

Supplementary info

Experimental and Analytical Methods:

Starting Material

The silicate glasses with pyrolitic composition (McDonough and Sun 1995) without FeO were synthesized using levitation method. High purity oxides and carbonate (CaCO_3) doped with V, Cr, Ta, Nb (added as standard ICP solutions) were ground in ethanol in an agate mortar and then decarbonated, compressed and transformed into a glass in an Argon flux using aerodynamic levitation furnace coupled with 120 W CO_2 laser. Silicate glasses were analyzed by EPMA at Camparis to confirm the chemical homogeneity (Table S1) before polished down to ~ 20 μm thick and subsequently machined into small disks suitable for DAC loading using a picosecond laser machining system at IPGP. An additional pyrolite glass without FeO and any siderophile elements was also used following the same procedure described above in a parallel experiment (Table 1).

The metallic starting materials were either commercial reagent Fe-rich metal balls (91% Fe + 9% Si) or trace-element-bearing iron-nickel alloy synthesized in a piston-cylinder apparatus at IPGP. The piston-cylinder experiment was performed at 2 GPa and 1800 °C in a MgO capsule with graphite furnace and BaCO_3 cell assembly. Natural MORB was ground and mixed with high purity oxides (NiO and Cr_2O_3) and ICP vanadium standard solution and fired at 950 °C overnight and then mixed and equilibrated with silicon-bearing iron alloy under high P-T for 2

minutes. Synthesized metal was recovered and analyzed to be homogeneous (Table S1), and was then crushed and finely ground to serve as starting metal for DAC experiments.

Laser-Heated Diamond Anvil Cell Experiments

Symmetric DACs were used to generate high pressure. Diamond anvils with flat culet diameters of 200 μm or 300 μm were used. Re gaskets were pre-indented to 40-50 μm thick with a gasket hole of ~ 100 μm or 150 μm in diameter to serve as a sample chamber. Starting metals were sandwiched between two layers of silicate glasses, and the glasses were also served as thermal and chemical insulator during laser heating.

Sample assembly was compressed to a pressure of interest and subsequently laser-heated from both sides using a fiber laser ($\lambda = 1070$ nm, 200 W) with a focused beam size of ~ 20 μm in diameter. Typical heating lasted up to several minutes, with temperature ramping at first and then held for at least 60 s at target T before quench. Time series experiments under similar extreme conditions have demonstrated the achievement of equilibrium in a few seconds (Walter and Thibault 1995; Corgne et al. 2008). To make sure the pyrolite fully melted, all runs were conducted well above the liquidus of pyrolite (e.g. 4500 K at 93 GPa) (Fiquet et al. 2010; Andrault et al. 2011). Temperature was measured every second by fitting the visible portion of the black-body radiation (500–750 nm) from both sides of the heating spot to the Planck black-body function with an uncertainty around ± 250 K (Benedetti and Loubeyre 2004). Pressure was determined by diamond Raman spectroscopy before heating (Akahama and Kawamura 2004),

and corrected for thermal pressure following $\Delta P = 2.7 \text{ MPa/K}$ (Fiquet et al. 2010; Andraut et al. 2011; Siebert et al. 2012).

Sample Recovery and Chemical Analysis

Run products were decompressed slowly and then thin-sectioned using a focused ion beam (FIB) instrument equipped with a field emission gun (Zeiss Auriga FEG-FIB) at IPGP. Ga⁺ ion beam was used to mill the sample from both sides of the laser heating spot. Both secondary and backscattered electron images were used to monitor the sectioning. To avoid any possible contamination from adjacent phases in EDX or EPMA analysis, samples were sectioned down to 3-4 μm thick with the same geometry on both sides. Thin sections were removed from the center of the laser-heated spot by an in situ micromanipulator, and then welded to TEM copper grids with carbon deposit for further polishing and metalized for later analysis. An image of the recovered DAC sample is shown as an example in Figure 1.

Chemical analysis was performed using energy dispersive X-ray (EDX) spectroscopy on FEG-FIB at IPGP and electron probe micro-analysis (EPMA) on Cameca SX-five at Camparis. Excellent agreement was achieved for both techniques, and it has been tested that the apparent metal-silicate partition coefficients of Ni, Cr and V are the same within uncertainties regardless of the analysis methods employed, except for the run X16, which has a strong fluorescence effect from surrounding silicate when analyzing the metal with EPMA, due to the large beam relative to the metal. For consistency, we opt for EDX analysis in this work. Accuracy of the measurements is expected to be 1 % based on the analytical calibrants. An accelerating voltage of 15 kV, a beam current of 20 nA and a counting time of 120 s were used for both metallic and silicate phases. Special care was taken to avoid analytical contamination: when the size of quenched silicate or metallic melts was comparable to the interaction volume, small beam (a few

nanometers) was used and the analyzed spots were chosen far enough from the metal-silicate interface to avoid any secondary fluorescence from adjacent phases. For each phase in an individual run, 4-12 spots/windows were measured by EDX. Uncertainties were reported as 1 standard deviations of multiple measurements (Table S3).

Thermodynamics

To model the interactions in the metal, we used the thermodynamically consistent interaction parameter (ε) approach proposed by (Ma 2001). Following the method, the activity coefficients of the solvent (Fe) and N-1 solutes (i) for N components metallic solutions can be expressed as:

$$\begin{aligned} \ln \gamma_{Fe} = & \sum_{i=1}^{N-1} \varepsilon_i^i (X_i + \ln(1 - X_i)) - \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon_j^k X_j X_k \left(1 + \frac{\ln(1 - X_j)}{X_j} + \frac{\ln(1 - X_k)}{X_k} \right) \\ & + \sum_{i=1}^{N-1} \sum_{\substack{k=1 \\ (k \neq i)}}^{N-1} \varepsilon_i^k X_i X_k \left(1 + \frac{\ln(1 - X_k)}{X_k} - \frac{1}{1 - X_i} \right) + \frac{1}{2} \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon_j^k X_j^2 X_k^2 \left(\frac{1}{1 - X_j} + \frac{1}{1 - X_k} - 1 \right) \\ & - \sum_{i=1}^{N-1} \sum_{\substack{k=1 \\ (k \neq i)}}^{N-1} \varepsilon_i^k X_i^2 X_k^2 \left(\frac{1}{1 - X_i} + \frac{1}{1 - X_k} + \frac{X_i}{2(1 - X_i)^2} - 1 \right) \end{aligned} \quad (S1)$$

and

$$\begin{aligned} \ln \gamma_i = & \ln \gamma_{Fe} + \ln \gamma_i^0 - \varepsilon_i^i \ln(1 - X_i) - \sum_{j=1(j \neq i)}^{N-1} \varepsilon_i^j X_j \left(1 + \frac{\ln(1 - X_j)}{X_j} - \frac{1}{1 - X_i} \right) \\ & + \sum_{j=1(j \neq i)}^{N-1} \varepsilon_i^j X_j^2 X_i \left(\frac{1}{1 - X_i} + \frac{1}{1 - X_j} + \frac{X_i}{2(1 - X_i)^2} - 1 \right) \end{aligned} \quad (S2)$$

where γ_i^0 is the activity coefficient of solute i in liquid iron at infinite dilution, ε_i^j the interaction parameter of element j on element i and X_i the concentration of element i in the metal. We

calculated ε_i^j at the reference temperature 1873 K (T^0) and reported them in Table 1, together with γ_i^0 taken from *Steelmaking Data Sourcebook* (Japan Society for the Promotion of Science and the Nineteenth Committee on Steelmaking, 1988). ε_i^j and γ_i^0 were then extrapolated to run temperatures according to:

$$\ln \gamma_i^0(T) = \frac{T^0}{T} \ln \gamma_i^0(T^0) \quad (S3)$$

$$\varepsilon_i^j(T) = \frac{T^0}{T} \varepsilon_i^j(T^0) \quad (S4)$$

Following Eq. (2), the equilibrium constant K was calculated for data from literature and this study (Table S4-S6) and plotted in Fig. 2.

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