

Role of weathering of fine-grained micas in potassium management of Indian soils

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Abstract

Although the major soils of India (alluvial, ferruginous and black soils), endowed with fine-grained micas, are known as natural K suppliers to plants, crop response to K fertilizer treatment has been anomalous. The silt and clay fractions of 14 benchmark soils were subjected to repeated batch type Ba–K exchange to study the rate of K release. The significant positive correlation between cumulative K release in 25 extractions and X-ray intensity ratio of peak heights of the 001 and 002 basal reflections of mica in the silt ($r = 0.629$ at 1% level) and clay ($r = 0.729$ at 1% level) suggested that although the fine-grained muscovite and biotite co-exist in soils, the rate of K release and crop response to K are related primarily to the presence of biotite only while muscovite remains as an inert source of K in soils justifying the crop response to K fertilizers.

Soil micas under a scanning electron microscope (SEM) indicated that biotite particles were generally thick, showing layer separation with bending at edges due to the formation of vermiculite around their rims. The muscovites, on the other hand, were characterized by very minor layer separation at their edges. To resolve the issue of layer separation of micas through the release of K during the formation of soils, experimental studies of repeated Ba–K exchange were conducted with specimen muscovite and biotite and also on the mixture of the two micas. Experimental studies indicated that at ambient temperature and pressure, muscovite released negligible amount of K from its exposed surfaces and the weathering of muscovite was inhibited in the presence of biotite. This confirmed the observation that when muscovite and biotite co-exist, muscovite hardly weathers in soil environments. Hence, its enrichment in soils does not enhance the supply of K. Therefore, weathering products like di- and trioctahedral vermiculite and smectite are generally the products of the weathering of biotite mica.

The X-ray intensity ratio of 001 and 002 basal reflections of mica has been found to be an effective diagnostic parameter to find out the quality of mica and therefore to judge the K releasing potential of soils. However, actual quantification of fine-grained biotites of soils appears to be mandatory for the precise determination of K reserves in soils in order to predict release of K for sustainable K management. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fine-grained micas; Muscovite; Biotite; Vermiculite; Smectite; K-management

1. Introduction

Alluvial, black and ferruginous soils cover the major part (> 60%) of the total geographical area of

India. Next to nitrogen and phosphorus, potassium is the limiting element in Indian soils. Research endeavours on K have failed to achieve momentum over the past few decades due to the general impression that, except for highly weathered ferruginous soils, most Indian soils are well supplied with K and for most crops, there is a little need for K fertilizers

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(Sekhon and Ghosh, 1982). Although widespread responses to K fertilizer have been noticed (Sekhon and Ghosh, 1982) due to intensive agricultural activities during 1970–1980, comprehensive information on crop response to K fertilizers has not been available. In subsequent years, it was observed that crops do not respond to K fertilizers in many of these soils even over a long period of time (Pal and Mondal, 1980; Pal and Durge, 1987; Ghosh and Biswas, 1978; Rego et al., 1986).

The prime K-bearing minerals in 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). Despite this favourable natural mineral endowment, crop response to K fertilizers in many of these soils has been anomalous (Pal and Durge, 1987, 1989; Pal et al., 1993). Both di- and trioctahedral micas, which are mainly muscovite and biotite, are very common in these soils (Kapoor et al., 1981; Pal et al., 1987; Pal and Durge, 1987; Pal et al., 1993). Lack of crop response to K fertilizers has been ascribed to the rapid release of K from biotite, whereas response to K has been attributed to the much reduced rate of K release of mica with muscovitic character (Pal and Durge, 1993).

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-sized mica attains a character of both di- and trioctahedral micas in soils of semi-arid climates, and a muscovitic character 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 of biotite. However, these are contrary to the general understanding (Douglas, 1989) that trioctahedral vermiculite is an alteration product of biotite, whereas dioctahedral vermiculite and smec-

tite 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 not in accordance with the experimental 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 K into even 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 processes (Sarma, 1976) and may prove muscovite to be useless as a source of K in soils (Pal and Durge, 1989).

So far, attempts made in highlighting the precise nature of 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). In view of the diversity in the understanding of the weathering of muscovite in soil environments, it is imperative to examine the weathering features of muscovite and biotite micas as they co-exist in soil environments under the scanning electron microscope (SEM). In order to gain precise understanding of the relative weatherability of muscovite and biotite when they co-exist in soils, experimental studies of K release from a mixture of specimen muscovite and biotite are also warranted. It is hoped that despite the complexity of soil micas (Rich, 1972; Wilson, 1999), the present work will be of value to relate the weathering of micas to K management not only to soils in India but also to soils elsewhere that largely depend upon imports of K fertilizers to meet their domestic K requirements.

2. Materials and methods

The present study is based on 14 benchmark soils and identified soil series representing alluvial, black and ferruginous soils that have developed from various parent materials and are spread in different agro-climatic zones of the country (Table 1). Soil

Table 1

Soil type, location, climate, parent material and selected properties of the soils

Benchmark soil/soil series	State	Parent material	Bio-climatic zone	Texture	Soil reaction (pH 1:2)	Available K (mg/100 g)	Cumulative K release in 25 extractions (mg/100 g)	Crop response to K fertilizer
<i>Alluvial Soils (AS)</i>								
Holambi ^a (Udic Ustochrept)	Delhi	Indo-Gangetic alluvium (IGP)	Semi-arid (SA)	Sandy clay loam	Alkaline	10.0	17.5	No ^{b,c}
Hissar ^b (Typic Ustochrept)	Haryana	Indo-Gangetic alluvium	Semi-arid	Sandy clay loam	Alkaline	45.0	45.0	No ^{b,c}
Kanagarh ^d (Aeric Fluvaquent)	West Bengal	Indo-Gangetic alluvium	Sub-humid (SH)	Silty clay loam	Neutral	15.0	18.5	No ^{b,c}
Totpara ^b (Udic Ustochrept)	West Bengal	Indo-Gangetic alluvium	Moist sub-humid (MSH)	Sandy clay loam	Neutral	15.0	20.0	No ^{b,c}
Dahotia ^a (Typic Haplaquept)	Assam	Brahmaputra alluvium (BA)	Per-humid (PH)	Loam	Acidic	0.3	0.6	Yes ^{b,c}
Akahugaon ^a (Typic Haplaquept)	Assam	Brahmaputra alluvium	Per-humid	Clay	Acidic	0.3	0.8	Yes ^{b,c}
<i>Black Soils (BS)</i>								
Aroli ^e (Typic Chromustert)	Maharashtra	Deccan basalt alluvium	Sub-humid	Clay	Alkaline	16.2	5.0	No, for initial 3 years ^e
Nimone ^d (Typic Chromustert)	Maharashtra	Deccan basalt alluvium	Semi-arid	Clay	Alkaline	25.2	7.5	No, for initial 3 years ^e
Kasireddipalli ^d (Typic Pellustert)	Andhra Pradesh	Deccan basalt alluvium	Semi-arid	Clay	Alkaline	12.0	4.0	No, for initial 3 years ^e
Kheri ^d (Typic Chromustert)	Madhya Pradesh	Deccan basalt alluvium	Sub-humid	Clay	Neutral	15.0	3.0	No, for initial 3 years ^e
Sarol ^d (Typic Chromustert)	Madhya Pradesh	Deccan basalt alluvium	Sub-humid	Clay	Neutral	27.5	5.0	No, for initial 3 years ^e
<i>Ferruginous Soils (FS)</i>								
Patancheru ^d (Udic Rhodustalf)	Andhra Pradesh	Granite–gneiss	Semi-arid	Loamy sand	Acidic	7.0	8.0	No ^{f,g}
Nalgonda ^f (Udic Rhodustalf)	Andhra Pradesh	Granite–gneiss	Semi-arid	Sandy loam	Acidic	15.0	17.5	No ^{f,g}
Dyavapatna ^f (Udic Rhodustalf)	Karnataka	Granite–gneiss	Semi-arid	Loamy sand	Acidic	3.0	5.0	No, for initial 4 years ^{f,g}

^aPal et al. (1987).^bPal and Durge (1993).^cPal and Durge (1989).^dMurthy et al. (1982).^ePal and Deshpande (1987).^fPal and Durge (1996).^gPal et al. (1993).

type, location, climate, parent material and selected properties of these soils are given in Table 1.

Sand (2000–50 μm), silt (50–2 μm), and clay fractions (< 2 μm) of fine earth were separated after dispersion according to the size segregation procedure of Jackson (1979).

2.1. K release study of soils

Available K was obtained on 25 g of soil (< 2 mm) from 0–40 cm depth using a 0.1N BaCl_2 solution. Fifty milliliters of 0.1N BaCl_2 solution was added to the soil, contained in a 250-ml polypropylene bottle. The stoppered bottles, after thorough shaking, were placed in an oven at 35°C. After a reaction period of 3 days, the samples were centrifuged to a clear supernatant liquid that was removed and analysed for K. A fresh 50-ml 0.1N BaCl_2 solution was added to the soil and the process was repeated 25 times. The K released from each soil was expressed in mg K/100 g soil.

2.2. K release study of various size fractions of the specimens muscovite and biotite

Mica samples were obtained from Wards Natural Science Establishment (Rochester, New York). Muscovite (from Imperial County, CA) and biotite (from near Bancroft, Ontario, Canada) were ground in a blender and separated to particle size fractions of 100–50, 50–20, 20–6 and 6–2 μm equivalent spherical diameter by the method of Tanner and Jackson (1947).

One hundred milligrams of each fraction of each of muscovite and biotite was placed in the polypropylene centrifuge tubes and 10 ml of 0.1N BaCl_2 solution was added to each tube. The stoppered tubes, after shaking, were placed in an oven at 35°C. After reaction for 3 days, the samples were centrifuged to a clear supernatant liquid that was removed and analysed for K. A fresh 10-ml 0.1N BaCl_2 solution was added. This treatment was repeated 35 times. The released K of each fraction was expressed in mg K/100 g of mica.

One hundred milligrams of mica containing 50 mg of each fraction of muscovite and biotite was placed in the polypropylene centrifuge tubes and 10 ml of 0.1N BaCl_2 solution was added to each tube. The rest of the procedure was the same as above. A fresh 10-ml 0.1N BaCl_2 solution was added and this treatment was repeated 35 times. The total content of K in the biotite specimen was determined according to the method of Jackson (1958).

2.3. Qualitative and quantitative mineralogy

The silt and clay fractions were subjected to X-ray diffraction (XRD) analysis of the parallel-oriented Ca/K-saturated samples with a Philips diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation and a scanning speed of $2^\circ 2\theta/\text{min}$. Clay minerals were identified according to the procedure outlined by Jackson (1979). Semi-quantitative estimates of clay minerals in the silt and clay fractions were made following the principles outlined by Gjems (1967) with some modifications suggested by Kapoor

Table 2

Semi-quantitative estimates of clay minerals (%) of representative alluvial, black and ferruginous soils

Soils	Silt fraction (50–2 μm)								Clay fraction (< 2 μm)							
	M ^a	ML	V	Ch	S	K	Q	F	M	ML	V	Ch	S	K	Q	F
Holambi (AS of SA part of IGP)	23	5	5	5	Nil	5	27	30	54	6	6 ^T	5	14 ^T	5	5	5
Kanagarh (AS of SH part of IGP)	35	5	8	8	Nil	8	20	16	21	Nil	23 ^D	6	37 ^D	13	Trace	Trace
Dahotia (AS of PH part of BA)	20	Nil	5	Nil	Nil	15	50	10	23	9	21 ^D	5	Nil	36	6	Trace
Kasireddipalli	10	5	5	5	5	5	45	20	8	Nil	8 ^T	12	54 ^D	12	6	Trace
(BS of SA part of southern India)																
Patancheru	16	5	8	Nil	9	7	35	20	10	13	5 ^T	Nil	42 ^D	30	Trace	Trace
(FS of SA part of southern India)																

^aM = mica (a mixture of muscovite and biotite), ML = 10–14 Å minerals, V = vermiculite, Ch = chlorite, S = smectite, K = kaolinite, Q = quartz, F = feldspars, T = trioctahedral, D = dioctahedral.

(1972a) and are presented in Table 2. Information about the chemical structure of the clay fractions was obtained by examination of the (060) reflections and also by other diagnostic chemical methods (Harward et al., 1969; MacEwan and Wilson, 1980). After identification under the petrographic microscope, the sand-sized muscovites and biotites were picked up and fixed on an aluminium stub with LEIT-C con-

ductive carbon cement, coated with gold and examined under Philips SEM.

3. Results

The soils of the IGP are neutral to alkaline and have fairly high available K status, whereas those of

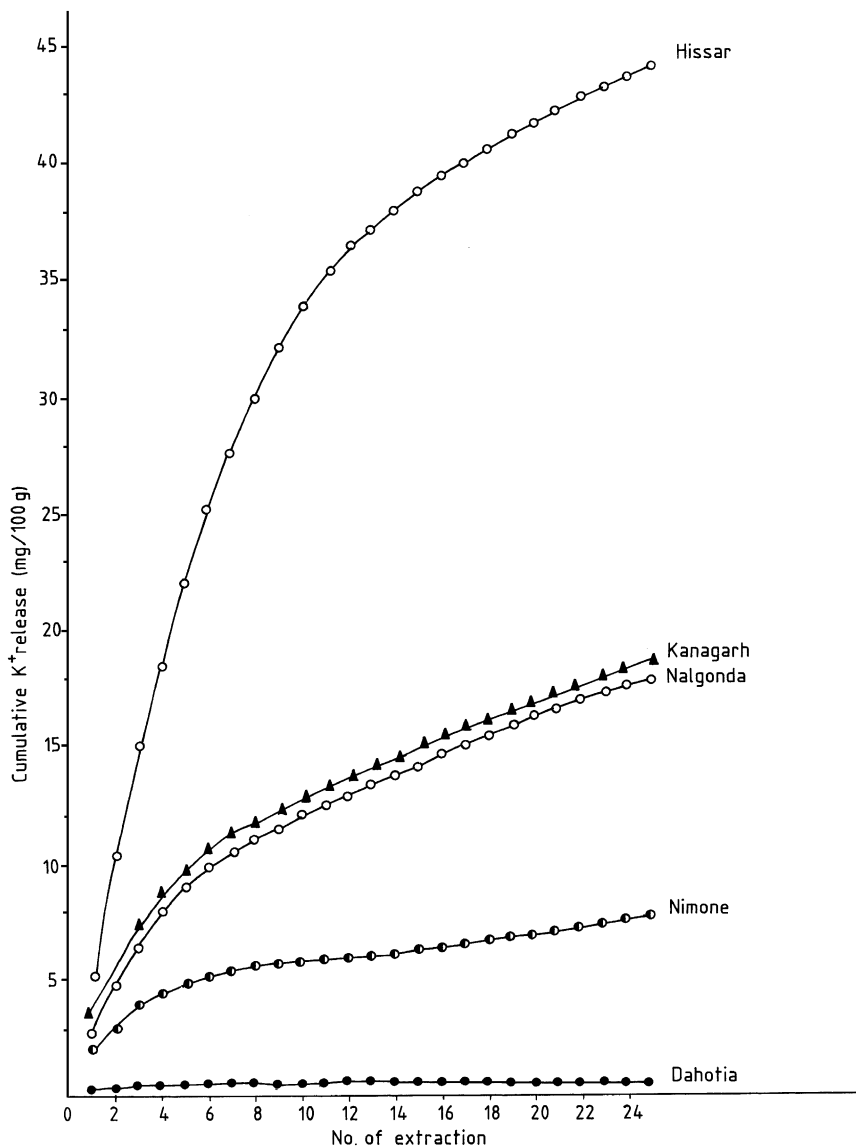


Fig. 1. Relation between cumulative K release of soils and number of extractions: Hissar, representative of IGP soils of SA climate; Kanagarh, representative of IGP soils of SH climate; Dahotia, representative of BA soils of PH climate; Nimone, representative of black soils of SA climate; Nalgonda, representative of ferruginous soils of SA climate.

the BA are acidic and have very low available K. Crops do not respond to K fertilizers in the former soils while they respond to the latter (Table 1). Black soils developed in alluvium of the Deccan basalt are neutral to alkaline and also have a high available K status. Despite a high level of K, crops respond to K fertilizers after 3 years of cropping (Table 1). Ferruginous soils developed on granite–gneiss are slightly acidic and have a moderate amount of available K. Crops do not, however, respond to K fertilizer application in these soils.

In order to assess the ability of these soils to release non-exchangeable K, an experimental study of Ba–K exchange was conducted. The cumulative amount of K released from 14 soils varied among them and also within the soil groups (Table 1). Soils of IGP released the highest amount of K. It ranged from 17.5 to 45.0 mg K/100 g soil. Black soils released 3.0–7.5 mg K/100 g only even though their available K status is high. Despite their advanced stage of weathering in a tropical humid climate in the past (Pal et al., 1989), ferruginous soils released much higher amounts of K (5.0–17.5 mg K/100 g) as compared to that of black soils. The soils of BA released the least amount of K (< 1 mg K/100 g). By and large, the rate of K release from soils was reduced with the increasing number of extractions (Fig. 1). This may be due to the fact that after most of the interlayer K had been removed by Ba^{2+} ions, the exchange fronts meet in the centre of the mica particles, where exchange of remaining K is considerably reduced (Reichenbach and Rich, 1969). The rate of K release was at a maximum in alluvial soils of IGP followed by ferruginous and black soils. The lowest rate of K release was observed in soils of the BA. These observations thus justified the crop response to K in the respective soils (Table 1). This suggests that it is not the quantity of mica but its nature that may restrict the rate of K release (Table 2).

The X-ray intensity ratio of peak heights of 001 and 002 basal reflections of mica is greater than unity in the silt and clay fractions of soils (Table 3). However, in soils of BA and black soils, this ratio is close to unity, especially in their clay fractions. The ratio > 1 suggests the presence of both muscovite and biotite minerals. If muscovite minerals were present alone, the ratio would have been close to

Table 3

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 μ m	< 2 μ m
Holambi (AS-SA) (Udic Ustochrept)	IGP ^a	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

^a IGP = Indo-Gangetic alluvium; DBA = Deccan basalt alluvium; GG = granite–gneiss.

unity (Tan, 1982). In the event of a mixture of these two micas, both will contribute to the intensity of the 10-Å reflections, whereas contribution of biotite to the 5-Å reflection would be nil or negligible, thus giving a higher value to the intensity ratio of these reflections (Kapoor, 1972b). This suggests that the silt fractions of all the soils and the clay fractions of IGP and ferruginous soils contain both muscovite and biotite, whereas the clay fractions of BA and black soils are more muscovitic in character. The dominance of muscovite in both silt and clay fractions in most of these soils finds support from the significant positive correlation at 1% level between cumulative K release in 25 extractions (Table 1) and

the 001/002 ratio of basal reflections of mica in the silt ($r = 0.629$) and clay ($r = 0.729$) fractions. The enrichment of soils with muscovite is therefore not favourable so far as the K release and available K status are concerned. Rausell-Colom et al. (1965) demonstrated that extractability of K from muscovite was extremely sensitive to solution K. Kapoor (1972b) observed that the K released from weathering biotite can inhibit the K release of muscovite when the two micas co-exist in soils. This sensitivity appears to have an important bearing on the persistence of muscovite in soils during the weathering process (Sarma, 1976), as confirmed through the SEM study of the morphology of the coarser fractions of two micas.

Petrographic examination of sand fractions of the soils confirmed the presence of muscovite and biotite in all soils except Patancheru and Nalgonda where muscovite was rare. 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. SEM examination of micas indicated that irrespective of soil type, biotites generally occurred as thick particles with different stages of layer separation. They were weathered with layer separations and bending at their edges (Fig. 2). At the edges of these particles, layer separation indicated the formation of a vermiculite rim around the particles. These features indicated the replacement of interlayer K of

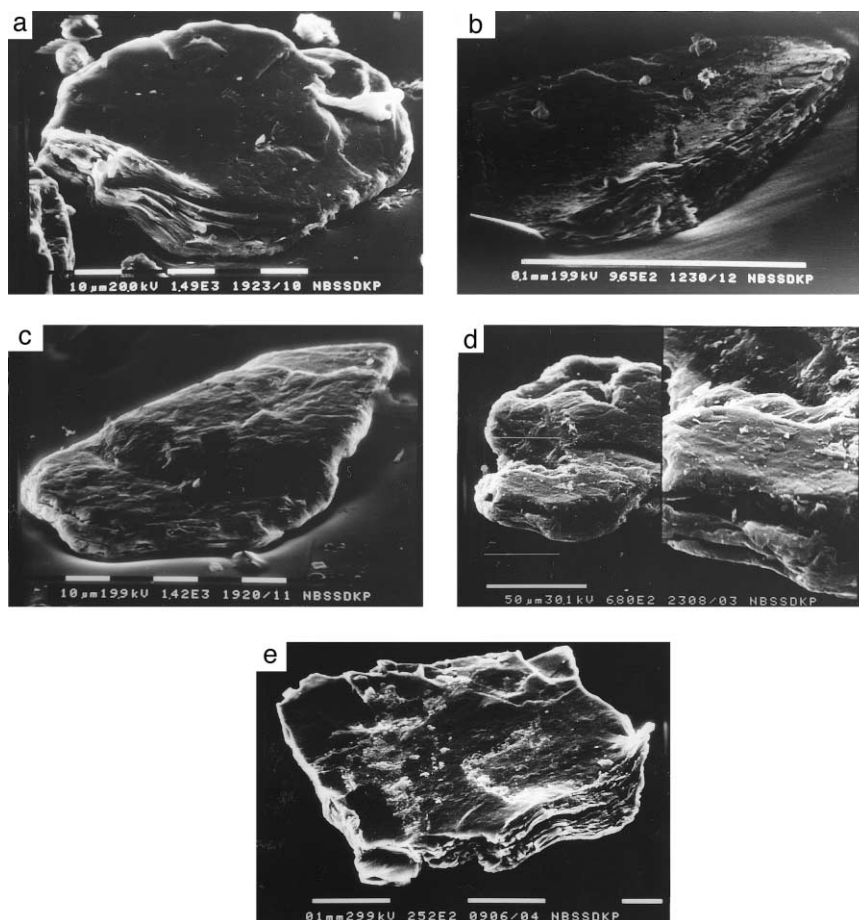


Fig. 2. SEM photographs of sand-sized biotite of representative alluvial, black and ferruginous soils: (a) IGP soils of SA climate, Holambi; (b) IGP soils of SH climate, Totpara; (c) BA soils of PH climate, Dahotia; (d) black soils of SA climate, Aroli; (e) ferruginous soils of SA climate, Dyavapatna.

biotite. The replacement of interlayer K of muscovite has not been substantial as evidenced from a general lack of interlayer opening (Fig. 3). However, in some soils, weak to moderate layer separation at the edge was observed (Fig. 4) possibly due to alteration prior to pedogenesis. These observations indicated that the weathering of muscovite was almost inhibited in the presence of biotite. A similar observation has recently been made by Srivastava et al. (1998) in soils of IGP. Despite this, minor layer separation in muscovite that was observed in this study and elsewhere (Sidhu and Gilkes, 1977) needs some explanation. It is difficult to conclude whether the observed layer separation in muscovite is due to K release

during soil formation or not. In order to confirm the feasibility of K release from muscovite in soil environments towards the formation of dioctahedral 2:1 expandable minerals, the repeated batch type Ba–K exchange experiments were carried out on mixtures of muscovite and biotite.

In the present experimental studies, the exchange systems were fairly close to equilibrium after the reaction period of 3 days. Cumulative amount of K released from a mixture (1:1) of muscovite and biotite in 35 extractions was 1240, 965, 950 and 854 mg K/100 g of mica from 100–50, 50–20, 20–6 and 6–2 μm fractions, respectively. Muscovite alone released 0.3, 0.4, 0.5 and 0.8 mg k/100 g mica from

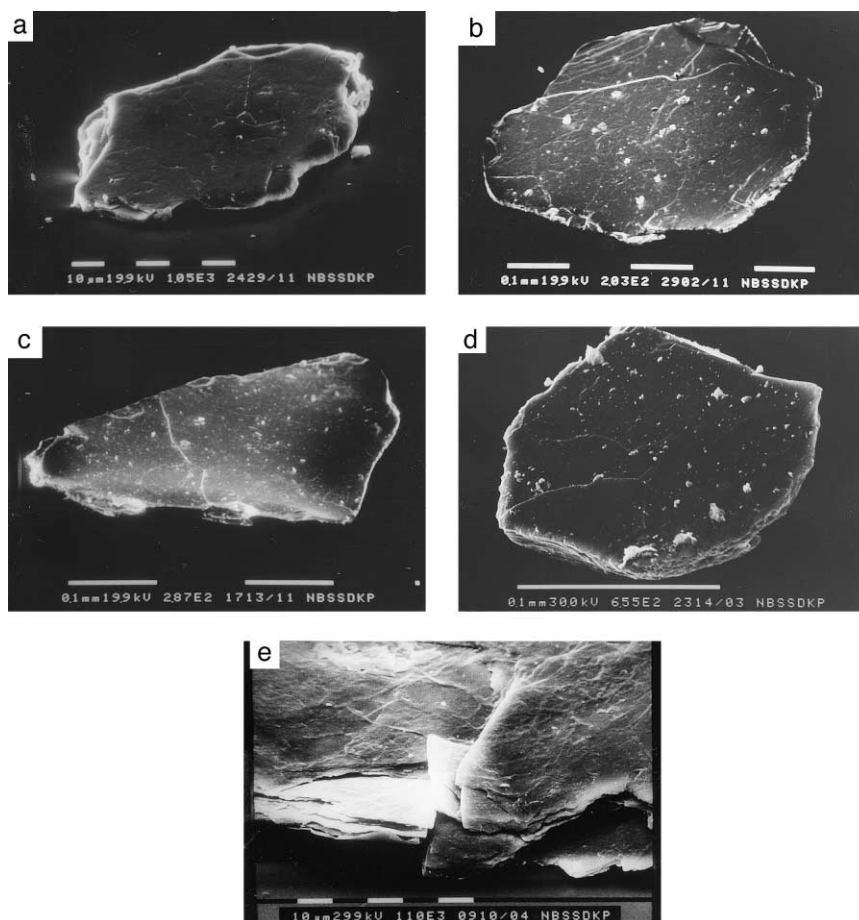


Fig. 3. SEM photographs of sand-sized muscovite of representative alluvial, black and ferruginous soils: (a) IGP soils of SA climate, Holambi; (b) IGP soils of SH climate, Totpara; (c) BA soils of PH climate, Dahotia; (d) black soils of SA climate, Aroli; (e) ferruginous soils of SA climate, Dyavapatna.

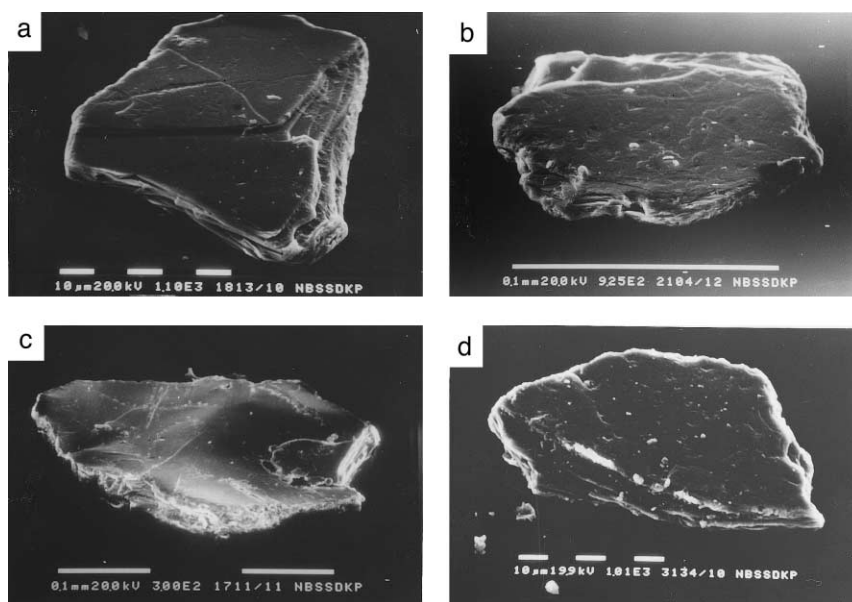


Fig. 4. SEM photographs of sand-sized muscovite with weak to moderate layer opening of representative alluvial, black and ferruginous soils: (a) IGP soils, Holambi; (b) IGP soils, Totpara; (c) BA soils, Dahotia; (d) black soils, Aroli.

the same size fraction, respectively, while biotite alone released 2295, 1216, 1167 and 1092 mg K/100 g, respectively (Table 4).

In view of the negligible amount of K released by muscovite, it can be safely presumed that the K released from the mica mixture can be attributed to

Table 4

Cumulative K release and X-ray intensity ratio of the peak heights of 001 and 002 basal reflections of mica

Size fractions (μm)	Cumulative K release in 35 extractions mg/100 g of mica	K ₂ O (%)		Ratio 001/002	
		Original amount	Loss of total content	Original	After 35 extractions
<i>Muscovite</i>					
100–50	0.3	–	–	1.56	1.57
50–20	0.4	–	–	1.70	1.72
20–6	0.5	–	–	1.64	1.67
6–2	0.8	–	–	1.89	1.83
<i>Biotite</i>					
100–50	2295	7.53	36.6	–	–
50–20	1216	7.33	20.0	–	–
20–6	1167	7.20	19.4	–	–
6–2	1092	6.95	18.8	–	–
<i>Muscovite + biotite</i>					
100–50	1240	–	–	5.54	5.00
50–20	965	–	–	11.33	5.75
20–6	950	–	–	7.69	5.52
6–2	854	–	–	17.45	5.93

that released from biotite only. In view of the inertness of muscovite in releasing K from mixtures, the cumulative amount of K release from the mixture should be comparable with those of biotite alone. It

is, however, observed that the amount of K release from any fraction of biotite is much higher than that of the mica mixture. This difference can be attributed to the change in mica/solution ratio in the sense that

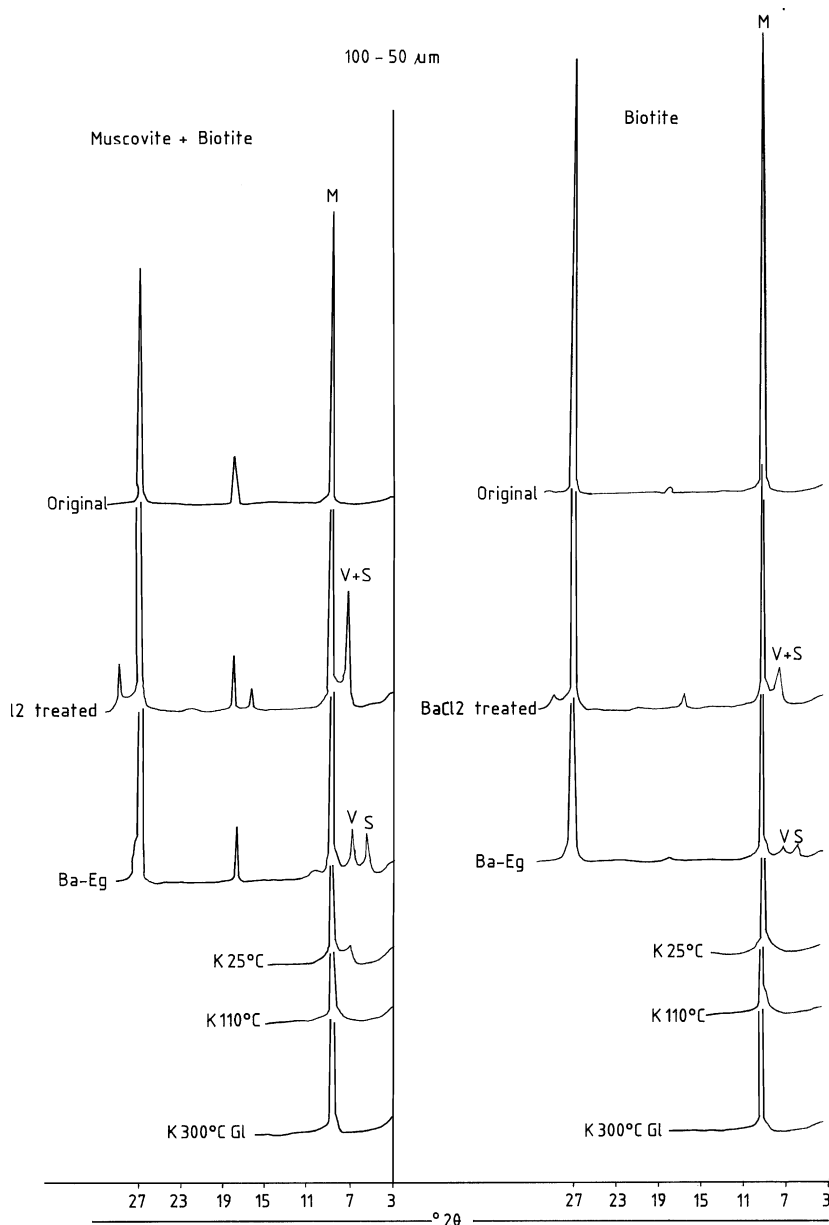


Fig. 5. Representative XRD patterns of 100–50-μm fraction of biotite and mixture of muscovite and biotite; M = mica, V = vermiculite, S = smectite; BaCl₂-treated = after 35 extractions with 0.1N BaCl₂ solution; Ba-Eg = Ba-saturated plus glycol vapour; K 25/100°C = BaCl₂-treated sample saturated with K and heated to 25/100°C; K-300°C Gl = BaCl₂-treated sample saturated with K, heated to 300°C and glycolated.

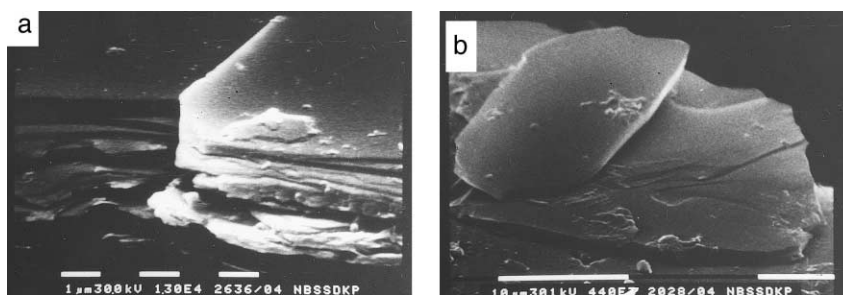


Fig. 6. SEM photographs of biotite (a) and muscovite (b) after 35 extractions with 0.1N BaCl₂ solution as representative of the 100–50-μm fraction of mixture of muscovite and biotite.

in the mixture of micas, the released K was calculated considering 100 mg of mica:100 ml of BaCl₂ solution while K release from muscovite was negligible. The inert role of muscovite was confirmed from the constancy of X-ray intensity ratio of peak heights of 001 and 002 basal reflections of each fraction of muscovite before and after the 35 extractions (Table 4), indicating that the mica remaining was still muscovite. The 001/002 ratio of mica of the mixture of muscovite and biotite after 35 extractions, however, indicated a decrease. This trend does not correspond to the one documented for dioctahedral micas (Brown, 1955; White, 1962) where intensity of the (001) reflection increased more rapidly than that of the (002) when interlayer K was depleted during weathering. The present observation strongly suggests that the decrease in the ratio was only due to the weathering of biotite. Both muscovite and biotite have strong first- and third-order reflections at 10 and 3.3 Å, respectively, and thus are characterised by their second-order reflection. The second-order reflection is almost absent in biotite compared to muscovite. When these two micas co-exist, the contribution of the former to the second-order mica reflection is thus almost negligible. During the weathering in the experimental studies, the concentration of biotite decreased and resulted in a greater decrease in the intensity of (001) reflection than (002). Similar observations were made for muscovite and biotite when they co-existed in soils (Kapoor, 1972b; Pal and Durge, 1993).

The transformation of micas to expandable 2:1 minerals by replacement of K with hydrated cations is a common phenomenon in soils. As expected, biotite altered vermiculite and smectite during the

Ba–K exchange reaction (Fig. 5). The smectite was a high-charge type as it readily collapsed to 10 Å upon K-saturation and heating to 110°C. Its high charge was further confirmed by non-expansion on the low angle side by glycolation of its K-saturated and heated (300°C) sample (Ross and Kodama, 1984). The appearance of the (060) reflection of the BaCl₂-treated biotites at 1.54 Å only indicated the trioctahedral nature of both vermiculite and smectite. Vermiculite and high-charge smectite were also detected during the Ba–K exchange reactions of muscovite and biotite mixtures (Fig. 5). This suggests that under ambient temperature and pressure as in soil environments, formation of trioctahedral 2:1 expandable minerals at the expense of biotite is a distinct possibility even in the presence of muscovite. This is evidenced from the morphology of the treated biotite and muscovite under SEM. Layer separation for the formation of vermiculite and smectite was observed around biotite alone and also with mixtures of micas (Fig. 6a). Muscovite particles did not show any perceptible layer separation after 35 extractions (Fig. 6b). This observation further supports the evidence that K released from weathering biotite inhibits the K depletion process in muscovite (Kapoor, 1972b) that is extremely sensitive to K in solution (Rausell-Colom et al., 1965). This suggests that the presence of muscovite appears to be useless as a K reserve in soils (Pal and Durge, 1989).

4. Discussion

Among the principal K-bearing minerals, feldspars contribute very little to the soil pool of K that can be

used by plants (Rasmussen, 1972) and the mere presence of micas may not necessarily justify the actual K release potential, as indicated in the present study. In order to describe the factors controlling interlayer K release from muscovite and biotite as well as soil micas, experimental conditions of the experiments were chosen in a way that the released K remained in the solution of the exchange system. With a specific concentration of the extractant and a definite mineral/solution ratio, the K released in each treatment of BaCl_2 will depend primarily on the K selectivity of the mica mineral, this being the determining factor for K equilibrium concentration of the solution phase. However, this is only applicable when the reaction periods are sufficiently long to establish an equilibrium (Reichenbach and Rich, 1969). The concentration of K in soil solutions can, however, be expected to approach equilibrium levels as the applicability of diffusion models to K release from micas depends on the presumption that diffusion gradients are kept constant with time; and this condition is not likely to be fulfilled in soils, particularly where rainfall is low or soil permeability is impeded (Reichenbach, 1972). In the present study, exchange systems of both soil and specimen micas were fairly close to equilibrium after the reaction period of 3 days. The cumulative amount of K release from both soil micas and specimen micas indicated the inert role of muscovite. This observation finds support from the crop response to K fertilizer in soils of BA of per-humid climates of Assam and in black soils of western and central peninsular India (Table 1) where mica in the clay fractions has a predominantly muscovitic character. During weathering in a per-humid climate, mica transformed into dioctahedral vermiculite (Table 2). It may be argued that the dioctahedral vermiculite and smectite can also be a weathering product of muscovite as suggested by many researchers (Robert, 1973; Churchman, 1980; Aoudjit et al., 1995; Taboada and Garcia, 1999). However, the formation of dioctahedral 2:1 expansible minerals at the expense of muscovite need not be regarded as the only transformation pathway. The 001/002 ratio of mica in the clay fractions of Totpara and Kanagarh soils of the sub-humid part of IGP is 2.73 and 1.60, respectively (Table 3), indicating that the clay–mica of these soils is not muscovitic although the mica of

these soils altered to dioctahedral vermiculite and smectite (Table 2). The 001/002 ratio above unity thus justified the lack of crop response to K fertilizers in these soils. Therefore, in the presence of biotite in coarser fractions of soils, it is quite likely that muscovites do not weather and the dioctahedral 2:1 expansible minerals in the finer fractions are the alteration product of biotite in sub-humid to per-humid climates as the formation of both di- and trioctahedral 2:1 expansible minerals is possible from biotite (Fanning and Keramidis, 1977). This result therefore questions the weatherability of muscovite in soil environments. This may explain the existence of almost unaltered muscovite even in advanced acid tropical weathering conditions in bauxite laterite (Anand and Gilkes, 1987). A lack of layer separation in muscovite at ambient temperature and pressure was also demonstrated experimentally in alkaline environments by Pal (1985). It was also noted in many reports on the formation of dioctahedral 2:1 expansible minerals from muscovite in experiments 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, the expanded layer separation observed in muscovites of soils may not be pedogenic.

5. Conclusions

The study indicates that the weathering of muscovite in the presence of biotite is improbable. Therefore, the quantity of muscovite cannot be used as an index of K reserve in soils wherever biotite and muscovite occur together in soil environments. Formation of dioctahedral 2:1 expansible minerals from biotite in humid climates is a distinct possibility in view of their unlikely formation from muscovite in the common soil situation where both forms of mica occur together. Crop response to K fertilizers will depend on the biotite reserves in various soil-size fractions. A selective quantification of biotite mica in the common situation in soils containing mixtures of biotite and muscovite could be an effective tool to determine the status of stock of K in soils. This information could be used to dictate the K fertilizer

requirement in various soils in many parts of India and elsewhere and will also help in making projections for K-fertilizer production in the future.

References

- Anand, R.R., Gilkes, R.J., 1987. Muscovite in Darling Range bauxitic laterite. *Aust. J. Soil Res.* 25, 445–450.
- Aoudjit, H., Robert, M., Elsass, F., Curmi, P., 1995. Detailed study of smectite genesis in granitic saprolites by analytical electron microscopy. *Clay Miner.* 30, 135–147.
- April, R.H., Hluchy, M.M., Newton, R.M., 1986. The nature of vermiculite in Adirondack soils and till. *Clays Clay Miner.* 34, 549–556.
- Brown, G., 1955. Intensities of 001 reflections of mica and chlorite type structures. *Miner. Mag.* 30, 657–665.
- Churchman, G.J., 1980. Clay minerals formed from micas and chlorites in some New Zealand soils. *Clay Miner.* 30, 135–147.
- Douglas, L.A., 1989. Vermiculites. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. 2nd edn. Soil Science Society of America, USA, pp. 635–674.
- Fanning, D.S., Keramidas, V.Z., 1977. Micas. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. 1st edn. Soil Science Society of America, Madison, WI, USA, pp. 195–258.
- Fritz, S.J., 1988. A comparative study of gabbro and granite weathering. *Chem. Geol.* 68, 275–290.
- Ghosh, S.K., Bhattacharyya, T., 1984. Mineralogy of soils of Bihar, Uttar Pradesh, Gujarat and Rajasthan. *Mineralogy of Soil Potassium. PRII Research Review Series*, vol. 1, Potash Research Institute of India, Gurgaon, India, pp. 15–29.
- Ghosh, A.B., Biswas, C.R., 1978. Potassium responses and change in soil potassium status with time. *Potassium in Soils and Crops*. Potash Research Institute of India, New Delhi, pp. 379–390.
- Gjems, O., 1967. Studies on clay minerals and clay mineral formation in soil profiles in Scandinavia. *Medd. Nor. Inst. Skogforsk.* 21, 303–415.
- Goswami, S.C., Kapoor, B.S., Gupta, Y., 1986. Clay mineral distribution in some alluvium derived soils of Bihar. *Trans. Int. 13th Congr. Soil Sci.* 4, 1449.
- Harward, M.E., Carstea, D.D., Sayegh, A.H., 1969. Properties of vermiculites and smectites: expansion and collapse. *Clays Clay Miner.* 16, 437–447.
- Jackson, M.L., 1958. *Soil Chemical Analysis*. Prentice Hall, Englewood Cliffs.
- Jackson, M.L., 1979. *Soil Chemical Analysis, Advanced Course*. 2nd edn. University of Wisconsin, Madison, WI, USA, 11th Printing, Published by the author.
- Kapoor, B.S., 1972a. Weathering of micaceous clays in some Norwegian podzols. *Clay Miner.* 9, 383–394.
- Kapoor, B.S., 1972b. Weathering of micaceous minerals. *Norsk. Geol. Tidsskr.* 52, 451–452.
- Kapoor, B.S., Singh, H.B., Goswami, S.C., Abrol, I.P., Bhargava, G.P., Pal, D.K., 1981. Weathering of micaceous minerals in some salt-affected soils. *J. Indian Soc. Soil Sci.* 29, 486–492.
- Kerns, R.L., Mankin, C.J., 1967. Compositional variation of a vermiculite as related to particle size. *Clays Clay Miner.* 15, 163–177.
- MacEwan, D.M.C., Wilson, M.J., 1980. Interlayer and intercalation complexes of clay minerals. In: Brindley, G.W., Brown, G. (Eds.), *Crystal Structures of Clay Minerals and their X-ray Identification*. Mineralogical Society, London, pp. 223–235.
- Murthy, R.S., Hirekerur, L.R., Deshpande, S.B., Venkat Rao, B.V., 1982. Benchmark Soils of India. National Bureau of Soil Survey and Land Use Planning, Nagpur, India, 374 pp.
- Nettleton, W.D., Flach, K.W., Nelson, R.E., 1970. Pedogenic weathering of tonalite in southern California. *Geoderma* 4, 387–402.
- Pal, D.K., 1985. Potassium release from muscovite and biotite under alkaline conditions. *Pedologie* 35, 133–146.
- Pal, D.K., Deshpande, S.B., 1987. Characteristics and genesis of minerals in some benchmark Vertisols of India. *Pedologie* 37, 259–275.
- Pal, D.K., Durge, S.L., 1987. Potassium release and fixation reactions in some benchmark Vertisols of India in relation to their mineralogy. *Pedologie* 37, 103–116.
- Pal, D.K., Durge, S.L., 1989. Release and adsorption of potassium in some benchmark alluvial soils of India in relation to their mineralogy. *Pedologie* 39, 235–248.
- Pal, D.K., Durge, S.L., 1993. Potassium release from clay micas. *J. Indian Soc. Soil Sci.* 41, 67–69.
- Pal, D.K., Durge, S.L., 1996. Potassium release reaction in ferruginous soils of southern India. *Clay Res.* 15, 1–6.
- Pal, D.K., Mondal, R.C., 1980. Crops response to potassium in sodic soils in relation to potassium release behaviour in salt solutions. *J. Indian Soc. Soil Sci.* 28, 247–254.
- Pal, D.K., Deshpande, S.B., Durge, S.L., 1987. Weathering of biotite in some alluvial soils of different agroclimatic zones. *Clay Res.* 6, 69–75.
- Pal, D.K., Deshpande, S.B., Venugopal, K.R., Kalbande, A.R., 1989. Formation of di- and trioctahedral smectite as an evidence of paleoclimatic changes in southern and central peninsular India. *Geoderma* 45, 175–184.
- Pal, D.K., Deshpande, S.B., Durge, S.L., 1993. Potassium release and adsorption reactions in two ferruginous (polygenetic) soils of southern India in relation to their mineralogy. *Pedologie* 43, 403–415.
- Rasmussen, K., 1972. Potash in feldspars. *Proc. Colloq. Int. Potash Inst.* 9, 57–60.
- Rausell-Colom, J.A., Sweatman, T.R., Wells, C.B., Norrish, K., 1965. Studies in the artificial weathering of mica. In: Hallsworth, E.G., Crawford, D.V. (Eds.), *Experimental Pedology*. Butterworths, London, pp. 40–72.
- Rebertus, R.A., Weed, S.B., Buol, S.W., 1986. Transformations of biotite during saprolite-soil weathering. *Soil Sci. Soc. Am. J.* 50, 810–819.
- Rego, T.J., Sahrawat, K.L., Burford, J.R., 1986. Depletion of soil potassium in an Alfisol under improved rainfed cereal/legume cropping system in the Indian SAT. *Trans. 13th Int. Congr. Soil Sci.* 3, 928–929.

- Reichenbach, H.G.Von., 1972. Factors of mica transformation. Proc. 9th Colloq. Int. Potash Inst., Switzerland, pp. 3–12.
- Reichenbach, H.G.Von., Rich, C.I., 1968. Preparation of dioctahedral vermiculites from muscovite and subsequent exchange properties. Trans. 9th Int. Congr. Soil Sci. 1, 709–718.
- Reichenbach, H.G.Von., Rich, C.I., 1969. Potassium release from muscovite as influenced by particle size. *Clays Clay Miner.* 17, 23–29.
- Rich, C.I., 1972. Potassium in soil minerals. Proc. 9th Colloq. Int. Potash Inst., pp. 15–31.
- Robert, M., 1973. The experimental transformation of mica towards smectite: relative importance of total charge and tetrahedral substitution. *Clays Clay Miner.* 21, 167–174.
- Ross, G.J., Kodama, H., 1984. Problems in differentiating soil vermiculites and soil smectites. *Agron. Abstr.*, Annual Meetings of ASA, CSSA, SSSA, Las Vegas, NV, 275 pp.
- Sarma, V.A.K., 1976. Mineralogy of soil potassium. *Bull. Indian Soc. Soil Sci.* 10, 66–77.
- Sekhon, G.S., Ghosh, A.B., 1982. Potassium. Review of Soil Research in India. Int. Congr. Soil Sci., 12th, Part 1, pp. 331–341.
- Sidhu, P.S., Gilkes, R.J., 1977. Mineralogy of soil developed on alluvium in the Indo-Gangetic Plain (India). *Soil Sci. Soc. Am. J.* 41, 1194–1201.
- Srivastava, P., Parkash, B., Pal, D.K., 1998. Clay minerals in soils as evidence of Holocene climatic change, central Indo-Gangetic Plains, north-central India. *Q. Res.* 50, 230–239.
- Stoch, L., Sikora, W., 1976. Transformation of micas in the process of kaolinisation of granites and gneisses. *Clays Clay Miner.* 24, 156–162.
- Taboada, T., Garcia, C., 1999. Smectite formation produced by weathering in a coarse granite saprolite in Galicia (NW Spain). *Catena* 35, 281–290.
- Tan, K.H., 1982. Principles of Soil Chemistry. Marcel Dekker, New York, 122 pp.
- Tanner, C.B., Jackson, M.L., 1947. Nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration. *Soil Sci. Soc. Am. Proc.* 12, 50–55.
- Tomita, K., Sudo, T., 1971. Transformation of sericite into an interstratified mineral. *Clays Clay Miner.* 19, 263–270.
- White, J.L., 1954. Reaction of molten salts with layer lattice silicates. *Nature* 174, 790–800.
- White, J.L., 1956. Layer charge and interlamellar lattice silicates. *Clays Clay Miner.* 4, 133–146.
- White, J.L., 1962. X-ray diffraction studies on weathering of muscovite. *Soil Sci.* 93, 16–21.
- Wilson, M.J., 1973. Clay minerals in soils derived from Lower Old Stand stone till: effects of inheritance and pedogenesis. *J. Soil Sci.* 24, 26–41.
- Wilson, M.J., 1999. The origin and formation of clay minerals in soils: past, present and future perspective. *Clay Miner.* 34, 7–25.