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THE THERMAL STABILITY OF PURIFIED TRIDYMITE: DISCUSSION

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In sharp contrast to Sosman's (1965) new review of the phases of silica, Rockett and Foster (1967) have made a commendable effort to acknowledge all contemporary workers interested in the classical silica polymorphs. Their observations provide very interesting data about the transformation rate of tridymite which calls for a few comments regarding their interpretation.

Tridymite prepared by the classical sodium tungstate flux method was "purified" by subjecting it to a prolonged leaching in NH_4Cl solution and electro dialysis to remove excess soda. It was then heated to 1670°C before transforming to cristobalite. The conclusion was reached that the closer the tridymite had approached pure silica, the more stable it had become. It is highly doubtful that the impurities were extracted from the tridymite lattice. Thus the tridymite phase proper had not been purified but rather its environment. The sluggishness of its inversion to cristobalite would then be typical of all reconstructive silica transformation in a "flux free" environment.

The only sure method of extracting the alkalis from a silica phase itself is by high temperature electrolysis, which must be performed in an atmosphere containing water vapor so that the alkalis can be replaced by water. The collapse and transformation of tridymite during electrolysis implies that the activity of water resulting from the replacement is insufficient to stabilize the tridymite structure. This view is consistent with the reported high water vapor pressures required for forming tridymite. The attempt by the authors to explain the electrolysis experiments is unrealistic in view of the very low current reported by Flörke (1956) and it is also contradicted by the transformation of tridymite to quartz below 1050°C .

The controversy and confusion about the nature of the tridymite phase seems to be a consequence of an oversimplified interpretation of heterogeneous equilibria and the phase rule. Specifically, the idea by Ricci (1951) that absolutely pure solid phases can be in equilibrium with a multicomponent liquid is, strictly speaking, incorrect. It is admittedly impractical to indicate minute solid solubility in an ordinary phase diagram without using an expanded scale drawing, but its existence must be kept in mind when considering various solid state characteristics of the phase (Holmquist, 1967).

Once it has been understood and recognized that thermodynamically

significant amounts of a second component must be present in all silica phases formed in binary systems, it is also necessary to inquire into the effect this solution has on the transformations between the various silica phases and their stability.

Inversion temperatures for solid phases may be depressed or elevated by solid solution and the degree is determined by the relative chemical activity of the solute rather than by its concentration in the solid phases. This effect must be accounted for in all phase diagrams having silica as one component, as did Keith and Tuttle (1952) in explaining the variability of the high-low inversion in quartz.

Fenner (1913) might not have insisted on his interpretation had he known then what is now well documented. He cautioned that "negative evidence, the fact that no change takes place is not sufficient; positive evidence must be found that changes do take place and that the direction of change is reversible at will under changes of conditions which are perfectly definite." He also explained that "in determining the transition points between quartz and tridymite and between tridymite and cristobalite, it was necessary to use a solvent or catalytic agent in order to cause the transformation to proceed at an appreciable rate, and sodic tungstate was selected for the purpose. The use of this material is permissible if it gives rise to no product which enters into solid solution with one or another form of silica. If such solution occurred, the inversion points would be displaced and the determinations made would have no special significance. It is necessary, therefore, to show that the artificial products do not represent solid solution."

Strictly speaking, Fenner studied silica in the three-component system $\text{SiO}_2\text{-Na}_2\text{O-WO}_3$. He apparently assumed the solid solubilities of the "flux" in all the crystalline forms of silica to be vanishingly small and hence that the transformation temperatures observed for the three-component system also applied to pure silica.

Because the properties of the synthetic silica minerals were in close agreement with those of the naturally occurring silica minerals, Fenner concluded that no significant solid solution had taken place, although chemical analyses indicated 0.2–0.6% impurities. He did not know or even suspect that natural tridymites could be and actually are solid solutions, as shown by Mason (1953) and Buerger (1954) and stressed by Frondell (1962).

Rockett and Foster (1966) provided another good example of the influence of solid solution when reporting that the tridymite-cristobalite transformation takes place at 1410°C in the system silica-sodium tetraborate, while Fenner (1913) located it at 1470°C. It should be recalled that Flörke (1961) reported complete transformation of tridymite to

cristobalite after one day of heating in air at 1350°C when the tridymite was prepared with the aid of cesium oxide.

This author (1967) has shown that tridymite is a binary phase in the silica-soda system and that it is stabilized at 1200°C in a narrow range when the activity of sodium oxide is approximately 10^{-9} units. The corresponding concentrations have not yet been determined.

It should be pointed out that none of the tridymite samples studied by Rockett and Foster seemed to correspond to tridymite-S as defined by Hill and Roy (1958).

It would have been interesting to learn from D.T.A. runs what changes took place in the high-low transformations of the tridymite samples after each heat treatment carried out by Rockett and Foster (1967).

In another paper by Buttermann and Foster (1967), the classical forms and the original transformation temperatures of silica was retained although they had never succeeded in forming tridymite by heating pure silica and zirconia. Thus there is a startling lack of internal consistency in Foster's interpretation of his observations.

REFERENCES

- BUERGER, M. J. (1954) Stuffed derivatives of the silica structures. *Amer. Mineral.* **39**, 600-14.
- BUTTERMAN, W. C. AND W. R. FOSTER (1967) Zircon stability and the ZrO_2 - SiO_2 phase diagram. *Amer. Mineral.*, **52**, 880-5.
- FENNER, C. N. (1913) Stability relations of the silica minerals. *Amer. J. Sci.*, **36**, (214) 331-84.
- FLÖRKE, O. W. (1961) Die Kristallarten des SiO_2 und ihr Umwandlungsverhalten. *Ber. Deut. Keram. Ges.*, **38**, 89-97.
- (1956), Ueber das Einstoffsystem SiO_2 . *Naturwissenschaften*, **43**, 419-20.
- FRONDELL, C. (1962) *The Dana System of Mineralogy. Vol. 3, Silica Minerals*. J. Wiley & Sons, Inc., New York, New York.
- HILL, V. G. AND R. ROY (1958) Silica structure studies VI on tridymites. *Trans. Brit. Ceram. Soc.* **57**, 496-510.
- (1967) The classical silica transformation and controlled sodium oxide activity. *Amer. Ceram. Soc. Basic Sci. Div. Fall Meet. Boston. (1967)*. Ext. Abst. **7-B-67F**.
- KEITH, M. L. AND O. F. TUTTLE (1951) Significance of variations in the high-low inversion of quartz. *Amer. J. Sci.* **Bowen Vol.**, 203-52.
- MASON, B. (1953) Tridymite and christensenite. *Amer. Mineral.*, **38**, 866-7.
- RICCI, J. E. (1951) *The Phase Rule*. Van Nostrand Co., New York, p. 79.
- ROCKETT, T. J. AND W. R. FOSTER (1966) The system silica-sodium tetraborate. *J. Amer. Ceram. Soc.*, **49**, 30-33.
- (1967) The thermal stability of purified tridymite. *Amer. Mineral.*, **52**, 1233-1240.
- SOSMAN, R. B. (1965) *The Phase of Silica*. Rutgers University Press, New Brunswick, New Jersey.