Incorporation of Fe and Al in MgSiO$_3$ perovskite: An investigation by $^{27}$Al and $^{29}$Si NMR spectroscopy

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ABSTRACT

We present $^{27}$Al and $^{29}$Si magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra of Al- and Fe-bearing, high-pressure pyroxene and perovskite samples, synthesized in a multi-anvil apparatus at 26 GPa and 1900 °C at targeted compositions of (Mg$_{1-x}$Fe$_x$)(Si$_{1-y}$Al$_y$)O$_3$ ($x = 0.01, 0.025, 0.05$). $^{27}$Al MAS-NMR spectra of the perovskite samples indicate that Al$^{3+}$ replaces both Si$^{4+}$ in the octahedral site and Mg$^{2+}$ in the larger 12-coordinated site. NMR signal loss caused by paramagnetic interactions is often a severe complication when performing NMR on materials containing Fe$^{2+,3+}$; however, careful measurement of signal loss and comparison to total Fe content in these samples sheds light on the nature of Al and Fe incorporation. NMR signal loss for the pyroxenes is linearly related to total Fe content as would be expected in the case of uncorrelated substitution of randomly distributed Al and Fe. However, $^{27}$Al signal loss for the perovskite samples increases only slightly between samples with $x = 0.01$ and $0.025$ indicating similar coordination of Al by Fe and non-random distribution. Complete signal loss at Fe/(Fe + Mg) = 0.05 suggests the upper limit of Fe$^{2+}$ and Fe$^{3+}$ concentration at which useful NMR data can be obtained for this system.

Keywords: NMR spectroscopy, perovskite, pyroxene, paramagnetic shifts, high-pressure studies

INTRODUCTION

The 660 km seismic discontinuity marking the boundary between the Earth’s upper and lower mantle is generally attributed to the dissociation of Mg$_2$SiO$_4$ ringwoodite into MgO periclase and MgSiO$_3$ perovskite in the lower mantle. The transition to the perovskite structure is notable as it marks the change from predominantly tetrahedrally coordinated Si in almost all common silicates to octahedrally coordinated Si. The ideal cubic perovskite structure contains one large 12-coordinated site (the A site) and one octahedral, 6-coordinated site (the B site). MgSiO$_3$ perovskite is distorted from the perfect cubic structure into a lower symmetry orthorhombic structure in which the Si octahedra are tilted, and four of the Mg-O bonds are lengthened and eight shortened (Ross and Hazen 1990; Fiquet et al. 2000). In the lower mantle, the most important secondary constituents in perovskite are expected to be FeO, Fe$_2$O$_3$, and Al$_2$O$_3$. The addition of either or all of these species may significantly affect lower mantle phase equilibria (Weidner and Wang 1998, 2000; Kubo and Akaogi 2000; Akaogi et al. 2002), elastic properties (Zhang and Weidner 1999; Brodholt 2000; Kubo et al. 2000; Daniel et al. 2001; Walter et al. 2004; Li et al. 2005; Andrau et al. 2007; Nishio-Hamane et al. 2008), and trace-element incorporation if these species affect the crystalline defect population.

It is well known that simultaneous incorporation of Fe and Al into perovskite greatly increases the solubility of both species while also dramatically raising the ferric iron content (Fe$^{3+}$/Fe$_{total}$) by the following charge-balancing co-substitution (Frost and Langenhorst 2002; Frost et al. 2004a):

$$\text{Mg}^{2+} + \text{Si}^{4+} \leftrightarrow \text{Fe}^{3+} + \text{Al}^{3+}. \quad (1)$$

Previous ab initio studies, in the absence of Fe, indicate the ability of Al$^{3+}$ to enter the lattice either through a charge-balanced substitution into both A and B sites

$$^{\text{A}}\text{Mg}^{2+} + {^{\text{A}}\text{Si}}^{4+} \leftrightarrow {^{\text{A}}\text{Al}}^{3+} + {^{\text{B}}\text{Al}}^{3+} \quad (2)$$

or by substitution into the B site with the concomitant creation of charge-balancing oxygen vacancies (Brodholt 2000; Brodholt et al. 2002; Yamamoto et al. 2003)

$${^{\text{B}}\text{Si}}^{4+} + \frac{1}{2} \text{O}^{2-} \leftrightarrow {^{\text{B}}\text{Al}}^{3+} + \frac{1}{2} \Box_0^0 \quad (3)$$

where $\Box_0^0$ is an oxygen vacancy. The presence of Al$^{3+}$ on both the A and B sites has been shown experimentally by XANES (Andrau et al. 1998) and NMR spectroscopy (Stebbins et al. 2001, 2003, 2006) although the substitutions both in Equations 2 and 3 may be important in some or all of these studies. Meanwhile, ab initio studies on Al- and Fe-bearing perovskite indicate the charge-balanced substitution of Fe$^{3+}$ on the large A site and Al$^{3+}$ on an adjacent octahedral B site (Richmond and Brodholt 1998). The presence of Fe$^{3+}$ on the A site and Al$^{3+}$ on the B site is born out by the XRD refinements of Vanpeteghem et al. (2006). While