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TANCOITE, A NEW LITHIUM SODIUM ALUMINUM PHOSPHATE FROM THE TANCO PEGMATITE, BERNIC LAKE, MANITOBA

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ABSTRACT

Tancoite, a new species from the Tanco mine, Bernic Lake, Manitoba, occurs as small crystals associated with apatite and lithiophosphate in a pegmatite. Chemical analyses gave Li_2O 5.2, Na_2O 20.0, CaO 0.5, Al_2O_3 18.3, P_2O_5 50.1 and H_2O 6.8, total 100.9 wt. %, leading to the formula $H_{1.13}Li_{0.98}Na_{1.82}Ca_{0.03}Al_{1.01}P_{1.99}O_8(OH)$, ideally, $HLiNa_2Al(PO_4)_2(OH)$. The presence of hydroxyl and the absence of molecular water are shown by IR spectrometry. Tancoite is orthorhombic, space group *Cmma*, *Cmmb*, *Cm2a* or *C2mb*, with *a* 7.041(2), *b* 14.130(3), *c* 6.975(2) Å and $Z = 4$. The strongest lines of the X-ray powder pattern are 4.672(100) (111), 3.413(90)(131), 3.150(100)(220,041,201), 2.479(90)(042,202), 1.760(40)(400) and 1.438(40). The crystals are generally equant and show the forms {010}, {111}, {001}, {100} and {021}. Tancoite is colorless to pale pink, and has a vitreous lustre, white streak, Mohs hardness of 4–4½, conchoidal fracture and fair cleavages {010} and {001}. The measured density is 2.752 g/cm³, and the calculated density is 2.724 g/cm³. Tancoite is optically biaxial negative; $2V\alpha = 23°$ (meas.), 24° (calc.), $r < v$ weak; refractive indices α 1.541(2), β 1.563(2), γ 1.564(2), with orientation of the indicatrix $X \parallel a$, $Y \parallel b$, $Z \parallel c$. The mineral is named for the Tanco mine.

Keywords: tancoite, Tanco pegmatite, Manitoba, phosphate, new mineral description.

SOMMAIRE

La tancoite, nouvelle espèce minérale, a été trouvée à la mine Tanco, lac Bernic (Manitoba), en petits cristaux associés dans une pegmatite à de l'apatite et du lithiophosphate. L'analyse chimique, Li_2O 5.2, Na_2O 20.0, CaO 0.5, Al_2O_3 18.3, P_2O_5 50.1, H_2O 6.8, total 100.9% (poids), donne la formule $H_{1.13}Li_{0.98}Na_{1.82}Ca_{0.03}Al_{1.01}P_{1.99}O_8(OH)$, d'où la formule idéale $HLiNa_2Al(PO_4)_2(OH)$. Les spectres *IR* montrent la présence de l'hydroxyle et l'absence d'eau moléculaire. Orthorhombique, groupe spatial *Cmma*, *Cmmb*, *Cm2a* ou *Cm2b*, *a* 7.041(2), *b* 14.130(3), *c* 6.975(2) Å, $Z = 4$. Les sept raies les plus fortes du cliché de poudre sont: 4.672(100) (111), 3.413(90)(131), 3.150(100)(220, 041, 201), 2.479(90)(042,202), 1.760(40)(400) et 1.438(40). Les cristaux, équidimensionnels en général, montrent les formes {010}, {111}, {001} et {021}. La tancoite est incolore à rose pâle, à éclat vitreux et rayure blanche; elle possède une dureté Mohs de 4 à 4½, une fracture conchoïde et des clivages assez bons suivant {010} et {001}. Sa densité est de 2.752 (mes.), 2.724 (calc.); biaxe négative, $2V$ 23° (mes.), 24° (calc.); dispersion $r < v$ faible; α 1.541(2), β 1.563(2), γ 1.564(2); orientation optique: $X \parallel a$, $Y \parallel b$, $Z \parallel c$. Son nom rappelle celui de la mine Tanco.

(Traduit par la Rédaction)

Mots-clés: tancoite, pegmatite Tanco, Manitoba, phosphate, description d'une espèce minérale nouvelle.

INTRODUCTION

Tancoite, $HLiNa_2Al(PO_4)_2(OH)$, is a new species from the Tanco mine, Bernic Lake, Lac-du-Bonnet area, Manitoba (50° 26′ N latitude, 95° 27′ W longitude). Prior to operation by the Tantalum Mining Corporation of Canada (TANCO), this pegmatite property was known variously as the Jack Nutt tin property, the Montgary property and the Chemalloy Minerals property. Recent studies of the geology of the deposit include those of Crouse & Černý (1972) and Crouse *et al.* (1979). To date, approximately seventy species have been identified from the Tanco pegmatite.

Three small hand specimens of spodumene-bearing pegmatite, containing lithiophosphate and a conspicuous pink apatite, were collected by one of the authors (R.A.R.) in 1974. Routine examination of these specimens revealed crystal druses of an unfamiliar mineral. The mineral was subsequently proven to be a new species; it was named tancoite (TĂN•KŌ•AIT) for the type locality, the Tanco mine. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The holotype hand specimen contains about 20 mg of tancoite (*M*36416); cotype specimens (*M*36417 and *M*36418) are preserved in the collections of the Royal Ontario Museum. Metatype fragments have been deposited in the National Museum of Natural Sciences, Ottawa (42900), the United States National Museum of Natural History (Smithsonian Institution), Washington, D.C. (*NMNH* 146284) and the University of Manitoba, Winnipeg (*M*5533 and *M*5534). Analyzed microprobe mounts of holotype tancoite are also housed in the Smithsonian Institution.

PHYSICAL PROPERTIES

Tancoite occurs as isolated crystals up to 1 mm in length and as druses of columnar individuals, oriented subparallel to [001]. Crystals are typically colorless to pale pink and transparent. Thin fragments are colorless. The mineral has a white streak, vitreous lustre, conchoidal fracture and a Mohs hardness of 4–4½. Two fair cleavages on {010} and {001} were observed. Very fine acicular inclusions, possibly of apatite, impart a chatoyancy to parts of some crystals. Tancoite does not fluoresce in ultraviolet for X radiation. However, exposure to high-intensity X radiation causes the mineral to turn greenish yellow. Tancoite is readily soluble in dilute nitric and hydrochloric acids.

Four clean crystals were suspended in tetrabromoethane–acetone mixtures, whose densities were determined with a pycnometer at 23°C. The densities of the crystals thus measured range from 2.751(4) to 2.758(4) g/cm^3, with a mean of 2.752 g/cm^3. The calculated density of tancoite, on the basis of chemical analytical data, is 2.724 g/cm^3, with $Z = 4$ and $V = 693.9$ Å^3. In comparison, the calculated density for tancoite of the ideal composition $HLiNa_2Al(PO_4)_2(OH)$ is 2.755 g/cm^3, assuming an identical unit-cell volume.

FIG. 1. Tabular crystals of tancoite associated with bundles of acicular apatite crystals. A porous mass of hydrous sodium phosphate is also present (upper-left corner). SEM image, scale bar is 200 μm.

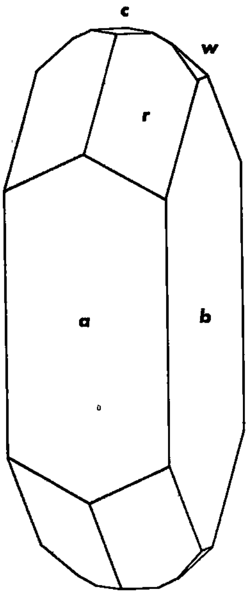

FIG. 2. Tancoite crystal, elongate [001], showing *a* {100}, *b* {010}, *c* {001}, *r* {111}, *w* {021}.

Tancoite is optitcally biaxial negative, $2V_\alpha$ = 23(2)°(meas,), 24°(calc.), $r < v$ weak. The refractive indices are α 1.541(2), β 1.563(2), γ 1.564(2) (Na light). The orientation of the indicatrix with respect to the crystallographic axes is $X \parallel a$, $Y \parallel b$, $Z \parallel c$. No optical zoning was observed.

The value of K_P or $(\bar{n}_{meas}-1)/D_{calc}$ is 0.204. [In comparison, K_c or $k_n\ p_n/100$, where p_n = wt. % of the component oxide and k_n represents the corresponding specific Gladstone–Dale constant given by Mandarino (1976)] is 0.202. Superior compatibility of the chemical and physical data is suggested by $1-K_P/K_C = -0.010$ (Mandarino 1979).

CRYSTALLOGRAPHY

Tancoite crystals are generally equant to tabular on (010); some are elongate [001]. Tabular crystals are illustrated in Figure 1, and one with elongate habit is shown in Figure 2. Tancoite crystals vary in perfection from crude and anhedral to well formed, and commonly show parallel multiple growth. The dominant forms on most well-formed crystals are {010}, {111}, {001} and {100}. All faces are bright and sharp, except for {100}, which is typically curved and somewhat dull; in addition, {001} is usually striated parallel [100]. Crystals are commonly modified by small {021} faces. Three crystals were measured with an optical goniometer. Observations on a nearly complete crystal give no indication that tancoite is noncentrosymmetric. Angle data for the forms of tancoite are given in Table 1.

TABLE 1. ANGLE TABLE FOR TANCOITE

Orthorhombic, *a* = 7.041, *b* = 14.130, *c* = 6.975 Å

Form	Measured		Calculated	
	ϕ	ρ	ϕ	ρ
c 001	0°	0°	0°00'	0°00'
b 010	0°	90°	0°00'	90°00'
a 100	90°	90°	90°00'	90°00'
w 021	0°	44°34'	0°00'	44°37'
r 111	63°37'	48°34'	63°30'	47°54'

The study of two tancoite crystals by precession and Weissenberg methods shows tancoite to be orthorhombic, *a* 7.04, *b* 14.12, *c* 6.97 Å, space group *Cmma*, *Cmmb*, *Cm2a* or *C2mb*. Least-squares refinement of 23 lines from the X-ray powder-diffraction data gave unit-cell parameters *a* 7.041(2), *b* 14.130(3) and *c* 6.975(2) Å. The refined unit-cell volume is 693.9 Å^3. X-ray powder-diffraction data for tancoite are given in Table 2.

CHEMICAL COMPOSITION AND THERMAL ANALYSIS

Chemical analytical data for tancoite are given

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR TANCOITE

I_{est}	d_{meas}(Å)	d_{calc}(Å)	*hkl*	I_{est}	d_{meas}(Å)	d_{calc}(Å)	*hkl*
20	7.06	7.065	020	15	2.011	2.011	331
20	6.95	6.975	001	5	1.999	1.999	133
100	4.672	4.676	111			1.957	260
10	3.520	3.533	040	5	1.952	1.952	062
		3.521	200	5	1.941	1.942	043
5	3.494	3.487	002			1.940	203
90	3.413	3.414	131	20	1.929	1.929	312
100	3.150	3.151	041	5	1.885	1.885	261
		3.151	220	2	1.871	1.871	223
		3.143	201			1.869	171
20	3.126	3.127	022			1.799	332
5	3.053	3.051	112	30	1.765	1.766	080
5	2.873	2.872	221	40	1.760	1.760	400
1	2.820 *					1.748	351
1	2.787 *			20	1.742	1.744	004
		2.604	132			1.712	081
20	2.494	2.494	240	5	1.706	1.707	262
90	2.479	2.482	042	10	1.699	1.700	243
		2.478	202	1	1.695	1.696	172
20	2.454	2.455	151	5	1.654		
10	2.349	2.355	060	1	1.639		
		2.348	241	5	1.603		
5	2.337	2.338	222	5	1.577		
10	2.324	2.325	003	5	1.558		
5	2.228	2.231	061	30	1.535		
7	2.209	2.208	023	10	1.525		
2	2.196	2.197	311	7	1.495		
10	2.181	2.181	113	5	1.489		
1	2.130$_b$			40	1.438		
				40	1.429		
1	2.096	2.096	152				
30	2.029	2.028	242				

12 additional lines observed to 1.224Å.
Guinier-de Wolff camera, CuK$_\alpha$ radiation; intensities estimated visually; b = broad; * may be due to apatite impurity.

TABLE 3. CHEMICAL DATA FOR TANCOITE

	Tancoite wt. %	$HLiNa_2Al(PO_4)_2(OH)$ theoretical wt. %
Li_2O	5.2	5.19
Na_2O	20.0	21.53
CaO	0.5	
Al_2O_3	18.3	17.71
P_2O_5	50.1	49.31
H_2O	6.8	6.26
Total	100.9	100.00

Li_2O by atomic absorption spectrophotometry, H_2O by TGA, all others by electron-microprobe analysis; accuracy of data ±3% of amount shown.

in Table 3. Crystals of tancoite were analyzed using an ARL–SEMQ electron microprobe at an operating voltage of 15 kV and a beam current of 0.15 μA. Of elements with $Z > 8$, only Na, Ca, Al and P were found in greater than trace concentrations; traces of Mg, Mn and F were detected. No zoning of these elements was noted. The following standards were utilized: maricite for Na, montgomeryite for Ca, Mg, Al and P, manganite for Mn, and fluorapatite for F. The data were corrected with Bence–Albee factors.

A diluted solution of 5 mg tancoite in concentrated HNO_3 was analyzed for lithium by atomic absorption spectrophotometry. A determination of 22% Na_2O by the same technique supports the sodium determination by microprobe analysis. Induction-coupled plasma analysis of the above solution gave 7.8 ppm beryllium in tancoite.

A simultaneous DTA – TGA – evolved-gas analysis was performed on 7 mg of tancoite, with a Mettler TA–1 Thermoanalyzer coupled to an Inficon IQ 200 quadrupole mass spectrometer. The sample was heated at 4°/min to 700°C in high vacuum. Water was evolved between 337 and 542°C, resulting in a 6.8% weight loss. The TGA curve (Fig. 3a) indicates that the loss occurred in three distinct stages: approximately 1.0% between 337 and 429°C, 5.2% between 429 and 472°C and 0.6% between 472 and 542°C. The H_2O partial pressure curve (Fig. 3b) shows pressure maxi-

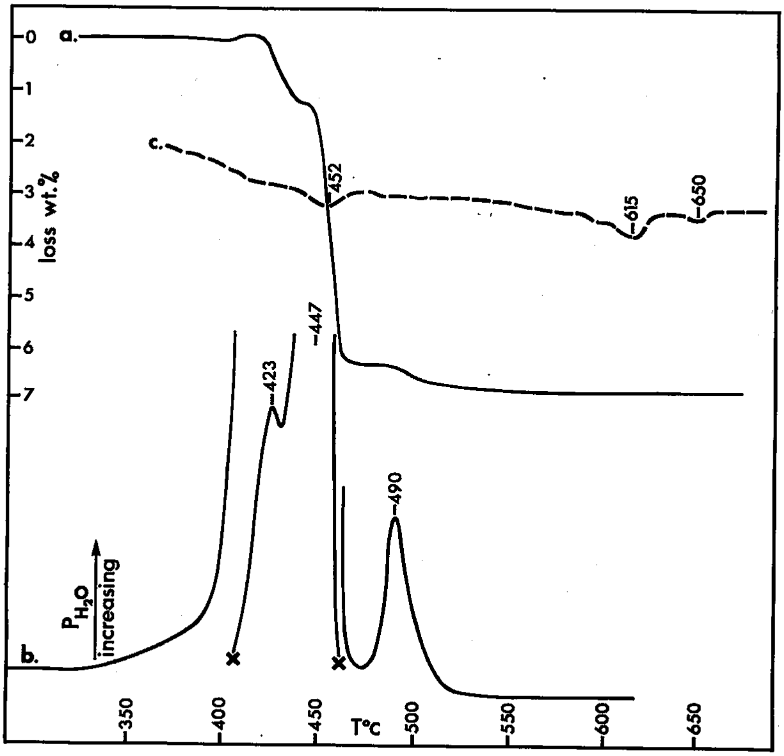

FIG. 3. Thermal analysis curves of tancoite: (a) TGA; (b) partial pressure of evolved H_2O (portion of curve between crosses was recorded at reduced sensitivity); (c) DTA (endothermic direction down).

ma at 423, 447 and 490°C. The three endothermic peaks on the DTA curve (Fig. 3c) correspond to decomposition (452°C), possible recrystallization (615°C) and fusion (650°C). No evolved gases other than H_2O were detected during the analysis.

Calculation of the analytical formula for tancoite, based on 9 oxygen atoms, gave $H_{1.13}Li_{0.98}Na_{1.82}Ca_{0.03}Al_{1.01}P_{1.99}O_8(OH)$ or, ideally, $HLiNa_2Al(PO_4)_2(OH)$. The presence of hydroxyl and absence of water groups in tancoite are indicated by IR spectrometry, to be discussed in the following section. In addition, water evolution in the range 337–542°C *in vacuo* is more consistent with the presence of hydroxyl than water of crystallization. The coordination of the charge-balancing hydrogen is uncertain, and the possibility of an HPO_4^{2-} group is not discounted.

The summation of empirical subscripts of H, Li, Na and Ca approximates a whole number, raising the possibility of substitution among these elements.

INFRARED ABSORPTION SPECTRUM

The IR spectrum of tancoite between 4000 and 400 cm^{-1} has strong absorption bands at 3565, 1145, 1060, 970, 694, 600, 535 and 456 cm^{-1} (Table 4). The sharp band with a maximum at 3565 cm^{-1} must be interpreted as a valent vibration of the OH bond. An absorption band in the interval 3600–3500 cm^{-1} may not necessarily be due to OH vibration, but could result from H_2O vibration, as is observed in the IR spectra of variscite, strengite and phosphophyllite (Moenke 1962, 1966, Farmer 1974). However, in the spectrum of tancoite, the absence of the δ_2 vibrational band of water molecules between 1600 and 1700 cm^{-1} indicates that the 3565 cm^{-1} band is due to OH vibration.

The absorption bands at 1145, 1060 and 970 cm^{-1} are assigned to the vibrations of v_3 P–O_4 bonds of slightly distorted PO_4 tetrahedra. However, it is possible that the wide band of absorption with a maximum at 970 cm^{-1} belongs to the band of vibration (δ) of OH bonds, as is observed in the IR spectra of augelite, hopeite, brazilianite and other phosphates (Moenke 1962, 1966, Povarennykh 1978).

The absorption band with a maximum at 694 cm^{-1} belongs to the valent vibration (v_3) of Al–O bonds. Two absorption bands with maxima at 600 and 535 cm^{-1} are attributed to the deformational vibrations (δ_4) of the P–O_4 bonds. The band with a maximum at 456 cm^{-1} may be the valent vibrational band of a Li–O_4 polyhedron, as it is for many Li-bearing phosphates (Moenke 1962, 1966, Farmer 1974, Povarennykh 1978). One referee kindly pointed out that this band may also be ascribed to δ_2 (P–O_4) of an HPO_4^{2-} group. A compilation of several monohydrogen phosphate spectra (Farmer 1974) shows the range 465–240 cm^{-1} for this vibration.

TABLE 4. ABSORPTION BANDS IN INFRARED SPECTRUM OF TANCOITE BETWEEN 4000 AND 400 cm^{-1}

$HLiNa_2Al(PO_4)_2(OH)$		Tentative Assignment**
cm^{-1}	I*	
3565	vs	ν OH
3400	vw	
2910	vw	ν OH (?)
2840	vw	
1145	vs	$\nu_3(P-O_4)$
1060	m	
970	vs	
694	m	$\nu_3(Al-O_6)$
600	vs	$\delta_4(P-O_4)$
535	vs	
456	m	$\nu_3(Li-O_4)$

*I = relative absorption band-intensity denoted as follows: vs very strong, m medium, vw very weak.

**ν bond-stretching vibration, δ bond-bending deformation.

OCCURRENCE

As the study was limited to specimens collected from the mine dump, details of the occurrence of tancoite within the pegmatite are not known. Tancoite occurs with pink apatite and colorless lithiophosphate crystals to 2 cm in length. Small cavities in granular apatite are commonly partly filled by a corroded and detached lithiophosphate crystal. These cavities are lined with acicular apatite crystals and with druses and individual crystals of tancoite (Fig. 1). Tancoite has been observed only in this environment. White granular masses and botryoidal growths of a sodium phosphate are commonly associated with tancoite in the cavities. Preliminary investigation suggests that this mineral is a new species, a natural occurrence of $Na_2HPO_4 \cdot 2H_2O$. A few minute crystals of quartz, barite and calcite were also noted in the cavities.

The above-mentioned phosphate suite occurs as masses in a spodumene–calcite–cookeite assemblage. The spodumene is present as small prismatic crystals, some of which have been surficially to completely replaced by montmorillonite. Coarse-grained calcite and a lesser amount of cookeite crystals are interstitial to the spodumene. Quartz crystals and abundant aggregates of cookeite are included in and border the phosphate-rich masses.

DISCUSSION

Early stages of the paragenetic sequence involving tancoite are obscure. However, it appears that the formation of lithiophosphate and quartz was followed by the etching of lithiophosphate and the sequential crystallization of granular, then acicular, apatite. Subsequently, tancoite, calcite, the hydrated sodium phosphate, barite and a second generation of quartz formed in the cavities. This sequence bears some resemblance to that of the secondary mineral assemblage 4 of Černý (1972), found in the spodumene-rich upper intermediate zone of the Tanco pegmatite: quartz–cookeite–cesian analcime – lithiophosphate – apatite – montmorillonite/illite (listed in the sequence of deposition).

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