Canadian Mineralogist
Vol. 24, pp. 449-453 (1986)

HOCHELAGAITE, A NEW CALCIUM–NIOBIUM OXIDE MINERAL FROM MONTREAL, QUEBEC

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ABSTRACT

The new mineral hochelagaite occurs as white globules, 150 μm across, in vugs of a dawsonite-bearing sill in the Francon limestone quarry, Montreal, Quebec. The globules consist predominantly of radiating bladed crystals with a vitreous lustre, white streak, hardness 4. Optically, we measure $n\alpha$ 1.72(1), $n\beta$ 1.81(1), $n\gamma$ 1.82(1), (-)2V 35(5)°; Z is parallel to the elongation (c) and α (b) is perpendicular to the blades. Microprobe analyses of four globules gave, in wt.%, CaO 6.3–7.7, SrO 0.0–1.2, Na_2O 0.0–1.3, Nb_2O_5 71.7–78.3, TiO_2 1.2–1.5, Al_2O_3 0.0–0.8, SiO_2 0.4–1.5, H_2O (by difference) 10.3–18.9; the results correspond to $(Ca,Na,Sr)(Nb,Ti,Si,Al)_4O_{11}\bullet nH_2O$, where n is probably 8. Indexing of the X-ray powder pattern gave a 19.88(1), b 12.83(1), c 6.44(1) Å, β 93.20(3)°. Measured densities range from 2.85 to 2.94 g/cm³, and calculated values range from 2.82 to 2.88 g/cm³ assuming $8H_2O$ and $Z = 4$. The strongest lines of the X-ray pattern are 10.0(10), 5.39(5), 4.96(5), 3.208(7), 3.115(8), 2.799(4). Many of the properties of hochelagaite are similar to those of franconite; on heating, however, hochelagaite decomposes to $CaNb_4O_{11}$, whereas franconite goes to $Na_2Nb_4O_{11}$. The new name is derived from Hochelaga, the original name for Montreal. UK–50 from Mont St-Hilaire is hochelagaite.

Keywords: hochelagaite, new mineral species, Ca–Nb oxide hydrate, Francon quarry, Montreal, Quebec, UK–50, Mont St-Hilaire, Quebec.

SOMMAIRE

La nouvelle espèce minérale hochelagaïte se présente sous forme de globules blancs, d'environ 150 μm de diamètre, dans les vacuoles d'un sill à dawsonite de la carrière de calcaire Francon, sur l'île de Montréal (Québec). Les globules sont constitués de cristaux rayonnant du centre, en lames d'aspect vitreux, à rayure blanche et de dureté 4. Optiquement, on a $n\alpha$ 1.72(1), $n\beta$ 1.81(1), $n\gamma$ 1.82(1), (-) 2V 35(5)°; γ parallèle à l'allongement (c) et α (b) normal au plan des lames. Les analyses à la microsonde de quatre de ces globules indiquent: CaO 6.3–7.7, SrO 0–1.2, Na_2O 0–1.3, Nb_2O_5 71.7–78.3, TiO_2 1.2–1.5, Al_2O_3 0–0.8, SiO_2 0.4–1.5, H_2O (par différence) 10.3–18.9% en poids, ce qui correspond à $(Ca,Na,Sr)(Nb,Ti,Si,Al)_4O_{11}\bullet nH_2O$, où n est probablement égal à 8. Les dimensions de la maille, obtenues à partir du cliché de poudre aux rayons X, sont a 19.88(1), b 12.83(1), c 6.44(1) Å, β 93.20(3)°. En supposant $8H_2O$ et $Z = 4$, on calcule $D_{calc} = 2.82$ à 2.88; $D_{mes} = 2.85$ à 2.94. Les raies les plus intenses du cliché de poudre sont: 10.0(10), 5.39(5), 4.96(5), 3.208(7), 3.115(8), 2.799(4). En nombre de propriétés, l'hochelagaïte ressemble à la franconite; au chauffage, l'hochelagaïte se décompose en $CaNb_4O_{11}$, tandis que la franconite se décompose en $Na_2Nb_4O_{11}$. Le nom adopté est dérivé d'Hochelaga, nom originel de Montréal. L'échantillon UK–50 du mont St-Hilaire est identifié comme hochelagaïte.

Mots-clés: hochelagaïte, nouvelle espèce minérale, oxyde hydraté de Ca–Nb, Montréal, Québec, UK–50, mont St-Hilaire, Québec.

INTRODUCTION

Dawsonite-bearing sills in the Francon limestone quarry at Montreal, Quebec, have been the source of several new minerals (Sabina 1979), of which the most recently described is franconite $(Na,Ca)_2(Nb,Ti)_4O_{11}\bullet nH_2O$ (Jambor *et al.* 1984). The new mineral *hochelagaite,* described herein, is intimately associated with franconite; the two minerals are related in composition and X-ray properties but may not be isostructural. The new name hochelagaite (HŌSHE. LĂ-GAWAĪT) is derived from Hochelaga, the original appelation for the City of Montreal and for the county that encompassed most of Montreal Island, including the site of the Francon quarry. The new mineral and its 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 (64285–64288) and at the Royal Ontario Museum (M37547, M37548).

PHYSICAL AND OPTICAL PROPERTIES

Hochelagaite occurs as polycrystalline white globules that average about 150 μm in diameter. Individual globules consist of radiating blades, each about 0.03 × 0.005 × 0.001 mm, or of a finer-grained compact core of random grains gradational to a radiating, bladed rim. Hochelagaite has a white streak, vitreous lustre, is nonfluorescent, brittle, and is unreactive in 1:1 HCl at room temperature. No cleavage was observed. The hardness, determined by abrasion of globules against micromounts of standard minerals, is about 4.

Hochelagaite is biaxial negative, with α 1.72(1), β_{calc} 1.81(1), γ 1.82(1), and with $2V = 35(5)°$ measured by universal stage. Extinction of the blades is parallel (±5°), with Z along the elongation and X perpendicular to the plane of the blades. Except for the higher indices of refraction, the optical properties and crystal shapes of hochelagaite are similar to those of franconite.

Hochelagaite is megascopically indistinguishable from franconite, and both occur predominantly on crystals of weloganite, calcite and quartz. Individual globules commonly contain both hochelagaite and franconite, and in some cases the compositions vary from blade to blade. Usually, however, there is segregation into areas in which the blades are of similar composition, and therefore reliable analyses can be obtained; heterogeneity in the globules diminishes and, in rare cases, is absent when compositions approach those of end-member franconite or hochelagaite. The stability of polished areas of sodium-poor hochelagaite distinguishes this mineral from franconite: franconite is extremely sensitive to moisture, and polished areas of the mineral characteristically swell even after a mere wipe with a damp tissue.

CHEMICAL COMPOSITION

Microprobe analyses of hochelagaite were obtained at the Geological Survey of Canada and at CANMET, using standards of synthetic $NaNbO_3$, synthetic TiO_2, titanite, celestite, orthoclase, kaersutite and halite. Operating conditions varied from 16 to 20 kV and 0.038 to 0.027 microamperes. The results of the analyses of four globules of Francon hochelagaite are given in Table 1. Two of the globules were checked with another microprobe capable of detecting fluorine and carbon, but these elements were not found. The water content of hochelagaite could not be determined because of the minute amount of pure material available, but based on the similarity of franconite and hochelagaite, the apparent absence of other anions in hochelagaite, and the breakdown of the mineral to $CaNb_4O_{11}$ on heating, the low analytical totals in Table 1 are attributed to the presence of H_2O. The substantial differences in calculated H_2O contents among the various sets of analytical data are considered to reflect variations in H_2O rather than analytical errors.

The analytical formula of hochelagaite corresponds approximately to $(Ca,Sr,Na)(Nb,Ti,Si,Al)_4O_{11}{\bullet}nH_2O$, and the simplified theoretical formula is $CaNb_4O_{11}{\bullet}nH_2O$. X-ray-diffraction and microbeam studies have indicated that the persistent presence of the minor elements does not

TABLE 1. COMPOSITION OF HOCHELAGAITE

	Francon quarry				Mont St-Hilaire				
	NMC 64285	NMC 64286	NMC 64287	NMC 64288	M37547		M37548		average (8 anal.)
					dark*	light*	dark*	light*	
wt.% CaO	6.7	7.7	7.0	6.3	6.6	8.3	7.6	7.8	7.3
SrO	1.2	0.2	0.5	0.0	0.0	0.0	0.0	0.0	0.3
Na_2O	0.7	0.0	0.3	1.3	1.9	0.7	0.7	0.8	0.8
Nb_2O_5	73.8	72.0	71.7	78.3	73.5	78.5	75.5	79.7	75.3
TiO_2	1.3	1.5	1.2	1.5	2.5	2.0	0.5	0.7	1.4
Al_2O_3	0.0	0.0	0.0	0.8	0.6	0.9	0.4	0.6	0.4
SiO_2	1.1	0.6	0.4	1.5	0.9	1.7	1.5	2.8	1.3
H_2O	15.2	18.0	18.9	10.3	14.0	7.9	13.8	7.6	13.2
formula ratios for (Nb,Ti,Si,Al)=4									
Ca	0.810	0.963	0.890	0.693	0.770	0.895	0.893	0.834	0.844
Sr	0.079	0.014	0.034	0.000	0.000	0.000	0.000	0.000	0.016
Na	0.153	0.000	0.069	0.259	0.401	0.137	0.149	0.155	0.165
	1.042	0.977	0.993	0.952	1.171	1.032	1.042	0.989	1.025
Nb	3.766	3.798	3.845	3.634	3.620	3.571	3.743	3.597	3.697
Ti	0.110	0.132	0.107	0.116	0.205	0.151	0.041	0.053	0.114
Al	0.000	0.000	0.000	0.097	0.077	0.107	0.052	0.071	0.051
Si	0.124	0.070	0.048	0.153	0.098	0.171	0.164	0.279	0.138
H_2O	5.7	7.0	7.5	3.5	5.1	2.7	5.0	2.5	5.47

Analytical data by electron probe, H_2O by difference from 100 wt.%. Ta not detected.

*Appearance in backscattered electron image; dark area is the principal phase. All four analyses also have 0.1 wt.% Cl (close to limit of detection and not included in totals).

originate from discrete contaminant phases, but nothing else is known about the nature or role of these elements; possibly their presence is essential in maintaining a hydrated structure, but this seems unlikely in view of the reported syntheses of various hydrated sodium niobates (Muller 1970), as well as the synthesis of compounds such as $K_2Ta_4O_{11}\cdot 3H_2O$ (Marshall & Laudise 1967). All compositions in Table 1 show a slight excess in the Nb position if 11 oxygen atoms are assumed, or a corresponding deficiency in O if the Nb position is adjusted to 4. Only minor substitution of OH is necessary to attain the chemical formula $CaNb_4(O,OH)_{11}$; for the average composition in Table 1 the cation charges are balanced by $O_{10.71}$ or $(O_{10.42}OH_{0.58})_{\Sigma 11}$.

Thermal decomposition

Globules of hochelagaite from hand specimen NMC 64286, heated in air to 150°C and 250°C, gave the same, unidentified X-ray patterns as were obtained from franconite heated to these temperatures (Jambor *et al.* 1984); hochelagaite heated to 350°C seems to be similar, but the material is largely amorphous and diffracts poorly. At 500°C and at higher temperatures, the product formed corresponds to $CaNb_4O_{11}$ as is indicated by the similarity of the X-ray powder pattern to that of $CaTa_4O_{11}$ (PDF 15-679).

X-RAY DATA

The fine grain-size of Francon hochelagaite precluded single-crystal X-ray studies; the powder pattern was indexed on the basis of its similarity to that of franconite. Although the measured values in Table 2 were obtained from a hochelagaite globule of unspecified composition, the data are representative and were chosen because of the superior sharpness of the X-ray pattern. Cell parameters calculated from the powder data (Table 2) give a cell volume of 1640 Å^3. X-ray patterns of grains NMC 64286 and 64287, of nearly end-member composition, have the inferior sharpness characteristic of most hochelagaite films; cell volumes of both are 1656 Å^3, based on calculated dimensions of *a* 19.98(2), *b* 12.88(1), *c* 6.446(6)Å, ß 93.41(8)°.

A sample of UK-50 from Mont St-Hilaire, Quebec, kindly provided by G.Y. Chao of Carleton University, Ottawa, gave an X-ray pattern identical to that of hochelagaite. A qualitative energy-dispersion analysis confirmed that Ca and Nb are the only major detectable elements, and no contaminants or heterogeneity were evident. A long-exposure X-ray oscillation photograph of a blade mounted along the elongation gave 6.4 Å for this axis, but additional unit-cell information could not be obtained. The 6.4 Å axis corresponds to the *c* value obtained from indexing of the powder pattern of Francon hochelagaite.

TABLE 2. X-RAY POWDER DATA FOR HOCHELAGAITE

I est	*d*meas	*d*calc	*hkl*	I est	*d*meas	*d*calc	*hkl*
10	10.0	9.93	200	1/2	2.693	2.694 2.693	440 $\bar{5}31$
2	6.18	6.22	$\bar{1}01$	1/2B	2.606	2.609	341
<1/2	5.61	5.60	$\bar{1}11$	2	2.541	2.543 2.542	701 $\bar{4}22$
5	5.39	5.39	220	<1/2	2.492	2.495 2.494	540 711
5B	4.96	4.96	400	1	2.276	2.275	522
<1/2	4.61	4.61	320	2	2.232	2.232	$\bar{2}42$
1	4.48	4.49	301	<1/2	2.197	2.195 2.195	$\bar{6}41$ 242
2B	4.24	4.24	311	2B	2.085	2.086	920
2B	3.93	3.93 3.93	230 420	2	2.020	2.019	$\bar{8}02$
1/2	3.61	3.59	330	3B	1.979	1.979	$\bar{2}52$
1	3.50	3.49	131	2B	1.890	1.890	$\bar{4}61$
7	3.208	3.208	040	<1/2	1.863		
1/2	3.161	3.167	140	1/2B	1.810		
8	3.115	3.118	012	2B	1.755		
2	3.059	3.055	112	1	1.708		
<1/2	2.936	2.936	$\bar{4}31$	1	1.690		
<1/2	2.854	2.852	431	1B	1.666		
4	2.799	2.798	$\bar{2}22$				

Camera diameter 114.6 mm, CoKα radiation (λ 1.7902 Å), intensities estimated visually. Indexed with *a* 19.882(6), *b* 12.831(4), *c* 6.438(2) Å, β 93.20(3)°. B refers to broad lines.

VARIATIONS IN COMPOSITION

Mont St-Hilaire

Two additional samples of UK-50 from Mont St-Hilaire were obtained from the Royal Ontario Museum (M37547, M37548). Several X-ray powder mounts of grains selected under a binocular microscope gave patterns suggestive of mixtures containing abundant hochelagaite, and none of the results could be duplicated. Nevertheless, part of a globule from each sample was mounted in a polished section, and each appeared to be largely homogeneous. Backscattered electron-imaging showed that the optically homogeneous areas of each globule contain a moderate-sized irregular patch having an average atomic number higher than that of the principal portion of each globule. Microprobe data for the principal and minor phases are given in Table 1. Although X-ray patterns of the analyzed areas are of poor quality, mainly because of the small amount of material available, the diffraction lines of the principal phase (lower average atomic number) correspond well with the *d* values and intensities of all of the main diffraction lines of hochelagaite. Data for the minor phase (higher average atomic number) are too poor to be conclusive; it might be relevant, however, that in all of the X-ray patterns obtained from megascopic grains, the strong 10 Å line is accompanied by another whose *d* value is so slightly higher that the pair appears as a single broad line or a barely resolved doublet. This feature suggests that hochelagaite with a variation in composition is present. As it is known that the principal phase in Table 1 approximates normal hochelagaite, the higher *d* values could represent the minor phase.

Comparison of the four St-Hilaire analyses (Table 1) shows that the higher average atomic number of the minor phase mainly reflects its lower H_2O content; as the *d*-value shift indicates an enlargement in the cell despite the lower H_2O, presumably the enlargement reflects a variation in Na and Ca rather than in H_2O.

Francon quarry

Numerous microprobe analyses of the core *versus* the rim of globules of Francon hochelagaite commonly show variations of 2 to 3 wt.% in the analytical totals, but no systematic spatial trends in the totals, nor in the direction of cation variation, could be found. The only clearly defined, consistent trend is that Na increases as Ca decreases, thus indicating that at least partial mutual substitution occurs between these elements.

To determine the range of solid solution, about 50 globules of hochelagaite and franconite were mounted in polished sections and checked by energy-dispersion analysis; more than half of the globules were quantitatively analyzed and examined by X-ray powder-diffraction patterns. Without referring to the analyses, the powder patterns were grouped into 5 categories: types A and B were subsequently found to correspond to franconite and calcian franconite (2.6 wt.% Ca), and type E matches end-member hochelagaite. Intermediate types C and D correlate well with compositions rich in both Na + Ca, but all of these X-ray patterns show line broadening as well as two lines in the 10 Å - 11 Å position. The displacement of the two lines from their normal positions in hochelagaite and franconite suggests that both franconite and hochelagaite of intermediate compositions are present, but the invariable appearance of two phases at these compositions suggests that the minerals are not isostructural.

The limit of sodium substitution in hochelagaite could not be determined because of the difficulty in precisely correlating X-ray powder-diffraction patterns with areas that were analyzed, and because of the apparent absence of homogeneous areas of suitable compositions. The microprobe and X-ray results suggest that increases in the Na content of hochelagaite are accompanied by increased heterogeneity in the samples. Thus, analyses of Na-rich hochelagaite commonly yield inconsistent alkali values; this inconsistency, which is not present for the other elements, is evident from pronounced rises in the homogeneity index for Na and Ca microprobe data (Boyd *et al.* 1967). Therefore, extreme caution is necessary in interpreting the analytical results; at this stage the Ca:Na ratio in the hochelagaite formula cannot be extended with confidence beyond 66:34. Although hochelagaite and franconite are closely related, an isostructural series seems unlikely in view of the necessity of substituting $2Na^+$ for each Ca^{2+} to maintain charge balance. Incomplete solid-solution is also suggested from the increase in heterogeneity that accompanies sodium-rich hochelagaite.

Density and water content

The density of Francon hochelagaite was determined by suspension of globules in heavy liquids. Careful selection and checking of the material were necessary because globules from a hand specimen usually vary considerably in composition, and because individual globules rarely contain hochelagaite of a single, uniform composition. Nevertheless, density determinations of globules from four different samples all fell in the range 2.8–2.9 g/cm^3, requiring that nH$_2$O be 8 or 9, which is similar to the H_2O contents suggested for franconite (Jambor *et al.* 1984). For NMC 64285, which contains numerous sodium-rich areas, the measured density is 2.89(1) g/cm^3 and the calculated density is 2.883 g/cm^3, assuming $8H_2O$ in the analytical formula (V 1656 Å^3, $Z = 4$). For NMC 64286 the calculated densities assuming $8H_2O$ and $9H_2O$ are 2.883 and 2.955 g/cm^3, respectively, and the measured density is 2.94(1) g/cm^3.

The discrepancies between the H_2O contents inferred from the microprobe analyses *versus* those necessary to obtain satisfactory calculated densities imply that hochelagaite, despite its much greater stability relative to franconite, is also susceptible to partial dehydration. Among the Francon quarry samples, the discrepancy is especially evident for NMC 64288, which has an apparent water content of only 3.5 H_2O per formula unit. The measured density of this globule was found to be 2.847(5) g/cm^3. The globule was subsequently mounted in a polished section, analyzed (Table 1) and confirmed by X-ray powder pattern to be hochelagaite with a slightly reduced cell-volume of 1640 Å^3. Whether the smaller cell-volume reflects the low content of water is not known, but the calculated densities assuming $8H_2O$ and $9H_2O$ are 2.823 and 2.896 g/cm^3. The implications from these results are that hochelagaite undergoes a partial dehydration in the microprobe, and that the water loss does not change the basic structure of the mineral. In other words, there is no evidence that the various H_2O levels in Table 1 signify the presence of structurally different hydrates; all compositions apparently are representative of hochelagaite. It is also noteworthy that the Francon quarry samples, which have provided the most reliable data, show a good correlation between increasing Na and decreasing H_2O, thereby suggesting that sodium-rich hochelagaite is susceptible to fluctuations in H_2O content and thus has the instability noted for franconite (Jambor *et al.* 1984).

If the average analytical composition in Table 1 is recalculated assuming $8H_2O$ in the formula, the chemical molar refractivity K_C is 0.2786. The three globules for which measured densities have been obtained similarly yield K_C values of 0.2778 to 0.2793. The physical molar refractivity is 0.2708 if the average of the measured densities is used, and is 0.2736 using the calculated densities and $8H_2O$ in the formulae; the respective K_P/K_C values are 0.9720 and 0.9821. Similar calculations showed that

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of Mandarino (1979).

ACKNOWLEDGEMENTS

Specimens of UK–50 from Mont St-Hilaire were obtained through the generosity of R.A. Ramik of the Royal Ontario Museum, Toronto, and G.Y. Chao of Carleton University, Ottawa. E.J. Murray and J.H.G. Laflamme kindly provided technical assistance at CANMET. Reviews by E.E. Foord and W.B. Simmons of an earlier version of the manuscript are much appreciated.

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Received June 27, 1985, revised manuscript accepted December 17, 1985.