

Response May 4, 2014

We would like to thank Anonymous Referee #1 for a very detailed evaluation of our paper “*Is there a layer deep in the Earth that uncouples heat from mechanical work?*” The reviewer implies the answer to our query is “no” based on simulations from density function theory, DFT, which shows no negative thermal expansion in the data sets evaluated. If you were to use our linear elastic data in the same volume range as DFT the answer would also be “no”. DFT data (for MgSiO₃ as described by Z. Zhang et. al.) has volumes that are much larger than the zero thermal expansion, regression curve volume discussed in our manuscript. We prefer volume over pressure because it describes the atomic space in the unit cell. This is discussed in some detail below but first we would like to answer the other comments from this Referee.

We used a linear elastic theory, well-established at several GPa of pressure and extrapolated our findings to pressures to near 50 GPa. As pointed out by Referee #1 this is a long extrapolation. We agree that non-linear terms should be introduced into our linear theory at pressures well below 50 GPa and thus the pressure values we find for creating near zero thermal expansion as predicted by our model may have substantial errors. That however is not the point: the major conclusion from our linear EOS is that some pressure can be found that will suppress expansivity for terrestrial constituents to have near zero thermal expansion coefficients. These pressures are close to Earth-mantle pressures especially in perovskite minerals, including MgSiO₃. We cite about 25 references related to several aspects of negative thermal expansion coefficients in broad classes of materials but especially the perovskites.

This Referee also suggested that we review Helffrich and Connolly who conclude that the thermal expansion coefficient can never be zero. In fact, the authors in this reference add terms to a modified Murnaghan equation of state, EOS, so as to mandate their thermodynamic expressions to explicitly avoid all zero thermal expansion coefficients. The justification for modifying the EOS is that zero thermal expansion is “non-physical behavior.” The references cited in our manuscript on negative thermal expansion do they describe “non-physical behavior”? We don’t think so. These authors also show how to calculate the pressures that result in zero thermal expansion coefficients including a non-linear pressure dependent term in the bulk modulus; the pressures found from our linear regression curve which we use to predict zero thermal expansion is a just a special case of their non-linear analysis: their value for P^* is that pressure where the thermal expansion coefficients are zero. They have $P^* = B / (\delta_T - K')$ where B is the bulk modulus, δ_T is Anderson-Gruneisen parameter and K' is the first derivative of the pressure dependence of the bulk modulus, typically taken as 4. Our linear theory, which leaves out all the pressure dependence of the bulk modulus (that is why it is called linear), i.e., $K' = 0$, predicts a regression curve where the thermal expansion coefficients are zero from which we approximate $P^* = B / (\delta_T)$ as shown in our equation 16.

There is an additional point from the reference to Helffrich and Connolly it can be seen in their equation 1 which is:

$$G(P, T) = G(P_r, T_r) + \int_{P_r}^P V(p) dp - \int_{T_r}^T S(t) dt \quad (1)$$

G is the Gibb's free energy; P and T are the pressure and temperature respectively. The subscript variables are reference states. The derivative of equation 1 with respect to P first and then T yields

$$dG(P, T) = V(P)dP - S(T)dT \quad (2)$$

Our equation 3 for incremental Gibbs free energy is written with $V(P, T)$ and $S(T, P)$ in equation 2. The thermal expansion coefficient is the temperature dependence of the volume or equivalently the negative of the pressure dependence of the entropy. (See equation 10 in our manuscript.) Their equation 1 formally precludes thermal expansion coefficients because thermodynamic interactions are not correctly represented in their Gibbs energy function. However, this early Gibbs function is somehow not a major description used latter in their text; this paper goes on to show that a Murnaghan and Birch-Murnaghan EOS including the pressure dependence of the bulk modulus gives rise to zero thermal expansion coefficients. Zero thermal expansion behavior is considered unrealistic by Helffrich and Connolly so they have arbitrarily modified Murnaghan and Birch-Murnaghan EOS so as to purposely exclude all zero thermal expansion coefficient behavior. The modified EOS is to us arbitrary. They have excluded exactly what we are interested in.

Returning to simulations using DFT and Anonymous Referee #1 reference to the work of Z. Zhang, L. Stixrude and J. Brodholt (Z. Zhang et. al. lists 10 other references that also cover this topic; the paper by Z. Zhang et. al. seems to us to be very carefully done and quite complete so it is representative of our response on DFT descriptions of solids.) The DFT simulation finds a local energy minimum from imposed conditions at each prescribed volume and temperature using exchange-correlation functionals on the orbital electrons. The simulation cell size typically contains 20 atoms in a 4x4x4 mesh about the k point in the reciprocal lattice; the authors also investigated a super-cell with 1280 atoms at reference or ambient conditions and report only minor differences from the smaller cell. These results should also predict in phase space all reconstructive and isostructural phase changes in $MgSiO_3$ and give all the thermophysical properties of this material. Our linear elastic model purposely excludes all first and second order phase changes which alter the linear elastic constants and thus the temperature dependence of the compressibility we used. The volume values used in the DFT simulations are always much larger than the volumes where we would look for a zero thermal expansivity on our regression curve. The cell volume is important as it changes the local environment of the electrons and the atoms. Linear theory predicts zero thermal expansion coefficients on the

regression curve when $\ell n(v/v_0)$ is between -0.50 and -1.20 but DFT's volumes (combining data from all 10 references) is larger than -0.288 in all their data sets; in our figure 1 the very first point on our regression curve is at -0.50 and we go from there to -1.2 indicating significantly smaller volumes. Thus, DFT is very far away from the volume region where we expect to find major reductions in thermal expansion coefficients. We believe that volume is more important than temperature or pressure although thermodynamics will have only two independent variables connected by the EOS.

The entropy on our regression line is at a minimum as explained in the text; entropy reduction to get to our regression line is very significant so higher pressures with lower temperatures including reduced entropy is the region where we encourage DFT investigations. In this state of volume and pressure, we predict thermal expansions coefficients will be very near zero. The reviewer asks how a material can have a zero thermal expansion coefficient. The material on an atomic level will act as an auxetic material: the overbearing pressure causes thermal excursions sideways between atoms. Cora Lind (see our references) in her review of negative thermal expansion materials attributes transverse vibrations to these materials. Large pressures restrict the motion of atoms so they move in the transverse direction hence our reference to auxetic solids.

Further investigation of DFT data from Table 1 in Z. Zhang, L. Stixrude and J. Brodholt can be checked using our equation 12. Equation 12 a thermodynamic identity that relates the temperature dependence of the isothermal compressibility, κ_T , to the pressure dependence of the thermal expansion coefficient, β as given by

$$\left. \frac{-\Delta\kappa_T}{\Delta T} \right|_P = \left. \frac{\Delta\beta}{\Delta P} \right|_T. \quad (3)$$

Equation 3 assumes Gibbs equilibrium while DFT uses Helmholtz equilibrium. Choosing T = 2500 K and P = 112.2 GPa in Table 1 and Figure 3(a) in Z. Zhang et. al. gives an evaluation of the slopes found in the left and right sides respectively of:

$$-3.81 \times 10^{-8} / GPa - K = -6.39 \times 10^{-8} / GPa - K \quad (4)$$

The values seen in equation 4 differ by about 50% and seem somewhat larger than the scatter from the slopes taken using their data. Use has been made of the temperature dependence of the adiabatic bulk modulus (not the isothermal bulk modulus) since it is listed in their paper.

The last point that we will comment on is that thermodynamics in most geophysical work uses strain energy found from 6 stresses and 6 strains plus temperature and entropy for a total of 14 variables with 7 independent. The energy per unit volume is converted to energy per atom by multiplying by the volume per atom, V(P, T). This conversion introduces an additional variable into the thermodynamic analysis; V(P, T) has no conjugate variable in a thermodynamic sense

and its use introduces errors when finding thermophysical properties. There a simple check see if the Gibbs Function used has addition energy terms: let the stress tensor be a matrix that is fully hydrostatic (with no shear terms) and calculate $dG(P, T)$ does it include extra terms? Or is it just

$$dG(P, T) = -S(P, T)dT + V(P, T)dP \quad (5)$$

as it should be. If there are extra incremental energy terms then this energy will have consequences in finding the thermo-physical properties of the material studied. It will change physical properties hopefully in some minor way.