Fe-properties in ultra-dense minerals of the lowermost Earth mantle: Tandem XANES-XRD analyses

Denis Andrault [1*], Manuel Muñoz [2], Nathalie Bolfan-Casanova [1] and Sakura Pascarelli [3]

[1] *Laboratoire Magmas et Volcans, Université Blaise Pascal, Clermont-Ferrand, France*
[2] *Lab. de Géodynamique des Chaînes Alpines, Université Joseph Fourier, Grenoble, France*
[3] *European Synchrotron Radiation Facility, Grenoble, France*

The lower mantle is the major Earth's reservoir, where -subducting slabs, -ascending hot spots, -denser primitive mantle reservoirs, and -contact with the hot outer core dominate its dynamical activity. Its vigorous convection is a major driving force for plate tectonics. The lower mantle extends at depths from 670 km to 2900 km, corresponding to pressures from 25 GPa to 135 GPa. It is composed of three major phases; the $(Mg,Fe)(Si,Al)O_3$ and $CaSiO_3$ perovskites (Pv) and the (Mg,Fe)O ferropericlase (Fp). At a mantle depth about 300 km above the core-mantle boundary, the $MgSiO_3$-Pv transforms to a post-Pv (PPv) $CaIrO_3$-type structure (*1*).

Despite their moderate concentrations, Fe [Fe/(Mg+Fe+Ca)~0.1] and Al [Al/Fe~1] dominate most of mantle properties; In particular, Fe is the main element presenting a variable oxidation state (Fe^0, Fe^{2+} and Fe^{3+}). Altogether, these two elements control -the lower mantle oxygen fugacity, -the thermal (if radiative) diffusivity, -the solubility of many minor and trace elements, -the mechanism of the various phase transformations, -etc. A major property is a great affinity between Al^{3+} and Fe^{3+} in the $MgSiO_3$-based Pv-structure (*2*). This affinity affects largely the Pv crystal chemistry, inducing presence of various types of point defects and a high $Fe^{3+}/\Sigma Fe$ content. On the other hand, a change of spin state in Fe has been observed in Fp and Pv at lower mantle pressure (*3*). Concerning the phase transition to the PPv structure, while this phase transition has been used to explain the peculiar seismological features of the lowermost mantle (*4, 5*), the effect of Fe and Al on this transition remained to be quantified experimentally.

By means of *in situ* study of the Fe K-edge XANES spectroscopy, we investigated the major phase relations between the different lower mantle minerals. The high P and T assemblages were synthesized using the laser-heated diamond-anvil cell (DAC) at pressures up to more than 135 GPa. The sample's mineralogy was first determined using *in-situ* X-ray diffraction (XRD) at the ID27 beamline (*6*). Using Rietveld refinements, we could refine the phase contents, such as the relative amount of Pv and PPv as a function of P and T. Then, we probed the Fe speciation, i.e. the Fe concentration in each phases, as well as the Fe oxidation state, *in-situ* in the DAC using the μ-XANES mapping technique available at the ID24 beamline (*7*). Both pieces of information were combined to retrieve the Fe partitioning coefficient between the different high-pressure phases.

We will discuss the implications of our results in terms of mineralogy of the deep mantle, phase relations between minerals, and we will develop preliminary interpretation for the seismological features reported for the lowermost mantle.

References:
[1] M. Murakami, K. Hirose, K. Kawamura, N. Sata, Y. Ohishi, *Science* **304**, 855 (2004).
[2] S. Lauterbach, C. A. McCammon, P. van Aken, F. Langenhorst, F. Seifert, *Contrib. Miner. Petrol.* **138**, 17 (2000).
[3] J. Badro *et al.*, *Science* **305**, 383 (2004).
[4] T. Lay, Q. Williams, E. J. Garnero, *Nature* **392**, 461 (1998).
[5] J. W. Hernlund, C. Thomas, P. J. Tackley, *Nature* **434**, 882 (2005).
[6] E. Schultz *et al.*, *High Press. Res.* **25**, 71 (2005).
[7] S. Pascarelli, O. Mathon, M. Muñoz, T. Mairs, J. Susini, *J. Synch. Rad.* **13**, 351 (2006).