

## Role of Minerals in Potassium Management of Indian Soils

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### Introduction

The principal K-bearing minerals in soils are potash feldspars and micas. Micas are more important than K-feldspars in supplying K to plants (Rich, 1972). Plant uptake of K is however related to the weathering of feldspars and micas in soil environments.

Following the surface reaction, the weathering of K-feldspars takes place and the K ions are replaced by hydrogen ions (Jenny, 1950). This release would be rapid with the decrease in size of the particles and would result in the formation of a K-free layer. The K-free layer, a few unit cells thick, has a high affinity for K (Nash and Marshall, 1957). This causes slower release of K from the interior of the particle because K ions have to diffuse out through this layer. Progressive release of K can take place by rupture of the Si-O-Al bonds when the mineral breaks down (Sarma, 1984). Both processes of K release are very slow reactions in natural soil environments and hence feldspars contribute very little to the soil pool of K that can be used by plants (Rasmussen, 1972).

In micas, large unhydrated K ion is held in the ditrigonal cavities of the basal plane of oxygens of the tetrahedral sheets by electrostatic bonds. This keeps the layers collapsed. It is generally understood that the release of interlayer K is the replacement of the unhydrated K ions by the hydrostable cations and the reaction proceeds inward from the edge of the platy mica particles (Sarma, 1984). The process may also take place at fissures and defects on the planar surfaces of the mineral (Reichenbach, 1972). Trioctahedral micas lose their K by weathering more easily than dioctahedral micas (Mortland *et al.*, 1957). This may be applicable to biotite with its content of structural  $\text{Fe}^{2+}$ ,

but the iron free mineral phlogopite also weathers more rapidly than muscovite (Arnold, 1960). It was observed by Serratos and Bradley (1958) that the proton of OH in trioctahedral micas is repelled equally by all the three octahedral cations, and lies on the normal to the basal plane, directed towards the interlayer space. In dioctahedral micas the proton is attracted to the vacant octahedral site and is displaced to one side of the normal. Bassett (1960) concluded that the K in trioctahedral micas is repelled to a certain extent by the proton, and is, therefore, in a less electronegative environment than K in dioctahedral micas. As a result, K in dioctahedral mica is held more strongly than in trioctahedral micas. However, the importance of the presence of mica should only be realized in terms of their actual K release potential.

### **Potassium Release, Adsorption Reactions and Mineralogy**

The most important factor that controls the rate of release of K from micas into solution is the concentration of K in solution. Muscovite is extremely sensitive to potassium concentration in soil solution and may not release K into dilute electrolyte solutions containing as little as 1 ppm K (Rausell-Colom *et al.*, 1965). In view of this experimental observation any attempt to relate K release reaction of Indian soils without ascertaining the nature and composition of soil micas may not be adequate enough to establish a relation between crop response to K fertilizers and nature of soil micas (Pal *et al.*, 2000).

Regarding the K adsorption/fixation reaction of Indian soils, it was often reported in the literature that micas, hydrous micas and vermiculites have high adsorption/fixation properties, and smectites and kaolinites have low capacities. However, if mica is understood a mineral that does not expand on being saturated with divalent cations, it is difficult to understand how it can adsorb/fix added K (Sarma, 1976). In such reactions interlayer charge density of the mineral is of fundamental importance. Kaolinites are of no significance in such a reaction while vermiculites will be converted to mica by layer contraction due to K. Smectites would not possess this property as their layer charge is too low (Brindley, 1966) and they do not adsorb K selectively (Rich, 1968) unless the charge density is high (Pal and Durge, 1989).

Research work in India on the fundamental aspects of K release and adsorption/fixation reactions in relation to the mineralogy of soils took momentum during 1985 to 2001 (Subba Rao and Srinivasa Rao, 1996; Srinivasa

Rao *et al.*, 2001). However, the first hurdle was in proper identification, let alone quantitative estimation of K-bearing soil minerals. In the following, a review has been attempted on the research results, hitherto, obtained to highlight the role of minerals that control the K release and adsorption/fixation reactions, so important and fundamental in potassium management of Indian soils.

**Fine-Grained Micas in Indian Soils:** The role of K-bearing minerals in releasing K from their reserve/non exchangeable fraction of Indian soils is well established (Dhillon and Dhillon, 1990; Srinivasa and Khera, 1994; Srinivasa Rao *et al.*, 1994, 1998, 2000). The prime K-bearing minerals in major soils (alluvial, black and ferruginous soils) of India are micas that are concentrated mainly in their silt and clay fractions (Ghosh and Bhattacharyya, 1984; Pal and Durge, 1987, 1989, 1993; Pal *et al.*, 1993; Pal *et al.*, 2000). Despite this favourable natural mineral endowment, crop response to K fertilizers in many of these soils has been anomalous (Pal and Durge, 1987; Pal *et al.*, 1993, 2000). Both di- and trioctahedral micas which are mainly biotite and muscovite are very common in these soils (Kapoor *et al.*, 1981; Pal *et al.*, 1987; Pal and Durge 1987; Pal *et al.*, 1993, 2000). Thus the release of K from fine-grained micas of soils are expected not to be similar because they are far from 'ideal' in structure and composition. Zones in a particle may contain layer minerals in different stages of expansion as demonstrated recently by Pal *et al.*, (2000, 2001). Therefore, many of the proposed relationships between K release and micas are based on results obtained from specimen micas and not from soil micas and thus they are speculative (Rich, 1972; Sarma, 1984; Wilson, 1999).

**Release of K from Soil Micas:** Release of K from biotite is accompanied by concomitant changes in the mica particles (Kapoor *et al.*, 1981; Pal *et al.*, 1987; Pal and Durge, 1989). With progressive and preferential weathering of biotite, clay size mica attains a character of both di- and trioctahedral micas in soils of semi-arid climates, and a muscovite in soils of tropical humid climates (Pal *et al.*, 1987). During weathering, biotite particles alter not only to dioctahedral vermiculite and smectite (Pal *et al.*, 1987), but also to trioctahedral vermiculite and smectite (Pal *et al.*, 1987, 1989). Similar observations were also made by several researchers for both dioctahedral (Kerns and Mankin, 1967; Robert, 1973; Stoch and Sikora, 1976; April *et al.*, 1986; Fritz, 1988; Taboada and Garcia, 1999) and trioctahedral (Nettleton *et al.*, 1970; Kapoor, 1972a; Wilson, 1973; Rebertus *et al.*, 1986) weathering products. However, these are not in accordance to the general understanding (Douglas, 1989) that trioctahedral vermiculite is an alteration product of biotite

whereas dioctahedral vermiculite and smectite are derived from muscovite (Churchman, 1980; Aoudjit *et al.*, 1995), suggesting that muscovite does weather to 2:1 expansible minerals in soil environments. However, this is contrary to the observations of Rausell-Colom *et al.* (1965) who demonstrated an extreme sensitivity of muscovite mica to K in solution to the extent that muscovite may not release any K into even very dilute electrolyte solutions. Kapoor (1972a) observed that the K released from the weathering of biotite can inhibit the weathering of muscovite when two micas co-exist in soils. The sensitivity of muscovite has an important bearing on the persistence of dioctahedral micas during weathering process (Sarma, 1976) and may prove muscovite to be useless as a source of K in soils (Pal *et al.*, 2000).

**Nature of Soil Micas:** So far attempts made in highlighting the precise nature of soil mica in the silt and clay fractions of Indian soils have been based on the X-ray intensity ratio of peak heights of 001 and 002 basal reflections of mica (Kapoor *et al.*, 1981; Goswami *et al.*, 1986; Pal *et al.*, 1987; Pal and Durge, 1987, 1993). The ratio is greater than unity in the silt and clay fractions of major soils of India (**Table 1**). However, in soils of Brahmaputra alluvium (BA) and black soils in alluvium of weathering Deccan basalt, this ratio is close to unity in their clay fractions in particular. The ratio >1 suggests the presence of both muscovite and biotite minerals. If muscovite minerals were present alone the ratio would have been very close to unity (Tan, 1982). In the event of a mixture of these two micas, both will contribute to the intensity of the 10A° reflections, whereas contribution of biotite to the 5A° reflection would be nil or negligible, thus giving a higher value to the intensity ratio of these reflections (Kapoor, 1972b). According to this criterion, silt fractions of alluvial soils of Indo-gangetic plains (IGP) and BA, ferruginous and black soils and also the clay fractions of soils of IGP and ferruginous soils contain both muscovite and biotite. But the clay fractions of soils of BA and black soils are more muscovitic in character (**Table 1**). The enrichment of soils with muscovite is not favourable so far as the K release and available K status are concerned. This is evidenced with the reduced rate of K release from black soils and soils of BA against much higher rate of K release from soils of IGP and ferruginous soils when they were subjected to repeated batch type of Ba-K exchange (Pal *et al.*, 2001).

**Examination of Soil Micas Under Microscope:** In view of the diversity in the understanding of the weathering of muscovite in soil environments, it became essential to examine the weathering features of muscovite and biotite micas as they co-exist in soil environments under scanning electron microscope

**Table 1. X-ray intensity ratio of the peak heights of 001/002 basal reflection in the silt and clay fractions**

Benchmark Soil/Soil Series	Parent material	Size fractions	
		50-2 mm	<2 mm
Holambi (AS-SA) ** (Udic Ustochrept)	IGP*	2.14	2.63
Hissar (AS-SA) (Typic Ustochrept)	IGP	2.05	2.57
Totpara (AS-SH) (Aeric Fluvaquent)	IGP	2.27	2.73
Kanagarh (AS-SH) (Udic Ustochrept)	IGP	1.48	1.60
Dahotia (AS-PH) (Typic Haplaquept)	BA	1.47	1.10
Akahugaon (AS-PH) (Typic Haplaquept)	BA	1.70	1.04
Aroli (BS-SH) (Typic Chromustert)	DBA	1.80	1.05
Nimone (BS-SA) (Typic Chromustert)	DBA	1.90	1.00
Kasireddipalli (BS-SA) (Typic Pellustert)	DBA	1.56	1.04
Kheri (BS-SH) (Typic Chromustert)	DBA	1.87	1.01
Sarol (BS-SH) (Typic Chromustert)	DBA	1.50	1.04
Patancheru (FS-SA) (Udic Rhodustalf)	GG	1.77	1.80
Nalgonda (FS-SA) (Udic Rhodustalf)	GG	2.00	1.87
Dyavapatna (FS-SA) (Udic Rhodustalf)	GG	2.25	2.16

\* IGP=Indo-Gangetic alluvium; DBA-Deccan basalt alluvium; GG=Granite-gneiss

\*\* AS-SA = Alluvial soil of semi-arid climate; AS-SH =Alluvial soil of sub-humid climate; AS-PH = Alluvial soil of per-humid climate; BS-SH = Black soil of sub-humid climate; BS-SA = Black soil of semi-arid climate; FS-SA = Ferruginous soil of semi-arid climate.

Source: Division of Soil Resource Studies, NBSSLUP, Nagpur.

(SEM) (Pal *et al.*, 2000, 2001). Petrographic examination of sand fractions of major soils of India confirmed the presence of muscovite and biotite in soils

of BA and IGP and also in black soils. Muscovite particles were very rare in ferruginous soils. In soils of IGP and BA, muscovite was more common than biotite. In black soils amounts of micas were low as compared to the other two soils and biotite was more common than muscovite (Pal *et al.*, 2001). SEM examination of micas by Pal *et al.* (2000, 2001) indicated that irrespective of soil type biotite generally occurred as thick particles with different stages of layer separation. They are weathered with layer separations and bending at their edges. At the edges of these particles, layer separation indicated the formation of a vermiculite rim around the particles as a result of replacement of interlayer K of biotite. In contrast, the replacement of interlayer K of muscovite was not substantial as evident from a general lack of interlayer opening. Pal *et al.* (2001) however demonstrated weak to moderate layer separation at the edge of muscovite in some soils. Pal *et al.* (2001) was of the opinion that minor layer separation in muscovite is due to alteration prior to pedogenesis. Lack of interlayer opening in general indicates that weathering of muscovite was almost inhibited in the presence of biotite. Srivastava *et al.* (1998) also indicated similar observations in soils of IGP. Pal *et al.* (2001), however, was of the opinion that minor layer separation in muscovite observed by them and elsewhere (Sidhu and Gilkes, 1977) needed some explanation.

**Weathering of Muscovite in Soil Environments:** In order to confirm the feasibility of K release from muscovite in soil environments towards the formation of dioctahedral 2:1 expansible minerals, the repeated batch type Ba-K exchange experiments were carried out on mixtures of specimen muscovite and biotite by Pal *et al.* (2001). The result of the Ba-K exchange reaction indicated that the X-ray intensity ratio of peak heights of 001 and 002 basal reflections of muscovite remained constant before and after the experiments, indicating that mica remaining was still muscovite. However, in alluvial soils of sub-humid and per-humid climate, mica transformed to dioctahedral vermiculite and smectite (Pal *et al.*, 1987). It may be thus argued that these 2:1 minerals can also be the weathering products of muscovite as suggested by many researchers (Robert, 1973; Churchman, 1980; Aoudjit *et al.*, 1995; Taboada and Garcia, 1999). Pal *et al.* (1987) however demonstrated that mica altered to dioctahedral vermiculite and smectite in alluvial soils of humid climates even when the 001/002 ratio of mica in their clay fractions is >1. These authors concluded that the dioctahedral expansible minerals are the alteration product of biotite mica as the formation of both di- and trioctahedral 2 : 1 expansible minerals are possible from biotite (Fanning and Keramidas, 1977). Thus the results obtained by Pal *et al.* (2001), therefore question the weatherability of muscovite in soil environments of India. This



also explains the existence of almost unweathered muscovite in advanced acid tropical weathering conditions in bauxitic laterite (Anand and Gilkes, 1987) and also in high alkaline conditions (Pal, 1985). Many reports on the formation of dioctahedral 2 : 1 expansible minerals from muscovite indicate the transformation in experiments conducted either at elevated temperature or at both elevated temperature and pressure, much higher than those of soil environments (White, 1954, 1956; Reichenbach and Rich, 1968, 1969; Tomita and Sudo, 1971; Wilson, 1999). Therefore, it can be concluded that the expanded layer separation observed in muscovites of soils may not be pedogenic (Pal *et al.*, 2001).

### **Soil Type, K Release and Crop Response to K Fertilizers**

**Alluvial soils:** Crops in micaceous alluvial soils of the semi-arid and sub-humid climates seldom respond to K fertilizers even under continuous cropping over long periods of time (Pal and Mondal, 1980) whereas in soils of the per-humid climate, crops do respond (Roy *et al.*, 1978). Following the repeated batch type exchange of Ba-K, a considerable amount of K was released by the silt and clay micas of three benchmark soils namely Holambi, Kanagarh and Dahotia. The K release from soil mica, however, increased with a decrease in particle size (Pal and Durge, 1989), a trend not in accordance with those of specimen micas (Reichenbach, 1972; Reichenbach and Rich, 1969; Pal, 1985), because the K release mainly occurred by edge weathering. With the higher number of extractions, the K release continued from biotite micas of Holambi and Kanagarh soils while in Dahotia soils, K release became almost nil after the first few extraction because of the muscovitic character of mica. The crop response to K fertilizer in Dahotia soils of per-humid climates indicates the uselessness of muscovite for K reserve in soils, and thus justifies the crop response to K fertilizer treatments. On the other hand, enormous K release by biotite in other two soils is the reason for seldom crop response to K fertilizer. Due to the presence of biotite, alluvial soils of the Indo-Gangetic Plains have a favourable rate of K replenishment even under intense cropping (Srinivasa *et al.*, 1994).

**Shrink-swell soil:** Vertisols appear to be adequately supplied with K and therefore responses to applied K are rarely observed (Finck and Venkateswarlu, 1982). The Vertisols developed in the alluvium of the Deccan basalt are dominated by smectite minerals and contain very small amount of sand and silt-size biotite and muscovite, and clay size muscovite (Pal and Deshpande,

1987; Pal and Durge, 1987). The silt mica consists of both muscovite and biotite whereas the coarse clay (<2 mm) mica is dominated by muscovite (**Table 1**, Pal and Durge, 1989). The sand and silt-size biotite, even though present in small amount, could be the major contributor to K release in these soils and soil K supply would be limiting after the exhaustion of soil available K (Pal *et al.*, 2000) because of their low mica content, biotite in particular (Pal and Durge, 1987).

**Ferruginous soils:** The predominance of kaolinite followed by illite keeps the nutrient holding capacity of ferruginous soils of the southern Peninsular India low and therefore application of balanced fertilizers including K is generally recommended. However, in many of these soils, crops do not respond to K fertilizer application (Ghosh and Biswas, 1978; Rego *et al.*, 1986). This suggests that these soils contain sufficient biotite mica that escaped the advanced stage of tropical weathering and are releasing the K to plants as and when necessary. Paleopedological studies demonstrated that the ferruginous soils are relict paleosols of polygenetic nature. As a result of climatic change from tropical humid to semi-arid during the Plio-Pleistocene transitional period, the upper layers of the soils of the preceding tropical humid climate were truncated by multiple erosional cycles. This exposed the relatively less weathered lower layer wherein considerable amount of unaltered biotite particles remained in the sand and silt fractions (Pal *et al.*, 1989; Srinivasa Rao *et al.*, 1997). Many of the proposed relationships between K release and mica particle size hitherto obtained either with soil mica or specimen mica may not, therefore, be valid in these polygenetic soils (Pal *et al.*, 1993). The cumulative amounts of K release from different size fractions of two benchmark ferruginous soils namely Patancheru and Nalgonda, indicated a fairly high rate of K release (Pal *et al.*, 1993). The observed data indicated a contrasting particle size-K release relationships between the silts and clays since K release increased with the decrease in clay particle but also increased with the increase of silt-size mica (**Table 2**). The zones in clay micas are at different stages of expansion (Pal *et al.*, 2001); and under such circumstances K release would occur mainly by edge weathering as evident from increased K release with the decrease in mica particle. On the other hand, because of almost unaltered silt biotites with more number of elementary layers (Pal *et al.*, 2001), K release increased with the increase in particle size of silt mica. Such relationship is normally obtained with specimen mica (Reichenbach, 1972; Reichenbach and Rich, 1969; Pal, 1985). Thus quite favourable K release rate from both silt and clay micas amply explains why crop response to K fertilizers is seldom obtained in many of these soils.



**Table 2.** The data of K release from and adsorption by various size fractions of ferruginous soils (Patancheru and Nalgonda) of southern India

Size fractions	Cumulative K release* (mg/100g of mica)		Adsorption of added K (mg/100g)**	
	Patancheru	Nalgonda	Patancheru	Nalgonda
50-20 mm	112	450	16	37
20-6 mm	70	182	36	44
6-2 mm	88	198	60	62
2-0.6 mm	101	134	128	133
0.6-0.2 mm	279	287	90	108
<0.2 mm	413	468	90	16

\* Following repeated batch type Ba-K exchange

\*\* K added was 0.1 mg/g of silt fractions and 0.2 mg/g of clay fractions

(Source : Pal *et al.*, 1993).

### Soil Type, K Adsorption/Fixation and Mineralogy

Schwertmann (1962) indicated that some soil smectites have a greater capacity to fix K than do many of the specimen type smectites. Bajwa (1980) pointed out that beidellite soil clays are greater fixers for added K followed by vermiculite clays, and fixation is not appreciable in clays consisting of montmorillonite. The fine clay smectites of benchmark Vertisols of central and western India is nearer to montmorillonite of the montmorillonite-nontronite series (Pal and Deshpande, 1987) and do not adsorb K selectively (**Table 3**) because of their low charge (Pal and Durge, 1987). However, the observed low K adsorption in these smectites is due to presence of vermiculite. This indicates that K loss due to adsorption/fixation in shrink-swell soils is very less. In contrast to the low charge dioctahedral smectite of shrink-swell soils, high charge trioctahedral smectites of some alluvial soils do adsorb K selectively (**Table 4**). These smectites expand to 17Å° on glycolation but contract readily to 10Å° on K saturation at 25°/110°C indicating their high layer charge density. Hence these minerals could be smectites of high charge density or vermiculite of low charge density (Pal *et al.*, 1989).

In the absence of vermiculite the observed K adsorption by various silt and clay fractions of ferruginous soils (**Table 2**) was thus attributed to soil smectite (Pal *et al.*, 1993). However, this fact is in contrast to the behaviour of dioctahedral smectite of the soil clays (Pal and Durge, 1987), is due to the

**Table 3. Adsorption of K in different size fractions of Vertisols**

Soil Series	Adsorption of added K (mg/100g)		
	Silt (50-2 mm)*	Coarse clay (2-0.2 mm)	Fine clay (<0.2 mm) **
Aroli	35	16.0	30.0
Sarol	4.5	23.0	25.0
Kasireddipalli	3.0	10.0	25.0
Nimone	13.0	20.0	28.0
Kheri	5.0	31.0	28.0

\* 0.25 mg K added per g of silt; 0.50 mg K added per g of coarse and fine clay, \*\* Fine clay smectites did not adsorb added K in proportion to their high amount indicating their no K-selectivity. (Source: Pal and Durge, 1987).

**Table 4. Adsorption of K in different size fractions of alluvial soils of IGP and BA**

Size fractions	Adsorption of added K (mg/100g)*		
	Holambi (IGP)	Kanagarh (IGP)	Dahotia (BV)
20-6 mm	6.6	9.7	0.5**
6-2 mm	11.8	19.1	1.0
2-0.6 mm	30.4	52.9	26.4
0.6-0.2 mm	45.5	63.7	31.0
<0.2 mm	67.7	79.3	50.0

\* K added 1 mg per g of silt and 2 mg per g of clay fractions, \*\*Showing high K selectivity of smectite. (Source: Pal and Durge, 1989).

presence of high charge trioctahedral smectite of the silt and clay fractions. The fine clay (< 0.2mm) dominated by low charge dioctahedral smectite did not however participate in the adsorption reaction. This then suggests ferruginous soils may have very less problem of K fixation (Pal *et al.*, 1993).

## Conclusions

Review on the role of minerals in potassium management of Indian soils indicates that weathering of muscovite in presence of biotite is improbable. Therefore, the quantity of muscovite can not be used as an index of K reserve in soils wherever biotite and muscovite occur together in soil environments. Crop response to K fertilizers will depend on the biotite reserves in various soil size fractions.

The adsorption/fixation of K is related to vermiculite and other 2:1 expansible minerals of high charge density like high charge di- and trioctahedral smectite or low charge di- and trioctahedral vermiculite. The detailed characterization and quantification of 2 : 1 expansible minerals are still needed to make judicious application of K fertilizers in different soil types.

### Perspectives

In view of ever continuing large import of K fertilizers to meet the domestic K requirements, a selective quantification of biotite mica is common situation in soils containing mixtures of biotite and muscovite could be an effective tool to examine the status of stock of K in soils. This information would be used to dictate the K fertilizer requirement in various soils of India. This will also help in making projection for K fertilizer production in future (Pal *et al.*, 2001).

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