

EQUILIBRIUM BOUNDARY BETWEEN KAOLINITE AND PYROPHYLLITE

TOSHIHIKO MATSUDA, MAKOTO KUROSAKI and KITINOSUKE HENMI*

*Department of Earth Sciences, Faculty of Science,
Okayama University, Tsushima-naka, Okayama 700, Japan*

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ABSTRACT

Hydrothermal experiments have been carried out to find the equilibrium conditions for the reactions:



As starting materials, a natural mixture of kaolinite-pyrophyllite-boehmite was used for the experiments. Determination of reaction direction was based upon X-ray diffraction patterns.

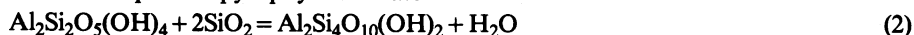
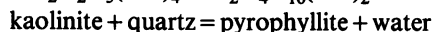
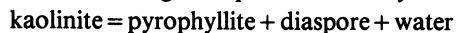
It has been confirmed that the equilibrium curve for the reaction (1) passes through the points $325 \pm 10^\circ\text{C}$ at 1kb and $330 \pm 10^\circ\text{C}$ at 2kb, and the curve for the reaction (2) passes through $250 \pm 10^\circ\text{C}$ at 1kb and $260 \pm 10^\circ\text{C}$ at 2kb. The present temperatures for the reaction (2) are lower than any other one reported so far.

Key words: Kaolinite, Pyrophyllite, Hydrothermal experiments, Equilibrium boundary

INTRODUCTION

It is important to determine the upper stability limit of kaolinite for the genetic interpretation of mineral assemblages found in hydrothermally altered rocks and low grade metamorphic rocks. Many attempts have been made to set the limit through experimental work, but the results of these studies are in disagreement with each other.

The boundaries along which kaolinite reacts to form pyrophyllite can only be considered as the upper stability limit of kaolinite. Therefore, the stable occurrence of kaolinite is limited on the high temperature side by the following two reactions:



In the reaction (1) boehmite, a metastable form of diaspore, can be found instead of diaspore in both laboratory and nature.

Solubility data of Hemley et al. (1980) in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ have given valuable contributions on the subject. However, with the exception of the results of Henmi and Matsuda (1975), most phase equilibrium data reported so far are not in agreement

*Present address: 1-9-20 Ishimacho, Okayama 700, Japan

with Hemley *et al.*'s (1980) solubility data. In this paper, we present the results of experimental work following after our previous report (Henmi and Matsuda, 1975).

PREVIOUS WORK

Roy and Osborn (1954) suggested that pyrophyllite is a stable phase above 420°C under varying water pressure, in all alumina-silica mixtures rich in silica. They used coprecipitated alumina-silica gels as starting materials. Carr and Fyfe (1960) used three different starting materials (amorphous Al₂O₃-quartz, kaolinite-amorphous silica, kaolinite-quartz) and three significantly different synthesis diagrams resulted. They concluded that the results using kaolinite-quartz might approach most closely to equilibrium conditions because the mixture was the closest approach to natural materials. Later, Carr (1963) examined the influence of experimental method on the nature of synthetic phases and on the extent of their synthesis fields. He reported that the kaolinite-pyrophyllite boundary using kaolinite-quartz mixture passes through the point 416°C at 2kb and the boundary using kaolinite-amorphous silica passes through 355°C at 2kb. Aramaki and Roy (1963) carried out a reexamination of the system Al₂O₃-SiO₂-H₂O up to 900°C and 6kb in sealed noble metal systems. The decomposition temperature for the reaction kaolinite → pyrophyllite + boehmite + H₂O was reported to be 405 ± 10°C (2–5kb). They suggested that mineral 'hydralsite', named by Roy and Osborn (1954), is a metastable step in the reorganization of the 1:1 layer lattice (kaolinite) to the 2:1 layer lattice (pyrophyllite) plus boehmite. Althaus (1966) used a mixture of natural kaolinite and quartz (68%, 32% respectively) as starting material. The decomposition temperature of kaolinite was reported to be 390 ± 10°C (2kb). Velde and Kornprobst (1969) reported the decomposition temperature of kaolinite to be 310°C (2kb). A mixture of natural kaolinite and silica gel was used as starting material.

Since 1970's, the attempts have been made to examine the equilibrium conditions for the reactions (1) and (2) rather than the synthesis fields. Thompson (1970) tried to find the equilibrium conditions for the reaction (2) by the single crystal experiments. The method was originally presented by Fyfe (1960). A mixture of a quartz crystal and powders of kaolinite and pyrophyllite was used as starting material. Determination of reaction direction was based upon the weight-change of the quartz crystal. The data showed the equilibrium temperature to be 345 ± 10°C (2kb). Henmi and Matsuda (1975) found out that the equilibrium boundaries for the reactions (1) and (2) are considerably different in temperature. Determination of reaction direction was based upon a comparison of X-ray diffraction patterns of the products and the starting materials. The data showed that the equilibrium curve for the reaction (1) passes through the points 333°C at 1kb and 340°C at 2kb, and the curve for the reaction (2) passes through 263°C at 1kb and 270°C at 2kb. They used a natural mixture of kaolinite-pyrophyllite-boehmite and the mixture plus silica gel as starting materials. Hemley and co-workers have paid attention to the composition of coexisting fluid phase (e.g., Hemley and Jones, 1964). By using an aqueous phase-mineral equilibrium approach, Hemley *et al.* (1980) investigated the stability relations of minerals in the system. They deduced from their solubility data that the equilibrium curve for the reaction (1) passes through the point 300 ± 10°C at 1kb and the curve for the

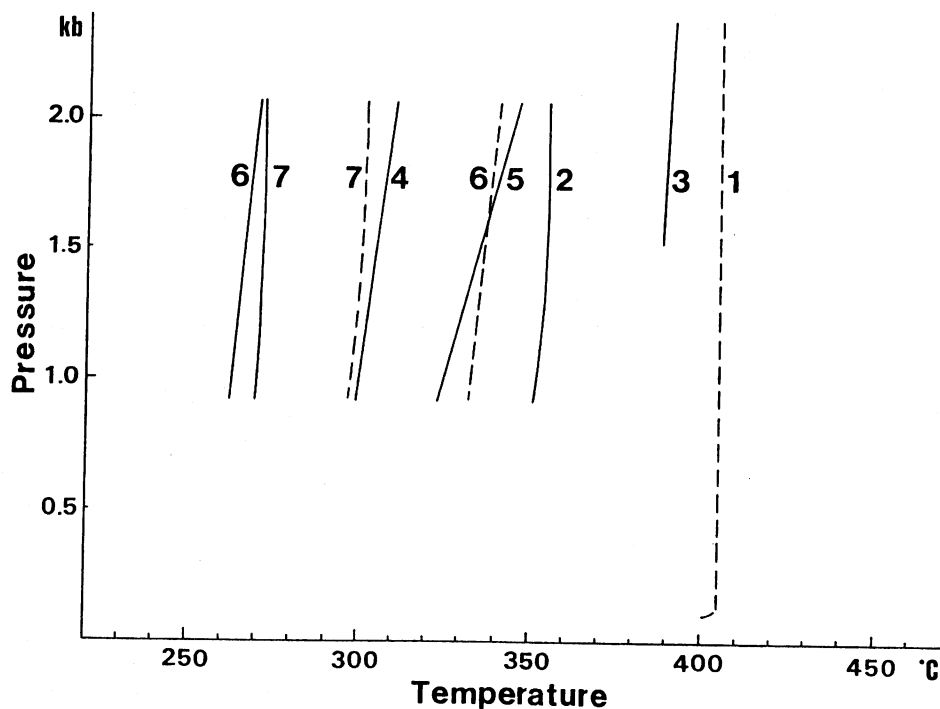


FIG. 1. Summary of previous studies. Broken line indicates the equilibrium boundary for the reaction (1). Solid line indicates the equilibrium boundary for the reaction (2). 1: Roy and Osborn (1954) and Aramaki and Roy (1963), 2: Carr (1963), 3: Althaus (1966), 4: Velde and Kornprobst (1969), 5: Thompson (1970), 6: Henmi and Matsuda (1975), 7: Hemley et al. (1980)

reaction (2) passes through $273 \pm 10^\circ\text{C}$ at 1 kb.

These results are summarized in Fig. 1.

EXPERIMENTAL

Equipment

The experiments were conducted in conventional test-tube type hydrothermal vessels. The vessel, or bomb, is a thick-walled test tube of stellite (20 cm long, 25 mm outer diameter, 5 mm inner diameter) closed at one end and the other attached to pressure line. The sample is placed in the bottom. The bomb is suspended vertically and heated in an electric furnace.

Temperature was measured with chromel-alumel thermocouple placed near the sample. The thermocouple rarely showed a variation of more than $\pm 2^\circ\text{C}$. Pressure was measured with a Bourdon gauge. Generally speaking the data presented are accurate to $\pm 10^\circ\text{C}$ and $\pm 5\%$ of the pressure.

Starting materials

Following three mixtures were used as starting materials.

1) kaolinite-pyrophyllite-boehmite (K-P-B)

For the reaction (1) in aluminous environment the natural mixture which was from Mitsubishi, Okayama Pref., Japan was used as starting material. From microscopic observation it is confirmed that the material consists of the minerals with fine-grained crystals (5–10 μm) and is mixed intimately each other. The chemical composition of the mixture is presented in Table 1. The atomic ratio Al/(Al + Si) is 0.49.

2) kaolinite-pyrophyllite-quartz (K-P-Q)

For the reaction (2) in siliceous environment the natural mixture which was from Yakuno, Kyoto Pref., Japan was used as starting material. From microscopic observation it is confirmed that the material consists of the minerals with relatively coarse-grained crystals (over 100 μm). The atomic ratio Al/(Al + Si) is 0.13 (Table 1).

3) kaolinite-pyrophyllite-boehmite plus silica gel

For the reaction (2) the mixture 1) plus silica gel was also used as starting material. The atomic ratio Al/(Al + Si) is 0.25 (Table 1).

Procedure

For each experiment the starting material (about 50mg) was sealed together with excess fluid (about 20mg of distilled water) in a gold or a silver-palladium ($\text{Ag}_{70}\text{Pd}_{30}$) capsule. The sealing was checked by weighing the capsule before and after each run. The reactant was held for periods from 2 to 66 days in the range of 0.5 to 2.0kb and 230 to 380°C. Each run was terminated by release of pressure and water quenching (about 30 seconds to room temperature). The product was smeared on a glass slide and analyzed by X-ray

TABLE 1. Chemical analyses of starting materials (wt.%)

	1)	2)	3)
SiO ₂	47.69	84.49	68.72
TiO ₂	0.11	0.10	0.05
Al ₂ O ₃	38.94	10.87	19.43
Fe ₂ O ₃	0.02	0.12	0.01
CaO	0.27	0.11	0.13
MgO	0.02	0.04	0.01
Li ₂ O	0.04	0.01	0.02
Na ₂ O	0.31	0.11	0.15
K ₂ O	0.25	0.22	0.12
P ₂ O ₅	0.01	0.03	0.00
H ₂ O(+)	10.14	3.06	5.05
H ₂ O(-)	1.82	0.93	5.89
Total	99.62	100.09	99.58
Al/(Al + Si)	0.49	0.13	0.25

1): kaolinite-pyrophyllite-boehmite, 2): kaolinite-pyrophyllite-quartz, 3): kaolinite-pyrophyllite-boehmite plus silica gel.

powder diffraction (XRD).

Determination of reaction direction at a given temperature and pressure was based upon a comparison of XRD patterns of the products and the starting materials. This method is the same as Henmi and Matsuda (1975) and Chernosky and Berman (1988).

RESULTS AND DISCUSSION

The critical experimental data are presented in Table 2. 'Stable mineral' in Table 2 shows the mineral whose peak height on XRD increased after each run. For example, at 300°C and 1kb, by using the mixture 3), pyrophyllite is regarded as the stable mineral (Fig. 2). Fig. 3 shows the equilibrium boundaries for the reactions (1) and (2) obtained from the data using the mixture 1) and the mixture 3) respectively. The boundary for the reaction (1) passes through the points 322°C at 0.5kb, 325°C at 1kb and 330°C at 2kb, and the boundary for the reaction (2) passes through the points 245°C at 0.5kb, 250°C at 1kb and 260°C at 2kb.

The problem on 'stable mineral' detection at the temperatures and pressures close to the equilibrium boundaries was that the results of shorter duration runs contradicted those of longer duration runs. As shown in Fig. 4, for example, according to the 2 days' run kaolinite is regarded as the stable mineral, whereas according to the 7 days' run pyrophyllite is regarded as the stable mineral (at 350°C and 1kb). One of the reasons for the contradictory seems to be in kinetics of reaction. In their study on the alteration process of sericite to pyrophyllite, Tsuzuki and Mizutani (1971) reported that at 270°C in relatively dilute KCl solution kaolinite increased in the earlier stage but decreased later while sericite decreased and pyrophyllite increased gradually with time, whereas at 190°C sericite was changed to kaolinite but pyrophyllite was not observed. Therefore, it is reasonable to conclude that the results of longer duration runs must indicate stable minerals. In other words, even in the pyrophyllite stability field, kaolinite can be regarded as stable mineral when the detection is based only upon the results of shorter duration runs.

To use highly reactive starting material is essential to the determination of the equilibrium boundaries within the time scale of most laboratory experiments because the silicate reactions are notoriously sluggish. Disagreement among the previous results might be caused by the difference of reactivity among the starting materials used. Coprecipitated alumina-silica gels (Roy and Osborn, 1954; Aramaki and Roy, 1963), mixtures of natural minerals (Carr and Fyfe, 1960; Carr, 1963; Althaus, 1966; Thompson, 1970), mixtures of natural mineral(s) and amorphous material (Carr and Fyfe, 1960; Carr, 1963; Velde and Kornprobst, 1969; Henmi and Matsuda, 1975), and natural mixtures of minerals (Henmi and Matsuda, 1975) have been used as the starting materials. The coprecipitated gels have yielded the highest equilibrium temperature for the reaction (1) (Aramaki and Roy, 1963) (Fig. 1). The temperature is too high. This kind of material has a nucleation problem and seeds of minerals must be needed to increase the rate of reaction. The mixtures of natural mineral(s) and amorphous material have yielded the temperatures for the reaction (2) in the range of 270 to 350°C at 2kb. The temperatures are lower than those yielded by using the mixtures of natural minerals, i.e. 345 to 416°C at 2kb. In the mixtures of natural mineral(s) and amorphous material the nucleation

TABLE 2. Critical experimental data

Run No.	T °C	P _{H₂O} kbar	Duration days	Results Stable mineral
Starting material: Mixture 1), K-P-B kaolinite = pyrophyllite + diaspore + water				
142	310	0.5	16, 32	K
133	320	0.5	14, 43	RND
76	330	0.5	21, 46	RND
195	340	0.5	23, 44	P
65	350	0.5	5, 15	P
75	360	0.5	7	P
205	300	1.0	10, 30	K
369	310	1.0	10, 40	K
151	320	1.0	31, 64	RND
67	330	1.0	14, 60	RND
370	340	1.0	14, 60	P
93	350	1.0	7, 20	P
101	360	1.0	2, 7	P
38	370	1.0	7	P*
160	300	2.0	14	K
204	310	2.0	14, 49	K
158	320	2.0	14, 48	K
105	330	2.0	30, 64	RND
82	340	2.0	14, 43	P
192	350	2.0	14, 33	P
98	360	2.0	14	P
36	370	2.0	8	P*
37	380	2.0	4	P*
Starting material: Mixture 3), K-P-B + silica gel kaolinite + quartz = pyrophyllite + water				
188	230	0.5	28, 66	K
189	240	0.5	28, 66	RND
289	250	0.5	20, 65	RND
197	260	0.5	29, 60	P
190	270	0.5	20, 46	P*
187	230	1.0	28, 62	K
181	240	1.0	11, 24	K
180	250	1.0	30, 52	RND
191	260	1.0	24, 60	P
174	270	1.0	7, 21	P
194	280	1.0	24, 25	P
206	290	1.0	20	P
152	300	1.0	20	P*
149	320	1.0	10	P*
171	240	2.0	13, 28	K
178	250	2.0	15, 35	K
168	260	2.0	14, 42	RND
172	270	2.0	14, 21	P
165	280	2.0	8, 16	P
159	300	2.0	14	P*
157	320	2.0	7	P*

K: kaolinite, P: pyrophyllite, *: kaolinite was decomposed completely
RND: reaction was not detected

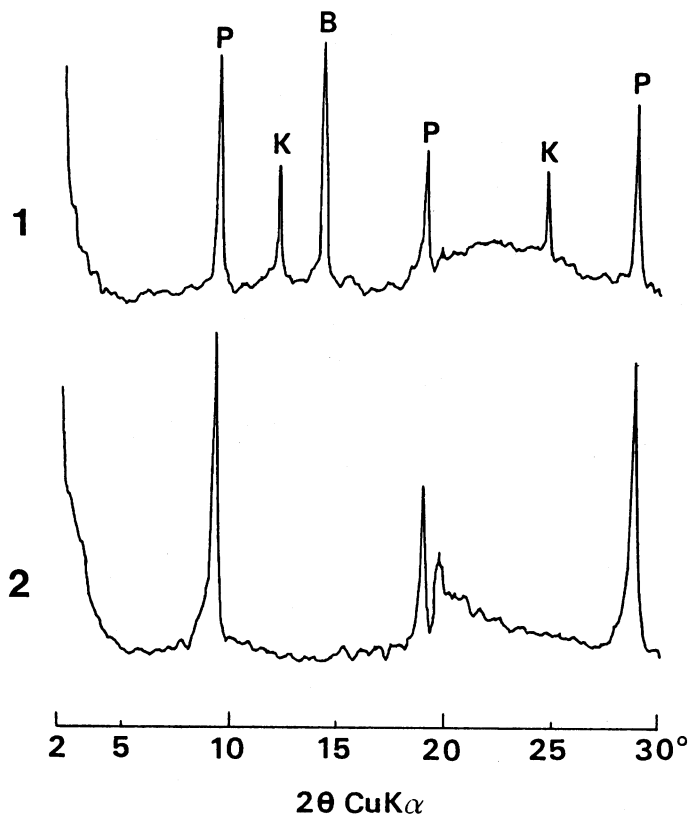


FIG. 2. XRD patterns of product and starting material. 1: starting material (the mixture 3), 2: product of 300°C and 1kb (20 days), P: pyrophyllite, K: kaolinite, B: boehmite

problem does not occur, and in this case the unstability of amorphous material may contribute to increasing the rate of reaction.

Natural mixture of minerals and the mixture plus amorphous material have been used in our successive work. It is evident in laboratory work that using natural mixture may be the best way to pursue the events taking place in nature. Therefore, in the beginning of the present experiments the mixture 2), which is a natural mixture of minerals and appropriate to the experiments for the reaction (2) in chemical composition and in mineral assemblage (Table 1), was also used. Since the mixture 1) had yielded defined equilibrium boundary for the reaction (1) (Table 2, Fig. 3), we expected that the mixture 2) would also yield the boundary for the reaction (2). However, against our expectation no apparent equilibrium boundary was detected (Table 3). As mentioned above, the two mixtures are different in grain size; that is, the mixture 1) consists of fine-grained minerals and the mixture 2) consists of relatively coarse-grained minerals. It is well known that decreasing grain size of reactant produces a corresponding increase in the rate of reaction (e.g.,

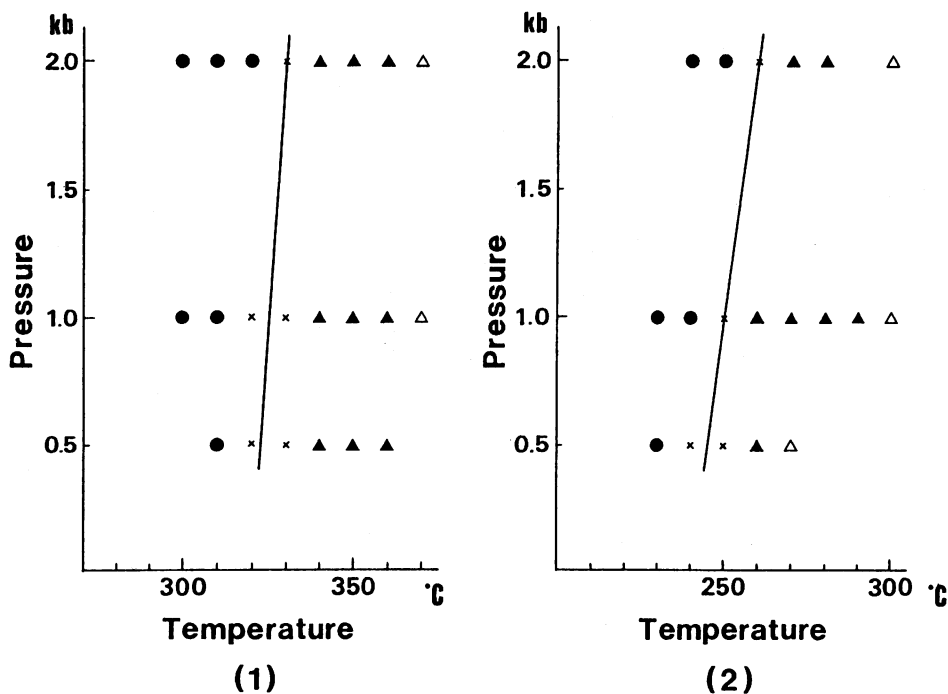


FIG. 3. P-T plots of run results for the reactions (1) and (2). Solid circle indicates that kaolinite has grown. Solid triangle indicates that pyrophyllite has grown. Open triangle indicates that kaolinite has decomposed completely. Cross indicates that reaction was not detected

Matthews, 1988). Therefore, it is anticipated that the difference of grain size between the two mixtures caused the difference of reactivity, which in turn affected the results of the experiments. We think it best to use natural mixture of 'fine-grained' minerals for starting material of hydrothermal experiments of this kind.

Reasonable equilibrium boundary for the reaction (2) was obtained by using the mixture 3) (Table 2, Fig. 3). The present equilibrium temperatures for the reaction (2) are lower than any other one reported so far. The mixture 3) contains boehmite. Therefore, the starting material is appropriate to the reaction (2) in chemical composition but not in mineral assemblage. From XRD patterns of the products, however, it is confirmed that boehmite disappeared in the earlier stage (e.g., Fig. 2). Since the stable mineral detection on the experiments by using the mixture 3) was based upon the comparison of XRD patterns of shorter duration runs and longer duration runs, the results are highly reliable.

Difference between diaspore and boehmite should be taken into consideration on the accuracy of the results for the reaction (1). Hemingway (1982) suggested that diaspore is the stable phase under surface weathering conditions and that gibbsite and boehmite are metastable phases whose presences are in large part due to slow rates of transformation (given in Peryea and Kittrick, 1988). Peryea and Kittrick (1988) concluded that the relative thermodynamic stability of the three minerals at 298K and 1atm is gibbsite < boehmite <

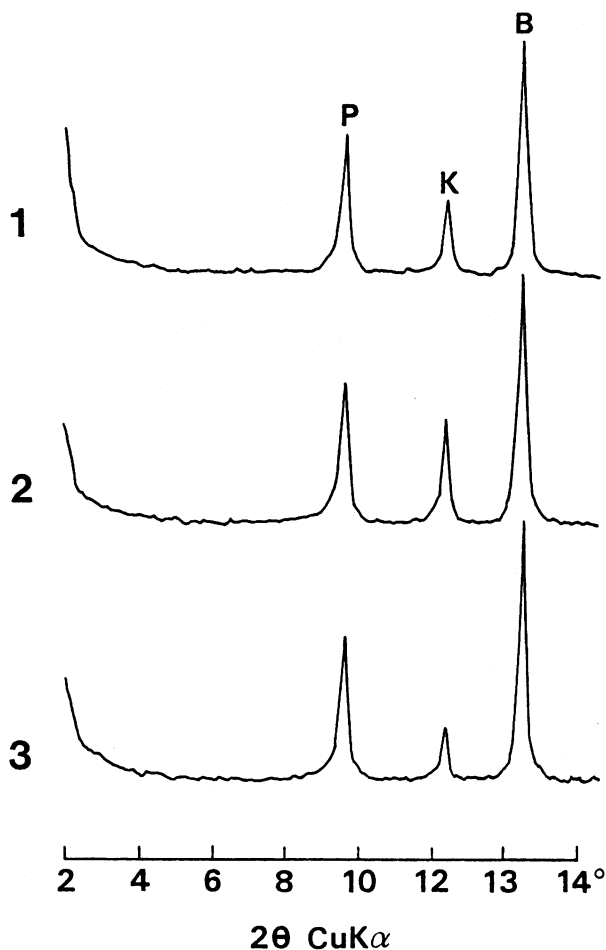


FIG. 4. XRD patterns of products and starting material. 1: starting material (the mixture 1), 2: product at 350°C and 1 kb (2 days), 3: product at 350°C and 1 kb (7 days), P: pyrophyllite, K: kaolinite, B: boehmite

diaspore. Hemley et al. (1980) indicated that the triple point of kaolinite-pyrophyllite-boehmite, in their stability diagram at 1 kb, is located in the higher temperature region compared to the point of kaolinite-pyrophyllite-diaspore. It is anticipated from these results that true equilibrium temperatures for the reaction (1) might be a little lower than those presented here.

The stability relationships of minerals in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 1 kb are shown in Fig. 5, in chemical composition-temperature diagram. The data of Haas and Holdaway (1973) are used above 330°C. In aluminous environment kaolinite is stable up to 325°C, whereas in siliceous environment it is stable up to 250°C. As shown in Fig. 5, in the

TABLE 3. Experimental data by using the mixture 2)

Run No.	T °C	P _{H₂O} kbar	Duration days	Results Stable mineral
Starting material: Mixture 2), K-P-Q kaolinite + quartz = pyrophyllite + water				
154	300	1.0	30	(K)
367	310	1.0	30	RND
220	320	1.0	14, 33	P
107	330	1.0	7	RND
368	340	1.0	30	P
92	350	1.0	7	P
100	360	1.0	7	P
222	300	2.0	7, 30	(K)
221	330	2.0	10, 30	P
86	340	2.0	7	RND
95	350	2.0	7	RND
102	360	2.0	7	P
51	370	2.0	7	P

K: kaolinite, P: pyrophyllite,
RND: reaction was not detected

intermediate chemical environment kaolinite and pyrophyllite are coexisting in equilibrium in the range of 250 to 325°C.

Henmi and Matsuda (1975) classified 'Roseki' deposits in Japan into three groups, based upon mineral paragenesis. That is: (1) Pyrophyllite type deposit; in which pyrophyllite and quartz are dominant, and kaolin minerals are subdominant. Diaspore and boehmite are found, but corundum and andalusite are not. (2) Complex type deposit; in which pyrophyllite, quartz and kaolin minerals are dominant. Corundum and andalusite are found. (3) Kaolin type deposit; in which kaolin minerals and quartz are dominant, and pyrophyllite is rarely found. Diaspore is found, but corundum and andalusite are not. The formation temperatures of these types under hydrothermal conditions can be estimated from Fig. 5, assuming that total pressure is 1 kb. The temperature of Pyrophyllite type may be in the range of 250 to 360°C in which pyrophyllite is stable. The presence of corundum and andalusite suggests that the temperature of Complex type is somewhat higher than that of Pyrophyllite type. Kaolin type may be formed below 250°C.

The present phase equilibrium data are in reasonable agreement with the solubility data of Hemley et al. (1980). However, it is suggested that the temperature range in which kaolinite and pyrophyllite are coexisting in equilibrium is wider than Hemley et al.'s (1980). The present range is about 70°C, and Hemley et al.'s (1980) is about 30°C. The range is also wider than that deduced from recently calculated phase relations in the system Al₂O₃-SiO₂-H₂O (e.g., Chatterjee et al., 1984; Berman, 1988).

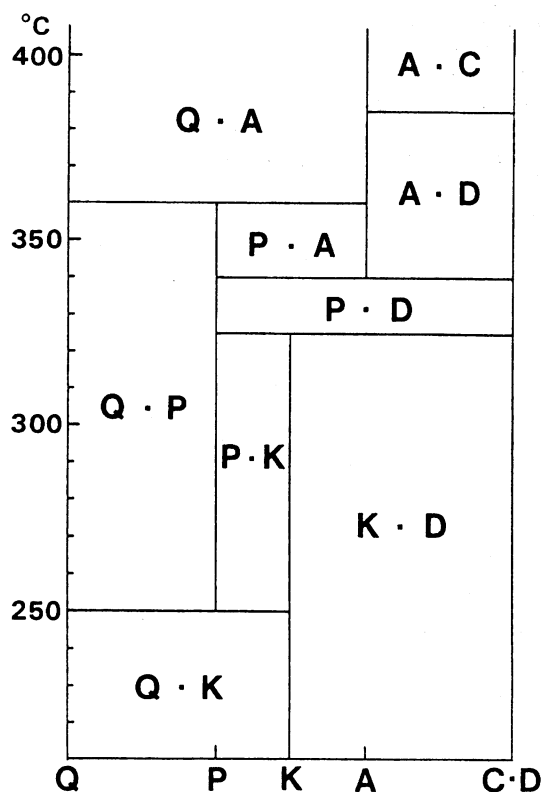


FIG. 5. Chemical composition - temperature diagram in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 1 kb. The data above 330°C are from Haas and Holdaway (1973). Q: quartz, P: pyrophyllite, K: kaolinite, A: andalusite, C: corundum, D: diaspore

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