

Thermoelastic properties of $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ ferropericlasel based on in situ X-ray diffraction to 26.7 GPa and 2173 K

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Abstract

We present 53 in situ measurements of the unit-cell volume (V) of polycrystalline $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ ferropericlasel (FP) at simultaneous high pressures (P) and temperatures (T) up to $P = 26.7$ GPa and $T = 2173$ K, including pressure–temperature conditions at the top of Earth's lower mantle. FP volumes were determined through in situ energy-dispersive synchrotron X-ray diffraction in a multi-anvil press, using gold and MgO as pressure markers. Our data, combined with 112 previously published P – V – T measurements for the same FP sample, were fitted to high-temperature Birch–Murnaghan and Mie–Grüneisen equations of state (EOS). Experimental data are reproduced accurately, with a standard deviation lower than 0.31 GPa for both EOS. EOS calculations show that the thermal expansion and P – T derivatives of the bulk modulus of this iron-rich FP are virtually identical to those of pure MgO to pressures >55 GPa and temperatures of 3000 K. This result is confirmed by measurements of the

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normalised unit-cell volumes for FP and MgO at identical simultaneous high P – T conditions, which are identical to within 0.6 per cent relative to 26.7 GPa and 2173 K. The pressure and temperature derivatives of the bulk modulus, and thermal expansion are concluded to be independent of iron content across the range of plausible FP compositions in Earth's lower mantle.

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1. Introduction

The Earth's lower mantle is thought to consist predominantly of a mixture of Mg–Fe silicate perovskite ($\text{Mg}_x\text{Fe}_{1-x}\text{SiO}_3$), ferropericlase ($\text{Mg}_y\text{Fe}_{1-y}\text{O}$), and Ca-rich silicate perovskite (CaSiO_3) (e.g., Irifune, 1994; Wood, 2000). Making accurate measurements of the thermodynamic properties of these phases at the high temperatures (T) and pressures (P) prevalent in the lower mantle is experimentally challenging at present. Instead, equations of state (EOS) are used to extrapolate thermodynamic properties measured at lower pressures and temperatures to lower mantle conditions. EOS link pressure and temperature to a mineral's unit-cell volume, allowing computation of density profiles in the lower mantle. Comparing these with density profiles inferred from seismology provides constraints on temperature and/or lower mantle composition (e.g., Stixrude et al., 1992; Wang et al., 1994; Jackson, 1998; da Silva et al., 2000; Marton and Cohen, 2002; Deschamps and Trampert, 2004). Here, we present new data constraining the thermal equation of state for a iron-rich ferropericlase (FP) with composition $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$.

Several studies have been published on the temperature and pressure effects on the unit-cell volume of periclase, the pure MgO end-member of the solid solution, see Jacobs and Oonk (2000) for a recent summary. Because FP in the Earth's mantle contains appreciable amounts of iron (~ 10 to ~ 20 mol%, e.g., Irifune, 1994; Katsura and Ito, 1996; Mao et al., 1997; Wood, 2000; Andrault, 2001), the effect of iron content on the elastic and thermal properties of FP needs to be quantified (e.g., Fei, 1999; Hama and Suito, 1999; Reichmann et al., 2000; Jacobsen et al., 2002; Kung et al., 2002).

To our knowledge, only two studies have measured unit-cell volumes of iron-bearing FP at simultaneous high static P and T (Fei et al., 1992; Zhang and Kostak, 2002), both for a relatively Fe-rich composition $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ that was originally synthesized by Rosenhauer et al. (1976). Using an externally

heated diamond-anvil cell, Fei et al. (1992) provided FP unit-cell volume data for this composition at pressures up to 30 GPa, with a maximum temperature of approximately 800 K. Zhang and Kostak (2002), using a multi-anvil press, measured unit-cell volumes at temperatures up to 1273 K, with a maximum pressure of 10.1 GPa. Fig. 1 shows both studies require substantial extrapolation to pressures and plausible temperatures even at the top of the lower mantle, as indicated by an approximate adiabatic mantle geotherm (Agee, 1998). In this study, unit-cell volumes of $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ ferropericlase are measured at simultaneous high P – T conditions to 26.7 GPa and 2173 K in a multi-anvil press, including for the first time likely temperatures at the top of the lower mantle. The parameters of the thermal equation of state are constrained by fitting a combination of our

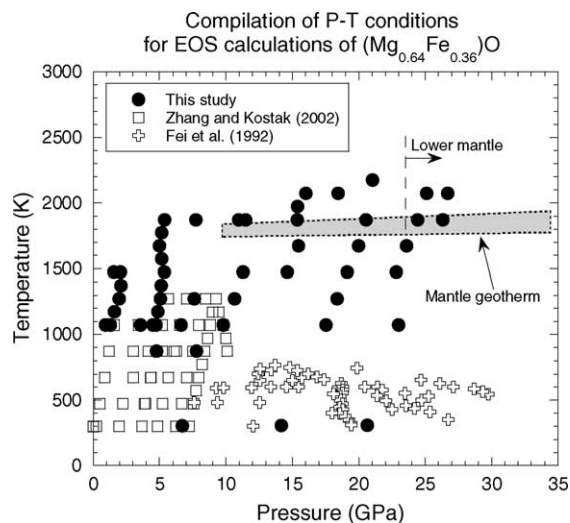


Fig. 1. Pressure–temperature conditions of in situ unit-cell volume measurements of $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ ferropericlase. Filled circles: this study; pluses: Fei et al. (1992); squares: Zhang and Kostak (2002). The grey field outlines an approximate adiabatic mantle geotherm (Agee, 1998), and the top of the lower mantle is indicated by the dashed vertical line.

data and the two prior studies of Fei et al. (1992) and Zhang and Kostak (2002), to provide improved constraints on possible variations in the elastic and thermal properties of FP as a function of iron content in FP.

2. Methods

2.1. Experimental methods

Experiments were performed using the 1500 ton Kawai-type multi-anvil apparatus on beamline BL04B1 at the SPring-8 synchrotron radiation facility (Hyogo prefecture, Japan). The high-pressure assembly, shown in Fig. 2a, is based on a Cr-doped MgO octahedron of 8 mm edge length (manufactured by Japan Ceramic Engineering Company, Inc). A rhenium foil heater of thickness 0.025 mm was wrapped within a LaCrO_3 insulating sleeve, inserted into the center of the octahedron. A 1 mm diameter cylindrical beam path was drilled through the octahedron, and filled with MgO rods to prevent absorption of synchrotron radiation by the octahedron material and LaCrO_3 sleeve. Pyrophyllite gaskets were used to separate the

eight second-stage Toshiba F-grade tungsten carbide (WC) cubes with 3 mm truncated-edge lengths.

Temperatures were measured using a W5%Re–W26%Re (type C) thermocouple. Thermocouple wires (0.13 mm diameter) were inserted axially through four-bore alumina rods. No account was taken of the effect of pressure on thermocouple electromotive force (emf). Temperatures were controlled to within 0.2 K. A disk of MgO mixed with finely dispersed gold powder (used as pressure markers) was packed in an MgO capsule around the thermocouple junctions. Au and MgO were used as pressure markers for several reasons: First, at a given pressure both Au and MgO have a significantly higher melting point than NaCl (used as a pressure marker in the study of Zhang and Kostak, 2002), considerably increasing the maximum attainable temperature. Second, the Au lattice parameter is more sensitive to pressure changes than other potential pressure standard metals with high melting temperatures such as Pt, resulting in more precise pressure estimates. Third, Fei et al. (2004) recently presented a gold EOS, based on the work of Shim et al. (2002), that was shown to be consistent with the recently published MgO EOS of Speziale et al. (2001). By combining these Au and MgO

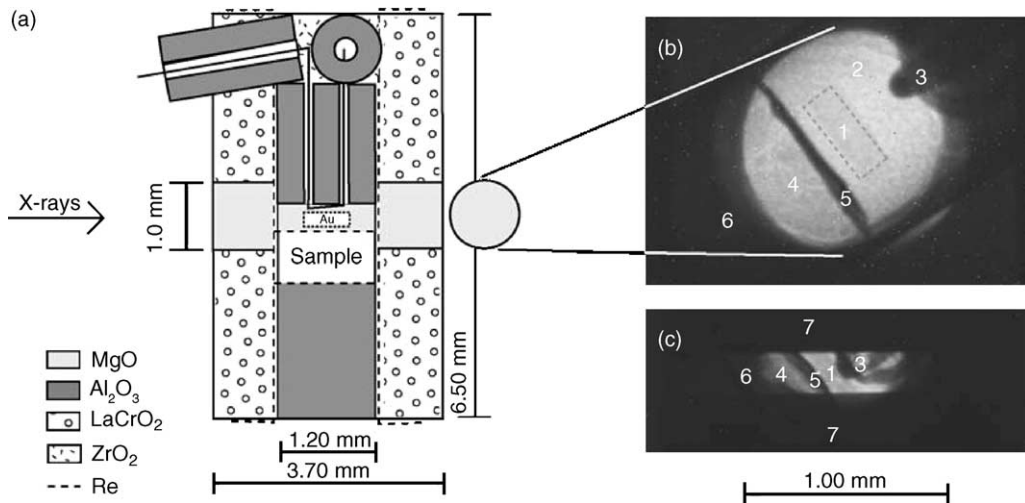


Fig. 2. (a) High-pressure assembly used in this study (see Section 2.1 in the main text for details). (b and c) Typical radiograph images, taken through the beam path indicated in (a), showing the assembly at ambient conditions (b) and during compression (c). 1: Au + MgO pressure marker; 2: MgO capsule; 3: thermocouple junction; 4: ferropericlase sample; 5: upper rhenium disk; 6: rhenium foil furnace; 7: tungsten carbide anvils. The gap between the opposing anvils (7) decreases as pressure is increased, but both pressure markers (1) and sample (4) remain accessible to X-rays. Images in (b) and (c) are tilted with respect to the sketch in (a), because of the geometry of the assembly in the SPring-8 multi-anvil press.

EOS it should therefore be possible to obtain consistent results for the FP EOS. Finally, a direct comparison of measured unit-cell volumes of pure MgO and FP at identical pressure–temperature conditions can shed more light on the question of whether or not the thermo-elastic properties (P – T dependence of the bulk modulus and thermal expansion) of FP vary significantly with iron content.

Finely ground polycrystalline FP was packed in direct contact with the Re heater and separated from pressure markers and alumina end cap by two 0.064 mm thick Re disks. Fig. 2 shows images of a typical experiment at room pressure (Fig. 2a and b) and high pressure (Fig. 2c). The thermocouple junction, pressure marker, Re disk and sample are radiographically imaged through the gap between the WC anvils, and through the MgO-filled holes drilled into the sides of the octahedron. At all times, FP samples were located within approximately 400 μm of the thermocouple junction, i.e., within the measured hot spot for this assembly (1 mm in length along the Re furnace axis, see van Westrenen et al., 2003).

Experiments were pressurized at room temperature, before heating to the maximum desired temperature. X-ray diffraction patterns were mostly obtained during cooling from the highest temperature to minimize non-hydrostatic effects. Typically, a total of 10–15 min were spent at each temperature to collect X-ray diffraction patterns. After quenching to room temperature, the pressure was increased again before the next series of measurements. Diffraction patterns from the sample and pressure markers were taken along several isotherms between 300 and 2173 K, at up to eight different pressures for each temperature (Fig. 1).

2.2. Analytical methods

Lattice parameters for Au, MgO and FP were obtained in situ during three separate experimental sessions covering the period April 2002–June 2003 using energy-dispersive synchrotron X-ray diffraction methods similar to those described by Irifune et al. (1998). Incoming white X-rays were collimated to a size of 50 μm $\times$ 200 μm , and positioned over either the pressure marker or sample region using a radiograph image on a CCD camera lowered into the beam path (Fig. 2b and c). The diffracted beam was then detected with a Ge solid state detector placed in the horizontal plane.

For all three sessions, energy calibrations for the detector were based on the detector channel positions of approximately 20 $\text{K}\alpha$ and $\text{K}\beta$ peaks of known energies in the range 8–85 keV, and four high-energy γ radiation peaks between 81 and 122 keV from radioactive sources. Residuals of linear fits to the data show no systematic variation with channel number, and quadratic fits did not improve calibrations significantly. The detector 2θ angle was calibrated before each experiment by fitting both Au (3 peaks) and MgO (2–3 peaks) diffraction patterns at ambient pressure and temperature conditions, and was found to be constant within error for each of the three sessions. At every P – T point, Au or MgO, and FP diffraction patterns were obtained, and the XRayAna program available at the beamline was used to calculate lattice parameters. Au and MgO lattice parameters were converted to pressures using the Fei et al. (2004) and Speziale et al. (2001) thermal equations of state for Au and MgO, respectively.

Major element compositions of the starting material and selected run products were determined on polished assembly cross-sections with a JEOL 8900 electron microprobe at the Geophysical Laboratory, using a focused beam with an accelerating voltage of 15 kV and a beam current of 15 nA. Counting times were 30 s on both peak and background. Zabargad olivine (for Mg, Fe, Si) and almandine (for Al) were used as calibration standards.

3. Results

3.1. Ferropericlase composition

Meaningful interpretation of our measurements requires sample composition to remain constant during the experiments. A first concern was the presence of Al_2O_3 assembly parts in proximity to the FP samples, as significant amounts of Al are known to dissolve in FP at high temperatures (e.g., van Westrenen et al., 2003). Notwithstanding the very high maximum temperatures, the aluminium content of samples confined by rhenium disks and heater is universally low (Table 1). Maximum Al concentrations (up to 0.20 wt.% Al_2O_3 in experiment S813) were found near the edges of the bottom rhenium disk, far removed from the central sample area where in situ measurements were made.

Table 1
Ferropellicle compositions (oxide wt.%) determined by electron microprobe^{a,b}

Run	$T_{\max}$ (K)	Capsule	Al ₂ O ₃	Al ₂ O ₃ (max)	FeO	MgO	Total	Average stoichiometry
Starting material	—	—	b.d.	b.d.	50.0(3)	49.9(2)	99.9(3)	Mg _{0.64} Fe _{0.36} O
S806	1873	Re disks	0.03(1)	0.06	50.2(8)	49.6(8)	100.0(4)	Mg _{0.64} Fe _{0.36} O
S813	2073	Re disks	0.11(8)	0.20	49.6(8)	50.1(8)	100.0(5)	Mg _{0.64} Fe _{0.36} O

^a b.d.: below detection limit.

^b Numbers in brackets are 1 σ errors in last digit.

A second concern was possible sample oxidation at elevated temperature, leading to increased Fe³⁺ and vacancy concentrations. All iron-bearing FP samples contain some Fe³⁺, either interstitially or in regular Fe lattice sites, charge-balanced mainly by cation vacancies (e.g., Reichmann et al., 2000; Jacobsen et al., 2002; O'Neill et al., 2003). Rosenhauer et al. (1976) report approximately 3.6 atomic per cent of our starting material's Fe is trivalent. This is consistent with models for the fraction of trivalent iron in FP in the presence of metallic Fe as a function of FP composition (e.g., Hilbrandt and Martin, 1998; O'Neill et al., 2003; Jung et al., 2004).

The oxygen fugacity (f_{O_2}) during our experiments was not buffered, but our in situ measurements provide lower and, more importantly, upper bounds. The intrinsic oxygen fugacity (f_{O_2}) of the starting material was close to that of the Fe–(Fe,Mg)O buffer. No Fe peaks were identified in any in situ diffraction patterns, and no metallic iron was found in any run products. Fe loss to the Re heater can also be excluded, as electron microprobe analyses (Table 1) show that the Fe/Mg ratio of the samples after experimentation is within error of the starting material ratio. The f_{O_2} therefore never fell below the Fe–(Fe,Mg)O buffer. This is consistent with the fact that the assembly parts surrounding the sample (Fig. 2a), in particular the Re furnace, favour more oxidising conditions. The particular assembly used would tend to increase f_{O_2} towards that of the Re–ReO₂ buffer, positioned 5–7 log units above the Fe–(Fe,Mg)O buffer (Pownceby and O'Neill, 1994). If the f_{O_2} of our FP samples reached this buffer at any stage, thermodynamic models of the Mg–Fe–O system (e.g., Jung et al., 2004) show that over 80% of all iron in FP should have become trivalent at the highest experimental temperatures.

The absence of magnetite from both X-ray diffraction patterns during, and run products after the

experiments, however, proves that such high oxygen fugacities were never reached. Magnetite should have formed at most temperatures reached in this study if the oxygen fugacity had been buffered by the Re–ReO₂ equilibrium. From these observations we estimate that the f_{O_2} of our FP samples likely exceeded the f_{O_2} of the Fe–(Fe,Mg)O buffer by a maximum of 3 log units. At the temperatures reached in this study, this increased f_{O_2} would lead to an increase in the percentage of total iron that is trivalent from 3.6 at.% to a maximum of 14 at.%, translating into a FP Fe³⁺ content change from 1.3 at.% to a maximum of 5 at.% for our particular FP composition. Jacobsen et al. (2002) recently showed that changes in FP Fe³⁺ content of this order have no measurable effect on elastic properties, so we consider this change in composition insignificant.

3.2. Lattice parameters

The number of resolvable peaks for sample and pressure markers varies due to overlaps with rhenium (from the upper rhenium disk bounding the sample) and preferred orientation of Au at high temperatures, both of which change as a function of P and T (and time in the case of preferred orientation). One to four 'clean' Au or MgO pressure marker peaks could be used for each pressure determination, and one to six peaks for the calculation of (Mg_{0.64}Fe_{0.36})O unit-cell volumes (V). Peak positions were determined using Gaussian peak fitting, and for all instances where the number of clean peaks exceeded one, lattice parameters were determined by least-squares fitting based on a cubic unit cell for sample and pressure markers.

Table 2 lists calculated lattice parameters and associated errors for all three phases, and pressure determinations obtained from these lattice parameters

Table 2

Pressure, temperature, and unit-cell volume measurements for (Mg_{0.64}Fe_{0.36})O ferropericlas (FP)

Run	T (K)	<i>a</i> (Å) ^a	<i>a</i> (MgO) ^a	<i>P</i> (GPa) ^b	<i>V</i> (FP) ^c	Δ <i>P</i> (BM) ^d	Δ <i>P</i> (MG) ^d
S806-13	303.5	4.029(1)		6.72(6)	74.344(12)	−0.14	−0.05
S806-34	306	3.983(1)		14.17(1)	71.534(10)	−0.21	−0.22
S813-18	308	3.949(1)		20.65(2)	69.552(40)	0.09	0.01
S955-08	873		4.2004	4.77	76.580(33)	−0.67	−0.59
S954-06	873		4.1756	7.77	75.540(19)	0.02	0.09
S1018-24	1073		4.2490(5)	0.92(3)	79.518(49)	−0.02	0.03
S1018-07	1073		4.2452(5)	1.29(3)	79.144(13)	−0.33	−0.28
S1018-25	1073		4.2229(4)	3.58(2)	77.851(81)	−0.54	−0.50
S1018-28	1073		4.2143(4)	4.50(2)	77.371(63)	−0.59	−0.56
S955-09	1073		4.2122	4.73	77.309(43)	−0.48	−0.45
S806-05	1073	4.070(6)		6.62(43)	76.579(9)	−0.14	−0.12
S806-12	1073	4.047(1)		9.80(9)	75.320(12)	0.20	0.22
S806-33	1073	3.997(1)		17.52(7)	72.422(20)	0.51	0.49
S813-17	1073	3.966(1)		22.99(7)	70.409(4)	−0.04	−0.09
S1018-10	1173		4.2489(2)	1.61(1)	79.432(22)	−0.13	−0.12
S1018-31	1173		4.2171(3)	4.86(2)	77.693(60)	−0.23	−0.22
S1018-14	1273		4.2526(7)	1.94(4)	79.781(36)	0.18	0.16
S1018-34	1273		4.2213(4)	5.07(2)	78.023(62)	−0.02	−0.04
S806-04	1273	4.074(6)		7.62(42)	76.853(8)	0.12	0.09
S806-09	1273	4.051(1)		10.65(8)	75.642(7)	0.45	0.42
S806-30	1273	4.000(2)		18.37(16)	72.638(13)	0.56	0.52
S1018-15	1373		4.2584(2)	2.09(1)	80.151(50)	0.33	0.29
S1018-36	1373		4.2271(7)	5.13(4)	78.159(38)	−0.35	−0.39
S1018-21	1473		4.2724(8)	1.57(4)	80.62(11)	−0.02	−0.10
S1018-20	1473		4.2668(6)	2.04(3)	80.57(18)	0.37	0.29
S1018-39	1473		4.2316(30)	5.34(18)	78.586(29)	0.03	−0.04
S806-08	1473	4.057(1)		11.29(4)	75.984(9)	0.52	0.45
S806-19	1473	4.034(1)		14.62(6)	74.690(25)	0.79	0.72
S806-29	1473	4.005(1)		19.13(13)	72.829(24)	0.45	0.39
S813-10	1473	3.983(1)		22.83(2)	71.409(52)	0.06	−0.01
S1018-40	1573		4.2404(10)	5.15(6)	78.933(21)	−0.15	−0.25
S1018-41	1573		4.2404(10)	5.15(6)	79.433(90)	0.79	0.69
S1018-43	1673		4.2492(9)	5.00(5)	79.380(46)	−0.13	−0.25
S806-23	1673	4.038(1)		15.46(7)	74.632(5)	0.10	0.02
S806-26	1673	4.008(1)		19.98(5)	73.106(36)	0.65	0.57
S813-09	1673	3.987(3)		23.60(35)	71.520	−0.27	−0.34
S1018-44	1773		4.2549(7)	5.17(4)	79.770(71)	0.10	−0.05
S1018-47	1873		4.2604(18)	5.38(9)	80.25(18)	0.51	0.34
S1018-49	1873		4.2347(16)	7.74(9)	78.88(20)	0.32	0.17
S1018-51	1873		4.2039(40)	10.98(25)	77.397(37)	0.57	0.44
S1018-54	1873		4.1995(14)	11.47(9)	76.706(45)	−0.42	−0.55
S1018-55	1873		4.1995(14)	11.47(9)	76.619(54)	−0.62	−0.74
S1018-57	1873		4.1674(29)	15.36(21)	75.309(10)	0.26	0.15
S1018-58	1873		4.1674(29)	15.36(21)	74.986(87)	−0.52	−0.63
S806-25	1873	4.014(1)		20.55(9)	73.282(61)	0.29	0.19
S813-06	1873	3.991(3)		24.43(29)	71.807	−0.02	−0.10
S813-14	1873	3.980(1)		26.33(4)	71.300	0.36	0.28
S1018-60	1973		4.1725(3)	15.38(2)	75.498(57)	0.04	−0.08
S1018-62	2073		4.1728(2)	16.01(1)	75.380(50)	−0.71	−0.44
S1018-64	2073		4.1540(6)	18.45(5)	74.234(29)	−0.31	−0.82
S813-05	2073	3.995(1)		25.11(1)	71.999	−0.20	−0.29

Table 2 (Continued)

Run	T (K)	a (Au) ^a	a (MgO) ^a	P (GPa) ^b	V (FP) ^c	ΔP (BM) ^d	ΔP (MG) ^d
S813-13	2073	3.986(1)		26.68(7)	71.658	0.36	0.28
S1018-69	2173		4.1401(2)	21.03(1)	73.59(34)	−0.53	−0.63

^a Lattice parameters a (in Å) for pressure markers Au and MgO. Numbers in brackets are 1σ error in last digit. No errors reported for measurements based on a single X-ray diffraction peak position.

^b Pressure (in GPa) calculated from Au EOS of Fei et al. (2004) and MgO EOS of Speziale et al. (2001). Numbers in brackets are 1σ error in last digit, derived from propagation of errors in lattice parameters a .

^c Measured unit-cell volume V (in Å³) for ferropericlas (FP). Numbers between brackets are 1σ error in last digit. No errors reported for measurements based on a single X-ray diffraction peak position.

^d ΔP (in GPa) denotes difference between measured P and P calculated for given T and FP unit-cell V using the FP Birch-Murnaghan (BM) and Mie-Grüneisen (MG) EOS parameters from Table 3.

using the thermal EOS of Fei et al. (2004) for Au and of Speziale et al. (2001) for MgO. A total of 53 P – V – T measurements were obtained for FP at pressures up to 26.7 GPa and temperatures up to 2173 K (Fig. 1). In Fig. 3, measured FP unit-cell volumes are plotted as a function of pressure for the range of temperatures chosen for this study. Unit-cell volumes increase with increasing temperature at any given pressure across the range of pressures studied (1.3–26.7 GPa), indicating internal consistency of the data set.

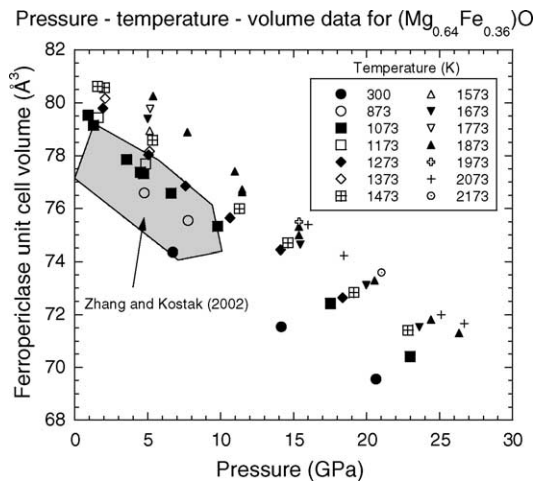


Fig. 3. Data compilation of measured (Mg_{0.64}Fe_{0.36})O ferropericlas unit-cell volumes as a function of pressure for the 14 isotherms in this study. The approximate P – V field from the study of Zhang and Kostak (2002) is shown in grey for comparison. 1σ errors are smaller than symbol size.

4. Equations of state

4.1. Room-temperature equation of state

In Fig. 4, our three room-temperature measurements are compared with previous results for this FP composition (Rosenhauer et al., 1976; Fei et al., 1992; Zhang and Kostak, 2002). The 23 data points in Fig. 4 were obtained with two different high-pressure techniques (diamond-anvil cells in Rosenhauer et al. (1976) and Fei et al. (1992), multi-anvil presses in the

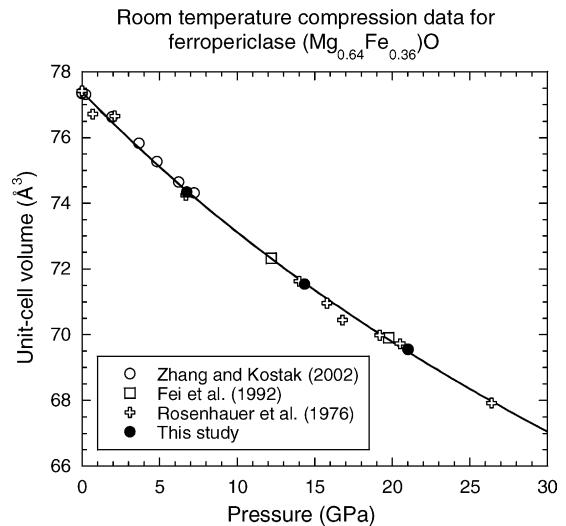


Fig. 4. Compilation of room-temperature compression data for (Mg_{0.64}Fe_{0.36})O. 1σ errors are smaller than symbol size. Line is best-fit third-order Birch-Murnaghan equation of state (Eq. (1) – best-fit parameters are given in Table 3).

other two studies) and two different pressure markers (Au in this study and Fei et al. (1992), NaCl in the case of Rosenhauer et al. (1976) and Zhang and Kostak (2002)). All data can be fit satisfactorily with a third-order Birch-Murnaghan equation of state (Birch, 1947),

$$P(V, 300 \text{ K}) = 3K_{T0}f(1 + 2f)^{5/2} \times \left(1 + \frac{3}{2}(K'_0 - 4.0)f\right), \quad (1)$$

where V is the unit-cell volume, V_0 is the unit-cell volume at zero pressure, K_{T0} is the isothermal bulk modulus at zero pressure, K'_0 is its pressure derivative, and f , the Eulerian strain, is defined as

$$f = \frac{1}{2} \left(\left(\frac{V_0}{V} \right)^{2/3} - 1 \right). \quad (2)$$

A non-linear least-squares fit (using EOSFIT software developed by R. Angel, described in Angel, 2000) gives $V_0 = 77.438 \pm 0.029 \text{ \AA}^3$, $K_{T0} = 154 \pm 3 \text{ GPa}$, and $K'_0 = 4.0 \pm 0.4$ (Table 3, errors given are 1σ). These parameters are within 2σ of previous analyses of room-temperature data (Rosenhauer et al., 1976; Fei et al., 1992; Zhang and Kostak, 2002).

4.2. High-temperature equations of state

A total of 165 P – V – T measurements are now available for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$: 52 from Zhang and Kostak

(2002), 60 from Fei et al. (1992) and 53 from this study. The three studies are to a large degree complementary, as seen by the P – T coverage in Fig. 1. We opted to fit all 165 data points simultaneously. Provided results from the three studies are mutually consistent, this approach should lead to the most precise description of the EOS for this FP composition. Data were fitted to two commonly used thermal equations of state, the high-temperature Birch-Murnaghan EOS and the Mie-Grüneisen EOS, using EOSFIT software (Angel, 2000), and custom-made Pascal software, respectively.

The high-temperature Birch-Murnaghan (BM) EOS is a simple extension of Eqs. (1) and (2), where the zero-pressure parameters V_0 and K_{T0} are varied with temperature (e.g., Duffy and Wang, 1998):

$$K_{T0}(T) = K_{T0}(300 \text{ K}) + \left(\frac{\partial K_{T0}}{\partial T} \right)_P (T - 300 \text{ K}), \quad (3)$$

$$V_0(T) = V_0(300 \text{ K}) \exp \int_{300 \text{ K}}^T \alpha(T) dT, \quad (4)$$

where $\alpha(T) = \alpha_0 + \alpha_1 T$ is the thermal expansion coefficient.

Table 3 lists the best-fit parameters and associated errors for weighted fits of all 165 P – V – T data to Eqs. (3) and (4). Experimental data are reproduced very well. In Fig. 5, the difference between observed pressures (Table 2, obtained using the Au EOS of Fei et al. (2004), the MgO EOS of Speziale et al. (2001),

Table 3

Best-fit parameters for Birch-Murnaghan (BM) and Mie-Grüneisen (MG) equations of state (EOS) for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ ferropericlase (FP), based on measurements from Rosenhauer et al. (1976), Fei et al. (1992), Zhang and Kostak (2002), and this study

Parameter	Room T EOS	High T BM EOS	High T MG EOS
No. of data points	23	165	165
V_0 ($\text{\AA}^3$)	77.438(29)	77.429(37)	77.369(8)
K_{T0} (GPa)	154(3)	155(2)	159(1)
K'_0	4.0(4)	3.8(1)	3.8(1)
$(dK/dT)_P$	–	–0.020(1)	–
α_0 ($\times 10^{-5} \text{ K}^{-1}$)	–	3.78(12)	–
α_1 ($\times 10^{-8} \text{ K}^{-2}$)	–	0.74(13)	–
δ_T	–	3.3(1)	–
θ_{D0} (K)	–	–	576 ^a
γ_0	–	–	1.63(2)
q	–	–	0.54(3)
$1\sigma(\Delta P)$ (GPa)	0.25	0.27	0.31

Numbers in brackets are 1σ error in last digit.

^a Fixed value, see text for details.

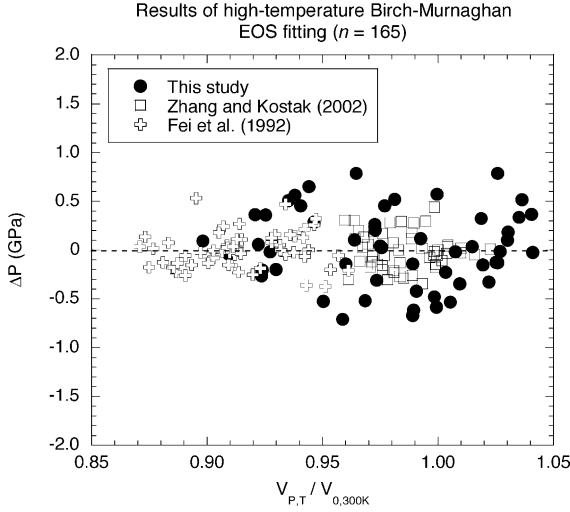


Fig. 5. The difference ΔP between experimentally measured pressure and pressure calculated using the high-temperature Birch-Murnaghan FP EOS parameters (Table 3), plotted against measured normalised FP unit-cell volume ($V_{P,T}/V_{0,300\text{K}}$). Both the overall distribution of pressure differences, and the distribution of individual data subsets are close to Gaussian, and centred around $\Delta P = 0$ (dotted line). This provides strong evidence for the absence of significant systematic errors between the EOS of Au, MgO, and NaCl used to calculate sample pressures, across the experimental P – T range shown in Fig. 1.

and NaCl EOS of Decker (1971)) and pressures calculated from the best-fit high-temperature BM EOS parameters (Table 3) is shown as a function of normalised unit-cell volume ($V_{P,T}/V_{0,300\text{K}}$). The distribution of resulting pressure differences is very nearly Gaussian, with an average difference of -0.006 GPa, and a standard deviation of 0.27 GPa. Within error, there is no systematic difference between the average pressure differences for the three data subsets. For the Zhang and Kostak (2002) data, the average pressure deviation is -0.03 GPa, with a standard deviation of 0.21 GPa. For the Fei et al. (1992) subset, values are -0.01 ± 0.18 GPa, and for our new data presented in Table 2 the pressure difference is $+0.02 \pm 0.39$ GPa. The standard deviation for the pressure differences is largest for data from this study, reflecting the significantly larger temperature range. The absence of any systematic differences between the three data sets indicates a high level of consistency among the Au, MgO, and NaCl pressure scales used, as previously shown, in the case of the Au and MgO scales, by Fei et al. (2004).

Best-fit V_0 , K_{T0} , and K'_0 are all within error of the values obtained from the fit to room-temperature data only (Section 4.1), and are consistent with the previous studies on this material. Thermal parameters α_0 , α_1 , and $(\partial K_{T0}/\partial T)_P$ differ slightly from previous studies. α_0 is larger, whereas α_1 and $(\partial K_{T0}/\partial T)_P$ are smaller than previously assumed. Using these BM EOS parameters, the Anderson–Grüneisen parameter,

$$\delta_T = -\frac{1}{\alpha_T K_T} \left(\frac{\partial K_T}{\partial T} \right)_P, \quad (5)$$

is derived to be virtually constant at 3.3 ± 0.1 at all temperatures between 300 and 3000 K, lower than the value 4.3 ± 0.5 derived by Fei et al. (1992), based on their smaller data set.

The Mie–Grüneisen (MG) EOS (e.g., Speziale et al., 2001) requires the introduction of the concept of thermal pressure, P_{Th} , resulting from a change in temperature from a reference temperature (300 K) at constant volume (e.g., Anderson et al. (1989), and references therein):

$$P(V, T) = P(V, 300 \text{ K}) + P_{\text{Th}}. \quad (6)$$

$P(V, 300 \text{ K})$ is taken from Eq. (1), and P_{Th} can be expressed through the Mie–Grüneisen equation,

$$P_{\text{Th}} = \frac{\gamma(V)}{V} (E(T, \theta_D) - E(300 \text{ K}, \theta_D)), \quad (7)$$

with the Grüneisen parameter

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0} \right)^q, \quad (8)$$

where γ_0 is the Grüneisen parameter at V_0 , and $q = (\partial \ln \gamma / \partial \ln V)_T$ describes its volume dependence. The Debye temperature, θ_D , is assumed to be a function of volume, and to be temperature independent:

$$\theta_D = \theta_{D0} \left(\frac{V}{V_0} \right)^{-\gamma(V)}, \quad (9)$$

with θ_{D0} the Debye temperature at V_0 . The thermal free energy E in Eq. (7) is calculated from the Debye model (Debye, 1912), using

$$E(T, \theta_D) = 9nRT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1}. \quad (10)$$

Notwithstanding the large number of available P – V – T data, simultaneous least-squares fitting of all parameters (V_0 , K_{T0} , K'_{T0} , q , γ_0 , and θ_{D0}) produced physically unrealistic results (among them, a Debye temperature below 60 K), because of strong correlations between the individual fit parameters q , γ_0 , and θ_{D0} . Following Speziale et al. (2001), we opted to fix the FP Debye temperature, θ_{D0} . θ_{D0} can be derived from calorimetric data, from spectroscopic data, or from acoustic velocity measurements. For iron-free MgO, the first two methods result in θ_{D0} values in the range 743–762 K. In the MgO EOS of Speziale et al. (2001) θ_{D0} was fixed to 773 K, from the calorimetric data of Watanabe (1982). Debye temperatures for pure MgO derived from acoustic measurements, however, are approximately 200 K higher (Anderson, 1998).

To our knowledge, neither calorimetric nor spectroscopic data are available for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$. To determine a θ_{D0} that is consistent with the value of 773 K for pure MgO assumed by Speziale et al. (2001), we therefore compared θ_{D0} values calculated from acoustic measurements, which were recently made for the complete range of compositions from MgO to FeO (Jacobsen et al., 2002). Acoustic θ_{D0} values can be calculated using

$$\theta_{D0} = \frac{h}{k} \left(\frac{3N_A \rho}{4\pi\mu} \right)^{1/3} v_m \quad (11)$$

where h is Planck's constant, k is Boltzmann's constant, N_A is Avogadro's number, ρ is density, μ is the mean atomic mass, and the mean sound velocity, v_m , is given by

$$\frac{3}{v_m^3} = \frac{2}{v_s^3} + \frac{1}{v_p^3} \quad (12)$$

where v_s and v_p are the measured P-wave and S-wave velocities. Using the empirical formulae for v_s and v_p as a function of FP composition and the measured densities of Jacobsen et al. (2002), Eqs. (11) and (12) lead to $\theta_{D0} = 959$ K for pure MgO. This value of θ_{D0} is in very good agreement with other acoustic data (Sumino et al., 1983; Isaak et al., 1989). For $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$, the acoustic data of Jacobsen et al. (2002) predict $\theta_{D0} = 715$ K, over 25% lower than the acoustic θ_{D0} for pure MgO. Clearly, θ_{D0} for FP shows a large dependence on Fe content. To reflect this dependence, and retain consistency with the MgO pressure scale used,

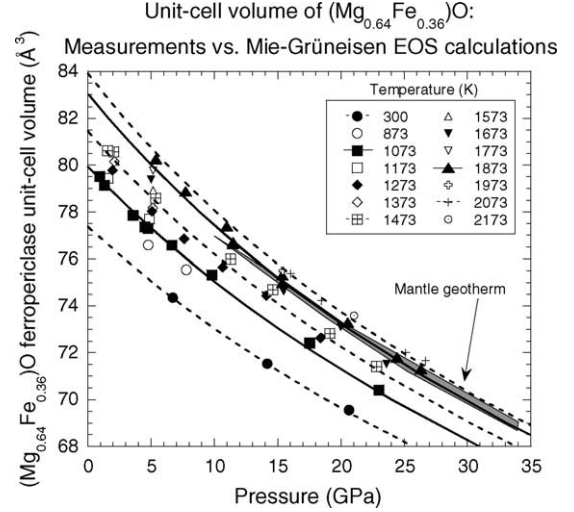


Fig. 6. Comparison between measured FP unit-cell volumes (symbols) and volumes calculated using the best-fit Mie-Grüneisen EOS parameters shown in Table 3 (curves). The mantle geotherm from Fig. 1 is shown in grey.

we reduced the θ_{D0} for pure MgO used by Speziale et al. (2001), by the same factor observed in the acoustic data, leading to $\theta_{D0} = 576$ K for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$. This value is close to $\theta_{D0} = 500 \pm 20$ K given in Fei et al. (1992), but significantly lower than θ_{D0} values used by Hama and Suito (1999).

The resulting best-fit MG EOS parameters V_0 , K_{T0} , K'_{T0} , γ_0 and q , at fixed $\theta_{D0} = 576$ K, are given in Table 3. Experimental data are reproduced very well, with a standard deviation equivalent to 0.31 GPa in pressure. Fig. 6 shows the good agreement between FP unit-cell volumes calculated using the MG EOS parameters, and measured volumes from Table 2. As was the case for the BM EOS, the MG EOS reproduces the three available data sets (Fei et al., 1992; Zhang and Kostak, 2002; and this study) equally well, again suggesting a high degree of consistency between the pressure scales used.

Best-fit V_0 , K_{T0} , and K'_{T0} are in good agreement with fits from the room-temperature and high- T Birch-Murnaghan EOS. Best-fit values for K'_{T0} are in the range (3.8 ± 0.1) – (4.0 ± 0.4) for the three EOS listed in Table 3. Jacobsen et al. (2002), on the basis of room-temperature FP single crystal X-ray diffraction measurements in a diamond anvil cell, recently suggested that K'_{T0} values for $(\text{Mg},\text{Fe})\text{O}$ solid solutions with compositions bracketing the one studied are sig-

nificantly higher (5.5 ± 0.1). Our results are not compatible with this elevated K'_0 . A room-temperature BM EOS fit with K'_0 set to 5.5 yields $K_{T0} = 142 \pm 3$ GPa, significantly lower than previously published FP bulk moduli, and lower than any of the fits shown in Table 3. A possible explanation for this discrepancy is the relatively smaller pressure range covered by Jacobsen et al. (2002), which has been observed previously to lead to higher fit values of K'_0 (e.g., Brown, 1999). Additional studies will be required to resolve these issues.

The best-fit Grüneisen parameter $\gamma_0 = 1.63 \pm 0.02$, slightly higher than the value of 1.50 ± 0.05 derived by Fei et al. (1992). The q value is 0.54 ± 0.03 , which is within the range given by Fei et al. (1992). We note that P – V – T measurements provide tight constraints on the average value of $\gamma(V)$ (Eq. (8)) across the volume range covered by the data (e.g., Jackson, 1998), rather than on γ_0 itself. It is therefore possible that different combinations of γ_0 and q , that lead to similar values of $\gamma(V)$ in Eq. (8), provide equally good fits to the P – V – T data.

5. Discussion

To quantify possible variations in the elastic and thermal properties of FP as a function of FP iron content, the thermoelastic properties of FP are compared with those of pure MgO. In Fig. 7, the calculated 1 bar expansion of the FP unit cell, based on the best-fit BM EOS thermal expansion coefficients ($\alpha_0 = (3.78 \pm 0.12) \times 10^{-5} \text{ K}^{-1}$, $\alpha_1 = (0.74 \pm 0.13) \times 10^{-8} \text{ K}^{-2}$, Table 3), is compared with the expansion calculated using previously published values $\alpha_0 = 3.40 \times 10^{-5} \text{ K}^{-1}$ and $\alpha_1 = 1.33 \times 10^{-8} \text{ K}^{-2}$ (derived by Zhang and Kostak (2002) from fitting a combination of their data and those of Fei et al. (1992)), and with the measured expansion of pure MgO (Dubrovinsky and Saxena, 1997). At temperatures up to approximately 1300 K, the two calculated expansions for FP are, within error, identical to each other and to the measurements for pure MgO. This temperature coincides with the maximum temperature for which experimental data were available to Zhang and Kostak (2002). At temperatures exceeding 1300 K, the calculations based on the new EOS show a slightly lower expansion than the calculations of Zhang and Kostak (2002). Agreement between the normalised FP unit-cell volumes calculated using

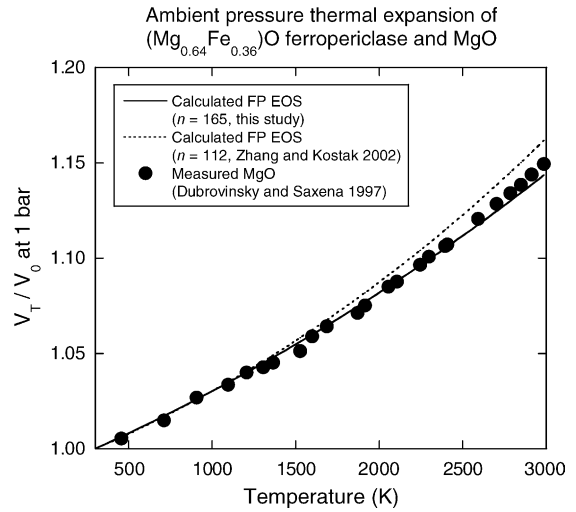


Fig. 7. Ambient pressure thermal expansion of $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ (FP) and MgO. Normalised FP unit-cell volumes (V_T/V_0) were calculated using the Birch-Murnaghan EOS thermal expansion parameters from this study (solid line) and from Zhang and Kostak (2002) (dotted line). Normalised MgO unit-cell volumes are measurements taken from Dubrovinsky and Saxena (1997). 1σ errors bars are smaller than symbol size.

the new BM EOS parameters from Table 3 and those measured for pure MgO remains within one standard deviation over the complete temperature range from 300 to at least 3000 K. Our Birch-Murnaghan EOS results strengthen previous suggestions (Zhang and Kostak, 2002) that the 1 bar thermal expansion of FP is identical to that of Fe-free MgO.

Our experiments provide a direct test for the assumption that this similarity in thermoelastic properties persists at simultaneous high pressures and temperatures. At 31 different P – T conditions, unit-cell volumes were measured for both pure MgO (for pressure determination) and FP (Table 2). Fig. 8 shows that measured thermal expansions of FP and pure MgO at simultaneous high P and T are identical to within 0.6 per cent relative, fully consistent with inferences from our BM EOS calculations (Fig. 7).

Fig. 9 shows the normalised unit-cell volumes for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ ferropervicite at pressures up to 55 GPa, along four isotherms ranging from 1073 to 3000 K, calculated using the two EOS derived in this study. Results from the two EOS are consistent with each other across the complete P – T range, as discussed in the previous section. Calculated normalised unit-cell

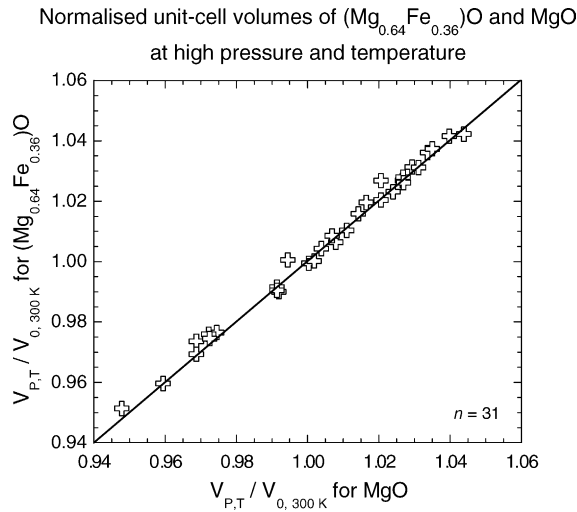


Fig. 8. Comparison between normalised unit-cell volumes for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ and MgO measured at identical high-pressure, high-temperature conditions (symbols, data from this study, Table 2). One-to-one line is a guide to the eye.

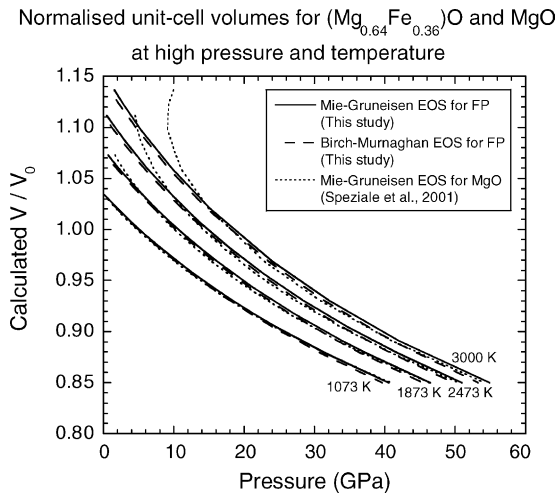


Fig. 9. Normalised unit-cell volumes (V/V_0) as a function of pressure in the temperature range 1073–3000 K for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ (FP) (calculated using the Mie-Grüneisen and Birch-Murnaghan EOS parameters listed in Table 3 – solid and dashed lines, respectively) and MgO (calculated using the Mie-Grüneisen EOS proposed by Speziale et al. (2001) – dotted line). Note the excellent agreement at high pressures and temperatures between the two high-temperature EOS for FP presented in Table 3, and between these EOS and data for pure MgO . Also note that the MgO EOS of Speziale et al. (2001) produces unrealistic results at conditions of simultaneous high temperature and low pressure (see text for discussion).

volumes for pure MgO , using the Speziale et al. EOS, are also plotted. At plausible pressures and temperatures in Earth's lower mantle, the FP and MgO EOS lead to very similar normalised volume calculations (to within 2% relative at 3000 K and 55 GPa). At temperatures exceeding approximately 2200 K, and normalised unit-cell volumes exceeding 1.05, the Speziale et al. EOS produces unrealistic results at lower pressures. This is a result of the special EOS term for the volume dependence of the Grüneisen parameter, used by Speziale et al. (2001) to correctly describe both low-pressure, static compression data and high-pressure Hugoniot data. Fig. 9 suggests the Speziale et al. (2001) EOS should not be used at simultaneous very high temperature and very low pressure. Note that our lowest-pressure, highest temperature experimental data (Table 2) were obtained at V - T conditions still allowing use of the Speziale et al. EOS for pressure determination (Table 2).

From Figs. 7–9 we conclude that both direct experimental measurements and equation of state analyses strongly suggest that the pressure and temperature derivatives of bulk modulus, and the thermal expansion of FP are independent of iron content.

6. Conclusions

New in situ P - V - T measurements for $(\text{Mg}_{0.64}\text{Fe}_{0.36})\text{O}$ ferropericlase provide improved constraints on the equation of state for this material. Based on best-fit EOS parameters, and a direct comparison of normalised unit-cell volumes for ferropericlase and pure MgO to 26.7 GPa and 2173, the thermal expansion and P - T derivatives of the bulk modulus of this iron-rich FP are virtually identical to those of pure MgO up to pressures exceeding 55 GPa and temperatures of 3000 K. FP thermoelastic properties (the pressure and temperature derivatives of bulk modulus, and the thermal expansion) of FP are independent of iron content across the range of plausible FP compositions in Earth's lower mantle.

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