

## LETTERS

### Crystal chemistry of Ca-bearing majorite

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#### ABSTRACT

Single crystals of Ca-bearing majorite, a garnet with composition  $(\text{Ca}_{0.49}\text{Mg}_{2.51})(\text{MgSi})\text{Si}_3\text{O}_{12}$ , have been synthesized at 18.2 GPa and 2050 °C. This sample is the first silicate garnet to display ordering on both octahedral and dodecahedral sites—behavior that may increase the compositional flexibility of garnet, affect element partitioning at high pressure, and stabilize the garnet structure in the transition zone and upper portion of the lower mantle. The garnet is tetragonal [space group  $I4_1/a$ ,  $Z = 8$ ,  $a = 11.5816(9)$ ,  $c = 11.5288(13)$  Å,  $V = 1546.39(29)$  Å<sup>3</sup>] and, like  $\text{MgSiO}_3$  majorite, displays twinning by twofold rotation about [110].

#### INTRODUCTION

The garnet structure, first identified in common rock-forming silicates, has been synthesized in a wide range of oxides and fluorides that incorporate at least 50 elements. The compositional flexibility of garnet has led to a wide range of applications, including grit for abrasive paper and cloth, crystals for lasers, wave-guide components for microwave communications, low-conductivity magnetic bubble domain devices, and semiprecious colored gemstones. Silicate garnets, furthermore, are a major rock-forming mineral and may account for as much as half of the volume of the Earth's transition zone between about 500 and 670 km in depth (Ita and Stixrude, 1991). In this study we describe a new, unanticipated ordering behavior of cations in silicate garnet—behavior that has implications for both geophysical modeling and materials science applications.

At crustal pressure, most garnets have cubic symmetry with the general formula  $\text{A}_3^{2+}\text{B}_2^{3+}\text{Si}_3\text{O}_{12}$ , where eightfold-coordinated A is usually Mg, Fe, Mn, or Ca and sixfold-coordinated B is Al, Fe, or Cr. Silicate garnets synthesized at high pressure commonly incorporate <sup>66</sup>Si, as in  $\text{Mn}_3(\text{MnSi})\text{Si}_3\text{O}_{12}$  (equivalent to  $\text{MnSiO}_3$ ), which has tetragonal symmetry because of the ordering of Mn and Si on octahedral sites (Ringwood and Major, 1967; Prewitt and Sleight, 1969). Garnets from the Coorara meteorite with more than three Si atoms per 12 O atoms were subsequently described by Smith and Mason (1970), who named the new mineral majorite. End-member  $\text{MgSiO}_3$  majorite was synthesized by Kato and Kumazawa (1985), and single crystals of  $\text{MnSiO}_3$  (Fujino et al., 1986) and

$\text{MgSiO}_3$  (Angel et al., 1989) provided samples for detailed structure investigation.

Studies of mantle minerals have emphasized the dominant roles of the oxides of Si and Mg and to a lesser extent Fe—components that together may account for as much as 94 mol% of the mantle (Ringwood, 1975; Basaltic Volcanism Study Project, 1981). The role of calcium oxide, which represents perhaps 3 mol% of the mantle's mass, might seem to be relatively unimportant in the mineral content of the Earth's deep interior. From a crystal chemical perspective, however, Ca may play an influential role in high-pressure silicates. The  $\text{Ca}^{2+}$  cation is significantly larger than other common divalent cations proposed to exist in the mantle. In eightfold coordination, for example, the radius of Ca is 1.12 Å, whereas the radii of Fe and Mg are 0.92 and 0.89 Å, respectively (Shannon, 1976). The presence of significant Ca, therefore, might lead to new structures or help to stabilize structures like garnet with appropriately large cation sites.

With this situation in mind, a number of researchers have investigated the system  $\text{CaO-SiO}_2$ . Their studies revealed transitions to new Ca-bearing phases, including perovskite-like  $\text{CaSiO}_3$ , titanite-type  $\text{CaSi}_2\text{O}_5$ , and  $\text{K}_2\text{NiF}_4$ -type  $\text{Ca}_2\text{SiO}_4$  (Finger and Hazen, 1991). The behavior of binary systems and end-member compositions, however, is not necessarily applicable to more complex systems. In this context, studies of phase equilibria in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  at transition zone conditions are of special interest (Gasparik, 1989, 1990). At intermediate compositions, a wide range of pyroxene and garnet compositions, including those with <sup>66</sup>Si, are stabilized (Angel

et al., 1988, 1989). These complex silicate phases are not only relevant to the multielement environment of the Earth's deep interior, but they also have implications for the crystal chemistry of synthetic analogues.

### EXPERIMENTAL METHODS

The sample, heated for 4 h to a maximum temperature of 2050 °C at 18.2 GPa in the USSA-2000 split-sphere anvil apparatus, produced numerous colorless crystals up to 100  $\mu\text{m}$  diameter, as described by Gasparik (1990: expt. no. SUNY 868). Less calcic majorite and  $\text{CaSiO}_3$  perovskite formed at the cooler end of the sample assembly, estimated to have reached a temperature no higher than 1850 °C. Our work focused on crystals from the hotter end of the sample assembly.

X-ray diffraction and electron microprobe study of the sample revealed both garnet and subcalcic diopside crystals in the experimental products of the sample assembly's hotter end. More than a dozen Ca-bearing majorite crystals were mounted for X-ray study, but most displayed multiple and smeared reflections. Only one crystal, an elongated shard approximately 30 and 70  $\mu\text{m}$  in minimum and maximum dimensions, respectively, proved suitable for X-ray diffraction study. Electron microprobe analysis revealed an average composition of  $(\text{Ca}_{0.49}\text{Mg}_{2.51})(\text{MgSi})\text{Si}_3\text{O}_{12}$ , slightly more calcic than the average composition of  $(\text{Ca}_{0.45}\text{Mg}_{2.55})(\text{MgSi})\text{Si}_3\text{O}_{12}$  reported by Gasparik (1990). A high-resolution multielement map of a portion of this crystal  $20 \times 20 \mu\text{m}$  revealed a generally uniform composition, but small areas display reduced Ca/Mg, corresponding to Ca contents as low as about  $(\text{Ca}_{0.4}\text{Mg}_{2.6})(\text{MgSi})\text{Si}_3\text{O}_{12}$ . Such compositional heterogeneity must contribute to the generally broad diffraction maxima observed for this sample.

Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer equipped with a rotating-anode generator operated at 45 kV and 180 mA. We used graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7093 \text{ \AA}$ ) to measure a hemisphere of data to  $(\sin \theta)/\lambda = 0.71$ . A total of 4814 symmetry-allowed diffraction peaks were measured by  $\omega$  step scans. Diffraction maxima were uniformly weak and broad, and <10% of the peaks with  $2\theta$  values above  $40^\circ$  were observed.

Most observed peaks were doublets, perhaps due to multiple crystals in close alignment. Doubling was not observed in  $\theta$ - $2\theta$  scans, indicating that peak splitting is not a consequence of pseudomerohedral twinning about [111], as observed in majorite (Wang et al., 1993). The other known twinning in majorite, rotation about [110], is merohedral and does not result in split reflections (Hatch and Ghose, 1989). One member of each split diffraction peak (presumably the component from the main crystal) was always well centered. Peaks were integrated by fitting step-scan data to multiple Gaussian functions; only the central peak was retained. Peaks that appeared to be single but significantly exceeded the expected peak width (implying an unresolved doublet) were rejected during this procedure, which yielded 801 observed reflections.

Intensities were corrected for Lorentz and polarization effects and reduced to structure factors. No correction was made for crystal absorption ( $\mu_l = 14.3 \text{ cm}^{-1}$ ). Systematic extinctions are consistent with space group  $I4_1/a$ , as previously reported for majorite (Angel et al., 1989). Reflections were averaged according to Laue group  $4/m$  ( $R_{\text{int}} = 0.050$ ), which yielded 195 symmetrically distinct observations ( $I \geq 3\sigma$ ).

### RESULTS AND DISCUSSION

We initiated the crystal structure refinement with parameters reported by Angel et al. (1989) for the Mg end-member,  $\text{MgSiO}_3$ . In addition to the scale factor and 25 variable atomic coordinates, we refined one occupancy parameter for Ca and Mg in D1 and D2, assuming a total composition of  $\text{Ca}_{0.49}\text{Mg}_{2.51}$ . We also refined a [110] twin fraction and five isotropic displacement factors (D1, D2, and one each of the other three site types, T, Oct, and O), for a total of 33 refined parameters. Initial refinements also included a parameter for Mg and Si ordering on Oct1 and Oct2, but preliminary results indicated complete Mg-Si order, and this parameter was omitted from later refinements. Refinements were performed with RFINE90, a version of RFINE4 (Finger and Prince, 1975). Refinement converged to a weighted  $R$  of 0.057 and unweighted  $R$  of 0.066 for 195 observations. The goodness of fit for the converged refinement is 1.39. Calculated and observed structure factors are available from the authors.

Refined positional and displacement parameters appear in Table 1, and unit-cell parameters, selected interatomic distances, and bridging-O angles appear in Table 2. Ca-bearing majorite has a calculated density of  $3.516 \text{ g/cm}^3$  for a composition of  $(\text{Ca}_{0.49}\text{Mg}_{2.51})(\text{MgSi})\text{Si}_3\text{O}_{12}$ .

Silicate garnets may be described in terms of a relatively rigid three-dimensional, corner-linked framework of silicate tetrahedra and octahedra (Fig. 1). This framework defines eightfold-coordinated sites that are occupied by divalent cations. Tetragonal garnets have three symmetry-independent  $\text{SiO}_4$  tetrahedra, all of which are nearly regular, with typical orthosilicate mean T-O distances close to 1.64  $\text{\AA}$ .

Octahedral Mg and Si order in the two symmetrically distinct octahedral sites, which are close to regular. This inflexible framework displays uniform bridging Oct-O-Si angles in all three specimens. The mean Oct1-O and Oct2-O distances, 2.012 and 1.754  $\text{\AA}$ , are typical of those found in  $\text{MgO}_6$  and  $\text{SiO}_6$  octahedra, respectively. The Oct2-O distances in  $\text{MgSiO}_3$  and  $\text{MnSiO}_3$  (1.807 and 1.795  $\text{\AA}$ , respectively), however, are significantly longer than end-member Si-O octahedral distances. Furthermore, refined octahedral occupancies for both end-member  $\text{MnSiO}_3$  and  $\text{MgSiO}_3$  garnets indicate up to 20% disorder. The reasons for these differences in degree of octahedral order are not obvious. The  $\text{MgSiO}_3$  (Angel et al., 1989) and  $\text{MnSiO}_3$  (Fujino et al., 1986) samples were synthesized at lower temperatures (1700 and 1500 °C, respectively) and for shorter experiment durations (<30 min) than Ca-bearing majorite (2050 °C for 4 h), so the latter

TABLE 1. Positional and displacement parameters from the refinement of Ca-bearing majorite

Site*	Atom	Occupancy	x	y	z	B (Å <sup>2</sup> )
D1**	Mg	0.917 (36)	0.1265 (11)	0.0137 (13)	0.2576 (12)	0.83 (28)
	Ca	0.083				
D2**	Mg	0.677	0	¼	0.6258 (22)	2.20 (39)
	Ca	0.323				
Oct1	Mg		0	0	½	0.44 (9)
Oct2	Si		0	0	0	0.44
T1	Si		0	¼	¾	0.59 (15)
T2	Si		0	¼	⅞	0.59
T3	Si		0.1259 (9)	0.0072 (11)	0.7575 (10)	0.59
O1	O		0.0251 (18)	0.0524 (17)	0.6666 (19)	0.61 (14)
O2	O		0.0420 (17)	-0.0462 (16)	0.8635 (19)	0.61
O3	O		0.2212 (17)	0.1100 (17)	0.7934 (16)	0.61
O4	O		0.2172 (18)	-0.0839 (18)	0.7026 (18)	0.61
O5	O		-0.0530 (16)	0.1585 (17)	0.4697 (19)	0.61
O6	O		-0.1024 (17)	0.2141 (18)	0.7842 (19)	0.61

\* The origin of atomic coordinates is shifted by ½,0,0 relative to the standard origin at the Wyckoff position 8c, to conform with previous descriptions of cubic garnets.

\*\* The total occupancies of each of these two sites are constrained to unity, with the total composition constrained to Ca<sub>0.45</sub>Mg<sub>0.55</sub>.

specimen might be expected to display more, not less, disorder.

The nearly complete octahedral ordering in Ca-bearing majorite may, in part, be coupled with the unanticipated ordering of Ca and Mg on the two symmetrically distinct dodecahedral sites, D1 and D2. Ca is concentrated in the

D2 site, which has a refined composition of Ca<sub>0.32</sub>Mg<sub>0.68</sub>, compared with Ca<sub>0.08</sub>Mg<sub>0.92</sub> for D1. These site compositions may be expressed as a distribution coefficient:  $K_D = (XCa_{D2}/XMg_{D2})/(XCa_{D1}/XMg_{D1}) = 5.4$ . This distribution coefficient is unusually large for a silicate quenched from high temperature: completely disordered sites have  $K_D = 1$ , whereas most crustal silicates quenched from high temperature have  $K_D < 2$ , especially for large cation sites that share edges and thus would seem to disorder easily (Hazen et al., 1993). Furthermore, these two dodecahedral sites are not appreciably different in size, which is a con-

TABLE 2. Unit-cell parameters and selected distances (Å) and angles (°)

a (Å)	11.5816 (9)
c (Å)	11.5288 (13)
c/a	0.9954
V (Å <sup>3</sup> )	1546.4 (3)
D1-O1	2.105 (25)
D1-O2	2.429 (24)
D1-O3	2.309 (25)
D1-O3'	2.522 (22)
D1-O4	2.084 (25)
D1-O4'	2.305 (24)
D1-O5	2.178 (24)
D1-O6	2.696 (25)
Mean D1-O	2.329
D2-O1[2]	2.354 (20)
D2-O2[2]	2.414 (18)
D2-O5[2]	2.177 (30)
D2-O6[2]	2.217 (30)
Mean D2-O	2.291
Oct1-O1[2]	2.035 (22)
Oct1-O4[2]	2.035 (22)
Oct1-O5[2]	1.967 (20)
Mean Oct1-O	2.012
Oct2-O2[2]	1.731 (22)
Oct2-O3[2]	1.730 (20)
Oct2-O4[2]	1.802 (20)
Mean Oct2-O	1.754
T1-O5[4]	1.640 (21)
T2-O6[4]	1.636 (20)
T3-O1	1.655 (22)
T3-O2	1.679 (22)
T3-O3	1.676 (23)
T3-O4	1.623 (23)
Mean T3-O	1.658
Oct1-O1-T3	127.2 (13)
Oct2-O2-T3	135.2 (12)
Oct2-O3-T3	136.2 (13)
Oct1-O4-T3	129.1 (13)
Oct1-O5-T1	127.2 (11)
Oct2-O6-T2	140.2 (13)
Mean Oct-O-T	132.5

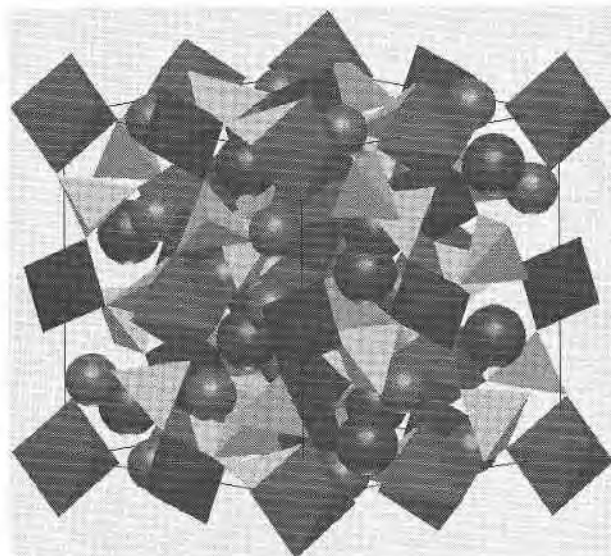


Fig. 1. The structure of tetragonal Ca-bearing majorite (shown with one a axis vertical and the c axis to the left and diagonally out from the page) features a corner-linked framework of SiO<sub>4</sub> tetrahedra, SiO<sub>6</sub> octahedra (smaller), and MgO<sub>6</sub> octahedra (larger), represented here as polyhedra. This framework defines two symmetrically distinct dodecahedral cation sites (spheres), which contain Ca and Mg. Ca concentrates in the D2 site, which is represented by the larger spheres.

trolling factor in cation ordering in some minerals. One possibly significant difference between D1 and D2 is the distribution of second-nearest neighbor cations (Fig. 1). Distances between adjacent D1 sites and between D1 and D2 are relatively short—approximately 3.5 Å. Distances between closest D2 sites, on the other hand, are >5.7 Å. Ordering of Ca onto D2 minimizes Ca-Ca interactions, which may be significant at the high pressure and temperature of Ca-bearing majorite synthesis.

This study reveals the surprising structural complexity of tetragonal garnets. Of its seven symmetrically distinct cation sites, only the three Si tetrahedra display similar crystal chemical behavior. Cation distributions in the two octahedra and two dodecahedra demonstrate that these four sites behave differently and thus may incorporate a wide variety of major and minor elements. In geological environments, these distinct sites may provide mechanisms for element partitioning. Furthermore, the presence of extensive garnet solid solutions may expand its stability into pressure and temperature ranges of the upper portion of the lower mantle (O'Neill and Jeanloz, 1994). Chemical analyses of mantle-derived garnets with more than three Si atoms per 12 O atoms underscore the chemical complexity of these high-pressure minerals (Moore and Gurney, 1985; Haggerty and Sautter, 1990). Garnet specimen JX-25 of Haggerty and Sautter, for example, has clinopyroxene exsolution lamellae in a garnet host, suggesting an original homogeneous composition of approximately  $(\text{Na}_{0.09}\text{Ca}_{0.72}\text{Mn}_{0.02}\text{Fe}_{0.36}\text{Mg}_{1.82})(\text{Mg}_{0.19}\text{Al}_{1.48}\text{Cr}_{0.08}\text{Si}_{0.23}\text{Ti}_{0.02})\text{Si}_3\text{O}_{12}$ . Garnet compositional complexity is further demonstrated by Gasparik's (1992) synthesis of compositions approximating  $(\text{NaMg}_2)(\text{AlSi})\text{Si}_3\text{O}_{12}$ ,  $\text{Mg}_3(\text{Mg}_{0.5}\text{AlSi}_{0.5})\text{Si}_3\text{O}_{12}$ , and  $(\text{Na}_2\text{Mg})\text{Si}_2\text{Si}_3\text{O}_{12}$ . High-pressure garnets are thus able to incorporate cations of valence 1+, 2+, 3+, and 4+ and cations of a wide range of size and electronic structure. Synthetic tetragonal garnets, though little explored, may display similar compositional complexities, as well as cation ordering—behavior that might enhance magnetic or optical properties.

This study on garnets underscores a growing recognition that high-pressure silicates, even those synthesized at temperatures near 2000 °C, display a marked tendency for cation ordering (Aikawa et al., 1985; Finger et al., 1993). Most mantle silicates have ordering systematics not expected for low-pressure phases. In the case of majorite-type garnets, the tendency to order octahedral and dodecahedral cations appears to be a driving force behind the reduction of symmetry from the more typical cubic garnet symmetry. If so, then a similar, as yet unrecognized, symmetry breaking might occur in high-pressure silicate perovskites of an intermediate composition, such as  $\text{CaMgSi}_2\text{O}_6$ .

#### ACKNOWLEDGMENTS

The synthesis of single crystals was performed in the Stony Brook High-Pressure Laboratory, which is jointly supported by the 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 no. EAR-9218845 and by the Carnegie Institution of Washington.

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