large quantum spin fluctuations (*6*) at low temperatures. The ordering temperature for a one- or two-dimensional Heisenberg spin lattice is 0 K, whereas a three-dimensional system would condense into long-range order at about (*17*) $3J_{dd}$, leading to small spin fluctuations at low temperature.

2) The large superexchange of the linear Cu-O-Cu bonds leads to large negative J_{dd} and hence to high-frequency spin waves.

3) In the CuO sheets and chains, oxygen $p\pi$ holes on adjacent oxygens have large matrix elements leading to high mobility (allowing the holes to move freely).

4) The ferromagnetic pairing between the localized oxygen $p\pi$ hole and the adjacent copper *d* electron couples the conduction electrons to the copper *d* magnons, leading to the attractive pairing responsible for superconductivity.

5) For the 1-2-3 system, the one-dimensional Cu-O chains may play more than one important role. Perfect chains would indeed lead to superconductivity; however, the specific value of T_c depends sensitively upon the average magnon polarization, τ. The ferromagnetic coupling between chains and sheets may lead to a decreased τ that increases T_c for superconductivity in both the chains and sheets. For values of y (in $Y_1Ba_2Cu_3O_y$) around $y = 6.5$ (and for the tetragonal phase), the observed superconductivity may be due to sheets.

6) The equations for T_c and Δ, Eqs. 21 and 22, clearly indicate those quantities that should be maximized and minimized in order to develop higher temperature superconductors.

A qualitative view of the magnon-pairing model is as follows. A conduction electron (oxygen $p\pi$-like) tends to repolarize the nearby copper *d* spins into local ferromagnetic order. As this oxygen $p\pi$ electron moves along, it tends to leave behind a wake with ferromagnetically paired copper spins. As a second conduction electron is scattered, it finds it favorable to be scattered into the wake of the first electron since there is already ferromagnetic polarization of the copper spins. The net result is the attractive interaction responsible for superconductivity.

One puzzle in understanding these systems concerns why $La_{2-x}Sr_xCrO_4$ is not a superconductor beyond $x = 0.3$ and why other systems (such as $La_4BaCu_5O_{13}$ and $La_5SrCu_6O_{15}$) (*18*) with similar sheets and chains and a high level of oxidation are semiconductors. In our mechanism, this is easily explained in terms of subtle shifts in the net Madelung energy at each oxygen (because of changes in location and charge of cations) that shifts the relative oxidation potential of various oxygens. This arises because the magnon-pairing model requires holes in the proper oxygen $p\pi$ orbital of the sheets and chains. Thus, Guo *et al.* (*4*) showed that changing x from 0 to 0.3 in $La_{2-x}SrCuO_4$ shifts the lowest ionization potential from the sheet oxygen to the apex oxygen (which does not contribute to superconductivity). This suggests that the above semiconducting cuprates might be made into superconductors by appropriate replacement of cations or changes in structure.

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Spectroscopic Evidence for Pressure-Induced Coordination Changes in Silicate Glasses and Melts

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Infrared spectra demonstrate that at pressures above 20 gigapascals and room temperature the regular tetrahedral coordination of oxygen around both silicon and aluminum ions is severely disrupted in SiO_2, $CaMgSi_2O_6$, and $CaAlSi_2O_8$ composition glasses. The spectra are consistent with gradual, pressure-induced increases in the coordination numbers of silicon and aluminum. A variety of coordination environments, from sixfold to fourfold, appears to be present at pressures as high as about 40 gigapascals. This apparent change in coordination is not quenchable at room temperature: on decompression, the glasses return to tetrahedral coordination. This continuous and reversible coordination change in amorphous silicates explains the lack of observation of coordination changes in silicate glasses quenched from high pressure, the shallow melting slopes observed for mantle silicates at high pressures, and the possible presence of neutrally buoyant magmas deep within the terrestrial planets.

THE PROPERTIES OF SILICATE MELTS, such as density, viscosity, and chemical diffusivity, control processes of differentiation by which the interiors of Earth and other terrestrial planets evolve over geological time. As melt properties are largely determined by the geometrical packing and coordinations of ions, there has been considerable interest in documenting how the structures of both melts and glasses change with pressure, or in the case of planets, with increasing depth.

At ambient conditions, silicate melts and glasses are structurally ordered in the sense that they exhibit a well-defined nearest neighbor coordination of four oxygen ions around silicon and aluminum ions. Under pressure, however, it is expected that the coordination increases from fourfold (tetrahedral arrangement) to sixfold (octahedral arrangement), resulting in a drastic change in melt properties (*1*). This expectation is based on the coordination changes observed among crystalline silicates under pressure. That such a change occurs in melts and

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glasses is supported by molecular dynamics simulations (*2*) and by the analysis of shock-wave compression measurements on liquids (*3*), but it has so far not been verified by direct observations under pressure. Thus, the purpose of our study was to determine by in situ, spectroscopic measurements whether or not the primary coordinations of noncrystalline silicates do change with pressure.

In this work, we have measured the mid-infrared absorption spectra of three silicate glasses to pressures of 40 GPa (*4*). Glasses of silica (SiO_2), anorthite ($CaAl_2Si_2O_8$), and diopside ($CaMgSi_2O_6$) compositions were examined in order to simulate the range of structures and compositions that is representative of silicate melts within Earth and terrestrial planets (*5*). The first two compositions consist of frameworks of corner-linked tetrahedra, with silica being a completely polymerized network of SiO_4 tetrahedra. In anorthite glass, half of the tetrahedra contain aluminum instead of silicon; also, calcium ions are inserted within the framework of tetrahedra. Finally, diopside glass is believed to contain chains of SiO_4 tetrahedra that are cross-linked by calcium and magnesium ions (*6*).

Room temperature infrared absorption spectra of silica, anorthite, and diopside glasses all exhibit major changes under compression (Fig. 1). Notably, the strong absorption bands observed initially near 1100 cm^{-1} decrease significantly in amplitude relative to the region between 600 and 900 cm^{-1} as pressure is increased (*7*). Whereas the absorption at about 1100 cm^{-1} is caused by SiO_4 (and, for anorthite, AlO_4) tetrahedral stretching vibrations, the increased absorption between 600 and 900 cm^{-1} at pressure is assigned to the stretching and O–Si–O bending vibrations of SiO_6 octahedra. These octahedral vibrations are assigned on the basis of their observed frequencies in crystalline phases (*8*). Thus, we interpret our spectroscopic observations as showing the loss of tetrahedral coordinations for silicon and aluminum in glasses, with the coordination of silicon (and probably aluminum) (*9*) increasing gradually from fourfold to sixfold above 10 to 20 GPa (*10*). For comparison, the crystalline equivalents of these glasses transform at lower pressures to phases containing octahedrally coordinated silicon and aluminum (*11*).

The coordination change commences at a lower pressure in the anorthite glass (~10 GPa) than in the diopside and silica glasses (~17 to 25 GPa). It is likely that this difference reflects the presence of aluminum, which changes coordination at a lower pressure than silicon and is only present within the anorthite composition glass (*11*). Both silica and diopside glasses exhibit measurable absorption at 950 to 1200 cm^{-1} implying that a range of coordinations, from fourfold to sixfold, is present even at the highest pressures of this study. Similarly, the lack of discrete peaks above 650 cm^{-1} in the high-pressure anorthite glass spectrum suggests that both aluminum and silicon are distributed over a range of sites with coordinations up to six, but with regular tetrahedral coordination being essentially nonexistent. Finally, the absorption at about 500 cm^{-1} is assigned to deformational motions of the silicon-oxygen framework that are present in all three glasses.

The structural transformations docu-

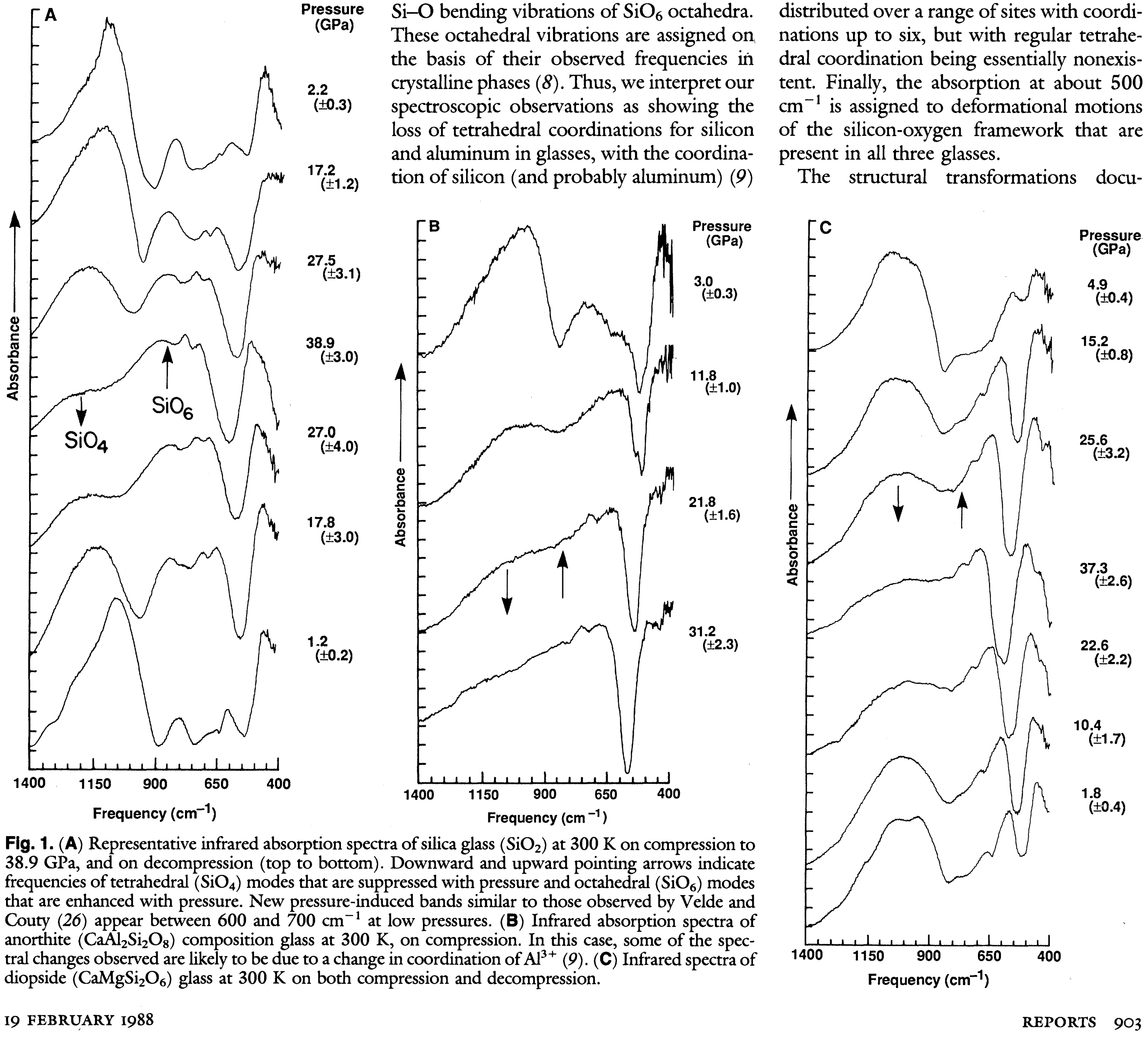

Fig. 1. (**A**) Representative infrared absorption spectra of silica glass (SiO_2) at 300 K on compression to 38.9 GPa, and on decompression (top to bottom). Downward and upward pointing arrows indicate frequencies of tetrahedral (SiO_4) modes that are suppressed with pressure and octahedral (SiO_6) modes that are enhanced with pressure. New pressure-induced bands similar to those observed by Velde and Couty (*26*) appear between 600 and 700 cm^{-1} at low pressures. (**B**) Infrared absorption spectra of anorthite ($CaAl_2Si_2O_8$) composition glass at 300 K, on compression. In this case, some of the spectral changes observed are likely to be due to a change in coordination of Al^{3+} (*9*). (**C**) Infrared spectra of diopside ($CaMgSi_2O_6$) glass at 300 K on both compression and decompression.

mented here for glasses under pressure differ in two important respects from the analogous transformations in crystalline silicates. First, the coordination changes in the glasses occur continuously over an extended pressure range. In contrast, crystals of the same composition exhibit coordination changes at discrete pressures associated with equilibrium phase transitions. The second and more remarkable difference is that coordination changes in the crystalline phases are hindered by kinetics, even at temperatures well above 300 K. The glasses, however, appear to transform reversibly at room temperature: the spectra of the glasses after quenching from high pressure are nearly identical to the spectra of the starting materials (*12*). This indicates that tetrahedral coordinations of both aluminum and silicon are reestablished when pressure is decreased. Our observation that glasses return to tetrahedral coordination on decompression probably explains the difficulties in quenching octahedral aluminum within silicate glasses from high pressures (*13*).

The reversibility that we observe for the coordination changes in silicate glasses is important in that it justifies the extension of our results to silicate melts. As the glass state is simply a kinetically frozen form of liquid that is achieved at low temperatures (well below the melting temperature), any reversible transformation found to occur in glass is also expected to occur in the corresponding but kinetically unhindered liquid (*14*). Recognizing that kinetic hindrances are significantly reduced at the high temperatures of the melt, we anticipate that the coordination changes observed here in glasses could occur at lower pressures in silicate melts of the same compositions. In fact, even more extreme coordinations could be achieved in the melts than in the glasses because of possible kinetic limitations on glass structure. In this sense, our observations on glasses lead to a conservative estimate of the structural changes that occur in silicate melts under pressure.

Based on our observations, as well as previous studies, the compression of silicate melts and glasses appear to be accommodated by three processes occuring between 0 and 30 GPa. Below 10 GPa, the average Si–O–Si angle between tetrahedra decreases upon compression. It is likely that this involves a decrease in the size of the rings of tetrahedra making up the structure, from five- to eight-membered toward three- and four-membered rings with increasing pressure (*15*). The range of Si–O–Si bond angles is also likely to narrow, with intertetrahedral angles remaining greater than 120° in order to minimize Si–Si repulsions (*16*).

Above 10 GPa, by analogy with crystalline equivalents, we expect the tetrahedra themselves to distort prior to the onset of the coordination change (*17*). Thus, the O–Si–O angle deviates from the ideal tetrahedral value (109.5°) with compression. We infer that this change in angle is associated with a breakdown of the strong sp^3 covalent bonding of the SiO_4 tetrahedra, and an approach toward mixed ionic and sp^3d^2 hybridized bonding present within both ideal and distorted SiO_6 octahedra. The change in Si–O bonding character and in the local symmetry of oxygen ions surrounding silicon ions probably causes the dramatic loss of the Raman spectrum of SiO_2 glass observed at high pressures (*18*).

At pressures above about 20 GPa the silicon coordination increases toward sixfold with distorted tetrahedra converted to distorted and regular octahedra. As noted above, the actual transition pressure is likely to depend somewhat on the temperature and composition of the melt or glass. Nevertheless, the structure can be described over a broad pressure range as consisting of a variety of distorted, corner-sharing and edge-sharing polyhedra of oxygen ions around cations. Equivalently, the structure above 15 to 20 GPa can be described as approaching a random close packing of oxygen ions (*19*), with cations placed interstitially. Because of the breakdown of the strong, tetrahedral Si–O bonds, we expect this densely packed structure to be characterized by weaker bonding and less pronounced polymerization than is present in silicate melts and glasses at low pressures (*20*). Both the bond weakening and the increased (and variable) coordination present at high pressures are likely to result in a significant enhancement of ion mobility and hence of the chemical diffusivity of silicate melts at high pressures. This conclusion is in accord with the results of previous molecular dynamic simulations (*2*). Such increases in ionic mobility within liquids are generally associated with decreases in their viscosity, as is reflected by the Stokes-Einstein relation (*21*). Thus, silicate magmas deep inside planets may have dramatically enhanced flow properties over those observed at shallower depths.

Our observation of a continuous shift in coordination number with increasing pressure also provides a rationale for the extremely shallow melting slopes observed for high-pressure mantle silicates: the change in the melting point of silicates with pressure in some cases exceeds 100 K/GPa at low pressures (*22*), but decreases to between 0 and 15 K/GPa at pressures greater than ~20 GPa (*23*). This decrease in the slope of the fusion curve may be ascribed to continuous changes in the structure of the liquid. As pressure is increased, the structure of the liquid becomes denser more rapidly than the coexisting solid because of the shift within the liquid to higher coordination. This produces a decrease in the volume change on melting and thus, by the Clausius-Clapeyron relation, a progressively smaller change in the melting temperature of mantle silicates with increasing pressure. Also, the pressure-induced depolymerization of the melt as it adopts higher coordinations may increase the entropy change on melting, accentuating this volumetric effect on the melting curve. Taking into account the compositional differences between coexisting melts and crystals for mantle silicates, the decrease in the volume change on melting at high pressures is likely to cause the melt density to equal or even surpass the density of the coexisting solid (*3, 23*).

The approach and possible crossover of the densities of liquid and solid silicates at high pressures could result in gravitationally stable melt layers existing within the transition zone of Earth's mantle (*3, 24*) (depth, 400 to 900 km; 13 to 30 GPa in pressure); at greater depths magmas could even sink, rather than rising as they do in the crust and upper mantle to produce volcanism at the surface. Thus, if large-scale melting occurred early in Earth's history (*25*), this melting would not only have produced extensive compositional stratification of the mantle within the transition zone, but possibly also between the upper and lower mantle. Indeed, the mechanism of terrestrial differentiation is principally governed by density differences, and the melt components with higher densities would thus tend to be enriched within the lower mantle. In contrast to the terrestrial mantle, however, the only region in which we would expect gravitationally stable melt layers to form in the lower pressure interior of Mars would be at the bottom of that planet's mantle. Although on Earth, and probably also on Venus, magmas may stably stratify or even sink at depth, the lack of neutrally or negatively buoyant melts on Mars will mean that Martian surface volcanism is more likely to sample the entire depth range of a relatively homogeneous mantle. Therefore, structural changes within melts at pressure may be one of the principal driving forces governing the differentiation histories of the mantles of terrestrial planets.

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4. All experiments were performed at room temperature on samples of commercially available SiO_2-Herasil glass, and anorthite and diopside glasses synthesized from $CaCO_3$, Al_2O_3, and SiO_2 gel. Anorthite and diopside composition glasses are from the same material used for shock compression measurements, and they are characterized elsewhere (*3*). The SiO_2 glass sample is the same as was used in a previous Raman spectroscopic investigation under pressure [R. Hemley, H. K. Mao, P. M. Bell, B. O. Mysen, *Phys. Rev. Lett.* **57**, 747 (1986)]. In order to ensure sufficiently low optical density for the infrared measurements, glasses were ground to powders with particle sizes below 4 μm and diluted to approximately 3% by weight in CsI. The CsI served as both an infrared window and a pressure medium. Pressures were generated with a modified Mao-Bell type diamond anvil cell equipped with type II diamonds with 500-μm culets. The ruby fluorescence technique [H. K. Mao, P. M. Bell, J. W. Shaner, D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978)] was used to measure pressures in the samples, with a system described elsewhere [Q. Williams and R. Jeanloz, *Phys. Rev. B* **31**, 7449 (1985)]. In order to accurately characterize pressure gradients, pressures were measured at 6 to 11 points in each sample. Samples were gasketed by means of spring steel with gasket holes varying in diameter between 150 and 275 μm. A Bomem DA3.02 Fourier transform interferometer with KBr beamsplitter, liquid He-cooled Ge:Cu detector, and globar source was used to collect all spectra. Spectra were recorded from 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}.
5. The only major magma components not represented in our glasses are iron and sodium oxides, each of which generally represents less than 10 mol% of natural silicate liquids; see the report of the Basaltic Volcanism Study Project, *Basaltic Volcanism on the Terrestrial Planets* (Pergamon, New York, 1981).
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7. Although our experiments are not hydrostatic, changes in pressure gradients (and resultant shear forces) do not appear to affect the results reported here: spectral changes occur at identical pressures in samples with different stress gradients. Also, the Raman spectrum of silica glass compressed under nearly perfectly hydrostatic conditions vanishes over the same pressure range at which we observe the major changes in the infrared spectra [Hemley *et al.* in (*4*)]. Therefore, the spectroscopic evidence for coordination changes appears to be independent of the state of stress within the glass samples (*18*).
8. At ambient pressures, infrared-active SiO_6 octahedral stretching vibrations of geophysically relevant crystalline phases lie between ~750 to 850 cm^{-1}, whereas Si–O–Si octahedral bending vibrations fall in a range between 440 and 690 cm^{-1}. The pressure shift of the stretching vibrations is generally between 2.2 and 2.7 cm^{-1}/GPa, so that at 30 GPa octahedral stretching vibrations lie between ~770 and 920 cm^{-1} [Q. Williams, R. Jeanloz, P. McMillan, *J. Geophys. Res.* **92**, 8116 (1987); A. Hofmeister, J. Xu, S. I. Akimoto, Abstracts with Program, 14th General Meeting of the International Mineralogical Association (Mineralogical Society of America, Washington, DC, 1986), p. 126]. We also note that there is no evidence in any of our spectra for pressure-induced crystallization of the glass samples. Additionally, the disappearance of the bands associated with tetrahedral stretching vibrations cannot be attributed to a pressure-induced change in the selection rules for infrared-active vibrations. Within an amorphous solid, all such symmetry-dependent selection rules are relaxed by the lack of periodicity within the glass structure (*14*). Finally, absolute band intensities depend on the derivative of the dipole moment of the vibration with respect to its normal coordinate. Pressure-induced changes within these derivatives cannot account for the presence of the new bands that we attribute to SiO_6 groups.
9. We infer that aluminum in fivefold and sixfold coordination contributes to the absorption between 600 and 900 cm^{-1} for anorthite under pressure on the basis of the frequencies observed in crystalline polymorphs with these coordinations [*Infrared Spectra of Minerals*, V. C. Farmer, Ed. (Mineralogical Society, London, 1974)]. We cannot uniquely separate this contribution from the absorption caused by silicon in octahedral coordination, however.
10. The lower frequency of the main absorption feature with increasing pressure is not attributable to vibrations of silicon or aluminum in tetrahedral coordination because, in general, pressure shifts infrared-active tetrahedral stretching bands to higher frequencies; see, for example, J. Xu *et al.*, *Carnegie Inst. Washington Yearb.* **82–83**, 352 (1983); Q. Williams, R. Jeanloz, M. Akaogi, *Phys. Chem. Miner.* **13**, 141 (1986); R. Couty and B. Velde, *Am. Mineral.* **71**, 99 (1986). Below 20 GPa, we observed the tetrahedral vibrational modes to increase in frequency with pressure, as expected.
11. Silicon is octahedrally coordinated in both the perovskite and rutile-structured polymorphs of silicates that are formed at high pressures. Under equilibrium conditions, diopside and anorthite crystals break down to assemblages involving $CaSiO_3$ perovskite at ~15 to 22 GPa, whereas SiO_2 converts to rutile-structured stishovite at ~8 GPa [L. G. Liu, in *The Earth: Its Origin, Structure and Evolution*, M. W. McElhinny, Ed. (Academic Press, Orlando, FL, 1979), pp. 177–202; S. M. Stishov and S. V. Popova, *Geokhimiya* **10**, 923, (1962)]. Aluminum in crystalline anorthite enters octahedral coordination with the formation of an assemblage containing kyanite and grossularite at ~3 GPa [F. R. Boyd and J. L. England, *Carnegie Inst. Washington Yearb.* **60**, 113 (1961)].
12. The tetrahedral stretching band appears at 1040 cm^{-1} in the quenched silica, compared with 1090 cm^{-1} in the starting material, implying that there is some irreversibility in the compaction process. Similarly, the tetrahedral bands at 950 to 1100 cm^{-1} in the quenched diopside glass are systematically shifted to lower frequency by 20 cm^{-1} relative to the starting material. We note, however, that these are small changes compared to those found here under pressure. They are consistent with previous infrared studies on both pressure and neutron-densified fused silica in suggesting that the force constant for the asymmetric stretching of the SiO_4 group decreases irreversibly upon compaction [I. Simon, *J. Amer. Ceram. Soc.* **40**, 150 (1957); S. Mochizuki and N. Kawai, *Solid State Commun.* **11**, 763 (1973); J. B. Bates, R. W. Hendricks, L. B. Shaffer, *J. Chem. Phys.* **61**, 4163 (1973); J. Arndt and D. Stoffler, *Phys. Chem. Glasses* **24**, 104 (1969)]. Additionally, the Si–O–Si bond angles in densified fused silica are irreversibly decreased from those in nondensified glass (*15*), which is believed to accompany a decrease in the average size of rings of silicate tetrahedra within the glass. The lowering of the force constant for the asymmetric SiO_4 stretching vibration can thus be ascribed to a combination of two effects, both of which are correlated with this irreversible narrowing of the range of Si–O–Si bond angles. Both experiments and theory have documented that a decrease in the Si–O–Si angle causes the Si–O bond to lengthen slightly, and thus to become weakened [R. A. B. Devine and J. Arndt, *Phys. Rev. B* **35**, 9376 (1987); G. V. Gibbs, E. P. Meagher, M. D. Newton, D. K. Swanson, in *Structure and Bonding in Crystals*, M. O'Keeffe and A. Navrotsky, Eds. (Academic Press, Orlando, FL, 1981), pp. 195–225]. Therefore, the force constant and frequency of vibrations involving Si–O stretching decrease. Additionally, the frequency of this vibration is lowered by the Si–O motion being directed along the bond at a smaller angle to the O–Si bond between the bridging oxygen and the next silicon in the network of the densified glass.
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15. This is suggested both by the irreversible decrease in the Si–O–Si angle in samples quenched from pressure [see (*12*); P. McMillan, B. Piriou, R. Couty, *J. Chem. Phys.* **81**, 4234 (1984); R. A. B. Devine, R. Dupree, I. Farnan, J. J. Capponi, *Phys. Rev. B* **35**, 2560 (1987)], and by the pressure-induced increase in amplitude of the D_1 and D_2 Raman "defect" bands [Hemley *et al.*, in (*4*)], which have been associated with four- and three-membered rings, respectively [S. K. Sharma, J. F. Mammone, M. Nicol, *Nature (London)* **292**, 140 (1981); F. L. Galeener, *Solid State Commun.* **44**, 1037 (1982)].
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17. For example, the compression mechanism of SiO_2-quartz is known to shift at high pressures from predominantly Si–O–Si angle changes to distortions of the tetrahedra [L. Levien, C. T. Prewitt, D. J. Weidner, *Am. Mineral.* **65**, 920 (1980)]. Additionally, the low pressure behavior of GeO_2 is thought to mimic the behavior of SiO_2 at high pressures, and quartz-structured GeO_2 is known to compress almost solely by tetrahedral deformations [J. D. Jorgenson, *J. Appl. Phys.* **49**, 5473 (1978)]. Finally, the Raman spectrum of GeO_2 glass undergoes a decrease in intensity at 8 GPa similar to that observed in the Raman spectrum of silica glass above 30 GPa [S. K. Sharma and J. F. Mammone, *Carnegie Inst. Washington Yearb.* **78**, 640 (1978)]. Indeed, it appears that the more weakly bound the cation-oxygen tetrahedra, the lower the pressure at which they break down: Tischer and Drickamer [*J. Chem. Phys.* **37**, 1554 (1962)] have documented a coordination change of cobalt tetrahedra in silicate glasses occurring continuously and reversibly at pressures of only 4 to 8 GPa.
18. We attribute this loss of intensity in the Raman spectrum of SiO_2 glass at high pressures, in accord with Hemley *et al.* [in (*4*)] to a combination of several complementary effects. First, the loss of short-range order around silicon cations, and the resultant presence of a large number of different silicon sites and coordinations could produce severe broadening and loss of peak intensity in the high-pressure spectrum [see also, P. McMillan and B. Piriou, *J. Non-Cryst. Solids* **53**, 279 (1982)]. Second, the coordination change may induce a decrease in the polarizability of the ions within the polyhedra, thus causing the amplitude of the Raman spectrum to decrease. Finally, pressure-induced puckering of originally planar rings may also play a role in the disappearance of the Raman spectrum [see F. Galeener in (*15*)].
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