The Threshold Dependencies of Thermal Conductivity and Implications on Mantle Dynamics

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Abstract. New experimental measurements of thermal diffusivity show that the lattice component of thermal conductivity for minerals becomes independent of temperature within experimental uncertainty above roughly 1200 to 1900 K. Recent revision of the formulation for an effective thermal conductivity due to radiative transfer shows that a different type of threshold dependence on the grain-size with greater complexity in the temperature dependence for large grains, and a dependence on Fe content. The combination of these threshold effects in thermal conductivity have ramifications on the style of mantle convection, since radiative transfer acts to stabilize the flow, whereas the lattice contribution tends to destabilize the boundary layer. However, radiative transfer can make convection chaotic and time-dependent as the sign of $\partial k_{\text{rad}}/\partial T$ is sometimes negative, e.g. for large, Fe-rich grains. The specific domains in thermal conductivity suggest sluggish lower mantle flow, but a strongly time-dependent pattern for the upper mantle-transition zone. That radiative transfer decreases as Fe/(Fe+Mg) increases beyond 0.1 suggests that thermo-chemical plumes can form at the base of the lower mantle through a positive feedback involving chemical enrichment, thermal conductivity, and viscosity. This mechanism would be particularly effective in stagnant points of the upwelling. The above cross-scaling connection of microscopic processes in solids with macroscopic transport mechanisms in the mantle plays an important role in differentiation of the Earth.

1. Introduction

The style of mantle convection depends on a balance between the transport properties (viscosity and thermal conductivity) and the buoyancy forces. Most geodynamicists have neglected variable thermal conductivity ($k$) and rather focused on variable viscosity (e.g.
Tackley, 1996) because the variations of $k$ with temperature are much smaller (e.g. Ziman, 1962: $1/T$ dependence) than the exponential dependence of viscosity on the temperature (an Arrhenius relationship). However, the simple $1/T$ dependence is associated with exchange of heat via lattice vibrations: the radiative component of thermal conductivity can have a much stronger temperature dependence and magnitude, leading Lubimova (1958) and MacDonald (1959) to conclude that radiative transfer was a key process in the Earth. Geophysical interest in thermal conductivity has been rejuvenated by the semi-empirical model based on solid-state physics of Hofmeister (1999). Most recently, changes in radiative transfer with depth, which could result from the low spin to high spin electronic transition of Fe$^{2+}$ in perovskite, have been suggested to impact lower mantle convection (Badro et al., 2004).

The role played by thermal conductivity in mantle convection has been assessed by Dubuffet et al. (1999, 2001) and van den Berg et al. (2001, 2002), whereas Starin et al (2000) and Branlund et al. (2001) probed lithospheric processes. Even for high Rayleigh numbers, a regime considered to be dominated by viscosity due to the vigor of flow, the effects wielded by variable thermal conductivity can still be felt (Dubuffet et al., 2000). Recent investigations of Yanagawa et al. (2004) and van den Berg et al. (2004) on the interaction between variable viscosity and variable thermal conductivity in mantle convection have shown that thermal conductivity can not be overridden by viscosity, even for a large viscosity contrast. It is thus important to consider variable thermal conductivity in dynamical studies, even though the effort, complexity, and computational costs are increased relative to constant $k$ (Dubuffet et al., 1999). The small changes in $k$ with $T$ has a disproportionately large effect on dynamical behavior, because the time-dependence of an infinite Prandtl number fluid such as the mantle is governed.
primarily by the temperature equation, which contains \( k \), and not by the momentum equation which viscosity dominates. In mathematical parlance (Haken, 1977) the temperature equation functions as a "master" equation, whereas the momentum equation responds instantaneously as the "slave" equation.

The thermal conductivity in the mantle is governed by two processes. The first intra-granular process involves the scattering of phonons within each individual mineral grain, the so-called lattice conductivity (\( k_{\text{lat}} \)). The second inter-granular process of diffusive radiative transport (\( k_{\text{rad,dif}} \)) involves the progressive attenuation of photons emitted by a given grain inside the material as this light traverses the other grains constituting the medium. For brevity, we drop the subscript “dif” in the remainder of the paper, as it should be clear that all heat transfer processes in the Earth are diffusive. The dichotomy of the relative roles played by \( k_{\text{lat}} \) and \( k_{\text{rad}} \) in mantle convection is the focus of this paper.

We report on a recent experimental discovery (Hofmeister, 2004a; in prep.) that \( k_{\text{lat}} \) decreases in two stages as the temperature increases: first rapidly with the temperature and then slowly, once a threshold temperature \( T_c \) is reached, \( k_{\text{lat}} \) asymptotes to a constant, low value. This behavior differs from the traditional \( 1/T \) dependence commonly assumed in geophysics (e.g. Schatz and Simmons, 1972) and the \( 1/T^b \), where \( b \) is below 1, obtained by curve-fitting data on minerals at low to moderate temperature (Hofmeister, 1999; Xu et al., 2004). We then discuss the revised model for \( k_{\text{rad}} \) introduced by Hofmeister (2004b), which, in contrast to previous models (Clark, 1957; Shankland et al., 1979; Hofmeister, 1999) accounts for the strong effects of emissivity and grain-size. This newly developed model also shows that \( k_{\text{rad}} \) has a threshold dependence with greater grain-size. The competition between the radiative and lattice
contributions to thermal conductivity discovered by Dubuffett et al. (2002) and the presence of threshold phenomenon (e.g. Drazin, 1992; Strogatz, 1994) in thermal conductivity affect the style of mantle convection. For example, feedback by thermal conductivity due to the compositional dependence can simultaneously engender deep mantle plumes and chemical layering. Scale-crossing between microscopic processes in solid-state physics and the macroscopic behavior in convection are relevant to differentiation of Earth’s mantle.

2. New measurements on $k_{\text{lat}}$

Thermal diffusivity:

$$D = \frac{k}{\rho C_p}$$

(1)

where $k$ is thermal conductivity, $\rho$ is density, and $C_p$ is heat capacity at constant pressure ($P$) was obtained using a Netzsch LFA 427 and the laser-flash technique first developed by Parker et al. (1961). Emissions from the upper surface of a sample held at some given temperature ($T$) are monitored remotely with an infrared (IR) detector. The bottom of the sample is heated by an optical pulse from a Nd-GGG laser. Sample sizes were ~8 to 13 mm in diameter by ~1 to 4 mm thick. Surfaces were graphite coated to enhance absorption of the laser pulse and to increase the intensity of IR emissions (Blumm et al., 1997). As heat from this pulse diffuses from the bottom surface to the top of the sample, the increased emissions are recorded by the IR detector, in the form of a time-temperature curve. Various mathematical models are used to extract $D$ from the time-temperature curve (Parker et al., 1961; Cape & Lehman, 1963; Cowan, 1963; Heckman, 1973; Clark & Taylor, 1975; and Azumi & Takabashi, 1981; Tan et al., 1991). This technique minimizes unwanted radiative transfer through the physical configuration and removes this effect with the mathematical models, and thus only the lattice contribution to $D$ is recorded.
Uncertainties are better than 2%. For details regarding the technique see Blumm et al. (1997); Buettner et al. (1998); and the above references. Details regarding these specific measurements will be published elsewhere (Hofmeister, 2004a, in preparation).

To compute $k_{\text{lat}}(T)$ from our measurements and for mantle-candidate minerals, we assume that the temperature derivative is constrained by the structure, i.e., that $\partial D/\partial T$ of SrTiO$_3$ represents the behavior of MgSiO$_3$. Densities of MgSiO$_3$ with the perovskite and majorite structures were computed using the temperature dependence of the thermal expansivity from Chopelas (2000). For diopside, a constant value of thermal expansivity was used (see Fei, 1995). For MgO, MgAl$_2$O$_4$, and Fo$_{90}$, tabulated values of $\rho(T)$ (Anderson and Isaak, 1995) were used. Formulae in Fabrichnaya (1995) reproduced the later three datasets. Heat capacities for olivine, diopside, spinel, pyrope, MgO were obtained using the formulation of Berman and Brown (1989). Majorite and pyrope have almost identical $C_p(T)$ (Geisting et al., 2004). For MgSiO$_3$ perovskite, $C_p(T)$ was taken from Lu et al. (1984).

For $T$ below $\sim$1200 K, $D$ is nearly proportional to $1/T^b$, where $b$ is near unity (Fig. 1ab). However, this fit does not adequately describe the high temperature behavior wherein $D$ becomes independent of $T$ within the experimental uncertainty. Very high-order polynomials provide equally good fits, but departures again occur at high temperature. In fitting $D$ to functions of $1/T$ and $\log(T)$, the same problems were encountered. These results indicate a type of threshold behavior, wherein $D$ follows $1/T^b$, $b$~1, at low to moderate temperature, but is constant above some high temperature. Thus $D$ exhibits a dual behavior with $T$, with $T_C$ being a threshold temperature separating the two regimes. This threshold quantity in $T$ is analogous to the threshold stress in the theory of plasticity (e.g. Hill, 1950).
Thermal conductivity behaves similarly to \( D \) (Fig. 1c). The direct comparison for MgO (Fig. 1a) shows that the low and moderate temperature slope for \( k_{\text{lat}} \) is less steep than that for \( D \), but that constant \( k_{\text{lat}} \) is also achieved at very high \( T \). Neither do the power law or other fits adequately describe the high temperature behavior of \( k_{\text{lat}} \). Above about 1200 K, \( \rho \) linearly (or nearly linearly) decreases with \( T \), whereas \( C_P \) linearly increases (e.g. Berman and Brown, 1984; Fabrichnaya, 1995). These competing effects roughly cancel in Eq. 1, and thus the temperature response of \( k_{\text{lat}} \) is largely that of \( D \) such that, the dependence of \( \rho \) and \( C_P \) on \( T \) cause constant \( k_{\text{lat}} \) to occur at slightly higher temperature than \( D \). For perovskite, for which our measurements of \( D \) barely resolve the threshold behavior, \( k_{\text{lat}} \) is not observed to become constants at the highest temperatures attained (2100 K) although the derivative is distinctly lower (Fig. 1c).

The results for \( D(T) \) can be understood by considering the spectroscopic model for thermal conductivity (Hofmeister 1999, 2001, 2004a; Giesting and Hofmeister, 2002; Giesting et al., 2004). Neglecting the slight (~3 \%) difference between \( C_P \) and \( C_V \) gives:

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

where \( u \) is the average sound speed, \( Z \) is the number of formula units in the primitive cell, \( M \) is the formula weight, and FWHM is the full width at half maximum of the IR peaks in the imaginary part of the dielectric function. The available spectroscopic data are insufficient to examine this relationship in detail. However, our data (Fig. 1ab) shows that the FWHM controls the temperature dependence of \( D \) insofar as \( u \) depends only weakly on temperature (e.g. Anderson and Isaak, 1995).
Achievement of constant $D$ at high $T$ is thus largely due to the widths becoming independent of temperature. As FWHM appears to be connected with the number of phonons available for scattering (within the primitive unit cell), the flat trend in $D$ at high $T$ results from saturation. At some high temperature, increasing $T$ no longer significantly changes the number of phonons. The behavior of FWHM is consistent with statistical thermodynamics descriptions of the population of states (overtone-combinations of the fundamentals) with temperature. It also parallels the behavior of the heat capacity which asymptotes to $3R$ (the gas constant) once $T$ exceeds the Debye temperature. That $D$ and $k_{1u}(T)$ are independent of $T$ at roughly double the Debye temperature is thus attributed to saturation of phonon densities, consistent with statistical thermodynamics.

A threshold temperature exists for all phases examined so far, including unpublished data on feldspars, basalts, and various glasses. This apparently universal behavior is consistent with the connection to statistical thermodynamics discussed above. From Fig. 1c, the threshold temperature tends to increase with stability at pressure, i.e. MgO and the perovskite structure have higher $T_C$ than the rest. Estimation of $T_C$ for MgSiO$_3$ perovskite from isostructural SrTiO$_3$ does not impact the analysis of the present paper as $T_C$ is an indicator of an asymptotic transition.

Threshold behavior abounds in nature and is associated with non-linear processes, such as the onset of convection in fluid dynamics and of plastic creep explored in materials science. For lattice thermal conductivity it is a threshold temperature, which demarcates the two regimes, one with a $1/T^b$ dependence, the other with an asymptotically flattening value, similar to the Dulong-Petit limit reached in heat capacity at high $T$. 
3. A revised model for diffusive radiative transfer

Unlike radiative transfer in atmospheres, which involves a non-local process use to the absorption and re-emission of photons (e.g. Chandrasekhar, 1960), radiative transfer inside the Earth is a locally diffusive process that is represented by an effective thermal conductivity ($k_{rad}$), calculated from spectroscopic data (e.g. Siegel and Howell, 1972). Numerical computations required for diffusion of light in mantle convection are simple compared to non-local formulations involving integral equations such as in models of stellar convection (e.g. Porter et al., 1990) and of other astrophysical environments (e.g. Tucker, 1975).

Previous geophysical models for $k_{rad}$ (e.g. Clark, 1957; Shankland et al., 1979; Hofmeister, 1999) ignored the effect of grain-size ($d$). Not only does finite grain-size shorten the mean free path of the photons through physical scattering, but the emission spectrum is affected by average grain-size in the mantle. Specifically, within the internally heated mantle, light produced by each grain diffuses locally to neighboring grains. The intensity contributed by an individual grain is the product of the emissivity with Planck’s blackbody function ($I_{bb}$).

Emissivity ($\xi$) is related to the absorptivity ($A$, defined below), which is commonly measured in the laboratory, through Kirchhoff’s law:

$$\xi(v) = 1 - \exp [-dA(v)],$$

(e.g. Brewster, 1992). Based on formulations for radiative transfer in engineering (e.g. Brewster, 1992), astronomy (e.g. Kaufmann and Freedman, 2002), and remote sensing (Hapke, 1993), Hofmeister (2004b, in review) revised the equations used in geophysics to account for the effects of grain-size on the emissions and on mean free path. This revision brings the formulation into compliance with local radiative equilibrium and diffusive conditions of the mantle, and also
accounts for light lost through back-reflections at interfaces, which varies with rock texture. Specifically, the mean free path (\( \lambda \)) is assumed to be affected by scattering and attenuation

\[
\frac{1}{\lambda} = \frac{1}{d} + A(\nu)
\]

where \( A_z = 2.3026 \ [a_{chem} + 2 \log (1-R)] \) is the true absorption coefficient and \( a_{chem} = \log (I_T/I_0) \) is the absorbance determined from measuring the transmission through a sample (e.g. Clark, 1957). The resulting equation for diffusive radiative transfer in a grainy medium (Hofmeister, 2004b, in review) is:

\[
k_{rad}(T,d,A) = \frac{4dn^2}{3} \sum_{n}^{} \int_{\nu_U}^{\nu_L} \left[ \frac{1-e^{-dA(\nu)}}{(1+dA)^2} \right] \frac{\partial I_{bb}(\lambda,T)}{\partial \nu} d\nu.
\]

The cutoff frequencies (\( \nu_U \) and \( \nu_L \)) and the discrete sum are needed because the integral is valid only for the frequency regions where the mineral partially transmits (Clark, 1957). Grains are opaque when the absorbance is high enough that the interface reflectance (obtained from Snell’s law) summed with the transmittance is 100%. Opacity occurs in the IR and far-UV, and also near the red for large and/or dark grains.

Important factors in radiative diffusion are grain-size, as \( d \) enters into Eq. 4 by itself, and temperature, as the blackbody intensity depends strongly on \( T \). Through \( A \) and Beer’s law, \( k_{rad} \) depends on \( Fe^{2+} \) content and other impurities. However, Eq. 4 is an integral over the product \( dA \), and thus \( k_{rad} \) depends largely on how dark (i.e., Fe-rich) the individual grains are, more than on the specific spectrum possessed by a given mineral phase. This essential behavior of \( k_{rad} \) is gleaned by considering the asymptotic limits:

For very low absorbance, as may be possible for minerals with Fe in the low spin state (Badro et al. 2004), and assuming that \( A \) is independent of frequency, reduces Eq. 4 to:
\[ k_{\text{rad}} \sim d^2 A T^3 \]  \hspace{1cm} (5)

The same limit is obtained for small \( d \). For either small \( d \) or small \( A \), diffusive radiative transfer is small because the emissions of the constituent grains are low, and physical scattering is strong. The opposite conclusion of large \( k_{\text{rad}} \) was reached by Badro et al (2004) because they did not consider the role of grain-size. For very high absorption coefficients, which can be achieved for high concentrations of Fe\(^{2+}\) or other impurities, and assuming that \( A \) is constant reduces Eq. 4 to:

\[ k_{\text{rad}} \sim T^3 / A, \]  \hspace{1cm} (6)

if the grain-size is small enough that the grains are not opaque. For opaque grains, \( k_{\text{rad}} = 0 \). For large grains, the same limit exists. For either large \( d \) or large \( A \), diffusive radiative transfer is low due to the darkness (opacity) of the medium. Thus, \( k_{\text{rad}} \) is largest at moderate \( A \) and moderate grain-size, where physical scattering is not overwhelming, significant light is emitted by individual grains inside the medium, and this light is not completely extincted by nearby grains. As Brewster (1992) pointed out, “lossy” media are effective at radiative transfer. This class includes Fe-rich minerals.

Radiative transfer is much more complex than \( T^3 \) law in Eq. 5 and 6 because \( A \) depends strongly on frequency. To probe \( k_{\text{rad}} \) in the mantle, we apply Eq. 4 to the relevant minerals olivine and perovskite, which have much different absorption characteristics. Recent visible spectra of olivine (Taran and Langer, 2001; Ullrich et al., 2002) merged with new IR data (Hofmeister, in review) show that \( k_{\text{rad}} \) depends non-linearly and strongly on \( d \), \( T \), and Fe\(^{2+}\) content. The behavior (Fig. 2a) is governed by many tradeoffs. Radiative transfer is blocked for very large and small grains, and behavior nearly \( T^3 \) occurs for smallish grains, as discussed above. At any given \( T \), \( k_{\text{rad}} \) has a maximum for a certain \( d \), as indicated in Fig. 2a, because
emissions are substantial when the grains are moderately large, but are still small enough that the mean free path of the photons is significantly longer than $d$. For moderate grain size, a local minimum occurs in $k_{\text{rad}}$ near $T = 2000$ K because at that temperature the peak position of the blackbody curve coincides with that of the strongly absorbing Fe$^{2+}$ peak in the visible. Larger $k_{\text{rad}}$ exists at lower and higher temperatures because mean free paths are longer in the transmitting near-IR and UV spectral regions.

Published spectra for Fe-bearing MgSiO$_3$ perovskite (Fig. 3) were acquired from polycrystalline samples, and therefore include scattering effects. Although the absorption spectra of all minerals strongly increase with $\nu$ in the UV, due to metal-oxygen charge transfer, this material property (the UV tail) is masked by scattering. We therefore use the baseline corrected spectra of Keppler et al. (1994) in the computations, and alter the limits of integration to determine how much the UV contribution could influence $k_{\text{rad}}$. Perovskite has a d-d electronic transition of Fe$^{2+}$ near 8000 cm$^{-1}$ with a band strength [$A \sim 80$/cm for Fe/(Fe+Mg) = 0.06] large compared to $A \sim 25$/cm for olivine with similar Fe content. In addition, perovksite has a charge transfer band in the visible region, attributed to Fe$^{2+}$-Fe$^{3+}$ charge transfer (about 10% of the total Fe in the samples is ferric).

The values for $k_{\text{rad}}$ for perovskite and olivine are surprising similar (Fig. 2b), especially for small grain-sizes, where the behavior of Eq. 5 dominates. To probe the effect of spectral details such as the missing UV tail, $k_{\text{rad}}$ was computed for perovskite with Fe/(Fe+Mg) = 0.12 and $d = 0.1$ cm both by integrating over the entire spectrum and by integrating only up to 10,000 cm$^{-1}$. Neglecting the charge transfer bands in the visible decreases $k_{\text{rad}}$ by about 50% because this part of the integral is important at mantle temperatures. This exercise suggests that the values
shown in Fig. 2b somewhat underestimate $k_{\text{rad}}$ for perovskite as the UV tail is unknown (Fig. 3). However, neglecting the temperature dependence of $A$ overestimates $k_{\text{rad}}$ at high $T$, as can be seen by comparing results for olivine and perovskite for $d = 1$ cm. As $T$ increases, the increase in absorbance of the $\text{Fe}^{2+}$ bands of olivine blocks radiative transfer in olivine until the blackbody curve passes into the UV window. For perovskite, the blocking effect should be greater as the charge transfer bands cover the visible (Fig. 3). Clearly $k_{\text{rad}}$ for perovskite is overestimated for $d = 1$ cm from the available spectral data. The reasonable comparison of $k_{\text{rad}}$ for olivine and perovskite in Fig. 2b, justifies use of olivine in radiative transfer models of the lower mantle, until better spectroscopic data are available for perovskite.

The effect of increasing Fe content is germane to geodynamics. For grain-sizes of 1 and 0.1 cm, doubling $A$ (i.e., doubling the Fe content) of olivine decreases $k_{\text{rad}}$ by $\sim 30\%$. This is due to very intense bands being better at blocking radiative transfer and to these sizes being relatively dark (Hofmeister, in review). For $d \sim 0.01$ cm, increasing $\text{Fe}/(\text{Fe}+\text{Mg})$ to 0.12 increases radiative transfer slightly (Fig. 2b) because optimal radiative transfer is not expected until high iron contents are reached. For olivine with $d = 0.01$, the maximum in $k_{\text{rad}}$ is below $\text{Fe}/(\text{Fe}+\text{Mg}) \sim 0.5$.

Clearly, $\partial k_{\text{rad}}/\partial X$ is negative for upper mantle iron content and grain-size. For the lower mantle, $k_{\text{rad}}$ would reach a maximum at lower Fe content because its strong absorption of perovskite in the visible blocks radiative transfer at substantially lower Fe contents. We conclude that increasing Fe content lowers radiative thermal conductivity for the lower mantle for all but the smallest grain-size ($\sim 0.01$ cm). The effect of Fe in any case on $d = 0.01$ cm is small, as the curves for perovskite (or olivine) with different Fe content are equal within the uncertainties of the calculation.
Evaluating Eq. 4 for perovskite and olivine shows that radiative transfer in the mantle exhibits several threshold effects, although the cut-ons and cut-offs are gradual. (1) At any given Fe content and temperature, a minimum grain-size is required to produce radiative transport, and beyond some large value of $d$, radiative transfer ceases. (2) At any given $d$ and $T$, a minimum Fe content is required to produce radiative transport, and beyond some large value of Fe/(Fe+Mg), radiative transfer ceases. (3) Thresholds in temperature exist as well, but the cut-on temperature is below mantle temperatures (Fig. 2). The cutoff temperature depends strongly on grain-size, but temperatures for $d < 2$ cm appears to be higher than $T$ expected for the mantle (Fig. 2a).

4. Competition between phonon and photon contributions to thermal conductivity

Most geophysicists since the days of Mac Donald and Lubimova have neglected the effects of radiative thermal conductivity (e.g. Balachandar et al., 1992, Tackley, 1996). But, a few works on mantle convection have been devoted to the influence of radiative heat transfer (Matyska et al., 1994; Dubuffet et al., 2002). Although the thermal conductivity depends on $P$ and $T$, it is the temperature dependence of $k$ that critically affects convection because of non-linear terms in the governing equations (e.g. Dubuffet et al., 2002; Yuen et al., 2000). The inferred behavior is complex and counterintuitive because the lattice component decreases with temperature whereas the diffusive radiative component increases with temperature (e.g. van den Berg et al., 2001). Specifically, $k_{\text{rad}}$ increasing with $T$ controls the time dependence and stabilizes the planiforms of mantle convection through positive feedback, whereas $k_{\text{lat}}$ decreasing with $T$ has a destabilizing influence, making convection more chaotic and time-dependent (Dubuffet et al., 2002).
Why $\partial k/\partial T$ is important is revealed by considering the temperature equation. The relevant term is

$$\nabla \cdot [k(T)\nabla T] = k(T)\nabla^2 T + (\partial k/\partial T)(\nabla T)^2$$

which constitutes part of the non-linear partial differential equation. For constant $k$, the temperature equation is simply a linear partial differential equation. Different classes of solutions are obtained for constant and temperature-dependent $k$, because the nature of the equations are not at all the same (e.g. Barenblatt, 1996).

At the boundary layers, where the $\nabla k$ and $\nabla T$ terms become larger than the terms involving $k(T)$ and the Laplacian of the temperature, the temperature equation assumes the character of a first-order non-linear partial differential equation, akin to the Eikonal equation (Barenblatt, 1996). The temperature equation for $k(T)$ changes order as one traverses across the edge of the thermal boundary layer. Therefore, different classes of equations are obtained, depending on whether $k$ is constant or temperature-dependent. Dubuffet et al. (1999) and Starin et al. (2000) found that the non-linear heat equation with $k(T)$ require more grid points that the linear heat equation associated with constant $k$. Yuen et al. (2000) demonstrated the drastic difference of heat advection and diffusion for various forms of $k(T)$, ranging from $\partial k/\partial T$ negative (phonon-type) to $dk/dT$ positive (photon-type).

The new experimental data confirm that $\partial k_{\text{lat}}/\partial T$ is negative and weaker than $1/T^2$, and in addition reveal that this derivative asymptotes to zero at temperatures expected near the top of the lower mantle (Fig. 4). The steepest trend is seen for MgO, as its $k_{\text{lat}}$ is nearly inverse with $T$. The small positive derivatives seen for olivine at high $T$ are due to experimental uncertainties.
and to imperfections in the polynomial fits. The temperature dependence of perovskite in Fig. 4 is a better representation of high $T$ behavior.

The revised formula for radiative transfer (Eq. 4) shows that $\partial k_{\text{rad}}/\partial T$ is positive and nearly linearly dependent on $T$ for small grain sizes (Fig. 4), due to such sizes being partially transparent from the IR to the UV (Hofmeister, 2004b). But for large grain-sizes, $\partial k_{\text{rad}}/\partial T$ changes sign and magnitude rapidly with temperature, due to blocking of radiative transfer in the visible for larger grain-size. Accounting for grain size adds considerable complexity in that radiative transfer can become destabilizing, even more so than the lattice contribution at temperatures consistent with the upper mantle and transition zone, as shown in Fig. 4.

The relative effectiveness of the lattice and radiative contributions are implicit in the competition factor,

$$\phi(T) = \frac{\partial k_{\text{lat}}/\partial T}{\partial k_{\text{rad}}/\partial T}$$

Where $\phi = 0$, convection is controlled by radiative processes, which can either weaken or invigorate convection, as the sign changes with grain-size and temperature. Negative $\phi$ indicates that radiative processes exert a stabilizing influence against convection while phonon scattering operates simultaneously but in a destabilizing fashion, making convection more chaotic and time-dependent. Positive $\phi$ implies that convection is envigorated by both processes. Where $\phi = \infty$, convection is controlled by phonon scattering.

The new results are compared to previous formulations in Fig. 5. The model of Hofmeister (1999) provides trends comparable to the medium grain sizes, but the critical value of $\phi = 0$ is never attained. This parameterization for $k_{\text{lat}}$ was derived by fitting measured $k_{\text{tot}}$ for
forsterite (Schatz and Simmons, 1972) and olivine at low temperature (Kanamori et al., 1968), and by modeling $k_{\text{rad}}$ from the lifetimes of the photons, obtained from the widths of the spectral features in the near-IR through the UV. The model of Shankland et al. (1979) combined with the $k_{\text{lat}}$ being proportional to $1/T$ (considered to be the expected trend at that time) gives a flat lying trend (Fig. 5) which does not attain the critical value. Shankland et al. (1979) computed $k_{\text{rad}}$ using their spectra of Fo$_{90}$ at temperature to determine the mean free path, but assumed that blackbody radiation was propagating through the mantle and that grain boundary scattering could be ignored. In summary, for the upper mantle and transition zone, the previous results are similar to the present model of radiative transfer for 0.1 cm grain sizes. However, the dynamics are quite unstable for the 1 cm size grains as $\phi$ is positive. The new results for the lower mantle differ significantly in that the critical value of $\phi = 0$ is attained.

Threshold phenomenon describe a wide range of systems and physical responses (Drazin, 1992; Strogatz, 1994).

5. Implications on the style of mantle convection

The response of thermal conductivity to physical conditions parallels that of rheology, which also involves multiple mechanisms on microscopic scales (diffusion vs. dislocation flow) as well as mesoscopic processes at grain-boundaries. The various mechanisms are affected by pressure, temperature, and other variables in different ways (e.g. Evans and Kohlstedt, 1995). As a consequence, the response of materials to stress are depicted on deformation maps (Weertman, 1978), wherein the flow behavior is categorized as cataclastic, brittle, ductile, or plastic, and localized or delocalized. The type of rheological behavior largely dictates the dynamical regimes in mantle convection (e.g. van den Berg and Yuen, 1996).
We therefore map mantle-relevant mechanisms for heat transfer onto a domain diagram which considers the effects of $T$, $P$ and grain-size (Fig. 6). Pressure negligibly affects radiative transfer, but because the lattice component increases with $P$, the effect of pressure is to expand the domain where $k_{\text{lat}}$ is important with causes the domain were both mechanisms operate to shrink. Existence of threshold temperature above which $k_{\text{lat}}$ is constant, defines one regime. In addition, just below the critical temperature a region exists where $k_{\text{lat}}$ is small but still relevant to heat flow, and $k_{\text{rad}}$ is large enough to be important. The transition at lower temperatures to purely phonon transport is gradational (Fig. 6ab). Grain-size effects add considerable complexity to the domain diagram. Radiative transfer is increasingly diminished as grain-size decreases, due to physical scattering and weak emissions (Eqs. 4 and 5, Figs. 2-5). Below some threshold, which is affected by temperature and Fe content, $k_{\text{rad}}$ is negligible. Similarly, once the grain-size is coarse enough that individual grains are opaque, radiation can no longer diffuse. This upper cut-off is also affected by $T$ and Fe content, creating another class of behavior in the domain diagram (Fig. 6b).

Lower mantle conditions are above $T_C$, and thus heat transfer is governed by radiative effects. Chemistry is not well-constrained as few mantle samples originate near 670 km, nothing has emerged from greater depths (Gasparik, 2000), and modeling seismic velocity distribution is equivocal due to tradeoffs in $T$, chemical composition, and phase (Deschampes and Trampart, 2003). Grain-size is crucial, but is not well-constrained (e.g. Ranalli, 2001). Growth is retarded by shear forces arising during flow, which disrupts and deforms the large grains. The present results for Fe/(Fe+Mg) = 0.1 are compatible with $d = 0.1$ cm in the lower mantle, as this provides not only large $k_{\text{rad}}$ values at high temperature (Fig. 2), but also high $\partial k_{\text{rad}}/\partial T$ (Fig. 4). Growth
into large grains is not only limited by shear, but such growth would also impede heat transfer leading to instabilities (plumes).

Efficient radiative transfer in the lower mantle provides a means of expelling heat without significant flow, and therefore tweaks the system to weak and sluggish convection. Vigor is provided largely by the size of the lower mantle in this case, as the properties in this region are generally slowly varying. A sluggish lower mantle system is consistent with the long wavelength patterns which seems to dominate the geoid and mantle tomographic images (e.g. Hager and Richards, 1989; Gu et al., 2000; see review by Romanowicz, 2003).

The existence of a critical point at large grain-size (Fig. 6) and the decrease in $k_{\text{rad}}$ as Fe content of the minerals increases suggest that positive feedback may be important to plume formation near the core-mantle boundary. The possible process, as sketched in Fig. 7, is described as follows. Earth’s core provides the source of Fe. In the boundary layers, flow is slow which allows grain-growth to proceed. The slowest regions within the boundary layers are stagnation points where plumes (or upwellings on the edges of the convecting cells) would form. Not only does grain growth in the stagnant regions aid incorporation of new material, e.g. Fe from the core, but moreover, increased grain-size means that very little increase in Fe content, due to the lowering of the solidus, is needed to reduce radiative transfer. Such positive reinforcement means that small changes in Fe content or grain size could initiate the process in Fig. 7. Whereas grain growth and Fe enrichment work together to initiate the process, it is the connection of reduced viscosity with Fe content which provides the feedback loop sustaining plume development. The process described here, wherein radiative transfer is altered by incorporation of Fe ions into the crystal lattice of silicates and oxides, differs substantially from
that envisioned by Manga and Jeanloz (1996), who considered that D’ could consist of a mechanical mixture of metal, sulfide, and silicate, on the basis of variations in the thermal conductivity of the lattice, but more closely resembles the redox driven incorporation of Fe discussed by Morse (2003). The scenario depicted in Fig. 7 can be explored with the Lagrangian-Eulerian schemed devised by Gerya and Yuen (2003) for modeling thermo-chemical plumes: this work will be carried out in the near future.

Our result addresses the seemingly contradictory result of Trampert et al. (2004) which associates high iron contents with lower mantle underlying the central Pacific, regions thought to be hotter than ambient due to the density being lower. The existence of thermo-chemical plumes (Yuen et al., 1993; Ishii and Tromp, 1999) engendered by iron enrichment further suggests both chemical differentiation of the lower mantle, and a density stratification favorable to inducing layered convection. Evidence for decoupling of the lower and upper mantle systems is summarized by Hamilton (2002, 2003), and Anderson (2001, 2002).

Heat transfer in the upper mantle and transition zone differ considerably from lower mantle. First, the temperatures are below \( T_C \) and in the region where both \( k_{\text{rad}} \) and \( k_{\text{lat}} \) are important. The existence of large grains is particularly destabilizing (Fig. 2-6), yet cm sized grains are common in available mantle xenoliths. Decoupled styles of upper and lower mantle cells is consistent with the largely 2-D aspect of plate tectonics which is characerized by higher degrees in spherical harmonics (e.g. Forte and Peltier, 1987; Wen and Anderson, 1995).

6. Cross-scaling in heat transport due to the behavior of thermal conductivity

All processes have an associated length scale, although non-linear processes can involve multiple scales. Commonly, processes operating on a microscopic scale affect macroscopic
phenomena. A classic example is that microscopic vibrations of a crystalline lattice determine the heat capacity of the solid, a bulk physical property, as was recognized by Einstein (1907) and Debye (1912). Processes relevant to geophysics are shown in Fig. 8, along with their characteristic length scales.

Two paths are the focus of this paper. The vibrations of atoms in a crystal lattice are quantized. Scattering of these quanta (phonons) transfers heat within each grains, and eventually beyond. This process exerts considerable control over mantle dynamics, due to the destabilizing effect it has on boundary layers. Exchange of radiation (photons) occurring between grains provides a competing mechanism which operates independently and over much longer length scales (Fig. 8). This mesosocopic process dictates the mode of convection at high temperature.

Mass diffusion provides another example of cross-scaling. It is coupled to radiative diffusion of heat as both are grain-size dependent, and to the lattice contribution in that defects in the crytal lattice (disorder) reduce $k_{\text{lat}}$.

7. Conclusions

The concept of thresholds in thermal conductivity has been introduced, which has important implications for mantle dynamics. Thresholds exist in temperature, grain-size and Fe content. The microscopic process of phonon heat transfer on scale of the crystal lattice and of diffusive radiative transfer on the scale of grain-size are link directly to the macroscopic process of conduction through time and space. The dynamics of mantle plumes are influenced in a different manner by cross-scaling relationships, in view of radiative thermal conductivity (Matyska et al., 1994; Dubuffet et al., 2002).
Cross-scaling relationships involving radiative heat transfer and Fe content are inferred to produce thick thermo-chemical plumes through positive feedback at stagnation points near the core-mantle boundary. Such a mechanism is suggested by seismological studies of low density regions (Trampert et al., 2004), and lends credence to the growing body of evidence for some form of layered mantle convection (see summaries by Anderson, 2002; Hamilton, 2003).

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**Figure Captions**

Figure 1. The lattice contribution to heat transfer for mineral structures present in the mantle.

(a) Dependence of $D$ and $k_{\text{lat}}$ on $T$ for ceramic MgO (from Aremco) with porosity of 4.5%. Open circles = individual data points for MgO. Dotted curves = power law fits, as shown. The data are best fit with an 8th order polynomial, but linear extrapolations are used below and above the range of measurements. Thermal conductivity was calculated from $D$ using published data on heat capacity and density.

(b) Measured values of $D$ vs. $T$. Circles = mantle garnet $[(\text{Mg}_{2.1}\text{Fe}_{0.75}\text{Ca}_{0.15})\text{Al}_2\text{Si}_3\text{O}_{12}]$. 


from Garnet Ridge, AZ). Open squares = olivine \((\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4)\) from Balsam Gap, N.C.). Gray diamonds = diopside (near end-member \(\text{CaMgSi}_2\text{O}_6\) from DeKalb, N.Y.). Triangles = hercynite (~\(\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Al}_2\text{O}_4\) from Parker Mine, Canada). Open crosses = synthetic \(\text{SrTiO}_3\) (from Morion Co.) with the perovksite structure. Symbols are individual data points. Polynomial fits are shown. The double arrow shows the range of critical temperatures for these solids.

(c) Values of \(k_{\text{lat}}\) calculated from \(D, \rho\) and \(C_P\). Square with cross = perovskite (computed using \(D_0\) from Osako and Ito (1991), with \(C_P(T)\) and \(\rho(T)\) for \(\text{MgSiO}_3\), but \(dD/dT\) for \(\text{SrTiO}_3\). Spinel values were computed from \(\partial D/\partial T\) for hercynite, but the remaining properties for end-member \(\text{MgAl}_2\text{O}_4\). Gray circle = \(k_{\text{lat}}\) for \(\text{MgSiO}_3\) majorite computed using \(\partial D/\partial T\) for garnet. Other symbols as in (a) and (b).

Figure 2. Dependence of diffusive radiative transfer on temperature, grain-size, and phase, with comparison to the phonon contribution.

(a) Olivine (Fo\(_{90}\)) vs. \(T\). Heavy lines = \(k_{\text{rad}}\) for various grain-sizes. Long dashes = \(d\) of 10 cm. Medium dash = 5 cm. Dotted = 1 cm. Broken = 0.5 cm. Solid = 0.1 cm. Dot-dashed = 0.01 cm. Thin dotted line = \(k_{\text{lat}}\) for olivine. The bump near 1500 K is an artifact due to fitting \(D(T)\) with a polynomial. Thin dashed line = \(k_{\text{lat}}\) for \(\text{MgAl}_2\text{O}_4\) which should be similar to that for \(\gamma\)-\(\text{Mg}_2\text{SiO}_4\). Thin solid line = \(k_{\text{lat}}\) estimated for \(\text{MgSiO}_3\) perovskite. Gray bars = threshold temperatures for \(k_{\text{lat}}\). Approximate temperatures for the subdivisions of Earth’s mantle are shown above the graph.

(b) Perovskite (Mg\(_{0.94}\text{Fe}_{0.06}\text{SiO}_3\)) vs. \(T\). Thin solid line = \(k_{\text{lat}}\) Gray bar = threshold for lower mantle. All other lines are \(k_{\text{rad}}\), where patterns indinctate grain-sizes (dotted = 1 cm;
solid = 0.1 cm, and dot-dashed = 0.01 cm). Olivine is shown as a medium black line, and perovksite as the heavy lines. Heavy black = perovskite with Fe/(Fe+Mg) of 0.6. Grey = perovskite with Fe/(Fe+Mg) of 0.12. Light grey shows the effect of neglecting the charger transfer band at high frequency for Fe/(Fe+Mg) = 0.12 and d = 0.1 cm.

Figure 3. Visible spectra of Fe-bearing magnesium silicate perovskite. Thin solid curve = raw absorbance data from Keppler et al. (1994) for a 50 µm thick sample with 6 % FeSiO$_3$. Heavy solid curve = baseline corrected spectra. The correction removed scattering effects, but may also have removed the intrinsic metal-oxygen charge transfer tail from the UV. Dotted curve = measurements of Shen et al. (1994) for 5 % FeSiO$_3$. Absorbance was not reported. The data are plotted to most closely follow the results of Keppler et al. (1994). The Fe$^{2+}$-Fe$^{3+}$ charge transfer band near 15000 cm$^{-1}$ appears to be sample specific.

Figure 4. Temperature dependence of $\partial k_{lat}/\partial T$ for three minerals and of $\partial k_{rad}/\partial T$ for various grain sizes. Thin lines = $\partial k_{lat}/\partial T$: long dashes for MgO, solid for perovskite, short dashes for olivine. Perovksite data are derived from thermal diffusivity on SrTiO$_3$, combined with $\rho$, $C_P$, and low $T$ measurements of $k$ for MgSiO$_3$. Thick lines = $\partial k_{rad}/\partial T$: dotted for $d = 1$ cm; solid for 0.1 cm, and dot-dashed for 0.01 cm. Derivatives of $k_{rad}$ were obtained from fit the calculations for olivine in Fig. 2a to polynomials (order 3 for $d = 0.01$ and 0.1 cm, order 8 for $d = 1$ cm). Derivatives of $k_{lat}$ were obtained directly from the data plotted in Fig. 2a. The waviness is due to experimental uncertainties being magnified in the derivative.
Figure 5. Competition factor, $\varphi = (\partial k_{\text{lat}}/\partial T)/(\partial k_{\text{rad}}/\partial T)$ as a function of temperature. Black lines use $k_{\text{lat}}$ of perovksite and $k_{\text{rad}}$ of Fo$_{90}$ from this work (dotted = $d$ of 1 cm; solid = $d$ of 0.1 cm; dot-dashed = $d$ of 0.01 cm). Solid grey curve computed from $k_{\text{lat}}$ (W/m-K) = $5/T$ and $k_{\text{rad}}$ from Shankland et al. (1979). Dotted grey curve computed from $k_{\text{lat}}$ (W/m-K) = $5/T^{1/2}$ and $k_{\text{rad}}$ from Hofmeister (1999). These earlier studies did not consider grain size. The initial value of 5 W/m-K used for the “generic” $k_{\text{lat}}$ formulas is close to those of MgSiO$_3$-perovskite (4.77 W/m-K) and olivine with Fe/(Fe+Mg) = 0.1 (4.9 W/m-K), and is the average of ringwoodite and solid solution majorite values.

Figure 6. Domain diagram mapping $k_{\text{rad}}$ and $k_{\text{lat}}$ onto the $T$ (shown vertically) vs. grain-size ($d$) or pressure ($P$) planes (shown horizontally). Dark gray areas = regimes where radiative transfer is important. Light gray areas = regimes where both phonon and photon processes are important. Slashed area = region where $k_{\text{lat}}$ is constant and radiative transfer is blocked. The temperature at which $k_{\text{lat}}$ becomes constant is independent of $P$ or $d$.

Radiative transfer disappears at small grain-size ($d_{c1}$) as the emission intensity approaches zero and scattering greatly shortens the mean free path, and also at large grain size ($d_{c2}$), as the particles become opaque due to strong absorbance combined with finite reflectivity at grain boundaries due to mismatch in indices of refraction.

Figure 7. Schematic of the role of positive feedback in production of thermo-chemical plumes in the deep mantle. Enrichment of Fe in perovskite locally decreases radiative transfer which turn provides hotter temperatures and lower viscosity, and the additional effects as shown.
Figure 8. Scale diagram connecting microscopic (solid state physics) to macroscopic (conduction vs convection) processes relevant to Earth science. Filled arrows = scale crossings producing heat transfer. Open arrows = scale crossings producing deformation. Shaded squares = processes focussed on in this study.
Fig. 1

MgO ceramic

\[ D = 15863 \ T^{1.2516} \]

\[ k_{lat} = 12151 \ T^{-0.99585} \]

measured thermal diffusivity

thermal conductivity
Chemical absorbance (a)

Shen et al. (1994) absorbance estimated
Keppler et al. (1994) baseline corrected

Perovskite
Mg$_{0.94}$Fe$_{0.06}$SiO$_3$

$\nu$, cm$^{-1}$
$0 5000 10000 15000 20000 25000$

Fe$^{2+}$ charge transfer
baseline corrected
raw data
Shen et al. (1994) absorption estimated
Keppler et al. (1994)

t = 50 µm

Fig. 3
Fig. 4

![Graph showing thermal properties of the Earth's interior](image-url)
fig. 5

Lithosphere | UM | TZ

Shankland et al. (1979)

Hofmeister (1999)

0.01 cm
0.1 cm
0.01 cm

0

φ

400 600 800 1000 1200 1400 1600 1800 2000

Temperature, K
Fig. 6. 

Fig. 7. 

higher Fe$^{2+}$ $\rightarrow$ lower $k_{rad}$ $\rightarrow$ hotter

higher entrainment $\rightarrow$ lower $\eta$ $\rightarrow$ lower $k_{rad}$ $\rightarrow$ hotter