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# PHASE RELATIONS BETWEEN CYMRITE, $BaAlSi_3O_8(OH)$, AND CELSIAN, $BaAl_2Si_2O_8$[1]

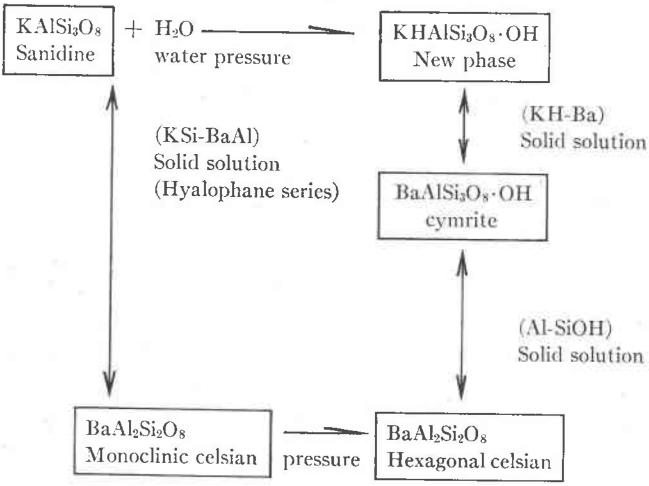
YÔTARÔ SEKI[2] AND GEORGE C. KENNEDY, *Institute of Geophysics and Planetary Physics, University of California, Los Angeles, Calif.*

## ABSTRACT

The chemical reaction: celsian+sanbornite+2 quartz+water$\rightleftharpoons$2 cymrite, has been experimentally studied in the temperature range of 200° to 850° C. and at pressures up to 35 kb by the simple squeezer. Hexagonal celsian forms a complete solid solution series with cymrite by substitution of $Al^{3+}$ for $[Si(OH)]^{3+}$ with increasing water pressure (and/or decreasing temperature). Some interpretations of the natural occurrence of monoclinic celsian, cymrite and sanbornite are presented.

## INTRODUCTION

The potassium and barium feldspars have been studied at length in this laboratory at high temperatures and pressures. Data on the potassium feldspars are appearing in a separate paper. The general relationships between the potassium and barium feldspars are shown in the following diagram.



Sanidine plus water goes to a new phase, $KHAlSi_3O_8\cdot OH$ at high pressure. This new phase is an analog of cymrite and an end member of a solid solution series involving cymrite. Cymrite, in turn is part of a solid solution series of which hexagonal celsian is the other end member.

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[1] Publication #304 Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California.

[2] Department of Earth Sciences, Saitama University, Urawa, Japan.

Hexagonal celsian is the high pressure-low temperature polymorph of monoclinic celsian. Monoclinic celisan is an end member of a solid solution series of which sanidine is the other member.

Cymrite was described as forming a vein within the manganiferous ore deposit of the Benallt mine in Wales by Smith *et al.* (1949). They reported the results of their microchemical tests and *x*-ray study and concluded that this mineral with the chemical composition $BaAlSi_3O_8(OH)$ probably had a very simple hexagonal framework type structure.

Hexagonal celsian was artificially prepared by Dittler and Lasch (1930), Yoshiki and Matsumoto (1951) and Davis and Tuttle (1952). Yoshiki and Matsumoto (1951) found two modifications ($\alpha$ and $\beta$) of hexagonal celsian. Takéuchi (1958) reexamined the crystal structure of these two types of "hexagonal celsian" in detail and showed that $\beta$-"hexagonal" celsian, which is stable below 300° C., is truly orthorhombic; and $\alpha$-hexagonal celsian, which is stable above 300° C., is hexagonal ($D^4 6h$). No significant difference can be observed between the *x*-ray powder patterns of the $\alpha$- and the $\beta$-form except peak shifts owing to lattice expansion. The similarity of *x*-ray patterns demonstrates the similarity of the basic frameworks of these two kinds of celsian. Neither hexagonal nor orthorhombic celsian has been found in nature.

*X*-ray powder data of natural cymrite are almost identical to those of synthesized hexagonal celsian as shown in Columns D and E in Table 1. This similarity is believed to show that these two materials have almost the same fundamental structure.

Another kind of barium-aluminum silicate, monoclinic celsian, has been described, particularly in manganiferous ore deposits (Bauer and Palache, 1926; Larsen *et al.*, 1941; Meier, 1939; Schaller, 1929; Segnit, 1946; Spencer, 1943; Vermaas, 1953; Villiers, 1951; Yoshimura, 1936, 1939). The stability relation between hexagonal celsian and monoclinic celsian has never been clarified.

It is well known that monoclinic celsian and monoclinic potassium feldspar form a complete or partial solid solution through the mineral hyalophane, which is intermediate both in chemical composition and in physical properties (Strandmark, 1903, 1904; Taylor *et al.*, 1934; Vermaas, 1953).

The present writers have recently succeeded in synthesizing a new phase, $KAlSi_3O_8 \cdot H_2O$, from potassium feldspar under high water pressure conditions (Seki and Kennedy, 1964). The *x*-ray powder patterns and unit-cell dimensions calculated for this new phase are quite similar to those of cymrite presented by Smith *et al.* (1949a).

In order to study the relation between two possible solid solution series: cymrite ($BaAlSi_3O_8(OH)$)-$KAlSi_3O_8 \cdot H_2O$ and monoclinic celsian

TABLE 1. *X*-RAY POWDER PATTERNS, UNIT-CELL DIMENSIONS, UNIT-CELL VOLUME AND OPTICAL PROPERTIES OF SYNTHESIZED CYMRITE-HEXAGONAL CELSIAN SERIES MINERALS AND NATURAL CYMRITE

| hkl | A | | B | | C | | D | | E | | F | | G | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Synthesized cymrite (500° C., 25 kb) | | Synthesized cymrite-hex. celsian solid (620° C., 5 kb) | | Synthesized cymrite-hex. celsian solid solution (725° C., 2 kb) | | Natural cymrite (Smith *et al.*, 1949) | | Hexagonal celsian synthesized from oxide mixture (room press. 600° C.) | | Synthesized β-hexagonal celsian (Takéuchi, 1958) | | Synthesized "Monoclinic" celsian (Thomas, 1950) | |
| | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I |
| **001** | 7.68 | 16 | 7.70 | 10 | 7.74 | 33 | 7.7 | 80 | 7.77 | 12 | 7.79 | 112 | 7.7 | w. |
| 010<br>100 | 4.62 | 8 | 4.62 | 8 | 4.58 | 10 | 4.6 | 10 | — | — | — | — | | |
| 011<br>101 | 3.96 | 100 | 3.96 | 100 | 3.94 | 100 | 3.95 | 100 | 3.94 | 100 | 3.963 | 47 | 3.96 | v.s. |
| 012<br>102 | 2.951 | 40 | 2.957 | 45 | 2.961 | 60 | 2.95 | 100 | 2.961 | 100 | 2.977 | 59 | 2.97 | v.s. |
| 110 | 2.671 | 72 | 2.656 | 27 | 2.648 | 67 | 2.67 | 80 | 2.643 | 48 | 2.659 | 15 | 2.65 | s. |
| 003 | 2.554 | 16 | 2.573 | 15 | 2.586 | 22 | 2.57 | 20 | 2.599 | 20 | 2.602 | 22 | | |
| 111 | 2.522 | 10 | 2.513 | 8 | 2.507 | 16 | 2.53 | 20 | 2.505 | 12 | — | — | | |
| 020<br>200 | 2.311 | 24 | 2.302 | 13 | 2.294 | 16 | 2.32 | 40 | 2.295 | 12 | 2.300 | 5 | | |
| 013<br>103 | 2.237 | 34 | 2.248 | 18 | 2.252 | 15 | 2.24 | 60 | 2.255 | 28 | 2.266 | 15 | 2.26 | w. |
| 201<br>021 | 2.214 | 50 | 2.206 | 23 | 2.199 | 20 | 2.21 | 60 | 2.199 | 28 | 2.206 | 11 | 2.20 | m. |
| 112 | 2.192 | 22 | 2.191 | 15 | 2.188 | 25 | | | 2.190 | 28 | — | — | | |

TABLE 1—(*continued*)

| hkl | A | | B | | C | | D | | E | | F | | G | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Synthesized cymrite (500° C., 25 kb) | | Synthesized cymrite-hex. celsian solid (620° C., 5 kb) | | Synthesized cymrite-hex. celsian solid solution (725° C., 2 kb) | | Natural cymrite (Smith *et al.*, 1949) | | Hexagonal celsian synthesized from oxide mixture (room press. 600° C.) | | Synthesized $\beta$-hexagonal celsian (Takéuchi, 1958) | | Synthesized "Monoclinic" celsian (Thomas, 1950) | |
| | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I | d(Å) | I |
| 202<br>022 | 1.981 | 16 | 1.978 | 10 | 1.975 | 22 | 1.990 | 40 | 1.974 | 20 | — | — | | |
| 004 | 1.917 | 20 | 1.932 | 10 | 1.940 | 15 | 1.920 | 50 | 1.943 | 16 | 1.951 | 60 | | |
| 113 | 1.847 | 17 | 1.850 | 23 | 1.850 | 22 | 1.849 | 60 | 1.850 | 32 | 1.860 | 6 | | |
| 014<br>104 | 1.771 | 6 | 1.781 | 15 | 1.786 | 22 | 1.783 | 20 | 1.788 | 8 | — | — | | |
| 201<br>120 | 1.749 | 6 | 1.740 | 5 | 1.734 | 7 | — | — | — | — | — | — | | |
| 121<br>211 | 1.705 | 20 | 1.697 | 13 | 1.691 | 25 | 1.705 | 50 | 1.691 | 20 | — | — | | |
| 122<br>212 | 1.591 | 22 | 1.586 | 15 | 1.582 | 35 | 1.594 | 50 | 1.582 | 20 | — | — | | |
| 114 | 1.558 | 12 | 1.563 | 10 | 1.565 | 7 | 1.565 | 40 | 1.565 | 17 | — | — | | |
| a<br>c | 5.34 (3) Å<br>7.66 (3) Å | | 5.31 (6) Å<br>7. 72 (6) Å | | 5.29 (6) Å<br>7.75 (7) Å | | 5.32 Å<br>7.67 Å | | 5.29 (0) Å<br>7.77 (1) Å | | 5.313±0.05 Å<br>7.805±0.05 Å | | | |
| Unit-cell volume | 189.3 Å³ | | 189.4 Å³ | | 188.8 Å³ | | 188.0 Å³ | | 189.0 Å³ | | 190.4 Å³ | | | |
| Refractive index | No=1.621<br>±0 .003<br>Ne=1.610 | | n=1600 | | n=1.580 | | No=1.6225<br>Ne=1.6125 | | n=1.575 | | Ne=1.573 | | | |

($BaAl_2Si_2O_8$)-sanidine ($KAlSi_3O_8$) and particularly to determine the physical conditions under which cymrite and Ba-bearing monoclinic feldspar are stable, we performed experimental work on the chemical reaction shown below:

$$\underset{BaAl_2Si_2O_8}{\text{celsian}} + \underset{BaSi_2O_5}{\text{sanbornite}} + \underset{SiO_2}{2\text{ quartz}} + \underset{H_2O}{\text{water}} \rightleftharpoons \underset{BaAlSi_3O_8(OH)}{2\text{ cymrite}}$$

under wide ranges of temperature and water pressure.

In the present paper, the solid solution relation between cymrite and hexagonal celsian and the stability field of monoclinic celsian will be described and their geological applications will be discussed.

## EXPERIMENTAL TECHNIQUES AND STARTING MATERIALS

Most of the experimental work in the present study was carried out in the piston-anvil, "simple squeezer," apparatus which has already been described in detail by Griggs and Kennedy (1956) and by Pistorius *et al.* (1960).

Three kinds of starting materials were used.

The first was a glass having the approximate chemical composition of cymrite. The glass was made by heating a finely ground mixture of the following materials to 1300° C. followed by rapid quenching in an air blast:

| | |
|---|---|
| $Ba(OH)_2 \cdot 8H_2O$ | 51.6% by weight |
| $Al_2O_3 \cdot xH_2O$ ($x \fallingdotseq 1$) | 9.8% by weight |
| $SiO_2 \cdot xH_2O$ ($x \fallingdotseq 1$) | 38.5% by weight |

The second starting material was an unfired mixture of the above hydrated materials. The mixture was ground under water and dried. This procedure was repeated 8 to 10 times in order to completely homogenize the mixture.

The third was mixtures of (1) hexagonal celsian, sanbornite and dibarium-trisilicate ($Ba_2Si_3O_8$) and (2) monoclinic celsian, sanbornite and $Ba_2Si_3O_8$. These mixtures were prepared in the simple squeezer from oxide mixes having the chemical composition of cymrite.

Water was added to all mixes before subjecting them to pressure. The pressure was raised to the desired value before heating in order to retain the water in the sample. We failed to synthesize any cystalline phase from the glass starting mixture even when the glass was kept at 700° and 30 kb pressure for 24 hours.

The oxide mixture of cymrite composition, on the other hand, readily transformed into a crystalline phase assemblage. At above 500° C. crystallization of the oxide mixtures was complete within fifteen minutes.

Mixtures of hexagonal or monoclinic celsian, sanbornite and dibarium-trisilicate formed from oxide mixture were used to confirm the reversibility of the two modifications of celsian along the boundary between the hexagonal celsian solid solution+sanbornite+quartz and monoclinic celsian+sanbornite+quartz fields.

The products were identified chiefly by means of *x*-ray powder patterns taken on a Philips diffractometer, using Cu radiation; as well as by means of the polarizing microscope. The *x*-ray patterns of starting materials and synthesized mineral assemblages are very distinctive and little difficulty was encountered in identifying even relatively small amounts of each phase. Quartz powder or silicon powder was used as an internal standard, in order to measure accurately the $2\theta$ CuK$\alpha$ values of diffraction peaks.

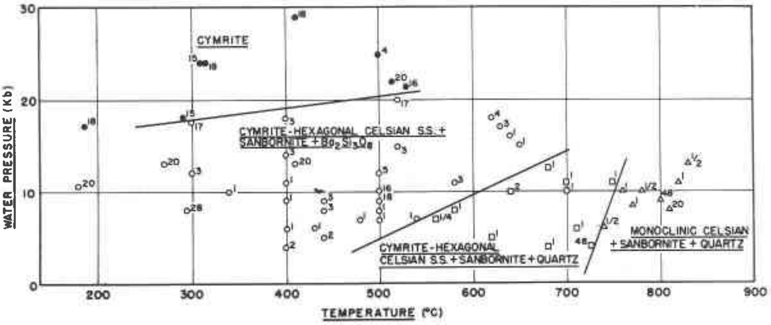

FIG. 1. Stability field of cymrite-celsian and their associated minerals formed by the chemical reaction of 2 cymrite$\rightleftharpoons$celsian+sanbornite+2 quartz+$H_2O$. Numbers represent the duration (in hours) of the runs.

## RESULTS

Figure 1 shows the stability fields of some mineral assemblages associated with the chemical reaction, celsian+sanbornite+2 quartz+$H_2O$ $\rightleftharpoons$2 cymrite.

*Cymrite-hexagonal celsian.* Column A in Table 1 shows the *x*-ray powder data, unit-cell dimensions, unit-cell volume and optical properties of cymrite synthesized from oxide mixture of cymrite composition. These data are practically the same as those of natural cymrite (Col. D in Table 1).

With decreasing pressures and/or increasing temperatures, *x*-ray data and optical properties of the mineral having the cymrite structure gradually approach those of hexagonal celsian (Cols. B, C, E and G, Table

1). A hexagonal mineral formed from the oxide mixture of cymrite composition at 725° C. under water pressure of 2 kilobars and associated with sanbornite and quartz (Col. C, Table 1) shows practically the same physical properties as those of pure hexagonal celsian synthesized under room pressure from an oxide mixture having the chemical composition of cymrite and celsian glass (Cols. E, F, Table 1). Column G in Table 1 contains the *x*-ray data reported by Thomas (1950) for the "monoclinic celsian" synthesized by him. A comparison between this column and Table 2 clearly shows that his "monoclinic celsian" actually was not monoclinic but was hexagonal celsian.

The most distinct *x*-ray diffraction peaks of cymrite are (101), (102) and (110). Among these three peaks, $2\theta$ values of (102) and (110) diffractions should clearly and regularly shift with the transition from pure cymrite to pure hexagonal celsian. Figures 2 and 3 show the shift of $2\theta$ $\text{CuK}\alpha$ values of these two *x*-ray diffractions of cymrite-hexagonal celsian mineral series synthesized under a wide range of physical conditions.

It is clear, from inspection of Figs. 2 and 3, that the chemical potential of all components in this difficult and complex system are not changing as regularly as might be desired. This probably stems from slight non-homogeneity of our oxide starting mix and from failure to retain water pressure exactly equal to confining pressure. More or less, the trend in the system is clear, with cymrite forming at high water pressures and low temperatures and hexagonal celsian forming at low water pressures and high temperatures. In addition, increasing chemical potential of silica with decreasing chemical potential of alumina would cause the stable field of cymrite to expand to much lower water pressures.

*Monoclinic celsian.* Monoclinic celsian was formed from the oxide mixture of cymrite composition under relatively high temperature and low pressure conditions (Fig. 1). Monoclinic celsian is associated with sanbornite and quartz as in the case of hexagonal celsian. *X*-ray data, unit-cell dimension and unit-cell volume of monoclinic celsian are shown under Column A in Table 2. Column C is *x*-ray powder data of "$3Al_2O_3 \cdot 2SiO_2$ (mullite)" synthesized by Thomas (1950) in his study of $BaO$-$Al_2O_3$-$SiO_2$ system. He said "the *x*-ray data lead to the conclusion, though such a conclusion is open to question and deserves further study, that all the points are probably mullite." It is clear, however, that his mullite is actually monoclinic celsian.

*Sanbornite.* Sanbornite ($BaSi_2O_5$) was formed in association with cymrite-hexagonal celsian series, monoclinic celisan, dibarium-trisilicate and quartz in our experiments.

TABLE 2. *X*-RAY POWDER DATA, UNIT-CELL DIMENSIONS AND UNIT-CELL VOLUMES OF MONOCLINIC CELSIANS

| hkl | Synthesized monoclinic Celsian 800°, 9 kb (this paper) | | | Natural monoclinic Celsian (Vermaas, 1953) | | Synthesized "$3Al_2O_3 \cdot 2SiO_2$" (Thomas, 1950) | |
|---|---|---|---|---|---|---|---|
| | Measured | | Calculated d(Å) | d(Å) | I | d(Å) | I |
| | d(Å) | I | | | | | |
| 020 | 6.51 | 41 | 6.51 | 6.39 | 40 | | |
| 021 | 4.59 | 18 | 4.60 | 4.57 | 20 | 4.6 | w |
| 130 | 3.79 | 38 | 3.79 | 3.77 | 3 | 3.80 | m |
| $\bar{2}21$ | 3.55 | 33 | 3.56 | — | — | | |
| $\bar{1}12$ | 3.51 | 80 | 3.51 | 3.44 | 60 | 3.45 | s |
| 220 | Quartz (101)[1] | | 3.336 | 3.33 | 70 | 3.33 | v.s. |
| $\bar{2}02$ | | | 3.321 | | | | |
| 002 | 3.273 | 74 | 3.276 | 3.24 | 70 | 3.25 | s |
| 040 | 3.259 | 74 | 3.262 | | | | |
| 131 | 3.014 | 75 | 3.014 | 3.00 | 70 | 3.00 | m |
| 041 | 2.912 | 30 | 2.916 | 2.901 | 40 | 2.91 | w |
| 201 | 2.834 | 10 | 2.836 | — | — | | |
| $\bar{1}32$ | 2.795 | 50 | 2.794 | 2.758 | 50 | 2.77 | w |
| 221 | 2.603 | 30 | 2.602 | — | — | | |
| $\bar{2}41$ | 2.589 | 100 | 2.589 | 2.574 | 100 | 2.57 | m |
| $\bar{2}03$ | 2.401 | 10 | 2.404 | 2.406 | 30 | | |
| $\bar{1}13$ | 2.354 | 10 | 2.354 | — | — | | |
| 042 | 2.312 | 15 | 2.312 | 2.316 | 30 | | |
| $\bar{2}23$ | 2.259 | 8 | 2.259 | 2.263 | 20 | | |
| 132 | 2.251 | 12 | 2.252 | — | — | | |
| 152 | 2.214 | 18 | 2.214 | — | — | | |
| 060 | 2.174 | 15 | 2.175 | 2.167 | 100 | | |
| $\bar{1}52$ | Quartz (200)[1] | | 2.122 | 2.104 | 10 | | |
| 311 | 2.080 | 10 | 2.082 | 2.056 | 10 | | |
| $\bar{4}22$ | 2.021 | 20 | 2.022 | — | — | | |
| | $a=$ 8.63 (1) Å<br>$b=$13.10 (2) Å<br>$c=$ 7.29 (4) Å<br>$\beta=$116°<br>unit-cell volume 185.2 Å$^3$ | | | $a=$ 8.63 Å<br>$b=$13.10 Å<br>$c=$ 7.29 Å<br>$\beta=$116°<br>unit-cell volume 185.0 Å$^3$ | | | |

[1] Hidden by peaks of associated quartz.

*X*-ray powder data and other physical properties of our sanbornite are represented in Table 3. $BaSi_2O_5$ was first synthesized by Bowen (1918). Eskola (1922) found that synthesized $BaSi_2O_5$ is orthorhombic. In 1932,

TABLE 3. *X*-RAY POWDER DATA, UNIT-CELL DIMENSIONS AND UNIT-CELL VOLUMES OF SANBORNITES

| Synthesized Sanbornite (This paper) | | | Natural Sanbornite (Douglass, 1958) | | |
|---|---|---|---|---|---|
| d(Å) | I | hkl | d(Å) | I | hkl |
| 6.74 | 12 | 002 | 6.79 | 30 | 002 |
| 5.05 | 20 | 012 | 5.08 | 30 | 012 |
| Hex. Celsian (011, 101)[1] | | | 3.97 | 100 | 110 |
| 3.81 | 16 | 102 | 3.82 | 10 | 102 |
| 3.419 | 60 | 112 | 3.422 | 50 | 112<br>004 |
| Quartz (101)[1] | | | 3.342 | 70 | 022 |
| 3.227 | 36 | 103 | 3.226 | 20 | 103 |
| 3.088 | 100 | 014 | 3.092 | 75 | 014 |
| 2.980 | 20 | 113 | 2.980 | 5 | 113 |
| 2.883 | 16 | 121 | 2.888 | 5 | 121 |
| 2.723 | 40 | 104 | 2.720 | 55 | 122<br>104 |
| 2.710 | 60 | 122 | | | |
| Hex. Celsian (003)[1] | | | 2.574 | 15 | 114 |
| 2.540 | 12 | 024 | 2.541 | 5 | 023 |
| 2.395 | 12 | 032 | 2.394 | 5 | 032 |
| 2.326 | 8 | 105 | 2.327 | 5 | 105 |
| 2.316 | 20 | 200 | 2.317 | 15 | 200 |
| — | — | — | 2.281 | <5 | 201 |
| Hex. Celsian (013, 103)[1] | | | 2.236 | 10 | 130<br>115 |
| 2.225 | 45 | 124 | 2.226 | 30 | 124 |
| 2.192 | 28 | 202<br>211 | 2.193 | 15 | 202<br>211 |
| 2.160 | 12 | 016 | 2.162 | 25 | 016 |
| Quartz (200)[1] | | | 2.130 | 40 | 132 |
| 2.108 | 28 | 212 | 2.109 | 10 | 212 |
| 2.038 | 16 | 034 | 2.038 | 5 | 034 |
| 2.026 | 15 | 106 | 2.025 | 15 | 106 |
| 1.995 | 12 | 125 | 1.990 | 10 | 125<br>213 |
| 1.991 | 15 | 213 | | | |
| 1.921 | 25 | 041 | 1.921 | 10 | 041 |
| 1.902 | 27 | 222 | 1.903 | 10 | 222 |
| Hex. Celsian (113)[1] | | | 1.850 | 20 | 214<br>042 |
| — | — | — | 1.815 | 5 | 223 |
| 1.793 | 28 | 126 | 1.793 | 20 | 126 |
| $a=$ 4.63 (7) Å<br>$b=$ 7.69 (0) Å<br>$c=$13.50 Å<br>Unit-cell volume 120.3 Å$^3$ | | | $a=$ 4.63 Å<br>$b=$ 7.69 Å<br>$c=$13.53 Å<br>Unit-cell volume 120.4 Å$^3$ | | |

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[1] Peaks hidden by the presence of peaks of celsian and quartz crystals associated with sanbornite.

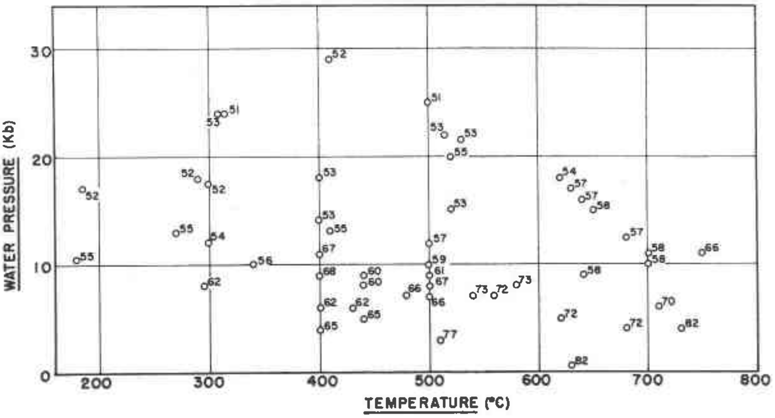

FIG. 2. $X$-ray diffraction peak of (110) of cymrite-hexagonal celsian solid solution series. Numbers represent the $2\theta$ CuK$\alpha$ value (example, $57=33.57$ degrees).

Rogers discovered a natural occurrence of $BaSi_2O_5$ in association with quartz, monoclinic celsian, diopside, gillespite and tourmaline forming a vein in metamorphic rocks, and proposed a new name sanbornite. Recently Douglass (1958) has studied in detail the crystal structure and related solid solution of sanbornite and has found that this mineral, previously described as triclinic by Rogers (1932), is truly orthorhombic. The presence of two polymorphic forms of $BaSi_2O_5$ (high temperature and low temperature forms) has been reported by Roth and Levin (1959). They stated the transition temperature of these two forms to be 1350° C. at room pressure. Sanbornite synthesized at 300–850° C. in our run is believed to be their low temperature form.

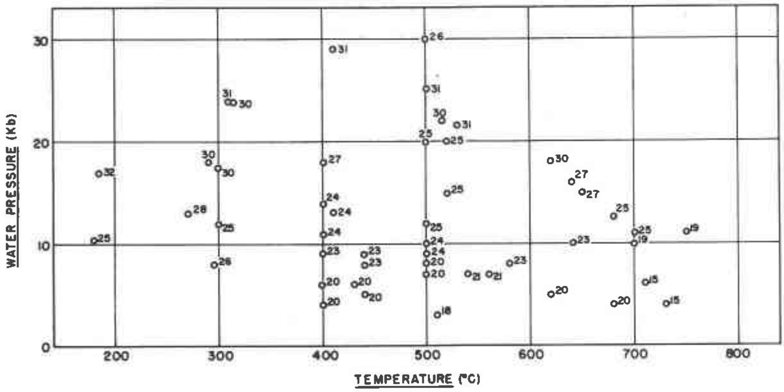

FIG. 3. $X$-ray diffraction peak of (102) of cymrite-hexagonal celsian solid solution series. Numbers represent the $2\theta$ CuK$\alpha$ value (example $30=30.30$ degrees).

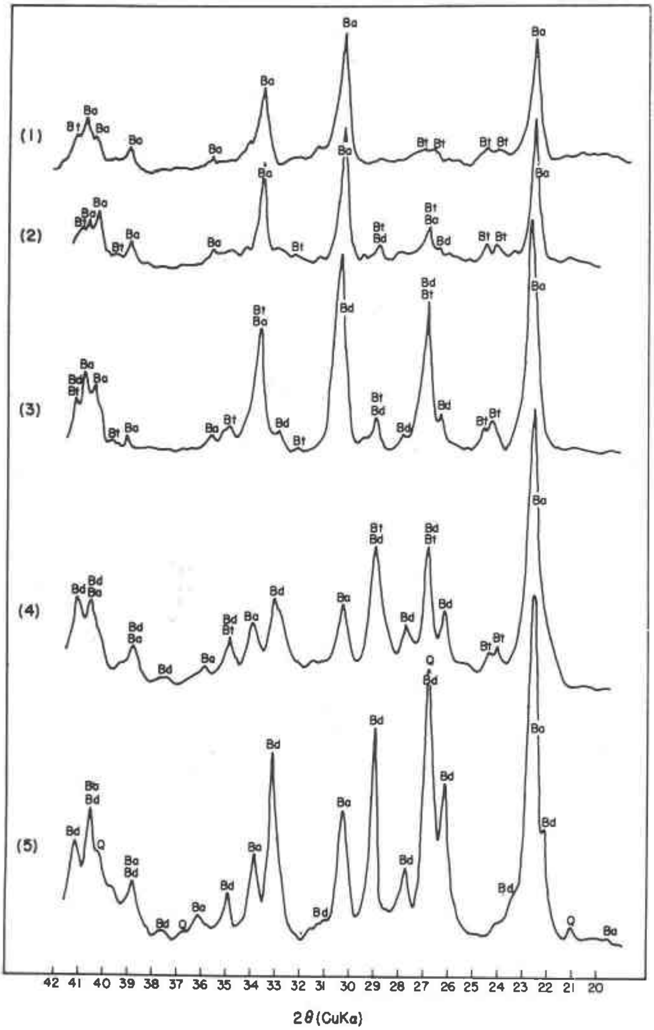

FIG. 4. *X*-ray diffraction figures of 2 cymrite$\rightleftharpoons$hexagonal celsian+sanbornite+2 quartz+$H_2O$ reaction at various physical conditions as follows: (1) 410°, 29 kb, (2) 520°, 20 kb, (3) 630° C., 17 kb, (4) 500° C., 10 kb, (5) 560° C., 7 kb; Ba: Cymrite-hexagonal celsian solid solution, Bd: Sanbornite, Bt: $Ba_2Si_3O_8$, Q: Quartz.

It must be noted that the relative amount of sanbornite synthesized in our runs, as estimated from the intensity of *x*-ray diffractions, gradually decreases with the increase of water pressure and/or decrease of temperature (Figs. 4, 5 and 6).

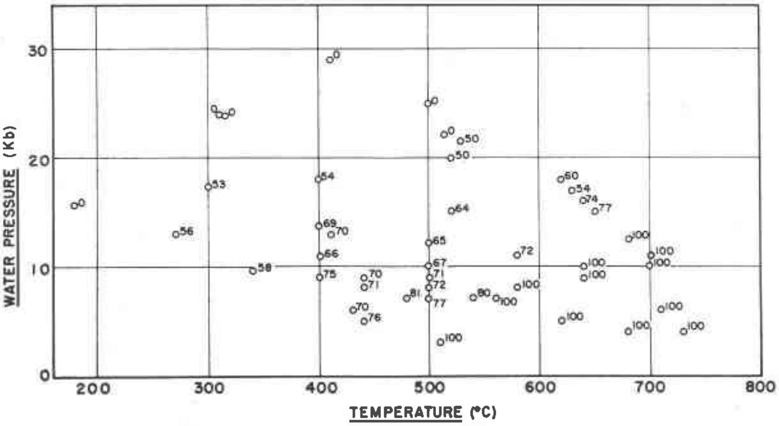

FIG. 5. Diagram showing the variation of the ratio

$$\frac{\text{I (014) sanbornite}}{\text{I (014) sanbornite} + \text{I } (d=3.711)\ Ba_2Si_3O_8} \times 100$$

in the chemical reaction of 2 cymrite$\rightleftharpoons$celsian+sanbornite+2 quartz+$M_2\theta$ at various physical conditions.

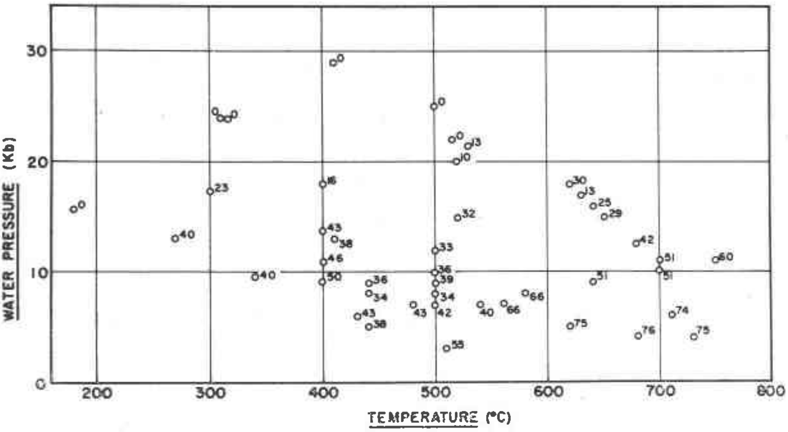

FIG. 6. Diagram showing the ratio of

$$\frac{\text{I (014) sanbornite}}{\text{I (102) cym.-cel. s. s.} + \text{I (014) sanbornite} + \text{I } (d=3.711)\ Ba_2Si_3O_8} \times 100$$

in the chemical reaction of 2 cymrite$\rightleftharpoons$celsian+sanbornite+2 quartz+$H_2O$ at various physical conditions.

*Dibarium-trisilicate* (*$Ba_2Si_3O_8$*). The appearance of dibarium-trisilicate ($Ba_2Si_3O_8$) is limited to higher pressure and lower temperature regions of the field of cymrite-hexagonal celsian series+sanbornite in Fig. 1. *X*-ray powder data of dibarium-trisilicate associated with cymrite-hexagonal celsian series and sanbornite in our runs are shown in Table 4.

The intensity ratio of *x*-ray diffraction peaks clearly show that in our runs the amounts of sanbornite and dibarium-trisilicate vary inversely with changing temperature and pressure. It is also noteworthy that dibarium-trisilicate has never been found in association with quartz or other silical minerals in our experimental work. Thus, with increasing pressure and decreasing temperature the following chemical reaction goes to the right:

2 Sanbornite ($BaSi_2O_5$)$\rightleftharpoons$dibarium-trisilicate ($Ba_2Si_3O_8$)$+SiO_2$

The $SiO_2$ thus liberated is used to form cymrite from hexagonal celsian. Winchell (1931) concluded from his interpretation of the data of Eskola (1922) that $Ba_2Si_3O_8$ and $BaSi_2O_5$ form a continuous series of mix-crystals. Levin and Ugrinic (1953) also said that $Ba_2Si_3O_8$ and $BaSi_2O_5$ form a complete solid solution though the *x*-ray data did not conclusively show a solid solution series. Keler and Glushkova (1956), Glushkova and Keler (1957) and Roth and Levin (1959) later denied the presence of a solid solution relation between these two components. Our experimental work clearly shows several double peaks which indicate the presence of both of these two phases in the same run and thus tend to substantiate the latter hypothesis.

*Quartz.* Quartz is always associated with hexagonal celsian, monoclinic celsian and sanbornite formed at relatively low water pressures in our runs. *X*-ray powder and microscope data show, with increasing water pressure and/or decreasing temperature, the amount of quartz associated with these minerals generally decreases; and finally under high water pressures quartz disappears and dibarium-trisilicate appears in association with cymrite-hexagonal celsian series, rich in cymrite molecule, and sanbornite.

## Summary of Results

Minerals or phases appearing in the chemical reaction: hexagonal or monoclinic celsian+sanbornite+2 quartz+water$\rightleftharpoons$2 cymrite are as follows:

cymrite
hexagonal celsian
monoclinic celsian
sanbornite
quartz

TABLE 4. X-RAY POWDER DATA OF $Ba_2Si_3O_8$

| $Ba_2Si_3O_8$ associated with cymrite-hex. celsian s.s. and sanbornite | | $Ba_2Si_3O_8$ (Levin *et al.*, 1953) | | $Ba_2Si_3O_8$ (Austin, 1947) | |
|---|---|---|---|---|---|
| d(Å) | I | d(Å) | I | d(Å) | I |
| — | — | 7.11 | 15 | 7.00 | 12 |
| — | — | 6.06 | 11 | 6.05 | 6 |
| — | — | — | — | 5.00 | 6 |
| 4.40 | 9 | — | — | 4.33 | 6 |
| — | — | 3.93 | 13 | — | — |
| 3.711 | 100 | 3.79 | 100 | 3.75 | 100 |
| 3.651 | 75 | 3.71 | 75 | 3.68 | 80 |
| — | — | 3.51 | 10 | 3.43 | 6 |
| — | — | 3.44 | 10 | | |
| Sanbornite[1] | | 3.33 | 87 | 3.30 | 70 |
| 3.211 | 25 | 3.28 | 76 | 3.26 | 42 |
| Sanbornite[1] | | 3.15 | 48 | 3.13 | 35 |
| Cym.-hexagonal celsian[1] | | — | — | 2.99 | 6 |
| 2.756 | 25 | 2.78 | 74 | 2.78 | 75 |
| 2.621 | 35 | — | — | — | — |
| 2.581 | 48 | 2.61 | 8 | 2.60 | 9 |
| Cym.-hexagonal celsian[1] | | — | — | 2.55 | 6 |
| — | — | 2.41 | 8 | 2.40 | 9 |
| 2.345 | 9 | 2.36 | 35 | 2.35 | 14 |
| 2.268 | 24 | 2.28 | 45 | 2.27 | 23 |
| Cym.-hexagonal celsian[1] | | 2.23 | 32 | 2.23 | 23 |
| Cym.-hexagonal celsian[1] | | 2.21 | 24 | 2.21 | 13 |
| 2.143 | 45 | 2.14 | 60 | 2.14 | 41 |
| 2.097 | 25 | 2.09 | 22 | 2.08 | 18 |
| 2.043 | 21 | 2.04 | 12 | 2.04 | 12 |
| Cym.-hexagonal celsian[1] | | 1.981 | 20 | 1.98 | 17 |
| 1.919 | 25 | 1.918 | 14 | 1.91 | 14 |
| — | — | 1.881 | 8 | 1.88 | 7 |
| 1.865 | 10 | — | — | 1.86 | 7 |
| 1.817 | 20 | 1.825 | 14 | 1.83 | 16 |
| 1.784 | 9 | 1.789 | 25 | 1.79 | 20 |
| Cym.-hexagonal celsian[1] | | 1.760 | 11 | 1.76 | 16 |
| 1.733 | 10 | 1.745 | 11 | — | — |
| Cym.-hexagonal celsian[1] | | — | — | 1.71 | 8 |
| 1.644 | 15 | 1.654 | 22 | 1.65 | 12 |
| 1.629 | 14 | 1.636 | 10 | 1.63 | 6 |
| — | — | 1.617 | 7 | 1.62 | 6 |
| Cym.-hexagonal celsian[1] | | — | — | 1.60 | 6 |
| — | — | — | — | 1.58 | 6 |
| Cym.-hexagonal celsian[1] | | 1.557 | 11 | 1.56 | 8 |
| 1.514 | 10 | 1.518 | | 1.52 | 8 |
| 1.504 | 8 | 1.513 | | 1.51 | 6 |

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[1] Hidden by cymrite-hex. celsian and sanbornite.

Pure cymrite was synthesized under high water pressure and/or low temperatures, but pure hexagonal celsian was formed only under low water pressures (Fig. 1).

Figure 7 shows how the quantitative ratios of cymrite-hexagonal celsian series, sanbornite and dibarium-trisilicate vary under wide ranges of temperature and water pressure. From this Fig. 7 it is clear that the amount of cymrite-hexagonal celsian series formed in our runs generally increases with increasing water pressure.

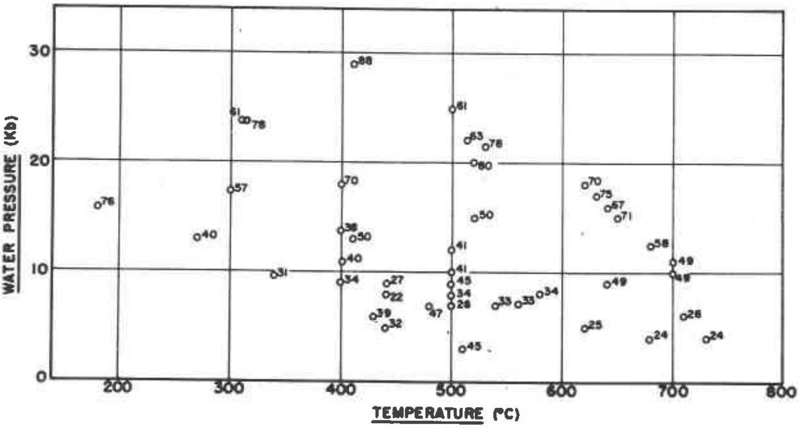

FIG. 7. Diagram showing the variation of the ratio of

$$\frac{I\ (102)\ \text{cymrite - hexagonal celsian s.s.}}{I\ (102)\ \text{cym.-hex.cel. s.s.} + I\ (014)\ \text{sanbornite} + I\ (d=3.711)\ Ba_2Si_3O_8}$$

in the chemical reaction of 2 cymrite$\rightleftharpoons$celsian+sanbornite+2 quartz+$H_2O$ at various physical conditions.

Figures 8 and 9 represent the relations between the amount of cymrite-hexagonal celsian series formed in our experimental work and $2\theta$ CuK$\alpha$ values of (102) and (110) diffractions of this mineral series. Both of these figures clearly show that the composition of cymrite-hexagonal celsian solid solution becomes richer in the cymrite molecule with the increase of the amount of the solid solution in the experimental products (Figs. 2, 3, Table 1).

## DISCUSSION

The volume relations in the chemical reaction are as follows:

| | hexagonal celsian | + sanbornite | + 2 quartz | + water $\rightleftharpoons$ | 2 cymrite |
|---|---|---|---|---|---|
| | $BaAl_2Si_2O_8$ | $BaSi_2O_5$ | $SiO_2$ | $H_2O$ | $BaAlSi_3O_8(OH)$ |
| molecular volume | 190 Å$^3$ | 120 Å$^3$ | (38×2) Å$^3$ | 30 Å$^3$ | (189×2) Å$^3$ |
| total volume | 416 Å$^3$ | | | | 378 Å$^3$ |

The chemical reaction, in going from the left to the right, involves the addition of water. Thus high water pressure as well as high hydrostatic pressure promote the formation of cymrite.

As previously noted, we found clear evidence showing a solid solution relation between pure cymrite and pure hexagonal celsian by the following substitution:

$$Al^{3+} \rightleftharpoons [Si(OH)]^{3+}$$

With substitution of $Al^{3+}$ by $Si^{4+}$ a space between the $(Al_2Si_2)O_8$ sheets of hexagonal celsian must have been occupied by $(OH)^-$.

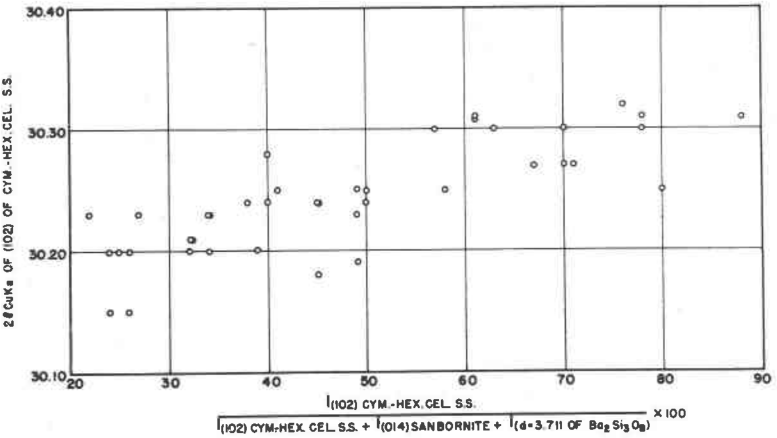

FIG. 8. Diagram showing the relation between $2\theta$ CuK$\alpha$ of (102) and the amount of cymrite-hexagonal celsian solid solution formed by the chemical reaction of 2 cymrite $\rightleftharpoons$celsian+sanbornite+2 quartz+$H_2O$ at various physical conditions.

Thus with the increase of water pressure the mineral assemblages in the chemical reaction we have studied change as follows:

(1) hexagonal celsian+sanbornite+quartz
(2) (cymrite-hexagonal celsian)+sanbornite+$Ba_2Si_3O_8$ solid solution
(3) (cymrite-hexagonal celsian)+dibarium-trisilicate solid solution
(4) cymrite

Our experimental work shows that in an anhydrous system or under low water pressures hexagonal and monoclinic modifications of $BaAl_2Si_2O_8$ are stable at high and low temperatures respectively. At atmospheric pressure, hexagonal celsian may be stable below about 700° C. However, natural occurrence of hexagonal celsian has never been reported.

Similar observations of hexagonal anorthite were made by Goldsmith and Ehlers (1952). Goldsmith and Ehlers (1952) and Donnay (1952) stated that hexagonal anorthite would not be isostructural with hexagonal celsian. However, as shown in Table 5 of the present paper, the similarity of *x*-ray powder patterns suggests that these two hexagonal phases are isostructural. The absence of an *x*-ray diffraction peak corresponding to (004) of hexagonal anorthite in our hexagonal celsian may suggest celsian has twice the unit-cell dimension *c* of the anorthite. The experimental work of Goldsmith and Ehlers (1952) shows hexagonal anorthite to be stable below 350° C., but hexagonal anorthite has never been reported to occur in nature.

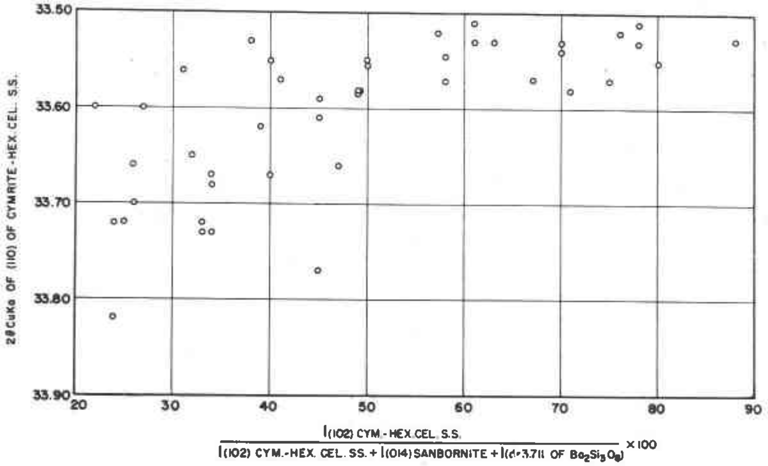

FIG. 9. Diagram showing the relation between $2\theta$ CuK$\alpha$ of (110) and the amount of cymrite-hexagonal celsian solid solution formed by the chemical reaction of 2 cymrite $\rightleftharpoons$ celsian + sanbornite + 2 quartz + $H_2O$ at various physical conditions.

It is noteworthy that monoclinic celsian is transformed into the hexagonal form, moderately rich in cymrite, under more than 4 kb water pressures in our experiments. Below 4 kb, monoclinic celsian does not change into the hexagonal form even at 650° C. for 33 hrs. Thus it is quite probable that monoclinic celsian persists into the low temperature field if water pressure is not high.

Sanbornite is a rather rare mineral but is usually associated with monoclinic celsian and quartz (Rogers, 1932).

Only one occurrence of cymrite in nature has been reported (Smith *et al.*, 1949a). The high water pressure or high chemical potential of water which is necessary for the formation of cymrite is believed to be a reason why this mineral is so rare in nature. The physical conditions which pre-

TABLE 5. SIMILARITY OF *X*-RAY POWDER DATA OF HEXAGONAL ANORTHITE TO THOSE OF HEXAGONAL CELSIAN

| Synthesized hexagonal anorthite (Davis *et al.*, 1952) | | | Synthesized hexagonal celsian (Takéuchi, 1958) | | |
|---|---|---|---|---|---|
| hkl | d(Å) | I | hkl | d(Å) | I |
| 002 | 7.37 | 85 | 001 | 7.79 | 112 |
| 100<br>010 | 4.43 | 7 | 100<br>010 | — | — |
| 102<br>012 | 3.80 | 30 | 101<br>011 | 3.963 | 100 |
| 004 | 3.68 | >100 | — | — | — |
| 104<br>014 | 2.84 | 40 | 012<br>102 | 2.977 | 59 |
| 110 | 2.555 | 9 | 110 | 2.659 | 15 |
| 006 | 2.456 | 14 | 003 | 2.602 | 22 |
| 112 | 2.414 | 3 | 111 | — | — |
| — | — | — | 020<br>200 | 2.300 | 5 |
| 106<br>016 | 2.147[1] | 11 | 103<br>013 | 2.266 | 15 |
| 202<br>022 | 2.119 | 4 | 201<br>021 | 2.206 | 11 |
| 008 | 1.842 | >100 | 004 | 1.951 | 60 |
| 116 | 1.770 | 9 | 113 | 1.860 | 6 |
| 108<br>018 | 1.701 | 1 | 104<br>014 | — | — |
| $a=5.110\pm0.02$ Å<br>$c=2\times7.369\pm0.02$ Å | | | $a=5.313\pm0.05$ Å<br>$c=7.805\pm0.05$ Å | | |

[1] Davis *et al.*, noted 2.417 but is probably a misprint.

vailed in the formation of the cymrite in Wales may have been below 300° C. and above 5 kb water pressure.

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