Interlayer potassium and its surrounding in micas: Crystal chemical modeling and XANES spectroscopy

M.F. Brigatti (1), D. Malferrari (1), M. Poppi(1), A. Mottana (2,3), G. Cibin (2,3), A. Marcelli (3) and G. Cinque (3)

(1) Dipartimento di Scienze della Terra, Università degli Studi di Modena e Reggio Emilia, Modena, Italy, (2) Dipartimento di Scienze Geologiche, Università degli Studi Roma Tre, Roma, Italy, (3) Laboratori Nazionali di Frascati, Frascati, Italy (brigatti@unimore.it / Fax: +39 059 2055887 / Phone: +39 059 2055805)

Crystal chemistry and topology of the interlayer cations in micas were detailed by several authors and readily appeared not only to be sensitive to the interlayer composition, but to mirror also the topology of other sites occurring in the mica structure (i.e., tetrahedral, octahedral and anionic sites). The aim of this work is to provide a detailed description of the interlayer site in trioctahedral true micas by combining crystal-chemical and spectroscopic evidence. Insights obtained are 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) was decomposed by calculation and extrapolated into a full in-plane absorption component ($\sigma_{||}$) and a full out-of-plane absorption component ($\sigma_{\perp}$). These two patterns reflect different structural features: $\sigma_{||}$ represents the arrangement of the atoms located in the mica interlayer space and facing tetrahedral sheets; $\sigma_{\perp}$ is associated to multiple-scattering interactions entering deep into the mica structure, thus reflecting also in-

teractions with the heavy atoms (essentially Fe) located in the octahedral sheet. The out-of-plane pattern also reflects somewhat the octahedral atoms electronic properties, such as their oxidation states (e.g., Fe^{2+} and Fe^{3+}) and their ordering (e.g., *trans-* vs. *cis*-setting). Distinction between fluoro- and hydrous micas is also possible due to peculiar absorption features originating from the F vs. OH occupancy of the O4 octahedral site. Thus, combining structural and spectroscopic information is shown to be a practical method that allows, on one hand, assigning the observed spectroscopic features to precise structural pathways followed by the photoelectron within the mica structure and, on the other hand, clarifying on the amount of electronic interactions and forces acting onto the individual atoms at the various structural sites.