

Interlayer potassium and its neighboring atoms in micas: Crystal-chemical modeling and XANES spectroscopy

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ABSTRACT

A detailed description of the interlayer site in trioctahedral true micas is presented based on a statistical appraisal of crystal-chemical, structural, and spectroscopic data determined on two sets of trioctahedral micas extensively studied by both X-ray diffraction refinement on single crystals (SC-XRD) and X-ray absorption fine spectroscopy (XAFS) at the potassium *K*-edge. Spectroscopy was carried out on both random powders and oriented cleavage flakes, the latter setting taking advantage of the polarized character of synchrotron radiation. Such an approach (AXANES) is shown to be complementary to crystal-chemical investigation based on SC-XRD refinement. However, the results are not definitive as they focus on few samples having extreme features only (e.g., end-members, unusual compositions, and samples with extreme and well-identified substitution mechanisms). The experimental absorption *K*-edge (XANES) for potassium was decomposed by calculation and extrapolated into a full in-plane absorption component (σ_{\parallel}) and a full out-of-plane absorption component (σ_{\perp}). These two patterns reflect different structural features: σ_{\parallel} represents the arrangement of the atoms located in the mica interlayer space and facing tetrahedral sheets; σ_{\perp} is associated with multiple-scattering interactions entering deep into the mica structure, thus also reflecting interactions with the heavy atoms (essentially Fe) located in the octahedral sheet. The out-of-plane patterns also provide insights into the electronic properties of the octahedral cations, such as their oxidation states (e.g., Fe²⁺ and Fe³⁺) and their ordering (e.g., *trans*- vs. *cis*-setting). It is also possible to distinguish between F- and OH-rich micas due to peculiar absorption features originating from the F vs. OH occupancy of the O4 octahedral site. Thus, combining crystal-chemical, structural, and spectroscopic information is shown to be a practical method that allows, on one hand, assignment of the observed spectroscopic features to precise structural pathways followed by the photoelectron within the mica structure and, on the other hand, clarification of the amount of electronic interactions and forces acting onto the individual atoms at the various structural sites.

Keywords: Crystal structure, X-ray absorption spectroscopy, XAFS, XRD, correlation, assignment