

## Amorphous silicates

## Easy transformations in glasses

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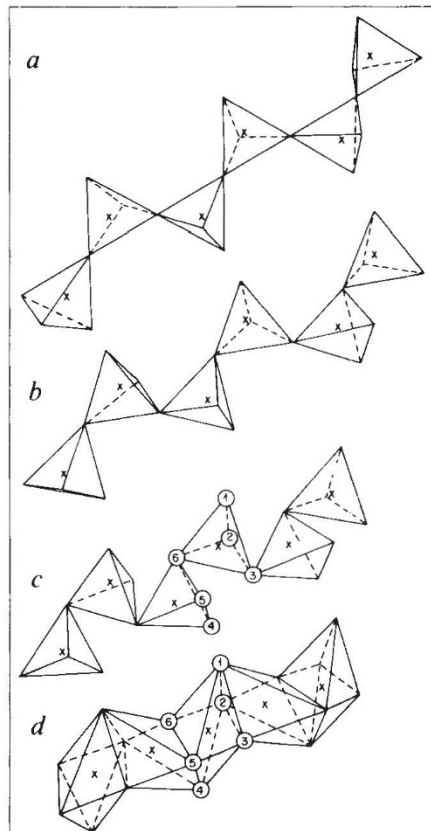
TETRAHEDRALLY coordinated  $\text{SiO}_4$  is the primary building block of silicate melts and glasses at the Earth's surface, but what about at depth? Does the silicon coordination of melts change with pressure? These are significant questions because melting is one of the primary mechanisms by which the planetary interior evolves; the atomic packing that largely determines the properties of silicate melts ultimately governs much of the Earth's internal dynamics. Edward M. Stolper and Thomas J. Ahrens have recently proposed<sup>1</sup> a model in which silicate melts and glasses transform continuously from tetrahedral to octahedral ( $\text{SiO}_6$ ) coordination under pressure. That such a transformation occurs has previously been inferred from the modelling of high-temperature shock-wave measurements on silicate melts: density increases so rapidly with pressure that it is most easily explained in terms of an increase in coordination<sup>2</sup>. What is new about this model is the idea that the change in atomic packing could be continuous and reversible, even at room temperature. This is surprising as one might expect that a major change in coordination would require bonds to be broken, an energetically costly process for the strong Si–O bond.

Stolper and Ahrens propose a displacive mechanism involving an accordion-like compression of the chains and rings of tetrahedra that make up the structures of amorphous silicates (Fig. 1). The corner-linked  $\text{SiO}_4$  tetrahedra are made to rotate toward each other to the point that only minor distortions are required to rearrange the oxygen ions into octahedral configurations around each silicon. The main motivation for such a proposal derives from our recent spectroscopic observations of pressure-induced coordination changes occurring in silicate glasses at room temperature<sup>3</sup>. Remarkably, the transformations are entirely reversible, although they proceed over a broad pressure range (several tens of gigapascals, depending on the glass composition). Moreover, the large increase in density observed in high-temperature samples subjected to shock waves takes place over the same pressure interval, thus confirming that the activation energy involved is negligible. In short, the data indicate a displacive rather than a thermally activated mechanism.

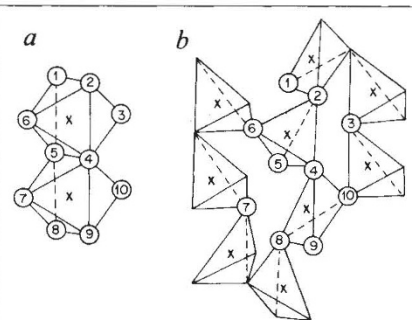
The new model of Stolper and Ahrens is entirely geometrical, emphasizing the survival of undistorted tetrahedra to large compressions. To make the point that octahedral and tetrahedral coordinations of oxygen around silicon can be viewed as

geometrically closely related, Stolper and Ahrens show how the structure of stishovite, the high-pressure crystalline polymorph of  $\text{SiO}_2$ , can be described in terms of irregular rings of distorted tetrahedra (Fig. 2). Although surprising, this does not mean that the transformation of crystalline silicates from tetrahedral to octahedral coordination is displacive. Experiments clearly exclude this possibility<sup>4,5</sup>.

A key point in Stolper and Ahrens' model is that the tetrahedra are allowed to distort in the last step of the coordination change, once Si–O–Si bond angles of  $100^\circ$  are achieved. That such distortion is required is evident from the locations of the silicon ions, most of which must move through edges or faces of the tetrahedra as the octahedra are formed (Fig. 1c and d). It is precisely this step that seems to require a large activation energy in crystalline structures, yet occurs at essentially no



**Fig. 1** Stolper and Ahrens' model for the continuous transformation of tetrahedral  $\text{SiO}_4$  to octahedral  $\text{SiO}_6$ . a–c, The reduction of the Si–O–Si bond angle from  $180^\circ$  to  $140^\circ$  to  $100^\circ$ . d, The new octahedral coordination with the oxygen ions located in the same positions as in c. Oxygen ions are at the vertices (numbers show equivalent ions); crosses, silicon ions. (From ref. 1.)



**Fig. 2** Description of oxygen packing in stishovite: a, edge-sharing octahedra, usual view; b, in terms of distorted tetrahedra. Oxygen ions at vertices (numbers show equivalent ions); crosses, silicon ions. (From ref. 1.)

energetic cost in the less constrained environment of silicate glass and melt structures. How this might be is still unclear, but it is interesting that previous measurements of crystallization from glass provide independent support for this aspect of the model (M. Aziz, personal communication). Specifically, the rate at which quartz grows in  $\text{SiO}_2$  glass is strongly enhanced with pressure, and the activation energy for this bond rearrangement process is expected to vanish above 10–15 gigapascals (ref. 6). Distortion of the tetrahedra towards an octahedral configuration could thus begin at much smaller compressions than invoked by Stolper and Ahrens<sup>3,7</sup>. This has the advantage that Si–O–Si bond angles need not become smaller than about  $120^\circ$ , agreeing with empirical and theoretical results indicating very high energies for smaller angles<sup>8,9</sup>.

The main point of Stolper and Ahrens' article is that coordination changes in amorphous silicates, even in solid glasses, occur much more easily under pressure than in the corresponding crystals. A displacive rather than a thermally activated mechanism seems to be involved in transforming the silicon from a tetrahedral to an octahedral environment. Thus, it seems inevitable that the physical properties of silicate melts deep inside the Earth are strongly influenced by these surprisingly easy coordination changes<sup>10</sup>. □

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