

**BOBTRAILLITE, (Na,Ca)₁₃Sr₁₁(Zr,Y,Nb)₁₄Si₄₂B₆O₁₃₂(OH)₁₂•12H₂O,
A NEW MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC: DESCRIPTION,
STRUCTURE DETERMINATION AND RELATIONSHIP TO BENITOITE AND WADEITE**

ANDREW M. McDONALD[§]

Department of Earth Sciences, Laurentian University, Sudbury Ontario P3E 2C6, Canada

GEORGE Y. CHAO[¶]

Ottawa–Carleton Geoscience Centre, Department of Earth Sciences, Carleton University, Ottawa Ontario K1S 5B6, Canada

ABSTRACT

Bobtraillite is a new, complex zirconosilicate found in igneous breccias and nepheline syenite pegmatites at the Poudrette quarry, Mont Saint-Hilaire, Quebec. It is associated with a burbankite-group mineral, donnayite-(Y), clinoamphibole, albite, aegirine, pyrrhotite, pyrite, annite, analcime, microcline, a white mica (muscovite?), yellow titanite, clinopyroxene and calcite. Crystals are commonly grey to brown in color, blocky to prismatic, elongate along [001], with a maximum length of 2 mm. It is generally found as isolated single crystals or simple parallel intergrowths with two or three members, rarely in small (<0.1 mm) rosettes. It is transparent with a vitreous luster and a white streak, and is non-luminescent. The Mohs hardness is 5½; no cleavage is evident. It is brittle and has an uneven to conchoidal fracture. The calculated density is 3.16 g/cm³. Bobtraillite is nonpleochroic, uniaxial positive, with ω 1.627(1) and ϵ 1.645(1). Seven analyses made on one crystal gave: Na₂O 5.62, CaO 1.11, SrO 17.76, BaO 0.40, B₂O₃ (calc.) 3.38, Y₂O₃ 1.15, SiO₂ 40.51, ZrO₂ 25.32, HfO₂ 0.48, Nb₂O₅ 1.32 and H₂O (calc.) 5.25, total 102.30 wt.%, corresponding to (Na_{11.20}Ca_{1.22})Σ_{12.42}(Sr_{10.59}Ba_{0.16})Σ_{10.75}(Zr_{12.69}Y_{0.63}Nb_{0.61}Hf_{0.14})Σ_{14.07}Si_{41.64}B₆O₁₃₂(OH)₁₂•12H₂O on the basis of 156 anions, or ideally, (Na,Ca)₁₃Sr₁₁(Zr,Y,Nb)₁₄Si₄₂B₆O₁₃₂(OH)₁₂•12H₂O. The mineral is trigonal, space group *P*3̄c1, *a* 19.720(1), *c* 9.9788(5) Å, *V* 3360.7(1) Å³ and *Z* = 1. The strongest six lines on the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 2.752(100)(332), 3.13(70)(331), 3.96(51)(212), 3.76(49)(302), 6.46(38)(210), and 5.43(33)(211). The structure of bobtraillite was refined to *R* = 3.49% and *wR*² = 10.88% for 1575 reflections [*F*_o > 4σ(*F*_o)]. Isolated ZrO₆ octahedra are linked by (Si₃O₉) rings to form a pinwheel-like motif similar to that found in wadeite. Additional (Si₃O₉) and [Si₂BO₇(OH)₂] rings complete a two-dimensional, giant pinwheel motif along [001]. Bonding between three-membered rings and ZrO₆ octahedra along [001] completes the structure in three dimensions. Channels along [001] are occupied by Na, H₂O and Sr. Bobtraillite shares chemical and crystal-structure features with benitoite, wadeite and catapleite, and should be considered as a structural hybrid of these minerals. The presence of essential B, Sr, H₂O and its trigonal symmetry make it unique. We discuss the group classification of minerals based on frameworks containing isolated MO₆ and three-membered rings of tetrahedra. The mineral is paragenetically late, arising from unusual, hydrous fluids enriched in B, Sr, Na and Zr. There are similarities between the fluid resulting in the crystallization of bobtraillite in igneous breccias and that responsible for the assemblages exotic minerals in altered marble xenoliths at Mont Saint-Hilaire. The name of the new species honors Robert (“Bob”) J. Traill, formerly mineralogist at the Geological Survey of Canada, Ottawa.

Keywords: bobtraillite, new mineral species, zirconosilicate, crystal structure, cyclosilicate, wadeite, benitoite, igneous breccias, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La bobtraillite, nouvelle espèce minérale, est un zirconosilicate complexe découvert dans une brèche ignée et des venues de pegmatite de syénite néphélinique à la carrière Poudrette, au mont Saint-Hilaire, Québec. Elle est associée à un membre du groupe de la burbankite, donnayite-(Y), clinoamphibole, albite, aegirine, pyrrhotite, pyrite, annite, analcime, microcline, un mica blanc (muscovite?), titanite jaune, clinopyroxène et calcite. En général, les cristaux sont gris à brun, et en blocs trappus ou prismatiques, allongés selon [001], avec une longueur maximale de 2 mm. Les cristaux sont généralement isolés ou en intercroissances de deux ou trois individus, et rarement en petites rosettes (<0.1 mm). Les cristaux sont transparents, avec un éclat vitreux et une rayure blanche, et sans luminescence. La dureté de Mohs est 5½; aucun clivage n'est évident. C'est un minéral

[§] E-mail address: amcdonald@nickel.laurentian.ca

[¶] Present address: 2031 Delmar Drive, Ottawa, Ontario K1H 5P6, Canada.

caissant, avec une fracture inégale à conchoïdale. La densité calculée est 3.16 g/cm³. La bobtraillite est nonpléochroïque, uniaxe positive, avec ω 1.627(1) et ε 1.645(1). Sept analyses effectuées sur un cristal ont donné: Na₂O 5.62, CaO 1.11, SrO 17.76, BaO 0.40, B₂O₃ (calc.) 3.38, Y₂O₃ 1.15, SiO₂ 40.51, ZrO₂ 25.32, HfO₂ 0.48, Nb₂O₅ 1.32 et H₂O (calc.) 5.25, pour un total de 102.30% (poids), ce qui correspond à (Na_{1.20}Ca_{1.22}) Σ 12.42(Sr_{10.59}Ba_{0.16}) Σ 10.75 (Zr_{12.69}Y_{0.63}Nb_{0.61}Hf_{0.14}) Σ 14.07 Si_{41.64}B₆O₁₃₂(OH)₁₂•12H₂O sur une base de 156 anions ou, idéalement, (Na,Ca)₁₃Sr₁₁(Zr,Y,Nb)₁₄Si₄₂B₆O₁₃₂(OH)₁₂•12H₂O. Le minéral est trigonal, groupe spatial *P*3*c*1, *a* 19.720(1), *c* 9.9788(5) Å, *V* 3360.7(1) Å³ et *Z* = 1. Les six raies les plus intenses du spectre de diffraction X, méthode des poudres [*d* en Å(*hkl*)], sont: 2.752(100)(332), 3.13(70)(331), 3.96(51)(212), 3.76(49)(302), 6.46(38)(210), et 5.43(33)(211). La structure a été affinée jusqu'à un résidu *R* de 3.49% (*wR*² = 10.88%) en utilisant 1575 réflexions [*F*_o > 4σ(*F*_o)]. Les octaèdres isolés ZrO₆ sont liés à des anneaux (Si₃O₉) pour former des assemblages à motif de virement comme on en trouve dans la wadeïte. Des anneaux supplémentaires (Si₃O₉) et [Si₂BO₇(OH)₂] complètent un agencement à virement géant en deux dimensions le long de [001]. Les liaisons entre les anneaux à trois membres et les octaèdres ZrO₆ le long de [001] complètent la structure en trois dimensions. Le Na, H₂O et Sr logent dans les canaux le long de [001]. La bobtraillite partage des propriétés chimiques et structurales avec la bênioïte, la wadeïte et la catapléïte, et serait un hybride structural de ces minéraux. La présence de B, Sr, H₂O essentiels et une symétrie trigonale assurent son statut unique. Nous discutons la classification des minéraux ayant une trame contenant des octaèdres MO₆ isolés et des anneaux à trois tétraèdres. Le minéral est paragénetiquement tardif, et cristallise à partir d'une phase fluide hydrothermale enrichie en B, Sr, Na et Zr. Cette phase fluide ressemble à celle qui est responsable des assemblages de minéraux exotique retrouvés dans les xénolithes de marbre altérés au mont Saint-Hilaire. Le nom honore Robert ("Bob") J. Traill, minéralogiste autrefois à la Commission géologique de Canada à Ottawa.

(Traduit par la Rédaction)

Mots-clés: bobtraillite, nouvelle espèce minérale, zirconsilicate, structure cristalline, cyclosilicate, wadeïte, benitoïte, brèche ignée, mont Saint-Hilaire, Québec.

INTRODUCTION

Bobtraillite, (Na,Ca)₁₃Sr₁₁(Zr,Y,Nb)₁₄Si₄₂B₆O₁₃₂(OH)₁₂•12H₂O, is a new addition to the growing list of minerals discovered in the hyperagpaitic nepheline syenites at Mont Saint-Hilaire, Quebec. It was tentatively referred to as UK69 (Chao *et al.* 1990), owing to an incomplete chemical formula and questions regarding its true space-group symmetry. Subsequent analyses have clarified these matters, and the mineral has been recognized as a new species. It has been named after Dr. Robert ("Bob") James Traill (b. 1921), mineralogist and former head of the Mineralogy Section at the Geological Survey of Canada (1953–1986), in recognition of his contributions to mineralogy. Dr. Traill coauthored mineral descriptions of hawleyite, molybdenite-3*R* and the lunar minerals pyroxferroite and armalcolite. He also authored the *Catalogue of Canadian Minerals* (editions published in 1969, 1973 and 1980). Both the mineral and mineral name were approved by the Commission on New Minerals and Mineral Names (CNMMN), IMA (2001–041). It should be noted that some data pertaining to bobtraillite (chemical formula, space group) have changed slightly from that reported in the submission to the CNMMN, IMA. The changes have been reported to, and accepted by, the Chairman of the CNMMN, IMA, Prof. E.A.J. Burke. The holotype material, consisting of one matrix specimen (1.5 × 1.3 × 1 cm) and a single-crystal mount (used in the intensity-data collection for refinement of the crystal structure) is housed in the collection of the Canadian Museum of Nature, Ottawa, catalogue number CMNMC 83718.

OCCURRENCE

Bobtraillite was originally discovered in green vuggy zones of breccia blocks from the lower level on the west side of the Poudrette quarry (formerly the Demix quarry), Mont Saint-Hilaire, Rouville County, Quebec. None of the boulders were found *in situ* and, according to some collectors, may have been exposed for quite some time. Many of the samples used in this study were collected by Mr. Garry Glenn (Niagara Falls, Ontario) in September, 1988. Whereas the majority of bobtraillite specimens have been recovered from igneous breccia, the mineral has also been rarely encountered in cavities of pegmatites in nepheline syenite. This pattern of distribution suggests the presence and subsequent migration of an unusual fluid (or fluids) through both rock types.

The mineral is clearly a late-stage phase, typically developing in cavities within the breccia. Associated minerals include a fibrous white burbankite-group mineral, green donnayite-(Y), a green acicular to prismatic clin amphibole, white, blocky albite (commonly translucent with a clear, colorless rim), aegirine, pyrrhotite, pyrite, annite, analcime, microcline, a white mica (muscovite?), yellow titanite, and calcite. The mineral occurs in thin (two to four millimeters wide) discontinuous pockets, intimately associated with blocky albite, green amphibole and calcite (with rare inclusions of green clin amphibole); the pocket margins also contain rounded aggregates of sulfides. A powder X-ray diffractogram of the matrix material indicates the presence of nepheline, albite, microcline, annite, a white mica and a clinopyroxene (inferred to be aegirine).

Bobtraillite is chemically and structurally related to benitoite, wadeite and catapleiite. Details of these relationships will be discussed below.

PHYSICAL AND OPTICAL PROPERTIES

Crystals of bobtraillite are blocky to prismatic, elongate along [001], up to 2 mm and averaging <0.5 mm in length. Very rarely are crystals found as plates, flattened along [001]. The mineral generally occurs as isolated single crystals or simple parallel intergrowths with two or three members, rarely in small (<0.1 mm) rosettes. It is most commonly gray to pale green or brown in color (Fig. 1), and very rarely, almost black. The mineral commonly develops in euhedral to subhedral crystals exhibiting the prism {100} and pinacoid {001}. One unique characteristic useful in recognizing the mineral is the presence of dark greenish to black rims. Such a rim is most noticeable on the pinacoids, the coloration of which is most likely due to inclusions of clin amphibole. Bobtraillite is transparent, has a vitreous luster, a white streak and shows no fluorescence in either short- or long-wave ultraviolet radiation. The mineral has a Mohs hardness of 5½ with no observable cleavage. It is brittle and has an uneven to conchoidal fracture. The density could not be determined owing to a dearth of pure, inclusion-free crystals. The calculated density of 3.12 g/cm³ was determined using the empirical chemical formula and the unit-cell parameters derived from the crystal-structure analysis.

Bobtraillite is nonpleochroic, uniaxial positive, with ω 1.627(1) and ε 1.645(1). A Gladstone–Dale calculation, using the empirical formula and the unit-cell parameters from the crystal-structure analysis, gave a compatibility index of 0.003, considered superior (Mandarino 1981).

CHEMICAL COMPOSITION

Bobtraillite was analyzed using a Cambridge Microscan MK5 electron microprobe using an operating voltage of 15 kV, and a beam current of 10 nA. The mineral is unstable under the electron beam; Na, in particular, was found to be quite volatile. To minimize sample degradation, the electron beam was defocused to approximately 40 μ m. Wavelength-dispersion data were collected using the following standards: albite (NaK α), Kakanui hornblende (CaK α , SiK α), celestine (SrL α), Ba glass (BaL α), YIG (YL α), zircon (ZrL α), hafnium (HfL α) and Na–Nb glass (NbL α). Also sought, but not detected, were K, Mg, Ti, Mn, Fe, Al, La, Ce, Th, U, P, F and Cl. Seven analyses made on one crystal gave, as an average: Na₂O 5.62 (5.30–6.02), CaO 1.11 (0.53–1.46), SrO 17.76 (16.56–18.28), BaO 0.40 (0.36–0.48), B₂O₃ (calc.) 3.30, Y₂O₃ 1.15 (1.07–1.24), SiO₂ 40.51 (39.84–41.17), ZrO₂ 25.32 (24.95–25.80), HfO₂ 0.48 (0.44–0.52), Nb₂O₅ 1.32 (1.12–1.86) and H₂O

(calc.) 4.28, total 101.25 wt.%. The presence of H₂O was confirmed by infrared spectroscopy (see below), and results from the crystal-structure analysis. Boron was also initially identified on the basis of results of the crystal-structure analysis, and its presence was subsequently confirmed by qualitative wavelength-dispersion scans. The empirical formula based on 156 anions and a stoichiometric amount of B is: (Na_{11.20}Ca_{1.22}) Σ 12.42 (Sr_{10.59}Ba_{0.16}) Σ 10.75 (Zr_{12.69}Y_{0.63}Nb_{0.61}Hf_{0.14}) Σ 14.07 Si_{41.64}B₆O₁₃₂(OH)₁₂•12H₂O or, ideally, (Na,Ca)₁₃Sr₁₁(Zr,Y,Nb)₁₄Si₄₂B₆O₁₃₂(OH)₁₂•12H₂O. Low totals for the alkali and alkaline-earth sites may be due to element migration under the electron beam or the presence of structural vacancies. The mineral does not effervesce in 1:1 HCl at room temperature.

INFRARED ANALYSIS

The infrared spectrum of bobtraillite (Fig. 2) was obtained using a Bomem Michelson MB–120 Fourier transform infrared spectrometer equipped with a mercury–cadmium telluride (MCT) detector. A single crystal was mounted in a Spectra-Tech low-pressure diamond-anvil microsample cell. The spectrum was obtained over the range 4000–660 cm^{–1} from a total of 200 co-added scans. Absorption bands were identified using data from Farmer (1974). The spectrum shows a medium-intensity band centered at the 3567 cm^{–1} (O–H stretching) and a relatively weak band at 1639 cm^{–1} (H–O–H bending). The spectrum also shows a shoulder of medium-intensity band at 1082 cm^{–1}, three strong, sharp bands at 1020, 977 and 938 cm^{–1} (asymmetric O–Si–O, O–B–O stretching) and a strong, somewhat sharp, band at 750 cm^{–1} (symmetric Si–O–Si, O–B–O stretching). As the ranges in the frequency modes for tetrahedra of BO₄ and SiO₄ directly overlap [asymmetric stretching: 1100–850 cm^{–1} for BO₄ versus 1200–900 cm^{–1} for SiO₄; symmetric stretching: 850–700 cm^{–1} for BO₄ versus 800–400 cm^{–1} for SiO₄; Farmer (1974)], it is not possible to unequivocally assign absorption bands in these regions.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray powder-diffraction data were collected with a Debye–Scherrer camera 114.6 mm diameter employing Ni-filtered CuK α radiation (λ = 1.5418 Å). Intensities were determined using a scanned image of the powder pattern, normalized to the measured intensity of d = 2.752 Å (I = 100). Whether or not an hkl plane significantly contributes to a reflection was determined from the powder pattern calculated using the atom parameters from the crystal-structure analysis and the program POWDERCELL (Nolze & Kraus 1998). Overall agreement between the observed and calculated patterns is reasonably good (Table 1). As a note, the calculated

powder-diffraction pattern indicates the presence of the reflection (110) at $d(\text{calc.}) = 17.08 \text{ \AA}$ with $I(\text{calc.}) = 44$. However, given the low-order nature of the reflection, it was not observed on routine powder-patterns of the mineral made with a standard Gandolfi camera (diameter = 114.6 mm) using 0.5 or 0.3 mm collimators. This reflection was, however, observed on a powder pattern collected with a Debye–Scherrer camera (diameter = 57.3 mm) equipped with a modified beamtrap of reduced diameter (A.C. Roberts, pers. commun.).

X-ray intensity data were collected on a Bruker *P4* diffractometer equipped with a SMART 1K CCD detector and a crystal-to-detector distance of 4.045 cm. Initially, a single crystal of dimensions $0.13 \times 0.14 \times$

0.08 mm exhibiting a strong optical extinction was selected for collection of the intensity data. However, preliminary Laue photographs of this crystal indicated significant splitting of diffractions spots, possibly arising due to the presence of multiple crystallites or twinning. It was gently crushed, which produced three irregular grains of subequal dimensions. Subsequent Laue photographs of one of these fragments (measuring $80 \times 80 \times 20 \text{ }\mu\text{m}$) was found to produce sharp diffraction-spots and was thus selected for collection of the intensity data. A total of 31995 reflections were measured out to $2\theta = 60.02^\circ$ using framewidths $0.2^\circ \omega$ and count times of 90 s per frame. Of the 3275 unique reflections, 1575 were considered as observed [$|F_o| \geq$



FIG. 1. Photograph of bobtraillite in igneous breccia. Note the associated clinoamphibole. Crystal is 1 mm in length.

$4\sigma F$]; the low number of unique reflections is attributable to the paucity of observable data beyond $2\theta = 40^\circ$. The data were corrected for Lorentz, polarization and background effects using the program SAINT. Absorption corrections were applied using the program SADABS, the crystal being modeled as an ellipse. All reflection data were then merged using the program XPREP. Information pertinent to the data collection and structure determination is provided in Table 2.

Solution and refinement of the crystal structure were accomplished using the *SHELX-93* package of programs (Sheldrick 1993). The crystal structure was solved using direct methods, with scattering curves and anomalous scattering factors taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. Phasing of a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 1.049. Considering the mean values $|E^2 - 1|$ of 0.968 (centric) and 0.736 (acentric) and the observed morphology of the crystals, the centrosymmetric space-group $P\bar{3}c1$ (#165) was selected as the preferred choice from a listing of potential space-groups. The phase-normalized structure-factors were used to give an *E*-map on which were located the Zr, one Sr, three Si and several O sites. The remaining Na, Si, O sites were located on subsequent difference-maps. Results from this model indicated one of the tetrahedrally coordinated sites to have bond distances of ~ 1.51 Å, too short for a Si–O bond length, but consistent with that of B–O. In light of this finding, a qualitative wavelength-dispersion scan was made that confirmed the presence of B. Refinement of the electron scattering at this site (assuming B) gave 6.4(1) electrons. On the basis

of these data, the B has thus been assigned to this site. Determination of those O sites likely occupied by OH or H₂O was made on the basis of bond-valence calculations in conjunction with charge-balance considerations. Anisotropic refinement of this model indicated those sites assigned to Na1, Na2 and Sr to have lower-than-ideal site-occupancy factors (SOF), *i.e.*, 0.837(7), 0.24(1) and 0.916(9), respectively. Final least-squares refinement of this model gave residuals of $R = 3.49\%$ and $wR^2 = 10.88\%$, and the difference map calculated at this stage did not reveal any positive maxima greater than $1 e^{-}/\text{Å}^3$. Whereas the results of the crystal-structure refinement are reasonable, a check for evidence of higher symmetry was carried out using the program MISSYM (Le Page 1987). Results of this test suggested the presence of additional elements of symmetry, including *m* perpendicular to $[1\bar{1}0]$, $[210]$ and $[120]$, and a six-fold rotational axis (rather than three-fold), all of which are consistent with the non-centrosymmetric space-group $P6_3cm$ (#185). Given that the presence of heavy elements in the crystal structure of a mineral can result in pseudosymmetry [*e.g.*, parasite-(Ce); Ni *et al.* 2000], and unreliable $|E^2 - 1|$ statistics (Sheldrick 1993), and that a significant concentration of essential Sr is present in bobtrillite, we considered it a possibility that its true crystal structure might be non-centrosymmetric. Thus a refinement of the crystal structure was repeated assuming the correct space group to be $P6_3cm$. Final least-squares refinement of this model gave residuals of $R = 3.46\%$ and $wR^2 = 11.33\%$, values virtually identical to those obtained for the $P\bar{3}c1$ model. However, one of the SiO₄ tetrahedra from the $P6_3cm$ model exhibited unreasonable Si–O bond distances (1.44, 1.72 Å) and both displacement parameters and their associated errors for all atoms were on average one order of magnitude greater than those obtained for the $P\bar{3}c1$ model. In light of these results, $P\bar{3}c1$ is considered to be the correct space-group.

Table 3 contains the final positional and displacement parameters, selected interatomic distances are in Table 4, and bond-valence sums, in Table 5. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of bobtrillite contains five tetrahedrally coordinated ions, four Si and one B. The SiO₄ tetrahedra all have normal $\langle \text{Si-O} \rangle$ bond distances, with average $\langle \text{Si-O} \rangle$ values ranging from 1.609 to 1.622 Å (Table 4). The other tetrahedral complex is $[\text{BO}_2(\text{OH})_2]^{4-}$. The B–(OH) bond distance corresponds to the longest in the tetrahedral unit, and its presence explains the lower-than-ideal bond-valence sum calculated for B (Table 5). All tetrahedra are linked into three-membered rings.

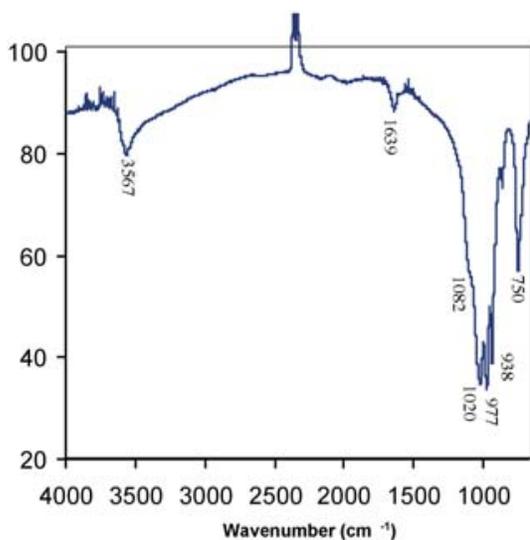


FIG. 2. The infrared spectrum of bobtrillite. The artifact at 2400 cm^{-1} corresponds to O stretching in atmospheric CO₂.

There are two MO_6 octahedra present, identified as $Zr(1)O_6$ and $Zr(2)O_6$. Both exhibit normal $\langle Zr-O \rangle$ bond distances (Table 4), with $Zr(1)O_6$ having a greater dispersion in individual bond-lengths and a shorter average $\langle Zr-O \rangle$ bond distance. The calculated bond-valence summations for $Zr(1)$ is slightly high (4.129 *v.u.*), and may be evidence for substitution of Zr by an ion of greater valence (*e.g.*, Nb^{5+}).

The crystal structure of bobtrillite is complicated, and as a first step, is most easily considered in terms of a two-dimensional [001] slab. The mineral is a cyclosilicate containing two basic kinds of three-membered rings, $(Si_3O_9)^{6-}$ and $[Si(3)_2BO_8(OH)]^{6-}$. Those rings containing only Si may be further subdivided into one of composition $[Si(1)Si(2)_2O_9]^{6-}$ and the other, $[Si(4)_3O_9]^{6-}$, using the formal designations given in Table 4. There are six $[Si(1)Si(2)_2O_9]^{6-}$ rings radially distributed about a central $Zr(2)O_6$ octahedron (Fig. 3). This produces a simple pinwheel-like configuration that resembles the basic structural motif present in wadeite $[K_2Zr(Si_3O_9)]$; Sakai *et al.* 2000] and will be referred to henceforth as the Wadeite Pinwheel Motif (WPM). The WPM is different than that observed in benitoite, wherein three three-membered silicate rings are arranged around a central TiO_6 octahedron (Fig. 3). Continuing to expand the structure in the [001] plane, the $Si(2)O_4$ tetrahedra of the $[Si(1)Si(2)_2O_9]^{6-}$ ring are joined to peripheral $Zr(1)O_6$ octahedra along [110] through O(3) and O(8) (Fig. 3). The $Zr(1)O_6$ octahedra are further joined to two $Si(3)O_4$ tetrahedra from the $[Si(3)_2BO_7(OH)_2]^{5-}$ rings, resulting in the formation of a giant pinwheel-like motif or GPM (Fig. 4). A two-dimensional slab in the [001] plane is principally

achieved by $[Si(4)_3O_9]^{6-}$ rings linking $Zr(1)O_6$ octahedra from adjacent GPM together along [110].

Several linkages along [001] are made that complete the octahedron-tetrahedron zirconosilicate framework in three dimensions. It should be noted that the ZrO_6 octahedra are isolated, with all linkages between adjacent octahedra occurring principally *via* SiO_4 tetrahedra. In terms of the WPM, the $[Si(1)Si(2)_2O_9]^{6-}$ rings link both adjacent $Zr(1)O_6$ and $Zr(2)O_6$ octahedra. These particular rings directly superimpose on one another, leading to the formation of infinite channels along [001].

Moving further outward into the larger GPM, $Zr(1)O_6$ octahedra are joined along [001] by SiO_4 tetrahedra belonging to the $[Si(3)_2BO_7(OH)_2]^{5-}$ rings and the $[Si(4)_3O_9]^{6-}$ rings. Whereas this configuration leads to the respective superposition of both types of rings along [001], the resulting development of channels is different depending on the type of ring. For example, alternating $[Si(4)_3O_9]^{6-}$ rings are counter-rotated 30° relative to one another, a disposition similar to that observed in benitoite (Hawthorne 1987). This configuration produces infinite channels whose voids geometrically approach an octahedron. The $[Si(4)_3O_9]^{6-}$ rings are significant in that they serve to join adjacent GPM both parallel and perpendicular to [001] (Fig. 4). The $[Si(3)_2BO_7(OH)_2]^{5-}$ rings from adjacent GPM also are directly superimposed, but are rotated 180° relative to one another, so continuous channels are not produced.

The three-dimensional tetrahedron-octahedron framework structure of bobtrillite contains a number of infinite channels along [001], but not all are occupied. In the discussion of the crystal chemistry of benitoite and related minerals, Hawthorne (1987) elucidated the important role that local bond-strength arrangements have on influencing selection of channel occupants. Some of the lines of reasoning used therein have been adopted in the discussion of the channel occupants in bobtrillite that follows.

TABLE 1. BOBTRILLITE: X-RAY POWDER-DIFFRACTION DATA

<i>l</i> meas	<i>l</i> calc	<i>d</i> meas Å	<i>d</i> calc Å	<i>hkl</i>	<i>l</i> meas	<i>l</i> calc	<i>d</i> meas Å	<i>d</i> calc Å	<i>hkl</i>
	44		17.08	100		1		2.207	314
23	13	9.87	9.86	110	6	5	2.145	2.152	630
38	39	6.46	6.46	210		3		2.140	622
26	30	5.71	5.69	300	6	4	2.014	2.015	504
33	34	5.43	5.42	211	7	9	2.008	2.003	542
14	5	5.02	4.99	002	27	43	1.990	1.987	334
11	2	4.93	4.93	220	2	2	1.934	1.929	623
12	4	4.76	4.74	310	13	32	1.901	1.898	900
11	4	4.28	4.27	400	2	2	1.827	1.827	543
51	60	3.96	3.95	212		2		1.824	642
49	46	3.76	3.75	302	2	4	1.806	1.802	614
18	15	3.44	3.44	312	3	12	1.777	1.774	902
23	29	3.30	3.29	330	3	8	1.736	1.734	830
70	55	3.13	3.12	331	10	18	1.719	1.718	624
12	11	2.970	2.957	213	4	10	1.641	1.638	832
5	7	2.857	2.846	600	2	3	1.615	1.610	216
19	26	2.831	2.818	502	1	3	1.599	1.596	306
100	100	2.752	2.745	332	4	11	1.561	1.561	662
12	17	2.503	2.495	004	3	9	1.512	1.510	904
5	4	2.403	2.398	522	9	16	1.4864	1.4840	336
3	8	2.370	2.368	620	3	6	1.4245	1.4238	834
3	3	2.291	2.285	304	3	8	1.3751	1.3723	664
6	3	2.210	2.210	442	3	6	1.3416	1.3388	952
					2	3	1.3121	1.3078	337

TABLE 2. MISCELLANEOUS INFORMATION FOR BOBTRILLITE

Space group	$P \bar{3}c1$ (#165)	Diffractometer	Broker P4
<i>a</i> (Å)	19.720(1) *	Radiation	MoK α (50 kV, 40 mA)
<i>c</i>	9.9788(5) *	Monochromator	Graphite
<i>V</i> (Å ³)	3360.7(1)	Crystal Size	0.08 × 0.08 × 0.02 mm
<i>Z</i>	1	μ (MoK α)	1.97 mm ⁻¹
Chemical formula: (Na,Ca) ₁₁ Sr ₁₁ (Zr,Y,Nb) ₁₄ Si ₄₂ B ₆ O ₁₃₂ (OH) ₁₂ ·12H ₂ O			
Intensity-data collection		θ : 2 θ scan mode	
2 θ limit		60°	
Number of unique reflections		3275	
Number of observed reflections		1575	
Criterion for observed reflections		$F_o > 4\sigma(F_o)$	
GoOF		1.183	
Final <i>R</i> for all observed reflections		3.49%	
Final <i>wR</i> ² for all observed reflections		10.88%	

* values refined from four-circle diffractometer data.

Starting with the *WPM*, channels generated by overlapping $[\text{Si}(1)\text{Si}(2)_2\text{O}_9]^{6-}$ rings are occupied by the H_2O molecules, OW14 (Fig. 3). Moving slightly outward, rectangular channels (dimensions $\sim 2.8 \times 4.6 \text{ \AA}$) are formed between the $[\text{Si}(1)\text{Si}(2)_2\text{O}_9]^{6-}$ rings and both the $\text{Zr}(1)\text{O}_6$ and $\text{Zr}(2)\text{O}_6$ octahedra. These are occupied by $^{18}\text{Na}(1)$ ions (Fig. 4), which are coordinated in $\text{Na}(1)\text{O}_6(\text{H}_2\text{O})_2$ polyhedra, consisting of six relatively long bonds and two shorter ones (the latter made with OW14). The configuration of channel occupants observed here differs from that in benitoite, wherein large, [12]-coordinated sites accommodate Ba. In bobtraillite, the smaller, lower-coordination sites and local bond-valence sums allow for smaller, lower-valence ions like Na as occupants.

The presence of H_2O as part of the $\text{Na}(1)\text{O}_6(\text{H}_2\text{O})_2$ polyhedra likely also plays a role in minimizing local imbalance in charges. By joining to Na, H_2O effectively converts a “strong” Na–O bond to two weaker O–H bonds, thus reducing the Lewis acidity of Na and making it more appropriate in terms of its bond-valence contribution. The presence of Na and H_2O as channel occupants is not observed in wadeite, benitoite or any minerals related to benitoite. However, a geometrically identical configuration is observed in catapleite, ($\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$; Ilyushin *et al.* 1981) which, although lower in symmetry (monoclinic; Table 6), has a

topology similar to that of wadeite (Sakai *et al.* 2000), *i.e.*, both are based on the *WPM*. The crystal structures of these two minerals differ in the way in which the (Si_3O_9) rings are arranged about the central ZrO_6 octahedron (a radial concentric arrangement in wadeite *versus* a linear concentric arrangement in catapleite) and the type of channel occupants present (Na + H_2O in catapleite and K in wadeite), which in turn influence their respective space-group symmetries. Whereas bobtraillite shares the *WPM*, the disposition of its (Si_3O_9) rings and the scheme of channel occupants are more consistent with that found in catapleite rather than wadeite (Fig. 3). Additional channels, generated between the $[\text{Si}(1)\text{Si}(2)_2\text{O}_9]^{6-}$ and $[\text{Si}(3)_2\text{BO}_7(\text{OH})_2]^{5-}$ rings and the $\text{Zr}(1)\text{O}_6$ octahedra in bobtraillite, are located near the periphery of the *GPM* (Fig. 4). These are occupied by disordered $^{18}\text{Na}(2)$ ions and vacancies.

Finally, large irregular channels at the periphery of the *GPM* are occupied by ^{10}Sr (Fig. 4), which participates in eight short ($< 2.80 \text{ \AA}$) and two long bonds ($3.272, 3.275 \text{ \AA}$). The asymmetry of the $\text{SrO}_8(\text{OH})_2$ polyhedron is similar to that observed in benitoite, wherein BaO_{12} contains six short ($< 2.767 \text{ \AA}$) and six long bonds (3.434 \AA). The channels occupied by Sr are bounded by $[\text{Si}(4)_3\text{O}_9]^{6-}$ rings belonging to adjacent *GPM*, and both $[\text{Si}(3)_2\text{BO}_7(\text{OH})_2]^{5-}$ and $\text{Zr}(2)\text{O}_6$

TABLE 3. POSITIONAL AND DISPLACEMENT PARAMETERS FOR BOBTRAILLITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{eq}
Na1	0.7823(1)	0.8913(2)	0.9997(2)	0.024(2)	0.027(2)	0.031(2)	0.013(1)	0.002(1)	0.012(1)	0.028(1)
Na2	0.6719(6)	0.6718(6)	0.4947(19)	0.037(6)	0.034(6)	0.050(7)	0.025(5)	0.021(6)	0.001(4)	0.048(3)
Sr	0.43604(4)	0.56401(1)	0.50000(6)	0.0126(1)	0.0124(3)	0.0152(3)	-0.0010(3)	-0.0012(3)	0.0049(2)	0.0140(1)
Zr1	0.56592(3)	0.78293(3)	0.50000(4)	0.0100(2)	0.0096(3)	0.0068(2)	0.0001(2)	0.0001(2)	0.0050(2)	0.0088(1)
Zr2	0	0	½	0.0076(3)	0.0076(3)	0.0045(5)	0	0	0.0038(2)	0.0066(2)
Si1	0.8702(1)	0	¾	0.0108(7)	0.013(1)	0.012(2)	0.0002(8)	0.0001(4)	0.0067(5)	0.0118(4)
Si2	0.69223(8)	0.91164(9)	0.7501(1)	0.0094(7)	0.0128(7)	0.0126(8)	0.0005(6)	0.0002(6)	0.0040(6)	0.0123(3)
Si3	0.56438(9)	0.65133(7)	0.7500(2)	0.0117(7)	0.0116(7)	0.0113(8)	-0.0005(6)	-0.0008(6)	0.0079(6)	0.0106(3)
Si4	0.42971(8)	0.74333(8)	0.7500(2)	0.0089(7)	0.0104(7)	0.0104(8)	0.0002(6)	0.0003(5)	0.0058(6)	0.0095(3)
B	0.4798(3)	0.4798(3)	¾	0.018(3)	0.018(3)	0.010(4)	0.001(1)	-0.001(1)	0.009(3)	0.015(2)
O1	0.4776(2)	0.7846(2)	0.6164(3)	0.018(2)	0.016(2)	0.014(2)	0.003(2)	0.006(2)	0.009(2)	0.0156(8)
O2	0.4779(2)	0.6932(2)	0.3824(3)	0.015(2)	0.016(2)	0.013(2)	-0.006(1)	-0.006(2)	0.007(1)	0.0150(8)
O3	0.6517(2)	0.8683(2)	0.6164(4)	0.032(2)	0.030(2)	0.015(2)	-0.008(2)	-0.009(2)	0.016(2)	0.026(1)
O4	0.7809(2)	0.9237(2)	0.7497(4)	0.011(2)	0.009(2)	0.041(2)	0.003(2)	0.001(2)	0.002(1)	0.0216(8)
O5	0.9999(2)	0.0885(2)	0.3860(4)	0.026(2)	0.025(2)	0.027(2)	0.008(2)	0.001(2)	0.012(2)	0.026(1)
O6	0.5585(2)	0.8674(2)	0.3870(3)	0.017(2)	0.021(2)	0.011(2)	0.004(1)	-0.001(1)	0.011(2)	0.0158(8)
O7	0.5584(2)	0.6911(2)	0.6141(3)	0.015(2)	0.015(2)	0.011(2)	0.003(1)	0.001(1)	0.006(2)	0.0143(8)
O8	0.6516(2)	0.7836(2)	0.3843(4)	0.036(2)	0.028(2)	0.015(2)	0.001(2)	0.010(2)	0.016(2)	0.026(1)
O9	0.4893(2)	0.5618(2)	0.7498(3)	0.010(2)	0.010(2)	0.020(2)	-0.001(1)	-0.001(1)	0.003(1)	0.0146(8)
O10	0.4005(2)	0.6492(2)	0.7498(3)	0.003(2)	0.003(2)	0.027(2)	0.001(1)	-0.001(1)	-0.001(1)	0.0119(7)
O11	0.6423(2)	0.6423(3)	¾	0.013(2)	0.013(2)	0.017(3)	-0.001(1)	0.001(1)	0.009(2)	0.013(1)
O12	0.7028(2)	0	¾	0.009(2)	0.010(2)	0.041(4)	-0.040(2)	-0.002(1)	0.005(1)	0.020(1)
OH13	0.4418(2)	0.4418(2)	0.6216(4)	0.026(2)	0.027(2)	0.024(2)	-0.007(2)	-0.006(2)	0.015(2)	0.025(1)
OW14	0.7762(3)	0.9998(3)	0.0907(5)	0.058(3)	0.049(3)	0.061(4)	0.000(3)	0.015(3)	0.023(3)	0.058(1)

octahedra. In summary, the complete structure of bobtrallite includes features common to both benitoite and catapleite; it may be considered as a hybrid structure of the two.

RELATED STRUCTURES

The crystal chemistry of the benitoite and related minerals, including those whose crystal structures contain (Si_3O_9) rings, was discussed by Hawthorne (1987). Structurally, they can be described as having octahedron-tetrahedron frameworks composed of isolated $M^{4+}\text{O}_6$ octahedra ($M = \text{Zr, Ti, Sn}$) linked by (Si_3O_9) rings into pinwheel-like motifs. In the so-called benitoite-group minerals [benitoite, bazirite, pabstite; informally defined as such by Hawthorne (1987)], the (Si_3O_9) rings are alternately counter-rotated 30° about $[001]$; they thus differ from wadeite and catapleite, in

which the (Si_3O_9) rings directly superimpose. All these cyclosilicates have channels in which alkali and alkaline-earth ions (Na, Ba, K) are accommodated.

As elucidated by Hawthorne (1987), the type of ion that is accommodated can be rationalized in terms of bond-valence requirements. In the benitoite structure-type, a large divalent cation (Ba) occupies a $[12]$ -coordinated site on a three-fold axis (Fig. 3). The absence of additional silicate rings in benitoite is curious. Although there is sufficient space to accommodate such rings, it is possible they are not present as this would lead to an oversaturation of charge on the divalent alkaline earth to which they would be bonded. In the wadeite structure-type, the sites are of lower coordination (9) and only monovalent cations (K, Na) can be accommodated if bond-valence restrictions are considered. It should be noted that both wadeite and catapleite have structures based on the *WPM*, despite differences in their respec-

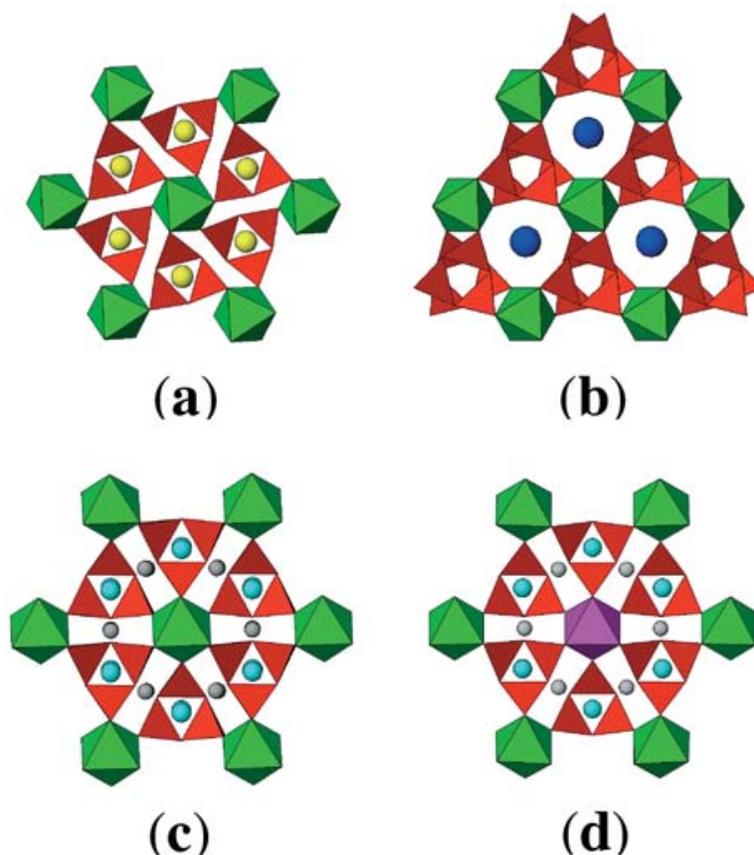


FIG. 3. The $[(\text{Zr/Ti})\text{Si}_5\text{O}_{13}]^{2-}$ pinwheel motifs and channel occupants in (a) wadeite (K: yellow spheres), (b) benitoite (Ba: blue spheres), (c) catapleite (Na: grey spheres; H_2O blue spheres) and (d) bobtrallite [Na(1): grey spheres; H_2O blue spheres], projected along $[001]$. In bobtrallite, the $\text{Zr}(1)\text{O}_6$ octahedra are shown in green, the $\text{Zr}(2)\text{O}_6$ octahedron, in purple, and the $\text{Si}(1,2)\text{O}_4$ tetrahedra, in red.

tive symmetries (Table 6). These differences arise owing to the differing radii of K *versus* Na: in wadeite, the larger K ion is positioned along the three-fold axis, but Na with a smaller radius is displaced from the three-fold axis, leading to a reduction in symmetry. Interestingly, catapleite may undergo a transition to higher symmetry (hexagonal) above 140°C, possibly owing to disordering of Na and minor shifts of other atoms (Chao *et al.* 1973). Both the benitoite and wadeite structure-types are dimensionally consistent with one another (Table 6), whereas those possessing the benitoite structure have the same space-group symmetry ($P\bar{6}2c$), that of wadeite is slightly different ($P6$ or $P6_3/m$; Table 6), and differences between the two are attributable to a combination of configurations of the silicate rings and type of channel occupant.

If the crystal structure of bobtraillite is compared to those of benitoite and wadeite, there are obvious fea-

tures suggesting a relationship among these minerals. At the same time, there are certain chemical and structural aspects that make bobtraillite unique. First, it contains three distinct types of three-membered rings, one similar to that in wadeite $\{[\text{Si}(1)\text{Si}(2)_2\text{O}_9]^{6-}\}$, a second similar to that in benitoite $\{[\text{Si}(4)_3\text{O}_9]^{6-}\}$, and a third that is unique $\{[\text{Si}(3)_2\text{BO}_7(\text{OH})_2]^{5-}\}$; second, a large divalent cation (Sr^{2+}) and a smaller monovalent cation (Na^+) *both* occupy channels along [001]; third, it is the first mineral of this group found to contain B, and fourth, it is the only mineral of this group that accommodates Na and H_2O and retains overall hexagonal symmetry. Dimensionally, the bobtraillite cell is effectively tripled along [100] ($a_{\text{benitoite}} \cong 6.7 \text{ \AA}$, $a_{\text{bobtraillite}} = 19.720 \text{ \AA}$, thus $3a_{\text{benitoite}} = a_{\text{bobtraillite}}$), owing to the presence of the three distinct types of three-membered rings that are present. Given the existence of bobtraillite and the fact that it possesses chemical and geometrical aspects common to

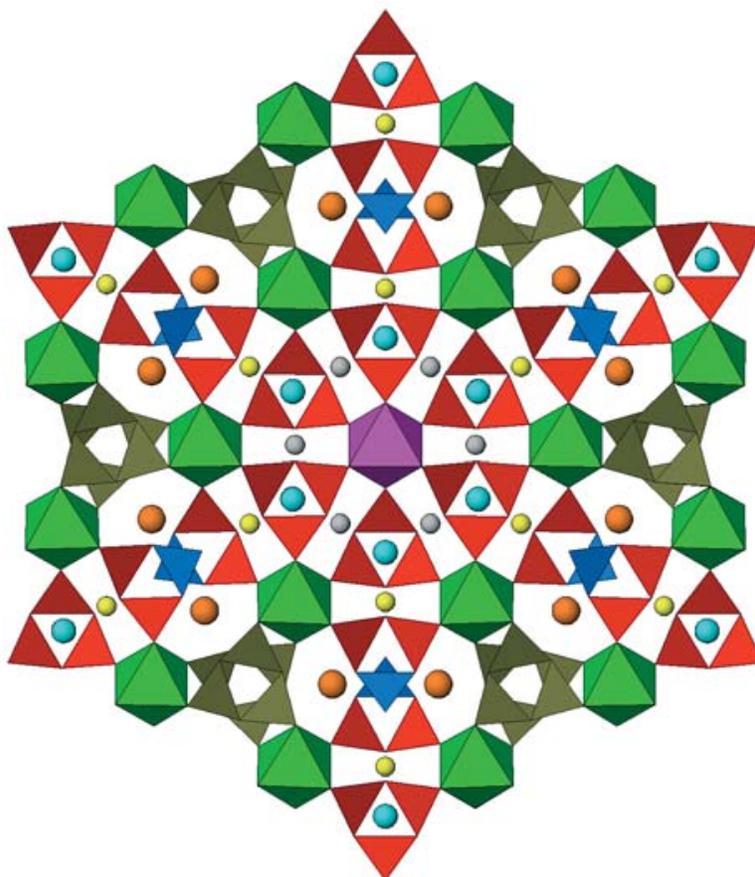


FIG. 4. The giant pinwheel motif (*GPM*) in bobtraillite, projected along [001]. Legend as in Figure 3c, with BO_4 tetrahedra in blue, $\text{Si}(4)\text{O}_4$ tetrahedra in khaki, $\text{Na}(2)$ ions shown as yellow spheres, and Sr ions, as orange spheres.

both benitoite and wadeite, other chemical and structural variants may occur in nature.

As noted earlier, the benitoite-mineral group has only been informally defined (Hawthorne 1987). Such a group should reflect not only the similarities between benitoite and its isostructural phases, but would also have to be flexible enough to include those minerals that are chemically and structurally related, albeit in a more distant manner (*e.g.*, wadeite, catapleite, hilairite, walstromite, pseudowollastonite, *etc.*; *cf.* Hawthorne 1987). It would also have to include bobtraillite, in addition to another new, related mineral discovered at Mont Saint-Hilaire and temporarily designated UK99 (Wight & Chao 1995). The latter mineral has been accepted as a new species by the CNMMN, IMA (2003–019), and a description is currently being prepared (McDonald & Chao, *in prep.*). Whereas it would be enticing to formally propose a mineral group encompassing benitoite, wadeite and related minerals, doing so is deemed to be beyond the scope of the current work, given its focus and set objectives.

ORIGIN

The genesis of bobtraillite is both intriguing and unclear. At Mont Saint-Hilaire, the igneous breccia has been described as fragments of early-formed lithologies (nepheline syenite, gabbro, pyroxenite, *etc.*) cemented by fine-grained albite (Horváth & Gault 1990). The fragments are generally angular, commonly tens of centimeters in size, and show evidence of resorption (Horváth & Gault 1990). The exotic minerals found therein typically occur in small cavities, interstices or seams between the fragments, attesting to the late-stage nature of the fluid(s) from which these minerals, including bobtraillite, crystallized. Interestingly, similar exotic minerals are found in both the igneous breccia and altered marble xenoliths (McDonald & Chao 2004), suggesting that a similar (if not the same) late-stage fluid was responsible for the late-stage mineralogical assemblages of both microenvironments.

In the specific case of bobtraillite, the late-stage fluid was clearly aqueous (reflected in both the composition of the mineral and its ubiquitous, intimate association with a clinoamphibole) and enriched in Zr, Sr and B. Whereas Zr is commonly considered to be immobile during hydrothermal alteration, there is overwhelming experimental and empirical evidence suggesting that it can be mobile under highly alkaline (agpaitic) conditions (Rubin *et al.* 1993, Olivo & Williams-Jones 1999, Salvi *et al.* 2000). Thus many of the exotic zirconosilicates found in hyperagpaitic environments are probably secondary in nature. At Mont Saint-Hilaire, some of the important secondary zirconosilicates include elpidite ($\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$; *Pbm2*), gaidonnayite ($\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$; *P2₁nb*) and hilarite ($\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$; *R32*), with catapleite ($\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$; *B2/b*) probably being the most common and widespread of

these minerals. Whereas alkaline rocks are generally enriched in Sr, the number of minerals containing essential Sr at Mont Saint-Hilaire is surprisingly rather limited [*e.g.*, ancylite-(Ce), burbankite-(Ce), donnayite-(Y), lamprophyllite, khomyakovite, *etc.*]. Such minerals tend to be late-stage in origin and although rare, are rather widespread in their occurrence. That both a burbankite-group mineral and donnayite-(Y) are associated with bobtraillite highlights the fact that the late-stage fluid moving through the igneous breccia must have been somewhat enriched in Sr. Finally, the presence of B in bobtraillite is significant, as the number of minerals containing B as an essential element at Mont Saint-Hilaire is extremely low. Interestingly enough, some of the more abundant of these [*e.g.*, tadjikite-(Ce), leucosphenite, stillwellite-(Ce)] have also been found as late-stage phases both within igneous breccia and altered marble xenoliths, again reinforcing the hypothesis that a similar fluid was responsible for the late-

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN BOBTRAILLITE

Na(1)O ₈ polyhedron			Na(2)O ₈ polyhedron		
Na1	-OW14	2.382 (6)	Na2	-OW14	2.27 (1)
	-OW14'	2.390 (6)		-O12	2.52 (2)
	-O4	2.579 (4)		-OH13	2.52 (1)
	-O4'	2.580 (5)		-O11	2.61 (2)
	-O5	2.630 (4)		-O3	2.66 (1)
	-O5'	2.632 (4)		-O8	2.67 (1)
	-O8	2.645 (4)		-O6	2.72 (1)
	-O3	<u>2.653</u> (4)		-O7	<u>2.73</u> (1)
<Na1	-O>	2.561	<Na2	-O>	2.59
Sr(10) polyhedron			Zr(1)O ₈ octahedron		
Sr	-O1	2.532 (3)	Zr1	-O8	2.041 (4)
	-O2	2.535 (3)		-O3	2.049 (4)
	-O6	2.708 (3)		-O6	2.076 (3)
	-O7	2.711 (3)		-O7	2.081 (3)
	-O9	2.714 (3)		-O2	2.104 (3)
	-O9'	2.717 (3)		-O1	<u>2.107</u> (3)
	-OH13 × 2	2.751 (4)	<Zr1	-O>	2.076
	-O10	3.272 (3)			
	-O10'	<u>3.275</u> (3)	Zr(2)O ₈ octahedron		
<Sr	-O>	3.176	Zr2	-O5 × 6	2.084 (4)
Si(1)O ₄ tetrahedron			Si(2)O ₄ tetrahedron		
Si1	-O5 × 2	1.582 (4)	Si2	-O3	1.570 (4)
	-O4 × 2	<u>1.648</u> (4)		-O8	1.576 (4)
<Si1	-O>	1.615		-O4	1.642 (4)
				-O12	<u>1.648</u> (2)
			<Si2	-O>	1.609
Si(3)O ₄ tetrahedron			Si(4)O ₄ tetrahedron		
Si3	-O7	1.600 (3)	Si4	-O2	1.601 (3)
	-O6	1.609 (3)		-O1	1.601 (3)
	-O11	1.633 (3)		-O10	1.640 (3)
	-O9	<u>1.642</u> (3)		-O10'	<u>1.646</u> (3)
<Si3	-O>	1.621	<Si4	-O>	1.622
BO ₄ tetrahedron					
B	-OH13 × 2	1.485 (5)			
	-O9 × 2	<u>1.531</u> (5)			
<B	-O>	1.508			

stage mineralogy of both microenvironments. Whereas the actual source of the B is enigmatic, as it is geochemically associated with alkalis, alkaline earths, Zr, REE etc., which typify apaitic magmas, the implication is that it is magmatic in origin. This source is also plausible considering that alkaline magmatic rocks can exhibit B concentrations up to 100 ppm (Leeman & Sisson 1996).

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TABLE 5. EMPIRICAL BOND-VALENCES (*v.u.*) FOR BOBTRAILLITE*

	Na1	Na2	Sr	Zr1	Zr2	Si1	Si2	Si3	Si4	B	ΣV^{**}
O1			0.327	0.632					1.064		1.996
O2			0.324	0.637					1.064		1.998
O3	0.100	0.097		0.739			1.157				2.003
O4	0.122					0.937 ⁺²¹	0.953				2.093
	0.121										
O5	0.106 ⁺²¹				0.672 ⁺⁶	1.120 ⁺²¹					1.969
O6		0.084	0.203	0.687				1.041			1.934
O7		0.082	0.201	0.678				1.067			1.949
O8	0.102	0.096		0.755			1.139				2.002
O9			0.200					0.953		0.649 ⁺²¹	1.983
			0.198								
O10			0.044 ⁺²¹						0.958		1.984
									0.942		
O11		0.111 ⁺²²						0.976 ⁺²²			2.090
O12		0.144 ⁺²²					0.937 ⁺²²				2.053
OH13		0.141	0.181 ⁺²¹							0.735 ⁺²¹	1.116
OW14	0.207	0.279									0.410
	0.203										
ΣV	1.067	1.034	1.903	4.128	4.032	4.114	4.186	4.037	4.028	2.77	

* Parameters from Brese & O'Keefe (1991). Calculated using the refined site-occupancy factors of 0.837, 0.24 and 0.916 for Na(1), Na(2) and Sr, respectively.

TABLE 6. DATA FOR BENITOITE AND RELATED MINERALS

Mineral	Formula	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
Benitoite ¹	BaTiSi ₃ O ₉	<i>P</i> $\bar{6}2c$	6.6410(7)		9.760(1)			
Bazirite ²	BaZrSi ₃ O ₉	<i>P</i> $\bar{6}2c$	6.742(1)		9.930(2)			
Pabstite ²	BaSnSi ₃ O ₉	<i>P</i> $\bar{6}2c$	6.7307(7)		9.824(2)			
Wadeite ^{3,4}	K ₂ ZrSi ₃ O ₉	<i>P</i> $\bar{6}$ or <i>P</i> _{6₃/m}	6.918(2)		10.151(3)			
Bobtraillite ⁵	(Na,Ca) ₁₃ Sr ₁₁ (Zr,Y,Nb) ₁₄ Si ₄₂ B ₆ O ₁₃₂ (OH) ₁₂ •12H ₂ O	<i>P</i> $\bar{3}c1$	19.720(1)		9.9788(5)			
Catapleite ⁶	Na ₂ ZrSi ₃ O ₉ •2H ₂ O	<i>B2/b</i>	23.917(2)	20.148(2)	7.432(1)		147.46(1)	
Margarosamite ⁷	Ca ₂ PbSi ₃ O ₉	<i>P</i> $\bar{1}$	6.768(4)	9.575(4)	6.718(5)	69.40(3)	102.98(4)	96.98(5)
Wälstromite ⁸	Ca ₂ BaSi ₃ O ₉	<i>P</i> $\bar{1}$	6.743(5)	9.607(5)	6.687(5)	69.85	102.23	96.11
"Pseudowollastonite" ^{9,10}	CaSiO ₃	<i>P</i> $\bar{1}$ or <i>C2/c</i>	6.8394(5)	11.8704(9)	19.6313(9)		90.667(6)	

1. Fischer (1969), 2. Hawthorne (1987), 3. Blinov *et al.* (1977), 4. Sakai *et al.* (2000), 5. this study, 6. Ilyushin *et al.* (1981), 7. Freed & Peacor (1969), 8. Alfors *et al.* (1965), 9. Yamanaka & Mori (1981), 10. Yang & Prewitt (1999).

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