



Article

Ammoniotinsleyite, $(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, a new mineral species from the guano deposit at Pabellón de Pica, Iquique Province, Chile

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Abstract

The new leucophosphate-group mineral ammoniotinsleyite is found in a guano deposit located on the Pabellón de Pica Mountain, Iquique Province, Tarapacá Region, Chile. Associated minerals are halite, gypsum, salammoniac and clay minerals. Ammoniotinsleyite occurs as pink to pale violet globular aggregates up to 3 mm across with individual single crystals ~10–15 µm. The mineral is brittle. Its Mohs hardness is 4. $D_{\text{meas.}} = 2.42(2) \text{ g cm}^{-3}$ and $D_{\text{calc.}} = 2.451 \text{ g cm}^{-3}$. The IR spectrum shows the presence of NH_4^+ and PO_4^{3-} groups and H_2O molecules. Ammoniotinsleyite is optically biaxial (+), $\alpha = 1.557(2)$, $\beta = 1.559$ (calc.), $\gamma = 1.563(2)$ ($\lambda = 589 \text{ nm}$); and $2V_{\text{meas.}} = 75(10)^\circ$. The chemical composition (K, Mg, Ca, Al, Fe and P from electron-microprobe data; H, C and N measured by gas chromatography on products of ignition at 1200°C; wt.%) is: $(\text{NH}_4)_2\text{O}$ 7.25, K_2O 1.50, MgO 0.42, CaO 0.34, Al_2O_3 29.91, Fe_2O_3 2.36, P_2O_5 43.97, H_2O 14.89, CO_2 below detection limit, total 100.64. The empirical formula is $[(\text{NH}_4)_{0.88}\text{K}_{0.10}\text{Ca}_{0.02}]_{\Sigma 1.00}(\text{Al}_{1.86}\text{Fe}_{0.09}\text{Mg}_{0.03})_{\Sigma 1.98}(\text{PO}_4)_{1.96}(\text{OH})_{1.05}\cdot 2.11\text{H}_2\text{O}$. The idealised formula is $(\text{NH}_4)_2\text{Al}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$. The crystal structure of ammoniotinsleyite was refined based on powder X-ray diffraction data, using the Rietveld method. The final agreement factors are: $R_p = 0.0071$, $R_{\text{wp}} = 0.0093$ and $R_{\text{obs}} = 0.0167$. The new mineral is isostructural with tinsleyite, spheniscidite and leucophosphate. It is monoclinic, space group $P2_1/n$, $a = 9.5871(1) \text{ \AA}$, $b = 9.6089(1) \text{ \AA}$, $c = 9.6467(2) \text{ \AA}$, $\beta = 103.4461(8)^\circ$, $V = 864.31(2) \text{ \AA}^3$ and $Z = 4$. The strongest reflections of the powder X-ray diffraction pattern [$d, \text{ \AA}(I, \%) (hkl)$] are: 7.56(23)($\bar{1}01$), 6.71(79)(011, 110), 5.947(100)(101, $\bar{1}11$), 4.676(36)(002, 200), 3.032(28)($\bar{1}13$, 031, 130), 2.958(25)($\bar{2}22$, 310, $\bar{1}31$) and 2.635(29)($\bar{2}31$).

Keywords: ammoniotinsleyite, new mineral, leucophosphate group, phosphate, crystal structure, guano, Pabellón de Pica, Chile

(Received 8 April 2020; accepted 30 May 2020; Accepted Manuscript published online: 5 June 2020; Associate Editor: Ian T. Graham)

Introduction

The guano deposit situated on Pabellón de Pica Mountain, 1.5 km south of Chanabaya village, Iquique Province, Tarapacá Region, Chile (20°55'S, 70°08'W) belongs to the famous belt of guano occurrences of the Atacama Desert stretching along the northern coast of Chile (Ericksen, 1981; Pankhurst and Herve, 2007; Appelton and Nothold, 2002; Bojar *et al.*, 2010). Pabellón de Pica is one of the most interesting mineralogical occurrences in this area being the type locality of several nitrogen-bearing and organic minerals: ammineite, $\text{CuCl}_2(\text{NH}_3)_2$ (Bojar *et al.*, 2010), joanneumite, $\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2$ (Bojar *et al.*, 2017), chana-bayaite, $\text{Cu}_4(\text{N}_3\text{C}_2\text{H}_2)_4(\text{NH}_3)_4\text{Cl}_2(\text{Cl}, \text{OH})_2\cdot \text{H}_2\text{O}$ (Chukanov *et al.*, 2015a), shilovite, $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ (Chukanov *et al.*, 2015b), antipinite, $\text{KNa}_3\text{Cu}_2(\text{C}_2\text{O}_4)_4$ (Chukanov *et al.*, 2015c), möhnite, $(\text{NH}_4)\text{K}_2\text{Na}(\text{SO}_4)_2$ (Chukanov *et al.*, 2015d) and triazolite, $\text{NaCu}_2(\text{N}_3\text{C}_2\text{H}_2)_2(\text{NH}_3)_2\text{Cl}_3\cdot 4\text{H}_2\text{O}$ (Chukanov *et al.*, 2018).

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Cite this article: Chukanov N.V., Möhn G., Pekov I.V., Zubkova N.V., Ksenofontov D.A., Belakovskiy Dmitry I., Vozchikova S.A., Britvin S.N. and Desor J. (2020) Ammoniotinsleyite, $(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, a new mineral species from the guano deposit at Pabellón de Pica, Iquique Province, Chile. *Mineralogical Magazine* 84, 705–711. <https://doi.org/10.1180/mgm.2020.45>

Specimens with the new mineral ammoniotinsleyite, ideally $(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, were collected at Pabellón de Pica in 2019 by one of the authors (G.M.). Ammoniotinsleyite is named as the ammonium analogue of tinsleyite, $\text{KAl}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, with prevailing of NH_4^+ over K^+ . The new mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2019-128, Chukanov *et al.*, 2020). The holotype specimen is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5510/1.

Occurrence, general appearance and physical properties

Ammoniotinsleyite occurs in a guano deposit on the lower part of the steep southern slope of Pabellón de Pica Mountain. It forms globular, partly porous polycrystalline aggregates up to 3 mm across in cavities of granular aggregates of associated minerals (Figs 1 and 2). Sizes of elongate single-crystal fragments are below 10–15 µm. Associated minerals are halite, gypsum, salammoniac and clay minerals.

Aggregates of ammoniotinsleyite are translucent to transparent. The colour is pink to pale violet. The lustre is vitreous. The



Fig. 1. Aggregates of ammoniotinsleyite (pink) in association with gypsum and halite. FOV 0.7 mm. Photo: A.V. Kasatkin, cotype specimen.

streak is white. Mohs hardness is 4. Ammoniotinsleyite is brittle. Cleavage was not observed and the fracture is uneven. Density measured by flotation in heavy liquids (mixtures of bromoform with benzene) is $2.42(2) \text{ g cm}^{-3}$ while the density calculated using the empirical formula is 2.451 g cm^{-3} .

Ammoniotinsleyite is optically biaxial (+), $\alpha = 1.557(2)$, $\beta = 1.559$ (calculated using $2V_{\text{meas.}}$), $\gamma = 1.563(2)$ ($\lambda = 589 \text{ nm}$); $2V_{\text{meas.}} = 75(10)^\circ$. Dispersion of optical axes is not observed. Under the polarising microscope, the mineral is pale pink and non-pleochroic. The Gladstone-Dale compatibility index (Mandarino, 1981) is: $1 - (K_p/K_c) = 0.042$ (good) with $D_{\text{calc.}}$ and 0.030 (excellent) with $D_{\text{meas.}}$.

Infrared spectroscopy

In order to obtain infrared (IR) absorption spectra (Fig. 3), powdered samples of ammoniotinsleyite and tinsleyite (used for comparison) were mixed with dried KBr, pelletised, and analysed using an ALPHA FTIR spectrometer (Bruker Optics) in the range $360\text{--}4000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . A total of 16 scans were collected for each spectrum. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Wavenumbers of IR absorption bands of ammoniotinsleyite and their assignments are (cm^{-1} ; s – strong band, w – weak band, sh – shoulder): 3510s, 3419s, 3375s (O–H stretching vibrations of OH groups and H_2O molecules), 3232, 3164, 3056s, 2857 (N–H stretching vibrations of NH_4^+ cations), 1652, (bending vibrations of H_2O molecules), 1455, 1434 (bending vibrations of NH_4^+ cations), 1195, 1120s, 1098s, 1080sh, 1020s [$\nu_3(\text{F}_2)$ asymmetric stretching vibrations of PO_4^{3-} ions], 893 [$\nu_1(\text{A}_1)$ symmetric stretching vibrations of PO_4^{3-} ions], 786w (Al...O–H bending vibrations), 665, 613, 590 [$\nu_4(\text{F}_2)$ – asymmetric bending vibrations of PO_4^{3-} ions], 547sh, 515s (Al–O stretching vibrations), 467, 404 (lattice modes, possibly involving Fe^{3+} –O and Mg–O stretching vibrations, librational vibrations of H_2O molecules and $\nu_2(\text{E})$ symmetric bending vibrations of PO_4^{3-} ions]. The band assignment was carried out in accordance with Nakamoto (2008, 2009), Chukanov (2014), and Chukanov and Chervonnyi (2016).

The IR spectrum of ammoniotinsleyite differs from that of tinsleyite by the presence of distinct bands of NH_4^+ in the ranges

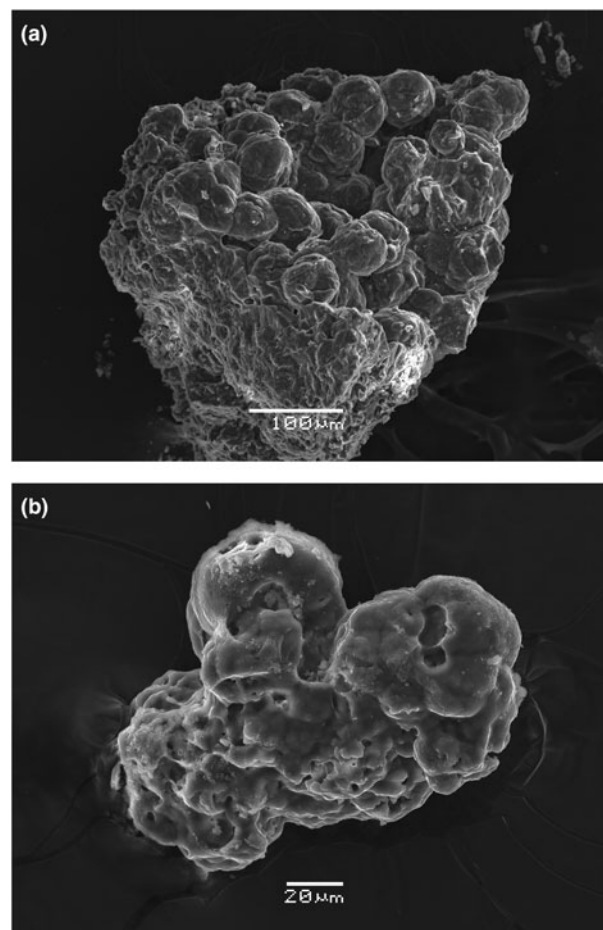


Fig. 2. (a,b) Scanning electron microscopy (secondary electron) images of aggregates of ammoniotinsleyite, holotype specimen.

$1400\text{--}1500$ and $2800\text{--}3300 \text{ cm}^{-1}$. In addition, most bands in the IR spectrum of tinsleyite are observed at lower frequencies than analogous bands of ammoniotinsleyite which is due to the differences in masses of the NH_4^+ and K^+ cations as well as hydrogen bonds formed by NH_4^+ .

Chemical data

Four chemical analyses were carried-out using a Tescan VEGA-II XMU scanning electron microscope equipped with an energy dispersive spectrometer INCA Energy 450 (EDS mode, 20 kV, 600 pA, beam diameter $0.16\text{--}0.18 \mu\text{m}$) for K, Mg, Ca, Al, Fe and P. The beam was rasterised on an area $16 \mu\text{m} \times 16 \mu\text{m}$ to minimise unstable sample damage.

Gas chromatography on products of ignition in an oxygen stream at 1200°C was used to determine H, N and C. Contents of carbon and other elements with atomic numbers higher than 6 are below detection limits. Analytical data are given in Table 1.

The charge-balanced empirical formula (based on 11 O apfu) is $[(\text{NH}_4)_{0.88}\text{K}_{0.10}\text{Ca}_{0.02}]_{\Sigma 1.00}(\text{Al}_{1.86}\text{Fe}_{0.09}\text{Mg}_{0.03})_{\Sigma 1.98}(\text{PO}_4)_{1.96}(\text{OH})_{1.05} \cdot 2.11\text{H}_2\text{O}$. Minor excess of H_2O relative to the idealised formula may be due to adsorbed water. The idealised formula is $(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$ which requires $(\text{NH}_4)_2\text{O}$ 8.27, Al_2O_3 32.37, P_2O_5 45.06, H_2O 14.30, total 100.00 wt.%.

Evolution of NH_3 from ammoniotinsleyite on moderate heating in air was detected organoleptically (by smell) and with a wet

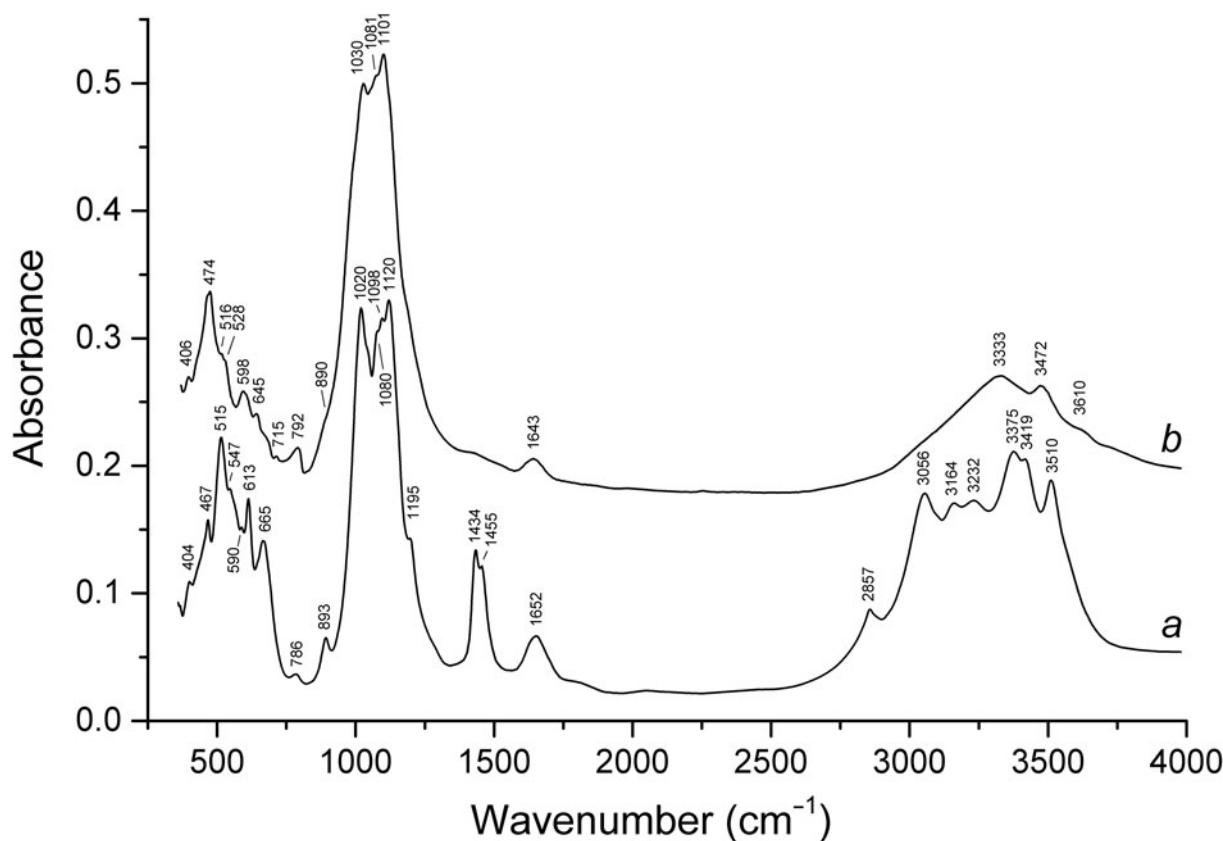


Fig. 3. Powder infrared absorption spectra of (a) ammoniotinsleyite and (b) Fe-rich tinsleyite with the composition $(K_{0.86}Ca_{0.10}Na_{0.04})(Al_{1.36}Fe_{0.57}Mg_{0.05})(PO_4)_2 \cdot 0.00(OH) \cdot 2H_2O$ from Mejillones Peninsula, Mejillones, Antofagasta, Chile.

pH-paper. No gas evolution was observed in 20% HCl, confirming the absence of CO_3^{2-} groups.

X-ray diffraction and crystal structure

Single-crystal X-ray diffraction studies of ammoniotinsleyite could not be carried-out due to the absence of suitable single crystals: aggregates of ammoniotinsleyite (Figs 1 and 2) are polycrystalline and consist of very small imperfect individuals. For this reason, the crystal structure of ammoniotinsleyite was refined based on powder X-ray diffraction data, using the Rietveld method.

Table 1. Chemical composition of ammoniotinsleyite.

Constituent	Content, wt.%	Range	S.D.	Probe standard
$(NH_4)_2O^*$	7.25			
K_2O	1.50	1.30–1.74	0.16	Sanidine
MgO	0.42	0.32–0.48	0.04	Diopside
CaO	0.34	0.25–0.43	0.06	Wollastonite
Al_2O_3	29.91	29.26–31.07	0.72	Albite
Fe_2O_3	2.36	1.87–2.70	0.31	Fe
P_2O_5	43.97	43.27–44.43	0.47	$LaPO_4$
H_2O^{**}	14.89			
CO_2	Below detection limit			
Total	100.64			

Total iron was measured as Fe_2O_3 ; S.D. = standard deviation.

*The value of 7.25 wt.% for $(NH_4)_2O$ is calculated from 3.9 wt.% N determined by gas chromatography.

**The value of 14.89 wt.% for H_2O is calculated from the rest of hydrogen after subtraction of H in NH_4^+ cations. The total H content determined by gas chromatography is 2.79 wt.% which corresponds to 24.9 wt.% H_2O .

Powder X-ray diffraction data (Table 2) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector (radius 127.4 mm) using Debye-Scherrer geometry, $CoK\alpha$ radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA and 15 min exposure. Angular resolution of the detector is 0.045° (for 2θ) and pixel size is 0.1 mm. The data were integrated using the software package *Osc2Tab* (Britvin *et al.*, 2017).

Diffraction peaks are well indexed in the monoclinic unit cell, space group $P2_1/n$. The unit-cell parameters calculated from the powder data are: $a = 9.5871(1)$, $b = 9.6089(1)$, $c = 9.6467(2)$ Å, $\beta = 103.4461(8)^\circ$ and $V = 864.31(2)$ Å³.

Refinement of the crystal structure of ammoniotinsleyite was performed using the Rietveld method using the structure of tinsleyite (Dick, 1999) as the starting model except for H atoms which were excluded from the refinement. Data treatment and the Rietveld structure analysis were carried-out using the *JANA2006* program package (Petříček *et al.*, 2006). The profiles were modelled using a pseudo-Voigt function. The structure was refined in isotropic approximation of atomic displacements. The P–O and Al–O interatomic distances were softly restricted nearby the values obtained for the synthetic tinsleyite (Dick, 1999). A small amount of K (12%) was added to the N site and fixed during the refinement assuming the K + Ca admixture according to chemical data. The final agreement factors are: $R_p = 0.0071$, $R_{wp} = 0.0093$, $R_{obs} = 0.0167$. The observed and calculated powder X-ray diffraction diagrams demonstrate a very good agreement (Fig. 4). Coordinates and thermal displacement parameters of atoms are given in Table 3 and selected interatomic

Table 2. Powder X-ray diffraction data (d in Å) of ammoniotinsleyite.

l_{obs}	d_{obs}	l_{calc}^*	d_{calc}	hkl
23	7.56	29	7.549	$\bar{1}01$
79	6.71	63, 41	6.713, 6.692	011, 110
100	5.947	31, 100	5.957, 5.936	101, $\bar{1}11$
36	4.676	21, 33	4.691, 4.662	002, 200
15	4.271	3, 15	4.276, 4.271	021, 120
20	4.193	10, 2, 18, 2	4.216, 4.195, 4.183, 4.168	012, 210, $\bar{1}12$, $\bar{2}11$
4	4.056	3	4.053	$\bar{1}21$
20	3.743	5, 26	3.775, 3.740	$\bar{2}02$, 121
5	3.568	3, 3	3.571, 3.562	112, 211
6	3.516	7	3.513	$\bar{2}12$
8	3.344	4, 6	3.346, 3.340	220, $\bar{1}22$
3	3.181	2	3.179	$\bar{3}01$
28	3.032	16, 15, 2	3.034, 3.031, 3.029	$\bar{1}13$, 031, 130
20	3.005	11, 11	3.003, 2.997	122, 221
25	2.958	8, 10, 20	2.968, 2.957, 2.949	$\bar{2}22$, 310, $\bar{1}31$
22	2.846	29	2.845	212
21	2.799	8, 23	2.804, 2.796	$\bar{2}13$, $\bar{3}12$
13	2.659	6, 7, 5	2.668, 2.662, 2.651	113, $\bar{1}23$, $\bar{3}21$
29	2.635	38	2.633	$\bar{2}31$
4	2.531	5	2.532	222
4	2.518	3	2.516	$\bar{3}03$
2	2.499	2	2.497	$\bar{3}22$
6	2.459	7	2.458	231
2	2.442	1	2.442	$\bar{2}32$
5	2.402	3, 1, 4	2.404, 2.402, 2.396	123, 040, 321
12	2.334	9, 9, 5	2.339, 2.331, 2.327	$\bar{1}14$, 400, 041
3	2.263	3	2.263	$\bar{1}33$
5	2.230	3, 3	2.231, 2.228	330, 141
5	2.157	1, 6	2.163, 2.155	$\bar{2}33$, $\bar{1}24$
3	2.133	2	2.132	$\bar{2}41$
6	2.109	7	2.107	114
3	2.073	1, 3	2.075, 2.070	$\bar{3}14$, $\bar{4}13$
2	2.035	1, 2	2.038, 2.027	142, $\bar{2}42$
5	1.980	8	1.979	$\bar{3}33$
2	1.963	3	1.961	421
3	1.941	3	1.940	$\bar{4}23$
5	1.921	3, 1, 2	1.923, 1.921, 1.919	204, $\bar{1}43$, $\bar{4}31$
5	1.903	6, 2	1.905, 1.901	043, 340
5	1.878	1, 5	1.880, 1.875	412, $\bar{4}32$
3	1.857	1, 2	1.856, 1.855	$\bar{3}42$, 512
4	1.781	3, 3, 1	1.784, 1.781, 1.778	431, 422, 052
4	1.770	5	1.768	$\bar{4}33$
3	1.738	1, 4	1.738, 1.738	520, $\bar{3}43$
2	1.680	3, 2	1.682, 1.678	$\bar{5}23$, 044
4	1.669	1, 5	1.670, 1.667	$\bar{2}44$, 314
5	1.647	2, 5, 1	1.647, 1.645, 1.644	521, $\bar{3}51$, 531
3	1.637	1, 3, 1	1.636, 1.635, 1.634	514, 350, 235
2	1.601	2	1.601	441
2	1.591	2, 2	1.590, 1.590	602, $\bar{4}43$
2	1.578	1, 2	1.579, 1.578	061, 160
3	1.572	1, 1, 4	1.573, 1.571, 1.571	611, $\bar{4}25$, $\bar{3}35$
1	1.543	2	1.544	135
2	1.537	3, 1	1.538, 1.534	531, 610
2	1.532	2	1.529	$\bar{3}16$
3	1.515	2, 2, 3	1.516, 1.515, 1.514	062, 260, $\bar{1}62$
3	1.478	1, 3, 3	1.481, 1.479, 1.478	$\bar{2}54$, 045, 162
3	1.474	4	1.472	414
1	1.443	2, 1	1.445, 1.442	614, $\bar{3}45$
3	1.424	3, 1, 2	1.427, 1.424, 1.423	631, 360, 424
3	1.400	3	1.399	325
2	1.383	2, 1	1.382, 1.381	602, 353
1	1.358	1	1.359	$\bar{1}17$

*For the calculated pattern, only reflections with intensities $\geq 1\%$ are given. The strongest lines are given in bold.

distances in Table 4. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Table 3. Coordinates and isotropic displacement parameters (U_{iso} , in Å²) of atoms for ammoniotinsleyite.

Site	x	y	z	U_{iso}
$A = N_{0.88}K_{0.12}$	0.5159(3)	0.1907(3)	0.8951(3)	0.014(1)
Al(1)	0.3870(2)	0.5400(2)	0.3730(2)	0.0194(7)
Al(2)	0.6023(2)	0.2278(2)	0.3163(2)	0.0194(7)
P(1)	0.7983(2)	0.0293(2)	0.1524(2)	0.0151(6)
P(2)	0.7959(2)	0.1914(2)	0.6385(2)	0.0155(6)
O(1)	0.9533(2)	0.0870(3)	0.2036(3)	0.012(11)
O(2)	0.6893(3)	0.1278(3)	0.1937(3)	0.024(1)
O(3)	0.7589(3)	0.0178(3)	-0.0148(2)	0.022(12)
O(4)	0.7110(3)	0.3840(2)	0.2815(3)	0.0136(1)
O(5)	0.9512(2)	0.2396(4)	0.6617(2)	0.030(1)
O(6)	0.7812(3)	0.0480(2)	0.7110(2)	0.027(1)
O(7)	0.7076(3)	0.2979(3)	0.6983(3)	0.010(1)
O(8)	0.7398(3)	0.1773(3)	0.4779(2)	0.027(1)
O(9) = OH	0.4957(2)	0.3609(2)	0.4486(2)	0.016(1)
O(10) = H ₂ O	0.4978(3)	0.0613(2)	0.3556(3)	0.016(1)
O(11) = H ₂ O	0.3162(3)	0.1460(3)	0.5349(4)	0.004(1)

Table 4. Selected interatomic distances (Å) in the structure of ammoniotinsleyite.

A–O(1)	2.796(4)	Al(2)–O(5)	1.848(2)
A–O(3)	2.829(4)	Al(2)–O(8)	1.857(3)
A–O(5)	2.862(4)	Al(2)–O(2)	1.865(4)
A–O(4)	2.962(4)	Al(2)–O(4)	1.902(3)
A–O(2)	3.033(4)	Al(2)–O(10)	1.970(3)
A–O(7)	3.109(4)	Al(2)–O(9)	2.217(3)
A–O(8)	3.199(4)	<Al(2)–O>	1.943
A–O(11)	3.281(4)		
A–O(10)	3.403(4)	P(1)–O(2)	1.529(4)
<A–O>	3.053	P(1)–O(4)	1.546(3)
		P(1)–O(1)	1.556(3)
		P(1)–O(3)	1.573(3)
		<P(1)–O>	1.551
Al(1)–O(7)	1.852(3)		
Al(1)–O(6)	1.857(3)		
Al(1)–O(3)	1.899(3)		
Al(1)–O(1)	1.903(3)	P(2)–O(8)	1.523(3)
Al(1)–O(9)	2.056(3)	P(2)–O(7)	1.524(4)
Al(1)–O(9)	2.057(2)	P(2)–O(5)	1.525(3)
<Al(1)–O>	1.937	P(2)–O(6)	1.566(3)
		<P(2)–O>	1.535

Discussion

Ammoniotinsleyite, $(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, is a member of the leucophosphate group with the general formula $AB_2[\text{PO}_4]_2(\text{OH})\cdot 2\text{H}_2\text{O}$ ($A = \text{NH}_4$ or K ; $B = \text{Al}$ or Fe^{3+}). This new mineral is the ammonium analogue of tinsleyite, $\text{KAl}_2(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, with prevailing NH_4^+ over K^+ and the aluminium analogue of spheniscidite, $(\text{NH}_4)\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH})\cdot 2\text{H}_2\text{O}$, with prevailing Al^{3+} over Fe^{3+} (Table 5). The synthetic analogue of ammoniotinsleyite is well-known (Parise, 1984; Pluth *et al.*, 1984; Aubert *et al.*, 2003; Parnham *et al.*, 2006; Vaughan *et al.*, 2012). A crystal chemical review on minerals of the leucophosphate group and related synthetic compounds was reported by Yakubovich *et al.* (2012).

In the structure of ammoniotinsleyite (Fig. 5), Al cations occupy two crystallographically non-equivalent sites with octahedral coordination. As mentioned in previous work (Yakubovich *et al.*, 2012 and references therein), the remarkable feature of the crystal structure of members of the leucophosphate group is the occurrence of tetrameric units of four AlO_6 octahedra built by two Al(1) octahedra sharing an edge and two additional Al(2) octahedra attached at each side of this common edge *via*

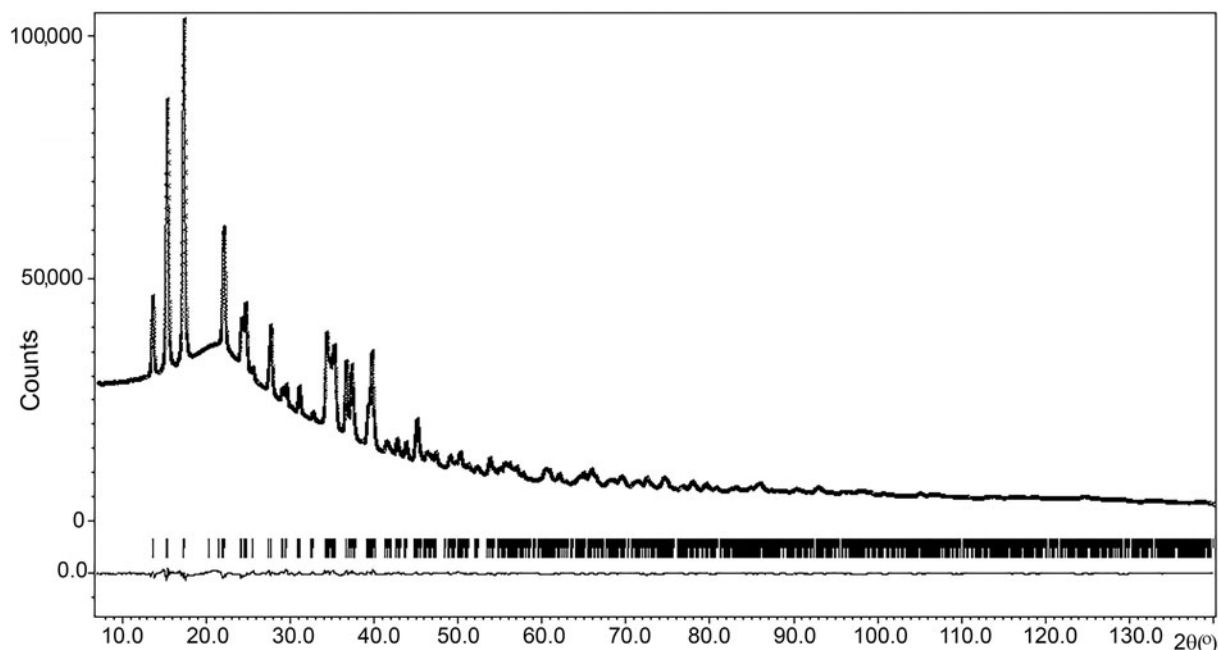


Fig. 4. Observed and calculated powder X-ray diffraction patterns of ammoniotinsleyite. The solid line corresponds to calculated data, the crosses correspond to the observed pattern and vertical bars mark all possible Bragg reflections. The difference between the observed and calculated patterns is shown by the curve at the bottom.

Table 5. Comparative data for ammoniotinsleyite, tinsleyite and spheniscidite.

Mineral	Ammoniotinsleyite	Tinsleyite	Spheniscidite
Formula	$(\text{NH}_4)\text{Al}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$	$\text{KAl}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$	$(\text{NH}_4)\text{Fe}_2^{3+}(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2/n$ or Pn	$P2_1/n$?
a (Å)	9.58711	9.602	9.75
b (Å)	9.60888	9.532	9.63
c (Å)	9.64670	9.543	9.70
β (°)	103.4461	103.16	102.6
V (Å ³)	864.31	850.5	889
Z	4	4	4
Strongest reflections of the powder	7.56 (23)	6.68 (100)	7.62 (40)
X-ray diffraction pattern: d , Å (l , %)	6.71 (79)	5.91 (80)	6.79 (100)
	5.947 (100)	4.157 (50)	5.99 (90)
	4.676 (36)	3.723 (50)	4.75 (35)
	3.032 (28)	3.006 (70)	4.26 (35)
	2.958 (25)	2.836 (50)	3.358 (35)
	2.846 (22)	2.616 (60)	3.053 (45)
	2.799 (21)		
	2.635 (29)		
Density, (g cm ⁻³)	2.42 (meas.)	2.69 (meas.)	
	2.451 (calc.)	2.62 (calc.)	3.08 (calc.)
Optical data			
α	1.557	1.591	No data;
β	1.559 (calc.)	1.597	$n_{\text{mean}} \approx 1.7$
γ	1.563	1.604	
$2V$ (°)	75	86	
Optical sign	+	+	
Strong and characteristic bands in the IR spectrum (cm ⁻¹)	3510	3472	3465
	3375	3333	3330
	3056	1101	3020
	2857	1030	2835
	1455	598	1428
	1434	474	1064
	1120		985
	1020		633
	613		529
	515		
References	This work	Dunn <i>et al.</i> , 1984; Chukanov and Chervonnyi, 2016	Wilson and Bain, 1986; Chukanov, 2005, 2014

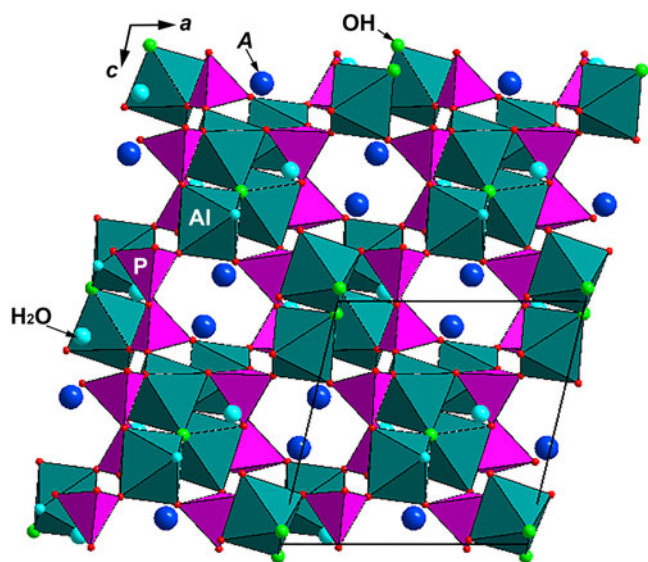


Fig. 5. The crystal structure of ammoniotinsleyite: view along the *b* axis (positions of O atoms of OH groups are shown as green circles, O atoms of H₂O molecules are given as blue circles). The unit cell is outlined.

common corners. These octahedral units are cross-linked by PO₄ tetrahedra, thus forming a heteropolyhedral pseudo-framework with channels running along the *a*, *b* and *c* axes which in ammoniotinsleyite host large NH₄⁺ ions (with K admixture) and H₂O molecules. There are two crystallographically non-equivalent sites of water molecules [O(10) and O(11)]; O(10) participates in the coordination polyhedra of Al(2) and NH₄ cations whereas O(11) is only involved in the coordination polyhedron of NH₄⁺.

Ammoniotinsleyite is a product of a deep alteration of bird guano over the course of geologically long time processes. Obviously, guano was the primary source of N and P in this mineral, and the host rock was the source of Al.

Comparative data for ammoniotinsleyite and related minerals are given in Table 5. As one can see from these data, wave-numbers of IR bands can be considered as a reliable diagnostic characteristic of ammoniotinsleyite.

Acknowledgements. The authors are grateful to Béla Fehér and two anonymous reviewers for valuable comments. This work was supported by the Russian Foundation for Basic Research, grants nos. 18-29-12007-mk. A part of this work (IR spectroscopy and chemical analyses) was carried-out in accordance with the state task, state registration number AAAA-A19-119092390076-7. The authors thank the X-ray Diffraction Centre of Saint-Petersburg State University for instrumental and computational resources.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2020.45>

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