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Variation of thermal conductivity and heat flux at the Earth’s core mantle boundary

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Highlights

- The thermal conductivity of post-perovskite is 50\% larger than that of perovskite.
- Enhanced heat flux into cold regions of D" where post-perovskite is stable.
- The conductivity of post-perovskite is anisotropic and thus varies with texture.
- Potential for feedback between convection, deformation and conduction in D".
Abstract

The two convective systems that dominate Earth’s internal dynamics meet at the boundary between the rocky mantle and metallic liquid core. Energy transfer between processes driving plate tectonics and the geodynamo is controlled by thermal conduction in the lowermost mantle (D’). We use atomic scale simulations to determine the thermal conductivity of MgSiO$_3$ perovskite and post-perovskite under D’ conditions and probe how these two convective systems interact. We show that the thermal conductivity of post-perovskite (∼12 W/mK) is 50% larger than that of perovskite under the same conditions (∼8.5 W/mK) and is anisotropic, with conductivity along the a-axis being 40% higher than conductivity along the c-axis. This enhances the high heat flux into cold regions of D’ where post-perovskite is stable, strengthening the feedback between convection in the core and mantle. Reminiscent of the situation in the lithosphere, there is potential for deformation induced texturing associated with mantle convection to modify how the mantle is heated from below. We test this by coupling our atomic scale results to models of texture in D’ and suggest that anisotropic thermal conductivity may help to stabilise the roots of mantle plumes over their protracted lifetime.

Key words: Lowermost mantle, Thermal conductivity, Perovskite, Post-perovskite, D’, CMB heat flux

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Thermal interaction between the core and mantle is central to our understanding of the Earth's energy budget (Gubbins, 2003; Lay et al., 2008). In the absence of substantial chemical mixing heat is only transported across the core mantle boundary (CMB) by conduction in the lowermost mantle ($D''$).

The rate of cooling of the top of the core and heating of the base of the mantle is therefore controlled by the temperature difference between the core and the interior of the mantle and the thermal conductivity of materials such as (Mg,Fe)SiO$_3$ perovskite and post-perovskite found in $D''$. However, the thermal conductivity of these materials under high pressure ($P \sim 135$ GPa) and temperature ($T \sim 2000$–$4000$ K) conditions is unknown. Historically, estimates of thermal conductivities at the CMB from low pressure or low temperature experiments, theoretical considerations and extrapolations are 4–29 W/mK (e.g. Osako and Ito, 1991; Hofmeister, 1999, 2008). Ongoing experimental work is aimed at refining these estimates but, as yet, it is still not possible to measure thermal conductivity under the conditions of simultaneously high $P$ and $T$ found at the CMB. Manthilake et al. (2011) performed measurements on MgSiO$_3$ perovskite and MgO to 14 GPa and 1273 K in a multi-anvil cell. Goncharov et al. (2009) and Dalton et al. (2013) measured the thermal conductivity of MgO at 300K to 32 GPa and 60 GPa, respectively, using a diamond anvil cell to generate pressure. Goncharov et al. (2010) performed a similar experiment on perovskite at 125 GPa and 300 K. The latest experimental results (Ohta et al., 2012) reach 144 GPa and include both MgSiO$_3$ perovskite and post-perovskite but are limited to near-ambient temperatures (300–436 K). These results reveal that post-perovskite has $\sim 60\%$ larger con-
ductivity than perovskite and that the conductivity of perovskite increases from 8 to 37 W/mK as pressure increases from 8 to 144 GPa.

Recently, to avoid the formidable experimental challenges in determining thermal conductivity to high pressure and temperature, considerable effort has been expended in the development of tools to make use of atomic scale simulations to calculate the thermal conductivity of lower mantle phases. Much of this work, reviewed by Stackhouse and Stixrude (2010), has focused on MgO where a range of different techniques have been used. For example, Cohen (1998) made use of equilibrium molecular dynamics (MD), interatomic potentials and Green-Kubo theory, Tang and Dong (2009) used anharmonic lattice dynamics (LD) truncated to third-order and density functional theory (DFT), de Koker (2009, 2010) combined DFT, MD and LD in the harmonic approximation, and Stackhouse et al. (2010) used DFT and non-equilibrium molecular dynamics (NEMD). Importantly, results of these studies are broadly in agreement with each other, and with the available experimental data (see Stackhouse and Stixrude, 2010, Figure 6).

There has been less attention focused on MgSiO$_3$ perovskite or post-perovskite, despite these phases dominating the mineralogy of the lower mantle and D$''$, respectively. As discussed below Stackhouse et al. (2009) reported preliminary results for perovskite using DFT and NEMD. Very recently Haigis et al. (2012) used an interatomic potential model, MD and Green-Kubo theory to predict the thermal conductivity of MgO and the two MgSiO$_3$ phases to CMB conditions while Dekura et al. (2013) made use of anharmonic LD and DFT to probe the conductivity of perovskite. At low temperature the results of Haigis et al. (2012) give thermal conductivities substantially higher than the available experimental data and these authors appeal to an isotopic correction to reduce
their calculated conductivities to values in better agreement with experiment (phonon scattering by atoms with a mass different to their replicas in adjacent unit cells will reduce the thermal conductivity). However, an isotopic correction is not applied by Cohen (1998), de Koker (2009, 2010) or Stackhouse et al. (2010) but their results for MgO are in reasonable agreement with the experiments (although the focus is not always on the low temperature properties where isotopic effects are most important). The LD calculations (Dekura et al., 2013) give good agreement with experiment at low temperature but the results deviate from the experiments of Manthilake et al. (2011) at higher temperatures. There is clearly further work needed to fully understand these methods at low temperature where the conductivity is most difficult to predict (e.g. where the effect of isotopic disorder is maximised). Work reported by, e.g. Sellan et al. (2010), Hu et al. (2011) and Beck et al. (2013) is a significant step in this direction. Nevertheless, under the high temperature conditions interesting for core-mantle interaction the various computational approaches are in good agreement and this motivates the current study, which has the aim of using atomic scale simulation to probe the variation of thermal conductivity in D″.

Before outlining our approach it is important to note that all these calculations only capture the portion of heat transport caused by interactions between lattice vibrations (phonons). This lattice conductivity is believed to dominate in insulating solids like the mantle silicates and we neglect the electronic conductivity (important in metals, see Pozzo et al., 2012) and radiative heat transport, which is expected to be altered by the iron spin transition at high pressure (see Lin et al., 2013, for a recent review). The importance of the radiative heat transport is disputed (Hofmeister, 1999; Keppler et al.,
2008; Goncharov et al., 2008), but this process will contribute a maximum of 50% of the total conductivity (5 W/mK, Keppler et al., 2008), and probably much less (0.5 W/mK, Goncharov et al., 2008) in perovskite, and certainly in post-perovskite (Goncharov et al., 2010).

2 Methodology

We use the so-called direct scheme (Müller-Plathe, 1997; Nieto-Draghi and Avalos, 2003; Stackhouse and Stixrude, 2010) and invoke non-equilibrium molecular dynamics to calculate the thermal conductivity of perovskite and post-perovskite. In this method, physical reality is inverted in the sense that one imposes a heat flux leading to a thermal gradient (instead of a thermal gradient leading to a heat flux). The single crystal thermal conductivity $k$ is then given by the ratio of the time-averages of the heat flux $\langle J \rangle$ across a unit area and the temperature gradient $\langle dT/dx \rangle$:

$$k = -\frac{\langle J \rangle}{\langle dT/dx \rangle}.$$  

(1)

The heat-flux is imposed by virtual elastic scatters between two atoms in separated sections of a long simulation cell. The atom with the highest kinetic energy in the designated cold section and the one with the lowest kinetic energy in the hot section swap their momenta, effectively transferring heat from the cold to the hot section (see Stackhouse and Stixrude, 2010, for details).

In order to avoid the high computational costs and system-size limitations one encounters using density functional theory (DFT), which are particularly heavy for the large unit cells of perovskite and post-perovskite, we primarily
made use of the two established interatomic potential parameterisations of Murakami et al. (2004) and Oganov et al. (2000). The choice of interatomic potential is critical to the success of our calculations and we note that a recent appraisal of 27 possible choices found that the Oganov et al. (2000) model and similar parameterisations were the most successful (Chen et al., 2012). The Murakami et al. (2004) model was not included in the study of Chen et al. (2012). In order to undertake these calculations we modified the code GULP (Gale and Rohl, 2003) to implement the direct scheme for arbitrarily complex systems. The use of interatomic potentials allowed us to perform simulations with up to 11,520 atoms while maintaining predictive power. System-size effects were corrected by extrapolating to infinite cell size (Schelling et al., 2002) and by checking convergence on the cross-sectional area (see below). We also perform DFT simulations of smaller supercells as a test of the interatomic potentials. These calculations were performed with a modified version of the VASP code (Stackhouse and Stixrude, 2010).

To determine the cell parameters as a function of pressure and temperature we first performed equilibrium molecular dynamics (MD) for both phases at a constant pressure and constant temperature using the modified Nosé-Hoover thermostat (Melchionna et al., 1993) in $3 \times 3 \times 3$ super-cells. We used a time-step of 1 fs and the thermo- and barostat parameters both set to 0.05. After equilibration for 5 ps the time averages over a production run of 20 ps were used. The resulting parameters (pressure, temperature, unit cell parameters) are tabulated the Supplementary Information. These parameters were used to calculate cell volumes for the non-equilibrium molecular dynamics runs used to calculate the thermal conductivity.

NEMD simulations were performed at a constant volume and a constant tem-
perature using a Nosé-Hoover-thermostat (Nosé, 1984; Hoover, 1985) with a thermostat parameter of 0.05 and time-step of 1 fs. After 5 ps equilibration with MD, we started the NEMD simulation which ran for 100 ps. Following convergence testing (Figure 1) energy was swapped every 20 fs (i.e., every 20th time-step). This established a thermal gradient across the simulation cell, and the temperatures of the slices within our simulation cell reached a constant temperature after about 30 ps. To calculate $k$ the simulation cell of dimensions $N \times D \times D$ was divided into $2N$ slices each containing an equal numbers of atoms. As shown in Figure 2 we fitted weighted straight lines following York (1966, 1967) and calculated errors of our time-averages of temperatures and energy-flux with the blocking method (Flyvberg and Petersen, 1989). The thermal gradients in the simulation cells were fitted to the central 33% of all slices between the hot and cold slice. However, for the smallest cells ($N \times 3 \times 3$ when $N = 6$ and 8) we excluded only the hot and cold slice for the fitting procedure. The same weighted linear fitting method was used to extrapolate from finite cell-length to infinite cell length (Schelling et al., 2002), see Figure 3 for examples, and to calculate the errors on the fitting parameters (slope and zero-intersect). We found that the effect of increasing the cross-sectional area ($D \times D$) is to reduce the thermal conductivity. As shown in Figure 3, converged results can be obtained for a $2 \times 2$ unit cell cross-sectional area for perovskite (irrespective of direction), a $2 \times 1$ unit cell ($b \times c$) for the conductivity along $a$ in post-perovskite and $3 \times 1$ unit cell ($a \times c$) along $b$ in post-perovskite. We used these values for the DFT simulations while for the interatomic potential simulations we used $3 \times 3$ cross-sectional areas to give full convergence.

In order to begin to explore the effect of iron-(II) impurities on thermal conductivity we performed some simulations with the interatomic potentials with
randomly chosen magnesium ions replaced with iron (with “iron” in the sim-
ulations being simply a magnesium atom with an atomic weight of 56 g/mol).
These simulations, which are only possible to such low concentrations (down
to 1% of Mg-sites occupied with Fe) because of the large size of the simulation
cells, should allow us to capture the leading effect of the inclusion of a vari-
able amount of iron in perovskite and post-perovskite on the lattice thermal
conductivity. We do not, however, capture the possibility that the spin tran-
sition in iron ions could dramatically alter the radiative contribution to the
conductivity or the potential effect of other impurities such as aluminium or
iron-(III). While provisional, these calculations highlight an important ben-
efit of the use of computationally efficient interatomic potential models: as
long as they can be validated for pure systems using the predictive power of
DFT they can be used to probe the effect of a wide range phenomena such as
solid-solution, defects (including grain boundaries) and impurities on thermal
conductivity.

Geophysically, the thermal conductivity is of interest because it controls the
movement of heat and we complete our study by combining our calculated val-
ues of $k$ for single crystal perovskite and post-perovskite with previous models
of texture and temperature in D’” (Walker et al., 2011) to build a model of
CMB heat flux. We concentrate on a simple model were the temperature, tex-
ture and phase distribution is fixed and consider how different assumptions
for the state of the lowermost mantle alter the heat flux. In a more sophis-
ticated model changing the heat flux would lead to changes in temperature
that would alter the distribution of perovskite and post-perovskite, the pat-
tern of convection and, in turn, that of conductivity and introduce a number
of feedback mechanisms. In calculating the heat flux for plausible models of
the lower mantle, without allowing these feedbacks or necessarily generating a model that is self consistent, we aim to determine how changes in lowermost mantle conductivity might alter deep mantle convection. We do not attempt to directly model the effect of variable and anisotropic conductivity on deep mantle convection because current knowledge of how perovskite or post-perovskite deform is not sufficiently advanced for this task. In order to proceed we recall that, in three dimensions, the heat flux $q_i$ in direction $x_i$ ($i = 1, 3$) is given by Fourier’s law:

$$q_i = -K_{ij} \frac{dT}{dx_j},$$

where $K$ is the second order thermal conductivity tensor for the polycrystal and $T$ is the temperature. The repeated index on the right hand side implies a summation for values $j = 1, 3$. In order to calculate the heat flux across the thermal boundary layer above the CMB we therefore need to combine two models: one for the thermal conductivity of the rock forming the lowermost mantle and one for its temperature. Full details of these two models are given in the Supplementary Information but, briefly, they consist of the following components. The one-dimensional geotherm of Stacey and Davis (2008) and local temperature perturbations taken from Simmons et al. (2009) is used to calculate the thermal gradients in the layer above the CMB. This model is identical to that used by Walker et al. (2011) to evaluate the phase stability and lattice preferred orientation (LPO, calculated using the VPSC code of Lebensohn and Tomé, 1993) in D'' (a model which used data from: Mitrovica and Forte, 2004; Oganov and Ono, 2004; Simmons et al., 2009; Forte et al., 2013). To calculate the bulk conductivity, $K$, we take the mean of the Voigt and Reuss bounds of single crystal conductivities, $k$, taking account of the temperature dependant phase transition between perovskite and post-perovskite
and either assuming $D''$ is isotropic, or that it exhibits an LPO as modelled by Walker et al. (2011).

3 Results

Results of the atomic scale simulations are summarised in Figures 4 and 5 with further details given in the Supplementary Information. Both phases show the expected decrease in conductivity with increasing temperature and increase in conductivity with increasing pressure. Post-perovskite is consistently more conducting than perovskite. Both sets of interatomic potentials give good agreement with the results from DFT, however, the extrapolations to infinite cell-size differ in terms of the resulting anisotropy. Nevertheless, DFT and interatomic potentials give values within error of each other for the isotropic average thermal conductivity. To capture the effect of pressure and temperature on the thermal conductivity we fitted the temperature-dependence of our data (along all crystallographic axes) with functions of the form: $k \propto \alpha + \beta/\sqrt{T}$, and used a linear fit to interpolate between the pressures. This leads to a four-parameter equation we use to describe our results:

$$k = \alpha_0 + \alpha_P \cdot P + \frac{\beta_0 + \beta_P \cdot P}{\sqrt{T}}.$$  \hspace{1cm} (3)

The parameters $\alpha_0$, $\alpha_P$, $\beta_0$ and $\beta_P$ for both phases and potential models are given as a function of direction in the crystal in Table 1.

As expected, the result of including iron in our calculations is to reduce the thermal conductivity. However, as shown in Figure 6, the reduction is variable between phase, crystallographic direction and interatomic potential and
rapidly saturates with increasing iron content. Our approach probably gives a lower bound on the effect of iron impurities (as additional changes in the atomic interactions associated with the difference in chemistry of iron and magnesium will increase any anharmonicity and thus the magnitude of the phonon scattering). Indeed, the reduction in thermal conductivity in perovskite is about half of the 50% reported by Manthilake et al. (2011). The reason for this discrepancy is probably the presence of Fe$^{3+}$ in these experiments (and in the mantle) and we note that our approach could be used to study this in more detail if suitable transferable interatomic potentials for these impurities were to be produced. In the meantime, our results show that thermal conductivity can vary quickly with the addition of a small quantity of impurities, but that this effect can change and saturate as the impurity concentration grows. This non-linear behaviour needs to be considered if experimental results, such as those of Manthilake et al. (2011), are extrapolated to other impurity contents.

In order to gain further confidence in our approach we compare the calculated conductivity with all the available experimental determinations of thermal conductivity in MgSiO$_3$ perovskite (Osako and Ito, 1991; Goncharov et al., 2010; Manthilake et al., 2011; Ohta et al., 2012) in Figure 5a. We derive a conductivity that is slightly ($< 2$ W/mK) lower than the 26 GPa experimental data (Manthilake et al., 2011) and agrees with the lower bound of low precision provisional data from Goncharov et al. (2010) at 125 GPa. Furthermore, there is good agreement with new 300 K data above 80 GPa (Ohta et al., 2012). Early experiments by Osako and Ito (1991) at ambient conditions give a thermal conductivity of 5 W/mK. This is substantially lower than our results of $14\pm 1$ W/mK under these conditions and is not compatible with
the 26 GPa experimental data (Manthilake et al., 2011). This discrepancy may be due to the presence of a large number of defects in the metastable perovskite sample measured at low pressure leading to substantial phonon scattering and a reduction in thermal conductivity or to the effect of decompressed grain boundaries. For post-perovskite there are no experimental data above 300 K (Ohta et al., 2012). However, the agreement with the 300 K data and with DFT results (Figure 5b) lends support to the results of the present calculations.

Our results show that post-perovskite conducts heat more easily than perovskite but what are the geophysical implications? Figure 7 shows the thermal conductivity along the mantle geotherm of Stacey and Davis (2008); for most of the lower mantle increasing pressure (which increases thermal conductivity) overcomes the effect of increasing temperature (which decreases it). In the thermal boundary layer above the CMB the rapid increase in temperature leads to a decrease in conductivity for both perovskite and post-perovskite, but post-perovskite still conducts heat 50% faster than perovskite. Another factor that can lower the conductivity is the presence of impurities (e.g. Fe or Al) but this effect is hard to quantify in the lowermost mantle as we do not know how these impurity elements partition between perovskite, post-perovskite and periclase. However, the saturation of the change in thermal conductivity with relatively small quantities of iron could suggest that the impurity effect is homogeneous across the lowermost mantle as compositionally pure phases are unlikely. Figure 7 also illustrates a second potentially important difference between the two phases. Thermal conductivity in perovskite is nearly isotropic but there could be a strong anisotropy for post-perovskite.

To illustrate the potential importance of these results we modelled heat flux
in the thermal boundary layer above the CMB. We quantify the effects of temperature dependent thermal conductivity, the increase in thermal conductivity across the phase transition and anisotropic thermal conductivity in post-perovskite, and compare these effects with the expected variation in temperature in D''. To do this we evaluate the heat flux on a 5° by 5° grid using models of the thermal conductivity and temperature field described above. We evaluate the three components of the temperature gradient by finite difference of the temperature model described in detail in the Supplementary Information, which also includes full results for all our heat flux models. The chosen geotherm (Stacey and Davis, 2008) implies a baseline CMB heat flux for a 1D isotropic Earth that is \sim 40% higher if it is controlled by post-perovskite compared to a perovskite controlled case. The absolute values reported in the S.I. are largely controlled by the temperature drop across the CMB and should only be considered as a reference point in the current work; choosing a different geotherm will change the absolute values of the heat flux. However, the temperature of the core and lowermost mantle is poorly constrained, and we thus focus on how the heat flux varies across the lowermost mantle rather than the total heat flux out of the core. We emphasise that these results cannot simply be scaled to account for a different temperature field or for different heat production rates in the core or mantle because the model includes important non-linear effects. We address this topic in more detail in the Conclusions, below.
The spatial pattern of heat flux across the CMB has the potential to influence convection in the outer core and thus the pattern and evolution of the Earth’s magnetic field (Biggin et al., 2012). This may control the patterns of geomagnetic reversals (Glatzmaier et al., 1999), lead to a distinctive pattern of high magnetic flux (Gubbins et al., 2007) and even control how the inner core grows (Aubert et al., 2008). Even with uniform thermal conductivity hot regions of \( D'' \) will lead to low, and cold regions to high, heat flux. Previous workers have used this information with tomographic images to set a spatially varying heat flux boundary condition at the CMB for models of the geodynamo (Glatzmaier et al., 1999; Gubbins et al., 2007). Our data and models confirm that temperature variation in \( D'' \) is the most important control on variation in heat flux but modifies this view in two important ways. First, the temperature dependence of the thermal conductivity will lead to a further increase in the heat flux into cold regions and a decrease into hotter regions. Our temperature model has a range of \( \pm 500 \) K from the value defined by the geotherm and this dominates the pattern of radial heat flux through \( D'' \), which is positively skewed as the area covered by hot material is smaller than the area covered by cooler mantle (Figure 8). Changing the conductivity (by comparing models with a constant 10 W/mK conductivity with those of temperature dependent conductivity controlled by perovskite) shows that the pattern of high heat flux in cold areas remains but the skewness increases slightly. A larger effect is seen when comparing perovskite with post-perovskite. For post-perovskite dominated lowermost mantle the maximum, mean and modal values of local heat flux all increase compared to the perovskite case and its distribution
broadens. Going from perovskite to post-perovskite increases the maximum heat flux from 0.04 to 0.06 W/m². A second effect arises from the positive Clapeyron slope of the phase transition (Hirose et al., 2006) meaning that post-perovskite is expected to be found in colder regions of D″. This leads to an interesting mixed phase case (where the phase, and thus thermal conductivity, depends on the temperature) and results in the high maximum and high modal flux as the post-perovskite case but reduces the heat flux in hotter regions giving a strongly bimodal heat flux distribution (Figure 8c and d). Together these two effects will, for any assumed relationship between mantle temperature and seismic velocity, substantially stretch and modify the range of heat flux variation, enhancing the potential for mantle control on convection in the core and thus on the magnetic field.

As well as spatial variation on how quickly the core is cooled, the conductivity step across the perovskite to post-perovskite transition can change the behaviour of the mantle itself. Geodynamic models show that increasing the thermal conductivity of D″ increases the size of plumes from the CMB (Naliboff and Kellogg, 2006; Tosi et al., 2010). In two-dimensional models of mantle convection increasing the conductivity across the phase transition gives higher velocity downwellings and larger asymmetry of the convective planform compared to cases where the conductivity of the two phases are identical (Hunt et al., 2012; Tosi et al., 2013). The increase in thermal conductivity across the phase transition is thus expected to be crucial for convection in the mantle and core. Intriguingly, this may be a transitory effect over the history of the Earth (e.g. Oganov and Ono, 2004; Kameyama and Yuen, 2006). In the past it is likely that the mantle was warmer, suppressing the formation of post-perovskite close to the CMB and reducing the heat flux variation. In the future
the core and mantle could be cooler, perhaps with a thick post-perovskite layer everywhere above the core. We expect the three regimes to yield measurably different dynamics, for example changing the nature of plumes rising from the lowermost mantle (Matyska and Yuen, 2006), and it would be interesting to know if this produced a signature in the palaeomagnetic or tectonic records. Depending on size and internal structure, larger or cooler terrestrial planets could enter the ‘future Earth’ regime more quickly while smaller or warmer planets may never develop into a mixed phase regime.

Changing anisotropy of conductivity across the phase transition may also be important. Seismic studies (e.g., Lay and Young, 1991; Kendall and Silver, 1996; Nowacki et al., 2010, 2011) show that D″ is elastically anisotropic and this is likely to be the signature of lattice preferred orientation (LPO) of post-perovskite generated by solid-state deformation from mantle convection (Panning and Romanowicz, 2004; Merkel et al., 2007; Wenk et al., 2011; Walker et al., 2011; Nowacki et al., 2013). If correct, the bulk thermal conductivity of post-perovskite bearing D″ material must also be anisotropic reflecting the LPO and single crystal conductivity. A similar argument has been made for the upper mantle where seismic anisotropy is believed to originate from the flow-induced reorientation of olivine. This is proposed to alter the conductive heat flux in regions with LPO developed by past or present convection leading to cooling of old conductive lithospheric roots (Mimouni and Rabinowicz, 1988) and to fast conduction parallel to strain and deformation induced weakening (Tommasi et al., 2001; Gibert et al., 2003). As the conductive anisotropy of olivine is similar in magnitude to that calculated for post-perovskite, similar arguments can be made for D″. It turns out that anisotropy plays a minor role in altering the radial CMB heat flux but can, as discussed in the supplementary
material, rotate the heat flux vector and thus change its horizontal components in a way that is dependent on the active slip systems. Figure 9 shows one interesting effect in the South East Pacific, close to the possible source of the Galápagos hot spot (flow in this region is discussed in more detail by Forte et al., 2013). As illustrated in the cartoon (Figure 9e), anisotropy has the effect causing heat traverse across the temperature gradient oblique to the maximum slope, rather than to flow directly down the thermal gradient parallel to the direction of maximum decreases in temperature, as expected in the isotropic case. This has the effect causing the horizontal components of the heat flux, when viewed from the surface, to be reversed, leading to conduction towards the plume increasing its buoyancy. We emphasise that heat is still conducted from hot to cold; what changes is that the heat is no longer conducted towards the coldest location as expected for the isotropic case. What happens to the heat flux into the base of the plume if it shifts on the CMB? Immediately after this movement some of the conductive heating of the plume base is lost, potentially reducing its buoyancy until the texture has time to evolve. This suggests that there may be a resistance to movement of the base of a plume across the CMB caused by the development of LPO and anisotropic conductivity in D″. This might contribute to the apparent fixity of the locations of plumes through geological time. However, quantification of this effect awaits fully anisotropic dynamic modelling of convection and texture development in the lowermost mantle.
Although the conductivities of perovskite and post-perovskite are both within the historical range of estimates, we argue that the change in conductivity and its anisotropy across the phase transition have important implications for the dynamics of the core and mantle. In our simplified models including the higher thermal conductivity of post-perovskite increases the heat flux across the CMB by almost 40%, implying a change in core or mantle temperature if this were permitted to vary in the model. Even though our models maximise the effect of anisotropy the global effect is a minor increase or decrease in the total heat flux. Locally, the effect may be more significant, but the details of the depend on the active slip system. Our approach is simplified and should only be taken as an illustration of some of the effects of variable thermal conductivity at the CMB. The model makes use of a fixed temperature field as input rather than the more challenging approach of attempting to construct a self-consistent thermal model based on heat production in the mantle and core. More importantly, there is no feedback between the conductivity, flow field and resulting distribution of perovskite and post-perovskite. While it is possible to build a self-consistent global model based on a radial viscosity profile and mapping between density and temperature (e.g. Forte and Woodward, 1997; Glišović et al., 2012), in the lowermost mantle lateral variations, exemplified by the perovskite to post-perovskite phase transition with its steep Clapeyron slope, makes such an approach difficult. Other important effects that would have to be considered include the viscosity and chemistry of D'' and the possibility of phase separation between (Mg,Fe)O and post-perovskite. Models with softer post-perovskite (Hunt et al., 2009; Ammann et al., 2010; Dobson
et al., 2012) give a higher heat flux (Tosi et al., 2010; Nakagawa and Tackley, 2011) and chemical impurities can decrease the conductivity (Manthilake et al., 2011) and potentially its lateral variation. On the other hand, (Mg,Fe)O could segregate into bands or layers parallel to the CMB and this could open new conductive paths parallel to these layers. In this case the anisotropy of conductivity in the lowermost mantle would increase reenforcing the pattern shown in Figure 9. New, more sophisticated convective models are required if we are to explore the dynamical consequences of a textured and heterogeneous D′ including lenses of rheologically weak, chemically distinct, thermally conducting and anisotropic post-perovskite.

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Table 7

Parameters for Equation 3 describing the variation in thermal conductivity (in W/mK) of perovskite and post-perovskite with pressure (in GPa), temperature (in K) and direction. Results for individual pressures and temperatures are given in the Supplementary Information.

<table>
<thead>
<tr>
<th>Phase and direction</th>
<th>$\alpha_0$</th>
<th>$\alpha_P$</th>
<th>$\beta_0$</th>
<th>$\beta_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perovskite, isotropic average$^a$</td>
<td>$-1.1676$</td>
<td>$-0.0014$</td>
<td>$211.19$</td>
<td>$2.6212$</td>
</tr>
<tr>
<td>Perovskite, parallel to $a$-axis$^a$</td>
<td>$-0.0349$</td>
<td>$0.0029$</td>
<td>$244.30$</td>
<td>$1.4842$</td>
</tr>
<tr>
<td>Perovskite, parallel to $c$-axis$^a$</td>
<td>$3.0495$</td>
<td>$-0.0597$</td>
<td>$144.97$</td>
<td>$4.8951$</td>
</tr>
<tr>
<td>Post-perovskite, isotropic average$^a$</td>
<td>$-3.5501$</td>
<td>$-0.0254$</td>
<td>$678.95$</td>
<td>$3.0203$</td>
</tr>
<tr>
<td>Post-perovskite, parallel to $a$-axis$^a$</td>
<td>$-13.0000$</td>
<td>$0.0100$</td>
<td>$1309.60$</td>
<td>$0.5600$</td>
</tr>
<tr>
<td>Post-perovskite, parallel to $b$-axis$^a$</td>
<td>$7.8513$</td>
<td>$-0.1018$</td>
<td>$0.5950$</td>
<td>$7.8658$</td>
</tr>
<tr>
<td>Post-perovskite, parallel to $c$-axis$^a$</td>
<td>$-5.1953$</td>
<td>$0.0130$</td>
<td>$727.09$</td>
<td>$0.6318$</td>
</tr>
<tr>
<td>Perovskite, isotropic average$^b$</td>
<td>$-1.0618$</td>
<td>$0.0105$</td>
<td>$203.74$</td>
<td>$2.3210$</td>
</tr>
<tr>
<td>Perovskite, parallel to $a$-axis$^b$</td>
<td>$2.4414$</td>
<td>$-0.0186$</td>
<td>$141.20$</td>
<td>$2.7199$</td>
</tr>
<tr>
<td>Perovskite, parallel to $c$-axis$^b$</td>
<td>$-0.3872$</td>
<td>$0.0098$</td>
<td>$328.82$</td>
<td>$1.5232$</td>
</tr>
<tr>
<td>Post-perovskite, isotropic average$^b$</td>
<td>$-16.8163$</td>
<td>$0.0606$</td>
<td>$1194.20$</td>
<td>$0.5096$</td>
</tr>
<tr>
<td>Post-perovskite, parallel to $a$-axis$^b$</td>
<td>$-68.0000$</td>
<td>$0.3900$</td>
<td>$4478.00$</td>
<td>$-19.8900$</td>
</tr>
<tr>
<td>Post-perovskite, parallel to $b$-axis$^b$</td>
<td>$22.1088$</td>
<td>$-0.1900$</td>
<td>$-1098.48$</td>
<td>$14.5315$</td>
</tr>
<tr>
<td>Post-perovskite, parallel to $c$-axis$^b$</td>
<td>$-4.3000$</td>
<td>$-0.0200$</td>
<td>$202.90$</td>
<td>$6.8600$</td>
</tr>
</tbody>
</table>

$^a$ Using the potentials from Oganov et al. (2000)

$^b$ Using the potentials from Murakami et al. (2004)
Fig. 1. Thermal conductivity as a function of the generated temperature gradient for different heat exchange intervals. Perovskite (left) at 130 GPa, 1000 K in a $16 \times 3 \times 3$ supercell and post-perovskite (right) at 120 GPa, 2000 K in a $12 \times 3 \times 3$ supercell. (The temperature gradient is generated along the $a$-axis for both phases). For all but the longest exchange interval (80 fs), perfect linear correlation has been found, confirming the validity of heat equation.

Fig. 2. Temperatures (blue dots; squares are averages between left and right half of simulation cell indicating that steady state has been reached) of the slices across the simulation-cell ($64 \times 3 \times 3$, post-perovskite at 120 GPa and 2000 K). Green line: fitted linear thermal gradient across cell after 100 ps of simulation time.
Fig. 3. The effect of the cross-sectional area on the thermal conductivity of perovskite (20 GPa and 2000 K) along $a$ (top) and post-perovskite (120 GPa and 2000 K) along $a$ (centre) and $b$ (bottom) as a function of the simulation-cell length. Squares mark values for different simulation-cell lengths, lines are the linear extrapolations to infinite cell-size (see text for details).
Fig. 4. Thermal conductivities of perovskite and post-perovskite as functions of temperature with the potential from Murakami et al. (2004) (top) and Oganov et al. (2000) (bottom). Shown are the thermal conductivities at different pressures along different crystal axis as marked. Squares are the calculated conductivities with lines being $1/T^2$ least-square fits and their appropriate error bounds. Post-perovskite is anisotropic particularly at lower temperatures.
Fig. 5. Comparison of the calculated thermal conductivities of perovskite (a) and post-perovskite (b) as a function of temperature and pressure compared with the available experimental data. Solid and dashed lines: results from non-equilibrium molecular dynamics where, for any pressure, lower conductivities are found with increasing temperature (typical error bars are shown in the key). Symbols: experimental data or results from atomic scale calculations with error bars (colours refer to temperature; the DFT data points shown for perovskite were previously presented by Stackhouse et al. (2009) and will form the basis for a future publication, we do not plot the 300 K, 135 GPa data of Haigis et al. (2012) for post-perovskite because it lies so far from the rest of the plotted data). For the low precision provisional data (Goncharov et al., 2010) the lower bound of the conductivity is shown (the very large errors reported in these experiments are due to lack of knowledge of the conductivity of other components in the sample assembly). Above about 80 GPa our calculations using interatomic potentials agree with all available data for both phases.
Fig. 6. Thermal conductivities as functions of iron concentration using the potentials from Oganov et al. (2000), left, and Murakami et al. (2004), right. The thermal conductivity quickly saturates with increasing iron concentration.

Fig. 7. Calculated single crystal thermal conductivity of perovskite and post-perovskite along a geotherm (Stacey and Davis, 2008). Note the large (factor of 1.5) increase in conductivity across the phase transition and the large anisotropy for post-perovskite exhibited by the potential of Murakami et al.
Fig. 8. Calculated radial heat flux distribution across the CMB. (a) – (c) show the spatial variation in heat flux for conductivity dominated by perovskite, post-perovskite and a mixed-phase assemblage, respectively. (d) Histogram of the heat flux distribution showing the low, unimodal distribution for perovskite, the higher unimodal distribution for post-perovskite and the bimodal distribution for the mixed phase case. Integrated CMB heat flux for these three cases are 3.48, 4.93 and 4.83 TW, respectively. Further details of these models are given in the Supplementary Information.
Fig. 9. Calculated heat flux distribution across the CMB around the south east Pacific centred on an up-welling in the TX2008.V2 mantle flow model. Upper panels show the horizontal (arrows) and vertical (red contour fill) component of the heat flux for an isotropic (a; close up of Figure 8c) and anisotropic (b; anisotropy derived from TX2008.V2.P100 polycrystalline deformation model, results for other proposed slip systems can be found in the Supplementary Information). Blue – red contours in the lower panels show the magnitude of the horizontal heat flux resolved in the direction towards the centre of the upwelling, U_{plume}, for the isotropic (c) and anisotropic (d) cases. (e) Cartoon showing how a change in the direction of the heat flux vector results in a change in the horizontal components.