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DERBYLITE FROM BUCA DELLA VENA MINE, APUAN ALPS, ITALY

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ABSTRACT

The second occurrence of derbylite is reported. The mineral occurs within microcrystalline barite and in cavities within dolomite in the metasomatic mineralization of the Buca della Vena iron mine, Apuan Alps, Italy. Derbylite is black with a metallic lustre; it commonly occurs as twins consisting of two or three individuals. New data are given for the mineral, including its X-ray powder-diffraction pattern; the strongest five lines [*d* in Å (I) (*hkl*)] are: 2.853(100) (131), 2.674(73)($\bar{2}$31), 3.186(43) (140, 121), 2.479(23) ($\bar{1}$02) and 2.393(23) (060). Analytical data were determined for uncontaminated material. Derbylite from Buca della Vena contains more titanium than reported for the sample from Diamantina, Brazil. The higher charge due to titanium is balanced by substitution of Fe^{2+} for Fe^{3+}. The chemical data lead to the structural formula $Fe^{2+}_{\geq 0.45}Fe^{3+}_{\leq 2.90}Ti^{4+}_{3.66}Sb_{0.99}O_{\leq 13.11}(OH)$.

Keywords: derbylite, powder pattern, structural formula, Apuan Alps, Italy, iron, titanium, antimony.

SOMMAIRE

Nous décrivons ici le deuxième gîte de derbylite. Le minéral est inclus dans une baryte microcristalline et à l'intérieur de cavités dans la dolomie du gisement métasomatique de la mine de fer de Buca della Vena, dans les Alpes apouennes (Italie). La derbylite, noire, à éclat métallique, se présente communément sous forme de macles formées de deux ou trois cristaux. Nous présentons de nouvelles données sur cette espèce, en particulier le diagramme de diffraction X de poudre; les cinq raies les plus intenses [*d* en Å(I)(*hkl*] sont: 2.853(100)(131), 2.674(73)($\bar{2}$31), 3.186(43)(140, 121), 2.479(23)($\bar{1}$02) et 2.393(23)(060). De plus, on présente des données chimiques obtenues sur matériau pur. La derbylite de la mine Buca della Vena a une teneur en titane plus élevée que celle d'un échantillon de Diamantina (Brésil). La substitution de Fe^{2+} au Fe^{3+} compense l'excédent de charge positive résultant de la teneur élevée en titane. L'analyse chimique donne la formule structurale $Fe^{2+}_{\geq 0.45}Fe^{3+}_{\leq 2.90}Ti^{4+}_{3.66}Sb_{0.99}O_{\leq 13.11}(OH)$.

(Traduit par la Rédaction)

Mots-clés: derbylite, cliché de poudre, formule structurale, Alpes apouennes, Italie, fer, titane, antimoine.

INTRODUCTION

Derbylite was discovered by Hussak & Prior (1897) and was described as an antimonotitanate of iron found in the placers of Tripuhy, near Ouro Prieto, Minas Gerais, Brazil. The mineral was thought to originate from the weathering of nearby muscovite schist. Although Hussak & Prior (1897) described the main physical properties of the mineral, they incorrectly assigned it to the orthorhombic system, and they were not able to obtain a chemical analysis from uncontaminated material.

Using crystals from Diamantina, Minas Gerais, Brazil, Moore & Araki (1976) found that derbylite is monoclinic $P2_1/m$, and has the formula: $Fe^{3+}{}_4Ti^{4+}{}_3Sb^{3+}O_{13}(OH)$. Derbylite proved to be a closed-packed (...*chh*...) oxide structure, with iron and titanium located within the octahedral voids. An anion position is not occupied by oxygen atoms, but by a slightly displaced and ψ-tetrahedrally coordinated antimony atom.

Notwithstanding the conclusive nature of the structural study, neither the X-ray powder-diffraction pattern nor a chemical composition determined on uncontaminated material was available. The lack of these data and the scarcity of derbylite led us to describe this second occurrence from Buca della Vena mine, Apuan Alps, Italy.

OCCURRENCE

The Buca della Vena iron mine is located north of Stazzema, in the upper Versilia valley, central Italy. Iron ore (magnetite, hematite and minor pyrite) occurs within a microcrystalline mass of barite. The mineralization is attributed to metasomatism by medium-temperature hydrothermal fluids introduced along the contact between phyllite and dolomite (Carmignani *et al.* 1977). A full description of the many mineral species found here is in preparation by P. Orlandi. Veins of recrystallized dolomite and barite occur within the microcrystalline mineralized body as well as at the contact between this body and the surrounding dolomite country rock. Derbylite occurs in these veins, in cavities inside the veins or embedded within the recrystallized dolomite or barite. Associated minerals are pyrite, sphalerite, bournonite, schafarzikite, versiliaite and apuanite. Derbylite is very rare; less than ten specimens are known. Derbylite from the two occurrences is present as euhedral, black crystals up to 2 mm long, with a metallic lustre and conchoidal fracture. The habit is prismatic, and the forms {*hk0*} are the most developed.

Twins consisting both of two and three individuals have been observed (Figs. 1, 2). The composition plane of the twins is ($\bar{1}$53). The drawing in Figure 1 is slightly idealized in that a ß angle of 103.4° instead of 104.7° was used to effect closure of the twin. The three crystals giving rise to the twin are characterized by a nearly parallel orientation of the (100) faces. The observed forms are: {100}, {110}, {120}, $\{\bar{1}01\}$, {010}}, $\{\bar{1}02\}$, $\{\bar{2}01\}$, $\{\bar{1}11\}$, $\{\bar{2}11\}$, $\{\bar{2}31\}$.

In reflected light, derbylite from Buca della Vena Mine is grey with bluish green reflections. Reflectivities measured at λ values of 470, 546, 586 and 650 nm give R_1 21.7, 19.9, 19.2 and 18.4 and R_2 19.7, 17.9, 17.0 and 16.6%, respectively. Metatype derbylite is deposited in the mineralogical collection of our Department (#4498).

X-RAY CRYSTALLOGRAPHY

Single-crystal X-ray-diffraction patterns of derbylite from Buca della Vena mine agree well with the data given by Moore & Araki (1976). The crystals are monoclinic; systematic extinctions in 0*k*0, $k = 2n+1$, indicate $P2_1$ or $P2_1/m$ as the possible space-groups. Unit-cell parameters refined by least-squares fitting of the X-ray powder-diffraction lines (Table 1) are: *a* 7.156(2), *b* 14.354(4), *c* 4.980(1) Å, ß 104.69(2)°; Moore & Araki (1976) obtained *a* 7.160(1), *b* 14.347(3), *c* 4.970(1) Å, ß 104.61(2)°. The close correspondence between the two sets of parameters seems to exclude large compositional differences, at least for cations of grossly different radii.

CHEMICAL COMPOSITION

Results of a qualitative XRF analysis of derbylite show abundant iron, titanium and antimony, with

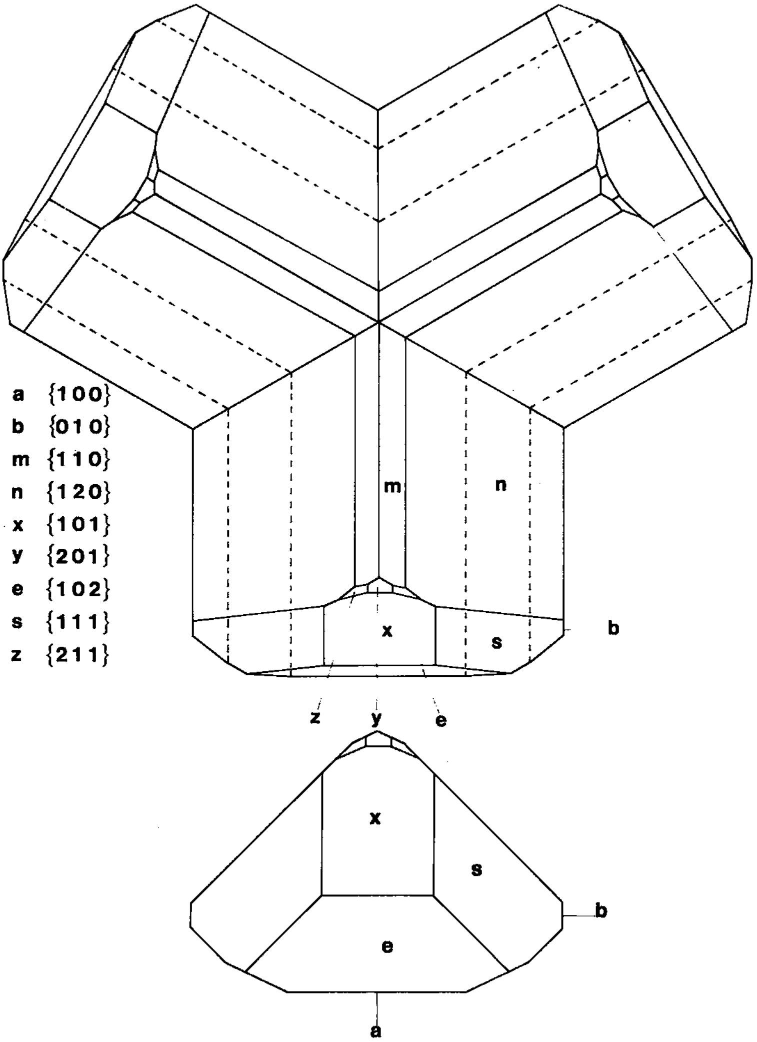

Fig. 1. A well-developed twin of derbylite.

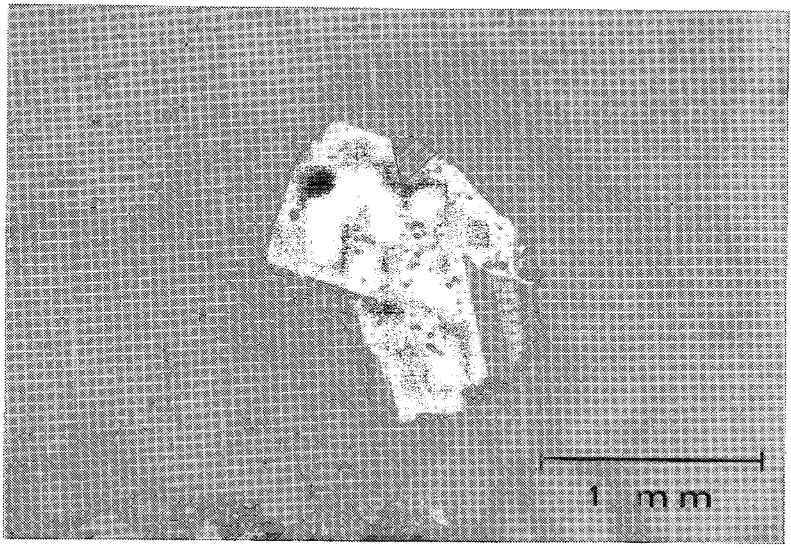

Fig. 2. Typical habit of triple twins of derbylite.

no other element with $Z > 11$. The quantitative analysis was done with an ARL-SEMQ fully automated electron-microprobe analyzer, using a 15 kV acceleration voltage, beam size of approximately 5 μm in diameter, crystal spectrometers and standards of natural ilmenite, magnetite and stibnite. Raw data from eight different points were averaged and corrected by the MAGIC IV program to produce the data given in column a of Table 2.

The low sum of the oxides (93.75 wt.%, apart from water) led us to check the iron and titanium contents by atomic absorption spectrometry. Whereas the iron content did not change significantly, a considerably higher titanium content was obtained (Table 2). Although the reason for this bias in the microprobe analysis is not known, it seemed appropriate to combine the chemical data given, as is done in columns c and d of Table 2. The values used are the atomic absorption for titanium, the microprobe analytical result for antimony and an average value for iron. The water content was calculated assuming one hydroxyl per formula unit, as indicated by Moore & Araki (1976). The same solution used for the atomic absorption analysis was tested also for the Fe^{2+}/Fe^{3+} ratio by conventional analytical wet methods. This test, in this case, gives only the lower limit of the FeO content (13.4% of the total iron). In fact, the strongly oxidizing reagents used to dissolve derbylite were also expected to be eventually able to oxidize the ferrous iron.

The value of density, determined by torsion balance on several fragments of derbylite, whose weight ranged from 1.5 to 3.0 mg, is 4.62(14)

TABLE 1. X-RAY POWDER-DIFFRACTION PATTERN FOR DERBYLITE

d_{obs}	d_{calc}	I/I_o	*hkl*
6.24	6.24	12	110
4.98	4.98	4	120
4.811	4.817	10	001
4.529	4.529	9	101
4.322	4.319	3	$\bar{1}11$
3.997	4.000	18	021
3.934	3.936	2	130
3.830	3.830	16	$\bar{1}21$
3.588	3.588	8	040
3.554	3.554	2	101
3.461	3.461	2	200
3.453	3.450	2	111
3.366	3.365	6	210
3.223	3.225	7	$\bar{2}01$
3.186	3.186*	43	140
	3.185		121
3.136	3.146	8	$\bar{2}11$
3.118	3.118	33	220
2.942	2.942	5	$\bar{2}21$
2.877	2.878	8	041
2.853	2.853	100	131
2.813	2.813	14	$\bar{1}41$
2.674	2.674	73	$\bar{2}31$
2.524	2.525*	5	141
	2.524		201
2.485	2.491	5	240
	2.486*		221
2.479	2.478	23	$\bar{1}02$
2.466	2.466	7	051
2.425	2.425	2	$\bar{1}51$
2.393	2.392	23	060
2.292	2.293	8	$\bar{3}11$
2.279	2.278	3	310
2.260	2.261	5	160
2.232	2.233*	12	151
	2.232		231
2.206	2.210	3	$\bar{3}21$
	2.209		250
	2.200		$\bar{1}32$
	2.197		320
2.145	2.144*	17	$\bar{2}51$
	2.143		061
2.112	2.115	6	$\bar{1}61$
	2.114		102
2.091	2.092	4	112
	2.090		$\bar{3}31$
2.055	2.064	2	241
	2.047		$\bar{2}32$
2.028	2.028	8	122
1.999	2.000	4	042
1.916	1.915	6	$\bar{2}42$
1.836	1.838	5	321
1.806	1.806	6	$\bar{3}51$
1.776	1.778	9	$\bar{4}01$
	1.778		$\bar{2}52$
	1.777*		202
	1.776		171
1.764	1.767	7	331
	1.765		$\bar{4}11$
	1.764		270
	1.763		212
1.721	1.721	14	$\bar{1}62$
1.612	1.612*	10	$\bar{4}02$
	1.612		$\bar{2}13$

Diffractometer, Mn-filtered radiation (λ 1.9372 Å), LiF internal standard, speed 0.5° min^{-1}. Only unambiguously indexed reflections were used in the least-squares refinement. The starred d^*_{calc} values correspond to the most likely assignment of indices, based on the structure factors of Moore & Araki (1976).

TABLE 2. CHEMICAL DATA FOR DERBYLITE FROM BUCA DELLA VENA MINE

	a	b	c	d	e
TiO_2	37.36	40.20	40.20	40.20	3.66
FeO	-----	-----	-----	4.44	0.45
Fe_2O_3	36.59	36.79	36.69	31.83	2.90
Sb_2O_3	19.80	-----	19.80	19.80	0.99
H_2O	-----	-----	1.24	1.24	1.00
				97.51	O=14.11

a) Microprobe data; b) Atomic absorption data; c) Combined data
d) Combined data with iron shared between FeO and Fe_2O_3;
e) Atoms per unit formula, on the basis of eight cations.

g/cm³. This value must be compared with a calculated density of 4.762 g/cm³. Correct ratios were also obtained between the numbers of octahedral and ψ-tetrahedral antimony cations. The ferrous iron content (0.45 atoms per formula unit) is in accord with the number of titanium atoms (0.66 per formula unit), which exceeds the proportions in the ideal formula proposed by Moore & Araki (1976).

CRYSTAL CHEMISTRY OF DERBYLITE

The titanium content of derbylite from the Buca della Vena mine is higher than that given by Moore & Araki (1976) for derbylite from Diamantina. Consequently, iron is present not only as Fe^{3+}, but also as Fe^{2+} to maintain charge balance. Ideally, (4-x) iron atoms are present in the formula unit for (3 + x) titanium atoms. Of these, (4–2x) represent the ferric content and x the ferrous iron. The resulting idealized crystal-chemical formula, $Fe^{2+}{}_{x}Fe^{3+}{}_{(4-2x)}Ti^{4+}{}_{(3+x)}Sb^{3+}O_{13}(OH)$, compares favorably with the determined formula: $Fe^{2+}{}_{0.45}Fe^{3+}{}_{2.90}Ti^{4+}{}_{3.66}Sb_{0.99}O_{13.11}(OH)$. Of the four independent octahedral positions, the one designated $M(2)$ seems to be the most appropriate for the Fe^{2+} cations. This is the largest octahedral site, and its average bond-distance of 2.045 Å fits a site population of $0.32Fe^{2+} + 0.68Fe^{3+}$, calculated using the ionic radii given by Shannon & Prewitt (1969) and assuming three coordinated oxygen atoms.

Such a site-population factor corresponds to 0.64 Fe^{3+} cations per formula unit. As stressed by Moore & Araki (1976), $M(1)$ is fully occupied by titanium cations, whereas $M(3)$ and $M(4)$ share the remainder fairly equally. The formula: $Ti(Fe^{2+}{}_{0.45}Fe^{3+}{}_{1.55})(Fe^{3+}{}_{0.67}Ti^{4+}{}_{1.33})(Fe^{3+}{}_{0.67}Ti^{4+}{}_{1.33})Sb_{0.99}O_{13.11}(OH)$ gives the contents of M sites from $M(1)$ to $M(4)$. The slightly larger dimensions of the $M(4)$ site compared to $M(3)$ may indicate a slightly higher Fe^{3+} content in $M(4)$. The cationic distributions within the $M(2)$ site on the one hand and the $M(3)$, $M(4)$ sites on the other are probably related: when $M(2)$ is occupied by Fe^{2+}, $M(3)$ and $M(4)$ are enriched in titanium. When $M(2)$ is occupied by Fe^{3+}, more Fe^{3+} is present in the $M(3)$ and $M(4)$ sites. Ordered schemes of distribution within these sites might lead to the lower symmetry $P2_1$.

Moore & Araki (1976) have stressed the coexistence of Fe^{3+} and Sb^{3+} in derbylite, despite the redox potentials, which would favor the pair Fe^{2+} and Sb^{5+}. The coexistence must now be expanded to include Fe^{2+}. This assemblage of oxidation states is not new; it was first found in versiliaite $Fe^{2+}{}_4Fe^{3+}{}_4Fe^{3+}{}_4Sb^{3+}{}_{12}O_{32}S_2$ and apuanite $Fe^{2+}{}_4Fe^{3+}{}_8Fe^{3+}{}_8Sb^{3+}{}_{16}O_{48}S_4$ (Mellini *et al.* 1979, Mellini & Merlino 1979, Perchiazzi 1982). These two minerals occur with derbylite at the Buca della Vena mine; all probably crystallized under very similar physical and chemical conditions.

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