

## BRIEF COMMUNICATION

The Synthesis and Characterization of a One-Dimensional Aluminophosphate:  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$ Martin P. Attfield,\* Russell E. Morris,\* Izya Burshtein,† Charles F. Campana,‡ and Anthony K. Cheetham\*<sup>1</sup>

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$\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  (orthorhombic, *Pbcm*,  $a = 15.279(3)$  Å,  $b = 14.660(3)$  Å,  $c = 6.9470(10)$  Å,  $V = 1556.1(5)$  Å<sup>3</sup>, and  $Z = 4$ ) was prepared hydrothermally in a steel autoclave at 473 K. The structure was solved using room-temperature single-crystal X-ray diffraction data from 1544 observed reflections ( $I > 4\sigma(I)$ ),  $R(F^2) = 6.27\%$ ,  $R_w(F^2) = 16.14\%$ ,  $S(F^2) = 1.044$ .  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  contains  $[\text{Al}(\text{PO}_4)_2(\text{OH}^{4-})]_n$  chains that run parallel to the [001] direction, which are held together in a three-dimensional structure by their interaction with the sodium cations that reside in the channels between the chains. The structure is very similar to that of the mineral tancoite,  $\text{LiNa}_2\text{HAl}(\text{PO}_4)_2(\text{OH})$  © 1995 Academic Press, Inc.

## INTRODUCTION

The discovery of a series of microporous aluminum phosphates by Wilson *et al.* (1, 2) led the way to the synthesis of many novel zeolitic materials with interesting sorption and catalytic properties. Some of these materials adopt the same framework structures as those of naturally occurring or synthetic aluminosilicate zeolites, e.g.,  $\text{AlPO}_4\text{-37}$  (faujasite) (3) and  $\text{AlPO}_4\text{-34}$  (chabazite) (3), but others, e.g., VPI-5 (4), are unique. Further work has shown that aluminophosphates can be synthesized with one- and two-dimensional framework structures, e.g.,  $(\text{Et}_3\text{NH})\text{H}_2\text{AlP}_2\text{O}_8$  (5) and  $1.5[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{Al}_3\text{P}_4\text{O}_{16}$  (6), such structures having previously been found only in minerals. The charge-compensating cations in these structures are typically derivatives of organic amines. Unlike the aluminosilicates, which contain only tetrahedral Si and Al, the aluminophosphate framework may contain four-, five-, or six-coordinated aluminum.

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In this work we describe the preparation and crystal structure of a synthetic one-dimensional aluminophosphate,  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$ , in which the charge-compensating species are alkali metal cations, as is commonly found in aluminosilicates. The structure is closely related to that of tancoite,  $\text{LiNa}_2\text{HAl}(\text{PO}_4)_2(\text{OH})$ , a phosphate mineral discovered at the Tanco Mine, Bernic Lake, Manitoba (7).

## EXPERIMENTAL

$\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  was prepared hydrothermally, in a 25-ml capacity Teflon-lined steel autoclave, from a starting mixture containing  $\text{H}_3\text{PO}_3$  (2 g),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1 g), 1, 4-diazobicyclo[2.2.2.]octane (DABCO) (1 g) in 15 ml of deionized water. Solid NaOH was added until the pH of the solution was approximately 10. The reaction mixture was heated at 473 K for 4 days, removed from the oven, and allowed to cool to room temperature. The resulting solid product, which contained colorless, needle-like crystals, was recovered from the product mixture by suction filtration and dried in air.

A suitable crystal for structure determination was mounted on a CAD4-MACH diffractometer and room temperature diffraction data were collected, the details of which are outlined in Table 1. The orthorhombic cell constants were determined from the positions of 25 centered reflections and optimized by least-squares refinement; the resulting lattice parameters are given in Table 1. Data were collected in the  $\omega$ - $2\theta$  scanning mode. Three standard reflections were monitored throughout the data collection; no significant variation in intensity was noted. Data reduction was performed using the program XCAD4 (8).

The systematic absences were consistent with those of space groups  $P2_1ab$  (No. 29) and  $Pmca$  (No. 57), but

TABLE 1  
Crystal Data and Structure Refinement for  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$

Formula	$\text{Na}_8\text{Al}_2\text{P}_4\text{O}_{18}\text{H}_2$
$F_w$	651.78
Crystal system	Orthorhombic
Space group	$Pbcm$
$F(000)$	1280
$a$	15.279(3) Å
$b$	14.660(3) Å
$c$	6.9470(10) Å
$V$	1556.1(5) Å <sup>3</sup>
$Z$	4
$D_c$	2.782 Mg/m <sup>3</sup>
Radiation (Nickel filtered)	$\text{CuK}\alpha$ ( $\lambda = 1.54178$ Å)
Crystal size	0.49 × 0.04 × 0.03 mm
$\mu$	8.882 mm <sup>-1</sup>
No absorption correction	
$\theta$ Range	2.89° to 71.87°
$hkl$ Range	-1 to 18; -1 to 18; -1 to 8
No. of reflections	2081
No. of independent refs.	1544
$R_m$	0.0332
No. of parameters	175
$S$ ( $F^2$ )	1.044
$R$ ( $F^2$ ) [ $I > 4\sigma(I)$ ]	0.0627
$R_w$ ( $F^2$ ) [ $I > 4\sigma(I)$ ]	0.1614
$R$ ( $F^2$ ) (All data)	0.0772
$R_w$ ( $F^2$ ) (All data)	0.1773
Extinction coefficient	0.00047(13)
$\Delta\rho$ min/max	-1.266/1.821 eÅ <sup>-3</sup>
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1212P)^2 + 3.37P]$ where $P = 1/3[\max(0 \text{ or } F_o^2) + 2F_c^2]$

structure solution was possible only in the latter and the successful completion of the refinement validates this choice. The aluminum, phosphorus, and some of the sodium atomic positions were found using the direct-methods program SHELXTL4.2 (9); all remaining atoms were located from subsequent difference Fourier syntheses. None of the remaining peaks in the final difference Fourier synthesis could be refined as other atoms. The final cycle of least-squares refinement, against  $F^2$ , included anisotropic temperature factors for all non-H atoms; the hydrogen atoms' temperature factors were left unrefined.

All least-squares, Fourier, and subsidiary calculations were performed using SHELXL-93 (10). Complex neutral atom scattering factors were obtained from Ref. (11). Final fractional atomic coordinates, equivalent isotropic temperature factors, and selected bond distances and angles are given in Tables 2, 3, and 4.

#### DISCUSSION

The structure of  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  is shown in Fig. 1. It consists of infinite  $[\text{Al}(\text{PO}_4)_2(\text{OH})^{4-}]_n$  chains which run

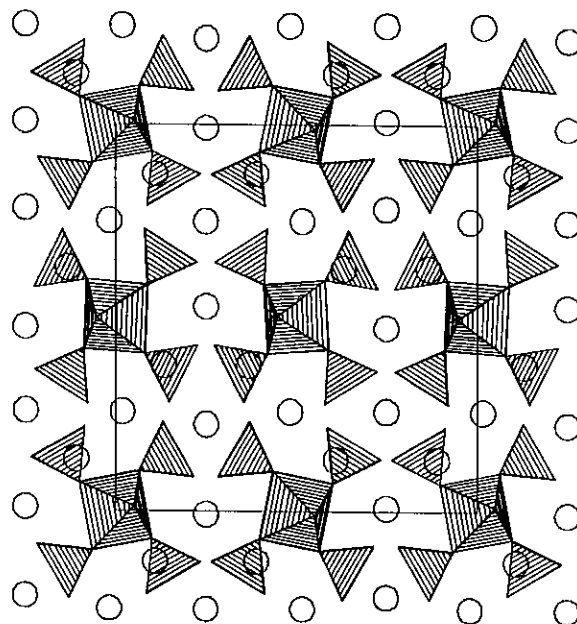


FIG. 1. The structure of  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  viewed along the [001] direction.

TABLE 2  
Final Atomic Coordinates and Equivalent Temperature Factors for  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$

Atom	$x$	$y$	$z$	$U_{eq}$ (Å <sup>2</sup> )
P(1)	0.3800(1)	0.8643(1)	0.25	0.011(1)
P(2)	0.1288(1)	0.6207(1)	0.25	0.011(1)
P(3)	0.6332(1)	0.6202(1)	-0.25	0.011(1)
P(4)	-0.1246(1)	0.8705(1)	-0.25	0.011(1)
Al(1)	0.5	1.0	0.0	0.010(1)
Al(2)	0.0	0.5	0.0	0.010(1)
Na(1)	0.1312(2)	0.3901(2)	0.25	0.020(1)
Na(2)	0.2546(1)	0.9825(1)	0.0200(3)	0.023(1)
Na(3)	0.5270(2)	0.75	0.0	0.023(1)
Na(4)	0.2225(2)	0.75	0.0	0.029(1)
Na(5)	-0.0086(2)	0.75	0.0	0.022(1)
Na(6)	0.2556(2)	0.25	0.0	0.048(1)
Na(7)	0.6253(2)	1.1325(2)	0.25	0.024(1)
O(1)	0.4264(3)	0.7735(3)	0.25	0.018(1)
O(2)	0.2801(3)	0.8535(3)	0.25	0.017(1)
O(3)	0.4046(2)	0.9202(2)	0.0673(4)	0.015(1)
O(4)	0.0891(3)	0.7158(3)	0.25	0.018(1)
O(5)	0.1022(2)	0.5646(2)	0.0708(4)	0.015(1)
O(6)	0.2286(3)	0.6295(3)	0.25	0.016(1)
O(7)	0.6389(3)	0.7245(3)	-0.25	0.017(1)
O(8)	0.7252(3)	0.5797(3)	-0.25	0.021(1)
O(9)	0.5833(2)	0.5889(2)	-0.0692(4)	0.015(1)
O(10)	-0.1324(3)	0.7658(3)	-0.25	0.015(1)
O(11)	-0.0721(2)	0.8983(2)	-0.0681(4)	0.013(1)
O(12)	-0.2149(3)	0.9133(3)	-0.25	0.020(1)
O(13)	-0.0104(3)	0.4491(3)	0.25	0.012(1)
O(14)	0.4979(3)	1.0518(3)	0.25	0.011(1)
H(1)	-0.0613(3)	0.4258(3)	0.25	0.05
H(2)	0.4501(3)	1.0842(3)	0.25	0.05

TABLE 3  
Selected Bond Distances (Å) for  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$

P(1)–O(1)	1.509(4)	P(1)–O(2)	1.534(4)
P(1)–O(3 <sup>a</sup> )	1.557(3)	P(1)–O(3)	1.557(3)
P(2)–O(4)	1.521(4)	P(2)–O(5)	1.547(3)
P(2)–O(6)	1.529(4)	P(2)–O(5 <sup>a</sup> )	1.547(3)
P(3)–O(7)	1.532(4)	P(3)–O(8)	1.526(4)
P(3)–O(9)	1.539(3)	P(3)–O(9 <sup>b</sup> )	1.539(3)
P(4)–O(10)	1.539(4)	P(4)–O(11)	1.552(3)
P(4)–O(11 <sup>b</sup> )	1.552(3)	P(4)–O(12)	1.516(4)
Al(1)–O(9 <sup>c</sup> )	1.884(3)	Al(1)–O(9 <sup>d</sup> )	1.884(3)
Al(1)–O(14)	1.896(2)	Al(1)–O(14 <sup>e</sup> )	1.896(2)
Al(1)–O(3 <sup>e</sup> )	1.927(3)	Al(1)–O(3)	1.927(3)
Al(2)–O(5 <sup>f</sup> )	1.891(3)	Al(2)–O(5)	1.891(3)
Al(2)–O(13)	1.897(2)	Al(2)–O(13 <sup>f</sup> )	1.897(2)
Al(2)–O(11 <sup>g</sup> )	1.913(3)	Al(2)–O(11 <sup>d</sup> )	1.913(3)
Na(1)–O(8 <sup>h</sup> )	2.239(5)	Na(1)–O(10 <sup>f</sup> )	2.286(4)
Na(1)–O(13)	2.328(5)	Na(1)–O(11 <sup>g</sup> )	2.390(3)
Na(1)–O(11 <sup>h</sup> )	2.390(3)	Na(1)–O(5 <sup>a</sup> )	2.878(4)
Na(1)–O(5)	2.878(4)		
Na(2)–O(2)	2.506(4)	Na(2)–O(5 <sup>d</sup> )	2.510(3)
Na(2)–O(8 <sup>j</sup> )	2.376(3)	Na(2)–O(3)	2.488(3)
Na(2)–O(6 <sup>k</sup> )	2.525(3)	Na(2)–O(9 <sup>c</sup> )	2.992(3)
Na(3)–O(1 <sup>h</sup> )	2.345(3)	Na(3)–O(1)	2.345(3)
Na(3)–O(7 <sup>l</sup> )	2.465(4)	Na(3)–O(7)	2.465(4)
Na(3)–O(9 <sup>d</sup> )	2.559(3)	Na(3)–O(9)	2.559(3)
Na(4)–O(2)	2.469(3)	Na(4)–O(2 <sup>h</sup> )	2.469(3)
Na(4)–O(6 <sup>k</sup> )	2.479(3)	Na(4)–O(6)	2.479(3)
Na(4)–O(4 <sup>k</sup> )	2.724(4)	Na(4)–O(4)	2.724(4)
Na(5)–O(4)	2.344(3)	Na(5)–O(4 <sup>h</sup> )	2.344(3)
Na(5)–O(11 <sup>d</sup> )	2.428(3)	Na(5)–O(11)	2.428(3)
Na(5)–O(10)	2.578(3)	Na(5)–O(10 <sup>h</sup> )	2.578(3)
Na(6)–O(7 <sup>h</sup> )	2.400(3)	Na(6)–O(7 <sup>m</sup> )	2.400(3)
Na(6)–O(10 <sup>n</sup> )	2.571(4)	Na(6)–O(10 <sup>l</sup> )	2.571(4)
Na(7)–O(6 <sup>o</sup> )	2.234(5)	Na(7)–O(1 <sup>p</sup> )	2.212(5)
Na(7)–O(14)	2.278(4)	Na(7)–O(3 <sup>e</sup> )	2.380(3)
Na(7)–O(3 <sup>e</sup> )	2.380(3)		
O(13)–H(1)	0.849(5)	O(14)–H(2)	0.871(5)

Note. Key for Tables 3 and 4. Symmetry operations needed to produce equivalent atoms. (a)  $x, y, -z + 0.5$ ; (b)  $x, y, -z - 0.5$ ; (c)  $-x + 1, y + 0.5, z$ ; (d)  $x, -y + 1.5, -z$ ; (e)  $-x + 1, -y + 2, -z$ ; (f)  $-x, -y + 1, -z$ ; (g)  $-x, y - 0.5, z$ ; (h)  $-x + 1, -y + 1, -z$ ; (i)  $-x, y - 0.5, -z + 0.5$ ; (j)  $-x + 1, y + 0.5, -z - 0.5$ ; (k)  $x, -y + 1.5, z - 0.5$ ; (l)  $x, -y + 1.5, z + 0.5$ ; (m)  $-x + 1, -y + 1, z - 0.5$ ; (n)  $-x, y - 0.5, z$ ; (p)  $-x + 1, y + 0.5, -z + 0.5$ ; (q)  $-x + 1, y - 0.5, -z - 0.5$ .

parallel to the [001] direction. The  $[\text{Al}(\text{PO}_4)_2(\text{OH})_2]^{4-}_n$  chains contain  $\text{AlO}_4(\text{OH}_2)$  octahedra sharing *trans* vertices to form an infinite  $\text{MO}_5$  chain. Adjacent  $\text{AlO}_4(\text{OH})_2$  octahedra are bridged by two phosphate groups, via the sharing of two of each of the phosphate group's vertices, to form the  $[\text{Al}(\text{PO}_4)_2(\text{OH})_2]^{4-}_n$  chain as shown in Fig. 2. The  $[\text{Al}(\text{PO}_4)_2(\text{OH})_2]^{4-}_n$  chains are pseudo-body-centered, but the structure is of lower symmetry due to the arrangement of the Na atoms, as confirmed by use of the program MISSYM (12). The chains are held together in a three-dimensional structure, primarily by the interaction of the remaining two O atoms in the phosphate groups and the Na atoms [Na(2) to Na(6)] that lie in the channels between

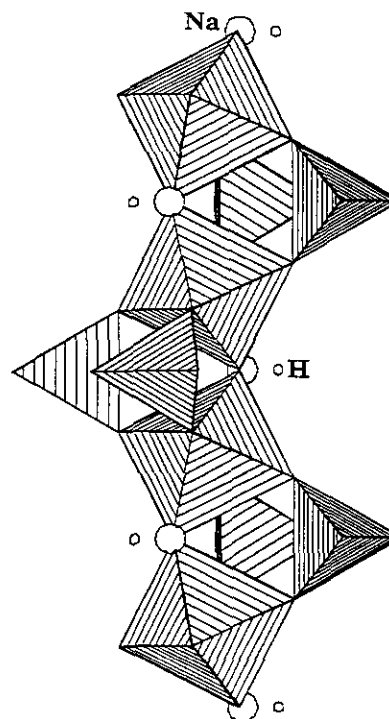


FIG. 2. The  $[\text{Al}(\text{PO}_4)_2(\text{OH})_2]^{4-}_n$  chain.

TABLE 4  
Selected Bond Angles (°) for  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$

O(1)–P(1)–O(2)	112.1(2)	O(1)–P(1)–O(3 <sup>a</sup> )	110.6(2)
O(2)–P(1)–O(3 <sup>a</sup> )	107.1(2)	O(1)–P(1)–O(3)	110.5(1)
O(2)–P(1)–O(3)	112.5(1)	O(3 <sup>a</sup> )–P(1)–O(3)	109.2(2)
O(4)–P(2)–O(5)	112.5(1)	O(6)–P(2)–O(5)	107.9(1)
O(4)–P(2)–O(5 <sup>a</sup> )	107.2(2)	O(6)–P(2)–O(5 <sup>a</sup> )	107.9(1)
O(5)–P(2)–O(5 <sup>a</sup> )	109.6(2)	O(4)–P(2)–O(6)	108.6(2)
O(8)–P(3)–O(7)	109.0(2)	O(8)–P(3)–O(9 <sup>b</sup> )	109.9(2)
O(7)–P(3)–O(9 <sup>b</sup> )	109.0(2)	O(8)–P(3)–O(9)	109.9(2)
O(7)–P(3)–O(9)	110.0(2)	O(9)–P(3)–O(9 <sup>b</sup> )	109.4(2)
O(12)–P(4)–O(10)	107.6(1)	O(12)–P(4)–O(11)	111.2(2)
O(10)–P(4)–O(11)	111.2(2)	O(10)–P(4)–O(11 <sup>b</sup> )	107.6(1)
O(12)–P(4)–O(11 <sup>b</sup> )		O(11)–P(4)–O(11 <sup>b</sup> )	109.1(2)
	180		
O(9 <sup>c</sup> )–Al(1)–O(9 <sup>d</sup> )	93.14(14)	O(9 <sup>c</sup> )–Al(1)–O(14)	89.86(14)
O(9 <sup>d</sup> )–Al(1)–O(14)	86.86(14)	O(9 <sup>c</sup> )–Al(1)–O(14 <sup>e</sup> )	93.14(14)
O(9 <sup>d</sup> )–Al(1)–O(14 <sup>e</sup> )	91.67(12)	O(14)–Al(1)–O(14 <sup>e</sup> )	180
O(9 <sup>c</sup> )–Al(1)–O(3 <sup>e</sup> )	89.55(14)	O(9 <sup>d</sup> )–Al(1)–O(3 <sup>e</sup> )	88.33(12)
O(14)–Al(1)–O(3 <sup>e</sup> )	88.33(12)	O(14 <sup>e</sup> )–Al(1)–O(3 <sup>e</sup> )	90.45(14)
O(9 <sup>c</sup> )–Al(1)–O(3)	180	O(9 <sup>d</sup> )–Al(1)–O(3)	91.67(12)
O(3 <sup>e</sup> )–Al(1)–O(3)	89.55(14)	O(14)–Al(1)–O(3)	90.45(14)
O(14 <sup>e</sup> )–Al(1)–O(3)	180		
O(5 <sup>f</sup> )–Al(2)–O(5)	91.59(14)	O(5 <sup>f</sup> )–Al(2)–O(13)	88.41(14)
O(5)–Al(2)–O(13)	88.41(14)	O(5 <sup>f</sup> )–Al(2)–O(13 <sup>f</sup> )	91.59(14)
O(5)–Al(2)–O(13 <sup>f</sup> )	91.23(12)	O(13)–Al(2)–O(13 <sup>f</sup> )	180
O(5 <sup>f</sup> )–Al(2)–O(11 <sup>g</sup> )	88.15(14)	O(5)–Al(2)–O(11 <sup>g</sup> )	88.77(12)
O(13)–Al(2)–O(11 <sup>g</sup> )	91.23(12)	O(13 <sup>f</sup> )–Al(2)–O(11 <sup>g</sup> )	91.85(14)
O(5 <sup>f</sup> )–Al(2)–O(11 <sup>d</sup> )	88.15(14)	O(13)–Al(2)–O(11 <sup>d</sup> )	91.85(14)
O(13 <sup>f</sup> )–Al(2)–O(11 <sup>d</sup> )	91.23(12)	O(11 <sup>g</sup> )–Al(2)–O(11 <sup>d</sup> )	180
O(5)–Al(2)–O(11 <sup>d</sup> )			

Note. For key, see Table 3.

the  $[\text{Al}(\text{PO}_4)_2(\text{OH})^{4-}]_n$  chains. Further interchain linkages are provided by the remaining Na atoms [Na(1) and Na(7)], which lie between phosphate groups and are *cis* to the hydroxyl H atom (Fig. 2).

The bond distances in the almost regular tetrahedral phosphate groups agree well with those found for other phosphate entities; the mean P–O distance in  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  is 1.537 Å (standard deviation = 0.015), compared to 1.537 Å for  $(\text{Et}_3\text{NH})\text{H}_2\text{AlP}_2\text{O}_8$  (5) and 1.516 Å for  $\alpha$ -berlinite (13). The aluminum atoms are octahedrally coordinated by four O atoms and two hydroxyl groups, the mean Al–O distance being 1.901 Å (standard deviation = 0.015). The Na atoms show a wide range of coordination and bond distances; the five Na atoms that reside in the channels between chains [Na(2)–Na(6)] are six-coordinated (except Na(6), which is four-coordinated) with short bond distances to oxygen varying between 2.34 and 2.58 Å and long bonds varying in the range 2.72–2.99 Å. The two Na atoms [Na(1) and Na(7)] that are not in the channels both have five short bond distances to oxygen of order 2.21–2.39 Å, with Na(1) having an additional two longer bonds to oxygen at 2.88 Å.

Bond valence calculations (14), in addition to the atomic positions determined from the difference Fourier maps, confirm that the protons in the structure are connected to the Al–O–Al bridging oxygens, O(13) and O(14). All other atoms in the structure have their expected valence.

The  $[\text{M}(\text{TO}_4)_2\phi]$  chain ( $\phi$ , unspecified ligand) is a fairly common feature in minerals, as discussed by Hawthorne (15). The mineral tancoite,  $\text{LiNa}_2\text{HAl}(\text{PO}_4)_2(\text{OH})$  (15), has the same empirical formula and a similar structure to that described here. The only significant difference is in the positions of the Li and H atoms surrounding the chains which alters the symmetry of the structure. The fact that all the countercations in  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  are sodium ions, suggests the unit cell dimensions in directions perpendicular to the chain direction should be significantly larger, while the unit cell axis along the chain direction should be similar in length. This is seen to be the case:

#### Tancoite

$$a = 1/2a' = 6.948(2) \text{ \AA}$$

$$b = b' = 14.089(4)$$

$$c = 2c' = 14.065(34)$$

#### $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$

$$a' = 15.279(3) \text{ \AA}$$

$$b' = 14.660(3)$$

$$c' = 6.9470(10).$$

Sulfate and silicate analogues of the  $[\text{M}(\text{TO}_4)_2\phi]$  chain are also known. Examples of those with chain arrangements similar to that in  $\text{Na}_4\text{Al}(\text{PO}_4)_2(\text{OH})$  are discussed by Hawthorne (15) and include the minerals sideronatriite  $\text{Na}_2[\text{Fe}(\text{SO}_4)_2(\text{OH})] \cdot 3\text{H}_2\text{O}$  (16), metasideronatriite (I)  $\text{Na}_2[\text{Fe}(\text{SO}_4)_2(\text{OH})]$  (17), yftsite  $(\text{Y}, \text{Ln})_4(\text{F}, \text{OH})_6[\text{Ti}(\text{SiO}_4)_2\text{O}]$  (18), nenadkevichite  $(\text{Na}, \text{K})_{2-x}[(\text{Nb}, \text{Ti})\text{Si}_2\text{O}_6(\text{O}, \text{OH})] \cdot 2\text{H}_2\text{O}$  (19), and labuntsovite  $(\text{K}, \text{Ba}, \text{Na})[(\text{Ti}, \text{Nb})\text{Si}_2\text{O}_6(\text{O}, \text{OH})] \cdot 3/4\text{H}_2\text{O}$  (20). The  $[(\text{Ti}, \text{Nb})\text{Si}_2\text{O}_6(\text{O}, \text{OH})]^{n-}$  chains in the latter two minerals behave slightly differently than the others as they actually polymerize, through the O atoms of the silicate groups, to form a three-dimensional framework. Minerals are also known which contain layers of  $[\text{M}(\text{TO}_4)_2\phi]$  chains, as opposed to the three-dimensional arrangement found in the materials discussed previously. The layers of chains are held together by  $\text{M}^{2+}\text{O}_2(\text{H}_2\text{O})_4$  octahedra. Examples of these minerals are the phosphates jahnsite  $\text{CaMnMg}_2[\text{Fe}(\text{PO}_4)_2(\text{OH})]_2 \cdot 8\text{H}_2\text{O}$  (21), overite  $\text{Ca}_2\text{Mg}_2[\text{Al}(\text{PO}_4)_2(\text{OH})]_2 \cdot 8\text{H}_2\text{O}$  (22), and segelerite  $\text{Ca}_2\text{Mg}_2[\text{Fe}(\text{PO}_4)_2(\text{OH})]_2 \cdot 8\text{H}_2\text{O}$  (22).

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