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Hydrolytic Weakening of Quartz and Other Silicates*

David Griggs

Summary

Rocks at high pressure and temperature become weak when exposed to an aqueous environment. Four different weakening processes have been found: (1) Increase in pore pressure reduces the effective confining pressure, thus negating the strengthening effect of confining pressure (Terzaghi). (2) Penetration of water into the intergranular boundaries reduces the cohesive strength. This is believed to have occurred in the dehydration weakening found in gypsum (Heard & Rubey) and in serpentinite (Raleigh & Paterson). (3) Water promotes recrystallization, greatly reducing the strength at low strain-rates at temperatures above the critical temperature for recrystallization. (4) Water permeates most silicate crystals so far tested and causes hydrolytic weakening of the component crystals of rocks.

The most revealing experiments on hydrolytic weakening have been those on single crystals of synthetic quartz with varying water content (Griggs & Blacic). The water content inferred from 3 micron infra-red absorption varies from 0·0015 to 0·13 wt % (100–9000 H/10^6 Si) in the nine crystals tested. All crystals became weak at a critical temperature dependent on the water content, varying from 380 °C at 0·13% to 1070 °C at 0·0015%. The weakening process is thermally activated, is reversible, and is rate dependent. The mechanism of deformation is intracrystalline glide. McLaren has shown by transmission electron microscopy that deformed weakened synthetic quartz contains dislocation densities similar to those found in strong dry quartz deformed in the ductile regime. Annealing of water-weakened quartz removes most of the dislocations and causes the formation of bubbles. These are believed to be water bubbles formed by the reaction $Si(OH)_4 \rightarrow SiO_2 + 2H_2O$, the water migrating through the lattice.

The Frank–Griggs hypothesis of hydrolytic weakening is that easy slip occurs only when Si–O–Si bridges adjacent to a dislocation are hydrolyzed by the migration of water. No Si–O bonds need be broken, for dislocation motion can occur by hydrogen bond exchange.

All the evidence in hand suggests that hydrolytic weakening is general in silicates containing very small amounts of water. This phenomenon is expected to be important in the mantle, leading to a rate-dependent strength.

Introduction

It has long been known that rocks tested at high pressure and temperature may be greatly weakened by exposure to fluid pressure. Terzaghi's (1936) concept of *effective* stress has been found to hold under many conditions at high pressure where fluids permeate the interstices of the rocks. The *effective* stress is defined as the

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total stress minus the fluid pressure. When the interstitial fluid pressure is equal to the confining pressure in a triaxial test, the strength is generally found to be reduced to that with no confining pressure. Hubbert & Rubey (1959) cite many examples of such behaviour in tests on concrete, sandstone and clay. Heard (1960) describes an apparent exception in his tests on Solenhofen Limestone.

In triaxial compression tests of jacketed specimens of rocks, it is universally found that the strength is substantially reduced if the jacket leaks, admitting the pressure fluid to the sample. If the fluid is water, disaggregation commonly occurs at elevated temperatures, leading to brittle behaviour. (Griggs, Turner & Heard 1960, Griggs & Heard, unpublished work.)

It has recently been found (Heard & Rubey 1963, 1966, Raleigh & Paterson 1965, Raleigh—this symposium) that when a rock composed of hydrous minerals is heated to the dehydration temperature, the strength drops below the zero pressure strength, and in Raleigh & Paterson's serpentinite, the rock becomes brittle. The writer believes that this weakening below the *effective* strength is due to penetration of the released water into the intergranular boundaries, reducing the cohesive strength and leading to brittle fracture.

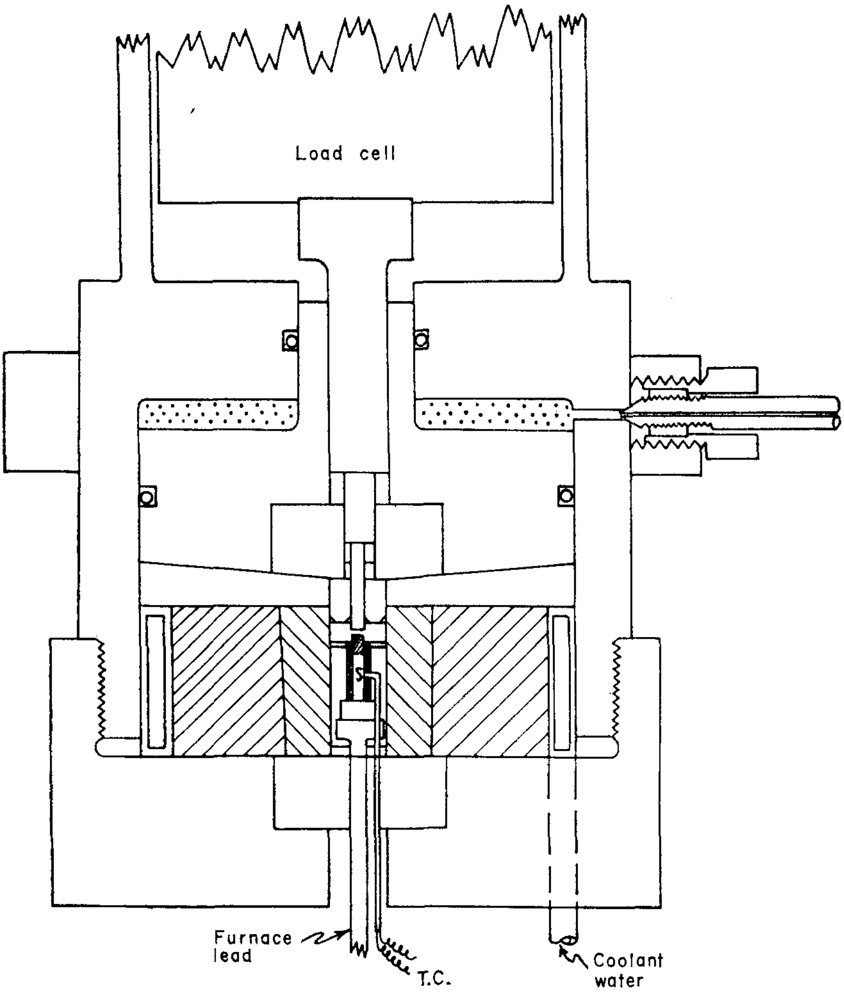


FIG. 1. Schematic drawing of apparatus.

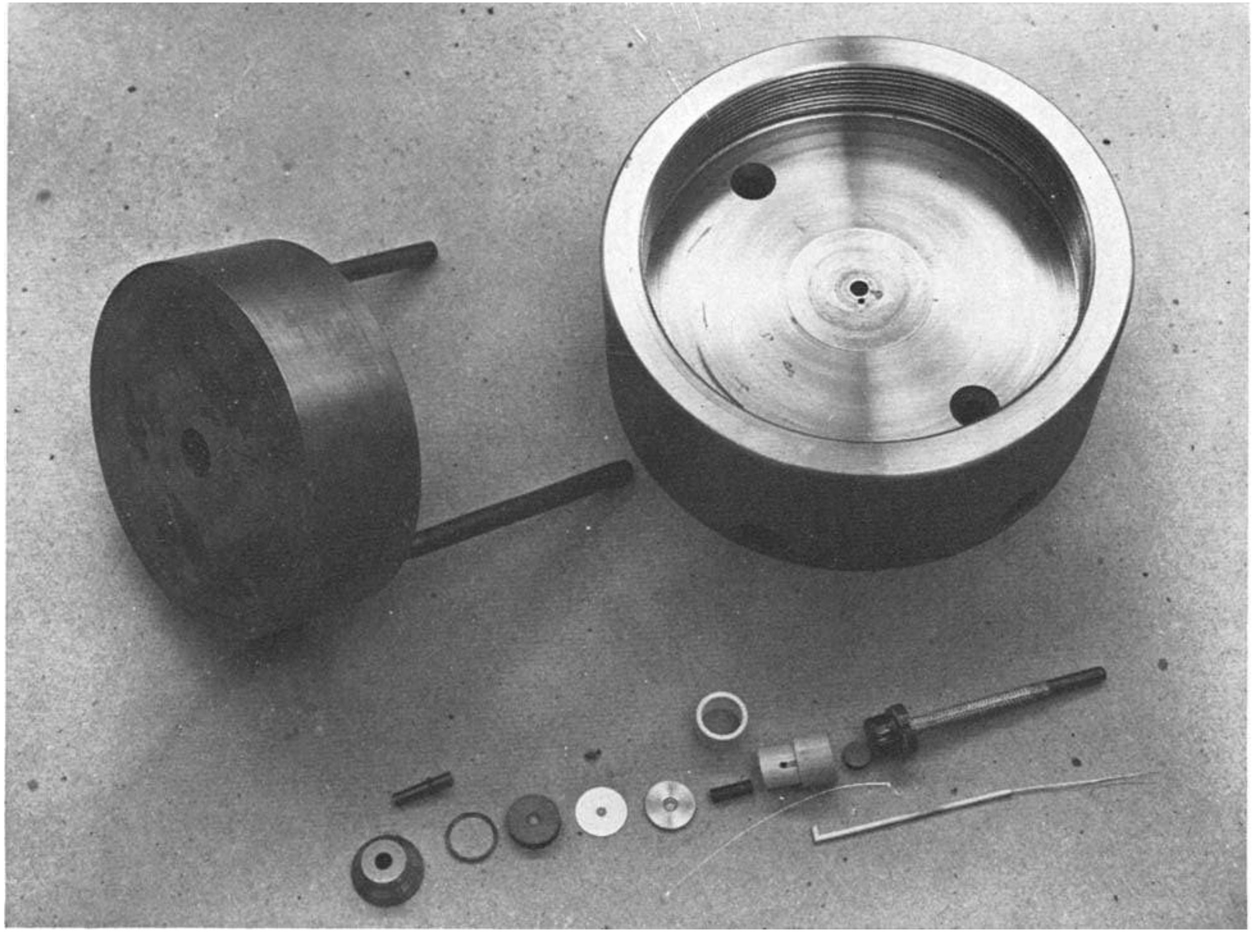


FIG. 2. Exploded high pressure assembly left to right: above—cylinder with cooling jacket, retaining cap; below—outer piston, inner piston, packing ring, silver chloride disk, silver buffer washer, copper furnace lead, graphite furnace containing specimen, talc sleeves, carboloy end plate, furnace lead, a thermocouple (bottom).

A third weakening effect of water in tests at high temperature and pressure is due to its common ability to promote recrystallization of rock forming minerals. Quartz, olivine, and some other silicates have been found to flow at low stresses by recrystallization at temperatures of 800–1000 °C, 15 kb confining pressure, when exposed to water —whereas these substances are strong when tested dry at the same temperature and pressure (Griggs & Blacic, unpublished work).

A new type of water-weakening or softening has been found in quartz and several silicates and is called *hydrolytic weakening* because there is evidence that it is specifically associated with hydrolysis of the Si–O–Si or Si–O–M bridges in the silicate structure. The weakened crystals deform plastically by dislocation-propagated slip. This is the only case known to the writer in which the critical resolved shear stress for slip in a nearly perfect single crystal has been drastically lowered by trace concentrations of an impurity. This paper will be concerned only with hydrolytic weakening and will concentrate on the effects observed in single crystals of quartz with which we have the most experience and the greatest variety of evidence.

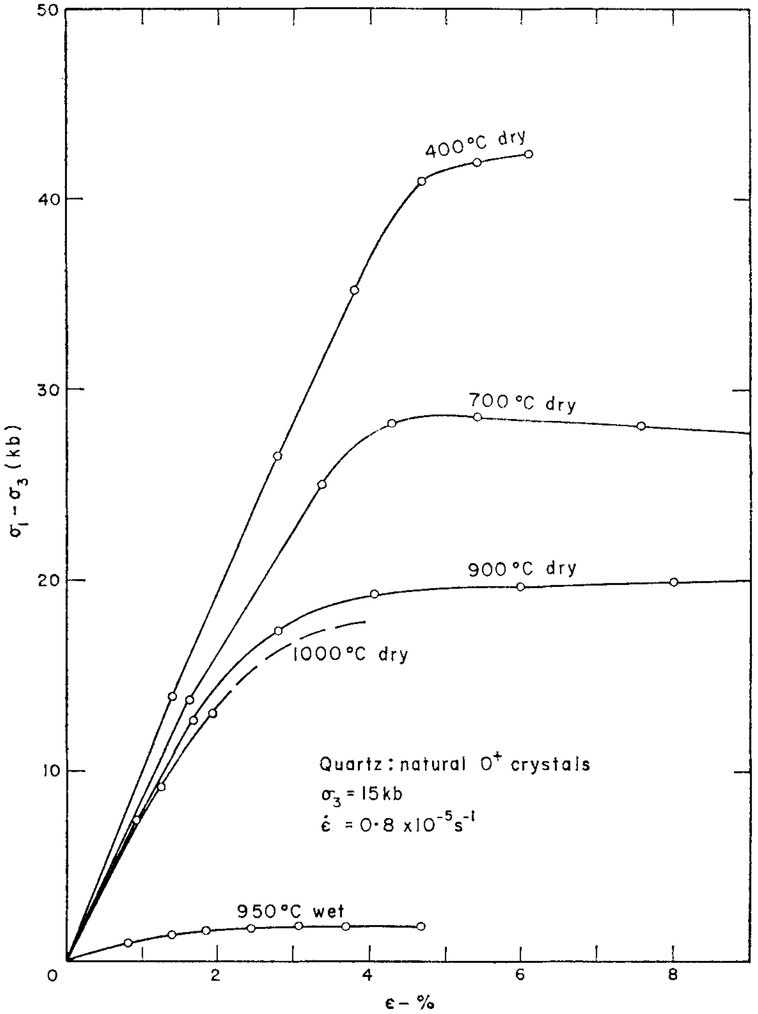


FIG. 3. Stress–strain curves of wet and dry natural quartz crystals.

Apparatus and results

A new type of constant strain-rate apparatus has been developed and has been in operation in this laboratory for two years. In this apparatus, confining pressure up to 20 kb and temperatures up to the melting point of any rock are readily attained. The apparatus is so designed that pressure and temperature may be maintained indefinitely. Four units are now in operation and nearly 300 experiments have been performed at strain rates from $0{\cdot}8 \times 10^{-4}$ to $0{\cdot}8 \times 10^{-7}\,\mathrm{s}^{-1}$ (half-hour to one month duration).

The apparatus is shown schematically in Fig. 1. The specimen is enclosed in a graphite furnace which is surrounded by an insulating sleeve of talc. Nearly hydrostatic confining pressure is applied to the specimen by the annular piston which bears on a silver chloride disk above the copper ring that grounds the upper end of the furnace to the cylinder wall. After the desired confining pressure and temperature have been attained, the specimen is compressed longitudinally by the inner piston which is driven by an electric motor through a gear train and a ball screw actuator. The components of the high-pressure assembly are shown in Fig. 2. The water-cooled double-ring cylinder is at left above, the closure cap at right. The specimen assembly components are, from left to right: (1) the confining pressure piston, (2) inner piston, (3) packing ring, (4) silver chloride disk, (5) silver buffer sheet, (6) copper ground ring, (7) specimen in the graphite furnace, (8) talc filler—above, (9) talc insulation, (10) carboloy end piece, (11) furnace lead, pusher plate and insulation, (12) thermocouple—below.

The temperature is measured by the thermocouple which penetrates the furnace and is in direct contact with the specimen. The e.m.f. of this thermocouple is also

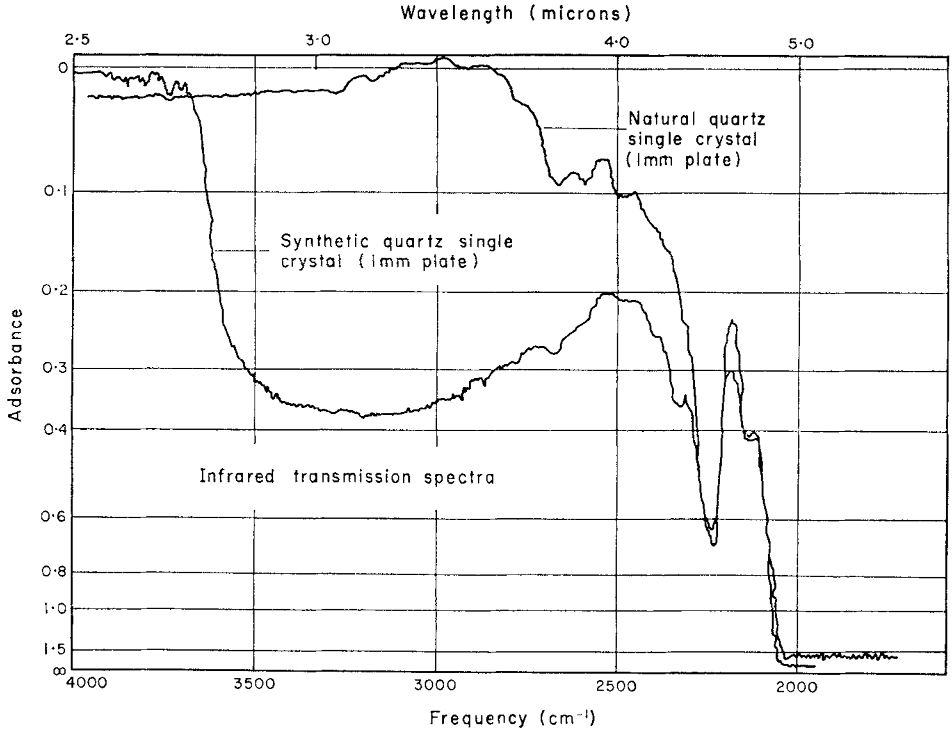


FIG. 4. Infra-red absorption spectrum of natural quartz ($1{\cdot}4 \times 10^{-4}$ H/Si) and synthetic quartz ($8{\cdot}8 \times 10^{-3}$ H/Si).

used to regulate the furnace temperature through home-made servos. Confining pressure is measured by pressure cells in the hydraulic ram fluid. Longitudinal differential compressive stress in the specimen is determined by measuring the force applied to the inner piston through the load cell, subtracting the force due to confining pressure plus friction which is measured in every run. Strain is determined by measuring displacement of the inner piston and correcting for the calibrated elastic distortion of the apparatus.

Fig. 3 shows stress–strain curves of specimens cut from a single crystal of optically clear untwinned natural quartz, all tested at the same confining pressure and strain-rate. The initial slope of the 400 °C curve corresponds closely to that expected from the elastic constants for quartz measured at one atmosphere. Note that there is nearly 5% of elastic deformation before the yield point. The combination of high strength and low elastic constants leads to greater elastic deformation than has ever been found in any single crystal except 'whiskers' and other tiny crystals carefully grown to be free from dislocations. MacKenzie (1949) has shown that the theoretical shear strength of crystals (without resorting to dislocation weakening) may be as low as $\mu/30$ ($\mu = 570$ kb for basal shear in quartz at room temperature and pressure) corresponding to a compressive strength in our crystals of about 40 kb.

Thus it is perhaps not surprising that Christie & Green (1964) have identified ten different slip systems in single crystals of quartz appropriately oriented to favour these systems. There is no easy slip system in dry quartz, and as the theoretical strength is approached, slip may occur with nearly equal ease on many crystallographic planes. The O^+ crystals of Fig. 3 are oriented to favour basal slip parallel to an *a* axis—the easiest slip in quartz at temperatures up to 700 °C.

The 'dry' crystals of Fig. 3 actually contain some water and the infra-red absorption shows $1{\cdot}4 \times 10^{-4}$ H/Si. Tests on these crystals at varying temperatures and strain rates yield an activation energy of 18 kcal/mole. Kats, Haven & Stevels (1962) report an activation energy of 19 kcal/mole for diffusion of H from the low-energy infra-red absorption bands in α quartz. The rate-limiting process in these crystals thus may be H, OH, or H_2O diffusion.

The 'wet' crystal in Fig. 3 was soaked for two hours at 950 °C, 15 kb to allow water liberated by dehydration of the talc jacket to diffuse into the quartz crystal. It was not possible to determine the water content in the specimen after deformation. Examination of a thin section of this specimen showed that the deformation had occurred by slip primarily on prismatic and basal slip systems. No fracturing or recrystallization was observed in this water-weakened crystal.

Synthetic crystals

A synthetic quartz crystal from Bell Labs (X_0) was tested under similar conditions (Griggs & Blacic 1965). This crystal contains $8{\cdot}8 \times 10^{-3}$ H/Si as shown by infra-red absorption (Fig. 4). Its strength as a function of temperature is shown in Fig. 5. Above a critical temperature of 380 °C, its strength was reduced by a factor of 10–20. Fig. 6 shows the appearance of thin sections of specimens deformed at 300, 400 and 600 °C. The 300° specimen (Fig. 6(a)) deformed primarily by basal slip in prismatic kink bands. The 400° specimen deformed primarily by prismatic slip in the broad basal kink band. The 600° specimen seems to have deformed primarily by prismatic slip, but there has been much recovery eliminating the evidences of slip, and there may be some recrystallization.

An experiment on this crystal showed that the weakening effect is reversible. In Fig. 7, the specimen was first heated to 600 °C for an hour, then cooled to 200 °C and loaded. The stress rose normally to 45 kb. Hence the weakening effect was recovered on cooling. This must mean that the weakening is not caused by migration of the H_2O

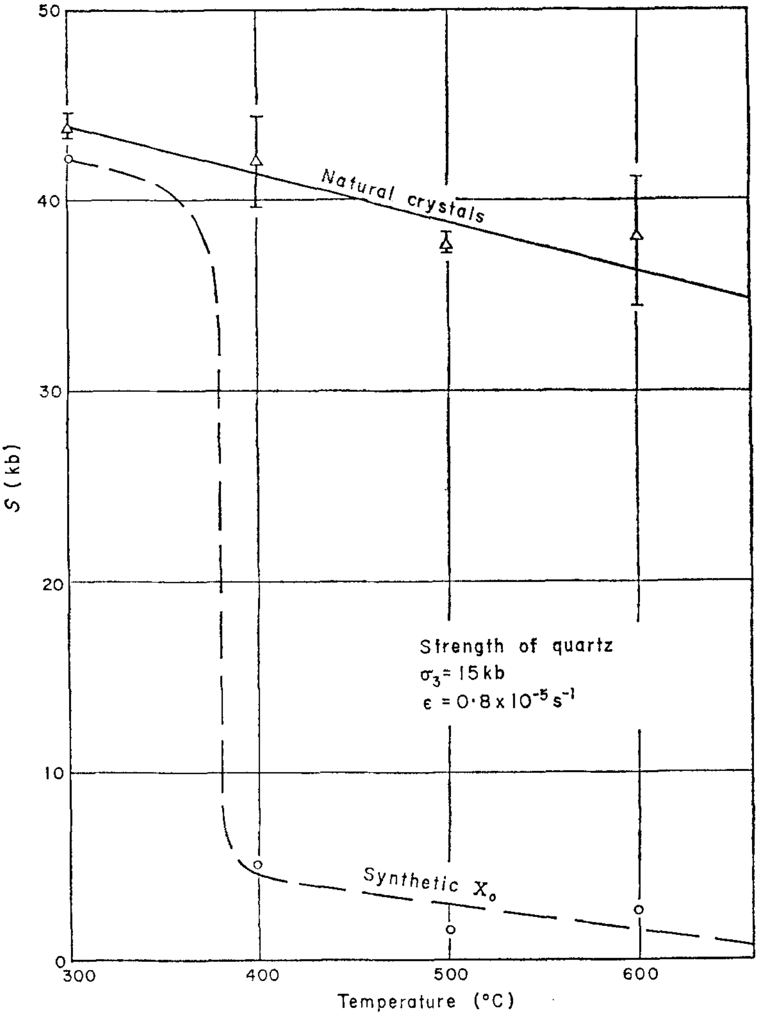


FIG. 5. Strength of natural and synthetic quartz crystals vs temperature.

to structural sites which cause an intrinsic weakening, but that the deformation process in the weakened condition is thermally activated.

To explore this thermal activation, a series of relaxation tests at stepwise increased temperatures was performed on this crystal, eight other synthetic crystals with varying water content, and on three natural crystals. The right-hand part of the force record in Fig. 7 shows such a relaxation test. At intervals of 20 min the temperature was increased 50 °C and the stress relaxation recorded. The change in slope at 400 °C is evident.

When the fractional stress drop during each interval is plotted against temperature, this sudden weakening becomes more apparent. Fig. 8 shows the curve for this experiment (140) and for a representative sample of synthetic and natural crystals. Each synthetic crystal has a sharp change in slope which characterizes the onset of weakening. The two natural crystals show two such inflections. Those at lower temperature (720 and 780 °C) correspond to the change from basal to prismatic slip reported earlier by Griggs & Blacic (1964), while the higher temperature inflections (950 and 1070 °C) seem to be associated with water-weakening.

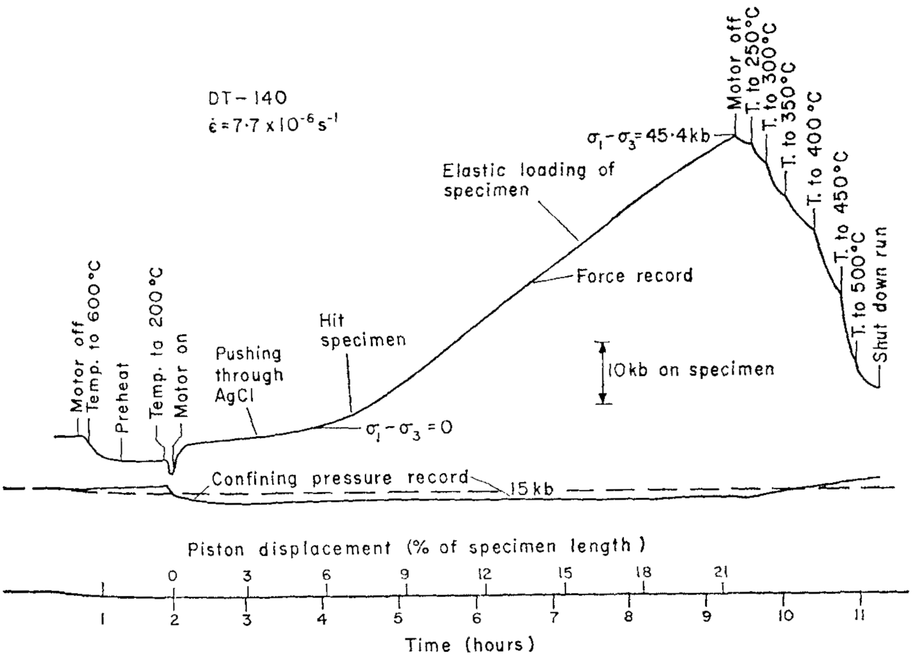


FIG. 7. Tracing of force record on specimen of synthetic crystal X_0, 14–15kb confining pressure. Left to right: initial heating at 600°C; cool to 200°C; motor on; force increases slowly as piston is pushed through AgCl; piston hits specimen and force increases to 45·4 kb elastic loading of specimen; motor off; successive relaxation in 50°C increments of temperature. The piston displacement during 'elastic loading' includes apparatus distortion. The elastic strain computed is 4·5% at 45 kb.

The critical weakening temperature decreases as the water content of the crystal increases, in such a way that H/Si $\propto e^{-A/RT}$ as shown in Fig. 9. If one treats this as a diffusion problem, with the rate of diffusion proportional to the inverse cube-root of the H/Si concentration, this yields an activation energy of 9·7 kcal/mole. This is only half that for hydrogen diffusion mentioned above, but is within the expected range for the hydrogen bond which will be discussed later.

McLaren's transmission electron microscopy

McLaren & Phakey (1964, 1965) developed a novel technique for transmission electron microscopy of quartz crystals. McLaren *et al.* (1967) report the results of this technique on our experimentally deformed quartz crystals. In natural crystals deformed at low temperature (500°C), McLaren found only basal faults as shown in Fig. 10. No dislocations of any sort were observed. By similarity with his findings on Brazil twins in amethyst (McLaren & Phakey 1966) he reasons that these basal faults are actually thin (50–300 Å) Brazil twins formed by partial basal dislocations of Burgers vector *a*/2 (2·955 Å). No such dislocations are seen, however. Since the stress in these experiments is approximately equal to the theoretical strength, as noted above, it seems possible that the crystal slips bodily without dislocation propagation as required to form Brazil twins in these very thin layers.

Study of the right-hand and left-hand crystal structure of quartz reveals that there is a translation, parallel to an *a* axis, of one lattice distance per unit cell which transforms a right- to left-hand lattice or vice versa. If such a uniform shear takes place in a layer parallel to the basal plane, the result curiously enough is a Brazil twin displaced by *a*/2 from the host structure, which is just what McLaren's electron microscope observations require.

At somewhat higher temperatures (600–750 °C) in the natural crystals, basal faults of the same characteristics were found, but basal dislocations were also found in profusion, frequently associated with the basal faults as shown in Fig. 11. These dislocations seem to be predominantly ones with their dislocation line parallel to one *a* axis and their Burgers vector parallel to another *a* axis which in these crystals is

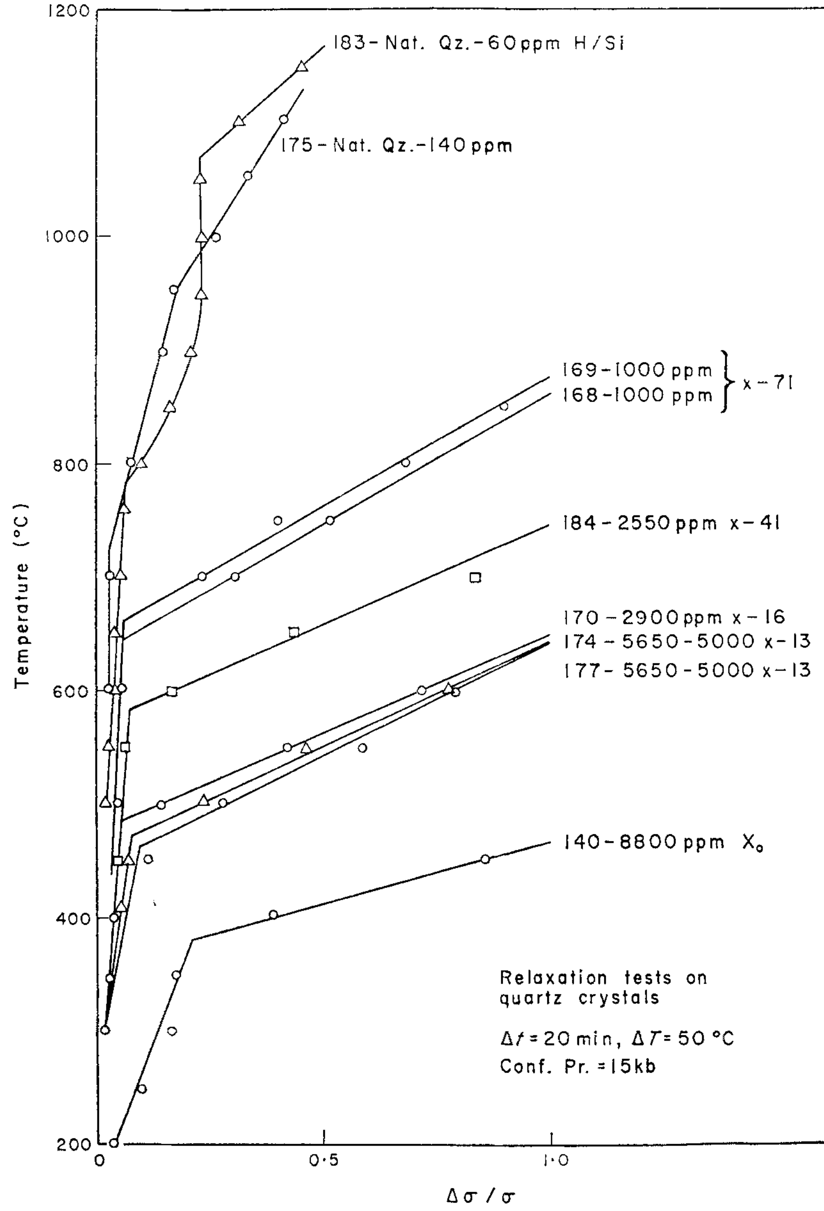
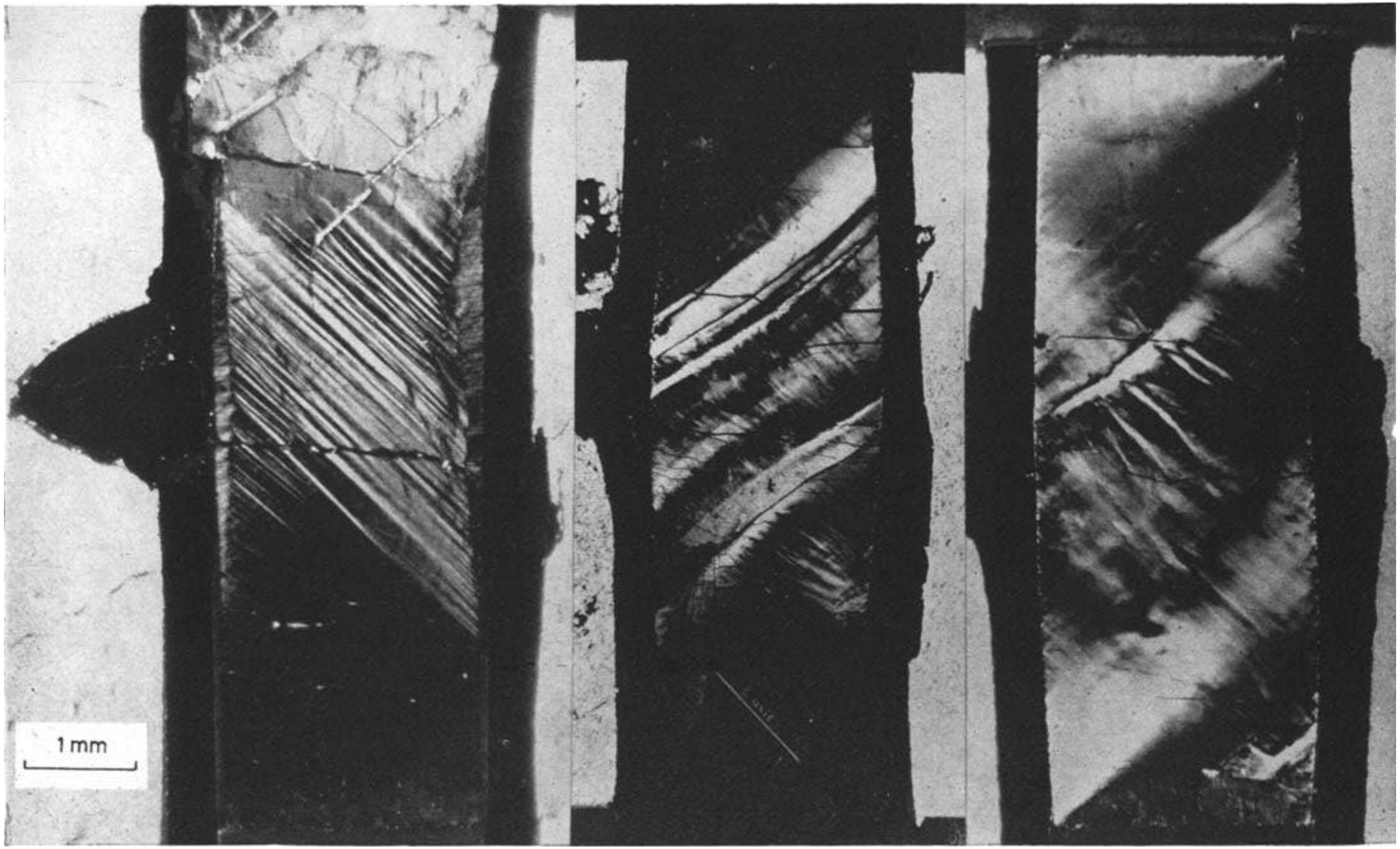


FIG. 8. Relaxation plots of typical synthetic and natural quartz single crystals with varying amounts of contained water. Note knee in each curve at the critical weakening temperature.



(a) (b) (c)

FIG. 6. Thin sections of synthetic quartz crystal X_0 deformed in compression at a strain rate of $0{\cdot}8\times10^{-5}$ s^{-1} at 15 kb confining pressure. All specimens cut so that *c* and *a* axes are in the plane of the thin section with the *c* axis trending NW. (a) 300 °C, 6·2% shortening, strength 42 kb. Prismatic kink bands (NW) produced by basal slip. (b) 400 °C, 9·6% shortening, strength 1 kb. NE trending kink band produced by predominant prismatic slip. (c) 600 °C, 5% shortening, strength 0·4 kb. No strong lamellae or kink bands.

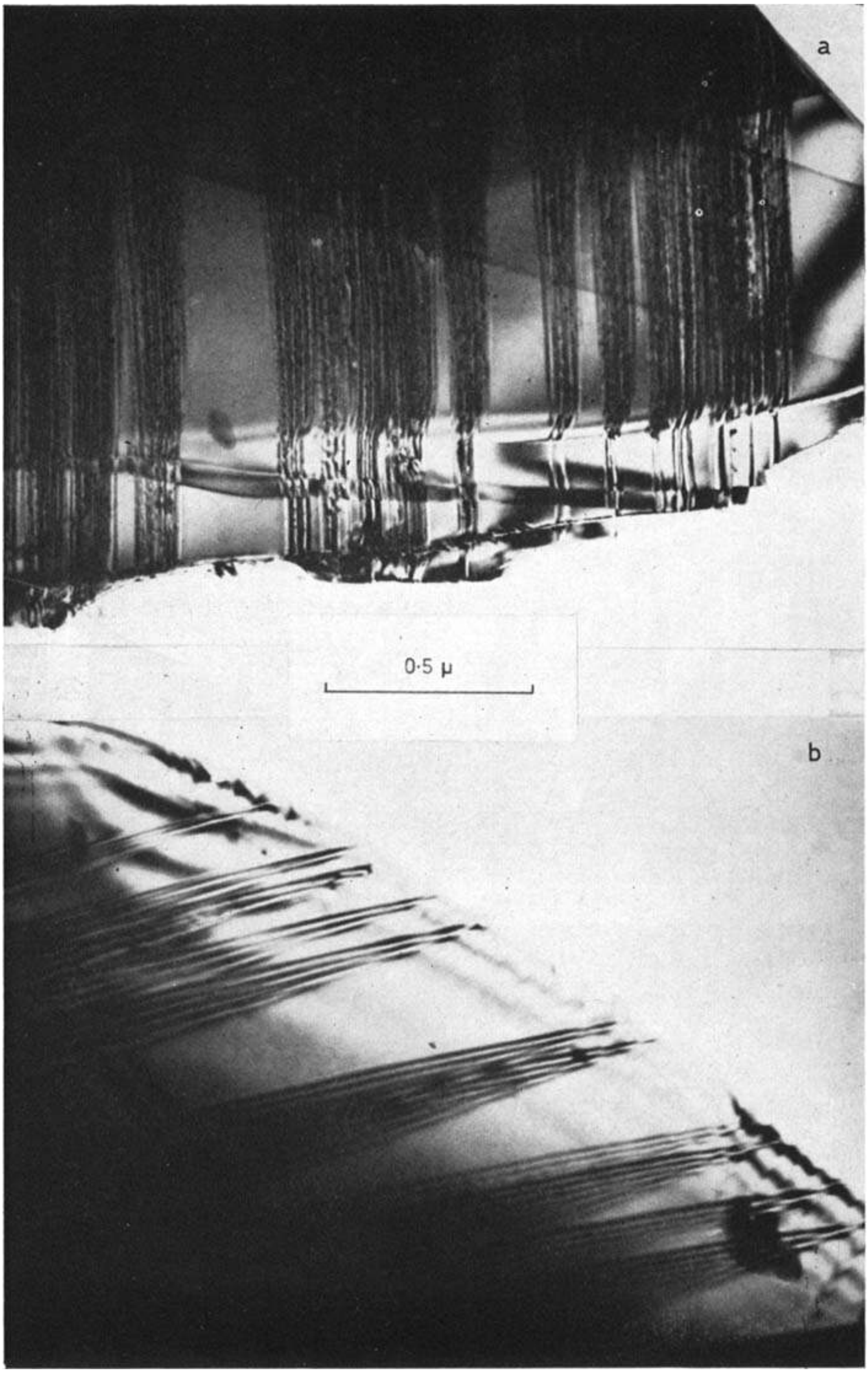


FIG. 10. Transmission electron micrographs of flakes of a single crystal of natural quartz deformed at 500 °C, 20 kb confining pressure. (a) Basal faults nearly normal to flake—slight radiation damage. (b) Basal faults inclined to flake. Asymmetry of fringes shows Brazil twinning in thin segments (see McLaren *et al.* 1967).

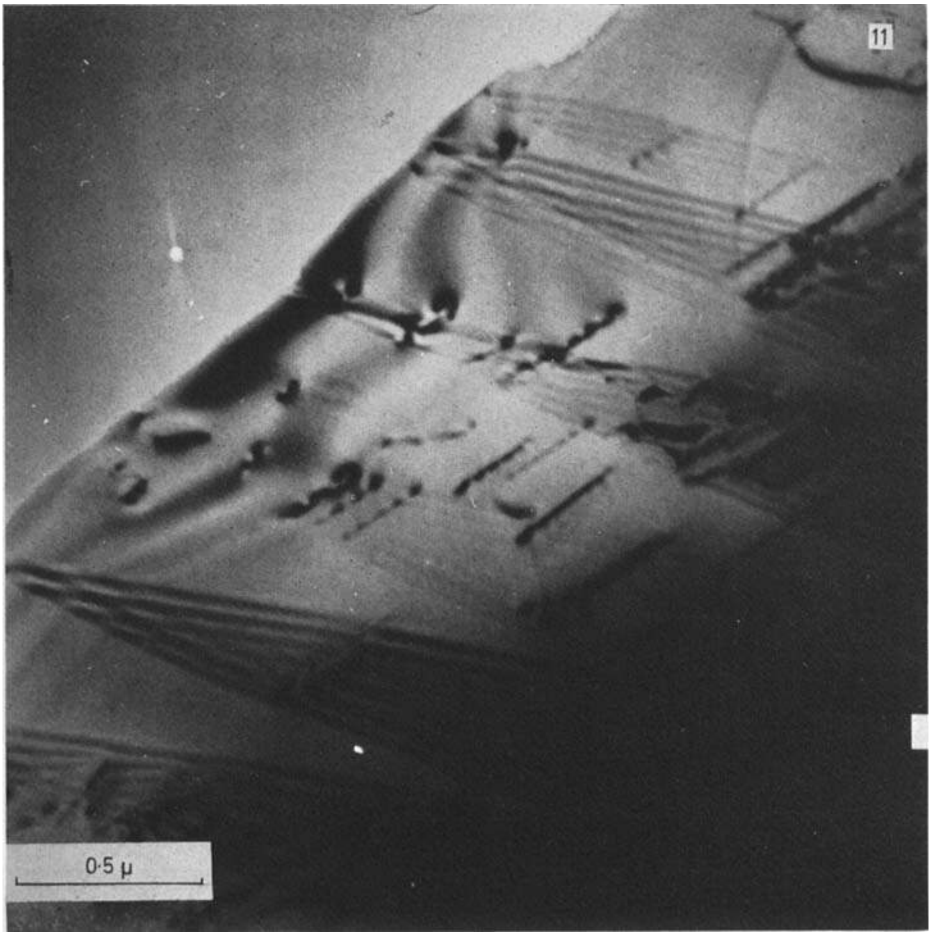


FIG. 11. Specimen deformed at 700 °C, 15 kb confining pressure. Note basal dislocations (11a) lying in basal faults.

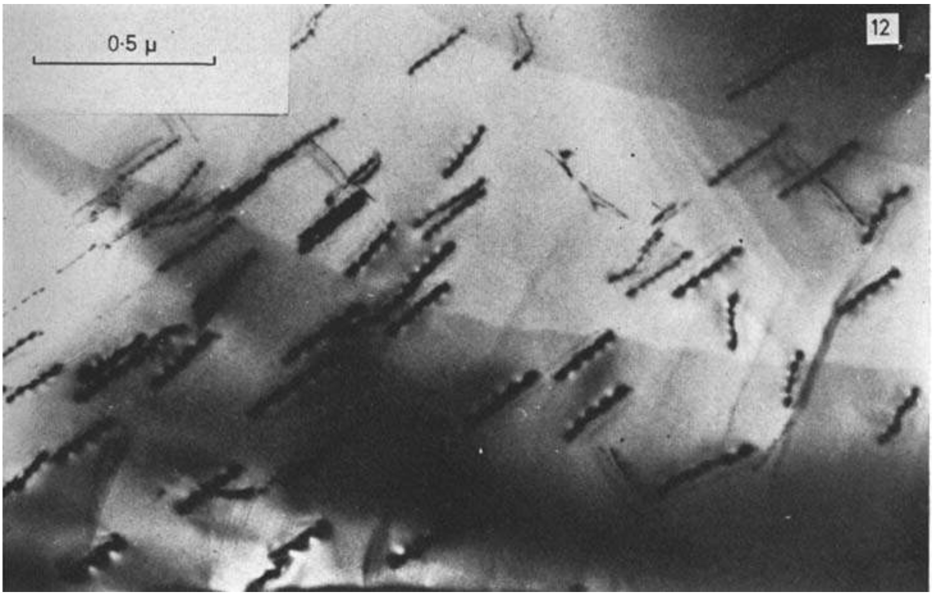


FIG. 12. Dislocations predominantly parallel to one *a* axis characteristic of higher temperature experiments on natural quartz. Dislocation lines inclined to

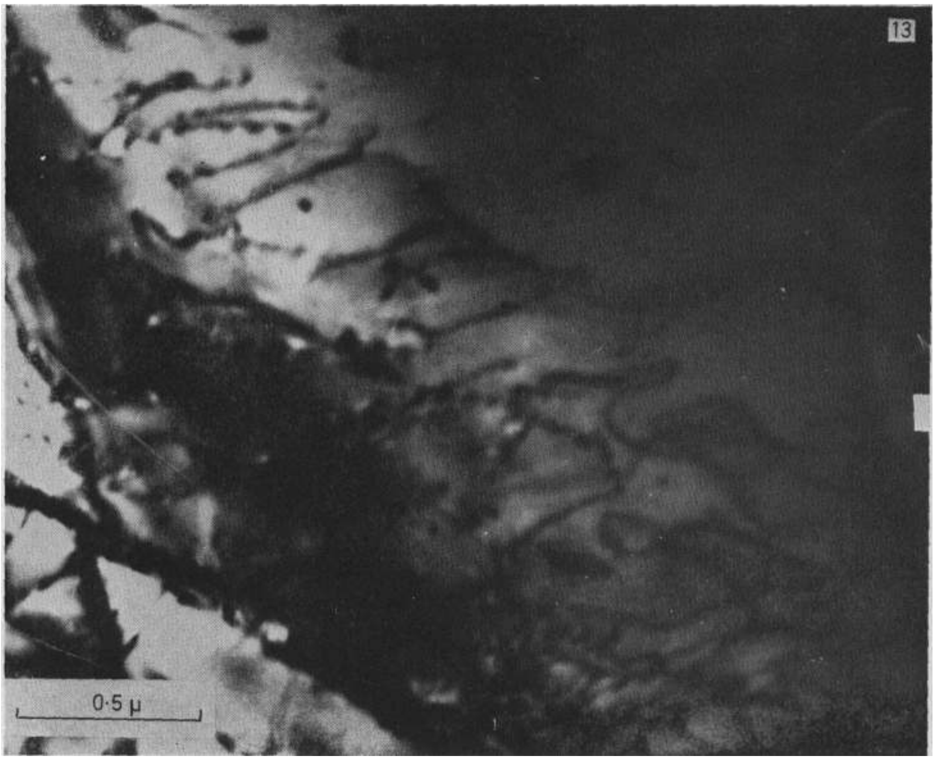


FIG. 13. Synthetic quartz crystal deformed under conditions of hydrolytic weakening. Dislocation lines curved and tangled in contrast to Fig. 12.

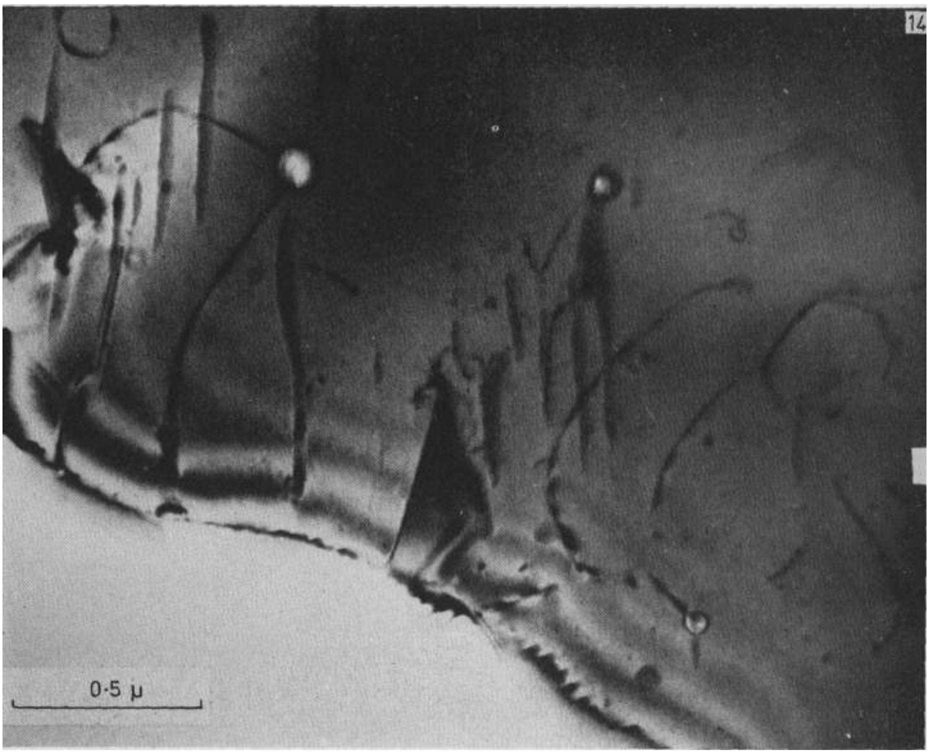


FIG. 14. Same specimen as Fig. 13 after annealing at 1 atm, 300 °C, for 24 h. Note disappearance of dislocations and formation of water bubbles by dissociation of the hydrolized bridges and water migration.

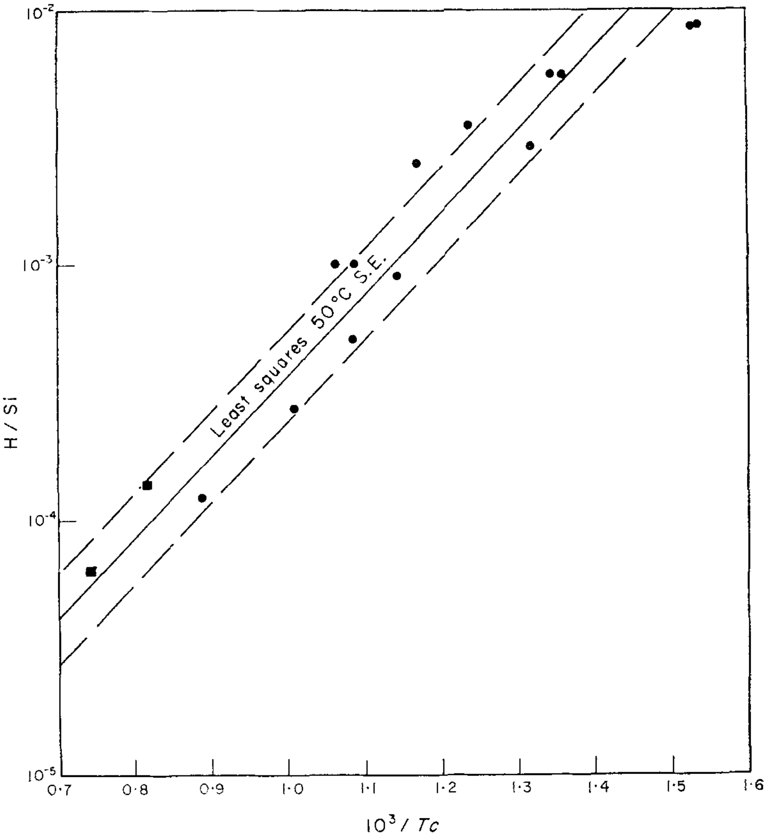


FIG. 9. Log water concentration (H/Si) versus $1/T_c$ (the critical temperature of weakening). Linear log H/Si vs $1/T$ gives activation energy of 9·7 ± 1·5 kcal/mole, in a diffusion model.

presumed to be the *a* axis with the maximum resolved shear stress. The resolved shear stress coefficients were: a_1: $-S_0 = 0{\cdot}50$, $a_2 + a_3$: $-S_0 = 0{\cdot}25$. It is seen in Fig. 11 that the basal faults contain many dislocations, and that in one instance a fault terminates in three dislocations. From these observations, it is deduced that, at the somewhat higher temperature and lower stress, there is a mixture of uniform shear and dislocation-propagated shear of the same sort, both producing thin Brazil twins.

At higher temperature, McLaren finds no basal faults, but only dislocations of the same orientation (Fig. 12). The dislocation density is about $10^9/\text{cm}^2$, and they are characteristically straight as shown in this photo.

In synthetic quartz deformed above the critical weakening temperature, McLaren finds about the same density of dislocations, but as shown in Fig. 13, the dislocations are curved and tangled and no longer show a preference for any particular crystallographic direction. The abundance of dislocations and the optical evidence leaves little doubt that these water-weakened crystals have been plastically deformed by dislocation propagation.

When McLaren annealed this specimen for 24 h at 300 °C, most of the dislocations disappeared and bubbles developed which are believed to have formed by migration of H_2O through the crystal (Fig. 14). Brunner, Wondratschek & Laves (1961) found similar bubbles formed by annealing of amethyst. They showed that the infra-red absorption bands of Si–OH in the original crystals were replaced by H–OH absorption bands after annealing, indicating the migration of H_2O to form steam bubbles. They suggested the reaction:

$$Si(OH)_4 \rightleftharpoons SiO_2 + 2H_2O$$

had run to the right at the annealing temperature. We believe this reaction may play an important role in the hydrolytic weakening process.

Hypothesis of hydrolytic weakening

The infra-red absorption bands in quartz have been shown to be predominantly due to Si-OH (Brunner *et al.* 1961, Kats *et al.* 1962), and the former paper suggests that the common mode of occurrence is as hydrolyzed silicon-oxygen bridges:

$$Si{-}O{-}Si + H_2O \rightarrow Si{-}OH.HO{-}Si.$$

In such a hydrolyzed bridge, the bond between the two SiOH groups would be a hydrogen bond—weaker by an order of magnitude than the Si-O or Si-OH bonds. The weakness of this hydrogen bond is believed to be the source of the hydrolytic weakening observed.

In a crystal containing dislocations, the preferred site for the H_2O ions must be to fill the dangling Si- and Si-O- bonds at the edge of the extra half plane in the dislocation lines. To saturate all such bonds in dislocations at the observed density of $10^9/cm^2$ requires only $1{\cdot}5 \times 10^{-6}$ H/Si. Griggs & Blacic (1965) suggested that: 'As the temperature is raised . . . the silanol groups (SiOH) become sufficiently mobile to move with the dislocations, breaking and reforming Si-O-Si bridges as they go.' It was then recognized that if the number of dislocations were the same as had been found in natural quartz ($10^9/cm^2$) less than one-thousandth of the water observed would take part in this dislocation motion. When McLaren found that the dislocation density was in fact about $10^9/cm^2$, and when it was found that the critical weakening temperature was a smooth function of the water concentration, as shown in Fig. 8, this hypothesis became untenable. Before proceeding further, it might be helpful to review the salient facts:

1. The fact that quartz is strong below the critical temperature shows that the hydrolyzed bridges and dislocations do not of themselves cause weakening.

2. The fact that strength is regained after cooling from above the critical temperature shows that the weakening is not due to movement of the H^+ and OH^- ions to sites which of themselves permit easy glide (as for instance, if the H_2O were to hydrolyze all bridges on a plane which could then slip at low shear stress).

3. The fact that the critical temperature decreases with increasing H_2O content shows that H_2O not at the dislocations plays a key role in the weakening process.

4. McLaren's observation of bubble formation in annealing suggests thermally activated decomposition of Si-OH.HO-Si bridges, diffusion of H_2O and re-formation of hydrolyzed bridges in equilibrium under the conditions of pressure and temperature at which weakening occurs. It is presumed that such decomposition does not occur sufficiently below the critical temperature to accomplish weakening.

5. The activation energy of 9·7 kcal/mole derived from the relation between ln H_2O concentration and $1/T_c$ suggests that the rate limiting process is the breaking of the hydrogen bond in the hydrolyzed bridges.

6. The critical weakening temperature depends on the strain-rate. As the rate of strain is increased, the criticial temperature is increased. This effect has been observed qualitatively, but the quantitative relation has not yet been determined.

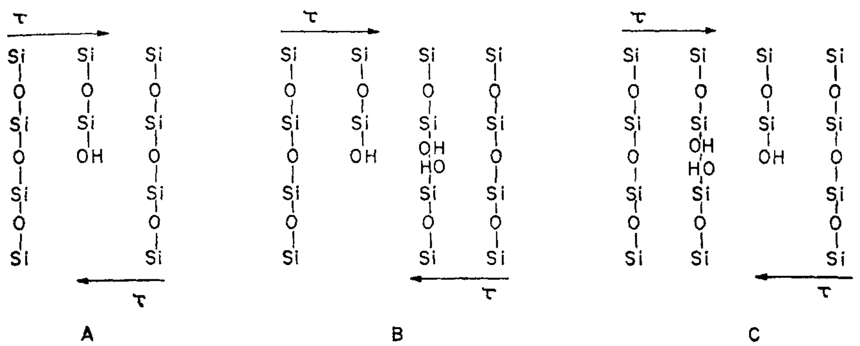


Fig. 15. Schematic model of the Frank–Griggs mechanism of dislocation motion by hydrolysis and hydrogen bond exchange. A. sessile hydrolyzed edge dislocation with anhydrous neighbours. B. Neighbouring bridge hydrolyzed by water migration. C. Dislocation moves by exchange of hydrogen bond with neighbouring bridge.

F. C. Frank made a key suggestion at an early date when the old hypothesis was becoming untenable, but long before most of the above facts were in hand. He suggested that the dislocations might propagate by kink migration and that the kinks would develop and move under low shear stress only when adjacent Si–O–Si bridges became hydrolyzed. Coupled with McLaren's observation of bubble formation, this concept is in accord with all our observations.

Our hypothesis then is that the easy glide which occurs in the hydrolytic state can only occur when the hydrolyzed dislocation can move by exchanging hydrogen bonds with a neighbouring silicon–oxygen bridge which has become hydrolyzed. This process is shown schematically in Fig. 15. Hydrolysis of the neighbouring bridges occurs by the diffusion of water through the lattice when the temperature is sufficiently high to decompose some of the hydrolyzed bridges. Since the migration of water will be random in its temporal distribution (though probably not random in space, since the *c* axis holes in the quartz structure should favour diffusion in that direction) the motion of the dislocations will not be as straight-line segments as in dry quartz, but will become curved, following the random hydrolysis of neighbouring bridges. Dislocation loops may be expected to form and to serve as Frank–Read sources for dislocation multiplication.

When the temperature is below that required for a sufficient rate of decomposition to maintain the imposed strain-rate, the strength will rise to that required to break the silicon–oxygen bonds as in dry quartz. For higher water content, the critical temperature will be lower, since the diffusion distance is smaller on the average and hence the rate of decomposition and diffusion required is lower.

The strength should be proportional to the bond strength in dry and wet crystals, since the mechanism of deformation is so similar. The observed strength drop of a factor of 10 or somewhat more is consistent with the ratio of ionic to hydrogen bond strength (Pimentel & McClellan 1960).

Thus, all the observations seem to be consistent with this hypothesis of hydrolytic weakening.

Applications to other silicates

All silicates contain Si–O–Si bridges of the type found in quartz, and M–O–Si bridges in addition. Hydrolysis of these bridges would be expected to produce weakening of all silicates similar to that observed in quartz. Such weakening has been observed in plagioclase feldspar, olivine, hypersthene, tourmaline and beryl—all the silicates so far tested. In these experiments, samples were tested dry and in an aqueous environment provided by talc decomposition, all at 950 °C, 15 kb confining pressure. In all cases the wet experiment was an order of magnitude weaker than the dry experiment. Lamellae and deformation bands were found in the individual crystals, indicating that the deformation had occurred by intracrystalline flow in the water-weakened specimens.

The strength of the mantle

Predictions as to the strength of the mantle on the hypothesis of hydrolytic weakening require a more complete understanding of the theory and experimental tests over a wider range of strain rates than have been done to date. All we can say is that we have discovered a phenomenon which produces a tenfold reduction in strength of silicates in the ductile regime. Such small concentrations of water are required that it seems reasonable to expect that abundant water for this process occurs throughout the mantle. It is perhaps noteworthy that the apparent elastic constants of the hydrolytically-weakened quartz are greatly reduced even at low stresses (Fig. 3). This must mean that we are in fact observing an inelastic rate-dependent behaviour which fortuitously gives a linear stress-strain relation at stresses well below the 'strength' referred to above. This in turn must mean that the long-term strength of interest in the mantle must be much lower than the strength of 2·3 kb at 950 °C and 1·1 kb at 1000 °C measured in hydrolytically weakened natural quartz at a strain rate of 10^{-5}/s.

It is too early to tell whether or not this hydrolytic weakening will produce lower strengths in the mantle than the other water-weakening processes mentioned in the introduction. In the light of these recently discovered weakening processes which all seem applicable to the mantle, it seems that the mantle may be very weak indeed at the low strain rates required by tectonic processes.

Acknowledgments

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