SELECTIVE SORPTION AND FIXATION OF CATIONS BY CLAY MINERALS: A REVIEW

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Abstract — Investigations concerning selective sorption and fixation of K and similar cations by clay minerals and soil clays and the mechanisms of these reactions are reviewed. In particular, recent observations on selective sorption of these ions in dilute solutions by weathered micas and vermiculite in relation to the interlayer structures are discussed in detail. Also, implications of the resistance to weathering of small mica particles to cation selectivity by soils are described. Despite the increased understanding of sorption and fixation reactions, the following aspects remain unclear.

First, the mechanism of the collapse of alternate layers in vermiculite on K or Cs sorption has not been unequivocally established. Second, factors that impart stability to the central core of mica particles so that K extraction becomes progressively difficult are not known. Third, inability of Ca or Mg ions to expand interlayers of Cs-saturated vermiculite in contrast to K-saturated vermiculite is not completely understood.

INTRODUCTION

SORPTION of cations from solution by clay minerals and by soils and sediments containing these minerals is usually considered a simple ion exchange process. In non-selective sorption, the amounts of cations sorbed are proportional to their relative concentrations in solution and their sorption can be described by the laws of mass action. Certain cations are, however, sorbed more selectively than others and are held more tightly against replacement by other cations. Potassium, NH_4^+ and other large monovalent cations are sometimes held so strongly that they are said to be fixed.

Selective sorption of K^+, NH_4^+, and Cs^+ ions by clays has been observed by a number of investigators (Krishnamoorthy and Overstreet, 1950; Wiklander, 1950; Marshall and Garcia, 1959). Numerous early reports on K^+ fixation have been reviewed by Reitemeier (1951). Although fixation of K^+ and NH_4^+ ions by clay minerals had earlier been attributed to their close fit within the hexagonal cavities of basal oxygen planes (Page and Baver, 1940; Barshad, 1948, 1950; Stanford, 1948; Wear and White, 1951), low hydration energy of the ions is now considered to be the major factor in cation selectivity and fixation (Norrish, 1954; Shainberg and Kemper, 1966; Kittrick, 1966). Data showing greater sorption and fixation of Cs^+ and Rb^+ ions with smaller hydration energy than of K^+ ions (Coleman *et al.*, 1963; Sawhney, 1964; Marshall and McDowell, 1965) can be similarly explained.

Cations with low hydration energy, such as K^+, NH_4^+, Rb^+, and Cs^+ produce interlayer dehydration and layer collapse and are therefore fixed in interlayer positions. Conversely, cations with high hydration energy, such as Ca^{2+}, Mg^{2+}, and Sr^{2+}, produce expanded interlayers and are not fixed.

The layer charge on the mineral also effects the interlayer collapse and hence, the degree of cation fixation. For instance, in vermiculite, K^+-saturation effects interlayer collapse, producing a 10A structure, whereas in montmorillonite with a smaller layer charge than vermiculite, K^+-saturation effects only a partial interlayer collapse, producing a 12A structure. Consequently, K^+ is fixed by vermiculite but K^+-saturated montmorillonite must be heated to collapse interlayers to 10A to fix K^+. Within the montmorillonite mineral group, the greater the layer charge, the greater is the K^+ fixation (Weir, 1965). Similar relationships have been observed for K^+ or Cs^+ fixation in vermiculite (Sawhney, 1969b). It has been observed also that K^+ ions are held more tightly in dioctahedral than in trioctahedral minerals (Jackson and Sherman, 1953; Newman and Brown, 1966). Although the exact reasons for this difference are not known, the following two factors may contribute to greater fixation of K^+ in dioctahedral minerals. First, the vertically oriented OH-dipole of the hydroxyls in trioctahedral layer silicates results in a weaker bonding of K^+ than the inclined OH-dipole in the dioctahedral layer silicates (Serratosa and Bradley, 1958). Second, the smaller size of the octahedral layer in dioctahedral minerals produces shorter

K—O bonds, hence K^+ is held more tightly in dioctahedral minerals (Radoslovich, 1962; Rich, 1968).

Role of frayed edges in selective sorption

Interest in radioactive fallout and in the disposal of radioactive effluents containing small amounts of $^{137}Cs^+$ led to investigations that revealed the role of different exchange sites in selective sorption and fixation of K^+ and Cs^+ ions. Results of Jacobs and Tamura (1960) and Tamura and Jacobs (1960) indicated that illite, with a smaller cation exchange capacity than vermiculite, sorbed more Cs than vermiculite from dilute solutions in the range of 10^{-5} M Cs. They attributed this to the selective sorption of Cs in the interlayer space near particle edges. Coleman et al. (1963) and Sawhney (1964, 1965) further demonstrated the selective sorption of Cs^+ over Ca^{2+} and Na^+ ions. Although selective sorption of Cs^+ from dilute solutions was ascribed to the edge sites, the mechanism of selective sorption was not clear.

Evidence for the existance of exchange sites with different selectivities for K^+ ions was obtained by Bolt et al. (1963) in experiments on removal of K^+ from a soil illite. These authors recognized three different sites, basal surface, edge-interlayer and interlayer sites. Potassium ions held on basal surfaces and at the edges were exchangeable with other cations. Bolt et al. estimated that while the selectivity of basal surfaces of illite for the sorption of K^+ was twice that of Ca^{2+}, the selectivity of edge interlayer sites was about 500-fold greater. The release of K^+ from interlayer sites was extremely slow, however, and was possibly controlled by a solid- or film-diffusion process as suggested by Mortland and Ellis (1959).

Other investigations have provided additional data illustrating the importance of edge-interlayer sites in selective sorption of K^+ and Cs^+ ions and have provided a possible mechanism for the selectivity of partially weathered micas and vermiculites with collapsed interlayers. Schwertmann (1962a, b) observed preferential sorption of K^+ over Ca^{2+} ions by a number of soil clays from dilute solutions. Jackson (1963) and Rich (1964) suggested that the selective sorption of K^+ in soils is due to the presence of frayed edges resulting from weathering in micas. Selective sorption of K^+ by soil clays has also been observed by Keay and Wild (1961), Rich and Black (1964) and Dolcater et al. (1968). As demonstrated by optical observations in the laboratory, weathering in mica proceeds from the edges inwards (Walker, 1956, 1959; Mortland, 1958; Reed and Scott, 1962; Rausell-Colom et al., 1965; Scott and Smith, 1966; Boyle et al., 1967;

Sawhney and Voigt, 1969). Thus, partially weathered mica (illite) in soils should consist of a collapsed 10A central core and expanded frayed edges. Cations such as K^+, NH_4^+, Rb^+ and Cs^+ which produce interlayer collapse would be selectively sorbed at the frayed edges to produce more stable collapsed structure similar to that of the central core. Although selective sorption on scrolls and pits on surfaces of large mica particles has been observed using electron microscope (Raman and Jackson, 1964) and electron microprobe (LeRoux et al., 1970), it should be small compared to sorption on frayed edges of weathered micas.

Because the selectivity of frayed edges of weathered micas for K^+ and Cs^+ ions is ascribed to the ease of collapse of frayed edges and because interlayers in vermiculite also collapse on sorption of these ions, relative selectivities of the two minerals have been evaluated. Sawhney (1970) found that illite and micas had larger selectivity than vermiculite at low concentrations of K^+ and Cs^+ ions, presumably due to larger selectivity of frayed-edge sites in illite and mica than interlayer sites in vermiculite. As the concentrations increased, selectivity of illite and micas became less than that of vermiculite. At higher concentrations, as the highly selective sites of frayed edges become saturated with the cation, sorption occurs on nonselective sites in addition to the selective sites; consequently, the overall selectivity of illite and mica decreases. Although selectivity of vermiculite also decreases with increased K or Cs saturation, the decrease is less in vermiculite than in illite and partially weathered micas because of the smaller ratio of the non-selective to selective sites. The decrease in selectivity of illite for K^+ (Bolt et al., 1963; Schouwenburg and Schuffelen, 1963; Tucker, 1967b), of illite and soil clays for Cs^+ (Coleman and LeRoux, 1965; Sawhney, 1970) and of hydrobiotite for Rb^+ (Reichenback, 1968) on increased saturation with the ion is thus explained by sorption on less selective sites in addition to the highly selective frayed edges.

The higher selectivity of frayed edges than the expanded interlayers requires that as frayed edges in mica are increased by removal of the interlayer K^+, the selectivity for K^+ or Cs^+ should increase. However, when essentially all the interlayer K^+ is removed and the layers expand, the selectivity should decrease. This phenomenon has been demonstrated by LeRoux and Rich (1969), who observed that selectivity of micas for Rb^+ ions first increased on removal of interlayer K^+ and then decreased. Increased sorption of Cs^+ by soil clays of larger CEC (Sawhney and Frink, 1964), presumably due to increased weathering of mica edges, and partially weathered biotite (Sawhney,

1967a) may thus be explained by increased area of the frayed edges.

The ease of collapse of frayed edges resulting in their large selectivity for K^+ or Cs^+ ions may be due to the following forces, as illustrated in Fig. 1 for one interlayer edge, where the forces are resolved into horizontal and vertical components (as shown by arrows). First, the vertical component of the force of attraction due to the K^+ ion in the interlayer position near the frayed edge and the negative layer charge tends to bring the two ends of the frayed edge together as the cation in the forked edge moves out to be replaced by a K^+ ion. Then, the approaching K^+ ion further increases the attraction between the two ends and collapses the edge to produce the stable structure as that of the central core. Consequently, K^+ and other ions with low hydration energy would be selectively sorbed by the frayed edges of the weathered micas. Large hydrated cations, as Ca^{2+}, on the other hand, tend to keep the edges apart and prevent the formation of a stable structure as that of the core and hence, are neither selectively sorbed nor fixed.

Role of interlayer collapse in vermiculite on K^+ or Cs^+ sorption

Sorption of K^+ or Cs^+ ions by montmorillonites and vermiculites produces a collapse in their interlayers. Montmorillonites collapse to give a 12A c-axis spacing on K^+ or Cs^+ saturation while vermiculites give a 10A spacing on saturation with K^+ and 10·8A on saturation with Cs^+. When progressively larger amounts of these cations are sorbed by these minerals, in the expanded state produced by saturation with Ca^{2+}, random collapse of interlayers occurs in montmorillonite. In vermiculite, K^+ or Cs^+ sorption causes collapse in alternate layers producing regularly interstratified 10A and 15A layer sequences (Sawhney, 1967b, 1969a). A vermiculite sample from Libby gave a sharp 15A diffraction peak and its higher orders on saturation with Ca^{2+}. As the interlayer Ca^{2+} was progressively exchanged by K^+ (or Cs^+), a regularly interstratified component with a 25A spacing increased in amount while the 15A component decreased. When approximately half of the interlayer $Ca^{2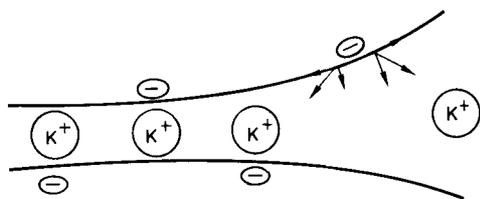+}$ was replaced by K^+ (or Cs^+), the entire sample was changed to a regularly interstratified mixture. Further sorption of K^+ (or Cs^+) produced collapse of the 15A layers within the interstratified mixture until the entire sample was converted to 10A layers. Similar layer collapse in Mg^{2+}-saturated vermiculite (Rhoades and Coleman, 1967) and in K^+-depleted micas (Weed and Leonard, 1968) has been observed. Sawhney and Norrish (unpublished) have observed that sorption of successively larger amounts of K^+ produced regular interstratification in vermiculites obtained by removal of almost all interlayer K^+ from biotite, phlogopite and biotite-vermiculite mixtures.

Conversely, the replacement of K^+ in collapsed 10A layers by Mg^{2+} or Ca^{2+} produced expansion in alternate layers (Bassett, 1959; Rausell–Colom et al., 1965; Farmer and Wilson, 1970). Bassett suggested that the removal of K^+ from one layer strengthens the K—O bonds in the adjacent layer so that K^+ removal does not occur in the adjacent but occurs in the next layer, effecting expansion of the alternate layers. Farmer and Wilson proposed that the oxidation of the Fe^{2+} ions in the two silicate layers on either side of a hydrated interlayer should lead to a stronger retention of K^+ in the two adjacent layers and consequently produce regular interstratification.

Interlayer collapse in alternate layers of vermiculite on K^+ sorption should be the reverse of the expansion of alternate layers of mica on K^+ removal. Thus, it has been hypothesized (Sawhney, 1967b; Rhoades and Coleman, 1967) that collapse in one layer of vermiculite on K^+ sorption reduces the charge density of the adjacent layer. Consequently, the bonding energy of K^+ to the silicate sheet of reduced charge is smaller than the hydration energy of the Ca^{2+} or Mg^{2+} ions, hence K^+ would not enter this layer but would enter the next layer, producing regularly interstratified layer sequences. Weed and Leonard (1968) ascribed the prevention of K^+ entry to greater hydration of the layer of reduced charge.

Although these hypotheses have been advanced to explain the expansion of alternate layers in mica on K^+ removal and the collapse of alternate layers in vermiculite on K^+ sorption, no comprehensive treatment of these changes has emerged yet and the mechanism of regular interstratification remains unclear.

Comparison of fixation of K^+ and Cs^+ by clays

Just as the fixation of K^+ and Cs^+ ions is accompanied by interlayer collapse, the release of these ions should occur by expansion of the interlayers. Thus, when micas and K^+-saturated vermiculite are exhaustively leached with solutions of cations, such as Ca^{2+} and Mg^{2+}, that produce interlayer

Fig. 1. Selective sorption of a K^+ ion in a frayed edge of a weathered mica sheet.

expansion, K^+ is replaced by these cations. Conversely, K^+ is not replaced effectively by cations, such as NH_4^+, that produce interlayer collapse in minerals (Barshad, 1948, 1950). Indeed, K^+ retained against replacement by NH_4^+ has been commonly used as a measure of K^+ fixation. Furthermore, the presence of small amounts of ions such as NH_4^+ in solutions of Ca^{2+} and Mg^{2+} salts used for extracting K^+ inhibits the release of K^+ (Scott and Smith, 1966; Wells and Norrish, 1968).

Recent observations, however, revealed that in contrast to K^+ fixed in the interlayers of vermiculite, a portion of the K^+ in illite and certain soils is more readily replaced by NH_4^+ than by Ca^{2+} or Mg^{2+} ions (Bolt et al., 1963; Rich and Black, 1964; Tucker, 1967a). As discussed above, K^+ fixed by illite and weathered micas in soil clays occupies edge-interlayer sites that are highly specific for K^+ and other similar cations. Because of the similarity of K^+ and NH_4^+ ions and the small diffusion distance from solution to these sites, NH_4^+ ions are effective in replacing K^+. Conversely, hydrated ions Ca^{2+} and Mg^{2+} are not selectively sorbed by these sites, hence they are not as effective in replacing K^+.

Fixation of Cs^+ by layer silicates appears to be similar to that of K^+ at the edge-interlayer sites of partially weathered micas and not as K^+ fixation in interlayers of vermiculite or montmorillonite. Several investigations show that K^+ and NH_4^+ ions replace Cs^+ fixed at the edge-interlayer sites as well as in the interlayer positions more readily than Ca^{2+} and Mg^{2+} ions (Schulz et al., 1960; Coleman et al., 1963; Sawhney, 1964). Similarly, Cs^+ fixed in soils and soil clays was replaced more readily by K^+ than Ca^+ (Klechkovsky et al., 1959; Schulz et al., 1960; Nishita et al., 1962; Coleman and LeRoux, 1965). Cesium ions with a smaller hydration energy than K^+ ions hold the layers together more strongly than K^+ ions so that hydrated Ca^{2+} and Mg^{2+} ions which can expand layers held by K^+ ions are ineffective in producing layer expansion in Cs^+-saturated minerals. Consequently, Cs^+ ions are not as readily replaced by these ions as are the K^+ ions. Smaller retention of Cs^+ against replacement by K^+ than Ca^{2+} or Mg^{2+} ions has been suggested to be related to interlayer distances (Coleman et al., 1963). For example, Cs^+ fixed by vermiculite or heated montmorillonite produces interlayer distances (basal spacing = 10·8A) large enough to permit K^+ ions to diffuse into the interlayers and replace the Cs^+ ions but greatly restrict the entry of hydrated Ca^{2+} or Mg^{2+} ions. Although these hypotheses appear logical, lack of precise measurements of the bonding energies of different cations and of the forces involved in interlayer collapse and expansion preclude an unequivocal explanation for the differences in the interlayer fixation of K^+ and Cs^+ ions.

Release of K^+ from naturally-occurring micas and implication in cation selectivity and fixation

Most of the K^+ in naturally-occurring hydrothermal micas is fixed in the interlayer positions and is not exchangeable, while a small portion that is present on basal surfaces is exchangeable with other cations. When micas are weathered artificially by treatment with a neutral salt solution, interlayer K^+ is slowly replaced by the cation of the neutral salt and the interlayers are expanded to form vermiculite. It has been suggested that in addition to the removal of K^+, the net negative charge on the layers also decreases during weathering (Jackson and Sherman, 1953; Raman and Jackson, 1966; Newman and Brown, 1966). Newman and Brown concluded that the changes in chemical composition of micas during weathering include the release of structural OH ions exposed on replacement of K^+ or the sorption of H^+ ions and oxidation of iron in the octahedral sheet or loss of divalent cations, resulting in the decrease in net negative charge. Brown and Newman (1970) observed that the removal of interlayer K^+ from micas also produces slight structural irregularities.

Studies of K^+ release in relation to particle size of micas (Mortland and Lawton, 1961; Reichenbach and Rich, 1969; Scott, 1968) show that initial release of K^+ from surface sites is somewhat greater in smaller particles, presumably due to the larger surface area and more surface K^+ on smaller particles. However, the total K^+ released decreases with decreasing particle size. Reichenbach and Rich showed that whereas extraction with $BaCl_2$ solution over a 5 day period replaced only about 60 me K^+ per 100g from less than $0·08\mu$ particles, the same treatment replaced about 200 me per 100g from 5 to 2μ particles. Scott also concluded that smaller particles resist the release of K^+; over 95% of K^+ was extracted from 60 to 50μ particles in 3 yr, using the extraction procedure of Scott and Smith (1966), but less than 70% of K^+ was extracted from 0·7 to $0·2\mu$ particles. Similarly, in our experiments (Sawhney and Norrish, unpublished), we found that after a 4-week treatment with $BaCl_2$ (Rich, 1968; slightly modified), 50–5μ particles of biotite and phlogopite retained about 2% and 1% K_2O respectively. An illite sample (about 1μ particle size) retained as much as 7·5% K_2O following the same treatment.

It appears that removal of interlayer K from micas proceeds from the edges inwards, leaving a stable central core as in Fig. 1. The amount of K^+ retained per unit weight is larger in smaller parti-

cles, as shown in Fig. 2 (data taken from Scott, 1968; Fig. 7). However, the number of K^+ ions retained per particle, and hence the size of the interlayer core increases with increasing particle size, as illustrated in Fig. 2. The diameter of the core was calculated from data of Scott (1968, Fig. 7), and was based on the assumptions that the particles are spherical, they initially contain 250 me K/100g, and each K^+ ion occupies 450Å^3 of interlayer space of dimensions $a = 5A$, $b = 9A$ and $c = 10A$. Over the range of particle sizes examined, the diameter of the central core does not appear to reach an upper limit. Extrapolating the data downwards to the point where the diameter of the particle and of the core are equal, it appears that the central core becomes extremely stable at a particle diameter of about 100A. The changes in configuration of electrical field which impart stability to the central core are not known, although the resistance of small particles to K^+ release may be related to better structural order in smaller particles. Smaller particles of kaolinite have been shown to be more highly ordered (Ormsby, *et al.*, 1962; Wiewiora and Brindley, 1969), though a similar relationship for illite has not been reported.

The resistance of small particles to release K^+ has important implications in cation selectivity and fixation by soil clays. Calculations from the data of Reichenbach and Rich (1969) and Scott (1968) on K^+ release by different particle size of micas reveal that the area of collapsed central core relative to the frayed edges is larger in the smaller particles. This should impart greater ease of collapse to the frayed edges in smaller particles. Con-
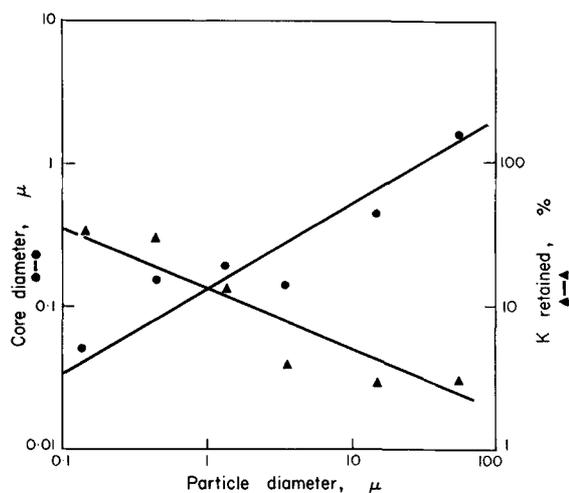
sequently, smaller particles would show greater selectivity for K^+ and similar ions, although the total capacity for fixation may be greater in larger weathered particles (Hill and Sawhney, 1969) due to greater K^+-depletion in them during weathering. The large selectivity of soils for K^+ in dilute solutions is, thus, attributed to the presence of fine partially weathered mica particles, illite, in soil clays.

Although the investigations reviewed here have described the selective sorption and fixation of K^+ and Cs^+ ions from dilute solutions, the following aspects of the reactions of these ions remain unanswered. First, the mechanism of the collapse of alternate layers in vermiculite on K^+ or Cs^+ sorption has not been unequivocally established. Second, factors that impart stability to the central core of mica particles so that K^+ extraction becomes progressively difficult are not known. And third, the inability of Ca^{2+} or Mg^{2+} ions to expand interlayers of Cs^+-saturated vermiculite in contrast to K^+-saturated vermiculite is not completely understood.

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Fig. 2. Relationship among particle size, diameter of collapsed central core and K retained by muscovite (calculated from data of Scott, 1968).

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Résumé – On passe en revue les recherches concernant la sorption sélective et la fixation de K et de cations similaires par les minéraux argileux et les argiles des sols ainsi que les recherches concernant les mécanismes de ces réactions. En particulier, des observations récentes sur la sorption sélective de ces ions en solutions diluées par les micas altérés et la vermiculite, en liaison avec les structures interfeuillets, sont discutées en détail. De même, on décrit les implications de la résistance à l'altération de petites particules de mica dans la sélectivité des sols pour le cation. En dépit d'une amélioration dans la compréhension des réactions de sorption et de fixation, les points suivants sont toujours mal éclaircis.

En premier lieu, le mécanisme de la fermeture de couches alternées dans la vermiculite lors de la sorption de K ou Cs n'a pas été établi sans équivoque. En second lieu, les facteurs qui confèrent la stabilité au noyau central des particules de mica, si bien que l'extraction de K devient de plus en plus difficile, ne sont pas connus. En troisième lieu, l'inaptitude des ions Ca ou Mg à ouvrir les espaces interfeuillets de vermiculite saturée par le Cs, ce qui contraste avec le comportement de la vermiculite saturée par le K, n'est pas complètement comprise.

Kurzreferat – Es werden Untersuchungen über die selektive Sorption und Fixierung von K und ähnlichen Kationen durch Tonminerale und Bodentone sowie die Mechanismen dieser Reaktionen überprüft. Insbesonders werden neuere Beobachtungen über selektive Sorption dieser Ionen in verdünnten Lösungen durch verwitterte Glimmer und Vermiculite in bezug auf die Zwischenschichtgefüge im Einzelnen erörtert. Ferner wird die Bedeutung der Widerstandes gegen Verwitterung kleiner Glimmerteilchen für die Kationenselektivität der Böden beschrieben. Ungeachtet des besseren Verständnisses der Sorptions-und Fixierungsreaktionen, sind die folgenden Aspekte weiter unklar.

Erstens ist der Mechanismus des Zusammenbruchs alternierender Schichten im Vermiculit bei K oder Cs Sorption nicht eindeutig festgelegt worden. Zweitens sind die Faktoren, die dem inneren Kern von Glimmerteilchen Stabilität verleihen, so dass die K-Extraktion fortschreitend schwieriger wird nicht bekannt. Drittens ist die Unfähigkeit von Ca oder Mg Ionen die Zwischenschichten von Cs-gesättigtem Vermiculit im Gegensatz zum K-gesättigten Vermiculit auszuweiten nicht ganz verständlich.

Резюме — Дан обзор исследований, посвященных селективному поглощению и фиксации К и аналогичных катионов глинистыми минералами и почвенными глинами, а также механизму подобных реакций. В частности, детально рассматриваются недавно проведенные исследо-

вания по селективному поглощению этих катионов в разбавленных растворах выветрелыми слюдами и вермикулитом с разной структурой межслоевого пространства. Стойкость к выветриванию небольших частиц слюды объясняется селективностью почв по отношению к катионам. Однако отмечается, что несмотря на все углубляющееся понимание механизма поглощения и фиксации остаются неясными следующие аспекты.

Во-первых, однозначно не установлен механизм сжатия чередующихся слоев в вермикулите в результате поглощения К или Са. Во–вторых, до сих пор не выяснены факторы, определяющие устойчивость центральных частей глинистых частиц, благодаря которым удаление К становится все более и более затруднительным. В–третьих, полностью не понята неспособность ионов Са или Mg вызывать разбухание межслоевых промежутков Сs–насыщенных вермикулитов в противоположность их действию на К–насыщенные вермикулиты.