The kinetic fragility of natural silicate melts

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Abstract
Newtonian viscosities of 19 multicomponent natural and synthetic silicate liquids, with variable contents of SiO_2 (41–79 wt%), Al_2O_3 (10–19 wt%), TiO_2 (0–3 wt%), FeO_{tot} (0–11 wt%); alkali oxides (5–17 wt%), alkaline-earth oxides (0–35 wt%), and minor oxides, obtained at ambient pressure using the high-temperature concentric cylinder, the low-temperature micropenetration, and the parallel plates techniques, have been analysed. For each silicate liquid, regression of the experimentally determined viscosities using the well known Vogel–Fulcher–Tammann (VFT) equation allowed the viscosity of all these silicates to be accurately described. The results of these fits, which provide the basis for the subsequent analysis here, permit qualitative and quantitative correlations to be made between the VFT adjustable parameters (A_{VFT}, B_{VFT}, and T_0).

The values of B_{VFT} and T_0, calibrated via the VFT equation, are highly correlated. Kinetic fragility appears to be correlated with the number of non-bridging oxygens per tetrahedrally coordinated cation (NBO/T). This is taken to infer that melt polymerization controls melt fragility in liquid silicates. Thus NBO/T might form an useful ingredient of a structure-based model of non-Arrhenian viscosity in multicomponent silicate melts.

1. Introduction

Future models for predicting the structural or rheological properties of silicate melts must find a means of partitioning the effects of composition across a system that shows varying degrees of non-Arrhenian temperature dependence [1].

Adequate understanding of the physical properties of silicate liquids plays a central role in the description of the system rheology during magmatic processes. In order to be useful over the volcanic evolution of magmatic systems, theories and empirical models of magma rheology must be sufficiently general to cope with temperature variations of over 1000 K from eruptive to solidification temperatures. Thus the deviation from Arrhenian behaviour—that is,

the 'fragility term'—plays a very significant role that accordingly needs to be described in an adequate, precise manner.

At present the description of the role played by the glass transition in silicate liquids is macroscopically relatively well constrained and predictable [2–5]. In contrast, little is known about the microscopic nature and mechanism of melt failure upon crossing the glass transition. Similarly, the physical meanings of the parameters currently being profitably employed in the description of the viscosity of magmatic melts are still under debate. The Vogel–Fulcher–Tammann (VFT) [6–8] temperature T_0, is, for example, generally considered to represent little more than a fit parameter useful for the description of the viscosity of a liquid. Correlations of T_0 with the Kauzmann temperature, T_K [9], have been described in the literature (e.g. [10]), but without a conclusive physical interpretation of this parameter.

The definition of a 'fragility term' (s.l.), which indicates, via the deviation from an Arrhenian behaviour, the kind of viscous response of a system to the applied forces, is still not unequivocally identified (e.g. [11–13]). Energy landscape (e.g. [14, 15]) and configurational entropy [16] theories correlate the fragility with the number of accessible basins of local potential energy minima or configurations available in the structure, respectively, with strong liquids having small values of these quantities. All these approaches have remained qualitative explanations to date. Thus, it appears likely at present that, at least in the short term, the algorithm for expanding the viscosity and its non-Arrhenian behaviour in terms of composition will probably derive from empirical study [1].

In a previous study, Russell and co-authors [1] have provided a numerical analysis of the nature and magnitude of correlations inherent in fitting a non-Arrhenian model (e.g. VFT function) to measurements of the melt viscosity from single sets of measurements. They pointed out that the non-linear character of the non-Arrhenian models forces strong numerical correlations between model parameters which may mask the effects of composition. They also showed, by using albite and diopside melts as representative of strong (nearly Arrhenian) and fragile (non-Arrhenian) melts, respectively, how the quality and the distribution of experimental data can affect covariances between model parameters. The present contribution constitutes a further step in that analysis, providing an approach to these problems and those related to the definition of the fragility by the investigation of the parameters constituting the VFT equation taken across 19 data-sets (not just a single one) representative of a wide range of compositions and a variety of sources [17–25].

2. Results and discussion

We approached the problem of defining the relationship between the fragility and some well known parameters by using Newtonian viscosity determinations performed in our group and previous studies from the literature. The viscosity data and the compositional details for the samples investigated are provided in [17–25]. The viscosities used here span a wide range of rheological behaviours, from strong to highly fragile, ranging over 6–7 orders of magnitude at a given temperature, and over a viscosity range from 10^{-1} to $10^{11.6}$ Pa s (figure 1). Viscosity data are accurately reproduced by using the VFT equation:

$$\log \eta = A_{VFT} + \frac{B_{VFT}}{(T - T_0)} \tag{1}$$

where A_{VFT}, B_{VFT}, and T_0 are adjustable parameters, termed the pre-exponential term, the pseudo-activation energy (related to the barrier of potential energy obstructing the structural rearrangement of the liquid), and the VFT temperature, respectively.

The values obtained for the VFT parameters are reported in table 1 for each of the liquids investigated.
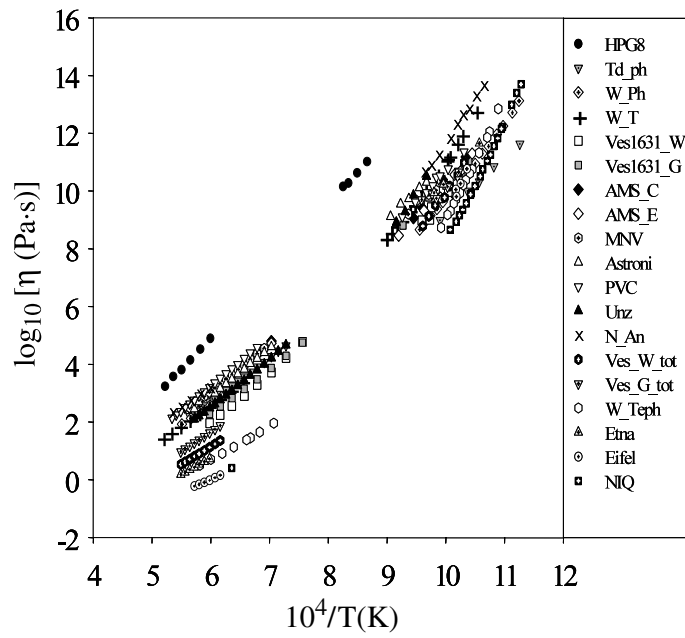
Figure 1. Dry viscosities (in log units (Pa s)) against the reciprocal of temperature. Also shown for comparison are results for natural and synthetic samples from previous studies [17–25].
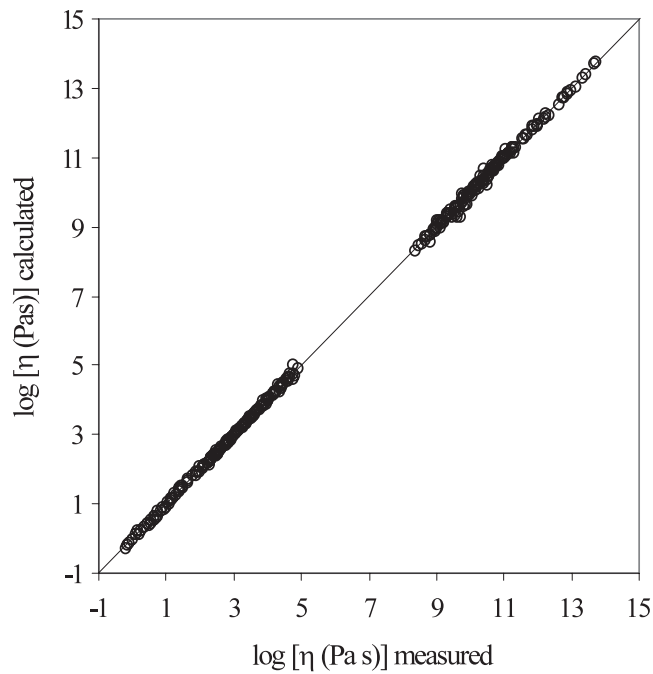

Figure 2. Comparison between the measured and the calculated data (equation (1)) for all the liquids investigated.
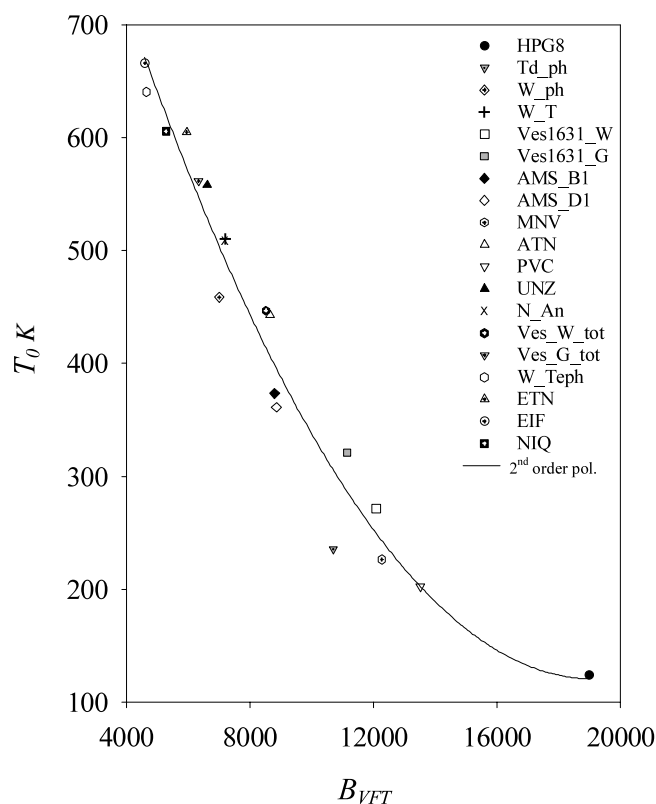
Figure 3. Calibrated Tammann–Vogel–Fulcher temperatures (T_0) versus the pseudo-activation energies (B_{VFT}) calibrated using equation (1). The curve represents the best-fit second-order polynomial which expresses the correlation between T_0 and B_{VFT}.

A comparison between the viscosity calculated using equation (1) and the measured viscosity is provided in figure 2 for each of the liquids investigated.

As shown in figure 3, the T_0- and B_{VFT}-values calculated over the 19 different sets of data appear to be highly correlated. T_0 increases when B_{VFT} decreases. This correlation would offer the possibility of reducing the number of fit parameters from three to two. At a first approximation, relatively basic liquids (those with low SiO_2 content), such as the basanite from Eifel (EIF) [18], the tephrite (W_Teph) [21], the synthetic foidite (NIQ) [21], and the basalt from Etna (ETN) [17], have higher VFT temperatures (T_0) and lower pseudo-activation energies B_{VFT}. In contrast, acidic melts (those with high SiO_2 content), such as the Povocao trachyte (PVC) [18] and the HPG8 haplogranite [23], have higher pseudo-activation energies and much lower T_0.

An important property that controls the fluid dynamic properties of magmatic systems is their ability to flow. A measure of the rapidity with which these properties change with temperature as they approach the glass transition temperature T_g is given by the fragility parameter. Fragility can be defined along with thermodynamic (thermodynamic fragility) or rheological (kinetic fragility) measurements (e.g. [31]).

On the basis of the rheological data analysed here, we compare two different definitions of fragility in the following—that is, the kinetic fragility F, defined as T_0/T_g, and the steepness index m (e.g. [31]).
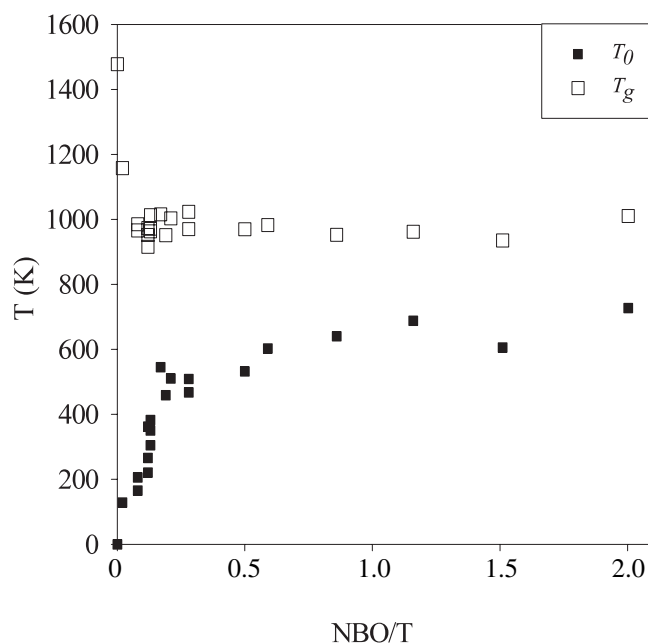
Figure 4. The relationships between the VFT temperature (T_0) and NBO/T, and the glass transition temperature (T_g) and NBO/T. $T_g = T_{11}$ indicates that T_g is defined as the temperature of the system where the viscosity is 10^{11} Pa s. T_0 increases with the addition of network modifiers. The two most polymerized liquids have high T_g. Melts with NBO/T ratios of >0.4–0.5 show a variation in T_g. The viscosimetric and calorimetric T_g are consistent.

We observed that there is a linear relationship between[1] F and T_0 for all the silicate liquids investigated (figure 5). This is due to the relatively small variation of the glass transition temperatures, calculated for each composition, that range over about 100° around the 1000 K value (figure 5). Exceptions are constituted by the two most polymerized liquids, HPG8 [24] and SiO_2 from [25] (included in the diagram as the extreme compositional limit), showing a significant deviation from the trend with much higher T_g-values. In contrast, the T_0-values vary widely. Diopside (Di) [27] has also been included in figures 4 and 6 as an extreme case of depolymerization.

For silicate liquids the degree of polymerization can be defined by means of the main SiO_4^{4-} tetrahedral units. The oxygen connecting two of these units is called a 'bridging oxygen' (BO). According to Mysen [33], the 'degree of polymerization' in these materials is proportional to the number of BO per cation that have the potential to be in tetrahedral coordination T (more frequently represented by Si^{4+}, Al^{3+}, Fe^{3+}, and Ti^{4+}). More commonly used is the term non-bridging oxygen per tetrahedrally coordinated cation, NBO/T, where NBO is an oxygen that bridges from a tetrahedron to a non-tetrahedral polyhedron. Addition of other oxides to silica (assumed as the base composition for all silicates) results in the formation of NBO [33].

Kinetic fragilities F, m and VFT temperatures T_0 increase as the structure becomes increasingly depolymerized (i.e. as NBO/T increases) (figures 5, 6). Consequently low values of the kinetic fragility correspond to high B_{VFT}-values and low T_0-values. Note that T_0-values

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[1] Along with what was observed from the comparison between the calorimetrically determined glass transition temperatures and the temperature at which the viscosity is calculated to be 10^{11} Pa s (figure 4) [32], T_g is here assumed as the temperature at which the viscosity is 10^{11} (table 1).
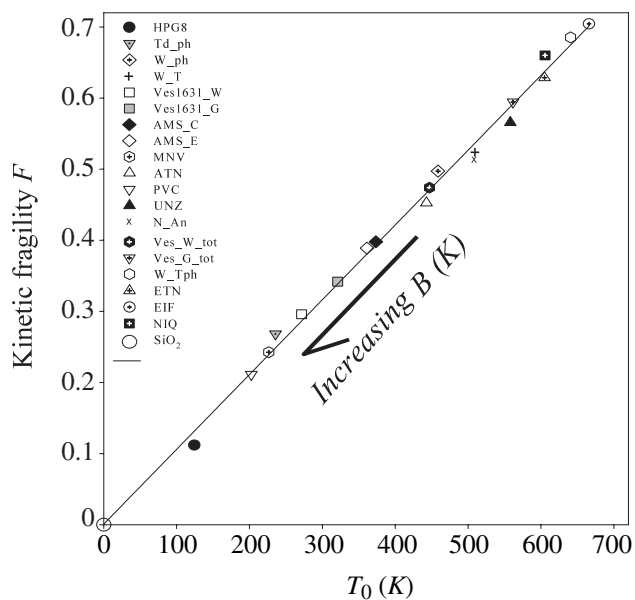
Figure 5. The relationship between fragility (F) and the VFT temperature (T_0) for all the samples investigated. SiO_2 is also included for comparison. Pseudo-activation energies increase with decreasing T_0 (as indicated by the arrow). The line is a best-fit equation through the data.

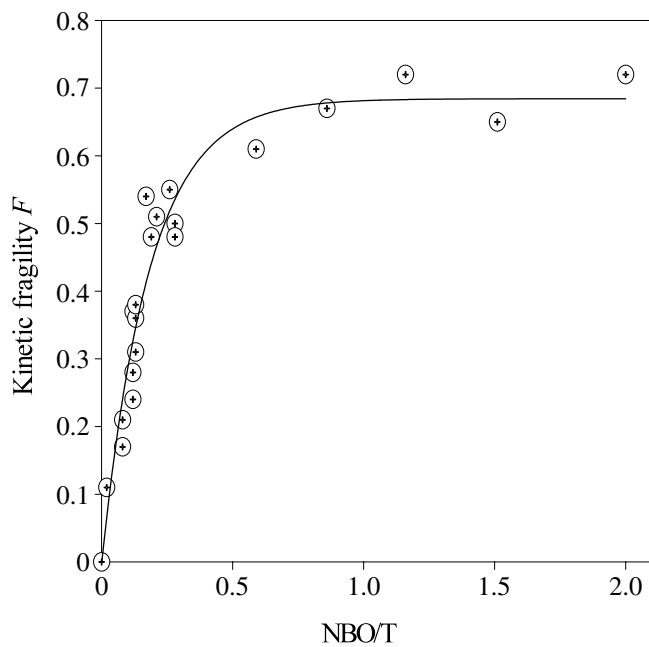**Figure 6.** The relationship between the fragilities (F) and the NBO/T ratios of the samples investigated. The curve in the figure was calculated using equation (2).
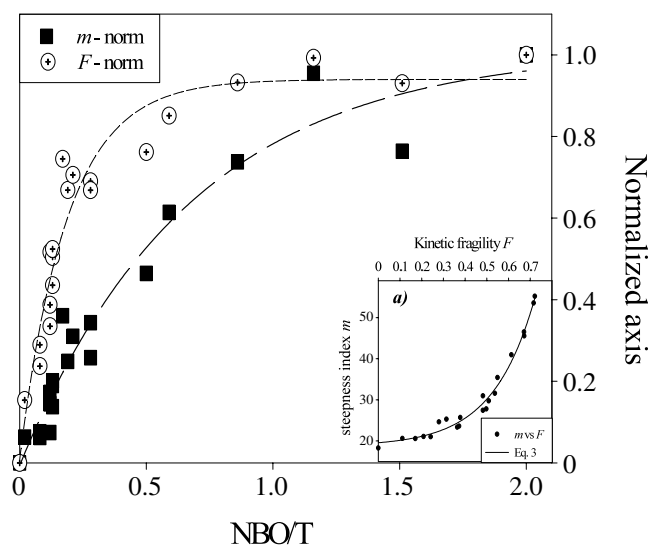
Figure 7. Comparison between F and the steepness index m versus NBO/T. Crossed circles and full squares correspond to the normalized F- and m-values derived from equation (1) (e.g. [10, 13]). In particular, the fine and the thick dashed curves correspond to regressions obtained by fitting the normalized F- and m-values versus NBO/T, according to an expression like equation (2). Inset (a) shows the high correlation between the two different expressions for the fragility for silicate melts.

varying from 0 to about 700 K correspond to F-values between 0 and around 0.7. There is a sharp increase in fragility with increasing NBO/T ratios up to NBO/T = 0.4–0.5. For the most depolymerized liquids (NIQ, ETN, EIF, W_Teph, Di), the fragility assumes an almost constant value (0.6–0.7). Such high fragility values are similar to those shown by molecular glass-formers, such as orthoterphenyl (OTP) [34] which is one of the most fragile organic liquids.

An empirical equation (represented by a solid curve in figure 6) enables F to be predicted, for all the liquids investigated, as a function of the degree of polymerization:

$$F = -0.0044 + 0.6887[1 - \exp(-5.4767\text{NBO/T})]. \tag{2}$$

This equation reproduces F within a maximum residual error of 0.13 for silicate liquids ranging from very strong to very fragile (see table 1). Calculations using equation (2) are more accurate for fragile than for strong liquids (table 1).

Figure 7 reports the comparison between F- and m-normalized patterns versus NBO/T. This figure clearly displays that F correlates with[2] NBO/T better than m.

All these observations suggest that the experimentally determined trends can be reconciled with the fragility linked to a chemical parameter serving as a proxy for the mean polymerization.

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[2] The solid curve in inset (a) represents the best-fit equation that correlates the two fragility terms:

$$m = 18.7026 + 0.8599\exp(5.1820F). \tag{3}$$

By using equation (3), steepness index values within a maximum relative error of about 7% can be recalculated starting from the F-values.

Table 1. The pre-exponential factors (A_{VFT}), pseudo-activation energies (B_{VFT}), and VFT temperature values (T_0) obtained by fitting the experimental determinations via equation (1). Column 5 reports the glass transition temperatures (T_{11}) calculated as the temperature at which the viscosity is 10^{11} Pa s. The fragilities F of the various samples are defined as the ratios T_0/T_g, whereas the F_{calc} are the fragilities calculated according to equation (2) as a function of NBO/T.

Sample	A_{VFT} (Pa s)	B_{VFT} (K)	T_0 (K)	$T_g = T_{11}$ (K)	F	F_{calc}, equation (2)
SiO_2[a]	−7.26	26 984	0	1477.60	0.00	—
HPG8[b]	−7.32	18 859	128.39	1157.74	0.11	0.07
Td_ph[c]	−4.94	11 069	220.81	915.31	0.24	0.33
W_ph[d]	−3.22	7 009	458.59	951.40	0.48	0.44
W_T[d]	−3.61	7 201	510.12	1002.98	0.51	0.47
Ves_W[e]	−6.76	12 183	265.80	951.80	0.28	0.33
Ves_G[e]	−6.34	11 559	304.77	971.33	0.31	0.35
AMS_B1[e]	−3.82	9 056	362.22	973.22	0.37	0.33
AMS_D1[e]	−3.86	9 108	350.20	963.15	0.36	0.35
MNV[c]	−6.05	13 654	165.02	965.91	0.17	0.24
ATN[c]	−4.99	10 078	382.53	1012.70	0.38	0.35
PVC[c]	−5.68	13 004	205.45	985.01	0.21	0.24
UNZ[c]	−3.63	6 879	545.14	1015.42	0.54	0.41
N_an[f]	−2.97	7 184	508.67	1022.93	0.50	0.54
VesGt	−4.98	6 987	531.99	969.35	0.55	0.52
VesWt	−5.05	8 070	467.16	969.79	0.48	0.54
W_Tph[g]	−3.93	4 663	639.99	952.39	0.67	0.68
ETN[c]	−4.84	6 019	602.38	982.35	0.61	0.66
EIF[c]	−4.24	4 171	687.91	961.56	0.72	0.68
NIQ[g]	−5.06	5 289	605.55	934.94	0.65	0.68
Di[h]	−4.42	4 351	728.15	1011.14	0.72	0.68

[a] Regression parameters are obtained using data from [26].
[b] Regression parameters are obtained using data from [23].
[c] Regression parameters are obtained using data from [18].
[d] Regression parameters are obtained using data from [22].
[e] Regression parameters are obtained using data from [20].
[f] Regression parameters are obtained using data from [24].
[g] Regression parameters are obtained using data from [21].
[h] Regression parameters are obtained using data from [27–30].

3. Conclusions

The dependence of T_g, T_0, F, and m on composition, for all the silicate liquids investigated, are shown in figures 5–7. An empirical equation, equation (2), which allows the kinetic fragility of silicate melts to be calculated in terms of the compositional (structure-related) parameter NBO/T is provided. This parameter is supposed, to at first approximation, to represent the atomic distribution present in the structure [33].

A comparison of F and the steepness index m [11] with NBO/T shows that these are both highly correlated (figure 7 and equation (3)) and suggests that, for silicate melts, the fragility term can indeed be correlated with the bulk atomic distribution. F rather than m provides accurate relationships with NBO/T.

The addition of generic network-modifying elements (expressed by increasing of the NBO/T ratio) has an interesting effect. Initial addition of such elements to a fully polymerized melt (e.g. SiO_2, NBO/T $= 0$) results in a sharp increase in F (figure 6). However, at NBO/T values above 0.4–0.5, further addition of network modifier has little or no effect on the fragility. This effect has to be interpreted as a variation in the distribution and size of the

configurational rearrangements [16] and rheological regimes of the silicate liquids due to the addition of structure modifier elements. The size of these rearrangements does not seem to vary significantly after a certain amount of modifier has been added to the initial base composition (SiO_2). A high mobility of modifying cations within the structure is derived.

This point of view may be consistent with hypotheses [35–38] that see silicate melts as having a disordered structure crossed by percolation channels. We suggest that work on complex dynamic simulations of multicomponent natural silicates as well as measurements of fast diffusivity should be focused on testing these hypotheses.

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