

A XANES studies of the iron oxidation state in upper mantle spinel

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The oxygen fugacity (fO_2) is a significant parameter which has a major effect on the evolution of Earth's crust and mantle. Spinel as a host mineral for ferric iron could be a proxy for determination of the oxygen fugacity through $Fe^{3+}/\Sigma Fe$ ratio.

We prepared 5 natural spinel samples from upper mantle xenoliths and obtain XANES, Mössbauer and EPMA data on two different grains on each sample. Calculation of $Fe^{3+}/\Sigma Fe$ was conducted through EPMA measurements (based on stoichiometry) and on Mossbauer data. For XANES spectra, after fitting was calculated integral intensity ratio $AFe^{3+}/A\Sigma Fe$.

Fe-K XANES spectra show systematic differences in the pre-edge region as a function of the shape of iron K-edge peak from iron oxidation state, as was previously shown for garnet [1], [2]. In addition, the main peak shift to lower energy noticed - in Cr-rich grains (44 and 95) with highest differences in $AFe^{3+}/A\Sigma Fe$ in comparison to Mössbauer and EPMA data. Noteworthy moment is that heterogeneity of spinel grains in $Fe^{3+}/\Sigma Fe$ is far larger than expected. A more detailed analysis of the issue requires further studies from rim to core on synthetic and natural samples.

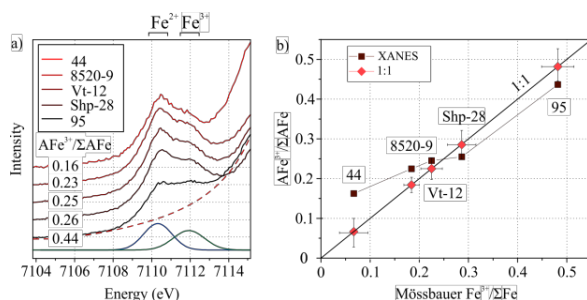


Figure 1. a) Fe-K pre-edge peak for natural spinel samples with out of scale illustration of systematic differences in the shape of peak from iron oxidation state; b) Mössbauer plotted versus Mössbauer (1:1), XANES $AFe^{3+}/\Sigma AFe$ plotted versus Mössbauer (XANES);

[1] Berry et al, (2010) *Chemical Geology* **278**, 31–37. [2] Yaxley et al, (2012) *Lithos* **140**, 142-151