tissue regions representing different stages of bone formation would result in different overall mineral compositions for the entire limb. Therefore, it must be realized that the percentage crystallinity value given for a whole limb represents an average assay of the mineral in a mixture of tissues comprising that limb.

The fact that young bone contains much more amorphous than crystalline mineral suggests that amorphous calcium phosphate may be the first mineral deposited during the overall process of bone formation. As a verification of this, we found, by x-ray diffraction analysis of chick bones, that mineral in the epiphyseal tissue is only 20 percent crystalline (80 percent amorphous), while in the metaphyseal tissue mineral is 60 percent crystalline and 40 percent amorphous (*8*).

The value for nonhaversian, 264-day-old compact rat bone mineral is identical with that obtained for haversian cortical cow bone by infrared analysis, which seems to indicate that amorphous calcium phosphate is present in all bone tissue, independent of microanatomical considerations. This is not surprising since, on a molecular level, amorphous calcium phosphate is a precursor of crystalline apatite in synthetic systems (*9*). These facts are consistent with evidence obtained by electron microscopy which indicates that a noncrystalline mineral phase appears prior to crystalline apatite during early stages of bone formation (*10*). Thus, it may be true that amorphous calcium phosphate can act as a metabolic precursor of crystalline apatite in bone.

We also analyzed surgically separated, adult human dentine and enamel. Enamel samples were 100 percent crystalline apatite, while the mineral portion of the dentine was 65 to 70 percent crystalline. Thus, dentine has a mineral composition akin to that of compact bone, while the much harder and more chemically inert dental enamel consists of only crystalline apatite.

The presence of amorphous calcium phosphate in hard tissues is an important parameter that must be considered in any discussion of the properties of these tissues. For example, there may actually be two separate and distinct mineral ion metabolic pools in skeletal tissue. Moreover, amorphous calcium phosphate may be the first mineral deposited during the calcification process and may subsequently act as a metabolic precursor of crystalline apatite in calcified tissues. The two-phased nature of bone mineral may prove to be a valuable aid in understanding the operative mechanisms of bone metabolism and the molecular basis of bone structure.

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## Electrical Resistivity Changes in Saturated Rock under Stress

Abstract. *Electrical resistivity of water-saturated crystalline rock such as granite, diabase, dunite, or quartzite changes by an order of magnitude prior to fracture of the rock in compression. The effect observed even under high confining pressure is due to formation of open cracks which first appear at one-third to two-thirds the fracture stress.*

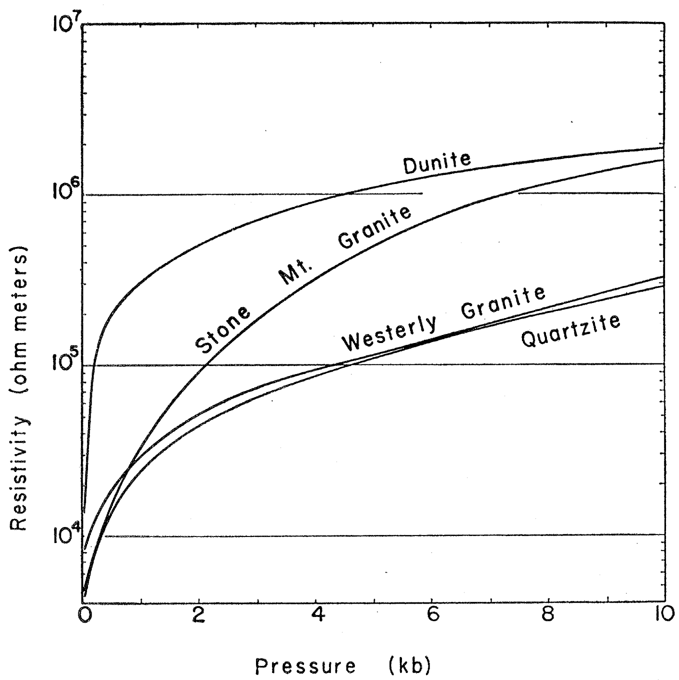
Fracture of brittle materials usually occurs without much warning. If a rock such as granite is stressed in compression, for example, there is little in the stress-strain curve preceding fracture which might predict the point of fracture. However, a number of subtle changes in the structure of the granite do occur prior to fracture. These changes, although not apparent in the axial stress-strain curve, exert a marked influence on certain properties. The most striking effect observed is on the electrical properties; electrical resistivity changes by an order of magnitude prior to fracture of water-saturated crystalline rocks.

Two observations suggested that large changes in resistivity might precede the fracture of rock. Sensitive measurements of volume change (*1*) showed that many rocks became dilatant, that is, they increased in volume slightly, as they were deformed in compression. Surprisingly, this was observed even when specimens were deformed at a confining pressure of 8 kb. The amount of volume increase, relative to elastic changes, was small; typically, it was of the order of a few tenths of a percent. Nevertheless, increase in volume could be detected at one-third to two-thirds the fracture stress. The increase in volume was traced to new cracks which were apparently open and which were strongly aligned parallel with the direction of maximum compression.

Conduction of electricity (through cracks and pore spaces) in a water-saturated crystalline rock such as dunite or granite is primarily ionic. In the laboratory samples the effect of hydrostatic pressure on conductivity is striking (*2*) because of the way in which cracks and pores change shape under pressure. An increase in confining pressure of 10 kb changes resistivity of common crystalline rocks by as much as three orders of magnitude (Fig. 1). A large percentage of this change occurs in the first 2 kb; measurements of linear compressibility and other elastic parameters in this range (*3*) suggest the reason. Most rocks such as granite have minute porosity in the form of cracks; these cracks are closed by a pressure of a few kilobars. The remaining pore spaces are more equant in shape so that further changes in the cross section of conduction paths take place much more slowly as pressure is raised.

When combined, these two sets of observations suggest that if a saturated rock is stressed in compression, one might first see resistivity increase (preexisting cracks forced shut) and then, at about one-third to two-thirds the fracture stress, see rapid decrease (rock becomes dilatant and new cracks form). To observe this effect one would have to ensure that water could move freely in and out of the rock, so that potential conduction paths would contain water.

We measured the effects of stress



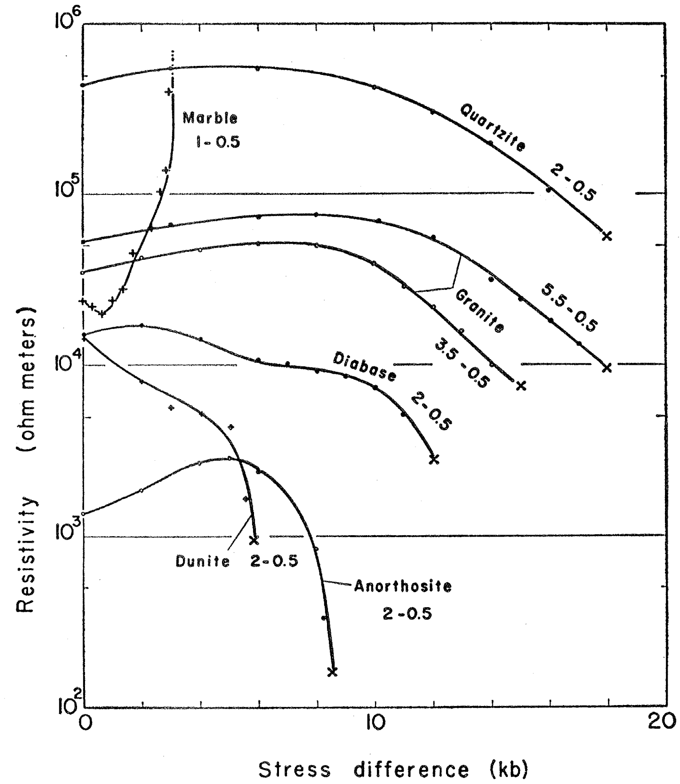




Fig. 1 (left). Effect of hydrostatic pressure on electrical resistivity. Rocks were saturated with tap water (2). Fig. 2 (right). Effect of stress on resistivity. (For greater clarity, the curves have been shifted to a vertical position.) The numbers after the names of the rocks give the total pressure and pore pressure in kilobars, respectively. Fracture in the experiments occurred at point X. The marble did not fracture. To obtain the correct value of resistivity, the value shown for quartzite is multiplied by $10^{-2}$, for granite (3.5 kb) by 0.5, for diabase by 10, for dunite by 10, and for anorthosite by $10^{2}$. Rocks were saturated with tap water and temperature was 50°C.

on resistivity for a variety of rocks (Fig. 2). Confining pressure and pore pressure were held constant and stress was raised (500 bars per hour) while resistivity (10 cy/sec) was measured across the ends of the specimen. The rocks were saturated with local tap water (resistivity, 40 ohm-meters).

Resistivity showed the predicted decrease for all rocks except marble. It began to fall at less than half the fracture stress and fell rapidly near fracture. Initially, most of the rocks showed a slight increase in resistivity. An effective hydrostatic pressure ranging from 500 to 5000 bars was applied before the rock was stressed; for this reason most initial cracks were closed before stress was applied.

Based on the volume of the new cracks, the order of magnitude change in resistivity (Fig. 2) is what one would expect. This new volume is a few tenths of a percent of the total volume of the rock and is close to the initial crack porosity for most of these rocks (*2, 3*). Therefore, decrease of resistivity as new cracks form (under stress) should be about the same as increase in resistivity with crack closure (under hydrostatic pressure).

The behavior of marble was quite different from that of the other rocks; this may have been due to its ductility. Although marble was also dilatant (*1*), new pore space may not have been interconnected. The ductility of the marble was probably responsible for sealing off the conduction paths as the material yielded under stress. Other ductile rocks may behave in the same way and show rather different electrical behavior as a class.

In rocks under stress, the changes in resistivity are far more pronounced than the changes of elastic properties (*4*) and are probably more pronounced than changes of any of the intrinsic properties (magnetic susceptibility, dielectric constant, or thermal conductivity) of the rock-forming minerals. This is due to the fact that the electrical properties of saturated rock are virtually independent of mineral content and depend only on the pore structure of the rock.

Because resistivity changes markedly with stress, electrical properties of saturated rocks might be used, for example, to reveal details of the fracture process in rocks, or to detect minute changes in the structure of a rock which is under stress. Stress measurement techniques usually depend on measurement of elastic strains and conversion of strains to stresses through elastic moduli. It might be simpler to base the measurement on resistivity as most rock in place is saturated with water and techniques for field measurement of resistivity are highly developed. On a larger scale, shallow crustal earthquakes may result from sudden release of accumulated elastic strain. By analogy with laboratory experiments, build-up of strain ought to be accompanied by changes in resistivity; these changes might warn of an impending earthquake (*5*).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