

**Title:** Heat transfer in plagioclase feldspars

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### Abstract

Laser Flash Analyses (LFA) of oriented sections of five natural plagioclase crystals provide thermal diffusivity ( $D$ ) as function of temperature (to  $\sim 1300$ - $1500$  K) and composition ( $An_{5-65}$ ).

Plagioclase has low thermal diffusivity; over much of the solid solution room temperature  $D$  is  $0.979$  to  $0.751$   $\text{mm}^2/\text{s}$  along **c**,  $0.919$  to  $0.767$   $\text{mm}^2/\text{s}$  along **b**, and  $0.632$  to  $0.868$   $\text{mm}^2/\text{s}$

perpendicular to **a** and **b**. The directionally averaged  $D$  is 30-45% lower than  $D$  of Amelia albite. Thermal conductivities calculated using measured  $D$  values are almost the same for all samples of  $An_{>20}$ , being about  $1.5 - 1.9 \text{ Wm}^{-1}\text{K}^{-1}$  and changing little with temperature.

Increasing Al/Si disorder causes  $D$  to decrease with increased An content, although sample structure causes more ordered samples to have higher  $D$  than more disordered samples.

Inflections in  $D(T)$  are connected with structural changes with  $T$ . Disorder with increased temperature or change to a  $C\bar{1}$  structural component lowers  $D$ . Structure dictates whether  $D$  along the **b** axis is greater or less than that along **c**, possibly because ordering in An-like domains increases  $D$  along **c** relative to **b**. Likewise, disorder during heating decreases  $D$  in albite along **c** but has little impact on  $D$  in the other directions. The anharmonic lattice effects that dictate both thermal expansivity and  $D$  are swamped by effects of disorder; the latter plays a major role in plagioclase  $D$ . Finally, measured  $D$  values confirm that plagioclase is more insulating than other major igneous rock-forming minerals.

### Introduction

Solving many geologic problems requires an understanding of the thermal nature of Earth's crust and mantle, and mineral heat transfer properties (thermal conductivity ( $k$ ) and thermal diffusivity ( $D$ )) provide the basis for such understanding. Therefore, we have been building a database of

mineral thermal diffusivities measured with Laser Flash Analysis (LFA). To date, several glass and mineral systems have been probed, including quartz, perovskite, olivine, clinopyroxene, orthopyroxene, garnet and spinel (Branlund and Hofmeister 2007; Hofmeister 2010; Pertermann and Hofmeister 2006, 2008; Hofmeister 2011, 2006, 2007). Data on low albite and low sanidine have been published (Pertermann et al. 2008; Hofmeister et al. 2009), but more-calcic plagioclase data are lacking. Given that feldspar is the most common rock-forming mineral, and plagioclase is prevalent in intermediate and mafic igneous rocks, it is especially important that ~~we~~ <sup>it is</sup> characterize heat transfer in plagioclase.

Plagioclase minerals are structurally complex (Figure 1). At high temperature, a true solid solution exists between the sodic and calcic end members of the plagioclase series, albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). Low albite is ordered such that Al always resides on the  $T_1O$  site, forming a  $C\bar{1}$  structure. With increased temperature <sup>diffuse</sup> the albite disorders forming high albite (still  $C\bar{1}$ ), because Al can <sup>move</sup> to other sites. At a higher temperature, the framework shears leading to a partially ordered monoclinic structure ( $C2/m$  space group) (Parsons 2010). In pure anorthite, each Al is surrounded by four Si and vice versa; the alternating layers of Si and Al tetrahedra double the length of the  $c$ -axis in the crystallographic unit cell (McConnell 2008); Like low albite, anorthite exhibits long-range order. Unlike albite, anorthite remains perfectly ordered (with the  $I\bar{1}$  structure) until melting. At low temperature (below about 500 K), The <sup>ital</sup> anorthite lattice distorts around Ca atoms, creating a  $P\bar{1}$  structure. Charge imbalances caused by <sup>-</sup> Na/Ca substitution in anorthite/albite are counteracted by Al/Si <sup>-</sup> exchange. Atomic ordering becomes complicated because Al-O-Al bonds are energetically expensive; intermediate plagioclase therefore consist of planar subdomains with slightly different structures, and these antiphase domains combine to form incommensurate superstructures. The two main

intermediate structures are the more Ab-rich  $e_2$  and the more An-rich  $e_1$  plagioclase, so named because of  $e$  reflections that appear in single-crystal x-ray photographs. McConnell (2008) proposed that  $e_2$  plagioclase contains alternating domains of albite-like ( $C\bar{1}$ ) and anorthite-like ( $I\bar{1}$ ) structures, whereas the  $e_1$  phase contains alternating incommensurate layers of ordered and partially ordered  $I\bar{1}$  structures. The widths of the domains are on the order of 20-50 nm, and orientations vary with An-content and temperature (e.g., Carpenter 1991; Grove 1977). At low temperatures, miscibility gaps exist in the solid solution, and intergrowths of the different structures form, creating peristerite ( $C\bar{1}$  and  $e_2$ ), Bøggliid ( $e_1 + e_2$ ) and Hüttenlocher ( $e_1 + I\bar{1}$ ) intergrowths (Figure 1). It is likely that the entire solid solution, with the exception of the two end members, is immiscible at temperatures ( $< \sim 400$  K) (Parsons 2010).

Because atomic diffusion is very sluggish in plagioclase, many samples retain a metastable structure (either  $C\bar{1}$ ,  $I\bar{1}$ ,  $e_1$  or  $e_2$ ). Only very slowly cooled plutonic samples and metamorphic samples will possess the intergrowths, whereas volcanic plagioclase are more disordered with structures that may reflect the high temperature solid solution. Plagioclase therefore does not simply fall into a “high” versus “low” category, but exhibits a wide range of order/disorder reflecting varied cooling histories.

In this study, we measure thermal diffusivity of natural plagioclase with compositions ranging from  $An_5$  to  $An_{65}$  at different temperatures, thus quantifying heat transfer for several different plagioclase chemistries and structures.

## Methods

### Samples

Low albite from Amelia County, Virginia, was previously studied along with Ab and An glasses (Hofmeister et al. 2009; note, the low albite was mistakenly called high albite in that paper). We add to this data from seven natural plagioclase samples with higher An contents, five of which were analyzed to high temperature (Table 1).

An anorthite mat was fabricated by cooling a synthetic  $\text{CaAl}_2\text{Si}_2\text{O}_8$  glass (see Hofmeister et al. 2009). The resulting sample is fine grained and polycrystalline, probably containing some glass.

Each ~~sample~~ <sup>crystal</sup> was cut along three orthogonal directions. Two sections were cut parallel to (001) and (010). A third section cut perpendicular to these two faces is designated “ $\perp$ ” because plagioclase is triclinic and therefore the perpendicular face is not (100). Values presented for (001) therefore quantify heat flow along **c** while (010) quantifies heat flow along **b**. Although **a** is almost perpendicular to **b**, it is oblique to **c** (angles range from  $115.5^\circ$ - $116.3^\circ$ ), thus the perpendicular orientation does not quantify heat flow along **a**.

~~Sample~~ <sup>samples</sup> sections were ground into discs about 1 cm in diameter and less than 1 mm thick. The top and bottom of each disc were polished to be parallel. Optical microscopy was used to identify any inclusions and twinning. Before analyzing *D*, samples were sputter coated with platinum and then spray coated with graphite. The graphite coating maximizes energy absorption, and ensures that absorbed energy is spread across the surface. The platinum coating helps reduce the amount of direct (or ballistic) radiation through these transparent samples.

Chips from each sample were analyzed using wavelength-dispersive analysis (WDS) on the JXA-8100 electron microprobe at Washington University in St. Louis to quantify major

element chemistry. Accelerating voltage was 15 kV, beam current was nominally 25 nA, beam diameter was 1  $\mu\text{m}$ , and counting times were near 30 s. Various oxide standards were used for calibration. Measurements of three points were averaged to give the chemical formulas of plagioclase samples (Table 1).

### **Measurement of thermal diffusivity**

Thermal diffusivity was measured with the Netzsch LFA427, a laser-flash apparatus. The instrument heats the sample's base briefly with a laser pulse, and records changes in emissions from the top of the sample using a remote IR detector. Basically,  $D$  is calculated using the time taken for the heat from the pulse to travel through a sample of given thickness. This technique is preferred because no contacts exist between thermocouples and the sample; such contacts limit measurements to  $\sim 1200$  K and provide an additional thermal resistance that artificially lowers measured  $D$  values. LFA accounts for the shape of the laser pulse and removes unwanted ballistic radiative transfer using the mathematical model of Mehling et al. (1998). For details, see Pertermann and Hofmeister (2006).

Thermal diffusivities of plagioclase samples were measured at 100 K increments from room temperature up to between 1150-1550 K. At each temperature step, at least three measurements were collected and averaged. Measurements with poor fits between the model and signal were not included in the average. Graphs presented herein show the average of successful measurements. Due to its small size,  $D$  of sample FSU $\perp$  could only be measured at room temperature. Samples FLT and FLC were also measured only at room temperature.

## Results

Plagioclase  $D$  generally decreases with temperature (Figure 2) and can be fit with a third-order polynomial, namely:

$$D = \frac{1}{A + BT + CT^2 + ET^3} \quad (1)$$

Coefficients for the different samples are given in Table 2.

Thermal diffusivity decreases with increased An content (Figure 3). For intermediate values of An, the  $D$  values are very similar; from An<sub>10</sub> and An<sub>65</sub>, room temperature  $D$  decreases from 0.979 to 0.751 mm<sup>2</sup>/s along **c** and 0.919 to 0.767 mm<sup>2</sup>/s along **b**. For comparison,  $D$  along **b** in pure albite is 1.689 mm<sup>2</sup>/s (Hofmeister et al. 2009). The measured value of  $D$  along **c** of 1.354 mm<sup>2</sup>/s is likely too low, because that section was cut too thick, and therefore lost heat through the sample edges. Fracturing along cleavages prohibited preparation of thinner samples. Thermal diffusivity of the anorthite mat is lower than the true anorthite value due to glass present in the polycrystalline sample. Because the anorthite primitive unit cell contains the same number of formula units as albite,  $D$  should be continuous across the series. Extrapolation of plagioclase data to higher An gives a  $D$  value (averaged over the three directions) for pure anorthite of 0.741 mm<sup>2</sup>/s at room temperature and about 0.574 at high temperature (about 1100 K).

For albite, even considering possible errors due to sample thickness,  $D$  along **b** (measured using (010) sample) is higher than along **c** for all temperatures measured (Figure 2a; Hofmeister et al. 2009). This is not the case for all other plagioclase samples studied. Like albite,  $D$  in sample FSU is significantly higher along **b** than **c** (Figure 2a). Although samples FLL and FBM also have greater  $D$  along **b** than **c**,  $D$  values are difficult to distinguish given experimental uncertainty, at least within certain temperature ranges. For sample FBM,  $D_{010}$  and  $D_{001}$  are similar from room temperature up to 768 K, such that  $D$  values diverge as temperature increases


(Figure 2a). Samples FON and FLN both had  $D_{001} > D_{010}$  at lower temperatures, although the  $D$  values crossed over, so that  $D_{010} > D_{001}$  at higher temperatures.

Except for FON and FLN, samples did not change appearance when compared before and after heating in the LFA. During LFA analysis, sample FON was heated above its melting temperature. At about 1580 K, large peaks of direct radiation were detected in FON001 and FON $\perp$ , suggesting that these samples cracked, probably during the growth of lower density melt pockets. Although intact, both samples were netted with two sets of microscopic fractures that formed at angles between 40° to 60° from the **a-c** plane. FON001 had a higher density of cracks, as well as two larger cracks, one ending in a conchoidal fracture, near the sample's edge. There was no evidence wholesale flow (no change in sample shape, for example). However, inclusions visible in this sample pre-heating were not visible after LFA runs, and chains of dark, small dots (glass) appeared mostly along (001) cleavages in FON $\perp$  and along fractures in FON001.

Thermal diffusivity decreases or is constant with temperature at all temperatures measured with three exceptions. Thermal diffusivity increases significantly above 1300 K in FLN001 and FLN010 ( $D$  increases 7-11% from 1320 to 1420 K) (Figures 2b and 4). Furthermore, additional measurements made on cooling show that in both FLN001 and FLN010,  $D$  remained higher upon cooling, at least until a temperature of ~800 K. Sample FLN $\perp$  was not analyzed to as high a temperature as the other two orientations; it might very likely show a similar increase in  $D$  if analyzed at higher temperatures. The recovered sample contains two sets of fractures, one which lines up with the black inclusions. FLN $\perp$  also cracked during analysis. The samples likely cracked on cooling, explaining the lower  $D$  measured during cooling below ~800 K. The cracks also lead to lower room temperature  $D$  measured at a later date (diamond and plus sign in Figure 4).

Sample FON001 has a 5% increase in  $D$  from 1260 to 1460 K (filled gray circles in Figure 2b). That  $D_{001}$  increases following premelting from 1260 to 1460 K may result from dehydration.

### Thermal diffusivity and plagioclase structure

Thermal diffusivity measurements may provide additional insights on plagioclase structure, the complexity of which is compounded by the sluggish kinetics (several samples retain their high temperature structures) and effects of Or and water. 

Thermal diffusivity of albite is much higher than <sup>+D</sup> other members of the plagioclase series. <sup>OF</sup> Likewise, albite is the only sample analyzed that should be well <sup>-</sup>ordered at room temperature. The addition of Al reduces order, and hence reduces  $D$ . Likewise, in intermediate plagioclase, more ordered samples (FON, FLN, FLC) have higher room temperature  $D$  than the more disordered samples (FLL and FBM) (Figure 3).

The direction of maximum  $D$  seems to depend on plagioclase structure (Figure 1b). For samples with  $C\bar{1}$  symmetry,  $D_{010} > D_{001}$ . For all other structures,  $D_{001} > D_{010}$ . In phases with a  $C\bar{1} + e_2$ , the direction of maximum  $D$  depends on the relative amounts of the two phases, which depends on An content. Samples with low An content such as FSU ( $An_5$ ) will have  $D_{010} > D_{001}$ , whereas samples with higher An content such as FON ( $An_{19}$ ) will have  $D_{001} > D_{010}$ . The division between these high and low An contents corresponds to the position of the  $C\bar{1} \leftrightarrow e_2$  boundary extrapolated to lower temperatures. The switch in orientation of maximum  $D$  may suggest that ordering associated with development of the anorthite-like component of the superstructure increases  $D$  preferentially along  $c$ . This would occur if antiphase domains orient such that  $c$  resides almost entirely in the more-ordered domain.



Several of the inflections and crossovers in the  $D^l(T)$  plots correspond to changes in the plagioclase structure. Albite  $D^l(T)$  can be fit linearly, as long as the lines break at about 625 K, a temperature that may mark the high-low albite boundary as the sample disorders upon heating (Figure 5a). The transition seen in LFA is lower than the equilibrium transition in Figure 1. Of the transitions in the phase diagram, only the low to high  $C\bar{1}$  transition does not involve a symmetry change. Similar to the way that LFA “sees” melting at different temperatures than do other techniques, such as viscosimetry (Hofmeister et al. 2009), LFA “sees” the low to high  $C\bar{1}$  transition at a lower temperature than other techniques. In (010), a second inflection occurs at about 1300 K which could mark the transition from  $C\bar{1}$  to  $C2/m$ . Given that this transition is accompanied by a symmetry change, the LFA inflection and equilibrium transition temperature are similar.

In FSU, small inflections at ~850 K in both orientations is close to the transition from low  $C\bar{1} + e_2$  to  $C\bar{1}$  (Figure 5b). The inflection at ~1250 K in  $D^l_{010}(T)$  occurs where expected for the  $C\bar{1} \leftrightarrow C2/m$  transition (1290 K; McConnell 2008). Inflections at about 1050 K in the  $D^l(T)$  plots for both (010) and (001) may reflect that the phase transition is gradual, the sample becoming more like  $C2/m$  with heating as proposed by Prewitt et al. (1976).

The peristerite intergrowths in FON will not diffuse during the brief heating times of the LFA. However, the two components may disorder. If the more Ab-rich component (with a low  $C\bar{1}$  structure) disorders at a different temperature than the intermediate  $e_2$  structure, multiple inflections could exist in the data. An inflection in all orientations at ~800 K corresponds to the expected change from  $e_2 \leftrightarrow C\bar{1}$  (Figure 5c). There is also an inflection in the plot for  $D_{\perp}$  at ~600 K, which may represent the disordering of the  $C\bar{1}$  component.

The crossover of  $D_{010}$  and  $D_{001}$  also results from the change in structure to  $C\bar{1}$  symmetry, even though the crossover temperature for sample FON is hard to pinpoint. The measured  $D$  values for FON001 are slightly larger to 868 K, and by 976 K diffusivity is larger along (010) than along (001), but error bars for  $D$  along the two orientations overlap between 378 and 996 K.

Thermal diffusivity of FON001 and FON $\perp$  drop drastically between 1200 and 1300 K., while  $D_{010}$  decreases slightly at the same temperature. The melting temperature for this composition is about 1400 K (McConnell 2008). Although the presence of OH and K will lower the solidus (Johannes et al. 1994; Parsons 2010), the decrease in  $D$  is consistent with the glass transition as seen by the LFA occurring at temperatures about 100 K lower than the melting temperature (Hofmeister et al. 2009). Because the melting temperature of plagioclase increases with An-content (Figure 1), the more Ab-rich component of the peristerite intergrowth will melt first. Because peristerite intergrowths parallel  $\sim(010)$ , melt will form in the **a-c** plane, and therefore affect  $D_{\perp}$  and  $D_{001}$  more than  $D_{010}$ . As further evidence for differential melting of peristerite, melt (as beads of glass seen in recovered samples) aligns with the (001) cleavage in FON $\perp$ . Beads of glass do not align with (100) in FON001, but follow fractures. This might be expected if melt formed along a **but** then accumulated in fractures. At 1460 K, enough melt exists to crack the sample, allowing direct radiation through the sample that aborted the run. bold

The crossover temperature of FLN is about 850 K, which matches the predicted transition from the Bøggliid intergrowth ( $e_1+e_2$ ) to a high  $C\bar{1}$  structure (about 886 K) (Figure 5d). The  $e_1$  portion of the structure should alter to  $C\bar{1}$  at a lower temperature than the  $e_2$  phase, which explains the width of the transition in temperature space. Above this temperature (in the  $C\bar{1}$  stability field),  $D$  of FLN is considerably lower than for other samples (Figure 2b), until about  $\sim 1400$  K, where  $D$  of both orientations increase to values similar to the other plagioclase samples

of about 0.6 mm<sup>2</sup>/s. Some aspect of FLN's structure, perhaps the Bøggliid intergrowths, restricts  $D$ . As temperature increases, the structure flexes, returning to that expected for  $C\bar{1}$  plagioclase with intermediate An values by 1600 K. The thermal history of the sample might also be responsible for the reset of  $D$  at high temperature. Although originally plutonic, the slowly-cooled anorthosite intrusions were later metamorphosed. Strain imparted during metamorphism might have overprint the lattice in a manner that affects  $D$ .

There are no clear inflections in the  $D^l(T)$  plots for sample FBM (Figure 5e).  $D_{010}$  is greater than  $D_{001}$  at all temperatures, implying that this sample has a  $C\bar{1}$  structure, and cooled quickly enough to preserve that  $C\bar{1}$  structure.

In sample FLL,  $D_{010}$  appears to exceed  $D_{001}$  at room temperature and above 1400 K (Figure 5f). However, the error bars for  $D_{001}$  and  $D_{010}$  in sample FLL overlap at room temperature and again at temperatures greater than 1100 K. Unlike the other samples,  $D_{\perp}$  is similar to the other orientations, being in between  $D_{001}$  and  $D_{010}$  at temperatures below 1000 and above 1400 K, but lower than  $D_{001}$  and  $D_{010}$  between those temperatures. The temperatures of the 1400 K crossover corresponds to the transition between the  $I\bar{1}$  and  $C\bar{1}$  structures, and the crossover is due mainly to a decrease in  $D_{001}$ . In addition to the inflection at 1400 K in  $D^l(T)_{001}$  and  $D^l(T)_{\perp}$ , possible inflections exist at ~1160 K in  $D^l(T)_{010}$ , and at ~1250 K in  $D^l(T)_{001}$ . Despite the fact that FLL is a volcanic sample, the inflections at ~1200 K correspond to the expected transition to an  $e_l$  structure, and suggest that when the crystal formed, cooling was slow enough for this sample to weakly order. The Lake County Labradorite cooled within a thick basaltic lava flow, which also explains the weak  $e$  reflections in the single-crystal x-ray photographs (Wenk 1980). Possible inflections at 600 K in  $D^l(T)_{010}$  and 800 K in  $D^l(T)_{\perp}$  and  $D^l(T)_{001}$  are unexplained, but could reflect a disordering of one of the antiphase domains in the  $e_l$

structure. A further decrease of  $D_{001}$  as temperatures approach 1600 K result from premelting effects.

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### **Thermal diffusivity and thermal expansion coefficient**

The volume coefficient of thermal expansion was calculated for different members of the plagioclase series from measured volumes from Hovis et al. (2010) and Tribaudino et al. (2010), using:

$$\alpha_v = \frac{1}{V_0} \frac{\partial V}{\partial T} \quad (2)$$

where  $V_0$  is the volume at room temperature. Linear fits to  $V(T)$  were appropriate and used to compute  $\alpha_v$ . To determine dependence of  $\alpha_v$  on An content, the two variables were plotted and linearly fit, using different fits for An<40 and An>40 (not shown).

Values of room temperature  $D^{-1}$  are compared with  $\alpha_v$  in Figure 6. As seen by the disagreements of values calculated from different volume data, large uncertainty exists in  $\alpha_v$  (Figure 6). Nonetheless, a clear trend shows that samples with lower thermal expansion coefficients have higher  $D^{-1}$  (lower  $D$ ) values. This is opposite of what was seen in halides (Yu and Hofmeister 2011) and endmember perovskites (Hofmeister 2010), where  $\alpha_v$  and  $D^{-1}$  are positively correlated. In those minerals, higher means the lattice is more responsive to temperature, hence causing more phonon scattering and higher  $D^{-1}$ . In plagioclase, disorder has reversed the trend. Samples with An>40 plot along different trends than do more sodic samples. Although offset, the trends do have similar slopes. The different trends reflect the different structures for minerals with these An contents; this is generally the boundary between  $C\bar{1}$  and

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I $\bar{1}$ . Although lattices of more An-rich samples should be less responsive to  $T$ , effects of higher amounts of Al-Si disorder swamp the lattice impact on  $D$ .

Directional  $D^{-1}(T)$  should go as  $\alpha_L T$ , reflecting the fact that both are governed by anharmonic effects. Because thermal changes in length are small,  $\alpha_L$  is most accurate in the middle of the temperature range. Therefore, lengths of **a**, **b** and **c** for albite (Tribaudino et. al 2010) were plotted at temperatures  $>500$  K and linearly fit.

For the (010) and  $\perp$  samples,  $\alpha_L T$  and  $D^{-1}(T)$  increase similarly with temperature, as expected (Figure 7). This behavior was similarly seen in perovskites and halides (Hofmeister 2010; Yu and Hofmeister 2011). The slope of  $\alpha_L T$  for the **c** orientation is much less than that for  $D^{-1}(T)$ , which causes  $\alpha_L T$  along **a** $>$ **b** $>$ **c**, but  $D^{-1}$  along **a** $>$ **c** $>$ **b**. Albite disorders upon heating. The mismatch in slopes for the (001) sample indicates that additional phonon scattering (due to something that is not the expected lattice effect) enhances  $D^{-1}$  along this orientation. That disordering decreases  $D$  in albite mimics the fact that ordering (due to formation An-like domains, for example) increases  $D$  preferentially along **c**.

### Thermal conductivity

Bulk thermal diffusivities of samples were calculated using:

$$D = \left[ \frac{1}{3} \left( \frac{1}{D_x} + \frac{1}{D_y} + \frac{1}{D_z} \right) \right]^{-1} \quad (5)$$

where  $D_x$ ,  $D_y$  and  $D_z$  are diffusivities along three orthogonal directions.

Thermal conductivity ( $k$ ) is then calculated as:

$$k = D \frac{c_p}{\rho} \quad (6)$$

Heat capacities vary only slightly for different members of the plagioclase solid solution (Figure 8). Nonetheless, thermal conductivities were calculated using An-specific heat capacity values from Benisek et al. (2009). Densities were calculated using temperature-dependent molecular volumes, which were assumed to vary linearly with An content, using albite and anorthite values from Holland and Powell (1998). Thermal conductivities are not very sensitive to the choice of density. Measured volumes from Tribaudino et al. (2010) give very similar  $k$  values. The resulting thermal conductivity values change little with temperature for all but the most albite-rich plagioclase (Figure 8).



### **Plagioclase when compared with previous studies and other major rock forming minerals**

Although albite and potassium feldspar minerals have been previously analyzed, measurements of plagioclase heat transfer properties are rare in the literature. An exception is a study by Magnitskiy (1971) of a labradorite (density of 2.67 g/cm<sup>3</sup>) and an oligoclase (density of 2.63 g/cm<sup>3</sup>). Specific An contents were not reported. Thermal diffusivities were measured to 1200 K with plane-periodic wave method, which involves one thermocouple attached to the sample; the samples were not oriented crystals. Their data is in decent agreement with our measurements; the oligoclase values are slightly higher than ours to 800 K, and their labradorite values are on the low end of our labradorite measurements at temperatures up to 1000 K (Figure 9).

Linville (1987) measured thermal diffusivity of Madagascar albite (Ab<sub>99</sub>An<sub>1</sub>, ρ=2.622), Nain labradorite (Ab<sub>48.7</sub>An<sub>48</sub>Or<sub>3.3</sub>, ρ=2.695), Lake St. John labradorite (Ab<sub>33</sub>An<sub>65.5</sub>Or<sub>2</sub>), and Lake

County labradorite ( $\text{Ab}_{31}\text{An}_{68}\text{Or}_1$ ,  $\rho=2.71$ ) at low temperatures using a divided bar technique and to about 500 K using the modified Ångström method. The long axes of the samples were 010 in albite,  $11\bar{2}$  in the Nain sample, and  $20\bar{3}$  in the Lake County sample. Orientations for the Lake St. John sample were not given. Data from attained with the modified Ångström method are shown in Figure 9. Lake County and Lake St. John data are slightly lower than ours, and data from the Nain labradorite are higher than ours, due to various amounts of radiative gains and contact losses.


When compared with other common rock-forming minerals, plagioclase has one of the lowest thermal diffusivities, both at room temperature and higher temperatures (Figure 10). Of the major families of rock-forming minerals, quartz and olivine have the highest thermal diffusivities. In general, thermal diffusivity is linked to the number of active IR modes in a mineral, which is determined by number of atoms and structure in a given unit cell. Quartz and olivine have few modes compared to orthopyroxene and garnets, and thus plot higher in Figure 10.

## Conclusions

Laser-flash analysis of plagioclase feldspars reveals clues about the feldspar structure, as inflections in the  $D(T)$  curves occur at temperatures expected for phase transitions. Fast heating and cooling during LFA measurements do not allow for atomic diffusion, but nonetheless result in structural changes to the tetrahedral framework. In all minerals,  $D$  decreases upon heating as more phonons lead to increased phonon scattering. Plagioclase  $D$  is further affected by disordering upon heating. For example,  $D$  drops in all samples during the transition to  $C\bar{1}$  symmetry.

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Likewise, disorder accompanying Al/Si substitution causes  $D$  of plagioclase to decrease with increasing anorthite content. The decrease seems mostly continuous across the solid solution, regardless of the crystallization temperature and/or cooling history of the sample. This suggests that ordering/disordering dictated by structure at a given composition is minimal compared with ordering/disordering dictated by An contents.

With regards to applying measured  $D$  values to geological problems, two main  conclusions can be reached. First, thermal conductivity values for plagioclase can easily be approximated. When combined with heat capacity and density,  $D$  give similar room temperature thermal conductivity values (between about 1.5 and 1.9  $\text{Wm}^{-1}\text{K}^{-1}$ ) for all plagioclase samples containing some Ca. Also, thermal conductivity changes little with temperature. Secondly, that  $D$  is lower for plagioclase (at all temperatures) than for other major rock-forming minerals suggests that plagioclase will dictate lower bounds of  $D$  and  $k$  in plagioclase-bearing rocks, especially mafic rocks in Earth's crust.

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## Figure captions

### Figure 1

Phase diagram for plagioclase showing (a) major structures (modified from Parsons (2010) and McConnell (2008), with the low to high  $C\bar{I}$  transition from Carpenter (1994)) and (b) the direction of maximum  $D$  for the different structures using measurements from the present study. Location of the  $C\bar{I}/I\bar{I}$  boundary (heavy black line) agrees with data from Carpenter et al. (1984). Pe, Bø, Hü are the peristerite, Bøggliid and Hüttenlocher intergrowths, respectively. More uncertainty exists in the low temperature portion of the diagram than in the upper due to sluggish kinetics. Locations of the upper phase boundaries are affected by Or contents. For example, adding K lowers  $T$  of the low to high  $C\bar{I}$  transition as well as the solidus (Parsons 2010). The solidus decreases with increased  $P_{H_2O}$  by up to 400 K (Johannes et al. 1994).

### Figure 2

Thermal diffusivities versus temperature for (a) samples FON (filled gray), FBM (open black), and albite (filled black, from Hofmeister et al. (2009)), and (b) samples FLN (filled gray), FSU (filled black), FLL (open black) and anorthite mat (black diamonds). Measurements made on (010) are shown as squares, on (001) are shown as circles, and on perpendicular sections are shown as triangles. Error bars are included, but many are smaller than the symbol size. Larger error bars for albite (001) reflect uncertainty due to ~~extreme~~ sample thickness.

excessively large

### Figure 3

Thermal diffusivity versus An content. Measurements made on (010), (001) and  $\perp$  are shown with squares, circles and triangles, respectively. Black symbols show values measured at room temperature, and gray symbols show values measured at about 1100 K. Measurements made on (010) are shown as squares, on (001) are shown as circles, and on perpendicular sections are shown as triangles. The high temperature square and circle symbols for FON plot in the same place.

### Figure 4

Thermal diffusivity measured as sample FLN cooled from 1600 K (filled symbols) was higher until about 800 K. Measurements made upon cooling at lower temperatures, as well as room

temperature  $D$  measured many days later (010=cross, 001=diamond), were lower than the original measurements (open symbols) due to cracks in the sample. Measurements made on (010), (001) and  $\perp$  are shown with squares, circles and triangles, respectively.

#### Figure 5

Inverse thermal diffusivities for samples (a) albite, (b) FSU, (c) FON, (d) FLN, (e) FBM and (f) FLL. Inflections in  $1/D$  plots (short double lines) correspond to approximate positions of phase transitions marked, and long double lines show the expected position of the solidus (see Figure 1). Measurements made on (010), (001) and  $\perp$  are shown with squares, circles and triangles, respectively. Fits from Table 2 are shown as lines in figure 5e. Arrows in figures 5c and 5f show the decrease in  $D$  due to melting or premelting. Larger error bars for albite (001) reflect uncertainty due to extreme sample thickness.

#### Figure 6

Correlation of room temperature values of  $1/D$  (averaged for the three orientations) with  $\alpha_v$ . Because only two orientations were measured, sample FLC is not shown in the diagram.  $\alpha_v$  was calculated using data from two different sources, squares= Tribaudino et. al (2010) and circles = Hovis et al. (2010). Linear fits to samples with  $An < 40$  and  $An > 40$  are shown (grey=Tribaudino; black= Hovis).

#### Figure 7

$D^{-1}(T)$  from fits in Table 2, and  $\alpha_L T$  calculated from unit cell parameters (Tribaudino et al. 2010) for the different samples measured to high temperature. Albite fits are from Hofmeister et. al (2009).

#### Figure 8

Heat capacity (dashed lines) is compared with thermal conductivity (various solid and dotted lines) for plagioclase samples. Albite heat capacity is shown in black, and thermal conductivity is shown with heavy black line. Also shown are thermal conductivities of FON (heavy dark gray), FLN (long dash-dot), FBM (thin black), and FLL (heavy light gray). Most thermal conductivities calculated with volumes from Tribaudino et. al (2010) are similar to those

calculated using Holland and Powell (1998), as shown for albite (dotted black). FON (gray dotted) shows more dissimilarity. Because  $D$  was only measured in two of the three orientations,  $k$  of FSU was not calculated.

#### Figure 9

Comparison of our data (shaded and outlined box) with data for labradorite (squares) and oligoclase (circles) samples from Magnitskiy (1971), and for labradorite samples (Linville 1987) from Nain (squares with crosses), Lake St. John (squares with diagonals) and Lake County (open squares).

#### Figure 10

Summary of thermal diffusivity of important mineral families; plagioclase  $D$  values (triangles) are among the lowest of all rock forming minerals, both at room temperature ( $D_{298}$ ) and at high temperature ( $D_{highT}$ ). Plagioclase  $D_{highT}$  measured at  $\sim 1350$  K for all samples measured in this study (does not include albite). Data for all orientations of other minerals are plotted along with lines of best fit; data were taken from the following references and used the following values for  $D_{highT}$ : quartz (open squares), with highT value from  $\beta$ -quartz at  $\sim 1100$  K (Branlund and Hofmeister 2007); olivine (gray diamonds), used “high temperature”  $D$  (Table 2, Pertermann and Hofmeister 2006); clinopyroxene (black squares), used  $D_{sat}$  (Pertermann and Hofmeister 2008); orthopyroxene (square with X), used  $D$  at  $\sim 1200$  K (Hofmeister, 2011); garnet (gray dots), used  $D_{sat}$  (Hofmeister 2006); spinel (black dots), used  $D$  at  $\sim 1000$  K (Hofmeister 2007). Sanidine ( $D_{highT}$  at  $\sim 1200$  K) and albite ( $D_{highT}$  at  $\sim 1075$  K) mark the alkali feldspar (open circles) trend (from Pertermann et al. 2008 and Hofmeister et al. 2009, respectively). Only single crystals with high temperature measurements of multiple orientations were plotted. The lines of best fit for clinopyroxene and orthopyroxene overlap, and are labeled “pyroxene.” Trends correlate with number of infrared (IR) modes as labeled.