

# Equations of state for $\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ "skiaigite" garnet and $\text{Fe}_2\text{SiO}_4$ – $\text{Fe}_3\text{O}_4$ spinel solid solutions

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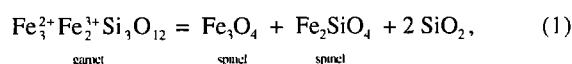
**Abstract.** The equations of state of  $\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ , or "skiaigite" garnet, and two  $\text{Fe}_2\text{SiO}_4$ – $\text{Fe}_3\text{O}_4$  spinel solid solutions were determined from room temperature hydrostatic compression experiments up to 11 GPa performed at the European Synchrotron Radiation Facility. These data indicate that there are no first-order phase transitions or changes in compression mechanism in skiaigite garnet or  $\text{Fe}^{3+}$ -bearing silicate spinel solid solutions up to 11 GPa at room temperature. Skiaigite garnet has an isothermal bulk modulus  $K_{0T} = 157.4(3.0)$  GPa and a pressure derivative of the isothermal bulk modulus  $K'_{0T} = 6.7(8)$ , where numbers in parentheses represent 1 estimated standard deviation of these values. Combination of this result with those for other silicate garnets reveals an inverse linear relationship between the octahedral cation-oxygen (Y-O) bond length and the bulk modulus. The dominating effect of the octahedral site on the bulk compression of garnet can be understood by considering that the octahedral-tetrahedral network has no rigid unit modes and that no cation substitution occurs on the tetrahedral sites in these garnets. It is apparent that the incorporation of  $\text{Fe}^{3+}$  and Cr acts to lower the bulk modulus of aluminosilicate garnets. Consideration of the effect of compression on the molar volume results in nonsystematic changes in calculated oxygen fugacity for garnet-bearing mantle peridotites that equilibrated at high pressures. The pressure-volume data obtained from two  $\text{Fe}^{3+}$ -bearing silicate spinel solid solutions with compositions  $X_{\text{fay}} = 0.45$  and  $X_{\text{fay}} = 0.57$  (fay, fayalite component) yielded similar enough values of  $K_{0T}$  and  $K'_{0T}$  to warrant a combined refinement with the data points scaled to the appropriate zero-pressure volumes. This gave  $K_{0T} = 168.9(1.2)$  GPa and  $K'_{0T} = 5.7(1.2)$  with  $\chi^2_w = 4.6$  (weighted  $\chi^2$ ) and  $K_{0T} = 175.5(1.4)$  GPa when  $K'_{0T}$  is fixed equal to 4 ( $\chi^2_w = 4.9$ ). Our solid solutions have significantly lower bulk moduli than either magnetite or  $\text{Fe}_2\text{SiO}_4$  spinel end-members or indeed many other spinels.

## 1. Introduction

Garnet and silicate spinel are important minerals in the Earth's mantle. Becoming stable at ~60 km depth in a peridotite bulk composition, garnet persists through the transition zone and into the upper portions of the lower mantle [e.g., *Irfune and Ringwood*, 1987; *O'Neill and Jeanloz*, 1994; *Yagi et al.*, 1997]. Silicate spinel becomes stable at ~520 km due to the transformation of wadsleyite [e.g., *Bina and Wood*, 1987; *Katsura and Ito*, 1989]. At higher pressures, silicate spinel breaks down to the assemblage of silicate perovskite and magnesiowüstite, and it is generally considered that this reaction is responsible for the 660 km seismic discontinuity.

Experimental studies suggest that in a "pyrolite" bulk composition this portion of the transition zone between 520 km and 660 km is essentially biminerallitic, consisting of silicate spinel and garnet [e.g., *Irfune and Ringwood*, 1987].

The incorporation of  $\text{Fe}^{3+}$  into garnet and silicate spinel has received much attention in recent years due to the implications this has for the redox state in these deeper portions of the upper mantle and transition zone [*O'Neill et al.*, 1993]. Studies of mantle-derived garnets [*Luth et al.*, 1990; *Canil et al.*, 1994; *Canil and O'Neill*, 1996; *Woodland and Peltonen*, 1999] and experimental investigations [*O'Neill et al.*, 1993; *Woodland and O'Neill*, 1993, 1995] indicate that  $\text{Fe}^{3+}$  can be readily incorporated into garnet and silicate spinel at high pressures and temperatures. The low-pressure stability of garnet in the simple  $\text{Fe}^{3+}$ - $\text{Fe}^{2+}$ -Si-O system is controlled by the equilibrium:



where  $\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$  is the "skiaigite" end-member garnet and the two spinel components occur as a solid solution [*Woodland and O'Neill*, 1993]. The volume change at 298 K and 1 bar  $\Delta V_{298, 1\text{bar}}$  for (1) is positive within the coesite stability field but becomes negative upon crossing into the stishovite field, suggesting that skiaigite garnet should be

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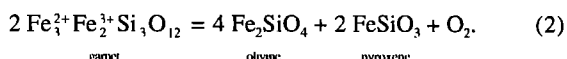
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destabilized at higher pressures. Understanding the behavior of this equilibrium at high pressures and temperatures requires knowledge of the relative compressibilities of garnet and silicate spinel solid solutions in addition to that of the  $\text{SiO}_2$  polymorphs.

The recent advent of quantitative  $\text{Fe}^{3+}/\text{Fe}^{2+}$  measurement in milligram-sized samples by Mössbauer spectroscopy [McCammon *et al.*, 1991], by electron energy loss spectroscopy (EELS) [van Aken *et al.*, 1998], or by other methods [e.g., McCammon, 1999] provides an opportunity to make estimates of the oxygen fugacity of very deep mantle samples, even from inclusions in diamonds (with the assumption that the mineral grains were in equilibrium). Such estimates can be made by considering the equilibrium between garnet, olivine, and orthopyroxene:



This equilibrium has been recently calibrated as an oxygen barometer by Gudmundsson and Wood [1995]. Although a correction for the pressure dependencies of the molar volumes of these phases is normally small and can be neglected, this will not be the case for samples that come from great depths (up to 670 km, ~22.0 GPa). In addition, accurate knowledge of the elastic properties of skiaegite garnet and  $\text{Fe}^{3+}$ -bearing silicate spinel is necessary when attempting to model the behavior of  $\text{Fe}^{3+}$  under conditions relevant to the transition zone.

Here we report the results from a room temperature study of the hydrostatic compression of the end-member skiaegite garnet and two  $\text{Fe}_2\text{SiO}_4$ - $\text{Fe}_3\text{O}_4$  spinel solid solutions up to 11 GPa. These results are then briefly compared with data from the literature on other, mostly  $\text{Fe}^{3+}$ -free, garnet and silicate spinel compositions. The implications for mantle phase equilibria such as (1) and (2) are discussed.

## 2. Synthesis of Garnet and Spinel

Samples of  $\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$ , skiaegite garnet, and  $\text{Fe}_2\text{SiO}_4$ - $\text{Fe}_3\text{O}_4$  spinel solid solutions were synthesized at 1100°C and 9.0-9.7 GPa from stoichiometric oxide mixes in a multi-anvil press at the Bayerisches Geoinstitut in Bayreuth, Germany. The method of synthesis is detailed by Woodland and O'Neill [1993]. Analysis of the skiaegite sample (experiment uhp-702) by X-ray powder diffraction with Si as an internal standard gave a unit cell parameter of  $a_0 = 11.7272(7)$  Å (where the number in parentheses represents 1 estimated standard deviation of the measured value), corresponding to a molar volume of 121.42 cm<sup>3</sup>. A small amount of stishovite and spinel (57 mol %  $\text{Fe}_2\text{SiO}_4$  and 43 mol %  $\text{Fe}_3\text{O}_4$ ) was also apparent in the powder diffraction pattern. A room temperature Mössbauer spectrum indicated that all  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were dodecahedrally and octahedrally coordinated in the garnet, respectively, confirming that no Fe-majorite component was present.

The spinel sample (experiment uhp-524) has a unit cell parameter of  $a_0 = 8.3147(11)$  Å and a composition as determined by the microprobe of 45 mol %  $\text{Fe}_2\text{SiO}_4$  and 55 mol %  $\text{Fe}_3\text{O}_4$ . It was also possible to simultaneously extract equation of state data for the spinel coexisting with the skiaegite garnet, thus providing a second data set for a  $\text{Fe}^{3+}$ -bearing silicate spinel solid solution with a composition that is different by ~10 mol %  $\text{Fe}_2\text{SiO}_4$ .

## 3. Diffraction Experiments and Data Reduction

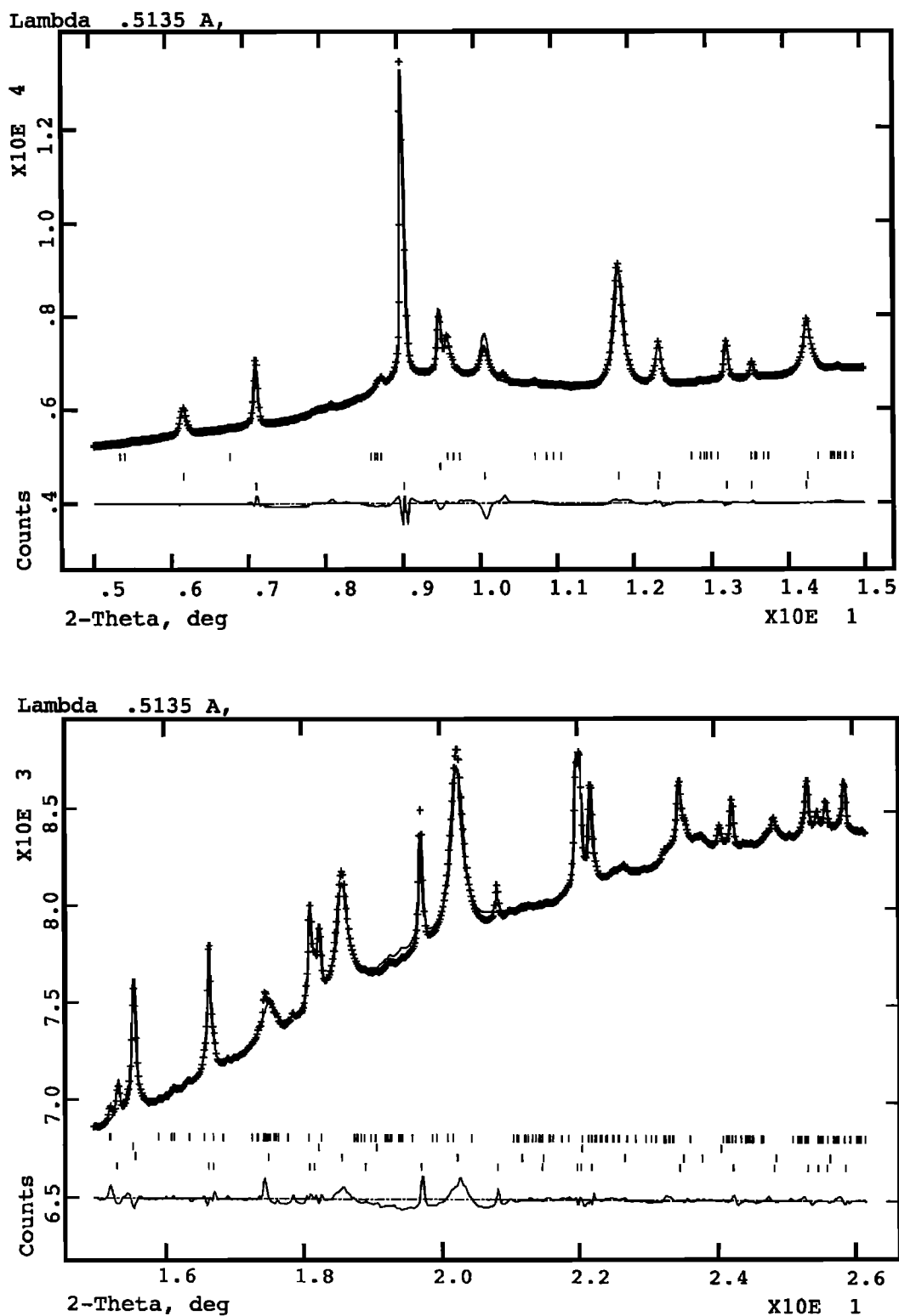
High-pressure powder diffraction was performed on beamline ID30 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Monochromatic radiation was selected with a double monochromator, and a wavelength of ~0.51 Å was chosen as it provided a reasonable compromise between signal to noise and the resolution of the diffraction pattern. Both samples were ground together with quartz, to act as a precise internal pressure standard [Angel *et al.*, 1997]. Samples were loaded into diamond-anvil pressure cells (DAC) of the Bayerisches Geoinstitut design [Allan *et al.*, 1996], using T301 steel gaskets together with a 4:1 methanol-ethanol mixture to serve as the pressure medium. Ruby was also added to serve as an approximate indicator of pressure for ease of changing pressure on the DAC during the course of the experiments.

Diffraction patterns were collected with an A3-size image plate located at ~29 cm behind the sample position. The precise sample-to-plate distance and the precise X-ray wavelength were determined by collecting a diffraction pattern from a standard silicon sample (distance of 29.65 cm, and wavelength of 0.5134(1) Å). The exposure time for each pattern was varied between 8 and 15 min depending on the current in the storage ring. Each image was corrected for plate tilts and aberrations using the Fit2d program written by A. Hammersley at the ESRF [Hammersley *et al.*, 1996; Hammersley, 1997]. The corrected image was then integrated to produce a one-dimensional intensity-2θ data set. Unit cell parameters of the samples and accompanying quartz were obtained by full-pattern *le Bail* refinement [le Bail, 1992] of the one-dimensional data sets using the GSAS program package [Larson and Von Dreele, 1988]. Refined parameters included: (1) the background parameters, (2) the peak profile parameters, (3) the 2θ zero offset, and (4) the cell parameters. A typical pattern along with its associated *le Bail* refinement is presented in Figure 1.

Three major sources of experimental error exist: (1) the reproducibility of the positioning of the image plate along the axis of the X-ray beam is estimated to be 5 μm, (2) the positioning of the sample (within the DAC) along the axis of the X-ray beam is achieved through rocking the cell and measuring the absorption curve, which may result in positioning errors of as much as 50 μm for thick samples, and (3) the wavelength selected by the monochromator may fluctuate by as much as 1 part in 5,000 as the refrigerator on the cooling water system cycles. The combined effect of all of these sources of errors is to produce an uncertainty  $\Delta V/V = 0.0014$ . Duplicate measurements on quartz at room pressure suggest an estimated standard deviation in the pressure determination of 0.03 GPa.

## 4. Results

Data for the skiaegite and spinel samples were collected at ~1.0 GPa intervals. At pressures above 11 GPa, line broadening was observable in the diffraction patterns due to nonhydrostatic stresses, and therefore only measurements made up to 11 GPa were used in determining the equation of state (EOS). The pressure was derived from the measured unit cell volume of the quartz in the sample, along with its corresponding estimated standard deviation (esd), via the EOS for quartz reported by Angel *et al.* [1997]. The variation in the molar volumes of



**Figure 1.** Example of a le Bail fit to an X-ray diffraction pattern of the  $\text{Fe}^{3+}$ -bearing silicate spinel solid solution with a composition  $X_{\text{Fe}^{3+}} = 0.45$  at 5.37 GPa. The residual is displayed below the diffraction pattern. Also displayed below the diffraction pattern are the reflections corresponding to the four phases that were refined in this sample; from top to bottom, quartz, silicate spinel solid solution, Si metal, and coesite.

skiaite and the two spinel samples with pressure is presented in Table 1 and Figures 2 and 3.

The pressure-volume ( $P$ - $V$ ) data were fit to a third-order Birch-Murnaghan EOS [Birch, 1947]:

$$P = 3K_0 f (1 + 2f)^{5/2} [1 + \frac{1}{2}(K' - 4)f],$$

where  $f = \frac{1}{2}[(V_0/V)^{2/3} - 1]$  by applying a fully weighted least-squares refinement of the  $P$ - $V$  data. The refined parameters were  $V_0$ , the isothermal bulk modulus  $K_0$ , and the pressure derivative of the isothermal bulk modulus  $K'_0$ . Weights were assigned to each data point using the estimated standard deviations in both the pressure and the measured volume. The results of the least-squares refinements are summarized in Table 2. For the skiaite garnet a  $K_0 = 157.4(3.0)$  GPa and  $K'_0 = 6.7(8)$  were obtained. Fixing  $K'_0 = 4$  yields a significantly higher  $\chi^2_w$  of 10.5 (weighted  $\chi^2$ ), indicating that the fit with  $K'_0 = 6.7$  is a statistically better fit. The pressure-volume data provide no evidence for a first-order phase transition or change in compression mechanism in skiaite garnet up to 11 GPa at room temperature (Figure 2). The pressure-volume data obtained from the two spinel solid solutions with compositions  $X_{\text{fay}} = 0.45$  and  $X_{\text{fay}} = 0.57$  (fay, fayalite component) yielded similar enough values of  $K_0$  and  $K'_0$  to warrant a combined refinement using all 24 data points scaled to the appropriate zero-pressure volumes. This gave  $K_0 = 168.9(1.2)$  GPa and  $K'_0 = 5.7(1.2)$  with  $\chi^2_w = 4.6$  and  $K_0 = 175.5(1.4)$  GPa when  $K'_0$  is fixed equal to 4 ( $\chi^2_w = 4.9$ ).

## 5. Discussion

### 5.1. Compression of Garnet

The bulk modulus of a variety of silicate garnets has been experimentally determined over the past thirty years with some variation apparent between studies on a given composition such as pyrope (see Olijnyk *et al.* [1991] and Knittle [1995] for a summary of data). Some of the scatter in the published data can be attributed to experimental or computational problems, which are sometimes revealed by an anomalous value for the pressure derivative of the bulk modulus (see, e.g.,

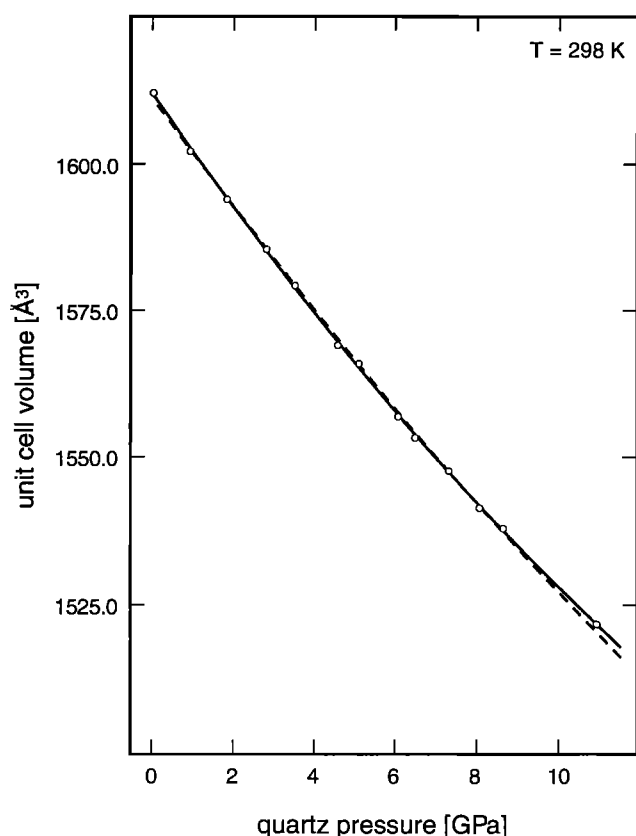
discussion by Hazen and Finger [1989]). In other cases, some of the reported variability is due to the inappropriate combination of data obtained from static compression measurements and elasticity measurements, which yield isothermal bulk moduli and adiabatic bulk moduli, respectively. Adiabatic bulk moduli always have slightly higher values compared with isothermal bulk moduli for the same substance [cf. Poirier, 1991; Anderson, 1995]. The systematics and mechanism(s) of compression of the garnet structure need to be investigated with these considerations in mind.

The garnet structure consists of a network of corner-sharing octahedra and tetrahedra within which the larger dodecahedral sites are situated and has a general formula  $\{X_3\}[Y_2](Z_4)O_{12}$  where {braces}, [brackets], and (parentheses) denote the dodecahedral, octahedral, and tetrahedral sites, respectively [e.g., Novak and Gibbs, 1971]. To help explain the observed variation in bulk modulus between different garnet compositions, a simple inverse relationship between the isothermal bulk modulus and molar volume has been applied, based upon the assumption that garnets approximate a Debye solid [Bass, 1989; Olijnyk *et al.*, 1991; Hazen *et al.*, 1994a; see Anderson, 1988]. Although a linear relationship for the Ca-bearing garnets andradite, uvarovite, and grossular was found, other aluminosilicate garnets such as pyrope and almandine deviate significantly from this trend, having much lower bulk moduli than their molar volumes would predict (Figure 4). Overbonding or crystal field effects relating to the dodecahedrally coordinated Mg and Fe<sup>2+</sup>, respectively, were invoked by Olijnyk *et al.* [1991] to explain this discrepancy. Skiaite garnet also deviates strongly from the linear relationship defined by the Ca-bearing garnets, having essentially the same bulk modulus as andradite (Figure 4). Thus the skiaite data further indicate that the simple relationship between bulk modulus and molar volume is not generally valid for garnets and that the dodecahedral site occupancy has little direct influence on the bulk modulus. In contrast, the similarity in bulk modulus between skiaite and andradite, together with the observed systematics of the Ca-bearing garnets, suggests that the octahedral site occupancy is an important factor; the smaller the octahedral cation, the larger the bulk modulus (i.e., the structure becomes stiffer). This relationship can be further quantified by plotting

**Table 1.** Variation in the Molar Volumes of Skiaite Garnet and Silicate Spinel Solid Solutions with Pressure

Skiagite garnet		Spinel $X_{\text{fay}} = 0.57$		Spinel $X_{\text{fay}} = 0.45$	
$P$ , GPa	$V$ , Å <sup>3</sup>	$P$ , GPa	$V$ , Å <sup>3</sup>	$P$ , GPa	$V$ , Å <sup>3</sup>
0.0001	1611.8(3)	0.0001	571.52(3)	0.0001	575.21(6)
0.900(8)	1602.24(16)	0.900(8)	568.19(15)	3.559(9)	563.96(10)
1.804(10)	1594.12(17)	1.804(10)	566.05(16)	5.370(12)	558.44(12)
3.489(13)	1579.36(17)	3.489(13)	560.92(15)	6.365(11)	555.80(11)
4.555(11)	1569.21(18)	4.555(11)	557.20(12)	7.333(11)	553.42(11)
6.479(19)	1553.64(23)	6.479(19)	552.17(19)	7.865(11)	551.71(10)
7.308(19)	1547.97(19)	7.308(19)	550.32(17)	0.633(5)	573.12(9)
8.064(24)	1541.73(25)	8.064(24)	548.12(21)	1.689(4)	569.71(7)
8.632(18)	1538.28(28)	8.632(18)	547.11(21)	2.777(9)	566.59(11)
5.070(17)	1566.16(20)	5.070(17)	556.41(18)	4.145(11)	562.31(12)
2.785(13)	1585.51(20)	2.785(13)	563.37(18)	5.153(10)	559.41(11)
6.057(25)	1557.15(14)	6.057(25)	553.02(29)		
10.916(26)	1522.15(21)	10.916(26)	541.33(19)		

Numbers in parentheses represent 1 estimated standard deviation in the measured values.



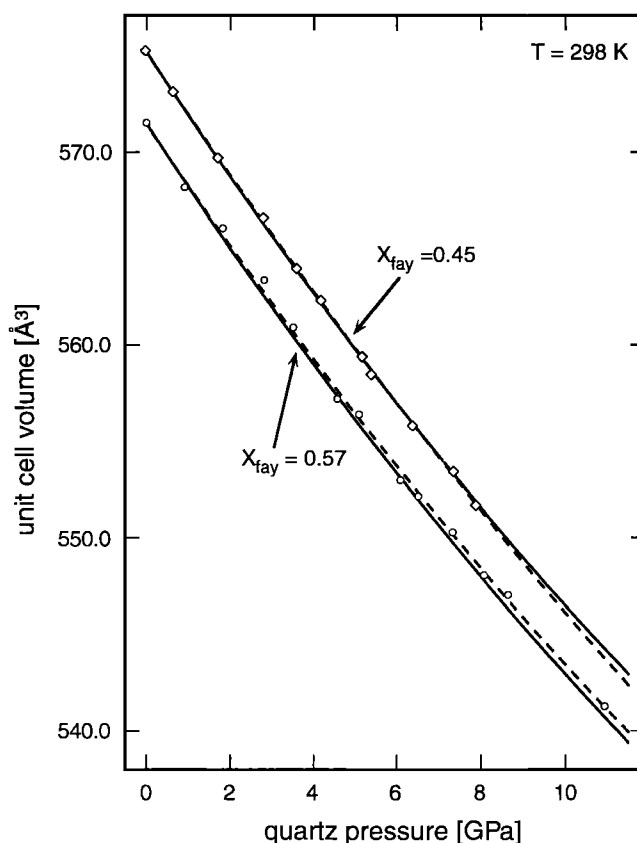
**Figure 2.** Plot of unit cell volume versus pressure for the "skiaigite" garnet with a third-order Birch-Murnaghan equation of state (EOS) fitted to the data. The dashed curve represents a fit with a fixed  $K'_{01}$  equal to 4. Quartz pressure refers to the use of the EOS of quartz to accurately determine the pressure. The propagated uncertainties in the volume and pressure measurements are smaller than the size of the symbols.

the bulk modulus against the Y-O bond length (Figure 5). The result is an inverse linear trend ( $r = 0.95$ ) with respect to bond length which is valid not only for the Ca-bearing garnets, but also for pyrope, almandine, and spessartine. The reason for this is that the Y-O bond length is not only a direct function of the octahedral site occupancy, but it is also indirectly influenced by the dodecahedral site occupancy since 6 of 12 octahedral edges are shared with neighboring dodecahedral sites [Novak and Gibbs, 1971; Woodland and Ross, 1994]. In addition,  $\text{MgSiO}_3$  majorite fits the trend when an average Y-O bond length of this tetragonal garnet is used, further supporting this simple relationship (Figure 5, data from Angel *et al.* [1989]). On the other hand, the bulk modulus appears to be unaffected by the geometry of the octahedral site. With respect to the 3-symmetry axis the octahedral site can either be elongated, as in skiaigite, or flattened, as in andradite, yet these two end-member garnets have very similar bulk moduli [Novak and Gibbs, 1971; Woodland and Ross, 1994] (Figure 5).

Two garnets deviate significantly from the inverse relationship between Y-O and bulk modulus depicted in Figure 5:  $\text{Mn}_2^{2+}\text{Mn}_2^{3+}\text{Si}_3\text{O}_{12}$  or "blythite" [Arlt *et al.*, 1998] and a Ca-Mg majorite solid solution [Hazen *et al.*, 1994a]. In the case of blythite, which is the Mn analogue of skiaigite garnet, the electronic configuration of the  $\text{Mn}^{3+}$  is such that dynamic Jahn-Teller distortion of the octahedral sites occurs, although

the "average" structure is still cubic [Arlt *et al.*, 1998]. This dynamic distortion is suppressed at high pressures, providing a second contribution to the compression of blythite in addition to the compression mechanism common to the garnet structure. As a result, the response of the Y-O bond length during compression should be different in comparison to other garnets which do not display such distortion. Tetragonal Ca-Mg majorite displays complete ordering of Mg and Si on the two distinct octahedral sites [Hazen *et al.*, 1994b], in contrast with partial disordering observed in  $\text{MgSiO}_3$  majorite [Angel *et al.*, 1989]. The environment of the two distinct octahedral sites are apparently different enough that a simple averaging of Y-O for the two sites is no longer a valid approximation for this tetragonal structure. Consequently, Ca-Mg majorite has a more compressible structure than would be expected from the octahedral bond length-bulk modulus systematics depicted in Figure 5.

Several studies have already emphasized the importance of the octahedral-tetrahedral network on the compressional behavior of silicate garnets, including those by Hazen and Finger [1989], Olijnyk *et al.* [1991], and particularly Hazen *et al.* [1994a]. In their compressional study of several types of majoritic garnets, including a Na majorite where the octahedral sites are nearly completely occupied with  $\text{Si}^{4+}$ , Hazen *et al.*



**Figure 3.** Plot of unit cell volume versus pressure for the two  $\text{Fe}^{3+}$ -bearing silicate spinel solid solutions. Quartz pressure refers to the use of the EOS of quartz to accurately determine the pressure. The solid lines are a third-order Birch-Murnaghan EOS fitted to all of the data. The dashed lines are separate fits to each of the spinel solid solutions. The propagated uncertainties in the volume and pressure measurements are smaller than the size of the symbols.

**Table 2.** Equations of State of Skiagite Garnet and Silicate Spinel Solid Solutions

	$n$	$P$ Range, GPa	$V_0$ , $\text{cm}^3 \text{mol}^{-1}$	$K_{or}$	$K'_{or}$	$\chi^2_{iv}$
Skiagite garnet	13	0.0 - 11	121.35(2)	157.4(3.0)	6.7(8)	4.7
				168.2(1.5)	4 <sup>†</sup>	10.5
Spinel <sub>ss</sub>						
$X_{\text{fey}} = 0.45$	11	0.0 - 7.9	43.31(1)	174(3)	4.0(9)	1.7
				174.0(9)	4 <sup>†</sup>	1.5
$X_{\text{fey}} = 0.57$	13	0.0 - 11	43.03(1)	173(4)	5.6(1.2)	4.4
				177.9(1.4)	4 <sup>†</sup>	4.7
Combined	24	0.0 - 11		168.9(1.2)	5.7(1.2)	4.6
				175.5(1.4)	4 <sup>†</sup>	4.9

\*Number of data points.

†Fixed value.

[1994a] proposed that the average valence of the octahedral cation is the primary factor in determining the compressibility of the octahedral-tetrahedral network. Although this may be true, the fact that Na majorite falls on the same trend as the other silicate garnets in Figure 5 suggests that the effect of higher valence merely reflects the shortening in the cation-O bond lengths going from  $\text{Al}^{3+}$ -O to  $\text{Si}^{4+}$ -O. In detail, Na majorite fits better to a quadratic function of Y-O (Figure 5). Deviation from the linear relationship to an even stiffer structure might be expected for such a short bond length compared with most phases possessing the garnet structure. In any case, a change in cation valence cannot explain the variation in

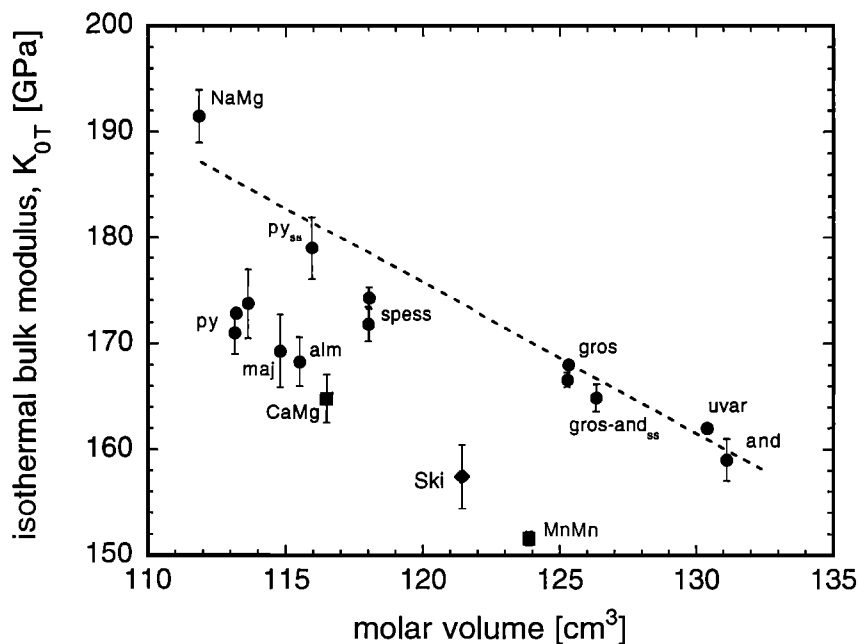
bulk modulus between andradite or skiagite and their Al-bearing analogues, grossular and almandine.

The relatively simple relationship between the bulk modulus and octahedral site occupancy can be understood by considering the fact that the octahedral-tetrahedral network of garnet has no rigid unit modes, which means that compression of the structure cannot be achieved by tilting of rigid polyhedra [Hammonds *et al.*, 1998]. Instead, compression or deformation of the crystal structure requires deformation of one or more of the polyhedral units, either the tetrahedra or the octahedra or both. Since the tetrahedral site environment remains more or less the same in all silicate garnets, it is the varying octahedral site that has the greatest direct influence on the bulk modulus. On the other hand, small differences in Si-O bond lengths do exist, dependent on the dodecahedral site occupancy [Novak and Gibbs, 1971; Woodland and Ross, 1994], and this could account for some of the scatter in Figure 5.

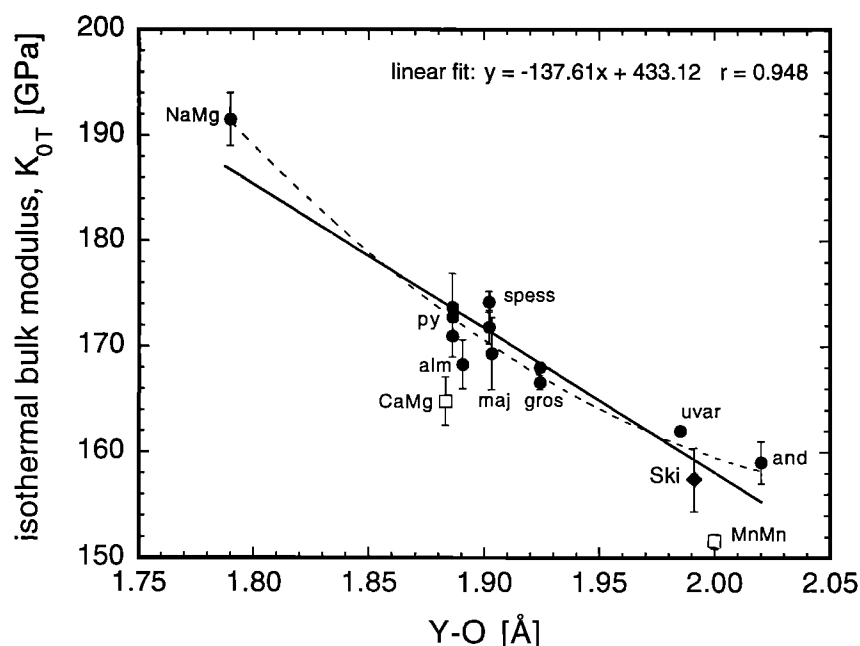
The pressure derivative of the isothermal bulk modulus for skiagite  $K'_{or} = 6.7(8)$  is similar to that determined for a variety of different garnet compositions: 4.4 for pyrope [Zhang *et al.*, 1998], 4.7(7) for uvarovite [Leger *et al.*, 1990], ~6 for grossular [Olijnyk *et al.*, 1991]; 6.38(19) for blythite [Arlt *et al.*, 1998], and 7.4(1.0) for spessartine [Leger *et al.*, 1990]. Although a variation with composition is apparent, it would seem that a relatively large initial compression is a general characteristic of silicate garnets.

## 5.2. Compression of Silicate Spinel Solid Solutions

As for skiagite garnet, our data indicate that no phase transition occurs in  $\text{Fe}^{3+}$ -bearing silicate spinel up to 11 GPa at



**Figure 4.** Variation of the isothermal bulk modulus,  $K_{0T}$ , with molar volume for a variety of silicate garnets. Data are given as follows: alm, almandine [Yagi *et al.*, 1987]; and, andradite [Hazen and Finger, 1989]; CaMg, Ca-Mg majorite [Hazen *et al.*, 1994a]; gros, grossular [Isaak *et al.*, 1992; Olijnyk *et al.*, 1991]; gros-and<sub>ss</sub>, grossular-andradite solid solution [Isaak *et al.*, 1992]; maj, majorite [Hazen *et al.*, 1994a]; MnMn, "blythite" [Arlt *et al.*, 1998]; NaMg, Na-Mg majorite [Hazen *et al.*, 1994a]; py, pyrope [Leger *et al.*, 1990; Hazen *et al.*, 1994a; Zhang *et al.*, 1998]; py<sub>ss</sub>, pyrope solid solution [Hazen and Finger, 1989]; ski, skiagite (this study); spess, spessartine [Leger *et al.*, 1990]; uvar, uvarovite [Leger *et al.*, 1990]. The dashed line was fit by eye and is provided for reference only. Note that many garnet end-members deviate from this linear trend.



**Figure 5.** Variation of the isothermal bulk modulus,  $K_{0T}$ , with the Y-O bond lengths for a variety of silicate garnets for which bond length data are available. Data are given as follows: alm, almandine [Armbruster *et al.*, 1992]; and, andradite [Armbruster and Geiger, 1993]; CaMg, Ca-Mg majorite [Hazen *et al.*, 1994b]; gro, grossular [Novak and Gibbs, 1971]; maj, majorite [Angel *et al.*, 1989]; MnMn, blythite [Arlt *et al.*, 1998]; Na-Mg, Na-Mg majorite (L. Finger, personal communication, 1998); py, pyrope [Zhang *et al.*, 1998]; ski, skiaegite [Woodland and Ross, 1994]; spess, spessartine [Novak and Gibbs, 1971]; uvar, uvarovite [Novak and Gibbs, 1971]. Sources for the bulk moduli are given in the caption to Figure 4. The data, excluding blythite and Ca-Mg majorite have been fit to a linear (solid line) and a quadratic (dashed line) function of Y-O.

room temperature. The two samples investigated here effectively lie in the middle of  $\text{Fe}_2\text{SiO}_4$ - $\text{Fe}_3\text{O}_4$  join, and it is of interest to compare their compression behavior with that of the two end-member phases, magnetite and  $\gamma$ - $\text{Fe}_2\text{SiO}_4$  spinel. Most end-member spinels, including the aluminates and silicate spinels, have bulk moduli of  $\sim 200$  GPa [e.g., Knittle, 1995]. Several static compression studies of magnetite yielded a bulk modulus of  $\sim 180$ - $185$  GPa [Mao *et al.*, 1974; Finger *et al.*, 1986; Nakagiri *et al.*, 1986], except for one anomalously low value of  $K_{0T} = 155(12)$  GPa from the work of W. A. Bassett *et al.* as reported by Wilburn and Bassett [1978]. Recent studies by Zerr *et al.* [1993] and Caldwell *et al.* [1998] on Mg-rich, Mg-Fe silicate spinel solid solutions arrived at bulk moduli of  $K_{0T} = 183$  GPa with  $K'_{0T} = 5.4$  and  $K_{0T} = 203(3)$  GPa with  $K'_{0T} = 6.3(3)$ , respectively. Thus it appears that our value for  $\text{Fe}^{3+}$ -bearing silicate spinel of  $K_{0T} = 168.9(1.2)$  GPa is significantly lower than either end-member as well as  $\text{Mg}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$  spinel solid solutions. A clear explanation for the lower bulk moduli in our solid solutions remains elusive. However, considering the crystal structure of spinel, with tetrahedra cross-linking strips of edge-sharing octahedra, it seems reasonable to expect that the compression behavior of the tetrahedral sites will have a dominant influence on the properties of the bulk crystal. The octahedral sites of our spinel solid solutions are occupied by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , which is the same as in magnetite, albeit with a different cation ratio. Since the ionic radii of octahedrally coordinated  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are similar [Shannon, 1976], it seems unlikely that additional amounts of  $\text{Fe}^{2+}$  relative to magnetite would have much effect on the com-

pression of the octahedral sites. In contrast, the tetrahedral sites in our solid solutions are occupied by essentially equal proportions of  $\text{Fe}^{3+}$  and  $\text{Si}^{4+}$ , two cations which have markedly different radii [Shannon, 1976]. It is tempting to attribute the more compressible nature of the spinel solid solutions to the presence of randomly distributed  $\text{Fe}^{3+}$  and  $\text{Si}^{4+}$  on the cross-linking tetrahedral sites. On the other hand, our value for  $K'_{0T}$ , 5.7(1.2), is consistent with most studies of magnetite and silicate spinels for which a pressure derivative of the bulk modulus is reported [Finger *et al.*, 1986; Nakagiri *et al.*, 1986; Zerr *et al.*, 1993]. A compressional study of  $\gamma$ - $\text{Fe}_2\text{SiO}_4$  spinel at  $400^\circ\text{C}$  by Plymate and Stout [1994] also yielded a comparable pressure derivative of the bulk modulus of 5.4(2.5).

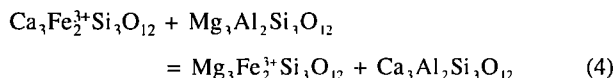
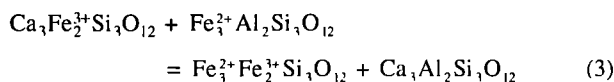
### 5.3. Petrological Considerations

The results presented here indicate that the bulk moduli of the  $\text{Fe}^{3+}$ -bearing silicate spinel and skiaegite garnet are similar. Therefore compression of garnet and spinel should not result in any change in sign of  $\Delta V$  of the breakdown reaction of skiaegite garnet (1). The fact that skiaegite remains stable in the stishovite stability field even though the  $\Delta V_{298 \text{ bar}}$  for (1) is negative must be due only to the concomitant change in the  $\Delta S$  of (1) in passing from the coesite to the stishovite stability field [e.g., Robie *et al.*, 1979].

The compression systematics for the silicate garnets depicted in Figure 5 indicate that the incorporation of  $\text{Fe}^{3+}$  and, to a lesser extent  $\text{Cr}^{3+}$  into aluminous garnets reduces their bulk moduli. The implications of this for the bulk physical prop-

erties of the Earth's mantle are limited, however, since the amount of  $\text{Fe}^{3+}$  present in mantle-derived garnets is small [Luth *et al.*, 1990; Canil and O'Neill, 1996; Woodland and Peltonen, 1999]. On the other hand, the Cr contents of garnet can be appreciable, especially in some inclusions in diamond where Cr can occupy in excess of 40% of the octahedral sites [e.g., Gurney *et al.*, 1979; Tsai *et al.*, 1979; Meyer, 1987]. These and other "subcalcic" garnets are considered to represent strongly depleted bulk compositions [e.g., Sobolev *et al.*, 1973]. According to the relation in Figure 5 the bulk modulus of garnet in such depleted portions of the Earth's mantle should be on the order of several percent lower compared to the Al-rich garnets in "normal" fertile mantle peridotite.

Estimates of the oxygen fugacity of deep mantle samples can be made via application of heterogeneous equilibria, such as (2). Our data on the elastic properties of skiaegite garnet together with those for fayalite and ferrosilite reported by Fei *et al.* [1991] allow a more accurate computation of the oxygen fugacity recorded in these samples. However, the lack of thermal expansion data for skiaegite and of the temperature derivative of the bulk modulus for skiaegite and other garnet components still does not permit full assessment of the pressure and temperature effects on the  $\Delta V$  of (2). The fact that natural garnet is a complex multicomponent solid solution means that internal equilibrium between various components must be accounted for when deriving the activity coefficient for the skiaegite component. This is accomplished by considering the reciprocal reactions between the garnet components [e.g., Wood and Nicholls, 1978], which have the following form:



with analogous equilibria involving the Cr-bearing components. The value of the free energy change of (3)  $\Delta G^\circ_3$  was reported by Woodland and O'Neill [1993] to be  $\Delta G^\circ_3$  (kJ mol<sup>-1</sup>) = 40.2 - 0.7P (GPa), and, based upon the crystal chemical similarities of Mg and  $\text{Fe}^{2+}$ , they considered  $\Delta G^\circ_4$  to have a similar value. Recent data on the molar volumes of grossular [Ganguly *et al.*, 1993] and andradite [Woodland and O'Neill, 1995], together with data from Woodland and O'Neill [1993] for skiaegite and almandine, indicate that the pressure dependence of  $\Delta G^\circ_3$  is somewhat smaller than that reported by Woodland and O'Neill [1993] and that value of  $\Delta V^\circ_{298,1\text{bar}} = -0.05 \text{ J bar}^{-1}$  is more reasonable for (3). Applying our compression data for skiaegite along with literature data for grossular [Olijnyk *et al.*, 1991], almandine [Yagi *et al.*, 1987] and andradite [Hazen and Finger, 1989] reveals that the pressure dependence of  $\Delta G^\circ_3$  becomes progressively smaller with increasing pressure. For example,  $\Delta V^\circ_{298} = -0.03 \text{ J bar}^{-1}$  at 6.0 GPa, which yields a contribution to  $\Delta G^\circ_3$  from the  $\Delta VP$  term of  $-1800 \text{ J mol}^{-1}$  compared with  $-4200 \text{ J mol}^{-1}$  calculated from the original expression given by Woodland and O'Neill [1993] at this pressure. This has a direct effect on the value of the activity coefficient for skiaegite that is applied in the redox equilibrium (2). Taking the subset of samples from Luth *et al.* [1990] and Woodland and Peltonen [1999] that equilibrated at pressures of 5.0-6.5 GPa, we find that the calculated log  $f\text{O}_2$  changes by +0.3 to -0.8 log units in response to explicitly accounting for the compression be-

havior of skiaegite, fayalite, and ferrosilite compared with the case when  $\Delta V^\circ_{298,1\text{bar}}$  is employed. Considering that the estimated uncertainties in the  $f\text{O}_2$  values are on the order of  $\pm 0.6$  log units [Gudmundsson and Wood, 1995], these observed changes should not be neglected. The resulting  $f\text{O}_2$  values range from -3.6 to -4.4 log units relative to the fayalite-magnetite-quartz reference equilibrium, which are just above the conditions for Fe metal saturation at this pressure [see Woodland and Peltonen, 1999]. The lack of a systematic shift in calculated  $f\text{O}_2$  is due to the fact that the activity of skiaegite at high pressures is a function not only of the molar volumes of skiaegite and other garnet components present in the reciprocal reactions (i.e., equilibria (3) and (4)) but also of the bulk composition of the garnet in the individual samples. This non-systematic shift makes it important to include the effect of compression on the molar volume of garnet when computing  $f\text{O}_2$  values for natural samples from the deep mantle. However, it should be reiterated that these calculations were performed without accounting for the effects of the thermal expansion on the molar volumes of the participating phases and phase components. Since thermal expansion and compression generally have compensating effects on the molar volume, the actual molar volumes at  $P$  and  $T$  could produce less of a change in calculated  $f\text{O}_2$  than that described above. An additional consideration is our observation of a lower bulk modulus for the spinel solid solutions relative to the corresponding end-member spinels. This raises the question of how to accurately predict the elastic properties of natural phases that are often complex solid solutions.

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## References

- Allan, D., R. Miletich, and R. J. Angel, A diamond-anvil cell for single-crystal X-ray diffraction studies to pressures in excess of 10 GPa, *Rev. Sci. Instrum.*, **67**, 840-842, 1996.
- Anderson, O. L., Simple solid-state equations for materials of terrestrial planet interiors, in *The Physics of the Planets*, edited by S. K. Runcorn, pp. 27-60, John Wiley, New York, 1988.
- Anderson, O. L., *Equations of State of Solids for Geophysics and Ceramic Sciences*, 405 pp., Oxford Univ. Press, New York, 1995.
- Angel, R. J., L. W. Finger, R. M. Hazen, M. Kanzaki, D. J. Weidner, R. C. Liebermann, and D. R. Velten, Structure and twinning of single-crystal  $\text{MgSiO}_3$  garnet synthesized at 17 GPa and 1800°C, *Am. Mineral.*, **74**, 509-512, 1989.
- Angel, R. J., D. Allan, R. Miletich, and L. Finger, The use of quartz as an internal pressure standard in high-pressure crystallography, *J. Appl. Crystallogr.*, **30**, 461-466, 1997.
- Arlt, T., T. Armbruster, R. Miletich, P. Ulmer, and T. Peters, High-pressure single crystals synthesis, structure, and compressibility of the garnet  $\text{Mn}^{3+}\text{Mn}^{2+}\text{Si}_3\text{O}_{12}$ , *Phys. Chem. Miner.*, **26**, 100-106, 1998.
- Armbruster, T., and C. A. Geiger, Andradite crystal chemistry, dynamic X-site disorder, and structural strain in silicate garnets, *Eur. J. Mineral.*, **5**, 59-71, 1993.
- Armbruster, T., C. A. Geiger, and G. A. Lager, Single crystal X-ray structure study of synthetic pyrope almandine garnets at 100 and 298 K, *Am. Mineral.*, **77**, 512-521, 1992.
- Bass, J. D., Elasticity of grossular and spessartite garnets by Brillouin spectroscopy, *J. Geophys. Res.*, **94**, 7621-7628, 1989.
- Bina, C. R., and B. J. Wood, Olivine-spinel transitions: Experimental and thermodynamic constraints and implications for the nature of the 400-km seismic discontinuity, *J. Geophys. Res.*, **92**, 4853-4866, 1987.
- Birch, F., Finite elastic strain of cubic crystals, *Phys. Rev.*, **71**, 809-824, 1947.



- Caldwell, W. A., S. V. Sinogeikin, J. D. Bass, A. Kavner, J. H. Nguyen, M. Kruger, and R. Jeanloz, Compressibility of natural  $(\text{Mg},\text{Fe})_2\text{SiO}_4$   $\gamma$ -spinel at transition zone pressures (abstract), *Eos Trans. AGU*, 79(45), Fall Meet. Suppl., F866-F867, 1998.
- Canil, D., and H. St.C. O'Neill, Distribution of ferric iron in some upper mantle assemblages, *J. Petrol.*, 37, 609-635, 1996.
- Canil, D., H. St.C. O'Neill, D. G. Pearson, R. Rudnick, W. F. McDonough, and D. A. Carswell, Ferric iron in peridotites and mantle oxidation states, *Earth Planet. Sci. Lett.*, 123, 205-220, 1994.
- Fei, Y., H.-K. Mao, and B. O. Mysen, Experimental determination of element partitioning and calculation of phase relations in the  $\text{MgO}$ - $\text{FeO}$ - $\text{SiO}_2$  system at high pressure and high temperature, *J. Geophys. Res.*, 96, 2157-2169, 1991.
- Finger, L. W., R. M. Hazen, and A. M. Hofmeister, High-pressure crystal chemistry of spinel ( $\text{MgAl}_2\text{O}_4$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ): Comparisons with silicate spinels, *Phys. Chem. Miner.*, 13, 215-220, 1986.
- Ganguly, J., W. Cheng, and H. St.C. O'Neill, Syntheses, volume, and structural changes of garnets in the pyrope-grossular join: Implications for stability and mixing properties, *Am. Mineral.*, 78, 583-593, 1993.
- Gudmundsson, G., and B. J. Wood, Experimental tests of garnet peridotite oxygen barometry, *Contrib. Mineral. Petrol.*, 119, 56-67, 1995.
- Gurney, J. J., J. W. Harris, and R. S. Rickard, Silicate and oxide inclusions in diamonds from the Finsch Kimberlite pipe, in *Kimberlites, Diatremes, and Diamonds: Their Geology, Petrology, and Geochemistry*, vol. 1, edited by H. O. A. Meyer and F. R. Boyd, pp. 1-15, AGU, Washington, D. C., 1979.
- Hammersley, A. P., FIT2D: An introduction and overview, *ESRF Internal Rep. ESRF97HA02T*, Eur. Synchrotron Radiat. Facil., Grenoble, France, 1997.
- Hammersley, A. P., S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Häusermann, Two-dimensional detector software: From real detector to idealized image or two-theta scan, *High Pressure Res.*, 14, 235-248, 1996.
- Hammonds, K. D., A. Bosenick, M. T. Dove, and V. Heine, Rigid unit modes in crystal structures with octahedrally coordinated atoms, *Am. Mineral.*, 83, 476-479, 1998.
- Hazen, R. M., and L. W. Finger, High-pressure crystal chemistry of andradite and pyrope: Revised procedures for high-pressure diffraction experiments, *Am. Mineral.*, 74, 352-359, 1989.
- Hazen, R. M., R. T. Downs, P. G. Conrad, L. W. Finger, and T. Gasparik, Comparative compressibilities of majorite-type garnets, *Phys. Chem. Miner.*, 21, 344-349, 1994a.
- Hazen, R. M., R. T. Downs, L. W. Finger, P. G. Conrad, and T. Gasparik, Crystal chemistry of Ca-bearing majorite, *Am. Mineral.*, 79, 581-584, 1994b.
- Irfune, T., and A. E. Ringwood, Phase transformations in primitive MORB and pyrolyte compositions to 25 GPa and some geophysical implications, in *High Pressure Research in Mineral Physics*, Geophys. Monogr. Ser. vol. 39, edited by M. Manghnani, and Y. Syono, pp. 231-242, AGU, Washington, D. C., 1987.
- Isaak, D. G., O. L. Anderson, and H. Oda, High-temperature thermal expansion and elasticity of calcium-rich garnets, *Phys. Chem. Miner.*, 19, 106-120, 1992.
- Katsura, T., and E. Ito, The system  $\text{Mg}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$  at high pressures and temperatures: Precise determination of stabilities of olivine, modified spinel, and spinel, *J. Geophys. Res.*, 94, 15,663-15,670, 1989.
- Knittle, E., Static compression measurements of equations of state, in *Mineral Physics and Crystallography: A Handbook of Physical Constants*, AGU Ref. Shelf, vol. 2, edited by T. J. Ahrens, pp. 98-142, AGU, Washington, D. C., 1995.
- Larson, A. C., and R. B. Von Dreele, GSAS manual, Rep. LAUR 86-748, Los Alamos Natl. Lab., Los Alamos, N. M., 1988.
- le Bail, A., Extracting structure factors from powder diffraction data by iterative full pattern profile fitting, in *Accuracy in Powder Diffraction II*, edited by E. Prince and J. K. Staljek, NIST Spec. Publ., 846, 213, 1992.
- Leger, J. M., A. M. Redon, and C. Chateau, Compressions of synthetic pyrope, spessartine and uvarovite garnets up to 25 GPa, *Phys. Chem. Miner.*, 17, 161-167, 1990.
- Luth, R. W., D. Virgo, F. R. Boyd, and B. J. Wood, Ferric iron in mantle-derived garnets, implications for thermometry and for the oxidation state of the mantle, *Contrib. Mineral. Petrol.*, 104, 56-72, 1990.
- Mao, H.-K., T. Takahashi, W. A. Bassett, G. L. Kinsland, and L. Merrill, Isothermal compression of magnetite up to 320 kbar and pressure-induced phase transformation, *J. Geophys. Res.*, 79, 1165-1170, 1974.
- McCammon, C. A., Methods for determination of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in microscopic samples, in *Proceedings of the VIIIth International Kimberlite Conference, P. H. Nixon Volume*, edited by J. J. Gurney, J. L. Gurney, M. D. Pascoe and S. H. Richardson, in press, RedRoof Design, Cape Town, South Africa, 1999.
- McCammon, C. A., V. Chaskar, and G. G. Richards, A technique for spatially resolved Mössbauer spectroscopy applied to quenched metallurgical slags, *Meas. Sci. Technol.*, 2, 657-662, 1991.
- Meyer, H. O. A., Inclusions in diamond, in *Mantle Xenoliths*, edited by P. H. Nixon, pp. 501-522, John Wiley, New York, 1987.
- Nakagiri, N., M. H. Manghnani, L. C. Ming, and S. Kimura, Crystal structure of magnetite under pressure, *Phys. Chem. Miner.*, 13, 238-244, 1986.
- Novak, G. A., and G. V. Gibbs, The crystal chemistry of the silicate garnets, *Am. Mineral.*, 56, 791-825, 1971.
- Olhnyk, H., E. Paris, C. A. Geiger, and G. A. Lager, Compressional study of katoite [ $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H})_3$ ] and grossular garnet, *J. Geophys. Res.*, 96, 14,313-14,318, 1991.
- O'Neill, B., and R. Jeanloz,  $\text{MgSiO}_3$ - $\text{FeSiO}_3$ - $\text{Al}_2\text{O}_3$  in the Earth's lower mantle: Perovskite and garnet at 1200 km depth, *J. Geophys. Res.*, 99, 19,901-19,915, 1994.
- O'Neill, H. St.C., D. C. Rubie, D. Canil, C. A. Geiger, C. R. Ross II, F. Seifert, and A. B. Woodland, Ferric iron in the upper mantle and in transition zone assemblages: Implications for relative oxygen fugacities in the mantle, in *Evolution of the Earth and Planets, Geophys. Monogr. Ser.*, vol. 74, edited by E. Takahashi, R. Jeanloz, and D. Rubie, pp. 73-88, AGU, Washington, D. C., 1993.
- Plymate, T. G., and J. H. Stout, Pressure-volume-temperature behavior of  $\gamma$ - $\text{Fe}_2\text{SiO}_4$  (spinel) based upon static compression measurements at 400°C, *Phys. Chem. Miner.*, 21, 413-420, 1994.
- Poirier, J. P., *Introduction to the Physics of the Earth's Interior*, 264 pp., Cambridge Univ. Press, New York, 1991.
- Robie, R. A., B. S. Hemingway, and J. R. Fisher, Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar ( $10^5$  Pascal) pressure and at higher temperatures, *U.S. Geol. Surv. Bull.*, 1452, 1979.
- Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr., Sect. A Cryst. Phys. Diff. Theor. Gen. Crystallogr.*, 32, 751-767, 1976.
- Sobolev, N. V., Yu. G. Lavrent'yev, N. Pokhilenko, and L. V. Usova, Chrome-rich garnets from kimberlites of Yakatia and their paragenesis, *Contrib. Mineral. Petrol.*, 40, 39-52, 1973.
- Tsai, H.-M., H. O. A. Meyer, J. Moreau, and H. J. Milledge, Mineral inclusions in diamond: Premier, Jagersfontein and Finsch kimberlites, South Africa, and Williamson Mine, Tanzania, in *Kimberlites, Diatremes, and Diamonds: Their Geology, Petrology, and Geochemistry*, vol. 1, edited by H. O. A. Meyer and F. R. Boyd, pp. 16-26, AGU, Washington, D. C., 1979.
- van Aken, P. A., B. Liebscher, and V. J. Strysa, Quantitative determination of iron oxidation states in minerals using Fe  $L_{2,3}$ -edge electron energy-loss near-edge structure spectroscopy, *Phys. Chem. Miner.*, 25, 323-327, 1998.
- Wilburn, D. R., and W. A. Bassett, Hydrostatic compression of iron and related compounds: An overview, *Am. Mineral.*, 63, 591-596, 1978.
- Wood, B. J., and J. Nicholls, The thermodynamic properties of reciprocal solid solutions, *Contrib. Mineral. Petrol.*, 66, 389-400, 1978.
- Woodland, A. B., and H. St.C. O'Neill, Synthesis and stability of  $\text{Fe}^{3+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  garnet and phase relations with  $\text{Fe}_3\text{Al}_2\text{Si}_4\text{O}_{12}$  -  $\text{Fe}^{3+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  solutions, *Am. Mineral.*, 78, 1000-1013, 1993.
- Woodland, A. B., and H. St.C. O'Neill, Phase relations between  $\text{Ca}_2\text{Fe}^{3+}\text{Si}_2\text{O}_{12}$  -  $\text{Fe}^{3+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  garnet and  $\text{CaFeSi}_2\text{O}_6$  -  $\text{Fe}_2\text{Si}_2\text{O}_6$  pyroxene solid solutions, *Contrib. Mineral. Petrol.*, 121, 87-98, 1995.
- Woodland, A. B., and P. Peltonen, Ferric iron contents of garnet and clinopyroxene and estimated oxygen fugacities of peridotite xenoliths from the Eastern Finland Kimberlite Province, in *Proceedings of the VIIIth International Kimberlite Conference, P. H. Nixon Volume*, edited by J. J. Gurney, J. L. Gurney, M. D. Pascoe and S. H. Richardson, in press, RedRoof Design, Cape Town, South Africa, 1999.
- Woodland, A. B., and C. R. Ross II, A crystallographic and Mössbauer spectroscopy study of  $\text{Fe}_3\text{Al}_2\text{Si}_4\text{O}_{12}$  -  $\text{Fe}^{3+}\text{Fe}^{2+}\text{Si}_3\text{O}_{12}$  (almandine-

- skiagite) and  $\text{Ca}_3\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$  -  $\text{Fe}_2^{3+}\text{Fe}_2^{2+}\text{Si}_3\text{O}_{12}$  (andradite-skiagite) garnet solid solutions, *Phys. Chem. Miner.*, 21, 117-132, 1994.
- Yagi, T., M. Akaogi, O. Shimomura, H. Tamai, and S. Akimoto, High pressure and high temperature equations of state of majorite, in *High-Pressure Research in Mineral Physics*, edited by M. H. Manghnani and Y. Syono, pp. 141-147, Terra Sci., Tokyo, 1987.
- Yagi, T., B. O'Neill, T. Kondo, N. Miyajima, and K. Fujino, Post garnet high-pressure transition: Effect of heterogeneous laser heating and introduction of some new techniques, *Eur. J. Mineral.*, 9, 301-310, 1997.
- Zerr, A., H. Reichmann, H. Euler, and R. Boehler, Hydrostatic compression of  $\gamma\text{-(Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$  to 50.0 GPa, *Phys. Chem. Miner.*, 19, 507-509, 1993.
- Zhang, L., H. Ahsbahs, and A. Kutoglu, Hydrostatic compression and crystal structure of pyrope to 33 GPa, *Phys. Chem. Miner.*, 25, 301-307, 1998.
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