Cation sites in Al-rich MgSiO₃ perovskites

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ABSTRACT

Local structure analysis of Al-containing magnesium silicate perovskite has been carried out with X-ray absorption spectra recorded at the Mg, Al, and Si K-edges using the SA32 beam-line of SuperAco (Orsay, France). The Al-XAFS spectrum of (MgSi₃₀₋ₓAlₓO₉)₃ perovskite (synthesized in a multi-anvil apparatus) cannot be explained by assuming that Al³⁺ occurs in octahedral or dodecahedral sites only. This conclusion is based on comparison between Al-spectrum and those recorded at the Mg and Si K-edges for the same structure, general trends found for Aℓ-spectra in various atomic sites, and ab-initio calculations using the FEFF-6 code. Thus, Al appears to be partitioned between both octahedral and dodecahedral perovskite sites. However, the structural accommodations needed to stabilize Al³⁺ cation in such different sites are not straightforward. Also, Mg K-edge spectra in enstatite and perovskite were compared with those previously reported at the Fe K-edge for the same structures, confirming that these two elements are located in the same polyhedra in both structures, and thus that Fe²⁺ enters the dodecahedra of the silicate perovskite.

INTRODUCTION

Although the first silicate perovskite synthesized in a diamond-anvil cell was prepared using pyrope as the starting material (Liu 1974), the site occupancy of Al in MgSiO₃, with the perovskite structure remains uncertain. MgSiO₃ perovskite can accommodate significant amount of Al³⁺ as pyrope (Mg₃Al₂Si₃O₁₂) and grossular (Ca₃Al₂Si₃O₁₂) were observed to transform fully into the perovskite-structure at 26.5 and 30.2 GPa, respectively (Irifune et al. 1992; Kesson et al. 1995; Yusa et al. 1995). One possibility is that two Al³⁺ cations substitute for a pair of Mg (or Ca) on the dodecahedral site and Si on the dodecahedral site in the silicate perovskite, maintaining electrical neutrality without formation of vacancies. However, the structural distortion needed to accommodate the same type of atom in both the octahedral and dodecahedral sites needs to be explained (the volume ratio in MgSiO₃ perovskite is about 4.3, see Andrault and Poirier 1991). This type of coupled substitution ocurs along the pyrope-majorite join, where two Al³⁺ substituted for a pair of Mg and Si in the octahedral site. The possibility of Al substitution on both perovskite sites is largely supported by recent ab-initio calculations showing that pure corundum could undergo a phase transformation to perovskite at very high pressures (Thomson et al. 1996).

The other possibility is that Al enters in only one of the two perovskite sites, more likely the octahedral site as observed in aluminous XAI0₃ perovskites (X³⁺ = Sc, Y, Gd . . .). In this case, either many charged vacancies should form to maintain electroneutrality (Al³⁺ substitutes for Mg²⁺ or Si⁴⁺ in MgSiO₃), or a consequent amount of Si or Mg should change coordination sites to form (Mg₀.₃₋ₓScₓ)(AlₓSi₁₋ₓ)O₉ or (MgₓAl₁₋ₓ)(Mg₁₋ₓScₓ)O₃ perovskite (A. Hofmeister, personal communication). In these cases, the volume ratio between octahedra and dodecahedra would most probably be affected, because Mg²⁺, Al³⁺, and Si⁴⁺ show significantly different ionic radii. This is in disagreement with previous reports showing that the Al₂O₃ substitution in MgSiO₃ occurs with reduced variation of the Pbnm orthorhombic distortion (see Table 1).

Obtaining quantitative information on the local structure around light elements remains an experimental challenge, especially for high-pressure minerals for which the available volume is smaller than 1 mm³. Spectroscopic studies, using X-ray absorption (XAFS) and electron energy loss (EELS), recently addressed changes of the local structure of Si in SiO₂ polymorphs (Li et al. 1994; Henderson et al. 1995; Sharp et al. 1996). Most of the reported experimental features are located near the absorption edge, and are thus related to photoelectron multiple scattering (X-ray absorption near edge spectroscopy, XANES; energy loss near edge spectroscopy, ELNES). Various theoretical approaches have been used to reproduce the experimental spectrum of stishovite. Good agreement on the energy position of the XANES features was first obtained after comparison with the theoretical density of state (Li et al. 1994). Multiple scattering calculations were then used to improve agreement between experiments and theory, in reproducing experimental intensities (Wu et al. 1996).