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THE THERMAL STABILITY OF PURIFIED TRIDYMITE

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Introduction

There exists today among ceramists, chemists and mineralogists a lively controversy as to the nature of tridymite. Over fifty years ago C. N. Fenner (1913) on the basis of the work of numerous earlier investigators and his own careful studies, delineated the relations of tridymite with the other two major forms of silica, quartz and cristobalite. According to the Fenner scheme tridymite is the stable form of SiO_2 between 867° and 1470°C, with quartz stable below 867°C, and cristobalite stable from 1470° to the melting point at 1713°C.

Many years elapsed without any serious disclaimer or doubt as to the validity of the general relationships defined by Fenner for the SiO_2 system. Then there appeared the first of a series of papers by O. W. Flörke (1955) which raised serious doubts as to the correctness of Fenner's views, and questioned the very existence of tridymite as a phase in the system SiO_2. Flörke regards quartz and cristobalite as the stable forms of SiO_2 below and above 1050°C, respectively. Tridymite is completely excluded in the belief that it is a compound or solid solution between silica and an additional chemical constituent.

A large group of workers, including Eitel (1957, 1958), De Keyser and Cypres (1957, 1961), Holmquist (1958, 1961), Grofcsik and Vago (1958), Wollast (1961), Coquerelle (1961), Wahl, Grim and Graf (1961), Cypres (1962, 1964), and Foster (1965) has joined Flörke in favoring the rejection of the traditional view. Flörke (1956, 1959, 1961, 1963) has followed his initial presentation with a succession of articles in like vein. In the face of these contrary opinions partisans of the Fenner school have been generally silent, with the exception of Roy and his associates (Shafer and Roy, 1956, 1957; Roy, Isaacs and Shafer, 1957; Hill and Roy, 1958; Miller, Dachille, Shafer and Roy, 1962; Roy and Roy, 1964).

When the authors (Rockett and Foster, 1965) recently undertook an investigation of the system SiO_2-B_2O_3, they were confronted with this controversy surrounding the status of tridymite. Several courses appeared open to them; to accept the traditional view that tridymite is a bona fide member of the silica family of minerals; to reject tridymite as a

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phase in the one-component system SiO_2; or, to attempt to provide additional data which might throw further light on this crucial question. The latter course was chosen, and the purpose of the present paper is to record the results of prolonged thermal treatment of purified synthetic tridymite, and the bearing of these results on the tridymite controversy.

BASIS FOR THE OPPOSING VIEWS

Much of the argument surrounding the true nature of tridymite stems from the difficulty, if not impossibility, of obtaining a pure silica phase possessing the tridymite structure. With few exceptions investigators of the silica minerals have agreed that it is not in practice possible to synthesize tridymite in the complete absence of some additional chemical constituent. There is disagreement, however, as to the specific role played by such added constituents. Flörke and his followers contend that these foreign ions are essential ingredients of the tridymite, without which the latter could neither form nor persist. Of the nonsilica ingredients, soda is regarded by Flörke as the one primarily responsible for the existence of tridymite, and a minimum of 0.1 per cent is believed by him to be required. Fenner, on the other hand, maintained that foreign ions acted merely as mineralizing catalysts without entering the tridymite lattice. There has long been ample evidence that foreign ions greatly facilitate the formation of tridymite, and on this point there has never been any quarrel between the two schools of thought. The realization that these foreign ions may enter the tridymite lattice is more recent, and calls for some modification of the original Fenner view. However, acceptance of these later findings does not necessarily weaken the overall Fenner position. Both cristobalite and quartz are also now known to accept foreign ions in their lattices, even in substantial amounts, yet it has never been suggested that cristobalite and quartz should be discredited as silica polymorphs. It should be added that cristobalite, unlike tridymite, does not require the presence of foreign ions for its formation. Quartz synthesis usually involves the presence of foreign ions, although it is claimed (Flörke, personal communication) that their presence is not essential.

The nature and behavior of hydrothermal tridymite have been major points of contention in the continuing tridymite controversy. When Hill and Roy (1958) reported tridymite synthesis with the aid of water vapor alone, Flörke (1959) and Holmquist (personal communication) suggested that water should be added to the list of effective tridymite stabilizers. Persistence of their hydrothermally synthesized tridymite after calcination at 1300°C convinced Hill and Roy that they had a pure water-free tridymite. Holmquist (personal communication) questioned this belief and suggested that heating to 1470°C in air might be required to release the essential water. Flörke (1959) too expressed dissatisfaction with Hill and Roy's heat-treatment of their tridymite.

Rejection of tridymite as a silica polymorph can be justified only if the added ingredients enter the lattice as essential rather than merely as incidental constituents. It would appear to follow that persistence of the tridymite lattice, at least in the face of severe thermal treatment, would depend upon the retention of such constituents. Indeed, Flörke (1959) and Holmquist (1961) have cited evidence for the collapse of the tridymite structure upon removal of the foreign ions. According to their view, tridymite, thus deprived of its very cause for being, should change to quartz or to cristobalite, depending upon whether the temperature is below or above 1050°C. Experimental evidence for such behavior is at best contradictory, and the results presently to be proffered are believed to support the Fenner rather than the Flörke viewpoint.

TABLE 1. SPECTROCHEMICAL ANALYSIS OF TRIDYMITE SAMPLES
(results in weight percent of elements)

	Tridymite No. 1	Tridymite No. 2	Silica glass (GE-204A) used for Tridymite No. 3
Na	0.04 ($\sim$0.05Na_2O)	0.01 ($\sim$0.01%Na_2O)	trace
W	0.80	0.05	—
Al	0.05	0.03	0.005
Fe	0.01	0.005	0.001
Others (trace)	Ca, Cu Ag, Mg	Ca, Mg, B	Ca, Li, B

Analyst: R. Heffelfinger, Battelle Memorial Institute, Columbus, Ohio.

EXPERIMENTAL MATERIALS AND DATA

Three samples of finely-powdered synthetic tridymite were used in these experiments. Tridymite No. 1[1] was prepared by the sodium tungstate flux method, followed by leaching with NH_4Cl solution and electrodialysis to remove excess soda. The analysis of this material as received is shown in the second column of Table 1, and reveals that Tridymite No. 1 contains only one-half of the minimum amount of alkali specified by Flörke. Tridymite No. 2 was prepared by subjecting a portion of Tridymite No. 1 to continuous treatment with NH_4Cl solution in a Soxhlet extractor for one week. Table 1 shows that the alkali content has been reduced to about one-tenth that considered by Flörke as the minimum for tridymite stability. Tridymite No. 3[1] was synthesized hydrothermally at 1100°C and 12,000 psi, using pure fused silica for which the analysis appears in the last column of Table 1. It is clear that the resulting sample, except for water or hydroxyl in undetermined amount, must be extremely pure.

[1] Obtained from Tem-Pres Research, Inc., State College, Pennsylvania.

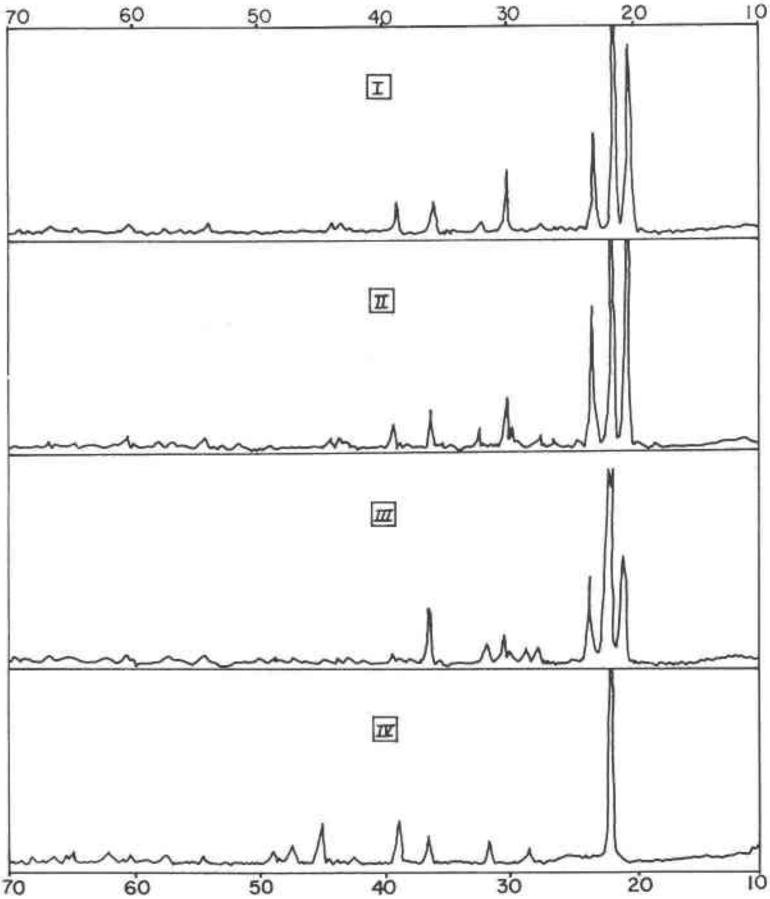

FIG. 1. Selected X-ray diffractometer patterns (Two-Theta range: 70° – 10°; Radiation: CuK$_\alpha$)—I: Tridymite-I; II: Tridymite-II; III: Tridymite-III; IV: Cristobalite formed from Tridymite-I after 16 hours at 1650°C.

Figure 1 presents x-ray diffractometer patterns of each of the three starting materials, and a sample of cristobalite. Tridymite-I and Tridymite-II consist entirely of tridymite, whereas Tridymite-III consists of roughly equal amounts of tridymite and cristobalite.

The above three tridymite samples were subjected to thermal treatment at selected elevated temperatures for periods of time as shown in Table 2, with results as indicated. A Marshall Products Company platinum-wound resistance furnace, closely controlled by a Leeds and Northrup saturable-core controller, was used. Temperatures were determined by a platinum/platinum 10% rhodium thermocouple, which was periodically calibrated against a similar thermocouple standardized by the Na-

TABLE 2. SELECTED RESULTS OF THERMAL TREATMENT OF SYNTHETIC TRIDYMITES

Temperature (°C)	Time (hrs)	Resulting Crystal Phases
	(Tridymite No. 1)	
1450	200	Tridymite
1500	24	Tridymite and cristobalite
1540	16	Tridymite and cristobalite
1600	24	Cristobalite and tridymite
1650	24	Cristobalite
	(Tridymite No. 2)	
1450	300	Tridymite
*1450	376	Tridymite and cristobalite
1500	100	Tridymite
1600	12	Tridymite
1670	4	Tridymite
1670	12	Tridymite
1670	30	Cristobalite
	(Tridymite No. 3—Hydrothermal)	
1000	800	Tridymite and cristobalite
1350	300	Tridymite and cristobalite
1400	200	Tridymite and cristobalite
1430 (in vacuum)	50	Tridymite and cristobalite
1450	40	Tridymite and cristobalite
1550	50	Tridymite and cristobalite
1600	50	Tridymite and cristobalite
1650	50	Tridymite and cristobalite
1690	50	Tridymite and cristobalite

* This run involved an initial 50:50 mixture of Tridymite No. 2 and cristobalite, to check the possible "seeding" effect of cristobalite on the tridymite-cristobalite conversion.

tional Bureau of Standards. The samples were in the form of pressed tablets contained in platinum crucibles. At the completion of a run the charge was quenched in mercury. The crystalline form or forms of silica present at the conclusion of a run were determined with a General Electric XRD-5 recording x-ray diffractometer, using copper radiation, and nickel filter. Since no attempt was made at mechanical separation of tridymite and cristobalite from partially converted samples, it is not possible to characterize these mixtures with respect to Flörke's (1955) polytype theory. It can be stated however that the diffractometer patterns of tridymite and cristobalite were sharp and distinctive, whether they appeared singly or in combination.

DISCUSSION OF RESULTS

Table 2 shows a significant difference in the thermal behavior of the two tridymites produced initially with the aid of sodium tungstate flux.

Treatment for twenty-four hours at 1500°C was sufficient to convert a substantial portion of Tridymite No. 1 to cristobalite. In contrast, Tridymite No. 2 showed no recognizable cristobalite after 100 hours at 1500°C. Indeed, cristobalite failed to appear until a considerably higher temperature was achieved. It is to be noted that Tridymite No. 2 differs from Tridymite No. 1 (from which latter it was derived) only in containing a lesser quantity of non-silica constituents. The conclusion appears inescapable that the closer the tridymite has approached pure silica the more stable it has become. This is the behavior to be expected if tridymite is a SiO_2-polymorph. If tridymite were, rather, a compound or solid solution involving additional ions, its stability should have decreased on approaching SiO_2. Its persistence, even 200° above 1470° stability limit for the tridymite-cristobalite inversion, is readily explained by the well-known tendency for increased sluggishness of reconstructive transformations with increased purity of the transforming phase.

The results shown in Table 2 for Tridymite No. 3 should provide at least a partial answer to the claim that hydrothermally synthesized tridymite exists only because of stabilizing hydroxyl ions. Assuming (Holmquist, personal communication) that heating at 1470°C in air would be sufficient to expel the stabilizing hydroxyl ions, the tridymite should have readily and completely changed to cristobalite, but it did not. Instead, tridymite persisted even after 50 hours at 1690°C, and in spite of the potential seeding effect of associated cristobalite. It is to be noted, too, that this sample, the purest of the three starting materials in terms of SiO_2, shows the strongest tendency for the persistence of tridymite.

The results briefly discussed above favor the Fenner over the Flörke scheme of silica polymorphs. They are thus in conflict with the electrolysis experiments described by Flörke (1956) and Holmquist (1961) in which removal of alkali ions from tridymite by passage of an electric current at 1300°C was found to convert the tridymite to cristobalite. The present authors are at a loss to explain these latter results, unless perhaps a resistance-heating effect due to the passage of the electric current might have heated the tridymite specimen well above the 1300° furnace temperature. Whether such a heating effect would carry the tridymite beyond the 1470° limit set by Fenner for the conversion of tridymite to cristobalite is problematical. In view of the contradictory results of the removal of foreign ions from tridymite the data of Table 2 cannot be considered conclusive in themselves. They should, however, serve to discourage a too-hasty rejection of the Fenner viewpoint. It is to be hoped that they may also induce other investigators to direct their attention to this interesting controversy.

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AN OCCURRENCE OF CORDIERITE-GARNET GNEISS IN GEORGIA

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Cordierite occurs in regionally metamorphosed rocks in Lincoln County near the Georgia-South Carolina boundary. Well-exposed outcrops are along Curry Creek and along Georgia Highway 79, three miles north of Lincolnton, Georgia (Fig. 1). The presence of cordierite is noteworthy because it is a rare regional mineral within the Appalachian province (Conant, 1935; Heald, 1950; Hurst, 1956; Barker, 1961; Barker, 1962) and because garnet is a common associate mineral.

The cordierite-bearing rock is fine-grained, generally contorted biotite gneiss. All outcrops show some weathering, and where weathering has been intense a dark red-brown soil has developed. This soil is readily identified by its distinctive color and very high content of fine-grained quartz and micas.

The area south of the cordierite-bearing rocks is underlain by the lower Paleozoic Little River series. The nature of the contact between the two units is not directly observable; however, the contact is delineated by the sharp contrast in soil types overlying each rock. The Little River series is the southwestern extension into Georgia of what in South Carolina is referred to as the Carolina slate belt. In Lincoln County, Georgia, this unit consists of a thick sequence of interbedded fine-grained metavolcanic and metasedimentary rocks. Most of the Little River series has a well-developed foliation that strikes about N45E and dips nearly vertical. North of the cordierite-bearing gneiss is a sequence of generally