

# THE EFFECT OF VARIOUS IMPURITIES ON THE CRYSTALLIZATION OF AMORPHOUS SILICIC ACID

L. S. BIRKS AND J. H. SCHULMAN, *Naval Research  
Laboratory, Washington 20, D. C.*

## ABSTRACT

Five added impurities were found effective in causing amorphous silicic acid to transform to quartz several hundred degrees above its stability limit. These were the carbonates of magnesium, calcium, strontium, barium, and manganese. Five other impurities,  $\text{Al}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NiCO}_3$  did not cause the transformation to quartz but did accelerate the transformation to cristobalite.  $\text{BeO}$  was the only impurity added for which no crystallization was observed. The lattice constant for the quartz formed in the presence of the five effective impurities was the same as for powdered natural quartz. No explanation is offered for the specific action of the impurities in effecting the crystallization to the quartz structure.

## INTRODUCTION

It was reported recently (1) that when a mixture of calcium carbonate and silicic acid was heated at  $1150^\circ\text{C}$ ., quartz as well as cristobalite was formed. This observation has since been confirmed by Bailey (2). Because of the unusual effect of the formation of quartz some  $300^\circ\text{C}$ . above its transition temperature, we decided to investigate the action of other impurities besides calcium carbonate. The impurities chosen were  $\text{MgCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{BeO}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Bi}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NiCO}_3$ ,  $\text{MnCO}_3$  and the percentage added to the silicic acid ranged from 0.25 to 10 mole per cent. The silicic acid was Mallinckrodt "Special Bulky" grade.

## METHOD AND RESULTS

The transformations of the silicic acid were studied in the high temperature  $x$ -ray diffraction apparatus described by Birks and Friedman (3). This comprised a focusing Geiger counter spectrometer with the specimen heated in a vacuum oven. Specimen preparation was as follows: A 100 mesh platinum gauze was spot welded to a  $1\frac{1}{4} \times 1\frac{1}{2}$  inch piece of 5 mil platinum foil to be mounted on the heater element. A platinum-platinum 10 per cent rhodium thermocouple was spot welded to the center of the gauze to measure the specimen temperature. Finally, the powder to be examined was pressed into the gauze and scraped off flush with the surface. The actual area of the specimen irradiated by the  $x$ -rays was restricted to a spot  $\frac{1}{2}$  inch square over which the temperature was uniform.

After pumping the apparatus to  $10^{-4}$  mm. of Hg., an  $x$ -ray pattern

was made at room temperature, and then the temperature was raised at 15° C. per minute to 1200° C. Another *x*-ray pattern was made as soon as the temperature reached 1200° C. and again after holding at

TABLE 1

Impurity added	Mole per cent of impurity	Observations
MgCO <sub>3</sub>	0.25-1%	Practically no crystallization.
MgCO <sub>3</sub>	2.5	Weak cristobalite and quartz at 1300° C. after 30 min.
MgCO <sub>3</sub>	5.0	Cristobalite and quartz at 1200° C. after 30 min.
MgCO <sub>3</sub>	10.0	Quartz on reaching 1200° C.
CaCO <sub>3</sub>	.25	No crystallization.
CaCO <sub>3</sub>	.5	Weak cristobalite on reaching 1300° C.
CaCO <sub>3</sub>	1.0	Quartz and cristobalite at 1300° C., both increasing after 30 min.
CaCO <sub>3</sub>	2.5	Quartz and cristobalite at 1300° C.
CaCO <sub>3</sub>	5.0	Quartz and cristobalite at 1300° C.
CaCO <sub>3</sub>	10.0	Cristobalite at 1200°, quartz at 1250 to 1300° C.
SrCO <sub>3</sub>	.25	No crystallization.
SrCO <sub>3</sub>	.5	Weak quartz and cristobalite at 1300° C. after 30 min.
SrCO <sub>3</sub>	1.0	Quartz and cristobalite at 1250° C.
SrCO <sub>3</sub>	5.0	Weak quartz and very weak cristobalite, some tridymite after 30 min.
SrCO <sub>3</sub>	10.0	Quartz, cristobalite and some tridymite after 30 min. at 1200° C.
BaCO <sub>3</sub>	.25-.5	No crystallization.
BaCO <sub>3</sub>	1.0	Strong cristobalite and weak quartz after 30 min. at 1250° C.
BaCO <sub>3</sub>	5.0	Cristobalite at 1250° C.
BaCO <sub>3</sub>	10.0	Cristobalite and perhaps quartz at 1200° C.
MnCO <sub>3</sub>	5.0	Weak cristobalite on reaching 1250°, cristobalite and quartz after 30 min. at 1250°.
BeO	5.0	No crystallization.
Al <sub>2</sub> O <sub>3</sub>	5.0	Weak cristobalite after 30 min. at 1300°.
Bi <sub>2</sub> O <sub>3</sub>	5.0	Cristobalite at 1250° C.
Li <sub>2</sub> CO <sub>3</sub>	5.0	Strong cristobalite at 1200° C. or lower.
Na <sub>2</sub> CO <sub>3</sub>	5.0	Strong cristobalite at 1200° C. or lower.
NiCO <sub>3</sub>	5.0	Weak cristobalite after 30 min. at 1300° C.
Silic acid with no impurity added	—	No crystallization after 30 min. at 1300° C.

1200° C. for a half hour. The temperature was then raised to 1250° C. and 1300° C. and the procedure repeated at each temperature.

In no case where quartz was formed, did its amount decrease with higher temperature. This indicated that once formed, it was stable at high temperature at least for periods up to two hours. The quartz and

crystalite formed at high temperature both persisted on cooling to room temperature, substantiating the interpretation of the earlier paper that the quartz did not form by transformation from cristobalite. The results for the various specimens are tabulated in Table 1.

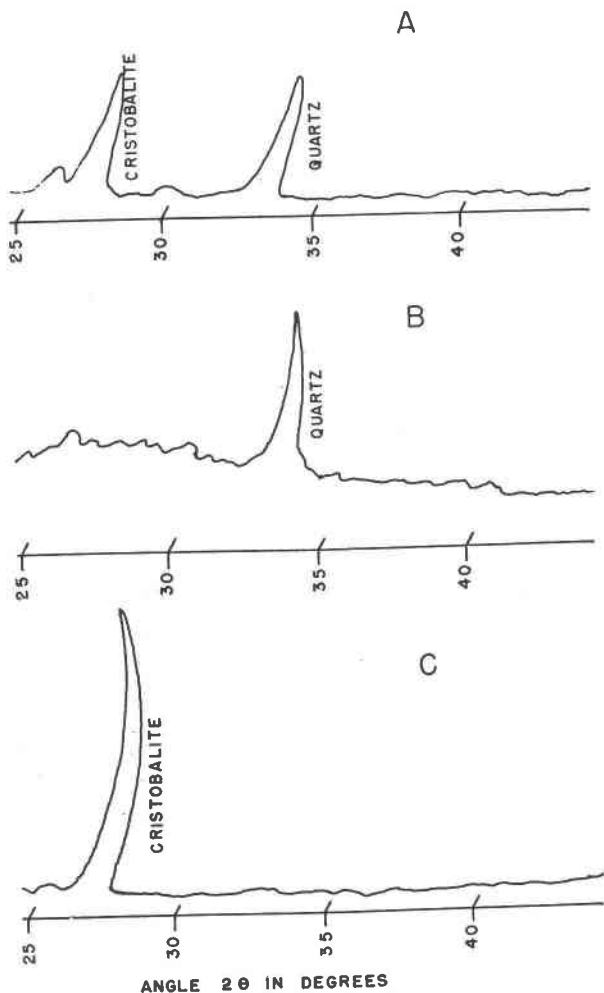


FIG. 1. Unretouched Geiger counter records of typical diffraction patterns. (A) 1%  $\text{CaCO}_3$ , after 30 minutes at  $1300^\circ\text{C}$ .; (B) 10%  $\text{MgCO}_3$ , after 10 minutes at  $1300^\circ\text{C}$ .; (C) 5%  $\text{LiCO}_3$ , after 30 minutes at  $1250^\circ\text{C}$ .

It may be seen from the table that four other impurities, in addition to the  $\text{CaCO}_3$  previously found effective, caused crystallization to the quartz structure. These effective impurities were Mg, Sr, Ba, and Mn.

Bailey (2) reported that MgO did not cause quartz to be formed; however the maximum temperature he used was 1150° C. We did not observe quartz until the temperature had reached 1200° C. which could account for the apparent discrepancy.

Typical *x*-ray patterns are shown in Fig. 1. (A) shows a transformation to both quartz and cristobalite, (B) shows only quartz and (C), only cristobalite.

An attempt was made to determine whether or not quartz, formed in the presence of additives, had appreciably different cell dimensions from pure quartz. Four samples of silicic acid, containing 5 mole per cent MgCO<sub>3</sub>, CaCO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub>, respectively, were heated for 8 hrs. at 1300° C. *X*-ray patterns made on a 10 cm. radius asymmetric focussing camera at room temperature showed no difference in lattice constant between any of these preparations and powdered natural quartz.

#### CONCLUSIONS

The crystallization of amorphous silicic acid into the quartz structure at temperatures several hundred degrees above the stability limit of quartz, has been shown to take place in the presence of four alkaline earth impurities and also in the presence of manganese. Precision lattice constant determinations gave no evidence that these impurities have entered into the quartz structure formed in their presence. In amounts of the order of one mole per cent or greater, most of the impurities studied very noticeably accelerated the crystallization of the silicic acid into the cristobalite structure, whether or not they were effective in producing quartz.

We can offer no explanation of the specific action of the five impurities found effective for quartz formation. The suggestion of Bailey that a liquid silicate is responsible for the conversions does not seem to be borne out by literature data (4), which show no liquidus in the alkaline earth oxide-SiO<sub>2</sub> systems in the temperature range investigated by him or by us.

#### ACKNOWLEDGMENT

We wish to thank Mr. R. T. Seal for his help in preparing the *x*-ray diffraction patterns and Mrs. Esther W. Claffy for preparing the samples.

#### REFERENCES

1. SCHULMAN, J. H., CLAFFY, E. W., AND GINTHER, R. J., *Am. Mineral.*, **34**, 68 (1949).
2. BAILEY, D. A., *Am. Mineral.*, **34**, 601 (1949).
3. BIRKS, L. S., AND FRIEDMAN, H., *R.S.I.*, **18**, 576 (1947).
4. HALL, F. P., AND INSLEY, H., *J. Am. Ceramic Soc.*, **30** (1947).