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ROUVILLEITE, A NEW SODIUM CALCIUM FLUOROCARBONATE MINERAL FROM MONT SAINT-HILAIRE, QUEBEC

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ABSTRACT

Rouvilleite, ideally $Na_3Ca_2(CO_3)_3F$, is a new mineral species from Mont Saint-Hilaire, Quebec. The mineral is transparent to translucent and occurs as tan, rusty brown and colorless crystalline masses, and rarely as transparent euhedral crystals, in an inclusion of sodalite syenite in nepheline syenite. Crystals are prismatic, elongate along [001], and are either terminated by {001} or by {101}, {023} and {03$\bar{2}$}. Associated minerals include villiaumite, shortite, aegirine, microcline, cancrinite, analcime, vuonnemite, cryolite, kogarkoite and others. Rouvilleite is brittle, Mohs hardness about 3, with a vitreous to slightly waxy luster, a white streak, an uneven fracture and imperfect {010} and good {001} cleavages. The mineral effervesces vigorously in 1:1 HCl and does not show fluorescence in ultraviolet light. It is optically biaxial negative with α 1.472(1), β 1.562(1), γ 1.569(1), $2V_{meas}$ 25(1)°, $2V_{calc}$ 30°, and a weak dispersion $r > v$. The orientation is b = Y, $c \wedge X = 6°$ in the acute β angle. Rouvilleite is monoclinic, *Cc* or *C2/c*, with a 8.043(4), b 15.812(5), c 7.030(3) Å, β 101.16(3)°, V 877.1(4) Å^3 and Z = 4. The strongest six lines of the X-ray-diffraction pattern (Gandolfi) [d in Å (I)(hkl)] are: 7.081(80)(110), 2.937(70)(150), 2.895(100)(20$\bar{2}$), 2.711(90)(22$\bar{2}$), 2.039(70)(242) and 1.869(75)(35$\bar{2}$). Averaged results of electron-microprobe analyses give Na_2O 25.95, CaO 26.47, MnO 6.83, FeO 0.52, MgO 0.01, F 5.65, CO_2(calc.) [37.21], $-F \equiv 2.38$, sum 100.26 wt.%, corresponding to $Na_{2.97}(Ca_{1.67}Mn_{0.34}Fe_{0.02})_{\Sigma 2.03}(CO_3)_3F_{1.06}$. Infrared-absorption spectroscopy confirms the presence of CO_2. $D_{meas.}$ 2.67(2), $D_{calc.}$ 2.69 g/cm^3. The name recalls Rouville County, within which Mont Saint-Hilaire occurs.

Keywords: rouvilleite, new mineral species, sodium calcium fluorocarbonate, Mont Saint-Hilaire, Quebec, X-ray data, chemical composition.

SOMMAIRE

La rouvilléite, de formule idéale $Na_3Ca_2(CO_3)_3F$, est une nouvelle espèce minérale provenant du mont Saint-Hilaire (Québec). Transparent à translucide, le minéral se trouve en amas cristallins de couleur beige à brun rouille, et plus rarement en cristaux idiomorphes transparents, dans une enclave de syénite à sodalite dans la syénite néphélinique. Les cristaux sont prismatiques, allongés sur [001], et montrent comme terminaisons les faces {001} ou {101}, {023} et {03$\bar{2}$}. Lui sont associés villiaumite, shortite, aegyrine, microcline, cancrinite, analcime, vuonnemite, cryolite et kogarkoïte. Elle est cassante, et possède une dureté de Mohs d'environ 3; son éclat est vitreux à légèrement cireux, et sa rayure, blanche. Le plan de clivage {001} est bon, et {010} imparfait; la cassure est irrégulière. Il y a effervescence vigoureuse à l'acide HCl 1:1; elle ne montre aucune fluorescence en lumière ultra-violette. Les cristaux sont biaxes négatifs, α 1.472(1), β 1.562(1), γ 1.569(1), $2V$ 25(1)° (mesuré), 30° (calculé), dispersion $r > v$. L'orientation est b = Y, $c \wedge X = 6°$ dans l'angle β aigu. La rouvilléite est monoclinique, *Cc* ou *C2/c*, avec a 8.043(4), b 15.812(5), c 7.030(3) Å, β 101.16(3)°, V 877.1(4) Å^3, et Z = 4. Les six raies les plus intenses du cliché de diffraction X [d en Å(I)(hkl)], obtenu avec une chambre de Gandolfi, sont: 7.081(80)(110), 2.937(70)(150), 2.895(100)(20$\bar{2}$), 2.711(90)(22$\bar{2}$), 2.039(70)(242) et 1.869(75)(35$\bar{2}$). Les analyses à la microsonde électronique donnent, en moyenne, Na_2O 25.95, CaO 26.47, MnO 6.83, FeO 0.52, MgO 0.01, F 5.65, CO_2 (calculé) [37.21], moins $F \equiv O$ 2.38, pour un total de 100.26% par poids, ce qui correspond à $Na_{2.97}(Ca_{1.67}Mn_{0.34}Fe_{0.02})_{\Sigma 2.03}(CO_3)_3F_{1.06}$. Les spectres d'absorption infra-rouge confirment la présence du CO_2. Densité mesurée 2.67(2), densité calculée 2.69. Le nom rappelle le comté de Rouville, où se trouve le mont Saint-Hilaire.

(Traduit par la Rédaction)

Mots-clés: rouvilléite, nouvelle espèce minérale, fluorocarbonate de sodium et de calcium, mont Saint-Hilaire, Québec, données de diffraction X, composition chimique.

INTRODUCTION AND OCCURRENCE

In the fall of 1988, a new mineral species, rouvilleite (formerly UK62), was found in a sodalite syenite inclusion (sodalite xenolith of Mandarino & Anderson 1989) of diameter 0.5 m within nepheline syenite, at the Poudrette Quarry, Mont Saint-Hilaire, Quebec. The mineral, moderately abundant in this particular inclusion, occurs most commonly as irregular crystalline masses up to 3 mm across, and rarely as euhedral crystals up to 1 mm across within cavities. Associated minerals include: aegirine, analcime,

TABLE 1. X-RAY-DIFFRACTION DATA FOR ROUVILLEITE

hkl	d_{calc} Å	d_{obs} Å	I
110	7.060	7.081	80
11$\bar{1}$	5.425	5.433	55
021	5.197	5.194	50
111	4.555	4.538	20
130	4.383	4.387	5
040	3.953	3.952	15
131	3.531	3.524	40
220	3.530		
$\bar{1}$12	3.334	3.326	15
150	2.935	2.937	70
20$\bar{2}$	2.888	2.895	100
240	2.792	2.791	50
22$\bar{2}$	2.713	2.711	90
060	2.635	2.637	60
132	2.579	2.580	55
202	2.378	2.377	20
15$\bar{2}$	2.319	2.321	35
222	2.278	2.277	20
260	2.191	2.193	5
170	2.172	2.169	45
331	2.118	2.118	10
062	2.094	2.096	25
242	2.038	2.039	70
$\bar{2}$62	1.947	1.946	20
312	1.906	1.906	25
35$\bar{2}$	1.870	1.869	75
$\bar{4}$22	1.825	1.825	40
332	1.804	1.805	45
280	1.767	1.767	55
$\bar{1}$14	1.746	1.746	60
190	1.715	1.716	55
082	1.715		
460	1.579	1.580	10
24$\bar{4}$	1.566	1.566	10
$\bar{4}$04	1.444	1.444	15
	Plus additional lines		

Visually estimated intensities, 114.6 mm Gandolfi camera, Ni-filtered Cu$K\alpha$ radiation (λ 1.5418 Å).

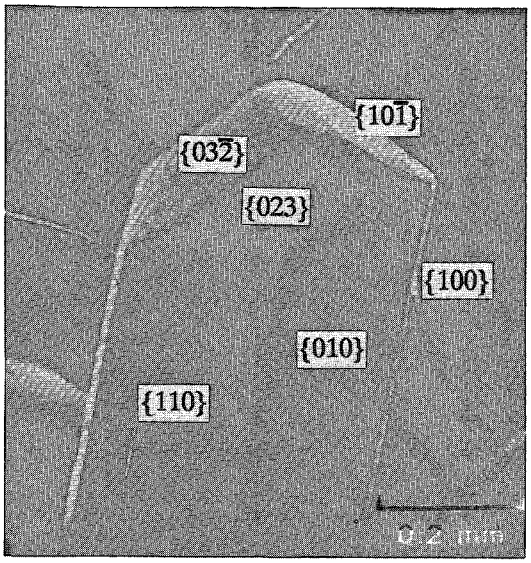

FIG. 1. A typical type-1 rouvilleite crystal.

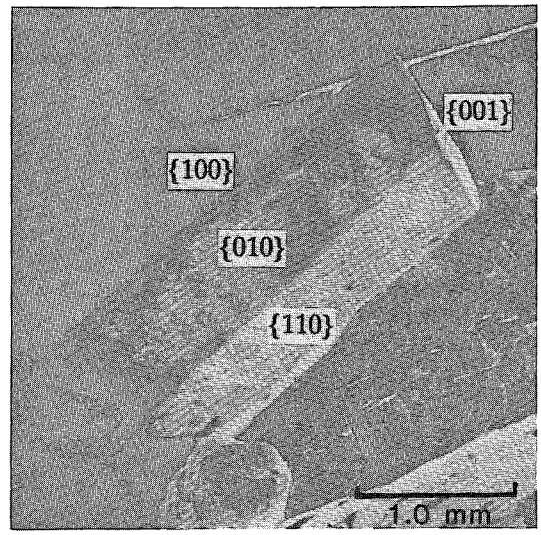

FIG. 2. A typical type-2 rouvilleite crystal.

burbankite, cancrinite, catapleiite, clinoamphibole, cryolite, eudialyte, fluorite, galena, kogarkoite, kupletskite, lorenzenite, microcline, molybdenite-2H, natrolite, pectolite, pyrophanite, serandite, shortite, sphalerite, sodalite, steenstrupine, thermonatrite, villiaumite, vinogradovite, vitusite, vuonnemite, and a metamict mineral. The occurrence of rouvilleite within villiaumite, and kupletskite within rouvilleite, suggests crystallization of rouvilleite after kupletskite and prior to villiaumite. The name of the mineral is inspired by Rouville County, within which the Monteregian hill, Mont Saint-Hilaire, is located. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The cotype specimens are deposited with the Royal Ontario Museum, Toronto (M44157, M44233) and the Canadian Museum of Nature, Ottawa (CMN54542).

CRYSTALLOGRAPHY

Precession photographs using Zr-filtered Mo$K\alpha$ radiation indicate that rouvilleite is monoclinic, with space group *Cc* (#9) or *C*2/*c* (#15). Cell parameters first obtained from single-crystal photographs, were refined using the least-squares program CELREF (Appleman & Evans 1973) and X-ray-diffraction data obtained with a Gandolfi camera. The refined values are: a 8.043(4), b 15.812(5), c 7.030(3) Å, β 101.16(3)°, V = 877.1(4) Å^3 and Z = 4. The Gandolfi diffraction pattern (Table 1) was indexed using the intensity of reflections on the precession photographs as a guide.

Although rare, euhedral crystals of rouvilleite have been found. These are prismatic, elongate along [001], and less than 1 mm in length; they occur in two distinct morphologies: type 1, bounded by the forms {010}, {110}, {100}, {10$\bar{1}$}, {023} and {03$\bar{2}$} (Fig. 1); and type 2, bounded by the forms {010} {110}, {100}, and {001} (Fig. 2). Both types give identical diffraction patterns. The faces {023} and {03$\bar{2}$} of the type-1 crystals, although indexable using a combination of optical and X-ray precession goniometry, are inconsistent with space groups *Cc* and *C*2/*c*. Two crystals exhibiting these forms have been found thus far.

Physical and Optical Properties

Rouvilleite is pale tan to colorless, but commonly appears reddish brown owing to inclusions of kupletskite. The mineral has a vitreous to slightly waxy luster and a white streak. Inclusion-free rouvilleite is transparent, but becomes slightly translucent as the amount of occluded material increases. The mineral is brittle, has a good {001} cleavage and an imperfect {010} cleavage, and possesses an uneven fracture. The Mohs hardness is about 3, and no fluorescence in long- or short-wave ultraviolet radiation was observed. A strong effervescence is noted when the mineral is placed in 1:1 HCl at room temperature. It is not soluble in water. The measured density, determined by flotation in a heavy liquid and a 25-mL pycnometer, is 2.67(2) g/cm^3, close to the value of 2.69 g/cm^3 calculated from the empirical formula and refined cell-dimensions.

Optically, rouvilleite is biaxial negative, with α 1.472(1), β 1.562(1), and γ 1.569(1), as measured in sodium light (λ 589.3 nm) on a spindle stage. The crystal used was a cleavage fragment previously oriented by the X-ray-precession method. The immersion liquids were checked using an Abbe refractometer. The 2*V* angle, measured by direct observation of the optic axes, is 25(1)°, whereas the calculated value is 30°. Rouvilleite possesses a sharp interference figure and shows a weak dispersion $r > v$. The optical orientation is b = Y, $c \wedge X = 6°$, in the acute β angle. It is nonpleochroic.

Chemical Composition

Both energy- and wavelength-dispersion analyses of rouvilleite were carried out on a Cambridge Microscan (MK) 5 electron microprobe. An acceleration voltage of 15 kV, a beam current of 25 nA (estimated), and a 75° fixed take-off angle were used for quantitative wavelength-dispersion (WDS) analyses. The following standards were used: tugtupite (Na), dolomite (Ca), rhodochrosite (Mn), Kakanui hornblende (Fe, Mg), and LiF (F). Samples were analyzed with a defocussed 10-μm beam to minimize the loss of Na and to maximize X-ray counts. Total elemental X-ray counts were obtained by averaging several sets of 20-second counts, except for Na, for which an average of six 2-second counts was used. Li was sought by atomic absorption, but not detected. The analytical results are listed in Table 2.

TABLE 2. CHEMICAL COMPOSITION OF ROUVILLEITE (wt.%)*

	1	2	3	4	5
Na_2O	25.53	26.59	25.72	25.95	26.60
CaO	25.99	26.50	26.91	26.47	32.21
MnO	6.52	5.85	8.13	6.83	-
FeO	0.29	0.63	0.64	0.52	-
MgO	0.03	-	-	0.01	-
CO_2**	(36.41)	(37.44)	(37.78)	(37.21)	37.92
F	5.49	5.40	6.07	5.65	5.46
Sum	100.26	102.41	105.25	102.64	102.19
O≡F	-2.31	-2.27	-2.56	-2.38	-2.19
Corr. Sum	97.95	100.14	102.69	100.26	100.00

1. Average of rouvilleite-1. 2. Average of rouvilleite-2.
3. Average of rouvilleite-3 4. Average of 1., 2., and 3.
5. Calculated components of the ideal formula, $Na_3Ca_2(CO_3)_3F$.
* Errors on wt.% values at the 2σ level (in wt. %): Na_2O (.21), CaO(.23), MnO(.18), FeO(.12), MgO(.1), F(.39).
** CO_2 calculated from stoichiometry.

The cation and F content in the unit cell, calculated from the averaged results of analyses, the refined cell-parameters and measured density, is: $4 \times [Na_{2.96}(Ca_{1.66}Mn_{0.34}Fe_{0.02})F_{1.06}]$. This suggest the ideal formula, $Na_3X_2(CO_3)_3F$, where $X = \Sigma Ca + Mn + Fe + Mg$. Therefore, 10 (O + F) is used as the basis to calculate the empirical formula, $Na_{2.97}(Ca_{1.67}Mn_{0.34}Fe_{0.02})_{\Sigma 2.03}(CO_3)_3F_{1.06}$. Using the Gladstone–Dale constants (Mandarino 1981), $1-(k_P/k_C) = -0.026$, which indicates excellent compatibility between chemical and physical data.

Infrared-Absorption Spectroscopy

The infrared-absorption spectrum of rouvilleite, shown in Figure 3, was obtained from a pellet composed of 3.5 mg of the mineral, and 400 mg of KBr (kept at 140°C). The pellet was run on a Perkin-Elmer 1600 series FTIR infrared-absorption spectrophotometer (4 cm^{-1} resolution capability), with the background subtracted prior to data collection.

The spectrum is characterized by strong vibration in the region 1600–1250 cm^{-1}, attributable to carbonate (White 1974). There is also a weak vibration in the region 3600–3100 cm^{-1}, which is attributable to adsorbed water (consistent with TGA–EGA results). The doubling of the ν_5 (1497 cm^{-1}, 1457 cm^{-1}) and ν_2 bands (1100 cm^{-1}, *etc.*) (following the notation of Fujita *et al.* 1962) suggests the presence of at least two nonequivalent carbonate groups.

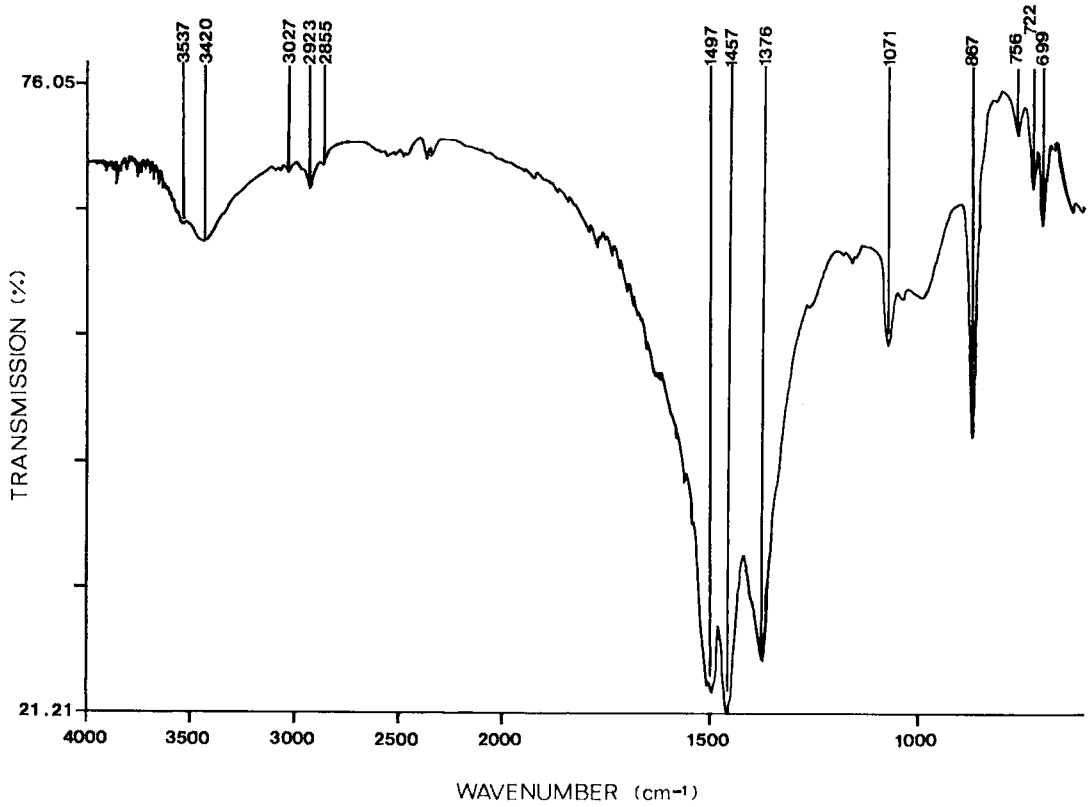

FIG. 3. The infrared-absorption spectrum of rouvilleite.

TGA–EGA ANALYSIS

Simultaneous thermogravimetric analysis (TGA) and evolved gas analysis (EGA) were performed on 8.293(6) mg of crushed and purified rouvilleite, using a Mettler TA–1 thermoanalyzer in conjunction with an Inficon IQ200 Quadrupole mass spectrometer at the Royal Ontario Museum. The starting material was visually estimated to be 98–99% pure, and no extra X-ray-diffraction lines were observed.

The sample was subjected to a preliminary high-vacuum treatment, which resulted in a loss of 1.5(5) wt.% (presumably adsorbed water). It was then heated at a rate of 10°C/min to a maximum temperature of 1400°C. The TGA–EGA curves show five peaks; the first one at 255°C, represents a loss of 0.3(1) wt.% water between 150 and 280°C. The four remaining peaks occur at 525, 715, 910 and 1195°C and represent a combined weight-loss (after a pressure correction) of 61.8 wt.%, which brings the total weight-loss over the interval 150 – 1400°C to 63.6 wt.%.

The evolved-gas analysis shows two volatile species, with masses of 32 and 44 atomic mass units, respectively, which are lost between 525 and 1195°C. The latter is clearly CO_2, and the former could represent S or O_2. However, as S was not detected by electron-microprobe analysis, this species must be O_2. The EGA also indicates that O_2 and CO_2 were given off contemporaneously, except for the 1195°C peak, which was solely ascribable to O_2. Peak-area calculations indicate a CO_2 molecular abundance approximately five times that of O_2.

Three phases are megascopically present in the heterogeneous residue; a thin, white layer, a light grey-brown powdery material with minor surficial black splotches, and a hard, darker grey-brown glass. An X-ray-diffraction investigation (Gandolfi camera) of the residue showed it to be composed principally of CaO and $Ca(OH)_2$, plus traces of an unidentified compound. Quantitative WDS analysis of this unidentifed compound indicate that it is composed essentially of Mn and Ca, with no detectable Na or F.

The significant amount of evolved O_2 is interpreted to be the result of the decomposition of Na_2O for two reasons: (a) the sum of the Na_2O, CO_2 and F estimated from the microprobe data, minus O ≡ F, is 66 wt.%, which approximates the

high-temperature TGA loss of ~ 62 wt.%; (b) Na_2O melts at 917°C, at presumably ambient pressure, and decomposes into $2Na + \frac{1}{2}O_2$ (Brewer & Margrave 1955). It is conceivable, therefore, that the melting point, and hence the decomposition temperature, of Na_2O could be lowered somewhat under the conditions of vacuum induced for TGA–EGA analysis.

In the TGA–EGA run, F was not detected, nor was it found in the TGA–EGA residue by wavelength-dispersion analysis. It is possible that F was released from the mineral in the form of NaF. NaF would not be detected by the mass spectrometer used, as the path leading to the spectrometer is not sufficiently heated to prevent the condensation of this volatile compound.

Synthesis

Both Mn-bearing (Mn:Ca ratio of 1:9) and Mn-free rouvilleite were hydrothermally synthesized at 680–700°C and 1.5 kbars pressure, using stoichiometric mixtures (approximately 70 mg) of reagent-grade Na_2CO_3, $MnCO_3$, $CaCO_3$, NaF and doubly distilled, deionized H_2O (approximately 20 mL). Four-cm-long gold capsules were used to enclose the starting materials. The successful synthesis of Mn-free material suggests that Mn is not essential to rouvilleite. Unfortunately, the products were found to be extremely fine-grained and to contain other phases, so that neither optical nor physical properties of the synthetic material could be accurately determined.

Acknowledgements

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References

Appleman, D.E. & Evans, H.T., Jr. (1973): Job 9214: indexing and least-squares refinement of powder diffraction data. *U. S. Geol. Surv., Comp. Contrib.* **20** (NTIS Doc. **PB2–16188**).

Brewer, L. & Margrave, J. (1955): The vapour pressure of lithium and sodium oxides. *J. Phys. Chem.* **59**, 421-425.

Fujita, J., Martell, A.E. & Nakamoto, K. (1962): Infrared spectra of metal chelate compounds. VIII. Infrared spectra of Co(III) carbonato complexes. *J. Chem. Phys.* **36**, 339-345.

Mandarino, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

_____ & Anderson, V. (1989): *Monteregian Treasures: The Minerals of Mont Saint-Hilaire, Quebec.* Cambridge University Press, Cambridge, England.

White, W.B. (1974): The carbonate minerals. *In* The Infrared Spectra of Minerals (V.C. Farmer, ed.). Mineral. Soc., London (227-284).

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