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Al, Fe substitution in the $MgSiO_3$ perovskite structure: A single-crystal X-ray diffraction study

C.B. Vanpeteghem[a,*], R.J. Angel[a], N.L. Ross[a], S.D. Jacobsen[b], D.P Dobson[c], K.D. Litasov[d], E. Ohtani[d]

[a] *Crystallography Laboratory, Department of Geosciences, Virginia Polytechnic Institute and State University, Derring Hall, Blacksburg, VA 24061, USA*
[b] *Geophysical Laboratory, Carnegie Institute of Washington, 5251 Broad Branch Road, NW, Washington DC 20015, USA*
[c] *Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK*
[d] *Institute of Mineralogy, Petrology and Economic Geology, Tohoku University, Sendai 981-8578, Japan*

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Abstract

We have determined by single-crystal X-ray diffraction the crystal structure of three Fe–Al–$MgSiO_3$ perovksite samples containing up to 9.5 wt% of Al_2O_3 and 19 wt% of FeO. We find that there is no evidence for Fe (Fe^{3+} or Fe^{2+}) on the octahedral site. Therefore, we deduce that the two dominant substitution mechanisms for the combined substitution of Al and Fe into the perovskite structure are: (i) ${Mg_A}^{2+} + {Si_B}^{4+} \Leftrightarrow {Fe_A}^{3+} + {Al_B}^{3+}$, where the excess of Fe is accommodated by (ii) ${Mg_A}^{2+} \Leftrightarrow {Fe_A}^{2+}$. This is in agreement with all past theoretical and experimental work and solves the long-debated issue of Fe^{3+} occupancy in the perovskite structure.

Keywords: Single-crystal; X-ray diffraction; Cation partitioning; Site occupancy

1. Introduction

Magnesium silicate perovskite ($MgSiO_3$) is believed to be the dominant phase in Earth's lower mantle, co-existing with magnesiowüstite (Mg,Fe)O and $CaSiO_3$ perovskite (e.g. Kesson et al., 1998; Serghiou et al., 1998; Shim et al., 2004). The physical and chemical properties of perovskite and magnesiowüstite, and the distribution of major elements between these phases should therefore account for the bulk seismic properties of the lower mantle. In particular, partitioning of iron (Fe^{2+} and Fe^{3+}) and aluminum between the various phases is expected to influence the elasticity and rheology of the lower mantle (e.g. Jackson, 1998; Kung et al., 2002; Yamazaki and Karato, 2002), its bulk transport properties (e.g. Xu et al., 1998) as well as possible compositional layering (e.g. Kellogg et al., 1999; Badro et al., 2003). Since cation partitioning is ultimately controlled by structure, a detailed picture of silicate perovskite crystal chemistry with varying Fe and Al substitution is necessary to further our understanding of the lower mantle assemblage.

Over the past 10 years, much effort has been made to determine the effect of Al substitution on the physiochemical properties of Fe–$MgSiO_3$ perovskite (e.g. McCammon, 1997; Richmond and Brodholt, 1998; Wood, 2000; Brodholt, 2000; Lauterbach et al., 2000; Andrault et al., 2001). Previous work by Wood and

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* Corresponding author. Tel.: +1 540 231 5539; fax: +1 540 231 3386.
E-mail address: carine@vt.edu (C.B. Vanpeteghem).

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Rubie (1996) and Frost and Langenhorst (2002) indicated that the presence of Al causes a significant increase in the partioning of Fe into Fe–$MgSiO_3$ perovskite coexisting with magnesiowüstite. It is, therefore, of critical importance to determine site occupancies of all possible cations that could be hosted by magnesium silicate perovskite.

The perovskite structure, generally ABO_3, is composed of a corner-linked octahedral framework (B cation site) with the octahedra sharing triangular faces with a larger dodecahedral A cation site formed by the spaces within the three-dimensional octahedral network. The structure of Al–Fe–$MgSiO_3$ perovskite (space group *Pbnm*) is an orthorhombic distortion from the ideal cubic perovskite structure with space group *Pm*3*m* (Horiuchi et al., 1987).

Previous studies (Horiuchi et al., 1987; Kudoh et al., 1990; McCammon et al., 1992; Fei et al., 1994; McCammon, 1998; Jackson et al., 2005) determined that Fe on its own substitutes into $MgSiO_3$ by the following exchange mechanisms:

$$\mathrm{Mg_A}^{2+} + \mathrm{Si_B}^{4+} \Leftrightarrow \mathrm{Fe_A}^{3+} + \mathrm{Fe_B}^{3+} \qquad (1)$$

$$\mathrm{Mg_A}^{2+} \Leftrightarrow \mathrm{Fe_A}^{2+} \qquad (2)$$

where the subscripts A and B refer to the dodecahedral A-site and octahedral B-site, respectively. McCammon (1998) reported that in the presence of oxygen vacancies, Fe^{3+} is located on the octahedral site but as the concentration of Fe^{3+} increases in phases synthesized at higher oxygen fugacity, Fe^{3+} occupies both sites. Lauterbach et al. (2000) showed that an additional substitution mechanism can operate along with mechanisms (1) and (2) through creation of oxygen vacancies when Fe^{3+} replaces Si^{4+} as follows: $\frac{1}{2}\mathrm{O_2}^{-} + \mathrm{Si_B}^{4+} \Leftrightarrow \frac{1}{2}\mathrm{V_o} + \mathrm{Fe_B}^{3+}$. This mechanism is analogous to that described for Fe substitution in $CaTiO_3$ (Becerro et al., 1999).

In Fe-free $MgSiO_3$, Al substitution is accommodated by two mechanisms analogous to those found for Fe substitution (Kesson et al., 1995; Andrault et al., 1998; Stebbins et al., 2001, 2003; Yamamoto et al., 2003; Navrotsky et al., 2003; Akber-Knutson and Bukowinski, 2004):

$$\mathrm{Mg_A}^{2+} + \mathrm{Si_B}^{4+} \Leftrightarrow \mathrm{Al_A}^{3+} + \mathrm{Al_B}^{3+} \qquad (3)$$

$$\tfrac{1}{2}\mathrm{O_2}^{-} + \mathrm{Si_B}^{4+} \Leftrightarrow \tfrac{1}{2}\mathrm{V_o} + \mathrm{Al_B}^{3+} \qquad (4)$$

The vacancy substitution mechanism (4) is suppressed by increasing pressure and is only significant in the uppermost part of the lower mantle (Brodholt, 2000).

In addition, numerous previous synthesis and phase-equilibrium studies of Al incorporation into Fe–$MgSiO_3$ (e.g. Wood and Rubie, 1996; McCammon, 1997; Richmond and Brodholt, 1998; Wood, 2000; Brodholt, 2000; Lauterbach et al., 2000; Andrault et al., 2001; Frost and Langenhorst, 2002) have shown that (i) the Fe^{3+} content of $MgSiO_3$ perovskite increases with Al content and is independent of oxygen fugacity, (ii) Fe^{2+} partitioning is independent of Al_2O_3 content and (iii) the substitution of 3+ cations is coupled with Al substitution, where the highest level of cations are for X = Fe, Sc, Ga and Y (Andrault et al., 2001; Andrault, 2003).

In summary, previous studies indicate that Fe^{2+} occupies the dodecahedral A-site, whereas the location of Fe^{3+} within the silicate perovskite structure remains unclear. Therefore, we have carried out a single-crystal X-ray diffraction study on several well-characterized Fe–Al–$MgSiO_3$ crystals to determine the site occupancies of Al and Fe, and hence deduce the possible substitution mechanisms. Our results, based on the three samples studied here, are in agreement with all previous experimental and theoretical work and solve the question of Fe^{3+} occupancy in the lower mantle perovskite structure.

2. Experimental methods

Five different synthetic samples of Mg-perovskites have been used in this study and their compositions are summarized in Table 1. The Mg-perovskites were synthesized at 24–25 GPa and 1750–2000 °C in a multi-anvil press apparatus available at the Bayerisches Geoinstitut by Bolfan-Casanova (2000) and Dobson and Jacobsen (2004). Al and Fe-bearing samples were synthesized by Dobson and Jacobsen (2004) at the Bayerisches Geoinstitut and by Litasov and Ohtani (2002) in a Kawai-type (MA8) multi-anvil press at Tohoku University (Litasov and Ohtani, 2002). Bolfan-Casanova (2000) used oxide mixtures of MgO, SiO_2 and $Mg(OH)_2$ as a starting material. The temperature was held at ~1750 °C for up to 10 h before rapid quenching and slow decompression lasting 12–30 h. Chemical analyses were performed with a Cameca SX50 electron microprobe at 15 nA and 15 kV.

Dobson and Jacobsen (2004) synthesized large pure-Mg and Al–Fe–Mg-perovskite crystals up to 300 μm in size by fluxing the system in molten NaCl at 24 GPa. Temperature cycling between 1850 and 2050 °C was used to enhance grain growth, before rapid quenching and ~15 h decompression. The chemical compositions of the samples were determined using a JEOL 733 electron microscope on as-grown (not polished) crystals at 2 nA and 15 kV.

Two additional samples of Al–Fe–Mg-perovskite, one corresponding to peridotite and the other having closer to MORB composition, were synthesized from