SOME OBSERVATIONS ON THE CRYSTALLIZATION OF AMORPHOUS SILICA

R. M. CARR AND W. S. FYFE, *University of Otago, Dunedin, New Zealand.*

ABSTRACT

Experiments have been carried out to determine the effect of pressure and temperature on the rate of formation of quartz from silicic acid. The rate is much more sensitive to pressure than temperature and this is discussed in terms of possible mechanisms. Cristobalite and silica-K appear as intermediate phases before quartz is formed in appreciable quantity. In this system increasing pressure favours the attainment of equilibrium more than increasing temperature.

INTRODUCTION

In most experimental studies designed to determine phase relations in a mineral system the starting materials chosen are those which allow reaction to proceed in a reasonable time. The constituents are often used in some amorphous reactive condition, a glass or gel, which also assists in the final x-ray analysis to determine the phases present. It is always desirable that the phases which are grown at a given pressure and temperature, be those having the lowest possible free energies of formation and thus represent the thermodynamically stable assemblage. But by using the most reactive starting materials the difficulty of obtaining stable products may be at a maximum. From such unstable reactants many metastable assemblages, more stable than the reactants, may easily be formed.

It has been recognized for a long time that during hydrothermal crystallization of amorphous silica, metastable phases commonly are formed and persist for considerable periods. As an understanding of such phenomena appears fundamental in the interpretation of experimental results a more detailed study of the crystallization of amorphous silica was undertaken.

EXPERIMENTAL PROCEDURE

The general procedure followed was to allow samples of amorphous silica to react with water at a fixed pressure and temperature for various times and then to rapidly cool the reaction vessels. The products were then examined with an x-ray diffractometer. The silica used in this study was powdered A. R. silicic acid (100 mesh) manufactured by Mallinckrodt Chemical Co. This material was not completely amorphous but an x-ray pattern showed a broad diffuse hump (see Fig. 1) with a centre close to the position of the strongest line of cristobalite. Hydrothermal experiments were carried out in test-tube bombs with the sample

in a silver capsule with ends pinched off to avoid contamination. The tubes were not sealed. Temperature control was to $\pm 3°$ C.

Experimental Results

In Table I, data from a series of experiments are summarized.

Discussion

The reproducibility of the times of conversions is not high but in general anomalies were less than 20%. Temperature has a rather small effect on the rate, but pressure has a very marked effect and an error in pressure could cause a significant variation, particularly at low pressures. Only three experiments were conducted at 15,000 p.s.i. where the times were inconveniently long and the results, while being of the order of time expected are anomalies with respect to temperature. This anomaly could be explained by pressure uncertainty.

From an inspection of the results in Table I a number of conclusions which have important bearing on the mechanism are apparent. These are:

1. Quartz does not appear in significant quantities until two other phases have formed.
2. Cristobalite is the first phase to form although in some series where run times are short a really sharp cristobalite pattern may not develop.
3. When cristobalite is well developed, silica K is normally present.
4. Silica-K appears to change rapidly to quartz once it is well formed.
5. In all runs the assemblages recorded are quartz, quartz and silica-K, silica-K and cristobalite, cristobalite. In one run only a very small amount of quartz was observed along with major silica-K and minor cristobalite.
6. Tridymite was not formed in any experiments in sufficient quantity to appear in an x-ray pattern.
7. Pressure has a much greater influence than temperature on the reaction rate in the temperature range studied.
8. In this system a pressure increase of 1000 bars favours the attainment of equilibrium more than a temperature increase of 100° C. This may not have been anticipated from the great mass of chemical data on temperature effects on reaction kinetics.

We may now consider what details of mechanism may be deduced from these observations. It is certain that the path followed in these reactions is:

almost amorphous silica $\rightarrow$ cristobalite $\rightarrow$ silica-K $\rightarrow$ quartz.

The change silica-K to quartz appears to occur more rapidly than stages leading to silica-K. A set of typical x-ray patterns illustrating these changes is shown in Fig. 1. It should be noted that in some longer runs at lower pressures cristobalite develops more strongly before silica-K appears. In Fig. 2 data are plotted to illustrate the effect of pressure on
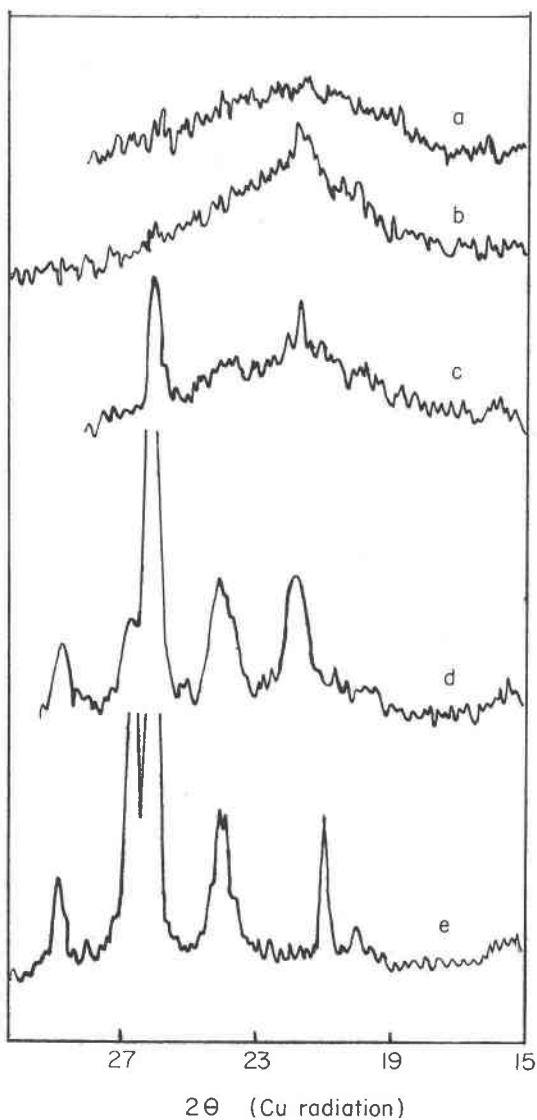
FIG. 1. A set of diffractometer patterns illustrating changes in structure with time, taken from runs at 45,000 p.s.i. and 430° C.

(a) Largely amorphous SiO_2.
(b) Cristobalite developing.
(c) Silica-K developing with cristobalite.
(d) Silica-K the major phase with cristobalite and a small amount of quartz.
(e) Silica-K the major phase with strong quartz. Cristobalite has disappeared.

TABLE 1. PHASES FORMED BY HYDROTHERMAL CRYSTALLIZATION OF SILICIC ACID AT VARIOUS PRESSURES, TEMPERATURES AND TIMES

Pressure (p.s.i.)	T° C.	t (hours)	Products
Set 1			
59,000	428	6	poor C
	440	7	K+Q
	448	8	Q
	440	9	Q
Set 2			
59,000	340	8	poor C
	330	9	Poor C
	340	10	Q
	325	12	Q
Set 3			
45,000	435	7	poor C
	442	8	poor C
	440	9	poor C
	425	9	K+C (minor Q)
	433	10	K+C
	440	12	Q+K
	440	12	K+Q
	426	13	Q
	436	14	Q
	430	14	Q
Set 4			
45,000	330	14	poor C
	330	15	K+Q
	330	16	Q
	337	18	Q
Set 5			
30,000	430	24	C
	430	48	Q+K
	438	72	Q+K
	440	96	Q
	430	120	Q
Set 6			
30,000	325	48	poor C
	334	72	K+poor C
	335	96	Q+K
	330	120	Q
Set 7			
15,000	438	576	C
	426	840	K+C
	335	840	Q

(*Note:* C=cristobalite, K=silica-K or keatite, Q=quartz. A mixture K+Q signifies that silica-K is the major phase).

the time necessary for the 100% conversion to quartz. A qualitative picture of the process is illustrated diagrammatically in Fig. 3.

The process of the formation of a new phase may be considered to involve the following steps listed on page 912.
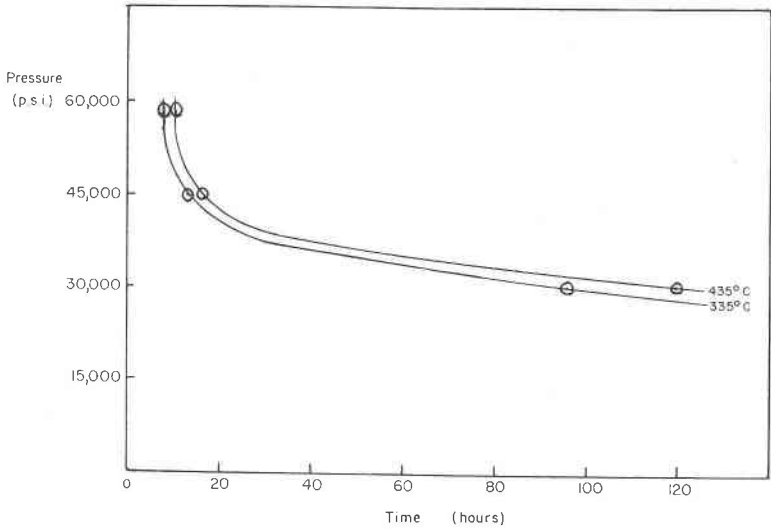
Fɪɢ. 2. The variation with pressure of the time for 100% conversion to quartz.

(a) the starting materials pass into solution,
(b) nuclei of the new phase form,
(c) nuclei of the new phase grow by transfer of material from the de-
     caying phase.

Any of these three steps can be rate controlling.

Some selection of these possibilities can be made and with this in view
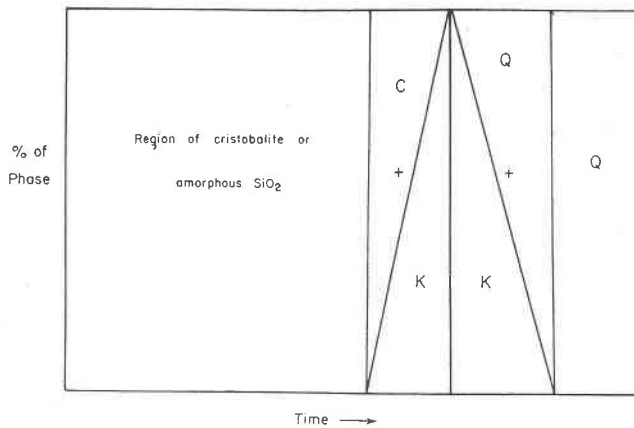some measurements were made of the rate of solution of quartz and its

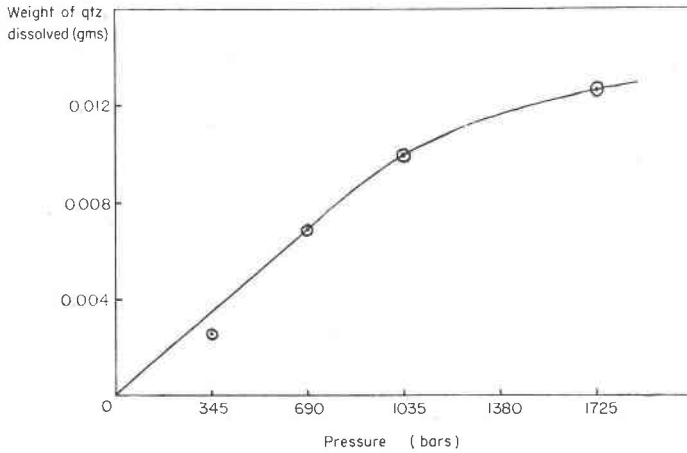Fɪɢ. 3. Diagrammatic representation of phase assemblages during typical runs.

Fɪɢ. 4. Effect of pressure on the rate of solution of quartz at 400° C.

variation with temperature and pressure. While quartz was used in these experiments, it is not unreasonable to assume that the rate of solution of the other phases of silica will show similar variation. In these experiments a single quartz crystal was suspended in a pressure vessel for a given time at constant pressure and temperature. The amount of silica which had passed into solution was determined by weight loss. It is obvious that the rate is proportional to surface area but this factor can be made negligible by using the same crystal in all experiments forming a set, and as the amount lost in each is very small a fairly constant surface area can be assumed. In Fig. 4 some results are shown for the amount dissolved in one hour at 400° C. and varying pressures. It will be noticed that the amount dissolved in unit time increases fairly steadily with pressure but tends to fall off as higher pressures are reached. In Fig. 5 data are given to illustrate the effect of temperature at constant pressure for a time of one hour. The temperature effect is quite large and tends to increase with temperature. Inspection of these results indicates no correlation with the rates of transformation with respect to both pressure and temperature. For example from the temperature effect we would anticipate a four-fold increase in the rate for 100° C. if the rate of solution was controlling. The data indicates a very much smaller effect. It is thus reasonable to assume that the rate of solution does not control the overall rate.

A study of the rate of solution at constant pressure and temperature indicated that the solution obeys an equation of the type
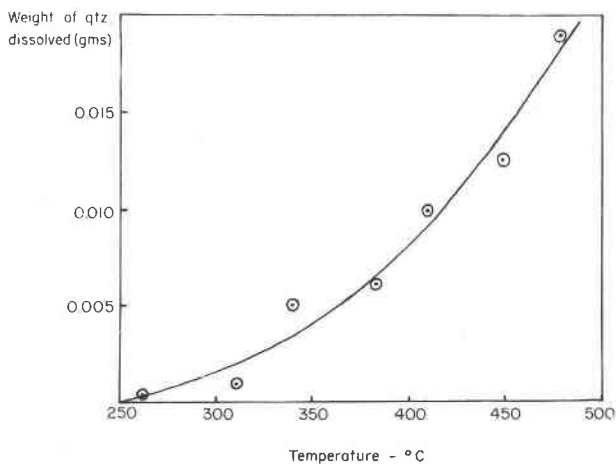
$$\frac{dw}{dt} = K(W_s - w)$$

FIG. 5. Effect of temperature on the rate of solution of quartz at 15,000 p.s.i.

This is typical of many solution processes. (1) ($w =$ weight dissolved, W_s is the weight at saturation. K is the rate constant including constant terms for the volume of the system and surface area). On integration this becomes

$$Kt = \ln \left(\frac{W_s}{W_s - w} \right)$$

and

$$\ln \left(\frac{W_s}{W_s - w} \right)$$

should be a linear function of time. A plot for a typical set of results is shown in Fig. 6. We have found, however, that the data is not of sufficient accuracy to allow calculation of other kinetic functions.

A few experiments were attempted to obtain information on the rate of growth of a quartz crystal in a solution saturated with amorphous silica. Results were erratic and present data indicate little more than that pressure increases the rate of growth. It is probably possible to eliminate rate of solution as the major factor on the following grounds. A phase should grow most rapidly in an environment where the supersaturation is largest. Thus if quartz nuclei were forming at the start of crystallization, then they should grow rapidly in the presence of amorphous silica, perhaps more so than the other possible phases. Experiments indicate that quartz does grow very rapidly from silica-K, in a small fraction of the total time, even though the supersaturation with respect to quartz must be less than in an environment with amorphous silica or cristobalite.

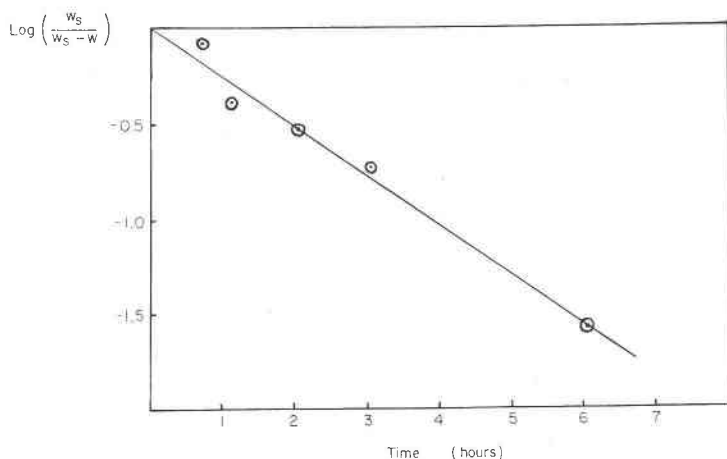If rates of growth and solution are not the controlling processes then

FIG. 6. Test of rate equation for solution of quartz, at 400° C. and 15,000 p.s.i.

we must examine the possibility that nucleation is rate controlling. The main problem in this respect is to explain the order of appearance of the phases. Normally it would be anticipated that a phase would form nuclei in a medium where the supersaturation factor is large. This is not in accord with these observations. However, in this system the amount of supersaturation cannot be very large and the results suggest that nucleation is induced on solid phases already present. Thus the starting material shows some order suggesting a relationship to cristobalite and cristobalite is the first phase of form. The general physical properties of silica-K such as density and refractive index (2) suggest that it is intermediate between cristobalite and quartz and in this case it may form nuclei on cristobalite with greater ease than quartz. Similarly, quartz might form nuclei readily on silica-K.

On this model of induced nucleation it might be expected that early formed cristobalite would produce silica-K and that this in turn would produce quartz and all would appear together. This is not typical of what is observed. An explanation can be made along the following lines. Nucleation is an unfavourable reaction and can be considered to start from a suitably oriented group of atoms condensed on a surface. It is obvious that the greater the area of suitable surface available the greater is the chance of this process occurring. In this way the number of nuclei of silica-K forming becomes large only when a large, rapidly growing surface of cristobalite is present and similarly the rate of nucleation of quartz becomes large only when a large surface of silica-K is present. This relationship to surface also explains why an added seed crystal has little effect as it presents relatively little new surface. It is also commonly observed in the experiments that pseudomorphs initially form such as

balls of cristobalite covered with a high index skin of silica-K (cf. the remarks of Keat (2) on the difficulties of refractive index determinations).

If the above arguments are reasonable then nucleation induced on other phases is the overall rate controlling process, coupled to some extent with growth. It remains to explain why this is so sensitive to pressure and less sensitive to temperature in the range examined. It is well known that alkalis catalyse the reaction and this may perhaps provide a clue. We have observed complete conversion to quartz, from the same starting materials, in a few hours in the presence of dilute KOH at 250° C. If hydroxyl ions catalyse the reaction it is possible that nucleation is controlled by the number of some species of silicate anion. The behaviour reported is not opposed to such a proposition. In the absence of alkali the silicate ion concentration will be controlled by the dissociation constants of silicic acid and dissociation constants vary steadily with pressure. Franck (3) has carried out extensive calculations on the variation of the ionic product of water in the supercritical region and one would expect other weak acids to show similarities. Pressure has a large effect on the dissociation, increasing at low pressures. The effect of temperature varies greatly depending on the region. For example, at 1000 bars and 350° C., log K_w is -10.97, while at 450° C. and 1000 bars the value is -10.90. At both these temperatures a change to 2000 bars increases the strength by a much larger factor. At other temperatures, both higher and lower, temperature may have a larger effect. With silica, as well as the acid strength increasing, the concentration in solution increases with pressure. An analysis of the kinetics suggests, however, that for the pressure effect to be explained qualitatively on the basis of a silicate ion concentration this ion would have to be doubly charged. Before any final statement can be made a wider temperature range should be studied.

It should be emphasized that the pattern followed in this series of experiments is not always observed. In a great number of experiments when glasses and mixes of compositions corresponding to Na_2O, Al_2O_3, 6–$10SiO_2$ were crystallized mixtures of quartz and cristobalite were formed but never silica-K. Tridymite did not appear even at temperatures above 800° C. A few experiments with a much less dense sample of silica gel indicated that the rate was much slower. In all these runs the same pressure sensitivity was observed.

REFERENCES

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3. E. U. Franck, "Ionendissoziation von HCl, KOH und H_2O in überkritischem Wasser," *Zeit. Phys. Chemie*, **8**, 192, (1956).