CLAY MINERALS IN THE MIOCENE LOW-GRAD
METAMORPHIC ROCKS, TANZAWA MOUNTAINS,
KANAGAWA PREFECTURE,
CENTRAL JAPAN

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INTRODUCTION

Early Miocene basic pyroclastic rocks
are widely distributed in the Tanzawa
Mountains, about 70 km west of Tokyo, central Japan (Fig. 1). These pyroclastic
rocks (roughly 10,000 meters in total thick-
ness) suffered low-grade metamorphism of
regional scale ranging from the zeolite facies
to the amphibolite facies (Seki et al., 1969;
Shimazu et al., 1971). As the result, various
kinds of clay minerals occur associated with
zeolites, prehnite, pumpellyite and epidote
in the low-grade metamorphosed rocks.

For the last few years, the present
writer has been conducting a mineralogical
study of various kinds of clay minerals
found in the Miocene pyroclastic sediments
(Green Tuff) in Japan. The purpose of the
present paper is to describe some mineralologi-
cal data of clay minerals in the Tanzawa
Mountains and to discuss their origin and
petrological significance.

GEOLOGICAL SETTING

The geology of the Tanzawa Mountains
has been surveyed in detail by many investi-
gators (Mikami, 1962; Ishihara, 1964; Shi-

Fig. 1 Geologic map in the eastern part of
the Tanzawa Mountains (Shimazu et
al., 1971).

Susugaya subgroup
1: Ochiai conglomerate.
2: Teraya sandstone with mudstone.
3: Osawa dacitic tuff.
4: Fudojiri dacitic lapilli tuff.

Oyama subgroup
5: Karasawa basaltic tuff.
6: Fukawa basaltic breccia.
7: Yakeyama basaltic breccia.
8: Hondani basaltic tuff.
9: Shiomizu basaltic breccia.
10: Otaki basaltic tuff.

Togatake subgroup
11: Shizunhasse basaltic tuff.
12: Ogusadaira dacitic tuff.
13: Yodorigi basaltic breccia.
14: Kamagi basaltic breccia.

Intrusive rocks
15: Gabbro.
16: Quartz diorite.

(Manuscript received, May 31, 1973)
mazu et al., 1971). According to Mikami (1962), Neogene Tertiary strata in the eastern part of the Mountains are divided into two groups; Aikawa group and Tanzawa group. Shimazu et al. (1971) who studied the geology and petrology of the Tanzawa group in the eastern part of the Tanzawa Mountains reported the stratigraphical succession of this district as follows (Fig. 1):

**Aikawa group:**

* Tanzawa group:
  - Susugaya subgroup: [Hayato F., Osawa F., Karasawagawa F., Hontanigawa F.]
  - Oyama subgroup: [Hontanigawa F.]
  - Togatake subgroup: [Shizuhasse F., Yodorigizawa F.]

It is noteworthy that the Tanzawa group from upper horizon to lower one is characterized by an enormous amount of basaltic pyroclastic rocks.

The Tanzawa group outcropping along R. Hayato in the eastern part of the Tanzawa Mountains has generally strike of NNW-SSE and dips about 70°ENE. It forms a monoclinal structure in this district whereas in the north of R. Hayato it forms an overturned structure. The total thickness of the group exposed along R. Hayato attains to about 10,000 m. The Tertiary quartz diorite mass intrudes into the group in the central part of the Tanzawa Mountains. The pyroclastic rocks surrounding the diorite mass are altered to green rocks characterized by the presence of calcic amphibole.

**METHOD OF STUDY**

About seventy rock samples were collected from the Tanzawa group along R. Hayato in the eastern part of the Tanzawa Mountains. The mode of occurrence of alteration products was studied in thin sections under the microscope. Microcrystalline minerals such as zeolites were detected by X-ray diffraction method. Furthermore, clay minerals were studied in detail by the following method: The rock sample is crushed into fine powder in a stainless mortar, and conglomerate, andesitic pyroclastic rocks dispersed in distilled water. After settling for 8 hours, clay fractions less than 2 microns are collected from the dispersed-system and are concentrated by a centrifuge. A few drops of the concentrated fractions are smeared on the glass slide and dried in room air for X-ray analysis. The other fractions are also dried in room air for chemical, X-ray and differential thermal analyses.

**GENERAL DESCRIPTION OF METAMORPHISM**

Metamorphosed rocks in this district can be divided into the following seven zones, on the basis of the stability relation of some critical alteration products (Shimazu et al., 1971):

- **Zone I**: mordenite-stilbite-heulandite-montmorillonite
- **Zone IIa**: laumontite-saponite
- **Zone IIb**: laumontite-prehnite-pumppellyte-chlorite/montmorillonite mixed-layer
Fig. 2 Stability ranges of alteration products in the eastern part of the Tanzawa Mountains (Shimazu et al., 1971).

Fig. 3 The distribution of metamorphic zones in the eastern part of the Tanzawa Mountains (Shimazu et al., 1971).

Zone IIIa: prehnite-pumpellyite-chlorite
Zone IIIb: prehnite-pumpellyite-epidote-chlorite
Zone IV: epidote-actinolite-chlorite
Zone V: biotite-hornblende

These metamorphic zones are distributed surrounding the Tanzawa quartz diorite mass. Wairakite occurs locally in Zone IIIa and Zone IIIb. The mineral assemblages are summarized in Fig. 2 and the zonal distribution map of the metamorphic zones in the eastern part of the Mountains is shown in Fig. 3. Roughly speaking, calcium zeolites appear in the lowest grade zone while calciferous amphiboles appear in the highest one. Prehnite and pumpellyite are found in the intermediate grade zone. On the other hand, ferromagnesian clay minerals occur ranging from the lowest grade zone to the higher one.

**MINERALOGY OF ALTERATION PRODUCTS**

The modes of occurrence and mineralogical properties of alteration products in the Tanzawa group exposed along R. Hayato are described in this section.

1) Zeolites

As given in Fig. 4, heulandite and stilbite occur in the uppermost horizon (Susugaya subgroup) of the Tanzawa group (heulandite-stilbite zone). Heulandite occurs in aggregate of tabular crystals with distinct cleavage, replacing glass shards or filling cavities. Stilbite associated with iron-rich saponite or montmorillonite also occurs replacing glass shards. Analcime is found in the middle to lower part of the heulandite-stilbite zone, filling cavities. Laumontite appears as a stable zeolite in the lower part of the Osawa formation to the upper part of the Karasawagawa formation (laumontite zone), in which neither heulandite nor stilbite occur. Laumontite replaces plagioclases and volcanic glass shards, and sometimes fills interstitial spaces of pyroclastic rocks in close association with interstratified chlorite-saponite. Wairakite is found in a limited area in the uppermost member of the Hontanigawa formation. It fills cavities in association with prehnite, pumpellyite and epidote.
(3) Clay minerals

Various kinds of clay minerals, such as montmorillonite, iron-rich saponite, interstratified chlorite-saponite and chlorite, occur commonly in the low-grade metamorphic rocks of the Tanzawa Mountains. Mineralogical properties of these clay minerals have been briefly described by Seki et al. (1969) and Shimazu et al. (1971), but no detailed description of these minerals based on the field evidence is found in these papers. The present writer describes in detail some mineralogical properties of these clay minerals found in this district.

(A) Montmorillonite and iron-rich saponite

Montmorillonite and iron-rich saponite were confirmed in the following way: The 15 Å reflection of these minerals expands to 17 Å and 18 Å ones after treatments with ethylene glycol and glycerol respectively. After boiled with 1N ammonium nitrate or potassium chloride solution, the 15 Å peak is replaced by a 12.5 Å one. After heating at 300°C for one hour, it contracts to 10 Å. Montmorillonite and iron-rich saponite as smectite group show the same behaviour in thermal and chemical treatments. However, since saponite has a trioctahedral structure whereas montmorillonite has a dioctahedral one, we can distinguish the former from the latter by the value of $b_0$ parameter obtained from the (060) spacing in X-ray powder pattern.

Montmorillonite is found only in the Teraya sandstone with mudstone member, lower part of the Hayato formation. It occurs as an aggregate of micro-fibroid crystals filling interstitial spaces or replacing glass shards associated with chlorite (probably detrital) and heulandite. The (060)
spacing at 1.50 \text{"Å"} gives clearly a dioctahedral structure.

\textit{Iron-rich saponite} with 1.53 \text{"Å"} of (060) spacing is widely observed in upper horizon of the Tanzawa group. It occurs as interstitial-film and aggregate of microcrystals replacing glass shards associated with heulandite, stilbite and analcime. Differential thermal analysis (DTA) curves of the iron-rich saponite (H-1 and H-2) in the upper member of the Hayato formation are quite similar to that of a dioctahedral montmorillonite (H-7) in the upper member of the Hayato formation (Fig. 5). A broad endothermic peak at about 500\text{"°C"}, which may be due to the interleaved brucite (Mackenzie, 1957), is recognized in these specimens.

Fig. 5 DTA curves of trioctahedral iron-rich saponites (H-1 and H-2) and dioctahedral montmorillonite (H-7) in the Hayato formation.

Fig. 6 DTA curves of iron-rich saponites associated with heulandite and stilbite in the Osawa formation.

Fig. 7 X-ray diffraction patterns of an interstratified chlorite-saponite (H-27) associated with laumontite before and after various treatments.

U.T.: untreated, 300\text{"°C"}, 450\text{"°C"}, 600\text{"°C"}, 800\text{"°C"}: heated at each temperature for one hour, \text{NH}_4\text{NO}_3: treated with ammonium nitrate, E.G.: treated with ethylene glycol.
Table 1 Chemical compositions of clay minerals in the Tanzawa group.

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Total (%) 100.59 101.00 101.05 100.76 99.52

H-9: iron-rich saponite (Analyst: K. Kimbara)
H-28: chlorite (Ib+IIb) associated with interstratified chlorite-saponite (Analyst: K. Kimbara)
H-43: interstratified chlorite-saponite associated with a small amount of chlorite (I Ib) (Analyst: K. Kimbara)
H-45: interstratified chlorite-saponite (Analyst: K. Kimbara)
H-47: chlorite (Ib) associated with a small amount of interstratified chlorite-saponite (Analyst: K. Kimbara)

It is a noteworthy fact that specimens H-1 and H-2 show a weak endothermic reaction at about 700°C as in the case of dioctahedral montmorillonite. This reaction may be attributed to dehydroxylation of silicate layer. Thus the iron-rich saponites (H-1 and H-2) are very similar to dioctahedral montmorillonite in regard to DTA curve. Judging from the field evidence and microscopic observation, they are considered to have been formed from basic glass at an earlier stage of diagenesis.

On the other hand, DTA curves of other iron-rich saponites (H-15, H-16, H-18 and H-20) do not give an endothermic peak at about 700°C (Fig. 6). This result reveals that these iron-rich saponites are close to normal trioctahedral montmorillonite (saponite) in regard to DTA curve.

An iron-rich saponite (H-9) occurring in dacitic tuff breccia from the uppermost member of the Osawa formation belongs to a group of the normal trioctahedral montmorillonite (saponite) in regard to DTA curve. Chemical composition of the specimen is given in Table 1. It is characterized by considerably large amounts of iron, magnesium and aluminum. The structural formula can be calculated on the basis of O₁₀(OH)₂ as follows:

\[
\begin{align*}
&\left[\text{Si}_{0.072}\text{Al}_{0.928}\right] / \left[\text{Al}_{0.174}\text{Fe}^{3+0.879}\text{Fe}^{2+0.942}\text{Mn}_{0.002}\right] \\
&\times 4.000 \\
&= 2.487
\end{align*}
\]

\[
\text{M}_{\text{51.097}}\left[\text{Ca}_{0.354}\text{Na}_{0.218}\text{K}_{0.070}\text{O}_{10}(\text{OH})_{2}\cdot\text{nH}_2\text{O}\right] \\
= 0.981
\]

The total number of octahedral cations clearly shows deficiency. When all ferric iron converts into ferrous one, the structural formula can be recalculated as follows:

\[
\begin{align*}
&\left[\text{Si}_{0.111}\text{Al}_{0.889}\right] / \left[\text{Al}_{0.345}\text{Fe}^{2+1.241}\text{Mn}_{0.033}\text{Mg}_{0.142}\right] \\
&\times 4.000 \\
&= 2.751
\end{align*}
\]

\[
\left[\text{Ca}_{0.348}\text{Na}_{0.312}\text{K}_{0.073}\text{O}_{10}(\text{OH})_{2}\cdot\text{nH}_2\text{O}\right] \\
= 0.981
\]

Although the total number of octahedral cations becomes close to ideal one 3, the deficiency still remains. X-ray powder diffraction data of iron-rich saponites (H-9 and H-38) are given in Table 2.

(B) Interstratified mineral of chlorite and saponite

As shown in Fig. 4, regularly interstratified mineral of chlorite and saponite appears extensively ranging from the laumontite zone to upper part of the prehnite-pumpellyte zone in the Karasawagawa formation. In the laumontite zone, the interstratified chlorite-saponite occurs replacing glass shards and filling interstitial spaces as cement of the pyroclastic rocks. These interstratified minerals are associated with
chlorite having Ib (β=90°) and/or IIb (β=97°) structure. The interstratified chlorite-saponite also occurs in the upper part of the prehnite-pumpellyite zone, replacing glass shards and/or filling interstitial spaces or cavities of the pyroclastic rocks. These interstratified minerals are associated with chlorite having IIb (β=97°) polytype structure.

X-ray powder diffraction data of an interstratified mineral (H-27), which is associated with laumontite and a small amount of chlorite, are given in Table 2. X-ray diffraction patterns and the basal spacings before and after various treatments are given in Fig. 7 and Table 3 respectively. X-ray diffraction data of an interstratified mineral (H-45) associated with prehnite are given in Tables 2, 4 and Fig. 8. These two specimens (H-27 and H-45) having quite similar mineralogical properties are clearly identified as regularly interstratified mineral of chlorite and saponite. Chemical composition of the specimen H-45 is given in Table 1. From the chemical composition, the following structural formula was calculated on the basis of O_{20} (OH)_{10} equivalents:

\[
\text{Mg}_{1.376}(\text{Ca}_{0.633}\text{Na}_{0.400}\text{K}_{0.006})\text{O}_{20}(\text{OH})_{10}\cdot n\text{H}_{2}\text{O}
\]


\[
\text{Table 2 X-ray powder diffraction data of clay minerals in the Tanzawa group.}
\]

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*: reflection of chlorite, **: reflection of Ib chlorite.
Table 3 Basal reflections of specimen H-27 before and after various treatments.

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Mean d(002)* 29.36 24.41 24.19 23.74 23.89 21.82 30.63 27.69

U.T.: untreated, 300°C, 450°C, 600°C, 700°C, 800°C: heated at each temperature for one hour.
E.G.: treated with ethylene glycol, NH₄NO₃: treated with ammonium nitrate.
*: calculated from the basal spacings.

Table 4 Basal reflections of specimen H-45 before and after various treatments.

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</table>

Mean d(002)* 29.36 24.28 24.15 24.16 23.94 23.02 30.95 27.38

*: The abbreviations are the same as given in Table 3.

The total number of octahedral cations in this formula shows deficiency due to oxidation of ferrous iron.

DTA curves of interstratified minerals associated with laumontite are shown in Fig. 9. DTA curves of interstratified minerals associated with prehnite and pumpellyite are shown in Figs. 10 and 11. As revealed by these figures, in the laumontite zone (Fig. 9), a broad endothermic peak due to dehydroxylation of brucite layer appears at about 500°C and a weak exothermic peak is clearly observed between 800°-900°C, whose peak shape agrees well with that of Mg-Fe chlorite. In the prehnite-pumpellyte zone (Figs. 10 and 11), on the other hand, a
Table 5 Basal spacings of chloritic clay minerals before and after various treatments.

<table>
<thead>
<tr>
<th>H-32</th>
<th>U.T.</th>
<th>300°C</th>
<th>450°C</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
<th>NH₄NO₃</th>
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<td>d(Å)</td>
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<th>600°C</th>
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</table>

<table>
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<th>H-52</th>
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<th>450°C</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
<th>E.G.</th>
<th>NH₄NO₃</th>
</tr>
</thead>
<tbody>
<tr>
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<td>d(Å)</td>
<td>1</td>
<td>d(Å)</td>
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<td>2.855</td>
<td>11</td>
<td>2.855</td>
<td>11</td>
</tr>
</tbody>
</table>

The abbreviations are the same as given in Table 3.

+: reflection of interstratified chlorite-saponite.

strong endothermic reaction due to dehydroxylation can be detected at 550°C, which is higher than the temperature in the laumontite zone. A distinct endothermic peak, which is followed by an exothermic peak, is recognized between 800° and 900°C in all specimens. This peak system closely resembles that of Mg-chlorite.

(C) Chlorite

Chlorite commonly appears as a stable alteration product in the prehnite-pumpellyite zone, although it is sometimes associated with interstratified chlorite-saponite in the upper part of this zone. On the other hand, chlorite found in the heulandite-stilbite zone and the laumontite zone is associated with iron-rich saponite and/or interstratified mineral.

(a) Chlorite in the heulandite-stilbite zone:

A small amount of authigenic chlorite associated with iron-rich saponite occurs in the heulandite-stilbite zone. The 14 Å peak becomes broad after thermal treatment at 450°–600°C (Fig. 12). Hence, this authigenic chlorite may be called "sedimentary chlorite" (Johns et al., 1954) or "heat-labile chlorite" (Dunoyer de Segonzac, 1970) or "clay chlorite". The mineralogical properties of the chlorite could not be confirmed.
because of its being an admixture with a large amount of iron-rich saponite. In the light of the mode of occurrence, this chlorite is assumed to have been formed from iron-rich saponite under the aggradation condition. Chlorite associated with iron-rich saponite is also found in the upper to middle member of the Karasawagawa formation, which is equal to the lower part of the laumontite zone. The thermal stability of this chlorite, however, is almost the same to that of normal chlorite (Fig. 13).

(b) Chlorite in the laumontite zone:
Chlorite associated with interstratified chlorite-saponite is commonly found in the laumontite zone. Specimen H-28 occurs as interstitial-film associated with laumontite.
in basaltic tuff breccia of the Karasawagawa formation. X-ray powder diffraction data between 35°-45° (2θ CuKα) show that this material is a mixture of Ib (β=90°) and IIb (β=97°) trioctahedral chlorites (Table 2). Basal reflection data which obtained before and after various treatments give clearly that this material is composed of two kinds of minerals, that is, chlorite and interstratified chlorite-saponite (Table 5 and Fig. 14). As given in chemical data (Table 1), specimen H-28 contains large amounts of ferrous and ferric irons (about 27%), whereas the content of aluminum is extremely low (9%) like vermiculite or saponite. It is noticeable that the contents of cations such as Ca, Na and K are relatively high like smectite. DTA curve of specimen H-28 shows three principal peaks (Fig. 15): (1) A strong endothermic peak at 90°C is followed by a weak endothermic peak at 160°C. This double endothermic peak is attributed to loss of adsorbed water. (2) A strong endothermic peak at 530°C due to dehydro-
Fig. 14 X-ray diffraction patterns of a chlorite (admixture of Ib and IIb polytypes) (H-28) associated with interstratified chlorite-saponite in the laumontite zone. The abbreviations are the same as given in Fig. 7.

Fig. 15 DTA and TG curves of a chlorite (admixture of Ib and IIb polytypes) (H-28) associated with interstratified chlorite-saponite in the laumontite zone.

Specimen H-25 as well as specimen H-28 associated with interstratified mineral occurs also in the laumontite zone. X-ray powder diffraction data (Table 2) of the specimen gives Ib (β = 90°) polytype structure according to Brown and Bailey (1962). Thus, it is noteworthy that the most

of chlorites in the laumontite zone belong to Ib (β = 90°) polytype, whereas IIb (β = 97°) polytype is rare.

(c) Chlorite in the prehnite-pumpellyite zone:

Chlorite appears as a stable alteration product in the prehnite-pumpellyite zone, although in the upper part of this zone it is still associated with interstratified chlorite-saponite (Fig. 16). As given in X-ray diffraction data (Table 2) and columnar section (Fig. 4), chlorite in this zone has IIb (β = 97°) structure in all specimens. Chemical compositions of specimens H-43 and H-47 show higher content of magnesium than those of chlorite in the laumontite zone (H-28) and iron-rich saponite in the heulandite-stilbite zone (H-9) (Table 1). This chemical data agree well with the DTA data. This fact strongly suggests that magnesium content of chlorite from the Tanzawa group increases with increasing metamorphic grade or burial depth as in the case reported by Muravjew and Salyn (1969) and Dunoyer de Segonzac (1970).

DTA curves (Fig. 17) show clearly two endothermic peaks at 550°C and 600°C. This double endothermic reaction tends to appear more clearly in strongly chloritized speci-
Fig. 16 X-ray diffraction patterns of a chlorite (Ilb polytype) (H-52) associated with a small amount of interstratified chlorite-saponite before and after various treatments. The abbreviations are the same as given in Fig. 7.

mens. However, the weakly chloritized specimens associated with interstratified chlorite-saponite show a single endothermic peak at 550°C. Judging from these results, an endothermic peak at about 550°C may be attributed to dehydroxylation of brucite layer accompanied by interstratified chlorite-saponite-like mineral, and another one at 600°C may be due to that of chlorite-like mineral.

DISCUSSION

Clay minerals such as iron-rich saponite, interstratified chlorite-saponite and chlorite occur extensively in the low-grade metamorphic rocks of the Tanzawa Mountains. In the light of some field evidences, iron-rich saponite seems to convert gradually into chlorite through interstratified mineral with increasing metamorphic grade. The crystallochemical change from saponite to chlorite, however, is not so clear.

Eckhardt (1958) has suggested that Mg-chlorite is considered to be formed from Al-montmorillonite when added with Mg as
shown by the following equation:
\[ \text{Al-montmorillonite} + 1.6 \text{MgO} \rightarrow \text{Al-saponite} + 0.8 \text{SiO}_2 \]
\[ 2\text{Al-saponite} + 3\text{MgO} + 3\text{H}_2\text{O} \rightarrow \text{corrensite} \]
\[ \text{corrensite} + 3\text{MgO} + 3\text{H}_2\text{O} \rightarrow 2\text{Mg-chlorite} \]

These mineralogical changes were confirmed by hydrothermal syntheses (Wayart and Sabatier, 1967). All chloritic minerals in the Tanzawa group are rich not only in magnesium and also in iron (Table 1). The iron-rich saponite can also be expected to have been transformed into chlorite with increasing metamorphic grade. This transformation must also be accompanied by substitution of Al for Si in the tetrahedral sites.

Iron-rich saponites (H-1 and H-2) show a weak endothermic peak at 700°C due to dehydroxylation of silicate layer (Fig. 5). The same endothermic peak is commonly observed in a dioctahedral montmorillonite (H-7). Judging from the field evidence, this “iron-rich saponites” are considered to have been formed from basic glass during an earlier stage of diagenesis. In regard to the chemical composition (Table 1), all iron-rich saponites may be called “Al-saponite” proposed by Eckhardt (1958).

In the next diagenetic stage, the iron-rich saponite begins to form an “island-like brucite” in the interlayer space. Consequently, “clay chlorite” or “sedimentary chlorite” or randomly interstratified chlorite-saponite appears in this stage. DTA curves in Fig. 6 represent this stage. A broad endothermic peak at about 500°C, which is lower than that of normal chlorite, may be due to dehydroxylation of this “incomplete” brucite layer. When the iron-rich saponite adsorbs a more “complete” brucite layer in the interlayer space, it was transformed into normal chlorite or regularly interstratified chlorite-saponite as those commonly observed in the laumontite zone (Figs. 9 and 15).

The adsorption of brucite layer becomes more complete in the prehnite-pumpellyite zone. Consequently, the endothermic reaction due to dehydroxylation in chlorites of the prehnite-pumpellyite zone occurs at higher temperatures (about 550°C) than those of chloritic minerals in the laumontite zone (Figs. 10 and 11). Finally, DTA curves show two endothermic reactions at 550° and 600°C due to the loss of hydroxyl water with advancing chloritization. As described already in this paper, the reaction at 550°C is quite similar to that of interstratified chlorite-saponite. The one at 600°C may be attributed to dehydroxylation of brucite layer of normal chlorite.

Hayes (1970) estimated the sequence of the formation of chlorite polytypes during the post-sedimentary evolution as follows:
\[ \text{Ibd} \rightarrow \text{Ib} (\beta=97°) \rightarrow \text{Ib} (\beta=90°) \rightarrow \text{IIb} (\beta=97°) \]
\[ \text{Ib} (\beta=90°) \text{chlorite converts to IIb} (\beta=97°) \text{at} 150°C. \]

Karpova (1969) has also observed the following ranks of chlorite polytypes at the post-sedimentary alteration in the Bolshoy Donbas district, USSR:
\[ \text{Fe}7\text{Alb} (\beta=97°) \rightarrow \text{Fe}14\text{Alb} (\beta=90°) \rightarrow \text{Mg-Fe}14\text{Alb} (\beta=97°) \rightarrow \text{Fe-Mg}14\text{Alb} (\beta=97°) \]

Interstratified chlorite-montmorillonite occurs in association with Ib (\(\beta=90°\)) chlorite.

In the Tanzawa Metamorphic terrain, Ib(\(\beta=90°\))chlorite associated with interstratified mineral of chlorite and saponite appears in the laumontite zone. The chlorite seems to convert to IIb (\(\beta=97°\)) chlorite in the prehnite-pumpellyite zone by the increase of metamorphic grade. This process agrees well
with above noted Karpova's data. Ib chlorite in the laumontite zone contains a larger amount of iron than that of IIb chlorite in the prehnite-pumpellyite zone. This fact supports Karpova's data (1969) that IIb chlorite is usually more magnesian than Ib chlorite, and also supports Hayes' consideration (1970) that the stabilities of chlorite polytype must be controlled more by structural details and environment of formation. However, Hayes stated that the stabilities of chlorite polytype were controlled less by compositional difference. In conclusion, chemical compositions and the stratigraphical positions of chlorite in the Tanzawa group strongly suggest that the polytype stabilities between Ib and IIb chlorites have close relations to both the chemical composition of chlorite and environment of the formation.

The paragenetic relations between clay minerals and Ca-Al silicates in the Tanzawa group are summarized as follows:

<table>
<thead>
<tr>
<th>Clay minerals</th>
<th>Ca-Al silicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>saponite</td>
<td>heulandite-stilbite-analcime</td>
</tr>
<tr>
<td>chlorite-saponite</td>
<td>laumontite</td>
</tr>
<tr>
<td>mixed-layer+chlorite (Ib)</td>
<td>prehnite-pumpellyite</td>
</tr>
<tr>
<td>chlorite (IIb)</td>
<td></td>
</tr>
</tbody>
</table>

Yoshimura (1964, 1971) reported that the stable association of laumontite and interstratified chlorite-montmorillonite is commonly recognized in the Miocene pyroclastic rocks from the Oshima-Fukushima district, Hokkaido. Afterwards, many investigators reported the similar mode of occurrence of the interstratified mineral from the Green Tuff region of Japan (Seki et al., 1969; Kimbara, 1970; Motojuku Research Group, 1970; Shimazu et al., 1971; Kimbara and Sudo, 1973). Kossovskaya (1972) reported an occurrence of laumontite associated with interstratified chlorite-mont-morillonite in cavities of basalt. The association of chlorite with laumontite was also been reported from low-grade metamorphic rocks (Coombs, 1960; Packham and Crook, 1960; Brown and Thayer, 1963; Carrigy and Mellon, 1964). Few associations of laumontite and saponite or montmorillonite, however, has been reported until recent. These data show that laumontite usually occurs in physical conditions in which interstratified chlorite-saponite and/or chlorite are stable.

Recently, the P-T stability range of laumontite was determined from the following reaction (Fig. 18) (Liou, 1971a, b, c): stilbite→laumontite+3SiO₂+3H₂O
laumontite→wairakite+2H₂O

On the other hand, the P-T stability rela-
Fig. 19 Depth-temperature diagram showing the stability range of chlorite and montmorillonite estimated from their natural occurrences.

Data sources:
Muffler and White (1969)
(1) Sportsman No 1, Salton Sea.
(1)' I.I.D. No 1, Salton Sea.
(1)'' Wilson No 1, Salton Sea.
Steiner (1968)
(2) drillhole 225, Wairakei.
Khitarov and Pugin (1966)
(3) upper limit of montmorillonite
Sigvaldason and White (1961)
(4) GS-2, Steamboat.
Sigvaldason (1962)
(5) Hveragerdi, Iceland.
(5)' Reykjavik, Iceland.
Iijima and Utada (1970)
(6) Shimoigarashi, Niigata Pref.
(6)' Obuchi, Niigata Pref.
(6)'' Yabase, Akita Pref.

tions among the chloritic clay minerals are not well known because of the lack of synthetic study of these clay minerals. However, we can tentatively estimate the P-T stability relations of these clay minerals from the data of active geothermal area such as Salton Sea (Muffler and White, 1969), Iceland (Sigvaldason, 1962), Steamboat (Sigvaldason et al., 1961), Wairakei (Steiner, 1968) and of the present-day diagenesis in geosynclinal deposits (Iijima and Utada, 1970) (Fig. 19).

According to Fig. 19, montmorillonite must disappear at about 100°C whereas chlorite begins to appear at about 140°C. Therefore, mixed-layer chlorite-montmorillonite are presumably stable between 100° and 140°C. Since in the Liou's experiments the water pressure is equal to the total pressure, natural laumontite should appear at lower temperature than 150°C (1Kb) obtained from the equilibrium reaction stilbite $\rightarrow$ laumontite+3 SiO$_2$+3 H$_2$O. In this case, it must be noted that the lower stability limit of chlorite agrees well with that of laumontite. This fact strongly suggests that the laumontite-chlorite assemblage which is commonly observed in the Miocene pyroclastic rocks (Green Tuff) of Japan must represent an equilibrium product.

ACKNOWLEDGMENTS

The writer to thank Professor T. Sudo of Tokyo University of Education for his valuable suggestions. Thanks are also due to Dr. T. Yoshimura of Niigata University and Mr. A. Tabuchi of Power Reaction and Nuclear Fuel Development Corporation, Japan for their advices on the geology of the Tanzawa group.

REFERENCES


--- (1971), Interstratified clay minerals in the Miocene pyroclastic formations from...
丹沢山地中新世変成度岩中の粘土鉱物

金原啓司

丹沢山地は新第三紀中新世に堆積した大量の玄武岩質火薬岩からなり、その層厚は 10,000 m にも達し、沸石相からふどう石・バンペリー石相をへて緑色片岩相にいたる変成作用を受けている。このうち丹沢山地東部早戸川流域に見られる丹沢層群中の粘土鉱物を検討してみたところ、埋没深層の増加に伴い粘土鉱物とその他の変成鉱物の間に次のような共生関係が認められた。

A. 鉄サポナイト（+緑泥石）
B. 緑泥石-サポナイト混合層（+緑泥石） 溶液石
C. 緑泥石-サポナイト混合層（+緑泥石） ふどう石・バンペリー石
D. 緑泥石（+緑泥石-サポナイト混合層） ふどう石・バンペリー石

A の鉄サポナイトは上部層では熱的に di, tri 型のモンモリロナイトに近く、下部では tri, 型のサポナイトになる。化学組成は Fe と Al に富む。共生する自在緑泥石の耐熱性は低く、B の混合層は長周期反射を示し、ブルーサイトの (OH) 脱水は約 500°C で起こり、これと共生する緑泥石は Mg-Fe 質で Al が少なく Ilb (β=90°) が多い。C の混合層は B とは異なり Fe-Mg 質で、(OH) 脱水は約 550°C に認められ、これに共生する緑泥石もやはり Fe-Mg 質で Iib (β=97°) である。D ではさらに緑泥石化が進み、Fe-Mg 質で (OH) 脱水は 550°C のほかに 600°C にも新しく認められる。ポリタイプは Iib (β=97°) である。以上の粘土鉱物の鉱物学的変化は、地層が深部に埋没する過程で進行していったものと考えられる。