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DONNAYITE, $NaCaSr_3Y(CO_3)_6 \cdot 3H_2O$, A NEW MINERAL FROM MONT ST-HILAIRE, QUÉBEC

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ABSTRACT

Donnayite occurs in pegmatite dykes, miarolitic cavities and interstices in nepheline syenite at Mont St-Hilaire, Québec. Usually associated with microcline, analcime, calcite, natrolite, chlorite, aegirine, arfvedsonite and other minerals, donnayite commonly occurs in syntactic intergrowths with ewaldite, a Sr analogue of ewaldite, mckelveyite, and rarely with synchysite. Crystals, 0.05 to 2 mm, vary in habit from platy, tabular, columnar, saucer-shaped, barrel-shaped to irregularly granular; they are usually pale yellow to yellow, but also colorless, white, grey, brown to reddish brown, with a white streak and vitreous lustre. Hardness = 3. D_{obs} = 3.30 and D_{calc} = 3.266 g/cm^3. Basal cleavage indistinct to fair. Dissolves in HCl with strong effervescence. Optically, biaxial negative, with α 1.551–1.561, β 1.646, γ 1.652, $2V$ 0–20°, $X \simeq c^*$. Donnayite is isomorphous with weloganite (as shown by the following unconventional setting): triclinic P1, a 9.000, b 8.999, c 6.793Å, α 102.77, β 116.28, γ 59.99°, Z = 1. The nine strongest powder diffraction lines are: 6.103 (4) (001), 4.368 (7) (120, 21$\bar{1}$, 1$\bar{1}$0), 3.209 (3) (121, 1$\bar{1}$1, 21$\bar{2}$), 2.839 (10) (211, 1$\bar{1}\bar{2}$, 12$\bar{2}$), 2.598 (4) (33$\bar{1}$, 030, 30$\bar{1}$), 2.038 (3) (3$\bar{1}$0, 11$\bar{3}$, 212, 00$\bar{3}$), (2.018 (3) (242, 22$\bar{2}$, 420), 1.978 (3) (33$\bar{3}$, 303, 03$\bar{2}$, 032, 301, 331), 1.694 (3) (54$\bar{2}$, 51$\bar{2}$, 14$\bar{0}$, 150, 4$\bar{1}\bar{1}$, 45$\bar{1}$, 21$\bar{4}$, 1$\bar{1}$3). Twinning by rotation about [103]$_{120°}$ and by reflection across (010), (30$\bar{1}$) or ($\bar{3}\bar{3}$1) is extremely common. Electron microprobe analysis gives: Na_2O 3.37, CaO 5.75, BaO 0.85, SrO 35.8, Y_2O_3 13.1, Nd_2O_3 1.83, La_2O_3 0.45, CO_2 (30.98), H_2O (6.34), sum 98.47%. CO_2 and H_2O are assumed to be stoichiometric. The analysis corresponds to $Na_{0.93}(Ca_{0.87}Nd_{0.09}La_{0.03})(Sr_{2.95}Ba_{0.05})Y_{0.99}(CO_3)_6 \cdot 3H_2O$, or ideally $NaCaSr_3Y(CO_3)_6 \cdot 3H_2O$. New data show that mckelveyite is also triclinic, isomorphous with weloganite and donnayite; its original analysis may be recalculated to $(Na_{1.29}K_{0.02})(Ca_{0.73}U_{0.17})(Ba_{2.72}Sr_{0.17})(Y_{0.70}RE_{0.32})(CO_3)_6 \cdot 3.48H_2O$, close to $NaCaBa_3Y(CO_3)_6 \cdot 3H_2O$.

SOMMAIRE

La donnayite se présente dans des dykes pegmatitiques, cavités miarolitiques et fissures dans la syénite à néphéline du mont St-Hilaire, dans la province de Québec. Elle s'y trouve ordinairement associée aux espèces suivantes: microcline, analcime, calcite, natrolite, chlorite, aegyrine, arfvedsonite. Elle forme des groupements syntaxiques avec l'éwaldite, l'éwaldite strontique, la mackelveyite et, mais rarement, avec la synchisite. Le faciès des cristaux est variable: aplati, tabulaire, prismatique, en forme de soucoupe ou de tonnelet, en masses grenues. Ces cristaux, dont la taille oscille entre 0.05 et 2mm, sont normalement de couleur jaune ou jaune pâle, parfois incolores, blancs, gris, bruns à rougeâtres, à poussière blanche et éclat vitreux. Dureté 3. D_{obs} 3.30, D_{calc} 3.266. Clivage parallèle à la base (plan du faciès tabulaire), indistinct ou assez bon. Ce minéral est soluble dans HCl avec forte effervescence. Observations optiques: α 1.551 – 1.561, β 1.646 γ 1.652, $2V$ (–) 0-20°, $X \simeq c^*$. La donnayite est isomorphe de la weloganite, triclinique $P1$, a 9.000, b 8.999, c 6.793Å, α 102.77, β 116.28, γ 59.99°, Z = 1 (maille non-conventionnelle pour montrer l'isomorphie). Pour les neuf raies les plus intenses du diagramme de poudre, 6.103 (4) (001), 4.368 (7) (120, 21$\bar{1}$, 1$\bar{1}$0), 3.209 (3) (121, 1$\bar{1}$1, 21$\bar{2}$), 2.839 (10) (211, 1$\bar{1}\bar{2}$, 12$\bar{2}$), 2.598 (4) (33$\bar{1}$, 030, 30$\bar{1}$), 2.038 (3) (3$\bar{1}$0, 11$\bar{3}$, 212, 003), 2.018 (3) (24$\bar{2}$, 22$\bar{2}$, 420), 1.978 (3) (33$\bar{3}$, 30$\bar{3}$, 03$\bar{2}$, 032, 301, 331), 1.694 (3) (54$\bar{2}$, 51$\bar{2}$, 140, 150, 4$\bar{1}\bar{1}$, 45$\bar{1}$, 21$\bar{4}$, 1$\bar{1}$3). Macles très fréquentes: par rotation [103]$_{120°}$; par réflexion (010), (30$\bar{1}$), ($\bar{3}\bar{3}$1). La sonde électronique donne Na_2O 3.37, CaO 5.75, BaO 0.85, SrO 35.8 Y_2O_3 13.1, Nd_2O_3 1.83, La_2O_3 0.45, CO_2 (30.98), H_2O (6.34), total 98.47% (on admet que CO_2 et H_2O sont stoechiométriques). Cette analyse correspond à $Na_{0.93}(Ca_{0.87}Nd_{0.09}La_{0.03})(Sr_{2.95}Ba_{0.05})Y_{0.99}(CO_3)_6 \cdot 3H_2O$, soit idéalement $NaCaSr_3Y(CO_3)_6 \cdot 3H_2O$. La mackelveyite, réexaminée, s'avère triclinique, isomorphe de weloganite et donnayite; sa composition originelle peut s'écrire $(Na_{1.29}K_{0.02})(Ca_{0.73}U_{0.17})(Ba_{2.72}Sr_{0.17})(Y_{0.70}RE_{0.32})(CO_3)_6 \cdot 3.48H_2O$, soit $NaCaBa_3Y(CO_3)_6 \cdot 3H_2O$ comme formule idéale.

(Traduit par la Rédaction)

INTRODUCTION

In 1973 a specimen from mont St-Hilaire, Québec, labeled "brockite" was sent by D. W. Richerson to one of us (GYC) for verification. The specimen is composed of arfvedsonite, aegirine, calcite, sphalerite and minor amounts of catapleiite filling the interstices of coarse microcline crystals. The so-called "brockite" occurs as aggregates of approximately 0.5mm tabular crystals which usually display rough, irregular

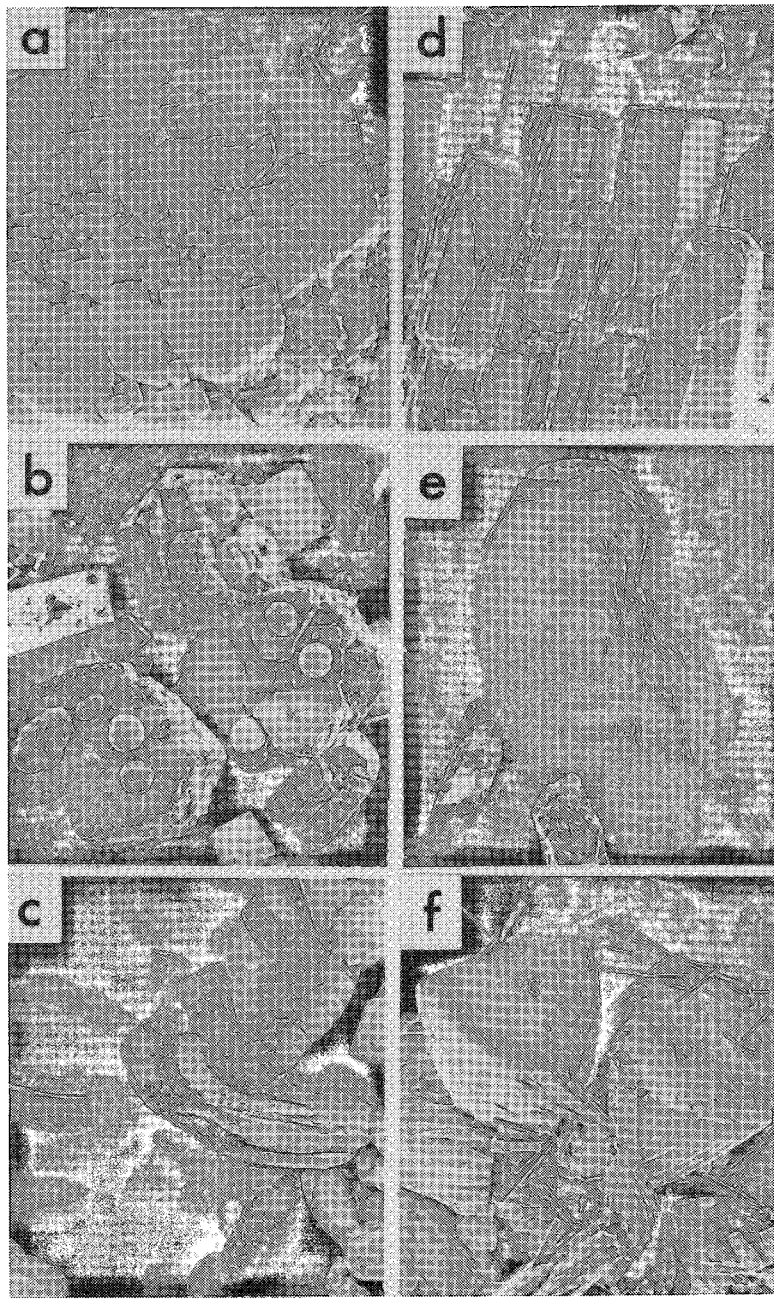

FIG. 1. Scanning electron photomicrographs of donnayite. (a) Parallel growth or twinned crystal aggregate (1 mm dia.). (b) White tabular crystals (1 mm) of donnayite with brownish-red globular gaidonnayite crystals. (c) Saucer-shaped crystals (0.2 mm). (d) Columnar (1 mm long) aggregates displaying crystals with pedial termination. (e) Barrel-shaped crystal (1.5 mm long). (f) Hemimorphic crystals (0.2 mm) with pedial termination.

and somewhat curved surfaces with an overall hexagonal crystal outline. Some crystals are transparent with a pale yellow color but most crystals show a gradation of color from pale yellow and transparent near the rim to dark reddish brown and almost opaque toward the core. Under high magnification, with a scanning electron microscope, each "crystal" was found to be composed of numerous individuals in sub-parallel to parallel growth (Fig. 1a), too small to be separated for single-crystal X-ray work. Preliminary optical and X-ray studies together with electron microprobe analyses indicated the mineral to be a new species, a Y-bearing analogue of weloganite ($Na_2Sr_3Zr(CO_3)_6 \cdot 3H_2O$: Chen & Chao 1975, Grice & Perrault 1975). However, due to the small amount of material available and the lack of truly single crystals, a complete description of the mineral was not possible and the mineral was therefore tentatively designated *UK*33.

A year later, the mineral was again encountered in small quantities in varied mineral associations, habits and colors on newly collected specimens and on specimens sent to us for verification from several advanced mineral collectors. It became possible, therefore, to gather sufficient data for characterizing this new species. The mineral has been named donnayite, after Professors J. D. H. Donnay and G. Donnay, in recognition of their contributions to the fields of crystallography and mineralogy. Both the mineral and its name have been approved by the Commission on New Minerals and Mineral Names, I. M. A. The type specimens are deposited at the National Museum of Natural Sciences, Ottawa (Specimen #39394, 39395, 39396) and the Royal Ontario Museum, Toronto (specimen #*M*35222).

Occurrence and Physical Properties

Donnayite occurs in small quantities in the pegmatite dykes, miarolitic cavities and interstices in the nepheline syenite at Mont St-Hilaire, Québec. The mineral is usually associated with microcline, analcime, natrolite, calcite, chlorite, aegirine, arfvedsonite and minor amounts of siderite, rhodochrosite, ancylite, pyrite, sphalerite, hematite, goethite, pyrophanite, catapleiite, gaidonnayite and astrophyllite. Crystals are usually very small, from 0.05 to 1.0mm, rarely 2.0mm. The mineral is commonly pale yellow to yellow, but also colorless, white, grey and rarely reddish brown due to hematite inclusions. The streak is white. The mineral is transparent with a vitreous lustre, but the white and grey varieties are opaque and earthy. Crystals with vitreous lustre have a hardness about 3 on the Mohs scale whereas the earthy material is apparently softer. An indistinct to fair basal cleavage is present. Density determined by the flotation method is 3.30(1) g/cm^3. The mineral dissolves rapidly in 1:1 HCl with strong effervescence.

Donnayite crystals generally display apparent trigonal or hexagonal symmetry with various habits from platy, tabular (Fig. 1b), saucer-

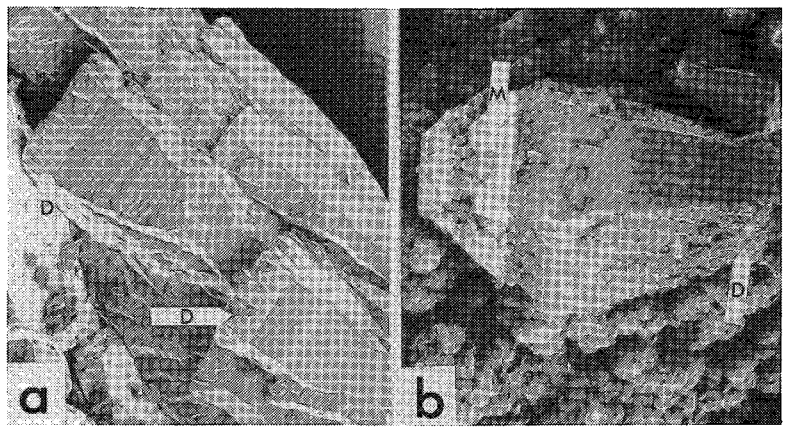

FIG. 2. Scanning electron photomicrographs of polycrystals produced by syntactic intergrowth of donnayite with other minerals. (a) Hemimorphic polycrystals (1.5-2.0 mm long) of ewaldite (dark bands) and donnayite (lighter bands) with a donnayite "cap"(D). The polycrystals are white and opaque, the "caps" are pale yellow and transparent. (b) A doubly terminated hemimorphic polycrystal (2.0 mm long) of ewaldite and its Sr analogue with "caps" of donnayite(D) and mckelveyite(M).

shaped (Fig. 1c), columnar (Fig. 1d), barrel-shaped (Fig. 1e) to irregularly granular. Some crystals are clearly hemimorphic, with curved trigonal pyramidal faces converging toward a point on one end and terminated with a flat pedion on the other (Fig. 1f). As with the minerals in the bastnaesite–synchysite family (Donnay & Donnay 1953), donnayite commonly forms syntactic intergrowths with other minerals of similar structure and chemical composition. Ewaldite, $Ba(Na,Ca,Y,RE)(CO_3)_2$ (Donnay & Donnay 1971), a Sr analogue of ewaldite, mckelveyite, and rarely synchysite have been found in such intergrowths with donnayite. Donnayite may occur as a "cap" on ewaldite crystals as shown in Figure 2a. In one case, a hemimorphic polycrystal of ewaldite was found to have a "cap" of donnayite on one end and a "cap" of mckelveyite on the other (Fig. 2b).

Optically, donnayite is biaxial negative with α 1.551–1.561(2), β 1.646(2), and γ 1.652(2). The $2V$ varies from crystal to crystal and from point to point on the same crystal from 20° to almost 0°, the most commonly observed values being 5 to 10°. The X principal vibration axis is approximately parallel to c^* with a maximum deviation from parallelism of 5°. Prismatic sections of well-formed crystals always show sharp and nearly parallel extinctions between crossed polars whereas the basal sections either show patchy extinction or no extinction at all. On these basal sections the orientation of the optic plane has been observed to vary from point to point corresponding to rotations of 60° or 120° about c^*, strongly suggesting twinning. The acute-bisectrix interference figures often show complications and various degrees of distortion, probably due to overlapping twinned individuals.

X-Ray Crystallography

Crystals of donnayite used for the single-crystal X-ray diffraction study were first checked optically for identity and possible intergrowth of other minerals using a spindle stage and then by X-ray using a 114.6 mm diameter Gandolfi camera. The precession photographs show that donnayite is triclinic, pseudorhombohedral and isomorphous with weloganite (Table 1). The space group is $P\bar{1}$ by virtue of the hemimorphic crystal morphology (Fig. 1f). The cell parameters of donnayite given in Table 1 are results of a least-squares refinement using powder diffraction data (Table 2). A non-conventional cell is used here in order to bring out the pseudosymmetry ($a = b$, $\gamma = 60°$) and to allow a direct comparison with the cell of weloganite. Due to the strong pseudosymmetry, there are two equally acceptable choices of the reduced cell (Table 3) which may be derived from the adopted cell by the matrices $\bar{1}0\bar{1}/1\bar{1}0/001$ and $101/0\bar{1}0/00\bar{1}$. The difference between the two reduced cells is well within the error of measurement.

As with weloganite, twinning in donnayite is the rule rather than the exception. Many unsuccessful attempts were made to obtain untwinned fragments by repeatedly splitting twinned crystals. Significant changes in the volume ratio of the twin individuals were obtained, in the best cases, which permitted the recognition of the triclinic symmetry from the X-ray photographs. Two twin laws are operative either individually or simultaneously. These may be stated as a rotation about $[103]_{120°}$ or $[001]^*_{120°}$ and a reflection across (010), $(30\bar{1})$ or $(\bar{3}\bar{3}1)$. The twin axis corresponds to the pseudo three-fold axis and the twin planes

TABLE 1. CELL PARAMETERS OF DONNAYITE AND RELATED MINERALS

	Donnayite $NaCaSr_3Y(CO_3)_6\cdot 3H_2O$		Weloganite $Na_2Sr_3Zr(CO_3)_6\cdot 3H_2O$		McKelveyite $NaCaBa_3Y(CO_3)\cdot 3H_2O$	
	This study	Chen & Chao 1975	Grice & Perrault 1975	Sabina et al. 1968	This study	Milton et al. 1965
Symmetry	P1	P1	P1	$P3_{1.2}$	P1	$P\bar{3}$*
a (Å)	9.000(1)	8.988(1)	8.966(1)	8.96	9.170(3)	9.174(2)
b	8.999(1)	9.988(1)	8.980(2)		9.169(3)	
c	6.793(1)	6.730(1)	6.730(1)	18.06	7.075(2)	19.154(7)
α(°)	102.77(1)	102.84(1)	102.72(2)		102.50(3)	
β	116.28(1)	116.42(2)	116.65(1)		115.63(3)	
γ	59.99(1)	59.99(1)	60.06(1)		59.99(3)	
V (Å)	427.4	421.6	419.6	3x418.5	464.5	3x465.4
Z	1	1	1	3	1	3
D_{obs} (g/cm^3)	3.30(1)			3.22(3)		3.62
D_{calc}	3.266	3.208		3.260		3.47-3.58

* Also P3 or P3m1, Desautels (1967).

TABLE 2. X-RAY POWDER DIFFRACTION DATA OF DONNAYITE(1)

	Donnayite			Weloganite(2)		
hkl	d_{calc}	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
010	7.792	7.768	1	7.784	7.786	3
100				7.149	7.143	3
001	6.094	6.103	4	6.027	6.022	5
$10\bar{1}$				5.898	5.901	1
011				4.766	4.765	1/2
$01\bar{1}$				4.765		
$21\bar{1}$	4.370			4.361		
120	4.369	4.368	7	4.362	4.362	8
$1\bar{1}0$	4.369			4.361		
$12\bar{1}$	4.037			4.024		
$1\bar{1}1$	4.037	4.041	2	4.024	4.022	4
210	4.037			4.024		
101				3.909	3.906	1
111				3.909		
$21\bar{2}$	3.207			3.187		
121	3.206	3.209	3	3.188	3.187	5
$1\bar{1}1$	3.206			3.187		
002	3.047	3.050	2	3.013	3.013	5
$1\bar{1}2$	2.838			2.817		
$12\bar{2}$	2.838	2.839	10	2.817	2.817	10
211	2.837			2.818		
$33\bar{1}$	2.598			2.595		
030	2.598	2.598	4	2.594	2.594	7
$30\bar{1}$	2.598			2.594		
330	2.390			2.384		
$30\bar{2}$	2.390			2.383		
$03\bar{1}$	2.390	2.391	2	2.383	2.382	6
031	2.390			2.383		
300	2.389			2.383		
$21\bar{3}$	2.259			2.239		
$1\bar{1}2$	2.259	2.261	<1	2.239		
122	2.259			2.239		
$22\bar{1}$	2.233			2.230	2.233	7
$24\bar{1}$	2.233	2.233	2	2.230		
$42\bar{1}$	2.233			2.230		
220	2.184	2.183	<1	2.180	2.181	2
240	2.184			2.180		
$1\bar{1}3$	2.038			2.019		
$3\bar{1}0$	2.037	2.038	3	2.032	2.024	1
212	2.037			2.019		
003	2.031					
$24\bar{2}$	2.019			2.012		
$22\bar{2}$	2.018	2.018	3	2.012	2.012	7
420	2.018			2.012		
003				2.010		
$33\bar{3}$	1.977			1.966		
$30\bar{3}$	1.977			1.966		
$03\bar{2}$	1.977	1.978	3	1.966	1.966	7
032	1.977			1.966		
301	1.977			1.966		
331	1.977			1.966		
$42\bar{3}$	1.917			1.908		
241	1.916	1.916	3	1.909	1.907	7
$22\bar{1}$	1.916			1.908		
$21\bar{4}$	1.694			1.677	1.676	4
$1\bar{1}3$	1.694			1.677		
$54\bar{2}$	1.694			1.691		
$51\bar{2}$	1.693			1.691		
$1\bar{4}0$	1.693	1.694	3	1.691	1.691	4
$15\bar{0}$	1.693			1.691		
$41\bar{1}$	1.693			1.691		
$45\bar{1}$	1.693			1.691		
033	1.600			1.589		
$03\bar{3}$	1.600			1.588		
$30\bar{2}$	1.600			1.588		
$30\bar{4}$	1.600	1.600	2	1.588	1.589	6
$51\bar{3}$	1.594			1.590		
$14\bar{1}$	1.594			1.590		
$4\bar{1}0$	1.594			1.590		
151	1.594			1.590		
441	1.561					
401	1.561					
213	1.559	1.560	2			
$1\bar{1}4$	1.559					
$12\bar{4}$	1.559					
050	1.559					
$54\bar{0}$	1.542			1.538		
$15\bar{2}$	1.542			1.537		
$41\bar{3}$	1.542	1.541	<1	1.537	1.538	4
$14\bar{2}$	1.542			1.537		
$5\bar{1}0$	1.542			1.537		
$33\bar{1}$	1.500			1.498		
$36\bar{1}$	1.500	1.499	<1	1.498	1.497	3
$63\bar{2}$	1.500			1.498		
$36\bar{3}$	1.346	1.345	<1	1.341	1.341	1
$33\bar{3}$	1.346			1.341		

Plus many more lines

(1) CuKα radiation, λ = 1.5418Å, 114.6 mm camera, Si standard, visual intensities.
(2) Data from Chen & Chao (1975).

correspond to the pseudo mirror planes of the pseudorhombohedral lattice.

Electron Microprobe Analysis

Donnayite was analyzed using a Cambridge MK5 electron microprobe for the following elements using the standards shown in parentheses: Ca, Y, La (rare earth glass REE3, Drake & Weill 1972), Nd (REE2), Ba (synthetic barium ferrite), Sr (strontianite), and Na (sodium niobate). K, Zr, Si, Al, F, Nb, Ce and other rare-earth elements were also looked for but not detected. The analyses were performed at 15kV using a slightly defocused beam. To avoid producing a crater on the specimen, which would reduce the Na count-rate with time, the specimen was translated across the beam at 10 μm per minute. Raw X-ray data with fixed carbon weight percentage were processed using the ZAF correction procedure of EMPADR VII (Rucklidge & Gasparrini 1969).

Several crystals, representative of different habits and mineral associations, were initially selected and prepared for analysis. However, all except one crystal were shown to be unsuitable owing to the presence of intimate syntactic intergrowths with other minerals. The analysis (Table 4) was, therefore, obtained from one crystal only. The CO_2 and H_2O values given in Table 4 were calculated on the basis of $6CO_3^{2-}$ and $3H_2O$ per formula by analogy with weloganite. This analysis corresponds to $Na_{0.93}(Ca_{0.87}Nd_{0.09}La_{0.03})(Sr_{2.95}Ba_{0.05})Y_{0.99}(CO_3)_6 \cdot 3H_2O$, or ideally, $NaCaSr_3Y(CO_3)_6 \cdot 3H_2O$. Assuming one formula unit per cell, the density calculated

TABLE 3. THE REDUCED CELLS OF DONNAYITE

	(1)	(2)
a(Å)	8.544	8.544
b	8.998	8.999
c	6.793	6.793
α(°)	102.81	102.77
β	109.19	109.19
γ	110.51	110.55

Transformation matrix from adopted cell to reduced cell (1) = $10\bar{1}/1\bar{1}0/001$ and to (2) = $101/0\bar{1}0/00\bar{1}$.

TABLE 4. ELECTRON MICROPROBE ANALYSIS OF DONNAYITE

	Wt%		Wt%
Na_2O	3.37	Nd_2O_3	1.83
CaO	5.75	La_2O_3	0.45
BaO	0.85	CO_2	(30.98)
SrO	35.8	H_2O	(6.34)
Y_2O_3	13.1	Total	98.47

Contents of CO_2 and H_2O were calculated on the basis of $6CO_3$ and $3H_2O$ per formula.

from the empirical formula is 3.266g/cm³, in good agreement with the observed value of 3.30g/cm³.

Discussion

The isomorphous relationship between donnayite and weloganite may be extended to mckelveyite which also has been found in small amounts, forming syntactic intergrowths with donnayite at Mont St-Hilaire. Mckelveyite from the Green River Formation, Wyoming was originally described by Milton *et al.* (1965) as trigonal $P\bar{3}$, a 9.174(2), c 19.154(7)Å, with two units of $Na_{1.9}Ba_{4.0}Ca_{1.1}Sr_{0.2}RE_{1.5}U_{0.3}(CO_3)_9 \cdot 5H_2O$ per cell. The space group was later given as $P3$ or $P3ml$ by Desautels (1967) based on morphological evidence. The isomorphism, suggested by the strong similarity of its powder diffraction pattern (Milton *et al.* 1965) with those of donnayite and weloganite, was confirmed by X-ray study of a single crystal obtained by repeatedly splitting a twinned crystal. The parameters of the triclinic cell of mckelveyite derived from least-squares refinement using the powder data given by Milton *et al.* (1965) are compared with those of donnayite and weloganite in Table 1. The original analysis of mckelveyite may be recalculated, on the basis of $6CO_2$ per formula, to $(Na_{1.29}K_{0.02})$ $(Ca_{0.73}U_{0.17})$ $(Ba_{2.72}Sr_{0.17})$ $(Y_{0.70}RE_{0.32})$ $(CO_3)_6 \cdot 3.48H_2O$. Despite the analytical difficulties stated by the authors (mainly due to large amounts of inclusions of organic matter, acmite, biotite and quartz) the recalculated formula is surprisingly close to the expected ideal formula $NaCaBa_3Y(CO_3)_6 \cdot 3H_2O$. Thus, mckelveyite is clearly the Ba analogue of donnayite. The two minerals probably form a solid solution but the extent of the solid solution is not yet known.

The Na:Ca ratios in donnayite and mckelveyite are both very close to 1:1; therefore, it is reasonable to assume that Na and Ca atoms are ordered in the two distinct positions occupied by Na in the weloganite structure (Grice & Perrault 1975).

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