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LETTER

Crystal structure of a new spinelloid with the wadsleyite structure in the system Fe_2SiO_4-Fe_3O_4 and implications for the Earth's mantle

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ABSTRACT

A new spinelloid polytype with a composition $Fe_{2.45}Si_{0.55}O_4$ has been synthesized at 1100 °C and 5.6 GPa that is isostructural with wadsleyite [$\beta-(Mg,Fe)_2SiO_4$]. The refined parameters (space group *Imma*) are: a = 5.8559(2) Å, b = 11.8936(4) Å, c = 8.3684(2) Å, V = 582.84(2) Å^3. Tetrahedrally coordinated Fe^{3+} and Si are completely disordered and the substitution of Fe^{3+} for nearly one-half of the Si results in a significant expansion of the tetrahedra. This is the first direct evidence that significant amounts of Fe^{3+} can be incorporated into the wadsleyite-type structure. Because the β form of Fe_2SiO_4 is unstable, the implication is that Fe^{3+}, by the substitution mechanism: $2Fe^{3+} = Si^{4+} + Fe^{2+}$, acts to stabilize the wadsleyite structure. It is possible that the addition of Fe^{3+} could stabilize $(Mg,Fe)_2SiO_4$ wadsleyites to lower pressures, which would influence the exact position of the ''410 km'' discontinuity. The apparent compatibility of Fe^{3+} in the wadsleyite structure, suggests that available Fe^{3+} will be readily incorporated in the modally dominant phase in the upper parts of the transition zone, thereby leading to a low f_{O_2} in this region of the mantle.

INTRODUCTION

In some current mineralogical models of the Earth's mantle, wadsleyite, the β polymorph of $(Mg,Fe)_2SiO_4$, is considered to be the dominant phase in the upper portions of the transition zone (e.g., Irifune and Ringwood 1987). In addition, the transition of olivine into the wadsleyite structure (i.e., the α–β transition) has been implicated as the cause for the observed discontinuity in seismic wave velocities near 410 km depth (e.g., Ringwood 1975; Bina and Wood 1987; Katsura and Ito 1989). Therefore, the stability and crystal chemical behavior of wadsleyite is of interest to petrologists and geophysicists. Wadsleyite is one of various spinelloid polytypes, which are derivatives of the spinel structure and differ from each other in the degree of polymerization of the octahedral and tetrahedral sites. In the case of wadsleyite (space group *Imma*), three distinct octahedral sites are corner-linked to T_2O_7 dimers that are oriented parallel to b (Horiuchi and Sawamoto 1981). Double columns of M3 octahedra, oriented parallel to a, are cross-linked by chains of edge-sharing M1 and M2 octahedra running parallel to b. Experimental and theoretical studies indicate that the stability of wadsleyite is limited to the Mg-rich portion of the $(Mg,Fe)_2SiO_4$ binary system, with Fe/(Fe + Mg) ≤ 0.25 (Bina and Wood 1987; Akaogi et al. 1989; Katsura and Ito 1989; Fei et al. 1991). Although wadsleyite with a much higher Fe content [Fe/(Fe + Mg) = 0.4] has been recently synthesized, it is clear that the presence of Fe acts to destabilize the wadsleyite structure even if there is no obvious crystallographic reason for this (Finger et al. 1993). At the Fe_2SiO_4-end-member composition, olivine transforms directly to the spinel structure (γ-Fe_2SiO_4) without any intervening β phase (Yagi et al. 1987).

In other systems, up to five different spinelloid polytypes have been observed. Based upon work in the $NiAl_2O_4$-Ni_2SiO_4 system, these have been designated phases I–V (Ma 1974; Akaogi et al. 1982). Wadsleyite and Ni-aluminosilcate phase III are isostructural. A type V spinelloid has been recently synthesized at high pressure in the system Fe_2SiO_4-Fe_3O_4 (Canil et al. 1991; Ross et al. 1992). This polytype has space group *Pmma*, is intermediate to the spinel and β-phase structures, and consists of alternating strips of these two types of structural units with Fe^{3+} substituting for both Fe^{2+} and Si on the octahedral and tetrahedral sites, respectively. Refined site occupancies indicate that Fe^{3+} prefers the less distorted isolated tetrahedral sites in the spinel-like layers (Ross et al. 1992). The compatibility of Fe^{3+} in the β-phase structure is an open question. The behavior of Fe^{3+} in the wadsleyite (spinelloid III) structure has implica-

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TABLE 1. Fractional atomic coordinates and anisotropic displacement parameters for Fe^{3+}-substituted wadsleyite

Atom	*x/a*	*y/b*	*z/c*	B_{eq} (Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M1	0	0	0	0.94	0.0067(2)	0.00174(4)	0.0033(1)	0	0	0.00000(5)
M2	0	¼	0.96966(9)	0.87	0.0062(2)	0.00170(4)	0.0028(1)	0	0	0
M3	¼	0.12496(4)	¼	1.02	0.0082(2)	0.00194(4)	0.00300(8)	0	−0.00003(7)	0
T	0	0.11991(5)	0.6180(1)	0.74	0.0051(2)	0.00144(5)	0.0025(1)	0	0	0.00000(5)
O1	0	¼	0.2255(5)	0.96	0.0057(11)	0.0022(3)	0.0031(5)	0	0	0
O2	0	¼	0.7234(6)	1.50	0.0065(12)	0.0047(3)	0.0033(5)	0	0	0
O3	0	−0.0041(3)	0.2544(4)	1.29	0.0042(9)	0.0038(2)	0.0042(4)	0	0	−0.0017(2)
O4	0.2556(4)	0.1222(1)	0.0014(3)	1.04	0.0092(7)	0.0038(14)	0.0039(3)	0.00012(16)	−0.0018(3)	−0.00005(15)

Notes: Numbers in parentheses represent estimated standard deviations for the last digits. The refined site occupancy of the T site is 0.454(6)Fe + 0.546(6)Si, subject to the constraint of a total occupancy of unity.

tions for the relative oxygen fugacity, f_{O_2}, of the transition zone, which in turn has wider petrological and geochemical ramifications from element partitioning to the generation of partial melts through ''redox melting'' (Taylor and Green 1988). Mixed valence substitutions also provide a mechanism for the incorporation of H into nominally anhydrous phases.

This paper reports the synthesis and crystal structure of a new spinelloid in the system Fe_2SiO_4-Fe_3O_4 that is isostructural with wadsleyite. Its crystal chemistry and implications for the Earth's transition zone are briefly discussed.

Experimental methods

Synthesis

The spinelloid sample was synthesized in a belt apparatus at the Institut für Mineralogie, Universität Frankfurt, Germany. The pressure assembly and pressure and temperature calibration are described in detail by Brey et al. (1990). The starting material was a stoichiometric mixture of fayalite and magnetite (ground under acetone and dried) with a nominal composition of 55 mol% Fe_2SiO_4−45 mol% Fe_3O_4. Magnetite was synthesized from high-purity Fe_2O_3 (99.99%) in a 1 atm gas-mixing furnace at 1100 °C and a log $f_{O_2} = -9.1$, as measured by a Y-stabilized zirconia electrolyte cell, and drop-quenched into water. The fayalite was prepared in an analogous way from a stoichiometric mixture of high-purity SiO_2 (99.999%) and Fe_2O_3 at 1100 °C except with a CO_2/CO ratio of ¼, which yields an f_{O_2} just below the iron-wüstite oxygen buffer. Several cycles of grinding and firing were necessary to achieve homogeneity. The experiment (no. mt45-fr1062) was performed with a dry powder at 1100 °C and 5.6 GPa using a silver capsule with a friction-fitting lid and had a duration of 45 h. The chemical composition of the sample was determined by electron microprobe (Cameca SX-51, 15 kV, 20 nA sample current with 20 s counting times on the peak and background) to have a bulk magnetite content of X_{mt} = 0.454(11). The crystals are black and ferromagnetic.

X-ray diffraction

Powder X-ray diffraction patterns over the 2θ range 30–120° were collected from the samples (with Si added as an internal diffraction standard) with a Stoe STADI-P diffractometer equipped with Co X-ray tube and a focusing monochromator. Unit-cell parameters were determined by least squares fit to the positions of 82 peaks from the sample, corrected through use of peak positions from the Si standard (NBS 640). Refined parameters are: a = 5.8559(2) Å, b = 11.8936(4) Å, c = 8.3684(2) Å, and V = 582.84(2) Å^3. In this high-resolution pattern, no peak-splitting was evident that would indicate symmetry below orthorhombic (cf. Smyth et al. 1997).

X-ray intensity data were collected from a single crystal (a hexagonal-shaped plate 35 μm thick and ≈110 μm in diameter) with an Enraf-Nonius CAD4 diffractometer equipped with a Mo X-ray tube operated at 50 kV and 50 mA, with $K\alpha$ radiation selected with a graphite monochromator. All reflection positions corresponding to a primitive unit cell were scanned in one hemisphere of reciprocal space for $2\theta < 30°$ to determine the diffraction symbol. Only 13 reflections of 288 that would violate the diffraction conditions for diffraction symbol *I*–(*ab*) had integrated intensities greater than three standard deviations as estimated from counting statistics. As the intensities were marginally above 3σ and the profiles off-center in the scans, these can all be attributed to either double diffraction or to contributions from a small second crystal fragment. A data set of a hemisphere of reflections permitted by the *I*-lattice to $2\theta < 60°$ was then collected with constant precision ω-scans, yielding 1660 reflections consistent with diffraction symbol *I–(ab).* Lorentz, polarization, and absorption corrections (μ_l= 121.7 cm^{-1}) were performed with a program based upon ABSORB (Burnham 1966). Averaging in point group *mmm* (R_{int} = 0.026) yielded a unique set of 393 reflections with $I > 3\ \sigma_I$ for subsequent analysis. Intensity statistics [N(Z) and E statistics] clearly indicated the presence of a center of symmetry and hence space group *Imma.* A structure refinement with RFINE90 (based upon RFINE4, Finger and Prince 1975) starting from published wadsleyite structures converged to R_u = 0.023, R_w = 0.026, G_{fit} = 1.04 for 44 variables including anisotropic temperature factors for all atoms and the site occupancy of the T site (Table 1). Complex scattering factors for neutral atoms were taken from the *International Tables for Crystallography* (Creagh and McAuley 1992; Maslen et al. 1992). The refined occupancy of 0.454(6)Fe + 0.546(6)Si for the T site agrees well with electron microprobe analyses of the

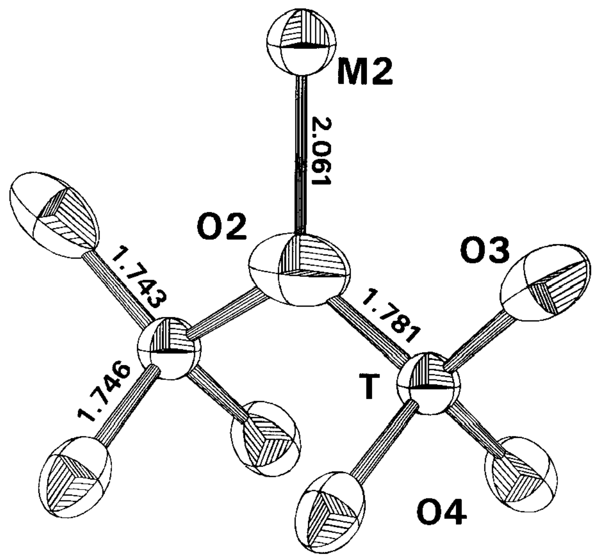

Figure 1. A thermal ellipsoid plot of the T_2O_7 group and adjacent M2 site in wadsleyite-structured $Fe_{2.45}Si_{0.55}O_4$ (drawn with Atoms; Dowty 1995), with bond lengths indicated in Å. Elongation of the ellipsoids of the O atoms toward the T sites arise from the averaging of positions corresponding to T occupancy by Fe or Si.

Table 2. Selected bond lengths (Å) in Fe^{3+}-substituted wadsleyite

	T	M1	M2	M3
O1			2.141(4)	2.097(1) ×2
O2	1.781(2)		2.061(5)	
O3	1.743(3)	2.129(3) ×2		2.121(2) ×2
O4	1.746(2) ×2	2.087(2) ×4	2.150(2) ×4	2.081(2) ×2
Average	1.754	2.101	2.134	2.100
V (Å³)	2.76	12.35	12.75	12.28
Q.E.	1.0022	1.0005	1.011	1.0033
A.V.	9.08	1.28	37.20	11.51

Notes: Q.E. are the quadratic elongations and A.V. the angle variances of the polyhedra as defined by Robinson et al. (1971).

bulk sample that yielded a magnetite content of 0.454(11). Based upon this composition and measured unit-cell volume, the calculated density of Fe^{3+}-substituted wadsleyite at 1 atm is 4.95 g/cm³.

The structure refined in space group *Imma* contains only a single symmetrically distinct T site, occupied by Fe and Si. The anisotropic displacement parameters (adp) of the O atoms coordinated to the T site show significant elongation along the direction of the T-O bonds (Table 2, Fig. 1). The adp represent an average mean square displacement along the T-O bonds of 0.16 Å, compared to 0.10 Å along M-O bonds. The reported structure is therefore an ''average'' structure, with the refined positions of O2, O3, and O4 representing an average of positions occupied when T = Si or T = Fe. The question is whether this average is an artifact due to twinning of an ordered structure, incorrect choice of space group, or whether it represents disorder on a local scale. Two further refinements to the same data set were performed to investigate these possibilities. A wadsleyite-type structure with the acentric space group *Im*2*a* (Smyth et al. 1997) would possess two distinct tetrahedral sites. Complete ordering of Fe^{3+} and Si^{4+} between these two sites would result in each T_2O_7 group being a $FeSiO_7$ group, thereby reducing the formal charge balance on the central O2 atom of the dimer. However, structure refinements in *Im*2*a* with complete Fe-Si ordering yielded greatly increased *R*-values (R_w = 0.12), and no distinction in geometry between the two T sites. Refinement of the Fe/Si distribution between the two sites resulted in a completely disordered model, consistent with space group symmetry *Imma.* Similarly, a model in *Im*2*a* with twinning on (010) also yielded R_w = 0.12. Therefore, *Imma* is the correct space group for this new spinelloid in the Fe_2SiO_4-Fe_3O_4 system, making it isostructural with wadsleyite and Ni-aluminosilicate III. As in Ni-aluminosilicate III (Ma and Sahl 1975), the tetrahedral cations in Fe^{3+}-substituted wadsleyite are completely disordered, on the length scale probed by X-ray diffraction.

Crystal chemistry

The crystal structure of $Fe_{2.45}Si_{0.55}O_4$ determined here retains the general features of the orthorhombic wadsleyite structure (e.g., Horiuchi and Sawamoto 1981), but has some significant differences compared to wadsleyites on the $(Mg,Fe)_2SiO_4$ join. Finger et al. (1993) showed that the geometry of the Si_2O_7 group of $(Mg,Fe)_2SiO_4$ wadsleyites is essentially invariant with Fe/Mg ratio. In contrast, substitution of Fe^{3+} for nearly one-half of the tetrahedral Si in the T site of $Fe_{2.45}Si_{0.55}O_4$ significantly expands the TO_4 tetrahedron (Table 2). The average T-O bond length of 1.754 Å compares well with a value of 1.758 Å obtained by linear interpolation between 1.887 Å for the $Fe^{3+}O_4$ tetrahedra in magnetite (Hill et al. 1979) and 1.652 Å for the SiO_4 tetrahedra in $(Mg,Fe)_2SiO_4$ wadsleyites (Finger et al. 1993). In the latter structures the Si-O2 bond is 0.07 Å longer than the other three Si-O bonds because of overbonding (valence sum of 2.33 based upon formal charges) of the bridging O2 atom. Substitution of Fe^{3+} for 50% of the Si^{4+} reduces the formal valence sum at O2 to 2.00, and the tetrahedron is therefore much less distorted, with T-O2 being only 0.04 Å longer than the other three T-O bonds. The relaxation of the sites in tetrahedral sublattice provides a structural explanation for the stabilization of the wadsleyite structure through substitution of Fe^{3+} for Si in Fe_2SiO_4.

In the absence of octahedral Si^{4+} in the crystal structure, the three octahedral sites must have an overall average occupancy of 0.225 Fe^{3+} + 0.775 Fe^{2+}, if formal charges are a valid description of the electronic state of the structure. Comparison of the M-O bond lengths with those in structures of the $(Mg,Fe)_2SiO_4$ system hints at the distribution of Fe^{3+}. Extrapolation of the average bond lengths reported for several compositions by Finger et al. (1993) gives values of 2.12, 2.13, and 2.13 Å for the average bond lengths of M1, M2, and M3 in a hypothetical $Fe^{2+}_2SiO_4$ wadsleyite. These values are only exceeded in $Fe_{2.45}Si_{0.55}O_4$ by ⟨M2-O⟩ (Table 2), suggesting that this site is occupied primarily by Fe^{2+}. The values of ⟨M1-O⟩ and ⟨M3-O⟩ are less than the predicted values, suggesting that the smaller Fe^{3+} cation is significantly partitioned into these two octahedral sites. An attempt to determine the Fe^{2+} and Fe^{3+} site occupancies by Mössbauer spectroscopy was precluded by the complexity of the room temperature absorption spectrum. Spectroscopic measurements at low temperature are planned to characterize the distribution of Fe^{2+} and Fe^{3+}.

Discussion

This new spinelloid in the Fe_2SiO_4-Fe_3O_4 system provides the first direct evidence that significant amounts of Fe^{3+} can be incorporated into a wadsleyite-type structure. This is also the first reported Fe-silicate to possess the wadsleyite structure, except for the true wadsleyite rich in Mg. The fact that the β form of Fe_2SiO_4 is unstable implies that the addition of Fe^{3+}, through the substitution mechanism: $2Fe^{3+} = Si^{4+} + Fe^{2+}$, stabilizes the wadsleyite structure. An additional spinel-like TO_4 site, as in the spinelloid V polytype (Ross et al. 1992), is not required for large amounts of Fe^{3+} to be incorporated into a spinelloid structure. In fact, there exists at least one additional spinelloid polytype in the Fe_2SiO_4-Fe_3O_4 system (Woodland and Angel 1997).

Additional experiments in the Fe_2SiO_4-Fe_3O_4 system with the same starting materials and procedures used here document that the stability field of Fe^{3+}-substituted wadsleyite extends up to 20 mol% Fe_3O_4 ($\approx 0.30 < X_{mt} < \approx 0.50$) and that this spinelloid polytype is preferentially stabilized at high temperature (> 1000 °C, Woodland and Angel, unpublished data). This result is consistent with the observation in other systems that spinelloids, including the β-polytype, are high-entropy phases (Akaogi and Navrotsky 1984; Leinenweber and Navrotsky 1989). The wadsleyite structure can accommodate at least a limited range of solid solution in the Fe_2SiO_4-Fe_3O_4 system, with up to 50% of the tetrahedral sites being occupied by Fe^{3+}. Complete phase relations in the Fe_2SiO_4-Fe_3O_4 system will be presented elsewhere.

The stability of Fe^{3+}-substituted wadsleyite in the *P-T* range of 5.0 to 6.0 GPa at 1100–1200 °C contrasts with the much higher pressures necessary for stabilizing $(Mg,Fe)_2SiO_4$ wadsleyites (i.e., 12 GPa at 1200 °C, Katsura and Ito 1989). This difference suggests that the addition of Fe^{3+} could act to stabilize $(Mg,Fe)_2SiO_4$ wadsleyites to lower pressures compared with the Fe^{3+}-free system, which could shift the position of the ''410 km'' seismic discontinuity merely through a change in redox state. A large modal abundance of wadsleyite in the upper portions of the transition zone in a ''pyrolite'' mantle (Irifune and Ringwood 1987) implies that the available Fe^{3+} will be distributed throughout a relatively large volume, rather than being concentrated in modally minor phases, as is the case in the upper mantle (O'Neill et al. 1993b). This occurrence should lead to a significant lowering of the f_{O_2} in the transition zone, thereby increasing the feasibility of ''redox melting'' as a viable process for melt generation in the deeper portions of the upper mantle (i.e., O'Neill et al. 1993b). However, the extent of solid solution between Fe^{3+}-substituted wadsleyite and the true Mg_2SiO_4-rich wadsleyites relevant to the Earth's mantle remains unknown, although small amounts of Fe^{3+} are often present in such experimentally sythesized materials (Fei et al. 1992; O'Neill et al. 1993a; Finger et al. 1993).

The recently reported hydrous ''wadsleyite II'' is a spinelloid-like structure related to spinelloid III (true wadsleyite), with the unit cell being expanded in the *b* direction (Smyth and Kawamoto 1997). Although this spinelloid derivative has not yet been found in the Fe_2SiO_4-Fe_3O_4 system, Fe is considered essential for the stabilization of ''wadsleyite II'' (Smyth and Kawamoto 1997). In fact, much of the Fe in the ''wadsleyite II'' sample of Smyth and Kawamoto (1997) is the ferric state (J. Smyth, personal communication), suggesting a possible link between the incorporation of H and Fe^{3+} in this phase. Clearly, the roll of Fe^{3+} in helping to stabilize hydrous forms of $(Mg,Fe)_2SiO_4$ wadsleyite also awaits further investigation.

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