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Synthesis, composition, thermal stability, and thermodynamic properties of bicchulite, $Ca_2[Al_2SiO_6](OH)_2$

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Abstract

Single-phase bicchulite has been synthesized and its composition established as $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$. Bicchulite crystallizes in space group $I\bar{4}3m$, with $a = 8.825 \pm 0.001$ A. Seven reversal brackets have been obtained experimentally for the dehydration reaction bicchulite = gehlenite + H_2O in the P_{H_2O} range 500 to 7000 bars. The equilibrium constant, K, for this reaction may be expressed as $\log K = \log f_{H_2O} = 9.02 - 5750/T + 0.0699(P - 1)/T$, with P indicated in bars and T in °K. Based on these experimental data, the standard state thermodynamic parameters for bicchulite are found to be:

$$H^0_{f,298} = -4364.511 \text{ kJ/mol}$$

$$S^0_{298} = 216.0 \text{ J/°K-mol}$$

$$G^0_{f,298} = -4098.169 \text{ kJ/mol}$$

$$V^0_{298} = 10.3496 \text{ J/bar}$$

Data available on the CaO-rich portion of the system $CaO–Al_2O_3–SiO_2–H_2O–CO_2$, where the compositions of simplified bicchulite-bearing metamorphic rocks would plot, suggest that bicchulite will be restricted to assemblages with a vapor of extremely low X_{CO_2}.

Introduction

Carlson (1964) first described a synthetic phase of possible composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$, a gehlenite monohydrate, during his study of the system $CaO–Al_2O_3–SiO_2–H_2O$. More recently, Henmi *et al.* (1973) discovered the natural equivalent of this phase from skarns of Fuka (Honshu Island, Japan) and from a high-grade contact aureole of northern Ireland; they named this mineral bicchulite. Preliminary investigations on the stability relations of this phase at P_{H_2O} up to 1000 bars were made by Henmi *et al.* (1973) and Shoji (1975). In the present study, the synthesis of single-phase bicchulite was achieved and its composition was established. Furthermore, the decomposition of bicchulite to gehlenite plus H_2O vapor has been determined reversibly to 7000 bars P_{H_2O}. On the basis of seven reversal brackets of this equilibrium, the standard thermodynamic properties of bicchulite have been derived. The crystal structure of synthetic bicchulite, which has been demonstrated to belong to the group of the framework silicates, has been reported elsewhere (Sahl and Chatterjee, 1977).

Previous work

Carlson (1964) reported the result of hydrothermal synthesis runs on various bulk compositions near gehlenite in the system $CaO–Al_2O_3–SiO_2–H_2O$. He noted that the maximum yield of the cubic phase gehlenite monohydrate was achieved on the composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot xH_2O$; however, even here, it was invariably accompanied by minor amounts of hydrogrossular. Gravimetric determination of H_2O on a number of high-yield preparations gave an average of 1.08 (range 1.00 to 1.19) moles of H_2O per mole of $2CaO \cdot Al_2O_3 \cdot SiO_2$. From these observations, Carlson (1964, p. 452) deduced that it was impossible to state whether or not "the proposed formula $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$ is actually correct." Several years later Henmi *et al.* (1973) demonstrated that the mineral bicchulite is identical to Carlson's gehlenite monohydrate. Their experimental studies showed

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that bicchulite structure is capable of some MgSi = AlAl type substitution. Moreover, they also established the thermal stability of bicchulite in the P_{H_2O} range 300 to 1000 bars in the system $Ca_2Al_2SiO_7$–H_2O.

More recently, another phase on the join $Ca_2Al_2SiO_7$–H_2O, a gehlenite octahydrate, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, has been described from a limestone xenolith in a basalt from Mayen, Eifel, Germany, under the name strätlingite (Hentschel and Kuzel, 1976). Strälingite is a sheet silicate, crystallizing in space group $R3$ or $R\overline{3}$ (Kuzel, 1976), and contains eight (OH)-groups in addition to four H_2O molecules. With rising temperature, strätlingite tends to lose the water molecules reversibly (Kuzel, 1976). As indicated by Carlson (1964), under hydrothermal conditions gehlenite octahydrate decomposes to bicchulite + hydrogrossular ± boehmite. This implies that the anhydrous composition of bicchulite must be more aluminous and less siliceous than that of strätlingite (*cf.* Fig. 1). However, no compelling evidence exists so far to substantiate this hypothesis. Indeed, no information is available on the upper thermal stability of strätlingite or on the lower thermal stability of bicchulite. The only other data available on the phase relations in the system $Ca_2Al_2SiO_7$–H_2O concern the equilibrium gehlenite + H_2O = liquid (Huckenholz and Yoder, 1974).

Experimental procedure

High-pressure apparatus

Conventional cold-seal hydrothermal apparatus was used for all runs up to 5 kbar P_{H_2O}. Temperatures were measured with chromel–alumel thermocouples. Calibration of the bomb-furnace assembly was achieved by using thermocouples calibrated against the melting points of NaCl, NaI, and metallic Pb, and measuring temperatures inside the pressure vessels under operating conditions. The cumulative uncertainty in the stated temperature due to calibration, measurement, and control is within ± 5°C. Pressures were measured by Bourdon tube gauges, and are believed to be accurate to ± 100 bars in the pressure range 1 to 5 kbar and to ± 50 bars at 500 bars.

The hydrothermal runs at 7 kbar P_{H_2O} were conducted in an internally-heated pressure vessel, with argon as the pressure medium. Temperatures were measured with a Pt–Pt90Rh10 thermocouple, and are believed to be correct to ± 10°C. The pressure-dependence of the thermocouple e.m.f. has been disregarded in stating the temperatures. Pressure measurements was effected through a manganin cell; the reported pressure are thought to be accurate to ± 100 bars.

Experimental techniques

The starting material, along with deionized water, was welded shut into thin-walled gold tubes and subjected to the desired pressure–temperature conditions. Following termination of the runs, the tubes were checked for leakage, cut open, dried, and the run products examined under the polarizing microscope and by X-ray diffractometry.

The P_{H_2O}–T reversal brackets for the univariant reaction bicchulite = gehlenite + H_2O were obtained from hydrothermal runs, using a starting material consisting of synthetic gehlenite seeded with 10 weight percent of synthetic single-phase bicchulite, in presence of excess H_2O vapor. Runs lasting up to 10 days were usually sufficient to demonstrate drastic growth of one of the phases at the expense of the other.

Starting materials

Single-phase synthetic gehlenite was used as starting material for the hydrothermal synthesis of bicchulite. The gehlenite was prepared from an oxide mix of its own composition. The oxide mix was made from reagent-grade $CaCO_3$, γ-Al_2O_3 (2.03 per cent H_2O), and purified Brazilian quartz. After homogenizing, the mix was ignited at 500° for 1 day, followed by raising the temperature by 100° steps each day to 1000°C. The final ignition was at 1330°C for 1 day. This material was then subjected to hydrothermal treatment at 710°C, 1 kbar P_{H_2O} for 7 days. The final product was a single-phase gehlenite, as determined both optically and by X-ray diffractometry.

Experimental results

Phases synthesized

Gehlenite was synthesized hydrothermally as stated above. Its cell dimensions were obtained from X-ray diffractogram using KI (a = 7.06516 ± 0.00010 A; calibrated against diamond) as internal standard. In all, 40 lines in the range 16 to 66° $2\theta_{CuK\alpha}$ could be unambiguously indexed, using powder-diffraction intensities calculated on the basis of space group $P\overline{4}2_1m$ and the refined atomic coordinates of gehlenite (Louisnathan, 1971). The least-squares refinement of the cell dimensions made use of the computer program by Appleman and Evans (1973) and converged to an observed standard error unit weight of 0.013°

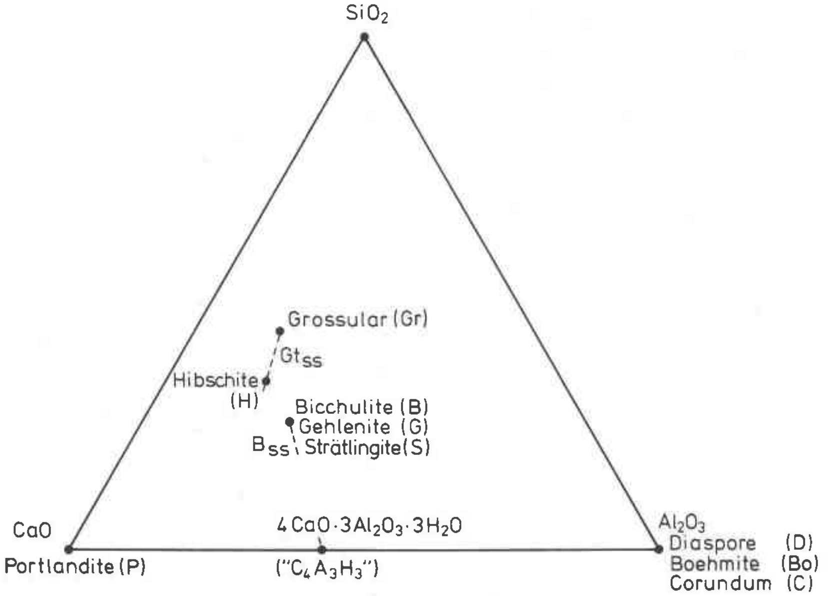

Fig. 1. Crystalline phases in the system $CaO–Al_2O_3–SiO_2–H_2O$ pertinent to this study shown in a projection from the H_2O apex onto the water-free base of the tetrahedron. Abbreviations for phases indicated in parentheses; Gt_{ss} stands for hydrogrossular crystalline solution.

$2\theta_{CuK\alpha}$. The cell dimensions are: $a = 7.6874 \pm 0.0015$, $c = 5.0641 \pm 0.0012$ A, and $V = 299.27 \pm 0.12$ A^3 (*esd* at 3σ-level). A remarkable agreement in observed and calculated X-ray diffraction intensities suggests that our synthetic gehlenite is possibly similar to the gehlenite examined by Louisnathan (1971), as far as ordering of Si and Al in the T_{3-6} type tetrahedra (point symmetry $mm2$) is concerned; the remaining Al, therefore, occupies the T_{1-2} type tetrahedra (point symmetry $\bar{4}$). Thus, the structural formula of the synthetic gehlenite may be written as $Ca_2Al(Al_{0.5}Si_{0.5})_2O_7$.

Bicchulite was prepared hydrothermally from synthetic single-phase gehlenite. As indicated by Carlson (1964), hydration of gehlenite to bicchulite is invariably accompanied by the formation of hydrogrossular crystalline solution. In most cases, the first-formed bicchulite enclosed minute grains of hydrogrossular along with small remnants of unreacted gehlenite. Hydrothermal treatment of gehlenite at 540°C, 1 kbar P_{H_2O} over periods of 1, 4, 12, and 30 days, with repeated grinding between each treatment, finally led to complete disappearance of hydrogrossular as well as the gehlenite starting material, yielding single-phase bicchulite. Idiomorphic single crystals ranging in size up to 50 μm were obtained (Sahl and Chatterjee, 1977). Microprobe analyses for Ca, Al, and Si on 5 of these crystals demonstrated that they were chemically homogeneous, their anhydrous composition corresponding within the limits of analytical uncertainties to stoichiometric gehlenite. Furthermore, microchemical H_2O determination on two separate batches of synthetic bicchulite gave 6.08 and 6.23 percent H_2O, agreeing excellently with the theoretical value of 6.16 percent H_2O in gehlenite monohydrate. Thus, the composition of bicchulite is unequivocally established as gehlenite monohydrate, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$.

Carlson's (1964, p. 452) failure to prepare single-phase bicchulite, as well as the considerable difficulty we encountered in synthesizing single-phase material on its own composition, warrants some discussion regarding the nature of the first-formed bicchulite during the hydration of gehlenite. In this discussion, only those runs made on the composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot xH_2O$ will be considered. Carlson (1964, Table 1) conducted a large number of synthesis runs on that composition under a variety of conditions. Whenever bicchulite formed, it was accompanied by hydrogrossular, occasionally with small amounts of boehmite. Furthermore, Carlson (1964, p. 450) noted that the hydrogrossular formed grew progressively less hydrous and more siliceous with increasing run temperatures. In our study, only hydrogrossular was observed. Determination of its cell dimensions on the basis of 5 diffraction lines gave $a = 11.878 \pm 0.004$ A (*esd* at 3σ-level). According to data furnished by Olesch (1973, p. 34), a lattice constant of 11.878 A indicates a composition of approximately 70 grossular, 30 hibschite. Since most of Carlson's runs were performed at lower temperatures than in the present study, his hydrogrossulars must have been richer in the hibschite end member [$Ca_3Al_2Si_2(OH)_4O_8$; Deer *et al.*, 1962, p. 79]. These observations can be tentatively interpreted in terms of formation of a *metastable* subsiliceous bicchulite at the beginning of the synthesis runs. The possible accompanying phase on the bulk composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot xH_2O$ will be hydrogrossular (hibschite$_{30}$) at temperatures around 540°C, as in the present case. At substantially lower temperatures, the coexisting hydrogrossular will be even less siliceous; as such, an aluminous phase (diaspore or boehmite) will show up in addition, as indicated by Carlson (1964). At temperatures higher than ~ 540°C, the garnet composition will shift toward H_2O-free grossular, and consequently, a calcic phase (portlandite?) will appear in addition. These alternate possibilities have been illustrated in Figure 2.

The question that arises now concerns the nature of the substitution that leads to such a silica-poor bicchulite. From a structural point of view, either of the following two substitutions seem to be possible: (a) $Si^{4+} + OH^- = Al^{3+}$, or (b) $Si^{4+} = Al^{3+} + H^+$. The former substitution leads from ideal stoichiometric bicchulite to the compound $4CaO \cdot 3Al_2O_3 \cdot H_2O$, the latter substitution to $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ ("$C_4A_3H_3$"). The compound $4CaO \cdot 3Al_2O_3 \cdot H_2O$ has apparently not been reported so far; however, $C_4A_3H_3$ is known to exist at the P_{H_2O}–T conditions of the synthesis runs described here. Moreover, both bicchulite (Sahl and Chatterjee, 1977) and $C_4A_3H_3$ have sodalite-type structure, the latter demonstrating an orthorhombic distortion of the basic structure type (Ponomarev *et al.*, 1970). It may, therefore, be tentatively concluded that silica-poor bicchulite can be derived from stoichiometric bicchulite by the substitution $Si^{4+} = Al^{3+} + H^+$. The Al so introduced goes into the framework of tetrahedral four-fold rings (Sahl and Chatterjee, 1977), while the proton

Table 1. X-ray powder diffraction data for synthetic bicchulite prepared at 540°C, 1 kbar PH_2O in 47 days

h k l†	d_{cal} (Å)	d_{obs} (Å)	I_{cal}*	I_{obs}**
2 0 0	4.41	4.41	1	3
2 1 1	3.603	3.600	93	78
2 2 0	3.120	3.120	9	7
3 1 0	2.791	2.790	100	100
2 2 2	2.548	2.547	25	34
3 2 1	2.359	2.358	24	25
4 0 0	2.206	2.205	12	13
3 3 0	2.080	2.080	22	40
4 1 1			33	
4 2 0	1.973	1.974		
3 3 2	1.882	1.882	3	4
4 2 2	1.801	1.802	8	9
4 3 1	1.731	1.731	9	12
5 1 0			5	
5 2 1	1.611	1.612	8	6
4 4 0	1.560	1.560	44	41
5 3 0	1.514	1.513	1	19
4 3 3			23	
4 4 2	1.471	1.471	3	6
6 0 0			3	
6 1 1	1.432	1.432	3	8
5 3 2			6	
6 2 0	1.395	1.395	1	1
5 4 1	1.362	1.362	6	8
6 2 2	1.330	1.331	10	8
6 3 1	1.3012	1.3013	3	3
7 1 0	1.2481	1.2483	1	5
5 4 3			5	
6 3 3	1.2010	1.2009	2	4
5 5 2			1	
7 2 1			1	
6 4 2	1.1793	1.1795	3	3
7 3 0	1.1588	1.1588	14	10
7 3 2	1.1208	1.1208	2	5
6 5 1			4	
8 0 0	1.1032	1.1031	3	4
8 1 1	1.0863	1.0864	2	8
7 4 1			7	
5 5 4			2	
6 4 4	1.0702	1.0704	2	1
6 5 3	1.0548	1.0549	1	1
8 2 2	1.0401	1.0402	2	2
8 3 1	1.0259	1.0260	4	5
7 4 3			3	
7 5 0			1	
6 6 2	1.0123	1.0123	3	2
7 5 2	0.9993	0.9993	1	1
8 4 0	0.9867	broad	1	1
8 4 2	0.9629	0.9629	2	2
9 2 1	0.9517	0.9517	2	3
7 6 1			2	
6 5 5			1	
6 6 4	0.9408	0.9408	1	1
8 5 1	0.9303	0.9302	4	3
9 3 2	0.9102	broad	1	1
8 4 4	0.9907	0.9908	8	5
8 5 3	0.8915	0.8915	2	4
9 4 1			2	
7 7 0			2	
8 6 0	0.8825	broad	1	1
8 6 2	0.8654	0.8655	3	3
9 5 0	0.8572	broad	1	2
9 4 3			2	
10 2 2	0.8492	0.8492	3	2
6 6 6			1	
10 3 1	0.8415	0.8415	3	3
7 6 5			1	
9 5 2			2	
8 5 5	0.8266	0.8265	2	8
7 7 4			8	
8 6 4	0.8194	0.8194	1	3
10 4 0			6	
9 6 1	0.8124		3	2
10 3 3			1	

a = 8.8254 ± 0.0003 Å, *V* = 687.39 ± 0.08 Å^3 ; *Space group:* $I\bar{4}3m$, *Z* = 4

† *X-ray diffraction lines with* I_{cal} < 1 *has not been listed*

* d_{cal} *and* I_{cal} *are from refined atomic parameters for synthetic bicchulite (Sahl and Chatterjee,1977)*

** I_{obs} *are integral peak area intensities*

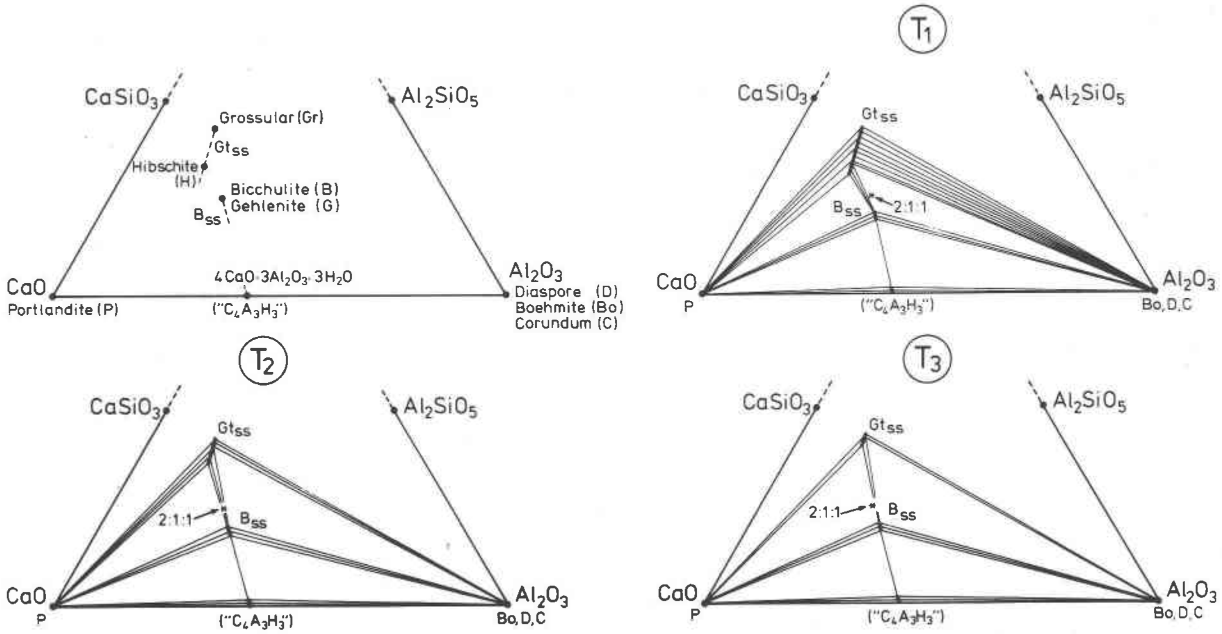

Fig. 2. Possible alternative topologies of phase diagrams at three different temperatures for the anhydrous bulk composition $2CaO\cdot Al_2O_3\cdot SiO_2$ (2:1:1), shown in a projection from the H_2O apex onto the H_2O-free base $CaO–Al_2O_3–SiO_2$. T_2 corresponds to $T \sim 540$°C, T_1 to substantially lower temperatures, and T_3 to temperatures higher than T_2. Abbreviations as in Fig. 1. *Note that the metastable miscibility of bicchulite has been strongly exaggerated for clarity of presentation.*

combines with one of the oxygens of the $Ca–(O/OH)_6$ octahedra. The ultimate implication is that the first-formed bicchulite is a subsiliceous crystalline solution which, however, reacts with coexisting hydrogrossular (± diaspore or boehmite) at the same T and P_{H_2O} with longer run durations to yield the final stoichiometric bicchulite. In other words, the first-formed bicchulite on $2CaO\cdot Al_2O_3\cdot SiO_2\cdot xH_2O$ composition is a *metastable* crystalline solution.

The cell dimension of bicchulite has been refined on three separate samples, both from Guinier photographs with Si as internal standard and from powder X-ray diffractograms using BaF_2 (a = 6.1971 ± 0.0002 A; calibrated against diamond) as an internal standard. The results obtained overlap within 3σ uncertainties. The powder-diffraction data reproduced in Table 1 are from the diffractometer measurements. The observed intensities correspond to the peak *areas;* the calculated intensities are based on space group and atomic coordinates indicated by Sahl and Chatterjee (1977). The excellent agreement between the observed and calculated intensities should be noted. It is also worthwhile to point out that the single-phase bicchulite (a = 8.825 ± 0.001 A; *esd* at 3σ-level) we synthesized has a slightly smaller lattice constant compared to those reported earlier (a = 8.83 A, Carlson, 1964; a = 8.837, Henmi *et al.*, 1973). This is best explained by the probable sub-siliceous composition of the bicchulite synthesized by the previous workers.

The equilibrium: bicchulite = gehlenite + H_2O

Reversal runs to establish the univariant $P_{H_2O}–T$ equilibrium bicchulite = gehlenite + H_2O were performed on a starting material made up of synthetic gehlenite seeded with 10 weight percent of synthetic single-phase bicchulite. Run data are listed in Table 2.

In all, seven reversal brackets have been obtained in the P_{H_2O} range 500 to 7000 bars; these are indicated on a $\log f_{H_2O} + \Delta V^0_{298,s}(P-1)/2.3026\,RT$ *vs.* $1/T$°K plot (Fig. 3). A curve fitted to pass through these brackets will have a slope equivalent to $-\Delta H°/2.3026\,R$ (Chatterjee, 1977, p. 141). It is seen that only a straight-line fit can be obtained through these brackets, indicating that the ΔH^0 of the reaction bicchulite = gehlenite + H_2O is constant for the range of temperature explored experimentally. An extrapolation of this straight line to lower temperatures shows that it also passes through the 300 bar bracket established experimentally by Henmi *et al.* (1973). The equilibrium constant for the reaction bicchulite = gehlenite + H_2O was derived from a linear least-squares fit of these eight reversal brackets; thus,

Table 2. Critical hydrothermal runs demonstrating reversal of the reaction bicchulite = gehlenite + H_2O vapor

Run No.	P_{H_2O} (kbar)	T (°C)	Run duration (days)	Condensed run products*
0.5-5	0.5	607	12	Bi(+), Ge(-)
0.5-2	0.5	617	10	Bi(+), Ge(-)
0.5-6	0.5	627	12	Ge(+), Bi(-)
0.5-1	0.5	637	7	Ge only
Reaction interval: 617-627°C/0.5 kbar P_{H_2O}				
1-4	1.0	638	7	Bi only
1-3	1.0	648	7	Ge only
1-1	1.0	659	8	Ge only
Reaction interval: 638-648°C/1.0 kbar P_{H_2O}				
2-5	2.0	649	8	Bi(+), Ge(-)
2-2	2.0	660	8	Bi(+), Ge(-)
2-4	2.0	670	8	Bi(+), Ge(-)
2-1	2.0	680	8	Ge only
2-3	2.0	690	5	Ge only
Reaction interval: 670-680°C/2.0 kbar P_{H_2O}				
3-4	3.0	680	7	Bi(+), Ge(-)
3-3	3.0	690	6	Bi(+), Ge(-)
3-2	3.0	700	8	Ge only
3-1	3.0	721	7	Ge only
Reaction interval: 690-700°C/3.0 kbar P_{H_2O}				
4-2	4.0	690	8	Bi(+), Ge(-)
4-3	4.0	700	8	Bi(+), Ge(-)
4-1	4.0	711	5	Ge only
4-4	4.0	721	8	Ge only
Reaction interval: 700-711°C/4.0 kbar P_{H_2O}				
5-1	5.0	711	5	Bi(+), Ge(-)
5-2	5.0	721	7	Bi(+), Ge(-)
5-3	5.0	731	5	Ge(+), Bi(-)
Reaction interval: 721-731°C/5.0 kbar P_{H_2O}				
Mirw-1	7.1	720	2	Bi(+), Ge(-)
Mirw-3	6.98	741	2	Bi(+), Ge(-)
Mirw-2	7.05	760	2	Ge only
Reaction interval: 741°C/6.98 kbar to 760°C/7.05 kbar P_{H_2O}				

* *Abbreviations: Bi, bicchulite; Ge, gehlenite; relative growth or diminution of phases indicated by (+) or (-) respectively.*

$\log K = \log f_{H_2O} = 9.02 - 5750/T + 0.0699(P - 1)/T$, with P expressed in bars and T in °K.[2]

Thermodynamic considerations

Standard thermodynamic data for bicchulite may be extracted from phase-equilibria measurements of the reaction bicchulite = gehlenite + H_2O, because thermodynamic data for gehlenite and H_2O are available. The method of data retrieval applied in this study is the so called "curve-fitting" technique, described in detail elsewhere (Chatterjee, 1977, p. 144 *ff*).

Hemingway and Robie (1977) have recently tabulated $H^0_{f,298}$ and S^0_{298} for a gehlenite having the structural formula $Ca_2Al(Al_{0.5}Si_{0.5})_2O_7$. As pointed out earlier, our synthetic gehlenite has an identical structural formula, so these tabulated data were adopted for our calculation. V^0_{298} for gehlenite, as measured by us, was used. Thermodynamic data for H_2O were obtained by combining those given by Robie and Waldbaum (1968) with the H_2O fugacity data tabulated by Burnham *et al.* (1969). Using these data as input, the following thermodynamic data were derived for bicchulite:

$$\begin{aligned} H^0_{f,298} &= -4364.511 \text{ KJ/mol} \\ S^0_{298} &= 216.0 \text{ J/°K-mol} \\ (S^0_{f,298} &= -893.315 \text{ J/°K-mol) and} \\ G^0_{f,298} &= -4098.169 \text{ KJ/mol.} \end{aligned}$$

As noted earlier, the bicchulite structure (Sahl and Chatterjee, 1977) involves random mixing of two Al

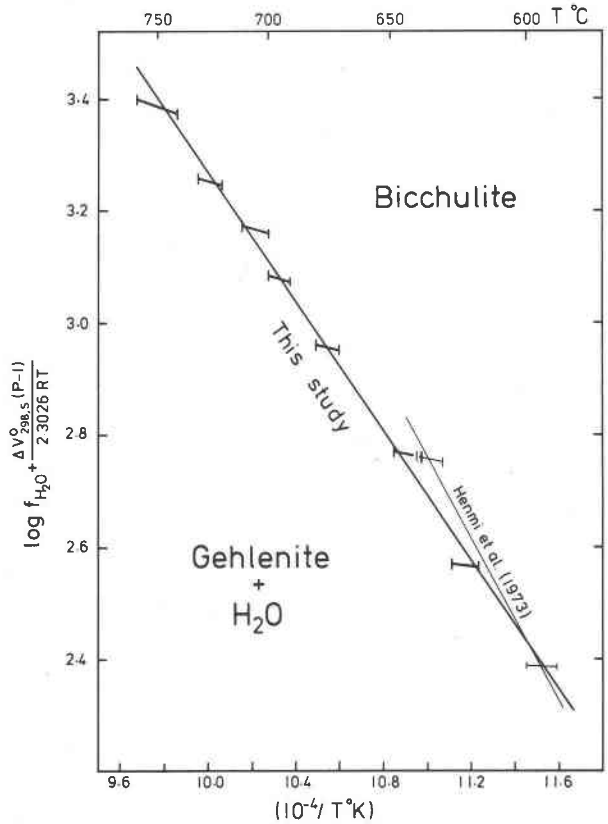

Fig. 3. A $\log f_{H_2O} + \Delta V^0_{298,s}(P - 1)/2.3026\,RT$ *vs.* $1/T$°K plot of the reversal brackets for the reaction bicchulite = gehlenite + H_2O vapor. Seven heavy brackets are from the present work, the two thin ones are from Henmi *et al.* (1973).

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[2] After completion of the experimental work on this project, it became known to us that a similar study has been undertaken at Munich by Huckenholz (H. G. Huckenholz, personal communication, April 4, 1977).

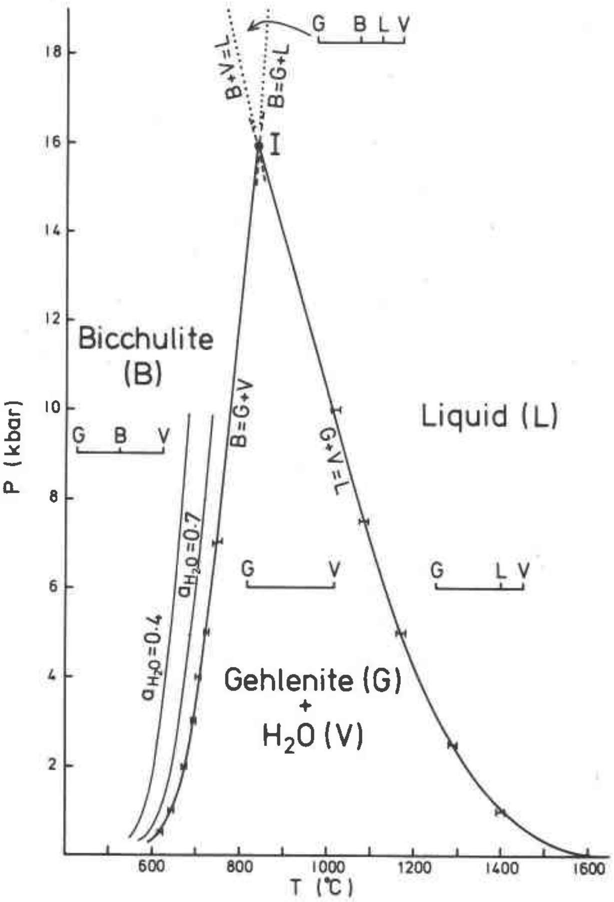

Fig. 4. Phase relations among bicchulite (B), gehlenite (G), a hydrous liquid (L) and H_2O vapor (V) in the system $Ca_2Al_2SiO_7$–H_2O projected onto the $P_{H_2O}(= P_{total})$ *vs.* T °C plane. The equilibrium curves for the decomposition of bicchulite to gehlenite + H_2O vapor at a_{H_2O} equalling 0.7 and 0.4 were calculated from thermodynamic data given in the text.

and 1 Si on 3 tetrahedrally coordinated sites per formula unit. This implies an ideal molar configurational entropy of 15.819 J/°K for bicchulite. It should be stressed, however, that the value of S^0_{298} derived above utilizing the curve-fitting technique already includes the configurational contribution to the total standard molar entropy (*cf.* Chatterjee, 1977, p. 151).

Phase relations and geological application

Bicchulite is known to occur as a product of the hydration of gehlenite during the cooling episode of contact metamorphism or metasomatism. Its occurrence in association with phases such as calcite, wollastonite, spurrite, tilleyite, gehlenite, rankinite, hydrogrossular, portlandite, *etc.* suggests that the system CaO–Al_2O_3–SiO_2–H_2O–CO_2 might serve as a suitable model system for a discussion of its phase relations. Unfortunately, the lack of knowledge of compatibility relations of phases in the CaO-rich part of the system CaO–Al_2O_3–SiO_2–H_2O–CO_2 will inevitably make any detailed discussion of the phase relations of bicchulite premature. Only the salient features of its stability relations are indicated in the following.

The join $Ca_2Al_2SiO_7$–H_2O contains three solids, *i.e.* strätlingite ($Ca_2Al_2SiO_7 \cdot 8H_2O$), bicchulite ($Ca_2Al_2SiO_7 \cdot H_2O$), and gehlenite ($Ca_2Al_2SiO_7$), in addition to a H_2O-bearing melt and a H_2O-rich fluid. The phase relations among these phases, with the exception of strätlingite, are indicated in Figure 4. The univariant curve for the decomposition of bicchulite to gehlenite + H_2O is from the present study, whereas that of the hydrous melting of gehlenite is from Huckenholz and Yoder (1974). These two univariant curves intersect at an invariant point located approximately at 840°C and 16 kbar P_{H_2O}. At P_{H_2O} in excess of 16 kbar, bicchulite will become a liquidus phase. If, however, the equilibrium activity of H_2O, a_{H_2O}, becomes less than unity, the subsolidus decomposition curve of bicchulite will be shifted to lower temperatures, as shown in Figure 4; at the same time, the hydrous melting curve of gehlenite will slide to higher temperatures, so that the invariant point involving bicchulite, gehlenite, liquid, and H_2O vapor will move to yet higher pressures. Since magmatic rocks will seldom, if ever, have a very high a_{H_2O}, bicchulite will not be expected to occur in magmatic rocks, even if appropriate bulk compositions are available.

Phase relations of bicchulite in the system CaO–Al_2O_3–SiO_2–H_2O–CO_2 can be discussed at present only in the context of the gehlenite stability (Hoschek, 1974, Fig. 2). Recalling that bicchulite decomposes to gehlenite + H_2O at 643 ± 5°C and 1 kbar P_{H_2O}, it is seen immediately that the occurrence of bicchulite in the CO_2-bearing system will be restricted to rather low X_{CO_2}. At fluid pressures higher than 1 kbar, the corresponding X_{CO_2} value would be yet smaller.

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