STUDIES IN THE SYSTEM BaO-Al₂O₃-SiO₂ I. THE POLYMORPHISM OF CELSIAN[1]

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Abstract

Prolonged anhydrous and hydrothermal heating experiments made with natural and synthetic materials have confirmed the following polymorphic relations: Monoclinic celsian is stable from room temperature up to 1590°C, where it inverts sluggishly and reversibly to hexagonal hexacelsian. The latter, stable to the melting point at about 1760°C, readily persists metastably on cooling below 1590°, and inverts rapidly and reversibly to an orthorhombic form on cooling through 300°C. Paracelsian appears to be a metastable phase, and changes monotropically through hexacelsian to celsian at temperatures at least as low as 500° and possibly at lower temperatures also.

Introduction

Four distinct crystalline forms of $BaAl_2Si_2O_8$ are recognized. Celsian and paracelsian, both monoclinic, are known as natural minerals of limited occurrence (Deer, Howie and Zussman, 1963). The remaining two are encountered only in synthetic products (Yoshiki and Matsumoto 1951). A fifth form has been postulated (Yoshiki, Koide and Waki, 1954), but no real supporting evidence has been offered.

The interrelationships of the four well-authenticated $BaAl_2Si_2O_8$ polymorphs are the subject of considerable disagreement, even among recent investigators. Only with respect to the two synthetic forms does there appear to be general agreement. A readily reversible inversion at about 300°C is believed to separate the lower temperature orthorhombic form from the higher temperature hexagonal form (hexacelsian). At least four different stability schemes relating celsian and hexacelsian have been proposed. The relations of paracelsian to the other three polymorphs have received scant attention. The present investigation attempts to resolve the conflicting views on $BaAl_2Si_2O_8$-polymorphism, and to select the most plausible phase diagram for the system.

Conflicting views on $BaAl_2Si_2O_8$ polymorphism. Figure 1 represents our attempt to picture schematically the earlier interpretations of polymorphism, by means of conventional pressure-temperature phase diagrams. In each case the synthetic low-temperature orthorhombic form has been included, in addition to hexacelsian and celsian. No quantitative

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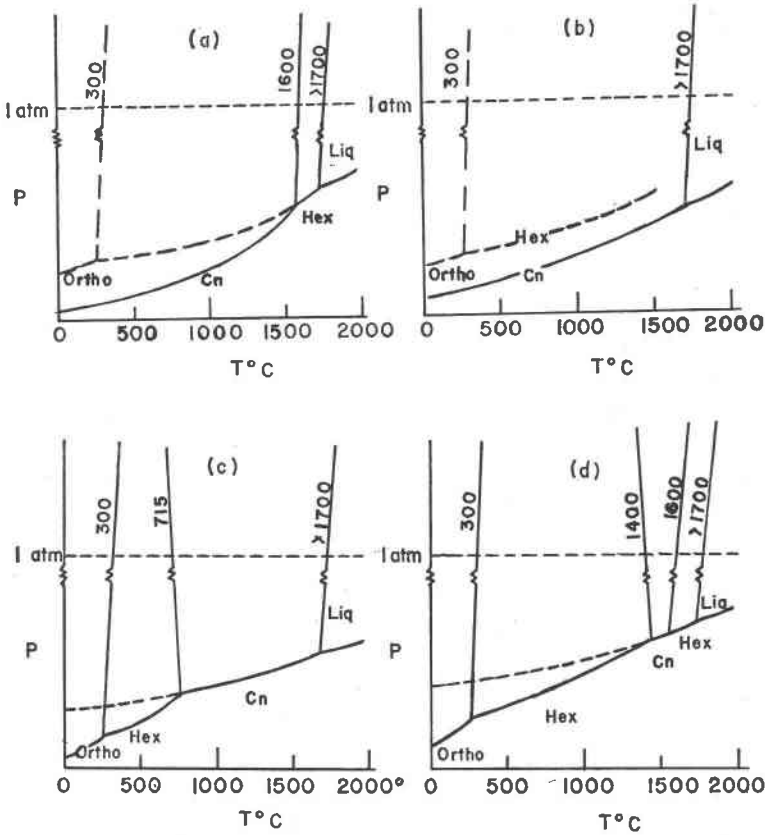
FIG. 1. Hypothetical phase diagrams for the system $BaAl_2Si_2O_8$ deduced from earlier investigations as follows:

  (a) Yoshiki and Matsumoto (1951); Planz and Müller-Hesse (1963)
  (b) Davis and Tuttle (1952); Grabenshchikov (1963); Sorrell (1962); Wisely and Thomas (1953)
  (c) Yoshiki, Koide and Waki (1954); Seki and Kennedy (1964)
  (d) Ivukina and Panova (1964).
  Cn = celsian, Hex = hexacelsian, Ortho = orthorhombic form, Liq = liquid.

significance is to be attached to distances measured on the pressure axis. The hypothetical vapor pressure curves of the several polymorphs and of the liquid are identified by appropriate symbols. Inversion and melting temperatures are located by the intersection of the appropriate hypothetical transformation curves with the 1-atmosphere isobar. The slopes of these curves are consistent with known or inferred density relations among the several forms. Curves depicting stable conditions are solid curves, whereas those representing metastable conditions are dashed.

Yoshiki and Matsumoto (1951) prepared hexagonal $BaAl_2Si_2O_8$ (hexacelsian) by electrofusion, and concluded that it is the stable high temperature polymorph of celsian. Planz and Müller-Hesse (1963) presented a similar view, and established the celsian-hexacelsian inversion temperature at 1600°C (Fig. 1a). Some of their data, however, suggested that the inversion occurs as low as 1400°C.

A contrary view, which finds support in the results of several other investigators (Davis and Tuttle, 1952; Grebenshchikov, 1963; Sorrell, 1962; Wisely and Thomas, 1953), considered celsian as the only truly stable form, persisting from room temperature to the melting point, beyond 1700°C. Hexacelsian is considered to be a metastable phase, with an everpresent tendency to change monotropically, at all temperatures, to the stable celsian (Fig. 1b).

A third relation is that proposed by Yoshiki, Koide and Waki (1954), according to which hexacelsian and its orthorhombic polymorph are stable low temperature phases (Fig. 1c). They indicated that hexacelsian inverts at approximately 1200°C to celsian, which is stable from 1200°C to the melting point. Essentially the same view has recently been espoused by Seki and Kennedy (1964), whose hydrothermal results led them to set the hexacelsian-celsian inversion at about 715°C.

Still another view (Ivukina and Panova, 1964) incorporates aspects of both the first and third configurations (Fig. 1d). This scheme depicts celsian as the stable form between 1400°C and 1600°C. Two stability ranges are alloted to hexacelsian, the one below 1400°C and the other above 1600°C.

Experimental materials and methods. The samples used in this study included natural paracelsian from the Benallt mine, Rhiw, Wales, synthetic hexacelsian, synthetic celsian, and various mixtures of the three. The synthetic materials were compounded from C. P. Baker's Analyzed Reagent barium carbonate (purity, 99.5%), Linde Type B-5125 fine abrasive gamma-alumina (purity, 99.9%) and Pennsylvania Glass Sand Corporation 5-micron MIN-U-SIL silica (purity, 99.9%). Prolonged calcination at selected elevated temperatures, yielded the desired individual polymorph (hexacelsian or celsian) or mechanical mixtures of the two, as judged by careful X-ray powder diffractometry.

Anhydrous experiments at moderate temperatures (900–1100°C) were carried out on the above materials in a small laboratory furnace (Blue M Model M-10-A-1A), the temperature being controlled through a chromel-alumel thermocouple. Higher temperature runs were made in Tem-Pres Model QF-1C and Harrop quenching furnaces operating up to 1650°C. For temperature control Barber-Colman Model 357-A

digiset Null Balance Controllers were used. The temperature is believed to be reliable to $\pm 2°C$. The platinum-platinum/rhodium 10 percent thermocouples were calibrated against the melting points of gold (1063°C), diopside (1391.5°C) and gehlenite (1590°C). A few experiments were made using a platinum strip-furnace (Roberts and Morey, 1930).

Hydrothermal experiments were carried out in the temperature range 400°–700°C at 1 kilobar of water pressure. Samples were sealed in gold, silver or platinum capsules and placed in cold-seal Tuttle-type pressure vessels with sufficient distilled water to produce the required water pressure. These Tuttle bombs were then heated in a Tem-Pres Model HR-1B-4 hydrothermal unit. West Guardsman proportional controllers, with chromel-alumel thermocouples placed at the side wall of the bomb, were used to regulate temperature. The thermocouples were calibrated against the melting points of aluminum (659.7°C), silver (960.8°C) and gold (1063°C). Temperature control is believed to be good to $\pm 10°C$. A Bourdon-type gauge, calibrated against a dead-weight gauge tester, was used to measure the water pressure within the bomb. The value measured is believed to be reliable within 10% of the reported values. At the end of a run, the bomb was quenched first with an air-blast and then with water.

Products of the anhydrous and hydrothermal heating experiments were identified from room-temperature X-ray powder patterns recorded on a Norelco high-angle diffractometer, using pressed powder mounts, CuK_α radiation, goniometer scanning speed, 2° two-theta per minute, and a Geiger counter or scintillation counter. Relative changes in peak heights of certain selected diffraction maxima characteristic for each crystalline phase were used as an index of changes in phase proportions during heat treatment.

EXPERIMENTAL DATA

Anhydrous experiments at high temperature (1500° to 1700°C) were conducted primarily to test the celsian-hexacelsian relations depicted in Figure 1a. Typical results are presented in Table 1. Moderate temperature (900° to 1100° C) anhydrous experiments were designed to throw some light on the little-studied problem of the stability of paracelsian. Table 2 incorporates results typical of these tests. Hydrothermal experiments at lower temperature (400° to 700°C) were designed to study possible interconversions, such as the hexacelsian-celsian relations shown in Figure 1c, and for further clarification of paracelsian stability, under the catalyzing influence of water vapor. Data selected from these experiments are shown in Table 3.

The melting point of hexacelsian was determined to be approximately 1760°C, using a platinum strip furnace (Roberts and Morey, 1930) with an optical pyrometer for temperature measurement, and synthetic gehlenite (melting point 1590°C) and platinum (melting point 1755°C) as calibrants. In one strip-furnace run the hexacelsian melted with platinum strip intact, whereas in another such run the platinum strip melted before the crystalline hexacelsian became molten. These observations are interpreted as indicating a $BaAl_2Si_2O_8$ melting point not far removed from the melting-point of platinum, and consistent with the 1760°C value assigned above. For comparison, earlier reported values for the melting points of $BaAl_2Si_2O_8$ are 1710°C (Yoshiki, Koide and Waki, 1954), "above 1700°C" (Kracek, 1963), 1715°C (Yoshiki and Matsumoto, 1951), 1720°C (Dittler and Lasch, 1931), 1740°C (Grebenshchikov, 1963), and 1780°C (Rieke, 1910).

INTERPRETATION OF DATA

Identification of the various $BaAl_2Si_2O_8$ polymorphs was effected with the aid of reference X-ray powder diffractometer patterns which agreed

TABLE 1. ANHYDROUS EXPERIMENTS ON CELSIAN-HEXACELSIAN RELATIONS

Temp. (°C)	Time (hrs)	Results of X-ray examination
Starting material: synthetic celsian		
1700	2	complete conversion to hexacelsian
1625	$3\frac{1}{2}$	about $\frac{1}{3}$ conversion to hexacelsian
1600	4	no detectible change
1595	8	development of trace of hexacelsian
Starting material: synthetic celsian+2% (by wt.) LiF		
1600	4	celsian with trace of hexacelsian
1595	8	celsian with trace of hexacelsian
1590	10	no detectible change
Starting material: synthetic celsian-hexacelsian mixture (1:1)		
1632	27	complete conversion to hexacelsian
1595	34	increase in hexacelsian
1585	50	increase in celsian
1575	100	increase in celsian
1500	181	complete conversion to celsian
1300	136	celsian with trace of hexacelsian

TABLE 2. ANHYDROUS EXPERIMENTS ON PARACELSIAN STABILITY

Temp. (°C)	Time (days)	Results of X-ray examination[a]
	Cumulative run on natural paracelsian (unfired)	
900	1	paracelsian unchanged
	$2\frac{1}{2}$	paracelsian unchanged
	7	paracelsian with trace of hexacelsian
	Cumulative run on natural paracelsian (unfired)	
1000	21	paracelsian:hexacelsian:celsian = 75:15:10
	103	paracelsian:hexacelsian:celsian = 70:20:10
	215	paracelsian:hexacelsian:celsian = 60:20:17
	Cumulative run on natural paracelsian (after 7 days at 900°C)	
1000	1	paracelsian with trace of hexacelsian
	7	paracelsian with minor hexacelsian
	Cumulative run on natural paracelsian (after 7 days at 900°C and 7 days at 1000°C)	
1100	1	paracelsian:hexacelsian:celsian = 75:25:0
	3	paracelsian:hexacelsian:celsian = 60:40:trace
	7	paracelsian:hexacelsian:celsian = 30:65:5
	11	paracelsian:hexacelsian:celsian = 20:70:10
	18	paracelsian:hexacelsian:celsian = 10:75:15
	42	paracelsian:hexacelsian:celsian = trace:80:20
	55	paracelsian:hexacelsian:celsian = 0:80:20

[a] Phase proportions derived from peak-height ratios, using the following peaks: paracelsian-4.00 Å; hexacelsian-3.95 Å; celsian-3.35 Å.

closely with data from the A.S.T.M. card file. In those experiments in which a single polymorph was used as starting material, or in which a mixture of polymorphs showed essentially complete elimination of one of the phases, interpretation of the X-ray patterns was simple and straightforward. It was merely necessary to observe the appearance or disappearance of characteristic diffraction maxima (*e.g.*, the 4.00 Å peak of paracelsian, the 3.95 Å peak of hexacelsian, or the 3.35 Å peak of celsian) in order to conclude that a change had occurred. Most of the data recorded in Tables 1, 2 and 3 are based on such evaluations. In certain critical experiments involving celsian-hexacelsian mixtures (Table 1) the two forms were substantially present in both starting material and product. The interpretation of the X-ray patterns in such

TABLE 3. HYDROTHERMAL EXPERIMENTS ON BaAl$_2$Si$_2$O$_8$ POLYMORPHS

Temp. (°C)	Water Pressure (Kb)	Time (days)	Results of X-ray examination
		Starting material: natural paracelsian	
700	1	4	complete conversion to celsian
600	1	4	complete conversion to celsian
549	1	15	celsian > paracelsian > hexacelsian
536	1	19½	complete conversion to celsian
524	1	15	paracelsian unchanged
489	1	15	paracelsian unchanged
393	1	15	paracelsian unchanged
		Starting material: synthetic celsian-hexacelsian mixture (1:1)	
700	1	4	complete conversion to celsian
600	1	4	complete conversion to celsian
544	1	15	complete conversion to celsian
489	1	15	complete conversion to celsian
393	1	15	complete conversion to celsian
		Starting material: paracelsian-hexacelsian-celsian mixture (2:1:1)	
500	1	10	complete conversion to celsian

cases was more difficult, and the following scheme patterned after one recently described by Richardson, Gilbert and Bell (1967) was adopted. It was first established that the 3.35Å:3.95Å peak ratio for the original 1:1 celsian-hexacelsian mixture ranged from 0.78 to 1.24, as determined from 20 recordings on 10 different samples of the mixture. If after thermal treatment a sample of this material yielded a pattern with a peak ratio less than 0.78, the celsian content was judged to have decreased relative to hexacelsian. If, on the other hand, the peak ratio exceeded 1.24, celsian was judged to have increased at the expense of hexacelsian. Peak ratios between 0.78 and 1.24 were dismissed as inconclusive evidence for any change.

The experimental results recorded in Tables 1, 2 and 3 indicate a wide range of stability for celsian, the monoclinic polymorph of BaAl$_2$Si$_2$O$_8$ most commonly observed in nature. Hexacelsian has been converted to celsian as low as 393°C and as high as 1585°C. Such behavior is at odds with the opinion of Seki and Kennedy (1964) that hexacelsian is stable at temperatures below about 715°C. In the present study, hydrothermal runs at 393°, 489°, 544°, 600° and 700°C strongly suggest that hexacelsian

is metastable with respect to celsian in this temperature range. Seki and Kennedy's runs were in general considerably shorter than those recorded in Table 3, which ranged from 4 to 15 days in length. On the other hand, their experiments were conducted at water vapor pressures up to 20 or more kilobars, whereas those of the present study were confined to one kilobar. It is here suggested that the prolonged runs at one kilobar are the more significant as indicators of the polymorphic relations at atmospheric pressure. Yoshiki Koide and Waki (1954) propose that hexacelsian is stable below about 1200°C. The 900°, 1000°, and 1100°C anhydrous experiments on paracelsian recorded in Table 2, although not a clearcut refutation of this claim, strongly suggest that paracelsian is gradually changing, first to hexacelsian, then to celsian in this temperature range. Ivukina and Panova (1964) have proposed that hexacelsian is more stable than celsian below 1400°C However, experiments such as the 1300°C 136-hour run recorded in Table 1, wherein a 1:1 celsian-hexacelsian mixture has been converted almost completely to celsian, cast considerable doubt on such a relation.

The hexacelsian-celsian results thus far enumerated are at odds with the interpretation of Figure 1c based on the views of Seki and Kennedy (1964) and of Yoshiki, Koide, and Waki (1964) as well as Figure 1d, based on the opinion of Ivukina and Panova. They are not in themselves at variance with the interpretation of Figure 1b, based on data of Davis and Tuttle (1952), Wisely and Thomas (1953), Sorrell (1962), and Grebenshchikov (1963). But additional experiments of the present study dispute the implication of Figure 1b that hexacelsian is a completely metastable form, and that celsian is stable to the melting point, in excess of 1700°C. The runs at 1625° and 1700°C, in particular, give unequivocal proof of the high-temperature conversion of monoclinic celsian to hexacelsian below the melting point. That the inversion is reversible is indicated by the 100 hour run at 1575°C. The best estimate of the actual inversion temperature from the data of Table 1 is 1590° ± 5°C. It is to be noted that, although Planz and Müller-Hesse (1963) assigned a similar temperature value for the inversion (1600°C), certain of their data suggested that it might be as low as 1400°C. The present data therefore serve to resolve any uncertainty in their published findings. It is ironic that Yoshiki and Matsumoto (1951) originally favored this view, but it was rejected several years later by Yoshiki, Koide and Waki (1954).

The combined anhydrous and hydrothermal experiments on paracelsian clearly show that at temperatures above 500°C and at pressures not exceeding one kilobar, paracelsian is less stable than hexacelsian and celsian. They strongly suggest that the order of increasing stability is paracelsian→hexacelsian→celsian in the 500°–1000°C temperature

range covered by the experiments, in apparent conformity to the well-known Ostwald step-wise rule of successive reactions. The distinct contrast between the results of the hydrothermal run at 536°C (complete conversion to celsian) and that at 524°C (paracelsian unchanged) at first suggested the possibility of a reversible paracelsian-celsian inversion at 530° ± 6°C with paracelsian stable below and celsian stable above that temperature. The 500°C run, however, indicates that when celsian is present as a "seed," paracelsian will change completely to celsian at least 30° below the supposed reversible inversion temperature. This is taken as strong indication, although not conclusive proof, that paracelsian is less stable than celsian at all temperatures. As far as the available data are concerned, then, paracelsian is to be regarded as a metastable form.

On the basis of the foregoing data and discussion the following phase relations are indicated for the system $BaAl_2Si_2O_8$. The monoclinic form corresponding to the natural mineral, celsian, is stable over the entire temperature range up to 1590°C. At that temperature it undergoes a sluggish reversible inversion to hexacelsian, which is stable to the melting point at about 1760°C. Hexacelsian can be readily cooled metastably below 1590°C. The present study gives no evidence for the rapid reversible inversion of hexacelsian to an orthorhombic form on cooling through about 300°C. However, this has been clearly established by Yoshiki and Matsumoto (1951) and Takeuchi (1958). Paracelsian is believed to be a completely metastable form, which changes monotropically through metastable hexacelsian to the stable celsian, in accordance with Ostwald's rule. These relations have been incorporated in Figure 2, which is proposed as the most plausible phase diagram to date for the system $BaAl_2Si_2O_8$.

A noteworthy feature of the present study is the sluggishness of transformation of one polymorph to another in the absence of water vapor or other effective mineralizer. Natural paracelsian was only partly converted to the other forms after 235 hours at 1000°C. Only at temperatures above 1600°C was conversion of celsian to hexacelsian complete. Inversion occurs more readily in mixtures than in single-polymorph samples. But even here the unequivocal demonstration of the reversible celsian-hexacelsian inversion at 1590°C was difficult because of the sluggishness of change, and required the special precautions described earlier. As might be expected, hydrothermal conditions were much more effective in promoting inversion than were anhydrous conditions. Thus, paracelsian and hexacelsian changed completely to celsian in a hydrothermal bomb at 500°C whereas the anhydrous materials showed little more than incipient change until 1000°C was attained. Another striking
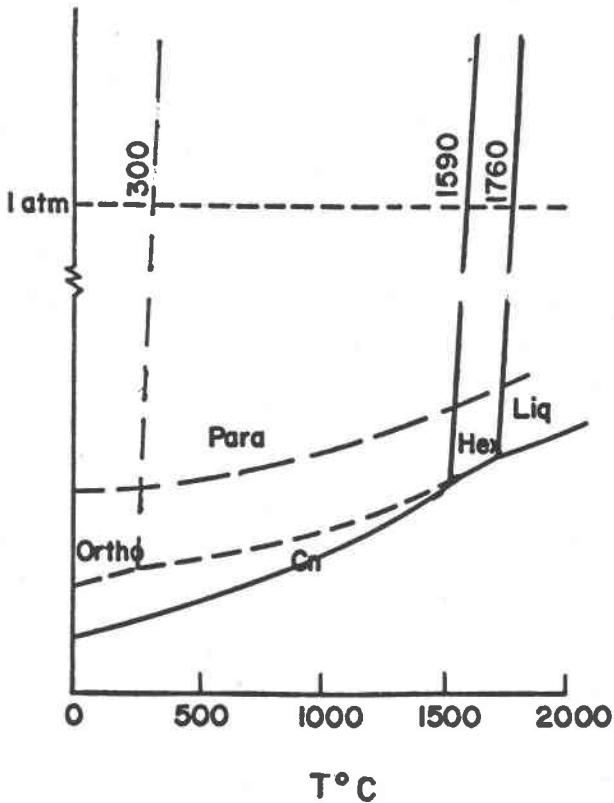
FIG. 2. Hypothetical phase diagram for the system $BaAl_2Si_2O_8$ as deduced from the present study. Cn=celsian, Hex=hexacelsian, Ortho=orthorhombic form, Para=para-celsian, Liq=liquid.

feature of the experiments was the readiness with which hexacelsian developed and persisted metastably throughout a wide temperature range. Indeed, the development of celsian in its own stability range was always preceded by the formation of metastable hexacelsian. This phenomenon, coupled with the sluggishness with which the metastable hexacelsian gives way to the stable celsian, may account largely for the conflicting data and interpretations of previous investigators.

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