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GAIDONNAYITE, $Na_2ZrSi_3O_9 \cdot 2H_2O$, A NEW MINERAL FROM MONT ST. HILAIRE, QUEBEC

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ABSTRACT

Gaidonnayite occurs at Mont St. Hilaire, Quebec, in miaroles in nepheline syenite both as crystals on analcime and in cavities in dense natrolite aggregates; it is mainly associated with hilairite, aegirine, calcite, and siderite. Gaidonnayite also occurs in altered pegmatite dykes mainly with catapleiite, elpidite, hilairite, albite, microcline, chlorite, aegirine, epididymite, and goethite.

The mineral is orthorhombic, space group $P2_1nb$, $a = 11.740$, $b = 12.820$ and $c = 6.691$Å. $Z = 4$, D(calc) $= 2.10$, D(meas) $= 2.67$ g/cm^3, $H = 5$. It has conchoidal fracture and no noticeable cleavage. The mineral is colourless, white to beige, with vitreous luster. Crystals are bladed on (010), elongate along [100], bounded by {010}, {120}, and {100} with striations on {010} and {120} parallel to [001]. Twinning by $[012]_{180°}$ is common. The mineral is optically biaxial with $\alpha = 1.573$, $\beta = 1.592$, $\gamma = 1.599$, $2V_z = 121°$, $X = a$, $Y = b$ and $Z = c$.

Electron microprobe analysis gave SiO_2 42.51; ZrO_2 30.21; Nb_2O_5 3.00; TiO_2 0.42; Na_2O 13.11; K_2O 2.20; H_2O (by TGA to 1000°C) 9.25; sum 100.70%. The analysis corresponds to $(Na_{1.72}K_{0.19})(Zr_{1.00}Nb_{0.09}Ti_{0.02})\ Si_{2.88}O_9 \cdot 10H_2O$ or ideally $Na_2ZrSi_3O_9 \cdot 2H_2O$.

Dehydration began immediately on thermogravimetric analysis and was complete at about 400°C; water lost was not re-absorbed on cooling.

The mineral is a dimorph of catapleiite and is similar in many properties to α-catapleiite.

INTRODUCTION

Gaidonnayite, an orthorhombic dimorph of catapleiite, was first discovered in 1967 from a vug in nepheline syenite at Mont St. Hilaire, Quebec. Only two small crystals (approximately 0.5 mm) of this mineral were found among small crystals of siderite and aegirine protruding from large analcime crystals. One of the crystals was kept intact as reference material and the other was detached and broken up for qualitative spectrographic analysis, optical studies and powder and single-crystal *x*-ray diffraction. Although it was recognized at that time that the mineral was possibly a new species, a complete description, especially of its chemistry, was not possible and the mineral was designated UK23. In the summer of 1972 more than a hundred small crystals of the same mineral were found on a natrolite specimen from a vug. Quantitative chemical analysis was carried out and much of the previous work was repeated with the new material. Gaidonnayite is named after Prof. Gabrielle Donnay, McGill University, Montreal. The mineral and its name have been approved by the Commission on New Mineral Names, I.M.A. The type specimens (T73/2-1 and T73/2-2) are deposited with the National Museum of Canada, Ottawa.

OCCURRENCE

Gaidonnayite occurs in miaroles in nepheline syenite, Mont St. Hilaire, as small well-formed crystals on large analcime crystals and in cavities in dense aggregates of natrolite. It is commonly associated with hilairite (Chao *et al.* 1974), aegirine, calcite, siderite and minor amounts of albite, catapleiite, zircon, pyrochlore, ancylite and burbankite. The gaidonnayite crystals are often partly covered by sprays of minute brown flakes of an unidentified, chlorite-like mineral. Gaidonnayite was also found in altered pegmatite dykes which are characterized by chloritized aegirine and amphibole, goethite and limonite pseudomorphous after a rhombohedral carbonate (probably siderite), and a botryoidal amorphous dark-brown to black material. In the altered pegmatites gaidonnayite was found in the interstices of aggregates of catapleiite as poorly-formed, translucent to opaque crystals frequently enclosed by hilairite. Other minerals in the dykes are microcline, albite, elpidite, aegirine, epididymite, calcite, sphalerite and galena.

CRYSTALLOGRAPHY

Measurements by optical goniometry showed that a typical crystal of gaidonnayite (Figs. 1 and 2) is bounded, in order of prominence, by {010}, {011}, {120}, and {100} forms. An additional small {101} form is present on some crystals. The crystals are slightly bladed, flattened on (010) and elongated along [100].

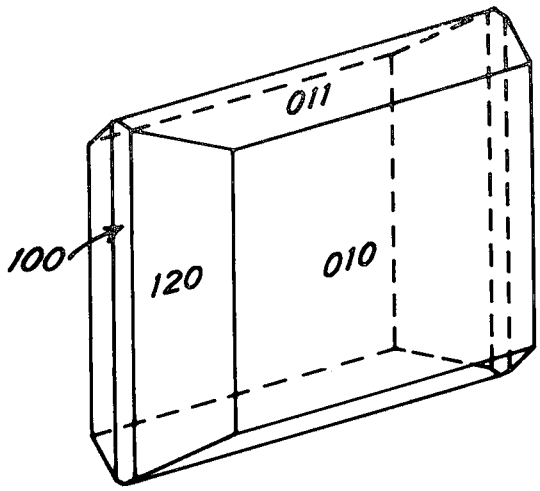

FIG. 1. Crystal drawing of gaidonnayite.

Heavy striations parallel to [001] are very common on {010} and less common on {120}. Twinning by $[012]_{180°}$ is very common (Fig. 3). In a twinned crystal, one individual appears to be rotated relative to the other by 90° about *a*. The composition plane is usually irregular.

Weissenberg and precession *x*-ray photographs show that gaidonnayite is orthorhombic. The systematic extinctions are consistent with the space groups $P2_1nb$ and $Pmnb$. The latter space group was eliminated by crystal structure analysis (Chao 1973). The preliminary cell parameters obtained from single-crystal *x*-ray photographs were refined by a least-squares method using powder diffraction data (Table 1) obtained with Cu$K\alpha$ radiation, using metallic Si as an internal standard. The refined values are $a = 11.740(3)$, $b = 12.820(3)$ and $c = 6.691(1)$Å.

PHYSICAL PROPERTIES

Gaidonnayite crystals from miaroles are colourless, transparent with vitreous luster; some crystals are white to beige and are translucent to opaque. Some clear transparent crystals have an opaque to translucent core which was shown by *x*-ray diffraction to be identical to the transparent material. Most crystals from the altered pegmatite dykes are poorly-formed without well-defined crystal faces. They are translucent and are pale yellowish-green when viewed against a white background.

Gaidonnayite is brittle, with a Mohs hardness of approximately 5. It has conchoidal fracture and no noticeable cleavage. Determinations of density by floatation in a heavy liquid for three different crystals gave the average value 2.67 (1) g/cm³. All crystals of gaidonnayite tested have bright green fluorescence in short-wave ultra-violet light.

Optical properties of gaidonnayite were determined at 24°C using a spindle stage and a sodium vapor lamp as an illuminator. Colour-

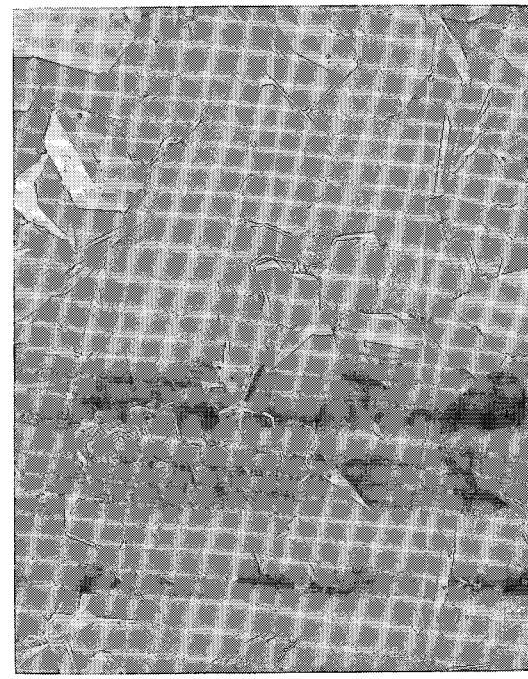

FIG. 2. Scanning electron photomicrograph of gaidonnayite crystals (average 0.5 mm long).

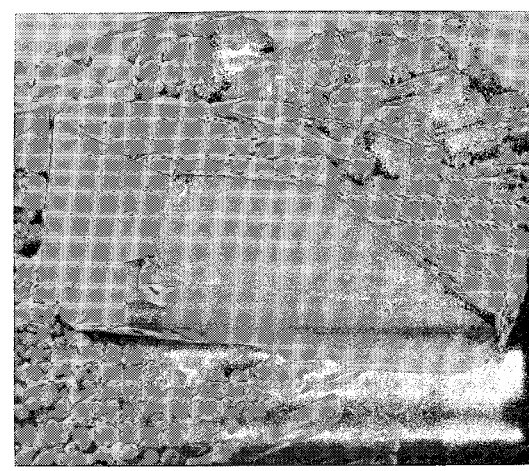

FIG. 3. Scanning electron photomicrograph of a twinned gaidonnayite crystal (0.5 mm long) on natrolite aggregate with small clusters of a chlorite-like mineral.

less crystals previously oriented on a precession *x*-ray camera were used. All Cargille immersion liquids used were checked by an Abbé refractometer.

TABLE 1. *X*-RAY POWDER DIFFRACTION DATA FOR GAIDONNAYITE

hkl	d_{calc} Å	d_{obs} Å	I_{est}	*hkl*	d_{calc} Å	d_{obs} Å	I_{est}
020	6.410	6.42	30	060	2.137	2.135	5
011	5.931	5.93	80	160	2.102	2.102	10
200	5.867	5.84	80	441	2.059	2.056	5
101	5.812			213	2.057		
120	5.625	5.63	50	061	2.035	2.037	20
111	5.293	5.28	10	052	2.035		
021	4.628	4.64	10	260	2.008	2.007	10
220	4.328	4.31	30	152	2.005		
121	4.305			600	1.955	1.950	10
211	4.166	4.17	15	133	1.949		
221	3.634	3.618	20B	261	1.923	1.921	30
031	3.601			252	1.923		
131	3.443	3.441	30	512	1.900	1.897	10
301	3.377	3.376	5	360	1.875		
320	3.339	3.337	5	233	1.873	1.875	10
012	3.236	3.224	5	620	1.871		
040	3.205			611	1.857		
112	3.120	3.124	100	451	1.855	1.854	5
140	3.092	3.094	80	323	1.854		
321	2.987	2.990	5	361	1.806		
400	2.934	2.931	40	352	1.805	1.804	5
122	2.875	2.873	20	621	1.801		
212	2.834	2.831	30	062	1.801		
141	2.806	2.806	30	413	1.758	1.758	10
240	2.813			460	1.727	1.725	5
331	2.649	2.647	20			1.670	30
241	2.593	2.594	20			1.637	40
132	2.570	2.564	5			1.617	5
312	2.494	2.488	10			1.606	5
340	2.479					1.591	5
232	2.403	2.403	10			1.545	20
431	2.274	2.269	5			1.512	5
251	2.217	2.217	5			1.488	5
501	2.215					1.471	5
013	2.197	2.195	20			1.450	5
103	2.191					1.409	10
440	2.164	2.161	5			1.376	5
113	2.159					1.287	5

Data obtained by 114.6 mm camera at room temperature using metallic silicon as internal standard with Cu K_α radiation (λ=1.5418Å). B=broad line.

TABLE 2. COMPARISON OF PROPERTIES OF GAIDONNAYITE, CATAPLEIITE, α-CATAPLEIITE AND HILAIRITE

	gaidonnayite	catapleiite[1]	α-catapleiite[2]	hilairite[3]
Symmetry	orthorhombic	monoclinic	orthorhombic	rhombohedral
	$P2_1nb$	$I2/a$		$R\bar{3}m$, $R3m$, $R32$
a(Å)	11.740(3)	12.779(9)		10.556(1)
b	12.820(3)	7.419(5)	1.727:1:1.336	--
c	6.691(1)	20.157(8)		15.851(2)
β(°)	90	90.41(4)	90	--
α	1.573(1)	1.588(1)	1.575	(ε) 1.596(1)
β	1.592(1)	1.591(1)	1.590	
γ	1.599(1)	1.624(1)	1.605	(ω) 1.609(1)
$2V_z$(meas.)	121(1)°	40(1)°	(-)2E large	--
$2V_z$(calc.)	119.5°	34°	92.6°	
X	a	--	c	--
Y	b	b	a	--
Z	c	$Z_{\wedge c}$=4°	b	--
D_{meas} (g/cm³)	2.67(1)	2.80(1)	2.658	2.724(4)
D_{calc} (g/cm³)	2.70	2.79	--	2.739
Hardness	5	5	5	>4

1. Mont St. Hilaire, Quebec (Chen & Chao 1973). Other authors (*e.g.* Brunowsky 1936) reported hexagonal, $P\bar{6}gmc$.
2. Narssarssuk, Greenland (Gordon 1925).
3. Mont St. Hilaire, Quebec (Chao *et al.* 1974).

The properties of gaidonnayite are summarized in Table 2 where they are compared with those of catapleiite, α-catapleiite, and hilairite.

Chemical Analysis

Gaidonnayite was analysed using a Cambridge MK5 electron microprobe initially at 15 and 20 kv with a beam approximately 2 μm in diameter. The analyses showed that the major elements (with standards used) were K (synthetic fluorphlogopite), Na and Si (jadeite), Zr (synthetic zirconia), Ti (metallic Ti) and Nb (synthetic $NaNbO_3$), and that Al, Ca, F, Mg, Mn, and Y were less than 0.01% by weight. The major elements were re-analysed at 12 kv with a defocused (30 μm) beam because Na *x*-ray counting rates decreased drastically with time using the more intense beam. The *x*-ray data were computer-corrected for generation (atomic number) absorption and fluorescence effects using the program EMPADR 7 (Rucklidge & Gasparrini 1969). The results given in Table 3 are averages of 8 to 12 sets of 10-second counts on each of three grains. The H_2O content was determined separately by thermogravimetric analysis.

The analysis was recalculated, on the basis of 9 oxygen atoms per formula, to $(Na_{1.72}K_{0.19})$ $(Zr_{1.00}Nb_{0.09}Ti_{0.02})$ $Si_{2.88}O_9 \cdot 2.10H_2O$, or ideally $Na_2ZrSi_3O_9 \cdot 2H_2O$. With Z=4, this analysis gave a calculated density of 2.70 g/cm³, which is in good agreement with the measured density of 2.67 g/cm³.

TABLE 3. CHEMICAL ANALYSIS OF GAIDONNAYITE

	Wt.%	Number of atoms based on 9 oxygens atoms per formula	
SiO_2	42.51	Si	2.884
ZrO_2	30.21	Zr	1.000
Nb_2O_5	3.00	Nb	0.092
TiO_2	0.42	Ti	0.022
Na_2O	13.11	Na	1.724
K_2O	2.20	K	0.191
H_2O*	9.25	H_2O	2.095
Sum	100.70		

* Determined by TGA to 1000°C.

Thermal Studies

Thermogravimetric analysis of gaidonnayite was made in air at a heating rate of 10°C/min using a 12.70 mg hand-picked sample of the transparent material. Dehydration began immediately on heating and was complete at about 400°C; the total weight loss was 9.25%. No

further weight loss was detected from 400° to 1000°C. The quenched product (probably $Na_2ZrSi_3O_9$) from 1000°C showed signs of melting but gave a fairly sharp powder diffraction pattern which is very similar to that of wadeite ($K_2ZrSi_3O_9$).

Separate TGA runs were made with the translucent-to-opaque material containing 1-2% of the unidentified chlorite-like mineral. In one run, after heating to 400°C where the dehydration curve began to level off, the sample was allowed to cool slowly to room temperature and held for 24 hours. No significant rehydration (weight gain) occurred. The *x*-ray powder pattern of this heated material showed only a few diffuse lines attributable to gaidonnayite, indicating the collapse of the structure. In other runs, products quenched from 450° and 900°C gave wadeite-like diffraction patterns.

Related Minerals

Gaidonnayite is an orthorhombic dimorph of catapleiite. Gaidonnayite has a single-chain structure (Chao 1973), with the chains of SiO_4 tetrahedra parallel to [101] and [10$\bar{1}$] repeating at every sixth tetrahedron, whereas catapleiite has a benitoite structure based on three-membered rings of SiO_4 tetrahedra (Brunowsky 1936). Hilairite, $Na_2ZrSi_3O_9 \cdot 3H_2O$, which is closely associated with gaidonnayite, contains one more H_2O molecule per formula than gaidonnayite. The relationships of the three phases are not certain. Attempts to synthesize gaidonnayite and hilairite hydrothermally in the temperature-pressure range 150° - 600° and 0.5-2.5 kb always produced elpidite at low temperatures (200-400°C) and catapleiite at high temperatures (300-500°C). However, the textural relationships observed in hand specimens indicate that gaidonnayite was formed earlier than hilairite and later than catapleiite. Gaidonnayite can be distinguished easily from catapleiite and hilairite by its *x*-ray powder diffraction pattern, crystal morphology, and other physical properties (Table 2).

Gordon (1925) described a mineral, α-catapleiite, from Narssarssuk, Greenland, which occurred in a small vug in augite-syenite with natrolite, aegirine, minor albite and siderite. The mineral was thought to be a low-temperature analog of catapleiite but no chemical analysis was made to confirm its composition due to scarcity of material. Crystals of α-catapleiite are orthorhombic with {100}, {110} {203}, {301}, and {013} forms. Gaidonnayite and α-catapleiite are similar in many properties, including refractive indices, density, colour, luster, crystal habit and occurrence (Table 2). However, the two minerals may be distinguished from each other by differences in their cell geometry and optical orientation.

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