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NUMANOITE, $Ca_4CuB_4O_6(OH)_6(CO_3)_2$, A NEW MINERAL SPECIES, THE Cu ANALOGUE OF BORCARITE FROM THE FUKA MINE, OKAYAMA PREFECTURE, JAPAN

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Abstract

Numanoite, the Cu analogue of borcarite, is found in an irregular patch in crystalline limestone near gehlenite–spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. Numanoite (up to 1 mm across) is observed as a core or zones in borcarite crystals up to 5 mm long. The mineral is also found as veinlets up to 0.4 mm wide in aggregates of borcarite crystals. The associated minerals are nifontovite, bultfonteinite, calcite and an unidentified magnesium silicate mineral. In hand specimen, the mineral is blue-green to colorless and transparent with a vitreous luster. The streak is white to pale blue-green. Numanoite is monoclinic, space group $C2/m$, a 17.794(2), b 8.381(1), c 4.4494(7) Å, β 102.42(2)° and $Z = 2$. The strongest seven lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are 7.57(100)(110), 2.671(84)($\bar{4}21$), 2.727(68)(221), 1.887(52)(041,440), 2.272(48)($\bar{3}31$), 2.899(44)(600) and 1.698(34)(640). Electron-microprobe and thermogravimetric analyses gave B_2O_3 24.09, CaO 38.11, CuO 10.32, MgO 1.02, ZnO 0.51, CO_2 15.80, H_2O 9.75, sum 99.60 wt.%. The empirical formula, calculated on the basis of O = 18, is $Ca_{3.898}(Cu_{0.744}Mg_{0.145}Zn_{0.036})_{\Sigma 0.925}B_{3.969}O_{5.615}(OH)_{6.208}(CO_3)_{2.059}$, ideally $Ca_4CuB_4O_6(OH)_6(CO_3)_2$. The mineral is optically biaxial negative, α 1.618(2), β 1.658(2), γ 1.672(2), and $2V_{calc} = 60°$. The mineral has perfect cleavages in two directions. The density is 2.96(2) g/cm^3 (meas.) and 2.93 g/cm^3 (calc.). The Vickers microhardness is 376 (290–464) kg/mm^2 (25 g load), and the Mohs hardness number is 4½. The differential thermal analysis curve shows two endothermic peaks at 489° and 692°C. It is likely that numanoite from the Fuka mine formed by precipitation from late Cu- and Mg-bearing hydrothermal solutions.

Keywords: numanoite, borcarite, hydrothermal solution, gehlenite–spurrite skarn, Fuka mine, Japan.

Sommaire

La numanoïte, analogue à dominance de Cu de la borcarite, a été découverte dans un amas irrégulier de calcaire recristallisé près des cipolins à gehlenite–spurrite à la mine Fuka, dans la préfecture d'Okayama, au Japon. La numanoïte, atteignant une

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taille d'un millimètre, se présente comme noyau ou en zones dans des cristaux de borcarite atteignant 5 mm. La numanoïte se présente aussi en veinules d'une largeur de 0.4 mm dans des agrégats de cristaux de borcarite. Lui sont associés nifontovite, bultfonteinite, calcite et un silicate de magnésium non identifié. Le minéral est bleu-vert à incolore et transparent, avec un éclat vitreux. La rayure est blanche à bleu-vert pâle. La numanoïte est monoclinique, groupe spatial $C2/m$, a 17.794(2), b 8.381(1), c 4.4494(7) Å, β 102.42(2)° et $Z = 2$. Les sept raies les plus intenses du spectre de diffraction X, méthode des poudres [d en Å(I)(hkl)] sont: 7.57(100)(110), 2.671(84)($\bar{4}21$), 2.727(68)(221), 1.887(52)(041,440), 2.272(48)($\bar{3}31$), 2.899(44)(600) et 1.698(34)(640). Les analyses obtenues avec une microsonde électronique et par thermogravimétrie ont donné B_2O_3 24.09, CaO 38.11, CuO 10.32, MgO 1.02, ZnO 0.51, CO_2 15.80, H_2O 9.75, pour un total de 99.60% (poids). La formule empirique, calculée sur une base de 18 atomes d'oxygène, est $Ca_{3.898}(Cu_{0.744}Mg_{0.145}Zn_{0.036})_{\Sigma 0.925}B_{3.969}O_{5.615}(OH)_{6.208}(CO_3)_{2.059}$ ou, de façon idéale, $Ca_4CuB_4O_6(OH)_6(CO_3)_2$. Le minéral est optiquement biaxe négatif, α 1.618(2), β 1.658(2), γ 1.672(2), et $2V_{calc} = 60°$. Les clivages sont parfaits en deux directions. La densité est 2.96(2) g/cm^3 (mes.) et 2.93 g/cm^3 (calc.). La microdureté de Vickers est 376 (290–464) kg/mm^2 (charge de 25 g), et la dureté de Mohs est 4½. L'analyse thermique différentielle montre deux pics endothermiques, à 489° et 692°C. Il est probable que la numanoïte se soit formée par précipitation à partir de solutions hydrothermales tardives enrichies en Cu et Mg.

(Traduit par la Rédaction)

Mots-clés: numanoïte, borcarite, solution hydrothermale, cipolin à gehlenite–spurrite, mine Fuka, Japon.

INTRODUCTION

New boron-bearing minerals such as henmilite (Nakai *et al.* 1986), takedaite (Kusachi *et al.* 1995), parasibirskite (Kusachi *et al.* 1998) and okayamalite (Matsubara *et al.* 1998) have been identified from veins and small irregular patches in crystalline limestone near the gehlenite–spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. In recent examinations in the same area, a blue-green mineral in the core of colorless crystals of borcarite was observed in small irregular patches. Electron-microprobe analyses, X-ray diffraction, infrared absorption spectrum and thermal analysis confirmed the mineral to be the Cu analogue of borcarite, $Ca_4MgB_4O_6(OH)_6(CO_3)_2$ (Pertsev *et al.* 1965). This mineral is only fourth borate of copper.

The Cu analogue of borcarite is named numanoite after Dr. Tadayuki Numano (1931–2001), Emeritus Professor of Okayama University, in recognition of his notable and valuable contributions to the field of mineralogy. The mineral data and the mineral name were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (No. 2005–050). The type specimen of numanoite is deposited in the Department of Geology, National Science Museum, Tokyo, Japan, under the registration number NSM–M28813.

OCCURRENCE

The Fuka mine is located about 40 km west–northwest of Okayama City, western Japan (Lat. 34°46' N, Long. 133°26' E). The geological map of the Fuka mine area is given in Figure 1. Skarn formation in the Fuka mine has been documented by Satish-Kumar *et al.* (2004). Here, extensive mining of highly crystalline pure limestone has been carried out along the four levels of tunnels, and the retaining pillars and quarry face expose fresh skarn. Generally, the skarns consist of spurrite or products of its alteration, and surround monzodiorite. Patches and streaks of gehlenite up to few centimeters across occur randomly inside the monomineralic spurrite skarn. In the second to fourth levels, small irregular patches composed of boron-bearing minerals occur in the crystalline limestone in the vicinity of the skarns. Takedaite, olshanskyite, pentahydroborite and nifontovite are major constituents of the irregular patches, which also contain henmilite, frolovite, sibirskite, parasibirskite, uralborite, inyoite, borcarite, ettringite-group minerals, cuspidine, tenorite, cahnite, johnbaumite, bultfonteinite, andradite, bornite, chalcopyrite, pyrite, chalcocite and unidentified minerals. Frolovite, henmilite, nifontovite, pentahydroborite and uralborite usually form euhedral crystals (Takada *et al.* 2005).

Numanoite was found in an irregular patch, up to 7 m long and 3 m wide, at the fourth level in the Fuka mine. It forms grains up to 1 mm across as a core or in zones in borcarite crystals up to 5 mm long (Fig. 2a) and as veinlets up to 0.4 mm wide in aggregates of borcarite crystals (Fig. 2b). The numanoite–borcarite assemblages occur on cavity walls in patches of nifontovite and along cracks cutting crystalline limestone. The associated minerals are nifontovite, bultfonteinite, calcite and an unidentified magnesium silicate mineral.

PHYSICAL AND OPTICAL PROPERTIES

Numanoite is blue-green to colorless and transparent with a vitreous luster. The streak is white to pale blue-

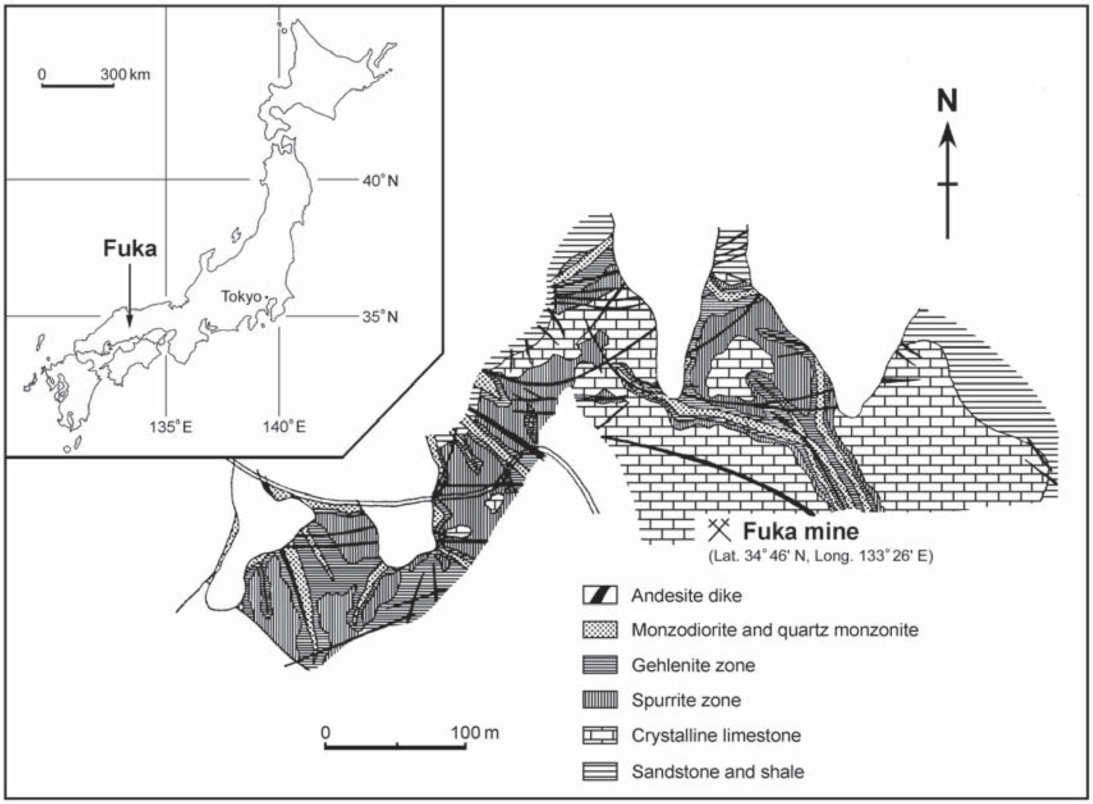

FIG. 1. Geological map around the Fuka mine, Okayama Prefecture, western Japan (modified from Omae *et al.* 2002).

green. In thin sections, the mineral is colorless to pale blue-green and non-pleochroic. The mineral has perfect cleavages in two directions. Twinning is not observed in the samples studied. Numanoite occurs as a core or zones in borcarite crystals (Figs. 3, 4a). Optically, the mineral is biaxial negative, α 1.618(2), β 1.658(2), γ 1.672(2), with $2V_{\text{calc}}$ equal to 60°. The density, measured using hand-picked pure crystals in heavy liquid, is 2.96(2) g/cm^3, and the calculated density using the empirical formula is also 2.93 g/cm^3. The Vickers microhardness (25 g load) and the Mohs hardness are reported in Table 1. The mineral is not fluorescent under short- or long-wave ultraviolet light. Numanoite is easily dissolved with effervescence in dilute hydrochloric acid. The properties of numanoite are compared with those of borcarite reported by Kusachi *et al.* (1997) in Table 1.

The infrared absorption spectra of numanoite and the associated borcarite in KBr pellets were measured using an infrared spectrophotometer (Hitachi 270–50) at Okayama University of Science for the wavenumber region 4000 to 250 cm^{-1} (Fig. 5). The spectrum of

TABLE 1. PHYSICAL AND OPTICAL PROPERTIES OF NUMANOITE AND BORCARITE FROM THE FUKA MINE

	Numanoite	Borcarite
Color	Blue-green to colorless	Bluish green to colorless
Color in thin section	Colorless to pale blue-green	Colorless
Luster	Vitreous	Vitreous
Indices of refraction		
α	1.618	1.592
β	1.658	1.653
γ	1.672	1.655
Birefringence	0.054	0.063
$2V_{\text{calc}}$ (°)	60	20
Sign	Biaxial (–)	Biaxial (–)
D_{meas} (g/cm^3)	2.96	2.56
D_{calc} (g/cm^3)	2.93	2.80
VHN_{25} (kg/mm^2)	376 (290–464)	370 (287–429)
MHN	4.5	4.5
Reference	Present work	Kusachi *et al.* (1997)

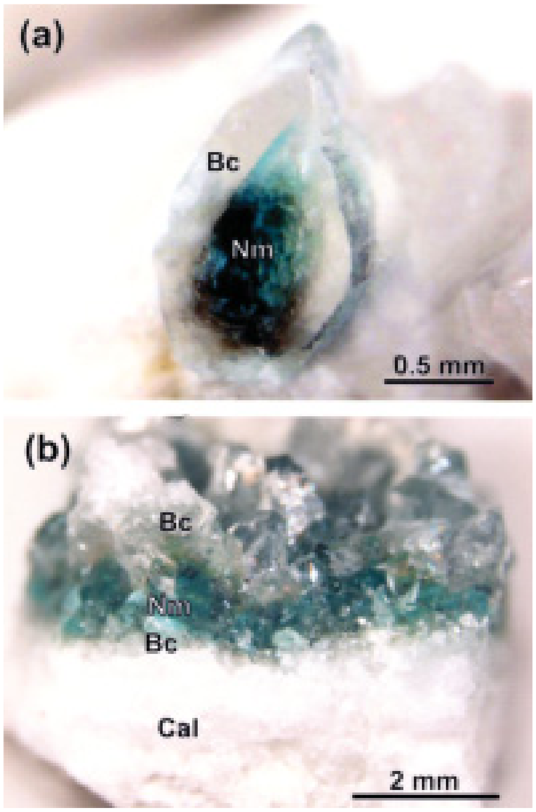

FIG. 2. Photographs of numanoite from the Fuka mine. (a) Core of borcarite crystal. (b) Veinlet in aggregates of borcarite crystals. Abbreviations: Nm: numanoite, Bc: borcarite, Cal: calcite.

TABLE 2. CHEMICAL COMPOSITION OF NUMANOITE AND BORCARITE FROM THE FUKA MINE AND STANDARDS USED IN ANALYSES

	Numanoite n* = 27 Average	Range	Borcarite n* = 3 Average		Standard used
B_2O_3 wt%	24.09	23.43 – 25.39	26.68		Nifontovite
CaO	38.11	37.52 – 38.66	40.32		Takedaite
CuO	10.32	8.55 – 11.90	0.05		Cu metal
MgO	1.02	0.34 – 1.76	6.81		Periclase
ZnO	0.51	0.04 – 1.08	0.73		Sphalerite
CO_2	15.80**		15.81**		
H_2O	9.75**		9.78**		
Total	99.60		100.18		
B *apfu*	3.969		4.169		
Ca	3.898		3.912		
Cu	0.744	0.920	0.003	0.972	
Mg	0.145		0.920		
Zn	0.036		0.049		
C	2.059		1.954		
H	6.208		5.907		
Cu/(Cu + Mg)	0.837		0.003		

* Analyzed spots; ** results of a thermogravimetric analysis. The compositions are reported in atoms per formula unit (*apfu*) based on 18 atoms of oxygen.

numanoite shows absorption bands at 3540 and 3260 cm^{-1} attributed to O–H stretching vibrations, 1410, 870 and 290 cm^{-1} for the vibrations of the carbonate group, and 1450, 1215 and 390 cm^{-1} for the vibrations of $B(O,OH)_4$ tetrahedra (Burns & Hawthorne 1995). A vibration due to H–O–H bending was not observed in the analysis. It should be noted that the spectra of numanoite and associated borcarite are virtually identical.

CHEMICAL COMPOSITION

Chemical analyses carried out using an electron-microprobe analyzer (JEOL JXA–8900R) at Okayama University of Science with wavelength-dispersion spectrometry (WDS) revealed the presence of B, Ca, Cu, Mg and Zn. The element-distribution maps of Ca*K*α, Cu*K*α and Mg*K*α in a crystal of numanoite including borcarite (Figs. 4b to 4d) were carried out using a scanning electron microscope (JEOL JSM–5410CL) with

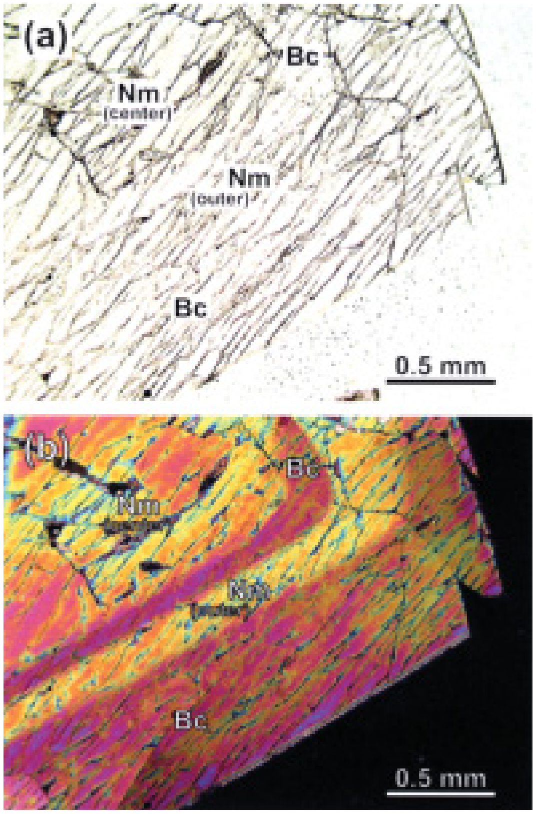

FIG. 3. Photomicrographs of the core of numanoite in borcarite from the Fuka mine. (a) Plane light. (b) Crossed nicols.

energy-dispersion spectrometer (Oxford Link ISIS 300) at Okayama University of Science. The concentration of B, Ca, Cu, Mg and Zn in numanoite and associated borcarite were obtained with WDS analyses. The conditions of measurement for each element were: accelerating voltage 15 kV, beam current 12 nA, and beam diameter 10 µm. The peak and backgrounds were measured for 10 and 5 seconds, respectively. The ZAF method was used for the corrections. The average values of the chemical composition near the core and rim of borcarite crystals (Figs. 3, 4a), and veinlets in aggregates of borcarite crystals (Fig. 2b) were almost the same. For the determination of CO_2 and H_2O contents by thermogravimetric analysis (TGA), numanoite specimens were selected by hand-picking under a binocular microscope. The empirical formula of numanoite calculated from the average results on the basis of O = 18 is $Ca_{3.898}(Cu_{0.744}Mg_{0.145}Zn_{0.036})_{\Sigma 0.925}B_{3.969}O_{5.615}(OH)_{6.208}(CO_3)_{2.059}$ or, ideally, $Ca_4CuB_4O_6(OH)_6(CO_3)_2$ (Table 2).

X-RAY CRYSTALLOGRAPHY

X-ray powder-diffraction data (Table 3) were obtained for numanoite and associated borcarite with a Rigaku RINT–2500V diffractometer at Kurashiki University of Science and the Arts with graphite-monochromatized Cu$K\alpha_1$ radiation generated at 40 kV and 240 mA. Single-crystal X-ray-diffraction data were obtained for numanoite on a four-circle diffractometer (Rigaku AFC–5R) at Okayama University with graphite-monochromatized Mo$K\alpha$ radiation generated at 50 kV and 200 mA. The crystal fragment (0.2 × 0.1 × 0.1 mm) was picked out of a polished section after its identity was confirmed using BSE images and electron-microprobe analyses. Numanoite is monoclinic, space group *C*2/*m*, *a* 17.799(2), *b* 8.389(2), *c* 4.451(2) Å, β 102.49(3)° and *Z* = 2. The unit-cell parameters refined by least squares from the X-ray powder-diffraction data are nearly identical (Table 3); reflections were indexed

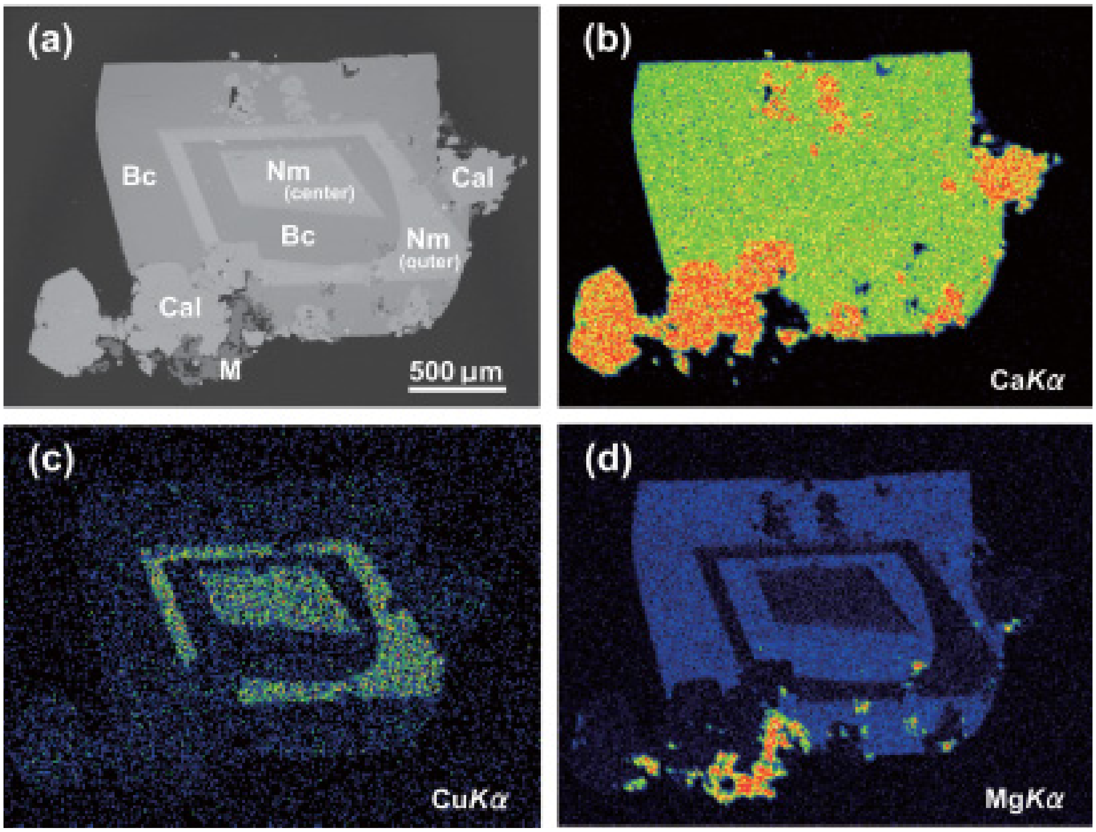

FIG. 4. BSE image and X-ray images of element distribution in numanoite from the Fuka mine. (a) BSE image, (b) Ca$K\alpha$ image, (c) Cu$K\alpha$ image and (d) Mg$K\alpha$ image. Abbreviation: M: unidentified magnesium silicate mineral.

TABLE 3. REPRESENTATIVE X-RAY POWDER-DIFFRACTION DATA FOR NUMANOITE AND BORCARITE FROM THE FUKA MINE

Numanoite						Borcarite	
h	*k*	*l*	*d* calc	*d* meas	*I*	*d*	*I*
2	0	0	8.69	8.73	6		
1	1	0	7.55	7.57	100	7.57	88
3	1	0	4.77	4.78	18	4.78	10
0	0	1	4.35	4.35	8	4.36	20
4	0	0	4.34				
$\bar{2}$	0	1	4.27	4.27	4		
0	2	0	4.19	4.2	6	4.19	18
$\bar{1}$	1	1	3.93	3.928	8	3.917	8
2	2	0	3.775	3.783	4		
2	0	1	3.59	3.593	8	3.607	18
$\bar{4}$	0	1	3.468	3.469	6	3.461	12
5	1	0	3.21	3.213	14	3.225	30
0	2	1	3.017	3.019	10	3.019	8
$\bar{2}$	2	1	2.992	2.988	10	2.978	32
3	1	1	2.961	2.961	18		
6	0	0	2.896	2.899	44	2.912	88
$\bar{5}$	1	1	2.869	2.868	4		
4	0	1	2.787	2.788	10	2.801	12
1	3	0	2.758	2.759	14	2.761	8
2	2	1	2.726	2.727	68	2.73	64
$\bar{4}$	2	1	2.672	2.671	84	2.665	100
3	3	0	2.516	2.517	14	2.517	12
6	2	0	2.383	2.384	14	2.384	40
$\bar{1}$	3	1	2.366	2.365	20	2.359	6
1	3	1	2.294	2.295	6	2.296	10
$\bar{3}$	3	1	2.272	2.272	48	2.266	58
$\bar{1}$	0	2	2.215	2.218	8		
6	0	1	2.201	2.201	28	2.215	54
5	3	0	2.178	2.176	10	2.178	18
0	0	2	2.173				
7	2	0	2.136	2.136	20	2.135	22
$\bar{4}$	0	2	2.136				
$\bar{8}$	0	1	2.135				
$\bar{3}$	1	2	2.124	2.122	10	2.116	8
0	4	0	2.095	2.096	22	2.093	26
$\bar{5}$	3	1	2.061	2.062	18	2.058	26
1	1	2	2.038	2.037	4	2.035	10
2	4	0	2.037				
2	0	2	2.009	2.007	2	2.013	4
$\bar{5}$	1	2	1.993	1.99	4		
$\bar{2}$	2	2	1.964	1.963	6	1.959	10
7	1	1	1.927	1.927	6	1.938	4
3	0	2	1.904	1.903	20	1.901	26
$\bar{4}$	2	2	1.903				
$\bar{8}$	2	1	1.903				
0	4	1	1.887	1.887	52	1.886	68
4	4	0	1.887				
5	3	1	1.849	1.852	4	1.857	12
2	2	2	1.811	1.811	26	1.811	36
2	4	1	1.81				
4	0	2	1.795	1.795	8	1.789	4
5	4	0	1.795				
8	0	1	1.795				
$\bar{6}$	2	2	1.769	1.769	6	1.763	8
$\bar{1}$	3	2	1.736	1.735	8	1.746	18
$\bar{8}$	0	2	1.734				
6	4	0	1.698	1.698	34	1.698	46
1	5	0	1.669	1.668	6	1.667	6
4	2	2	1.65	1.65	18	1.656	24
8	2	1	1.65				
7	3	1	1.615	1.614	10		
$\bar{10}$	2	1	1.614				
10	2	0	1.605	1.606	20	1.611	36
9	3	0	1.588	1.589	8	1.594	16
$\bar{11}$	1	1	1.571	1.571	2	1.574	4
11	1	0	1.552	1.551	4	1.559	6
$\bar{2}$	4	2	1.525	1.525	8	1.522	18
6	4	1	1.518	1.517	10	1.512	4
0	4	2	1.508	1.508	4	1.509	4
8	4	0	1.508				
$\bar{4}$	0	3	1.473	1.472	4	1.477	2
$\bar{12}$	0	1	1.472				
$\bar{4}$	1	3	1.45	1.449	4	1.455	4
2	4	2	1.45				
0	0	3	1.449				
12	0	0	1.448				
$\bar{1}$	1	3	1.448				
0	1	3	1.427	1.426	2	1.424	4
12	1	0	1.427				
$\bar{4}$	2	3	1.389	1.388	6	1.389	6
7	5	0	1.389				
$\bar{12}$	2	1	1.389				
$\bar{7}$	0	3	1.388				
$\bar{11}$	3	1	1.388				
2	6	0	1.379	1.379	2		
$\bar{7}$	1	3	1.369	1.369	2	1.367	6
0	2	3	1.369				
$\bar{12}$	2	0	1.369				
4	4	2	1.363	1.363	4		
8	4	1	1.363				
$\bar{13}$	0	1	1.363				
$\bar{6}$	2	3	1.348	1.348	4		

	Numanoite	Borcarite
a (Å)	17.794 (2)	17.849 (4)
b (Å)	8.381 (1)	8.368 (2)
c (Å)	4.4494 (7)	4.448 (2)
β (°)	102.42 (2)	102.07 (3)
V (Å^3)	648.0 (2)	649.7 (3)

from the single-crystal X-ray-diffraction data. It should be noted that the data for numanoite are in close agreement with those for borcarite.

Thermal Analysis

The thermogravimetry (TG) and differential thermal analysis (DTA) of numanoite and the associated

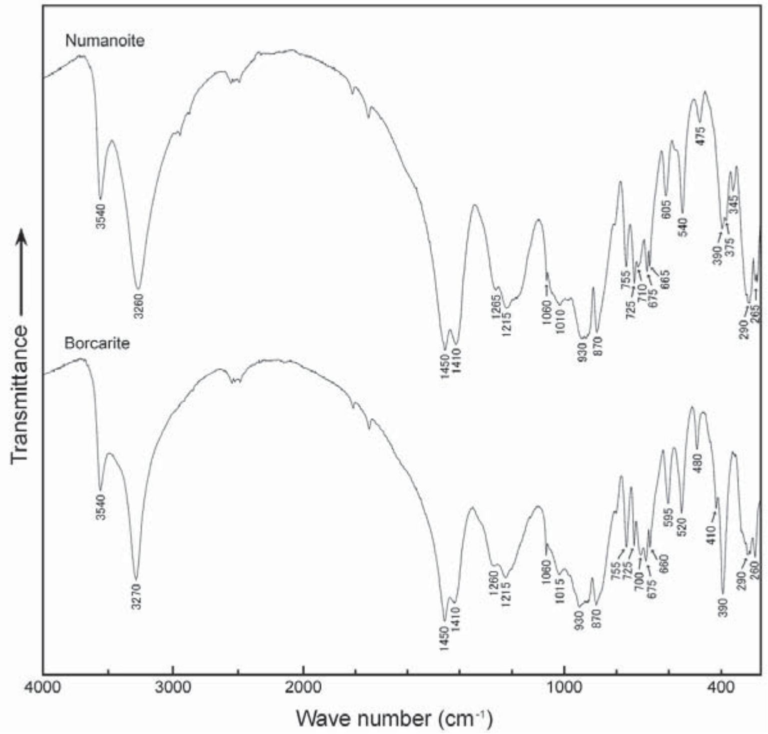

FIG. 5. Infrared absorption spectra of numanoite and borcarite from the Fuka mine.

borcarite were carried out using a thermal analyzer (Rigaku TG–8120) at Okayama University in air from room temperature to 900°C at a rate of 10°C min^{-1} (Fig. 6). The TG–DTA curves of numanoite closely resemble those of borcarite. Numanoite has a sharp endothermic peak at 489°C corresponding to the loss of H_2O, and a small endothermic peak at 692°C corresponding to the loss of CO_2 (Fig. 6a). On heating numanoite at 900°C, calcium borate ($Ca_2B_2O_5$) and copper oxide (CuO) appeared as crystalline phases according to the following reaction:

$$Ca_4CuB_4O_6(OH)_6(CO_3)_2 = 2Ca_2B_2O_5 + CuO + 3H_2O + 2CO_2 \quad (1)$$

DISCUSSION

The unit-cell parameters, symmetry, infrared spectrum and thermal behavior of numanoite are consistent with those of borcarite. The differences in color, indices of refraction and density result from the dominance of Cu in numanoite and the dominance of Mg in borcarite.

As shown in Figure 7, the composition of numanoite plots in the range of Cu-dominance. The range of Cu varies from 0.61 to 0.89 atoms per formula unit (*apfu*), and Mg varies from 0.04 to 0.25 *apfu*. The Cu/(Cu + Mg) value varies over the range 0.72 to 0.96, and the compositional variation shows an inverse linear relationship. On the other hand, the composition of borcarite plots near the Mg end-member. The Zn content of numanoite and borcarite is the same (0 to 0.02 Zn *apfu*). In the sample studied, there is a compositional gap between numanoite and borcarite. The gap is also evident in Figure 8. The sharply defined zones in Figures 3 and 4 lead to two possible interpretations: (1) a major miscibility-gap between nearly end-member borcarite and magnesian numanoite, (2) abrupt changes in composition of the fluids in which the borcarite–numanoite crystals grew, and there was no fluid yielding intermediate borcarite–numanoite composition.

As explained earlier, in the exposure of the irregular patches at the Fuka mine, numanoite occurs in the core of borcarite crystals in association with nifontovite, bultfonteinite, calcite and an unidentified magnesium silicate mineral. Kusachi *et al.* (1997) reported that

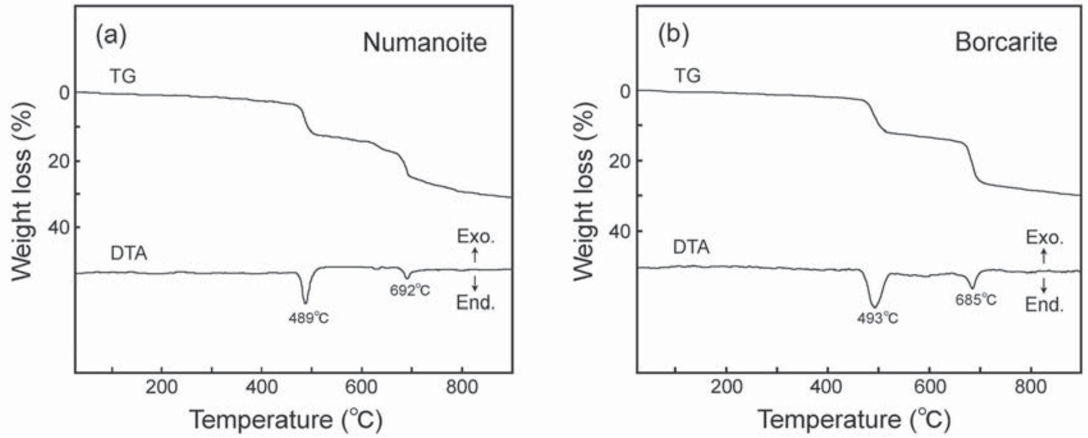

FIG. 6. TG–DTA curves for numanoite and borcarite from the Fuka mine.

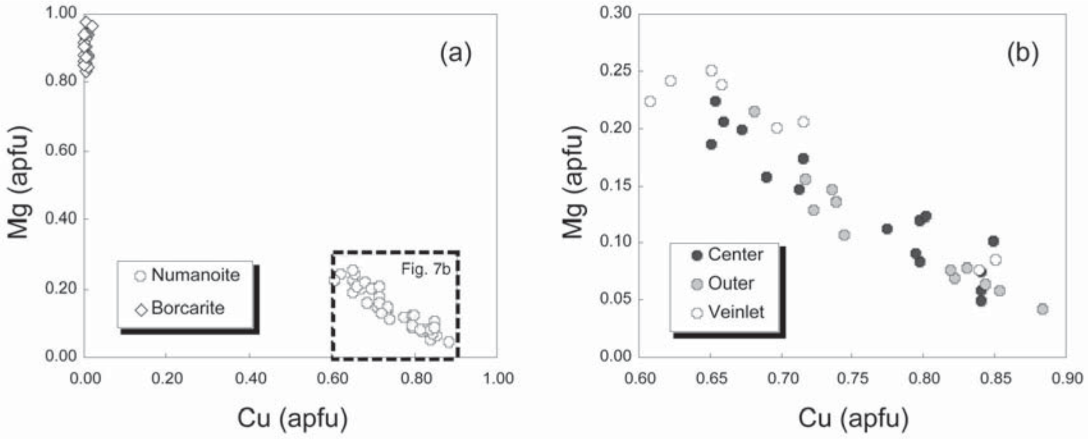

FIG. 7. Compositional variation of Cu *versus* Mg in numanoite and borcarite from the Fuka mine. Center, outer and veinlet reveal the result of the chemical analyses in Nm (center), Nm (outer) (Figs. 3, 4a), and Nm veinlet (Fig. 2b), respectively.

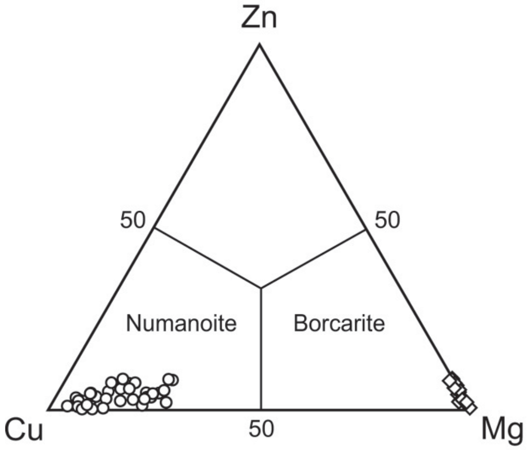

FIG. 8. The compositions of numanoite and borcarite from the Fuka mine in terms of the components Cu–Mg–Zn. Symbols are the same as in Figure 7a.

borcarite in association with takedaite was formed as a secondary mineral from brucite. However, numanoite is not associated with brucite, and occurs on the wall of cavities in a vein of nifontovite or in fractures in a crystalline limestone. From the mode of occurrence, it is likely that numanoite formed from Cu- and Mg-bearing late hydrothermal solutions, and numanoite and borcarite formed alternately in succession as an overgrowth on early-formed numanoite owing to differences in composition of the hydrothermal solutions.

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