

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 Ba(FeMg)₃(SiFe³⁺)O₁₀(OH)S and a microprobe-derived formula of (Ba_{0.96}K_{0.03}Na_{0.01})_{Σ=1.00}(Fe_{2.01}²⁺Mg_{0.46}Fe_{0.28}³⁺Al_{0.10}Mn_{0.04}³⁺Mn_{0.04}²⁺Ti_{0.01})_{Σ=2.93}(Si_{2.60}Fe_{1.40}³⁺)_{Σ=4.00}O₁₀[(OH)_{0.96}S_{0.84}Cl_{0.16}F_{0.04}]_{Σ=2.00}, where S²⁻ primarily substitutes for (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 β = 95.046(1)°. 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 ~95°. Subgroup symmetry of *Am* results from tetrahedral sheets within layers that are non-centrosymmetric with unequal compositions (Si_{0.61}Fe_{0.39}³⁺ vs. Si_{0.79}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 (Δ*z* = -0.110 and 0.011 Å and across the interlayer Δ*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

INTRODUCTION

Anandite, ideally Ba(FeMg)₃(SiFe³⁺)O₁₀(OH)S, where S > OH and Cl,F if present (Rieder et al. 1998), is a trioctahedral brittle mica that has been identified from the Wilagedera iron ore prospect, North Western Province, Sri Lanka (Pattiaratchi et al. 1967; Giuseppetti and Tadani 1972). The sample, identified in a drill core, occurs in a banded magnetite-barite-sulfide ore deposit within a meta-sedimentary series (granulite facies) of calc-schists and calc-gneisses of Precambrian age (Pattiaratchi et al. 1967). In addition to an association with chalcopyrite, pyrite, and pyrrhotite as reported by Pattiaratchi et al. (1967), we have identified small amounts of ferrosilite in the sample.

Other occurrences of anandite have been reported in Rush

Creek and Big Creek, Fresno County, California (Basciano et al. 2001), and Sterling Hill, New Jersey (Tracy 1991). However, sulfur was neither reported in the Sterling Hill mica nor at the California locations, thereby suggesting that these micas are probably not anandite as defined by Rieder et al. (1998). Anandite is of crystal-chemical interest because of structural S, substantial Fe³⁺ tetrahedral substitutions, interlayer Ba, and the nature of the layer stacking. Substitution of S²⁻ for OH⁻ was established by Lovering and Widdowson (1968) by microprobe analysis, by structural refinement of Giuseppetti and Tadani (1972) and Filut et al. (1985), and is further described in this paper. A 2*M*₁ polytype was indexed by powder pattern by Pattiaratchi et al. (1967), and the crystal structure of a 2*O* polytype was refined by Giuseppetti and Tadani (1972) and later by Filut et al. (1985).

Because of the very unusual chemical composition of anandite, our initial interest was to determine if the presence of

* E-mail: xtal@uic.edu

sulfur affected the crystal structure differently than described for anandite-2O. Our initial examination of precession photographs, for what had been identified initially as anandite-1M, was intriguing because the unit-cell geometry appeared to be more consistent with a 2M₁ polytype ($\beta = 95^\circ$, two-layer repeat) than a 1M polytype. Finally, the *A* centering and weak reflections were of further interest, and prompted a structure determination. We discuss this polytype of anandite; although based on a one-layer polytype, it is better described as 2M.

EXPERIMENTAL METHODS

Powder patterns

To determine polytype information, Gandolfi powder patterns were obtained using a Bruker AXS D8 SMART/APEX three-circle diffractometer using monochromatized MoK α radiation (0.7107 Å) following the procedure of Guggenheim (2005). Data were collected from single crystals with a collimator aperture size of 0.3 mm for small crystals and 0.5 mm for larger crystals using a CCD detector with 1024 × 1024 pixel resolution and a crystal-to-detector distance of 120 mm. One mounting was used for each of the 10 crystals examined. All crystals showed preferred orientation, which is attributed to the limited number of orientations achievable with each mounting. Therefore, one crystal was mounted in three different orientations in an attempt to minimize apparent preferred orientation. Visual inspection of six Debye-Scherrer patterns (five collected with Fe radiation and one with Cu radiation) also showed preferred orientation. The intensity peaks of the patterns are approximately similar for all crystals analyzed and the patterns are most similar to a 1M polytype. As a consequence of preferred orientation, Table 1 shows a composite powder pattern produced from the 10 Gandolfi patterns.

Precession and pseudo-precession photos

To find a high-quality crystal for further study, 60 well-formed, platy anandite crystals were examined using rotation frames (photos) collected on the Bruker

system as described above. In addition, precession camera photos and pseudo-precession photos (Bruker APEX 2 software) were obtained of exceptional crystals that showed minimal reflection streaking to further verify quality, to examine for twinning/intergrowths, and to examine the polytype symmetry (see below).

Zero- and first-level pseudo-precession and camera photos were indexed so that the *c* axis described the stacking direction, as is conventional for phyllosilicate minerals. The unit cell is nearly *A*-centered with the exception of 10 very weak violating reflections present near the origin. Weak reflections of the type $l = 2n + 1$ in the *Ok**l* net and $h + l = 2n + 1$ in the *h**0**l* net indicate a 20 Å unit cell, which suggested that the structure was based on a two-layer polytype. However, these reflections are uniformly weak, and if omitted, all photos are indiscernible from 1M nets (β near 100°), indicating a strong similarity to a 1M polytype. The two-layer characteristics are evident in the *Ok**l* net showing a slight resemblance to a 2O precession photo and the *h**0**l* net (β near 95°). Both the 10 Å *c*-axis spacing (neglecting weak reflections) and $\beta \neq 90^\circ$ in the *h**0**l* net indicate that: (1) only set I cations (Bailey 1984) are occupied (i.e., the orientation of the triangles formed by the octahedral positions around central OH, S groups/atoms of each six-member ring is the same); (2) the structure is not a 2O polytype; and (3) there is no component of 2O intergrowth. The inspection of additional precession camera photos confirmed no intergrowths and allowed us to reject the presence of any twinning attributable to mica twin laws, including rotation of the layers about the normal to (001) or mirror relationships.

Data processing

Single-crystal X-ray data collection was performed on a rectangular grain measuring 0.296 × 0.201 × 0.061 mm using the Bruker diffractometer and a 0.3 mm Monocap collimator. The crystal showed no observable streaking on either precession camera photographs or APEX pseudo-precession frames. Data were collected with a crystal-to-detector distance of 60 mm and frame time exposure of 25 s. The unit-cell determination was performed using three sets of 30 frames collected at 25 s each and resulted in an *A*-centered cell with monoclinic geometric dimensions of: $a = 5.4431(3)$, $b = 9.4719(6)$, $c = 20.042(1)$ Å, and $\beta = 95.046(1)^\circ$, which was in agreement with our assessment of the precession photos. Data reduction and integration were performed using SAINT. A Gaussian absorption correction was performed using a linear absorption coefficient (μ) of 9.574 mm⁻¹ calculated from

TABLE 1. X-ray powder diffraction data

d_{obs}	l_{obs}	d_{calc}	l_{calc}	(<i>hkl</i>)	d_{obs}	l_{obs}	d_{calc}	l_{calc}	(<i>hkl</i>)
9.98	40.7	9.9824	15.4	(0 0 2)	1.6119	4.5	1.6112	6.1	(2 4 $\bar{6}$)
8.61	2.7*	8.5576	4.5	(0 1 1)	1.5669	32.8	1.5731	38.6	(3 3 1)
4.92	23.6*	4.9912	25.7	(0 0 4)	1.5436	8.0	1.5430	21.1	(1 3 $\bar{1}$)
4.76	4.0*	4.7360	1.7	(0 2 0)	1.4903	4.9	1.4940	4.4	(1 1 $\bar{1}$)
4.52	1.2*	4.5040	9.3	(1 1 1)	1.4644	2.0*	1.4680	1.2	(2 2 10)
4.28	10.1	4.2788	22.8	(0 2 2)	1.4264	2.1	1.4261	1.5	(0 0 14)
3.99	29.5	3.9883	32.4	(1 1 $\bar{3}$)	1.4027	4.8*	1.4101	3.2	(2 2 $\bar{1}$)
3.707	47.5	3.7109	47.8	(1 1 3)	1.3609	16.4	1.3597	14.1	(2 6 $\bar{2}$)
3.428	51.6	3.4355	49.4	(0 2 4)	1.3281	9.2	1.3294	9.0	(3 3 9)
3.288	6.6*	3.2990	1.3	(1 2 2)	1.2970	1.6	1.2958	1.4	(4 0 $\bar{6}$)
3.172	54.0	3.1661	53.4	(1 1 $\bar{5}$)	1.2775	1.8*	1.2784	1.4	(4 2 2)
2.927	42.5	2.9360	45.1	(1 1 5)	1.2557	5.8	1.2551	2.1	(1 7 $\bar{5}$)
2.717	42.0	2.7226	37.0	(0 2 6)	1.2368	3.9*	1.2377	1.3	(4 0 $\bar{8}$)
2.686	100.0*	2.6874	100.0	(1 3 1)	1.2132	2.4	1.2146	1.2	(3 1 $\bar{1}$)
		2.6765	49.1	(2 0 $\bar{2}$)	1.1807	3.4	1.1802	1.3	(2 2 14)
2.548	11.7	2.5260	21.9	(1 1 7)	1.1458	6.9	1.1452	1.2	(0 6 12)
2.480	26.2*	2.4862	31.1	(1 3 3)	1.1036	2.9	1.1038	5.8	(2 6 10)
2.474	18.2	2.4753	15.3	(2 0 4)	1.0996	1.9*	1.0993	3.0	(4 0 $\bar{1}$)
2.358	19.4*	2.3605	11.7	(1 1 7)	1.0551	1.9	1.0554	1.7	(3 3 15)
2.300	3.6	2.2990	3.0	(2 0 4)	1.0286	2.7	1.0284	2.9	(4 6 0)
2.200	52.9	2.2077	37.2	(1 3 5)	1.0146	2.1*	1.0139	1.2	(5 3 5)
		2.1986	19.1	(2 0 6)	1.0043	1.4*	0.9963	1.8	(2 0 18)
2.126	5.9*	2.1394	7.2	(0 4 4)	0.9940	2.9	0.9955	3.6	(1 3 $\bar{1}$)
2.055	3.9	2.0682	5.9	(2 2 4)	0.9785	3.4	0.9789	1.7	(0 6 16)
2.015	47.1	2.0166	47.3	(1 3 $\bar{7}$)	0.9387	0.9	0.9306	2.4	(1 9 9)
1.9276	2.9	1.9293	3.2	(0 4 6)	0.9260	3.2	0.9265	2.6	(5 3 $\bar{1}$)
1.8502	1.2*	1.8555	1.1	(2 2 6)	0.9025	1.6	0.9028	1.8	(5 3 9)
1.6806	75.1	1.6851	36.2	(1 3 9)	0.8788	1.1*	0.8799	1.2	(2 6 $\bar{1}$)
		1.6797	18.1	(2 0 $\bar{1}$)	0.8609	1.4*	0.8437	1.9	(3 3 19)
1.6462	8.3*	1.6495	6.8	(2 4 4)					

Note: Intensities, *d* spacings, and Miller indices calculated using: $a = 5.4431(3)$, $b = 9.4719(6)$, $c = 20.042(1)$ Å, $\beta = 95.046(1)^\circ$, and *Am* symmetry. Collected using Gandolfi powder-pattern simulations (Guggenheim 2005) and MoK α radiation.

* Peak not present in all crystals owing to apparent preferred orientation. In addition, calculated peaks at $d = 3.328$ ($l = 17.4$) and 4.66 ($l = 6.3$) were not observed.

the chemistry obtained by electron microprobe analysis (Filut et al. 1985). Filut et al. (1985) obtained similar electron microprobe results for three different anandite grains from the same drill-core sample used here; therefore their analysis was initially used. The absorption correction, space group determination, and data merging were performed using XPREP, a part of the SHELXTL software package. Because *A* centering is not a conventional monoclinic or triclinic space group recognized by XPREP, space-group determination and data merging were initially performed as *C* centered. Several data sets were prepared: a centrosymmetric monoclinic data set with Friedel pairs merged, a non-centrosymmetric monoclinic data set without merging Friedel pairs, and triclinic non-centrosymmetric data sets.

Structure determination

A data set merged as centrosymmetric monoclinic, containing 1383 reflections, was used for a structure solution. Phases were determined by direct methods using SHELXS. *C* centering, with *a* as the longest axis, was initially used for simplification and the symmetry was described tentatively in *C*2/*m*, which is the highest symmetry allowable. Barium is the heaviest atom and was placed at the origin; all other atom positions were systematically found using Fourier difference peaks.

Refinement

The refinement procedure was completed using XSHELL and XL in the SHELXTL software package. Miller indices were transformed to the *A*-centered space group for refinement. Initially, *A*2/*m* was assumed based on systematic absences (or lack thereof) in the precession/pseudo-precession photos. Several refinement cycles were performed in *A*2/*m* symmetry and models involving subgroup symmetry (*A*2, *Am*, and *A*1) were explored before site chemistry was considered to find a best-fit model to the data. In the non-centric space groups, the interlayer site, *A*1, was fixed at the origin. Refinement in each space group went through 8–10 cycles, in which all atoms were refined independently after expanding atom coordinates appropriately for each subgroup symmetry model. *Am* was the space group that yielded the lowest *R*-factor (to *R*₁ = 0.1393, a drop of 0.0544) and this space group was chosen for further refinement involving site chemistry. Additionally, other refinements were performed in which site chemistry was refined (see below) in space groups *A*1 and *A*2 to determine if subgroup symmetries (other than *Am*) better described the structure. The final *R* parameters for the *A*1 space group are higher than those of the *Am* refinement with an expanded atom set and the *A*2 refinement was insufficiently stable to allow a complete refinement. A summary of results is given in Table 2 for *A*2/*m* before occupancy refinement, *A*1, *A*2, and *Am*.

The chemical composition of the tetrahedral sites was determined by using electron densities and by comparing observed bond lengths to Si–O and Fe³⁺–O distances, which are 1.620 and 1.8757 Å, respectively (Filut et al. 1985). Partial Al substitution was also considered in the tetrahedral sites, but inclusion of Al caused an increase in the *R*-factor. Interlayer chemistry was derived directly from microprobe results of Filut et al. (1985) and was a best fit throughout the refinement process. Octahedral and S,OH site chemical compositions varied from the microprobe results and thus, were used only initially to constrain site occupancy factors (SOF). A trial-and-error approach was later implemented using Fourier difference map peaks and M–O, S bond distances.

Site chemistry and atom positions for S and OH were difficult to determine. The data indicated that positional disorder occurs, although the close proximity of the atoms in the (average) unit cell would not allow reasonable displacement factors (small atom displacements are possibly the cause for the weak symmetry-violating reflections near the origin in precession photos). Because of the difficulty in determining displacement factors, S and OH could not be refined anisotropically.

TABLE 2. Final refinement parameters

Parameter	<i>A</i> 1	<i>A</i> 2*	<i>Am</i>	<i>A</i> 2/ <i>m</i> †
<i>R</i> ₁ ‡	0.0497	0.1536	0.0443	0.1920
<i>F</i> ₀ > 4σ (<i>F</i> ₀) reflections	5018	2777	2874	1296
<i>R</i> ₂ ‡	0.0538	0.1640	0.0473	0.1999
All reflections	5761	3107	3219	1383
w <i>R</i> ₂ §	0.1547	0.6462	0.1232	0.7081
S§	0.742	6.535	0.657	8.160
C.C.	0.848	–0.789	0.842	0.895

* Was not refined anisotropically.

† Occupancy was not refined.

‡ *R*₁ = Σ||*F*₀|| – ||*F*_c||/Σ||*F*₀|| for number of reflections directly below it in the table.

§ w*R*₂ = {Σ[w(*F*₀² – *F*_c²)]/Σ[w(*F*₀²)]^{1/2}.

|| Absolute greatest correlation coefficient (maximum or minimum).

Partial Cl and F substitution were also attempted in these sites, but resulted in elevated *R*-values and were not considered further.

The final refinement cycle was fully anisotropic (except S,OH) and 22 strong outlier reflections of the type 20*l*, 33*l*, 00*l*, and 13*l* were removed from the data set to increase precision, resulting in 3219 reflections. The weighting scheme used during the refinement was defined as: weight (*w*) = 1/[σ²(*F*₀²) + (*a* · *P*)² + *b* · *P*], where *P* is (*F*₀² + 2 · *F*_c²)/3 or zero (the greater of the two), and *a* and *b* are refined. The default values of *a* = 0.1 and *b* = 0.0 were used initially and *a* = 0.1088 and *b* = 31.9026 were refined in the final run. The final refinement cycle, after the absolute structure of the *Am* refinement was considered (but could not be determined significantly), resulted in a decrease of *R*₁ and w*R*₂ (Table 2). Final atom coordinates, displacement parameters, and selected calculated bond lengths and angles are in Tables 3–6, respectively.

For purposes of comparison to refinements of the anandite-2*O* polytype, an *F* refinement was performed, which duplicated the *F*² refinement as close as possible (i.e., chemistry, same number of reflections, isotropic S,OH parameters). In the *F* refinement, the *R*₁ and w*R*₂ are nearly the same (0.051 and 0.052, respectively) and compared to *F*² results, the *R*₁ is similar and w*R*₂ is less than half. These results suggest that the precision of the Filut et al. (1985) refinement of anandite-2*O*, based on *F* (*R*₁ = 0.052 and w*R*₂ = 0.064), is similar to our refinement for anandite-2*M*.

DISCUSSION

General appearance of diffraction pattern and choice of unit cell

Peak intensities and *d* values of the powder patterns (Table 1) are significantly different than the anandite 2*M*₁ pattern (Pattiaratchi et al. 1967), superficially similar to the 2*O* pattern (Filut et al. 1985), and most similar to a calculated 1*M* pattern, suggesting that the structure is a 1*M* polytype or a modified 1*M* polytype. Overall, precession work also indicates that the structure is based on a 1*M* polytype with differences between adjacent layers to produce a two-layer periodicity. Structure refinement indicates a two-layer sequence (2*M*) induced by ordering, hereafter referred to as anandite-2*M*. Figure 1 shows the structure of anandite-2*M* and the 1*M* cell in relation to the *A*-centered 2*M* unit cell. The 1*M* cell is not viable owing to cation ordering and anion (S,OH) positional disorder (discussed below). The stacking arrangement follows a 1*M* pattern, where there is no rotation of the layers relative to each other so that the *a*/3 intralayer shifts are all parallel and the octahedral cations are all organized in a set I configuration. This stacking dominates the pattern and produces strong reflections, and the generally weaker reflections are produced by secondary effects, such as order-disorder. Precession and powder patterns for anandite-2*M* also show a superficial resemblance to anandite-2*O*. Both the 2*M* and 2*O* have layer stacking along one *a* axis and this produces a similarity in overall appearance. Of course, the composite layers of the 2*O* are rotated 180° relative to each other, unlike the 2*M* structure.

Cation order

The ordering scheme in the octahedral and tetrahedral sites was determined by site occupancy refinement, cation-oxygen/sulfur bond distances, and bond-valence sum calculations (Brown 1992; Table 7) and is given in Table 8. In the tetrahedral sites, the occupancy refinement and observed bond-length derived occupancy differ slightly; the occupancy refinement resulted in T2a as the most Fe³⁺-rich and T2b as the most Si-rich, but the occupancy derived from observed bond lengths resulted in T1a and T1b as the most Si- and Fe³⁺-rich, respectively. However, each method results in T1a and T2b as Si-rich and T1b and T2a as Si-poor. The occupancy refinement precludes Al in tetrahedral

TABLE 3. Atomic coordinates

Anandite-2M				Anandite-2O (Filut et al. 1985)*			
Atom	x	y	z	Atom	x	y	z
A1	0.0	0.0	0.0	A	0.0	0.0	0.0
A2	0.5042(1)	0.5	0.0070(0)	A	0.5035	0.5	0.0106
M11	0.7531(5)	0.0	0.2545(1)	M1	0.7517	0.0	0.2553
M12	0.2515(4)	0.5	0.2537(1)	M2	0.2517	0.5	0.2553
M21	0.2528(3)	0.1692(1)	0.2538(1)	M4	0.2517	0.1690	0.2553
M22	0.7533(3)	0.3375(1)	0.2538(1)	M3	0.7517	0.3441	0.2553
T1a	0.5407(5)	0.1643(2)	0.1154(1)	T1	0.5397	0.1617	0.1166
T1b	0.4679(4)	0.3330(2)	0.3940(1)	T2	0.4679	0.3333	0.3956
T2a	0.0382(4)	0.3326(2)	0.1142(1)	T2	0.0356	0.3333	0.1150
T2b	0.9666(5)	0.1639(3)	0.3933(1)	T1	0.9638	0.1617	0.3940
O11a	0.025(2)	0.5	0.0784(5)	O6	0.0302	0.5	0.0742
O11b	0.970(3)	0.0	0.4202(5)	O5	0.9699	0.0	0.4209
O12a	0.534(3)	0.0	0.0845(5)	O5	0.5336	0.0	0.0897
O12b	0.468(2)	0.5	0.4291(4)	O6	0.4733	0.5	0.4364
O21a	0.771(1)	0.243(1)	0.0831(3)	O4	0.7684	0.2329	0.0819
O21b	0.731(1)	0.239(1)	0.4267(3)	O4	0.7351	0.2329	0.4287
O22a	0.279(1)	0.237(1)	0.0847(3)	O3	0.2833	0.2293	0.0847
O22b	0.224(1)	0.237(1)	0.4260(3)	O3	0.2202	0.2293	0.4259
O31a	0.572(1)	0.1642(5)	0.1958(3)	O1	0.5735	0.1625	0.1977
O31b	0.444(2)	0.3334(6)	0.3054(4)	O2	0.4446	0.3312	0.3059
O32a	0.062(1)	0.3328(5)	0.1995(3)	O2	0.0589	0.3312	0.2047
O32b	0.936(1)	0.1626(6)	0.3090(3)	O1	0.9300	0.1625	0.3129
S1a	0.0600(8)	0.0	0.1717(3)	OH	0.0676	0.0	0.2044
S1b	0.9423(7)	0.5	0.3306(2)	S	0.9458	0.5	0.3391
S2a	0.5574(5)	0.5	0.1664(2)	S	0.5577	0.5	0.1715
S2b	0.4329(7)	0.0	0.3021(3)	OH	0.4359	0.0	0.3062

* Atomic coordinates in the 2M setting to facilitate comparison.

TABLE 4. Displacement factors for anandite-2M

Atom	U_{eq}^*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A1	0.0351(3)	0.0298(4)	0.0343(4)	0.0415(8)	0.0	0.0050(4)	0.0
A2	0.0290(2)	0.0305(3)	0.0371(4)	0.0192(3)	0.0	0.0014(2)	0.0
M11	0.0107(2)	0.0098(4)	0.0097(4)	0.0122(5)	0.0	-0.0007(3)	0.0
M12	0.0125(2)	0.0124(3)	0.0099(3)	0.0148(4)	0.0	-0.0007(4)	0.0
M21	0.0113(1)	0.0095(3)	0.0112(3)	0.0134(3)	0.0003(5)	0.0013(2)	-0.0008(4)
M22	0.0146(2)	0.0101(3)	0.0206(3)	0.0133(3)	-0.0008(5)	0.0021(2)	-0.0019(4)
T1a	0.0146(4)	0.0164(9)	0.016(1)	0.0112(9)	0.0010(5)	-0.0007(6)	0.0017(5)
T1b	0.0099(3)	0.0085(7)	0.0133(8)	0.0078(8)	-0.0007(4)	0.0003(5)	-0.0007(4)
T2a	0.0158(3)	0.0174(8)	0.0184(8)	0.0115(7)	-0.0004(4)	0.0013(5)	0.0020(4)
T2b	0.0135(4)	0.0134(9)	0.014(1)	0.013(1)	0.0011(6)	0.0027(7)	0.0004(5)
O11a	0.030(2)	0.028(4)	0.030(4)	0.032(5)	0.0	0.005(3)	0.0
O11b	0.049(3)	0.12(1)	0.016(4)	0.012(5)	0.0	0.003(6)	0.0
O12a	0.030(2)	0.064(6)	0.013(4)	0.013(4)	0.0	-0.003(3)	0.0
O12b	0.031(2)	0.036(5)	0.049(6)	0.009(3)	0.0	0.002(3)	0.0
O21a	0.030(1)	0.031(3)	0.045(4)	0.014(3)	-0.014(3)	0.010(2)	0.010(2)
O21b	0.030(1)	0.023(3)	0.044(4)	0.024(3)	0.003(3)	0.007(2)	0.005(3)
O22a	0.028(1)	0.020(2)	0.051(4)	0.011(2)	0.016(2)	-0.004(2)	0.005(2)
O22b	0.031(1)	0.028(3)	0.040(4)	0.024(3)	-0.002(3)	-0.002(2)	0.005(3)
O31a	0.0102(9)	0.010(2)	0.012(2)	0.009(2)	0.002(2)	-0.002(2)	0.001(1)
O31b	0.018(1)	0.017(3)	0.010(2)	0.027(3)	0.001(2)	0.003(2)	-0.002(2)
O32a	0.0098(9)	0.007(2)	0.013(2)	0.009(2)	0.002(2)	-0.001(2)	0.002(2)
O32b	0.014(1)	0.014(2)	0.015(2)	0.012(2)	0.002(2)	0.002(2)	-0.000(2)
S1a	0.0072(8)	†					
S1b	0.0180(7)	†					
S2a	0.0045(4)	†					
S2b	0.0205(7)	†					

Note: Displacement parameters of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

* Isotropic equivalent displacement factor.

† Refined values.

sites, therefore it was assigned to octahedral sites and best fitted into M11 and M21. Filut et al. (1985) noted also the lack of ^{IV}Al in anandite-2O.

The S₂OH sites have positional disorder and vary between pure OH and predominantly S (S1b and S2a are S-rich and S1a and S2b are S-poor, Table 8). The S-rich sites are within the coordination of the larger *trans* M12 and *cis* M22 sites and the S-poor sites are coordinated by the smaller *trans* M11 and *cis* M21 sites (Fig. 2). The larger M sites contain only Fe²⁺ and Fe³⁺

[as indicated by Mössbauer analysis as reported in Filut et al. (1985), bond lengths, and site occupancy refinement] and the smaller sites contain Fe in addition to Al, Mg, and Mn. Both observed bond lengths and the occupancy refinement indicate there is more Fe³⁺ present in the M sites of the crystal reported here than found by Mössbauer analysis, however, bond-valence sums suggest that there are only R²⁺ cations present, which is accounted for in the best-fit composition. Discrepancies between microprobe results and occupancy may relate to possible inho-

TABLE 5. Calculated tetrahedral bond lengths (Å) and angles (°)

Tetrahedral				
T1a-O31a	1.605(6)			About T
T1a-O21a	1.641(9)	O12a-O21a	2.64(1)	105.7(6)
T1a-O22a	1.651(8)	O12a-O22a	2.64(1)	105.1(6)
T1a-O12a	1.674(4)	O12a-O31a	2.713(9)	111.6(3)
Average	1.643	O21a-O22a	2.68(1)	108.9(4)
		O21a-O31a	2.695(8)	112.2(3)
		O31a-O22a	2.711(8)	112.7(3)
T1b-O12b	1.731(4)			About T
T1b-O21b	1.763(8)	O12b-O21b	2.86(1)	109.8(4)
T1b-O31b	1.769(6)	O12b-O22b	2.82(1)	107.2(4)
T1b-O22b	1.777(8)	O12b-O31b	2.932(9)	113.8(3)
Average	1.760	O21b-O22b	2.76(1)	102.6(4)
		O21b-O31b	2.912(9)	111.0(3)
		O31b-O22b	2.937(9)	111.8(3)
T2a-O32a	1.704(6)			About T
T2a-O22a	1.738(8)	O11a-O21a	2.80(1)	107.0(5)
T2a-O11a	1.739(5)	O11a-O22a	2.84(1)	109.7(5)
T2a-O21a	1.749(8)	O11a-O32a	2.89(1)	114.2(4)
Average	1.733	O21a-O22a	2.77(1)	104.9(4)
		O21a-O32a	2.833(9)	110.3(3)
		O32a-O22a	2.825(8)	110.3(3)
T2b-O22b	1.643(8)			About T
T2b-O11b	1.643(4)	O11b-O21b	2.62(1)	105.2(6)
T2b-O21b	1.657(8)	O11b-O22b	2.63(1)	106.3(6)
T2b-O32b	1.684(6)	O11b-O32b	2.703(9)	108.6(4)
Average	1.657	O21b-O22b	2.68(1)	108.6(4)
		O21b-O32b	2.792(9)	113.4(4)
		O32b-O22b	2.791(9)	114.1(4)

mogeneous grains within the rock sample. Note that results differ between samples and analyses [e.g., the wet chemical analysis of Pattiaratchi et al. (1967) differs from Lovering and Widdowson (1968) and Filut et al. (1985)].

Within the tetrahedral sheets, alternating bands of Si- and Fe³⁺-rich tetrahedra are oriented along *b* (Fig. 3) and within each layer, these bands are parallel to each other. Across the interlayer, the tetrahedral bands alternate along *c* and the *m*-planes create a “bow-tie” effect of corner-sharing tetrahedra oriented along *b*. The succession of bands results in small tetrahedral rings (R1) and large tetrahedral rings (R2), which surround the interlayer cation (Fig. 4). Distortions caused by R1 and R2 across the interlayer. As expected, the large rings are primarily coordinated by the larger M12 and M22 octahedral sites and small rings by the smaller M11 and M21 sites. In the tetrahedral rings, the corner sharing Fe³⁺ creates an ordering pattern unlike other layer silicates, which commonly involve a pattern of Si and R³⁺ alternation around the rings. This corner-sharing pattern appears to be stable in anandite because bridging O atoms between two Fe³⁺-rich tetrahedra are sufficiently charge saturated by coordinating Ba²⁺ cations (see bond-strength calculations and Ba shift in the following section). In addition, repulsive forces across the interlayer are minimized by the alternation of O atoms of Fe- and Si-rich tetrahedra across the interlayer as required by *A* centering.

Interlayer

Ba²⁺ is the abundant interlayer cation in anandite-2M, and the higher charge and field strength of Ba results in differences from K-rich micas. The interlayer separation of anandite-2M is 3.141 Å (0.242 Å less than in most K-rich micas; Table 6), and the reduced symmetry allows for two unique interlayer cation

sites. The tetrahedral rings are superimposed across the interlayer so that the bridging O atoms lie directly across from each other along *c* (Figs. 3 and 4). The interlayer coordination polyhedra are asymmetric and differ slightly in dimensions mainly owing to the topology of the basal O atoms, the shift of the A cation (and S, discussed below; Table 9), and the sizes of the tetrahedra. Each A site is bonded closer to four of the six basal O atoms of the small R1 ring than with the corresponding four basal O atoms of the large R2 ring. The A sites are also bonded closer to two basal O atoms from R2 than the two corresponding basal O atoms from R1. Moreover, the two more closely bonded basal O atoms from the large rings are exclusive to either A1 or A2 (i.e., O12a,b are unique to A1 and O11a,b are unique to A2). This coordination arrangement does not allow an inner/outer octahedral coordination with the interlayer cations, which is common in K-rich micas. The dissimilar sized tetrahedral rings, the topology of the basal O atoms (discussed below), and the shift of the interlayer cation are responsible for the coordination about the Ba.

Unlike the OH-rich sites, the S-rich sites are shifted within the large tetrahedral rings, away from the octahedral cation plane, and toward the interlayer cations. Furthermore, the interlayer cations are shifted toward the S-rich sites. Conversely, the OH groups are located further away than the S relative to the A sites. The shift is sufficient so that S can be considered the 13th neighbor of the coordination polyhedra of the interlayer cations. This arrangement is similar to that in anandite-2O (Filut et al. 1985).

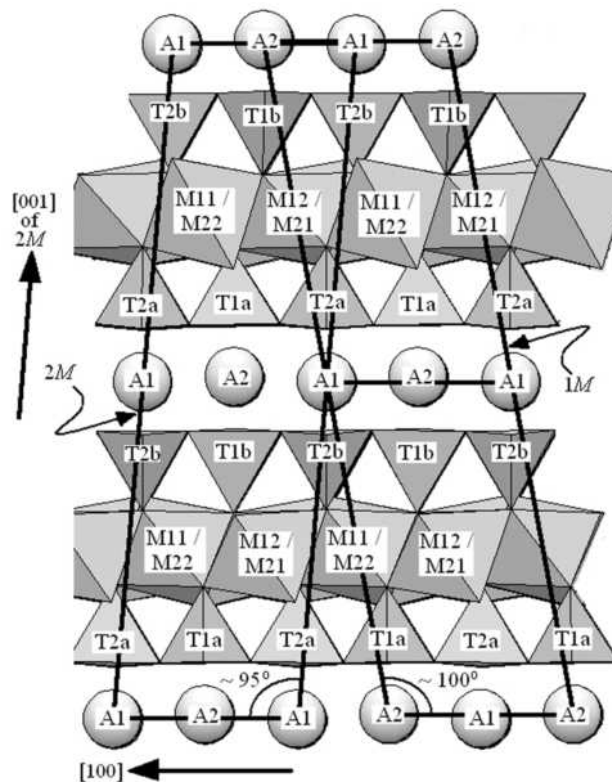


FIGURE 1. The structure of anandite-2M, projected down the *b* axis, showing the 1M cell in relation to the *A*-centered 2M unit cell. Note the differences between the layers in the 1M cell.

TABLE 6. Calculated octahedral and interlayer bond lengths (Å) and angles (°)

Octahedral						Interlayer	
M11			M12			A1	
M11-S2b	2.060(4)		M12-O31b (x2)	2.114(6)		A1-O12b	3.02(1)
M11-O32b (x2)	2.090(6)		M12-O32a (x2)	2.133(6)		A1-O12b'	3.11(1)
M11-O31a (x2)	2.138(6)		M12-S1b	2.380(4)		A1-O22a (x2)	3.131(8)
M11-S1a	2.455(5)		M12-S2a	2.519(3)		A1-O21a (x2)	3.163(9)
Average	2.162		Average	2.232		A1-O21b (x2)	3.166(8)
Unshared		Shared	Unshared		Shared	A1-O12a	3.17(1)
O31a-S1a (x2)	3.151(7)	O31a-S2b (x2)	2.796(7)	O32a-S2a (x2)	3.244(7)	O32a-S1b (x2)	3.185(7)
O31a-O31a	3.111(7)	O31a-O32b (x2)	2.879(9)	O32a-O32a	3.168(7)	O32a-O31b (x2)	2.837(9)
O32b-S2b (x2)	3.136(7)	O32b-S1a (x2)	3.274(7)	O31b-S1b (x2)	3.231(8)	O31b-S2a (x2)	3.308(6)
O32b-O32b	3.080(8)	Average	2.983	O31b-O31b	3.155(8)	Average	3.110
Average	3.128			Average	3.212		
M21			M22			A2	
M21-S2b	2.073(3)		M22-O31b	2.053(7)		A2-O11a	3.06(1)
M21-O31b	2.094(6)		M22-O32a	2.082(7)		A2-O11a'	3.08(1)
M21-O32a	2.113(6)		M22-O32b	2.183(6)		A2-O22b (x2)	3.093(8)
M21-O32b	2.128(7)		M22-O31a	2.194(6)		A2-O21b (x2)	3.099(8)
M21-O31a	2.175(7)		M22-S1b	2.350(3)		A2-O21a (x2)	3.16(1)
M21-S1a	2.464(3)		M22-S2a	2.499(2)		A2-O11b	3.20(2)
Average	2.175		Average	2.227		A2-O22a (x2)	3.231(9)
Unshared		Shared	Unshared		Shared	A2-O11b'	3.25(2)
O31a-O32a	3.208(9)	O31a-O31b	2.855(8)	O31a-O32a	3.105(9)	O31a-O31b	2.855(8)
O31a-S1a	3.191(7)	O31a-S2b	2.796(7)	O31a-S2a	3.234(5)	O31a-O32b	2.879(9)
O32a-S1a	3.201(5)	O32a-O31b	2.837(9)	O32a-S2a	3.191(7)	O32a-O32b	2.855(8)
O31b-O32b	3.21(1)	O32a-O32b	2.855(8)	O31b-O32b	3.13(1)	O32a-S1b	3.185(7)
O31b-S2b	3.159(6)	O32b-S1a	3.274(7)	O31b-S1b	3.140(8)	O31b-S2a	3.308(6)
O32b-S2b	3.124(7)	S1a-S2b	3.164(6)	O32b-S1b	3.225(6)	S2a-S1b	3.743(8)
Average	3.182	Average	2.964	Average	3.171	Average	3.138

TABLE 7. Bond valence sums (Σs) in valence units (v.u.) for anandite-2M

A1	A2	M11	M12	M21	M22	T1a	T1b	T2a	T2b	Σs^*
O11a	0.12							0.86		1.97
O11a'	0.12									1.96
O11b	0.09								1.00	2.17
O11b'	0.07									2.15
O12a	0.09					0.90				1.99
O12a'	0.08									1.96
O12b	0.14						0.91			2.11
O12b'	0.11									2.05
O21a	0.09 (x2)	0.10 (x2)				0.99		0.84		2.02
O21b	0.09 (x2)	0.11 (x2)					0.84		0.96	2.01
O22a	0.10 (x2)	0.08 (x2)				0.96		0.86		2.00
O22b	0.09 (x2)	0.11 (x2)					0.81		1.00	2.01
O31a		0.33 (x2)		0.31	0.30	1.09	0.83			2.02
O31b			0.37 (x2)	0.38	0.44					2.01
O32a			0.35 (x2)	0.36	0.40			0.95		2.06
O32b		0.38 (x2)		0.35	0.31				0.90	1.93
S1a		0.14		0.14						0.42
S1b	0.19		0.55		0.60					1.94
S2a		0.33	0.38		0.40					1.51
S2b		0.41		0.40						1.22
Σs	1.36	1.53	1.98	2.38	1.93	2.44	3.39	3.51	3.86	

Notes: Calculated using $s = \exp[(R_0 - R)/B]$ (Brown 1992), where R is the observed bond length, $B = 0.37$ Å, and R_0 is from Brese and O'Keeffe (1991). Hybrid M and T sites calculated using weighted averages of occupancies.

* Symmetry equivalent sites factored into bond valence sums are not shown.

Differences in individual bond lengths between the two interlayer coordination polyhedra (Table 6) are mainly related to the size of the surrounding tetrahedra. Of the two larger of the four tetrahedra, T2a is smaller than T1b causing the basal O atoms to move closer to A2. Of the two smaller tetrahedra, T1a is smaller than T2b, bringing the basal oxygen closer to A1. Because the size differences among large and small tetrahedra are of different magnitudes (Table 5), the basal O atoms are closer to one of the two A sites.

Assuming an idealized end-member composition, bond-valence computations suggest three possible arrangements: a

basal O atom is surrounded by either: (1) two Fe and two Ba; (2) an Fe, Si, and two Ba; or (3) two Si and two Ba nearest cation neighbors. If a basal O atom receiving a combined charge of 2.0 electrostatic valency units (e.v.u.) is charge balanced, then: case (1) results in an undersaturated oxygen with respect to charge [Pauling bond strength (PBS) = $2 \cdot (2/12) + 2 \cdot (3/4) = 1.833$ e.v.u.]; case (2) results in a slightly oversaturated oxygen (PBS = 2.083 e.v.u.); and case (3) results in an oversaturated oxygen (PBS = 2.333 e.v.u.). These configurations will result in the Ba shifting toward the undersaturated oxygen and the Fe³⁺ rich tetrahedra [i.e., between layers 1 and 2 (as defined in Fig. 3), A1 is shifted

TABLE 8. Tetrahedral, octahedral, and S site occupancies

Site	Occupancy refinement	Observed bond lengths*	Bond valence
T1a	Si _{0.80} Fe _{0.20} ³⁺	Si _{0.91} Fe _{0.09} ³⁺	Si _{0.94} Fe _{0.06} ³⁺
T1b	Si _{0.68} Fe _{0.32} ³⁺	Si _{0.45} Fe _{0.55} ³⁺	Si _{0.38} Fe _{0.62} ³⁺
T2a	Si _{0.43} Fe _{0.57} ³⁺	Si _{0.56} Fe _{0.44} ³⁺	Si _{0.51} Fe _{0.49} ³⁺
T2b	Si _{0.91} Fe _{0.09} ³⁺	Si _{0.86} Fe _{0.14} ³⁺	Si _{0.86} Fe _{0.14} ³⁺
M11	Fe _{0.59} ³⁺ Al _{0.15} Mg _{0.16} Mn _{0.10}	Fe _{0.84} Al _{0.16} ³⁺	R _{1.00} ²⁺
M12	Fe _{0.55} ³⁺ Fe _{0.45} ²⁺	Fe _{0.60} Fe _{0.40} ²⁺	R _{0.62} R _{0.38} ²⁺
M21	Fe _{0.90} ³⁺ Al _{0.01} Mg _{0.07} Mn _{0.02}	Fe _{0.76} Fe _{0.05} Al _{0.11} Mg _{0.03} Mn _{0.05} ³⁺	R _{1.00} ²⁺
M22	Fe _{0.60} ³⁺ Fe _{0.40} ²⁺	Fe _{0.65} Fe _{0.35} ²⁺	R _{0.56} R _{0.44} ²⁺
S1a	OH _{1.00}	—	OH _{1.00}
S1b	S _{0.52} OH _{0.48}	—	S _{0.94} OH _{0.06}
S2a	S _{0.58} OH _{0.42}	—	S _{0.50} OH _{0.50}
S2b	S _{0.30} OH _{0.70}	—	S _{0.22} OH _{0.78}

Site	Best fit composition	Filut et al. (1985)
T1a	Si _{0.88} Fe _{0.12} ³⁺	Si _{1.00}
T1b	Si _{0.50} Fe _{0.50} ³⁺	Fe _{0.70} Si _{0.30} ³⁺
T2a	Si _{0.50} Fe _{0.50} ³⁺	Fe _{0.70} Si _{0.30} ³⁺
T2b	Si _{0.88} Fe _{0.12} ³⁺	Si _{1.00}
M11	Fe _{0.48} ³⁺ Fe _{0.28} ²⁺ Al _{0.10} Mg _{0.09} Mn _{0.05} ²⁺	Fe _{0.70} Fe _{0.30} ²⁺ Mg _{0.53} Al _{0.07}
M12	Fe _{0.51} ³⁺ Fe _{0.49} ²⁺	Fe _{0.70} Fe _{0.30} ²⁺
M21	Fe _{0.55} ³⁺ Fe _{0.30} ²⁺ Al _{0.04} Mg _{0.07} Mn _{0.02} ²⁺ Mn _{0.02} ³⁺	Fe _{0.70} Mn _{0.20} Mn _{0.04} Mg _{0.04} Al _{0.07} ²⁺
M22	Fe _{0.56} ³⁺ Fe _{0.44} ²⁺	Fe _{0.83} Fe _{0.17} ²⁺
S1a	OH _{1.00}	—
S1b	S _{0.73} OH _{0.27}	—
S2a	S _{0.54} OH _{0.46}	—
S2b	S _{0.26} OH _{0.74}	—

* Derived from ionic radii (Shannon 1976; tetrahedral Fe³⁺ radius from Filut et al. 1985).

in one direction along the *c* axis toward the O12b atoms and A2 is shifted in the opposite direction toward the O11a atoms], and away from the oversaturated O atoms and Si tetrahedra to compensate for charge (i.e., between layers 1 and 2, A1 is shifted away from the O12a atoms and A2 is shifted away from O11b atoms). Case 2 will not cause Ba to shift significantly, because the bridging basal oxygen is already nearly charge satisfied. The interaction between Ba, the tetrahedra, and S is reflected in the bond valences around the interlayer cations where the values are larger for A1-O12b and A2-O11a than for A1-O12a and A2-O11b.

Assuming the radius of an S²⁻ anion to be 1.81 Å (Filut et al. 1985) and that of an apical O atom to be 1.38 Å (Shannon 1976) in a four coordinated site, and an unshifted S to be in contact with the octahedral cation, then an unshifted S would exceed the distance of the apical O atoms along *c* by 0.43 Å (=1.81–1.38 Å). The difference in distance between the observed location and the ideal location along *c* gives the shift of S toward the interlayer

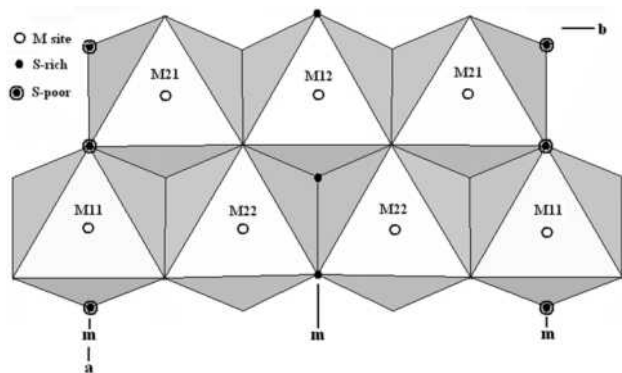


FIGURE 2. Octahedral sheet of the first layer projected down the *c* axis.

cation. The shift along *c* of S-rich sites (S1b, S2a) and S-poor sites (S1a, S2b) is given in Table 9. S1b and S2a have larger shifts, and S1a and S2b have very little and no shifts, respectively. The relatively large difference in shift between S1b and S2a is attributed to positional disorder and possibly compositional differences. The charge interaction between S and A sites causes the interlayer cation to also shift (Table 9) toward the S site from the median plane of the interlayer. This shifting is evidence for the bonding of Ba and S and for S being present in the structure as S²⁻. An inspection of bond valence sums of S sites (Table 7) indicates that the A cations and S prefer to be shifted toward each other to achieve near charge balance.

Displacement ellipsoids of the interlayer cations appear circular when projected down the [001] direction (Fig. 4). However, when projected down the [100] (Fig. 5) or [010] direction (not shown), the projections are not circular. The A1 cation ellipsoid is elongated along *c* and A2 is flattened along *c*. This is interpreted as positional disorder among unit cells, possibly an effect of the variable tetrahedral compositions; the basal O atoms of the Fe³⁺ tetrahedra attract the Ba, Si tetrahedra repel the Ba. Moreover, S and OH sites are variable in composition and the presence of S on the opposite side of the interlayer cation would cause changes in A site ellipsoid shape.

Structure and distortions

The absence of a twofold axis and inversion center permits the tetrahedral sheets within a layer to be symmetrically inequivalent and to vary in thickness by 0.209 Å (Fig. 3; Table 9). This variation is related to tetrahedral cation-occupancy differences between the sheets and possibly the variable composition and displacement of the S, OH sites. This is in agreement with the observed bond-length and bond valence calculations of occupancy, where the designated *a* sheet (Fig. 3) contains less Fe³⁺ than does

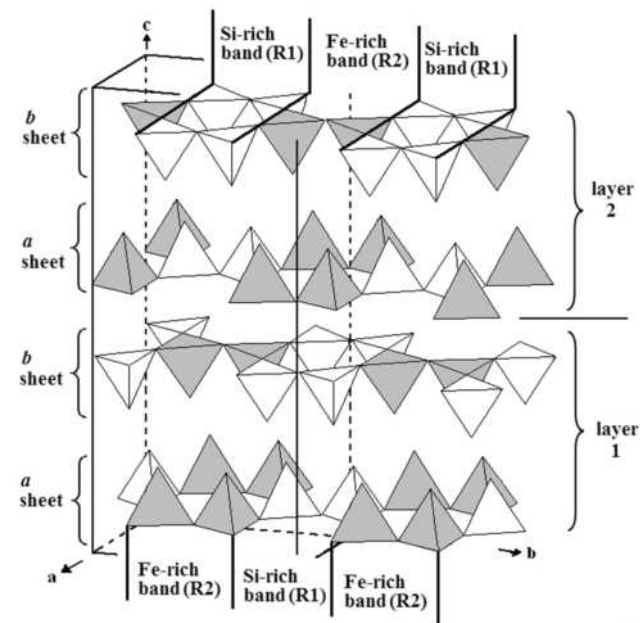


FIGURE 3. Diagram showing tetrahedral sheets with Fe- and Si-rich bands in two unit cells of anandite-2M. Shaded tetrahedra are Fe-rich.

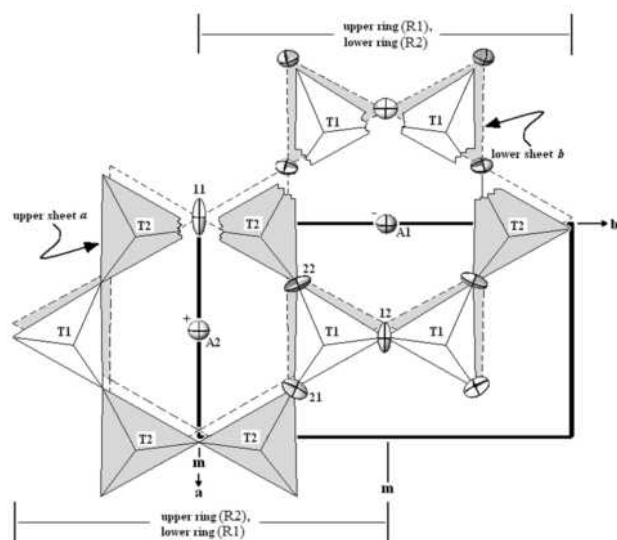


FIGURE 4. Diagram showing small (R1) and large (R2) tetrahedral rings and displacement parameters of the interlayer between layer 1 and 2 projected down the c axis. Shaded tetrahedra are Fe-rich; bands alternate between layers 1 and 2; and sulfur atoms are projected below (–) site A1 and above (+) site A2.

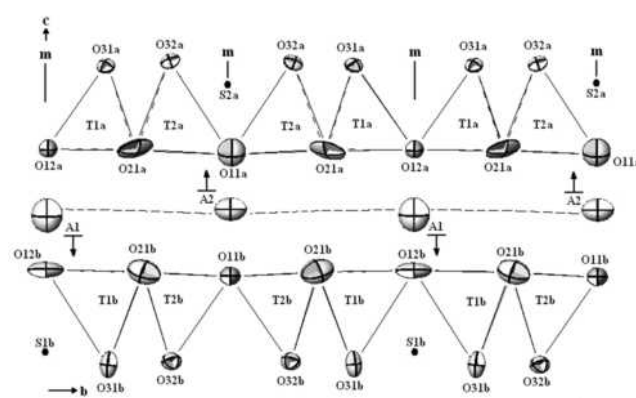


FIGURE 5. Diagram showing the A site cations, tetrahedra, S-rich sites, and displacement ellipsoids in and near the interlayer between layers 1 and 2.

the b sheet. As expected, the larger b sheet has less tetrahedral rotation and higher O_a -T- O_b (τ) averages (Table 9).

Similar to other micas, basal oxygen corrugation in anandite-2M is a result of distortion of the *trans* M sites and tetrahedral tilting. Anandite-2M has an unusual corrugation, similar to anan-

TABLE 9. Calculated structural parameters

Tetrahedral rotation (α)		Sheet thickness ($\text{\AA}$)	
a sheet	0.92°	Tetrahedral a sheet	2.0968
b sheet	0.83°	Tetrahedral b sheet	2.3062
Basal oxygen Δz ($\text{\AA}$)		Octahedral	2.4386
O11a	0.110	Interlayer separation	3.1409
O12a	0.011§	Total	9.9825
O11b	0.121§	Angle Variance (σ_a^2)*	
O12b	0.007	M11	29.22
Tetrahedral angle (τ)		M12	15.38
T1a	112.19°	M21	37.11
T2a	111.60°	M22	28.12
T1b	112.20°	T1a	11.31
T2b	112.04°	T1b	15.85
Flattening angle (ψ)		T2a	10.25
A1	60.14°	T2b	13.41
A2	60.05°	Quadratic elongation (λ)†	
M11	55.67°	M11	1.0131
M12	56.89°	M12	1.0141
M21	55.89°	M21	1.0158
M22	56.80°	M22	1.0158
Shift along c axis ($\text{\AA}$)		T1a	1.0026
A1,A2	0.070	T1b	1.0040
S2a	0.195	T2a	1.0024
S1b	0.038	T2b	1.0039
S1a	0.084	β_{ideal} 95.194°	
S2b	–0.328		

Note: Braces denote the average.

$$* \lambda = \sum_{i=1}^n (l_i / l_0)^2 / n$$

where l_0 is the center-to-vertex distance of an undistorted polyhedron with n coordinating ions around the central atom and a volume equal to the distorted polyhedron with center-to-vertex distances of l_i (Robinson et al. 1971).

$$† \sigma_0^2 = \sum_{i=1}^m (\theta_i - 90^\circ)^2 / (m - 1)$$

where θ_i is the observed O-M-O or O-T-O angle and m is the number of angles in the polyhedron.

§ Basal O atom in coordination with Si-rich tetrahedra (negative in Filut et al. 1985).

dite-2O, where the basal O atoms of one tetrahedral sheet form crests and troughs in a wave-like fashion and are in phase with the basal O atoms across the separation (e.g., O11a is in a trough at the bottom of the *a* sheet and O11b is in an opposite trough in the *b* sheet; Fig. 5). Individual troughs and crests run parallel to or on *m* planes, and therefore are also parallel to the intralayer *a*/3 shift and Fe³⁺- and Si-rich tetrahedral bands (Fig. 3).

Both O32b-O32b and O32b-O32a pairs are pushed apart to fit the larger octahedra (see Filut et al. 1985), which causes the O11a and O12b bridging O atoms of the Fe³⁺-rich tetrahedral bow-ties to fold away from the interlayer, similar to bridging basal O atoms of the Si-rich tetrahedra. Because the bridging O atom of Fe-rich tetrahedral bow-ties shifts toward the interlayer and cause the basal O atoms to fold into the interlayer, a reduction in the frequency of troughs and crests results. The attraction of the Ba and the undersaturated basal oxygen (see PBS calculations above and bond valencies, Table 7) pulls this O atom toward the positively charged Ba and away from the negatively charged S.

Comparison of polytypes

Atomic coordinates, site occupancies, and unit-cell dimensions of anandite-2M are compared with anandite-2O (Filut et al. 1985) in Tables 3, 8, and 10, respectively. Atomic coordinates and unit-cell parameters of anandite-2O are referred to the origin of the 2M polytype and are presented in the 2M setting for direct comparison. The greatest difference between structures is the 180° rotation of the second layer of the 2O structure. However, the topology of the layers is similar. Comparison of unit cells (Table 10) shows that the *a* axes are nearly the same, the *b* axis is smaller (by 0.0371 Å), the *c* axis is larger (by 0.08 Å), and β is smaller (by 0.089°) for 2M relative to 2O. The difference in *c* axis lengths is related to the thicknesses of the octahedral sheets and the interlayer separation, which are both larger for 2M. The thickness of the octahedral sheet is a function of the flattening angle (ψ), which is smaller for all M sites in 2M. The larger ψ angles of 2O also have the effect of laterally expanding the sheet to cause a larger *b* axis. Consequently, the basal oxygen corrugations are larger in 2O than in 2M to compensate for octahedral expansion. Moreover, the overall sizes of the 2O tetrahedra are larger, also contributing to the larger *b* axis length. The larger β in 2O is a function of ψ, the greater the octahedral flattening, the larger the value of β. Note that α and τ are the same, within errors, for both polytypes.

On average, the Si-rich tetrahedra of 2M are 0.030 Å larger and the Fe-rich tetrahedra are 0.053 Å smaller than in 2O. This leads to larger R2 rings, and to a lesser extent, smaller R1 rings. In addition, the Fe-rich tetrahedra of 2O contain more Fe³⁺, and therefore less residual positive charge, than do 2M tetrahedra. This allows the interlayer cations of 2O to settle into ring R2 more than in the 2M structure (0.1 vs. 0.07 Å, respectively), decreasing the interlayer separation.

Filut et al. (1985) asserted that the in-phase nature of the wave structure of the basal O atoms is only possible in a 2O structure with a primitive unit cell. This conclusion is based on geometry, which requires a two-layer structure with all *a*/3 shifts within the layers parallel to each other. In addition, a second layer must be shifted by the *C*-centering vector ($\frac{1}{2} \frac{1}{2} 0$) relative to the first

TABLE 10. Unit-cell dimensions comparison between anandite-2M and anandite-2O

Type	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
2M	5.4431(3)	9.4719(6)	20.042(1)	95.046(1)
2O*	5.439	9.509	19.958	95.135

* Cell dimensions in the 2M setting to facilitate comparison.

layer, which occurs in the ideal symmetry of the 2O polytype. The present study shows that the in-phase wave structure of the interlayer is not restricted to an orthorhombic *P* cell. The non-centrosymmetric symmetry (lacking a twofold axis) of the 2M structure also allows the interlocking characteristic wave structure and conforms to the requirements as outlined by Filut et al. (1985), i.e., a two-layer structure with parallel *a*/3 shifts and a loss of the twofold axis owing to the ordering pattern.

Filut et al. (1985) speculated that the ordering pattern and the “interlocking wave forms” in the interlayer are the explanation for the abundance of anandite-2O polytype in anandite samples of the same composition. However, anandite-2M has similar ordering and “interlocking wave forms” and is also prevalent in the zone of anandite in the Wilagedera, Sri Lanka, drill cores.

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