Spin crossover and iron-rich silicate melt in the Earth's deep mantle

It is known that iron included in (Mg,Fe)O ferropericlase changes its spin state from low-spin to high-spin at high pressure corresponding to the Earth's lower mantle. Such iron spin crossover has been reported to occur in $(Mg,Fe)SiO_3$ perovskite as well at a similar pressure range. The change in the spin state of iron strongly affects the partitioning of iron between the coexisting phases.

We have performed X-ray emission spectroscopy measurements on $(Mg_{0.95}Fe_{0.05})SiO_3$ glass at beamline **BL12XU** [1]. The spectra were collected at 300 K in a diamond-anvil cell (DAC) with increasing pressure from 8 to 85 GPa (Fig. 1). At low pressures, the Fe $K\beta$' satellite peak was clearly observed at 7,045 eV, showing high-spin Fe^{2+} in the glass sample. The satellite peak diminished weakly at 59 GPa and vanished at 77 GPa. This indicates a high-spin to low-spin crossover of ferrous iron included in the glass.

In order to evaluate the effect of such iron spin crossover on the partitioning of iron, additional experiments have been performed at beamline **BL10XU** [1]. By using the laser-heated DAC techniques, we melted the $(Mg_{0.89}Fe_{0.11})_2SiO_4$ sample, in which $(Mg,Fe)SiO_3$ perovskite or post-perovskite coexisted with partial melt. The samples were then recovered from the DAC and examined with a high-resolution field-emission-type electron probe micro-analyzer (FE-EPMA) (Fig. 2). Quenched melt was found at the center of the sample, where the temperature was highest and surrounded by perovskite above 36 GPa, a primary mineral in the Earth's lower mantle. On the basis of the chemical analyses of coexisting quenched melt and perovskite, we have determined the Fe-Mg distribution coefficient K_D = $([Fe^{Pv}]/[Mg^{Pv}])/([Fe^{melt}]/[Mg^{melt}])$ between the two. The results obtained in a pressure range from 36 to 159 GPa are demonstrated in Fig. 3. The K_D values were approximately constant at 0.22-0.29 below 73 GPa. On the other hand, melt composition suddenly became Fe-rich and the K_D dropped to 0.07±0.02 at 76 GPa. It was again almost constant at 0.06-0.08 to 159 GPa.

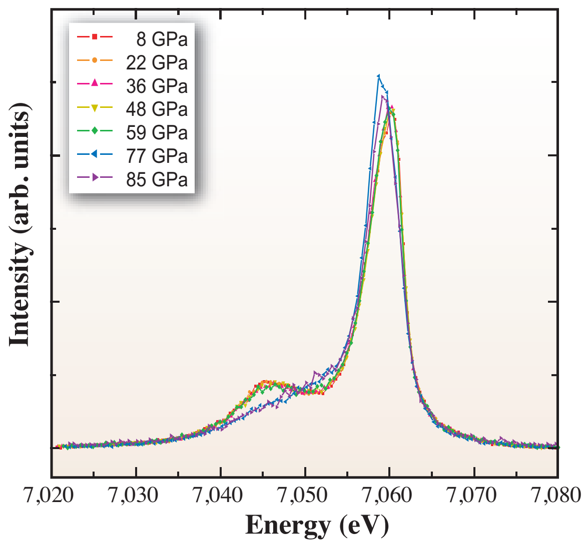

Fig. 1. Evolution of X-ray emission spectra of $(Mg_{0.95}Fe_{0.05})SiO_3$ glass with increasing pressure.

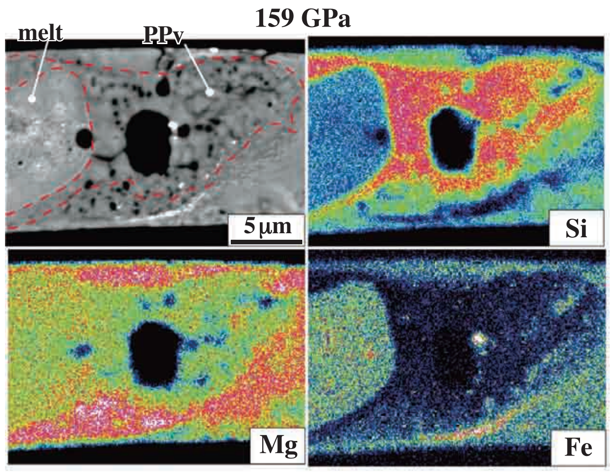

Fig. 2. Backscattered electron images and the X-ray maps for Si, Mg, and Fe for samples recovered from high-pressure melting experiments at 159 GPa. Partial melt is surrounded by post-perovskite (PPv).

The pressure range of the spin crossover observed in our glass matches the pressure where K_D changed dramatically (Fig. 1). Insofar as the glass is a good analogue for the liquid state, a high-spin to low-spin crossover of iron observed in the glass may also occur in melt at a similar pressure range, thus providing an explanation for the measured jump in Fe-enrichment in partial melt (Fig. 3).

A strong change in iron partitioning suggests that partial melt becomes more dense above 76 GPa, corresponding to 1,800-km depth in the Earth's deep mantle. We calculated the density of $(Mg,Fe)SiO_3$ liquid in equilibrium with $(Mg_{0.92}Fe_{0.08})SiO_3$ perovskite, a typical composition for the Earth's lower mantle, at 4,000 K as a function of pressure (Fig. 4). For simplicity, we used K_D = 0.25 below 75 GPa and K_D = 0.07 at higher pressures. While (Mg,Fe)SiO_3 melt is buoyant compared to any of the typical lower mantle minerals below 75 GPa, it suddenly becomes more dense at higher pressures (at depths greater than 1,800 km). The density difference between the solid mantle and partial melt reaches 8% at the base of the mantle.

Seismological studies show the presence of ultra-low velocity zone at the base of the mantle, suggesting the presence of melt at ~2,900 km depth. The present results indicate that such melt is gravitationally stable. Moreover, in Earth's early history when the mantle was much hotter, a stable melt layer below the solid mantle could be as thick as around 1,000 km [2]. The bottom ~1,000 km layer comprises about 25% of the mantle's mass. Upon cooling, fractional crystallization and sequestering of incompatible heat producing elements (e.g., U, Th) in the melt layer would therefore account for the mass of "missing" chondritic complement of these species expected to be sequestered in a reservoir inside the mantle [3]. The residual liquid now possibly observed as ultra-low velocity zone above the core-mantle boundary may be enriched in such heat producing elements.

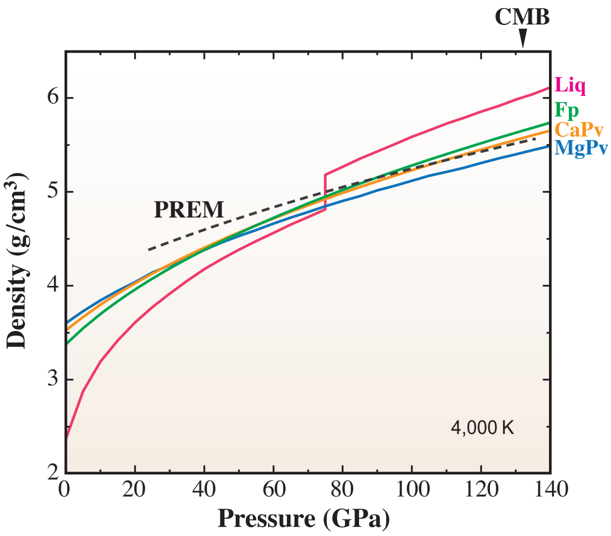

Fig. 4. Density of (Mg,Fe)SiO_3 liquid coexisting with $(Mg_{0.92}Fe_{0.08})SiO_3$ perovskite is calculated at 4,000 K using newly obtained Fe-Mg partitioning data. Those of $(Mg_{0.86}Fe_{0.14})$ O ferropericlase, Ca-perovskite, and PREM (seismic observation) are also shown for comparison.

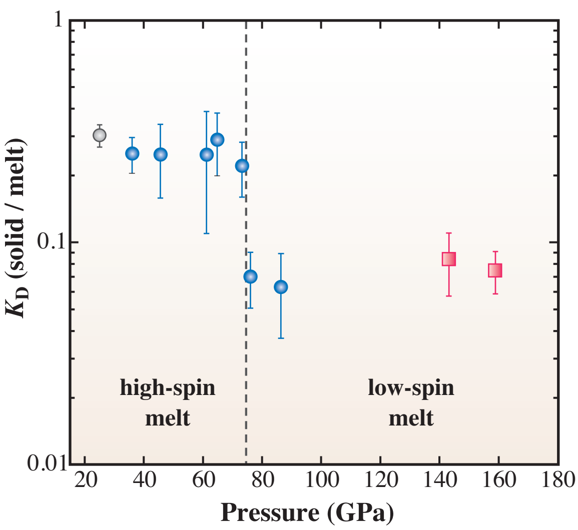

Fig. 3. Change in Fe-Mg distribution coefficient between perovskite and melt.

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References

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[2] S. Labrosse *et al.*: Nature **450** (2007) 866.
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