TRANSFORMATION OF SERICITE INTO AN INTERSTRATIFIED MINERAL

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Abstract—Sericite was K-depleted with molten LiNO₃. The sample was changed into an interstratified structure in the presence of a small amount of LiNO₃ after prolonged treatment, and in the presence of a considerable amount of LiNO₃ a similar structure was formed after about 3 hr of reaction. In the case of the presence of the proper amount of NaCl, a mixed-layer structure was easily obtained by treatment for a long period of time with a considerable amount of molten LiNO₃.

The interstratified mineral had a basal spacing of 22 Å–23.3 Å which was expanded to 25 Å–27.6 Å by treatment with ethylene glycol.

INTRODUCTION

INTERSTRATIFIED minerals have been reported by many investigators, but only a few experiments concerning synthesis of interstratified minerals have been reported.

Mica weathering in soils has been attributed to a loss of K and a gain in water. Loss of K changed micas into expanded layer silicates (Jackson and Sherman, 1953). Various chemical methods of extracting interlayer K from mica in the laboratory under the condition of room pressure have been carried out with aqueous salt solutions (Barshad, 1948, 1954; Mortland, 1958; Ransell-Colom et al., 1965) and laboratory weathering of the micaceous mineral to mixtures of vermiculite and regularly and randomly interstratified mica-vermiculite was reported by Rich and Cook (1963). A large part of the interlayer K in muscovite has been extracted by treating the mineral with molten LiNO₃ at 300°C (White, 1956, 1958). The application of NaTPB to the extraction of interlayer K from micaceous minerals was initiated by Hanway (1956), De Mumbrum (1959, 1963), Scott, Hunziker and Hanway (1960), Scott and Reed (1962a, 1962b) and K depletion of micas has produced more interstratification when the particles are smaller (Scott, 1968), but formation of regularly interstratified minerals in the process of the extraction of K from micaceous minerals have not been reported. The present writers succeeded in forming an interstratified mineral from sericite using molten LiNO₃. As shown in the previous study by the writers (Tomita and Sudo, 1968a, 1968b), an interstratified structure was formed from sericite at room pressure.

EXPERIMENTAL

Starting material and methods

Sericite from Goto mine, Nagasaki Prefecture, Japan, was used as a starting material. Fractions less than 2μ were collected by the sedimentation method. The untreated < 2μ material was dried in air, and was used for experiments. The untreated sericite sample was investigated, and it was confirmed that the sericite is assigned to the 2M₁ type in polytype notation and does not contain any interstratified minerals. The X-ray powder data of the untreated sample are listed in Table 1.

Reactions of sericite with lithium nitrate and sodium chloride were carried out at 300°C. The reactions with molten LiNO₃ were carried out in porcelain crucible in an electric furnace. After the reaction the sample was washed with distilled water by filtering and excess salt was removed. The reacted sample was dried in air, and its properties were investigated by X-ray analysis, chemical analysis, infrared absorption analysis, thermal analysis and electron microscopic observation. Total lithium and potassium of the reacted sample were determined using flame photometer.
Table 1. X-ray powder data for the untreated sericite and the altered specimen. $\lambda$(CuKα) = 1.5418 Å

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(Å)</th>
<th>I</th>
<th>hkl</th>
<th>d(Å)</th>
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<td>000</td>
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</tbody>
</table>

A—untreated sericite; B—altered sericite (specimen 1368); C—treated with ethylene glycol; D—heated at 300°C for 1 hr.
* Indicates peaks of montmorillonite.
† Indicates peaks of sericites.

Reactions were followed by means of X-ray diffractometer.

RESULTS

Reaction of sericite with lithium nitrate and sodium chloride

The < 2μ sericite was treated with LiNO₃ and NaCl at 300°C. The specimens were then parallel oriented and changes in basal spacings of the regular and ethylene glycolated samples were determined by X-ray diffraction. The effect of time of reaction of 0-2 g of sericite in 2 g of LiNO₃ and 0-01 g of NaCl is shown in Fig. 1. Reaction period varied from 0-25 to 291 hr.

Specimen 1389 which is a reaction product after treatment for 15 min showed a small peak of 11 Å, and ethylene glycol caused the 11 Å reflection to shift to 17 Å. This expansion was due to the more rapid reaction of lithium nitrate with the fine fraction of the material used. A small 26 Å peak appeared by treatment with ethylene glycol. Specimen 1386 which was formed in 2 hr reaction showed a strong 11 Å peak and a weak 22 Å peak. Specimen 1368 which was formed in 75 hr reaction showed a strong 11 Å peak and a weak 22 Å peak. The specimen gave a rational series of reflections corresponding to a d(001) of 22 Å on X-ray analysis. The 291 hr reaction product (specimen 1377) showed a broad 11 Å reflection which was divided into two peaks, 26.6 Å and 17 Å, upon treatment with ethylene glycol. Decrease in intensity of the 10 Å peak and increase in intensity of the 11 Å peak with reaction time in this experiment are shown in Fig. 1.

Influence of the amount of sodium chloride on the reflections of reacted samples is shown in Fig. 2. The weight of sericite was always 0-2 g and that of LiNO₃ was 2 g, and the amount of sodium chloride varied from 0-005 g to 0-04 g. Reaction time was always 75 hr. Diffraction pattern of specimen 1378 (NaCl:0-005) shows a strong 11 Å reflection which moved to 17 Å by treatment with ethylene glycol. In the pattern of specimen 1378, a small 22 Å reflection was observed. Specimen 1368 (NaCl:0-01 g) showed a clear 22 Å reflection and a 11 Å reflection. Basal reflections at submultiples of the 22 Å spacing were observed. Intensity of the 11 Å peak is larger than that of the 10 Å peak in this specimen. The 22 Å peak expanded to a 26 Å by treatment with ethylene glycol. The (002) reflection of the 26 Å showed a broad peak which is probably due to mixing of a 17 Å and a 13 Å spacings. Specimen 1372 (NaCl:0-04 g) showed also a strong 11 Å peak and a weak 22 Å peak. When only 2 g of LiNO₃ was used, montmorillonite was formed.
This phenomenon suggests that NaCl plays an important role in restricting the expansion of some layers or completing extraction of K ion in interlayers of sericite.

**Reaction between sericite and lithium nitrate**

Sericite was changed into a montmorillonite type mineral showing a 15 Å peak of \( d(001) \) by treatment with a large amount of LiNO\(_3\) for a long period of reaction time as reported by White (1956). But in the presence of a small amount of LiNO\(_3\), an interstratified structure was formed even after a long period of reaction. In the presence of a considerable amount of LiNO\(_3\), an interstratified structure was only formed when the reaction time was about 3 hr.

**Properties of an interstratified mineral formed from sericite by treatment with LiNO\(_3\) and NaCl**

The specimen 1368 was selected from many specimens which were formed from sericite by treatment with LiNO\(_3\) and NaCl, and the sample was investigated.

**X-ray analysis.** As mentioned in the preceding section, the sample showed a 22 Å peak and ethylene glycol caused the 22 Å reflection to shift to a 26 Å. Solvation with ethylene glycol produced a rational sequence of 001 reflections indicating complete expansion of the clay. After heating to 300°C, the 22 Å peak disappeared giving one at 10 Å. The X-ray powder data for the altered specimen are listed in Table 1. The powder data and the behaviour of the basal reflection upon treatment with ethylene glycol and heat show that this specimen is nearly a regularly interstratified mineral of mica and hydrous mica having one layer of water molecules with certain amounts of cations between silicate layers. The properties of the altered specimen are similar to "allevardite" (Brindley, 1956). Nature of the interstratification of the specimen could not be investigated as correct integrated intensity of the sample could not be measured due to overlapping of some reflections of mica.

**Differential thermal analysis.** Differential thermal analysis curves of the altered specimen and the untreated sericite are shown in Fig. 3. The endothermic peak at about 650°C is considered to be due to dehydroxylation which in the curve of the altered specimen appeared at a slightly lower temperature as compared with the untreated sericite. This phenomenon suggests that the altered sample has a weaker structure than that of the untreated sericite. Endothermic peaks at 100°C and 190°C in the curve of the altered specimen were due to dehydration of non-cation associated and cation associated water, respectively. This suggests that hydration probably occurred when the LiNO\(_3\), NaCl-treated sample was washed with water.

**I.R. absorption spectra.** I.R. absorption spectrum of the altered specimen is shown in Fig. 4 together with that of the untreated sericite. The untreated sericite had bands at 3640, 1020, 920, 825 and 800 cm\(^{-1}\). The band at 3640 cm\(^{-1}\) is due to the O–H
stretching vibration and the band at 920 cm\(^{-1}\) is assigned to the O–H–Al\(^{2+}\) vibration (Stubičan and Roy, 1961a, 1961b). The altered specimen showed absorption bands at about 3640 cm\(^{-1}\) and 1640 cm\(^{-1}\). The 1640 cm\(^{-1}\) band is due to vibration of adsorbed water. In addition to these bands, a broad absorption band at 3400 cm\(^{-1}\) is observed. This is due to the adsorbed water in interlayers and is considered to be the same kind as that observed in absorption spectra of montmorillonite and hydrated halloysite. Hydration in interlayers in the untreated sericite occurred after it was treated with LiNO\(_3\) and NaCl. This fact agrees with the experimental result of differential thermal analysis. Double absorption bands in the range of 800–830 cm\(^{-1}\) which are characteristic to regularly interstratified mica–montmorillonite minerals as reported by Oinuma and Hayashi (1965) are observed in the absorption spectra of the altered specimen. Muscovite of the 2\(M\) type shows double bands in the range of 800–830 cm\(^{-1}\) in its infrared absorption spectrum and that of muscovite of 1\(M\) type shows single band in the same range. This suggests that regularly interstratified mica–montmorillonite minerals are related to mica of 2\(M\) type.

Fig. 2. X-ray diffraction patterns of specimens formed from various compositions after 75 hr reaction. 1378, sericite(0.2 g) + LiNO\(_3\)(2 g) + NaCl(0.005 g); 1368, sericite(0.2 g) + LiNO\(_3\)(2 g) + NaCl(0.01 g); 1369, sericite(0.2 g) + LiNO\(_3\)(2 g) + NaCl(0.02 g); 1374, sericite(0.2 g) + LiNO\(_3\)(2 g) + NaCl(0.025 g); 1372, sericite(0.2 g) + LiNO\(_3\)(2 g) + NaCl(0.04 g).
TRANSFORMATION OF SERICITE

Chemical analysis. Chemical analysis data for the altered specimen are listed in Table 2 together with that of the untreated sericite. The data show that the untreated sample has a higher content of K₂O and lower content of H₂O(⁻) as compared with the altered specimen. These facts indicate that some of the potassium ions between silicate layers were removed by treatment with molten LiNO₃ and hydration in interlayers has occurred.

It is a well-established fact that if Li ions move into the vacant octahedral positions in muscovite, less K is needed to satisfy the negative charge generated by Al³⁺ for Si⁴⁺ substitution.

Electron microscopy. As indicated in Fig. 5 an electron micrograph of the altered specimen showed a hexagonal shape, the same as that of the untreated sericite. This fact suggests that the potassium ions between the silicate layers were removed without decomposition of the sericite structure.

Amounts of exchangeable cations. Amounts of exchangeable cations of the altered specimen were measured by the Schollenberger and Simon method (Schollenberger and Simon, 1945). The sample was pulverized in an agate mortar and 0.2 g of powdered sample was mixed with quartz powder. Ammonium acetate solution (pH = 7, 1N, 100 ml) was passed through the sample for 7 hr. The amounts of exchangeable potassium, sodium and lithium ions were determined by flame photometry. The results are listed in Table 3. Considerable amounts of exchangeable Li ions exist in the interlayers with water.

Table 2. Chemical compositions of the altered sericite (a) and the untreated sericite (b)

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<thead>
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<th>(b)</th>
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<tr>
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<td>TiO₂</td>
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<td>Al₂O₃</td>
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<td>FeO</td>
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<td>H₂O⁺</td>
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<td>H₂O⁻</td>
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<tr>
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<td>99.58%</td>
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</table>

Analyst: K. Tomita.
Fig. 4. I.R. absorption spectra of the untreated sericite and the altered sericite. 1—untreated sericite; 2—altered sericite.

DISCUSSION
In treatment of sericite (0.2 g) with LiNO₃ (2 g) and NaCl, the amount of NaCl needs to be adjusted between 0.01 g and 0.04 g in order to form a regular type of mixed-layer structure. In the presence of 0.01 g of NaCl, an interstratified structure was formed in the reaction period ranging from 2 to 75 hr, but after 291 hr reaction, the powder pattern of the reaction product showed a broad peak at about 11 Å, which was divided into two peaks, 27.6 Å and broad 14 Å, upon treatment with ethylene glycol.

Sericite was changed into a montmorillonite type mineral in the presence of a large amount of LiNO₃ after a long period of reaction time. This agrees with the experimental results of White

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<td>Na</td>
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</tr>
<tr>
<td>K</td>
<td>6</td>
</tr>
<tr>
<td>Li</td>
<td>83</td>
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</table>
Fig. 5. Electron micrograph of the altered specimen.
(1956). In the presence of a small amount of LiNO₃ (about 0.4 g), an interstratified structure was formed regardless of the period of reaction. On the other hand, as long as the reaction time is about 3 hr, an interstratified structure was formed even in the presence of a large amount of LiNO₃.

Judging from the facts mentioned above, the formation of a regular type of mixed layer structure can be ascribed to removal of potassium ions from alternate layers of mica by molten LiNO₃ and that a proper amount of LiNO₃ is required to form an interstratified structure in the absence of NaCl. In the presence of a proper amount of NaCl, an interstratified structure was formed in spite of the presence of a considerable amount of LiNO₃.

The present results suggest an ordered alternation of layer charge distribution in mica (2M₁ type), as has been predicted by Sudo, Hayashi and Shimoda (1962). In most montmorillonite minerals, random interstratification resulted from treatment with ethylene glycol as indicated by Greene-Kelly (1955), and Tettenhorst and Johns (1963). This was suggested to be due to random distribution of layer charge.

Acknowledgments—The writers wish to thank Drs. K. Oinuma and S. Shimoda of the Geological and Mineralogical Institute, Tokyo University of Education, for their valuable comments. Thanks are also due to Dr. H. Hayashi for i.r. analysis.

REFERENCES


Kurzreferat—Mit Hilfe von geschmolzenem LiNO$_3$ wurde einem Sericit Kalium entzogen. In Gegenwart einer geringen Menge von LiNO$_3$ wurde die Probe nach längerer Behandlung in ein zwischengeschichtetes Gefüge verwandelt, und in Gegenwart einer größeren Menge von LiNO$_3$ wurde ein ähnliches Gefüge bereits nach drei Stunden Reaktionszeit gebildet. Bei Anwesenheit der entsprechenden Menge von NaCl konnte eine Gemischschichtstruktur leicht erhalten werden durch Behandlung über eine längere Zeitspanne mit einer beträchtlichen Menge von geschmolzenem LiNO$_3$.


Резюме—Серicit был подвергнут обработке расплавленным LiNO$_3$ с целью удаления K. Образец претерпел превращение в смешаннослоиную структуру в присутствии небольшого количества LiNO$_3$ при продолжительной обработке или же в присутствии достаточно большого количества LiNO$_3$ в течение трех часов. В присутствии достаточного количества NaCl смешаннослоиная структура легко получалась при обработке в течение длительного периода времени большим количеством расплавленного LiNO$_3$.