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THE BARIUM ANALOG OF BREWSTERITE FROM HARRISVILLE, NEW YORK

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ABSTRACT

The barium analog of brewsterite, ideally $BaAl_2Si_6O_{16}{\cdot}5H_2O$, occurs in cavities in prehnite at the Gouverneur Talc Co. No. 4 wollastonite mine southwest of Harrisville, Lewis County, New York. The mineral forms pale yellow to colorless aggregates of pinacoidal crystals up to 1 mm, associated with prehnite, quartz, diopside, calcite, wollastonite and microcline. It is brittle, with a conchoidal fracture and perfect {010} cleavage. It has a colorless streak and a Mohs hardness of ~4, and fluoresces bright yellow-green in shortwave ultraviolet light. The barium analog of brewsterite is biaxial positive, with α 1.513, β 1.517, γ 1.527, $2V$(meas.) 57(5)°, $2V$(calc.) 64(10)°, with $X \wedge c$ 36° (β obtuse) and $Z \parallel b$. Pleochroism and dispersion were not observed. The mineral is monoclinic, space group $P2_1/m$ or $P2_1$, with refined unit-cell parameters a 6.780(3), b 17.599(9), c 7.733(2) Å, β 94.47(3)°, V 919.9(4) Å^3, a:b:c 0.385:1:0.439. Electron-microprobe analyses show the mineral to be commonly zoned with respect to Ba and Sr. An analysis of the most Ba-rich zone gave BaO 19.12, SrO 1.99, CaO 0.06, K_2O 0.08, Na_2O 0.06, Al_2O_3 15.49, SiO_2 52.48, sum 89.28 wt.%, corresponding to $(Ba_{0.85}Sr_{0.13}Ca_{0.01}K_{0.01}Na_{0.01})(Al_{2.07}Si_{5.95})O_{16}{\cdot}5H_2O$, based on 21 anions and assuming $5H_2O$. D(meas.) is equal to 2.50 g/cm^3, and D(calc.), to 2.52 g/cm^3 for the observed empirical formula with $Z = 2$. Exchange of Ba and Sr is not appreciable in this structure; the existence of Ba-rich and Ba-poor zones probably reflects compositional fluctuations in the fluid phase that caused the late hydrothermal mineralization.

Keywords: barium, barium analog, brewsterite, ion exchange, zeolite, Gouverneur deposit, New York.

SOMMAIRE

Un analogue baryfère de la brewsterite, possédant la formule idéale $BaAl_2Si_6O_{16}{\cdot}5H_2O$, tapisse les cavités de la prehnite dans la mine de wollastonite dite Gouverneur Talc Co. No. 4, au sud-ouest de Harrisville, comté de Lewis, dans l'état de New York. C'est un minéral jaune pâle à incolore, qui se présente en agrégats de cristaux pinacoïdaux jusqu'à 1 mm de longueur, associés à: prehnite, quartz, diopside, calcite, wollastonite et microcline. Il est cassant, avec une fracture concoïdale, et un clivage {010} parfait. Sa rayure est incolore, et sa dureté de Mohs, environ 4. Lorsqu'exposé à la lumière ultra-violette à onde courte, il émet une fluorescence de couleur jaune-vert brillant. Il est biaxe positif, avec α 1.513, β 1.517, γ 1.527, $2V$ (mesuré) 57(5)°, $2V$(calculé) 64(10)°, avec $X \wedge c$ 36° (dans l'angle β obtus), et $Z \parallel b$. Nous n'avons pas décelé de pléochroïsme, ni de dispersion. C'est un minéral monoclinique, groupe spatial $P2_1/m$ ou $P2_1$, avec les paramètres réticulaires suivants: a 6.780(3), b 17.599(9), c 7.733(2) Å, β 94.47(3)°, V 919.9(4) Å^3, a:b:c 0.385:1:0.439. Les données à la microsonde électronique montrent que les cristaux sont généralement zonés en Ba et Sr. Une analyse de la zone la plus riche en Ba a donné BaO 19.12, SrO 1.99, CaO 0.06, K_2O 0.08, Na_2O 0.06, Al_2O_3 15.49, SiO_2 52.48, total 89.28% (en poids), ce qui correspond à $(Ba_{0.85}Sr_{0.13}Ca_{0.01}K_{0.01}Na_{0.01})(Al_{2.07}Si_{5.95})O_{16}{\cdot}5H_2O$ pour une formule de 21 anions, en supposant $5H_2O$. La densité mesurée est de 2.50, et la densité calculée est de 2.52 pour la formule empirique observée, avec $Z = 2$. Le Ba et le Sr ne semblent pas échangeables dans cette structure; l'existance de zones riches et pauvres en Ba témoignerait donc de fluctuations dans la phase fluide responsable de la minéralisation hydrothermale tardive.

(Traduit par la Rédaction)

Mots-clés: baryum, analogue baryfère, brewsterite, échange d'ions, zéolite, gisement de Gouverneur, New York.

INTRODUCTION

The mineral described herein was first brought to our attention in 1985 by a private collector, Wayne Holt (deceased) of Rochester, New York, who submitted it to one of us (GWR) for identification. The specimen was quickly identified by X-ray powder diffraction as "brewsterite" and dismissed. Five years later, while examining another group of specimens from the same locality by SEM, an EDS X-ray spectrum of the "brewsterite" was acquired and its anomalously high Ba peak noted. Subsequent investigation has proven this mineral to be the Ba analog of brewsterite. The specimens used in this study are deposited at the Canadian Museum of Nature, Ottawa, Ontario (CMN #82457).

The data presented in this paper were submitted to the Commission on New Minerals and Mineral Names, IMA in July, 1990. At present, no decision can be made as to the acceptability of this mineral as a new species, since the findings of the Zeolite Subcommittee on the rules for designation of new species and nomenclature have not been made available. In view of this long-standing problem, the authors have decided to present their new data with their opinion (but not with IMA approval) that the barium analog of brewsterite should be considered a distinct mineral species.

OCCURRENCE AND PHYSICAL PROPERTIES

The barium analog of brewsterite occurs in cavities in prehnite at the Gouverneur Talc Company's No. 4 open-pit wollastonite mine (Valentine property), on New York Route 3, southeast of Lake Bonaparte, near Harrisville, Lewis County, New York. Associated species include prehnite, quartz, diopside, calcite, wollastonite and microcline. This assemblage seems to postdate the wollastonite orebody, and probably formed by hydrothermal mineralization along fractures (Brown 1987, Gerdes 1991).

The barium analog of brewsterite forms transparent, vitreous, pale yellow to colorless, platy aggregates of flattened, pinacoidal crystals up to 1 mm across (Fig. 1). Individual crystals are tabular on {010} and show the forms {001}, {010} and {001}. Twinning is optically visible on the {010} plane. The mineral is brittle, with a conchoidal fracture, and shows perfect cleavage parallel to {010}. It has a colorless streak and a Mohs hardness of approximately 4. The density, measured by suspension in bromoform diluted with butyl alcohol, is 2.50(1) g/cm^3. It fluoresces bright yellow-green in shortwave ultraviolet light; it gives a Fourier-transformed infrared (FTIR) spectrum essentially identical to that of brewsterite from Strontian, Scotland, with broad absorption bands with peaks at 465, 585, 715, 1025, 1150, 1630, 2360 and 3500 cm^{-1}.

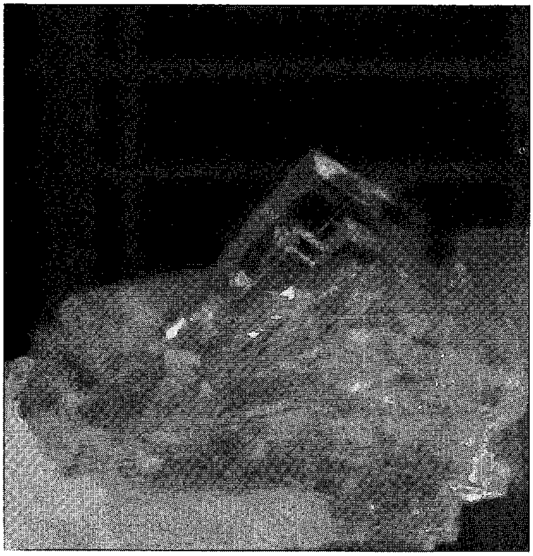

FIG. 1. Photomicrograph of the barium analog of brewsterite. Crystal aggregate is approximately 0.5 mm.

The barium analog of brewsterite is colorless in thin fragments and shows neither pleochroism nor dispersion. It is biaxial positive, with indices of refraction α 1.513(1), β 1.517(1), γ 1.527(1), $2V$(meas.) 57(5)° (for a λ of 590 nm) and $2V$ (calc.) 64°. The optical orientation is $X \wedge c$ 36° (in β obtuse) and $Z \parallel b$. The indices of refraction are higher than those of brewsterite.

X-RAY CRYSTALLOGRAPHY

Single-crystal X-ray precession photographs show the barium analog of brewsterite to be monoclinic, with space group either $P2_1/m$ or $P2_1$. These findings confirm the crystallographic findings of Perrotta & Smith (1964), but could not confirm the triclinic setting of Akizuki (1987), which results from a slight distortion in the crystal structure due to order involving Si and Al. Unit-cell dimensions were refined from X-ray powder-diffraction data collected on a 114.6 mm Debye–Scherrer camera using Cu$K\alpha$ radiation: a 6.780(3), b 17.599(9), c 7.733(2) Å, β 94.47(3)° and V 919.9(4) Å^3. The strongest eight lines in the powder-diffraction pattern [d in Å (I)(hkl)] are 2.926(10)(230), 4.68(8)(031), 6.31(8)(110), 3.27(6)(141), 5.07(3)(111), 4.53(3)(121), 2.018(3)(270) and 1.663(3)(234). The complete powder-diffraction data are not reproduced here, as they are essentially identical to those given for brewsterite in the JCPDS mineral powder-diffraction file (PDF 15–582).

CHEMICAL COMPOSITION

The barium analog of brewsterite was analyzed by wavelength-dispersion electron-microprobe spectrometry using a JEOL 733 Superprobe, and the data reduced with the Tracor–Northern 5600 program ZAF. Analyses were carried out using an operating voltage of 15 kV and a beam current of 25 nA measured on a Faraday cup. Both defocussed (50 μm) and scanning beam techniques were employed to minimize volatilization, with negligible differences noted. Back-scattered-electron imaging demonstrated the crystals to be compositionally zoned (Fig. 2); these images were used together with the energy-dispersion spectra (EDS) to select barium-dominant zones for both chemical analysis and determination of physical properties. Sanbornite (Ba$L\alpha$, Si$K\alpha$), celestine (Sr$L\alpha$), almandine (Ca$K\alpha$), sanidine (K$K\alpha$), albite (Na$K\alpha$) and YAG (Al$K\alpha$) were used as standards. No other

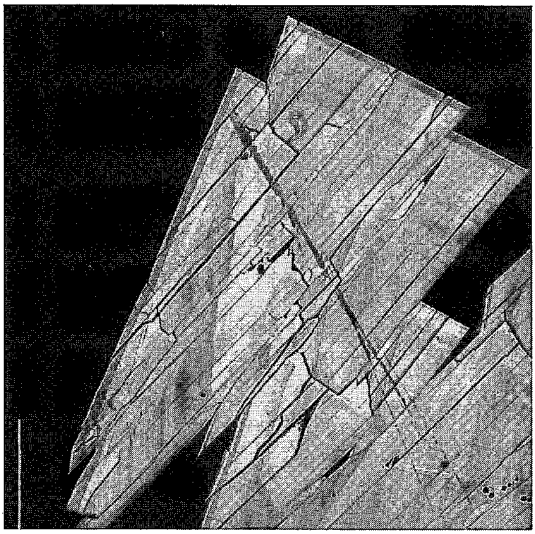

FIG. 2. Back-scattered-electron image of the barium analog of brewsterite, showing Ba–Sr zoning (the darker areas are enriched in Sr). Scale bar: 100 μm.

elements with an atomic number of 9 or greater were detected. Analysis of the most barium-rich zone observed gave BaO 19.12(34), SrO 1.99(3), CaO 0.06(1), K_2O 0.08(1), Na_2O 0.06(1), Al_2O_3 15.49(8), SiO_2 52.48(26), sum 89.28 wt%. The presence of H_2O was confirmed qualitatively by FTIR spectroscopy using a diamond microsample cell, and determined quantitatively to be 17.2 wt% by thermogravimetric microanalysis. However, we consider this value to be too high, probably owing to the small amount of sample available (0.932 mg). The resulting empirical formula, based on 21 anions and assuming the presence of $5H_2O$, is $(Ba_{0.85}Sr_{0.13}Ca_{0.01}K_{0.01}Na_{0.01})(Al_{2.07}Si_{5.95})O_{16}\cdot 5H_2O$, or an ideal end-member formula $BaAl_2Si_6O_{16}\cdot 5H_2O$.

The calculated density based on the observed composition and unit-cell volume is 2.52 g/cm^3, in close agreement with the measured value. The compatibility index $(1 - K_P/K_C)$ based on the Gladstone–Dale relationship is 0.0304, indicating excellent agreement between the physical and chemical data (Mandarino 1979).

ION-EXCHANGE CAPACITY

Brewsterite is not a common zeolite. Relatively few localities have been reported, along with correspondingly few compositions. Whereas the substitution of barium for strontium in brewsterite is well documented, it seldom exceeds 30 mole % (Tschernich 1992). To date, only one other occurrence of Ba-dominant brewsterite has been noted (Cabella *et al.* 1993). Since little is known about the capacity for cation exchange in brewsterite, a simple experiment was conducted. Individual crystals of brewsterite from Strontian, Scotland, found by microprobe to contain both Ba- and Sr-rich zones, were crushed to approximately 0.1 – 0.3 mm, ultrasonically cleaned in deionized water, and dried in air at room temperature. Individual portions were separated and placed in solutions of ammonium acetate, ammonium chloride, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, barium chloride and cobalt chloride. The samples were kept in these solutions at room temperature for two weeks and ultrasonically agitated for ten minutes daily. After two weeks, the samples were removed from the solutions, rinsed in deionized water and dried in air at room temperature. The samples were then mounted in epoxy and prepared for examination by electron microprobe. No evidence of cation exchange was observed in the back-scattered-electron images or EDS X-ray spectra for any of the samples in either the Ba- or Sr-rich zones. Thus it appears that these cations are not readily exchangeable in the brewsterite structure.

This result is predictable, since the two main channels in the structure have minimum free apertures of 2.7 and 2.3 Å across, which is considerably smaller than in other zeolite structures in which cation exchange is prevalent (Breck 1974). These small apertures would not allow for the exchange of such large cations as Ba^{2+}, Sr^{2+} and Ca^{2+}, and hence they remain in distinct chemical zones within a single crystal. Exchange involving monovalent species would require modification of the Si/Al ratio in the framework to maintain charge balance. The existence of Ba-rich and Ba-poor zones probably reflects compositional fluctuations in the fluid phase that caused the late hydrothermal mineralization.

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