Experimental Study of Amorphous Silica Crystallization in Na_2CO_3–$NaHCO_3$ Solutions as a Source of Chert Formation in Lake Magadi

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Amorphous silica was treated with Na_2CO_3–$NaHCO_3$ and Na_2CO_3–$NaHCO_3$–NaCl solutions, which are related to the alkaline brine in Lake Magadi in East Africa; its transformation was followed as a function of time under various temperatures (100—160 °C) and pHs (8—12). The reaction occurred in steps. Three kinds of sodium silicates (magadiite, kenyaite, and SiO_2-X_2) appeared as intermediate phases in solutions with various pH, and finally converted into quartz. The rate of formation of naturally occurring silicates and quartz (chert) was roughly estimated by extrapolating the basis of the data on the temperature dependence of the conversion rate. From those crystallization observations, the preparation conditions for obtaining well-crystallized silicates were determined, and kenyaite was synthesized, which has note yet been obtained as a highly crystallized compound.

In 1967 two new hydrous sodium silicates, magadiite ($Na_2Si_{14}O_{29}\cdot nH_2O$) and kenyaite ($Na_2Si_{22}O_{45}\cdot nH_2O$), and chert (quartz) were found in the lake beds of Lake Magadi, Kenya.[1)] It was thought that magadiite chemically precipitated from the alkaline lacustrine brines, and that the percolating waters converted the magadiite to kenyaite and eventually to chert. Magadiite was subsequently identified in Oregon and California.[2,3)] It occurred in the playa sediments of Alkali Lake, Oregon. The brines in these lakes were highly alkaline sodium carbonate–sodium hydrogencarbonate waters containing abundant SiO_2 attributed to weathering. It is important to determine the reaction mechanism of the formation of magadiite, kenyaite, and quartz (chert) in nature, because this inorganic mechanism may explain the formation of many bedded cherts.

On the other hand, three silicates, which appear as intermediates, are constructed as layered structures which are able to accomodate a guest molecule or ion by an intercalation reaction, such as clay minerals. From the standpoint of the preparation of a host compound, Beneke and Lagaly[4)] synthesized magadiite and kenyaite from aqueous suspensions containing amorphous silica and NaOH at 100—150 °C. At 100 °C, magadiite generally precipitated as the first reaction product, and was then altered to kenyaite with quartz being the stable end product. They concluded that the transformations were in fair agreement with the field observations of Eugster[1)] and McAtee et al.[5)]

Kitahara et al.[6)] and Muraishi[7—9)] examined the crystallization of amorphous silica into quartz in various alkaline hydrothermal solutions. It was observed that amorphous silica transformed into quartz through various sodium silicates (i.e., amorphous silica → magadiite → SiO_2-X_2 → quartz).

In this study, the crystallization of amorphous silica was investigated in Na_2CO_3–$NaHCO_3$ and Na_2CO_3–$NaHCO_3$–NaCl solutions, which are implicated in chert formation in Lake Magadi in East Africa and in Alkali Lake, Oregon. The effects of the temperature, pH, and sodium concentration of the solution on the crystallization were studied in order to obtain a clue concerning the process of the formation of magadiite, kenyaite, and quartz in an alkali lake. In addition, the other object of this study was to find suitable conditions for preparing well-crystallized silicates based on the crystallization data.

Materials and Methods

Reagents: Commercially available silica gel (Wako Pure Chemical, Wakogel Q-22) was used as a starting material, and aerosil (Japan Aerosil) and laboratory manufactured silica gel (produced by the hydrolysis of sodium silicic acid) were used as comparison samples.

Experimental Operation: The medium solution for the crystallization of silica gels was prepared by mixing 1/2 M Na_2CO_3 and 1 M $NaHCO_3$ ($1\ M=1\ mol\,dm^{-3}$) at a definite rate and adjusting for each 0.4—1.2 pH unit. The crystallization experiments were carried out in the respective solution adjusted to various pHs. The starting material (0.5 g silica gel) was suspended in 15 ml of the solution. The suspensions were treated for a definite time and quenched to room temperature. They were then filtered off under reduced pressure. The filtrate was measured by a pH meter, and the residue was identified by an X-ray diffractometer and TGA-DTA after washing and drying. The filtrate changed in pH by about 0.3 unit before and after the run. A vessel made of Teflon with a 10—100 ml capacity was used as the reaction vessel. The vessel containing the suspension was placed in a pressure-resistant vessel made of stainless steel, and was heated in an electric furnace. The reaction products were identified using a Rigaku XGC-20 X-ray diffractometer and a Rigaku TGA-DTA. The chemical composition of the products was determined by atomic adsorption.

Results and Discussion

1. Effect of the pH of the Solution on the Crystallization Process. Amorphous silica was first treated with Na_2CO_3–$NaHCO_3$ solutions with various pH values (pH=8.2, 8.6, 9.0, 9.4, 9.8, 10.5, and 11.7), which were prepared by mixing Na_2CO_3 with $NaHCO_3$ in various molar ratios. Three types of pathways for the transformation of amorphous silica to quartz were observed, and can be summarized as follows:

At pH values above 10

$$am\,SiO_2 \rightarrow \mathrm{mag} \rightarrow X_2 \rightarrow \mathrm{qtz} \tag{1}$$

In a pH range of 9.5—10

$$am\,SiO_2 \rightarrow X_2 \rightarrow \mathrm{qtz} \tag{2}$$

At pH values below 9.5

$$am\,SiO_2 \rightarrow \mathrm{ken} \rightarrow \mathrm{qtz} \tag{3}$$

In the above, *am* SiO_2, mag, ken, X_2, and qtz represent amorphous silica, magadiite, kenyaite, SiO_2-X_2, and quartz, respectively. SiO_2-X_2 is an alkali silicate ($M_2Si_{20}O_{41}\cdot nH_2O$, M=K, Na, n=8—10), which was named by Mityuku,[10] and is very similar to kenyaite regarding its XRD structure.[9]

It was also observed that the appearance period of those intermediate products (magadiite, kenyaite, and SiO_2-X_2) and the time of 100% conversion to quartz varied with the pH of the alkaline medium solution. These results are summarized as functions of the pH and reaction time in Fig. 1. (In Fig. 1, two kinds of lines are depicted to compare with the pathway for the transformation in Na_2CO_3–$NaHCO_3$ solution (broken line) and those in Na_2CO_3–$NaHCO_3$–NaCl solution (solid line)).

Some characteristic results are shown in Fig. 1.

(1) All sodium silicates (magadiite, kenyaite, and SiO_2-X_2) were metastable in an alkaline solution.

(2) The pH dependence of the rate of crystallization of amorphous silica and the conversion to quartz differs markedly at around pH 10.

The stability relations for sodium silicates[11] in this way were mainly dependent on the pH of the solution, because the solutions were supersaturated with respect to amorphous silica, and were held constant at 1 mol dm^{-3} of sodium ion. However, only the pH value could not explain the drastic changes at about pH 10. It is thought that the changes would be attributable to an alteration in the species of soluble silica with the pH.[12—14] The solubility of amorphous silica in water (around neutrality) is in the range of 100—150 ppm at 20—30 °C. The soluble species is $Si(OH)_4$ (or H_4SiO_4), which is an uncharged molecular species,

$$SiO_2 + 2H_2O = Si(OH)_4. \tag{4}$$

In this case, the solubility of silica is little affected by a change in the pH of the solution. When a solution is above pH 9, the solubility is about 1000 ppm or more. The soluble species is altered mainly to $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ as

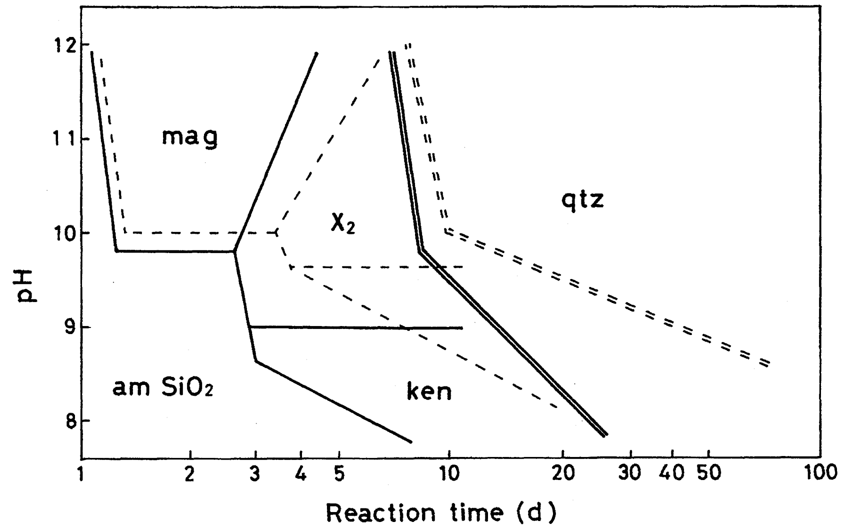

Fig. 1. Effect of pH on amorphous silica crystallization in Na_2CO_3–$NaHCO_3$ (- - -) and Na_2CO_3–$NaHCO_3$–NaCl (—) solutions as a function on time. Reaction temperature: 160 °C, concentration of Na: 1 M for Na_2CO_3–$NaHCO_3$ solution and 2 M for Na_2CO_3–$NaHCO_3$–NaCl solution. am SiO_2: amorphous silica, mag: magadiite, X_2: SiO_2-X_2, ken: kenyaite, qtz: quartz.

$$H_4SiO_4 + OH^- = H_3SiO_4^- + H_2O \qquad (5)$$

and

$$H_3SiO_4^- + OH^- = H_2SiO_4^{2-} + H_2O. \qquad (6)$$

The solubility of silica therefore increases linearly with an increase in pH. It is thought that the variation in these soluble species with the pH value induces different chemical processes (e.g., dissolution–precipitation process) and different physical processes (e.g., nucleation process) for the crystallization of amorphous silica. As a results, the mode of the formation of silicates and the rate of crystallization into quartz may have drastically changed at around pH 10.

In fact, magadiite could be easily prepared in solution above pH 10, irrespective of the kind of alkali (e.g., the Na_2CO_3–$NaHCO_3$ system, NaOH–NaCl system, or Na_2CO_3 alone). On the other hand, kenyaite was prepared only by adding a large quantity of $NaHCO_3$ to a solution of the Na_2CO_3–$NaHCO_3$ system.

2. Effect of the Na^+ Ion Concentration on Crystallization. In Lake Magadii, NaCl is the principal constituent of the lake as well as Na_2CO_3 and $NaHCO_3$. The Na_2CO_3–$NaHCO_3$–NaCl solution was used for investigating the effect of the concentration of the Na^+ ion on the rate of crystallization of amorphous silica. When 1 mole of NaCl was added to 1 mol dm^{-3} Na_2CO_3–$NaHCO_3$ solutions, the formation of sodium silicates (magadiite, SiO_2-X_2, and kenyaite) was shifted to a lower pH region, and the rate of crystallization of amorphous silica and the transformation to quartz was accelerated. The results are shown in Fig. 1 (illustrated by solid lines). This alteration upon the addition of NaCl is explicable as follows. The solubility equilibrium is represented by the following equation:

$$\underset{\text{(magadiite)}}{Na_2Si_{14}O_{29}\cdot 10H_2O} + 2H^+ + 17H_2O = 2Na^+ + \underset{\text{(soluble silica)}}{14H_4SiO_4} \qquad (7)$$

The addition of Na^+ ion therefore caused sodium silicates to precipitate, even in a lower pH solution. Na^+ ion also acts as a catalyst, which accelerates the rate of nucleation and crystallization. The effect of the Na^+ ion concentration on the rate was remarkable at pH 9.5 or below, at which soluble silica is mainly a neutral species (H_4SiO_4, as shown in Eq. 4). However, the addition of NaCl in the Na_2CO_3–$NaHCO_3$ solutions did not cause any significant change in the kinds of intermediate phases and the quartz formation process.

3. Effect of Temperature on the Conversion to Quartz. The process of the conversion and the rate of crystallization of amorphous silica to quartz were observed at various temperatures (100, 120, 140, and 160 °C). In all runs, the Na_2CO_3–$NaHCO_3$ solution adjusted to a pH of 10.5 was used as the medium solution. The resulting conversion curves as a function of time are shown in Fig. 2. In this figure, the ordinate represents the relative amounts of products measured by X-ray diffractometry. The abscissa indicates the reaction time. The parenthesized numbers represent the time (t_q) to 100% conversion to quartz.

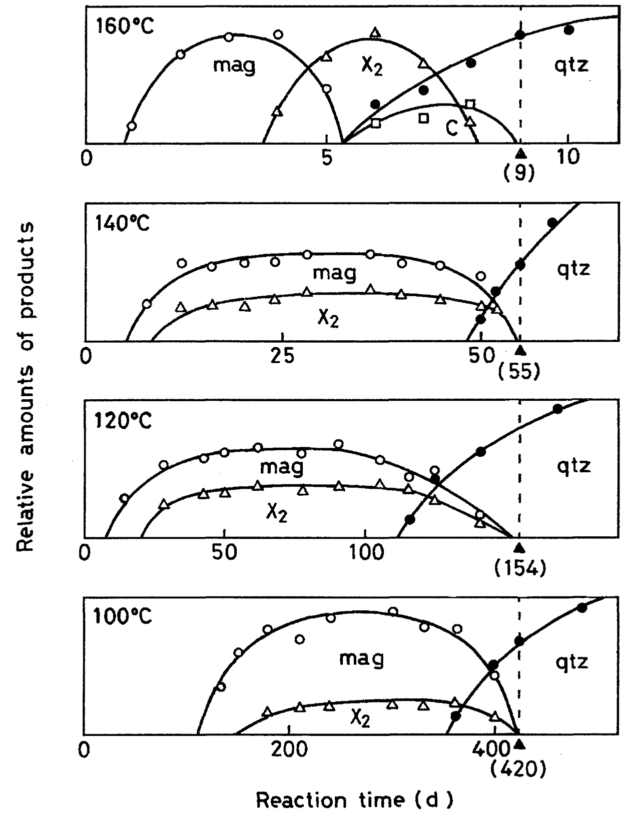

Fig. 2. Effect of temperature on amorphous silica crystallization in Na_2CO_3–$NaHCO_3$ solution in the temperature range 100 to 160 °C. The ordinate represents relative amounts of products. The parenthesized numbers represent the time of 100% conversion to quartz. The abbreviations are the same as that of Fig. 1.

At a temperature of 160 °C, magadiite was transformed consecutively into SiO_2-X_2, cristobalite, and the final product quartz, as follows;

$$am\ SiO_2 \rightarrow \text{mag} \rightarrow X_2 \rightarrow \text{csb} \rightarrow \text{qtz} \qquad (8)$$

where csb represents cristobalite.

At a temperature of 140 °C or below, magadiite precipitated as the chief intermediate product along with SiO_2-X_2,

$$\begin{tikzcd} am\ SiO_2 \arrow[r] \arrow[dr] & \text{mag} \arrow[r] & \text{(csb)} \arrow[r] & \text{qtz} \\ & X_2 \arrow[ur] & & \end{tikzcd} \qquad (9)$$

The lifetime of these intermediate products increased along with a decrease in the temperature, and the formation of SiO_2-X_2 decreased quantitatively with it.

In some additional experiments below 100 °C, no SiO_2-X_2 could be observed. Thus, magadiite finally becomes the only intermediate product in the course of the crystallization of amorphous silica below 100 °C,

$$am\,\mathrm{SiO_2} \rightarrow \mathrm{mag} \rightarrow \mathrm{qtz}. \tag{10}$$

This simple route is thought to be part of the quartz (chert) formation process in a natural alkali saline lake.

Using these results concerning the temperature dependence of the rate of crystallization, we then tried to estimate the time of conversion to quartz (chert) from amorphous silica under the condition at 30 °C, which is the average temperature in Lake Magadi in East Africa.

The experimental data were analyzed as follows. The time of conversion to quartz was used as an indicator of the reaction rate. The logarithms of the reciprocal of the time to 100% conversion to quartz ($\log(1/t_\mathrm{q})$) were plotted as a function of the reciprocal of the reaction temperature ($1/T$), which corresponds to the Arrhenius plot of $\log k$ versus $1/T$ to obtain the activation energy. For this reaction, the reciprocal of the time to 100% conversion to quartz $1/t_\mathrm{q}$ was used instead of k, which is a rate constant, as described above; $1/t_\mathrm{q}$ represents the mean rate of the reaction. The results are shown in Fig. 3. It can be seen that a plot of $\log(1/t_\mathrm{q})$ versus $1/T$ gives a straight line, except for plot of the data for 160 °C. This linear relationship seems to be based on a similar reaction mechanism. The slope for the straight line is represented by

$$\log(1/t_\mathrm{q}) = -3.4\times 10^3/T + 6.5. \tag{11}$$

The time for quartz formation at a temperature below 100 °C, even at an ordinary temperature, can be estimated by extrapolation, provided that the reaction mechanism does not change over the range of these temperatures. Using this equation (Eq. 11), the time of quartz formation in an alkaline solution at 30 °C was roughly estimated for 150 years. These extrapolated results are particularly surprising because quartz is considered to be formed over a period of thousands of years or longer at ordinary temperatures.[14)]

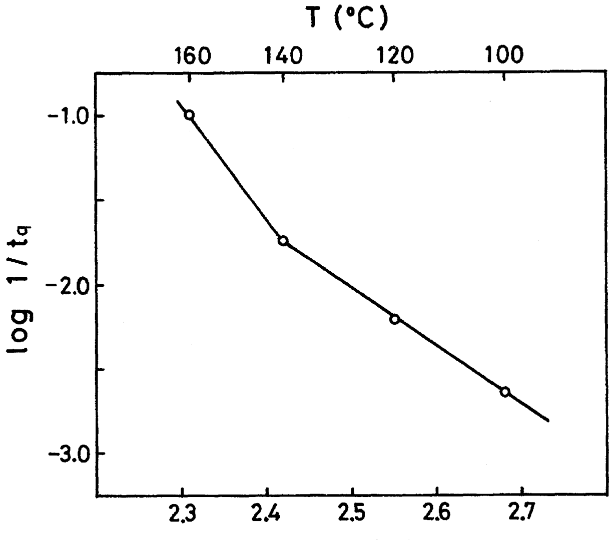

Fig. 3. Relationship between $\log(1/t_\mathrm{q})$ and $1/T$. The symbol "t_q" represents the time of 100% conversion to quartz obtained in Fig. 2.

It has been thought that the temperature of both the brines and the inflow waters in an alkali lake is considerably above 25 °C, in some cases reaching 85—90 °C, and that the brines are supersaturated with both silica and kenyaite, or magadiite in many cases.[15)] The pH of the brines may be as high as 11.0, and the silica contents can exceed 2500 ppm. These data suggest that the precipitation of magadiite increases very rapidly with increasing temperature, and that its solubility also increases with it. It is considered from those facts that amorphous silica transformes rapidly into quartz in an alkali saline lake, such as Lake Magadi.

4. Characterization of the Formation of Magadiite and Kenyaite. It was found that magadiite, kenyaite, and chert (quartz) have coexisted in the lake beds of Lake Magadi. The formation of those silicates and silica has been thought to be based upon the following consecutive reaction:

$$\underset{\text{(silicic acid)}}{am\,\mathrm{SiO_2}} \rightarrow \mathrm{mag} \rightarrow \mathrm{ken} \rightarrow \underset{\text{(chert)}}{\mathrm{quartz}} \tag{12}$$

This reaction was proposed by Eugster[2)] and Rooney et al.[3)] Their view can be represented as follows. Magadiite may have precipitated directly in a solution that was substantially supersaturated with respect to amorphous silica. When magadiite reacted with fresh water,

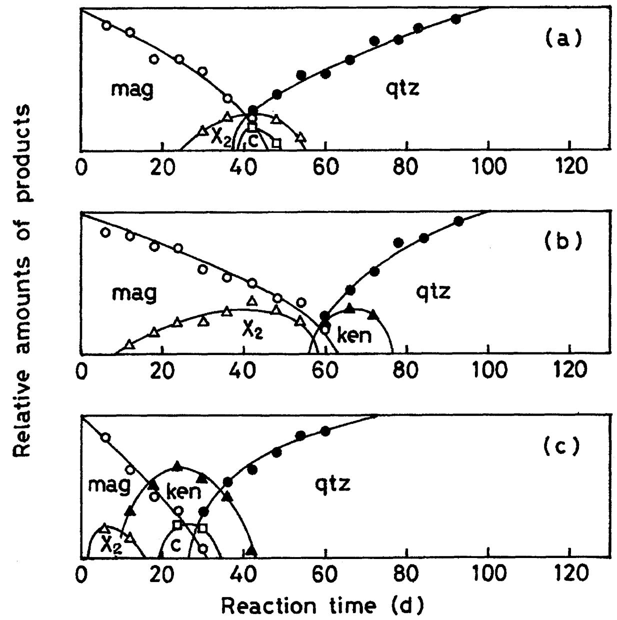

Fig. 4. Transformation of magadiite in the various solutions at 140 °C. (a): The reaction in distilled water, (b): The reaction in the $\mathrm{Na_2CO_3}$–$\mathrm{NaHCO_3}$ solution adjusted at pH 9.5, (c): The reaction in the solution adding amorphous silica to the solution used in run (b). The ordinate represents relative amounts of products as shown in Fig. 2.

the chemical transition took place only by the removal of Na^+ ion according to the following equation, and partial hydration and dehydration:

$$\underset{\text{(magadiite)}}{Na_2Si_{14}O_{29}\cdot nH_2O} \xrightarrow{-Na^+} \underset{\text{(kenyaite)}}{Na_2Si_{22}O_{45}\cdot nH_2O} \xrightarrow{-Na^+} \underset{\text{(chert)}}{SiO_2} \tag{13}$$

This stepwise reaction was not observed in our run in a definite alkaline solution. To ascertain the possibility that magadiite transforms into kenyaite, the stepwise reaction was followed using magadiite as a starting material in various medium solutions:

(1) First, magadiite was reacted with various amounts of fresh water at 140 °C. Magadiite transformed into quartz through SiO_2-X_2 and cristobalite without forming kenyaite in any case. One of the results is shown in Fig. 4(a).

(2) Next, magadiite was reacted with a Na_2CO_3–$NaHCO_3$ solution adjusted to pH 9.5 or below, in which amorphous silica was transformed into kenyaite, as described above. It was found that kenyaite was not directly transformed from magadiite, but was formed through SiO_2-X_2, such as in the magadiite → SiO_2-X_2 → kenyaite → cristobalite → quartz transformation. The result is shown in Fig. 4(b).

(3) When magadiite was reacted with a Na_2CO_3–$NaHCO_3$ solution supersaturated with respect to amorphous silica adjusted to pH 9.5 or below, magadiite directly transformed into kenyaite. A reaction like this may be represented by

$$\underset{\text{(magadiite)}}{Na_2Si_{14}O_{29}\cdot 10H_2O} + 8SiO_2 = \underset{\text{(kenyaite)}}{Na_2Si_{22}O_{45}\cdot 10H_2O} \tag{14}$$

The results is shown in Fig. 4(c).

From these results, it was found that the transformation of magadiite into kenyaite could have taken place when the compositions of the alkali-medium solutions were altered after the formation of magadiite from amorphous silica, e.g., (1) when magadiite was exposed to an alkaline solution diluted with an inflow of water into the alkali lake, and (2) when magadiite was exposed to alkaline solutions which were abundant in silicic acid or sodium hydrogencarbonate.

5. Preparation Conditions of Magadiite, Kenyaite, and SiO_2-X_2 as a Single Phase. It is important to synthesize well-crystallized magadiite, kenyaite, and SiO_2-X_2 as a single phase, because the structure of these silicates has not yet been analyzed, but kenyaite and SiO_2-X_2 are especially indistinct. Those compounds are also of great value as functional substances for intercalation.

Those silicates can be obtained by controlling such factors as the pH, ratios of Si/Na, and temperature. These silicates appeared as intermediate products, which were finally converted into quartz, even when the solid came to nearly equilibrium with its medium solution. Therefore, the reaction time also becomes a dominant factor in the formation of silicates.

In this section, the method of synthesis of those well-crystallized silicates, which was obtained by observing the crystallization processes in the solutions as a source of chert formation, is mainly described.

Well-crystallized magadiite was easily obtained in a solution with a pH greater than 10 (Figs. 5a and 5b). The ratio of Si/Na was widely variable (e.g., 3—10 g silica gel in 100 ml of alkali solution containing 0.1 mole Na^+ ion), and the ratios caused only a difference in the reaction time (e.g., 2—7 d at 160 °C).

The synthesis of kenyaite has seemed to be difficult because kenyaite has been considered to appear as a alteration product of magadiite.[1,2] In fact, the transformation, magadiite kenyaite quartz, was observed when NaOH or Na_2CO_3 was used as alkali sources, and the reaction temperatures were as high as 130—160 °C. The kenyaite synthesized in this manner was usually a poorly crystalline product and a mixture with quartz.

Beneke and Lagaly reported that kenyaite can be directly formed in 100 °C runs with high $SiO_2/NaOH$ ratios (>16) without forming magadiite. A relatively well-crystallized kenyaite was obtained from suspensions held for 3 to 24 months.[4]

In our study it was found that well-crystallized kenyaites could be formed in the temperature range of 100—160 °C when a weak base, $NaHCO_3$, was used as an alkali source. For example, when 10 g silica gel was dispersed in 100 ml of alkaline solution (e.g., 0.17 M-Na_2CO_3–0.67 M-$NaHCO_3$ solution), kenyaite formed at 140 °C in 15 d (Figs. 5c and 5d). The resulting kenyaite was a more crystalline product, as determined by X-ray and microscopy, than that synthesized by the other methods.[4,15]

SiO_2-X_2 is regarded as being a layered silicate like kenyaite, including some distortion of the lattice, but is distinguishable from kenyaite in terms of titration curves with a 0.1 M HCl solution, thermal behavior, and formation conditions.[9] For example, SiO_2-X_2 formed in the solutions of the Na_2CO_3–$NaHCO_3$ or K_2CO_3–$KHCO_3$ system (produced as Na- and K-form silicates, respectively) (Figs. 5e and 5f), but kenyaite formed only in the Na_2CO_3–$NaHCO_3$ system solution (produced as Na-form silicates).

Conclusions

(1) Magadiite, kenyaite, and SiO_2-X_2 appeared as intermediate phases during the transformation of amorphous silica into quartz in Na_2CO_3–$NaHCO_3$ and Na_2CO_3–$NaHCO_3$–$NaCl$ solutions.

(2) Magadiite and SiO_2-X_2 appeared consecutively in a solution rich in Na_2CO_3; then, SiO_2-X_2 decreased in amount with decreasing temperature. Magadiite was finally produced as the only intermediate phase at a temperature below 100 °C. The simple reaction pathway (silica → mag → chert) was thought to be the process of chert formation in nature.

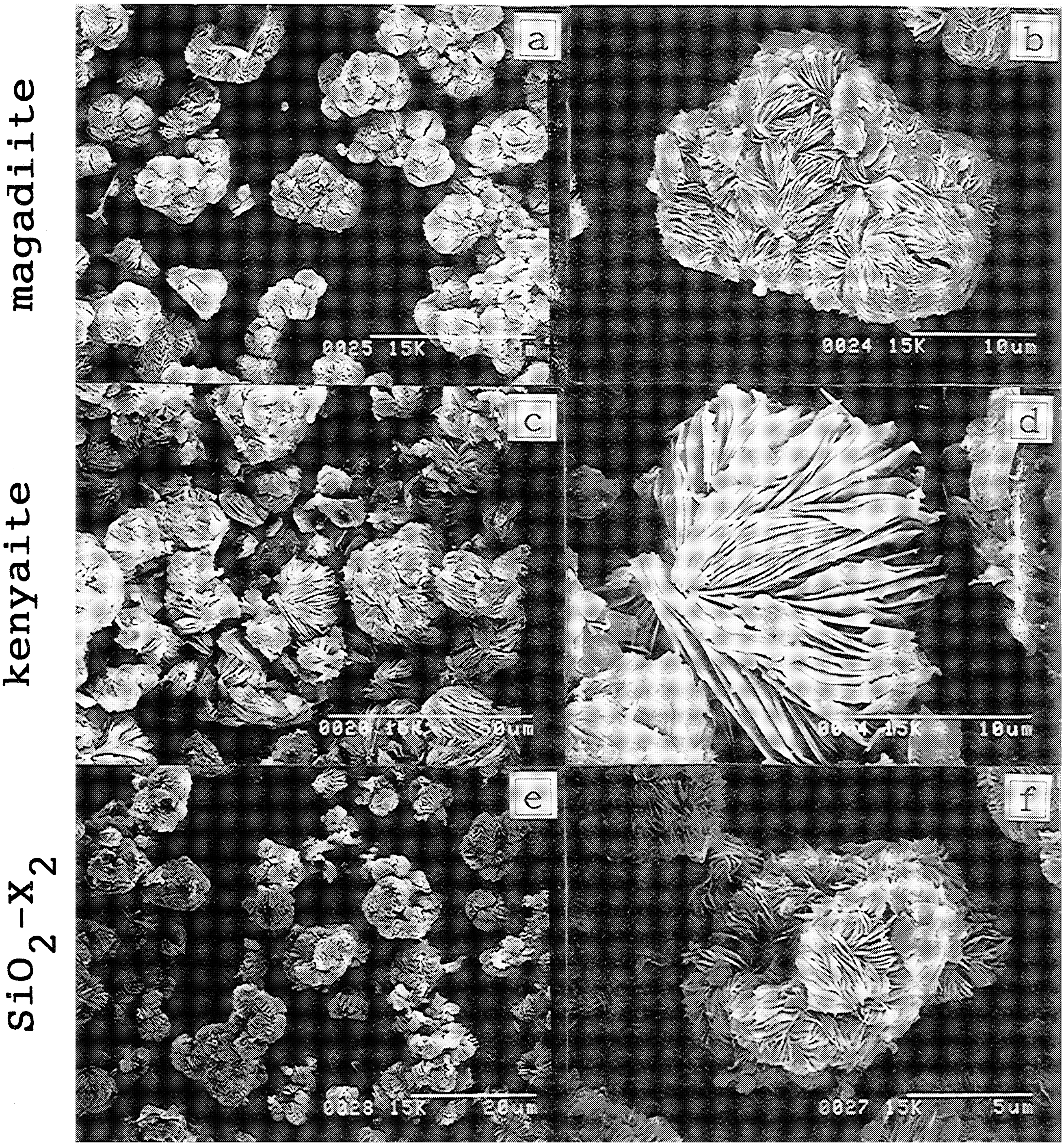

Fig. 5. Scanning electron micrographs of synthesized magadiite, kenyaite, and SiO_2-X_2 ((a), (c), and (e), and its details of a particle ((b), (d), and (f)). (a), (b): magadiite; synthesized in 1%-NaOH–1 M-NaCl solution at 140 °C, 7 days. (c), (d): kenyaite; synthesized in 0.17 M-Na_2CO_3–0.67 M-$NaHCO_3$ solution at 160 °C, 16 days. (e), (f): SiO_2-X_2; synthesized in 0.33 M-K_2CO_3–0.33 M-$KHCO_3$ solution at 140 °C, 6 days.

(3) Kenyaite formed through magadiite when lower pH solutions containing abundant SiO_2 and/or $NaHCO_3$ were added after precipitating magadiite. Kenyaite also precipitated directly from a solution rich in $NaHCO_3$ at pH 8—9.5. From these results, the most suitable conditions for the preparation of well-crystallized silicates were determined.

(4) When NaCl was added to Na_2CO_3–$NaHCO_3$ solutions, the rate of transformation was accelerated, and kenyaite and SiO_2-X_2 were precipitated in a lower pH solution.

(5) The time to 100% conversion to quartz at 30—50 °C was estimated by extrapolation so as to presume the time of chert formation in nature. Quartz was formed from scores of years to hundreds of years, at most.

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