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CHEMICAL REACTIONS AMONG CLAY MINERALS, CALCIUM CARBONATE, AND AMMONIUM CHLORIDE

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ABSTRACT

Various kinds of clay minerals mixed with calcium carbonate and ammonium chloride were heated at a specific temperature in the range of 500–1000° C. for one hour, and the reaction products were examined. The kinds of reaction products depend upon the chemical compositions of the clay minerals. In the case of clay minerals rich in aluminum, formation of such minerals as hydrogrossularite, wollastonite, haüyne, larnite, etc., was observed. With clay minerals rich in magnesium, crystallization of such minerals as periclase, forsterite, monticellite, spurrite, etc., was observed. For clay minerals containing both aluminum and magnesium, such minerals as periclase, forsterite, hydrogrossularite, and monticellite were formed. When calcium carbonate alone was used, the crystallization temperatures usually rose higher than those in the case when both ammonium chloride and calcium carbonate were used, the kinds of reaction products differed, particularly in clay minerals rich in aluminum; gehlenite was noticed as one of the principal reaction products. Probably chlorine acts on calcium ions forming calcium chloride, which reacts with silicates. Hydrogen in ammonium ions released from ammonium chloride may play an important role in the formation of hydrogarnet.

INTRODUCTION

The authors have taken an interest in chemical reactions among silicates or volcanic glass and various kinds of alkali-earth salts or metal oxides under a specific chemical environment in which catalytic reactions are suggested (Sudo and Matsuoka, 1959; Ueda and Sudo, 1963). In relation to this, the authors have investigated the chemical reaction in the process of the Smith method (1871) which has long been used in the chemical analysis for alkalies. In a preliminary report (Sudo, *et al.* 1960), the authors reported the formation of hydrogrossularite and periclase from leuchtenbergite. In the present work, the experiments were extended by using various kinds of clay minerals as starting materials, and the formation of various kinds of reaction products, which are usually found in nature as skarn minerals, was revealed. The results of these experiments revealed that a volatile material such as ammonium chloride plays an important role in promoting complicated chemical reactions among clay minerals, ammonium chloride and calcium carbonate. In this connection, the authors refer to the work of Gorgeu who, in 1883, reported the possibility of the synthesis of grossularite by passing hydrogen and steam over a mixture of pipe clay (pyrophyllite) and calcium chloride in a platinum crucible.

STARTING MATERIALS

The following clay minerals were used as starting materials:

(a) Illite from Yoji, Gumma Prefecture. It occurs as a hydrothermal alteration product of granodiorite (Kodama, 1957).

(b) Pyrophyllite from Yoji, Gumma Prefecture. It occurs as a hydrothermal alteration product of shale (Kodama, 1958).

(c) Montmorillonite from Endani, Tottori Prefecture. It occurs as clay veins cutting granite (Yoshikawa and Sudo, 1960).

(d) Leuchtenbergite from the Wanibuchi mine, Shimane Prefecture. It occurs in the alteration area around the hydrothermal replacement bodies of gypsum in Tertiary tuffs or volcanic rocks (Sakamoto and Sudo, 1956).

(e) Kaolinite from the Kampaku mine, Tochigi Prefecture. It occurs as a hydrothermal alteration product of liparite around gold-quartz vein.

(f) Antigorite from Haruyama, Iwate Prefecture.

(g) Vermiculite from Gobangumi, Fukushima Prefecture. It occurs in serpentine near the contact with granite.

(h) Talc from Akihata, Gumma Prefecture.

(i) Hydrated halloysite from the Zuihō mine, Taiwan and from the Jōshin mine, Gumma Prefecture. The former occurs as a gangue mineral of gold-quartz veins, and the latter occurs as a hydrothermal alteration product of andesite (Sudo and Ossaka, 1952).

(j) Allophane from Ōya, Tochigi Prefecture. It occurs as a weathering product of pumice fragments in the surface soil (Sudo and Ossaka, 1952).

The chemical compositions of these starting materials are shown in Table 1.

EXPERIMENTS

The starting materials are free of impurities as far as the detection limit of the usual *x*-ray diffractometer recording. Each sample was directly pulverized in an agate mortar into fine powder and its size was set below 5 microns by decantation. The sample was mixed with calcium carbonate (reagent grade) and ammonium chloride (reagent grade) in various molecular ratios. The weight of the mixture was set at 0.5 g throughout the experiments. Each mixture was heated at every 100° temperature, namely 100° C., 200° C., . . . , 1000° C., for one hour at a mean heating rate of 20° C. per minute. The mixture was kept at a specific temperature for one hour and then cooled immediately. After cooling to room temperature, the content of the crucible was put into boiling water for 15 minutes to one hour; then it was filtered, and washed with distilled water to remove the water-soluble products completely. The residue thus obtained was dried at 100∼110° C. and examined by an *x*-ray diffractometer.

REACTION PRODUCTS

Experimental data are given in Table 2. Table 3 shows the rise and fall of the amounts of reaction of clay mineral: $CaCO_3$: NH_4Cl.

TABLE 1. CHEMICAL COMPOSITIONS OF THE STARTING MATERIALS

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
SiO_2	47.63%	62.02%	48.90%	29.07%	44.77%	41.44%	25.06%	38.97%
TiO_2	0.10	—	tr.	0.32	0.05	0.12	—	—
Al_2O_3	37.03	32.24	18.40	21.82	35.70	0.95	27.68	34.43
Fe_2O_3	0.01	tr.	1.12	0.83	0.40	1.56	1.24	2.06
FeO	tr.	tr.	0.01	3.67	—	1.79	—	—
MgO	0.04	0.18	1.88	29.90	0.84	41.06	0.59	—
CaO	tr.	0.04	2.25	0.19	tr.	0.11	1.59	—
MnO	tr.	none	—	—	—	0.04	—	—
Na_2O	0.76	—	0.35	0.35	0.04	0.10	—	—
K_2O	9.02	—	0.28	tr.	0.16	none	—	—
$H_2O(+)$	4.97	6.06	8.44	10.76	13.25	10.58	13.90	24.66
$H_2O(-)$	0.73		17.64	2.76	4.33	2.12	20.82	
P_2O_5	0.02	—	0.05	—	—	0.02	—	—
Total	100.31%	100.54%	99.32%	99.67%	99.54%	99.89%	(90.88%)	100.12%

(a) Illite, Yoji, Gumma Prefecture (Kodama, 1957).

(b) Pyrophyllite, Yoji, Gumma Prefecture (Kodama, 1958).

(c) Montmorillonite, Endani, Tottori Prefecture (Yoshikawa and Sudo, 1960).

(d) Leuchtenbergite, Wanibuchi mine, Shimane Prefecture (Sakamoto and Sudo, 1956).

(e) Kaolinite, Kampaku mine, Tochigi Prefecture (Iwai and Kuroda, 1960).

(f) Antigorite, Haruyama, Iwate Prefecture (Analyst: the authors).

(g) Allophane, Oya, Tochigi Prefecture (Sudo and Ossaka, 1952, analyst: Hideo Minato).

(h) Hydrated halloysite, Joshin mine, Gumma Prefecture (Sudo and Ossaka, 1959, analyst: Geological Survey of Japan).

Illite: In the range of the following proportions, illite:$CaCO_3$:NH_4Cl $=1:0\sim5:2\sim10$, the crystallization of the minerals such as anorthite, hydrogrossularite ($Ca_3Al_2(SiO_4)_{3-m}(OH)_{4m}$), a cancrinite-like mineral with main reflections; 4.77 Å (relative intensity=69), 3.69 Å (96), 3.28 Å (100), 2.92 Å (16), 2.76 Å (28), 2.65 Å (51), 2.45 Å (31), 2.127 Å (40), 1.781 Å (16), and an undetermined mineral was observed. Hydrogrossularite tends to be formed when the ratio of $CaCO_3$ is relatively higher. The chemical composition of the residue obtained in the ratio of illite:$CaCO_3$:$NH_4Cl$$=1:4:8$, heated at 900° C., is as shown in Table 4a.

Pyrophyllite: In the case of such a ratio as pyrophyllite:$CaCO_3$:NH_4Cl $=1:5:10$, the crystallization of pseudowollastonite, hydrogrossularite, and haüyne was noticed.[1] As the temperature rose, haüyne disappeared,

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[1] Identification of haüyne was only based on the principal x-ray powder reflections. Although the general formula of haüyne is given as $(Na, Ca)_{4\sim8}Al_6Si_6O_{24}(SO_4, S)_{1\sim2}$, it is

pseudowollastonite and hydrogrossularite remained, and successively the growth of hydrogrossularite was enhanced.

Montmorillonite: The starting material contains a small amount of quartz, which could hardly be removed by the sedimentation method. The results obtained, using the original sample, are as follows; in the ratio of montmorillonite:$CaCO_3$:NH_4Cl=1:4:8, the formation of such minerals as hydrogrossularite, pseudowollastonite and wollastonite was observed. The reflections of pseudowollastonite and hydrogrossularite gradually increase with increasing temperature.

Vermiculite: In the ratio of vermiculite:$CaCO_3$:NH_4Cl=1:4:8, the crystallization of minerals such as hydrogrossularite, monticellite and periclase was obtained. The reflections of monticellite are weak, but those of hydrogrossularite were gradually enhanced with rising temperature.

Leuchtenbergite: In the ratio of leuchtenbergite:$CaCO_3$:NH_4Cl=1:4∼5:10, the crystallization of the minerals such as hydrogrossularite, periclase, larnite (Ca_2SiO_4) and spurrite ($2\ Ca_2SiO_4 \cdot CaCO_3$) was observed. The reflections of periclase and hydrogrossularite were gradually enhanced with rising temperature, and spurrite and larnite were found only at a high temperature in association with periclase and hydrogrossularite.

The residue obtained under the conditions of the ratio 1:5:10 and 900° C. was analyzed chemically (Table 4b). The oxide ratio is obtained as $3.1CaO \cdot Al_2O_3 \cdot 2.4SiO_2 \cdot 1.9H_2O + 3.2MgO$, which corresponds to the composition of a mixture of hydrogrossularite and periclase in a molecular ratio of nearly 1:3.

Talc: In the ratio of talc:$CaCO_3$:NH_4Cl=1:0∼6:8, the formation of the minerals such as enstatite, diopside, monticellite, spurrite and merwinite ($Ca_3MgSi_2O_8$) was observed. Enstatite was only formed in the case without $CaCO_3$, hence it is appropriately inferred that enstatite is a firing product of talc itself.[2] The formation of monticellite was clearly confirmed in the range of $CaCO_3$:2∼6, and 600∼1000° C. When a product, which was obtained at 800° C. from a mixture having the ratio of talc:$CaCO_3$:NH_4Cl=1:4:8, was fused at 1100° C. for 3 hours, it was transformed into a mixture of åkermanite ($Ca_2(Mg, Si_2)O_7$) and monticellite.

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strongly suggested that, in the present material, Ca is considered in place of Na, and CO_3 or Cl are considered in place of SO_4.

[2] Although the numbers and sharpness of the powder reflections are not sufficient for the identification of the polytype of this material, the relative intensities of the strong reflections are closer to enstatite rather than proto-enstatite as described by Smith (1959).

TABLE 2. EXPERIMENTAL DATA FOR THE CHEMICAL REACTIONS AMONG CLAY MINERALS, AMMONIUM CHLORIDE AND CALCIUM CARBONATE

Exp. No.	Illite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
1/8~9	1	0	8	920~960° C.	Il
1/10	1	1	2	900	Um+An
1/11	1	1	6	900	An
1/16	1	2	4	900	Um+Ca+Hg
1/17	1	2	8	1000	An
1/18	1	3	6	900	Ca+Hg+Um
1/19	1	3	6	1000	Ca+Hg+An
1/20~21	1	4	8	900~1000	Ca+Hg
1/1~2	1	5	10	400~500	Il+$CaCO_3$
1/3	1	5	10	600	Il+Hg+$CaCO_3$
1/4~5	1	5	10	700~800	Il+Hg+Ca
1/6~7	1	5	10	900~1000	Hg+Ca

Exp. No.	Pyrophyllite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
2/1	1	5	10	400° C.	Py+$CaCO_3$
2/2	1	5	10	500	Py
2/3~5	1	5	10	600~800	Pw+Ha+Hg
2/6	1	5	10	900	Pw+Hg
2/7	1	5	10	1000	Pw+Hg+Um
2/8~11	1	4	0	500~830	Py+$CaCO_3$
2/12	1	4	0	1000	Ge+Pw

Exp. No.	Montmorillonite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
3/1	1	4	8	400° C.	Mm+$CaCO_3$
3/2	1	4	8	500	Hg+Pw
3/3~7	1	4	8	600~1000	Hg+Pw+Wo
12/8~10	1	4	0	500~680	Mm+$CaCO_3$
12/11	1	4	0	860	Ge+CaO
12/12	1	4	0	1000	Ge+Um

Exp. No.	Vermiculite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
4/1	1	4	8	400° C.	Vm+$CaCO_3$
4/2	1	4	8	500	Hg+$CaCO_3$
4/3~7	1	4	8	600~1000	Hg+Pe+Mc

Exp. No.	Leuchtenbergite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
5/1~2	1	5	10	400~500° C.	Le+$CaCO_3$
5/3	1	5	10	600	Le+Hg+Pe+$CaCO_3$
5/4~6	1	5	10	700~900	Hg+Pe
5/7	1	5	10	1000	Hg+Pe+Fo+La
5/16	1	3	6	800	Hg+Fo+Pe
5/17~18	1	4	0	520~600	Le+$CaCO_3$
5/19	1	4	0	700	Le+Ca+$CaCO_3$
5/20	1	4	0	900	CaO+En+Pe+$CaCO_3$

Abbreviation: An: Anorthite, At: Antigorite, Ca: Cancrinite(?), Di: Diopside, En: Enstatite, Fo: Forsterite, Ge: Gehlenite, Ha: Haüyne, Hg: Hydrogrossularite, Hh: Hydrated halloysite, Il: Illite, Ka: Kaolinite, La: Larnite, Le: Leuchtenbergite, Mc: Monticellite, Me: Merwinite, Mm: Montmorillonite, Pe: Periclase, Pw: Pseudowollastonite, Py: Pyrophyllite, Sp: Spurrite, Ta: Talc, Um: Undetermined mineral, Vm: Vermiculite, Wo: Wollastonite, amorph. subst.: Amorphous substance.

TABLE 2—(*continued*)

Exp. No.	Leuchten-bergite	$CaCl_2 \cdot 2H_2O$	NH_4Cl	Temperature	Reaction Products
5/11~12	1	4	0	420~500° C.	Le
5/13	1	4	0	670	Le+Fo+Hg+Pe
5/14~15	1	4	0	850~1000	Hg+Fo+Pe+Mc
5/9	1	3	0	800	Fo+Ha

Exp. No.	Talc	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
6/8~12	1	0	8	400~800° C.	Ta
6/13	1	0	8	870	Ta+En
6/14~15	1	0	8	900~1000	En
6/16~18	1	1	8	400~620	Ta+$CaCO_3$
6/19~20	1	1	8	710~800	Ta+Di
6/21~22	1	1	8	900~1000	Di
6/23~24	1	2	8	400~500	Ta+$CaCO_3$
6/25	1	2	8	600	Ta
6/26~29	1	2	8	700~1000	Mc+Di
6/30~31	1	3	8	410~520	Ta+$CaCO_3$
6/32	1	3	8	610	Ta
6/33~36	1	3	8	720~1000	Mc+Di+Sp
6/1~2	1	4	8	400~500	Ta+$CaCO_3$
6/3	1	4	8	640	Ta+Mc+Sp
6/4~7	1	4	8	700~1000	Mc+Di+Sp
6/37~38	1	5	8	410~520	Ta+$CaCO_3$
6/39	1	5	8	640	Ta+Mc+$CaCo_3$
6/40~41	1	5	8	700~800	Mc+Sp
6/42~43	1	5	8	900~1000	Mc+Um
6/44~46	1	6	8	400~600	Ta+$CaCO_3$
6/47~48	1	6	8	700~800	Mc+Sp
6/49~50	1	6	8	900~1000	Mc+Um
6/52~54	1	0	0	600~800	Ta
6/55~56, 75	1	0	0	850~1000	En
6/57~58	1	2	0	600~700	Ta+$CaCO_3$
6/59	1	2	0	800	Ta+Me
6/60~61	1	2	0	900~1000	En+Me
6/62~66	1	4	0	400~770	Ta+$CaCO_3$
6/67, 72	1	4~6	0	800	Ta+Me
6/68~69	1	4	0	900~1000	Mc+Me
6/70~71	1	6	0	600~700	Ta+$CaCO_3$
6/73~74	1	6	0	900~1000	Me+Pe+La

Exp. No.	Antigorite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
7/1~2	1	4	8	380~450° C.	At+$CaCO_3$
7/3~6	1	4	8	500~800	Mc+Fo+Pe
7/7~8	1	4	8	900~1030	Mc+Pe
7/9	1	4	0	570	At+$CaCO_3$
7/10	1	4	0	650	At+$CaCO_3$+CaO
7/11	1	4	0	750	CaO+Fo
7/12	1	4	0	980	CaO+Fo+Pe+La

(*continued on next page*)

TABLE 2—(*continued*)

Exp. No.	Kaolinite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
8/1~3	1	4	8	380~400° C.	Ka+$CaCO_3$
8/4	1	4	8	500	Ha+(Hg)+($CaCO_3$)
8/5	1	4	8	600	Ha+Hg+(Ca)
8/6~7	1	4	8	700~800	Ha+Hg+Ca
8/8	1	4	8	930	Hg+Ca
8/9~10	1	4	8	1000~1050	Hg+La
8/22	1	3	8	490	$CaCO_3$
8/23	1	3	8	530	$CaCO_3+CaCl_2\cdot nH_2O$?
8/24~25	1	3	8	600~650	amorph. subst.
8/26	1	3	8	730	Um
8/27	1	3	8	970	Um+Ha+Ca
8/28~30	1	4	0	570~670	$CaCO_3$
8/31	1	4	0	820	CaO
8/32	1	4	0	980	CaO+Ge

Exp. No.	Hydrated halloysite	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
9/1	1	4	8	400° C.	Hh+$CaCO_3$
9/2~5	1	4	8	500~800	Hg+Ha+Ca
9/6	1	4	8	900	Hg+(Ha)+(Ca)
9/7~8	1	4	8	1060~1100	Hg+La
13/1	1	4	8	500	Hg+Ha
13/2	1	4	8	600	Ha+Ca+Um
13/3~5	1	4	8	700~900	Hg+Ca
13/6~7	1	4	0	150~370	Hh+$CaCO_3$
13/9~10	1	4	0	500~590	$CaCO_3$
13/11~12	1	4	0	750~840	CaO
13/13	1	4	0	1100	Ge+La

Exp. No.	Allophane	$CaCO_3$	NH_4Cl	Temperature	Reaction Products
10/1	1	4	8	400° C.	$CaCO_3$
10/2~3	1	4	8	500~600	Hg+Ha
10/4	1	4	8	700	Hg
10/5~7	1	4	8	800~1000	Hg+La
10/8~10	1	4	0	150~370	$CaCO_3$
10/11~13	1	4	0	500~830	CaO+Ge
10/14~15	1	4	0	950~1100	La+Ge

Antigorite: In the ratio of antigorite:$CaCO_3$:NH_4Cl=1:4:8, the formation of forsterite, monticellite and periclase was observed. The reflections of forsterite became just visible at 800° C., and at higher temperatures, both monticellite and periclase remained (Table 5). The chemical composition of the residue obtained at 800° C. is shown in Table 4c. Disregarding the very small amount of forsterite, the composition agrees well with the composition of monticellite and periclase in a molecular ratio of nearly 2:1.

Kaolinite: In the ratio of kaolinite:$CaCO_3$:NH_4Cl=1:4:8, the crystallization of such minerals as haüyne, hydrogrossularite, cancrinite-like

TABLE 3. RISE AND FALL OF REACTION PRODUCTS IN THE CHEMICAL REACTIONS AMONG CLAY MINERALS, AMMONIUM CHLORIDE AND CALCIUM CARBONATE

Starting materials	Products	500° C.	600° C.	700° C.	800° C.	900° C.	1000° C.
Illite (1:5:10)	Cancrinite(?)				·	++	+++
	Hydrogrossularite		+	++	+++	+++	+++
Pyrophyllite (1:5:10)	Pseudowollastonite		+	++	+++	++	+
	Haüyne		++	+	·		
	Hydrogrossularite		+	++	+++	+++	+++
Montmorillonite (1:4:8)	Wollastonite		·	·	·	·	·
	Pseudowollastonite	+	++	++	++	+++	+++
	Hydrogrossularite	+	++	++	++	+++	+++
Dehydrated montmorillonite (1:4:8)	Cancrinite(?)	++					
	Pseudowollastonite		+	+	++	+++	+++
	Hydrogrossularite		+	+	++	+++	+++
Vermiculite (1:4:8)	Periclase		·	·	·	·	·
	Monticellite		·	+	+	+	+
	Hydrogrossularite	+	++	+++	+++	+++	+++
Leuchtenbergite (1:5:10)	Periclase		·	++	++	++	+++
	Spurrite						+
	Larnite						+++
	Hydrogrossularite		·	++	+++	+++	+++
Leuchtenbergite (1:4; $CaCl_2 \cdot 2H_2O$)	Periclase			·	·	·	·
	Monticellite			·	·	+	+
	Forsterite		·	+	+	·	·
	Hydrogrossularite		+	+++	+++	+++	+++
Talc (1:4∼5:8)	Spurrite			++	++	++	+++
	Diopside			+	+	++	++
	Monticellite		+	+++	+++	+++	+++
Antigorite (1:4:8)	Periclase	·	·	+	+	++	++
	Forsterite	++	+	·	·		
	Monticellite	++	++	++	+++	+++	+++
Kaolinite (1:4:8)	Haüyne	+	+	+	·	·	
	Larnite(?)						·
	Cancrinite(?)		+	+	+	·	
	Hydrogrossularite		+	++	+++	+++	+++
Hydrated halloysite (1:4:8)	Haüyne	++	+	+	·	·	
	Larnite						+
	Cancrinite(?)	++	+	+	·	·	
	Hydrogrossularite	+	+	++	++	++	+++
Allophane (1:4:8)	Haüyne	+	+	·			
	Larnite			·	+	+	+
	Hydrogrossularite	+	++	+++	+++	+++	+++

The ratio means the relative proportion of clay mineral against the reagents such as calcium carbonate and ammonium chloride. For example, 1:5:10 = clay mineral: $CaCO_3$:NH_4Cl. Estimation of relative amounts is shown with notations, ·, +, ++, +++, in increasing order.

mineral and larnite was observed. The weak reflections of haüyne gradually declined at 600∼700° C., thereafter the reflections of hydrogrossularite were enhanced.

The relative amount of $CaCO_3$ has an effect upon the kinds of reaction products. For example, in the case of the ratio of kaolinite: $CaCO_3$: NH_4Cl = 1:3:8, at 600° and 650° C., the firing product is composed principally of amorphous material which is probably metakaolin.

TABLE 4. CHEMICAL COMPOSITIONS OF THE RESIDUE OBTAINED IN THE CHEMICAL REACTIONS OF CLAY MINERALS, AMMONIUM CHLORIDE AND CALCIUM CARBONATE

	(a)	(b)		(c)	
SiO_2	32.33%	24.37%	0.4058	31.66%	0.5271
TiO_2	—	0.05		tr.	
Al_2O_3	26.89	17.32	0.1699	0.37	
Fe_2O_3	—	0.98		2.33	
FeO	—	0.24		—	
CaO	34.31	29.22	0.5210	29.71	0.5298
MgO	0.82	21.66	0.5372	30.89	0.7661
Na_2O	0.80	0.35		1.15	
K_2O	0.75	0.19		0.40	
$H_2O(+)$	3.38	5.77	0.3195	3.00	
$H_2O(-)$	0.38	0.13		0.45	
P_2O_5	—	0.16		0.03	
Total	99.66%	100.44%		99.99%	

(a) Illite: $CaCO_3$: NH_4Cl = 1:4:8; temperature, 900° C. *X*-ray diffraction data showed that the residue is composed of hydrogrossularite and a cancrinite-like mineral.

(b) Leuchtenbergite: $CaCO_3$: NH_4Cl = 1:5:10; temperature, 900° C. *X*-ray reflections showed that the residue is composed of hydrogrossularite and periclase. The molecular ratio of the principal composition is given as,

$$3{,}2MgO \text{ (periclase)} + 3.1CaO \cdot Al_2O_3 \cdot 2 \cdot 4SiO_2 \cdot 1.9H_2O \text{ (hydrogrossularite)}.$$

(c) Antigorite: $CaCO_3$: NH_4Cl = 1:4:8; temperature, 800° C. *X*-ray reflections showed that the residue is composed of monticellite and periclase; the reflections of forsterite are just visible. The molecular ratio of the principal composition can be approximately given as, 1.0MgO (periclase) + $2.0CaMgSiO_4$ (monticellite).

Hydrated halloysite: In the ratio of hydrated halloysite: $CaCO_3$: NH_4Cl = 1:4:8, a result similar to that in the case of kaolinite was obtained. The formation of hydrogrossularite, cancrinite-like mineral, larnite, and haüyne was observed. The reflections of larnite are observed only at about 1000° C.

Allophane: In the ratio of allophane: $CaCO_3$: NH_4Cl = 1:4:8, the crystallization of such minerals as hydrogrossularite, larnite and haüyne was noticed.

DISCUSSION

(I) When the starting materials were heated with calcium carbonate only, the reaction temperatures clearly rose higher than those under the condition when both ammonium chloride and calcium carbonate were used. The kinds of reaction products tended to differ; the formation of gehlenite was noticed from clay minerals rich in aluminum. In the case

Table 5. *X*-Ray Powder Diffraction Data for the Residue Obtained Under the Condition That Antigorite:$CaCO_3$:NH_4Cl=1:4:8, Heated at 800° C. for One Hour (CuKα)

d(Å)	I		d(Å)	I	
5.57	15	Mc.	2.22	15	Mc.
4.21	30	Mc.	2.108	40	Pe.
3.90	10	Fo.	2.109	5	Mc.
3.86	20	Mc.	1.918	15	Mc.
3.65	80	Mc.	1.819	70	Mc.
3.20	35	Mc.	1.778	10	Mc.
3.18	20	Mc.	1.752	15	Mc., Fo.
3.04	10	Mc.	1.722	20	Mc.
2.94	50	Mc.	1.704	10	Mc.
2.88	5		1.685	10	Mc.
2.77	15	Mc., Fo.	1.596	30	Mc.
2.72	20	Mc.	1.583	10	Mc.
2.67	100	Mc.	1.544	10	Mc.
2.59	75	Mc.	1.503	15	Mc.
2.54	35	Mc., Fo.	1.491	20	Pe.
2.48	15	Mc., Fo.	1.453	5	Mc.
2.44	5		1.425	5	Mc.
2.40	45	Mc.	1.390	5	Mc.
2.36	15	Mc.	1.383	5	Mc.
2.28	5	Fo.	1.360	5	Mc.

Mc.: Monticellite, Fo.: Forsterite, Pe.: Periclase

of clay minerals rich in magnesium, no remarkable difference was noticed with respect to the kinds of reaction products, but usually their crystallization temperatures increased over that in the case in which both ammonium chloride and calcium carbonate were used (Table 2).

When the starting materials were heated with calcium chloride alone, instead of both ammonium chloride and calcium carbonate, no remarkable difference was noticed with respect to the crystallization temperatures and the kinds of the principal reaction products. For example, in the case of the ratio of leuchtenbergite:$CaCl_2$:$2H_2O$=1:3$\sim$4, the crystallization of the minerals such as forsterite, haüyne, hydrogrossularite, periclase and monticellite was noticed in the range of 700–1000° C. (Table 2, 3).

Also, when dehydrated clay minerals were used as starting materials, no remarkable difference was seen. For example, when montmorillonite was heated at 700° C. for three hours, air quenched, and then heated with calcium carbonate and ammonium chloride in the ratio of firing montmorillonite:$CaCO_3$:NH_4Cl=1:4:8, the formation of hydrogrossu-

TABLE 6. *X*-RAY POWDER DIFFRACTION DATA FOR HYDROGROSSULARITE (CuKα).

	(a)		(b)	
hkl	d(Å)	I	d(Å)	I
211	4.96	20		
311	3.65	5		
321	3.23	10		
400	3.03	50	2.98	40
420	2.71	100	2.67	100
322	2.58	10	2.54	10
422	2.47	40	2.43	20
510, 431	2.37	10	2.33	15
521	2.21	15	2.17	15
440	2.10	5	2.103	5
611, 532	1.961	10	1.929	20
444	1.743	10	1.716	15
710, 550, 543	1.710	5		
640	1.675	25	1.649	20
642	1.613	25	1.588	35
800	1.512	5	1.486	10

(a) The experimental condition: Leuchtenbergite:$CaCO_3$:NH_4Cl = 1:5:10, temperature, 900° C. Periclase was dissolved completely by boiling with water for four hours.

(b) Hydrogrossularite from Rodin River, New Zealand.

larite and pseudowollastonite was observed in the range of 600–1000° C. (Table 3).

The results of the experiments stated above strongly suggest the following; (a) Ammonium chloride played an important role in promoting the chemical reactions by lowering the reaction temperatures and giving rise to a specific assemblage of reaction products. (b) Chemical agencies of the present chemical reactions are due to the volatile component such as ammonium chloride. It is strongly suggested that the chemical reactions were particularly promoted by the reaction between clay minerals and calcium chloride,[3] which was produced by reaction of chlorine gas upon calcium carbonate. (c) Water molecules in clay minerals are not a requisite condition for the formation of hydrogrossularite.

(II) It is worthy of notice that hydrogrossularite is one of the principal reaction products. Although we could not obtain a reaction product consisting of hydrogrossularite only, it was easy to identify it in *x*-ray powder reflections of a sample composed largely of hydrogrossularite

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[3] The extent of the duplication of these reactions by use of $CaCl_2$ is observed clearly in the kinds of the principal reaction products. The kinds of minor products have not been duplicated by use of $CaCl_2$ only.

TABLE 7. *X*-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC AND NATURAL HYDROGROSSULARITE HEATED AT 700° C. AND 1100° C. RESPECTIVELY, AND THOSE OF NATURAL GROSSULARITE (CuKα)

	(a)		(b)		(c)	
hkl	d(Å)	I	d(Å)	I	d(Å)	I
400	2.97	40	2.97	50	2.96	8
420	2.66	100	2.66	100	2.65	10
322	2.54	10	2.54	10	2.53	2
422	2.43	20	2.42	20	2.41	6
431, 510	2.33	20	2.33	15	2.33	5
521	2.171	20	2.168	10	2.16	6
440	2.101	5	2.103	5	2.10	1.5
532, 611	1.929	25	1.926	20	1.92	7
444	1.716	15	1.714	10	1.71	6
640	1.647	20	1.647	15	1.65	8
			1.642	10		
642	1.589	35	1.585	25	1.58	9
800	1.485	10	1.484	10	1.485	5

(a) Natural hydrogrossularite heated at 700° C. Rodin River.
(b) Synthetic hydrogrossularite heated at 1100° C. (Exp. No. 5/6).
(c) Natural grossularite (Yoder, 1952).

(Table 6). The reaction product obtained from leuchtenbergite (leuchtenbergite:$CaCO_3$:NH_4Cl = 1:5:10, temperature 900° C.) was a favorable sample in which to identify hydrogrossularite. The *x*-ray powder reflections are composed of those of hydrogrossularite and periclase. From these reflections, the reflections attributed to garnet structure can be selected (Table 6), which well agree with those of natural hydrogrossularite from Rodin River. The spacings are slightly larger than those of grossularite and an $a = 12.07$ Å was obtained, which indicated that the chemical composition is closest to $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The chemical composition of the residue is shown in Table 4b. The molecular ratio of the principal compositions can be written as $3.1CaO \cdot Al_2O_3 \cdot 2.4SiO_2 \cdot 1.9H_2O + 3.2MgO$, which agrees with the composition of a mixture of hydrogrossularite and periclase in a molecular ratio of nearly 1:3. Further it was noticed that the spacings of powder reflections come to agreement with those of natural grossularite when the sample was heated at 1100° C. for three hours (Table 7).

In these experiments, hydrogrossularite was most widely produced, but the *a*-spacing is not necessarily unique, being slightly variable. The variations are due to slightly modified ratios of silica to water.

(III) In the present chemical reactions, some components evaporate during the heating, and the alkalies are dissolved in water. Hence, it is difficult to write chemical equations explicitly. However, in the case of clay minerals of relatively simple chemical compositions, equations may be written as follows:

(a) The residue obtained from the mixture of pyrophyllite:$CaCO_3$:NH_4Cl=1:5:10, heated at 900° C., is shown to be composed of hydrogrossularite and pseudowollastonite by *x*-ray investigation.

$$Al_2Si_4O_{10}(OH)_2+5CaCO_3+10NH_4Cl\rightarrow Ca_3Al_2Si_2O_{10}\cdot 2H_2O+2CaSiO_3$$

(b) The following equation may be given for the chemical reaction under the condition of leuchtenbergite:$CaCO_3$:NH_4Cl=1:3:6, at 800° C.:

$$Mg_5Al_2Si_3O_{10}(OH)_8+3CaCO_3+6NH_4Cl\rightarrow Ca_3Al_2Si_2O_{10}\cdot 2H_2O \\ \cdot 2H_2O+Mg_2SiO_4+3MgO.$$

The chemical reaction under the condition of leuchtenbergite:$CaCO_3$:NH_4Cl=1:5:10, at 900° C., may be expressed as follows:

$$3Mg_5Al_2Si_3O_{10}(OH)_8+15CaCO_3+30NH_4Cl\rightarrow 5Ca_3Al_2Si_2O_{10}\cdot 2H_2O \\ +15MgO.$$

(c) The residue obtained under the condition of antigorite:$CaCO_3$:NH_4Cl=1:4:8, heated at 800° C., is composed of periclase and monticellite, accompanied by a very small amount of forsterite. Disregarding the formation of forsterite, the following equation would be established:

$$Mg_3Si_2O_5(OH)_4+4CaCO_3+8NH_4Cl\rightarrow 2CaMgSiO_4 \\ +MgO+2CaCl_2 \text{ (soluble).}$$

(IV) The chemical reactions occurring in the process of Smith's method for alkali are very interesting as they indicate the crystallization of various kinds of reaction products, most of which are found as the skarn minerals in nature. Referring to the general problem of individuality of minerals, it can be anticipated that the present reaction products really have slight modifications from natural minerals because of differences in the environments, particularly in pressure. The author could not confirm these modified properties in the present situation because of the difficulty in obtaining macroscopic single crystals; this will be attempted in the future under conditions of higher pressures.

Although it is premature to state that the experimental conditions are those to be formed in natural skarnization, the present experiments may indicate that a volatile component plays an important role in chemical reactions of silicates, particularly in the formation of hydrogrossularite and monticellite.

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