Spin state and electronic environment of iron in basaltic glass in the lower mantle

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ABSTRACT

The spin states of iron in deep magmas are one of the most important properties that affect the partitioning of iron between magmas and minerals and, thus, the gravitational stability of magmas in the Earth. We investigated the spin state and electronic environments of iron in a basaltic glass containing ~70 $Fe^{3+}/\Sigma Fe$ at room temperature and pressures from 1 bar to 130 GPa using a diamond-anvil cell combined with energy domain synchrotron ⁵⁷Fe Mössbauer source spectroscopy. The basaltic glass represents an analog of a multi-component magma typical for the Earth. The Mössbauer spectra could be fitted by a two pseudo-Voigt doublet model including a high quadrupole splitting (OS) doublet and a low OS doublet, which were assigned to high-spin Fe^{2+} and high-spin Fe^{3+} , respectively. The high-spin states of Fe²⁺ and Fe³⁺ remained up to 130 GPa corresponding to the pressure in the lowermost mantle. The center shift values of high-spin Fe²⁺ and Fe³⁺ did not show large changes with pressure, ruling out sharp electronic changes in the basaltic glass. Therefore, a sharp and complete spin crossover of Fe²⁺ from the high-spin to the low-spin state does not appear to occur in the basaltic glass although the possibility of a partial spin transition cannot be fully excluded. The QS values of Fe²⁺ increased slightly at 0–20 GPa and above 100 GPa, and the higher value was preserved after decompression to ambient conditions. This behavior may be related to distortion of Fe^{2+} polyhedra due to short-range ordering on compression. Such a distortion of Fe^{2+} polyhedra could gradually stabilize Fe^{2+} in the basaltic glass with pressure compared to bridgmanite according to the Jahn-Teller effect, and thus could gradually enhance the partitioning of iron into deep magmas in the lower mantle.

Keywords: Silicate glass, deep magma, spin transition, lower mantle, Synchrotron Mössbauer spectroscopy, diamond-anvil cell