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MOSAIC STRUCTURE IN QUARTZ*

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ABSTRACT

Natural quartz crystals have a pronounced mosaic structure. The smallest mosaic units are tiny rods approximately 0.0009 mm. in diameter by 0.009 to 0.05 mm. long. The rods are laid side by side to form sheets. Several sheets produce the "shingle" appearance seen when the quartz is etched with distilled water under elevated temperatures (up to 360° C.) and pressures (up to 300 bars).

The anomalous solubility of quartz surfaces produced by grinding is attributed to a mechanical loosening of the rods and sheets to produce a relatively large surface easily attacked by solvents. The existence of an amorphous layer to account for the anomalous solubility is questioned.

The nature of the forces or cementing holding the rods together is of considerable geological interest.

INTRODUCTION

A mosaic crystal is simply a large one made up of many discrete smaller crystals. A brick wall might be an example of a mosaic crystal in which the individual bricks would be the crystallites. This is a good example because many natural crystals are much like brick walls. The individual bricks may all be more or less perfectly aligned. However, slight departures from perfect alignment are quite common, especially where the bricks can be physically disturbed.

Grinding the surface of crystals disturbs the alignment of the building bricks or crystallites. The manner in which the intensity of x-ray reflections are increased by grinding and subsequently decreased by further polishing or etching furnishes a method of classifying crystals according to the degree to which the crystallites or mosaic units are perfectly aligned (Sakisaka, 1930). Measurements of this kind also enable one to calculate the approximate size of the individual blocks and their angular departure from perfect alignment (Armstrong, 1946).

The sizes of the mosaic blocks have been calculated by several methods. The blocks are said by many authors to be about 10^{-4} cm. on an edge for

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many metals and salts. Work designed to yield information on residual stresses in metals has usually been based on a crystal model consisting of a mosaic of small regions within which the lattice is essentially perfect. The size of these blocks exceeds 10^{-5} cm. (1000 Å) on an edge. The literature on this topic is reviewed by Barrett (1943, pp. 219–223). If the mosaic units are no smaller than this, it should be possible to see them directly under an ordinary microscope.

Resolution of a Microscope

The smallest distance d two spots must be separated to be recognized as two distinct spots is expressed by

$$d = \frac{1.22\lambda}{2\mu \sin \alpha}$$

where λ is the wave length of light used, μ is the index of refraction of the media (usually air) between the objects being observed and the objective of the microscope, and α is half the angular distance between the spots and the edge of the objective lens. If an oil immersion lens is used, μ is commonly taken as 1.52. The maximum value for α is 67°. Since sin

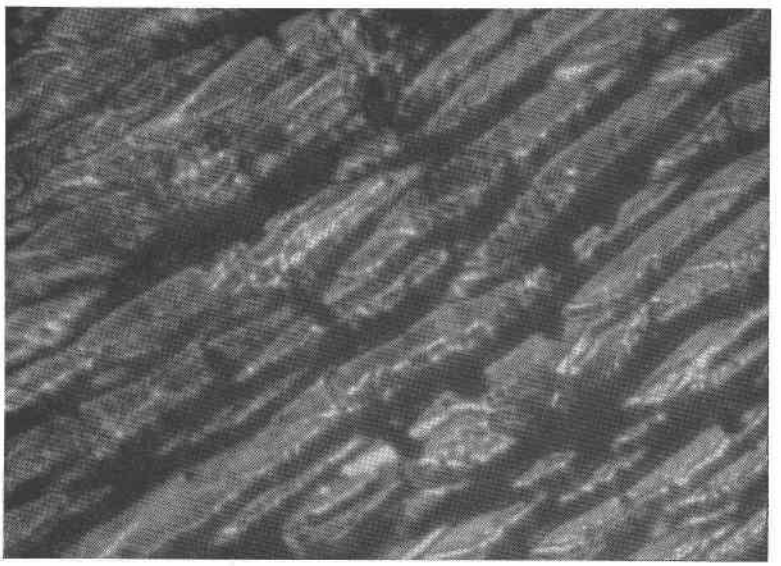

Fig. 1. Mag. 100×. Ordinary photomicrograph of the surface of a water-etched quartz crystal. Highly inclined transmitted illumination was used. The surface has the general appearance of a stack of shingles. By adjusting the illumination so that light enters the "rear" part of the shingles, the size of the individual layers can be clearly seen. The most interesting detail is that the layers seem to be made up of individual rods. The shingles are made up of layers and each layer consists of a series of rods laid side by side.

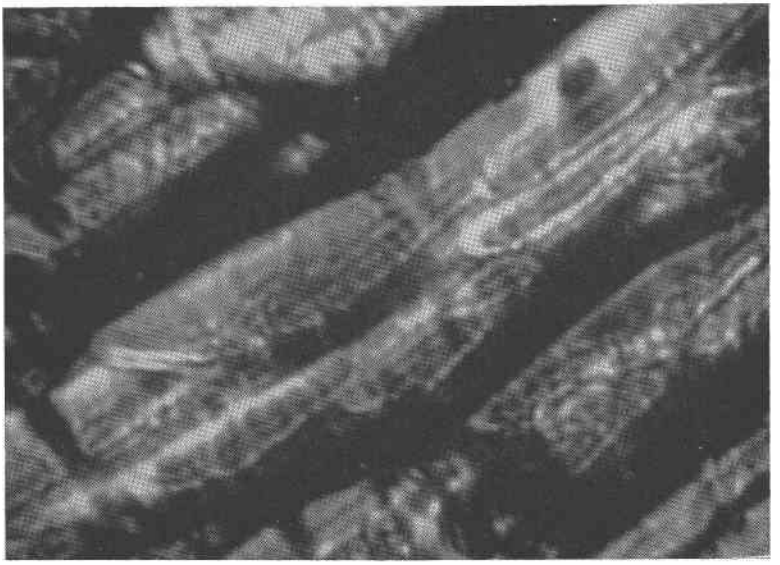

FIG. 2. An enlargement (200×) of the same area shown in Fig. 1. Here the regularity of the layers and the individual rods can be clearly seen. An isolated rod in a layer can be seen in the upper left part of the photomicrograph.

67° equals 0.92, substitution of these figures in the above formula shows that it should be possible to resolve detail separated by as little as $\lambda/2$. Inasmuch as the arbitrary figure of 1.22 is considerably too high and that a higher index oil may be used, it is theoretically possibly to resolve objects separated by as little as 0.3 (Meyer, 1933 p. 208). With the use of highly inclined illumination (Frederickson, 1953) twice this resolution should be possible. If light of $\lambda = 5 \times 10^{-5}$ cm. is used, the predicted mosaic blocks should be clearly visible.

The study of the size and regularity of etch pits and Widmanstätten figures indicates that mosaic blocks of this size exist. Work of this kind however, has been severely criticized by Buerger (1934) and others who believe that the apparent regularity in both etch pits and Widmanstätten figures is illusory. Although etch-pit and Widmanstätten-figure evidence may not be conclusive, modified etching techniques applied to quartz reveals a highly regular mosaic structure (Fig. 1) made up of units of approximately the same size as predicted by earlier workers.

MOSAIC STRUCTURES OBSERVED IN QUARTZ

Small quartz crystals, $\frac{1}{2}$ to 1 inch in length, were etched by suspending them in a bomb partially filled with distilled water. The system was heated to 300° C. for various lengths of time ranging up to 48 hours. The pressure in the bomb was 300 bars.

Prism faces consist of a series of overlapping plates giving the crystal a shingle-like appearance. By arranging the light so that it appears to enter the ends of the plates, individual layers within the shingles can be clearly seen (Figs. 1 and 2). Each little plate lights up much like a plastic rod held on the end of a flashlight. The thickness of these layers can be measured directly: each layer is approximately 0.0009 mm. thick.

Some layers are better illuminated and appear much brighter than others. Slight movement of the stage on which the crystal is mounted causes different layers to be more intensely illuminated. This indicates that all of the layers are not in perfect alignment. Armstrong (1946) has studied the disorientation of mosaic blocks in quartz by x-ray rocking-crystal techniques. She showed that large "blocks" may be disoriented as much as 4°. "Blocks" disoriented by more than three degrees were thought to be broken loose from the parent crystal. She estimated that

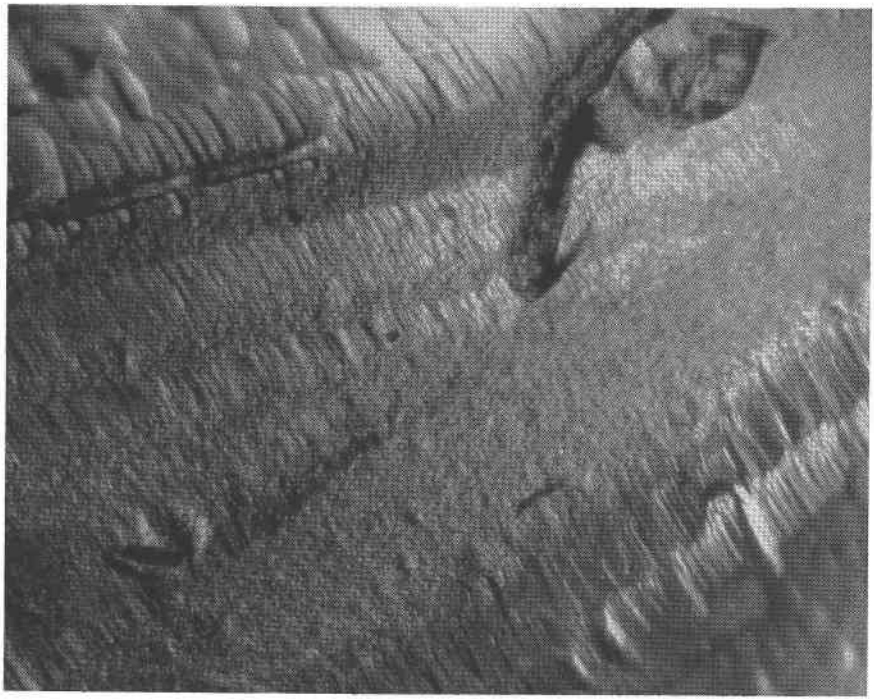

FIG. 3. Mag. 21×. This is the beveled intersection of two prism faces of a quartz crystal naturally etched during weathering. Here we see the individual rods stacked up like piles of cord wood. The length to width ratio of individual rods varies within wide limits; the width of the rods is highly uniform. The rods are not all straight. Maybe the reason why a crystal grows faster in one direction than another is related to whether the material must be added onto the end of a rod or if more rods must be formed and stacked onto the parent crystal.

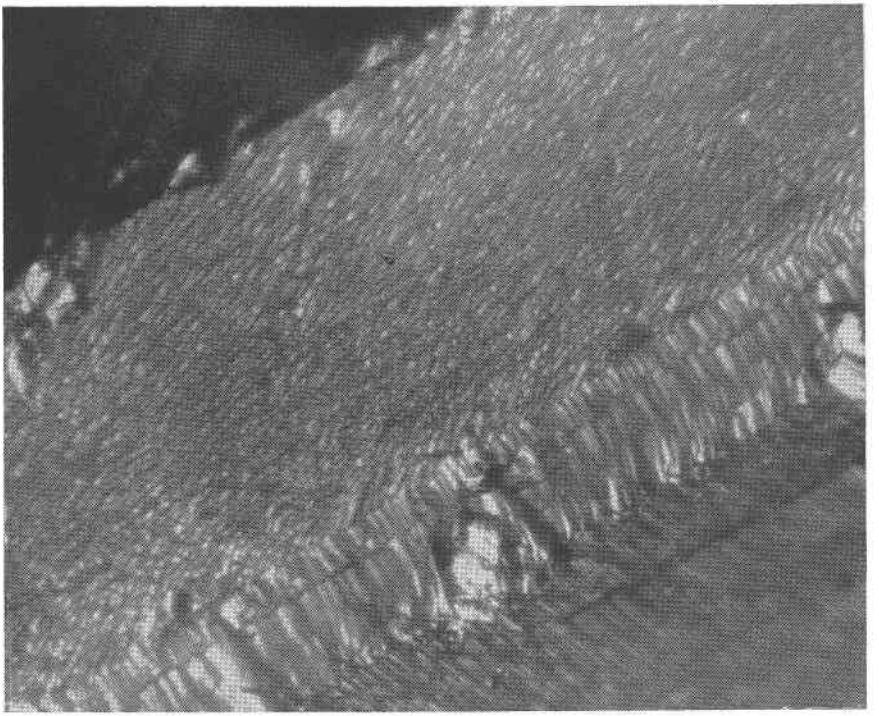

FIG. 4. Mag. 30×. Here we see a small *s*-face on a water-etched quartz crystal. The edges of the shingles appear as tiny rods on the *r*-face in the foreground. The shingles are quite irregular and apparently quite brittle. The very ragged appearance of the beveled edge between the *r* and *s* faces must have been due to its rapid solution in the hydrothermal solution of the bomb. The shingles upended into the *r*-face are almost of the same length. They seem to be separated from the crystal by an irregular crack. At present, no satisfactory answer can be given concerning the parallelism of the irregular line with the intersection of the two faces.

for 3° of disorientation, the "blocks" would have to possess a length to width ratio of 26:1 to keep from breaking. She concluded that there was no experimental evidence for the existence of such rods.

Careful observation of the individual layers in Fig. 2 reveals that they consist of a series of bright spots which are very close together. These spots look like the ends of tiny rods. Figure 3 shows that the basic units making up the individual layers actually are tiny rods.[1] The diameter of a rod in a "shingle" is approximately 0.0009 mm. whereas the length ranges from 0.005 up to 0.09 mm. The length to width ratio is as high as

[1] The diameter of the rods shown in Fig. 3 is about 10 times as large as those in the shingles. This is the only exception to the 0.0009 mm. diameter figure we have observed. At present no satisfactory explanation can be offered as to why these are so much larger than all of the others studied.

100:1 for some of the rods although most of them have a ratio closer to 40 or 50:1. Armstrong's conclusion that "blocks" misoriented by more than 3° must be broken from the bulk crystal is therefore not correct. The crystals were buffed on rough canvas cloth and rephotographed. The same area can be found by use of an odd-shaped ridge or channel as a guide. Careful comparison of the two photomicrographs did not indicate any differences. Even tiny, thin, quartz platelets (Fig. 4) were not removed by this treatment; hence, it appears that both the thin plates and the narrow rods are quite firmly fixed onto the parent crystal.

Crystallinity of Crystal Faces and Interfaces

A large literature exists which deals with the physical nature of polished surfaces and interfaces of many types of crystals. The classic Beilby layer (1921) is supposed to be an amorphous layer occurring on surfaces and interfaces. It is usually reserved for metallic systems but is also thought to exist on quartz (Demster and Ritchie, 1952). The basic experimental fact supporting the idea that an amorphous layer develops from grinding or otherwise "working" the surface is that the thin surface "layer" is often much more soluble in various solvents than the bulk of the crystal.

Metals are not reduced to the amorphous state by cold work (Barrett, 1942, p. 229). Only under severe shearing strains and high compressive stress can crystalline fragments be reduced to the state where they give typical amorphous *x*-ray patterns (Bridgman, 1937, p. 328). If metals cannot be reduced to an amorphous state by ordinary cold working, it is almost certain that much less ductile materials like silicates cannot develop amorphous layers when ground.

Electron diffraction photographs (Armstrong, 1946, p. 153) of freshly ground quartz surfaces show a series of rings analogous to those produced by powders. Even though of small particle size, this material must be well crystallized to give such a pattern. After the crystal surface was scrubbed with water and a toothbrush, the rings are replaced by Laue spots. Apparently the first, very loose material resulting from grinding can be easily removed leaving a surface which produces a single-crystal pattern. These experiments clearly contradict the opinion of Dempster and Ritchie (1952):

"The evidence suggests that there exists on powdered quartz particles a vitreous skin, produced by surface-flow during grinding, and blending via a transitional layer into the truly crystalline core."

Grinding apparently fractures the crystal surface and loosens the piles of rods (Figs. 3 and 5) which, because of their greater surface area, are much more soluble in acids or other solvents than the undisturbed por-

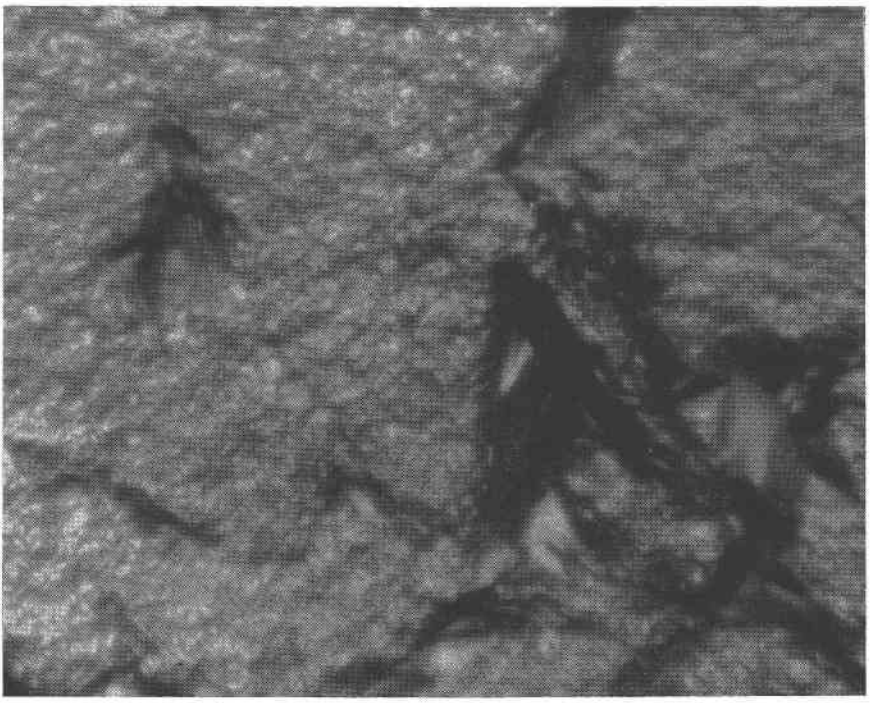

FIG. 5. Mag. 98×. A quartz wafer suitable for piezoelectric purposes was etched in the bomb. The wafer was first acid etched (in HF) and then placed in the bomb to reveal surface detail. The hydrofluoric acid etched deep pits and left irregular ridges that made focussing difficult. The wafer was then polished and again put in the bomb. The surface produced is shown here. The deep pits are remnants of the acid etch. The rest of the surface consists of a mass of rod-shaped aggregates. Some of the shingles can be seen on the sides of the acid etch pits.

tions of the crystal. In unground crystals, the quartz along the "pore-spaces" between the rods and the plates is first removed to produce the relief features shown in the photomicrographs. This material is removed first for the simple reason that it forms the external surface of the crystallites which the etchant first encounters.

Unetched surfaces look as if tiny chips had been gouged from them by a curved chisel (Fig. 6). Although these concave hollows vary considerably in size, they are of the same order of magnitude as the length of the rods. These surfaces are relatively smooth. Some sort of cementing material must bind the rods together and fill up the irregularities between them. Because the rods are not perfectly aligned, the cementing material must have a lower degree of order and consequently slightly different properties from the rods; the solubility of the cement, for example, should

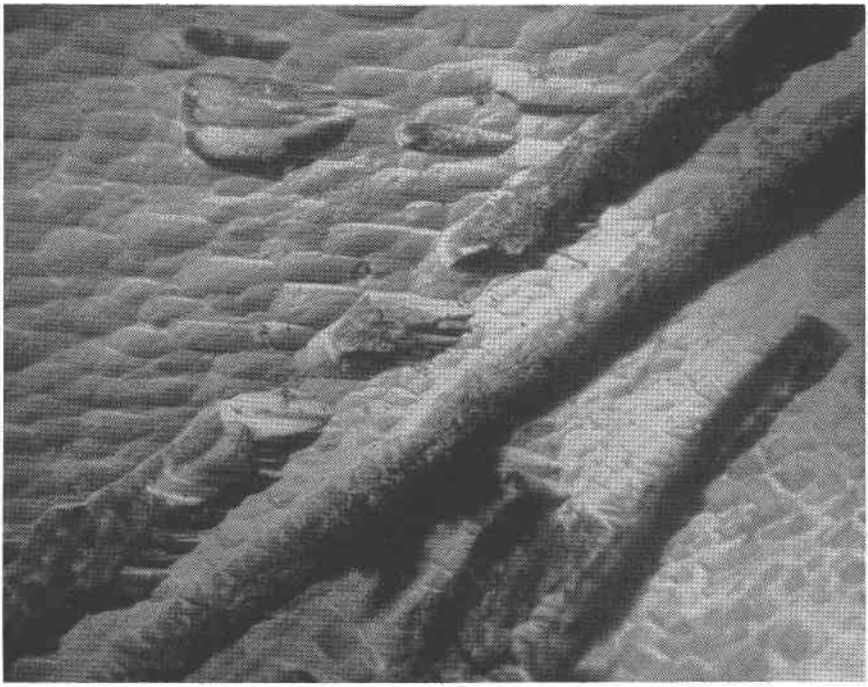

FIG. 6. Mag. 22×. This crystal was water-etched in a bomb for a short period of time. The dark rectangular-shaped zones actually are etch pits or channels. Notice the septa across the large channel. These channels are thought to be molecular sieve zones from which much of the silica was removed from around some of the rods by natural solutions before it was placed in the bomb. Channels of this kind are common in many metamorphic rocks, but this is the first time it has been seen on a single crystal.

Irrespective of interpretation as to their origin, the quartz that was differentially etched from the channels must have had a greater apparent "solubility" than the bulk of the crystal.

Unetched faces of quartz look as if a chisel had grooved small flakes from the quartz surface as shown here. The long dimension of these grooves is about the same as the length of the rods shown in Fig. 3. These surfaces look as if they were formed by piling up a stack of rods and cementing them together much like concrete is poured into a suitable mold containing a bundle of reinforcing rods.

be different than that of the rods. Are these the "pore spaces" through or along which hydrothermal solutions, ions or ichors migrate?

ACKNOWLEDGMENTS

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