each case a separate distinct pattern was obtained. This indicates that in the reaction of zirconium tetramandelate with ammonia and sodium bicarbonate, no extensive hydrolysis takes place but a new salt-like compound is formed.

These studies show that zirconium tetramandelate must be a chelate type compound as postulated by Feigl. The reaction of ammonia with an excess of zirconium tetramandelate can be formulated

$$H_4Zr(C_8H_6O_3)_4 + 3NH_4OH \longrightarrow (NH_4)_3HZr(C_8H_6O_3)_4 + 3H_2O$$

An alternate explanation would be that three molecules of mandelic acid form a chelate ring with zirconium whereas the fourth molecule of mandelic acid forms a simple salt-like linkage. This would require that zirconium have a coördination number of 7, which is unlikely.

When an excess of ammonia is added, some of the tetrabasic salt $(NH_4)_4Zr(C_8H_6O_3)_4$ is formed. The reaction, however, is not stoichiometric as indicated by the molar ratio 1:3.5 of zirconium tetramandelate to ammonia. With other weak bases and basic salts, like sodium carbonate, corresponding reactions take place. With strong bases, however, hydrolysis takes place and zirconium hydroxide is precipitated. Because of the lack of stoichiometry the above reactions are not suitable as analytical methods.

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Oxygen Exchange in the Hydrothermal Growth of Quartz[1]

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During investigation of the mechanism of the isothermal formation of α-quartz at 400° and 340 atm. in sodium fluoride solutions, several oxygen exchange experiments were performed. By assuming that all of the oxygen atoms were equivalent and that the exchange was controlled by a homogeneous phase reaction between dissolved silica and water, complete isotopic exchange was observed.[2] On the basis of similar assumptions it has recently been shown that at 750° and at 960° the exchange reaction follows first-order kinetics.[3] In the latter experiments, however, the product was not identified and the degree of oxygen exchange per mole of silica was not determined.

The purpose of this note is to report some additional experiments on the exchange of oxygen in the silica–water system in the absence of fluoride ion.[4] Two sets of results were obtained. In the first of these all of the silica reacting was in the water phase, *i.e.*, dissolved, during all or most of the reaction time of 48 to 144 hours, and complete isotopic exchange was observed. On the other hand in those experiments where silica glass was converted into α-quartz, only partial isotopic exchange was observed.

Three different nutrient solutions prepared with water having a sevenfold O^{18} enrichment were used. These were 2 *M* sodium carbonate, 0.025 *M* sodium hydroxide and 0.025 *M* sodium chloride adjusted to a *p*H of 10 with sodium hydroxide. In the isothermal experiments using the sodium hydroxide and sodium chloride solutions the autoclaves and control equipment, the experimental procedure for the hydrothermal conversion of silica glass to α-quartz, the method of analysis for O^{18} and the procedure for calculating the degree of oxygen exchange were the same as those described previously.[2,5]

In the two experiments made with the 2 *M* sodium carbonate solutions, the gradient method of Nacken[6] was used, *i.e.*, the top and the bottom of the autoclaves were maintained at 380 ± 5° and 360 ± 5°, respectively, for 144 hours. In one of these experiments (No. 869) using 30 g. of α-quartz as the source of silica, 13.6 g. of the silica was found as an alkali soluble sludge in the bottom of the autoclave. In the second experiment (No. 872) using 30 g. of silica glass, 14 g. of the source material was found as an alkali-soluble sludge while the remainder was converted into α-quartz. The silica found in the sludge corresponds to the solubility of α-quartz in sodium carbonate solutions at 350–400°[7] and was probably present as soluble silica during the experiment.[6,7]

In order to calculate the degree of oxygen exchange in the gradient runs it was first necessary to determine the degree of exchange between water and sodium carbonate and between water and soluble silica under the conditions of our experiments. Accordingly separate runs were made with sodium carbonate and with disodium dihydrogen silicate solutions. As a further check on the procedure, additional experiments were also made using sodium sulfate solutions. The results of these various experiments are listed in Table I and indicate that complete oxygen exchange should occur in both the water-carbonate and the water-soluble silica systems during the gradient runs. This was confirmed in experiment no. 869 in which α-quartz was used as the source of the silica (see Table II). In the second gradient experiment in which silica glass was converted into α-quartz the degree of oxygen exchange was calculated by assuming that complete oxygen exchange occurred between the carbonate initially present and the silica ultimately found in the sludge. The results of this experiment are included in Table II.

The results of the isotopic exchange experiments in which silica glass was completely converted into α-quartz under isothermal conditions at 400° and 340 atm. using the sodium hydroxide and the sodium chloride solutions are summarized in Table III.

The complete isotopic exchange which is reported in Table I for the water–dihydrogen silicate system at 100° and in Table II for experiment No. 869 indicates that during the course of these experiments equilibria involving monomeric[8] silica had

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[1] The results and interpretations presented here are derived from work supported on contract between Antioch College and the U. S. Army Signal Corps through its Signal Corps Engineering Laboratories at Fort Monmouth, New Jersey.

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Table I

Oxygen Exchange with Water Soluble Oxy-ions

Soln.	Temp., °C.	Time, hr.	No. of runs	F
2 M Na_2CO_3	370	144	3	0.98 ± 0.01
0.1 M $Na_2H_2SiO_4 \cdot 8H_2O$	100	48	2	1.00 ± .02
2 M Na_2SO_4	400	48	2	0.54 ± .01

Table II

Summary of H_2O–SiO_2 Exchange under Gradient Conditions[a]

Run no.	Silica source	Products, g.	F
869	α-Quartz	16.4 α-quartz, 13.6 amorphous silica	1.00[b]
872	Silica glass	16 α-quartz, 14 amorphous silica	0.42[c]

[a] Top of bomb 380 ± 5°, bottom 360 ± 5°, 144 hours, 30 g. source, 2 M Na_2CO_3, 50% filling. [b] Calculated only for amorphous silica found as an alkali-soluble sludge. [c] Calculated for silica converted into α-quartz assuming complete exchange for the remainder.

Table III

Summary of H_2O–SiO_2 Exchange under Isothermal Conditions[a]

Soln.	Initial pH	No. of runs	F
0.025 M NaCl	10[b]	5	0.72 ± 0.03
.025 M NaOH	12.4	4	0.61 ± .02

[a] 400°, 350 atm., 48 hours, 50% filling, silica glass source. [b] Adjusted with NaOH.

been obtained. Secondly, the partial oxygen exchange observed in those experiments in which silica glass was converted to α-quartz indicates that the mechanism of the exchange reaction is different from that required for the crystallization of α-quartz and that, under the conditions of these experiments, the latter reaction is the more rapid. It seems reasonable, then, that the exchange reaction in the water–silica system, like that of the water–carbonate[9] and water–hydrogen sulfate systems,[10] would involve the neutral acid, $Si(OH)_4$, while the crystallization process involves a silicate ion.[11] This would be in agreement with the observation noted in Table III that under isothermal conditions a lower pH favors the degree of oxygen exchange. That the crystallization of α-quartz involves a silicate ion rather than a neutral molecule has also been demonstrated in this Laboratory from the results obtained when silica glass is heated at 400° in buffered solutions at various pH's.[4]

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