

2) As the Iapetus Ocean (predecessor of the Atlantic) opened in latest Precambrian or early Cambrian time, extensional faults formed. Most were probably normal faults, forming both west of Giles County and at least as far east as a large gravity gradient that passes about 50 km to the southeast (1, 9). Such a fault is the most likely candidate to be active under Giles County today.

3) After a period of thrusting, the Atlantic Ocean opened in Mesozoic time. Additional northeast-oriented extensional faults formed, many as sedimentary basin border faults, but these faults are not known as far to the northwest as Giles County.

From seismologic and core data, the upper crust in Giles County appears to be subject to roughly homogeneous, northeast- to east-trending compressive stress (10). Thus, a midcontinent stress province (11) may extend eastward into the basement under the thrust faults of the Valley and Ridge province. A fault striking northeast that was reactivated in such a stress regime would be a right-reverse fault, consistent with but not required by the sparse first-motion data from Giles County (1, 10).

We have assumed that the seismic zone we have defined was the source of the 1897 shock, but the assumption cannot be tested. The intensity data demonstrate that the meizoseismal area was, indeed, in Giles County (2, 12, 13). Campbell (14) reported, "The shock of May 31 was probably more severe in and about Pearisburg than any other point from which I have information." Pearisburg, being the largest town in the county, may have produced the most and more detailed intensity reports. The earthquakes of 1886 in Charleston, South Carolina, and 1811–1812 in New Madrid, Missouri, are also associated with zones of continuing earthquake activity (15).

Our results provide direct instrumental evidence of a tabular seismic zone in Virginia and an active zone in the Southeast that does not parallel the surficial tectonic fabric. Whether they are representative or atypical of a larger region is not yet known.

We draw four main conclusions (1).

1) The Giles County seismic zone, centered at Pearisburg, strikes northeast and dips nearly vertically. It is about 40 km long, 10 km wide, and 5 to 25 km deep.

2) The seismic zone is in the basement beneath the rocks detached by thrusting. It lies 20° counterclockwise to the trend of the detached structures of the southern Appalachian region.

3) Although low-dip thrust faults have been found to, or suggested to, produce large earthquakes elsewhere (16), such is not the case for the Giles County seismic zone.

4) Although conclusive evidence is lacking, it is likely that (i) this seismic zone is the same one that produced the 1897 shock and that the events felt in the last two decades suggest an apparent resumption of strain energy release after a seismic quiescence of four to five decades and (ii) the northeast-trending seismic zone is most probably the result of reactivation of one or more normal faults from Iapetan time.

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Zeolite Molecular Sieve 4A: Anomalous Compressibility and Volume Discontinuities at High Pressure

Abstract. *Unit cell parameters of synthetic zeolite 4A were measured at several pressures to 40 kilobars with both water and an alcohol mixture as hydrostatic pressure media. Compression in water was normal, with no observed phase transitions. Compression in alcohols was twice as great as in water, and three volume discontinuities were observed. These volume changes in alcohol were rapid with increasing pressure but sluggish in reverse. High-pressure "phases," all of which are dimensionally cubic, are progressively more compressible at high pressure. These unusual high-pressure phenomena, which indicate significant interactions between zeolite 4A and the hydrostatic media, are consistent with differences in zeolite adsorption of water and alcohols.*

A-type zeolites are synthetic, hydrous, alkali aluminosilicates, with exceptionally large structural channels and cavities (1). This cubic framework structure has been employed extensively as a selective sorbent for drying gases and solvents. Aluminosilicate framework compounds, especially those of high symmetry, commonly display "polyhedral tilt" transitions, in which corner-linked networks of AlO_4 and SiO_4 tetrahedra distort at high pressure (2). Zeolite A was selected for crystallographic study at high pressure on the basis of the prediction that the unusually open cubic framework would undergo such revers-

ible tilt transitions. The zeolite crystals instead displayed a series of gradual transitions of a type not previously recorded. In particular, the high-pressure behavior of zeolite A was found to be dependent on the nature of the hydrostatic, pressure-transmitting fluid. These striking and unexpected phenomena are described in this report.

Cube-shaped crystals of fully hydrated zeolite A (Linde Molecular Sieve 4A, space group $Fm\bar{3}c$, $a = 24.55 \text{ \AA}$, $12\text{NaAlSiO}_4 \cdot 27\text{H}_2\text{O}$) were provided by J. V. Smith (Department of Geophysical Sciences, University of Chicago). A 70- μm cube was selected for high-pressure

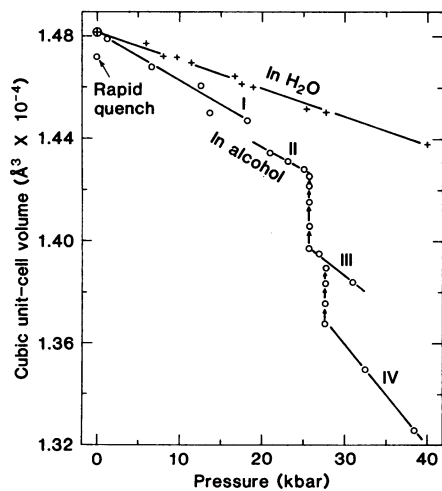


Fig. 1. Unit cell volume of zeolite 4A versus pressure. Plus signs represent unit cell volume in water; compression is normal. Circles represent unit cell volume in a 4:1 mixture of methanol and ethanol; three volume discontinuities are observed.

study and was mounted in a gasketed diamond anvil cell for single-crystal, x-ray diffraction (3). In the first set of experiments a 4:1 mixture of methanol and ethanol was used as the hydrostatic pressure medium; distilled water was employed in the second series. Ruby chips approximately 10 μm in diameter were included as an internal pressure standard in all mounts (4).

Unit cell dimensions of zeolite at 17 different pressures (in the alcohol mixture) from 1 bar to 39 kbar were determined by the procedure of King and Finger (5), in which as many as 12 reflections were measured in eight equivalent positions on an automated, four-circle, x-ray diffractometer. Molybdenum $K\alpha$ radiation was used in all experiments.

Zeolite A is dimensionally cubic at all pressures up to 39 kbar. In a series of unit cell measurements with increasing pressure, three distinct volume discontinuities were observed, at 20, 25, and 32 kbar, as illustrated in Fig. 1. For convenience the four distinct pressure-volume regions are designated phases I to IV. Crystal-fluid interactions complicate the definition of phase in zeolite 4A-alcohol system, however, and details of phase equilibria are not yet resolved. The volume changes of 0.5, 1.9, and 2.1 percent, for transitions I \leftrightarrow II, II \leftrightarrow III, and III \leftrightarrow IV, respectively, occurred in less than the 0.5-hour duration of preliminary unit cell determinations. Additional unit cell measurements were made at a series of decreasing pressures, and whereas compression appeared to be rapidly reversible within each phase region, volume changes from phase IV to III (at 32 kbar) and from III to II (at 25 kbar) were

gradual, taking more than 1 and 4 days, respectively. Volume changes at constant pressure during these transformations varied linearly with the logarithm of time, as illustrated in Fig. 2. Upon reapplication of pressure the original rapid sequence of transitions was again observed. When quenched rapidly from 39 kbar, however, and removed from the pressure fluid within 15 seconds, the crystal was found to have sustained an irreversible reduction in the unit cell volume of 0.40 ± 0.05 percent. The reversible compression behavior of zeolite 4A is dependent on sufficient time to equilibrate with the pressure-transmitting fluid.

A remarkable feature of these transformations is that compressibility is progressively greater for each of the four phases. Compressibilities of the four phases are 1.4 ± 0.1 , 1.6 ± 0.2 , 2.0 ± 0.2 , and $2.8 \pm 0.2 \times 10^{-3} \text{ kbar}^{-1}$, in order of increasing pressure. Thus, the densest of the four zeolite 4A phases is twice as compressible as the phase at room pressure.

A second crystal of zeolite 4A, with the same initial unit cell volume as the previously studied specimen, was mounted with distilled water as the hydrostatic pressure fluid. Ten sets of unit cell parameters were measured from 1 bar to 40 kbar. No volume discontinuities were observed, and thus the zeolite transformations observed in the alcohol mixture, if they occur at all in water, must be at much higher pressure. Furthermore, the compressibility of zeolite 4A in water was approximately half ($0.74 \pm 0.06 \text{ kbar}^{-1}$) the value measured in alcohols (Fig. 1). Zeolite 4A in water thus behaves in a dramatically different way than zeolite 4A in alcohol.

An important conclusion of these high-pressure experiments is that zeolite 4A interacts in a complex way with water and alcohol hydrostatic pressure media. Zeolite 4A has a continuous three-dimensional network of channels approximately 4 \AA in diameter, in addition to larger "cages" approximately 7 \AA in diameter (1). Water molecules (effective diameter $< 2 \text{\AA}$) are easily adsorbed into these channels and cages. When water is used as the hydrostatic pressure medium the internal pressure in these open portions of the structure must rapidly approach the hydrostatic pressure in the diamond cell. The observed compression is thus representative of the aluminosilicate framework alone, independent of channel or cage compression. Zeolite 4A in water thus appears to be relatively incompressible, with no volume discontinuities.

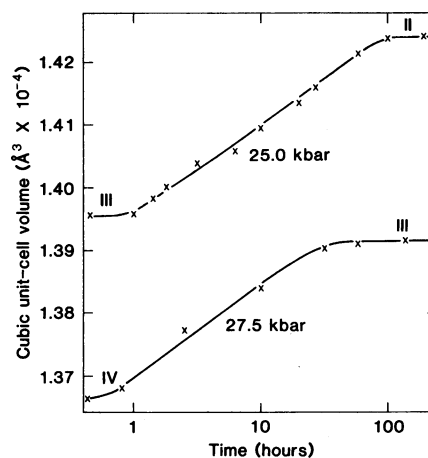


Fig. 2. Variation of unit cell volume of zeolite 4A versus time during transitions from phase IV to III and from III to II.

Methanol (effective diameter approximately 4 \AA) is adsorbed slowly into zeolite 4A under room conditions, whereas ethanol (effective diameter greater than 4 \AA) is excluded from the zeolite 4A channels. In an alcohol pressure fluid, therefore, the internal pressure of channel constituents is probably less than external pressure, and the compression of channels is correspondingly greater than in water.

The reasons for volume discontinuities of zeolite 4A in alcohol are not immediately obvious. The transformation behavior of zeolite 4A is atypical of polyhedral tilting. Known polyhedral tilt transitions involve reductions in symmetry of the tilted, high-pressure phase, whereas in zeolite 4A no change in cubic dimensional symmetry is detected through the three volume discontinuities. In addition, known polyhedral tilt transitions are rapid, whereas the volume discontinuities of zeolite 4A are gradual from high to low pressure. Polyhedral tilting, if present, is thus not the primary cause of these transformations.

The unusual kinetics of the zeolite 4A volume changes are evidence for a diffusion-controlled mechanism. Each of the volume changes is relatively rapid with increasing pressure, but the second and third transformations are gradual upon release of pressure. A diffusion-controlled mechanism could account for the transition kinetics from phase IV to III and III to II, for which volume varies as the logarithm of time (Fig. 2). The unreversed volume change of the rapidly quenched crystal is further evidence of diffusion; the crystal, which was quickly removed from the pressure fluid, had insufficient time to completely reabsorb channel contents, and thus suffered a volume loss.

Methanol may be the diffusing species. Volume discontinuities perhaps correspond to pressures at which specific fractions of methanol (that is, methanol adsorbed into specific positions in the zeolite framework) are squeezed out. As methanol molecules are removed from the channels and cages the entire crystal becomes progressively more compressible. Gradual reabsorption of methanol into compressed channels and cavities could explain the sluggish reversal of the volume discontinuities. Other possible diffusing species are alkali cations or water molecules, for which rapid movement in zeolite channels might be impeded by the larger methanol molecules.

This novel transition and compression behavior is not restricted to zeolite 4A; preliminary experiments on the potassium-exchanged zeolite 3A reveal the same sequence of volume discontinuities in alcohols, though shifted approximately 3 kbar to higher pressure. It is antic-

ipated that studies on other large-channel zeolites, as well as with other pressure-transmitting fluid media, will also reveal fluid-dependent compression and diffusion-controlled, high-pressure transformations.

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Primitive Helium in Diamonds

Abstract. *Thirteen diamond stones from various unspecified mines in South Africa were analyzed for the isotopic ratio of helium-3 to helium-4. Values of the ratio ranged from less than 10^{-7} to $(3.2 \pm 0.25) \times 10^{-4}$. The latter value is higher than the primordial helium-3/helium-4 ratio in meteorites and close to the ratio for solar-type helium. Such extremely high values may represent primitive helium that evolved very little (that is, showed very little increase in radiogenic helium-4) since the formation of the earth.*

Characterization of the state of noble gases in the mantle is important for constraining models of the evolution of the earth's atmosphere. A number of attempts have been made to do this by examining the noble gases in mantle-derived materials. Diamonds are unique among such materials because of their extremely high resistance to chemicals and high temperatures, which promises better preservation of the noble gases. In addition, diamonds are thought to originate in the deeper mantle, whose nature cannot be inferred from a study of volcanic rocks. Previous studies on batches of diamond stones (1), where 10 to 15 stones were analyzed at one time in order to obtain sufficient noble gases, showed that the diamonds had a higher $^3\text{He}/^4\text{He}$ ratio than atmospheric helium. We report here the results of measurements of the $^3\text{He}/^4\text{He}$ isotopic ratio in single diamond stones.

We studied 13 industrial-grade diamond stones (1 to 2 carats each) that were commercially available and thought to come from various unspecified mines in South Africa. The diamonds were kept in hot HNO_3 (80°C) overnight and then

rinsed with acetone and distilled water. Noble gases were extracted by graphitization (1); the diamond stones were heated to 2050°C in a vacuum and completely converted to graphite. Helium isotopic measurements were made with a mass spectrometer equipped with a double collector and having a resolution of about 600. The mass spectrometer has never been used for extraterrestrial samples. Repeated analyses of atmospheric helium ($^4\text{He} \cong 5 \times 10^{-6} \text{ cm}^3\text{STP/g}$) gave a $^3\text{He}/^4\text{He}$ ratio of $(1.16 \pm 0.016) \times 10^{-6}$.

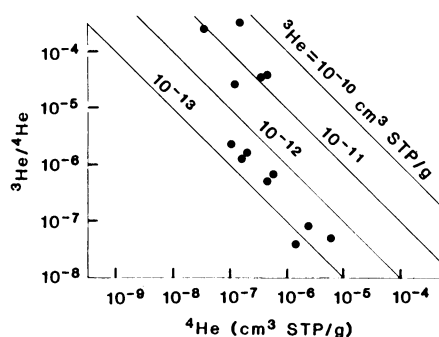


Fig. 1. Plot of $^3\text{He}/^4\text{He}$ versus ^4He for diamond samples.

The measured $^3\text{He}/^4\text{He}$ value (R) was represented as its ratio to the average value in air ($R_a = 1.16 \times 10^{-6}$), which eliminates the effect of instrumental mass discrimination in the final results. The results are shown in Table 1. The errors in R/R_a were calculated as the sum of all the possible errors in the ^3He and ^4He measurements and in the hot blanks—that is, 50 percent of the hot blanks—and must therefore be considerably overestimated. Hence we consider that the very high $^3\text{He}/^4\text{He}$ values observed in some samples cannot be attributed to experimental uncertainty but must represent the helium in the diamonds. Two diamond samples have values of the $^3\text{He}/^4\text{He}$ ratio that are higher than the primordial ratio in meteorites, He-A [$^3\text{He}/^4\text{He} = (1.42 \pm 0.2) \times 10^{-4}$] (2) and are close to the solar value ($^3\text{He}/^4\text{He} \sim 4 \times 10^{-4}$) (3).

The only way to explain the extremely high $^3\text{He}/^4\text{He}$ ratio seems to be to attribute it either to indigenous mantle helium trapped in the diamonds or to a nuclear reaction $^6\text{Li}(n,\alpha)^3\text{H} \rightarrow ^3\text{He}$ in the diamonds. First we consider the latter possibility. Since some diamond mines in South Africa, such as the Premier Mine, are known to have originated as much as 1.2×10^9 years ago (4), it is possible that some diamonds resided for more than 10^9 years in the crust, where the thermal neutron flux could have been high enough to produce significant amounts of ^3He in the diamonds. Assuming $t = 1.2 \times 10^9$ years for the age of the diamonds and taking $\phi =$ eight neutrons per square centimeter per day for the neutron flux in the crust, which was estimated for average granitic rocks (5), we find that the amount of lithium needed to account for the observed amount of ^3He ($\sim 4 \times 10^{-11} \text{ cm}^3\text{STP/g}$) in sample 82401 is

$$n(\text{Li}) = \frac{\text{Li}}{^6\text{Li}} \times \frac{n(^3\text{He})}{\sigma\phi t} \approx 44 \text{ ppm}$$

where σ is the cross section for the reaction $^6\text{Li}(n,\alpha)^3\text{H}$ ($\sigma = 930 \times 10^{-24} \text{ cm}^2$). Although there are no reported data on the lithium content of diamonds, we consider such a high lithium content ($\sim 44 \text{ ppm}$) extremely unlikely for the following reason. The potassium content of diamonds seldom exceeds 10 ppm even for highly inclusion-rich samples (4, 6). Since the K/Li ratio does not vary much in crustal rocks or volcanic rocks, being about 10^3 (7), it is safe to assume that the lithium content of diamonds is much less than the potassium content, say less than 1 ppm.

Figure 1 shows the $^3\text{He}/^4\text{He}$ values plotted against the ^4He content of dia-