

Crystallization of silica gel in alkaline solutions at 100 to 180 °C: Characterization of SiO₂-Y by comparison with magadiite

HARUTO MURAISHI

Department of Chemistry, Fukuoka University of Education, Akama, Munakata, Fukuoka 811-41, Japan

ABSTRACT

SiO₂-Y, an intermediate product of the transformation of silica gel to quartz, was synthesized from KOH or NaOH solution containing SiO₂ and NaCl with a molar ratio of SiO₂:H₂O:Na⁺:OH⁻ equal to 1:100:2–4:0.5 at 100–180 °C. In almost all reaction processes, SiO₂-Y appeared as the first crystal phase and then was transformed into SiO₂-X₂, cristobalite, and finally quartz. The characterizations based on the chemical and physical data for SiO₂-Y showed that SiO₂-Y is magadiite (Na₂Si₁₄O₂₉·xH₂O, x = 9–11), which was discovered at Lake Magadi (an alkali lake), Kenya, and has been considered to be an important precursor of inorganic bedded cherts.

INTRODUCTION

Hydrothermal crystallization of amorphous silica was investigated in the binary system SiO₂-H₂O at high temperature and high pressure, and the transformation via some metastable phases (cristobalite, keatite) to quartz was observed (Keat, 1954; Carr and Fyfe, 1958). When alkali-metal or alkaline-earth salt was added in aqueous media, the transformation to quartz occurred at lower temperatures with various intermediate phases that always contain some alkali ions and so are not crystal phases in the one-component SiO₂ system.

Heydemann (1964) observed that amorphous silica in KOH solution crystallizes via SiO₂-X and cristobalite to quartz at 100–250 °C, and characterized the nature and properties of SiO₂-X. Mitsyuk et al. (1973, 1976) described many intermediate phases that appear at 150–280 °C when alkali-metal or alkaline-earth salt is added to an alkaline medium. SiO₂-Y, which is one of the intermediate crystal phases, was formed in 0.5–2% KOH solutions containing NaCl in the temperature range 150–180 °C at 0.5–4.0 kbar. This is a sodium silicate that has the composition Na₂O·21SiO₂·12H₂O–Na₂O·29SiO₂·14H₂O, depending on the nature of the reaction medium. This compound was found to have a high capability for cation exchange. Kitahara et al. (1982) and Muraishi and Kitahara (1986) observed the effects of seed crystals, some metal oxides, and alkali-metal salts on the crystallization of silica gel in KOH solution at temperatures below 300 °C, under which conditions SiO₂-X, SiO₂-X₂, and SiO₂-Y mainly formed as intermediate phases.

On the other hand, Eugster (1967) described new hydrous sodium silicates, the mineral magadiite [reportedly NaSi₇O₁₃(OH)₃·3H₂O] and kenyaite [NaSi₁₁O_{10.5}(OH)₄·3H₂O] from Lake Magadi, Kenya. It is thought that magadiite precipitates from alkaline lacustrine brines and converts to kenyaite and finally to quartz (chert). Its synthesis has been reported by McCulloch (1952) and Lagaly

et al. (1973). Lagaly et al. (1975) have since shown that natural and synthesized magadiite is a sodium silicate with the composition Na₂Si₁₄O₂₉·11H₂O.

We also obtained the product identified as SiO₂-Y in NaOH, KOH, and Na₂CO₃ solutions containing NaCl at 100–180 °C at the autogenous pressure of an autoclave at a given temperature. In this paper, the transformation of amorphous to crystal phases under hydrothermal conditions was further examined on the basis of the run duration, temperature, and concentration of alkali-metal and alkaline-earth salts. The preparation condition of SiO₂-Y was determined from the experimental observations, and its synthesis was attempted. The nature of SiO₂-Y was determined and compared with that of the other silicates. The results showed that SiO₂-Y is indeed magadiite. The details of the chemical properties and the X-ray diffraction data of SiO₂-X₂, from which it was determined to be a quasi-kenyaite, will be reported in a subsequent paper.

EXPERIMENTAL DETAILS

Hydrothermal experiments on the transformation of silica gel were carried out in the temperature range 100–180 °C in 1–2 wt% (0.18M–0.36M, M ≡ mol/L) KOH solutions containing 0.2, 0.5, 1.0, and 2.0M NaCl. We used Teflon bottles with a volume of 15, 50, and 100 cm³ as reaction vessels. Usually a 15-cm³ bottle was used, and 0.3 g of starting silica (Wako's silica gel Q-22, through 200 mesh) was put in the bottle together with 7.5 mL of the solution. The Teflon bottle was closed with a Teflon plug, and it was placed in a stainless-steel autoclave that was designed to accommodate the bottle. After the autoclave was kept at a given temperature for a definite time, it was quenched rapidly with water. The reaction products were taken out of the autoclave and washed with NaOH solution (pH 10), since SiO₂-Y has good cation exchange below a pH of 10. Some of the conditions for preparing SiO₂-Y are described in Table 2.

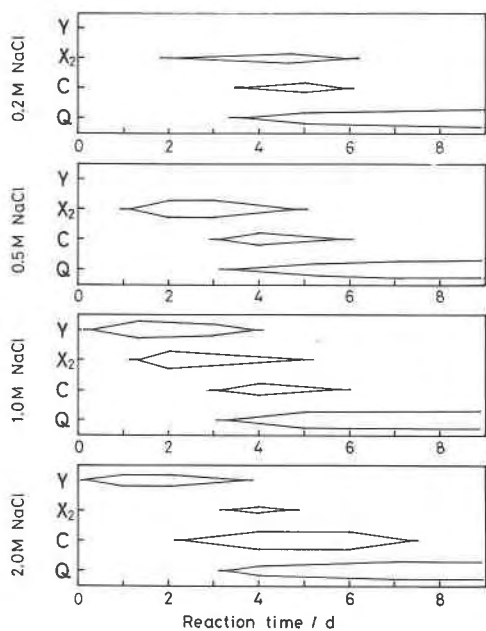


Fig. 1. Effect of NaCl concentration in 1% KOH solution in the composition of $\text{SiO}_2\text{:OH}^-:\text{Na}^+ = 3:1:1.1\text{--}11.0$ at 160°C on the crystallization sequence of $\text{SiO}_2\text{-Y}$ (Y), $\text{SiO}_2\text{-X}_2$ (X_2), cristobalite (C), and quartz (Q) as a function of reaction time.

Magadiite was synthesized by heating mixtures of the ratio of 9 mol of SiO_2 , 2 mol of NaOH, and 75 mol of H_2O at 100°C for 4 weeks, according to the method described by Lagaly et al. (1975). As it is known that magadiite as well as $\text{SiO}_2\text{-Y}$ exhibits a cation-exchange capability, synthetic magadiite was also treated with the same method described above for $\text{SiO}_2\text{-Y}$.

The reaction products were identified by the use of a Rigaku xgc-20 X-ray diffractometer. Chemical composition of the products was determined by conventional gravimetric methods for silica and by atomic absorption for Na and K. The water content was measured by a thermogravimetric method.

RESULTS AND DISCUSSION

Preparation conditions of $\text{SiO}_2\text{-Y}$ and magadiite

It was observed that $\text{SiO}_2\text{-Y}$, $\text{SiO}_2\text{-X}_2$, and cristobalite, as intermediate crystal phases appearing in the order listed, form in the $100\text{--}180^\circ\text{C}$ experiments in 1% (0.18M) KOH solutions containing various amounts of NaCl. The final product is quartz. The results of the reaction sequence of 160°C experiments are shown in Figure 1. In this figure (and in Fig. 2 also), the schematic line breadth for each phase was determined on the basis of the intensity of a main X-ray diffraction peak. Increasing the NaCl concentration induces the formation of $\text{SiO}_2\text{-Y}$ and cristobalite. Further addition of NaCl seems to result in preventing $\text{SiO}_2\text{-X}_2$ from appearing, in which situation $\text{SiO}_2\text{-Y}$ is directly followed by cristobalite. The same experimental results were also observed for the reaction at

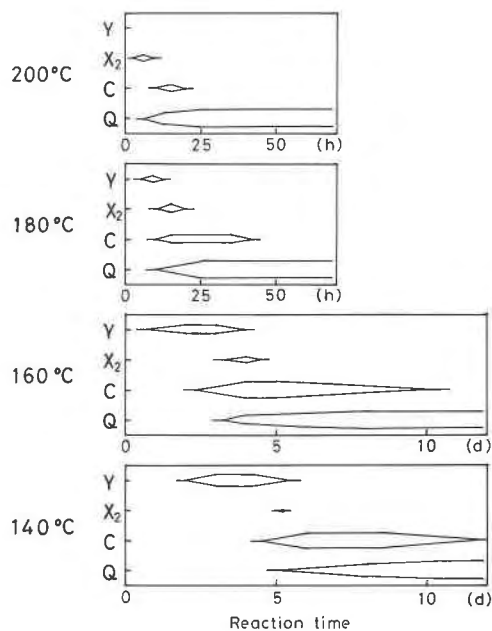


Fig. 2. Effect of temperature for a 1% KOH solution containing NaCl of 2 mol/L on the crystallization sequence defined in Figure 1 as a function of reaction time.

lower temperatures (e.g., below 120°C) in the 1% KOH-NaCl or 0.5M Na_2CO_3 solutions. When NaOH is used as an alkali source instead of KOH (i.e., using NaOH-NaCl solutions), a well-crystallized $\text{SiO}_2\text{-Y}$ is synthesized. When KOH is used instead of NaCl (i.e., using KOH-KCl solutions), $\text{SiO}_2\text{-X}_2$ is directly formed and transformed into cristobalite, which then goes to quartz. This difference is understandable from the fact that $\text{SiO}_2\text{-Y}$ is a sodium silicate and $\text{SiO}_2\text{-X}_2$ is formed as a combination of both sodium and/or potassium silicates as described below.

Figure 2 shows the effect of temperature on the crystallization of silica gel for a 1% KOH solution containing 2M NaCl. It has been reported that $\text{SiO}_2\text{-Y}$ is formed in a temperature range of $150\text{--}180^\circ\text{C}$ under high pressure (Mitsyuk et al., 1973). In our investigation, the period over which $\text{SiO}_2\text{-Y}$ was stable was found to increase with a decrease in the temperature, and it was synthesized even at 100°C . Comparatively well-crystallized $\text{SiO}_2\text{-Y}$ was obtained after a reaction time of 1 to 3 months at 100°C . $\text{SiO}_2\text{-Y}$ was stable for several months and slowly transformed into quartz. Thus, a lower temperature was advantageous for the formation of $\text{SiO}_2\text{-Y}$ compared with $\text{SiO}_2\text{-X}_2$. In addition, the amount of solid phase in the alkaline solutions was followed through the reaction term. The solid phase decreased in the initial stage of the reaction and then increased with reaction time up to constant amounts. These results suggest that the transformation process of silica gel to $\text{SiO}_2\text{-Y}$ may be a dissolution-precipitation process.

The appearance of $\text{SiO}_2\text{-Y}$ varied as a function of NaCl

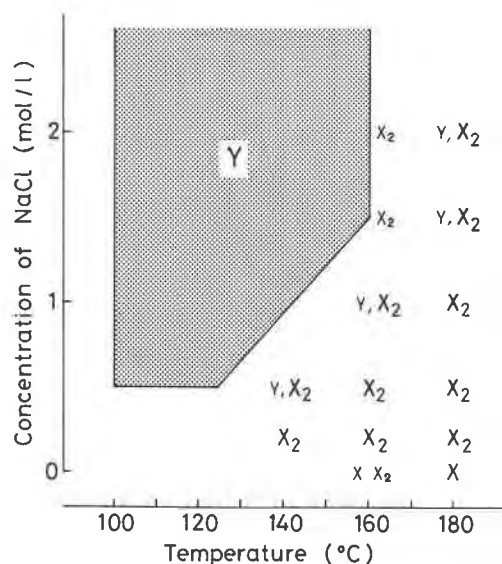


Fig. 3. The range of $\text{SiO}_2\text{-Y}$ appearance as a function of NaCl concentration and temperature for a 1% KOH solution. (The crystals indicated with small letters are minor phases as determined by X-ray diffraction patterns.) $\text{SiO}_2\text{-X}$ (X); other abbreviations as in Figure 1.

concentration and reaction temperature for a 1% KOH solution, as shown in Figure 3. $\text{SiO}_2\text{-Y}$ appears separately in the dotted region and is more stable under conditions of lower temperature and higher NaCl concentrations. In the other region, $\text{SiO}_2\text{-Y}$ forms together with the other intermediate phases or does not form at all.

Figure 4 shows the composition of the solutions in which $\text{SiO}_2\text{-Y}$ and magadiite were prepared. For the preparation of $\text{SiO}_2\text{-Y}$, a relatively large amount of water was used, and the concentration of Na^+ in the solution was made to vary independently against that of OH^- . This is different from the procedure to synthesize magadiite, which was done at 100–120 °C in suspensions typically containing 1 mol of NaOH, 2 to 6 mol of SiO_2 , and 10 to 60 mol of H_2O (Lagaly et al., 1973).

The results of the conversion of crystalline phases with time (Figs. 1 and 2) show the following reaction path: amorphous silica \rightarrow $\text{SiO}_2\text{-Y}$ \rightarrow $\text{SiO}_2\text{-X}_2$ \rightarrow cristobalite \rightarrow quartz. Sometimes it was observed that the crystal growth of $\text{SiO}_2\text{-Y}$ and $\text{SiO}_2\text{-X}_2$, however, did not proceed consecutively, but simultaneously, and that cristobalite was formed prior to the appearance of $\text{SiO}_2\text{-X}_2$. If these results have any fundamental significance, the reaction path ought to be expressed by the process including the parallel reactions in which $\text{SiO}_2\text{-Y}$ and $\text{SiO}_2\text{-X}_2$ are independently rather than consecutively formed.

X-ray diffraction and chemical composition of products

The X-ray diffraction peaks of the $\text{SiO}_2\text{-Y}$ and synthetic magadiite prepared by us are given in Table 1 and compared with those of $\text{SiO}_2\text{-Y}$ from Mitsyuk et al. (1973)

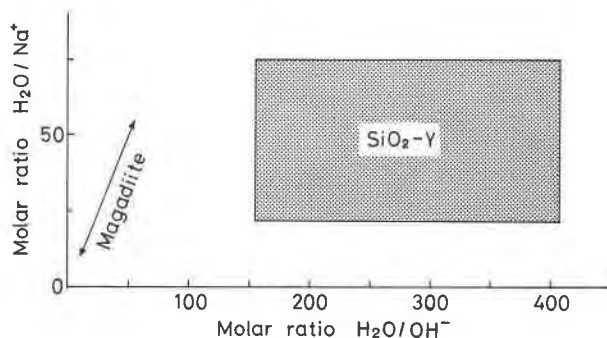


Fig. 4. Chemical composition of the solutions required for the formation of $\text{SiO}_2\text{-Y}$ at 100–150 °C and magadiite at 100 °C. The amount of silica in the solutions is $\text{SiO}_2/\text{OH}^- = 2\text{--}6$.

and natural magadiite from Brindley (1969). As seen in Table 1, there is little difference between the X-ray diffraction peaks of natural magadiite and those of the synthesized material. The slight difference may be caused by a variety of impurities included in natural magadiite. The patterns of the two kinds of synthesized silicates—magadiite and $\text{SiO}_2\text{-Y}$ —are similar to each other except for the differences in intensity, I , resulting from their differences in crystallinity.

Thermal changes in $\text{SiO}_2\text{-Y}$ and magadiite were determined by means of differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). The DTA-TGA curves for both silicates drying in air are shown in Figure 5, and the results actually overlap each other. It was found from the TGA curves that the dehydration occurred mainly in four steps. The dehydration at temperatures below 100 °C may be assigned to adsorbed H_2O and some water of crystallization, which are easily released. When these samples were stored in a desiccator using silica gel for a desiccant, the ignition loss below 100 °C was no longer observed. At about 130 and 190 °C, some 50% to 90% of the total ignition loss was released. The bulk of the contained water was lost by heating to 550 °C. The water content in the preparations varied slightly with the conditions of synthesis and storage. On the other hand, DTA curves have a small broad endothermic peak at about 680 °C and an exothermic peak at about 750 °C. The former was assigned to the destruction of the lattice of $\text{SiO}_2\text{-Y}$ (or magadiite) and to the formation of quartz, and the latter was assigned to its reconstitution into tridimite.

Table 2 summarizes the molar ratio of Na and Si in some of the $\text{SiO}_2\text{-Y}$ and magadiite samples prepared under various conditions. From these results, the chemical formula of $\text{SiO}_2\text{-Y}$ was determined to be $\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$. It was deduced from ignition loss that the amount of water of crystallization, x , equaled 8.5–11. It is worth noting that $\text{SiO}_2\text{-Y}$ was usually free from K^+ . This characteristic of $\text{SiO}_2\text{-Y}$ distinguishes it from $\text{SiO}_2\text{-X}_2$, which can contain as structural atoms both Na and K in any proportion.

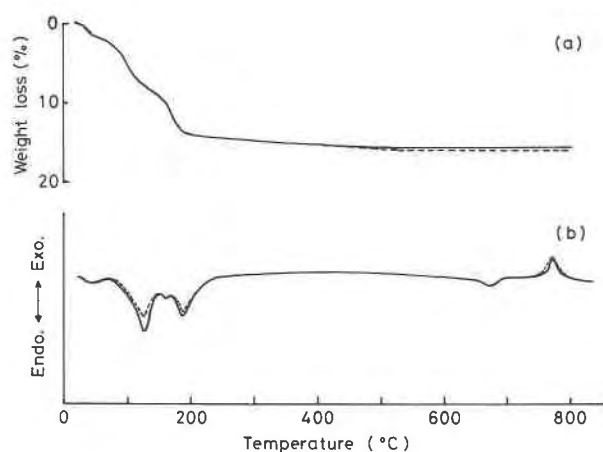


Fig. 5. Thermal behavior of synthesized $\text{SiO}_2\text{-Y}$ (solid lines) and magadiite (dashed lines). (a) Weight-loss curves; (b) DTA diagram.

Properties

$\text{SiO}_2\text{-Y}$ and magadiite were suspended in water after drying in air and grinding into fine powders through 200 mesh to determine ion-exchange properties. The suspensions were titrated continuously with 0.1M HCl solutions using an automatic titrator with a rate of addition of 1.0 mL/h. The results are shown in Figure 6. The titration curves of both silicates showed that half of the alkali in the crystal is neutralized at approximately pH 7, and al-

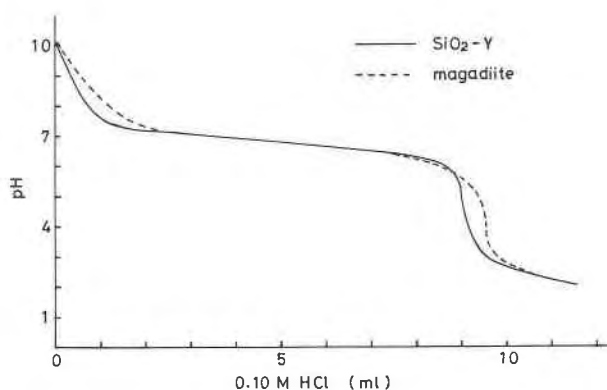
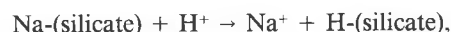


Fig. 6. Typical titration curves of $\text{SiO}_2\text{-Y}$ and magadiite suspensions with 0.10M HCl. Suspension, 0.5 g of silicate per 50 mL of water; rate of addition of HCl, 1.0 mL/h; temperature, 25.0 °C.

most all of it at $\text{pH } 4.4 \pm 0.1$. This is closely analogous to that of crystalline sodium polysilicate $\text{Na}_2\text{O} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$ investigated by Iler (1964). The result proves that these sodium silicates [abbreviated as Na-(silicate)] have high exchangeability in acidic solution and high selectivity for H^+ and then suggests that the following reaction goes to completion:



where H-(silicate) is crystalline silicic acid from sodium silicate. The pH value of 4.4, which is the pH of the

TABLE 1. X-ray diffraction patterns of $\text{SiO}_2\text{-Y}$ and magadiite

$\text{SiO}_2\text{-Y}$						Magadiite			
1		2		3		4		5	
$d(\text{\AA})$	l	$d(\text{\AA})$	l	$d(\text{\AA})$	l	$d(\text{\AA})$	l	$d(\text{\AA})$	l
15.50	100	15.78	90	15.64	65	15.56	100	15.64	65
7.76	20	7.80	16	7.76	15	7.77	9	7.90	12
6.26	5							7.26	8
5.17	30	5.20	23	5.20	23	5.18	18	5.22	20
(4.44)	—	4.48	13	5.03	13	5.00	14		
4.23	10	4.23	8	4.48	20	4.46	18	4.48	13
				4.02	13	4.01	8	4.02	10
3.877	10			3.920	10				
3.637	30	3.641	21	3.648	23	3.626	13	3.663	23
		3.550	27	3.550	33	3.544	19	3.569	23
3.450	90	3.453	100	3.445	100	3.434	75	3.460	100
3.304	80	3.308	65	3.308	65	3.298	40	3.314	65
						3.197	11		
3.160	90	3.153	81	3.151	74	3.145	60	3.159	72
						2.989	6	2.998	8
		2.864	7	2.876	9	2.866	6	2.880	8
2.831	10	2.827	9	2.823	9	2.821	10	2.831	8
						2.639	7		
2.578	10	2.585	8	2.603	7	2.599	11	2.600	7
(2.36)	—	2.356	6	2.353	8	2.353	12	2.350	9
2.289	10	2.287	5	2.273	5				
2.012	10					2.067	12		
1.937	10								
1.833	30	1.830	20	1.826	18	1.822	30	1.833	20

Note: Columns are as follows: (1) 155 °C, in KOH + NaCl solution (Mitsyuk et al., 1976). (2) 150 °C, 5 days, in 1% KOH + 1.5M NaCl solution (this work). (3) 100 °C, 8 weeks, in 1% KOH + 1M NaCl solution (this work). (4) Natural magadiite (Trinity County, California) (Brindley, 1969). (5) 100 °C, 8 weeks, in the solution with molar ratio of $\text{SiO}_2\text{:NaOH:H}_2\text{O} = 9\text{:}2\text{:}75$ (this work).

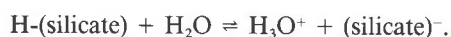
TABLE 2. Reaction conditions and analysis of products

Run*	T (°C)	Time (d)	Molar ratio of solution				Atomic ratio of product		
			OH ⁻	Na ⁺	SiO ₂	H ₂ O	Na	Si	K
Y-1	140	5	0.25	1.36	1	50	1.91	14	0.03
Y-2	150	5	0.32	1.80	1	100	1.94	14	0.02
Y-3	140	5	0.64	1.36	1	100	1.98	14	0.03
Y-4	150	3	0.32	5.41	1	100	2.01	14	0.01
Y-5	140	5	0.34†	1.70	1	50	1.99	14	—
M-1	100	60	0.22†	0.22	1	8	2.03	14	—

* Y, SiO₂-Y; M, magadiite.

† NaOH was used as an alkaline source.

solution at the equivalence point in Figure 6, corresponds to the concentration of hydronium ion formed by the reaction of the resulting silicic acid from ion exchange with water:



The ionization constant pK_a of the silanol groups on the crystalline silicic acid was estimated to be about 6.9 on the basis of the concept of weak acid solutions. This is in good agreement with some estimates based on titration curves for amorphous silica, which are about 6.5 to 7.7 (Schindlar and Kamber, 1968; Strazenko et al., 1974).

Both SiO₂-Y and magadiite, synthesized by us, have a refractive index of 1.481 ± 0.003 . This value is the same as that reported for natural magadiite by Eugster (1967), who gave an average value of 1.48.

Therefore, from the results previously stated, it is concluded that SiO₂-Y is indeed magadiite.

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