REVIEW

Glass structure, melt structure, and dynamics: Some concepts for petrology

JONATHAN F. STEBBINS^{1,*}

¹Department of Geological Sciences, Stanford University, Stanford, California 94305, U.S.A.

ABSTRACT

1916 December 2016 American Mineralogist Centennial

The thermodynamic and transport properties of the aluminosilicate melts at the heart of most magmatic processes vary in complex ways with composition, temperature, and pressure. Insights into these properties can come from information on the structure of the melts themselves, and more commonly from their glassy, quenched equivalents. Although most such connections remain qualitative or semi-quantitative, they are fundamentally important in interpretation of observations on igneous systems in nature and the labora-

tory, and in the formulation of physically accurate models. This review presents some of the important concepts of aluminosilicate glass and melt structure and dynamics that are most relevant to furthering our understanding of the igneous processes so central to how our planet has formed and evolved. The relationships among glasses, melts, and crystals are introduced. The structural underpinnings of temperature and pressure effects on melt free energies, densities, and viscosities, constraints on the extent of order/disorder among cations and anions in melts, why silica activity varies so strongly with composition, and how liquid-liquid phase separation can be understood, are discussed. Some simple, but useful, general views are presented on melt disorder and the shapes of liquidus surfaces (key to magmatic phase equilibria), as are links between atomic-scale dynamics and viscous flow and diffusion.

Keywords: Silicate melt, glass structure, phase equilibria, viscosity, igneous process, Invited Centennial article, Review article

INTRODUCTION

After decades of research using many experimental and theoretical approaches, much is now known about the structure of aluminosilicate glasses. These materials are of interest not only to igneous processes in nature, but in advanced technologies as well. Less well-defined are the high-temperature (and often high pressure) liquids themselves, but work on glasses has provided a basic framework, and growing numbers of in situ, high T, high P, and even high P-T experiments are becoming feasible. However, as may be inevitable in a developing field, the specialized language and concepts of the discussion, and the focus on ever-finer quantitative details, can limit accessibility by non-experts. This can, in turn, limit motivating inputs from those studying petrological processes into future directions of investigations on the atomic scale. Conversely, phenomenological models that are generated to make pragmatic predictions of melt properties, such as compositional fits of phase equilibria or physical property data, may have limited physical accuracy if they are not well informed by structural concepts. And, a more general understanding, by a wider scientific community, of the fundamental roots of well-known petrological phenomena may lead to new insights into how igneous processes occur in nature as well as the laboratory or industrial glass production facility. Increasingly accurate, and more automated, tools have been developed for calculating the behavior of melts, which often now

It is thus the purpose of this review to present some of the basic concepts of melt structure and properties in a brief, nontechnical form that may increase their accessibility to students and researchers of real-world igneous processes, and enhance the two-way cross-fertilization that can enhance progress across the entire spectrum. Given the breadth of this field, and the limitations of a relatively short article, not much detail can be provided. Recent introductions to the field (Calas et al. 2006; Dingwell 2006; Galoisy 2006; Henderson et al. 2006), as well as, more extensive reviews, provide not only greater conceptual depth but the background literature from experiment and theory that lies beneath the generalizations given here (Greaves and Sen 2007; Lee et al. 2004; Mysen 1990; Mysen and Richet 2005; Richet and Bottinga 1986; Richet and Neuville 1992; Stebbins et al. 1995a, 2013; Stebbins and Xue 2014). Several areas of particular interest in petrology, where some real progress has been made in connecting melt structure with macroscopic properties, are also neglected here for length reasons, notably the role of volatile components such as H₂O and crystal-melt partitioning. Insights from quantum chemical calculations and computer simulations, which have long been important in thinking about melt structure

appear as "black box" software packages. The very success of such modeling efforts can actually insulate users from underlying connections between structure, atomic-scale process, and melt properties, obscuring fundamental and intriguing questions. For example, why do the heats and entropies of fusion for minerals, buried in a model algorithm, vary so greatly, and why does this matter so much for geological systems?

^{*} E-mail: stebbins@stanford.edu

and properties (deJong and Brown 1980; Navrotsky et al. 1985; Tossell and Vaughn 1992) and that are increasingly being extended to large-scale Earth processes (Ghosh et al. 2014; Richet and Ottonello 2014; Stixrude et al. 2009), also largely fall outside the scope of this article.

CRYSTALS VS. LIQUIDS VS. GLASSES

Melting, crystallization, and the glass transition

The processes of melting and crystallization are, of course, of key importance in igneous systems and are ultimately controlled in part by the atomic-scale structure of the melt. However, these are not the main subjects of this review. On the other hand, quenching of silicate melts to glasses does happen to be a common phenomenon in nature, especially during rapid cooling of magmas on the sea floor and in explosive eruptions. More generally, much of what we know about the atomic-scale structure of silicate melts comes from diffraction and spectroscopic studies of glasses. It is thus important to know just what a glass is, what it is not, and what it represents.

When a crystalline solid melts to a liquid, there are abrupt changes in first-order thermodynamic properties including enthalpy, entropy, and volume, as well as their "second-order" temperature and pressure derivatives, namely constant pressure heat capacity (C_P), thermal expansivity ($\alpha = [dV/dT]/V$), and compressibility ($\beta = -[dV/dP]/V$). Under equilibrium conditions, melting occurs as heat energy (enthalpy) is added to break bonds and rearrange and (usually!) expand the structure, with an entropy increase to balance the free energy change to zero. The crystal, defined by long-range as well as at least partial short-range order, transforms from a relatively rigid state to a more fluid, more disordered state in which ions or molecules are much more mobile.

Going the opposite direction, the kinetics of crystal nucleation and growth can be relatively slow. Especially in liquids where the viscosity at the melting point (T_m , or the liquidus temperature) is relatively high, as is often the case for silicate melts, the temperature can be lowered below $T_{\rm m}$ without crystallization taking place, into the metastable, "supercooled" liquid region. High viscosity is closely associated not only with slow diffusion of the components that need to assemble to make a complex crystal from the liquid, but also with the short-range bond breaking and re-arrangements that are needed to go from the disordered melt structure to what may be a quite different structure in the crystal. With falling temperature, all of these dynamics slow down as the viscosity rises; if cooling is sufficiently rapid, crystallization may be avoided completely. With cooling, the structure of the liquid itself continuously re-arranges and becomes more ordered as its entropy decreases. At some point, however, the kinetics of the local structural changes needed to maintain metastable equilibrium in the melt become too slow to keep pace with the decreasing temperature. Over a temperature interval that is typically only a few to tens of degrees, the liquid falls out of equilibrium and the melt structure "freezes in" to form a rigid glass. At typical laboratory cooling rates this occurs at a viscosity of about 1012 Pas, whether the liquid is a geologically interesting basalt, a multi-component borosilicate in a production line making glass for computer displays, or a simple organic molecular liquid such as glycerol.

The transition from liquid to glass involves often a large decrease in second-order properties—heat capacity, thermal expansivity, and compressibility—over a fairly narrow temperature interval, without abrupt changes in first-order properties. It thus in some ways can resemble a second-order phase transition in a crystal. However, the glass transition is inherently a kinetic phenomenon depending on thermal history and structural dynamics, and is thus a disequilibrium process. Glasses do have physical properties that clearly define them as solids, not just as "really viscous liquids," but they lack the long-range translational symmetry and order of crystals.

Fictive and glass transition temperatures

A measure of where a liquid transforms to a glass during cooling is the "fictive temperature" (T_f), which approximates the point where the melt structure was "frozen into" that of the glass (Mysen and Richet 2005). T_f will be higher if cooling is more rapid (Fig. 1); correspondingly, the liquid will behave rigidly (and potentially fracture) at a higher temperature and lower viscosity if deformation is very rapid (Dingwell and Webb 1990). Obtainable laboratory cooling rate variations over 6 or 8 orders of magnitude typically can change T_f by only up to about 200 °C, however. This means that some structural details important in liquids at much higher temperatures are potentially not detectable in any glass that can be formed and must be observed in situ or



FIGURE 1. Qualitative sketch of how a first-order thermodynamic property such as molar volume, entropy, or enthalpy varies with temperature for a glass-forming liquid. The stable liquid enters the metastable ("supercooled") field on cooling below the melting point of the corresponding crystal, T_m . On further cooling, the rate at which the structure of the melt becomes more ordered slows to the point where it falls out of equilibrium, transforming to a solid glass. The properties of the glass are strongly dependent on this point of transition, T_t , which is higher for faster cooling. The colored area represents the "configurational" contribution to the property of the liquid. Note that in reality, curves are not linear, the changes in slope vary widely, and the glass transition takes place over a range in temperature, not at a single discontinuity.

in computer simulations. The closely related term "glass transition temperature" (T_g) is often used in a similar sense to T_f , but most commonly designates the point at which a glass, heated at a standard rate such as 10 °C/min, transforms back to a metastable supercooled liquid with a measurable change in $C_{\rm P}$ or α . It is very important to note that the melt structure recorded in the glass should depend only on the cooling rate through the glass transition range and not on the initial temperature, assuming that the original stable liquid is truly a single phase (no residual crystals or bubbles) and that cooling is isochemical. In some systems the latter may not be the case, as temperature can drive compositional changes, most obviously variations in oxidation state of Fe and other redox-variable elements. Because such kinetics may involve longer-range diffusion of chemical components, their structural consequences may occur much more slowly than the processes that control local isochemical structure and viscosity.

A glass with a faster cooling rate and higher $T_{\rm f}$ will thus have a greater enthalpy of formation and a greater molar volume (lower density) than the same composition glass with a lower $T_{\rm f}$, differences that can often be readily measured in the lab on experimental (Tischer 1969) and sometimes on natural glassy materials (Dingwell 2006; Nichols et al. 2009). A glass with higher $T_{\rm f}$ will also inherit a higher degree of structural disorder from the metastable liquid.

CONFIGURATIONAL PROPERTIES OF MELTS: WHY STRUCTURE MATTERS

Thermodynamic properties, most obviously free energy and its first (entropy, volume) and second temperature and pressure derivatives (involving $C_{\rm P}$, α , β), control melting and crystallization and thus define the phase diagrams at the heart of igneous processes. Melt properties, and how they change with composition, are closely linked to melt structure. While it is not yet possible to accurately predict the details of phase equilibria from structural measurements alone, knowledge of these connections is critical to testing and improving models as well as fundamental in understanding the atomistic roots of complex geological processes.

The heat capacity of both crystalline and glassy solids is usually dominated by the energy put into interatomic vibrations with increasing temperature, and increases with temperature. For materials such as silicates that have relatively high melting and glass transition temperatures, it has long been observed that the heat capacity (most precisely the constant volume heat capacity $C_{\rm V}$, which for solids usually differs from $C_{\rm P}$ by only a few percent) tends to approach the classical vibrational limit of about $3 \times$ the gas constant R per mole of atoms (Mysen and Richet 2005; Richet 1984). Heat capacities well above this value may be observed when extra energy needs to be added to change the structure itself with increasing temperature. This involves rearranging the atoms or molecules and the bonds between them, and associated increases in $C_{\rm P}$ are often thus considered as "configurational" $(C_{P,conf})$. Such effects can be observed in some crystalline phase transitions involving cation or anion disorder, and in crystalline molecular solids in which whole molecules can begin to rotate or exchange positions. C_{P,conf} for silicate melts is sometimes approximated simply as the excess over 3R per mole of atoms, or more commonly as the increment in $C_{\rm P}$ between glass and liquid at $T_{\rm g}$, which is usually similar. In most melts more complex than SiO₂ itself, such configurational heat capacities are quite significant (10 to as much as 50% above the 3R "limit"), are readily observed on heating through T_g , and, when integrated up in temperature to melting points, have large effects on overall entropy, enthalpy, and free energy. For example, the heat of fusion of diopside (CaMgSi₂O₆) at its melting point would be estimated as about 86 kJ/mol if the configurational component of C_P were neglected, that is, if the liquid heat capacity were taken as that of the glass; the actual value is about 138 kJ/mol (Richet and Bottinga 1986). Increases in thermal expansivity and compressibility are usually even larger than those in C_P , often growing by a factor of two or three from glass to liquid (Mysen and Richet 2005; Richet and Neuville 1992). If these property changes are "configurational," the obvious and fundamental questions are "what is the structure?" and "how is it changing so much with temperature?"

As a preview to structural concepts discussed below, it is useful to compare the properties of albite liquid (NaAlSi₃O₈) with those of a lower silica composition such as diopside (CaMgSi₂O₆). As a rough starting point, the former may be considered to represent something resembling a high-silica rhyolite, the latter a mafic, even ultramafic magma. The structures of the feldspar and pyroxene crystals are of course very different, and it is safe to assume that the melt structures will also be very different. The enthalpies and entropies of melting, per mole of atoms, are also very different: ΔH_m and ΔS_m for diopside are 13.8 kJ/mol of atoms (138 kJ/mol divided by10 atoms per formula unit) and 8.3 J/(K·mol) of atoms, but for albite are 4.9 kJ/mol of atoms and 3.5 J/(K·mol) of atoms. Increases in heat capacity on heating through T_g are also quite different, about 31% vs. 8% for diopside and albite liquids, respectively (Richet and Bottinga 1986).

Beyond the obvious importance of configurational (structural) changes and consequent effects on thermodynamic properties to phase equilibria, heat budgets, melt density, and buoyancy, etc., there is a remarkable and fundamental connection between transport properties of melts, most obviously viscosity, and the configurational heat capacity and entropy. As noted above, for typical cooling rates the viscosity of almost any glass forming liquid is about 1012 Pa·s at its transition to glass, including for example, a rhyolite and a basalt, or albite and diopside as illustrated here; and T_{g} values for all of these typically differ by only about 100 K. However, the rate at which viscosity (η) decreases with T above T_g , and the shape of the curve on a plot of log η vs. inverse 1/T (an "Arrhenius" plot) differ greatly (Fig. 2). Liquids such as silica, albite, and anhydrous rhyolites have such curves that are nearly linear ("Arrhenian" behavior) over as much as 1000 K, and have been labeled as "strong" liquids (Angell 1985). The configurational components of their heat capacities are relatively small, suggesting that structural change with T is limited. In contrast, η for a composition such as diopside or a mafic basalt decreases much more rapidly above T_s , then curves to a shallower slope at high T, resulting in a viscosity in the magmatic temperature range that may be many orders of magnitude below that of a "strong" liquid. (Of course, basaltic magmas in nature are generally much hotter than rhyolitic magmas, which accentuates their difference in viscosities.) Such liquids are described as more "fragile." Their systematically higher increases in $C_{\rm P}$ at $T_{\rm g}$ suggest more rapid structural disordering with rising temperature. Models that

parameterize viscosity as functions of composition, regardless of their theoretical basis, must include this sometimes highly "non-Arrhenian" temperature dependence to be accurate and useful over a wide-temperature range (Giordano et al. 2006; Hess et al. 1996; Mauro et al. 2009).

These fundamental relations, which apply to many types of glass formers from simple organic molecular liquids and polymers, molten salts, and even some aqueous solutions, as well to more conventional silicate-based systems, were highlighted by physicists and chemists working on the intriguing general issue of the nature of the glass transition (Angell 1985). The "Adam-Gibbs" equation (Mysen and Richet 2005; Richet 1984) draws the quantitative connections

$$\log \eta = A + B/(T\Delta S_{conf}) \tag{1}$$

where S_{conf} is the configurational entropy of the liquid, based on the value at T_{s} and integration up in temperature of its derivative, $C_{P,conf}/T$, from T_g . A and B are fitting parameters needed to match the shape of the viscosity curve, but may be correlated with each other in a given type of material. The applicability of the Adam-Gibbs equation to silicate melts of interest in the geoscience community has been well-demonstrated by calorimetry and viscosity studies in both pioneering early studies (Richet 1984) and recent re-confirmations (Richet 2009); it has often been inverted to estimate configurational entropies from viscosity data on complex silicate melt solutions and test models of mixing (Neuville and Richet 1991; Toplis et al. 1997a). The exact physical explanation of the Adam-Gibbs equation in such liquids remains incompletely understood, but it again points out how fundamental the liquid structure, and how it changes with temperature, must be to the melt properties that control igneous processes.



FIGURE 2. Plot of log_{10} of viscosity (Richet 1984) for albite (Ab, NaAlSi₃O₈) and diopside (Di, CaMgSi₂O₆) liquids vs. inverse temperature. Straight lines (pure "Arrhenian" behavior) are shown for comparison. The glass transitions are at about 10^{12} Pa·s.

CONCEPTS OF MELT STRUCTURE: TIES TO MAGMA PROPERTIES

The known structures of crystalline silicates, familiar ground for most Earth scientists, provide the basic starting point for concepts of glass and melt structure, but can only take us so far into the disordered, dynamical realm of high-temperature liquids. The literature of glass structure is vast because of widespread interest not only in the geosciences but in technology, condensed matter physics, and solid-state chemistry. Here I will highlight a few basic concepts that have some obvious bearing on petrologic processes.

The silica network and network-modifying oxides

The common beginning for such discussions is pure silica (SiO₂). Glasses of this composition are quite important in technology in optical components and data transmission fibers, but are found in nature only in fulgurites and rare types of impactites (e.g., Libyan Desert glass). As in the low-pressure crystalline forms of silica, it is well known that the glass is comprised of a threedimensionally linked, corner-shared network of SiO₄ tetrahedra, with some degree of disorder in the ring structure, bond angles, and distances. The oxygen links between the Si4+ "network forming" cations are denoted "bridging" O atoms (BO). Si-O bonds in such tetrahedra are among the strongest in silicate materials. Silica liquid thus is the epitome of a "strong" liquid in the sense that its viscosity drops relatively slowly on heating above T_{\circ} , and its heat capacity increase from glass to metastable liquid at T_{o} is minimal. It is thus not surprising that cristobalite, the crystalline polymorph stable at the 1 bar melting point, has the lowest known heat and entropy of fusion of any silicate [3.0 kJ/mol of atoms, 1.5 J/(K·mol) of atoms] (Richet and Bottinga 1986). This simple fact has a huge impact on silicate phase equilibria and on magmatic differentiation, as will be discussed below. A two-dimensional "cartoon" view of the relatively minor structural differences between crystalline and glassy silica is shown in Figure 3.

When an oxide of another element with +1 or +2 valence $(M_2O \text{ or } MO, \text{ such as an alkali or alkaline earth oxide) is added to liquid silica, there are too many oxygen anions <math>(O^{2-})$ for them to all connect to two tetrahedrally coordinated Si⁴⁺ cations. As a result, some must be bonded to only one SiO₄ group and thus become "non-bridging" O atoms (NBO). In standard models, which are good first approximations, exactly two NBO are formed from one BO and one added O²⁻ ion (Fig. 4a)

$$\text{Si-O-Si} + \text{M}_2\text{O} \leftrightarrow 2\text{Si} - \text{O}^- + 2\text{M}^+.$$
 (2)

When enough modifier oxide has been added so that the molar ratio O/Si is greater than the coordination number of Si (4), then there must be O^{2-} ions that are bonded only to the modifier cations, forming so-called "free" oxide ions. Magmas this poor in silica (<33.3 mol%, as in olivine) are rare in nature, but are of major importance in the technology of ore smelting, where the properties of molten "slags" are key to the controlled reduction and purification of molten metals such as iron. This species can also be present in minor amounts at higher silica contents, at least when the "modifier" cation has a relatively high charge and/or small radius (e.g., Mg²⁺) (Nasikas et al. 2012; Sen and Tangeman 2008), tends to form relatively covalent bonds (e.g., Pb²⁺) (Lee and Kim 2014), or is part of an OH⁻ group bonded only to modifier cations (Xue 2009).

Locally, the negative charge on each NBO (formally -1) must be balanced by coordination with several modifier cations, each of which is shared, in turn, with other O atoms, just as in crystalline silicates. And, of course, the energetically stable coordination number of the modifier cation is generally much greater than the 1 or 2 NBO produced per cation by reaction 2. Therefore, also as in crystals, at silica contents above the olivine composition, there are usually not enough NBO to make up the full first-shell coordination of each modifier cation, which thus must then include some BO. Many of the differences between effects of different cations are captured by the variable "cation field strength," which is the valence divided by the sum of the cation and oxide ion radii (e.g., $Mg^{2+} > Ca^{2+} > Na^+ > K^+$) (Brown et al. 1995). If multiple types of modifier cations (M) are present in the melt, they may "compete" for the formation of small coordination shells with short M-NBO distances, with the higher field strength cation expected to "win," again as can be seen in some crystal structures. For example, Ca2+ in crystalline diopside has 4 NBO and 4 BO neighbors, while smaller Mg2+ has 6 neighbors, all NBO. Modifier cations will thus interact with not only the NBO in

silica-like "crystal"





FIGURE 3. Sketch of a two-dimensional analog of a silica-like "crystal" vs. "glass." Here and in Figure 5, oxygen anions are shown explicitly as larger circles, cations as smaller circles. Note the relatively small number of ways that the "glass" structure is disordered relative to that of the "crystal," e.g., angles between polyhedra, ring sizes.

their first shells, but with any BO present as well. In liquids these interactions are dynamic, transient, and likely to be important in breaking BO-Si bonds, which is required for viscous flow to occur in all but the most silica-poor melts. Mixing of different modifier cations, if it occurs, will add to configurational entropy of the melt, affecting its viscosity curve and fundamental thermodynamics. For example, unlike in the crystal, there is evidence of a randomized Ca/Mg distribution in diopside glass and liquid, with a large contribution of this mixing to the entropy of fusion (Allwardt and Stebbins 2004; Cormier and Cuello 2013; Richet and Bottinga 1986; Stebbins et al. 1984). Another 2D "cartoon" view of the wide range of possibilities for structural disorder in a complex, lower silica composition such as multi-component chain silicate is shown in Figure 5. As in crystals, most modifier cations can themselves have a range of coordination numbers in melts and glasses, which can vary in complex ways with composition, temperature, and pressure (Brown et al. 1995; Farges et al. 1994, 1996; Galoisy 2006; Guignard and Cormier 2008; Skinner et al. 2012; Wilke et al. 2007).

Composition, structure, and "fragility" in simple binary systems

It is not really the modifier cations that "break up" the silica network (as is often stated in introductions to this topic), but the accommodation of the added oxide ions into the network, which must reduce the number of bridges between the Si cations if the latter remain coordinated by exactly 4 O atoms. However,



FIGURE 4. Sketch of a two-dimensional analog for adding a networkmodifying oxide (M_2O) to a network liquid such as SiO₂, B_2O_3 , or GeO₂. Here, network cation polyhedra are shown instead of the oxygen anions that mark each of their corners. (**a**) Most appropriate for silicates at low pressure, the added oxide forms two NBO (dark blue circles) from a bridging oxygen connecting two "tetrahedra." The nominal –1 charge on the NBO's are relatively concentrated. (**b**) Most appropriate for germanates or borates at low pressure (during initial modification of the network), or possibly silicates at high pressure. Here, the added oxide increases the coordination number of a network cation. Instead of forming NBO, oxygen bridges between the higher and lower coordinated network cations (light blue circles) are formed, whose partial negative charges are more dispersed than in **a**. In both cases, the M cations (yellow circles) are distributed to balance the charges on the O atoms. Reprinted from Stebbins et al. (2013) with permission from Elsevier. modifier cation-BO interactions do weaken the silicate network by pulling some electron density out of the Si-O-Si linkages, and bonds among the modifier cations and the NBO are generally more ionic, weaker, and longer than Si-O bonds. The liquid thus becomes more "fragile" as more modifier oxide is added and viscosity at $T > T_g$ drops farther and farther below that of liquid silica. Heat capacity increase at T_g becomes larger and larger as well, and the liquid structure becomes disordered more and more rapidly with increasing temperature. As noted above, heats and entropies of fusion tend to increase with decreasing silica content, at least in part because of the greater number of ways that a lowsilica melt can be disordered. Some aspects of these changes in disorder are known, many are still to be determined.

Clustering and liquid-liquid phase separation

The size and charge of the modifier cation systematically affect the quantitative details of property changes with composition. For example, modifier cations usually are energetically stabilized more effectively by NBO than by BO. This can lead to preferential clustering of NBO with these cations, and eventually to liquidliquid phase separation. Two-liquid fields extend systematically to higher temperatures and wider ranges of silica contents with

chain silicate "crystal"



chain silicate "glass"



FIGURE 5. As in Figure 3: sketch of a two-dimensional analog of a compositionally complex "chain silicate" "crystal" vs. "glass." Here there are two types of network-forming cations (Si and Al) and two types of network-modifying cations (e.g., Na and K). Some of the bridging O atoms (BO) and non-bridging O atoms (NBO) are labeled. Compared with Figure 3, there are many more ways of disordering the structure: randomization of each pair of cations; change from a single to multiple types of anionic groups; even the formation of over-coordinated Al.

higher modifier cation field strength. One of the highest field strength modifiers that is abundant in magmas, and that is often concentrated during differentiation under $low_{-f_{O_2}}$ conditions, is FeO. It is thus not coincidental that the only common observation of silicate liquid-liquid phase separation in nature is in very FeO-rich residual melts trapped in some crystallizing basalts. As will discussed below, closely related effects of field strength and network species distributions have petrologically critical effects on one of the most important chemical parameters, the thermodynamic activity of silica. Some cation and NBO clustering may be common even in single-phase melts, leading to the possibility of through-going "ion channels" (Greaves and Sen 2007) that may greatly augment diffusion in both liquids and glasses (Fig. 6).

Melt structure vs. mineral structure

In a general sense, the continuous change with composition in a "snapshot" view of melt structure at high temperature, or in the quenched-in structure at the glass transition that can actually be observed at room temperature, resembles the discontinuous progression in the structures of crystals as the modifier oxide/ silica ratio increases, and hence the ratio of NBO to tetrahedral cations (NBO/T). In the Na2O-SiO2 system, for example, crystalline $Na_2Si_2O_5$ ($Na_2O/SiO_2 = 0.5$) is a sheet silicate analogous to a mica: the average NBO/T must be 1 (reaction 1). It happens that each SiO₄ group in the crystal actually has just one NBO and three BO, although other distributions could be imagined in a more complex structure of the same composition. At $Na_2O/SiO_2 = 1.0$ the chain silicate Na₂SiO₃ forms with each tetrahedron having exactly two NBO; at $Na_2O/SiO_2 = 2.0$ an olivine-like structure Na4SiO4 is stable and each SiO4 has four NBO and no BO. In rockforming minerals the progression from sheet silicates to pyroxenes to olivines follows the same pattern, although compositions are often more complex. Spectroscopy (e.g., Raman and NMR) on simple-composition glasses can detect and sometimes count SiO₄ tetrahedra with varying numbers of BO and NBO (Koroleva et al. 2013; Maekawa et al. 1991; Malfait et al. 2007b; Mysen and Richet 2005). In some early literature these were described as "sheet-like," "chain-like" (etc.) units by analogy with the crystals. However, these terms may inadvertently carry implications about longer range structure and dynamics for which we have little real information. Hence, a terminology has been adopted that fixes the description to the measureable local structure of SiO₄ groups ("Quaternary," with four bonds) with varying number (n = 0 to 4) of bridging O atoms, "Qn species." Low-pressure crystalline silica is thus solely comprised of Q⁴ units, pyroxenes of only Q² units, olivines of Q⁰ and so forth. An obvious question for melt and glass structure thus becomes how do distributions of Qⁿ species relate to those known to be present in the crystals.

Network speciation, modifier cations, and silica activity

One of the early hints about the nature of structural disorder in glasses, and of its quantitative extent, relates to such network speciation, and is closely linked to one of the most important thermodynamic parameters needed to understand and predict magmatic phase equilibria, namely the activity of silica (a_{siO_2}). As introduced by slag chemists and as highlighted for petrologists in the seminal work of I.S.E. Carmichael (Carmichael et al. 1974), silica activity controls not only the solubility of silica minerals but equilibria between pairs of major rock-forming silicate minerals such as feldspars-feldspathoids and pyroxenesolivines. It is thus fundamental to magmatic evolution and even to standard igneous rock classification schemes. It has been known since early phase diagram studies (Hess 1995; Ryerson 1985) that modifier cation field strength systematically and dramatically affects the activity coefficient of silica in melts ($\gamma_{SiO_2} = a_{SiO_2}/X_{SiO_2}$).



FIGURE 6. As in Figure 4: sketch of a two-dimensional analog of a modified network liquid, but showing implications for longer-range structure. The upper panel corresponds to Figure 4a, with all "tetrahedral" network cations (triangles in 2D) and abundant NBO. Note clustering or "channeling" of modifier cations. The lower panel corresponds to Figure 4b, with partially charged BO between lower and higher coordinated network cations. Note the much greater dispersion of the modifier ("charge balancing") cations. A transition from the upper to lower type of structure might take place in aluminosilicate melts with increasing pressure. Reprinted from Stebbins et al. (2013) with permission from Elsevier.

Figure 7 (Ryerson 1985) shows the silica saturation curves (liquidi) for a series of alkaline earth and alkali oxide-silica binaries. In each such binary phase diagram, isothermal points on the cristobalite liquidus each must have the same silica activity. The mole fraction of silica at such points steadily decreases as the field strength increases from K⁺ to Na⁺ to Li⁺ to Ba²⁺ to Sr²⁺ to Ca²⁺ to Mg²⁺ (see Brown et al. 1995 for field strength values). The activity coefficient γ_{SiO_2} must thus increase, by a factor of almost 2, in this same sequence. Similar systematics have also long been known in three-component phase equilibria where a_{SiO_2} is fixed by mineral pairs such as forsterite-enstatite (Hess 1995; Ryerson 1985).

This systematic effect continues into complex multicomponent magmatic liquids, as can be explored by calculation of a_{SiO_2} using the pMELTS software package (Ghiorso et al. 2002), in the composition, temperature, and pressure range where it is well calibrated, such as for basaltic melts at 1600 °C and 1 GPa. For a standard MORB composition (51 mol% SiO₂), 1 mol% CaO can be systematically replaced with 1 mol% of K₂O, Na₂O, MgO, or FeO (Fig. 8). Here, the same qualitative trend as expressed in the simple binary and ternary systems is readily apparent, with a steady increase in a_{SiO_2} with smaller and/or higher charged modifier cations. In an extreme example of replacing 6% MgO in a typical MORB with Na2O, the average modifier cation field decreases from 0.39 to 0.32 and γ_{SiO_2} drops by a factor of 2.5; a typical K- and Na-rich, Ca- and Mg-poor nephelinite (average cation field strength of 0.34, 41 mol% SiO₂) has γ_{SiO_2} about 4× lower than the unmodified, low-alkali, high-Mg MORB.

This dramatic effect is well, if qualitatively, correlated with findings on glass and melt structure. A melt of the same composition as a simple binary silicate crystal, such as $Na_2Si_2O_5$ or MgSiO₃, could be imagined to have exactly the same Qⁿ speciation as the crystal, i.e., all Q³ or all Q² in these examples.



FIGURE 7. The liquidus curves for cristobalite in a series of alkaline earth and alkali silicate binary phase diagrams (Ryerson 1985), showing dramatic effect of modifier cation field strength ($Mg^{2+} > Ca^{2+} > Sr^{2+} >$ $Ba^{2+} > Li^+ > Na^+ > K^+$). Any series of isothermal points on the liquidi have the same silica activity, as illustrated by red dots and dashed line.

Spectroscopy on glasses and melts has shown instead that "disproportionation" reactions take place, probably driven by the entropy generated by mixing of a greater variety of Qⁿ species than is necessitated by composition alone, such as

$$2Q^3 \leftrightarrow Q^4 + Q^2 \tag{3}$$

$$2Q^2 \leftrightarrow Q^3 + Q^1. \tag{4}$$

The right-hand sides of such reactions are generally favored by higher field strength modifier cations (Davis et al. 2011; Maekawa et al. 1991; Malfait et al. 2007a; Mysen and Richet 2005), as groups with lower Qⁿ numbers have more concentrated local negative charge (more NBO in one place). As a "side effect," the concentration of Q4 units is higher in such systems (e.g., Li > Na > K), which correlates systematically with higher γ_{SiO_2} . For example, in the alkali disilicate glasses $(M_2Si_2O_5)$, which could be comprised of only Q³ units, about 17, 11, and 7% Q4 species have been detected for Li vs. Na vs. K by ²⁹Si NMR spectroscopy (Maekawa et al. 1991), balanced by corresponding concentrations of Q² and other groups. Quantitative connections between such structural details and the phase diagrams have been made in models of simple alkali silicate binaries (Gurman 1990; Vedishcheva et al. 1998); extending them to detailed structure-free energy links in complex magmatic systems remains for the future. The mixing of Qⁿ species contributes significantly to the overall configurational entropy of the melt but is by no means the predominant term. Reactions such as 3 and 4 generally seem to have positive enthalpy changes and thus shift to the right at higher temperatures, but much remains to be learned about such details even in simple systems.



FIGURE 8. Activities of silica (taken here as Si_4O_8) and of alumina (Al₄O₆) calculated using the pMelts software package (Ghiorso et al. 2002) for a typical mid-ocean ridge basalt at 1600 °C and 1 GPa. Five compositions, each with 1 mol% of an added modifier oxide component (replacing 1% CaO), are compared to assess the effects of cation field strength in these complex compositions.

Aluminum, network order/disorder, and silica activity

The Al³⁺ cation is only slightly larger than Si⁴⁺, and thus at low pressures is largely four-coordinated in aluminosilicate melts and glasses of geological compositions. If Al2O3 (or, more clearly for comparison with SiO₂, AlO_{3/2}) is added to a binary modifiersilicate melt, there is a per-cation deficit of oxygen relative to SiO₂. This means that to provide four O atoms to coordinate the Al, NBO must be converted to BO (Fig. 9). Unlike the effectively charge-neutral BO connecting two SiO₄ groups, those linking AlO₄ groups to other network-formers have a net partial negative formal charge, -1/4 in the case of Al-O-Si and -1/2 in the case of Al-O-Al. These charges are based on simple considerations of bond valence sums (Brown et al. 1995; Brown and Shannon 1973), e.g., Al^{3+} with four Al-O bonds contributes +3/4 to each O, an adjacent Si⁴⁺ with four Si-O bonds contributes +4/4, and the difference between the O^{2-} valence and 7/4 is -1/4. Actual electron distributions, for example as calculated by ab initio methods (Vuilleumier et al. 2011), will be somewhat different and will vary with details such as bond angles and distances, but the relative trends illustrated by such approximations have long been shown to be useful starting points in thinking about both crystal and melt structure. Advanced theoretical methods can, of course, be very useful in elucidating the fundamentals of cation-oxygen interactions in this context (Gatti et al. 2012).

As AlO₄ tetrahedra become part of the strongly bonded silicate network in glasses and melts, the mixing of Al and Si, and of three instead of one distinct type of bridging oxygen, add much complexity and many more options for the generation of configurational order/disorder that is so important to bulk properties. Partial negative charges on Al-O-Si and Al-O-Al BO need to be locally balanced, generally by the "modifier" cations, which in this role are often labeled as "charge compensators." In the case of relatively large, low-charge cations (e.g., K⁺ or Na⁺), it can be difficult to fit enough neighbors to compensate the -1/2 charge on Al-O-Al: if the K⁺ is eight coordinated, for example, each cation will contribute only +1/8, in principle requiring 4 K⁺ neighbors around an Al-O-Al bridging oxygen. This becomes difficult simply for local volumetric reasons [sometimes called "steric hindrance" (Mysen and Richet 2005)]. The consequence is what has long been known as "aluminum avoidance," meaning that Al-O-Al linkages are minimized in favor of Si-O-Al plus Si-O-Si, which is possible if overall Al/Si < 1 as in all natural magmas. Equilibria such as that below are therefore shifted to the left.



FIGURE 9. As in Figure 4: sketch of a two-dimensional analog of addition of alumina to a modified silicate network. Here, the concentrated negative charges on the NBO (dark blue circles) are converted to more dispersed, small negative charges (light blue circles) on BO-linking Si and Al (green triangle). Reprinted from Stebbins et al. (2013) with permission from Elsevier.

$$2(\text{Si-O-Al})^{-1/4} \leftrightarrow (\text{Si-O-Si})^0 + (\text{Al-O-Al})^{-1/2}$$
(5)

The consequences of the ordering that can result have long been explored in the thermodynamics of feldspars and other crystalline aluminosilicates (Putnis 1992); "Al avoidance" is known to be especially prevalent in alkali feldspars and feldspathoids, especially those formed at low temperature where enthalpy is more likely to prevail over entropy. The presence of smaller, higher charged "compensating" cations (e.g., Mg2+ or Ca²⁺ vs. Na⁺ or K⁺) can more readily balance the charge on the Al-O-Al bridging O atoms, allowing such linkages to form in disordered high-temperature phases such as crystalline anorthite (CaAl₂Si₂O₈) near its melting point (Phillips et al. 1992) and high-temperature cordierite (Mg₂Al₄Si₅O₁₈) (Putnis et al. 1985). In such materials the disordered structure is stabilized by the extra entropy of mixing of Al and Si in the network. The same is certainly expected in melts. This has indeed been demonstrated by spectroscopic studies of simple, ternary aluminosilicate glasses: some Al-O-Al can be observed in Na aluminosilicates, but much less than in a fully random distribution of Al and Si; comparable Ca aluminosilicates are more disordered (Lee and Stebbins 2000; Stebbins et al. 1999). Limited evidence from glasses prepared with different fictive temperatures shows the expected increased randomness at higher T (Dubinsky and Stebbins 2006). Network order-disorder is schematically illustrated in Figure 10. Here, one sketch shows complete "avoidance" of presumably energetically costly Al-Al pairs, the other a random distribution with a much higher



less disordered "glass": few AI-O-AI (low T?)

FIGURE 10. As in Figure 9: an expanded view of a 2D analog structure for a glass/melt with equimolar Si and Al, to illustrate the range of possibilities from complete "aluminum avoidance" (lower panel, no Al-O-Al or Si-O-Si) to a disordered arrangement (upper panel, abundant Al-O-Al and Si-O-Si). Modified from Henderson et al. (2006).

configurational entropy. In favorably cases, ¹⁷O NMR and other methods can actually count the distributions of the different O atoms (Al-O-Al, Al-O-Si, Si-O-Si) in glasses and minerals, allowing development of thermodynamic models (Dirken et al. 1997; Lee and Stebbins 2000).

In melts with high Al/Si, such as NaAlSiO₄, the disorder generated by mixing of Si and Al (and of the three kinds of BO) can be a substantial fraction of the overall configurational entropy (Stebbins 2008); in natural magmas with much lower Al/Si the effects are smaller. However, because higher field strength modifiers push reactions such as 5 to the right, the concentration of silica-like species, and thus of silica activity, is again enhanced. In more silica-rich systems with few NBO and low probability of Al-O-Al, analogous re-distributions of Al and Si neighbors around a given SiO₄ group probably also play a role (Murdoch et al. 1985). For example, for silicate Q⁴ groups connected to various numbers of AlO₄ groups (the rest being SiO₄), an equilibrium can be written (one of many possible for different network species)

$$2Q^{4}[1A1] \leftrightarrow Q^{4}[0A1] + Q^{4}[2A1]. \tag{6}$$

As for the right-most species in reactions 3 and 4 (i.e., lower Q^n numbers) and reaction 5 (i.e., Al-O-Al), the right-most species in reaction 6 has the highest local negative charge concentration, and is stabilized by higher field strength modifier cations. All three reactions point to an accompanying greater concentration of locally silica-like species, and thus higher γ_{SiO_2} . This is in fact again seen in analysis of simple pseudobinary phase diagrams such as Ca_{0.5}AlO₂-SiO₂ and NaAlO₂-SiO₂ (Ryerson 1985), where a shift in silica liquidus compositions analogous to those in simple binary silicates has long been known.

In summary, alkali-rich melts will have much lower silica activities than MgO-, CaO-, or FeO- rich melts of the same molar proportions. The products of magmatic differentiation in nature of course do not lend themselves to such a direct comparison (e.g., the Earth does not produce rhyolites containing mostly MgO as the modifier oxide, instead of Na₂O), but nonetheless such effects of composition should be inherent in any model of bulk thermodynamics, phase equilibria, and magmatic properties. Models that treat all modifier oxide components as equivalent must thus be only first approximations.

Suppression of phase separation by alumina

When alumina is added to an alkali or alkaline earth binary silicate liquid, the negative charges on NBO are spread out among multiple BO (Figs. 9 and 10), resulting in less tendency for clustering and ultimately less tendency for liquid-liquid phase separation. Two-liquid solvi are greatly suppressed in all such ternary phase diagrams, and, instead of being nearly universal as in binary silicate systems, often are reduced to no significance at all in the aluminosilicates that comprise most magmas. Less clustering of modifier cations and NBO into "channels" is also a consequence of alumina addition, expected to affect diffusivities significantly. In parallel, a great deal of advanced technology also depends on this drastic effect of structure on phase diagrams, for example the alkaline earth aluminoborosilicate glasses used in computer display screens.

Potential for ordering among different modifier cations in aluminosilicate melts

In compositions with total modifier oxide contents higher than alumina (e.g., "peralkaline" compositions, and most "metaluminous" intermediate and mafic magmas), NBO could be distributed over AlO₄ and/or SiO₄ groups. The latter generally "win," at least at the low temperatures captured by glasses (Allwardt et al. 2003; Mysen 1997). As discussed above for simple Al-free melts, the non-network cations can be distributed in many different ways with different combinations of NBO and BO neighbors, with the expectation that larger, lower charged cations (e.g., alkalis) may be more likely to be coordinated by BO such as Si-O-Al and smaller, higher charged cations (e.g., Mg²⁺) may associate more with the NBO. This phenomenon is clearly seen in some crystalline silicates. For example, in biotite, the higher field strength Mg²⁺ and Fe²⁺ cations are coordinated only by NBO (and OH-) in the octahedral sheets, while larger, monovalent K⁺ cations are surrounded by Si-O-Al BO in the interlayers. There is some evidence for this kind of ordering in glasses (Allwardt and Stebbins 2004; Kelsey et al. 2008; Mysen and Richet 2005); it provides another potential source of configurational entropy and heat capacity on disordering above T_{g} . Furthermore, such energetic "preferences" of different cations in different coordination environments must certainly matter in models of how they diffuse in melts, of central importance to problems of crystal growth, melting, and mixing.

Alumina content, viscosity, and variations from standard models of structure

As more and more alumina is added to a simple binary silicate melt, the fraction of O atoms that are NBO, and the NBO/T ratio, systematically decrease. The melt "fragility" and configurational entropy decrease, and high-temperature viscosity goes up. In the standard model approximation, when the modifier oxide/alumina ratio is reduced to 1, all O atoms are bridging and the composition of the melt will be along a "1:1" join such as SiO2-NaAlSiO4 or SiO2-CaAl2Si2O8. As in the calculation of a CIPW norm, the local structure of such melts (e.g., anhydrous high-silica rhyolites) can be approximated by locally feldsparand silica-like structures with some disorder in mixing of both charge compensating and network cations, bond angles and ring sizes, etc. But how is it that such a "strong" liquid can flow at all? Both physical property and structural data indicate that the dynamics of such BO-rich systems are particularly sensitive to structural "imperfections," in particular the introduction of NBO and weakening of BO links by fugitive and mobile components such as H₂O. Even anhydrous melts generate their own "defects" that fall outside of standard structural models, however. For example, 17O NMR spectroscopy of glasses on 1:1 joins has shown that they do contain small amounts of NBO, and these concentrations again are higher for higher charged modifiers (e.g., Ca²⁺ vs. K⁺) (Thompson and Stebbins 2011). Such non-standard species may have important effects on transport properties, and in fact were predicted from detailed studies of composition vs. viscosity in ternary aluminosilicate melts (Mysen and Toplis 2007; Toplis and Dingwell 2004; Toplis et al. 1997b).

AL AND SI COORDINATION, NETWORK DEFECTS, AND EFFECTS OF PRESSURE

The roles of non-tetrahedral Al and Si

Another key approximation of standard models of glass and melt structure is that all Al³⁺ cations have exactly four oxygen neighbors for compositions in which the modifier oxides exceed or equal the alumina contents; formation of higher coordinated Al in peraluminous composition has long been suggested to accommodate local charge balance, but such Al-rich magmas are uncommon in nature. ²⁷Al NMR has now clearly shown that even in strongly peralkaline (e.g., Na₂O/Al₂O₃ >> 1) and "peralkaline earth" (e.g., $CaO/Al_2O_3 >> 1$) ternary aluminosilicate glasses, some five-coordinated Al (VAl), and even some VIAl, are indeed present (Kelsey et al. 2009a; McMillan and Kirkpatrick 1992; Neuville et al. 2006, 2008b; Toplis et al. 2000). Once again, the field strength of the modifier cation has a big effect, producing typically 5 to 8% VAl in the well-studied Ca aluminosilicates and even more in Mg aluminosilicates. The formation of "nonstandard" VAl may be related to that of "non-standard" NBO, but there is not a simple 1 to 1 relationship (Thompson and Stebbins 2011). Both probably increase with increasing T above T_{g} , contributing further to the configurational entropy and to reducing the "strength" of the liquid (Stebbins et al. 2008). X-ray and neutron scattering methods, applied to aluminosilicate glasses and even in situ to high-temperature melts, are also important in observing and modeling deviations from the conventional structural picture (Guignard and Cormier 2008; Jakse et al. 2012; Neuville et al. 2008a).

Five-coordinated network cations (VAl and VSi), and the longer, weaker bonds that go with them, have long been suggested as "transition states" or "reaction pathways" in the local bondbreaking and rearrangement that must occur for viscous flow, and diffusion of Si, Al, and O, to happen in such highly connected structures (Fig. 11). This was suggested by early computer simulations of melts (Angell et al. 1982; Brawer 1985). The discovery of small concentrations of VSi even in low-pressure alkali silicate glasses (Stebbins and McMillan 1993), and now of much more abundant ^vAl, has been particularly interesting for this reason. As Earth scientists know so well, both Si and Al coordination increases in crystalline silicates (most commonly to the six-coordinated structures, of course) are fundamental in high-pressure transformations in the deep crust and mantle. Intriguingly, some of the first indirect evidence for such coordination shifts in silicate melts came from anomalous viscosity decreases with increasing pressure of relatively "strong" compositions such as K₂Si₄O₉ and NaAlSi₂O₆ (Angell et al. 1982; Wolf and McMillan 1995). These contrast with the increases in viscosity with pressure expected for "normal" liquids simply because of density increase and tighter ionic packing. The latter behavior is indeed seen for "weaker" silicate melts such as CaMgSi₂O₆ and mafic basalts (Liebske et al. 2005). Although quantifying the interplay of network cation coordination and melt viscosity remains elusive, it is an intriguing issue for rationalizing both compositional and pressure effects on this petrologically critical property, which can vary over at least 12 orders of magnitude in natural silicate liquids.

As in minerals, the most obvious connection between pressure-

induced increases in Al and/or Si coordination in silicate melts and their properties is through density or molar volume. Radical changes in structure of simple oxide and silicate glasses at lower mantle pressures have been reported from in situ diffraction and spectroscopic studies (Farber and Williams 1996; Majérus et al. 2004; Wolf and McMillan 1995), but glasses compressed under such conditions may revert at least partially on decompression to lower-pressure structures, making more detailed structural studies difficult. Nonetheless, it is likely that at very high pressures (>30 GPa?), Si and Al cations in melts all have six oxygen neighbors, and behave more like dense ionic liquids than the strongly connected network liquids that are familiar to us at near-surface pressures.

At more modest pressures (to at least 10-12 GPa, representing deeper regions of the Earth's upper mantle), many silicate and aluminosilicate melts can be quenched to glasses, which can then be decompressed for detailed structural studies at room temperature and pressure. These densified glasses may be up to 15 to 20% denser than the same glass initially melted at 1 bar. In one recent study of aluminosilicates similar in composition to rhyolitic to intermediate magmas (Malfait et al. 2014), melt densities measured by in situ X-ray methods to 3.5 GPa were compared to those calculated from recovered glass density and its measured elastic constants. Agreement within uncertainties in the experimental measurements involved suggested that inelastic volume relaxation during decompression of the glass at room temperature was not important, and thus that the recovered glass structure was a good representation of the melt structure at high pressure and T_{g} . Other very recent studies (Bista et al. 2015; Gaudio et al. 2015) have also shown, however, that significant, transient pressure drops can take place on quenching of a high-temperature melt in a solid medium high-pressure apparatus, and that experiments with initial temperatures near to $T_{\rm g}$ will retain greater structural and density changes, if crystallization can be avoided. Many published estimates of structural changes in glasses quenched from high pressure may thus be minimum values. In any case, Al-free alkali silicate glasses quenched from melts initially at 10 to 12 GPa contain up to at least 15% of VSi and VISi (Allwardt et al. 2004; Gaudio et al. 2008; Xue et al. 1991). NBO-rich aluminosilicate compositions, which are about 95% ^{IV}Al when melted at 1 bar, can be recovered from 6 to 10 GPa with the majority of Al converted to VAI and VIAI (Kelsey et al. 2009a). As noted above for 1 bar glasses, higher field strength modifier cations (Mg²⁺ > Ca²⁺ > Na⁺ > K⁺) greatly promote the formation of higher coordinated Al at high pressure, but such effects on Si coordination are much less well known (Allwardt et al. 2005; Kelsey et al. 2009b). There is good evidence that a relatively easy pathway for conversion of both ^{IV}Si and ^{IV}Al to higher coordination involves conversion of NBO to "bridging" or "intermediate" oxygen links involving the higher coordinated cations (Allwardt et al. 2004; Lee et al. 2004; Yarger et al. 1995). Thus, such changes in NBO-poor liguids (e.g., rhyolites in contrast to basalts) probably happen more gradually, by different mechanisms, and at higher pressures. The most common magmas formed in the mantle of the modern Earth are mafic basalts, which not only have high proportions of NBO but high concentrations of high field strength cations (notably Mg²⁺ and Fe²⁺), which will both promote coordination increase of at least Al. Recent studies indicate that even at the "modest" upper mantle pressures where most basaltic magmas commonly arise (say, 2–3 GPa), high concentrations of ^vAl and even ^{v1}Al are present, which may have to be considered in refinements of models of melt properties (Bista et al. 2015).

As mentioned above, species such as VAI and VSi have been implicated in mechanisms of viscous flow and the diffusion of network components in melts, and this role may be accentuated at higher pressures. In fact, VSi- or VISi-rich melts may become so "fragile" that they cannot be readily quenched to glasses, placing limits on what can be recovered for ex-situ spectroscopy. What about the most obviously expected high-pressure property change, namely density? In recovered glasses that do contain measurable amounts of high-coordinated Al and/or Si, the effects of this structural change can be compared with measured density increases in the glasses, by using models of partial molar volumes of oxide components and substituting, for example, a "corundumlike" volume for alumina. It has been found that even in the most densified, VAI- and VIAI-rich glasses, this observed structural change can account for only a relatively minor part of the density increase (Allwardt et al. 2005). Most of the densification in this pressure range is probably thus accommodated by compression of "softer" cation sites, i.e., those of the modifier cations, and some accompanying topological reconfiguration of the network. We have hints about these kinds of changes from apparent reductions in network bond angles (Mysen and Richet 2005) and in ²³Na NMR spectra suggesting smaller Na sites (Kelsey et al. 2009a), but a detailed picture of this process remains to be determined.



FIGURE 11. Schematic model of a possible mechanism of exchange between silicon and oxygen species in a liquid. O atoms are shown as large open circles, cations as smaller filled circles. In step 1, a modifier cation moves away from an NBO (blue circle), which then forms a short-lived Si-O bond to create a ^VSi (black circle). If this step reverses (double arrow), there is no net diffusion, exchange, or flow. In step 2, the bonds break differently, converting the ^VSi back to ^{IV}Si, a former BO (green) to an NBO, and a former NBO (blue) to an NBO. If all of the unlabeled O atoms are bonded to other Si (not shown), then during this same process a Q³ group (A) is converted to a Q⁴ group and a Q⁴ group (B) is converted to a Q³ group. Cation and anion diffusion, species exchange, and a viscous flow step all have occurred. Modified from Calas et al. (2006).

The development of abundant high-coordinated Al and Si at high pressure also will greatly alter the oxygen speciation in the network, will contribute to increased configurational complexity, and is expected to have major effects on thermodynamic and transport properties (Lee 2004; Lee et al. 2004).

Alumina activity and Al coordination?

As discussed above for silica activity, compositional effects on the local structural environments of Al³⁺ cations should have effects on component activities. It might be expected, for example, that the formation of more highly coordinated Al would increase the activity of melt components related to the formation of minerals containing VIA1. Accurate data on the 1-bar liquidus surfaces for such phases, such as corundum and mullite, are limited, so that it is difficult to make the sort of direct comparison of the effects of, say, modifier cation field strength, as were described above for a_{SiO_2} . Such equilibria are even more poorly constrained at high pressures where high-coordinated Al becomes abundant. However, the Al2O3 component in a model such as pMELTS (Ghiorso et al. 2002) may represent the activity of non-tetrahedral Al, as tetrahedral Al can be accounted for by feldspar or feldspathoid-like components. Alumina activity is constrained at least in part by high-pressure liquid-crystal equilibria with VIAl-containing phases such as spinels and Alrich pyroxenes, even in the metaluminous compositions that comprise most of the model database. If this is the case, then known systematic effects of modifier cation field strength on Al coordination might be expected to systematically change $a_{Al_{2}O_{2}}$. Using the same "isochemical" substitutions of MgO vs. FeO vs. CaO vs. Na2O vs. K2O as described above for silica, this correlation is indeed found (Fig. 8). This structure-activity correlation is admittedly speculative, but suggests that direct experiments with well-constrained phase equilibria in simple peraluminous systems could be worth attempting.

Models of melt properties based on "non-structural" oxide components, or on simple low-pressure mineral components, will become more and more difficult to accurately constrain at higher and higher pressures. The need for multicomponent models that explicitly account for major structural changes (notably in Si coordination) has been recognized and important steps made in their formulation (Ghiorso 2004). At this time the structural "data" for these models has come largely (and necessarily) from computer simulations; we might hope that in the future more data from both ex-situ and in situ structural measurements will become available to constrain such petrologically important computational tools.

PRESSURE EFFECTS ON MELT STRUCTURE AND PROPERTIES: INSIGHTS FROM NON-SILICATE ANALOG SYSTEMS

Two other well-studied families of glass-forming oxide melts may provide some qualitative insights into some of the composition/structure/property effects to be expected in high-pressure aluminosilicates (Stebbins et al. 2013). In contrast to silicon in simple silicates at 1 bar pressure, boron in binary borate crystals and melts has two coordination states with oxygen, ^{III}B and ^{IV}B, that are energetically close enough so that both can readily form. In germanate melts and crystals, structures with ^{IV}Ge, ^VGe, and ^{VI}Ge are all readily accessible at

1 bar. In both systems, the binaries with alkali oxides have the widest glass-forming ranges and are most fully studied. In both cases, the pure network forming glass (B_2O_3, GeO_2) is known to contain only the low-coordination state (IIIB, IVGe). As alkali oxide is added, the initial structural change is not to primarily form NBO as in silicates, but to accommodate the added oxide ion by increasing the coordination of the network cation (^{IV}B and ^{V,VI}Ge), illustrated by Figure 4b. This is found in liquids, glasses, and crystals out to roughly 20 mol% added modifier oxide. To this point, the modifier cations are coordinated primarily by bridging O atoms, some of which will have partial negative charges, e.g., [^{III}B-O-^{IV}B]^{-1/4} or [^{IV}Ge-O-^VGe]^{-1/5}. At alkali oxide higher contents, NBO do begin to form and the network cation coordination goes back down, eventually to again being dominated by the low-coordination numbers. The variation with composition in melt and glass properties, such as viscosity, T_{g} , and most obviously molar volume, is highly non-linear because of these complex structural changes (Stebbins et al. 2013), and are often analyzed with models containing multiple components representing different local structures. These kinds of systems may represent some of the complex effects of changing composition in aluminosilicate melts at intermediate pressures, where more than one coordination of Si or Al can readily form, and again, point out the possible complexity of models needed to accurately capture non-linear property variation. To date however, the experimental data sets for neither high-pressure melt properties nor structure are wide enough in scope to begin to define such transitions. As suggested by the 2D analog portrayed in Figure 6, a shift with pressure from primarily ^{IV}Al and ^{IV}Si to a mix with ^{V,VI}Al and ^{V,VI}Si is also expected to have large effects on the configurational entropy, the dispersion vs. concentration of charges on oxygen species, liquid immiscibility, and heterogeneity/homogeneity of modifier cation distribution.

MELT DISORDER AND THE ROOTS OF MAGMATIC PHASE EQUILIBRIA

As mentioned above, we now have qualitative, and in many cases quantitative insights into many different, if inter-related, aspects of structural disorder in silicate glasses and melts, and, in some cases, to how this increases with temperature. These include ordering/disordering of different network-modifying/ charge-compensating cations (e.g., Na⁺, Ca²⁺, Mg²⁺, Fe²⁺) in sites with varying oxygen coordination, of different types of network-forming cations (e.g., Si⁴⁺, Al³⁺) and of the consequent different types of bridging O atoms, of NBO and BO, and even of varying coordination states of Si and Al. It is likely that other less readily measurable contributions to disorder, for example the high-energy defects that must be formed in higher and higher concentrations as cations diffuse more and more rapidly, make important contributions to configurational properties in melts, but as yet are poorly characterized (Stebbins 2008). Nonetheless, it is clear that many potential sources of structural disorder in melts, and for increases in disorder with temperature, increase as the "simple" network of pure silica is broken apart by modifier oxides. Apart from obvious effects on melt fragility and hence on diffusivity and viscosity, one outcome is a systematic increase in enthalpies and entropies of fusion of silicate minerals as the

fraction of non-bridging O atoms increases (Richet and Bottinga 1986; Stebbins et al. 1984). Large differences can also be seen among ΔS_m even for oxides of simple compositions, which are also obviously related to their network-forming ability. For partially covalent, network-forming SiO₂, ΔS_m is the lowest known [1.5 J/(K·mol) of atoms], contrasting with estimated values for oxides of larger tetravalent cations such as TiO₂ [9.9 J/(K·mol) of atoms (Chase et al. 1985)] and ZrO₂ [9.8 J/(K·mol) of atoms] that form liquids with higher cation and anion coordination, longer bonds, and more ionic interactions.

As pointed out in the ground-breaking igneous petrology textbook of Carmichael, Turner, and Verhoogen (Carmichael et al. 1974), a simple calculation of binary phase diagrams suggests that this relationship between what are now known as structural differences, and the silica content of the crystal and melt, has fundamental consequences for magmatic phase equilibria. If we assume no solid solution, and ideal solution in the liquid (often very rough assumptions, but useful in this context), the equilibrium constant for melting of a single-mineral component i simply becomes the mole fraction of i in the liquid, $X_{i,Liq}$. With the further approximations of constant ΔH_m (and thus ΔS_m) of melting, the Van't Hoff equation gives

$$d(\ln X_{i,\text{Liq}})/dT = \Delta H_{\text{m}}/(RT^2)$$
(7)

Simply inverting to examine the effects of dilution of component i in the liquid (i.e., how much does the liquidus temperature drop as other components are added to the melt), it is easy to see that, with all else equal, a mineral with a small enthalpy and entropy of fusion, and thus greatest mineral-melt structural similarity, will have a liquidus curve that drops more steeply with decreasing X_i than that of a mineral with a high enthalpy and entropy of fusion, and thus greatest melt disorder relative to crystal. Eutectic temperatures are thus lowered and eutectic compositions (the last liquid to crystallize or the first liquid produced on melting) are enriched in the components with smaller $\Delta H_{\rm m}$ and $\Delta S_{\rm m}$ (Fig. 12). Given that the silica polymorphs, and alkali feldspars as well, have much lower $\Delta H_{\rm m}$ and $\Delta S_{\rm m}$ values than mafic silicates such as Mg-rich olivines and pyroxenes, it is thus not surprising that most natural magmas become enriched with silica and alkali feldspar components as they differentiate, as these minerals generally come into equilibrium only at low temperatures at high concentrations of these components. Of course real magmatic phase equilibria are highly complex and often involve highly non-ideal solutions in both liquids and solids, but the steep liquidus curve for silica, required by its low $\Delta H_{\rm m}$ and $\Delta S_{\rm m}$, must be a key part of the eventual enrichment of magmas in silica and the low temperature of appearance of silica phases in magmas, in spite of the relatively high pure-phase melting point of silica. In fact, the overall progressions in the succession of minerals to form during differentiation, as summarized by Bowen's reaction series, from olivines to pyroxenes to sheet silicates and from Ca-rich to Na,K-rich feldspars and eventually quartz, can in some sense be viewed as a progression from the crystallization of highly disordered melt components to highly ordered components. There are thus deep melt structural roots to the most basic of natural magmatic processes.

STRUCTURE AND DYNAMIC PROCESSES IN MELTS

Fundamental connections between melt structure and viscosity, as illustrated by the Adam-Gibbs relationship between the shape of the viscosity curve and configurational entropy (Eq. 1), have already been made above. In silicate melts, knowledge is still very limited on the mechanistic details of links between non-vibrational atomic motions, such as cation site hopping, bond breaking and re-arrangement, and petrologically crucial processes of viscous flow and diffusion. Many ideas about these links have come, and will continue to come, from atomistic computer simulations, often termed "molecular dynamics" (MD, although this label is not so appropriate for mostly non-molecular silicate liquids), but space does not allow detailed discussion of this important field (Ghosh et al. 2014; Guillot and Sator 2007; Martin et al. 2009; Stixrude et al. 2009). A few examples of experimental insights will be given here, along with some basic theoretical concepts.

One key concept is the "shear relaxation time" (τ_s) for a liquid, for which an average value can be estimated from the "Maxwell" equation (Dingwell 2006; Dingwell and Webb 1990; Mysen and Richet 2005), the viscosity, and the infinite frequency shear modulus G_{x} . The latter represents deformation going on at very short length scales in the melt, and is typically about 1 to 3×10^{10} Pa in molten silicates

$$\tau_{\rm s} = \eta/G_{\infty} \tag{8}$$

 $τ_{s}$, although based on macroscopic measurements, is often presumed to be some measure of the inverse of the rate of some small-scale dynamic process (or processes) that controls viscous flow. Estimated values of $τ_s$ vary just as widely as do those for viscosity in magmas, for example a few nanoseconds in an alkali basalt near its liquidus ($η = 10^1$ Pa·s) to a few seconds in a rhyolite dome ($η = 10^{11}$ Pa·s). In a few cases, we actually have quantitative data on the average lifetimes of small-scale structural units in simple molten silicates, such as Qⁿ species and BO vs. NBO. As Si-O bonds break and rearrange during flow (and the closely related process of diffusion of these network ions), these local species exchange back and forth, as illustrated in an MD-inspired cartoon view in Figure 11. In situ, high-temperature NMR data



FIGURE 12. Hypothetical liquidus curves for two phases A with the same melting point but very different heats of melting. The intersecting liquidus for B is the same in both cases. For $\Delta H_{\rm m} = 60$ kJ/mol, the eutectic (arrow) is at $X_{\rm A} = 0.38$ and 1580 K, for 3 kJ/mol, it is at $X_{\rm A} = 0.84$ and 1000 K.

has measured these rates in a few alkali silicate liquids with relatively high silica contents, and they can be close to the inverse of τ_s estimated from the Maxwell equation (Farnan and Stebbins 1990, 1994; Sen 2008; Stebbins et al. 1995b). The fundamental conclusion here is that although the concept of "polymerization" is deeply embedded in the glass structure literature as a description of the extent of network connectivity, the silicate melts for which we have data do not dynamically behave anything like organic polymers, whose viscosities are primarily controlled by the coordinated motions of large, weakly interacting molecules. These are built with strong carbon-carbon bonds whose lifetimes are vastly longer than the time scale set by τ_s . This view is supported by a few measurements of silicates and borates that show no retention of local structural alignment of structural groups when rapidly deformed during cooling to glass (Stebbins et al. 1989; Wu et al. 2009), again in stark contrast to organic polymers. It is possible that in much lower silica liquids, viscous flow may be dominated by breaking and re-forming of weaker bonds among NBO and modifier cations, with longer-lasting Si-O bonds in small "molecule-like" fragments, but as yet we have almost no experimental data in such systems.

If viscous flow is closely linked to the rate of network bond breaking, then it should also be closely related to tracer diffusion of network cations and anions. In fact, such relationships are often at least approximately seen in silicate melts (within better than a log₁₀ unit), through analysis of data using the Eyring equation, that links the diffusion constant D to atomic site hopping at a mean timescale of τ_E and a jump distance of d. For network species τ_E is expected to be closely related to τ_s and d to a typical Si-Si or O-O distance

$$D = d^2/6\tau_E.$$
 (9)

The "Einstein-Smoluchowski" relationship connects viscosity to network ion diffusivity directly (Stebbins 1995), given k_B as the Boltzmann constant:

$$\eta = k_{\rm B} T / dD. \tag{10}$$

In fact, measurements of diffusivities of Si and/or of O can be used as at least rough proxies of melt viscosity, when the latter can be very challenging to measure, for example at high pressure (Poe et al. 1997; Reid et al. 2003; Tinker et al. 2004). Si and O atomic motions can thus be described as highly "coupled" to network structural dynamics.

In contrast, weakly bonded network modifier cations, most notably the alkalis, can move about in the melt much more rapidly, and can be considered to be "decoupled" from the network. Long-range diffusion of weakly bonded ions may be facilitated if NBO are concentrated in domains or channels that allow "percolation" through the network, rather than being dispersed evenly with BO (Greaves and Sen 2007) (Fig. 6 vs. Fig. 10). The formation of this kind of "intermediate-range" structure is related to the same interactions that can give rise to liquid-liquid phase separation, as discussed above. Network bond breaking "freezes out" at the glass transition. However, rapid diffusion of alkalis at temperatures well below T_g may be important not only in geochemical processes, but is at the heart of technologies involving Li-ion conducting glasses and the alkali exchange employed in the chemical tempering of glass sheets made to protect mobile phone displays. Network-modifier cations with higher charge, notably Mg²⁺, Ca²⁺, and Fe²⁺ in magmas, may have intermediate dynamical behavior, with diffusive timescales coupled to those of the network at higher temperature, but "decoupling" at lower temperature (George and Stebbins 1998).

In multicomponent, "chemical" diffusion that is so important in transporting the building blocks of crystals and in homogenizing liquids after melting and mixing, complex interactions among components are expected through mutual effects on chemical potentials, the need for local as well as overall charge balance. These may appear as correlations among diffusivities that can seem to suggest the diffusion of larger structural units, e.g., "molecules" of feldspar. Given the close relationship of network bond breaking, viscous flow, and network tracer diffusivities noted above, it seems unlikely that the lifetime of such multi-cation structural units is long enough for them to move, intact, for significant distances. However, just as mineral-like components have long been useful in models of free energies and phase equilibria in melts, correlated grouping of atoms may be useful in models of diffusion to capture some of the dynamical consequences of short-range structural interactions.

IMPLICATIONS AND PROGNOSIS

Most silicate melts in nature have large "configurational" components to their thermodynamic properties, meaning that structural changes with pressure, composition, and temperature have direct relationships to petrological processes from melting and crystallization to temperature and pressure-caused density changes. The differences in entropies and enthalpies of fusion among various silicate minerals, which exert a first-order control on magmatic phase equilibria, have obvious relationships to differences in melt structure. Links between melt structure and magmatic transport properties, including diffusion and viscous flow, are also fundamental. Many of these connections are now beginning to be understood at a qualitative and sometimes quantitative level, and should be useful concepts to those working on the complex realities of magmatic systems in both nature and the laboratory, to guide interpretations of data and help to formulate more physically based models. In turn, the questions and phenomena of petrology should inform ongoing directions of structural studies. There is a bright future for experimental and theoretical work on melt structure and processes, both through the relatively accessible "window" provided by quenched, glassy samples, and in the challenging world of in situ, high-temperature and high-pressure measurements.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation, grants EAR-1019596 and EAR-1521055 to J. Stebbins. I thank Pascal Richet (IPGP) for a helpful review of this manuscript, as well as for decades of excellent data and inspiring ideas, as well as a second, anonymous reviewer.

REFERENCES CITED

- Allwardt, J.R., and Stebbins, J.F. (2004) Ca-Mg and K-Mg mixing around non-bridging oxygens in silicate glasses: An investigation using oxygen-17 MAS and 3QMAS NMR. American Mineralogist, 89, 777–784.
- Allwardt, J.R., Lee, S.K., and Stebbins, J.F. (2003) Bonding preferences of non-bridging oxygens in calcium aluminosilicate glass: evidence from ¹⁷O MAS and 3QMAS NMR on calcium aluminate and low-silica Ca-aluminosilicate glasses. American

Mineralogist, 88, 949-954.

- Allwardt, J.R., Schmidt, B.C., and Stebbins, J.F. (2004) Structural mechanisms of compression and decompression in high pressure K₂Si₄O₉ glasses: An investigation utilizing Raman and NMR spectroscopy of high-pressure glasses and crystals. Chemical Geology, 213, 137–151.
- Allwardt, J.R., Stebbins, J.F., Schmidt, B.C., Frost, D.J., Withers, A.C., and Hirschmann, M.M. (2005) Aluminum coordination and the densification of high-pressure aluminosilicate glasses. American Mineralogist, 90, 1218–1222.
- Angell, C.A. (1985) Strong and fragile liquids. In K.L. Ngai and G.B. Wright, Eds., Relaxation in Complex Systems, 3–11. Office of Naval Research, Washington, D.C.
- Angell, C.A., Cheeseman, P.A., and Tamaddon, S. (1982) Pressure enhancement of ion mobilities in liquid silicates from computer simulation studies to 800 kilobars. Science, 218, 885–887.
- Bista, S., Stebbins, J.F., Hankins, B., and Sisson, T.W. (2015) Aluminosilicate melts and glasses at 1 to 3 GPa: Temperature and pressure effects on recovered structural and density changes. American Mineralogist, 100, 2298–2307.
- Brawer, S. (1985) Relaxation in viscous liquids and glasses. American Ceramic Society, Columbus, Ohio.
- Brown, G.E. Jr., Farges, F., and Calas, G. (1995) X-ray scattering and X-ray spectroscopy studies of silicate melts. Reviews in Mineralogy, 32, 317–410.
- Brown, I.D., and Shannon, R.D. (1973) Empirical bond-strength–bond-length curves for oxides. Acta Crystallographica, A29, 266–282.
- Calas, G., Henderson, G.S., and Stebbins, J.F. (2006) Glasses and melts: Linking geochemistry and materials science. Elements, 2, 265–268.
- Carmichael, I.S.E., Turner, F.J., and Verhoogen, J. (1974) Igneous Petrology, 739 p. McGraw-Hill, New York.
- Chase, M.W., Davies, C.A., Downey, J.R. Jr., Frurip, D.J., McDonald, R.A., and Syverud, A.N. (1985) JANAF Theromochemical Tables, Third ed. American Institute of Physics, New York.
- Cormier, L., and Cuello, G.J. (2013) Structural investigation of glasses along the MgSiO₃-CaSiO₃ join: Diffraction studies. Geochimica et Cosmochimica Acta, 122, 498–510.
- Davis, M.C., Sanders, K.J., Grandinetti, P.J., Gaudio, S.J., and Sen, S. (2011) Structural investigations of magnesium silicate glasses by ²⁰Si 2D magic-angle flipping NMR. Journal of Non-Crystalline Solids, 357, 2787–2795.
- deJong, B.H.W.S., and Brown, G.E. Jr. (1980) Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions-II. The network modifying effects of Mg²⁺, K⁺, Na⁺, Li⁺, OH⁻, F⁻, Cl⁻, H₂O, CO₂ and H₃O⁺ on silicate polymers. Geochimica et Cosmochimica Acta, 44, 1627–1642.
- Dingwell, D.B. (2006) Transport properties of magmas: Diffusion and rheology. Elements, 2, 281–286.
- Dingwell, D.B., and Webb, S.L. (1990) Relaxation in silicate melts. European Journal of Mineralogy, 2, 427–449.
- Dirken, P.J., Kohn, S.C., Smith, M.E., and van Eck, E.R.H. (1997) Complete resolution of Si-O-Si and Si-O-Al fragments in an aluminosilicate glass by ¹⁷O multiple quantum magic angle spinning NMR spectroscopy. Chemical Physics Letters, 266, 568–574.
- Dubinsky, E.V., and Stebbins, J.F. (2006) Quench rate and temperature effects on framework ordering in aluminosilicate melts. American Mineralogist, 91, 753–761.
- Farber, D.L., and Williams, Q. (1996) An in-situ Raman spectroscopic study of Na₂Si₂O₅ at high pressures and temperatures: Structures of compressed liquids and glasses. American Mineralogist, 81, 273–283.
- Farges, F., Brown, G.E. Jr., Calas, G., Galoisy, L., and Waychunas, G.A. (1994) Temperature-induced structural transformations in Ni-bearing silicate glass and melt. Geophysical Research Letters, 21, 1931–1934.
- Farges, F., Brown, G.E., Navrotsky, A., Gan, H., and Rehr, J.R. (1996) Coordination chemistry of Ti(IV) in silicate glasses and melts. 3. Glasses and melts from ambient to high temperatures. Geochimica et Cosmochimica Acta, 60, 3055–3065.
- Farnan, I., and Stebbins, J.F. (1990) A high temperature ²⁹Si NMR investigation of solid and molten silicates. Journal of the American Chemical Society, 112, 32–39.
 (1994) The nature of the glass transition in a silica-rich oxide melt. Science, 265, 1206–1209.
- Galoisy, L. (2006) Structure-property relationships in industrial and natural glasses. Elements, 2, 293–297.
- Gatti, C., Ottonello, G., and Richet, P. (2012) Energetics and bonding in aluminosilicate rings with alkali metal and alkaline-earth metal charge-compensating cations. Journal of Physical Chemistry A, 116, 8584–8598.
- Gaudio, S.J., Sen, S., and Lesher, C.E. (2008) Pressure-induced structural changes and densification of vitreous MgSiO₃. Geochimica et Cosmochimica Acta, 72, 1222–1230.
- Gaudio, S.J., Lesher, C.E., Maekawa, H., and Sen, S. (2015) Linking high-pressure structure and density of albite liquid near the glass transition. Geochimica Cosmochimica Acta, 157, 28–38.
- George, A.M., and Stebbins, J.F. (1998) Structure and dynamics of magnesium in silicate melts: A high temperature ²⁵Mg NMR study. American Mineralogist, 83, 1022–1029.
- Ghiorso, M.S. (2004) An EOS for silicate melts. III. Analysis of stoichiometric liquids at elevated pressure: Shock compression data, molecular dynamics simulations and mineral fusion curves. American Journal of Science, 304, 752–810.
- Ghiorso, M.S., Hischmann, M.M., Reiners, P.W., and Kress, V.C. (2002) The pMelts: A revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. Geochemistry,

Geophysics, Geosystems, 3, 1030.

- Ghosh, D.B., Karki, B.B., and Stixrude, L. (2014) First-principles molecular dynamics simulations of MgSiO₃ glass: Structure, density and elasticity at high pressure. American Mineralogist, 99, 1304–1314.
- Giordano, D., Mangiacapra, A., Potuzak, M., Russell, J.K., Romano, C., Dingwell, D.B., and Di Muro, A. (2006) An expanded non-Arrhenian model for silicate melt viscosity: A treatment for mataluminous, peralumuninous, and peralkaline liquids. Chemical Geology, 229, 42–56.
- Greaves, G.N., and Sen, S. (2007) Inorganic glasses, glass-forming liquids and amorphizing solids. Advances in Physics, 56, 1–166.
- Guignard, M., and Cormier, L. (2008) Environments of Mg and Al in MgO-Al₂O₃-SiO₂ glasses: A study coupling neutron and X-ray diffraction and Reverse Monte Carlo modeling. Chemical Geology, 256, 111–118.
- Guillot, B., and Sator, N. (2007) A computer simulation study of natural silicate melts. Part II: High pressure properties. Geochimica et Cosmochimica Acta, 71, 4538–4556.
- Gurman, S.J. (1990) Bond ordering in silicate glasses: A critique and re-solution. Journal of Non-Crystalline Solids, 125, 151–160.
- Henderson, G.S., Calas, G., and Stebbins, J.F. (2006) The structure of glasses and melts. Elements, 2, 269–274.
- Hess, P.C. (1995) Thermodynamic mixing properties and structure of silicate melts. Reviews in Mineralogy, 32, 145–189.
- Hess, K.U., Dingwell, D.B., and Rössler, E. (1996) Parameterization of viscositytemperature relations of aluminosilicate melts. Chemical Geology, 128, 155–163.
- Jakse, N., Bouhadja, M., Kozaily, J., Drewitt, J.W.E., Hennet, L., Neuville, D.R., Fischer, H.E., Cristiglio, V., and Pasturel, A. (2012) Interplay between non-bridging oxygen, triclusters, and fivefold Al coordination in low silica content calcium aluminosilicate melts. Applied Physics Letters, 101, 201903.
- Kelsey, K.E., Allwardt, J.R., and Stebbins, J.F. (2008) Ca-Mg mixing in aluminosilicate glasses: An investigation using ¹⁷O MAS and 3QMAS and ²⁷Al MAS NMR. American Mineralogist, 93, 134–143.
- Kelsey, K.E., Stebbins, J.F., Mosenfelder, J.L., and Asimow, P.D. (2009a) Simultaneous aluminum, silicon, and sodium coordination changes in 6 GPa-sodium aluminosilicate glasses. American Mineralogist, 94, 1205–1215.
- Kelsey, K.E., Stebbins, J.F., Singer, D.M., Brown, G.E. Jr., Mosenfelder, J.L., and Asimow, P.D. (2009b) Cation field strength effect on high pressure aluminosilicate glass structure: Multinuclear NMR and La XAFS results. Geochimica et Cosmochimica Acta, 73, 3914–3933.
- Koroleva, O.N., Anfilogov, V.N., Shatskiy, A., and Litasov, K.D. (2013) Structure of Na₂O-SiO₂ melt as a function of composition: In situ Raman spectroscopic study. Journal of Non-Crystalline Solids, 375, 62–68.
- Lee, S.K. (2004) Structure of silicate glasses and melts at high pressure: Quantum chemical calculations and solid-state NMR. Journal of Physical Chemistry B, 108, 5889–5900.
- Lee, S.K., and Kim, E.J. (2014) Probing metal-bridging oxygen and configurational disorder in amorphous lead silicates: In sights from ¹⁷O solid-state nuclear magnetic resonance. Journal of Physical Chemistry C, 119, 748–756.
- Lee, S.K., and Stebbins, J.F. (2000) The structure of aluminosilicate glasses: Highresolution ¹⁷O and ²⁷Al MAS and 3QMAS NMR study. Journal of Physical Chemistry B, 104, 4091–4100.
- Lee, S.K., Cody, G.D., Fei, Y., and Mysen, B.O. (2004) Nature of polymerization and properties of silicate melts and glasses at high pressure. Geochimica et Cosmochimica Acta, 68, 4189–4200.
- Liebske, C., Schmickler, B., Terasaki, H., Poe, B.T., Suzuki, A., Funakoshi, K., Ando, R., and Rubie, D.C. (2005) Viscosity of peridotite liquid up to 13 GPa: Implications for magma ocean viscosities. Earth and Planetary Science Letters, 240, 589–604.
- Maekawa, H., Maekawa, T., Kawamura, K., and Yokokawa, T. (1991) The structural groups of alkali silicate glasses determined from ²⁹Si MAS-NMR. Journal of Non-Crystalline Solids, 127, 53–64.
- Majérus, O., Cormier, L., Itié, J.-P., Galoisy, L., Neuville, D.R., and Calas, G. (2004) Pressure-induced Ge coordination change and polyamorphism in SiO₂-GeO₂glasses. Journal of Non-Crystalline Solids, 345–346, 34–38.
- Malfait, W.J., Halter, W.E., Morizet, Y., Meier, B.H., and Verel, R. (2007a) Structural control on bulk melt properties: Single and double quantum ²⁹Si NMR spectroscopy on alkali-silicate glasses. Geochimica et Cosmochimica Acta, 71, 6002–6018.
- Malfait, W.J., Zakaznova-Herzog, V.P., and Halter, W.E. (2007b) Quantitative Raman spectroscopy: High-temperature speciation of potassium silicate melts. Journal of Non-Crystalline Solids, 353, 4029–4042.
- Malfait, W.J., Seifert, R., and Sanchez-Valle, C. (2014) Densified glasses as structural probes for high-pressure melts: Configurational compressibility of silicate melts retained in quenched and decompressed glasses. American Mineralogist, 99, 2142–2145.
- Martin, G.B., Spera, F.J., Ghiorso, M.S., and Nevins, D. (2009) Structure, thermodynamic, and transport properties of molten Mg₂SiO₄: Dynamics simulations and model EOS. American Mineralogist, 94, 693–703.
- Mauro, J.C., Yue, Y., Ellison, A.J., Gupta, P.K., and Allan, D.C. (2009) Viscosity of glass-forming liquids. Proceedings of the National Academy of Sciences, 106, 19780–19784.
- McMillan, P.F., and Kirkpatrick, R.J. (1992) Al coordination in magnesium alumino-

silicate glasses. American Mineralogist, 77, 898-900.

- Murdoch, J.B., Stebbins, J.F., and Carmichael, I.S.E. (1985) High-resolution ²⁹Si NMR study of silicate and aluminosilicate glasses: The effect of network-modifying cations. American Mineralogist, 70, 332–343.
- Mysen, B.O. (1990) Effect of pressure, temperature and bulk composition on the structure and species distribution in depolymerized alkali aluminosilicate melts and quenched glasses. Journal of Geophysical Research, 95, 15733–15744.
- ——(1997) Aluminosilicate melts: Structure, composition and temperature. Contributions to Mineralogy and Petrology, 127, 104–118.
- Mysen, B.O., and Richet, P. (2005) Silicate Glasses and Melts, Properties and Structure. 544 p. Elsevier, Amsterdam.
- Mysen, B.O., and Toplis, M.J. (2007) Structural behavior of Al³⁺ in peralkaline, metaluminous, and peraluminous silicate melts and glasses at ambient temperature. American Mineralogist, 92, 933–946.
- Nasikas, N.K., Edwards, T.G., Sen, S., and Papatheodorou, G.N. (2012) Structural characteristics of novel Ca-Mg orthosilicate and suborthosilicate glasses: Results from ²⁹Si and ¹⁷O NMR spectroscopy. Journal of Physical Chemistry B, 116, 2696–2702.
- Navrotsky, A., Geisinger, K., McMillan, P., and Gibbs, G.V. (1985) The tetrahedral framework in glasses and melts: Inferences from molecular orbital calculations and implications for structure, thermodynamics and physical properties. Physics and Chemistry of Minerals, 11, 284–298.
- Neuville, D.R., and Richet, P. (1991) Viscosity and mixing in molten (Ca, Mg) pyroxenes and garnet. Geochimica et Cosmochimica Acta, 55, 1011–1019.
- Neuville, D.R., Cormier, L., and Massiot, D. (2006) Al coordination and speciation in calcium aluminosilicate glasses: effects of composition determined by Al-27 MQ-MAS NMR and Raman spectroscopy. Chemical Geology, 229, 173–185.
- Neuville, D.R., Cormier, L., de Ligney, D., Roux, J., Flank, A.-M., and Lagarde, P. (2008a) Environments around Al, Si, and Ca in aluminate and aluminosilicate melts by X ray absorption spectroscopy at high temperature. American Mineralogist, 93, 228–234.
- Neuville, D.R., Cormier, L., Montouillout, V., Florian, P., Millot, F., Rifflet, J.C., and Massiot, D. (2008b) Structure of Mg- and Mg/Ca aluminosilicate glasses: ²⁷Al NMR and Raman spectroscopy investigations. American Mineralogist, 93, 1721–1731.
- Nichols, A.R.L., Potuzak, M., and Dingwell, D.B. (2009) Cooling rates of basaltic hyaloclastites and pillow lava glasses from the HSDP2 drill core. Geochimica et Cosmochimica Acta, 73, 1052–1066.
- Phillips, B.L., Kirkpatrick, R.J., and Carpenter, M.A. (1992) Investigation of short-range Al, Si order in synthetic anorthite by ²⁹Si MAS NMR spectroscopy. American Mineralogist, 77, 484–495.
- Poe, B.T., McMillan, P.F., Rubie, D.C., Chakraborty, S., Yargar, J., and Diefenbacher, J. (1997) Silicon and oxygen self-diffusivities in silicate liquids measured to 15 Gigapascals and 2800 Kelvin. Science, 276, 1245–1248.
- Putnis, A. (1992) Introduction to Mineral Sciences, 457 p. Cambridge University Press, U.K.
- Putnis, A., Fyfe, C.A., and Gobbi, G.C. (1985) Al, Si ordering in cordierite using "magic angle spinning" NMR. Physics and Chemistry of Minerals, 12, 211–216.
- Reid, J.E., Susuki, A., Funakoshi, K.-I., Terasaki, H., Poe, B.T., Rubie, D.C., and Ohtani, E. (2003) The viscosity of CaMgSi₂O₆ liquid at pressures up to 13 GPa. Physics of Earth and Planetary Interiors, 139, 45–54.
- Richet, P. (1984) Viscosity and configurational entropy of silicate melts. Geochimica et Cosmochimica Acta, 48, 471–483.
- (2009) Residual and configurational entropy: Quantitative checks through applications of Adam-Gibbs theory to the viscosity of silicate melts. Journal of Non-Crystalline Solids, 355, 628–635.
- Richet, P., and Bottinga, Y. (1986) Thermochemical properties of silicate glasses and liquids: A review. Reviews of Geophysics, 24, 1–25.
- Richet, P., and Neuville, D.R. (1992) Thermodynamics of silicate melts: configurational properties. In S.K. Saxena, Ed., Thermodynamic Data, p. 132–161. Springer-Verlag, New York.
- Richet, P., and Ottonello, G. (2014) The Earth as a multiscale quantum-mechanical system. Comptes Rendues Geoscience, 346, 317–325.
- Ryerson, F.J. (1985) Oxide solution mechanisms in silicate melts: Systematic variations in the activity coefficient of SiO₂. Geochimica et Cosmochimica Acta, 49, 637–650.
- Sen, S. (2008) Differential mobility and spatially heterogeneous dynamics of oxygen atoms in a supercooled glass-forming network liquid. Physical Review B, 78, 100201.
- Sen, S., and Tangeman, J. (2008) Evidence for anomalously large degree of polymerization in Mg₂SiO₄ glass and melt. American Mineralogist, 93, 946–949.
- Skinner, L.B., Benmore, C.J., Weber, J.K.R., Tumber, S., Lazareva, L., Neuefeind, J., Santodonato, L., Du, J., and Parise, J.B. (2012) Structure of molten CaSiO₃: Neutron diffraction isotope substitution with aerodynamic levitation and molecular dynamics study. Journal of Physical Chemistry B, 116, 13439–13447.
- Stebbins, J.F. (1995) Dynamics and structure of silicate and oxide melts: Nuclear magnetic resonance studies. Reviews in Mineralogy, 32, 191–246.
- (2008) Temperature effects on the network structure of oxide melts and their consequences for configurational heat capacity. Chemical Geology, 256, 80–91.
- Stebbins, J.F., and McMillan, P. (1993) Compositional and temperature effects on five coordinated silicon in ambient pressure silicate glasses. Journal of Non-Crystalline Solids. 160, 116–125.
- Stebbins, J.F., and Xue, X. (2014) NMR spectroscopy of inorganic Earth materials.

Reviews in Mineralogy and Geochemistry, 78, 605-653.

- Stebbins, J.F., Carmichael, I.S.E., and Moret, L.K. (1984) Heat capacities and entropies of silicate liquids and glasses. Contributions to Mineralogy and Petrology, 86, 131–148.
- Stebbins, J.F., Spearing, D.R., and Farnan, I. (1989) Lack of local structural orientation in oxide glasses quenched during flow: NMR results. Journal of Non-Crystalline Solids, 110, 1–12.
- Stebbins, J.F., McMillan, P.F., and Dingwell, D.B. (1995a) Structure, dynamics, and properties of silicate melts. Reviews in Mineralogy, 32, 616.
- Stebbins, J.F., Sen, S., and Farnan, I. (1995b) Silicate species exchange, viscosity, and crystallization in a low-silica melt: In situ high-temperature MAS NMR spectroscopy. American Mineralogist, 80, 861–864.
- Stebbins, J.F., Lee, S.K., and Oglesby, J.V. (1999) AI-O-AI oxygen sites in crystalline aluminates and aluminosilicate glasses: High-resolution oxygen-17 NMR results. American Mineralogist, 84, 983–986.
- Stebbins, J.F., Dubinsky, E.V., Kanehashi, K., and Kelsey, K.E. (2008) Temperature effects on non-bridging oxygen and aluminum coordination number in calcium aluminosilicate glasses and melts. Geochimica et Cosmochimica Acta. 72, 910–925.
- Stebbins, J.F., Wu, J., and Thompson, L.M. (2013) Interactions between network cation coordination and non-bridging oxygen abundance in oxide melts and glasses: Insights from NMR spectroscopy. Chemical Geology, 346, 34–46.
- Stixrude, L., de Koker, N., Mookherjee, M., and Karki, B.B. (2009) Thermodynamics of silicate liquids in the deep Earth. Earth and Planetary Science Letters, 278, 226–232.
- Thompson, L.M., and Stebbins, J.F. (2011) Non-bridging oxygen and high-coordinated aluminum in metaluminous and peraluminous calcium and potassium aluminosilicate glasses: High-resolution ¹⁷O and ²⁷Al MAS NMR results. American Mineralogist, 96, 841–853.
- Tinker, D., Lesher, C.E., Baxter, G.M., Uchida, T., and Wang, Y. (2004) High-pressure viscometry of polymerized silicate melts and limitations of the Eyring equation. American Mineralogist, 89, 1701–1708.
- Tischer, R.E. (1969) Heat of annealing in simple alkali silicate glasses. Journal of the American Ceramic Society, 52, 499–503.
- Toplis, M.J., and Dingwell, D.B. (2004) Shear viscosities of CaO-Al₂O₃-SiO₂ and MgO-Al₂O₃-SiO₂ liquids: Implications for the structural role of aluminum and the degree of polymerization of synthetic and natural aluminosilicate melts. Geochimica et Cosmochimica Acta, 68, 5169–5188.
- Toplis, M.J., Dingwell, D.B., Hess, K.U., and Lenci, T. (1997a) Viscosity, fragility, and configurational entropy of melts along the join SiO₂-NaAlSiO₄. American Mineralogist, 82, 979–990.
- Toplis, M.J., Dingwell, D.B., and Lenci, T. (1997b) Peraluminous viscosity maxima in Na₂O-Al₂O₃-SiO₂ liquids: The role of triclusters in tectosilicate melts. Geochimica et Cosmochimica Acta, 61, 2605–2612.
- Toplis, M.J., Kohn, S.C., Smith, M.E., and Poplett, I.J.F. (2000) Five coordinate aluminum in tectosilicate glasses observed by triple quantum MAS NMR. American Mineralogist, 85, 1556–1560.
- Tossell, J.A., and Vaughn, D.J. (1992) Theoretical Geochemistry: Applications of quantum mechanics in the earth and mineral sciences, 514 p. Oxford University Press, U.K.
- Vedishcheva, N.M., Shakhmatkin, B.A., and Wright, A.C. (1998) A thermodynamic approach to the structural modeling of oxide melts and glasses: Borate and silicate systems. Glass Physics and Chemistry, 24, 308–311.
- Vuilleumier, R., Sator, N., and Guillot, B. (2011) Electronic distribution around oxygen atoms in silicate melts by ab initio molecular dynamics simulations. Journal of Non-Crystalline Solids, 357, 2555–2561.
- Wilke, M., Farges, F., Partzsch, G.M., Schmidt, C., and Behrens, H. (2007) Speciation of Fe in silicate glasses and melts by in-situ XANES spectroscopy. American Mineralogist, 92, 44–56.
- Wolf, G.H., and McMillan, P.F. (1995) Pressure effects on silicate melt structure and properties. Reviews in Mineralogy, 32, 505–562.
- Wu, J., Deubener, J., Stebbins, J.F., Grygarova, L., Behrens, H., Wondraczek, L., and Yue, Y. (2009) Structural response of a highly viscous aluminoborosilicate melt to isotropic and anisotropic compression. Journal of Chemical Physics, 131, 104504.
- Xue, X.Y. (2009) Water speciation in hydrous silicate and aluminosilicate glasses: Direct evidence from ²⁹Si-¹H and ²⁷Al-¹H double-resonance NMR. American Mineralogist, 94, 395–398.
- Xue, X., Stebbins, J.F., Kanzaki, M., McMillan, P.F., and Poe, B. (1991) Pressure-induced silicon coordination and tetrahedral structural changes in alkali silicate melts up to 12 GPa: NMR, Raman, and infrared spectroscopy. American Mineralogist, 76, 8–26.
- Yarger, J.L., Smith, K.H., Nieman, R.A., Diefenbacher, J., Wolf, G.H., Poe, B.T., and McMillan, P.F. (1995) Al coordination changes in high-pressure aluminosilicate liquids. Science, 270, 1964–1967.

MANUSCRIPT RECEIVED APRIL 24, 2015 MANUSCRIPT ACCEPTED JULY 14, 2015 MANUSCRIPT HANDLED BY DON BAKER