

mounted; this block is a pre-war model borrowed from the College Park Station of the Bureau of Mines, where it had been extensively used by myself and others. Except for a minor adjustment of the clearing bar, it has required no attention.

It is stated on page 1 of the original description that true Rosiwal analyses have not been made since introduction of the Shand micrometer in 1916, but this error is corrected in a hastily inserted footnote. The use of traverses so spaced that a single grain may be cut more than once does in fact violate a major condition specified by Rosiwal and places the procedure beyond the pale as far as the excellent study of Lincoln and Reitz (*Econ. Geol.*, 1913) is concerned. But this modification was suggested first by Wentworth, not by Shand. The use of evenly spaced traverses is now so ingrained that it has hardly been mentioned since it was first suggested by Wentworth in 1923, and in reviewing my typescript even such a meticulous critic as Dr. Shand himself failed to notice the error.

A NOTE ON THE CONVERSION OF AMORPHOUS SILICA TO QUARTZ

DONALD A. BAILEY, *The Saranac Laboratory, Saranac Lake, New York.*

In an earlier paper (1) it was pointed out that quartz or amorphous silica can be converted to cristobalite when heated for ten to thirty minutes with alkali fluxes at temperatures in the vicinity of 1150° C. A further investigation of several commercially prepared, finely divided amorphous silicas disclosed that crystallization of these substances could be brought about during ignition at temperatures between 1070° C. and 1100° C., provided CaO or CaCO₃ were present in amounts of five to ten per cent by weight. Before an opportunity to present the results had been realized, a paper on the crystallization of silicic acid by Schulman, *et al.* (2), appeared in a recent issue of the *American Mineralogist*. The authors show that quartz and cristobalite can form from silicic acid heated at 1150° C. for three hours in the presence of calcium, added as CaCO₃ or CaSiO₃. The present writer finds his results to be consistent with the observations of Schulman and his co-workers. Additional points revealed in the writer's investigation but not covered by Schulman's paper are discussed below.

In the experiments dealing with the conversion of silica to cristobalite (1), one sample in the series was a commercially prepared, finely divided amorphous silica. Following ignition of this sample at temperatures between 1070° C. and 1100° C., it was noted that over one-half of the substance was converted to quartz. The original material consisted of fine aggregates and sub-microscopic particles, and contained approximately

five per cent calcium carbonate, the latter ranging in particle size from thirty microns to less than one micron. An *x*-ray powder photograph of the material prior to ignition showed no crystalline component aside from the calcium carbonate, and yielded a diffuse ring similar to that observed in *x*-ray diffraction patterns of vitreous silica (3). This diffuse ring was found to be in the position which it occupies in patterns of hydrated silica, such as opal and silica gel.

The discovery that quartz had been formed by igniting a sample of sub-microscopic amorphous silica that contained lime was an unexpected

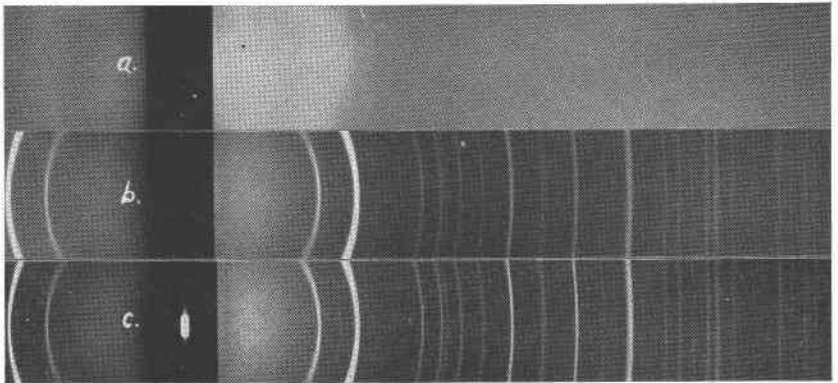


FIG. 1. *X*-ray powder diffraction patterns, Cu radiation, Ni filter. Samples held in wedge holder.

- (a) Amorphous silica, containing 5 per cent calcium carbonate.
- (b) Sample (a) after ignition at 1070° C. to 1100° C. for thirty minutes.
- (c) Standard pattern for quartz.

finding which called for further study. Ignition of this finely divided silica had been carried out by heating for thirty minutes a 200-milligram sample in a covered platinum crucible supported over a Meker burner. The substance lost approximately 11 per cent by weight and showed a marked shrinkage in volume. Microscopic examination between crossed nicols revealed that all of the calcite had been decomposed. The bulk of the material now had the appearance of cryptocrystalline quartz. Individual particles showed aggregate polarization and usually did not exceed twenty microns in size. The heated sample also contained fused masses having a refractive index near 1.63. This substance seems to be wollastonite. A powder photograph of the heated material + an internal standard showed a quartz pattern accounting for approximately 60 per cent of the sample. A faint line in the position of the principal wollastonite line and a very weak line indicating a trace of cristobalite were also apparent.

A photograph without the internal standard shows a strong pattern for quartz (Fig. 1).

Following these observations on this one sample, a number of finely divided amorphous silicas were similarly heated for from five to thirty minutes after the addition of CaO or CaCO₃, or, in one case, CaSiO₃. Each sample, together with the flux employed, was moistened with alcohol and thoroughly mixed in a mullite mortar before and after the heat treatment. The materials chosen for the tests and the approximate percentages of crystalline silica formed, as determined by means of x-ray diffraction, are indicated in the Tables, 1 to 4. One test was included in which MgO was used. This material failed to bring about the conversion of amorphous silica to quartz. It is to be noted that the sample designated as "Silica No. 1" occurs in spherical particles ranging in diameter from 0.2 micron to less than 0.02 micron, as determined from electron micrographs. It contains 3.23 per cent CaO, 0.22 per cent MgO and 0.36 per cent alkalies (Na₂O+K₂O). The colloidal silica gel contains 0.18 per cent

TABLE 1

Silica No. 1 plus 10 Per Cent by Weight CaO Ignited at 1070° C. to 1100° C. Showing Effect of Time		
Mixture after Ignition		Ignition time
Quartz per cent	Cristobalite per cent	minutes
n.f.	n.f.	0.5
15	n.f.	2
55	n.f.	5
55	trace	30

TABLE 2

Colloidal Silica Gel (contains 0.18% CaO) Ignited Alone and with Fluxes at 1070° C. to 1100° C. for 30 minutes		
Substance added	Mixture after Ignition	
	Quartz per cent	Cristobalite per cent
none	n.f.	n.f.
CaCO ₃ 10%	55	trace
CaO 10%	55	trace
CaSiO ₃ 10%	3	trace
MgO 10%	n.f.	n.f.

TABLE 3

Various Silicas Ignited with 10 Per Cent CaO at 1070° C. to 1150° C. for 30 Minutes		
<i>Silica</i>	Mixture after Ignition	
	<i>Quartz</i> per cent	<i>Cristobalite</i> per cent
Silica No 1	55	trace
Colloidal Silica gel	55	trace
Vitreous Silica, 1-3 μ	30	2
Diatomaceous Earth	17	30

TABLE 4

Vitreous Silica Ignited with 10 Per Cent CaO at 1070° C. to 1150° C. for 30 Minutes Showing Effect of Size		
<i>Vitreous Silica</i> Size in microns	Mixture after Ignition	
	<i>Quartz</i> per cent	<i>Cristobalite</i> per cent
1-3	30	2
10-30	10	trace
75-200	2	trace

CaO. Samples of relatively coarse vitreous silica were also included among the tests.

An approximate estimate of the ignition temperature necessary to bring about conversion was made. Samples held at 820° C. and at 850° C. in a muffle furnace equipped with a pyrometer remained amorphous. Portions of these same samples when spread over the bottom of the platinum crucible to a depth of one millimeter and kept over the Meker flame for five minutes readily underwent conversion to quartz. The temperature on the inside bottom of the covered crucible was found to lie between the melting point of K_2SO_4 (1070° C.) and that of albite (1100° C.). The same burner was used in all of the tests, and efforts were made to maintain the gas and air supplies at constant levels.

RESULTS

It may be noted that where the grain size is sufficiently small, as in precipitated silicic acid and in samples of silica fume, conversion to quartz will take place in the presence of CaO within a few minutes, once

the charge has reached the proper temperature (Table 1). These experiments do not exclude the possibility that some crystallization of the quartz may occur during the cooling of the samples and at temperatures somewhat lower than the maximum heat attained. CaO and CaCO₃ seem equally effective in bringing about conversion (Table 2). CaSiO₃ produced little quartz at the temperature employed, while MgO was inactive. Sosman (4) has suggested that liquid silicates, formed by the interaction of SiO₂ with certain oxides, including CaO, may act as fluxes, assisting in the sluggish inversions. It has been demonstrated that lime and silica when heated together at temperatures covering the range here explored will form calcium silicate (5). On the basis of the evidence, it seems probable that the true flux responsible for the conversions here noted is in every case a liquid silicate.

Anhydrous silica and silica gel yielded similar amounts of quartz when heated with CaO (Table 3). An increase in the grain size of vitreous silica retarded the rate of conversion to quartz (Table 4). In the diatomaceous earth sample, where small percentages of alkalis were present (Na₂O+K₂O=0.7 per cent), cristobalite was found to be in excess of quartz in the treated sample (Table 3).

ACKNOWLEDGMENT

The writer wishes to thank Mr. Thomas M. Durkan of the Saranac Laboratory for determining the lime content of two samples tested, and for advice regarding the preparation of this manuscript.

REFERENCES

- (1) BAILEY, D. A., Conversion of silica during ignition: *J. Ind. Hyg. and Tox.*, **29**, 242 (1947).
- (2) SCHULMAN, J. H., CLAFFY, E. W., AND GINTHER, R. J., Some observations on the crystallization of silicic acid: *Am. Mineral.*, **34**, 68 (Jan.-Feb. 1949).
- (3) WARREN, B. E., The basic principles involved in the glassy state: *J. Applied Physics*, **13**, 602-610 (1942).
- (4) SOSMAN, R. B., The properties of silica: The Chemical Catalogue Co., New York (1927).
- (5) STROKOV, F. N., MUSYAKOV, V. A. AND VOLKOV, V. S., High temperature reactions of calcium carbonate and silica, and the hydrochemical treatment of the products: *Chem. Abstr.*, **37**, 2890 (1943).