Thermal diffusivity of clinopyroxenes at elevated temperature

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Abstract: The phonon component of thermal diffusivity (D) was measured from 8 single-crystals and 2 polycrystalline clinopyroxene samples at temperatures (T) up to a maximum of ~1000 to 1600 K, using laser-flash analysis. Electron microprobe analysis shows that we have two samples of near end-member diopside, two augites, one end-member and one impure jadeite, aegerine, and three near end-member spodumenes. Hydroxyl contents determined from near-IR spectroscopy range from ~0 to 70 ppm as H2O. Two directions constrain D for clinopyroxenes, consistent with phonon symmetry. Anisotropy = (D∥sat − D⊥)/D∥ is near 40 % for all samples and independent of T, where | and ⊥ indicate the direction heat flows relative to the c-axis. Thermal diffusivity decreases with increasing T and approaches a constant (D∥sat) near 1400 K. The temperature dependence of 1/D is well described by low-order polynomial fits. At 298 K and for near end-member compositions, cation mass and bond lengths strongly affect D∥ whereas D⊥ is essentially constant and large, 3.9 mm²/s⁻¹. For solid solutions, D at 298 K decreases from end-member values as impurity content increases, but D at saturation is little affected. Excluding Li-rich clinopyroxenes, D∥sat ~ 0.5 mm²/s⁻¹ and D⊥sat ~ 0.9 mm²/s⁻¹. The values pertain to lithospheric and mantle compositions of clinopyroxene above 1400 K, and lead to bulk thermal conductivity at saturation being 2.4 Wm⁻¹K⁻¹. Pressure derivatives are predicted from models as ∂(ln k)/∂P = 4.2 to 4.7 %GPa⁻¹.

Key-words: Laser-flash method, high-temperature, thermal diffusivity, thermal conductivity, IR spectroscopy, clinopyroxene.

Introduction

Monoclinic pyroxenes are important rock-forming minerals containing a wide range of ionic substitutions (e.g., Cameron & Papke, 1980). Compositions rich in end-member diopside (CaMgSi₂O₆) occur in metamorphic rocks, basalts, and mantle xenoliths. Those rich in aegirine (NaFe³⁺Si₂O₆) crystallize from alkaline magmas. Low-temperature, high-pressure metamorphic rocks contain clinopyroxenes near jadeite (NaAlSi₂O₆) composition. Augites contain solid solutions of the above end-members, with additional substitution of Fe²⁺, Ti, and Cr, and are essential components of gabbros and basalts. Rare spodumene is near end-member (LiAlSi₂O₆) and exists in granitic pegmatites. Model compositions of Earth’s upper mantle contain 10–20 % diopсидic clinopyroxene (e.g., Agee, 1998), and the oceanic crust consists of an upper layer of basalt underlain by mafic and ultramafic cumulates, all containing substantial clinopyroxene (e.g., Best, 1982).

Heat transport properties of minerals are poorly constrained, despite their importance to models of conductive and convective heat flow. For clinopyroxenes, thermal diffusivity (D) or thermal conductivity

\[ k = \rho C_p D \]  

have been studied by contact methods (Horai, 1971; Kobayashi, 1974), which underestimate k or D near 298 K due to losses at interfaces between sample and heater or thermocouple, but overestimate results above ~600 K due to unwanted radiative transfer (e.g., Hofmeister, 2006, 2007a; Pertermann & Hofmeister, 2006; Hofmeister et al., 2007). The present report uses contact-free, laser-flash analysis (LFA; e.g., Parker et al., 1961) which removes spurious photon transfer and accurately (~2 % uncertainty) provides the component of heat transfer originating through phonon scattering (lattice conductivity, kphonon).

We measured D(T) for eight different clinopyroxene single-crystals and two polycrystalline samples. The only type not represented is pigeonite (low Ca, high Mg and Fe), due to lack of homogeneous, large samples. All samples crystallize in C2/c. Specimens were characterized by electron microprobe analysis and optical spectroscopy. Comparison with the damped harmonic oscillator (DHO) model (e.g., Hofmeister, 1999; Hofmeister et al. 2007) is made to better understand microscopic origins of heat transport.
We show that pyroxenes are more efficient in transporting heat than previously thought, and use our results to provide $D(T, P)$ and $k(T, P)$ for compositions considered appropriate to Earth’s mantle.

**Experimental methods**

**Sample preparation**

Samples were oriented using a microscope, and then cut, ground, and polished into slabs of 6–16 mm diameter with thicknesses of 0.6–2.8 mm. After spectroscopic and electron microprobe measurements, samples were sand-blasted with alumina grit of 50–150 μm to roughen the surface. For (010) of Na-rich diopside only, a thin Au sputter coat about 1/2 μm thick was applied and overcoated with graphite spray. The remaining samples were spray coated with graphite only. Total coating thicknesses of ~1 μm negligibly affect measurements of $D$. See Pertermann & Hofmeister (2006) for details.

**Selection of crystallographic orientation and polarization**

Four measurements are needed to define the principle axes for $D$ in monoclinic structures (Nye, 1985). Anisotropy in $D$ is linked to behavior of the phonons. For clinopyroxenes, only two symmetry species exist for its infrared (IR) modes (Zulumyan et al., 1975): $A_x$ species absorb when the electric field is parallel to the $y$-axis (the $β$ polarization) whereas $B_x$ species have the maximum absorption anywhere in $x$-$z$ plane, (010). The structure contains chains of silica tetrahedra along the $z$ axis, which suggests that the $z$ direction and (by default) $x$ in (010) are likely to depict the maximum contrast in absorption or in thermal diffusivity, as is the case for the IR vibrations (Zulumyan et al., 1975). We therefore obtained $D$ from (001), a few sections not quite perpendicular to $c$, and at least one of (100), (010), or the cleavage plane (110). The size and shape of the crystal determined which sections were used. Furthermore, clinopyroxenes have strong (110) cleavage. For (100) and (010) orientations, heat diffusing upwards crosses cleavage planes, which may contribute thermal resistance by providing "gaps" through which phonons cannot propagate (e.g., Fried, 1969). For (110), the cleavage planes are oriented vertically and should not impede flow of heat.

Optical spectra were collected along and perpendicular to the optical directions and/or crystallographic axes.

**Chemical characterization**

Wavelength-dispersive analysis (WDS) was performed using the JXA-8100 electron microprobe at Washington University. Accelerating voltage was 15 kV, beam current was nominally 25 nA, beam diameter was 1 μm, and counting times were near 30 s. Various oxide standards were used for calibration. Two points were measured on each sample as most of the material appeared to be optically homogeneous. For spodumene, Li contents were assumed. These two compositions were averaged and reported as formula such that the sites were filled and the charge was balanced (Table 1). Some cases required iron to be ferric.

**Near-IR to visible spectroscopy**

We used an evacuated Bomem DA3.02 Fourier transform interferometer with an SiC source, a InSb detector, a CaF$_2$ beamsplitter, and a wire-grid polarizer. This instrument is accurate to 0.01 cm$^{-1}$, and thus peak breadth largely determines uncertainties in peak positions. About 2000 scans were collected at room temperature from ~1800–6000 cm$^{-1}$ at a resolution of 2 cm$^{-1}$. A calcite polarizer, quartz lamp and quartz beamsplitter were used for ~5000–12 000 cm$^{-1}$. A Si-avalanche detector was used for ~10 000 to 21 000 cm$^{-1}$, but because this region added little information, it is not reported. Spectral segments were merged and absorption coefficients ($A$) were calculated from thickness ($t$):  

$$A t = -\log(I_{\text{trans}}/I_0).$$

(2)

Hydroxyl contents (X, in ppm H$_2$O by weight) can be reliably determined for Ca-rich clinopyroxenes using the calibration of Bell et al. (1995):

$$X = qA^*/L$$

(3)

where the calibration coefficient $q = 0.141 \pm 0.006$, $L$ is thickness in cm, and $A^*$ in cm$^{-1}$ is total integrated peak absorbance over 3200–3650 cm$^{-1}$. Ideally, $A^*$ is the sum of areas from each of the three polarizations, which were baseline corrected. Our samples have bands up to 3680 cm$^{-1}$, and this area was included in the computation. Using a larger interval does not add much uncertainty because some polarizations were not measured and their contributions were assumed to be similar to those of the other polarizations. For Na- and Li-rich samples, equation (3) provides estimates only, see Koch-Müller et al. (2004) for discussion.

**Laser-flash analysis and data processing**

Thermal diffusivity was measured with an LFA 427 apparatus manufactured by Netzsch Gerätebau, Germany. Specimens are suspended in a graphite holder, allowing analysis of a circular area with diameter of 6 or 10 mm. The sample is in an Ar gas atmosphere in the hot-spot zone of a furnace and the temperature dependence of $D$ is obtained by varying furnace temperature. Graphite coatings on the sample (which block laser light and enhance absorption of the pulse and sample emission) and the graphite sample holder buffer oxygen fugacity. A single pulse from an Nd-GGG laser heats the sample from below. As heat difuses from the bottom to the top of the sample, emissions are monitored by an InSb detector mounted above the sample. Because sample temperature is directly related to emissions,
raw data are acquired as time-temperature curves (Fig. 1). Accuracy in \( D \) is \( \pm 2 \% \), as verified against opaque and soft standard reference materials. Uncertainties are largely associated with determining sample thickness. For details and calibration procedures, see Blumm & Lemarchand (2002), Hofmeister (2006) and Pertermann & Hofmeister (2006).

Data were obtained at \( \sim 50 \) K intervals with three acquisitions at each temperature. The algorithm of Mehling et al. (1998) was used to extract thermal diffusivity from the raw data (Fig. 1). Their model accounts for both 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 detailed values of optical properties are not needed. The measured shape of the laser pulse was taken into account (Blumm & Opfermann, 2002). The amount of direct radiative transfer is negligible at all \( T \) for dark samples (Ti-rich augite, aegirine). Small amounts of radiative transfer that increased with temperature were seen for jadeite and spodumene: large amounts were not seen because high temperatures were not reached. For pale diopside and augite, the amount of radiative transfer is small at low \( T \) and steadily increases, becoming quite large at the maximum temperatures, but is still reproduced by the model (see examples in Fig. 1). The amount of radiative transfer decreases as absorbance increases. Absorbance differences exist between the various orientations, due to polarized behavior of the d-d transitions in the near-IR. For any given orientation, the increase is caused by an increase in Fe content.

**Sample descriptions and characteristics**

**Spectroscopic characterization of hydroxyl and transition metal ions**

Ti-rich augite was too absorbent for quantitative analysis using optical spectroscopy. Large amounts of physical scattering prohibited spectral acquisition for cloudy spodumene and jadeite.

Hydroxyl absorptions vary in widths (Fig. 2). Full widths at half maximum of roughly 6, 20, 60, 90, and 160 cm\(^{-1}\) for kunzite, Fe-rich diopside, Na-rich diopside, augite, and aegirine, respectively, correlate with the amount of cation substitutions and the number of sites affected. However, the spectrum of Na-rich diopside indicates alteration and Fe-rich diopside has amphibole bands (Fig. 2b), common in pyroxene (Skogby et al., 1990). Our aegirine spectra resemble those of omphacite (Koch-Müller et al., 2004) and our diopside and augite spectra resemble those of other calcic clinopyroxenes (Skogby et al., 1990).

Water contents obtained from equation (3) (Table 1) also correlate with extent of cation substitutions. Uncertainties are \( \sim 20 \% \) for the calcic samples, but \( \text{OH}^- \) content may be overestimated by a factor of 2 for kunzite and aegirine. Hydroxyl contents are similar to amounts determined for the 51 pyroxenes surveyed by Skogby et al. (1990). We included alteration and amphibole water in our estimates (Table 1).

Our spectrometer probes the d-d transitions of \( \text{Fe}^{2+} \) in the clinopyroxenes. None were detected in spodumene, consistent with presence of ferric iron and manganese. The overall absorbance in the near-IR and visible regions increases in the order Na-rich diopside, Fe-rich diopside, augite, and aegirine, \( \text{i.e.} \), as indicated by the coloration (described in Table 1).

Ca-rich pyroxenes have a weak, broad band near 4300 cm\(^{-1}\) that has been assigned to \( \text{Fe}^{2+} \) at the M2 site (see Rossman, 1980, 1988). The intensity of the band increases with \( \text{Fe}^{2+} \) content for the three samples, but a quantitative comparison was not made because different orientations were examined (Fig. 2a, b). Peak positions, relative intensities and polarizations are similar to those of augite examined by Rossman (1980).

Thicknesses appropriate for thermal diffusivity measurements are too large to obtain good quality optical spectra from aegirine. The noisy spectra (not shown) for \( \text{E|x and E|y} \) each have a band near 4600 cm\(^{-1}\), similar to previous results (Amthauer & Rossman, 1984).
Table 1. Sample characteristics and chemical composition.

<table>
<thead>
<tr>
<th>Name</th>
<th>Location</th>
<th>Source</th>
<th>Formula*</th>
<th>X* ppm H₂O</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-rich diopside</td>
<td>DeKalb, NY</td>
<td>NMN‡</td>
<td>[Na₄₀₂₆Ca₉₄₆(OH)₅](Mg₀₉₄₆Fe₀₂₄₆Mn₀₀₃₆Al₀₉₆₅(Ti₀₀₆₅Si₁₉₉₅)O₆</td>
<td>4</td>
<td>Pale green</td>
</tr>
<tr>
<td>Fe-rich diopside</td>
<td>Piedmont, Italy</td>
<td>Excalibur</td>
<td><a href="Mg%E2%82%80%E2%82%89%E2%82%80%E2%82%83%E2%82%85Mn%E2%82%80%E2%82%80%E2%82%83%E2%82%86">Ca₁₀₁₀</a>Si₁₀₀₃₅O₆</td>
<td>15</td>
<td>Light green</td>
</tr>
<tr>
<td>Augite</td>
<td>Unknown, Forstburg, Germany</td>
<td>ThaiGem</td>
<td>[Na₀₂₀₆Ca₀₉₄₆(OH)₅](Ca₄₀₃₈Mg₀₉₃₆Fe₀₉₃₆Mn₀₀₃₆Al₀₉₆₅(Ti₀₀₆₅Si₁₉₉₅)O₆</td>
<td>70</td>
<td>Medium green</td>
</tr>
<tr>
<td>Ti-rich augite</td>
<td>Washington U.</td>
<td>ThaiGem</td>
<td>[Fe₀₉₃₆Al₀₉₃₆Si₁₉₉₅](Ca₄₀₃₈Mg₀₉₃₆Fe₀₉₃₆Mn₀₀₃₆Al₀₉₆₅(Ti₀₀₆₅Si₁₉₉₅)O₆</td>
<td>n.d.</td>
<td>Black, mineral inclusions</td>
</tr>
<tr>
<td>Aegirine</td>
<td>Mt. Malosa, Zomba, Malwi</td>
<td>Excalibur</td>
<td>[Fe₀₉₃₆Al₀₉₃₆Si₁₉₉₅](Mn₀₀₃₆Fe₀₉₃₆Mn₀₀₃₆Fe₀₉₃₆Mn₀₀₃₆Al₀₉₆₅(Ti₀₀₆₅Si₁₉₉₅)O₆</td>
<td>60</td>
<td>Dark green</td>
</tr>
<tr>
<td>Jadeite</td>
<td>Burma</td>
<td>ThaiGem</td>
<td><a href="Al%E2%82%81%E2%82%80%E2%82%80%E2%82%80%E2%82%85Al%E2%82%80%E2%82%80%E2%82%80%E2%82%81Si%E2%82%81%E2%82%89%E2%82%89%E2%82%85">Na₀₉₇₄Ca₀₉₄₆(Mg₀₀₀₁Fe₀₀₀₁Mn₀₀₀₁Al₀₀₀₁)</a>O₆</td>
<td>n.d.</td>
<td>Very pale green fibrous mat</td>
</tr>
<tr>
<td>Fe³⁺-bearing jadeite</td>
<td>Clear Creek, San Benito Co, CA</td>
<td>U.C. Davis</td>
<td><a href="Al%E2%82%81%E2%82%80%E2%82%80%E2%82%80%E2%82%85Al%E2%82%80%E2%82%80%E2%82%80%E2%82%81Si%E2%82%81%E2%82%89%E2%82%89%E2%82%85">Na₀₉₇₄Ca₀₉₄₆(Mg₀₀₀₁Fe₀₀₀₁Mn₀₀₀₁Al₀₀₀₁)</a>O₆</td>
<td>n.d.</td>
<td>Lt. grey-green Fibrous mat</td>
</tr>
<tr>
<td>Spodumene</td>
<td>Ambatomoninty, Madagascar</td>
<td>Excalibur</td>
<td><a href="Al%E2%82%80%E2%82%80%E2%82%80%E2%82%81Si%E2%82%81%E2%82%89%E2%82%89%E2%82%85">Li₀₉₉₆Mn₀₀₀₁Fe₀₀₀₁Al₀₉₆₅</a>O₆</td>
<td>&lt; 1</td>
<td>Colorless</td>
</tr>
<tr>
<td>Spodumene C Gerais, Brazil</td>
<td>Araçuaí, Minas Whittington</td>
<td>A.G.</td>
<td><a href="Al%E2%82%80%E2%82%80%E2%82%80%E2%82%81Si%E2%82%81%E2%82%89%E2%82%89%E2%82%85">Li₀₉₉₆Mn₀₀₀₁Fe₀₀₀₁Al₀₉₆₅</a>O₆</td>
<td>n.d.</td>
<td>Cloudy white</td>
</tr>
<tr>
<td>Kunzite</td>
<td>Resplendor, Brazil</td>
<td>Schooler’s</td>
<td>[Li₀₉₉₆Mn₀₀₀₁Al₀₉₆₅Si₁₉₉₅]O₆</td>
<td>8</td>
<td>Light pink</td>
</tr>
</tbody>
</table>

*Water contents are approximate, and include alteration present within the sample; n.d., not determined due to sample being too dark (Ti-rich augite) or opaque due to physical scattering (jadeite, cloudy spodumene).
†Fe is ferrous unless indicated otherwise. For the three spodumenes, Li assumed to be 1 pfu in computing the oxide totals, which may have led to the Si site being slightly underfilled, since a small amount of Na exists, replacing the Li. [ ] = large octahedral site, ( ) = small octahedral site, { } = tetrahedral site.
‡National Museum of Natural History, sample number R18682.
Thermal diffusivity of clinopyroxenes at temperature

**Thermal diffusivity results**

**General trends**

Thermal diffusivity is highest at room temperature, and decreases with rising temperature, such that the slope $|\partial D/\partial T|$ decreases as $T$ increases unless the sample transforms (Fig. 3). Sections containing the $c$-axis [(100), (010), or (110)] all have nearly the same thermal diffusivity (designated $D_{lc}$ to emphasize the direction of heat flow) which is $\sim 40\%$ less than $D$ than from (001), denoted $D_{lc}$. Sections slightly misoriented from (001) have lower $D$ than (001), confirming that maximum heat transfer occurs parallel to $c$. Because (010) slabs are a special direction (the crystallographic $b$-axis and the principle axis $\beta$ and polarization of $A_u$ modes all coincide) and other planes containing the $c$-axis all give the same $D$ values as (010), as shown below, two directions suffice to characterize $D$ in the clinopyroxenes studied here.

Above $\sim 1400$ K, thermal diffusivity becomes constant ($D_{sat}$), within the uncertainties of measurement. Such a high temperature was not reached for jadeite, as the...
Fig. 3. Thermal diffusivity of clinopyroxene as a function of temperature. Solid or broken curves = fits listed in Table 1, unless labeled otherwise. Symbols show the average of three datapoints (six at room temperature). Error bars are generally smaller than the symbol, except at room temperature, where the uncertainty in \( D \) is about twice the size. Squares = (001) sections; triangles = slabs nearly (001); circles = (100); diamonds = (010); plus, cross, or \( X = (110) \). Right-triangles = polycrystals. (a) Near end-member diopsides. \( D \) of (110), (010), and (100) lie on the same trends. The Na-rich (grey, open circles, square with cross) and Fe-rich samples (+, filled black symbols) fall on the same trends. (b) Solid solution clinopyroxene. Black squares, + and \( X = aegerine \). Filled circles = Ti-rich augite. Grey and triangles = augite. Distinct trends are seen for Ca- and Na-rich samples, which are lower than \( D(T) \) for diopside (shown as dotted lines). (c) Jadeite. Samples are as labeled. Dotted curves = fits for single-crystal aegirine (approximately NaFeSi\(_2\)O\(_6\)). (d) Spodumene. \( D \) of the cloudy sample (open square and cross) is lower than that of the inclusion-free kunzite (grey) and spodumene (X, filled square and triangle). Dotted curve = fits for nearly pure NaAlSi\(_2\)O\(_6\), close to (110).

Polycrystalline mats deformed at about 900 K, nor for spodumene, which shattered near 1100 K. Samples with more extensive solid solution tend to reach saturation at lower temperature and have greater curvature (aegirine, Na-rich diopside, and Fe\(^{3+}\)-bearing jadeite). Results below saturation are best represented by fitting \( 1/D \) to a low-order polynomial in \( T \) (Table 2), consistent with the damped harmonic oscillator model, such that the coefficients for all chemical compositions are fairly well constrained and near 0 mm\(^2\) s\(^{-1}\), +0.002 mm\(^2\) K\(^{-1}\) s\(^{-1}\), and \(-6 \times 10^{-7}\) mm\(^2\) K\(^{-2}\) s\(^{-1}\), respectively. For samples that reached saturation, the fit describes the curvature up to the flat region (Table 2). However, this polynomial fit can be extrapolated to a few hundred K above the fitted region. Other functions or fitting \( D \)
to a polynomial in $T$, do not describe the data well: see Hofmeister (2006, 2007a) and Hofmeister et al. (2007).

### Diopside

Accurately oriented sections of these two samples give virtually the same $D(T)$ (Fig. 3a). The greatest difference ($<0.02 \text{ mm}^2 \text{s}^{-1}$) occurs at 298 K (Table 2). This behavior is consistent with these two samples having similar amounts of impurity atoms: both samples are within $\sim 8\%$ of end-member, such that the Na-rich sample is purer, but all sites are affected by substitution, whereas only MI of the Fe-rich sample is involved. Large amounts of radiative transfer between the graphite layers (Fig. 1) and the expectation of melting just below 1670 K limited our runs to $\sim 1600$ K. Saturation occurs for $T > 1400$ K, within the uncertainties of measurement. Simple power-law fits match $D(T)$ only at very low temperature ($<500$ K, Fig. 3a). Polynomial fits to $1/D$ are needed to describe values over a wide range of temperatures (Table 2).

Sections containing to the c-axis ([010], [001], and [110]) have nearly the same trends in $D(T)$. Large amount of radiative transfer in (100) (Fig. 1), decreases the accuracy of determinations of $D$ at very high $T$. Section (010) of Na-rich diopside provides the most accurate data because cleavage was absent and coating with Au reduced radiative

### Table 2. Run conditions and fits to thermal diffusivity at temperature.

<table>
<thead>
<tr>
<th>Name</th>
<th>face</th>
<th>$L$</th>
<th>$S$</th>
<th>$D_{293}$</th>
<th>$D_{473}$</th>
<th>$T_{sat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-rich diopside</td>
<td>100</td>
<td>1.24</td>
<td>~ 7</td>
<td>2.54(8)</td>
<td>0.47</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>010</td>
<td>1.07</td>
<td>~ 7</td>
<td>2.40(5)</td>
<td>0.57</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>~ 001</td>
<td>1.05</td>
<td>6 x 8</td>
<td>3.83(4)</td>
<td>-</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>001</td>
<td>1.30</td>
<td>~ 6</td>
<td>3.97(30)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Fe-rich diopside</td>
<td>100</td>
<td>1.074</td>
<td>10 x 12</td>
<td>2.33(4)</td>
<td>0.46</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>1.18</td>
<td>11 x 13</td>
<td>2.31(4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Augite</td>
<td>010</td>
<td>0.605</td>
<td>6 x 8</td>
<td>1.55(1)</td>
<td>~ 0.50</td>
<td>~ 1400</td>
</tr>
<tr>
<td></td>
<td>001</td>
<td>1.141</td>
<td>8 x 8</td>
<td>2.73(8)</td>
<td>0.88</td>
<td>1400</td>
</tr>
<tr>
<td>Ti-rich augite</td>
<td>100</td>
<td>1.685</td>
<td>12 x 15</td>
<td>1.19(3)</td>
<td>-</td>
<td>1.5633</td>
</tr>
<tr>
<td>Aegirine</td>
<td>110</td>
<td>1.279</td>
<td>8 x 11</td>
<td>1.42(3)</td>
<td>0.49</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>1.13</td>
<td>12 x 14</td>
<td>1.48(3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>001</td>
<td>1.28</td>
<td>8 x 10</td>
<td>2.76(5)</td>
<td>0.94</td>
<td>-</td>
</tr>
<tr>
<td>Jadeite</td>
<td>n.a.</td>
<td>2.745</td>
<td>10 x 12</td>
<td>2.79(9)</td>
<td>0.86  &gt; 1000</td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$-bearing jadeite</td>
<td>n.a.</td>
<td>1.555</td>
<td>10 x 12</td>
<td>1.84(10)</td>
<td>0.71</td>
<td>1100</td>
</tr>
<tr>
<td>Spodumene</td>
<td>010</td>
<td>1.10</td>
<td>12 x 12</td>
<td>2.28(4)</td>
<td>~ 0.7</td>
<td>~ 1200</td>
</tr>
<tr>
<td></td>
<td>001</td>
<td>1.42</td>
<td>~ 10</td>
<td>3.93(5)</td>
<td>~ 1.1</td>
<td>~ 1200</td>
</tr>
<tr>
<td>Spodumene C</td>
<td>110</td>
<td>1.655</td>
<td>12 x 15</td>
<td>2.10(9)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kunzite</td>
<td>110</td>
<td>0.789</td>
<td>~ 6</td>
<td>2.19(4)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Notes:** All fits had residuals better than 0.99.

*Low temperature only.
†Sample warped above $\sim 900$ K.
‡Sample shattered near 1100 K.
§Obtained from fitting data.
¶Fit combines the data from two different slabs of (110).
||Best representation of diopside data.
@Adding an offset of $-0.04 \text{ mm}^2 \text{s}^{-1}$ this fit will provide $1/D$ for a correctly aligned (001) section.
|||Fitting all data up to 1200 K provides $1/D = -0.10654 + 0.0017602T - 5.0944 \times 10^{-7} T^2$ (in $\text{mm}^2 \text{s}$).
|To reproduce $D_{tt}$ near 298 K requires a third order fit $1/D = -0.15313 + 0.0021475T - 12.417 \times 10^{-7} T^2 + 2.72 \times 10^{-10} T^3$ (in $\text{mm}^2 \text{s}$).
transfer. For (001), the larger section of Fe-rich diopside is preferred because higher temperatures were reached. Anisotropy is substantial, \( D \) from (001) is 38 % higher than \( D \) from (110) and is independent of temperature within experimental uncertainty.

**Extensive solid-solution clinopyroxenes**

For augite, (010) lacked visible cleavage and should provide accurate values at high \( T \). Multiple runs made on several sections of both aegirine and augite ensure reproducibility. Radiative transfer is considerably lower in the solid-solution clinopyroxene than in diopside (Fig. 1) and did not limit our maximum temperatures. However, we terminated the runs when \( D \) appeared constant and also to avoid melting. For augite, a third-order polynomial is needed to accurately portray \( D_0 \) near 298 K, but for higher temperature, second-order is acceptable (Table 2).

Solid solution clinopyroxene has much lower \( D \) near 298 K than diopside, but as \( T \) increases, differences in \( D \) are greatly reduced (Fig. 3b, Table 2). The degree of solid solution and \( D \) values are about the same for aegirine and augite, but \( D \) for Ti-rich augite is much lower. Inclusions in Ti-rich augite could affect the results so this sample is not discussed further. For augite, \( D \) from (001) is 39 % larger than \( D \) from (010) and is nearly independent of temperature (increases to 41 % at saturation), as for diopside. Aegirine has a larger anisotropy (Fig. 3b) of 47 % at 298 K, increasing to 52 % at the maximum temperature attained. Given that saturation was not reached for (001), the observed change in anisotropy with \( T \) is not as accurate as the ~40 % observed at saturation for diopside and augite.

**Na-rich clinopyroxenes**

Near end-member jadeite occurs as a compact, tough mat of fine-grained polycrystalline lathes without apparent preferred orientation, consistent with the description of Sorensen et al. (2006). Fe-rich jadeite has a similar habit, but is coarser grained and may have some degree of preferred orientation. Orientation is difficult to quantify given the thickness of our samples and inhomogeneity. Much higher \( D \) values exist for the near end-member at low \( T \), compared to Fe-rich jadeite with substitutions involving M1 and M2. The trends extrapolate to similar values at high temperature, such that the solid-solution seems to attain saturation at lower temperature. The end-member value of 0.88 mm\(^2\) s\(^{-1}\) for \( D_{\text{sat}} \) of NaAlSi\(_2\)O\(_6\) is much higher than that for (001) of CaMgSi\(_2\)O\(_6\) (cf. Fig. 3a and 3c) and attributable to mass effects, see below.

Aegirine has the simplified composition of \((\text{Na}_{0.9}\text{Ca}_{0.1})\text{FeSiO}_6\), ignoring the small amounts of Mg, Mn, Al, Ti, and also of Fe\(^{3+}\) which provides charge neutrality. Its trend for (110) parallels that of the nearly pure jadeite, but with lower \( D \), attributable to mass effects. The solid-solution jadeite has a shallower trend that lies between jadeite and aegirine.

**LiAlSi\(_2\)O\(_6\) clinopyroxenes**

Trace impurities in near-endmember Li samples scarcely affect \( D \) (Fig. 3d). However, the cloudy spodumene has lower \( D \) for both orientations. Due to the prominent cleavage, it was difficult to prepare (001) slabs for the clear sample. We used data on ~ (001) to extrapolate results for the well aligned section to high temperature. Anisotropy is 42 % at 298 K and is nearly independent of temperature. Saturation was not reached because these samples disintegrated near 1100 K. The trends for \( D(T) \) of LiAlSi\(_2\)O\(_6\) are nearly parallel to those of NaAlSi\(_2\)O\(_6\) (Fig. 3d).

**Discussion**

**Comparison to previous results from contact methods at 298 K**

Kobayashi (1974) applied the modified Ångström method to single-crystal diopside (CaMg\(_0.95\)Fe\(_{0.05}\)Si\(_2\)O\(_6\)) from Quebec (Canada) and found that \( D_{001} = 1.18 \text{ mm}^2\text{s}^{-1}\), \( D_{010} = 1.28 \text{ mm}^2\text{s}^{-1}\), and \( D_{003} = 1.81 \text{ mm}^2\text{s}^{-1}\) at 298 K. Radiative transfer was evident as upturns at ~600 K. The composition of Kobayashi’s (1974) sample is virtually the same as our Fe-rich diopside, but our \( D \) values at 298 K are ~50 % larger (Table 2). This discrepancy is more than observed for other single-crystal samples: typically, dual-contact methods are 20 % lower than LFA (Hofmeister, 2007b; Hofmeister et al., 2007).

Osako et al. (2004) cite their own unpublished data on jadeite with \( k = 6.8 \text{ W m}^{-1}\text{K}^{-1} \) at 298 K. Because composition was not reported, only rough comparison can be made. End-member density is 3.34 g cm\(^{-3}\) (Smyth & Bish, 1998), heat capacity is 164.13 J mol\(^{-1}\) K\(^{-1}\) (Hemingway et al., 1998), and \( M \) is 202.1 g mol\(^{-1}\) providing \( D = 2.5 \text{ mm}^2\text{s}^{-1}\) which is 10 % lower than our end-member and greater than our solid solution.

Horai (1971) studied three samples with similar localities and compositions (indicated by density) to ours, using the needle-point method. Diopside from New York with \( k = 5.58 \text{ W m}^{-1}\text{K}^{-1} \) has endmember density (3.27 g cm\(^{-3}\)) of \( 98 \text{ for NaAlSi}_2\text{O}_6 \) (Horai, 1971) studied three samples with similar localities and compositions (indicated by density) to ours, using the needle-point method. Diopside from New York with \( k = 5.58 \text{ W m}^{-1}\text{K}^{-1} \) has endmember density (3.27 g cm\(^{-3}\)) of (cf. Fig. 3a and 3c) and attributable to mass effects, see below.

Using \( C_P = 166.78 \text{ J mol}^{-1}\text{K}^{-1} \) (Robie & Hemingway, 1995) implies \( D_{\text{bulk}} = 2.22 \text{ W m}^{-1}\text{K}^{-1} \), which is 30 % lower than \( D_{\text{bulk}} = 2.95 \text{ mm}^2\text{s}^{-1}\) from LFA. Jadeite from California has \( k = 4.62 \text{ W m}^{-1}\text{K}^{-1} \) and \( \rho = 3.35 \text{ g cm}^{-3} \), suggesting end-member, so \( D = 1.45 \text{ mm}^2\text{s}^{-1} \), which is 48 % lower than LFA values. Spodumene has \( k = 5.65 \text{ J mol}^{-1}\text{K}^{-1} \) and \( \rho = 3.155 \text{ g cm}^{-3} \) suggesting end-member composition. Using \( C_P = 158.93 \text{ J mol}^{-1}\text{K}^{-1} \) (Robie & Hemingway 1995) and \( M = 186.08 \text{ g mol}^{-1} \) gives \( D = 2.10 \text{ mm}^2\text{s}^{-1} \), which is 22 % lower than \( D_{\text{bulk}} = 2.71 \text{ mm}^2\text{s}^{-1}\) from LFA. Direct comparison of our results with Horai’s (1971) other pyroxenes is precluded because reported densities suggest substitution of Fe that differs from our samples. It is clear, however, that the needle-point method systematically underestimates thermal transport properties not only for pyroxenes (average of ~33 %), but for other structures as well (average of ~15 % for olivine, quartz and garnet: Hofmeister et al., 2007). Roughly, the needle-point method is 20 % low, similar to the average discrepancy.
between LFA results and dual-contact methods for pyroxenes (above) and other samples (Hofmeister, 2007b). From the present and previous results, contact methods underestimate \(D\) and \(k\) by about 10% per contact due to thermal resistance at the interfaces between sample and either the heater or thermocouple.

**Isolation of vibrational from radiative transfer in LFA results and trends above 298 K**

Our samples are either (1) optically thin in the near-IR to visible region associated with blackbody emissions above 298 K, having moderately to weakly absorbing bands associated with transition metal ions (Fig. 2), and hence radiative transfer should be removed by the algorithm of Mehling et al. (1998), or (2) are effectively opaque (e.g., polycrystalline jadeite) and thus the temperature-time curves depict vibrational transport only and are described by the model of Cowan (1963). The consistent behavior (Fig. 3) for a variety of compositions, opacity and color is attributable to isolation of the lattice component in our measurements.

Model fits are less than perfect when emissions due to radiative transfer comprise over half of the total rise in the temperature-time curves (Fig. 1). Derivation of \(D\) under such conditions is less accurate than the 2% uncertainty associated with the technique. Data points involving excessive radiative transfer (> half the total rise) were not included with fitting \(D\) vs. \(T\).

For conventional methods involving contact, strong increases in \(\partial D/\partial T\) with \(T\) at high \(T\) have been observed (e.g., Kanamori et al., 1968; Kobayashi, 1974). Strong, positive slopes for \(\partial D/\partial T\) at high \(T\) are not due to diffusive radiative transfer because some light crosses the small (~5 mm) samples unattenuated (as shown in Fig. 2 at ~2500 and ~8000 cm\(^{-1}\); also see discussion of Pertermann & Hofmeister, 2006), in violation of the requisite optically thick conditions (Hofmeister, 2005). Consequently, previous contact measurements of \(D\) for pyroxenes above 298 K consist of unknown proportions of lattice and direct radiative transport, and are not discussed further. Note that polycrystals are not immune from this problem, but rather have smaller amounts of spurious radiative transfer than single-crystals.

Contact measurements do not provide reliable determinations of the temperature dependence of \(D\) or \(k\) for minerals or rocks due to radiative transfer effects, and do not provide correct absolute values, even at room temperature, due to thermal resistance at interfaces. These two problems alter \(D\) from the intrinsic values in different directions and to various degrees, depending on experimental details.

**Comparison with models**

The observed behavior is consistent with the damped harmonic oscillator model:

\[
D(T) = \frac{\langle u(T) \rangle^2}{6\pi(\text{FWHM}(T))} = \frac{\langle u(T) \rangle^2 \langle \tau(T) \rangle}{3Z} = \frac{\langle u(T) \rangle \langle \lambda(T) \rangle}{3Z}
\]

where \(\langle u \rangle\) is an average phonon speed (group velocity) which is similar to sound speeds, \(Z\) is the number of formula units in the primitive cell, and (FWHM) is the average full width at half maximum of the peaks in the dielectric function obtained from IR reflectivity data. Mean free lifetimes (\(\tau\)) or mean free paths (\(\lambda\)) of the phonons decrease smoothly with \(T\), largely due to increasing the number of states populated, see Hofmeister (2006, 2007b); Hofmeister et al. (2007) for detailed discussion of this model including comparison to earlier efforts.

Thermal diffusivity approaches a constant above 1400 K for diopside and at somewhat lower temperature for solid solutions. In the DHO model, constant \(D\) is connected with saturation of the number of modes once the continuum becomes populated, and is analogous to the Dulong-Petit limit of heat capacity. As observed for olivines (Pertermann & Hofmeister, 2006), garnets (Hofmeister, 2006), and spinels (Hofmeister, 2007a), the flat region occurs at roughly double the Debye temperature (which is ~650 K for diopside and ~720 for jadeite: Kieffer, 1980). The high-temperature asymptote was previously connected with the mean free path (\(\lambda = ur\)) approaching the size of the unit cell (or lattice constant) in the acoustic model (e.g., Ziman, 1962). It is true that \(D_{sat}\) of diopside, augite, and aegirine are nearly the same and these varieties have similar lattice constants (cell volumes = 438, 440, 429 Å\(^3\), respectively, see compilation of Cameron & Papike, 1980), but, jadeite and spodumene have significantly smaller volumes (401 and 388 Å\(^3\), respectively) and larger \(D_{sat}\) which is the opposite expected from the right hand side of equation (4) using lattice constants. The DHO model better fits the available data.

Different trends for \(D(T)\) of endmember and solid solution clinopyroxene are also consistent with the DHO model. At low \(T\), solid solutions have more scattering centers, shortening the mean free path and lowering \(D\). As temperature rises, overtones-combination bands become increasingly populated, providing more phonons and more scattering, and lower \(D\). However, solid solutions have broader bands and fewer distinct overtones, so as \(T\) increases, the endmembers and solid solutions converge to the same values. Because of this behavior, mantle values for clinopyroxenes are best represented by augite (Fig. 3b).

**Mass and structural controls on thermal diffusivity of clinopyroxenes**

For clinopyroxenes, the value of \(D\) depends on whether heat flow is perpendicular or parallel to the \(c\)-axis, i.e., to the chains of silica tetrahedra. The percent difference between \(D\) for flow \(|e\) and \(-e\) is independent of temperature. The importance of structural control is further emphasized in the low variability of 38, 39, 42, and 47% anisotropy for our single-crystals. This consistency allows us to estimate values for jadeite. Given the size and charge of the cations, NaAlSi\(_2\)O\(_6\) should have anisotropy like that of LiAlSi\(_2\)O\(_6\) (47%) or NaFeSi\(_2\)O\(_6\) (42%). Assuming no preferred orientation, i.e. \(D_{ave} = (D_{hc} + 2D_{lc})/3\), we estimate values for jadeite and Fe-jadeite as \(D_{hc} = 3D_{ave}/(1 + 2x)\) and...
$D_{\perp c} = (1 - x)D_{\parallel c}$, where $x =$ degree of anisotropy. These equations hold at all temperatures.

Thermal diffusivity at 298 K linearly correlates with cation mass for near end-member olivine (Pertermann & Hofmeister, 2006). Olivine with extensive solid solution does not follow the same trend, attributable to mean free paths being shortened by the presence of additional scattering centers (the impurity ions). We therefore separately examine our near end-member and solid-solution clinopyroxenes for both flow directions, $\parallel c$ and $\perp c$ (Fig. 4). The degree of solid solution does affect $D$, but because all our samples have about 10% impurities on two of the three sites, the effect of cation substitution should be similar for all samples, although not be exactly equal.

Inferred $D$-values for oriented end-member jadeite are consistent with the trends defined by the other three near end-members (Fig. 4). The results suggest that the lower amount anisotropy, like that of sodic aegirine, pertains. Fe-rich jadeite has larger grains and may be somewhat oriented. We believe that this is the case, given the similar $D$ values for Na- and Fe-rich diopside, and suggest that we have underestimated $D$ in Fig. 4. The less regular trends for solid solutions could be connected with this problem, but the degree of solid solution pertains as well. Because of this potential problem, and the similar behavior of end-members and solid solutions (Fig. 4), we focus on near end-member behavior and also use equation (4) to explore the link of heat transport to microscopic behavior in clinopyroxene.

For endmembers, mass does not affect $D_{\parallel c}$, but $D_{\perp c}$ increases as mass increases (Fig. 4a), which is the opposite of how olivines respond. A strong connection also exists with bond lengths (Fig. 4b). Trends for M1 and M2 individually are similar to those shown for average bond lengths. Flow $\parallel c$ is not affected, whereas $D_{\perp c}$ increases with bond length. Change in mass and bond length are related because heavier cations are larger and expand the lattice. The increase in $D$ with bond length for flow perpendicular to $c$ is consistent with expansion of the lattice which increases $\lambda$ and thus $D$ (Eq. (4)). Expansion associated with chemical substitution occurs mainly in the $a$ and $b$ directions, with changes in the $c$ direction being about 1/20th as large (see Tables in Smyth & Bish, 1988), consistent with the lack of an effect of bond length for heat flow parallel to $c$. Heat transport is most efficient along the $SiO_4$ chains (Fig. 4). The primitive cell volume is $1/2$ the size of the crystallographic unit cell, such that $c$ is the same for these cell types. However, the average of the primitive lattice constants $a^*$ and $b^*$ are still greater than $c$, so differences in mean free path unlikely cause the anisotropy. We suggest that high speeds cause $D$ to be largest along $c$. The chains possess high frequency vibrations ($Si-O$ stretching and bending modes). High frequencies in theory are associated with high speeds (Hofmeister, 2001).

**Calculation of thermal conductivity**

Thermal conductivity is obtained from equation (1) and the relation $\rho = M/V$. End-member values were obtained from the literature. For CaMgSi$_2$O$_6$, fits to $V(T)$ by Richet et al. (1998) were used. Comparison of these measurements to $V$ projected from 298 K using constant $\alpha$ suggests uncertainties in $\rho$ of $< 1\%$ for the remaining end-members, for which constant thermal expansivity (Cameron et al., 1973) was used. For $C_p(T)$ of CaMgSi$_2$O$_6$, NaAlSi$_2$O$_6$, and NaFeSi$_2$O$_6$, we used polynomial fits from Berman &
Brown (1989). For CaFeSi$_2$O$_6$ and LiAlSi$_2$O$_6$, we used data compiled by Robie & Hemingway (1995). Using the above with $D(T)$ for Na-rich diopside, jadeite, and spodumene, allows calculation of $k(T)$ for end-members CaMgSi$_2$O$_6$, NaAlSi$_2$O$_6$, and LiAlSi$_2$O$_6$.

For our solid solution samples (Fe-bearing jadeite, augite, and aegirine) we used our fits for $D(T)$ in Table 2. For $M$, $V$, and $C_P$, we added end-member components, assuming the following simplified compositions: Fe-rich diopside = 0.93CaMgSi$_2$O$_6$ + 0.07CaFeSi$_2$O$_6$; Fe-rich jadeite = 0.89NaAlSi$_2$O$_6$ + 0.11CaFeSi$_2$O$_6$; augite = 0.93CaMgSi$_2$O$_6$ + 0.07CaFeSi$_2$O$_6$; and aegirine = 0.88NaFeSi$_2$O$_6$ + 0.12CaFeSi$_2$O$_6$. This additive representation should suffice for the impurity levels in these samples. We neglect the effect of Al substituting for Si, and the minor substitutions at M2 or M1 associated with charge compensation.

Thermal conductivity decreases from 200 to ~1200 K, becoming constant at very high $T$ (Fig. 5). Fits and values at room temperature and saturation are provided in Table 3. For slight compositional differences, the asymptotic values are not affected, but substantial substitution of a heavier cation lowers $k_{sat}$. Saturation temperatures are a few hundred K below melting, except for augite, for which saturation was not reached. For jadeite and spodumene, runs were terminated when the sample cracked or flowed, and saturation is an approximation. It may be that $k$ and $D$ are not truly independent of temperature at high $T$, but rather are constant within the uncertainties of our measurements.

Pressure derivatives

Thermal diffusivity at pressure has been determined only for jadeite and with a contact method (Osako et al., 2004), but data were not shown. The value $\frac{\partial (\ln k)}{\partial P} = 4.6$ %/GPa is similar to measurements on other hard minerals, summarized by Hofmeister (2007b). This value is higher than the prediction of 3.7 %/GPa from the DHO model:

$$\frac{\partial (\ln(k_{sat}))}{\partial P} = \frac{1}{K_T} \left( 4\gamma_\theta + \frac{1}{3} \right).$$

(5)

The alternative relationship:

$$\frac{\partial (\ln(k_{sat}))}{\partial P} \approx \frac{1}{K_T} \frac{\partial K_T}{\partial P} = \frac{K'}{K_T}$$

(6)

omits terms $\sim 1/10th$ of $K'/K_T$ and gives 3.2 %/GPa. The sample is doubtless polycrystalline, which means that pore space could be compressed and the measurements may overestimate $\partial (\ln k)/\partial P$. Pressure derivatives from contact methods are affected also by the maximum pressure attained and whether the derivative is determined from comparison with $k$ at ambient pressure or from $k$ obtained at two different elevated pressures (Hofmeister, 2007b).

Heat transport associated with clinopyroxene in oceanic lithosphere and upper mantle

Diffusive radiative transfer, which is described as an effective thermal conductivity ($k_{rad}$) is important inside the Earth (Dubuffet et al., 2002). Because blackbody emissions depend entirely on temperature, $k_{rad}$ is strongly $T$ dependent and weakly $P$ dependent (Hofmeister, 2005). Given the similarity of visible spectra of Fe$^{2+}$ in pyroxenes to that of olivine, $k_{rad}(T)$ calculated for olivine is a reasonable substitute.

We assume that the $P$ and $T$ dependencies of $k$ are separable, as commonly assumed for the related physical property, bulk modulus. Temperatures in the lithosphere vary from 298 to ~1275 K at the base of the lithosphere, roughly 60 to 100 km. Upper mantle clinopyroxene has significant substitution of Na,Cr, and Al with Fe/Mg $\sim$ 0.1 (see Boyd & Meyer, 1979). The best representative is augite, because Cr and Fe$^{3+}$ should have about the same effect. This sample has less Na, but more Al than mantle samples, and the substitutions involve M2 and T sites, whereas mantle chrome diopsides have substitutions at M1 and M2. Augite fits (Tables 2 and 3) are also appropriate for the oceanic lithosphere.

Temperatures in the upper mantle reach a maximum of 1800 K at 410 km, as suggested by experimental constraints of Katsura & Ito (1986) on the $\alpha$-$\beta$ transition of olivine at 13 GPa. The lower limit is set by the solidus of basalt. Saturation values reasonably approximate behavior in the upper mantle, which are $D_{sat} = 0.5$ and 0.9 mm$^2$ s$^{-1}$ for the two directions of clinopyroxene (Table 2). This result compares closely with $D_{sat} = 0.51$,
Table 3. Fits to thermal conductivity with temperature.

<table>
<thead>
<tr>
<th>Name</th>
<th>Flow</th>
<th>$k_{98}$</th>
<th>$k_{30}$</th>
<th>$T_{sat}$</th>
<th>Fit of 1/k vs. $T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ CaMgSi2O6</td>
<td>†e</td>
<td>6.86</td>
<td>2.48</td>
<td>1400</td>
<td>0.01335 + 0.000477057 - 14.465 x 10^-5 $T^2$</td>
</tr>
<tr>
<td></td>
<td>†c</td>
<td>11.38</td>
<td>4.04</td>
<td>1500</td>
<td>0.012043 + 0.000271387 - 7.7142 x 10^-5 $T^2$</td>
</tr>
<tr>
<td>Augite</td>
<td>†e</td>
<td>3.84</td>
<td>&lt; 1.90</td>
<td>&gt; 1600</td>
<td>0.1641 + 0.000319357 - 4.1436 x 10^-5 $T^2$ + 6.2711 x 10^-11 $T^3$</td>
</tr>
<tr>
<td></td>
<td>†c</td>
<td>6.57</td>
<td>&lt; 3.11</td>
<td>&gt; 1600</td>
<td>0.045162 + 0.000422817 - 24.739 x 10^-5 $T^2$ + 5.6882 x 10^-11 $T^3$</td>
</tr>
<tr>
<td>Aegirine</td>
<td>†e</td>
<td>2.67</td>
<td>1.81</td>
<td>1100</td>
<td>0.01145 + 0.00101087 - 57.903 x 10^-5 $T^2$ - 9.543 x 10^-11 $T^3$</td>
</tr>
<tr>
<td></td>
<td>†c</td>
<td>3.79</td>
<td>1.23</td>
<td>1300</td>
<td>0.063027 + 0.000301057 - 11.192 x 10^-5 $T^2$</td>
</tr>
<tr>
<td>~ NaAlSi2O6</td>
<td>bulk</td>
<td>5.68</td>
<td>2.84</td>
<td>1170</td>
<td>0.00462666 + 0.000490097 - 19.541 x 10^-5 $T^2$</td>
</tr>
<tr>
<td>Fe3+-bearing jadeite</td>
<td>bulk</td>
<td>4.59</td>
<td>2.84</td>
<td>1050</td>
<td>0.11361 + 0.000405137 - 0.0175 x 10^-5 $T^2$</td>
</tr>
<tr>
<td>~ LiAlSi2O6</td>
<td>†e</td>
<td>5.83</td>
<td>3.00</td>
<td>1200</td>
<td>0.019635 + 0.000607347 - 38.201 x 10^-8 $T^2$ + 7.672 x 10^-11 $T^3$</td>
</tr>
<tr>
<td></td>
<td>†c</td>
<td>10.64</td>
<td>4.72</td>
<td>1300</td>
<td>0.025518 + 0.000266947 - 9.5359 x 10^-8 $T^2$</td>
</tr>
</tbody>
</table>

* Directions of heat flow are indicated, i.e. †e depicts measurements from (001) sections.
† All fits had residuals better than 0.99. Fits are up to $T_{sat}$ ~ + 200 K.
§ Saturation not reached.

0.79, and 0.87 mm$^2$ s$^{-1}$ for the three directions of olivine (Pertermann & Hofmeister, 2006) and 0.66 mm$^2$ s$^{-1}$ for upper mantle garnets (Hofmeister, 2006). We assume that orthopyroxene behaves similarly to clinopyroxene because contact measurements give similar D for enstatite and diopside (Kobayashi, 1974).

We estimate k(P) for mantle varieties of pyroxene from the above equations as 4.2 to 4.7 %GPa$^{-1}$ for Ca-rich compositions expected in the oceanic lithosphere and upper mantle. These derivatives and the saturation values listed above (also see Fig. 3 and 4) constrain the lattice component of heat transport in the upper mantle.

Conclusions

We provide thermal diffusivity and conductivity data at temperature that are free of artifacts for three very different end-member compositions and several solid solutions of clinopyroxene. The trends with temperature resemble previous laser-flash studies of olivine and garnets. For example, D at high T asymptotes to a constant that varies little among the diverse chemical compositions studied here, and the anisotropy of all samples is near 40 %. Given the consistency, values of D for the mantle can be roughly estimated from our on augite. Our results can be used to constrain D and k of the oceanic lithosphere and Earth’s upper mantle, if it is assumed that the present data represent orthopyroxene.

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