Abstract

Combining new measurements of thermal diffusivity ($D$) and viscosity ($\eta$) of 13 silica-rich glasses and their melts with previous data reveals specific effects of Al, Ca, and Fe cations on heat and mass transport for diverse glasses and melts. We investigated rhyolites, tektites, leucogranite, haplogranite, and chemically complex commercial glasses. Highly polymerized samples, with high Al but low Ca contents, yield high values for $\eta$, $D$, and glass transition temperatures ($T_{g,12}$), whereas less polymerized samples with high Ca but low Al contents, have
low $\eta$, D, and $T_{g,12}$. Upon crossing the glass transition, $D$ decreases substantially, to $\sim 0.35$ mm$^2$s$^{-1}$ for Ca-rich melts, but $D$ decreases only weakly, to $\sim 0.52$ mm$^2$s$^{-1}$ for Al-rich melts. The magnitude of the decrease in $D$ at $T_{g,12}$ correlates with the melt fragility, and also to the configurational heat capacity. High Ca contents result in low $D$ for glasses and melts, whether or not Al is present. At high $T$, $\partial D/\partial T$ is positive for glasses and melts containing Fe$^{2+}$, which we attribute to diffusive radiative transfer involving electronic-vibronic coupling. Thermal conductivity of all glasses increases with $T$, flattening out as the transition is approached. For melts with $\geq 1$ wt.% FeO$_{total}$, $\partial k/\partial T$ is positive. We predict that upon melting, I-type arc granite liquids should have lower thermal diffusivity than calcium-poor A- or S-types, and calc-alkaline basalts will have lower $D$ than tholeiitic basalts, such that $D$ of granitic melts is $\sim 0.2$ mm$^2$s$^{-2}$ higher than basaltic. Ferrous iron enhancing heat transport could alter the predicted order at higher temperatures.

Keywords, laser-flash analysis, high-temperature, thermal diffusivity, viscosity, hydration, impurities, glass, melt

INTRODUCTION

Transport properties of rocks and magmas strongly influence igneous processes (e.g., Nabelek et al. 2012). Mass transport of a melt is described by viscosity ($\eta$), for which several predictive models exist as functions of temperature and composition (e.g., Hui and Zhang 2007; Giordano et al. 2008). Heat transport is described by thermal conductivity ($k$). Direct measurements of $k$ of melt using contact methods are not reliable, because at the high temperatures ($T$) required, ballistic radiative transfer gains, exceed the lattice contribution (e.g., Hofmeister et al. 2007; 2009). Ballistic (direct or boundary-to-boundary) radiative transfer,
which goes roughly as $T^3$, is not a material property and is due to light passing essentially
unattenuated through the sample. This ballistic radiative transfer does not occur in geological
settings, but over the small length-scales encountered in the laboratory it occurs at all
temperatures, even cryogenic (e.g., Hofmeister, 2010; Hofmeister and Whittington 2012).

Thermal diffusivity ($D$) can be measured a few hundred K above the glass transition
using laser-flash analysis (LFA), thereby providing information on the liquid state. The contact-
free LFA technique (Parker et al. 1961) lacks systematic errors associated with conventional
methods, such as thermal losses at interfaces of ~10% per contact. Furthermore, ballistic
radiative transfer gains are removed after Diegiovanni et al. (1994) and Mehling et al. (1998),
making the LFA technique essential for measuring thermally insulating, but highly transparent,
glasses and melts with a high degree of accuracy (±2%). Combining our data with heat capacity
$(C_P)$ and density ($\rho$) data, which are generally available or can be estimated with reasonable
accuracy (e.g. Richet 1987; Lange 1997), therefore constrains thermal conductivity ($k$) associated
with vibrational modes, needed for thermal models of igneous processes,

$$k_{\text{lat}} = \rho C_P D.$$  \hfill (1)

Previously, we focused on simple glass compositions corresponding to the stoichiometry
of crustal minerals, quartz (SiO$_2$); alkali feldspar (XAlSi$_3$O$_8$ where X = Li, K, Na), anorthite
(CaAl$_2$Si$_2$O$_8$), and clinopyroxene (XYSi$_2$O$_6$ where XY = CaMg, LiAl, NaAl) (Pertermann et al.
(Romine et al. 2012) showed that minor amounts of crystals significantly increase thermal
diffusivity, due to their $D$-values being much larger than $D$ of the glass matrix. In the absence of
microcrystals, mass and heat transport properties are linked to chemical composition such that a
dichotomy exists between properties of mafic and felsic liquids, with the latter having higher viscosity and higher thermal diffusivity (Hofmeister et al. 2009).

To probe the effects of specific cations on thermal diffusivity, and to test whether the observed correlation of mass and heat transport properties holds for all high-silica chemical compositions, we examined diverse types of samples: natural glasses, laboratory synthetics and various commercial glasses, antique and modern. The 13 glasses selected have high silica contents (71-80 wt.% SiO₂), but variable quantities of other cations (Al₂O₃, FeO, MgO, CaO, Na₂O, K₂O). We present $D$ vs. $T$ for four highly polymerized Al-rich samples and five less polymerized Na- and Ca-rich samples, and compare these data to results for chemically similar remelted rhyolites of Romine et al. (2012), which lack crystallites. Our results above the glass transition provide reliable temperature derivatives for $D$ of silicate melts, and further suggest that lattice thermal heat transport involves a form of radiative transport in the infrared, in addition to phonon scattering. We also include viscosity measurements of the molten state for compositions not heretofore investigated, which substantiate our previous demonstration that mass and heat transport properties are linked, and confirm that a dichotomy exists between transport properties of felsic and mafic melts. The new results imply differences in transport properties between granitic melts of different chemical types, and by extension also for basaltic melts of different types.

EXPERIMENTAL METHODS
Sample compositions and synthesis procedures

Our samples fall into two groups. One group includes two tektites, remelted leucogranite and rhyolites, and a synthetic haplogranite, which all have high Al contents and low abundances of other cations. The other group consists of antique and modern commercial glasses with high Na and Ca, but low Al contents. Antiques are typically bubbly and often inhomogeneous due to starting materials being more variable and manufacturing processes being less controlled. Within each of these groups lesser variations exist in other cations, e.g., Fe, Mg and K (Table 1).

Moldavite is especially SiO₂-rich (>80 wt.%) whereas indochinite contains 5 wt % total FeO. Remelted leucogranite from Harney Peak in the Black Hills, SD is described by Whittington et al. (2009a). For obsidian from Mono Craters, California see Romine et al. (2012). One of the rhyolite remelts was contaminated by the alumina crucible, providing a composition with an Al/Si ratio like that of indochinite, but with low Fe. We also prepared a synthetic haplogranite (corresponding to the 2 kbar H₂O-saturated minimum melt composition in the NaAlSi₃O₈-KAlSi₃O₈-SiO₂ ternary system) by grinding appropriate combinations of SiO₂, Al₂O₃, Na₂CO₃ and K₂CO₃ powders under acetone, then heating slowly in a platinum crucible to 1650°C, driving off CO₂. Mass losses were consistent with full decarbonation. The liquid was quenched to glass by cooling in air, then ground under acetone, and fused again. A third fusion over 72 hours at 1650°C allowed air bubbles to escape and ensured homogeneity.

Sample preparation

For parallel plate viscometry, cylindrical samples were cored from glass lumps using a diamond core drill, avoiding visible bubbles. The cylinders were cut to lengths of 5 to 10 mm
using a diamond wafer saw, polished on successively finer grit papers, and parallel faces were verified using a micrometer. For LFA, sections were sawed and ground into disks of ~12 mm diameter with 0.5 to 1.1 mm thicknesses and nearly parallel surfaces, and sand-blasted with 50–150 µm alumina grit. For spectroscopic measurements, double-polished sections were prepared. Polished chips were used in electron microprobe analysis.

Chemical analyses

Samples were characterized by wavelength dispersive analysis (WDS) and standard procedures on the JEOL-733 and JXA-8200 electron microprobes at Washington University, using “Probe for Windows” for data reduction (see http://www.probesoftware.com/). The measured data were corrected with CITZAF after Armstrong (1995). Oxide and silicate standards were used for calibration (e.g., Amelia albite for Na, Si; microcline for K; Gates wollastonite for Ca; Alaska Anorthite for Al; synthetic fayalite for Fe; synthetic forsterite for Mg; synthetic TiO2 for Ti; synthetic Mn-olivine for Mn; synthetic Cr2O3 for Cr).

Near-IR to ultraviolet spectroscopy and analysis of water contents

Our evacuated Bomem DA3.02 Fourier transform interferometer has an SiC source, a InSb detector, a CaF2 beamsplitter. About 2000 scans were collected at room temperature from ~1800 to ~9000 cm⁻¹ at a resolution of 2 cm⁻¹. Unpolarized spectra from 9090 to 52630 cm⁻¹ were collected using a double-beam Shimadzu UV-1800 with 1 nm resolution. Absorption coefficients (A) were calculated from thickness (L) measured using a digital micrometer from,

\[ AL = -\log(I_{\text{trans}}/I_0) \]  

(2)

Water content of glass was determined from,
\[ H_2O \text{ wt } \% = 1802 \frac{a}{(\rho \varepsilon L)}, \quad (3) \]

where \( \rho \) has units of gL\(^{-1}\) (see Table 2) and thickness \( L \) has units of cm. We used \( \varepsilon = \)

75 L mol\(^{-1}\)cm\(^{-2}\) for the \( \sim 3500 \) cm\(^{-1}\) peak from Okumura et al. (2003) because their rhyolite compositions are similar to our Al-rich samples. Uncertainties are \( \sim 5\% \), mainly from that of \( \varepsilon \).

We report the total water content as ppm OH\(^{-}\), because water is expected to be dissolved mostly as hydroxyl at the low concentrations observed (Stolper 1982), although small amounts of H\(_2\)O molecules may be present.

For Na-Ca glasses, \( \varepsilon = 42 \) L mol\(^{-1}\)cm\(^{-2}\) is accepted for the high-\( \nu \) peak (Shelby, 2005). We used this value in Eq. 3 for the additional O-H stretch near 2900 cm\(^{-1}\) (Fig. 1) and summed the results. Relative concentrations are accurate, but absolute concentrations could vary by \( \sim 30\% \) for the Na-Ca glasses, due to \( \varepsilon \) being estimated for the low-\( \nu \) peak (Table 2). However, given that hydroxyl only lowers \( D \) by 0.006 mm\(^2\)s\(^{-1}\) per wt % H\(_2\)O (Hofmeister et al., 2006) and that these samples have so little water that an effect on \( D \)-values would be difficult to ascertain, we did not attempt to verify water contents by another method.

**Density determinations**

Glass density was obtained before and after viscosity measurements using the Archimedean method, with ethanol as the immersion liquid. Repeat measurements indicate precision is \( \pm 2 \) kg m\(^{-3}\). A small initial bubble fraction (<0.2 volume %) present in some samples should not significantly impact viscosity measurements.
Viscosity measurements

Viscosity was measured using a Theta Instruments Rheotronic III parallel plate viscometer, with a constant uniaxial load of 1500 g, and a maximum temperature of 1000°C. Viscosity is calculated from the measured longitudinal strain rate, known load and calculated instantaneous surface area, assuming perfect slip between sample and plates. Relatively low finite strains were used (≤ 20%); samples remained cylindrical after measurement. Temperatures in this study ranged from 520 to 988°C; viscosity ranged from $3.1 \times 10^8$ to $7.9 \times 10^{13}$ Pa s. The accuracy and precision of the measurements are ±0.06 log units, confirmed by repeat measurements on multiple cores. For experimental protocol and instrument calibration see Whittington et al. (2009b). For the rhyolites, viscosity was also measured at superliquidus conditions using a Theta Instruments Rheotronic II 1600C Rotating Viscometer, equipped with a Brookfield HBDV-III Ultra measuring head, which can measure over the range 1 to $10^5$ Pa s with accuracy and precision of ±0.03 log units, based on repeat measurements of NIST standard glasses. For experimental protocols and calibration see Getson and Whittington (2007).

Thermal diffusivity measurements

Our LFA 427 apparatus is manufactured by Netzsch Gerätebau, Germany. Specimens are held in a furnace in an Ar gas atmosphere using graphite holders. The temperature dependence of $D$ is obtained by varying furnace temperature, which is measured to within ~1°C using calibrated W-Re thermocouples. A pulse with ~ 0.5 ms width from a 400 W Nd-GGG laser heats the sample from below, providing a difference of ~<4°C across the sample. As heat diffuses from the bottom to the top of the sample, emissions upward are recorded as a function of time with an
InSb detector. Graphite coatings on the sample serve to block laser light, enhance absorption of the laser pulse and sample emissions, and buffer oxygen fugacity at high temperatures to C-CO. Some samples (as noted) were sputter coated with Pt prior to graphite coating, to further block unwanted direct (ballistic) light transfer through the sample. Data were obtained at 50-100 °C intervals with several acquisitions at each temperature, and processed using the algorithm of Mehling et al. (1998) to extract thermal diffusivity from the time-dependent emissions. This model accounts for radiative surface losses to the surroundings and spurious radiative transfer through the sample between the top and bottom graphite coats, and allows for absorbance being frequency dependent, although the detailed values of optical properties are not needed. The measured shape of the laser pulse is accounted for (Blumm and Opfermann 2002). Thermal diffusivity is accurate to 2%, verified against opaque reference materials.

CHEMICAL COMPOSITIONS, FE SPECIATION, AND WATER CONTENTS

All investigated samples have high silica contents, spanning the range 71-80 wt % (Table 2). Granitic glasses and tektites have high Al$_2$O$_3$ (10-14 wt %) and moderate K$_2$O (2.5-4.6 wt %) whereas commercial glasses have high CaO (7-14 wt %) and high Na$_2$O (12-16 wt %). A few other cations are significant, the “1960” and modern Na-Ca glasses contain moderate MgO (up to 4.6 wt%), and the indochinite contains 4.8 wt % FeO. Laboratory synthetics inherited some trace impurities from the starting materials. The chemical composition of our moldavite is consistent with that of 93 samples from the main strewn field (Bouška 1998) and with those from the stated location (Philpotts and Pinson 1966). Our indochinite is most similar to the normal
australites, but has slightly lower Ca, Na and Mg. This difference is insignificant because few samples were previously analyzed (Chapman and Scheiber 1969; Koberl 1986).

To make comparisons with our previously examined samples with feldspathic stoichiometry, Table 1 provides “formulae” based on eight O atoms. Polymerization is often quantified by the nominal ratio of non-bridging oxygens to tetrahedrally-coordinated cations (NBO/T). In Table 2, NBO/T is calculated assuming that all Si, Ti, Al and Cr are network-forming tetrahedral cations and all other cations either play a charge-balancing role for tetrahedral Al and Cr, or are network-modifying cations that result in some non-bridging oxygens. Although unlikely to be strictly correct, these assumptions provide a useful first-order assessment of the state of polymerization of the glass structures. For most samples, Fe contents are low and are unimportant to our evaluation. The tektites and leucogranites with high Fe mostly have Fe$^{2+}$ (see spectra below) and thus are represented correctly in our NBO/T calculation. Antique glasses have high NBO/T values in the range 0.63-0.79, which are more typically associated with basalts and mafic melts, whereas Al-rich granites and rhyolites have low NBO/T below 0.02, and the tektites have NBO/T = 0.07.

Infrared spectra for high Al glasses prior to heating have a broad, asymmetric band near 3550 cm$^{-1}$ (e.g. indochinite, Fig. 1), as do rhyolites of Okamura et al. (2003), whose calibration we used to quantify hydration. The profile indicates hydroxyl (OH$^-\$). Water contents are low and decreased upon heating during LFA (Table 2). Water contents of our impact melts agree with previous determinations of 70 -130 ppm for moldavites (Luft 1983) and of 20-190 ppm H$_2$O in indochinites and australites (Gilchrist et al. 1969). Water contents are too low to observe overtone-combination bands at higher frequency (Fig. 2a).
Low Al (high Ca) glasses have a second broad peak near 2900 cm\(^{-1}\) (e.g., 1926, Fig. 1). The position indicates hydrogen bonding associated with nearby O\(^{2-}\) atoms (e.g., Rossman 1988a). If scattering baselines are accounted for, the two peaks decrease together with heating. Because hydroxyl contents of the glasses are similarly low, trends in thermal diffusivity are attributed to variations in cations other than H.

Visible spectra (Fig. 2) show d-d electronic transitions of iron, assigned by comparison to mineral spectra of Rossman (1988b). Bands for octahedrally coordinated Fe\(^{2+}\) are present at >0.1 wt % FeO, and in the antiques with lower FeO contents, but not in modern glass or haplogranite, which have much weaker UV tails, consistent with the absence of Fe\(^{2+}\) that interacts with existing Fe\(^{3+}\) (as observed for orthopyroxenes, Hofmeister 2012). The position of the main Fe\(^{2+}\) band shifts from 8930 cm\(^{-1}\) in the Al-rich glasses to 10000 cm\(^{-1}\) in the Na-Ca glasses. Sharp bands for tetrahedrally coordinated Fe\(^{3+}\) occur at 22833, 23780, and 26260 cm\(^{-1}\) for Na-Ca glasses, and at slightly higher positions for haplogranite. For leucogranite and rhyolite with higher FeO (1.0 wt %), these Fe\(^{3+}\) transitions are at similar positions but are broader. We conclude that Fe\(^{3+}\) bands in both tektites are too broad to be resolved as shoulders on their strong UV tail. For the four Al-rich glasses with >1 wt % FeO, an additional broad band exists near 18460 cm\(^{-1}\). We assign this to intervalence charge transfer (IVCT) due to its spectral profile and position, and evidence for both charge states of Fe. In the moldavite the broad band is not resolvable but is the cause of high absorbance in the visible (Fig. 2). Indochinite spectra are like moldavite, but more intense (not shown). To locally balance charge, Fe\(^{3+}\) is likely preferentially located adjacent to Fe\(^{2+}\). This conclusion is supported by comparing the strength of the Fe\(^{2+}\) absorption in Fig. 2a to the total FeO content. Relative band strengths for 1895 and leucogranite are proportional to their FeO contents, but the band for moldavite is ~50% stronger and that of
indochinite is ~100% stronger, compared to low Fe glasses. Band enhancement connected with IVCT is well-known (Rossman 1988b). Rhyolite spectra are similar to the leucogranite, but have slightly stronger IVCT, attributed to specific site locations. Similarly, disproportionately large band strengths for Fe$^{3+}$ in 1960 compared to the other low Fe glasses are attributed to interactions without charge transfer, as observed in minerals (e.g., Rossman 1988b).

RESULTS ON TRANSPORT PROPERTIES

Viscosity

Near the glass transition, viscosity is close to a linear function of inverse temperature for all samples, although the antique liquids have lower viscosity and steeper slopes than the tektites and granites (Fig. 3; Table 3). Both viscosity and the viscometric glass transition temperature, taken to be the temperature of the 10$^{12}$ Pa s isokom ($T_{g,12}$), decrease with decreasing melt polymerization from granites to tektites to antiques (Table 4). A decrease in $T_{g,12}$, and in viscosity at any given temperature, accompanies increasing Al/Si ratio from haplogranite to leucogranite, and from moldavite to indochinite, whereas decreasing $T_{g,12}$ correlates with increasing Na/Ca in the commercial specimens.

Datasets were fitted with the Tamman-Vogel-Fulcher (TVF) equation,

$$\log \eta = A + B/(T-C)$$  \hspace{1cm} (4)

where A, B and C are adjustable parameters. Best-fit values are given in Table 4. It is generally accepted that all silicate melts tend towards a common value of about 10$^{-4.5}$ Pa s at very high temperatures (Russell et al. 2003), so the antique liquids, which have a relatively low glass transition temperature but also a steep slope on Figure 3, must show pronounced non-Arrhenian
behavior at higher temperatures than investigated here. Although the best fits for many of our samples return an A value in the range -4 to -5, we did not force all the fits to a common value. Given the large number of viscosity data for each sample, all three TVF parameters are tightly constrained, allowing extrapolation of viscosity with a high degree of confidence up to the highest temperatures at which samples were analyzed by LFA, which is useful in interpreting changes in D observed at high temperatures.

One way to quantify the degree of non-Arrhenian behavior, or “fragility”, is to calculate the gradient of the viscosity curve at the glass transition temperature on a reduced temperature scale (Plazek and Ngai 1991); see Table 4. Melt fragility is directly related to configurational heat capacity, $C_P^{conf}$, which is the difference between $C_P$ of the glass at $T_{12}$ and of the melt (Richet et al. 1986). From the temperature dependence of relaxation times in viscous liquids (Adam and Gibbs 1965), the viscosity of a liquid can be related to its configurational entropy ($S^{conf}$) through,

$$\log \eta = A_e + \frac{B_e}{T S^{conf}_e} (T)$$

where $T$ is temperature, $A_e$ is a constant, and $B_e$ is another constant reflecting the Gibbs free-energy barriers hindering co-operative rearrangements in the liquid (Richet 1984). Highly polymerized melts with small values of $C_P^{conf}$ have small changes in $S^{conf}$ with temperature, and hence exhibit near-Arrhenian or “strong” behavior (Richet and Bottinga 1995). Conversely, less polymerized melts with large values of $C_P^{conf}$ have correspondingly large changes in $S^{conf}$ with temperature, and hence exhibit distinctly fragile, non-Arrhenian, behavior. Calculated values of fragility for our samples show the expected positive correlation with NBO/T (Table 4), such that granites (NBO/T = 0) are the least fragile, the tektites (NBO/T = 0.07) are intermediate, and the Ca-rich compositions (NBO/T = 0.63 to 0.79) are the most fragile.
Thermal diffusivity

Thermal diffusivity of glasses is highest at room temperature, decreases with increasing temperature, and becomes nearly constant at high $T$ (Fig. 4), as observed for other silicates (e.g., Hofmeister et al. 2009). Greater variability is associated with the antiques (Fig. 5ab), attributed to inhomogeneities such as the presence of tiny bubbles, and variations in fictive temperature and internal strain induced by different annealing and/or quenching rates (see notes in Table 1). For samples with high Al and Fe$^{2+}$ contents, which remained glass to high $T$, $\partial D/\partial T$ is slightly positive above 800 K (Figs. 4 and 5cd), similar to the behavior of SiO$_2$ glass from $\sim$1000 K up to the glass transition (Hofmeister and Whittington 2012).

As in our previous studies, $D$ decreases substantially across the glass transition (Fig. 5). Our measurements probe relaxed melt, starting at $T$ corresponding to a viscosity of $\sim$2×10$^8$ Pa s (e.g., Pertermann et al. 2008; Hofmeister et al. 2009). The temperature of the transition in LFA being higher than in viscometric experiments can be understood by considering the relaxation timescale ($\tau$) calculated from the Maxwell relationship ($\eta = G_\infty \tau$) where $G_\infty \sim$10 GPa, see Dingwell and Webb 1990 and Whittington et al. 2012) is $\sim$1–10 ms, consistent with the duration of the laser pulse in LFA. Glass transition temperatures in our heat transfer experiments ($T_{g,LFA}$) occur at substantially higher temperatures and lower viscosities than in viscometry experiments ($T_{g,12}$) simply due to the short timescale on which the laser interrogates the sample. At moderate $T$ only a little above $T_{g,12}$, viscous liquid appears frozen (glassy) on the short timescale of the laser pulse, although it can still flow over the longer (minutes to hours) timescale of a viscosity measurement. Although the state immediately above the glass transition is supercooled (metastable) liquid, thermal diffusivity measured above $T_{g,LFA}$ represents that of structurally
relaxed melt up to and including superliquidus conditions, and is denoted $D_{\text{melt}}$. For brevity, we refer to this state as liquid.

The glass-to-liquid transition occurred at very low temperatures for the Na-Ca specimens (Fig. 4). The melt was initially viscous and flowed slowly, permitting acquisition of $D$ of supercooled liquid over intervals of up to 300 K for some compositions (Fig. 5b) compared to narrower ranges of <200 K previously. Because flow near 1200 K for the Na-Ca liquids is accompanied by thickening and sagging, followed by thinning, as well as by loss of the small amounts of water in the samples, the highest temperature points may not provide reliable measurements. As discussed by Hofmeister and Whittington (2012), LFA samples are thin and suspended by their edges so flow occurs below the sagging temperature, which is derived from flow of lumps. Examining the recovered sample allowed us to estimate whether flow was extensive, moderate, or slight, and to provide a similar assessment regarding the growth of bubbles. Table 6 excludes suspect $D$ values, such as 1926-1 (see below). Constant $D_{\text{melt}}$ was observed for the Na-Ca samples, which become liquid at relatively low temperatures, whereas upturns (quantified below) exist for Al-rich samples for which higher temperatures were reached (see Fig. 4). When degassing occurs, it is evident as bubbles appearing in the recovered samples and reduction of O-H peaks in the IR spectra (Fig. 1, Table 2). Because the presence of OH$^-$ lowers the glass transition temperature, upon degassing, the material can return to the glass state ($D$ increases) and then become liquid once again as temperature increases: this behavior is evident in only a few samples (Al-rich leucogranite and moldavite) and is marked by arrows in Fig. 5cd. This process is not seen for Na-Ca samples which have stronger hydrogen bonding, as indicated by lower O-H frequencies (Fig. 1) and thus require higher temperatures for dehydration, at which point flow dominates over degassing. Note that the water contents (Table
2) are too small to measurably affect values of $D$ (see Hofmeister et al., 2006), only the

temperature of the transition from glass to melt is affected by water loss.

Because variations in thermal history and internal strain strongly affected $D$ of pure silica
glass (Hofmeister and Whittington, 2012), we performed multiple runs to different maximum
temperatures ($T_{\text{max}}$). High Na>Ca glass (the 1960 insulator) initially had a much steeper trend
than any other low Al glass, but above $T_{g,\text{LFA}}$, the temperature dependence of $D_{\text{melt}}$ was like that
of the other commercial samples (Fig. 5a). Very little water was lost (Table 2), consistent with
the change in behavior being due to either removal of strain, or diffusion of the tiny bubbles. A
second disc of 1960 was run, but the cover had tilted so we do not show this suspect dataset. The
reruns of both discs of 1960 had low $D$-values (Fig. 5a), consistent with the presence of strain
developing as the sample sagged under its own weight but the trends resemble those of other
Na-Ca glasses and melts.

Rolled Na~Ca glass from 1926 has a wide range of initial values (Fig. 5b), which is likely
due to variable amounts of strain. However, $D$ of liquid for disc #1 is much higher than for other
discs (#2-4), which are equal within uncertainty and resemble chemically similar vase and
modern liquids (Fig. 4). Melts are relaxed and thus strain cannot cause this difference. The
compositions are essentially the same (Table 2), so neither is chemistry the source. Hofmeister
and Whittington (2012) found that overly thick coats of Au on silica glass artificially elevated $D$
and also produced flatter trends than graphite coats. Because both features are observed for disc
#1 of 1926, which was Pt coated, we do not discuss the data for this disc further. Although
coatings of metals are desired for suppression of ballistic transfer, the very low $D$-values of
glasses being easily perturbed by coatings thicker than optimal, leads us to conclude that graphite
coatings alone are preferred.
Haplogranite had similar $D$ for all three runs, as we observed for our previous laboratory synthetics (Perterman et al. 2008; Hofmeister et al. 2009). Slightly more variability was observed in the rhyolites, but these are the same within measurement uncertainty.

We considered several different formulae in fitting the $T$ response for $D$ of glass. The $T^{-1}$ form expected for phonon scattering (e.g., Julian 1965) is obviously too steep for these flat lying trends. Instead, data for Na-Ca glasses could be fit to a simple power law, $T^{-0.1}$ to $T^{-0.4}$, but with low correlation coefficients ($R \sim 0.96$, indicating a less than optimal fit). This behavior, coupled with observed upturns at high $T$ for SiO$_2$ glass (Hofmeister and Whittington 2012) and Al-rich samples (Fig. 5cd) suggests one possible form,

$$D = a + bT^{-1} + cT.$$  (6)

With the additive constant, the linear $cT$ term was not needed for the high Na-Ca glasses, but it significantly improved the fit for the Al-rich glasses (Table 5). Importantly, phonon scattering is not precisely inverse with $T$. Calculations for MgO, which has few IR modes, indicate a stronger inverse dependence, $\sim T^{-1.4}$ (e.g., de Koker 2010; Tang and Dong 2010), which is compatible with fits to LFA data on MgO (Yu and Hofmeister 2011). Hofmeister et al. (in prep.) found that LFA data on crystals are well-represented by

$$D = fT^{-g} + hT,$$  (7)

where $g$ depends on crystal structure. For feldspar crystals with many IR modes, $g = 0.3$ to 0.85, such that $g$ increases as Al-Si and Na-Ca ordering increases. For our glasses, which are highly disordered, we used $g = 0.4$, which describes the steep $\partial D/\partial T$ of sample 1960-1, and provided good fits (Table 5). Above $T_{g,LFA}$, we use a simpler fit, $D_{\text{melt}} = a + cT$.

**DISCUSSION**
Comparison with previous measurements of heat transport properties

Some contact-free measurements exist on melts with compositions similar, but not identical, to ours, including Ca-Al-Si slags (Erikson and Seetharaman 2004) and Na-Ca-Si oxide glasses used as standards in Japan (Shibata et al. 2005). The steep increase in $D$ with $T$ for all slags of Erikson and Seetharaman (2004) is due to not accounting for the large amounts of spurious radiative transfer which are present at high $T$ (> 1600 K), and is discounted. Results of Shibata et al. (2005) are roughly consistent with our data, given that the compositions differ slightly. However, Shibata et al. (2005) used a non-standard geometry that does not permit measuring heat crossing the sample, did not account for radiative transfer, and did not benchmark their results, so accuracy is not yet established for their technique.

We do not compare our results to contact measurements of thermal conductivity because techniques such as the hot wire method involve both contact losses of ~10% per contact and radiative gains that can more than double intrinsic $D$ (discussed by Hofmeister et al. 2007).

Dependence of thermal diffusivity values on melt chemistry

Figure 6 further shows that trends in $D$ of liquid against cation contents are generally similar to trends in $D_{298}$ of glasses, although variations in $D$ of the liquid are typically larger. The average decrease in $D$ from glass prior to the transition to relaxed melt is 0.15 mm$^2$s$^{-1}$, irrespective of temperature of the glass transition. Overall, the spread in $D$ among different melts is similar to the spread among glasses at room temperature. The consistency in Figure 6 indicates that we provide accurate values for $D$ of melts above the glass transition, but before significant flow or crystallization onsets.
We examined the variation of $D$ as a function of the concentrations of various cations for both glasses and melts studied by LFA. The strongest correlations were found with Ca and Al content (Fig. 6), increasing concentrations of either cation lowers $D$. However, we recognize that multiple compositional effects coexist. For example, in Figure 6b, the three alkali feldspar compositions lack Ca and so their values depend on other factors, e.g., the size of the substituting cation. Importantly, high Ca contents clearly result in low values of thermal diffusivity whether or not Al is present (c.f. anorthite and diopside). This finding is consistent with the known large effect of Ca on thermal expansivity of melts (Fluegel et al. 2008) since $D$ is connected with thermal expansivity for crystals and glasses (Hofmeister 2010; Hofmeister and Whittington 2012).

Our results suggest that high Ca content, and to a lesser extent high Al content, are the main chemical variables that reduce $D$ in silicic melts. Therefore, Ca-rich magmas such as tonalities, trondhjemites, granodiorites, and I-type arc granites, are expected to have lower thermal diffusivity than similar, but calcium-poor rocks (A-type or S-type granites). At subliquidus conditions, the relatively high $D$ of crystals compared to melt may become more important than variations in $D$ caused by differences in melt chemistry. The crystallization history of the magma is itself a function of the thermal history, thus illustrating the potentially complex feedbacks between the two, mediated by magma transport properties.

**Dependence of thermal diffusivity on structural properties**

The decrease in $D$ at $T_g$ is consistent with configurational changes and similar behavior of $C_p$ and $D^{-1}$ (see Hofmeister et al. 2009; Hofmeister and Whittington 2012). Configurational changes in the liquid upon heating are approximated by the melt fragility. The nominal degree of
polymerization (NBO/T) is less useful because all feldspathic and haplogranitic melts are nominally fully polymerized, yet they show a considerable range in $D$. Generally, both $D$ of glass and melt decrease as fragility increases (Fig. 7a). Other factors must also be important, as indicated by divergence of silica and the Na-Ca glasses from the trend of our feldspar, pyroxene, and various Al-bearing glasses. Nevertheless, this well-defined trend is pertinent to igneous melt compositions, and provides further confirmation of the link between heat and mass transport properties suggested by Hofmeister et al. (2009).

Density reflects both structural and chemical characteristics. The overall decrease in $D_{\text{melt}}$ as melt density increases (Fig. 7b) is attributed to increased phonon interactions, i.e. more phonons in an equal volume of melt. Silicic melts typically have high $D$ and $\eta$, and low fragility and $\rho$, again linking heat and mass transport.

**Increase in $D$ with $T$ for glass and liquid**

The initial decrease in thermal diffusivity with increasing temperature has long been attributed to phonon scattering (Liebfried and Schlömann 1954; Julian 1965). At ~500 K, increases in thermal diffusivity have been previously observed due to ballistic radiative transfer between the heater and thermocouple, which do not actually involve the sample (see e.g., Hofmeister et al., 2007). In our LFA measurements, this unwanted ballistic radiative transfer has been removed at all $T$. In the present study and in our study of SiO$_2$ glasses, we found that $D$ of the glass increases linearly with $T$ above 1000 K, for samples that remained glassy at these high temperatures (Fig. 5bc; also see Hofmeister and Whittington, 2012).

Our Fe- and Al-rich samples have obvious upturns and similar values for the linear coefficient (Eqs. 6 and 7) for both glasses and their melts (Tables 5 and 6). Fitting suggests that
positive linear coefficients exist for the other samples, although slopes are poorly constrained for Na-Ca melts due to their low $T_{g,LFA}$ and proclivity to flow at temperatures only a little higher (e.g. Figs. 4,5a). Given scatter in the data and uncertainties in fitting, the linear coefficients for glasses and melts are described approximately as, $<<10^{-5}$ K$^{-1}$ for Na-Ca (glasses only) and haplogranite; $0.3\times10^{-4}$ K$^{-1}$ for leucogranite and the rhyolites, and $1.5\times10^{-4}$ K$^{-1}$ for the tektites. At higher temperatures, silica glass and melt both show positive $\partial D/\partial T$ of about $10^{-4}$ mm$^2$s$^{-1}$K$^{-1}$ (Fig. 5; Hofmeister and Whittington 2012). The present data show a strong correlation of the upturns with Fe$^{2+}$ content and/or charge transfer between Fe$^{2+}$ and Fe$^{3+}$ (Fig. 2; Table 2).

It is possible that some of the increase in $D$ observed in glasses at high temperature may be due to removal of defects by annealing, and for melts some of the increase could be due to flow of the sample within the experimental apparatus. However, this cannot be the case immediately above $T_{g,LFA}$ where the liquid is relaxed, yet still too viscous for flow to affect the measurements significantly.

It is unlikely that the increase in $D$ with $T$ is due to configurational entropy. Heat capacity and $D^{-1}$ depend similarly on temperature (e.g., Hofmeister and Whittington 2012) so that across the glass transition, $D$ drops whereas $C_P$ increases. The magnitudes of the changes in $D$ and $C_P$ correlate (Fig. 12 in Hofmeister et al., 2009). The increase in $D$ with $T$, if configurational, would mean that configurational heat capacity decreases with temperature, which is inconsistent with available data that suggest high temperature heat capacities of silicate liquids are constant or increase with temperature (see review by Mysen and Richet 2005, and references therein).

The positive correlation in the present study of the $cT$ term in Equation 7 with Fe$^{2+}$ is consistent with a radiative process, because the high frequency electronic transitions of Fe$^{2+}$ are
coupled with vibronic transitions, as indicated by their extremely large bandwidths (cf. d-d transitions of Fe$^{3+}$ to Fe$^{2+}$ in Fig. 2). In intervalence charge transfer, electrons cross Fe$^{2+}$-O$^{2-}$-Fe$^{3+}$ bonds, and thus lattice vibrations are involved. The present data suggest that reduction in heat transport due to cation disorder offset by the increase of $D$ with $T$ attributed to radiative effects. Consequently, despite the decrease in $D$ with increasing fragility, iron-rich tholeiitic melts may have relatively high thermal diffusivity values at high (liquidus) temperatures, especially compared to relatively iron-poor calc-alkaline basalts. Refining this speculation requires quantifying the linear term in Eqs. 6 and 7 and its dependence on Fe content for glasses and melts, and whether a similar enhancement exists for crystals, will require additional study.

**THERMAL CONDUCTIVITY**

Using Eq. 1 requires data on density and heat capacity. For $C_P$, we used the model of Stebbins et al. (1984) for liquid and that of Richet (1987) for glass. Rhyolite data are from Neuville et al. (1993). Density of soda lime melts are reproduced by the model of Fluegel et al. (2008) as a function of composition within a 95% confidence level, with a linear temperature-dependence (Table 7). Except for highest Ca sample (No. 1926), these results are close to the formulation of Lange (1997), which also yields density that depends linearly on $T$. Because the model of Fluegel et al. (2008) reproduces experimental data for industrial glasses and melts, and the effect of Ca is known to be large, we use the Lange (1997) model for the Al-rich melts, which have compositions similar to measurements underlying her model. For the Al-rich glasses, no data exists on $\rho(T)$. Given the calculated expansivity values for soda-lime silica glasses reported in Table 7, we use $\alpha_{glass} = 20 \, \mu K^{-1}$ combined with measured room temperature density (Table 1). Changes in density are minor compared to changes in $D$ and $C_P$ as a function
of temperature, for crystals, glasses and melts. Note that the largest uncertainty in \( k \) is due to how accurately \( C_P \) is modeled. For this reason our report has centered on thermal diffusivity.

Thermal conductivity of glasses increases with \( T \) (Fig. 8) due to the strong increase of \( C_P \) with temperature overwhelming the weak decreases of density and of thermal diffusivity (Figs. 4 and 5). Because \( k \) is the product of \( C_P \) and \( D \), which respond oppositely to increasing temperature, and the models of \( C_P \) have uncertainties, configurational effects on \( k \) are not easily resolved, and we leave this issue for later studies. For the melts, thermal conductivity depends linearly on \( T \) (Table 8) because all three inputs have this form. Whether \( \partial k/\partial T \) is positive or negative depends on the relative sizes of the input derivatives. For the Na-Ca glasses, \( C_P \) was estimated as constant, whereas this property could increase slightly due to anharmonicity. If this is indeed the case, then \( k \) of the Na-Ca melts is approximately temperature independent, and equal to the value obtained at the transition. For the Al-rich melts, within uncertainty, the positive \( \partial k/\partial T \) trend obtained for the glass extrapolates into the melt field (Fig. 8b). These strong melts have very small configurational heat capacities, so crossing the glass transition should result in only modest changes in physical properties, as observed.

**Implications for Geologic Melts**

This paper provides high \( T \) measurements of \( D \) that are free from experimental artifacts such as ballistic radiative transfer gains and contact losses. Key findings are: (1) The cations Ca, Al and Fe strongly affect values of heat and mass transport properties of silicate glasses and melts, whereas substitution of Na and K have a minor effect. Polymerization has a strong effect, as described by melt fragility, but both are overridden by the presence of Ca. The physical cause for the decrease in \( D \) with Ca content is tentatively attributed to Ca vibrations being at low
frequency, which promote mode-mixing with acoustic phonons, which species largely control phonon-phonon scattering (e.g., Tang and Dong, 2010) and to optical phonons being slower (less efficient) than acoustic. (2) Thermal diffusivity of glass and melt can increase with $T$ at high $T$, and the magnitude of the increase is correlated with the presence of Fe. (3) Regular variations of glass and melt properties with chemical composition previously discovered for simple glass compositions also hold for more chemically complex glasses.

These inferences, along with the trends of $D_{\text{melt}}$ with composition and physical properties, permit estimation of thermal diffusivity near liquidus of melts associated with common igneous and volcanic rocks (Fig. 9). Felsic melts with low Ca contents are expected to have high $D_{\text{melt}} \sim 0.5$ mm$^2$s$^{-1}$. This projection includes most granite and granitoid melts, and involves little uncertainty due to little variation in the end-member values. However, more calcic I-type arc granite melts are expected to have lower thermal diffusivity than calcium-poor A-type or S-type granites. Mafic melts will have low $D_{\text{melt}} \sim 0.3$ mm$^2$s$^{-1}$. This projection is less certain because of $D_{\text{melt}}$ of olivine was estimated and because the effect of Fe cations is strong, as shown in the present paper. Consequently, we also predict that calc-alkaline basalts will initially have lower thermal diffusivity than tholeiitic basalts. At high temperature the converse could hold due to the higher Fe content of tholeiitic magmas.

**ACKNOWLEDGMENTS**

Support from NSF grants EAR-0748411, EAR-0911428, EAR-1321857 and EAR-0911116 is appreciated. We thank Paul Carpenter (W.U.) for providing microprobe analysis.

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**FIGURE CAPTIONS**

**Fig. 1.** Unpolarized absorption spectra of the O-H fundamental region for selected samples. Thicknesses of the samples (L) are labeled but spectra as shown are scaled to represent 1 mm thickness. Baseline corrections are not shown. Due to imperfect surface polish, true absorbance near 4000 cm⁻¹ is zero. Grey = natural samples with similar patterns (dashed = indochinite; solid = moldavite; dots = spectra from a 4.4 mm Al-rich rhyolite). The rise to high frequency is due to Fe²⁺ transitions. Black = effect of heating on 1926 window glass, which has the same profile as the other Na-Ca commercial glasses. The rise to high ν for heated samples (from L = 0.9 mm) is
due to imperfect surface polish. Thickness was 2.4 mm for the fresh sample. Overtones of Si-O lattice modes are near 2400 cm\(^{-1}\).

**Fig. 2** Unpolarized absorption spectra of d-d electronic transitions of Fe ions. Thicknesses of the samples \((L)\) are labeled but spectra as shown are scaled to represent 1 mm thickness. (a) Near-IR data, as labeled, on ferrous iron in octahedral coordination. Light vertical lines show that the same positions exist for the high Al glasses, but that the Ca-rich glasses have broader bands. Thickness was 2.7 and 3.5 mm for the high and low frequency spectral segments of 1895.

(b) Visible-UV region showing ferric iron, if present. For the thin curves, solid line = 1895 from thickness of 0.10 mm for the UV and 2.705 mm for the visible; dotted line = 1960 with L = 0.787 to 0.917 mm; dashed line = “modern” with L = 1.124 mm; dot-dashed line = 1926 from L = 0.608 to 0.848 mm. * = Fe\(^{3+}\) transitions in a tetrahedral site. Vertical line = Fe\(^{2+}\) transitions in a tetrahedral site or intervalence charge transfer (IVCT). Double vertical line indicates Fe\(^{2+}\) in an octahedral site.

**Fig. 3.** Viscosity data for supercooled liquids near the glass transition. Lines are TVF curves. Filled symbols listed on left = Al-rich samples. Open symbols listed on right = Na-Ca samples. Leucogranite data from Whittington et al. (2009a).

**Fig. 4.** Thermal diffusivity, comparison of high-Al rhyolite to Na-Ca glasses and liquids. Symbols are the average of 3 datapoints (>6 at room temperature). Double arrow = transition interval. Curves are fits in Table 5 and 6, unless stated otherwise. Dots = remelted rhyolite as quenched for two different discs. The three different pieces represent varying amounts of residual strain. The fit is to all data. Squares = modern Na-Ca glass, fit by \(D = 1.00T^{-0.124}\), Open squares = modern liquid. Diamonds = vase, was fit by \(D = 1.18T^{-0.155}\). Open diamonds = vase liquid. + = 1890. X = 1884. Flow (sagging) onsets above 1200 K.
Fig. 5. Thermal diffusivity vs. temperature. (a) Antique and modern commercial samples with high Na contents, showing power law fits. Triangles = 1895 which melted gradually, then flowed at the highest temperature accessed. Two sequential runs are shown for disc #1 of 1960 (filled squares, crossed squares). A fit was not made to data for the dry sample because data points were widely spaced. Filled diamonds = a second disc from 1960. (b) 1926 with power law fits as labeled. The wide variation in $D$ is attributed to strain in this rolled glass. (c) Granitic glasses and liquids. Filled and open square = 1st sample of haplogranite. Square with plus = 2nd sample of haplogranite. Leucogranite (diamonds) has much higher Fe content. Just above melting, leucogranite $D$ increased slightly, connected with degassing. (d) Tektites and Al-rhyolite with K>Na. Above $T_g$ moldavite back transformed to glass, attributed to loss of water.

Fig. 6. Dependence of thermal diffusivity on chemical composition. Circles = $D$ at 298 K. Squares = $D$ upon melting. Also included are data from Hofmeister et al. (2009). Dotted and dashed lines are linear fits. Solid lines are trends within the Al-rich glasses and liquids. (a) $D$ vs Al content per 8 O atoms (b) $D$ vs. Ca content per 8 atoms. Alkali feldspar melts (square with plus) are not included in the fit.

Fig. 7. Dependence of thermal diffusivity of glasses and liquids on physical properties. Additional data from Pertermann et al. (2008); Hofmeister et al. (2009); Whittington and Hofmeister (2012). (a) $D$ of glass and melt vs. fragility. Symbols for liquid are as labeled, except unlabeled crossed squares are alkali feldspar melts. For glass, the same symbols are used, but are grey. Lines are not fits, but indicate ranges of values. (b) $D$ upon melting vs. density.

Fig. 8. Thermal conductivity. Lines are labeled, such that heavier weight lines represent liquid. (a) Soda-lime compositions, for which melt density is well-known. (b) Al-rich samples, for which we assumed $\alpha_{glass} = 20 \times 10^{-6}$ K$^{-1}$, as measured for phonolitic glass (Bouhifd et al. 2001).
Fig. 9. Ternary diagrams of thermal diffusivity for common igneous melts. Left = felsic rocks. Right = mafic rocks. Letters indicate samples of (I) indochinite, (M) moldavite, (R) rhyolite, (L) leucogranite and (H) haplogranite. Other labels indicate melts of mineral stoichiometry. Olivine melt was projected using Fig. 7.
1926, fresh

OH⁻ stretching region

Wavenumber, cm⁻¹

Absorption coefficient, mm⁻¹

1st heating

2nd heating

moldavite
L = 1.96 mm

indochinite
L = 1.57 mm
Absorption coefficient, mm$^{-1}$

Wavenumbers, cm$^{-1}$

- **Fe$^{2+}$ bands**
- **Indochinite**  
  - L = 0.643 mm
- **Moldavite**  
  - L = 1.96 mm
- **Leucogranite**  
  - L = 9 mm

5500 cm$^{-1}$

8930 cm$^{-1}$

1895 cm$^{-1}$
Absorption Coefficient, mm$^{-1}$

Wavenumber, cm$^{-1}$

Moldavite  
$L = 0.433$ mm

Leucogranite  
$L = 1.98$ mm

Haplogranite  
$L = 0.521$ mm

Fe$^{2+}$ oct.  
Al-rhyolite  
2.19 mm

IVCT  
1895

Fe$^{3+}$ tet.  
1960

modern  
1926

1.10$^4$  
1.50$^4$  
2.00$^4$  
2.50$^4$  
3.00$^4$
Na > Ca
antique insulators

1960-1 rerun
1960-2 rerun

1895

D, mm²s⁻¹

T, K

D_{melt}

T_{g,LFA}
Figure b shows a graph of diffusion coefficient ($D$, mm$^2$s$^{-1}$) vs. temperature ($T$, K) for Na, Ca window glass. The graph includes data for runs #1, #2, #3, and #4, with #3 rerun. The graphs are described by the equations:

- $D = 1.15T^{-0.11}$
- $D = 1.34T^{-0.17}$

The data points indicate warping and thickening effects. The Tg, LFA temperatures are also marked on the graph.
glasses similar to granitic magmas

Temperature, K

D, mm$^2$s$^{-1}$

- haplogranite Fe-free
- leucogranite (low Fe)
- 2nd sample
- 1st run
- 2nd run
- Fe-free melt
- degassing

2nd sample

1st run

D$_{\text{melt}}$
Tektites
Al > Na > K
fit to \( D = fT^{-g} + hT \)

- Al-rich rhyolite
- Moldavite
- Indochinite

Degassing; remelting

\( \text{D}_{\text{melt}} \)
Thermal diffusivity, mm·s⁻¹

Number of Ca per 8 O atoms

room temperature

initial melt

NaCa

anorthite

diopside

moldv
haplo
leuco
rhyo
indo

feldspars
spodumene
at 298 K

upon melting

Diopside

Ca-Na

Spodumene

Silica

Leuco.

Moldv.

Haplo.
Melt thermal diffusivity, mm s⁻¹ vs. Melt density, kg m⁻³
FIGURE 9

\[ \text{qtz} = 0.45 \]

\[ \text{kspar} = 0.475 \]

\[ \text{albite} = 0.5 \]

\[ \text{D}_{\text{melt}} = 0.5 \]

\[ \text{D}_{\text{melt}} = 0.3 \]

\[ \text{cpx} = 0.30 \]

\[ \text{plag} = 0.35 \]

\[ \text{projected olv} = 0.15 \]

\[ \text{granites} \]

\[ \text{gabbro, basalt} \]
<table>
<thead>
<tr>
<th>Sample Year</th>
<th>Key elements*</th>
<th>Density kg m(^{-3})</th>
<th>Origin and/or Source</th>
<th>Color†</th>
<th>“Formula”*</th>
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<td>1895</td>
<td>high Na&gt;Ca</td>
<td>2480</td>
<td>antique insulator from telephone line‡</td>
<td>aqua blue</td>
<td>Na(<em>{1.40})K(</em>{0.05})Ca(<em>{0.33})Mg(</em>{0.10})Fe(<em>{0.02})Al(</em>{0.15})Si(_{3.30})O(_8)</td>
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<td>high Na&gt;Ca</td>
<td>2476</td>
<td>antique insulator from telephone line§</td>
<td>colorless</td>
<td>Na(<em>{1.37})Ca(</em>{0.36})Mg(<em>{0.28})Al(</em>{0.053})Si(_{3.32})O(_8)</td>
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<tr>
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<td>ground glass from Edmund Scientific</td>
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<td>Na(<em>{1.21})Ca(</em>{0.40})Mg(<em>{0.31})Al(</em>{0.08})Si(_{3.28})O(_8)</td>
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<td>Na(<em>{1.22})K(</em>{0.005})Ca(<em>{0.678})Mg(</em>{0.025})Fe(<em>{0.005})Al(</em>{0.028})Si(_{3.315})O(_8)</td>
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<td>Na(<em>{1.12})K(</em>{0.007})Ca(<em>{0.660})Mg(</em>{0.025})Fe(<em>{0.007})Al(</em>{0.031})Si(_{3.327})O(_8)</td>
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<td>antique window pane¶</td>
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<td>laboratory synthetic</td>
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<td>Habri, Czech Republic, from Excaliber</td>
<td>green</td>
<td>Na(<em>{0.09})K(</em>{0.19})Ca(<em>{0.11})Mg(</em>{0.12})Fe(<em>{0.05})Al(</em>{0.49})Si(_{3.44})O(_8)</td>
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<td>Indochinite</td>
<td>Al&gt;Fe<del>K</del>Mg</td>
<td>2425</td>
<td>Kohn Khaen, Thailand, Ebay purchase</td>
<td>dark brown</td>
<td>Na(<em>{0.03})K(</em>{0.14})Ca(<em>{0.08})Mg(</em>{0.13})Fe(<em>{0.18})Al(</em>{0.73})Si(_{3.20})O(_8)</td>
</tr>
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</table>

*Notes: For the antiques, the sample number is the year of manufacture, if known. The remelted rhyolites are samples NCAR (rhyolite) and NCr (Al-rhyolite) described by Romine et al. (2012). The last digits are uncertain.*
*Detailed in text and tables. Cations most abundant after Si are listed. The commercial glasses with significant Ca have two sites for OH⁻. “Formula” are given for comparison with glasses previously studied. Trace Ti is grouped with Si.

†Color is related to presence of Fe³⁺

‡Manufactured at the Hemingray factory in Covington, KY between 1894 and 1895. Commonly produced in blue to green hues, due to use of sand from dunes at Michigan Beach, Michigan which are impure. At this time, recycled glass was often added to the vats to reduce cost. Many bubbles are present due to crude molding techniques and furnace temperatures being close to glass melting temperature. Found in Missouri.

§Among the last glass made at the Hemingray factory located in Muncie, IN. Embossed with year of manufacture. At this time Hemingray Co. primarily produced glass windows and blocks for residential use, using pure quartz sandstone. Few bubbles are present due to mechanized molding techniques and furnace temperatures well exceeding glass melting temperature. Found at a farm in south central Ohio.

||This vase was purchased at Treasure Isles Antique Mall, 2317 South Big Bend Blvd. St. Louis MO 63143 USA. Its probable date of manufacture lies between the 1930’s thru 1960’s.

@ From the ruins of the National Memorial Church of God in Christ, located at 460 North Spring Avenue, St. Louis MO USA. Completed in 1884, the church burned down in 2001, only the exterior remains are still standing. The glass sample was in hte soil beneath one of the windows.

#From the ruins of the Sheahan Quarries private railroad engine house located in Elephant Rocks State Park, MO USA. Constructed during the 1890’s this structure was created out of the same granite which was being quarried at the site. The glass sample was dug out of the soil directly beneath an opening in the side wall where the window and floor used to exist.

¶Date reflects construction of the depression era house at 2561 Circle Dr., Maplewood MO. Manufactured using a plate glass process, because the float glass technique originated subsequently (Pilkington, 1969) and the appearance is slightly wavy, like that of rolled glass. Few impurities exist due to use of mined quartz sandstones.
Table 2. Chemical compositions (in wt %) and hydroxyl contents (in ppm by wt)

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<td>SiO₂</td>
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Notes: Chemical analyses of the remelted rhyolites are provided by Romine et al. (2012). The last digit is uncertain, unless noted.
OH⁻ contents determined initially and after LFA runs to the temperatures indicated. Initially, Al-rhyolite has 130 ppm OH, whereas rhyolite had 230 ppm (Romine et al. 2012).

NBO/T is the nominal ratio of non-bridging oxygens to tetrahedral cations, calculated according to NBO/T = (FeO+MnO+MgO+CaO+Na₂O+K₂O – 2Al₂O₃ – 2Cr₂O₃)/(SiO₂ + TiO₂ + 2Al₂O₃ + 2Cr₂O₃) on a molar basis, and using average compositions for the 1890 glass. For rhyolite and Al-rhyolite, NBO/T = 0.02 and 0, respectively.

Includes 0.263 wt% SO₂ and 0.003 wt % V₂O₃.

Contains only Fe³⁺, whereas the remaining samples contain both Fe³⁺ and Fe²⁺.

Includes 0.05 wt% SO₂.

Microprobe analysis after heating
Table 3a. Viscosity measurements: Ca-Na rich melts

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Notes: The last digit is uncertain.
Table 3b. Viscosity measurements: Al-rich melts

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<td>8.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: Viscosity data for leucogranite are given by Whittington et al. (2009b). The last digit is uncertain.
Table 4. Fits to viscosity data of the form: \( \log \eta = A + \frac{B}{(T - C)} \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B(K)</th>
<th>C(K)</th>
<th>( T_{12}(K) )</th>
<th>number</th>
<th>RMS error</th>
<th>fragility&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1895</td>
<td>-4.69</td>
<td>5998.5</td>
<td>446.7</td>
<td>806</td>
<td>9</td>
<td>0.02</td>
<td>37.4</td>
</tr>
<tr>
<td>1926</td>
<td>-4.44</td>
<td>5999.5</td>
<td>477.5</td>
<td>842</td>
<td>10</td>
<td>0.04</td>
<td>38.0</td>
</tr>
<tr>
<td>1960</td>
<td>-4.51</td>
<td>5998.4</td>
<td>445.2</td>
<td>809</td>
<td>11</td>
<td>0.04</td>
<td>36.7</td>
</tr>
<tr>
<td>Vase</td>
<td>-4.37</td>
<td>5999.5</td>
<td>449.0</td>
<td>815</td>
<td>11</td>
<td>0.05</td>
<td>36.4</td>
</tr>
<tr>
<td>Haplogranite</td>
<td>-1.87</td>
<td>9001</td>
<td>494.4</td>
<td>1143</td>
<td>26</td>
<td>0.02</td>
<td>24.4</td>
</tr>
<tr>
<td>Leucogranite&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-6.98</td>
<td>18000</td>
<td>145.0</td>
<td>1093</td>
<td>36</td>
<td>0.02</td>
<td>21.9</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>-4.65</td>
<td>12600</td>
<td>313.4</td>
<td>1070</td>
<td>22</td>
<td>0.08</td>
<td>23.5</td>
</tr>
<tr>
<td>Al-rhyolite</td>
<td>-7.30</td>
<td>17388</td>
<td>212.2</td>
<td>1113</td>
<td>27</td>
<td>0.05</td>
<td>23.8</td>
</tr>
<tr>
<td>Moldavite</td>
<td>-3.08</td>
<td>8997</td>
<td>488.5</td>
<td>1085</td>
<td>12</td>
<td>0.03</td>
<td>27.4</td>
</tr>
<tr>
<td>Indochinite</td>
<td>-3.16</td>
<td>8042</td>
<td>493.5</td>
<td>1024</td>
<td>36</td>
<td>0.03</td>
<td>29.3</td>
</tr>
</tbody>
</table>

Notes: The RMS error pertains to the fitting. Coefficient A has no units but is based on \( \log (\text{Pa s}) \) per convention. Coefficient B has a similar basis. The last digit in the fitting parameters is uncertain.

<sup>a</sup> Calculated from the TVF parameters according \( m = \frac{B}{(T_{12}[1 - C/T_{12}])^2} \)

<sup>b</sup> Data and TVF fit from Whittington et al. (2009b)
Table 5. Thermal diffusivity values and fitting parameters for glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness</th>
<th>$T$</th>
<th>$D_{298}$</th>
<th>$D$</th>
<th>$T_{\text{max}}$</th>
<th>$D = a + bT^{-1} + cT$</th>
<th>$T_{\text{max}}^a$</th>
<th>$D = fT^{-0.4} + hT$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm</td>
<td>°C</td>
<td>mm$^2$s$^{-1}$</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>R</td>
<td>f</td>
</tr>
<tr>
<td>1895</td>
<td>0.55$^d$</td>
<td>25.3</td>
<td>0.55</td>
<td>0.428</td>
<td>34</td>
<td>0</td>
<td>0.98</td>
<td>900</td>
</tr>
<tr>
<td>1960-1</td>
<td>0.91$^d$</td>
<td>22.2</td>
<td>0.66</td>
<td>0.336</td>
<td>98</td>
<td>0</td>
<td>0.99</td>
<td>800</td>
</tr>
<tr>
<td>1960-1 rerun</td>
<td>0.672</td>
<td>22.4</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1960-2 rerun</td>
<td>0.91</td>
<td>22.2</td>
<td>0.49</td>
<td>0.348</td>
<td>38</td>
<td>0</td>
<td>0.97</td>
<td>870</td>
</tr>
<tr>
<td>Vase</td>
<td>0.576</td>
<td>19.9</td>
<td>0.50</td>
<td>0.382</td>
<td>33</td>
<td>0</td>
<td>0.98</td>
<td>850</td>
</tr>
<tr>
<td>Modern</td>
<td>1.124$^{bd}$</td>
<td>24.8</td>
<td>0.50</td>
<td>0.400</td>
<td>29</td>
<td>0</td>
<td>0.98</td>
<td>900</td>
</tr>
<tr>
<td>1884</td>
<td>0.467</td>
<td>20.1</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1890</td>
<td>0.51</td>
<td>21</td>
<td>0.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1926-2</td>
<td>0.951</td>
<td>24.8</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1926-3</td>
<td>0.848$^d$</td>
<td>26.5</td>
<td>0.53</td>
<td>0.383</td>
<td>40</td>
<td>0</td>
<td>0.97</td>
<td>700</td>
</tr>
<tr>
<td>1926-4</td>
<td>0.74</td>
<td>24.0</td>
<td>0.57</td>
<td>0.422</td>
<td>45</td>
<td>0</td>
<td>0.99</td>
<td>900</td>
</tr>
<tr>
<td>Haplogranite</td>
<td>0.6-0.8$^e$</td>
<td>20</td>
<td>0.70</td>
<td>0.440</td>
<td>69</td>
<td>0.62$\times10^{-4}$</td>
<td>0.99</td>
<td>1300</td>
</tr>
<tr>
<td>Leucogranite</td>
<td>0.772$^d$</td>
<td>24.3</td>
<td>0.67</td>
<td>0.40</td>
<td>70</td>
<td>0.88$\times10^{-4}$</td>
<td>0.99</td>
<td>1200</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>0.4-0.9$^e$</td>
<td>21</td>
<td>0.63</td>
<td>0.44</td>
<td>51</td>
<td>0.54$\times10^{-4}$</td>
<td>0.95</td>
<td>1250</td>
</tr>
<tr>
<td>Al-Rhyolite</td>
<td>0.962</td>
<td>20.0</td>
<td>0.63</td>
<td>0.375</td>
<td>65</td>
<td>0.97$\times10^{-4}$</td>
<td>0.99</td>
<td>1260</td>
</tr>
<tr>
<td>Moldavite</td>
<td>0.84$^d$</td>
<td>22.4</td>
<td>0.68</td>
<td>0.32</td>
<td>87</td>
<td>1.9$\times10^{-4}$</td>
<td>0.97</td>
<td>1000</td>
</tr>
<tr>
<td>Indochinite$^c$</td>
<td>0.86$^d$</td>
<td>22.7</td>
<td>0.64</td>
<td>0.31</td>
<td>82</td>
<td>1.6$\times10^{-4}$</td>
<td>0.98</td>
<td>1100</td>
</tr>
</tbody>
</table>

Notes: Uncertainty in $D$ is 2%, from benchmarking. R is the linear correlation coefficient for the fits. The last digit of each fitting coefficient (a,b,c,f,g) is uncertain, except for leucogranite and rhyolite, where c is uncertain by 20%. Two fits are provided. Units of coefficient $a$ are mm$^2$s$^{-1}$; units of $b$ are mm$^2$Ks$^{-1}$; units of $c$ and $h$ are mm$^2$s$^{-1}$K$^{-1}$; units of $f$ are mm$^2$s$^{-1}$K$^{0.4}$.

$^a$ $T_{\text{max}}$ is the limit to which all these fits can be projected to.

$^b$ The room temperature values for modern glass were obtained using thinner pieces.

$^c$ Bubbles formed during the run.

$^d$ Sputter coated with Pt before applying graphite.

$^e$ Fit includes runs on multiple sections.
Table 6. High temperature thermal diffusivity values

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{sat}}$</th>
<th>$D_{\text{sat}}$</th>
<th>$T_{\text{melt}}$</th>
<th>$D_{\text{melt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>mm$^2$s$^{-1}$</td>
<td>K</td>
<td>mm$^2$s$^{-1}$</td>
</tr>
<tr>
<td>1895</td>
<td>750-930</td>
<td>0.47</td>
<td>1000-1200</td>
<td>0.38</td>
</tr>
<tr>
<td>1960-all</td>
<td></td>
<td></td>
<td>950-1200</td>
<td>0.32</td>
</tr>
<tr>
<td>Vase</td>
<td></td>
<td></td>
<td>950-1250</td>
<td>0.35</td>
</tr>
<tr>
<td>Modern</td>
<td></td>
<td></td>
<td>950-1300</td>
<td>0.36</td>
</tr>
<tr>
<td>1926-3</td>
<td>800-950</td>
<td>0.43</td>
<td>940-1170</td>
<td>0.35</td>
</tr>
<tr>
<td>1926-4</td>
<td></td>
<td></td>
<td>1000-1260</td>
<td>0.37$^a$</td>
</tr>
<tr>
<td>Haplogranite</td>
<td>940-1320</td>
<td>0.57</td>
<td>1390-1650</td>
<td>0.54</td>
</tr>
<tr>
<td>Leucogranite</td>
<td></td>
<td></td>
<td>1320-1450</td>
<td>0.47+0.36×10$^{-4}$</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>1100-1350</td>
<td>0.54</td>
<td>1350-1450</td>
<td>0.52</td>
</tr>
<tr>
<td>Al-rhyolite</td>
<td>1350-1550</td>
<td>0.35+1.2×10$^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moldavite</td>
<td>1250-1420</td>
<td>0.35+1.6×10$^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indochinite</td>
<td>1150-1310</td>
<td>0.32+1.4×10$^{-4}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: Uncertainties in $D$ are 2% for the glass and 4% for the melt. Fits have linear correlation coefficients of 0.90 to 0.97

$^a$The sample flowed during melting at high temperature, adding uncertainty to $D$-values.
Table 7. Volumetric thermal expansivity of glasses at 298 K and of melts at 1200 K, along with melt density

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha_{\text{glass}}$ $^a$</th>
<th>$\rho_{\text{melt}}$ $^b$</th>
<th>$\alpha_{\text{melt}}$ $^b$</th>
<th>$\rho_{\text{melt}}$ $^c$</th>
<th>$\alpha_{\text{melt}}$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\times10^{-6}$ K$^{-1}$ kg m$^{-3}$</td>
<td>$\times10^{-6}$ K$^{-1}$ kg m$^{-3}$</td>
<td>$\times10^{-6}$ K$^{-1}$ kg m$^{-3}$</td>
<td>$\times10^{-6}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>1895</td>
<td>29.4</td>
<td>2364</td>
<td>62.5</td>
<td>2370</td>
<td>61.5</td>
</tr>
<tr>
<td>1960</td>
<td>28.1</td>
<td>2390</td>
<td>62.8</td>
<td>2385</td>
<td>62.1</td>
</tr>
<tr>
<td>Vase</td>
<td>27.5</td>
<td>2400</td>
<td>58.3</td>
<td>2389</td>
<td>61.3</td>
</tr>
<tr>
<td>Modern</td>
<td>28.6</td>
<td>2411</td>
<td>62.2</td>
<td>2403</td>
<td>62.2</td>
</tr>
<tr>
<td>1926</td>
<td>27.2</td>
<td>2374</td>
<td>93.0</td>
<td>2393</td>
<td>57.2</td>
</tr>
<tr>
<td>Haplogranite</td>
<td></td>
<td>2308</td>
<td></td>
<td></td>
<td>24.62</td>
</tr>
<tr>
<td>Leucogranite</td>
<td></td>
<td>2327</td>
<td></td>
<td></td>
<td>24.54</td>
</tr>
<tr>
<td>Rhyolite</td>
<td></td>
<td>2326$^d$</td>
<td>22.24$^d$</td>
<td></td>
<td>22.24$^d$</td>
</tr>
<tr>
<td>Moldavite</td>
<td></td>
<td>2353</td>
<td>20.83</td>
<td></td>
<td>20.83</td>
</tr>
<tr>
<td>Indochinite</td>
<td></td>
<td>2426</td>
<td>24.47</td>
<td></td>
<td>24.47</td>
</tr>
</tbody>
</table>

Notes: Measured densities of the glasses are in Table 1. From comparing the two models, uncertainties are 2% for density and generally 5% for $\alpha_V$.

$^a$Thermal expansivity was calculated after Fluegel (2005) whose method is not geared to Al-rich melts. Results for 1884 and 1890 are similar to 1926 glass.

$^b$Density of the melt was calculated after Flugel et al. (2008), whose method is not geared to Al-rich melts. Results for 1884 and 1890 are similar to 1926 and closely resemble measured $\rho(T)$ for Na-Ca melts.

$^c$Calculated after Lange (1997) and Lange and Carmichael (1990).

$^d$Al-rhyolite is assumed the same as rhyolite.
**Table 8. Fits to thermal conductivity in Wm\(^{-1}\)K\(^{-1}\)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(k_{\text{glass}} = a + bT + cT^2 + dT^3)</th>
<th>(k_{\text{melt}} = a + bT)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>1895</td>
<td>0.669</td>
<td>0.00196</td>
</tr>
<tr>
<td>1960</td>
<td>0.647</td>
<td>0.00147</td>
</tr>
<tr>
<td>Vase</td>
<td>0.601</td>
<td>0.00180</td>
</tr>
<tr>
<td>Modern</td>
<td>0.572</td>
<td>0.00197</td>
</tr>
<tr>
<td>1926-3</td>
<td>0.695</td>
<td>0.00153</td>
</tr>
<tr>
<td>Haplogranite</td>
<td>0.734</td>
<td>0.00213</td>
</tr>
<tr>
<td>Leucogranite</td>
<td>0.737</td>
<td>0.00199</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>0.703</td>
<td>0.00202</td>
</tr>
<tr>
<td>Moldavite</td>
<td>0.795</td>
<td>0.00158</td>
</tr>
<tr>
<td>Indochinite</td>
<td>0.792</td>
<td>0.00151</td>
</tr>
</tbody>
</table>

*Notes:* The last digit of the fits are uncertain. Linear correlation coefficients are ~0.99.

Units of coefficient \(a\) are Wm\(^{-1}\)K\(^{-1}\); units of \(b\) are Wm\(^{-1}\)K\(^{-2}\); units of \(c\) are Wm\(^{-1}\)K\(^{-3}\); units of \(d\) are Wm\(^{-1}\)K\(^{-4}\)

\(^a\)The fit for the melt is Al-rhyolite shifted to match the result upon melting for rhyolite.