

SIMILARITIES OF REHYDRATION AND REHYDROXYLATION PROPERTIES OF RECTORITE AND 2M CLAY MICAS

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Abstract—Various dehydroxylated micas and rectorites were acid-treated. Rectorite-type mixed-layer mineral was formed from $2M_1$ and $2M_2$ mica and random mixed-layer mineral from $1M$ and $1Md$ mica. Rectorite was formed again from dehydroxylated rectorite. The rehydration and rehydroxylation properties of dehydroxylated rectorite and $2M$ sericites were found to be similar.

INTRODUCTION

Three mechanisms of formation are considered with regard to the origin of long-spacing (mica-montmorillonite) minerals having regular or nearly regular alternation of layers of two kinds. These mechanisms are: (1) primary formation from amorphous materials (Iiyama and Roy, 1963) or rocks; (2) formation from

montmorillonite by an unmixing of the interlayer cations (Brindley and Sandalaki, 1963); and (3) formation from $2M_1$ mica by leaching of alternate interlayers of potassium ions and hydration (Tomita and Sudo, 1968a, b, 1971; Tomita and Dozono, 1972). In this paper the author describes the relationship between mica polymorphs and mixed-layer minerals based on the third mechanism.

Table 1. Identification and sampling location of the starting specimens

Sample identification	Location	Reference
Sericites		
$1M$	Masuda, Gifu Prefecture, Japan	Kanaoka and Kato (1972)
$1Md$	Makurazaki, Kagoshima Pref., Japan	
$2M_1$	Goto mine, Nagasaki Pref., Japan	Tomita and Sudo (1968a,b)
$2M_2$	Izumiyama, Saga Pref., Japan	Kanaoka and Kato (1972)
Montmorillonites		
Oguni sample	Oguni, Niigata Pref., Japan	
Aterazawa sample	Aterazawa, Yamagata Pref., Japan	Tomita (1967)
Natural rectorites		
Iwato sample	Iwato, Kagoshima Pref., Japan	Tomita and Dozono (1973)
Kawanabe sample	Kawanabe, Kagoshima Pref., Japan	Tomita <i>et al.</i> (1969)
Synthetic rectorites		
Specimen altered from $2M_1$ sericite with 0.8 N H_2SO_4		Tomita and Sudo (1968a, b)
Specimen altered from $2M_1$ sericite with $LiNO_3$		Tomita and Sudo (1971)
Specimen altered from $2M_1$ sericite with sodium tetraphenylboron		Tomita and Dozono (1972)

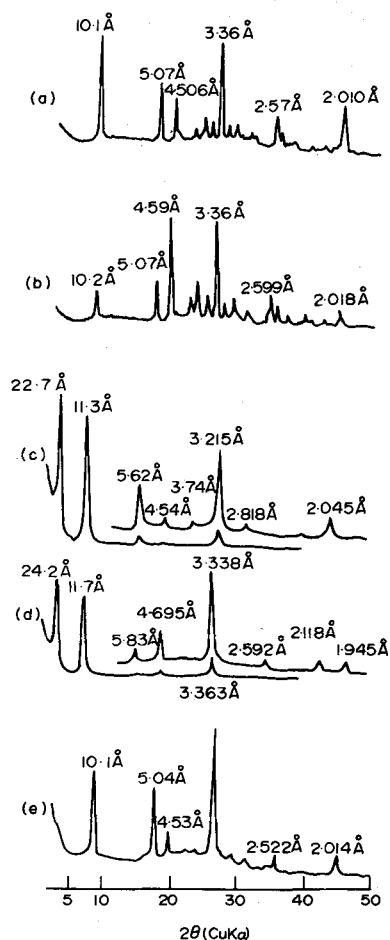


Fig. 1. X-ray powder patterns of $2M_2$ sericite after various treatments. (a) Unheated $2M_2$ sericite; (b) heated to 800°C for 1 hr; (c) specimen altered from the heated sericite by treatment with $0.8\text{ N H}_2\text{SO}_4$ for 20 hr; (d) treated with ethylene glycol; (e) heated to 800°C for 1 hr.

MATERIALS AND METHODS

In these experiments various micas, montmorillonites, and natural and synthetic mixed-layer minerals were used as starting materials. Sample description and identification are given in Table 1. Particles less than $2\ \mu\text{m}$ were obtained by sedimentation. All experiments were carried out on this fraction. Air-dried specimens were heated to 800 or 850°C for 1 hr, quenched to room temperature and boiled with $0.8\text{ N H}_2\text{SO}_4$. After boiling for several hours, the sample was washed with distilled water until the filtrate showed no acid reaction. In the acid treatment, 0.1 g of pre-heated sample was boiled in the 50 cm^3 of sulphuric acid solution (0.8 N). The washed sample was dried in air. Preferred particle orientation was used for X-ray analysis.

RESULTS

Sericites

$2M_1$ type. Mineralogical data for the specimen prepared from dehydroxylated $2M_1$ sericite have already been published; a regularly interstratified mineral was formed (Tomita and Sudo, 1968a,b). The first reflection of the interstratified mineral moved to $10.1\ \text{\AA}$ after heating to 800°C for 1 hr. A rectorite-type mineral was formed again from the heated mineral by treatment with acid.

$2M_2$ type. X-ray powder patterns of sericite heated at 800°C and treated with acid after heating are shown in Fig. 1. The peak intensity of the (002) reflection of the heated sample is weaker than that of the unheated one. The pattern of a sample acid-treated for 20 hr shows an interstratified mineral with a long spacing of about $22.7\ \text{\AA}$ (Fig. 1c) which moved to $24.2\ \text{\AA}$ upon treatment with ethylene glycol (Fig. 1d), and to $10.1\ \text{\AA}$ upon heating to 800°C (Fig. 1e). MacEwan's (1956) transform method was used to deduce the nature of the interstratification of the mineral. The $|F|^2$ values of a dioctahedral mica layer with 1 K^+ , $1\text{ H}_2\text{O}$ in the interlayer were used for the transform. The combined Lorentz-polarization factor function used was $(1 + \cos^2 2\theta)/\sin 2\theta$. In Fig. 2, which shows the result of the transform of the basal reflections, A represents a mica layer and B a hydrous mica layer. Peaks of types AB and $ABAB$ are outstanding and indicate a marked tendency for alternation of two different layers. A similar mixed-layer mineral was again formed by acid treatment of the mixed-layer mineral heated at 800°C for 1 hr.

$1M$ type. X-ray powder patterns of the sample heated to 800°C and of a sample treated with acid after heating are shown in Fig. 3. The peak intensity of the (001) of the heated sample is stronger than that of the (002) reflection. This phenomenon is different from the cases of $2M_1$ and $2M_2$ sericites. The X-ray powder pat-

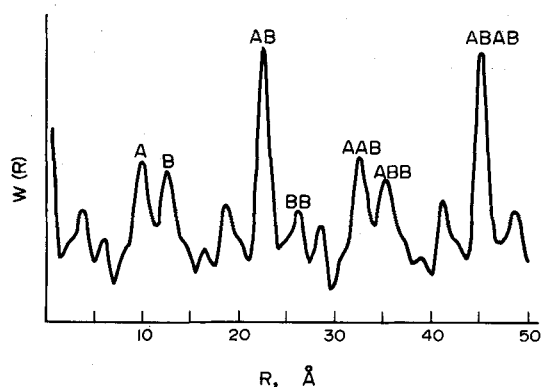


Fig. 2. Fourier transform of basal reflections of the interstratified mineral formed from $2M_2$ sericite.

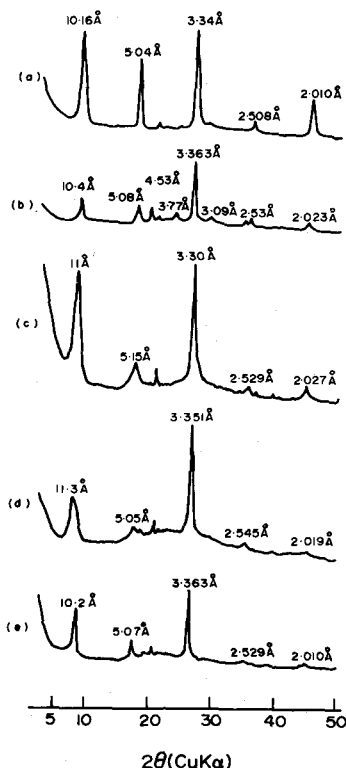


Fig. 3. X-ray powder patterns of 1 M sericite after various treatments. (a) Unheated 1 M sericite; (b) heated to 800°C for 1 hr; (c) specimen altered from the heated sericite by treatment with 0.8 N H₂SO₄ for 8 hr; (d) treated with ethylene glycol; (e) heated to 800°C for 1 hr.

tern of the acid-treated sample is very different from that of the specimen altered from 2M₁ or 2M₂ sericite by treatment with acid after heating. No reflection having a long *d*-spacing appeared in the X-ray powder pattern. The 11 Å peak of the acid-treated sample (Fig. 3c) moved to 11.3 Å by treatment with ethylene glycol (Fig. 3d) and shifted to 10.2 Å after heating to 800°C (Fig. 3e). The acid-treated sample is a random mixed-layer mineral of mica and hydrous mica. Figure 4, the

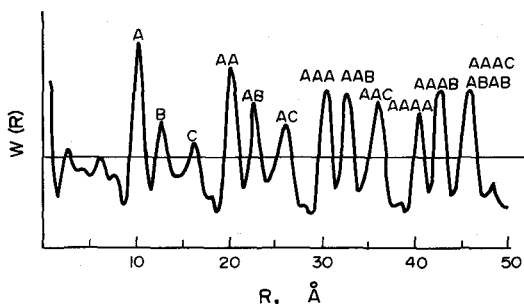


Fig. 4. Fourier transform of basal reflections of the altered specimen from 1 M sericite.

result of Fourier transform of the basal reflections of the random mixed-layer mineral, includes two kinds of hydrous layer mineral. One is a mineral having one layer of water molecules between silicate layers, the other one has two layers. In the figure, *A* represents a mica layer, *B* a hydrous mica layer having one layer of water molecules, and *C* a hydrous mica layer having two layers of water molecules.

1Md type. X-ray powder patterns of the sample heated to 800°C for 1 hr and a sample treated with acid after heating are shown in Fig. 5. The X-ray powder pattern of the heated sample is similar to that of the heated 1M sericite. The X-ray pattern of the sample treated with acid shows a 11.3 Å reflection (Fig. 5c), which was shifted by ethylene glycol solvation to 11.6 Å (Fig. 5d). After heating to 800°C the 11.3 Å reflection dropped to 10.2 Å (Fig. 5e). Judging from the X-ray patterns after various treatments, this specimen is a random mixed-layer mineral of mica and hydrous mica.

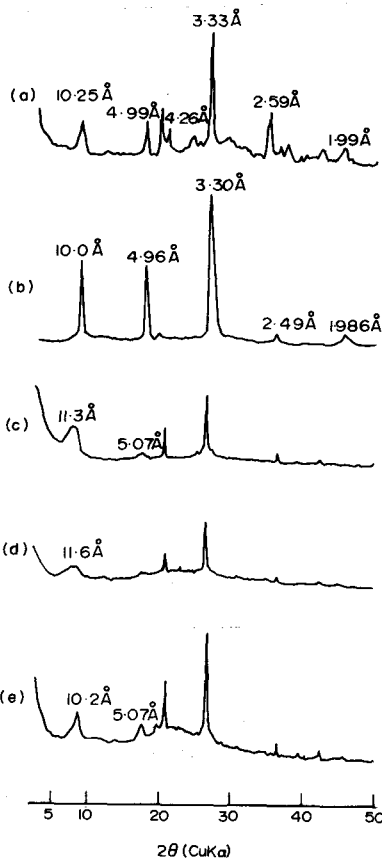


Fig. 5. X-ray powder patterns of 1 Md sericite after various treatments. (a) Unheated 1 Md sericite; (b) heated to 800°C for 1 hr; (c) specimen altered from the heated 1 Md sericite by treatment with 0.8 N H₂SO₄ for 8 hr; (d) treated with ethylene glycol; (e) heated to 800°C for 1 hr.

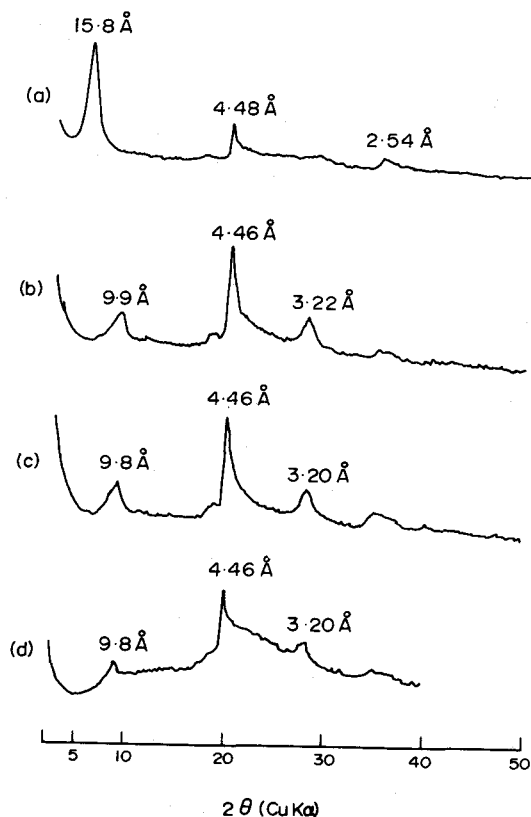


Fig. 6. X-ray powder patterns of montmorillonite after various treatments. (a) Unheated montmorillonite; (b) heated to 800°C for 1 hr; (c) specimen altered from the heated montmorillonite by treatment with 0.8 N H₂SO₄ for 8 hr; (d) treated with ethylene glycol; (e) heated to 800°C for 1 hr.

Montmorillonites

Montmorillonite from Oguni. X-ray powder diffraction patterns of a sample heated to 800°C and a sample treated with acid after heating are shown in Fig. 6. The $d_{(001)}$ value of the heated sample is about 9.9 Å (Fig. 6b) and no change was observed in the sample treated with acid (Fig. 6c). Ethylene glycol treatment for the acid treated sample gave no spacing change (Fig. 6d). These results mean that rehydration never occurred in the heated sample.

Montmorillonite from Aterazawa. This mineral showed the same behavior as the Oguni sample.

Natural rectorites

Iwato sample. This mineral was described by Tomita and Dozono (1973). Since the mineral has high rehydration ability, a specimen heated to 850°C was used for the experiment. X-ray powder patterns of the heated sample and of a sample treated with acid after heating are shown in Fig. 7. The heated sample shows

a mica pattern (Fig. 7b); the specimen treated with acid shows a 24.5 Å reflection (Fig. 7c). This peak moved to a 28.5 Å treatment with ethylene glycol (Fig. 7d) and to 10.0 Å after heating to 800°C (Fig. 7e).

Kawanabe sample. This specimen, described by Tomita *et al.* (1969), shows a 26.8 Å reflection. A specimen treated with acid after heating to 850°C for 1 hr showed the same long spacing as the unheated sample and also showed the same behavior with various treatments.

Synthetic rectorites

A rectorite-type mixed-layer mineral formed from 2M₁ sericite by treatment with hydrosulphuric acid (0.8 N) for 2 hr. This sample was formed from 2M₁ sericite by Tomita and Sudo's method; the properties of the specimen were described in their papers (Tomita and Sudo, 1968a,b). The X-ray pattern of the specimen

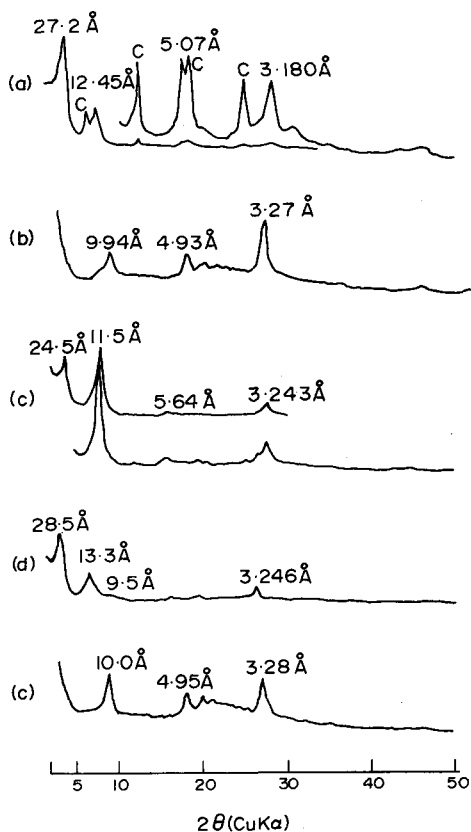


Fig. 7. X-ray powder patterns of natural rectorite after various treatments. (a) Unheated rectorite; (b) heated to 850°C for 1 hr; (c) specimen altered from the heated rectorite by treatment with 0.8 N H₂SO₄ for 0.5 hr; (d) treated with ethylene glycol; (e) heated to 800°C for 1 hr.

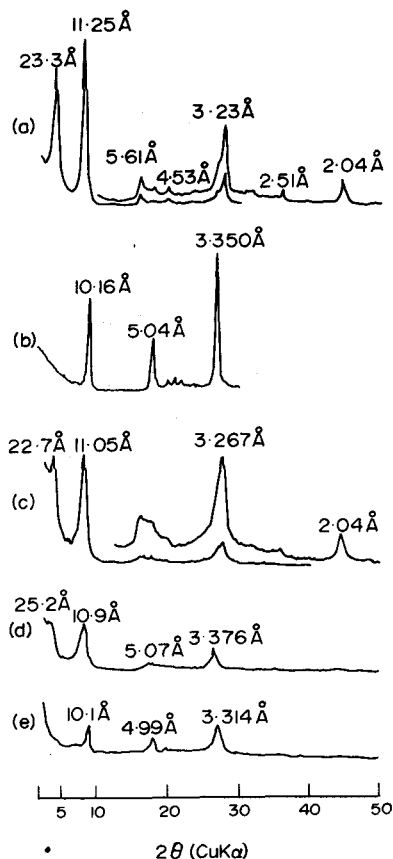


Fig. 8. X-ray powder patterns of synthetic rectorite after various treatments. (a) Unheated synthetic rectorite; (b) heated to 850°C for 1 hr; (c) specimen altered from the heated specimen by treatment with 0.8 N H₂SO₄ for 0.5 hr; (d) treated with ethylene glycol; (e) heated to 800°C for 1 hr.

showed a 23.3 Å reflection (Fig. 8a), which contracted to 10.16 Å by heating at 800°C (Fig. 8b). The heated specimen possessed a mica pattern. The X-ray pattern of a specimen treated with acid after heating to 800°C had a 22.7 Å reflection (Fig. 8c), which expanded to 25.2 Å by treatment with ethylene glycol (Fig. 8d) and contracted to 10.1 Å upon heating to 800°C (Fig. 8e). The sample treated with acid showed the same behavior as did the untreated synthetic specimen for various treatments.

A rectorite-like mineral synthesized from 2M₁ sericite with sodium tetraphenylboron after Tomita and Dozono's method (Tomita and Dozono, 1972). This specimen showed the same behavior as did the mixed-layer mineral formed from 2M₁ sericite by treatment with acid.

A rectorite-like mineral altered from 2M₁ sericite with LiNO₃ after Tomita and Sudo's method (Tomita and Sudo, 1971). This specimen also showed the same

behavior as did the mixed-layer mineral formed from 2M₁ sericite by treatment with acid.

DISCUSSION

Mixed-layer minerals of rectorite-type were formed from 2M₁ and 2M₂ types of mica. Random mixed-layer minerals were formed from 1M and 1Md types of mica by treatment with acid (0.8 N H₂SO₄) after heating the micas to 800°C for 1 hr. Rectorite-type minerals were again formed from dehydroxylated forms of natural and synthetic rectorites by treatment with acid (0.8 N H₂SO₄). Rehydroxylation and rehydration properties of dehydroxylated natural rectorite and dehydroxylated forms of 2M₁ and 2M₂ types of sericite are similar to each other. The differential thermal analysis curve and the i.r. spectra of the specimen altered from 2M₁ sericite (Tomita and Sudo, 1968b) are similar to those of natural rectorites. Similarity of i.r. spectra of rectorite and 2M micas was reported by Oinuma and Hayashi (1965). The differential thermal analysis curves of the rehydroxylated natural rectorite from dehydroxylated rectorite by treatment with 0.8 N H₂SO₄ and of the rehydroxylated 2M₁ sericite from dehydroxylated 2M₁ sericite by treatment with acid are shown in Fig. 9. They are similar to each other. Based on the phenomena mentioned

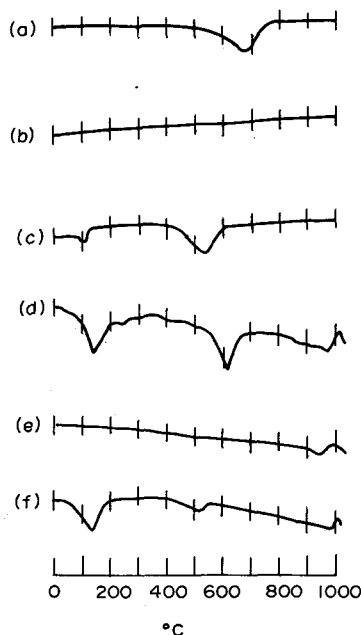


Fig. 9. Differential thermal analysis curves of: (a) unheated 2M₁ sericite; (b) heated to 800°C for 1 hr; (c) specimen altered from the heated sericite by treatment with 0.8 N H₂SO₄ for 8 hr; (d) unheated natural rectorite from Iwato; (e) heated to 900°C for 1 hr; (f) specimen altered from the heated rectorite by treatment with 0.8 N H₂SO₄ for 0.5 hr.

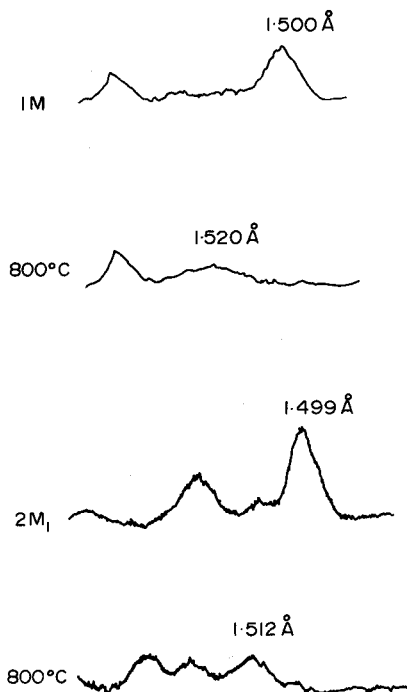


Fig. 10. X-ray diffraction traces of the 1-50 Å region of the powder patterns of unheated and heated 1 M and 2 M_1 sericites.

above, rehydroxylation and rehydration properties of the dehydroxylated rectorite and 2 M sericites are similar. This conclusion suggests that their dehydroxylated structures are alike.

The $d_{(060)}$ reflections for the dehydroxylated samples of 2 M_1 and 1 M sericites were used to measure the b -dimensions. X-ray diffraction traces of the 1-50 Å region of these sericites are shown in Fig. 10. Upon dehydroxylation, $d_{(060)}$ of 2 M_1 sericite moved from 1.499 Å to 1.512 Å. At 800°C $d_{(060)}$ of 1 M sericite moved from 1.500 Å to 1.520 Å. The 1.520 Å peak was broad. The b -dimensions of both samples therefore increased after heating to 800°C. This increase in b may weaken or stretch the K-O bond sufficiently to enhance K^+ release (Burns and White, 1963a,b; Leonard and Weed, 1967, 1970), but this hypothesis does not explain the phenomenon of K^+ leaching from alternate interlayers of 2 M_1 or 2 M_2 sericite. These results suggest that studies on the crystal structure of dehydroxylated 2 M micas can solve one of the mechanisms of formation of rectorite.

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Résumé—On a traité en milieu acide plusieurs micas et rectorites deshydroxylés. Le minéral interstratifié du type rectorite était formé de mica $2M_1$ et $2M_2$ et le minéral interstratifié au hasard, de mica $1M$ et $1Md$. La rectorite s'est reformée à partir de la rectorite deshydroxylée. Il a été montré que les propriétés de rehydratation et rehydroxylation de la rectorite et des séricites $2M$ deshydroxylées étaient semblables.

Kurzreferat—Verschiedene deshydroxylierte Glimmer und Rectorite wurden mit Säure behandelt. Wechsellagerungsminerale vom Rectorittyp wurden aus $2M_1$ - und $2M_2$ -Glimmer und zufällig wechselgelagerte Minerale aus $1M$ - und $1Md$ -Glimmer gebildet. Rectorit wurde wiederum aus deshydroxyliertem Rectorit gebildet. Die Rehydratisierungs- und Rehydroxylierungseigenschaften des deshydroxylierten Rectorits und der $2M$ -Sericite wurden für ähnlich befunden.

Резюме— Разные дегидроксилированные слюды и ректориты перерабатываются кислотой. Из слюд $2M_1$ и $2M_2$ образовался минерал типа ректорита, состоящий из чередованных пластов разного происхождения, а из слюды $1M$ и $1Md$ —минерал с произвольно смешанной прослойкой. Из дегидроксилированного ректорита вновь образовался ректорит. Характеристики регидратации и регидроксилирования дегидроксилированного ректорита и $2M$ серицитов оказались аналогичными.