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HILAIRITE, $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$, A NEW MINERAL FROM MONT ST. HILAIRE, QUEBEC

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ABSTRACT

Hilairite occurs as small, very pale brown, transparent crystals in miarolitic cavities and as flesh-pink porcelain-like opaque crystals in altered pegmatites in nepheline syenite at Mont St. Hilaire, Quebec. The most abundant associated minerals are analcime, natrolite, microcline, catapleite, elpidite, aegirine and chlorite.

Hilairite crystals are trigonal, bounded by $\{11\bar{2}0\}$ and $\{01\bar{1}2\}$. The space group is $R\bar{3}2$, $R\bar{3}m$ or $R\bar{3}m$; $a = 10.556(1)$ and $c = 15.851(2)$ Å. Multiple twinning by $[2201]_{180^\circ}$ and $[0001]_{180^\circ}$ is very common. $D(\text{cal.}) = 2.739$ and $D(\text{meas.}) = 2.724(4)$ g/cm³. Hardness > 4 . No obvious cleavage was observed. It is optically uniaxial negative with $\epsilon_D = 1.596(1)$ and $\omega_D = 1.609(1)$.

Averaged electron microprobe analyses gave SiO₂ 42.08; Al₂O₃ 0.03; ZrO₂ 29.72; TiO₂ 0.04; CaO 0.20; MgO 0.01; total Fe as FeO 0.03; MnO 0.02; Na₂O 13.43; K₂O 0.52; H₂O 13.54 (by TGA to 1000°C); total = 99.62%. The analysis corresponds to $\text{Na}_{1.85}\text{K}_{0.05}\text{Ca}_{0.02}\text{Zr}_{1.03}\text{Si}_{2.99}\text{O}_9 \cdot 3.2\text{H}_2\text{O}$ or ideally $\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$.

Water in hilairite is zeolitic in nature; on heating hilairite loses all of its water at 220°C and at least 95% of the original water is recovered on cooling from 85°C to room temperature. Attempts at hydrothermal synthesis were unsuccessful.

INTRODUCTION

A new mineral species from Mont St. Hilaire, Quebec, was recognized simultaneously at the Royal Ontario Museum and Carleton University in 1965 and was designated as ROM#1 or UK#20 (Chao *et al.* 1967). A preliminary report on the properties of this mineral was given by

Mandarino *et al.* (1965). Due to the very small amount of this mineral available at that time no complete description, especially of its chemistry, was possible. This new mineral, a hydrated sodium zirconium silicate, is hilairite, named after the locality. The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA (Sept. 1972). Type specimens (T73/1) are deposited with the National Museum of Canada, Ottawa.

OCCURRENCE

Hilairite occurs as 0.1 to 1.0 mm, nearly equidimensional, crystals and more commonly as aggregates in miarolitic cavities and altered pegmatite dikes in nepheline syenite at Mont St. Hilaire, Quebec. About 200 mg of hilairite have been collected.

In the miarolitic cavities hilairite crystals are found on analcime, microcline, or natrolite, usually associated with calcite, aegirine, albite, catapleite and gaidonnayite (a new mineral, an orthorhombic dimorph of catapleite; Chao 1973). The hilairite crystals in miaroles are pale brown, always clear, transparent and are often coated with a thin veneer of fine-grained dark-green or dark-brown chlorite.

The altered pegmatite dikes are characterized by the ubiquitous occurrence of chlorite, limonite and goethite. The last two minerals are often found in pseudomorphs after a rhombohedral carbonate, presumably siderite. The hilairite crystals of the dikes are characterized by white to flesh pink color, opacity and their porcelainous luster. Minerals closely associated with hilairite

are catapleite, elpidite, gaidonnayite, albite microcline, chlorite and minor amounts of powdery calcite, epididymite, natrolite, fluorite, pyrite, sphalerite and galena.

CRYSTALLOGRAPHY

Careful optical goniometry measurements on well-formed doubly-terminated crystals indicated that hilairite is trigonal with only two forms, hexagonal prism $\{01\bar{1}2\}$ and rhombohedron $\{01\bar{1}2\}$ (Fig. 1). The prism is usually slightly more prominent than the rhombohedron, causing the crystals to be slightly elongate along the c -axis. Twinning is very common and often obscures the true symmetry. Two twin laws, $[2\bar{2}01]_{180^\circ}$ and $[0001]_{180^\circ}$, were observed. Crystals are often multiple-twinned according to both twin laws, involving four, eight or more individuals (Figs. 2 and 3).

Weissenberg and precession studies on single crystals confirmed the trigonal symmetry established by optical goniometry. The systematic extinctions observed on single crystal x -ray photographs are consistent with those required for the space groups $R32$, $R3m$ or $R\bar{3}m$. The preliminary cell parameters obtained from single crystal photographs were refined by a least-squares method using powder diffraction data (Table 1) obtained at room temperature with a 114.6 mm diameter camera and $\text{CuK}\alpha$ radiation. Metallic silicon was used as an internal standard. Indexing of the powder diffraction lines was based on comparison between observed and calculated d -values with the aid of a set of Weissenberg photographs. The refined values are $a =$

10.556(1) and $c = 15.851(2)$ Å. The angle $(0001) \wedge (01\bar{1}2)$, $41^\circ 02'$, calculated from the refined cell parameters is in good agreement with the value, $40^\circ 55'$, measured on a two-circle optical goniometer.

Mandarino *et al.* (1965) reported for ROM#1 a monoclinic cell ($a = 12.24$, $b = 10.57$, $c = 8.06$ Å and $\beta = 101^\circ 10'$) which can be derived from the present rhombohedral cell by the transformation $\bar{1}11/010/-2/3, -1/3, -1/3$.

PHYSICAL PROPERTIES

Hilairite from miaroles is very pale brown with vitreous luster; small fragments are colorless. It has conchoidal fracture and shows no obvious cleavage. Its hardness is greater than 4 on the Mohs scale. Density was determined by suspension in a mixture of bromoform and acetone and then by a micro-pycnometer (10 cc capacity). Two independent determinations at 24°C gave $D(\text{meas.}) = 2.724(4)$ g/cm³.

Hilairite is attacked slightly by 1:1 HCl and HNO_3 but not by 1:1 H_2SO_4 at room temperature.

Hilairite is uniaxial negative with $\epsilon = 1.596(1)$ and $\omega = 1.609(1)$. All the measurements were made at 24°C using a spindle stage on crystals previously oriented with the precession camera. A sodium vapor lamp was used as the source of illumination. All the Cargille refractive index

TABLE 1. X-RAY POWDER DIFFRACTION DATA OF HILAIRITE *

I	d_{obs} Å	d_{calc} Å	hkl	I	d_{obs} Å	d_{calc} Å	hkl
60	6.00	5.988	012	5	1.719	1.7188	128
100	5.28	5.278	110	20	1.688	1.6879	422
		5.284	003	20	1.661	1.6601	054
5	3.636	3.6359	104	10	1.607	1.6077	152
50	3.168	3.1673	122	10	1.584	1.5836	244
40	3.046	3.0472	300	<5	1.562	1.5612	318
30	2.994	2.9942	024			1.5618	1.0.10
30	2.639	2.6389	220	5	1.524	1.5236	600
		2.6397	033	10	1.516	1.5168	514
5	2.604	2.6043	214	10	1.4759	1.4765	342
10	2.416	2.4149	312	30	1.4643	1.4638	520
5	2.362	2.3624	116	10	1.4408	1.4402	238
10	2.197	2.1959	042			1.4407	2.1.10
15	2.135	2.1357	134	10	1.3734	1.3730	612
30	2.027	2.0274	232	5	1.3439	1.3437	508
30	1.996	1.9948	410			1.3441	1.3.10
		1.9961	306			1.3195	440
5	1.866	1.8670	226	15	1.3194	1.3198	606
10	1.852	1.8536	324			1.2886	072
5	1.820	1.8179	208	10	1.2884	1.2886	532
40	1.759	1.7593	330				
Plus many more lines							

* Intensities estimated visually. 114.6 mm camera, Si standard, $\text{CuK}\alpha$ radiation, $\lambda = 1.5418$ Å.

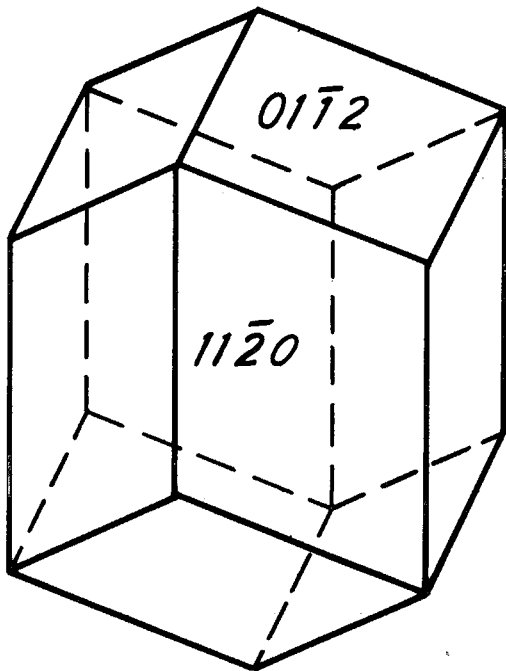


FIG. 1. Crystal drawing of hilairite.

liquids used were checked on an Abbe-3L refractometer. Some crystals of hilairite examined optically have inclusions of minute needle-shaped crystals, possibly elpidite, which are often arranged in radiating clusters.

CHEMICAL ANALYSIS AND FORMULA

Hilairite was analyzed using the Cambridge MK5 electron microprobe for the following ele-

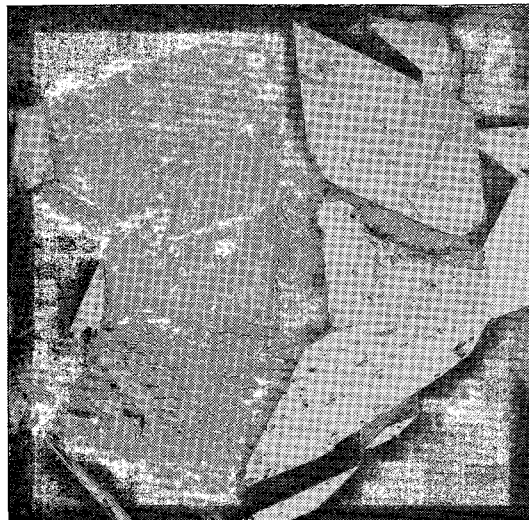


FIG. 2. Scanning electron photomicrograph of multiple twinned hilairite crystals (approximately 1 mm).

ments using the standards shown in parentheses: Si and Na (jadeite), Zr (synthetic zirconia), Al and Ca (synthetic anorthite), Fe, Mn and Ti (pure metals), K and Mg (synthetic fluorophlogopite). Analyses were performed at 15 kv with a static beam of approximately 1 μm diameter. To maintain a stable count rate and homogeneous Na concentration, Na analyses were done at 10 kv with a beam enlarged to 30 μm and the specimen was translated across the beam at 10 μm per minute.

The x-ray data were computer-corrected for generation (atomic number), absorption and

TABLE 2. ELECTRON MICROPROBE ANALYSIS OF HILAIRITE

wt %		Number of atoms based on 9 oxygen atoms per formula		
SiO ₂	42.08	Si	2.99	} 2.99
Al ₂ O ₃	0.03	Al	0.002	
ZrO ₂	29.72	Zr	1.03	} 1.03
TiO ₂	0.04	Ti	0.002	
CaO	0.20	Ca	0.02	} 1.92
MgO	0.01	Mg	0.001	
FeO	0.03	Fe	0.002	
MnO	0.02	Mn	0.001	
Na ₂ O	13.43	Na	1.85	
K ₂ O	0.52	K	0.05	
H ₂ O*	13.54	H ₂ O	3.21	3.21
Total	99.62			

* Determined by TGA to 1000°C.

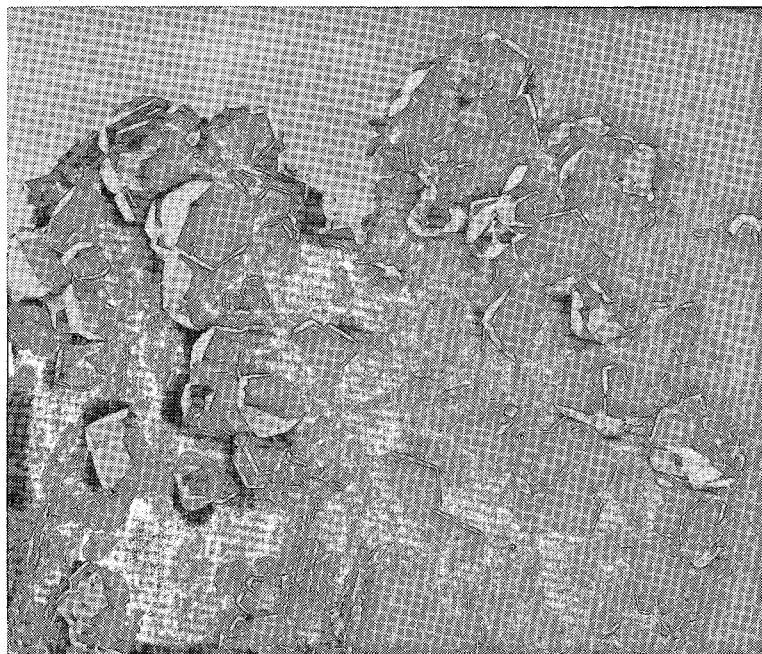
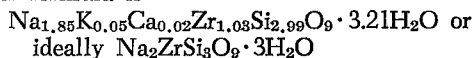


FIG. 3. Scanning electron photomicrograph of multiple twinned crystals of hilairite (average 0.5 mm) on natrolite.

fluorescence effects using the program EMPADR 7 (Rucklidge & Gasparrini 1969). Data in Table 2 are averages of from 8 to 24 sets of ten-second counts on a grain of hilairite. The H₂O content was determined by TGA to 1000°C on 18 mg of hand-picked sample.

The chemical formula, calculated from the averaged analysis on the basis of 9 oxygen atoms per formula is



Assuming six formula units per cell, the density calculated from the analysis is 2.739 g/cm³ and is in good agreement with the measured density of 2.724 g/cm³.

THERMAL ANALYSES

Thermal gravimetric analyses showed that dehydration of hilairite began almost immediately on heating and continued until completion at about 220°C. The dehydrated material was stable up to at least 855°C at the heating rate of 10°C/min., but broke down between 855°C and 950°C to a mixture of ZrO₂ and unidentified compounds. On cooling from 855°C rehydration began when the temperature dropped to 220°C. At least 95 per cent of the original water content was recovered within 15 hours at room temperature. The x-ray powder pattern of the rehydrated material is identical to that of the unheated hilairite. Thus water in hilairite is zeolitic in nature. When one single crystal was heated to 855°C and allowed to cool to room temperature the rehydrated crystal became opaque with a porcelainous luster and changed from pale brown to flesh color, similar to the hilairite crystals found in the altered pegmatites. This suggests that hilairite in the altered pegmatites may have experienced a similar dehydration-rehydration process during late-stage magmatic hydrothermal activity.

Differential thermal analysis has not been attempted due to the limited amount of available material.

RELATED MINERALS

Hilairite is similar to catapleite and gaidonnayite, two polymorphs of Na₂ZrSi₃O₉ · 2H₂O, in

both chemical composition and some physical properties. It differs primarily in the water content. Nevertheless, hilairite can be easily distinguished from these chemically similar minerals by its crystal morphology and x-ray powder diffraction pattern.

The unusual association of several hydrated sodium zirconium silicate minerals at Mont St. Hilaire prompted an attempt to determine their relative stabilities by hydrothermal syntheses at various temperature and pressure conditions. Synthesis of hilairite and gaidonnayite was not successful from 0.5 to 2.5 kb and between 150° and 600°C. Between 1.0 and 2.5 kb the synthetic products were either elpidite at high temperatures (300-500°C) or catapleite at low temperatures (200-400°C).

The sequence of crystallization deduced from textural relationships is elpidite, catapleite, gaidonnayite, hilairite. Elpidite needles were always found to penetrate the relatively large catapleite crystals. Gaidonnayite and hilairite were found to fill the interstices between catapleite crystals and hilairite was sometimes found to enclose gaidonnayite.

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