ON THE NATURE OF PRESSURE-INDUCED COORDINATION CHANGES IN SILICEOUS MILTS AND GLASSES

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Abstract: Progressive decreases in the Si-O-Si angles between ceramics and silicate metal glasses with increasing pressure can be attributed to arrangements of oxygen atoms that can be observed in terms of edge- or face-shared oxygen tetrahedra. This mechanism of compression can account for the gradual, continuous increases in metal and glass density from values at low pressure that indicate discontinuously coordinated states of Si in glasses. The absence of tetrahedrally coordinated Si in glasses until they are highly compressed, the gradual and reversible transformation from tetrahedral to octahedral coordination in glasses once the transformation is detectable spectroscopically, and the fact that this transformation takes place in glasses at room pressure as well as higher pressures. It may also have relevance to pressure-induced transformations from crystalline to glassy phases, the difficulty in achieving some metastable high pressure crystalline phases at low pressures, and the observed differences between the pressures required for phase transformations in shock wave experiments on glasses and crystals.

Introduction

It is generally accepted that silicon is tetrahedrally coordinated by oxygen ions in silicate melts and glasses. In a large number of experiments, it has been established that the four oxygen ions forming the tetrahedron are statistically distributed, and that the coordination of oxygen to silicon is described by the T-O-Si bond angle. The T-O-Si bond angle can be observed in terms of edge- or face-shared oxygen tetrahedra. This mechanism of compression can account for the gradual, continuous increases in metal and glass density from values at low pressure that indicate discontinuously coordinated states of Si in glasses. The absence of tetrahedrally coordinated Si in glasses until they are highly compressed, the gradual and reversible transformation from tetrahedral to octahedral coordination in glasses once the transformation is detectable spectroscopically, and the fact that this transformation takes place in glasses at room pressure as well as higher pressures. It may also have relevance to pressure-induced transformations from crystalline to glassy phases, the difficulty in achieving some metastable high pressure crystalline phases at low pressures, and the observed differences between the pressures required for phase transformations in shock wave experiments on glasses and crystals.

Several observations contain possible variations of compression in silicate glasses and melts: (1) Shock waves modify the structure of molten glasses in the same way that they modify the structure of solid ceramics. (2) The coordination of oxygen to silicon is described by the T-O-Si bond angle. The T-O-Si bond angle can be observed in terms of edge- or face-shared oxygen tetrahedra. This mechanism of compression can account for the gradual, continuous increases in metal and glass density from values at low pressure that indicate discontinuously coordinated states of Si in glasses. The absence of tetrahedrally coordinated Si in glasses until they are highly compressed, the gradual and reversible transformation from tetrahedral to octahedral coordination in glasses once the transformation is detectable spectroscopically, and the fact that this transformation takes place in glasses at room pressure as well as higher pressures. It may also have relevance to pressure-induced transformations from crystalline to glassy phases, the difficulty in achieving some metastable high pressure crystalline phases at low pressures, and the observed differences between the pressures required for phase transformations in shock wave experiments on glasses and crystals.

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The Proposal

What must be sought in a mechanism of compression (2) - the same with only tetrahedral compression at low pressure and then continuously to octahedral coordination at high pressure. (2) does not generate spectroscopically observable tetrahedral coordinated silicon until after substantial compression; (3) proceeds, with increasing pressure, a continuous transformation of amorphous to octahedral coordination as detected by infrared spectroscopy as pressure above the first appearance of octahedrally coordinated silicon; (4) proceeds at room temperature; and (5) is reversible and virtually unquenchable.

Figure I illustrates the kind of mechanism we propose can satisfy these constraints. A chain of octahedrally coordinated Si-amides at Si-O-Si angle of 107° (Figure 1a) is compressed by increasing its angle. Figure 1b shows various stages in its continuous compression. A comparison of Figures 1a and 1f, both of which have the same placement of oxygen atoms (Si-O-Si = 107° in Figure 1f) illustrate our basic point. This configuration of oxygen atoms can be viewed either as a highly distorted and compressed chain of tetrahedra or as a chain of face-shared octahedra. Figure 1c illustrates a possible mechanism by which a low pressure, low density arrangement of oxygen atoms can transform continuously into a closely packed arrangement of oxygen octahedra. Although we have not calculated it, the chain of octahedra shown in Figure 1c could also have been compressed into a chain of edge-shared tetrahedra.

Although the end product of compression of the chain of tetrahedra shown in Figure 1a is a chain of face-shared octahedra (which based on Pwist's view is not expected to be an energetically favorable configuration), edge-shared octahedral arrangements can also be produced by a direct compression of a group of face-shared tetrahedra. Figure 2a shows two highly distorted, linked rings of silicate tetrahedra; Figure 2b shows that the central portion of this configuration of oxygen atoms can also be viewed to two edge-sharing tetrahedra. Both Figures 2a and 2b are actually portions of the crystal structure of chlorite, the arrangement of oxygen atoms in crystalline chlorite, which is usually viewed as linked chains of edge-shared octahedra, could also be viewed as a network of trigonal, corner-shared tetrahedra.

In transforming from Figure 1a to 1f or 2a to 2b, there is no movement of oxygen atoms. There will, however, be movement of Si atoms. In the transition shown, the coordination of Si atoms is not only chemically justified to form oxygen atoms, but also two other oxygen atoms. If the Si ions in these two additional oxygen ions, it would be expected to move across one face of the oxygen tetrahedra to be to be more correctly located within the octahedral defined by the Si-O-Si oxygen atoms.

Discussion

The proposal that the transformation of Si from tetrahedral to octahedral coordination in melts and glasses with increasing pressure is...
Fig. 2. Two views of a part of the structure of 

due to a continuous variation of polymer structure caused by the change from high pressure to low pressure.

(1) The gradual, continuous compression of amorphous silicas from high pressure to low pressure is readily achieved by this model. In particular, the mechanism of compression by decreasing Si-O-Si angles between adjacent tetrahedra can remain the same all the way from 1 to several tens of GPa. Once the configuration has reached the critical packing, the melt or glass will be expected to soften considerably. This has been observed in shock studies (Weast et al., 1986; Piggin et al., 1977). The proposed mechanism of compression may also help to explain why under shock compression the density of silica glass increases smoothly and approaches that of silicovar in lower pressure than does the density of shockcompressed crystalline quartz (Schaff, 1987), because the glass, unstructured by crystal structure, can more readily disorder into the proposed high density arrangement of oxygen polyhedra.

(2) It is not clear how a packing of oxygen polyhedra consistent with octahedral coordination of Si has been achieved, the material will necessarily give up its tetrahedral bonding environment. Thus, for example, it is conceivable that a glass could remain in a tetrahedral network (e.g., Figure 24) to very high pressures and temperatures. Such materials, however, would be highly disordered, and their properties at room temperature and room pressure were determined by the number of oxygen atoms that are being pressed in and brought to a high pressure. The disorder of the high-pressure ordered arrangement of oxygen polyhedra can be observed in an amorphous glass (Williams).
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and freuden, 1987). It is clear, however, that in the early stages of coordination (e.g., Figures 1b, d), nothing but tetrahedral units are present in the glass or melt. This would explain why vibrational spectra of dense glasses, whether obtained at high pressures or at low pressures on peritectically densified glasses, have revealed only tetrahedrally coordinated silicate.

(3) To first order, we would expect the compression of glasses and melts by the proposed mechanism to be stearic; that is, when we apply to the chain in Figure 7a, the Si-O-Si angle decreases, and when we release the pressure, it will spring back. In the range of compression over which the loading and unloading change from isostatic to octahedral, we would still observe the transformation to be stearically reversible. We have utilized the observation that the transformation from tetrahedral to octahedral coordination of Si in amorphous glass is irreversible (Williams and Jeanteur, 1987). In addition, when viewed in this light, it is not surprising that the transformation from low to high pressure packing of oxygen appears to be so difficult to pressure- quicken, it may also explain why octahedrally coordinated Al, whose presence has been inferred to melt at rather low pressures (e.g., Freuden, 1984), has so far only been observed in glasses pressure- quickened to 1 atm.

We note that in reality, coordination of a glass or melt or in several tens of GPa probably would not be entirely stearic, even in the mechanism that we have proposed to describe. In Figure 1, for example, the chain of tetrahedra may be bend by thermal motion among several silicon or polymer, and these bonds would probably have to break as the silicate chain coalesces and may not readily return on release of pressure. Likewise, although it is possible to describe a network of octahedral chains in terms of distorted rings of analogues (Figure 2b), a given low pressure starting configuration of the silicate tetrahedra may not necessarily map directly onto a three-dimensional network of octahedra. Thus, some bond breaking and diffusion would probably accompany the octahedral compression of complex melts and glasses. It is to this extent that we would explain the pressure densification of glasses and systems of Si-O-Si polyhedra in which the octahedrally coordinated Si would spring back to the low pressure tetrahedrally coordinated configuration.

(4) It is important to emphasize that the proposed change of oxygen packing from the expanded low pressure tetrahedral network to a collapsed configuration involving octahedral packing pressures would not be limited by diffusion. The collapse of the structure and change in oxygen packing will take place essentially contemporaneously, and except for a possible activation energy involved in switching over from tetrahedral to octahedral, the process would not play an important role in the kinetics of such pressure-induced transition to octahedral coordination. This may explain why the major pressure induced changes in glasses occur mostly reversibly and on release of temperature (Hersey et al., 1988, 1987, and Jeanteur, 1987).

The pressure for coordination changes in melts and glasses may also be understood of observed crystal-glass transitions. For example, the high pressure crystalline phases yield glasses on pressure-quenching (e.g., Lin and Ringwood, 1975, Lin, 1975). Its pressure to high pressure phase can be described in terms of networks of silicate tetrahedra to which the phases deceptively rely on release of pressure. The quickness of solvus, however, which can be described in terms of a network (Figure 2a), indicates that such structures are not necessarily irreversible. Similarly, it would be that transformation of the net that transmits a role in the conversion of crystalline to glass under pressure at room temperature (e.g., Hersey, 1987, Williams and Jeanteur, 1987). In such cases, we would propose that conversion is the stable, high pressure silicate phase is absent by the use for metastable transformations; conversion to some high pressure crystalline phase, however, is not difficult for phases low temperature conditions because it can be achieved merely by distortion of the low pressure framework. Likewise, glass formation may be favored in certain shock wave experiments either at high pressures or upon unloading from a high pressure-pretransition state. Acknowledgments: We thank Dr. Bass, G. S. Brown, K., J. Jeanteur, and Q. Williams for suggestions that helped us to develop the ideas presented in this paper, and K. J. Hersey, K. Holloway, and C. Maede for comments and criticism. We also thank R. Myers for assistance with the computer graphics. This work was supported by NSF Grant EAR-8407374 and EAR-8518548. California Division of Geologic and Planetary Sciences Contribution 4671.

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