

Interactive comment on “Is there a layer deep in the Earth that uncouples heat from mechanical work?” by S. J. Burns and S. P. Burns

Responses to Reviewers 1 & 2, Manuscript Changes

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10 First, we thank the Anonymous Reviewer for the detailed comments about our manuscript and Peter Dorogokupets for posting the recent article by Sokolova et al. (2013) which includes MgO properties. Both reviewers feel that negative thermal expansion in the deep earth is impossible. We have responded to both reviewers' comments by adding two new tables, two new figures, and Appendix A to our manuscript. We have also extensively expanded the text in section 2.2 to discuss these new additions. The changes and new additions to the manuscript are listed at the end of this response.

15 The new text in section 2.2 directly addresses the positive thermal expansion coefficients found in density-functional theory, DFT, with descriptions of MgSiO₃ properties at high pressures and temperatures. In addition, using an *ab initio* Helmholtz potential of MgO, the Sokolova et al. (2013) paper suggested by Peter Dorogokupets, also shows positive thermal expansion coefficients at high pressures and temperatures. We have added a new section with a thermodynamic identity based only on Gibbs equilibrium; the first identity was in our original manuscript, the second is now in the added section. In addition, we now include an Appendix with the properties from MgSiO₃ and MgO. We have elaborated and explained in some detail the new Compressibility and Thermal identities. These identities establish basic relationships among physical properties at all pressures and temperatures for all materials. These identities must be satisfied for any material in equilibrium. In our newly added Appendix we take data found in the DFT paper on MgSiO₃ and data on MgO to establish that there is a significant inconsistency between the temperature dependence of the compressibility and the pressure dependence of the thermal expansion coefficient in MgO. In addition, the pressure dependence of the heat capacity and the temperature dependence of the thermal expansion coefficient are inconsistent in both MgO and MgSiO₃. The MgSiO₃ data from DFT and the MgO data thus show there are problems with the specific *ab initio* assumptions.

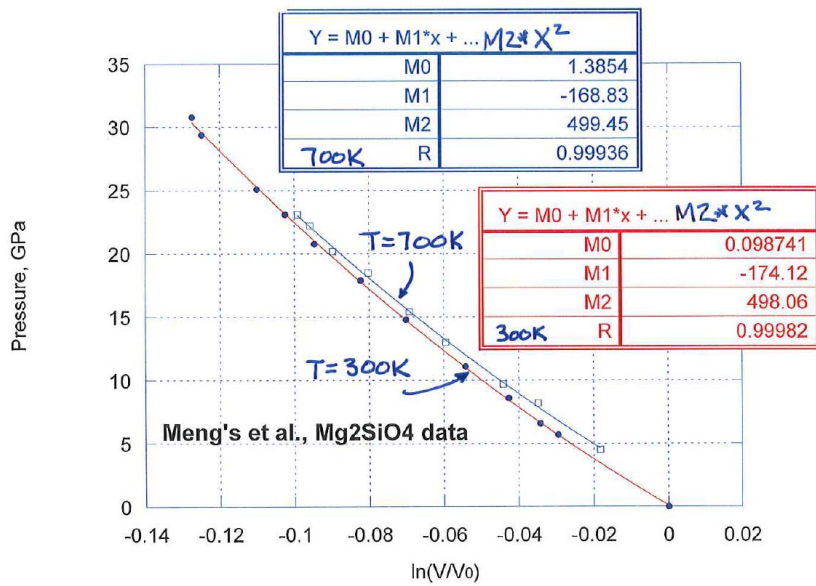
35 We argue that any data that describes physical properties but is internally inconsistent can't describe a real material. Thus, the data from DFT and Helmholtz potentials while very carefully done do not preclude the main hypothesis of our paper that pressure will suppress the thermal expansion even to zero as in our linear model and describe a deep Earth layer that uncouples heat from work.

40 The Anonymous Reviewer pointed out a reference to non-linear Birch-Murnaghan and Murnaghan equations of state that have zero thermal expansion coefficients at very high pressures. Our linear equation of state is just a special case of the more general non-linear theories. The non-linear pressures are significantly larger than the linear value we have found. We have included the specific form of the pressure that achieves zero-thermal expansion coefficients in non-linear models; we have now included this value in our text.

This reviewer also questioned if the data from Meng et al. (1994) had two isotherms touching. We have changed the statement in the paper on this point. Included in our response is her

45 data plotted as log natural volume/reference volume versus pressure all from her observed
values at two temperatures in their Table 1. The extrapolated curve from 300 K will cross the
extrapolated curve from 700 K at a pressure of 77 GPa. Figure R1 attached to this response
shows the raw data and the equations for both second order curve fits. The reviewer will note
50 that the temperature dependence of the compressibility in the linear term is the major reason
that these curves cross. The higher order pressure term has little effect on how pressure
suppresses thermal expansion coefficients, although, it does raise the pressure where the two
lines cross.

The second reviewer, Peter Dorogokupets, states that no real material has a thermal expansion
coefficient that is zero due to pressure. He then referred us to a paper in which he is a co-
55 author with an extensive list of physical properties, none of which shows zero thermal expansion
coefficients. We have shown in Appendix A that the thermal expansion coefficient of one of
the materials in his paper (the only one we tested) is inconsistent with basic thermodynamic
identities. This suggests that the properties described are not properties of real materials as
described by thermodynamics. As stated in our Introduction finding the interaction energies are
60 quite difficult in *ab initio* calculations.



$$P_{300K} = P_{700K} = 77.14 \text{ GPa}$$

$$\ln(V/V_0) = \ln(V_0/V_0) = -0.2556$$

$$Y = \text{pressure} ; x = \ln(V/V_0)$$

Figure R1 Measured data from Meng, et al. (1994) plotted as pressure versus true strain at $T=700\text{K}$ and $T=300\text{K}$. The curve fits cross at $p=77$ GPa.

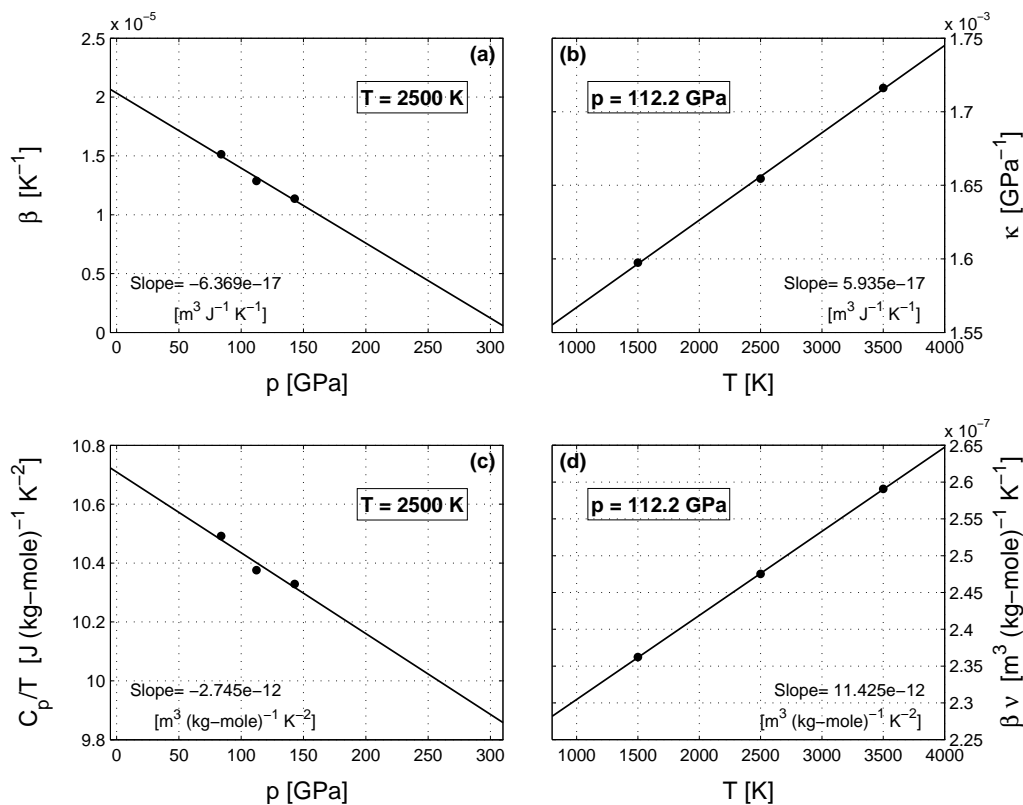


Fig. 3. A check of the thermodynamic relationships of MgSiO₃ based on state properties determined by Zhang et al. (2013). Values shown are (a) volumetric thermal expansion coefficient β versus pressure p , (b) isothermal compressibility κ versus temperature T , (c) heat capacity at constant pressure C_p divided by T versus p , and (d) the specific volume ν times β versus T . The solid line is a linear fit through the data with the slope of the line provided in the lower corner in SI units.

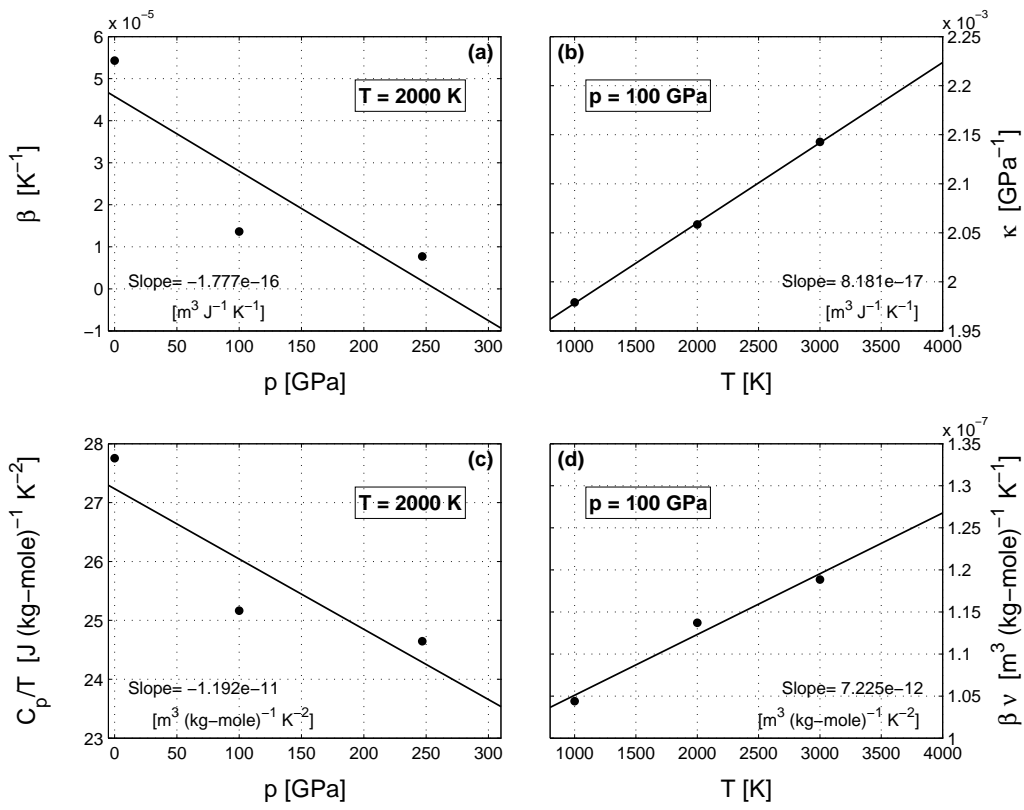


Fig. 4. As in Fig. 3, except for the mineral MgO using data from Sokolova et al. (2013).

Table 2. The thermal expansion coefficient β , ratio of the heat capacity at constant pressure to temperature C_p/T , isothermal compressibility κ , and β times the specific volume ν for the mineral MgSiO₃ at a selected temperature ($T = 2500$ K) and pressure ($p = 112.2$ GPa). These data are from Zhang et al. (2013) (their Table 1) and are used to calculate linear slopes with varying pressure and temperature as shown in the far-right column. SI units are used throughout. These data are plotted in Fig. 3 so judgments on regression and quality of the comparison can be assessed.

for $T = 2500$ K	Range of Pressure Values			Slope with Δp
	83.9 GPa	112.2 GPa	142.9 GPa	
β [K ⁻¹]	1.514×10^{-5}	1.287×10^{-5}	1.137×10^{-5}	-6.38×10^{-17} [m ³ J ⁻¹ K ⁻¹]
C_p/T [m ³ (kg-mole) ⁻¹ K ⁻²]	10.492	10.376	10.329	-2.74×10^{-12} [m ³ (kg-mole) ⁻¹ K ⁻²]
for $p = 112.2$ GPa	Range of Temperature Values			Slope with ΔT
	1500 K	2500 K	3500 K	
κ [GPa ⁻¹]	1.597×10^{-3}	1.655×10^{-3}	1.716×10^{-3}	5.94×10^{-17} [m ³ J ⁻¹ K ⁻¹]
$\beta\nu$ [m ³ (kg-mole) ⁻¹ K ⁻¹]	2.362×10^{-7}	2.475×10^{-7}	2.591×10^{-7}	11.425×10^{-12} [m ³ (kg-mole) ⁻¹ K ⁻²]

Table 3. As in Table 2, for the mineral MgO using data taken from Sokolova et al. (2013) (their Table 5). SI units are used throughout.

for $T = 2000$ K	Range of Pressure Values			Slope with Δp
	0 GPa	100 GPa	246.86 GPa	
β [K ⁻¹]	5.428×10^{-5}	1.363×10^{-5}	0.770×10^{-5}	-17.78×10^{-17} [m ³ J ⁻¹ K ⁻¹]
C_p/T [J(kg-mole) ⁻¹ K ⁻²]	27.755	25.165	24.645	-11.92×10^{-12} [m ³ (kg-mole) ⁻¹ K ⁻²]
for $p = 100$ GPa	Range of Temperature Values			Slope with ΔT
	1000 K	2000 K	3000 K	
κ [GPa ⁻¹]	1.979×10^{-3}	2.059×10^{-3}	2.143×10^{-3}	8.18×10^{-17} [m ³ J ⁻¹ K ⁻¹]
$\beta\nu$ [m ³ (kg-mole) ⁻¹ K ⁻¹]	10.440×10^{-8}	11.372×10^{-8}	11.885×10^{-8}	7.23×10^{-12} [m ³ (kg-mole) ⁻¹ K ⁻²]

Revised section 2.2 in the manuscript:

65 2.2 Additional expressions for the thermal expansion coefficient

There is a second interpretation for thermal expansion coefficient which comes from the Maxwell relation from the Gibbs energy function, g ,

$$\beta = -\frac{1}{\nu} \left. \frac{\partial s}{\partial p} \right|_T. \quad (10)$$

70 On any isotherm where $\beta < 0$ the entropy will increase as pressure is increased; for any material with $\beta > 0$ a larger pressure will decrease entropy. The entropy is thus an extremum on any isotherm where the pressure forces $\beta = 0$. Entropy is a minimum in the case proposed here. This is one of the reasons why Bridgman (1952) attempted to pressurize materials to conditions of zero thermal expansion as this condition represents an extremum in entropy.

75 The third mixed derivative of the free energy function g leads to another thermodynamic identity for the thermal expansion coefficient that is particularly useful:

$$\frac{\partial^3 g}{\partial T \partial p^2} = \frac{\partial^3 g}{\partial p \partial T \partial p}, \quad (11)$$

or

$$-\left. \frac{\partial \kappa}{\partial T} \right|_p = \left. \frac{\partial \beta}{\partial p} \right|_T. \quad (12)$$

80 Equation (12) has been previously found by Birch (1952). Birch lists an unnumbered equation at the top of p. 255 at the right side of a three term expression. Here Eq. (12) is called the “Compressibility Identity” which can be used to compare material properties on the left side to the material properties on the right side. This expression is a thermodynamic relation that assumes Gibbs equilibrium and applies to all geophysical properties that the thermodynamic system describes. The term Compressibility Identity is used because Eq. (11) has two p 's and one T in the derivative of the Gibbs function. In Appendix A, Eq. (12) evaluates the thermodynamic consistency of geophysical properties from density functional theory (DFT) and approximate forms of the Helmholtz potential applied to several high pressure Earth minerals.

The integration of Eq. (12) with β_0 as the constant of integration, yields

$$\beta = -\int_0^p \left. \frac{\partial \kappa}{\partial T} \right|_p dp + \beta_0. \quad (13)$$

90 Equation (13) is the same as Eq. (7). In Eq. (13) the left side with $\left. \frac{\partial \kappa}{\partial T} \right|_p$ is that value at the specific pressure under consideration. β_0 , the constant of integration, is a general function of temperature and here represents the thermal expansion coefficient when $p = 0$, a value very close to atmospheric pressure. Equation (12) shows that it is the temperature dependence of the compressibility that governs the approach to zero thermal expansion, not the pressure dependence of the compressibility. Equation (12) also show that if a power series in pressure and temperature were used to describe κ then the pressure part alone does not enter into how β approaches zero at high pressures. Again, Eq. (13) leads directly to Eqs. (8) and (9) for $\beta = 0$ without any presumptions about the EOS.

100 The Anderson–Grüneisen parameter (Anderson and Isaak, 1993), δ_T , at atmospheric pressure, is closely related to p^* since

$$\delta_T = \frac{-1}{\beta_0 B_T} \left. \frac{\partial B_T}{\partial T} \right|_p, \quad (14)$$

with B_T the isothermal bulk modulus' temperature dependence measured at atmospheric pressure. Because $\kappa = (B_T)^{-1}$, it follows that,

$$\left. \frac{\partial \kappa}{\partial T} \right|_p = -\frac{1}{B_T^2} \left. \frac{\partial B_T}{\partial T} \right|_p. \quad (15)$$

105 Comparing Eqs. (14) and (15) with Eq. (8), we find

$$p^* = \frac{B_T}{\delta_T}. \quad (16)$$

Typical values of δ_T at atmospheric pressure are about 5 so p^* is about 20 % of the isothermal bulk modulus in many materials found within the Earth. The bulk modulus is known from Murnaghan's EOS (i.e., Murnaghan, 1944) to increase linearly under pressure. Thus, Eq. (16) may describe a value of p^* larger than the measured values of B_T and δ_T . β_0 is used in Eq. (14) thus δ_T is the value at atmospheric pressure. We would like the readers to concentrate on pressures that are so large that the thermal expansion coefficient is effectively reduced to zero in our linear elastic Hookian solid.

115 Helffrich and Connolly (2009) using the non-linear, isothermal, EOS from Murnaghan and Birch-Murnaghan found that the thermal expansion coefficient went to zero at a pressure of

$$p^* = \frac{B_T}{\delta_T - K'}. \quad (17)$$

where K' is the pressure derivative of the isothermal bulk modulus; it often taken to be approximately 4.

120 Other theoretical descriptions of a material's thermal expansion coefficient at geophysical conditions are found in the literature. For example, density functional theory is applied to MgSiO_3 by Zhang et al. (2013) which is an excellent example of DFT used to evaluate an important Earth mineral. Zhang et al. (2013) has tables of the geophysical properties of this material in p and T space. There is also, thermal expansion coefficients obtained from direct representation of the Helmholtz free energy by Sokolova et al. (2013): they give a complete description of thermodynamic properties none of which show negative thermal expansion coefficients and thus seem to be in contradiction to the main hypothesis of our paper. However, these materials are shown in Appendix A to be inconsistent in physical properties and directly violate the thermodynamic identity established above or the thermodynamic identity derived below. The Gibbs free energy relationship (i.e., Eq. (3)) also gives the following relation,

$$130 \frac{\partial^3 g}{\partial p \partial T^2} = \frac{\partial^3 g}{\partial T \partial p \partial T}, \quad (18)$$

or,

$$-\left. \frac{\partial(C_p/T)}{\partial p} \right|_T = \left. \frac{\partial \beta \nu}{\partial T} \right|_p, \quad (19)$$

135 where C_p is the heat capacity at constant pressure. Equation (19) is called the "Thermal Identity" and like the Compressibility identity (i.e., Eq. (12)) it places restrictions on the physical properties of all materials including geophysical materials. Equations (12) and (19) are very general and are based only on Gibbs equilibrium. Data obtained for MgSiO_3 from Zhang et al. (2013), at $T = 2500$ K and $p = 112.2$ GPa are described in Table 2. The method to construct Table 2 is described in Appendix A. Figure 3a is the right hand side of the Compressibility identity and Fig. 3b is the left hand side. It is seen that the data from Zhang et al. (2013) (also see Table 2) are consistent with the Compressibility identity, showing about 7% variation in comparison of the slopes of the two physical properties. Figure 3c is the data in Eq. (19) plotted from the same source. It is now seen to have over 300% in disagreement and thus inconsistent with

this basic thermodynamic identity. This basic disagreement on the Thermal identity calls into question the validity of the data on the thermal expansion coefficient describing MgSiO_3 using DFT. Physical descriptions of real materials cannot (in our opinion) violate thermodynamics as seen in Figs. 3c and 3d and listed in Table 2.

We have also looked at the data for periclase or MgO . The properties are taken with $T = 2000$ K and $p = 100$ GPa from the data of Sokolova et al. (2013): Table 2 shows the data calculated with Eqs. (12) and (19). Again, the physical properties do not satisfy either the compressibility or the thermal identity. If both thermodynamic identities were satisfied then the physical properties would be at least self-consistent; comparison with experimental data would establish validity. However, with inconsistent physical properties derived from a theoretical description of a material the properties found are surely called into serious question. We are unaware of real materials that violate any thermodynamic identities.

The Compressibility identity seems better supported by the DFT data for MgSiO_3 while the reverse seems to be true for the MgO data (see Table 2). In either case, accurate descriptions of the thermal expansion coefficients in Earth minerals are not well supported by either theory. The central importance of the temperature dependence of the compressibility in describing the reduction of the thermal expansion coefficient in Eq. (12) is easily seen in Fig. ?? where two isotherms with different slopes cross and form part of a regression curve that describes pressures and temperatures with zero thermal expansion coefficients. Equation (12) establishes this point at all pressures and for all non-linear theories.

If we were to ask what additional pressure is needed for MgSiO_3 to reach zero thermal expansion coefficients, then, since,

$$d\beta = \left. \frac{\partial\beta}{\partial p} \right|_T dp + \left. \frac{\partial\beta}{\partial T} \right|_p dT, \quad (20)$$

it follows that,

$$\Delta\beta = \left. \frac{\partial\beta}{\partial p} \right|_T \Delta p + \left. \frac{\partial\beta}{\partial T} \right|_p \Delta T, \quad (21)$$

where the partial derivatives of β are known from Eqs. (12) and (19) above. Equation (19) gives the required derivative from the Thermal identity as,

$$\left. \frac{\partial\beta}{\partial T} \right|_p = \frac{1}{\nu} \left. \frac{\partial(\nu\beta)}{\partial T} \right|_p - \beta^2. \quad (22)$$

It is seen from the DFT data of MgSiO_3 that if pressure alone were to reduce the thermal expansion coefficient to zero than an additional 216 GPa would be needed so at 328 GPa the thermal expansion coefficient would be reduced to zero. We have used the data in Table 2 with Eqs. (20) and (21) to linearize where $\beta = 0$ starting from a pressure p and temperature T . We have shown that thermal expansion coefficients at deep Earth pressures are inconsistent so predictions using those data is going to be suspect.

The remainder of this paper discusses material behavior when the thermal expansion coefficient is positive, negative and very near zero. Pressures can be thought of as equivalent depths for homogeneous compositions in the Earth so Eqs. (8) and (16) define a shell related to the pressure p^* where $\beta = 0$; deeper material would have β negative and shallower material have β positive based on the linear model proposed here.

Appendix A

Thermodynamic consistency check of selected earth minerals

185 *Ab initio* calculations of material properties are quite widely used to predict material behavior at conditions that are difficult to measure experimentally. Two data sets are used here because both show non-zero thermal expansion coefficients at high pressures and high temperatures. The full set of properties of the Earth minerals MgSiO₃ and MgO are from Zhang et al. (2013) and Sokolova et al. (2013), respectively.

190 The two thermodynamic identities in Eqs. (12) and (19) are used to compare to the published properties which have been found using *ab initio* calculations. A point has been selected at a pressure and temperature and then neighboring points were used for the partial derivatives needed for Eqs. (12) and (19). These surrounding points in pressure or temperature are listed in Table 2 to obtain the required partial derivatives. The data in Table 2 for MgSiO₃ and Table 3 for MgO shows the values of the properties used which were obtained from the cited
195 references. The atomic mass units (amu) for MgSiO₃ and MgO were taken to be 100.39 amu and 40.31 amu, respectively. For MgSiO₃, we have used $Nk_B = R = 8316.62 \text{ J (kg-mole)}^{-1} \text{ K}^{-1}$ for converting relative heat capacity to absolute values. If you examine Eq. (12) for MgSiO₃ then,

$$-\left. \frac{\partial \kappa}{\partial T} \right|_p = -5.94 \times 10^{-17} \frac{\text{m}^3}{\text{JK}} \stackrel{?}{=} -6.38 \times 10^{-17} \frac{\text{m}^3}{\text{JK}} = \left. \frac{\partial \beta}{\partial p} \right|_T. \quad (\text{A1})$$

200 The linear fit and slopes are shown in Fig. 3a and 3b for the left and right sides of Eq. (A1). The difference in slopes is about 7% and this is a verification of the self-consistency of the Compressibility identity. The Thermal identity is also checked for MgSiO₃. Based on the data in Table 2, we find,

$$-\left. \frac{\partial(C_p/T)}{\partial p} \right|_T = 2.74 \times 10^{-12} \frac{\text{m}^3}{\text{kg-mol K}^2} \stackrel{?}{=} 11.425 \times 10^{-12} \frac{\text{m}^3}{\text{kg-mol K}^2} = \left. \frac{\partial \beta \nu}{\partial T} \right|_p, \quad (\text{A2})$$

205 The difference in slopes is about 300% and does not support the self-consistency of the data in Zhang et al. (2013) (their Table 1). In fact, if the thermal expansion coefficient were to be reduced on the thermal side by a factor of 4 then negative thermal expansions would be obtained at the pressures listed. The data and linear fits are shown in Figs. 3c and 3d for the left-side and right-side of Eq. (A2), respectively.

210 The MgO data from Sokolova et al. (2013) shown in Table 3 are also checked for thermodynamic consistency. Starting with the Compressibility identity, we find:

$$-\left. \frac{\partial \kappa}{\partial T} \right|_p = -8.18 \times 10^{-17} \frac{\text{m}^3}{\text{JK}} \stackrel{?}{=} -17.78 \times 10^{-17} \frac{\text{m}^3}{\text{JK}} = \left. \frac{\partial \beta}{\partial p} \right|_T. \quad (\text{A3})$$

215 There is about a 100% difference in slopes between the right and left sides of Eq. (A3). Thermodynamics would expect the values to be identical. MgO's thermal expansion coefficient seems to be reduced by pressure more than MgSiO₃. More importantly is that the tabulated data seems to show an inconsistency in representation of the thermal expansion coefficient. Figures 4a and b are the data plotted from which the slopes are found. The Thermal identity for
220 MgO was also checked based on data in Table 3,

$$-\left. \frac{\partial(C_p/T)}{\partial p} \right|_T = 11.92 \times 10^{-12} \frac{\text{m}^3}{\text{kg-mol K}^2} \stackrel{?}{=} 7.23 \times 10^{-12} \frac{\text{m}^3}{\text{kg-mol K}^2} = \left. \frac{\partial \beta \nu}{\partial T} \right|_p, \quad (\text{A4})$$

The slopes differ by a factor of 1.65 with the thermal part on the left being larger. Figures 4c and 4d are the respective left and right sides. The MgO data has quite large steps in both

pressure and temperature so there is more scatter when compared to MgSiO_3 . Regression
225 analysis in the figures is supportive of well-established slopes for several examples.

We conclude that the thermal expansion coefficient may be zero in materials at extreme pressures and that *ab initio* calculations alone give data that have sufficient inconsistencies to not exclude the main hypothesis of our paper: the thermal expansion coefficients may go to zero at very high pressures.

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