

TRANSFORMATION OF SERICITE INTO AN INTERSTRATIFIED MINERAL

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Abstract—Sericitic was K-depleted with molten LiNO_3 . The sample was changed into an interstratified structure in the presence of a small amount of LiNO_3 after prolonged treatment, and in the presence of a considerable amount of LiNO_3 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 LiNO_3 .

The interstratified mineral had a basal spacing of 22 \AA – 23.3 \AA which was expanded to 25 \AA – 27.6 \AA 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 LiNO_3 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 Mumbum (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 LiNO_3 . 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 $< 2\mu$ 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 $2M_1$ 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 LiNO_3 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. $\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$

A			B			C		D	
<i>hkl</i>	<i>d</i> (\AA)	<i>I</i>	<i>hkl</i>	<i>d</i> (\AA)	<i>I</i>	<i>d</i> (\AA)	<i>I</i>	<i>d</i> (\AA)	<i>I</i>
002	10.0	84	001	22	4	26	80	10.0	100
004	5.01	37	002	11	69	14.8*	100	5.0	37
110	4.47	12		10.3†	35	10.1	34		
11 $\bar{1}$			003			8.93	13	3.33	47
111	4.29	3	004	5.54	24			2.50	3
022	4.11	4		5.04†	37	5.37	14		
11 $\bar{2}$	3.95	2	005	4.50	2	5.04	20	2.003	23
11 $\bar{3}$	3.90	6	006	3.70	1	4.42	5		
02 $\bar{3}$	3.74	9		3.34	95				
114	3.49	9	007	3.08	100	3.74	2		
024	3.34	100		2.57	2	3.34	73		
006									
114	3.20	11		2.508	7				
11 $\bar{5}$	3.12	1	0011	2.006					
025	2.99	16							
11 $\bar{5}$	2.868	11							
11 $\bar{6}$	2.797	8							
131	2.585	9							
200									

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 $< 2\mu$ sericite was treated with LiNO_3 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 LiNO_3 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 26.8 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 LiNO_3 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 ($\text{NaCl}:0.005$) 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 ($\text{NaCl}:0.01$ 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 ($\text{NaCl}:0.04$ g) showed also a strong 11 Å peak and a weak 22 Å peak. When only 2 g of LiNO_3 was used, montmorillonite was formed.

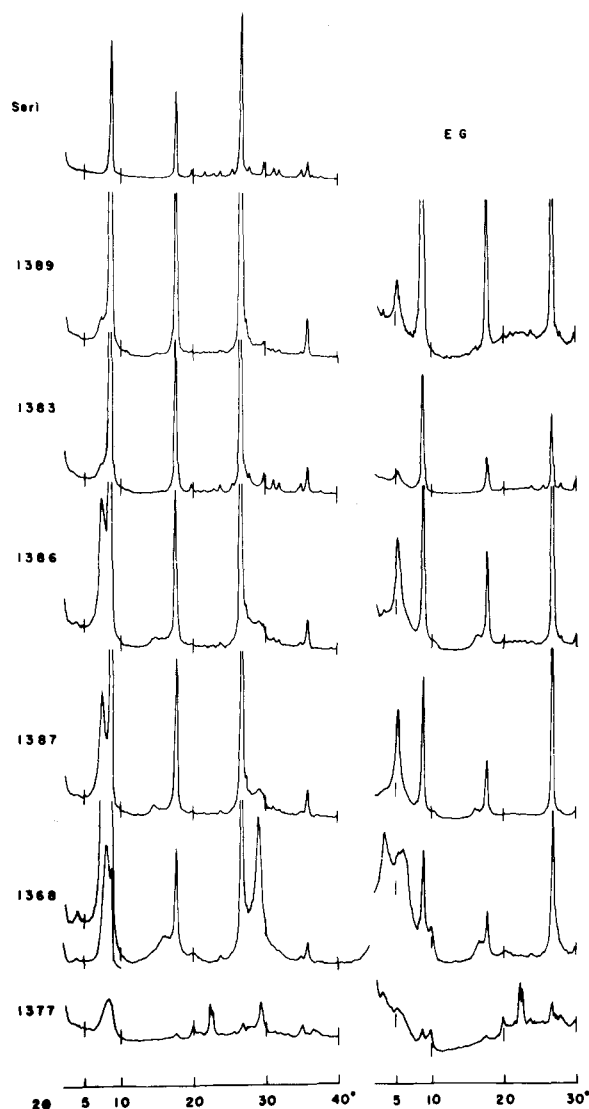


Fig. 1. X-ray diffraction patterns of specimens formed from a mixture (0.2 g of sericite, 2 g of LiNO_3 and 0.01 g of NaCl) under various reaction periods. seri: untreated sericite; 1389, 0.25 hr reaction; 1383, 1 hr reaction; 1386, 2 hr reaction; 1387, 18 hr reaction; 1368, 75 hr reaction; 1377, 291 hr reaction.

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 \AA 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 \AA peak and ethylene glycol caused the 22 \AA reflection to shift to a 26 \AA . Solvation with ethylene glycol produced a rational sequence of $00l$ reflections indicating complete expansion of the clay. After heating to 300°C , the 22 \AA peak disappeared giving one at 10 \AA . 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 "alleverdite" (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



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).

stretching vibration and the band at 920 cm^{-1} is assigned to the O-H-Al^{3+} 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 $800\text{--}830\text{ cm}^{-1}$ 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 $2M$ type shows double bands in the range of $800\text{--}830\text{ cm}^{-1}$ in its infrared absorption spectrum and that of muscovite of $1M$ type shows single band in the same range. This suggests that regularly interstratified mica-montmorillonite minerals are related to mica of $2M$ type.

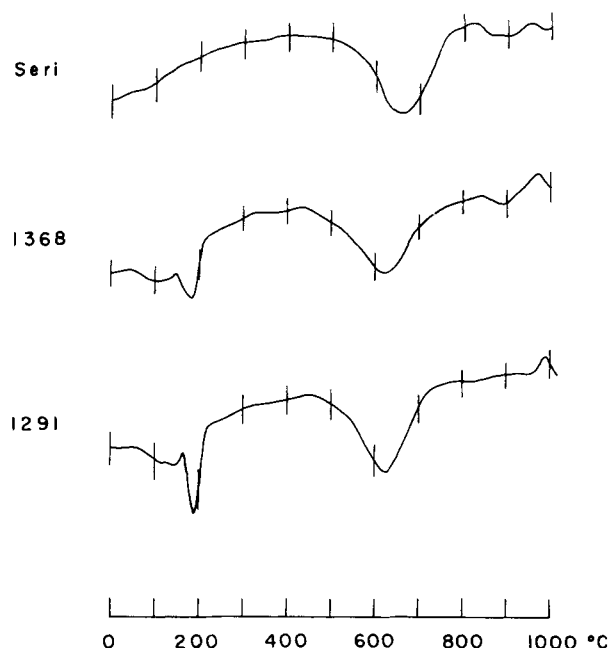


Fig. 3. Differential thermal analysis curves of the untreated sericite and the altered sericites. seri, untreated sericite; 1368, specimen formed from a mixture (sericite(0.2 g) + LiNO₃(2 g) + NaCl(0.01 g)) after 75 hr reaction; 1291, specimen formed from a mixture of 0.2 g of sericite and 2 g of LiNO₃ after 3 hr reaction.

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

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

	(a)	(b)
SiO ₂	46.07%	47.24%
TiO ₂	0.61	0.38
Al ₂ O ₃	32.75	35.04
Fe ₂ O ₃	0.39	0.59
FeO		
MnO	tr.	tr.
MgO	0.31	0.21
CaO	0.30	0.16
K ₂ O	6.10	8.75
Na ₂ O	2.00	1.37
Li ₂ O	2.70	tr.
H ₂ O(+)	5.39	5.52
H ₂ O(-)	3.17	0.32
Total	99.79%	99.58%

Analyst: K. Tomita.

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.

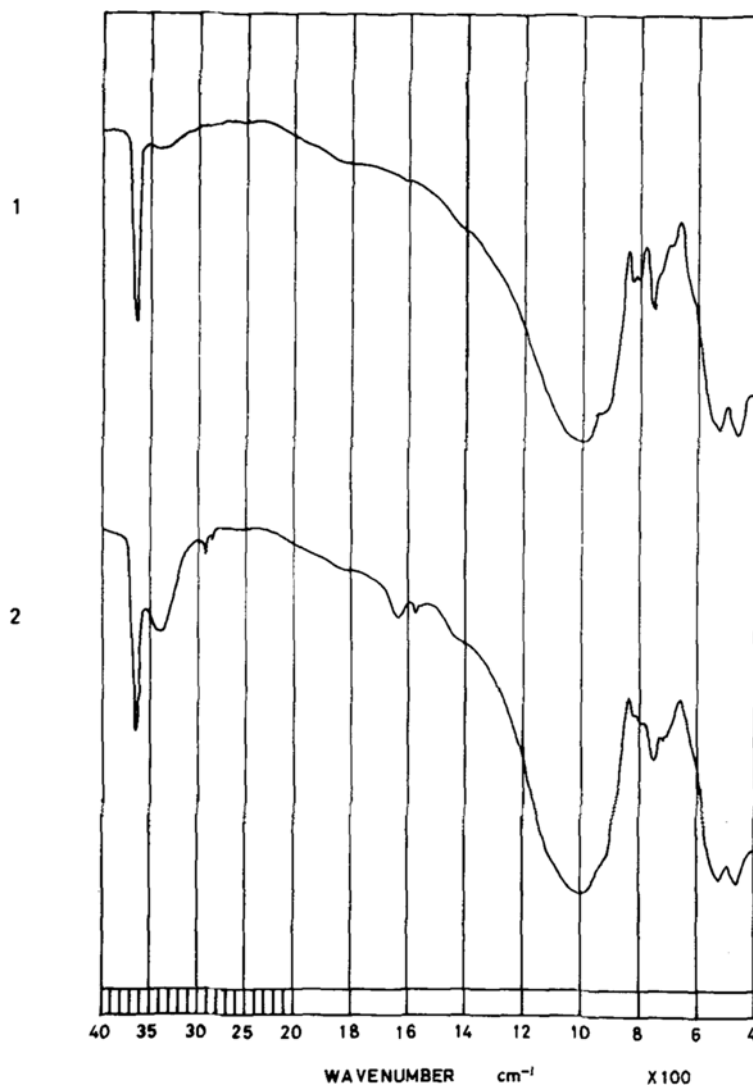


Fig. 4. I.R. absorption spectra of the untreated sericite and the altered sericite. 1—untreated sericite; 2—altered sericite.

DISCUSSION

In treatment of sericite (0.2 g) with LiNO_3 (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 LiNO_3 after a long period of reaction time. This agrees with the experimental results of White

Table 3. Amounts of exchangeable cations of the altered sericite (me/100 g)

Na	8
K	6
Li	83

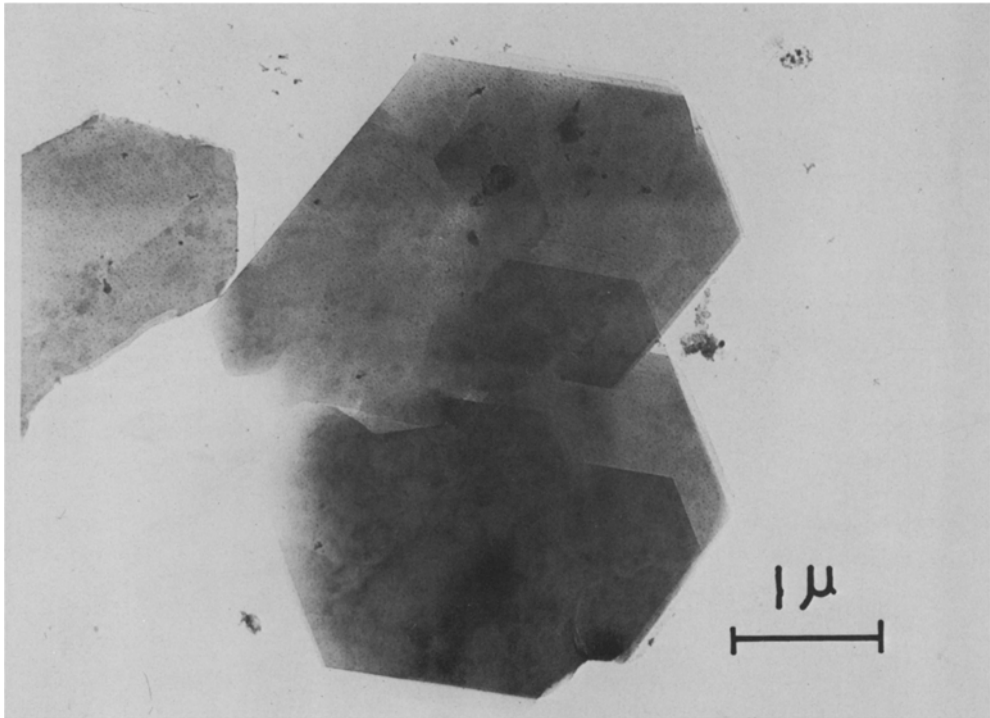


Fig. 5. Electron micrograph of the altered specimen.

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(1956). In the presence of a small amount of LiNO_3 (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 LiNO_3 .

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 LiNO_3 and that a proper amount of LiNO_3 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 LiNO_3 .

The present results suggest an ordered alternation of layer charge distribution in mica ($2M_1$ 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.

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Résumé—Une séricite a été épuisée en potassium par LiNO_3 fondu. L'échantillon a été transformé en une structure interstratifiée en présence d'une petite quantité de LiNO_3 après un traitement prolongé; en présence d'une quantité importante de LiNO_3 , une structure similaire s'est formée après environ trois heures de réaction. Dans le cas où une quantité appropriée de NaCl est présente, une structure interstratifiée a été facilement obtenue par un traitement de longue durée avec une quantité importante de LiNO_3 fondu.

Le minéral interstratifié a un espacement basal de 22–23,3 Å qui gonfle à 25–27,6 Å après traitement à l'éthylène-glycol.

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 Gemischtstruktur leicht erhalten werden durch Behandlung über eine längere Zeitspanne mit einer beträchtlichen Menge von geschmolzenem LiNO_3 .

Das zwischengeschichtete Mineral hatte einen basalen Abstand von 22 \AA – $23,3 \text{ \AA}$ der durch Behandlung mit Äthylenglykol auf 25 \AA – $27,6 \text{ \AA}$ erweitert wurde.

Резюме — Серицит был подвергнут обработке расплавленным LiNO_3 с целью удаления К. Образец претерпел превращение в смешаннослойную 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 смешаннослойная структура легко получалась при обработке в течение длительного периода времени большим количеством расплавленного LiNO_3 .

Смешаннослойный минерал характеризуется базальным межплоскостным расстоянием 22 – $23,3 \text{ \AA}$, которое увеличивается до 25 – $27,6 \text{ \AA}$ при обработке этилен-гликолем.