

CANAVESITE, A NEW CARBOBORATE MINERAL FROM BROSSO, ITALY

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ABSTRACT

Canavesite occurs as milky-white rosette-like aggregates of fibers on ludwigite and magnetite skarns in the abandoned iron mine of Brosso (Piedmont, Italy). It is monoclinic (diffraction symbol $2/mP-/-$) with a 23.49(2), b 6.164(6), c 21.91(2) Å, β 114.91(9)°; D_{calc} 1.790 g cm⁻³ for $Z = 12$. The strongest reflections in the X-ray powder pattern are: 9.54(100) (202), 8.12(40)(201), 7.80(18)(102,301), 4.56(21) (501,503) and 3.110 Å (19)(407). The fibers are elongate [010] and show one or more $\{h0l\}$ cleavages; optically they are biaxial, $2V$ very large, $Z = b$, n_{α} 1.485(4), n_{β} 1.494(4), n_{γ} 1.505(2). DTA, TGA and high-temperature X-ray powder analyses document several breakdown reactions, finally leaving an assemblage of $Mg_3(BO_3)_2$ and MgO above 800°C. TGA, in particular, gives cumulative weight losses of 10, 20, 30, 39, 43, 50 and 56% at 95, 190, 300, 410, 475, 625 and 875°C, respectively. The infrared absorption spectrum shows OH⁻, CO₃²⁻ and BO₃³⁻; the CO₃ analysis gives the formula $Mg_{2.03}(CO_3)_{1.09}(HBO_3)_{0.94} \cdot 4.91H_2O$.

SOMMAIRE

La canavésite se présente sous forme de fibres d'un blanc laiteux, groupées en rosettes dans des skarns à ludwigite et à magnétite dans la mine de fer abandonnée de Brosso (Piémont, Italie). Elle est monoclinique (symbole de diffraction $2/mP-/-$) avec a 23.49(2), b 6.164(6), c 21.91(2) Å, β 114.91(9)°; D_{calc} 1.790 g cm⁻³ pour $Z = 12$. Les raies les plus intenses du diagramme de poudre sont: 9.54(100) (202), 8.12(40)(201), 7.80(18)(102,301), 4.56(21) (501,503) et 3.110 Å (19)(401). Les fibres sont allongées suivant [010] et présentent un ou plusieurs clivages $\{h0l\}$; optiquement elles sont biaxes, $2V$ très grand, $Z = b$, n_{α} 1.485(4), n_{β} 1.494(4), n_{γ} 1.505(2). Les analyses ATD et ATP, ainsi que les clichés de poudre aux rayons-X à hautes températures, ont mis en évidence des réactions de décomposition qui donnent comme produits $Mg_3(BO_3)_2$ et MgO au-dessus de 800°C. En particulier, l'ATP montre des pertes pondérales de 10, 20, 30, 39, 43, 50 et 56% à 95, 190, 300, 410, 475, 625 et 875°C, respectivement. Le spectre d'absorption infrarouge

indique la présence de OH⁻, CO₃²⁻ et BO₃³⁻. D'après l'analyse chimique, la formule s'écrit $Mg_{2.03}(CO_3)_{1.09}(HBO_3)_{0.94} \cdot 4.91H_2O$.

INTRODUCTION

The iron mines of Brosso and of Traversella (Province of Torino, Piedmont, Italy) are well-known sources of fine minerals developed near the contact between the Traversella monzonite stock and marbles interbedded in the mica schists of the Sesia-Lanzo zone. Giussani & Vighi (1964) described boron mineralization, with ludwigite and szaibelyite occurring just at the contact, in magnetite skarns of the Brosso pyrite mine; they listed the principal references concerning Brosso and Traversella. The recent discovery of arsenic minerals is reported by Abbona *et al.* (1969).

In the spring of 1972 Messrs. V. Farina and M. Rapazzini of the Gruppo Mineralogico Lombardo found the first specimens of the new mineral at the same locality, level 373 of the Vola Gera tunnel, after the mine had been abandoned. These were brought to our attention by Dr. V. de Michele, curator of the mineralogical section of the Museo Civico di Storia Naturale di Milano where type material is deposited. Since 1973 samples of canavesite have been widely collected and occasionally traded as nesquehonite.

Canavesite (pronounced KĀNAVĚZAIT) represents, with carboborite, Ca₂Mg(CO₃)(B₂O₃)·10H₂O (Hsieh *et al.* 1964), the only examples of carboborates.

The mineral is named after the district, Canavese, in which the village and the mine of Brosso occur, near the town of Ivrea. The name and species have been approved by the IMA Commission on New Minerals and Mineral Names.

PARAGENESIS

Canavesite occurs as milky rosette-like aggregates (Fig. 1) of very thin [010] elongated fi-



FIG. 1. Rosette-like canavesite with spheres of a hydromagnesite-like mineral (see text); scale bar 2mm (photo C. Bevilacqua).

bers on surfaces and along fractures of ludwigite and magnetite skarns. It seems clearly to have formed since mine operations ceased by reaction of carbonatic solutions with ludwigite. Canavesite is associated with spheres of an earlier-formed mineral upon which the needles may be implanted (Fig. 2a). The properties of the spheroidal aggregates suggest the unnamed hydromagnesite-like mineral $Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O$ (Suzuki & Ito 1973) or dypingite $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$ (Raade 1970). Further investigations are in progress.

PHYSICAL AND CRYSTALLOGRAPHIC PROPERTIES

From the silky aggregates, fragile but slightly flexible fibers having vitreous lustre (Fig. 2b) extend for about 1 mm. They show no fluorescence under ultraviolet light; under the polarizing microscope they appear as flat, colorless and transparent crystals with very weak dispersion and maximum cross-section of about $5 \times 30 \mu m$. Under the scanning electron microscope, the fibers appear as textures with an uneven distri-

bution of lamellae around the needle axis (Fig. 2c). The habit of the material and its easy alteration, beginning at about $40^\circ C$ (see below), made troublesome and imprecise the measurement of the following optical characteristics: biaxial positive, $2V$ very large, $Z=b$, refractive indices (Na light) n_α 1.485(4), n_β 1.494(4) and n_γ 1.505(2); n_α and n_β actually correspond, respectively, to the minimum (more frequent) and the maximum value observed perpendicular to the needle axis.

Very rare single crystals with prismatic hexagonal habit (Fig. 2d) were observed at higher resolution only. Fracture leaves uneven sections across the fiber axis; along this direction one or more unidentified $\{h0l\}$ cleavages or partings (?) were observed.

The X-ray diffraction pattern of the fibers was very weak; oscillation photographs took no less than two days of exposure to produce patterns exhibiting a mirror plane coincident with the zero-layer line and a fiber period of 6.16 \AA . The corresponding zero-level Weissenberg films showed, at best, half a dozen faint spots considerably elongated in the ω direction; usually

TABLE 1. X-RAY DATA FOR CANAVESITE

l	d_{obs}^a (Å)	hkl	d_{calc}^a (Å)
100	9.54	$\bar{2}02$	9.54
40	8.12	201	8.08
18	7.80	102;301	7.83;7.81
14	7.53	302	7.45
8	7.20	T03	7.25
2	5.40	$\bar{4}03$	5.41
10	5.00	004	4.97
7	4.78	203; $\bar{4}04$	4.79;4.77
21	4.56	501;503	4.58;4.56
7	4.014	410; $\bar{3}14$	4.030;3.991
12	3.693	511	3.677
11	3.332	015; $\bar{7}02$	3.340;3.330
9	3.180	$\bar{6}14$;606	3.188;3.181
19	3.110	$\bar{4}07$	3.106
4	2.993	512;121	2.996;2.988
5	2.889	$\bar{6}07$;611	2.889;2.886
3	2.772	$\bar{4}17$;323	2.774;2.774
7	2.726	$\bar{7}07$;722	2.726;2.724
2	2.690	603;405	2.693;2.688
5	2.607	306; $\bar{3}22$	2.610;2.607
4	2.571	421; $\bar{8}15$	2.573;2.573
3	2.505	801	2.505
13	2.407	703	2.408
4	2.397	525;406	2.398;2.396
6	2.282	526	2.283
14	2.233	416	2.233
3	2.201	506;118	2.204;2.200
2	2.147	T27	2.143
2	2.048	813; $\bar{7}28$	2.051;2.046
2	2.015	230;820	2.017;2.015
5	1.949	232; $\bar{7}28$	1.947;1.947
6	1.910	334;525	1.913;1.912
2	1.900	034; $\bar{7}23$	1.899;1.897
3	1.824	035	1.825
6	1.585	831;237;038	1.589;1.586;1.583

Average results from films and counter data with $FeK\alpha$ and $CuK\alpha$ radiations.

no spots at all were detectable. Electron diffraction patterns obtained with the beam roughly perpendicular to the fiber axis confirmed the repetition period along this direction and the needle texture showed by SEM. On the basis of the fiber period and a few d_{h0l} values measured on oscillation and Weissenberg films, the X-ray powder spectrum (Table 1) was indexed with a 23.49(2) b 6.164(6) c 21.91(2) Å β 114.91(9)°. No systematic absences were observed; the space group is presumably one included in the diffraction symbol $2/mP-/-$, but owing to the scarcity of single crystal data, twinned triclinic symmetry cannot be excluded. The pseudo-hexagonal dimensions of the cell could account for the hexagonal habit, which probably reflects the presence of the pinacoids $\{100\}$, $\{001\}$ and $\{\bar{1}01\}$.

COMPOSITIONAL DATA

The infrared spectrum of canavesite (Fig. 3) is not easily comparable with those of well-known families of minerals; broad and strong bands near 3500, 1450 and 1000 cm^{-1} could be interpreted as due to OH $^-$, CO $_3^{2-}$ and, with greater uncertainty, to BO $_3^{3-}$. The products of heating to 900°C, after 56% weight loss, were identified as a mixture of Mg $_3$ (BO $_3$) $_2$ and MgO (Table 2).

Canavesite effervesces with dilute HCl at room temperature. The chemical analysis, made by a combination of several methods on 100 mg of fibers selected under the binocular microscope, is given in Table 3. On the basis of eleven oxygens the analytical formula is Mg $_{2.03}$ (CO $_3$) $_{1.09}$ (HBO $_3$) $_{0.94}$ •4.91H $_2$ O, ideally Mg $_2$ (CO $_3$)(HBO $_3$)•5H $_2$ O or, perhaps, Mg $_2$ (CO $_3$,HBO $_3$) $_2$ •5H $_2$ O.

Because of the habit of the material, only an approximate measurement of the density was possible by the heavy-liquid method; the value, approximately 1.8 g cm $^{-3}$, requires 12 idealized unit formulae in the cell (D_{calc} 1.790 g cm $^{-3}$; V 2877.3 Å 3 ; $M.W.$ 258.559). For the ideal formula the Gladstone-Dale law suggests a D'_{calc} of

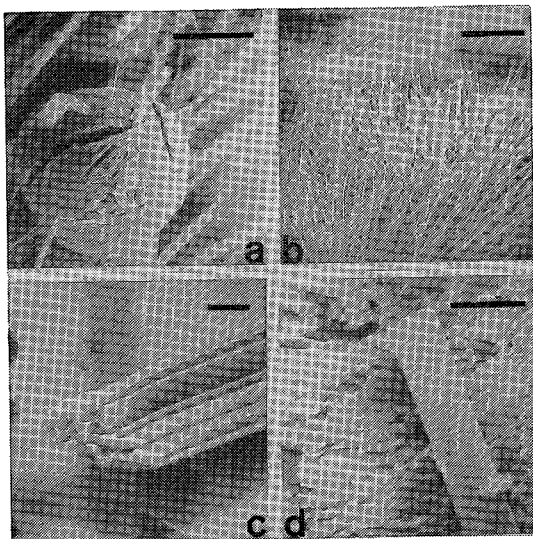


FIG. 2. a. Canavesite implanted on a spherical aggregate of a hydromagnesite-like mineral; SEM, scale bar 0.05mm. b. Close view of a rosette; SEM, scale bar 0.1mm. c. Needle texture; SEM, scale bar 0.01mm. d. Single crystal with hexagonal habit (only two faces are visible); SEM, scale bar 0.005mm.

1.908 and of 1.921 with the specific refractive energies reported by Larsen & Berman (1934) and by Mandarinò (1976), respectively. The discrepancy between D_{calc} and D'_{calc} , which requires $Z=13$, can be ascribed to several independent or concurrent causes, e.g., imprecise refractive indices, minor content of water, disorder in the crystal structure with a fractional Z in the cell.

THERMAL STABILITY

The TGA curve (Fig. 4) has inflections at 95, 190, 300, 410, 475, 625 and 875°C, which correspond to cumulative weight losses of 10, 20,

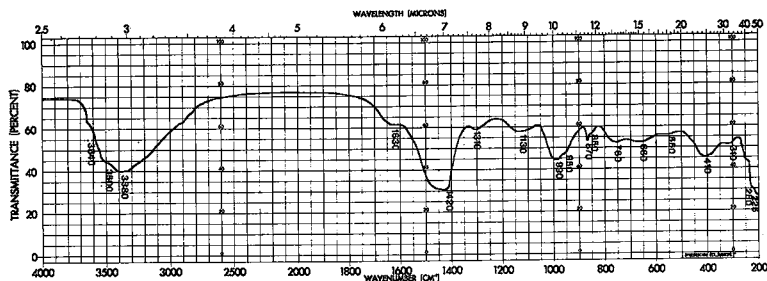


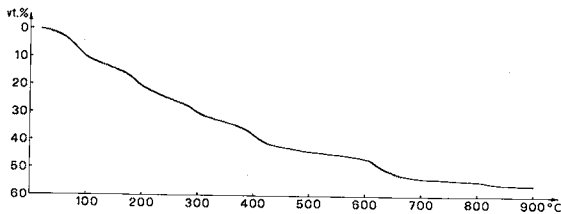
FIG. 3. Infrared spectrum of canavesite; 0.6mg in 100mg KBr disk.

TABLE 2. X-RAY POWDER DATA FOR PHASES OBTAINED BY HEATING CANAVESITE

I		II		III		IV		V		VI		
40-90°C		90-165°C		165-275°C		275-525°C		525-790°C		790-1050°C		
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	
7.55	m	7.13	mw	3.53	m	4.20	w	3.98	vw	1.960	vw	
4.93	s	4.93	s	2.938	mw	3.76	w	3.75	vw	1.931	vw b	
4.19	vw	4.20	vw	2.553	ms	3.53	w	3.63	m	1.872	vw	
3.53	w	3.53	w	1.733	s	3.48	m	3.54	vw	1.818	m	
3.30	w	3.30	vw	1.486	vw	2.951	s	3.48	m	1.743	w	
3.06	mw	3.06	mw			2.436	ms	2.953	s	1.708	w b	
3.00	vw	2.978	m			2.398	ms	2.791	m b	1.659	vw	
2.940	vw	2.943	mw			1.749	w	2.641	s	1.559	vw	
2.895	vw	2.898	w			1.542	w	2.459	vw	1.522	w	
2.547	ms	2.548	ms					2.429	ms c	1.502	m c	
2.434	mw	2.429	mw					2.190	ms	1.467	vw	
1.941	vw	2.037	vw					2.127	s bc	1.457	vw	
1.906	vw									1.344	w b	
1.560	w											
											2.304	w a
											2.263	s a
											2.201	s a
											2.136	vs ac
											2.099	w a
											2.055	vw a
											1.684	ms a
											1.675	vw a
											1.650	vw a
											1.622	vw a
											1.590	w a
											1.573	mw a
											1.550	w a
											1.534	m a
											1.507	s ac
											1.490	w a
											1.413	vw a
											1.379	w a
											1.373	mw a
											1.334	vw a

Guinier-Lenné (Nonius) camera, CuK α radiation; maximum measurable $d=8$ Å.
 w=weak, m=medium, s=strong, vw=very weak, vs=very strong.
 a=Mg₃(BO₃)₂, b=MgCO₃, c=MgO.

30, 39, 43, 50 and 56% respectively; secondary effects are indicated by the derivative curve only (not reported) at 45, 365, 475, 650, 690, 760 and 825°C. With some approximation the above temperatures reflect endothermic reactions in the DTA pattern (Fig. 4), where effects occur at 80, 105 and 125 (shoulders), 175, 195 (shoul-



der), 260, 325, 350-400 and 480-600 (broad peaks), 665, 700 and 790-840°C (broad peak).

The complexity of the thermal behavior of canavesite is confirmed and in part clarified by a continuous X-ray powder spectrum (Table 2) taken between 20 and 1050°C. The unambiguously identified phases MgCO₃ and MgO appear near 530°C; Mg₃(BO₃)₂ and MgO are present above 800°C. The range 165-530°C is characterized by poor crystallinity (unidentified X-ray patterns III and IV in Table 2). In the range 40-165°C, X-ray patterns I and II differ only in their first reflection, and differ from that of canavesite by shifts, mainly towards higher angles, of the majority of the lines. Phases I and II could represent partly dehydrated canavesite, with 2 and 3 water molecules lost, respectively,

TABLE 3. CHEMICAL ANALYSIS

	A	B	C	D	E
MgO	31.50 ^a	31.70 ^a		31.60	31.21
B ₂ O ₃	12.80 ^b	12.60 ^b	12.70 ^b	12.70	13.40
CO ₂	18.83 ^c	18.32 ^c		18.57	17.03
H ₂ O	37.56 ^c	37.32 ^c	56.00 ^d	37.44	38.35
Total	100.69	99.94		100.31	100.00

D. Average values of the analyses A, B and C.

E. Mg₂(CO₃)(HBO₃)₂·5H₂O.

a. Colorimetry. - b. Titration with NaOH of a HCl solution in presence of mannitol. - c. C. Erba 1104 elemental microanalyser. - d. Total wt. loss at 900°C.

Fig. 4. TGA (top) and DTA (bottom) curves; 10mg of canavesite with 10 and 20°C/min. speed, respectively.

but without a breakdown of the crystal structure. Breakdown surely occurs in the range of low crystallinity with, firstly, the complete loss of H₂O below 300°C and, subsequently, at around 400°C, of OH⁻. The presence of MgCO₃ in pattern V (Table 2) shows that the loss of CO₂ occurs only after complete dehydration.

The stability field of canavesite confined below 40°C and its occurrence on surfaces in a tunnel of an abandoned mine clearly show that the mineral formed at or near room temperature.

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REFERENCES

- ABBONA, F., COMPAGNONI, R. & FERRARIS, G. (1969): Contributo alla conoscenza di minerali arsenicali. Nota I. Ricerche su nuovi minerali di Brosso (Torino). *Period. Mineral.* **38**, 245-284.
- GIUSSANI, A. & VIGHI, L. (1964): Caratteristiche e genesi dei minerali di boro ludwigite, ferroludwigite, szaibelyite e camsellite della miniera di Brosso (Ivrea). *Period. Mineral.* **33**, 471-500.
- HSIEH HSIEN-TE, CHIEN TZE-CHIANG & CIU LAI-PAO (1964): The new mineral carboborite MgCa₂(CO₃)(B₃O₃)•10H₂O. *Scientia Sinica* **13**, 813-821.
- LARSEN, E. S. & BERMAN, H. (1934): The microscopic determination of the nonopaque minerals. *U.S. Geol. Surv. Bull.* **848**.
- MANDARINO, J. A. (1976): The Gladstone-Dale relationship—Part I: Derivation of new constants. *Can. Mineral.* **14**, 498-502.
- RAADE, G. (1970): Dypingite, a new hydrous basic carbonate of magnesium from Norway. *Amer. Mineral.* **55**, 1457-1465.
- SUZUKI, J. & ITO, M. (1973): A new magnesium carbonate hydrate mineral, Mg₅(CO₃)₄(OH)₂•8H₂O, from Yoshikawa, Aichi Prefecture, Japan. *J. Japan. Assoc. Mineral. Petrog. Geol.* **68**, 353-361.

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