Supplementary Information

APT analysis of W enrichments at exsolution boundaries

Utilizing the proxigram technique for a comprehensive 3D compositional analysis perpendicular to iso-concentration surfaces[21], elemental gradients from the exterior to the interior of MgO nanoparticles were quantified (Extended Data Fig. 1) from the atom probe tomography (APT) results. This revealed an exterior rich in Fe (84 at%) and Ni (7 at%), with lower average concentrations of Mg and O of 2.3 at% and 4.8 at%, respectively, which increased towards the nanoparticle cores. As the gradient moved inward, the contents of Fe and Ni decreased, while those of Mg and O increased, reaching approximately 40 at% and 52 at%, respectively. Notably, the average W content rose from 0.5 at% at the exterior to 1.8 at% at the boundaries, then dropped to 0.2 at% inside the MgO nanoparticles, revealing W enrichment at the MgO boundaries, likely due to W adsorption on the core-exsolved oxides. At these boundaries, Fe and Mg contents were approximately 28 at%, and the W content peaked at 1.8 at% with a thickness of about 3 nm. Additionally, we observed that W tails approximately 6 nm and 3 nm thick on the Fe and MgO regions, respectively. Trace elements such as Pt were primarily found in Fe-rich areas and showed no enrichment at the MgO boundaries.

Further analysis of a 10-nm-thick thin section from the specimen's midsection intersected two MgO nanoparticles, providing insights into the spatial distribution of W, particularly at the nanoparticle boundaries (Extended Data Fig. 10). The right MgO nanoparticle visually displayed a higher W content around its boundary. However, no obvious W was observed at the boundaries of one MgO nanoparticles on the left side of the section, suggesting variations in W content at the nanoparticle boundaries. Two regions of interest (ROIs) of dimensions 3 × 5 × 100 nm (Cube ID: 17) and 3 × 5 × 60 nm (Cube ID: 4) were defined within this thin section. The first ROI traversed two large MgO nanoparticles, and the second passed through a large and a small nanoparticle. 1D concentration profile along the long edges of these ROIs confirmed W enrichment at the boundaries of large MgO nanoparticles, and show W enriched within small MgO nanoparticles (Extended Data Fig. 10). To further evaluate W thickness at the MgO boundaries, a single MgO nanoparticles on the right was selected. A cylindrical ROI, perpendicular to the relatively flat MgO boundary, was established with a diameter of 2 nm (Extended Data Fig. 11a). The element distribution at the MgO nanoparticle's boundary (Extended Data Fig. 11b) showed W enrichment at the boundary, with minimal W detected within the adjacent Fe and MgO regions. The W thickness at the MgO nanoparticle boundary was also about 3 nm.

APT analysis revealed W enrichment at the MgO nanoparticle boundaries, with an average W content of 1.8 at% and an average thickness of about 3 nm. The average W content inside the MgO nanoparticle was about 0.2 at%, and the average content within the Fe region was approximately 0.5 at%.

Size of the ferropericlase exsolution

As discussed in our recent study[59], the size of ferropericlase nanoparticles exsolved from the core is controlled by two key parameters: 1) the critical nucleus size, i.e., the minimum size from which an particle is thermodynamically stable; 2) the critical size above which the particle's buoyancy overcomes convective stirring, causing it to rise and ascend into the mantle. The critical nucleus size is given by

$$d_{\text{nuc}} = \frac{2\sigma}{\Delta G} \tag{1}$$

Here, σ represents the interfacial free energy between the oxides and the core fluid, and ΔG denotes the Gibbs free energy difference per unit volume between the liquid and solid phases during exsolution. Interfacial energies under core-mantle boundary (CMB) conditions are poorly constrained. We estimate this parameter using the interfacial energy for solid MgO and molten steel under ambient pressure (~1.8 J m^{-2})[60]. The value of ΔG can be estimated using a thermodynamic database[61]. This yields critical nucleus sizes of ~3 nm for ferropericlase.

While ferropericlase is naturally buoyant in the metallic outer core, the strong convective flow may carry exsolved crystals if the force of convective entrainment exceeds gravitational settling. To determine the minimum crystal size required for sedimentation towards the CMB, we estimate the critical exsolution size using

$$d_{\text{sed}} = \sqrt{\frac{\eta_c \alpha g F}{C_p}} \frac{1}{\Delta\rho_c g S_h} \tag{2}$$

In this equation, α, η_c, and C_p represent the thermal expansion coefficient (2×10^{-5} K^{-1})[62], viscosity (0.01 Pa s)[63], and isobaric heat capacity (800 J kg^{-1} K^{-1})[62] of the outer core, respectively; F is the heat flux across the CMB (25 TW)[64]; g (10 m s^{-2}) is gravitational acceleration; and $\Delta\rho$ (~5 g cm^{-3}) is the density difference between the core fluid and exsolved ferropericlase[9]. The Shields number (S_h) is a dimensionless parameter representing the ratio of tangential stress from convective flow to buoyancy stress. Sedimentation occurs when Sh falls below 0.1–0.2[65]. The critical radius given by this equation is ~2 nm.

Therefore, the radius of core-exsolved ferropericlase nanoparticles is set to 2–3 nm in our calculations and the radius-dependent partition coefficients are shown in Extended Data Fig. 12.

W isotope fractionation during adsorption

The adsorption of metal species onto mineral surfaces may lead to significant isotopic fractionation[66]. Potential fractionation of W isotopes during the adsorption process may prevent core-derived W from fully retaining the μ^{182}W value of the core, which may, in turn, impact our interpretation of μ^{182}W anomalies in OIBs. Although the isotopic fractionation of W between the oxide surfaces and metallic liquid has not been studied, previous experiments suggest that lighter W isotopes are preferentially adsorbed on both Fe and Mn oxides from the aqueous solution with the equilibrium fractionation $\Delta^{186/183}\text{W}_{\text{liquid}-\text{solid}}$ values of 0.76±0.09‰ for ferrihydrite and 0.88±0.21‰ for δ-MnO$_2$[67]. Here $\Delta^{186/183}\text{W}_{\text{liquid}-\text{solid}} = \delta^{186/183}\text{W}_{\text{dissolved}} - \delta^{186/183}\text{W}_{\text{adsorbed}}$, where $\delta^{186/183}$W denotes the deviations in ^{186}W/^{183}W from a laboratory standard in per mil. However, these results were obtained at 25°C, and isotopic fractionation significantly diminishes at very high temperatures[68].

The isotopic fractionation as a function of temperature is well fitted using the following polynomial[69–71]

$$\Delta_{A-B} = 1000 \ln \alpha_{A-B} = ax + bx^2 + cx^3 \tag{3}$$

where $x = 10^6/T^2$; T is the temperature in Kelvin; Δ is the equilibrium isotope fractionation between phases A and B in per mil (e.g., $\Delta^{186/183}\mathrm{W}_{\mathrm{liquid-solid}}$); α is the isotopic fractionation factor; a, b, and c are constants. The first term in Eq. 3 is usually the dominant term at room temperature and above[69–71], where the Δ_{A-B} value is approximately proportional to $1/T^2$[68]. The temperature-dependent isotopic fractionation during adsorption process has been studied for Mo[72] and V[69] and their DFT results both support this trend.

Therefore, we can assume that the $\Delta^{186/183}\mathrm{W}_{\mathrm{liquid-solid}}$ value is proportional to $1/T^2$ to roughly estimate $\Delta^{186/183}\mathrm{W}_{\mathrm{liquid-solid}}$ at CMB temperatures based on experimental results at 298 K[67]. The results suggest that $\Delta^{186/183}\mathrm{W}_{\mathrm{liquid-solid}}$ is less than 5 ppm for temperatures above 4000 K, and the smaller mass difference between ^{182}W and ^{184}W would lead to even weaker fractionation compared to ^{186}W and ^{183}W. Thus, the μ^{182}W value of core-exsolved oxides would differ from that of the core ($\mu^{182}\mathrm{W} = -220$,[6]) by no more than 5, and the W isotopic fractionation is neglected in our calculations.