U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1152

Part of Journal of Research of the National Bureau of Standards, Volume 21, December 1938

OBSERVATIONS ON CRYSTALLINE SILICA IN CERTAIN DEVITRIFIED GLASSES

By Arthur Q. Tool and Herbert Insley

ABSTRACT

Samples of a borosilicate glass having a relatively high silica content were devitrified at temperatures in the range between 625° and 950° C by heat treatments of various durations. The crystals in these samples, and in certain other devitrified siliceous materials, were studied by examining their form and general appearance and by comparing the characteristics of their endothermic and exothermic effects which develop in heating and cooling curves, respectively, as a result of "rapid" inversions. In general agreement with the experience of other investigators, it was found that the devitrification developed approximately as follows: Heat treatments at points above 700° C caused cristobalite to appear within a month or less and in considerable quantities. Increasing the duration of treatment caused this material to disappear while tridymite developed coincidentally at a fairly rapid rate. When the duration of a treatment approached 6 months at temperatures near 800° but below 870° C, quartz in turn almost completely displaced the tridymite.

The results indicate that ultimately wedge-shaped twins always displace the earlier formed plates as the tridymite development is advanced by increasing the duration of treatment at any reasonable temperature below a point which may greatly exceed 1,000° C, and that coincidentally the inversion effects are shifted from the 150° to the 100° C range. The fact that the crystalline plates and practically all inversion effects at temperatures above the lower range were made to disappear almost completely by imposing relatively long heat treatments suggests the possibility that each of the two recognized inversion ranges of tridymite belongs to one of two low-temperature tridymite types, each of which possesses but one inversion range. It would also seem that the type inverting in the 100° C range was the stable form from 870° C to well above 1,000° C at least.

[Vol. 21

CONTENTS

I. INTRODUCTION

Many glasses when heated in certain temperature ranges for any considerable time will show some evidences of devitrification, although the extent and nature of the crystal development and the temperatures at which the rate of this development is highest may vary greatly with the composition. If the "devitrification range" of a glass is defined as the temperature range within which noticeable evidences of devitrification develop during heat treatments of appropriate duration, this range will usually be found to lie entirely above the normal annealing range. That is, most of the glasses in common use devitrify very slowly or not at all during ordinary annealing treatments, and their devitrification proceeds at an appreciable rate only when the viscous deformability exceeds that required for such treatments. In other words, lowering the temperature into or below the annealing range so reduces the mobility of the glass that a sort of physical stability is imposed upon the more or less accidental molecular space pattern which developed during the melting process.

In order to gain certain desirable changes in the properties of glass it is occasionally necessary to depart from those compositions yielding this stability which prevents a massing of any of the constituents into possible crystal formations. Such departures may not only affect the rate of devitrification and its ultimate extent but may also change very greatly the breadth and position of the devitrification range. The composition is naturally the chief factor in determining the type of crystals developed, but often the treating temperature and the duration of the treatment are additional factors.

Certain borosilicate glasses present examples of this use of compositions which result in very desirable properties at the expense of stability; and some of these glasses devitrify rather extensively when heated for moderately long periods at any temperature in a rather wide range above 600° C. Temperature not only determines the necessary duration of a treatment required to produce obvious devitrification in a given glass, but it also limits the ultimate extent of the devitrification, and together with the duration of a treatment it often determines the type of crystals found in a devitrified material. For example, treatments lasting several days at 700° C will in many cases develop cristobalite as practically the only crystalline product in these glasses, while an equal period at 800° C will yield tridymite as the chief product. Actually cristobalite appears first in both cases, and if the treatments are prolonged sufficiently at these temperatures, quartz ultimately appears and becomes practically the only form present.

II. OBSERVATIONS ON THE GENERAL EFFECTS OF DEVITRIFICATION IN CERTAIN BOROSILICATE GLASSES

This paper [1] deals chiefly with results obtained by the devitrification of certain specimens of borosilicate glasses at temperatures between 650° and 950° C. The first visual evidences of devitrification in many of the samples were very fine surface cracks, which probably developed during the period of cooling from the treating to the observing temperature. The best examples of such surface cracks appeared in the polished surfaces of some samples that were being intermittently treated for a total duration of several days near 700° C in the course of some experiments designed to demonstrate that the refractive index and density reach stable values after not more than a few hours' treatment. The surface effects did not appear until long after the desired stability was reached, but extending the treatments beyond 3 or 4 days often developed them rapidly without causing detectable changes in the properties being studied. At this stage the glass was soon encased in a thin translucent film which usually could be ground and polished away leaving apparently only clear undeteriorated glass. Occasionally, however, in some of the more inhomogeneous samples certain cords developed a cloudiness throughout their extent during these treatments; and the surface deterioration often appeared first at the polished ends of some of these cords.

In samples such as rods made by the gathering process, these nonuniformities in the deterioration rate at different points were especially noticeable. That is, the devitrification often developed more rapidly and to a greater extent in one or two than in the rest of the concentric cylindrical shells that are often apparent in glass rods. Probably because of the occasional coolings required for close observation and test, these shells sometimes separated during a series of treatments at temperatures near and below 700° C. These separations usually occurred early in such a series and before any visible evidence of devitrification developed. Their detection occurred only after the samples were immersed in oil and then reheated. This caused the shells to be outlined by very thin carbon films or mirrors within the body of the rod. Later it was noted that in other rods, apparently similar inner shells often were outlined by films of crystals which developed rapidly and were among the first to appear. On some occasions these films even preceded those developing on the outer surface. Ultimately the devitrification spread throughout the mass of the glass, but these observations indicate that the distribution of the crystals probably never became uniform. Moreover, it is apparent that the rates of development of the various crystalline phases at any efficacious treating temperature were not likely to be the same in all parts of the glass at any time. Consequently, well-developed quartz crystals might often appear in certain shells while cristobalite was still predominant in others.

---

[1] The greater part of the results presented here were included in an informal progress report entitled "Some Observations on a Devitrified Glass," which was read at the Washington meeting of the American Ceramic Society on February 9, 1932.

Numerous preliminary tests showed that the devitrification of such glass rods developed much more rapidly at 800° C than at 700° C. After 3 days a rod would often be encased in a dense white crystal-rich shell approximately 0.5 mm thick. At this time some of the inner shells might remain practically clear, while others would be highly devitrified. When rods in this condition were cooled, the outer shell broke away from the remainder of the glass as 200° C was approached. This happened because of the relatively large contraction of cristobalite at its inversion point. A treatment of 14 days entirely devitrified such rods and the cristobalite was to a great extent transformed into tridymite. Cooling the samples under these conditions caused no breaking up of the glass, and its hardness and density seemed to be greater than originally. In one case, for example, the density of the original glass was 2.2407 and after 2 weeks of treatment it was 2.2684. Regardless of the possible density changes occurring at the treating temperature because of devitrification, the change [2] noted here should be attributed chiefly to the difference between the expansivity coefficients of the residual and original glasses and to the contraction of the tridymite at its inversion points.

III. TREATMENT AND TESTING OF GLASS

The samples used in the major portion of the tests described in section IV were cut from a glass rod [3] (approximately 1 cm in diameter) that was procured from the general glass supply of the National Bureau of Standards. Placed in a platinum boat, these samples were treated in an electric furnace, the treating temperatures in which were maintained within 10° C of the desired point. Extended treatments at temperatures above 700° C caused the glass to adhere more or less to the container, and above 800° C. considerable deformation developed.

The devitrification changes in the samples were followed closely by making frequent heating and cooling curve tests, and also by examination with a petrographic microscope. Occasionally X-ray patterns were procured and in certain cases expansivity measurements [4] were included in the tests. In the heating and cooling curve tests, the heating rate was usually somewhat in excess of 3° C per minute throughout the test range, but the cooling rate dropped from about 5° at 500° C to about 1° per minute at 90° C. The test sample, reduced to small granules by cracking, weighed 1.5 g and the neutral body required in differential pyrometry consisted of granular Al_2O_3. The difference in temperature between neutral body and sample and the temperature of the latter were determined at intervals ranging, respectively, from ¼ to 2 minutes and from 5 to 10 minutes by the usual combined differential and simple thermocouple system in which one wire was platinum and the other two were 90 Pt–10 Rh. The differences in temperature were indicated by galvanometer deflections. A 1° difference at 500° C corresponded to a double deflection of about 46 mm. A potentiometer was used in determining the sample temperature.

---

[2] This density increase at room temperature caused by devitrification is somewhat larger than the unrelated density change that (as shown in a previous paper, Trans. Soc. Glass Tech. **9**, 185 (1925)) can be produced in undevitrified glasses of the same type by reducing the annealing temperature from 700° to 450° C and that can be reversed by reannealing at 700° C.

[3] According to an analysis made by the Chemistry Division of this Bureau, the percentages of the chief constituents of this Pyrex glass were: SiO_2, 80.6; B_2O_3, 11.9; Al_2O_3, 2.2; Na_2O, 3.9; and K_2O, 0.07.

[4] *Expansion effects on the inversion of silica crystals in certain devitrified glasses*, A. Q. Tool and J. B. Saunders, J. Research NBS **21,** 773 (1938) RP1153.

IV. EXPERIMENTAL RESULTS

SAMPLE 1

This sample was treated for 25 days at 725° C. Contrary to earlier experiences described in the preceding section, the resulting devitrification was reasonably uniform throughout the glass. The treatment caused some deformation and the two pieces of rod comprising the sample adhered strongly at their points of contact. During the cooling after removal from the furnace the sample broke into several large pieces as it passed through the range of the high-low inversion of cristobalite.

All of the observed heat effects which could be ascribed to crystalline inversions in this sample fell in the temperature range (80° to 300° C) covered by the heating and cooling curves represented in figure 1. The curves *A* (heating) and *A′* (cooling) were obtained on the glass previous to any heat treatment. Neglecting the depression[5] just above 100° C in *A*, they show no inversion or other heat effects. In the heating curve *B*, obtained on the devitrified glass, the depression is so unusually deep that a large part of it must be ascribed to endothermic effects resulting from crystalline inversions. The three minima falling near 120°, 160°, and 210° C indicate that a large por-

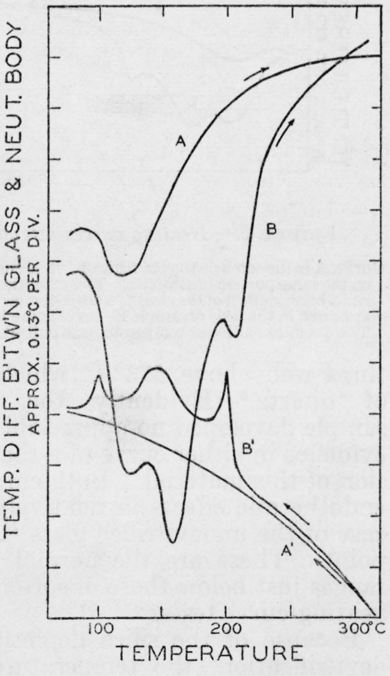

FIGURE 1.—*Curves showing inversion effects of tridymite and cristobalite in a devitrified glass.*

Curves *A* and *A′* are the heating and cooling curves obtained before devitrification. Curves *B* and *B′* are the corresponding curves obtained after devitrification. Curves were obtained by differential thermocouple method. On the average, observations were taken at intervals of 2° C or less. All observations are covered by the breadth of the curves in this and the following graphs with the exception of figure 5 where the individual points are shown. In figures 1 and 2 the heating curves for the undevitrified and particularly for the devitrified glass are greatly distorted in the range just above 100° C by an endothermic effect which is supposedly caused by the vaporization of moisture from the surfaces of the glass dust particles which remained after the samples were crushed and sifted for test.

---

[5] This depression is unimportant in this connection because it is presumably a moisture effect and is usually observed in the first heating curve of any granular sample of undevitrified glass from which the fine dust formed by crushing has not been carefully sifted out. The similar endothermic effect in curve *B* has an even greater magnitude, which seems excessive even after a reasonable allowance is made for the probable contribution from a low-high inversion of the tridymite present. Probably the combined effect was excessive because the partial crystallization of the silica had so increased the alkali content of the residual glass that its dust absorbed more moisture than did that of the original glass. Whenever a crushed sample of the glass was re-treated at high temperatures the supposed moisture effects were markedly diminished in the later tests. This reduction may have been caused by a decrease in the free dust after the sintering.

tion of the depression was the result of three inversions. The cooling curve B′ shows three corresponding exothermic effects; but because of the test conditions and the nature of such inversions, the temperatures determined by the maxima in *B′* are somewhat lower than those determined by the minima in *B*.

The low-high inversions causing the minima near 120° and 160° C may be ascribed to tridymite, while the inversion causing a minimum near 210° C indicates the presence of a considerable quantity of cristobalite. It may seem that the cristobalite inversion should have been expected near this temperature because of the relatively low developing temperature.[6]

The heating curves for both the undevitrified glass[7] (curve *A*) and the devitrified sample (curve *B*) are extended in figure 2 to temperatures well above 573° C, which is the approximate inversion point of quartz.[8] Evidently the heat treatment imposed on this sample developed no appreciable quantity of quartz, since there is no evidence in either curve of a thermal effect corresponding to an inversion of this material. Both curves, however, do show the presence of endothermic effects in relatively high temperature ranges, and in the case of the undevitrified glass the range includes the quartz inversion point. These are the normal effects always found in temperature ranges just below those of softening whenever glasses are subjected to heating-curve tests.

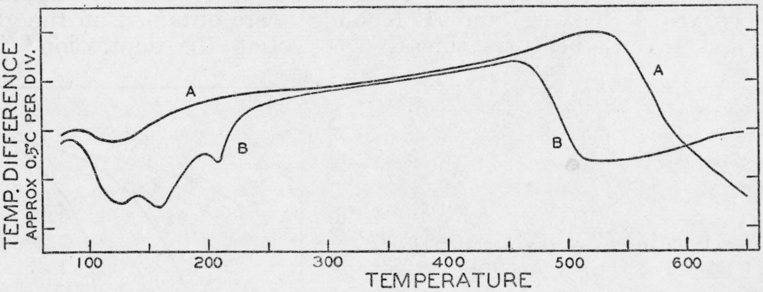

Figure 2.—*Heating curves extended into the softening range of the glasses.*

Curve *A* is the same as that in figure 1. The curves designated by *B* in the two figures were not obtained on the same portion of sample 1. This extension of the curves shows that devitrification shifts the normal endothermic effect of the glass to a lower-temperature range and that no appreciable quartz-inversion effect appeared in the tests of sample 1. As in figure 1, the ordinates were adjusted for temperatures near 300° C. The deviation at lower temperatures is indicated approximately in figure 8.

Because of the silica depletion suffered by the glass phase from devitrification, the temperature range of this glass-effect in *B* is lowered considerably with respect to that in *A*. Judging from the beginning temperatures of the effects, this lowering amounts to approximately 60° C (approximately from 530° to 470° C), but the actual lowering is even greater because (as should be expected) the width of the range was materially reduced by the devitrification. The lowering of the range of the endothermic effect indicates an approximately equivalent lowering of the softening range, while the reduction in its width indicates a material increase in the rate of softening with

---

[6] Fenner, Am. J. Sci. **36**, 331 (1913), procured data which indicate that the low-high inversion point of this material decreases from 277° to 220° C as the developing temperature is reduced from 1,600° to 1,025° C, approximately.

[7] Heating curves extending to still higher temperatures have been obtained on similar glasses and were presented in a previous publication (J. Am. Ceram. Soc. **8**, 1 1925").

[8] Bates and Phelps. Phys. Rev. [2] **18**, 115 (1921).

temperature. These results explain the unexpectedly large deformation sometimes obtained by devitrification treatments. They also agree with the common experience that devitrifiable glass tubes or bulbs subjected to continued heating at temperatures approaching their softening ranges ultimately lose their normal ability to withstand pressure at those points where devitrification develops.

To the unaided eye this devitrified sample had a uniform milky appearance throughout the body of the glass, except that one cylindrical layer parallel to the axis of the rod was much more opaque than the remainder of the glass. This condition suggested not only a greater but also a more advanced degree of crystalline development in this layer. By microscopic examinations of powdered samples and of a thin section cut normal to the axis of the rod so that a ring of the more highly devitrified layer was included, tridymite occurring usually as plates, but sometimes as wedge-shaped twins, was readily identified in all parts of the sample. Because of the small size of these crystals and the presence of the enveloping glass their index of refraction could not be determined with precision, but it was near that given in the literature for tridymite. In the main body of the glass, cristobalite appeared to be predominant although it was identified with difficulty. It was found on examining the material with an oil-immersion objective that cristobalite occurred as very minute rounded pellets or as short rods in which no double refraction could be observed, and that its index of refraction was near the accepted value for cristobalite. In the layer showing the greatest devitrification, tridymite, associated with a few quartz crystals, was the major product. Some of these quartz crystals reached a length of 10 microns, their pyramidal faces were well developed, and the prismatic faces, although not so large, were also present.

An X-ray diffraction pattern obtained from a powdered sample contained faint lines of both cristobalite and tridymite. Those of the former were more intense, and this indicated a possible predominance of this form. None of the characteristic quartz lines could be detected, presumably because the amount of this material in the sample was very small.

SAMPLE 2

This sample of the glass rod was treated twice at 675° C, once for 18 days and again for 19 days. After the first treatment a marked devitrification such as developed in the first sample had appeared only in the outer shell to a depth of possibly 1 mm. This shell in peeling while cooling naturally caused the whole sample to shatter. The heat effects near 200° C in the heating and cooling curves obtained on this shell were very large and sharp with respective minima and maxima at 214° and 199° C. There were no indications of heat effects at lower temperatures.

After the second treatment, during which the shell and relatively clear core were kept separate, both parts appeared from a visual examination to have reached about the same stage of devitrification. The magnitude of the cristobalite heat effects by being almost equal for the two parts (although 25 percent smaller than that obtained on the shell after the first treatment) supported the visual observation. In the case of the core, the minimum and maximum of the effects were at 218° and 201° C, respectively, and these values were duplicated within one degree after 2 weeks on another part of the sample. In the cooling curve (curve 1, fig. 3) very slight indications of heat effects were detectable near 160° and 100° C. In the case of the shell, the minima and maxima were at 216° and 200° C, respectively, and there was some indication of a moderately large and closely bound subordinate member on the low-temperature side of the endothermic effect. A similar and less pronounced indication was noted in only one of the heating curves obtained on the core.

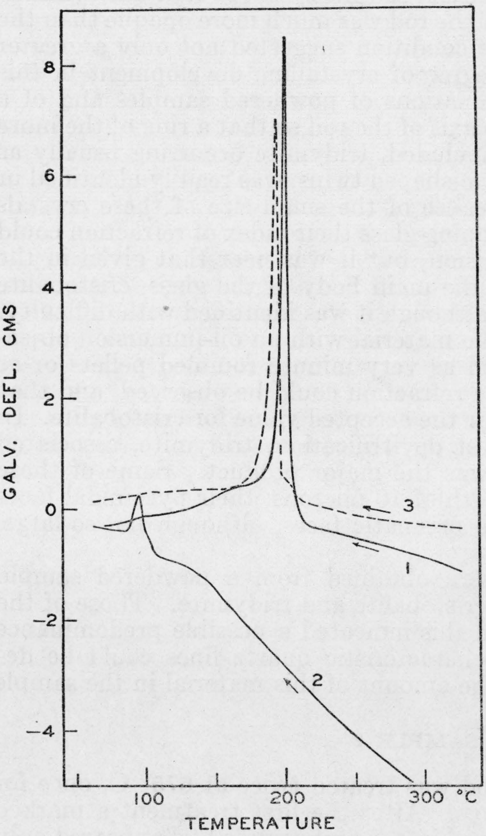

Figure 3.—*Cooling curves showing cristobalite and tridymite inversion effects.*

Curve 1 obtained on sample 2 after 37 days at 675° C. Large cristobalite effect followed by very small tridymite effect. Curve 2 obtained on same sample after six additional days at 800° C. Indefinite tridymite effect centering on 136° C followed by definite effect near 95° C. Curve 3 obtained on sample 3 after 33 days at 625° C. Ordinates are double galvanometer deflections.

By microscopic examination after the second treatment, the core was found to contain (in addition to the residual glass) both cristobalite and tridymite, although the former was by far the more abundant. Cristobalite occurred as long thread-like chains of minute beads with threads radiating in many places from a common center. The double refraction of these crystals was extremely weak and their index of refraction was normal for cristobalite, although determinations of the usual precision were impossible because the crystals were so small. The tridymite occurred as plates which were clearly visible only when on edge. They had the index of refraction and other optical properties (double refraction and character of elongation) of such tridymite crystals, and seemed to be concentrated in certain parts of the sample. No quartz could be found. An X-ray diffraction pattern showed clearly defined critobalite lines which were more intense than those found in sample 1. Besides these lines there were two extremely faint lines corresponding to the strongest lines in a pattern obtained on relatively pure tridymite.

The outside shell when examined microscopically after the second treatment was found to contain cristobalite, tridymite, and quartz. Cristobalite was the most abundant and occurred either as fine fibers often radiating from centers or as short rods arranged along branching fibers. The shape of the rods could be distinguished only with the oil-immersion objective, and while the index of refraction of the fibers could not be determined accurately, it was 1.48 ±0.01. Tridymite, present only in small amounts, was in the form of hexagonal plates. The quartz occurred as aggregates of interlocking grains. In an X-ray pattern (see fig. 4 (A)) the cristobalite lines were well developed and only slightly fainter than those obtained from the reference material (cristobalite obtained by heating quartz at 1,500° C). Only two extremely faint lines corresponding to the strongest lines in the quartz pattern were present.

After these treatments and examinations, a portion of the core was further heat treated for 6 days at 800° C. The cooling curve then obtained (curve 2, fig. 3) indicated a very definite inversion effect with its peak or maximum at 95° C and its beginning at 108° C. The latter temperature was somewhat lower than that of the minimum of a relatively small and indefinite effect which appeared in the heating curve and may have been caused by moisture.[9] There was also an indication of a broad indefinite effect between 150° and 120° C in the cooling curve but no corresponding effect of even that weak character appeared in the heating curve. There was also no indication of cristobalite effects in any of the heating or cooling curves nor was there any definite evidence of quartz-inversion effects. In a superficial microscopic examination at this stage the tridymite crystals appeared to be plates turned on edge, but a more careful examination with an oil-immersion objective (1.9 mm) showed an abundance of wedge-shaped twins which may have been composed of parallel growths of plates. Skeleton twins and interpenetration twins were also common.

SAMPLE 3

A 33-day treatment at 625° C devitrified only a very thin outer layer of this sample of the rod, and the greater part of this layer cracked into small flakes during the cooling. These were easily peeled from the clear inner glass which was broken up by the bursting of the outer layer at 200° C. Heating and cooling curves obtained on this outer shell indicated no inversion effects except those of cristobalite. The respective minimum and maximum of the low-high and high-low effects were at 207° and 194° C, which are 7° and 5° lower than the corresponding temperatures obtained on sample 2 after the first of the 675° C treatments. This again is a result that seems to agree with the usually reported experience that reducing the devitrifying temperature lowers the inversion temperature. A slight hump on the high-temperature side of the base of the principal effect (curve 3, fig. 3) indicated the presence of a subordinate effect which in regard to temperature coincided rather more closely than its principal to the cristobalite effect shown in curve 1, figure 3. The smallness of this hump suggests that it was accidental, but its persistence in duplicate curves tended to remove this possibility. Moreover, such evidences of possible satellites were often noted in other samples (see fig. 5) on one side or the other of both cristobalite and tridymite effects. In almost every case such evidences indicated two or more

---

[9] It was found later that the definite endothermic effect which usually appears at, or near, 115° C and corresponds to the exothermic effect occurring below 100° C often did not develop to a detectable magnitude at any temperature. Apparently this happened when the tridymite crystals were only partially transformed from plates to wedge-shaped twins. In fact, the magnitude of the exothermic effect appears under such conditions to increase in a more or less erratic manner as the preheating temperature preceding cooling tests is increased. This suggests that the endothermic effect is distributed over a wide range of temperatures which may reach almost 400° C as long as the transformation to wedge-shaped twins is in its initial stages. This occasional nonappearance of a clear-cut endothermic effect in a restricted range just above 100° C is likely to be overlooked in the presence of the moisture-dust effect.

effects which were separated by intervals of several degrees. Possibly this separation may be explained by a difference in the devitrification development in different portions of the sample. At times it also appeared that increasing the period of treatment erased a satellite on the high-temperature side, and at others that it shifted a major effect into the approximate position previously occupied by a satellite. Such shifts were usually toward lower temperatures.

When a portion of the shell was examined microscopically under the highest power available, minute branching fibers with an average width of less than 1 micron could be distinguished. Their index of refraction could not be determined but they showed an extremely weak double refraction and a positive elongation, both of which are properties of cristobalite. An X-ray pattern (fig. 4 (B)) gave faint but characteristic cristobalite lines. No other lines were present.

SAMPLE 4

This sample when cooled after a treatment of 11 days at 800° C did not disintegrate, presumably because the cristobalite was almost completely converted to tridymite. The heating curve had a large endothermic effect with a minimum at 152° C, but there were no significant indications of cristobalite effects. There was also strong evidence of an effect near 120° C, but a definite inversion temperature was not indicated. The general appearance of the cooling curve indicated effects much like those shown in figure 6 for sample 8 after a 12-day treatment. The main exothermic effect with a maximum at 144° C was broad although quite pronounced. Its breadth was exaggerated by a small hump near 160° C. There was also a small and very definite effect with a maximum at 99° C. No indication of quartz or cristobalite was detected.

Only three phases (glass, tridymite, and quartz) were identified in this sample by the petrographic examination. Because of being mixed with so much tridymite the index of refraction of the glass could not be determined definitely.

Tridymite plates were scattered throughout the sample and probably constituted the most abundant crystalline phase. In general, the plates were small but were considerably larger than those in sample 1 treated at 725° C. A layer of plates larger than the average occurred in a thin cylindrical coaxial layer having a radius which was about two-thirds that of the rod. The characteristics of the plates were negative elongation on upturned plates, low double refraction, and refractive index slightly less than that of the surrounding glass. A reexamination of powdered and thin section specimens of this sample showed a few forms like the skeleton and interpenetration twins found in sample 2.

The quartz crystals occurred in two localities, on the surface of the rod, and in the cylindrical layer containing the larger tridymite plates. They were small (30 microns or less in the largest dimension) but larger than those in sample 1, and appeared microscopically as six-sided figures.[10] The determined index agreed with that of quartz, and the form was essentially that of a rhombohedron.

---

[10] Dana, System of Mineralogy, 184, figure 4. Sixth edition (1911).

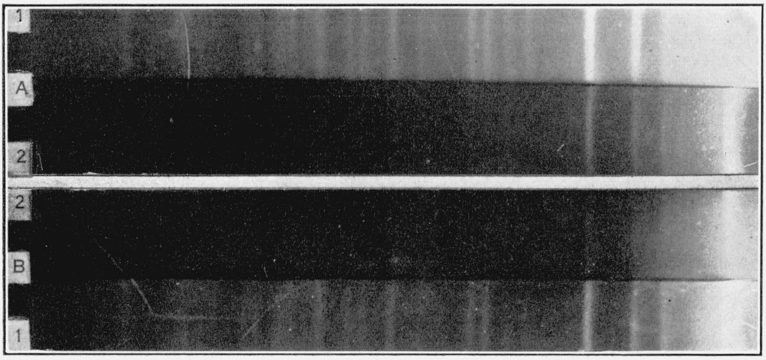

Figure 4.—*X-ray patterns of samples 2 and 3.*

A1 is a pattern of the reference material. *A2* is a pattern of sample 2 after 37 days at 675° C. The original photograph shows both cristobalite and quartz lines, although the latter do not appear in the reproduction. *B1* is a pattern of the reference material. *B2* is pattern of sample 3. Cristobalite a lines are relatively faint in the reproduction.

SAMPLE 5

This sample of the rod was treated 10 days at 750° C and on cooling broke up more completely near 200° C than sample 1. Moreover, the devitrification was concentrated to a somewhat greater extent near the outer surface. After separating the core from the thick and more densely devitrified shell as well as possible, heating and cooling curves were taken on them individually. For both portions these curves showed large definite inversion effects near 200° C, and much smaller ones near 150° C, while only the cooling curve indicated a very slight effect near 100° C. The minima for the largest effect fell at 214° for both shell and core and the maxima fell, respectively, at 201° and 203° C. These temperatures agree reasonably well with those obtained for the same inversion in sample 2 after its first treatment at 675° C. The minima for the intermediate effect were at 164° and 162° C and the maxima at 155° and 150° C, respectively, for core and shell.

After these tests the two parts of the sample were subjected to a second treatment of 12 days at 750° C and retested. Neither the heating nor the cooling curves now gave any clear indication of the cristobalite effect near 200° C and in general, the results for the shell and core were almost identical. The cooling curves corresponded roughly to those obtained on sample 8 after 18 days of treatment at 800° C (fig. 6), although the effect near 100° C for sample 5 was somewhat broader and consequently less definite. Furthermore, a comparison of the magnitude of this effect with that of the effect near 150° C in the two cases indicated that the low-temperature effect in sample 5 was relatively smaller than that in sample 8 after 18 days. This suggests that the devitrification of the latter sample was somewhat further advanced than that of the former. For the shell the minimum and maximum were, respectively, at 154° and 145° C for the upper tridymite effect, and the maximum for the lower effect was at 96° C; for the core the corresponding temperatures were 152°, 144°, and 96° C. The minima for the lower effect (if such existed) were submerged to some extent by the moisture effect, although in these particular tests this spurious effect could not have been large.

Finding from these tests that the two parts of the sample were in almost identical stages of devitrification, the core was again treated at 750° C for 10 days and the shell at 800° C for 6 days. In neither case did the heating and cooling tests indicate a definite effect near 150° C, although there was a trace of a small broad effect between 150° and 120° C in the cooling, and within a slightly higher range in the heating curves. Apparently the portion treated at the lower temperature now lagged somewhat in its stage of devitrification since it was noted that its tridymite effect (that obtained near 100° C by cooling) was broader and less pronounced than that of the portion treated at 800° C. In the latter case the effect indicated a stage between that represented by curve 2, figure 3, and that by the curve for sample 8 after 30 days of treatment at 800° C (fig. 6). The maxima for this effect now fell at 92° and 94° C, respectively, for shell and core. The tests were not carried into the quartz range.

In comparing these samples under the microscope after the second treatment no perceptible difference was noted in the degree of crystalline development. The material of the shell, for example, consisted of tridymite, glass, and quartz. Quartz was present in small amounts, but the crystals were fairly large (20 to 30 microns in length) and had well developed faces. The tridymite crystals generally appeared as flat plates in random orientation, but these plates sometimes appeared to be so joined as to form the semblance of wedge-shaped twins.

SAMPLE 6

This sample was treated six successive times at 900° C and was tested after each treatment. The treating periods totaled 1, 2, 4, 9, 51, and 251 days for the respective tests in the series. Heating and cooling curves after the first day of treatment (when the crystal concentration was much greater near the surface than in the core) showed large inversion effects with corresponding minima and maxima at 201° and 192° C, respectively. No indications of other effects were

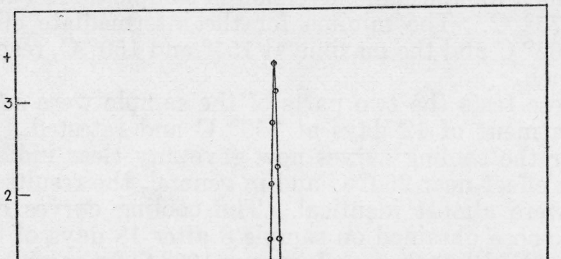

FIGURE 5.—*Cristobalite inversion effect with satellite.*

Cooling curve obtained on sample 6 after 1 day at 900° C.

present except that the cooling curve definitely indicated a satellite[11] on the high-temperature side of the high-low inversion effect (fig. 5). The heating curves gave no evidence of a corresponding satellite, but this may be explained on the assumption that a large heat effect closely followed by a much smaller one usually masks the latter completely. It will also be noted that the values obtained here for the temperatures of the cristobalite effects are lower than those obtained on either sample 2 or 3. It seems unlikely that these differences in position are a matter of uncertainty in the determinations because all duplicate tests indicated that the maximum deviation should not exceed ±2.0° C when the effects are (as they were in these cases) nearly the same in magnitude. Consequently, it no longer appears that increasing the developing temperature in this range (below 1,000° C) necessarily raises the cristobalite inversion point.

After the second day of treatment a cooling curve only was procured, and it indicated a still larger exothermic effect with a maximum at 195° C. There was no evidence of other effects except that the satellite, which apparently had also grown in magnitude, had practically merged with the main effect. It was estimated that the satellite, if it had not been followed by the larger effect, would have produced a maximum near 201° C.

The first cooling curve test after the fourth day of treatment yielded a maximum at 195° C and a definite hump on the high-temperature side still persisted; but a second test on another part of the sample gave an effect with a maximum at 198° C and a hump on the low-temperature side at approximately 192° C. These results point to the possibility that the sample contained two slightly different types of nonuniformly distributed crystalline materials. Both cooling tests indicated very small inversion effects with maxima between 160° and 150° C.

At the end of the ninth day of treatment the exothermic effect near 200° C was very small. There were, however, two additional effects, a small and rather indefinite one extending from 170° to 120° C with a maximum near 136° and a small but more definite one with a maximum near 88° C. Except that their magnitude was much smaller, these effects apparently corresponded closely to the devitrification stage represented by the curve in figure 6 for the 18-day treatment at 800° C. During this series of tests it was noted that treatments at temperatures well above 800° C never produced as large an upper tridymite effect (with a maximum near 150° C) as treatments of a proper duration at points below that temperature almost invariably produced.[12]

---

[11] Effects of this nature and the small effects which sometimes develop in the range between 170° and 190° C would presumably be ascribed to the influence of certain impurities by some investigators. R. Weil (Compt. rend. **183**, 753; 1926), for example, believed that the position of the inversion ranges of portions of certain cristobalite crystals which he studied was affected by the presence of impurities in the form of the oxides of the alkali and some other metals.

[12] Possibly this difference in the effects produced can be ascribed to the relatively excessive fluxing effect of the residual glass on the transformation of the intermediate stages at the higher temperatures. That is, under such conditions certain intermediate stages may transform into final or succeeding stages at almost the same rate as they develop from preceding or initial stages. In consequence, no great concentrations of crystals of such intermediate types appear. The persistence of crystals in the preceding (or final) cristobalite stage will not be so seriously affected by this fluxing effect because a relatively large concentration of cristobalite must develop, presumably, before the silica depletion is sufficient to cause the fluxing effect to become excessive.

The treatment of 51 days caused the effect near 200° C to disappear and practically erased the one or more effects between 170° and 120° C, but it developed very considerably the low-temperature effect which had now become quite sharp and definite with its maximum at 82° and its beginning just above 90° C. Increasing the treatment to 251 days did not materially alter the results except that it broadened and possibly increased slightly the height of the effect occurring below 100° C. Two cooling curves obtained on the same charge gave 82° and 85° C as the temperature of the maximum of this effect. In both cases it began at 100° and ended at 75° C.

When examined petrographically at this stage tridymite appeared to be the only crystalline constituent. The crystals were moderately large and wedge-shaped and interpenetration twins were common.

Following these treatments at 900° C the sample was treated twice at 950° C, and the total treating periods for the two tests following these treatments were 4 and 52 days. In neither case was there an indication of any effect above 100° C in the cooling curves, and the effect below that point was practically unchanged except that the maximum was raised to 88° C.

SAMPLE 7

The results from the cooling tests after a 9-day treatment of this sample at 900° C were, in general, similar to those obtained on the previous sample after the same period of treatment. That is, the cristobalite effect was practically nonexistent, there was a small effect with a maximum near 88° C, and an indefinite effect of small magnitude extending from 170° to 120° C, which, in this case, appeared to have maxima at 156° and 127° C. Corresponding to these, the heating curve possessed a minimum at about 145° C. As before, the results of both the heating and cooling curve tests indicated that the intermediate effects near 150° C were relatively much smaller after treatments near and above 900° C than they were after treatments near and below 800° C. On the other hand, the greatest magnitude ultimately attained by the effect occurring below 100° C in the cooling curves was practically the same after long treatments in either range. Assuming that the original samples were identical, this would indicate that the ultimate quantity of the crystalline phase which could be developed did not vary materially with the treating temperature for this range between 750° and 950° C. Naturally, this is based on the assumption that the rate of transformation from tridymite to quartz below 800° C was relatively quite low as compared with that from cristobalite to tridymite.

After a total of 22 days at 900° C, a cooling curve on this sample indicated no effects above 100° C. The lower inversion effect of the cooling tridymite began at this point, was relatively broad, and reached a maximum at 86° C. At this stage the material was examined petrographically in both powder form and in thin section. Under crossed nicols it was found to be faintly birefringent, and areas with the same extinction position (representing presumably sections of single crystals) were elongate in shape with very poorly defined limits. More sharply defined needles were scattered through this cloudy material, and they, together with the less well defined areas, had a negative character of elongation. No wedge-shaped twins were positively identified, but it was impossible to determine the exact character and shape of indefinite birefringent areas.

SAMPLE 8

The tests so far described were undertaken chiefly to ascertain the results of changing the treating temperature. These results indicate that for this glass 800° C is a favorable treating temperature for following the course of the changes in the "prompt" inversions from the time of the development of cristobalite until quartz becomes predominant. In consequence, this sample was subjected to a series of treatments at that temperature, and cooling curves (and occasionally heating curves) were obtained when the duration of the series of heat treatments totaled 3, 6, 9, 12, 18, 30, 55, 116, and 313 days. The

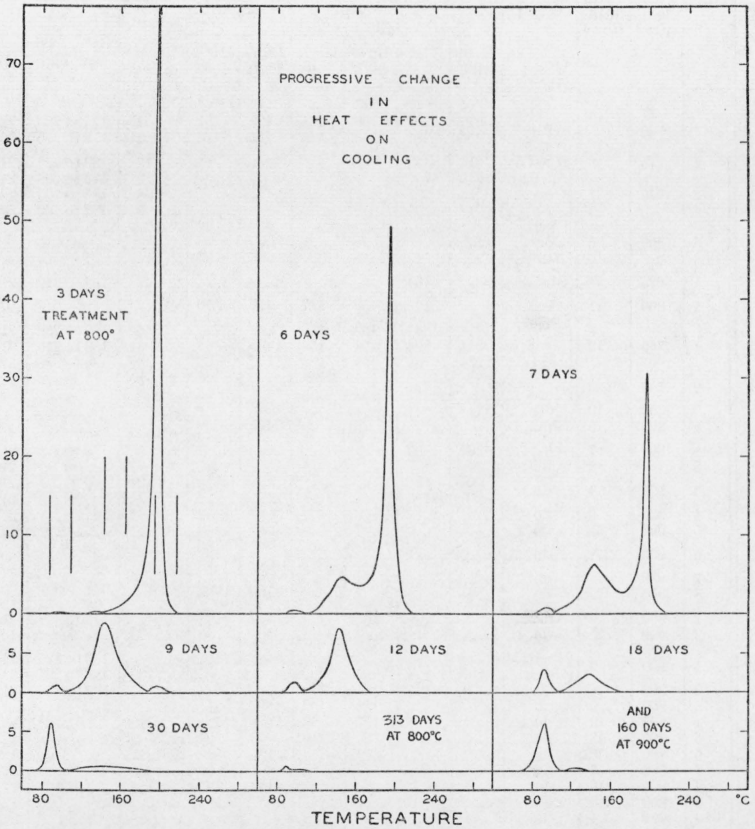

FIGURE 6.—*Progressive changes in exothermic effects as duration of devitrifying treatments increased.*

Only those portions of the cooling curves are presented which were affected by inversions occurring below 300° C. The procedure followed in procuring these portions was equivalent to the subtraction of curve *A′* from curve *B′* in figure 1. The three pairs of vertical lines in the first section show the approximate limits of the ranges within which the maxima of the three major effects usually occurred. At its greatest magnitude the intermediate heat effect is relatively indefinite since it covers a rather broad range in comparison to its height. It will be noted that the last effect to appear after the treatment at 900° C is about 50 percent greater than the similar effect after 30 days at 800° C, although the heights are almost the same in terms of double galvanometer deflections.

cooling curves obtained after the first six and the ninth total periods are represented in figure 6, and the indicated inversion temperatures are presented in table 1. These are difference curves procured by subtracting the ordinates of curves obtained on the untreated glass from those obtained on the treated glass; that is, a similar curve would have been obtained if the differences between the ordinates of curves *A′* and *B′*, figure 1, had been plotted. The curve for a treatment of

TABLE 1.—*Cristobalite and tridymite inversions* [a]

Sample No.	Test No.[b]	Treatment		Portion of sample tested	Indicated inversion temperature						Approximate relative height of cristobalite high-low effects	Approximate range of cristobalite effects	
		Temperature[c]	Total duration[d]		Cristobalite		Tridymite						
							First		Second				
					Low-high	High-low	Low-high	High-low	Low-high	High-low		Low-high	High-low
		°C	Days		°C	°C	°C	°C	°C	°C		°C	°C
1	1	725	25	All	210	201	160	145	[e] 120	101	2½	175 to 260	220 to 175
					209	201	160	146	120	100	2½	175 to 260	220 to 175
2	1	675	18	Shell	214	199	------	------	------	------	12	180 to 250	217 to 180
	2	675	37	Shell	216	200	------	------	------	------	9	175 to 250	217 to 180
				Core	218	201	------	------	------	------	8	185 to 260	220 to 180
				do	217	201	------	------	------	------	9	182 to 260	220 to 178
	3	800	6	Shell	------	------	------	------	(g)	92	------	------	------
				Core	------	------	------	------	(g)	95	------	------	------
				do	------	------	------	------	(g)	95	------	------	------
3	1	625	33	Shell	207	194	------	------	------	------	7	182 to 240	212 to 170
4	1	800	11	All	------	------	152	144	[e] 120	99	------	------	------
5	1	750	10	Shell	214	201	162	150	------	------	6	180 to 260	216 to 176
				Core	214	204	164	155	------	------	6	180 to 260	216 to 175
				do	214	202	164	155	------	------	6	180 to 250	220 to 176
	2	750	22	Shell	------	------	154	145	110	96	------	------	------
				Core	------	------	152	144	110	96	------	------	------
	3	750	10	Core	------	------	------	------	(g)	94	------	------	------
	3′	800	6	Shell	------	------	------	------	105	92	------	------	------
6	1	900	1	All	201	192	------	------			5	170 to 228	212 to 174
	2	900	2	do	(g)	195	------	------	------	------	7½	(g)	212 to 176
	3	900	4	do	(g)	195	------	------	------	------	2	(g)	210 to 178
					(g)	198	------	------	------	------	3½	(g)	212 to 174
	4	900	9	do	------	------	(g)	136	(g)	88	------	------	------
	5	900	51	do	------	------	------	------	(g)	82	------	------	------
	6	900	251	do	------	------	------	------	109	82	------	------	------
									(g)	85	------	------	------
	7	950	4	do	------	------	------	------	(g)	88	------	------	------
	8	950	52	do	------	------	------	------	109	88	------	------	------
7	1	900	9	All	------	------	145	127	------	------	------	------	------
	2	900	22	do	------	------	------	------	(g)	86	------	------	------
8	1	800	3	Shell	208	198	------	------	------	------	7	180 to 225	214 to 176
				Core	207	198	------	------	------	------	3	186 to 225	214 to 182
	2	800	6	All	201	194	155	145	------	------	4	175 to 225	213 to 174
	3	800	9	do	------	------	155	143	------	------	------	------	------
	4	800	12	do	------	------	152	143	------	------	------	------	------
	5	800	18	do	------	------	(g)	140	(g)	94	------	------	------
	6	800	30	do	------	------	------	------	107	89	------	------	------
	7	800	55	do	------	------	------	------	107	90	------	------	------
	8	800	116	do	------	------	------	------	109	91	------	------	------
	[f] 9	800	313	do	------	------	------	------	------	------	------	------	------
	[f] 10	900	4	do	------	------	------	------	------	------	------	------	------
	11	900	59	do	------	------	------	------	114	92	------	------	------
	12	900	160	do	------	------	------	------	114	93	------	------	------
8′	1	800	7	All	205	197	155	143	------	------	2½	184 to 228	214 to 180

---

[a] The more prominently indicated inversion points found in the glass samples devitrified during this investigation.

[b] Test numbers also signify the number of treatments received previous to test.

[c] After each treatment the samples were cooled to room temperature and prepared for test. Consequently, a sample was whole only during the first treatment.

[d] The duration of the second and all additional treatments at a given temperature is shown by the difference between the corresponding value tabulated and the next preceding for the same sample portion.

[e] Values uncertain because of added effect from vaporization of moisture.

[f] Quartz effects only were appreciable.

[g] Necessary heating curves not procured or effects were of doubtful origin.

7 days was obtained on the companion sample of No. 8 and was introduced to fill a rather wide gap in the stages of the disappearance of the cristobalite effect. A close correspondence between these companions cannot be expected, however, because one was broken up after 3 days, while the other was whole during its entire treatment (7 days).

During the treatment of these samples quartz probably began to develop quite soon, but the quantity did not become sufficient to produce significant effects in either heating or cooling curves until approximately the 30th day of treatment. After 55 days the quartz-inversion effect (fig. 7) had nearly reached the magnitude of the cristobalite effect after 6 days and its height was approximately doubled and tripled after 116 and 313 days, respectively. For these last three periods of treatment its maxima in the cooling curves were between 570° and 572° C and its minima in the heating curves fell between 574° and 576° C.

The tridymite effect which has its maximum between 100° and 80° C still maintained approximately the same magnitude after the 55th day that it had had after the 30th, but after the 116th day it had noticeably diminished and after the 313th day it had almost disappeared, as shown in figure 6. There were no observable exothermic effects in the range between 120° and 300° C after any of the last three treating periods.

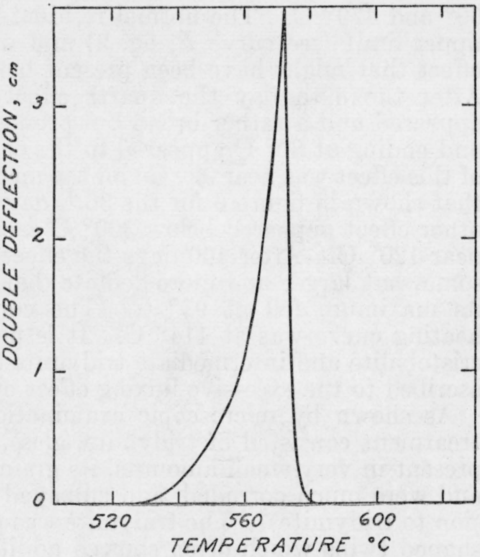

FIGURE 7.—*Quartz-inversion effect in cooling curve.*

At this stage (55th day of treatment) the effect in sample 8 was increasing very rapidly with duration of treatment, and after the treatment totaled 313 days at 800° C the height was tripled.

Examination with the microscope after the 3d day disclosed two fairly well defined internal zones of devitrification. The inner one centered on the axis of the cylinder and the outer one was about midway between the axis and periphery. The remainder of the glass was fairly clear. Most of the crystalline material occurred as minute rounded and faintly birefringent particles which were arranged along lines radiating from centers. This material which occurred in the characteristic habit of cristobalite was so interspersed with glass that no good determinations of the refractive index could be made, but it was in the vicinity of 1.48. A small amount of material was crystallized in roughly quadrangular forms. Possibly this was tridymite but no optical properties distinguishing it from cristobalite could be obtained.

After the 30th day, quartz was an abundant crystalline constituent, and although its crystal habit was difficult to determine, it apparently occurred as rhombohedrons with perhaps additional short prismatic faces. Tridymite was also relatively abundant and a number of wedge-shaped twins (more frequently the skeleton wedge-shaped forms) were present, but individual plates could also be observed. No cristobalite was identified. After the 313th day no tridymite or cristobalite was found and the crystalline material appeared to be entirely quartz.

Since quartz after these treatments was the only crystalline phase present in sufficient quantity to register very appreciable effects in heating and cooling curves or to be observed petrographically, the sample was now treated at 900° C in order to change this phase ultimately to tridymite, and curves were procured after the 4th, 59th, and 160th day of treatment. The first of these reduced the quartz effect very materially but developed no effects in the range between 60° and 470° C. The normal residual glass effect appeared at this upper limit (see curve *B*, fig. 2) and would have masked any small effect that might have been present between that point and 520° C. After the 59th day the quartz effect had almost completely disappeared and a rather broad but pronounced effect beginning at 116° and ending at 80° C appeared in the cooling curves. The maximum of this effect was near 92° C and the magnitude was almost as great as that shown in figure 6 for the 30th day of treatment at 800° C. No other effect appeared below 300° C except possibly a very small one near 120° C. After 160 days the effect between 116° and 80° C was somewhat larger and more definite than it was after the 59th day and its maximum fell at 93° C. The corresponding minimum in the heating curve was at 114° C. It is possible that the failure of the cristobalite and intermediate tridymite effects to appear can again be ascribed to the excessive fluxing effect of the residual glass.

As shown by microscopic examination, the sample after the last treatment consisted of tridymite, glass, and quartz. The latter was present in very small amounts, its grains showed no crystalline faces, and were much corroded, and embayed (possibly owing to the inversion to tridymite). The tridymite was present very largely as wedge-shaped twins which often showed additional polysynthetic twinning. The composition planes of the polysynthetic twins were apparently parallel to the edges of the wedge-shaped crystals.

The following results were obtained on materials that contained crystalline silica and were gathered from various sources. These results are presented for comparison with those described above.

SAMPLE *A*

This sample, developed from fused quartz under unknown conditions, contained a high percentage of cristobalite. Being fine powder, it was not so suitable for heating and cooling curve tests as the previously described samples containing much lower percentages of cristobalite. Only about 0.4 g could be used as a charge without increasing the volume that was ordinarily employed and considered rather large for satisfactory work. Nevertheless, the cristobalite inversion effects (curves *A* and *A′*, fig. 8) were relatively large with a maximum on cooling at 218° and a minimum at 260° C on heating. Both effects started at approximately 240° C. These large effects were respectively followed and preceded by small trailing effects which by some might be ascribed to final and initial adjustments which accompany the real inversion. No other indications of inversions were noted.

No tridymite could be seen when the material was examined petrographically. The cristobalite occurred as minute rounded pellet which showed a very low but easily perceptible birefringence. In many cristobalite samples this birefringence is not discernible.

SAMPLE *B*

This was reported to be a powdered flint treated 5 hours at 1,400° C, and its inversion effects were broad and about one-fourth as large as those of sample *A*. The effect on heating appeared to be more definite than that on cooling, because the latter seemingly approached the doublet form with the larger member on the low-temperature side. (Curves *B* and *B'*, fig. 8.) In the heating curve the inversion effect began at approximately 210° and the curve minimum fell at 236° C. In the cooling curve it began at 260° and the curve maximum fell at 222° C with a possible secondary near 240° C. No other inversion effects were observed below the quartz range.

As shown by microscopic examination, the sample was composed largely of quartz but also contained some cristobalite which was usually on the borders of the quartz grains. The refractive index of the cristobalite was just above 1.48 but there was no perceptible birefringence. No tridymite could be identified.

SAMPLE *C*

This sample was reported to be silicic acid treated for 5 hours at 1,400°. It had an even finer texture than samples *A* and *B*. The inversion effects were again broad and had about the same magnitude as those of sample B, but unlike them, the effect on cooling was more definite than that on heating because the latter had a slight likeness of a doublet. On heating, the effect began at about 160°, the curve minimum was reached at 220° C, and

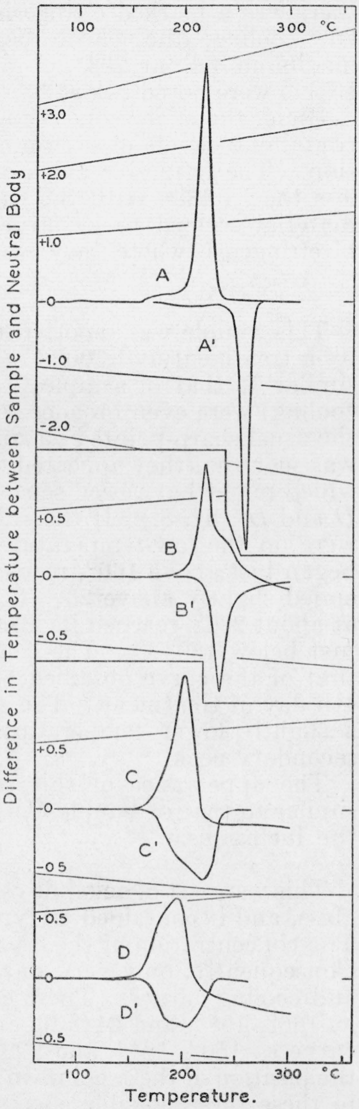

FIGURE 8.—*Inversion effects of various silica materials.*

The original ordinates, double galvanometer deflections, have been transformed into the corresponding temperature differences in order to give a suggestion of the relative temperature change developed during the inversions. The indicated temperature differences are approximately correct at 100° and 300° C where the necessary factors for the transformations were experimentally determined. Elsewhere, the ordinates are also within the probable error of the determinations, although the relation between the deflections and temperature differences is nonlinear, particularly in this range. The primed and unprimed letters indicate heating and cooling curves respectively. Only those portions of the curves near the effects are shown. Some of the curves show peculiarities which possibly signify an approaching transformation of cristobalite into tridymite.

there was a marked change in curvature as 200° C was approached. On cooling, the effect began just above 220° and the curve maximum fell at 203° C. (Curves *C* and *C′*, fig. 8.) No other effects were noted below 300° C.

Under the microscope the material seemed to be composed of grains containing clouds of very minute inclusions which obscured observation. The refractive index of these inclusions or particles was much less than 1.48. With the exception of these low-index particles the material seemed to be structureless, and it showed no perceptible birefringence where they were absent.

SAMPLE *D*

This sample was reported to have been developed from silicic acid by a treatment at 1,300° C for an unspecified time. Its texture was similar to that of sample C, but its inversion effects (especially on cooling) were even broader with blunted tops and bottoms instead of the usual sharp-pointed maxima and minima. In fact, their character was such that they appeared to be made up of two almost equal effects which might have been separated by approximately 20° C. (Curves *D* and *D′*, fig. 8.) If the effects were doublets the smaller members were on the low-temperature side. In the heating curve the effect began just above 160°, reached its greatest depth at about 204°, and ended slightly above 230° C. In the cooling curve the effect began at about 230°, reached its maximum at approximately 195°, and ended just below 150° C. The general appearance of curve *D* approached that of the curve obtained by the second test on sample 6 after the 4th day of treatment. The effect in *D*, however, was smaller, was in a slightly lower temperature range, and gave less indication of a secondary peak.

The appearance of this sample under the microscope was very similar to that of sample *C*, especially with regard to the character of the inclusions.

SAMPLE *E*

This was part of a nodule caused by the devitrification of a soda-lime glass, and it contained tridymite plates and considerable cristobalite. The concentration of the crystalline phases in the glass was very low. Consequently, only very small effects were obtainable in the heating and cooling curves. These consisted of minima in the heating curve at 166°, 198°, and 214° C, and corresponding maxima in the cooling curve at 150°, 184°, and 209° C. Tests on another charge changed the position of these points in no case by more than 2° C. In addition to these three possible effects, no others were indicated in the range from 80° to 300° C.

SAMPLE *F*

This was another specimen of a devitrified glass, but it came from a different and unknown source. It contained chiefly thin flat tridymite plates, but each plate was composed of a number of small tridymite individuals. (See reproduction of photomicrograph, fig. 9.) A large number of these individuals were twinned, either polysynthetically, in a wedgelike form, or both. The outer form of the wedge twins was never displayed. The concentration of the crystalline phase in the glass was again very low and the possible heat effects detected near 115° and 166° and near 150° and 80° C in the heating and cooling curves, respectively, were extremely small. A second cooling test confirmed the 150° and 80° C points.

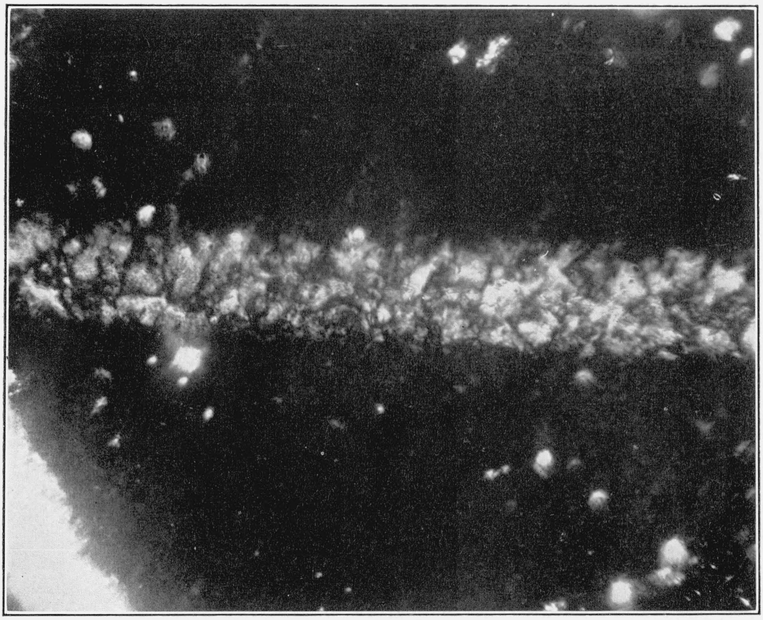

Figure 9.—*Reproduction of photomicrograph of tridymite crystal.*

Crossed nicols, magnification × 80. With unpolarized light this crystal from sample *F* appeared as a homogeneous plate.

SAMPLE G

This was a portion of a silica brick transformed by use and was composed largely of tridymite in the form of wedge-shaped twins. The nature of the sample was excellent for making heating and cooling-curve tests and there was only one significant effect in each curve. The effect in the cooling curve was relatively large and definite. It began at 110° and ended at 84° C. The curve maximum was at 98° C, while the minimum in the heating curve developed at 124° C. The effect in the heating curve was, however, not so clear-cut and there was some indication that it was followed by a small effect which extended to about 160° C. These temperatures for the maxima and minima are among the highest obtained for the low-temperature tridymite inversion effect during this investigation.

V. GENERAL COORDINATION AND POSSIBLE SIGNIFICANCE OF RESULTS

From the experience obtained in performing the various series of tests described above as representative examples of more numerous tests, it seems that the results may be coordinated as follows:

1. Borosilicate glasses with a relatively high silica content when held at treating temperatures near or within a considerable range below 800° C first develop a cristobalite that yields inversion effects at points usually somewhat above 200° C, both when heated and cooled. If the duration of the treatment is increased after these effects reach their maximum, they then decrease with a rapidity that depends on the treating temperature.
2. Increasing the duration of the heat treatments at these temperatures causes the temperatures, indicated respectively by the maxima and minima of the cristobalite effects in the cooling and heating curves, to shift over intervals which are greater than the probable error of determination.
3. Even before the cristobalite effects begin to decrease, tridymite plates appear in considerable numbers and small heat effects make their first appearance in the range between 190° and 150° C. Curve 1, figure 3, gives some evidence of one of the smaller effects noted in this range.
4. If the duration of the heat treatments is further increased, the number of plates multiplies rapidly and the small heat effects continue to grow into large but broad and rather indefinite tridymite effects, the maxima and minima of which usually indicate high-low and low-high inversion temperatures between 140° and 160° C. In the meantime, the cristobalite effects dwindle toward insignificance.
5. As these effects near 150° C approach their maximum size, wedge-shaped tridymite twins also begin to develop rapidly and a high-low inversion with its maximum usually somewhat below 100° C coincidently appears. The corresponding low-high effect with its minimum at a somewhat higher temperature is not so easily and consistently located, possibly because some remnants of the moisture effects supposedly associated with glass dust interfere, although such dust should now be eliminated by sintering. For another possibility see footnote 9.
6. Continuing the treatments causes the effects near 150° C to diminish steadily and also greatly reduces the number of plates, so

that they are few in comparison to the number of twins. At the same time, the tridymite effects near 100° C grow rather rapidly and become so definite in comparison to the earlier and much larger effects near 150° C that the maximum of the high-low and the minimum of the low-high inversion can be easily and precisely located. These effects and also those near 150° C shift their positions, however, as the duration of the treatments increases.

7. Still longer treatments practically eliminate the tridymite plates and almost completely destroy the tridymite effects near 150° C, leaving only very small seeming remnants of those effects near 120° and 140° C in the heating and cooling curves, respectively. (The 30-day treatment brought sample 8 into about the middle of this stage.) There are, therefore, at this stage no really manifest inversion effects from these points to approximately 570° C where the quartz effects have now begun to grow with relative rapidity. As the duration of the treatments of various samples is increased, the indicated temperatures of the effects near 150° and also of those near 100° C shift about over ranges which appear to be appreciably larger than should be expected in view of the estimated probable uncertainties of determination. The relatively narrow and consequently definite tridymite effects in the cooling curves occur almost wholly within the range between 80° and 100° C with maxima near 90° C, while the almost equally definite effects in the heating curves have minima near 110° C.

8. Greatly increasing the duration of the heat treatments almost completely removes the inversion effects near 100° C and transforms practically all of the wedge-shaped tridymite twins into quartz. The quartz now yields very large and definite effects with maxima and minima (in cooling and heating curves, respectively) between 570° and 576° C.

9. Subjecting the material at this stage to heat treatments at 900° C (as in the case of sample 8, for example) transforms the quartz with relative rapidity into wedge-shaped tridymite twins. The inversion effects near 100° C reappear with a greater magnitude than they had previously since they are now at least equally high (or deep) and definitely broader. The cristobalite effects apparently fail to develop, and the intermediate tridymite effects near 150° C, if present, are too small to be located with any certainty. (See paragraph 11 also.)

10. Treatments of the original glass at 900° C develop cristobalite as the first crystalline product, and its large definite inversion effects occur at temperatures which are at least as low as those usually obtained after treatments at lower temperatures.

11. The development of tridymite from the cristobalite at 900° C follows much the same course as in the case of treatments at 800° C or lower, except that the inversion effects near 150° C are usually no more than barely detectable. Consequently, they never reach that prominence they attain as a result of the treatments at lower temperatures. This difference in prominence must, it would seem, be ascribed to an increase at the higher temperature in the transformation rates of intermediate crystalline forms. Possibly the increased fluxing power of the residual glass at 900° C causes these rate increases almost entirely.

12. The effects near 100° C, when the original glass is treated at 900° C, ultimately become larger than those appearing at any time as a result of treatments at 800° C and lower; presumably, because tridymite becomes the end product as soon as 870° C is exceeded. (Also see paragraph 9 and fig. 6.) That is, the absence of any loss to quartz must more than offset the possible increase in the solubility of crystalline silica in the residual glass as the temperature rises through this range near 870° C.

13. Occasionally the inversion effects occurring near 200° C when the cristobalite is developed at 900° C or lower appear to be double or to cover unusually broad ranges (see last column, table 1). Similar conditions often develop in the tridymite inversion effects near 150° C and possibly to some extent in the more definite effects near 100° C.

It seems further that the significance of these results may be outlined as follows:

1. The results indicate that the shift in prominence from the tridymite effects near 150° C to those near 100° C is related to the change in crystal habit from plates to wedge-shaped twins. In any case it would seem that the "high-temperature" inversion effects are predominant only when the tridymite is "young" and that they are displaced in this role by the "low-temperature" effects as the material becomes more "mature" (age being measured in terms of the duration of treatment and the effectiveness of the other conditions which enter into the development of the crystals).

2. The above suggests that there are at least two kinds of low tridymite which may exist normally at room temperatures, and that each kind has a rapid inversion range in which it transforms to a high form that has no rapid inversions at still higher temperatures. That is, it appears that these high forms can only change into other high forms through very sluggish transformations which probably occur in most cases at relatively high temperatures as compared with those of the rapid inversions. Verification of this would signify that a sample is a composite of two kinds of tridymite whenever (as is usual) both of the established inversions occur in it.

3. If two such low temperature types of tridymite exist, the high form of the one inverting near 150° C is not an end product at treating temperatures between 870° and 950° C. Whether it is such a product at higher temperatures may also be doubtful.

4. If both inversions, the one near 150° and that near 100° C, should ever be found in what appeared to be a single crystal, such a crystal, as well as the whole sample, would then assume the character of a composite. In that case it would seem that similar conditions might appear in cristobalite or in any other silica crystals if a sluggish transformation has caused only a partial change from one form of crystal to another. Presumably, such composites would resemble some of those crystals in which multiple inversions were investigated optically by Weil. (See footnote 11, page 755.)

5. If close association of two or more forms within the same crystal should influence the inversion characteristics of the forms, it may well be that this influence in the suspected composites would be the cause of minor shifts such as were observed in the indicated inversion temperatures of many of the samples and which were often larger than the estimated errors in locating such temperatures. This possibility, if

established, would also explain some of the wide divergences in the published results of other investigators for the various inversion points. Moreover, it should throw some light on the cause of the rather large temperature hysteresis effects which have been observed in certain cases.

VI. INCIDENTAL DISCUSSION

Certain of the variations in the results outlined in the preceding sections can no doubt be ascribed to two kinds of inhomogeneity in the original material. The most evident of these inhomogeneous conditions caused the devitrification to develop and to proceed through the mass in more or less well defined waves. These waves corresponded to the crystal growths in various portions of the glass sample that were differentiated by the cords or striae contained.

The other condition, which also can be considered as a type of inhomogeneity, existed at the air-glass surfaces, and it usually so hastened devitrification there that it was often more potent than any of the cords in causing an early wave of crystal development. Moreover, this potency was greatly enhanced and other complications were probably introduced whenever the glass was broken up. Such a multiplication of the air-glass surface was introduced whenever a sample was prepared by crushing, and the sample was always crushed for the test made between the first and second of a series of treatments. As a result of the fragmentation the second treatment probably developed a relatively pronounced second wave of newly developed crystals which followed the older crystals of the first treatment through the various transformations. When the lag was sufficient, these waves probably remained more or less distinct even after the development of tridymite and the practical disappearance of cristobalite.

To a certain degree these inhomogeneities and the resultant waves of devitrification may account for the lack of definiteness in some of the heat effects of inversion and for the occasional satellites of these effects. This possibility requires, however, that the indicated inversion temperatures (of cristobalite, for instance) changed either with the duration of treatment at the temperatures employed or with the position of the crystals in the sample. In either case it would seem that the changes in the indicated inversion temperatures were caused by the same factors that influence growth and sluggish transformations of the crystals. Consequently, it appears logical to suppose that both inversion temperature and temperature hysteresis change as the crystals grow or proceed through some sluggish transformation which is induced by continued heat treatment. Since the treating temperatures were all below the cristobalite stability range in the heat treatments described above, the cristobalite-tridymite transformation was probably proceeding continuously from the appearance and until the disappearance of the cristobalite. At such treating temperatures there is, however, the possibility that other transformations or changes also develop and affect the inversion characteristics. These changes may or may not have something of the nature of those postulated by Sosman[13] in seeking an explanation for the apparent decrease in the inversion temperatures of cristobalite as its formation temperature is reduced.

---

[13] The Properties of Silica. Page 259 (1927).

According to Sosman's hypothesis the proportion of oxygen atoms in undefined or haphazard positions increases and decreases with the treating (or formation) temperature of the cristobalite. It is then further postulated that the inversion temperature of the crystals increases and decreases with the relative number of such haphazard atoms. To account for still other peculiarities of the crystals he also postulates that there is a certain type of heterogeneity in the structure of cristobalite. Granting these highly speculative possibilities, it seems reasonable to suspect that the relative number of haphazard atoms and the degree of heterogeneity are to some extent not only coordinate but related; or at least, that they are both affected by practically the same factors. At any rate uniformity in the proportion of such atoms should scarcely be expected to exist throughout even a single crystal. Any lack of such uniformity would of itself constitute heterogeneity. Moreover, it would seem that a heterogeneity of whatever nature should affect the inversion temperature.

If changes developed in the proportion of haphazard atoms by treatments at high temperatures are to affect the inversion temperatures, it is necessary that the proportion established by any treatment shall be susceptible to preservation during a cooling of the material to the inversion points or lower. Presumably this preservation is accomplished by cooling through the higher temperature ranges at comparatively rapid rates. As a matter of fact, however, a drastic rate does not seem to be required anywhere except possibly within the cristobalite range. This, at least, is the impression one would gain from certain of Fenner's experiments. The susceptibility to preservation suggests that the changes in the relative number of haphazard atoms must have the nature of sluggish transformations.

It is possible therefore that at most temperatures the duration of treatment is, along with the temperature of treatment, a real factor in determining the inversion temperature of the resulting cristobalite crystals. It may as a matter of fact be the more important of the two. At least, it may easily be so when the treating temperature is below the cristobalite range, and, especially, when the condition of the material is such that all transformations develop slowly. That is, the duration of treatment required to develop any condition may be considered as always depending on the nature of the silica material as well as on its temperature. In view of the nature of the material and of the treatments employed, this consideration of the experimental factors which may determine the inversion temperature of cristobalite suggests that the variations observed in the cristobalite inversions—as noted at various points in the previous discussion—are to be expected since undoubtedly the age of the crystals even in a single sample varied greatly. It also corroborates the belief that the obvious inhomogeneities of the original glass and the consequent waves of devitrification may account for the satellites of some of the inversion effects. Furthermore, variations in the effective duration of treatment becomes a possible explanation for the occasional marked deviations in Fenner's[14] data from the general trend on which the dependence of the inversion temperature on that of formation or treatment is chiefly based.

---

[14] Am. J. Sci. 36, 369 (1913). Some of the inversion temperatures deviate from 5° to 30° C from any curve which might reasonably represent the supposed dependence of these temperatures on those of formation or treatment.

In the formation and treatment of crystals there are two possibilities which should be considered. That is, the crystals may be formed and treated at the same or at different temperatures. In the latter case, treatment will produce a change in the relative number of haphazard atoms if the hypothesis fits the actual conditions. In the other case, however, it may be a matter of uncertainty as to whether or not any such change takes place. The proportion of such atoms and the degree of heterogeneity corresponding to the formation temperature may be attained immediately at incipiency and remain unchanged throughout the growth and any further treatment of the crystal at that temperature. As a matter of conjecture, it seems more likely, however, that the conditions in incipient crystals are, regardless of the temperature, much the same unless there are two or more kinds of high cristobalite. Even in that event the incipient form would usually be the same if the usual course of the transformations of crystalline silica when heated is followed. Conceding that the incipient condition is independent of the formation temperature and that the condition corresponding to that temperature is gradually developed, it follows that the mass of crystals in a sample at any intermediate stage of devitrification would represent a wide range of development stages and a correspondingly broad interval of inversion temperatures. This may account for the rather peculiar effects of samples *B*, *C*, and *D* in figure 8.

At this point it should be noted that Greig[15] has reported that the heat effects of inversion in certain samples containing cristobalite did not develop sharply at any temperature when the samples were cooled through the inversion range. He also observed that many of the small crystals, when mechanically attached to the surrounding glass, failed to invert and consequently reached atmospheric temperatures in the high form. Other investigators have also reported observations which suggest that in certain cases the cristobalite inversions may be very lethargic and that such persistence of the high form is not uncommon. There is no doubt some similarity between such observations and certain of those presented in the previous pages. These observations include the broad inversion ranges, the variability of the indicated inversion temperature, marked temperature hysteresis, and certain peculiarities noted in the cristobalite crystals when the samples were examined microscopically.

If the chief cause of the lethargy of inversion lies in the surrounding or attached materials, it seems obvious that the incipient or very small crystals would be most affected, especially since they should be the least capable of breaking away from those materials. Such a crystal with its attached material may be considered as a very heterogeneous structure. A structure of this sort may well be incapable of inverting sharply at a definite temperature and any delay in the inversion should depend on the degree of heterogeneity. Since there is in the usual artificially prepared sample a great variety of crystal sizes and degrees of attachment it follows that the inversion ranges should be correspondingly broad. Obviously, the attached material may be crystalline as well as glassy. Consequently, this broadening of inversion effects should appear whenever any transformation is only partially accomplished. To what extent the restraint exerted by

---

[15] J. W. Greig, Am. J. Sci. **13**, 40 (1927); J. Am. Chem. Soc. **54**, 2846 (1932).

attached materials on the inversions of small newly developed crystals is mechanical (as has been suggested) is, however, a matter for further consideration.

Whatever may be the nature of the changes which cause the variations in the inversion effects of cristobalite, it seems possible that the development of tridymite also includes changes of a somewhat similar nature since it was noted that within certain limited temperature ranges its inversion points also appeared to be variable especially when either the treating temperature or period was changed. At least two distinct tridymite inversion ranges [16] are known to exist and these may be considered as centering on 150° and 100° C when both the low-high and high-low effects are considered. As stated before, the sequential appearance (and disappearance) of the effects in these two ranges as the treatments were prolonged leads to the possibility that each inversion range belongs to a more or less distinct crystalline type that has but two modifications (high and low). Of these types only the one inverting in the vicinity of 100° C appears to possess a high modification that is stable in the lower part of the tridymite stability range. Whether the high modifications of the possible two or more tridymite types divide this range between them will require further study since it may well be that the types appearing first and inverting at the higher temperatures are never really stable.

The indication that there is a sluggish development of one tridymite from another suggests that this transformation is the source of the suspected heterogeneity of tridymite crystals. Even so, this heterogeneity might have something of the nature of that postulated by Sosman, or of that suggested as a possibility by Fenner who, in discussing the significance of his results took cognizance of Smits' theory of allotropy in this connection. This idea that sluggish transformations cause the possible tridymite heterogeneity suggests further, however, that any apparently individual tridymite crystal can be considered as a more or less heterogeneous and intimate mixture of decadent (or disappearing) and of immature (or developing) forms which are unevenly distributed throughout not only the sample as a whole but also the seemingly individual component crystals.

Certain parts of any such mixed crystal should, however, be relatively homogeneous in their structure and, consequently, each of these probably resembles rather closely in its structure some one of the various crystalline forms entering into the series of transformations undergone by the crystal as a whole. In that case these fragmentary parts are presumably cemented together by layers of less homogeneous material which has its disorganized and more or less haphazard structure because all of the various intermediate stages of the transformations are represented in it. Granting the existence of such composites, it seems probable that the very different but more homogeneous parts exert through this cementing layer considerable mutual influence upon their individual inversion characteristics.

On the basis of this mixture hypothesis several relatively large inversion effects appearing at points separated by more or less definite temperature intervals would show the presence of a corresponding

---

[16] It will be presumed for the time being that only these two particular inversion ranges are involved although some indication of another range centering on approximately 130° C was noted. Furthermore, another possible range near 440° C has been reported by Travers and Goloubinoff, Rev. Metall. **23**, 27, 100 (1926).

number of distinct and rather persistent crystalline types within the sample. Minor variations in the inversion temperatures from their normal position and any exceptional broadening of the inversion effects would be the result of a mutual influence exerted by the various types within composite crystals upon the inversions of the components. Presumably, such variations would be relatively insignificant in the case of very predominant types having large inversion effects, but these variations should increase if the predominance of the type waned as the sluggish transformations continued. Masses of heterogeneous crystals containing a predominant type with inversions that are easily influenced should, if all possible degrees of heterogeneity are present, yield rather broad inversion effects such as those of tridymite near 150° C. Exceptional broadening of this nature may cause the observable effects to be unexpectedly small in many cases, just as they were in sample F for instance.

Experience with these materials would seem to show that crystals or crystalline fragments must ordinarily be exceedingly small before their inversions can be materially modified by the nature of their surroundings. Conceivably, however, the inversions in composites made up of closely associated fragments may be materially modified by such association if the fragments do not too greatly exceed the submicroscopic scale. Moreover, the fragments may not possess the uniformity of structure suggested by their appearance, and elements of the transition layers may permeate them to some extent. The crystal shown in figure 9 may be an example of such a composite of tridymites if elements of the plate structure still persist in the transition layers or elsewhere. Presumably, the transformation in this crystal is well advanced, but in the beginning of a transformation the heterogeneous regions may be even less obvious and constitute little more than a film over the surface of an otherwise perfectly uniform crystal.

Composites with modified inversions may also be formed during the cristobalite to tridymite transformation. Possibly the crystals studied by Weil [17] possessed a heterogeneity of this kind, although he ascribed the observed differences in the inversion ranges of various portions of the same crystal to the effect of impurities. With respect to such effects from impurities, the results of Fenner's experiments [18] testing this point indicate that cristobalite from specially purified silica yields practically the same variations in its inversions as does cristobalite from melts containing considerable impurities or flux.

Obviously, the development of the original crystalline growth and of any other later sluggish transformations must proceed much more slowly in relatively pure than in fluxed silica unless the developing temperatures for the purer material are considerably higher. Consequently, Weil [19] in subjecting cristobalite crystals to alkali vapors probably caused regions of incipient tridymite to develop very rapidly but only on the crystal surfaces during that time when the temperature was below the cristobalite range. Such an action would presumably cause inversion changes very similar to those he observed. This suggests that he may have been dealing with composite crystals of the type discussed in the previous paragraphs rather than with a direct effect of impurities on the inversions as he assumed.

---

[17] Compt. rend. **180**, 1949 (1925).
[18] Am. J. Sci. **36**, 363, 370 (1913).
[19] Compt. rend. **183**, 754 (1925).

Moreover, it is clear that the acid treatments which he later applied [20] should in most cases have removed any such possible incipient tridymite from the surfaces of the vapor-treated cristobalite almost as easily as it would have removed the film of alkaline glass that was undoubtedly formed. On account of this action the temperature of the inversion effects should have been raised by the acid treatment. In general, however, the acid treatment would fail in this action if the tridymite was more deeply embedded, since any dissolving away of probable surface films of glass would normally release only those tridymite structures that were on the surfaces. The development of deeply embedded structures would presumably require relatively long treatments and fairly large original cristobalite crystals. Some of the natural crystals with two inversion ranges did not entirely lose their apparent inhomogeneity on being subjected to the acid treatment. Weil ascribed this resistance to the protection which a deeper permeation into the crystals afforded the impurities. He apparently did not consider the possibility that the displaced inversion effects were caused by deep seated regions of incipient tridymite although some of the natural crystals which showed peculiar inversion effects were classed as tridymite.

If by any chance impurities were not the direct cause of the nonuniformity of the inversions of these crystals, it would seem that the evidences of heterogeneity actually observed by Weil in what appeared to be relatively large individual crystals may be as well explained on the basis of composite crystals of cristobalite and small portions of incipient tridymite as on any other. Moreover, some of the crystals classed as tridymite may have contained small amounts of decadent cristobalite especially when their inversion effects extended to comparatively high temperatures. Granting that the crystals were composites of this nature, his results on various individual crystals then give a much clearer insight as to the possible structure of such composites than can be obtained by experiments which require large masses of crystals where the masses presumably include crystals representing all of the possible stages of heterogeneity which may be developed during a sluggish transformation.

The possibility that decadent fragments of cristobalite may enter into tridymite composites and influence the tridymite inversions makes the comparative indefiniteness and the relatively great breadth of the inversion effect of that tridymite form which appears to be intermediate between cristobalite and the final tridymite even less surprising. This follows, since some of the crystals of this intermediate form will invert at abnormally low temperatures because of the influence of the final tridymite, while other crystals will invert at abnormally high temperatures because of the influence of cristobalite. Finally, there is a possibility that the medium which transmits this influence is made up of the silica threads or chains which are discussed by Sosman. That is, such chains may in many cases lead through several incomplete structures at certain times during the progress of any transformation or series of transformations. Between the more regular incomplete structures, the threads at such times would presumably be tangled and twisted to a considerable extent. This condition in some cases may actually approach that of silica glass. If

---

[20] Compt. rend. 183, 753 (1926).

this picture is at all representative of actual conditions, it seems, when the persistence usually ascribed to these chains is considered, that it may be along them that a structure exerts the influence which resists or abets the inversion of its intimate neighbors.

VII. SUMMARY

1. A series of tests was made for the purpose of following in a devitrifying glass the well-known series of transformations—noncrystalline silica to cristobalite to tridymite to quartz—which can be completed under proper conditions at temperatures below 870° C.

2. The devitrifying or transformation temperatures employed ranged from 625° to 950° C, and the material treated consisted of a high silica borosilicate glass which devitrified readily at temperatures above 750° C.

3. The devitrification products were studied mainly by procuring heating and cooling curves which extended over the whole temperature range of possible rapid inversions. In addition, several of the samples were examined microscopically, and X-ray patterns were also obtained occasionally.

4. The apparent inversion points of the cristobalite ranged from 201° to 218° on heating and from 192° to 240° C on cooling (as indicated by the endothermic and exothermic effects).

5. The points similarly determined for the upper inversion of the tridymite ranged from 145° to 164° C and from 127° to 155° C on heating and cooling, respectively.

6. The corresponding points for the lower inversion of the tridymite fell between 107° and 120° C and between 82° and 101° C.

7. The inversion points of the quartz as determined in the same way, all fell between 570° and 576° C, and it appears that much of this spread can be ascribed to the relatively high rates (approximately 5° C per minute) employed in this range both on heating and cooling.

8. The inversion effects in the upper tridymite range were usually broad and often indefinite, and they always disappeared completely soon after the effects in the lower inversion range of this material reached their maximum.

9. Ordinarily, the interval between the complete disappearance of the effects in the upper inversion range and the full growth of those in the lower range seemed to coincide with the period within which the tridymite crystals were transformed from plates to wedge-shaped twins.

10. Certain speculations concerning the significance of this coincidence and of the results, in general, are incorporated in a discussion.

WASHINGTON, July 1, 1938.