Structure of Glasses of Geological Interest: Applying Spectroscopic Techniques

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Introduction

Glasses are a minor fraction of Earth materials. However, all igneous processes within the Earth involve a melt phase (magma), and our understanding of the physical and chemical features of these processes is contingent upon an adequate understanding of the melt phase itself. In particular, we wish to relate the behavior of such melts to their composition and structure in the range of physical and chemical conditions in which they occur. The physical conditions of many of these processes are particularly difficult to reproduce in the laboratory, and the ability to predict behavior under such conditions is the goal. From a geological viewpoint, the primary interest is in silicate melts because of the composition of the Earth's lithosphere and mantle. There are significant experimental difficulties in looking at the behavior of silicate melts, so much work has focused on glasses as melt analogues since spectroscopic data on silicate glasses and melts (Figure 1) are similar.[1,2]

Silicate glasses are also of considerable industrial interest, and early work in the geological field borrowed heavily from materials science. However, the thrust to understand natural magmas led geologically based work into more complex chemical systems (e.g., hydrous alkali-alkaline-earth-aluminosilicates) and their behavior at high pressures.

The structure of glasses is a complex issue, and many different experimental techniques are needed to resolve the details of their structure. Here I will focus on the following techniques: IR (infrared), Raman, Mössbauer, EXAFS (extended x-ray absorption fine structure) and XANES (x-ray absorption near-edge spectroscopy) spectroscopies. MAS NMR (magic angle spinning nuclear magnetic resonance) and scattering methods are obviously of key importance, and are dealt with elsewhere in this issue. Detailed introductions to these techniques and their use in characterizing geological materials are given elsewhere.[3] The following discussion is organized not in terms of technique, but in terms of structural features.

Glass Structure and Energetics

Without loss of generality, we may consider a glass as a graph in which the nodes correspond to atoms and the edges correspond to chemical bonds. This is a useful way in which to consider a glass, both from an energetic viewpoint and with regard to the interpretation of many types of spectroscopic data. It can describe any model of glass structure just by specifying the type of graph that is congruent with the connectivity of the model.

The electronic energy DOS (density of states) of a molecule or crystal can be generated by inversion of the moments of the electronic energy DOS, and these have their origin in the topological details of the bond network.[4] This formulation of the electronic energy DOS is obviously not useful in calculating the energetics of a glass (which one could consider as an infinite molecule) or a crystal, as one becomes embroiled in "infinite sum" problems. However, the qualitative model provides important conceptual insights. The most important differences between two structures involve the lowest disparate moments of their respective electronic energy DOS.[5] The low moments are therefore of greatest interest. This then suggests a qualitative answer to the general question of what constitutes a good description of a glass structure. An exact description of a glass structure would involve specifying the relative spatial coordinates of Avogadro's number of atoms, obviously an impracticality. However, let us consider the energetic descriptions of both a glass and a mixture of constituent oxides or a single crystalline phase of the same composition formulated within the graphical model and apply the method of moments. In general, the lowest moments of both materials will be identical; let us designate this as the local volume. The first few moments that differ between the structures contain the dominant energetic differences between the structures; this we designate as the intermediate volume. The essentially infinite number of higher moments contributes greatly to the total energy of both structures, but contributes negligibly to the energy difference between the structures; let us designate this as the distant volume. The key factors in any description of a glass are therefore the local volume (as we will see, this specifies such properties as the chemical composition) and the intermediate volume. Variations in the charac-

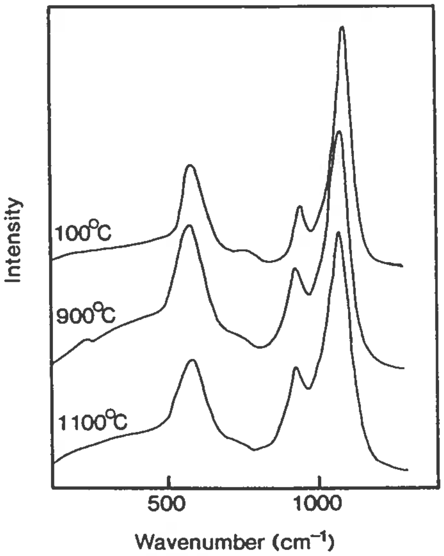


Figure 1. Temperature-reduced Raman spectra of glass (100°C) and melt (900 and 1100°C) of composition $Na_2O{:}2SiO_2{:}0.027NaAl_2O_4$*; the liquidus temperature is 850°C. Note the similarity of the spectra of the glass and the melts. (After Reference 2).*

ter of the distant volume do not materially affect the energetics of the local and intermediate volumes.

Let us now consider what are the chemical and structural aspects of the local and intermediate volumes. A single moment constitutes a closed walk, and the order of the moment specifies the length of the walk. A zero-order moment constitutes a walk "in place" and specifies the type of atom at the origin of the walk; the sum of the zero-order moments specifies the chemical compostion of the glass. In isochemical systems, the sums of the zero-order moments are hence identical. Second-order moments specify which atoms are bonded to which and what are the coordination numbers, factors that are extremely important from an energetic viewpoint. Higher-order moments specify how coordination polyhedra are linked together; it is here that structural and energetic differences between glasses and crystals become important, and it is here that the thrust of current work primarily focuses.

General Features of (Alumino-)Silicate Glass Structure

The modern study of glasses was initiated by that prominent mineralogist W.H. Zachariasen.[6] He proposed that silica glass is made up of $(SiO_4)^{4-}$ tetrahedra that share corners so that each oxygen is linked to two Si atoms. This idea was adopted by B.E. Warren[7] (who solved the crystal structures of diopside, tremolite, and vesuvianite) in his diffraction studies of silica glass, and the idea of silica glass as a continuous random network developed from this. Note that the beginning of this model was the definition of the lowest moments in the structure: silicon is bonded to oxygen, and the coordination numbers of silicon and oxygen are four and two respectively. The chemical features of most natural melts (and glasses) ensure that their structures will have broadly similar features—a continuous or discontinuous network of corner-linked tetrahedral oxyanions with additional cation species occupying interstices within this framework. Spectroscopic studies have confirmed this as a general model. However, it should be noted that both [5]- and [6]-coordinated Si have been reported[8,9] in glasses quenched from melts at very high pressure, and from glasses at high pressure,[10] although there is some contention[11] concerning vibrational spectroscopic evidence for glasses at high pressure. The principal thrusts of current work are to determine coordination numbers for components in addition to Si, to determine details of local tetrahedral connectivity, and to try and characterize details of intermediate-range tetrahedral connectivity (i.e., smallest sizes of rings of tetrahedra within the framework).

There are five topologically distinct local tetrahedral linkages; these are illustrated in Figure 2, which also shows the different types of terminology used by different "breeds" of spectroscopists. Anions (oxygens) that bridge (are linked to) two tetrahedra are denoted as bridging anions; anions that bond to only one tetrahedrally coordinated cation are denoted as nonbridging anions. Nonbridging anions obviously interrupt the connectivity of a tetrahedral network. When there are no nonbridging anions, the general formula of the glass is $T\varnothing_2$ ($\varnothing$ = unspecified anion) and the linkage is denoted as tectosilicate (for a silicate glass), Q^4 and NBO/T = 0. A decrease in the number of bridging anions produces the sequence of units shown in Figure 2, ending with an orthosilicate unit, Q^0 and NBO/T = 4, in which there is no tetrahedral linkage (polymerization) at all. Tetrahedral stoichiometries intermediate between the discrete values of Figure 2 can be produced by networks that consist of mixtures of the individual connectivities shown. Questions of bulk composition, coordination number and (tetrahedral) network connectivity are not completely independent. There are long-range and short-range charge-balance requirements to be satisfied, and frequently the determination of network connectivity can also solve problems of cation coordination number, and vice versa.

Local Connectivity

Two principal spectroscopic methods have been used to derive local (tetrahedral) connectivity information in silicate and aluminosilicate glasses—vibrational (Raman and IR spectroscopies) and MAS NMR spectroscopy. The latter is considered by J.F. Stebbins,[12] and has been particularly important in determining small amounts of unusual coordinated elements (e.g., $^{[5]}$Si, $^{[5]}$Al) that may represent quenched transient species in the melt.

Raman spectroscopy has played a major role in characterizing local aspects of network connectivity in silicate and aluminosilicate glasses.[13,14] Figure 3 shows a schematic representation of the major bands or groups of bands as a function of silica content in alkali and alkaline-earth silicate glasses. Systematic trends are immediately apparent, and an adequate interpretation of the bands will provide information on local structure. The spectrum of SiO_2 glass[12] shows two weak depolarized bands near 1,200 and 1,060 cm^{-1}, usually assigned to asymmetric Si–O stretching vibrations within the fully con-

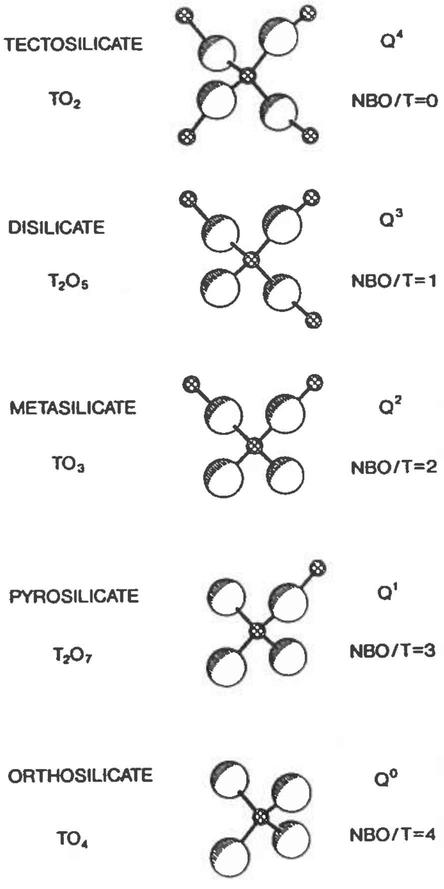


Figure 2. The five topologically distinct local tetrahedral linkages possible in a glass or crystal; small cross-hatched circles denote tetrahedrally coordinated cations (e.g., Si,Al); large partly shaded circles denote oxygen anions. The different terminologies used to denote these species are also shown, together with the stoichiometry of a network formed solely by each species.

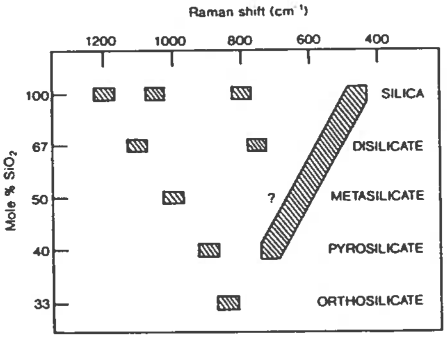


Figure 3. Frequency variation of the major Raman bands as a function of silica content and long-range connectivity in alkali and alkaline-earth silicate glasses. (After Reference 13).

nected (Q^4) tetrahedral network. Glasses of composition near $X_nSi_2O_5$ (X = alkali or alkaline-earth cations) show a band in the range 1,100–1,050 cm^{-1}, the frequency of which decreases with increasing field strength of the X cation. This band has a low depolarization ratio (0–0.2)[15] consistent with a symmetric vibration of a tetrahedral group with noncubic point symmetry. The compositional details of these glasses suggest that this group is a disilicate (Q^3, one nonbridging anion per $T\phi_4$ group) type because the intensity of this band peaks at the $X_nT_2O_5$ composition and decreases rapidly toward the metasilicate composition. As the latter composition is approached, a strong band is observed in the region 1,000–950 cm^{-1}; there is the suggestion of fine-structure within this band, but the details are not clear. Again, the low depolarization ratio and composition are consistent with a symmetric vibration of a metasilicate (Q^2, two nonbridging anions per $T\phi_4$ group) group. Similarly, the bands at 900 cm^{-1} and 850 cm^{-1} for the pyrosilicate and orthosilicate compositions are consistent with symmetric vibrations of pyrosilicate (Q^1) and orthosilicate (Q^0) groups, respectively. Thus for any specific glass composition, the relative intensities of these five bands give the relative frequency of the different connectivity species in the glass,[16] and this has proved an important technique in characterizing tetrahedral network connectivity in compositionally complex silicate glasses.

Coordination Number

In addition to Si, the most important (cationic) components of magmas are Al, Na, K, Ca, Fe, and Mg. Except at high pressure (or in unusual structural or crystal-chemical compositions), Si is always [4]-coordinated. However, the other cations show a range of coordination numbers (from [4] to [12] in minerals), and the coordinations adopted at any specific glass composition and conditions of preparation need to be characterized. When tetrahedrally coordinated, cations are designated as *network formers* (Figure 4a); in other (higher) coordinations, cations are designated as *network modifiers* (Figure 4b), because their occurrence interrupts the connectivity of the tetrahedral network, giving rise to nonbridging anions. Some cations (e.g., Fe) may be either network formers or network modifiers, depending on glass composition and conditions of synthesis. Other cations (e.g., Na, Ca) may be network modifiers or *interstitials* (Figure 4c) (i.e., occupying holes within the tetrahedral framework without modifying its connectivity). Hence, characterization of the coordination number is of major importance in understanding the properties and behavior of glasses and melts. Since different elements may behave differently *and* are sensitive to different types of spectroscopy, each element will be examined separately.

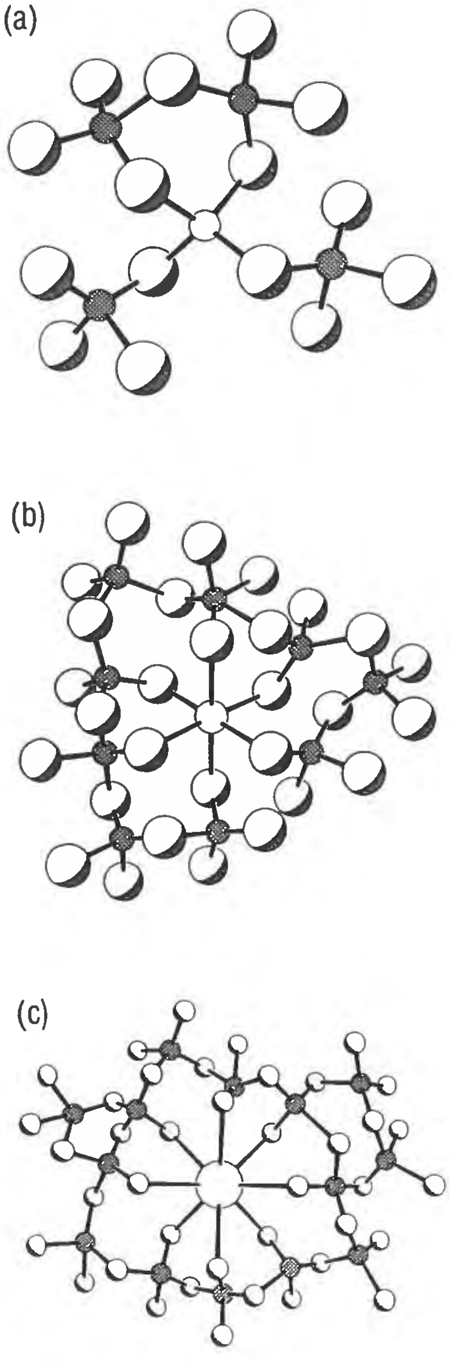
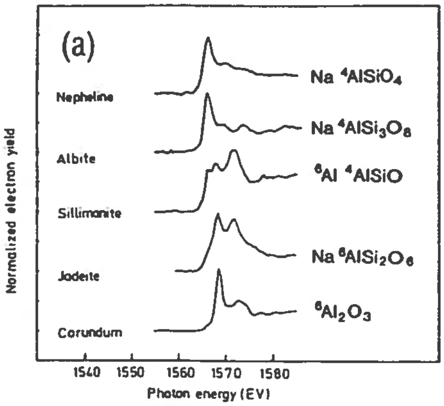


Figure 4. The different types of cation coordination in glasses: (a) network former, where the cation is part of the tetrahedral network; (b) network modifier, where the cation interrupts the connectivity of the tetrahedral network; (c) interstitial, where the cation occupies a hole (or cavity) within the tetrahedral framework without modifying its connectivity. Small circles are cations, large circles are anions; cross-hatched cations are part of the tetrahedral network, dotted cations show the different roles from (a)-(c).

Aluminum

Al adopts [4]-, [5]- and [6]-coordinations in crystals, and potentially can adopt any of these in glasses. In tetrahedral coordination, Al is a network former; in [5]- or [6]-coordination, Al is a network modifier. Simple bond-strength arguments suggest that the role of Al is a function of melt composition. It has often been suggested that when in a substitutional role (e.g., Na + Al $\rightleftharpoons$ Si in a silicate glass), Al will be a network former, and when in an additive role (e.g., Al_2O_3 + a silicate glass → peraluminous glass), Al will be a network modifier because of the local coordination requirements of the additional anions introduced into the system. The most effective probe for resolving Al coordination is MAS NMR spectroscopy, but vibrational and x-ray absorption spectroscopies are also important techniques. In alkali aluminosilicate glasses,[15-17] the Raman spectra are similar to spectra of analogous alkali silicate glasses in the region 1,200–800 cm^{-1}. With increasing Al/(Al + Si) ratio, the higher frequency bands all shift to lower wavenumbers,[15,18] band assignments being the same in both the aluminosilicate and silicate glasses. This shift may be due to the superposition of bands due to discrete NNN (next-nearest-neighbor) configurations, or may be due to a continuous shift in frequencies with change in composition (i.e., longer-range coupling). This point is not adequately resolved at present. With changing Al/(Al + Si) ratio, the relative intensities of these bands also change. In particular, the Q^4 band decreases rapidly in intensity, whereas the Q^3 band increases in relative intensity and Q^2, Q^1, and Q^0 are relatively unaffected, with regard to either relative intensity or frequency.[17,19] One may thus conclude that Al preferentially orders at Q^4 (fully polymerized) tetrahedra in alkali aluminosilicate glasses, this preference increasing with increasing Al/(Al + Si) ratio. Different behavior is exhibited by alkaline earth aluminosilicate glasses.[20] Increasing Al/(Al + Si) ratio (for constant degree of polymerization) promotes ordering of Al at Q^3 sites. The situation for peraluminous melts is less clear. It has frequently been suggested that Al may act as a network former and a network modifier. Raman spectroscopy can give information on this via the change in Q species resulting from changes in the role



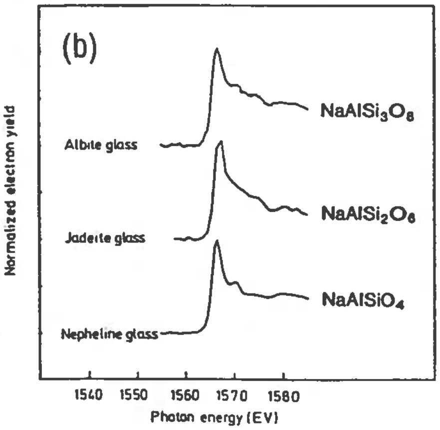


Figure 5. Comparison of Al K-edge structure and XANES spectra for aluminosilicate crystals and glasses: (a) spectra for minerals, in which the Al coordination is known from crystal structure work; (b) spectra of glasses of analogous compositions. (After Reference 21).

of Al in the glass, but the interpretation is somewhat contentious at present.

More direct evidence of Al coordination can be gained from x-ray absorption spectroscopy.[21,22] Comparison of Al K-XANES spectra for crystalline aluminosilicates of known structure with aluminosilicate glasses[23] shows the Al K-edge energies in alkali aluminosilicate glasses to be compatible with [4]-coordination (Figure 5); compare the glass spectra with those of nepheline ($NaAlSiO_4$) and albite ($NaAlSi_3O_8$) (both with [4]-coordinated Al) versus those of jadeite ($NaAlSi_2O_6$) and corundum (Al_2O_3) (both with [6]-coordinated Al). These results are confirmed by analogous Al EXAFS results.[24] ⟨Al-O⟩ distances of 0.174 nm and Al coordination numbers close to [4] were obtained for alkali aluminosilicate glasses; this compares with $\langle ^{[4]}$Al-O⟩ and $\langle ^{[6]}$Al-O⟩ distances of 0.176 and 0.192 nm, respectively, in sillimanite ($^{[6]}Al^{[4]}AlSiO_4$).

Iron

Fe occurs in both divalent and trivalent states in minerals, and can have coordination numbers of [4]–[8] and [4]–[6], respectively. Thus both Fe^{2+} and Fe^{3+} could potentially be both network formers and network modifiers; their field strengths are too strong for them to occur as interstitials. Thus Fe is a much more complex constituent than the nontransition metals discussed here, and it is perhaps fortunate that ^{57}Fe is a Mössbauer-sensitive nucleus,[3] enabling us to rapidly distinguish valence state and coordination number with only a modicum of controversy.

Ranges of IS (isomer shift in mm/s relative to Fe^0) for Fe in different valence states and coordinations are shown in Figure 6. Spectral resolution can sometimes be a problem in the more complex minerals, and this problem is exaggerated for glass, in which ranges of similar environments lead to significant *substitutional broadening* of lines. However, resolution of such key issues as $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratios and principal coordination numbers is still feasible (Figure 7), and Mössbauer spectroscopy can determine oxidation ratios as accurately as calorimetric methods.[25] In most complex glasses, Fe^{2+} has been assigned to octahedral coordination, although it shows considerable range in IS with glass composition.[26] Most spectra usually show just two maxima corresponding to a $^{[6]}Fe^{2+}$ doublet; however, these doublets are frequently asymmetric and often have obvious shoulders, indicating that more than one Fe^{2+} doublet is present. Such spectra have often been resolved into two discrete doublets corresponding to Fe^{2+} in two distinct octahedrally coordinated environments.[27,28] However, the situation here is far from clear. The range of IS values that have been assigned to $^{[6]}Fe^{2+}$ include 0.64–0.83 mm/s in Fe-bearing $NaAlSi_2O_6$ glasses[29] and 0.89–0.99 mm/s in Na_2SiO_3-$NaFeSi_2O_6$ glasses,[30] even though IS values for $^{[4]}Fe^{2+}$ in silicate minerals generally overlap these values (Figure 6). This has led some studies to refrain from assigning coordination numbers in Fe-bearing silicate glasses[31] with IS values in this range. However, more unequivocal evidence comes from EXAFS work on $Na_2FeSi_3O_8$, $K_2FeSi_3O_8$ and Fe_2SiO_4 glasses,[32,33] which shows Fe^{2+} to be tetrahedrally coordinated. Thus, more sophisticated models are needed for the Mössbauer spectra of silicate glasses in terms of both spectrum fitting and interpretation.

The behavior of Fe^{3+} is more complicated. Fe^{3+} may be [4]-coordinated, [6]-coordinated or both, depending on glass composition and fO_2 conditions of synthesis. For oxidized glasses [$Fe^{3+}/(Fe^{2+} + Fe^{3+}) > 0.5$], the IS values are characteristic of [4]-coordination, with Fe^{3+} in a network-forming role. There may be two distinct Fe^{3+} doublets (corresponding to two distinct tetrahedrally-coordinated Fe^{3+} sites),[27] but there are problems in fitting the spectra with this model. In reduced glasses [$Fe^{3+}/(Fe^{2+} + Fe^{3+}) << 0.5$], the IS values are characteristic of [6]-coordination, with Fe^{3+} in a network-modifying role. At intermediate conditions [$0.5 > Fe^{3+}/(Fe^{2+} + Fe^{3+}) > 0.3$], the spectra show both [4]- and [6]-coordinated Fe^{3+} to be present.

Variation in $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ obviously changes the polymerization of the tetrahedral network when $^{[4]}Fe^{3+}$ is present. As $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ is a function of fO_2, temperature (T) and pressure (P) of synthesis, it obviously has a significant effect in controlling polymerization-related melt properties such as viscosity and density, and is thus of great interest with regard to magmatic processes. As discussed above, low fO_2 promotes [6]-coordinated Fe^{3+} and reduced tetrahedral network connectivity; increasing fO_2 promotes $^{[6]}Fe^{3+} \rightarrow {}^{[4]}Fe^{3+}$ and increased network connectivity. However, tetrahedral connectivity is also related to other factors (T, P, composition), and thus $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ also interacts with these other factors. For a specific network connectivity, the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio is a linear function of the Al/(Al + Si) ratio and the field strength of the constituent alkali or alkaline-earth cation.[28] These interactions are also a function of temperature,[34] and the actual structure of the glass is controlled through the mutual interaction of all these factors. The effect of pressure is also of great interest from a geological viewpoint, as it is a physical parameter that

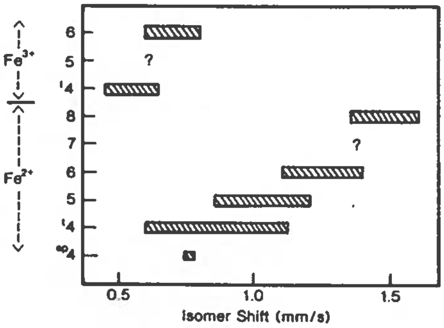


Figure 6. Variation in isomer shift as a function of valence state and coordination number in ^{57}Fe Mössbauer spectra of minerals of known structure; t = tetrahedral, sp = square planar. (After Reference 3).

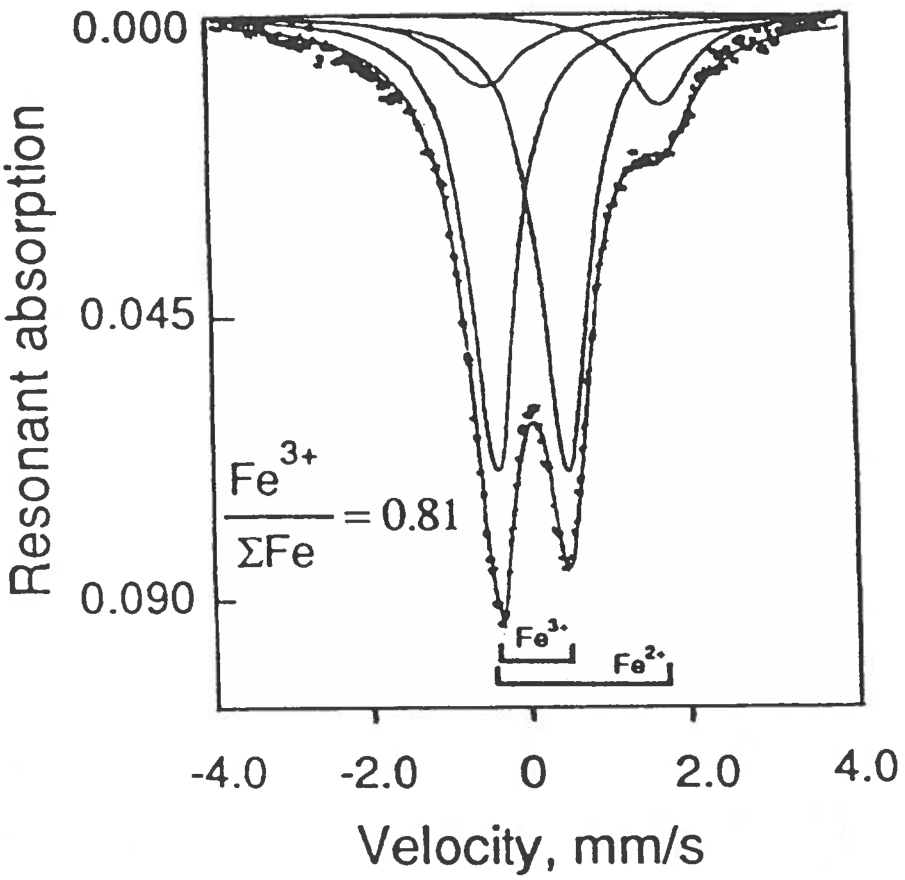


Figure 7. The ^{57}Fe Mössbauer absorption spectrum of quenched melt (at 298 K) in the system Na_2O-Al_2O_3-SiO_2-Fe-O; the melt was formed at 1250°C and at an oxygen fugacity of 10^{-3}. (After Reference 27).

can change rapidly during magmatic processes. For some glass compositions,[25] increasing P promotes the reactions $^{[4]}Fe^{3+} \rightarrow {}^{[6]}Fe^{3+}$ and $Fe^{3+} \rightarrow Fe^{2+}$, and this causes a considerable decrease in the degree of connectivity of the tetrahedral network (hence decreasing viscosity), suggesting that magmatic transport is enhanced at depth within the Earth. For other compositions,[31] no change is seen in Fe^{3+} coordination up to 30 kb. Hence this effect seems to be quite sensitive to composition, and there is room for much more work in this area.

Magnesium

Magnesium is one of the most important components in magmatic liquids, but there is little direct information on its coordination in analogue glasses. Raman spectra of $MgSiO_4$-$MnSiO_4$ glasses[35] show a band at ~400 cm^{-1} that has been assigned to octahedral (MgO_6) groups. This is in accord with molecular dynamics simulations of $MgSiO_4$ liquid structure[36] and diffraction analysis of $MgSiO_3$ glass.[37]

Calcium

Calcium is a network modifier (or perhaps even an interstitial for some compositions), and it is difficult to gain any information on coordination from vibrational spectroscopy. However, XAS has been important in this regard.[38] EXAFS measurements on anorthite and amorphous $CaAl_2Si_2O_8$ indicate ⟨Ca-O⟩ distances of 0.264 and 0.260 nm, respectively, and coordination numbers of [7]. For diopside and amorphous $CaMgSi_2O_6$, the EXAFS-derived distances are 0.264 and 0.250 nm with coordination numbers of [8] and [7], respectively. These values are in line with the densities of the four materials; in addition, one does not necessarily expect the coordination to be the same in $CaMgSi_2O_6$ glass as in diopside, as the conformation of the rather distorted [8]-coordination in diopside is dictated primarily by the linkage requirements of the two distinct polyhedral structural units. As the structures of glasses and melts are far more flexible in terms of geometrical details, it seems likely that Ca adopts a much smaller range of coordination numbers in glasses and melts than in minerals.

Low frequency (200–250 cm^{-1}) vibrational bands have recently been assigned to Ca-O modes.[20] Changes in the frequency of this mode correlate with the Al/(Al + Si) ratio and with the number of nonbonding oxygens per tetrahedral cation. This is interpreted as being due to a change in the role of Ca (from network modifier to interstitial). When in an interstitial role, one expects weak Ca-O bonds and high coordination numbers, and hence a low frequency band. When in a network-modifying role, one expects stronger Ca-O bonds and lower coordination numbers, and hence a higher frequency band.

Sodium

Sodium is a network modifier or interstitial, and information on coordination has been derived primarily by XAS. EXAFS studies of Na-bearing aluminosilicate glasses[24] show Na coordination numbers from less than [6] to above [7], increasing Na coordination correlating with decreasing Al content, together with a ⟨Na-O⟩ distance of 0.261 nm. As with Ca, a low-frequency vibrational mode can be associated with an Na-O deformation that changes in frequency with changing network connectivity.

Rare-Earth Elements

The partitioning of REEs between different minerals and between minerals and melt are extremely sensitive indicators of igneous processes. In particular, partial melting and fractional crystallization are important processes and involve the distribution of REEs between minerals and a melt phase. Adequate models for crystal-melt partitioning need to incorporate details on coordination, and little information has been available until recently. As REEs are only present in trace amounts in melts and glasses of geological interest, an element-selective method must be used to characterize their environment.

EXAFS results[39] on Yb^{3+}, Gd^{3+}, and La^{3+}-bearing glasses from $NaAlSi_3O_8$ to $Na_2Si_3O_7$ show that coordination is a function of both size and glass composition. Yb^{3+} is [5]- to [6]-coordinated with ⟨Yb-O⟩ = 0.221 nm. Gd^{3+} ranges from [6]-coordinated (⟨Gd-O⟩ = 0.230 nm) in albite glass to [8]-coordinated (⟨Gd-O⟩ = 0.243 nm) in sodium trisilicate glass. La^{3+} is [7]-coordinated (⟨La-O⟩ = 0.243 nm) in sodium trisilicate and intermediate glasses, but is [8]- to [9]-coordinated (⟨La-O⟩ = 0.259 nm) in albite glass; the latter result is thought to be caused by La^{3+} occupying a large tetrahedral cage in albite glass. Similar work on La^{3+}-bearing K_2O-SiO_2 glasses[40] also shows La^{3+} to be [7]-coordinated with $\langle \text{La-O} \rangle = 0.242$ nm.

Of particular geological interest is the addition of halogens (F,Cl) to REE-bearing systems. The REEs complex strongly with F (but not Cl) in the glass.[41] Yb^{3+} and Gd^{3+} bond solely to F; they are both [8]-coordinated with $\langle \text{Yb-F} \rangle = 0.223$ nm and $\langle \text{Gd-F} \rangle = 0.230$ nm On the other hand, La^{3+} forms mixed (O,F) complexes; it is [8]-coordinated by (on average) 4 oxygens ($\langle \text{La-O} \rangle = 0.245$ nm) and 4 fluorines ($\langle \text{La-F} \rangle = 0.246$ nm). This substantiates the many suggestions that REEs complex preferentially with fluorine in the melt/fluid phase.

Titanium

Ti is one of the more important of the minor elements in rocks and minerals. It is usually quadrivalent (Ti^{4+}), although a few examples of Ti^{3+} are known. In minerals, it is usually [6]-coordinated, although [5]-coordination is not uncommon and [4]-coordination does occur. The most informative work on Ti in glasses has been by XAS. XANES spectra are particularly sensitive to Ti^{4+} coordination number. Typical spectra show strong pre-edge features (Figure 8) that have been assigned to an electronic transition of the type $1s \rightarrow 3d$. Such transitions are formally forbidden, but can occur if there is mixing of the metal d-states with ligand p-states. Such mixing is forbidden if the metal occurs in a centrosymmetric environment, but occurs increasingly with deviation from this condition. Thus [4]-coordinated Ti^{4+} will show a relatively strong absorption due to this transition, whereas [6]-coordinated Ti^{4+} will only show a weak absorption.

The pre-edge features in Ti-bearing cordierite[42] and spodumene[43] glasses show the Ti to be [4]-coordinated at low Ti concentrations. EXAFS results confirm this, and give a $\langle \text{Ti-O} \rangle$ distance of 0.182 nm. Calas et al.[21] note the strong medium-range disorder exhibited by Ti-rich glasses, and suggest that (TiO_4) groups are not easily incorporated into the normal tetrahedral framework of aluminosilicate glasses. In the system K_2O-TiO_2-$2SiO_2$, EXAFS data[44] indicate [5]-coordinated Ti, with Ti-O distances of 0.164 (×1) and 0.193 (×4) nm, similar to the square pyramidal coordination shown by Ti in some minerals.

Intermediate-Range Disorder

Until recently, there has been little information available on intermediate-range ordering in aluminosilicate glasses. Some techniques are not sensitive at this scale; others have low resolution because of the considerable disorder that always acts to broaden and reduce signal intensity. Various indirect methods have been used to try and extract some information or test possible models, but these have not been very successful. Tetrahedral networks can be topologically characterized by the types of rings (or circuits) that they contain. There have been efforts to identify vibrational (deformational) modes that are characteristic of particular ring sizes, but no specific scheme has met with general acceptance. EXAFS data can provide mean nearest and next-nearest-neighbor distances (i.e., $\langle \text{Si-O} \rangle$ and $\langle \text{Si-Si} \rangle$), from which an average ring size can be calculated. However, it is not clear if this has the resolution to characterize multiple ring (e.g., 4- and 6-ring, 5- and 6-ring) structures.

Although diffraction methods are not the principal topic of this article, they must be considered here since recent work promises to change our views on intermediate-range ordering in silicate glasses. As glasses are structurally isotropic, the maximum information that can be gained from a diffraction experiment is a correlation function in one dimension.[45] Thus we can never hope to derive the three-dimensional structure, but we can test structural models. The problem with such correlation functions is one of resolution and of identification of specific interatomic distances. In an extremely elegant experiment, Gaskell et al.[46] use neutron scattering by isotopically substituted (^{nat}Ca and ^{44}Ca) Ca silicate glass to produce a Ca-Ca pair correlation function. This shows prominent Ca-Ca separations of 0.38 and 0.64 nm compatible with sheets of edge-sharing CaO_6 octahedra that resemble the octahedral motif in the compositionally similar wollastonite structure, and incompatible with a random filling of interstices in an SiO_2 network. This well-developed intermediate-range order is in remarkable contrast to our previous views of glass structure. This isotopic double-difference neutron scattering technique seems the best way to approach such questions of intermediate-range order, and promises great advances in our knowledge of glass structure in the next few years.

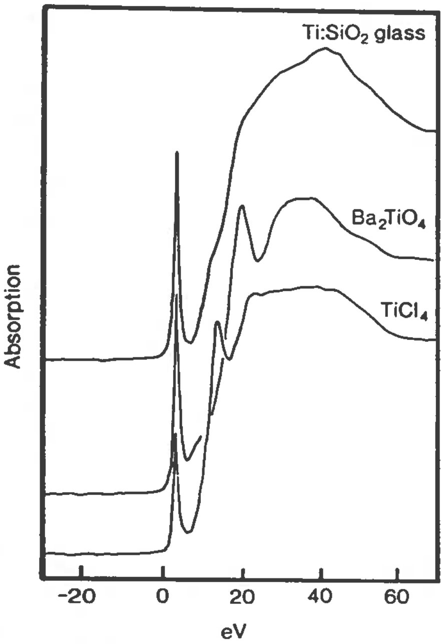


Figure 8. Near-edge K-absorption spectra of [4]-coordinated Ti in crystalline phases ($TiCl_4$, Ba_2TiO_4) and SiO_2 glass doped with 3 wt% TiO_2; note the strong pre-edge feature at 3 eV. (After Reference 53)

H_2O in Silicate Melts

H_2O is an extremely important constituent in silicate magmas. H_2O exerts a major effect on such properties as temperature of crystallization and viscosity, and has a key role in controlling the nature of volcanic eruption (explosive versus quiescent). Consequently, there has been considerable effort within the geological community to characterize the solubility and speciation of H_2O in analagous quenched glasses.

The addition of small amounts of H_2O (ppm) results in a sharp band at ~3,600 cm^{-1} in both the Raman and infrared spectra,[47] diagnostic of OH groups. This is accompanied by a weak highly polarized band at 967 cm^{-1} that may be assigned to a tetrahedral [SiO_3OH] stretching vibration, and an overtone band near 4,500 cm^{-1} that results from the combination of these two stretching vibrations. This indicates that at low concentrations, H_2O dissolves in silicate glasses as OH (hydroxyl) groups.

The addition of large amounts of H_2O (wt%) produces very different vibrational spectra. The envelope in the OH-stretching region now contains two components, a sharp band that can be assigned to an OH stretch, as in the low-H_2O glass, and a broad asymmetric band that is similar to H_2O stretching bands in hydrous minerals. The appearance of the characteristic H-O-H bending mode at 1,630 cm^{-1} and the combination mode (H_2O stretch + H-O-H bend) at ~5,200 cm^{-1} indicate the presence of molecular H_2O at these much higher H_2O concentrations.

There has been considerable recent work to characterize the factors that control both speciation and solubility. This has been aided by the development of quantitative micro-IR spectroscopy,[48] whereby total dissolved H_2O and the concentrations of individual H-bearing species can be determined precisely and nondestructively over a wide compositional range (ppm to wt%). The microprobe nature of the technique allows crystals, vesicles and alteration to be avoided (something not feasible with bulk analytical techniques).

At low H_2O contents, OH is the dominant species. When H_2O is in the range 0.1–1.0 wt%, molecular H_2O is dominant. Essentially, the OH content of a melt initially increases with increasing total H_2O content, but saturates when H_2O is of the order of a few weight percent, with additional H_2O dissolving as molecular H_2O. Thus H_2O content is the dominant factor controlling speciation in glasses of geological interest. However, both temperature and glass composition also affect speciation of H_2O. Increasing (synthesis) temperature for rhyolitic glasses correlates with increasing OH content (for a constant H content) and can be interpreted in terms of the dissolved species reaction $H_2O + O^{2-} = 2OH^-$ via a regular solution model.[49] Not surprisingly, bulk glass composition also influences speciation. In aluminosilicate glasses, both increasing Si content and K/Na ratio correlate with increasing H_2O (molecular) relative to OH.[50]

Summary and Future Prospects

Spectroscopic techniques have contributed significantly to our understanding of the structure of glasses of geological interest. Their primary contribution has been to the characterization of local structure, particularly coordination number. Whether a species is a network former, network modifier or interstitial strongly affects the physical properties (e.g., viscosity) of a magma. The character of the coordinating anions (e.g., O^{2-}, OH^-, Cl^-, F^-) gives information on complexing and transport of different elements in the melt. These details of coordination also strongly impact our interpretation of element fractionation between the melt and crystallizing minerals. Raman and infrared spectroscopy have been important in characterizing local connectivity in the tetrahedral network, and this has played an important role in understanding the physical properties of melts. Two-dimensional-shift correlated (COSY) MAS NMR shows promise in further defining local connectivity.[51] There has been less success at characterizing intermediate-range structure. Some lines in the Raman spectra of silicate and germanate glasses have been assigned to ring deformation modes; however, this is still somewhat controversial. In addition, there can be strong matrix enhancement of symmetric vibrational modes in Raman spectra,[52] and hence such signals do not necessarily represent a dominant structural motif.

Spectroscopic methods will continue to contribute significantly to studies on geological glasses. In particular, the local behavior of most major and trace elements in magmas is of great interest, and we have barely begun work in this area. EXAFS and neutron diffraction hold most promise as useful experimental probes of intermediate-range structure, and the next few years should see significant expansion in the use of these two methods. Until recently, geochemistry tended to ignore the structural aspects of silicate liquids and glasses because of their experimental intractibility. However, this situation is now changing and significant advances have been made in the past few years. This should continue at an accelerating rate in the near future.

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