

## THE CRYSTAL CHEMISTRY OF THE “NICKELALUMITE”-GROUP MINERALS

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### ABSTRACT

The crystal structure of “nickelalumite”, ideally  $\text{NiAl}_4(\text{SO}_4)(\text{OH})_{12}(\text{H}_2\text{O})_3$ , from the Kara–Tangi uranium deposit, Batken region, Kyrgyzstan, monoclinic,  $a$  10.2567(5),  $b$  8.8815(4),  $c$  17.0989(8) Å,  $\beta$  95.548(1)°,  $V$  1550.3(1) Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 4$ ,  $D_{\text{calc}}$  2.231 g/cm<sup>3</sup>, has been solved by the Patterson method and refined to an  $R_1$  index of 5.7% for 1554 unique ( $F_o > 4\sigma F$ ) reflections collected on a Bruker single-crystal P4 diffractometer with a 4K CCD detector and MoK $\alpha$  X-radiation. “Nickelalumite” occurs with quartz, calcite, aluminohydrocalcite, allophane, crandallite and kyrgyzstanite. An electron-microprobe analysis gave  $\text{Al}_2\text{O}_3$  39.94,  $\text{SiO}_2$  0.17,  $\text{SO}_2$  12.16,  $\text{V}_2\text{O}_5$  0.29,  $\text{FeO}$  0.15,  $\text{NiO}$  8.00,  $\text{ZnO}$  6.21,  $(\text{H}_2\text{O})_{\text{calc}}$  31.87, sum 98.79 wt.%; the amount of  $\text{H}_2\text{O}$  was determined by crystal-structure analysis. There is one tetrahedrally coordinated  $S$  site, with  $\langle S-O \rangle$  1.468 Å. There are five octahedrally coordinated sites. At the  $M$  site, Ni is dominant over Zn, with  $\langle M-O \rangle = 2.079$  Å. Four sites are occupied solely by Al, with a grand  $\langle Al-O \rangle$  distance of 1.900 Å. There are 19 anion sites: four sites are occupied by O atoms, 12 sites by (OH) groups, and three sites by (H<sub>2</sub>O) groups. The main building unit of the “nickelalumite” structure is a (001) sheet of Al and  $M$  octahedra. The Al and  $M$  octahedra share common edges to form an interrupted sheet of the form  $[MAl_4(\text{OH})_{12}]^{2+}$ . Intercalated between the  $M$ –Al–OH sheets are layers of (SO<sub>4</sub>) tetrahedra and (H<sub>2</sub>O) groups. All H atoms of (OH) and (H<sub>2</sub>O) groups were located, and details of hydrogen bonding are discussed. The structure of “nickelalumite” is similar to those of alvanite,  $\text{ZnAl}_4(\text{VO}_3)_2(\text{OH})_{12}(\text{H}_2\text{O})_2$ , and ankinovichite,  $\text{NiAl}_4(\text{VO}_3)_2(\text{OH})_{12}(\text{H}_2\text{O})_2$ , and stoichiometry and cell dimensions suggest that mbobomkulite and hydrombobomkulite also are related to “nickelalumite”. All structures are based on a positively charged sheets of octahedra of the form  $[\square M^{2+} M^{3+}_4 (\text{OH})_{12}]^{2+}$  that are intercalated with interstitial complexes of oxyanions and (H<sub>2</sub>O) groups. The Lewis acidity of the structural unit is 0.167 *vu*, and the character of the interstitial complexes is constrained by the valence-sum rule of bond-valence theory. Possible interstitial oxyanions are (SO<sub>4</sub>)<sup>2-</sup>, (NO<sub>3</sub>)<sup>1-</sup><sub>2</sub> and [VO<sub>3</sub>]<sup>1-</sup><sub>2</sub>, whereas (SiO<sub>4</sub>)<sup>4-</sup>, (BO<sub>3</sub>)<sup>3-</sup><sub>2</sub>, (PO<sub>4</sub>)<sup>3-</sup> and (BO<sub>4</sub>)<sup>5-</sup> have Lewis basicities that are too high and hence cannot form “nickelalumite”-type structures.

*Keywords:* “nickelalumite”, crystal structure, electron-microprobe analysis, hydrogen bonding.

### SOMMAIRE

Nous avons résolu la structure cristalline de la “nickelalumite”, dont la formule idéale serait  $\text{NiAl}_4(\text{SO}_4)(\text{OH})_{12}(\text{H}_2\text{O})_3$ , provenant du gisement d’uranium de Kara–Tangi, région de Batken, au Kyrgyzstan, monoclinique,  $a$  10.2567(5),  $b$  8.8815(4),  $c$  17.0989(8) Å,  $\beta$  95.548(1)°,  $V$  1550.3(1) Å<sup>3</sup>, groupe d’espace  $P2_1/n$ ,  $Z = 4$ ,  $D_{\text{calc}}$  2.231 g/cm<sup>3</sup>, par méthode de Patterson, et nous l’avons affiné jusqu’à un résidu  $R_1$  de 5.7% en utilisant 1554 réflexions uniques ( $F_o > 4\sigma F$ ), prélevées avec un diffractomètre Bruker P4 muni d’un détecteur CCD 4K, avec rayonnement MoK $\alpha$ . On trouve la “nickelalumite” avec quartz, calcite, aluminohydrocalcite, allophane, crandallite et kyrgyzstanite. Une analyse avec une microsonde électronique a donné  $\text{Al}_2\text{O}_3$  39.94,  $\text{SiO}_2$  0.17,  $\text{SO}_2$  12.16,  $\text{V}_2\text{O}_5$  0.29,  $\text{FeO}$  0.15,  $\text{NiO}$  8.00,  $\text{ZnO}$  6.21,  $(\text{H}_2\text{O})_{\text{calc}}$  31.87, pour une somme de 98.79% (poids); la quantité de  $\text{H}_2\text{O}$  a été établie par ébauche de la structure cristalline. Il y a un site  $S$  à coordinence tétraédrique, avec  $\langle S-O \rangle$  1.468 Å. Il y a cinq sites à coordinence octaédrique. Au site  $M$ , le Ni est dominant par rapport au Zn, avec  $\langle M-O \rangle = 2.079$  Å. Quatre sites sont remplis uniquement par Al, avec une longueur moyenne  $\langle Al-O \rangle$  de 1.900 Å. Il y a 19 sites anioniques: quatre sites sont occupés par des atomes O, 12 sites par des groupes (OH), et trois sites par des groupes (H<sub>2</sub>O). L’unité structurale principale de la “nickelalumite” est un feuillet (001) d’octaèdres Al et  $M$ . Les octaèdres Al et  $M$  partagent des arêtes communes pour former un feuillet interrompu de composition  $[MAl_4(\text{OH})_{12}]^{2+}$ . Des couches de tétraèdres (SO<sub>4</sub>) et des groupes (H<sub>2</sub>O) sont intercalés entre les feuillets  $M$ –Al–OH. Tous les atomes H des groupes (OH) et (H<sub>2</sub>O) ont été situés, et les détails des liaisons hydrogène sont évalués. La structure de la “nickelalumite” est semblable à celle de l’alvanite,  $\text{ZnAl}_4(\text{VO}_3)_2(\text{OH})_{12}(\text{H}_2\text{O})_2$ , et de l’ankinovichite,  $\text{NiAl}_4(\text{VO}_3)_2(\text{OH})_{12}(\text{H}_2\text{O})_2$ , et la stoechiométrie et les dimensions de la maille font penser que la mbobomkulite et la hydrombobomkulite sont aussi apparentées à la “nickelalumite”. Toutes ces structures seraient fondées sur la présence de feuillets d’octaèdres à charges positives de la forme  $[\square M^{2+} M^{3+}_4 (\text{OH})_{12}]^{2+}$  qui sont intercalés avec des complexes interstitiels

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d'oxyanions et de groupes (H<sub>2</sub>O). L'acidité de Lewis de l'unité structurale est 0.167 unités de valence, et le caractère des complexes interstitiels est régi par la règle des sommes des valences dans le contexte de la théorie des valences de liaisons. Les oxyanions possibles sont (SO<sub>4</sub>)<sup>2-</sup>, (NO<sub>3</sub>)<sup>1-</sup> et [VO<sub>3</sub>]<sup>1-</sup>, tandis que (SiO<sub>4</sub>)<sup>4-</sup>, (BO<sub>3</sub>)<sup>3-</sup>, (PO<sub>4</sub>)<sup>3-</sup> et (BO<sub>4</sub>)<sup>5-</sup> possèdent une basicité de Lewis trop élevée, ce qui ne leur permettrait pas de former des structures de type "nickelalumite".

(Traduit par la Rédaction)

*Mots-clés:* "nickelalumite", structure cristalline, données de microsonde électronique, liaisons hydrogène.

## INTRODUCTION

"Nickelalumite", (Ni<sub>0.75</sub>Cu<sub>0.25</sub>)<sub>Σ1.00</sub>Al<sub>4</sub>[SO<sub>4</sub>]<sub>Σ0.75</sub>(NO<sub>3</sub>)<sub>Σ0.50</sub>(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>3</sub>, was described as a new mineral species from the Mboobo Mkulu cave, Nelspruit district, eastern Transvaal, in association with two other new minerals: mbobomkulite, (Ni,Cu<sup>2+</sup>)Al<sub>4</sub>[(NO<sub>3</sub>),(SO<sub>4</sub>)<sub>2</sub>](OH)<sub>12</sub>(H<sub>2</sub>O)<sub>3</sub>, and hydrombobomkulite, (Ni,Cu<sup>2+</sup>)Al<sub>4</sub>[(NO<sub>3</sub>),(SO<sub>4</sub>)<sub>2</sub>](OH)<sub>12</sub>(H<sub>2</sub>O)<sub>12</sub> (Martini 1980). [Unfortunately, the name is in the literature without the approval of the IMA – CNMMN, hence the quotation marks.] The unit-cell parameters were determined for all three minerals, but their crystal structures are not known. There are five minerals that have stoichiometries related to "nickelalumite": mbobomkulite, hydrombobomkulite, chalcoalumite, alvanite and ankinovichite (Table 1). They are characterized by the general formula MAl<sub>4</sub>(OH)<sub>12</sub>(TO<sub>3</sub>,SO<sub>4</sub>)<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub>, where M = Ni, Zn, Cu<sup>2+</sup>; T = N<sup>3+</sup>, V<sup>5+</sup>; m = 1, 2; 2 < n < 12. All minerals are monoclinic with unit-cell parameters a ≈ 8.9, b ≈ 10, c ≈ 17 Å and β in the range 90–95°. Previously, "nickelalumite" was considered as the nickel analogue of chalcoalumite (Williams & Khin 1971), the crystal structure of which also is not known.

Here, we report on the structure of "nickelalumite" and examine the structures and chemical compositions of related phases in terms of the Lewis acidities and basicities of their constituent structural units and interstitial complexes.

## EXPERIMENTAL

The crystal structure of "nickelalumite" has not been established because it has been extremely difficult to find a single crystal suitable for structure refinement. "Nickelalumite" crystals are fragile, transparent flakes that deform under the slightest touch. After much effort, we extracted a crystal with minimal damage from an aggregate embedded in a rock matrix. The sample of "nickelalumite" used here is from the Kara-Tangi uranium deposit, Batken region, Kyrgyzstan, where it occurs in the zone of hydrothermal alteration of U–V-bearing carbon-bearing silicified schists, in association with quartz, calcite, alumohydrocalcite, allophane, crandallite and kyrgyzstanite (Karpenko *et al.* 2004b, Agakhanov *et al.* 2005).

X-ray-diffraction data for "nickelalumite" were collected with a Bruker P4 diffractometer equipped with a 4K CCD detector (MoKα radiation) from a single crystal of "nickelalumite" with dimensions 0.10 × 0.06 × 0.02 mm. The intensities of 7103 reflections with  $\bar{1}0 < h < 10$ ,  $\bar{9} < k < 9$ ,  $\bar{1}8 < l < 18$  were collected to 59.99° 2θ using 30 s per 0.2° frame. An empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters were obtained from 3365 reflections with  $I > 10\sigma I$ . There were no observed data in the high-angle region between 45 and 59.99°, and the data were truncated at 44.42°. Details of the data collection and structure refinement are given in Table 2. The crystal structure of "nickelalumite" was

TABLE 1. COMPARISON OF DATA FOR "NICKELALUMITE", MBOBOMKULITE, HYDROMBOBOMKULITE, CHALCOALUMITE, ALVANITE AND ANKINOVICHITE

Mineral name	Ideal* or general formula	Space group	a (Å)	b (Å)	c (Å)	β (°)	Z	Ref.
"Nickelalumite"*	NiAl <sub>4</sub> (OH) <sub>12</sub> (SO <sub>4</sub> )(H <sub>2</sub> O) <sub>3</sub>	P2 <sub>1</sub> /n	10.2567(5)	8.8815(4)	17.0989(8)	95.548(1)	4	(1)
Mbobomkulite	(Ni,Cu <sup>2+</sup> )Al <sub>4</sub> (OH) <sub>12</sub> [(NO <sub>3</sub> ),(SO <sub>4</sub> ) <sub>2</sub> ](H <sub>2</sub> O) <sub>3</sub>	–	10.171	8.865	17.145	95.37	4	(2)
Hydrombobomkulite	(Ni,Cu <sup>2+</sup> )Al <sub>4</sub> (OH) <sub>12</sub> [(NO <sub>3</sub> ) <sub>2</sub> ,(SO <sub>4</sub> )](H <sub>2</sub> O) <sub>12</sub>	–	10.145	17.155	20.870	90.55	4	(2)
Chalcoalumite	CuAl <sub>4</sub> (OH) <sub>12</sub> (SO <sub>4</sub> )(H <sub>2</sub> O) <sub>3</sub>	P2 <sub>1</sub>	17.090	8.915	10.221	95.88	4	(3)
Alvanite*	ZnAl <sub>4</sub> (OH) <sub>12</sub> (VO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	P2 <sub>1</sub> /n	17.808(8)	5.132(3)	8.881(4)	92.11(3)	2	(4)
Ankinovichite*	NiAl <sub>4</sub> (OH) <sub>12</sub> (VO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	P2 <sub>1</sub> /n	17.8098(8)	5.1228(2)	8.8665(4)	92.141(1)	2	(5)

\* Ideal formulae are given for minerals of known crystal-structure; general formulae are given for minerals of unknown structure. References: (1) This work; (2) Martini (1980); (3) Williams & Khin (1971), Larsen & Vassar (1925); (4) Pertlik & Dunn (1990); (5) Karpenko *et al.* (2004a).

solved by the Patterson method and refined to  $R_1 = 5.7\%$  and a  $GoF$  value of 1.059 for 1554 independent reflections (281 refined parameters including extinction) with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 1997). The occupancy of the  $M$  site was refined with the scattering curve of Ni, and all H positions were softly constrained by setting the O–H distances equal to 0.98 Å. Final atom-parameters are given in Table 3, selected interatomic distances in Table 4, details of hydrogen bonding in Table 5, and bond valences in Table 6. A structure-factor table may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

#### CHEMICAL COMPOSITION

The crystal used for X-ray diffraction was mounted on a Perspex disc, ground, polished, carbon-coated and analyzed with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 keV, a specimen current of 3 nA, a beam size of 20  $\mu\text{m}$ , and counting times on peak and background of 20 and 10 s, respectively. The following standards and crystals were used for K X-ray lines: Al: andalusite, Si: titanite, S: anhydrite, V:  $\text{VP}_2\text{O}_7$ , Ni:  $\text{Ni}_2\text{Si}$ , Zn: gahnite, Fe: fayalite, and Cu:  $\text{CuFeS}_2$ . Data were reduced using the X-PHI procedure of Merlet (1992). The amount of  $\text{H}_2\text{O}$  was calculated from the results of the structure refinement. Table 7 gives the chemical composition and empirical formula unit based on 4 (Al + Si) cations:  $(\text{Ni}_{0.55}\text{Zn}_{0.39}\text{V}_{0.02}\text{Fe}_{0.01})_{\Sigma 0.97}(\text{Al}_{3.99}\text{Si}_{0.01})_{\Sigma 4.00}[\text{SO}_4](\text{OH})_{12}(\text{H}_2\text{O})_3$ ,  $Z = 4$ .

#### DESCRIPTION OF THE STRUCTURE

##### Cation sites

In the crystal structure of “nickelalumite”, there are five sites octahedrally coordinated by (OH) groups. The  $M$  site is Ni-dominant with considerable Zn and

minor V and Fe:  $(\text{Ni}_{0.55}\text{Zn}_{0.39}\text{V}_{0.02}\text{Fe}_{0.01})_{\Sigma 0.97}$ . The good agreement between the refined [27.8(2)] and calculated (27.8 *epfu*) site-scattering values confirms this site assignment. Four sites are occupied solely by Al, with  $\langle \text{Al-OH} \rangle = 1.900$  Å. There is one tetrahedrally coordinated  $S$  site, with  $\langle \text{S-O} \rangle = 1.468$  Å.

##### Topology of the structure

In the crystal structure of “nickelalumite”,  $[\text{Al}(\text{OH})_6]$  octahedra link through common edges to form a dioctahedral sheet of the form  $[\square\text{Al}_2(\text{OH})_6]$  that occurs in the structure of muscovite,  $\text{KAl}_2[\square(\text{AlSi}_3\text{O}_{10})](\text{OH})_2$ . In “nickelalumite”, half of the octahedron vacancies are occupied by  $M$  cations, predominantly Ni and Zn, and half of the octahedra remain vacant to produce an interrupted sheet of the form  $[\square(\text{Ni,Zn})\text{Al}_4(\text{OH})_2]^{2+}$

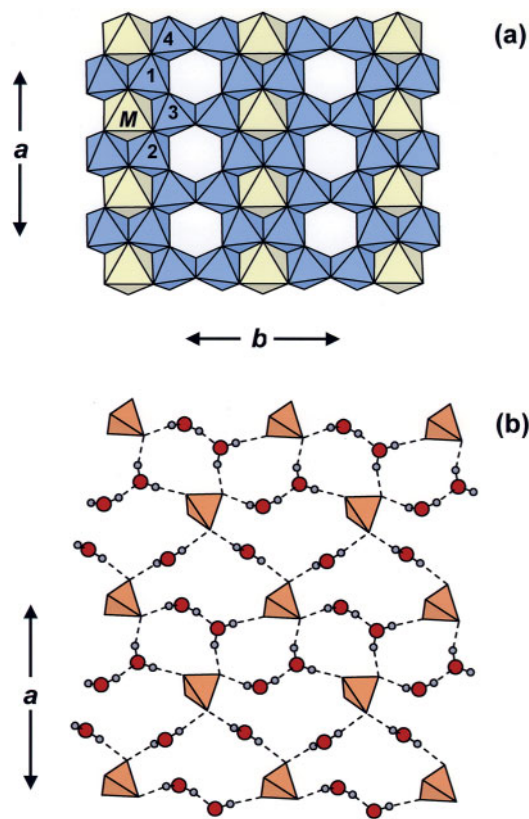


FIG. 1. Two fragments of the structure of “nickelalumite” showing (a) the muscovite-like sheet parallel to (001), and (b) the linkage of  $(\text{SO}_4)$  groups and  $(\text{H}_2\text{O})$  groups through hydrogen bonding. The  $M$  octahedra are honey yellowish, Al octahedra are blue,  $S$  tetrahedra are orange, oxygen atoms are shown as red circles, hydrogen atoms of  $(\text{H}_2\text{O})$  groups are shown as small gray circles,  $\text{O}_w\text{-H}$  bonds are shown as black solid lines, and hydrogen bonds are shown as black dashed lines.

TABLE 2. MISCELLANEOUS DATA CONCERNING THE STRUCTURE REFINEMENT OF “NICKELALUMITE”

$a$ (Å)	10.2567(5)	Crystal size (mm)	$0.10 \times 0.06 \times 0.02$
$b$	8.8815(4)	Radiation	MoK $\alpha$
$c$	17.0989(8)	Monochromator	graphite
$\beta$ ( $^\circ$ )	95.548(1)	$2\theta$ range for data	
$V$ (Å $^3$ )	1550.3(2)	collection ( $^\circ$ )	44.42
Space group	$P2_1/n$	$R(\text{int})$ (%)	2.82
$Z$	4		
Absorption coefficient ( $\text{mm}^{-1}$ )	1.71	Reflections collected	26624
$F(000)$	1064.0	Unique reflections	15173
$D_{\text{calc}}$ ( $\text{g}/\text{cm}^3$ )	2.231	Independent reflections	1959
		$F_o > 4\sigma F_o$	1554
Refinement method		Full-matrix least squares on $F^2$ , fixed weights $\propto 1/\sigma F_o^2$	
Goodness of fit on $F^2$	1.059		
Final $R_{\text{obs}}$ (%) [ $F_o > 4\sigma F_o$ ]		$R1 = 5.66$	
$R$ indices (%) (all data)		$R1 = 7.04$	
		$wR2 = 16.72$	
		$GoF = 1.054$	

TABLE 3. FINAL POSITIONS AND DISPLACEMENT PARAMETERS (Å) OF ATOMS IN "NICKELALUMITE"

	x	y	z	$U_{eq}^*$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
M**	0.74867(8)	0.49993(8)	0.49280(5)	0.0068(4)	0.0026(6)	0.0023(7)	0.0157(7)	-0.0003(3)	0.0017(4)	-0.0001(3)
Al(1)	0.0001(2)	0.3286(2)	0.5016(1)	0.0081(6)	0.0061(13)	0.0053(13)	0.0128(13)	-0.0002(8)	0.0004(10)	-0.0001(8)
Al(2)	0.5005(2)	0.6741(2)	0.5045(1)	0.0083(6)	0.0055(13)	0.0054(13)	0.0140(13)	-0.0004(8)	0.0006(10)	0.0003(8)
Al(3)	0.2485(2)	0.1611(2)	0.4976(1)	0.0076(6)	0.0059(12)	0.0032(13)	0.0136(13)	-0.0001(8)	0.0014(10)	0.0002(8)
Al(4)	0.2496(2)	-0.1606(2)	0.5001(1)	0.0075(6)	0.0057(12)	0.0024(13)	0.0143(13)	-0.0004(8)	0.0007(10)	-0.0004(8)
S	0.4887(2)	0.1094(2)	0.7406(1)	0.0107(5)	0.0115(10)	0.0112(9)	0.0094(10)	0.0002(7)	0.0011(7)	-0.0005(8)
O(1)***	0.5816(5)	0.4971(4)	0.5540(3)	0.0066(12)	0.0052(25)	0.0054(27)	0.0092(26)	-0.0020(18)	0.0003(20)	0.0016(18)
O(2)	0.9219(5)	0.4993(4)	0.4427(3)	0.0078(12)	0.0065(26)	0.0060(27)	0.0104(27)	-0.0008(18)	-0.0016(21)	-0.0013(18)
O(3)	0.6497(5)	0.3211(5)	0.4375(3)	0.0072(11)	0.0089(27)	0.0060(25)	0.0065(25)	-0.0002(19)	-0.0005(21)	-0.0001(19)
O(4)	0.8473(5)	0.3246(5)	0.5567(3)	0.0073(11)	0.0085(27)	0.0030(24)	0.0099(26)	-0.0017(19)	-0.0016(22)	-0.0024(19)
O(5)	0.1068(5)	0.1938(5)	0.5588(3)	0.0100(12)	0.0103(28)	0.0083(26)	0.0120(27)	0.0022(20)	0.0034(22)	0.0001(21)
O(6)	0.1820(5)	-0.0011(4)	0.4376(3)	0.0084(12)	0.0073(27)	0.0072(27)	0.0098(27)	0.0002(19)	-0.0043(21)	0.0004(19)
O(7)	0.6477(5)	0.6824(5)	0.4430(3)	0.0063(11)	0.0051(26)	0.0053(25)	0.0083(25)	-0.0025(19)	-0.0006(21)	-0.0008(19)
O(8)	0.8500(5)	0.6749(5)	0.5559(3)	0.0079(11)	0.0079(27)	0.0067(25)	0.0094(26)	0.0026(19)	0.0018(22)	-0.0016(19)
O(9)	-0.1058(5)	0.1949(5)	0.4421(3)	0.0100(12)	0.0092(28)	0.0085(26)	0.0131(27)	-0.0048(20)	0.0040(21)	-0.0012(21)
O(10)	0.6104(5)	0.8037(5)	0.5629(3)	0.0099(11)	0.0094(28)	0.0081(26)	0.0126(27)	-0.0033(20)	0.0028(22)	-0.0038(21)
O(11)	0.3947(5)	-0.1945(5)	0.4453(3)	0.0097(11)	0.0096(27)	0.0059(25)	0.0140(27)	0.0037(20)	0.0037(22)	0.0014(20)
O(12)	0.3126(5)	0.0016(4)	0.5595(3)	0.0079(12)	0.0044(26)	0.0072(27)	0.0110(27)	-0.0005(19)	-0.0045(21)	-0.0010(18)
O(13)	0.5242(5)	0.0252(5)	0.6717(3)	0.0186(13)	0.0295(32)	0.0138(27)	0.0132(28)	0.0033(21)	0.0056(24)	-0.0013(23)
O(14)	0.9158(6)	0.4892(6)	0.2890(3)	0.0297(15)	0.0403(38)	0.0351(35)	0.0150(31)	0.0004(24)	0.0089(27)	0.0223(27)
O(15)	0.6095(5)	0.1637(6)	0.7855(3)	0.0212(13)	0.0206(30)	0.0242(30)	0.0171(29)	0.0008(22)	-0.0067(23)	-0.0075(24)
O(16)	0.4075(5)	0.2392(6)	0.7142(3)	0.0241(13)	0.0248(31)	0.0211(30)	0.0257(30)	-0.0037(23)	-0.0003(24)	0.0144(24)
O(17)	-0.1529(5)	-0.2224(6)	0.2225(3)	0.0245(13)	0.0223(32)	0.0228(30)	0.0293(33)	0.0024(25)	0.0066(25)	0.0011(25)
O(18)	0.7271(7)	0.4018(8)	0.6938(4)	0.0518(19)	0.0623(49)	0.0602(50)	0.0342(38)	-0.0060(35)	0.0110(34)	-0.0357(39)
O(19)	-0.0255(7)	0.0065(6)	0.3135(3)	0.0339(16)	0.0446(41)	0.0292(36)	0.0265(35)	0.0051(25)	-0.0035(30)	-0.0056(28)
H(1)	-0.246(2)	-0.208(7)	0.228(4)	0.0294						
H(2)	-0.124(6)	-0.318(5)	0.247(4)	0.0294						
H(3)	0.775(9)	0.490(7)	0.717(5)	0.0622						
H(4)	0.703(9)	0.334(8)	0.735(4)	0.0622						
H(5)	-0.034(8)	0.088(5)	0.275(3)	0.0406						
H(6)	-0.061(8)	-0.087(4)	0.289(3)	0.0406						
H(7)	0.620(2)	0.484(7)	0.609(2)	0.008						
H(8)	0.892(7)	0.497(7)	0.386(1)	0.0094						
H(9)	0.648(7)	0.317(7)	0.3797(8)	0.0087						
H(10)	0.844(7)	0.320(7)	0.6140(9)	0.0088						
H(11)	0.088(6)	0.118(6)	0.598(3)	0.012						
H(12)	0.130(6)	0.003(7)	0.386(2)	0.0101						
H(13)	0.626(6)	0.697(7)	0.386(1)	0.0076						
H(14)	0.865(7)	0.678(7)	0.6139(8)	0.0095						
H(15)	-0.087(6)	0.118(6)	0.403(3)	0.012						
H(16)	0.596(7)	0.874(6)	0.606(3)	0.0119						
H(17)	0.411(7)	-0.134(6)	0.399(2)	0.0116						
H(18)	0.371(6)	0.011(7)	0.609(2)	0.0094						

\*  $U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ . \*\*  $M = Ni_{0.55} Zn_{0.39} V_{0.02} Fe_{0.01}^{2+}$ . \*\*\* O(1-12) = (OH), O(13-16) = O, O(17-19) = H<sub>2</sub>O.

that is parallel to the (001) plane (Fig. 1a). Intercalated between these sheets are layers of isolated (SO<sub>4</sub>) tetrahedra and (H<sub>2</sub>O) groups (Fig. 1b), linked through a network of hydrogen bonds. The sheet and the layer alternate along the *c* direction (Fig. 2), and are linked by an extensive network of hydrogen bonds (Fig. 3).

#### Hydrogen bonding

There are two types of hydrogen bonds in the crystal structure of "nickelalumite". Hydrogen bonds of the first type occur between H atoms of (H<sub>2</sub>O) groups and O atoms of the (SO<sub>4</sub>) groups, and are located within

the (H<sub>2</sub>O)-(SO<sub>4</sub>) layer (Fig. 1b). Hydrogen bonds of the second type occur between H atoms of the (OH) groups of the M-Al-OH sheet and O atoms of the (H<sub>2</sub>O)-(SO<sub>4</sub>) layer (Fig. 3). Table 5 gives the stereochemical details of the hydrogen bonds. All H atoms are involved in strong hydrogen bonds, with H...A in the range 1.70-2.04 Å. Almost all D-H...A angles are close to 161°, typical of fairly unstrained hydrogen bonds. There is one hydrogen bond between two (H<sub>2</sub>O) groups, O(19)-H(6)...O(17) (Fig. 4a), whereas the third (H<sub>2</sub>O) group is connected to (SO<sub>4</sub>) tetrahedra and the M-Al-(OH) sheet (Fig. 4b). The O atoms of the (SO<sub>4</sub>) group receive from 2 to 3 hydrogen bonds each, and the

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN "NICKELALUMITE"

M-O(1)	2.093(5)	S-O(13)	1.470(5)
M-O(2)	2.045(5)	S-O(14)	1.460(5)
M-O(3)	2.065(5)	S-O(15)	1.474(5)
M-O(4)	2.104(5)	S-O(16)	1.468(5)
M-O(7)	2.062(5)		
M-O(8)	2.107(5)	<S-O>	1.468
<M-OH>	2.079		
Al(1)-O(2)	1.933(5)	Al(2)-O(1)	1.935(5)
Al(1)-O(2)a	1.949(5)	Al(2)-O(1)b	1.964(5)
Al(1)-O(4)	1.906(5)	Al(2)-O(3)	1.913(5)
Al(1)-O(5)	1.839(5)	Al(2)-O(7)	1.922(5)
Al(1)-O(8)	1.903(5)	Al(2)-O(10)	1.837(5)
Al(1)-O(9)	1.847(5)	Al(2)-O(1)	1.831(5)
<Al(1)-OH>	1.896	<Al(2)-OH>	1.900
Al(3)-O(5)	1.894(5)	Al(4)-O(3)	2.006(5)
Al(3)-O(6)	1.859(5)	Al(4)-O(4)	1.968(5)
Al(3)-O(7)	1.972(5)	Al(4)-O(6)	1.867(5)
Al(3)-O(8)	1.948(5)	Al(4)-O(9)	1.877(5)
Al(3)-O(10)	1.894(5)	Al(4)-O(11)	1.858(5)
Al(3)-O(12)	1.851(5)	Al(4)-O(12)	1.842(5)
<Al(3)-OH>	1.901	<Al(4)-OH>	1.903

a: x - 1, y, z; b: -x + 1, -y + 1, -z + 1.

TABLE 5. HYDROGEN BONDING IN THE CRYSTAL STRUCTURE OF "NICKELALUMITE"

D-H...A	D-A (Å)	D-H (Å)	H...A (Å)	∠D-H...A (°)
O(1)-H(7)...O(18)	2.822(5)	0.99(1)	1.88(1)	157.7(1)
O(2)-H(8)...O(14)	2.625(5)	0.99(1)	1.70(1)	153.6(1)
O(3)-H(9)...O(17)	2.765(4)	0.99(1)	1.79(1)	170.2(1)
O(4)-H(10)...O(18)	2.837(4)	0.99(1)	2.04(1)	137.1(1)
O(5)-H(11)...O(19)	2.998(5)	0.99(1)	2.02(1)	168.9(1)
O(6)-H(12)...O(19)	2.858(4)	0.99(1)	1.93(1)	156.6(1)
O(7)-H(13)...O(16)	2.782(4)	0.99(1)	1.81(1)	169.5(1)
O(8)-H(14)...O(15)	2.707(5)	0.99(1)	1.72(1)	174.0(1)
O(9)-H(15)...O(19)	2.944(5)	0.99(1)	1.98(1)	165.6(1)
O(10)-H(16)...O(13)	2.904(3)	0.99(1)	1.94(1)	164.1(1)
O(11)-H(17)...O(13)	2.698(4)	0.99(1)	1.73(1)	166.2(1)
O(12)-H(18)...O(13)	2.762(5)	0.99(1)	1.82(1)	157.4(1)
O(17)-H(1)...O(16)	2.926(5)	0.98(1)	2.03(1)	151.4(6)
O(17)-H(2)...O(14)	2.863(4)	0.98(1)	1.89(1)	174.5(5)
O(18)-H(3)...O(15)	2.870(5)	0.99(3)	1.95(1)	154.1(4)
O(18)-H(4)...O(15)	2.958(4)	0.97(2)	2.03(1)	158.9(4)
O(19)-H(5)...O(16)	2.869(5)	0.98(1)	1.91(1)	163.8(5)
O(19)-H(6)...O(17)	2.805(4)	0.98(1)	1.86(1)	162.8(1)
∠H(1)-O(17)-H(2)	109(2)			
∠H(3)-O(18)-H(4)	111(3)			
∠H(5)-O(19)-H(6)	109(2)			

TABLE 6. BOND-VALENCE\* TABLE FOR "NICKELALUMITE"

	M	Al	Al	Al	Al	S	Σ	Anion	H	H	H	H	H	H	H	H	H	H	H	H	H	H	Σ				
	(1)	(2)	(3)	(4)					(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	
O(1)	0.33	0.46						1.22 (OH)						0.84												2.06	
		0.43																									
O(2)	0.38	0.47						1.30 (OH)						0.78													2.08
		0.45																									
O(3)	0.36	0.49		0.38				1.23 (OH)								0.81											2.04
O(4)	0.32	0.50		0.43				1.25 (OH)								0.88											2.13
O(5)		0.60		0.52				1.12 (OH)								0.88											2.00
O(6)				0.57	0.56			1.13 (OH)									0.86										1.99
O(7)	0.36	0.48	0.42					1.26 (OH)									0.82										2.08
O(8)	0.32	0.51	0.45					1.28 (OH)										0.78									2.06
O(9)		0.59		0.54				1.13 (OH)										0.87									2.00
O(10)		0.61	0.53					1.14 (OH)											0.86								2.00
O(11)		0.62	0.57					1.19 (OH)												0.79							1.98
O(12)			0.58	0.60				1.18 (OH)													0.82						2.00
O(13)					1.52	1.52	O														0.14	0.21	0.18				2.05
O(14)					1.56	1.56	O		0.16					0.22													1.94
O(15)					1.50	1.50	O			0.14	0.12									0.22							1.98
O(16)					1.53	1.53	O	0.12			0.45									0.18							1.98
O(17)					0	(H <sub>2</sub> O)	0.88	0.84			0.17			0.19													1.98
O(18)					0	(H <sub>2</sub> O)		0.86	0.88			0.16			0.12												2.02
O(19)					0	(H <sub>2</sub> O)			0.85	0.83						0.12	0.14				0.13						2.07
Σ	2.07	3.12	3.09	3.07	3.08	6.11			1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

\* The bond-valence parameters for Ni<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup> and S<sup>6+</sup> are taken from Brown & Altermatt (1985).

"isolated" (SO<sub>4</sub>) group is well connected to the other fragments of the structure.

#### RELATED STRUCTURES

##### Structure and chemical formulae

The structure of "nickelalumite", ideally NiAl<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>3</sub>, is similar to those of alvanite, ideally

ZnAl<sub>4</sub>(VO<sub>3</sub>)<sub>2</sub>(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>2</sub> (Pertlik & Dunn 1990), and ankinovichite, ideally NiAl<sub>4</sub>(VO<sub>3</sub>)<sub>2</sub>(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>2</sub> (Karpenko *et al.* 2004a). All three structures are based on a positively charged interrupted sheet of octahedra of the form [□M<sup>2+</sup>M<sup>3+</sup><sub>4</sub>(OH)<sub>12</sub>]<sup>2+</sup> that is intercalated with layers of oxyanions and (H<sub>2</sub>O) groups; a similar structural motif occurs in minerals of the hydrotalcite group (Hawthorne *et al.* 2000). Related minerals for which there is no detailed crystal-structure information

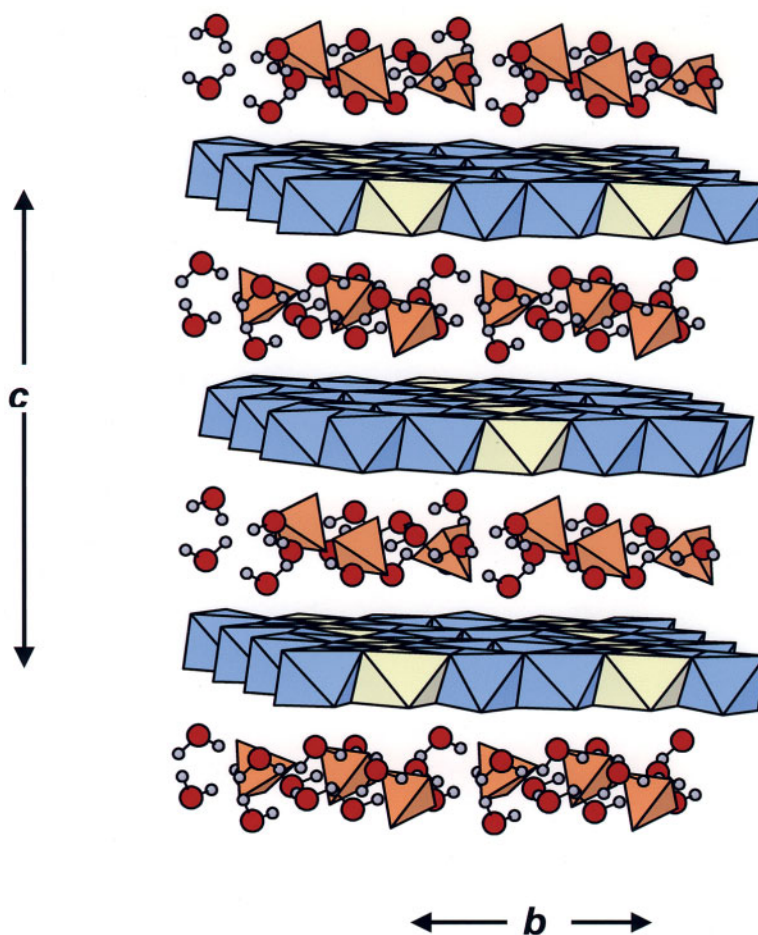


FIG. 2. Perspective view of the crystal structure of "nickelalumite". Legend as in Figure 1.

available are also listed in Table 1. Inspection of the formulae, cell dimensions and space group (where available) indicate that these minerals are all based on the same  $[\square M^{2+}Al_4(OH)_{12}]^{2+}$  sheet with  $M^{2+} = Ni, Zn$  and  $Cu^{2+}$ . However, there is considerable variation in cell size, presumably related to the arrangements of atoms in the much more variable layer that is intercalated between the  $[\square M^{2+}Al_4(OH)_{12}]^{2+}$  sheets. Moreover, the formula for mbobomkulite is not written correctly. The charge on the  $[\square M^{2+}Al_4(OH)_{12}]^{2+}$  sheet is  $2^+$  *pfu*. Hence the interstitial sheet must bear a charge of  $2^-$  *pfu*, and can be either  $(SO_4)$  or  $(NO_3)_2$  for a total charge of  $2^-$  in each case, but *not*  $[(NO_3),(SO_4)]_2$  as is written in Martini (1980) and Mandarino & Back (2004).

#### *Interstitial components*

Hawthorne & Schindler (2000) and Hawthorne & Sokolova (2002) have considered similar minerals as decorated sheet structures, and have provided hierarchical connections between similar structures that rationalize their chemical compositions in terms of bond topologies. The structures of Table 1 are interestingly different than those previously examined. The sheet unit of their structures is positively charged, rather than negatively charged or neutral, and the principal differences among these structures occur in the negatively charged interstitial complex. In the sheet structures examined by Hawthorne & Schindler (2000) and Hawthorne & Sokolova (2002), sheet units of their

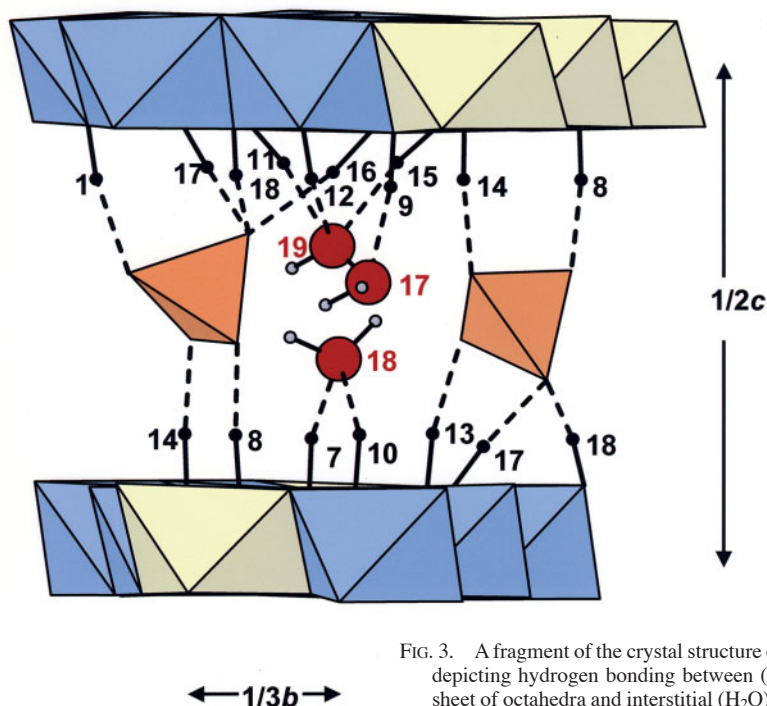
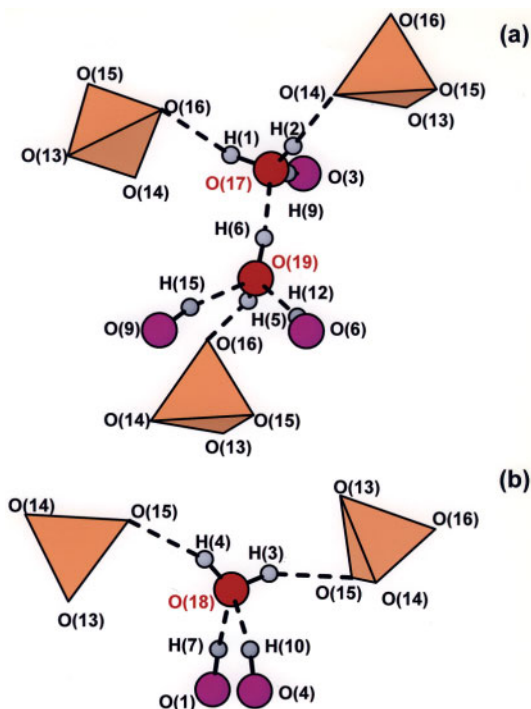


FIG. 3. A fragment of the crystal structure of "nickelalumite", depicting hydrogen bonding between (OH) groups of the sheet of octahedra and interstitial (H<sub>2</sub>O) and (SO<sub>4</sub>) groups. Legend as in Figure 1; hydrogen atoms of the (OH) groups are shown as black circles.

FIG. 4. Details of hydrogen bonding for (a) two (H<sub>2</sub>O) groups with central O(17) and O(19) oxygen atoms; (b) the (H<sub>2</sub>O) group with O(18) central oxygen atom. Legend as in Figure 1; oxygen atoms of the (OH) groups are shown as magenta circles.

structures are negatively charged, and the principal differences among these structures occur in these sheets as well as in the neutral or positively charged interstitial complexes. Let us examine this issue in terms of the ideas of Hawthorne (1985, 1990, 1997) and Schindler & Hawthorne (2001). The structures are considered as binary entities, a structural unit and an interstitial complex, and the interaction between these two components is examined using the valence-matching principle (Brown 1981, Hawthorne 1997, Schindler & Hawthorne 2001). The Lewis acidity of the [ $\square M^{2+}Al_4(OH)_{12}$ ]<sup>2+</sup> sheet is the charge on the sheet divided by the number of bonds emanating from the sheet. As there are 12 hydrogen bonds emanating from the sheet, the Lewis acidity of the sheet is  $2 / 12 = 0.167$  *vu* (valence units). Hence by the valence-matching principle, the Lewis basicity of the interstitial components of the layer must also be 0.167 *vu*. The Lewis basicity



of the  $(\text{SO}_4)^{2-}$  group, (0.17 *vu*, Brown 1981) matches the Lewis acidity of the  $[\square M^{2+} \text{Al}_4(\text{OH})_{12}]^{2+}$  sheet, and a stable structure is formed. If this is the case, why are there three  $(\text{H}_2\text{O})$  groups in the interstitial layer? Inspection of Table 6 shows that the  $(\text{H}_2\text{O})$  groups do not act as bond-valence transformers, but occur to carry bond valence from  $(\text{OH})$  groups distant from the  $(\text{SO}_4)$  groups to the simple anions of those groups [*e.g.*, see O(7) and O(10), Fig. 3].

Inspection of Table 1 shows that  $(\text{NO}_3)^{1-}$  also occurs as an interstitial oxyanion in mbobomkulite and hydro-mbobomkulite, and as discussed above, there are two  $(\text{NO}_3)^{1-}$  groups in these minerals, as distinct from one  $(\text{SO}_4)^{2-}$  in “nickelalumite” and chalcophyllite. Brown (2002) listed the Lewis basicity of the  $(\text{NO}_3)^{1-}$  group as 0.111 *vu*. There is significant mismatch between the Lewis acidity of the sheet, 0.167 *vu*, and the Lewis basicity of the interstitial  $(\text{NO}_3)^{1-}$  group, 0.111 *vu*. However, the structural details of these two minerals are not known, and it is possible that the  $(\text{H}_2\text{O})$  groups are acting as hydrogen-bond transformers and modulating the Lewis acidity of the bonds from the sheet to match with the Lewis basicity of the  $(\text{NO}_3)^{1-}$  group.

Consider next the  $[\text{VO}_3]^{1-}$  chain that occurs in alvanite and ankinovichite. In this chain, two simple anions of the  $(\text{VO}_4)^{3-}$  group bridge the length of the chain; their bond-valence requirements are satisfied, and the terminal anions each receive 1.5 *vu* from the central  $^{4+}\text{V}^{5+}$  cation. Assuming a mean interstitial coordination number of [3] for the terminal anions of the  $(\text{VO}_4)^{3-}$  group, the Lewis basicity of the  $[\text{VO}_3]^{1-}$  unit is thus  $(2.0 - 1.5) / 3 = 0.167$  *vu*, and the valence-matching principle is satisfied.

Thus  $(\text{SO}_4)^{2-}$ ,  $(\text{NO}_3)^{1-}$  and  $[\text{VO}_3]^{1-}$  satisfy the valence-matching principle for the  $[\square M^{2+} \text{Al}_4(\text{OH})_{12}]^{2+}$  sheet in these minerals. Could other oxyanions also fill this role? Note that  $(\text{SiO}_4)^{4-}$ ,  $(\text{BO}_3)^{3-}$ ,  $(\text{PO}_4)^{3-}$  and  $(\text{BO}_4)^{5-}$  have Lewis basicities of 0.33, 0.33, 0.25 and 0.42 *vu*, respectively, and hence cannot occur as interstitial species, as they cannot match the Lewis acidity of the  $[\square M^{2+} \text{Al}_4(\text{OH})_{12}]^{2+}$  sheet. However, the Lewis acidity of the  $[\square M^{2+} \text{Al}_4(\text{OH})_{12}]^{2+}$  could be modified by substitution of other cations of different valence for either Ni or Al. Replacement of Ni by a trivalent cation would change the Lewis acidity of the

sheet to  $3 / 12 = 0.25$  *vu*. This matches the Lewis basicity of the  $(\text{PO}_4)^{3-}$  group, suggesting that the composition  $[\text{Fe}^{3+} \text{Al}_4(\text{OH})_{12}](\text{PO}_4)(\text{H}_2\text{O})_3$  could be a stable phase with the “nickelalumite” structure; however, the chemical study of Karpenko *et al.* (2004b) shows no significant Fe or P to be present. Replacement of Al by tetravalent or pentavalent cations would also change the Lewis acidity of the sheet. Thus replacement of Al by  $\text{Ti}^{4+}$  would also produce a structure of composition  $[\text{NiAl}_3\text{Ti}^{4+}(\text{OH})_{12}](\text{PO}_4)(\text{H}_2\text{O})_3$  that obeys the valence-matching principle. Replacement of Al by  $\text{V}^{5+}$  will change the Lewis acidity of the sheet to  $4 / 12 = 0.33$  *vu*. This value matches the Lewis basicity of the  $(\text{SiO}_4)^{4-}$  group, suggesting the composition  $[\text{NiAl}_3\text{V}^{5+}(\text{OH})_{12}](\text{SiO}_4)(\text{H}_2\text{O})_3$  as a stable phase. Karpenko *et al.* (2004b) have examined variations in composition of “nickelalumite” from Kara–Chahgyr in South Kirgizia and have shown that significant amounts of V and Si are incorporated into the structure, presumably by the substitution  $\text{V}^{5+} + \text{Si} \rightarrow \text{Al} + \text{S}^{6+}$ .

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TABLE 7. CHEMICAL COMPOSITION AND UNIT FORMULA OF ‘NICKELALUMITE’

$\text{Al}_2\text{O}_3$ wt.%	39.94	Al <i>apfu</i>	3.99
$\text{SiO}_2$	0.17	Si	0.01
$\text{SO}_2$	12.16	S	1.00
$\text{V}_2\text{O}_5$	0.29	V	0.02
NiO	8.00	Ni	0.55
ZnO	6.21	Zn	0.39
FeO	0.15	Fe	0.01
$\text{H}_2\text{O}^*$	31.87	H	18.00
Total	98.79		

\* calculated from structure refinement.



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