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Spin and valence dependence of iron partitioning in Earth’s deep mantle

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We performed laser-heated diamond anvil cell experiments combined with state-of-the-art electron microanalysis (focused ion beam and aberration-corrected transmission electron microscopy) to study the distribution and valence of iron in Earth’s lower mantle as a function of depth and composition. Our data reconcile the apparently discrepant existing dataset, by clarifying the effects of spin (high/low) and valence (ferrous/ferric) states on iron partitioning in the deep mantle. In aluminum-bearing compositions relevant to Earth’s mantle, iron concentration in silicates drops above 70 GPa before increasing up to 110 GPa with a minimum at 85 GPa; it then dramatically drops in the postperovskite stability field above 116 GPa. This compositional variation should strengthen the lowermost mantle below 1,800 km depth and 2,000 km depth, and weaken it between 2,000 km depth and the D"" layer. The succession of layers could dynamically decouple the mantle above 2,000 km from the lowermost mantle, and provide a rheological basis for the stabilization and nonentrainment of large low-shear-velocity provinces below that depth.

iron partitioning | lower mantle | spin state | valence state | viscosity

The relative concentration (partitioning) of iron in minerals constituting mantle rocks is a critical parameter controlling their physical properties and, consequently, the dynamical properties of the mantle. In a pyrolite mantle, the lower-mantle mineral phase assemblage consists of bridgmanite (Brg)—which transforms to postperovskite (PPv) at pressures higher than 110 GPa (1–4)—ferropericlase (Fp), and calcium silicate perovskite. Only Brg/PPv (hereafter referred to as “silicate” and abbreviated Sil) and Fp can accommodate significant amounts of iron in their structure (5). Density, elasticity, viscosity, and thermal or electrical conductivities, along with associated phase relations, melting temperatures, and relative melt/solid buoyancy, are all linked to the concentration, valence, and spin state of iron in lower-mantle minerals. The seismic observation of global-scale heterogeneities such as large low-shear-velocity provinces (LLSVPs) (6, 7), and that of experimental iron spin-pairing in mantle minerals at lower-mantle depths (8, 9), has fueled a number of investigations of iron partitioning in the lower mantle (10–22).

Despite remarkable advances in experimental and analytical techniques in the last two decades (Supporting Information), stark discrepancies have been reported, depending on the composition of the starting material (San Carlos olivine vs. pyrolite) and differences in iron valence (Fe2+ and Fe3+). San Carlos olivine has a molar (Mg + Fe)/Si = 2 and contains only iron as Fe3+, whereas pyrolite has a molar (Mg + Fe)/Si = 1.4, contains Ca and Al, and contains iron as Fe2+ and Fe3+ (23). Therefore, the parameters controlling iron partitioning in deep mantle conditions are complex (12), and hinder any attempts to infer large-scale geophysical or geochemical consequences on the mantle.

To disentangle valence (15, 23), spin (18, 24), and compositional (12) effects on iron partitioning, we measured iron concentration and iron valence (Fe2+ and Fe3+ concentrations) in silicates and Fp at lower-mantle conditions, in two bulk compositions intermediate between the widely studied San Carlos olivine (10, 11, 17–19, 24, 25) and pyrolite (16, 21, 22) compositions. These are (i) an alumina-bearing olivine and (ii) a calcium-free pyrolite. Neither composition exists in nature, and they were therefore synthesized in the laboratory to be used as compositionally intermediate compounds: Al-bearing olivine is a San Carlos olivine (Mg#90) with the addition of 2 wt.% Al2O3, and has an iron valence distribution similar to that of pyrolite. Ca-free pyrolite has the same iron valence as pyrolite, but contains no Ca, eliminating CaPv from the phase assemblage; as CaPv contains negligible Fe, it is not relevant to Fe partitioning at lower-mantle conditions.

Materials and Methods

Al-bearing olivine and Ca-free pyrolite glasses were produced in an aerodynamic levitation laser furnace, compressed in symmetrical diamond anvil cells at pressures between 28 GPa and 118 GPa, and laser-heated from both sides to temperatures between 2,100 K and 2,700 K, sticking as close as possible to a mantle geotherm (26) (Table S1). The samples were heated for 10 min to 20 min to ensure full equilibration of the sample and to grow large enough crystal grains for accurate chemical quantification (Fig. 1A and Supporting Information). The samples were then quenched and decompressed, and thin sections suitable for transmission electron microscopy (TEM) analysis were prepared using the focused ion beam (FIB) lift-out technique (Fig. S1) using Zeiss Nissros 40 (Centre Interdisciplinaire de Microscopie Electronique (CIME), Ecole Polytechnique Federale de Lausanne (EPFL)) and Zeiss Auriga (Institut de Physique du Globe de Paris (IPGP)) instruments. Quantitative chemical maps and analyses were obtained in scanning TEM (STEM) mode (Fig. 1B–D and Supporting Information) using energy dispersive X-ray (EDX) spectroscopy (Fig. S2) performed on an FEI Tecnai Osiris TEM (CIME, EPL). Iron valence state (Fe2+ and Fe3+ distribution) (Fig. S3) was measured on aberration-corrected electron microscopes, with high spatial resolution and high analytical sensitivity, by electron energy loss spectroscopy (EELS) on a JEOL ARM 200 instrument (LeRoy Eyring Center for Solid Materials and Methods

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Significance

We studied high-pressure and high-temperature phase equilibria using state-of-the-art microanalytical techniques to measure iron partitioning and valence in iron-bearing lower-mantle rocks. Our data allow us to reconcile the discrepancies observed in previous reports, and to propose a comprehensive model of the evolution of iron partitioning in the lower mantle. We reveal an intricate interplay between spin and valence states. Our results suggest a mineral physics basis for rheological variations in the deep lower mantle as a process for stabilizing large thermochemical piles and large low-shear-velocity provinces.

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up to 118 GPa, as observed at lower pressures up to 100 GPa, whereas the Al-bearing system shows a relative enrichment of iron in the Brg is the result of the coupled substitution Fe\(^{2+}\) + Si\(^{4+}\) = Fe\(^{3+}\) + Al\(^{3+}\) (Fig. S4), stabilizing Fe\(^{3+}\) in that phase (28, 29).

The pressure effects on \(K_{\text{eff}}\) are more complex. At pressures up to 70 GPa, \(K_{\text{eff}}\) is effectively constant (Fig. 2A) in both types (Al-free and Al-bearing) of systems. The invariance of \(K_{\text{eff}}\) demonstrates that iron partitioning between lower-mantle minerals is constant with depth down to about 1,700 km depth, regardless of Al content and iron valence distribution, and is consistent with the absence of strong geophysical signature in the lower mantle to those depths (6, 30). 70 GPa corresponds to the onset of iron spin-pairing in Fp (8, 31), whereas iron enrichment was predicted (32, 33) in this phase. This enrichment is observed in both systems (Fig. 2A) through the decrease of \(K_{\text{eff}}\) above 70 GPa, with a notable difference, however: The Al-free system shows a gradual and constant decrease in \(K_{\text{eff}}\) (in this case equal to \(K_{\text{D}}\)) with pressures up to 100 GPa, whereas the Al-bearing systems show a peculiar behavior, in which \(K_{\text{eff}}\) decreases to a minimum value at 85 GPa and then increases up to 110 GPa.

In the PPv (3, 4) stability field, a sharp decrease in \(K_{\text{eff}}\) is observed in the Al-bearing system whereas a sharp increase is observed in the Al-free system. It is noteworthy, however, that \(K_{\text{eff}}\) then becomes identical (within uncertainties) in both Al-free and Al-bearing systems. This particularity is preserved at higher pressures in the PPv stability field, and both systems exhibit similar partitioning with \(K_{\text{eff}}\) decreasing with pressure; this is the only pressure range, corresponding to the lowermost mantle, where iron partitioning in both Al-free and Al-bearing systems is identical.

The comprehensive dataset clearly distinguishes two types of behavior: Al-free ferrous-iron-bearing systems (San Carlos olivine starting compositions, blue colors in Fig. 2A) and Al-bearing systems, containing both ferrous and ferric species (pyrolite, Ca-free pyrolite, and Al-bearing olivine, orange colors in Fig. 2A). This resolves the long-standing discrepancy in iron partitioning behavior previously reported in the literature, as being due to the inappropriate comparison of experimental data from Al-bearing and Al-free lithologies. Our data also confirm that iron partitioning in the Al-bearing system is more complicated than that in the Al-free system. The mechanism is explained by changes in iron valence in the silicate at high pressure coupled with changes in spin state. Iron depletion in the silicate (Brg or PPv) is systematically associated with a drop in Fe\(^{3+}\) concentration (Fig. 2B), and conversely; the evolution trends of \(K_{\text{eff}}\) (Fig. 2A) and Fe\(^{3+}\) concentration in the silicate (Fig. 2B) are identical. A drop in Fe\(^{3+}\) implies an increase in Fe\(^{2+}\) concentration, and the latter has a strong affinity for Fp as shown by the partitioning behavior in the Al-free system, especially above 70 GPa when it turns to the low-spin state. Therefore, iron depletion from the silicate is expected with decreasing Fe\(^{3+}\) and increasing Fe\(^{2+}\) concentration, due to the preferential partitioning of Fe\(^{2+}\) in Fp; that partitioning is spin-state-dependent, and becomes more extreme at pressures above 70 GPa, where iron becomes low-spin in Fp.

The combined dataset presented here also shows that iron partitioning in all Al-bearing systems (pyrolite, Ca-free pyrolite, Al-bearing olivine) is identical within uncertainties, regardless of bulk composition, and argues that our results are applicable to Earth’s mantle. With the silicate phase being the dominant interconnected phase in the lower mantle, it should strongly...
influence transport properties (34–36) and, most notably, viscosity (37). Although there are no compositional-dependence deformation data on Brg, experiments on olivine (38) and Fp (39) have shown an inverse correlation between iron content and strength; Minerals with higher iron concentrations are softer. Assuming that the strength of Brg/PPv follows a similar compositional dependence, an increase in $K_{\text{eff}}$ should result in decreased strength. Because Brg/PPv is the major interconnected phase in the lower mantle, this should result in lowering mantle viscosities (9).

We found a striking correlation (Fig. S5) between mantle viscosity profiles obtained by geophysical inversion (40) and iron partitioning ($K_{\text{eff}}$); a viscosity maximum observed at 2,000 km depth corresponds to a minimum in both $K_{\text{eff}}$ and Fe$^{3+}/\Sigma$Fe observed at 85 GPa (Fig. 2), whereas the viscosity minimum at 2,550 km depth fits with a maximum in both $K_{\text{eff}}$ and Fe$^{3+}/\Sigma$Fe at 100 GPa (Fig. 2). The lack of sensitivity at those depths, however, precludes the accurate inference of depth-dependent deformation experiments or calculations on Brg, the question remains open from a point of view of mineral physics.

It has been proposed that the viscosity high at 1,000 km (40, 42, 43) is correlated with stagnating slabs and fast regions inferred from seismic tomography (44). If the viscosity contrast between 80 GPa and 120 GPa predicted here were to affect mantle dynamics below 1,800 km, this would provide a unique explanation to the remanence of LLSVPs. These structures are currently thought of as being primordial (7), dating back to the initial settling and freezing of Earth’s Magma Ocean after accretion 4.5 Gya ago. The question of their stability (45), and how they anchor above the core–mantle boundary over geological time, is still unsolved. The top of the weak layer inferred by our partitioning data sits above those structures. We propose that a weak lowermost mantle (below 2,000 km) topped by a stiffer mantle (1,800 km to 2,000 km) could dynamically decouple the base of the mantle from the overlying mantle, which could, in turn, isolate and stabilize these large structures.

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