Fe3+-bearing post-perovskite phase in a subducted MORB crust

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A number of experimental studies demonstrated that (Al,Fe)-bearing $MgSiO_3$ perovskite, a predominant mineral in the lower mantle, contains substantial amounts of Fe^{3+}. The high Fe^{3+} content in perovskite has large effects on electrical conductivity, radiative thermal conductivity, elasticity, and Mg-Fe partitioning. Recently Murakami et al. [2004] discovered that the $MgSiO_3$ perovskite undergoes phase transition to a post-perovskite phase under the lowermost mantle conditions. Does the post-perovskite phase also include certain amount of Fe^{3+}? Major element compositions of post-perovskite formed in natural peridotitic mantle and MORB bulk compositions were reported [Murakami et al., 2005; Hirose et al., 2005], but the valence state of iron has never been measured yet. By analogy with perovskite, Fe^{3+} in post-perovskite possibly has significant effects on its physical and chemical properties. In addition, it may have large but opposite effect from that of Fe^{2+} on the stability of post-perovskite phase. Moreover, iron metal is likely present in the lower mantle together with Fe^{3+}-rich perovskite. The Fe^{3+}/total Fe ratio in post-perovskite is also important for the fate of such metallic iron in the D" region. Recently, the Fe^{3+}/total Fe ratio is quantitatively determined with a nm-scale spatial resolution by ELNES spectroscopy [van Aken et al., 1998].

In this study, the Fe^{3+}/total Fe ratios in both (Al,Fe)-bearing $MgSiO_3$ post-perovskite phase and Ca-ferrite-type Al-phase, synthesized in a natural mid-oceanic ridge basalt (MORB) composition at 113 GPa and 2240 K, were determined by electron energy-loss near-edge structure (ELNES) spectroscopy. Results demonstrate that post-perovskite includes significant Fe^{3+} much more than Fe^{2+} with Fe^{3+}/total Fe ratio of 0.59-0.69. The high Fe^{3+} concentration in post-perovskite may have significant effects on its physical properties, phase stability, and iron partitioning. In contrast, Ca-ferrite-type Al-phase, which is the second Fe-bearing phase in a subducting MORB crust, is enriched in Fe^{2+} rather than Fe^{3+} with Fe^{3+}/total Fe ratio of 0.15-0.29.

The Fe^{3+}/total Fe ratio in Mg-perovskite has been extensively studied, showing that the concentration of Fe^{3+} strongly correlates with the Al^{3+} content and is independent from the oxygen fugacity [e.g., Frost and Langenhorst, 2002]. Present study of (Al,Fe)-rich $MgSiO_3$ post-perovskite showed that it contains 0.254 Al^{3+} and 0.223 Fe^{3+} in two-cations formula. This relation between Al^{3+} and Fe^{3+} observed in post-perovskite is quite consistent with that of perovskite. Since Al^{3+} contents are similar in perovskite and post-perovskite in a given MORB bulk composition, both should include similar amounts of Fe^{3+}. This suggests that the whole rock Fe^{3+}/total Fe ratio in a subducting MORB crust does not change remarkably at the post-perovskite phase transition in the lowermost mantle.