

CdS will occur when the chemical potentials of the solid and liquid phases are equal. If the assumption of a three-phase equilibrium between a spherical solid particle, a liquid particle of the same mass, and vapor is made, changes in T_m compared to that of the bulk are given by (5)

$$T_b - T_m = \frac{2T_m}{L \rho_{\text{sol}} R_{\text{sol}}} \left[\gamma_{\text{sol}} - \gamma_{\text{liq}} \left(\frac{\rho_{\text{sol}}}{\rho_{\text{liq}}} \right)^{2/3} \right] \quad (1)$$

where T_b is the bulk melting temperature, T_m is the melting temperature for a particle of radius R , L is the molar latent heat of fusion, and γ and ρ are the surface tension and density, respectively. All parameters for this equation are known or are reliably estimated, with the exception of the surface tensions. A fit of Eq. 1 to T_m as a function of reciprocal particle radius yields a difference in surface tensions $\gamma_{\text{sol}} - \gamma_{\text{liq}}$ of 0.42 N m^{-1} . Thus, if either surface tension is determined independently, both are known.

The surface tension of the solid can be obtained from the contraction of the lattice with decreasing size at room temperature (Fig. 3). The slope of this plot is related to γ by

$$\frac{\Delta a}{a} = \frac{2}{3} \frac{\gamma \kappa}{R} \quad (2)$$

where κ is the isothermal compressibility ($\kappa_{\text{CdS}} = 1.56 \times 10^{-11} \text{ m}^2 \text{ N}^{-1}$). High-pressure studies have shown that the isothermal compressibility of the nanocrystals is the same as for the bulk (26). These plots yield a value of $\gamma_{\text{sol}}(111)$ for capped particles of $1.74 \pm 0.11 \text{ N m}^{-1}$, whereas γ_{sol} for the bare nanocrystals is 2.50 N m^{-1} (Fig. 3). This compares with an experimental bulk CdS₍₁₁₁₎ surface tension of 0.750 N m^{-1} (27, 28) and a calculated value of 0.865 N m^{-1} (29). The fit of Eq. 1 is obtained with a value for $\gamma_{\text{sol}} - \gamma_{\text{liq}}$ of 0.42 N m^{-1} and the values of ρ_{sol} and L , which are 4830 kg m^{-3} and $50.6 \text{ kcal mol}^{-1}$, respectively. The density of liquid CdS is assumed to be 4200 kg m^{-3} . The large increase in surface tension for CdS nanocrystals, compared to that of the bulk, is consistent with observations in metallic systems such as Al (30), Pt, and Au (31). Surface stress coefficients for the (422) faces of Pt and Au are 4.44 and 3.19 N m^{-1} , respectively, whereas the corresponding bulk surface tensions are approximately 3.1 and 1.8 N m^{-1} . Solliard and Flueli have argued that this increase in surface tension for the nanocrystals, compared to that of the bulk, is attributable to a weak dilation of the surface (31).

The marked reduction in T_m for semiconductor nanocrystals has several important implications. First, the optimum annealing temperature for preparation of high-quality,

defect-free nanocrystals can be expected to be a small fraction of the bulk annealing temperature. Second, the ability to fuse nanocrystals to form a film at relatively modest temperatures indicates that nanocrystals may provide a new low-temperature route to thin-film growth. Finally, as the dimension of active domains is reduced to the nanometer length scale, the thermal stability of the new devices may be limited. Large changes in the phase diagram as well as in the electronic properties must be considered in semiconductors of reduced dimensionality.

REFERENCES AND NOTES

1. D. A. B. Miller, D. S. Chemla, S. Schmitt-Rink, in *Optical Nonlinearities and Instabilities in Semiconductors*, H. Haug, Ed. (Academic Press, Orlando, FL, 1988), p. 325.
2. M. L. Steigerwald and L. E. Brus, *Annu. Rev. Mater. Sci.* **19**, 471 (1989).
3. G. D. Stucky and J. E. Mac Dougall, *Science* **247**, 669 (1990).
4. A. Henglein, *Top. Curr. Chem.* **143**, 113 (1988).
5. Ph. Buffat and J.-P. Borel, *Phys. Rev. A* **13**, 2287 (1976).
6. S. J. Peppiat and J. R. Sambles, *Proc. R. Soc. London Ser. A* **345**, 387 (1975).
7. M. Y. Hahn and R. L. Whetten, *Phys. Rev. Lett.* **61**, 1190 (1988).
8. P. Sheng *et al.*, *J. Phys. C* **14**, L565 (1981).
9. C. Solliard, *Surf. Sci.* **106**, 58 (1981).
10. C. J. Coombes, *J. Phys. F* **2**, 441 (1972).
11. P. Pawlow, *Z. Phys.* **66**, 549 (1909).
12. C. L. Briant and J. J. Burton, *J. Chem. Phys.* **63**, 2045 (1975).
13. R. S. Berry, J. Jellinek, G. Natanson, *Phys. Rev. A* **30**, 919 (1984).
14. W. D. Kristensen, E. J. Jensen, R. M. Cotterill, *J. Chem. Phys.* **11**, 4161 (1974).
15. J. D. Honeycutt and H. C. Andersen, *ibid.* **91**, 4950 (1987).
16. K.-J. Hanzen, *Z. Phys.* **157**, 523 (1960).
17. M. Hasegawa, K. Hoshino, M. Watabe, *J. Phys. F* **10**, 619 (1980).
18. M. L. Steigerwald *et al.*, *J. Am. Chem. Soc.* **110**, 3046 (1988).
19. Y. Nosaka *et al.*, *Chem. Lett.* **1988**, 605 (1988); A. P. Alivisatos *et al.*, *Mater. Res. Soc. Symp. Proc.* **195**, 597 (1990); V. L. Colvin, A. N. Goldstein, A. P. Alivisatos, *J. Am. Chem. Soc.*, in press.
20. E. P. Butler and K. F. Hale, in *Dynamic Experiments in the Electron Microscope*, A. M. Glauret, Ed. (Van Nostrand, New York, 1981), vol. 9, pp. 112–119.
21. B. Gale and K. F. Hale, *Br. J. Appl. Phys.* **12**, 116 (1961).
22. J. Ling, *ibid.* **18**, 991 (1967).
23. C. R. Wronski, *ibid.*, p. 1731.
24. H. Reiss and I. B. Wilson, *J. Colloid Sci.* **3**, 551 (1948).
25. A. Zangwill, *Physics at Surfaces* (Cambridge Univ. Press, Cambridge, 1988).
26. M. Haase and A. P. Alivisatos, *Mater. Res. Soc. Symp. Proc.* **206**, 233 (1991); *J. Phys. Chem.*, in press.
27. B. F. Ormont, *Dokl. Akad. Nauk SSSR* **124**, 132 (1959).
28. S. N. Sadumkin, *Fiz. Tverd. Tela* **2**, 880 (1960).
29. B. N. Oshcherin, *Phys. Status Solidi A* **34**, K181 (1976).
30. J. Woltersdorf, A. S. Nepijko, E. Pippel, *Surf. Sci.* **106**, 64 (1981).
31. C. Solliard and M. Flueli, *ibid.* **156**, 487 (1985).
32. We thank V. Colvin for preparing the samples. We thank J. H. Turner and M. A. O'Keefe for assistance in digitizing the electron diffraction patterns obtained in this study. We also thank the National Center for Electron Microscopy for the use of their facilities. This work was supported by the Director, Office of Basic Energy Sciences, Division of Materials Sciences, of the U.S. Department of Energy under contract DEAC03-76SF00098.

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Pressure-Induced Coordination Changes in Alkali-Germanate Melts: An in Situ Spectroscopic Investigation

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The structure of liquid $\text{Na}_2\text{Ge}_2\text{O}_5 \cdot \text{H}_2\text{O}$, a silicate melt analog, has been studied with Raman spectroscopy to pressures of 2.2 gigapascals. Upon compression, a peak near ~ 240 wavenumbers associated with octahedral GeO_6 groups grows relative to a peak near ~ 500 wavenumbers associated with tetrahedral GeO_4 groups. This change corresponds to an increase in octahedral germanium in the liquid from near 0% at ambient pressures to $>50\%$ at a pressure of 2.2 gigapascals. Silicate liquids plausibly undergo similar coordination changes at depth in the Earth. Such structural changes may generate decreases in the fusion slopes of silicates at high pressures as well as neutrally buoyant magmas within the transition zone of the Earth's mantle.

Pressure-induced changes in the coordination number of silicon from four- to sixfold with respect to oxygen profoundly alter the physical and chemical properties of minerals in the deep Earth (1). However, comparable structural changes in silicate melts

have only been inferred to occur at high pressures. Resolving the structure of melts at high pressures and temperatures requires actual experiments on pressurized, high-temperature liquids. We describe spectroscopic measurements made on a silicate-analog (germanate) liquid in situ at simultaneous high-pressure and high-temperature conditions.

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Coordination changes in silicate melts at high pressures have been previously inferred to occur on the basis of five primary lines of indirect evidence: (i) from molecular dynamic simulations of compressed silicate liquids (2–4); (ii) from studies of glasses compressed at ambient temperature (5–7); (iii) from the probing of glasses formed by fusion at high pressures and quenched to ambient pressures and temperatures (8, 9); (iv) from the volumes of shock-compressed silicate melts at high pressures (10, 11); and (v) from inferences derived from fusion-curve analysis (12). However, each of these lines of evidence for changes in coordination is ambiguous. The results of molecular dynamic simulations vary depending on the interatomic potential used (2–4, 13, 14). In addition, simple compression of glasses at 300 K is unlikely to access fully the equilibrium structural state of compressed liquids (6, 9, 15). Also, glasses quenched to ambient conditions do not fully preserve their high-pressure structures (5–7). Finally, volumetric measurements and thermochemical analysis of melting curves provide no direct constraints on the actual microstructure of melts.

We examined liquids of the composition $\text{Na}_2\text{Ge}_2\text{O}_5\cdot\text{H}_2\text{O}$ at high pressures and temperatures with Raman spectroscopy (16, 17). The rationale for studying this composition is

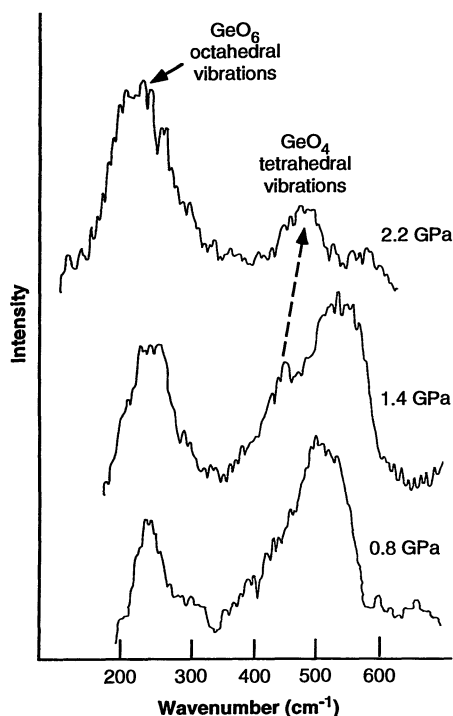


Fig. 1. Representative in situ high-pressure Raman spectra of liquid $\text{Na}_2\text{Ge}_2\text{O}_5\cdot\text{H}_2\text{O}$ spanning a pressure range of 0.8 to 2.2 GPa at temperatures of 1040 ± 20 K. The modes correlated with octahedral germanium (GeO_6) increase in amplitude relative to those attributable to germanium in tetrahedral (GeO_4) coordination.

threefold. First, germanates are known to undergo polymorphic transitions similar to those in silicates, but at lower pressure conditions; therefore, germanates have been extensively used as analogs for high-pressure silicate structural polymorphism (1). Second, the zero-pressure liquidus phase and glass of this composition both contain germanium in octahedral coordination (18). As such, this composition is plausibly at the cusp of undergoing a pressure-induced coordination change at ambient pressure, and we expected that profound structural changes would occur in a moderate pressure range. Third, at temperatures greater than ~ 1070 K in air, the windows of externally heated diamond anvil cells decompose to graphite. Therefore, we analyzed a relatively low melting temperature hydrous melt in order to generate a melt uncontaminated by coexisting crystals within our pressure-generating apparatus. Our rationale for examining a germanate melt was thus related to the comparatively low pressures and temperatures at which these liquids are anticipated to undergo major structural changes.

The Raman spectra of $\text{Na}_2\text{Ge}_2\text{O}_5\cdot\text{H}_2\text{O}$ liquid exhibited extreme changes as pressure was increased (Fig. 1). In particular, the intensity of a band near 240 cm^{-1} increased with pressure, while the amplitude of a band initially centered at 510 cm^{-1} decreased. The band near 500 cm^{-1} is associated with bridging Ge-O-Ge tetrahedral linkages, whereas the band near 250 cm^{-1} has been plausibly attributed to octahedrally coordinated germanium on the basis of Raman spectra of both crystalline and amorphous germanates (19). The precise atomic displacements involved in this latter vibration are ill-constrained; however, by analogy with the vibrational spectra of a range of octahedral species, it could be associated with bending vibrations of the GeO_6 octahedra. We thus interpret these spectral changes to represent a gradual in-

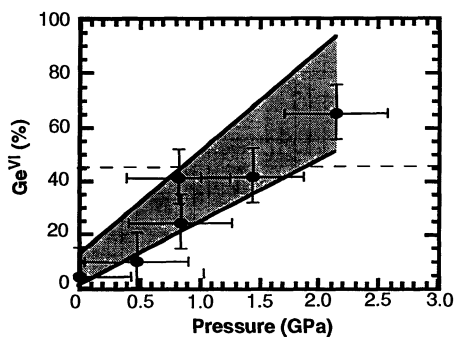


Fig. 2. Estimated percentage of octahedral germanium as a function of pressure. The stippled region represents the uncertainty in the estimated relative scattering cross sections of tetrahedral and octahedral germanium, while the dashed horizontal line represents the percentage of octahedral germanium found in the equilibrium liquidus phase, $\text{Na}_4\text{Ge}_9\text{O}_{20}$.

crease in the amount of octahedrally coordinated germanium (Ge^{VI}) in this melt with increasing pressure [and a corresponding decrease in the fraction of tetrahedrally coordinated germanium (Ge^{IV})] (20).

We estimated the relative amounts of octahedral and tetrahedral germanium in the liquid by determining the relative Raman scattering cross sections of these two species from spectra of $\text{Na}_2\text{Ge}_2\text{O}_5$ glass at ambient pressure from the amounts of Ge^{VI} in these glasses determined from x-ray and neutron-scattering studies (21) (Fig. 2). It is apparent from this analysis that the proportion of Ge^{VI} within the melt increased systematically with increasing pressure. Notably, even our most conservative estimate of the amount of Ge^{VI} present within the melt at 2.2 GPa is greater than the amount present in the liquidus phase $\text{Na}_4\text{Ge}_9\text{O}_{20}$ (18).

Changes in bond angle represent one of several mechanisms that could explain the dramatic densification of silicate melts with pressure (10, 11, 22). Our data do not preclude such changes in bond angle as a possible subsidiary mechanism of liquid germanate compression but rather document that the primary compressional mechanism in $\text{Na}_2\text{Ge}_2\text{O}_5$ liquid between 0 and 2.2 GPa is the change in coordination from Ge^{IV} to Ge^{VI} (23). Similar coordination changes have been observed in silicate and germanate glasses, but under more extreme pressures and at ambient temperature (5–7). However, in the pressure range below 5 GPa, the dominant compressional mechanism in glasses seems to be a reduction of the $\text{Ge}(\text{Si})\text{-O-Ge}(\text{Si})$ angle (5–7).

The maintenance of a relatively uniform peak width (24) in the high-pressure, high-temperature liquid spectra (Fig. 1) suggests that these high-pressure liquids maintain reasonably well-defined coexisting fourfold and sixfold coordinate species. This contrasts with the behavior of compressed glasses, which clearly undergo major tetrahedral distortions at high pressures; these distortions plausibly culminate in an increase in average silicon or germanium coordination (5–7). Thus, it appears that the added structural degrees of freedom available to the liquid allow a continuous (and, within our resolution, uniform) rate of increase in the number of octahedra present relative to tetrahedra. The observation of a continuous change in the coordination of germanium in these compressed liquids is consistent with previous predictions based on compression of glasses (6) and on molecular dynamic simulations of silicate liquids (2–4). Furthermore, these two species coexist over a large volume range; we estimate that this liquid underwent about 8.5% volume compression between 0 and 2.2 GPa (25).

These data provide a structural basis for many of the inferred and observed high-

pressure properties of silicate magmas. Although it is well known that silicate melts densify approximately an order of magnitude faster than isochemical crystalline silicates, the structural basis for this notable compressibility remains controversial (4, 14, 26, 27). The results shown in Fig. 2 provide evidence for densification of germanate liquids through coordination changes of germanium and indicate that the rapid densification of silicate melts observed under shock-loading also occurs through changes in the coordination of silicon in the melt.

Our results indicate that coordination changes in liquids occur over a pressure range in which mixed-coordination crystalline phases exist. Thus, while recognizing that we have examined an analog system, we believe that our observations indicate that shifts in the silicon coordination in ultrabasic silicate liquids plausibly take place in the pressure range over which majorite-garnets, which contain both octahedral and tetrahedral silicon, are the liquidus phase (22). This pressure range, from ~12 to 24 GPa, exists in most of the deep transition zone of the upper mantle, at depths between 400 and 700 km.

These data also support earlier inferences that changes in the transport properties of aluminosilicate liquids at high pressures are produced by coordination changes of aluminum from fourfold to sixfold coordination (28): by analogy with their crystalline equivalents, these changes plausibly occur at pressures less than 5 GPa (1). In addition, coordination-induced densification of silicate liquids may produce liquids denser than their coexisting solids. Such a crossover between the density of ultrabasic liquids and majorite-garnet has been proposed to occur at pressures above ~20 GPa (11), and we attribute this to coordination changes in the liquid. Moreover, such structurally generated decreases in the volume difference between liquids and solids would produce a shallowing of the fusion slopes of silicates at high pressure, as is observed in a range of compositions (12, 22). If the early Earth was extensively melted, then changes in sign of the density contrast between compressed silicate melts and their coexisting solids at depth imply that melt coordination changes controlled the pattern of liquid segregation in a solidifying early Earth (29). Thus, structural changes in melts could have played a primary role in the early differentiation and geochemical evolution of the planet.

REFERENCES AND NOTES

1. L. G. Liu and W. A. Bassett, *Elements, Oxides, Silicates: High Pressure Phases with Implications for the Earth's Interior* (Oxford Univ. Press, New York, 1986).
2. C. A. Angell, P. A. Cheeseman, S. Tamaddon, *Science* **218**, 885 (1982); *Bull. Mineral.* **106**, 87 (1983); Y. Matsui, K. Kawamura, Y. Syono, in *High Pressure Research in Geophysics*, S. Akimoto and M. Manghnani, Eds. (Center for Academic Publishing, Tokyo, 1982), pp. 511–524.
3. J. R. Rustad, D. A. Yuen, F. J. Spera, *Phys. Rev. A* **42**, 2081 (1990).
4. ———, *J. Geophys. Res.* **96**, 19665 (1991).
5. R. J. Hemley *et al.*, *Phys. Rev. Lett.* **57**, 747 (1986); J. P. Itie *et al.*, *ibid.* **63**, 398 (1989).
6. Q. Williams and R. Jeanloz, *Science* **239**, 902 (1988).
7. D. J. Durben and G. H. Wolf, *Phys. Rev. B* **43**, 2355 (1991).
8. B. Velde and I. Kushiro, *Earth Planet. Sci. Lett.* **40**, 137 (1978); J. F. Stebbins and P. F. McMillan, *Am. Mineral.* **74**, 965 (1989); X. Xue, J. F. Stebbins, M. Kanzaki, R. G. Tronnes, *Science* **245**, 962 (1989); Q. Williams, *Geophys. Res. Lett.* **17**, 635 (1990).
9. X. Xue *et al.*, *Am. Mineral.* **76**, 8 (1991).
10. S. M. Rigden *et al.*, *J. Geophys. Res.* **94**, 9508 (1989); S. M. Rigden, T. J. Ahrens, E. M. Stolper, *Science* **226**, 1071 (1984).
11. G. H. Miller, E. M. Stolper, T. J. Ahrens, *J. Geophys. Res.* **96**, 11831 (1991).
12. C. W. Burnham, in *Chemistry and Geochemistry of Solutions at High Temperatures and Pressure*, D. T. Rickard and F. E. Wickman, Eds. (Pergamon, New York, 1981), pp. 197–229; A. Boettcher, Q. Guo, S. Bohlen, B. Hanson, *Geology* **12**, 202 (1984); T. Irfune and E. Ohtani, *J. Geophys. Res.* **91**, 9357 (1986); E. Knittle and R. Jeanloz, *Geophys. Res. Lett.* **16**, 421 (1989).
13. Indeed, some molecular dynamic simulations of compressed liquids do not produce such transitions [L. V. Woodcock *et al.*, *J. Chem. Phys.* **65**, 1565 (1976); J. D. Kubicki and A. C. Lasaga, *Am. Mineral.* **73**, 945 (1988); (14)]. Recent work by J. R. Rustad, D. A. Yuen, and F. J. Spera [(3, 4); *Phys. Earth Planet. Inter.* **65**, 210 (1991)] has indicated that high-pressure structural and spectroscopic properties in the SiO_2 system may be reproduced in molecular dynamic simulations that incorporate large numbers of particles and accurate potentials.
14. L. Stixrude and M. S. T. Bukowski, *Science* **250**, 541 (1990).
15. S. A. Brawer, *Relaxation in Viscous Liquids and Glasses* (American Ceramic Society, Columbus, OH, 1985).
16. The starting composition was synthesized from the appropriate molar proportions of Puratronic-grade NaOH and quartz-structured GeO_2 . The powders were both ground by hand and then mixed in a ball mill. Comparisons between Raman spectra obtained from the fused starting material and published spectra of sodium germanate glasses [T. Furukawa and W. B. White, *J. Chem. Phys.* **95**, 776 (1991)] document that the composition was accurate to better than ± 2 mol percent GeO_2 . All measurements were made in a modified Merrill-Bassett-type diamond anvil cell, and samples were contained in rhenium gaskets. Modifications to the standard Merrill-Bassett design included using low-thermal expansion bolts and surrounding the cell with mica thermal insulation. Temperatures were generated by a heater external to the gasket and the diamond anvils, and they were monitored with a Pt/Pt-13%Rh thermocouple in contact with the gasket and the diamond anvils. The reported temperatures have been corrected for the difference between that at the diamond surface and that within the sample chamber by calibration against a thermocouple placed between the diamond anvils [X. Li and R. Jeanloz, *Phys. Rev. B* **36**, 474 (1987); L. C. Ming *et al.*, in *High Pressure Research in Mineral Physics*, M. H. Manghnani and Y. Syono, Eds. (American Geophysical Union, Washington, DC, 1987), pp. 69–74]. Including the uncertainty in the calibration, our errors on measured temperatures within the sample chamber are less than ± 20 K. Pressures within the cell were measured with the fluorescence of the Y1 and Y2 bands of Sm:YAG grains added to the sample [N. J. Hess and D. S. Schiferl, *J. Appl. Phys.* **68**, 1953 (1990)], with a nonlinear inversion of the full peak shapes performed with the method of C. Xu [*J. Optim. Theory Appl.* **65**, 555 (1990)]. The reported errors in pressure include both the error in the Sm:YAG calibration [± 0.3 GPa (Hess and Schiferl, cited in this note)] and an error estimated from the reproducibility of our inversion. An argon-ion laser tuned to 488 nm was used for both excitation of the Raman scattering and the fluorescence of Sm:YAG; typical laser powers at the sample were less than 100 mW, and signals were collected from a $5 (\pm 1)$ - μm -diameter spot in the sample with a Quantar Technologies multichannel system. The configuration of our micro-Raman system is described by S. Kraft, E. Knittle, and Q. Williams [*J. Geophys. Res.* **96**, 17997 (1991)]. Typical spectral collection times were ~600 s, and in all runs the measured temperature variation over this time was less than ± 3 K. Spectral resolution is 4 to 5 cm^{-1} .
17. In all experiments, the presence of liquid was detected visually by observing motion of the Sm:YAG grains used as our pressure calibrant as well as by observing the annihilation of grain boundaries within the sample. Also, melting was monitored spectroscopically through the change in peak shape from the characteristically sharp crystalline lines [full width at half maximum (FWHM) $< 20 \text{ cm}^{-1}$] to the broad (FWHM $> 60 \text{ cm}^{-1}$) features associated with the liquid. Before fully melting, the sample recrystallized to form an assemblage containing $\text{Na}_4\text{Ge}_3\text{O}_{20}$. Only in samples that ruptured at high temperatures did we observe the evolution of a hydrous vapor phase. All high-pressure, high-temperature spectra were corrected for thermally induced phonons by the application of a Bose-Einstein-type correction factor [B. O. Mysen, *Structure and Properties of Silicate Melts* (Elsevier, Amsterdam, 1988)]. Bands in all liquid spectra were fit with Gaussian peaks with the same algorithm used to fit the Sm:YAG spectra.
18. The composition $\text{Na}_2\text{Ge}_2\text{O}_5$ lies to the Ge-rich side of the zero-pressure eutectic (~1045 K) in the system Na_2GeO_3 - $\text{Na}_4\text{Ge}_3\text{O}_{20}$ [M. K. Murthy and J. Aguiayo, *J. Am. Ceram. Soc.* **47**, 444 (1964)]. The structure of $\text{Na}_4\text{Ge}_3\text{O}_{20}$ contains 44% octahedral germanium, and the remaining germanium is in tetrahedral coordination [N. Ingri and G. Lundgren, *Acta Chem. Scand.* **17**, 617 (1963)]; this phase is the liquidus phase throughout the pressure range of this study. Numerous studies have examined the changes in physical and spectral properties of glasses across the Na_2GeO_3 - GeO_2 binary at zero pressure [C. R. Kurkjian and J. T. Krause, *J. Am. Ceram. Soc.* **49**, 134 (1965); M. K. Murthy, *Nature* **201**, 285 (1964); J. E. Shelby, *J. Am. Ceram. Soc.* **57**, 436 (1974); M. K. Murthy and B. Scroggie, *Phys. Chem. Glasses* **6**, 162 (1965); Murthy and Aguiayo, cited in this note; M. K. Murthy and E. M. Kirby, *Phys. Chem. Glasses* **5**, 144 (1964); M. Ueno *et al.*, *Phys. B* **120**, 347 (1983); S. Fukushima *et al.*, *J. Am. Ceram. Soc.* **68**, 490 (1985); K. Kamiya *et al.*, *J. Non-Cryst. Solids* **91**, 279 (1987)], and all have invoked the presence of Ge^{VI} to explain anomalous changes in physical properties between the GeO_2 and Na_2GeO_3 compositions. Indeed, x-ray and neutron-scattering studies of Na_2O - GeO_2 glasses have found the abundance of Ge^{VI} to increase from 0% GeO_2 glass to a maximum of 22% Ge^{VI} between 14 and 20 mol percent Na_2O and to return to 0% Ge^{VI} between 35 and 40 mol percent Na_2O , although one recent study has questioned whether Ge^{VI} exists in these glasses [G. Henderson and M. E. Fleet, *ibid.* **134**, 259 (1991)].
19. In situ Raman spectroscopic measurements of GeO_2 glass under compression also show the growth with pressure of a band at ~240 cm^{-1} ; this band is attributed to a change in coordination of germanium from four- to sixfold (7). Furthermore, Raman spectra of crystalline phases with germanium in point-sharing octahedra all show strong features in the region near ~200 cm^{-1} [P. F. McMillan and N. Ross, *Phys. Chem. Miner.* **16**, 21 (1988); N. Ross and A. Navrotsky, *Am. Mineral.* **73**, 1355 (1988); D. J. Durben, G. H. Wolf, P. McMillan, *Phys. Chem. Miner.* **18**, 215 (1991)]. Raman band assignments for sodium germanate glasses in the region between 700 and 100 cm^{-1} have been made by a number of researchers [H. Verweij and J. Buster, *J. Non-Cryst. Solids* **34**, 81 (1979); G. E. Walrafen, *J. Chem. Phys.* **42**, 485 (1965); T. Furukawa and W. B. White, *J. Mater. Sci.* **15**, 1648 (1981); Furukawa and White, in (16)]. In $\text{Na}_2\text{Ge}_2\text{O}_5$ glass, there are four

resolvable Raman bands in this spectral region at 653, 600, 530, and 330 cm^{-1} . The weak bands at 653 and 600 cm^{-1} are similar in frequency to strong bands at 648 and 608 cm^{-1} in crystalline $\text{Na}_4\text{Ge}_3\text{O}_{20}$ and have been assigned to symmetric stretching of Ge-O-Ge linkages between octahedra. The strong band at 530 cm^{-1} has been generally assigned to symmetric stretching or deformation of Ge-O-Ge linkages between germanium tetrahedra. The weak band at 330 cm^{-1} compares favorably in frequency with a strong band at 309 cm^{-1} in crystalline $\text{Na}_4\text{Ge}_3\text{O}_{20}$, and the intensity of a feature near 300 cm^{-1} in glasses in the $\text{K}_2\text{O-GeO}_2$ system is clearly correlated with the intensities of bands at 645 and 603 cm^{-1} (Verweij and Buster, cited in this note).

20. The effect of the added H_2O in our samples is easily discerned. In the zero-pressure spectrum of anhydrous $\text{Na}_2\text{Si}_2\text{O}_5$ glass, there are strong bands at 867 and 790 cm^{-1} . Both of these bands are associated with vibrations of relatively polymerized units of tetrahedrally coordinated germanium [Verweij and Buster; Walrafen; Furukawa and White; all in (18)]. In our lowest pressure spectra of the hydrated liquid, these bands are reduced in amplitude to the degree that they are unresolvable. Thus, added water produces depolymerization of the liquid relative to the anhydrous glass, in accord with the solution mechanisms of H_2O in silicate liquids [E. M. Stolper, *Contrib. Mineral. Petrol.* 81, 1 (1982)].

21. We utilized a range of abundances of Ge^{VI} (between 3 and 8% [Ueno *et al.* and Fukushima *et al.*, respectively, in (18)]) and the areas under the ~ 500 and ~ 300 cm^{-1} bands in the zero-pressure Raman spectrum of anhydrous $\text{Na}_2\text{Ge}_2\text{O}_5$ glass to calculate relative scattering cross sections of the two species in the glass. Estimated relative Raman scattering cross sections of octahedral to tetrahedral species range from 0.39 to 2.6. Our data are plotted with an average value of 1.5, but the stippled region of Fig. 2 incorporates the entire range of values.

22. Other possible mechanisms for densification include both simple bond compaction and more complex changes in polyhedral packing involving changes in second or more distant neighbor distances. The sequence with increasing pressure of the liquidus phases of ultrabasic melts of olivine, pyrope-majorite solid solutions (up to 25% Si^{VI}), and MgSiO_3 perovskite (100% Si^{VI}) suggests that the dominant structural change over the pressure range of the transition zone is the conversion of fourfold silicon to sixfold silicon [E. Takahashi, *J. Geophys. Res.* 91, 9367 (1986); K. Wei, R. G. Tronnes, C. M. Scarfe, *ibid.* 95, 15817 (1990)].

23. The shoulder present at ~ 425 cm^{-1} in the spectrum at 1.4 GPa grew with increasing pressure to become the dominant component in this spectral region (400 to 600 cm^{-1}) at the highest pressures of this study (Fig. 1). This shift in frequency suggests a change in the local tetrahedral environment upon compression. We believe that the decrease in the frequency of this vibration is produced by the tetrahedra in the high-pressure liquid sharing oxygens with a greater proportion of relatively weakly bound GeO_6 octahedra. Such a weakening of the tetrahedral environment would be expected to lower the vibrational frequency of this band, as is observed. However, we cannot preclude that the peak at 425 cm^{-1} is not associated with more highly coordinated germanate units. If this is the case, then our estimates of the amount of GeO_6 octahedra within the liquid are conservative.

24. The amplitude and the FWHM of the ~ 500 cm^{-1} peak decreased with increasing pressure, but neither peak broadens by a factor of ~ 3 to 4 with compression, as is seen in spectra of compressed germanate glasses (7). Thus, the local environment of the germanium may be less distorted in the liquid than in the compressed glass.

25. The zero-pressure bulk moduli of $\text{Na}_2\text{Ge}_2\text{O}_5$ glass and $\text{Na}_2\text{Si}_2\text{O}_5$ glass are 33 and 40 GPa, respectively [R. R. Shaw, *J. Am. Ceram. Soc.* 54, 170 (1970); G. K. White, J. A. Birch, M. H. Manghnani, *J. Non-Cryst. Solids* 23, 99 (1977)]. This similarity

indicates that the elasticity of $\text{Na}_2\text{Si}_2\text{O}_5$ liquid may be used to conservatively estimate the compression of $\text{Na}_2\text{Ge}_2\text{O}_5$ liquid. The bulk modulus of metastable $\text{Na}_2\text{Si}_2\text{O}_5$ liquid at 940 K is 20 GPa [V. C. Kress, Q. Williams, I. S. E. Carmichael, *Geochim. Cosmochim. Acta* 52, 283 (1988)]; over the pressure range of our experiments, this would produce a volume compression of $\sim 8.5\%$ (note that the presence of water will probably decrease the bulk modulus of the liquid, again rendering this estimate conservative). The volume compression in silicate liquids in a pressure range over which they are inferred to undergo coordination changes (8 to 25 GPa) is comparable with the compression occurring in this germanate melt under lower pressure conditions (10, 11).

26. H. S. Waff, *Earth Planet. Sci. Lett.* 28, 254 (1975); E. M. Stolper and T. J. Ahrens, *Geophys. Res. Lett.* 14, 1231 (1987); J. D. Kubicki and A. C. Lasaga, *Phys. Chem. Miner.* 17, 661 (1991).

27. Our observations of coexisting and interconverting Ge^{IV} and Ge^{VI} preclude some models for high-pressure coordination changes in liquids. Models that involve uniform distortion and deformation of tetrahedra until octahedral coordination is generated are inconsistent with our observation of extensive coexistence of two distinct coordination states (for example, Stolper and Ahrens [in (26)]). However, our results are consistent with structural models of compressed alkali halide liquids that rely on coex-

isting coordination states [J. L. Tallon, *Phys. Lett.* 72, 150 (1979)]. Furthermore, on the basis of our observations of a mixed-coordination liquid, we concur with Rustad *et al.* (4) that molecular dynamic simulations utilizing potentials in which the coordination number of silicon is fixed at four are unlikely to produce geophysically relevant results [for example, (14)].

28. J. A. Tyburczy and H. S. Waff, *J. Geophys. Res.* 88, 2413 (1983); I. Kushiro, *ibid.* 81, 6347 (1976); *Earth Planet. Sci. Lett.* 41, 87 (1978); N. Shimizu and I. Kushiro, *Geochim. Cosmochim. Acta* 48, 1295 (1984).

29. W. B. Tonks and H. J. Melosh, in *Origin of the Earth*, H. E. Newsom and J. H. Jones, Eds. (Oxford Univ. Press, New York, 1990), pp. 151–174; C. B. Agee, *Nature* 346, 834 (1990); G. H. Miller, E. M. Stolper, T. J. Ahrens, *J. Geophys. Res.* 96, 11849 (1991).

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Small Earthquakes, Tectonic Forces

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Earthquake scaling and frequency-of-occurrence relations require that small earthquakes be just as important as larger ones in redistributing the forces that drive relative displacements across active faults of any dimension, including plate boundaries.

According to the Gutenberg-Richter frequency-of-occurrence relation (1), small earthquakes (2) occur in vastly greater numbers than large ones:

$$\log N = a - bM \quad (1a)$$

In Eq. 1a, N is the cumulative number of earthquakes that exceed or are equal to a given magnitude M in a chosen area for a chosen time interval. The constant a depends on the overall seismicity rate, which can vary greatly from one region to the next. The constant b , however, is almost always ≈ 1 , although recent studies have suggested that $b < 1$ at very small magnitudes ($M \lesssim 2$) (3, 4) and have shown that $b \approx 1.5$ at large magnitudes (5). The distribution function corresponding to Eq. 1a is of the same form: the number of earthquakes ΔN within a magnitude increment ΔM centered on M is

$$\log \Delta N \left(M \pm \frac{\Delta M}{2} \right) = a' - bM \quad (1b)$$

where the constant a' now depends on a , ΔM , and b (if different from 1).

Because of their greater numbers, microearthquakes have played an important role in illuminating faintly seismogenic structures (6). Otherwise, the physical significance of small earthquakes has been debated for decades, at least since the time of the first energy-magnitude studies (7) of the 1940s and 1950s, which showed that small earthquakes contributed negligibly to seismogenic energy budgets, either globally or regionally. By the early 1970s, seismologists had also learned that small earthquakes contribute neither to seismic moment sums nor to long-term displacement rates along active faults (8).

Numerous studies of the past two decades, however, have revealed that earthquake stress drops, in the midst of considerable scatter, are sensibly constant for small earthquakes and large (9), for interplate earthquakes and intraplate (10), and for shallow earthquakes and deep (11). For equidimensional sources of circular radius r , the stress-drop $\Delta\sigma$ relation is

$$\Delta\sigma = (7/16)M_0/r^3 \quad (2a)$$

whereas for large earthquakes with fault length l much greater than fault width w ,

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