

Reports

Tridymite Pseudomorphs after Wood in Virginian Lower Cretaceous Sediments

Abstract. Fossil wood composed of tridymite is abundant in Patuxent (Lower Cretaceous) arkose on Hazel Run, Fredericksburg, Virginia. X-ray diffraction studies of the tridymite indicate that it has a disordered structure in which hexagonal close packing predominates. The specimens, which contain trace amounts of aluminum, iron, and other elements, are soft and fibrous, varying from white to shades of brown.

X-ray diffraction analyses of fragments of fossil wood from Patuxent (Lower Cretaceous) arkose in Fredericksburg, Virginia, have shown that they are composed of tridymite—the first known occurrence of tridymite in fossil wood. The occurrence of tridymite in material formed at relatively low temperatures is also unexpected, since in the classical interpretation tridymite is a high-temperature form of silica.

Recently, however, Sato (1) found the mineral with opaline silica in silicified andesite from Japan; he mentions a similar occurrence where tridymite is associated with hydrated halloysite. The appearance of tridymite in rocks of Lower Cretaceous age is also noteworthy, since the mineral rarely occurs in rocks older than Tertiary (2).

The x-ray diffraction data for Virginian tridymite (Table 1) represent averaged values derived from measurements from five separate, although nearly identical, films made in two cameras (11.46 cm in diameter) with $\text{CuK}\alpha$ radiation. Although these data are obviously from tridymite, they do not correspond exactly with published data for the mineral. Rarely do any two natural low-tridymite specimens give exactly identical x-ray data.

The tridymite situation is complicated by the fact that interstratification of tridymite layers (similar to hexagonal close packing, as in the high-tridymite 2H structure) and cristobalite layers (similar to cubic close packing, as in the high-cristobalite 3C structure) may occur in low tridymite; interstrati-

fication may be random or systematic (3). Systematic interstratifications may form various polytypes. Frondel (2) has summarized data for natural polytypes with 2, 4, 10, and 20 layers. Hill and Roy (4) have studied synthetic tridymite, finding two main types, referred to as tridymite-M (metastable) and tridymite-S (stable). Further studies of synthetic materials by Sato (5, 6) have indicated that tridymite-M is a ten-layered orthorhombic structure; tridymite-S, a two-layered monoclinic structure (referred to as tridymite-S1).

Table 1. Comparison of x-ray diffraction data for Virginian tridymite and Sato's synthetic tridymite-S4 (6). Intensities for tridymite-S4 were determined from diffractometer charts loaned by Sato. Abbreviations: s, strong; v, very; m, medium; w, weak; B, broad.

Virginian tridymite d (Å), intensity	Tridymite-S4	
	d (Å), intensity	hkl
4.33, s	4.370, s	10·0
4.11, vs	4.118, vs	00·2
3.87, mwB	3.862, ms	10·1
	2.995, m	10·2
2.50, ms	2.523, mw	11·0
	2.325, w+	10·3
2.13, vvwB	2.152, vvw	11·2
2.09, vvwB	2.114, w—	20·1
2.05, vwB	2.059, w	00·4
	1.930, vvw	20·2
	1.863, vw	10·4
	1.710, w—	20·3
1.63, wB	1.651, vw	21·0
1.61, wB	1.619, vw+	21·1
	1.542, w	10·5
	1.531, vvw	21·2
1.45, vwB		
1.36, vvwB		
1.20, vwB		

Upon heating, the tridymite-S1 structure changes to two other structures: two-layered orthorhombic (tridymite-S2) and two-layered hexagonal (tridymite-S4 or tridymite-2H). A domain structure of the tridymite-S2 and tridymite-S4 structures, having the c -axis in common, was designated tridymite-S3.

Comparison of the Virginian data with the structures of Sato (5) and Hill and Roy (4) shows some similarity to tridymite-M, especially a correlation with the most intense x-ray reflections at 4.33, 4.11, and 3.87 Å. On the other hand, strong tridymite-M reflections, 3.25, 3.17 and 2.97 Å, are very weak in or absent from the Virginian material. The tridymite-S1 structure of Sato (6) has a different intensity distribution for the three most intense reflections, and has numerous doublets and other reflections that are absent from the Virginian material.

As to the remaining data of Sato (6), the tridymite-S4 structure (which is the same as hexagonal close packing of high-tridymite 2H) matches the observed data best (Table 1); the most obvious difference is the absence of the $10\cdot2$ (2.995 Å) reflection from the Virginian data. The absence or broadening of reflections corresponding to the tridymite-S4 $h0\cdot l$ reflections (broadening in the case of $10\cdot1$) is probably due to randomness in the stacking of the successive layers of structure, a phenomenon well-known for other polytypic substances. Apparently the Virginian tridymite is not an ordered two-layered hexagonal structure (tridymite-S4 or tridymite-2H), but is a disordered structure in which hexagonal close packing (ideally 2H) predominates over cubic close packing.

A semiquantitative spectrographic analysis was made of a sample of the fossil wood. As expected, the principal constituent is SiO_2 . The following (reported as oxides) are also present: Al, 1.5 percent; Fe, 1 percent; Ti, 0.15 percent; Mg, 0.12 percent; Ca, 0.12 percent; Ba, 0.025 percent; and Mn, Cu, Zr, Sr, and Cr, each a trace. The sample was a clean white piece of fossil wood, but it is not certain whether the trace elements mentioned are in the tridymite structure or present as admixed impurities. Analyses of tridymite from other localities commonly show aluminum, iron, and other trace elements (2, 7). The role played by trace elements in formation and stabilization of the tridymite structure is not known for certain, but it

is thought to be very important (8).

The wood replaced by tridymite varies in color from white to yellow-brown, to brownish-gray, to dark brown; it is very soft, dull, and fibrous (asbestiform), resembling decayed wood. The fibers are easily pulled apart, but they lack the tensile strength of asbestos. An x-ray study of several fibers showed the tridymite to be present as exceedingly fine, randomly oriented grains unrelated to the fiber axis. The wood fragments range from very small to several centimeters in length. The material is very abundant in the host rock, an impure, gray, medium-grained arkose.

The arkose, which is composed of gray quartz and kaolinized feldspar, is also host to small pyrite concretionary masses; gray clods of a mixture of kaolinite, white mica, and quartz; large quartz pebbles; and charcoal-like fragments (amorphous to x-rays) often having pyrite inclusions. Casts of large tree limbs ranging up to 2 m in length are also in the rock. Although I made no attempt to identify plant materials, other studies (9) of the Patuxent formation, based primarily upon leaf impressions in clay, have shown a flora composed of numerous species. A study of weathering products and secondary minerals associated with the arkose, and an underlying montmorillonite bed at the exposure (10), has shown cobaltian pickeringite, alunogen, melanterite, and jarosite.

The exposure, a low, overhanging cliff about 50-m long, is on Hazel Run within the city of Fredericksburg, about half-way between Lafayette Boulevard and Jefferson Davis Highway.

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References and Notes

1. M. Sato, *Mineral. J. Tokyo* 3, 296 (1962).
2. C. Frondel, *Dana's System of Mineralogy* (Wiley, New York, ed. 7, 1962), vol. 3, pp. 259-72.
3. O. W. Flörke, *Ber. Deut. Keram. Ges.* 32, 369 (1955).
4. V. G. Hill and R. Roy, *Trans. Brit. Ceram. Soc.* 57, 496 (1958).
5. M. Sato, *Mineral. J. Tokyo* 4, 115, 131 (1963).
6. ———, *ibid.*, p. 215 (1964).
7. R. W. Grant, *Amer. Mineralogist* 52, 536 (1967).
8. O. W. Flörke, *Ber. Deut. Keram. Ges.* 38, 89 (1961).
9. L. C. Strange, "Geology of the Patuxent sandstone of northeastern Virginia," thesis 732, Univ. of Virginia, 1934; J. R. Burns, "The geology of Fredericksburg, Virginia, and vicinity," thesis 1652, Univ. of Virginia, 1950.
10. J. P. Terry and R. S. Mitchell, *Virginia J. Sci.*, in press.
11. J. P. Terry assisted in the collection of materials in the field.

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Manganese and Related Elements in the Interstitial Water of Marine Sediments

Abstract. Analyses for manganese, nickel, iron, cobalt, sodium, and lithium in the interstitial water of cores from the southern California borderland and six deep-sea cores in the area of the East Pacific Rise show great variation in concentration of trace elements. Oxidizing near-shore sediments showed a 50-fold enrichment in manganese in contrast to sulfide-rich reducing sediments, which showed no enrichment. Deep-sea sediments were variable in their concentration of the trace metals. All but one core showed a high enrichment in dissolved manganese, with a maximum of 6.6 parts per million. Two cores showed a 100-fold enrichment in nickel and cobalt. The manganese appears to be in solution either as Mn^{2+} or as a complex. The results appear to support manganese nodule formation in deep-sea sediments through a diffusion of manganese from depth to the surface.

Concentrations of manganese in deep-sea sediments are high compared with terrestrial igneous and sedimentary rocks, and many workers (1-5) have speculated about the origin of the manganese. Earlier work has been confined mainly to analysis of the solid phase, owing to lack of sensitive methods for the analysis of interstitial waters.

A sensitive analytical technique has recently been developed in our laboratory for the analysis of dissolved trace metals in the parts-per-billion range by a combination of solvent extraction and atomic absorption spectrophotometry (6). This method has been applied to the analysis of several constituents in interstitial water from sediments of the California continental margin (7) and in several deep-sea cores collected by the Scripps Institution of Oceanography in the East Pacific area.

The results reported in this study are from the two areas described above and shown in Fig. 1. The California Borderland sediments were collected in a (25- by 40-cm) polystyrene-coated stainless-steel box corer, and deep-sea cores were taken in a polythene-lined pipe 5 cm in diameter. The interstitial water was removed via a Teflon-lined, gas-operated squeezer (8). Eh and pH measurements were made on the water immediately after removal, minimizing changes occurring through gas exchange. The water was then filtered through a 0.45- μ millipore filter and acidified to pH 3. Manganese, iron, nickel, and cobalt were complexed by adding ammonium pyrrolidine dithiocarbamate to the samples and to standard controls, and extracting the complexes into a small volume of methylisobutyl ketone. Incomplete extraction is corrected for by comparing the samples with standards extracted in the same way (6).

The extracts were analyzed within 30 minutes of phase separation. In all but two cores (Nos. 2 and 8) manganese concentration was sufficiently high for direct analysis of the interstitial water. Sodium and lithium were determined directly by flame emission analysis, with diluted seawater used as a standard for both elements (7). The solid sediment was analyzed by atomic absorption spectrophotometry after decomposition of the sediment with aqua regia, evaporation, and resolution of the metal ions in dilute hydrochloric acid.

The analytical results for the waters are given in Table 1. Sodium was analyzed in all samples as a reference in order to indicate if salinities were similar to average seawater. It can be seen that the California Borderland samples were on the average 1 to 2 percent higher, whereas the deep-sea brines were about 4 to 5 percent higher than values for coastal seawater.

In the waters from the two coastal sediments, iron and nickel showed higher concentrations in the reducing, sulfide-rich Santa Barbara Basin (core No. 2) than in the oxidizing Santa Cruz Basin (core No. 1). Cobalt showed little concentration in relation to seawater, although the highly reducing interstitial water appeared to be somewhat more enriched, especially at the surface of the core.

In view of the published thermodynamic data on manganese (2, 9, 10), it was expected that manganese should follow iron and would be most soluble in the Santa Barbara Basin at a low Eh. The results of the analysis show, however, that in the Santa Barbara Basin, manganese was slightly depleted with respect to its normal concentration in seawater, whereas in the oxidizing Santa Cruz Basin sediments it was concentrated by a factor of 30 to 50.