

High pressure  
thermal expansion

S. J. Burns and  
S. P. Burns

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# Is there a layer deep in the Earth that uncouples heat from mechanical work?

S. J. Burns<sup>1</sup> and S. P. Burns<sup>2,3</sup>

<sup>1</sup>Materials Science Program, Department of Mechanical Engineering, University of Rochester, Rochester, New York 14627, USA

<sup>2</sup>National Center for Atmospheric Research, Boulder, Colorado 80301, USA

<sup>3</sup>Department of Geography, University of Colorado, Boulder, Colorado 80309, USA

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Correspondence to: S. J. Burns (stephen.j.burns@rochester.edu)

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## Abstract

The thermal expansion coefficient is presented as the coupling between heat energy and mechanical work. It is shown that when heat and work are uncoupled then very unusual material properties occurs: for example, acoustic  $p$  waves are not damped and heat is not generated from mechanical motion. It is found that at pressures defined by the bulk modulus divided by the Anderson–Grüneisen parameter, then the thermal expansion coefficient approaches zero in linear-elastic models. Very large pressures always reduce thermal expansion coefficients; the importance of a very small or even negative thermal expansion coefficient is discussed in relation to physical processes deep in the core and mantle of Earth. Models of the thermal expansion coefficients based on interatomic potentials which are always relegated to isometric conditions preclude any changes in volume due to temperature changes. However, it is known that the pressures in the Earth are large enough to effectively reduce thermal expansion coefficients to near zero which decouples heat from mechanical work.

## 1 Introduction

The mineralogical constituents and the physical properties of the Earth's materials are important to understanding geological processes within the Earth and modeling the dynamic evolution of the Planet. There are excellent measurements and reviews of the high pressure properties for many terrestrial constituents (e.g., Isaak, 1992; Anderson, 1995; Mitra, 2004). High pressures obtained on small samples in the diamond anvil cell have provided a revolutionary wealth of crystallographic data for comparisons to equation of state, EOS, models with materials at high pressures (Jayaraman, 1983; Mao and Hemley, 2007; Bassett, 2009; Wang et al., 2010). These cells have also provided extensive evidence for pressure driven solid state phase changes. Laser induced compression has led to even higher pressures for selected materials (Sawada, 2008). Structural phase changes in perovskites of olivine,  $Mg_xFe_{(1-x)}SiO_3$ , (Jeanloz

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and Thompson, 1983; Murakami et al., 2004; Duffy, 2008) are particularly relevant and useful as these mineral compositions make up most of the Earth's mantle. This paper is concerned with the interaction between heat energy and mechanical work. It is shown later that thermal expansion coefficients couple heat to work. In this introduction thermal expansion coefficients are extensively reviewed to better understand the conditions that minerals might experience to promulgate thermal expansion coefficients that are effectively zero in a linear elastic approximation.

Thermal vibration along a line connecting atoms in asymmetric atomic potentials is our physical understanding of the atomic bonding basis for thermal expansion coefficients; as the atomic vibrations increase the material expands. Materials under pressure will do mechanical work during expansion so at very large pressures, the mechanical work suppresses the asymmetry in the interatomic potential and vibrations may become skewed to interatomic bond directions: atomic vibrations don't necessarily lead to positive thermal expansion coefficients at extreme pressures where the interatomic cores are heavily compressed. Most materials and our everyday experiences are with positive thermal expansion coefficients: we expect hot fluids to rise, while cool fluids sink. However, there are anomalous materials that have negative thermal expansion coefficients: water is the most widely quoted substance with a negative thermal expansion coefficient from 0 to 4°C (Chappuis, 1907). This condition gives rise to the seasonal rotation and the sinking of lake surface water near freezing which is well known to oxygenate the bottom of lakes.

Negative thermal expansion coefficients are present in Type IV elements and III–V compounds at atmospheric pressures and low temperatures; silicon (Novikova and Strelkov, 1959; Lyon et al., 1977; Swenson, 1983), germanium (Gibbons, 1958) and diamond (Biernacki and Scheffler, 1989), are the best known elements with negative thermal expansion coefficients below 122 K, 50 K and 125 K respectively. The other thermodynamic properties of these materials are well behaved although there are reports of residual entropy near absolute zero in some Type IV elements and compounds (Giauque, 1949) with silicon the poster child material for measured entropy. Some III–V

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compounds with negative thermal expansion coefficients at low temperature are InSb, InP, GaP, InAs and GaAs (Carr et al., 1965; Slack and Bartram, 1975; Sirota et al., 1984). Zero thermal expansion in single crystals of calcite occurs on conic crystallographic sections: the single crystal has two negative thermal expansion coefficients on axes that are perpendicular to the triad axis. The triad has a positive thermal expansion coefficient so a conic orientation has a zero thermal expansion coefficient in specific crystallographic directions. See for example, the room temperature data of calcite in Nye (1964, pp. 106–109). In addition, magnetic transitions in FeNi alloys and FeNiCo alloys can have very low and sometimes negative thermal expansion coefficients at atmospheric pressures near room temperatures. Rubbers and chain molecule solids typically have negative thermal expansion coefficients.

Bridgman (1952) in his classic work compressed materials to synthesize diamonds but he also attempted to achieve high pressures where the thermal expansion coefficient would approach zero. In his early work, physical samples were large and very high pressures that led to extremely large forces so mechanical cells were difficult to design, construct and seal. Bridgman achieved pressures of 10 GPa with some difficulty. The measurements were static but extreme pressures like the 300 GPa found at the center of the Earth were not obtainable. Kitahara and Kennedy (1964) using opposing anvil methods achieved slightly higher pressures but still well below deep Earth core pressures. The advent of diamond anvil cells with small samples, after optimization, and with X-ray diffraction analysis has led to pressures that can approach the pressures at the Earth's core (Bassett, 2009). Shock loaded material properties under quasi-isentropic or Hugoniot conditions have been reported with very large pressures even well beyond the pressures at the center of the Earth (e.g., Ahrens, 1993; Grieve and Pesonen, 1996; Swift et al., 2004; Fan et al., 2005; Sawada, 2008; Lang and Gupta, 2010; LLNL, 2013).

Nernst's theorem requires equilibrium materials to have zero thermal expansion at 0 K where all atomic vibrations cease. Materials in thermodynamic equilibrium should have zero thermal expansion coefficients when 0 K is approached. In this paper, we are

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concerned with pressures that might create near zero thermal expansion coefficients in the mineralogical constituents found in the Earth. These compounds normally have positive thermal expansion coefficients at atmospheric pressures. It is known that very large pressures suppress and significantly reduce the coefficient of thermal expansion because the expansion does work against the applied pressure.

Anderson (1966, 1967) has proposed that a log–log plot of the ratio of the volume at a high pressure to volume at atmospheric pressure is proportional to the ratio of the high pressure thermal expansion coefficient to the atmospheric thermal expansion coefficient. The slope of this relationship is the Anderson–Grüneisen parameter which describes the anisotropy in the interatomic potential (Anderson, 1988; Anderson and Isaak, 1993). In this model, zero thermal expansion coefficients can only be achieved at pressures that reduce the volume to zero, a theoretical impossibility. Thus, zero thermal expansion is precluded by this model. This model’s derivation is based on Grüneisen’s constant which subsequently was shown by Burns et al. (1992) to be restricted to constant volume conditions. Therefore, the Anderson (1967) relationship on thermal expansion and volume is suspect.

In contrast, there is strong evidence that many compounds show negative thermal expansion especially perovskites: cubic zirconium tungstate (Mary et al., 1996; Mittal et al., 2004; He et al., 2010) with  $\text{ZrO}_2$  octahedral and  $\text{WO}_4$  tetrahedral units share an open framework and have negative thermal expansion from about 0.3 K to 1050 K, while  $\text{AX}_2\text{O}_8$  ( $A = \text{Zr, Hf}$ ;  $X = \text{W, Mo}$ ) has isotropic negative thermal expansion to very high temperatures (Mukherjee et al., 2005). These ceramic, oxide perovskites have negative thermal expansion coefficients with increasing temperature. According to reviews, the octahedrons in the unit cell rotate and increase the packing density with increasing temperature or pressure (e.g., Stillinger and Stillinger, 1997; Sikka, 2004; Barrera et al., 2005; Lind, 2012). Data on  $\gamma\text{-Mg}_2\text{SiO}_4$  (Meng et al., 1994) shows a zero thermal expansion coefficient under pressure: experimental data that was curve fit using a third-order Birch–Murnaghan equation shows the volume vs. pressure for two temperatures; the difference between these two volume curves at constant pressure

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divided by the temperature difference is the thermal expansion coefficient. Since the curves touch at about 30 GPa, the thermal expansion coefficient is zero. Other examples of materials that show a change from positive to negative thermal expansion coefficients at high pressures are both cesium (Christensen et al., 2000), and diamond (Xie et al., 1999).

EOS are used for many things. They describe the coexistence tie-line between different structural phases in materials of the same composition; density-functional theory (Tsuchiya et al., 2005) is often used to predict phase changes in the solid state and structural changes in crystallographic cells assuming thermodynamic equilibrium. EOS are also used for describing physical properties and inter-relationships among properties. Grüneisen (1926) found from an early EOS that there was a simple dimensionless “constant” that relates volume, thermal expansion coefficient, heat capacity at constant volume and isothermal compressibility. This constant is frequently embedded into EOS and forms the basis of most atomic interaction potentials such as Born–Mie potentials. Although, it has been shown that Grüneisen’s relation is restricted to isochoric conditions; isobaric conditions lead to a different Grüneisen “constant” which should be used when comparing physical properties on isobars since most thermal properties are typically measured at constant atmospheric pressure (Burns et al., 1992).

Many equations of state add energy terms but often neglect interaction energies. Hooks’ Law which relates volumetric strain to hydrostatic stress and temperature dependent elastic constants plus temperature dependent thermal strains is one of the very oldest equations of state. It assumes a parabolic temperature dependent energy potential and explicitly includes interactions through the thermal expansion coefficients. Hooke’s law relates stresses to strains with temperature dependent compliances and expansivities; Lamé’s equations relate strains to stresses and generally does not include thermal expansion effects (Landau and Lifshitz, 1959). In the work presented here, the volume is the dependent variable and the pressure and temperature are the independent variables.

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This paper proposes a hypothesis that at very high pressures, the thermal expansion coefficients which are typically positive at atmospheric pressures will become zero in a linear model. Nonlinear materials at very high pressures will have thermal expansion very close to zero. Materials with zero thermal expansion as might occur at some layer in the Earth will have very unique properties. It is shown that conversion of mechanical work as in acoustic damping can not be converted into heat because the thermal properties are decoupled from the mechanical system under these conditions.

## 2 Thermodynamic relationships

### 2.1 Thermal expansion coefficient based on a linear elastic Hookian solid

The first law of thermodynamics (Bridgman, 1925) in incremental form is

$$du = Tds - pdv, \quad (1)$$

where  $u$  is the internal energy per unit mass,  $T$  is the absolute temperature,  $s$  is the entropy per unit mass,  $p$  is the pressure and  $v$  is the volume per unit mass.  $Tds$  is the incremental heat added to the internal energy system and  $pdv$  is the incremental work done by the system on the surroundings. The difference between these two incremental terms is the change in the internal energy of the system. The Gibbs free energy per unit mass,  $G$ , is related to  $u$  by

$$G = u - Ts + pv. \quad (2)$$

It follows that,

$$dG = -sdT + vdp. \quad (3)$$

The independent variables  $T$  and  $p$  are used to define the isothermal compressibility,  $\kappa$

$$\kappa \equiv -\frac{1}{v} \left. \frac{\partial v}{\partial p} \right|_T, \quad (4)$$

and the volumetric, thermal expansion coefficient,  $\beta$

$$\beta \equiv \frac{1}{v} \left. \frac{\partial v}{\partial T} \right|_p. \quad (5)$$

In the general case,  $\kappa$  and  $\beta$  are functions of both independent variables,  $T$  and  $p$ . Typically  $\beta$  is determined by measuring  $v$  vs. temperature at atmospheric pressure.

Equation (5) evaluated at atmospheric pressure will be designated as  $\beta_0$ ; a general nonlinear temperature dependence is still included in  $\beta_0$ . As shown below, Eqs. (4) and (5) can be integrated. First with  $T$  held constant in Eq. (4) and then with  $p$  held constant in Eq. (5), this leads to the oldest equation of state for a solid, i.e., Hooke's Law:

$$\ln \left( \frac{v}{v_0} \right) = - \int_0^p \kappa dp + \int_0^T \beta_0 dT. \quad (6)$$

The first term on the right is the material compression due to the pressure; the second term is the expansivity of the material as measured at atmospheric pressure.  $v_0$  is a reference volume per unit mass at atmospheric pressure and zero temperature.  $\kappa$ , in general, depends on both  $T$  and  $p$ . Experimental data on the  $T$  dependence of  $\kappa$  is typically reported for the part of  $\kappa$  at low pressure while there is also the  $p$  dependence of  $\kappa$  which is extensively reported. However the  $T$  dependence of this second part is typically not measured. It follows that an approximate thermal expansion at any pressure is given by applying Eq. (5) to Eq. (6) which yields,

$$\beta = - \int_0^p \left. \frac{\partial \kappa}{\partial T} \right|_p dp + \beta_0. \quad (7)$$

Figure 1 shows a schematic of Eq. (6) assuming  $\kappa$  is independent of  $p$  but has  $T$  dependence;  $\beta_0$  is  $T$ -dependent especially at temperatures below the characteristic

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Debye temperature,  $\theta_D$ . The curves that just touch in Fig. 1 have the thermal expansion coefficient zero and define a regression curve in pressure-volume-temperature space. The vertical line  $\nu = \nu_0$  is marked in Fig. 1. This line typically will never intersect the regression curve as is seen in the figure. Continuing with the approximation that  $\left. \frac{\partial \kappa}{\partial T} \right|_p$  is only  $T$ -dependent, it can be taken out from under the integral sign, then  $p^*$  is that pressure where the thermal expansion coefficient is taken to be zero, i.e.,

$$p^* = \beta_0 / \left( \frac{d\kappa}{dT} \right). \quad (8)$$

However, if  $\left. \frac{\partial \kappa}{\partial T} \right|_p$  is represented by a power series in  $p$  and  $T$  then additional terms are needed to find the pressures where  $\beta = 0$ . The authors are well aware of the pressure dependence of the bulk modulus and thus on  $\kappa$  used here. Higher order  $p$  terms alone will not be included in Eq. (7) but mixed  $p, T$  terms will remain and are not included in  $\kappa$  (so we underestimate  $p^*$ ). In Table 1,  $p^*$  is tabulated for a selection of materials and discussed later in this text.

Combining Eqs. (7) and (8) we find,

$$\beta = \beta_0 \left( 1 - \frac{p}{p^*} \right). \quad (9)$$

The thermal expansion coefficients are positive for pressures less than  $p^*$  and negative for pressures larger than  $p^*$  as can be seen in Eq. (9). If the regression curve were to collapse into a point i.e., with  $p^*$  constant as shown in Fig. 2, then all thermal expansion coefficients would be positive for pressures less than  $p^*$  and negative for higher pressures. Generally,  $\beta_0$  and  $\frac{d\kappa}{dT}$  are both positive quantities. It is shown below that  $p^*$  is closely related to the bulk modulus and the Anderson–Grüneisen parameter  $\delta_T$ .

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## 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,  $G$ .

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

- 5 On any isotherm where  $\beta < 0$  will have larger entropy 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.

10 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

$$15 -\left. \frac{\partial \kappa}{\partial T} \right|_p = \left. \frac{\partial \beta}{\partial p} \right|_T. \quad (12)$$

The integration of Eq. (12) with  $\beta_0$  as the constant of integration, yields

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

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.  $\beta_0$ , the constant of integration, is a general

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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  $\kappa$  then the pressure part alone does not enter into how  $\beta$  approaches zero at high pressures. Again, Eq. (13) leads directly to Eqs. (8) and (9) for  $\beta = 0$  without any presumptions about the EOS.

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

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

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

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

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

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

Typical values of  $\delta_T$  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  $\delta_T$ .  $\beta_0$  is used in Eq. (14) thus  $\delta_T$  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.

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  $\beta$  negative and shallower material have  $\beta$  positive based on the linear model proposed here.

### 3 Material stability with negative and positive thermal expansion

#### 3.1 Positive thermal expansivity

Materials that are heated typically expand and the volume increases. This is very common experience in our surrounding as it drives atmospheric pressure changes, jet streams, ocean and lake currents, and many other physical phenomena. In the interior of the Earth, material in a fluid state will rise when it is warmer; the driving forces for solids or fluids cause hot materials to rise. Convective buoyancy sets up an advective circulation cell driven by the force from the less dense hotter material. Dense cooler material will sink in a fluid. For the Earth, it is thought that the cooler outer crust becomes more dense relative to the same hot magma while being countered by the compressibility of the material which increases the density. The convective circulation cells set up by upwelling and sinking crusts are reported to drive continental drift and are a major source of earthquakes. Hot materials will only be more buoyant when the thermal expansion coefficient is positive. Most equation of state models are directed to understanding the compressibility and isocompositional phase changes in the materials as high pressures are applied. Models of the Earth also describe the motion in the mantle from thermal effects and convection or advection. Our understanding of com-

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position within the mantle comes from measured acoustic wave speeds and ray tracing coupled with reflections from compositional and anisotropic changes (Long, 2009).

### 3.2 Negative thermal expansivity

Materials that have negative thermal expansivity will shrink when heated and become denser. The hotter the material becomes, the denser it is. This behavior is very different from our normal experiences. Material will sink and remain stable with a density profile going from very dense material near the center of the Earth with very hot material being even denser because of negative thermal expansivity. Material with negative expansivity will be stable and not form convective or advective cells. In this case, the driving force for both compression and heating aid in densification. Mixing of different layers should not occur as both heat and pressure aid in compressing the solid or liquid. The negative thermal expansivity implies experiences we typically don't see in nature at atmospheric pressures especially in gases. It might be argued that  $\text{MgSiO}_3$  undergoes a phase change from perovskite to another crystal structure (Murakami et al., 2004; Tsuchiya et al., 2005) called post-perovskite and thus our  $\rho^*$  values in Table 1 are not appropriate for the deep Earth phases. However, if a hypothetical material (with no phase changes allowed) undergoes a change in thermal expansion properties as we described, then our very simple equation of state with emphasis on the thermal expansion coefficients should be considered. Negative thermal expansion is very much the exception at atmospheric pressure but will be more likely at very high pressures where thermal expansion is pressure suppressed.

### 3.3 Layered shell with zero thermal expansion coefficient

The ratio of the incremental heat to the incremental mechanical work in an isothermal process is given thermodynamically by,

$$\frac{T}{p} \frac{\partial s}{\partial v} \Big|_T = \frac{\beta T}{\kappa p}. \quad (17)$$

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Thermal energy can couple into mechanical work proportional to the ratio given by Eq. (17). The magnitude of this quantity for an ideal gas is 1 so the heat and mechanical work are equal but for solids or liquids it will change sign if  $\beta$  is positive or negative. In the case when  $\beta = 0$  then the mechanical system can not couple into the thermal properties. For example, an acoustic wave will not be able to dissipate heat nor cool or heat the material with pressure excursions as the wave propagates. The change in the temperature with changes in pressure adiabatically as in an acoustic wave is

$$\left. \frac{\partial T}{\partial p} \right|_s = \frac{\beta v T}{C_p}, \quad (18)$$

where  $C_p$  is the heat capacity at constant pressure. It follows that a wave propagating adiabatically in media that has a zero thermal expansion coefficient will neither heat nor cool the surrounding media nor transfer mechanical energy to thermal energy; acoustic damping is thus eliminated. There should be no acoustic damping in this layer as thermal damping will be zero. The adiabatic and isothermal compressibility are the same and the heat capacities at constant volume and constant pressure are also equal. The damping of acoustic waves is not possible because there is neither local heating nor cooling to cause temperature differences needed for Coulomb heat flow. The mechanical work can not be converted into heat energy without any temperature difference to drive the heat flow. The conversion of mechanical energy into thermal energy which is generally the major dissipation in media is not viable when  $\beta = 0$ . It is hypothesized here that the  $D''$  layer in the Earth (e.g., Lee, 2009; Shu, 2012) has  $\beta \approx 0$ . This hypothesis would imply that at even higher pressures the thermal expansion coefficient and the expansivity are negative as seen in Fig. 1. At depths that are less than  $D''$  the coefficients of thermal expansion are positive while continuing to decrease as seen by Eq. (9).

## 4 Conclusions

We have found that there is a characteristic pressure,  $p^*$ , for which the thermal expansion coefficient goes to zero based on a simple linear EOS: at very large pressures the expansion coefficient is negative; at smaller pressures it is positive. The characteristic pressure was found in two ways: first, from a linear, elastic EOS with a temperature dependent compressibility and explicit temperature dependent expansivity. This used the thermal expansion coefficient taken at zero pressure in the EOS; secondly, from the direct integration of a thermodynamic identity taken from the third derivative of the Gibbs free energy function with no modeling. Thus, our equation for  $\beta$  is not only based on the EOS. The characteristic pressure is related to the atmospheric pressure Anderson–Grüneisen parameter which describes the asymmetry of the interatomic potential. It is noted in the text that internal energy theories of solids from the very earliest days are based on constant volume assumptions. This assumption mandates that changes in temperature impose quite large pressures on the material to experimentally verify the nuances of the models and compare to heat capacity measurements. Isometric and isobaric paths lead to very different state conditions: thus thermal measurements made isobarically are not the same as isometric thermal measurements. Figure 1 shows very clearly that temperature changes with a fixed value on the abscissa gives rise to very large pressures. The limit of the possible pressures at all temperatures is significantly less than the pressures needed to suppress thermal expansion coefficients.

Thermal expansion is the slope of the natural log of the volume vs. temperature on an isobar without any presumptions about EOS or how it behaves. Direct thermal expansion measurements at very high pressures are quite rare and can be very difficult to achieve. Shock wave or laser implosions under Hugoniot conditions preclude thermal expansion measurements because the entropy is constrained as seen in Eq. (10); thus measuring thermal expansion with shock conditions is not possible.

Emphasis on the thermal expansion coefficient's role in the thermodynamic interaction between heat and mechanical work has shown that modeling the physical pro-

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cesses of the Earth will change dramatically if there are pressures where the thermal expansion coefficient is effectively zero. An Earth with a near zero thermal expansion coefficient will possess very unusual interactions between heat and work. The standard mechanism for acoustic damping will cease to exist at the characteristic pressure,  $p^*$ .

5 There are excellent measurements of the bulk modulus having a pressure dependence which implies that the linear theories as used here will have higher order pressure dependencies. Higher order terms may change the value of  $p^*$  by a factor of 2 or 3 or even more as the bulk modulus has been reported to change by that much at very large pressures.

10 It might be argued that the materials emphasized in this paper are not the same phases (Murakami et al., 2004; Duffy, 2008) as those found deep in the Earth. However, there is some phase deep in the Earth and that material will behave similar to what we have described here. That thermal expansion coefficients will be reduced at higher pressures can not be doubted: it is proposed here that they go very close to zero  
15 at a very large characteristic pressure which requires dramatic changes in modeling physical processes in the Earth.

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**Table 1.** Physical properties of selected materials used to find a characteristic pressure,  $p^*$ .

Material	Chemical composition	$d\kappa/dT$ ((GPaK) <sup>-1</sup> )	$\beta_0$ (K <sup>-1</sup> )	$p^* =$ $\beta_0/(d\kappa/dT)$ (GPa)	References
Olivine	(Mg, Fe) <sub>2</sub> SiO <sub>4</sub>	$973 \times 10^{-9}$	$38.6 \times 10^{-6}$	39.7	A
Forsterite	Mg <sub>2</sub> SiO <sub>4</sub>	$946 \times 10^{-9}$	$37 \times 10^{-6}$	39.1	B
Fayalite	Fe <sub>2</sub> SiO <sub>4</sub>	$1580 \times 10^{-9}$	$37.8 \times 10^{-6}$	23.9	C
PostPerovskite	MgSiO <sub>3</sub>	$2810 \times 10^{-9}$	$14.8 \times 10^{-6}$	52.6	D
Garnet Pyrope	Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	$879 \times 10^{-9}$	$13.4 \times 10^{-6}$	15.2	E
Chromium Spinel (e.g., Chromite)	FeCr <sub>2</sub> O <sub>4</sub>	$128 \times 10^{-9}$	$70 \times 10^{-6}$	54.6	F
Iron	$\epsilon$ -Fe (HCP)	$1599 \times 10^{-9}$	$61.2 \times 10^{-6}$	38.3	G
Periclase	MgO	$1515 \times 10^{-9}$	$45.5 \times 10^{-6}$	30.1	H
Corundum	Al <sub>2</sub> O <sub>3</sub>	$300 \times 10^{-9}$	$27.1 \times 10^{-6}$	90.3	I

A. See Isaak (1992): Olivine (OLA) 1200 K, Table 4a (p. 1881) and Table 5 (p. 1881) converted to compressibility data.

B. See Mitra (2004): Thermal expansion coefficient at 1000 K, Table 6.3 (p. 521); and Isaak (1992): Table 5 (p. 1881) converted to compressibility data.

C. See Mitra (2004):  $\alpha$  phase, thermal expansion coefficient at 1200 K, Table 6.3 (p. 521) and Table 6.4 (p. 522). Original data from Fabrichnaya (1995).

D. See Guignot et al. (2007), Table 2.

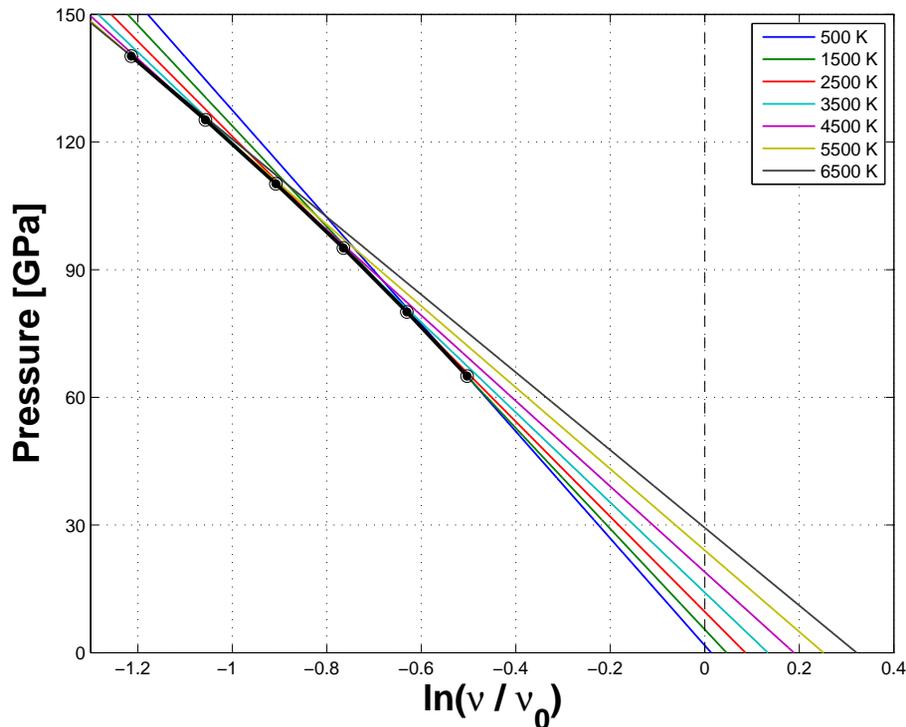
E. See Pavese et al. (1995): Thermal expansion coefficient at 975 K; temperature dependence of compressibility is from Sinogeikin and Bass (2002).

F. See Fan et al. (2008).

G. See Dubrovinsky et al. (1998).

H. See Mitra (2004): Thermal expansion coefficient at 1000 K, Table 6.3 (p. 521) and Table 6.4 (p. 522). Original data from Fabrichnaya (1995).

I. See Dubrovinsky et al. (1998).



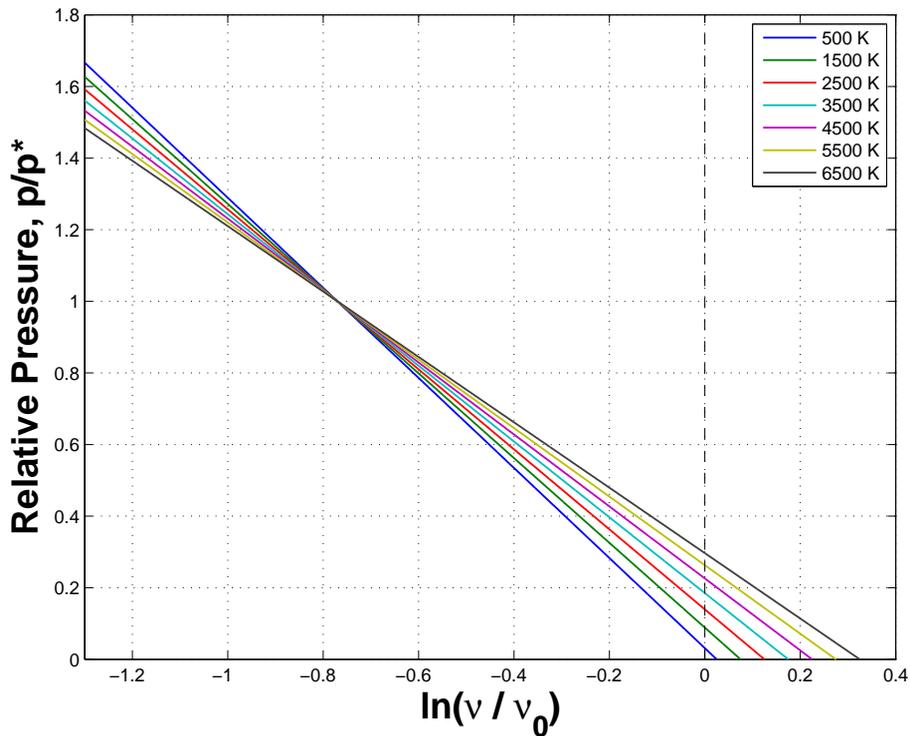
**Fig. 1.** A schematic of the volumetric strain,  $\ln(v/v_0)$ , vs. pressure at selected temperatures. The vertical dashed line at zero strain corresponds to the reference volume,  $v_0$ . The upper left lines are negative thermal expansion coefficients and the lower right lines are positive. The black dots are points where two adjacent temperatures cross approximating zero thermal expansion coefficients between those two temperatures. These dots are points on the regression curve at the selected temperatures.

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**Fig. 2.** A schematic with the regression curve reduced to a point; all lines with  $p > p^*$  have negative thermal expansion coefficients; at pressures less than  $p^*$  they have positive thermal expansion coefficients.

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