

Systematic compositional zoning in the quartz fibers of agates

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Abstract

Etched sections of agates examined by scanning electron microscopy show three types of compositional zonation: (1) two-unit oscillatory sequences in which the successive zones are of the same width, on a micron scale, but show a uniform difference in the content of (OH) in structural sites; (2) three-unit oscillatory sequences of various palindromic types in which successive zones are of the same width, on a micron scale, but show a uniform difference at three levels of (OH) content; and (3) disordered sequences in which the zone width is variable, on a micron to millimeter scale, and the (OH) content varies in a high-low but non-uniform way. All three types range in length up to thousands of successive zones, and often occur intermixed. These types of zonation constitute the whole of the fibrous parts of agates in general.

The oscillatory zonation is the result of a cyclic interplay between growth rate and diffusion rates at a crystal/solution interface. In agates the process operates at the interface between the quartz fibers growing on the cavity wall and the inner solution and is imposed on all fibers simultaneously. It is identical in crystallochemical mechanism with the coarse random zonation seen in large individual crystals of Type B quartz.

Introduction

The idealized agate represents the infilling of a spheroidal cavity by quartz fibers. The fibers tend to grow radially inward. They can be described as forming a crust on the cavity wall that thickens up to the point of complete filling. A color zonation caused by pigmenting impurities usually is imposed during the course of infilling. Agates are usually described as seen in sawn diametral cross-section. The color zonation then appears as a succession of concentric bands. The width of the bands varies randomly in the millimeter range. The bands usually have been interpreted, incorrectly as will be seen, as marking separate stages or layers of deposition.

When polished agate cross-sections are etched and examined by scanning electron microscopy, the visual banding is resolved into a concentric succession of zones on a micron to submicron scale. Study by infrared, X-ray diffraction, optical and thermal techniques has established that the successive zones involve variation in the content of (OH) in structural sites in the quartz itself (FrondeL, 1982). The systematic nature of the variation is described in this paper.

The compositional zonation is effected at the interface between the inner crystallizing solution and the growing fiber crust on the cavity wall. It is imposed on all fibers simultaneously and can be properly described as a compositional variation along their length. Individual fibers in the converging array may show a succession of hundreds of thousands of such zones or compositional units.

The crystallographic characters of the quartz fibers of agates have been described elsewhere (FrondeL, 1978, 1982).

In brief, the fibers are elongated along $[11\bar{2}0]$, are polar and hence are piezoelectric and show unlike growth rates in opposite senses along $[11\bar{2}0]$, are chiral, and show stereospecific twisting along their length. The fibers range in thickness up to about $0.5 \mu\text{m}$ and in length up to a few centimeters. They are not cylindrical but tend toward a lath-like shape.

The study is based on the examination of several hundred sawn agates, from world wide localities, contained in the Harvard mineral collection or obtained from commercial dealers. Ideal study material is provided by complete diametral thin sections of the nearly colorless long-fiber agates from the Antelope area, Oregon.

Compositional zonation

Three different types of sequencing have been recognized in the compositional zonation that constitutes agates.

1. *Oscillatory two-unit sequences.* These comprise orderly sequences in which successive units of constant length oscillate between two different but uniform levels of (OH) content (Fig. 1). The two units are designated as H (higher content of (OH)) and L (lower content of (OH)). The length of the ... LHLH ... sequences usually ranges from a few hundred to a few thousand units, but examples have been found with up to 15,000 successive units. The length of the individual units is essentially constant in a given agate specimen, with the L units slightly longer in some instances. The length varies in different specimens from sub-micron dimensions up to about three microns. The difference in (OH) content between successive zones also is constant in a given specimen but differs in different specimens.

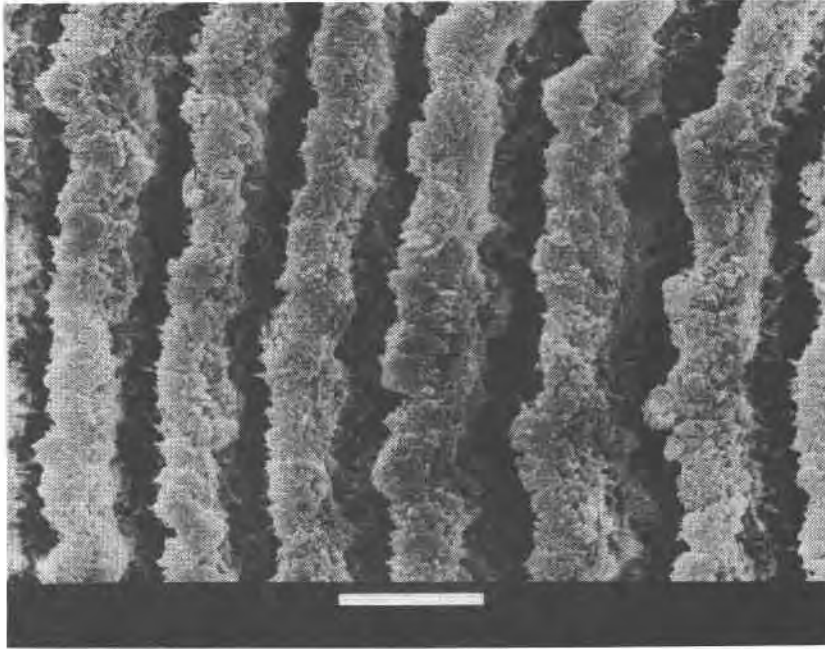


Fig. 1. Relatively coarse two-unit oscillatory sequence. Deeply etched, with the L zones in relief. The platy or lath-like nature of the quartz fibers can be discerned. Bar is 10 microns. This and the accompanying figures are from a single agate from Antelope, Oregon. Harvard specimen no. 124129.

This is shown by the relative depth of etching and, more precisely, by differences in the angular separation of the X-ray reflection angles of the H and L units in different bulk samples of ... LHLH ... sequences. The reflection angles and the etching rate increase with increasing content of (OH), but the relation has not been calibrated.

Two-unit sequences as seen in transmitted light also have been illustrated by Reis (1920), Heinz (1930), and Jones (1952). The extended sequences act as optical diffraction gratings in transmitted light and yield the so-called iris agate described by Brewster (1843), Jones (1952), and by Raman and Jayaraman (1953). Many agates were found here to contain oscillatory zonations of appropriate dimension but that were not sufficiently translucent to display the iris effect. An iris effect also has been observed in garnets containing two-unit oscillatory compositional sequences on a submicron scale (Akizuki et al., 1984).

2. *Oscillatory three-unit sequences.* Numerous types of orderly three-unit oscillatory sequences were observed. The unit length is constant and three different but uniform levels of (OH) content are involved. These are designated as H, L, and M (intermediate content of (OH)). The most common three-unit sequence is ... LHMHLHMH ... Other orderly sequences included ... LHMHLHMH ... and similar sequences with longer L to L separation in the identity period (Fig. 2). Sequences of the type ... LHLHMHLHHL ... also were observed. The identity periods of the orderly sequences, such as LHMHL in the sequence first cited, in all instances are palindromic. (Palindromes read the same forward and back. They may have

either a center or a line of symmetry such as, in their familiar expression as words or sentences, the examples Madam and Hannah.) All observed quartz fiber sequences are centrosymmetrical and hence odd-numbered, without any periodic variation in unit length such as represented by the even-numbered sequence LHMMHL.

Three-unit sequences are less common than two-unit sequences and on average are shorter in length. Different

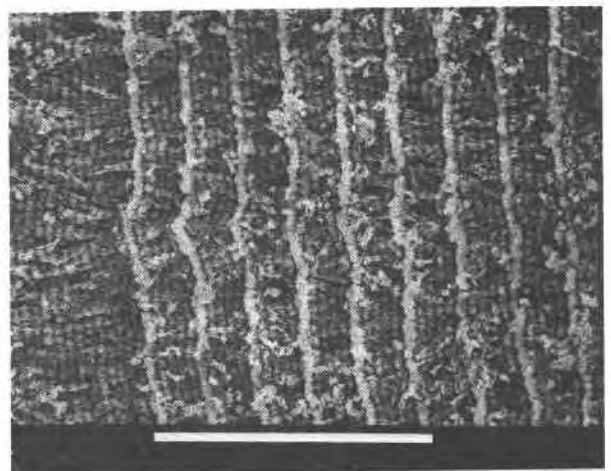


Fig. 2. Three-unit oscillatory sequence, HLMLMLMLH, merging into a two-unit oscillatory sequence on left. Bar is 100 microns.

three-unit sequences often occur intercalated with each other and with two-unit sequences along the fiber length (Figs. 2, 3). Such mixed sequences range up to tens of thousands of units in length and may include or be preceded by disordered sequences, described below. Some mixed sequences are locally centrosymmetrical, as in ... LHMHLHMHLHMHLHMHLHMHL ... Four-unit sequences have not been found.

Another feature of both two-unit and three-unit orderly sequences is the occasional occurrence of gaps in the sequence along the fiber length (Fig. 4). The gaps are composed of H, or of quartz with still more (OH) than the oscillatory H zones, and as far as can be told are multiples of the unit length. They usually are short but range up to about 150 μm in length. X-ray diffraction examination of bulk samples of three-unit sequences does not show three separate peaks for the H, L, and M quartz; usually one peak is distinct and the others blurred. There is also an indication in some three-unit sequences that the correlation between etching rate and (OH) content between H, L, and M is not uniform but varies in a wave-like fashion over the identity period. It is not known how the (OH) content of the M units quantitatively relates to that of H and L.

3. *Disordered sequences.* In addition to orderly oscillatory zoning, agates also show sequences of units that vary randomly in length. The (OH) content in successive units, however, does not vary randomly but is systematic in that it is alternately higher or lower but not, as in orderly sequences, in a uniform way. Disordered zoning is common and may constitute the whole of the agate, although close examination often shows a few intercalated very short two-unit sequences. In some instances the disordered zoning is on two scales, one involving fairly broad zones of H and L quartz and the second representing a less distinct and smaller scale zonation within the H zones that is itself disordered or ordered. These may be the disordered equiv-

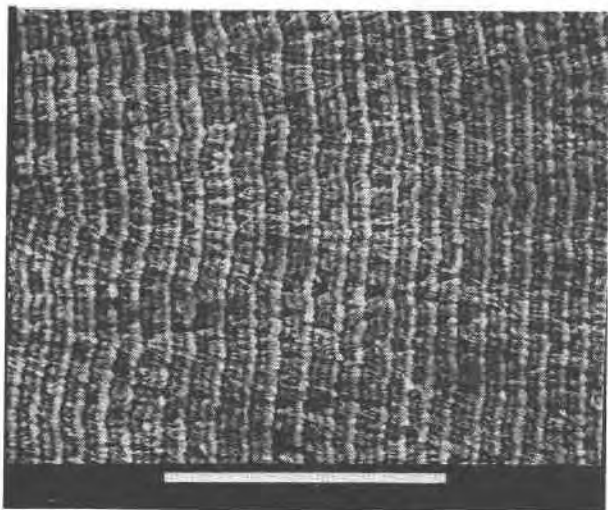


Fig. 3. Intermixed three-unit sequences, HLMLH and HLMLMLH. Bar is 100 microns.

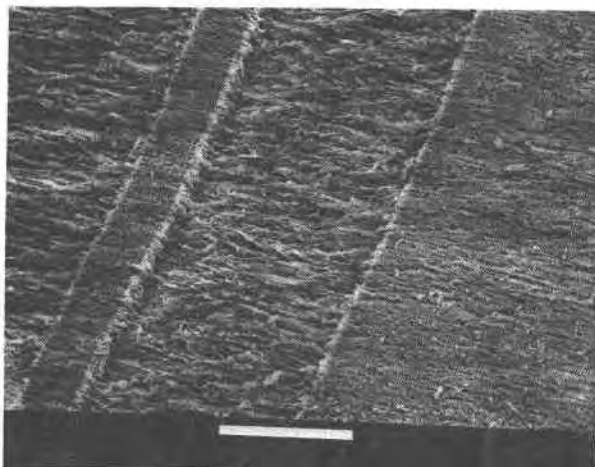


Fig. 4. Gaps in two-unit oscillatory sequence, showing fibers. Bar is 100 microns.

alent of three-unit orderly sequences. Rarely a sequence of three or four units was observed in which the (OH) content appeared to be progressively and non-uniformly higher or lower. The relation is difficult to determine when one or more intervening zones are extremely thin. The disordered sequencing tends to develop in the early stages of cavity filling and the orderly sequencing in the closing stages. The disordering is suggestive of a varying imbalance between two interacting processes. It is not known whether the average amount of (OH) in adjoining units tends to vary along the length of disordered sequences analogous to the Ca/Na ratio in the disordered zonation of plagioclase feldspar.

X-ray diffraction patterns of bulk samples of disordered sequences show extremely broad single reflections at high angles, occasionally with one or a few very weak superimposed peaks. The width of the reflections presumably is caused by a wide and virtually continuous range of (OH) content in the zonation.

In general it appears that all or virtually all of the compositional zoning that constitutes agates is systematic, either orderly or disordered, and is not due to chance. The coarse visual color banding is an independent feature imposed on the compositional zonation by relatively long-term chance variations in the deposition of pigmenting impurities. It does not bear on the origin of agates.

Mechanism of zonation

Oscillatory compositional zonation in plagioclase (Sibley et al., 1976), sphalerite (Oen et al., 1980), and other crystals has been modeled in terms of a cyclic interplay between the rate of crystal growth and rates of diffusion to the crystal/solution interface. If the growth rate is fast relative to the diffusion rates, the supersaturation may become reduced in the layer of solution immediately adjacent to the interface. This slows or stops growth until the super-

saturation is restored by diffusion from the body of the solution. The physical nature of the interface, whether planar, stepped, or irregular is a factor, as is the dissipation of the latent heat of crystallization at the interface.

Modeling of the oscillatory zonation in agates on this basis is complicated by lack of knowledge of the composition of the crystallizing solution and of the mode of formation of agates in general. To a first approximation agates are deposited from a solution of silica in water at a pH upwards of 7. The composition of silica-depositing hot springs associated with igneous action may be relevant; they usually contain up to about 300 ppm SiO_2 with a pH up to about 9 (White et al., 1956, 1963). The monomers for silica in water solution, depending on the pH and temperature, are $\text{Si}(\text{OH})_4$ and polynuclear complexes. At values of the pH over about 9.5, charged silicate monomers also come into consideration (Iler, 1979; Nolan et al., 1981; Crerar et al., 1981).

The zonation in terms of the OH content of the quartz may involve a relatively slow diffusion rate of the bulky silica monomer, as compared to that of $(\text{OH})^-$ ions yielded by the hydrolysis of dissolved strong electrolytes in the solution. A fast-slow cyclic variation in the growth rate of the quartz fibers based on the diffusion of the silica monomer may then be accompanied by a variation in the $\text{Si}(\text{OH})_4/(\text{OH})^-$ ratio in the layer of solution adjacent to the interface. Another factor may be the dehydration of the silica monomer at the interface as it enters the structure of quartz; $\text{Si}(\text{OH})_4$, for example, yields 1.6 volumes of water per unit volume of SiO_2 deposited. The dilution thus effected would influence the supersaturation at the interface.

Models of oscillatory zonation based on growth and diffusion rates lead to two-unit or high-low sequences. The oscillatory three-unit sequences in agates apparently have not been observed in other substances. They present a special problem. A possibility is the generation of pyroelectric potentials on the interface by release of the latent heat of crystallization. If thermal conduction from the interface is slower than diffusion from the solution, the thermal cycling of such potentials may become out of phase with the growth cycling. This could modulate the accession of the $(\text{OH})^-$ ions. In the preferred fiber orientation observed, with +X in piezoelectric notation facing the solution, an increase in the temperature of the interface would create a negative potential thereon and restrain the accession of $(\text{OH})^-$ ions. Static quartz surfaces in contact with water normally are negatively charged (Iler, 1978, 1979; Nolan et al., 1981).

Containment

It is evident that containment of a solution in small volume is needed to give expression to the diffusive and perhaps also electromechanical processes involved in the orderly zonations. Such zonations are not observed in quartz fibers formed in open systems, including sedimentary and diagenetic deposits such as chert and flint, and vein or replacement deposits of chalcedony. More-or-less distinct color banding and a coarse optical zonation

probably of a compositional nature is sometimes seen, however, in chalcedony deposited under localized circumstances such as in small cracks and as a replacement of fossils. Polar preferred orientation to an interface, as in agates, also is lacking in quartz fibers formed in open systems.

Differentially etched compositional zonation also occurs parallel to the growth faces of large single crystals of both natural and synthetic quartz. The literature is summarized by Sosman (1964) and Frondel (1982). The successive zones in Type A natural quartz vary widely in thickness up into the millimeter range, are few in number, and tend to develop during the later stages of growth of the crystal. In one described instance (Shin-Paw, 1945), the differentially etched zones are thin, closely spaced, and seem to approach a disordered sequence. This also is true of some crystals of synthetic Type B quartz (Dodd and Fraser, 1967). The crystallochemical mechanism of the zonation in the quartz fibers of agates also is of Type B. The difference between the zonation in agates and synthetic crystals is only in the nature of the interface, in the former between a solution and a layer of quartz fibers and in the latter between a solution and a single crystal.

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