

THE AMERICAN MINERALOGIST, VOL. 53, MARCH-APRIL, 1968

THE THERMAL STABILITY OF PURIFIED TRIDYMITE: REPLY

W. R. FOSTER, *Department of Mineralogy, The Ohio State University, Columbus, Ohio 43210.*

Holmquist's comments may give a misleading picture of our recent data on tridymite (Rockett and Foster, 1967) and other related work (Butterman and Foster, 1967). His belief that leaching removes alkali from the environment, but leaves it in the lattice, may or may not be correct. In any event, it is irrelevant to our thesis. Our point is that, as tridymite is shown to contain less and less alkali (regardless of how it is present) the allegedly essential role of alkali in stabilizing tridymite becomes less and less convincing. It is of note that the alkali content of our leached tridymite is only 1/50 to 1/100 of the 1/2 to 1 percent once considered by Holmquist (1961) as essential to his binary tridymite phase.

We have already indicated (p. 1238) our inability to explain satisfactorily the published results of high-temperature electrolysis experiments. However, we regard them as no more damaging to the Fenner viewpoint than are our results for the thesis of Flörke and Holmquist.

Holmquist notes that high water pressure is necessary to form hydrothermal tridymite, which he regards as a binary silica-water phase. But there is evidence that silica and silicate structures are weakened rather than strengthened by the introduction of water into their lattices (Donnay *et al.*, 1959; Frondel, 1953; Griggs *et al.*, 1965, 1966; McConnell, 1963). Furthermore, such water is expelled at temperatures of the order of 1000°C or less. It appears to be wishful thinking, therefore, to ascribe the stability of hydrothermal tridymite to water, when available evidence points to exactly the opposite effect.

We think that it beclouds the issue to attribute the controversy and confusion to an oversimplified interpretation of binary phase diagrams. We are well aware of the role of solid solution in systems of silica with other oxides, especially in ternary systems in which Al^{3+} replaces Si^{4+} , and electrical balance is restored by interstitial Na^{1+} or Ca^{2+} . But comparable solid solution in binary alkali-silica systems has not been convincingly demonstrated. In the case under discussion alkali solid solution in SiO_2 , if present at all, is of the order of parts per ten thousand. Perhaps, then, there is justification in borrowing a cogent phrase, used by Bowen (1953) in a similar connection, to suggest that Holmquist "... aims at rigor, but this is rigor mortis."

It is futile to speculate as to what Fenner might think if he knew then what we know now, and the use of Fenner's (1913) description of poly-

morphism to support the contrary thesis is unwarranted. Fenner and Holmquist are discussing entirely different phenomena: the former deals with the effect of binary or ternary solid solution on the inversion temperature between two bona fide polymorphs of a one-component system; the latter with the relations between a pure end-member phase (or its solid solution) and a binary phase alleged to have no existence whatsoever in the one-component system.

Holmquist comments that one of our samples seemed to be tridymite-S (Hill and Roy, 1958), and that DTA runs would have been interesting. If the implication is that the use of tridymite-S and of DTA techniques would have yielded contrary results, to the detriment of our case, the logic of such reasoning escapes us. If the tridymites shown by us to be thermally stable were the less stable tridymites-M or -U, one should scarcely expect lesser thermal stability upon purification and heat-treatment of the more stable tridymite-S.

In their proposed phase diagram for the zirconia-silica system, Butterman and Foster (1967) included tridymite as one of the silica phases. The study was concerned primarily with zircon-stability; no attempt was made to synthesize tridymite nor any other specific form of silica or zirconia. Nevertheless, inclusion of tridymite was entirely consistent with the Fenner viewpoint espoused by the authors, and with the findings of Rockett and Foster (1967) on the thermal stability of tridymite. We fail to see here any "startling lack of internal consistency," as alleged by Holmquist.

REFERENCES

- BOWEN, N. L. (1953) Petrology and silicate technology. *J. Amer. Ceram. Soc.*, **26**, 285-301.
- BUTTERMAN, W. C. AND W. R. FOSTER (1967) Zircon stability and the ZrO_2 - SiO_2 phase diagram. *Amer. Mineral.*, **52**, 880-885.
- DONNAY, G., J. WYART AND G. SABATIER (1959) Structural mechanism of thermal and compositional transformations in silicates. *Z. Kristallogr.* **112**, 161-168.
- FENNER, C. N. (1913) Stability relations of the silica minerals. *Amer. J. Sci.*, **36**, (214) 331-384.
- FRONDEL, C. (1953) Hydroxyl substitution in thorite and zircon. *Amer. Mineral.*, **38**, 1007-1018.
- GRIGGS, D. T. AND J. D. BLACIC (1965) Quartz: anomalous weakness of synthetic crystals. *Science*, **147**, 292-295.
- GRIGGS, D. T., J. D. BLACIC, J. M. CHRISTIE, A. C. MCLAREN AND F. C. FRANK (1966) Hydrolytic weakening of quartz crystals. *Science*, **152**, 674.
- HILL, V. G. AND R. ROY (1957) Silica structure studies, VI. On tridymites. *Trans. Brit. Ceram. Soc.*, **57**, 496-510.
- HOLMQUIST, S. B. (1961) Conversion of quartz to tridymite. *J. Amer. Ceram. Soc.*, **44**, 82-86.
- MCCONNELL, D. (1963) Hydrogen ion incorporation in crystals. *Science*, **141**, 171.
- ROCKETT, T. J. AND W. R. FOSTER (1967) The thermal stability of purified tridymite. *Amer. Mineral.*, **52**, 1233-1240.