Pressure Enhancement of Ion Mobilities in Liquid Silicates from Computer Simulation Studies to 800 Kilobars

Abstract. *Ion dynamics computer simulation methods show that for many liquid silicates, like silica itself, the component diffusion coefficients show anomalous pressure dependences. This implies that their viscosities have negative pressure dependences. Overall, there is an interesting degree of analogy between the fundamental binary solutions of geochemistry and the aqueous solutions of common experience; however, due to the stronger bonding in silicate systems, the anomalies are much more persistent. Diffusivity maxima occur at pressures of 200 to 300 kilobars and are correlated with a prevalence of fivefold coordination of silicon ions. The relevance of these findings to planetary dynamics and thermophysical modeling problems is briefly considered.*

A remarkable degree of similarity exists between water and liquid silica, the progenitors of the natural world's two most important classes of liquid solution. The thermodynamic and transport properties of these solutions are strongly dependent on the analogously anomalous characteristics of the pure solvents themselves. The foremost shared anomaly, discussed in an earlier report (*1*), is the existence of a density maximum, the temperature and sharpness of which depend strongly on the pressure under which it is observed.

A related shared anomaly is the increase in particle mobility that accompanies an increase in density under pressure. In water this phenomenon is well studied, and the fluidity in particular is known to exhibit a maximum value at about 1500 bars (150 MPa). In silica the parallel phenomenon is known only through the results of a molecular dynamics computer simulation study of oxygen and silicon diffusivities (*2*), although an experimental study of the closely analogous liquid GeO_2 has shown a dramatic increase in fluidity with increasing pressure to at least 10 kbar (*3*). Furthermore, several liquid silicate systems have shown the presence of similar anomalous effects (*4*).

In this report we explore this phenomenon in silicates to very high pressures, seeking to establish where a maximum value for the mobility occurs, to what structural features it is related, and under what circumstances it can be eliminated. Since laboratory experiments extending into the requisite temperature and pressure range are not feasible, we use the method of ion dynamics computer simulation, which was applied successfully in earlier studies of silicate and borate glasses by Soules (*5*) and Angell and co-workers (*1, 6*) and extended recently to the geochemically interesting cases of $MgSiO_3$ and Mg_2SiO_4 by Matsui and Kawamura (*7*).

The origin of the parallels in behavior of water and silica is almost certainly the circumstance that their lowest energy states are reached when the constituent particles are arranged in rather open network structures. In this respect the silicates are of special interest because there are many combinations of ions besides Si^{4+} and O^{2-} which yield the same open network structural characteristics; thus there may exist a potentially very large family of "anomalous" liquids. For instance, BeF_2, BPO_4, and $AlPO_4$, as well as the charge-compensated framework aluminosilicates (such as $NaAlSi_3O_8$, albite, and $CaAl_2Si_6O_{16}$, anorthite) that make up much of the mineral world, should behave like water and SiO_2. Although the high-pressure crystal phase jadeite, $NaAlSi_2O_6$, has Al^{3+} ions in sixfold coordination, its liquid state at 1 atm has a more expanded structure in which Al^{3+} is four-coordinated and the existence of a strongly anomalous pressure dependence of the viscosity has been demonstrated to 40 kbar at 1350°C by Kushiro (*4*). We therefore commenced our investigation by seeking to verify and extend Kushiro's observations on this substance. We then studied the consequences of breaking up the SiO_2 network with additions of oxide ion as Na_2O.

The ion dynamics calculations imitate nature by allowing each particle to respond, according to Newton's second law, to the unbalanced force exerted on it by all the other particles within a modest distance of it. The unbalanced forces are continuously reassessed so that a complete record of the energy and position, hence motion, of each particle is accumulated.

The only inputs to the calculation are pair potentials of very simple form for the various possible pairs of interacting ions in the system; the potentials consist only of Coulomb repulsion and attraction

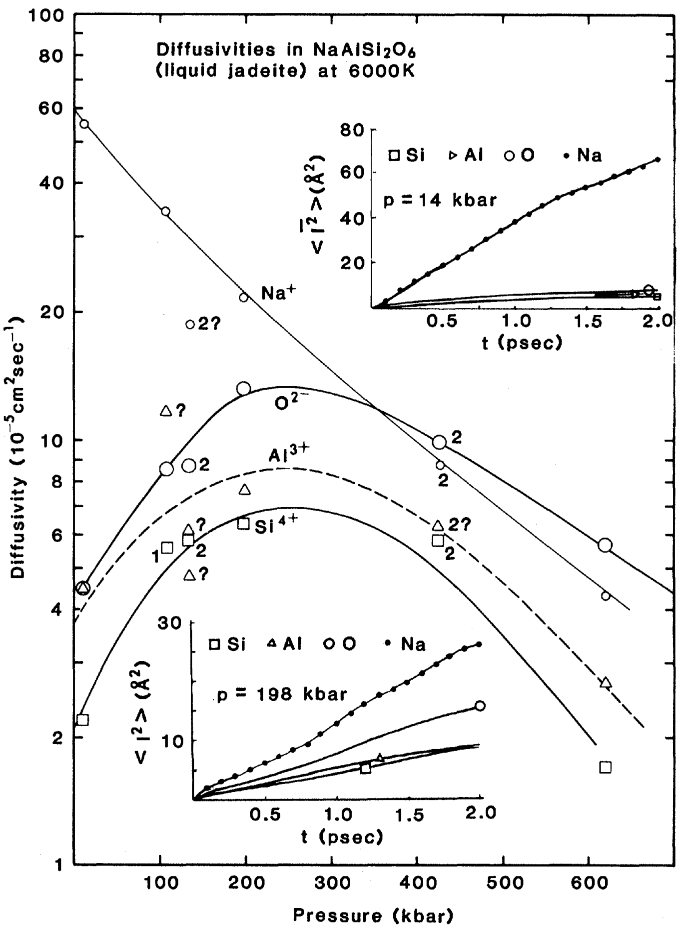

Fig. 1. Contrasting pressure dependences of diffusion coefficients of network (Si^{4+}, Al^{3+}, O^{2-}) and non-network (Na^+) components of liquid jadeite. Note maximum diffusivities for the former at 150 to 300 kbar. Discrepant results for Al^{3+} are indicated with question marks (Al^{3+} has the poorest statistics because of the combination of small number of ions in the sample and small mobility). Subscripts 1 and 2 refer to results obtained during the first and second cycles in pressure. The second cycle, commenced after expanding the system to zero pressure at the end of the first increasing-pressure series, was intended to test for reproducibility. (Insets) Mean square displacement versus time for ionic constituents of liquid jadeite at low and intermediate (maximum diffusivity) pressures.

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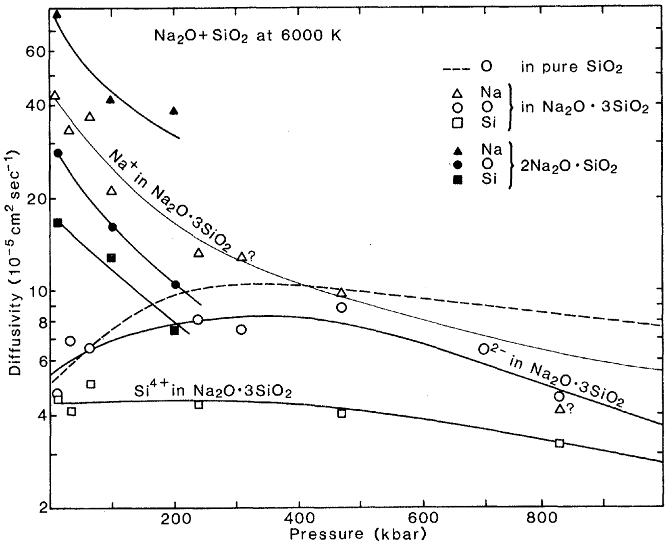

Fig. 2. Dependence on pressure of ionic diffusivities for polymerized and depolymerized compositions in the system SiO_2 + Na_2O. Note that for the depolymerized (orthosilicate) melt, the pressure coefficients of diffusivity are of normal sign for all species at all pressures.

terms and exponential repulsions. Due to the dominance of these two types of force in the present systems and the absence of an absolute or even a refined crystal data basis for the potential functions, there is little justification for use of more complex potentials. Details of the calculations, the periodic boundary conditions by which the undesirable effects of surfaces are avoided, the parameters in the potential functions we used, and various checks against experiments are all available in various literature sources (*1, 5, 6*).

The "experimental error" in the "data" can be considerable. In the first place it is necessary, starting from an arbitrary configuration of the particles of interest, to allow the system time to find its correct chemical structure. Basic coordination relations are established in very short periods of real time, but when there are different possible configurations that differ slightly in potential energy and require the surmounting of considerable configurational barriers for their sampling, a possibility of obtaining results for inappropriate structures exists. The basic criterion for successful equilibration in these calculations lies in the demonstration of absence of history dependence of the results. We tested this by carrying out the study in a pressure cycle, returning to the same high pressure more than once.

Even when structural equilibration has been assured, there remain errors due to the statistical nature of the processes being studied. Thus, the curves of mean square displacement versus time, from which the particle diffusivities are most conveniently assessed, will not be identically linear in two separate runs and will not have the same average slopes. Our practice has been to run our system at sufficiently high temperatures that structural relaxation occurs in a fraction of a picosecond (this requires diffusion coefficients of 5×10^{-5} cm^2 sec^{-1} or greater), then to run each new pressure temperature point for 3 psec, of which the first picosecond is discarded before the plot of mean square displacement versus time is constructed. For test cases we have continued the run for twice as long to reassure ourselves that we have sampled sufficient of the system's characteristic motions, but for the most part computing time limitations have led us to choose more data points at the expense of larger uncertainties.

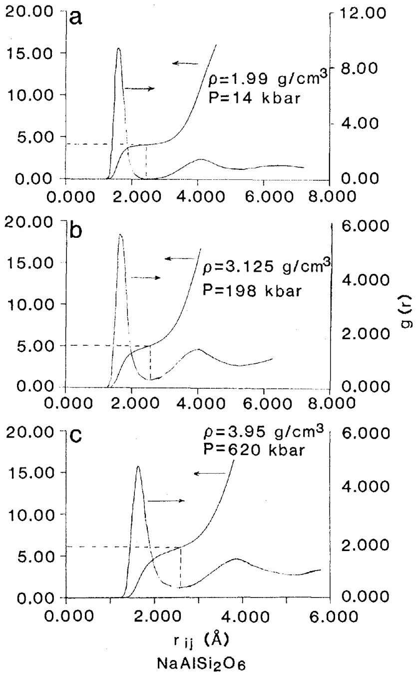

Fig. 3. Silicon-oxygen pair distribution functions and coordination numbers at 6000 K and three pressures spanning the range of this study. Note that the pressure which gives an average five-coordination of silicon by oxygen is that which produces the highest diffusivities for these ions.

The important diffusivity results are summarized in Figs. 1 and 2. Figure 1 shows that in liquid jadeite increasing the pressure increases the mobilities of all "network-forming" ions up to 150 to 300 kbar; beyond this range (which is necessarily uncertain in this work) the effect of pressure returns to normal. In the same range of 0 to 300 kbar, however, the alkali cations, which occupy network channel positions where they compensate the trivalent aluminum ions to maintain local electrical neutrality and network integrity at the same time, show a normal pressure dependence. We may assume that the mobilities of the network-forming constituents will determine the viscosity of the liquid, hence that the viscosity will decrease with increasing pressure up to about 250 kbar. It might be expected that the pressure at the viscosity minimum would be somewhat lower in the laboratory (and geochemically interesting) temperature range in which Kushiro (*4*) observed the viscosity of jadeite decreasing sharply with increasing pressure to 40 kbar, the limit of the experimental technique.

Given that the viscosity varies inversely with the network ion mobilities, we note that the Stokes-Einstein equation fails even qualitatively to predict the behavior of the alkali (or non-network) cation. A similar failure for a non-network cation in a related liquid (aluminosilicate) has been noted for the case of calcium diffusion in experiments by Watson (*8*). It seems safe to generalize this observation to all non-network components, and identify as its cause the closing up of the network channel structure with increasing pressure. This does not require, at least initially, that coordination changes occur, since considerable economy in packing can be obtained simply by distorting the tetrahedral network such as to decrease the average Si–O–Si or Si–O–Al bond angles.

At sufficiently high pressures, coordination numbers certainly change. Figure 3 shows a sequence of Si-O pair distribution functions and the related coordination number functions at three pressures spanning our range. It may be observed that the diffusivity maximum corresponds approximately to a prevalence of five-coordination of silicon by oxygen. This finding is consistent with Brawer's observation (*9*), in his study of the analogous BeF_2 and BeF_2 + alkali fluoride systems, that the five-coordinated beryllium cation was a center of unusual dynamic activity. Stereoscopic displays of the ionic arrangement and printouts of nearest neighbor instantaneous configurations both show that the five-coordination is very irregular.

Figure 2 shows how the anomalous pressure dependence of network ion diffusivities in the silicates can be removed by sufficient breakdown of the tetrahedral network structure. For clarity, we have omitted data points for the original SiO_2 system (which first showed the existence of anomalous pressure dependences of transport in such inorganic systems) (*2*). In the sodium trisilicate case, in which the network structure is only partly broken down, an anomalous pressure dependence of the silicon and oxygen mobilities remains, consistent with the observation of a negative pressure dependence of the viscosity in this system (*4*). The orthosilicate structure, on the other hand, shows the normal pressure dependence observed in ionic liquids (*2*). Results for the metasilicate composition are given elsewhere (*10*).

The outstanding difference between the network and the orthosilicate liquids is the volume that must be assigned to the system to produce a pressure of about zero. Particularly at the high temperatures of these calculations, the normal pressure density of the orthosilicate (and metasilicate) compositions is very low. This is consistent with extrapolations (*10*) to the temperatures of our study of precise density data obtained by Bockris *et al.* (*11*) at lower temperatures.

Network (or framework) compounds are the predominant materials of the earth's crust. It seems clear from these studies, supported by the direct experimental studies of viscosity (*4*), that all these framework minerals in the liquid state, and probably also in the defect crystal state, will show anomalous pressure dependences of the framework ion mobilities. This characteristic is of interest in relation to the problem of modeling planetary evolution and even that of interpreting creep-dependent crustal displacements during the current epoch of the earth's geological history. Most planetary bodies pass through stages in their evolution in which they are molten, and in which the interior temperature may be somewhat closer to that chosen for the present study than is the case with the earth at present. While we are not competent to pursue this matter in any depth, it seems that the interior viscosity of a molten SiO_2-rich planetary body would be much smaller than the viscosity at the surface, since it seems that, at least to pressures of 150 kbar, increasing pressure acts in the same way as increasing temperature to decrease the viscosity. Experience with viscous liquids shows that, in general, pressure effects become much more pronounced as temperature decreases; hence, increases of several orders of magnitude in fluidity and a zone of maximum fluidity deep within the molten body are possibilities which should be considered in discussions of the hydrodynamics and long-term evolution of planets. From studies of aqueous systems (*12*) it seems that the pressure at which the viscosity minimum would occur would move to lower values as the temperature decreases.

By contrast, in liquid silicates poor in SiO_2, such as the olivine-type (orthosilicate) compositions believed to constitute the earth's mantle, behavior qualitatively similar to that for Na_4SiO_4 in Fig. 2 must be expected. In this case pressure and temperature will act in opposite directions at all pressures, giving less interesting profiles of viscosity (or creep rate) versus depth.

It is unfortunate that the time scale for the study of creep in stable (unsuperheated) crystals is too long for fruitful simulation studies at this time. However, the fact that simulation "samples" have no free surfaces (thanks to the periodic boundary conditions used) makes the study of fast-creeping superheated solids no less feasible than the study of supercooled liquids. Qualitative features of superheated solid behavior, such as the sign of the pressure dependences of creep rates, would probably be relevant to stable-state behavior, and we believe such studies would represent a worthwhile extension of the present work.

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13. Supported by NSF grant DMR-8007053.

12 April 1982; revised 28 July 1982

Monoclonal Antibodies to Hypothalamic Growth Hormone–Releasing Factor with Picomoles of Antigen

Abstract. *Monoclonal antibodies specific for rat hypothalamic growth hormone–releasing factor (rGRF) have been produced by in vitro immunization of mouse spleen cells with less than 1 nanomole of rGRF in a partially purified preparation. Hybridoma supernatants were screened for anti-rGRF activity by use of a pituitary culture assay system that can detect growth hormone–releasing factor in the femtomole range. Such highly sensitive in vitro techniques permit the use of picomole quantities of an antigen in partially purified preparations for the isolation of monoclonal antibodies, which can in turn be used in biological studies and in immunochemical procedures for large-scale purification and isolation of that antigen.*

When specific high-affinity antibodies to a biologically active molecule are available, a variety of powerful techniques can be used to purify and characterize that molecule or study its physiological functions. A consistent problem, however, during the characterization of some biologically active molecules, such as neuropeptides present in brain tissue in amounts of only picomoles per gram, has been the difficulty of producing sufficient quantities of high-purity materials to be used as antigens to produce antibodies by standard in vivo immunization procedures. Although hypothalamic growth hormone–releasing factor is obtained in picomole amounts as a highly purified material, it has not been characterized yet, primarily because of its extremely low concentration (*1*) in the hypothalamus. We combined an in vitro immunization for hybridoma production (*2*) with a highly sensitive in vitro assay (*3*) to achieve the production of unlimited amounts of monoclonal antibodies to rat hypothalamic growth hormone–re-

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