Spin Transition of Iron in Amorphous Mg-Silicates at Mantle-Related Pressures

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A sharp increase in iron partitioning into melt with respect to mineral phases was reported at 70 GPa in an Al-free system [Nomura *et al.* 2011]. Based on the report, it was proposed that melt may be neutrally or negatively buoyant in the deep mantle. Nomura *et al.* [2011] attributed the iron partitioning change to a sharp high-spin to low-spin change in iron, which was found in their measurements on a Fe-diluted (5%) Mg-silicate glass at a similar pressure. However, Andrault *et al.* [2012] found no sharp change in iron partitioning between silicate melt and minerals in an Al-bearing system up to 120 GPa.

We measured the electronic configuration of iron in two differernt iron-rich (20%) Mg-silicate glasses at high pressure and 300 K in the diamond-anvil cell combined with X-ray Emission Spectroscopy (XES) and Nuclear Forward Scattering (NFS): Al-free glass up to 135 GPa and Al-bearing glass up to 93 GPa. We found no sharp changes in the spin state of iron up to our maximum pressure. Instead, the population of low-spin iron increases gradually from 1 bar in both glasses, but significant population of iron still remains high spin (40-50%) even at 90-135 GPa. Our observation is consistent with the expectation of gradual response of disordered systems to compression due to the existence of diverse coordination environments for iron in the glasses and continuous structural adjustment of the disordered system with pressure. If our results on Mg-silicate glasses can provide some insights for iron in mantle melts, the spin transition in iron should be gradual and further smeared out at the high temperatures of mantle melts [Sturhahn *et al.*, 2005], and therefore unlikely to induce a sharp change in iron partitioning in the deep mantle.

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Volatile element content of the mid-ocean ridge mantle

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Volatile element (H_2O, CO_2, F, Cl, S) budget of mid-ocean ridge mantle (DMM) is crucial for understanding mantle melting, rheology, and convection. The isotopic composition of MORB demonstrates that the mantle beneath ridges is heterogeneous. MORB from Garrett transform fault and Macquarie Island defines the depleted and enriched end-members respectively. We have analyzed H_2O, CO_2, F, Cl, S contents of Garrett TF and Macquarie Is. MORB to determine the volatile budget of these end-member components.

28 glasses from Garrett TF [1] and 52 glasses from the Macquarie Is. [2] were analyzed for major, trace, and volatile elements by triplicate analyses. Previous works reported the isotopic composition of a subset of our samples from the Garrett TF [3] (minimum $^{87}Sr/^{86}Sr$ = 0.7022) and the Macquarie Is. [2] (maximum $^{87}Sr/^{86}Sr$ = 0.7033), which correlates with the degree of trace element enrichment (e.g. Th/La) indicating a long-lived depletion and enrichment of their mantle sources.

We first considered shallow level processes, such as volatile degassing, sulfide saturation and interaction of melt with hydrothermally altered material. Degassing has affected the CO_2 concentration of the glasses except for a few CO_2 undersaturated samples, but it did not affect H_2O, F, Cl, and S. Samples that were sulfide saturated [4] and contaminated by seawater or hydrothermally altered material (high Cl/K) were filtered out.

The CO_2/Nb of the depleted MORB determined using the CO_2 undersaturated Garrett TF glasses MORB is 250, consistent with Saal *et al.* [5]. We use Cl-Nb-CO_2 correlations to determine a CO_2/Nb of ~ 600 for degassed Macquarie Is. MORB, consistent with the work by Cartigny *et al.* [6]. The H_2O/Ce of the depleted and enriched sources are 120 and 170 respectively. The F/Nd, Cl/K, and S/Dy ratios of our samples expand beyond the range of previous reported values.

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