

Natropalermoite, $\text{Na}_2\text{SrAl}_4(\text{PO}_4)_4(\text{OH})_4$, a new mineral isostructural with palermoite, from the Palermo No. 1 mine, Groton, New Hampshire, USA

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ABSTRACT

Natropalermoite, ideally $\text{Na}_2\text{SrAl}_4(\text{PO}_4)_4(\text{OH})_4$, the Na-analogue of palermoite, is a new mineral from the Palermo No. 1 mine, Groton, New Hampshire, USA. Associated minerals are palermoite, eosphorite and quartz. Natropalermoite crystals are prismatic with striations parallel to the direction of elongation (the a axis) up to $200\ \mu\text{m} \times 50\ \mu\text{m} \times 45\ \mu\text{m}$ in size. The mineral is colourless, transparent with a white streak and vitreous lustre and is visually indistinguishable from palermoite. It is brittle with subconchoidal fracture and has a Mohs hardness of 5.5. Cleavage is perfect on $\{001\}$, fair on $\{100\}$ and no parting was observed. The calculated density is $3.502\ \text{g cm}^{-3}$. Natropalermoite is biaxial (–), $\alpha = 1.624(1)$, $\beta = 1.641(1)$, $\gamma = 1.643(1)$ (589 nm), $2V_{\text{meas}} = 43(4)^\circ$, $2V_{\text{calc}} = 38^\circ$. An electron microprobe analysis yielded an empirical formula (based on 20 O apfu) of $(\text{Na}_{1.69}\text{Li}_{0.31})_{\Sigma 2.00}(\text{Sr}_{0.95}\text{Mg}_{0.04}\text{Ca}_{0.02}\text{Ba}_{0.01})_{\Sigma 1.02}(\text{Al}_{3.82}\text{Mn}_{0.03}\text{Fe}_{0.03})_{\Sigma 3.88}(\text{P}_{1.01}\text{O}_4)_4(\text{OH})_4$.

Natropalermoite is orthorhombic, space group $Imcb$, $a = 11.4849(6)$, $b = 16.2490(7)$, $c = 7.2927(4)$ Å, $V = 1360.95(17)$ Å³, $Z = 4$. Natropalermoite is isotypic with palermoite, but substitution of the larger Na for Li results in substantial increase of the b cell parameter. Four of the seven Na–O distances are longer than their equivalents in palermoite, resulting in a more regular 7-fold coordination polyhedron about Na. The eight strongest peaks in the calculated X-ray powder diffraction are [d_{calc} (Å), $I_{\text{rel}}\%$, (hkl)]: [3.128, 100, (321)], [4.907, 68, (121)], [3.327, 48, (022)], [4.689, 45, (220)], [3.078, 45, (202)], [2.453, 38, (242)], [2.636, 35, (411)], [2.174, 35, (422)].

KEYWORDS: natropalermoite, new mineral, phosphate, Palermo No. 1 mine, pegmatite.

Introduction

A new mineral species, natropalermoite, ideally $\text{Na}_2\text{SrAl}_4(\text{PO}_4)_4(\text{OH})_4$, was found in a sample from the Palermo No. 1 mine, Groton, New Hampshire. The name reflects the presence of sodium (sodium) and the structural isomorphism to palermoite. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2013-118). The holotype sample is deposited in the collections of the Mineral Museum of the University of Arizona,

Tucson, Arizona, USA, catalogue number 19735, and the RRUFF Project, deposition number R130092 (<http://rruff.info/R130092>). This paper describes the physical and chemical properties of natropalermoite and the characterization of the structure based on single-crystal X-ray diffraction data.

Sample description and experimental methods

Occurrence, physical and chemical properties and Raman spectra

Natropalermoite was found in a sample from the Palermo No. 1 mine, Groton, Grafton County, New Hampshire, USA which exploited a complex,

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FIG. 1. The sample on which natropalermoite was found.

phosphate-bearing granite pegmatite for mica, feldspar and beryl (Cameron *et al.*, 1954; Page and Larrabee, 1962). Associated minerals include palermoite, childrenite, lefontite, mixed iron oxides and quartz (Fig. 1). Natropalermoite is of secondary origin, formed as a result of hydrothermal alteration of primary triphylite pods in the core-margin zone of the pegmatite (Page and Larrabee, 1962; Segeler *et al.*, 1981). Palermoite in association with natropalermoite shows cores of near end-member composition with rims richer in Na, indicating that natropalermoite forms later than palermoite. The Palermo No. 1 mine was brought into the mineralogical spotlight by the host of secondary phosphate phases found there, and is the type locality for 12 phosphate species, not including natropalermoite: palermoite, whitlockite, goedkenite, schoonerite, bjarebyite, whitmoreite, wolfeite, xanthoxenite, foggite, samuelsonite, falsterite and nizamoffite (Kampf *et al.*, 2013 and references therein).

Natropalermoite crystals are prismatic, up to $200\ \mu\text{m} \times 50\ \mu\text{m} \times 45\ \mu\text{m}$ in size, elongated and striated along the *a* axis (Fig. 2). In transmitted light, natropalermoite is colourless and transparent, with a vitreous lustre. It is brittle, has perfect cleavage on {001}, fair on {100} and no parting was observed. Fracture is sub-conchoidal to fibrous. Hardness was not measured but is most likely 5.5 by analogy with palermoite. Natropalermoite is non-pleochroic, biaxial (-), $\alpha = 1.624(1)$, $\beta = 1.641(1)$, $\gamma = 1.643(1)$ (589 nm), $2V_{\text{meas}} = 43(4)^\circ$, $2V_{\text{calc}} = 38^\circ$, dispersion $v > r$, medium to weak. Because of the paucity of crystals, no density was measured. The calculated density is $3.502\ \text{g cm}^{-3}$. Natropalermoite is insoluble in water and acetone.

The chemical composition of natropalermoite was determined using a CAMECA SX100 electron microprobe with beam conditions of 15 kV, 4 nA

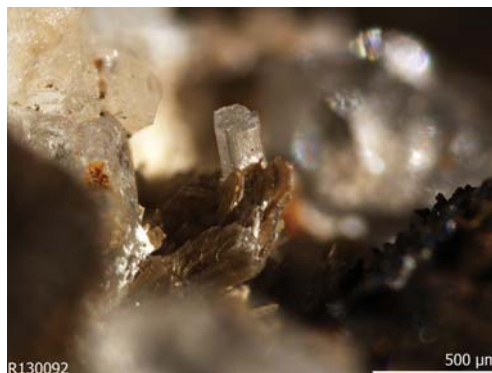


FIG. 2. Prismatic crystal of natropalermoite growing on greyish brown childrenite. Note weak striations parallel to the axis of elongation *a*. The top portion of this crystal was used for X-ray, chemistry and optical data collection.

and a beam diameter of $5\ \mu\text{m}$. Standards used were K-feldspar for Al, albite for Na, synthetic apatite for Ca and P, synthetic SrTiO_3 for Sr, rhodonite for Mn, forsterite for Mg, fayalite for Fe and baryte for Ba. The presence of OH was confirmed by both structural determination and Raman spectroscopic measurements (see below), and the amount of OH was estimated by stoichiometry from the crystal-structure refinement. Not enough material was available for the direct determination of Li_2O , which was estimated by stoichiometry from the crystal-structure refinement. An average of 10 spot analyses (Table 1) yielded an empirical formula of $(\text{Na}_{1.69}\text{Li}_{0.31})_{\Sigma 2.00}(\text{Sr}_{0.95}\text{Mg}_{0.04}\text{Ca}_{0.02}\text{Ba}_{0.01})_{\Sigma 1.02}(\text{Al}_{3.82}\text{Mn}_{0.03}\text{Fe}_{0.03})_{\Sigma 3.88}(\text{P}_{1.01}\text{O}_4)_4(\text{OH})_4$ based

TABLE 1. Microprobe data for natropalermoite, standard deviation in weight percent are indicated by numbers in parenthesis.

Constituent	wt.%	Range	Probe standard
Al_2O_3	28.6(2)	28.39–28.95	K-feldspar
Mn_2O_3	0.36(9)	0.17–0.50	Rhodonite
Fe_2O_3	0.35(4)	0.31–0.41	Fayalite
Na_2O	7.68(10)	7.56–7.87	Albite
Li_2O	0.69		*
MgO	0.26(3)	0.22–0.31	Forsterite
CaO	0.16(4)	0.11–0.20	Apatite, synthetic
SrO	14.5(4)	14.23–15.29	SrTiO_3
BaO	0.14(4)	0.10–0.21	Barite
P_2O_5	42.28(13)	42.06–42.46	Apatite, synthetic
H_2O	5.29		*
Total	100.29		

*Estimated from structure refinement stoichiometry.

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TABLE 2. Summary of crystal data and refinement results for natropalermoite.

Natropalermoite (R130092, New Hampshire)	
IMA-defined chemical formula	$\text{Na}_2\text{SrAl}_4(\text{PO}_4)_4(\text{OH})_4$
Effective structural formula	$(\text{Na}_{1.69}\text{Li}_{0.31})_{\Sigma 2.00}$ $(\text{Sr}_{0.95}\text{Mg}_{0.04}\text{Ca}_{0.02}\text{Ba}_{0.01})_{\Sigma 1.02}$ $(\text{Al}_{3.82}\text{Mn}_{0.03}\text{Fe}_{0.03})_{\Sigma 3.88}$ $(\text{P}_{1.01}\text{O}_4)_4(\text{OH})_4$
Space group	<i>Imcb</i>
<i>a</i> (Å)	11.4849(6)
<i>b</i> (Å)	16.2490(7)
<i>c</i> (Å)	7.2927(4)
<i>V</i> (Å ³)	1360.95(17)
<i>Z</i>	4
ρ_{calc} (g cm ⁻³)	3.328
λ (Å)	0.71073
μ (mm ⁻¹)	4.73
2 θ range for data collection	<65.19°
No. of reflections collected	5970
No. of independent reflections	1257
No. of reflections with $I > 2\sigma(I)$	1132
No. of parameters refined	86
R(int)	0.0271
Final R_1 , wR_2 factors [$I > 2\sigma(I)$]	0.0207, 0.0564
Final R_1 , wR_2 factors (all data)	0.0252, 0.0564
Goof	1.034

on 20 O atoms per formula unit (apfu), which can be simplified to $\text{Na}_2\text{SrAl}_4(\text{PO}_4)_4(\text{OH})_4$.

The Raman spectrum of natropalermoite was collected from a randomly oriented crystal on a Thermo Almega microRaman system, using a 532-nm solid-state laser with a thermoelectric cooled CCD detector. The laser is partially polarized with 4 cm⁻¹ resolution and a spot size of 1 μm .

X-ray crystallography

Due to the paucity of material, powder X-ray diffraction data of natropalermoite (Table 2) were calculated from the determined structure using the program *XPOW* (Downs *et al.*, 1993).

Single-crystal X-ray diffraction data (Table 3) of natropalermoite were collected using a Bruker X8

TABLE 3. Calculated powder X-ray diffraction data for natropalermoite.

<i>I</i> _{rel}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>
33	6.653	0	1	1
14	5.743	2	0	0
68	4.907	1	2	1
45	4.689	2	2	0
20	4.347	2	1	1
32	3.399	1	1	2
48	3.327	0	2	2
100	3.128	3	2	1
45	3.078	2	0	2
17	2.968	0	5	1
19	2.637	2	5	1
35	2.636	4	1	1
21	2.606	3	1	2
22	2.479	1	6	1
38	2.453	2	4	2
24	2.396	4	3	1
27	2.171	0	6	2
35	2.174	4	2	2
17	2.031	0	8	0
13	1.843	4	1	3
31	1.663	0	4	4
15	1.658	4	8	0
15	1.611	4	5	3

Only calculated lines with $I_{\text{calc}} > 12$ are included. The strongest lines are given in bold.

APEX2 CCD diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation, with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed based on an orthorhombic unit cell. The intensity data were corrected for X-ray absorption using the Bruker program *SADABS*. *SHELX97* (Sheldrick 2008) was used for structure determination and refinement. The final crystal structure was solved and refined with space group *Imcb* resulting in $R_1 = 0.021$, $wR_2 = 0.0564$ for 1257 reflections with $F_o > 4\sigma(F_o)$. Final atom positions, occupancies and isotropic and anisotropic displacement parameters are given in Table 4, and selected bond distances are given in Table 5. For the refinement, site occupancies were refined for sites Sr and Na to account for substitution of Ca for Sr and Li for Na, respectively, ignoring other trace elements. The refinement showed 0.04 Ca apfu replacing Sr and 0.05 Li apfu replacing Na, compared to 0.02 Ca apfu measured and 0.16 Li apfu estimated from the microprobe analysis.

TABLE 4. Coordinates and displacement parameters for natropalermoite. Assumed average position of H2 is included for completeness.

Atom	x	y	z	U_{eq}	Occ. (<1)	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sr	0.25	0.5	0.5	0.01173 (10)	0.962(4)	0.01685 (17)	0.01113 (15)	0.00722 (14)	0	0	0
Ca	0.25	0.5	0.5	0.01173 (10)	0.038(4)	0.01685 (17)	0.01113 (15)	0.00722 (14)	0	0	0
Li	0.5	0.28990 (6)	0.24295 (14)	0.0185 (3)	0.047(6)	0.0322 (7)	0.0071 (5)	0.0162 (5)	0	0	0.0013 (3)
Na	0.5	0.28990 (6)	0.24295 (14)	0.0185 (3)	0.953(6)	0.0322 (7)	0.0071 (5)	0.0162 (5)	0	0	0.0013 (3)
P1	0.25	0.28936 (3)	0.5	0.00567 (12)		0.0051 (2)	0.0057 (2)	0.0062 (2)	0	0.00005 (16)	0
P2	0	0.46228 (3)	0.76986 (7)	0.00647 (12)		0.0077 (2)	0.0063 (2)	0.0054 (2)	0	0	-0.00014 (16)
Al	0.13198 (4)	0.37236 (3)	0.13801 (6)	0.00707 (11)		0.0054 (2)	0.0074 (2)	0.0084 (2)	-0.00058 (14)	0.00156 (15)	-0.00068 (14)
O1	0.14274 (9)	0.26571 (7)	0.03332 (14)	0.0092 (2)		0.0069 (5)	0.0080 (5)	0.0128 (5)	0.0010 (3)	0.0001 (4)	-0.0018 (4)
O2	0.22871 (9)	0.34742 (7)	0.33754 (14)	0.0094 (2)		0.0096 (5)	0.0106 (5)	0.0080 (5)	-0.0011 (4)	-0.0012 (4)	0.0028 (4)
O3	0	0.40980 (10)	0.6008 (2)	0.0141 (3)		0.0210 (8)	0.0141 (7)	0.0073 (7)	0	0	-0.0034 (5)
O4	0	0.40464 (9)	0.9440 (2)	0.0101 (3)		0.0156 (8)	0.0078 (7)	0.0070 (6)	0	0	0.0014 (5)
O5	0.11018 (9)	0.48323 (7)	0.22553 (14)	0.0091 (2)		0.0067 (5)	0.0093 (4)	0.0111 (5)	0.0000 (3)	0.0000 (4)	-0.0001 (4)
O-H1	0	0.34231 (9)	0.2617 (2)	0.0074 (3)		0.0066 (6)	0.0096 (6)	0.0059 (6)	0	0	0.0002 (5)
O-H2	0.25	0.41142 (11)	0	0.0124 (3)		0.0149 (8)	0.0089 (7)	0.0136 (7)	0	0.0085 (6)	0
H1	0	0.359 (3)	0.376 (5)	0.037 (10)							
H2*	0.25	0.47	0								

*Assumed average position of H2.

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TABLE 5. Selected bond distances (Å) in natropalermoite.

Sr	-O5 ×4	2.5806(10)	P1	-O2 ×2	1.5341 (11)
	-O2 ×4	2.7587(11)		-O1 ×2	1.5419 (11)
	Avg.	2.6697		Avg.	1.5380
Na	-OH1	2.1487(16)	P2	-O3	1.4990(16)
	-O3	2.2568(19)		-O5 ×2	1.5447(11)
	-O4	2.3095(18)		-O4	1.5778(16)
	-O1 ×2	2.4831(13)		Avg.	1.5427
	-O1 ×2	2.6270(13)			
	Avg.	2.4248			
Al	-OH2	1.8036(8)			
	-OH1	1.8303(9)			
	-O2	1.8751(11)			
	-O1	1.8977(12)			
	-O5	1.9277(12)			
	-O4	2.1390(12)			
	Avg.	1.9122			

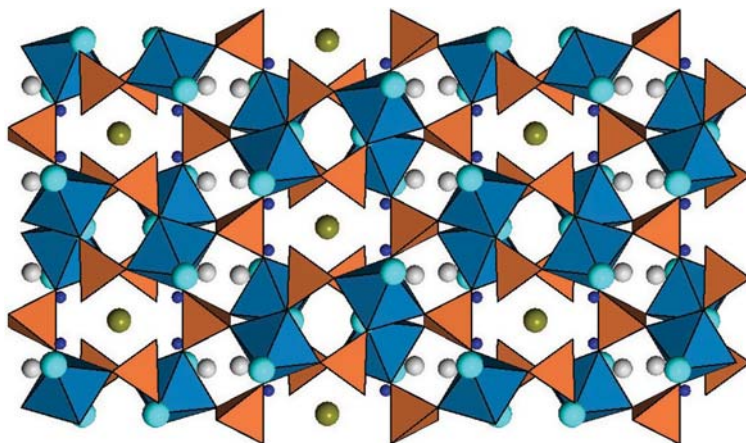


FIG. 3. The crystal structure of natropalermoite, viewed along [100]. Grey, golden, sky blue and blue spheres represent Na, Sr, OH and H respectively. Orange tetrahedra are PO_4 groups and cerulean octahedra are AlO_6 groups.

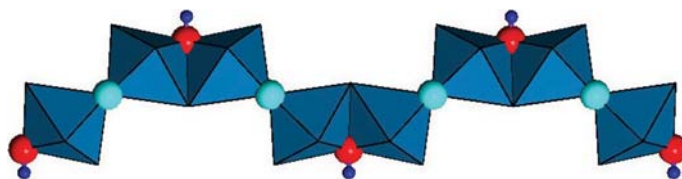


FIG. 4. The zigzag chain of $\text{Al}_2\text{O}_7(\text{OH})_3$ dimers, looking down [010], [100] is horizontal. Cerulean octahedra are AlO_6 octahedra, red spheres represent O-H1, while light-blue spheres represent the OH2 group.

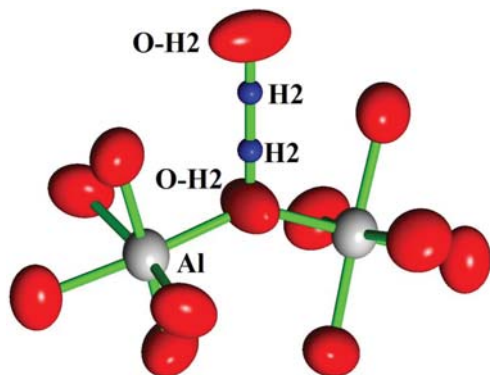


FIG. 5. The Al dimer, with each atom shown as an ellipsoid of 99.999% probability. In particular note the elongated O–H2 ellipsoid indicating significant libration in the direction perpendicular to the Al–O–Al plane. The H2 position is the average likely position that must also have significant motion related to riding on O–H2 and repulsion from its neighbouring H2 atom.

Discussion

Crystal structure

Natropalermoite, $\text{Na}_2\text{SrAl}_4(\text{PO}_4)_4(\text{OH})_4$, is isostructural with palermoite, $\text{Li}_2\text{SrAl}_4(\text{PO}_4)_4(\text{OH})_4$, the structure of which was described by Moore and

Araki (1975). The natropalermoite structure contains five non-H cation sites: one each for Sr^{2+} , Na^+ , Al^{3+} , and two for P^{5+} (P1 and P2), and two non-equivalent H atoms. The crystal structure of natropalermoite is shown in Fig. 3. Two $\text{AlO}_4(\text{OH})_2$ octahedra form edge-sharing $\text{Al}_2\text{O}_7(\text{OH})_3$ dimers. These dimers are corner-linked to one another through (OH)₂, forming infinite zigzag chains along [100] (Fig. 4). The chains themselves are hexagonal close-packed, accounting for the pseudo-hexagonal prismatic morphology of the crystals. The zigzag chains are interconnected by PO_4 groups, which share all four O atoms with Al. Sodium and Sr atoms are 7- and 8-coordinated, respectively, and are located in two distinct types of channels parallel to [100]. When viewed along [100], the Na atoms are staggered within their respective channels, forming a ‘double-stack’ arrangement, while the Sr atoms are ‘single-file’ (Fig. 3). Most remarkably, due to the substitution of Na for Li, the unit cell *b* dimension of natropalermoite is significantly longer than that of palermoite: the larger Na atoms increase the width of their accommodating channels in the [010] direction, lengthening the overall *b* dimension of the unit cell. As the channels widen along [010], the angle between the two octahedra in the $\text{Al}_2\text{O}_7(\text{OH})_3$ dimer narrows, resulting in the

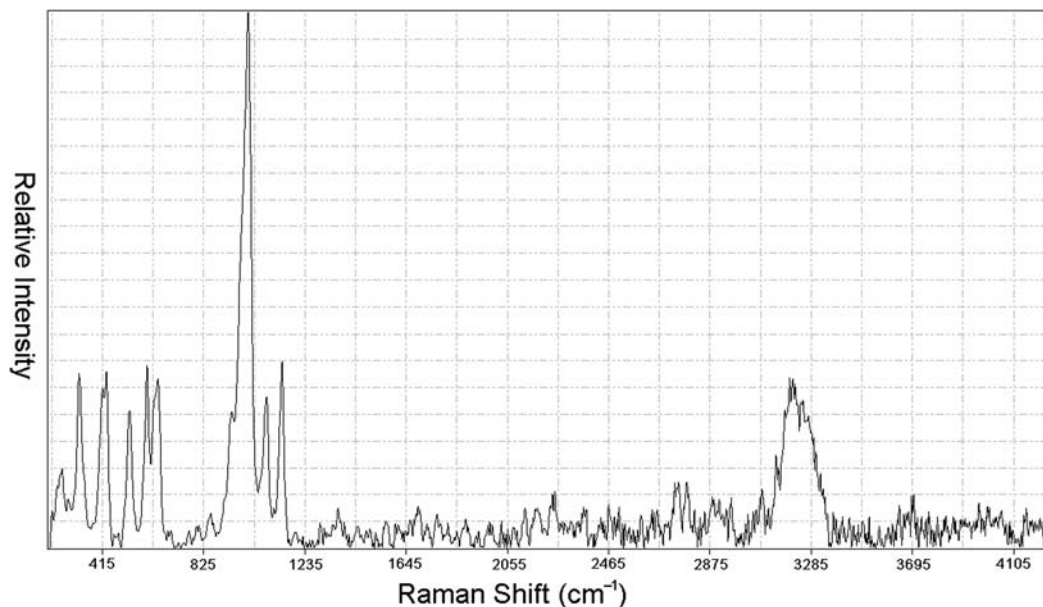


FIG. 6. Raman spectrum of natropalermoite, showing acoustic and optical modes (left) and a broad band at 3215 cm^{-1} attributed to O–H stretching.

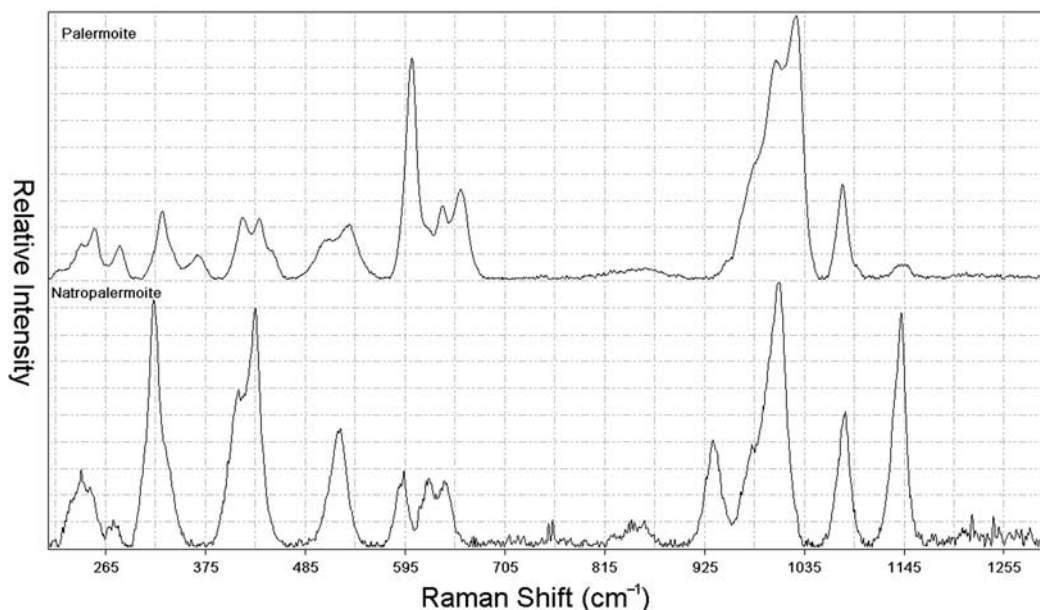


FIG. 7. The Raman spectrum of natropalermoite (*lower*) compared with that of palermoite (*upper*).

shortening of the $a = 11.4849(6)$ and $c = 7.2927(4)$ Å dimensions of natropalermoite versus those of palermoite: $a = 11.577(1)$ and $c = 7.3276(7)$ Å. The b cell edge is the distinguishing crystallographic parameter which can be used to differentiate natropalermoite from palermoite.

The position of the H1 atom was determined during the structure refinement, indicating the presence of OH in natropalermoite. The H1 atom is bonded to O–H1, which is one of the two atoms in the shared edge of the $\text{Al}_2\text{O}_7(\text{OH})_3$ dimer. Coordinates for the second H2 atom could not be refined, however valence considerations point to O–H2, the bridging atom linking dimers. The average position of atom H2 was assumed to be $x = 0.25, y = \sim 0.47, z = 0$. This position must represent an average because O–H2, which links two AlO_6 octahedra, undergoes considerable libration, demonstrated by its elongated displacement ellipsoid, oriented perpendicular to the Al–O–Al plane (Fig. 5), making it extremely difficult to observe the electron density associated with the H2 atom.

Natropalermoite is structurally related to carminite, $\text{PbFe}_2^{3+}(\text{AsO}_4)_2(\text{OH})_2$. The structures of natropalermoite and carminite contain the same zig-zag chain of $M_2\text{O}_7(\text{OH})_3$ edge-sharing dimers linked by OH2, with individual chains interconnected by TO_4 tetrahedra (Moore and Araki, 1975). The difference between natropalermoite and

carminite lies in accommodation of Na in natropalermoite. Two equivalent Na atoms of site-symmetry m in natropalermoite take the place of the single Pb2 atom of site-symmetry $2/m$ in carminite. For a detailed comparison between palermoite and carminite, see Moore and Araki (1975).

Raman spectroscopy

The Raman spectrum of a natropalermoite crystal in unknown orientation is shown in Fig. 6. The band at 3215 cm^{-1} can be attributed to O–H stretching vibrations. Bands between 1142 cm^{-1} and 524 cm^{-1} are interpreted as P–O stretching and bending vibrations. Bands between 295 and 462 cm^{-1} are interpreted as metal-oxygen stretching vibrations. The broad bands below 295 cm^{-1} are interpreted as translational lattice vibrations. The Raman spectra of natropalermoite and palermoite are virtually indistinguishable (Fig. 7).

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