

Crystal structure determination of anandite-2*M* mica

THOMAS J. BUJNOWSKI,¹ STEPHEN GUGGENHEIM,^{1,*} AND TOSHIO KATO²

¹Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, Illinois 60607, U.S.A.

²Institute of Earth Sciences, Faculty of Liberal Arts, Yamaguchi University, Yoshida, Yamaguchi 753-8511, Japan

ABSTRACT

Anandite, a trioctahedral mica, has an ideal chemical formula of $\text{Ba}(\text{FeMg})_3(\text{SiFe}^{3+})\text{O}_{10}(\text{OH})\text{S}$ and a microprobe-derived formula of $(\text{Ba}_{0.96}\text{K}_{0.03}\text{Na}_{0.01})_{\Sigma=1.00}(\text{Fe}_{2.01}^{2+}\text{Mg}_{0.46}\text{Fe}_{0.28}^{3+}\text{Al}_{0.10}\text{Mn}_{0.04}^{2+}\text{Mn}_{0.04}^{2+}\text{Ti}_{0.01})_{\Sigma=2.93}(\text{Si}_{2.60}\text{Fe}_{1.40}^{3+})_{\Sigma=4.00}\text{O}_{10}[(\text{OH})_{0.96}\text{S}_{0.84}\text{Cl}_{0.16}\text{F}_{0.04}]_{\Sigma=2.00}$, where S^{2-} primarily substitutes for $(\text{OH})^-$. A single-crystal, X-ray structure determination of anandite-2*M* was refined to $R_1 = 0.0443$ and $wR_2 = 0.1232$ on F^2 in space group *Am*. Cell parameters are: $a = 5.4431(3)$, $b = 9.4719(6)$, $c = 20.042(1)$ Å, and $\beta = 95.046(1)^\circ$. Layer stacking is analogous to a 1*M* stacking pattern (parallel unidirectional $a/3$ shifts within layers and octahedral set I only occupied), however cation order and (S,OH) positional disorder produce a two-layer repeat with β equaling $\sim 95^\circ$. Subgroup symmetry of *Am* results from tetrahedral sheets within layers that are non-centrosymmetric with unequal compositions ($\text{Si}_{0.61}\text{Fe}_{0.39}^{3+}$ vs. $\text{Si}_{0.79}\text{Fe}_{0.21}^{3+}$) and thicknesses (difference of 0.209 Å), and there is positional and site-occupancy disorder (four sites with S of 0, 30, 52, and 58%) of (S,OH). Characteristics of anandite-2*M*, which are similar to those of anandite-2*O*, include (1) alternation of smaller tetrahedral rings containing four Si-rich tetrahedra (T1a: 1.643 Å, T2b: 1.657 Å) and two Fe³⁺-rich tetrahedra (T2a: 1.733 Å, T1b: 1.760 Å) and larger rings containing four Fe³⁺-rich tetrahedra and two Si-rich tetrahedra within each layer; (2) nearly in-phase wave forms of basal O atoms across the interlayer ($\Delta z = -0.110$ and 0.011 Å and across the interlayer $\Delta z = -0.121$ and 0.007 Å); and (3) attraction that results in Ba being shifted toward S (0.070 Å) and S being shifted toward Ba (0.117 Å average) along the *c* axis, relative to the ideal. Bond-valence calculations show that Ba is shifted toward the undersaturated, bridging-basal O atoms of the Fe³⁺-rich tetrahedra and toward S-rich sites to achieve charge balance. Comparison of anandite-2*M* and anandite-2*O* shows that they possess unit cells (2*M* setting) that have nearly equal *a* axes, unequal *b* and *c* axes, and β (anandite-2*M* is smaller by 0.0371 Å, larger by 0.08 Å, and smaller by 0.089°, respectively). Moreover, anandite-2*O* exhibits larger Fe³⁺-rich tetrahedral rings than anandite-2*M*, which allow for a greater shift in Ba (difference of 0.03 Å). The ordering and consequent absence of a twofold axis in anandite-2*M* allows the in-phase wave structure of basal O atoms, which was previously thought only possible in the orthorhombic *P* cell.

Keywords: Anandite mica, single-crystal X-ray diffraction, two-layer monoclinic mica polytypes, phyllosilicate, Ba-rich mica, S-rich mica, Fe-rich mica