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THERMAL EXPANSION OF MANTLE MINERALS AT HIGH PRESSURES - A THEORETICAL STUDY

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Abstract. Recent experimental work has shown that the pressure dependence of the thermal expansion coefficient can be expressed as:

$$(\alpha/\alpha_0) = (\rho/\rho_0)^{-\delta T} \quad (1)$$

where δ_T, the Anderson-Gruneisen parameter, is assumed to be independent of pressure, and for the materials studied has a value that lies between 4 and 6. Calculation of δ_T from seismic data, however, appears to suggest a contradictory value of between 2 and 3 for mantle-forming phases. Using an atomistic model based on our previously successful many-body interatomic potential set (THB1), we have performed calculations to obtain values of δ_T for four major mantle-forming minerals. Our model results are in excellent agreement with experimental data, yielding values of between 4 and 6 for forsterite and MgO, and values in the same range for $MgSiO_3$-perovskite and γ-Mg_2SiO_4. Moreover, the calculations confirm that δ_T is indeed constant with pressure up to the core-mantle boundary. The apparent conflict between the values of δ_T predicted from seismic data and those obtained from experiment, and now from theory, is discussed.

Introduction

An understanding of the effect of pressure on the thermal expansion of silicates is of great geophysical importance, as it is required in order to calculate mineral densities under mantle pressure and temperature conditions independently from the adiabatic gradient assumption. O.L.Anderson (1967) first showed that thermal expansion can be related to density by the equation (1). δ_T is the so-called Anderson-Gruneisen parameter, and is defined as:

$$\delta_T = (\partial \ln K_T/\partial \ln \rho)_P = -(1/K_T\alpha)(\partial K_T/\partial T)_P \quad (2)$$

and is assumed to be constant with pressure.

From basic thermodynamic relations, it .can be shown that (Anderson and Yamamoto, 1987):

$$\delta_T = -(\partial \ln \alpha/\partial \ln \rho)_T \quad (3)$$

Assuming that δ_T is constant with pressure, and separating variables, yields equation (1).

Despite its importance, there is considerable uncertainty both concerning the values of the Anderson-Gruneisen parameters for mantle minerals, and concerning the validity of the assumption that δ_T is essentially pressure independent. Indeed, there is a conflict between the values of δ_T obtained from experiments (see Chopelas and Boehler, 1989 for a review) and those obtained from seismic data (e.g. D.L. Anderson, 1987). Thus, in this study we have used an atomistic computer simulation approach, based on our previously successful potential models (e.g. Price et al., 1987a) and free-energy minimization code PARAPOCS (Parker and Price, 1989), to predict the high pressure and temperature densities of four major mantle-forming phases. Specifically, we have attempted (1) to verify that equation (1) holds for the whole mantle (i.e. that δ_T is indeed relatively insensitive to pressure), and (2) to fix some bounds on the value of δ_T for MgO, forsterite, γ-Mg_2SiO_4, and $MgSiO_3$-perovskite.

In the following, we present first a summary of the different values of δ_T inferred from various experimental measurements and from the seismic equation of state. This is followed by a brief description of the methodology of our computer simulations, and a discussion of our predicted values for δ_T, which are in excellent agreement with what experimental data are available. We finally discuss the discrepancy between our calculated data and those obtained from seismology.

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Measurements and estimates of δ_T

The Anderson-Gruneisen parameter has previously been inferred for several minerals (see Table 1) from various experimental approaches, including:

1) measurements of their thermal expansion coefficient, isothermal bulk modulus and their respective temperature dependence, that allow δ_T to be retrieved from equation (2) (Isaak et al.,1989a, b).

2) direct measurement of thermal expansion at high pressure, that allows δ_T to be measured directly (Yagi et al., 1987; Boehler et al., 1989).

3) spectroscopic measurements at various pressures that allow, by means of vibrational spectra modelling (e.g. Kieffer, 1979), the calculation of the pressure dependence of thermodynamic properties, which Chopelas (1989a, b) has recently used to estimated the thermal expansion pressure dependence of forsterite and MgO.

D.L. Anderson (1987) has developed an independent estimation of δ_T under lower mantle conditions, from lateral variations of seismic wave velocities. Assuming an adiabatic gradient for the lower mantle, and that the lateral (i.e. isobaric) variations of V_s and V_p are only due to temperature, he defined the parameters g and δ_s:

$$g = (\partial \ln G/\partial \ln \rho)_P = -(1/G\alpha)(\partial G/\partial T)_P \quad (4)$$

$$\delta_s = (\partial \ln K_s/\partial \ln \rho)_P = -(1/K_s\alpha)(\partial K_s/\partial T)_P \quad (5)$$

which are equivalents of the Anderson-Gruneisen parameter δ_T for G and K_s respectively. Given the observed values of lateral wave velocity variations (Hager et al., 1985) and the assumptions above, he obtained values of $g = 5.8$ to 7.0 and $\delta_s = 1.0$ to 1.8. From the relation $K_T = K_s/(1+\alpha\gamma T)$, it can be shown that:

$$\delta_T \approx \delta_s + \gamma \quad (6)$$

where γ, the Gruneisen parameter, is taken to be unity thus yielding values of $\delta_T \approx 2$ to 3.

Thus, on the one hand, there is a great consistency in the δ_T values from structural, elastic and spectroscopic measurements, but on the other hand, the estimate of δ_T for the lower mantle seismic data is a factor of two smaller than the experimental data. D.L. Anderson (1987, 1989) concluded that the results obtained under laboratory conditions (i.e. moderate P and T relative to the lower mantle) can not be extrapolated to the extreme conditions of the mantle. Thus, in an attempt to establish whether such extrapolation of laboratory data is indeed invalid, we have performed atomistic computer simulations to calculate the pressure dependence of thermal expansion for major mantle-forming minerals at temperatures and pressures directly appropriate to mantle conditions.

The atomistic model

In order to perform reliable computer simulations of the free energy of a system, an accurate description of both the static and vibrational behaviour of atoms in mineral structures is required (Price et al., 1987a, b; Wolf and Bukowinski, 1987). We use an approach based upon the Born model of solids in which the interaction between atoms is described by a potential of the form (Born and Huang, 1954):

$$U = \sum_{ij} e^2 q_i q_j r_{ij}^{-1} + \sum_{ij} A_{ij} \exp(-r_{ij}/B_{ij}) - C_{ij} r_{ij}^{-6} \quad (7)$$

where the first term represents the Coulombic energy (with e the

TABLE 1. Experimental values of δ_T for various minerals.

Compound	δ_T $T<\theta_D$	$T>\theta_D$	
Forsterite	6.0	5.4	(1)
	6.5	5.5	(4)
MgO	5.3	4.7	(1)
	6.1	5.5	(4)
Garnets	7.0	6.0	(2)
Iron	6.0-7.0		(3)

(1) Isaak et al. (1989a, b): resonance measurements;
(2) Yagi et al. (1987), (3) Boehler et al. (1989): High Pressure-High Temperature X-ray measurements;
(4) Chopelas (1989ab): spectroscopic measurements.

electron charge, q_i and q_j the point charges associated with the ions i and j, and r_{ij} the distance between them), and the second term models the short range repulsive potential and Van der Waals interactions, where A_{ij}, B_{ij}, C_{ij} are derivable constants. In order to model the directionality of the Si-O bonds, a bond-bending term is included in the potential, of the form:

$$U = \sum_{ijk} k^B_{ijk} (\theta_{ijk}-\theta_0)^2 \quad (8)$$

where k^B_{ijk} is a derivable spring constant, θ_{ijk} is the O-Si-O bond angle and θ_0 the ideal polyhedron bond angle (109°47' for tetrahedral and 90° for octahedral coordination). Finally the polarizability of the oxygen ion is modelled by a core-shell interaction, where a massless shell of charge Y is coupled to the core containing all the mass by an harmonic spring:

$$U = \sum_i k_s r_i^2 \quad (9)$$

where k_s is the spring constant and r_i the core-shell separation.

For the THB1 potential used in this study (see Table 2), the parameters were derived from fitting either to quantum mechanical energy surfaces or to the structural and elastic properties of simple binary oxides (see Price et al., 1987a, for a full reference). The

TABLE 2. THB1 potential parameter set. (Short range cutoff = 10A)

q_{Mg}	+2.0	B_{Mg-O} A	0.2945
q_{Si}	+4.0	B_{Si-O} A	0.3205
$q_{O\text{-shell}}$	-2.848	B_{O-O} A	0.1490
$q_{O\text{-core}}$	+0.848	C_{O-O} eVA^6	27.88
A_{Mg-O} eV	1428.5	C_{Si-O} eVA^6	10.66
A_{Si-O} eV	1283.9	k^S eVA^{-2}	74.92
A_{O-O} eV	22764.3	k^B eVrad^{-2}	2.09

structural, elastic, and thermodynamic properties, in association with phonon frequencies, are calculated at various simulated pressures and temperatures using energy minimization procedures available via the code PARAPOCS (Parker and Price, 1989). Of particular relevance to this study, the thermal expansion α is calculated self-consistently during the energy minimisation procedure from:

$$\alpha = \gamma_{th} Cv/K_T V \quad (10)$$

where γ_{th} is estimated from the average mode Gruneisen parameter:

$$\langle\gamma\rangle = \sum_i (Cv_i\gamma_i)/Cv \quad (11).$$

THB1 has been found to be successful in describing the strucure and lattice dynamics of forsterite and its high-pressure polymorphs (Price et al., 1987a, b).

Some of the calculated room temperature and pressure properties of the minerals considered in this study, namely the forsterite and spinel polymorphs of Mg_2SiO_4, MgO and $MgSiO_3$-perovskite, are reported in Table 3, and are compared with the observed values. One can see that the thermal expansion coefficients as well as the Gruneisen parameters are systematically underestimated (by up to 40% for α) as pointed out by Price et al. (1987b), because of some shortcomings in the potential and because of the inherent limitations of the quasi-harmonic approximation used in the energy minimization procedure. This is also a consequence of the assumption that $\gamma_{th} = \langle\gamma\rangle$ which is adopted in the calculation of α. Experimental measurements of $\langle\gamma\rangle$ from high-pressure IR and Raman spectroscopy on several mantle minerals (Chopelas, 1989ab; Hofmeister et al., 1989;

TABLE 3. Calculated and measured values of volume, thermal expansion, bulk modulus and Gruneisen parameter at 300K and 1 bar for the four simulated minerals.

		V A^3	α $10^{-5}K^{-1}$	K_T Mbar	αK_T $MbarK^{-1}$	γ
α-Mg_2SiO_4	calc	296.1	1.89	1.50	2.84	1.09
	obs	289.9	2.72(a)	1.28(b)	3.45	1.29(b)
γ-Mg_2SiO_4	calc	519.7	1.13	2.44	2.76	0.95
	obs	524.6	1.86(c)	1.84(d)	3.42	1.27(c)
MgO	calc	74.9	1.94	2.32	4.50	1.41
	obs	73.8	3.12(e)	1.62(f)	5.05	1.52(f)
$MgSiO_3$	calc	161.3	1.35	3.37	4.55	1.32
	obs	162.5	1.71(g)	2.47(h)	4.22	1.60(i)

a, quoted in Isaak et al., 1989a; b, Isaak et al., 1989a; c, Suzuki et al., 1979; d, Weidner et al., 1984; e, Suzuki, 1975; f, Isaak et al., 1989b; g, Ross and Hazen, 1989; h, Kudoh et al., 1987; i, estimated.

Chopelas, personal communication), shows it to be systematically lower than the thermal Gruneisen parameter, γ_{th}, by between 10 and 20%, and therefore give virtually indentical results to those predicted from THB1. However, both of these Gruneisen parameters are, by definition related to the frequency shifts of the vibrational modes. As THB1 has proved successful in modelling both the ambient (e.g. Price et al., 1987a) and high pressure (unpublished results) lattice dynamics of mantle minerals, we are therefore confident that this potential will allow accurate prediction of the variation with pressure of both the Gruneisen parameter and thermal expansion.

Predicted thermal expansion pressure derivatives

The structural and thermodynamic properties of the four quoted minerals were calculated for different pressures over their stability fields along two isotherms, (1) at room-temperature (i.e. below the Debye temperature), and (2) at 1200K for Mg_2SiO_4 polymorphs and 2000K for MgO and $MgSiO_3$-perovskite, in order to remain far above their respective Debye temperatures even at very high pressure. At such temperatures, intrinsic anharmonic effects are important at low pressures but are mostly supressed at high pressure (Hardy, 1980). Therefore, we may expect the quasi-harmonic approximation to be valid under such high pressure conditions. The calculated ratios of α/α_0 to V/V_0 are reported on figure 1 and derived values of δ_T for the four simulated minerals are listed in Table 4.

The predicted values are in very good agreement with the experimental data for forsterite and MgO. We find the same trends

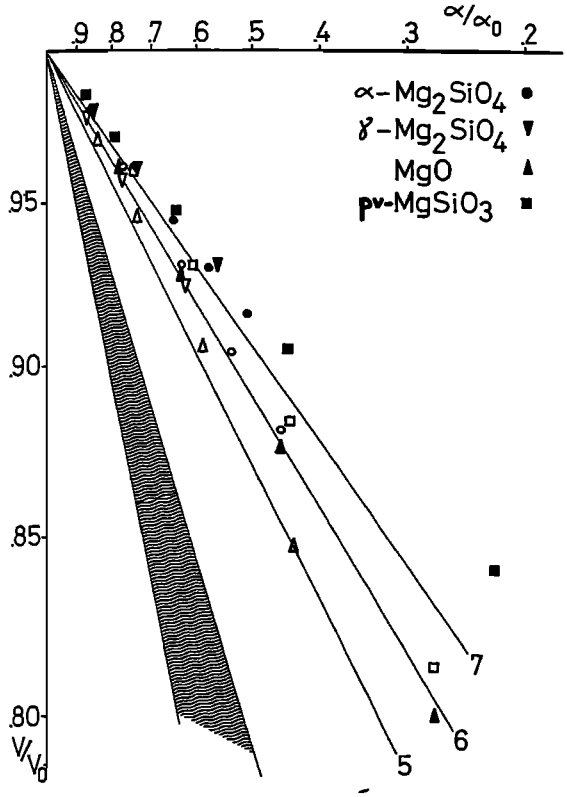

Fig. 1. Log-log plot of the calculated α/α_0 vs. V/V_0 ratios. The lines correspond to different values of δ_T as indicated. The stippled area corresponds to δ_T values inferred from the seismic equation of state of the lower mantle (D.L. Anderson, 1987). Filled symbols: $T<\theta_D$; open symbols: $T>\theta_D$

for the calculations as for the experiments, namely, (1) δ_T is fairly independent of pressure, and (2) δ_T decreases by a value of one to two above the Debye temperature, but remains in the experimental range of 4 to 6 under mantle conditions.

In addition, we confirm that the Anderson-Gruneisen parameter can be assumed to be constant with pressure up to the core-mantle boundary, so that equation (1) holds for the whole mantle. Finally, THB1 allows the prediction of δ_T for high-pressure polymorphs, such as γ-Mg_2SiO_4 and $MgSiO_3$-perovskite, for which metastability (especially for $MgSiO_3$ perovskite) precludes structural studies over a wide range of temperature (Ross and Hazen, 1989). Furthermore, using an approach based on the modified electron-gas theory, Wolf and Bukowinski (1987) have presented the simulated properties of $MgSiO_3$-perovskite at high pressures and temperatures. From an analysis of their data, we infer that their calculations predict a similar Anderson-Gruneisen parameter, confirming that in spite of some apparently minor short-comings and its empirical nature, the potential set THB1 appears to be remarkably robust and highly versitile in modelling a wide range of perfect (e.g Price et al., 1987a, b) and defect properties (e.g. Wall and Price, 1989; Wright and Price, 1989) of minerals at high pressures and temperatures.

TABLE 4. Calculated values of the Anderson-Gruneisen parameter δ_T at various pressures and temperatures.

	Fo		Sp		MgO		Pv	
T(K)	300	1200	300	1200	300	2000	300	2000
P(kbar)								
50	7.6	6.5	7.5	6.3	6.3	5.9	-	-
100	7.6	6.4	7.9	6.1	6.2	5.6	8.0	7.0
200	7.8	6.2	8.1	6.0	6.1	5.3	8.0	7.0
400	-	-	-	-	5.9	5.0	8.1	6.6
800	-	-	-	-	5.8	4.7	8.7	6.3
1200	-	-	-	-	5.9	4.6	10.1	6.5

Discussion and Conclusion

Chopelas and Boehler (1989) have stressed that, from experimental evidence, the pressure dependence of thermal expansion, expressed as the Anderson-Gruneisen parameter δ_T, lies between 4 and 6 for oxide minerals under mantle conditions. Using atomistic simulation techniques, we have confirmed these results for forsterite and MgO, and shown that γ-Mg_2SiO_4 and $MgSiO_3$-perovskite, for which experimental values were lacking, behave similarly. Our calculations show that δ_T can indeed be assumed independent of pressure, up to at least the core-mantle boundary conditions, and decreases by about one above the Debye temperature, thus remaining in the observed experimental range of 4 to 6 over the whole mantle. The implications for the lower mantle composition of δ_T being in the range 4-6 have been discussed by Chopelas and Boehler (1989), who showed that for such a situation a pyrolitic composition mantle (2 perovskite + 1 magnesiowustite) could account for the densities of the PREM model (Dziewonski and Anderson, 1981) below the 670km-discontinuity.

Having confirmed the findings of the experimentists, it is now essential to try to find an interpretation of D.L. Anderson's seismically inferred values of the Anderson-Gruneisen parameter. It must be noted that the estimate given by D.L. Anderson is based on the assumptions that (1) the geothermal gradient is adiabatic in the lower mantle (i.e. no account is given for possible superadiabaticity), and (2) the lateral seismic velocity variations are due only to temperature variations. It is widely held that in the upper mantle, the discrepancy between the "seismic" and experimental δ_T might be explained by partial melting, which strongly affects the rigidity (i.e. V_s) and weakly affetcs the bulk modulus (i.e. V_p), yielding an apparently low δ_T. The fact that in the lower mantle partial melting is unlikely, led D.L. Anderson to describe the V_s and V_p isobaric variation as a temperature effect. Nevertheless, in addition to changing the elastic properties of the lower mantle minerals (perovskite and Mg-wustite), temperature can also affect the composition of the coexisting phases (different Fe/Mg equilibrium constant) and/or their structure. Variations of Fe/Mg ratios have been shown to have a strong differential effect on the rigidity and bulk modulus for the (Mg,Fe)O solid solution (Sumino and Anderson, 1984), and could thus explain the greater variation in rigidity (V_s) than in bulk modulus (V_p) in an isochemical lower mantle. Unfortunately, no data are available for the $(Mg,Fe)SiO_3$-perovskite solid solution, and the temperature dependence of the equilibrium constant between (Mg,Fe)O and $(Mg,Fe)SiO_3$ is not clearly elucidated (Guyot et al., 1989). An alternative explanation is that orthorhombic $MgSiO_3$-perovskite undergoes a ferroelastic phase transition at high-temperature, transforming to a higher symmetry tetragonal or cubic polymorph (Yeganeh-Haeri et al., 1987). This would also result in a large variation in rigidity, compared with bulk modulus, in the vicinity of the transition boundary, leading to the observed high $(\partial \ln V_s/\partial \ln V_p)_p$ ratios. Further experiments and simulations are needed to establish whether either of these proposals are a viable alternative interpretation of the apparently anomalous V_s-V_p systematics of the lower mantle.

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