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Nitrogen solubility in magnesiowüstite and ferropericlase at lower mantle conditions

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Nitrogen and hydrogen are dominant volatile elements making up the Earth atmosphere and hydrosphere. In an effort to describe how and when habitability was set on Earth, the budget of N and H in planetary interiors has become a major field of investigation in the last decades. In this context, magnesiowüstite has recently been established as a major nitrogen reservoir in Earth's lowermost mantle [1]. Secundary ion mass spectrometry, transmission electron microscopy and Raman spectroscopy analysis showed that nitrogen could dissolve at the weight% level in magnesiowüstite. A compositional dependence was also proposed, nitrogen being orders of magnitude more soluble in Fe-rich magnesiowüstite as compared to ferropericlase. However, inherent spatial resolution limits of these techniques prevent some further conclusions to be drawn.

Here, we used atom probe tomography to unravel the spatial distribution of nitrogen and hydrogen (that was not analyzed previously) in a ferropericlase-magnesiowüstite-bridgmanite assemblage (at metallic iron saturation). The sample was synthesized at 1700°C and 24 GPa for 5 hours. It was previously characterized in [1]. Recovered samples were machined by FIB (ThermoFisher Helios 5 Dual Beam) and analyzed on a CAMECA LEAP 5000 XR (GPM, Rouen, France) atom Probe. Atomic scale elemental reconstructions demonstrate the lack of any volatile inclusion in all studied minerals. Conversely, nitrogen and hydrogen are always randomly distributed in the host matrix. Based on local and bulk composition, nitrogen most certainly substitutes for oxygen in the magnesiowüstite crystal lattice. Furthermore, a clear positive correlation between H, N and Fe is established. Nitrogen and hydrogen partitioning were also determined without any ambiguities related to nanoscale inclusions and heterogeneities. Further indirect conclusions concerning the atomic mobilities in N- and H-saturated magnesiowüstite is derived from the very thin Fe-Mg composition gradients at ferropericlase/magnesiowüstite interfaces.

The exceptional storage capacity of Fe-rich magnesiowüstite for nitrogen is thus further established. If such an iron-rich phase is present in the lower mantle, the high nitrogen solubility could explain the apparent subchondritic Earth's N/C.

[1] Rustioni et al., 2024. GPL2401.