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 pseudo-hexagonal, with maximum dimensions 0.01 x 0.001 mm, biaxial negative with 2V ~ 85°, c ~ 1.74(2), α ~ 1.85(1), X nearly perpendicular to the plates. Analyses gave Na₂O 20.7, CaO 0.2, ZrO₂ 39.1, HfO₂ 0.47, TiO₂ 12.0, CO₂ 27.1, total 99.57 wt. %. Sabinaite is anhydrous and has low or negligible F. The analytical formula is (Na,Ca)₉₋₁(Sz,Hf)ₐ₋₁(Zr,Hf)ₖ₋₁(Ti,Hf)₉₋₈O₈₋₅(CO₃)₈₋₇ where k = 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, β ~ 90°. Dcalc is 3.41 g/cm³ for Z = 8 (analytical formula), whereas Dmeas is 3.36 g/cm³. Strongest lines of the powder pattern are 8.97(10), 2.991(6), 2.017(5), 1.847(6), 1.646(5). The infrared spectrum of sabinaite confirms the presence of carbonate and the absence of H₂O and OH. DTA and TGA gave a weight loss of 28.1%, with decomposition mainly to monoclinic ZrO₂. Sabinaite is named in honor of Ann Phyllis Sabina, of the Geological Survey of Canada.

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

INTRODUCTION

Dawsonite-bearing silicocarbonatite sills exposed in a limestone quarry at St-Michel, Montréal 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 (Sabinna 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 (M35902).

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.

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/cm³.

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 d₁₀₀ = 10.2, d₀₁₀ = 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, β = 90° (Table 1).
TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR SABINAITE

<table>
<thead>
<tr>
<th>hkl</th>
<th>( d_{\text{calc}} )</th>
<th>( d_{\text{meas}} )</th>
<th>wt. %</th>
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<tr>
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<td>8.974</td>
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<td>3.00</td>
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</tr>
<tr>
<td>12</td>
<td>2.628</td>
<td>2.621</td>
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Guinier focusing camera, CuKα radiation. Indexed with \( \alpha = 6.605(3), \beta = 10.186(5), \gamma = 37.94(5) \) \(^\circ\). \( \beta \) = broad line.

**CHEMICAL COMPOSITION**

Numerous samples of the silicocarbonatite were examined under a binocular microscope, 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 recrystallized 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 Na₂O, CO₂, and F were determined by wet-chemical methods at the Geological Survey of Canada. No other elements were detected by microprobe.

The analyses in Table 2, recalculated to 100 wt. %, yield a formula of \((Na, Ca)_{2.94}(Zr, Hf)_{1.24}TiO_2(CO_3)_{8.10}\), approximately \(Na_2(Zr, Hf)_4TiO_3(CO_3)_{8.67}\) 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 smallest amount of fluorine obtained initially (Table 2) seemed likely to be nonessential; the "fines" sample was therefore used to re-determine 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 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/cm\(^3\). Using the density obtained with the unit-cell volume, \(K_p/K_o\) (Mandarino 1979) is 0.234/0.228 = 1.026; utilization of the measured density leads to \(K_p/K_o\) = 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 (Durtrizac 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 CO₂ 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 ZrO₂.

A 7.3-mg sample of sabinaite run in a N₂ 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 CO₂, corresponding to a calculated decrease in weight of 20.2%. Further CO₂ 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°C is 28.1%. The end product is monoclinic ZrO₂, with faint traces of cubic ZrO₂ and Na₂ZrO₃ 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 ZrO₂ with a 5.05 Å; Katz (1971) reported that pure cubic ZrO₂ 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 H₂O 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 CO₂. 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 ν₃ (CO), that at 1330 cm⁻¹ is ν₅ (CO), and that at 1080 cm⁻¹ is probably ν₃ (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 carbonate 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-
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References


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