Implications of Ferric Iron in the Lower Mantle: Mineralogy, Density, and the Disproportionation of Ferrous Iron

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Abstract

The amount of ferric iron in the lower mantle is unknown; however, recent work has shown that ferric iron Fe^{3+} may explain seismic anomalies in the lower mantle (Kurnosov et al., 2017) and has a strong effect on mantle mineralogy and corresponding assemblage density (Gu et al., 2016). In order to fully understand the implications of Fe³⁺ on lower mantle mineralogy, we conducted laser-heated diamond-anvil cell experiments to lower mantle pressures and temperatures on two nearly identical synthetic glass samples approximating an ocean island basalt parent body [MIX1G; Hirschmann et al., 2003]). The pyroxenite mixtures differed in ferric iron content; with one sample more oxidizing (Fe³⁺/ Σ Fe ~ 55%) and one more reducing (Fe³⁺/ Σ Fe ~11%). The samples were examined with in-situ x-ray diffraction (XRD) and electron probe microanalysis (EPMA). The resulting mineral assemblages and densities were drastically different between the two sets of samples. For the reducing composition, we observed an assemblage of bridgmanite, calcium silicate perovskite, calcium-ferrite structured phase, alumina, stishovite, and metallic iron (in descending order of abundance). We observed the coupled substitution of Fe^{3+} and Al, along with Fe^{2+} into the bridgmanite structure. In addition, we observed the disproportionation of Fe^{2+} into metallic iron, which was confirmed by XRD and EPMA. In contrast, in the oxidizing material, we only observed two phases: bridgmanite (~95%), where Mg and Ca formed a solid solution in the perovskite structure, and a calcium-ferrite structured phase. We directly observed the absorption of all Fe³⁺, Al, and Ca into the bridgmanite structure. These results show that large amounts of Fe³⁺ content could potentially hinder the formation of secondary minerals in the lower mantle such as calcium silicate perovskite, which could have important implications on the interpretation of deep mantle geochemistry. Overall, the reduced sample assemblage is 3-4% greater in density than the oxidized sample. As a result, a reduced assemblage would have slower seismic velocities than the oxidized material. Therefore, variations in seismic velocities in the lower mantle as observed in global tomography models may be a result of varying ferric iron content.

Gu, Tingting, et al. "Redox-induced lower mantle density contrast and effect on mantle structure and primitive oxygen." *Nature Geoscience* 9.9 (2016): 723-727. Hirschmann, Marc M., et al. "Alkalic magmas generated by partial melting of garnet pyroxenite." *Geology* 31.6 (2003): 481-484.

Kurnosov, A., et al. "Evidence for a Fe3+-rich pyrolitic lower mantle from (Al, Fe)bearing bridgmanite elasticity data." *Nature* 543.7646 (2017): 543-546.