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A Study of Rock Alteration Process Based on Kinetics of Hydrothermal Experiment

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Abstract. Experimental investigation was made on hydrothermal alteration of sericite in acid solution. It is found that the sericite is changed to pyrophyllite through kaolinite at 270° C and 260° C, and the alteration is considered to be a consecutive reaction involving two steps, from sericite to kaolinite and from kaolinite to pyrophyllite. On the other hand, pyrophyllite is not formed at 190° C and the sericite is altered to kaolinite. The rate of reaction in each step of this hydrothermal alteration is dependent on reaction temperature and chemical composition of the solution. From the results of the quantitative analyses of the experimental products, kinetic constants and related parameters were obtained.

By using these numerical values, an alteration process can be followed in a given model. Computed results for some cases of an alteration of sericite in acid solution are presented. Geological phenomena such as rock alteration or weathering are thought to progress in a disequilibrium state and in an open system. An attempt described in this paper is a physico-chemical approach to treat an alteration process accompanied with material transfer occurring in an open system from a kientic viewpoint.

Introduction

Generally, mineral paragenesis has been interpreted as a result of various reactions in a final equilibrium state. However, it is doubtful that the paragenesis really represents the equilibrium state. In any phenomenon in which reaction concerned is sluggish enough in rate to reach the equilibrium state, process of the reaction is much more important than the equilibrium state itself, and kinetics is necessarily required to study it. One of the authors (Mizutani, 1966, 1967) reported an experimental study of kinetics of transformation of amorphous silica to cristobalite and quartz under hydrothermal condition, and he examined natural siliceous deposits in relation to their genetic conditions and ages. Since this transformation was considered isochemical, it was treated as a reaction in a closed system.

In a reaction accompanied with material transfer, e.g., metasomatism, wall-rock alteration or weathering, the rate of attainment of equilibrium depends largely on a relative rate of reaction to material transfer. When the material transfer is rapid, marked disequilibrium might be the rule even if the reaction rate is fairly high as discussed by Hemley and Jones (1964). It is practically significant for us to trace a progressive change with time in a system where material transfer takes place. Therefore, we should study kinetics of the reaction in such an open system. Though thermodynamics by assuming partial or mosaic equilibrium as discussed by J. B. Thompson (1955), Korzhinskii (1959), Helgeson (1968), and Helgeson, Garrels and Mackenzie (1969) gives us a theoretical clue to explain mineral paragenesis in open systems, the kinetic treatment is necessary for us to gain a better understanding of a natural phenomenon in which a reaction does not really attain an equilibrium state and some metastable phases are retained. For example, Curtis and Brown (1969) stated that kinetic considerations lead to a much satisfactory analysis of a metasomatic development of zoned ultrabasic bodies.

There are, however, few kinetic data available to geology, and suitable kinetic experiments should be performed. Since any geological process accompanied with material transfer cannot be exactly reproduced by experimental method, an attempt is made to explain such process in an open system by numerical calculation in terms of parameters obtained experimentally for closed system. Mechanism of a complicated process can be made clear when it is overhauled to elementary reactions and reconstructed again by combining them. In other words, kinetic experiments are performed on one mineral, which is a constituent of rock, in various solutions. As an example, alteration by acid solution of a rock consisting of sericite and sufficient amount of silica was considered. A preliminary report of this study has been published by the present authors (Tsuzuki and Mizutani, 1969; Tsuzuki, 1970).

Experimental and Results

Material. Starting material for the hydrothermal alteration experiments was prepared from sericite from Furikusa, Aichi Prefecture, Japan. The sericite has a well crystallized $2M$ structure and is stained a little by iron compounds. It was purified by eliminating the fraction coarser than 4 microns by sedimentation, and iron stain was removed by Mackenzie's method (1954).

Method. About 0.03 g of the sericite was placed in a 17 ml silica tube, into which 10 ml of various acid solutions from 0.4 to 0.05 molar HCl and from 0 to 0.8 molar KCl were poured; the tube was then sealed. For each run the solution was prepared so that the ratio of the cations, H^+/K^+, falls into the kaolinite field in the diagram given by Hemley (1959). The amount of solution greatly exceeded that of the pulverized sericite, and its composition may be assumed to remain practically unchanged during the reaction.

The tubes were placed in an autoclave together with distilled water, and heated in an electric furnace. Many experimental runs were performed at various temperatures from 130° C to 270° C. The amount of material in each tube was sufficiently small to ensure the presence of two phases, solution and vapor, at that temperature. In consequence, the pressure of the solution was held at its equilibrium vapor pressure at that temperature. After various time intervals, from 2 to 158 days, the products were taken out of the tubes in the autoclave and the mineralogical compositions were quantitatively determined by X-ray diffraction method.

Product. Among the alteration products, sericite, kaolinite and pyrophyllite were usually detected. Peaks of kaolinite are sharp, whereas those of pyrophyllite are broad as shown in Fig. 1. The basal spacing of the pyrophyllite is larger than that of natural pyrophyllite as reported by Roy and Osborn (1954) on their synthetic pyrophyllite (Table 1). The basal spacing decreases with the reaction time, and $d(004)$ is changed from 4.783 to 4.656 Å during 1320 hours in an experimental series. Similar tendency was found in kaolinite formed from Al-OH-montmorillonite in HCl solution by Poncelet and Brindley (1967). Only in two samples treated for a short period with acid alone, without potassium chloride, small amounts of boehmite were found.

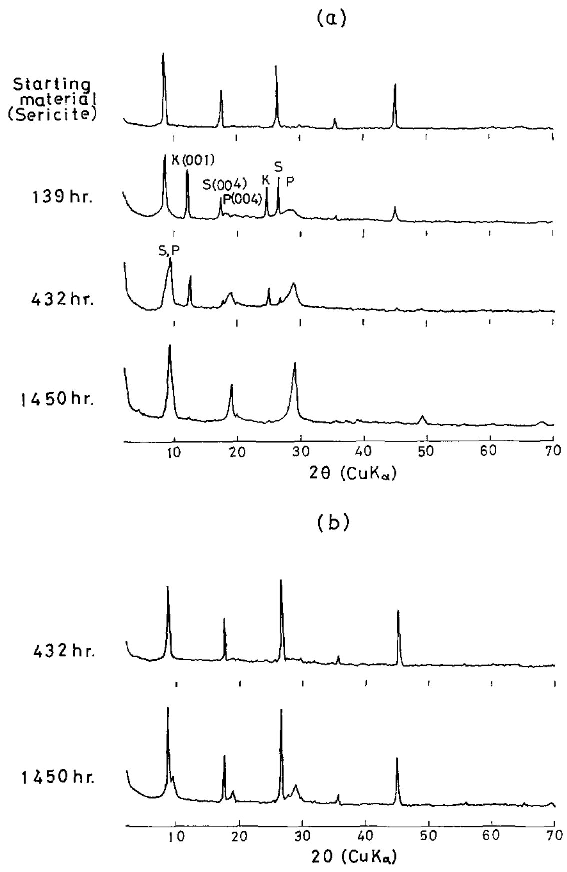

Fig. 1a and b. X-ray diffraction patterns of oriented specimen of sericite treated in acid solution during various durations at 270° C. (a) $^{\mathrm{m}}\mathrm{HCl} = 0.1$, $^{\mathrm{m}}\mathrm{KCl} = 0$, (b) $^{\mathrm{m}}\mathrm{HCl} = 0.1$, $^{\mathrm{m}}\mathrm{KCl} = 0.1$. *S* sericite; *K* kaolinite; *P* pyrophyllite

Fractions of the minerals were determined on an oriented specimen by using calibration curves made by natural sericite, kaolinite and pyrophyllite. Some errors at estimation of the relative amounts of these minerals are unavoidable, because the cristallinity of the latter two minerals is different from that of the same minerals produced in the experiment. For the quantitative determination, peaks of 7.2 Å—(001) of kaolinite—, 5.0 Å—(004) of sericite—and 4.7 Å—(004) of pyrophyllite—were exclusively used. An intensity of a peak was obtained by measuring the peak area. The fraction of a mineral was expressed by the ratio of the mineral to the summation of sericite, kaolinite and pyrophyllite in weight. Even if another phase, e.g., amorphous phase, appeared, it was eliminated. The phase was, however, not clearly observable in every experimental run. The results of the experiments are shown in Table 2 and some of X-ray diffraction patterns are illustrated in Fig. 1.

In the experimental runs made at 270° C in relatively dilute KCl solution, sericite decreased gradually with time, kaolinite increased in the earlier stage, but decreased later and eventually almost disappeared, while pyrophyllite exhibited a sigmoidal increase as shown in Fig. 2a. In the experimental products

Table 1. *X-ray diffraction data for pyrophyllite*

Synthetic				Natural		
Tsuzuki and Mizutani[a] (this paper)		Roy and Osborn (1954)		Gruner (1934)		
d	*I*	*d*	*I*	*d*	*I*	*hkl*[b]
9.41	100	9.32	90	9.16	40	002
7.18	5					kaolinite
		4.94	15			?
4.656	54	4.634	20	4.58	13	004
4.463	4	4.439	100	4.46	40	020
		4.280	30	4.13	25B	111; 11$\bar{2}$; 021; 11$\bar{1}$
		4.077	30			
		3.786	5	3.86	6B	11$\bar{3}$; 022
3.589	3					kaolinite
		3.420	15	3.35	30	113
		3.186	5			?
3.090	92	3.084	90	3.05	100	006
2.546	3	2.571	40	2.529	25B	13$\bar{2}$
		2.543	60			200
2.420	3	2.424	70	2.406	40B	20$\bar{4}$; 132
2.312	5	2.309	5	2.292	25B	008
2.159	2	2.166	20	2.146	20B	20$\bar{6}$; 134
2.065	2	2.078	40	2.075	13	204
				2.048	13	13$\bar{6}$
				1.885	6	136
1.849	11	1.843	20	1.832	40	0, 0, 10
1.650	3			1.639	30	138
				1.624	20	2, 0, $\overline{10}$
				1.570	4B	208; etc.
1.490	2			1.488	30B	060; 33$\bar{2}$
				1.466	10	33$\bar{4}$; 062; 330
				1.435	6	1, 3, 10
				1.422	6	2, 0, $\overline{12}$
1.378	5			1.380	40	2, 0, 10
				1.365	40	1, 3, $\overline{12}$

[a] Experimental no. ACTM 47, an oriented specimen on a glass slide. It was altered from sericite in solution (^{m}HCl = 0.1, ^{m}KCl = 0.0) during 1450 hr at 270° C.

[b] Indices after Gruner (1934).

in relatively concentrated KCl solution shown in Fig. 2b, kaolinite scarcely observed. The amount of sericite decreased and that of pyrophyllite increased correspondingly.

It is considered that pyrophyllite is the final product and kaolinite is an intermediate one at 270° C and even at 260° C, though the rate of formation of pyrophyllite is slow at the latter condition. The temperature is far below the lowest stability temperature of pyrophyllite, when compared with synthetic experiments reported by Roy and Osborn (1954), Hemley (1959) and Carr and Fyfe (1960). Althaus (1966) described in his report on the hydrothermal experiment of mixtures

Table 2. *Experimental result*

Experimental run no.	Starting material	Solution		Temp.	Time	Mineral composition in wt. %			
		$^{m}\mathrm{HCl}$	$^{m}\mathrm{KCl}$	(°C)	(h)	sericite	kaolinite	pyrophyllite	others
ACTM									
24	sericite	0.4	0	270	138	14	0	86	
23	sericite	0.4	0.05	270	138	100	0	0	
22	sericite	0.4	0.2	270	138	100	0	0	
48[a]	sericite	0.1	0	270	46	nd.	nd.	nd.	boehmite
28	sericite	0.1	0	270	139	26	32	42	
55	sericite	0.1	0	270	166	22	21	57	
46	sericite	0.1	0	270	432	2	8	90	
47	sericite	0.1	0	270	1450	0	1	99	
43	sericite	0.1	0.005	270	432	41	7	52	
45	sericite	0.1	0.005	270	953	3	2	95	
44	sericite	0.1	0.005	270	1450	0	1	99	
27	sericite	0.1	0.01	270	138	89	11	0	
40	sericite	0.1	0.01	270	432	49	3	48	
42	sericite	0.1	0.01	270	953	7	1	92	
41	sericite	0.1	0.01	270	1450	3	1	96	
37	sericite	0.1	0.05	270	432	76	0	24	
39	sericite	0.1	0.05	270	953	62	0	38	
38	sericite	0.1	0.05	270	1450	46	0	54	
26	sericite	0.1	0.1	270	138	91	1	8	
34	sericite	0.1	0.1	270	432	89	0	11	
36	sericite	0.1	0.1	270	953	69	0	31	
35	sericite	0.1	0.1	270	1450	61	0	39	
25	sericite	0.1	0.8	270	953	83	0	17	
31	sericite	0.05	0	270	139	66	21	13	
30	sericite	0.05	0.01	270	139	76	16	8	
29	sericite	0.05	0.05	270	139	86	5	9	
33[a]	sericite	0.01	0	270	139	nd.	nd.	nd.	boehmite
69	sericite	0.1	0	260	720	10	56	34	
70	sericite	0.1	0.01	260	720	77	15	8	
71	sericite	0.1	0.1	260	720	91	2	7	
64	sericite	0.1	0	190	3065	23	77	0	
65	sericite	0.1	0.01	190	3065	49	51	0	
66	sericite	0.1	0.1	190	3065	100	0	0	
59	sericite	0.1	0	130	3790	100	0	0	
60	sericite	0.1	0.01	130	3790	100	0	0	
61	sericite	0.1	0.1	130	3790	100	0	0	
49	ordered kaolinite	0.1	0	270	214	0	100	0	
54	disordered kaolinite	0.1	0	270	166	0	100	0	
50	disordered kaolinite	0.1	0	270	214	0	100	0	
58	disordered kaolinite	0.1	0.005	270	166	0	100	0	
57	disordered kaolinite	0.01	0	270	166	0	100	0	
53	disordered kaolinite	0.01	0	270	214	0	100		
51	sericite + disordered kaolinite (1:5)	0.1	0	270	214	0	100	0	
56	sericite + disordered kaolinite (1:1)	0.1	0	270	166	0	100	0	
52	powdered silica glass + disordered kaolinite (1:5)	0.1	0	270	214	0	100	0	
72	pyrophyllite	0.1	0	260	720	0	0	100	
73	pyrophyllite	0.1	0.1	260	720	0	0	100	
67	pyrophyllite	0.1	0	190	3065	0	0	100	
68	pyrophyllite	0.1	0.1	190	3065	0	0	100	
62	pyrophyllite	0.1	0	130	3790	0	0	100	
63	pyrophyllite	0.1	0.1	130	3790	0	0	100	

[a] ACTM 48 and ACTM 33 contain a small amount of boehmite and mineral composition was not determined.

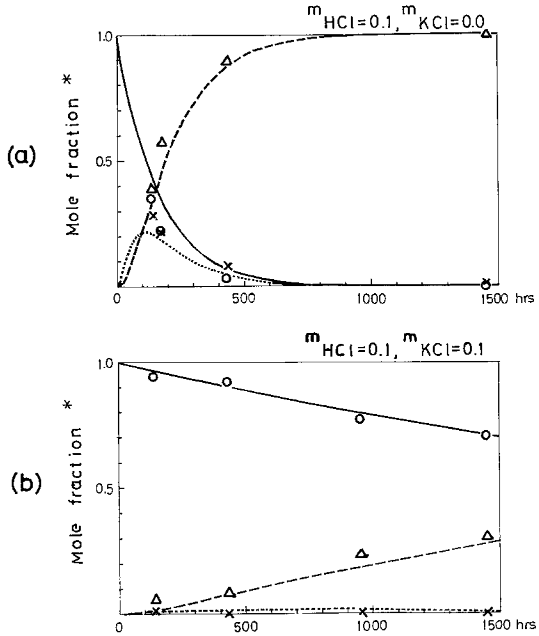

Fig. 2a and b. Changes in mineral composition (reduced mole fraction) during hydrothermal alteration experiments at 270° C. (a) $^{m}HCl = 0.1$, $^{m}KCl = 0$, (b) $^{m}HCl = 0.1$, $^{m}KCl = 0.1$. ○ sericite observed; × kaolinite observed; △ pyrophyllite observed. —— sericite calculated; ------ kaolinite calculated; — — — pyrophyllite calculated

of kaolinite and quartz that strong acids bring about a remarkable shift of the lower stability limits of pyrophyllite down about 260° C. Recently, A. B. Thompson (1970) studied equilibrium temperatures for breakdown of kaolinite plus quartz to pyrophyllite plus water and showed equilibrium at 325 ± 20° C at 1 kb, 345 ± 10° C at 2 kb and 375 ± 15° C at 4 kb (water pressure = total pressure). It is probable that the stability field pyrophyllite may extend down to much lower temperature under lower pressure conditions. In fact, on a basis of field evidence, Roy and Osborn (1954) also suggested that pyrophyllite is stable at 280° C, and Chennaux and Dunoyer de Segonzac (1967) and Füchtbauer and Goldschmidt (1959) described authigenic pyrophyllite in sedimentary rocks. On the other hand, natural kaolinite prepared in a starting material was not changed to pyrophyllite at 270° C. The reason why kaolinite produced from sericite is liable to be altered to pyrophyllite, and why natural kaolinite is not is unknown.

In all experimental runs at 190° C, sericite is changed to kaolinite, but pyrophyllite was not observed. Pyrophyllite is considered unstable at this temperature. In this temperature region, however, natural pyrophyllite prepared in a starting material was unchanged, probably because the rate of change is very low. Sericite was not changed at 130° C even after 158 days.

Electron Micrography. Electron micrograph of sericite from Furikusa used as a starting material is shown in Fig. 3a. In an experimental series in a solution ($^{m}H^{+} = 0.1$, $^{m}K^{+} = 0$) at 270° C, the specimen was changed from Fig. 3a to b. The electron micrographs reveal that the solution reacts on crystals from outside inwards, and a reaction rim is observed. Aggregate of the reaction product in the rim did not have any textural relation to the original crystal and it shows

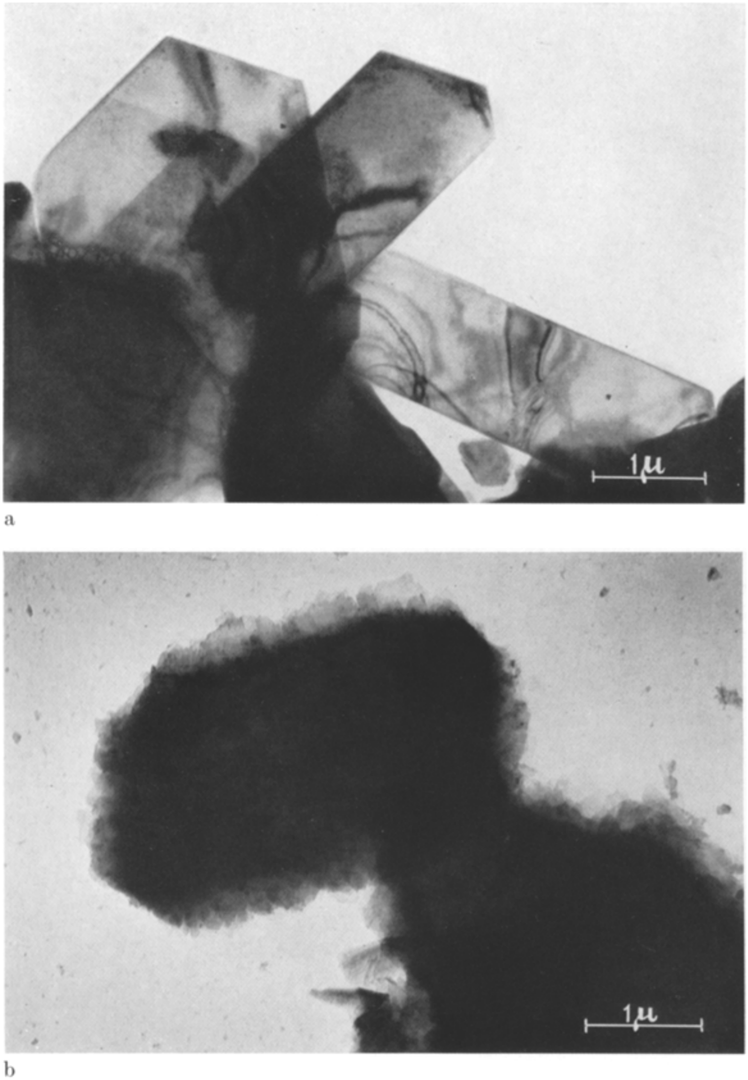

Fig. 3a and b. Electron micrographs of sericite. (a) Sericite from Furikusa —— starting material, (b) treated in solution ($^{m}HCl = 0.1$, $^{m}KCl = 0$) at 270° C, after 432 hours

an irregular aggregation of minute flakes. In the experiments in a solution containing much KCl ($^{m}H^{+} = 0.1$, $^{m}K^{+} = 0.05$, 1450 hours), the reaction rim was more smooth as shown in Fig. 4a, probably because the reaction progressed rather gently. It is unknown, however, whether a part of the product, for example, irregular aggregate in Fig. 4a was precipitated from solution or was the flakes of the altered product separated from the original crystal. Specimen treated at 190° C ($^{m}H^{+} = 0.1$, $^{m}K^{+} = 0$, 3065 hours) shows well crystallized flakes as shown in Fig. 4b, and a large amount of kaolinite was detected by the X-ray diffraction.

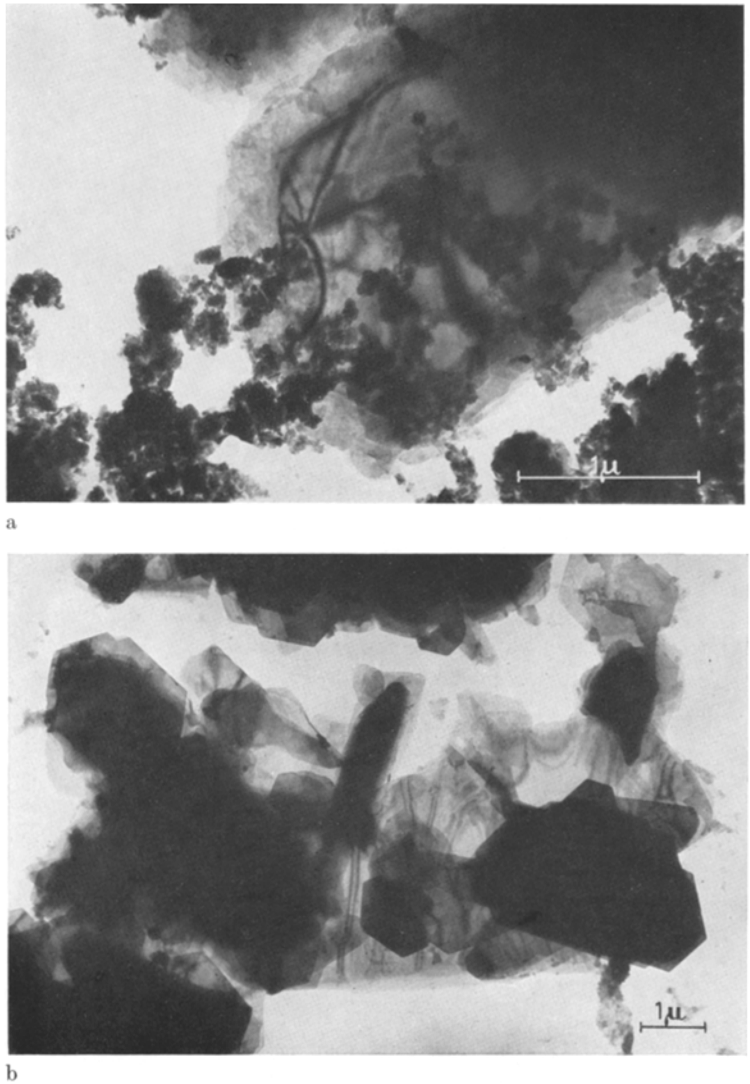

Fig. 4a and b. Electron micrographs of sericite. (a) Treated in solution ($^{m}HCl = 0.1$, $^{m}KCl = 0.05$) after 1450 hours at 270° C; (b) in solution ($^{m}HCl = 0.1$, $^{m}KCl = 0$) after 3065 hours at 190° C

This may be ascribed to the slow reaction at low temperature and to no further reaction from kaolinite to pyrophyllite.

Reaction Kinetics

A reaction found in the experimental runs described above appears to be a consecutive type, i.e., sericite → kaolinite → pyrophyllite. The alteration reaction can be expressed by the formula

$$\underset{\text{sericite}}{KAl_2(AlSi_3O_{10})(OH)_2} + H^+ + \tfrac{3}{2} H_2O \rightarrow \tfrac{3}{2}\underset{\text{kaolinite}}{Al_2(Si_2O_5)(OH)_4} + K^+ \qquad (1)$$

followed by

$$\underset{\text{kaolinite}}{Al_2(Si_2O_5)(OH)_4} + 2H_4SiO_4 \rightarrow \underset{\text{pyrophyllite}}{Al_2(Si_4O_{10})(OH)_2} + 5H_2O. \quad (2)$$

For the following calculation, it is more convenient to convert the molar amounts of kaolinite and pyrophyllite obtained into values equivalent to that of the sericite from which they were produced, by multiplying by $\frac{2}{3}$. The mole fractions of three species were thus recalculated, and the values in Fig. 2 are expressed in terms of the resulting fractions.

By assuming that the alteration involves two first-order steps, it may be kinetically expressed as follows:

$$\frac{d\mathrm{S}}{dt} = -k_1\mathrm{S}, \quad (3)$$

$$\frac{d\mathrm{K}}{dt} = k_1\mathrm{S} - k_2\mathrm{K}, \quad (4)$$

and

$$\frac{d\mathrm{P}}{dt} = k_2\mathrm{K}, \quad (5)$$

where S, K and P are the corrected mole fractions of sericite, kaolinite and pyrophyllite, respectively, and k_1 is the rate constant for the change from sericite to kaolinite and k_2 that from kaolinite to pyrophyllite. In each series of experiments, the rate constant k_1 is obtained from the equation

$$\mathrm{S} = \exp(-k_1 t) \quad (6)$$

and the rate constant k_2 is computed by successive approximation from the equation

$$\mathrm{K} = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)]. \quad (7)$$

The rate constant k_1 apparently depends on both concentrations of H^+ and K^+. By examining the results of the experiment, the following relation is found. At a constant concentration of H^+, the relation of k_1 and the concentration of K^+ is expressed by equation

$$\left(\frac{1}{k_1} - \frac{1}{k_1^0}\right) = a_1[\mathrm{K}^+] \quad (8)$$

where a_1 is a constant and it amounts to 40900 at 270° C, $[\mathrm{K}^+]$ is the molar concentration of K^+, k_1^0 is a rate constant at $K^+ = 0$, and it varies with the concentration of H^+, that is,

$$k_1^0 = \frac{1}{a_2}\sqrt{[\mathrm{H}^+]} \quad (9)$$

where a_2 is a constant and it amounts to 52.0 at 270° C, and $[\mathrm{H}^+]$ is the molar concentration of H^+. Hence, k_1 at arbitrary $[\mathrm{H}^+]$ and $[\mathrm{K}^+]$ is given by

$$k_1 = \frac{1}{a_1[\mathrm{K}^+] + \frac{a_2}{\sqrt{[\mathrm{H}^+]}}}. \quad (10)$$

On the other hand, the rate constant k_2 is practically dependent merely on the concentration of H^+ and irrespective of K^+, and is tentatively expressed by the equation

$$k_2 = k_2(0.1,\ 0.0) \times \frac{[H^+]}{0.1} \tag{11}$$

where $k_2(0.1,\ 0.0)$ is the rate constant of the second step in a solution of $^{m}H^+ = 0.1$ and $^{m}K^+ = 0.0$, and it amounts to 0.015/hour at 270° C. An example of the comparison of the experimental results with the calculated ones is illustrated in Fig. 2.

By using the results of the experiments at different temperature, the rate constants k_1 and k_2 in various solutions at various temperatures are roughly determined. For the rate constant k_1 in a solution of $^{m}H^+ = 0.1$ and $^{m}K^+ = 0.0$, the activation energy $E_1(0.1,\ 0.0)$ is calculated at 17 kcal/mole, though it is doubtful whether a solution remains in the same state at a different temperature condition for calculation of activation energy, because the equilibrium constant varies with temperature. By assuming that this activation energy is invariable irrespective of the concentration of the cation concerned, that is, the kinetic constant is related only with the frequency factor, we can obtain the frequency factor in the solution designated as A_1, by the following equation,

$$A_1 = \frac{k_{1,543}}{\exp\left[-\frac{E_1(0.1,\ 0.0)}{R \times 543}\right]} \tag{12}$$

where $k_{1,543}$ means k_1 at 270° C or 543 °K and it can be given by Eq. (10), and R is the gas constant. Then k_1 at T °K, $k_{1,T}$, in a solution is given by the following equation

$$k_{1,T} = A_1 \exp\left[-\frac{E_1(0.1,\ 0.0)}{RT}\right]. \tag{13}$$

For the rate constant k_2 in a solution of $^{m}H^+ = 0.1$ and $^{m}K^+ = 0.0$, the activation energy $E_2(0.1,\ 0.0)$ and the frequency factor $A_2(0.1,\ 0.0)$ are also calculated, and $E_2(0.1,\ 0.0) = 141$ kcal/mole and $\log A_2(0.1,\ 0.0) = 55$. Then, k_2 in various solutions at T °K is given by the following equation,

$$k_{2,T} = A_2(0.1,\ 0.0) \exp\left[-\frac{E_2(0.1,\ 0.0)}{RT}\right] \times \frac{[H^+]}{0.1}. \tag{14}$$

Since pyrophyllite was not found at every experiment at a temperature lower than 255° C, the rate constant k_2 is 0.0, but k_1 is given by the same equations applied for the reactions at a temperature higher than 255° C. Pyrophyllite once formed, however, is considered to be not changed to kaolinite which latter may be a stable phase at this temperature range.

Alteration of Rock and Formation of Alteration Zone

On a basis of the result of kinetic experiments, progressive steps of alteration in an open system can be traced numerically. As an example, let us consider an alteration by acid solution attacking a rock which consists of sericite and

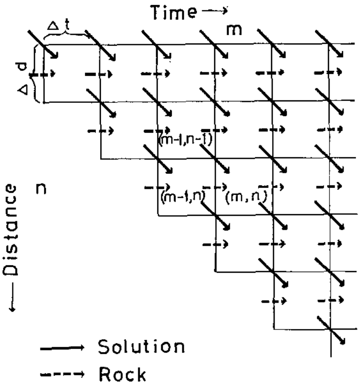

Fig. 5. A schematic time-space diagram of rock alteration by solution in an open system. Assume that rock comes in contact with a solution in a channel. Let the ordinate be distance from the channel and the abscissa be time in order to express the compositional change of rock and solution with time. Solution at a time-space unit reacts with rock. After a time interval Δt, compositions of rock and solution are changed. The compositional change of the rock is shown by a horizontal arrow parallel to the abscissa of time-axis. On the other hand, the solution whose composition is changed in the preceding reaction will instantaneously migrate Δd into the adjacent part of the field, and will react with rock at this place. The compositional change of the solution is expressed by a diagonal arrow

sufficient amount of silica. It is assumed that a solution having a given initial concentration of K^+ and H^+ reacts with the surrounding rock, and steadily migrates, and this process continues till the supply of the solution stops.

During the alteration of sericite to kaolinite, one mole of H^+ in the solution gets into one mole of sericite, while one mole of K^+ in the sericite is released into the solution, as shown in Eq. (1). Consequently, the concentration of H^+ decreases and that of K^+ increases according to the following equation,

$$\frac{d[H^+]}{dS} = -\frac{d[K^+]}{dS} = p \tag{15}$$

where p is a constant related with porosity or void ratio of the rock, and

$$p = \frac{\text{volume of sericite in unit volume}}{\text{volume of solution in unit volume}} \times \frac{1000}{\text{volume of 1 mole of sericite}}\,.$$

At first, the solution permeates into a small portion of a rock and reacts with it to some extent. Both compositions of the rock and solution are changed by this reaction. The solution then migrates into the adjacent part of the rock and reacts with it. The rate of reaction in this part differs from the first, because the chemical composition of solution has been changed. At the same time, a new solution enters into the first portion and reacts with it. Thus, both compositions of the rock and solution are changed either with time or with place. These step-like changes are schematically illustrated in Fig. 5.

Let Δd be the thickness of a layer of the rock into which the solution migrates and Δt the time of reaction with the rock. After the time interval Δt, the solution migrates into the next layer, where it reacts with the rock during the next time interval. Thus, reaction and migration occur alternately. Value $\varDelta d$ corresponds to the distance through which the solution migrates during the time interval $\varDelta t$. If the kinetic formula is established according to the relation described in the preceding chapter, the reaction at a portion during $\varDelta t$ can be known, and changes in chemical composition of both solution and rock are obtained from the reaction formulae.

In the schematic time-space diagram (Fig. 5), the solution at time-space unit (m, n) comes from time-space unit $(m-1, n-1)$, while the rock in time-space unit (m, n) is changed from time-space unit $(m-1, n)$. At the beginning of a time interval at time-space unit (m, n), the concentration of H^+ and K^+ in the solution is $[H^+]^{m-1}_{n-1}$ and $[K^+]^{m-1}_{n-1}$, respectively; similarly, fractions of constituent minerals of the rock at the unit are S^{m-1}_n, K^{m-1}_n and P^{m-1}_n. Since the time interval $\varDelta t$ is small relative to the rate of reaction, changes of mineral composition during $\varDelta t$ at time-space unit (m, n) are calculated by the following equations;

$$\varDelta S^m_n = -\varDelta t\, k^m_{1n} S^{m-1}_n, \tag{16}$$

$$\varDelta K^m_n = \varDelta t\, k^m_{1n} S^{m-1}_n - \varDelta t\, k^m_{2n} K^{m-1}_n, \tag{17}$$

$$\varDelta P^m_n = \varDelta t\, k^m_{2n} K^{m-1}_n, \tag{18}$$

where k^m_{1n} is obtained from Eq. (10) and k^m_{2n} from Eq. (11).

The changes in concentration H^+ and K^+ are estimated from Eq. (15) as follows,

$$\varDelta [H^+]^m_n = p \varDelta S^m_n \tag{19}$$

and

$$\varDelta [K^+]^m_n = -p \varDelta S^m_n. \tag{20}$$

Evidently, the solution does not migrate into time-space unit (m, n) if $m < n$, and sericite remains unchanged. Since the constants a_1, a_2 and $k_2(0.1, 0.0)$ were experimentally determined at 270° C, Eqs. (16)–(20) can be applied to an alteration process at that temperature by substituting various initial concentrations of H^+ and K^+ and various p and $\varDelta t$. Conveniently, distance is expressed by number of layers, i.e., number of unit distance.

A result of the calculation is shown in Figs. 6 and 7, where the field is maintained 270° C, the initial concentration of H^+ is 0.1 mole, that of K^+ is 0.0, p is 28.7, which is given by (volume of sericite in unit volume)/(volume of solution in unit volume) $=4$, and $\varDelta t$ is 1 hour. As is seen in these figures, there is an intermediate zone between the sericite and the pyrophyllite zone. The intermediate zone, in which sericite, kaolinite and pyrophyllite coexist, migrates from inner part to outer one, and its width becomes wider with time. In other words, sericite rock is changed to pyrophyllite rock passing through an intermediate zone, and the zone is found earlier in the inner part and later in the outer one.

When there is a temperature gradient in the field, and/or temperature at a portion is changed with time, the rate constants, being a function of temperature, are given by Eqs. (8)–(14).

When temperature is lower than 255° C, k_2 is 0.0. Pyrophyllite once formed is, however, retained as it was even below 255° C. In order to calculate the pro-

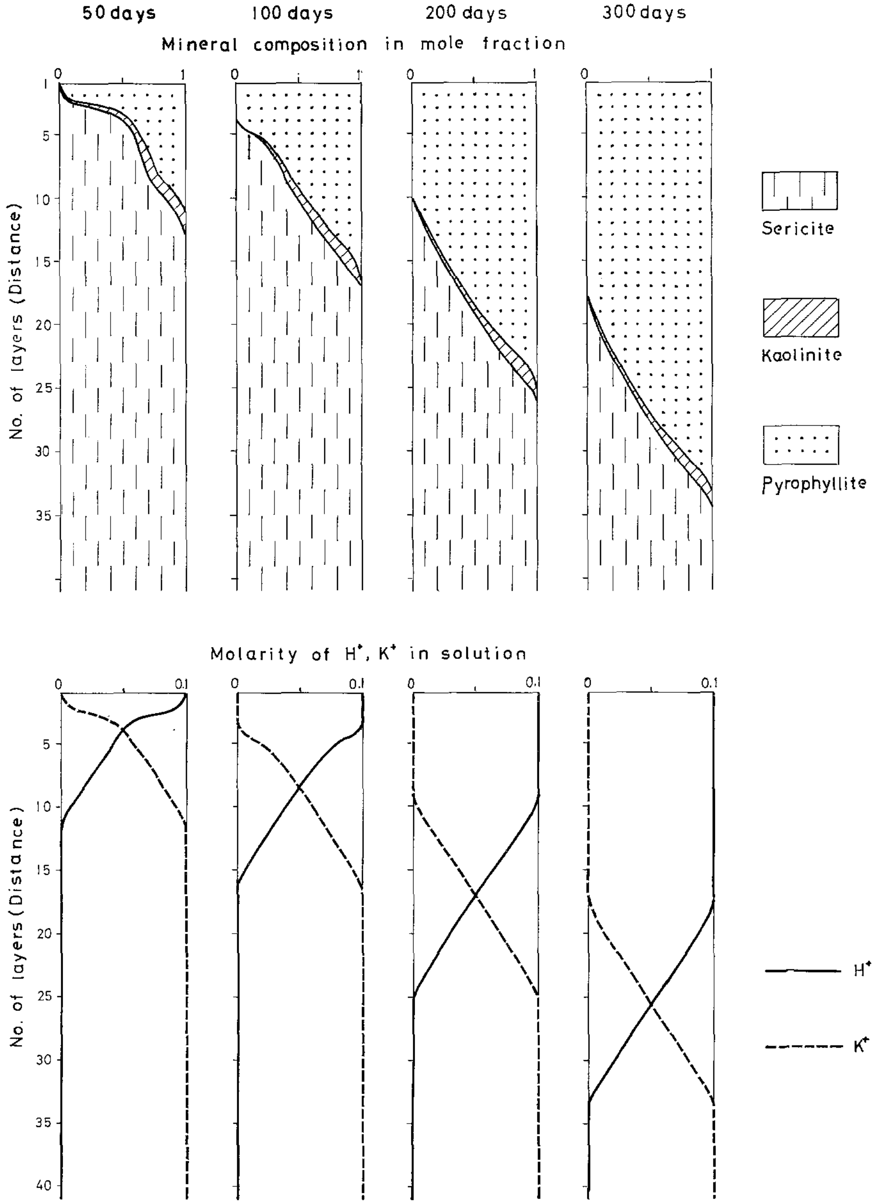

Fig. 6. Calculated result of changes with time of composition of silica-containing sericite rock altered by solution ($^{m}\mathrm{HCl}=0.1$, $^{m}\mathrm{KCl}=0$). Temperature = 270° C; pressure = vapor pressure of the solution; $p=28.70$

gressive change, temperature must be expressed as a function of time (m) and space (n), and this function should be given in advance. Figs. 8 and 9 demonstrate an example of the result of calculation at the following case: temperature gradient is 0.01° C/layer, temperature at the innermost layer decreases from 280° C at a

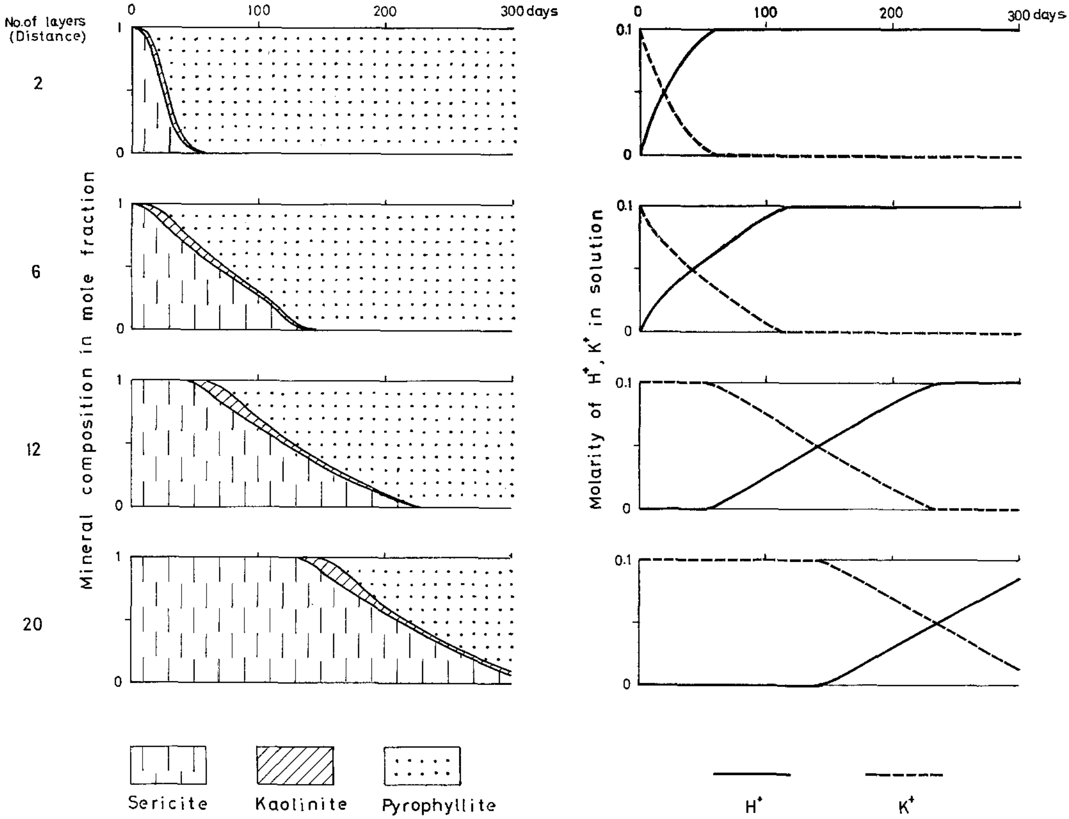

Fig. 7. Calculated result of changes with position of composition of silica-containing sericite rock altered by solution (^{m}HCl = 0.1, ^{m}KCl = 0). Temperature = 270° C; pressure = vapor pressure of the solution; $p = 28.70$

rate 0.0091° C/hour, and the other chemical and mineralogical condition is the same as an isothermal example at 270° C already described.

In this example, the thermal gradient in the rock is too small to give its effect to the zonation. The pyrophyllite zone is formed in the inner part during an incipient higher temperature condition, and the kaolinite zone is formed in the outer part during the later lower temperature condition. If temperature decreases with time, temperature gradient in the rock is not always required for making such zonation. In other words, a zonation characterized by so-called high-temperature and low-temperature minerals may be established when temperature decreases with time without any thermal gradient.

As expressed above, thickness of a layer Δd corresponds to the distance through which solution migrates during Δt, and it is given by seepage velocity. The seepage velocity can be calculated according to Darcy's law, $v = CJ$, where v is the seepage velocity, C is the seepage coefficient and J is a gradient of piezometric head. For example, if C is assumed to be 0.0001 cm/sec for solidified rock, as estimated by Polubarinova-Kochina (1962), and the gradient of the piezo-

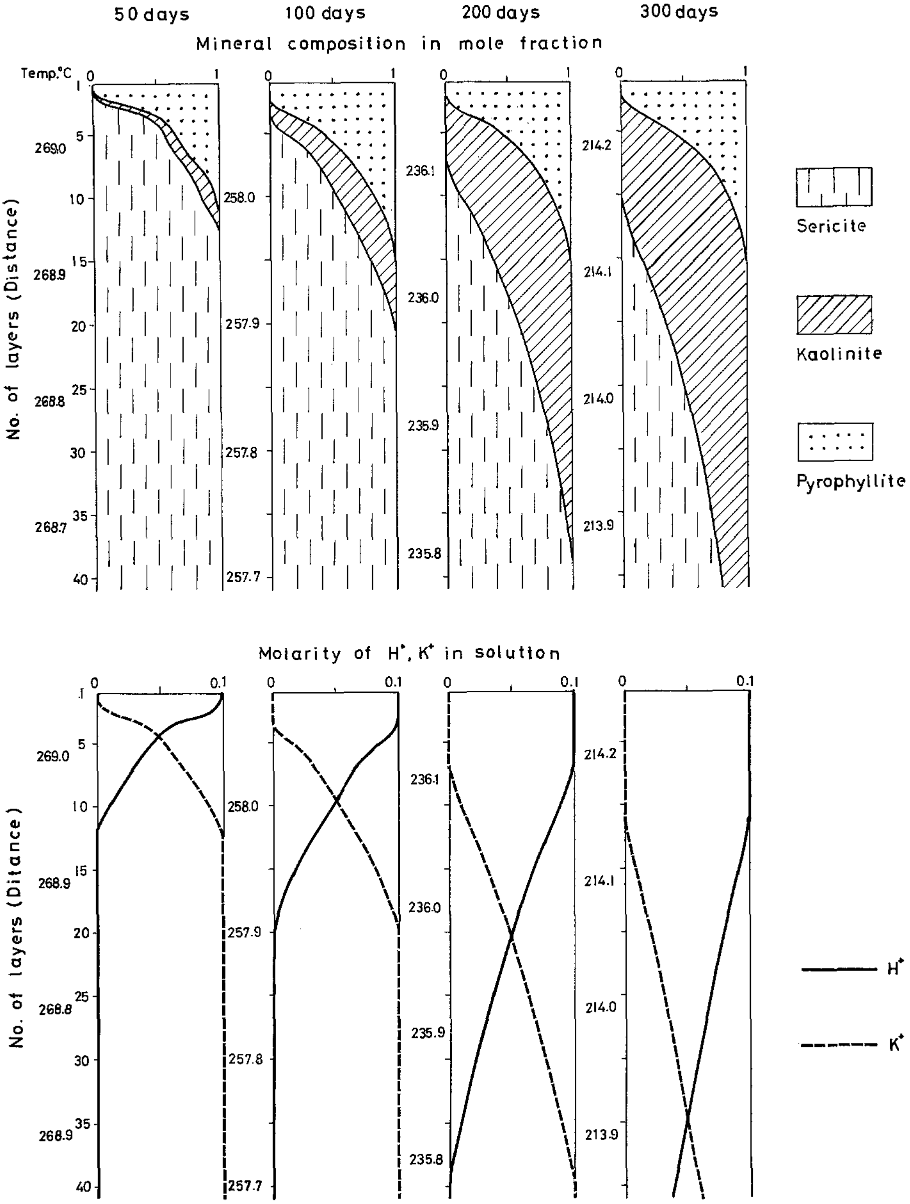

Fig. 8. Calculated result of changes with time of composition of silica-containing sericite rock altered by solution (${}^{m}HCl=0.1$, ${}^{m}KCl=0$). Temperature gradient $= 0.01°$ C/layer; temperature decrease at the innermost layer from 280° C at the rate of 0.0091° C/hour; pressure = vapor pressure of the solution

metric head to be about 1.0, we obtain $v=0.36$ cm/hour. When the time interval $\Delta t=1$ hour, then Δd is obtained as 0.36 cm, and thickness of the pyrophyllite zone after 300 days is 6.5 cm in Fig. 6.

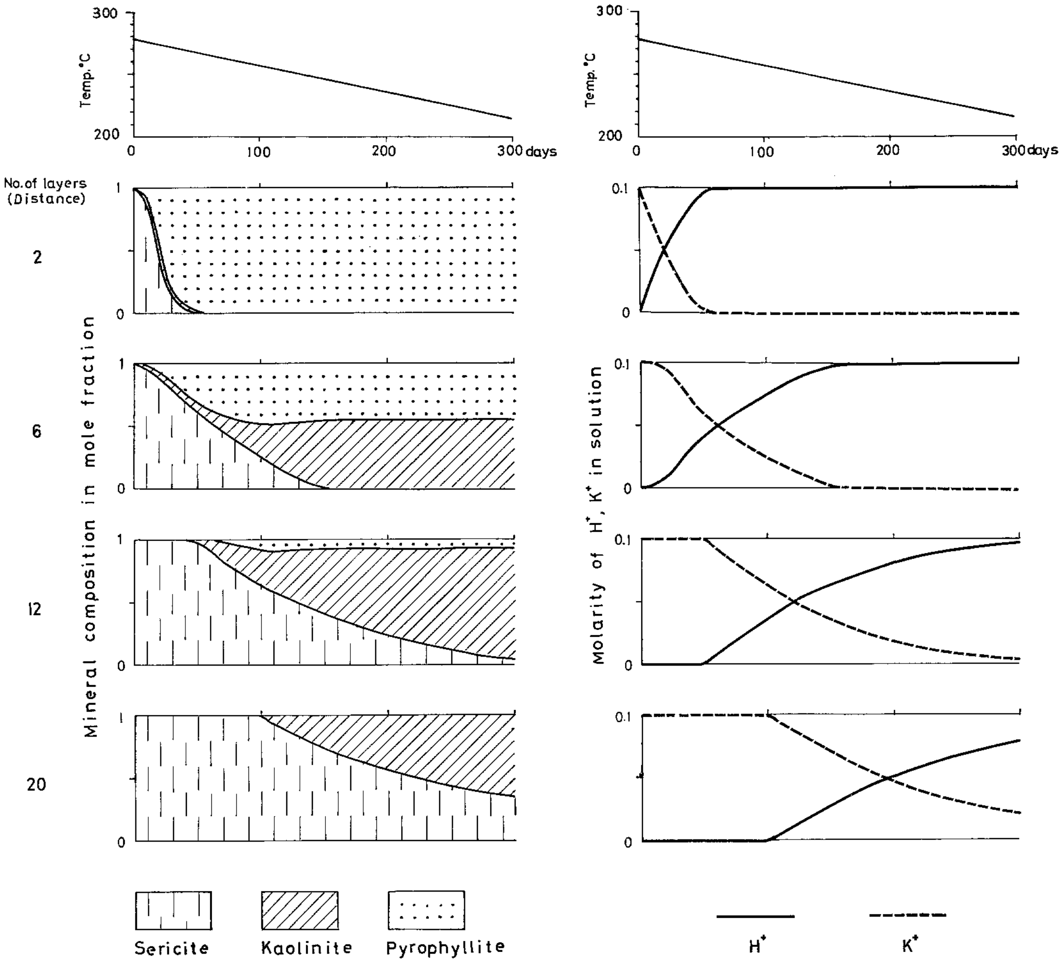

Fig. 9. Calculated result of changes with position of composition of silica-containing sericite rock altered by solution ($^{m}HCl = 0.1$, $^{m}KCl = 0$). Temperature gradient = 0.01° C/layer; temperature decrease at the innermost layer from 280° C at the rate of 0.0091° C/hour; pressure = vapor pressure of the solution

Discussion

In this paper, the authors described an attempt kinetically to illustrate geological processes in open systems, and presented some models. Little evidence that a rock consisting of sericite and sufficient amount of silica had existed and it was altered thereafter by acid solution has been known. However, Fujii (1968) reported alteration of sericite rock to pyrophyllite rock at Shin-yo Mine, Nagano Prefecture, Japan. Sumi (1968, 1969) stated that there is found to occur pyrophyllite zone adjacent to the alteration zones characterized by montmorillonite, kaolinite and alunite in the Matsukawa geothermal area, Iwate Prefecture, Japan, and he suggested the pyrophyllite zone was formed at higher temperature stage than

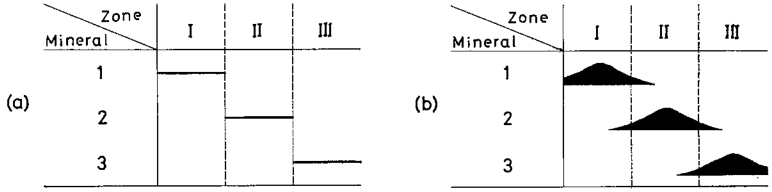

Fig. 10. Graphic representation of mineral paragenesis in two different ways

the other, because the present temperature measured in the pyrophyllite zone is lower than the temperature required for the formation of pyrophyllite. It may be conceivable that the occurrence of pyrophyllite found in these area is reasonably explained by the kinetic scheme discussed here.

As described by Zen (1961), three phase assemblage, pyrophyllite—kaolinite—quartz, in Al_2O_3—SiO_2—H_2O system may indicate that H_2O behaved as a fixed component during the formation of the pyrophyllite deposits, contrary to the general situation in regional metamorphism. On the other hand, the present kinetic study suggests the three phase assemblage can be found even when H_2O is a mobile component. In this report, it is assumed that H^+, K^+ and H_2O are perfectly mobile, whereas Al_2O_3 and SiO_2 are innert.

The scheme presented here is useful when seepage velocity is relatively high to the rate of diffusion, but when the velocity is much lower, the diffusion of ions due to gradient of the chemical potential may become a main factor governing transfer of material as discussed by Garrels, Dreyer and Howland (1949) and Curtis and Brown (1969).

At present, the result of calculation as shown in Figs. 6–9 is surely conceptional, because precise information about kinetic and related data, for example, temperature, composition of the initial solution, and void ratio of rock, is not available for accurate discussion. It will become much more quantitative, if many data are accumulated. Most important is that geological process is numerically describable on coordinates of space and time. By combining kinetic parameters with spacial ones, the process in an open system will be successfully depicted on the kinetic scheme as discussed here.

Mineral paragenesis is generally displayed by many solid lines representing existence or non-existence of minerals participating in an alteration. An example shown in Fig. 10a demonstrates that zone *I* is characterized by the presence of mineral 1 and absence of 2 and 3. Graphic representation of this kind implies on a basis of equilibrium or partial equilibrium that a certain condition definitely governs the existence of a mineral. In other words, it is thought that the mineral represents the final equilibrium state. However, a system would not be placed abruptly in a condition, but it would reach the condition gradually from the different one. Even if change of the condition occurred abruptly, the alteration does hardly ensue. In addition, the change of condition would probably accompany material transfer. Accordingly, the mineral paragenesis would be better displayed by many lenticular bands instead of lines as shown in Fig. 10b. The explanation of this lies in a fact that many relict minerals, zonal structure of a crystal or mixed-layer minerals are frequently encountered in various kinds of rocks. Sometimes, there are found to occur ambiguous and obscure zones difficult to define the boundary of zonal arrangement of minerals. In these cases, kinetic treatment in open systems is very useful for clarifying the actual mineral paragenesis.

Thermodynamics is usually applied to an idealized state, that is, equilibrium state, and it suggests where the reaction goes to. On the other hand, kinetics is more realistic, and it provides us with another information: how fast it occurs. Alteration process occurring in a disequilibrium state and in an open system will be understood much more exactly by the method described in this paper.

Conclusion

Hydrothermal experiments show that sericite in acid solution is altered to pyrophyllite through kaolinite under temperature conditions higher than 255° C, and the alteration process is found seemingly to be a consecutive reaction consisting of two first-order steps. In temperature conditions lower than 255° C, the alteration involves only one step of the first-order reaction, that is, from sericite to kaolinite, and pyrophyllite is no longer formed. From the result of quantitative analysis of the experimental products, the kinetic constants are obtained.

The rate constant of each step in this alteration is more or less dependent on the concentrations of cations in solution. The interrelationship between these rate constants and the concentration of cations are tentatively formulated. Activation energy and frequency factor relevant to these reactions are also obtained.

It is stressed that alteration process should be expressed on coordinates of space and time. The process would be thoroughly traced numerically on these coordinations, if the kinetic constants and related parameters are known. By using the numerical results obtained in the experimental investigation, some examples of progressive alteration of a rock composed of sericite and sufficient amount of silica are presented. Such kinetic analysis is to be very essential and instrumental to study a disequilibrium process especially accompanied with material transfer, that is, reaction in an open system.

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