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A STUDY OF THE TEXTURE AND COMPOSITION OF CHERT

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ABSTRACT. Electron microscope study of fracture surfaces of chert, using the replica technique, has shown that at least two and possibly three types of surfaces are present. Specimens which under the light microscope consist of microcrystalline quartz (minute, equant grains) show sharply defined polyhedral blocks with smooth, slightly curved faces—exactly like the shapes occupied by the air cells in soap froth. Arkansas novaculite, a very homogeneous type of chert, possesses this type of surface to a marked degree. Specimens which under the light microscope are composed of chalcedonic quartz (radiating fibers) have a more or less spongy surface, with no evidence of fibrous character when examined with the electron microscope. The sponginess is caused by the presence of abundant spherical water-filled cavities, all very nearly 0.1 micron in diameter. The bubbles impart a brownish color to the chalcedonic quartz as seen in the light microscope and decrease the density and refractive index in proportion to their abundance. Chalcedonic quartz without bubbles has the same refractive index as normal quartz. The properties of chert and chalcedony are adequately explained by the hypothesis that they consist of fine-grained quartz plus a variable quantity of water-filled cavities; there is no evidence of admixed opal. The fracture surface features are related to the mode of origin of the various types of chert.

INTRODUCTION

IT has long been known that sedimentary silica exists in at least three major modifications, those of normal quartz, chalcedony, and opal. The sequence from quartz through chalcedony on to opal is marked by decreasing grain size, increasing water content, and decreasing refractive index and density. The two end-members, quartz and opal, are distinct minerals, since opal gives the X-ray pattern of cristobalite (Levin and Ott, 1932) and is isotropic. However, the relation of chalcedony (including microcrystalline quartz) to other members of the group is less clear. Its variation in refractive index, density, and water content, combined with the fact that it yields the X-ray pattern of quartz, indicates that it is a mixture of two phases in varying proportions: quartz plus some hydrous material of lower density and refractive index. Correns and Nagelschmidt (1933) postulated that this interstitial material ("zwischenmittel") was opal. Their work was later enlarged upon by Donnay (1936b).

The purpose of this paper is to show that in the cherts that have been examined, the "interstitial material" is present, not as opal, but as very minute cavities containing water, and that all properties of chert or chalcedony may be explained by the combination of quartz with water-filled cavities.

THE HYPOTHESIS OF CORRENS AND NAGELSCHMIDT: CHALCEDONY AS A MIXTURE OF QUARTZ WITH OPAL

Correns and Nagelschmidt (1933) and Donnay (1936b) developed the theory that chalcedony is a mixture of fibers of quartz with interstitial opal. They measured the density of chalcedony, and from this figure obtained the proportion of opal presumably present in the mixture. By using the Wiener and Christiansen formulas, they computed the refractive index that would result from such a mixture, and found that the computed value agreed closely with actual measurements of the refractive index. They also attempted to determine the amount of opal by measuring the quantity dissolved by alkalies. However, no direct evidence was obtained for the existence of admixed opal in chalcedony. Donnay states (1936b, p. 301),

"Il n'a pas été prouvé directement que le constituant jouant le rôle de milieu interstitiel soit de l'opale. C'est évidemment l'hypothèse la plus plausible."

The present investigation has revealed no evidence in support of the opal hypothesis. X-ray diffraction patterns show no trace of the cristobalite pattern which should be present if opal were contained in chalcedony. Electron microscope study reveals only two phases: solid masses interpreted as quartz, and cavities. Inasmuch as quartz is harder than opal, fibers of quartz amid softer opal (as postulated by Correns and Nagelschmidt) should be readily visible on fracture surfaces when examined with the electron microscope. Such is not the case even in chalcedony specimens which are strikingly "fibrous" under the light microscope.

Although no evidence of opal was found in the specimens of chert and chalcedony studied, some intergrowths of quartz and opal may exist. However, in all the specimens we have examined, cavities containing water and not opal have been found to be the diluent of the quartz.

INVESTIGATION OF TEXTURE AND COMPOSITION

Outline of the work

Under the light microscope, chert specimens usually con-of chert and chalcedony studied, some intergrowths of quartz and optically fibrous chalcedonic quartz. Both varieties were found to contain minute water-filled cavities which decrease the refractive index and density. Under the electron microscope these two micro-forms of quartz were studied in greater detail.

Chalcedonic quartz versus microcrystalline quartz

The micro-forms of quartz, as they occur in chert, may be divided petrographically into two classes: microcrystalline quartz (following the usage of Keller, 1941), and chalcedonic quartz (plate 1, fig. 1). Microcrystalline quartz forms the bulk of most chert nodules, and is composed of subsequent interlocking grains in random orientation.[1] The individual grains in most specimens average three to five microns in diameter, and the aggregate has "pin-point" birefringence; but in other specimens, the grains are so small as to make the aggregate appear nearly isotropic. Each grain in a thin section appears to possess undulose extinction, which is due in part to the effect of many superimposed grains, but in part may also be a property of the individual microcrystal.

Chalcedonic quartz under the light microscope appears to be composed of radiating or sheaf-like bundles of fibers, each fiber not more than a few microns in diameter and ranging up to 200 microns or more in length. The fibers are not physically separable, for no fibrous structure is evident on fracture surfaces studied with the electron microscope. The break between microcrystalline and chalcedonic quartz seems to be rather sharp, although transitions do exist.

In addition to the micro-forms of quartz, chert nodules may also contain ordinary quartz of larger crystal size, showing straight extinction and normal refractive index. This "drusy" quartz usually forms the final deposit in the center of cavity fillings, while chalcedonic quartz lines the walls. This is probably due to a decreasing rate of precipitation

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[1] X-ray diffraction patterns of thin sections of chert contain reflections which have the same relative intensities as reflections from powdered specimens of quartz.

because of the diminishing rate of supply of solution as consolidation proceeds. In some formations (Taliaferro, 1934) cherts are associated with large, entirely isotropic, masses of opal with low index of refraction, but the two occupy discrete areas and are not so intimately mixed that the opal affects the physical properties of the chalcedonic or microcrystalline quartz.

Presence of water-filled cavities in chert

In transmitted light, chalcedonic quartz (and, to a lesser degree, microcrystalline quartz) often appears to contain brownish zones. In reflected light, these zones become milky white. The movement of the Becke line indicates that they have a lower refractive index than the surrounding clear chalcedony. Under 1000x magnification, the brownish areas are found to be made up of a swarm of very minute, pale brownish dots. The largest of these are one or two microns in diameter, are isotropic, and have a moderate relief with refractive index below that of the enclosing chalcedony. These features are similar to the water-filled cavities in the quartz of igneous rocks. On the basis of this similarity, the brownish dots in chalcedony are also interpreted as water-filled cavities. It is believed that the cavities are filled with water and not gas, because (1) gas-filled cavities have an extreme negative relief, much greater than the relief of the observed cavities; (2) chemical analyses of chalcedony show a content of water, which, as shown later, is not present as opal, and therefore must be present as free water. The brownish color is probably due to some complex dispersion effect, caused by the difference in index.

The refractive index is a direct function of the abundance of water-filled cavities, as evidenced by the depth of brownish coloration. Bubble-free chalcedony has the same index of refraction (ordinary ray) as normal quartz. The fact that brownish areas in chalcedony have a lower refractive index was first noticed by Sargent (1929, p. 407). He ascribed it to a greater degree of hydration, but did not specify how this hydration was accomplished.

Collodion replicas were made of the surfaces of chalcedonic quartz specimens which contained most bubbles as seen under the light microscope. Electron microscope study of the replicas revealed that the surfaces were very heavily crowded with holes, most of them spherical and about 0.1 micron in diameter. This fact indicates that the brownish dots seen in the light microscope are cavities and do not represent spherical particles of a solid such as opal.

Electron microscope study

Freshly fractured, unpolished surfaces of chert specimens were studied with the electron microscope, using the replica technique. Because of the low penetrating power of the electron beam, it is impossible to study chert specimens directly, and a very thin replica or mold of the actual surface must be made with a plastic film. One drop of a solution of amyl acetate with two per cent collodion is placed on the surface of the vertically held specimen, and allowed to spread very thinly over it. After the film has dried, the specimen is immersed in hydrofluoric acid to dissolve the chert and free the collodion film. The inner side of the plastic is then a negative replica of the surface of the chert. The replica, mounted on a 200-mesh screen, is "shadowed" with vaporized chromium to accentuate the relief, and examined with the electron microscope at magnifications of 1500 to 10,000 times.

Two distinct end-points of surface morphology were observed, together with a third, perhaps transitional type. The first we have called the "novaculite" type, because Arkansas novaculite (a very homogeneous white chert) gives the best example of this type of surface (Bates, 1949). It is characterized by sharply defined, equant polyhedral blocks with slightly curved surfaces, all blocks being about the same size (plate 1, fig. 2; plate 3). The blocks are remarkably similar in appearance to the air cells produced in a soap froth. Individual blocks which break in half usually show a featureless interior, but occasionally a somewhat terrace-like or platy structure is observed, and more rarely a conchoidal fracture appears. The novaculite-type surface occurs with varying degrees of distinctness, and shows a complete transition to the "intermediate" type. A few blocks contain small swarms of beautifully defined spherical cavities, which are almost uniformly 0.1 micron in diameter (plate 3, fig. 2).

The second, "spongy" type of surface, is found exclusively in specimens that are classed petrographically as chalcedonic quartz. The appearance of the replica is somewhat like a piece of swiss cheese or a sponge (plate 2, fig. 1; plate 4); that is, the surface of the chert contains no discrete grains, but is permeated with tremendous numbers of small hemispherical holes, many of which coalesce to form vague tubules (plate 2, fig. 1) which tend to be parallel to each other and perpendicular to the orientation of the fibers as seen in the light microscope. Cavity-rich zones alternate with zones poor in cavities, just as seen in the light microscope. There is no evidence of fibrous character under the electron microscope.

The third, "intermediate" type of surface apparently represents a transitional stage between the novaculite and spongy types. It consists of highly irregular, somewhat indistinct areas of low relief without many cavities (plate 2, fig. 2). It sometimes contains patches showing the novaculite type surface. This intermediate type seems to be characteristic of oolitic cherts, and also of some cherts composed of massive microcrystalline quartz.

The correlation of surface morphology shown by the electron microscope with internal morphology as revealed by the light microscope is depicted in figure 1, in which the width

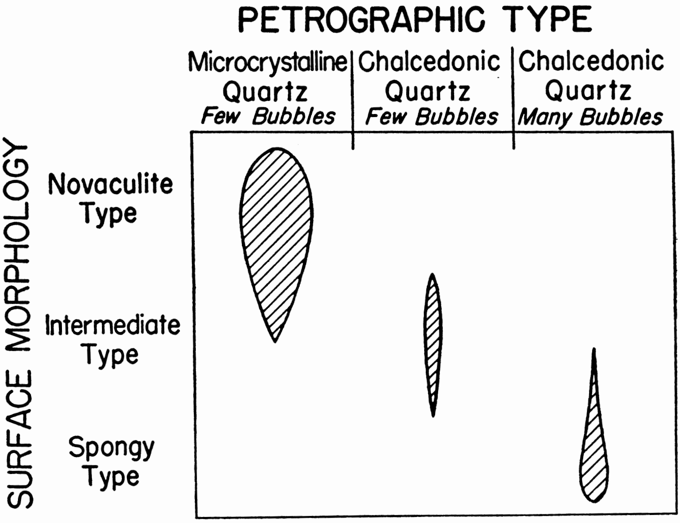

Fig. 1. Diagram showing the correlation between surface morphology and petrographic type. Width of the lenses shows the estimated relative volumetric importance of the three varieties of quartz.

of the lenses shows the relative volumetric importance of the types.

Effect of water-filled cavities on physical properties

The presence of water-filled cavities should result in a decrease of the density and refractive index of the chalcedony. To check this, the physical properties of several pieces of novaculite, which contains but few bubbles, were compared with those of several pieces of bubbly chalcedony. The novaculite is uniform petrographically, and consists entirely of microcrystalline quartz. The chalcedony, on the other hand, is composed of a chalcedonic quartz, and contains bubble-rich and bubble-free zones.

Density measurements. Replicate measurements were made on one specimen of novaculite and one of chalcedony. A five to ten gram fragment was dried in a desiccator and weighed. Then it was placed in a wire sling of known weight, submerged in distilled water at known temperature and weighed again. From each specimen, three fragments were cut, and the experiments were replicated four times; hence, twelve measurements were obtained for each specimen. The average experimental error was ± 0.0019.[2] The following results were obtained (± range refers to one standard deviation, using n−1 = 3 degrees of freedom):

A. Novaculite, specimen homogeneous with few cavities:

	densities	
Piece #1	2.6422±0.0018	
Piece #2	2.6437±0.0028	
Piece #3	2.6412±0.0021	
Arithmetic mean	2.6424±0.0021	(95% confidence limits)

B. Chalcedony, microscopically fibrous with many cavities:

	densities	
Piece #1	2.6067±0.0010	
Piece #2	2.6145±0.0025	
Piece #3	2.6098±0.0014	
Arithmetic mean	2.6103±0.0037	(95% confidence limits)

It is evident that the large number of cavities lowers the density significantly.

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[2] In terms of standard deviation.

PLATE 1

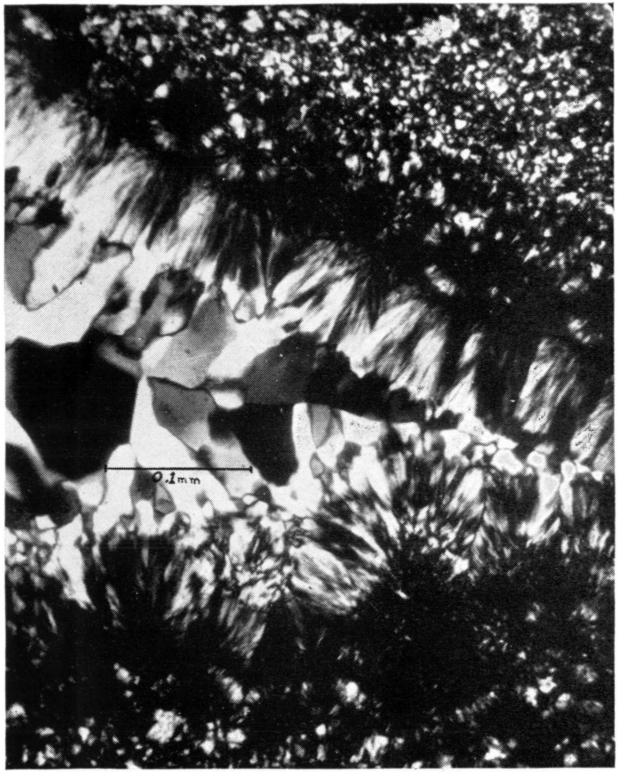

Fig. 1. Light microscope, crossed nicols, x 216. Thin section showing the three petrographic types of quartz: microcrystalline quartz, forming minute, equant grains; chalcedonic quartz, forming fibrous bundles; and normal quartz, forming large equant grains. The latter two varieties fill a geode in the specimen. Chert from Lower Ordovician Bellefonte dolomite, State College, Pa.

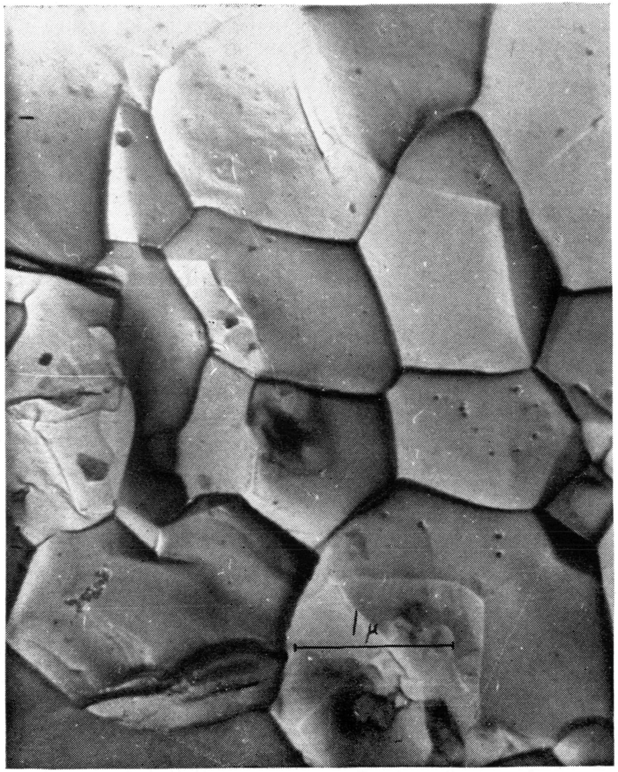

Fig. 2. Electron micrograph, x 27,700. Novaculite-type surface, showing well-defined blocks with somewhat curved surfaces. Note presence of a few well-defined bubbles. Chert from the Permian Phosphoria formation, southwest Montana.

PLATE 2

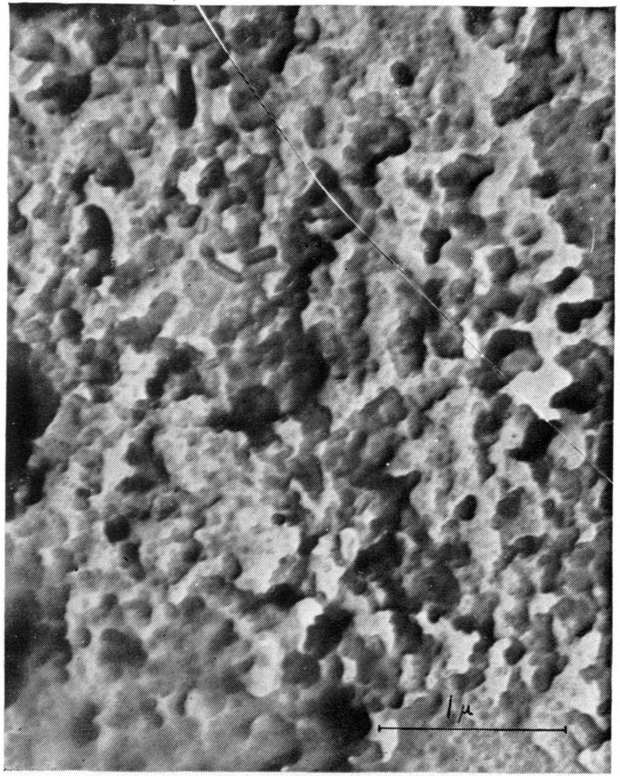

Fig. 1. Electron micrograph, x 26,650. Spongy surface, showing coalescence of bubbles to form parallel vaguely expressed tubules. Thin line is a crack in the glass negative. Chalcedony, locality unknown.

Fig. 2. Electron micrograph, x 11,750. Intermediate-type surface, showing sub-planar areas of low relief. Chert from Permian Phosphoria formation, southwest Montana.

PLATE 3

Fig. 1. Electron micrograph, x 3,290. Typical area of novaculite-type surface. Chert from the Permian Phosphoria formation, southwest Montana.

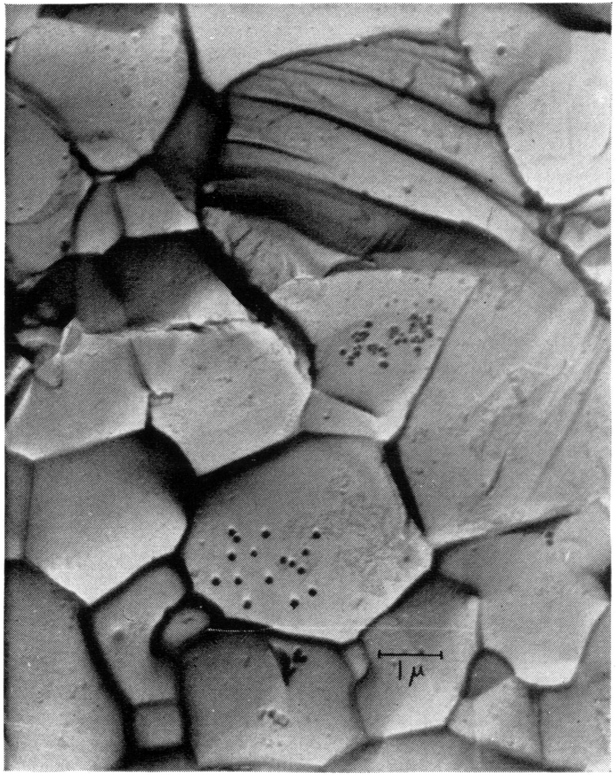

Fig. 2. Electron micrograph, x 9,400. Novaculite-type surface. One block contains a swarm of nicely-defined spherical bubbles. Chert from the Permian Phosphoria formation, southwest Montana.

PLATE 4

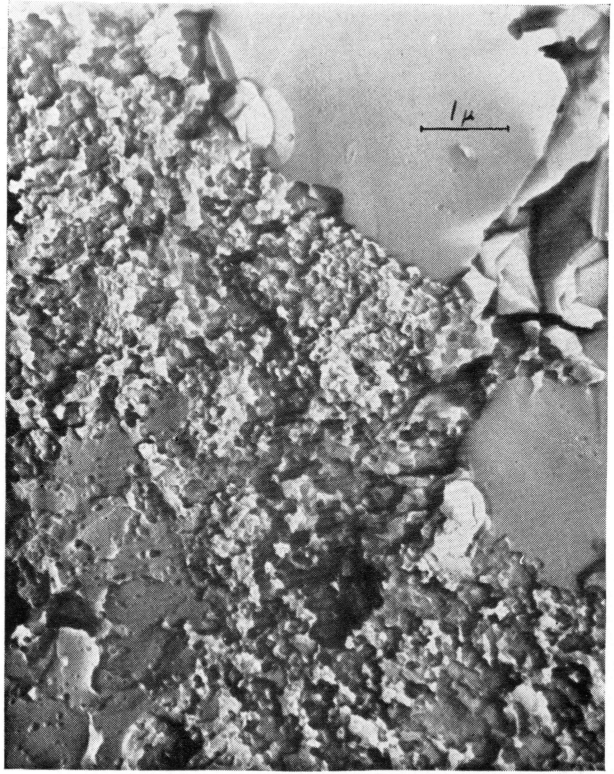

Fig. 1. Electron micrograph, x 12,690. Spongy surface, caused by the abundance of bubbles. Passes abruptly into area of rather poorly developed novaculite-type surface. Brecciated white chert from the lead-zinc deposits at Joplin, Missouri.

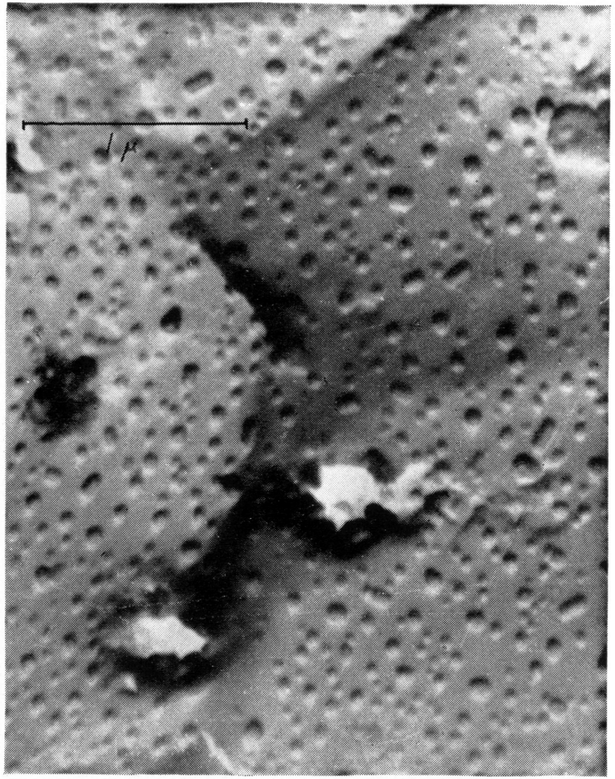

Fig. 2. Electron micrograph, x 31,490. Spongy surface, as shown in a piece of bubbly chalcedonic quartz. Note abundant spherical bubbles, and lack of fibrous structure. Milky chalcedony, locality unknown.

Index of refraction. The index of refraction of the ordinary ray was measured for both chalcedony and novaculite. The extraordinary ray was not measured because of its variation due to orientation. In all index measurements, crushed fragments of a clear quartz crystal were mixed with the fragments of novaculite and chalcedony to serve as a standard. Determinations were made by using index liquids and monochromatic sodium light. The refractive index of novaculite was found to be 1.544, the same as that of quartz. The refractive index of chalcedony varied from 1.544 where the chalcedony was colorless (hence free of cavities) to 1.540 in places where the chalcedony was brownish and filled with cavities. Due to the close spacing of bubbly and non-bubbly zones, no mathematical correlation between refractive index and density was attempted. The concept of form birefringence (Donnay, 1936a) is not believed to be applicable because it requires the existence of fibers or plates of one substance embedded in another substance of differing refractive index; in the chalcedony studied, quartz plus cavities are the only two phases, and there is no evidence of physically discrete fibers or plates.

Other physical properties. In order to ascertain the elements that might be present in traces in the water contained in the cavities, one sample of chalcedony and one of novaculite were sent to Mr. Howard W. Jaffe, of the U. S. Bureau of Mines for spectrographic analysis. He obtained the following results:

Estimated percentage	*Chalcedony*	*Novaculite*
0.5 - 5.		Fe
0.1 - 1.	Al	
0.01 - 0.1	Na, Fe, Mg	
0.01	Ca	Na, Al, Ba, Sr, Mg

No definite conclusions can be drawn from two samples; however, the presence of appreciably more sodium and magnesium in the chalcedony may indicate the presence of saline water in the cavities.

Differential thermal analysis showed the normal quartz inversion at 573°C, although it was somewhat subdued. X-ray patterns revealed nothing but the normal quartz structure.

HYPOTHESIS ON THE FORMATION OF CHERT

Any hypothesis concerning the origin of chert should take into account the following properties of the two types of quartz of which it is composed:

Microcrystalline quartz: Optically, it consists of minute equant grains in random orientation, and under the electron microscope it shows distinct, polyhedral equant grains. Generally there are few cavities. This form usually occurs as a replacement of limestone.

Chalcedonic quartz: Optically, this consists of radiating bundles of fibers. Under the electron microscope, it seems to be massive and homogeneous with no evidence of fibrous nature or of distinct grains. There are alternating zones containing few to many cavities, which give the fracture surface a spongy appearance under the electron microscope. This material usually occurs as a direct precipitate or cavity-filling and much less commonly replaces limestone.

Origin and growth

Using the above facts, the writers have developed the following hypothesis to account for these characteristics as a function of the manner of growth.

The primary factor determining whether microcrystalline or chalcedonic quartz will form is believed to be the spacing of the centers of crystallization. It is suggested that microcrystalline quartz results when crystal growth begins at very numerous, closely spaced centers arranged in a three-dimensional array. The individual microcrystals, in random orientation, grow in all directions until they meet the advancing edges of adjacent microcrystals. If all crystallization centers are evenly spaced, the resulting microcrystals will form equant, polyhedral blocks of sub-uniform size such as those observed with the electron microscope. The surfaces of the blocks are slightly curved because they do not represent crystal faces, but merely the interface between two conformable masses—exactly as the interfaces between separate air cells in a soap froth have curved surfaces, defining equant, polyhedral, rather uniformly-sized blocks. The rate of formation presumably governs the closeness of the spacing, and this in turn determines the grain size of the chert.

Chalcedonic quartz, on the other hand, starts formation from only a few centers of crystallization, and because of the limited interference gives rise to optically continuous fibrous structures. The most favorable condition for the formation of chalcedonic quartz occurs when crystallization begins at a few centers spaced along a *surface*, in which case outward growth is unhampered. More rarely, chalcedonic quartz may also result from a three-dimensional array of centers, providing these are widely spaced.

Inherently, then, it would appear that either microcrystalline or chalcedonic quartz could form by replacement, and either type could form by direct precipitation, inasmuch as the sole controlling factor governing the type of quartz produced is the spacing and distribution of crystallization centers. However, petrographic evidence shows that most microcrystalline quartz forms by replacement. Evidently, when carbonates, either as an ooze or possibly as a consolidated mud, are replaced by chert, the silica begins to form essentially simultaneously at centers spaced closely throughout the rock, resulting in the formation of the polyhedral blocks described. On the other hand, almost all directly precipitated cavity-fillings are composed of chalcedonic rather than microcrystalline quartz. This is to be expected, because crystallization starts at centers spaced along the surface of the cavity. In cases where fossils have been replaced by chalcedonic quartz, replacement starts from a few centers spaced along the shell boundary, the quartz eating its way through the shell. Here again, crystallization starting from a surface favors the production of chalcedonic rather than microcrystalline quartz. These ideas are summarized in the table at the bottom of page 508.

Chemistry of growth

A possible explanation of the two types of fracture surfaces of chert can be derived by applying principles of surface chemistry advanced by Weyl (1948). When a crystal consists of highly polarizable anions of large size, together with small, highly charged cations, then the anions will be pushed to the surface of the crystal and the cations will be recessed. Thus in a microcrystal of quartz oxygen ions predominate at the surface, while the silicon ions are depressed. It is believed that each microcrystal of quartz then has a negatively charged "skin," and effectively repels adjacent randomly oriented microcrystals. When a specimen of chert composed of microcrystalline quartz is broken, fracture probably takes place between the polyhedral blocks because of the surface repulsion forces.

In chalcedonic quartz, on the other hand, it appears likely that large continuously oriented masses are built up by the regular accretion of ions at the edge of the growing lattice. Because of the uniform orientation over large areas, no negatively charged surface of oxygen ions is formed, and the chalcedonic quartz as seen in the electron microscope shows a continuous surface with no evidence of distinct grains or fibers. The bond strength between the subparallel lattices of adjoining fibers is strong enough so that the material does not fracture between the fibers. Of course, the fibrous character observed in the light microscope shows that the quartz lattice is arranged in a radial fashion, but the change in orientation is apparently so gradual that no anion skin results.

Mode of Formation	*Probable Rate of Formation*	*Arrangement of Crystallization Centers*	*Type of Quartz Resulting*	*Volumetric Importance*
Replacement of Carbonates	rapid	3-dimensional, close	fine-grained microcrystalline	Extremely abundant
	slow	3-dimensional, distant	Coarse-grained microcrystalline, transitional to fine-grained chalcedonic	Uncommon
	slow	2-dimensional, distant	fine-grained chalcedonic, somewhat transitional to types above and below.	Uncommon
Direct Precipitation into cavities	slow	2-dimensional, distant	coarser-grained chalcedonic	Fairly abundant
	rapid	2-dimensional, close	microcrystalline	Rare
Recrystallization of gel, or of opal.			Either type, depending on arrangement of crystallization centers.	Uncommon

Water bubbles are much more abundant in chalcedonic quartz, apparently because the latter usually grows by direct precipitation into water-filled cavities, thereby trapping a large amount of the water. This process is presumably facilitated by the hydrophilic character of quartz. Zonal variation in the abundance of bubbles may be caused by changes in the hydrophilic tendency, depending on rate of growth, temperature, or chemical character of the solution. Microcrystalline quartz, on the contrary, traps less water because it commonly forms as a replacement of limestone, which may either be solid (as in the case of limestone pebbles) or unconsolidated lime ooze. The nature of the replacement process, entailing volume-for-volume substitution of the quartz lattice for the calcite lattice, may inhibit the formation of water bubbles for reasons yet unknown.

CONCLUSIONS

1. Chert specimens are composed of two petrographic end-members: microcrystalline quartz and optically fibrous chalcedonic quartz. In the specimens studied there is no evidence for the presence of any opal admixed in chalcedony or chert.
2. Minute cavities present in zones in chalcedonic quartz are recognized by their apparent brownish color in the light microscope, and are easily seen in the electron microscope. It is believed that these cavities are filled with water.
3. Water-filled cavities are the cause of the lower refractive index and density of microcrystalline quartz and chalcedony as compared with normal quartz; and the values of the physical properties change in proportion with the abundance of the cavities. Chalcedony and microcrystalline quartz have the same properties as ordinary quartz when free of bubbles.
4. Electron microscope studies reveal that fracture surfaces of microcrystalline quartz aggregates consist of well-defined, polyhedral blocks, and that surfaces of bubbly chalcedonic quartz have a very spongy appearance. An intermediate type shows poorly defined sub-planar areas.
5. It is suggested that the spacing of the initial centers of crystallization governs whether microcrystalline or chalcedonic quartz will form. Replacement generally favors close spacing, resulting in the formation of microcrystalline quartz. Direct precipitation into cavities favors wide spacing and the formation of bubbly chalcedonic quartz.

ACKNOWLEDGMENTS

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