A Novel Topological Compression Mechanism in a Covalent Liquid

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Monte Carlo simulations of tetrahedrally bonded SiO_2 liquid show that pressure induces large changes in the topology of its four-coordinated framework structure but leaves the average properties of local coordination environments virtually unchanged. Ring statistics are used to describe the liquid's topology; the observed changes paradoxically indicate that the liquid compresses primarily by increasing the size of its rings. A theory for the effects of ring formation on density, which also explains the density of crystalline tectosilicates, accounts for the compression of the liquid.

ALTHOUGH IT HAS BEEN KNOWN for a long time that condensed matter is compressible (1), the notion that pressure can induce fundamental rearrangement of its atomic structure is relatively recent: the first correct identification of a high-pressure structure (the B2 phase of the Rb-halides) came from the work of Bridgman (2). Most of our current ideas about compression mechanisms in condensed matter found expression in these early experiments. Thus, in simple monatomic materials as well as more complex structures such as the crystalline silica polymorphs (3, 4), compression can be described by a shrinking of nearest neighbor interatomic distances (described in Bridgman's work as a compression of the atoms themselves). Further increases in pressure nearly always induce phase transitions (the rare gases are exceptions to this rule) that involve rearrangement to a more efficient packing of the atoms, usually facilitated, as with Rb- and other alkali-halides, by an increase in nearest neighbor coordination. In this report, we describe a different type of compression mechanism that we have observed in Monte Carlo simulations of a covalently bonded liquid (SiO_2). The mechanism involves neither decreases in nearest neighbor distances nor changes in coordination number, but rather relies on changes in the bonding topology of the liquid's structural framework. These compression mechanisms are relevant to the highly polymerized structures common to natural silicate magmas, whose formation and transport play a central role in the thermal and chemical evolution of our planet (4).

The unusual nature of the compression of SiO_2 liquid is a result of its strong covalent bonding. Unlike ionic, metallic, and Van der Wall's bonded structures, which are determined mostly by the packing efficiency of nearly spherical atoms, the directional properties of the covalent bond result in a much greater variety of structures, all of which tend to be relatively open. Thus, the packing fraction of the diamond structure, assumed by covalently bonded Si, Ge, and C, is only 46% of cubic close packing (5). Framework or tectosilicates, of which SiO_2 liquid is an example, assume still more open structures. We can think of these structures, which are based on continuous three-dimensional networks of corner-sharing SiO_4 and AlO_4 tetrahedra, as being derived from a network of tetrahedrally coordinated (T) atoms (Si and Al) each linked to four others through a shared O atom. (Thus, for example, the cristobalite structure, assumed by SiO_2 at high temperature, is a derivative of the diamond structure.) Although the T-T coordination number of these frameworks (four) is invariant, and nearest neighbor T-T distances are nearly so, the some 80 topologically distinct framework types vary in packing fraction (0.22 to 0.45) and framework density (number density of T-atoms) by a factor of 2 (12.9 to 29.3 nm^{-3}) (6, 7). By examining variations in ring and cluster statistics across the spectrum of crystalline frameworks, we have shown that these extreme variations in density are the result of variations in bonding topology (6). Liquid SiO_2 encounters similar topological changes with increasing pressure that lie at the heart of its compression mechanism. The mechanism is very efficient compared with those in crystals (4), and if similar mechanisms operate in natural magmas, they may help facilitate liquid-crystal density inversions even at the modest pressures of Earth's upper mantle (10 to 20 GPa or 300 to 500 km depth) (8).

Liquid silica is expected to retain its tetrahedral framework structure to about 20 GPa. At higher pressures a gradual pressure-induced four- to sixfold Si-O coordination change probably also contributes to compression (9). In order to focus exclusively on framework compression, we base our simulations on a covalent potential model specialized to tetrahedral Si-O bonding (3). The model is a limiting case that effectively disallows coordination changes—the strong tetrahedral Si-O bonds maintain nearly perfect tetrahedral coordination in the liquid up to the highest pressure considered (50 GPa) (4). But the model is expected to be otherwise realistic: it reproduces the observed equation of state, compression mechanisms, and phase stability of tetrahedral crystalline phases; and the structure, density, and bulk modulus of SiO_2 liquid (3, 4). Thus, our approach isolates tetrahedral framework compression mechanisms from the effects of coordination changes, which may be important at very high pressures.

Monte Carlo simulations are ideal for investigating the rich and complex structural variations in covalent liquids. Current experimental methods can yield spherically averaged liquid structures (x-ray diffraction) or information about local coordination environments (nuclear magnetic resonance and vibrational spectroscopy), but simulations provide complete structural information, including medium-range structural variations (length scales of 5 to 15 Å). We performed simulations in the NPT (constant particle number, pressure, and temperature) ensemble with 192 total atoms repeated with periodic boundary conditions to minimize finite-size effects. We performed simulations at seven different pressures along the 2000 K isotherm, ranging from 0 to 50 GPa. At each pressure, we performed two separate simulations with different cooling histories to investigate the reproducibility of simulated liquid properties (10).

The results show that even though the maximum pressure causes a nearly twofold increase in density, the average structure of local coordination environments remains nearly invariant. Not only does the liquid retain its tetrahedral coordination, but local geometries are also similarly unaffected by large increases in pressure: the pressure-induced changes in nearest neighbor Si-O, O-O, and Si-Si distances are far short of the amount needed to account for the increase in density (4). This result is in sharp contrast to the behavior of crystals whose compression, as observed experimentally and accurately reproduced by our model, can be accounted for almost entirely by decreases in nearest-neighbor Si-Si distances (3, 4).

Although local coordination environments in the liquid change their average properties only slightly with pressure, they are not static. Because the bonding model specifies that Si atoms bond only to the four nearest O atoms (and O atoms only to the two nearest Si atoms), coordination environments are in a dynamic steady state in which Si-O bonds are constantly broken and reformed: at 2000 K the simulated liquid encounters approximately one bonding

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change every 2000 Monte Carlo configurations or several thousand total changes for a typical simulation of 8 million configurations at each pressure. It is precisely these changes in bonding topology, and the con-
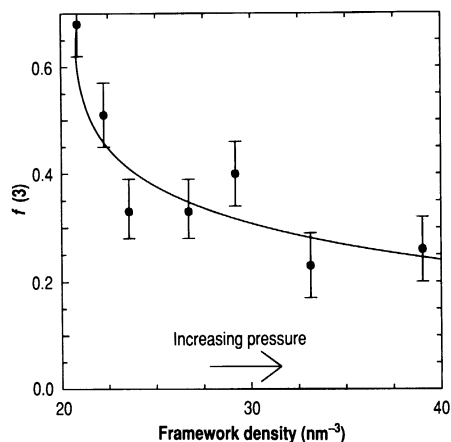

Fig. 1. Results of the Monte Carlo simulations of liquid SiO_2 at 2000 K showing the average number of three-membered rings passing through a tetrahedron in the liquid, $f(3)$, as a function of framework density. The points represent averages of the two simulations at each pressure (10). The error bars indicate the uncertainty, estimated by the average difference between the two simulations. The line is an empirical fit to guide the eye.
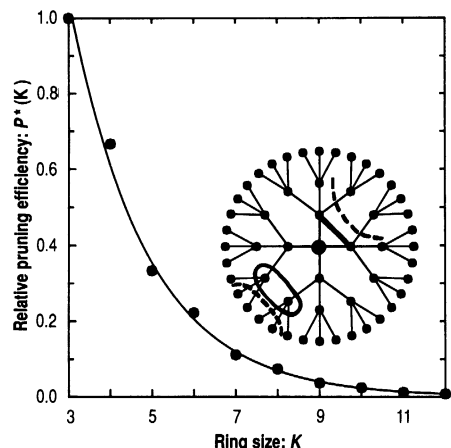

Fig. 2. The relative pruning efficiency, $P^*(K)$ (Eq. 1), plotted as a function of ring size K. The inset schematically shows the effect of forming a three-membered ring (upper right) and a four-membered ring (lower left) on the topology of the initially ringless Bethe lattice (tree). A three-membered ring is formed by linking two of the first neighbors of the central T-atom (indicated by the bold solid line). The constraint of four-coordination then requires that two branches originating in the second linked neighbor shell be pruned from the tree, as indicated by the bold dashed line. Forming a four-membered ring means that two second linked neighbors coalesce, indicated schematically by the bold line encircling two T-atoms. The constraint of four-coordination requires that four branches, originating in the third linked neighbor shell, be pruned from the tree, as indicated by the bold dashed line [after (6)].

sequent modification of the liquid's ring statistics, that lead to compression.

Rings, closed circuits of connected tetrahedra in a tectosilicate structure, provide a convenient, easily visualized characterization of different frameworks. Thus, cristobalite, which contains only six-membered rings, is easily distinguished from quartz, which also contains eight-membered rings. We used a newly developed definition of a fundamental ring that is free of the ambiguities of earlier ones (11) and an algorithm described in (6) to determine the ring statistics of our simulated liquid. These measurements show that the ring statistics vary widely with pressure (Table 1).

The most obvious change in ring statistics with increasing pressure is, seemingly paradoxically, a decrease in the number of smallest rings (three members): at 50 GPa, the number of three-membered rings is less than half that at zero pressure (Fig. 1). Furthermore, the observation that populations of larger rings do not behave systematically suggests that the liquid density is most strongly affected by the smallest rings. Thus, although an association of smaller volumes (higher pressures) with small rings might have been expected, the liquid appears to compress mainly by eliminating them.

We have developed a simple theory for the effects of ring formation on framework density that explains these observations (6). We assume that the relative effects of different sized rings on density are the same regardless of framework type, which allows us to focus on a particularly simple framework, the four-coordinate Bethe lattice (12). Because of the constraint of four-coordination, ring formation reduces density by pruning an exactly calculable number of T-

atoms from the Bethe lattice. The basic result of the theory, the relative ability of different sized rings to reduce framework density, is given by the pruning efficiency, $P^*(K)$, which is the number of T-atoms pruned by a K-membered ring in an infinite Bethe lattice normalized to the number pruned by a three-membered ring (13). Pruning efficiency is an exponentially decreasing function of K:

$$P^*(K) = \begin{cases} 1/3^{1/2(K-3)} & K = \text{odd} \\ 2/3^{1/2(K-2)} & K = \text{even} \end{cases} \quad (1)$$

Thus, the theory predicts that ring formation always reduces density (by way of the topological pruning mechanism) and that forming small rings is exponentially more effective at reducing density than forming larger rings (Fig. 2). This effect accounts for not only the decrease in the number of three-membered rings with increasing pressure, but also their apparently greater importance in determining density.

Although only the proportion of three-membered rings shows a systematic trend with pressure, we can relate the complete ring statistics of the liquid to compression by defining a single characteristic ring size, K^*, a weighted average in which $P^*(K)$ is used to take into account the greater importance of small rings

$$K^* = \Sigma\, K f(K)P^*(K)/\Sigma\, f(K)P^*(K) \quad (2)$$

where $f(K)$ is the number of K-rings. Because of the exponentially decaying form of $P^*(K)$, large fluctuations in the number of large rings (apparent in Table 1) are damped, commensurate with the relatively weak effect of such fluctuations on density, and K^* increases relatively smoothly with pressure (Fig. 3). We have observed a simi-

Table 1. Pressure, P; framework density, FD; characteristic ring size, K^* (Eq. 2); and the average number of K-membered fundamental rings passing through a tetrahedron, $f(K)$, in the simulated liquid at 2000 K for the seven pressures considered. The first entry for each pressure is for simulations cooled directly from 6000 K, the second for those cooled from 4000 K (10). After an initial equilibration period, variations in $f(K)$ and K^* during a simulation were typically less than 1% and always less than the differences between the two cooling histories. Rings larger than 12-membered (up to 17-membered rings were found) are not listed because they have a negligible effect on K^* (see text).

| P (GPa)	FD (nm^{-3})	K^*	$f(K)$ for K =									
			3	4	5	6	7	8	9	10	11	12
0	21.65	4.54	0.61	0.69	1.09	0.63	0.55	0.47	0.83	1.13	0.78	2.25
0	20.09	4.53	0.75	0.81	0.86	0.75	0.97	1.09	0.80	1.11	1.86	0.86
1	21.87	4.74	0.56	0.75	1.33	1.11	0.88	0.88	0.56	0.28	2.34	1.03
1	22.65	5.04	0.47	0.50	1.56	0.75	1.42	1.38	2.92	0.31	0.80	0.00
2	23.68	5.18	0.38	0.56	1.33	1.39	0.88	2.22	0.84	1.22	1.95	0.66
2	23.47	5.29	0.28	0.63	1.33	1.78	2.19	0.81	1.08	1.52	1.36	0.11
5	27.40	5.51	0.33	0.63	0.94	1.69	1.42	4.11	2.81	0.00	1.14	0.14
5	26.03	5.38	0.33	0.81	0.86	1.69	1.31	1.50	4.48	1.22	1.64	0.30
10	29.16	5.79	0.23	0.63	0.70	2.25	2.73	2.73	3.33	2.11	0.45	0.19
10	29.22	5.11	0.56	0.38	1.09	0.97	2.30	1.84	1.08	1.31	0.47	1.55
20	33.48	5.44	0.23	0.88	1.02	1.50	1.84	0.97	2.53	1.38	4.67	0.66
20	32.77	5.50	0.23	1.19	0.94	1.41	1.97	2.50	3.23	1.86	2.83	2.36
50	38.99	5.68	0.19	0.50	1.25	1.27	1.52	1.83	1.80	1.64	1.98	2.25
50	39.04	5.85	0.33	0.56	0.63	1.69	2.41	3.72	2.33	3.16	3.16	1.20

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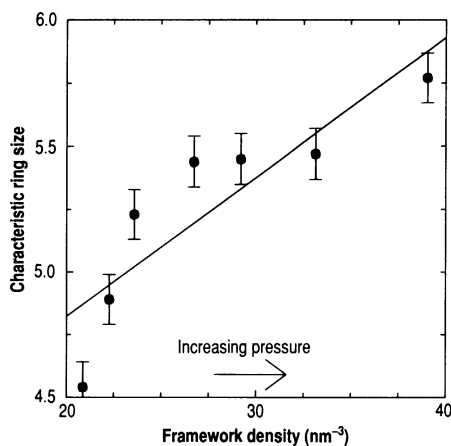
Fig. 3. The characteristic ring size, K^* (Eq. 2), calculated from the simulated structures of SiO_2 liquid at 2000 K as a function of framework density. The points represent averages of the two simulations at each pressure (10). The error bars indicate the uncertainty, estimated by the average difference between the simulations. Deviations from the linear trend in excess of the error bars are likely because of the simplifying assumptions built into the theory: the standard deviation from the best fit line (0.072) is similar to that observed in the much larger sample of crystalline tectosilicates (0.054) (6).

lar increase in K^* with increasing framework density in crystalline tectosilicates (6). We attribute these results to the greater pruning efficiency of small rings and their consequent tendency to form sparse, low-density frameworks. Thus, our theory illustrates the close relation between ring statistics and the density of framework structures and rationalizes compression in the liquid.

Our simulations illustrate the remarkable degree of topological variation possible in a tetrahedrally bonded liquid. Pressure-induced changes in the liquid's topology are systematic and are mimicked by crystalline framework structures (6)—both show a tendency for characteristic ring size to increase with increasing density. These results do not support the intuitive association of small rings with high density and lead us to conclude that the liquid compresses primarily by increasing the size of its rings. The topological compression mechanism, which is unavailable to crystals, may also facilitate efficient compression of natural magmas and liquid-crystal density inversion in Earth's upper mantle.

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8. Liquid-crystal density inversion is important geologically because it determines the direction (up or down) of liquid transport in Earth and thereby the direction of terrestrial chemical evolution. It implies that magmas produced below a certain depth, instead of rising to the surface, will sink to greater depths. Other factors that probably contribute to the density inversion are element partitioning, particularly of Fe [C. B. Agee and D. Walker, *J. Geophys. Res.* **93**, 3437 (1988)], and coordination changes in the liquid (9). The latter is expected to occur at higher pressures (20 to 30 GPa, corresponding to the upper mantle–lower mantle boundary region near 670 km depth) than the compression mechanisms we described.
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10. For each pressure, we initiated one 2000 K simulation by isobarically cooling the equilibrated 6000 K liquid directly to 2000 K and the other by first isobarically cooling the 6000 K liquid to 4000 K and re-equilibrating it at this intermediate temperature before finally isobarically cooling it to 2000 K. The simulations are identical to those in (4), which contains a detailed description of the method.
11. C. S. Marians and L. W. Hobbs, *J. Non-Cryst. Solids*, in press. A fundamental ring is defined as one which cannot be divided into two smaller ones. Thus, the new definition explicitly resolves the ambiguities which were often caused, under previous definitions, by the potential division of large rings. Furthermore, while previous definitions consider only six rings per T-atom, the new definition allows for the common occurrence of greater ring

populations (6) (cristobalite, for example, contains 12 six-membered rings per T-atom). See (6) and J. V. Smith [*Am. Mineral.* **62**, 703 (1977)] for critical discussions of the definition of a ring.
12. The four-coordinate Bethe lattice is the simplest possible tetrahedral framework because it contains no rings. It consists of a central atom, its four first-linked neighbors, the three additional atoms linked to each of these four for a total of $4 \times 3 = 12$ second-linked neighbors, $12 \times 3 = 36$ third-linked neighbors, and so on. The inset of Fig. 2 illustrates a four-coordinate Bethe lattice complete through the third-linked neighbor shell.
13. The number of Qth-linked neighbors in the four-coordinate Bethe lattice is $4 \times 3^{Q-1}$. One can show, then, that the total number of atoms pruned from a Bethe lattice complete through the Qth-linked neighbor shell, $P(Q,K)$, by the formation of a ring of size K is $3^{Q-S} - 1$ for odd K, and $2 \times 3^{Q-S} - 1$ for even K, where S is the linked neighbor shell in which a ring closes: S is $(K-1)/2$ for odd rings, and $K/2$ for even rings (6). The expression (Eq. 1) for the relative pruning efficiency, $P^*(K)$, is derived by taking the large Q limit of $P(Q,K)$ normalized to $P(Q,3)$

$$P^*(K) = \lim_{Q \to \infty} P(Q,K)/P(Q,3)$$

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Tetraplex Formation of a Guanine-Containing Nonameric DNA Fragment

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A combination of spectroscopic and calorimetric techniques has been used to characterize the structures formed by a family of short, guanine-containing DNA single strands of the form d[GGTTXTTGG], X = A, C, G, T. In 1 molar NaCl at low temperatures, these molecules do not behave like single strands, but rather exhibit properties consistent with tetraplex formation. The standard state enthalpies, entropies, and free energies for formation of each tetraplex have been measured, as have preliminary nuclear magnetic resonance (NMR) spectra. In 1 molar KCl, the melting behavior of the structure or structures is more complex than in 1 molar NaCl. This observation may be related to the recently proposed "sodium-potassium switch."

A FOUR-STRANDED FORM OF DNA with guanine self-pairing (so-called G4 DNA) has been proposed by Sen and Gilbert (1) to play a key role in meiosis. In this tetraplex model, repetitive, guanine-rich regions initiate the required alignment of four chromatids by formation of parallel, four-stranded structures in which sets of four guanine bases are arranged in planar tetrads by means of Hoogsteen hy-

drogen bonding (Fig. 1). Guanine-rich regions occur both at the ends of chromosomes, called telomeres (2), and within them, at recombination hot spots (3). Guanine tracts also occur in gene regulatory regions (4). For these reasons, guanine tetrads may represent biologically significant structures that participate in functionally important mechanisms. Several closely related models involving guanine self-pairing have been proposed recently for the specialized structures that occur in telomeres. The guanine-rich strand at the end of many chromosomes is 12 to 16 bp longer than the cytosine-rich strand and may fold back on

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