

## **Single-crystal structure refinements and crystal chemistry of synthetic trioctahedral micas $\text{KM}_3(\text{Al}^{3+}, \text{Si}^{4+})_4\text{O}_{10}(\text{OH})_2$ , where $\text{M} = \text{Ni}^{2+}, \text{Mg}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}$ , or $\text{Al}^{3+}$**

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### **ABSTRACT**

To study structural changes with changing chemical composition in the octahedral sheet of trioctahedral potassium-rich *1M* micas, 3 natural and 12 synthetic micas were examined by single-crystal X-ray diffraction. Samples with  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Al}^{3+}$  in the octahedral sheet and with  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$  and one sample with  $\text{Ga}^{3+}$  in the tetrahedral sheet were prepared at high temperatures and pressures, which yielded crystallites  $\leq 200 \mu\text{m}$  in size. For samples with approximately  $\text{AlSi}_3$  composition of the tetrahedral sheet and with no octahedral  $\text{Al}^{3+}$ , mean M1-O and M2-O octahedral bond lengths correlate very well with the mean ionic radius of the octahedral cations. For these samples, the M1 and M2 sites are found to be very similar or identical within experimental error in terms of mean M-O bond lengths, bond angles, and polyhedral distortion parameters. Octahedral distortion is negatively correlated with the size of the octahedral cation. Octahedra in  $\text{Ni}^{2+}$ -mica show the largest deviation from ideal octahedral geometry, whereas those in annite are closest to ideal octahedral geometry, but they are still significantly flattened. Octahedral  $\text{Al}^{3+}$  prefers the M2 site. This causes the mean M1-O bond length to decrease less with increasing  $\text{Al}^{3+}$  content as compared to the mean M2-O distance. This  $\text{Al}^{3+}$  preference for M2 also causes the M2 site to become smaller and more distorted than the M1 site. Refinement of the Mg-Fe ratios in the octahedral sites along the annite-phlogopite join shows that the two cations are statistically distributed over M1 and M2. Tetrahedra are regular and show only a small elongation along  $c^*$ . Tetrahedral distortion parameters for the  $\text{AlSi}_3$  micas show no correlation with chemistry of the octahedral layer. However, the mean T-O bond lengths increase slightly with increasing size of the octahedral cation. With decreasing size of the lateral dimension of the octahedral sheet in the (001) plane, the tetrahedral sheet shows increasing ditrigonal distortion. Largest tetrahedral rotation angles are observed for synthetic near end-member siderophyllite with  $\alpha = 11.5^\circ$  and for tetra-gallium-phlogopite  $\text{KMg}_3\text{GaSi}_3\text{O}_{10}(\text{OH})_2$  with  $\alpha = 10.8^\circ$ .