

**A new mineral bicchulite, the natural analogue
of gehlenite hydrate, from Fuka, Okayama
Prefecture, Japan and Carneal, County
Antrim, Northern Ireland***

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ABSTRACT

The natural analogue of gehlenite hydrate synthesized by Carlson (1964) was found as an alteration product of gehlenite from Fuka, Okayama Prefecture, Japan, and as a crust on wollastonite from Carneal, Northern Ireland.

The chemical analyses of the impure Fuka material substantiate the validity of Carlson's formula $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ with minor substitution of AlAl by MgSi. X-ray powder patterns are indexed on a body-centred cubic cell with $a=8.829\pm 0.002 \text{ \AA}$ (Fuka), $8.82\pm 0.01 \text{ \AA}$ (Carneal), $8.837\pm 0.002 \text{ \AA}$ (synthetic material). The strongest lines of the Fuka mineral are: 3.60 (90)(211), 2.786 (100)(310), 2.547 (30)(222), 2.354 (35)(321), 2.079 (40)(411), 1.599 (50)(440), 1.514 (25)(530). The unit cell contains 4 molecules of $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ ($\text{Ca}_2\text{Al}_2\text{SiO}_7\cdot\text{H}_2\text{O}$).

Bicchulite is white or gray in colour. The hardness could not be

* A report on the Fuka mineral was read at the Annual Meeting of the Mineralogical Society of Japan held in the National Science Museum, Tokyo, Japan, on June 8, 1972.

measured because of its powdery nature. Colourless and isotropic in thin section. The index of refraction is $n=1.625$ for the Carneal specimen and 1.628 for the synthetic material. The observed specific gravity is 2.75 for the synthetic material and 2.813 calculated for the synthetic material.

The name is for Bicchu, another spelling of Bitchu [bitʃu:], the name of the town including type locality in Japan.

Introduction

During the mineralogical survey of skarns from Fuka, Okayama Prefecture, Japan, the first natural occurrence of gehlenite hydrate originally synthesized by Carlson in 1964 was recognized by the first three authors. After the mineralogical description and the synthesis and hydrothermal studies of natural and synthetic materials were completed, they submitted the study to the Commission of New Minerals and Mineral Names, I. M. A. A few days later, the last two authors inquired of the Commission about the natural occurrence of gehlenite hydrate, having found it in County Antrim, Northern Ireland. The time difference between the two letters was so short that a joint paper between the two groups was recommended by the Chairman of the Commission (M. Fleisher). This was approved in 1973 together with its name.

The present paper deals with chemical and X-ray studies, and also includes some of the results of hydrothermal experiments which were used to show the similarities between the natural and synthetic materials.

Occurrences and some physical properties

At Fuka, the Town of Bitchu, Okayama Prefecture, the occurrences of skarn minerals such as spurrite, tilleyite, gehlenite, rankinite, and perovskite have been reported as the products of high temperature metamorphism and metasomatism of limestone. In subsequent retrograde hydration reactions bicchulite was formed as an alteration product of gehlenite. Bicchulite occurs in associ-

ation with vesuvianite with or without hydrogrossular, gehlenite and calcite and forms black or gray mixtures. Because of its extremely fine grain size and the presence of contaminating calcium silicates, the specific gravity, hardness, and optical properties of the Fuka material could not be determined.

At Carneal, Northern Ireland, a Tertiary olivine-dolerite volcanic plug that intrudes Tertiary lavas incorporates blocks of (Cretaceous) chalk from below, a soft limestone with siliceous flint nodules. The rocks are converted by intense contact-metamorphism to larnite, wollastonite, spinel, scawtite, spurrite, merwinite, sphene, and related assemblages while the dolerite is desilicated to melilite- and wollastonite-bearing pyroxene-rich and alkaline hybrids. Hydrated and secondary minerals include hydrogrossular, thomsonite, xonotlite, tacharanite, tobermorite, gyrolite, portlandite, calcite, and allophane.

The bicchulite occurs mixed with hydrogrossular and melilite in a buff-coloured coating to a wollastonite-rock (no NI 1597). The mineral is colourless under the microscope and isotropic with refractive index $n=1.625$, which is comparable with that of synthetic material, $n=1.628$ (Carlson, 1964). The specific gravity measured on synthetic material is 2.75. The calculated value on synthetic material is 2.813, when the unit-cell edge measured in this study (8.837 \AA) is employed, and is 2.792, when Gladstone-Dale's Law (1864) is adopted.

Chemical analyses

Two samples of Fuka material were chemically analysed. One contained vesuvianite and the other gehlenite, vesuvianite, and hydrogrossular as impurities (Table 1). Analysis for the associated gehlenite, and the theoretical values for the pure phase $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ were also listed for comparison. An accurate chemical composition of bicchulite can not be derived directly for the chemical analyses shown in Table 1 are interpreted as mixtures of minerals

Table 1. Chemical analyses, wt. percent.

	1	2	3	4
SiO ₂	28.51	23.77	25.81	20.55
TiO ₂	0.09	0.92	0.35	
Al ₂ O ₃	21.79	23.59	26.37	34.90
Fe ₂ O ₃	2.66	6.72	2.57	
FeO	0.25	0.20	0.19	
MnO	0.03	0.02	0.01	
MgO	2.72	2.00	2.05	
CaO	35.26	36.89	38.28	38.40
Na ₂ O	0.25	0.14	0.38	
K ₂ O	0.18	0.11	0.15	
H ₂ O(+)	8.03	4.79	2.73	6.16
H ₂ O(-)	0.43	0.40	0.93	
P ₂ O ₅	0.02	0.02	0.01	
Total	100.22	99.57	99.83	100.01

1. Bicchulite mixed with vesuvianite. Fuka, Okayama, Japan.
2. Bicchulite contaminated by small amounts of gehlenite, vesuvianite and hydrogrossular. Fuka, Okayama, Japan.
3. Unaltered gehlenite. Fuka, Okayama, Japan.
4. Theoretical $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$.

as detected by X-ray powder diffraction techniques.

Carlson (1964) showed in his study on the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ that the approximate chemical composition of gehlenite hydrate is $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$. Using hydrothermal techniques the authors succeeded in preparation of gehlenite hydrate containing minor magnesium and having a unit cell edge of $a=8.830 \text{ \AA}$. This value is closer to that of the Fuka material ($a=8.829 \text{ \AA}$) than the value for synthetic magnesium-free gehlenite hydrate ($a=8.837 \text{ \AA}$). Various evidences indicate that the ideal formula of bicchulite is $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ or $\text{Ca}_2\text{Al}_2\text{SiO}_7\cdot\text{H}_2\text{O}$ with four formulae per unit cell. This is also supported by specific gravities calculated from X-ray data (2.813) and Gladstone-Dale's Law (2.792), both being very close to the measured value (2.75) on the synthetic material.

Table 2. X-ray powder data for bicchulite.

<i>hkl</i>	1		2		3		4		
	<i>d</i> (Å)	<i>I</i>	<i>d</i> (cal.)	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
110			6.243						
200			4.415	4.40	10	4.44	4	4.42	7
211	3.60	90	3.604	3.60	100	3.62	90	3.607	93
	3.49	10	ve*						
220	3.12	10	3.122	3.11	10	3.13	8	3.122	9
	3.04	40	cal*						
	2.96	40	ve*						
310	2.786	100	2.792	2.787	100	2.794	100	2.793	100
	2.753	95	ve*						
	2.597	50	ve*						
222	2.547	30	2.549	2.545	20	2.554	33	2.549	32
	2.460	40	ve*						
321	2.354	35	2.360	2.38	b	2.366	28	2.360	29
400	2.205	20	2.207	2.21	b	2.210	14	2.208	15
	2.135	10	ve*						
411)	2.079	40	2.081	2.081	30	2.083	42	2.081	42
330)									
420	1.984	10	1.974	1.97	b	1.979	5	1.974	8
332	1.890	10	1.882	1.880	5	1.886	4	1.882	4
422	1.801	15	1.802	1.804	10	1.806	13	1.801	12
	1.763	15	ve*						
510)	1.732	10	1.732	1.727	10	1.732	13	1.730	13
431)									
	1.665	15	ve*						
	1.625	30	ve*						
521			1.612			1.614	7	1.611	10
440	1.559	50	1.561	1.558	40	1.564	42	1.559	38
530)	1.514	25	1.514	1.513	30	1.518	20	1.513	21
433)									
	<i>a</i> = 8.829 Å		<i>a</i> = 8.82 Å		<i>a</i> = 8.837 Å		<i>a</i> = 8.83 Å		

1. Bicchulite from Fuka. Cu/Ni radiation. Diffractometer method.
* Contaminated minerals. cal: calcite, ve: vesuvianite.
2. Bicchulite from Carneal. Co/Fe radiation. Camera method. (film × 6448). Intensities estimated visually by comparison with a standard intensity scale. Lines for hydrogrossular, melilite and calcite omitted unless overlapping with bicchulite lines.
b: broad line that coincides with a strong hydrogrossular line.
3. Synthetic bicchulite. Cu/Ni radiation. Diffractometer method. The present work.
4. Synthetic bicchulite. Cu/Ni radiation. Camera method. Carlson (1964).

X-ray powder study

X-ray powder data for Fuka and Carneal bicchulites and of those synthesized by the authors and by Carlson (1964) are compared in Table 2. The patterns indicated a body-centred cubic structure with a from 8.82 to 8.837 Å. There are minor but significant differences in their unit-cell edges, that is, the natural minerals are smaller than the synthetic materials. In order to obtain a better understanding of this cell-edge variation material with smaller unit-cell edges were prepared by hydrothermal experiments (Table 3). The unit-cell edge of material prepared from a synthetic melilite with the composition Ak_1Ge_6 is 8.830 Å, which is nearly equal to that of Fuka material. This is explained by the existence of a coupled substitution of AlAl by MgSi as seen in the well known melilite series.

Table 3. Cell dimensions of bicchulite.

		a (Å)
Natural	from Kuka at 20°C	8.829(2)
	at 300°C	8.842*
	at 500°C	8.851*
Synthetic	from Carneal	8.82 (1)
	present study (free from Mg)	8.837(2)
	(containing Ma†)	8.830(2)
	Carlson (1964)	8.83

* These results show that the thermal expansion coefficient of bicchulite is $5.2 \times 10^{-6}/^\circ\text{C}$.

† Synthesized from synthetic melilite with the composition of Ak_1Ge_6 .

Syntheses and hydrothermal changes

Carlson (1964) synthesized gehlenite hydrate (bicchulite) during the course of some hydrothermal studies in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and showed the limits of the compositions of starting materials to produce gehlenite hydrate.

In this study, the stability relation between gehlenite and bicchulite and the differences between the products from pure gehlenite and from gehlenite with various amounts of magnesium were investigated by hydrothermal techniques. The P-T boundary between gehlenite and bicchulite was also determined (Fig. 1). The conditions and the results were listed in Tables 4 and 5. All starting materials and products were examined with an X-ray diffractometer. The P-T boundary for the natural material from Fuka were in good agreement with that for synthetic one. As shown in Fig. 1, the boundary of gehlenite and bicchulite lies at $635 \pm 5^\circ\text{C}$ and 1 kbar, and at $595 \pm 5^\circ\text{C}$ and 300 bar water pressure.

The starting materials, which were tried to treat in the present work (Table 5), include not only the gehlenite end of melilite but also melilite with various akermanite components. Mixed oxides

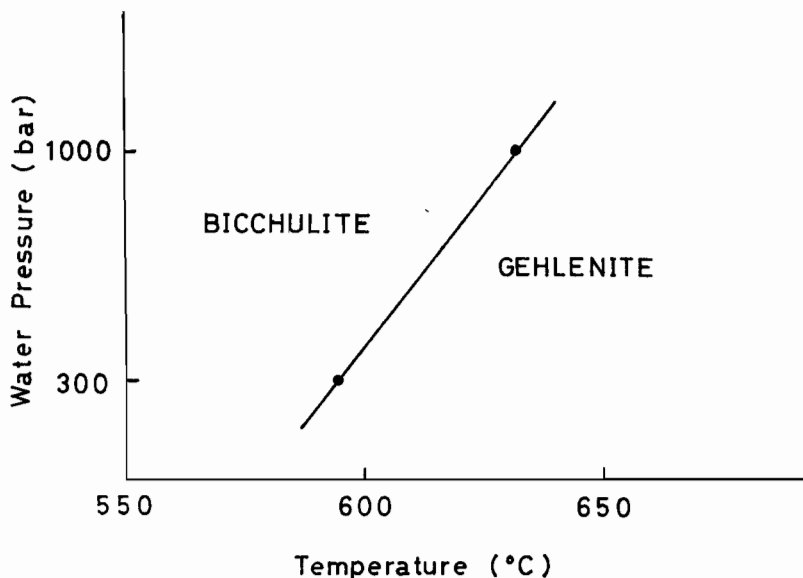


Fig. 1. Stability boundary between gehlenite and bicchulite. There was no distinct difference between the Fuka mineral and the synthetic one.

were used after sintering. The gehlenite composition yielded pure bicchulite and the composition of melilite rich in gehlenite (Al_1Ge_6) yielded also only bicchulite whose cell dimensions were slightly

Table 4. The results of hydrothermal treatments.

Starting materials*	T, °C	P, bar	Time, days	Results (increased mineral)
Natural	550	1000	2	bicchulite
Synthetic	"	"	"	"
Natural	630	"	"	"
Synthetic	"	"	"	"
Natural	635	"	"	not distinct
Synthetic	"	"	"	gehlenite
Natural	640	"	"	"
Synthetic	"	"	"	"
Natural	580	300	6	bicchulite
Synthetic	"	"	"	"
Natural	590	"	4	"
Synthetic	"	"	"	"
Natural	600	"	"	gehlenite
Synthetic	"	"	"	"

* Mixtures of gehlenite and bicchulite in both natural (Fuka) and synthetic materials were used.

Table 5. Hydrothermal products from melilite with various compositions.

Compositions of starting material*				T, °C	P, bar	Time, hours	Results†
MgO:	CaO:	Al ₂ O ₃ :	SiO ₂				
2	1	1		550	1000	90	(B)ss
1	14	6	8	"	"	"	(B)ss
1	12	5	7	"	"	"	(B)ss, (V)s
1	6	2	4	"	"	"	(B)ss, (V)m, (G)w
2	6	1	5	"	"	"	(V)m, (unid)s
1	2		2	"	"	"	(M)s, (W)m, (unid)w

* As the starting materials, mixed oxides after sintering were used.

† B: bicchulite, V: vesuvianite, G: grossular, M: monticellite, W: wollastonite, unid: unidentified material.

ss: very strong, s: strong, m: medium, w: weak.

smaller than those of the material from pure gehlenite. The yield of bicchulite decreased with increasing akermanite component in the starting material, and in such cases vesuvianite or hydrogrossular or both appeared.

Name and type mineral

The name of bicchulite* is for the first locality, the Town of Bitchu. The town of Bitchu was named in allusion to old country name of the district, and the mineral name is also indirectly related to the old district name. The Japanese name of Bitchu may be also spelled as Bicchu, and the authors preferred the latter spelling.

Type specimens of the mineral from Fuka and from Carneal have been deposited at Department of Earth Sciences, Faculty of Science, Okayama University, Okayama, Japan and at Institute of Geological Sciences, London, England respectively.

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* Pronunciation written in International Phonetic Alphabet is [bitʃu:lait].