

## X-RAY ABSORPTION SPECTROSCOPIC (XAS) STUDY OF $\text{Fe}^{3+}$ AND $\text{Ti}^{4+}$ IN TRIOCTAHEDRAL MICAS

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Micas are involved in many petrogenetic reactions in a wide range of geological environments and contribute significantly to the storage and release of water in the mantle. However, the complexity of mica composition constitutes a major obstacle to draw petrologic inferences, because the choice of a proper activity model depends on the assessment of the correct substitution mechanisms. This is particularly true for petrologic significant cations, such as  $\text{Ti}^{4+}$  and  $\text{Fe}^{3+}$ . Characterisation of substitution mechanisms is not straightforward in the case of micas and requires chemical, spectroscopic and diffraction techniques. Indeed, multimethodic investigations have ascertained that  $\text{Fe}^{3+}$ -oxy and Ti-oxy substitutions play a major role both in metamorphic and igneous phlogopites [1-2]. Associated to these substitutions is the geometric distortion of the octahedral site M2. Diffraction methods clearly show an “average” distortion of the octahedral site hosting the two species, but do not allow to determine any local structural modification. Moreover, the accuracy of Mössbauer Fe speciation is often affected by inhomogeneity of large sample amount. As a result discrepancies between spectroscopic and diffraction results occur. Moreover, Ti oxidation state is often inferred by crystal-chemistry considerations and rarely directly measured.

In this work we took advantage of the element selectivity and short-range structural probing of XAS to get information on the local environment around Ti and Fe and determine their oxidation states in natural trioctahedral micas. Six samples with Ti 0.02-0.20 a.p.f.u. and  $\text{Fe}^{3+}$  0.20-0.80 a.p.f.u., already characterized by several techniques including single-crystal X-ray diffraction, were analysed. Spectra at the Fe-K and Ti-K edges were collected at XAFS beamline of the ELETTRA facility (Trieste, Italy) at room temperature in fluorescence mode using single crystal flakes.

Analysis of the XANES spectral features confirms that  $\text{Ti}^{4+}$  preferentially enters the octahedral site, which is always distorted, with sample SA showing the maximum and IgnB the minimum degree of distortion. The Fe-K pre-edge region indicates the presence of tetrahedral  $\text{Fe}^{3+}$  in sample MA only. Indication on Fe oxidation state in all samples was derived on the basis of the Fe-edge positions compared to those measured for  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  standards. All samples show a mixed oxidation state for Fe, with Vut215 being the most and BHG the least oxidized sample. These results are in agreement with previous crystal-chemical considerations [2-6]. The  $\langle\text{Fe}-\text{O}\rangle$  and  $\langle\text{Ti}-\text{O}\rangle$  distances derived from EXAFS will be discussed and compared with the XRD results. It is confirmed that  $\text{Ti}^{4+}$  is in M2 site.

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