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### CHALCEDONY AND QUARTZ CRYSTALS IN SILICIFIED CORAL

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Silicified corals and mollusks from the Tampa formation at Ballast Point, Florida are well-known for their intrinsic beauty and exceptionally good preservation. Ballast Point has been a popular collecting ground for professional scientists and amateurs alike, and by as early as 1842 fine specimens were reported by Conrad (1846) to be rare. Occasionally good specimen material is still found by collectors who are willing to grabble through the mud adjacent to the Point at low tide.

The silicified coral masses from Ballast Point are of varying sizes and shapes. Some are globose and range up to a foot or more in diameter, some are tubular, and others are irregular in shape. Many of the masses are hollow, and the preserved "shell" is commonly only 2 or 3 cm thick or less. The "shell" is characteristically comprised of two distinct layers. The outer layer consists of replaced coral in which the features are preserved in remarkable detail, and the inner part consists of either banded chalcedony or banded chalcedony over which quartz crystals have grown. Most of the hollow forms are lined with colloform chalcedony, a few are lined with small quartz crystals, and less commonly specimens are partitioned and lined with both kinds of material, each in a separate chamber.

Two of the partitioned variety were collected and lent to the writer by Meade Norman, who was at the time a student of his at Florida State University. The two specimens are essentially alike and differ only in such minor details as size, shape, thickness of chalcedony bands, and size of quartz crystals.

In the specimen shown in Fig. 1, the wall ranges in thickness from about 1 to 2 cm. The outer layer in which the coral structures are preserved ranges from less than 1 mm. to about 2 cm. thick. The next is a series of very thin layers of white and gray chalcedony. Part of these layers appears to have been removed by corrosion, and they are therefore not continuous. They are common to the walls of both chambers, however, so were deposited before the partition which separates the interior into two distinct chambers was completed.

Covering the first series of chalcedony layers is a second series which is not so finely laminated as the first. The earlier part of the second series is a thin yellowish layer that is discontinuous because of corrosion, but is common to the walls of both chambers. It grades into a thicker layer of brown chalcedony. During the deposition of the second series the partition, consisting partly of replaced coral, was completed. On one side of

the partition the brown chalcedony continued to be deposited for a time, but on the other side its deposition apparently stopped much sooner, for on the one side the thickness is about 2 to 3 times that on the other side. In the one chamber where chalcedony continued being deposited, the interior is lined with a thin white layer with a botryoidal surface. In the other chamber quartz crystals were developed and they line the interior of that chamber. The total thickness of deposited silica in both chambers is about equal. Details in the layering and similar total thickness of de-

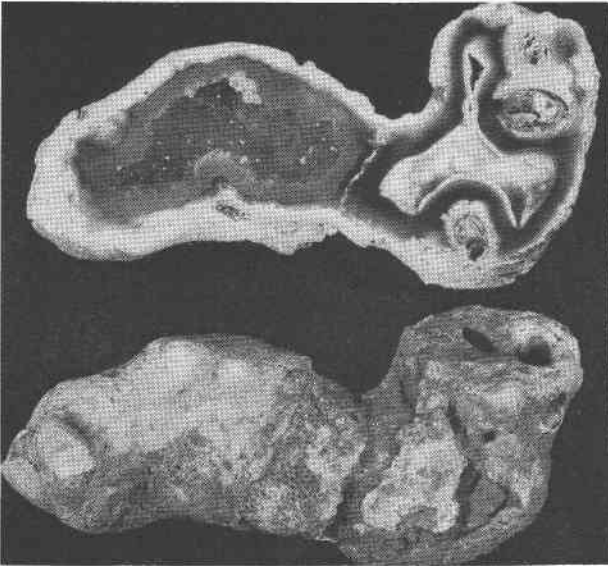


FIG. 1. Exterior and interior views of silicified coral.

posited silica in both chambers suggest that both the chalcedony and the coarsely crystalline quartz were deposited at the same time and at about the same rate. This poses a problem in the genesis of the silica.

The silicification of the corals and other fossils at Ballast Point is part of the general silicification that has taken place in the Tampa formation there. The silicified part of the formation has been referred to as the "silex bed," although it has no stratigraphic significance. Cooke and Mossom (1929) believe the silicification is a surface or near-surface process and that it is still going on. They state that the famous "silex bed" of Ballast Point is merely a superficial accumulation and that it is not confined to any particular stratigraphic level. In places the near-surface part of the formation consists almost wholly of chert in which fossil molds and silicified forms are abundant.

A basic premise to solving the problem of the silicification of the Ballast Point fossils is that silica is transported in true molecular solution rather than in colloidal solution or suspension. Until recently geologists generally believed that silica in natural water is in a colloidal state rather than in true molecular or ionic solution. Observations by Alexander, Heston, and Iler (1954) indicate that silica in low concentrations is in true solution. They found the solubility of amorphous silica to be between 120 and 140 p.p.m. at 25° C. and in the pH range between 5 and 8. Later observations by Krauskopf (1956) and White, Brannoch, and Murata (1956) are in accordance with those of Alexander and co-workers. Krauskopf states:

"In natural waters silica may be in either colloidal or in true solutions, but the colloidal particles are unstable and will disappear spontaneously in the course of a few days or weeks (provided total silica is less than about 100 p.p.m.). Hence the great majority of natural waters should have silica in true solution only."

The solubility of amorphous silica is about 10 times that of alpha quartz. Two values calculated by Siever (1957) are 7.25 p.p.m. and 14 p.p.m.

Most ground waters are low in dissolved silica. The Data of Geochemistry (1924) gives values ranging from 5 to 30 p.p.m. The subsurface water at Ballast Point is probably no exception.

Closely related to the concept that silica in natural waters is transported as a colloid is the belief that chalcedony is formed first as a gel from the colloidal silica and is later reconstituted into crystalline chalcedony. This origin for chalcedony is plausible in certain cases, as with the waters of many hot springs in which the amount of dissolved silica is unusually high, but it seems not to be applicable to a situation in which ordinary groundwater is the solvent. I therefore believe that both the quartz crystals and the banded chalcedony in the coral specimens were deposited as quartz from true solutions. The specimens indicate that chalcedony and quartz crystals can form under similar conditions of temperature, pressure, and concentration of silica in solution.

A feature that may give a clue to why two varieties of quartz have formed under essentially the same environmental conditions is a small opening a few millimeters in diameter in the wall of the chalcedony-lined chamber. The wall of the chamber lined with quartz contains no visible openings. The opening in the wall of one chamber gave the solutions free access, and perhaps at times permitted the cavity to be drained. In this chamber chalcedony was precipitated. In the other chamber, the relative imperviousness of the wall probably allowed the chamber to remain continuously filled with silica-bearing solutions, and quartz crystals were able to grow in this aqueous medium.

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## VOLBORTHITE FROM BRITISH COLUMBIA

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Volborthite,  $\text{Cu}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ , is present as a weathering product of a thin, interlava sedimentary rock of Upper Triassic age which crops out west of Menzies Bay on Vancouver Island, and north of Gowland Harbour on Quadra Island, British Columbia.

The vanadium-bearing rock is a black, extremely finely laminated, fossiliferous, non-clastic sediment which consists chiefly of carbonaceous matter and microcrystalline to cryptocrystalline quartz. Spectrographic analyses indicate that the carbonaceous material contains vanadium. Hypogene chalcocite is generally an additional major constituent of the sediment, in some cases making up over 50% of the rock. The associated volcanic flows are predominantly pillowform and massive porphyritic basalts, andesites, and spilites which are commonly amygdaloidal. The amygdule material is largely quartz, calcite, chlorite, zeolites, epidote, and pumpellyite. Prehnite, chalcocite, chalcopyrite, bornite, and native copper, as amygdule fillings, are widespread in small amounts; analcite, heulandite, and greenockite are of rare occurrence.

Minor quantities of volborthite coat exposed surfaces of the laminated sediment, but the mineral is more abundant along planes exposed by splitting the rock along the laminae.

## PHYSICAL PROPERTIES

The vanadate assumes many colors and habits, most of which are briefly summarized below: