

The dynamics of Fe oxidation in amphiboles: electronics processes vs. local structural strain by means of simultaneous XRD and XAS experiments

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Iron is the most abundant metallic element on the Earth, having a variable oxidation state that is extremely sensitive to the geochemical environment. Characterization of its valence state is therefore important in geology for defining the condition of formation of the rocks where the iron minerals under investigation are found. In particular, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of minerals is widely used in mineralogy and its evaluation is addressed typically by Mössbauer spectroscopy, a technique with extremely difficult access to micro-scale information. At variance, X-ray absorption spectroscopy (XAS) has been successfully applied to study $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in a variety of geological materials also at micro-scale. In this work we investigate the oxidation behaviour of a synthetic richterite, ideally $\text{K}(\text{NaCa})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, by using simultaneous XANES (X-ray Absorption Near Edge Spectroscopy) spectroscopy and X-ray diffraction experiments collected at the energy of 8 keV up to $\sim 750^\circ\text{C}$ performed at beamline B18 at the Diamond Light Source, the UK synchrotron radiation facility at Oxford.

From X-ray Diffraction (XRD) patterns we observe an abrupt drop of cell dimensions above 300°C , which can be associated to a deprotonation process. This rearrangement is accompanied in the same temperature range by an anomalous increase in the monoclinic cell angle (β). This behaviour points out a structural adjustment, involving also a sliding of the silicate double chains. From the analysis of the XANES spectra at the iron K-edge we find that the oxidation process occur slightly earlier ($\sim 310^\circ\text{C}$) than the structural variations monitored by our XRD data, in agreement with previous works conducted on the same system without simultaneous acquisition methods.

Combining these results with previous studies performed on similar samples by single-crystal structure refinement, Mössbauer, Raman and High Temperature-Fourier Transform IR (HT-FTIR) spectroscopy we show that the structural evolution in Fe-amphiboles is a multi-step process. We may also demonstrate for the first time that the structural dynamics is driven by the oxidation of iron in the M1 sites and by the local structural strains induced by the distortions of iron sites in the chains of octahedra.