INTRODUCTION

Many studies have been devoted to the definition of structure and layer topology in micas. An overview of the theoretical and experimental knowledge so far acquired may be attained from numerous reviews (e.g., Mottana et al. 2002b; Fleet 2003). Despite this work, mostly based on single-crystal X-ray diffraction (SC-XRD) techniques, many structural and crystal chemical aspects still require further investigation by complementary methods, such as spectroscopy.

The general formula of the mica group of phyllosilicates (cf. Rieder et al. 1998) can be written as:

$$\text{A}^{\text{M}}_{2–3}\text{M}^{\text{I}}_{1–0}\text{T}^{\text{T}}_{4}\text{O}^{\text{T}}_{10}\text{W}^{\text{W}}_{2}$$

where

- $\text{A}^{\text{M}} = \text{K, Na, Ca, Cs, NH}_{4}$, $\text{Rb, Ba, …}$ is the interlayer cation;
- $\text{M}^{\text{I}} = \text{Mg, Fe, Al, Ti, Li, Mn, Zn, Cr, V, …}$ is the octahedral cation, which is located in a trioctahedral site when divalent and in a dioctahedral one when trivalent,
- $\text{T}^{\text{T}} = \text{Si, Al, Fe, Be, B, …}$ is the tetrahedral cation; and
- $\text{W}^{\text{W}} = \text{OH, F, Cl, O, and S …}$ is the anion located at the O4 site of the octahedral sheet.

Starting from the formula of phlogopite, $\text{K}_{2}\text{Mg}_{3}\text{Si}_{3}\text{O}_{10}\text{(OH,F)}_{2}$, the trioctahedral mica prototype end-member, all other trioctahedral end-members are easily derived by using appropriate exchange vectors; e.g., annite by the $\text{Fe}^{2+}\text{Mg}–1\text{Fe}^{3+}\text{Al}–1\text{Fe}^{2+}\text{Li}–1\text{Si}–1\text{Fe}^{2+}\text{Si}–1\text{F}–1\text{OH}$ exchange vectors, using horizontally polarized synchrotron radiation. Experimental spectra are interpreted by the multiple scattering theory following decomposition according to the angular dependence approach of Brouder (1990). The experimental spectra sum up anisotropic effects deriving from in-plane and out-of-plane photoelectron interactions with the potassium near- and next-neighbor atoms to the fifth/sixth coordination sphere. For the first time, the absorption edge of a low Z atom is decomposed so as to produce two partial patterns giving, respectively, the full in-plane absorption spectrum ($\sigma_{||}$) and the full out-of-plane spectrum ($\sigma_{\perp}$). They fully describe the complete X-ray absorption dichroic behavior of layered compounds, of which mica is a prototype. $\sigma_{||}$ essentially reflects the arrangement of the atoms located in the mica interlayer space and facing tetrahedral sheets. Differences among the four micas depend on structural changes induced by the adaptation of their tetrahedral sheets to the increasing sizes of their octahedral sheet due to chemical substitutions (i.e., the $\text{Fe}^{2+}\text{Mg}–1\text{Fe}^{3+}\text{Al}–1\text{Fe}^{2+}\text{Li}–1\text{Si}–1\text{Fe}^{2+}\text{Si}–1\text{F}–1\text{OH}$ vector). By contrast, $\sigma_{\perp}$ reflects multiple-scattering interactions entering deep into the mica structure, beyond the tetrahedral sheet and well into the octahedral sheet. Such contributions reflect both changes in the anions coordinating the octahedral cations and increasing total amount of heavy atoms (essentially Fe), and differ based on electronic properties such as oxidation states (e.g., $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$). Therefore, angle-dependent XANES spectroscopy is one of the rare spectroscopic techniques able not only to detect, but also to quantify structural effects in the atoms at the medium- to long-range order.

**Keywords:** Mica, XAS, polarized XANES, potassium K-edge, trioctahedral micas, crystal structure