

## Crystallization of analcime solid solutions from aqueous solutions

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### Abstract

Sodium aluminosilicate gels containing an extremely small quantity of alumina changed initially to clear solutions on heating. Analcime solid-solution crystals formed directly from them at 100°C, under atmospheric pressure.

The chemical compositions of the analcimes were governed by the initial ratios of soda, alumina, and silica in the gels, and were independent of the depletion of nutrient with the elapse of reaction time. According to the isomorphous substitution  $\text{Si}^{4+} \rightleftharpoons \text{Na}^+\text{Al}^{3+}$ , an increase of soda and alumina concentrations caused a decrease of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the analcime crystals, whereas an increase in silica resulted in an increase of the ratio.

Analcime crystals grew uniformly in size in runs of 120 hrs or shorter duration and had trapezohedral crystal habit. When analcime seeds were added to the freshly-prepared gels, they grew longer on heating in all cases. The composition of the growth zones on the crystals also was governed by the initial compositions of the fresh gels and was independent of the composition of the added seed and the length of growth time.

These results can be readily explained by assuming the existence of active chemical species of sodium aluminosilicates, a hypothesis which was proposed first by Kerr (1966). We propose that they possess fixed compositions and incipient ordered structures identical to analcimes and that they polymerize to form analcime crystals.

### Introduction

In the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , many kinds of synthetic zeolites have been obtained from active gels at temperatures below 200°C. In this system, however, only a few studies of zeolite syntheses in the low-alumina region have been reported. Notable exceptions are the mordenite syntheses by Barrer (1948), Barrer and White (1952), Domine and Quobex (1968), Sand (1968), and Culfaz and Sand (1973).

The present investigation focused on the crystallization of analcime solid solutions from chemically-reactive gels having an extremely low alumina content. In the gel compositions, the ratios of  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ranged from 1/70 to 1/200 and 1/40 to 1/320, respectively. In the experiments, in addition to analcime, hydroxysodalite and zeolite B were obtained as crystalline phases.

Studies on the synthesis of analcimes have been made by many investigators in the field of geology, mineralogy and chemistry: Barrer and White (1952), Guyer *et al.* (1957), Barrer *et al.* (1959), Saha (1959, 1961), Campbell and Fyfe (1965), and Senderov and

Khitarov (1971). In our work, however, the state of the prepared gels and the conditions of synthesis were considerably different from those of the previous studies. Conventional methods for zeolite synthesis are characterized by the use of gels consisting of heterogeneous phases with amorphous solid and aqueous solutions coexisting until the conversion of amorphous materials to zeolite crystals is completed. The extremely low-alumina gels used in this investigation were readily changed to clear solutions on heating long before the crystallization of analcimes began. The present synthesis of analcimes was carried out using the clear solutions at 100°C under atmospheric pressure.

In the experiments, the following two problems were examined: (1) the effects of initial concentrations of soda, alumina, and silica of the gels on the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the synthesized analcime, and (2) the type of growth on analcime seeds in the freshly-prepared clear solution with a composition different from that of the seeds. The results yield useful information regarding the crystallization mechanism of zeolites.

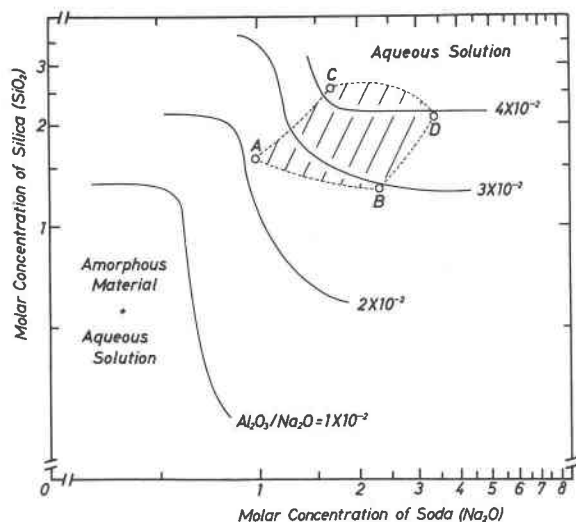


Fig. 1. Boundary curves between soluble and insoluble amorphous solid gels for various initial molar concentrations of silica ( $\text{SiO}_2$ ) and soda ( $\text{Na}_2\text{O}$ ) at constant  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  ratios. The gels were prepared from 10M solutions of sodium hydroxide, sodium aluminate, and aqueous colloidal silica sol. The diagram is based on 250 observed values.

So far, two theories which were reviewed in detail by Zhdanov (1971) have been proposed for the crystallization mechanism of zeolites. Breck and Flanigen (1968), McNicol *et al.* (1971, 1972), and Aiello *et al.* (1971a,b) support the theory of conversion of amorphous solid gel to crystalline phases. However, Kerr (1966, 1968), Ciric (1968), Culfaz and Sand (1973) and Cournoyer *et al.* (1975) support the theory of crystallization from solution. Other authors who have examined the mechanism of zeolite crystallization are Meise and Schwochow (1975) and Polak and Cichoki (1973).

### Experimental

Gels with the original compositions  $10 \text{ Na}_2\text{O} \cdot (0.05-0.15) \text{ Al}_2\text{O}_3 \cdot (6-16) \text{ SiO}_2 \cdot (168-592) \text{ H}_2\text{O}$  were prepared from a 10M solution of sodium hydroxide (90 volume percent as  $\text{H}_2\text{O}$ ), sodium aluminate (35.05 weight percent as  $\text{Na}_2\text{O}$  and 42.36 weight percent as  $\text{Al}_2\text{O}_3$ ), aqueous colloidal silica sol (0.2374 g/ml as  $\text{SiO}_2$ ), and distilled water. The total volume of each gel was adjusted to 50 ml.

The procedures for preparation were as follows. Known amounts of the 10M sodium hydroxide solution, sodium aluminate, and water were introduced into 100 ml teflon bottles used as reaction vessels. These mixtures were heated at  $100^\circ\text{C}$  in a water bath until the added sodium aluminate was completely dissolved. Subsequently, a calculated amount of

aqueous colloidal silica sol was pipetted into the bottle and stirred (*ca.* 600 rpm) with a magnetic stirrer for 2 min. Thereafter, the vessel was heated again at  $100^\circ\text{C}$  for 3 to 288 hrs. To prevent evaporation, the system was fitted with a reflux condenser.

Immediately after the preparation, a milky turbidity was observed, which disappeared within 5 min after heating. Because this turbidity of the gel was controlled by the initial concentrations of three components, the compositional boundaries between soluble and insoluble solid gels were determined by varying the proportions of silica ( $\text{SiO}_2$ ) and soda ( $\text{Na}_2\text{O}$ ), and holding the  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  ratio constant. The curves of the compositional boundaries are depicted in Figure 1. When the gel was alumina-free, *i.e.*,  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0$ , no amorphous material was observed. As the  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  ratio was increased, however, the region of the two phases enlarged in the direction of higher concentrations of silica and soda. The dashed area (ABDC) indicates the concentration ranges of silica and soda used in the present investigation (in this region the  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  ratio  $\leq 1.5 \times 10^{-2}$ ).

In all cases, analcime crystals were obtained in measurable amounts from clear solutions in 3 to 5 hrs after heating the solutions at  $100^\circ\text{C}$ . The crystal dimensions were in the range of 15 to  $25\mu\text{m}$ . At the completion of the runs, the reaction products were separated from the solution through a teflon filter with a pore size of  $0.2\mu\text{m}$  and examined by X-ray diffractometer ( $\text{CuK}\alpha$  radiation) analysis, optical microscopy, scanning electron microscopy, and by DTA. Chemical analyses were made on several specimens by gravimetric methods. The quantity of soda was determined by flame photometry.

Experiments on the growth of analcime seeds were carried out as follows. First, the seed crystals with a uniform grain size ranging from 6 to  $7\mu\text{m}$  were prepared from a few gels with selected compositions by heating for 48 to 72 hrs. Subsequently, a known amount of seed crystals was added to other freshly-prepared gels, and the mixture was heated at  $100^\circ\text{C}$  for 20 to 66 hrs. The resulting crystals were separated from the solution and examined by the methods described above.

### Results and discussion

#### Analcime solid solutions

Saha (1959) has shown that analcime solid solutions can be produced from glasses varying in composition from albite to anhydrous natrolite, and that the

Table 1. Relationship between  $\Delta\theta$  values and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios for analcime solid solutions

$\Delta\theta$ value	1.587°	1.656°	1.700°	1.718°	1.771°	1.844°
$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	3.24	3.52	3.74	3.81	4.04	4.39

The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios were determined by chemical analysis.  $\Delta\theta$  value:  $2\theta$  (Analcime (639)) -  $2\theta$  (Silicon (331)) (scanning speed 1°/16 min.; chart speed 1cm/min.)

unit-cell dimensions of the analcimes decrease linearly with increasing  $\text{SiO}_2$  content. He has pointed out also that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio can be determined by the difference of the  $2\theta$  angles between the diffraction peak (639) for analcime and (331) for silicon (internal standard). Because the  $2\theta$  angles are in the range of 77.9° to 78.5° for the former and 76.47° for the latter, the difference ( $\Delta\theta$ ) increases with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratios. In our investigation this method was applied to determine  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the analcimes. Both the  $\Delta\theta$  values and the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios for the specimens whose compositions were previously determined are listed in Table 1. These results are in good accord with those of Saha and thus were used for calibration. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the analcime solid solutions obtained were in the range of 3.2 to 4.8.

By varying initial molar concentrations of soda, alumina, and silica in the gels, the  $\Delta\theta$  values for the analcimes could be changed. In order to investigate the effect of the concentrations of  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  on the resulting  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios for analcime, the  $\Delta\theta$  values were measured as a function of one component, while the other two were kept constant. Some of the observed values are plotted in Figure 2. It should be noted that on the abscissa the scale for alumina is  $10^2$  times that of soda and silica.

The increase of initial soda concentration, holding alumina and silica constant, caused a reduction of the  $\Delta\theta$  values, as seen from curves 1 through 5 in Figure 2. These five curves were obtained for gels having different concentrations of alumina and silica, as can be seen from the footnote in Figure 2, but the concentrations of these two components remained constant for each curve. Similar effects were observed as a function of initial alumina concentration, with soda and silica kept constant. Curves 6 through 10 in Figure 2 were drawn in the same manner. However, the increase of initial silica concentration brought about a reverse change, as is shown by curves 11, 12, and 13.

These results reflect the isomorphous substitution

of silicon by aluminum,  $\text{Si}^{4+} \rightleftharpoons \text{Na}^+\text{Al}^{3+}$ , to maintain electrical neutrality. From the curves in Figure 2, the variation of the  $\Delta\theta$  value, which was caused by variation of 1 percent in the initial concentration of one component, was calculated and converted to the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in analcime as follows: 0.02° by soda, 0.002° to 0.004° by alumina, and 0.01° to 0.02° by silica.

The amount of crystals formed was determined as a function of reaction time, and two examples are tabulated in Table 2. The rate of crystallization increases gradually with reaction time and beyond 100 hrs the rate increment is slight. A similar tendency was observed in the crystallization of analcimes from other gels. Using the observed values listed in Table

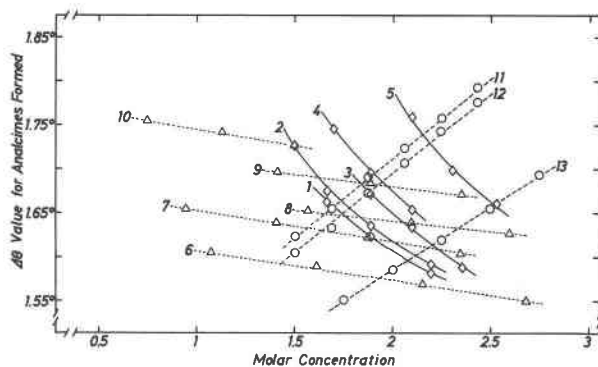


Fig. 2. Variations in  $\Delta\theta$  values for analcime solid-solution crystals as a function of initial molar concentration of one component, keeping those of the other two components constant. Diamond-shaped symbols on curves 1 to 5, triangles on curves 6 to 10, and circles on curves 11 to 13 indicate the values obtained as a function of soda, alumina, and silica, respectively. The scale along the abscissa is correct for soda and silica, but the concentration of alumina has been multiplied by a factor of  $10^2$ . For curves 1, 2, 3, 4, and 5 the constant molar concentrations of alumina and silica were  $1.80 \times 10^{-2}$  and 1.50,  $1.5 \times 10^{-2}$  and 1.50,  $2.23 \times 10^{-2}$  and 1.88,  $1.50 \times 10^{-2}$  and 1.88, and  $1.5 \times 10^{-2}$  and 2.53, respectively. For curves 6, 7, 8, 9, and 10 the constant molar concentrations of soda and silica were 2.14 and 1.50, 1.88 and 1.50, 2.03 and 1.88, 1.88 and 1.88, and 1.50 and 1.50, respectively. For curves 11, 12, and 13 the constant molar concentrations of soda and alumina were 1.88 and  $1.88 \times 10^{-2}$ , 1.88 and  $2.34 \times 10^{-2}$ , and 2.50 and  $2.50 \times 10^{-2}$ , respectively.

2, the percentage reduction in concentrations of three oxide components in the solution was calculated and plotted as a function of reaction time (see Fig. 3). In this illustration, a 100 percent reduction would mean that the concentration of alumina has become zero because of the formation of analcime crystals. As the reaction time was increased, the concentration of alumina was reduced greatly, by 60 or 80 percent after a 288 hr period; silica and soda concentrations remained very similar during 288 hr periods. The reduction of silica and soda was in a range of 4 percent and 1 percent, respectively.

We therefore suggest that, at an early stage of crystallization, alumina-rich solid solutions of analcime were formed, and that at a later stage alumina-poor analcimes crystallized. However,  $\Delta\theta$  values for the analcime were unchanged even after 288 hrs. The variation of  $\Delta\theta$  values as a function of reaction time was measured and is listed in Table 3. The results indicate that the composition of the solid solutions was governed by the concentrations of the initial components of the original gel and was independent of the length of the reaction time.

#### Hydroxysodalite and zeolite B

These zeolite species were also produced as single phases from clear solutions, but their crystallization occurred in chemical environments different from that for analcimes. Compared with analcime, hydroxysodalite was stable in highly alkaline solutions, whereas zeolite B crystallized from less alkaline solu-

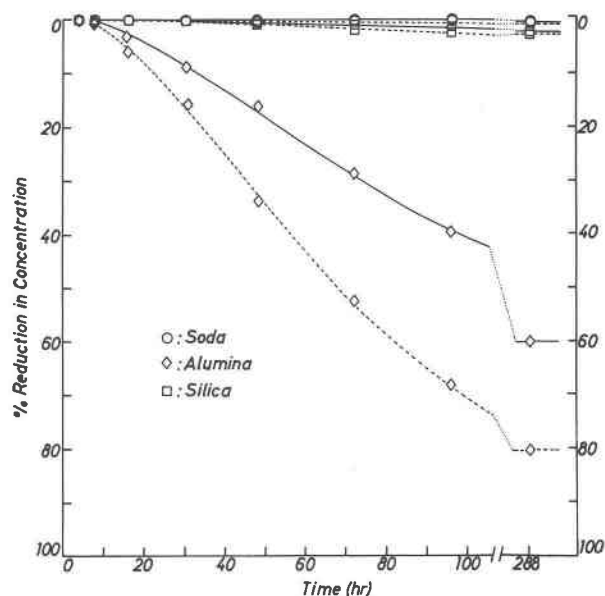


Fig. 3. Reduction in concentrations of soda, alumina, and silica in solutions as a function of reaction time. 100 percent reduction means that the concentration has become zero because of the formation of analcime crystals. Solid line: ref. (\*1) in Table 2; broken line: ref. (\*2) in Table 2.

tions. Accordingly, these two species did not coexist with each other, but both were found to coexist with analcime.

#### Growth of analcime crystals

The scanning electron photomicrograph (Fig. 4) shows that analcime crystals grew uniformly in size for runs shorter than about 120 hrs, and they had several polyhedral crystal habits. Barrer (1963) noted that single crystals of synthetic Na-analcimes consist mainly of polyhedra with predominating trapezohedral {211} and truncating cube {100} forms. In this study, the crystal forms are assumed to be analogous to the trapezohedron, but actual morphological data are not available.

As the crystals grew with reaction time, they became uneven in their dimensions and irregular in shape because the surface adhesion between crystals affected their growth. At this stage of development, single crystals were no longer observed. Neck growth occurred often, and spherical growths projected from the surface of large crystals.

Attempts to grow analcime seeds were made in freshly-prepared gels of two types. In one type the composition of the fresh gels was identical with that of gels used to prepare added seeds (case I), and in the other type it was different from the initial composition of the gels of added seeds (case D). In both

Table 2. Weight percent of analcime crystals formed from clear solutions as a function of reaction time

Reaction time (hrs)	Weight % of crystals formed	
	1 Exp. 1001-7(*1)	2 Exp. 1001-10(*2)
4	0.26	0.49
8	1.22	2.13
16	3.45	6.18
30	9.21	16.38
48	16.12	33.88
72	28.47	52.54
96	39.46	67.99
288	60.01	80.18

The 100 wt.% level was defined by assuming that the initial concentration of alumina becomes zero as it is consumed by the formation of analcime.

(\*1) and (\*2): The original gel compositions were  $10\text{Na}_2\text{O} \cdot 0.1\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 \cdot 259\text{H}_2\text{O}$  and  $10\text{Na}_2\text{O} \cdot 0.1\text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 370\text{H}_2\text{O}$ , respectively. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios for the frameworks were 3.22 in Exp. 1001-7 and 3.91 in Exp. 1001-10.

Table 3. Relationship between observed  $\Delta\theta$  values for precipitated analcimes and reaction time

1				2		
Initial composition of gel				Reaction time, hrs.		
Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	H <sub>2</sub> O	48hr	96hr	288hr
10	0.075	10	370	1.755°	—	1.752°
10	0.075	11	407	—	1.800°	1.803°
10	0.1	7	259	1.582°	1.585°	1.583°
10	0.1	8	296	—	1.636°	1.633°
10	0.1	9	333	—	1.683°	1.682°
10	0.1	10	370	1.739°	1.736°	1.738°
10	0.125	8	256	1.585°	1.587°	1.584°
10	0.125	10	295	1.681°	1.680°	1.682°

$\Delta\theta$  value:  $2\theta(\text{Analcime}_{(639)}) - 2\theta(\text{Silicon}_{(331)})$   
(Scanning speed 1°/16 min.; chart speed 1cm/min.)

cases, two kinds of crystals with different dimensions were observed. They are clearly distinguishable, as is shown in Figure 4c. The large particles correspond to the grown seeds, and the smaller ones are newly-formed crystals from the fresh gel. These particles, which consist of three phases [(i) seed, (ii) growth zone, and (iii) newly-formed crystal], are schematically represented in Figure 5.

In case D, X-ray diffraction patterns showed splitting of peaks due to the existence of two kinds of solid solution, whereas in case I no peak splitting was observed. Our investigation of the mechanism of growth was based on experiments of case D.

The interplanar spacings  $d$  of coexisting solid solutions did not change with growth time, but their intensity ratios varied over a wide range. From this variation, the chemical composition of growth zones on the surface of a seed was determined. The experimental results are tabulated in Table 4.

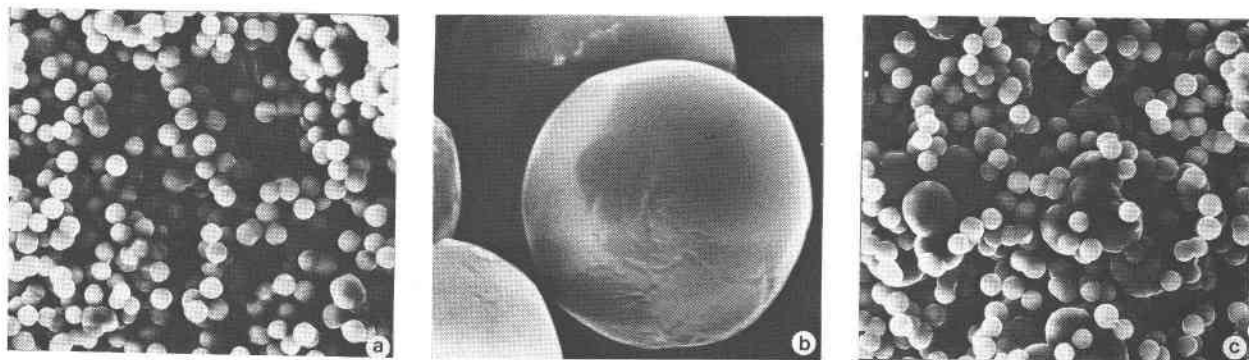


Fig. 4. Scanning electron photomicrographs of analcime crystals. (a) Crystallites resulting from a clear solution with composition  $10\text{Na}_2\text{O} \cdot 0.1\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot 333\text{H}_2\text{O}$  after heating at  $100^\circ\text{C}$  for 72 hrs ( $400\times$ ). (b) Enlargement of a ( $5400\times$ ). (c) Larger crystals represent enlarged seeds, and smaller grains are crystals newly formed from freshly-prepared gel ( $560\times$ ).

In Table 4 the initial compositions of both gels, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the framework for phases S and phase N, the growth time, the total amount of crystallites after the run ( $W_t$ ), the original quantity of phase S ( $W_s$ ), and the  $W_s/W_t$  ratio (percent), are listed. The  $W_s/W_t$  ratio decreases with growth time because of the assumption that  $W_s$  does not change. However, the weights of phases G and N could not be determined separately.

The X-ray intensities of very finely powdered samples were measured on the  $K\alpha_1$  peak of the (639) spacing according to the procedure of Keating (1959). The intensities due to phases S, G, and N are expressed as  $I_s$ ,  $I_g$ , and  $I_n$ , respectively; and the total intensity ( $I_t$ ) is given as  $I_t = I_s + I_g + I_n$ .

As shown in column 2 of Table 4, phase S always differs from phase N in composition. Therefore, phase G should be the same in composition as either phase N or S as shown in Figure 5. If phase G has the same composition as phase N (Fig. 5a), the quantity of phase S must remain constant with growth time, and its diffraction peak does not overlap those of the others. In this case, the measurement of the  $I_s/I_t$  ratio (percent) is easy and sufficient. The observed values are listed in the last column of Table 4. They diminish markedly with growth time in all cases and prove to be in close agreement with the  $W_s/W_t$  ratios listed in column 6. Such a direct comparison is reasonable because of the relation  $I_s/I_t = k(W_s/W_t)$  where  $k = \text{constant}$ .

However, if the composition of phase G is the same as that of phase S (Fig. 5b),  $I_g$  cannot be determined independently, although the ratio  $(I_s + I_g)/I_t$  can be calculated as before. The amount of phase G depends on both the number of seed crystals and the length of growth time. The former is assumed to be maintained constant throughout the growth time, because

Table 4. Experimental results for the growth of analcime seeds in freshly-prepared gels

1				2				3	4	5	6	7		
Initial composition of gels				SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratios of framework				Growth time	W <sub>t</sub> (*4)	W <sub>s</sub> (*5)	W <sub>s</sub> /W <sub>t</sub> ratio (%)	I <sub>s</sub> /I <sub>t</sub> (*6)		
Gel for preparing seed		Gel freshly prepared		phase S(*2)	phase N(*3)		(hrs)	(mg)	(mg)		(%)			
Na <sub>2</sub> O:Al <sub>2</sub> O <sub>3</sub> :SiO <sub>2</sub> :H <sub>2</sub> O				Na <sub>2</sub> O:Al <sub>2</sub> O <sub>3</sub> :SiO <sub>2</sub> :H <sub>2</sub> O										
10	0.1	7	259	10	0.1	10	370	3.22	3.91	20	85.4	20	23.7	21.7
10	0.1	7	259	10	0.1	10	370	3.22	3.91	42	190.9	20	10.5	11.5
10	0.1	7	259	10	0.1	10	370	3.22	3.91	66	225.3	20	8.9	9.7
10	0.1	7	259	10	0.075	11	407	3.22	4.20	20	61.9	20	32.2	32.1
10	0.1	7	259	10	0.075	11	407	3.22	4.20	42	124.1	20	16.2	15.4
10	0.1	10	370	10	0.1	7	259	3.91	3.22	20	65.7	20	30.4	28.1
10	0.1	10	370	10	0.1	7	259	3.91	3.22	42	152.9	20	13.1	11.7
10	0.1	10	370	10	0.1	7	259	3.91	3.22	66	222.4	20	9.0	7.8
	(*1)			10	0.1	7	259	4.01	3.22	42	193.0	20	10.3	9.8
	(*1)			10	0.1	7	259	4.01	3.22	66	257.0	20	7.8	6.7

(\*1): Natural analcime from Igarashi, Akita prefecture, Japan was used as seed; it was powdered to a grain size ranging from about 1 to 50μm and was irregular in shape. Synthetic seed crystals were in the range of 6 to 7μm in average dimension.  
 (\*2): Added seed. (\*3): Newly formed crystals from fresh gel. (\*4): Total weight of whole crystals after run. (\*5): Amount of added seed. (\*6): Ratio, x-ray intensity of phase S/total intensity of whole crystals. (scanning speed 1°/32min.; chart speed 1 cm/min.)

growth rates were approximately equal for phases G and N, and the growing seed crystals were comparatively uniform in dimensions, as can be seen in Figure 4c. Because the radii of grown seeds grew to about twice the size of the original ones after 66 hrs, the final volume became about 7 times the original volume of phase S. The increase in the weights is probably of a similar magnitude, and consequently the ratio (I<sub>s</sub> + I<sub>g</sub>)/I<sub>t</sub> should become much higher than the ratio I<sub>s</sub>/I<sub>t</sub> with growth time.

As a result of these studies, we conclude that the compositions of the growth zone are governed by the initial compositions of the freshly-prepared gels and have no relation to either the seeds or growth time. When natural analcime is used as a seed, the growth takes place in the same manner. Such growth is to be expected because the structural misfit between phases S and G is only 3 percent maximum, as indicated by the difference in their lattice dimensions.

Our results appear to support the hypothesis that active complex chemical species play an important role in zeolite crystallization, as was first proposed by Kerr (1966). Both the crystallization and growth of analcime can be readily explained by consideration of the behavior of the chemical species which were dissolved in the clear solutions.

At the beginning of the reaction, a large portion of silica in the original mixture promptly dissolved in

the liquid phase and was converted to ionic species such as occurs when sodium metasilicate is dissolved in water. The Tyndall phenomenon of colloidal dispersions was not observed before crystallization began. As can be seen from the concentration range (ABCD) in Figure 1, the silica content of the starting materials ranged from 1.3 to 2.5M, but the formation of amorphous materials due to polymerization did not occur in the clear solution over a long period of time.

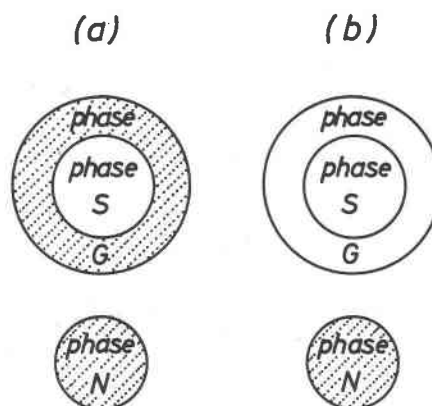


Fig. 5. Schematic representation of a growing seed and newly-formed crystal from fresh gel. S represents seed, G growth zone, and N newly formed crystal. Dashed areas indicate the same composition as phase N; (a) means that G is the same as N in composition, whereas (b) means that it is the same as S.

As the first step in crystallization, we propose that chemical species composed of sodium aluminosilicates formed rapidly in an early stage. The clusters once formed were unchanged on heating but were chemically active. As the next step, we propose that a partial polymerization of the clusters took place. Presumably they were being superposed on each other in complete alignment like the stacking of building blocks, and this polymerization led to a stage of stable nuclei, and finally to the growth of crystals. From the homogeneous crystal growth observed in the early stages, as shown in Figure 4a, the number of the nuclei probably converged to a certain range.

Kerr (1966) theorizes a soluble active species that probably is a colloidal particle rather than a simple molecular or ionic species, but its nature remains unknown. Ciric (1968) has reported that the soluble species probably consist of an aluminosilicate dimer or tetramer containing two negative charges. These conclusions were derived from his investigations of the crystallization of zeolite A.

On the basis of the experimental results, the formation and growth of analcime might be explained by assuming a complex building block model for the active chemical species. We suggest that such clusters possess definite compositions and rigid structures identical with those of analcimes, although their compositions and structures have not yet been determined directly.

The dimensions of the active chemical species and the critical radii of the nuclei of analcimes are unknown for discussions of the results of the present study, but are a subject for future investigations.

### Summary

Initial gels of composition  $10\text{Na}_2\text{O} \cdot (0.05\text{--}0.15)\text{Al}_2\text{O}_3 \cdot (6\text{--}16)\text{SiO}_2 \cdot (168\text{--}592)\text{H}_2\text{O}$  were prepared using aqueous solutions of sodium hydroxide, sodium aluminate, and aqueous colloidal silica sol. These gels changed to clear solutions within 5 min on heating at  $100^\circ\text{C}$  under atmospheric pressure, and after 3 to 5 hrs crystals of analcime solid solution formed from them. The following conclusions are made. (1) The effects of the initial concentrations of soda and silica components on the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the crystals were important, whereas the effect of alumina was small. (2) By the isomorphous substitution  $\text{Si}^{4+} \rightleftharpoons \text{Na}^+\text{Al}^{3+}$ , an increase in the initial concentrations of soda and alumina caused a decrease in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the framework, whereas an increase in silica resulted in an increase of the ratio. (3) The compositions of the analcime solid-solution crystals

were governed only by the initial concentrations of three components in the gels and were independent of the variation of their concentrations with reaction time. (4) Analcime crystals grew uniformly in size over a period of about 120 hrs and had trapezohedral crystal habit. (5) Analcime seed crystals grew in freshly-prepared gels even if the compositions of the fresh gels differed from those gels used for the preparation of the added seed. (6) The composition of the growth zones surrounding the seed was governed by the initial concentrations of three components in the fresh gels and was independent of the composition of the added seed and of the growth time. The crystallization and growth of analcimes can be explained by assuming the existence of active chemical species composed of sodium aluminosilicates. We propose that these species possess fixed compositions and rigid structures identical with those of the analcimes formed.

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