

Compressibility of zeolite 4A is dependent on the molecular size of the hydrostatic pressure medium

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Unit-cell parameters of synthetic zeolite 4A were determined at several pressures to 4.0 GPa in four different hydrostatic pressure media: ethanol, methanol, glycerol, and an organofluorine compound, $C_8F_{16}O$ (FC-75). These data, when combined with previously published results on zeolite in water and a water-bearing 4 : 1 methanol : ethanol mixture, reveal that compression of zeolite depends on the relative sizes of the hydrostatic fluid molecules compared with the structural channels in the zeolite framework. Zeolite 4A is most compressible ($\Delta V/V\Delta P = \beta = 0.046 \text{ GPa}^{-1}$) in glycerol and FC-75, which have molecular dimensions that are larger than the zeolite channels. Zeolite is least compressible ($\beta = 0.007 \text{ GPa}^{-1}$) in water, which has a maximum molecular dimension that is significantly smaller than the channel diameter. In methanol and ethanol alcohols, which have intermediate molecular diameters, zeolite 4A also has intermediate compressibility. This zeolite in alcohols, furthermore, progressively undergoes a series of transitions to more compressible states as pressure is raised.

Zeolites, with their exceptionally large structural channels and cavities, may interact with molecular fluids in complex ways. The sorbent and catalytic properties of these hydrous alkali aluminosilicates, for example, are well known.¹ Recent high-pressure studies of zeolite 4A in water and an alcohol mixture demonstrate that the compressibility of zeolite is dependent on the nature of the pressure fluid.² We undertook the present study of the compressibility of zeolite 4A to document further the relationships between fluid molecular size and zeolite compression.

Crystals of zeolite 4A (space group $Fm\bar{3}c$, $a = 24.55 \text{ \AA}$, $12 \text{ NaAlSi}_3\text{O}_8 \cdot 27\text{H}_2\text{O}$) were provided by J. V. Smith (Department of Geophysical Sciences, University of Chicago). Cube-shaped single crystals of edge length 0.07–0.09 mm were mounted in a gasketed diamond-anvil cell for single-crystal x-ray diffraction.³ Ruby chips, approximately 0.01 mm in maximum dimension, were included as internal pressure standards.⁴ Zeolite unit-cell parameters at several pressures to 4.0 GPa were determined by measuring as many as twelve reflections in eight equivalent positions on an automated four-circle x-ray diffractometer.⁵ Molybdenum K_{α} radiation was used in all experiments.

In previously reported experiments² zeolite 4A was observed to be relatively incompressible ($\Delta V/V\Delta P = \beta = 0.007 \text{ GPa}^{-1}$) in water,⁶ which has a maximum molecular dimension significantly smaller than the 4- \AA channels of the zeolite. In a "standard" pressure fluid of 4 : 1 methanol : ethanol that contains water as a result of atmospheric exposure, however, a complex sequence of sluggish, reversible volume discontinuities versus pressure was observed. Furthermore, each successive high-pressure phase was more compressible. It was suspected on the basis of these experiments that zeolite 4A might be significantly more compressible in a fluid with larger molecules that cannot penetrate channels than in water or methanol, which enter the framework.

The compressibility of zeolite 4A was measured in glycerol ($C_3O_3H_6$) and organofluorocarbon FC-75 ($C_8F_{16}O$), both of which are pressure media with diameters significantly greater than 4 \AA and both of which remain hydrostatic to 4.0 GPa. Compressibility was also measured in pure, dried methanol and ethanol alcohols. Pressure-volume (PV) data for zeolite in these four fluids, as well as previously untabulated PV data for zeolite in water and an alcohol mixture, are recorded in Table I.

The compressibility of zeolite 4A in glycerol and FC-75 ($\beta = 0.046 \text{ GPa}^{-1}$) is more than six times greater than in water (Fig. 1). A phase transition is suggested by a probable 3% volume discontinuity, a dramatic decrease in diffraction intensity, a broadening of diffraction maxima, and a discontinuity in compressibility in both media at 1.0 GPa. This behavior is typical of a polyhedral tilt transition,⁷ in which the low-pressure cubic zeolite framework distorts to an intimately twinned, lower symmetry variant at high pressure. The compressibility of the high-pressure phase ($\beta = 0.038 \text{ GPa}^{-1}$) is 20% less than that of the room-pressure phase.

Compression of zeolite 4A in pure, dried ethanol (C_2H_5OH) is similar to compression in the water-saturated 4 : 1 methanol : ethanol mixture.² A possible volume discontinuity at 2.0 GPa is also similar to the 1.8 GPa discontinuity observed during experiments with the alcohol mixture (Fig. 1). Ethanol crystallizes and becomes nonhydrostatic above 2.7 GPa, which was the highest pressure attempted in these experiments.

The compression behavior of the zeolite in pure dried methanol (CH_3OH) is more complex than in other pure pressure media (Fig. 2). During the first cycle of compression experiments, which were performed over a period of eight days, the zeolite compressed significantly more than in water or the alcohol mixture, but less than in the two larger molecule liquids. Upon reduction of the pressure to 0.1 GPa and reapplication of pressure, however, a different compression

TABLE I. Pressure-volume data for zeolite 4A in several pressure media.

Pressure (GPa)	a (Å) ^a	V (Å ³) ^a	V/V_0	Pressure (GPa)	a (Å) ^a	V (Å ³) ^a	V/V_0
<u>Water</u>				<u>Methanol (continued)</u>			
0.0001	12.280(1) ^b	1851.9(4)	1.0000	1.68	12.202(5)	1817(2)	0.9812
0.59(3)	12.269(3)	1846.8(10)	0.9972	1.70	12.202(5)	1817(2)	0.9812
0.81(3)	12.254(3)	1840.1(10)	0.9936	(26 day hiatus)			
0.97(3)	12.254(3)	1840.1(10)	0.9936	2.13	12.188(5)	1810(2)	0.9774
1.17(3)	12.251(3)	1838.6(10)	0.9917	2.35	12.163(5)	1800(2)	0.9720
1.66(3)	12.234(3)	1831.1(10)	0.9888	2.85	12.124(5)	1782(2)	0.9623
1.74(3)	12.224(3)	1826.8(10)	0.9864	3.18	12.078(5)	1762(2)	0.9515
1.92(3)	12.222(3)	1825.6(10)	0.9858	3.90	12.005(5)	1730(2)	0.9342
2.54(3)	12.195(3)	1813.6(10)	0.9793	0.22	12.272(5)	1848(2)	0.9979
4.00(3)	12.160(3)	1798.1(10)	0.9709	1.54	12.210(5)	1820(2)	0.9828
<u>Glycerol</u>				2.54	12.126(5)	1783(2)	0.9628
0.0001	12.280(1)	1851.9(4)	1.0000	3.64	12.008(5)	1732(2)	0.9353
0.23(2)	12.230(1)	1829.5(6)	0.9879	0.06	12.288(5)	1855(2)	1.0017
0.38(2)	12.224(3)	1826.6(10)	0.9863	<u>Ethanol</u>			
0.53(2)	12.168(2)	1801.8(9)	0.9729	0.0001	12.280(1)	1851.9(4)	1.0000
0.82(2)	12.106(3)	1774.2(12)	0.9580	0.56(2)	12.249(5)	1837.8(16)	0.9924
0.87(2)	12.085(3)	1764.9(11)	0.9530	1.87(2)	12.190(3)	1811.2(10)	0.9780
0.99(2)	12.034(2)	1742.8(8)	0.9411	1.97(2)	12.181(3)	1807.5(10)	0.9760
1.38(2)	11.990(1)	1723.9(4)	0.9309	2.05(2)	12.157(3)	1796.9(10)	0.9703
<u>FC-75</u>				2.70(2)	12.121(3)	1780.8(10)	0.9616
0.0001	12.280(1)	1851.9(4)	1.0000	<u>Alcohol Mixture (4:1 methanol:ethanol, not dried; see reference 2)</u>			
0.35(2)	12.234(6)	1831(2)	0.9887	0.0001	12.280(1)	1851.9(4)	1.0000
0.52(2)	12.178(3)	1806.2(10)	0.9753	0.15(3)	12.276(6)	1850(2)	0.9990
0.93(2)	12.107(1)	1774.7(2)	0.9583	0.65(3)	12.244(3)	1835.6(5)	0.9912
1.10(2)	12.024(3)	1738.6(10)	0.9388	1.25(3)	12.221(5)	1825.4(12)	0.9857
1.76(2)	11.925(6)	1696(2)	0.9158	1.42(3)	12.194(6)	1813(2)	0.9790
<u>Methanol (in sequence of experiments)</u>				1.82(3)	12.184(3)	1808.7(5)	0.9767
0.0001	12.280(1)	1851.9(4)	1.0000	2.08(3)	12.150(5)	1793.5(12)	0.9685
0.88	12.183(5)	1808(2)	0.9763	2.23(3)	12.140(6)	1789(2)	0.9660
1.51	12.126(5)	1783(3)	0.9628	2.45(3)	12.133(6)	1786(2)	0.9644
2.43	12.055(5)	1752(2)	0.9460	2.56(3)	12.048(3)	1749(1)	0.9444
3.32	11.967(5)	1714(2)	0.9255	+ 4 days ^c	+ 4 days ^c	+ 4 days ^c	
3.58	11.953(5)	1708(2)	0.9223	2.56(3)	12.119(3)	1780(1)	0.9612
0.84	12.245(5)	1836(2)	0.9914	2.64(3)	12.042(4)	1746.6(9)	0.9431
0.23	12.274(5)	1849(2)	0.9984	2.75(3)	11.956(3)	1709(1)	0.9228
1.10	12.234(5)	1831(2)	0.9887	+ 3 days ^c	+ 3 days ^c	+ 3 days ^c	
1.42	12.222(5)	1826(2)	0.9860	2.75(3)	12.025(3)	1739(1)	0.9390
1.82	12.194(5)	1813(2)	0.9790	3.07(3)	12.005(2)	1730.2(5)	0.9343
2.97	12.051(5)	1750(2)	0.9450	3.23(3)	11.904(6)	1687(2)	0.9110
				3.82(3)	11.836(3)	1658(1)	0.8953

^aUnit-cell edge (a) and volume (V) are recorded for the 12-Å zeolite subcell. Actual unit-cell edge is $2a$ (volume is $8V$) for the phase at room pressure.

^bParenthesized figures represent estimated standard deviations.

^cSee reference 2 for a description of the time-dependent experiments on zeolite 4A in an alcohol mixture.

behavior was observed. In this and all subsequent cycles, zeolite 4A in methanol was less compressible than in the alcohol mixture (Fig. 2).

The variable compression behavior of zeolite 4A in different pressure fluids may be interpreted as a consequence of fluid-crystal interactions. Larger diameter molecules, such as glycerol and FC-75, cannot enter the zeolite framework; the resultant pressure response is the intrinsic compression of zeolite 4A and is analogous to volume changes of most silicates in hydrostatic media. The bulk modulus of this zeolite in glycerol and FC-75 (21 GPa) is similar to bulk moduli of other open framework compounds, and is significantly smaller than that observed for close-packed silicates (typically 125–200 GPa). Water molecules, on the other hand, are small enough to pass through all the zeolite channels. At high water pressure the crystal is, in effect, compressed inter-

nally; the resultant bulk modulus (145 GPa) corresponds to the pressure response of the corner-linked tetrahedral elements of the structure.

The more complex, time-dependent behavior of zeolite 4A in methanol and the alcohol mixture may be a consequence of the similar cross-section dimensions of zeolite channels and these alcohol molecules. Molecules of ethanol or methanol gradually enter and fill the channels and cavities of zeolite 4A, perhaps displacing some structurally bonded water in the process, thus causing the time-dependent compression effects observed in these experiments. The details of fluid-crystal interactions are not certain, but the logarithmic variation of unit-cell volume with time observed by Hazen² is suggestive of a diffusion-controlled process.

A significant anomaly of these results is that first-cycle compression of zeolite 4A in methanol is greater than in

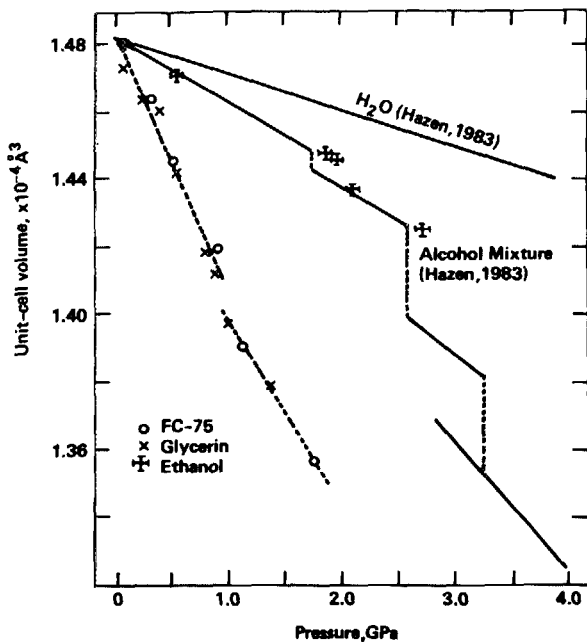


FIG. 1. Compression of zeolite molecular sieve 4A in different hydrostatic pressure fluids. In water, compressibility is 0.007 GPa^{-1} , but in larger molecule liquids such as glycerol and organofluorocarbon FC-75 the compressibility is more than six times greater (0.046 GPa^{-1}). In an alcohol mixture and in pure dried alcohols an intermediate compressibility with several volume discontinuities is observed.

ethanol. This anomaly may be an artifact of the time-pressure history of the experiments; zeolite in ethanol was first studied near room pressure and then at 0.56 GPa for the first three days of the experiments, whereas zeolite in methanol was studied at 0.86 GPa within the first 24 hours of being mounted. The crystals, therefore, may have had more time to equilibrate in ethanol than in methanol. This anomaly underscores the complexity of zeolite-fluid interactions at high pressure. Whatever the structural origin of crystal-fluid interaction, it is important to consider these effects in high-pressure studies of compounds with structural channels and cavities.

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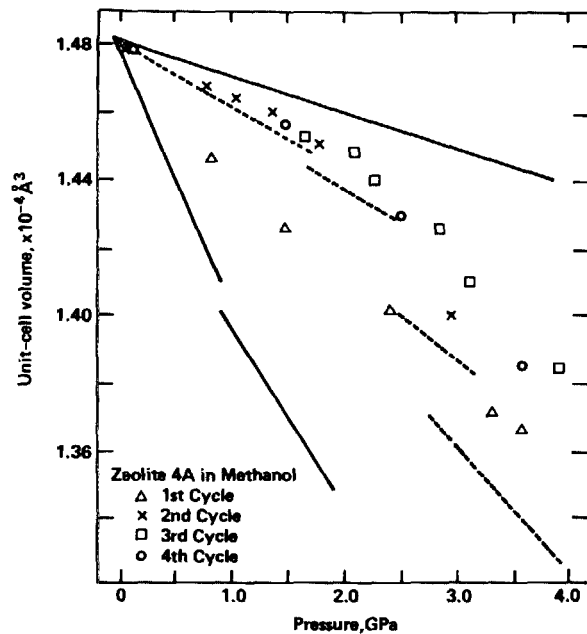


FIG. 2. Compression of zeolite molecular sieve 4A in methanol changes with pressure history. The zeolite was more compressible during the first pressure cycle, which lasted eight days, than in subsequent cycles. This behavior indicates complex fluid-crystal interactions that are not understood in detail.

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⁶Compressibilities and bulk moduli are calculated from regression analysis of PV data in Table I with a first-order Birch-Murnaghan equation of state in which a value of 4 was assumed for K' . The equation is $P = \frac{1}{2}K_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}]$.

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