uncertainty. Since it is now known that units of the Idaho batholith contain a widespread varied assemblage of U-Th-Nb-Ta species as accessory constituents and since no similar assemblages, either in igneous rocks or derived placers, are reported for the Boulder batholith, this relationship might offer an additional characteristic for correlating these intrusive units.

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HYDROXYL ION CATALYSIS OF THE HYDROTHERMAL CRYSTALLIZATION OF AMORPHOUS SILICA; A POSSIBLE HIGH TEMPERATURE pH INDICATOR

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INTRODUCTION

A study has been made of the effect of hydroxyl ion concentration on the time for the formation of quartz from silicic acid at 245° C. The time appears to be almost a linear function of reciprocal hydroxyl ion concentration. It is considered that all observations on this crystallization can be explained by a mechanism involving the concentration of a singly charged silicate anion as the rate controlling species. The effect of other mineral substances, in particular silicates, on this reaction may provide a method of determining the extent of hydrolysis of these minerals at moderate temperatures.

Previously a number of workers have found that when amorphous silica is crystallized under hydrothermal conditions, a number of intermediate phases tend to develop before the stable phase quartz is formed. Corwin et al. (1953) have shown that in a fixed time either cristobalite or quartz is produced, quartz being favored by high pH. Carr and Fyfe

(1958) studied the effect of pressure, and to a less extent temperature, on the process in pure water and found that the reaction was much more sensitive to pressure changes than temperature and that quartz formed only after the appearance of both cristobalite and silica-K (keatite). They considered that the rate was controlled basically by induced nucleation and that the pressure sensitivity might by explained with reference to the effect of pressure on the dissociation of silicic acid.

The present experiments were designed to obtain more data on the effect of hydroxyl ion concentration so that some definite selection of the rate controlling species might be possible.

Experimental

Small stainless steel test-tube bombs with a capacity of 1.5 ml. were used. Ignited silicic acid was sealed in a silver tube with 0.1 ml. of carbonate free sodium hydroxide. The amount of silica used was always sufficient to maintain a molar ratio of silica to hydroxide of the order of one hundred. This silver tube was placed in the bomb and sodium hydroxide solution added on the outside to balance the pressure in the tube. The pressure in the vessel must be nearly that of pure water at 245° C.,

Table 1. Products of Crystallization of Amorphous Silica

NaOH Concentration	Time (Hours)	Products	
		Cristobalite	Quartz
0.100 Molar	15	poor	—
0.100 Molar	16	poor	v. weak
0.100 Molar	17	poor	weak
0.100 Molar	18	poor	weak
0.100 Molar	19	—	almost 100%
0.100 Molar	20	—	100%
0.017 Molar	20	poor	—
0.017 Molar	40	poor	—
0.017 Molar	70	weak	—
0.017 Molar	80	strong	weak
0.017 Molar	90	weak	strong
0.017 Molar	100	—	almost 100%
0.017 Molar	110	—	100%
0.012 Molar	50	poor	—
0.012 Molar	70	weak	—
0.012 Molar	90	strong	—
0.012 Molar	120	strong	weak
0.012 Molar	130	V. strong	weak
0.012 Molar	140	—	100%

i.e. 36 bars. The starting material, powdered silicic acid (Mallinckrodt Chem. Co.) was ignited at 700° C. for 24 hours before use. This was found necessary, as otherwise water from silicic acid dilutes the alkali during the course of the run. *X*-ray patterns indicated that no detectable change in structure of the material occurred with this heating and the broad hump in the region of the strong cristobalite line remained little altered. Identification of all phases formed was by means of a Phillips *x*-ray diffractometer.

RESULTS AND DISCUSSION

Experiments were carried out at three hydroxyl ion concentrations to find the minimum time for complete formation of quartz. Obviously, a greater range of concentrations was difficult to use as times were either too short or inconveniently long. A summary of critical results from some 56 runs is given in Table 1. With short time runs, normally at least four were carried out and the behavior was reproducible to within one hour.

The results in the above table support a number of conclusions that may have bearing on the mechanism of the reaction.

1. Quartz does not appear until cristobalite has first been formed. How well the cristobalite develops depends on the strength of the sodium hydroxide used, and hence on the length of the run.
2. When cristobalite is well developed, quartz is usually present.
3. Tridymite and silica-K were not formed in sufficient quantity to show on an *x*-ray pattern.
4. The change cristobalite to quartz is much more rapid than the reaction amorphous silica to cristobalite.

Analysis of the above results indicates, that within the experimental uncertainty, the time for 100% formation of quartz is a linear function of 1/[NaOH]. For each strength of sodium hydroxide it is possible to estimate the concentrations of various possible reacting species present, in particular $Si(OH)_4$, OH^-, $H_3SiO_4^-$ and $H_2SiO_4^{--}$. In this range experimental values of K_w are available from Noyes and Kato (1907). Values for the first and second dissociation constants of silicic acid were taken from Greenberg and Price (1957) and Harman (1927). These latter values were extrapolated to 245° C. using a relation suggested by Pitzer (1937) which appears to hold fairly well to temperatures near 250° C. but is not adequate at higher temperatures (Ellis and Fyfe, 1957). Data on the solubility of quartz and amorphous silica were taken from Kennedy (1950). At 250° C. a saturated solution of amorphous silica has a concentration of 2.1×10^{-2} molar while a solution saturated with respect to quartz is 8.3×10^{-3} molar. The solutions used are always saturated with silica and Alexander, Heston and Ihler (1954) have shown that in such

TABLE 2. ESTIMATED CONCENTRATIONS OF IONIC SPECIES IN SILICA-SODIUM HYDROXIDE SOLUTIONS

[NaOH] (Initial)	0.100	0.017	0.012
$[H_3SiO_4^-]$	0.100	0.017	0.012
$[OH^-]$	1.5×10^{-2}	2.5×10^{-3}	1.8×10^{-3}
$[H_2SiO_4^{--}]$	2.3×10^{-4}	6.0×10^{-6}	3.1×10^{-6}

solutions the dominant species are $Si(OH)_4$ and $H_3SiO_4^-$. The hydroxyl ion concentration is given by the expression

$$[OH^-] = K_w[H_3SiO_4^-]/K_{a1}[Si(OH)_4]$$

and the concentration of $H_2SiO_4^{--}$ by the expression

$$[H_2SiO_4^{--}] = K_{a1}K_{a2}[Si(OH)_4][OH]^2/K_w^2.$$

It is assumed that the concentration of $H_3SiO_4^-$ is the same as the added sodium hydroxide. As the silicic acid is converted to quartz, the concentration of $Si(OH)_4$ in solution will decrease and the concentrations listed in Table 2 refer to initial experimental conditions. Using the concentrations in Table 2 and the experimental time for the 0.017 molar sodium hydroxide solution it is possible to predict the times required at the other concentrations. These predicted values are compared with the experimental values in Table 3. It is apparent that either OH^- or $H_3SiO_4^-$ could be rate controlling.

CONCLUSIONS

The results of crystallization in alkaline solutions indicate that either OH^- or $H_3SiO_4^-$ is the rate controlling species in the reaction. It might also be argued that the total amount of silica in solution determines the rate. This latter possibility can probably be eliminated by consideration of the pressure sensitivity in pure water found by Carr and Fyfe (1958) which is of a different order of magnitude to the effect of pressure on the solubility. Further, that hydroxyl is rate controlling can also be eliminated from consideration of the pressure effect. As silicic acid is a stronger acid than water and as the dissociation will increase with pressure (Ellis and Fyfe, 1957) then the concentration of hydroxyl in a pure water solu-

TABLE 3. ESTIMATED QUARTZ CRYSTALLIZATION TIMES

Strength of NaOH solution	0.100	0.012
Time if $[OH^-]$ rate controlling	17	140
Time if $[H_2SiO_4^{--}]$ rate controlling	3	190
Time if $[H_3SiO_4^-]$ rate controlling	17	140
Experimental values	18	140

tion should decrease with increasing pressure. It should be emphasized that both these arguments are only qualitative for they do not take into account changes in the rate constant with pressure and as yet data do not allow a sufficiently accurate analysis to completely settle the argument. It does appear, however, that all results can be reasonably explained if it is assumed that the rate is proportional to the concentration of $H_3SiO_4^-$ or a singly charged silicate anion. Goto (1955) has found that hydroxyl ions accelerate the polymerization of silicate ions in solution and it is not surprising that the present process involves similar factors.

From silica crystallization studies two features which have some general bearing on hydrothermal studies emerge. First, if the time for formation of quartz from a given type of silicic acid or amorphous silica is a measurable function of hydroxyl ion activity, then this time can be used as a pH indicator in more complicated environments. Chemists have long used catalytic effects of hydrogen ions as pH indicators in systems where chemical complications exclude the use of more direct techniques. As yet, we certainly do not have any simple method of measuring pH at elevated temperatures directly. It is planned to explore this aspect of the work in the very near future. It is hoped that it will be possible to obtain some information on the hydrolysis of complex aluminosilicate anions. Second, the results show clearly that it is possible to catalyze silicate reactions and to reduce the time for attainment of equilibrium by factors of the order of hundreds and thousands. At low temperatures it is a most difficult problem to obtain anything approaching equilibrium in silicate systems (e.g. Coombs et al., 1959) and it appears that serious consideration should be given to the mechanism of some more complex crystallizations so that possibilities of catalysis are fully appreciated.

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