

KINETIC AND ELECTRON OPTICAL STUDIES OF THE REACTION PROCESSES BETWEEN KAOLINITE AND SODIUM CARBONATE

YASUSHI KUBO,¹ GORO YAMAGUCHI, AND KOMEI KASAHARA, *Department of Industrial Chemistry, The University of Tokyo, Hongo, Tokyo.*

ABSTRACT

The system kaolin-1.5 Na₂CO₃ was studied at temperatures 650° to 800°C, and inversion of the high-carnegieite-like phase (L-phase) to nepheline was examined in relation to the starting materials. The L-phase from metakaolin inverts more readily to nepheline than that produced from well-crystallized kaolinite. Excess alkali (>1 mole Na₂CO₃) stabilizes an alkali-rich carnegieite at around 800°C.

Electron-optical examinations at various stages of the reaction reveal topotactic relationships between the original and product phases. From these observations and kinetic data, the process is interpreted in terms of the random distribution of Na ions in the L-phase which has a similar Si-O framework to that of the starting material.

INTRODUCTION

Investigations of solid-state reactions to form nepheline-carnegieite minerals reveal two different reaction series according to differences in starting materials (Kubo *et al.*, 1966, 1967). One is a sequence, starting mixture → high-carnegieite-like phase (designated tentatively as the L-phase) → nepheline → high-carnegieite, and the other, starting mixture → nepheline → high-carnegieite. The former was observed in the systems, kaolinite—, dehydroxylated kaolinite—, and coprecipitated aluminosilicic gel—Na₂CO₃, and the L-phase was interpreted as a disordered phase of high-carnegieite. Temperatures of the inversion to nepheline, which are at variance in different starting materials, are characteristic of the L-phase. On the other hand, mixtures of alumina-hydrate or γ -alumina with sodium disilicate followed the latter sequence, which is consistent with the thermodynamic stability relationship. In both cases, topotactic relationships between the original and product phases were observed. This indicates that structural inheritance is an important aspect in these reactions. Water and impurities have little effect on the observed reaction series.

In the present investigations, isothermal experiments at various temperatures were carried out and an attempt was made to measure the yields of new phases at various stages of reaction. Kaolin minerals were mixed with 1.5 moles of powdered sodium carbonate and the percentages

¹ Present address: The Institute of Industrial Science, The University of Tokyo, Roppongi, Tokyo.

of formation of the L-phase and of its inversion to nepheline were estimated at various reaction stages. Electron-optical observations were also made of the entire processes. The experimental rate determinations of each phase and the topotactic relationships between the original and product phases are described in detail, but no attempt has been made to obtain the activation energies for reactions because of the complexity involved in the entire processes.

EXPERIMENTAL

The materials used in the present experiments were well-crystallized Zettlitz kaolinite and Korean halloysite as determined by X-ray diffraction and by electron microscopy. X-ray examination indicated the presence of a small amount of illite in the former but no discernable impurity in the latter. Metakaolin was made from Zettlitz kaolinite by heating at 700°C for two hours. The weight loss by this procedure was 12.69 percent corresponding to 97.56 percent dehydroxylation of the original kaolinite. Table 1 gives the chemical compositions of these starting materials.

TABLE 1. CHEMICAL COMPOSITIONS OF ZETTLITZ KAOLINITE AND KOREAN HALLOYSITE (%)

	Ignition loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Total
Zettlitz Kaolinite	14.05	45.13	37.17	0.55	0.83	0.49	98.22
Korean Halloysite	13.33	45.60	37.43	0.32	0.77	0.78	98.23

For the determination of the reaction rates, two different mixtures, kaolinite+1.5 Na₂CO₃ and metakaolin+1.5Na₂CO₃, were made by dry milling in a pot-mill for 16 hours. Specimens in platinum crucibles were placed in the center of an electric furnace at a pre-determined temperature for set lengths of time. At the end of the run, the specimens were quenched in air and examined by X-ray powder diffraction and with the electron microscope.

In this procedure, five to seven minutes were needed for the specimen to reach the furnace temperature. Therefore, the measurement of the reaction time (duration of the reaction) was made with its origin at a point just after the specimen had reached the furnace temperature. Some ambiguity was unavoidable for the reactions of short duration. The reaction temperatures used in the present experiments were 650°C, 700°C, 750°C, and 800°C, respectively, and the reaction times ranged from 15 minutes to 32 hours.

Estimation of the yields of product phases was made by means of X-ray powder diffraction. The integral intensities of product phases were measured on the diffractometer traces obtained at a constant scanning speed of 2°/min. For this purpose, the 220 intensity ($2\theta_{\text{CuK}\alpha} \sim 35^\circ$) of the L-phase and the 21.0 ($2\theta_{\text{CuK}\alpha} \sim 27^\circ$) of nepheline were used. In this case, when both phases coexist, the 220 of the L-phase is superposed on the 22.0 of nepheline. The 22.0 intensity of nepheline was estimated from its 21.0 reflection on the same diffractometer traces by making use of the ratio, 22.0/21.0, obtained by a pure nepheline. The 22.0 intensity of nepheline thus obtained was then subtracted from the total intensity at $2\theta \sim 35^\circ$ to obtain the intensity of the 220 for the L-phase.

A few remarks should be made here concerning the conversion of the X-ray intensity to the yield of each phase. The electron microscopic observation revealed that at an early stage of the reaction, the original platy shape of kaolinite was maintained, whereas its deformation took place as the reaction proceeded. This certainly causes the variation of the orientation of crystals as the reaction proceeds, and reduces the accuracy of the estimation of the yield of the products. As there was no means to estimate the degree of orientation in the present experiments, only the approximate estimates were made, neglecting the orientation effects mentioned above, and were used to estimate a general tendency.

For the conversion of the X-ray intensity to the yield of products, the intensities of pure L-phase and nepheline, I_{L100} and I_{N100} respectively, were obtained as follows. Two specimens were prepared; one heated at 700°C for 16 hours and the other for 32 hours. In these specimens, the reaction between kaolinite and sodium carbonate was assumed completed. The only difference between them is in the degree of inversion of the L-phase into nepheline.

Therefore, the following two equations are obtained.¹

$$I_{L^{16}}/I_{L100} + I_{N^{16}}/I_{N100} = 1$$

$$I_{L^{32}}/I_{L100} + I_{N^{32}}/I_{N100} = 1$$

where $I_{L^{16}}$, $I_{N^{16}}$, $I_{L^{32}}$, and $I_{N^{32}}$ represent the intensities of the L-phase and nepheline in the specimens heated for 16 hours and 32 hours, respectively. These four intensities are obtained by the procedure described before. The unknown quantities in these equations are I_{L100} and I_{N100} . Therefore, by solving these equations, I_{L100} and I_{N100} are obtained and used for the estimation of the yield of products.

In practice the experimental error, as well as the one due to the incorrectness involved in this procedure, gave rise to an anomalous result that the total yield of the L-phase and nepheline exceeded 100 percent at some points. Therefore, in Figs. 1 and 2 which give the variation of yield with increasing reaction time, further correction was made of the values of I_{L100} and I_{N100} tentatively to make the maximum total yield 100 percent. Since the present data of the yields are used to show a general tendency of the reaction process qualitatively, this error does not affect the entire discussions.

For a more quantitative purpose, the value $v = (dN(t)/dt)/L(t)$ was used. In the formula, $N(t)$ and $L(t)$ indicate the amounts of nepheline and the L-phase at time t , respectively, expressed in terms of the mole fraction, and v means the rate of nepheline formation per unit amount of the L-phase at time t . In view of the error involved in the estimation of the yield, this value may be more reliable, since the experimental error due to the effect of crystal habit is cancelled in the ratio, $dN(t)/L(t)$.

RESULTS

Yield. The variation of the yield of new phases with time at 700°C is shown in Figures 1 and 2. Those at 650°C and 750°C also exhibited the

¹ These equations are derived by solving the following four equations.

$$I_{L100}(1 - x_{16}) = I_{L^{16}}$$

$$I_{N100} \cdot x_{16} = I_{N^{16}}$$

$$I_{L100}(1 - x_{32}) = I_{L^{32}}$$

$$I_{N100} \cdot x_{32} = I_{N^{32}}$$

where x_{16} and x_{32} indicate the mole fractions of the inversion of the L-phase to nepheline at 16 hours and 32 hours, respectively.

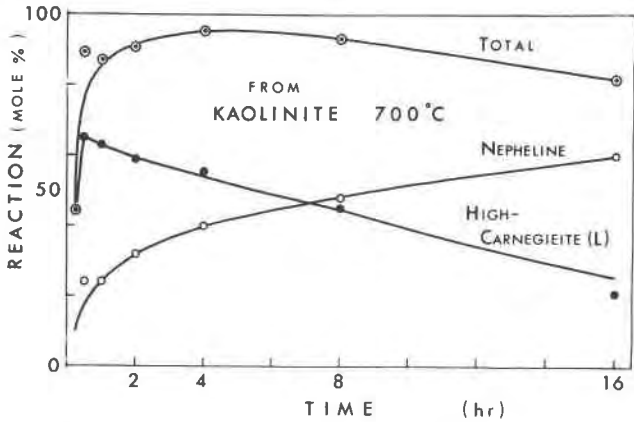


FIG. 1. Variation of the yield of product phases with time in the kaolinite-1.5 Na_2CO_3 system at 700°C.

same tendency regardless of the difference in the rate of reaction. As can be seen in the figures, the total yield, L-phase+nepheline, reached a maximum after 2~4 hours followed by a slight decrease. The reason for this decrease, however, can not be given, as there are unestimated errors involved in the yield data as mentioned above.

At an early stage of reaction at 800°C, the inversion of the L-phase into nepheline followed the same scheme as outlined above, but after about one hour, an increase of a phase with high-carnegieite structure, which must be different from the L-phase, accompanied by a decrease of nephe-

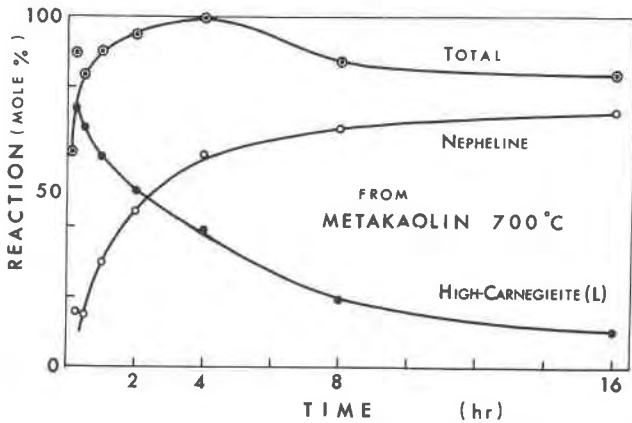


FIG. 2. Variation of the yield of product phases with time in the metakaolin-1.5 Na_2CO_3 system at 700°C.

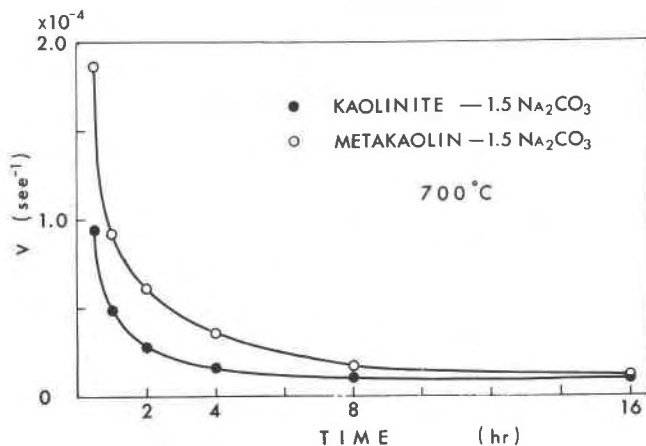


FIG. 3. Rate of L-phase-nepheline inversion at 700°C.

line took place with a maximum formation of nepheline at around one hour. This may indicate that the nepheline phase was transformed to the alkali-rich carnegieite phase that may be the most stable at this temperature.

As a criterion for the difficulty of the inversion of the L-phase to nepheline, the rate of nepheline formation per unit amount of the L-phase at time t , $v = (dN(t)/dt)/L(t)$ as described above, was calculated from the experimental curves at 700°C and is shown in Figure 3. The v is higher in the metakaolin than in the kaolinite system, indicating that the inversion to nepheline is easier in the former. In both cases, these values rapidly decrease at an early stage of reaction but gradually reach a constant value of $0.1 \times 10^{-4} \text{ sec}^{-1}$.

Electron-optical observation. A large number of crystal flakes, obtained from these systems and also from the halloysite—1.5 Na₂CO₃ system at various stages of reaction, were examined at 80 KV with a JEM-7 electron microscope. The shapes and the selected area diffraction patterns of crystal flakes were observed. Although there were crystal flakes at various extent of reaction even at the same temperature, a large number of observations made it possible to obtain an average extent of reaction at each stage. In the following, therefore, the representative patterns will be given.

The reaction sequence is well represented in a series of photographs given in Figures 4 and 5, in which the shapes and the selected area diffraction patterns of the products in a kaolinite—1.5 Na₂CO₃ system at 650°C,

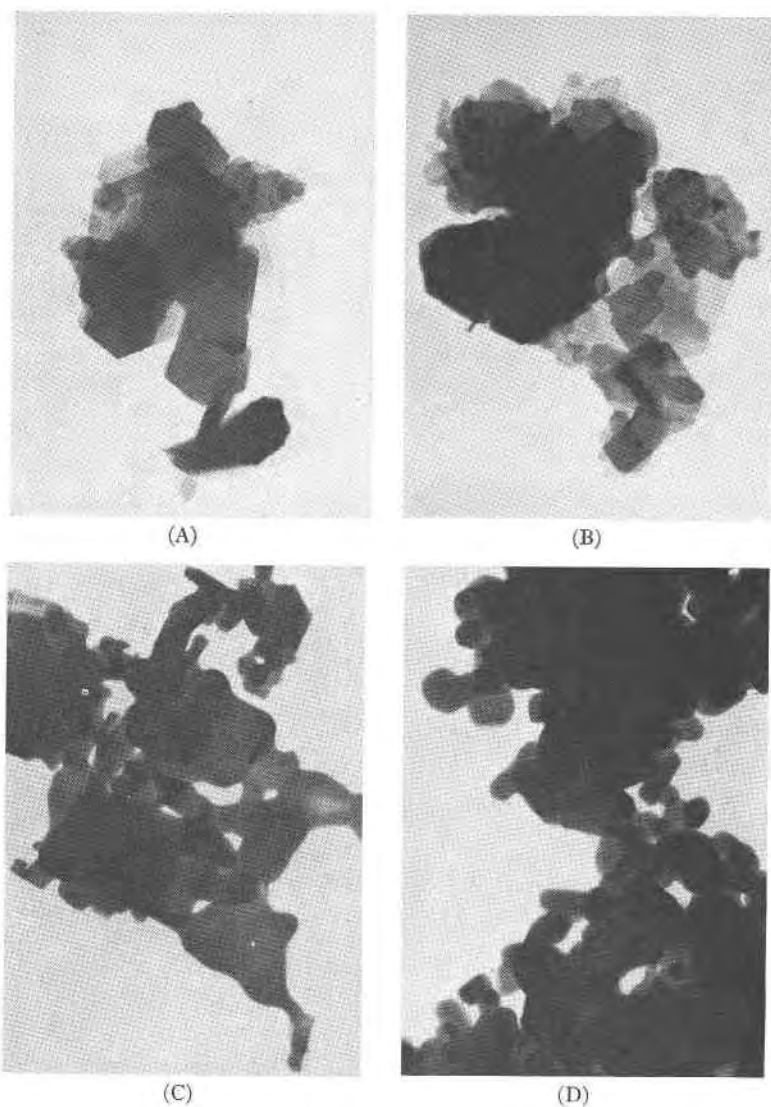


FIG. 4. Electron-micrographs of the products at 650°C ($\times 20,000$): (A) After 30 min. Grains of Na_2CO_3 are seen at a lower part of the photograph. Some are probably between the overlapping kaolin flakes. (B) After 2 hr. (C) After 8 hr. (D) After 32 hr.

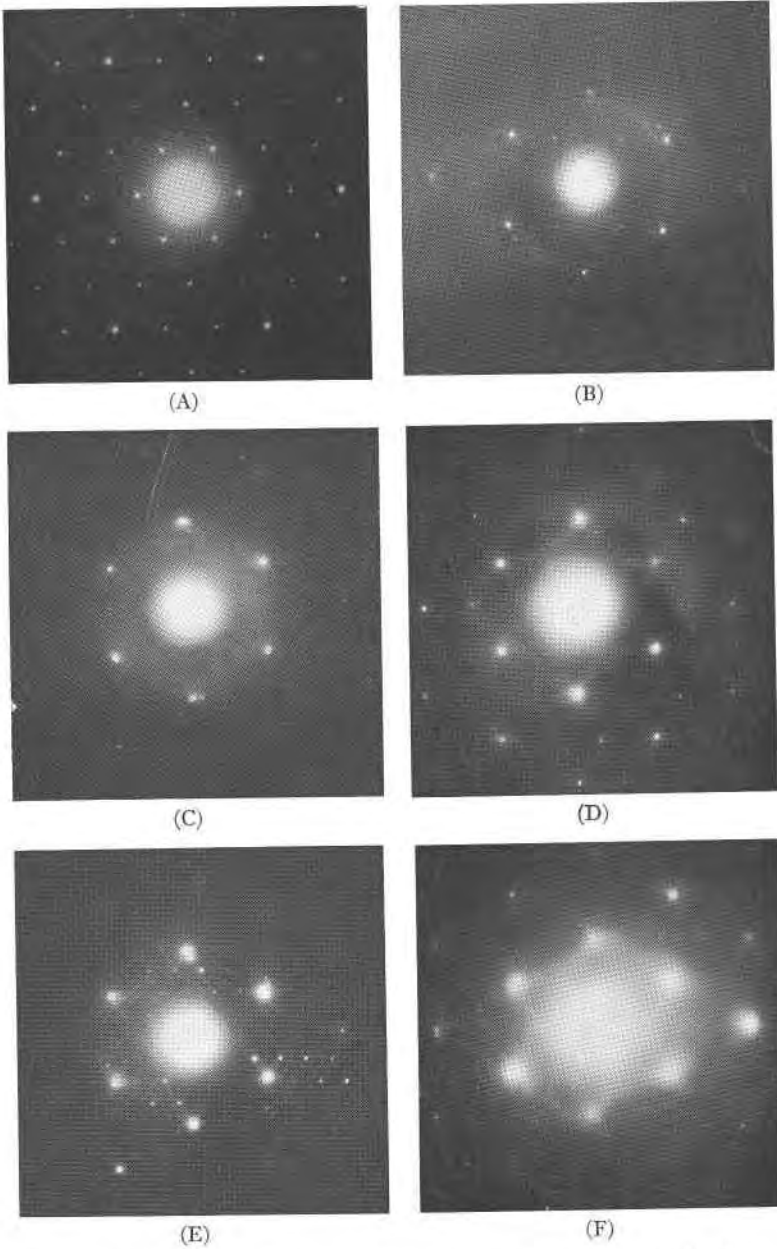


FIG. 5. Selected area diffraction patterns of the products at 650°C: (A) Metakaolin corresponding to Fig. 4(A). (B) Coexisting metakaolin and L-phase, corresponding to reaction stages between Figs. 4(A) and (B). (C) L-phase. (D) (E) Transitional stages of L-phase to nepheline. (F) Transitional stage of L-phase to nepheline in a halloysite-1.5 Na₂CO₃ system at 920°C. Note the pronounced diffuse scattering.

are shown. The original hexagonal shape is well maintained at the stages of metakaolin and the L-phase (Figs. 4(A) and (B)). The corresponding diffraction patterns are given in Figures 5(A) and (B). In Figure 5(B), the coexistence of metakaolin and the L-phase is observed which helps to establish the axial relationships between the original and product phases. Judging from the high background and a small number of diffraction spots as shown in (C) which is of the L-phase, this phase seems to be highly disordered.

As the reaction proceeds, corrosion at the edges of flakes takes place and eventually flakes of nepheline with a globular shape are produced (Figs. 4(C) and (D)). However, the diffraction patterns at these stages still exhibit clearly single crystal characteristics as shown in Figs. 5(D) and (E).

As has been observed in the kinetic studies, the L-phase inverts to nepheline upon prolonged heating. This is also clearly shown in Figures 5(D) and (E) in which diffuse streaks connecting the strong spots of the L-phase start developing (D) and eventually sharp spots along these streaks and clear layer lines of nepheline are generated (E). This indicates clearly a topotactic inversion of the L-phase to nepheline.

A few remarks should be made concerning a halloysite— $1.5 \text{ Na}_2\text{CO}_3$ system. A same sequence as outlined above, but of a more disordered character, was obtained with this system. This is shown in Figure 5(F) in which profound disordering in the inversion of the L-phase to nepheline is indicated.

DISCUSSION

Topotactic relations. The present experiments suggest the metastability of the L-phase and the topotactic transformations throughout the entire process. In a previous report (Kubo *et al.*, 1967) an assumption was put forward that the L-phase was of a disordered high-carnegieite type and the disordering was higher in the L-phase produced from a halloysite system (disordered kaolinite) than that from a kaolinite system. Evidence for this is given in the diffraction studies of the present investigation. Therefore, in order to interpret the reaction process, much attention will be directed towards the structural relationships between the original and product phases.

A schematic representation of the interrelation between the diffraction patterns of metakaolin, L-phase, and nepheline is given in Figure 6(A). The c^* direction of metakaolin is parallel to the (111) of the L-phase and the c -axis of nepheline, respectively. In metakaolin, its 020 is equivalent to its 110 and $\bar{1}\bar{1}0$ in terms of a two-dimensional lattice. There is no means to discriminate between these three spots on the diffraction pattern.

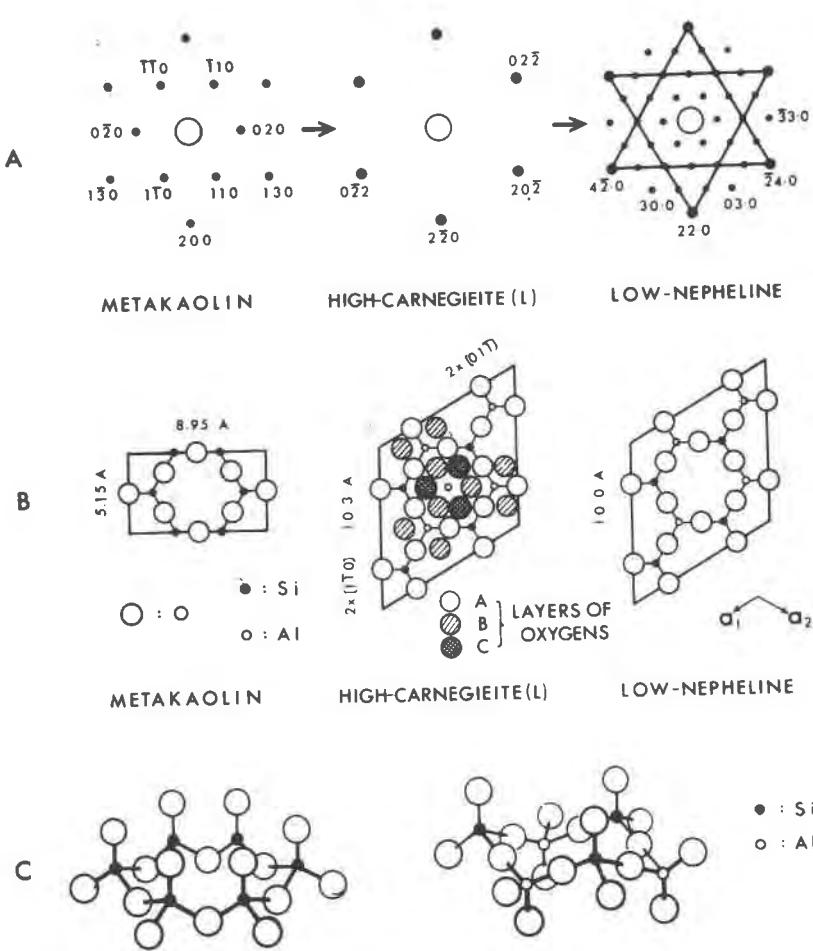


FIG. 6. Schematic representation of the topotactic relationships between the phases. (A) Correlation between the diffraction patterns of metakaolin, L-phase, and nepheline. (B) Orientational relationships between the structures of these phases. (C) Distribution of Si^{4+} and Al^{3+} ions in the Si—O hexagonal rings of metakaolin, and L- and nepheline phases.

Therefore, in the figure, one of this series of reflections is taken arbitrarily as $0\bar{2}0$.

The $\{200\}$ of metakaolin corresponds to the $\{2\bar{2}0\}$ of the L-phase, and the latter, in turn, is inherited by the $\{22\cdot0\}$ of nepheline. These orientational relationships imply the interrelation between the actual structures as shown in Figure 6(B).

Reaction to form the L-phase. In Figure 6, it can easily be seen that almost

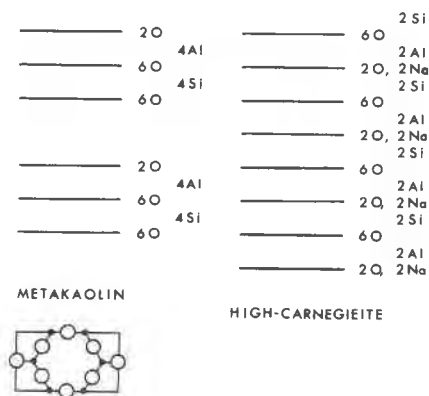


FIG. 7. Sequences of oxygen layers in metakaolin and L-phase.
(Sequence in metakaolin (Brindley and Nakahira, 1959).)

all the oxygen layers of metakaolin have been maintained in the structure of the L-phase. A schematic representation of this relation is given in Fig. 7 in which the distribution of the oxygen layers along the normal of the metakaolin sheet is illustrated.

In the transformation to the L-phase, the Al^{3+} and Si^{4+} ions in metakaolin rearrange themselves in the oxygen framework. This is illustrated in Figure 6(C) where it can be seen that the rearrangement of these cations induces little change in the oxygen framework resulting in a silicon—oxygen framework of the cristobalite or tridymite type. This is also illustrated in the layer sequence shown in Figure 7.

Although some corrosion of the metakaolin flakes seems to have taken place during the formation of the L-phase, it is nevertheless evident that the L-phase is produced within the original metakaolin framework. In view of the structural relation between the two phases, it is safe to think that the reaction is controlled by a diffusion of sodium ions into the metakaolin framework. In this case, if all the Si^{4+} and Al^{3+} ions in the latter remain within the original oxygen framework, an oxygen ion per two sodium ions must be added to metakaolin in order to keep the charge neutrality. Since the metakaolin structure has an open space around the original hydroxyl layer (2 O layer in Fig. 7), this can easily be done by a diffusion of Na and O ions, into this open space. The subsequent diffusion of Na^+ ions through the entire framework forms and stabilizes the L-phase.

An alternative interpretation for the maintenance of the electrical neutrality in the L-phase is that some of the Si^{4+} and Al^{3+} ions diffuse out of the metakaolin framework. This mechanism involving the cation

vacancies may rather be usual in many cases. In the present system, however, because of the open structure of metakaolin, extra oxygens along with sodium ions may easily be taken up in the metakaolin structure to form a more stable phase, the L-phase. From this reason, the former explanation seems more likely in this case.

Stacking disorder of the Si-O layer arising from the variable stacking of the starting materials, and a random distribution of the Na ions account for the various degrees of disordering in the resulting L-phase. As the reaction proceeds, an increasing stability of the L-phase is induced by a stable distribution of the Na ions at the given temperature, and this, in turn, makes the inversion of the L-phase to nepheline more difficult. The decrease in v with increasing time (Fig. 3) can be interpreted in terms of the stabilization of the L-phase. Diffusion of Na ions will be enforced by a rise in temperature which will result in a rapid stabilization of the L-phase, and eventually producing a stable alkali-rich carnegieite. This is a more stable phase than nepheline. The kinetic data at 800°C reflect a reaction sequence of this sort.

Inversion of the L-phase to nepheline. With the excess-alkali systems as in the present investigation, the L-phase, which is a disordered type of high-carnegieite, is always produced prior to the more stable nepheline at an early stage of reaction. At higher temperatures, the nepheline phase again transforms to an alkali-rich carnegieite phase. This indicates that at the present temperature range the stability of the phase increases in the sequence, L-phase→nepheline→alkali-rich carnegieite.

The structures of these phases are similar to one another as can be seen in Figure 6(B). Therefore, if the energy is insufficient at low temperatures, the inversion of the L-phase to nepheline may take place in preference to the formation of an alkali-rich carnegieite. Redistribution of Na ions in the L-phase causing inversion into nepheline may be reflected in the diffuse streaks and the subsequent appearance of the clear layer lines of nepheline in Figures 5(D) and (E).

ACKNOWLEDGEMENT

The authors wish to express their hearty thanks to Dr. M. Nakahira, University of Tokyo, for his kind discussions and instructions. Thanks are also due to Japan Electron Optic Co. for its help with the electron optical work.

REFERENCES

- BRINDLEY, G. W. AND M. NAKAHIRA (1959) The kaolinite-mullite reaction series; II. Metakaolin. *J. Amer. Ceram. Soc.*, **42**, 314-318.
- KUBO, Y., G. YAMAGUCHI, AND K. KASAHARA (1966) Inverted phase relation in the for-

mation of nepheline and carnegieite from the system kaolinite—sodium carbonate. *Amer. Mineral.*, **51**, 516–521.

———, ———, AND ——— (1967) Reaction processes to form nepheline-carnegieite minerals from various starting materials. *Mineral. J. (Tokyo.)*, **5**, 213–223.

Manuscript received, August 2, 1966; accepted for publication, March 5, 1968.