

FRANCONITE, A NEW HYDRATED Na-Nb OXIDE MINERAL FROM MONTREAL ISLAND, QUEBEC

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ABSTRACT

The new mineral species *franconite* occurs as white 150- μm globules on crystals of weloganite, calcite and quartz in vugs in a dawsonite-bearing sill in the Francon limestone quarry, Montreal, Quebec. The globules consist of bladed crystals, which show vitreous lustre, white streak, basal parting and have $n\alpha$ 1.72(1), $n\beta$ 1.78(1), $n\gamma$ 1.79(1), $(-2V$ 35(5) $^\circ$; Z is parallel to the elongation, and X is perpendicular to the blades. Franconite contains ~ 21 wt.% H_2O , but partial dehydration occurs in the vacuum conditions used for microprobe analyses. For the fully hydrated mineral the average composition deduced from chemical analysis of five globules corresponds to $(\text{Na}_{1.69}\text{Ca}_{0.12}\text{Sr}_{0.01})_{\Sigma 1.82}(\text{Nb}_{3.81}\text{Ti}_{0.09}\text{Al}_{0.01}\text{Si}_{0.09})_{\Sigma 4.00}\text{O}_{10.88}\cdot 9\text{H}_2\text{O}$. Indexing of the X-ray powder pattern gave the cell a 22.22(1), b 12.857(5), c 6.359(4) Å, β 92.24(6) $^\circ$, which for the average composition gives D_{calc} 2.71 g/cm 3 for $Z = 4$; $D_{\text{meas}} = 2.72$ (1) g/cm 3 . Strongest lines of the X-ray powder pattern [d in Å (hkl)] are: 11.0(10)(200), 5.55(7)(400), 4.73(6)(301), 3.18(6)(002), 3.21(5)(040), 2.626(5)(322). Heating of franconite to 500 $^\circ\text{C}$ produces $\text{Na}_2\text{Nb}_4\text{O}_{11}$. The name refers to the type locality.

Keywords: franconite, new mineral species, Na-Nb oxide hydrate, Montreal Island, Quebec.

SOMMAIRE

La nouvelle espèce minérale *franconite* se présente sous forme de globules blancs d'environ 150 μm de diamètre, à la surface de cristaux de weloganite, de calcite et de quartz dans les vacuoles d'un sill à dawsonite, dans la carrière de calcaire Francon, sur l'île de Montréal (Québec). Ces globules sont constitués de cristaux en lames qui possèdent un aspect vitreux, un trait blanc, un plan de fracture préférentiel, et $n\alpha$ 1.72(1), $n\beta$ 1.78(1), $n\gamma$ 1.79(1), $(-2V$ 35(5) $^\circ$; Z est parallèle à l'allongement et X est normal au plan des lames. La franconite contient approximativement 21% en poids d'eau, mais une déshydratation partielle se produit dans le vide que requiert une analyse à la microsonde. La composition déduite à partir des résultats d'analyse de 5 globules pour le minéral, hydraté à son maximum, correspond à $(\text{Na}_{1.69}\text{Ca}_{0.12}\text{Sr}_{0.01})_{\Sigma 1.82}(\text{Nb}_{3.81}\text{Ti}_{0.09}\text{Al}_{0.01}\text{Si}_{0.09})_{\Sigma 4.00}\text{O}_{10.88}\cdot 9\text{H}_2\text{O}$. Les dimensions de la maille, obtenues à partir du cliché de poudre aux rayons X, sont a 22.22(1), b 12.857(5), c 6.359(4) Å, β 92.24(6) $^\circ$. On calcule, à partir de la composition moyenne et pour Z

$= 4$, $D_{\text{calc}} = 2.71$; $D_{\text{mes}} = 2.72$ (1). Les raies les plus intenses du cliché de poudre [d en Å (hkl)] sont: 11.0(10)(200), 5.55(7)(400), 4.73(6)(301), 3.18(6)(002), 4.21(5)(130), 3.21(5)(040), 2.626(5)(322). Le chauffage à 500 $^\circ\text{C}$ de la franconite donne comme produit $\text{Na}_2\text{Nb}_4\text{O}_{11}$. Le nom rappelle la carrière Francon.

Mots-clés: franconite, nouvelle espèce minérale, oxyde hydraté de Na-Nb, île de Montréal, Québec.

INTRODUCTION

Dawsonite-bearing sills exposed in the Francon limestone quarry in the St-Michel district of Montreal, Quebec, contain an unusual suite of at least sixty minerals (Sabina 1979), of which several have this site as their type locality. Almost all of the new minerals, including the one described here, were recognized and characterized by X-ray-diffraction patterns in 1967, but in some cases it has taken years of persistent collecting to obtain sufficient material for an adequate mineral-description. The new species described here is a hydrous Na-Nb oxide that was referred to previously as unidentified No. 10 (Sabina 1976, 1979), and is now named *franconite* (fränkänite, fränkänait), derived from the name of the quarry. The new mineral species and name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Holotype specimens are in the National Mineral Collection at the Geological Survey of Canada (62094, 63748-63750) and at the Royal Ontario Museum, Toronto (M 39041).

PHYSICAL AND OPTICAL PROPERTIES

Franconite occurs as white globules in vugs in the sill in the upper levels of the quarry. The mineral is present most frequently on weloganite crystals, and less commonly on crystals of quartz and calcite. Globule diameter averages about 150 μm , but clustering is common, and groups up to 0.5 mm in diameter have been found.

Franconite has a vitreous lustre, but each globule consists of radiating, bladed crystals that collectively impart a silky lustre to new surfaces of split



FIG. 1. Bladed habit, two-face terminations, and basal parting of franconite. SEM photograph. Bar scale represents 1 μm .

globules. Individual blades commonly are terminated by two faces whose crystallographic angles could not be determined (Fig. 1). A basal parting is evident on broken blades, but cleavage was not observed. The streak of franconite is white; hardness could not be determined. The mineral does not fluoresce in ultraviolet light, does not effervesce in HCl, and is not readily consumed by this acid. Suspension of franconite globules in heavy liquids gave a density of 2.72(1) g/cm^3 .

Optical properties of franconite were determined on material verified by a Gandolfi X-ray pattern. The mineral is biaxial negative, with $2V = 35(5)^\circ$ measured by universal stage, and α 1.72(1), β_{calc} 1.78(1), γ 1.79(1). The bladed grains have parallel, or almost parallel, undulatory extinction, an effect that probably arises from the presence of overlapping blades. The undulatory extinction and small grain-size have prevented a more precise determination of the optical constants. The plane of the blade contains Z parallel to the elongation and Y normal to it; X is perpendicular to the blades.

CHEMICAL COMPOSITION

Microprobe analyses of franconite were obtained at the Geological Survey of Canada and at CANMET using various standards and operating conditions. Celestite and synthetic NaNbO_3 were used as standards in all analyses; dolomite, titanite, kaersutite and orthoclase were also utilized. Most analyses were done at 20 kV and specimen currents

from 0.020 to 0.028 μA . The results obtained from 6 globules of franconite from four specimens are given in Table 1.

The microprobe study showed that franconite is variable in composition, with the results interpreted as corresponding to a general formula $(\text{Na,Ca})_2(\text{Nb,Ti})_4\text{O}_{11} \cdot n\text{H}_2\text{O}$. The principal variations are in water and alkali contents; all analyses show minor to substantial alkali deficiencies (Table 1). Alkali contents commonly fluctuate within individual globules, but the other elements show no systematic variations that might be associated with these fluctuations. Some globules decrease in Na_2O and have a corresponding increase in CaO from core to rim, but the variation usually amounts to no more than a 0.5 wt.% increase in CaO . Numerous supplementary analyses have confirmed that potassium is usually absent, but some grains have been found to contain up to 0.2 wt.% K_2O . Checks for fluorine and carbon proved negative.

The alkali deficiency in franconite is most notable in sample 580a (Table 1), the composition of which is very close to $\text{NaNb}_3\text{O}_8 \cdot n\text{H}_2\text{O}$. Other globules from the same specimen (Table 1) gave higher alkali contents that, although low, are in better agreement with the results obtained from other specimens. X-ray powder-diffraction patterns of grains 580a and 580b prior to analysis showed negligible differences in cell dimensions, thus suggesting that the structural sites of the alkalis are encompassed in a niobium-oxygen framework that permits easy interchange of Na^+ and Ca^{2+} and readily tolerates alkali vacancies.

Water content

The shortfall in the analytical totals in Table 1 is attributable to H_2O , the presence of which is evident in the first two broad bands at 3350 and 1640 cm^{-1} in the infrared absorption spectrum (Fig. 2). H_2O also was confirmed by using mass spectrometry to monitor the products evolved from heated franconite. The total water content of the mineral is 21–22 wt.%, but a partial loss occurs in the vacuum conditions used for microprobe analyses. Despite this instability, specific checks showed that additional deterioration did not occur during microprobe analysis.

The H_2O content of a 5.86-mg sample of franconite was determined by using the Mettler Thermal analyzer and integrated mass-spectrometer at the Royal Ontario Museum. At a static temperature of 25°C and a vacuum of 10^{-6} to 10^{-7} torr applied for 20 hours, the sample lost 14.1 wt.% H_2O . Upon heating, the only additional H_2O losses were 3.75 wt.% between 25°C and 191°C , and 3.67 wt.% between 191° and 502°C , for a total loss of 21.5 wt.%. These results suggest that the value of n in the formula is 9. For the compound $\text{Na}_2\text{Nb}_4\text{O}_{11} \cdot 9\text{H}_2\text{O}$, the

TABLE 1. COMPOSITION OF FRANCONITE

wt. %		NMC 62094			NMC 63750	NMC 63748	NMC 63749
		580a	580b	580c			
	Na ₂ O	6.1	8.6	7.7	7.8	7.0	8.5
	CaO	1.1	0.7	0.7	1.3	1.8	0.7
	SrO	0.0	0.0	0.0	0.1	0.4	0.0
	Nb ₂ O ₅	78.0	79.6	78.6	74.2	75.5	75.4
	TiO ₂	1.2	1.0	1.0	1.3	1.2	0.9
	Al ₂ O ₃	0.5	0.2	0.2	0.0	0.0	0.0
	SrO ₂	0.2	0.4	0.6	1.3	0.4	0.5
	H ₂ O	12.9	10.1	11.2	14.0	13.7	13.0
formula ratios for (Nb,Ti,Si,Al)=4							
	Na	1.280	1.788	1.611	1.688	1.532	1.818
	Ca	0.128	0.080	0.081	0.154	0.218	0.083
	Sr	0.000	0.000	0.000	0.007	0.027	0.000
		1.408	1.868	1.692	1.849	1.777	1.901
	Nb	3.817	3.857	3.835	3.745	3.853	3.758
	Ti	0.098	0.080	0.081	0.110	0.102	0.076
	Al	0.064	0.020	0.020	0.000	0.000	0.000
	Si	0.021	0.043	0.065	0.145	0.045	0.166
	H ₂ O	4.657	3.396	4.031	5.212	5.157	4.781

Analytical data obtained by electron microprobe; H₂O by difference from 100 wt. %.

water content is 21.45 wt.%, and for the average of the last five compositions in Table 1, the nonhydrate contains 21.86 wt.% H₂O. In the vacuum conditions used for the microprobe analyses, stabilization apparently occurs at hydration levels approaching the tetrahydrate or pentahydrate (Table 1).

Further evidence supporting the proposed course of dehydration for franconite was obtained by charting weight losses from a 4.6-mg sample exposed to a desiccant. Sample weight remained unchanged after 4 hours in the desiccator, but a loss was detected in

the next 2 hours, and maximum dehydration with a weight loss of 15% occurred after 6 days (Fig. 3). This loss correlates well with that obtained at room temperature in the Mettler Thermalanalyzer, and indicates the removal of 6 or 7 molecules of H₂O. The desiccated product is amorphous, as revealed by X-ray powder patterns of grains sealed in a glass capillary to avoid atmospheric contact.

Upon re-exposure to room conditions, the desiccated product experienced a surge in uptake of atmospheric moisture, with peak absorption approaching the equivalent of about 26 H₂O in the formula (Fig. 3). Much of this H₂O presumably is not structurally bound. Moisture influx was extremely rapid, and recrystallization to give a diffuse X-ray pattern, possibly that of a lower hydrate of franconite, occurred within less than 6 hours (Table 3). This, and subsequent behavior, are plotted in Figure 3, wherein the humidified environment refers to a sealed container in which humidity was sufficiently high that condensation occurred on the container walls. Fluctuations in the water content of the end-product of the experiment are thought to reflect minor variations in atmospheric humidity and temperature.

The desiccator and Thermalanalyzer data indicate that water is bonded in at least two different ways in franconite. Part of the water that is readily drawn off by vacuum or low humidity may be absorbed, but most must be very weakly bound essential water, as indicated by the structural collapse that attends its removal. The residual water amounts to about 7.4 wt.% and is expelled in almost equal proportions upon heating: the first loss is centred at a temperature of about 110°C, and the more tenacious remainder, at about 356°C. Segregation of the weakly bound and residual waters suggests that the general formula

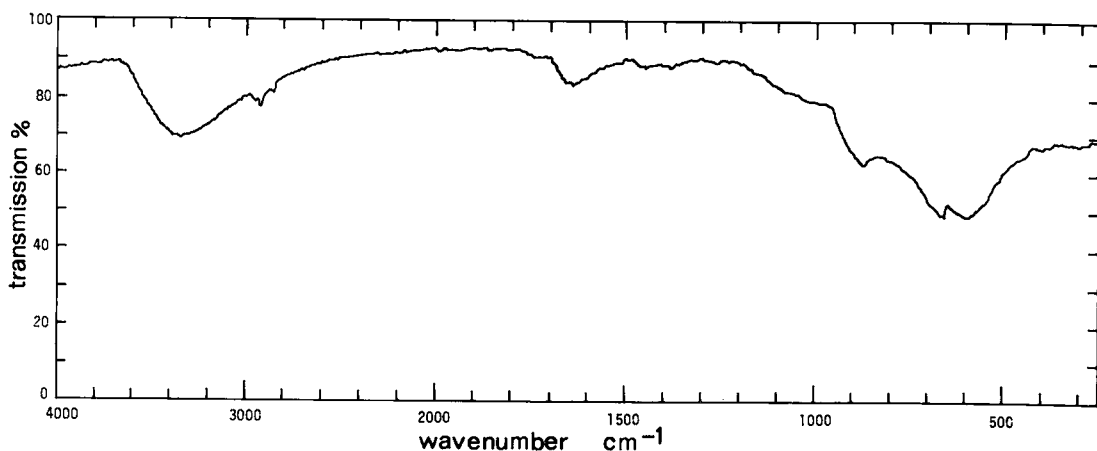


FIG. 2. Infrared absorption spectrum of franconite.

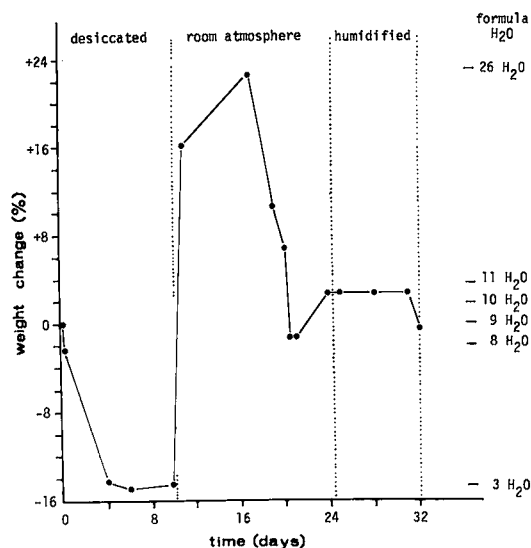


FIG. 3. Dehydration and rehydration of franconite at room temperature and pressure.

of end-member franconite may be $\text{Na}_2\text{Nb}_4\text{O}_{11}(\text{H}_2\text{O})_{2-3} \cdot n\text{H}_2\text{O}$, where n is approximately 6. It is possible that the niobium–oxygen framework is structurally stable and that alkali deficiency is charge-compensated by hydroxyl occupation of some of the oxygen positions in the framework.

Thermal decomposition

Globules of franconite heated to 150°, 250° and 350°C in air gave identical X-ray patterns that could not be identified; based on the Thermal analyzer data, the products presumably are $\text{Na}_2\text{Nb}_4\text{O}_{11}(\text{H}_2\text{O})_n$, where n is approximately 1. Samples heated to 500°, 600° and 700°C gave X-ray patterns identified as $\text{Na}_2\text{Nb}_4\text{O}_{11}$ by comparison with published data (PDF 20-1145), and by comparison with $\text{CaTa}_4\text{O}_{11}$ synthesized by J.E. Dutrizac at CANMET.

X-RAY DATA

Franconite is too fine grained for single-crystal X-ray study. An electron-diffraction pattern of fragments showing the elongate, bladed habit of franconite was obtained through the kindness of G.C. Weatherly of the Department of Metallurgy, University of Toronto. The diffraction pattern, which is presumably that of a lower hydrate of franconite, shows an orthogonal array $12.7 \times 6.4 \text{ \AA}$. With these values as starting points, the powder-diffraction pattern (Table 2) was indexed satisfactorily with $a 22.22(1)$, $b 12.857(5)$, $c 6.359(4) \text{ \AA}$, $\beta 92.24(6)^\circ$. For the average composition ($\text{Na}_{1.706}$

TABLE 2. X-RAY POWDER DATA FOR FRANCONITE

I_{est}	d_{meas}	d_{calc}	hkl	I_{est}	d_{meas}	d_{calc}	hkl
10	11.0	11.10	200	2	2.258	2.259	042, 351
4	6.06	6.05	101*	2	2.258	2.258	740
7	5.55	5.55	400*	2	2.220	2.220	10.0.0, 622
4	5.09	5.10	410	2	2.187	2.188	10.1.0*
3	4.92	4.92	301*	3	2.143	2.143	060
6	4.73	4.73	301*	3	2.099	2.099	10.2.0*
4	4.53	4.52	021	4	2.075	2.073	113, 442
5	4.21	4.21	130*	4	2.052	2.051	802
4	4.08	4.10	401	2	2.017	2.017	651*
1	3.90	3.90	321*	1	1.993	1.993	261*
2	3.82	3.81	321*	4	1.955		
1	3.71	3.71	330, 501	1	1.942		
1	3.58	3.57	501*	1	1.922		
4	3.43	3.44	511	1	1.883		
5	3.21	3.21	040*	2	1.857		
6	3.18	3.18	002*	4	1.834		
4	3.12	3.12	521*	1	1.806		
4	3.09	3.09	202*	4	1.772		
1	3.025	3.023	202*	4	1.755		
1	2.952	2.948	340*	2	1.724		
4	2.891	2.886	312	1	1.701		
1	2.839	2.838	141*	B	1.671		
1	2.776	2.775	800*	B	1.626		
4	2.690	2.690	341, 322	1	1.587		
5	2.626	2.627	322*	1	1.557		
2	2.565	2.567	441*	4	1.530		
4	2.503	2.505	250, 232	1	1.500		
4	2.430	2.429	350, 541	1	1.474		
4	2.322	2.324	251	1	1.441		
4	2.297	2.296	622	1	1.418		

Camera diameter 114.6 mm, CoK α radiation ($\lambda = 1.79021 \text{ \AA}$), intensities visually estimated. Indexed with $a 22.22$, $b 12.857$, $c 6.359 \text{ \AA}$, $\beta 92.24^\circ$. Lines with an asterisk were used for the least-squares refinement.

$\text{Ca}_{0.124}\text{Sr}_{0.007})(\text{Nb}_{3.851}\text{Ti}_{0.091}\text{Al}_{0.008}\text{Si}_{0.094})\text{O}_{11} \cdot 9\text{H}_2\text{O}$, which is based on the last five entries in Table 1, the calculated density is 2.736 g/cm^3 for $Z = 4$. For the same average composition adjusted to (Nb,Ti,Al,Si) = 4, the calculated density is 2.713 g/cm^3 . Suspension of franconite globules containing 1.3 to 1.7 wt. % CaO gave a measured density of $2.72(1) \text{ g/cm}^3$. The same specimen (NMC 62094) was used to obtain the powder-diffraction pattern.

Using the data of Mandarino (1976, 1979) on the Gladstone–Dale relationship, the above average formula with (Nb,Ti,Si,Al) = 4 yields a chemical molar

TABLE 3. X-RAY POWDER DATA FOR DEHYDRATED FRANCONITE

desiccated, partly rehydrated		heated to 250°C	
I_{est}	$d_{\text{meas}} (\text{Å})$	I_{est}	$d_{\text{meas}} (\text{Å})$
6 VB	10.4	8	6.36
3 B	6.3	10	4.55
2 VB	5.44	7	4.40
4 VB	4.53	1	3.73
1 VB	3.74	2	3.64
10	3.20	5	3.19
6	3.15	7	3.17
1 B	3.07	1	2.88
4 VB	2.96	5	2.641
3	2.67	2	2.568
2	2.63	1	2.258
2 B	2.55	2	2.031
5	2.253	2	1.986
1 VB	2.10	4	1.946
1 B	2.03	1	1.896
3 B	1.98	2	1.728
		1	1.686
		1	1.589

Camera diameter 114.6 mm, CoK α radiation ($\lambda = 1.7902 \text{ \AA}$). B broad, VB very broad.

refractivity K_C of 0.279. The physical molar refractivity K_P , obtained from the mean index of refraction and measured density, is 0.281, so that $K_P/K_C = 1.007$.

The X-ray powder pattern obtained from desiccated franconite re-exposed to air for only a few hours is given in Table 3. The desiccated product is thought to approximate $\text{Na}_2\text{Nb}_4\text{O}_{11}(\text{H}_2\text{O})_3$, but the amount of additional water re-absorbed during the initial X-ray filming is not known. Subsequent reruns of the same X-ray spindle over a two-year period have shown that rehydration leads to a product whose X-ray pattern is similar to that of franconite but which differs most notably in the appearance of a doublet in the 10–11 Å position.

RELATED MINERALS

X-ray data for UK43 from Mont St. Hilaire, Quebec (Chao & Baker 1979) and qualitative energy-dispersion analysis of a fragment of this mineral indicate that it is probably franconite. Specimens of franconite from Montreal Island commonly contain substantial amounts of calcium, but the extent of Na–Ca solid solution has not been resolved, mainly because multiple phases appear at intermediate compositions.

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