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TRIDYMITE-CRISTOBALITE RELATIONS AND STABLE SOLID SOLUTIONS

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ABSTRACT

Experiments in sealed platinum containers have been directed towards establishing the extent and stability of crystalline solutions in tridymite-M, tridymite-S and cristobalite, and lend unexpected support to the validity of the 1470° inversion in pure SiO_2. Fluxes not entering into crystalline solution in either tridymite or cristobalite cause tridymite to be formed below, and cristobalite above, $1470° \pm 30°$ C. Those forming crystalline solutions (Na+Al, Li+Al, and Ca+Al) cause a lowering of the inversion temperature. Similar experiments performed with quartz and tridymite suggest that the 870° inversion should not be hastily abandoned as a reconstructive transformation in SiO_2.

INTRODUCTION

Most published phase diagrams involving SiO_2 arbitrarily assign 1470° as the temperature for the tridymite-cristobalite inversion, although it is common knowledge that in a large number of systems cristobalite crystallizes from liquid within the so-called tridymite stability range. It has, in fact, been the contention of Flörke (1955, 1961) that tridymite is not really a phase in the system SiO_2, but that it depends on the presence of impurities for its existence. Tuttle and England (1955), however, demonstrated the formation of tridymite in the presence of no impurity other than water. Hill and Roy (1958a) established the existence of a unique stable tridymite phase in the system SiO_2, and they further pointed out the relationship between this and metastable forms of tridymite. In a parallel study, Hill and Roy (1958b) investigated chemically pure cristobalites and showed that highly ordered 3C cristobalite is only formed at high temperatures, and that the phase which is frequently formed within the tridymite stability range is a disordered cristobalite. The latter study showed also that the degree of order in the cristobalite structure is most easily detected by observing variation in the cristobalite inversion temperature.

Since the present work was first reported (Roy and Roy, 1959) studies have been made of the effect of various types of treatment, such as neutron bombardment (Krisement and Trömel, 1960), (Buhsmer and Roy, 1962), impurities (Trömel, 1959) and stress (Bogardus and Roy, 1962) on the cristobalite α-β inversion temperature. The present study attempts to test the validity of the 1470° tridymite-cristobalite inversion by studying in detail the effect of a number of additives, to make observations of the effect on the cristobalite α-β inversion temperature of components contained in crystalline solution, and to obtain similar data on the quartz-tridymite inversion.

Experimental Method

Binary mixtures were prepared using various forms of pure SiO_2 and in many cases sufficient "flux" component to produce 20–50% liquid phase. It is extremely important to note that we used the pre-formed *stable* crystalline phases (for the temperature range of study). Hence, any change in composition of the pure phase is a *certain* indication of the fact that the pure SiO_2phase is NOT the stable phase in the chosen temperature-composition environment. The same cannot, of course, be said if the starting material were a glass or other metastable (crystalline) phase, since the formation of a crystalline solid solution of tridymite or cristobalite is NOT then an indication of greater thermodynamic stability compared to the pure phase.

The starting materials used included the following highly purified forms:

Silica glass
Silicic acid
Quartz (Lake Toxaway, purified with HCl washing.)

Pure tridymite formed from Na_2WO_4 and silicic acid fusion, electrodialyzed: Spectrographic analysis:

MgO	0.003%	TiO_2	0.005	Na_2O, $K_2O<0.005$
Fe_2O_3	0.007%	CaO	<0.002	
Al_2O_3	0.007%	W	Trace	

Pure 3C cristobalite from silica glass prepared 8 hours at 1,600° C., analyzed as follows:

MgO	0.0006%	TiO_2	0.005
Fe_2O_3	0.003	CaO	<0.002
Al_2O_3	0.009	K_2O	<0.005

Binary additions to these various forms of silica of the following compositions:

1. $Na_2O\cdot 2SiO_2$ and $K_2O\cdot 4SiO_2$ glasses.
2. $LiAlO_2$, and $NaAlSiO_4$ and $KAlSi_3O_8$ glass.
3. Na_2WO_4, Li_2WO_4, and K_2WO_4.

In addition, gels of Li_2O, Na_2O or $K_2O+(Al_2O_3+SiO_2)$ prepared by method of Roy (1956) were used.

The samples were held in sealed Pt 20 Rh tubes or, where volatility was not a concern, in Pt envelopes, and heated for periods varying from one to twelve days. The products were examined on a Norelco wide range diffractometer using filtered Cu radiation for phase detection, and lattice spacings were measured precisely using slow scanning speeds and standardized with silicon. Some differential thermal analysis (DTA) patterns were also obtained to study the α-β cristobalite or the tridymite low-temperature inversions.

RESULTS

Three types of observations were made to obtain evidence on the tridymite-cristobalite inversion and the nature of the crystalline phases: 1) phase evidence, *i.e.*, presence or absence of tridymite or cristobalite after extended runs at a given temperature, 2) change in unit cell dimension, and 3) change in temperatures of metastable rapid transitions, *e.g.*, the α-β cristobalite inversion.

PHASE EVIDENCE FOR TRIDYMITE-CRISTOBALITE TRANSFORMATION

Examples of *x*-ray diffractometer traces on which identification of phases were made are given in Fig. 1. At the upper left, the principal tridymite-S (stable) and (3C-)cristobalite-O (ordered) peaks obtained at a slow scanning speed are superimposed, and more complete patterns obtained at higher speeds are given at the right. A mixed sample of 3C-cristobalite and tridymite-S at slow scanning speed showing optimum peak separation is given in the middle left. The lower left shows a mixture of crystalline solutions of tridymite and cristobalite, in which peak separation is adequate at slow scanning speeds. The same sample at fast speed, in which identification would be difficult, is shown in the lower middle, while the lower right shows much better separation obtained with a mixture of pure tridymite and cristobalite even at fast speeds.

Figure 2 summarizes some results obtained by reacting different forms of SiO_2 with a number of salt "fluxes" at various temperatures. These fluxes are such that it is difficult to propose a reasonable crystal chemical model by which the ions may be admitted into the structure in appreciable ($\sim$0.1–1.0%) amounts. The lower part of the diagram shows products of binary fluxes (which would not be expected to enter substantially into crystalline solution) reacted with tridymite, cristobalite, silica glass or quartz. In general, a constant inversion temperature of 1470 ± 30° C. is obtained, above which essentially all yield cristobalite, and below which they yield tridymite. An exception is Li_2WO_4 which favors cristobalite.

The upper part of the diagram summarizes results with the added components $Na^+ + Al^{3+}$, $Li^+ + Al^{3+}$, $K^+ + Al^{3+}$ and $Ca^{2+} + Al^{3+}$, which assemblages may, on crystal chemical grounds, be expected to enter the SiO_2 structures. Gels shown in the middle of the diagram having different

$Li_2O \cdot Al_2O_3:SiO_2$ and $Na_2O \cdot Al_2O_3:SiO_2$ ratios formed a cristobalite phase at all temperatures studied. Expanded cristobalite structures were formed as low as 1320° C. from $NaAlSiO_4$ and $CaAl_2O_4$ added to stable and metastable tridymite and 3C-cristobalite, indicating that the tridymite-cristobalite inversion is lowered by at least 150° by these substitutions. (Reaction was too sluggish at lower temperatures to produce definitive results below 1300° C.)

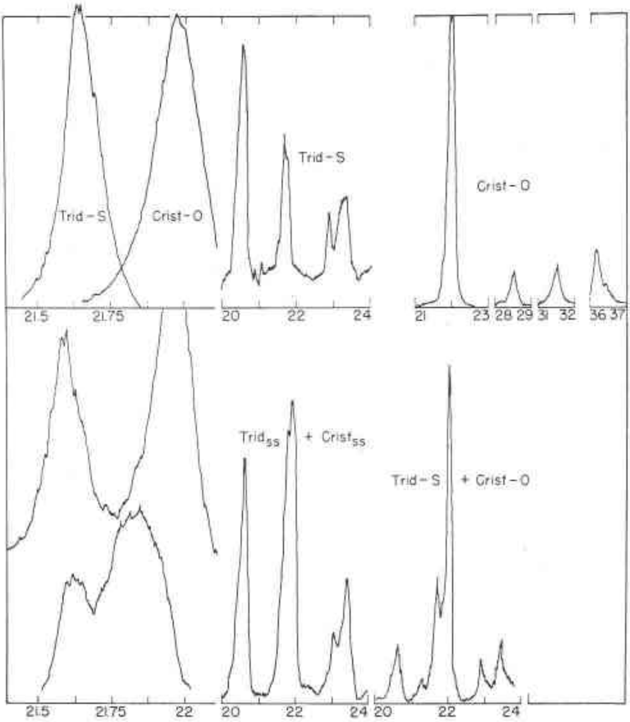

FIG. 1. X-ray diffractometer traces of typical tridymite and cristobalite phases using CuKα radiation. Upper left, slow scanning speed, superimposed patterns of stable tridymite and ordered cristobalite. Upper middle and upper right, same samples at fast speed. Middle left, mixture of trid-S and crist-O at slow speed showing adequate peak separation; lower left, mixture of solid solutions showing poorer separation. Lower middle and lower right, same two samples at fast speed.

K^+ and Al^{3+} added to tridymite, however, caused a slightly expanded tridymite structure to be formed as high as 1500° C., suggesting an increased stability range for tridymite. On addition of $K^+ + Al^{3+}$ to cristobalite, an expanded cristobalite was formed in the same temperature range. Both crystalline solutions obviously cannot be stable phases at the same temperatures; however, some suggestion of partial conversion of cristobalite to tridymite at lower temperatures was observed, suggesting that an increased range of tridymite stability is the correct interpretation.

Cell Dimension Measurements

The magnitude of change of lattice spacing on formation of cristobalite crystalline solutions (referred to pure cristobalite) is illustrated in Fig. 3, which gives a few measurements for $d_{(111)}$. All samples except those starting with tridymite were reacted at about 1400° C. Both $Na^+ + Al^{3+}$ and $K^+ + Al^{3+}$ substitution appear to reach a maximum by about 2 mole % $NaAlO_2$ (or $KAlO_2$), resulting in an increase in cell edge of about 0.3%. The gels produce what are, no doubt, metastable structures. The phases formed from tridymite have larger cell dimensions than those which started with 3C-cristobalite, suggesting a high degree of disorder

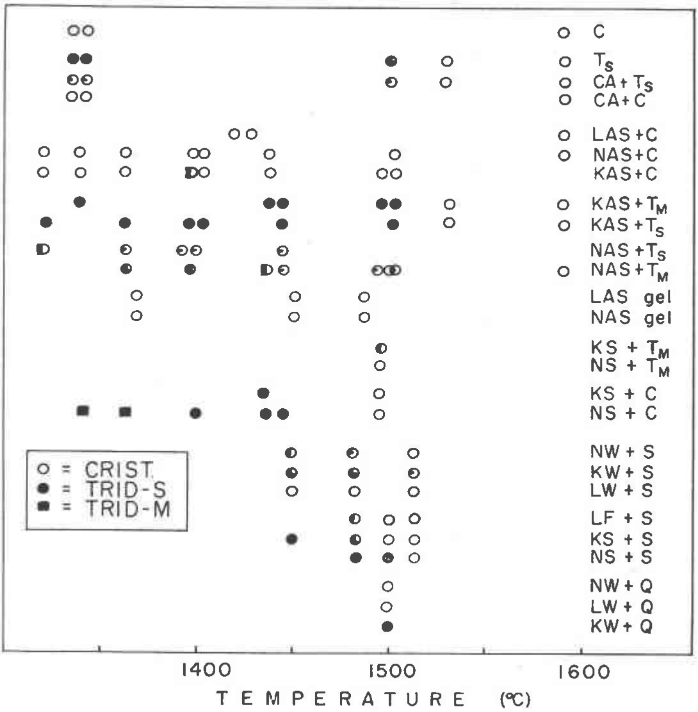

Fig. 2. Phases formed as a function of temperature by reaction of SiO_2 modifications with various fluxes. Abbreviations: C = 3-C cristobalite, T_s = stable tridymite, T_m = metastable tridymite, CA = $CaO\cdot Al_2O_3$, LAS = $Li_2O\cdot Al_2O_3$-SiO_2 mixtures, NAS = $NaAlSiO_4$ glass, KAS = $KAlSi_3O_8$ glass, KS = $K_2O\cdot 4SiO_2$ glass, NS = $Na_2O\cdot 2SiO_2$ glass, NW = Na_2WO_4, KW = K_2WO_4, LW = Li_2WO_4, S = SiO_2 glass, Q = quartz.

which should approach the stable equilibrium structure given sufficient time. The higher 2θ value of the two measurements given for 2% $NaAlO_2$ +tridymite was obtained at 1530° (*vs.* 1480° for the more expanded cell). Presumably, the difference is caused by the fact that the higher-temperature reaction product has more nearly attained equilibrium rather than to differences in equilibrium solubility at the two temperatures. For comparison, cristobalites (formed above 1470°) with $Na_2O \cdot 2SiO_2$, $K_2O \cdot 4SiO_2$, Li_2WO_4, K_2WO_4, Na_2WO_4 and LiF fluxes would have 2θ values of 21.96° or higher, indicating very little or no crystalline solution with these added components.

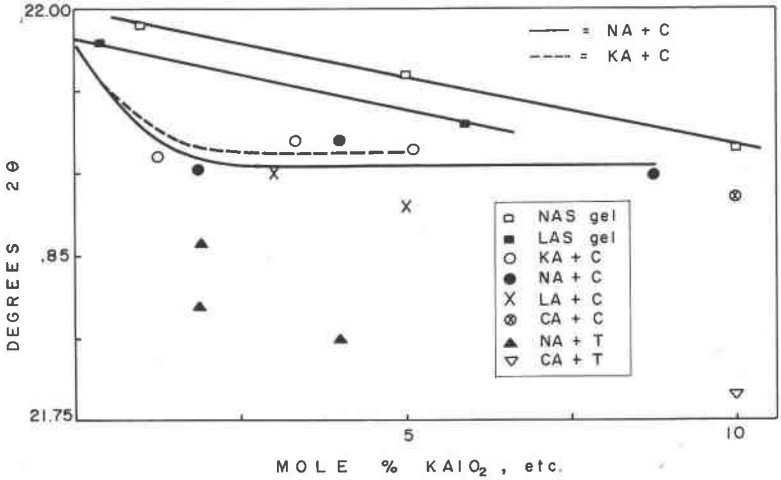

FIG. 3. *X*-ray spacings $d_{(111)}$ of cristobalite crystalline solutions using slow scanning speeds and CuKα radiation. Abbreviations same as Fig. 2.

Figure 4 shows representative measurements for tridymite samples using a variety of starting materials. Except for the two squares, all would be considered tridymite-S. The two exceptions are tridymite-M formed from Na_2WO_4 and $K_2WO_4 + SiO_2$ glass, and are therefore not comparable. Although there is much less variation between samples than with cristobalite, the values fall into two groups: 1) those from $K^+ + Al^{3+}$ which form slightly expanded structures with apparently some crystalline solution, and 2) the rest which show very little or no crystalline solution. Within each of the groups, a second trend toward slightly increasing crystalline solution with increasing temperature is observed.

Effect on high-low metastable inversions. Although the present investigation was principally concerned with the tridymite-cristobalite transformation, some observations were made of the effect of crystalline solution on the rapid high-low inversions. Table I gives some data on inversion temperatures obtained on various cristobalite samples, comparing the original cristobalite with the crystalline solutions.

In each case the incorporation of a second component in the structure results in a lowering of the α-β cristobalite inversion temperature. The well-known hysteresis effect—higher temperature on heating than cooling—which has been described by Hill and Roy (1958b) for pure cristobalites, is less pronounced with the crystalline solutions. In fact, the direc-

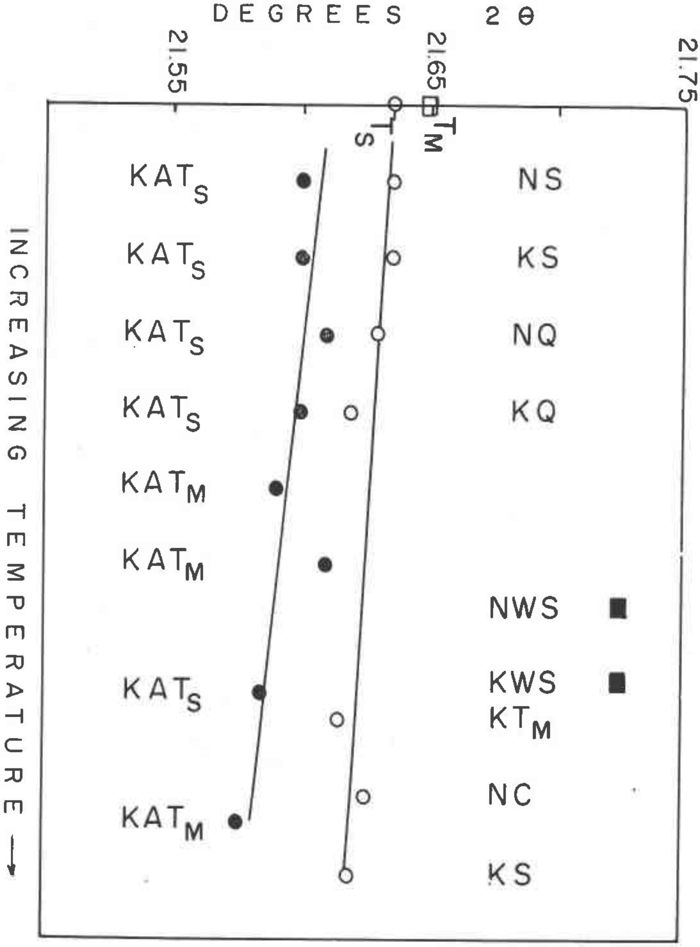

FIG. 4. X-ray spacings of tridymite samples using CuKα radiation. Solid circles correspond to compositions on left, open circles and squares to compositions on right. Abbreviations same as for Fig. 2.

TABLE I. INVERSION TEMPERATURES OF CRISTOBALITE CRYSTALLINE SOLUTIONS BY DTA

Sample No.	Composition	Preparation Conditions	Temp. of Heat Effects (°C)	
			Heating	Cooling
Crist-4	3C-cristobalite (pure)	SiO_2 glass 1550° 24 Hrs.	265	244
NAC-5 No. 25	3C-cristobalite +NA (66.7 mole % SiO_2) (33.3 mole % $NaAlSiO_4$)	1335° 6 days	231.5	228
CAC No. 1198	3C-cristobalite +CA (94 mole % SiO_2) (6 mole % $CaAl_2O_4$)	1340° 14 days	217	228
NAS No. 184	NAS gel (6 mole % $NaAlSiO_4$) (93.6 mole % SiO_2)	1340° 2 days	190	190
CAT No. 199	Electrodialyzed Tridymite $+CaAl_2O_4$ (91.5 mole % SiO_2) (8.5 mole % $CaAl_2O_4$)	1340° 14 days	170	186 (166)

tion of hysteresis is reversed in the sample formed from tridymite; this may be explained by a high degree of metastability.

A few tridymite samples were examined, but the results were inconclusive. Little variation in the DTA patterns was found, partly because the samples used were small and detail was limited because of the small size of the heat effect. However, in view of the relatively minor change in lattice constant of tridymite crystalline solutions relative to the pure phase less drastic effects are expected than those observed in cristobalite.

Quartz-tridymite inversion. Parallel experiments to those for the tridymite-cristobalite transformation were performed for the quartz-tridymite inversion, using quartz, tridymite, cristobalite and SiO_2 glass as starting materials. The results summarized in Fig. 5 give evidence to support the existence of a stable quartz-tridymite inversion at 870 ± 20° C. This is based on: 1) conversion of tridymite, cristobalite, or SiO_2 glass to quartz below this temperature by reacting with $Na_2O \cdot 2SiO_2$, Na_2WO_4, Li_2WO_4 or LiF; 2) conversion of quartz or SiO_2 glass to tridymite above this temperature by reaction with $Na_2O \cdot 2SiO_2$, $K_2O \cdot 4SiO_2$, Li_2WO_4 or Na_2WO_4. Exceptions are the failure to convert quartz to tridymite by reaction with K_2WO_4 or LiF as high as 915°, and the previously recognized failure to crystallize quartz from $K_2O \cdot 4SiO_2$ glasses at atmospheric pressure. The explanation for the Li peculiarity may be due to preferential crystalline solution in the quartz structure, but the K^+ failure may either be the result of kinetic considerations or of crystalline solution in the tridymite structure. The exact mechanism of such crystalline solution is not clear; some means of maintaining electrostatic balance must be achieved, such as stuffing the structures with excess oxygen ions.

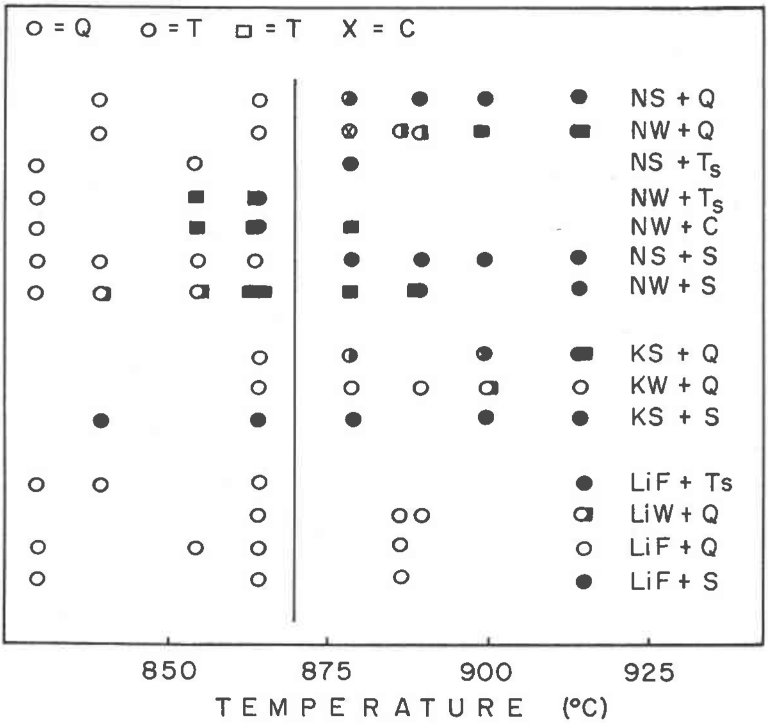

FIG. 5. The quartz-tridymite transformation. Abbreviations: NS = $Na_2O \cdot 2SiO_2$ glass, NW = Na_2WO_4, S = SiO_2 glass, KS = $K_2O \cdot 4SiO_2$ glass, KW = K_2WO_4, LW = Li_2WO_4, Q = quartz, T_s = tridymite-S, C = cristobalite. Solid circle = T_s, Solid square = T_m.

Since this work was completed, Holmquist (1961) showed that NaCl was ineffective as a flux for the quartz-tridymite transformation, and suggested that oxide solid solution was necessary to form tridymite. An alternative explanation, however, can involve merely the kinetics of the quartz-tridymite transformation, which may depend on solubility in the melt and rate of diffusion in the crystal through exchange with ions in the melt.

SUMMARY AND CONCLUSIONS

This investigation presents additional evidence for the existence of a polymorphic transformation between stable tridymite and stable crystobalite. The relationships between the various metastable forms of tridymite (Hill and Roy, 1958a) and cristobalite (Hill and Roy, 1958b) appear to be explained best by polytypic stacking disorder (Flörke, 1955, 1961), with a gradual transition toward the most stable polymorphs (Hill and Roy, 1958b). The (tridymite-S)–(3C-cristobalite) transformation may indeed be a special end-member case of a polytypic transformation. The experimentally observed variation in the temperature for the reconstructive transformation of tridymite to cristobalite may be explained by crystalline solubility in the polymorphs, which results in varying degrees of stacking disorder. When reactions of various forms of SiO_2 are carried out with fluxes expected to have a very minor amount of crystalline solubility in either tridymite or cristobalite, the transformation between tridymite-S and 3C-cristobalite occurs reversibly at 1470° within the rather broad limits of ±30° C. Moreover, no significant change in lattice spacings is observed in these cases. If one had to accept the view that SiO_2 did not exist in a tridymite form when "pure," it becomes necessary then to postulate a series of coincidences by which in *each* case with totally different ions, a "compound" is formed with very small amounts of an unknown ion(s). The coincidence required becomes even worse since it is also necessary for each of these compounds to have essentially the same stability temperature vis-à-vis cristobalite. On the other hand, reactions of the same starting materials with fluxes containing components expected to enter into crystalline solution produce quite normal measurable changes in the lattice spacings, a drastic effect on the temperature of the reconstructive transformation, and (in the case of cristobalite) also a significant change in the temperature of the low-temperature metastable displacive transformation.

The temperature of the quartz-tridymite inversion is less well established undoubtedly in part because of the low temperature and, hence, relative sluggishness of the reaction. Indeed, the ignoring of the fantastically slow reaction rates in this system leads to much of the speculation. However, in view of the variety of fluxes which may be used to bring about this reversible transformation, the existence of a stable reconstructive transformation at about 870° C. should not be hastily denied.

Following the great, if gloomy, Dane (Kierkegaard, 1848) it becomes necessary to add a concluding unscientific postscript. There is in the papers by Flörke and Holmquist the presumptive argument that it somehow rests with the "defenders" of the existence of tridymite to establish its existence. Furthermore, it is also implied that the only acceptable preparation is to prepare the phase, so to speak, with both hands tied behind one's back, *viz.* in the absence of any catalyst. The most interesting corollary of this type of reasoning is the elimination of all the crystalline phases of SiO_2 except 3C-cristobalite, since that is the only one which can be made from another form of SiO_2 without a mineralizer. The conversion to pure quartz of any other crystalline form of SiO_2 without some additive has yet to be achieved.

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REFERENCES

BOGARDUS, E. H. AND R. ROY (1962) Use of phase transitions as indications of residual stresses in crystalline and glass-crystalline aggregates (abs.). *Bull. Am. Ceram. Soc.* **41**(4), 225.

BUHSMER, C. P. AND R. ROY (1962) Effect of radiation-induced defects on first-order displacive transitions (abs.). *Bull. Am. Ceram. Soc.* **41**(4), 223.

FLÖRKE, O. W. (1955) Strukturanomalien bei Tridimyt und Cristobalit. *Ber. deut. Keram. Ges.* **32,** 369–381.

——— (1961) Die Kristallärten des SiO_2 und ihr Umwandlungsverhalten. *Ber. deut. Keram. Ges.* **38**(3), 89–97.

HILL, V. G. AND R. ROY (1958a) Silica structure studies, VI. On tridymites. *Trans. Brit. Ceram Soc.* **57,** 496–510.

——— (1958b) Silica structure studies, V. The variable inversion in cristobalite. *Jour. Am. Ceram. Soc.* **41**(12), 532–537.

HOLMQUIST, S. B. (1961) Conversion of quartz to tridymite. *Jour. Am. Ceram. Soc.* **44,** 82–86.

KRACEK, F. C., N. L. BOWEN AND G. W. MOREY (1929) The system potassium-metasilicate-silica. *Jour. Phys. Chem.* **33,** 1857–1879.

KRISEMENT, O. AND G. TRÖMEL (1960) Change of the properties of cristobalite on irradiation with fast neutrons and by incorporation of impurity atoms. *Zeit. Naturforsch.* **15a,** 634–640.

ROY, D. M. AND R. ROY (1959) Tridymite-cristobalite relations and stable solid solutions. *Bull. Geol. Soc. Am.* **71,** 1666 (Abstract).

ROY, R. (1956) Aids in hydrothermal experimentation: II, Methods of making mixtures for both "dry" and "wet" phase equilibrium studies. *Jour. Am. Ceram. Soc.* **39**(4), 145–146.

TUTTLE, O. F. AND J. L. ENGLAND (1955) Preliminary report on the system SiO_2-H_2O. *Bull. Geol. Soc. Am.* **66,** 149–152.

TRÖMEL, G. (1959) Optical determination of the transformation of cristobalite crystals and statistical evaluation. *Zeit. Naturforsch.* **14a,** 685–686.

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