Absence of pressure-induced electron spin-state transition of iron in silicate glasses upon compression

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Invited highlight and Breakthrough article for Z. Mao et al. "Spin and valence state of iron in Al-bearing silicate glass at high pressures studied by synchrotron Mossbauer and X-ray emission spectroscopy (in press)"

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Abstract. Upon compression, silicate melts in the Earth's interior are expected to be subject to successive structural transitions with multiple densification mechanisms that are distinct from those of their crystalline analogues. Experimental verification of this phenomenon remains a major target of glass-melt studies. Early studies of Fe spin-state transitions in silicate glasses under compression used synchrotron X-ray emission spectroscopy (XES) to develop seemingly irreconcilable interpretations that vary from complete transitions to low spin states at high pressure to a prevalence of high spin states. In an effort to reconcile the controversy, Mao et al showed that the XES data must be properly handled with a correct reference spectrum for each spin state and suggested that the subtle effect of pressure-induced broadening in the spectra be considered. Based on the new analyses, they concluded that no pressure-induced spin-state transitions exist in iron-bearing silicate glasses at high pressure. Thanks to several series of experimental studies, the illusive spin state in glasses under compression is being revealed, rendering the spin state of iron among the best understood for glasses at high pressure.

Understanding the electronic structures of the non-crystalline silicates such as glasses and melts in Earth's lower mantle is essential to account for the chemical and physical evolution of the Earth. However, detailed knowledge of the pressure-induced bonding transitions in silicate glasses and melts has remained a challenge within earth materials science (e.g., Lee 2011; Mysen and Richet 2005; Wolf and McMillan 1995 and references therein). This is in stark contrast to the crystalline phases where methodological advances in synchrotron x-ray techniques have revealed details of the bonding transitions at high pressure. Particularly, the advent of synchrotron x-ray emission spectroscopy (XES), combined with Mössbauer spectroscopy (SMS), shed light on an opportunity to probe the previously unknown effects of pressure on the spin transitions [from high-spin (HS) to low-spin state (LS)] and the valence states of Fe in crystalline oxides and silicate polymorphs (e.g, Bedro et al. 2003; Lin et al. 2012; 2013 and references therein). The spin transitions in perovskite and ferropericlase have provided insight into the changes in the thermo-mechanical and transport properties of Earth's lower mantle (see Lin et al. 2013 for a review).

The spin states of Fe in the silicate melts may also affect the diverse melt properties including the density and element partition coefficient between the melts and crystals (e.g., Andrault et al. 2012; Nomura et al. 2011). Although the structural role of Fe in silicate melts

and glasses at high pressure remains elusive largely due to a lack of suitable experimental probes and the increased topological disorder inherent in the glasses (e.g., Mysen and Richet 2005), pioneering efforts have been made to determine the pressure-induced spin transitions in silicate glasses (Nomura et al. 2011; Gu et al. 2012). These studies have provided seemingly incompatible results, including abrupt and complete spin transitions to the LS state in iron-bearing Mg-silicate glasses (Nomura et al. 2011) and prevalence of HS state evidenced by a gradual but slight decrease in the total spin momentum in Al-bearing and Al-free Mg-Fe-silicate glasses (Gu et al. 2012). This discrepancy in the spin state of Fe could be partly due to diverse intrinsic differences (i.e., the composition, Fe contents, presence of Al) and extrinsic uncertainties associated with the experimental setup and the manner in which the experimental data were handled (e.g., de Groot 2001; Vankó et al. 2006). Resolving these discrepancies is critical to determining the possible link between the changes in pressure-induced properties and the potential spin transitions. Additional research and analysis to reconcile these discrepancies has been greatly anticipated.

In their recent article, Mao et al. addressed the effects of these extrinsic factors on the estimation of the total spin momentum of iron in cold-compressed Fe-bearing magnesium aluminosilicate glass up to 120 GPa using high-pressure SMS and XES measurements (Mao et al. 2014). In agreement with an earlier study (Gu et al. 2012), Mao et al. observed the slight and apparent reduction of the Kβ' satellite peak intensity from high-pressure XES measurements, which could indicate a reduction in spin momentum. However, rather than utilizing a conventional intergraded absolute difference (IAD) method, which has proven useful in providing a rigorous estimation of total spin momentum of Fe in crystals (e.g., Gu et al. 2012; Vankó et al. 2006), Mao et al. slightly modified the approach to include the effects of satellite peak broadening. Additionally, rather than utilizing strongly correlated Fe metal, the authors chose to use oxides with a diluted Fe concentration—enstatite at 1 atm and ferropericlase at 90 GPa for the HS and LS references, respectively (Mao et al. 2014). While the utility of the references may require further testing, both Gu et al. (with an Fe metal reference) and Mao et al. provide careful and robust methods for estimating spin momentum from the XES spectra of glasses under compression. Based on new analysis that considers the pressure-induced spectral broadening effect, Mao et al. indicated that total spin momentum of both the Fe^{2+} and Fe^{3+} ions in the glass does not change at all but remains in a HS state.

Although earlier studies have reported that melt structures at high pressure differ from those of their crystalline analogues (see Wold and McMillan 1995; Poe et al 1995; Lee 2010 and reference therein), these previous studies of melts and glass structures at high pressures (particularly those not based on x-ray techniques) may not receive sufficient credit from the mineral physics community. These studies are less well recognized partly because the compositions of the glasses examined in these studies were mainly model silicate glasses (e.g., Na silicates) because the topological disorder and thus peak broadening in the NMR and vibrational spectroscopy that are more prevalent in the geologically relevant Mg-silicate and multi-component glasses (Lee 2010; Mysen and Richet 2005; Poe et al. 1995). Along with their careful experimental data and analyses, Mao et al. expended great effort to provide full credit to earlier studies on glasses and melts under compression using diverse spectroscopic and scattering tools (see Mao et al. 2014 and references therein). The cited references will

also be valuable to both experimental and theoretical mineral physicists seeking to understand the detailed atomic structures and properties of silicate glasses at high pressure.

Compared with other structural information regarding glasses under compression, the spin and valence states of iron in silicate glasses at high pressure were among the least studied aspects. However, thanks to series of experiments by earlier pioneers along with Mao and coworkers, the details of this hidden information are being revealed, enabling the spin-state of iron in the glasses to be relatively well understood (Gu et al. 2012; Mao et al. 2014; Nomura et al. 2011). Additional progress is also expected toward understanding the pressure-induced changes in the diverse structural details of iron silicate glasses. While the XES results may not be heavily affected by variations in the glass composition, the spin states of Fe in more complex mantle melts under compression require further exploration. In addition to its role in network modifying, pressure is expected to change the role of Fe from network modifier, into charge balancing cation, and perhaps, to network former as the fraction of non-bridging oxygen linked to the network-modifying cations decreases with pressure (see Lee 2010). While the presence of Al in the crystalline oxides and silicates may not affect the Fe spin state at high pressure, Al in the silicate liquids may compete with Fe as a network former at high pressure and could affect the spin states of the iron, necessitating further investigation. Furthermore, the current study provides insight into the spin states of cold-compressed glass, the nature of which is somewhat different from those of quenched glass at high pressure (representing the structure of a supercooled liquid at high pressure) and silicate melts at high temperature. Therefore, the spin transition in complex silicate *melts* and the effect of temperature on the spin and valence states of Fe in silicate melts, including the pressure-induced changes in the Fe^{2+}/Fe^{3+} ratio, remain uncertain.

Mao et al. also demonstrated that quadrupole splitting (QS) for both the high-spin Fe^{2+} and high-spin Fe^{3+} gradually increases with pressure, indicating an increase in the topological disorder around Fe consistent with the earlier study (Gu et al. 2012). Although a pressure-induced increase in the QS value in the glass was partly attributed to an increase in the coordination number, the deviation from perfect cubic symmetry in the $^{[n]}$Fe sites in the glasses may decrease as the coordination number n increases, as observed for other framework quadrupolar nuclides with potentially similar structural roles such as Al, resulting in a decrease in the magnitude of the quadrupolar interaction (Lee 2010). Thus, the microscopic origins of the increased QS value for the Fe in the glasses and the precursor liquids requires further confirmation.

Finally, the authors provide the necessary details, including simulations and results fitting, for the readers to evaluate the robustness of the analysis. In their details, the results of the study by Mao et al. differ somewhat from those of the earlier study by Gu et al.; however, both provided high-quality experimental data and analysis of the iron-bearing Mg silicate glasses and the Al-bearing Mg-Fe silicate glasses (Gu et al. 2012; Mao et al. 2014). Because XES is an inefficient experimental technique requiring relatively long collection times to yield spectra with sufficient signal/background ratios, confirming the reproducibility of the experimental results is difficult. However, a further reconciliation with previous results for an Al-free glass that exhibits a drastic drop in the total electron spin momentum remains to be performed. Despite the further challenges, resolutions and clarifications ahead, the progress in both measurement and analysis may hold promise for

further exploring the details of electronic spin-state of Fe in more complex iron-bearing silicate melts at high pressure and high temperature.

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