Micro-XANES study on iron oxidation state in amphiboles of mantle xenoliths from Persani Mt., Romania

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Studying Fe^{3+} bearing minerals are the easiest way to gain information about the oxidation state of the Earth mantle. Among these minerals, spinel is generally present in the mantle, but amphiboles are present only in special cases as a product of metasomatism (interaction of fluid-rich melt and mantle rock). Among the mantle xenoliths of the Carpathian-Pannonian region, those originating from the Persani Mt. (E-Transylvanian Basin) are indeed special rocks because the fluid-rich melt forming amphiboles [1] are related to such tectonic events as subduction [2]. Ferric iron rich amphiboles from mantle rocks of Persani Mt. were equilibrated with Fe^{2+} rich mantle at different conditions. Mössbauer spectroscopy has generally been used for oxidation state determination of iron in different materials, including rocks. However, Mössbauer method is not suitable for analysis of small (ca. 60 μm) individual grains. Since the amphibole grains are from different rocks and from different distribution of these rocks (i.e. in the middle or at the wall of the vein), the accurate analyses of individual grains at microscopic scale is essential. Therefore, microbeam X-ray absorption near-edge structure (micro-XANES) was selected which can deliver information on the oxidation state of Fe at microscopic scale [3]. Twenty one amphibole grains from 7 xenolith samples were selected for the analyses.

The experiments were performed at the micro-fluorescence beamline L of HASYLAB. The white beam of the bending magnet was monochromatized by a Si(111) double monochromator. A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of 3×1.5 mm^2 down to a spot size of 15 μm. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the K absorption edge of Fe (7112 eV) by stepping the Si(111) monochromator. The X-ray fluorescence photons were detected by a silicon drift detector with 50 mm^2 active area (Radiant Vortex). The used step size varied between 0.5 (edge region) to 2 eV (more than 50 eV above edge). The measuring time for each energy point was set to 5 s. Powdered standards of known Fe oxidation state were prepared from pro analysis grade chemicals of $FeCO_3$, Fe_2O_4 and Fe_3O_4. Similar size microscopic grains of the standards as well as of the unknown amphiboles were selected for the measurements, in order to minimize the difference of self-absorption between the standards and the samples. Background removal and normalization of the micro-XANES spectra was performed using the ATHENA software package [4]. The oxidation state of Fe in the microscopic amphibole grains was determined based on the calibration of the chemical shift of the absorption edge using standards.

The applied micro-XANES method clearly revealed that the mantle wall rock has low ferric iron content indicating its reductive environment, whereas the amphibole-bearing veins, occurring in the mantle, show at least twice higher Fe^{3+} content (Fig. 1). This oxidative environment corresponds to source of the fluid causing metasomatic alteration, namely formation of amphibole, in the mantle. Such circumstances are characteristic for, among others, subduction related geodynamic environment.

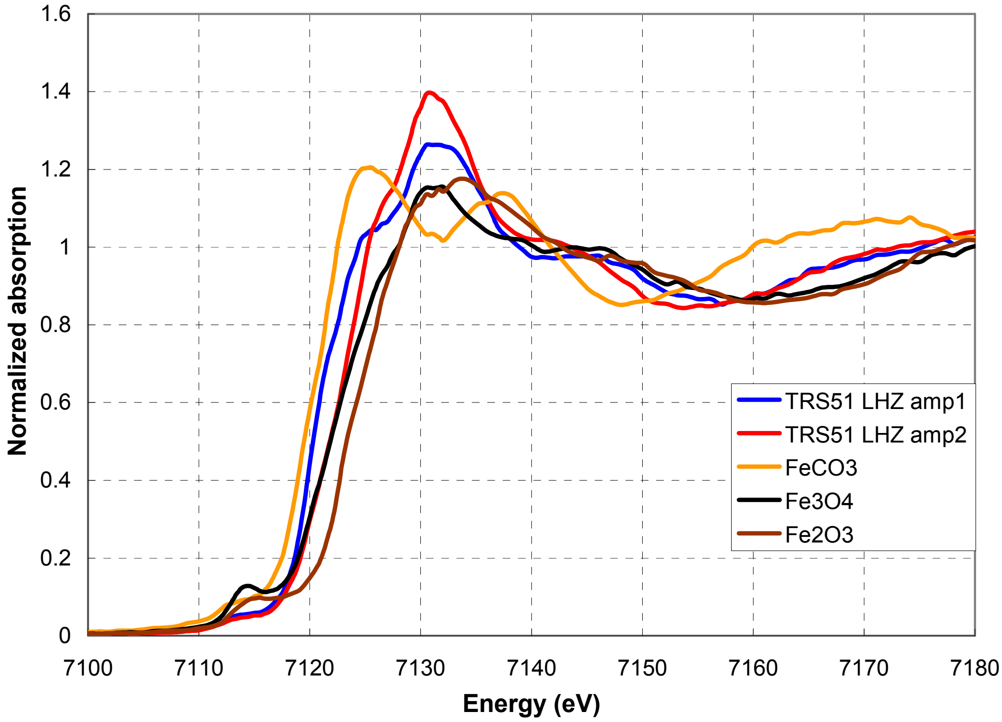

Figure 1: Fe-K edge micro-XANES spectra of microscopic grains of standards and amphibole grains.

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