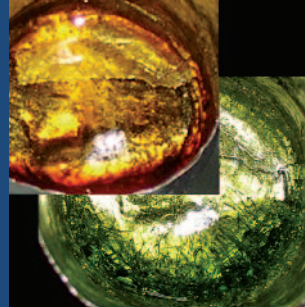


The Structure of Silicate Glasses and Melts

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Green Cr-containing glasses turn yellow at ca. 500°C, a direct illustration of the thermal expansion of cation sites in glasses. PHOTO COURTESY OF O. VILLAIN

Much progress has been made in elucidating the complex structures of silicate glasses and melts. X-ray and neutron scattering, spectroscopy, and theoretical calculations now provide a reasonably clear picture of many aspects of the short-range structure of glasses (which approximates the melt structure at the glass transition temperature). Critical effects of redox conditions and volatiles on structure have been clarified. Qualitatively, links between structure and properties such as molar volume, entropy, cation partitioning, and viscosity have been established, but quantitative connections remain challenging. Effects of temperature and pressure on structure have been the subject of much recent work.

KEYWORDS: melts, structure, properties, cations, heterogeneous, coordination, polyamorphism

INTRODUCTION

Glasses and melts have unique physical and chemical properties, which vary as a function of temperature, pressure, and chemical composition. Understanding these properties requires an accurate structural description. The amorphous nature and complex chemical composition of glasses and melts do not allow the construction of a unique, crystal-like structural model. Nevertheless, despite the lack of periodicity and long-range order, glasses and melts retain a characteristic short-range order, which obeys basic crystal-chemical rules. However, only a limited amount of information exists about changes in a glass structure with temperature or pressure or both. Obtaining this information requires a combination of experimental and theoretical approaches. The connections between structural observations and melt properties are less well known, even at the qualitative level, although progress has been and continues to be made. Melt structure, properties, and dynamics were reviewed a decade ago (Stebbins et al. 1995) and are discussed in detail in a recent book (Mysen and Richet 2005); we provide here only a few examples.

DETERMINING THE STRUCTURE OF MELTS AND GLASSES: A COMBINATION OF STRUCTURAL METHODS AND NUMERICAL MODELING

The structure of melts and glasses is primarily determined from diffraction (scattering) and spectroscopic methods. These techniques have benefited from the development of

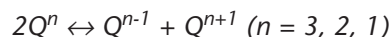
user facilities, such as synchrotron and neutron sources (see *Elements* volume 2, issue 1). Due to the lack of periodicity, neutron and wide-angle X-ray scattering result in one-dimensional information, but give access to interatomic distances, bond angles, and coordination numbers (Brown et al. 1995). Chemically selective spectroscopic methods, such as nuclear magnetic resonance (NMR) spectroscopy, X-ray absorption spectroscopy (XAS), optical absorption spectroscopy, and Mössbauer spectroscopy, are sensitive to the local geometry, site

symmetry, and the nature of the chemical bonds (see Hawthorne 1988). We will focus mostly on XAS (see e.g. Brown et al. 1995; Henderson 2005) and NMR (Stebbins et al. 1995). Most methods that have been applied to glasses have now also been used to investigate melts at high temperatures, in spite of their associated experimental challenges and loss of sensitivity and/or resolution. In addition, there is an increasing number of structural studies of glasses and melts at high pressure.

Numerical simulations [*ab initio* and classical molecular dynamics (MD) and Reverse Monte Carlo (RMC) simulations] are also used to gain insights into the possible atomic-level structure of glasses. The advantage of these approaches is that they provide access to the melt structure and atomic mobility at temperatures and pressures not reachable with experimental methods. Furthermore, RMC simulations can improve the analysis of the theoretical results by allowing the extraction of three-dimensional atomic models from the data that are in quantitative agreement with experiment.

Networks

Decades of experimental evidence have shown that the tetrahedron is the basic structural unit of silicate glasses. The tetrahedra have a well-defined geometry and are linked to each other through their corners in a manner similar to the connection between tetrahedra in crystalline SiO₂. Beyond adjacent tetrahedra, the medium- or intermediate-range structure contains rings of tetrahedra and other interconnected units whose exact structures are not well understood. The addition of a network modifier (such as an alkali oxide) results in the generation of non-bridging oxygens and distributions of Q species within the structure, which have been quantified by Raman and NMR spectroscopy (cf. Stebbins et al. 1995). The distribution of Qⁿ species in silicate glasses is governed by equilibria in the precursor liquids:



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where the extent of the reactions depends on the type of modifier, temperature, and pressure. These distributions make important contributions to the overall order/disorder (i.e. entropy, hence free energy) of the melt, as does mixing or ordering among different types of network cations (e.g. Si, Al). Modifier cations interact with the silicate network in ways that are still poorly known. However, the local structural environments around many cations are now relatively well understood.

The Peculiar Structural Organization Around Cations in Glasses and Melts

In silicate glasses, an intriguing picture is given by the peculiar geometry of cationic sites, the relationships between modifier and “intermediate” cations and the glass network, and evidence of a non-homogeneous distribution of such cations. Cation site geometry is often well defined, but cation coordination numbers are generally lower in glasses than in corresponding crystals. Some cations resemble network formers by occurring in tetrahedra connected to the polymeric network: such is the case for tetrahedral Ni^{2+} , Zn^{2+} , and Fe^{3+} . Other cations such as Ca^{2+} and Sr^{2+} are 6- or higher-coordinated and act as network modifiers. An interesting case is presented by Zr^{4+} , which occurs in regular octahedral coordination in glasses with local charge compensation (Farges et al. 1991). This unusual coordination, encountered in alkali zirconosilicates, was previously suspected from Zr geochemistry (Watson 1979).

An unusual feature of glass structure is the frequent occurrence of 5-fold coordination (cf. FIG. 1A). For example, in silicate glasses, ^{51}Ti coexists with ^{47}Ti , their relative proportions depending on glass composition (Henderson and Fleet 1995). Five-coordination has now been recognized for a wide range of cations, including Mg^{2+} (George and Stebbins 1998), Ni^{2+} (Galoisy and Calas 1993), and Fe^{2+} (see e.g. Jackson et al. 2005), as well as for network cations (Al and Si) in glasses quenched from high-pressure melts (Stebbins et al. 1995; Allwardt et al. 2005).

The same cation may be located in two or more different sites. This is more conveniently observed by symmetry-sensitive spectroscopic methods than by site-averaging diffraction methods. For instance, the presence of low field strength cations (i.e. K^+) can decrease the mean coordination number of the coexisting cations. These can compete more effectively for oxygen ligands, in some cases clearly affecting partial molar volumes of melt components (Liu and Lange 2001). A similar effect has also been noted for five-coordinated Al in both ambient- and high-pressure glasses (Allwardt et al. 2005). The chemical dependence of cation speciation may directly affect mineral/melt partition coefficients, as well as mineral component activities and thus solubilities. In the specific case of transition elements, crystal field splitting energy is also dependent on glass/melt chemistry.

The medium-range organization of cations involves a heterogeneous distribution with a clear structural ordering revealed by cation–cation distances. This information may be obtained directly by neutron scattering coupled with isotopic substitution, and indicates the presence of cation-rich regions extending over at least a 9–10 Å radius and based on edge- or corner-sharing of polyhedra. Such cation-rich regions are illustrated in FIGURE 1B.

Oxygen Surroundings: A Sensitive Witness of Glass Structure

Recently, a complementary view of glass structure has been obtained using methods that reveal the local structure around anions in glasses and melts, especially the all-important oxide ion. Two-dimensional, “triple-quantum

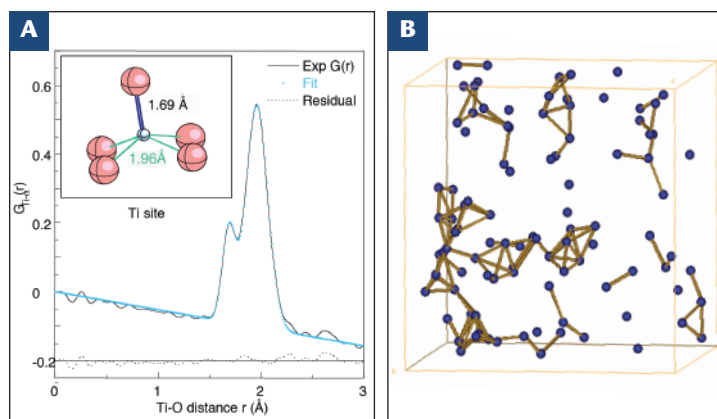


FIGURE 1 (A) Partial Ti–O radial distribution function of 5-coordinated Ti in a $\text{K}_2\text{O}\cdot\text{TiO}_2\cdot 2\text{SiO}_2$ glass, obtained using neutron scattering and isotopic substitution; the inset represents the geometry of the site with a short, non-bonding Ti–O bond (after Cormier et al. 2001). (B) Reverse Monte Carlo simulation of neutron scattering data, showing the structural position of Ti atoms in a $\text{K}_2\text{O}\cdot\text{TiO}_2\cdot 2\text{SiO}_2$ glass. The brown lines represent Ti-sites directly interconnected (after Cormier et al. 2001).

magic-angle spinning” (3QMAS) NMR of ^{17}O has been especially interesting, as it can directly quantify the extent of ordering (e.g. “aluminum avoidance”) among network components Si, Al, and B (Lee and Stebbins 2000) and of modifier cations around non-bridging oxygens. Another approach is oxygen K-edge XANES, which is proving to be useful where other methods are not available to directly measure network cation coordination, such as for Ge in alkali germanate glasses (Wang and Henderson 2004). Here, the electronic processes responsible for the oxygen XANES are strongly influenced by the cationic environment, and consequently the O K-edge XANES is sensitive to changes in the coordination geometry and environment of the cation bound to the oxygen.

FROM GLASSES TO MELTS

When glasses are heated through their glass transition temperatures (T_g , ranging from about 450 to 800°C for most anhydrous silicates), values of the second-order thermodynamic properties increase abruptly. For example, increases in heat capacity at constant pressure (C_p) are typically 10 to 50% (cf. Angell et al. 2000). The glass transition marks the transformation from a disequilibrium amorphous solid to a metastable supercooled liquid. Because the heat capacity just below T_g is commonly near the classical vibrational limit of three times the gas constant R per mole of atoms, the “extra” C_p at higher temperature is thought to be the consequence of additional energy being added to change the structure of the liquid via the onset of dynamic bond breaking and an increase in disorder. When integrated up in temperature from T_g to stable melting points, this “configurational” contribution to thermodynamic properties is often large. For example, the enthalpy and entropy differences between diopside ($\text{CaMgSi}_2\text{O}_6$) and the corresponding liquid at the equilibrium melting point are about twice those between the crystal and the glass at T_g . While it has long been appreciated by those modeling the properties and phase equilibria of magma systems that data for liquids, not just glasses, must be included, it is perhaps less well appreciated that the inherent nature of this distinction is that the liquid structure *must* change significantly with temperature. Extrapolation from studies of glass structure to models of melts at high temperature is thus a key problem.

Perhaps the most intuitive connection between melt structure and critical thermodynamic properties is the entropy associated with structural disorder. Just as in models of site mixing in solids, we can imagine the mixing of various structural units in molten silicates, which gives rise to a configurational contribution to the entropy. Similar concepts connect the configurational components of the thermal expansivity and compressibility to the large, decidedly non-solid-like effects of temperature and pressure on the densities of molten silicates (Richet and Neuville 1992).

Free energy is at the heart of calculations of magmatic phase equilibria; enthalpy is at the center of models of heat flow and transport. The configurational entropy bears obvious relations to these thermodynamic properties through the heat capacity, but a direct connection to a transport property such as viscosity is less obvious. Nonetheless, it has been known for some time that liquids with large heat capacity increases at T_g also show the most rapid decreases in viscosity just above T_g , as well as the most pronounced upward curvatures on plots of the logarithm of viscosity versus inverse temperature, i.e. “non-Arrhenian” behavior (Angell and Sichina 1976). The result is differences in viscosities at high temperatures that vary by many orders of magnitude from one magma composition to another. Remarkably, for silicate liquids a *quantitative* link between the configurational entropy and viscosity has been demonstrated for many systems via the “Adam-Gibbs” relationship (cf. Richet and Neuville 1992 and references therein). Thus, the structural basis of the configurational disorder and the effect of temperature upon it become critical to explaining and predicting a host of chemical and physical processes involving magmas.

STRUCTURAL MODIFICATIONS WITH TEMPERATURE

A simple alkali silicate melt such as $\text{Na}_2\text{Si}_2\text{O}_5$ might contain only Q^3 units. However, results from Raman (Mysen and Richet 2005) and ^{29}Si NMR spectroscopy (Stebbins et al. 1995) demonstrate that the glass network is more disordered than this and is better described by reactions of the type $2\text{Q}^3 = \text{Q}^2 + \text{Q}^4$. If these species mix randomly, they could account for as much as half of the entropy difference between glass and crystal at T_g . Further NMR studies on glasses prepared with varying cooling rates demonstrate that the reaction moves to the right at higher temperature, making an important (but by no means dominant) contribution to the configurational heat capacity (Stebbins et al. 1995). In situ high-temperature Raman studies have confirmed this type of change and have greatly extended the temperature and compositional ranges explored (Mysen and Richet 2005). Temperature-induced changes in the networks of alkali silicate melts, possibly reflecting changes in ordering at intermediate length scales, have also been reported from in situ neutron diffraction (Majérus et al. 2004a).

The tetrahedral networks of magmatic liquids are dominated by interconnected SiO_4 and AlO_4 tetrahedra. Just as Si–Al order/disorder is a key variable in the thermodynamics and phase equilibria of crystalline feldspars and other minerals, it is likely to be important to the properties of melts, although most models of free energies have performed assumed ideal and thus fully random mixing. Aluminosilicate melts often show anomalous heat capacities, suggesting a role for changes in Si–Al ordering (Mysen and Richet 2005). In Ca-, Li-, and Na-aluminosilicate glasses, ^{29}Si and ^{17}O NMR demonstrate that at least in melts at T_g , “aluminum avoidance,” although far from complete, can cause considerable ordering (Lee and Stebbins 2000). The increase in disorder with higher temperatures, which was predicted by

statistical mechanical modeling, was recently quantitatively confirmed by studies of glasses with varying cooling rates and thus varying fictive temperature (FIGS. 2A AND 2B) (Dubinsky and Stebbins 2006). Increases in the randomness of mixing with temperature may account for as much as about half of the configurational heat capacity at T_g in aluminous melts such as $\text{NaAlSi}_3\text{O}_8$ but probably cannot explain their increases in C_p at higher temperature.

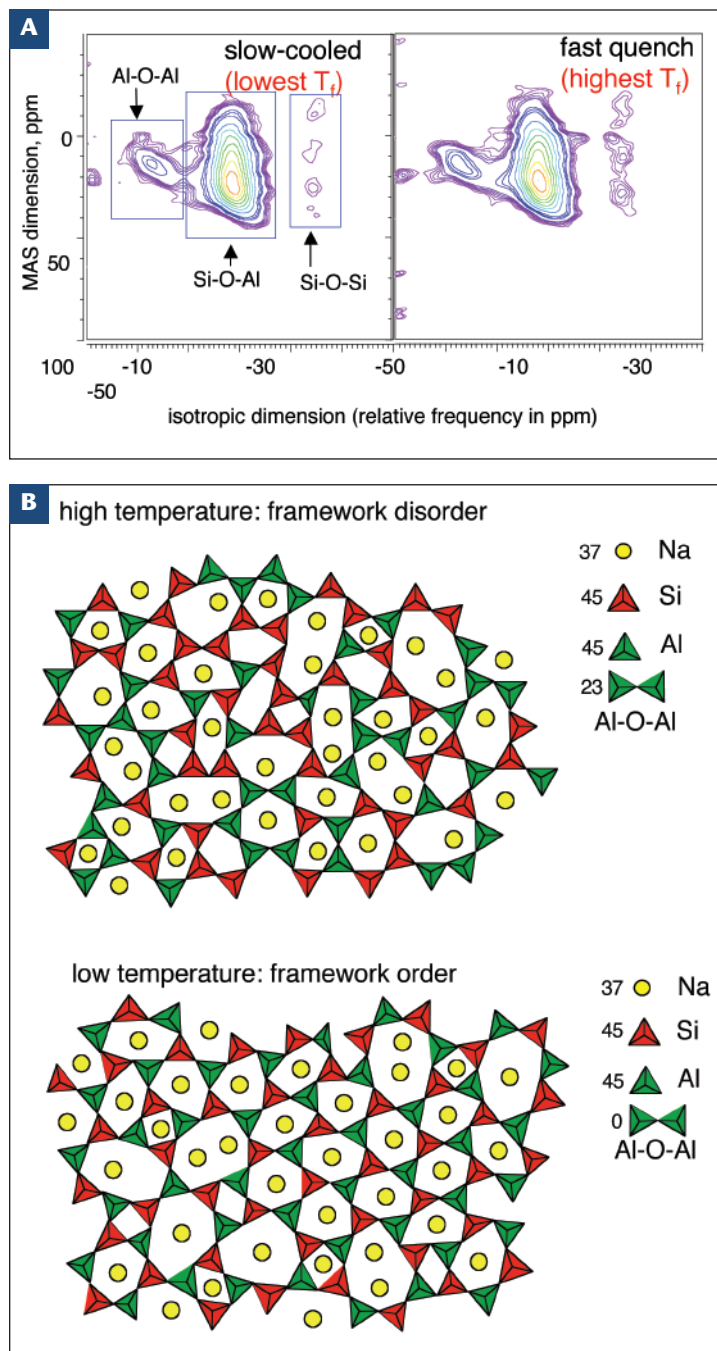


FIGURE 2 (A) Triple-quantum magic-angle spinning ^{17}O NMR spectra (9.4 Tesla field) of $\text{NaAlSi}_3\text{O}_8$ glasses prepared with different cooling rates and thus different fictive temperatures. Blue boxes show peaks for different bridging oxygen species. Intensities for the Al–O–Al and Si–O–Si peaks are slightly higher at higher T_f , indicating greater network disorder. Modified from Dubinsky and Stebbins 2006. (B) Two-dimensional cartoon of temperature effects on network disorder in “ $\text{NaAlSi}_3\text{O}_8$ ” melt, showing extremes of order (Si–O–Al linkages only) and disorder (random linkages between Si and Al).

Increasing temperature causes important structural modifications for cations, such as site thermal expansion, local disorder, and enhanced rates of motion. A recent quantification of the thermal expansion in glasses has indicated values similar to those encountered in minerals (Calas et al. 2006), a confirmation that cations organize their own surroundings in glasses and melts. These effects are enhanced for alkalis due to a low ionic potential and large bond thermal expansion. In the melt and supercooled liquid, alkali motion is decoupled from the structural relaxation of the network without discontinuity through the glass transition (Majérus et al. 2004a). Despite these modifications, the modified random network model still prevails in silicate melts, as in the corresponding glasses. With the temperature-enhanced mobility of alkalis, some cations undergo coordination changes in melts and supercooled liquids: in this case, the glass can no longer be considered as a frozen image of a silicate melt. Recent in situ high-temperature studies have detected changes in the coordination numbers of transition metals and other cations between glasses and high-temperature melts. For example, XAS studies of nickel cations in a variety of glasses and melts have indicated a decrease in the Ni coordination number at higher temperature (Farges et al. 2001). In contrast, in situ NMR has suggested increases with temperature in the average coordination number and/or cation–oxygen bond distance for Na, Mg, and Al in melts (George and Stebbins 1998), possibly as energetically less favorable, larger sites are explored by rapidly diffusing cations. Experimentally daunting, in situ structural studies of hydrous melts at simultaneous high pressure and high temperature have recently been carried out using externally heated diamond anvil pressure cells (Wilke et al. 2006). Some of these studies provide important new insights into the petrologically critical problem of temperature effects on water speciation in melts, which controls solubility and thus many eruptive processes (Behrens and Gaillard 2006).

PRESSURE-DRIVEN TRANSFORMATIONS

Pressure-induced structural transformations of glasses and melts are of major interest for understanding the geophysical properties of deep magmas. While modifier cations may also be affected, the most dramatic consequences of these transformations involve the silicate network. These may be at the origin of the densification of glasses and melts at high pressure, the latter having major consequences for magma transport and differentiation (cf. Stebbins et al. 1995 and references therein; Allwardt et al. 2005). The difficulty comes from the prediction of the changes in melts at high pressure and temperature (as opposed to recovered glasses) and from the partial reversibility of the pressure-induced coordination changes, particularly in glasses that are compressed at ambient temperature only. In situ measurements are thus especially important but are particularly difficult on high-temperature and high-pressure melts. Some structural modifications may be quantified using high-pressure XAS measurements on germanate analogs. The Ge coordination change in the tetrahedral framework of $\text{SiO}_2\text{--GeO}_2$ glasses depends on composition and occurs at higher pressure and over a broader pressure range as the SiO_2 content increases (Fig. 3). XAS data agree with a model based on a mixing of ^{41}Ge and ^{61}Ge , in agreement with a kinetically hindered, first-order transformation at room temperature (Majérus et al. 2004b). Furthermore, 5-fold Ge (^{51}Ge) appears not to be significant, although further work needs to be done.

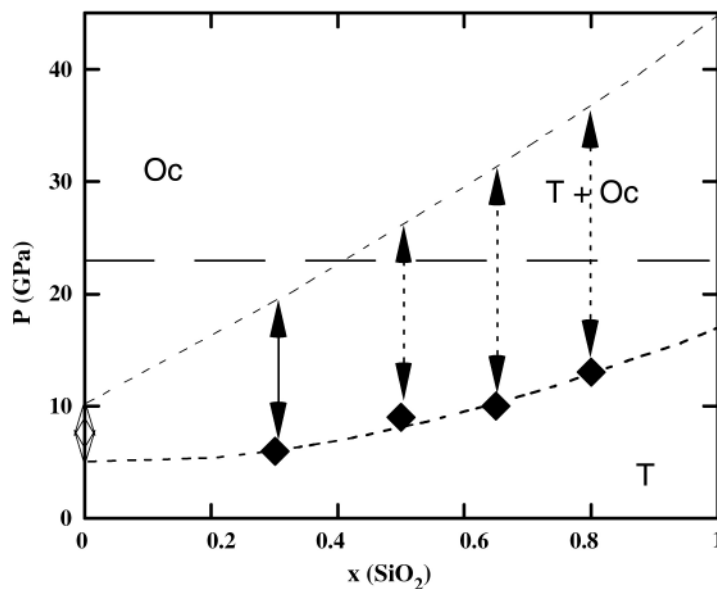


FIGURE 3 Pressure–composition diagram in $x\text{SiO}_2 - (1-x)\text{GeO}_2$ glasses, depicting the pressure-range of the Ge coordination change according to the composition. Diamonds are the pressure thresholds of the coordination change. T: tetrahedral; Oc: octahedral. The dashed curves delimit the intermediate domain in which a mixing of ^{41}Ge (T) and ^{61}Ge (Oc) prevails (after Majérus et al. 2004b)

“Polyamorphism,” implying a relatively abrupt structural change, is a widely discussed topic for silicate glasses and melts at high pressure (McMillan 2004). For example, SiO_2 glass appears to undergo polyamorphic transitions at 8 and 28 GPa (Inamura et al. 2004), with that at 8 GPa resembling the crystalline α - to β -cristobalite transition. Spectroscopic studies of glasses quenched from high-pressure and high-temperature melts are beginning to provide insights into mechanisms of structural changes in melts, although at best they record the structure at T_g and may undergo some still incompletely known structural changes during decompression. NMR studies of alkali and calcium silicate glasses from pressures to 10 or 12 GPa clearly record increases in Si coordination (Stebbins et al. 1995); in aluminosilicates the recovered structural changes are dominated by the development of five- and six-coordinated Al (Lee 2004; Allwardt et al. 2005). Observed structural changes are often well correlated with measured density increases, providing a good prognosis for future structurally constrained models of melt properties (Ghiorso 2004; Stixrude and Karki 2005).

FINAL THOUGHTS

We have not addressed here many of the fascinating structural questions that have direct bearing on the behavior of melts in nature and in technology. For example, intermediate-range order, involving organization at nanometer and longer length scales, is still a major challenge but must be of critical importance to kinetics of crystal nucleation and diffusive transport. For the mechanisms that control dynamical processes such as viscous flow, only tantalizing experimental glimpses have been obtained for the simplest systems; an example is the role of transient, high-coordinated Si in bond exchange in alkali silicates (Stebbins et al. 1995). The structural understanding of component activities in melts, or the effect of melt structure on trace element partitioning, are long-lasting questions, which make a link between molecular-scale and global processes. For these

examples and many others, development of new and improved experimental techniques and of new analytical facilities, as well as the making of in situ high P and T measurements and the application of advanced theoretical methods, are providing major insights. The further development of such approaches can only benefit our understanding of these intriguing and complex materials.

ACKNOWLEDGMENTS

We thank Becky Lange for a helpful review. Any errors or omissions are the fault of the authors, and we apologize if we do not cover all areas of interest to the community in these few pages. GSH acknowledges financial support from NSERC in the form of a discovery grant; JFS thanks the NSF for support through grant EAR-0408410. This is IPGP contribution # 2163. ■■

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