

## BOBDOWNSITE, A NEW MINERAL SPECIES FROM BIG FISH RIVER, YUKON, CANADA, AND ITS STRUCTURAL RELATIONSHIP WITH WHITLOCKITE-TYPE COMPOUNDS

KIMBERLY T. TAIT<sup>§</sup>

*Department of Natural History, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6, Canada*

MADISON C. BARKLEY, RICHARD M. THOMPSON, MARCUS J. ORIGLIERI, STANLEY H. EVANS,  
 CHARLES T. PREWITT AND HEXIONG YANG

*Department of Geosciences, University of Arizona, 1040 E. 4th Street, Tucson, Arizona 85721-0077, U.S.A.*

### ABSTRACT

A new mineral species, bobdownsite, the F-dominant analogue of whitlockite, ideally  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{F})$ , has been found in Lower Cretaceous bedded ironstones and shales exposed on a high ridge on the west side of Big Fish River, Yukon, Canada. The associated minerals include siderite, lazulite, an arrojadite-group mineral, kulanite, gormanite, quartz, and collinsite. Bobdownsite from the Yukon is tabular, colorless, and transparent, with a white streak and vitreous luster. It is brittle, with a Mohs hardness of ~5; no cleavage, parting, or macroscopic twinning is observed. The fracture is uneven and subconchoidal. The measured and calculated densities are 3.14 and 3.16 g/cm<sup>3</sup>, respectively. Bobdownsite is insoluble in water, acetone, or hydrochloric acid. Optically, it is uniaxial (-),  $\omega = 1.625(2)$ ,  $\varepsilon = 1.622(2)$ . The electron-microprobe analysis yielded  $(\text{Ca}_{8.76}\text{Na}_{0.24})_{\Sigma 9.00}(\text{Mg}_{0.72}\text{Fe}^{3+}_{0.13}\text{Al}_{0.11}\text{Fe}^{2+}_{0.04})_{\Sigma 1.00}(\text{P}_{1.00}\text{O}_4)_6(\text{P}_{1.00}\text{O}_3\text{F}_{1.07})$  as the empirical formula. Bobdownsite was examined with single-crystal X-ray diffraction; it is trigonal with space group  $R\bar{3}c$  and unit-cell parameters  $a$  10.3224(3),  $c$  37.070(2) Å,  $V$  3420.7(6) Å<sup>3</sup>. The structure was refined to an  $R_1$  factor of 0.031. Bobdownsite is isotypic with whitlockite, whose structure and relationships with other phosphate compounds have been studied extensively. Its structure is characterized by the  $[\text{Mg}(\text{PO}_4)_6]^{16-}$  ligand, or the so-called "Mg pinwheel". The isolated pinwheels are held together by intralayer Ca cations to form layers parallel to (001), which are linked together by interlayer Ca cations along [001]. The Raman spectra of bobdownsite strongly resemble those of whitlockite and merrillite. Bobdownsite represents the first naturally formed phosphate known to contain a P-F bond. It has subsequently been found in the Tip Top mine, Custer County, South Dakota, USA. On the basis of our study, we conclude that the "fluor whitlockite" found in the Martian meteorite SaU 094B also is bobdownsite.

*Keywords:* bobdownsite, whitlockite, phosphate, crystal structure, X-ray diffraction, Raman spectra, Big Fish River, Yukon, Canada.

### SOMMAIRE

Nous décrivons la bobdownsite, nouvelle espèce minérale, l'analogue à dominance de fluor de la whitlockite, de formule idéale  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{F})$ , découverte dans les minerais de fer argileux et les shales d'âge crétacé inférieur du côté ouest de la rivière Big Fish, au Yukon, Canada. Lui sont associés sidérite, lazulite, un minéral du groupe de l'arrojadite, kulanite, gormanite, quartz, et collinsite. La bobdownsite holotype se présente en cristaux tabulaire, incolores, et transparents, avec une rayure blanche et un éclat vitreux. Elle est cassante, avec une dureté de Mohs d'environ ~5; nous n'avons décelé aucun clivage, plan de séparation, ou macle macroscopique. La fracture est inégale et sub-conchoïdale. Les densités mesurée et calculée sont 3.14 et 3.16 g/cm<sup>3</sup>, respectivement. La bobdownsite est insoluble dans l'eau, l'acétone, et l'acide chlorhydrique. Optiquement, il s'agit d'un minéral uniaxe (-),  $\omega = 1.625(2)$ ,  $\varepsilon = 1.622(2)$ . Une analyse effectuée avec une microsonde électronique a donné la formule empirique  $(\text{Ca}_{8.76}\text{Na}_{0.24})_{\Sigma 9.00}(\text{Mg}_{0.72}\text{Fe}^{3+}_{0.13}\text{Al}_{0.11}\text{Fe}^{2+}_{0.04})_{\Sigma 1.00}(\text{P}_{1.00}\text{O}_4)_6(\text{P}_{1.00}\text{O}_3\text{F}_{1.07})$ . Nous avons examiné la bobdownsite par diffraction X sur monocristal; elle est trigonale, groupe spatial  $R\bar{3}c$ , avec paramètres réticulaires  $a$  10.3224(3),  $c$  37.070(2) Å,  $V$  3420.7(6) Å<sup>3</sup>. Nous en avons affiné la structure jusqu'à un résidu  $R_1$  de 0.031. La bobdownsite est un isotype de la whitlockite, dont la structure et les relations avec d'autres composés phosphatés ont été étudiées en détail. Sa structure contient le ligand  $[\text{Mg}(\text{PO}_4)_6]^{16-}$ , que l'on a nommé "virevent à Mg". Les virevents isolés sont retenus grâce à des cations Ca intracouches parallèles à (001), qui sont interconnectés par des cations Ca interfoliaires de long de [001]. Les spectres de Raman de la bobdownsite

<sup>§</sup> E-mail address: ktait@rom.on.ca

ressemblement fortement à ceux de la whitlockite et de la merrillite. La bobdownsite serait le premier exemple naturel d'un phosphate contenant la liaison P–F. On l'a trouvé par la suite à la mine Tip Top, comté de Custer, Dakota du Sud. Compte tenu de nos travaux, la "fluor whitlockite" trouvés dans la météorite martienne SaU 094B correspondrait à la bobdownsite.

(Traduit par la Rédaction)

*Mots-clés:* bobdownsite, whitlockite, phosphate, structure cristalline, diffraction X, spectres de Raman, rivière Big Fish, Yukon, Canada.

## INTRODUCTION

A new member of the whitlockite group, bobdownsite, ideally  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{F})$ , has been found in Big Fish River, Yukon, Canada. Phosphate minerals belonging to the whitlockite group include whitlockite  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$ , strontio whitlockite  $\text{Sr}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$ , merrillite  $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$ , IMA2006–039  $\text{Ca}_9\text{NaFe}(\text{PO}_4)_7$ , as well as bobdownsite  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{F})$ . These minerals are characterized by the  $[\text{M}(\text{PO}_4)_6]^{16-}$  ligands, or the so-called "M pinwheels" ( $M = \text{Mg}, \text{Fe}$ ), which are held together by intralayer  $\text{Ca}^{2+}$  cations to form layers parallel to (001). These layers are further linked by interlayer  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Sr}^{2+}$  cations along [001] (Gopal & Calvo 1972, Calvo & Gopal 1975, Schroeder *et al.* 1977, Hughes *et al.* 2006, 2008, Nestola *et al.* 2009). In this paper, we describe the physical and chemical properties of bobdownsite and its structural relationships with related phosphates based on single-crystal X-ray diffraction and Raman spectroscopic data. To our knowledge, bobdownsite represents the first naturally formed phosphate known to contain a P–F bond, although several synthetic phosphate compounds have been reported to contain  $\text{PO}_3\text{F}$  groups, such as  $\text{NaK}_3(\text{PO}_3\text{F})$  (Durand *et al.* 1975) and  $\text{LiNH}_4(\text{PO}_3\text{F})$  (Durand *et al.* 1978).

The new mineral species is named after Dr. Robert (Bob) Terrance Downs (born October 14, 1955), professor of mineralogy in the Department of Geosciences at the University of Arizona, for his outstanding contributions to the field of mineralogy, particularly his work on the American Mineralogist Crystal Structure Database (AMCSD: <http://ruff.geo.arizona.edu/AMS/amcsd.php>) and his dedication on the development of the RRUFF project, an Internet-based, internally consistent and integrated database of Raman spectra, X-ray diffraction, and chemical data for minerals (<http://ruff.info>). Bob Downs lived and worked in the Yukon Territory in the 1970s, where this mineral was found. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2008–037). Part of the cotype sample has been deposited at the University of Arizona Mineral Museum (catalogue # 18820) and the RRUFF project (deposition # R050109).

## BACKGROUND INFORMATION

Whitlockite,  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$ , crystallizing in trigonal symmetry (space group  $R3c$ ), is one of the primary phosphate minerals, along with apatite-group minerals, that occur in lunar rocks, Martian meteorites, and in many other groups of meteorites. Under terrestrial conditions, whitlockite is mainly found as an uncommon secondary mineral in complex zoned granitic pegmatites and in phosphate deposits. It is also known as a biogenic mineral (pathogenic mineralization in organisms) and as a cave mineral of secondary biogenic origin (*e.g.*, Anthony *et al.* 2000, Lagier & Baud 2003, Jolliff *et al.* 2006, Hughes *et al.* 2008, Orlova *et al.* 2009). Recently, Ionov *et al.* (2006) reported the discovery of whitlockite in mantle xenoliths from Siberia, and suggested that this mineral may be an important host for some lithophile trace elements in the Earth's upper mantle. Furthermore, whitlockite-type phosphates are holding great promise as potential hosts for radioactive wastes because of their high resistance to environmental corrosion (*e.g.*, Fong *et al.* 2007, Orlova *et al.* 2009). They have also served as the base for the crystallochemical design of compounds with nonlinear-optical, catalytic, ferroelectric, ion-conductive and luminescent properties (Belik *et al.* 2001, Guo *et al.* 2010, Du *et al.* 2011).

## DESCRIPTION

### *Occurrence, physical and chemical properties*

Bobdownsite was first misidentified as whitlockite in a sample from Big Fish River, Yukon, Canada (at about Latitude  $68^\circ 28' \text{N}$ , Longitude  $136^\circ 30' \text{W}$ ). The sample was recovered from the Lower Cretaceous bedded ironstones and shales exposed on a high ridge on the west side of the river, upstream from phosphatic nodule slopes, in the summer of 2001. At the exposure, bobdownsite occurs in an east–west-trending faulted vein. The vein is largely choked with fault gouge composed of anhedral bobdownsite, but euhedral crystals occur as well. Vein width ranges from 0 to 4 cm maximum. South-facing undulations in the vein create the largest openings, where the best specimens are exposed. Bobdownsite occurs with siderite, lazuli-

lite, an arrojadite-group mineral, kulanite, gormanite, quartz, and collinsite. Crystals range from microscopic to 2.7 cm wide and 0.4 cm thick (Fig. 1). The mineral has subsequently been found in samples from the Tip Top mine, Custer County, South Dakota, USA, and in a Martian meteorite. Big Fish River is the type locality.

Bobdownsite from the Yukon is tabular, colorless in transmitted light, transparent with a white streak and a vitreous luster. The Tip Top mine material is found as druses of pale purple, yellow or transparent colorless rhombohedral crystals. It is brittle, with a Mohs hardness of ~5; no cleavage, parting or macroscopic twinning is observed. The fracture is uneven and subconchoidal. The measured and calculated densities are 3.14 and 3.16 g/cm<sup>3</sup>, respectively. Bobdownsite is insoluble in water, acetone, or hydrochloric acid. The new mineral is uniaxial (-),  $\omega = 1.625(2)$ ,  $\varepsilon = 1.622(2)$ , and it does not fluoresce under long- or short-wave

ultraviolet light. The compatibility index [ $1 - (K_P/K_C)$ ] is 0.005 (superior).

Chemical analyses were conducted with a Cameca SX-50 electron microprobe at 15 kV and 10 nA. For comparison, we examined three samples: bobdownsite from Big Fish River, bobdownsite from the Tip Top mine, and the type whitlockite from the Palermo #1 quarry, Grafton County, New Hampshire (Harvard University ISGN:HRV000XO6 95030), which are designated as R050109, R070654, and R080052, respectively, hereafter. We used the following standards: anorthite (Al), sellaite (F), albite (Na), diopside (Mg, Ca), apatite (P), and fayalite (Fe). Based on 28 O atoms, an empirical formula of  $(Ca_{8.76}Na_{0.24})_{\Sigma 9}(Mg_{0.72}Fe^{3+}_{0.13}Al_{0.11}Fe^{2+}_{0.04})_{\Sigma 1}(P_{1.00}O_4)_6(P_{1.00}O_3F_{1.07})$  is obtained for bobdownsite R050109, and  $(Ca_{8.99}Na_{0.05})_{\Sigma 9.04}(Mg_{0.96}Al_{0.04})_{\Sigma 1.00}(P_{1.00}O_4)_6\{P_{1.00}O_3[F_{0.85}(OH)_{0.15}]_{\Sigma 1}\}$  for bobdownsite R070654, leading to a



FIG. 1. Tabular, colorless, euhedral crystals of bobdownsite from Big Fish River, Yukon, Canada.

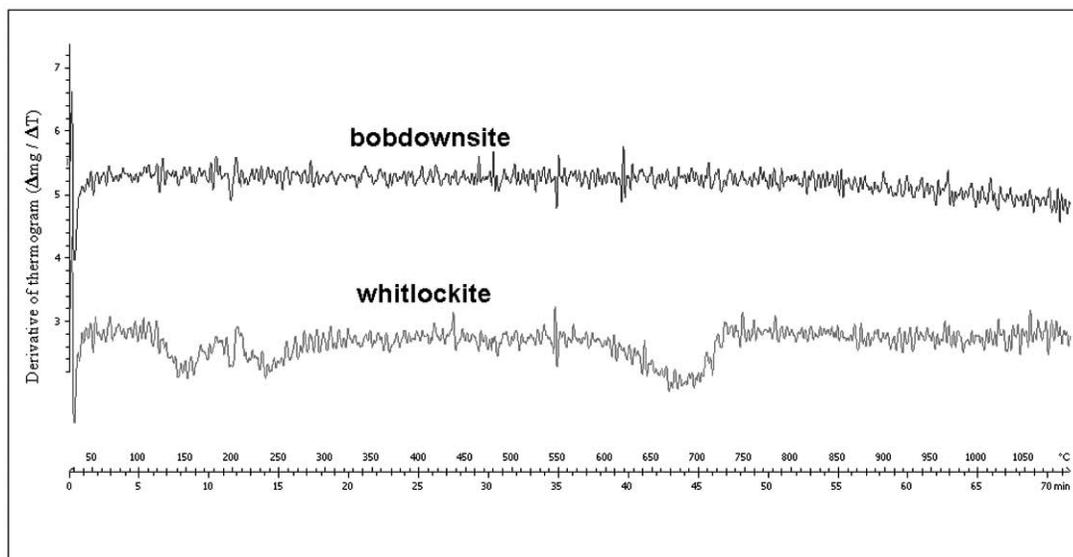


FIG. 2. Comparison of thermal gravimetric analyses (TGA) of bobdownsite R050109 and whitlockite R080052. The weights of the starting materials are 5.8912 mg and 2.3223 mg for R050109 and R080052, respectively.

simplified formula  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{F})$ . The chemical formula for the type whitlockite was determined to be  $(\text{Ca}_{8.82}\text{Na}_{0.18}\text{Sr}_{0.01})_{\Sigma 9.00}(\text{Mg}_{0.62}\text{Fe}^{2+}_{0.18}\text{Fe}^{3+}_{0.17}\text{Mn}_{0.02}\text{Al}_{0.02})_{\Sigma 1.01}(\text{P}_{1.00}\text{O}_4)_6(\text{P}_{1.00}\text{O}_3\text{OH})$  (Table 1).

The OH content of bobdownsite was examined by the thermal gravimetric analysis (TGA). The data for bobdownsite R050109, along with those for type whitlockite R080052 for comparison, are presented in Figure 2. All data were collected on a Mettler Toledo TGA/SDTA 851 Thermogravimetric Analyzer, using a heating rate of  $15^\circ\text{C}/\text{min}$ . Some weight loss for whitlockite below  $300^\circ\text{C}$  may be related to absorbed or non-essential water. The weight loss observed in whitlockite at  $\sim 700^\circ\text{C}$  is interpreted to be a result of dehydration. In contrast, bobdownsite does not display any significant weight loss up to  $1100^\circ\text{C}$ , consistent with the lack of OH in this mineral. Note that Gopal *et al.* (1974) measured the thermal dehydration curves of both synthetic and natural whitlockite and observed two major dehydration events, one at  $\sim 720^\circ\text{C}$  and the other at  $\sim 1000^\circ\text{C}$ . However, they did not offer an interpretation for the dehydration event at  $\sim 1000^\circ\text{C}$ . We did not observe the dehydration event in the type whitlockite up to  $1100^\circ\text{C}$ .

The Raman spectra of bobdownsite R050109 and R070654, as well as of type whitlockite R080052, were collected on randomly oriented crystals from nine scans at 30s and 100% power per scan on a Thermo Almega microRaman system, using a solid-state laser (100% power) with a wavelength of 532 nm and a thermo-

electrically cooled CCD detector. The laser is partially polarized with  $4\text{ cm}^{-1}$  resolution and a spot size of  $1\ \mu\text{m}$ .

#### X-ray crystallography

Powder X-ray-diffraction data for the type bobdownsite were collected on a Bruker D8 Advance diffractometer with  $\text{CuK}\alpha$  radiation (Table 2). On the basis of a trigonal symmetry, the unit-cell parameters determined from these data using the CRYSTALSLEUTH software (Laetsch & Downs 2006) are  $a\ 10.3440(2)$ ,  $c\ 37.0998(8)\ \text{\AA}$ , and  $V\ 3437.8(1)\ \text{\AA}^3$ .

Single-crystal X-ray-diffraction data for bobdownsite R050109, along with R070654 and type whitlockite R080052, were collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized  $\text{MoK}\alpha$  radiation. All data were collected from nearly equidimensional crystals cut from each sample, with a frame width of  $0.5^\circ$  in  $\omega$  and 30 s counting time per frame. All reflections were indexed on the basis of a trigonal unit-cell (Table 3). The intensity data were corrected for X-ray absorption using the Bruker program SADABS (Sheldrick 1996). The systematic absences of reflections ( $hkl$ :  $h + k + l = 3n$ ;  $hh0l$ :  $h + l = 3n$  and  $l = 2n$ , and  $000l$ ,  $l = 6n$ ) indicate possible space-group  $R3c$  (#161) or  $R\bar{3}c$  (#167). All crystal structures were refined using SHELX97 (Sheldrick 2008) in space group  $R3c$ . The positions of all atoms were refined with anisotropic displacement parameters. Final fractional coordinates and displacement parameters of atoms for the type bobdownsite are listed in Table 4, and selected

bond-distances are listed in Table 5. Final fractional coordinates and displacement parameters of atoms for bobdownsite R070654 and type whitlockite R080052 are recorded in Table 6 and Table 7, respectively. Bobdownsite R070654 from the Tip Tip mine contains  $[\text{F}_{0.85}(\text{OH})_{0.15}]$ ; together with the fully hydrated whitlockite sample, it provides complementary structural information as a function of the F/OH value. A table of structure factors for the bobdownsite samples and a cif file have been sent to the Depository of Unpublished Data on the MAC website [document Bobdownsite CM49\_1065].

## RESULTS

### Crystal structure

Bobdownsite is isotypic with whitlockite, whose structure and relationships with other phosphate compounds have been studied extensively (Gopal & Calvo 1972, Gopal *et al.* 1974, Calvo & Gopal

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF BOBDDOWNSITE R050109 FROM BIG FISH RIVER, BOBDDOWNSITE R070654 FROM THE TIP TOP MINE, AND THE TYPE WHITLOCKITE R080052 FROM PALERMO #1 QUARRY, NEW HAMPSHIRE

sample number average of	R050109 25 points	R070654 11 points	R080052 12 points
P <sub>2</sub> O <sub>5</sub> wt.%	46.4(3)	46.4(2)	46.9(3)
CaO	45.9(2)	47.0(6)	46.6(2)
MgO	2.70(5)	3.6(2)	2.37(5)
Na <sub>2</sub> O	0.70(5)	0.13(4)	0.53(5)
Al <sub>2</sub> O <sub>3</sub>	0.51(13)	0.2(2)	0.12(2)
Fe <sub>2</sub> O <sub>3</sub>	0.93(8)*	n.d.	-
FeO	0.28(2)*	n.d.	2.38(8) <sup>†</sup>
MnO	n.d.	n.d.	0.13(3)
SrO	n.d.	n.d.	0.14(6)
F	1.9(3)	1.5(2)	n.d.
Subtotal	99.3	98.8	99.2
F <sub>2</sub> =-O	0.80	0.6	-
Total	98.5(7)	98.2(7)	99.2(3)
P <i>apfu</i>	7.00	7.00	7.02
Ca	8.76	8.96	8.82
Na	0.24	0.04	0.18
Mg	0.72	0.96	0.62
Al	0.11	0.04	0.02
Fe <sup>2+</sup>	0.04	-	0.35
Fe <sup>3+</sup>	0.13	-	-
Mn	-	-	0.02
Sr	-	-	0.01
F	1.07	0.84	-

The compositions are recalculated on the basis of 28 atoms of oxygen per formula unit (*apfu*) in the case of bobdownsite and 27.5 atoms in the case of whitlockite. Notes: n.d.: not detected. The composition of bobdownsite R050109:  $(\text{Ca}_{8.76}\text{Na}_{0.24})_{\Sigma 9.00}(\text{Mg}_{0.72}\text{Fe}^{3+}_{0.13}\text{Al}_{0.11}\text{Fe}^{2+}_{0.04})_{\Sigma 1.00}(\text{P}_{1.00}\text{O}_4)_6(\text{P}_{1.00}\text{O}_3\text{F}_{1.07})$ ; FeO and Fe<sub>2</sub>O<sub>3</sub> readjusted after charge balance as  $\text{FeO}^* = (0.25 \times \text{Fe}_2\text{O}_3 \text{ tot}) / 1.11145$ ;  $\text{Fe}_2\text{O}_3^* = 0.75 \times \text{Fe}_2\text{O}_3 \text{ tot}$ , where  $\text{Fe}_2\text{O}_3 \text{ tot} = 1.24(11)\%$ . The composition of bobdownsite R070654:  $(\text{Ca}_{8.96}\text{Na}_{0.04})_{\Sigma 9.00}(\text{Mg}_{0.96}\text{Al}_{0.04})_{\Sigma 1.00}(\text{P}_{1.00}\text{O}_4)_6(\text{P}_{0.84}\text{O}_3[\text{F}_{0.84}(\text{OH})_{0.16}])_{\Sigma 1.00}$ ; OH estimated by difference and charge balance. The composition of type whitlockite, R080052:  $(\text{Ca}_{8.82}\text{Na}_{0.18}\text{Sr}_{0.01})_{\Sigma 9.01}(\text{Mg}_{0.62}\text{Fe}^{2+}_{0.35}\text{Mn}_{0.02}\text{Al}_{0.02})_{\Sigma 1.01}(\text{P}_{1.00}\text{O}_4)_6(\text{P}_{1.02}\text{O}_3\text{OH})$ . <sup>†</sup> Total Fe expressed as FeO.

1975, Schroeder *et al.* 1977, Hughes *et al.* 2008). The principal structural component of bobdownsite is the  $[\text{Mg}(\text{PO}_4)_6]^{16-}$  ligand, referred to as the "Mg pinwheel" after Hughes *et al.* (2006). The Mg pinwheels are flat in the *c* direction and can be thought of as defining oblate ellipsoids whose short axes are parallel to *c* and that form a regular packing arrangement. The isolated pinwheels, held together by intralayer Ca1 cations, form

TABLE 2. POWDER X-RAY-DIFFRACTION DATA FOR BOBDDOWNSITE R050109

<i>l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>h</i>	<i>k</i>	<i>l</i>
6	8.0740	8.0670	0	1	2	5	2.2311	2.2313	1	1	15
8	6.4544	6.4436	1	0	4	4	2.1769	2.1771	4	0	4
<b>16</b>	<b>5.1759</b>	<b>5.1722</b>	<b>1</b>	<b>1</b>	<b>0</b>	7	2.1477	2.1479	3	0	12
8	4.0354	4.0335	0	2	4	2	2.0866	2.0869	1	2	14
<b>18</b>	<b>3.4279</b>	<b>3.4277</b>	<b>1</b>	<b>0</b>	<b>10</b>	7	2.0169	2.0168	0	4	8
5	3.3716	3.3720	2	1	1	8	1.9170	1.9174	4	0	10
4	3.3315	3.3310	1	2	2	6	1.8790	1.8790	2	3	8
3	3.2231	3.2236	1	1	9	6	1.8642	1.8640	1	4	6
<b>100</b>	<b>3.1815</b>	<b>3.1807</b>	<b>2</b>	<b>1</b>	<b>4</b>	1	1.8166	1.8165	0	1	20
<b>19</b>	<b>2.9857</b>	<b>2.9862</b>	<b>3</b>	<b>0</b>	<b>0</b>	1	1.7979	1.7978	3	2	10
<b>58</b>	<b>2.8578</b>	<b>2.8572</b>	<b>0</b>	<b>2</b>	<b>10</b>	2	1.7592	1.7592	0	5	4
<b>16</b>	<b>2.7344</b>	<b>2.7347</b>	<b>1</b>	<b>2</b>	<b>8</b>	<b>32</b>	<b>1.7139</b>	<b>1.7139</b>	<b>2</b>	<b>0</b>	<b>20</b>
5	2.6890	2.6890	3	0	6	2	1.6239	1.6240	2	3	14
2	2.6543	2.6537	1	1	12	1	1.4547	1.4545	4	3	4
<b>13</b>	<b>2.5864</b>	<b>2.5861</b>	<b>2</b>	<b>2</b>	<b>0</b>	1	1.4287	1.4286	0	4	20
6	2.5008	2.5010	2	1	10	1	1.3108	1.3107	1	0	28
2	2.4779	2.4791	1	3	1	1	1.2930	1.2931	4	4	0
9	2.2446	2.2448	1	0	16	1	1.2505	1.2505	4	2	20
						4	1.1721	1.1721	2	3	26

Powder lines with relative intensities above 10 are marked in bold. The *d* values are expressed in Å.

TABLE 3. SUMMARY OF CRYSTALLOGRAPHIC DATA AND REFINEMENT RESULTS FOR BOBDDOWNSITE AND WHITLOCKITE

	bobdownsite R050109	bobdownsite R070654	type whitlockite R080052
Ideal formula	Ca <sub>8</sub> Mg(PO <sub>4</sub> ) <sub>6</sub> (PO <sub>3</sub> F)	Ca <sub>8</sub> Mg(PO <sub>4</sub> ) <sub>6</sub> (PO <sub>3</sub> F)	Ca <sub>8</sub> Mg(PO <sub>4</sub> ) <sub>6</sub> (PO <sub>3</sub> OH)
Space group	R3c	R3c	R3c
<i>a</i> (Å)	10.3224(3)	10.3394(3)	10.3590(3)
<i>c</i> (Å)	37.070(2)	37.084(2)	37.086(2)
<i>V</i> (Å <sup>3</sup> )	3420.7(6)	3433.2(2)	3446.5(3)
Z	6	6	6
ρ <sub>calc</sub> (g/cm <sup>3</sup> )	3.16(2)	3.055	3.135
θ range for data collection (°)	2.4–34.41	1.7–35.5	1.7–32.4
No. of reflections collected	7868	11117	9233
No. of independent reflections	2282	3031	2518
No. of reflections with <i>F</i> > 4σ( <i>F</i> )	2055	2774	2326
<i>R</i> <sub>int</sub>	0.0363	0.0301	0.0304
<i>R</i> <sub>1</sub> [ <i>F</i> <sup>2</sup> > 4σ( <i>F</i> <sup>2</sup> )]	0.0309	0.0274	0.0281
w <i>R</i> ( <i>F</i> <sup>2</sup> )	0.0730	0.0711	0.0682
Goodness-of-fit	0.989	1.046	1.064
No. of parameters refined	149	146	150

TABLE 4. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN BOBDDOWNSITE R050109

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Ca1	0.29205(9)	0.15618(8)	0.67232(2)	0.0351(5)	0.0176(4)	0.0151(3)	-0.0081(3)	-0.0111(3)	0.0197(4)	0.0198(2)
Ca2	0.28036(7)	0.14639(7)	0.56518(2)	0.0105(3)	0.0097(3)	0.0094(3)	-0.0014(2)	-0.0006(2)	0.0057(2)	0.0096(1)
Ca3	0.38694(8)	0.17961(7)	0.76765(2)	0.0116(3)	0.0093(3)	0.0096(3)	-0.0006(3)	-0.0021(2)	0.0051(2)	0.0102(1)
M	0	0	-0.00027(5)	0.0094(4)	0.0094(4)	0.0092(6)	0	0	0.0047(2)	0.0093(3)
P1A	0	0	0.75327(6)	0.0086(5)	0.0086(5)	0.0148(16)	0	0	0.0043(3)	0.0107(6)
P1B	0	0	0.7323(3)	0.004(3)	0.004(3)	0.002(5)	0	0	0.002(1)	0.003(3)
P2	0.31741(11)	0.14328(10)	0.86398(2)	0.0092(4)	0.0089(3)	0.0080(3)	0.0005(3)	-0.0000(3)	0.0053(3)	0.0084(2)
P3	0.35016(11)	0.15740(9)	0.96736(2)	0.0086(4)	0.0086(4)	0.0072(3)	0.0004(3)	-0.0001(3)	0.0044(3)	0.0081(2)
O1	0.2746(3)	0.0922(3)	0.82484(6)	0.0234(13)	0.0203(12)	0.0091(10)	-0.0001(9)	0.0006(9)	0.0126(11)	0.0169(5)
O2	0.2480(3)	0.2337(3)	0.87774(6)	0.0174(11)	0.0195(12)	0.0137(10)	0.0004(9)	0.0019(9)	0.0145(10)	0.0146(5)
O3	0.2734(2)	0.0020(2)	0.88653(6)	0.0110(10)	0.0082(10)	0.0100(9)	0.0016(7)	0.0021(8)	0.0026(8)	0.0107(4)
O4	0.4895(3)	0.2418(2)	0.86809(7)	0.0078(11)	0.0084(10)	0.0179(12)	0.0014(8)	0.0021(9)	0.0023(9)	0.0122(5)
O5	0.4034(3)	0.1966(3)	0.00672(6)	0.0239(13)	0.0165(11)	0.0076(10)	-0.0019(8)	-0.0032(9)	0.0124(10)	0.0150(5)
O6	0.3984(3)	0.0473(3)	0.95383(6)	0.0131(10)	0.0158(11)	0.0118(9)	-0.0027(8)	-0.0019(8)	0.0097(9)	0.0125(4)
O7	0.4155(3)	0.3033(3)	0.94638(6)	0.0164(11)	0.0124(11)	0.0122(10)	0.0050(8)	0.0023(9)	0.0049(9)	0.0147(5)
O8	0.1779(3)	0.0789(3)	0.96373(7)	0.0085(11)	0.0109(10)	0.0142(10)	0.0002(8)	-0.0002(8)	0.0038(9)	0.0117(5)
O9	-0.0191(3)	0.1299(3)	0.74208(7)	0.0178(12)	0.0134(10)	0.0274(14)	0.0042(9)	0.0084(10)	0.0100(10)	0.0186(5)
F1A	0	0	0.7971(2)	0.035(2)	0.035(2)	0.045(4)	0	0	0.018(1)	0.038(2)
F1B	0	0	0.6893(7)							0.016(6)

Notes: (1) Ca1 =  $\text{Ca}_{0.92}\text{Na}_{0.08}$ ; Ca2 = Ca; Ca3 = Ca; M =  $(\text{Mg}_{0.72}\text{Fe}^{3+}_{0.13}\text{Al}_{0.11}\text{Fe}^{2+}_{0.04})$ ; P1A = 0.85 P + 0.15 vacancy; P1B = 0.15 P + 0.85 vacancy; F1A = 0.85 F + 0.15 vacancy; F1B = 0.15 F + 0.85 vacancy. (2) The F1B atom was only refined with an isotropic displacement parameter.

TABLE 5. SELECTED BOND-DISTANCES (Å) IN BOBDDOWNSITE R050109

M-	O4	x 3	2.049(3)	Ca2-	O2	2.744(3)	P1a-	O9	x 3	1.508(2)
M-	O8	x 3	2.079(3)	Ca2-	O3	2.495(2)	P1a-	F		1.625(7)
<M-	O>		2.064	Ca2-	O4	2.460(2)	<P-	O,F>		1.537
				Ca2-	O4	2.478(3)				
Ca1-	O1		2.535(2)	Ca2-	O5	2.430(3)	P1b-	O9	x 3	1.495(4)
Ca1-	O2		2.404(2)	Ca2-	O6	2.460(2)	P1b-	F1b		1.59(3)
Ca1-	O3		2.385(2)	Ca2-	O7	2.314(2)	<P1b-	O,F>		1.519
Ca1-	O5		2.456(2)	Ca2-	O9	2.458(3)				
Ca1-	O5		2.535(3)	<Ca2-	O>	2.480	P2-	O1		1.532(3)
Ca1-	O6		2.377(2)				P2-	O2		1.521(3)
Ca1-	O7		2.654(3)	Ca3-	O1	2.367(3)	P2-	O3		1.540(2)
Ca1-	F1b		2.687(6)	Ca3-	O2	2.457(2)	P2-	O4		1.551(3)
<Ca1-	O,F>		2.504	Ca3-	O3	2.365(2)	<P2-	O>		1.536
				Ca3-	O6	2.628(3)				
				Ca3-	O7	2.628(3)	P3-	O5		1.540(3)
				Ca3-	O8	2.440(3)	P3-	O6		1.534(2)
				Ca3-	O8	2.463(2)	P3-	O7		1.520(3)
				<Ca3-	O>	2.464	P3-	O8		1.548(3)
							<P3-	O>		1.530

layers parallel to (001) (Fig. 3). These layers are linked by interlayer Ca2 and Ca3 cations.

Figure 4 shows that the anionic units in each pinwheel layer form a perfectly eutactic, *i.e.*, closest-packed, planar arrangement. The term "eutaxy" (O'Keeffe & Hyde 1996) is preferred to "closest-packing" because neither the atoms nor the ligands can be considered to be in contact with each other. The arrangement of anionic units is distorted and eutactic in three dimensions. The term "cubic eutaxy" will be

used because the ligands form a distorted cubic-closest packed arrangement (O'Keeffe & Hyde 1996).

Eutactic arrangements create tetrahedral and octahedral interstitial sites. The octahedral interstitial sites in bobdownsite contain the second structural component, namely isolated  $\text{PO}_3\text{F}$  tetrahedral groups (Fig. 4). The three oxygen atoms that form the base of a  $\text{PO}_3\text{F}$  tetrahedron are located approximately in the midplane between the two pinwheel layers and are each coordinated to the closest two interlayer Ca cations (Fig. 4), in addition to  $\text{P}^{5+}$ . The  $\text{P}^{5+}$  position in the  $\text{PO}_3\text{F}$  group

is split; it is randomly located either just above or just below the midplane between the two pinwheel layers, leading the apical  $F^-$  anion of the  $PO_3F$  tetrahedron to point either along  $+c$  or  $-c$ .

The whitlockite-type compounds contain a metal atom ( $M = Mg, Fe, Mn$ ) that is slightly offset from the origin along  $c$ . This atom is octahedrally coordinated

and resides at the center of an  $M$  pinwheel. For any compound isostructural with whitlockite, an atom  $M$  at the origin will result in a perfect cubic eutactic arrangement of  $M$  atoms if  $c = 2\sqrt{6}a$ , and the  $M$  pinwheel layers are constrained to be in perfect planar eutaxy for any value of the cell-edge ratio. Hence, distortion from

TABLE 6. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN BOBDDOWNSITE R070654

Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Ca1	0.29139(8)	0.15560(7)	0.672376(16)	0.0370(4)	0.0196(3)	0.0172(2)	-0.0084(2)	-0.0118(2)	0.0212(3)	0.02147(13)
Ca2	0.28027(6)	0.14660(5)	0.565209(12)	0.0110(2)	0.0103(2)	0.01016(19)	-0.00140(16)	-0.00061(16)	0.00593(18)	0.01020(10)
Ca3	0.38790(6)	0.18026(5)	0.767658(12)	0.0121(3)	0.0091(2)	0.0107(2)	-0.00070(18)	-0.00259(16)	0.00510(19)	0.01073(14)
$M$	0	0	-0.00029(5)	0.0125(4)	0.0125(4)	0.0124(5)	0	0	0.0063(2)	0.0125(3)
P1A	0	0	0.75328(4)	0.0084(4)	0.0084(4)	0.0162(11)	0	0	0.0042(2)	0.0110(5)
P1B	0	0	0.7314(2)	0.011(2)	0.011(2)	0.007(4)	0	0	0.0054(12)	0.009(2)
P2	0.31797(8)	0.14350(8)	0.864081(15)	0.0091(3)	0.0094(3)	0.0092(2)	0.0007(2)	0.0004(2)	0.0052(2)	0.00896(12)
P3	0.35050(8)	0.15790(7)	0.967265(14)	0.0087(3)	0.0098(3)	0.0083(2)	0.0007(2)	0.0002(2)	0.0044(2)	0.00905(12)
O1	0.2750(2)	0.0930(2)	0.82489(5)	0.0238(10)	0.0209(10)	0.0109(7)	-0.0002(7)	-0.0004(6)	0.0113(8)	0.0185(4)
O2	0.2478(2)	0.2336(2)	0.87747(5)	0.0175(9)	0.0191(9)	0.0152(7)	0.0007(6)	0.0025(6)	0.0140(8)	0.0151(3)
O3	0.2732(2)	0.0018(2)	0.88617(5)	0.0112(7)	0.0098(7)	0.0120(6)	0.0022(5)	0.0019(6)	0.0033(6)	0.0118(3)
O4	0.4892(2)	0.24185(19)	0.86830(5)	0.0082(8)	0.0088(8)	0.0181(8)	0.0018(6)	0.0026(6)	0.0031(7)	0.0122(3)
O5	0.4036(2)	0.1970(2)	0.00671(5)	0.0249(10)	0.0193(9)	0.0085(7)	-0.0010(6)	-0.0018(6)	0.0132(8)	0.0166(4)
O6	0.3991(2)	0.0484(2)	0.95381(5)	0.0146(8)	0.0181(9)	0.0132(7)	-0.0018(6)	-0.0010(6)	0.0111(7)	0.0140(3)
O7	0.4153(2)	0.3037(2)	0.94631(5)	0.0151(8)	0.0125(8)	0.0159(7)	0.0032(6)	0.0001(6)	0.0037(7)	0.0159(3)
O8	0.1790(2)	0.0788(2)	0.96363(5)	0.0083(8)	0.0106(8)	0.0157(7)	0.0002(6)	0.0008(6)	0.0041(7)	0.0118(3)
O9	-0.0201(2)	0.1298(2)	0.74149(5)	0.0177(9)	0.0113(8)	0.0297(10)	0.0050(6)	0.0070(7)	0.0083(7)	0.0191(4)
F	0	0	0.79715(15)	0.043(2)	0.043(2)	0.049(3)	0	0	0.0217(12)	0.0454(19)

Notes:  $M = 0.96Mg + 0.04Al$ , P1A = 0.81 P + 0.19 vacancy; P1B = 0.16 P + 0.84 vacancy; F = 0.85 F + 0.15 vacancy.

TABLE 7. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN TYPE WHITLOCKITE R080052

Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Ca1	0.29278 (8)	0.15662 (7)	0.672195 (18)	0.0364 (5)	0.0188 (3)	0.0160 (3)	-0.0086 (3)	-0.0126 (3)	0.0208 (3)	0.0206 (2)
Ca2	0.28035 (7)	0.14623 (6)	0.565199 (14)	0.0104 (3)	0.0095 (3)	0.0088 (2)	-0.0011 (2)	-0.0004 (2)	0.0056 (2)	0.0093 (1)
Ca3	0.38769 (7)	0.18008 (6)	0.767655 (13)	0.0107 (3)	0.0089 (3)	0.0095 (2)	-0.0009 (2)	-0.0024 (2)	0.0048 (2)	0.0098 (1)
$M$	0	0	-0.00028 (3)	0.0082 (3)	0.0082 (3)	0.0088 (4)	0	0	0.0041 (2)	0.0084 (3)
P1A	0	0	0.75326 (5)	0.0074 (5)	0.0074 (5)	0.0184 (14)	0	0	0.0037 (3)	0.0111 (6)
P1B	0	0	0.7318 (4)	0.000 (4)	0.000 (4)	0.000 (8)	0	0	0.000 (2)	0.000 (4)
P2	0.31690(9)	0.14343(9)	0.864280(17)	0.0085(4)	0.0089(3)	0.0074(3)	0.0012(3)	0.0012(3)	0.0049(3)	0.0080(2)
P3	0.35083(10)	0.15788(9)	0.967182(16)	0.0086(4)	0.0090(3)	0.0070(3)	0.0004(3)	0.0000(3)	0.0045(3)	0.0082(2)
O1	0.2758(3)	0.0936(3)	0.82513(5)	0.0251(12)	0.0207(12)	0.0077(8)	-0.0005(8)	0.0002(7)	0.0130(10)	0.0171(4)
O2	0.2462(2)	0.2328(2)	0.87771(5)	0.0158(10)	0.0174(11)	0.0149(8)	0.0017(8)	0.0027(7)	0.0133(9)	0.0138(4)
O3	0.2724(2)	0.0016(2)	0.88627(5)	0.0110(10)	0.0081(9)	0.0115(8)	0.0017(7)	0.0021(7)	0.0028(8)	0.0111(4)
O4	0.4877(2)	0.2415(2)	0.86884(6)	0.0096(11)	0.0075(9)	0.0170(9)	0.0012(7)	0.0031(8)	0.0031(9)	0.0119(4)
O5	0.4029(3)	0.1961(2)	0.00664(5)	0.0211(12)	0.0164(11)	0.0075(8)	-0.0022(7)	-0.0022(7)	0.0114(9)	0.0141(5)
O6	0.3999(2)	0.0489(2)	0.95358(5)	0.0148(10)	0.0156(11)	0.0126(8)	-0.0030(7)	-0.0008(7)	0.0110(9)	0.0128(4)
O7	0.4167(2)	0.3045(2)	0.94644(5)	0.0147(10)	0.0114(11)	0.0133(8)	0.0046(7)	0.0021(7)	0.0033(9)	0.0146(4)
O8	0.1793(2)	0.0794(2)	0.96326(6)	0.0075(10)	0.0098(10)	0.0140(8)	-0.0004(7)	0.0004(8)	0.0026(8)	0.0112(4)
O9	0	0	0.79758(15)	0.030(2)	0.030(2)	0.047(3)	0	0	0.0151(11)	0.0359(18)
O9B	0	0	0.6893(7)	0.015(9)	0.015(9)	0.032(14)			0.007(4)	0.020(7)
O10	-0.0193(2)	0.1295(2)	0.74202(5)	0.0183(12)	0.0095(9)	0.0269(11)	0.0040(7)	0.0086(9)	0.0089(9)	0.0174(5)

Notes:  $M = (0.62 Mg + 0.35 Fe + 0.02 Mn + 0.02 Al)$ ; P1A = 0.85 P + 0.15 vacancy; P1B = 0.09 P + 0.91 vacancy; O9B = 0.17 O + 0.83 vacancy.

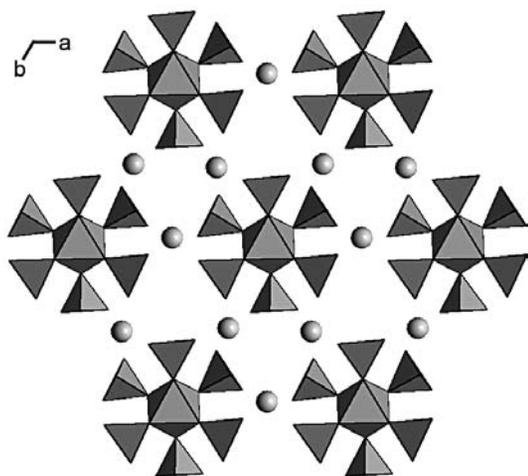


FIG. 3. A portion of a layer perpendicular to  $c$  showing  $[\text{Mg}(\text{PO}_4)_6]^{16-}$  "pinwheels" (Hughes *et al.* 2006). The anionic units form a perfectly closest-packed planar arrangement. The spheres represent intralayer Ca1 cations.

perfect cubic eutaxy depends only on the distortion from the ideal  $c : a$  ratio of  $2\sqrt{6}$ .

In Table 8, we compare selected crystal-chemical data and a quantitative measure of packing efficiency for bobdownsite and some isostructural compounds, together with packing efficiency for a hypothetical ideal eutactic whitlockite-type structure and several model whitlockite-type structures with  $a = 10 \text{ \AA}$  and  $c : a$  varying from 3.6 to 4.75. The measure of packing efficiency,  $U_{\text{cp}}$ , described by Thompson & Downs (2001), is calculated by fitting an arrangement of 675 ideal cubic closest-packed spheres to their observed equivalents such that the mean square distance between observed and ideal atoms is minimized. Minimization is accomplished by allowing the ideal arrangement to scale, rotate, and translate. The parameter  $U_{\text{cp}}$  is the minimal mean square displacement, which is zero for a perfectly eutactic arrangement of spheres, or in this case pinwheel ligands. The value of  $U_{\text{cp}}$  increases as an arrangement becomes more distorted from perfect eutaxy.

Values of  $U_{\text{cp}}$  for observed whitlockite-type compounds range from 23.7 to 28.3  $\text{\AA}^2$ . These values represent extreme distortion from perfect eutaxy and result from the fact that the items being packed together are far from spherical, more closely resembling disks, as their height to diameter ratio equals 0.51, which drastically reduces the  $c : a$  cell-edge ratio from its ideal eutactic value of  $2\sqrt{6}$ . The distortion from eutaxy represented by non-zero  $U_{\text{cp}}$  values can result from distortion of the cell parameters from ideal, the distortion of atomic positions from ideal, or a combination of both. The whitlockite structure is an example of the

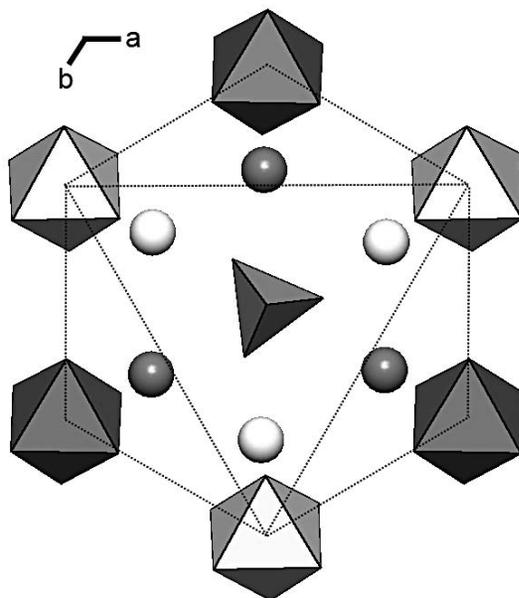


FIG. 4. A portion of two layers from a cubic closest-packed arrangement of Mg octahedra looking down  $c$  showing an isolated  $\text{PO}_3\text{F}$  tetrahedron in the large octahedral void formed by six of the octahedra. The "arms" of the Mg pinwheels, the six  $\text{PO}_4$  groups for every Mg octahedron, have been left off for clarity (see Fig. 3), as have the intralayer calcium cations. The gray octahedra are in the lower layer ( $z_{\text{Mg}} = 0.3331$ ), the white ones, in the upper layer ( $z_{\text{Mg}} = 0.4997$ ). The spheres are interlayer  $\text{Ca}^{2+}$  cations with gray ones (Ca2) at  $z = 0.3985$  and white (Ca3) at  $z = 0.4343$ . The base of the tetrahedron is in the midplane between the two layers of octahedra. In this illustration,  $\text{P}^{5+}$  has adopted the upper possibility of its split position, just above the midplane (instead of just below), and so the tetrahedron points along  $+c$ , instead of  $-c$ .

unusual case where the atom positions are ideal so that all distortion results from non-ideal cell-edge ratios.

Figure 5 is a plot of  $U_{\text{cp}}$  versus  $c/a$  for the observed whitlockite-type structures in Table 8 (solid circles) and some model structures (open circles). The model structures all have  $a = 10 \text{ \AA}$  and are included to add additional insight into the whitlockite structure-type. A quadratic trendline fits the model datapoints exactly. The values of  $U_{\text{cp}}$  for the observed structures do not fall exactly on the trendline because  $U_{\text{cp}}$  is a measure of the Euclidean distance, and is therefore affected to a small degree by differences in unit-cell volume in all cases except perfect eutaxy, which invariably has  $U_{\text{cp}} = 0$  for any cell size. These results suggest that there is little difference in principle between the processes that take place where oxygen anions with charge  $-2$  are forced into close proximity and those that occur where much larger ligands with charge  $-16$  get close to each other.

Figure 6 shows the structure of a  $\text{PO}_3\text{F}$ -bearing synthetic compound,  $\text{NaK}_3(\text{PO}_3\text{F})_2$  (Durand *et al.* 1975). The fundamental structural unit of this material is the Na-centered pinwheel polymerized by sharing tetrahedra to form a planar polymer. In this case, the  $\text{PO}_3\text{F}$  tetrahedra are not interstitial, but are part of the pinwheels. Like Mg in bobdownsite, the Na atoms form perfectly eutactic planar arrangements. In three dimensions, however, eutaxy is not maintained because the planes of Na pinwheels are stacked directly above each other, AAA... These planes are held together by  $\text{K}^+$ . Also like bobdownsite, the apical anion is  $\text{F}^-$  pointing

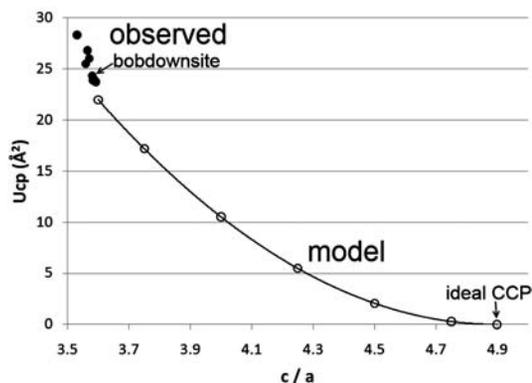


FIG. 5. A plot of packing efficiency,  $U_{cp}$ , versus axial ratio for the observed whitlockite-type structures of Table 8 (solid circles) and several model whitlockite-type structures with a fixed 10 Å and variable  $c/a$  (open circles). A value of zero for  $U_{cp}$  represents perfect eutaxy, whereas values for the observed structures represent extreme distortion. CCP: cubic closest packing.

along the stacking vector of the planes and is bonded only to  $\text{P}^{5+}$  in the  $\text{PO}_3\text{F}$  tetrahedron and the interplanar  $\text{K}^+$  cations.

The synthetic compound  $\text{LiNH}_4\text{PO}_3\text{F}$  (Durand *et al.* 1978) is also a layer structure (Fig. 7), with  $\text{F}^-$  at the apices of the  $\text{PO}_3\text{F}$  tetrahedra pointing into the interlayer space and  $\text{NH}_4^+$  playing the role of the interlayer cation. However, the layers themselves are very different, and although they stack in ABAB... fashion along  $c$ , there is no obvious eutaxy. These layers can be described as chains of corner-sharing  $\text{LiO}_4$  tetrahedra cross-connected by  $\text{PO}_3\text{F}$  tetrahedra (Durand *et al.* 1978).

All of the structures examined above share the common feature that  $\text{PO}_3\text{F}$  groups point into interlayer

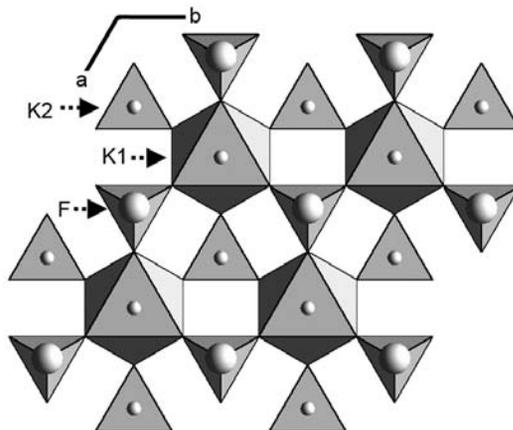


FIG. 6. The crystal structure of  $\text{NaK}_3(\text{PO}_3\text{F})_2$  (Durand *et al.* 1975), viewed down  $c$ .

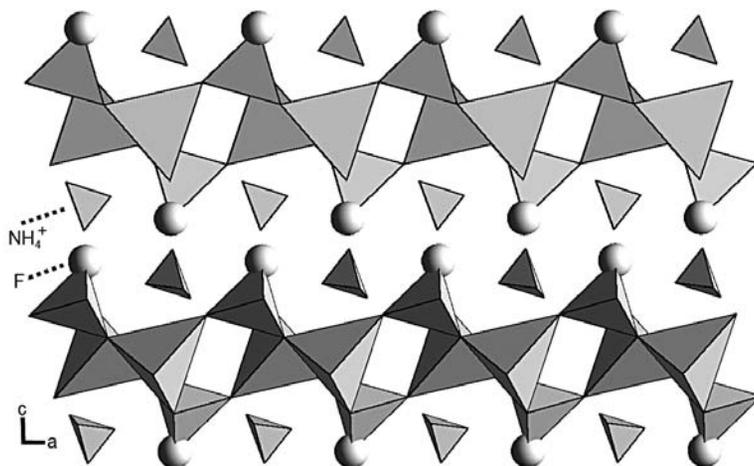


FIG. 7. The crystal structure of  $\text{LiNH}_4\text{PO}_3\text{F}$  (Durand *et al.* 1978), viewed down  $b$ .

spaces with F<sup>-</sup> at the apices either dangling or weakly bonded to the interlayer cations that bind the layers together. In bobdownsite, F<sup>-</sup> is 3.7 Å away from the nearest cation (Ca1) outside its tetrahedron, but only 2.7 Å from the nearest oxygen atom (O1) outside the PO<sub>3</sub>F group, suggesting that it is bonded only to P<sup>5+</sup>. In NaK<sub>3</sub>(PO<sub>3</sub>F)<sub>2</sub>, F<sup>-</sup> is part of the K2 coordination shell at a distance of 2.6 Å from K2, along with six oxygen atoms at 2.9 Å. In LiNH<sub>4</sub>PO<sub>3</sub>F, F<sup>-</sup> is 2.1 Å from one of the hydrogen atoms belonging to NH<sub>4</sub><sup>+</sup>. In these phases, F<sup>-</sup> does not form strong bonds with more than one cation.

### Series trends

It would be useful if bobdownsite could be distinguished from whitlockite on the basis of unit-cell parameters. Figure 8 shows a plot of *c* / *a* for the three members of the solid solution analyzed in this paper: Bobdownsite R050109 with F% [= F/(F + OH)] = 100, bobdownsite R070654 intermediate with F% = 84, and type whitlockite R080052 with F% = 0. This plot appears to show a correlation between the *c* / *a* ratio and

fluorine content. Table 9 provides the numerical data for these samples and for prior refinements of end-member whitlockite. All of the previous data have F% = 0, but their *c* / *a* values cover a greater range than our three samples. The analysis is complicated by the variable composition of the *M* site and the F site. Besides OH<sup>-</sup>, O<sup>2-</sup> may substitute at the F site, as in merrillite. This necessitates the addition of a new partially occupied cation site for charge balance. In future studies, one should verify a relationship between fluorine content and cell parameters given chemical constraints on other sites, but these constraints themselves will limit the value of any such discovery.

### Relationship to merrillite

Merrillite, like whitlockite, is another important phosphate mineral found in lunar rocks (Albee *et al.* 1970, Griffin *et al.* 1972, Lindstrom *et al.* 1985, Jolliff *et al.* 1993, 2006). It is also found in Martian and various other types of meteorites (Delaney *et al.* 1984, Davis & Olsen 1991, Prewitt & Rothbard 1975). In the labora-

TABLE 8. A COMPARISON OF SOME CRYSTALLOGRAPHIC PARAMETERS FOR BOBDOWNSITE WITH ISOSTRUCTURAL COMPOUNDS AND SOME MODEL STRUCTURES

	<i>c/a</i>	U <sub>op</sub>	REE1	REE2,3	<i>M</i>	<i>T</i>	Reference
bobdownsite	3.5912	23.75728	Ca	Ca	Mg	P	this work
bobdownsite F <sub>0.84</sub>	3.5867	24.00177	Ca	Ca	Mg	P	this work
whitlockite	3.5801	24.33555	Ca	Ca	Mg	P	this work
aluminocerite-(Ce)	3.5715	26.03169	Nd,Ce,Pr	Ce,La,Ca	Al,Fe	Si	Nestola <i>et al.</i> (2009)
cerite-(Ce)	3.531	28.34486	Ce	Ce	Mg	Si	Moore & Shen (1983)
cerite-(La)	3.5647	26.81851	La,Ce,Ca	La,Ce,Ca	Fe,Ca,Mg	Si	Pakhomovsky <i>et al.</i> (2002)
merrillite	3.5832	23.90210	Ca	Ca	Mg,Fe	P	Hughes <i>et al.</i> (2006)
whitlockite	3.5918	23.77217	Ca	Ca	Mg,Fe	P	Calvo & Gopal (1975)
whitlockite	3.5591	25.49985	Ca	Ca	Mn	P	Kostiner & Rea (1976)
whitlockite	3.5922	23.74322	Ca	Ca	V	P	Tsirlin <i>et al.</i> (2006)
model	3.6	21.99801					
model	3.75	17.21089					
model	4	10.53606					
model	4.25	5.49086					
model	4.5	2.07529					
model	4.75	0.28936					
ideal CCP	2√6 = 4.9	0					

TABLE 9. THE RELATIONSHIP BETWEEN COMPOSITION AND UNIT-CELL PARAMETERS FOR THE BOBDOWNSITE-WHITLOCKITE SOLID SOLUTION

% F	<i>a</i> (Å)	<i>c</i> (Å)	<i>c</i> / <i>a</i>	<i>M</i> site	<i>F</i> site	reference
100	10.3224	37.070	3.5912	Mg <sub>0.72</sub> Fe <sub>0.17</sub> Al <sub>0.11</sub>	F	Bobdownsite (this work)
84	10.3394	37.084	3.5867	Mg <sub>0.96</sub> Al <sub>0.04</sub>	F <sub>0.84</sub> OH <sub>0.16</sub>	Bobdownsite (this work)
0	10.3590	37.086	3.5801	Mg <sub>0.65</sub> Fe <sub>0.35</sub> Mn <sub>0.02</sub> Al <sub>0.02</sub>	OH	Whitlockite (this work)
0	10.347	37.099	3.5855	Mg	OH	Whitlockite (Gopal <i>et al.</i> 1974)
0	10.330	37.103	3.5918	Mg <sub>0.8</sub> Fe <sub>0.2</sub>	OH <sub>0.84</sub> O <sub>0.16</sub>	Whitlockite (Gopal & Calvo 1972)
0	10.330	37.103	3.5918	Mg <sub>0.585</sub> Fe <sub>0.415</sub>	OH <sub>0.81</sub> O <sub>0.19</sub>	Whitlockite (Gopal & Calvo 1975)
0	10.361	37.096	3.5803	Mg <sub>0.53</sub> Fe <sub>0.38</sub> Mn <sub>0.09</sub>	OH <sub>0.69</sub> O <sub>0.31</sub>	Whitlockite (Hughes <i>et al.</i> 2008)

tory, merrillite can be readily obtained by dehydrating whitlockite (Gopal *et al.* 1974, Hughes *et al.* 2008). Merrillite crystals with considerable amounts of F and traces of Cl are found in several Martian meteorites, including LEW 88516 (Gleason *et al.* 1997, Treiman *et al.* 1994, Lodders 1998), EETA79001A (Zipfel *et al.* 2000, Folco *et al.* 2000, Wadhwa *et al.* 2001, Mikouchi *et al.* 2001), SaU 005 and 008 (Zipfel 2000), and SaU 094 (average F = 1.1 wt%) (Gnos *et al.* 2002). Gnos *et al.* (2002) suggested that the F content in the Martian meteorites are the result of a solid solution with a structurally analogous “fluor whitlockite.” Based on our study on bobdownsite, we conclude that whitlockite with F content greater than ~0.9 wt%, including the F-bearing “merrillite” in SaU 094B (Gnos *et al.* 2002), is bobdownsite. Fully fluorinated bobdownsite contains ~1.8 wt% F.

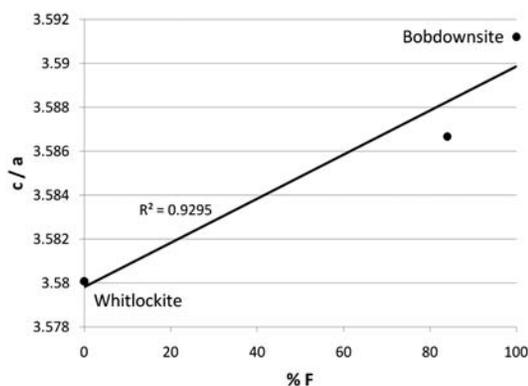


FIG. 8. The relationship between fluorine content and cell parameters for the bobdownsite–whitlockite solid solution. The best-fit line is drawn to guide the eye.

### Raman spectra

The Raman spectra of bobdownsite and whitlockite are plotted in Figure 9. They are remarkably similar to each other. Moreover, the Raman spectrum of our bobdownsite R070654 from the Tip Top mine strongly resembles that of whitlockite examined by Jolliff *et al.* (2006), which was also from the Tip Top mine. Unfortunately, no detailed chemical composition, especially in terms of F content, was provided by Jolliff *et al.* (2006). On the basis of previous Raman spectroscopic studies on whitlockite and merrillite (Cooney *et al.* 1999, Jolliff *et al.* 1996, 2006, Xie *et al.* 2002, Ionov *et al.* 2006), we made a tentative assignment of major Raman bands for bobdownsite (Table 10). The strongest band in the 950–975  $\text{cm}^{-1}$  region is attributed to the symmetric stretching ( $\nu_1$ ) mode of the  $\text{PO}_4$  groups. Interestingly, this band is a well-resolved doublet in our bobdownsite R070654 and the whitlockite studied by Jolliff *et al.* (2006), but a very poorly resolved doublet in bobdownsite R050109 and type whitlockite R080052. This observation, according to Jolliff *et al.* (2006), may be related to the complex substitutions

TABLE 10. TENTATIVE ASSIGNMENTS OF RAMAN BANDS IN BOBDOWNSITE

Bands ( $\text{cm}^{-1}$ )	Intensity	Assignment
1080–1100	Weak	$\nu_3$ ( $\text{PO}_4$ ) asymmetric stretching
950–975	Very strong, sharp	$\nu_1$ ( $\text{PO}_4$ ) symmetric stretching
923	Relatively strong, sharp	$\nu_1$ ( $\text{PO}_3\text{F}$ ) symmetric stretching
500–600	Weak	$\nu_4$ ( $\text{PO}_4$ ) / ( $\text{PO}_3\text{F}$ ) asymmetric bending
400–500	Weak	$\nu_2$ ( $\text{PO}_4$ ) / ( $\text{PO}_3\text{F}$ ) symmetric bending
<400	Weak	Lattice, Mg–O and Ca–O vibrational modes

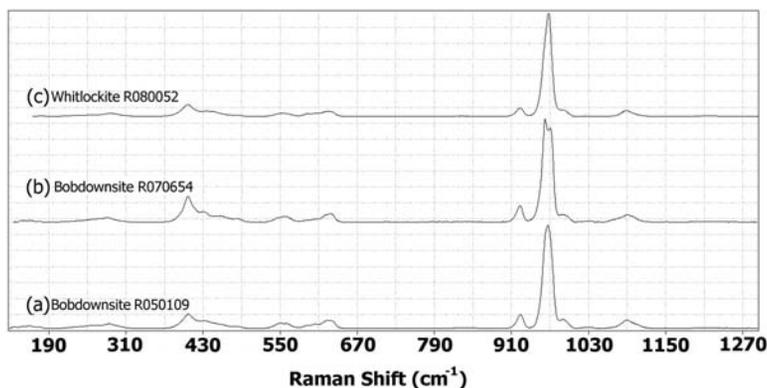


FIG. 9. Raman spectra of (a) bobdownsite R050109, (b) bobdownsite R070654, and (c) type whitlockite R080052.

at the Ca and Mg sites, resulting in a more uniform bonding environment for all PO<sub>4</sub> groups. Indeed, the chemical compositions of bobdownsite R050109, (Ca<sub>8.76</sub>Na<sub>0.24</sub>)<sub>Σ9</sub>(Mg<sub>0.72</sub>Fe<sup>3+</sup><sub>0.13</sub>Al<sub>0.11</sub>Fe<sup>2+</sup><sub>0.04</sub>)<sub>Σ1</sub>(PO<sub>4</sub>)<sub>6</sub>(PO<sub>3</sub>F<sub>1.07</sub>), and type whitlockite R080052, (Ca<sub>8.82</sub>Na<sub>0.18</sub>Sr<sub>0.01</sub>)<sub>Σ9</sub>(Mg<sub>0.62</sub>Fe<sup>2+</sup><sub>0.18</sub>Fe<sup>3+</sup><sub>0.17</sub>Mn<sub>0.02</sub>Al<sub>0.02</sub>)<sub>Σ1.01</sub>(PO<sub>4</sub>)<sub>6</sub>(PO<sub>3</sub>OH), are much more complicated than the composition of bobdownsite R070654, (Ca<sub>8.99</sub>Na<sub>0.05</sub>)<sub>Σ9.04</sub>(Mg<sub>0.96</sub>Al<sub>0.04</sub>)<sub>Σ1</sub>(PO<sub>4</sub>)<sub>6</sub>{PO<sub>3</sub>[F<sub>0.85</sub>(OH)<sub>0.15</sub>]<sub>Σ1</sub>} (Table 1).

There is a relatively strong and sharp peak at ~923 cm<sup>-1</sup> in both bobdownsite and whitlockite, but it is not observed in anhydrous merrillite (Cooney *et al.* 1999, Xie *et al.* 2002, Jolliff *et al.* 2006, Ionov *et al.* 2006). This band is, therefore, assigned to the symmetric stretching ( $\nu_1$ ) mode of the PO<sub>3</sub>F group in bobdownsite or the PO<sub>3</sub>OH group in whitlockite. It should be pointed out that the Raman-active O–H stretch of the weakly acidic OH in the PO<sub>3</sub>OH group in whitlockite may give rise to a weak band in the 2100–2700 cm<sup>-1</sup> region (Jolliff *et al.* 2006). Nonetheless, this band is not observed in the type whitlockite R080052 or the whitlockite specimen examined by Jolliff *et al.* (2006), who ascribed this to the strong background fluorescence in this region.

#### SUMMARY

1) A new mineral species, bobdownsite, named after Robert Terrance Downs, the F-analogue of whitlockite, ideally Ca<sub>9</sub>Mg(PO<sub>4</sub>)<sub>6</sub>(PO<sub>3</sub>F), has been discovered at Big Fish River, Yukon, Canada.

2) Bobdownsite is found to be isostructural with whitlockite, trigonal with space group R3c. Its structure is characterized by the [Mg(PO<sub>4</sub>)<sub>6</sub>]<sup>16-</sup> ligand, or the so-called “Mg pinwheel”. The isolated pinwheels are held together by intralayer Ca cations to form layers parallel to (001), which are linked together by interlayer Ca cations along [001].

3) The Raman spectra of bobdownsite strongly resemble those of whitlockite and merrillite.

4) Bobdownsite represents the first naturally formed phosphate known to contain a P–F bond.

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