Upper limit of the tetrahedral rotation angle and factors affecting octahedral flattening in synthetic and natural 1M polytype C2/m space group micas

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ABSTRACT

We have used recently developed quantitative crystal chemical models and a simple structural free-energy model to examine and interpret: (1) previously reported powder X-ray diffraction data for several trioctahedral mica solid solution series (64 synthetic powder samples between the Mg, Co, Ni, and Fe end-members, with different degrees of oxidation, vacancy contents, and Al/Si ratios; index as 1M polytype, space group C2/m; supplemented here by 57Fe Mössbauer spectroscopy to obtain accurate iron-site populations of 6Fe3+, 6Fe2+, and 6Fe2+), and (2) 175 previously published single-crystal refinements comprising 138 natural and 37 synthetic 1M mica samples refined in space group C2/m. The crystal chemical models were validated by comparisons between predicted and measured relations between structural parameters, and needed model parameters and their uncertainties were extracted, using the single-crystal refinements. Two main results arise. First, an observed limit value of the b lattice parameter in certain synthetic solid solution series is shown to correspond to an upper limit value for the tetrahedral rotation angle $\alpha$ of $\alpha_{\text{max}} = 9.5^\circ$ for AlSi3 tetrahedral sheets in K-rich micas. This upper limit is also clearly seen in the single-crystal refinement data for those K-rich single-crystals that have near-AlSi3 tetrahedral compositions. We argue that the (tetrahedral sheet composition dependent) upper limit of tetrahedral rotation is an intrinsic property of the tetrahedral sheet (presumably corresponding to an intra-tetrahedral-sheet bond-bending limit) rather than arising either from interactions with the interlayer cations or from an octahedral sheet lateral-contraction limit. Second, we find that, except in the extreme cases where one approaches the lower ($\alpha = 0^\circ$) or upper ($\alpha = \alpha_{\text{max}}$) tetrahedral rotation limits, the magnitude of the octahedral flattening angle $\psi$ is predominantly determined by octahedral cation stereo-chemical bonding requirements (and other intra-octahedral-sheet properties such as intra-sheet bond bending and intra-sheet electrostatic forces) rather than arising from tetrahedral-octahedral inter-sheet interactions (as generally argued or assumed). In addition, we corroborate a previously reported difference in the crystal chemical behaviors of trivalent octahedral cation (Fe3+, Al3+) and vacancy-bearing trioctahedral micas relative to samples that contain only divalent octahedral cations (e.g., Fe-Mg, Fe-Ni, Mg-Ni, and Co-Mg synthetic series); their $b$ vs. average octahedral metal-oxygen bond-length behaviors are dramatically different, a result that is consistent with our proposed dominant stereo-chemical control of $\psi$.

Keywords: Crystal chemistry, layer silicate, mica, tetrahedral rotation, inter-sheet matching, octahedral flattening

INTRODUCTION

Tetrahedral rotation and octahedral flattening are the two main structural distortion mechanisms which ensure the matching of octahedral and tetrahedral sheets in the mica structure (e.g., Bailey 1984; Brigatti and Guggenheim 2002; Ferraris and Ivaldi 2002) and in layer silicates in general (e.g., Bailey 1988). The degrees of these distortions can be expressed by the tetrahedral rotation angle $\alpha$ and the mean flattening angle $\psi$ of the octahedra (e.g., Donnay et al. 1964a; Hazen and Burnham 1973; Takeda and Morosin 1975). Tetrahedral rotation reduces the lateral extent of tetrahedral sheets, whereas octahedral sheets are laterally expanded by octahedral flattening.

Physical limits to possible mica structures owing to the relative sizes of octahedral and tetrahedral sheets appear to exist. In annite, for example, the ideal end-member stoichiometry

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