

MORPHOLOGICAL EFFECTS ON ILLITE AS A RESULT OF POTASSIUM DEPLETION*

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Abstract—Several illites and a mixed-layer illite-montmorillonite developed fractures in some particles during progressive removal of interlayer potassium by solutions containing sodium tetraphenylboron. The appearance of the splinters in bundles, some connected to incompletely broken plates, suggests the process is related to the differential release of stresses known to exist as a consequence of octahedral-tetrahedral misfit. The formation of splinters produces additional surface area for ion removal and may influence the rate of vermiculite development.

INTRODUCTION

FACTORS controlling the release of interlayer potassium from micaceous minerals have received considerable attention because of both their agricultural importance and their significance in interpreting the post-depositional history of clays. The application of sodium tetraphenylboron (NaBPh_4) to the potassium-extracting solutions in experimental studies of clays and micas (Scott *et al.*, 1960) has aided greatly in overcoming the difficulty of progressive ion displacement. It permits a constant exchange gradient to be maintained through continuous precipitation of released potassium, which would otherwise tend to block the release of other ions. In this way it has become possible to determine potassium depletion rates for particles under a variety of conditions.

Particular emphasis has been given to particle size (Reichenbach and Rich, 1969; Mortland and Lawton, 1961; Scott, 1968) and charge density (Ross and Kodama, 1970; Bassett, 1959) as factors most affecting potassium mobility in dioctahedral, aluminous, layer silicates although other authors point out that stage of weathering, type of interstratification, and structural change due to grinding (e.g. Lodding, 1970) should also be taken into consideration.

Reichenbach and Rich (1969) suggest that the high retention of potassium in the 0.08–0.2 μ fraction of a prepared muscovite indicates a higher potassium selectivity than in the coarser 5–20 μ fraction, and that potassium removal proceeds more by silicate dissolution than, as is the case with the larger particles, by ion exchange and layer bending. Scott (1968) has documented the relationship be-

tween particle size and the percentage of exchangeable potassium, and shows that below 2 μ , various micas plus illite behave in a non-linear fashion. For particles larger than 2 μ the relationship is notably more linear. As a mechanism Scott (1968) and Scott and Smith (1966) suggest that larger particles lose potassium by a process of edge weathering whereas smaller particles lost potassium by layer weathering, thus producing an interstratified material. The operation of the diffusion process involved is explored in detail by Reed and Scott (1962) and by Mamy (1970).

The purpose of this investigation is to examine differences produced by potassium depletion of several illites and related minerals, and to determine whether or not particle morphology is affected in the process.

MATERIALS AND METHODS

The materials used are the Beavers Bend illite from the Silurian Blaylock formation of Oklahoma (Mankin and Dodd, 1963), the API reference Fithian and Morris illites obtained from Ward's Natural Science Establishment, an illite from the middle Devonian Silica shale of northern Ohio, a glauconite from the Cambrian Franconia sandstone of Wisconsin, and a regularly interstratified illite-montmorillonite (Chattanooga K-bentonite) from the middle Ordovician of Tennessee.

Less than 2 μ fractions were prepared by sedimentation and centrifugation after the removal of carbonate and organic material and subjected to a series of treatments with a mixture of NaCl and NaBPh₄ followed the technique described by Smith and Scott (1966). Samples were agitated very briefly by ultrasonics and then allowed to sit overnight before being decanted, washed with acetone, and

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subjected to fresh solution. Periodically, portions were removed for X-ray diffraction and transmission electron microscope examination. Oriented specimens for diffraction analysis were prepared by sedimentation on glass, petrographic slides and allowed to dry at room temperature. They were run on a General Electric XRD-5 unit with Cu radiation, 0.1° Soller slit, Ni filtration, and a recorder speed of $2^\circ 2\theta$ per min. The same specimens were re-run after being placed in a container with an ethylene glycol saturated atmosphere and allowed to stand overnight. Specimens selected for microscope study were replicated by carbon

with platinum shadowing and examined with an RCA EMU-2D electron microscope.

RESULTS

X-ray diffraction

For each sample investigated, potassium depletion results in a vermiculite-type lattice with a first-order basal spacing for air-dried particles at about 12.5 \AA and an integral series of peaks completing the rest of the pattern (Figs. 1-3). With saturation by ethylene glycol the lattice expands to about 14.2 \AA . A particular exception is the sample of Morris illite, which shows an expanded

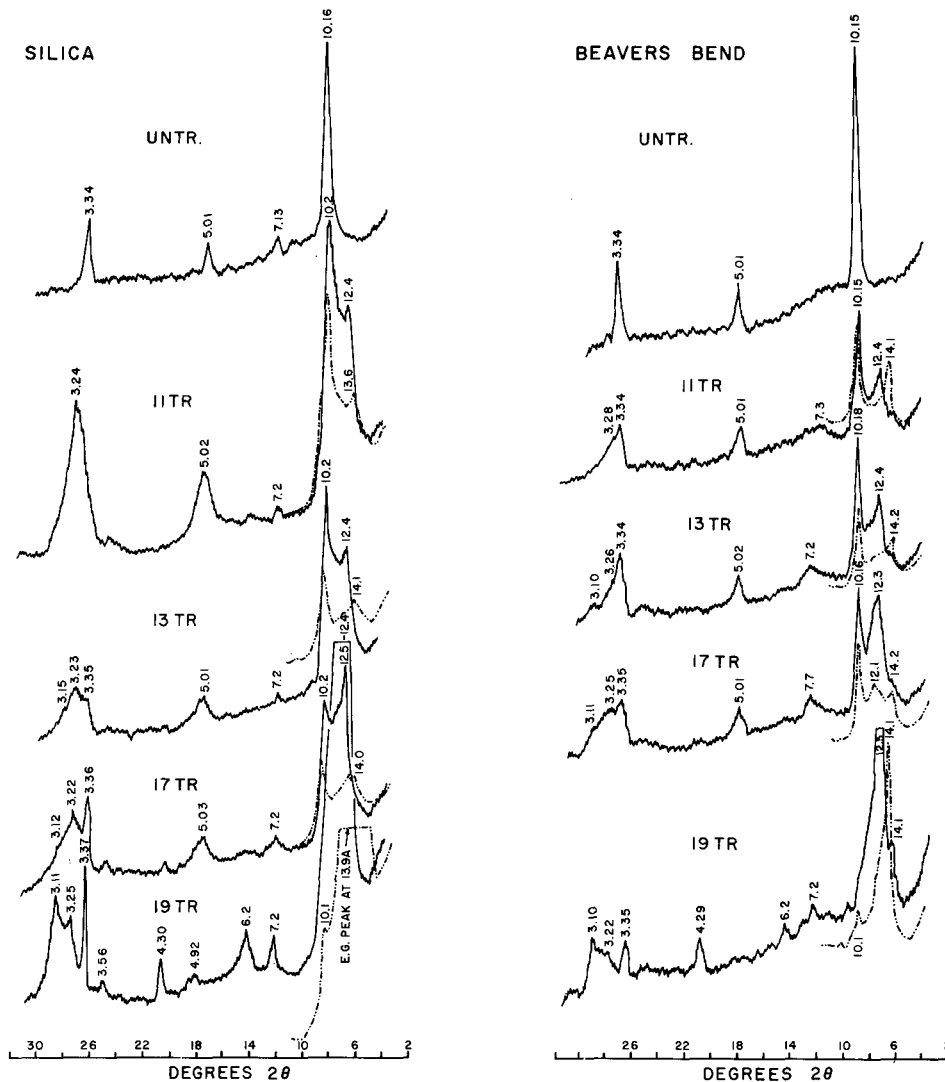


Fig. 1. Diffraction tracings of the Silica and Beavers Bend illites showing changes after successive treatments with NaBPh_4 . Glycolated patterns are indicated by dotted line.

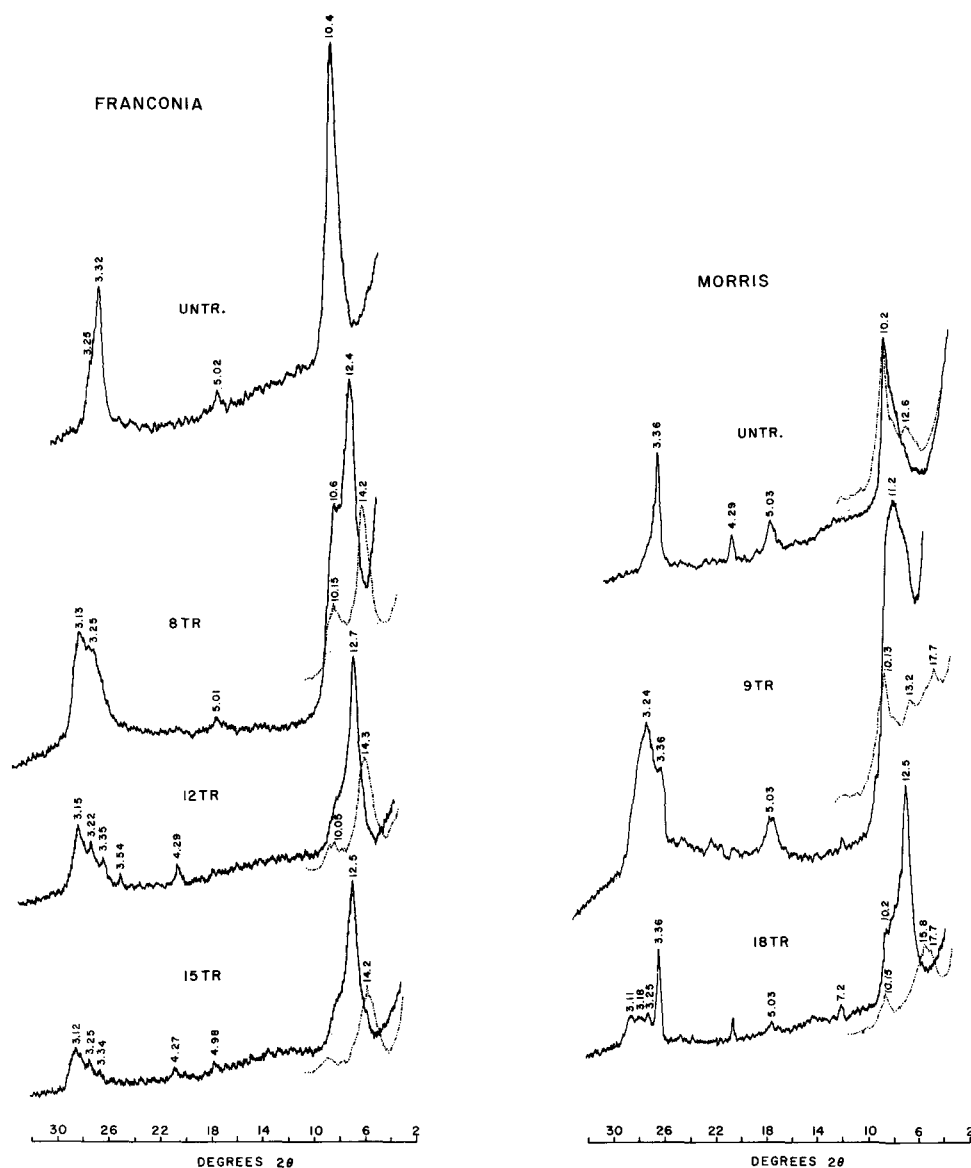


Fig. 2. Diffraction tracings of Morris illite and Franconia glauconite after successive treatments with NaBPh_4 . Glycolated patterns are indicated by dotted line.

reflection at 15.8 and 17.7 Å following potassium removal. The higher spacing is generally characteristic of Ca-montmorillonite and is the only instance here noted of spacings similar to those reported by White (1951). It can be seen, however, that the original, untreated material contains a small amount of an expandable component which registers a 12.6 Å reflection with glycol solvation. Thus in the likelihood that the Morris material is

in fact an ordered illite-montmorillonite, it is doubtful that the 17.7 Å peak represents a complete transformation from pure illite to montmorillonite under these experimental conditions.

For the sample of K-bentonite only three treatments were required to remove the 10 Å reflection from the diffraction pattern. This component constitutes approximately 80% of the total structure, and its ease of conversion tends to support the

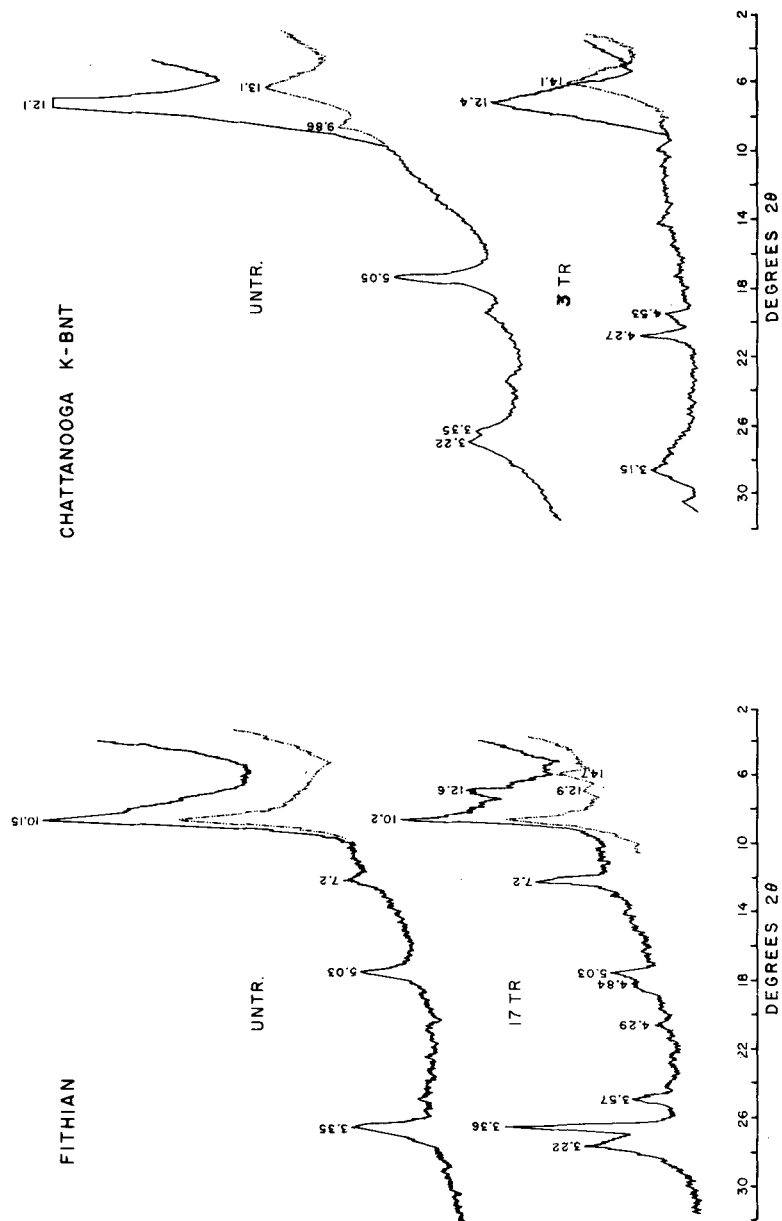


Fig. 3. Diffraction tracings of Fithian illite and Chattanooga K-bentonite after successive treatments with NaBPh₄. Glycolated patterns are indicated by dotted line.

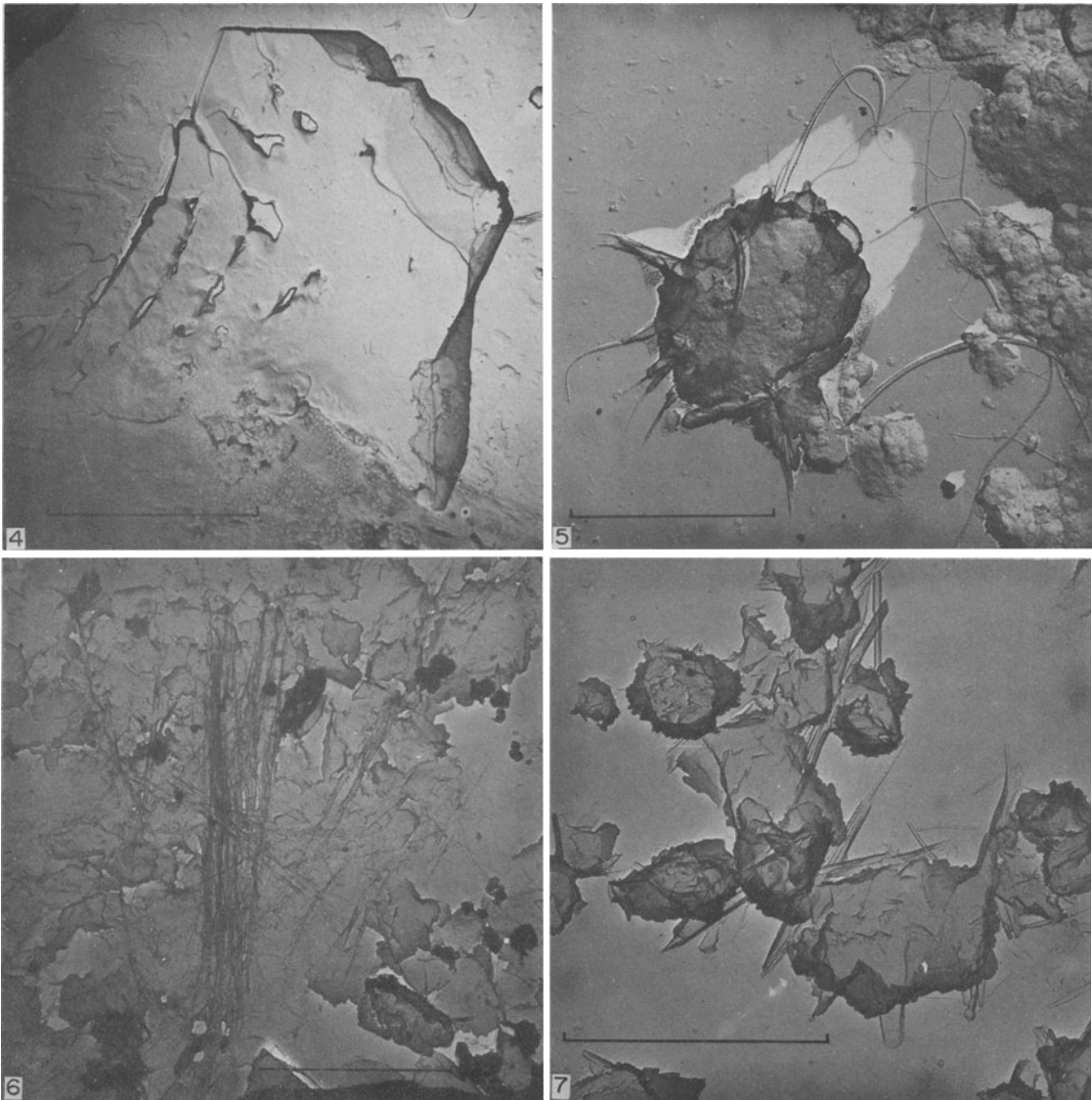


Fig. 4. Morris illite after 7 treatments. Scale indicates 1μ .

Fig. 5. Morris illite after 18 treatments. Scale indicates $\frac{1}{2} \mu$.

Fig. 6. Silica illite after 19 treatments. Scale indicates 1μ .

Fig. 7. Chattanooga K-bentonite after 3 treatments. Scale indicates $\frac{1}{2} \mu$.

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conclusion of Weaver (1953), Huff (1963), and others that K-bentonites are derived by potassium adsorption and fixation in montmorillonite. The relatively quick release of potassium contrasts sharply with the more tightly held ions in illite and probably reflects an overall lower layer charge. In addition, as will be shown later, the formation of newly exposed surface area due to crystallite fracturing probably enhanced this process even further.

While no effort was made here to measure the rate of potassium removal by periodic chemical analyses, this aspect having been closely examined by previous authors, it can be seen that, given basically the same experimental conditions, the development of vermiculite spacings proceeds differently for each sample. For the Franconia gluconite, eight treatments were sufficient to develop a strong reflection at 12.4 Å, while Fithian illite retained its prominent 10 Å peak even after seventeen treatments. The general dissimilarity rather than the actual number of treatments is to be noted here since, as Scott and Smith (1966) point out, it is recognized that slight changes in the ratio of NaCl to NaBPh₄ can affect the potassium withdrawal rate for various micaceous minerals.

Despite the difficulties in removing potassium from illite compared with other layer silicates (Scott, 1968), the position of first-order reflections measured here is generally higher than those indicated for muscovite (e.g. Reichenbach and Rich, 1969). A first-order spacing of 12.1–12.3 Å seems typical for air-dried muscovite after maximum potassium withdrawal, but for illites the variation in spacings extends to 12.7 Å. A possible explanation may be the effect of crystallite size on diffraction patterns. Ross (1968), for example, points out diffraction maxima of thin crystals appear to shift toward higher spacings compared with thicker ones.

For glycolated specimens the appearance of spacings up to 17.7 Å with intermediate peaks between 12.0 and 16.0 Å, in the case of illites, indicates the development of mixed-layer phases. Presumably a certain portion of each sample possesses sufficiently high layer charge to act like muscovite and resist complete potassium loss. That this portion varies between samples is indicated by the varying degrees of completeness of development of the 12 Å peak and the appearance of intermediate reflections. It is difficult to determine the exact nature of the interlayering formed, however, since additional second-, third-, and fourth-order peaks are not always well developed.

Electron microscopy

Electron micrographs of depleted particles

reveal changes in appearance in the form of fractures parallel to the *c* axis. Figures 4 and 5 show particles of Morris illite following seven treatments with NaBPh₄ (Fig. 4) and eighteen treatments (Fig. 5). Figure 6 is Silica illite after nineteen treatments and Fig. 7 shows Chattanooga K-bentonite following three treatments. In each case there is a noticeable fracturing of clay plates into narrow laths and fibers, an aspect that is lacking in photographs of the untreated material. Figure 4 reveals parallel rows of elongated openings in a single particle which suggest an incipient stage in lath development after partial potassium loss. With further potassium removal these openings appear to enlarge and finally merge forming distinct laths on the order of 0.1 μ in width. These in turn may further divide to form flexible fibers on the order of 0.01–0.05 μ in width and 0.5 μ in length as shown in Fig. 5. This photograph reveals what is essentially a stack of plates in a single floccule with varying degrees of splintering developed from individual layers. This additional splitting produces arrays or bundles of fibers, many incompletely separated from parent particles. Partial separation may be due to incomplete potassium removal in individual particles, or perhaps to an insufficient release of stress needed to produce discrete fibers. The ones that are produced are remarkable in the straightness of their sides and in their flexibility. Figure 6 illustrates the most complete development of fibers observed.

The frequency of fractured crystallites varied among the six samples, from common in the Morris, Silica, and Chattanooga clays through occasional in the Beavers Bend and Franconia clays to rare in the Fithian illite. In the first three instances potassium removal was high while in the latter case the persistence of a strong 10 Å reflection indicates high potassium retention, even after seventeen treatments (Fig. 3). These examples certainly suggest a direct correlation between potassium loss and particle disruption, but the absence of extensive splitting in the other two samples indicates that at least for some illites the relationship is not clear cut. Diffraction data show the Beavers Bend and Franconia samples lost considerable potassium without developing sufficient stress to cause widespread fracturing. For the Morris, Chattanooga, and, to a lesser extent, Silica samples, however, the apparently accelerated ease of potassium withdrawal may indeed be related to the exposure of fresh particle edges through fracturing.

DISCUSSION

Lath morphology is well known in clay micas although published photographs of potassium de-

pleted clays (Tomita and Sudo, 1971; Kitagawa and Watanabe, 1970) show no noticeable tendency toward fracturing. Brown and Rich (1968) and Reichenbach and Rich (1969) show micrographs of potassium depleted muscovite in which views normal to (001) planes reveal the preferential development of layers with varying potassium release. The latter authors suggest the layer separation may represent growth step planes in which ordering is less than in other layers. However, no disruption parallel to prismatic directions is seen. Robert (1971) records biotite flakes that show plate fracturing following potassium loss, but the particles produced tend to be irregularly shaped rather than fibrous.

From the present study there seems to be at least some basis for suspecting that fundamental zones of weakness within the clay structure are exploited by layer distortion during potassium loss and eventually yield by splitting. Construction of a model for this process could begin with the generally accepted thesis of Radoslovich (1963) that internal stresses within layer silicates can be compensated by rotation of the Si-O tetrahedra and a consequent reorientation of oxygen atoms in a ditrigonal arrangement in the surface of the tetrahedral layer. This, together with shearing produced by the misfit of adjacent layers and augmented by the loss of interlayer potassium may be sufficient to produce splitting as observed here.

If, as suggested by Reichenbach and Rich (1969), Bassett (1959), and others, the release of interlayer potassium from small particles proceeds by layer weathering rather than edge weathering then perhaps we can see this reflected in the selective breakdown of certain plates.

From the standpoint of experimental work, discriminate fracturing of clay plates can complicate efforts to relate variation in particle size to the rate of potassium loss. In particular, it raises the possibility of a variable increase in the amount of edge area available for rapid potassium removal. In such a situation these broken fragments might become preferential sites for potassium movement as opposed to the interiors of larger plates.

Smith and Scott (1966) point out in their discussion of the effects of ultrasonics on clay particles, that if all particles were continually fractured during potassium withdrawal one would expect the rate of potassium loss to be constant. Most published studies show that it is not, but rather that it follows a decreasing curve with time. The present study demonstrates that while none of the samples experienced complete particle disruption during potassium removal, in some cases significant fracturing did occur and may have accelerated the illite-vermiculite transformation.

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REFERENCES

1. Bassett, W. A. (1959) The origin of the vermiculite deposit at Libby, Montana: *Am. Mineralogist* **44**, 282–299.
2. Brown, J. and Rich, C. I. (1968) High resolution electron microscopy of muscovite: *Science* **161**, 1135–1137.
3. Huff, W. D. (1963) Mineralogy of Ordovician K-bentonites in Kentucky: *Clays and Clay Minerals* **11**, 200–209.
4. Kitagawa, Y. and Watanabe, Y. (1970) Preparation of dioctahedral vermiculite from muscovite: *Clay Sci.* **4**, 31–36.
5. Lodding, W. (1970) On potassium release from micas: *Clays and Clay Minerals* **18**, 67.
6. Mamy, J. (1970) Extraction of interlayer K from phlogopite special effects of cations, role of Na and H concentrations in extracting solutions: *Clays and Clay Minerals* **18**, 157–163.
7. Mankin, C. J. and Dodd, C. G. (1963) proposed reference illite from the Ouachita Mountains of southeastern Oklahoma: *Clays and Clay Minerals* **11**, 372–379.
8. Mortland, M. M. and Lawton, K. (1961) Relationships between particle size and potassium release from biotite and its analogues: *Soil Sci. Soc. Am. Proc.* **25**, 473–476.
9. Radoslovich, E. W. (1963) Cell dimension studies on layer lattice silicates, a summary: *Clays and Clay Minerals* **11**, 225–228.
10. Reed, M. G. and Scott, A. D. (1962) Kinetics of potassium release from biotite and muscovite in sodium tetraphenylboron solutions: *Soil Sci. Soc. Am. Proc.* **26**, 437–440.
11. Reichenbach, H. Graf von and Rich, C. I. (1969) Potassium release from muscovite as influenced by particle size: *Clays and Clay Minerals* **17**, 23–29.
12. Robert, M. (1971) Étude expérimentale de l'évolution des micas (biotites): *Ann. Agron.* **22**, 155–181.
13. Ross, G. J. and Kodama, H. (1970) Differential release of potassium from interstratified mica clay minerals as related to probable differences in their mica layer components: *Clays and Clay Minerals* **18**, 151–156.
14. Ross, M. (1968) X-ray diffraction effects by non-ideal crystals of biotite, muscovite, montmorillonite, mixed-layer clays, graphite, and periclase: *Z. Krist.* **126**, 80–97.
15. Scott, A. D. (1968) Effect of particle size on interlayer potassium exchange in micas: *Trans. 9th Int. Cong. Soil Sci.* **2**, 649–660.
16. Scott, A. D., Hunziker, R. R. and Hanway, J. J. (1960) Chemical extraction of potassium from soils and micaceous minerals with solutions containing sodium tetraphenylboron—I. Preliminary experiments: *Soil Sci. Soc. Am. Proc.* **24**, 191–194.

17. Scott, A. D. and Smith, S. J. (1966) Susceptibility of interlayer potassium in micas to exchange with sodium: *Clays and Clay Minerals* **14**, 69–81.
18. Smith, S. J. and Scott, A. D. (1966) Extractable potassium in grundite illite: I. Method of extraction: *Soil Sci.* **102**, 115–122.
19. Tomita, K. and Sudo, T. (1971) Transformation of sericite into an interstratified mineral: *Clays and Clay Minerals* **19**, 263–270.
20. Weaver, C. E. (1953) Mineralogy and Petrology of some Ordovician K-bentonites and related limestones: *Bull. Geol. Soc. Am.* **64**, 921–943.
21. White, J. L. (1951) Transformation of illite into montmorillonite: *Soil Sci. Soc. Am. Proc.* **15**, 129–133.

Résumé—Plusieurs illites et un interstratifié illite–montmorillonite montrent le développement de fractures dans certaines particules au cours de l'élimination progressive du potassium interfeuillet par des solutions contenant du tétraphénylborate de sodium. L'apparition d'éclats en gerbes, certains d'entre eux étant attachés à des plaques incomplètement brisées, suggère que le phénomène est relié à la disparition différentielle des contraintes provenant des défauts de raccordement entre couches octaédriques et tétraédriques. La formation des éclats produit une surface supplémentaire pour l'élimination des ions et peut influencer la vitesse du développement de la vermiculite.

Kurzreferat—Mehrere Illite und ein gemischtschichtiger Illit–Montmorillonit entwickelten Risse in einigen Teilchen während der fortschreitenden Entfernung von Zwischenschichtkalium durch Lösungen, die Natrium–Tetraphenylbor enthielten. Das Auftreten von Splittern in Bündeln, manche mit unvollständig gebrochenen Platten verbunden, deutet darauf hin, dass der Vorgang mit der unterschiedlichen Freigabe von Spannungen in Beziehung steht, die bekanntlich als Folge oktaedrischem Nichtpassens bestehen. Die Bildung von Splittern führt zu zusätzlicher Oberfläche für die Entfernung von Ionen und kann die Geschwindigkeit einer Entwicklung von Vermiculit beeinflussen.

Резюме — Во время прогрессивного удаления межслоевого калия растворами содержащими тетрафинилборный натрий в частицах иллита и в частицах смешанных слоев монтмориллонита–иллита появились трещины. Появление осколков в сростаниях, приводит к предположению, что процесс относится к дифференциальному снятию напряжения, которое существует, как известно, вследствие октаэдрического–тетраэдрического несовмещения. Образование осколков представляет добавочную поверхностную площадь для удаления ионов и может повлиять на скорость образования вермикулита.