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SABINAITE, A NEW ANHYDROUS ZIRCONIUM-BEARING CARBONATE MINERAL FROM MONTREAL ISLAND, QUÉBEC

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ABSTRACT

Fine-grained, white, powdery coatings and chalky aggregates of sabinaite occur in vugs in a dawsonite-rich silicocarbonatite sill at Montreal Island, Québec. The mineral is platy, roughly pseudohexagonal, with maximum dimensions 0.01 x 0.001 mm, biaxial negative with $2V$ 85°, α 1.74(2), β 1.80(2), γ 1.85(1), X nearly normal to the plates. Analyses gave Na_2O 20.7, CaO 0.2, ZrO_2 39.1, HfO_2 0.47. TiO_2 12.0, CO_2 27.1, total 99.57 wt. %. Sabinaite is anhydrous and has low or negligible F. The analytical formula is $(Na,Ca)_{8.84}(Zr,Hf)_{4.20}Ti_{1.98}O_{8.70}(CO_3)_{8.10}$, theoretically $Na_9Zr_{4+x}Ti_2O_9(CO_3)_8$ where $x = 0.25$. The mineral is unreactive in cold acids but is soluble with effervescence in warm HCl. Sabinaite is monoclinic; cell dimensions, obtained partly by electron diffraction and partly from the powder X-ray pattern, are a 6.605(3), b 10.186(5), c 37.94(5) Å, $\beta \sim 90°$. D_{calc} is 3.41 g/cm^3 for $Z = 8$ (analytical formula), whereas D_{meas} is 3.36 g/cm^3. Strongest lines of the powder pattern are 8.97(10)(012), 2.991(6)(036), 2.017(5)(240), 1.847(6), 1.646(5). The infrared spectrum of sabinaite confirms the presence of carbonate and the absence of H_2O and OH. DTA and TGA gave a weight loss of 28.1%, with decomposition mainly to monoclinic ZrO_2. Sabinaite is named in honor of Ann Phyllis Sabina, of the Geological Survey of Canada.

Keywords: sabinaite, silicocarbonatite, St-Michel quarry, Montréal, dawsonite, anhydrous carbonate of zirconium and titanium.

SOMMAIRE

On trouve la sabinaïte en enduits blancs, finements grenus, pulvérulents et en agrégats crayeux dans les vacuoles d'un sill de silicocarbonatite à dawsonite sur l'île de Montréal (Québec). Elle se présente en plaquettes pseudo-hexagonales mesurant au maximum 0.01 x 0.001 mm. Biaxe négative, $2V$ 85°, α 1.74(2), β 1.80(2), γ 1.85(1), X presque perpendiculaire aux plaquettes. L'analyse donne Na_2O 20.7, CaO 0.2, ZrO_2 39.1, HfO_2 0.47, TiO_2 12.0, CO_2 27.1, total 99.57 (poids). La sabinaïte est anhydre; sa teneur en fluor est négligeable; sa formule est $(Na,Ca)_{8.84}(Zr,Hf)_{4.20}Ti_{1.98}O_{8.70}(CO_3)_{8.10}$ soit, idéalement, $Na_9Zr_{4+x}Ti_2O_9(CO_3)_8$, $x = 0.25$. Elle ne réagit pas avec les acides froids, mais est soluble avec effervescence dans HCl chaud. La sabinaïte est monoclinique; les dimensions de la maille, obtenues en partie par diffraction électronique et en partie aux rayons X sur cliché de poudre, sont: a 6.605(3), b 10.186(5), c 37.94(5) Å, $\beta \sim 90°$. $D_{calc} = 3.41$ pour $Z = 8$ (formule analytique), D_{mes} 3.36. Les cinq raies les plus intenses du cliché de poudre sont: 8.97(10)(012), 2.991(6)(036), 2.017(5)(240), 1.847(6), 1.646(5). Le spectre infrarouge confirme la présence de carbonate et l'absence de H_2O et d'OH. Par ATD et ATG, on obtient une perte de poids de 28.1% et surtout du ZrO_2 monoclinique comme produit de décomposition. La nouvelle espèce est dédiée à Ann Phyllis Sabina, de la Commission géologique du Canada.

(Traduit par la Rédaction)

Mots-clés: sabinaïte, silicocarbonatite, carrière St-Michel, Montréal, dawsonite, carbonate anhydre de zirconium et de titanium.

INTRODUCTION

Dawsonite-bearing silicocarbonatite sills exposed in a limestone quarry at St-Michel, Montreal Island, Québec, contain a varied mineralogy that includes several unique barium- and zirconium-bearing carbonates and a few as-yet-unidentified minerals (Sabina 1979). In 1967 a new Na–Zr–Ti mineral was recognized and subsequently designated as mineral No. 5 (Sabina 1976, 1979) For almost a decade only a minute amount of this mineral was available, but persistent collecting and X-ray identifications by A.P. Sabina eventually resulted in the acquisition of sufficient material for a chemical analysis and characterization. The new mineral is named *sabinaite* in honor of Ann Phyllis Stenson (*née* Sabina), whose initial work led to the recognition of the unusual mineral assemblage at the St-Michel quarry, and whose perseverance in collecting and identifying these rare minerals has provided the main impetus toward their study. The new mineral and name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. Cotype specimens of sabinaite are in the National Mineral Collection at the Geological Survey of Canada, Ottawa (61017 to 61024 inclusive), and in the Royal Ontario Museum, Toronto (*M*35902).

PROPERTIES

Physical and optical properties

Sabinaite occurs in silicocarbonatite in the upper levels of the quarry, where it forms white, powdery coatings and compact, chalky aggregates in vugs. The mineral is microscopically flaky, with maximum dimensions of about 0.01 mm in width and 0.001 mm in thickness. Compact aggregates have a vitreous lustre, but in some cases flakes are aligned and impart a silky lustre to thin coatings. The hardness of the mineral could not be determined.

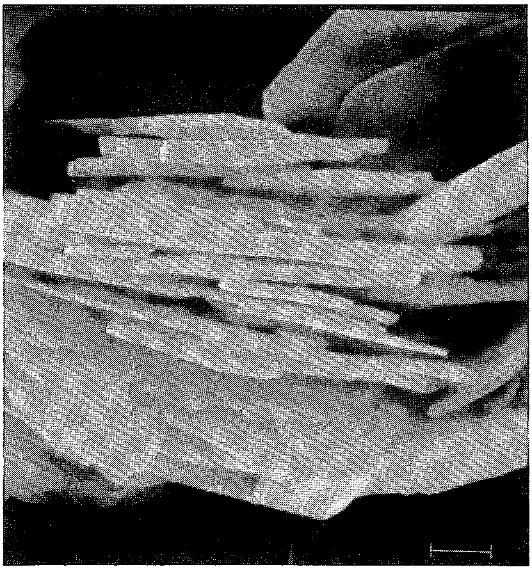

FIG. 1. SEM photograph showing the typical platy habit and crystal shape (top right) of sabinaite. Bar represents 1 μm.

Optical and scanning electron microscopy of sabinaite shows that it is platy and commonly roughly pseudohexagonal. Grains are generally equant, but most of the prism edges are irregular. A few grains are well formed (Fig. 1) and have crystal edges that intersect at 115 to 120°, thus accounting for the pseudohexagonal crystal shape. Perfect basal cleavage is evident from the persistent flaky habit of ground samples; a good cleavage normal to the base is visible in some SEM photographs.

Sabinaite is optically transparent and colorless, biaxial negative with $2V$ (universal stage) 85(5)°, α 1.74(2), β 1.80(2), γ 1.85(1). X is perpendicular (or nearly) to the plates.

Sabinaite does not fluoresce in ultraviolet radiation. However, in some specimens this inertness is obscured by the presence of films of a gibbsite-type mineral (No. 3 of Sabina 1976, 1979) that has an intense, white fluorescence under long-wave ultraviolet light. Sabinaite shows no reaction in dilute and concentrated (1:1) hydrochloric acid at room temperature, but is readily soluble with effervescence in warm HCl. Pycnometer measurement of an approximately 300-mg sample used for the chemical analysis of sabinaite gave a density of 3.36 g/cm^3.

X-ray data

Sabinaite is too fine grained for standard single-crystal X-ray study. Electron-diffraction patterns of flat-lying plates show a net that can be interpreted as orthogonal, with $h + k = 2n$ and $d_{100} = 10.2$, $d_{010} = 6.6$ Å. Observed forms for sabinaite therefore become {100} and {110}, platy {001}, with cleavages {001} and {100}. Attempts to obtain the third cell parameter by tilting the plates were not successful because of multiple diffraction and reciprocal lattice streaking. Controlled tilting experiments about [100] do not give identical patterns and indicate that the unit cell is not precisely orthorhombic. Therefore, either monoclinic or triclinic symmetry would be possible, but the systematic $hk0$ extinctions indicate that the cell is monoclinic.

The X-ray powder pattern of sabinaite was indexed by using the orthogonal dimensions from the electron-diffraction pattern and calculating c and β from the powder data. Satisfactory indexing was obtained with $c = 37.94$ Å, $\beta = 90°$ (Table 1).

TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR SABINAITE

I_{est}	d_{meas}	d_{calc}	*hkl*	I_{est}	d_{meas}	d_{calc}	*hkl*
10	8.97	8.974	012	1	2.243	2.244	048
1	5.10	5.093	020	1	2.153	2.150	0.2.16
<½	4.57	4.568	106	<½B	2.126	2.124	148
2	4.48	4.487	024	1	2.109	2.108	0.0.18
1	4.30	4.299	018	5	2.017	2.017	240
1	3.307	3.303	200	2	1.946		
<½B	3.277	3.279	033	6	1.847		
2	3.252	3.254	202	2	1.824		
1	3.009	3.010	131	3	1.795		
6	2.991	2.991	036	<½	1.730		
<½B	2.942	2.937	133	<½	1.693		
<½	2.768	2.771	220	3	1.687		
<½B	2.742	2.742	222	5	1.646		
1	2.724	2.725	136	<½	1.624		
<½	2.665	2.660	224	<½B	1.601		
<½B	2.628	2.621	1.2.11	<½	1.569		
1	2.494	2.496	043				
		2.491	2.0.10				

Guinier focusing camera, CuKα radiation. Indexed with *a* 6.605(3), *b* 10.186(5), *c* 37.94(5)Å, β 90°. B = broad line.

Chemical Composition

Numerous samples of the silicocarbonatite were examined under a binocular microscrope, and their mineral contents were checked by Debye–Scherrer X-ray patterns. About 30 samples containing clean, homogeneous areas of verified sabinaite were hand-picked and reconcentrated with methylene iodide to remove inadvertently incorporated contaminants such as quartz and dawsonite. The main purified concentrate weighed approximately 300 mg. A much smaller sample of recovered "fines" was used for supplementary chemical analyses. Compact aggregates of pure sabinaite selected from hand specimens were mounted in a polished section for microprobe study.

Initial semiquantitative microprobe analyses for Na, Zr, Hf and Ti were obtained by A.G. Plant of the Geological Survey of Canada; these results agree well with the quantitative data obtained subsequently (Table 2). The final analyses for Ti, Zr and Hf were obtained by neutron activation using the SLOWPOKE facility operated under the supervision of R.G.V. Hancock at the University of Toronto. Ca was determined by microprobe at CANMET, and Na_2O, CO_2 and F were determined by wet-chemical methods at the Geological Survey of Canada. No other elements were detected by microprobe.

TABLE 2. ANALYSES OF SABINAITE

wt.%	main sample	fines sample	values selected	recalc. to 100 %	nos. of ions for 33 O	
Na_2O	20.7		20.7	20.79	Na 8.788	8.84
CaO	0.2		0.2	0.20	Ca 0.047	
ZrO_2	39.4	38.8	39.1	39.27	Zr 4.174	4.20
HfO_2	0.47	0.46	0.47	0.47	Hf 0.030	
TiO_2	12.2	11.8	12.0	12.05	Ti 1.976	1.98
CO_2	27.1		27.1	27.22	C 8.100	8.10
F	0.6	<0.1	0.0		O 33.000	33.00
			99.57	100.00		

Analytical formula $(Na,Ca)_{8.84}(Zr,Hf)_{4.20}Ti_{1.98}O_{8.70}(CO_3)_{8.10}$

Theoretical formula $Na_9Zr_{4+x}Ti_2O_9(CO_3)_8$

The analyses in Table 2, recalculated to 100 wt. %, yield a formula of $(Na,Ca)_{8.84}(Zr,Hf)_{4.20}Ti_{1.98}O_{8.70}(CO_3)_{8.10}$, approximately $Na_9(Zr,Hf)_{4+x}Ti_2O_9(CO_3)_8$ assuming 33 O atoms and no F atoms. The analytically derived value of *x* is 0.18 to 0.20, whereas the theoretical value is 0.25. The slight deficiency in Ti (Table 2) is within the limits of analytical error; Ti and Zr are assigned separate positions as their mutual substitution is unlikely (Pyatenko & Voronkov 1978). From our evaluation of the various alternative formulae for sabinaite, the small amount of fluorine obtained initially (Table 2) seemed likely to be nonessential; the "fines" sample was therefore used to redetermine this element. The low value obtained (< 0.1 % F) supports the supposition that F is nonessential, but the reason for the difference between the two analytical results is not known.

The analytically derived, 33-oxygen formula (Table 2) yields a calculated density of 3.41 g/cm³ for $Z = 8$, in reasonable agreement with the measured value of 3.36 g/cm³. Despite this agreement, alternative formulas for sabinaite are possible; for example, *Z* may be 2 and (Zr,Hf) 17. The 33-oxygen formula also has (Zr,Hf): $CO_3 = 1.93$, whereas ideally this value probably is 2.00. However, manipulation of the analytical formula is difficult to justify at this time.

The mean refractive index of sabinaite and the specific refractivity (Mandarino 1979) obtained from the chemical analysis recalculated to 100 wt. % yield a density of 3.496 g/cm³. Using the density obtained with the unit-cell volume, K_p/K_c (Mandarino 1979) is $0.234/0.228 = 1.026$; utilization of the measured density leads to $K_p/K_c = 0.237/0.228 = 1.04$.

Neutron-activation analyses yield Hf/Zr ratios (wt. % x 100) of 1.37 for sabinaite and 1.28 for weloganite; microprobe analyses of zircon separates from the silicocarbonatite sill give Hf/Zr = 1.16. In zircon from Mont St-Hilaire, Hf/Zr = 1.24 (Dutrizac 1978).

DTA–TGA and Infrared Spectrum

DTA and TGA curves of sabinaite were obtained with a Mettler Thermoanalyzer at the Royal Ontario Museum. A 6.8-mg sample heated at 8° C/min in a CO_2 atmosphere (flow rate 6.7 l/h) showed a two-step weight loss: 0.9% from 430 to 470°C and 14.9% from 470 to

558°C (cumulative 15.8%). In the second stage, only 0.15% is lost from 811 to 895°C and 2.8% from 917 to 998°C, but the reaction is incomplete. The product of heating to 998°C is monoclinic ZrO_2.

A 7.3-mg sample of sabinaite run in a N_2 atmosphere, at flow and heating rates as above, gave much more pronounced reactions and a similar two-stage loss: to 450°C the weight loss is only 1.1%, but a major, sharp endothermic peak is centred at 519°C and the cumulative losses to 550 and 650°C are 18.8% and 20.3% respectively. The endothermic peak may signal the evolution of 6 CO_2, corresponding to a calculated decrease in weight of 20.2%. Further CO_2 evolution is signaled by the occurrence of a second endothermic peak between 660 and 780°C and a 7.9% weight loss. Only minor additional loss occurs between 780 and 900°C, and the cumulative total to 1010° is 28.1%. The end product is monoclinic ZrO_2, with faint traces of cubic ZrO_2 and Na_2ZrO_3 also evident on the X-ray pattern. A duplicate run to 587°C was used to examine the product formed after the first-stage weight loss. The X-ray powder pattern obtained was that of stabilized cubic ZrO_2 with *a* 5.05 Å; Katz (1971) reported that pure cubic ZrO_2 has a cell edge of 5.09 Å.

The infrared spectrum of sabinaite is shown in Figure 2. Sabinaite is a most unusual compound in that no other anhydrous zirconium carbonates are known to occur either naturally or in synthetic systems. Although normal carbonates of zirconium and hafnium have eluded synthesis, several hydrated zirconium salts with basic carbonato anions have been isolated (Bradley & Thornton 1973, Dervin *et al.* 1974). The notable absence of absorption bands in the 3000–3900 and 900–1000 cm^{-1} regions of sabinaite (Fig. 2) confirms the absence of H_2O and OH in the mineral.

Because of the unusual composition of sabinaite, the possibility that part of the carbon might be structurally bound as oxalate was considered. The first strong absorption band in the infrared spectrum of sabinaite is centred at about 1660 cm^{-1}. The equivalent band in oxalates is in the range 1600-1630 cm^{-1} whereas carbonates generally have this band at lower wave-numbers. However, chemical analysis of sodium oxalate by the identical method used for sabinaite gave negligible CO_2. Moreover, comparison of the infrared spectrum of sabinaite with spectra of carbonate compounds of zirconium (Kharitonov *et al.* 1967) shows that the absorption band at 1600 cm^{-1} is ν_1 (CO), that at 1330 cm^{-1} is ν_5 (CO), and that at 1080 cm^{-1} is probably ν_2 (CO). According to literature cited in Kharitonov *et al.* (1967), ν (ZrO) should appear as an intense, narrow absorption band between 800 and 1000 cm^{-1}; such a band appears in the spectrum of sabinaite at about 830 cm^{-1}. The positions of the CO absorption bands in sabinaite indicate that linkage of zirconium and carbonato groups is most likely bidentate or bridging rather than unidentate.

Associated Minerals

Sabinaite is commonly present in the silicocarbonatite in small amygdule-like pockets and as coatings in cavities lined with calcite, daw-

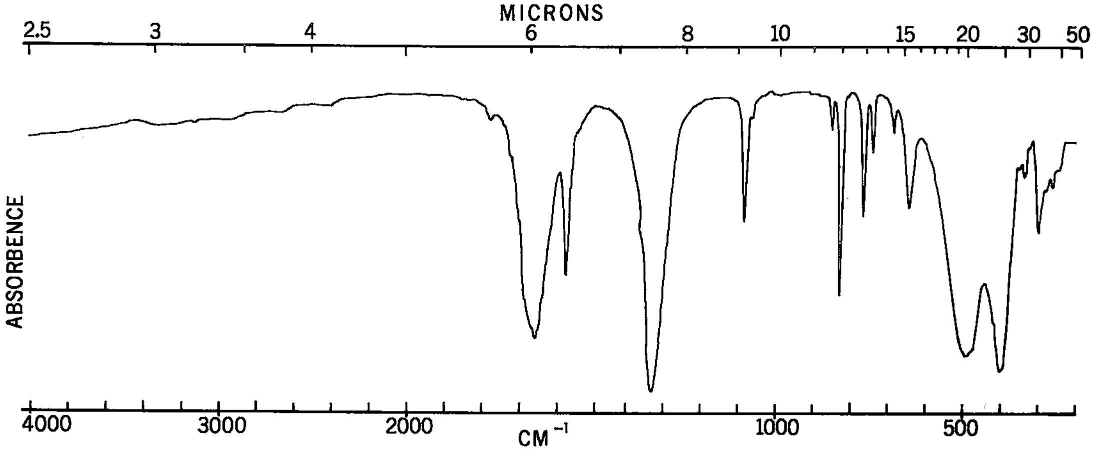

Fig. 2. Infrared spectrum of sabinaite.

sonite and quartz. The most persistent associate is a fluorine-bearing gibbsite-type mineral whose characterization has not been completed. Sabinaite coats all of the above minerals, as well as weloganite and cryolite. Pyrite, galena, pink barite, plates of ilmenorutile, and yellowish ankerite and siderite have been noted as inclusions in sabinaite. These observations indicate that sabinaite was formed late in the depositional sequence of the vug minerals. Films of blackish hydrocarbon have been observed as coatings on weloganite, quartz and calcite crystals; in one unusual case, sabinaite coats massive white dawsonite, pink garnet, and grey quartz and calcite that occur in a pod containing graphite flakes.

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