THE EXPERIMENTAL TRANSFORMATION OF MICA TOWARD SMECTITE*; RELATIVE IMPORTANCE OF TOTAL CHARGE AND TETRAHEDRAL SUBSTITUTION

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Abstract – This article emphasizes the influence of crystal-chemical composition on the ease of transformation of micas to vermiculite or more smectite-like minerals. The swelling test, with glycerol, of Mg-saturated mineral is used to characterize the degree of transformation.

The main structural factors of this evolution are tetrahedral substitution of Si by Al, and total charge. There is a relation between these two factors, i.e. the lower the tetrahedral substitution, the greater can be the charge without affecting the smectite swelling behavior.

In this respect there is a contrast between tri and dioctahedral micas. In the first, tetrahedral Al is so high (>1.20 for Si_4O_{10}) that transformation into smectite must imply modification of the tetrahedral layer. For dioctahedral micaceous phyllites (illites, glauconites) where tetrahedral charge is lower, transformation can be easier. Only a lowering of total charge is needed and reduction-oxidation seems to play a very important role in this process.

INTRODUCTION

IT is usual to present the alteration of mica minerals according to the continuous sequence: mica \rightarrow vermiculite \rightarrow smectite.

These successive steps of weathering are generally defined and identified on the basis of their behavior, especially with respect to interaction with polyalcohols. Hence, if we consider glycerol and minerals with interlayer Mg, vermiculites will sorb one layer of glycerol (d(001) = 14 Å), while smectites will take up two layers (d(001) = 17 or 18 Å).

Many studies (Barshad, 1950; Foster, 1956a; Walker, 1958) have established a relationship between this behavior and the total charge of the mineral (which is related to the number of interlayer cations). Thus, micas with a total charge in the range 0.7-1 (for Si₄O₁₀) will first alter to vermiculite with a low charge (0.6-0.8), and then to smectite with a charge less than 0.6. From this sequence we deduce that the alteration is a progressive transformation of the structure with a lowering of charge.

This paper considers: how this kind of alteration by simple transformation can occur experimentally for the different mica minerals, dioctahedral or trioctahedral; what are the structural properties that seem preponderant; and whether total charge is a good index for following this alteration.

EXPERIMENTAL PROCEDURES

Several micas or micaceous phyllites, trioctahedral (phlogopite-biotite), or dioctahedral (glauconites-illites-sericite-phengite-muscovite), were used in these experiments. Their total analyses are given in Table 1, and structural formulas are calculated from these data (Tables 2 and 3).

Potassium was extracted from the minerals by various treatments. For trioctahedral micas, N NaCl at 65°C was used to treat a concentration of mica in the suspension equal to about 1.0 g/l. of solution. For dioctahedral micas, the treatment used either 0.2 N NaCl, barium acetate (0.2 or0.4 N) at 65°C, or sodium cobaltinitrite at 25°C, on a suspension which contained about 30-50 mg of mica in 1 l. of solution. After the extraction of K, ferrous iron was oxidized by treatment with H_2O_2 at pH 4.3 (15 per cent-24 hr at 40°C). The treated mineral was then placed in a centrifuge tube and elutriated three times by N MgCl₂, and twice by a mixture of glycerol-ethanol. The specimens were then X-rayed by the method of Barshad (1960).

In this first study, differentiation between smectite and vermiculite will be based on the expansion of the Mg²⁺-saturated mineral after glycerol treat-

^{*}This general term refers to all expansible minerals of the montmorillonite group.

	Biotite, Varennes (a)	Biotite open (Na Cl) (b)	Glauconite (Cormes, France) (c)	Illite (Fithian) (d)	Illite (Grundite) (e)	Illite (Puy) (f)	Sericite (g)	Muscovite (Madagascar) (h)
SiO ₂	36.92	35.37	48.72	49.51	46.17	49.50	46.58	45.32
Al_2O_3	14.69	13.76	9.39	23.80	24.59	21.13	27.32	33.57
TiO ₂	3.94	3.78	0.08	0.54	0.62	0.62	0.19	0.12
Fe_2O_3	1.11	11.60	20.40	4.01	5.43	6.17	5.14	3.99
FeO	17.74	7.71	0.75	2.04	1.13	0.58	2.12	1.48
MgO	11.53	11.19	2.80	2.09	1.84	3.67	0.36	0.41
MnO	0.35	0.31				0.15		0.54
CaO	0.35	0.21	1.10	0.25	0.25	0.90	0.39	0.02
Na ₂ O	0.31	4.40	0.26	0.85	0.30	0.24	0.13	0.60
K_2O	8.55	0.04	7.20	5.78	4.97	7.90	8.46	10.15
H_2O	2.52	10.72	9.37	9.64	11.65	9·10	7.32	4.40
apatite	(1.30)	(0.91)	100.01	00 51	06.05	00.07	00.01	100 45
_Total	99.31	100.00	100.01	98.51	96.95	99.96	98 .01	100.65

Table 1. Total analysis of minerals (Analyst G. Veneau)

Table 2. Structural formulae of biotite before and after transformation: (a) Biotite without treatment. (b) Biotite after opening by NaCl

Calculations are made for (a and b) on the basis of all oxygens in one unit cell.

 $(b) \quad Ca_{0\cdot017}K_{0\cdot003}Na_{0\cdot661}[(Al_{0\cdot004}Ti_{0\cdot220}Fe_{0\cdot677}^{3+})(Fe_{0\cdot499}^{2+}Mg_{1\cdot295}Mn_{0\cdot02})](Al_{1\cdot254}Si_{2\cdot746})O_{10}(OH)_{2}$

ment. This test is considered to be specific for this purpose by many authors (Walker, 1958; Schultz, 1969; Harward *et al.*, 1969), but its exact meaning will be discussed in a short paper Robert and Barshad (in press).

TRANSFORMATION OF TRIOCTAHEDRAL MICA

Related experimental studies during the last few years have mainly been concerned with the transformation of mica into vermiculite. This process consists essentially of exchange and diffusion reactions coupled with replacement of the interlayer K by more hydrated cations (Na, Ca, Mg). This hydration of the interlayer space is the main morphological aspect of the transformation as seen with a scanning microscope (Seddoh and Robert, 1972). With X-rays the transformation manifests itself by the appearance of basal spacings at 12 Å or 14 Å. During the process the essential structure is maintained because the loss of structural elements is small (<5 per cent) if the pH is not too far from neutrality.

One must distinguish vermiculization, which can be called "opening" of the layers, from oxidation which can occur as an ancillary process after the opening. This oxidation reaction causes a more important change, an increase of octahedral positive charge and thus a lowering of the net negative layer charge. This increase is compensated in three ways (Robert, 1971), which are difficult to differentiate quantitatively. Compensation can occur by a lowering of interlayer charge (expulsion of exchangeable cations in vermiculite), by the expulsion of octahedral cations (e.g. iron and eventually Mg) and by a change in the hydroxyl content.

During opening of phlogopite which contains little ferrous iron, the charge remains about 0.8(Robert, 1971). The products obtained are typical vermiculites (sorption of one layer of glycerol).

In the experiments on a biotite rich in ferrous iron (Table 2), a vermiculite with a total charge of 0.7 results from complete "opening" with NaCl at 80° C. (Oxidation has occurred for 50 per cent of the ferrous iron originally present, mainly during the last renewals of the treating solution). If the vermiculite so obtained is completely oxidized by treatment with H₂O₂, a mineral is obtained (Robert, 1971) which has a charge of 0.5, within the charge range of smectite. However, if glycerol expansion of such a Mg²⁺-saturated sample is used as a basis for identification, the expansion involves only one layer of glycerol, as in true vermiculite.

These results on trioctahedral micas show that the parameter of total charge is insufficient to distinguish the different steps of mica alteration. This parameter must be supplemented by a consideration of whether the origin of this charge is tetrahedral or octahedral (Mering and Pedro, 1969). In our experiments, although the composition of the interlayer space and the octahedral sheet are changed, the tetrahedral substitution of Si by Al remains the same (Al > 1.20 for 4 tetrahedra)*.

TRANSFORMATION OF DIOCTAHEDRAL MICA

It is not possible to experiment with trioctahedral micas containing less tetrahedral Al, because the required species do not exist (Foster, 1960). However in the dioctahedral micas, there is a continuous trisilicic-tetrasilicic series (Foster, 1956). We have chosen for study a few members of this series which are either: (1) dioctahedral micaceous phyllites with mica structure but lower charge and lower tetrahedral substitution of Si by Al; and (2) true dioctahedral micas having higher charge and substitution.

TRANSFORMATION OF DIOCTAHEDRAL MICACEOUS PHYLLITES

Ferric phyllites (glauconites) and aluminous phyllites (illites) have been studied.

(1) Glauconites. These minerals are distinguished by a low tetrahedral substitution (< 0.4). One of the samples used came from a sandy formation of Cenomanien age from Cormes, France. Chemical and structural compositions, of material isolated with a magnetic separator, are given in Tables 1

*In all cases, the numbers of 4-fold coordinated aluminum are given for 4 tetrahedra i.e. per half-unitcell. †Spectra done by R. Prost (Versailles). and 3. The other sample came from Villers; the structural formula in Table 3 was taken from Besson *et al.* (1966).

These minerals, very similar to those described by Hendricks and Ross (1941) and by Sabatier (1949), have a high content of both K_2O and Fe_2O_3 and a low degree of interstratification with an expanded mineral. Examples of such glauconites are given by Burst (1958); Hower (1961); Cimbalnikova (1971) and Thompson (1973).

During the experiments, the potassium released, as measured by atomic absorption, was greater than 60 per cent of the total interlayer cations.

X-ray diffraction of the Cormes glauconite, after opening followed by Mg^{2+} -saturation and hydration, gave a basal spacing of 14 Å which increased to 18 Å upon glycerol treatment. Extraction of potassium gave only one species which possessed the swelling behavior of smectite. Treatment with H_2O_2 (oxidation) or with $Na_2S_2O_4$ (reduction) did not change the behavior of this mineral.

Figure 1 represents the diffractograms of glauconite before and after opening. The relatively low spacing at 17.40 Å can be due to some interstratification with unopened glauconite; when K extraction is more complete, a spacing greater than 18 Å occurs. In Fig. 2 are superimposed infrared spectra† of the treated and untreated minerals in the region of hydroxyl vibration. There is no apparent change in the hydroxyl absorption bands, but after opening some hydration water obviously remained in the KBr pellet. This last spectrum is very similar to that of nontronite.

The Villers glauconite, after extraction of K,

 Table 3. Structural formulae of glauconites and illites: (Analyst G. Veneau): Calculations are made with 11 oxygens in the unit cell. For glauconite of Villers, refer to Besson

Glauconite (Villers, France)	$Ca_{0\cdot07}K_{0\cdot64}[(Al_{0\cdot47}Fe_{1\cdot02}^{3+})(Fe_{0\cdot11}^{2+}Mg_{0\cdot37})](Al_{0\cdot22}Si_{3\cdot78})O_{10}(OH)_{2}$
Glauconite (Cormes, France) (100-200 µm)	$Ca_{0\cdot08}K_{0\cdot68}Na_{0\cdot03}[(Al_{0\cdot45}Fe_{1\cdot14}^3)(Fe_{0\cdot04}^{2+}Mg_{0\cdot31})](Al_{0\cdot37}Si_{3\cdot63})O_{10}(OH)_2$
Illite (Puy, France) $(< 2 \mu m)$	$Ca_{0\cdot07}K_{0\cdot71}Na_{0\cdot03}[(Al_{1\cdot23}Ti_{0\cdot03}Fe_{0\cdot32}^{3+})(Fe_{0\cdot03}^{2+}Mg_{0\cdot38}^{2+})](Al_{0\cdot52}Si_{3\cdot48})O_{10}(OH)_2$
Illite (Fithian) (0·3-0·5 µm) Na	$Ca_{0\cdot02}K_{0\cdot52}Na_{0\cdot07}[(Al_{1\cdot47}Ti_{0\cdot03}Fe_{0\cdot21}^{3+})(Fe_{0\cdot12}^{2+}Mg_{0\cdot22})](Al_{0\cdot50}Si_{3\cdot50})O_{10}(OH)_{2}$
Illite (Grundite) (0·3–0·5 µm) Mg	$Ca_{0\cdot02}K_{0\cdot47}Na_{0\cdot04}Mg_{0\cdot07}[(Al_{1\cdot50}Ti_{0\cdot03}Fe_{0\cdot30}^{3+})(Fe_{0\cdot08}^{2+}Mg_{0\cdot13})](Al_{062}Si_{3\cdot38})O_{10}(OH)_{2}$

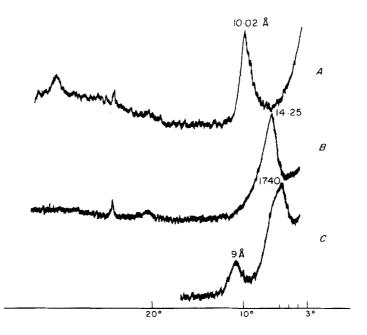


Fig. 1. X ray diffractograms of glauconite (Cormes) before and after K extraction. A-Glauconite; B-Open glauconite (Mg saturation); C-Open glauconite (Mg saturation + glycerol).

gave a basal spacing of 14 Å with glycerol. Oxidation by H_2O_2 resulted in an increase of this spacing to 18 Å.

For both Cormes and Villers glauconites, tetrahedral aluminum is low (near 0.3), and smectite swelling behavior can occur for a total charge of 0.7or 0.8, far above the smectite range.

For some glauconites this swelling behavior will appear directly after K extraction, while others will need the presence of ferrous iron in the structure to permit lowering of charge by oxidation.

(2) Illites. Potassium has been extracted from Fithian and Grundite illites in the size range $0.3-0.5 \,\mu\text{m}$. The samples were respectively Na⁺ and Mg²⁺ saturated before the opening treatment.

Extraction of K was done until about 60 per cent of the total content. To go above this level a more drastic treatment would have been necessary Smith and Scott (1966).

The total analyses of these illites are given in Table 1, the structural formulas in Table 3. If the structural formula is calculated on the basis of 11 oxygens, the total charge and the aluminum in tetrahedral position are relatively low and coincide with the values given by Foster (1956a) and Hower and Mowatt (1966). If free silica was removed by KOH treatment, and the structural formula calculated to include some extra structural water, both the charge and the tetrahedral aluminum increased. The X-ray results, presented in Table 4, are as follows.

Hydrated Grundite, after opening, showed a 14 Å spacing after Mg^{2+} -saturation. After glycerol treatment, the opened illite showed the presence of two species, one with a 14 Å spacing (one layer) and one with an 18 Å spacing (two layers). The first was similar to vermiculite in swelling behavior; the second, to smectite. If the remaining ferrous iron of the opened sample were oxidized, we then obtained, after Mg^{2+} -saturation, only one species which swelled to 18 Å. In this illite Gaudette *et al.* (1966) found some expanding mineral, which could

Table 4. Variation of micas basal reflexions during their transformation (Mg + glycerol samples)

Mineral	After K extraction	After oxidation following K extraction
Phlogopite	14.28	14.28
Biotite	14.25	14.25
Sericite	14.06	14.06
Phengite	14.06	14.06
Glauconite (Villers)	13.96	18.00
Glauconite (Comers)	18.20	18.20
Illite (Grundite)	14.59	18.30
. ,	17.36	
Illite (Fithian)	14.39	17.45
Illite (Puy)	13.96	13.70

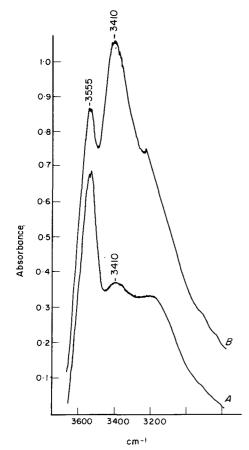


Fig. 2. I.R. spectra of glauconite (Cormes) before (A) and after (B) K extraction.

represent part of the second species. The important point is that after oxidation the opened sample showed only smectite swelling behavior.

Opening of Fithian illite gave only one species, with a basal spacing of 14 Å even after glycerol treatment. After oxidation with H₂O₂, however, glycerol treatment swelled the sample to 18 Å. The charge reduction by oxidation could only be about 0.1 or 0.2 (for a structural formula of Si₄O₁₀) but this amount was enough to change the swelling behavior from that of vermiculite to smectite. These results are in agreement with the work of White (1950), who, however, extracted only 20 per cent of the total potassium. The results are not in agreement with other authors who have also 'opened' illites. In illites there is more tetrahedral aluminum than in glauconites and the total charge must be reduced to near 0.6 to have smectite behavior. With Fithian illite and Grundite it is possible to reach such a charge only by extraction of K and oxidation of ferrous iron. These results cannot be generalized to all illites because of the complexity of these minerals. Preliminary experiments on illite from Puy (France) showed that opening gave vermiculite, and that the ferrous iron content was not enough to produce smectite behavior by oxidation.

Transformation of true dioctahedral micas

Many experiments have been performed on muscovite, for example, by Reichenbach and Rich (1969) and Scott and Reed (1966). In this work a phengite (with high content of Fe_2O_3) and a sericite were studied.

In these two cases, extraction of potassium produced a dioctahedral vermiculite which expanded to only one layer of glycerol when Mg^{2+} -saturated. Oxidation by H_2O_2 did not change this behavior. The charge after opening remained very high and the amount of ferrous iron present in the structure was not enough to reduce the charge.

It should be possible to obtain smectite behavior with a more fundamental change in structure. White (1956), working with muscovite, and more recently Tomita and Sudo (1971), working with sericite, have reduced charge by incorporation of cations in the octahedral sheet by fusion with $LiNO_3$. With a value of tetrahedral aluminum around 0.9 it seems possible to obtain smectite behavior if the total charge is lowered sufficiently by this Li⁺ incorporation.

DISCUSSION AND CONCLUSIONS

The main results of the transformation of micaceous phyllosilicates are summarized in Table 5. The general sequence of alteration remains valid. The total charge of the mineral is a good indication of transformation to a first approximation, but more detail must be considered.

In particular, the steps of transformation will be different according to the crystal-chemical constitution. For trioctahedral micas, simple transformation leads only to a vermiculite, due apparently to a high tetrahedral substitution (Al ≥ 1.2) (Foster, 1960).

For dioctahedral micas (muscovite, phengite or even sericite), with tetrahedral aluminum in less than one of every four tetrahedral sites, the extent of this substitution should no longer be an obstacle to transformation to smectite. However, because the charge remains high, this alteration is also limited to the vermiculite state. For dioctahedral phyllites, analogous to micas, which commonly occur in soils and in which tetrahedral aluminum is lower, the charge is also lower and the M. ROBERT

		Type of behavior			
Total charge	Mica type	After K extraction	After oxidation		
Trioctahedral					
	Phlogopite	 Vermiculite (high charge 0.9-0.8) 	Vermiculite		
>0.9	Biotite —	Vermiculite (0·7)	Vermiculite (low charge 0.5)		
Dioctahedral					
	Glauconite - (Cormes)	→ Smectite	→ Smectite		
< 0.9	Glauconite - (Villers)	→ Vermiculite	→ Smectite		
	Illite – (Grundite)	→ Vermiculite + Smectite	\rightarrow Smectite		
	. ,	→ Vermiculite	\rightarrow Smectite		
	· · · ·	→ Vermiculite	→ Vermiculite		
	Phengite -	→ Vermiculite high charge			
	Sericite -	→ Vermiculite high charge			
	Muscovite -	→ Vermiculite high charge			

Table 5. Transformation of different micas by extraction of K and Fe^{2+} oxidation

mineral obtained can more easily have a smectite behavior. Thus, glauconites, with only 0.3 tetrahedral Al can transform directly into smectite without an intervening vermiculite state.

For some illites, the postulated sequence of alteration to vermiculite and then to smectite is found, whereas in others both vermiculite and smectite occur together indicating that there were two differently charged species before transformation. Glauconite has the same maximum total charge as illite; after opening, it behaves more like a smectite because the amount of tetrahedral aluminum is smaller.

In all these experiments, structural changes in structure are minor and consist mainly of hydration of the layers and modification of the octahedral composition. To go beyond the degree of transformation considered here would involve more drastic structural modification. For example, reduction in charge of muscovite requires entry of cations into the octahedral sheet, as was demonstrated for Li⁺ by White (1956). In nature, Mg²⁺ may play a similar role. Similarly reduction of tetrahedral substitution in trioctahedral micas requires entry of Si and release of Al (Tardy, 1969). Cardenite, a trioctahedral smectite derived from biotite, has only 0.8 Al in tetrahedra (MacEwan, 1954), still a lot of Al^{1V} per total unit cell, but less than the Al^{1V} in biotite.

From our results it appears easier to reduce the charge by means other than modification of the tetrahedral substitution. The process of oxidationreduction appears important, not only for ferrous biotite but also for dioctahedral phyllites which contain only a small quantity of ferrous iron. Some of these results were quite unexpected. For example, alteration of trioctahedral micas to vermiculite is easy, but not alteration all the way to smectite. For dioctahedral micas and particularly for illites and glauconites, the alteration toward smectite is easier.

A first consequence of this work deals with our knowledge of micaceous phyllites. If all glauconites after opening behave alike with glycerol, they may be considered similar to high charge potassium smectite. As we have seen, illites are more complex and show the presence of different species. If, for opened Grundite and Fithian illites, the swelling behavior remains the same until K extraction is complete, their charge is not as high as muscovite or phengite type minerals.

Another consequence concerns the interpreta-

tion of natural weathering where one characterizes the type of alteration by the presence of a particular clay mineral. If such characterization can be correct for neogenesis of clay minerals, it will not be necessarily the case during transformation of minerals, a process in which inherited structural characteristics may be more important then conditions of the altering medium. In this respect, tetrahedral occupancy by aluminum, or ferrous iron in octahedral sites are important and can determine the type of swelling clay mineral (vermiculite or smectite) obtained during alteration. Smectites derived from micaceous minerals can be called "transformation smectites". It will be seen elsewhere that if they show smectite behavior with glycerol, they have also other special properties which allow differentiation from true smectites generally formed by neogenesis.

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Résumé – Cet article souligne l'influence de la composition cristallochimique sur la facilité avec laquelle les micas se transforment en vermiculite ou en minéraux d'un type smectite plus marqué. Le test de

M. ROBERT

gonflement au glycérol appliqué au minéral saturé par Mg est utilisé pour caractériser le degré de transformation.

Les facteurs structuraux principaux de cette évolution sont la substitution tétraédrique de Si par Al et la charge totale. Il y a une relation entre ces deux facteurs, à savoir que la charge qui n'affecte pas le comportement gonflant de la smectite est d'autant plus grande que le taux de substitution tétraédrique est bas.

A cet égard, il existe un contraste certain entre les micas tri et dioctaédriques. Dans les premiers, la teneur en Al tétraédrique est si élevée (>1,20 pour Si₄O₁₀) que la transformation en smectite doit impliquer une modification de la couche tétraédrique. Pour les phyllites micacées dioctaédriques (illites et glauconites) où la charge tétraédrique est plus basse, la transformation peut être plus facile. Seul un abaissement de la charge totale est nécessaire, et l'oxydoréduction semble jouer un rôle très important dans ce processus.

Kurzreferat- Die Arbeit behandelt den Einfluß der kristallchemischen Zusammensetzung auf die Neigung der Glimmer, sich in Vermikulite oder in Smektit-ähnliche Minerale umzuwandeln. Zur Kennzeichnung des Umwandlungsgrades wird der Quellungstest mit Glycerin an Mg-gesättigten Mineralen benutzt.

Die wichtigsten strukturellen Faktoren dieser Umwandlung sind tetraedrischer Ersatz von Si durch Al und Gesamtladung. Zwischen diesen beiden Faktoren besteht eine Beziehung. Je geringer die Substitution in den Tetraedern ist, desto größer kann die Ladung sein ohne daß das Quellungsverhalten des Smektits beeinflußt wird.

In dieser Hinsicht besteht ein Gegensatz zwischen tri- und dioktaedrischen Glimmern. Bei ersteren ist der Gehalt an tetraedrischem Al so hoch (>1,20 je Si₄O₁₀), daß die Umwandlung in Smektit eine Veränderung der Tetraederschicht voraussetzt. Bei dioktaedrischen glimmerartigen Schichtsilikaten (Illiten, Glaukoniten), bei denen die Tetraederladung niedriger ist, kann die Umwandlung leichter erfolgen. Es ist lediglich eine Verminderung der Gesamtladung erforderlich, und Reduktions- und Oxidationsvorgänge scheinen bei diesem Prozeß eine sehr wichtige Rolle zu spielen.

Резюме — В этой работе подчеркивается влияние кристаллохимического состава на легкость превращения слюд в вермикулит или в более смектитообразные минералы. Для характеризации степени трансформации, минерал насыщенный Mg подвергается испытанию набуханию с глицерином.

Главные структурные изменения — это тетраэдральное замещение Si Al, и полный заряд. Между этими двумя факторами имеется связь, то есть чем ниже тетраэдральная замена, тем выше может быть заряд не влияющий на поведение разбухания смектита.

В этом отношении между три и диоктаэдральной слюдами имеется контраст. В первой содержание тетраэдрального Al так высоко (>1,20 для Si_4O_{10}), что трансформация в смектит ведет за собой изменение тетраэдрального слоя. В диоктаэдральных слюдистых филлитах (иллиты, глаукониты) у которых тетраэдральный заряд ниже, превращение происходит с большей легостью. Требуется только понижение общего заряда, а пониженное окисление, по-видимому, играет важную роль в этом процессе.

174