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ARTIFICIAL CRYSTALLIZATION OF VOLCANIC GLASS TO CARNEGIEITE, NEPHELINE AND ALBITE AT ROOM PRESSURE

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ABSTRACT

Glass powder separated from natural glassy rhyolite tuff by the sedimentation method was heated at room pressure with NaOH, γ-Al_2O_3 and other metal oxides such as BeO, MgO, ZnO, CdO, SrO, BaO, TiO_2, and V_2O_5, etc. at temperatures from 500° C. up to 800° C. for one hour. We set up the following experimental condition with three variables, as temperatures, amounts of γ-Al_2O_3 and each metal oxide, and with definite amounts of glass powder as 0.300 g and NaOH as 0.16 g and 0.24 g. Crystallization of these minerals was usually accelerated with addition of metal oxides than without them. The formation of carnegieite was favored by the use of metal oxides as BeO, MgO, ZnO, CdO and the formation of nepheline or albite was gradually accelerated by the use of oxides of metal ions with relatively higher valencies as V_2O_5. The *a* parameters of carnegieite showed larger values with rising temperatures of synthesis at a definite amount of each metal oxide, and smaller values were obtained with smaller radii of metal ions of the oxides at a definite temperature of synthesis; the temperature effect may be due to substitution disorder of Si-Al at higher temperatures, whereas the cause giving rise to the radius effect is uncertain except we can say that the metal oxides act as mineralizers. Behavior of the synthesized albite is intermediate between high and low albites corresponding to the temperatures of synthesis from 500° C. up to 800° C.

INTRODUCTION

In the course of the mineralogical study on glassy rhyolite tuffs which are widely found in Japan, our attention has frequently been drawn to the problem concerning artificial crystallization of the glass at room pressure, and we have taken a particular interest in the problem whether or not we can find out a material which plays an important role in acceleration of crystallization of the glass. The earlier study (Sudo and Matsuoka, 1959; Sudo *et al.* 1960) was carried out from such a viewpoint. Successively we took interest in the role of NaOH in dry condition at high temperatures, that is, sodium-rich high temperature dry condition. Also, we noticed various kinds of oxides playing important roles to accelerate crystallization, and also noticed that addition of Al_2O_3 was effective to extend the kind of reaction products. On account of these, we studied the system of glass-NaOH-γ-Al_2O_3-metal oxides.

In the stage of preparation of the present paper, we could refer to the recent work of Rigby and Hutton (1962) who have studied the chemical reaction of sodium carbonate mixed with V_2O_5 on synthetic silica-alumina mixtures of pure silica and alumina, and obtained albite, nepheline, jadeite, cristobalite and tridymite etc., at 800° C. to 1600° C. at room pressure. They suggested that V_2O_5 may play an important role as a mineralizer in these chemical reactions.

ACKNOWLEDGMENTS

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STARTING MATERIAL

In this study we used glassy tuff from Koichi, Nagano Prefecture. It occurs as white powder; *x*-ray examination revealed fragments of feldspar and quartz in glass particles. These fragments were removed by the sedimentation method, and the residue was pulverized in an agate mortar into fine powder to be used in the present experiment. Its chemical composition is shown in Table 1. *X*-ray powder diffraction data for the specimen thus obtained show a broad band due to glass, and in the detection limit of *x*-ray diffraction in the present study, we could not detect the presence of any crystalline materials. But its chemical composition shows a considerable amount of water, which suggests that the glass has partly been altered by weathering. In the light of these data, the present material may be called a pozzolanic material. It is anticipated that slightly weathered fine-grained glassy tuff may be more reactive with reagents. On account of this, Koichi material was used in the present study.

NaOH: Reagent-grade chemical was used. There are ways to use other sodium salts as

TABLE 1. CHEMICAL ANALYSIS OF VOLCANIC GLASS OBTAINED BY THE SEDIMENTATION METHOD FROM LIPARITE GLASSY TUFF

(Analyst: UEDA, 1959)

SiO_2	72.00%
TiO_2	0.15
Al_2O_3	12.15
Fe_2O_3	0.25
FeO	—
MnO	—
MgO	—
CaO	tr.
Na_2O	5.16
K_2O	3.96
H_2O	0.83
Ig. loss[1]	5.30
Total	99.80%

[1] Above 105° C.

sodium carbonate, sodium chloride, etc. but we were interested in using NaOH, because (OH) is one of the important anions in rock-forming minerals.

Alumina: As one of the sources of aluminum, we used γ-Al_2O_3 (reagent-grade). The reason of using γ-Al_2O_3 is its strong absorptive powder which is capable of prompt chemical reaction.

Metal oxides: The following metal oxides (reagent-grade) were used; BeO, MgO, ZnO, CdO, CaO, SrO, BaO, CuO, NiO, Bi_2O_3, Cr_2O_3, MnO_2, TiO_2 and V_2O_5.

EXPERIMENTS

Glass particles separated from glassy tuff were pulverized in an agate mortar into fine powder less than 100 mesh. The powder was mixed with γ-Al_2O_3, NaOH and a metal oxide, and the mixture was packed into a small silver crucible and heated at a definite temperature with mean heating rate of 20° C. per minute. The junction of the thermocouple was set directly on the surface of the powder cake in the crucible. After heating at a definite temperature the sintered mass was quenched in room air, pulverized in an agate mortar and washed with hot water until all soluble materials were completely dissolved. The residue was pulverized in an agate mortar into fine powder and packed into an aluminum holder and was examined by x-ray diffractometer under the experimental condition as Cu, K_α-radiation, 35 KV, 15 MA.

It can be considered that the present chemical reactions may be affected by such conditions as temperature of synthesis, heating time, relative amounts of starting materials, γ-Al_2O_3, NaOH, and each metal oxide. It was very difficult to trace the chemical reactions under these multifold conditions, hence we took three variables: temperature of synthesis, and amounts of γ-Al_2O_3 and NaOH. Other conditions were held constant. The amount of the starting material was 0.300 g. The amount of γ-Al_2O_3 was in the range of 0.000–0.100 g and that of each metal oxide in the range of 0.000–0.200 g. An excess of NaOH caused the mixture to be more easily melted even at relatively lower temperatures; the consolidated mass was amorphous under x-ray. An insufficient amount of NaOH caused poor crystallization. With the amount of NaOH in a proper range, we could obtain a sintered state in most wide ranges of temperatures, in which the crystallization of glass powder was particularly accelerated. After many trial experiments, we determined the amount of NaOH as 0.16 g; in this case, the sintering temperature range was 500°–800° C. Above 800° C. the powder melted, and the consolidated mass became amorphous. Below 500° C., crystallization was insufficient to permit identification of the reaction products. The amount of NaOH was 0.16 g throughout the present experiments, but, as will be stated in the next paragraph, the effect obtained by increasing the amount of NaOH, for example to 0.24 g, was also examined.

GENERAL RESULTS

We obtained the following results:

(1) In the present study, in the system of glass $+\gamma$-Alumina$+$NaOH$+$metal oxides, we can confirm the crystallization of carnegieite, nepheline and albite.

(2) In general, the crystallization of these minerals was remarkably accelerated under the condition of coexistence of metal oxides; their x-ray powder reflections were stronger than in the case without them.

(3) Two examples are illustrated; one is glass $+NaOH+\gamma$-Al_2O_3+ZnO (Fig. 1), and the other is glass $+\gamma$-$Al_2O_3+NaOH+V_2O_5$ (Fig. 2).

Glass$+NaOH+\gamma-Al_2O_3+ZnO$

The field of formation of carnegieite develops where the amounts of V_2O_5 and $\gamma-Al_2O_3$ are extremely small, and its development is restricted at extremely high temperatures. The field of formation of albite develops where the amount of V_2O_5 is larger and the amount of $\gamma-Al_2O_3$ is relatively smaller. The area of formation of nepheline develops with a wide range in the amount of $\gamma-Al_2O_3$ and an intermediate range in the amount of V_2O_5; the latter develops, however, with rising temperature of synthesis. The area of coexistence of albite and nepheline develops where the amounts of both $\gamma-Al_2O_3$ and V_2O_5 are larger, and it is restricted with increase in temperature of synthesis. The area of coexistence of carnegieite and nepheline develops with a wide range of the amount of $\gamma-Al_2O_3$ and with a small amount of V_2O_5.

CARNEGIEITE

We noticed slight shifts of x-ray powder reflections according to the experimental conditions, and later we noticed that a slight increase of the amount of NaOH caused better formation of carnegieite and more remarkable shifts of the reflections under the experimental conditions. We examined the shifts of x-ray powder reflections in detail under the following experimental conditions: glass powder: 0.300 g, NaOH: 0.24 g, $\gamma-Al_2O_3$: 0.050 g, ZnO: 0.050 g. We maintained these experimental conditions for each of the metal oxides and confirmed the following:

(1) The formation of carnegieite was favored by using metal oxides as BeO, MgO, ZnO, CdO, whereas the formation of nepheline seems to be promoted when the oxides with metal ions of relatively higher valencies are used (Table 2).

(2) It was noteworthy that a clearly correlative relationship was confirmed between the amount of shifts of the principal reflections and the temperature of synthesis. Figures 3 and 4 show the results obtained in the case which in ZnO was used.

As these figures show, values of a parameters are larger with higher temperatures of synthesis when a definite metal oxide is used. This fact can be appropriately ascribed to substitution disorder of Si-Al in the

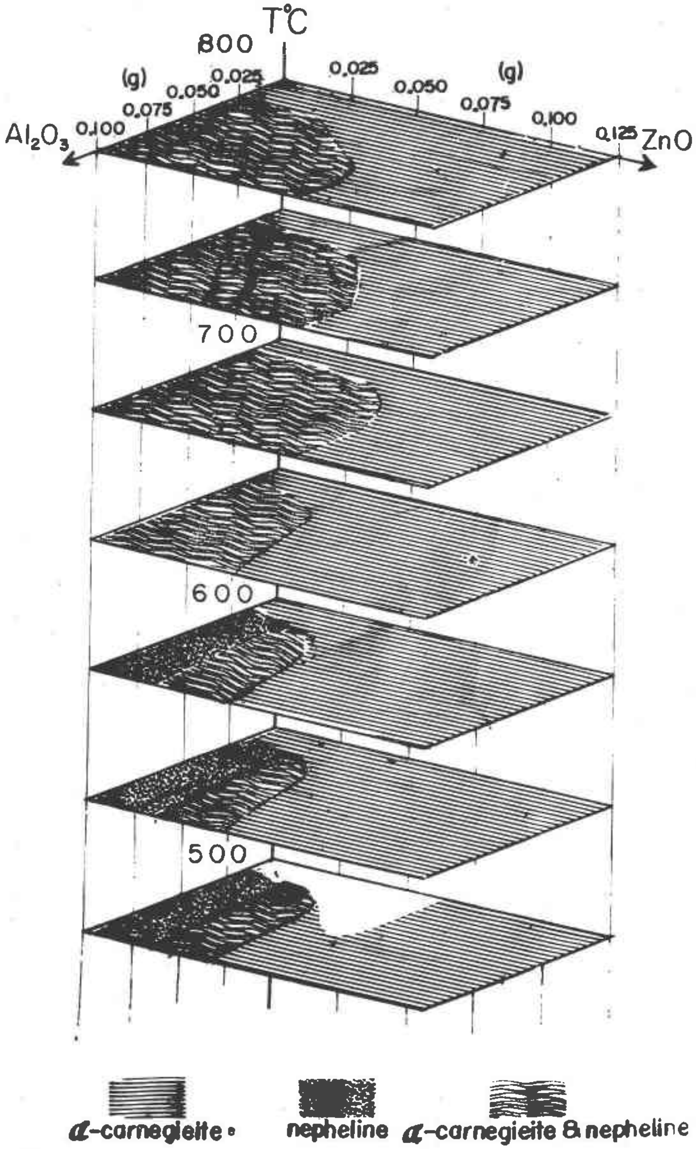

FIG. 1. Diagram showing formations of carnegieite and nepheline and their associations under the following condition: glass powder: 0.300 g, NaOH: 0.16 g, γ-Al_2O_3 and ZnO: various amounts, temperature: 500°–800° C. A blank field in the section at 500° C. means the area where any products cannot be confirmed. The areas were determined on the basis of the experimental results obtained from two hundred coordinates on the plane of each temperature.

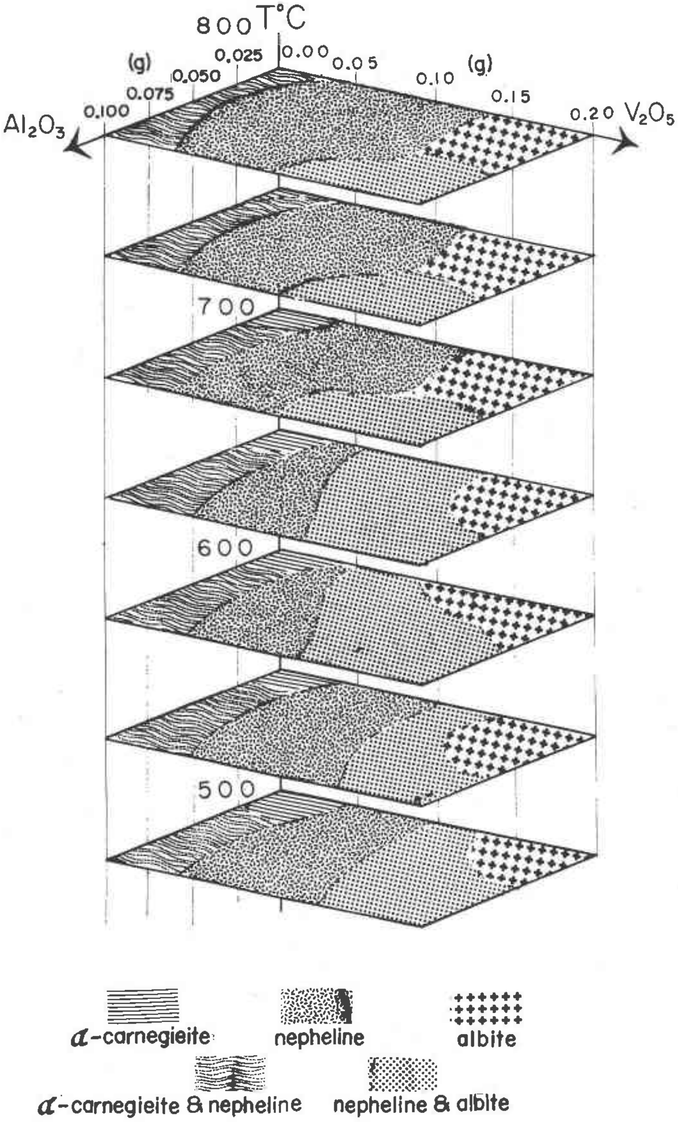

FIG. 2. Diagram showing formations of carnegieite, nepheline and albite and their associations under the following condition: glass powder: 0.300 g, NaOH: 0.16 g, γ-Al_2O_3 and V_2O_5: various amounts, temperature: 500°–800° C. The areas were determined on the basis of experimental results obtained from two hundred coordinates in each temperature plane.

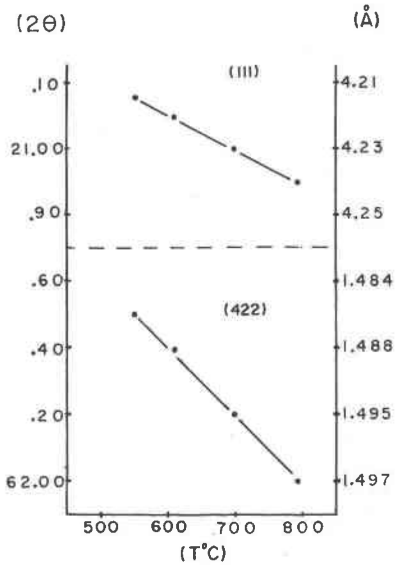

FIG. 3. Relationship between the spacing of x-ray powder reflections of carnegieite and the temperatures of its synthesis. The experimental conditions are as follows: glass powder: 0.300 g, NaOH: 0.24 g, ZnO: 0.050 g, γ-Al_2O_3: 0.050 g.

tetrahedral coordination. In rising temperatures, the distribution probably tends to have disordered configuration, which may give rise to a slight expansion of the unit cell of carnegieite.

(3) We also noticed a clearly correlative relationship between the amount of shifts of the principal reflections of carnegieite and the kind of metal oxides (Fig. 5). It is worthy of note that in the case of Be, which is the smallest ion in the metals under consideration, each of the principal reflections occurred as a single peak at 700° C. (Fig. 5 (B)), but at 800° C.

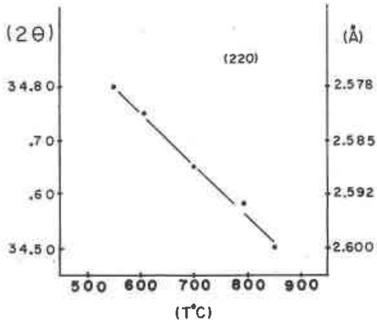

FIG. 4. Relationship between the spacing of x-ray powder reflections of carnegieite and the temperatures of its synthesis. The experimental conditions are as follows: glass powder: 0.300 g, NaOH: 0.24 g, ZnO: 0.050 g, γ-Al_2O_3: 0.050 g.

TABLE 2. KINDS OF METAL OXIDES FAVORING THE FORMATION OF CARNEGIEITE OR NEPHELINE, OR THEIR ASSOCIATION

Carnegieite	BeO, MgO, ZnO, CdO
Carnegieite and Nepheline	CaO, SrO, BaO CuO, NiO Bi_2O_3, Cr_2O_3, MnO_2
Nepheline	TiO_2, V_2O_5

it occurred as a distinct doublet (Fig. 5F). As shown in Fig. 6, we could confirm a clearly correlative relationship between the amount of shifts of the principal reflections of carnegieite and the radius of metal ions in the oxides used. As shown in Table 3, values of the *a* parameters of carnegieite were smaller when the radii of the metal ions of the oxides were smaller.

The above facts suggest that a metal ion of the oxide is included in the carnegieite lattice by isomorphous replacement as follows: (Na, M) (Al, Si)O_4; M: metal ions. But it is very difficult to confirm this. Metal ions in the residues were analysed chemically; usually they occurred in small amounts, and we could not confirm any distinct correlation between these amounts and *a* parameters (Table 4). But this fact does not necessarily deny the possibility of isomorphous replacement for the following reasons: (a) under the microscope, the residues are still composed of fine particles, (b) usually the

TABLE 3. *X*-RAY POWDER DIFFRACTION DATA FOR THE PRINCIPAL REFLECTIONS AND *a* PARAMETERS OF CARNEGIEITE (Cu, Kα: 1.5418 Å)

hkl	3A[1]	3B(BeO)	3C(MgO)	3D(ZnO)	3E(CdO)[2]	3F(BeO)
	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)
111	4.25	4.13	4.24	4.25	4.27	4.13 4.23
222	2.600	2.536	2.600	2.605	2.614	2.529 2.585
422	1.499	1.459	1.499	1.501	1.506	1.457 1.492
a (Å)	7.36	7.158	7.347	7.361	7.389	7.148 7.316

[1] Without metal oxides.

[2] Carnegieite coexists with a small amount of nepheline.

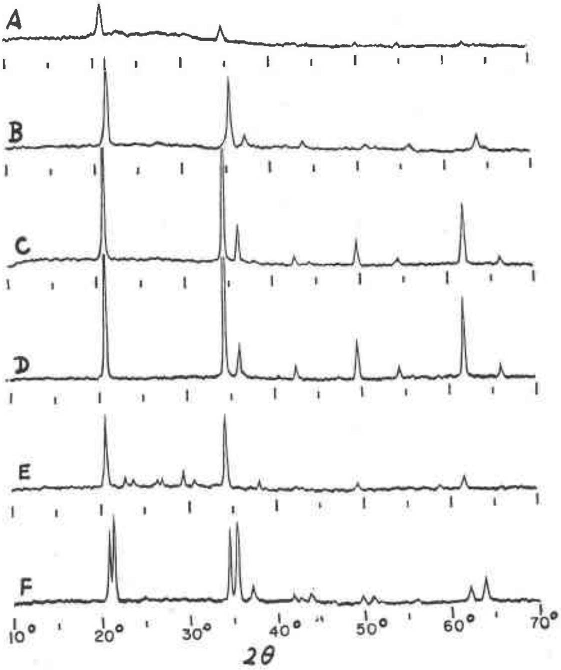

FIG. 5. *X*-ray powder diffraction data of carnegieite obtained under the following condition: glass powder: 0.300 g, NaOH: 0.24 g, γ-Al_2O_3: 0.050 g, metal oxides: 0.050 g. The temperature of the experiment was 700° C. in the cases of A to E, and 800° C. in F. The conditions concerning metal oxides are as follows: A: without metal oxide, B: BeO, C: MgO, D: ZnO, E: CdO, F: BeO.

reflections of synthesized carnegieite developed well, but actually we could notice a sign that a very broad band overlaps the reflections of carnegieite, which suggests that insoluble amorphous materials are still included in residues in association with carnegieite, (c) hence, it is probable that part of the metal ions of the oxides may be included in the amorphous glassy material.

But it is very difficult to confirm whether this inference is true or not be-

TABLE 4. CHEMICAL ANALYSIS OF MgO OF THE RESIDUE SHOWING X-RAY POWDER REFLECTIONS OF CARNEGIEITE OBTAINED IN THE FOLLOWING EXPERIMENTAL CONDITIONS

Specimen	Chem. composition				Experimental condition			
	MgO	Al_2O_3	Na_2O	Total	Glass powder	Al_2O_3	NaOH	Temp. of Synthesis
2K	3.01%	17.45%	21.27%	47.73%	0.300 g	0.050 g	0.24 g	600° C.
4K	0.86	24.11	17.70	42.67	0.300	0.050	0.24	800° C.
Before treatment	9.77	40.88	16.90	67.55				

Table 5. *X*-Ray Powder Diffraction Data for Nepheline (Cu, Kα: 1.5418 Å)

Natural nepheline[1]		Ex. 24–5 C_1		Ex. 24–5 d_1		Ex. 30–FU_1	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
4.67	6			4.62	3		
4.35	18	4.35	3	4.35	4	4.33	15
4.21	50	4.23	17	4.21	15	4.19	25
3.867	65	3.87	17	3.87	16	3.85	30
3.66	10						
3.290	55	3.29	12	3.29	12	3.27	21
3.23	10			3.19	2		
3.028	72	3.03	21	3.02	20	3.01	28
2.894	40	2.903	10	2.894	9	2.885	12
2.585	24	2.592	13	2.585	9	2.578	6
2.508	17	2.508	4	2.508	5	2.501	5
2.411	17	2.411	4	2.404	3	2.404	4
2.356	40	2.356	9	2.350	9	2.344	14
2.315	23	2.308	5	2.315	5	2.304	10
2.171	6	2.176	2	2.171	2		
2.132	8	2.132	3	2.127	2	2.122	4
2.099	17	2.103	4	2.099	4	2.094	5
1.937	11	1.941	4	1.933	3		
1.892	6	1.895	2	1.895	2		
1.801	8			1.798	2		
1.698	8			1.698	2		
1.639	5						
1.623	8			1.621	2	n.d.	
1.605	6			1.605	2		
1.568	18	1.566	5	1.566	4		
1.528	4			1.528	2		
1.475	6	1.475	2	1.473	2		
1.435	8	1.437	3	1.435	3		
1.400	5						
1.389	16	1.839	4	1.389	3		
1.377	5						
Glass powder		0.300 g		0.300 g		0.300 g	
Al_2O_3		0.050 g		0.075 g		0.025 g	
NaOH		0.16 g		0.16 g		0.16 g	
Metal oxide		0.000 g		0.000 g		0.100 g (V_2O_5)	
Temp. of synthesis		700° C.		700° C.		500° C.	

[1] From Korea.

cause of difficulty of separating carnegieite from the glassy material. Hence we could not arrive at the final conclusion from the results in Table 4. Thus we cannot present any additional comments except that the ions in the oxides play a role of mineralizers in these chemical reactions.

NEPHELINE

As already stated in the general statement, nepheline tends to form where certain metal oxides with metal ions of higher valencies are used. We could not confirm noticeable changes in the parameter of nepheline (Table 5). In the above experiment carnegieite was formed commonly coexistence with nepheline. In such a case, one of the principal reflections of carnegieite occurring at 21° (2θ) (111) overlaps one of the nepheline reflections. Nepheline gives the characteristic strong reflection at 29.5° (2θ). In the case of nepheline without carnegieite, the intensity ratio I (21°)/I (29.5°) is about 3/5. Hence, we regarded coexistence of carnegieite and nepheline in the case where the ratio was clearly larger than 3/5, and also we confirmed the reflection at 29.5° (2θ) (Table 6).

ALBITE

(1) The formation of albite was observed only when a large amount of V_2O_5 was used (Table 7).

(2) In the case of coexisting albite and nepheline, boiling for 2 minutes in 2% nitric acid entirely dissolved nepheline, leaving albite behind. Hence, the powder reflections of albite were more clearly developed, and their weak reflections were more easily and distinctly measured. From

TABLE 6. *X*-RAY POWDER DIFFRACTION DATA FOR THE PRINCIPAL REFLECTIONS OF MIXTURE OF CARNEGIEITE AND NEPHELINE (Cu, Kα: 1.5418 Å)

hkl	Carnegieite[1]	4C	4D	Ex. 24−5m$_1$
	d(Å)	d(Å)	d(Å)	d(Å)
111	4.29	4.23	4.23	4.21
	—	3.027	3.030	3.020
220	2.610	2.600	2.585	2.578
Glass powder		0.300 g	0.300 g	0.300 g
Al_2O_3		0.075 g	0.075	0.025 g
NaOH		0.16 g	0.16 g	0.16 g
Metal oxide		0.050 g (ZnO)	0.025 g (ZnO)	0.025 g (ZnO)
Temp. of synthesis		700° C.	800° C.	700° C.

[1] ASTM.

TABLE 7. *X*-RAY POWDER DIFFRACTION DATA FOR ALBITE (Cu, Kα: 1.5418 Å)

hkl	Albite[1]		Ex. 30		Ex. 30		Natural Albite[2]	
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
020	6.417	5	6.463	9	6.463	7	6.371	30
$11\bar{1}$	5.829	1R	5.867	2	5.867	2	5.906	4
$1\bar{1}\bar{1}$	5.644	1R	5.680	3	5.718	2	5.609	4
$20\bar{1}$	4.040	10R	4.058	34	4.058	19	4.022	34
$1\bar{1}1$	3.883	7R	3.900	8	3.900	5	3.850	12
$1\bar{3}0$	3.754	10	3.770	24	3.747	18	3.786	43
130	3.648	8	3.661	11	3.661	10	3.661	30
$1\bar{3}\bar{1}$	3.480	2	3.480	4	3.480	3	3.507	12
$1\bar{1}\bar{2}$	3.363	2R	3.389	5	3.389	4	3.376	15
040	3.209	10	3.220	65	3.220	60	3.189	100
002	3.175	10R	3.187	50	3.187	37		
220	3.132	9R	3.164	12	3.153	9		
$1\bar{3}1$	3.018	3R	3.018	7	3.018	6	2.969	20
$04\bar{1}$								
$02\bar{2}$	2.950	1	2.950	8	2.950	9	2.931	22
$22\bar{2}$	2.921	1	2.921	8	2.921	8		
131	2.831	4	2.858	7	2.858	7	2.867	15
$1\bar{3}\bar{2}$	2.652	2	2.675	3	2.683	4	2.637	9
$1\bar{1}2$	2.522	4	2.529	10	2.529	10	2.564	12
			2.455	2	2.462	2	2.442	9
			2.423	2	2.423	2	2.411	4
			2.386	3	2.386	2	2.386	4
			2.309	2	2.309	2	2.321	7
			2.287	2	2.292	2	2.281	3
060	2.141	3R	2.146	5	2.151	7	2.186	5
			2.122	3	2.122	3	2.127	8
Glass tuff			0.300 g		0.300 g			
Al_2O_3			0.025 g		0.000 g			
NaOH			0.16 g		0.16 g			
Metal Oxide			0.200 g (V_2O_5)		0.150 g (V_2O_5)			
Temp. of synthesis			700° C.		700° C.			

[1] After Donnay and Donnay (1952).

[2] From Amelia, Virginia, U.S.A.

the *x*-ray chart of the residue treated with nitric acid, we measured the θ value of $2\theta\,(131) - 2\theta\,(1\bar{3}1)$ appearing in the range of 29°–32°(2θ) (Fig. 7), which falls in the intermediate range between high and low albites, corresponding to temperatures of synthesis from 500° C. up to 800° C. (Fig. 8). Below 500° C. the crystallization of glass powder was just visible and we could not estimate the θ value accurately. In Fig. 8 the results of the data obtained by Mackenzie (1957) are compared with our results. In

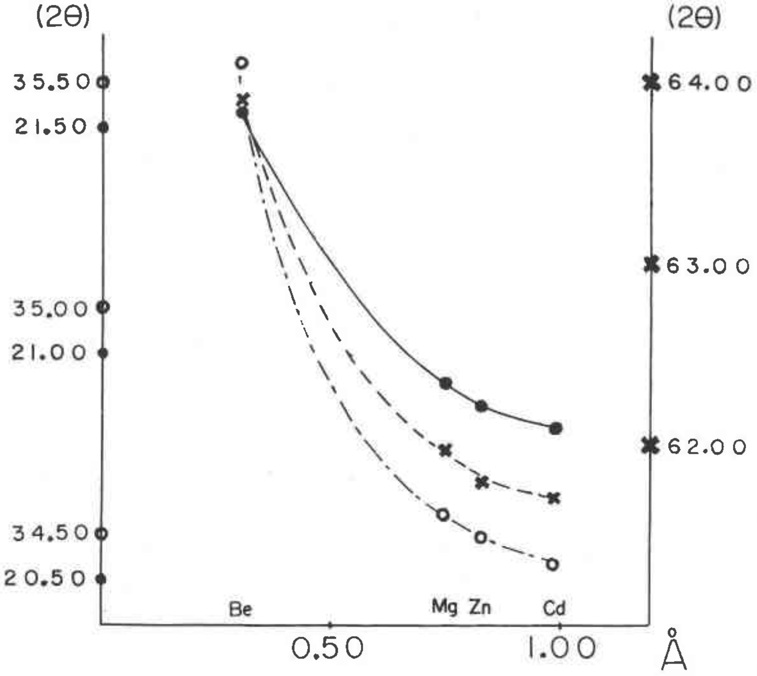

Fig. 6. Relationship between the amount of shift of x-ray powder reflections of carnegieite and the radius of metals of oxides used. Experimental conditions: glass powder: 0.300 3, NaOH: 0.24 g, γ-Al_2O_3: 0.050 g, metal oxide: 0.050 g, temperature: 700° C.

Mackenzie's experiment, a very long heating time was necessary in order to obtain intermediate albites. In our experiment, we could obtain the θ value corresponding to an intermediate albite even during one-hour heating; this fact may be due to a mineralizer role of V_2O_5.

(3) It is a question whether or not V_2O_5 is included isomorphously in

Table 8. Chemical Analysis of Vanadium in the Residues

Sample	Temp. of Synthesis	V_2O_5 (%)	Experimental conditions			
			Glassy tuff	Al_2O_3	NaOH	V_2O_5
FK_1	500° C.	1.03	0.300 g	0.050 g	0.16 g	0.200 g
$2K_1$	550	1.08	0.300 g	0.050 g	0.16 g	0.200 g
$3K_1$	600	1.15	0.300 g	0.050 g	0.16 g	0.200 g
$4K_1$	650	1.05	0.300 g	0.050 g	0.16 g	0.200 g
$5K_1$	700	0.74	0.300 g	0.050 g	0.16 g	0.200 g
$6K_1$	800	0.71	0.300 g	0.050 g	0.16 g	0.200 g

the albite lattice. Chemical analyses for vanadium in the residues are shown in Table 8. We could not confirm a distinct correlation between the temperature of synthesis and the amount of vanadium. But it seems that this fact does not necessarily reject the conclusion that vanadium is included in the albite lattice by isomorphous substitution, because of the following reasons:

(a) the *x*-ray reflections of synthesized albite were usually weaker than those of natural albite under the same experimental condition, and on the *x*-ray chart of synthesized albite,

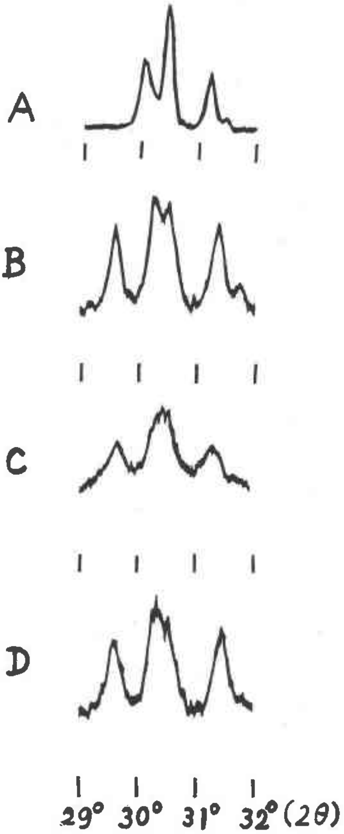

FIG. 7. *X*-ray powder diffraction data for synthesized albite in the range of 29°–32° (2θ).

A: Natural albite, Amelia, Virginia, U.S.A.

B: The experimental condition: glass powder: 0.300 g., NaOH: 0.16 g, γ-Al_2O_3: 0.025 g, V_2O_5: 0.200 g, temperature: 700° C.

C: Experimental conditions same as B except temperature: 650° C.

D: Experimental conditions same as B except temperature: 800° C.

a very broad band due to an insoluble amorphous material overlaps those of albite reflections, (b) hence, it is considered that an amorphous glassy material is included in residues in association with albite, (c) it is probable that vanadium may be partly included also in the glassy material.

Confirmation of the above, however, is very difficult because of difficulty in separating the albite from this glassy material. No additional comment can be given here except that V_2O_5 may play the role of a mineralizer, combining with NaOH.

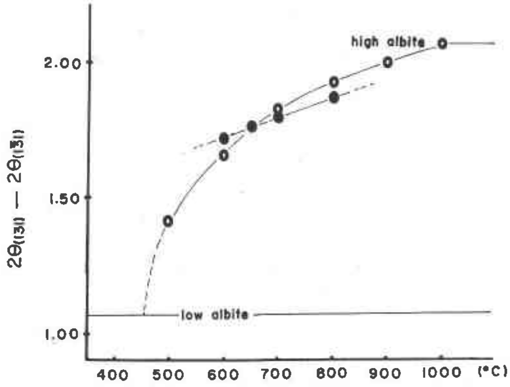

FIG. 8. Relationship between the value of $2\theta(131)–2\theta(1\bar{3}1)$ and the temperatures of synthesis of albite. Solid circle: data for albite obtained in the present experiments. Open circle: data for the albite obtained by hydrothermal synthesis by Mackenzie (1957).

DISCUSSION

(1) It should be noticed that, in the present experiment, Al and Na are in two different chemical situations; one exists in Si-Al networks in glass and the other in separate compounds as an oxide and hydroxide. It may be natural to consider that chemical reactions may be affected by the crystallochemical nature of Si, Al and Na in the starting material, for example, whether they exist entirely as constituents of a network structure, or they entirely exist as separated compounds. For the purpose of examining these points, the following experiments have been carried out:

(2) Other starting materials, such as pitchstone or reagent-grade silica-gel, were prepared.

(3) By using pitchstone or perlite glass as the starting material, the same result as in the case of glass particles in tuff was obtained.

(4) Reagent-grade silica-gel was used as the starting material, mixed with $\gamma-Al_2O_3$; an experiment was carried out maintaining conditions corresponding to the conditions kept in the albite-nepheline field, where glass powder was used as the starting material. By this experiment we

could still confirm crystallization of albite at 650° C., and in this case cristobalite has formed commonly in association with albite. It is noteworthy that the θ value of albite synthesized in the experiment using silica-gel was larger, approaching that of high albite rather than that obtained in the case of glass powder. It has been considered that substitutional disorder of Si/Al is one of the important causes of producing albite polymorphs. Hence, the fact suggests that substitutional disorder is more pronounced in the albite obtained in the experiment from silica-gel than in the case of glass particles. In the case of silica gel, crystallization of cristobalite was distinctly confirmed even below 500° C., for example at 450° C.

REFERENCES

DONNAY, G. AND J. D. H. DONNAY (1952) *Am. Jour. Sci.* (*Bowen Volume*), 115–132.
MACKENZIE, W. S. (1957) *Am. Jour. Sci.*, **255**, 481–516.
RIGBY, G. R. AND R. HUTTON (1962) *Jour. Am. Ceram. Soc.* **45**, 68–73.
SUDO, T. AND M. MATSUOKA (1959) *Geochim. Cosmochim. Acta*, **17**, 1–5.
——— S. UEDA AND S. IWAMOTO (1960) *Nature* **188**, 223–224.

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