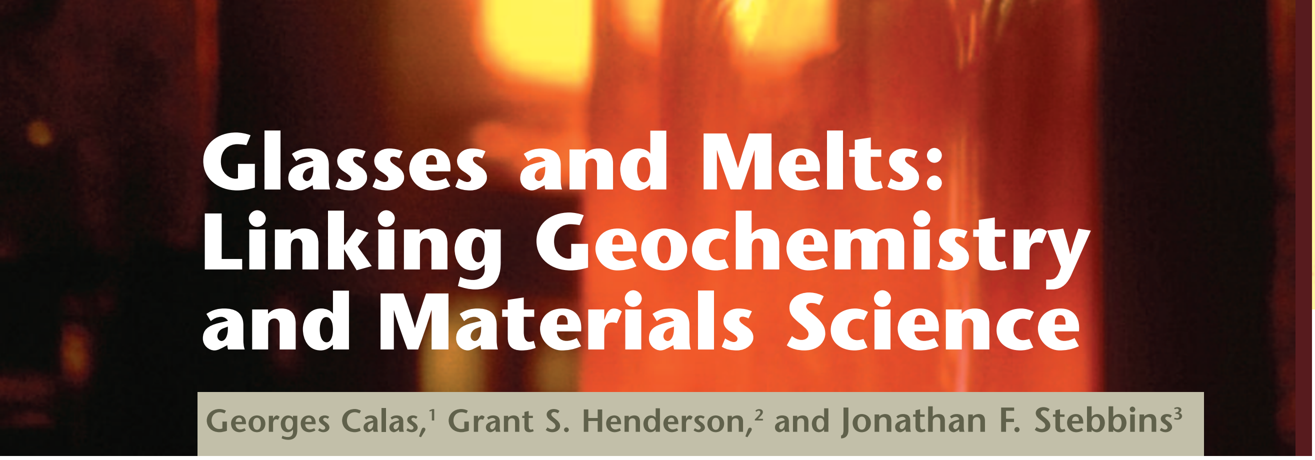

Glasses and Melts: Linking Geochemistry and Materials Science

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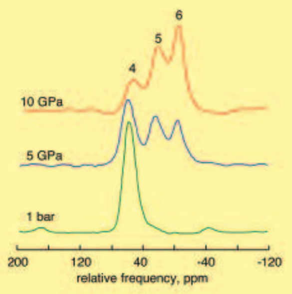

^{27}Al NMR spectra of Ca-aluminosilicate glasses quenched from melts at 1 bar, 5 GPa, and 10 GPa. Peaks for 4-, 5-, and 6-coordinated Al are shown (Allwardt et al. 2005).

Silicate melts are major components of magmatic activity and of its most spectacular expression, volcanic eruptions. The "hidden part" is even more fascinating, as silicate melts are directly involved in matter and heat transfer within the Earth and planets. Silicate glasses, often investigated as a frozen picture of their molten counterparts, are also materials of major importance in technology. Despite the difficulties in rationalizing physical and chemical properties of glasses and melts, due to an incomplete knowledge of their structure, major progress has been made recently in synthetic and natural systems. This issue of *Elements* reviews the properties of silicate glasses and melts from the molecular to the field scale. It includes insights into their technological applications and describes some recent advances in this fast-evolving field.

Keywords: magmas, volcanology, geochemistry, glasses, silicate materials

INTRODUCTION

Silicate glasses and melts have been of interest to mineralogists, geochemists and igneous petrologists for many decades. Silicate melts are essential components of igneous processes, participating actively in Earth differentiation, heat transfer and global geodynamics, and geochemical cycles. Melt viscosity can decrease some 20 orders of magnitude below that of corresponding solids, and timescales for transport properties are dramatically reduced in the presence of a liquid-phase. In addition, melts relevant to volcanological processes contain various amounts of volatiles, mainly H_2O, CO_2, and sulfur-bearing species. Models for Earth's formation propose a period of substantial melting of the planet during the later stages of accretion, due to the extremely high energies involved in a probable Moon-forming "giant impact" event. As properties of deep magmas must be experimentally constrained, researchers studying melts and glasses participate actively in current experimental developments in Earth sciences, such as in situ experiments at high temperature (T) and high pressure (P) and numerical modeling of complex systems. Many of these experiments are designed to aid in developing an understanding at the atomic level of the structure and dynamics of silicate melts under the P–T conditions of Earth's crust and mantle. Current issues range from the conditions of formation of planetary systems to volcanological monitoring and Earth's dynamics.

Silicate glasses and melts have been of interest in ceramic science, glass technology, and metallurgy for centuries, and more recently in the management of wastes (municipal, industrial and nuclear). A glass plant typically produces 600–1000 tons/day of silicate melts. These applications represent a major field of connection between Earth sciences and industry, and provide job opportunities for students. In addition, studies of archeological and historical glasses make them interesting as analogs for the long-term evolution of waste matrices and give insights into ancient technologies and sources of trade.

This broad interest in glasses and melts stems not only from their roles in Earth sciences and technology, but from their peculiar physicochemical properties, which are correlated to structural organization at the atomic scale. Terms used to describe glass/melt structure are defined in the glossary. The atomic structure and dynamic processes that occur at high temperature provide a basis for understanding the relationships between melt structure, thermodynamic properties, and rheology in these liquids. These fundamental relations permit extrapolation from laboratory-scale simplified melt compositions to multicomponent geological systems. For instance, atomic motion, favored by the high temperatures of silicate melts, is at the origin of the rheological properties of magmas. Element diffusion and gas dissolution are also enhanced relative to solid rocks; this gives magmas their unique geochemical properties.

This issue of *Elements* presents some aspects of glass and melt science and shows that defining structure–property relationships (Calas et al. 2003a; Mysen and Richet 2005) and linking microscopic to macroscopic phenomena (Stebbins et al. 1995) are especially intriguing fields of research.

THE STRUCTURE OF SILICATE GLASSES AND MELTS: SOME BASICS

Information about the molecular-scale structure of silicate glasses and melts and the dynamics of silicate melts is needed to understand their properties at a fundamental level. This task is a challenge because silicate melts possess no long-range structural periodicity or symmetry. Even today the structure of a simple network glass such as SiO_2 remains controversial, with no consensus as to its precise nature (cf. Henderson 2005). However, silicate glasses and melts do possess short-range order, usually manifested as polyhedral units such as tetrahedra, 5-, or 6-coordinated

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sites. The most detailed information on the local atomic environments comes from a combination of spectroscopic and diffraction measurements and bulk property determinations. These data are used to construct a working model of the glass and melt structure. In addition, their structure has some medium-range order, depending on bulk composition and temperature. Insight into the structural organization beyond this limit is mostly obtained from numerical modeling.

The structure of glasses and melts depends on their chemical composition. To a first approximation, a silicate glass or melt can be understood as a network of tetrahedra (Fig. 1a) bonded by non-bridging oxygens to network-modifying cations, such as Na$^+$ and Mg^{2+}, which depolymerize the silicate network. However, in the presence of trivalent tetrahedral cations, such as Al^{3+} and B^{3+}, cations are charge compensators and then contribute to increasing the connectivity of the network. This connectivity, defined by the relative abundances of Q^n species, has a strong influence on the viscosity of silicate melts and other melt properties. The lack of periodic structure and disorder effects are a major limitation for the structural description of silicate glasses and melts. Figure 1b shows how disorder can act in the absence of a periodic structure: silicate tetrahedra are free to rotate, which causes a loss of information over the medium-range structure scale. Numerical modeling provides the possibility of describing the structure of multicomponent glasses. It confirms recent experimental observations that the structure of most glasses and melts, in contrast to silica and other network glasses, e.g. glasses of feldspar composition, is not simply the continuous random network illustrated in the majority of textbooks. Figure 1c represents the simulated structure of a borosilicate glass and illustrates the heterogeneous distribution of cations (Henderson et al. 2006).

A direct visualization of the existence of well-defined sites in silicate glasses is provided by the magnificent coloring of medieval stained glass: the optical absorption bands arising from crystal field effects indicate the oxidation state and site geometry of transition elements (Fig. 2).

MELTS AND GLASSES

Any liquid might become glassy if cooled rapidly enough. The glass transition is characterized by a change in thermodynamic properties (e.g. heat capacity), from solid-like to liquid-like values, with changing temperature. The glass transition temperature depends on thermodynamic and kinetic parameters (Wong and Angell 1976). Glasses provide a frozen image of the melt "structure" at T$_g$; in the reverse direction, a glass gradually softens to a molten state above T$_g$. This property is at the origin of glass making. Blowing the supercooled liquid remains a dramatic aspect of the glass craft industry. Figure 3 depicts the progressive cooling of an industrial silicate melt.

As a melt is cooled, its structure rearranges more and more slowly. At some point (if crystallization is avoided by slow kinetics), the rate of this ordering process can no longer keep pace with the rate of cooling. The melt falls out of equilibrium, forming a glass, with the melt structure "frozen in" at a certain "fictive temperature" (T$_f$). Faster cooling thus leads to a higher T$_f$, allowing the melt structure to be sampled over a range in temperatures and studied conveniently and precisely at ambient temperature. This method is limited to the experimentally obtainable

GLOSSARY

Amorphous material – A solid that lacks a periodic crystalline structure, i.e. it lacks translational symmetry, or a liquid

Bridging oxygen (BO) – Oxygen atoms that are shared between two network formers

Charge compensator – A cation or anion that is in close proximity to another cation or anion in order to provide an overall neutral charge to a polyhedral unit, e.g. Na$^+$ charge compensates Al^{3+} near [AlO$_4$]$^-$ tetrahedra.

Clusters – Small groupings of atoms or polyhedra that have some sort of directionality or non-randomness associated with them

Disorder (structural) – Applied to arrangements of atoms that cannot be described by well-defined bond angles and distances and/or more-random distributions of adjacent cations or anions

Fictive temperature (T$_f$) – The temperature at which a liquid was last in thermal equilibrium during cooling to form a glass. It therefore characterizes the thermal history of the glass and is higher for more rapid cooling.

Glass – An amorphous material that exhibits the glass transition

Glass transition – A relatively narrow temperature region over which second-order thermodynamic properties, such as heat capacity and thermal expansivity of a glass, decrease from liquid-like to solid-like values

Glass transition temperature (T$_g$) – A specific point on the temperature curve of a glass property measured at a standard heating rate; often associated with a viscosity of 10^{12} Pa

Intermediate cation – Cations that may act as either a network former or a network modifier depending upon coordination

Magma – A naturally occurring high-temperature melt, generally containing dissolved gases and often mixed with bubbles or crystals or both

Medium- or intermediate-range order (MRO, IRO) – Structural arrangement out to a radial distance that incorporates next-nearest neighbors. This arrangement can also incorporate polyhedral organization such as rings.

Melt – Hot molten liquid found in magmas

Network – A three-dimensional structure composed of network formers. It may or may not be continuous, ordered or disordered.

Network former – Cations that bond to bridging oxygens to form the network. They usually have coordination numbers of 3 or 4.

Network modifier – Cations that disrupt the network and produce non-bridging oxygens. They usually have a coordination number of 6.

Non-bridging oxygen (NBO) – Oxygen atoms that are bonded to only one network former

Order (structural) – Applied to arrangements of atoms that can be described by well-defined bond angles and distances and/or non-random distributions of adjacent cations or anions

Polyamorphism – Two liquids or glasses with the same composition but different structures

Polymerization – The bonding together of polyhedral units to form two- and three-dimensional structures

Q^n species – A network former that has 0 to 4 bridging oxygens (n = 0–4) bound to the cation

Short-range order (SRO) – Structural arrangement out to a radial distance that incorporates nearest neighbors

Topology – The interconnections between atoms that describe the network

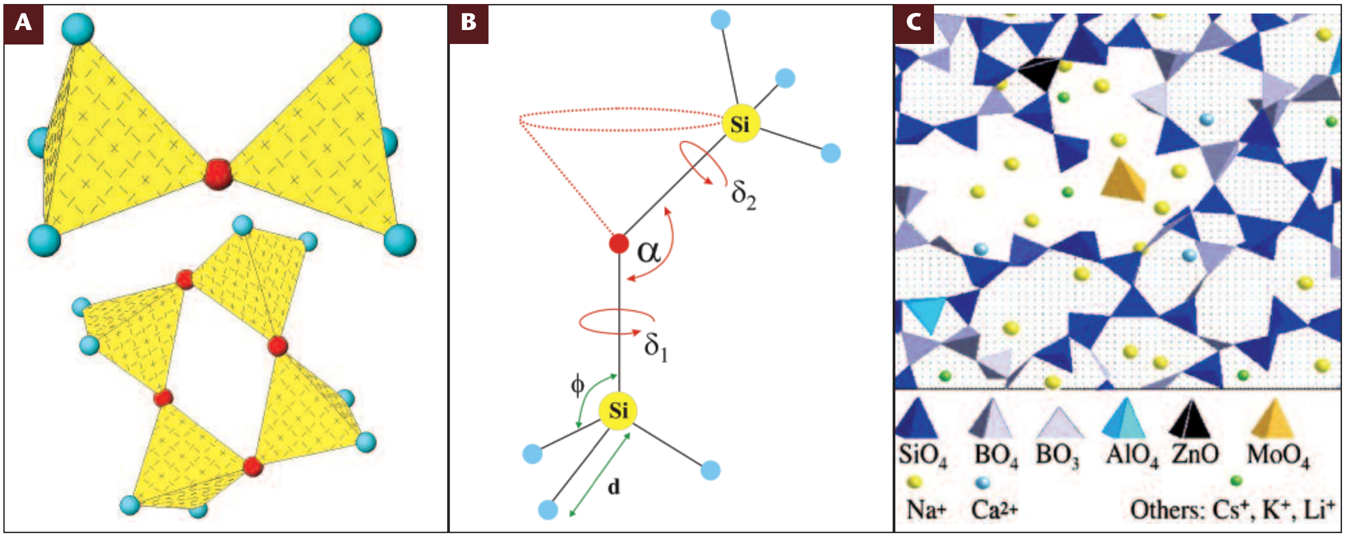

FIGURE 1 (**A**) (Left) Schematic of two SiO_4 tetrahedra containing 3 NBO (blue) and bound together through a BO (red). Each tetrahedron is a Q^1 species. (Right) Schematic of four SiO_4 tetrahedra containing 2 NBO (blue) and 2 BO (red). Each tetrahedron is a Q^2 species. (**B**) Structural disorder occurs through variation in the intertetrahedral angle (α) and the two torsional angles δ_1 and δ_2. The tetrahedral angle (ϕ) and Si–O bond lengths (d) remain relatively unchanged. (**C**) Schematic representation of the local structure of a borosilicate glass derived from an initial molecular dynamics simulation and showing heterogeneous distribution of cations (AFTER CALAS ET AL. 2003B).

range of cooling rates (six to eight orders of magnitude), which fixes the obtainable range of T_f to generally only about 150 to 250K above the "normal" (slow cooled) T_g (Dubinsky and Stebbins 2006).

An important property is the excess volume of silicate melts relative to their crystalline counterparts, as this property is at the origin of magma ascent through the mantle and crust. However, at high pressures, the high compressibility of melts may lead to important density inversions. For example, perovskite may be neutrally buoyant in a chondritically derived liquid at the core–mantle boundary in a deep magma ocean (Miller et al. 1991).

Understanding melt thermodynamics is important, as the free energy is needed to calculate phase equilibria. However, changes of melt structure with increasing temperature are indicated by the observation that liquid-state heat capacities and thermal expansions are generally considerably higher than the solid-like values of glasses, requiring significant "configurational" components (Mysen and Richet 2005). These must be considered to develop accurate structure-based models of melt properties.

The Dynamics of Silicate Melts

Silicate melts are not static mixtures of silicate polymer species and cations, but contain dynamic, rapidly exchanging chemical environments, with bond-breaking and ionic exchange between structural units occurring on a timescale comparable with those of viscous flow and chemical diffusion. In particular, the Adam-Gibbs theory of relaxation allows a quantitative link to be made between the timescale for viscous flow and the configurational entropy of the melt (Mysen and Richet 2005). Silicate melts are viscoelastic liquids, with a finite relaxation time related to dissipation of the strain induced by chemical, mechanical or thermal stress. Relaxation time increases with decreasing temperature down to the glassy state.

A schematic diagram of an oxygen-diffusion mechanism is shown in FIGURE 4A (Farnan and Stebbins 1994). The diffusion mechanism is initiated when a non-bridging oxygen of the SiO_4 tetrahedron A (probably with three other bridging oxygens) impinges on a tetrahedron B, where all oxygens are bridging oxygens (e.g. to tetrahedron C among others). In this situation, B transforms to an intermediate five-fold-coordinated species ($^{[5]}$Si, step 1). Diffusion occurs when $^{[5]}$Si dissociates, and an oxygen that was initially bonded to B (e.g. green circle) is now associated with a neighboring tetrahedron such as C (step 2). The increase of higher-coordinated species is consistent with increasing diffusivity in the liquid, which implies that viscosity decreases, since diffusivity and viscosity are inversely correlated. These atomic-scale mechanisms are at the origin of important transport properties, such as diffusivity or viscosity (FIG. 4B).

FIGURE 2 Detail of a stained glass, Notre Dame de Chartres, France (early thirteenth century). Glass coloration originates from crystal field transitions of minor transition elements. PHOTO COURTESY OF THE DATABANK PALISSY, MINISTÈRE DE LA CULTURE ET DE LA COMMUNICATION, FRANCE.

IN THIS ISSUE

In the articles that follow, the unique structures and properties of glasses, melts, and magmatic systems are further explored. Grant Henderson, Georges Calas and Jonathan Stebbins give insight into the peculiar aspects of the atomic-scale structure of glasses and melts, including the major changes observed at high temperature and at high pressure. Harald Behrens and Fabrice Gaillard discuss the

FIGURE 3 A silicate melt emerging from an industrial furnace and being transformed into a bottle. PHOTO COURTESY OF SAINT-GOBAIN COMPANY

influence of volatiles on the properties of silicate melts. They show how the speciation of these volatiles affects their solubility, the rheology and redox state of magmas, and the stability of minerals. The parameters controlling the transport properties of magmas, mostly diffusion and rheology, are addressed in the article by Don Dingwell. He brings attention to the major experimental and theoretical advances in viscous behavior and diffusion, which give a new perspective on magma migration and volcano dynamics. Bruce Marsh discusses the dynamic aspects of magmatic systems, setting this question in a historical perspective. Field studies, including investigations on the fascinating Sudbury complex, provide the real-scale validation of laboratory experiments and outline pertinent parameters, such as marginal solidification fronts and magma ascent. The final contribution presents examples of properties of industrial and natural glasses. Laurence Galoisy emphasizes the role of transition elements in defining glass coloration and stability, and in defining the formation conditions of volcanic and impact glasses.

Silicate glasses and melts play a critical role in many geological and technological processes. From the molecules to the planetary scale, they constitute a broad though still largely unknown universe, in which the mineralogist, the geologist, and the materials scientist must often find original ways to solve the many questions that are still open. This issue of *Elements* shows the rapid progress that has been made recently. We hope it will encourage young scientists to enter this fascinating field!

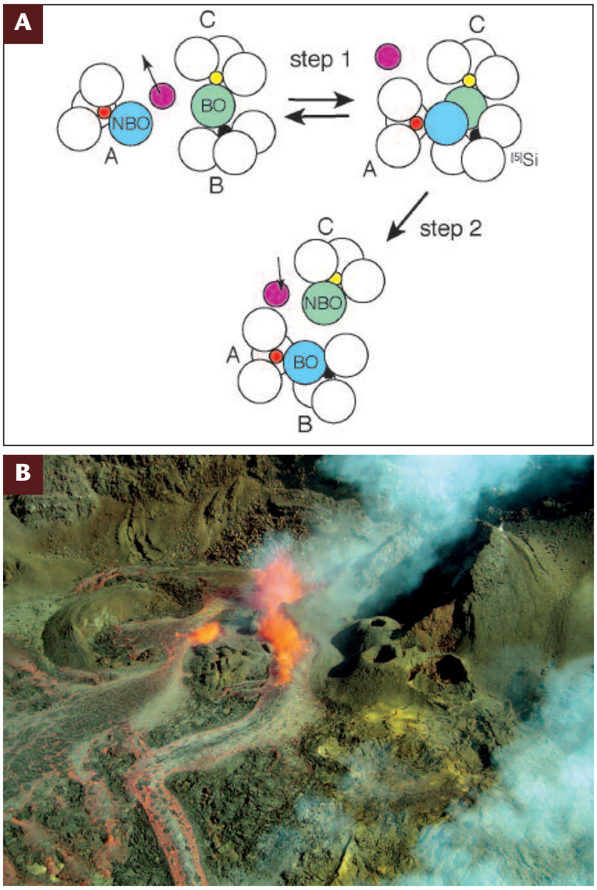

FIGURE 4 (**A**) A cartoon of a possible atomistic mechanism for viscous flow based on the presence of an intermediate 5-fold Si species. Large circles: oxygens; smallest circles: network forming cations; intermediate circles: network modifier cations. (**B**) Fluid lavas flowing during the October 4, 2005, eruption of the Piton de la Fournaise, Réunion Island. PHOTO COURTESY OF INSTITUT DE PHYSIQUE DU GLOBE DE PARIS

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We thank the authors of the articles presented in this issue, who give a synthetic and interdisciplinary view of the complex world of glasses and melts. Editors Pierrette Tremblay and Bruce Watson are thanked for their efforts in bringing this issue together. This is IPGP contribution.

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