

EXPERIMENTAL EVIDENCE FOR A HIGHLY REDUCED EARTH'S UPPER MANTLE. A. Rohrbach^{1,2,3}, C. Ballhaus¹, U. Golla-Schindler², P. Ulmer³ and D. Schönbohm¹, ¹Mineralogisches Institut und Museum, Universität Bonn, Poppelsdorfer Schloss, 53115 Bonn, Germany, arno.rohrbach@erdw.ethz.ch ²Institut für Mineralogie, Universität Münster, Corrensstr. 24, 48149 Münster, Germany, ³Institut für Mineralogie und Petrographie, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland

Introduction: At the time of core formation, the Earth's silicate mantle was presumably in redox-equilibrium with the metallic iron core, which means—assuming an olivine composition of Mg# 0.9—about IW-2[1]. On the other hand, samples representative for the modern upper mantle such as abyssal peridotites or melts that originate in the upper mantle (MORB, OIB, IAB) are considerably more oxidized[2]. Questions arising are: Which process may have caused secular mantle oxidation? Is the entire upper mantle as oxidized as the shallow mantle, or are there systematic changes in relative fO_2 with increasing depth in the upper mantle, leaving parts of the upper mantle in redox equilibrium with the metallic core?

Experimental: To investigate the redox evolution of the upper mantle with increasing depth we performed experiments in Fe^o capsules from 1 to 14 GPa and 1220 to 1650°C with a modified fertile mantle composition. We subtracted 30 wt% olivine from the composition in order to increase the amount of potentially Fe³⁺-rich phases like pyroxene and garnet. The starting composition was enriched in FeO (Mg# of 0.5) to raise the FeO content of the minerals, which results in more precise counting statistics during EELS measurements.

Experiments in the piston cylinder press were performed at 1 to 3 GPa and 1220°C to 1400°C at the Institute for Mineralogy, University of Münster. Run temperatures were measured with WRe₃-WRe₂₅ thermocouples (type D). Experiments from 6 GPa to 14 GPa were performed with the 600 and 1000t multi anvil presses (Walker type modules) of the High Pressure Lab of the Institute for Mineralogy and Petrology at ETH Zürich. Temperatures ranged from 1400°C to 1650°C. Experiments were run with 32 mm WC anvils, a stepped LaCrO₃ furnace combined with MgO/Cr₂O₃ ceramic octahedra, and pyrophyllite gaskets. Temperatures were measured with PtRh₆-PtRh₃₀ thermocouples, and both pressure and temperature were computer-controlled during the entire run duration.

Analytical: The run products were documented with backscattered electron imaging and phases were analyzed for major elements with an electron microprobe-analyzer. The samples were subsequently thinned with a Gatan Duo-mill ion thinning system at 5 kV and 14° beam angle to electron transparency. EELS analyses were performed with a Zeiss Libra 200 FE-TEM operated at 200 kV at the ICEM, University

of Münster. The energy resolution of the Zeiss Libra is 0.9 eV, measured as full width at half maximum of the zero loss peak. We analyzed 7 to 15 grains of each mineral phase per experimental run product. The spectra were quantified with respect to Fe³⁺/ΣFe using the “universal curve”[3,4]. We observed no beam-induced oxidation of the samples during the measurements, not even when counting times were increased to 5 minutes.

Results and Discussion: The 1 GPa run (1220°C) crystallized olivine and two pyroxenes. In the 3 to 6 GPa runs, stable silicate phases were subcalcic pyroxene of pigeonitic composition plus an almandine rich garnet. The 7 to 12 GPa runs also crystallized subcalcic pyroxene and garnet, but in this pressure range garnet becomes increasingly majoritic in composition, with Si cations per 12 oxygens ranging from 3.11 ± 0.02 (7 GPa) to 3.36 ± 0.02 (12 GPa). In the highest-pressure run (14 GPa) the only stable silicate phase was a distinctly majoritic garnet, with Si = 3.66 ± 0.02 pfu. In addition to these phases, all experimental charges were peppered with micrometer-sized grains of metallic iron, both distributed along grain boundaries and as inclusions in silicates, suggesting that redox equilibrium between the silicate phases and metallic Fe was achieved throughout.

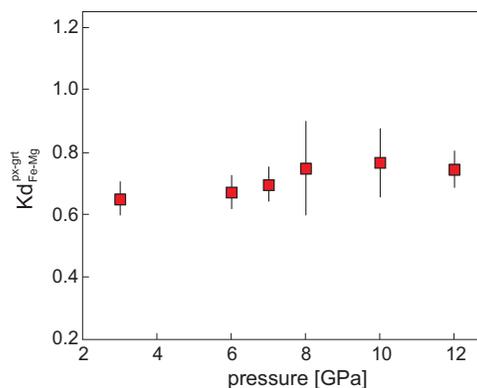


Figure 1. Kd_{Fe-Mg}^{px-grt} versus pressure. Kd is constant within error (95% confidence) around 0.7 and indicative for the attainment of Fe–Mg exchange equilibrium between pyroxene and garnet during experimentation.

This assumption is supported by the fact that the value for Kd_{Fe-Mg}^{px-grt} is within error uniformly around 0.7 in all charges (Figure 1) and appears to be largely independent of pressure, bulk FeO/MgO, and temperature. Note that the FeO content used to calculate Kd was

derived by subtracting the proportion of ferric iron as determined by EELS from bulk FeO as analyzed by EPMA. The fact that the K_d remains constant with pressure strongly suggests that the ferric iron determinations by EELS are robust. EELS analyses reveal that subcalcic pyroxene and majoritic garnet increasingly incorporate ferric iron above 7 GPa pressure despite these phases being in equilibrium with metallic iron. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet strongly correlates with the amount of majorite component dissolved in garnet (Figure 2). At ~ 8 GPa pressure, metal saturated subcalcic pyroxenes and majoritic garnets can incorporate more ferric iron than the 2000 ppm Fe_2O_3 present in fertile upper mantle. Hence, the Earth's upper mantle at > 250 km depth is likely to be saturated with an (Fe,Ni) metal phase[5].

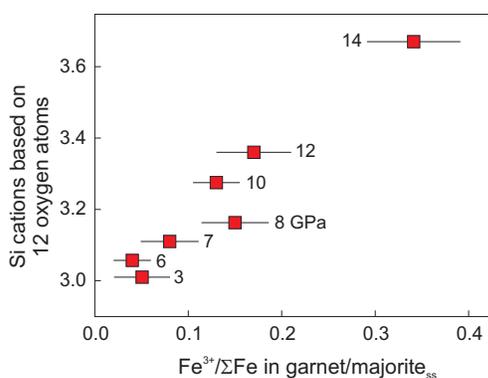


Figure 2. Si cations vs. $\text{Fe}^{3+}/\Sigma\text{Fe}$ garnet-majorite_{ss} (modified after ref 5).

We re-determined the P–T position of the $\text{Fe}^\circ\text{--Fe}_{1-x}\text{O--Fe}_3\text{O}_4$ triple point in the Fe–O system (at $\sim 570^\circ\text{C}$ at 10^5 Pa) to verify if pressure induced disproportionation of FeO to $\text{Fe}^\circ + \text{Fe}_2\text{O}_3$ is an effective mechanism responsible for the elevated Fe^{3+} contents measured in the experiments. The in-situ determination of the wüstite–magnetite phase transition in the presence of metallic Fe in the MAX80 high-pressure device, using white synchrotron radiation confirms the results of ref 6 that the disproportionation reaction has a steep negative slope in P–T space (Figure 3). Consequently, disproportionation of FeO solely induced by pressure is not effective in stabilizing ferric iron components in the upper mantle. Rather, the role of pressure is to stabilize silicate phases with high affinities for ferric iron (e.g. majorite), thereby lowering the activities of the ferric iron components at given bulk Fe_2O_3 and causing relative reduction.

We therefore interpret the oxidized nature of the Earth's upper mantle as a direct consequence of mantle convection: Downward convection (compression) results in relative reduction, upward convection (decom-

pression) results in relative oxidation. If material originating from the deeper mantle is within the stability field of majoritic garnet and convects upwards, majorite becomes unstable and the Fe_2O_3 is released. Fe_2O_3 comports with Fe° to form FeO until the mantle material has lost the metal phase completely. The only requirement to achieve relative oxidation (higher relative $f\text{O}_2$) during upward mantle convection is that the bulk mantle contains more free oxygen in the form of Fe_2O_3 than the amount balanced by Fe° . This is obviously the case. The metal-free fertile upper mantle contains 2000 ppm Fe_2O_3 [8]. This is “excess” Fe_2O_3 that is left over after ferric iron has reacted with metallic Fe to FeO. The excess Fe_2O_3 is potentially the result of the core-forming event where a small fraction of the internally produced Fe° is removed from the lower mantle. McCammon [9] argues that the removal of 10% of the ~ 1 wt% metal phase stable in the lower mantle[10] explains the excess Fe_2O_3 observed in upper mantle rocks. Implicit in this is that the lower mantle has never lost the internally produced metal phase entirely, not even at the time of core formation.

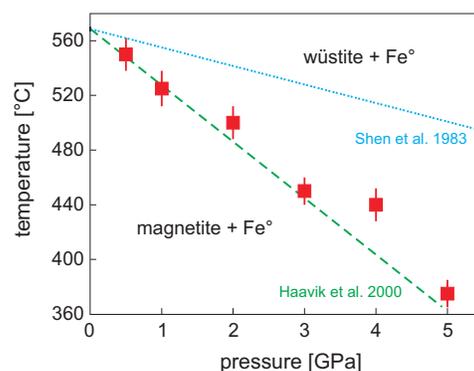


Figure 3. Magnetite+ Fe° –wüstite+ Fe° phase boundary in P–T space. Squares this study, dashed line ref 6, dotted line ref 7.

References: [1] O'Neill H.St.C. (1991) *Geochim. Cosmochim. Acta*, 55, 1159–1172. [2] Ballhaus, C.G. (1993) *Contrib. Mineral. Petrol*, 114, 331–348. [3] van Aken, P.A. and Liebscher, B. (2002) *Phys. Chem. Miner.*, 29, 188–200. [4] van Aken, P.A. et al. (1998) *Phys. Chem. Miner.*, 25, 323–327. [5] Rohrbach, A. et al. (2007) *Nature*, 449, 456–458. [6] Haavik, C. et al. (2000) *Am. Mineral.*, 85, 514–523. [7] Shen, P. et al. (1983) *Geochim. Cosmochim. Acta*, 47, 773–778. [8] O'Neill, H.St.C. et al. (1993) *Geophys. Monograph*, 74, pp. 73–88. [9] McCammon, C.A. (2005) *Science*, 308, 807–808. [10] Frost, D.J. et al. (2004) *Nature*, 428, 409–412.