability. The reason is hydrogen bonding. Unlike ionic, covalent, and metallic bonds, hydrogen bonds form only between hydrogen atoms and other atoms and usually involve water. Although water molecules are neutral, the sites of the hydrogen atoms within the water molecules have a weak positive charge. Because

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the opposite sides of the water molecules have a small negative charge, they behave as tiny dipole magnets. Hydrogen bonds, also called polar bonds, form when these faintly positive poles of water molecules attract the electrons of other atoms. Because hydrogen bonds are strongest at low temperatures, the instability of hydrous minerals increases significantly at elevated temperatures. Interestingly, hydrogen bonding between water molecules is the force that holds water together as ice at low temperatures. (Ice is accepted as a valid mineral, though it obviously is stable only at temperatures below freezing. Its chemical formula is H₂O, and it belongs to the hexagonal crystal system, forming particularly beautiful six-rayed stars in the characteristic habit we call snow. Its Dana's classification number is 4.1.2.1, and it is grouped with other simple oxides such as cuprite, zincite, corundum, and hematite.)

As a particularly unstable hydrous mineral, ikaite loses water of hydration at temperatures only nominally above the freezing temperature of water, when it breaks down into water and calcite, or anhydrous calcium carbonate (CaCO₃). This instability is explained by ikaite's atomic structure. Within the ikaite crystal, calcium ions are arranged in flat arrays, with the position of each coordinated by the placement of the carbonate ion and six water molecules. These discrete CaCO₃·6H₂O units are linked together only by weak hydrogen bonding, which is easily broken at elevated temperatures. Within each discrete CaCO₃·6H₂O unit, the water molecules have a greater attraction between themselves than they do to the calcium carbonate. Elevated temperatures thus cause the relatively rapid separation of water of hydration from the parent calcium carbonate.

Ikaite's instability makes it difficult to collect or study, because at room temperature it quickly disintegrates into a "mush" of freed hydration water and calcite crystals. Because ikaite is easily overlooked unless mineral samples are specially preserved, researchers now believe that it may be much more common than previously thought.

Ikaite is the natural mineral form of the compound calcium carbonate hexahydrate, which has been synthesized in laboratories. This unstable synthetic form of ikaite can exist only in cold-water environments rich in calcium and carbonate ions and in the presence of a calcite nucleation inhibitor (a compound that interferes with calcite crystal formation). While these laboratory conditions are quite specific, similar conditions also exist in nature.

Ikaite can form in two ways. One is the free growth of crystals that build from an attached base and grow upward in a cold-temperature, highly saline, lacustrine or marine environment. Such crystals can form remarkably large structures, such as those at ikaite's type locality, Ikka Fjord in Greenland, where large, underwater ikaite stalagmites develop in ideal conditions.

At Ikka Fjord, sea-bottom springs emanate from a carbonatite formation (an igneous body rich in calcium and magnesium carbonates) that provides an abundance of carbonate ions and traces of phosphorus and other ions. This ion-enriched springwater vents into the bottom of the fjord into cold, saline seawater that is rich in calcium ions. Normally, the combination of calcium and carbonate ions would precipitate as hexagonal crystals of calcite (CaCO₃). But in the near-freezing temperatures and in the presence of calcite-nucleation inhibiting phosphate ions, the calcium and carbonate ions precipitate as monoclinic crystals of ikaite.

Ikaite also forms by displacive growth (crystal growth which displaces other materials) within organic-rich marine sediments as crystal clusters and nodules. The conditions for displacive growth are similar to those needed for free growth: cold temperatures and the presence of calcium ions, carbonate ions, and a calcite-nucleation inhibitor. Displacive ikaite crystal growth occurs within organic-rich marine sediments

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September 2003 Mineral of the Month: Ikaite

saturated by calcium-rich seawater. Decomposition of organic matter produces phosphate ions and carbon dioxide (CO₂). The carbon dioxide reacts with water to form carbonic acid (H₂CO₃), a source of carbonate ions. The carbonate ions bond with calcium ions in the seawater, while the phosphate ions that are present inhibit the nucleation of calcite, thus favoring the precipitation of ikaite in small clusters of radiating crystals.

If temperatures remain constant, these sediment-bound crystal clusters remain as ikaite. But if seawater temperatures increase because of geologic uplift or changing climate, the unstable ikaite converts to calcite. These pseudomorphic crystals can then be covered by secondary growths of calcite in its normal hexagonal crystal structure. This forms a rounded calcite nodule, the interior of which clearly shows the form of the original ikaite crystals. These crystal pseudomorphs are commonly known as "glendonites."

COLLECTING LOCALITIES

Ikaite has been collected from only a few localities. The best known is the type locality at Ikka Fjord at Invigtut in southwestern Greenland, where spectacular submarine ikaite spires rise 60 feet from the fjord floor nearly to the surface. The largest spires form from the coalescence of several individual spires and have base diameters of 20 feet! Ikaite crystal clusters have been recovered by sediment-core drilling in the Nankai Trough southwest of Japan at depths of 13,000 feet; from the Zaire-Congo deep sea fan off western equatorial Africa; from estuarine sediments off arctic Alaska; and from the shelf basin of Antarctica's Bransfield Strait at depths of 6,000 feet

In winter, small crystals of ikaite grow as calcareous encrustations called "rimstone" in springs on Japan's Hokkaido Island, and at springs on the south shore of California's Mono Lake. With warmer spring temperatures, these crystals lose their water of hydration and convert to calcite. Ikaite probably also occurs at other cold, saline springs around the world, but goes unrecognized due to its ephemeral nature.

Calcite after ikaite crystal clusters and nodules are found in many parts of northern temperate, subarctic, and arctic regions. A prime source of calcite after ikaite nodules and crystal clusters are the mudflats at the mouth of the Olenitsa River on Russia's Kola Peninsula on the shore of the White Sea, where the nodules are exposed at low tide.

JEWELRY & DECORATIVE USES

Ikaite's instability precludes any jewelry or decorative uses, as does the softness of its calcite pseudomorphs. However, calcite after ikaite nodules, when cut and polished, make interesting and unusual display pieces.

HISTORY & LORE

Ancient Inuit tales and Viking sagas tell of invaders being driven onto the thin ice of a frozen Greenland fjord (Ikka Fjord?) where they plunged to their deaths in the icy waters to become rooted on the bottom as frozen statues. Taller underwater spires at Ikka Fjord terminate in multi-pronged forms reminiscent of upraised arms and hands. According to the ancient tales, these spires are the forms of the drowned warriors of legend whose arms still reach upwards toward air.

By means of scuba-diving, a team of British geologists closely examined these ikaite spires and described them this way, in *Divers Magazine*: "The more slender, delicate pillars, were spectacular-- only a few centimeters in diameter, but rising several meters from the bottom. By contrast, massive broad growths,

September 2003 Mineral of the Month: Ikaite

meters wide, rose up a full eighteen meters toward the surface. They would terminate in clusters of knobby spires, often growing into each other, like the flying buttresses of some great cathedral." Sounds breathtaking! The article also mentioned a plethora of sea creatures living on the nearby sea floor, including crabs, starfish, sea cucumbers, slugs, muscles, sea squirts, and many others. Later, a group of scientists from a number of institutes formed the Ikka Project to study in depth our featured mineral and these remarkable columns at Ikka Fjord. This group has also undertaken a mapping of many characteristics of the fjord.

Ikaite was synthesized long before it was found in nature. British chemist John Daniell (1790-1845) described hydrous calcium carbonate in 1819. In 1831, French chemist Jules Pelouze (1807-1867) synthesized calcium carbonate hexahydrate. Mineralogists assumed that calcium carbonate hexahydrate was too unstable to exist in nature.

But in 1962, Danish geologist Hans Pauly was working for a Greenland company mining cryolite, a calcium fluoride (CaF_2) used in aluminum production. After discussing the submarine spires in Ikka Fjord with Danish naval officers, Pauly asked a navy diver to recover samples. When the samples disintegrated on the surface, Pauly suspected that he had found a new mineral. The diver recovered additional samples, which Pauly kept cold until he returned to his Copenhagen laboratory, where he identified the mineral as a hydrous calcium carbonate. In tests, he determined that the mineral was a hexahydrate, based on the weight of the lost water of hydration. In 1964, the International Mineralogical Association recognized ikaite as a new mineralogical species.

Ikaite was next found in 1982 in deep-sediment core-drill samples off Antarctica. Researchers then realized that ikaite was the precursor of a number of the enigmatic calcite pseudomorphs first described in 1827, which have since been found worldwide and throughout the geological record from the Precambrian Era to the Quaternary Period. Geologists now believe that the spectacular tufa (a porous, calcareous rock deposited by springs or streams) "chimneys" sub-aerially exposed on the south shore of California's Mono Lake are calcite after ikaite, the latter apparently with an origin similar to that of the Ikka spires.

As we might expect with a rare and unstable mineral like ikaite, nothing has been written about its lore. One metaphysical writer speculates that glendonites help one to discover their life's purpose, and are all about home and family and creating a loving environment. Calcite, of course, is seen by metaphysical believers as a world teacher and a multi-directional energy distributor.

TECHNOLOGICAL USES

Although ikaite has no material uses, it does have peripheral value in science and industry. In stratigraphic and sediment studies, geologists and paleontologists use ikaite and calcite-after-ikaite pseudomorphs as paleo-thermometers-minerals that offer clues to seawater temperatures in ancient times. Whether or not ikaite has converted to calcite in deep sediments indicates whether temperatures have risen since the ikaite originally formed. This information is valuable in assessing geological uplifting, paleoclimatic change, and tectonic plate movement.

Ikaite is chemically similar to methane hexahydrate ($\text{CH}_4 \cdot 6\text{H}_2\text{O}$). Like ikaite, this gas hydrate crystallizes in low temperatures, sometimes causing blockages in natural-gas pipelines in cold climates. Studies of the nucleation inhibitors that help ikaite form are helping to solve pipeline blockage problems, and are also advancing water-softening technology.

September 2003 Mineral of the Month: Ikaite

ABOUT OUR SPECIMENS

Ikaite now becomes the third mineral we have featured from one of Russia's most prolific mineral sources, the Kola Peninsula, after staurolite in May 2000 and astrophyllite in July 2001. The astrophyllite write-up contains much information on this peninsula, with this introduction: "The Kola Peninsula has an area of about 40,000 square miles, most of which lies above the Arctic Circle, in the northwestern corner of Russia. As you can see from the map, the Barents Sea lies to the north and east, the White Sea to the south, with the borders of Finland and Norway to the west. Murmansk is the principle city, and is the world's largest city north of the Arctic Circle. The Peninsula has been highly modified by the

action of glaciers and ice sheets. The Russians have a word for the treeless plains characteristic of Arctic regions, with black muck soil, permanently frozen subsoil (permafrost), and low-growing vegetation: *tundra*, from which our English word "tundra" is derived. This is a land of harsh winters and short summers, with little snow or rainfall."

Our specimens come from of the mouth of the Olenitsa River, where it flows into the White Sea, on the southern shores of the Peninsula, as seen on the map. Here the specimens can be found at low tide, washed up from the depths of the sea. Our Junior size specimens display the rosette crystal habit of ikaite, with the crystals jutting out in every direction from the center in an attractive way. Our Deluxe specimens are likewise crystals that later attracted a layer of mineral matter that became attached in a typical round or oval shape. Cutting and polishing reveals the crystal form of the original ikaite. Occasionally, some crystals jut out of the surrounding matter, making for a very strange and fascinating form. After ninety months of examining mainly minerals that form deep in the Earth, we are happy to have this mineral that forms deep in the sea!

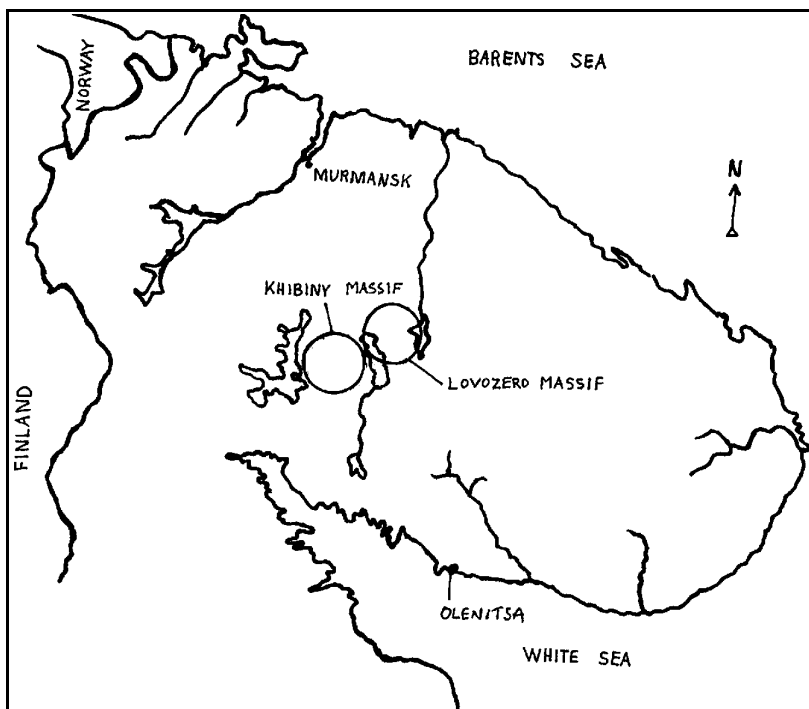


Figure 2 Map of Kola Peninsula

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