

THE TANCO PEGMATITE AT BERNIC LAKE, SOUTHEASTERN MANITOBA. XV. ERCITITE, $\text{Na Mn}^{3+} \text{PO}_4 (\text{OH}) (\text{H}_2\text{O})_2$, A NEW PHOSPHATE MINERAL SPECIES

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ABSTRACT

Ercitite, ideally $\text{Na Mn}^{3+} (\text{PO}_4) (\text{OH}) (\text{H}_2\text{O})_2$, is a new mineral species from the Tanco pegmatite, southeastern Manitoba. Ercitite forms 200–400 μm irregular aggregates of lath-like crystals in fan-like divergent sprays. The mineral occurs in a 5-cm nodule embedded in a quartz + spodumene pseudomorph after petalite in the upper intermediate zone (5) of the pegmatite. The outer rind of the nodule contains pink rhodochrosite, green and blue apatite, and minor yellow sphalerite, and the inner region is comprised of orange-brown lithiophilite. The core of the nodule consists of an assemblage of altered lithiophilite, locally stained red (hematite?), colorless lithiophosphate and dark brown-black clots of ercitate on collinsite, fairfieldite, whitlockite and two unidentified phosphates; the new species and associated minerals are alteration products of lithiophilite. Individual laths of ercitate are light brown with a beige streak and a vitreous luster. Laths are generally $\leq 20 \mu\text{m}$ across and $\leq 200 \mu\text{m}$ long, elongate along $[\bar{1}01]$ and flattened on $\{101\}$. Ercitite is brittle, with an irregular fracture on ends of laths, and has two very good orthogonal cleavages, parallel to $\{101\}$ and $\{010\}$. Mohs hardness is 3–4, and the calculated density is 2.75 g/cm^3 . Ercitite is biaxial positive, with α 1.699(2), β 1.715(5), γ 1.737(5), $2V(\text{obs.}) = 86^\circ$, $2V(\text{calc.}) = 82^\circ$, strongly pleochroic with X yellowish green, Y yellowish brown, Z very dark brown, with absorption $Z \gg Y > X$ and $X = b$, $Y \wedge c = 34^\circ$ (in β acute), $Z \wedge a = 53^\circ$ (in β obtuse). Ercitite is monoclinic, space group $P2_1/n$, a 5.362(5), b 19.89(1), c 5.362(5) Å, β 108.97(8)°, V 540.8(6) Å³, $Z = 4$. The seven strongest lines in the X-ray powder-diffraction pattern [$d(\text{in } \text{\AA})(h k l)$] are: 9.90(10)(0 2 0), 2.644(8)(1 4 1), 3.273(6)(1 4 $\bar{1}$), 3.126(6)(1 5 0, 0 5 1), 4.92(5)(0 1 1, 1 1 0), 2.542(4)(2 0 0, 0 0 2), 2.376(4)(1 7 $\bar{1}$). Chemical analysis by electron microprobe gave P_2O_5 32.37, Al_2O_3 0.34, Mn_2O_3 18.81, Fe_2O_3 16.51, ZnO 0.08, MgO 0.12, CaO 1.09, Na_2O 12.44, H_2O (calc.) 20.44, sum 102.20 wt.%, where the valence states of Mn and Fe, and the amount of H_2O , were determined by crystal-structure analysis. The resulting empirical formula on the basis of seven anions (including OH and 2 H_2O) is $(\text{Na}_{0.89}\text{Ca}_{0.04})_{\Sigma 0.93} (\text{Mn}^{3+}_{0.53}\text{Fe}^{3+}_{0.46}\text{Al}_{0.01})_{\Sigma 1.00} (\text{PO}_4)_{1.01} (\text{OH}) (\text{H}_2\text{O})_2$. Ercitite is structurally similar to bermanite, $\text{Mn}^{2+} \text{Mn}^{3+}_2 (\text{PO}_4)_2 (\text{OH})_2 (\text{H}_2\text{O})_4$, and is related by the substitution $2\text{Na} \rightarrow \text{Mn}^{2+} + \square$ (vacancy).

Keywords: ercitate, bermanite, tsumcorite, lithiophilite, granitic pegmatite, new mineral, Tanco, Manitoba, Canada.

SOMMAIRE

L'ercitite, $\text{Na Mn}^{3+} (\text{PO}_4) (\text{OH}) (\text{H}_2\text{O})_2$, est une nouvelle espèce minérale découverte dans la pegmatite granitique de Tanco, dans la partie sud-est du Manitoba. L'ercitite se présente en agrégats irréguliers de 200–400 μm , formés de cristaux en lattes disposés en houppes ou en gerbes. Le minéral se trouve dans un nodule de 5 cm, enchâssé dans une intercroissance quartz + spodumène remplaçant la pétalite par pseudomorphose, dans la zone intermédiaire supérieure (5) de la pegmatite. Le cortex de ce nodule est fait de rhodochrosite rose, d'apatite verte et bleue, avec un peu de sphalérite jaune, et la partie interne est constituée de lithiophilite brun orangé. Au cœur du nodule se trouve un assemblage de lithiophilite altérée, localement teintée de rouge (hématite?), de lithiophosphate incolore et de petits amas brun foncé à noirs d'ercitite sur la collinsite, fairfieldite, whitlockite, et deux phosphates non identifiés; la nouvelle espèce et les minéraux associés sont des produits d'altération de la lithiophilite. Les cristaux isolés d'ercitite sont brun clair avec une poussière beige et un éclat vitreux. Les lattes n'atteignent généralement pas 20 μm de large et 200 μm de long; elles sont allongées selon $[\bar{1}01]$ et aplaties sur $\{101\}$. L'ercitite est cassante, avec une fracture irrégulière à l'extrémité des lattes, et possède deux clivages orthogonaux très bons, parallèles à $\{101\}$ et $\{010\}$. La dureté sur l'échelle de Mohs est de 3–4; la densité calculée est de 2.75. Le minéral est biaxe positif avec α 1.699(2), β 1.715(5), γ 1.737(5),

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$2V(\text{obs.}) = 86^\circ$, $2V(\text{calc.}) = 82^\circ$, fortement pléochroïque avec X vert jaunâtre, Y brun jaunâtre, Z brun très foncé, avec $Z \gg Y > X$ et $X = b$, $Y \wedge c = 34^\circ$ (dans l'angle β aigu), $Z \wedge a = 53^\circ$ (dans l'angle β obtus). L'ercitite est monoclinique, avec le groupe spatial $P2_1/n$, a 5.362(5), b 19.89(1), c 5.362(5) Å, β 108.97(8)°, V 540.8(6) Å³, $Z = 4$. Les sept raies les plus intenses du radiogramme de poudre [$d(\text{en Å})$]($h k l$) sont: 9.90(10)(0 2 0), 2.644(8)(1 4 1), 3.273(6)(1 4 $\bar{1}$), 3.126(6)(1 5 0, 0 5 1), 4.92(5)(0 1 1, 1 1 0), 2.542(4)(2 0 0, 0 0 2) et 2.376(4)(1 7 $\bar{1}$). L'analyse chimique à la microsonde électronique a donné P_2O_5 32.37, Al_2O_3 0.34, Mn_2O_3 18.81, Fe_2O_3 16.51, ZnO 0.08, MgO 0.12, CaO 1.09, Na_2O 12.44, H_2O (calc.) 20.44, total 102.20% en poids, dans laquelle l'état de valence de Mn et Fe, ainsi que la quantité de H_2O , ont été déterminés par l'analyse structurale. Sur la base de sept anions (incluant OH et 2 H_2O), on peut établir la formule empirique $(Na_{0.89}Ca_{0.04})_{\Sigma 0.93}(Mn^{3+}_{0.53}Fe^{3+}_{0.46}Al_{0.01})_{\Sigma 1.00}(PO_4)_{1.01}(OH)(H_2O)_2$. L'ercitite montre des analogies structurales avec la bermanite, $Mn^{2+}Mn^{3+}_2(PO_4)_2(OH)_2(H_2O)_4$, de laquelle elle se rapproche par la substitution $2Na \rightarrow Mn^{2+} + \square$ (lacune réticulaire).

Mots-clés: ercitite, bermanite, tsumcorite, lithiophilite, pegmatite granitique, nouvelle espèce minérale, Tanco, Manitoba, Canada.

INTRODUCTION

In 1983, some of the current authors (AMF, PČ and FCH) initiated a paragenetic and geochemical study of lithiophilite from the Tanco granitic pegmatite, south-eastern Manitoba (Fransolet *et al.* 1997). In 1996, AMF noticed a patchy brownish black crust on lithiophilite sample TRT-38, earmarked for separation and wet-chemical analysis of the lithiophilite. X-ray powder-diffraction study of this material gave results that could not be matched to any known mineral species. Results of an electron-microprobe analysis indicated a rather simple stoichiometry of the main components, but could not be matched to any known mineral species.

Successful refinement of the crystal structure complemented collection of other data and resulted in approval of the new mineral species by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The mineral is named in honor of T. Scott Ercit (b. 1957) of the Research Division, Canadian Museum of Nature, an eminent student of the mineralogy of granitic pegmatites. The holotype, and so far the only specimen, of ercitite is stored in the collection of the Canadian Museum of Nature, Ottawa, Ontario (catalogue # CMNMC82944).

THE PARENT PEGMATITE

The Tanco granitic pegmatite has been the subject of numerous mineralogical and geochemical studies over the last fifty years. This giant subhorizontal body, about $1990 \times 1060 \times 100$ m in size, consists of nine zones with diverse mineral assemblages, textural attributes and positions within the body. The pegmatite belongs to the petalite subtype of rare-element pegmatites (*cf.* Černý 1991), and ranks as a major producer of tantalum-mineral concentrate, refractory-grade spodumene and pollucite. The literature and current state of knowledge of the Tanco pegmatite were summarized by Černý *et al.* (1998) and Stilling (1998).

PARAGENESIS OF ERCITITE

Ercitite was found on a fracture cross-cutting a nodule of lithiophilite from zone (5) of the Tanco pegma-

tite. This zone is characterized by the coarsest grain-size and a relatively simple mineral assemblage: microcline perthite, quartz, petalite (largely converted into a pseudomorphic assemblage of spodumene + quartz) and amblygonite-montebrazite, with minor lithiophilite, albite and pollucite, and (Ta,Sn)-oxide minerals, apatite, eucryptite and zircon as accessory phases. The ercitite-bearing nodule of lithiophilite is enclosed in a spodumene + quartz pseudomorph after petalite, and is surrounded by a narrow pale-green halo of cookeite replacing spodumene. The outer rind of the nodule contains pink rhodochrosite, green and blue apatite, and minor yellow sphalerite. The lithiophilite has the composition $Li(Mn_{0.84}Fe_{0.16})PO_4$. Alteration of lithiophilite has resulted in (hematite?) stains associated with colorless lithiophosphate and dark brown-black clots of ercitite, which overgrows a dispersed assemblage of very fine-grained phosphates (largely less than 25 μm): collinsite-fairfieldite with a Ca/Na value (at.) of 46 to 10, a Mg/Mn value of 16 to 0.4, and a Mn/Fe value of 3.7 to 9.6, whitlockite with $(Mn > Fe) > Mg$, and an unidentified phase "C" with $(Ca > Na) : (Fe > Mn > Mg > Zn) : P$ very close to 4 : 1 : 3. Another unidentified mineral, "A", which forms subround grains 5 to 7 μm across imbedded in ercitite, shows the ratio of its main components $Na : (Mn > Fe \gg Mg > Zn) : P : F$ as 3 : 2 : 2 : 2 (Fig. 1).

PHYSICAL PROPERTIES

Ercitite consists of irregular aggregates, 200 to 400 μm across, of lath-like crystals in fan-like divergent sprays (Fig. 1). The aggregates are dark brown to black, whereas individual laths are pale brown; the streak is beige, the luster, vitreous. The laths are generally $\leq 20 \mu\text{m}$ across and $\leq 200 \mu\text{m}$ long, elongate along $[\bar{1}01]$ and flattened on $\{101\}$. There are two very good orthogonal cleavages parallel to $\{101\}$ and $\{010\}$ (Fig. 1a). Ercitite is brittle and easily splinters into fine fibers if mechanically disturbed (Fig. 1b); it shows an irregular fracture at the ends of these lath-shaped fibers. Hardness is difficult to measure accurately because of the minute size of individual crystals, but it is between 3 and 4. The density could not be measured; the calculated density is 2.77 g/cm³. Optical properties were

measured with the Bloss spindle stage for the wavelength 590 nm using a gel filter. The indices of refraction are α 1.699(2), β 1.715(5), γ 1.737(5), the calculated birefringence $\gamma - \alpha$ is 0.038, (+)2V(meas.) 86°, 2V(calc.) 82°; orientation $X = b$, $Y \wedge c = 34^\circ$ (β acute), $Z \wedge a = 53^\circ$ (β obtuse). Pleochroism is strong with X yellowish green, Y yellowish brown, and Z very dark brown, absorption $Z \gg Y > X$.

CHEMICAL COMPOSITION

Crystals were analyzed with a Cameca SX-50 electron microprobe operating in the wavelength-dispersion mode, with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 5 μ m. The following standards were used: albite (Na), apatite (Ca, P), spessartine (Mn), almandine (Fe), pyrope (Al), forsterite (Mg) and gahnite (Zn). The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1984, 1985).

The presence and quantity of OH and H₂O groups were established by crystal-structure solution and refinement (Hawthorne & Grice 1990, Cooper & Hawthorne, in prep.); their presence was also confirmed by infrared spectroscopy, using the experimental method described by Roberts *et al.* (1994) (Fig. 2). A sharp absorption band at 3564 cm⁻¹ is attributed to the stretching vibrations of (OH) groups, whereas the broad envelope centered at 3200 cm⁻¹ and the narrow band at 1620 cm⁻¹ correspond to H₂O stretching and bending vibrational modes, respectively. Table 1 gives the chemical composition and formula unit based on seven anions (including 1 OH and 2 H₂O groups) *pfu* (per formula unit). The excess of wt.% total over 100 is probably caused by slight dehydration of the mineral during electron-microprobe analysis, which would increase the percentages of non-H₂O components.

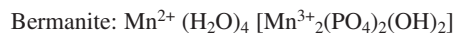
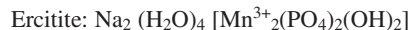
X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded with a Gandolfi camera using FeK α X-radiation. Table 2 shows the X-ray powder-diffraction data for ercinitite, together with the refined unit-cell dimensions. Unit-cell dimensions were also determined on a Nicolet P4 automated 4-circle diffractometer with a CCD detector: a 5.3757(5), b 19.955 (2), c 5.3750(5) Å, β 108.915(2)°, V 545.5(1) Å³, $Z = 4$; the space group is $P2_1/n$, and the point group is $2/m$.

DISCUSSION

Structure, chemical composition and related species

Solution and refinement of the crystal structure of ercinitite (Cooper & Hawthorne, in prep.) shows ercinitite to be structurally related to bermanite (Kampf & Moore 1976):



These two minerals have similar cell dimensions (Table 3), but the space group of bermanite is $P2_1$, whereas the space group of ercinitite is $P2_1/n$. Bermanite has an ordered distribution of Mn²⁺ and □ (vacancy) relative to the arrangement of 2Na in ercinitite. Complete details are discussed by Cooper & Hawthorne (in prep.).

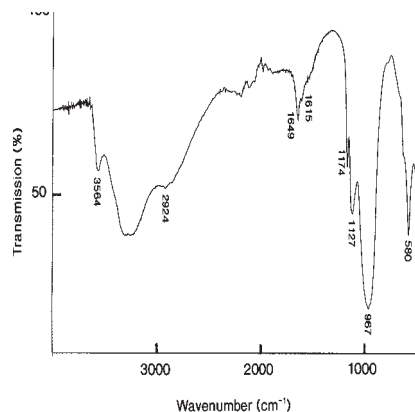


TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ERCINITITE

l_{obs}	d_{obs} (Å)	d_{calc} (Å)	h	k	l	l_{obs}	d_{obs} (Å)	d_{calc} (Å)	h	k	l
10	9.9	9.94	0	2	0	2	1.902 *	1.913	2	5	2
5	4.92	4.91	0	1	1	"	"	1.892	2	7	0
"	"	4.91	1	1	0	"	"	1.892	0	7	2
<1	4.27	4.26	1	1	1	<1	1.824	1.823	2	6	2
2	3.983	3.996	1	2	1	"	1.756 *	1.775	2	8	0
6	3.273	3.280	1	4	1	"	"	1.775	0	8	2
6	3.126	3.130	1	5	0	"	"	1.759	3	2	1
"	"	3.130	0	5	1	"	"	1.759	1	2	3
<1	2.968	2.972	1	2	1	1	1.705	1.703	1	11	0
8	2.644	2.640	1	4	1	"	"	1.703	0	11	1
4	2.542	2.535	2	0	0	3	1.684 *	1.684	3	1	0
"	"	2.535	0	0	2	"	"	1.684	0	1	3
3	2.475 *	2.479	1	7	0	"	"	1.682	3	4	1
"	"	2.479	0	7	1	"	"	1.682	1	4	3
"	"	2.457	2	2	0	2	1.658	1.657	0	12	0
"	"	2.457	0	2	2	2	1.633 *	1.640	2	8	2
3	2.446	2.450	2	3	1	"	"	1.638	3	3	0
"	"	2.450	1	3	2	"	"	1.638	0	3	3
4	2.376	2.381	1	7	1	"	"	1.630	3	5	1
1	2.282	2.259	2	4	0	"	"	1.630	1	5	3
"	"	2.259	0	4	2	3	1.574	1.573	3	6	1
2	2.161	2.160	1	8	1	"	"	1.573	1	6	3
2	2.129	2.138	2	5	0	3	1.558 *	1.565	2	10	0
"	"	2.138	0	5	2	"	"	1.565	0	10	2
1	2.074	2.073	2	3	2	"	"	1.557	2	0	2
1	1.942	1.943	1	8	1						

* not used in cell refinement.
Weak lines due to impurity at 8.95, 7.27, 5.24, 3.039, 2.948 (Å);
 $a = 5.362(5)$, $b = 19.89(1)$, $c = 5.362(5)$ Å, $\beta = 108.97(8)^\circ$, $V = 540.8(6)$ Å³,
FeK α (Mn-filtered radiation).

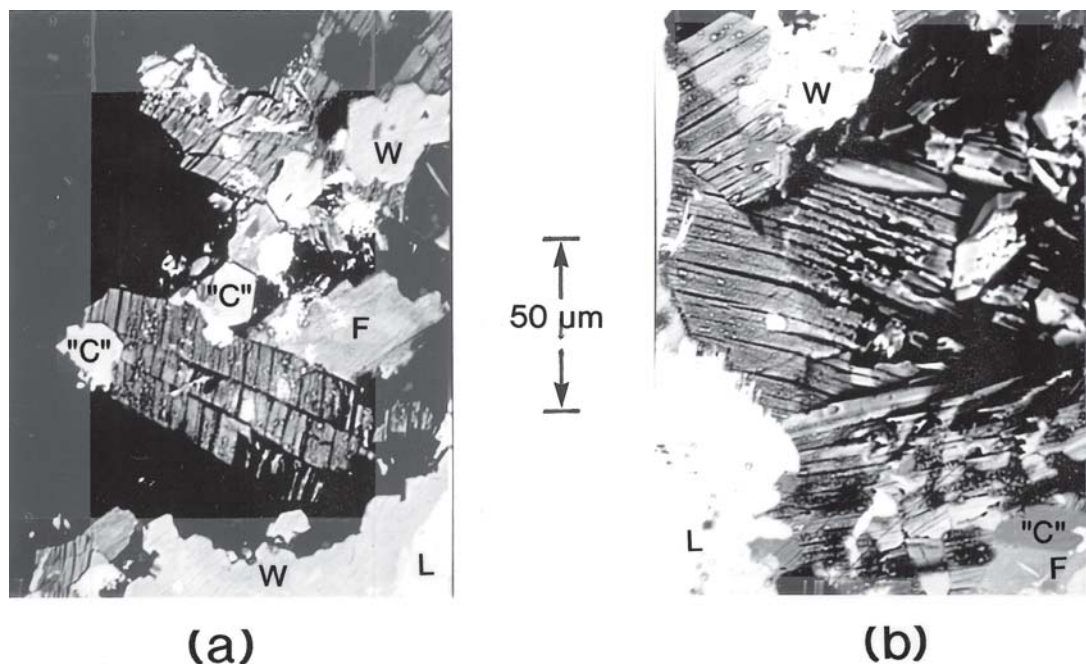


FIG. 1. Back-scattered electron images of ercrite (medium grey) and associated phosphates. Ercrite shows lath-shaped habit and cleavages (a) and splintering on mechanical disturbance (b). Black: epoxy-filled cavities, L: lithiophilite, W: whitlockite, F: fairfieldite, C: collinsite, "C": unidentified ($\text{Ca} > \text{Na}$, $\text{Fe} > \text{Mn} > \text{Mg} > \text{Zn}$) phosphate; tiny white spots near-central to the largest crystals of ercrite in both a and b are (relics of?) the unidentified ($\text{Na}, \text{Mn}, \text{F}$) phosphate "A". The 50 μm scale bar applies to both (a) and (b).

The structure of ercrite is also similar to that of tsumcorite, $\text{Pb}^{2+} [\text{Zn}_2 (\text{AsO}_4)_2 (\text{OH})_2]$ (Tillmanns & Gebert 1973), which has a topologically identical structural unit. The structural units in tsumcorite are linked solely by interstitial Pb^{2+} , with no interstitial H_2O present, whereas in ercrite, the structural units are linked by interstitial Na and a network of hydrogen bonds.

TABLE 3. CELL DIMENSIONS AND SPACE GROUPS FOR ERCRITE AND BERMANITE

	Ercrite	Bermanite*
<i>a</i> (Å)	5.36	5.45
<i>b</i>	19.89	19.25
<i>c</i>	5.36	5.43
β (°)	108.9	110.3
Sp. Gr.	$P2_1/n$	$P2_1$

* Data from Kampf & Moore (1976)

As is apparent from the above discussion, ercrite can be formally derived from bermanite by the substitution $2\text{Na} \rightarrow \text{Mn}^{2+} + \square$ at the interstitial sites in this structure type. In the crystals examined here, Mn^{3+} is only slightly dominant over Fe^{3+} (Table 2), and the occurrence of an Fe^{3+} -dominant analogue of ercrite seems a distinct possibility.

Origin

Ercrite is undoubtedly a product of alteration and oxidation of lithiophilite and its local breakdown products, collinsite-fairfieldite and the unidentified (Na , Ca , Mn , Fe , Mg)-bearing phases "A" and "C". Conditions must have been strongly oxidizing, as all Fe and Mn are in the trivalent state. This, and the presence of H_2O groups in the structure, indicate that ercrite formed below $\sim 200^\circ\text{C}$, rather than by leaching and alteration in a higher-temperature hydrothermal environment (Moore 1982).

Ercrite is the first phosphate mineral in granitic pegmatites to have the Na-Mn^{3+} pair in its chemical formula. In phosphate parageneses from granitic

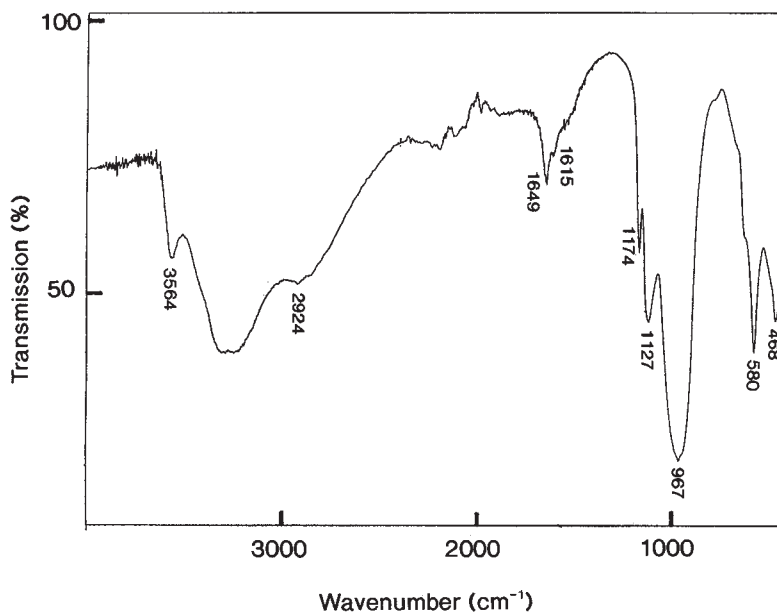


FIG. 2. The infrared spectrum of ercitate

pegmatites that allow recognition of successive steps in alteration of the primary phosphates, the combinations Li-Fe³⁺, Na-Fe³⁺, K-Fe³⁺, and Ca-Fe³⁺ (associated or not with Mn²⁺) are well known in many phases. In contrast, Mn³⁺ is present largely in heterosite-purpurite, (Fe³⁺, Mn³⁺) PO₄. These phases are typical of the Quensel-Mason sequence, characterized by intense alkali leaching (particularly Li) with concomitant oxidation of both Fe and Mn. Among the phosphates described as typical products of weathering (such as bermanite; Leavens 1967), the only cation pairing known to involve Mn³⁺ at present is that of Ca-Mn³⁺ (with subordinate Fe³⁺) in robertsite and pararobertsite.

Ercitite represents a noteworthy and unexpected phase in the complex alteration processes of primary phosphates. In general, these successive transformations lead to independent pathways for Fe and Mn, particularly at the end of the hydration stage (Fransolet *et al.* 1985). During systematic leaching of Li and Na at this stage, Fe³⁺ is initially accompanied by Mn²⁺ in diverse hydrous phosphates (*e.g.*, laueite, stewartite, strunzite). Ferric iron finally occurs virtually alone in H₂O-rich minerals such as phosphosiderite, and coupled with Na, K or Ca in, *e.g.*, cyrilovite, leucophosphate or mitridatite. Where Mn²⁺ becomes oxidized at low temperature, it leaves the phosphates after the heterosite-purpurite stage and forms distinct phases of its own, such as cryptomelane (Fontan 1978) and other complex oxides (Shigley & Brown 1985, Keller & von Knorring 1989).

In the Tanco pegmatite, lithiophilite is not extensively altered. The absence of substantial oxidation can be tentatively explained by the Fe-poor composition of the primary lithiophilite (Fontan *et al.* 1976). However, the location of the pegmatite deep below the water table must also have been a major factor. Oxidizing near-surface water has been introduced into the pegmatite only *via* drill holes in the last fifty years. The association of ercitate with lithiophosphate seems to be rather fortuitous. Lithiophosphate is a rather widespread product of the alteration of amblygonite-montebrasite at Tanco. However, it does not usually occur with any low-temperature (Fe,Mn)-bearing phosphates, despite the occasional close association of altered amblygonite-montebrasite and lithiophilite; the association of lithiophilite with Na-, Mn³⁺- and H₂O-rich ercitate is the only exception.

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