

## Comparative Compressibilities of Majorite-Type Garnets

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Received March 14, 1994/Revised, accepted June 6, 1994

**Abstract.** Relative compressibilities of five silicate garnets were determined by single-crystal x-ray diffraction on crystals grouped in the same high-pressure mount. The specimens include a natural pyrope [(Mg<sub>2.84</sub>Fe<sub>0.10</sub>Ca<sub>0.06</sub>)Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>], and four synthetic specimens with octahedrally-coordinated silicon: majorite [Mg<sub>3</sub>(MgSi)Si<sub>3</sub>O<sub>12</sub>], calcium-bearing majorite [(Ca<sub>0.49</sub>Mg<sub>2.51</sub>)(MgSi)Si<sub>3</sub>O<sub>12</sub>], sodium majorite [(Na<sub>1.88</sub>Mg<sub>0.12</sub>)(Mg<sub>0.06</sub>Si<sub>1.94</sub>)Si<sub>3</sub>O<sub>12</sub>], and an intermediate composition [(Na<sub>0.37</sub>Mg<sub>2.48</sub>)(Mg<sub>0.13</sub>Al<sub>1.07</sub>Si<sub>0.80</sub>)Si<sub>3</sub>O<sub>12</sub>]. Small differences in the compressibilities of these crystals are revealed because they are subjected simultaneously to the same pressure. Bulk-moduli of the garnets range from 164.8 ± 2.3 GPa for calcium majorite to 191.5 ± 2.5 GPa for sodium majorite, assuming  $K' = 4$ . Two factors, molar volume and octahedral cation valence, appear to control garnet compression.

### Introduction

Equation-of-state data play a central role in efforts to describe the layered mineralogical structure and convective dynamics of the earth's deep interior. Experiments defining the molar volume as a function of pressure clarify the nature and character of phase transitions that may occur in the crust and mantle and, furthermore, provide valuable constraints on models of bonding in minerals.

High-pressure studies of compositionally-similar minerals are often hampered by the difficulty of calibrating pressure. Unit-cell parameters, for example, may be measured to a few parts in 10<sup>4</sup> by routine single-crystal x-ray diffraction procedures, but pressure measurements are limited to no better than about ±1 percent below 10 GPa. Resolving small differences in the compressibilities of two similar specimens is thus impossible using conventional methods, in which two or more crystals are studied in separate experiments.

This experimental difficulty has been overcome by preparing a high-pressure mount with several crystals,

all compressed by the same hydrostatic pressure medium (Hazen 1981, 1993). Relative, rather than absolute, volumes at several pressures thus provide a precise measure of the relative compressibility:

$$\beta_1/\beta_2 \approx [(V_p/V_0)_1 - 1]/[(V_p/V_0)_2 - 1],$$

where  $\beta_1$  and  $\beta_2$  are compressibilities of two different crystals, and  $V_0$  and  $V_p$  are their unit-cell volumes measured at room pressure and high pressure. Small compressibility differences in compositionally-similar suites of wustites (Hazen 1981), feldspars (Angel et al. 1988), pyroxenes (McCormick et al. 1989), wadsleyites (Hazen et al. 1990), and silicate spinels (Hazen 1993) have thus been documented, even though individual compressibilities calculated from the same pressure-volume data may be in error by several percent.

In this study we describe the compression behavior of high-pressure garnets containing octahedrally-coordinated silicon – minerals assumed to comprise as much as half of the earth's transition zone (Ita and Stixrude 1992). Most garnets from the crust have cubic symmetry with the general formula  $A_3^{2+}B_3^{3+}Si_3O_{12}$ , where eight-coordinated  $A$  is usually Mg, Fe, Mn, or Ca, and six-coordinated  $B$  is Al, Fe, or Cr. High-pressure silicate garnets may incorporate six-coordinated silicon and thus approach a pyroxene composition, such as the synthetic garnet MnSiO<sub>3</sub>, which corresponds structurally to Mn<sub>3</sub>(MnSi)Si<sub>3</sub>O<sub>12</sub> (Fujino et al. 1986). This garnet displays tetragonal symmetry because Mn and Si order on two symmetrically distinct octahedral sites (Ringwood and Major 1967; Prewitt and Sleight (1969).

Smith and Mason (1970) described a natural garnet with more than 3 silicons per 12 oxygens from the Coorara meteorite; they named the new mineral majorite. Kato and Kumazawa (1985) synthesized end-member MgSiO<sub>3</sub> majorite, and single-crystal samples of MnSiO<sub>3</sub> (Fujino et al. 1986) and MgSiO<sub>3</sub> (Angel et al. 1989) were examined in subsequent detailed structure studies.

Work of Gasparik (1989, 1990, 1992) has revealed a broad stability range and unexpected compositional complexity in high-pressure garnets in the Na<sub>2</sub>O–

**Table 1.** Unit-cell parameters versus pressure and equation-of-state parameters for five silicate garnets

	Na-majorite	Intermediate	Pyrope	Majorite	Ca-majorite
Pressure (GPa)	a-cell (Å)				
0.00	11.4104(11)	11.4610(11)	11.4715(17)	11.5085(8)	11.5816(9)
0.39 <sup>a</sup>	11.4015(8)	11.4524(9)	11.4612(8)	11.5009(22)	11.5783(12)
0.99	11.3895(12)	11.4390(10)	11.4488(15)	11.4896(15)	11.5664(24)
1.62	11.3769(8)	11.4257(12)	11.4361(9)	11.4755(22)	11.5490(20)
2.23	11.3681(10)	11.4137(16)	11.4215(22)	11.4651(18)	11.5363(36)
2.42	11.3643(12)	11.4100(11)	11.4205(14)	11.4631(16)	11.5321(25)
3.24	11.3484(12)	11.3942(9)	11.4020(11)	11.4413(17)	11.5147(20)
4.10	11.3317(11)	11.3751(9)	11.3837(8) <sup>b</sup>	11.4238(13)	11.5010(26)
4.72	11.3201(10)	11.3631(14)	11.3715(14) <sup>b</sup>	11.4115(19)	11.4838(25)
Pressure (GPa)	c-cell (Å)				
0.00				11.4784(14)	11.5288(13)
0.39 <sup>a</sup>				11.4921(26)	11.5180(15)
0.99				11.4834(17)	11.4957(31)
1.62				11.4680(26)	11.4840(24)
2.23				11.4520(23)	11.4691(37)
2.42				11.4500(21)	11.4712(37)
3.24				11.4343(34)	11.4496(26)
4.10				11.4127(19)	11.4268(64)
4.72				11.3991(27)	11.4129(21)
Pressure (GPa)	Volume (Å <sup>3</sup> )				
0.00	1485.60(41)	1505.44(44)	1509.58(68)	1520.25(27)	1546.40(30)
0.39 <sup>a</sup>	1482.12(31)	1502.06(37)	1505.54(33)	1520.07(61)	1544.07(37)
0.99	1477.43(48)	1496.81(41)	1500.67(57)	1515.94(43)	1537.91(74)
1.62	1472.55(33)	1491.57(48)	1495.66(37)	1510.18(64)	1531.72(62)
2.23	1469.13(38)	1486.87(62)	1489.95(88)	1505.36(51)	1526.39(105)
2.42	1467.67(45)	1485.44(42)	1489.53(55)	1504.56(48)	1525.55(80)
3.24	1461.53(47)	1479.29(35)	1482.32(44)	1496.79(60)	1518.06(62)
4.10	1455.06(42)	1471.84(36)	1475.19(33)	1489.41(37)	1511.45(109)
4.72	1450.59(37)	1467.20(52)	1470.45(54)	1484.42(56)	1505.11(69)
Equation of State					
V <sub>0</sub> <sup>c</sup>	1485.5(3)	1505.4(2)	1509.3(3)	1524.6(5)	1547.0(3)
K	191.5(25)	175.1(13)	173.7(32)	169.3(34)	164.8(23)

<sup>a</sup> This pressure was determined from the Birch-Murnaghan equation of state for the intermediate structure

<sup>b</sup> These cell parameters were obtained as the cube root of the cell volumes determined at their respective pressures

<sup>c</sup> In order to determine the Birch-Murnaghan equations of state, the value for K' was fixed at 4.0, while the values of K and V<sub>0</sub> were varied

MgO–CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (NMCAS) system. Gasparik documented many high-silicon garnets, including a sample close to the end-member composition (Na<sub>2</sub>Mg)Si<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> [Namaj], intermediate compositions in the Pyrope-Majorite-Namaj ternary, and specimens on the majorite-CaSiO<sub>3</sub> join.

This study, part of an ongoing effort to characterize specimens from Gasparik's synthesis program, documents the comparative compressibility of five garnets from the NMCAS system.

## Experimental

### Specimen Descriptions

We optically examined numerous crystals from each of twelve garnet-bearing synthesis runs and selected single crystals that appeared uniform and isotropic. Suitable crystals were subsequently studied by single-crystal x-ray precession photography. Promising crystals

were further characterized with a Rigaku AFC-5 four-circle diffractometer equipped with a rotating-anode generator operated at 45 kV and 180 mA. Approximately 90 percent of the crystals examined by these x-ray techniques proved too poorly crystallized to employ in determining precise lattice parameters. They displayed broad and multiple diffraction peaks that result, in part, from twinning and multiple crystallites in similar orientations. Electron microprobe analysis, furthermore, revealed significant compositional zoning and mottling in many of these synthetic garnets samples – characteristics that may explain the extreme peak broadening observed by the x-ray techniques.

Five crystals, representing a range of available compositions, were selected for further study.

1. Natural pyrope, [(Mg<sub>2.84</sub>Fe<sub>0.10</sub>Ca<sub>0.06</sub>)Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, cubic space group *Ia3d*]: Natural pyrope (designated PYR) was provided by J.D. Bass. The same material was used by O'Neill et al. (1991) in their study of pyrope elastic properties, and by Rossman et al. (1989) in their study of hydrous garnets. We broke an angular fragment, approximately 50 × 60 × 80 μm from a clear, colorless crystal (sample GRR1266) from the Dora Maira Massif, Italy as described by Rossman et al. (1989), who note slight Fe–Mg zoning in this specimen. We mounted our fragment in an epoxy cement,

polished one surface, and determined the composition with a JEOL JXA-8900 electron microprobe. Our sample has slightly less Fe than the specimen measured by O'Neill et al. (1991). The crystal after removal from the microprobe mount measured approximately  $40 \times 50 \times 70 \mu\text{m}$ .

2. Majorite,  $[\text{Mg}_3(\text{MgSi})\text{Si}_3\text{O}_{12}]$ , tetragonal space group  $I4_1/a$ : We used the same single crystal of majorite (designated MAJ) described by Angel et al. (1989). The clear, colorless  $30 \times 40 \times 60 \mu\text{m}$  crystal was synthesized in a 2000-ton split-sphere apparatus (USSA-2000) at approximately 17 GPa and  $1700^\circ\text{C}$ . The 10-minute run used enstatite glass starting material plus PbO flux. Angel et al. (1989) report that MAJ is tetragonal, space group  $I4_1/a$ , with pervasive twinning by reflection on (110).

3. Calcium-bearing majorite  $[(\text{Ca}_{0.49}\text{Mg}_{2.51})(\text{MgSi})\text{Si}_3\text{O}_{12}]$ , tetragonal space group  $I4_1/a$ : We used the same calcium majorite single crystal (designated CAMAJ) studied by Hazen et al. (1994). The  $30 \times 40 \times 70 \mu\text{m}$  clear and colorless crystal came from SUNY run 868 (Gasparik 1990), heated for 4 hours to maximum temperature  $2050^\circ\text{C}$  at 18.2 GPa in the USSA-2000 apparatus. Structure analysis of CAMAJ by Hazen et al. (1994) revealed complete Mg–Si ordering on two octahedral sites, as well as Ca–Mg ordering on two dodecahedral sites. This tetragonal garnet displays twinning by reflection on (110), as observed in majorite.

4. Sodium majorite,  $[(\text{Na}_{1.88}\text{Mg}_{1.12})(\text{Mg}_{0.06}\text{Si}_{1.94})\text{Si}_3\text{O}_{12}]$ , cubic space group  $Ia3d$ : We selected a single crystal of sodium majorite (hereafter NAMAJ) from SUNY run TG835, the same sample described by Pacalo et al. (1992) and Pacalo and Gasparik (1994). We used an optically isotropic, clear, colorless  $40 \times 40 \times 100 \mu\text{m}$  single crystal, synthesized at 16.5 GPa and  $1600^\circ\text{C}$ .

5. Intermediate composition,  $[(\text{Na}_{0.37}\text{Mg}_{2.48})(\text{Mg}_{0.13}\text{Al}_{1.07}\text{Si}_{0.80})\text{Si}_3\text{O}_{12}]$ , cubic space group  $Ia3d$ : A single crystal of a ternary garnet in the system PY-MAJ-NAMAJ (hereafter INTER) from SUNY run 997 (Gasparik 1992) was selected from material synthesized at 14 GPa and  $2250^\circ\text{C}$  for 29 minutes. The clear, colorless, rounded crystal, approximately  $40 \times 50 \times 50 \mu\text{m}$ , was mounted in an epoxy cement, carefully polished, and studied with a JEOL JXA-8900 electron microprobe analysis. The  $30 \times 30 \mu\text{m}$  polished area of the garnet was homogeneous within the sensitivity of the instrument; the average of eight point analyses yields the structural equation noted above. The final size of the crystal, after removal from the microprobe mount, was approximately  $30 \times 40 \times 50 \mu\text{m}$ .

#### High-Pressure X-ray Diffraction

The five garnet crystals described above were mounted in a single high-pressure mount. We used a Merrill-Bassett diamond anvil cell with 0.75-mm anvil faces, an Inconel 750X gasket with 0.45-mm hole, and a 4:1 methanol:ethanol pressure fluid. The position  $R_1$  and  $R_2$  fluorescence lines from ruby chips approximately  $10 \mu\text{m}$  in diameter provided an internal pressure calibration, as described by Hazen and Finger (1982).

The sequence of experimental pressures was 0.39, 1.62, 0.99, 3.24, 2.42, 4.64, 4.10, 2.23 GPa, and room pressure (in the cell). All pressures (except for the 0.39 GPa value; see below) were measured before and after each experiment; these two values agreed within the estimated pressure uncertainty ( $\pm 0.05$  GPa) except in the case of the highest-pressure experiments. The initial pressure reading for this experiment was 4.96 GPa, but the cell relaxed during the next 24 hours, after which x-ray measurements commenced. The first pressure, estimated to be 0.39 GPa, was initially assumed to be close to room pressure because it represented the lowest pressure at which all air bubbles disappeared. The measured unit-cell volumes of the five garnets, however, reveal that the pressure was significant. The 0.39 GPa estimate is based on an interpolation from pressure-volume data for INTER, which has the best constrained equation of state of the five garnets studied.

Unit-cell parameters were determined on a Picker automated four-circle diffractometer from the centering of as many as 27 reflections from each crystal ( $14^\circ < 2\theta < 29^\circ$ ) at eight positions, as described by Hamilton (1974), and adapted for high-pressure stu-

dies by King and Finger (1979). All measured reflections were from cubic classes (004), (024), (444), (046), (246), and (008). Unit-cell parameters were calculated without constraints (i.e., as triclinic); values conformed to the appropriate cubic (PYR, INTER, and NAMAJ) or tetragonal (MAJ and CAMAJ) dimensions except for PYR at the two highest pressures. PYR was the thickest crystal, and at the highest pressure it became slightly strained between the diamond anvils. The reported unit-cell edge,  $a$  in Table 1, was calculated as the cube root of the observed unit-cell volume at those two pressures.

Each experiment began and ended with measurement of unit-cell parameters for NAMAJ, which displayed the strongest diffraction peaks. At all pressures these before and after measurements agreed within one estimated standard deviation, providing further evidence that pressures remained constant throughout each experiment. Unit-cell parameters and volumes for the five garnet crystals at several pressures appear in Table 1.

## Discussion and Conclusions

### Garnet Equations of State

Pressure-volume data may be analyzed in several ways. All P-V data may be represented on a graph of pressure versus  $V/V_0$  (Fig. 1). From this plot it appears that garnet compressibility increases in the order: NAMAJ < INTER  $\leq$  PYR < MAJ < CAMAJ. The P-V results for each garnet crystal may also be fit to a second-order Birch-Murnaghan equation of state for which the pressure derivative of bulk modulus,  $K'$ , is fixed to a value of 4, while bulk modulus,  $K$ , and room-pressure unit cell volume,  $V_0$ , are varied. The total compression of garnet between room pressure and 5 GPa is only about 2 percent – not enough of a change to derive a meaningful value of  $K'$ . If a value of  $K'$  closer to 5 is more appropriate, as suggested by Webb (1989), Duffy and Anderson (1989), and Rigden et al. (1994), then bulk moduli reported here would be approximately 3 to 4 GPa smaller.

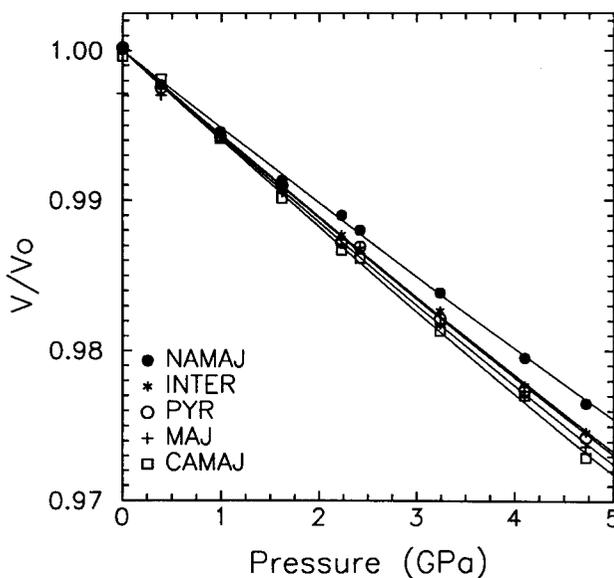
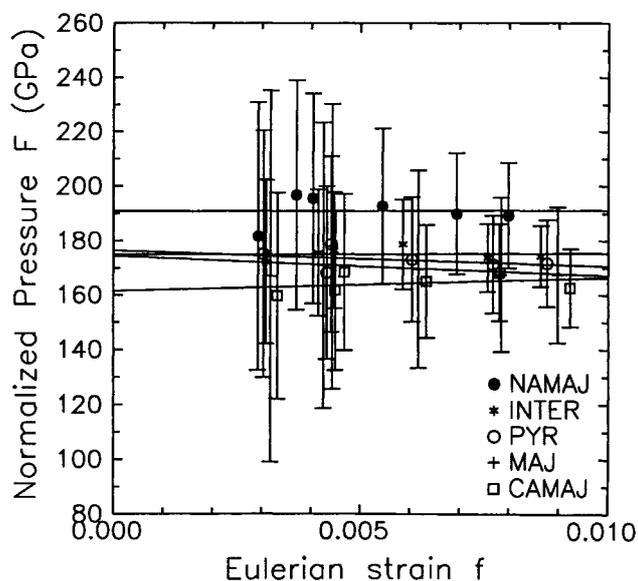


Fig. 1. Relative volumes ( $V/V_0$ ) versus pressure (in GPa) for five compositions of silicate garnet

Bulk moduli of the five garnets (Table 1) range from  $164.8 \pm 2.3$  GPa for CAMAJ ( $V_0 = 1547.0 \pm 0.3 \text{ \AA}^3$ ) to  $191.5 \pm 2.5$  GPa for NAMAJ ( $V_0 = 1485.5 \pm 0.3 \text{ \AA}^3$ ). Samples PYR, MAJ, and INTER have intermediate values of  $K$  and  $V_0$ , and an approximately inverse relationship is observed between unit-cell volumes and bulk moduli. Note that the two tetragonal specimens, MAJ and CAMAJ, display nearly isotropic compression (Table 1), although pervasive twinning in these samples decreased our ability to resolve compression anisotropies.

These values are, for the most part, consistent with previous measurements of garnet bulk moduli. We observe pyrope bulk modulus of  $174 \pm 3$  GPa, compared to a value of 173 GPa reported for the same specimen by O'Neill et al. (1991). Similarly, we observe majorite bulk modulus of  $169 \pm 3$  GPa, compared to values of approximately 170 GPa extrapolated from data of Yeganeh-Haeri et al. (1990), and  $161 \pm 4$  GPa for MAJ powder by Yagi et al. (1992). Equation-of-state parameters have not been reported previously for garnets near compositions CAMAJ and INTER.

Our value of  $191.5 \pm 2.5$  GPa for the NAMAJ bulk modulus differs significantly from the previously reported 173.5 GPa bulk modulus of NAMAJ (Pacalo et al. 1992) based on Brillouin spectroscopy. Our bulk modulus is greater than for any other silicate garnet, though it is consistent with crystal chemical arguments for this unique variant with all octahedral sites occupied by silicon (see below). The discrepancy between the two studies may arise, in part, from our use of  $K' = 4$ . A  $K'$  greater than 5 would reduce our bulk modulus to less than 190 GPa.



**Fig. 2.** A plot of Eulerian strain,  $f$ , versus Birch's normalized stress,  $F$ , for five silicate garnet compositions provides equation-of-state information. Lines are weighted linear regression fits to  $F-f$  data. The zero-pressure bulk modulus is given by the  $F$ -axis intercept; these data indicate that NAMAJ is significantly less compressible than other silicate garnets. Deviation of the  $f$  versus  $F$  slope from zero corresponds to the deviation of  $K'$  from 4; slopes for all five garnets are consistent with  $K' = 4$

Another possibility, suggested by D.J. Weidner (personal communication), is that NAMAJ undergoes a change in compression mechanism at about 2 GPa, resulting in a stiffening of the structure. Our P-V data below 2.23 GPa yield a bulk modulus of  $179 \pm 6$  GPa, significantly lower than that of the full P-V data set. Further studies of NAMAJ are required to examine this effect.

Finite-strain analysis of pressure-volume data highlights compositional effects on both  $K$  and  $K'$  (Jeanloz and Hazen 1991). Eulerian strain,  $f = [(V/V_0)^{-2/3} - 1]/2$ , plotted against Birch's normalized pressure,  $F = P/[3f(1+2f)^{2.5}]$ , intersects the  $F$  axis at the zero-pressure bulk modulus, while the slope indicates deviations of  $K'$  from 4. Garnet data, illustrated in Fig. 2, reveal that  $K'$  is close to 4 for all five samples, though slopes of  $F$  versus  $f$  lines are subject to large uncertainties owing to the small relative compression (maximum  $\Delta V/V \approx 0.025$ ) attained in these experiments.

#### Factors Controlling Garnet Compression

The garnet structure consists of a relatively rigid, corner-linked framework of alternating silicate tetrahedra and octahedra with,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ , or  $\text{Si}^{4+}$  in the octahedral sites for the samples of this study. The interstices in the framework define larger dodecahedral (8-coordinated) cation sites, containing  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , or  $\text{Na}^+$  in our specimens. The compressibility of garnet, therefore, depends almost entirely on the extent to which the tetrahedral-octahedral framework varies with pressure. All known silicate garnets have essentially full occupancy by silicon of the tetrahedra, giving an average tetrahedral cation valence of +4.

In most crustal silicate garnets, average cation valences for octahedral and dodecahedral sites are +3 and +2, respectively. Octahedral cation occupancies and valences, however, differ significantly in the specimens examined in this study:  $\text{Al}_2^{+3}$  in PYR, ( $\text{Mg}^{+2}\text{Si}^{+4}$ ) in MAJ and CAMAJ, ( $\text{Mg}_{0.13}\text{Al}_{1.07}\text{Si}_{0.80}^{+4}$ ) for INTER, and close to  $\text{Si}_2^{+4}$  for NAMAJ. In the case of NAMAJ, the increase in octahedral cation valence is compensated by a decrease in average dodecahedral cation valence – from +2 in MAJ, CAMAJ, and PYR, to +1.33 in NAMAJ.

Silicates may be modeled as ionic compounds with bond strengths determined to a first approximation by coulombic forces. Bridgman (1923), for example, demonstrated empirical inverse correlations between bulk modulus and molar volume and described his results in terms of an electrostatic model of interatomic forces. Bulk modulus-volume relationships have since become useful for predicting behavior of oxides, halides, silicates, and many other isomorphous, isoelectronic series (Anderson and Nafe 1965; Anderson and Anderson 1970).

In the case of natural silicate garnets, the bulk modulus-volume relationship provides some rationale for the observed variations in bulk moduli, from about 160 to 180 GPa, for isoelectronic silicate garnets. Garnets with

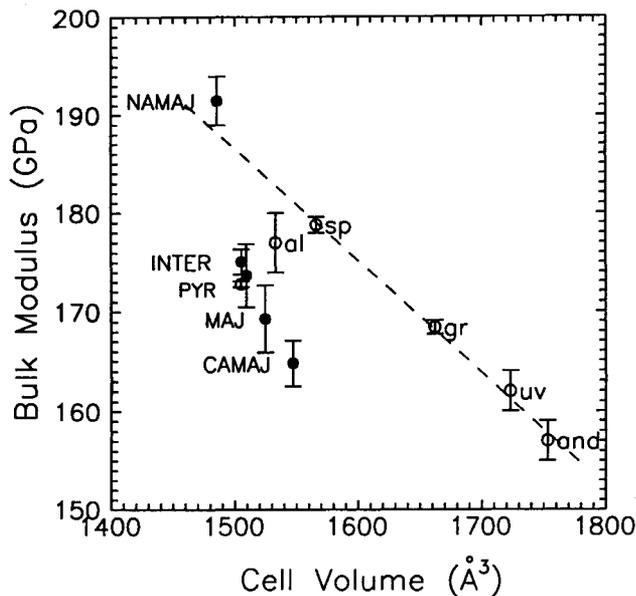


Fig. 3. A plot of garnet bulk modulus (in GPa) versus unit-cell volume (in  $\text{\AA}^3$ ) reveals bulk modulus-volume systematics. Solid circles represent the five specimens from this study, while open circles are: "and" = andradite (Bass 1986), "uv" = uvarovite (Bass 1986), "gr" = grossular (Bass 1989), "sp" = spessartine (Bass 1989), "al" = almandine (Bass 1989), "pyr" = pyrope (O'Neill et al. 1991). The dashed line represents a bulk modulus-volume trend defined by andradite, uvarovite, grossular, and spessartine. Note that NAMAJ, a garnet with  $\text{Si}^{4+}$  filling both octahedral cation sites, is significantly less compressible than the other garnets recorded. MAJ and CAMAJ with  $\text{Mg}^{2+}$  and  $\text{Si}^{4+}$  in octahedral sites lie below the general bulk modulus-volume trends defined by other garnets

trivalent octahedral cations and relatively large dodecahedral cations ( $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$ ), including grossular, uvarovite, andradite, and spessartine, have relatively large unit-cell volumes and display an inverse bulk modulus-volume trend (Bass 1986, 1989; Olijnyk et al. 1991; see Fig. 3). However, pyrope and almandine, with relatively small dodecahedral cations ( $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ ) are much more compressible than suggested by these systematics (Bass 1989; O'Neill et al. 1991). This increased compressibility of Mg- and Fe-garnets may result from the lack of structural support for the octahedral-tetrahedral framework provided by relatively small dodecahedral cations. Indeed, all previously measured Mg- or Fe-garnets with unit-cell volumes less than about  $1600 \text{\AA}^3$  have bulk moduli close to about 176 GPa, and thus do not follow the bulk modulus-volume trend of garnets with greater unit-cell volumes.

The PYR and INTER samples of the present study have bulk moduli of approximately 174 and 175 GPa, respectively, and thus conform to the behavior for other garnets with +3 octahedral cations and small dodecahedral cations (Fig. 3). MAJ, CAMAJ, and NAMAJ, which incorporate +2 and +4 octahedral cations, however, lie significantly off the trend. Majorite and calcium majorite, with divalent magnesium cations in half of the octahedral sites, are more compressible than garnets of similar volume with all trivalent octahedral cations, even though the average cation valence is +3 for these tetra-

gonal garnets. We suggest that the  $\text{Mg}^{2+}$  octahedra are significantly more compressible than those of  $\text{Al}^{3+}$  or  $\text{Si}^{4+}$ , and thus contribute to a lower garnet bulk modulus. On the other hand, sodium majorite, with relatively incompressible  $\text{Si}^{4+}$  in all octahedral sites, has the largest bulk modulus reported for any silicate garnet. This value, combined with its small unit-cell volume ( $1485.5 \pm 0.3 \text{\AA}^3$ ), places NAMAJ above the bulk modulus-volume trend defined by andradite, uvarovite, grossular, and spessartine (Fig. 3).

These results reveal an important and previously unrecognized aspect of garnet compression. Hazen and Finger (1989) documented the high-pressure crystal structures of pyrope and andradite ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ) and observed that garnet bulk compression approximately equals that of the dodecahedral sites. In andradite, for example, bulk moduli for the dodecahedral site and the crystal are 160 and 159 GPa, respectively. This result was mistakenly taken as evidence that dodecahedral site compression represented the primary factor in garnet bulk compressibility. Garnet was described as having a framework that tilted or collapsed about the more compressible large polyhedron. In fact, it now appears that the dodecahedral site merely scales with the compression of the much more rigid tetrahedral-octahedral framework. Furthermore, the compressibility of this framework is determined primarily by the valence of the octahedral cations.

Two lines of evidence support this contention. First, the magnitudes of dodecahedral site bulk moduli as determined by Hazen and Finger (1989) are significantly greater than those predicted on the basis of bulk modulus-volume systematics for other polyhedra (Hazen and Finger 1982). Predicted dodecahedral compression in pyrope and grossular, for example, are approximately 125 and 110 GPa, respectively, compared to the observed values close to 175 GPa. If dodecahedral site behavior alone governed garnet compressibility, then all crustal garnets should be approximately 50 percent more compressible than observed, based on these systematics.

The unusually large NAMAJ bulk modulus provides additional evidence for the hypothesis that garnet compression results primarily from the behavior of the octahedral sites. In NAMAJ the dodecahedral site is occupied primarily by monovalent Na, a cation with a predicted dodecahedral modulus of approximately 70 GPa – less than for any other garnet. If dodecahedral site compression governed the bulk properties of garnets, then NAMAJ would have the smallest bulk modulus of all silicate garnets. In fact, the opposite is true. This behavior must reflect the unique all-silicate framework of  $(\text{Na}_2\text{Mg})\text{Si}_2\text{Si}_3\text{O}_{12}$ , with +4 valence of both octahedral and tetrahedral cations. By the same token, MAJ and CAMAJ with  $\text{Mg}^{2+}$  in half of the octahedral sites are much more compressible than expected from other systematics. We thus conclude that the behavior of the rigid garnet framework, not the dodecahedral sites, controls garnet compression.

Further studies on garnets with more than 4 silicons per 12 oxygens would elucidate compression systematics and help to quantify the role of octahedral cation va-

lence. Of special interest would be the high-pressure synthesis of a phosphate garnet such as  $\text{Na}_3\text{Si}_2(\text{Si}_2\text{P})\text{O}_{12}$ , which is a plausible composition based on garnet crystal chemical systematics. This garnet has +1, +4, and +4.33 average valences for dodecahedral, octahedral, and tetrahedra, respectively. If garnet compression is a function of framework rather than dodecahedral cations, as suggested by our model, then this phosphate garnet should have a bulk modulus significantly greater than the 190 GPa value of NAMAJ.

*Acknowledgements.* We benefited from discussions and constructive reviews by J.D. Bass, R.C. Liebermann, J.R. Smyth, and D.J. Weidner. The synthesis of single crystals was performed in the Stony Brook High-Pressure Laboratory, which is jointly supported by NSF Center for High-Pressure Research and the State University of New York. X-ray diffraction work at the Geophysical Laboratory is supported by NSF grant EAR9218845 and by the Carnegie Institution of Washington.

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