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 Fe3+/ΣFe 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 (QS) doublet and a low QS doublet, which were assigned to high-spin Fe2+ and high-spin Fe3+, 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 Fe3+ 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 Fe3+ polyhedra due to short-range ordering on compression. Such a distortion of Fe3+ polyhedra could gradually stabilize Fe3+ 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

INTRODUCTION

The existence of magmas in the deep Earth is important for understanding deep Earth processes and evolution of the Earth. New geophysical observations and advances in high-pressure and high-temperature experiments have provided new insight on deep magmatism in the Earth’s mantle (e.g., Andrault et al. 2014; Kawakatsu et al. 2009; Lay et al. 2004; Ohtani and Maeda 2001; Pradhan et al. 2015; Sakamaki et al. 2013; Schmandt et al. 2014; Schmerr 2012; Song et al. 2004; Williams and Garnero 1996). Since partial melting can explain seismic velocity anomalies of ultralow-velocity zones (ULVZ) in the lowermost mantle, dense deep magmas have been considered to exist above the core-mantle boundary (CMB) (e.g., Berryman 2000; Lay et al. 2004; Komabayashi et al. 2009; Ohtani and Maeda 2001; Williams and Garnero 1996). Such deep magmas may cause superplumes relating to hot spots (e.g., Lay et al. 2004; Murakami et al. 2014). On the other hand, the observed anomalies in the lowermost mantle have also been explained by the existence of metallic iron from the outer core (Otsuka and Karato 2012).

The controversies regarding the ULVZ arise partly from a lack of knowledge about the stability of deep magmas. To discuss the possible existence of deep magmas, we need to understand the physical and chemical properties of magmas under extreme high-pressure conditions. For instance, the gravitational stability of deep magmas can depend on the density contrast between solid and melt (e.g., Ohtani and Maeda 2001; Agee and Walker 1993) or the permeability of the melt through mantle mineral assemblages (i.e., dihedral angles between melt and minerals). However, magmas are technically difficult to study in high-pressure and high-temperature experiments. As an alternative, silicate glasses have been used as analogs of deep magmas because they are considered to preserve the structures of quenched silicate melts (e.g., Lee 2011; Lee et al. 2012; Williams and Jeanloz 1988). The spin state of iron is one of the most important factors affecting the gravitational stability of deep magmas because iron is an abundant and relatively dense element among the major elements of the Earth. The partitioning of iron into silicate melt was reported to be enhanced at pressures greater than ~76 GPa, which could cause the formation of iron-rich dense melt above