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STABILITY, LATTICE PARAMETERS, AND THERMAL EXPANSION OF β-CRISTOBALITE

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ABSTRACT

β-cristobalite was synthesized on heating the zeolite stilbite beyond 920° C. Unusual conditions allowed this high temperature form of silica to survive indefinitely in a metastable, well crystalline condition, below its minimum inversion temperature of 220° C. Precise determination of the resultant cell parameters at room temperature has shown that the latter are dependent on previous thermal history: the lattice parameter "a" is inversely proportional to the maximum temperature of annealment. The discrepancies recorded by previous workers are explained. The thermal expansion characteristics of a sample previously heated to 1400° C. indicate that a maximum cell volume exists at 1000° C. The linear thermal expansion coefficient is $10.9\times10^{-6}\Delta L/L/°$ C. for the range 100° C. to 500° C., decreasing to 1.7×10^{-6} between 500° C. and 1000° C.

INTRODUCTION

Thermal transformations of stilbites from the Tertiary basalts of the Garron Plateau, Antrim, N.E. Ireland, and from the Triassic basalts of the North Mountains, Nova Scotia, were investigated, using high temperature diffractometry techniques, with a Siemens diffractometer converted by the author for work in the range of room temperature to 1400° C. (Aumento, 1965). Samples were also heated in vacuum to known temperatures beyond 1400° C. in graphite crucibles with an induction furnace, and were examined on cooling. Possible extraneous effects arising from different rates of heating and cooling, and from varying durations of maximum temperature, were minimized by heating all samples at rates of +5° C. to +10° C./minute, maintaining them at the required temperature for periods of $1\frac{1}{2}$ to 2 hours, and cooling them at rates of −5° C. to −10° C./minute. Photographic methods (Debye-Scherrer and Guinier focusing techniques) were used in conjunction with precision diffractometry to study the cooled samples.

The compositions of the original stilbite specimens were determined by rapid wet chemical analyses, the results of which are given in Table 1. A semi-quantitative examination of heat-treated material was carried out by means of an "Elion" electron-probe micro-analyser.

SYNTHESIS

Stilbite undergoes a number of transformations on heating from room temperature to 740° C. These will be reported in a later paper. At 740° C. and up to 920° C., and on cooling from these temperatures, there remains

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TABLE 1. RAPID CHEMICAL AND *X*-RAY FLUORESCENCE ANALYSES FOR STILBITE

	(1)	(2)
SiO_2	57.73	55.08
TiO_2	0.05	—
Al_2O_3	16.20	16.54
Fe_2O_3	—	—
FeO	0.12	0.10
MnO	0.03	Tr.
CaO	6.09	7.63
MgO	0.92	0.20
K_2O	0.35	0.53
Na_2O	0.53	0.93
CO_2	—	—
P_2O_5	0.03	—
SrO	Tr.	Tr.
H_2O^+	16.15	14.65
H_2O^-	2.00	4.22
Zn	Tr.	—
Y	Tr.	Tr.
Ag	Tr.	—
Total:	100.20%	99.88%

(1) Garron Plateau, Antrim, N.E. Ireland.
(2) Cape Blomidon, North Mountains, Nova Scotia, Canada.
tr. = Trace detected.
— = No trace detected.
Analyst: F. Aumento.

no crystalline trace of the original stilbite or its transforms, but diffraction patterns exhibit a broad band between 3 Å and 4 Å, which can be accounted for by the presence of a semi-crystalline silicate phase.

At 920° C. the broad band begins to fade. It is completely replaced on reaching 965° (and on cooling) by a simple pattern of sharp peaks. All but one of the diffraction peaks match the diffractogram of β-cristobalite with the accepted face-centered cubic space group *Fd3m*. The synthesis of a crystalline silica phase is to be expected when a semi-crystalline material of equivalent composition is subjected to increasing temperature. The alkali oxides present in such glass may accelerate the synthesis of β-cristobalite at these elevated temperatures. There is also a strong coincidence between the main spacing for β-cristobalite ($d = 4.11$ Å) and the broad band at 4 Å for the semi-crystalline silicate phase. The additional reproducible peak at $d = 3.18$ Å might be assumed erroneously to belong to β-cristobalite if indexed as (210); however such an assumption would require that β-cristobalite have a primitive cubic cell.

The diffraction pattern of β-cristobalite is found to improve with increasing temperature, and a second set of weaker lines appears at 1000° C. These lines, together with that at 3.18 Å, belong to a minor second phase, which has been identified as anorthite/bytownite. The calcic composition of the original stilbite would contribute to the synthesis of an anorthite-rich plagioclase feldspar.

The crystallinity of β-cristobalite improves with increasingly high temperatures up to the limit of 1400° C. imposed by instrumentation. At this point an exceedingly sharp cubic *x*-ray pattern is obtained.

The room temperature diffraction patterns of β-cristobalite obtained from those experiments which have not exceeded 1340° C. approach the sharpness attributable to good crystalline material. The proportion of crystallites to matrix is high enough to give good diffraction patterns. The metastable β-cristobalite kept at room temperature was re-examined at periods of six and twenty months from its synthesis, but no sign of inversion or loss of crystallinity was detected. No traces of inversion from β-cristobalite to α-cristobalite have been detected at any time during this study. Heating beyond 1340° C. produces a greater number and size of crystallites, but these do not survive on cooling, and the material is completely amorphous to *x*-rays when examined at room temperature.

LATTICE PARAMETERS

The unusually good quality of the room temperature diffractograms for β-cristobalite afforded a unique opportunity to determine with precision its room temperature lattice parameter. Previous attempts had either failed or yielded very inaccurate results. Room temperature diffractograms of β-cristobalite with a tungsten internal standard (Table 2) were taken on a Siemens diffractometer under the following conditions:

Iron radiation at 40 kV, 14 mA with Mn Kβ filter.
Scanning speed of 1/8°/minute.
1° divergence slits and 0.1 mm receiving slit.
Chart speed of 1 cm/minute = 8 cm/°2θ on chart.
Statistical error of 0.5% (= time constant).
Water cooled scintillation counter with discriminator.

Peak maxima, rather than centers of gravity, were taken as the 2θ positions. A wide range of different values in room temperature cell parameters, from 7.106 ± 0.005 Å to 7.148 ± 0.005 Å was obtained (Fig. 1). Any possibility of these differences arising from experimental techniques was ruled out, and a correlation was eventually reached between the values determined and the previous thermal history of the samples.

It was found that samples of β-cristobalite which had been taken to higher temperatures gave smaller cell parameters at room temperature

TABLE 2. ROOM TEMPERATURE DIFFRACTOGRAM OF RESIDUE FROM STILBITE HEATED AT 1260° C. FOR TWO HOURS

Iron radiation ($K\alpha_1 = 1.93597$ Å), tungsten internal standard ($a = 3.1648$ Å). Diffractogram shows superimposed β-cristobalite and weaker anorthite patterns.

Line no.	I_{100}	d obs.Å	d calc.Å	β-cristobalite	
				hkl	a.Å
1	15	6.518			
2	7	4.555			
3	100	4.112	4.108	111	7.122
4	16	4.040			
5	4	3.902			
6	5	3.780			
7	7	3.706			
8	8	3.463			
9	8	3.432			
10	15	3.403			
11	20	3.214			
12	38	3.195			
13	3	2.907	2.905	211	7.120
14	4	2.811			
15	8	2.547			
16	18	2.516	2.516	220	7.116
17	3	2.421			
18	8	2.231			
19	7	2.209			
20	5	2.144	2.146	311	7.112
21	5	2.085			
22	5	2.053	2.054	222	7.112
23	3	1.975	1.974	320	7.120
24	2	1.925			
25	4	1.802			
26	3	1.780	1.779	400	7.119
27	3	1.773			
28	4	1.769			
29	3	1.738			
30	4	1.633	1.635	331	7.118
31	5	1.600			
32	5	1.526			
33	4	1.463			
34	4	1.453	1.453	422	7.117
35	2	1.405			
36	6	1.370	1.370	511	7.118
37	6	1.258	1.258	440	7.118
38	2	1.203	1.203	531	7.117
39	2	1.125	1.125	620	7.117
40	3	1.088	1.088	533	7.117
41	3	1.047			
42	8	1.043			

Average value of "a": 7.117 Å.

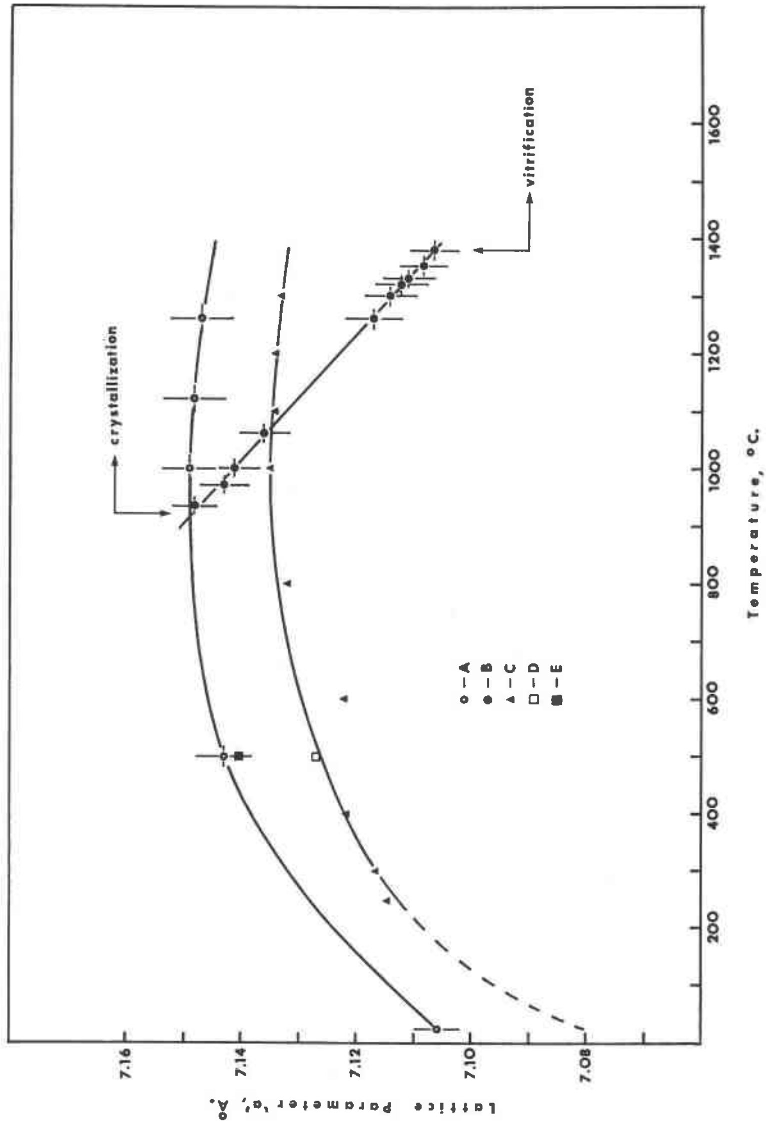

FIG. 1. Lattice parameters of β-cristobalite: A. Aumento (1965): thermal expansion of synthetic β-cristobalite previously heated to 1380° C. B. Aumento (1965): Room temperature lattice parameters of β-cristobalite cooled from the temperatures indicated. C. Büssem *et al.* (1935): Thermal expansion of β-cristobalite. D. Wyckoff (1925): cell parameter of β-cristobalite at 500° C. E. Barth and Ponsjak (1932): cell parameter of β-cristobalite at 500° C.

than samples cooled from lower temperatures. An inverse linear relationship has been found to exist between maximum temperature reached and cell parameter on cooling to room temperature. Results are plotted in Fig. 1. It is interesting to note that the resultant straight line graph intersects the thermal expansion graph (see next section) of a sample cooled from 1380° C. (as examined by high temperature diffractometry) at a point denoted by 920° C. and 7.149 Å.

THERMAL EXPANSION

The expansion of the unit cell of β-cristobalite has been investigated by Büssem *et al.* (1935) and Lukesh (1942). Lukesh erroneously calculated a value of 8.53×10^{-6} $\Delta L/L/°$ C. for α, the coefficient of linear expansion, from his two cell parameters, whilst Büssem *et al.* calculated an approximate value of 8×10^{-6} for the linear coefficient of expansion between 250° C. and 800° C. Büssem *et al.* also noted that the cell volume has a maximum value at 1000° C., when $a=7.1348$ Å, and contracts to 7.1329 Å by 1300° C. The present determinations with the high temperature diffractometer (employing a tungsten internal standard, optical pyrometer and thermocouple temperature control), show a somewhat higher average coefficient of expansion at the lower temperatures: 10.9×10^{-6} $\Delta L/L/°$ C. between 100° C. and 500° C., decreasing to only 1.7×10^{-6} between 500° C. and 1000° C. The resulting maximum cell parameter is 7.149 Å at 1000° C. Figure 1 also shows unit cell measurements by Wyckoff (1925) and Barth and Posnjak (1932) converted to Ångström units at 500° C. by Swanson and Tatge (1953).

DISCUSSION

The survival of β-cristobalite below its minimum inversion temperature can be readily explained by two basically different hypotheses:

(1) Greig (1932) suggested that since the inversion from the high temperature to the low temperature form is accompanied by a considerable decrease in volume, the inversion may be mechanically arrested if the high temperature crystallites are physically embedded in opal (as in naturally occurring samples) or other amorphous glasses which prevent their transformation. Natural opals consist of a sub-microcrystalline aggregate of crystallites of cristobalite with a somewhat disordered internal structure, containing much non-essential water. Increased internal ordering of the crystallites results in a closer approximation to the β-cristobalite configuration.

(2) A more recent approach to the problem, as presented by Eitel (1957), and others, suggests that the inversion temperature may be lowered by the action of solid-solution and disorder in the packing of the three-layered structure of β-cristobalite. Solid-solution would produce a disordered stuffed structure in which the Si has been partly replaced by cations such as Al, Ca, Mg, together with H_2O and OH.

Greig's matrix constraint hypothesis. An attempt was made to follow visually the different growth stages of the β-cristobalite crystals. Thin sections of samples cooled from 920° C.–980° C. show no visible traces of β-cristobalite crystals. Therefore, on crystallizing from a semi-amorphous silicate matrix at 920° C., β-cristobalite crystals are extremely small, and could be under full mechanical influence of their embedding glass matrix. Their cell parameter of $a=7.148$ Å at 920° C. could be retained on cooling by the restraining mechanical action of the glass matrix.

On heating above 920° C., not only do the crystallites expand with the expanding glass matrix, but they also grow in size due to further crystallization of the semi-crystalline glass onto the seed crystals. This growth improves the diffraction patterns, and may reduce the restraining effect of the glass matrix on cooling. With decreasing temperature these larger crystals could therefore contract a little more than the previous minimum value of 7.148 Å.

Thin sections of samples cooled from above 1000° C. contain the first visible β-cristobalite zones. These consist of small (less than 5μ) spherical particles, the centers of which appear to be hollow. These spheres increase to a maximum external diameter of 20μ in samples cooled from 1300° C.; the size of the cavities within these spheres also increases, with diameters up to 15μ in the larger spheres. The crystals now give excellent diffraction patterns at high temperatures and also on cooling to room temperature, when the cell parameter contracts to 7.114 Å.

The crystals continue their growth above 1340° C. The resultant ratio of crystal to glass increases so rapidly as to minimize the restraining action of the glass matrix on the β-cristobalite. On cooling, therefore, much of the β-cristobalite is destroyed to give a glass. Some of the unchanged β-cristobalite remains, giving the lowest recorded cell parameter in this study ($a=7.106$ Å).

Stuffed lattice hypothesis. Crystallization of β-cristobalite in the lower temperature range of 920° C.–1000° C. is subject to unfavorable conditions. Slow diffusion rates at such temperatures cannot allow complete exolution of foreign cations trapped in the incipient β-cristobalite nuclei. This would result in poor homogeneity within the new phase, which would be stuffed with cations from the original stilbite crystals. The possibilities of defects within the structure will therefore be very high. The diffuse *x*-ray diffraction lines of low intensity recorded from samples at, and cooled from, this temperature range, may therefore also be attributable to defects in the structure, rather than to number and size of crystallites alone.

With increasing temperature, the increased rate of cation diffusion could reduce stuffing and subsequent structural defects, thereby healing the β-cristobalite structure. This may account for the sharper and more intense lines of diffractograms in the higher temperature range. Indeed, one can observe, in thin sections of the material, that the areas immediately surrounding the hollow spheres of β-cristobalite often show dense clouds of exolved matter, from the original stilbite composition, which is not acceptable to the β-cristobalite structure.

In an attempt to provide some chemical data for the synthesised β-cristobalite, a polished section mount was prepared containing numerous samples previously heated to different temperatures, together with a grain of the original stilbite, and grains of silica and alumina standards. The mount was examined with a modified "Elion" electron micro-probe for the elements Si, Al, Ca, and Fe. The minimum electron beam diameter which was available was in the order of 5μ; the minimum effective analyzed spot was consequently about 10μ in diameter. It was therefore impossible to carry out quantitative determinations of the β-cristobalite sphere walls alone, since these had a maximum wall thickness of 5μ. Analyses were further complicated by the lack of precise optical microscopic sightings of the areas illuminated by the electron beam.

It was possible, however, to obtain semi-quantitative data on the composition of the β-cristobalite. Specimen current images showed darker borders surrounding many of the hollow spheres, suggesting a greater concentration of higher atomic number elements (relative to the matrix) in these positions. Scans made across these spheres clearly indicated higher concentrations of Si and Al relative to the matrix in the β-cristobalite zones, with Fe concentrated on the outer parts of these zones. Spot analyses made on a sample cooled from 1200° C showed one 10μ diameter area containing some 85% SiO_2, the remainder being Al_2O_3, with a small amount (about 1%) of CaO. As explained above, in view of the beam diameter, this determination necessarily included some of the adjacent matrix.

Although the electron probe analyses are inconclusive, they clearly indicate that zones identified optically as β-cristobalite contain a very high percentage of SiO_2 with considerable amounts of Al_2O_3. Larger concentrations of CaO were not detected. It is quite possible, therefore, that the β-cristobalite structure is stuffed with aluminum in solid-solution.

Conclusions

The lattice parameter of β-cristobalite, when measured at any one particular temperature, is primarily dependent on previous thermal treatment. This dependence can be explained either by the mechanical restraining action of the glassy matrix on the embedded crystallites, in accordance with the theory postulated by Greig (1932), or by stuffing of the structure by Al in solid solution with Si.

Whilst the electron probe analyses do not eliminate the possible existence of pure β-cristobalite crystallites (too small to be analyzed individually by the electron beam) the existence of Al-stuffed β-cristobalite would appear more feasible than unstuffed crystals physically restrained by the matrix. This view is especially supported by the survival of the β-cristobalite on grinding the cooled specimens for x-ray powder diffraction preparation. Had the β-cristobalite been restrained by the matrix, the grinding would have released a good number of crystallites.

The dependence of cell parameters on previous thermal history accounts for the wide discrepancies obtained by previous workers.

The very low values of Lukesh (1942) ($a = 7.031$ Å at 275° C$_1$, and $a = 7.044$ Å at 480° C.), however, seem unacceptable. Büssem *et al.* (1935) had extrapolated (with the assistance of an unreliable determination at room temperature on an opal giving broad, faint β-cristobalite lines) the room temperature cell parameter of β-cristobalite from a graph which they had plotted for values of the unit cell from 1300° C. to 250° C., slightly above the minimum inversion temperature. They arrived at a room temperature value of $a = 7.079$ Å (Fig. 1), somewhat lower than any of the values of the present study. On re-examination of Büssem's graph, the author finds that extrapolation could have yielded any value between 7.095 Å and 7.075 Å for the cell dimension at room temperature; the higher of the two values is more in accordance with the new experimental evidence.

A true thermal expansion curve must therefore be derived only from determinations on pure β-cristobalite crystals, *i.e.*, crystals which are not subject to solid-solution effects. The expansion curve given in Figure 1 by the author approximates this condition. Discrepancies in the expansion curves given by previous workers are possibly due to the stuffing effect, together with other thermal treatment conditions.

This study indicates the possibility of a new tool for the determination of temperatures of formation or annealment of natural β-cristobalites (and of material used by other workers). However, in this study the effects of rate of heating, duration of maximum temperature, and rate of cooling have been reduced to a minimum by standardizing the heat treatment procedures. It is not known to what extent these additional factors, which necessarily come into effect in nature, will affect the lattice parameter of β-cristobalite. The availability of cations from different materials will also vary; the extent to which these compositional variations will affect solid solution is not known. It would therefore be unwise to predict temperatures of formation or annealment of samples before further investigations have been made on the effects of time and other variables. Variations due to the duration of maximum temperature and rate of cooling are now under investigation.

Even if all the above variables could be accounted for, it would still be difficult to determine the temperature of formation of natural opals, because of the poor quality of the diffractograms from the embedded β-cristobalite crystals. However, examination at slightly elevated temperatures may improve the diffractograms sufficiently to provide parameters with the accuracy required for temperature determinations.

The dependence of lattice parameters on previous thermal treatment for crystals with open structures, as has been demonstrated here, is known to be applicable to other, more common, mineral species. These crystals need not be in metastable conditions for their lattice parameters to be influenced by solid-solution; wider, more useful, occurrences of this phenomenon may exist.

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