

Structural hydroxyl in chalcedony (Type B quartz)

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Abstract

Chalcedony including flint, chert and agate is shown by infrared and X-ray study to contain (OH) in structural sites in addition to several types of non-structural water, already recognized, held in association with internal surfaces and pores. The content of structural (OH) varies zonally both in chalcedony fibers and in natural and synthetic crystals of the same spectral type as chalcedony. The (OH)-rich zones are more rapidly etched, have lower X-ray reflection angles, lower indices of refraction, and whiten on heating to 550–600°C.

Chalcedony and its varieties together with colorless quartz crystals and amethyst formed at low temperatures in association with chalcedony, and synthetic quartz crystals, have a distinctive infrared absorption spectrum in the 3200 cm^{-1} to 3600 cm^{-1} region (Type B quartz). A different spectrum in this region is afforded by natural quartz crystals formed at higher temperatures (Type A quartz). The structural (OH) is housed by different mechanisms in these two types of quartz, apparently depending on the structural role and availability of Al.

The generally fibrous nature of low-temperature natural Type B quartz appears to be a character deriving from the content of (OH) and its effect on dislocations.

Introduction

Knowledge of compositional variation in quartz and of the attendant variation in physical properties almost wholly relates to single crystals. It is difficult to investigate these matters in quartz formed at low to ordinary temperatures since it then commonly occurs as microcrystalline fibrous aggregates, comprising chalcedony and its varieties flint, chert, and agate. In such material the general presence of much non-structural water and of finely divided foreign material precludes the precise measurement of the properties of the quartz itself as distinct from characters of the aggregate. The present study was undertaken after recognition that the concentric zonation typical of chalcedony cavity fillings is accompanied by a variation in the X-ray interplanar spacings. This is presumptive evidence of compositional variation in the quartz.

The zonation in chalcedony is accentuated by etching sawn sections in HF or hot alkaline solutions and by water alone at high temperatures and pressures. The thickness of the zones varies randomly from submicron dimensions up to the millimeter range. The zonation sometimes is oscillatory,

consisting of orderly alternations of two or of three sets of zones of constant thickness with each set uniform in properties (Fig. 1). The zones can be described in terms of the relative etching rate of each set, with the notation H (high), L (low), and M (intermediate). This type of oscillatory zonation has been earlier recognized from optical evidence (Fron del, 1978).

X-ray data

Chalcedony, especially flint, gives weak and broad X-ray powder reflections as compared to quartz crystals, due to the small fiber thickness, which ranges below 1000Å, and probably also to strain associated with the strongly dislocated and twisted nature of the fibers. In chalcedony the attainable precision using film in a 114.6 mm powder camera generally is about ± 1 in the fourth significant figure in the measurement of the *a* and *c* cell dimensions. This is not sufficient to recognize the variation in cell dimensions as a function of composition already known in quartz crystals. This variation usually appears in the fifth significant figure or beyond.

In the technique employed here, diffractometer



Fig. 1. SEM photograph of differentially etched oscillatory zoning in chalcedony. The light bands are approximately 1 micron wide.

scans were made manually at $0.01^\circ 2\theta$ intervals over the higher angle reflections using total counts over fixed time. The highest angle reflection in chalcedony that generally is sufficiently sharp and strong to be used is α_1 ($3\bar{1}42$), with $2\theta \text{ CuK}\alpha_1 \sim 90.82^\circ$. Measurements were made on chalcedony samples showing the 1:1 type of oscillatory zoning, on samples of flint, chert, and randomly zoned chalcedony crushed in bulk, and on density fractions obtained from zoned chalcedony.

The X-ray measurements were made on two voltage-controlled Norelco diffractometers using scintillation counters and filtered Cu radiation. The baseline and window settings on the pulse height analyzer were determined by the method of Parrish and Kohler (1956), using a symmetrical diminution of the total beam intensity ranging from 5 to 20 percent with baseline settings usually above background. Pressed mounts of <10 micron powders were employed. Si, and an analyzed quartz crystal

(C105) for which precise measurements of the cell dimensions have been reported by Frondel and Hurlbut (1955), were used as internal standards when relevant. The goniometer scanning direction in all measurements was up angle. Experimentation generally is needed for each sample or reflection to determine the optimum time constant and other instrumental settings. In some samples doublets could be resolved without pulse height analysis but with some loss of definition. Less satisfactory data were afforded by moving chart recording at low scanning speeds.

Flint, chert and zoned chalcedony crushed in bulk gave only single broad reflections. In chalcedony with 1:1 oscillatory zoning, however, both the α_1 and α_2 components of ($3\bar{1}42$) and of lower angle reflections with sufficient dispersion are resolved into double peaks representing the H and L components (Fig. 2). The angular separation between the paired peaks of α_1 ($3\bar{1}42$) varied in different samples up to $0.08^\circ 2\theta$. At $\sim 90.82^\circ 2\theta$ a 0.01° interval corresponds to $\sim 0.0001\text{\AA}$ in $d \alpha_1$ ($3\bar{1}42$). Peak separations of 0.02° or $0.03^\circ 2\theta$ and irregularities found in relatively broad reflections observed in reconnaissance runs with relatively short counting times were checked by reruns with reduced counting errors as estimated from the data of Klug and Alexander (1954). Poorly resolved doublets and

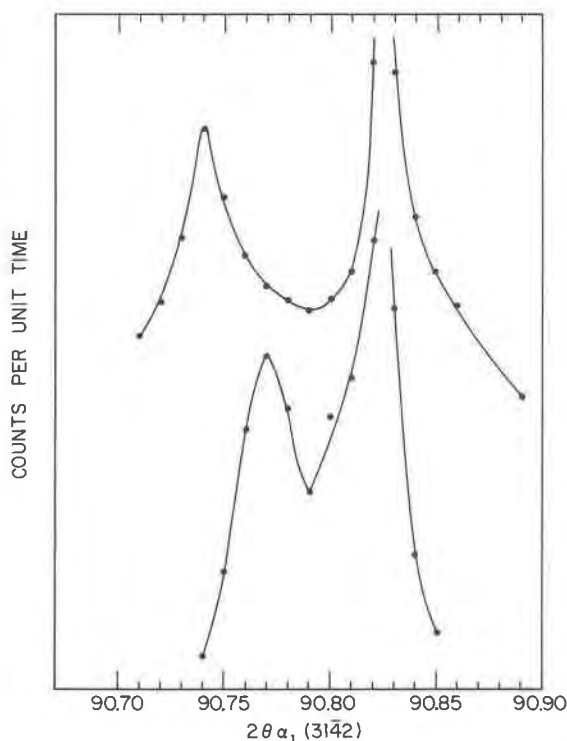


Fig. 2. Paired reflections of α_1 ($3\bar{1}42$) in chalcedony with 1:1 oscillatory zoning.

multiple peaks with separations up to $0.10^\circ 2\theta$ were observed in some samples with non-oscillatory zoning and in some density fractions (Fig. 3).

The quartz with the lower angle of reflection in the paired reflections is found to represent the relatively rapidly etched H zones. Admixture of Si as an internal standard, using $\text{Si}\alpha_1$ (422) at 88.030° and α_1 (333) at 94.952° to measure quartz ($3\bar{1}\bar{4}2$), established that the high angle or L component of the paired reflections has reflection angles close to the average $2\theta\alpha_1$ ($3\bar{1}\bar{4}2$) value of ordinary quartz crystals (90.829° for $\text{CuK}\alpha_1$ radiation as given by Frondel (1962) and 90.823° as found in standard CIO5). Admixture of a few percent of quartz CIO5 as internal standard gave sharp reflections that centered on and enhanced the intensity of the diffuse L reflections. It seems evident that the measurements represent a solid solution series, with the L component at or near a limiting composition and the mechanism of compositional variation therefrom involving a decrease in reflection angle. Infrared spectra obtained from zoned chalcedony and observations on zoning in single crystals of quartz, described in following sections, indicate

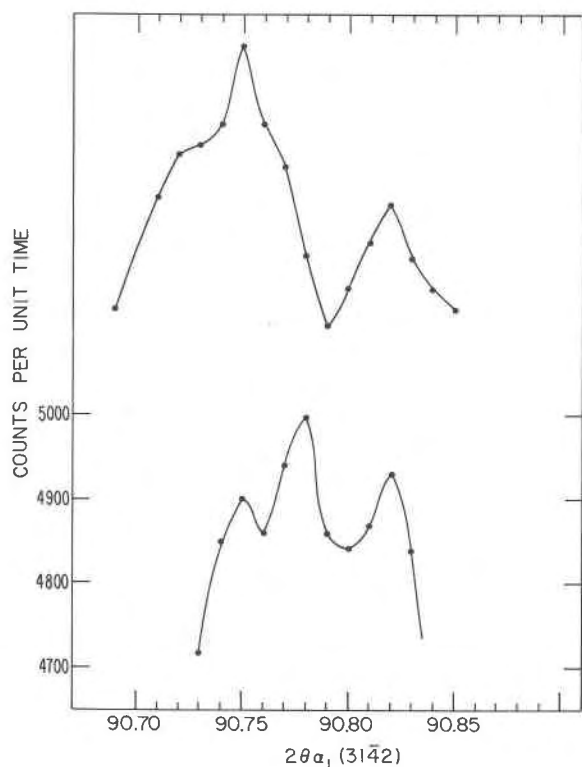


Fig. 3. Multiple peaks in α_1 ($3\bar{1}\bar{4}2$) in a density fraction with $d \sim 2.597$ (above), and in a bulk sample of randomly zoned chalcedony (below).

that the compositional variation in chalcedony is due to (OH) in structural sites.

In chalcedony the precision of measurement of reflections other than ($3\bar{1}\bar{4}2$) does not justify calculation of the cell dimensions and axial ratio to five significant figures. Assuming an arbitrary and unvarying value, 1.10005, for the axial ratio, a decrease of $0.01^\circ 2\theta$ in α_1 ($3\bar{1}\bar{4}2$) increases a by 0.00042 and c by 0.00045\AA . The indicated total variation is large as compared to those found in natural and synthetic quartz crystals (Cohen and Sumner, 1958; Bambauer, 1961; Frank-Kamenetski, 1961, 1962; Frondel, 1962; Tsinober and Kamentsev, 1964).

Infrared spectra and water content

It is difficult to identify and quantitatively measure the various kinds of "water" present in chalcedony. Extending the model of Pelto (1956), three different categories can be recognized:

(1) Molecular water loosely held in pores and cracks and, ideally, released at relatively low temperatures. The water reported lost from powdered chalcedony in the range from 100° to 200°C generally is from 0.1 to 0.4 wt.%. Pelto (1956), however, has shown that molecular water held in tightly sealed pores can be retained as vapor to high temperatures.

(2) Hydrogen-bonded (OH) and (OH) held over a range of bond energies in association with internal surfaces including fiber boundaries, imperfectly crystalline regions adjacent thereto, and dislocations. This (OH) is responsible, together with the molecular water of category 1, in part for the very strong continuous absorption centering at about 3440 cm^{-1} in the infrared spectrum of chalcedony. The earlier infrared studies of chalcedony by Pelto (1956) and Scholze (1960) identified only "water" of these types. Thermal analyses by Reis (1918), Braitsch (1957), Micheelsen (1966) [flint] and the writer (Table 1) establish that the bulk of the total water in the chalcedony, generally in the range from 0.8 to 1.6 wt.% is lost continuously up to about 600°C with very little loss, up to a few tenths of a percent, in the range from 600° to 1000°C . Weight loss at 1000°C , however, is an arbitrary and imprecise measure of the total water in all categories. Barker and Somner (1974) report from analyses made by mass spectrometry that "water" in quartz crystals can be retained up to the melting point.

(3) Hydrogen-bonded (OH) and (OH) held in structural sites in the quartz itself, independently of the non-structural "water" in categories 1 and 2, and yielding characteristic infrared band spectra.

The infrared spectrum of quartz crystals in the (OH) region from 3200 cm^{-1} to 3600 cm^{-1} are of two distinct types. That designated here as Type A includes apparently all natural and smoky crystals from hydrothermal veins, Alpine-type crevices, pegmatites and other deposits formed at relatively elevated temperatures. The (OH) content of such

Table 1. Water loss in chalcedony

	1.	2.	3.
Density	2.615	2.590	2.56
Mean \bar{n}	1.540	1.537	1.533
Loss at 120°C	0.25	0.18	0.27
Loss, 120°-400°	0.38	0.49	1.13
Loss, 400°-600°	0.48	0.49	0.59
Loss, 600°-800°	0.02	0.13	0.09
Loss, 800°-1000°	0.00	0.01	0.00
Total loss	1.13	1.30	2.08

Data obtained on air dried < 40 micron powders by heating to constant weight.

quartz and the crystallochemical mechanisms by which the (OH) is housed have been investigated especially by Bambauer (1961), Bambauer *et al.* (1961, 1962, 1963), Cohen (1960), Kats (1962), and Chakraborty and Lehmann (1976a, b). In Type A quartz Al is a characteristic trace element and stands in an approximately stoichiometric relation to the content of (OH) and alkalis.

Synthetic quartz crystals and both natural and synthetic amethyst have a different spectrum in the 3200 cm^{-1} to 3600 cm^{-1} region, here called Type B. It has been described by Wood (1960), Kats (1962), Kopp and Staats (1970), Tsyganov *et al.* (1975), Chakraborty and Lehmann (1976a, b), Kekulawala *et al.* (1978) and others. In synthetic Type B crystals there is no relation between the amount of (OH) and that of Al and alkalis, as found by Kats (1962), Atkinson (1972), and Chakraborty (1976). The mechanism by which the (OH) is housed is not clearly established.

The Type A spectrum is characterized by strong bands at 3370 cm^{-1} and 3430 cm^{-1} among other features (Fig. 4). The Type B spectrum, as seen in both synthetic and natural crystals, is characterized by a strong band at 3585 cm^{-1} , a weak band at 3614 cm^{-1} , and by relatively strong broad bands, in comparison to Type A quartz, at 3440 cm^{-1} and 3400 cm^{-1} (Fig. 5). The two types also have some absorption bands in common including overtone and combination bands at $\sim 3200 \text{ cm}^{-1}$ and $\sim 3300 \text{ cm}^{-1}$, a faint band at 3595 cm^{-1} , and somewhat variable bands, usually weak or not observed in Type B quartz, at 3565 cm^{-1} and 3370 cm^{-1} . A comparison of the two types of spectra also is given by Kats (1962, Fig. 4.4) and by Chakraborty and

Lehmann (1976b, Table 1). Both types vary somewhat in detail depending on thermal treatment, the content of (OH) and trace elements, and the experimental conditions under which the spectra are obtained.

Infrared spectra were obtained at room temperature, using unpolarized radiation, through 30 polished sections of chalcedony including flint, chert, and agate. Additional measurements were made on sections cut from the colorless and amethystine quartz crystals commonly found lining the central cavity in chalcedony geodes and agates. The turbidity of chalcedony and the strong continuous absorption around 3440 cm^{-1} necessitate the use of sections about 20 to 200 microns thick. This is a disadvantage since the intensity of the band spectra from the quartz itself is thereby much reduced. The data were obtained on a Nicolet FT-IR Model 7199 spectrometer.

The main features of the chalcedony spectrum are a broad and strong continuous absorption centering at about 3440 cm^{-1} , a distinct band at 3585

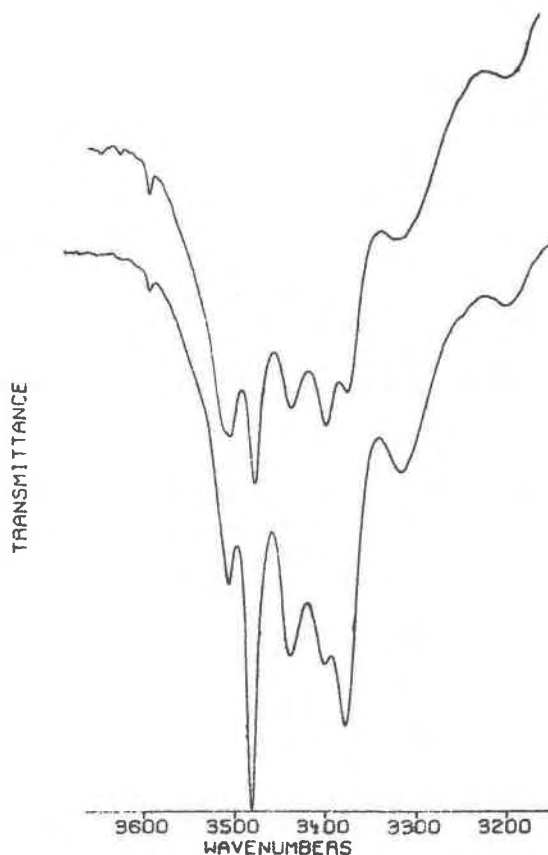


Fig. 4. Type A infrared spectra in the 3200 cm^{-1} to 3600 cm^{-1} region in natural quartz crystals.

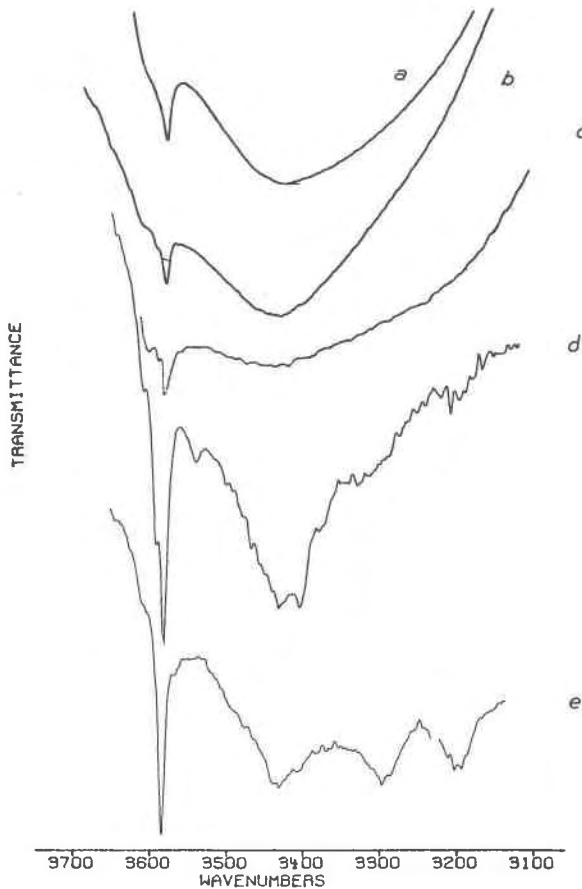


Fig. 5. Type B spectra in the 3200 cm^{-1} to 3600 cm^{-1} region for chalcedony (a and b), natural crystals associated with chalcedony (c and d), and synthetic quartz (e).

cm^{-1} and an inflection or weak band at 3614 cm^{-1} , both diagnostic of Type B quartz, with a faint somewhat variable inflection or band at 3595 cm^{-1} . The associated natural quartz crystals, usually quite small in size and difficult to section, show a sharper and a more detailed Type B spectrum. The absorption around 3440 cm^{-1} is much reduced in intensity relative to the strong 3585 cm^{-1} band, as compared to chalcedony, and usually is resolved, depending on the thickness and quality of the sections, into separate bands at 3440 cm^{-1} and 3400 cm^{-1} . A weak band at 3565 cm^{-1} is sometimes also seen.

In chalcedony the continuous absorption from "water" associated with pores and internal surfaces is superimposed on the structural 3440 cm^{-1} and 3400 cm^{-1} bands. An analogous feature is found in Type A quartz crystals containing clouds of microscopic liquid inclusions, in which a very strong continuous absorption centering at about

3440 cm^{-1} totally obscures the underlying band spectra; a variable band at 2325 cm^{-1} due to liquid CO_2 is often present in addition.

The total absorption around 3440 cm^{-1} varies in different specimens. It is relatively strong in flint and in fine-fibrous chalcedony and may then virtually obscure the 3585 cm^{-1} band. It also differs in adjacent broad zones in a single specimen. The zones in the micron-scale 1:1 oscillatory zonation cannot be separately resolved but the bulk spectrum is identical with that of chalcedony in general.

"Water" content of Type B quartz

In unheated sections of chalcedony and flint the extinction coefficient α_{3440} varied in different specimens from 76 to 150. The corresponding content of H-bonded OH in weight percent is approximately $0.01 \alpha_{3440}$ where α_{3440} = absorbance divided by the sample thickness in cm. (Chakraborty and Lehmann, 1976a; Dodd and Taylor, 1967). The range of values obtained, 0.7 to 1.5 wt.% H-bonded OH, corresponds roughly to the range of "water" lost thermally by chalcedony up to $\sim 600^\circ\text{C}$. It did not prove possible to discriminate between non-structural "water" and any structural H-bonded OH contributing to the absorption around 3440 cm^{-1} . Sections heated for 78 hours at 150° , 200° , 400° and 500°C showed a small decrease in the total absorbance, as found by Micheelsen (1962) in Danish flint, but there was no resolution of the presumed underlying structural bands at 3440 cm^{-1} and 3400 cm^{-1} . The absorbance cannot be followed to higher temperatures since the sections turn white and become virtually opaque at $550\text{--}600^\circ\text{C}$. The whitening is characteristic of Type B synthetic quartz crystals, as described by Cohen and Hodge (1958), Dodd and Fraser (1965) and Bambauer *et al.* (1969), and also was observed here in natural Type B colorless crystals. The thermal whitening is not observed in natural Type A crystals.

In chalcedony an added band at 3744 cm^{-1} becomes perceptible in sections heated at 400°C and increases in intensity at 600° and 800°C . This band is due to isolated SiOH groups on surfaces and is formed by the thermal decomposition of more complex surface (OH) groupings (McDonald, 1956, 1957; Iler, 1979).

The measured values for α_{3440} obtained on random sections of colorless and faintly amethystine crystals of natural Type B quartz ranged from 0.3 to 13.5, corresponding to 0.003 to 0.13 wt.% H-bonded OH. In Type B synthetic crystals the content of H-

bonded OH generally is well over 0.001 wt.%, with high values of 0.05 indicated by the data of Dodd and Fraser (1967), from α_{3500} , and of 0.059 (infrared) or 0.046 (thermal) by Godbeer and Wilkins (1977). Type B crystals in general appear to contain more "water" than natural Type A colorless and smoky crystals. These usually contain less than 0.001 wt.% H₂O, although 0.028 wt.% has been reported in (OH)-rich zones in Type A quartz (Bambauer, 1961; Bambauer *et al.*, 1961, 1962, 1963).

Density and optical properties

The values reported in the literature for the density and the indices of refraction of chalcedony vary downward over a wide range from the nominal values d 2.651 and ω 1.5442 of ordinary quartz crystals. The variation is primarily caused by the chance porosity and water content of the fibrous aggregates, making it difficult to recognize any small systematic variation related to the (OH) content of the quartz itself. The aggregates also are absorbent, especially after heating and readily measurable changes in ω or the mean index of refraction are effected by the absorption of liquids such as water ($n = 1.333$) or alpha-bromonaphthalene ($n = 1.659$). The nature of the medium occupying the available pore space, whether air, or a liquid acquired during sample preparation or measurement, hence affects the measured values of d and ω .

An optical and X-ray study was made of the density fractions obtained from two bulk samples of zoned agates. Sample 1 was composed of slices of 22 different agates from Uruguay, Brazil, Mexico, and California; these were combined, crushed, and ball-milled in water to below 40 microns. Sample 2 was a single colorless zoned agate from Oregon. The two samples were fractionated at intervals of from 0.002 to 0.007 in methylene iodide.

The size fraction below about 5 microns was removed by sedimentation in water. The remaining bulk sample was rapidly blotted dry to a flowing consistency and was stored over water before fractionation. The density change of the temperature controlled liquid over the dilution range, as obtained by pycnometric measurements, was initially calibrated by the use of quartz of precisely known density (ClO5) as internal standard.

A very small final float fraction differing significantly in density from the final chalcedony sink fraction was obtained from Sample 1. It consisted of melanophlogite and two unidentified platy silica minerals, possibly silica hydrates. Cristobalite was not identified in this fraction or in any chalcedony sample examined.

Prior to optical examination the density fractions were extracted in acetone, heated at 110°C, immersed in water, blotted dry, and stored over water. With decreasing fiber thickness and increasing randomness of fiber arrangement, the measurement of ω becomes difficult and ultimately only the mean index of refraction can be measured. Measurements of ϵ are unreliable; the angular divergence of the fibers from parallelism (Braitsch, 1957) and the common occurrence of twisting around the direction of fiber elongation, $[11\bar{2}0]$, contribute to the well known apparent low birefringence of chalcedony as compared to quartz crystals.

The fractionation yielded very small samples at the high and low ends of the range. About 50% of the total sample fell in the range from roughly 2.604 to 2.617 in Sample 1, and from 2.591 to 2.605 in the Oregon sample. Optical examination showed that the fractions, especially in the middle range, contained a large proportion of composite grains made up of two or more intergrown zones with different ω . The difference in ω ranged from a barely perceptible movement of the Becke line up to about 0.001. The H zones have the lower values. The values for ω given in Figure 6 represent the spread found in each fraction for essentially homogeneous grains. The average fiber thickness was noticeably smaller in the lower density fractions.

It is seen that ω increases with increasing density and extrapolates roughly to the value for quartz crystals, 1.544. The total variation in the measured range amounts to about 0.006 in ω and 0.08 in density. Both the total variation and the error of measurement in a single fraction, about 0.002, seem so large as to obscure any systematic variation in ω and density attending compositional variation in the quartz. The data of Heatherington and Jack (1962) on vitreous silica, if valid for crystalline quartz, and calculations based on assumed models for the mechanism of compositional variation, including

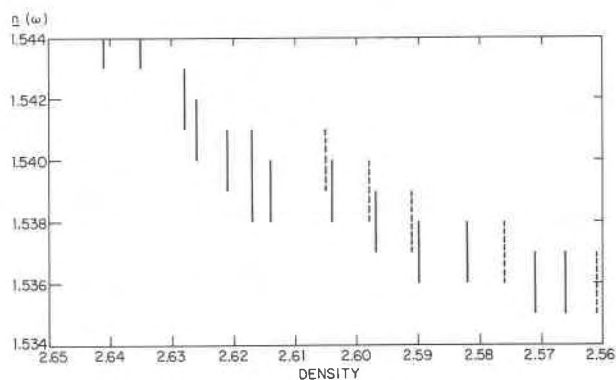


Fig. 6. Variation in ω as a function of density in chalcedony. Solid lines represent Sample 1; dotted lines Sample 2.

the omission of Si with accompanying substitution of $(OH)_4$ for O_4 , indicate that the entrance of 0.5 wt.% structural (OH), which is beyond any (OH) content so far found in quartz crystals, produces changes in the mean index of refraction only in the fifth significant figure.

The X-ray reflection angles of the quartz are independent of the porosity and offer a direct means of measuring the H and L components. The α_1 (3142) reflections of the nine density fractions of sample 1 were recorded against Si by both moving chart and manual scanning methods. The fractions with the highest bulk density and ω , composing about 2% of the total sample, gave relatively sharp single reflections at a high angle, near 90.82° , and evidently consist largely of L components. The middle range inhomogeneous fractions gave relatively broad irregular reflections with a poorly resolved but verified asymmetric doublet appearing in a fraction at d 2.597 (Fig. 3). The two lowest density fractions, composing about 1 percent of the sample, gave extremely broad irregular reflections whose center line could not be precisely located. The evidence suggests that the fractionation has effected a small separation of the H and L components, with the H components having either a lower true density or a higher characteristic porosity.

Correlations with zoned single crystals

The content of (OH), Al and alkalis often varies spatially within single crystals of natural and synthetic quartz, both in the growth loci of the external faces and in thin zones concentric to the growth surfaces. The latter type of compositional zonation, as seen in sawn and etched sections, has been described by Leydolt (1855), Weill (1931), Shin-Piaw (1945), and especially Bambauer *et al.* (1962, 1963). The latter authors also establish a relatively high content of (OH). The zones are differentially etched not only by HF but also by water at high temperatures and pressures (Kennedy, 1950). They also are accentuated by X-ray irradiation (Frondel, 1945; Cohen, 1960; Bambauer *et al.*, 1962, 1963). The rapidly etched zones in two Type A Brazilian crystals examined here had lower indices of refraction, as seen by movement of the Becke line in thin sections, and had lower X-ray reflection angles for α_1 (3142) (Fig. 7).

Type B synthetic crystals containing a series of thin zones parallel to the (0001) growth surfaces have been described by Dodd and Fraser (1967). The zones were shown to have a higher content of

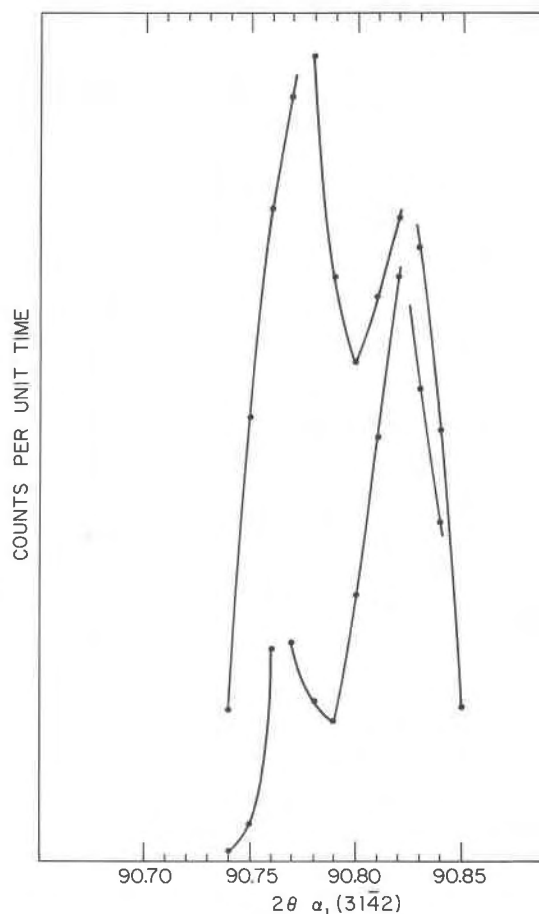


Fig. 7. Paired reflections of α_1 (3142) in zoned Type A quartz crystals with unlike proportions of H and L zones.

(OH) and lower indices of refraction than the bulk of the crystal. The zones turn white or milky when heated to about 550°C or more. The zoning is ascribed to fluctuations in the growth, the (OH) content increasing with increasing rate, as also found by Chakraborty (1976) for unzoned synthetic crystals.

An identical zonation is found in the small colorless Type B quartz crystals that commonly line or fill the central cavity in chalcedony geodes and agates. Photographs of such geodes and agates are given by Lund (1960) and by Murata and Norman (1976). In many instances, such as the chalcedony geodes from Tampa, Florida (Lund, 1960; Zeitner, 1979; Strom *et al.*, 1981) and Keokuk, Iowa (Van Tuyl, 1916), the crystals have formed from circulating ground water at essentially ordinary temperatures. The crystals examined here were identified as Type B by infrared spectra (7 specimens) and, with

less certainty, by turning milky or white when heated at 550°C (15 specimens). The crystals often contain scattered zones up to 30 microns in thickness that run parallel to the rhombohedral faces. The zones have lower indices of refraction, as seen by the Becke line effect under the microscope, are differentially etched, and turn white at 550°C. Zoned samples suitable for X-ray work could not be found. The deposition first of chalcedony fibers and then of single crystals appears to be a continuous process. The presumption is strong that the zoning in the chalcedony is carried on in the crystals by the same process.

Although the evidence is piecemeal, the rapidly etched H zones in Type B quartz crystals and chalcedony appear to have the higher (OH) content, lower X-ray reflection angles, lower indices of refraction and, unlike Type A crystals, whiten at about 550°C or more.

Discussion

In natural environments Type B quartz predominates at low to ordinary temperatures. The controlling factor may be the chemical composition of the crystallizing silica solution with reference to the presence of ions, especially Al, needed to effect Type A valence compensation. Al is strongly hydrolyzed or polymerized into basic polycations over the pH range common to meteoric waters and ocean water, rendering it unavailable for entrance substitutionally or interstitially into the quartz structure. The content of dissolved uncomplexed Al ions in such environments is below 1 ppm (Bell and Hem, 1978; Iler, 1979). Temperature also may be a factor. Dennen *et al.* (1970) report that the solubility of Al in quartz decreases with decreasing temperature, with values as low as ~20 ppm indicated for quartz formed at ~100°C. The actual trace element content of Type B natural quartz is not known. The reported analyses of chalcedony are not trustworthy because of the general presence of finely divided foreign material.

The formation of fibrous quartz (chalcedony) instead of single crystals is influenced by the degree of supersaturation and the rate of growth, with fibrous quartz favored by high supersaturation and high growth rates (White, Brannock, and Murata, 1950; Oehler, 1974). The formation of single crystals following the deposition of chalcedony may then result from the decrease in supersaturation and growth rate attending the final depletion of the silica solution. A crystallographic distinction between

quartz crystals and quartz fibers also is involved in the matter. In quartz crystals the growth rates along the three-fold symmetry-equivalent directions $\langle 11\bar{2}0 \rangle$ are equal; in quartz fibers one direction of this three-fold set is dominant, yielding the fiber elongation along $[11\bar{2}0]$ commonly observed. The (OH) content of the quartz may be the controlling factor here. In synthetic quartz the (OH) content weakens the crystal, by disruption of the Si–O–Si network through the substitution of (OH), promoting plastic deformation (Griggs and Blacic, 1965; Jones, 1975; Blacic, 1975; Kekulawala *et al.*, 1978) and decreasing the mechanical Q (Dodd and Fraser, 1965; Chakraborty and Lehmann, 1976). The introduction of structural imperfections attending the substitution of (OH) in chalcedony similarly may account for the development of the screw dislocations that, in the first place, cause the development of a one-dimensional fiber instead of a three-dimensional crystal in quartz (Frondel, 1978) and in whisker crystals generally.

Temperature seems to be an indirect rather than a direct factor in the formation of Type B quartz fibers since Type B synthetic crystals have been grown up to at least 400°C. The experimental hydrothermal crystallization of silica gels indicates that the upper limit for the formation of quartz fibers is about 250°–300°C (White and Corwin, 1961), with single crystals, of unknown spectral type, formed at higher temperatures. This may reflect the thermal stability of the dislocation system controlling the fiber growth, as is suggested by the very much lower incidence of dislocation-controlled stereospecific twisting in quartz formed at high temperatures (Frondel, 1978).

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