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SYNTHESIS AND ORIGIN OF CHALCEDONY*

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Abstract

Synthetic chalcedony has anomalous properties similar to those of natural chalcedony. These properties have been explained by submicroscopic holes and inferred disordered regions between fiber interfaces. The properties and origin of synthetic chalcedony are compatible with these concepts.

The chalcedony was made by transformation of solid silica in the presence of hydrothermal solutions at moderate temperature and pressure. Chalcedony was not directly precipitated from solution, but formed only by transformation of silica glass or cristobalite. In general, no conversion took place in slightly acid solutions, while complete, rapid conversion occurred in slightly alkaline solutions. The transformation proceeds indirectly by way of cristobalite and keatite.

Chalcedony is regarded as a secondary, metastable, transitional phase. The peculiar properties differentiating chalcedony from ordinary quartz may be a result of nucleation and growth in solid material (silica glass, opal, silica gel, or cristobalite).

Introduction

Chalcedony has certain distinguishing properties such as low, variable refractive indices and fibrous appearance or undulose extinction. In addition, it is commonly brown in transmitted light, biaxial, chemically more reactive than quartz, and shows suppression of the low-high transition of quartz as commented on by Pelto (1956), Hoss (1957), and Tuttle and Keith (1952). In this paper, the term chalcedony is restricted to material with the quartz structure but with refractive indices less than those of quartz. This essentially follows Pelto (1956). The term "chalcedonic quartz" probably should not be used for chalcedony, but can be conveniently used for textural varieties of quartz which look like chalcedony; *e.g.*, fibrous quartz which has the refractive indices of quartz.

In previous work, a chalcedonic variety of GeO_2 (quartz type), which was analogous to chalcedony, was produced hydrothermally (White, Shaw, and Corwin, 1958). Probably, the first acceptable synthesis of chalcedony was by Nacken (1948) who discussed the laboratory preparation of chalcedonic, geode-like structures and their bearing on the origin of agates.

Synthetic Chalcedony

Description and Comparison with Natural Chalcedony

The synthetic material, shown in Fig. 1, consists of microscopic, fibrous, fan-shaped aggregates which appear similar to natural chalced-

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* Summary in "Synthetic Chalcedony," *Nov. 1959 meeting Geol. Soc. Am., Pittsburgh, Pa.*

ony. The fibers range from approximate parallelism to strongly divergent groups. Most of the fiber groups show straight extinction, but some have inclined and undulose extinction. The fiber groups are usually length-fast, but some are length-slow, and correspond to the variety quartzine. Commonly, one or the other predominates in a given concentric zone. The complexity is similar in natural chalcedonic materials as considered by Braitsch (1957). The birefringence is about that of quartz. Some of the material is biaxial, optically positive, with 2V about 25°. Jones (1952) reported optically positive chalcedony with 2E about 50°.

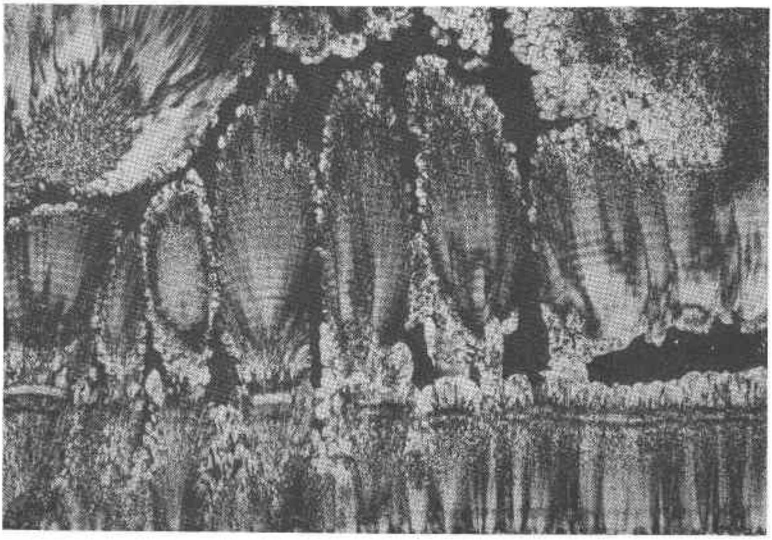


FIG. 1. Synthetic chalcedony showing texture, rhythmic banding, and gradation to quartz. Crossed nicols. ×25.

Much of the synthetic material is concentrically banded (Fig. 1) with changes of color and texture perpendicular to the length of the fiber groups. Rhythmic banding is also commonly present. In transmitted light, the color ranges from colorless, to a distinct brown, to murky along the length of the fiber groups.

The refractive indices are variable, but are mostly in the range 1.51 to 1.52. Indices of some of the fiber groups are gradational along the length ranging from as low as 1.48 to 1.55. Measurements of refractive indices and their comparison to natural chalcedony and quartz are given in Table I.

Folk and Weaver (1952) by using the electron microscope showed that water-filled submicroscopic holes, ranging from about .02 to .30 microns,

TABLE I. REFRACTIVE INDICES OF SYNTHETIC CHALCEDONY, CHALCEDONY, AND QUARTZ

Synthetic Chalcedony	Chalcedony
	1.470 (heat-treated, Pelto, 1956)
n_1 1.48	
n_2 1.49	
n_1 1.50	
n_2 1.51	
n_1 1.51	
n_2 1.52	1.528 (heat-treated, Pelto, 1956)
n_1 1.53	1.530 (Winchell, 1951)
n_2 1.54	1.533–1.539
n_1 1.54	
n_2 1.55	
Synthetic Quartz	Quartz
ω 1.544	1.544
ϵ 1.553	1.553

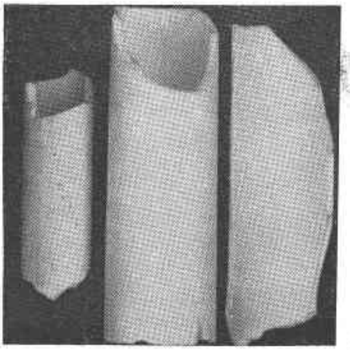
are present in chalcedony, and that these can account for the low indices as well as the brown color. The refractive index was shown to vary in proportion to the abundance of holes. Later, Pelto (1956), showed that the brown color is due to holes of suitable size which result in preferential scattering of blue light. Pelto also suggested there should be no sharp break between quartz and chalcedony. In describing the synthetic germanium analogue of chalcedony, White, Shaw, and Corwin (1958) noted low refractive indices and gradual change up to those of the quartz form of GeO_2. A relation between change in refractive index and color was also present. Synthetic chalcedony grades into ordinary quartz along with gradual changes in refractive index which in places accompany color changes.

The low-index material (Table I) is comparable to the heated natural material (Pelto, 1956) which develops a comparable range of indices and is as low as 1.47. Apparently upon heating, some of the water is lost and the index is lowered. A similar explanation appears reasonable for the low-index material which occurs in the central parts of the transformed glass and thus might contain less water.

X-ray powder patterns of the chalcedonic material indicate almost pure quartz, but lines indicating minor amounts of cristobalite and keatite (Keat, 1954) are present in many samples.

CONDITIONS OF ORIGIN

Silica glass, or in some experiments cristobalite, was placed in a 250 ml., stainless-steel autoclave containing 125 ml. of water solution of usually 0.025 N salt concentration. The pH of the solutions was varied in different experiments from about 3.5 to 12 by adding HCl or NaOH. The temperature, pressure, and time were respectively 400° C., 340 atm., and usually 48 hours, although longer and shorter runs were also made. Details of the equipment and procedure have been given by Swinnerton, Owen, and Corwin (1949) and Yalman and Corwin (1957). The silica was silica glass tubing and rods, and "standard" and "hyflo super-cel" (Johns-Manville) which are processed natural silica. This material is cristobalite as shown by *x*-ray powder patterns. The glass was high purity silica glass made by Thermal American Fused Quartz Co., transparent, one-half inch diameter. In some experiments, a quartz seed was also present.



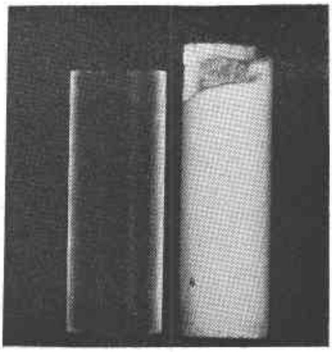


FIG. 2 (left). Glass tubing completely converted to chalcedony and quartz. Diameter of large tube 1.5 mm.

FIG. 2 (right). Unconverted glass rod on left. At right, partially replaced rod with unconverted core. Diameter of rods 13 mm.

Examination of the autoclave after a run generally showed crystalline material in one or more of the following places: on the quartz seed, on the walls of the autoclave, and as a replacement of original silica. Petrographic study of the material deposited on the walls of the autoclave and on the seed revealed in 30 samples the common presence of quartz or cristobalite, but no chalcedony. In contrast, the glass or cristobalite was commonly converted to chalcedonic quartz and chalcedony. In many cases glass tubing and rods maintained their original shape after conversion (Fig. 2).

A sequence of concentric layers is commonly shown by the converted silica (Fig. 3). When fully developed, the sequence from the outer surface inward is fibrous quartz, chalcedony, keatite, a thin zone of cristobalite, and finally a glass core if conversion is not complete. In detail, the cristobalite-glass contact is made up of hemispherical lobes of cristobalite directed into the glass. Identification is based on presence of cristobalite lines in the powder patterns, refractive index of 1.49, isotropic character, and assumed silica composition. The results are similar to those of Carr and Fyfe (1958), who found that the conversion of amorphous silica proceeded by way of cristobalite, keatite, and quartz. Similarly in the present work, the transformation proceeded as follows: *glass→cristobalite→keatite→chalcedony→quartz.*

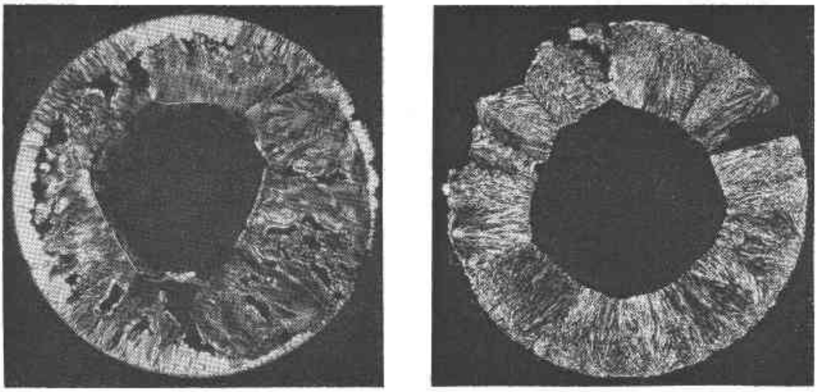


FIG. 3 (left). Cross section showing concentric layers of fibrous quartz, chalcedony, keatite, cristobalite and glass core. Growth proceeded from outer surface inward. Crossed Nicols. Diameter 13 mm.

FIG. 3 (right). Cross section of partially converted silica rod. Note radial fibrous texture and growth centers on outer surface. Core is glass. Crossed nicols. Diameter 13 mm.

Although chalcedony formed only by conversion of solid material, the character of the hydrothermal solutions determined whether the replacement or transformation would or would not take place under the given conditions of time, temperature and pressure. In pure water or very dilute acids, no reaction occurs. However, in very slightly alkaline solutions, the reaction is rapid and complete. This is in general agreement with Nacken (1948), and a similar control has been noted in experiments on the growth of quartz by precipitation from solution, *e.g.*, Yalman and Corwin (1957). A summary of data from 30 experiments pertaining to the influence of hydrothermal solutions and in particular the effect of pH on the presence or non-presence of chalcedony is given in Table II.

NATURAL CHALCEDONY AND CHERT

Conditions of Origin

It is known that natural chalcedony forms under near surface conditions at low temperatures. These conditions are restricted to sedimentary and low-temperature hydrothermal environments. Further well recognized features are the common and widespread association with opal and similar material and the conversion of opal to chalcedony (Pettijohn, 1957; Barth, 1952; Williams, Turner, and Gilbert, 1954; White, 1955; Pittman, 1959; and others). The experimental data support and complement these observations.

TABLE II. HYDROTHERMAL SOLUTIONS AND THE PRESENCE OR NON-PRESENCE OF CHALCEDONY

Number of Experiments	Solution	pH_f*	Product
4	Pure H_2O	6.0–7.5	Glass. No change in source material
3	HCl, .025 N	6.7–7.5	
2	$MgCl_2$, .025 N	4.0–4.5	
2	$BaCl_2$, .025 N	4.0	
2	$BaCl_2$, .025 N+ $Ba(OH)_2$ to pH 10	4.0	
2	BeF_2, .025 N	3.5	
3	KOH, .025 N	10.3	Chalcedony and Quartz. Replacement of original glass
4	NaOH, .025 N	10.2	
6	NaCl, .025 N+ NaOH to pH 10	8.0–9.0	
2	NaF, .025 N	5.0–8.0	

Source material—silica glass. Temp. 400° C.; Pressure 340 atm.; Time 48 hrs.
* pH_f is the final pH (measured).

Although chalcedony and quartz were formed rapidly at 400°, petrographic examination shows chalcedony is being converted to fibrous quartz and cannot persist. This was confirmed by longer runs (96 hours) which showed only fibrous quartz. From a consideration of solubility data (Kennedy, 1950) such transformations should take place at temperatures as low as about 300°, but below about 250° the recrystallization should be appreciably slower. That the critical temperature of water is not a factor is shown by the formation of the germania chalcedony (White, Shaw, and Corwin, 1958) at 200° C. Also Carr and Fyfe (1958) observed complete conversion of amorphous silica to quartz at 250° C. in a few hours in the presence of dilute alkaline solutions. Thus, an upper limit for the formation and persistence of chalcedony is suggested at about 300°. Concerning the lower limit, it has not been possible to grow quartz at temperatures below 100° C. This is also in line with natural occurrences, opal being the mineral present at lower temperature. White (1955) noted the rarity of opal in hot spring deposits at temperatures greater than 100°; its place being taken by chalcedony and quartz. White, Brannock, and Murata (1956) observed that opal probably forms at temperatures as high as 140° C. but is unstable and changes to chalcedony or quartz. Thus a temperature of formation on the order of 100–300° C. is indicated for chalcedony.

Pressure may be more important than temperature in controlling the occurrence of chalcedony. The important effect of pressure on the transition of amorphous silica to quartz has been demonstrated by Carr and Fyfe (1958). The pressure factor would restrict chalcedony to shallow depths.

In the formation of both synthetic and natural chalcedony, water solutions are necessary. Further, the nature of the solution seems to be of critical importance in determining whether chalcedony and quartz will form in a given time interval, or whether amorphous silica or cristobalite will persist. While many different ions may affect the rate of transformation, the experimental data suggest the presence or absence of chalcedony and secondary quartz in opaline, near-surface deposits may be primarily dependent on solutions of appropriate pH.

Flörke (1955), Hoss (1957), and others consider that much opal is essentially disordered low-cristobalite. In a study of cherts, Hoss concludes that the sequence of changes is probably: amorphous silica (or opal), to cristobalite, to chalcedony (or microcrystalline quartz). Braitsch (1957) describes natural examples of the apparent conversion of cristobalite to chalcedony, and notes silica gel may change to cristobalite-opal or directly to chalcedonic material, or in some instances cristobalite-opal later changes to chalcedony. The experimental results are similar but suggest keatite also may be found associated with opal and chalcedony.

This study supports the concept that most chalcedony and chert are secondary products and require the former presence of gelatinous silica, silica glass, opal or cristobalite. The extensive work on transport and precipitation of silica by Krauskopf (1956, 1959) is in agreement with these conclusions.

In the conversion, quartz may crystallize with submicroscopic holes because of negative volume change. Disordered regions between crystallite interfaces also might be expected. Nucleation and growth, as shown by the synthetic chalcedony, would generally start from a surface and proceed to other parts of the material producing the typical fibrous and radial textures.

REFERENCES

BARTH, TOM, F. W., 1952, Theoretical Petrology: John Wiley & Sons, New York.

BRAITSCH, OTTO, 1957, Über die natürlichen Fasen- und Aggregationens-typen beim SiO_2, ihre Verwachsungsformen, Richtungsstatistik und Doppelbrechung: *Heidelbg. Beitr. Mineral. u. Petrogr.*, **5,** 331–372.

CARR, R. M. AND FYFE, W. S., 1958, Some Observations on the Crystallization of Amorphous Silica: *Am. Mineral.*, **43,** 908–916.

FLÖRKE, O. W., 1955, Zur Frage des Hoch-Cristobalit in Opalen, Bentoniten, und Glässern: *Neues Jahrbuch für Mineralogie, Mh.*, H **10,** 217–223.

FOLK, ROBERT K. AND WEAVER, CHARLES EDWARD, 1952, A Study of the Texture and Composition of Chert: *Am. Jour. Sci.*, **250,** 489–510.

HOSS, H., 1957, Untersuchungen über die Petrographie kulmisher Kieselschiefer: *Beiträge zur Min. u. Petrog.*, **6,** 59–88.

JONES, FRANCIS T., 1952, Iris Agate: *Am. Mineral.*, **37,** 578–587.

KEAT, PAUL B., 1954, A New Crystalline Silica: *Sci.*, **120,** 328.

KEITH, M. L. AND TUTTLE, O. F., 1952, Significance of Variation in the High-Low Inversion of Quartz: *Am. Jour. Sci.*, *Bowen Volume,* **250,** 203–280.

KENNEDY, GEORGE C., 1950, A Portion of the System Silica Water: *Econ. Geol.*, **45,** 629–653.

KRAUSKOPF, K. B., 1956, Dissolution and Precipitation of Silica at Low Temperatures: *Geochim. Cosmochim. Acta,* **10,** 1–26.

KRAUSKOPF, K. B., 1959, The Geochemistry of Silica in Sedimentary Environments: Silica in Sediments, Soc. Econ. Paleon. and Mineralogists, Am. Assoc. Petroleum Geologists, 4–19.

NACKEN, R., 1948, Über die Nachbildung von Chalcedon-Mandeln: *Natur und Volk,* **B,** 78, 2–8.

PELTO, CHESTER R., 1956, A Study of Chalcedony, *Am. Jour. Sci.*, **254,** 32–50.

PETTIJOHN, F. J., 1957, Sedimentary Rocks: 2nd Edition, Harper and Bros., New York..

PITTMAN, J. S., JR., 1959, Silica in Edwards Limestone, Travis County, Texas: Silica in Sediments, Soc. Econ. Paleon. and Mineralogists, Am. Assoc. Petroleum Geologists, 121–134.

SWINNERTON, A. C., OWEN, G. E., AND CORWIN, J. F., 1949, Some Aspects of the Growth of Quartz Crystals: *Disc. Far. Soc.*, **5,** 172–180.

WHITE, DONALD E., 1955, Thermal Springs and Epithermal Ore Deposits: *Econ. Geology, Fiftieth Anniversary Volume,* Part I, Bateman, editor, 99–154.

WHITE, D. E., BRANNOCK, W. W., AND MURATA, K. J., 1956, Silica in Hot-Spring Waters: *Geochim. Cosmochim. Acta,* **10,** 27–59.

WHITE, J. F., SHAW, E. R., AND CORWIN, J. F., 1958, A Chalcedony-like Variety of Germania: *Am. Mineral.*, **43,** 580–584.

WILLIAMS, HOWELL, TURNER, FRANCIS J., AND GILBERT, CHARLES M., 1954, Petrography: Freeman and Company, San Francisco.

WINCHELL, ALEXANDER N. AND WINCHELL, HORACE, 1951, Elements of Optical Mineralogy, Part II. Description of Minerals: 4th Edition, John Wiley & Sons, Inc., New York, New York.

YALMAN, RICHARD G. AND CORWIN, JAMES F., 1957, Hydrothermal Reactions under Supercritical Conditions, III—The Effect of pH on the Crystallization of Silicon Dioxide: *Jour. Phy. Chem.*, **61,** 1432–1437.

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