Octahedral versus tetrahedral coordination of Al in synthetic micas determined by XANES

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ABSTRACT

We used the JUMBO monochromator at SSRL to measure the Al K-edge X-ray absorption spectra of synthetic micas having variable Al content and occupancy, from 0 to ⅓ in the octahedral M positions, and 0 to ⅔ in the tetrahedral T positions. The measured Al K edges differ markedly, but the differences may have a common explanation: (1) Micas containing ⅓ Al in M or ⅓ Al in T have K edges that differ in the energy and intensity of the first two features, which are related to interaction of Al with its first-shell nearest neighbors (O and OH or F). They are nearly identical to the K edges of reference minerals such as albite (tetrahedral Al only) or grossular (octahedral Al only). (2) Micas containing Al in both M and T have K edges that can be interpreted as a weighted combination of the simple edges.

INTRODUCTION

The 2:1 layer of micas, A(M,□)[T₂O₆(OH,F)₂], consists of an octahedral sheet sandwiched between two facing tetrahedral sheets. Three bridging ("basal") O atoms link the tetrahedral sites and form a hexagonal pattern on the outer surface of the 2:1 layer, whereas the fourth ("apical") O atom of all tetrahedra points toward the octahedral sheet. These apical O atoms plus the OH,F anions define the octahedral sheet with three M sites per formula unit (Fig. 1). In the trioctahedral micas, all three sites are occupied by M cations, and in the dioctahedral micas only two.

Al may occupy both types of sheets: (1) in the tetrahedral sheet, where Al substitutes for Si, contributing to the net negative charge of the 2:1 layer, which is compensated by the interlayer A cation, and (2) in the octahedral sheet, where Al can occupy at most two of the three available octahedra. The three octahedra are nonequivalent with respect to their nearest-neighbor (NN) configuration (Fig. 1b): One of them (M1) has its two OH groups located at opposite corners of the octahedron, symmetrically arranged astride the mirror plane, i.e., in a "trans" orientation with respect to the central cation; for the remaining two sites (M2), on the contrary, the two OH groups define the common edge between two adjacent mirror-equivalent octahedra ("cis" orientation) with all four of the O atoms lying on one side of the mirror plane.

Because of this complex crystal chemistry, micas must be investigated by a method that determines not only the Al coordination, but also the short-range order (SRO) at the T (T = Si, Be, Al) and M (M = Mg, Fe, Li, Al) sites, which complements the information on long-range order (LRO) obtained by X-ray structure refinement. So far the method of choice has been NMR (e.g., Müller et al. 1981; Herrero et al. 1985 a,b; 1987; Kinsey et al. 1985; Circone et al. 1991; Sanz and Robert 1992).

X-ray absorption near-edge structure (XANES) spectroscopy is also widely acknowledged as a local probe particularly sensitive to coordination and local environment, so that it could potentially be used to determine SRO patterns of micas (cf. Ildefonse et al. 1994). However, the Al and Si K edges lie in the soft X-ray range (at 1559 and 1839 eV, respectively), and because the performance inherent in XAS from the use of crystal monochromators in this energy range is believed to be poor, little work has actually been done on this matter. To our knowledge the only XANES studies of micas are non-systematic with regard to the Al content (Brytov et al. 1979; Ildefonse et al. 1994; Li et al. 1995), or they concern atoms other than Al (e.g., Jain et al. 1980; Jagannatha Rao and Chetal 1982; Waychunas et al. 1983; Güttler et al. 1989; Cruciani et al. 1995; Heald et al. 1995).

We intend to show the usefulness of Al K-edge XANES spectroscopy in unravelling the coordination and elec-