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# Thermal expansivity of mantle relevant magnesium silicates derived from vibrational spectroscopy at high pressure

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## ABSTRACT

Thermal expansivities for the $MgSiO_3$ phases of orthoenstatite, high clinoenstatite, ilmenite, and majorite; and for stishovite were estimated using the thermodynamic Maxwell relation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ where the entropies at high pressures were derived using a statistical method and spectroscopic data. The spectroscopically determined thermal expansivities for all minerals are in excellent agreement with previously determined volumetric data, where available. A value of $3.25(10) \times 10^{-5}$ $K^{-1}$ for orthoenstatite at room temperature was obtained; this value is situated in the middle of the large spread of reported values and is in excellent agreement with the two latest volumetric determinations. For high clinoenstatite, $\alpha$ at room $T$ is estimated as $2.56(9) \times 10^{-5}$ $K^{-1}$. This method provides good high temperature estimates of $\alpha$ for the high-pressure polymorphs, where data are scanty or unavailable. Included in this report are previous data for the $Mg_2SiO_4$ phases and MgO for completeness. The following equations may be used to extrapolate a to higher temperatures at 1 atm in $10^{-5}$ $K^{-1}$: $\alpha$(majorite) = 2.95 + 0.000521$x$; $\alpha(\gamma\text{-}Mg_2SiO_4)$ = 2.70 + 0.000648$x$; $\alpha$(ilmenite) = 2.64+ 0.000537$x$; $\alpha$(perovskite) = 2.51 + 0.000805$x$; and $\alpha$(stishovite) = 2.19 + 0.000485$x$, where $x$ is ($T$/$K$-750).

## INTRODUCTION

The topic "thermal expansivity" brought Orson Anderson and myself together during my early years in Mainz and lead to our collaborative work then and many fruitful exchanges in the ensuing years. It is my pleasure to be able to contribute this comprehensive article covering thermal expansivity of all mantle relevant magnesium silicates to a volume honoring Orson.

Thermal expansivity $\alpha$ of mantle minerals is of fundamental importance to physical and compositional models of the Earth in several ways. First, its knowledge allows for a more precise assessment of in situ mineral densities for comparison to seismic models. Accurate values at ambient conditions are important because these are used as a basis for extrapolation to mantle conditions. Secondly, dynamical models of the Earth are affected dramatically by the value of thermal expansivity especially at the bottom of the mantle. For example, a large decrease in $\alpha$ with depth narrows the calculated diameter of plumes or upwellings, more in line with the observations. Third, $\alpha$ is required to convert lateral velocity anomalies to lateral thermal anomalies. And last, $\alpha$ is required for calculating the adiabatic gradient of the Earth.

The value for $\alpha$ of the Earth relevant magnesium silicates is extremely small and its accurate measurement by volumetric methods tests the resolution limits of most equipment. The most common method for determining thermal expansivity is the X- ray determination of the lattice parameters vs. temperature. Powder diffractometry of the minerals of interest tends to be further complicated by the low symmetry of these materials. Reports of $\alpha$ even for common and abundant surface minerals such as $MgSiO_3$ enstatite may vary by over a factor of two as shown in the present work. Measurement of the even less compressible metastable deeper Earth phases at high temperatures and ambient conditions is even more of a challenge. Only scanty and incomplete data exist for the $MgSiO_3$ phases of majorite, high clinopyroxene, and ilmenite; and for stishovite.

I previously showed (Chopelas 1996) that thermal expansivity may be well constrained by using information obtained from vibrational spectroscopy at high pressure. The advantage of this method is that the measurements are performed at room temperature and the frequencies vs. pressure are very precisely determined. In all cases, several measurements were taken within the stability field of the phase. The pressure dependence of the vibrational frequencies did not change. The variation of frequency with pressure provides a basis for estimating entropy vs. pressure, which directly yields thermal expansivity through the Maxwell relation

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$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad (1)$$

where $S$ is entropy, $V$ is volume, $P$ is pressure, and $T$ is temperature. Thermal expansivity is then

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P . \quad (2)$$

To calculate $\alpha$ from the variation of entropy vs. pressure, the molar volume of the phase must be known at the pressure and temperature of interest. At 1 atm, the calculation of volume at higher temperatures is obtained by using the present expansivity results as temperature is increased. Note that the variation in $\partial S/\partial P$ greatly exceeds the variation in volume, thus the uncertainty in volume does not contribute significantly to the uncertainty in the resulting expansivity. At higher pressures, the bulk moduli and their pressure derivatives for each of the phases are used to calculate volumes at various pressures. Even though there are some variations in these values for the higher pressure polymorphs in the literature, the variations in the calculated volumes using the different elasticity values are much smaller than the uncertainties in $\partial S/\partial P$ obtained from the spectroscopic results. And again the volume uncertainty does not contribute significantly to the expansivity uncertainty. The most important parameter here is an accurate computation of the entropy rather than the volume.

For minerals in which no significant configurational entropy has been observed, as the ones in this study, the relationship of vibrational frequencies to thermal expansivity may be clearly seen by comparing expansivity to heat capacity. For pyrope (Suzuki and Anderson 1983), these two functions vs. temperature are identical in shape (Fig. 1). This is not a general relationship and may not be applied to many simple fourfold-coordinated compounds such as Si, Ge, or diamond, where negative expansivities are found at very low temperatures. The relationship of heat capacity to expansivity as shown in Figure 1 becomes clearer when the physical consequences

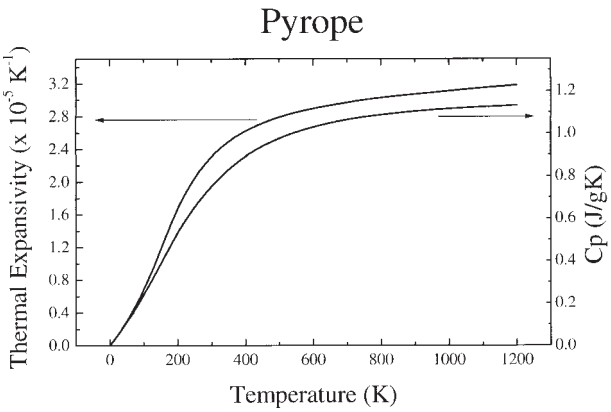


**FIGURE 1.** Comparison of the temperature dependence of the thermal expansivity (upper curve, left axis) to that for the constant pressure heat capacity, $C_P$, (lower curve, right axis). Data are obtained from the article by (Suzuki and Anderson 1983).

of raising the temperature of a mineral are considered. At room temperature, the normal modes or vibrations of a crystal lattice at or below about 300 cm$^{-1}$ are predominantly active in the crystal. This can be seen in the anti-Stokes spectrum where the modes above 300 cm$^{-1}$ have almost no intensity. As the temperature is increased, more of the higher frequency normal modes become activated; as seen by the intensity increase of the higher energy modes with increasing temperature in the anti-Stokes spectrum. This means more energy can be absorbed, meaning an increased heat capacity and its expansion is thus increased per unit temperature because more bonds (modes) become active in the expansion.

In my previous work (Chopelas 1996), thermal expansivity from spectroscopic data for MgO and $\gamma$-$Mg_2SiO_4$ was shown to closely match those measured volumetrically over a large temperature range at 1 atm. Furthermore, for MgO, the Anderson-Grüneisen parameter (Anderson 1967), $\delta_T = (\partial \ln a/\partial \ln V)_T$, derived from the spectroscopic method exactly matched that found from $\delta_T = -(1/aK_T)(\partial K_T/\partial T)_P$, where $K_T$ is the isothermal bulk modulus, at all temperatures (Isaak et al. 1989). The spectroscopic method was then applied to $MgSiO_3$ perovskite where previously reported volumetric measurements varied significantly from one another. The spectroscopic a results were consistent with the previous volumetric (lower) values measured by two laboratories, published in three different reports (Funamori and Yagi 1993; Utsumi et al. 1995; Wang et al. 1994). The spectroscopic method also provided valuable constraints for $\delta_T$ and $\gamma_{th}$, the thermal Grüneisen parameter, for perovskite.

In this report, I extend the application of the spectroscopic method for determining thermal expansivity to the remaining magnesium silicates relevant to the Earth's mantle, including $MgSiO_3$ orthoenstatite, high clinoenstatite, majorite, ilmenite, and $SiO_2$ stishovite. For completeness, I include the previous results for magnesium silicates. The thermal Grüneisen parameter $\gamma_{th} = \alpha K_T V/C_V$, where $C_V$ is the constant volume heat capacity, is also constrained for these minerals. The present $\alpha$ estimates for orthoenstatite provides an independent assessment in order to sort out the extreme variation in previously reported volumetric data. Moreover, determination of $\alpha$ for metastable high clinoenstatite and remaining high pressure magnesium silicates yield values in good agreement with the scant available data and consistent with the other thermoelastic parameters for these materials. The present estimates provide a good basis for extrapolation of $\alpha$ to mantle temperatures for these minerals.

## METHODOLOGY

Using the following equations to obtain entropy at various pressures and temperatures requires that a reasonable density of states be constructed whose spectrum and pressure dependency represents that observed experimentally. This can be obtained by careful enumeration of the modes using symmetry analysis, factor group analysis, and mode assignments based on cation or isotopic substitution, high pressure as well as variable temperature measurements of the vibrational modes. This has been done previously for all the minerals under examination here; their vibrational models are provided in the appendix for completeness.

For all minerals, the procedure for estimating entropy is the same. The constant volume heat capacity $C_V$ is estimated from

$$C_V = 3\,N\,\mathrm{k}\int_0^{\infty}\frac{e^x}{(e^x-1)^2}\;x^2\,g(\nu)\,d\nu \qquad (3)$$

where $N$ is the number of atoms in the unit cell, k Boltzmann's constant, $\nu$ the frequency of vibration, $x$ is $h\nu/kT$, h Planck's constant, and $g(\nu)$ the density of states. Then $C_V$ is converted to the constant pressure heat capacity, $C_P$, using the anharmonic correction of

$$C_P = C_V + T\,V\,\alpha^2\,K_T \qquad (4)$$

which may also be expressed as $C_V(1+\alpha\gamma T)$. The "anharmonic" correction "$\alpha\gamma T$" is very small until about 700 K. By 1000 K, it is about 5% of the total value of the heat capacity, most of which is due to the contribution from $T$. At high temperatures, $\gamma$ and $\alpha$ vary little little with pressure and temperature (Anderson et al. 1992). As mentioned later, $\alpha$ is solved by iteration. The soundness of the vibrational models checked for consistency by (1) the comparison of calorimetric data to those obtained using Equations 3 and 4, as done previously for all materials, and (2) comparison of the spectroscopically derived weighted average Grüneisen parameter $\langle\gamma\rangle = \sum C_i\,\gamma_i/\sum C_i$, where $C_i$ is the Einstein heat capacity and $\gamma_i$ the mode Grüneisen parameter of mode i, to $\gamma_{th}$ obtained as above. As seen in Table 1 for all minerals, all $\langle\gamma\rangle$ values are very near or match $\gamma_{th}$ well within the experimental uncertainties for the required parameters (found in Tables 2 and 3). For the $MgSiO_3$ high pressure phases of high clinoenstatite, majorite, and ilmenite, this study provides an a value at room $T$ so $\gamma_{th}$ may be calculated.

To obtain entropy, the following equation is integrated over temperature

$$\Delta S = \int_0^{T_1}\frac{C_P}{T}\,dT \qquad (5)$$

where $T_1$ is the temperature of interest. The entropy values are calculated at various pressures to find $S(P)$. Since $\alpha$ is used to calculate $C_P$, the results from Equation 2 are substituted back into Equation 4. The process is continued by successive iteration until convergence occurs.

To estimate entropy at higher pressures, the frequencies in the vibrational models (Appendix Tables 1–9) are shifted in accordance with measurements of $\nu(P)$, as represented by the mode Grüneisen parameters $\gamma_i = (K_T/\nu_0)(\partial\nu/\partial P)_T$ assigned to each frequency range. Fundamentally the resulting value of a depends on $\nu(P)$. Entropy as a function of pressure is fitted to a second order polynomial for use in Equations 1 and 2. In absence of high temperature measurements of $\nu(P)$, $S(P)$ at high temperature is obtained by varying $T$ in Equations 3 to 5, which is the quasi-harmonic approach. This method yields excellent results for most minerals. It may be surprising that the small frequency drop due to temperature does not need to be included in these calculations for accurate results, but this results in a small biasing of the entropy results which cancels when the pressure dependence of the entropy is computed. The quasi

**TABLE 3.** Comparison of spectroscopically determined thermal expansivity to those derived from volume measurements in $10^{-5}K^{-1}$

| Mineral | Spectroscopic | Volumetric |
|---|---|---|
| Forsterite | 2.40[a] | 2.72[a] |
| β-$Mg_2SiO_4$ | 1.89[a] | 2.01[a] |
| γ-$Mg_2SiO_4$ | 1.84[a] | 1.86[d] |
| MgO | 2.79[a] | 3.11[e] |
| Stishovite | 1.33(8)[a] | 1.42[a] |
| $MgSiO_3$ Orthoen. | 3.25(10)[a] | 2.2–4.7[f] |
| $MgSiO_3$ High Cen. | 2.59(10)[a] | Not measured |
| $MgSiO_3$ Majorite | 2.24(9)[a] | 2.36[f] |
| $MgSiO_3$ Ilmenite | 1.7(1)[a] | k |
| $MgSiO_3$ Perovskite | 1.8(1)[a] | 1.72[g] |

*Notes* a = Chopelas (1996), b = Kajiyoshi (1986), c = Suzuki et al. (1980), d = Suzuki et al. (1979), e = Isaak et al. (1989), f = this work, g = Fei et al. (1990); Ito et al. (1974a); Ito et al. (1974b), h = see Table 3, j = pyrope data from Suzuki and Anderson (1983), k = only averaged value between 298 and 876 K of $2\times4.1\,10^{-5}$ $K^{-1}$ reported Ashida et al. (1988), l = Funamori and Yagi (1993); Utsumi et al. (1995), m = Wet et al. (1994).

**TABLE 1.** Comparison of the weighted average of the spectroscopic mode Grüneisen parameters from $\langle\gamma\rangle = \sum C_i\gamma_i/\sum C_i$ to the thermal Grüneisen parameter $\gamma_{th} = \alpha\,K_T V/C_V$

| Mineral | $\langle\gamma\rangle$ | $\gamma_{th}$ |
|---|---|---|
| Forsterite | 1.19[a] | 1.29 |
| β-$Mg_2SiO_4$ | 1.29[a] | 1.39 |
| γ-$Mg_2SiO_4$ | 1.10[a] | 1.25 |
| MgO | 1.47[a] | 1.52 |
| Stishovite | 1.40[a] | 1.34 |
| $MgSiO_3$ Orthoenstatite | 1.20[a] | 1.28 |
| $MgSiO_3$ High Clinoen | 1.09[a] | 1.22 |
| $MgSiO_3$ Majorite | 1.32[a] | 1.28 |
| $MgSiO_3$ Ilmenite | 1.24[a] | 1.22 |
| $MgSiO_3$ Perovskite | 1.43[a] | 1.42 |

*Notes* Parameters for all minerals for calculation of $\gamma_{th}$ are found in Tables 2 and 3. a = Chopelas (1990), b = Chopelas (1991), c = Chopelas et al. (1994), d = Chopelas (1996), e = this study using α at room $T$ determined in this study

**TABLE 2.** Thermoelastic parameters for the minerals listed in Table 1

| Mineral | $V_0$ ($cm^3$/mol) | $K_T$ (GPa) | $K_0'$ | $C_V$ (J/mol-K) |
|---|---|---|---|---|
| Forsterite | 43.62[a] | 128[a] | 4.4[p] | 116.4[a] |
| β-$Mg_2SiO_4$ | 40.51[a] | 173[a] | 4.2[p] | 113.2[a] |
| γ-$Mg_2SiO_4$ | 39.53[a] | 183[a] | 5.0 | 112.1[a] |
| MgO | 11.25[a] | 161[a] | 4.1[q] | 36.7[m] |
| Stishovite | 14.02[a] | 303[a] | 2.8[a] | 41.4[a] |
| $MgSiO_3$ Orthoen. | 31.32[a] | 103[a] | 10.8[a] | 80.6[a] |
| $MgSiO_3$ High Cen. | 30.43[a] | 123[a] | 5.6[a] | 79.4[a] |
| $MgSiO_3$ Majorite | 28.58[a] | 160[a] | 4.5[a] | 79.9[a] |
| $MgSiO_3$ Ilmenite | 26.35[a] | 210[aa] | 4[bb] | 77.4[aa] |
| $MgSiO_3$ Perovskite | 24.44[a] | 263[cc] | 4[bb] | 81.9[dd] |

*Notes* a = Isaak et al. (1991), b = Li et al. (1996), c = Robie et al. (1982), d = Horiuchi and Sawamoto (1981), e = Sawamoto et al. (1984), f = Chopelas (1991), g = Akaogi et al. (1989), h = Weidner et al. (1984), i = Rigden and Jackson (1991), j = Chopelas et al. (1994), k = e.g., Isaak et al. (1989), l = Jackson and Niesler (1982), m = Robie et al. (1978), n = Hill et al. (1983), o = Ross et al. (1990), p = Hofmeister (1996), q = Ohashi (1984), r = Flesch et al. (1998); Zhao et al. (1995), s = Krupka et al. (1985a); Krupka et al. (1985b), t = Angel et al. (1992), u = Hugh-Jones and Angel (1994), v = Chopelas (1999), w = Angel et al. (1989), x = Yagi et al. (1992), y = Yusa et al. (1993), z = Ito and Yamada (1982), aa = Weidner and Ito (1985), aa = Ashida et al. (1988), bb = Assumed but fit the compressibility data with these $K_0'$s, cc = Weidner et al. (1993), dd = Akaogi and Ito (1993).

harmonic approach is less successful for the low pressure polymorphs of $Mg_2SiO_4$ (forsterite and β-$Mg_2SiO_4$) and of $MgSiO_3$ (the pyroxenes). For these materials, thermal expansivity is slightly underestimated at high temperatures, very likely due to the widely differing compressibilities of the two polyhedra, $MgO_6$ octahedra and $SiO_4$ tetrahedra, in these materials. This leads to a gap in the vibrational spectrum, where all the high energy modes are associated with the very incompressible $SiO_4$ tetrahedra and have very low mode $\gamma_i$ values. The underestimation of α at high temperatures suggests that as the higher energy vibrations become active, the pressure shifts of these modes will increase and likewise increase the estimated expansivity. Actual measurement of the mode pressure dependencies at the higher temperatures is thus required to accurately estimate α at higher temperatures. In contrast, the high energy modes of the high pressure polymorphs are intercoupled and are thus not separable into independent contributions from various polyhedral units. For the high-pressure polymorphs, thermal expansivities at high temperatures are in exact accord with previous volumetric measurements as seen in the following sections.

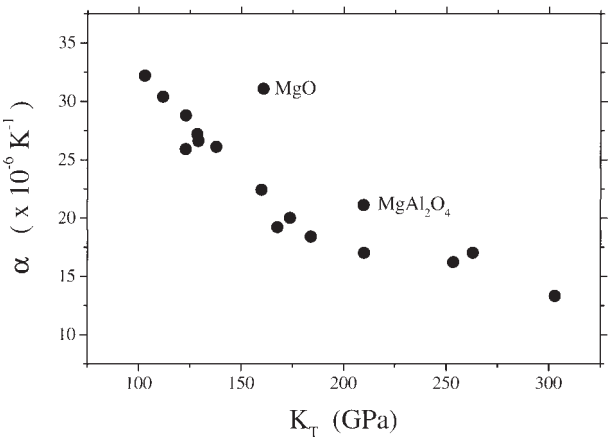


**FIGURE 2.** Plot of the volume thermal expansivity at room temperature vs. the isothermal bulk modulus for several minerals. Aside from those listed in Tables 2 and 3, values are also plotted for $MgAl_2O_4$ (198 GPa, $2.11 \times 10^{-5}$ $K^{-1}$), $Al_2O_3$ (254 GPa, $1.62 \times 10^{-5}$ $K^{-1}$), fayalite (138 GPa, $2.61 \times 10^{-5}$ $K^{-1}$), CaO (112 GPa, $3.04 \times 10^{-5}$ $K^{-1}$), pyrope (169 GPa, $2.36 \times 10^{-5}$ $K^{-1}$). The above data are in the article by Anderson et al. (1992).

**TABLE 4.** Thermal expansivity values for $Mg_2SiO_4$ orthoenstatite reported in the literature in $10^{-5}$ $K^{-1}$

| α | Source | α | Source |
|---|---|---|---|
| 3.6 | Sarver and Hummel (1962) | 2.35 | Yang and Ghose (1994) |
| 2.4 | Skinner (1966) | 3.08 | Zhao et al. (1995) |
| 4.77 | Frisillo and Buljan (1972) | 3.22 | Hugh-Jones (1997) |
| 2.08 | Dietrich and Arndt (1982) | 3.25(10) | This work |

## THERMAL EXPANSIVITY RESULTS

### Consistency checks

In general, the thermal expansivity is inversely proportional to the bulk modulus, which is fairly reasonable considering that $\gamma_{th}$, and $V/C_V$ vary little among the minerals, Tables 1 and 2. A graph of α vs. $K_T$ at room temperature shows this clearly (Fig. 2). All points except MgO and $Mg_2AlO_4$ in the figure follow a fairly narrow trend even though the structures and compositions of these materials vary significantly. So, it is reasonable to expect that very incompressible minerals such as stishovite will have the lowest α values whereas the more compressible minerals such as orthoenstatite with have one of the highest α values at room temperature. This correlation is corroborated by the following results for the minerals.

### Orthoenstatite

The value for α at room temperature reported in the literature over the years has varied by more than a factor of two, despite it being a common and important rock forming mineral (Table 4). Recently, two careful and thorough measurements of α on end-member $MgSiO_3$ Pbca orthoenstatite yielded room temperature values about in the middle of this range at 3.1 to $3.2 \times 10^{-5}$ $K^{-1}$ (Hugh-Jones 1997; Zhao et al. 1995). The present α estimate of $3.25(10) \times 10^{-5}$ $K^{-1}$ is in exact agreement with these recent volumetric measurements (Table 4), which also allows a more confident estimate for $\gamma_{th}$ of 1.28 for this mineral.

Furthermore, the rapid decline in α with pressure with a reported $\delta_T$ of 11.8 (Zhao et al. 1995) is also corroborated by the spectroscopic results. The Raman results for orthoenstatite vs. pressure show a large decrease in the pressure shifts of all frequencies at 5 GPa (Chopelas 1999). Thus, the pressure shift for entropy also decreases significantly, yielding a thermal expansivity of $2.28 \times 10^{-5}$ $K^{-1}$ at 5 GPa, in accord with the previous volumetric results. The present results yield a $\delta_T$ of about 10, approximately equal to the high $K' = (dK/dP)$ of about 10 observed for this mineral (Hugh-Jones and Angel 1994; Webb and Jackson 1993; Zhao et al. 1995), which is consistent with the empirically determined approximation that $\delta_T \approx K'_0$ (Anderson et al. 1992).

**TABLE 5.** Temperature dependence of the thermal expansivity for magnesium silicates in $10^{-5}$ $K^{-1}$

| Temperature (K) | γ-$Mg_2SiO_4$ Spectroscopic | Volumetric[a] | Majorite Spectroscopic | Pyrope Volumetric[b] | Ilmenite Spectroscopic | Volumetric[c] | Stishovite Spectroscopic | Volumetric[d] |
|---|---|---|---|---|---|---|---|---|
| 300 | 1.84 | 1.86 | 2.24 | 2.36 | 1.75 | 2.44 | 1.36 | 1.43 |
| 500 | 2.43 | 2.30 | 2.75 | 2.80 | 2.40 | 2.44 | 1.94 | 1.70 |
| 700 | 2.68 | 2.45 | 2.89 | 2.97 | 2.61 | 2.44 | 2.17 | 1.97 |
| 900 | 2.82 | 2.60 | 3.02 | 3.07 | 2.74 | 2.44 | 2.27 | 2.24 |
| 1000 | 2.87 | 2.60 | 3.09 | 3.11 | 2.77 | | 2.30 | 2.37 |

*Note* Uncertainties are approximately $0.10 \times 10^{-5}$ $K^{-1}$ for all spectroscopic estimates of α shown on Figures 4 to 6. a = Suzuki et al. (1979), b = garnet composition 72.6% pyrope, 15.7% almandine, 4.3% andradite, 6.1% uvarovite, and 0.6% spessartine (Sekiya et al. 1983), c = Ashida et al. (1988), d = Fei et al. (1990); Ito et al. (1974a); Ito et al. (1974b), e = for example, Suzuki (1975), f = Yagi (1993), and Yagi and Akimoto et al. (1993); Utsumi et al. (1995); Wang et al. (1994).

### High clinoenstatite (C2/c)

High clinoenstatite is a metastable phase converting to low clinoenstatite at about 4 GPa upon pressure release even at room temperature (see figure in Chopelas and Boehler 1992a). The volumetric measurement of $\alpha$ at 1 atm is thus not possible. Here the frequencies are linearly extrapolated to 1 atm, reflected in the vibrational model in Appendix Table 2, before applying Equations 1 to 5. A previous estimate of $\alpha$ using a systematic crystal chemical approach and data for other clinopyroxenes is $3.25 \times 10^{-5}$ K$^{-1}$ (Zhao et al. unpublished data), similar to that for orthoenstatite above. Such a high value for $\alpha$ for high clinopyroxene is however unlikely because the pressure shifts of the frequencies are significantly lower than for orthoenstatite and the estimated bulk modulus is suggested to be near that of forsterite (Angel et al. 1992; Zhao et al. unpublished data) and higher than that of orthoenstatite. The leads us to expect that $\alpha$ for this polymorph must be lower than that of orthoenstatite and near that of forsterite. Indeed, the spectroscopic $\alpha$ estimate is $2.56(10) \times 10^{-5}$ K$^{-1}$ for high clinoenstatite at room temperature.

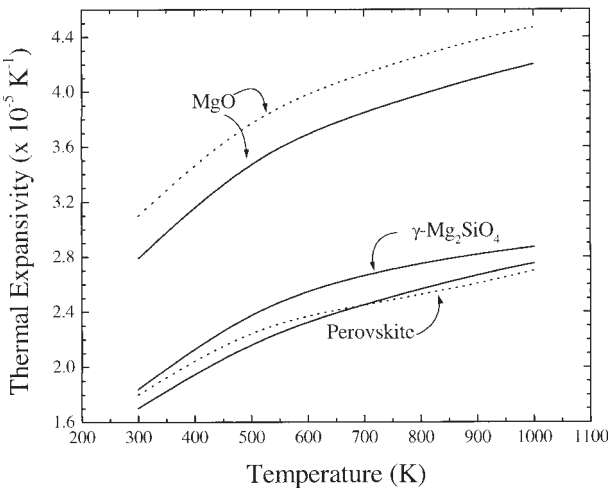


**FIGURE 3.** Plot of the spectroscopically estimated thermal expansivity vs. temperature at 1 atm (solid lines) compared with the volumetrically determined values (dotted lines) for MgO, $MgSiO_3$ perovskite, and $\gamma$-$Mg_2SiO_4$. The volumetrically determined values for $\gamma$-$Mg_2SiO_4$ are not plotted in the figure for clarity but examination of their values in Table 5 show that they are in accord with the present estimates plotted here. These values are from (Chopelas 1996).

**TABLE 5**—*Continued*

| MgO | | Perovskite | |
|---|---|---|---|
| Spectroscopic | Volumetric | Spectroscopic | Volumetric |
| 2.79 | 3.10 | 1.8 | 1.70 |
| 3.54 | 3.84 | 2.3 | 2.20 |
| 3.86 | 4.14 | 2.45 | 2.46 |
| 4.10 | 4.38 | 2.6 | 2.67 |
| 4.20 | 4.47 | 2.7 | 2.75 |

For all the remaining minerals examined in this study, comparisons of the room temperature thermal expansivities estimated by the spectroscopic method to those by volumetric methods, where available, show excellent agreement (Table 3).

### Majorite and Ilmenite

For the $MgSiO_3$ majorite and ilmenite phases, no atmospheric pressure volumetric measurements vs. temperature exist. That shown in Table 3 for majorite is the previously measured value for pyrope (Suzuki and Anderson 1983). For ilmenite, only an average $\alpha$ between 298 and 876 K of $2.44 \times 10^{-5}$ K$^{-1}$ has been reported (Ashida et al. 1988). It is expected that high tempera-

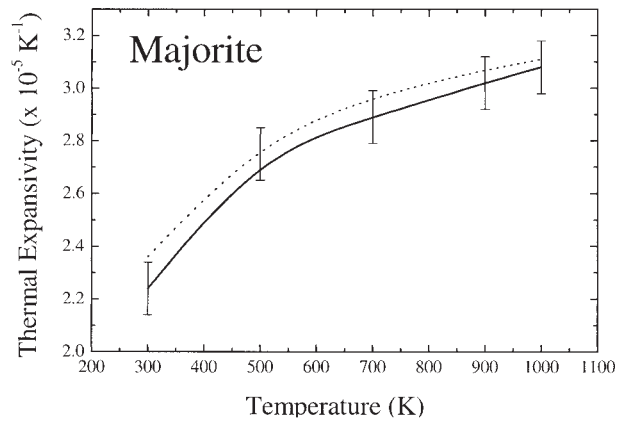


**FIGURE 4.** Comparison of the spectroscopically estimated thermal expansivity of $MgSiO_3$ majorite garnet vs. temperature at 1 atm (solid line) to the volumetrically determined values for pyropic garnet (dotted line) (Suzuki and Anderson 1983). The uncertainties for the spectroscopic values are shown in the figure.

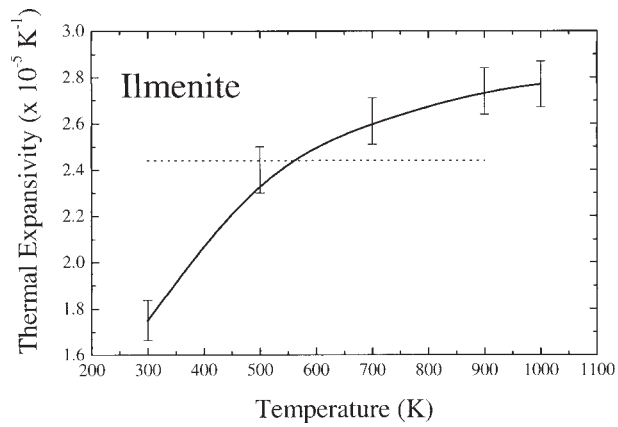


**FIGURE 5.** Comparison of the spectroscopically estimated thermal expansivity of $MgSiO_3$ ilmenite vs. temperature (solid line) to the volumetric determination averaged from 298 to 876 K (dotted line) (Ashida et al. 1988). The uncertainties for the spectroscopic values are shown in the figure.

ture estimates of α using the present method should be as successful as those for γ-$Mg_2SiO_4$, $MgSiO_3$ perovskite, and MgO (Chopelas 1996), shown in Figure 3 and Table 5, since these are also transition zone or lower mantle phases. Indeed, the results for majorite exactly match the previous pyrope results (Fig. 4 and Table 5), which is not surprising since pyrope and majorite have nearly the same bulk moduli, 169 GPa for the former (Suzuki and Anderson 1983) and 160 GPa for the latter (Yagi et al. 1992). For ilmenite, the high temperature results are consistent with the previous average value (Fig. 5 and Table 5). In both cases, the spectroscopic method provides a good basis for extrapolation of thermal expansivity to deep mantle conditions.

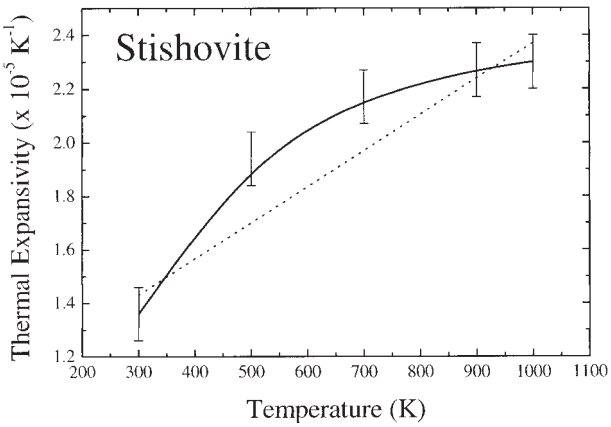


**FIGURE 6.** Comparison of the spectroscopically estimated thermal expansivity of stishovite vs. temperature (solid line) to the volumetric determination (dotted line) (Fei et al. 1990; Ito et al. 1974a; Ito et al. 1974b). The uncertainties for the spectroscopic values are shown in the figure.

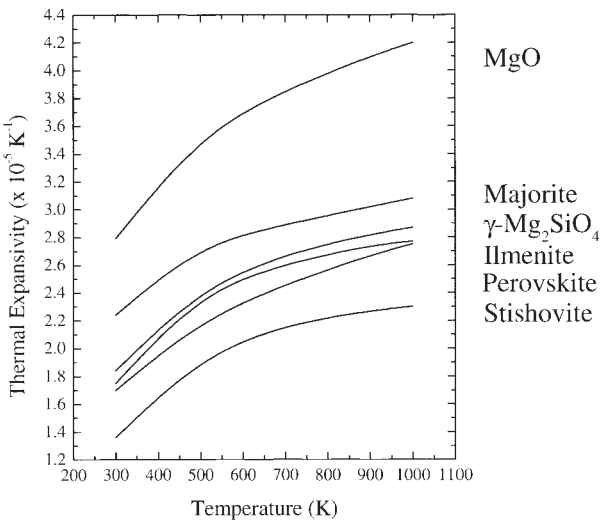


**FIGURE 7.** Comparison of the thermal expansivities vs. temperature from 300 to 1000 K for the minerals reported in this study. As bulk modulus increases, the thermal expansivity decreases.

**TABLE 6.** Parameters for extrapolation of thermal expansivity of the high pressure polymorphs to higher temperatures using $\alpha = \{A + B\cdot(T\text{-}750)\}\times 10^{-5}$ K$^{-1}$, where $T$ is in K

| Mineral | $A$ | $B \times 10^3$ |
|---|---|---|
| γ-$Mg_2SiO_4$ | 2.70 | 0.648 |
| $MgSiO_3$ majorite | 2.85 | 0.521 |
| $MgSiO_3$ ilmenite | 2.64 | 0.537 |
| $MgSiO_3$ perovskite | 2.51 | 0.805 |
| Stishovite | 2.19 | 0.485 |

### Stishovite

The α measured volumetrically for stishovite has been reported as a straight line function of $(1.02 + 0.00135\cdot T/K) \times 10^{-5}$ K$^{-1}$, (Fei et al. 1990; Ito et al. 1974a; Ito et al. 1974b), shown in Figure 6. The present results are in excellent agreement with the former measurements but provides a more physically realistic function for accurate extrapolation to deep mantle temperatures.

Figure 7 summarizes and compares the results for the minerals in this study and shows that the present expansivities for these phases increase in value as the bulk modulus decreases.

## EXTRAPOLATION OF α TO HIGH PRESSURES AND TEMPERATURES

For the above determinations of thermal expansivity for these mantle minerals to be useful for geophysical modeling, a simple relationship for extrapolation to higher temperatures and pressures is highly desirable. To extrapolate the 1 atm expansivities to higher temperatures, the slope of α vs. temperature above about 750 K is determined (Table 6). This simple relationship can then be further modified for pressure using (Chopelas and Boehler 1992b):

$$\alpha = \alpha_0 \left(\frac{V}{V_0}\right)^{\delta_T \cdot \frac{V}{V_0}}. \quad (6)$$

Because all of these materials have similar $K'$ values (Table 2), it is expected that all these materials will have similar values of $\delta_T$ (Anderson et al. 1992). For perovskite, a value of 5 for $\delta_T$ closely matched the high pressure behavior of α from 1 atm to 80 GPa at room temperature (Chopelas 1996). Other estimates for this parameter for perovskite also yield about 5 at room temperature and about 4 above the Debye temperature, for perovskite, about 1000 K (Anderson 1998). Thus, for parameterization in Earth models, a reasonable starting value for $\delta_T$ is 5 at room temperature and gradually reducing to 4 as the temperature rises to above 1000 K for all the materials listed in Table 6.

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## APPENDIX

Vibrational models for magnesium silicates in this study. The first three modes in each of the models represents the acoustic modes. The remainder are optic mode continua. Einstein oscillators are assigned very narrow frequency ranges to facilitate the calculations at high pressures. The mode Grüneisen parameters, $\gamma_i$, are used to obtain the pressure shifts of the frequency ranges using the bulk moduli listed in Table 2. Tables A1 through A5 are from Chopelas (1999).

**APPENDIX TABLE 1**. Pbca Orthoenstatite

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 65 | 1 | 0.2 |
| 0 | 67 | 1 | 0.3 |
| 0 | 110 | 1 | 1.23 |
| 83 | 90 | 3 | 2.32 |
| 110 | 120 | 3 | 3.26 |
| 120 | 140 | 5 | 3.3 |
| 140 | 168 | 10 | 1.46 |
| 168 | 223 | 12 | 1.75 |
| 223 | 245 | 12 | 1.23 |
| 245 | 323 | 28 | 1.25 |
| 323 | 350 | 12 | 1.93 |
| 350 | 362 | 12 | 1.1 |
| 380 | 390 | 8 | 1.1 |
| 398 | 447 | 32 | 0.7 |
| 516 | 553 | 20 | 0.7 |
| 580 | 630 | 16 | 0.6 |
| 656 | 752 | 16 | 0.63 |
| 853 | 903 | 12 | 0.36 |
| 886 | 937 | 16 | 0.55 |
| 1014 | 1035 | 20 | 0.62 |

**APPENDIX TABLE 2.** C2/c Clinoenstatite

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 95 | 1 | 0.80 |
| 0 | 104 | 1 | 0.80 |
| 0 | 172 | 1 | 2.4 |
| 120 | 155 | 2 | 1.10 |
| 165 | 484 | 6 | 1.7 |
| 216 | 280 | 2 | 0.90 |
| 229 | 416 | 11 | 1.4 |
| 380 | 577 | 20 | 0.64 |
| 680 | 682 | 2 | 0.57 |
| 714 | 716 | 2 | 0.46 |
| 829 | 831 | 5 | 0.43 |
| 1005 | 1007 | 4 | 0.54 |
| 1023 | 1026 | 3 | 0.62 |

**APPENDIX TABLE 3.** $I4_1/a$ Majorite

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 70 | 1 | 0.75 |
| 0 | 70 | 1 | 0.75 |
| 0 | 140 | 1 | 1.3 |
| 136 | 400 | 60 | 1.42 |
| 350 | 400 | 36 | 1.305 |
| 195 | 400 | 33 | 1.305 |
| 458 | 723 | 60 | 0.86 |
| 803 | 1081 | 48 | 0.86 |

**APPENDIX TABLE 4.** $R\bar{3}$ Ilmenite

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 168.7 | 1 | 0.75 |
| 0 | 184.5 | 1 | 0.75 |
| 0 | 301.3 | 1 | 1.3 |
| 287 | 337 | 2 | 1.6 |
| 337 | 595 | 13 | 1.35 |
| 595 | 700 | 10 | 1.1 |
| 735 | 799 | 2 | 1.1 |

**APPENDIX TABLE 5.** Pbmn Perovskite

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 130 | 1 | 0.85 |
| 0 | 150 | 1 | 0.85 |
| 0 | 223 | 1 | 2.5 |
| 240 | 335 | 12 | 1.8 |
| 335 | 440 | 12 | 1.1 |
| 440 | 540 | 15 | 0.95 |
| 590 | 680 | 9 | 0.75 |
| 700 | 780 | 7 | 0.75 |
| 890 | 891 | 2 | 0.75 |

**APPENDIX TABLE 6.** Pbnm Forsterite

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 98 | 1 | 1.1 |
| 0 | 99 | 1 | 1.1 |
| 0 | 171 | 1 | 1.6 |
| 105 | 145 | 2 | 1.2 |
| 170 | 227 | 7 | 0.92 |
| 240 | 385 | 12 | 1.45 |
| 280 | 410 | 12 | 1.35 |
| 305 | 470 | 12 | 1.4 |
| 405 | 505 | 8 | 0.6 |
| 505 | 644 | 12 | 0.63 |
| 838 | 839 | 4 | 0.49 |
| 868 | 869 | 3 | 0.46 |
| 916 | 917 | 4 | 0.38 |
| 975 | 976 | 5 | 0.66 |

From Chopelas (1990).

**APPENDIX TABLE 7.** Imma β-$Mg_2SiO_4$

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 118 | 1 | 0.95 |
| 0 | 118 | 1 | 0.95 |
| 0 | 198 | 1 | 1.45 |
| 86 | 140 | 1 | 1.65 |
| 140 | 185 | 2 | 1.6 |
| 185 | 232 | 3 | 1.5 |
| 232 | 340 | 8 | 1.35 |
| 250 | 330 | 6 | 0.9 |
| 360 | 505 | 12 | 0.85 |
| 340 | 485 | 4 | 1.65 |
| 350 | 520 | 12 | 1.4 |
| 430 | 580 | 4 | 1.1 |
| 505 | 645 | 11 | 0.82 |
| 530 | 580 | 2 | 1.35 |
| 710 | 711 | 2 | 0.83 |
| 795 | 796 | 2 | 1.1 |
| 810 | 930 | 8 | 0.82 |
| 965 | 966 | 2 | 0.85 |
| 1020 | 1021 | 2 | 0.85 |

From Chopelas (1991).

*Appendix continued on next page*

**APPENDIX TABLE 8.** Fd3m$\gamma$-$Mg_2SiO_4$

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 138 | 1 | 0.5 |
| 0 | 155 | 1 | 0.5 |
| 0 | 253 | 1 | 1.08 |
| 280 | 325 | 3 | 1.5 |
| 320 | 580 | 12 | 1.2 |
| 360 | 390 | 6 | 1.3 |
| 372 | 480 | 4 | 0.99 |
| 545 | 620 | 6 | 0.66 |
| 785 | 796 | 6 | 1.26 |
| 834 | 835 | 2 | 0.93 |

*Note:* From Chopelas et al. (1994).

**APPENDIX TABLE 9.** $P4_2$ Stishovite

| Lower limit | Upper limit | Number of modes | $\gamma_i$ |
|---|---|---|---|
| 0 | 186 | 1 | 1.3 |
| 0 | 227 | 1 | 1.3 |
| 0 | 405 | 1 | 1.7 |
| 190 | 470 | 2 | 0.7 |
| 470 | 585 | 3 | 1.6 |
| 580 | 700 | 3 | 2.3 |
| 836 | 1020 | 2 | 1.03 |
| 725 | 950 | 1 | 0.7 |
| 588 | 590 | 2 | 1.32 |
| 753 | 755 | 1 | 1.26 |
| 965 | 967 | 1 | 1.21 |

*Note:* Slightly modified version of that presented in Hofmeister and Ito (1992).