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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 between 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 pyrolitic mantle, the lower-mantle mineral phase assemblage consists of bridgmanite (Brg)—which transforms to postperovskite (PPv) at pressures higher than 110 GPa (1–4)—ferropericlasite (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 (Fe^{2+} and Fe^{3+}). San Carlos olivine has a molar $(\text{Mg} + \text{Fe})/\text{Si} = 2$ and contains only iron as Fe^{2+} , whereas pyrolite has a molar $(\text{Mg} + \text{Fe})/\text{Si} = 1.4$, contains Ca and Al, and contains iron as Fe^{2+} and Fe^{3+} (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 (Fe^{2+} and Fe^{3+} 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.% Al_2O_3 , 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 Nvision 40 [Centre Interdisciplinaire de Microscopie Électronique (CIME), École Polytechnique Fédérale 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 Tecnaï Osiris TEM (CIME, EPFL). Iron valence state (Fe^{2+} and Fe^{3+} 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

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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The authors declare no conflict of interest.

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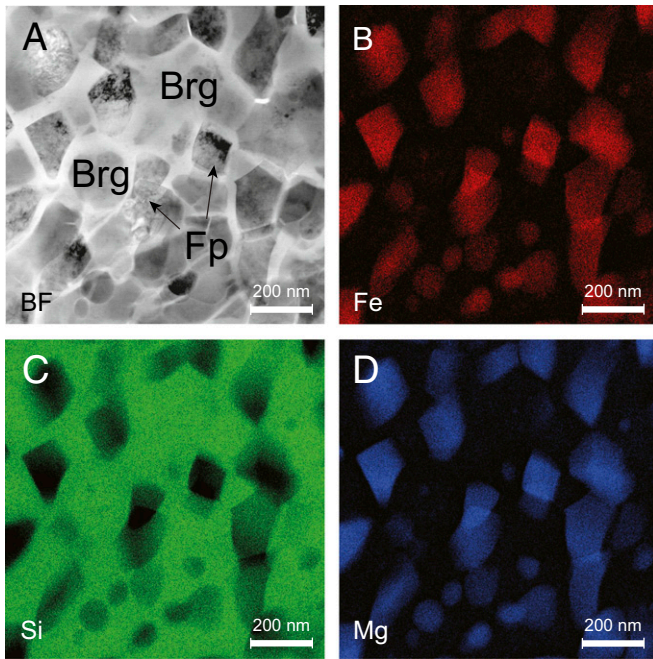
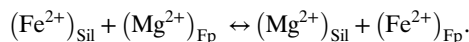


Fig. 1. TEM image and EDX chemical maps of a Brg and Fp assemblage heated for 15 min at 58 GPa and 2,400 K. Bright-field TEM image (A) of the assemblage and corresponding chemical maps for (B) iron, (C) silicon, and (D) magnesium. The geometry of Fp grains, as well as the identical composition of distinct grains across the sample, is indicative of equilibrium conditions. The central part of the sample shows smaller overlapping Fp and Brg grains; those were never used for quantification.

State Science, Arizona State University (ASU)] using a Gatan Enfium spectrometer, and on an FEI Titan Themis instrument (CIME, EPFL) using a Gatan GIF Quantum ERS high energy-resolution spectrometer. Quantitative chemical analyses of silicates and Fp phases are reported in Table S1 for all runs, and more details about sample preparation, synthesis, recovery, and analysis can be found in Supporting Information.

Results and Discussion

The EELS measurements confirm that Fp, like olivine at lower-pressure conditions, does not accommodate ferric iron (Table S1), and contains only Fe^{2+} up to 118 GPa, as observed at lower pressures (15). The silicate, however, contains both Fe^{2+} and Fe^{3+} , consistent with previous observations (23, 27), albeit with significantly lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ above 116 GPa (PPv stability field) than at lower pressure (Brg stability field). Ferric iron is therefore entirely contained in the silicate phase and doesn't exchange or partition between the silicate and Fp, whereas ferrous iron is distributed between both silicate and Fp through an Fe–Mg exchange reaction,



This reaction describes Fe^{2+} partitioning between both phases, and its exchange constant K_D is defined as $K_D = (X_{\text{Fe}^{2+}}^{\text{Fp}} X_{\text{Mg}^{2+}}^{\text{Sil}}) / (X_{\text{Fe}^{2+}}^{\text{Sil}} X_{\text{Mg}^{2+}}^{\text{Fp}})$, where X is the (molar) concentration of Mg and Fe^{2+} in Fp and the silicate. The effective equilibrium constant K_{eff} describes total iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$) partitioning between the two phases, $K_{\text{eff}} = (X_{\text{Fe}}^{\text{Fp}} X_{\text{Mg}}^{\text{Sil}}) / (X_{\text{Fe}}^{\text{Sil}} X_{\text{Mg}}^{\text{Fp}})$, where X is now the (molar) concentration of Mg and total Fe in Fp and the silicate. High values of K_{eff} therefore indicate iron-rich silicates, whereas low values indicate iron-rich Fp.

The compositional effect on K_{eff} is apparent in Fig. 2A, where our data are combined with laser-heated diamond anvil cell (LHDAC) data from the literature obtained with other bulk

chemistries (i.e., San Carlos olivine in blue, and pyrolite in orange). Our measurements in both Al-bearing olivine and Ca-free pyrolite are fully consistent with the previously published pyrolite dataset (16, 21, 22), corroborating the fact that iron partitioning is mainly controlled by aluminum content, and does not depend on the relative iron, magnesium, silicon, or calcium concentrations in the rock. Below 70 GPa, where partitioning is constant with pressure, K_{eff} in the Al-bearing system is significantly larger than in the Al-free system; this relative enrichment of iron in the Brg is the result of the coupled substitution $\text{Fe}^{2+} + \text{Si}^{4+} = \text{Fe}^{3+} + \text{Al}^{3+}$ (Fig. S4), stabilizing Fe^{3+} in that phase (28, 29).

The pressure effects on K_{eff} are more complex. At pressures up to 70 GPa, K_{eff} is effectively constant (Fig. 2A) in both types (Al-free and Al-bearing) of systems. The invariance of K_{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), where iron enrichment was predicted (32, 33) in this phase. This enrichment is observed in both systems (Fig. 2A) through the decrease of K_{eff} above 70 GPa, with a notable difference, however: The Al-free system shows a gradual and constant decrease in K_{eff} (in this case equal to K_D) with pressure up to 100 GPa, whereas the Al-bearing system shows a peculiar behavior, in which K_{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_{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_{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_{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_{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

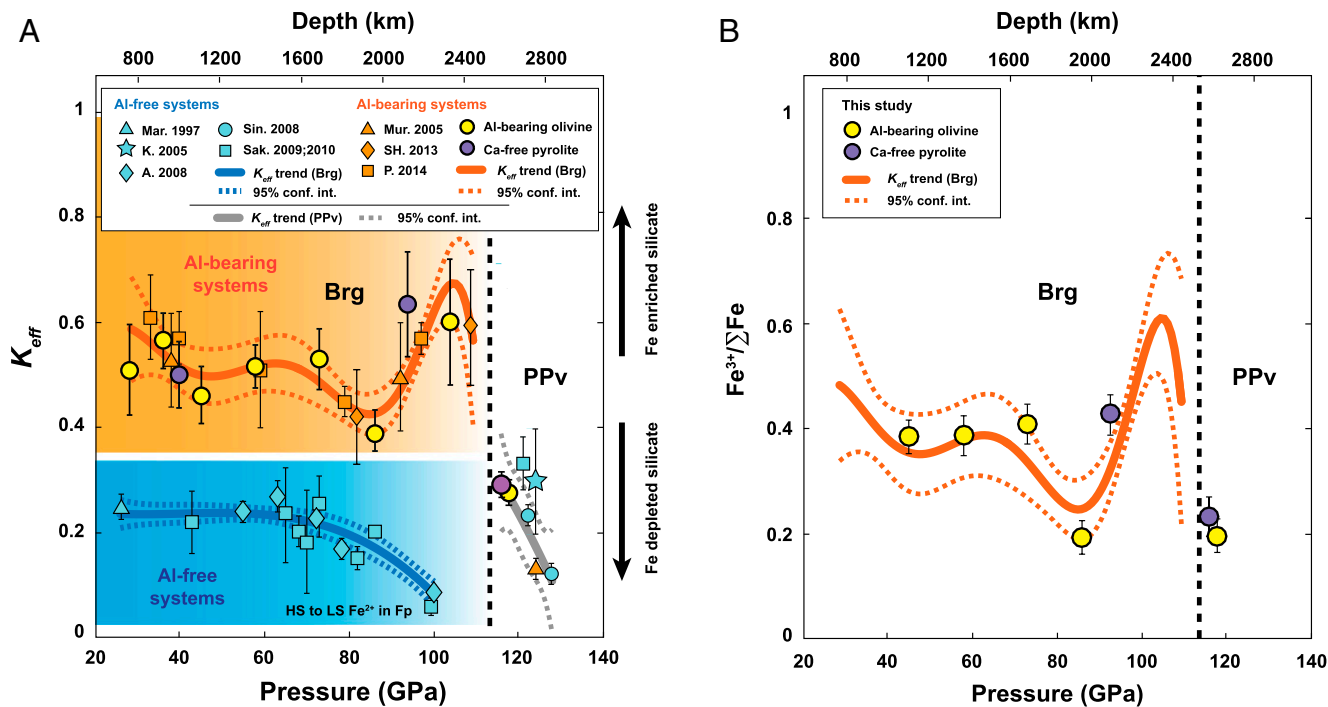


Fig. 2. Fe–Mg exchange coefficient between silicate (BRG and PPV) and Fp at lower-mantle pressures and temperatures. Brg and PPv stability fields are separated by the vertical dashed line at ~115 GPa. (A) Effective exchange coefficients K_{eff} obtained from EDX analyses (yellow and purple filled circles) are plotted as a function of pressure. K_{eff} values from previous studies in the San Carlos olivine system (11, 17–19, 24, 25) and in the pyrolyte system (16, 21, 22) are also plotted (see [Supporting Information](#) for details). The blue-shaded area delimits the K_{eff} range for Al-free systems, and the orange-shaded area delimits that of Al-bearing systems. Solid lines running through the data were obtained by linear least-squares regression, and the 95% confidence intervals were calculated from the linear model by propagating experimental uncertainties (see [Supporting Information](#)); these mostly serve the purpose of showing that K_{eff} variations above 70 GPa are statistically resolvable. (B) Fe^{3+} concentration in the silicate as a function of pressure from EELS measurements. The line is not fit to the data but is replicated from that obtained in A. The notable match is a strong indication that iron partitioning between lower-mantle minerals in an Al-bearing system follows the evolution of iron valence (i.e., Fe^{2+} and Fe^{3+}) distribution in the silicate.

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_{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_{eff}); a viscosity maximum observed at 2,000 km depth corresponds to a minimum in both K_{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_{eff} and $Fe^{3+}/\Sigma Fe$ at 100 GPa (Fig. 2). The lack of sensitivity at those depths, however, precludes the accurate inference of viscosity from geophysical data (41, 42). Moreover, without composition-dependent deformation experiments or calculations on Brg, the question remains open from the 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 remnant 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 Gy ago. The question of their stability (45), and how they anchor above the core–mantle boundary over geologic 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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