

Confidence Limits for Silicate Perovskite Equations of State

Craig R. Bina

Department of Geological Sciences, Northwestern University, 1847 Sheridan Road, Evanston, IL 60208, USA. (Fax: +1-708-491-8060; Email: craig@earth.nwu.edu)

Received January 18, 1995 / Revised, accepted April 13, 1995

Abstract. We examine thermoelastic equations of state for silicate perovskite based on data from recent static compression studies. We analyze trade-offs among the fitting parameters and examine data sets for possible effects of metastability and of Mg–Fe solid solution. Significant differences are found between equations of state based on low pressure measurements obtained for perovskite outside of its stability field. Increasingly consistent results are obtained when higher pressure data are used, despite differences in the zero-pressure parameters used to describe the equations of state. The results highlight the importance of measuring the thermoelastic properties of perovskite at high pressure, specifically within its stability field, and the potential problems associated with large extrapolations of equations of state in the analysis of seismic data.

Introduction

Constraints upon the composition and mineralogy of the Earth's mantle can be obtained by comparing the profiles of density and velocity which result from seismological studies with the elastic properties of candidate mineral assemblages under mantle conditions (Birch 1952). Measurements of elastic properties of minerals can now be performed over an increasingly large P – T range of the Earth's interior. For determining properties at very high P – T conditions, measured elastic properties of minerals must be modeled with suitable equations of state (Bina and Helffrich 1992).

The dominant minerals in the lower mantle are believed to be ferromagnesian silicate perovskite (Mg, Fe)SiO₃ and magnesiowüstite (Mg, Fe)O. The equation of state for magnesiowüstite is reasonably well constrained (Fei et al. 1992; Hemley et al. 1992), in part because this phase is stable from ambient to lower mantle conditions. The behavior of perovskite at high P and T is of particular interest, since it is this behavior that determines whether or not seismic velocity and density profiles require the lower mantle to be distinct in major

element composition from a pyrolite-like upper mantle (Jackson 1983; Knittle et al. 1986; Bina and Silver 1990; Zhao and Anderson 1994). However, (Mg, Fe)SiO₃ perovskite is thermodynamically stable only at high pressures (> 24 GPa), and most experimental studies of this phase have been performed outside of its stability field, thus necessitating significant extrapolation to lower mantle conditions. Despite experimental difficulties in studying perovskite, increasingly accurate measurements have been performed in recent years, and there is now good agreement among various groups on several of its thermoelastic properties (i.e., K_{T_0} , K'_{T_0} , and to a lesser extent α_p , the thermal expansivity under moderate pressures of 20–30 GPa) (Jeanloz and Hemley 1994).

Continued experimental study of the thermoelastic properties of silicate perovskites is needed over a wider range of P – T conditions. The significant pressure dependence of thermal expansivity determined by Mao et al. (1991) results in lower mantle densities for the perovskite which are close to those determined seismologically, a result that suggests silica (and possibly iron) enrichment in the lower mantle (Stixrude et al. 1992; Hemley et al. 1992; cf. Knittle et al. 1986; Jeanloz and Knittle 1989). In contrast, other measurements carried out at lower pressures find a lower thermal expansivity at low pressures and a very weak pressure dependence, suggesting that a pyrolite-like upper mantle composition fits the lower mantle density profile (e.g., Wang et al. 1991, 1994). Here we examine this issue by analysis of these and more recent data (Funamori and Yagi 1993; Yagi et al. 1993; Fei, unpublished). We study the trade-offs in the best-fit parameters and use the results to assess the validity of various measurements. We show explicitly the relationship among the parameters used in different approaches (e.g., q and δ_T).

Method

We are interested in an equation of state which relates pressure P , volume V , and temperature T (Zharkov and

Kalinin 1971). The pressure can be expressed as a function of volume and temperature simply by expanding the pressure in terms of its partial derivatives:

$$P(V, T) = \int \left(\frac{\partial P}{\partial V} \right)_T dV + \int \left(\frac{\partial P}{\partial T} \right)_V dT \quad (1)$$

Integrating the volume derivative first, at a reference temperature T_0 , gives the "cold" or room-temperature component of the pressure, and evaluating the temperature derivative second, at the volume of interest V , gives the "thermal" pressure:

$$P(V, T) = \int_{V_0}^V \left(\frac{-K_T}{\hat{V}} \right)_{T_0} d\hat{V} + \int_{T_0}^T \left(\frac{\gamma}{V} C_V \right) d\hat{T} \\ \equiv P_{\text{cold}} + P_{\text{thermal}}, \quad (2)$$

where K_T is the isothermal bulk modulus, γ is the Grüneisen parameter, C_V is the isochoric heat capacity, and V_0 is the reference volume corresponding to the reference temperature T_0 at the pressure $P=0$. (Note that the integrand for the thermal pressure term can be written equivalently as αK_T , where α is the volume coefficient of thermal expansion.) Since we wish to use our equation of state for extrapolation as well as for interpolation, we must employ functional forms that accurately reflect the underlying microscopic physics of the materials.

For the room-temperature isothermal equation of state, we employ the third-order Birch-Murnaghan equation from Eulerian finite strain theory (e.g., Birch 1952):

$$P_{\text{cold}} = 3 K_{T_0} f (1 + 2f)^{5/2} (1 - \xi f). \quad (3)$$

Here the strain variable f and the coefficient ξ are given by:

$$f \equiv \frac{1}{2} [(V_0/V)^{2/3} - 1], \quad \xi \equiv -\frac{3}{4} (K'_{T_0} - 4), \quad (4)$$

where K_{T_0} and K'_{T_0} denote the zero-pressure isothermal bulk modulus and its pressure derivative.

For the thermal pressure, we employ the Mie-Grüneisen-Debye equation based on quasi-harmonic lattice vibrations (Zharkov and Kalinin 1971). This approximation includes contributions from optical modes as an effective high-frequency cutoff for the acoustic modes. Although experiments and theory show that the density of vibrational modes of perovskite is manifestly non-Debye-like (Hemley and Cohen 1992), the thermoelastic properties of many such materials nonetheless can be well represented over a wide range of temperatures with such a model (e.g., Jeanloz and Knittle 1989; Hemley et al. 1992; Anderson et al. 1992; Stixrude and Hemley, unpublished). In this approximation, we write

$$P_{\text{thermal}} = \frac{\gamma_D}{V} E_{\text{th}}(V, T). \quad (5)$$

Here the thermal energy E_{th} is given by:

$$E_{\text{th}}(V, T) \equiv 9nRT \left(\frac{\theta_D}{T} \right)^{-3} \cdot \int_0^{\theta_D/T} \frac{t^3}{e^t - 1} dt, \quad (6)$$

where n is the number of atoms per formula unit and R is the gas constant. The Debye temperature and Grüneisen parameter, θ_D and γ_D , are given by:

$$\theta_D \equiv \theta_{D_0} (V_0/V)^{\gamma_D}, \quad (7)$$

$$\gamma_D \equiv \gamma_{D_0} (V_0/V)^{-q}, \quad (8)$$

in terms of their values θ_{D_0} and γ_{D_0} at the reference volume V_0 and the value of the additional parameter q . Implicit in the quasi-harmonic approximation [Eqs. (5)–(7)] is that γ_D (and hence θ_D) is independent of T . Secondary assumptions not fundamental to the theory, implicit in Eq. (8), are that γ_D has a V -dependence similar in form to that of θ_D and that q is independent of V . Alternatives to these secondary assumptions are the subject of ongoing study.

Given a set of experimental data points $\{P_i, V_i, T_i\}$, we construct a best-fit equation of state by employing the downhill simplex method (Press et al. 1986) to solve for some subset of the parameters $\{K_{T_0}, K'_{T_0}, \theta_{D_0}, \gamma_{D_0}, q\}$ which minimizes the mean-square misfit between the calculated and measured pressures.

The thermal pressure is most sensitive to γ_D [Eq. (5)], and hence to γ_{D_0} and q [Eq. (8)]. While previous studies have shown that $P-V-T$ data alone do not tightly constrain θ_{D_0} (Hemley et al. 1992), as confirmed by the trade-off analyses described below, additional constraints upon θ_{D_0} often can be obtained from vibrational, thermochemical, or phase equilibrium data.

Thermal equations of state are sometimes expressed in terms of the thermal expansivity α and the Anderson-Grüneisen parameter δ_T (giving the pressure dependence of α), rather than in terms of γ and q . The relationship between these two alternative representations is given by:

$$\gamma = \frac{\alpha K_T V}{C_V}, \quad q = 1 + \delta_T - K'_T - \left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T \quad (9)$$

Equation of State Analysis

We first employ the formulation for the room-temperature equation of state [Eqs. (3)–(4)] to solve for K_{T_0} and K'_{T_0} , using recent static compression data at $T_0 = 300$ K (Fig. 1) (Knittle and Jeanloz 1987; Mao et al. 1991; Funamori and Yagi 1993; Yagi et al. 1993; Fei, unpublished). The results are shown in Fig. 2a, which illustrates the well-known trade-off (e.g., Bell et al. 1987) between the best-fit values of K_{T_0} and K'_{T_0} . Statistical F -tests between one- and two-parameter fits (Lindgren et al. 1978) demonstrate that K'_{T_0} is indistinguishable from its null-hypothesis value of 4 at the 95% confidence level. Fixing K'_{T_0} at 4 and employing either all of the T_0 experimental data or a variety of subsets of the data yields best-fit K_{T_0} values which range from 261 to 263 GPa, in good agreement with independent Brillouin spectroscopy measurements (Weidner et al. 1993).

In contrast to this agreement for the room-temperature equation of state, different experimental results have been reported for the thermal expansion at low pressures (cf. Jeanloz and Hemley 1994). In particular, the data

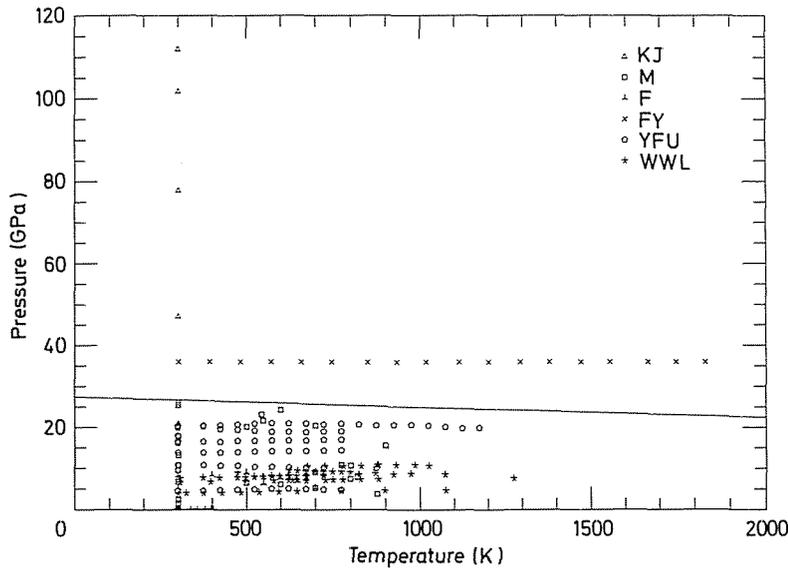


Fig. 1. Experimental data sets in pressure-temperature space. References are: KJ (Knittle and Jeanloz 1987), M (Mao et al. 1991), FY (Funamori and Yagi 1993), YFU (Yagi et al. 1993), F (Fei, unpublished), WWL (Wang et al. 1994). Dotted line shows ilmenite-perovskite phase boundary

Table 1. Best-fit thermal equation of state parameters for $\text{pv}(\text{Mg, Fe})\text{SiO}_3$. Isothermal equation of state parameters: $K_{T_0} = 261$ GPa and $K'_{T_0} = 4$. Data set references: KJ (Knittle and Jeanloz 1987), M (Mao et al. 1991), FY (Funamori and Yagi 1993), YFU (Yagi et al. 1993), F (Fei, unpublished), WWL (Wang et al. 1994)

Line	Data Sets	Points	θ_{D_0} (K)	γ_{D_0}	q
1	KJ + M + FY + YFU + F	131	1480	2.3	4.9
2	KJ + M + FY + YFU + F + WWL	210	1060	1.5	1.9
3	KJ + M + FY + YFU + F + WWL	210	950	1.4	1
(Fe-free samples)					
4	FY + YFU	89	1510	1.6	1
5	FY + YFU + WWL	168	1230	1.5	1
(metastability-weighted)					
6	KJ + M + FY + YFU + F	131	1190	1.7	2.4
7	KJ + M + FY + YFU + F	131	1100	1.5	1
8	KJ + M + FY + YFU + F + WWL	210	1030	1.5	1
(highest- P only)					
9	FY	18	1100-1600	1.5-1.6	1

of Wang et al. (1994) show an unusually weak pressure dependence of the thermal expansivity in comparison to the results of Mao et al. (1991) and Funamori and Yagi (1993). Accordingly, we have chosen to perform several separate analyses in order to explore the differences in the equation-of-state fits. Note that differences among the various data sets are not strictly associated with random errors; instead, there appear to be important systematic differences that have been difficult to establish experimentally. Hence, these fits may provide insight into possible systematic errors.

Adopting a 300 K isothermal equation of state characterized by K_{T_0} of 261 GPa and K'_{T_0} of 4, we incorporate the thermal pressure formulation [Eqs. (5)–(8)] to solve for θ_{D_0} , γ_{D_0} , and q , using recent static compression data at a variety of temperatures (Fig. 1) (Knittle and Jeanloz 1987; Mao et al. 1991; Funamori and Yagi 1993; Yagi et al. 1993; Fei, unpublished). The results are shown in Figs. 2b–d, which illustrate the trade-offs between θ_{D_0} and γ_{D_0} , between θ_{D_0} and q , and between γ_{D_0} and q . Statistical F -tests between two- and three-parameter fits demonstrate that q differs from its null-hypothesis value of 1 at the 99% confidence level. Since the ellipsoid sec-

tions in Fig. 2 are all shown with the same contour levels, it is evident that the trade-off between θ_{D_0} and q in Fig. 2c is the least well constrained. Employing these experimental data yields best-fit values of 1480 K for θ_{D_0} , 2.3 for γ_{D_0} , and 4.9 for q (Table 1, line 1). Stixrude et al. (1992) and Hemley et al. (1992) fit a limited set of these data; using information on phase boundaries as an additional constraint they obtained $\theta_{D_0} \approx 1100$ K but similarly high values for γ_{D_0} and q . These unusually large values for γ_{D_0} and q translate [Eq. (9)] into a strongly pressure-dependent volume coefficient of thermal expansion α (Fig. 3a) or, equivalently, a large Anderson-Grüneisen parameter δ_T (Fig. 3b).

We performed an additional set of fits including the data of Wang et al. (1994). Inclusion of this data set yields best-fit values of 1060 K for θ_{D_0} , 1.5 for γ_{D_0} , and 1.9 for q (Table 1, line 2). However, statistical F -tests between two- and three-parameter fits demonstrate that q is now indistinguishable from its null-hypothesis value of 1 at the 95% confidence level. As shown in Fig. 4c, the primary effect of incorporating this data set is to deform the trade-off ellipsoids between θ_{D_0} and q , thus simultaneously yielding smaller

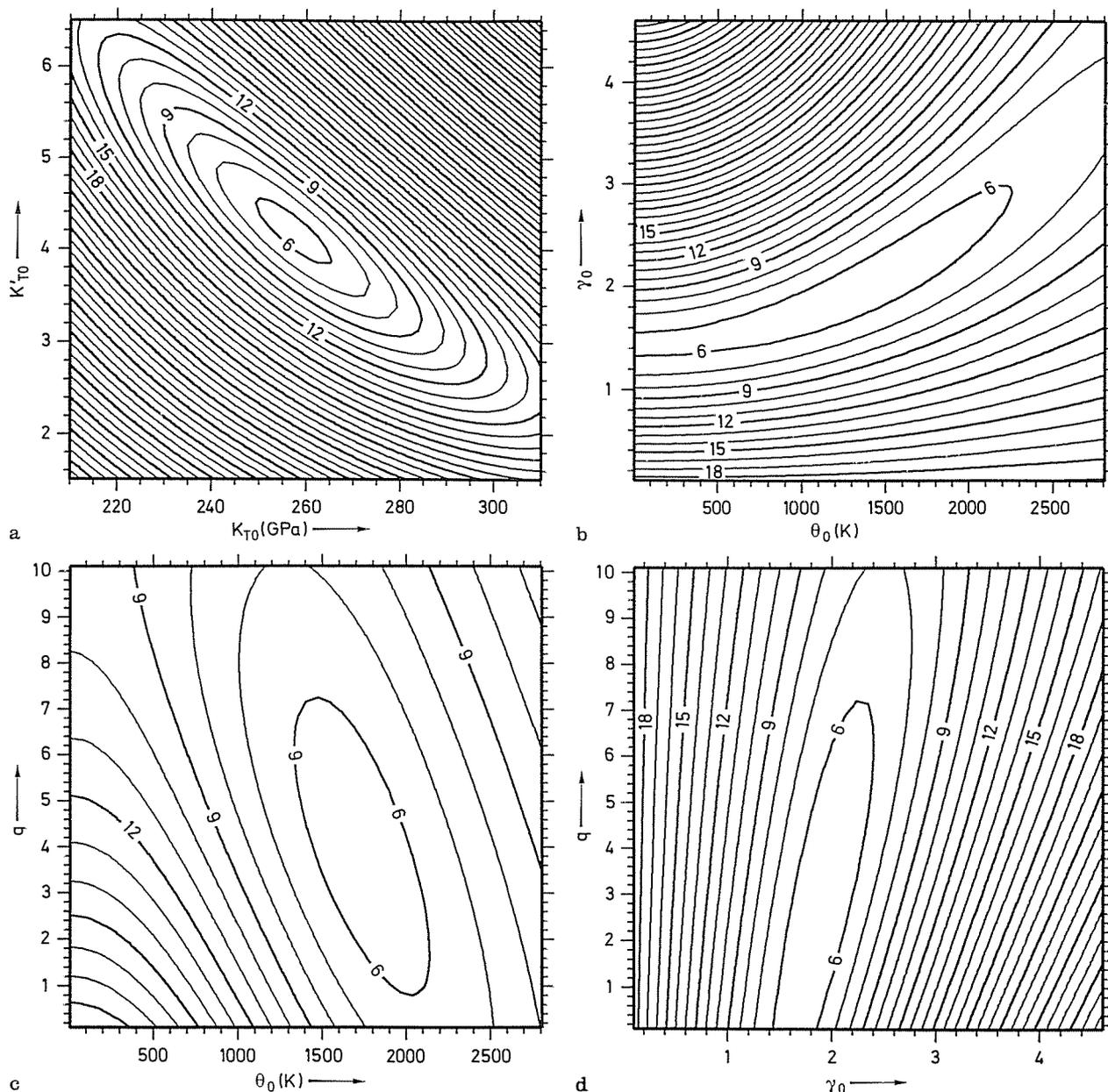


Fig. 2a-d. Contours of RMS misfit showing sections through five-dimensional hyper-ellipsoid about best-fit equation of state (Table 1, line 1). Four panels give complete illustration of parameter trade-offs. Contour values are of χ^2 where the normal estimator

$$\chi^2 \text{ is given by } \frac{1}{N} \sum_{i=1}^N \frac{1}{2} (\Delta P_i / \sigma_i)^2 \text{ for } \Delta P_i = P_i^{\text{exp}}(V_i, T_i) - P_i^{\text{calc}}(V_i, T_i)$$

with σ_i arbitrarily fixed at 0.1 GPa

values of γ_{D_0} through the trade-off between γ_{D_0} and q shown in Fig. 4d. Fixing q at 1 and employing all of the experimental data now yields best-fit values of 950 K for θ_{D_0} and 1.4 for γ_{D_0} (Table 1, line 3). These smaller values for γ_{D_0} and q translate [Eq. (9)] into a less strongly pressure-dependent volume coefficient of thermal expansion α (Fig. 3c) or, equivalently, a smaller Anderson-Grüneisen parameter δ_T (Fig. 3d) closer to a value of ~ 4 . The significant change in equation of state parameters resulting from incorporation of the Wang et al. (1994) data invites analysis of this data set in isolation, but the range of pressures spanned by the Wang et al.

(1994) data alone is too narrow to constrain simultaneously θ_{D_0} , γ_{D_0} , and q . However, this data set can be combined with those of Funamori and Yagi (1993) and Yagi et al. (1993), as discussed in the analysis of Fe-free perovskite below, to yield a similar low- γ_{D_0} equation of state (Table 1, line 5).

Discussion

We begin by considering possible effects of metastability upon measurements carried out at low pressures. First,

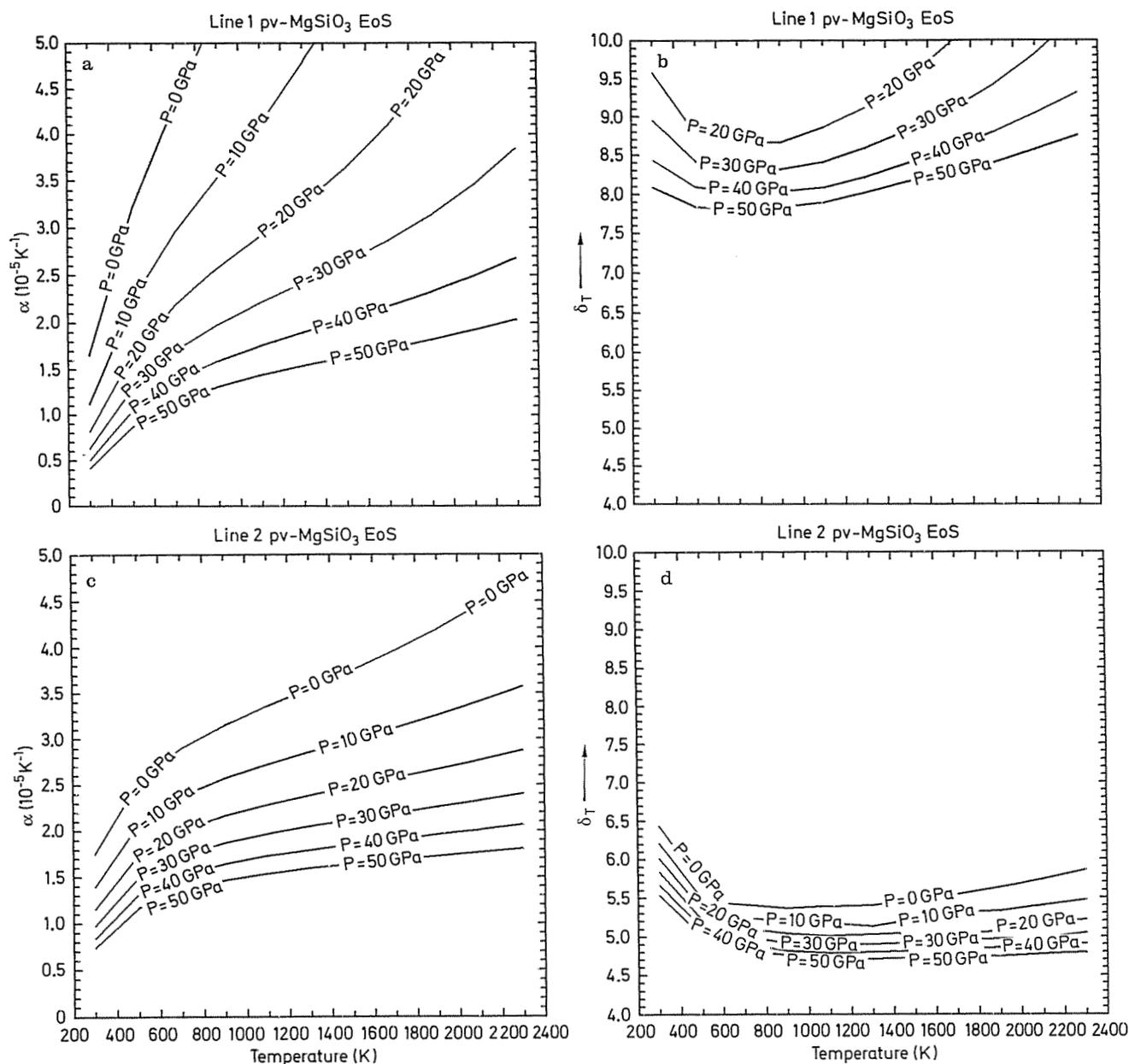


Fig. 3a–d. Volume coefficient of thermal expansion α and isothermal Anderson-Grüneisen parameter δ_T versus pressure and temperature as derived from best-fit equations of state. Panels a and b

are for the equation of state of Fig. 2; panels c and d are for that of Fig. 4

it is now well established that prolonged heating of perovskite at pressures below those of its stability field results in degeneration of the sample, so that measured elastic properties in some experiments may be influenced by partial amorphization, back-transformation to lower pressure phases, or change in $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio (cf. Hemley and Cohen 1992). While the thermal expansivity is reported to be reversible as a function of temperature in some studies, this does not prove that decomposition of the perovskite has not occurred and has not significantly affected the measured expansivity. Second, the thermal expansivity could be anomalously high at low pressures because the phase is close to an intrinsic (e.g.,

elastic or optic mode) instability in structure in the metastable state (Hemley and Cohen 1992). In this case, decomposition need not be invoked and the thermal expansivity will be reversible; it will be high as a result of increasing anharmonicity analogous to the increasing thermal expansivity of materials near melting (Ubbelohde 1965). Third, if the phase is close to an intrinsic instability in its thermodynamically metastable state, its structure may be highly sensitive to non-hydrostatic stresses which, for example, could drive metastable (and difficult to reproduce) crystalline-crystalline transitions. The latter phenomenon would compromise any determination of the true thermal expansivity of the material

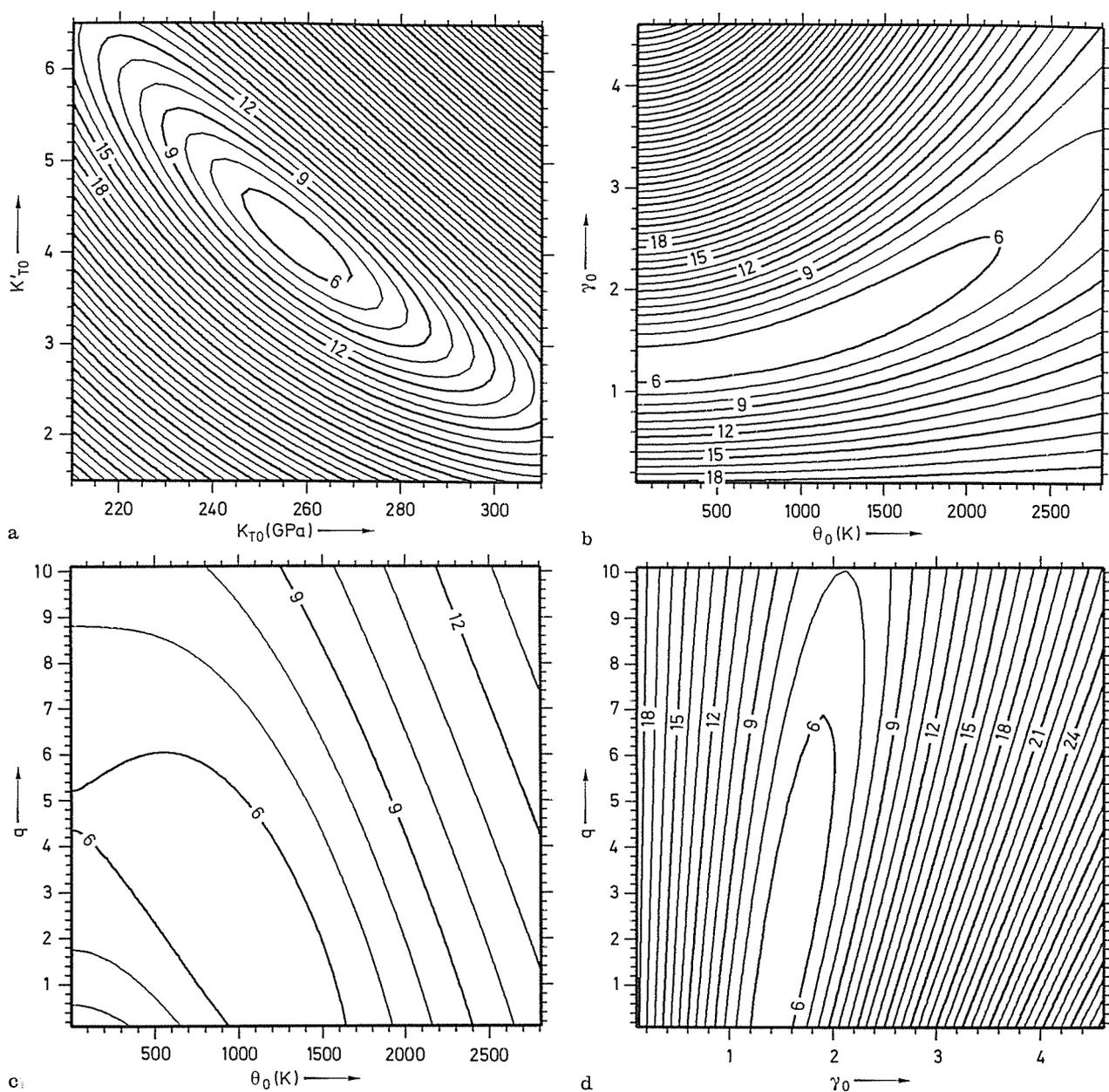


Fig. 4a–d. Contours of RMS misfit showing sections through five-dimensional hyper-ellipsoid about best-fit equation of state (Table 1, line 2). Four panels give complete illustration of parameter trade-offs. (Contour values as in Fig. 2)

in its stable structure and would reveal nothing about the phase in its stability field (and therefore in the lower mantle).

Furthermore, we consider possible effects of Mg–Fe solid solution. Direct measurements indicate that the room-temperature compression (K_{T_0}) is independent of iron content within experimental error [Mao et al. 1991], but the extent to which the thermal expansivity (and thus dK_T/dT) depends upon iron content has not been established. The data set that we have been using includes perovskite with up to 12% of FeSiO_3 component. If we use only those data points representing pure MgSiO_3 perovskite (Funamori and Yagi 1993; Yagi et al. 1993), we find that q is indistinguishable from 1

at the 95% confidence level, and the best fit values for θ_{D_0} and γ_{D_0} are 1510 K and 1.6, respectively (Table 1, line 4). Inclusion of the Wang et al. (1994) data, which are also for pure MgSiO_3 perovskite, yields 1230 K for θ_{D_0} and 1.5 for γ_{D_0} (Table 1, line 5). Thus, the exclusion of data from Fe-bearing samples yields low- γ_{D_0} equations of state.

Although evidence for greater instability of the Fe-bearing perovskite has been reported (Wang et al. 1994), it is important to note that even the MgSiO_3 end-member decomposes after prolonged heating at sufficiently low pressures (Hemley and Cohen 1992; Wang et al. 1991, 1994). Such a back-transformation could result in either a *higher* measured thermal expansivity in

the aggregate from the introduction of defects into the perovskite or a lower thermal expansivity from a compressive stress exerted by the glass on the perovskite (indeed, the latter is suggested by the reduction in zero-pressure volume after temperature cycling (Wang et al. 1991, 1994; Fei, unpublished).

In view of the possible problems with lower pressure data, we explored the consistency of the data at higher pressure by downweighting individual data points according to their distance from the perovskite stability field. We redetermined best-fit equations of state using the original data set (Knittle and Jeanloz 1987; Mao et al. 1991; Funamori and Yagi 1993; Yagi et al. 1993; Fei, unpublished) but weighting each point by the reciprocal of how far the experimental pressure falls below the ilmenite-perovskite phase boundary (Fig. 1) (Ito and Takahashi 1989). This approach results in values of 1190 K for θ_{D_0} , 1.7 for γ_{D_0} , and 2.4 for q (Table 1, line 6), similar to values obtained previously (Stixrude et al. 1992; Hemley et al. 1992). Statistical F -tests between two- and three-parameter fits indicate that q is distinguishable from its null-hypothesis value of 1 at the 95% but not the 99% confidence level, a marginal result. Fixing q at 1 yields 1100 K for θ_{D_0} and 1.5 for γ_{D_0} (Table 1, line 7), compared to 1030 K for θ_{D_0} and 1.5 for γ_{D_0} upon inclusion of the data of Wang et al. (1994) for which q is indistinguishable from 1 at the 95% confidence level (Table 1, line 8). Thus, downweighting of metastable measurements also yields low- γ_{D_0} equations of state, resulting in convergence between equations derived for data sets with and without the data of Wang et al. (1994).

Alternatively, we can simultaneously minimize both the effects of metastability and the necessity for extrapolation by considering only those data points closest to lower mantle conditions, those at the highest pressures (36 GPa) and temperatures (>1500 K) (Funamori and Yagi 1993). Although such a data set is too small to constrain θ_{D_0} (cf. Hemley et al. 1992) and q , values of 1100 K and 1, respectively, yield γ_{D_0} of 1.5, rising to 1.6 for θ_{D_0} of 1600 K (Table 1, line 9). This approach, too, yields low- γ_{D_0} equations of state.

Moreover, the latter analysis yields the density of the perovskite directly at pressures near 36 GPa and over a temperature range relevant to the lower mantle. Comparison to a seismological density profile (Dziewonski et al. 1975) at these pressures (assuming $T_{660} = 2000$ K at the top of a lower mantle adiabat) yields optimal Mg/(Mg+Fe) of 0.89, requiring no Fe-enrichment relative to a pyrolite upper mantle. On the other hand, constraints upon the Si/(Si+Mg+Fe) ratio require comparison to the bulk modulus or seismological bulk sound velocity (Kennett and Engdahl 1991). Such analyses based on the high- γ_{D_0} equations of state predict Si/(Si+Mg+Fe) > 0.8 , indicating Si-enrichment relative to pyrolite (Hemley et al. 1992; Stixrude et al. 1992). Compositions closer to pyrolite, for which Si/(Si+Mg+Fe) = 0.67, become permissible with the lower- γ_{D_0} equations of state described above or with colder mantle adiabats ($T_{660} < 1800$ K) (Bina and Silver 1990; Stixrude et al. 1992).

Conclusions

Metastability of silicate perovskite at low pressures and the effects of Mg-Fe solid solution appear to contribute to the scatter in reported thermal expansivity data well below its stability field. Results from fitting the lowest pressure data suggest the need for more flexible thermal equations of state than those used in conventional treatments, and care should be exercised in extrapolating such equations of state well beyond the measured data regime. One alternative would be to adopt a formulation which allows q to fall from high to low values with increasing compression (cf. Anderson et al. 1993; Stacey 1994), rather than assuming constant q . Another alternative would be to employ a high pressure (instead of zero-pressure) reference state in existing equation-of-state functions.

Increasingly consistent results for the thermoelasticity of (Mg, Fe)SiO₃ perovskites are obtained when higher pressure data are used. The data of Mao et al. (1991) and Funamori and Yagi (1993) together with the highest pressure data of Wang et al. (1994) yield a consistent high-pressure thermal expansivity (despite differences in zero-pressure parameters) at pressures characteristic of the top of the lower mantle (cf. Anderson and Masuda 1994). In particular, the current data sets suggest $\alpha \approx 2.0 \times 10^{-5} \text{ K}^{-1}$ at 20–30 GPa (cf. Jeanloz and Hemley 1994) in the temperature range 700–1000 K (Fig. 3).

While high- γ_{D_0} equations of state derived from perovskite thermoelastic data suggest silica enrichment in order to match to seismological density and velocity profiles at the top of the lower mantle, consideration of metastability and/or Mg-Fe solid solution effects yields low- γ_{D_0} equations of state consistent with a pyrolite lower mantle (cf. Anderson et al. 1995). These results illustrate the importance of making comparisons in regions, such as the upper portion of the lower mantle, where minimal extrapolation is required and where problems with metastability can be avoided by conducting measurements within the stability field of the perovskite. That such techniques have recently become available bodes well for improving compositional constraints on the lower mantle.

Acknowledgements. I thank Rus Hemley for helpful input throughout this project. I am grateful to Y. Fei, R.C. Liebermann, and T. Yagi for generously providing data prior to publication. I thank O. Anderson, D. Isaak, I. Jackson, A. Navrotsky, T. Shankland, F. Stacey, L. Stixrude, Y. Wang, D. Weidner, and an anonymous reviewer for helpful discussions and comments. I acknowledge the support of National Science Foundation grant EAR-9158594.

References

- Anderson OL, Masuda K (1994) A thermodynamic method for computing thermal expansivity, α , versus T along isobars at various pressures for silicate perovskite. *Phys Earth Planet Inter* 85: 227–236
- Anderson OL, Oda H, Chopelas A, Isaak DG (1993) A thermodynamic theory of the Grüneisen ratio at extreme conditions: MgO as an example. *Phys Chem Minerals* 19: 369–380
- Anderson OL, Isaak DG, Oda H (1992) High temperature elastic constant data on minerals relevant to geophysics. *Rev Geophys* 30: 57–90

- Anderson OL, Masuda K, Guo D (1995) Pure silicate perovskite and the PREM lower mantle model: A thermodynamic analysis. *Phys Earth Planet Inter*: in press
- Bell PM, Mao HK, Xu JA (1987) Error analysis of parameter-fitting in equations of state for mantle minerals. In: Manghnani MH, Syono Y (eds) *High-Pressure Research in Mineral Physics*. Terra Scientific, Tokyo, Washington DC, pp 447–454
- Bina CR, Helffrich GR (1992) Calculation of elastic properties from thermodynamic equation of state principles. *Ann Rev Earth Planet Sci* 20:527–554
- Bina CR, Silver PG (1990) Constraints on lower mantle composition and temperature from density and bulk sound velocity profiles. *Geophys Res Lett* 17:1153–1156
- Birch F (1952) Elasticity and constitution of the Earth's interior. *J Geophys Res* 57:227–286
- Dziewonski AM, Hales AL, Lapwood ER (1975) Parametrically simple earth models consistent with geophysical data. *Phys Earth Planet Inter* 10:12–48
- Fei Y, Mao HK, Shu J, Hu J (1992) $P-V-T$ equation of state of magnesiowüstite ($Mg_{0.6}Fe_{0.4}O$). *Phys Chem Minerals* 18:416–422
- Funamori N, Yagi T (1993) High-pressure and high temperature in situ x-ray observation of $MgSiO_3$ perovskite under lower mantle conditions. *Geophys Res Lett* 20:387–390
- Hemley RJ, Cohen RE (1992) Silicate perovskite. *Ann Rev Earth Planet Sci* 20:553–600
- Hemley RJ, Stixrude L, Fei Y, Mao HK (1992) $P-V-T$ measurements of $(Fe, Mg)SiO_3$ -perovskite and $(Fe, Mg)O$: Implications for lower mantle composition. In: Syono Y, Manghnani MH (eds) *High-Pressure Research in Mineral Physics: Application to Earth and Planetary Sciences*. Terra Scientific, Tokyo, Washington DC, pp 183–190
- Ito E, Takahashi E (1989) Post-spinel transformations in the system $Mg_2SiO_4 - Fe_2SiO_4$ and some geophysical implications. *J Geophys Res* 94:10637–10646
- Jackson I (1983) Some geophysical constraints on the composition of the earth's lower mantle. *Earth Planet Sci Lett* 62:91–103
- Jeanloz R, Hemley RJ (1994) Thermoelasticity of perovskite: An emerging consensus. *Eos Trans Am Geophys Union* 75:476–477
- Jeanloz R, Knittle E (1989) Density and composition of the lower mantle. *Phil Trans R Soc Lond A* 328:377–389
- Kennett BLN, Engdahl ER (1991) Traveltimes for global earthquake location and phase identification. *Geophys J Int* 105:429–465
- Knittle E, Jeanloz R (1987) Synthesis and equation of state of $(Mg, Fe)SiO_3$ perovskite to over 100 GPa. *Science* 235:668–670
- Knittle E, Jeanloz R, Smith GL (1986) The thermal expansion of silicate perovskite and stratification of the Earth's mantle. *Nature* 319:214–216
- Lindgren BW, McElrath GW, Berry DA (1978) *Introduction to Probability and Statistics*. Macmillan Publishing, New York
- Mao HK, Hemley RJ, Fei Y, Shu JF, Chen LC, Jephcoat AP, Wu Y, Bassett WA (1991) Effect of pressure, temperature, and composition on lattice parameters and density of $(Fe, Mg)SiO_3$ -perovskites to 30 GPa. *J Geophys Res* 96:8069–8079
- Press WH, Flannery BP, Teukolsky SA, Vetterling WT (1986) *Numerical Recipes*. Cambridge University Press, New York
- Stacey FD (1994) Theory of thermal and elastic properties of the lower mantle and core. *Surv Geophys*: submitted
- Stixrude L, Hemley RJ, Fei Y, Mao HK (1992) Thermoelasticity of silicate perovskite and magnesiowüstite and stratification of the Earth's mantle. *Science* 257:1099–1101
- Ubbelohde AR (1965) *Melting and Crystal Structure*. Clarendon Press, Oxford
- Wang Y, Weidner DJ, Liebermann RC, Liu X, Ko J, Vaughn MT, Zhao Y, Yeganeh-Haeri A, Pacalo REG (1991) Phase transition and thermal expansion of $MgSiO_3$ perovskite. *Science* 251:410–413
- Wang Y, Weidner DJ, Liebermann RC, Zhao Y (1994) $P-V-T$ equation of state of $(Mg, Fe)SiO_3$ perovskite: Constraints on composition of the lower mantle. *Phys Earth Planet Inter* 83:13–40
- Weidner DJ, Wang Y, Yeganeh-Haeri A (1993) Equation of state properties of mantle perovskites. *Eos Trans Am Geophys Union* 74 (suppl): 571
- Yagi T, Funamori N, Utsumi W (1993) Stability and thermal expansion of orthorhombic perovskite-type $MgSiO_3$ under lower mantle conditions. *Eos Trans Am Geophys Union* 74 (suppl): 571
- Zhao Y, Anderson DL (1994) Mineral physics constraints on the chemical composition of the Earth's lower mantle. *Phys Earth Planet Inter* 85:273–292
- Zharkov VN, Kalinin VA (1971) *Equations of State for Solids at High Pressures and Temperatures*. Consultants Bureau, New York