CLINOMETABORITE, NATURAL β-METABORIC ACID, FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

Clinometaborite, β-HBO_2, the monoclinic modification of metaboric acid, which has long been known as a synthetic product only, was found as a sublimate in an active medium-temperature intracrater fumarole at La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy. It forms aggregates of stout crystals up to 2 mm long in an altered pyroclastic breccia, associated with metaborite, sassolite and adranosite. The unaltered mineral is colorless and translucent, with a vitreous luster; it becomes chalky white after some months of exposure to open air. The crystal habit is prismatic; twinning was not observed. The strongest six lines in the X-ray powder-diffraction pattern [d_{obs} in Å(I)hkl] are: 3.078(100)201, 4.193(20)111, 6.773(15)001, 2.550(10)$\overline{1}$22, 3.224(8)$\overline{2}$01, and 2.702(8)031. The unit cell is monoclinic, space group $P2_1/a$, with a 7.127(2), b 8.842(3), c 6.773(2) Å, β 93.21(1)°, V 426.1(2) Å^3, Z = 12, values that virtually coincide with those of the synthetic compound. The calculated density is 2.049 g/cm^3. The structure was refined to a final R of 0.043 for 977 observed reflections [$I > 2\sigma(I)$]. Both the mineral and the mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2010–022).

Keywords: clinometaborite, β-metaboric acid, new mineral species, monotropism, Vulcano Island, Aeolian Islands, Italy.

SOMMAIRE

Nous avons découvert la clinométaborite, β-HBO_2, modification monoclinique de l'acide métaborique connu depuis longtemps comme produit de synthèse, dans une fumerolle active intercratérique de température modérée au cratère La Fossa, île de Vulcano, archipel aéolien, en Sicile, Italie. Les cristaux trappus, en agrégats d'une longueur de 2 mm dans une brèche pyroclastique altérée, sont associés à la métaborite, la sassolite et l'adranosite. Le minéral non altéré est incolore et translucide, avec un éclat vitreux; il devient blanc crayeux après quelques mois exposé à l'air. Les cristaux sont prismatiques; nous n'avons pas décelé de macle. Les six raies les plus intenses du spectre de diffraction X, méthode des poudres [d_{obs} en Å(I)hkl] sont: 3.078(100)201, 4.193(20)111, 6.773(15)001, 2.550(10)$\overline{1}$22, 3.224(8)$\overline{2}$01, et 2.702(8)031. La maille élémentaire est monoclinique, groupe spatial $P2_1/a$, avec a 7.127(2), b 8.842(3), c 6.773(2) Å, β 93.21(1)°, V 426.1(2) Å^3, Z = 12, valeurs qui coïncident pratiquement avec celles du composé synthétique. La densité calculée est 2.049 g/cm^3. Nous en avons affiné la structure jusqu'à un résidu final R de 0.043 en utilisant 977 réflexions observées [$I > 2\sigma(I)$]. Le minéral et son nom ont reçu l'approbation de l'Association internationale de Minéralogie, Commission des nouveaux Minéraux, Nomenclature et Classification (IMA 2010–022).

(Traduit par la Rédaction)

Mots-clés: clinométaborite, acide métaborique β, nouvelle espèce minérale, monotropisme, île de Vulcano, archipel aéolien, Italie.

INTRODUCTION

In the last few years, several new mineral species have been discovered at Vulcano, Aeolian Islands, Italy, as a result of a systematic investigation on the fumarolic products at the site (see Campostrini *et al*. 2011, Demartin *et al*. 2008a, 2008b, 2008c, 2009a, 2009b, 2009c, 2010a, 2010b, 2010c, 2010d, and references

therein). Here we report the discovery at La Fossa crater of an additional new mineral species: clinometaborite, β-HBO_2. It is the natural equivalent of β-metaboric acid or HBO_2 II, a substance already known as a synthetic product, and whose crystal structure has already been determined (Kracek *et al*. 1938, Zachariasen 1963, Freyhardt *et al*. 2000). The mineral is named after its composition and symmetry. Both the mineral and the

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mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2010–022). The holotype is deposited in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano (catalogue no. 2010–03).

OCCURRENCE AND PROPERTIES

Clinometaborite occurs in a medium-temperature (~250°C) intracrater fumarole developed on altered pyroclastic breccia, as stout crystals up to 2 mm long. It is accompanied by sassolite, adranosite, $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$ (Demartin $et\ al.$ 2010c), and metaborite; the last species is usually known to form good transparent rhombododecahedra in saline deposits (Lobanova & Avrova 1964), but its presence has never been noted in volcanic fumaroles.

The crystal habit is prismatic, but the faces are too rough for an assignment of indices (Fig. 1). Microscopic observations reveal that these "crystals" consist of aggregates of fibrous individuals and are most likely pseudomorphic. The unaltered material is transparent and colorless, the streak is white, and the luster is vitreous; it becomes chalk-white upon a few months' exposure to open air and is transformed into orthoboric acid. The mineral is not fluorescent either under short-wave or long-wave ultraviolet radiation. It is brittle, and a perfect cleavage can be observed. The calculated density is 2.049 g/cm^3. The optical properties of the synthetic compound reported by Kracek $et\ al.$ (1938) are: biaxial (–) with α 1.434, β 1.570, γ 1.588 (589 nm).

The infrared spectrum, recorded on a Jasco IRT–3000 spectrometer, shows absorption bands at 1194 and 1457 cm^{-1} typical of the E' vibration modes of the BO_2^- ion (Hisatsune & Haddock Suarez 1963).

Analyses with an electron microprobe (EDS mode) indicate only the presence of oxygen, a trace amount of Na due to contaminant material, and no elements with atomic number greater than 11. No attempt to analyze the mineral with WDS was made as its composition was unequivocally established by crystal-structure refinement.

X-RAY DATA AND REFINEMENT OF THE STRUCTURE

X-ray powder-diffraction data have been obtained at room temperature using a Philips PW1830 diffractometer, with CuKα radiation (Table 1). A least-squares fit of these data provided the following unit-cell parameters: monoclinic system, space group $P2_1/a$, with a 7.1243(6), b 8.8468(10), c 6.7699(7) Å, β 93.23(1)°, V 426.00(6) Å^3, $Z = 12$. These data are close to those of the corresponding synthetic compound (β-metaboric acid or HBO$_2$ II) reported by other authors (Table 2).

The crystal structure of the synthetic counterpart was determined and refined from single-crystal data by Zachariasen (1963) and Freyhardt $et\ al.$ (2000).

For our structure refinement of the natural material, single-crystal diffraction data were collected at room temperature by means of ω scans on a crystal fragment of about 0.20 × 0.03 × 0.02 mm, with MoKα radiation (λ = 0.71073 Å), using a BRUKER Apex II diffractometer equipped with a 2K CCD detector. A
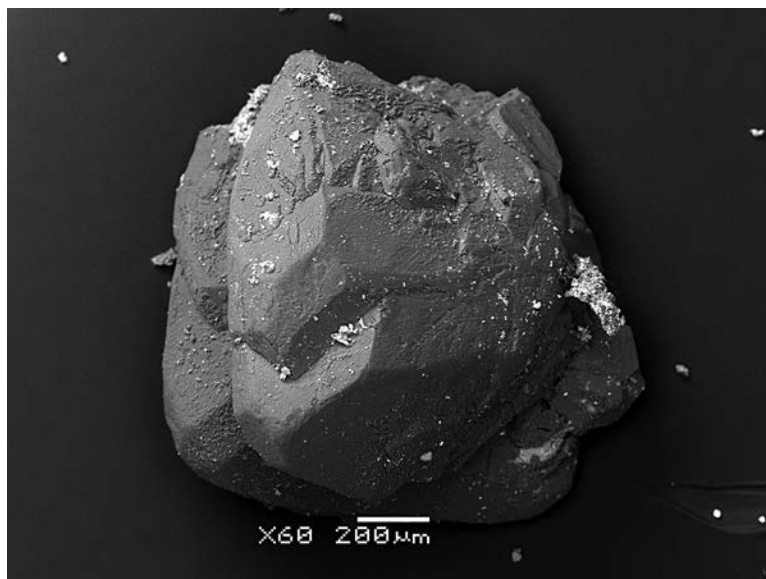

FIG. 1.   Scanning electron microscope (SEM) image (BSE) of clinometaborite.

one-minute exposure and 0.5° frame width were used. A total of 3218 reflections were measured, corresponding to a complete scan of the reciprocal lattice up to $2\theta_{max} = 63.54°$. Of these, 1372 were found to be unique ($R_{int} = 0.0256$). The unit-cell dimensions obtained from the single crystal were refined by least-squares from

1425 reflections with $I > 5\sigma(I)$; results are given in Table 3, together with other details concerning the data collection and refinement. The intensity data were reduced using the Bruker program SAINT, and corrected for Lorentz, polarization, and background. No violations of the systematic absences of the space group $P2_1/a$ were observed. An absorption correction was applied (maximum and minimum transmission factors 1.000 and 0.691, respectively) using the SADABS program (Sheldrick 2000). The structure was refined starting from the atom coordinates obtained by Freyhardt *et al.* (2000) and transformed into the $P2_1/a$ setting using the SHELXL97 program (Sheldrick 2008) implemented in the WINGX suite (Farrugia 1999). The final coordinates and displacement parameters of the atoms are reported in Table 4. The final R is 0.043 for 977 unique observed reflections [$I > 2\sigma(I)$]. A list of structure factors and a cif file are available from the Depository of Unpublished Data, on the Mineralogical Association of Canada website [document Chinometaborite CM49_1273].

RESULTS AND DISCUSSION

Metaboric acid exists in three crystalline phases, which are prepared by dehydration of orthoboric acid and subsequent heat treatment (Wells 1984, Cotton &

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR CLINOMETABORITE AND A COMPARISON WITH ITS SYNTHETIC COUNTERPART

	clinometaborite				synthetic**				
d_{obs} (Å)	d_{calc} (Å)*	I/Io	FWHM		d_{calc} (Å)	I/Io	h	k	l
6.773	6.759	15	0.16		6.753	33	0	0	1
					5.542	1	1	1	0
5.378	5.371	1	0.16		5.368	7	0	1	1
4.371	4.382	2	0.14		4.380	22	$\bar{1}$	1	1
4.193	4.197	20	0.17		4.195	100	1	1	1
3.557	3.556	5	0.20		3.556	5	2	0	0
3.318	3.255	4	0.20		3.324	5	$\bar{1}$	2	1
3.296	3.300	3	0.20		3.297	9	2	1	0
3.224	3.223	8	0.14		3.222	10	$\bar{2}$	0	1
					3.157	3	0	1	2
3.078	3.077	100	0.18		3.074	100	2	0	1
					3.027	2	$\bar{2}$	1	1
2.947	2.944	3	0.20		2.944	1	$\bar{1}$	1	2
2.836	2.831	4	0.20		2.831	2	1	1	2
					2.723	7	$\bar{1}$	3	0
2.702	2.703	8	0.15		2.701	10	0	3	1
2.685	2.685	3	0.15		2.685	10	0	2	2
2.550	2.546	10	0.14		2.550	11	$\bar{1}$	2	2
2.518	2.542	7	0.15		2.545	9	$\bar{1}$	3	1
					2.524	12	2	2	1
2.422	2.425	3	0.13		2.425	6	$\bar{2}$	1	2
2.385	2.384	1	0.13		2.383	1	2	0	2
					2.301	1	2	1	2
					2.290	2	3	1	0
					2.211	10	0	4	0
					2.206	8	$\bar{3}$	1	1
2.189	2.191	3	0.17		2.190	17	$\bar{2}$	2	2
					2.144	3	$\bar{1}$	3	2
					2.128	3	2	3	1
2.112	2.111	2	0.16		2.111	2	1	4	0
2.025	2.026	2	0.20		2.025	2	$\bar{1}$	4	1
2.007	2.008	4	0.20		2.008	15	0	2	3
1.958	1.958	3	0.18		1.958	6	$\bar{1}$	2	3
					1.916	1	$\bar{2}$	3	2
1.907	1.907	2	0.20		1.907	3	1	2	3
1.849	1.850	5	0.20		1.849	10	3	1	2
1.819	1.818	1	0.16		1.818	1	$\bar{3}$	2	2
					1.802	4	$\bar{3}$	3	1
					1.795	4	2	4	1
					1.791	3	0	3	3
1.778	1.778	2	0.18		1.778	2	4	0	0
					1.762	1	3	3	1
1.719	1.718	2	0.20		1.717	2	1	3	3
					1.711	3	0	5	1
1.697	1.696	3	0.25		1.696	2	4	0	1
					1.665	1	4	1	1
1.659	1.659	2	0.16		1.658	3	1	5	1
1.652	1.651	2	0.20		1.652	3	$\bar{3}$	1	3
					1.622	1	$\bar{4}$	2	1
					1.617	1	$\bar{3}$	4	0
1.612	1.612	1	0.20		1.612	1	$\bar{4}$	0	2
1.596	1.597	1	0.20		1.597	1	1	1	4
1.583	1.584	1	0.20		1.583	1	4	2	1

* Calculated from the unit cell obtained from least-squares refinement of the data in the first column using the program UNITCELL (Holland & Redfern 1997). E.s.d. on 2θ = 0.030°, average Δ2θ = 0.025°.
** PDF entry # 00–022–1109 (calculated pattern).

TABLE 2. CLINOMETABORITE: UNIT-CELL DIMENSIONS

	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
Our data (single crystal)	7.127(2)	8.842(3)	6.773(2)	93.21(1)	426.1(2)
Our data (powder diffraction)	7.1243(6)	8.8468(10)	6.7699(7)	93.23(1)	426.00(6)
Zachariasen (1963)	7.122(2)	8.842(2)	6.771(2)	93.26(1)	425.70(2)
Freyhardt *et al.* (2000)	7.075(2)	8.844(1)	6.758(1)	93.50(1)	422.07(2)

TABLE 3. CLINOMETABORITE: SINGLE-CRYSTAL DATA AND REFINEMENT PARAMETERS

Crystal system	monoclinic	Space group	$P2_1/a$ (no.14)
a (Å)	7.127(2)	β (°)	93.21(1)
b (Å)	8.842(3)	V (Å³)	426.1(2)
c (Å)	6.773(2)	Z	12
Radiation	Mo$K\alpha$	μ (mm⁻¹)	0.203
D$_{calc}$ (g/cm³)	2.049		
Measured reflections		3218	
hkl range		−10, 10/ −12,12/ −8, 9	
Independent reflections		1372	
Observed reflections [$I > 2\sigma(I)$]		977	
Parameters refined		94	
Final R and w$R2$		0.043, 0.144	
S		1.098	

Notes: $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (0.0885q)^2]$, where q = [max(0, Fo^2) + 2Fc^2)]/3; $S = \{\Sigma[w(Fo^2 - Fc^2)] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Wilkinson 1980). The present X-ray-diffraction data and structure refinement confirm the new mineral species to be the monoclinic polymorph of metaboric acid, β-HBO$_2$ or HBO$_2$ II.

In the cubic γ-HBO$_2$ phase (or HBO$_2$ I), corresponding to the mineral metaborite, all the boron atoms are equivalent by symmetry and display a tetrahedral coordination. The BO$_2$(OH)$_2$ tetrahedra are linked by sharing their corners to form a unique framework, analogous to that of cristobalite, so that the mineral can be classified as a mega-tectoborate, according to Strunz & Nickel (2001). A trigonal-planar coordination for all the boron atoms is observed instead in the orthorhombic α-HBO$_2$ phase (or HBO$_2$ III), known as a synthetic product only (Peters & Milberg 1964). Here the triangular building-blocks share their vertices to form [B$_3$O$_6$]$^{3-}$ rings that are linked by H$^+$ ions into pseudohexagonal sheets parallel to (001), and van der Waals interactions occur between sheets. Therefore the presence of isolated triborate anions allows one to classify this phase as neso-triborate.

The basic structural units observed in clinometaborite are six-membered B$_3$O$_3$ rings containing two three-coordinated boron atoms [B(2) and B(3)] and an additional boron atom [B(1)] in a distorted tetrahedral coordination, because of interaction with a H$_2$O molecule [O(5)]. The tetrahedral B(1) atom is displaced toward O(5) from the otherwise nearly planar

B$_3$O$_3$ ring by about 0.40 Å. In agreement with the fibrous aspect of the crystals, the six-membered rings are linked through the O(4) atoms to form polymeric chains extending along [010] in a zig-zag fashion (Fig. 2) and arranged to form layers parallel to (201). These chains are linked *via* hydrogen bonds between exocyclic O(6)–H(3) hydroxyl groups and endocyclic O(3) atoms within the same layer and *via* interlayer hydrogen bonds between the donor H$_2$O molecule O(5) and the acceptor O(1) and O(6) atoms of different layers (see Table 5, Fig. 3). Clinometaborite is therefore an ino-triborate. Three additional weaker contacts, reported in Table 5, may be considered as parts of a polyfurcated hydrogen-bonding system. Triborate rings like those found in clinometaborite, consisting of two triangular and one tetrahedral boron atoms, are rare, the only other known example being ameghinite, Na[B$_3$O$_3$(OH)$_4$] (Dal Negro *et al.* 1975), which is, however, a neso-triborate.

The discovery of the β-form of metaboric acid (or HBO$_2$ II) at Vulcano together with metaborite emphasizes the remarkable mineralogical and physicochemical interest of this locality. The overall complex picture points out the coexistence of different phases of boric acid, with the possibility of various combinations of planar BO$_3$ and tetrahedral BO$_4$ groups, depending on the conditions of formation. However, according to Wells (1962) and to Kracek *et al.* (1938), the polymorphism of HBO$_2$ provides a very good illustration

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS [$U_{eq}/U_{(i,j)}$, Å^2] OF ATOMS IN CLINOMETABORITE

Atom	X/a	Y/b	Z/c	$U_{eq}/U_{(i,j)}$
B(1)	0.23416(8)	-0.04313(6)	0.83071(7)	0.0149(1)
B(2)	0.26124(7)	0.21091(6)	0.97679(8)	0.0142(1)
B(3)	0.40077(7)	0.16241(6)	0.67183(8)	0.0146(1)
O(1)	0.21653(5)	0.06075(3)	0.99463(5)	0.0148(1)
O(2)	0.35331(5)	0.26191(4)	0.81577(5)	0.0193(1)
O(3)	0.35674(5)	0.01313(4)	0.68317(5)	0.0174(1)
O(4)	0.28810(5)	-0.19372(4)	0.87931(5)	0.0178(1)
O(5)	0.03355(5)	-0.04735(4)	0.72342(5)	0.0184(1)
O(6)	0.49777(5)	0.21595(4)	0.51815(5)	0.0202(1)
H(1)	0.012(1)	-0.130(1)	0.650(1)	0.0540(2)
H(2)	-0.068(1)	-0.048(1)	0.809(1)	0.0680(3)
H(3)	0.534(1)	0.136(1)	0.443(1)	0.0350(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B(1)	0.0221(2)	0.0106(2)	0.0128(2)	0.0012(2)	0.0078(2)	0.0004(2)
B(2)	0.0190(2)	0.0122(2)	0.0117(2)	0.0000(2)	0.0040(2)	0.0000(2)
B(3)	0.0208(2)	0.0116(2)	0.0119(2)	0.0011(2)	0.0046(2)	0.0000(2)
O(1)	0.0242(1)	0.0084(1)	0.0126(1)	-0.0018(1)	0.0068(1)	-0.0021(1)
O(2)	0.0322(2)	0.0110(1)	0.0159(1)	-0.0021(1)	0.0118(1)	-0.0040(1)
O(3)	0.0279(1)	0.0100(1)	0.0155(1)	0.0006(1)	0.0120(1)	-0.0009(1)
O(4)	0.0299(2)	0.0091(1)	0.0151(1)	0.0015(1)	0.0091(1)	0.0025(1)
O(5)	0.0229(1)	0.0157(2)	0.0169(1)	-0.0037(1)	0.0048(1)	-0.0010(1)
O(6)	0.0331(2)	0.0115(1)	0.0172(1)	0.0024(1)	0.0131(1)	0.0005(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[U_{11}h^2(a^*)^2 + ... + 2U_{12}hka^*b^* + ...]$;
$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE 5. CLINOMETABORITE: INTERATOMIC DISTANCES (Å) AND ANGLES (°)

B(1)–O(1)	1.4518(7)	B(2)–O(1)	1.3723(7)	B(3)–O(2)	1.3696(7)
B(1)–O(3)	1.4516(7)	B(2)–O(2)	1.3797(7)	B(3)–O(3)	1.3599(8)
B(1)–O(4)	1.4195(8)	B(2)–O(4)[a]	1.3502(7)	B(3)–O(6)	1.3660(7)
B(1)–O(5)	1.5676(7)				
<B(1)–O>	1.4726	<B(2)–O>	1.3674	<B(3)–O>	1.3652
O(1)–B(1)–O(3)	113.01(4)	O(3)–B(1)–O(5)	104.92(4)	O(2)–B(2)–O(4)[a]	121.40(5)
O(1)–B(1)–O(4)	116.75(4)	O(4)–B(1)–O(5)	108.26(4)	O(2)–B(3)–O(3)	121.09(5)
O(1)–B(1)–O(5)	104.70(4)	O(1)–B(2)–O(2)	120.59(4)	O(2)–B(3)–O(6)	118.39(5)
O(3)–B(1)–O(4)	108.39(4)	O(1)–B(2)–O(4)[a]	118.01(5)	O(3)–B(3)–O(6)	120.50(4)
B(1)–O(1)–B(2)	120.95(4)	B(2)–O(2)–B(3)	120.00(4)	B(1)–O(3)–B(3)	121.41(4)
B(1)–O(4) –B(2)	132.47(4)				

Hydrogen – bonding geometry

D – H•••A	D – H	H•••A	D•••A	D – H•••A
O(5) – H(1)•••O(6)[b]	0.893(8)	1.774(8)	2.658(1)	170.5(7)
O(5) – H(2)•••O(1)[c]	0.949(9)	1.752(9)	2.687(1)	167.5(8)
O(6) – H(3)•••O(3)[d]	0.917(6)	1.774(6)	2.682(1)	170.4(6)
O(5) – H(2)•••O(4)[e]	0.949(9)	2.559(9)	3.102(1)	116.6(7)
O(5) – H(2)•••O(2)[f]	0.949(9)	2.594(9)	2.916(1)	100.2(6)
O(5) – H(1)•••O(4)[e]	0.893(8)	2.771(9)	3.102(1)	103.4(5)
O(5) – H(1)•••O(5)[g]	0.893(8)	2.976(9)	3.151(1)	92.9(6)
O(6) – H(3)•••O(4)[d]	0.917(6)	2.633(7)	3.174(1)	118.5(5)

Symmetry codes: a = 1/2 – x, y + 1/2, 2 – z ; b = 1/2 – x, y – 1/2, 1 – z; c = –x, –y, 2 – z; d = 1 – x, –y, 1 – z; e = x – 1/2, –1/2 – y, z; f = x – 1/2, 1/2 – y, z; g = –x, –y, 1 – z.
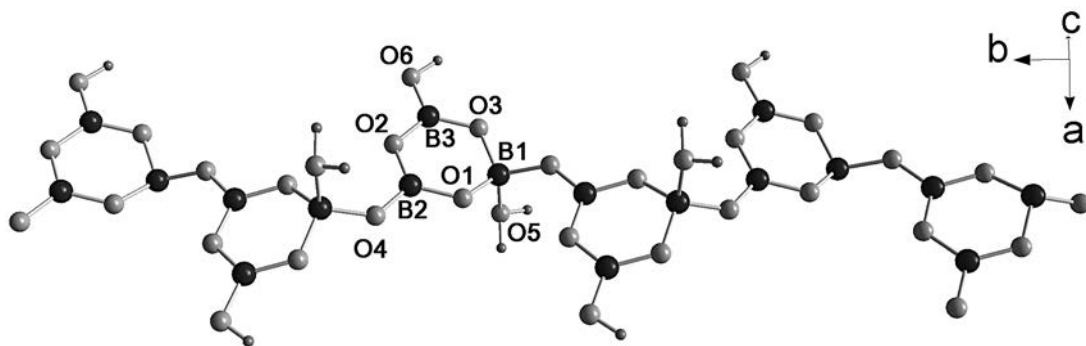

FIG. 2.   A polymeric chain in the structure of clinometaborite.

of monotropism, *i.e.*, of the actual existence of various forms, some of which (*e.g.*, clinometaborite) are not thermodynamically stable at any condition. For this reason, in view of absence of chemical equilibrium, the conditions of formation of this mineral cannot be deduced with a firm foundation. A suggestion from Wells (1962), that this form "is readily prepared by the dehydration of orthoboric acid in an open vessel at 130–140°C; heating it in a sealed tube for a long period at higher temperature gives the most stable [cubic] form" could well apply to our occurrence.

Such conditions should reasonably occur in some part of the fumaroles, where sassolite (orthoboric acid) is a common product.
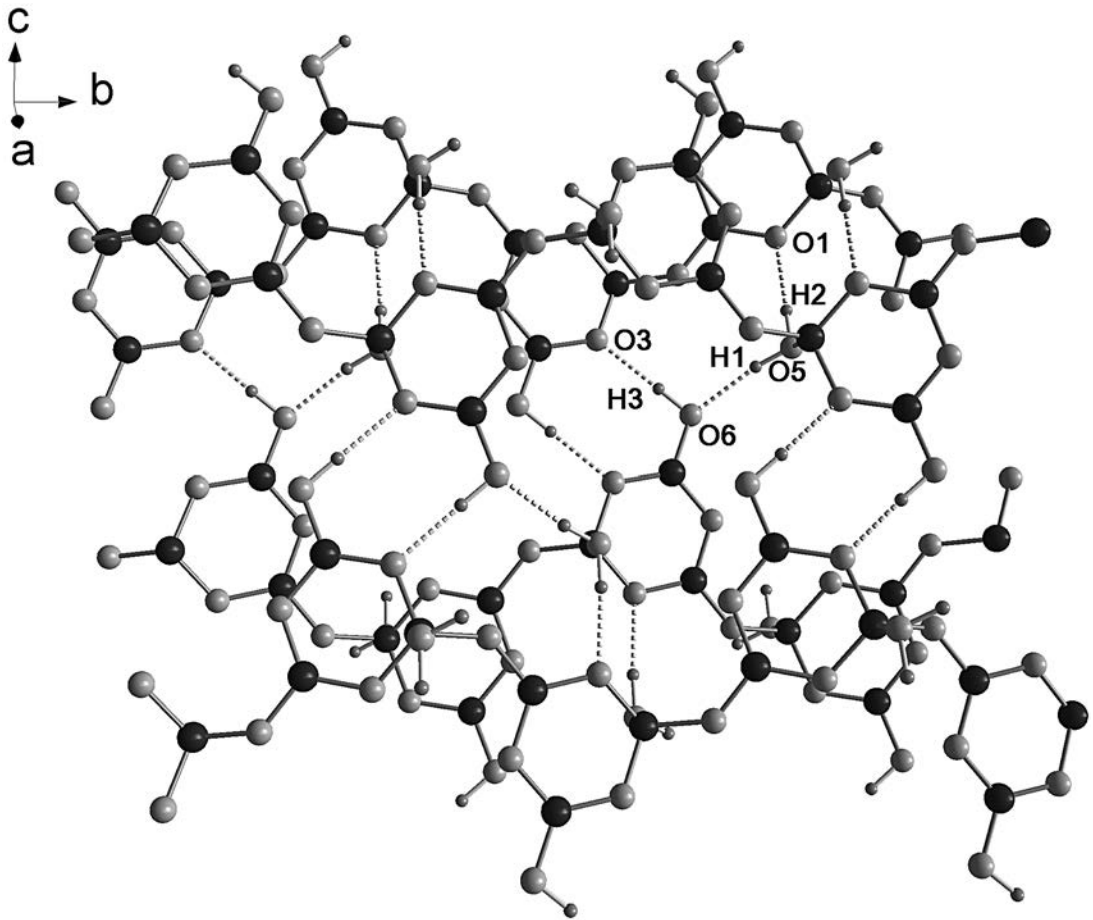
FIG. 3.   The pattern of hydrogen bonds in clinometaborite, with O...O interactions less than 2.7 Å.

REFERENCES

CAMPOSTRINI, I., DEMARTIN, F., GRAMACCIOLI, C.M. & RUSSO, M. (2011): *Vulcano. Tre secoli di mineralogia*. Associazione Micro-mineralogica Italiana Ed., Cremona, Italy [note that a review of this book is published in this issue].

COTTON, F.A. & WILKINSON, G. (1980): *Advanced Inorganic Chemistry* (4th ed.). Wiley Interscience, New York, N.Y.

DAL NEGRO, A., MARTIN POZAS, J.M. & UNGARETTI, L. (1975): The crystal structure of ameghinite. *Am. Mineral.* **60**, 879-883.

DEMARTIN, F., CAMPOSTRINI, I. & GRAMACCIOLI, C.M., (2009a): Panichiite, natural ammonium hexachlorostannate, $(NH_4)_2SnCl_6$, from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **47**, 367-372.

DEMARTIN, F., CASTELLANO, C., GRAMACCIOLI, C.M. & CAMPOSTRINI, I. (2010d): Aluminocoquimbite, $AlFe(SO_4)_3 \cdot 9H_2O$, a new aluminum iron sulfate from Grotta dell'Allume, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **48**, 1465-1468.

DEMARTIN, F., GRAMACCIOLI, C.M. & CAMPOSTRINI, I. (2009b): Demicheleite-(Cl), BiSCl, a new mineral from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Am. Mineral.* **94**, 1045-1048.

DEMARTIN, F., GRAMACCIOLI, C.M. & CAMPOSTRINI, I. (2009c): Brontesite, $(NH_4)_3PbCl_5$, a new product of fumarolic activity from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **47**, 1237-1243.

DEMARTIN, F., GRAMACCIOLI, C.M. & CAMPOSTRINI, I. (2010b): Pyracmonite, $(NH_4)_3Fe(SO_4)_3$, a new ammonium iron sulfate from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **48**, 307-313.

DEMARTIN, F., GRAMACCIOLI, C.M. & CAMPOSTRINI, I. (2010c): Adranosite, $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$, a new ammo-

nium sulfate chloride from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **48**, 315-321.

DEMARTIN, F., GRAMACCIOLI, C.M., CAMPOSTRINI, I. & ORLANDI, P. (2008a): Knasibfite, $K_3Na_4[SiF_6]_3[BF_4]$, a new hexafluorosilicate-tetrafluoroborate from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **46**, 419-425.

DEMARTIN, F., GRAMACCIOLI, C.M., CAMPOSTRINI, I. & ORLANDI, P. (2008b): Thermessaite $K_2[AlF_3|SO_4]$, a new ino-aluminofluoride-sulfate from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **46**, 693-700.

DEMARTIN, F., GRAMACCIOLI, C.M., CAMPOSTRINI, I. & ORLANDI, P. (2008c): Demicheleite, BiSBr, a new mineral from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Am. Mineral.* **93**, 1603-1607.

DEMARTIN, F., GRAMACCIOLI, C.M., CAMPOSTRINI, I. & PILATI, T. (2010a): Aiolosite, $Na_2(Na_2Bi)(SO_4)_3Cl$, a new sulfate isotypic to apatite from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Am. Mineral.* **95**, 382-385.

FARRUGIA, L.J. (1999): WINGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32**, 837-838.

FREYHARDT, C.C., WIEBCKE, M. & FELSCHE, J. (2000): The monoclinic and cubic phases of metaboric acid (precise redeterminations). *Acta Crystallogr.* **C56**, 276-278.

HISATSUNE, I.C. & HADDOCK SUAREZ, N. (1963): Infrared spectra of metaborate monomer and trimer ions. *Inorg. Chemistry* **3**(2), 168-174.

HOLLAND, T.J.B. & REDFERN, S.A.T. (1997): Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineral. Mag.* **61**, 65-77.

KRACEK, F.C., MOREY, G.W. & MERWIN, H.E. (1938): The system water–boron oxide. *Am. J. Sci.* **235-A**, 143-171.

LOBANOVA, V.V. & AVROVA, N.P. (1964): The new mineral metaborite – natural metaboric acid. *Zap. Vses. Mineral. Obshchest.* **93**, 329-334 (in Russian).

PETERS, C.R. & MILBERG, M.E. (1964): The refined structure of orthorhombic metaboric acid. *Acta Crystallogr.* **17**, 229-234.

SHELDRICK, G.M. (2000): *SADABS Area-Detector Absorption Correction Program.* Bruker AXS, Milwaukee, Wisconsin.

SHELDRICK, G.M. (2008): A short history of SHELX. *Acta Crystallogr.* **A64**, 112-122.

STRUNZ, H. & NICKEL, E.H. (2001): *Strunz Mineralogical Tables* (9th ed.). E. Schweizerbart'sche Verlaagsbuchhandlung, Stuttgart, Germany.

WELLS, A.F. (1962): *Structural Inorganic Chemistry* (3rd ed.). Clarendon Press, Oxford, U.K.

WELLS, A.F. (1984): *Structural Inorganic Chemistry* (5th ed.). Clarendon Press, Oxford, U.K.

ZACHARIASEN, W.H. (1963): The crystal structure of monoclinic metaboric acid. *Acta Crystallogr.* **16**, 385-389.