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LETTER

Crystal chemistry of Fe-bearing anhydrous phase B: Implications for transition zone mineralogy

ROBERT M. HAZEN, LARRY W. FINGER
Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington,
5251 Broad Branch Road NW, Washington, DC 20015-1305, U.S.A.
JAIDONG KO
Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11794, U.S.A.

ABSTRACT

Single crystals of an Fe-bearing high-pressure magnesium silicate "anhydrous phase B," $(Mg_{0.88}Fe_{0.12})_{14}Si_5O_{24}$, have been synthesized at 15 GPa and 1800 °C. A remarkable feature of this Fe-bearing variant is the significant partitioning of Fe into one of the six symmetrically distinct octahedral sites—a degree of Fe-Mg ordering not observed in any other rock-forming silicate quenched from very high temperature. The presence of Fe, as well as other octahedral cations such as Ca, Mn, or Al, may, therefore, expand the stability of anhydrous phase B into a pressure-temperature regime characteristic of the Earth's transition zone.

INTRODUCTION

Geophysicists predict the Earth's mantle mineralogy based in large part on phase equilibria in the system MgO-SiO_2, components believed to account for as much as 88 mol% of the mantle (Ringwood, 1975; Yoder, 1976; Basaltic Volcanism Study Project, 1981). Lesser amounts of FeO (≈6 mol%), CaO (≈3 mol%), Al_2O_3 (≈2 mol%) and alkalis (<1 mol%) have long been assumed to play a relatively minor role in the major mineral relations of mantle rocks. In particular, Fe has been thought to substitute freely for Mg in olivine, pyroxene, garnet, wadsleyite, and other silicates within the spinel, ilmenite, and perovskite structures. Phase equilibria observed for the Fe-free silicate system have been applied to the whole mantle, which actually possesses an Mg/(Mg + Fe) ratio of about 0.9.

In the paper, we describe the crystal structure of an Fe-bearing phase, $(Mg_{0.88}Fe_{0.12})_{14}Si_5O_{24}$, synthesized inadvertently in what were assumed to be the stable conditions for wadsleyite—a compound often invoked as the dominant mineral in the upper half of the Earth's transition zone. The unexpected synthetic compound adopts the anhydrous phase B structure, which has Si in both four- and sixfold coordination and is distinguished by Si octahedra that share all 12 edges with Mg-Fe octahedra to form a unique 13-cation cluster (Finger et al., 1991). In the Fe-free system, the anhydrous phase B stability region lies more than 100 °C above the presumed Earth geotherm (Kato and Kumazawa, 1985). This phase, though of considerable interest on crystal chemical grounds, was thus not thought to be a significant mantle mineral. The observation of Mg-Fe ordering in these crystals suggests the need to reexamine that assumption.

EXPERIMENTAL CONDITIONS AND RESULTS

Single crystals of Fe-bearing anhydrous phase B were synthesized in a split-sphere anvil apparatus (USSA-2000), starting from a dried and powdered mixture of forsterite and fayalite composition $(Mg_{1.6}Fe_{0.4})SiO_4$. The starting material was surrounded by Re foil, which was in turn jacketed by MgO and a cylindrical $LaCrO_3$ heater (Gasparik, 1989). The sample, heated for 1 h to 1800 °C at 15 GPa [well within the stability field for wadsleyite, β-$(Mg,Fe)_2SiO_4$], produced numerous crystals up to 150 μm in diameter. Microscopic inspection revealed at least two distinct types of birefringent crystals, indicating that the expected monomineralic synthesis of wadsleyite was not successful. Most grains are subequant pale green to dark green, but these crystals coexist with a few colorless flat plates.

Electron microprobe analyses of crystals from this experiment suggested the presence of at least three phases. Most abundant are anhydrous phase B crystals, $(Mg,Fe)_{14}Si_5O_{24}$, which display a range of atomic Mg/(Mg + Fe) from 0.88 to 0.93 (average of five analyses = 0.90). We observed no significant zoning in individual crystals, but compositional differences among grains are real. This range of Fe content, from 7 to 12%, is reflected in the continuous range of crystal color from pale to deep green. All anhydrous phase B analysis totals are within ±3% of 100%. Observed Si/(Fe + Mg) = 0.357 ± 0.003, the same

TABLE 1. Crystallographic data for $(Mg_{0.88}Fe_{0.12})_{14}Si_5O_{24}$

Atom	x	y	z	B_{eq}	Fe/ (Fe + Mg)
Si1	0	0	0	0.40(3)*	
Si2	½	0.31107(9)	0.17584(14)	0.40(2)	
Si3	0	0.37466(9)	0.99769(15)	0.36(2)	
Mg1	½	0	½	0.62(5)	0.119(6)
Mg2	½	0.17325(10)	0.35657(14)	0.63(4)	0.080(5)
Mg3	½	0	0	0.53(3)	0.409(6)
Mg4	0.24024(15)	0.00208(7)	0.25556(10)	0.51(2)	0.075(3)
Mg5	0	0.17678(10)	0.82023(15)	0.52(3)	0.088(4)
Mg6	0.24384(18)	0.16952(6)	0.08159(9)	0.50(2)	0.113(3)
O1	0	0.9136(2)	0.3471(3)	0.46(6)	
O2	0	0.5752(2)	0.3541(4)	0.50(6)	
O3	0	0.2419(2)	0.4960(4)	0.51(5)	
O4	½	0.0863(2)	0.1738(3)	0.54(6)	
O5	½	0.4248(2)	0.1700(4)	0.49(6)	
O6	½	0.7605(2)	0.4706(3)	0.56(6)	
O7	0.2323(4)	0.0881(1)	0.4207(2)	0.63(4)	
O8	0.2121(4)	0.4267(1)	0.4253(2)	0.47(4)	
O9	0.2834(4)	0.7622(1)	0.2521(2)	0.50(4)	

Note: Diffraction experiments with Rigaku AFC-5 diffractometer, rotating anode generator, Mo$K\alpha_1$ radiation, graphite monochromator, λ = 0.7093 Å, ω step scans to $2\theta = 60°$, ambient pressure and temperature; a = 5.908(2) Å, b = 14.241(3) Å, c = 10.069(3) Å, V_{cell} = 847.2(5) Å^3. Space group *Pmcb*; $Z = 2$; molecular mass = 913.8; ρ_{calc} = 3.582 g/cm^3; μ_l = 22.9 cm^{-1}; range of transmission factors = 0.82–0.94; four octants measured; internal agreement 5.6%. $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o| = 0.074$, $R_w = \Sigma\, \sigma_F^{-2}(F_o - F_c)^2/\Sigma\, \sigma_f^{-2}F_o^2 = 0.021$ for all 1357 independent data; $R = 0.049$, $R_w = 0.020$ for 1017 data with $F_o > 2\sigma_F$; goodness of fit = 0.8 for anisotropic temperature factors.

* Numbers in parentheses are the estimated standard deviation in the last quoted decimal place.

as the 0.357 value for stoichiometric $(Mg,Fe)_{14}Si_5O_{24}$. In addition, using electron microprobe and single-crystal X-ray analyses, we observed two distinct populations of orthosilicate crystals. The few colorless crystals are a forsteritic olivine with Mg/(Mg + Fe) ≈ 0.93 [orthorhombic, a = 4.756(5), b = 5.992(1), c = 10.224(3)], whereas the darkest green crystals are wadsleyite [β-$(Mg,Fe)_2SiO_4$] with Mg/(Mg + Fe) ≈ 0.87 [orthorhombic, a = 11.484(4), b = 8.291(11), c = 5.705(3)].

The three phases—olivine, wadsleyite, and anhydrous phase B—are not a stable assemblage in the $(Mg,Fe)_2SiO_4$ system, nor do they match the orthosilicate starting composition. We suspect that the brittle Re foil jacket split and perhaps fragmented during the experiment, allowing MgO to interact with the orthosilicate starting materials. We assume that anhydrous phase B formed at the MgO-rich rind of the sample chamber—the most magnesian samples at the outer edges—while the two-phase mixture of orthosilicates crystallized nearer the center of the cylindrical sample chamber.

A rectangular prismatic single crystal of the darkest green anhydrous phase B (presumably the most Fe rich), approximately 25 × 60 × 90 μm, was selected for structure analysis by X-ray diffraction. This crystal has an orthorhombic unit cell [space group *Pmcb*, a = 5.908(2), b = 14.241(3), c = 10.069(3)]. We initiated the crystal structure refinement of Fe-bearing anhydrous phase B with parameters observed for the Mg end-member (Finger et al., 1991). In addition to the scale factor and 35 variable atomic coordinates, we refined anisotropic temperature factors, an extinction parameter, and Mg/(Mg + Fe) for the crystal and each of the six symmetrically distinct Mg sites (Table 1). All atomic fractional coordinates are within ±0.002 of the Fe-free phase. Fe orders strongly into the M3 site, with 40% Fe, whereas the other five Mg octahedral sites have only 7–11% Fe.

A second anhydrous phase B crystal, this one of pale green, was also examined by single-crystal X-ray techniques. Preliminary refinements indicate Mg/(Mg + Fe) = 0.93, with an orthorhombic unit cell [a = 5.903(3), b = 14.229(2), c = 10.061(3)]. Fe in this specimen orders in an identical fashion to the 12% Fe crystal: M3 contains more than 30% Fe, whereas the other five Mg octahedral sites have only 4–7% Fe.

DISCUSSION

This study raises intriguing questions about the causes and consequences of Fe-Mg ordering in rock-forming silicates. The degree of ordering between two sites, M1 and M2, can be expressed as a distribution coefficient:

$$K_d = (Fe_{M1}/Mg_{M1})/(Fe_{M2}/Mg_{M2}).$$

A completely disordered mineral has a K_d equal to 1, whereas typical extreme values for common rock-forming silicates include 2.7 for wadsleyite (Finger et al., 1990), 1.8 for olivine (Finger and Virgo, 1971), and 2.3 for the amphibole grunerite (Finger, 1969). Orthopyroxenes, which have two very different octahedral sites, provide an interesting extreme case. When allowed to equilibrate at low temperature, Fe strongly orders into the larger and more distorted M2 site, while Mg prefers the smaller, undistorted M1 site. Distribution coefficients as large as 50 have been reported for samples annealed at temperatures below 500 °C, whereas samples heated to 1000 °C and rapidly quenched more typically have K_d values between 2 and 3 (Ghose, 1965). Above 1000 °C most other magnesium iron silicates also display nearly complete disorder (Virgo and Hafner, 1969). It has been tacitly assumed, therefore, that Fe-Mg ordering does not play a significant role in the high-temperature crystal chemistry of the Earth's mantle.

Anhydrous phase B calls this assumption into question. The sample was synthesized at 1800 °C and rapidly quenched, yet Fe is concentrated in the M3 site—the only octahedron to share two edges with the Si octahedra. The average distribution coefficient between M3 and the other five octahedral sites in the 12% Fe sample is 6.6 (in the 7% Fe sample it is greater than 9), significantly higher than for any other magnesium iron silicate quenched from high temperature. Furthermore, the K_d between M3 and M4 is 8.5, even though these two octahedra share edges. This pattern of Fe distribution, though unexpected, can be rationalized on crystal chemical grounds. The Si octahedron is significantly smaller (polyhedral volume = 7.85 Å^3) than the average Mg octahedra (≈12 Å^3). The close-packed O array, in which the smaller Si is surround-

TABLE 2. Selected interatomic distances for octahedra in $Mg_{14}Si_5O_{24}$ (AnhB) and $(Mg_{0.88}Fe_{0.12})_{14}Si_5O_{24}$ (Fe-AnhB)

	AnhB[a]	Fe-AnhB	% change
Si1-O2 [2]*	1.818(2)	1.819(3)	
Si1-O8 [4]	1.797(1)	1.796(2)	
Mean	1.804	1.804	0.00
Mg1-O5 [2]	2.008(2)	2.020(4)	
Mg1-O7 [4]	2.142(1)	2.171(2)	
Mean	2.097	2.117	0.94
Mg2-O4	2.224(2)	2.219(4)	
Mg2-O6	1.976(2)	1.980(3)	
Mg2-O7 [2]	2.099(1)	2.095(3)	
Mg2-O9 [2]	2.081(1)	2.107(2)	
Mean	2.093	2.101	0.36
Mg3-O4 [2]	2.112(2)	2.138(3)	
Mg3-O8 [4]	2.109(1)	2.133(2)	
Mean	2.110	2.135	1.17
Mg4-O1	2.108(1)	2.110(3)	
Mg4-O2	2.056(1)	2.078(3)	
Mg4-O4	2.095(1)	2.114(3)	
Mg4-O5	2.030(1)	2.032(2)	
Mg4-O7	2.072(1)	2.065(2)	
Mg4-O8	2.099(1)	2.120(2)	
Mean	2.077	2.087	0.48
Mg5-O1	2.112(3)	2.120(4)	
Mg5-O3	2.112(2)	2.116(4)	
Mg5-O8 [2]	2.192(1)	2.205(2)	
Mg5-O9 [2]	2.012(1)	2.022(2)	
Mean	2.106	2.115	0.43
Mg6-O2	2.061(1)	2.073(2)	
Mg6-O3	2.088(1)	2.100(2)	
Mg6-O4	2.119(1)	2.135(3)	
Mg6-O6	2.043(1)	2.060(2)	
Mg6-O8	2.081(1)	2.096(2)	
Mg6-O9	2.135(1)	2.146(2)	
Mean	2.088	2.102	0.65

* Numbers in square brackets indicate the multiplicity of the bond.

ed by 12 larger Mg octahedra, must become considerably strained in the vicinity of the 12 shared O-O edges.

An equal distribution of Fe among all six Mg sites in anhydrous phase B would exacerbate this misfit. By substituting the larger Fe for Mg in the M3 site, however, the lattice strain decreases. Si and M3 octahedra form edge-sharing strips parallel to the **a** crystallographic axis. These strips share edges with similar octahedral chains composed entirely of M4, the octahedron with the least Fe (Fig. 1). The extreme ordering of Fe between adjacent M3 and M4 sites results in Si-M3-Si-M3 and M4-M4-M4-M4 strips more nearly matched in size (Table 2). Ordering allows the structure to compensate in part for the misfit of Mg and Si octahedra.

The distinctive ordering behavior of M3, compared with the other five Mg octahedra, suggests that this site may provide a repository for other divalent cations larger than Mg. Other ordered high-pressure phases, such as $Mg_{12}Mn_2Si_5O_{24}$ or even $Mg_{12}Ca_2Si_5O_{24}$, should be considered as possible compositional variants. Alternatively, the coupled substitution of Al for octahedral Si plus Mg in M4 would also accomplish the required size compensation. An aluminous phase of composition $^{[6]}(Mg_{13}Al_2)$-$^{[4]}Si_4O_{24}$ might adopt the anhydrous B structure.

This study has implications regarding the seismic velocity and density distribution in the Earth's transition

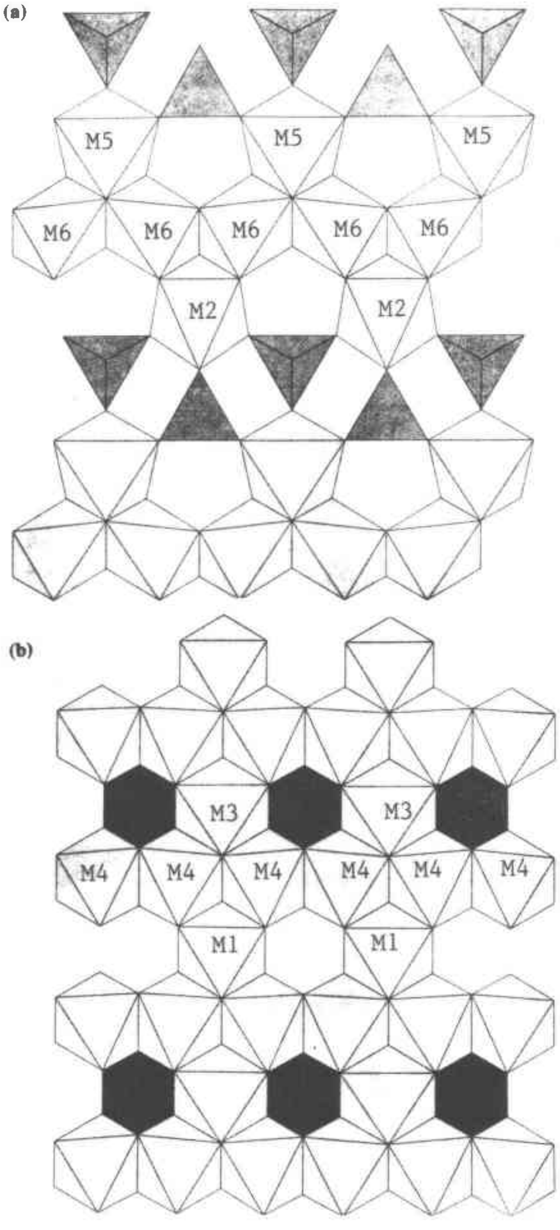

Fig. 1. Two types of (010) layers in the anhydrous phase B structure reveal a possible rationalization for extensive Mg-Fe ordering. Olivine-type layers (**a**) contain M2, M5, and M6 octahedra, all enriched in Mg. The (**b**) layers, on the other hand, contain Si octahedra surrounded by Mg-Fe octahedra. The Fe-rich site, denoted M3, is the only octahedron to share edges with two octahedral Si sites (in black). This concentration of Fe creates two chemically distinct kinds of edge-sharing octahedral strips parallel to **a**. Predominantly Mg sites form strips with equally sized M6 or M4 octahedra. Enclosed by these chains are strips in which smaller Si and larger (Mg,Fe) octahedra alternate. The concentration of larger Fe cations in the latter strips compensates for the smaller Si octahedra.

zone, a region critical for evaluating conflicting models of deep mantle chemistry (Ita and Stixrude, 1991). Some researchers argue for a lower mantle significantly enriched in Fe (Anderson, 1979; Jeanloz and Thompson, 1983), whereas others advocate a uniform composition across the 670-km seismic discontinuity (Ito and Takahashi, 1987; Bukowinski and Wolf, 1990; Wang et al., 1991). The differences in these compositional models have profound effects on models of mantle convection. In the past all mineralogical models have assumed the presence of Fe-bearing orthosilicate of approximate composition $(Mg_{0.9}Fe_{0.1})_2SiO_4$—as much as two-thirds by volume of the transition zone in some models.

Anhydrous phase B does not appear on the phase diagram for $(Mg,Fe)_2SiO_4$, and so has not been considered in models of mantle mineralogy. In the Fe-free system, anhydrous phase B is only seen in more Mg-rich (Si-poor) compositions, where it forms during incongruent melting of stoichiometric Mg_2SiO_4. This study demonstrates that the substitution of Fe for Mg significantly alters the stability of anhydrous phase B. If the expanded anhydrous phase B stability field approaches that of the orthosilicate at or near *P-T* conditions of the transition zone, or if it displaces orthosilicates with the addition of elements such as Ca or Al, many of the assumptions that underlie mantle model calculations will have to be revised.

The observed effect of Fe on the stability of anhydrous phase B should also hold true for the closely related hydrous phase B, which has been proposed as a major repository for H_2O in the Earth's mantle (Finger et al., 1989). The M3 sites of anhydrous and hydrous phase B are topologically identical, and their sizes, polyhedral distortions, and degree of misfit are the same within experimental error. Studies of phase equilibria in the system $MgO-SiO_2-H_2O$ at mantle conditions must be expanded to include an appropriate Fe component.

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