April, 1988] *Bull. Chem. Soc. Jpn., 61, 1071—1075 (1988)* 1071

# Studies of the Rate of the Formation of Talc under Hydrothermal Conditions at 400—460 °C

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(Received September 16, 1987)

The rate of the formation of talc from brucite powders with soluble silica under hydrothermal conditions was investigated in the temperature range of 400—460 °C, a range including the equilibrium temperature for the reaction: brucite+serpentine$\rightleftarrows$2 forsterite+3$H_2O$. Serpentine appeared as an intermediate phase below 415 °C, while above 430 °C forsterite appeared in addition to serpentine. The apparent reaction can be represented as:

$$\begin{tikzcd}
\text{(below 415° C)} & \text{brucite} \arrow[r] & \text{serpentine} \arrow[r] & \text{talc} \\
& & \text{serpentine} \arrow[dd] \arrow[dr] & \\
\text{(above 430° C)} & \text{brucite} \arrow[ur] \arrow[dr] & & \text{talc} \\
& & \text{forsterite} \arrow[ur] &
\end{tikzcd}$$

The reaction was apparently expressed as a pseudo-first-order reaction. The overall rate of the reaction did not increase with the increase in the temperature. Arrhenius plots of the rate constants for the overall reaction showed a curve with a maximum at about 415 °C and a minimum at about 445 °C which was caused by the alteration of the reaction by the appearance of forsterite at 430 °C.

The mechanism of the formation of silicates under hydrothermal conditions has been investigated from the standpoints of synthesis[1-3] and metamorphic reactions.[4-7] In spite of the many investigations into the synthesis of zeolite which have been done, however, the mechanism for the formation of zeolite has not yet been completely revealed. For the metamorphic reaction, though, the rates of hydration and dehydration (or forward and backward reactions) have been well investigated near the equilibrium temperature, and an effective rate constant has been obtained.

The kinetic study of solid-state reactions is generally attended with several problems. One of the problems with the reaction is that the observed overall rate of the reaction is usually controlled by the diffusion step (e.g., lattice diffusion) and is then influenced by the size and the shape of the starting materials. A physical process, such as diffusion, will not give useful information on surface reactions, nucleation, and intermediate formation. In order to obtain some information on these reactions of hydrothermal synthesis, it is necessary to simplify the reaction system and to set up a suitable reaction situation. From these points of view, we have now studied the hydrothermal synthesis of the $MgO$-$SiO_2$-$H_2O$ system.

It has been found that the reaction of brucite ($Mg(OH)_2$) with $SiO_2$ involved the dissolution process of $SiO_2$ and that the dissolved silica was adsorbed on the surface of brucite in the initial step of the reaction. The adsorption was chemisorption, and the surface of the silica-adsorbed brucite consisted of an amorphous silicate layer at atmospheric pressure.[8,9] When the resulting amorphous silicate on the brucite was treated hydrothermally, it crystallized as serpentine ($Mg_3Si_2O_5(OH)_4$) at temperatures below 400 °C and was further transformed into forsterite ($Mg_2SiO_4$) above 420 °C.[10] In addition, it was found from the kinetic study that the difference in the particle size of brucite powder influenced not only the overall reaction rate but also the rate-determining step.[11]

In this study, the formation of talc ($Mg_3Si_4O_{10}(OH)_2$) was followed as a function of the time at various temperatures (400—460 °C) including the equilibrium temperature for the reaction: brucite+serpentine$\rightleftarrows$2 forsterite+3 $H_2O$. The reaction was carried out under such conditions that the silica could react with the solid brucite in the state of soluble silica in an autoclave; the concentration was kept almost constant during the reaction by the use of a large excess of silica. This simplified reaction system led to a kinetic analysis of the formation of talc through intermediate products. The most reasonable process of the formation of talc around the equilibrium temperature will be discussed based on these results.

## Experimental

Two-tenths of a gram of $Mg(OH)_2$ powder, packed naturally into a basket mounted on a holder, was placed above 2.0 g of silica gel powder situated at the bottom of a modified Mory-type autoclave with a capacity of about 30 $cm^3$. The filling ratio of water in the autoclave was 35%; this ratio corresponds to a pressure of about 300—500 bars at 400—460 °C. A solution in an autoclave was kept saturated with soluble silica at a concentration of 700—900 ppm throughout the reactions in the temperature range of 400—460 °C, since a large excess of silica was used as the silica source.

After a definite time of heating, the autoclave was rapidly quenched with water and the materials were taken out. The reactant and products were identified by the use of X-ray diffractometry and DTA. Their quantities could be determined with a gravimetric technique (TGA) and by means of their X-ray diffraction patterns. These methods have been fully described in a previous paper.[11,12]

## Results and Discussion

**Analysis of Experimental Conversion Curves.** Figure

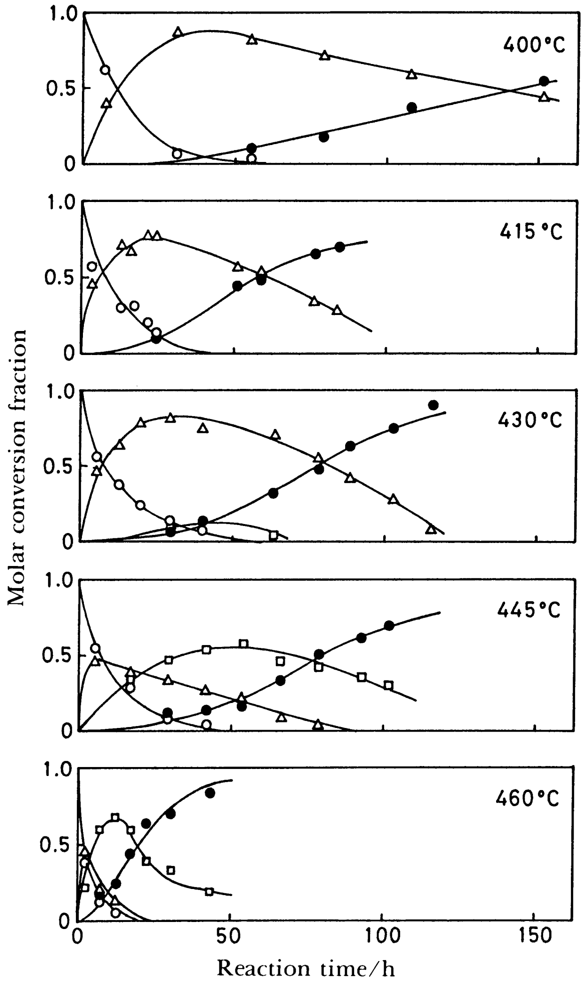

Fig. 1. Experimental conversion curves for the reaction of brucite with soluble silica at 400—460 °C. ○: brucite, △: serpentine, □: forsterite, ●: talc.

1 shows the molar conversion curves for the reaction of solid brucite with soluble silica at 400—460 °C. Talc was formed through serpentine at 415 °C or below and through serpentine and forsterite as intermediates above 430 °C. It was noted that the temperature where forsterite appeared in the present kinetic study was higher than that in the equilibrium data obtained previously by Bowen and Tuttle.[13] When serpentine alone appeared as an intermediate substance, the reaction represented, as has been described previously,[11] a first-order consecutive irreversible reaction:

$$\text{brucite} \rightarrow (\text{serpentine}) \rightarrow \text{talc} \qquad (1)$$

When forsterite appeared in addition to serpentine, its overall reaction, brucite→(serpentine, forsterite)→talc, may be summarized in the following apparent process including Reaction 1:

$$\begin{tikzcd} & \text{serpentine} \arrow[dd, shift right, "\text{Path 3}"'] \arrow[dr, "\text{Path 5}"] & \\ \text{brucite} \arrow[ur, "\text{Path 1}"] \arrow[dr, "\text{Path 2}"'] & & \text{talc} \\ & \text{forsterite} \arrow[uu, shift right, "\text{Path 3}'"'] \arrow[ur, "\text{Path 4}"'] & \end{tikzcd} \qquad (2)$$

Each reaction pathway can be expressed by the following reactions, which proceed in the direction of the most stable form under the present experimental conditions:

Path 1 $3Mg(OH)_2 + 2SiO_2 \rightarrow Mg_3Si_2O_5(OH)_4 + H_2O$ (3)

Path 2 $2Mg(OH)_2 + SiO_2 \rightarrow Mg_2SiO_4 + 2H_2O$ (4)

Path 3 $2Mg_3Si_2O_5(OH)_4 \rightarrow 3Mg_2SiO_4 + SiO_2 + 4H_2O$ (5)

Path 3′ $3Mg_2SiO_4 + SiO_2 + 4H_2O \rightarrow 2Mg_3Si_2O_5(OH)_4$ (6)

Path 4 $3Mg_2SiO_4 + 5SiO_2 + 2H_2O \rightarrow 2Mg_3Si_4O_{10}(OH)_2$ (7)

Path 5 $Mg_3Si_2O_5(OH)_4 + 2SiO_2 \rightarrow Mg_3Si_4O_{10}(OH)_2 + H_2O$ (8)

These equations are all similar in form to the reactions of magnesium compounds with silica. When the plural reactants except silica take part in magnesium silicate formation, the reaction are summarized in the following equations.

Path 2+3 $Mg(OH)_2 + Mg_3Si_2O_5(OH)_4 \rightarrow 2Mg_2SiO_4 + 3H_2O$ (9)

Path 2+3′ $4Mg(OH)_2 + Mg_2SiO_4 + 3SiO_2 \rightarrow 2Mg_3Si_2O_5(OH)_4$ (10)

Unfortunately, Reactions 9 and 10 may be actually indistinguishable from the sums of Reactions 4 and 5, and Reactions 4 and 6, respectively.

In order to quantitatively determine some experimental observations on the formation of talc, we tried to analyze the experimental conversion curves. Some preliminary discussion will, however, be useful before an analysis of the rate of solid-state reaction is attempted.

(a) The fraction reacted in a solid-state reaction is represented by a quantity of the reacting species, $\alpha_i$, instead of the concentration, $C_i$, in a homogeneous reaction, since the concept of concentration in the reactivity of a solid is meaningless:

$$\text{Rate} = kf(\alpha_i)$$

(b) The silica concentration in hydrothermal solutions was almost constant during the reaction times, as has been described above. The silica concentration ($C_{SiO_2}$) can, therefore, be considered to be a constant factor of the rate constant, $k$:

$$k = k' C_{SiO_2}$$

We can picture a generalized reaction scheme based on the apparent reaction process 2 as follows:

$$\begin{tikzcd} & A\,2 \arrow[dd, "k_{23}"] \arrow[dr, "k_{24}"] & \\ A\,1 \arrow[ur, "k_{12}"] \arrow[dr, "k_{13}"'] & & A\,4 \\ & A\,3 \arrow[ur, "k_{34}"'] & \end{tikzcd}$$

where Al and A4 are brucite as a starting material and talc as a final product respectively and where A2 and A3 are arbitrarily assigned to serpentine and forsterite as intermediate species in the reaction system. $k_{12}$, $k_{13}$, $k_{23}$, $k_{24}$, and $K_{34}$ are the rate constants for the reaction paths. If the reaction is a first-order reaction similar to Reaction 1, described previously, the differential rate equations will be expressed as follows:

$$\frac{d\alpha_1}{dt} = -(k_{12}+k_{13})\alpha_1 \tag{11}$$

$$\frac{d\alpha_2}{dt} = k_{12}\alpha_1 - (k_{23}+k_{24})\alpha_2 \tag{12}$$

$$\frac{d\alpha_3}{dt} = k_{13}\alpha_1 + k_{23}\alpha_2 + k_{34}\alpha_3 \tag{13}$$

$$\frac{d\alpha_4}{dt} = k_{24}\alpha_2 + k_{34}\alpha_3 \tag{14}$$

where $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$ indicate the numbers of moles of A1, A2, A3, and A4 respectively to one mole of the starting material, A1.

$$t=0 \quad \begin{cases} \alpha_1 = 1 \\ \alpha_2 = \alpha_3 = \alpha_4 = 0 \end{cases}$$

$$t=\infty \quad \begin{cases} \alpha_1 = \alpha_2 = \alpha_3 = 0 \\ \alpha_4 = 1 \end{cases}$$

The solutions of Eqs. 11, 12, 13, and 14 are given as:

$$\alpha_1 = \exp\{-(k_{12}+k_{13})t\} \tag{15}$$

$$\alpha_2 = \frac{k_{12}}{k_{23}+k_{24}+k_{12}-k_{13}}\,[\exp\{-(k_{12}+k_{13})t\} - \exp\{-(k_{23}+k_{24})t\}] \tag{16}$$

$$\begin{aligned}\alpha_3 = {} & \frac{1}{k_{34}-k_{12}-k_{13}}\left(k_{13}+\frac{k_{12}k_{23}}{k_{23}+k_{24}-k_{12}-k_{13}}\right) \times \exp\{-(k_{12}+k_{13})t\} \\ & - \frac{k_{12}k_{23}}{(k_{23}+k_{24}-k_{12}-k_{13})(k_{34}-k_{23}-k_{24})}\exp\{-(k_{23}+k_{24})t\} \\ & -\{\frac{1}{k_{34}-k_{12}-k_{13}}\left(k_{13}+\frac{k_{12}k_{23}}{k_{23}+k_{24}-k_{12}-k_{13})}\right) \\ & + \frac{k_{12}k_{23}}{(k_{23}+k_{24}-k_{12}-k_{13})(k_{34}-k_{23}-k_{24})}\}\exp(-k_{34}t)\end{aligned} \tag{17}$$

$$\alpha_4 = 1-\alpha_1-\alpha_2-\alpha_3 \tag{18}$$

These equations can be applied in any type of reaction which begins at A1 and terminates at A4 (e.g., A1→A2→A4, A1→A3→A4, A1→A2→A3→A4).

The experimental conversion curves shown in Fig. 1 were analyzed by a procedure which obtained a model curve fitted to the experimental data using a computer. These model curves are shown in Fig. 2 in comparison with the experimental data. It may be seen from this figure that the experimental observations are successfully represented by the theoretical equations except for the latter half-term of the formation of talc.

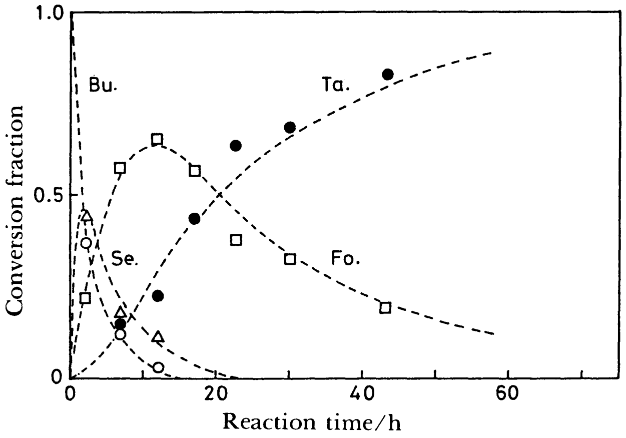

Fig. 2. Calculated conversion curves as compared to experimental conversion data at 460 °C.
Bu.: brucite, Se.: serpentine, Fo.: forsterite, Ta.: talc.

The reason why the experimental rate data are represented by a first-order equation is as follows:

(a) In the present study, the concentration of silica was not a variable in the rate equation, but one of the constant factors that were contained in the rate-constant term, since the silica concentration was almost constant throughout the reaction, as has been described previously. The reaction may, therefore, be simplified to a pseudo-first-order reaction.

(b) The brucite used as a starting material was found, by electron microscopy and X-ray diffractometry, to consist of smaller disk like grains (or crystallites) a few hundred angstromes in size. Moreover, it has been observed that the amount of brucite was reduced with the reaction time, while the crystallite size of the residual brucite was changed very little by the reaction. The crystallinity of the intermediate product was also small in size (such as brucite) and did not grow during the reaction term. These results suggest that crystallites are units of the reaction and that the conversion process is controlled by a surface reaction and/or nuclei formation rather than by mass transfer. This reaction may be expressed by this equation:

$$\alpha = 1-\exp(-kt^n) \tag{19}$$

which is universally applicable to nuclei formation and crystal growth.[14] When the rate-determining step is nuclei formation or a surface reaction, the value of $n$ is 1. The rate of the reaction, therefore, is expressed by this equation:

$$\ln(1-\alpha) = kt \tag{20}$$

which is equal to the first-order reactions in homogeneous reactions.

The rate constants obtained are shown in Table 1.

**Effect of the Equilibrium Temperature on the Overall Rate of the Reaction.** Figure 3 shows the plot of log $(1/t_{0.5})$ vs. $1/T$, where $t_{0.5}$ is the time for a 50%

Table 1. Rate Constants for the Reaction of Brucite with Soluble Silica

| Reaction temp | Rate constants $10^2k$/h$^{-1}$ | | | | |
|---|---|---|---|---|---|
| °C | $k_{12}$ | $k_{13}$ | $k_{23}$ | $k_{34}$ | $k_{24}$ |
| 400 | 6.8 | — | — | — | 0.63 |
| 415 | 11.0 | — | — | — | 1.4 |
| 430 | 8.5 | 0.22 | 0.05 | 0.11 | 1.1 |
| 445 | 8.0 | 2.7 | 3.5 | 1.3 | 0.42 |
| 460 | 28.0 | 8.1 | 19.0 | 4.0 | 3.1 |

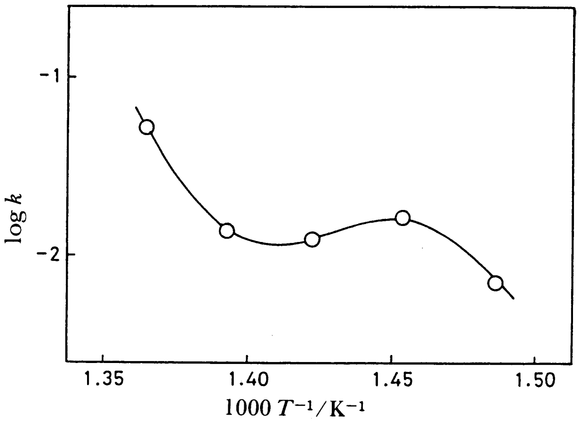

Fig. 3. Arrhenius plot of rate constant ($k=t_{0.5}{}^{-1}$) for the overall rate of talc formation.

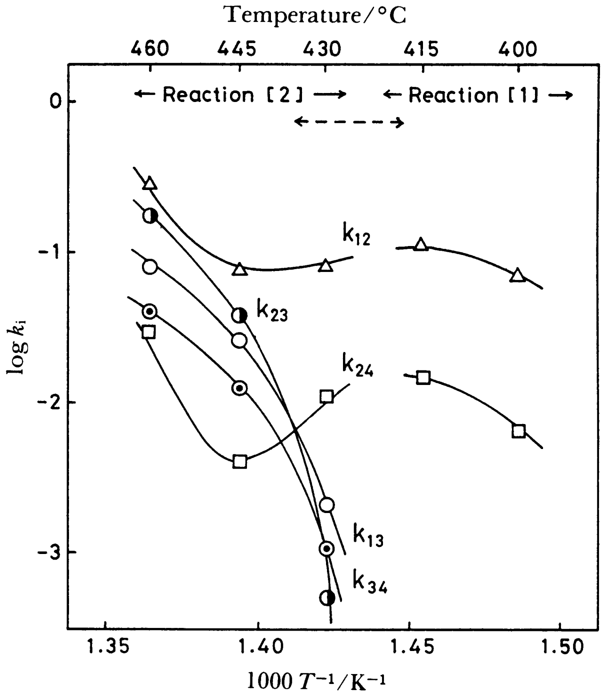

Fig. 4. Arrhenius plots of rate constants $k_{12}$, $k_{13}$, $k_{23}$, $k_{24}$, and $k_{34}$ for each reaction path.

formation of talc as the final product. The unit of the rate constant, $k=t_{0.5}{}^{-1}$, involves the h$^{-1}$ unit. The characteristic plot obtained has a double hump; this plot is given by a lowering of the reaction rate to near the temperature at which forsterite appeared. The plots for the rate constants below 415 °C and above 445 °C may reflect the apparent activation energies for Reactions 1 and 2 respectively. In the temperature range of 415—445 °C, a plot with a slightly positive slope with a negative activation energy was obtained. This region may reflect intermediate values, behaving as a weighted means of two kinds of apparent activation energies of Reactions 1 and 2. If the rate-controlling step (or the reaction path) in such reactions as $A \rightarrow B \rightarrow C$ and $A \begin{smallmatrix} \nearrow B \\ \searrow C \end{smallmatrix}$ changes at a particular temperature, typical plots in which two straight lines cross each other at that temperature will be obtained. In the present study, however, other factors further complicated the situation.

Arrhenius plots for the five rate constants given in Table 1 are shown in Fig. 4. The plots for $k_{13}$, $k_{23}$, and $k_{34}$ are found to have a steep slope. These rate constants for the formation of forsterite are essentially zero at the equilibrium temperature for the brucite+serpentine$\rightleftarrows$2 forsterite+3 $H_2O$ reaction. Since the direction of departure from the equilibrium temperature is also equal to the direction of the rise in the temperature, the slopes of the plots for these rate constants are larger than the others. The plots for $k_{12}$ and $k_{24}$ are similar to that for the overall reaction shown in Fig. 3. These plots may be divided into three regions as has been described above. The rate of Reaction 1, which is represented by $k_{12}$ and $k_{24}$ at the temperature of 415 °C and below, may essentially tend to increase with an increase in the temperature, even at the temperature of 430 °C, since there are no other factors that influence the kinetics of Reaction 1 except for the appearance of forsterite. However, a part of the serpentine produced at 430 °C is transformed into forsterite, and then the apparent rate of the formation of serpentine may be lowered. The rate of talc formation may also be lowered as a result of some distortion of the nucleation. Above 445 °C, forsterite is directly formed on brucite (Path 2) rather than through serpentine (Paths 1 and 3); that is, the main path of the formation of talc consists of Paths 2 and 4. It may, then, be said that the reaction path for forsterite becomes the most important factors controlling the overall reaction with an increase in the temperature.

**Some Considerations on the Formation of Intermediates.** The intermediates in talc formation appeared in the order of serpentine→frosterite, as may be seen in the experimental conversion curves above 445 °C (see Fig. 1). It has also been observed that silica-adsorbed brucite, when treated hydrothermally above 420 °C, was transformed into forsterite through serpentine-like silicate,[10] although, at higher temperatures, serpentine was no longer detectable. On the other hand, the equilibrium data on the stable phases of magnesium silicate in hydrothermal solutions containing sil-

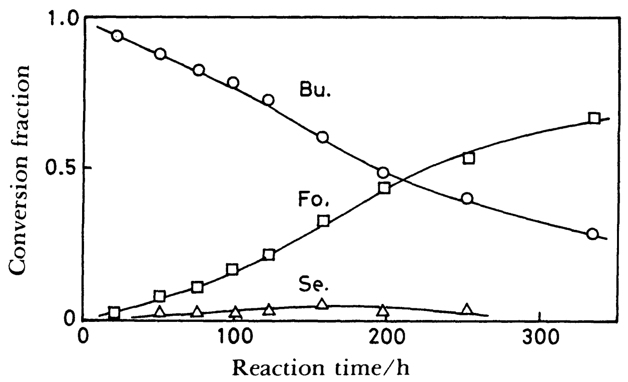

Fig. 5. Experimental conversion curve for the reaction of brucite with a low concentration solution of silica at 445 °C.

ica reported by Hemley et al.[15] are different. They reported that magnesium silicates were transformed from brucite into forsterite→serpentine→talc with increases in the concentrations of silica and that the $SiO_2/MgO$ ratios increase in that same order.

The reason why the kinetics of the formation of serpentine is much faster than that of forsterite is as follows: It may be presumed that the brucite surface is an excellent substrate for the nucleation of serpentine, since both brucite and serpentine are made of the same layered structure consisting of a Mg-O framework. The crystal nuclei of serpentine may, therefore, be generated with ease. In addition, since the formation of forsterite in accompanied by the severance of the Mg-O framework of brucite, it may require a large activation energy in the reconstructive reaction.

In order to obtain further information on the formation of serpentine and forsterite, a qualitative kinetic study was attempted under various conditions.

(a) Brucite was allowed to react under a low concentration of silica. A piece of quartz or serpentine, as a silica source, and same brucite were placed apart from each other in the same way. The reaction was very slow, and it produced a mere trace amount of serpentine. The conversion curves for the reaction of the brucite with the silica liberated from the serpentine are shown in Fig. 5.

(b) On the other hand, we employed a lod-like briquette consisting of the brucite powder as a starting material, with a smaller surface area, and examined it in the same manner as in the reaction of brucite with soluble silica. Its briquette was prepared by compressing the powder at a pressure of 50 $kg\,cm^{-2}$ by using a piston anvil. The reaction was very slow, similar to a diffusion-controlled bulk reaction in a solid. The reacted briquette was scrapped, step by step, from its surface and then evaluated. Talc, forsterite, and brucite were found to have been formed, in this order, from the surface toward the inner part. Only a small amount of serpentine was detected throughout the reaction.

In addition to the reaction rate, the differences in the reaction conditions influenced the appearance of intermediates. It can be seen from these results that the surface of the brucite powders contribute much to the nucleation of serpentine; when its surface is in contact with a higher concentration of silica solutions, they contribute still more. On the other hand, forsterite as a intermediate mainly appears when larger grains of brucite are used, when there is lower concentrated solution of silica, and at a temperature higher than the equilibrium temperature. Thus, in addition to the temperature, both the apparent (or net) grain size of the reactant and the silica concentration contribute to the appearance of an intermediate.

The author wishes to express his thanks to Dr. Shigeto Kitahara for his kind guidance and continuous encouragement throughout this work. The author also would like to thank Mr. Hideo Nagata for his assistance in the preparation of the silicate and in obtaining the X-ray diffraction data.

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