PHASE TRANSFORMATIONS IN SILICA AS EXAMINED BY CONTINUOUS X-RAY DIFFRACTION

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Abstract

The phase transformations of six different varieties of silica were examined by continuous x-ray diffraction while heated to 1400° C.

The (101) peak intensity changes which often accompany the α-β quartz inversion are a function of particle size. There is, however, no correlation between these changes and the gradual increase in the (101) d-spacing as the material is heated.

The crystallization temperature of β-cristobalite from a siliceous material is a consequence of the crystallinity and initial structural perfection of that material—the better the crystallinity, the higher the transition temperature. Rock crystal quartz gives β-cristobalite at 1200° C.; whereas, amorphous silica gel produces this phase of 900° C.

Tridymite was not detected as a transitional phase mineral in the silica system.

Introduction

During the past few decades many persons have studied the silica system and have presented data regarding the stability conditions of polymorphic silica minerals.

Previous methods and techniques used in examining the silica system were diversified. In an early fundamental investigation of this system, Fenner (1913) used static equilibrium conditions. Since that time, the thermochemical measurements of Mosesman and Pitzer (1941), the differential thermal studies of Keith and Tuttle (1952), and numerous other investigations by Sosman (1927), Jay (1933), Buerger (1954), Flörke (1955 and 1956), and Holmquist (1958), to mention only a few, have contributed greatly to our knowledge and understanding of this system.

The design and inception of continuous heating x-ray diffraction techniques now permit a new approach to the examination of certain problems regarding phase transformations within the SiO_2 system. This report is based on data obtained using this heating-diffraction technique. Of principal interest is the alpha-beta quartz inversion and the crystallization temperature for different initial forms of silica, and also the establishment of this technique for studying the effect of inherent structure of material upon consequent mineral phase transformations.

Samples and Procedure

Six varieties of silica representing different degrees of structural perfection and crystallinity were examined by continuous x-ray diffraction as they were heated to 1400° C. These were rock crystal quartz from near Hot Springs, Arkansas; chert from Dover, England; chalcedony

from Middle Park, Colorado; opal from Guanajuato, Mexico; silica gel, grade 42, Davison Chemical Company; and, silicic acid, 100 mesh, A. R. grade, Mallinckrodt Chemical Works.

Each of these materials was heated in the furnace in the x-ray diffraction unit at a program rate of 5° C. per minute. During the heating operation, diffraction data were logged for the 2θ interval containing the major diffraction reflections of the material under investigation. This traverse was normally restricted to a 2θ range of 19° to 27° and thus provided a continuous diffraction record of the (100) and (101) quartz peaks and the diagnostic (111) β-cristobalite reflection.

The furnace used was constructed on the same principle as that designed by G. Kulbicki and described by Grim and Kulbicki in 1957. It was adapted for use with a Philips recording diffractometer. All data to be presented herein were obtained using this type furnace and nickel-filtered copper radiation at 45 Kvp. and 18 ma.

The data curves shown in this report are a measure of the intensities of the diagnostic diffraction peaks as plotted against the temperatures at which they occurred. The resultant plot is a series of points representing the presence of a specific mineral phase at various temperatures. By connecting these representative points a curve is obtained for that particular mineral (Fig. 1). From the nature and configuration of this curve one can ascertain (a) the initial nucleation and growth of any new mineral phase, (b) the prevalence of any initial mineral with its consequent breakdown upon heating, and (c) the apparent rate of any structural inversion or new phase mineral formation.

Experimental Data

Rock Crystal Quartz

The α-β inversion in quartz was examined in detail. Rock crystal quartz was first crushed and then fractionated to obtain different size-grade materials. In addition to the unsized material the less-than-74 micron and less-than-2 micron fractions were isolated. Each of these fractions was x-rayed continuously while being heated to 1400° C.

A gradual shift in the d-spacing of the (101) reflection was observed as the quartz samples were heated. These values as recorded at specific temperatures are listed in Table 1, and plotted in Fig. 2. They show a gradual increase in the α-quartz (101) value of 3.34 Å as the sample is heated up to about 600° C. at which temperature a value of 3.38 Å is attained. Above this temperature, which is the temperature usually given for the α-β quartz inversion, there is again a gradual increase in this same value with the rate of increase becoming greater at higher temperatures. Taken as a whole there is a gradual increase in this dimension as the sample is
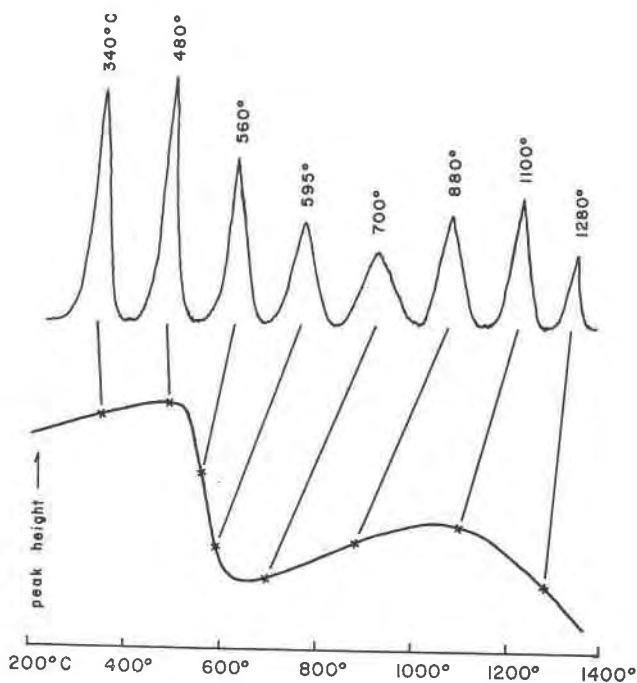
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Fig. 1. Method used in plotting x-ray diffraction data. The intensities of a characteristic diffraction peak at different temperatures are transferred to a curve.

heated upward from 200° C. with a slight break at about 600° C., which is essentially a reduction in rate of increase, and a final increase in rate just prior to the transformation to β-cristobalite. D.T.A. curves show an endothermic reaction at about 570° C. indicating some structural rearrangement at this temperature. A 3.42 Å β-quartz spacing was eventually

TABLE 1. SPACING VALUES OF THE (101) QUARTZ
REFLECTION AT VARIOUS TEMPERATURES

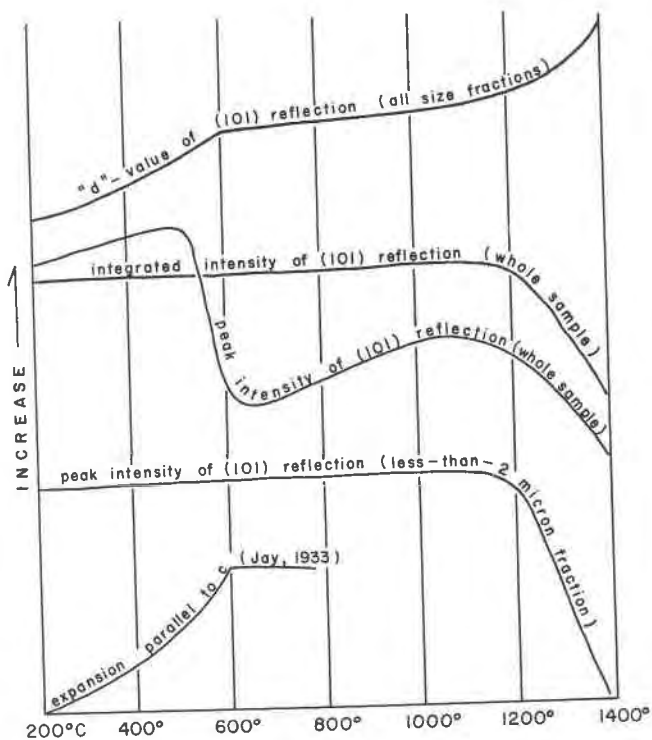| Temperature	d-value of (101) reflection
20° C.	3.34 Å
220° C.	3.35 Å
390° C.	3.36 Å
490° C.	3.37 Å
595° C.	3.38 Å
1120° C.	3.39 Å
1280° C.	3.40 Å
1340° C.	3.41 Å
1370° C.	3.42 Å

FIG. 2. Changes in quartz as heated to 1400° C.

reached at 1370° C. at the rate of firing used. It is important to note that the same increase in the (101) d-spacing of quartz was observed as each of the three different size fractions was heated.

Diffraction results from these three quartz fractions are shown in Fig. 3. The unsized fraction and the less than −74 micron fraction show a slight gradual increase in the peak height of the (101) quartz reflection with an increase in temperature up to about 500° C. Accompanying heating from 500° to 600° C. there is a sharp drop in peak height, but on heating to higher temperatures the intensity of this reflection gradually increases again. As the temperature of formation of cristobalite is approached the intensity of the quartz reflection decreases. Thus, there is a gradual increase in the intensity of this peak immediately preceding both the break in dimension change in α-β quartz (and the temperature of the thermal reaction) and the transformation to β-crystobalite. The change in the (101) quartz dimension between 500° and 600° C. is accompanied by an abrupt change in peak height, but not an overall change in diffrac-
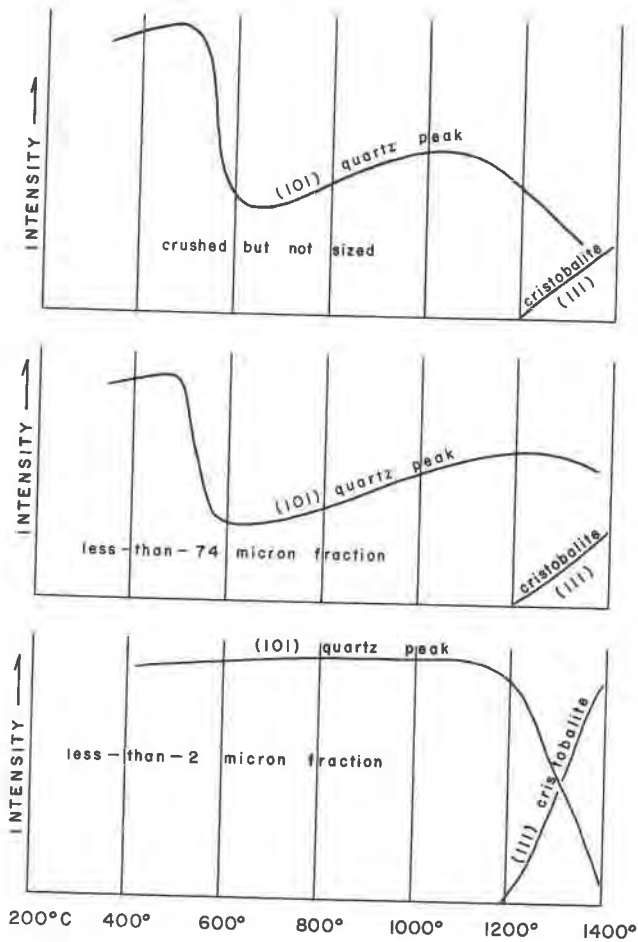
FIG. 3. Continuous x-ray diffraction results from rock crystal quartz.

tion intensity. The abrupt change in peak height is accompanied by an increase in peak width (Fig. 1) so that the integrated intensity is the same.

Rock crystal quartz (less-than-2 micron fraction), shows no comparable intensity change of the (101) reflection as the sample is heated from 400° to 800° C. In general there is only a slight increase in peak height prior to the formation of β-cristobalite at 1200° C. Following cristobalite nucleation the intensity decrease representing break-down of the existing phase is compatible with the intensity increase of the (111) cristobalite reflection indicative of the corresponding growth of this phase mineral. This loss of quartz and consequent formation of β-cristobalite was the same for all size fractions of the specimen.

In order to determine the effect of prolonged heating on the (101) d-spacing shift, less-than-2 micron quartz was held at various temperatures for different periods of time. After 20 hours at 520° C. the (101) reflection maintained a 3.37 Å dimension—the same value that was initially measured at 520° C. during the regular heating cycle. When held at 650° C. the same relationship was observed; namely, there was no additional shifting of the (101) reflection value from 3.38 Å, the initially recorded value at that temperature. With an additional temperature increase the d-spacing continues to increase, slowly at first but more rapidly above 1200° C.
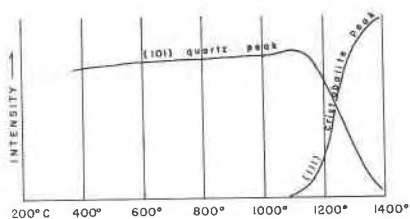

FIG. 4 (left). Continuous x-ray diffraction results from less-than-2 micron chert as heated to 1400° C.
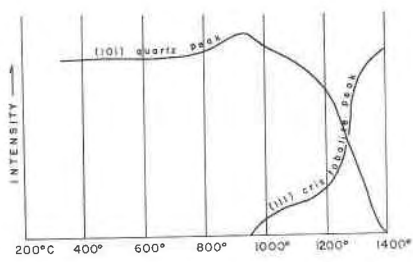
FIG. 5 (right). Continuous x-ray diffraction results from less-than-2 micron chalcedony as heated to 1400° C.

Chert

The heating curve for the less-than-2 micron chert sample (Fig. 4) is similar in configuration to that of less-than-2 micron quartz. No intensity variation of the initial α-quartz (101) diffraction peak accompanies heating from 400° to 800° C. There is a slight increase in the intensity of the (101) reflection just prior to cristobalite nucleation at 1050° C.

Chert also exhibits a gradual shift in the d-spacing as it is heated. The rate of this change is of the same approximate magnitude as that observed from rock crystal quartz; however, the maximum dimension attained at 1370° C. was only 3.39 Å instead of the 3.42 Å value recorded for the beta modification as derived from rock crystal quartz at that temperature.

Chalcedony

The less-than-2 micron chalcedony (Fig. 5) initially showed diffraction effects for α-quartz. There was no gradual intensity change of the (101) reflection on heating from 400° to 800° C. An increase in diffraction peak intensity suggesting an increase in structural perfection is indicated,

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however, just prior to the initial appearance of β-cristobalite at 950° C. With the nucleation and growth of cristobalite, there is a comparable decrease in the intensity of the quartz peak. That is, the quartz progressively decreases as the cristobalite increases. With the ultimate disappearance of quartz there is a leveling out of the β-cristobalite curve signifying complete conversion. A gradual shift in the d-spacing of the (101) reflection again accompanied the heating of this material. As with chert the maximum value attained for β-quartz was only 3.39 Å.
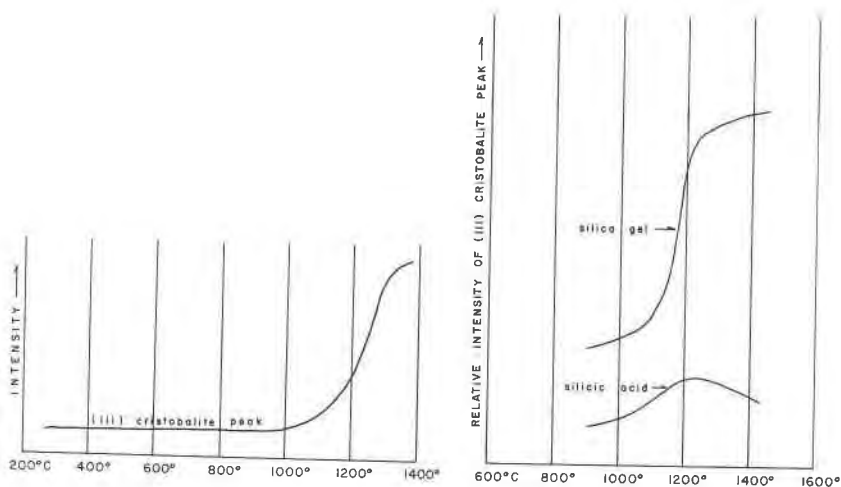

FIG. 6 (left). Changes in the cristobalite (111) peak intensity as opal is heated to 1400° C.

FIG. 7 (right). Curves depicting the formation of beta-cristobalite from silicic acid and silica gel.

Opal

Opal showed diffraction effects only for cristobalite. When heated, a definite increase in structural perfection of the initial cristobalite framework was indicated by a sharpening and increase in intensity of the (111) peak. This perfection and consequent intensity rise of the (111) reflection is not prominent, however, until the opal has been heated to 1000° C. Above this temperature the intensity increase is quite rapid until at 1400° C. a maximum is reached representing optimum structural perfection (Fig. 6).

Silicic acid

On heating, silicic acid showed no diffraction effects prior to 900° C. At that temperature, however, beta-cristobalite began forming. The cristobalite diffraction peaks increased gradually in intensity with continued

heating and attained a maximum at 1250° C. (Fig. 7). A measure of the beta-cristobalite (111) reflection peak intensity is regarded as an indication of the amount of nucleation of, or the degree of transformation to this modification: thus, the maximum intensity at 1250° C. represents the most complete conversion of the silicic acid to beta-cristobalite under these conditions of heating. At temperatures above 1250° C. there is a decrease in the peak intensity which accompanies partial fusion. It is noted that no diffraction data for other SiO_2 polymorphs were observed prior to the formation of beta-cristobalite, *i.e.*, no quartz or tridymite formed prior to the cristobalite.

Silica gel

Silica gel also gave no diffraction peaks prior to 900° C. At that temperature beta-cristobalite began forming (Fig. 7). The most rapid cristobalite growth as indicated by the (111) reflection peak intensity occurred between 1100° and 1200° C., and nearly complete transformation was reached by 1400° C. Neither α nor β-quartz, nor tridymite formed prior to the nucleation of β-cristobalite.

DISCUSSION

The sharpness and intensity of an x-ray diffraction peak can usually be regarded as an indication of the degree of crystallinity and perfection of atomic arrangement within the structural framework of a mineral. Thus, the nature of the (101) quartz reflection should be acceptable as a standard upon which the perfection of atomic arrangement of the alpha and beta forms of this mineral can be compared. Of particular interest are the diffraction data obtained while heating rock crystal quartz, chert, and chalcedony. Prior to heating each of these materials gave relatively sharp 3.34 Å diffraction peaks.

There was an abrupt decrease in peak height intensity of the (101) reflection as crushed-but-unsized quartz was heated from 400° to 800° C. which includes the temperature interval usually given for the alpha-beta quartz inversion; whereas, there was no intensity decrease of this same reflection when the less-than-2 micron fraction of the same specimen was heated through the identical temperature interval. Integrated peak area intensity measurements through the inversion interval are, however, the same for both fractions. Keith and Tuttle (1952) report that in the coarser-grained chert and novaculite samples which they examined, the observable heat effects were only weak; whereas, after fine grinding these same materials showed a measurable heat adsorption through the inversion.

The diffraction intensity data, dimensional values, and thermal data all suggest a relatively pronounced structural inversion at about 600° C.

It seems logical that in an aggregate the larger particles should require more time for complete inversion, especially if the actual transition starts at the surface of a grain and then proceeds inward as an advancing front along which the reaction occurs between two solid phases (Kracek,1951). However, the smaller size and uniformity of the less-than-2 micron material would not require as much time for complete particle inversion; thus, when the necessary temperature is reached, there should be a simultaneous and essentially complete transformation of all particles. Any intensity decrease of the (101) peak during this transition would be immediate and thus difficult to record, because following structural inversion the intensity of this reflection is virtually the same as that preceding structural transformation.

The gradual increase of the (101) lattice dimension of quartz is certainly a function of temperature. Jay (1933) reported a progressive increase in the dimensions of quartz as it was heated to the transition temperature, but he also observed a slight contraction parallel to c, above 600° C. Our data show a similar change in lattice dimension, but also indicate an additional progressive increase at higher temperatures until complete transformation to cristobalite is accomplished. After prolonged heating at 650° C., the (101) dimension is 3.38 Å—a value reported to be characteristic of β-quartz at that temperature. This gradual increase in d-spacing cannot be correlated with any increases or decreases in the (101) peak intensity measurements (Fig. 2), but it does follow closely the expansion measurements that Jay recorded up to 700° C. Even after some of the material has been converted to cristobalite at 1250° C. the (101) lattice dimension of the remaining quartz continues to increase.

In the literature there is a lack of agreement as to the unit cell dimensions for β-quartz. Bragg and Gibbs (1925) determined their measurements from quartz held at 700° C. for several hours and list dimensions of $c=5.446$ Å and $a=4.989$ Å. Wyckoff (1926) gives unit cell dimensions of $c=5.47$ Å and $a=5.01$ Å; whereas, the most recent A.S.T.M. data, based on quartz derived by firing to 1000° C., but measured at room temperature (Bradley and Grim, 1951), indicates dimensions of $c=5.37$ Å and $a=5.11$ Å. It is important to emphasize that the dimensions obtained are always dependent on the temperature at which the material is measured.

Wright and Larsen (1909) studied quartz optically as it was heated. They reported gradual changes in birefringence on heating to 1400° C. The fact that birefringence changes occur gradually, taking place over the entire temperature range, and are not restricted to the 570°–575° C. inversion temperature interval is significant. These continuous optical changes and the gradual d-spacing changes which we recorded both indicate a continuous gradual change in the internal atomic arrangement of

quartz as it is heated. The continual change in dimension through the temperature interval where an abrupt energy reaction occurs, and where optical characteristics change, is in accord with structural considerations brought out by Bragg (1925) and others.

Structural rearrangement begins with heating; however, not until approximately 570° C. is there an abrupt change in the Si-O-Si bonding arrangement of α-quartz to that of β-quartz. This is indicated by the sharp endothermic reaction on the thermal curve. With additional temperature increases, however, there is a continued preferential rearrangement of the silica tetrahedra within the newly developed structural framework to attain a more desired arrangement. The degree of tetrahedral organization is a direct function of temperature and as the temperature is increased, and the rearrangement accomplished, there is once again a progressive change in the lattice dimensions of the material. This additional change in dimension is slow between 600° and 1000° C., but increases more rapidly as the cristobalite crystallization temperature is reached (Fig. 2). This increase in dimension is of the same magnitude as that observed preceding the α-β quartz inversion. It is a predecessor of cristobalite density and depicts the beginning of a tetrahedral rearrangement which ultimately results in the cristobalite structure.

The inversion of the α-quartz structure requires more time in aggregates containing larger particles; whereas, in the smaller less-than-2 micron particles the breakdown is simultaneous. The tetrahedral reorganization which occurs above 600° C. takes place at the same rate regardless of particle size and is only a function of temperature. The ultimate degree of perfection that can be attained is contingent on the structural perfection of the α-quartz before inversion. Rock crystal quartz produces β-quartz with a (101) d-value of 3.42 Å; whereas, chert and chalcedony give β-quartz structures with maximum (101) values of approximately 3.39 Å. This is probably the consequence of larger crystals withstanding higher temperatures before their transformation to cristobalite.

The curves of quartz, chert, and chalcedony all show a gradual intensity increase of the (101) reflection prior to the breakdown of the β-quartz structure to form β-cristobalite. The magnitude of this increase, however, is different for each material (Figs. 3, 4, and 5), and appears to be directly related to the crystallization temperature of β-cristobalite and to the initial structural perfection of the type of silica. Such an intensity increase is again an indication of improved atomic arrangement within the β-quartz framework.

The actual temperatures at which β-cristobalite forms from each of the materials appears to be a consequence of the structural perfection of the starting material. Silicic acid and silica gel, which are mostly amorphous,

both crystallize to form β-cristobalite at 900° C. without any prior quartz phase; whereas, chalcedony, chert, and rock crystal quartz, which develop β-cristobalite at 950°, 1050°, and 1200° C. respectively, represent higher degrees of crystallinity and structural perfection in that order. The heating curves of the latter three materials also show a comparable reduction in the increase in the intensity of the quartz reflection prior to the cristobalite transition, i.e., quartz, which has the highest β-cristobalite crystallization temperature, also has the smallest increase in quartz intensity. This comparable reduction of any increase in the (101) peak intensity preceding transformation, when coupled with the higher temperature at which the structural transition occurs, would indicate that the crystallization temperature for β-cristobalite as it forms from any such siliceous material is a consequence of the initial structural perfection of that material. The better the initial structure, the smaller the (101) peak intensity increase which precedes the β-cristobalite formation, and also the higher the temperature of this transformation.

Because of this apparent relationship between the crystallization temperature of β-cristobalite and the initial perfection of the atomic arrangement or structure of the material, it is suggested that temperature alone be minimized as a major factor controlling this transformation. It is suggested that in the one-component SiO_2 system the formation temperature of β-cristobalite should not be considered as a fixed value, but rather that it be expressed as a function of the crystallinity and structural perfection of the material from which it develops. The formation of cristobalite at 900° C. from amorphous silicic acid and silica gel adds credence to this proposal.

The absence of tridymite when the different SiO_2 materials are heated is noteworthy. More than forty different heating trials were made during the course of our study and not once was any indication of the presence or formation of any tridymite observed. The normal transformation sequence was

$$\alpha\text{-quartz} \rightleftharpoons \beta \text{ quartz} \xrightarrow{\text{variable temp.}} \beta\text{-cristobalite.}$$
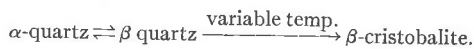
The absence of the tridymite "phase" is not unusual in studies of the one-component SiO_2 system; in fact, this modification has never been synthesized in the laboratory without the use of "mineralizers" which introduce foreign ions into the system and thereby result in "complex-stuffed" derivatives (Flörke, 1955).

Hill and Roy (1957) reportedly prepared pure tridymite hydrothermally at a pressure of several hundred atmospheres from all forms of silica; however, Holmquist (1958) states that under hydrothermal conditions the hydronium ion, H_3O^+, has the same effect as the mineralizing ion

potassium which, according to Flörke (1956) is the best promoter of the formation of tridymite.

Flörke (1955) questions the fact that tridymite can exist as a thermodynamically stable phase of pure silica at one atmosphere pressure. Holmquist (1958) re-examined, thermodynamically, the possible transformations of this system. He concludes that " . . . the mineral tridymite is not a stable phase of pure silica at one atmosphere but belongs in binary and multicomponent systems."

If tridymite is removed from the SiO_2 system, where should the inversion temperature between the stability fields of quartz and cristobalite be placed? Mosesman and Pitzer (1941) concluded such a hypothetical inversion point at about 1050° C. at ordinary pressures. Our data would support such a direct transformation; however, we would propose that the exact temperature at which this inversion takes place is a consequence of initial structural perfection when dealing with already crystallized materials.

SUMMARY

Phase transformations of various forms of silica on heating to 1400° C. were studied by continuous x-ray diffraction. Curves representing peak intensity of the silica phases versus temperature are presented for the different forms of silica.

On heating silica gel and silicic acid, β-cristobalite forms directly at 900° C. from both materials without any pure quartz phase. On heating chalcedony, chert, and quartz there is a gradual change in the (101) quartz spacing as the temperature increases from 60° to 1370° C. However, only in the case of rock crystal quartz was a 3.42 Å value attained. In the case of quartz in fairly coarse particles, the intensity of the (101) reflection sharply drops at the initiation of the α-β transition but increases again as the spacing of the β-form develops. This phenomenon is an indirect consequence of particle size, for integrated peak area intensity measurements show no such abrupt change.

The relatively abrupt change in structure at 570° C. is followed by a gradual preferential reorganization of the silica tetrahedra with additional temperature increases. This is suggested by gradual changes in crystal dimension that also accompany heating to higher temperatures. These dimensional changes, however, cannot be attributed solely to thermal expansion for they are often accompanied by a gradual increase in the intensity of the (101) quartz reflection prior to conversion to β-cristobalite. This increase is particularly pronounced for chalcedony and very scant for quartz, and could indicate a better arrangement of silicon and oxygen atoms within the β-quartz structure just prior to structural transformation. There is a more rapid change in dimension above

1000° C. as the cristobalite density is approached. This progressive change resembles that which precedes the α-β quartz inversion.

Variations in the crystallization temperatures of β-cristobalite as formed from different varieties of silica show that the better the crystallinity and structural perfection of the silica, the higher the β-cristobalite crystallization temperature. Rock crystal quartz forms beta-cristobalite at 1200° C., but silica gel produces this modification at 900° C.

A direct inversion from β-quartz to β-cristobalite is supported; however, the exact temperature of this transformation is believed to be a function of the crystallinity of the starting material.

At no time was tridymite identified; thus, the authors support those who would eliminate tridymite as a stable phase mineral in the one-component silica system.

REFERENCES

BRADLEY, W. F., AND GRIM, R. E., High temperature thermal effects of clay and related minerals: *Am. Mineral.*, **36,** 182–201 (1951).

BRAGG, W. H., AND GIBBS, R. E., The structure of α and β quartz: *Proc. Roy. Soc.*, **A109,** 405–427 (1925).

BUERGER, M. J., The stuffed derivatives of the silica structures: *Am. Mineral.*, **39,** 600–614 (1954).

EITEL, W., The silica system: The Physical Chemistry of the Silicates, Univ. of Chicago Press, 616–629 (1954).

FENNER, C. N., The stability relations of the silica minerals: *Am. Jour. Sci.*, **36,** 331–384 (1913).

FLÖRKE, O. W., Structural anomalies in tridymite and cristobalite: *Berichte der Deutschen Keramischen Gesellschaft*, **32,** 369–381 (1955): Translation by Eitel, W., *Bull. Am. Cer. Soc.*, **36,** 142–148 (1957).

FLÖRKE, O. W., Über das einstoffsystem SiO_2: *Naturwissenschaften*, **43,** 419–420 (1956).

GRIM, R. E., AND KULBICKI, G., Etude aux rayons X des reactions des mineraux argileux a haute temperature: *Bull. de la Societe Francaise de Ceramique*, 21–27 (1957).

HILL, V. J., AND ROY, R., New data on the tridymite problem: *Acta Crystallogr.*, **10,** 835 (1957).

HOLMQUIST, S. B., A note on the sluggish silica transformations: *Zeit. für Krist.*, **111,** 71–76 (1958).

JAY, A. H., Thermal expansion of quartz: *Proc. Roy. Soc.*, **142,** 237–247 (1933).

KEITH, M. L., AND TUTTLE, O. F., Significance of variations in the high-low inversion of quartz: *Am. Jour. Sci.* (Bowen Vol.), 203–280 (1952).

KRACEK, F. C., Phase transformations in one-component silicate systems: Phase Transformations in Solids, Ch. 9, (1951).

MOSESMAN, M. A., AND PITZER, K. S., Thermodynamic properties of the crystalline forms of silica: *Jour. Am. Chem. Soc.*, **63,** 2348–2356 (1941).

SOSMAN, R. B., The properties of silica: *Am. Chem. Soc. Monograph* **37** (1927).

WRIGHT, F. E., AND LARSEN, E. S., Quartz as a geologic thermometer: *Am. Jour. Sci.*, **27,** 421–447 (1909).

WYCKOFF, R. W. G., The crystal structure of the high temperature (β) modification of quartz: *Am. Jour. Sci.*, **11,** 101–112 (1926).