The electronic structure of iron in rhyolitic glass at high pressure

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The physical properties of silicate melts within the Earth's mantle affect the chemical and thermal evolution of the Earth's interior. To understand melting processes within the Earth, it is imperative to determine the structure of silicate melts at high pressure. It has been proposed that iron-bearing silicate melts may exist in the lower mantle just above the core-mantle boundary [1]. The behavior of iron in mantle melts is poorly understood, but in some cases may be approximated by iron-bearing silicate glasses. Previous studies have conflicting conclusions on whether iron in lower mantle silicate melts goes through a high-spin to low-spin transition [2-4]. Additionally, the average coordination environment of iron in glasses is poorly constrained. XANES experiments on MORB glasses have demonstrated that both four and six-fold coordinated iron may exist in significant amounts regardless of oxidation state [5] while conventional Mössbauer experiments have observed five-fold coordinated Fe^{2+} with small amounts of four and six-fold coordinated Fe^{2+} [6]. In an attempt to understand these discrepancies, we have measured the hyperfine parameters of iron-bearing rhyolitic glass up to ~115 GPa in a neon pressure medium using time-resolved synchrotron Mössbauer spectroscopy at the Advanced Photon Source (Argonne National Laboratory, IL). Our spectra are well explained by three high-spin Fe^{2+}-like sites with distinct quadrupole splittings. Our results indicate that iron experiences changes in the coordination environment with increasing pressure without undergoing a high-spin to low-spin transition. Changes in the electronic configuration, such as the spin state of iron affects the compressibility and thermal properties of melts. With the assumption that silicate glasses can be used to model structural behavior in silicate melts, our study predicts that iron in chemically–complex silicate-rich melts in the lower mantle likely exists in a high-spin state.

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