Electronic properties of iron in silicate glasses in the lower mantle

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Pressure-induced changes in chemistry and physical properties of melt are key to understanding the behavior of magma oceans and melt-rich layers in planetary interiors. The behavior of iron in mantle silicate melts is particularly important due to its control of melt density and redox state. In addition, electronic spin-pairing transitions in iron may affect elasticity, rheology and transport properties of melts. To investigate changes in coordination and spin states of iron in high-pressure silicate melts, we performed synchrotron X-ray spectroscopy experiments on silicate glasses as low-temperature analogues. ^{57}Fe-enriched glasses of almandine ($Fe_3Al_2Si_3O_{12}$) and enstatite-hematite solid solution ($(Mg,Fe)(Fe,Si)O_3$) compositions were examined by Mössbauer spectroscopy and X-ray emission spectroscopy in the diamond anvil cell to 91 GPa at 300 K. Results are consistent with a gradual high-to-low spin transition in Fe^{3+} between 1 bar and ~30 GPa. The new low-spin Fe^{3+} component exhibits quadrupole splitting of 1.8-2.0 mm/s and center shift 0.3-0.5 mm/s. The high-spin Fe^{2+} component, with average quadrupole splitting 2.0-2.2 mm/s and center shift 0.8-1.2 mm/s, broadens with pressure due to an increasing range of coordination environments of iron. These changes correspond to a darkening of the glass to black and an associated decrease in radiative thermal conductivity. Spin transitions in melts in the mantle should be broad with respect to glasses or crystalline materials: no discontinuities should be observed in density or transport properties of melts at depth.