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THERMAL EXPANSION OF MANTLE AND CORE MATERIALS AT VERY HIGH PRESSURES

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Abstract. The thermal expansivities (α) of MgO and high-pressure phases of CaO, $CaMgSi_2O_6$, and Fe at ultrahigh pressure are obtained by comparing existing shock compression and temperature measurements to 300 K compression curves constructed from ultrasonic elasticity and static compression data. For MgO, α can be represented by: $\alpha = \rho_o \gamma_o C_V (\rho_o/\rho)^{0.5\pm0.5} / K_T$ where γ is the Grüneisen parameter, C_V is the constant volume specific heat, K_T is the isothermal bulk modulus, and ρ is the density. Using this expression, the thermal expansivity of MgO is 28-32 x 10^{-6} K^{-1} at the pressure of the top of the lower mantle and 10-16 x 10^{-6} K^{-1} at its base (at 2000 K). New data for α of ε-Fe, together with an inner core temperature of 6750 K, constrain the density of the inner core to be 5 ± 2% less than the density of ε-Fe, implying the inner core contains a light element.

Introduction

The coefficient of thermal expansion under conditions of the Earth's deep interior is important for determining the composition, dynamic behavior, and thermodynamic properties of the Earth. Theoretical and semi-empirical expressions for the pressure dependence of α date back 26 years [Anderson, 1967; Birch, 1968] and attest to the long-standing interest in this quantity. By combining available shock compression and temperature data with room temperature densities from static compression or ultrasonic experiments, average thermal expansivities are constrained for the first time at very high pressure (150-200 GPa) for a number of geophysically important materials.

Dynamic and Static Equations of State

Shock compression data for single-crystal magnesium oxide (MgO) are shown in Figure 1 along with the 300 K isotherm derived from ultrasonic elasticity data to 3 GPa [Jackson and Niesler, 1982]. The isotherm was constructed by converting the measured bulk modulus and its pressure derivative from adiabatic to isothermal conditions and employing the Birch-Murnaghan equation.

The Hugoniot or shock compression curve can be related to a corresponding isotherm or adiabat using Mie-Grüneisen theory [McQueen et al., 1970]. This requires the volume-dependent Grüneisen parameter, γ:

$$\gamma = \frac{\alpha K_T}{\rho C_V} = \gamma_o \left(\frac{\rho_o}{\rho}\right)^q, \qquad (1)$$

where the subscript o represents ambient-pressure conditions. q is often assumed to be a constant equal to 1. Shock data reduced to an isotherm in this manner are used, for example, in establishing a pressure scale for diamond cell experiments. Calculated Hugoniots obtained from a 300 K adiabat constructed from ultrasonic data corrected to constant entropy conditions and for q equal to 0, 1, and 2 are shown in Figure 1. The Hugoniot pressure-volume data are best fit by $q = 0.3 \pm 0.7$. A slightly different value of q will be determined below from consideration of thermal expansion data.

Comparison of shock data with static compression or ultrasonic data may be complicated by shock-induced heterogeneities, material strength, and differences in thermodynamic state [Grady, 1977]. The single-crystal Hugoniot for MgO is coincident with the ultrasonic isotherm at low pressure, consistent with a significant loss of strength under dynamic compression, as determined independently from wave profile measurements [Grady, 1977]. At higher pressure, the Hugoniot and static isotherm diverge because of temperature differences. Thermal heterogeneities are expected to diminish when the pressure becomes larger than a few times a material's elastic limit [Grady, 1977]. The data of Vassiliou and Ahrens [1981] demonstrate that no phase change (with a volume change greater than 1.5%) occurs along the MgO Hugoniot to 200 GPa.

Svendsen and Ahrens [1987] reported four temperature measurements on shocked single-crystal MgO. Temperatures of initially transparent materials are measured by recording the spectral radiance of the shock-compressed sample with a high-speed optical pyrometer [Lyzenga and Ahrens, 1979]. Temperatures in opaque materials can be obtained from measurements of the interface temperature between the sample and an impedance-matching window [Bass et al., 1987]. The measured MgO temperatures are consistent with continuum calculations [McQueen et al., 1970] which include a temperature-dependent specific heat and q between 0 and 3. Comparison of measured temperatures with an MgO melting curve based on a Lindemann melting criterion indicates that the equilibrium melt boundary for MgO is >1500 K above the measured temperatures at 169-196 GPa [Svendsen and Ahrens, 1987].

For materials which undergo polymorphic phase transitions at high pressure, shock and static equations of state can be compared under the assumption that the Hugoniot high-pressure phase is the equilibrium assemblage. For CaO, the high-pressure Hugoniot phase has been identified as the B2 phase [Jeanloz et al., 1979]. Shock and room temperature equations of state for this material have been determined to 175 GPa [Jeanloz and Ahrens, 1980] and 135 GPa [Richet et al., 1989], respectively. Shock temperature measurements have been reported between 140 and 183 GPa [Boslough et al., 1984]. We assume that the ε-phase of Fe is stable along the Hugoniot between 13 and 200 ±

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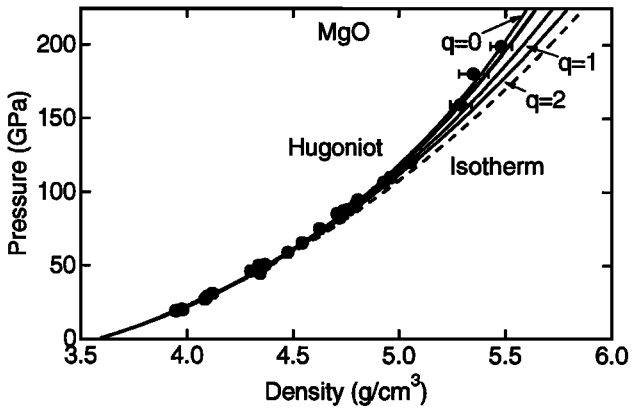

Fig. 1. Compression data for magnesium oxide. The heavy solid line is a fit to the shock data (symbols) [Carter et al., 1971; Vassiliou and Ahrens, 1981], and the dashed curve is the isotherm derived from ultrasonic data. Lighter solid lines show theoretical Hugoniots computed from ultrasonic data.

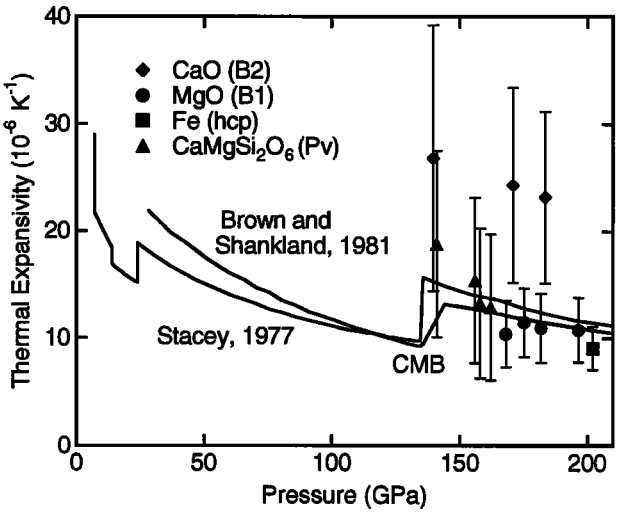

Fig. 2. α at high pressure from shock-wave data. The solid curves are estimated expansivities in the mantle and outer core obtained from Earth models. CMB indicates the core-mantle boundary.

2 GPa [Brown and McQueen, 1986]. A static isotherm for ε-Fe has recently been determined to 300 GPa [Mao et al., 1990] while the Hugoniot equation of state has been extensively studied (e.g., Brown and McQueen [1986]). A single shock temperature measurement plausibly within the stability field of ε-Fe has been reported [Bass et al., 1987]. For diopside ($CaMgSi_2O_6$), the equilibrium high-pressure assemblage is either a perovskite of diopsidic composition [Liu, 1987] or a mixture of $CaSiO_3$ and $MgSiO_3$ perovskites [Tamai and Yagi, 1989]. The static compression curve for these assemblages can be obtained by molar averaging the compression curves of $CaSiO_3$ [Mao et al., 1989] and $(Mg_{0.88}Fe_{0.12})SiO_3$ [Knittle and Jeanloz, 1987], where the latter is first corrected for the effect of iron. Shock equation of state and temperature data for diopside have been reported by Svendsen and Ahrens [1983] and [1990].

Results

Average high-pressure thermal expansion coefficients were determined from densities along the shock and room temperature compression curves at a given pressure using:

$$\alpha = \frac{\ln(\rho_{300}/\rho_H)}{T_H - 300}, \tag{2}$$

where ρ_{300} and ρ_H are the 300 K and Hugoniot densities, respectively and T_H is the measured shock temperature. The calculated α values are shown in Table 1 and Figure 2.

Also shown in Figure 2 are estimates of α in the Earth's interior obtained by combining seismic data with a thermodynamic model. For MgO and $CaMgSi_2O_6$, which represent the major structures expected in the lower mantle, the expansivities are similar to or larger than those found in Earth models at the base of the mantle. It is also noteworthy that α for ε-Fe is consistent with Earth model values for the liquid outer core.

Comparisons which use static compression data have the advantage that little or no extrapolation of the 300 K densities is required. However, the results depend on the static pressure scale, which is derived, in turn, from shock data on incompressible metals. The thermal corrections applied to these data are small and the static pressure scale is believed accurate to a few percent [Mao et al., 1990]. For CaO and $CaMgSi_2O_6$, there is the additional possibility of melting or other solid-solid phase changes along the Hugoniot [Boslough and Ahrens, 1984; Svendsen and Ahrens, 1990]. The MgO and $CaMgSi_2O_6$ results of Svendsen and Ahrens [1987] and [1990] have been corrected slightly to remove the effect of a thin (~1 μm) silver layer in front of the sample on the calculated Hugoniot pressure.

Thermal Expansion Models

Because of the extensive stability of MgO, high-pressure expansivity data for this material can be used with low-pressure thermodynamic data to test models for the pressure dependence of α. We begin with the following identity:

$$\left(\frac{\partial \alpha}{\partial P}\right)_T \equiv \frac{1}{K_T^2}\left(\frac{\partial K_T}{\partial T}\right)_P. \tag{3}$$

TABLE 1. Thermal Expansion Coefficients

Pressure (GPa)	ρ_H (g/cm^3)	ρ_{300} (g/cm^3)	T_H (K)	α (10^{-6}K^{-1})
		MgO (B1 phase)		
169(3)	5.340(0.038)	5.497(0.026)	3081(120)	10.4(3.1)
175(2)	5.375(0.038)	5.549(0.028)	3071(130)	11.5(3.2)
182(2)	5.417(0.038)	5.597(0.029)	3280(371)	11.0(3.2)
196(3)	5.495(0.040)	5.698(0.031)	3663(395)	10.8(3.0)
		CaO (B2 phase)		
140(8)	5.57(0.22)	6.11(0.10)	3749(178)	26.8(12.4)
171(10)	5.72(0.24)	6.46(0.12)	5333(238)	24.3(9.1)
183(11)	5.77(0.24)	6.60(0.12)	6038(225)	23.2(8.0)
		$CaMgSi_2O_6$ (perovskite phase)		
141(7)	5.264(0.142)	5.591(0.036)	3508(141)	18.8(8.7)
156(8)	5.365(0.154)	5.698(0.038)	4215(364)	15.4(7.7)
158(8)	5.396(0.155)	5.711(0.039)	4555(268)	13.3(7.0)
162(8)	5.417(0.158)	5.739(0.038)	4782(356)	12.9(6.8)
		Fe (ε-phase)		
202(3)	11.960(0.074)	12.505(0.072)	5200(500)	9.1(2.0)

Uncertainties are one standard deviation.

Anderson [1967] showed that if $\delta_T = -(\partial K_T/\partial T)_P/\alpha K_T$ is independent of pressure and temperature, (3) yields:

$$\alpha/\alpha_o = (\rho_o/\rho)^{\delta_{To}} . \quad (4)$$

Chopelas and Boehler [1989] found support for this equation from thermal expansion systematics. More recently, Chopelas and Boehler [1992] have suggested that δ_T is a linear function of compression, $(\delta_T + 1)/\eta = \text{const}$, where $\eta = \rho_o/\rho$. In combination with (3), this implies that:

$$\alpha = \frac{\alpha_o}{\eta} \exp\left[\delta_T - \delta_{To}\right] . \quad (5)$$

Birch [1968] proposed that $\alpha K_T \approx \text{const}$, based on the observation from shock data that $\rho\gamma/C_V \approx \text{const}$. A more general form of this obtainable from (1) is [Anderson, 1979]:

$$\alpha = \frac{\rho_o \gamma_o C_V}{K_T}\left(\frac{\rho_o}{\rho}\right)^{q-1} . \quad (6)$$

In Figure 3, this relation is used to compute α along a 2000 K isotherm, which is close to the mean temperature of the shock and ultrasonic data, for $q = 0, 0.5$, and 1. The pressure derivative of K_T at this temperature was taken from *ab initio* calculations [Isaak et al., 1990] and the results are not strongly sensitive to this quantity. The α data for MgO can be fit using (6) with $q = 0.5 \pm 0.5$, which is consistent with the previously determined value from Mie-Grünesien theory ($q = 0.3 \pm 0.7$).

Also shown in Figure 3 are α values calculated using (4) and (5) with δ_{To}=5.0 from high-T elasticity data [Isaak et al., 1989]. Equation (4) underpredicts the measured α values by a factor of 2.5. The value of δ_{To} required for (4) to fit the present data is 3.1 ± 0.7 at 2000 K, significantly lower than the ambient-pressure value. Fei et al. [1992] obtained a value of $\delta_{To} = 4.3 \pm 0.5$ from fitting high P and T diamond cell measurements on $(Mg_{0.6},Fe_{0.4})0$ to 30 GPa and 800 K. The disparity among these results suggests that δ_T has a significant pressure and/or temperature dependence.

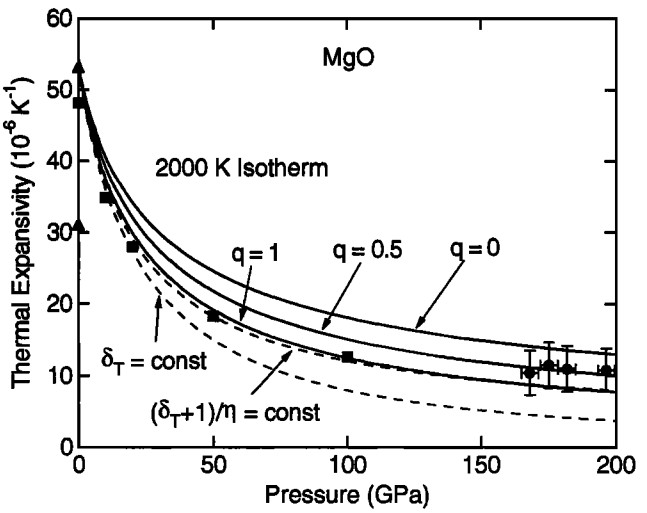

Fig. 3. Comparison of MgO expansion data (circles) with theoretical predictions. The solid lines are computed for a 2000 K isotherm using (6) and $q = 0, 0.5$, and 1. The dashed lines show expansivities at 2000 K using (4) and (5). The boxes show α values at 2000 K from the PIB model of Isaak et al. [1990]. The triangles are zero-pressure α values at 300 K and 2000 K [Isaak et al., 1989].

Equation (5) predicts expansivities that are consistent with the measured values. It is notable that this relation produces almost the same pressure dependence for α as (6) with $q = 1$ (which, at high temperature, is equivalent to Birch's relation, $\alpha K_T \approx \text{const}$). PIB model calculations for MgO [Isaak et al., 1990] also produce similar expansivities. While these relations are all consistent with the high-pressure MgO data, larger α values are also allowed. Using (6) and $q = 0.5 \pm 0.5$, the thermal expansivity of MgO at 2000 K and 24 GPa is 28-32 x 10^{-6} K^{-1} and decreases to 10-16 x 10^{-6} K^{-1} at 135 GPa. Results for $CaMgSi_2O_6$ suggest that silicate perovskite expansivities are equal to or greater than MgO values at high pressure, although this result is less secure because of the uncertain nature of the diopside high-pressure phase.

The α data for ε-Fe also have implications for the Earth's core. If the average temperature of the inner core is 6750 (± 1000) K as inferred from shock and static Fe melting data [Williams et al., 1987], then α and ρ of ε-Fe at inner core conditions, using (2), (6), and the data of Mao et al. [1990], are 6 x 10^{-6} K^{-1} and 13.45 ± 0.21 g/cm³, compared with the average inner core density from normal mode data of 12.85 ± 0.15 g/cm³ [Shearer and Masters, 1990]. This calculation ignores the small temperature-dependence of α at high pressure and assumes that $q = 1$ is appropriate for ε-Fe [Mao et al., 1990]. This result shows that the inner core is less dense than pure iron, in agreement with previous analyses [Jephcoat and Olson, 1987], and the density deficit of the inner core is 5 ± 2%. These conclusions are dependent on the inferred inner core temperature and significantly lower temperatures (4200 K) have been proposed based on other Fe melting data [Boehler, 1992].

Summary

The thermal expansivities of 3 minerals and 1 metal have been constrained at P > 140 GPa from shock and room temperature compression curves and measured Hugoniot temperatures.

It has been shown that expansivity values for MgO are consistent with several new and existing models for the pressure dependence of α. The widely used relation, $\alpha = \alpha_o(\rho_o/\rho)^{\delta_{To}}$, where δ_{To} is constant at its ambient-pressure value, underpredicts α at high pressure. Instead, we find that α is best given by:

$$\alpha = \frac{\rho_o \gamma_o C_V}{K_T}\left(\frac{\rho_o}{\rho}\right)^{-0.5\pm0.5}$$

This model yields 2000 K expansivities for MgO that vary from 28-32 x 10^{-6} K^{-1} at pressure corresponding to the top of the lower mantle and 10-16 x 10^{-6} K^{-1} at the pressure of the core-mantle boundary. Results for $CaMgSi_2O_6$ suggest that α in perovskite-structured materials could be equal to or greater than MgO values.

Data for ε-Fe extrapolated to inner core conditions indicate that ε-Fe is 5 ± 2 % denser than the inner core, implying the inner core is not pure iron.

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