

LETTERS

Crystal chemistry of ferromagnesian silicate spinels: Evidence for Mg-Si disorder

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ABSTRACT

Single-crystal X-ray diffraction data have been obtained for synthetic Fe-Mg silicate spinels, γ -(Mg_xFe_{1-x})₂SiO₄ ($x = 1.00, 0.40, \text{ and } 0.20$). The measurements on γ -Mg₂SiO₄ synthesized at 20 GPa and 1400 °C, compared with previous data on a specimen synthesized at 22 GPa and 1000 °C, provide evidence that approximately 4% of Si_{tot} enters octahedral coordination in the sample synthesized at higher temperature. Fe-bearing silicate spinels synthesized at lower pressures display no evidence for Fe-Si disorder.

INTRODUCTION

Ferromagnesian silicate spinels are thought to be major mineral phases in the Earth's transition zone. The spinel polymorphs of (Mg,Fe)₂SiO₄, which require minimum synthesis pressures of approximately 6–18 GPa for the Fe and Mg end-members, respectively, are approximately 3% denser than wadsleyite-type structures [β -(Mg,Fe)₂SiO₄] and 10% denser than olivines of the same composition (Smyth and Bish, 1988). The distribution and behavior of silicate spinels, therefore, may play an important role in the density contrasts and dynamics at the Earth's 410- and 660-km seismic discontinuities. Crystal chemical and thermochemical data on intermediate ferromagnesian silicate spinels are thus important in constraining models of the Earth's deep interior.

X-ray structure refinements of single-crystal silicate spinels have been recorded for end-member Co₂SiO₄ (Morimoto et al., 1974; Marumo et al., 1977), Ni₂SiO₄ (Marumo et al., 1974; Yagi et al., 1974), Fe₂SiO₄ (Yagi et al., 1974; Marumo et al., 1977), and Mg₂SiO₄ (Sasaki et al., 1982). In addition, Finger et al. (1979) reported high-temperature, high-pressure, and room-condition structure refinements of the synthetic nickel and iron silicate spinel samples described by Yagi et al. (1974).

Ideal, fully ordered, normal silicate spinels have two octahedrally coordinated divalent *M* cations for each ⁴Si. Thermochemical modeling (Navrotsky, 1977; Navrotsky et al., 1979) indicates that some *M*-Si disorder may occur, but X-ray structure analyses have not been able to resolve this problem. Several previous X-ray studies (Ma, 1972; Morimoto et al., 1974; Yagi et al., 1974; Marumo et al., 1974, 1977) suggested that silicate spinels may be slightly disordered, with a few percent Si entering octa-

hedral coordination, whereas divalent cations are in part fourfold coordinated. Studies of electron density by Marumo et al. (1974, 1977), for example, pointed to structural formulas of ⁶(Fe_{0.988}Si_{0.012})₂⁴(Si_{0.976}Fe_{0.024})O₄, ⁶(Co_{0.993}Si_{0.007})₂⁴(Si_{0.986}Co_{0.014})O₄, and ⁶(Ni_{0.9935}-Si_{0.0065})₂⁴(Si_{0.987}Ni_{0.013})O₄ for synthetic spinels. These cation distribution measurements are close to detection limits of the experiments, however, and subsequent studies by Finger et al. (1979), who modeled the temperature factors with anharmonic terms rather than standard anisotropic parameters, found no evidence for disorder in the Fe and Ni samples. Similarly, Sasaki et al. (1982) noted possible Mg-Si disorder in their Mg₂SiO₄ sample, but their bond distances were close to those expected for a fully ordered spinel, and they concluded, "results obtained thus far are inconclusive regarding the question of disorder in magnesium-silicate spinel." They also noted that "one way of providing additional information would be to refine occupancy parameters of crystals quenched from different temperatures."

In this paper we report for the first time the crystal structures of three intermediate ferromagnesian silicate spinels, as well as an end-member Mg₂SiO₄ spinel synthesized at significantly higher temperature than the sample of Sasaki et al. (1982). These data, when combined with the earlier studies, reveal strong evidence for a few percent cation disorder in the ferromagnesian silicate spinel solid solution.

EXPERIMENTAL

Single crystals of silicate spinels were synthesized in a split-sphere anvil apparatus (USSA-2000) starting from a dried powdered mixture of forsterite and fayalite com-

TABLE 1. A summary of the spinel refinements

Sample	SUNY 859	SUNY 1013	SUNY 1097	SUNY 1102
a-cell edge (Å)	8.0709(2)	8.1763(7)	8.2030(3)	8.2059(7)
Cell volume (Å ³)	525.73(4)	546.60(13)	551.98(7)	552.56(13)
μ_c (cm ⁻¹)	11.369	71.239	87.288	86.423
No. averaged/measured	52/806	56/893	56/897	56/893
No. obs. $I > 2\sigma_I$	41	51	52	48
Disagreement index on F	0.0187	0.0135	0.0273	0.0264
ρ^*	0.008	0.0061	0.009	0.0035
Weighted R	0.013	0.009	0.012	0.009
Unweighted R	0.015	0.010	0.011	0.010
Mg/(Mg + Fe)	1.0	0.383(6)	0.21(1)	0.218(8)
$\beta_{11}(M)^{**}$	263(11)	192(5)	180(6)	208(6)
$\beta_{12}(M)$	-16(9)	4(4)	1(4)	2(5)
$\beta_{11}(Si)$	199(9)	144(9)	147(11)	157(12)
x^\dagger	0.2441(1)	0.2420(1)	0.2415(1)	0.2418(1)
$\beta_{11}(O)$	197(14)	212(10)	209(13)	212(12)
$\beta_{12}(O)$	-4(13)	1(10)	-7(11)	37(27)

* Weights were computed as $w = (\sigma_c^2 + \rho^2 F^2)^{-1}$.

** Thermal parameters are of the form $\exp\{-\sum \sum h_i h_j \beta_{jk} \times 10^3\}$ and are constrained by symmetry to $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23}$ for all atoms, with $\beta_{12} = 0$ for Si.

† Positional parameters are constrained by symmetry to $[\frac{1}{6}\frac{1}{6}\frac{1}{6}]$ for Si, $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ for M, and (xxx) for O.

position. The starting material was surrounded by Re foil, which was in turn jacketed by MgO and a cylindrical LaCrO₃ heater (Gasparik, 1989). The Mg₂SiO₄ sample (SUNY experiment 859) was synthesized at 1400 °C and 20 GPa and was subsequently employed by Meng et al. (1992) in elasticity studies. The intermediate samples were synthesized at 1600 °C and 14.5 GPa for the sample with 40% Mg (SUNY experiment 1013), and 12.6 GPa for two samples with 20% Mg (SUNY experiments 1097 and 1102). Each experiment produced monomineralic spinel with crystals up to 200 μ m in diameter. All these samples, as well as the Ni and Fe end-members of Yagi et al. (1974), were employed by Hazen (1993) in a study of the comparative compressibilities of silicate spinels.

Electron microprobe analyses of the intermediate silicate spinels reveal uniform grains that closely match the starting compositions. Sample 1013 yielded a composition of (Mg_{0.409}Fe_{0.583})₂Si_{1.006}O₄, sample 1097 gave (Mg_{0.219}Fe_{0.769})₂Si_{1.010}O₄, and sample 1102 gave (Mg_{0.208}Fe_{0.778})₂Si_{1.012}O₄. In each of these samples, ⁵⁷Fe Mössbauer spectroscopy revealed 3–5% of Fe_{tot} as Fe³⁺, a common component in synthetic silicate spinels (Ross et al., 1992). The presence of Fe³⁺ may explain why the Mg + Fe totals for the three intermediate samples are slightly less than two cations per formula unit, although the cation totals from the microprobe analyses are stoichiometric within the estimated analytical uncertainty of about 1%. For example, the formula of sample 1013 might be recast as (Mg_{0.409}Fe_{0.567}Fe_{0.016}□_{0.008})₂SiO₄. Because the Fe³⁺ content of the intermediate Mg-Fe samples are poorly constrained and any deviations from stoichiometry are small, these specimens will be treated as stoichiometric (Mg,Fe)₂SiO₄ in the subsequent discussion.

Equant crystals approximately 100 μ m in diameter were selected for X-ray study. X-ray data were obtained using a Rigaku AFC-5 diffractometer with rotating anode generator and graphite monochromatized MoK α radiation ($\lambda = 0.7093$ Å). All crystals have cubic unit cells (space

group $Fd\bar{3}m$; $Z = 8$), with unit-cell edges and volumes as recorded in Table 1.

A hemisphere of intensity data was measured to $2\theta = 60^\circ$ [$(\sin \theta)/\lambda = 0.70$] using ω step scans for each of the four silicate spinel crystals. Data were corrected for absorption effects and averaged according to Laue symmetry $m\bar{3}m$ for all reflections. A summary of refinement conditions, including the number of measured structure factors, number of averaged observations, and internal agreement for averaged reflections, appears in Table 1. Calculated and observed structure factors, and standard deviations for the four silicate spinels appear in Table 2.¹

During initial refinements we placed no constraints on the occupancy of the tetrahedral site by Si, and all four samples yielded values within 1% (approximately ± 0.1 electron) of full occupancy by Si. Thus, Fe-Si disorder greater than a fraction of a percent can be ruled out in these specimens. Some Mg-Si disorder is possible because of the similar X-ray scattering behavior of these two cations. However, for the purposes of the final refinements we assumed complete ordering. Note that Marumo et al. (1977) demonstrated that this assumption has little influence on the refined value of the O positional coordinate.

RESULTS

The O coordinate and the unit-cell edge are the only variable parameters needed to determine all bond distances and angles in the spinel structure. In addition to the scale factor and O atomic coordinate, we refined anisotropic temperature factors and Mg/(Mg + Fe) for the octahedral site (see Table 1). Extinction was found to be negligible in initial refinements and subsequently ignored.

¹ A copy of Table 2 may be ordered from the authors or as Document AM-93-546 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 3. Calculated parameters

Sample	SUNY 859	SUNY 1013	SUNY 1097	SUNY 1102
$B_{eq}(\text{Si})$	0.520(7)	0.385(8)	0.40(1)	0.42(1)
$B_{eq}(\text{M})$	0.68(1)	0.514(5)	0.486(5)	0.561(5)
$B_{eq}(\text{O})$	0.51(1)	0.567(9)	0.56(1)	0.57(1)
$R(\text{SiO})$	1.6650(5)	1.6566(5)	1.6559(6)	1.6597(7)
$R(\text{OO})$	2.7190(8)	2.7052(8)	2.7041(9)	2.7103(10)
$V(\text{SiO}_4)$	2.369(2)	2.333(2)	2.330(2)	2.346(3)
$R(\text{MO})$	2.0664(3)	2.1117(3)	2.1223(3)	2.1211(4)
O-M-O	87.39(2)	86.50(1)	86.32(2)	86.41(2)
O-M-O	92.61(2)	93.50(1)	93.68(2)	93.59(2)
$V(\text{MO}_6)$	11.727(5)	12.483(5)	12.664(6)	12.646(6)

Note: values for B_{eq} represent isotropic equivalents of the anisotropic temperature factors in ångströms squared; R is in ångströms, V in ångströms cubed, and O-M-O in degrees.

Refinements converged to weighted R ($R_w = \sum w^2(F_o - F_c)^2 / \sum w^2 F_c^2$) between 0.009 and 0.013, and unweighted R ($R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$) between 0.010 and 0.015. The weights are inversely proportional to $\sigma_F^2 + (pF)^2$, where σ_F is obtained from counting statistics, and probability plot analysis (Abrahams and Keve, 1971; Hamilton, 1974) is used to determine the best value for p .

Unit-cell edge a for the four samples of this study and previously published values for the end-members demonstrate a simple linear trend vs. Mg/(Mg + Fe) and shows roughly a 2% increase from the Mg end-member ($a = 8.070$ Å) to the Fe end-member ($a = 8.235$ Å). Bond distances and angles for ferromagnesian silicate spinels are recorded in Table 3. The $^{60}\text{Mg,Fe}$ -O distance displays a linear trend with composition, as expected from the cell edge vs. composition systematics. The Mg-O and Fe-O distances for end-member silicate spinels are 2.066 and 2.136 Å, respectively.

The Si-O distances of these specimens are of special interest because the size of the spinel tetrahedron is sensitive to its composition. Any disorder between (Mg,Fe) and Si should be reflected in anomalously long Si-O distances. Orthosilicates typically have Si-O distances between 1.64 and 1.65 Å. Previously reported values for silicate spinels range from 1.646 Å for Co_2SiO_4 (Morimoto et al., 1974) to about 1.655 Å for the iron, nickel, and magnesium silicate spinels described by Yagi et al. (1974) and Sasaki et al. (1982). All the Si-O distances in this study, ranging from 1.6559 ± 0.0006 Å for sample 1097 to 1.6650 ± 0.0005 Å for the Mg_2SiO_4 specimen, are unusually long. In fact, the latter value appears to be the longest reported Si-O distance for any rock-forming orthosilicate (Smyth and Bish, 1988, their Table 11.2).

DISCUSSION

In this study of ferromagnesian silicate spinels, as in the previous work of Finger et al. (1979), we find no evidence for excess electron density on the tetrahedral site. Fe-Si disorder, if present at all, is therefore <1%. The observed Si-O distance in studies of $\gamma\text{-Fe}_2\text{SiO}_4$ is approximately 1.653 Å (Yagi et al., 1974; Marumo et al., 1977; Finger et al., 1979). Birle et al. (1968) and subsequent authors (Brown, 1982) demonstrate that the tetrahedral

Si-O distance (approximately 1.637 Å) in fully ordered $(\text{Mg,Fe})_2\text{SiO}_4$ olivine is unaffected by Fe-Mg ratio. Similarly, Hill et al. (1979) found that tetrahedral cation to O distances in a variety of nonsilicate spinels are determined almost entirely by cation radii. We assume the same behavior for ferromagnesian silicate spinels and propose that an Si-O distance of 1.653 Å represents an appropriate value for fully ordered samples.

Mg-Si disorder in silicate spinels has proved difficult to document on the basis of X-ray studies of electron distribution because of the similarity of Mg and Si scattering factors. The similar case of Al-Si disorder in silicates has been resolved through the use of $^{60}\text{Si,Al}$ -O bond distances as a sensitive measure of Al-Si ratio (Smith and Bailey, 1963). Observed tetrahedral bond distances in silicate spinels, similarly, may provide a sensitive measure of Mg-Si disorder. Comparison of the Mg_2SiO_4 refinement of Sasaki et al. (1982) and this study, for example, provides unambiguous evidence for Mg-Si ordering in silicate spinels.

The sample of Sasaki et al. (1982) was synthesized at 1000 °C and 22 GPa, whereas the present sample was prepared at 1400 °C and 20 GPa. If Mg and Si can disorder, then the higher temperature sample should display the greater disorder. This feature is readily observed in the Si-O and Mg-O bond distances, which are significantly different in these two refinements. Sasaki et al. (1982) reported a Si-O distance of 1.655(4), a value close to the assumed 1.653-Å value of fully ordered silicate spinel, whereas we find a significantly longer distance of 1.6650(5) Å in our higher temperature sample. Similarly, Sasaki et al. reported an Mg-O distance of 2.070(4), whereas we obtain a shorter distance of 2.0664(3) Å.

Shannon (1976) cited Si and Mg tetrahedral ionic radii of 0.26 and 0.57 Å, respectively. If 1.653 Å represents a typical Si-O distance for fully ordered silicate spinel, then 1.963 Å may be assumed to be an appropriate ^{60}Mg -O distance. Thus, the atom fraction of Mg in tetrahedral coordination, $x = \text{Mg}/(\text{Mg} + \text{Si})$, is related to the tetrahedral cation to O distance, d , by the linear relationship $x = [(d - 1.653)/0.31]$.

The 1.665-Å value of our $\gamma\text{-Mg}_2\text{SiO}_4$ sample, for example, corresponds to $x = 0.0387$, or a structural formula: $^{60}(\text{Mg}_{0.98}\text{Si}_{0.02})_2^{64}(\text{Si}_{0.96}\text{Mg}_{0.04})\text{O}_4$. Thus, approximately 4% of Si_{tot} appears to be in octahedral coordination. Investigation of ^{29}Si -enriched Mg_2SiO_4 samples by NMR would be particularly useful in confirming the presence of ^{60}Si in these samples (Stebbins and Kanzaki, 1991; Phillips et al., 1992).

The intermediate Fe-Mg samples also display unusually long Si-O distances (Fig. 1). Sample 1102 synthesized at 14.5 GPa and 1600 °C with approximately 20% Mg, for example, has $\text{Si-O} = 1.6597 \pm 0.0007$ Å. Our refinements detect no Fe in the tetrahedral site, and so the long Si-O distance must result exclusively from Mg-Si disorder.

Temperatures in the Earth's lower transition zone, approximately 500–660 km in depth, where silicate spinel may be the most abundant mineral, are estimated to ex-

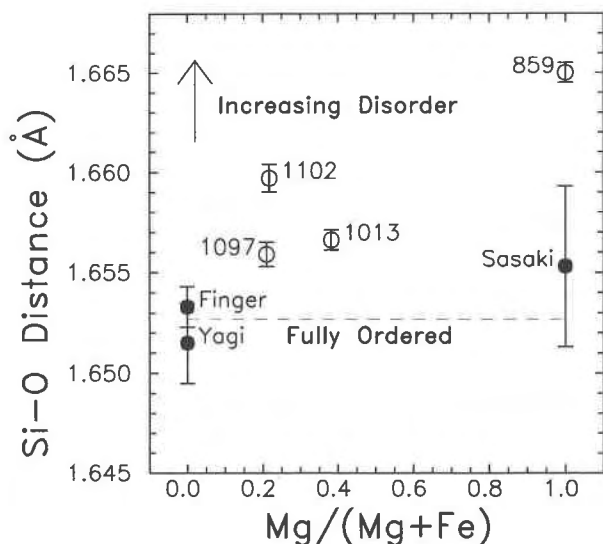


Fig. 1. Tetrahedral Si-O distances in ferromagnesian silicate spinels. Fully ordered samples have a Si-O distance of approximately 1.653 Å. Larger values result from Mg-Si disorder in these samples, up to a maximum of an estimated 4% of Si_{tet} in octahedral coordination for sample 859. Open circles are data from this study with Stony Brook sample numbers noted. Solid circles are data from Yagi et al. (1974), Finger et al. (1979), and Sasaki et al. (1982), as noted.

ceed 1500 °C (see, for example, Ita and Stixrude, 1992, and references therein). Under these conditions, significant Mg-Si disordering in silicate spinels is to be expected and must be incorporated into any thermochemical modeling of mantle phase equilibria.

These data on ferromagnesian silicate spinels add to a growing body of evidence that the behavior of Fe and Mg, which often play a common role in crustal silicates, deviate significantly in high-pressure phases (Navrotsky, 1987; Hazen, 1993). Our data on bond distances demonstrate clear evidence for Mg-Si disorder in Mg_2SiO_4 synthesized at 20 GPa and 1400 °C, yet no evidence for Fe-Si disorder is found in samples of $(\text{Mg}_{0.2}\text{Fe}_{0.8})_2\text{SiO}_4$ synthesized at 14.5 GPa and 1600 °C. We conclude, therefore, that Fe and Mg play significantly different roles in the crystal chemistry of silicate spinels.

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