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Linking water and ferric iron in Earth's lower mantle

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Earth's lower mantle constitutes the largest geochemical reservoir by mass and may host significant amounts of volatile elements critical to the habitability of Earth's surface. Magmas erupted at deep-rooted hotspots, such as oceanic island basalts (OIB), typically contain more H_2O than mid-ocean ridge basalts (MORB) and suggest the presence of volatile-rich regions in the lower mantle sampled by rising plumes. In some locations, high H_2O contents of plume-related magmas correlate with high $Fe^{3+}/\Sigma Fe$ ratios.

At pressures and temperatures of the lower mantle, the properties of many Fe-bearing minerals are affected by spin transitions. As potential host phases for H_2O in the lower mantle, high-pressure oxyhydroxide phases incorporate ferric iron and go through a spin transition. However, the impact of the spin transition of Fe^{3+} on the stability of oxyhydroxides and on the phase equilibria in mantle rocks remains unexplored. We studied the thermodynamics of the spin transition of Fe^{3+} in oxyhydroxides by performing high-pressure and high-temperature X-ray diffraction (XRD) and high-pressure nuclear resonant inelastic X-ray scattering (NRIXS) experiments. Based on our experimental results, we constructed thermodynamic models to assess the stability and phase equilibria of Fe-bearing oxyhydroxide phases in rocks of the lower mantle.

Our thermodynamic models suggest that the spin transition of Fe^{3+} in oxyhydroxide phases may reduce the H_2O activity in a coexisting fluid phase by several orders of magnitude. This finding implies that an Fe-bearing oxyhydroxide phase may form in mantle rocks with very low bulk H_2O contents. At a given H_2O activity, the spin transition may stabilize oxyhydroxide phases to higher temperatures that may exceed the temperature of the ambient mantle. As a consequence, Fe-bearing oxyhydroxides may host H_2O in large parts of the lower mantle and in particular in colder and in Fe-enriched regions. The spin transition of Fe^{3+} in high-pressure oxyhydroxide phases therefore creates a geochemical link between H_2O and ferric iron in Earth's lower mantle that might be reflected in the correlation between H_2O contents and $Fe^{3+}/\Sigma Fe$ ratios of OIBs and other plume-related magmas.