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Spin and valence states of iron in Al-bearing silicate glass at high pressures studied by synchrotron Mössbauer and X-ray emission spectroscopy

Zhu Mao[1,*], Jung-Fu Lin[1], Jing Yang[1], Junjie Wu[1,2], Heather C. Watson[3], Yuming Xiao[4], Paul Chow[4] and Jiyong Zhao[5]

[1]Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, Texas 78712, U.S.A.
[2]Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[3]Department of Earth and Environmental Science, Rensselaer Polytechnic Institute, Troy, New York 12180, U.S.A.
[4]HPCAT, Carnegie Institution of Washington, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.
[5]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

Abstract

High-pressure synchrotron Mössbauer (SMS) and X-ray emission (XES) spectroscopic measurements were conducted to investigate the spin and valence states of iron in (Al,Fe)-bearing magnesium silicate glass ($Mg_{0.79}Fe_{0.10}Al_{0.10}Si_{0.96}O_3$) up to 126 GPa and 300 K. By analyzing the Fe *K*β emission spectra using the integrated relative difference (IRD) method, which accounts for the spectral broadening effects, the derived total spin momentum (*S*) of the iron in the glass shows no observable changes with pressure within the experimental uncertainties. A two-doublet fitting model representing two diverse local iron atomic environments was used to satisfactorily simulate the high-pressure SMS spectra of iron in the glass. The doublet with an averaged quadrupole splitting (QS) value of 1.94(±0.25) mm/s and chemical shift (CS) of 1.02(±0.25) mm/s at ambient conditions was assigned to be high-spin Fe^{2+}, whereas the second doublet with QS = 0.83(±0.25) mm/s and CS = 0.49(±0.25) mm/s was assigned to be high-spin Fe^{3+}. Increasing pressure continuously elevates the QS of Fe^{2+} from ~2 mm/s at ambient pressure to 3.5 mm/s at 126 GPa, while Fe^{3+} only exhibits a slight increase in the QS to 1.34(±0.25) mm/s. Comparing with previous experimental and theoretical studies on the local geometries and hyperfine parameters of silicate glasses and minerals, we conclude that the occurrence of the extremely high QS of Fe^{2+} in our glass above ~40–50 GPa can be associated with the enhanced density and diverse distortions and geometries of the local Fe^{2+} environments. Our combined XES and SMS results show that both Fe^{2+} and Fe^{3+} ions in Al-bearing silicate remain in the high-spin state, rather than undergoing a spin-pairing transition as proposed previously. Assuming that the silicate glass results can be used as an analog for understanding silicate melts, our results here indicate that iron ions likely experience significant changes in the local environments yet remain overall in the high-spin state in silicate melts at the extreme pressure and temperature conditions of the deep mantle.

Keywords: Silicate glass, high pressure, synchrotron Mössbauer spectroscopy, X-ray emission spectroscopy, lower mantle