Brumadoite, a new copper tellurate hydrate, from Brumado, Bahia, Brazil

D. Atencio[1],*, A. C. Roberts[2], P. A. Matioli[3], J. A. R. Stirling[2], K. E. Venance[2], W. Doherty[2], C. J. Stanley[4], R. Rowe[5], G. J. C. Carpenter[6] and J. M. V. Coutinho[1]

[1] Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080, São Paulo, SP, Brazil
[2] Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, K1A 0E8, Canada
[3] Museu de Ciências Naturais José Bonifácio de Andrada e Silva (Jobas) − Largo Marquês de Monte Alegre, s/no., Valongo, Centro Histórico, 11010-260, Santos, SP, Brazil
[4] Department of Mineralogy, Natural History Museum, London SW7 5BD, UK
[5] Canadian Museum of Nature, PO Box 3443, Station D, Ottawa, Ontario, K1P 6P4, Canada
[6] Materials Technology Laboratories, Natural Resources Canada, 568 Booth Street, Ottawa, Ontario, K1A 0G1, Canada

ABSTRACT

Brumadoite, ideally $Cu_3Te^{6+}O_4(OH)_4 \cdot 5H_2O$, is a new mineral from Pedra Preta mine, Serra das Éguas, Brumado, Bahia, Brazil. It occurs as microcrystalline aggregates both on and, rarely, pseudomorphous after coarse-grained magnesite, associated with mottramite and quartz. Crystals are platy, subhedral, $1-2$ μm in size. Brumadoite is blue (near RHS 114B), has a pale blue streak and a vitreous lustre. It is transparent to translucent and does not fluoresce. The empirical formula is $(Cu_{2.90}Pb_{0.04}Ca_{0.01})_{\Sigma 2.95}$ $(Te^{6+}_{0.93}Si_{0.05})_{\Sigma 0.98}O_{3.92}(OH)_{3.84} \cdot 5.24H_2O$. Infrared spectra clearly show both (OH) and H_2O. Microchemical spot tests using a KI solution show that brumadoite has tellurium in the 6^+ state. The mineral is monoclinic, $P2_1/m$ or $P2_1$. Unit-cell parameters refined from X-ray powder data are a 8.629(2) Å, b 5.805(2) Å, c 7.654(2) Å, β 103.17(2)°, V 373.3(2) Å^3, Z = 2. The eight strongest X-ray powder-diffraction lines [d in Å,(I),(hkl)] are: 8.432,(100),(100); 3.162,(66),($\bar{2}$02); 2.385,(27),(220); 2.291,(12),($\bar{1}$22); 1.916,(11),(312); 1.666,(14),($\bar{4}$22,114); 1.452,(10),(323,040); 1.450,(10),(422,403). The name is for the type locality, Brumado, Bahia, Brazil. The new mineral species has been approved by the CNMNC (IMA 2008-028).

Introduction

BRUMADOITE, ideally $Cu_3Te^{6+}O_4(OH)_4 \cdot 5H_2O$, has been approved by the CNMNC (IMA 2008-028). The name is for the type locality, Brumado, Bahia, Brazil. The new mineral was found by Paulo A. Matioli and the late Carlos P. Barbosa in 1993 and is the only example, to date, to have been found. Part of the holotype material is deposited under the code DR679 in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, São Paulo, SP, Brazil (http://www2.igc.usp.br/museu/), and part under the code M5528 in the Museu José Bonifácio de Andrada e Silva, Santos, SP, Brazil (http://www.museujobas.hpg.ig.com.br/index2.htm). Microgram portions (with magnesite) are housed within the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa (NMC 068161). The polished section used for both the electron microprobe analyses and the reflectance study is preserved at the Natural History Museum, London, UK, as BM 2008, 32.

Occurrence

Brumadoite occurs in association with magnesite at the Pedra Preta mine, Serra das Éguas (14º30′S, 41º40′W), Brumado, Bahia, Brazil (Barbosa *et al.*, 2000). The prominent basement rocks in the Brumado area are Precambrian in age and consist predominantly of gneisses, schists, and amphibolites. A metamorphosed sequence, comprising a lower unit of dolomite and an upper unit of quartzite, overlies the basement rocks. The dolomite (with minor thin quartzite layers) is generally saccharoidal and ranges from grey to tan in colour. The upper unit consists of several hundred metres of white to grey quartzite that form prominent outcrops in the area. The deposits of magnesite are probably the result of replacement of dolomite and, to a lesser extent, of fracture filling. Evidently, the wealth of minerals found at Brumado is related to the intrusion of igneous dykes and associated hydrothermal mineralization. The following stages of mineralization are evident (Bodenlos, 1954; Cassedanne and Cassedanne, 1978):

(1) formation of the magnesite deposit as a hydrothermal replacement of pre-existing dolomite;

(2) deposition of coarse-grained magnesite in fractures and open spaces;

(3) deposition of quartz and several aluminosilicates in fissures;

(4) fracture filling of minor fractures with calcite, fine-grained magnesite, and other late-stage minerals.

Brumadoite occurs as a late fracture filling in the coarse-grained magnesite. It is associated with mottramite and quartz. The primary origin of the tellurium is unknown.

Habit and physical properties

Brumadoite occurs as microcrystalline aggregates both on and, rarely, pseudomorphous after magnesite (Fig. 1). Crystals are platy, subhedral, and scanning electron microscopy study shows them to be $1-2$ μm in size. Crust thickness does not exceed 100 μm. The pinacoid {100} form was confirmed by a convergent beam electron-diffraction (CBED) study. The mineral is blue in colour (similar to RHS 114B), its streak is pale blue and its lustre is vitreous. The mineral is transparent (as individual crystals) to translucent (massive). It is not fluorescent under either long- or short-wave ultraviolet light. Mohs hardness

FIG. 1. Brumadoite (blue) with mottramite (black) on magnesite from the Pedra Preta mine, Brumado, Bahia, Brazil. The longest dimension of the specimen is 6.5 cm.

could not be determined because insufficient pure material was available, but the mineral was easily crushed between two glass slides; tenacity is brittle. Neither cleavage nor parting was observed; fracture is uneven. The CBED shows multiple intergrowths on a submicrometric scale. The amount of available material is insufficient for a Berman balance density determination; the calculated density is 4.768 g/cm^3, based on the

TABLE 1. Reflectance data for brumadoite.

Reflectance (%)	Wavelength (nm)
11.4	400
11.0	420
10.6	440
10.3	460
10.2	470(COM)
10.0	480
9.7	500
9.4	520
9.0	540
8.9	546(COM)
8.7	560
8.4	580
8.3	589(COM)
8.3	600
8.3	620
8.3	640
8.3	650(COM)
8.4	660
8.5	680
8.6	700

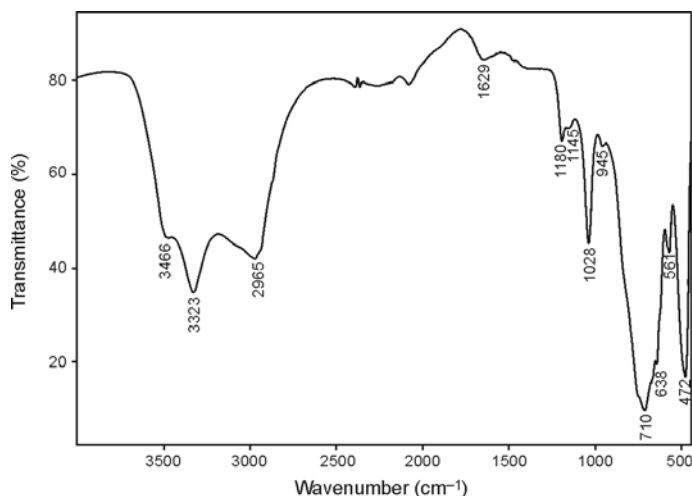COM: minimum requirements by the IMA-COM (Commission on Ore Minerals)

FIG. 2. IR spectrum of brumadoite.

empirical formula and unit-cell parameters refined from powder data.

Optical properties

In transmitted light, brumadoite has a mean refractive index (n) of ~1.79 (white light) and is pleochroic. In reflected light, the colour is grey with no discernible bireflectance. Anisotropic effects are masked by internal reflections (ubiquitous blue). Reflectance data were obtained in air from 400−700 nm using a Zeiss Axiotron microscope equipped with a Crystal Structures (Lanham) specimen − standard levelling super-stage and a J & M Tidas diode array spectrometer at the Natural History Museum, London. Measurements were made relative to a Zeiss SiC standard using Cavendish Instruments *Onyx*

software at intervals of 0.823 nm. Data were obtained in air (R′ because there was no detectable change on rotation of the stage) and are presented in Table 1. Oil data were impossible to collect due to internal reflections. Only one very small area (10 μm × 10 μm) was available for air data because of ubiquitous internal reflections. For $k = 0$, n at 589 nm = 1.81, which is in good agreement with that obtained from transmitted light.

Infrared spectroscopy

Infrared spectra (Fig. 2) clearly show both (OH) and H_2O. Strong bands at 2965, 3323 and 3466 cm^{-1} are due to O−H stretching in both the (OH) groups and the H_2O molecules; a small peak at 1629 cm^{-1} is due to the H−O−H bending

TABLE 2. Electron microprobe data for brumadoite.

Constituent	Wt.%	Range	Standard dev.	Probe standard
TeO_3	30.58	29.74−31.01	0.284	synthetic altaite (PbTe)
SiO_2	0.55	0.42−0.63	0.026	wollastonite
CaO	0.07	0.04−0.12	0.016	wollastonite
CuO	43.05	41.62−44.24	0.596	synthetic cuprite (Cu_2O)
PbO	1.70	1.44−2.08	0.135	synthetic PbO
H_2O*	24.05			
Total	100.00			

* By difference (based on H_2O confirmation and absence of carbonate bands by IR spectroscopy).

mode of H_2O. Other strong bands in the spectra are unassigned, but probably relate to Te−O and Cu−O interactions. There are no bands in the spectra that are indicative of carbonate groups.

Chemical data

Chemical analyses (16) were carried out by means of a Cameca SX50 electron microprobe: operated in wavelength dispersive spectrometry (WDS) mode, with an accelerating potential of 20 kV, a probe current of 10 nA, a 5 μm beam diameter and a counting time of 10 s on peak, 5 s on background.

H_2O bands were identified in IR spectra but there was insufficient pure material for the water content to be determined by classical methods. Infrared spectroscopy indicates that carbonate groups are absent.

The analytical results obtained are presented in Table 2.

Microchemical spot tests using a KI solution show that brumadoite has tellurium in the 6+ state. The KI solution was prepared with 2 g of reagent-grade KI crystals dissolved in 20 ml of 0.16 N ultra-high purity HNO_3 and doubly-distilled water. The spot tests were performed within 1 h of preparation on two tellurates, brumadoite and jensenite ($Cu_3Te^{6+}O_6 \cdot 2H_2O$), both totally unreactive in the KI solution, and on three tellurites, teineite ($CuTe^{4+}O_3 \cdot 2H_2O$), reagent-grade $Te^{4+}O_2$ (synthetic paratellurite, confirmed by X-ray powder diffractometer), and reagent-grade $K_2Te^{4+}O_3$, where almost immediate reaction with the KI solution occurred, turning orange-brown around the crystal. Consequently, we infer that brumadoite is a tellurate and it would appear that these spot tests are a reasonably simple way to differentiate tellurites from tellurates.

The empirical formula (based on 13 oxygen atoms) is $(Cu_{2.90}Pb_{0.04}Ca_{0.01})_{\Sigma 2.95}$ $(Te^{6+}_{0.93}Si_{0.05})_{\Sigma 0.98}O_{3.92}(OH)_{3.84} \cdot 5.24H_2O$. The end-member formula is $Cu_3Te^{6+}O_4(OH)_4 \cdot 5H_2O$, which can be expressed as: CuO = 44.16 wt.%, TeO_3 = 32.50 wt.% and H_2O = 23.34 wt.%, totalling 100 wt.%.

Crystallography

Single-crystal X-ray studies could not be carried out because of the very small crystal size. The symmetry and unit-cell parameters of brumadoite were determined by a combination of trial-and-error indexing and CBED studies. The mineral was sensitive to the electron beam, to the extent that a finely focused electron beam rapidly destroyed the thin grains. A number of electron-diffraction patterns were acquired, but interpretable ones were a challenge because of the small scale of the substructure and the pervasive submicrometer-scale multiple intergrowths. All observations are

TABLE 3. X-ray powder-diffraction data for brumadoite.

	I (%)	$d_{meas.}$(Å)	$d_{calc.}$(Å)	h	k	l
	100	8.432	8.402	1	0	0
	5	7.428	7.453	0	0	1
*	4	6.345	6.338	$\bar{1}$	0	1
*	4	4.576	4.580	0	1	1
	4	4.171	4.201	2	0	0
*	7	3.747	3.736	$\bar{1}$	0	2
*	7	3.724	3.726	0	0	2
	3	3.428	3.403	2	1	0
*	4	3.339	3.337	$\bar{2}$	1	1
*	**66**	3.162	3.169	$\bar{2}$	0	2
*	2	2.907	2.903	0	2	0
*	4	2.799	2.801	3	0	0
*	5	2.741	2.743	1	2	0
	2	2.567	2.554	$\bar{3}$	1	1
*	8	2.525	2.523	3	1	0
*	3	2.484	2.484	0	0	3
*	**27**	2.385	2.388	2	2	0
*	**12**	2.291	2.292	$\bar{1}$	2	2
*	2	2.136	2.135	1	2	2
*	2	2.101	2.101	4	0	0
*	7	2.016	2.015	3	2	0
*	**11**	1.916	1.914	3	1	2
*	5	1.868	1.868	$\bar{2}$	0	4
	14	1.666	1.669	$\bar{4}$	2	2
			1.664	1	1	4
	3	1.596	1.598	$\bar{1}$	2	4
			1.596	4	2	1
*	5	1.575	1.575	2	0	4
*	2	1.510	1.511	5	1	1
*	6	1.496	1.496	$\bar{3}$	2	4
*	**10**	1.452	1.453	3	2	3
			1.451	0	4	0
	10	1.450	1.450	4	2	2
			1.449	4	0	3
	4	1.428	1.430	1	4	0
			1.427	$\bar{3}$	3	3
	4	1.417	numerous			
	6	1.318	1.319	$\bar{2}$	4	2
			1.318	1	4	2
	6	1.260	numerous			
	5	1.249	1.248	3	4	1

* Lines used for unit-cell refinement.

consistent with the proposed monoclinic symmetry and unit-cell parameters, including the CBED observation of systematic absences along the 5.81 Å row, which is interpreted as $0k0$ with $k = 2n$ and allowed us to narrow the space-group choices to $P2_1/m$ or $P2_1$. X-ray powder-diffraction data, obtained by means of a Bruker microdiffractometer using Cu-$K\alpha_1$ radiation (1.54060 Å), are presented in Table 3. Unit-cell parameters refined from the powder data are a 8.629(2) Å, b 5.805(2) Å, c 7.654(2) Å, ß 103.17(2)°, V 373.3(2) Å^3, $Z = 2$. The a:b:c ratio calculated from the unit-cell parameters is: 1.4865:1:1.3185. The compatibility index $1 - (K_p/K_C) = 0.215$, poor (with $n = 1.79$), $= 0.195$, poor (with $n = 1.81$). The refractive indices measured in transmitted and reflected light were obtained independently, and are similar to each other. It is possible that the Gladstone-Dale constants for TeO$_3$ are in error: the average refractive index for brumadoite should be 2.006 for superior compatibility. According to J.A. Mandarino [his comments in CNMMN proposal 92-025 for the mineral macalpineite], "the poor compatibility is due to the unreliable nature of the GD constant for TeO$_3$". Nevertheless, for the well established minerals jensenite and frankhawthorneite there was absolutely no problem with the GD constants for TeO$_3$. Chemistry and X-ray powder-diffraction data reported here indicate that brumadoite is unique and bears no close resemblance to any other phases listed in the Powder Diffraction File (release 2007). In the absence of a crystal-structure determination, the mineral can be classified (Strunz and Nickel, 2001) as either a hydroxide (4.FM) or as a tellurate (7.DE). Xocomecatlite (Williams, 1975), mcalpineite (Roberts *et al.*, 1994) and jensenite (Roberts *et al.*, 1996) are the other copper tellurates having the same Cu:Te ratio. Crystal structure data are available only for jensenite (Grice *et al.*, 1996).

Acknowledgements

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