

# Ferric–ferrous iron ratios in upper mantle minerals

A. ROHRBACH<sup>1</sup> C. BALLHAUS<sup>2</sup> U. GOLLA–SCHINDLER<sup>1</sup>  
AND P. ULMER<sup>3</sup>

<sup>1</sup>Institut für Mineralogie, Westfälische Wilhelms–Universität  
Münster; rohrbaa@nwz.uni–muenster.de

<sup>2</sup>Mineralogisch–Petrologisches Institut, Universität Bonn

<sup>3</sup>Institut für Mineralogie und Petrographie, ETH Zürich

It is a matter of debate whether localized partial melting in some regions of the mantle is caused by elevated temperature (hotspots) or elevated volatile activity (wetspots). In the wetspot model proposed by Green and coworkers [1,2] partial melting is triggered by redox processes; oxidized (IW+4) lithospheric material is subducted into a reduced asthenosphere (IW+1), causing localized oxidation of reduced asthenospheric CH<sub>4</sub>–H<sub>2</sub> volatiles to CO<sub>2</sub> and H<sub>2</sub>O and thereby lowering the mantle solidus temperature and triggering partial melting. Implicit in this model is that the deeper asthenosphere is highly reduced, but until now proof for such highly reduced conditions has been lacking.

To understand redox controls in the upper mantle we have equilibrated Fe<sub>2</sub>O<sub>3</sub>–free synthetic fertile mantle material (~30% olivine) in metallic Fe<sup>0</sup> capsules between 1 and 10 GPa and 1400 to 1600°C. We have measured the Fe<sup>3+</sup>/ΣFe ratios of spinel, majoritic garnet, and subcalcic clinopyroxene in the run products with electron energy loss spectroscopy (EELS). To optimize the detection limits for Fe<sup>3+</sup>, all starting materials were enriched in FeO relative to natural mantle (Mg# from 50 to 70). The fO<sub>2</sub> conditions at which the charges equilibrated are approximated from the FeO content of the silicates to IW–0.5 to –1. Above a pressure of ~ 6 GPa, we detect significant concentrations in ferric iron in both pyroxene and majoritic garnet. The results confirm previous suggestions [3] that FeO disproportionates with increasing pressure to Fe<sup>0</sup> and Fe<sub>2</sub>O<sub>3</sub>. If the bulk Fe<sup>3+</sup>/ΣFe ratio of 0.023 determined by O'Neill et al. [4] is representative for the entire upper mantle, increasing depth causes closed–system reduction by FeO disproportionation. According to our experimental Fe<sup>3+</sup>/ΣFe – depth relations, fertile convecting upper mantle is expected to reach (Fe,Ni)<sup>0</sup> metal saturation at ~ 300 km depth. Well above this depth, C–H–O volatiles are already within the stability field of CH<sub>4</sub>–H<sub>2</sub>, with oxygen stored largely in Fe<sub>2</sub>O<sub>3</sub>.

## References

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