American Mineralogist, Volume 58, pages 717–720, 1973

Wood Opal—A Tridymite-like Mineral

RICHARD S. MITCHELL, AND SUSAN TUFTS[1]

Department of Environmental Sciences, University of Virginia,
Charlottesville, Virginia 22903

Abstract

Opalized fossil wood usually has a structure approaching high-tridymite. Only in rare cases does it resemble low-cristobalite, a structure often shown by other varieties of opal. Spectrochemical studies show that the silica of tridymite-like opals is chemically more pure than the silica of cristobalite-like or amorphous opals. These latter varieties usually contain more Al, Na, B, and Zr.

Introduction

Our recent X-ray diffraction studies of opalized fossil wood, from a variety of localities, have shown that this material usually has a tridymite-like structure, a somewhat disordered structure approaching orthorhombic high-tridymite (Dollase, 1967). Previously, when one of us (Mitchell, 1967) described fossil wood from Virginia showing this structure, the occurrence of tridymite in such material was believed to be very rare. It is obvious now that this is not the case.

In earlier X-ray diffraction studies of various opaline materials, Dwyer and Mellor (1932), Levin and Ott (1933), and Taliaferro (1935) suggested that some specimens of wood opal possess a high-cristobalite structure. Subsequent work (Raman and Jayaraman, 1953; Flörke, 1961; Tufts, 1971) has not supported the occurrence of high-cristobalite in opaline materials, although low-cristobalite may occur in precious opal, semi-opal, and some common opals (Tufts, 1971; Jones and Segnit, 1971). We reexamined the wood opal specimens in which Levin and Ott (1933) reported high-cristobalite (USNM 48095 and 93818), and found they have the typical disordered tridymite structure.

In Table 1 typical wood opal X-ray data (11.46 cm diameter cameras; Cu$K\alpha$ radiation) are compared with calculated interplanar spacings (Borg, 1973) for orthorhombic high-tridymite in which $a = 8.74$, $b = 5.04$, $c = 8.24$ Å, $C222_1$ (Dollase, 1967). Our observed data also compare well with the theoretical hexagonal $2H$ structure of Gibbs (1927). Every possible reflection through 1.37 Å is included in the calculations. Well crystallized tridymite has some reflections—for example 202, 112 (3.00 Å)—which were not observed in our data. Apparently these are absent in wood opal, or at least very weak and broad, due to random stacking (disorder) in the ideal structure of high-tridymite. Comparisons of our data with those for similar tridymite polytypes and related structures presented by Hill and Roy (1958), Frondel (1962), and Sato (1963a, 1963b, 1964) gave less satisfactory correlations. A more detailed consideration of these other structures was given by one of us earlier (Mitchell, 1967).

Experimental Methods

Thirty-two specimens from localities in eight states and three other countries were selected for study (Table 2). These range from soft asbestiform to massive resinous varieties. In each case the grain of the wood is well preserved. Limb casts were not included in the study. No attempt was made to identify the kind of wood. The material analyzed was selected so as to avoid obvious impurities and to be as homogeneous as possible. X-ray diffraction powder films (11.46 cm diameter cameras; Cu$K\alpha$ radiation) were made of the thirty-two specimens. In each case, additional powder was heated at 1000° C in air for 24 hours and also X rayed when cooled. Unlike the situation observed for amorphous and poorly crystalline cristobalite opals, the heat treatment had little effect on the specimens. In general the X-ray diffraction patterns were

---

[1] Present address: U. S. Geological Survey, Washington, D. C. 20242.

TABLE 1. X-ray Powder Diffraction Data for Orthorhombic High Tridymite and Wood Opal

	Orthorhombic tridymite		Wood opal	
hkl	d(calc)A	I(calc)	d(meas)A	I(obs)*
200,110	4.37	100	4.32	s
002	4.12	61	4.10	vs
201,111	3.86	57	3.87	mwB
202,112	3.00	16	--	--
310,020	2.52	13	2.50	m
311,021	2.41	1	--	--
203,113	2.33	7	2.34	vvw
312,022	2.15	1	2.13?	vvwB
401,221	2.11	5	2.09?	vvwB
004	2.06	2	2.05	wB
402,222	1.93	1	1.90?	vvw
204,114	1.86	2	--	--
403,223	1.71	3	1.73?	vvw
510,420,130	1.65	2	--	--
511,421,131	1.62	3	1.63	wB
314	1.60	0	--	--
205,115	1.54	4	--	--
512,422,132	1.53	2	--	--
404,224	1.50	1	1.51?	vvw
600,330	1.46	1	--	--
331	1.43	1	1.44	vwB
513,423,133	1.41	2	--	--
025	1.38	0	--	--
602,006,332	1.37	1	1.37	vvwB
			1.25	vvwB
			1.20	vwB

*Abbreviations: s, strong; v, very; m, medium; w, weak; B, broad

slightly enhanced and impurity reflections sometimes appeared—for example, hematite reflections occurred if the wood opal was very ferruginous. In some cases two samples were taken from the same specimen, one from the resinous interior and the other from the dull exterior. These samples disclosed that impurities were more abundant in the exterior portion. X-ray reflections from impurity phases appeared in each case after the exterior portions were heat treated, while the heat treatment of interior portions yielded only pure tridymite. The impurities probably were adsorbed during alteration subsequent to the formation of the wood opal.

Results

The major phase in all except two specimens was disordered tridymite, either alone or with quartz (rarely the presence of one or more additional weak X-ray reflections suggested calcite, cristobalite, or unknown substances). The two exceptions (UVA 4649b; USNM B5632) consisted of low-cristobalite opal instead of high-tridymite opal. In these two specimens the X-ray reflections for untreated samples were very weak and diffused; however, when heat treated the cristobalite reflections were enhanced.

The reason some opaline materials are tridymite-like while others are cristobalite-like is problematical. In a recent study of over 100 opaline specimens, we (Tufts, 1971) found that tripolite, geyserite, precious opal, hyalite, semi-opal, and

TABLE 2. Description and Composition of Wood Opal Specimens

No. *	Locality	Description	Composition †
USNM 81883-1	California	Resinous, compact, dark yellowish orange	T
USNM 81883-2	California	Resinous, compact, grayish orange	T+Q+c?
USNM 16058-2a	California (i)#	Resinous, compact, white to dark gray bands	T
USNM 16058-2b	California (e)#	Chalky resinous, compact, light gray	T+Q
USNM 118571	California Sonoma Co.	Chalky resinous, compact, light tan	T
USNM 13539	Colorado	Resinous, compact, yellowish brown	T+q
USNM B5630	Colorado	Resinous, compact, gray white	T+q
USNM 75588	Colorado Divide	Bright resinous, compact, white to brownish	T+Q
USNM 53091a	Idaho Lincoln Co. (i)#	Resinous, compact, yellow brown	T
USNM 53091b	Idaho Lincoln Co. (e)#	Dull chalky, porous, pale yellow	T
USNM R1708-2	Idaho, Blanche	Bright resinous, compact, yellow-brown	T
UVa 2690	Idaho Clover Creek (?)	Resinous, compact, grayish orange	T+u
USNM 75536-1	Montana, Logan Gallatin Co.	Dull resinous, compact, pinkish gray	T+Q
USNM 75536-2	Montana, Logan Gallatin Co.	Bright resinous, compact, dark yellow-orange	T+u
USNM 48095	Montana Gallatin Co. near Three Forks	Vitreous, compact, very light gray	T+q
USNM 46946-1	Montana Gallatin Co. Madison River	Dull resinous, compact, pale brown and white	T
USNM 46946-2a	Montana Gallatin Co. (i)# Madison River	Bright resinous, compact, brownish black	T
USNM 46946-2b	Montana Gallatin Co. (e)# Madison River	Dull earthy, asbestiform, very pale orange	T
USNM 93818	Nevada Esmeralda Co. Redlich	Dull earthy, asbestiform, light gray	T+Q
UVa 2684	Nevada Humboldt Co. Virgin Valley	Bright resinous, compact, dark brownish-black	T
UVa 7588	Nevada Humboldt Co. Virgin Valley	Dull resinous, compact, light grayish-white	T+Q
USNM 8997	Nevada Columbia district	Dull resinous, compact, pale yellowish-brown	T+Q
UVa 4317F	Nevada (?)	Bright resinous, compact, light yellow to tan	T+cal(?)
USNM 106147	New Mexico near Lamar	Resinous, compact, white	T+q
UVa 2686	Utah Millard Co.	Resinous, compact, pinkish gray	T
UVa V4168	Virginia Fredericksburg	Dull earthy, asbestiform, light brownish-gray	T+q
UVa 4649b	Australia Queensland Barcoo River	Dull resinous, compact, dark brown	c
USNM R1707	Hungary, Libethen	Bright resinous, compact, dark reddish brown	t
USNM B5632	Hungary, Erdo Benya, Zempliner Comitat	Resinous, compact, dark yellowish orange and tan	c
USNM C1341	Hungary	Bright resinous, compact, brown	T
USNM 47165	Japan, Itabashi Mura, Iwaki	Resinous, compact, light brownish-gray	T
USNM B5633	Japan, Buzen	Resinous, compact, reddish-brown	T

* USNM = U.S. National Museum; UVa = Lewis Brooks Museum, University of Virginia

† T,t = tridymite; Q,q = quartz; c = cristobalite-like; u = unidentified; cal = calcite. Major components are indicated by capital letters, minor components, lower case.

The interior of a specimen is designated by (i), while the exterior of the same specimen is designated by (e).

certain common opals are amorphous or cristobalite-like before heat treatment. Furthermore, the amorphous specimens became cristobalite-like after heat-treatment (1000°C, 24 hours in air). On the other hand most wood opals and many common opals are tridymite-like before and after heat treatment. Semiquantitative spectrographic analyses were made of twenty-nine representative specimens of various opaline types (including eight wood opals) to see if chemical differences could account for the different structures. Contrary to our predictions the cristobalite-like opals are less pure chemically than the tridymite-like opals. This fact is difficult to reconcile with the general argument of some investigators (Flörke, 1955; Eitel, 1957) who maintain that cristobalite is a pure crystalline phase of SiO_2 while foreign ions are necessary to the formation of the tridymite phase. However, in this instance we are dealing with substances of a much different origin from SiO_2 polymorphs formed at high temperatures.

The following generalizations can be drawn from a study of our twenty-nine analyses (eighteen cristobalite-like types, eleven tridymite-like types). Impurity elements which show a definite preference for cristobalite-like opals are Al, Na, B, and Zr. Aluminum was found in all specimens studied. Only two of the cristobalite opals had Al_2O_3 less than 0.25 percent (range 0.12 to 3.5 percent) whereas only one of the tridymite opals had Al_2O_3 greater than 0.25 percent (range 0.008 to 1.5 percent). Sato (1963a) showed that 2 percent Al_2O_3 is sufficiently effective for the formation of synthetic cristobalite from silica gel, while tridymite forms with lesser amounts. Twelve cristobalite opals contained appreciable Na_2O (range 0.1 to 2.5 percent) but only one tridymite opal (0.1 percent). Sixteen cristobalite opals contained appreciable B_2O_3 (range 0.01 to 0.35 percent) but only two tridymite opals (0.01 percent). Eleven cristobalite opals had ZrO_2 (range 0.002 to 0.08 percent) but only two tridymite opals (range 0.003 to 0.01 percent). The elements Mn, Fe, and Ca also seem to prefer cristobalite opals although the correlation is not as spectacular. Sixteen cristobalite opals had MnO (range 0.001 to 0.02 percent) but only four tridymite opals (range 0.001 to 0.007 percent). Iron was present in all opals studied (range 0.005 to 2.25 percent) without a definite differentiation between structural types, except values of 1 percent and greater were more frequently found in cristobalite types. Calcium was reported for all the opals analyzed (range 0.005 to 0.4 percent); values greater than 0.1 percent were more common in cristobalite types. Other common constituents in the opaline materials, which show no special affinity for type of opal structure, are: MgO (0.002 to 1.5 percent), BaO (0 to 0.12 percent), and TiO_2 (0 to 0.5 percent).

The semiquantitative spectrographic analyses of eight wood opals used in this study show that the unique cristobalite-like wood opal (USNM B5632) from Hungary contained slightly more Al, B, Zr, Mn, Fe, and Ca than the others, following the trends just outlined. An earthy asbestiform wood opal from Virginia (UVA V4168) possessed a tridymite-like structure, and contained more Al, Fe, and other less important trace elements than expected; however, we believe it to have been contaminated by adsorption of foreign cations from ground-water after its initial formation.

Studies of other data failed to show important differences between tridymite-like and cristobalite-like opals. The water content of the wood opals ranged from less than 2 percent to nearly 7 percent. Water percentages for cristobalite-like varieties often fall within this range, but higher values are also common. The index of refraction for the wood opal studied varied from $n = 1.410$ to 1.453, values commonly observed for other opal varieties. The specific gravity for the wood opal varied from 1.91 to 2.09, but here again no important difference was found between these values and those for other opal structural types.

In addition to its common occurrence in wood opal, the disordered high-tridymite structure also has been observed in other varieties of opaline materials, especially the common types including calcareous opal, jasper opal, milk opal, moss opal, and wax opal. Tridymite has also been observed in opaline materials by Sato (1962) and Sun (1962). Sun's data are essentially the same as those in Table 1. Other writers, including Raman and Jayaraman (1953), Eitel (1957), Franks and Swineford (1959), and Jones and Segnit (1971), suggest the possible occurrence of tridymite in opaline materials in combination with cristobalite.

Acknowledgments

We thank Dr. George Switzer of the U. S. National Museum for offering the use of specimens and facilities there. Research was aided by the Arthur A. Pegau Award of the University of Virginia and a Grant-in-Aid of Research from the Society of Sigma Xi.

References

Borg, I. Y. (1973) A personal communication in which data in the following publication are corrected: Borg, I. Y., and D. K. Smith (1969) Calculated x-ray powder patterns for silicate minerals. *Geol. Soc. Amer., Mem.* **122,** 896 p.

Dollase, W. A. (1967) The crystal structure at 220°C of orthorhombic high tridymite from the Steinbach meteorite. *Acta Crystallogr.* **23,** 617–623.

Dwyer, F. P., and D. P. Mellor (1932) A note on the occurrence of β-cristobalite in Australian opals. *Royal Soc. New South Wales J. and Proc.* **66,** 378–382.

Eitel, W. (1957) Structural anomalies in tridymite and cristobalite. *Amer. Ceram. Soc. Bull.* **36,** 142–148.

Flörke, O. W. (1955) Strukturanomalien bei tridymit und cristobalit. *Ber. Deut. Keram. Gessell.* **32,** 369–381.

——— (1961) Investigations of amorphous and microcrystalline SiO_2. *Silicates Inds.* **26,** 424–426.

Franks, P. C., and A. Swineford (1959) Character and genesis of massive opal in Kimball member, Ogallala formation, Scott County, Kansas, *J. Sed. Petrology,* **29,** 186–196.

Frondel, C. (1962) *System of Mineralogy of . . . Dana,* 7th ed., Vol. 3, John Wiley and Sons, New York, 334 pp.

Gibbs, R. E. (1927) The polymorphism of silicon dioxide and the structure of tridymite. *Proc. Roy. Soc. (London),* **113A,** 351.

Hill, V. G., and R. Roy (1958) Silica structure studies: on tridymites. *Trans. Brit. Ceram. Soc.* **57,** 496–510.

Jones, J. B., and E. R. Segnit (1971) The nature of opal. I. Nomenclature and constituent phases. *J. Geol. Soc. Aust.* **18,** 57–68.

Levin, I., and E. Ott (1933) X-ray study of opals, silica glass, and silica gel. *Z. Kristallogr.* **85,** 305–318.

Mitchell, R. S. (1967) Tridymite pseudomorphs after wood in Virginian Lower Cretaceous sediments. *Science,* **158,** 905–906.

Raman, C. V., and A. Jayaraman (1953) The structure of opal and the origin of its iridescence. *Indian Acad. Sci. Proc.* **A38,** 101–108.

Sato, M. (1962) Tridymite crystals in opaline silica from Kusatsu, Gumma Prefecture. *Mineral. J. (Tokyo),* **3,** 296–305.

——— (1963a) X-ray study of tridymite. (1) On tridymite M and tridymite S. *Mineral. J. (Tokyo),* **4,** 115–130.

——— (1963b) X-ray study of low tridymite. (2) Structure of low tridymite, type M. *Mineral. J. (Tokyo),* **4,** 131–146.

——— (1964) X-ray study of tridymite. (3) Unit cell dimensions and phase transition of tridymite, type S. *Mineral. J. (Tokyo),* **4,** 215–225.

Sun, M. S. (1962) Tridymite (low form) in some opal of New Mexico. *Amer. Mineral.* **47,** 1453–1455.

Taliaferro, N. L. (1935) Some properties of opal. *Amer. J. Sci.* **30,** 450–474.

Tufts, S. (1971) *An X-ray diffraction study of opaline material.* Master's thesis, University of Virginia, Charlottesville, Virginia, 69 pp.

Manuscript received, July 17, 1972;
accepted for publication, March 13, 1973.