Reports

Weakening of Dunite by Serpentine Dehydration

Abstract. *A shear press has been used to determine the mechanical behavior of serpentinized dunite and forsterite at normal pressures to 50 kilobars, temperatures to 900°C; and strain rates from* 10^{-1} *to* 10^{-4} *per second. The shear strength of dunite, containing less than 5 percent by volume of serpentine, is reduced by at least 30 percent as the temperature is raised from 300° to 520°C. Abundant kink bands develop at normal pressures above 35 kilobars at 27°C and at lower pressures as the temperature is increased.*

The strength of certain silicates is influenced significantly by the presence of water (*1*). Griggs and Blacic (*2*) found that the strength of synthetic single crystals of quartz, containing trace amounts of water, drops rapidly above 400°C, and ductility is enhanced without fracture. In fact, at 400°C the crystals had no measurable strength under a confining pressure of 2.5 kb and at a strain rate of 8×10^{-6} sec^{-1}. Natural quartz crystals also become very weak at much lower temperatures in a hydrous environment than under anhydrous conditions. Raleigh and Paterson (*3*) investigated the anomalous embrittlement and weakening of serpentinite at 300° to 600°C. They ascribe the weakening in part to reduction of effective confining pressure caused by pore pressure of water released by dehydration of serpentine. These results have important petrogenetic and geophysical significance, since they suggest that the strength of silicate rocks may be considerably reduced in the presence of hydrous minerals.

As part of a program to determine the mechanical properties of possible lower-crust and upper-mantle minerals under conditions of high pressure and temperature combined with shearing stress, we have tested serpentinized dunite and various olivine specimens to determine the effect of serpentine dehydration on shear strength.

An opposed anvil device, based on a design by Bridgman with later modifications by Griggs (*4*), which can attain simultaneous pressures and temperatures up to 60 kb and 1000°C, was used in the experiments. The samples were minus-400 mesh, pelletized powders, or thin slices of rock (0.38 mm thick). Shear was applied by rotation of the upper anvil at strain rates from 10^{-1} to 10^{-4} sec^{-1}.

A slightly serpentinized dunite from Addie, North Carolina, was chosen for the tests; veins of serpentine compose about 5 percent (by volume) of the rock. The olivine occurs as approximately equidimensional grains having diameters between 0.4 and 1 mm. The olivine is 87 percent forsterite (Fo_{87}). Some of the grains show natural deformation effects such as "translation lamellae" subparallel to (100) and undulatory extinction. In addition to the determination of shear strength of the olivine, deformation effects were studied microscopically in thin sections cut parallel and perpendicular to the specimen wafer after each test.

Figure 1 shows average shear strength for the dunite plotted against normal pressure; the lines connect isothermal tests. The steepening of the slope at about 30 kb normal pressure reflects a change in the behavior of the sample. The curve slope below 30 kb is caused predominantly by slip of the anvils over the sample, accompanied by some cataclastic deformation of the dunite. Numerous deformation bands are formed above 30 kb, particularly at high temperatures. This indicates that intragranular flow was induced in the olivine. The breadth of the transitional knee separating the two parts of the curves indicates the magnitude of the radial pressure gradients within the pellets (*5*). The average strain rates for these and subsequent tests are 10^{-1} sec^{-1}. Variations to 10^{-4} sec^{-1} produced only slight displacement of the data toward the ordinate.

The upper portion of the curve in Fig. 1 indicates a 30 percent decrease in strength of the dunite as the temperature was raised 220°C from 300° to 520°C. The weakening effect was most noticeable where sample compression was greatest and porosity was lowest (*6*). Higher temperature tests show minor weakening accounted for by increasing temperatures alone.

For comparison, Fig. 2 records strengths for synthetic forsterite (Fo_{100}, dashed lines), and for a serpentine-free olivine (Fo_{87}, triangles) from Hualalai Volcano, West Hawaii. The strengths are about 20 percent higher in unserpentinized materials than they are for the Addie, North Carolina, dunite. Shear strengths for dunite from Twin Sisters, Washington, and peridot from St. John's Island and Arizona also were very near those for the synthetic material.

Tests on serpentinite show very pronounced weakening (Fig. 3). As the temperature is raised from 300° to 500°C, in a sample from the American Miscellaneous Society's (AMSOC) Puerto Rico test hole there was a 55 percent decrease in strength from 5.5 to 2.7 kb at 40-kb normal pressure. Serpentinite sheared at 450°C or higher was always visibly damp after removal from between the anvils.

The olivine grains in all the sheared pellets, even at the lowest temperature and normal pressure, showed undulatory extinction. Well-developed deformation bands were formed at room temperature when the normal pressure exceeded 35 kb. As the temperature was increased, deformation bands developed at lower normal pressures. Compression tests made without applied shear also produced deformation bands, but the sheared samples generally contained more numerous and better-formed bands.

Universal-stage measurement of deformation bands in the sheared pellets showed a change in optical orientation across the band boundaries that is characteristic of kink bands. Figure 4 (left) shows a representative deformation band (30 kb normal pressure, 800°C, strain rate 10^{-1} sec^{-1}) and a stereo-

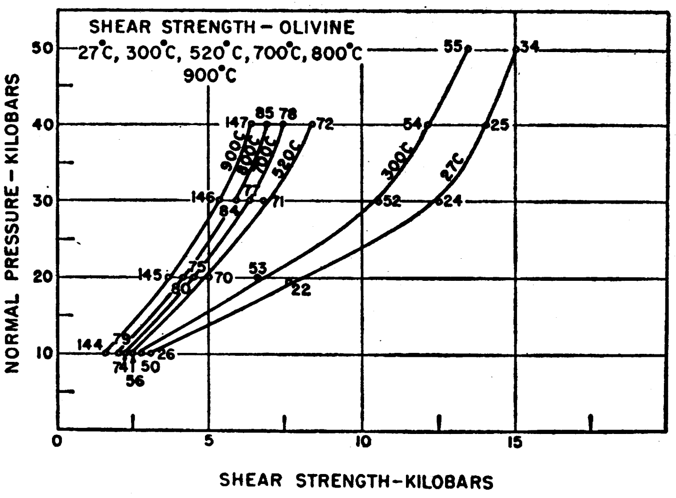

Fig. 1. (top left). Shear strength–normal pressure curves for Addie, North Carolina, dunite (5 percent serpentine veins) showing 30 percent reduction in strength as temperature is raised from 300° to 520°C.

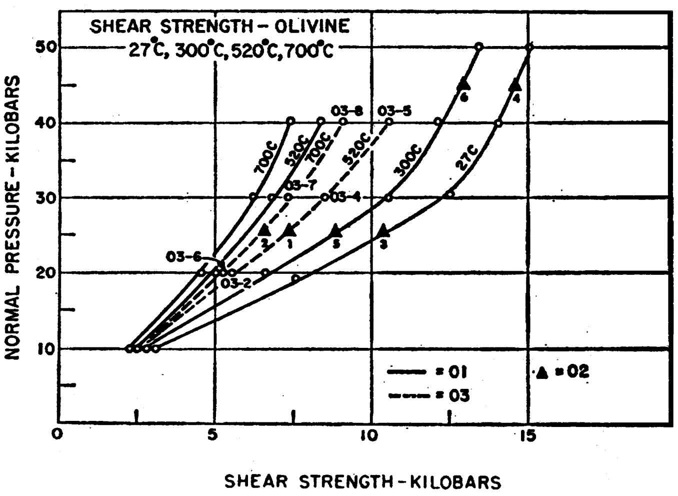

Fig. 2 (top right). Curves of shear strength plotted against normal pressure for synthetic forsterite and Hawaiian dunite showing greater strengths than for the serpentinized Addie dunite. Solid line, Addie dunite; triangles, Hawaiian dunite; dashed lines, synthetic forsterite.

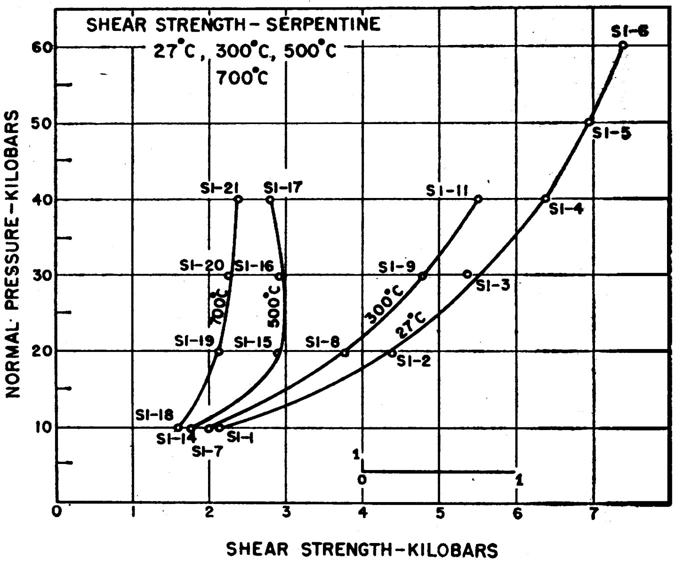

Fig. 3 (right). Shear strength–normal pressure curves for serpentinite from a test hole (148 m deep) in Puerto Rico; showing 55 percent weakening as temperature is raised through the dehydration temperature of serpentine.

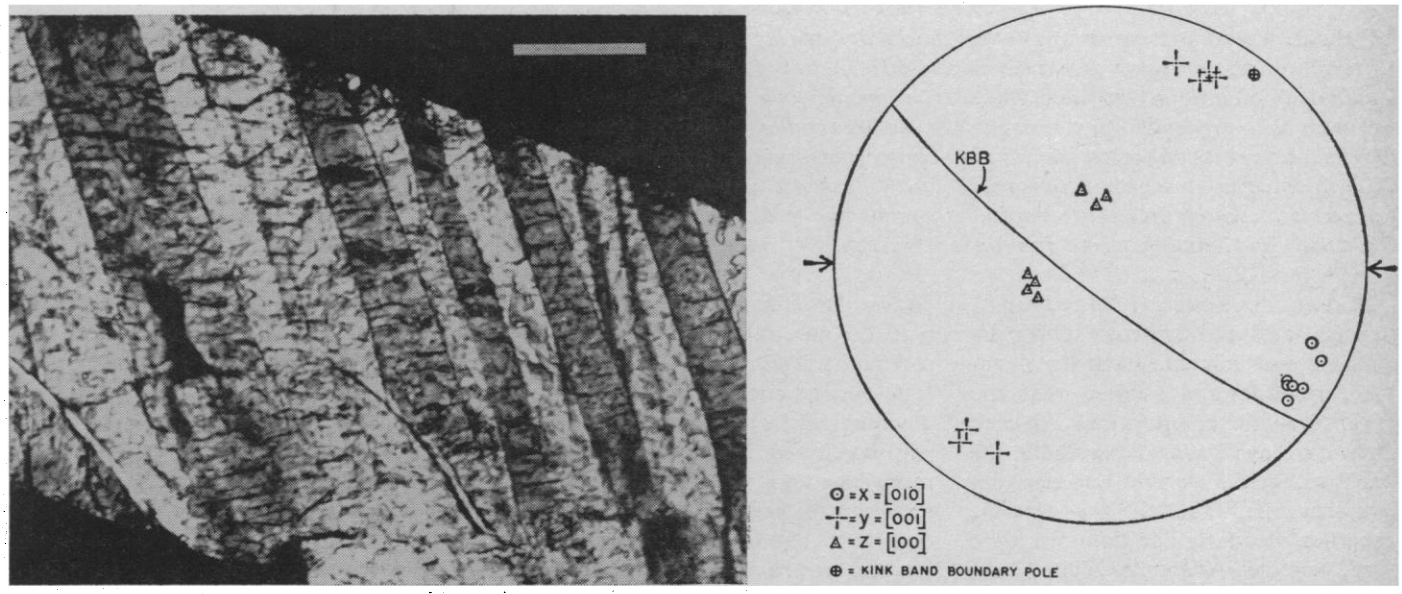

Fig. 4. (Left) Kink bands in experimentally deformed olivine. Thin section is cut normal to the pellet surface. Scale line indicates 0.1 mm. (Right) Stereographic projection of optical directions in kink bands shown at left. Slip system: T = (100); t = [001]. Arrows plotted normal to pellet surface.

graphic projection (Fig. 4, right) across several of the bands. By the criteria of Raleigh (*7*), the slip system was identified as T equal to (100); t equal to [001] (*8*). This is the most common glide system in the sheared olivine.

Preferred orientation apparently has been induced in those pellets sheared at high normal pressures. The x-ray powder transmission pattern, taken normal to the pellet surface, shows the characteristic arcuate pattern caused by preferred orientation. No evidence of recrystallization has been found, probably because the temperature was too low and the heating time too short.

The experiments demonstrate that a significant weakening mechanism, operating at temperatures higher than 300°C, causes a marked change in aggregate mechanical properties when the dunite is associated with even very small amounts of a hydrous mineral.

In addition to the reduction of normal pressure by serpentine dehydration, Raleigh and Paterson (*9*) suggest that the presence of new phases and new pores in grain boundaries may lead to a decrease of "cohesive strength" in the solid framework of the rock.

The classical Coulomb fracture theory for the generation of earthquakes requires prohibitively high shear stresses to overcome frictional resistance and shear strength. However, it is possible that at depths of 20 to 40 km the shear strength of rocks may be greatly reduced by dehydration effects.

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References and Notes

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2. D. T. Griggs and J. D. Blacic, *Science* **147**, 292 (1965).
3. C. B. Raleigh and M. S. Paterson, *Geophys. Res.* **70**, 3965 (1965).
4. R. E. Riecker, *Rev. Sci. Instr.* **35**, 1234 (1964).
5. R. E. Riecker, *J. Geophys. Res.*, in press.
6. An investigation of pressure gradients in opposed anvil devices demonstrates that sheared pellets are almost completely confined at high pressures. Little or no sample extrusion occurs at pressures above 20 kb.
7. C. B. Raleigh, thesis, University of California, Los Angeles, 1963.
8. Raleigh has restudied olivine kink bands using a polished section technique, and he has shown that $T = (110)$; $t = [001]$ is the most common glide system. Our U-stage results are reproducible; but, until such time as a polished section technique can be adapted to the sheared pellets, the possibility remains, especially where external rotations are small, that the kink bands may be described more accurately by another glide system. See C. B. Raleigh, *Science* **150**, 739 (1965).
9. C. B. Raleigh and M. S. Paterson, *ibid.* **70**, 3965 (1965).
10. We thank N. Haskell, H. Heard, N. Carter, and J. Handin for advice and assistance, H. Hess for the AMSOC serpentinite samples, and H. Powers for assistance in securing the Hawaiian olivine. The apparatus was fabricated under Dept. of Defense Advance Research Project Agency contract AF19(628)-1646.

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Oxygen Isotope Fractionation in the System Dolomite–Calcite–Carbon Dioxide

Abstract. *Oxygen isotopes were equilibrated between carbon dioxide and calcite at four temperatures in the range 350° to 610°C and between carbon dioxide and dolomite at 350° and 400°C. Carbon of unusual isotopic composition was used as a tracer to demonstrate the nature and extent of the exchange process. Extrapolation of these data at lower temperatures indicates that at 25°C dolomite is enriched in oxygen-18 by 6.8 per mil with respect to calcite. This result indicates that those natural dolomite-calcite assemblages which show very small fractionations were not formed in isotopic equilibrium.*

Clayton and Epstein (*1*) and Engel *et al.* (*2*) analyzed five coexisting pairs of quartz and dolomite from the Leadville formation and showed that the oxygen isotopic compositions of each mineral of a pair are essentially the same (within 3.5 per mil). These authors suggested that if the isotopic properties of quartz and dolomite were indeed similar, dolomite-calcite pairs could provide a useful geothermometer with about the same sensitivity as the quartz-calcite pair. This argument predicts a dolomite-calcite fractionation of 6 to 10 per mil at 25°C and 1 to 2 per mil at 500°C.

A succession of studies of natural dolomite-calcite assemblages ensued, with conflicting interpretations (*3*). Essentially, the problem involves the existence of large dolomite-calcite fractionations (2 to 4 per mil) in high-temperature rocks and small fractionations (0 to 1 per mil) in low-temperature rocks. Since isotopic fractionations increase with decreasing temperature, there is a basic incompatibility in the natural data and at least one of the types of rocks was not formed in isotopic equilibrium.

Whether or not the large fractionations found in the high-temperature assemblages are equilibrium fractionations can be resolved only by equilibration studies in the laboratory. Unfortunately, dolomite is very resistant to isotopic exchange with aqueous solutions in reasonable times. The first attempts to determine the equilibrium fractionations between dolomite and calcite were made by Epstein, Graf, and Degens (*4*). These authors synthesized dolomite-calcite mixtures by reacting calcium carbonate with magnesium chloride solutions and by decomposing magnesian calcite in the presence of water. The isotopic compositions of the starting materials were not such that values of the final fractionation factor could be bracketed (that is, equilibrium would be approached from only one direction). In addition, there may be unknown kinetic fractionation effects associated with the chemical reactions involved. The fractionations observed in the temperature range 400° to 600°C were approximately 2 per mil, in agreement with the natural hydrothermal results.

Northrop (*5*) and Northrop and Clayton (*6*) have derived a dolomite-water fractionation curve by graphically interpolating, to 100-percent exchange, data from experiments in which equilibration was incomplete. The temperature range studied was 300° to 510°C. Although different dolomites gave consistently different results, the combination of the average values with those of the previously determined calcite-water system (*7*) yielded a dolomite-calcite fractionation curve which extrapolates to a value of 5.6 per mil at 25°C. Due to the uncertainty involved in the extrapolation of the high-temperature data at 25°C, a range of 4 to 7 per mil was given for the dolomite-calcite fractionation at this temperature. These authors also studied carbonate-carbonate and carbon dioxide–carbonate systems but were unable to obtain consistent fractionations.

Our primary aim in this study was to determine dolomite-calcite equilibrium fractionations at some experimentally convenient temperatures in order to resolve the natural data incompatibilities previously mentioned. The only unambiguous way to determine an equilibrium fractionation factor be-