Crystal chemistry of the 1M mica polytype: The octahedral sheet

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ABSTRACT

This work provides a crystal-chemical description of the trioctahedral sheet in 1M mica polytypes of C2/m symmetry. Some octahedral parameters were found to be related strictly to octahedral chemical composition, whereas others were related to the overall layer chemistry. As a general rule, the M1 site is more affected by octahedral chemical composition than the M2 site, and octahedral distortions are more affected than octahedral size. This behavior is attributed to the constraints related to edge-sharing octahedra and octahedral-tetrahedral coupling, which involves the sharing of the apical tetrahedral oxygen atom between the tetrahedron and octahedron. A more quantitative explanation was sought by considering expressions that relate octahedral parameters as a function of atomic coordinates and unit-cell parameters. This procedure identified those parameters affected by local distortions and those that are a function of a more global effect and whose variation greatly affects the layer. Local distortions are obviously more likely a result of local chemical composition. The size and distortion of the octahedral sheet seem to be independent for the database of samples considered. The α angle was found to be a complex parameter required to: (1) fit tetrahedral and octahedral lateral dimensions; (2) fit tetrahedral topology to its local chemical composition, and (3) fit the interlayer cation electrostatic interactions.

INTRODUCTION

The crystal structure and composition of the micas were recently reviewed by Brigatti and Guggenheim 2002. Their review analyzed the influence of solid solution on the crystal structure and considered previous models that also addressed mica crystal chemistry (e.g., Mathieson and Walker 1954; Newnham and Brindley 1956; Zvyagin 1957; Bradley 1959; Radoslovich 1961; Radoslovich and Norrish 1962; Donnay et al. 1964; Hazen and Burnham 1973; Drits 1969, 1975; Takeda and Morosin 1975; Takéuchi 1975; Appelo 1978; Lee and Guggenheim 1981; Toraya 1981; Weiss et al. 1985, 1992).

The chemical composition and cation ordering in the octahedral sites have been recognized as important petrogenetic indicators. In addition, some authors (e.g., Weiss et al. 1985, 1992) quantitatively related the mean bond distances of individual octahedra to the chemical composition and geometry of each octahedral site, thus suggesting that the octahedra greatly control layer characteristics.

The 2:1 layer of the mica-1M structure is characterized by three translationally independent octahedral cation sites, i.e., the trans-site (usually called M1) and two cis-sites (M2 and M3, both referred as M2 when related by symmetry). Cis-octahedral sites are symmetrically equivalent and the layer follows C2/m symmetry where: (1) All three octahedra have the same cations (or a disordered-cation distribution) in trans- and cis-octahedra [i.e., the differences between the mean bond lengths and mean electron counts (m.e.c.) of trans- and cis-sites are equal within the respective standard deviations; this ordering is referred to as “homo-octahedral” by Dúrovíč (1981, 1994)]. Several phlogopite and tetra-ferriphlogopite crystals have this type of order. (2) The two cis-octahedra are occupied by the same cation (or by a disordered distribution of cations) and the trans-M1 site is occupied by a different cation (or a different average cation or “hybrid” cation) in an ordered way [i.e., the “meso-octahedral” ordering of Dúrovíč (1981, 1994)]. Crystals of the phlogopite-annite join, as well as some unusual end-members of true and brittle micas [e.g., norrishite, Tyrna and Guggenheim (1991); clintonite, MacKinney et al. (1988)], commonly show this type of order with one larger octahedron (M1) and two smaller, symmetrically equivalent octahedra (M2).

Some mica species (e.g., many Li-rich micas) show different M2 and M3 sites. The difference can be related to mean bond lengths or to m.e.c. resulting from either different cation or hybrid-cation occupancies. The ordering between cis-sites reduces the layer symmetry to C2 space group (Guggenheim and Bailey 1977; Guggenheim 1981; Backhaus 1983; Weiss et al. 1993; Brigatti et al. 2000a).

The octahedral sheet topology was described by various parameters, such as ψ (Donnay et al. 1964), which expresses the flattening of the octahedron; e/e, (Toraya 1981), which considers the ratio between the mean value of unshared and shared octahedral edges with octahedral flattening; φ (Newnham 1961; Appelo 1978; Lin and Guggenheim 1983), which defines the counter-rotation of upper and lower octahedral oxygen triads; or ECoN (Hoppe 1979; Weiss et al. 1985), which describes the effective coordination number of the octahedral cation. In addition, atomic coordinates can be used to calculate bond distances and angles, which may be used to determine the above distortions, as well as to compare individual