Fe^{3+}-rich oxidizing magma formed by Fe^{2+} redox disproportionation under high pressure

The valence state of iron oxides (Fe^{2+} and Fe^{3+}) in the mantle of terrestrial planets significantly affects the oxidation state of the mantle. This is because iron is the most abundant multi-valence state element in the mantle of terrestrial planets. Oxygen fugacity is controlled by the exchange reaction between Fe^{2+} and Fe^{3+} (i.e., $2FeO + O_2 = Fe_2O_3$); therefore, the valence state of the iron oxides determines the oxidation state of the mantle. Because volcanic gas compositions change substantially depending on the oxidation state of the mantle, constraining the valence state of iron oxides in the mantle is a quite important issue for understanding the atmospheric composition of terrestrial planets and perhaps planetary habitability.

Previous geological constraints on the oxidation state of the Earth's mantle inferred from the Ce anomaly of zircons suggest that the Earth's mantle was already oxidized close to the present level 4 billion years ago [1]. This has been profoundly challenging to the canonical model of the oxidation state of the early Earth's mantle because of the equilibration between the metallic core and the silicate mantle during its formation. The redox disproportionation of Fe^{2+} in a molten mantle (hereafter magma ocean) under high pressures has been proposed to explain the oxidation of the early Earth's mantle [2]. This mechanism produces Fe^{3+} and metallic iron (Fe^0) from Fe^{2+} (i.e., $3Fe^{2+} \rightarrow 2Fe^{3+} + Fe^0$). After removing Fe^0 from the metallic core, the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of the magma ocean increases and becomes more oxidizing than in the initial state. The redox disproportionation of Fe^{2+} in silicate melts was recently confirmed at pressures above 10 GPa [3]. However, determining the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of silicate melt equilibrating with metallic iron under the Earth's magma ocean conditions (peridotitic melt under high-pressure conditions >27 GPa) remains unconstrained and technically challenging due to its high-liquidus (completely molten) temperatures (>2400°C).

We optimized the cell assembly for high-pressure melting experiments and successfully melted peridotite samples under metal-saturated conditions up to 28 GPa [4] (Fig. 1). The $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of the silicate portion of the recovered samples was determined using X-ray absorption near-edge structure (XANES) measurements at SPring-8 **BL27SU**. The XANES spectra of the quenched samples showed a remarkable change at pressures between 15 and 28 GPa (Fig. 2), suggesting that the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio changes significantly under different pressure conditions. We found that the calculated $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of the quenched silicate melts from the XANES spectra increased from 0.13 to 0.52 with pressure (Fig. 3). These values are approximately one order of magnitude higher than the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of the Earth's upper mantle. These results suggest that the surface of the Earth's magma ocean after removing metallic iron into the core should be highly oxidizing, perhaps more than in the present state.

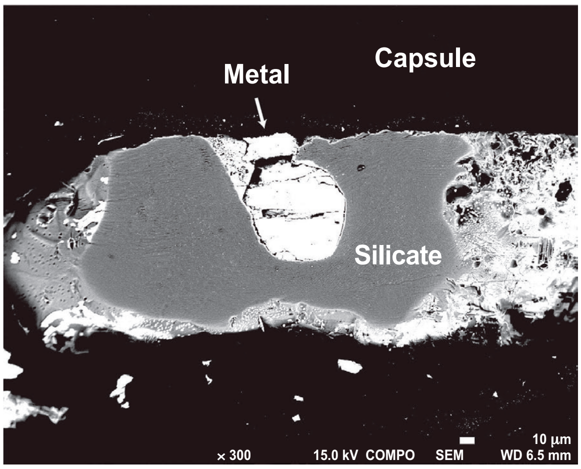

Fig. 1. The back-scattered electron image of the quenched sample at 28 GPa and 2600°C. The spheric metal surrounded by silicate indicates both phases were completely molten.

The oxidation state of the surface of the Earth's magma ocean having an $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of 0.2–0.5 would have created highly oxidizing conditions, more so than at present. However, the estimated oxygen fugacity of such a magma ocean around 4–7 log-units above the iron-wüstite buffer is partially consistent with those estimated for the Earth's upper mantle 4.0–4.4 billion years ago based on zircon records [1] within their analytical uncertainties. To explain the discrepancy in the oxidation state between the magma ocean and the present Earth's upper mantle, we propose that metallic iron in late accreting impactors after the formation of the Earth may have reduced the Earth's mantle [4].

The positive relationship between the pressure and redox disproportionation of Fe^{2+} in the magma provides another unique insight into the origin of the difference in the oxidation states of terrestrial planets and their atmospheric compositions, particularly during their formation. More specifically, Moon- or Mars-sized rocky bodies may have a relatively reduced

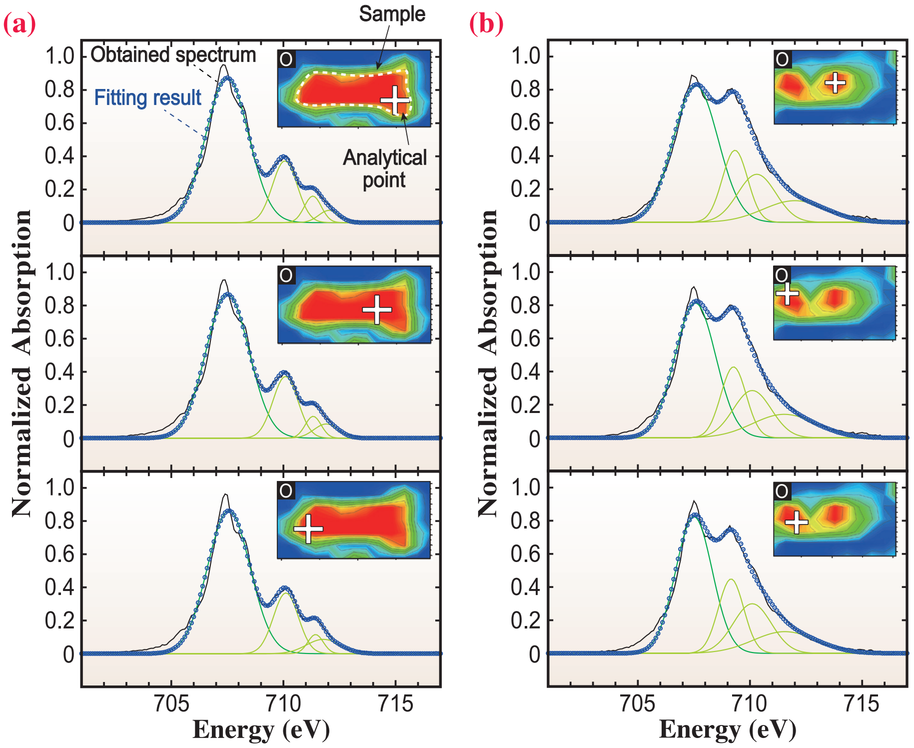

Fig. 2. Comparison of obtained XANES spectra of the silicate part of the recovered sample between **(a)** 15 GPa and **(b)** 28 GPa. The $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio was calculated from the area ratio of the first green-colored peak around 707 eV to all of the peaks. The inset of each figure shows an oxygen XRF map and analytical point indicated by **+**.

mantle and an atmosphere enriched in CH_4 and CO if the mantle is equilibrated with a metallic core. When a planet grows larger than Mars, the mantle may be significantly oxidized, and the atmospheric composition becomes rich in CO_2 and SO_2 [5]. The relationship between planetary size and atmospheric composition indicated in this study can be tested by future observations of exoplanetary atmospheres, particularly around young planets that likely have atmospheres equilibrated with the magma ocean.

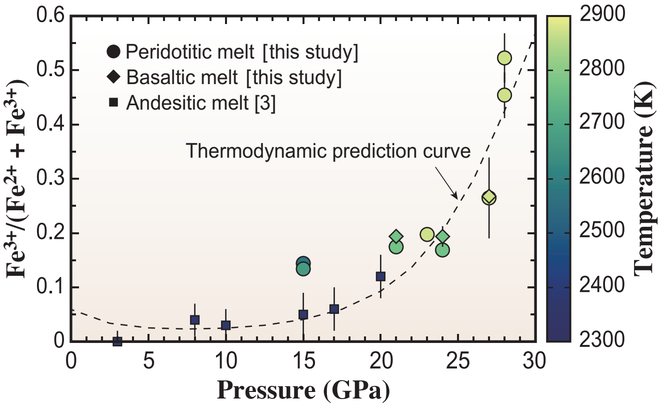

Fig. 3. Calculated $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio of quenched silicate melts equilibrating with metallic iron from XANES spectra. Data of andesitic melt were taken from [3]. The dashed curve indicates thermodynamic prediction based on experimental data [4]. At pressures above 20 GPa, Fe^{3+} in the melt is more stabilized than Fe^{2+}, and the $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ ratio rapidly increases with pressure.

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