

Clay Research, Vol. 31, No. 1, pp. 38-69 (2012)

Linking Minerals to Selected Soil Bulk Properties and Climate Change: A Review

D.K. PAL^{1,2}, T. BHATTACHARYYA, P. CHANDRAN AND S.K. RAY

Division of Soil Resource Studies, National Bureau of Soil Survey and Land Use Planning, Amravati Road, Nagpur, Maharashtra 440010, India

¹Resilient Dry Land Systems, International Crops Research Institute for the Semiarid Tropics, Patancheru 502 324, Andhra Pradesh, India

Abstract : *Reviews in the past on the significance of minerals indicated that despite our best management interventions the actual agricultural productivity does vary because factors beyond our control. One intrinsic factor in yield variation is soil type and clay is an important soil constituent that controls many properties. There is ample evidence to show that the amount and type of clay in a soil has a very important bearing on the genesis, characteristics, and physical and chemical properties and nutrient dynamics in soil plant continuum of soils. However, information with regard to significance that clay and other soil minerals have in major bulk properties of soils (edaphology) and in finding signatures of climate change in soils/sediments of the past (paleopedology) has been rare. A search for links between mineralogy and soil properties of agricultural importance and use of minerals in unravelling the climate of the past often poses problems because descriptions of soil minerals are inadequate or incomplete. This becomes more difficult as soil minerals do not remain as specimen minerals in soil environment. An endeavour made at NBSS&LUP in 2000 indicated that first hurdle lies in proper identification, let alone quantitative estimation, of soil clays and other minerals. However, through sustained efforts by the researchers at NBSS & LUP (ICAR) since then, further advances in knowledge has been possible and this demands for another critical review. Thus, this review is the synthesis of the updated knowledge, which has come out as state of the art information that will fulfill the need of a hand book to facilitate their better management for optimizing their productivity in the 21st Century even amidst the climatic adversities due to climate change.*

Minerals in soils are the result of both inheritance and authigenic formation of both primary and secondary minerals. Comprehensive reviews on the soil clay minerals and other minerals in the past indicate that there are not many attempts to show the influence of minerals in soil

genesis and management (Mukherjee *et al.*, 1971; Raman and Ghosh, 1974; Ghosh and Kapoor, 1982; Sarma and Sidhu, 1982; Ghosh and Bhattacharyya, 1983; Ghosh, 1997). A review in the past on this subject and related issues (Newman, 1984; Ghosh, 1997; Wilson, 1999) pointed out that the

increase in agricultural productivity during the middle of the twentieth century was due to human influence, which improved vastly the soil fertility on all types of soil. However, actual productivity does vary widely and this fact shows that there are other factors of productivity beyond our control. One intrinsic factor in yield variation is soil type, which is related to the soil composition and its position in the landscape. Clay is an important soil constituent controlling its properties. Despite the fact that there is ample evidence to show that the amount of clay in a soil has a very important bearing on the genesis, characteristics, and physical and chemical properties of soils, it would be more appropriate to see what significance clay mineral *type* and other soil minerals have in soils; pedology, paleopedology, polygenesis and edaphology in particular. A search for links between mineralogy and soil properties of agricultural importance is likely to be difficult because many a time the description of minerals actually present in a soil is inadequate or incomplete. Further, as soil minerals often differ from “type” minerals, it is very much necessary to investigate the properties of these minerals relevant to the properties of the soil in bulk. In this endeavour, Pal *et al.* (2000a) demonstrated a good number of examples that indicated despite soil clay minerals being a mixture of several components, adequate description is possible. However, for the last decade some more information on this important area of

soil research including the use of clay mineral as proxy to the climate change phenomena in the Peninsular and extra – Peninsular areas, has been generated at national level, specially at the National Bureau of Soil Survey and Land Use Planning (NBSS&LUP)(ICAR). Through synthesis of the present dataset on the nature and characteristics of primary and secondary minerals of Indian soils, this review as a state-of-the-art information is made, which has established a link between minerals and selected bulk soil properties and also climate change. It is hoped that this review will fulfil the need of a hand book for students and young researchers in earth science who would intend to assess the health and quality of soils while developing suitable management practices to enhance and sustain their productivity in the 21st Century.

Characteristics and nature of clay minerals in adsorption and desorption of major nutrients

Nitrogen adsorption and clay minerals

Increasing demand for nitrogen fertilizers to produce food has always stimulated research to gain knowledge on the various forms of nitrogen in soils. One of the forms of nitrogen (N) is the fixed $\text{NH}_4\text{-N}$. Despite many tropical soils being endowed with large amounts of fixed ammonium (Dalal, 1977), information on this important form of N is rare, especially in the semi-arid tropical (SAT) soils

(Burford and Sahrawat, 1989). Sahrawat (1995) determined the fixed $\text{NH}_4\text{-N}$ distribution in two of the benchmark (BM) Vertisols of Indian SAT, namely Kasireddipalli soils at ICRISAT Center, Patancheru and Barsi soils of Maharashtra state of western India. They reported that the amount of fixed $\text{NH}_4\text{-N}$ was 22 to 59% in the former and 16 to 31% in the latter in the total soil N. The 2:1 non-expanding minerals like vermiculites can only fix $\text{NH}_4\text{-N}$. Despite this knowledge, illites (micas) and smectites are considered as the minerals to fix $\text{NH}_4\text{-N}$ (Nommik and Vahtras, 1982). Smectites do not have any selectivity for non-hydrated monovalent cation like K because of their low layer charge (Brindley, 1966). The NH_4 ion being also a non-hydrated monovalent cation having almost the same ionic radii as that of K is not expected to be fixed in the interlayers of smectites. Similarly, it is difficult to understand the NH_4 ion fixing capacity of illites because illites do not expand when saturated with divalent cations (Sarma, 1976). Vertisols developed in the basaltic alluvium of the Deccan basalt of Peninsular India, are not devoid of vermiculite as reported (Mengel and Busch, 1982; Dhillon and Dhillon, 1991). However, the identification of vermiculite by XRD analysis in different soil size fractions is fraught with some difficulty in ubiquitous presence of chlorite and also because of its presence in small amounts in Vertisols and other soil types. Its presence is resolved by following the progressive reinforcement of

the 1.0 nm peak of mica while heating the K-saturated samples at 25, 110, 300 and 550°C (Fig.1) (Pal and Deshpande, 1987a;

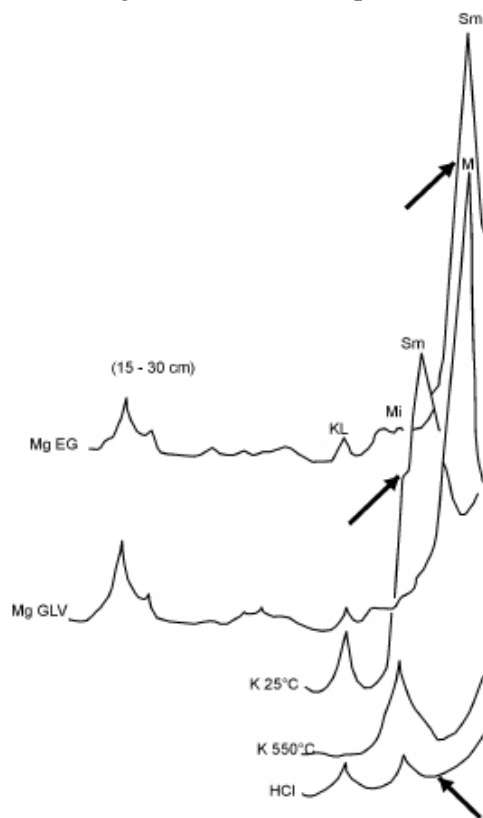


Fig. 1. Representative XRD diagram of fine clay ($< 0.2\mu\text{m}$) fraction of Vertisols. On glycolation it expands to 1.7 nm indicating the dominant presence of smectite (Sm). With glycerol vapour treatment it expands to about 1.8 nm, indicating that the smectite is nearer to montmorillonite. On K-saturation, its 1.0 nm region gets reinforced, indicating the presence of small amount of vermiculite which is not detected on glycolation. Adapted from Pal and Durge (1989).

Pal and Durge, 1987), and it is estimated semi-quantitatively following the method of Gjems (1967). Like other soil types, Vertisols do contain vermiculite in their silt (50-2 μ m), coarse clay (2-0.2 μ m) and fine clay (<0.2 μ m) fractions (Pal and Durge, 1987) and the content of vermiculite, determined quantitatively (Alexiades and Jackson, 1965) ranges from 2.0 to 3.5% in the silt, 3.5 to 10% in the coarse clay and 5.0 to 9.5 % in the fine clay fractions (Pal and Durge, 1987). Vermiculite is trioctahedral in nature, and is the alteration product of biotite in the presence of its dioctahedral variety (muscovite) (Pal and Durge, 1987; Pal *et al.*, 2001a). Both the micas are not part of the Deccan basalt and their origin in Vertisols has been attributed to the geomorphic history of the Deccan basalt landscape areas (Pal and Deshpande, 1987a). Thus, it would be prudent to attribute the observed N fixation in Vertisols (Sahrawat, 1995) and other soil as NH_4^+ , to the presence of vermiculite. Such basic understanding is essential to include fixed $\text{NH}_4\text{-N}$ in assessing the potentiality of N availability in Indian soils.

Phosphorous (P) adsorption and clay minerals

Soil properties that are linked to P adsorption by soil minerals include the nature and amount of clay, organic matter, and hydrous oxides of iron and aluminium (Sanyal and De Datta, 1991). Based on earlier findings these authors indicated a significant correlation of P sorption

parameters with clay content and opined that this may be a mere reflection of the effect of specific surface area on P adsorption.

Clays rich in 1:1 lattice mineral may contribute to P adsorption in highly weathered soils of humid tropical climate, especially at low soil pH, when the activity of iron and aluminium is also expected to be higher. Thus, the free hydrated oxides of iron and aluminium ordinarily present in ferruginous soils have considerable phosphate fixing ability (Biddappa and Venkat Rao, 1973). Kanwar and Grewal (1960) also reported that about 70 per cent of the phosphate fixing capacity of acid soils and 30 per cent of that of calcareous and alkali soils of Punjab were due to free sesquioxides. In soils hydrous oxides of iron and aluminium occur as fine coatings on surfaces of clay minerals (Greenland *et al.*, 1968; Haynes, 1983). These coatings having appreciably large specific surface area can adsorb large amounts of added P. This observation clearly implies that in P adsorption crystalline aluminosilicate minerals have a merely secondary role (Ryden and Pratt, 1980). However, hydroxides of iron and aluminium can adsorb negatively charged phosphate ions only when they remain as cations in highly acidic medium. Such soils (Ultisols) are highly acidic and their KCl pH values remain close to or greater than water pH (Bhattacharyya *et al.*, 2000; Chandran *et al.*, 2005), indicating the presence of

gibbsite and/or amorphous materials (Smith, 1986). A negative/zero/positive ΔpH indicates the presence of variable charge minerals such as gibbsite and /or sesquioxides (Uehera and Gillman, 1980; Bhattacharyya *et al.*, 1994). This indicates that gibbsite and /or sesquioxides in acidic soils showing a positive ΔpH could be a better substrate to absorb negatively charged phosphate ions. Therefore, reported adsorption of added phosphate ions by soils of the semi-arid and arid climates is difficult to reconcile since the soils in these regions are alkaline and sodic due to the formation of pedogenic CaCO_3 (Pal *et al.*, 2000b, 2009). In such pedo-environment layer silicates suffer congruent dissolution (Pal, 1985). This suggests that the highest surface area of 2:1 expanding clay minerals and/or hydroxides of iron and aluminium with no positive sites, have little role in the adsorption of added negatively charged phosphate ions in calcareous and mild to moderately alkaline soils. This supports the ICRISAT's classical experimental observations that P adsorption and desorption is not a major problem in Vertisols, and that all the adsorbed P is easily exchangeable by P^{32} and little amount of P is adsorbed in the non-exchangeable form (ICRISAT, 1988; Sahrawat and Warren, 1989; Shailaja and Sahrawat, 1990, 1994; Warren and Sahrawat, 1993).

Potassium release and biotite mica

The prime K-bearing minerals in major soils (alluvial, black and ferruginous soils)

of India are micas that are concentrated mainly in the silt and clay fractions. Despite this favourable natural mineral endowment, crop response to K fertilizers in many such soils has been anomalous (Pal *et al.*, 2000a, 2001a; Pal, 2003). Petrographic examination of sand fractions of major soils of India confirmed the presence of muscovite and biotite in soils of the Brahmaputra alluvium (BA) and Indo-Gangetic alluvium (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.*, 2001a). SEM examination of micas by Pal *et al.* (2000a, 2001a) indicated that irrespective of soil type biotite generally occurred as thick particles with different stages of layer separation. They are weathered through 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.* (2001a) however observed weak to moderate layer separation at the edge of muscovite in some soils and opined that this is due to alteration prior to pedogenesis. Thus the release of K from fine-grained micas of soils is 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 by Pal *et al.* (2000a, 2001a). 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).

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, 1972). 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 particularly in their clay fractions. The ratio >1 may apparently suggest the muscovitic character of mica but in reality it indicates the presence of both muscovite and biotite minerals (Pal *et al.*, 2000a). 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 1.0 nm reflections, whereas contribution of biotite to the 0.5 nm reflection would be nil or negligible, thus giving a higher value to the intensity ratio of these reflections (Fig.2) (Kapoor, 1972). 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 (Fig.3) (Pal *et al.*, 2001a).

A need of a selective quantification of biotite mica in the common situation in soils containing mixtures of biotite and muscovite was planned through an experiment by Pal *et al.* (2006a) wherein the contents of biotite in Vertisols and their size fractions were estimated through a rigorous and exhaustive Ba-K exchange reaction. The cumulative amount of K released at the end of final extraction when release of K almost ceased, was considered as released K mainly from biotite (Fig. 4). The amount of clay, silt and sand biotites in representative Vertisols of central India ranged from 1.0 to 1.6, 0.2 to 0.3 and 0.2 to 0.4 %, respectively. In <2 mm fine earth fraction, biotite quantity does not exceed 1%, which constitutes about 6-8% of total micas. For any size fraction, the cumulative amount of K released on biotite weight

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

Benchmark Soil/Soil Series	Parent material	Size fractions	
		50-2 mm	<2 mm
Holambi (AS-SA) ^c (Udic Ustochrept)	IGP ^b	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

^bIGP=Indo-Gangetic alluvium; DBA-Deccan basalt alluvium; GG=Granite-gneiss

^cAS-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.

^aAdapted from Pal *et al.* (2006a).

basis follows: > cumulative amount of K released on whole mica weight basis > cumulative amount of K released on weight basis of size fraction (Table 2). The

significant positive correlations between cumulative K release from sand, silt and clay and their corresponding total K contents, respectively (Table 3), indicates

Table 2. Cumulative K release from a representative Vertisol and its size fractions

Horizon	Depth (cm)	Fine earth (<2mm) cumulative K release in 75 extractions			Sand (2 - 0.05 mm) cumulative K release in 10 extractions			Silt (0.05 - 0.002 mm) cumulative K release in 35 extractions			Clay (<0.002 mm) cumulative K release in 60 extractions		
		SF*	MB	BB	SF	MB	BB	SF	MB	BB	SF	MB	BB
Ap	0-15	69	429	6059	20	272	7000	16	191	7004	114	561	6990
Bw1	15-41	41	277	4230	12	162	7006	15	195	7009	92	509	6998
Bw2	41-70	39	267	4097	23	297	6997	13	184	7011	88	502	6999
Bss1	70-95	45	261	4638	15	191	6986	14	161	6990	91	433	7000
Bss2	95-135	49	286	4793	24	334	6991	15	162	6991	92	462	6999
Bss3	135-155	37	235	3849	13	147	6907	16	184	7008	94	471	6984

*SF = on the basis of size fraction; MB = on the basis of mica content; BB = on the basis of biotite content
Adapted from Pal et al. (2006a)

that the K release is a function of total K content in micas and feldspars. However, the positive correlations between total K contents in sand, silt, clay and soil and their mica contents (Table 3) indicate the predominant influence of mica to supply K to the plants grown in Vertisols. Further, significant positive correlations between cumulative K release of sand, silt, clay and soil and their respective mica contents (Table 3) indicate that the K release from either the soils or different size fractions, are controlled mainly by mica. However, better correlations than those between cumulative K release of sand, silt, clay and soil and their biotite contents (Table 3) provide incontrovertible evidence that the K release in soils is primarily controlled by biotite mica. This further supports the earlier observations on the inertness of muscovite mica in releasing K in the presence of biotite (Pal *et al.*, 2001a).

Potassium (K) adsorption and low charge vermiculite/high charge smectite

Major soils of India do not adsorb/fix higher amount of K as evident from their low to moderate values of exchangeable potassium percentage (EPP) within 0.5 m of the profile; EPP for majority of the IGP soils ranges from 3 to 8 % (Pal *et al.*, 2010), for Vertisols (BS) it ranges from 1 to 2 % (Pal *et al.*, 2003a) and for ferruginous soils (FS) it ranges from 3 to 4 % (Murthy *et al.*, 1982). It is quite often reported in the literature that micas, hydrous micas and vermiculites have high adsorption/fixation

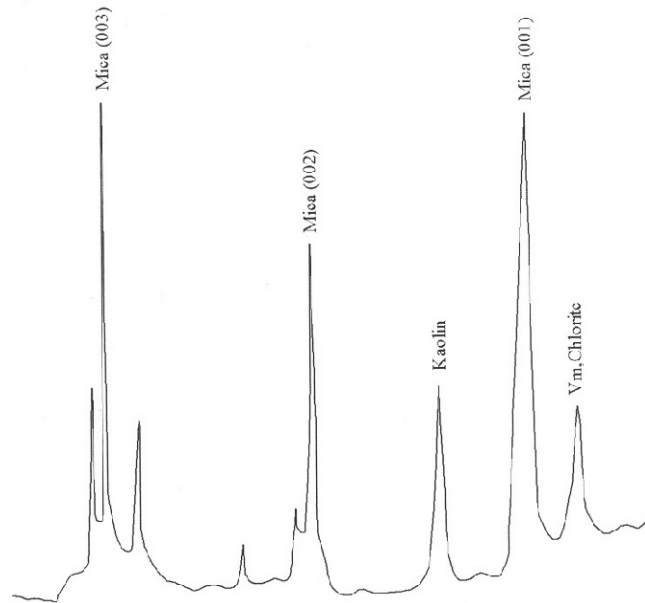


Fig. 2. XRD diagram showing the basal reflections of the micaceous minerals of soils. The ratio of the 001 and 002 reflections shows much more than a unity.

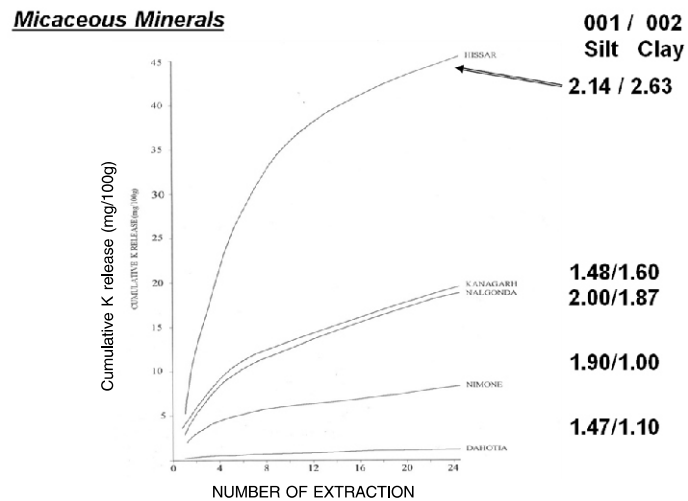


Fig.3. Relation between cumulative K release of soils and number of extractions: Hissar, representative of IGP soils of SA climate; Kanagarh, representative of IGP soils of SH climate; Dahotia, representative of BA soils of PH climate; Nimone, representative of black soils of SA climate; Nalgonda, representative of ferruginous soils of SA climate. (Please refer to 001/002 ratio of peak heights of mica in table 1).

Table 3. Coefficient of correlation among various soil characteristics.

	Parameter	r
Cumulative K of sand	Total K in sand	0.635**
Cumulative K of silt	Total K in silt	0.771 **
Cumulative K of clay	Total K in clay	0.822**
Total K in sand	Sand mica	0.933**
Total K in silt	Silt mica	0.766**
Total K in clay	Clay mica	0.981**
Total K in soil	Soil mica	0.979**
Cumulative K of sand	Sand mica	0.524*
Cumulative K of silt	Silt mica	0.694**
Cumulative K of clay	Clay mica	0.851**
Cumulative K of soil	Soil mica	0.429*
Cumulative K of sand mica	Sand biotite	0.894**
Cumulative K of silt mica	Silt biotite	0.917**
Cumulative K of clay mica	Clay biotite	0.978**
Cumulative K of soil mica	Soil biotite	0.435*

*Significant at 0.05 level; ** Significant at 0.01 level

Adapted from Pal *et al.* (2006a)

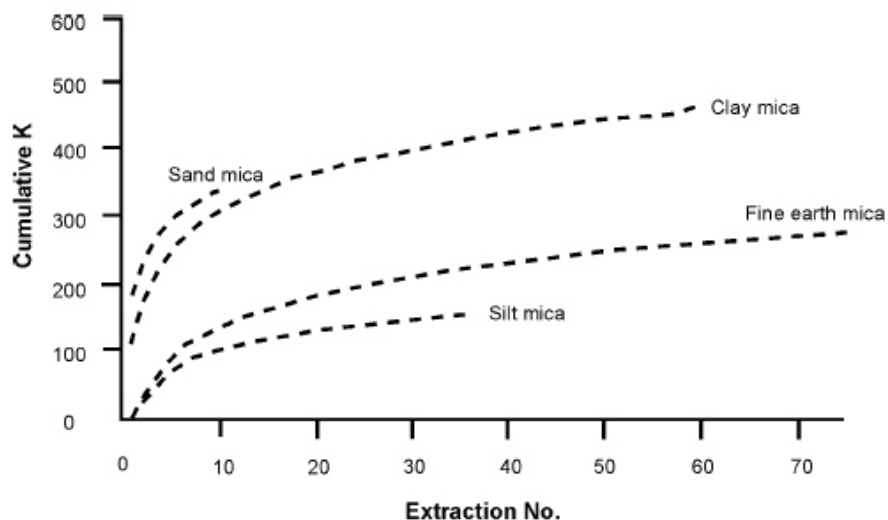


Fig. 4. Relationship between numbers of extractions and cumulative K release (mg/100 g⁻¹ mica) of micas in various size fractions of a Vertisol. Adapted from Pal *et al.*(2006a).

properties while 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). Schwertmann (1962) indicated that some soil smectites have a greater capacity to fix K than do many of the specimen type smectites. Bajwa (1980) has 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 content

of smectite in BS increases with the decrease in particle size and the fine clay fractions contain its highest amount. Despite this fact fine clay smectites do not participate in adsorption/fixation of added K as evident from their comparable amount of adsorbed K (Table 4). The reason is that the fine clay smectites of benchmark Vertisols of central and western India is nearer to montmorillonite of the montmorillonite-nontronite series (Pal and Deshpande, 1987a) and do not adsorb K selectively because of their low layer charge (Pal and Durge, 1987a). Therefore, the observed low K adsorption in these smectites (Table 4) is due to the presence of vermiculite, which is generally not detected on glycolation of Ca-saturated samples but can be detected by a progressive reinforcement of the 1.0 nm peak of mica while heating the K-saturated samples from 25 to 550°C (Fig. 1). Similar experience had also been expressed by Ruhlicke (1985) while reporting K

Table 4. Adsorption of K in different size fractions of Vertisols

Soil Series	Adsorption of added K (mg/100g)		
	Silt (50-2 μm) ^a	Coarse clay (2-0.2 μm)	Fine clay (<0.2 μm) ^b
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

^a0.25 mg K added per g of silt; 0.50 mg K added per g of coarse and fine clay; ^b Fine clay smectites did not adsorb added K in proportion to their high amount indicating their no K-selectivity.

Adapted from Pal and Durge (1987).

adsorption of 60 mg K/100g in bentonite (montmorillonite) deposit. The content of vermiculite was quantified following the method of Alexiades and Jackson (1965) by Pal and Durge (1987) and it ranged from 5 to 9% in the fine clay of Vertisols. Pal and Durge (1987) thus, concluded that the observed K adsorption by the silt and clay fractions is due to the presence of vermiculite and not due to smectite. This indicates that K loss due to adsorption/fixation in the Vertisols is very less. Similar observation was also made by Pal *et al.* (1993) for K adsorption in FS (Table 5). The fine clay fractions of FS though contained the highest amount of smectite did not participate in K adsorption because the fine clay smectite was mostly low charge dioctahedral smectite. The observed K adsorption in the coarser fractions of FS was attributed to vermiculite and in the finer fractions it was trioctahedral low

charge vermiculite/high charge smectite. This smectite could only be detected by their expansion to 1.7 nm on glycolation and by rapid contraction to 1.0 nm on K saturation at 110°C.

In contrast to the fine clay low charge dioctahedral smectites of Vertisols and FS, trioctahedral smectites of some alluvial soils do adsorb K selectively (Table 6) and rate of K adsorption is almost proportional to the content of smectite which increases with the decrease of particle size (Pal and Durge, 1989). These smectites are easily detected that expand to 1.7nm on glycolation but contract readily to 1.0 nm on K saturation at 110°C indicating their high layer charge density (Pal *et al.*, 1989).

Physical properties of soils and minerals

Hydraulic properties of soils and clay and other minerals

It is well known that the hydraulic properties of soils are impaired when they have dominance of Na⁺ ion on the exchange complex (Abrol and Fireman, 1977). In contrast, the Vertisols of dry climates of the Peninsular India do not have any salt-efflorescence on the soil surface as an evidence of soil sodicity but have poor drainage conditions. These soils do not qualify as salt-affected soils as per the United States Salinity laboratory criteria. However, the saturated hydraulic conductivity (sHC) of their subsoils is adversely affected due to clay dispersion and clogging of pores caused by

Table 5. The data of K adsorption by various size fractions of ferruginous soils (FS) (Patancheru and Nalgonda) of southern India

Size fractions	Adsorption of added K (mg/100g) ^a	
	Patancheru	Nalgonda
50-20 µm	16	37
20-6 µm	36	44
6-2 µm	60	62
2-0.6 µm	128	133
0.6-0.2 µm	90	108
<0.2 µm	90	16

^aK added was 0.1 mg/g of silt fractions and 0.2 mg/g of clay fractions

Adapted from Pal *et al.* (1993).

exchangeable magnesium (Balpande *et al.*, 1996; Vaidya and Pal, 2002). This confirms that saturation of Vertisols with Na⁺ and Mg²⁺ ions block small pores in the soil. In other words, Mg²⁺ ions are less efficient than Ca²⁺ ions in flocculating soil colloids (Rengasamy *et al.*, 1986), although the United States Salinity Laboratory (Richards, 1954) grouped Ca²⁺ and Mg²⁺ together as both the ions improve soil structure. The sHC is further impaired even by a low level of exchangeable sodium percentage (ESP) (> 5, < 15) (Balpande *et al.*, 1996) to < 5 mm/hr, causing > 50% reduction in cotton yield (Kadu *et al.*, 2003) because large amounts of smectite minerals (100g of soil may contain 40-50 g of smectite, Pal *et al.*, 2000a) in Vertisols. Thus, the current lower limit of 15 ESP of the United States Salinity Laboratory for all the soils is arbitrary thereby necessitating evaluation of lower limit of ESP. In order to validate this, Pal *et al.* (2006b) undertook an extensive study on Vertisols with and without soil modifiers (Ca-zeolites and gypsum), representing a

climosequence from sub-humid moist (SHM) to arid dry (AD) climate and occurring in major states of the Peninsular India. The results of this study indicate that the release of Ca²⁺ ions from soil modifiers prevented the rise in pH and ESP and modified sHC (>10 mm/hr) amidst high ESP, which supports fairly well the performance of rain-fed crops. Therefore, fixing a lower limit of sodicity at ESP > 40 for soils of the IGP (Abrol and Fireman 1977), at ESP > 5 but < 15 for Indian Vertisols (Kadu *et al.*, 2003), at ESP 6 for Australian soils or at ESP > 15 for all soil types (Soil Survey Staff, 1999) is incompatible with fairly well performance of crops in highly sodic Vertisols with soil modifiers especially of Ca-zeolites (Fig.5) (Pal *et al.*, 2006b). The impairment of sHC of soils mediated by dispersibility is the most important factor for soil degradation (Sumner, 1995), and thus, the characterization of sodic soils on the basis of sHC appears to be most appropriate parameter where 50% reduction in crop

Table 6. Adsorption of K in different size fractions of alluvial IGP and BV

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

^aK added 1 mg per g of silt and 2 mg per g of clay fractions-^bShowing high K selectivity of smectite. Adapted from Pal and Durge (1989).

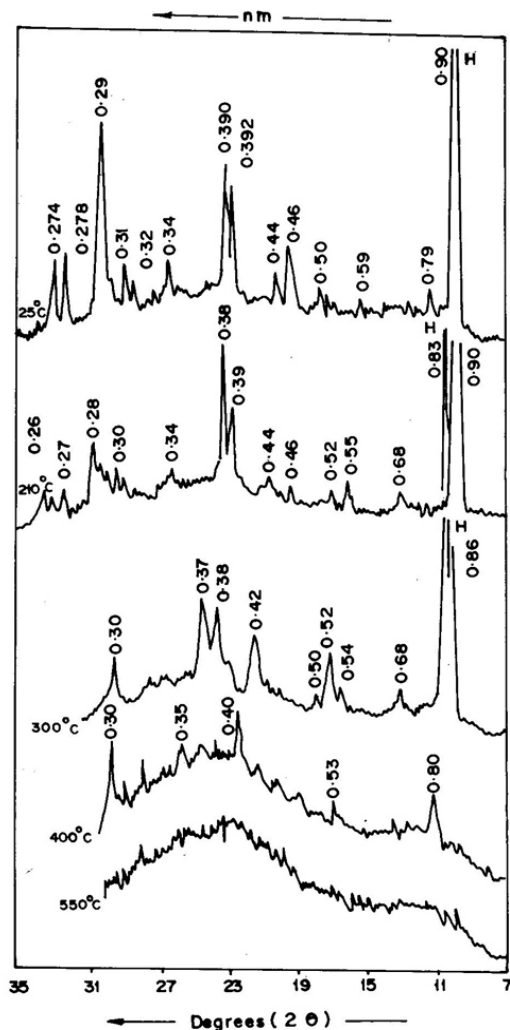


Fig. 5. Representative XRD diagrams of the powdered sand fractions of shrink-swells in semi-arid part of the Western Ghats: H=heulandites (Ca-zeolites). Adapted from Bhattacharyya *et al.* (1999).

yields has been recorded. Therefore, Pal *et al.* (2006b) advocated a value of sHC < 10 mm h⁻¹ (as weighted mean in 1m depth of soil) instead of ESP or SAR as the

important crop limiting soil factor. Therefore, the identification of Ca-zeolites and gypsum is very necessary. They can be easily detected by thin section studies and /or XRD technique. However, their presence can be readily realised when the summation of extractable bases are in excess of the CEC of soils (Bhattacharyya *et al.*, 1993; Pal *et al.*, 2003a, 2006b, 2011) due to release of extra Ca ions from soil modifiers by the exchanger solution during the extraction of exchangeable cations of soils.

Dispersibility of clay colloids impairing the sHC of soils is caused by ESP or to some extent exchangeable magnesium percentage (EMP) in the presence or absence of soil modifiers. However, the sHC of zeolitic Vertisols of Marathwada region in Maharashtra state of the semi-arid part of western India indicated a value <10 mm/hr, though they are non-sodic soils (Typic Haplusterts) (Zade, 2007). Such Vertisols have neutral to mildly alkaline pH, ESP < 5, but have increasing trend in EMP with depth, and in some pedons EMP is more than ECP (exchangeable calcium percentage) beyond 50 cm depth. Mineralogical studies indicate the presence of palygorskite mainly in the silt and coarse clay fractions (Fig. 6) (Zade, 2007; Kohle *et al.*, 2012). This mineral is the most magnesium rich among the common clay minerals (Weaver and Pollard, 1973; Singer, 2002). Therefore, Vertisols with palygorskite mineral are rich in EMP, which causes enormous dispersion of clay colloids

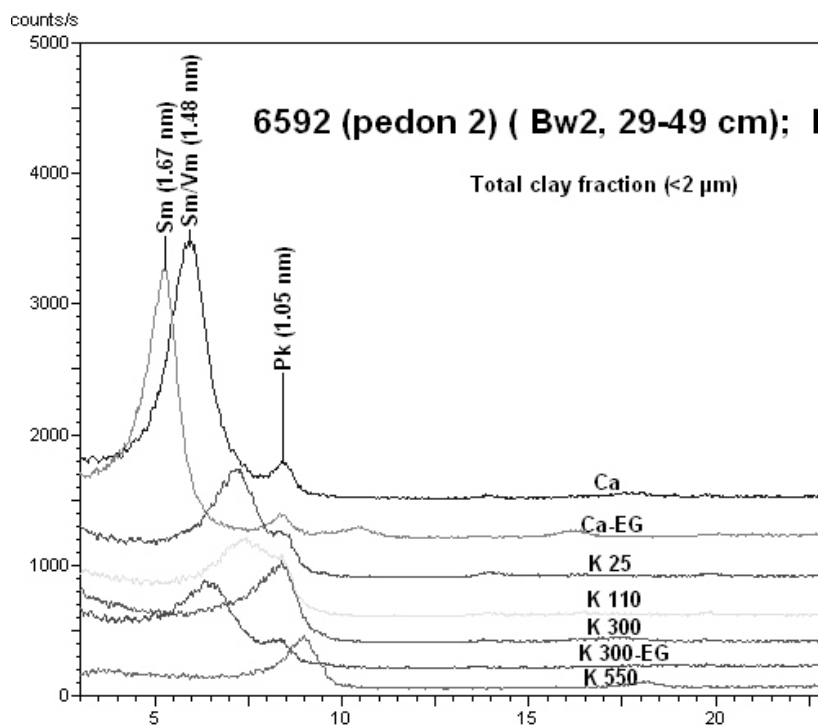


Fig. 6 .Representative X-ray diffractograms of total clay fractions of Pedon 1 (Sm=smeectite, Sm/Vm=smeectite or vermiculite, Pk=palygorskite, Ca = calcium saturated; CaEG = Ca-saturated and ethylene glycolated; K25°/K110°/K300°/K550° = K saturated and heated at 25, 110, 300 and 550°C. K300°EG= K saturated and heated at 300° and ethylene glycolated). Adapted from Kolhe *et al.* (2011).

that form a 3D mesh in the soil matrix. This causes drainage problem when such soils are irrigated, a predicament for crop production. In view of their poor drainage conditions and loss of productivity, non-sodic Vertisols (Typic Haplusterts) with palygorskite minerals needs to be considered as naturally degraded soils. Similar soils may be occurring elsewhere in the world and thus, a new initiative to classify them is warranted.

Climate change and minerals

Mineral formation in soils and sediments as signatures of climate change

Paleopedological research unravels the signatures of climate change that generally remain stored in soils and sediments of the past (Pal *et al.*, 2000a) and such soils are known as paleosols, formed on a landscape of the past (Valentine and Dalrymple, 1976). Studies on paleosols have caught the attention of the pedologists,

sedimentologists and soil mineralogists in India and abroad (Singer, 1980; Beckmann, 1984; Jenkins, 1985; Fenwick, 1985; Wright, 1986; Pal *et al.*, 1989, Srivastava *et al.*, 1998; 2007, 2009, 2010, Pal *et al.*, 2001b, 2009, 2011).

Identification of paleoclimatic signatures in paleosols forms the major challenge to soil scientists. Yaalon (1971) points to the fact that the products of the self-terminating, irreversible reactions such as calcareous or siliceous incrustations are among the most permanent and best indicators of paleo-environmental conditions. Whenever reliable paleoclimatic indicators, such as paleontological remains, pollen or isotope chemistry were absent or have failed, paleoclimatologists have turned to paleosols for clues as to the nature of climates of the past (Singer, 1980). The clay minerals of these paleosols are potential promising materials for documenting and resolving a wide spectrum of different genetic environments and reactions (Keller, 1970). The use of clay minerals in paleosols and saprolites (weathering profiles) for the purpose of paleoclimatic interpretation has been explained in detail by Singer (1980). It is often difficult to determine as to which minerals are diagnostic of different climatic zones. However, those clay minerals which occur most frequently can be considered to have climatic significance (Tardy *et al.*, 1973). For example, minerals such as kaolinite often remain unaltered through subsequent changes in climate, and

therefore, may preserve a paleoclimatic record. Singer (1980) indicated that other layered silicates at a less advanced stage of weathering may adjust to subsequent environmental changes and thus may lose their interpretative value for paleoclimatic signatures. However, several Indian researchers have considered minerals of intermediate weathering stage as potential indicators of paleoclimatic changes in parts of central India and Gangetic Plains (Pal *et al.*, 1989; Srivastava *et al.*, 1998; Pal *et al.*, 2009, 2011). They have demonstrated how secondary minerals like di- and trioctahedral smectites (DSm and TSm), smectite-kaolin interstratified minerals (Sm/K), hydroxy-interlayered smectite (HIS), hydroxy-interlayered vermiculite (HIV), pseudo-chlorite (PCh) of intermediate weathering stage, and CaCO₃ of pedogenic (PC) and non-pedogenic (NPC) origin can be regarded as potential indicators of paleoclimatic changes in major soil types of India and also in paleosols of the alluvial sediments of the Himalayan river systems and Cratonic source from Peninsular India.

Di- and trioctahedral smectite as evidence for paleoclimatic changes

Well crystallized dioctahedral smectites as the first weathering product of Peninsular Gneiss partly transformed to kaolin in ferruginous soils (Alfisols) formed in a pre-Pliocene tropical humid climate (Pal *et al.*, 1989). Such kaolin (KI) is not a discrete kaolinite as XRD diagrams of its Ca-saturated and glycolated sample indicates

the broad base of 0.72 nm peak and tails towards the low angle. On heating the K-saturated sample at 550°C, the 0.72 nm peak disappears, confirming the presence of kaolin and simultaneously reinforces the 1.0 nm region at much higher degree even in presence of 1.4 nm minerals, indicating the presence of KI-HIV/HIS (kaolin interstratified with either hydroxy-interlayered vermiculite, HIV or smectite, HIS) (Fig. 7). Later with the termination of humid climate, both these clay minerals were preserved to the present. Therefore, the ferruginous Alfisols overlying the saprolites dominated either by dioctahedral

smectite or kaolin are relict paleosols (Pal *et al.*, 1989; Chandran *et al.*, 2000), which have been affected by the climatic change from humid to drier conditions during the Plio-Pleistocene transition period. It is evidenced by the formation of trioctahedral smectite in the present dry climate from the sand and silt size biotite (Fig.8a), which survived weathering during the earlier humid climate. This smectite is high charge smectite or low charge vermiculite that expands to 1.7 nm on glycolation of Ca-saturated sample but contracts readily to 1.0 nm on K-saturation and heating to 110° C. The present day warm semi-aridic

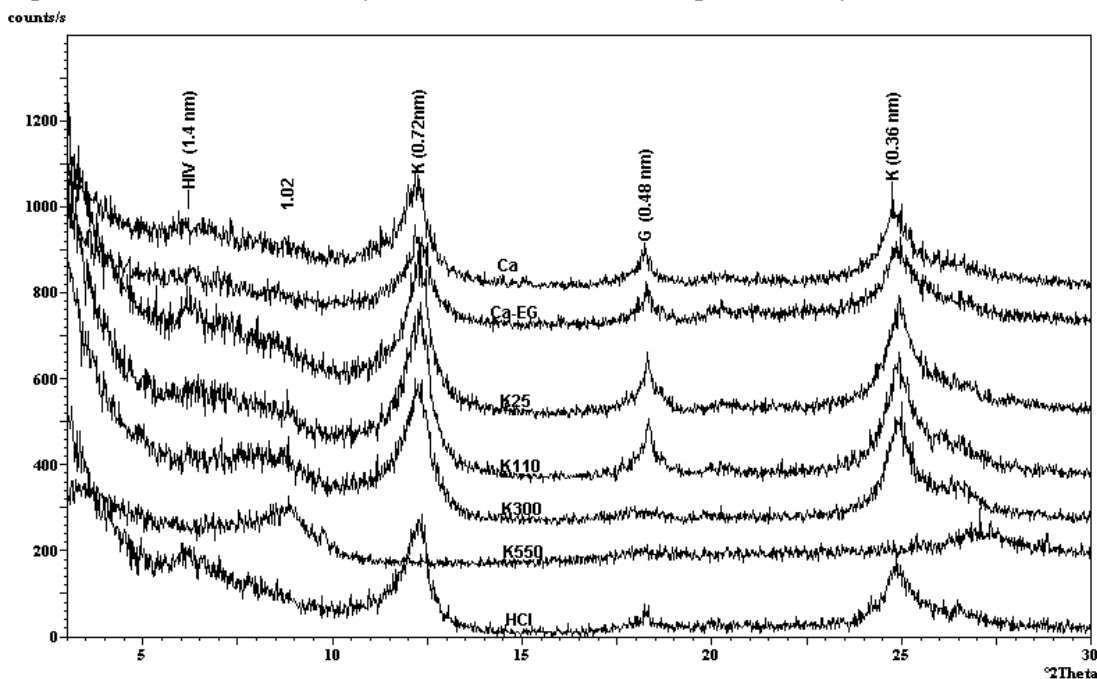


Fig.7. XRD diagram of fine clay of acid FS: Ca, Ca-saturated; Ca-EG, calcium-saturated and ethylene glycolated-solvated; K25, K110, K300, K550, K-saturated and heated to 25°, 110°, 300° and 550° C, respectively; HCl, treated with 6N HCl for 30 min at 90° C. HIV, hydroxy-interlayered vermiculite; K, kaolin; G, gibbsite. Adapted from Chandran *et al.* (2005).

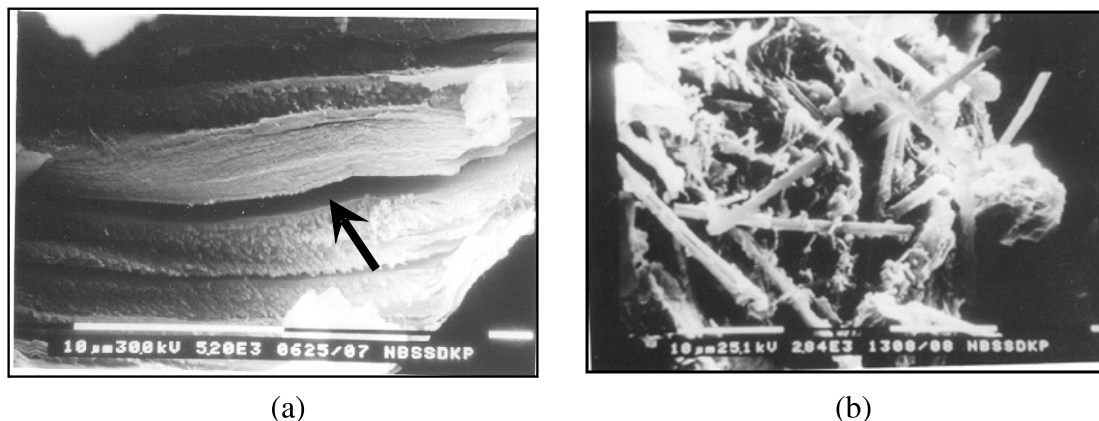


Fig. 8. Representative SEM photograph of the formation of vermiculite around biotite particles of ferruginous soils (Alfisols) (a), of PC (lubinites) in ferruginous soils (Alfisols) of semi-arid southern India (b). Adapted from Pal *et al.* (2000a).

climatic conditions also favoured the formation of pedogenic calcium carbonate (PC)(Fig.8b) by inducing the precipitation of CaCO_3 with a concomitant development of subsoil sodicity (Pal *et al.*, 2000b; 2011). These relict paleosol qualify to be polygenetic soils with strong paleoclimatic potential (Pal *et al.*, 1989).

Red and black soils in semi-arid climatic environments

Occurrence of spatially associated red ferruginous (Alfisols) and black (Vertisols) soils on gneiss under similar topographical conditions are very common in semi-arid region of southern Peninsular India (Pal and Deshpande 1987b). Ferruginous soil clays consist chiefly of kaolin and smectite whereas black soil clays are dominated by low charge dioctahedral smectite. The inverse relation between kaolin and smectite with pedon depth of ferruginous

soil clays (Pal *et al.*, 1989) indicated the transformation of smectite to kaolin even though prevailing semi-arid climate can not favour the formation of kaolin at the expense of smectite in slightly acid to moderately alkaline reaction. Similarly, the arid climate cannot yield the huge amount of smectite required for the formation of Vertisols. Earlier studies in southern Peninsular India (Murali *et al.*, 1978; Rengasamy *et al.*, 1978) suggested that kaolinite was formed in an earlier geological period with more rainfall and great fluctuations in temperature, as evidenced by the presence of granitic tors all around such area (Pal and Deshpande 1987b). Therefore, the smectite of Vertisols formed in the earlier humid climate. This was detached from the weathering gneissic rock and transported downstream and deposited in low-lying areas following the landscape reduction process and the typical

Vertisols were developed in the microdepressions (Fig. 9). After the peneplanation, red ferruginous soils on stable surface continued to weather to form kaolin mineral as the stability of the smectite was ephemeral in tropical humid climate (Bhattacharyya *et al.*, 1993). But due to termination of the humid climate during the Plio-Pleistocene transition, smectite and kaolin could be preserved to the present day (Pal *et al.*, 2000a).

Clay minerals in soils of the Indo-Gangetic Plains (IGP)

Transformation of clay minerals in a soil chrono-association comprising 5 fluvial surfaces (QGH1 to QGH5) of the IGP between Ramganga and Rapti rivers,

demonstrated that pedogenic smectite-kaolin (Sm/K) can be considered as a potential indicator for Holocene climatic changes from arid to humid conditions (Srivastava *et al.*, 1998). The ages of QGH1 to QGH5 are <500 yr BP, >500 yr BP, >2500 yr BP, 8000 Cal yr BP and 13,500 Cal yr BP, respectively. During soil formation, two major regional climatic cycles are recorded. Relatively arid to semi-arid cycles between 10,000-6,500 year BP and 4,000 year BP till present was punctuated by a warm and humid climate. Biotite weathered to trioctahedral vermiculite and smectite in the soils during arid conditions that was unstable and transformed to Sm/K during the following warm and humid climate phase (7400-4150

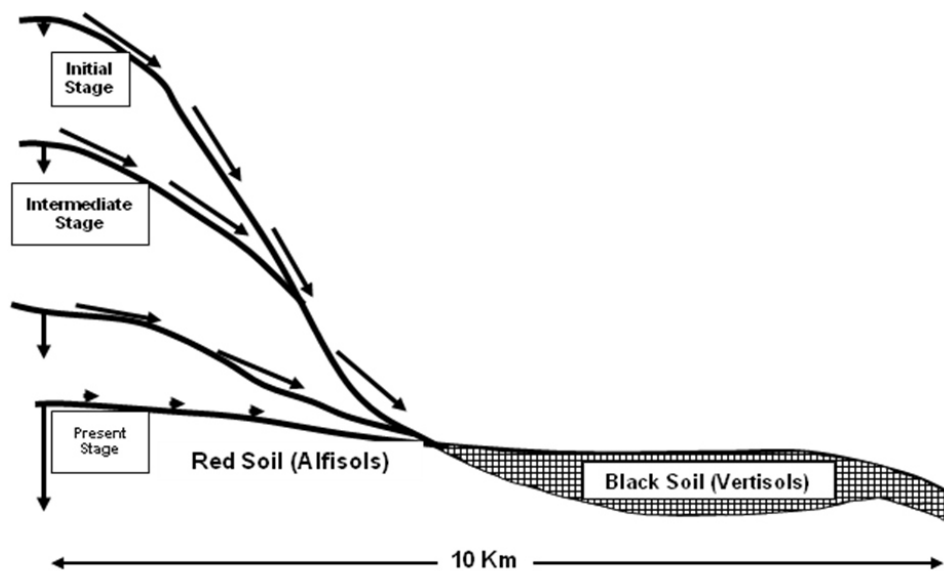


Fig. 9. Schematic diagram of the pedon site of red soils (Alfisols) and black soils, (Vertisols) showing the landscape reduction process explaining the formation of spatially associated red and black soils. Adapted from Pal (2008).

Cal year BP). When the humid climate terminated, vermiculite, smectite and Sm/K were preserved to the present. During the hot semi-arid climate that followed the humid climate, transformation of biotite into its weathering products like trioctahedral vermiculite and smectite did continue. Initiated by the formation of PC, fine clay vermiculite and smectite translocated downward in the profile as Na-clay, to make soils calcareous and sodic (Pal *et al.*, 1994, 2003b). This pedogenetic process with time become an example of self-terminating process (Yaalon, 1971) exhibiting their polygenetic features.

Vertisols, carbonate minerals and climate change

Smectitic Vertisols occur in humid tropical (HT), sub-humid moist (SHM), sub-humid dry (SHD), semi-arid moist (SAM), semi-arid dry (SAD) and arid dry (AD) climatic environments in Deccan basalt area (Pal *et al.*, 2009). It is well known that smectites are ephemeral in HT climate as they readily transform to kaolin (Pal *et al.*, 1989; Bhattacharyya *et al.*, 1993). The formation of Vertisols in HT climate has been possible because smectite of Sm/K and Ca-zeolites created conducive chemical environment necessary for the formation and persistence of Vertisols in lower topographic situation (Bhattacharyya *et al.*, 1993, 1999). It is equally difficult to understand the formation of Vertisols in SHM, SHD, SAM, SAD and AD climates, since a large amount of

smectite clay is required for their formation. However, in these climatic environments, the weathering of primary minerals contributes very little towards the formation of smectites. XRD analysis of fine clays (Fig. 10) indicates that smectites of Vertisols from sub-humid to arid climates are fairly well crystallized as evident from a regular series of higher order reflections and do not show any sign of transformation except for hydroxy-interlayering (HI) in the smectite interlayers (Pal *et al.*, 2000a; Srivastava *et al.*, 2002). Such interlayering

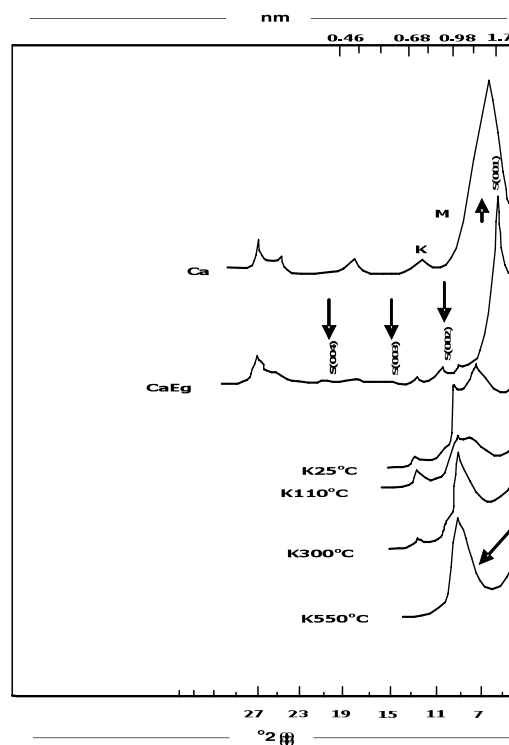


Fig. 10. Representative X-ray diffractograms of fairly well crystalline fine clay smectite of Vertisols despite having partial hydroxy-interlayering. Adapted from Pal (2003).

was also noticed in vermiculite of the silt and coarse clay fractions (Fig. 11) that resulted finally in the formation of pseudo-chlorite (PCh). HI in smectite interlayers is identified from the broadening of the low angle side of the collapsed 1.0 nm peak of K-saturated smectite heated to 550°C (Fig. 10). PCh is not a true chlorite as it shows a broad peak around 1.4 nm when K-saturated sample is heated to 550°C (Fig. 11). Thus the presence of hydroxy-interlayered dioctahedral smectite (HIS), hydroxy-interlayered vermiculite (HIV as an alteration product of biotite mica) and PCh (as a transformation product of HIV) is common in size fractions of Vertisols (Pillai *et al.*, 1996; Pacharne *et al.*, 1996; Vaidya and Pal, 2003). The hydroxy-interlayering in the vermiculite and smectite occurs when positively charged hydroxy-interlayer materials such as $[\text{Fe}_3(\text{OH})_6]^{3+}$, $[\text{Al}_6(\text{OH})_{15}]^{3+}$, $[\text{Mg}_2\text{Al}(\text{OH})_6]^+$, and $[\text{Al}_3(\text{OH})_4]^{5+}$ (Barnhisel and Bertsch, 1989) enter into the inter-layer spaces at pH much below 8.3 (Jackson, 1964). Moderately acidic conditions are optimal for hydroxyl interlayering of vermiculite and smectite and the optimum pH for interlayering in smectite and vermiculite is 5.0-6.0 and 4.5-5.0, respectively (Rich, 1968). The pH of the majority of Vertisols of subhumid to arid climates is either near to neutral or well above 8.0 throughout the profile. This suggests that in mildly to moderately alkaline conditions of soils, 2:1 layer silicates suffer congruent dissolution (Pal, 1985). Thus, it discounts the hydroxy-

interlayering of smectites and vermiculites during the post depositional period of the basaltic alluvium (Pal *et al.*, 2011), likewise the subsequent transformation of vermiculite to PCh. Therefore, the formation of HIS, HIV and PCh does not represent contemporary pedogenesis of Vertisols in the prevailing dry climatic conditions (Pal *et al.*, 2011). Vertisols of subhumid to arid climates have both NPC (relict Fe-Mn coated carbonate nodules) and PC (pedogenic CaCO_3) (Pal *et al.*, 2000b, 2009). Based on ^{14}C dates of carbonate nodules, Mermut and Dasog (1986) concluded that Vertisols with Fe-Mn coated CaCO_3 are older soils than those with PCs that are formed in soils of dry climate (Pal *et al.*, 2000b). Thus, NPCs were formed in a climate much wetter than the present, which ensured adequate soil water for reduction and oxidation of iron and manganese to form Fe-Mn coatings. The first weathering product of plagioclase-rich Deccan basalt is a low charge di-octahedral smectite (DSm) in aridic to humid climates (Pal and Deshpande, 1987b). Thus, the large amount of DSm formed in an earlier humid climate in the source area as an alteration product of plagioclase in tropical humid climates (Pal *et al.*, 1989; Srivastava *et al.*, 1998) and during this weathering vermiculite transformed to HIV, which may have transformed to PCh because HI in vermiculite would occur in acidic soil conditions. However, the formation of HIS in humid tropical climate did not continue as evidenced from the presence of very small

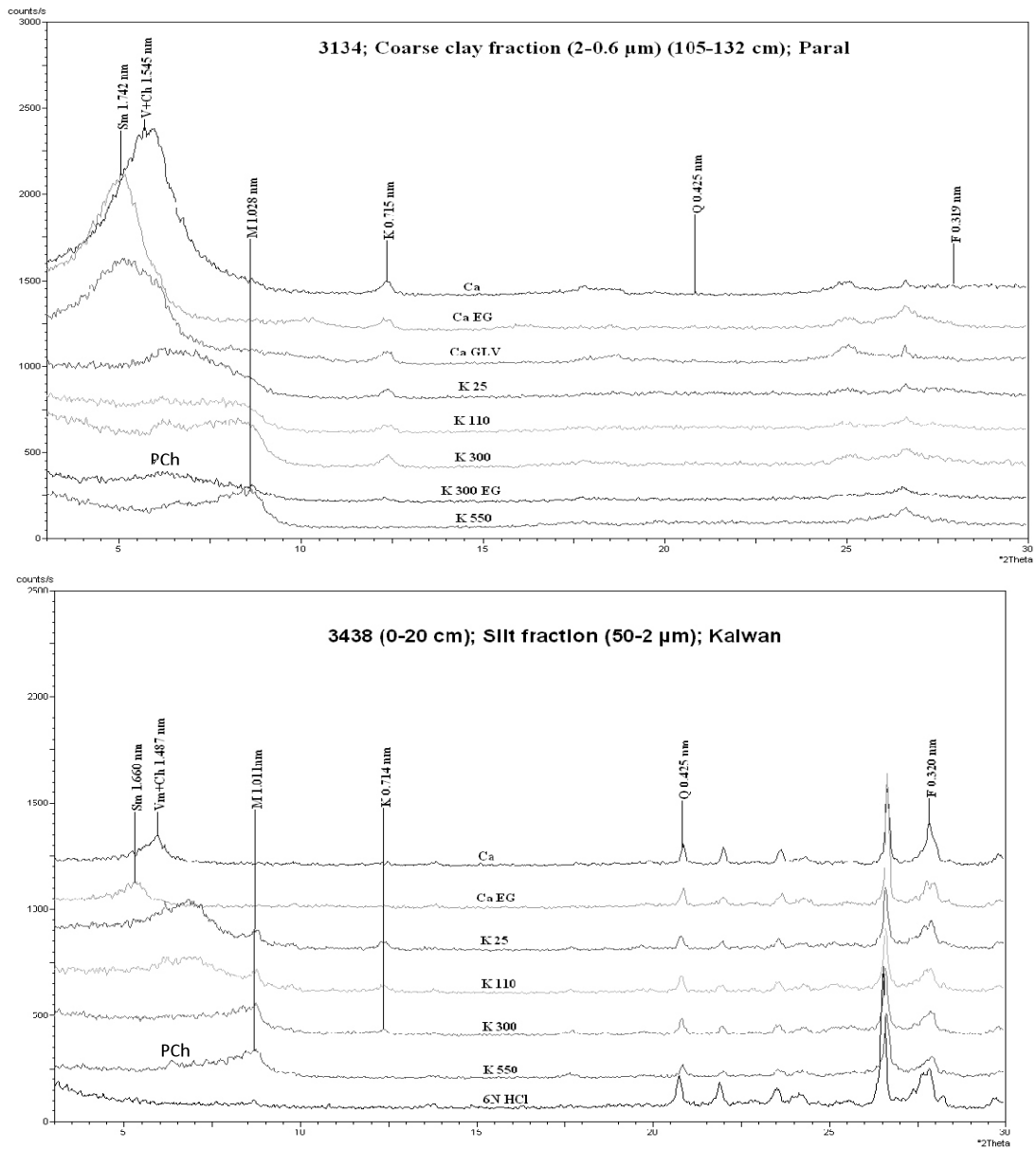


Fig. 11. Representative X-ray diffractograms of coarse clay (a), and silt (b) fractions of Vertisols of Peninsular India; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K25/110/300/550°C=K-saturated and heated to 25°, 110°, 300°, 550°C; 6NHCl = 6N HCl treated silt fraction; Sm = Smectite, V + Ch = vermiculite plus chlorite; PCh= Pseudo chlorite; K = Kaolin; F = Feldspars; Q = Quartz. Adapted from Pal et al.(2003a) and Bhople (2010).

amount of kaolin (Sm/K) in the fine clay fractions. In the event of prolonged formation of HIS, the content of kaolin should have been dominant (Bhattacharyya *et al.*, 1993). Thus, the smectite of Vertisols formed in an earlier and more humid climate. Its crystallinity, and also the PCh were preserved in the non-leaching environment of the latter dry climates (Pal *et al.*, 2009, 2011). The ^{14}C age of soil organic carbon of Vertisols was estimated to be between 3390 to 10,187 yr BP (Pal *et al.*, 2006b). This suggests that the change from humid to drier climate occurred in Peninsular India during the late Holocene (Pal *et al.*, 2001, 2003b, 2006b; Deotare 2006). In SAM, SAD and AD climates Vertisols became more calcareous and sodic (Pal *et al.*, 2006b) than those of SHM and SHD climates. Therefore, they qualify to be polygenetic (Pal *et al.*, 2001).

Clay minerals record from drill cores of the Ganga Plains

Climate change over the last 100 ka has been manifested in clay mineralogy of paleosols and sediments from two cores (~50 m deep) in the Ganga–Yamuna interfluvium in the Himalayan Foreland Basin, India (Pal *et al.*, 2011). Core sediments from the northern part of the interfluvium (IITK core) are micaceous and dominated by hydroxy-interlayered dioctahedral low-charge smectite (LCS) in fine clay fraction but by trioctahedral high-charge smectite (HCS) in silt and coarse clay fractions. In contrast, core sediments from the southern

part of the interfluvium (Bhognipur core) are poor in mica and both LCS and HCS are present in the upper 28 m of the core and the lower part is dominantly LCS in all size fractions. Paleosols are formed in the two cores in the sub-humid to semi-arid climatic conditions and this has resulted clay minerals such as 1.0-1.4 nm minerals, vermiculite, HCS and also preserved the LCS, hydroxy-interlayered vermiculite (HIV) and pseudo-chlorite (PCh), and kaolin that formed earlier in a humid climate. The preservation of LCS, HIV, kaolin and PCh bears the signature of climate shift from humid to semi-arid conditions in the Ganga Plains as their formation does not represent contemporary pedogenesis in the present alkaline chemical environment induced by the semi-arid climate. The abundance of LCS sediments in both the cores suggests the role of plagioclase weathering in the formation of LCS. The climatic records inferred from the typical clay mineral assemblages of the two interfluvium cores are consistent with the Marine Isotope Stages (MIS) over the last 100 ka. Typical clay mineral assemblage in humid interglacial stages (e.g. MIS 5, 3 and 1) is marked by HIV, LCS and PCh formed under acidic soil conditions. In a drier climate (MIS 4 and 2), formation of trioctahedral HCS from biotite weathering and precipitation of pedogenic CaCO_3 were the dominant processes that created conducive environment for illuviation of clays forming argillic (Bt) horizon in the paleosols of the

interfluvial.

Conclusions

A thorough knowledge and appreciation of minerals in soils is critical to our understanding and use of soil. Despite our general understanding on the role of minerals in soils it is necessary to investigate the properties of the minerals, especially clay minerals, their mixtures and surface modifications in the form that they occur in the soil. From the few examples under different agro-climatic situations cited here it is evident that unless the mineralogical description is accurate enough for the purpose intended, it would not be prudent to look for their significance in soils. With the use of high resolution micro-morphology, mineralogy, and age control data alongside their geomorphologic and climatic history, we can identify and explain many enigmatic situations in soils. Therefore, the future research endeavours should provide adequate knowledge that would explain discretely many of the pedo-edaphological aspects and also the impacts of climate change in soils in terms of minerals in general and clay minerals in particular and their significance for soil as a sustainable medium for plant growth. The mineralogical research work undertaken over the last several decades on important soil/paleosol types and the sediments demonstrates that the pedogenic clay minerals of intermediate weathering stages like HIS, Sm/K, HIV, PCh and pedogenic carbonates can be very useful paleoclimatic

indicators. This basic knowledge on soil clay minerals can serve as an important tool for the paleoclimatologists to infer climate change not only of India but elsewhere of the world. The state-of-the-art-information developed through this review has helped to establish a link between minerals and major soil properties and climate change phenomenon in geological time scale. It is hoped that this review serves as a hand book to assess the health and quality of soils while developing suitable management practices to enhance and sustain their productivity.

References

- Abrol, I.P., Fireman, M. 1977. *Alkali and Saline soils, Identification and Improvement for Crop Production*. Bull. No.4. Central Soil Salinity Research Institute: Karnal, India.
- Alexiades, C. A. and Jackson, M. L. 1965. Quantitative determination of vermiculite in soils. *Soil Sci. Soc. Amer. Proc.*, **29**: 522-527.
- Bajwa, I. 1980. Soil clay mineralogies in relation to fertility management: effect of soil clay mineral compositions on potassium fixation under conditions of wetland rice culture. *Com. Soil Sci. & Plant Anal.*, **11**: 1019-1027.
- Balpande, S. S., Deshpande, S. B. and Pal, D. K. 1996. Factors and processes of soil degradation in Vertisols of the Purna valley, Maharashtra, India. *Land Degrad & Dev.*, **7**: 313-324

- Barnhisel, R.I. and Bertsch, P. M. 1989. Chlorites and hydroxy-interlayered vermiculites and smectite. In: (J. B. Dixon and J. B. Weed, Eds.), *Minerals in Soil Environments*. Soil Science Society of America Book Series (Number 1): Wisconsin, USA, Second Edition, pp.729-788.
- Beckmann, G.G. 1984. Paleosols, pedoderm, and problems in presenting pedological data. *Aust. Geographer*, **16**:15-21.
- Bhattacharyya, T., Pal, D. K. and Deshpande, S. B. 1993. Genesis and transformation of minerals in the formation of red (Alfisols) and black (Inceptisols and Vertisols) soils on Deccan Basalt in the Western Ghats, India. *J. Soil Sci.*, **44**: 159-171.
- Bhattacharyya, T., Pal, D. K. and Srivastava, P. 1999. Role of zeolites in persistence of high altitude ferruginous Alfisols of the humid tropical Western Ghats, India. *Geoderma*, **90**: 263-276.
- Bhattacharyya, T., Pal, D. K. and Srivastava, P. 2000. Formation of gibbsite in presence of 2:1 minerals: an example from Ultisols of northeast India. *Clay Miner.*, **35**: 827-840.
- Bhattacharyya, T., Sen, T. K., Singh, R. S., Nayak, D. C. And Sehgal, J. L. 1994. Morphology and classification of Ultisols with kandic horizon in north eastern region. *J. Indian Soc. Soil Sci.*, **42**: 301-306.
- Bhople, B. S. 2010. Layer Charge Characteristics of Some Vertisol Clays of Maharashtra and its Relationship with Soil Properties and Management. Ph. D Thesis, Dr. P D K V, Akola, Maharashtra, India.
- Biddappa, C.C. and Venkat Rao, B.V. 1973. Studies on the relationship between sesquioxides, phosphorus contents and phosphorus fixing capacity of coffee soils of south India. *J. Indian Soc. Soil Sci.*, **21**:155-159.
- Brindley, G.W. 1966. Ethylene glycol and glycerol complexes of smectites and vermiculites. *Clay Miner.*, **6**: 237-259.
- Burford, J. R. and Sahrawat, K. L. 1989. Nitrogen availability in SAT soils: environment effects on soil processes. In: (Christianson, C. B, Ed.), *Soil Fertility and Fertility Management in Semi-Arid Tropical India*, Proc. Colloq. held at ICRISAT Centre, Patancheru, India, October 10-11, 1988, International Fertilizer Development Centre: Muscle Shoals, AL, pp. 53-60.
- Chandran, P., Ray, S. K., Bhattacharyya, T., Krishnan, P. and Pal, D.K. 2000. Clay minerals in two ferruginous soils of southern India. *Clay Res.*, **19**: 77-85.
- Chandran, P., Ray, S. K., Bhattacharyya, T., Srivastava, P., Krishnan, P. and Pal, D. K. 2005. Lateritic soils of Kerala, India: their mineralogy, genesis and taxonomy. *Austr. J. Soil Res.* **43**: 839-852.
- Dalal, R. C. 1977. Fixed ammonium and

- carbon-nitrogen ratios of Trinidad soils. *Soil Sci.*, **124** : 323-327.
- Deotare, B.C. 2006. Late Holocene climatic change: archaeological evidence from the Purna Basin, Maharashtra. *J. Geological Soc. India*, **68**: 517-526.
- Dhillon, S. K. and Dhillon, K. S. 1991. Characterization of potassium in red (Alfisols), black (Vertisols) and alluvial (Inceptisols and Entisols) soils of India using electro-ultra filtration. *Geoderma*, **50**: 185-196.
- Fenwick, I. 1985. Paleosols: problems of recognition and interpretation. In: (Boardman, J, Ed), *Soils and Quaternary Landscape Evolution*, John Willey & Sons Ltd. pp. 3-21.
- Ghosh, S. K. and Kapoor, B. S. 1982. Clay minerals in Indian soils. In: Review of Soil Research in India. *Transactions 12th International Congress Soil Science*, **2**: 703-710.
- Ghosh, S.K. and Bhattacharyya, T. 1983. Clay minerals – their distribution and genesis in Indian soils. In: *Advances in Soil Science*. Books and Periodicals Agency, New Delhi, pp.216-277.
- Ghosh, S.K. 1997. Clay research in India. 13th Prof. J.N. Mukherjee ISSS Foundation Lecture. *J. Indian Soc. Soil Sci.*, **45**:637-658.
- Gjems, O. 1967. Studies on clay minerals and clay mineral formation of soil profiles in Scandinavia. *Meddeleser fra det Norske Skogforsoksvesen* **21**: 303-415.
- Greenland, D. J. and Hayes, M. H. B. 1978. *The Chemistry of Soil Constituents*, John Wiley and Sons, USA.
- Haynes, R. J. 1983. Effect of lime and phosphate applications on the adsorption of phosphate, sulphate, and molybdate by a Spodosol. *Soil Sci.* **135**: 221-226.
- ICRISAT. 1988. Phosphorus in Indian Vertisols: Summary Proceedings of a Workshop, August 1988, ICRISAT Center, Patancheru, A.P.502324, India, pp.23-26.
- Jackson, M.L. 1964. Chemical composition of soils. In: (Bear, F. E, Ed.) *Chemistry of the Soil*. Oxford and IBH Publishing Co., Calcutta, pp.71-141.
- Jenkins, D.A. 1985. Chemical and mineralogical composition in the identification of paleosols. In: (Boardman, J, Ed.), *Soils and Quaternary Landscape Evolution*, Wiley: New York, pp. 23-43.
- Kadu, P. R., Vaidya, P. H., Balpande, S. S., Satyavathi, P. L. A. and Pal, D. K. 2003. Use of hydraulic conductivity to evaluate the suitability of Vertisols for deep-rooted crops in semi-arid parts of central India. *Soil Use & Magt.*, **19**: 208-216.
- Kanwar, J.S. and Grewal, J.S. 1960. Phosphate fixation in Punjab soils. *J. Indian Soc. Soil Sci.*, **8**: 211-218.
- Kapoor, B. S. 1972. Weathering of micaceous clays in some Norwegian Podzols. *Clay Miner.*, **9**: 383-394.

- Keller, W.D. 1970. Environmental aspects of clay minerals. *J. Sedimentary Petrology*, **40**:788-813.
- Kolhe, A. H., Chandran, P., Ray, S. K., Bhattacharyya, T. and Pal, D. K., 2012. Genesis of associated red and black shrink-swell soils of Maharashtra. *Clay Res.*, In Press.
- Mengel, K. and Busch, R. 1982. The importance of the potassium buffer power on the critical potassium level in soils. *Soil Sci.*, **133**: 27-32.
- Mermut, A. R. and Dasog, G. S. 1986. Nature and micromorphology of carbonate glaeboles in some Vertisols of India. *Soil Sci. Soc. America J.*, **50**: 382-391.
- Mukherjee, S. K., Das, S. C. and Raman, K.V. 1971. Soil mineralogy. In: (Kanwar, J.S. and Raychoudhuri, S. P, Eds.), *Review of Soil Research in India*, Indian Society of Soil Science, New Delhi, pp.169-194.
- Murali, V., Krishnamurti, G.S.R. and Sarma, V.A.K. 1978. Clay mineral distribution in two toposequences of tropical soils of India. *Geoderma*, **20**:257-269.
- Murthy, R. S., Bhattacharjee, J. C., Landey and R. J., Pofali, R. M. 1982. Distribution, characteristics and classification of Vertisols. In: *Vertisols and Rice Soils of the Tropics*, Symposia paper II, 12th International Congress of Soil Science, New Delhi, Indian Society of Soil Science, pp. 3-22.
- Nommik, H. and Vahtras, K. 1982. Retention and fixation of ammonium and ammonia in soils. In: (Stevensen, F. J, Ed.), *Nitrogen in Agricultural Soils. Agronomy*, **22**: 123-171.
- Pacharne, T., Pal, D. K. and Deshpande, S. B. 1996. Genesis and transformation of clay minerals in the formation of ferruginous (Inceptisols) and black (Vertisols) soils in the Saptadhara Watershed of Nagpur district, Maharashtra. *J. Indian Soc. Soil Sci.*, **44**: 300-309.
- Pal, D. K. 1985. Potassium release from muscovite and biotite under alkaline conditions. *Pedologie (Ghent)*, **35**: 133-146.
- Pal, D. K. 2003. Significance of clays, clay and other minerals in the formation and management of Indian soils. *J. Indian Soc. Soil Sci.*, **51**: 338-364.
- Pal, D. K. 2008. Soils and their mineral formation as tools in paleopedological and geomorphological studies. *J. Indian Soc. Soil Sci.*, **56**: 378-387.
- Pal, D. K. and Deshpande, S. B. 1987a. Characteristics and genesis of minerals in some benchmark Vertisols of India. *Pedologie (Ghent)*, **37**: 259-275
- Pal, D. K. and Deshpande, S. B. 1987b. Genesis of clay minerals in a red and black complex soils of southern India. *Clay Res.*, **6**: 6-13.
- Pal, D. K. and Durge, S. L. 1987. Potassium

- release and fixation reactions in some benchmark Vertisols of India in relation to their mineralogy. *Pedologie (Ghent)*, **37**: 103- 116.
- Pal, D. K. and Durge, S. L. 1989. Release and adsorption of potassium in some benchmark alluvial soils of India in relation to their mineralogy. *Pedologie (Ghent)*, **39**: 235-248.
- Pal, D. K., Deshpande, S. B., Venugopal, K. R. and Kalbande, A. R. 1989. Formation of di- and trioctahedral smectite as an evidence for paleoclimatic changes in southern and central Peninsular India. *Geoderma*, **45**: 175-184.
- Pal, D. K., Deshpande, S. B. and Durge, S. L. 1993. Potassium release and adsorption reactions in two ferruginous (polygenetic) soils of southern India in relation to their mineralogy. *Pedologie (Ghent)*, **43**: 403-415.
- Pal, D. K., Kalbande, A. R., Deshpande, S. B. and J. L. Sehgal. 1994. Evidence of clay illuviation in sodic soils of north-western part of the Indo-Gangetic plain since the Holocene. *Soil Sci.*, **158**: 465-473
- Pal, D. K., Bhattacharyya, T., Deshpande, S. B., Sarma, V. A. K. and Velayutham, M. 2000a. *Significance of Minerals in Soil Environment of India*, NBSS Review Series 1, NBSS&LUP, Nagpur, 68pp.
- Pal, D. K., Dasog, G. S., Vadivelu, S., Ahuja, R. L. and Bhattacharyya, T. 2000b. Secondary calcium carbonate in soils of arid and semi-arid regions of India. In: (Lal, R., Kimble, J. M., Eswaran, H. and Stewart, B. A, Eds.), *Global Climate Change and Pedogenic Carbonates*. Lewis Publishers, Boca Raton, Florida, pp.149-185.
- Pal, D. K., Balpande, S. S. and Srivastava, P. 2001b. Polygenetic Vertisols of the Purna Valley of Central India. *Catena*, **43**: 231-249.
- Pal, D. K., Srivastava, P., Durge, S. L. and Bhattacharyya, T. 2001a. Role of weathering of fine-grained micas in potassium management of Indian soils. *Applied Clay Sci.*, **20**: 39-52.
- Pal, D. K., Srivastava, P. and Bhattacharyya, T. 2003b. Clay illuviation in calcareous soils of the semi-arid part of the Indo-Gangetic Plains, India. *Geoderma*, **115**: 177-192.
- Pal, D. K., Bhattacharyya, T., Ray, S. K. and Bhuse, S. R. 2003a. *Developing a Model on the Formation and Resilience of Naturally Degraded Black Soils of the Peninsular India as a Decision Support System for Better Land Use Planning*. NRDMS, Department of Science and Technology (Govt. of India) Project Report, NBSSLUP (ICAR), Nagpur, 144pp.
- Pal, D. K., Nimkar, A. M., Ray, S. K., Bhattacharyya, T. and Chandran, P. 2006a. Characterisation and quantification of micas and smectites in potas-

- sium management of shrink-swell soils in Deccan basalt area. In: (Benbi, D. K., Brar, M. S. and Bansal, S. K, Eds.), *Balanced fertilization for Sustaining Crop Productivity*. Proceedings of the International Symposium held at PAU, Ludhiana, India, 22-25 Nov'2006 IPI, Switzerland, pp.81-93.
- Pal, D. K., Bhattacharyya, T., Ray, S. K., Chandran, P., Srivastava, P., Durge, S. L. and Bhuse, S. R. 2006b. Significance of soil modifiers (Ca-zeolites and gypsum) in naturally degraded Vertisols of the Peninsular India in redefining the sodic soils. *Geoderma*, **136**: 210-228.
- Pal, D. K., Bhattacharyya, T., Chandran, P., Ray, S. K., Satyavathi, P. L. A., Durge, S. L., Raja, P. and Maurya, U.K. 2009. Vertisols (cracking clay soils) in a climosequence of Peninsular India: evidence for Holocene climate changes. *Quat. Intern.*, **209**: 6-21.
- Pal, D. K., Sohan Lal, Bhattacharyya, T., Chandran, P., Ray, S. K., Satyavathi, P. L. A., Raja, P., Maurya, U. K., Durge, S. L. and Kamble, G. K. 2010. *Pedogenic Thresholds in Benchmark Soils under Rice-Wheat Cropping System in a Climosequence of the Indo-Gangetic Alluvial Plains*. Final Project Report, Division of Soil Resource Studies, NBSS&LUP (ICAR), Nagpur, 193pp.
- Pal, D. K., Bhattacharyya, T., Sinha, R., Srivastava, P., Dasgupta, A. S., Chandran, P., Ray, S. K. and Nimje, A. 2011. Clay minerals record from Late Quaternary drill cores of the Ganga Plains and their implications for provenance and climate change in the Himalayan Foreland. *Palaeogeography, Palaeoclimatology, Palaeoecology*, In Press.
- Pillai, M., Pal, D. K. and Deshpande, S. B. 1996. Distribution of clay minerals and their genesis in ferruginous and black soils occurring in close proximity on Deccan basalt plateau of Nagpur district, Maharashtra. *J. Indian Soc. Soil Sci.*, **44**: 500-507.
- Raman, K.V. and Ghosh, S. K. 1974. Identification and quantification of minerals in clays. *Bull. Indian Soc. Soil Sci.*, **9**: 117-142.
- Rengasamy, P., Sarma, V.A.K., Murthy, R.S. and Krishnamurti, G.S.R. 1978. Mineralogy, genesis and classification of ferruginous soils of the eastern Mysore plateau, India. *J. Soil Sci.*, **29** : 431-445.
- Rengasamy, P., Greene, R. S. B. and Ford, G. W. 1986. Influence of magnesium on aggregate stability in sodic red-brown earths. *Austr. J. Soil Res.*, **24**: 229-237.
- Richards, L. A. (Ed.). 1954. *Diagnosis and Improvement of Saline and Alkali Soils*. USDA Agricultural Handbook, Vol. 60. US Government Printing Office, Washington, D C.

- Rich, C. I. 1968. Hydroxy-interlayering in expansible layer silicates. *Clays Clay Miner.*, **16**: 15-30.
- Rich, C. I. 1972. Potassium in soil minerals. Proceedings 9th Colloquium International Potash Institute, pp.15-31.
- Ruhlicke, G. 1985. Layer charge of clay minerals in K fixing sedimentary soils. *Potash Review, Sub.*, **4**: 1-8.
- Ryden, J. C. and Pratt, P. F. 1980. Phosphorus removal from wastewater applied to land. *Hilgardia*, **48**: 1-36.
- Sahrawat, K. L. 1995. Fixed ammonium and carbon-nitrogen ratios of some semi-arid tropical Indian soils. *Geoderma*, **68**: 219-224.
- Sahrawat, K. L. and Warren, G. P. 1989. Sorption of labeled phosphate by a Vertisol and an Alfisol of the semi-arid zone of India. *Fert. Res.*, **20**: 17-25.
- Sanyal, S. K. and De Datta, S. K. 1991. Chemistry of phosphorus transformations in soil. In: (Stewart, B. A, Ed.), *Advances in Soil Science*. Springer-Verlag, New York, pp. 1-120.
- Sarma, V. A. K. 1976. Mineralogy of soil potassium. *Bull. Indian Soc. Soil Sci.*, **10**: 66-77.
- Sarma, V. A. K. 1984. Mechanisms and rate of release of potassium from potassium-bearing minerals in soils. *Mineralogy of Soil Potassium*, P^{RII} Review Series I, P^{RII}, Gurgaon, Haryana, pp. 55-61.
- Sarma, V.A.K. and Sidhu, P.S. 1982. Genesis and transformation of clay minerals. In: *Review of Soil Research in India. Transactions of the 12th International Congress of Soil Science 2*: 718-724.
- Schwertmann, U. 1962. Die Selective Kationensorption der Tonfraktion einiger Boden aus Sedimenten. *Z. Pflanz. Dung. Bodenkunde* **97**: 9-25.
- Shailaja, S. and Sahrawat, K. L. 1990. Adsorption and desorption of phosphate in some semi-arid tropical Indian Vertisols. *Fertl. Res.*, **23**: 87-96.
- Shailaja, S. and Sahrawat, K. L. 1994. Phosphate buffering capacity and supply parameters affecting phosphorus availability in Vertisols. *J. Indian Soc. Soil Sci.*, **42**: 329-330.
- Singer, A. 1980. The paleoclimatic interpretation of clay minerals in soils and weathering profiles. *Earth Sci. Reviews*, **15**: 303-326.
- Singer, A. 2002. Palygorskite and sepiolite. In: (Dixon, J. B and Schulze, D. G, Eds.), *Soil Mineralogy with Environmental Applications*. SSSA Book Series, vol. 7. Soil Science Society of America, Madison, WI, pp. 555-583.
- Soil Survey Staff, 1999. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. USDA-SCS Agricultural Handbook No 436, Second Edition. U.S. Govt. Printing Office, Washington, DC.

- Srivastava, P., Parkash, B. and Pal, D. K. 1998. Clay minerals in soils as evidence of Holocene climatic change, central Indo-Gangetic Plains, north-central India. *Quat. Res.*, **50**: 230-239.
- Srivastava, P., Bhattacharyya, T. and Pal, D. K. 2002. Significance of the formation of calcium carbonate minerals in the pedogenesis and management of cracking clay soils (Vertisols) of India. *Clays Clay Miner.*, **50**: 111-126.
- Srivastava, P., Singh, A.K., Parkash, B., Singh, A.K. and Rajak, M. 2007. Paleoclimatic implications of micromorphic features of Quaternary Paleosols of NW Himalayas and polygenetic soils of the Gangetic Plains - A comparative study. *Catena*, **70**: 169-184.
- Srivastava, P., Rajak, M. and Singh, L.P. 2009. Late Quaternary alluvial fans and paleosols of the Kangra Basin, NW Himalaya: Tectonic and paleoclimatic implications. *Catena*, **76** : 135-154.
- Srivastava, P., Rajak, M. K., Sinha, R., Pal, D. K. and Bhattacharyya, T. 2010. A high resolution micromorphological record of the Late Quaternary paleosols from Ganga-Yamuna Interfluvium: Stratigraphic and Paleoclimatic implications. *Quat. Intern.*, **227**: 127-142.
- Sumner, M. E. 1995. Sodic soils: new perspectives. In: (Naidu, R., Sumner, M. E. and Rengasamy, R, Eds.), *Australian Sodic Soils: Distribution, Properties and Management*, CSIRO Publications, East Melbourne: Victoria, Australia, pp. 1-34.
- Tan, K.H. 1982. *Principles of Soil Chemistry*. Marcel Dekker Inc.: New York, 122 pp.
- Tardy, Y., Bocquier, G., Paquet, H. and Millot, G. 1973. Formation of clay from granite and its distribution in relation to climate and topography. *Geoderma*, **10**: 271-284.
- Uehara, G. and Gillman, G. P. 1980. Charge characteristics of soils with variable and permanent charge minerals. *Soil Sci. Soc. America J.*, **44**: 250-252.
- Vaidya, P. H. and Pal, D. K. 2002. Microtopography as a factor in the degradation of Vertisols in central India. *Land Degrad & Dev.*, **13** : 429-445.
- Vaidya, P. H. and Pal, D. K. 2003. Mineralogy of Vertisols of the Pedhi Watershed of Maharashtra. *Clay Res.*, **22**: 43-58.
- Warren, G. P. and Sahrawat, K. L. 1993. Assessment of fertilizer P residues in a calcareous Vertisol. *Fert. Res.*, **34**: 45-53.
- Weaver, C. E. and Pollard, L. D. 1973. *The Chemistry of Clay Minerals*. Elsevier: Amsterdam.
- Wilson, M. J. 1999. The origin and formation of clay minerals in soils : past, present and future perspective. *Clay Miner.*, **34**: 7-25.

- Wright, V.P. 1986. *Paleosols their Recognition and Interpretation*. Blackwell Scientific Publications.
- Yaalon, D. H. 1971. Soil forming processes in time and space. In: (Yaalon, D. H, Ed.), *Paleopedology*. Israel University Press, Jerusalem.
- Zade, S. P. 2007. Pedogenic Studies of Some Deep Shrink-Swell Soils of Marathwada Region of Maharashtra to Develop a Viable Land Use Plan. Ph.D Thesis, Dr. P D K V, Akola, Maharashtra, India.

(Received 6th March, 2012; Accepted 17th July, 2012)