radioactive material in this study indicates that it originated in the stratosphere. This study indicates that long-lived fission-product activity in air at ground level is for the most part associated with airborne material having the same diameter as particles prevalent in the surrounding air. Studies of stratospheric activity show such activity to be associated with particles of smaller size (*9*). Furthermore, the long-lived nuclides present that emit gamma-radioactivity show the same particle size distribution, indicating that the dynamics of transfer of activity from the stratosphere act similarly on these six radionuclides.

There were no correlations between surface area, weight, and relative number of particles and the activity collected on a filter. This could be because the particles containing radioactivity amount to a small percentage of the total number of particles present. Particle size separations were not sufficiently distinct to determine accurately deposition in the pulmonary spaces. However, if particle densities from 1.0 to 2.0 are assumed, pulmonary deposition would vary from 25 to 60 percent for the majority of radioactive particles in this study (*10*).

BERNARD SHLEIEN
THOMAS P. GLAVIN
ALBERT G. FRIEND

Northeastern Radiological Health Laboratory, U.S. Public Health Service, Winchester, Massachusetts

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30 October 1964

Quartz: Anomalous Weakness of Synthetic Crystals

Abstract. *The strength of a synthetic quartz crystal drops rapidly at 400°C, and at 600°C is a hundredfold lower than at 300°C. Large plastic deformations can be produced without fracture. The predominant mechanism of deformation is translation gliding. The preferred explanation for this anomalous weakness is that this synthetic quartz contains water which has hydrolyzed the silicon-oxygen bonds. The silanol groups so formed are presumed to be rendered sufficiently mobile by elevating the temperature to 400°C so that they align themselves in dislocation lines and move through the crystal with the dislocation under the small applied shear stress.*

Under appropriate circumstances synthetic quartz crystals can be molded like putty. If silicates in general can be molded in similar fashion, it might be possible to form brittle silicate materials at considerably lower temperatures than those now used in glass technology.

Natural quartz is one of the strongest of common substances, rivaling tool steel in its compressive strength of 20 kilobars (*1*). Its strength is increased under confining pressure so much that at one time Bridgman seriously considered using quartz single crystals for the second-stage pistons of his high-pressure apparatus (*2*). Despite many attempts, quartz is the only material which has not been rendered ductile by high confining pressure at room temperature (*2, 3*). Quartz crystals retain high hardness and high strength to temperatures of 800° to 1000°C at low confining pressure (*4*).

At elevated temperatures and moderate confining pressures, quartz single crystals and aggregates have been plastically deformed, and the mechanisms of deformation have been determined (*5*). The strength of quartz has been measured in the ductile regime as a function of temperature and strain rate, at a confining pressure of 15 kb (*6*), and the natural quartz crystals become very weak when in the presence of water at temperatures of 800°C and above. Microscopic analysis of thin sections suggests that this weakness is caused by the diffusion of water throughout the crystal, hydrolyzing the silicon-oxygen bonds. In an anhydrous environment, natural quartz crystals have high strength at least up to 1000°C, the limit of our tests.

We have now studied in an anhydrous environment a large optically clear synthetic quartz crystal donated by the Bell Telephone Laboratories. At low temperatures, specimens cut from this quartz crystal have strengths similar to those of natural crystals. However, as the temperature is increased, the strength is drastically reduced.

The transition from high strength to great weakness in this synthetic quartz is accompanied by changes in the mechanisms of deformation which are readily apparent when thin sections of specimens are viewed in polarized light. A series of experiments at a constant confining pressure of 15 kb and strain rate of 8×10^{-6} sec^{-1} will be used to illustrate this transition with increasing temperature. At the lowest temperature of the series, 200°C, the specimen broke at an indicated longitudinal differential stress ($\sigma_1 - \sigma_3$) of 45 kb. The thin section exhibited primarily fracture (which occurred along basal planes) along with a few basal deformation lamellae. At 300°C considerable plastic flow occurred prior to fracture, and Fig. 1*A* shows this specimen, which has been shortened 6 percent by flow at a compressive stress of 42 kb before breaking at one end. The plastic deformation occurred primarily by basal slip concentrated in narrow kink bands subparallel to the quartz *c* axis. This behavior at 200° and 300°C is typical of that observed in natural quartz crystals at those temperatures. At 400°C, however, the strength was only 1 kb and the mechanism of deformation changed from basal to predominant prismatic slip (Fig. 1*B*). In natural crystals a change from basal to prismatic slip has also been observed, but at 700°C rather

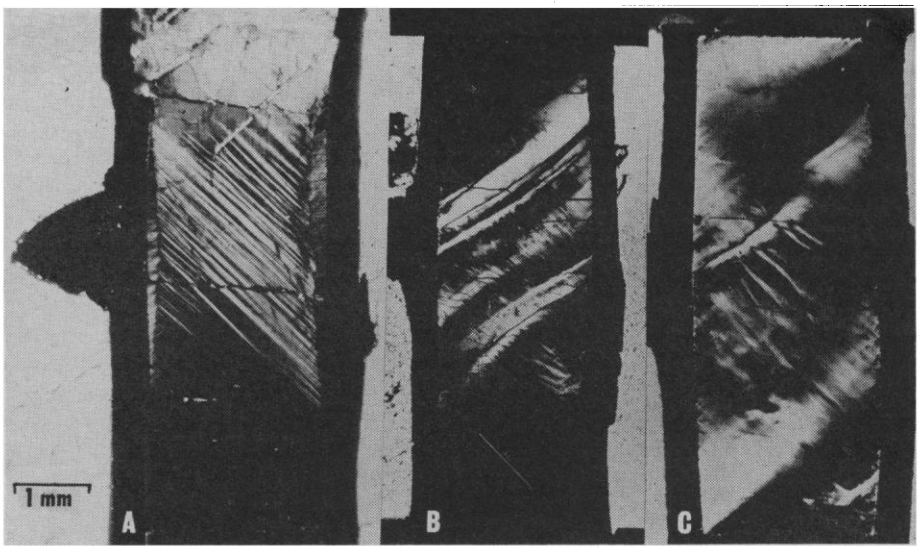

Fig. 1. Thin sections of cylindrical specimens (2.3 mm in diameter) cored from a synthetic quartz single crystal deformed in compression at a strain of 8 × 10^{-6} sec^{-1} at a confining pressure of 15 kb. All specimens were cut so that *c* and *a* axes are 45 degrees to the axis of the cylinder (direction of compression) and lie in the plane of the thin section with the *c*-axis trending NW. *A*, 300°C, 6.2 percent shortening. There are faint NE trending basal lamellae which produce NW kink bands. Strength, 42 kb. *B*, 400°C, 9.6 percent shortening. Whole central region is a broad NE trending kink band formed by slip on NW trending prismatic lamellae. Strength, 1 kb. *C*, 600°C, 6.5 percent shortening. No strong lamellae or kink bands. Very fine lamellae throughout of near basal and near prismatic orientation. Strength, 0.4 kb.

than 400°C. The compressive strength at 700°C in the natural crystals is 32 kb under these conditions.

At 600°C the synthetic crystals have very low strength and the character of deformation has further changed (Fig. 1*C*). The deformed crystal resembles natural crystals that have developed weakness when exposed to water at 800° to 1000°C. There is a characteristic blue-brown color change about the extinction position which has been observed previously in water-weakened specimens. Lamellae are still present, but are different in character from those seen in specimens deformed at lower temperatures. They are more pervasive, more closely spaced, and very much weaker in optical contrast, and, as a result, they are recognized only with difficulty in phase contrast illumination.

Faster strain rates appear to increase the weakening temperature. At the aforementioned strain rate (8 × 10^{-6} sec^{-1}) the synthetic quartz had no measurable strength at 600°C at a confining pressure of 2.5 kb, and a very low strength (perhaps 2 kb) at 500°C and 0.5 kb confining pressure—the lowest we can obtain in our present apparatus. Thus apparently no confining pressure is necessary to produce weakness in the synthetic quartz.

To determine whether the temperature weakening is reversible, a specimen was subjected to a confining pressure of 15 kb, heated to 600°C for 1 hour at hydrostatic pressure, then cooled to 200°C, and subjected to compressive strain in the normal manner. The stress rose elastically to 45 kb, indicating that the weakening is reversible. At this time the motor driving the deforming piston was turned off. The temperature was then raised in increments of 50° to 500°C. Figure 2 shows the progressive stress relaxation (weakening) as the temperature was increased. The thin section of this specimen shows an unusual pattern (Fig. 3). The fine bands have the appearance of recrystallized lamellae which have been observed in cold-worked natural quartz annealed at high temperatures (*5*, *7*). Temperatures of 900°C or more are required to produce this effect in natural quartz crystals.

The many analogies with the water-weakening of natural quartz suggested that the synthetic quartz might have an abnormal water content. This was tested by infrared absorption measurements, and Fig. 4 shows that the synthetic crystal has a broad absorption band in the region of 3 μ which is absent in untreated natural quartz. This absorption is characteristic of strongly bonded OH in crystals measured at room temperature. Integration of the area between the curves yields, by the method of Bambauer (*8*), a concentration of 1 atom of H for every 130 atoms of Si, or about 0.1 percent of water equivalent by weight. This concentration of OH is an order of magnitude larger than the maximum reported for natural quartz. It is of the same order as the

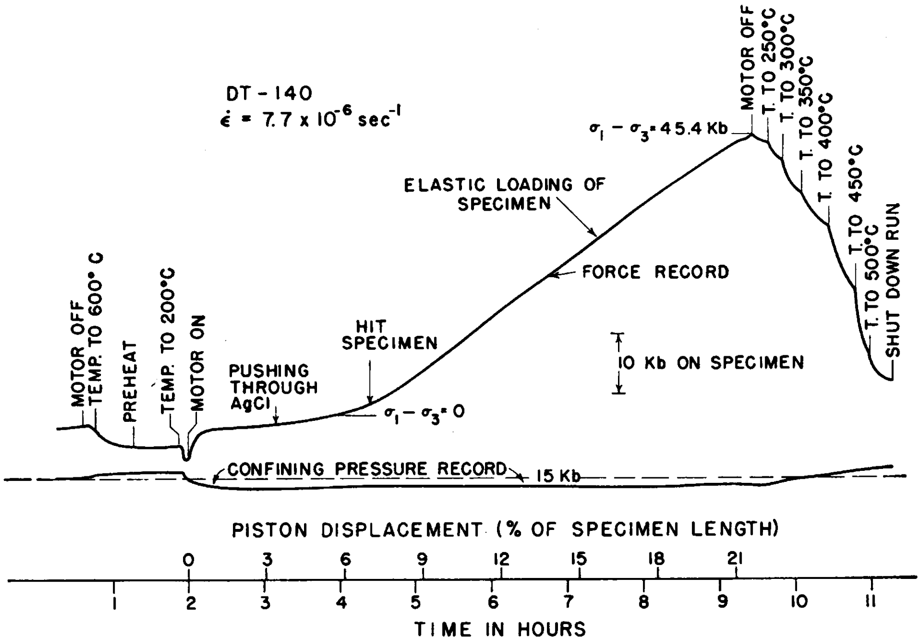

Fig. 2. Tracing of force record of DT-140. Time increases to the right. From left to right: initial heating at 600°C; cooling to 200°C; motor is turned on; force increases slowly while piston is being pushed through AgCl; the piston hits the specimen and the force increases linearly with time during the elastic loading of specimen; the motor is turned off; there is then successive relaxation at 200°, 250°, 300°, 350°, 400°, 450°, and 500°C. The piston displacement during "elastic loading" of the specimen includes apparatus distortion. The elastic strain computed from acoustically determined elastic constants is 4.5 percent at 45 kb.

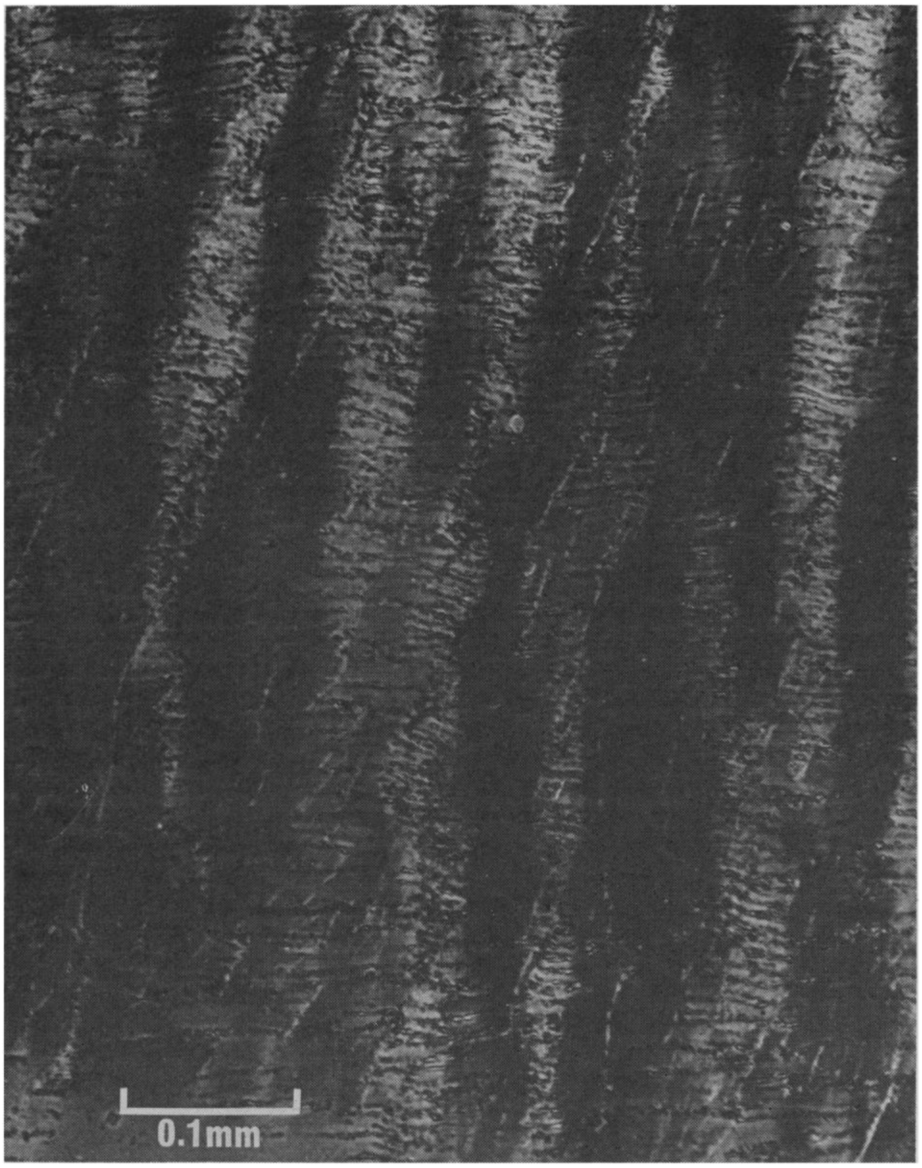

Fig. 3 (top left). Sepcimen DT-140 photographed in phase contrast illumination between crossed nicols. N-S bands are remnant kink bands subparallel to the *c*-axis. E-W worm-like features are recrystallized basal lamellae. The less prominent NNE trending features are recrystallized lamellae whose traces on the section are inclined 5° to 25° to the *c*-axis. At low temperature, specimen formed prismatic kink bands by basal slip. As the temperature was raised, stress relaxation was accompanied by recrystallization.

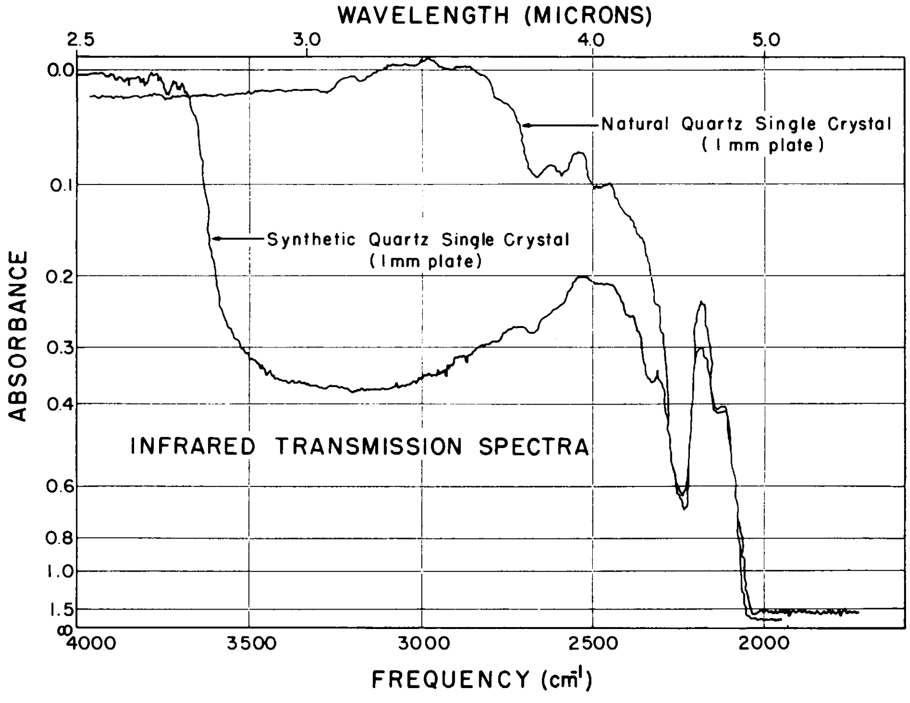

Fig. 4 (bottom left). Infrared absorption of natural quartz and synthetic quartz crystals, both 1 mm thick. (Courtesy M. Haugh.) Note essential absence of OH absorption in this natural quartz and large absorption in synthetic crystal, corresponding to 0.1 percent water equivalent (by weight).

water available in our earlier experiments with natural crystals.

Nuclear magnetic resonance analysis gave no measurable proton signal; this suggests that the OH is tightly bound and occurs at a variety of sites within the crystal. An x-ray analysis of this crystal by J. Starkey gave the same lattice constants as those published for quartz, ±0.001 Å (*9*).

We believe that the water may hydrolyze the Si — O — Si bridges to give two silanol groups, as suggested by Brunner *et al.* (*10*) as follows:

$$\mathrm{Si-O-Si} \qquad \begin{matrix} & \mathrm{HO} & \\ \mathrm{Si} & \vdots & \mathrm{Si} \\ & \mathrm{OH} & \end{matrix}$$

Two adjacent silanol groups would be bound to each other by only the relatively weak hydrogen bonding. Since fewer than 1 percent of the silicon-oxygen bonds would be so weakened, this would not be expected to cause appreciable weakening of the crystal unless these hydrolyzed bridges could catalyze fracture, recrystallization, or plastic deformation.

Fracture seems to have played no part in the deformation. The fractures observed (Fig. 1*B*, 1*C*) are of the type formed on release of confining pressure. Evidences of recrystallization are noted (Fig. 1*C*, Fig. 3) but do not occur in many weak specimens (Fig. 1*B*). All weak specimens, however, contain abundant lamellae. These lamellae have optical properties similar to those developed in natural quartz in which the lamellae have been shown to be arrays of edge dislocations, whose motion has caused the observed strain (*5*).

One picture of the way in which

water could facilitate such plastic flow is that hydrolysis takes place along preexisting dislocation lines where Si — O — Si bridges are already broken. As the temperature is raised this model would suggest that the silanol groups become sufficiently mobile to move with the dislocations, breaking and re-forming Si — O — Si bridges as they go. If the number of dislocations were 10^9 cm^{-2}, as found in natural quartz (*5*), then only one one-thousandth of the observed water would take part in this dislocation motion. Whatever the precise mechanism, the process is thermally activated, presumably as the mobility of the silanol groups is increased sufficiently.

Since all silicates have Si — O — Si or Si — O — M bridges (where M is a metal ion) which are susceptible to this type of hydrolysis, this temperature-induced water weakness may apply to silicates in general. We have observed such weakness in olivine and feldspar rocks, deformed in a hydrous environment.

These observations raise the possibility of great weakness in the earth's deeper crust and outer mantle at temperatures far below the melting point.

D. T. Griggs
J. D. Blacic

*Institute of Geophysics and
Planetary Physics, University
of California, Los Angeles*

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Permeability of Insect Cuticle to Water and Lipids

Abstract. *Insect cuticle presents a paradox: permeability to water may vary at different times, while lipids penetrate readily. Electron microscopy shows that the epicuticle is penetrated by filaments of wax 60 to 130 Å in diameter. These are believed to be lipid-water liquid crystals in the middle phase. The variable permeability to water, and other properties of the cuticle, may be due to phase changes.*

Some components of insect cuticle are among the most impermeable to water of all natural membranes. Typical rates of water loss by insects are lower than 0.1 mg cm^{-2} hr^{-1} (*1*). Lipids on the other hand penetrate the membrane fairly freely. In apparent contradiction of these observations, water passes through cuticle very rapidly under certain conditions: for example, when an insect is immersed in oil, drops of water soon appear all over its surface (*2*). In an atmosphere of high humidity water passes into mealworm larvae at a rate as high as 0.4 mg cm^{-2} hr^{-1}, compared with a maximum loss rate of 0.08 mg cm^{-2} hr^{-1} in dry air. Thus cuticle at different times can be permeable or impermeable to water and yet allow lipids to pass (*3*). An interpretation of some observations on the structure of the epicuticle may resolve this problem and throw light on other properties of this important membrane.

The epicuticle in various insects has been examined by electron microscopy. It consists of a clearly demarcated dense layer, the cuticulin, which is like a plasma membrane in that it can be resolved as a double layer; it overlays a thicker homogeneous region as thick as 1 μ. These layers are always penetrated by filaments of wax 60 to 130 Å in diameter which give rise to the surface wax layers (Fig. 1). An irregular porous layer of cement and a monolayer of lipid sometimes can be seen on the outside. The cement is frequently impregnated with wax which may form a white powdery bloom at the surface. The cuticulin and usually the dense layer completely cover the insect, except over some sensory areas. It is probable that the channels occupied by the wax filaments serve not only to bring wax to the surface, but also permit lipids to enter an insect.

Theories explaining the peculiar permeability properties of cuticle depend largely upon the nature of the wax filaments and the spaces they occupy. When first seen these structures were termed wax canal filaments and wax canals (*4*); lipid forms with this filamentous shape were then unknown. In material fixed with osmium and stained with lead, they appeared as dense lines of indefinite length in an orderly hexagonal array when densely packed. In some preparations the filaments have been resolved as tubes. They have, therefore, the structure expected for liquid crystals of lipid and water in the middle phase. These have been described on the basis of x-ray diffraction studies as "hexagonal arrays of cylinders of indefinite length, water is outside, and the hydrophilic groups of the lipid molecules sit on the surface" (*5*). The most probable arrangement of lipids in the epicuticle is shown in Fig. 2, in which the lipid-water liquid crystals are continuous with the monolayer and other lipids at the surface.

The properties of lipid-water systems of this sort are of particular interest. The arrangement gives the maximum surface area for reactions involving the lipids. Large amounts of lipid-soluble substances can be incorporated in solution in the regions occupied by the hydrocarbon ends of the chains. The main and subsidiary lipid components can diffuse freely within the liquid-crystalline structures, which can also flow in any direction towards regions where the lipid ceases to be in a liquid-crystalline phase.

These properties and the arrangement of molecules in the structure proposed in Fig. 2 can account for the following aspects of cuticle permeability.

The transport of wax to the surface of the cuticle is a general problem in insects. There has been no satisfactory explanation of the mechanism by which this insoluble, inert material is moved from the epidermal cells across a wide hydrophilic endocuticle and through the epicuticle. The structure proposed in Fig. 2 suggests that polar lipid molecules are synthesized by the cells and are continually added to the inner ends of the wax canal filaments which would flow through the epicuticle as the surface wax is absorbed in the