Clay Research, Vol. 31, No. 2, pp. 84-93 (2012)

Speciation of Smectites in two Shrink-swell Soils of Central Peninsular India

V.V. DESHMUKH, S.K. RAY*, P. CHANDRAN, T. BHATTACHARYYA AND D.K. PAL**

Division of Soil Resource Studies, National Bureau of Soil Survey and Land Use Planning, Amravati Road, Nagpur 440 033, Maharashtra
***Resilent Dryland Systems, ICRISAT, Pataneheru, Hyderabad, Andhra Pradesh*

Abstract: *Shrink-swell (Vertisols and their intergrades) soils cover an extensive area especially in Peninsular India with smectites as the dominant mineral. It was felt necessary to find out the species of smectites for better management of these soils. Hence, two benchmark Vertisols namely Seloo from Wardha and Saikhindi from Ahmadnagar districts of Maharashtra were chosen for the study. High resolution mineralogical analysis employed through X ray diffraction (XRD) techniques of the silt, total clay and fine clay fractions of both the pedons were carried out along with Greene-Kelly test with only fine clays. Silt (50-2 μm), total clay (<2 μm) and fine clay (<0.2 μm) fractions are dominated by smectite in both the soils; the smectites content increased gradually with decreasing size fraction. The fine clay fractions are mostly composed of smectite with small amounts of vermiculite and traces of chlorite, kaolin and feldspar. Greene-Kelly test indicated that both Seloo and Saikhindi soil fine clays are dominated by beidellite/nontronite over montmorillonite. The Seloo fine clay smectite is composed of 18-26 per cent and 74-82 per cent montmorillonite and beidellite/nontronite, respectively, and for Saikhindi it is composed of 32-41 per cent and 59-68 per cent for montmorillonite and beidellite/nontronite, respectively. However, these fine clay smectites are of low charge dioctahedral nature and therefore may not have any K selectivity. This property appears to have implications in K management of shrink-swell soils of Deccan basalt areas.*

Key words : Vertisols, smectite, speciation, montmorillonite, beidellite/nontronite, K management.

Shrink-swell (Vertisols and their intergrades) soils cover an extensive area especially in the Peninsular India. These soils occupy about 76.4 mha (Bhattacharyya *et al*., 2009; Mandal *et al*., 2012) out of which about 30 mha (41%) is in Maharashtra. These soils are developed in alluvium derived from weathering of Deccan Trap basalt. The black soils of the Deccan Trap of India are rich in plagioclase feldspars and yield dioctahedral smectite as the first weathering product (Pal and Deshpande, 1987; Bhattacharyya *et al*., 1993). Earlier these smectites were reported to be dominated by beidellite-nontronite type of minerals (Ghosh and Kapoor, 1982).

***Corresponding author :** e-mail: skraysrs@yahoo.com

But, the Mg-saturated clays expanded to about 1.8 nm with glycerol vapour. It was thus envisaged by Pal and Deshpande (1987) that the beidellite used for study by Harward *et al*. (1969) had apparently a higher tetrahedral charge. In spite of this fact, knowledge of exact species of smectite group may provide valuable inputs about the genesis of these soils. The information may also be helpful in better management of these soils. Therefore, the present study was undertaken which deals with the nature of speciation in smectites in two shrink-swell soils of the central Peninsular India.

Materials and Methods

Study Area

Two benchmark soils one is Seloo (Typic Haplusterts) from subhumid (dry) part of Wardha district and the other Saikhindi (Vertic Haplustepts), from semi-arid (dry) from Ahmadnagar district of Maharashtra were selected for the present study.

Physical and Chemical Characteristics of the Soils

The physical and the chemical characterization of the soils show higher clay and fine clay in Seloo soils compared to Saikhindi soils (Table 1). COLE and available water content was also higher in Seloo as compared to Saikhindi soils. Organic carbon content was comparable in both the soils. pH, $CaCO_3$ equivalent and ESP were higher in Saikhindi compared to Seloo. There is also slight to moderate problems of sodicity in Saikhindi soils, however, this is largely obliterated by possible presence of zeolites (Pal *et al.*, 2006).

Mineralogical analysis of the Soils

The silt (50-2 μm), total clay (<2 μm) and fine clay (<0.2 μm) fractions of each horizon of two pedons were analysed for qualitative mineralogy by X-ray diffraction (XRD) technique (Jackson, 1979) using a Philips X'Pert Pro diffractometer with Ni-

Table 1. *Some physical and chemical properties of the soils*

Property (units)	Seloo	Saikhindi
Clay (%)	51.5 – 58.2	39.2 – 45.1
Fine clay (%)	43.7 – 52.2	32.1 – 40.1
COLE	0.18 – 0.26	0.18 – 0.22
Available water content (%)	20.2 – 28.9	13.2 – 15.6
Organic carbon (%)	0.32 – 0.97	0.44 – 0.94
pH (1:2, soil: water)	8.0 – 8.4	8.5 – 9.0
$CaCO_3$ equivalent (%)	3.3 – 4.4	14.8 – 23.7
ESP	<1	5 – 8

filtered Cu-Kα radiation at a scanning speed of $2^{o}2\theta$/min. The semi-quantitative estimates of minerals in the silt, total clay and fine clay fractions were done by the method of Gjems (1967).

Hofmann-KIemen effect (1950) modified by Greene-Kelly (1953) and Lim and Jackson (1986) was performed only on fine clay samples (as total clay contained about 80-90 per cent of fine clays), and the glycerol solvation of the Li-saturated samples were prolonged upto 30-days (Pal and Deshpande, 1987; Kalbande *et al*., 1992; Bhattacharyya *et al*., 1993; Ray *et al*., 2008).

Results and Discussion

XRD analysis of the silt fractions (50-2 µm) of both the soils indicated the presence of smectite, vermiculite, chlorite, mica, kaolin, quartz and feldspar (Fig. 1). In the Seloo soils, silt fraction was dominated by smectites followed by quartz and feldspars and in Saikhindi soils silt fraction was dominated by smectites followed by feldspars and quartz.

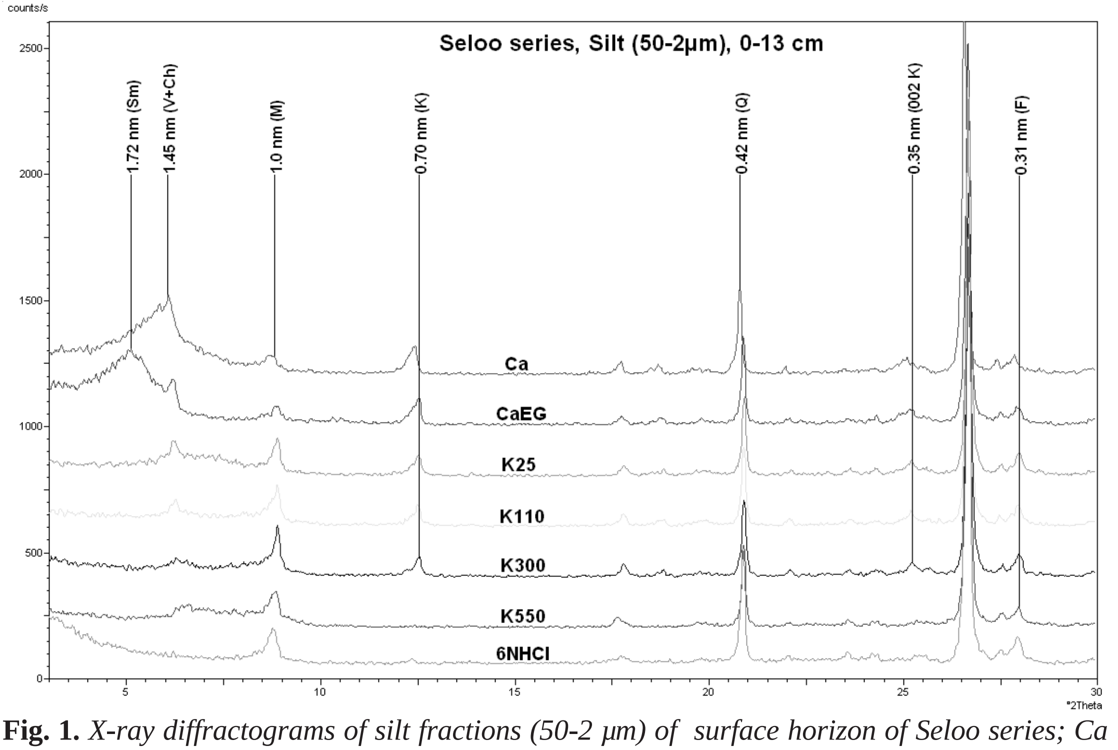


Fig. 1. *X-ray diffractograms of silt fractions (50-2 µm) of surface horizon of Seloo series; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K-saturated and heated to 25, 110, 300, 550°C. 6NHCl = 6N HCl treated fine clays; Sm = Smectite, V + Ch = Vermiculite plus Chlorite; K = Kaolin; F = Feldspars; Q = Quartz.*

The total clay fractions (<2 μm) for both the soils are dominantly composed of smectite followed by small amounts of vermiculite, chlorite, mica and feldspars (Fig. 2). The fine clay fractions are mostly composed by smectite with small amounts of vermiculite and traces of chlorite, kaolin and feldspar (Figs. 3a,b). The smectite content was higher in fine clays of Seloo soils (83-88%) compared to Saikhindi (78-84%). The smectite was slightly chloritised as evidenced by the broadening of the peak towards the lower angle side of 1.0 nm peak in K-saturated sample after subsequent heating to 550°C. Such chloritization is common in black soils of the Peninsular India (Pal and Deshpande, 1987; Bhattacharyya *et al*., 1993; Ray *et al*., 2008). However, chloritization in smectites was relatively less in black soils under study compared to some other soils from Maharashtra (Kapse, 2007; Thakare, 2008; Bhople, 2010; Ray *et al*., 2008).

Hofmann-KIemen effect (1950) modified by Greene-Kelly (1953) and Lim

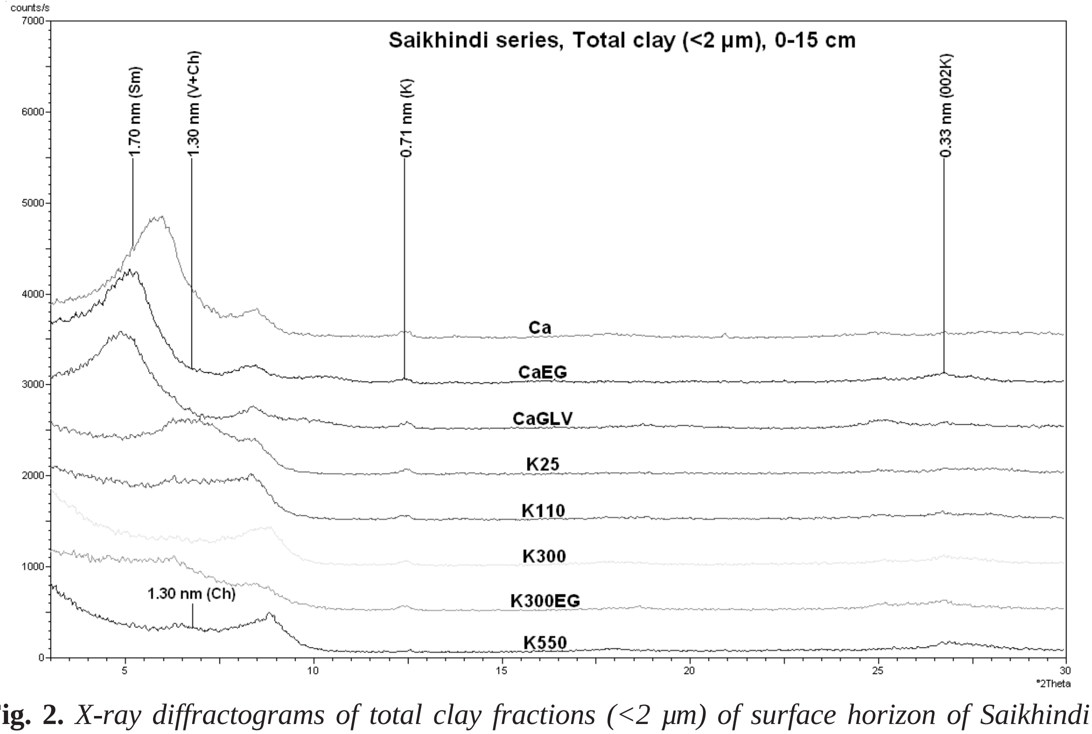


Fig. 2. *X-ray diffractograms of total clay fractions (<2 μm) of surface horizon of Saikhindi series; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K-saturated and heated to 25, 110, 300, 550°C. K300EG = K-saturated and heated to 300°C plus ethylene glycol vapour treated; V + Ch = Vermiculite plus Chlorite; Ch = Chlorite; K = Kaolin; F = Feldspars.*

and Jackson (1986) distinguishes between montmorillonite and beidellite by glycerol solvation of the Li-saturated and heated samples. Montmorillonite can be distinguished from beidellite/nontronite wherein Li-saturated samples when treated with glycerol, the former collapses to 0.95 nm and the latter expands to about 1.8 nm (Pal and Deshpande, 1987; Bhattacharyya *et al.,* 1993; Ray *et al.,* 2008). The soil fine clays in the present study shows the presence of both montmorillonite and beidellite/nontronite (Figs. 3a, b) as evidenced by the peaks at 0.95 to 1.00 nm and 1.80 to 1.86 nm, respectively. The ratio of peak heights of montmorillonite and beidellite/nontronite calculated as semi-quantitative estimates show that in both the samples beidellite/ nontronite dominated over montmorillonite. When these values were plotted in a graph as percentages (Figs. 4a, b), the Seloo fine clays showed 18 to 26 per cent and 74 to 82 per cent of montmorillonite and beidellite/nontronite, respectively. The values for Saikhindi fine clays were 32 to 41 per cent and 59 to 68 per cent of montmorillonite and beidellite/ nontronite, respectively (Deshmukh, 2009).

The glycerol solvated and Ca-treated samples for the same set of fine clays gave strong peaks between 1.75 and 1.85 nm (Figs. 3a,b). This led Pal and Deshpande (1987) to envisage that the beidellite studied by Harward *et al*. (1969) had apparently a higher tetrahedral charge than the fine clay smectites of Vertisols under study. In other words, fine clay smectite in these Vertisols is nearer to montmorillonite of the montmorillonite-beidellite series. They further logically stated that since the nontronite would behave similarly as beidellite does in Greene-Kelly test and the fine clay smectites studied is unstable to the HCl treatments releasing considerable iron, this mineral is nearer to the montmorillonite of the montmorillonite-nontronite series. Their study also highlights the importance and dominance of nontronite species in the shrink-swell soils of Peninsular India as otherwise not abundantly observed elsewhere (Sherman *et al*., 1962; Borchardt, 1989).

It is known that both beidellite and nontronite have more charge due to tetrahedral (IV) substitution compared to montmorillonite with octahedral (VI) substitution (Greene-Kelly, 1955; Lagaly, 1994). Semi-quantitative estimates show higher amount of beidellite/nontronite (74 to 82% in Seloo and 59 to 68% in Saikhindi) compared to montmorillonite (18 to 26% in Seloo and 32 to 41% in Saikhindi). Out of about 83 to 88% of smectites in the Seloo fine clays, about 67% is beidellitic/ nontronitic and about 11% is montmorillonitic (considering average values in a soil profile). Similarly out of about 74 to 84% of smectites in the Saikhindi fine clays, about 50% is beidellitic/ nontronitic and about 28% is montmorillonitic. The average layer charge determined by alkylammonium method for

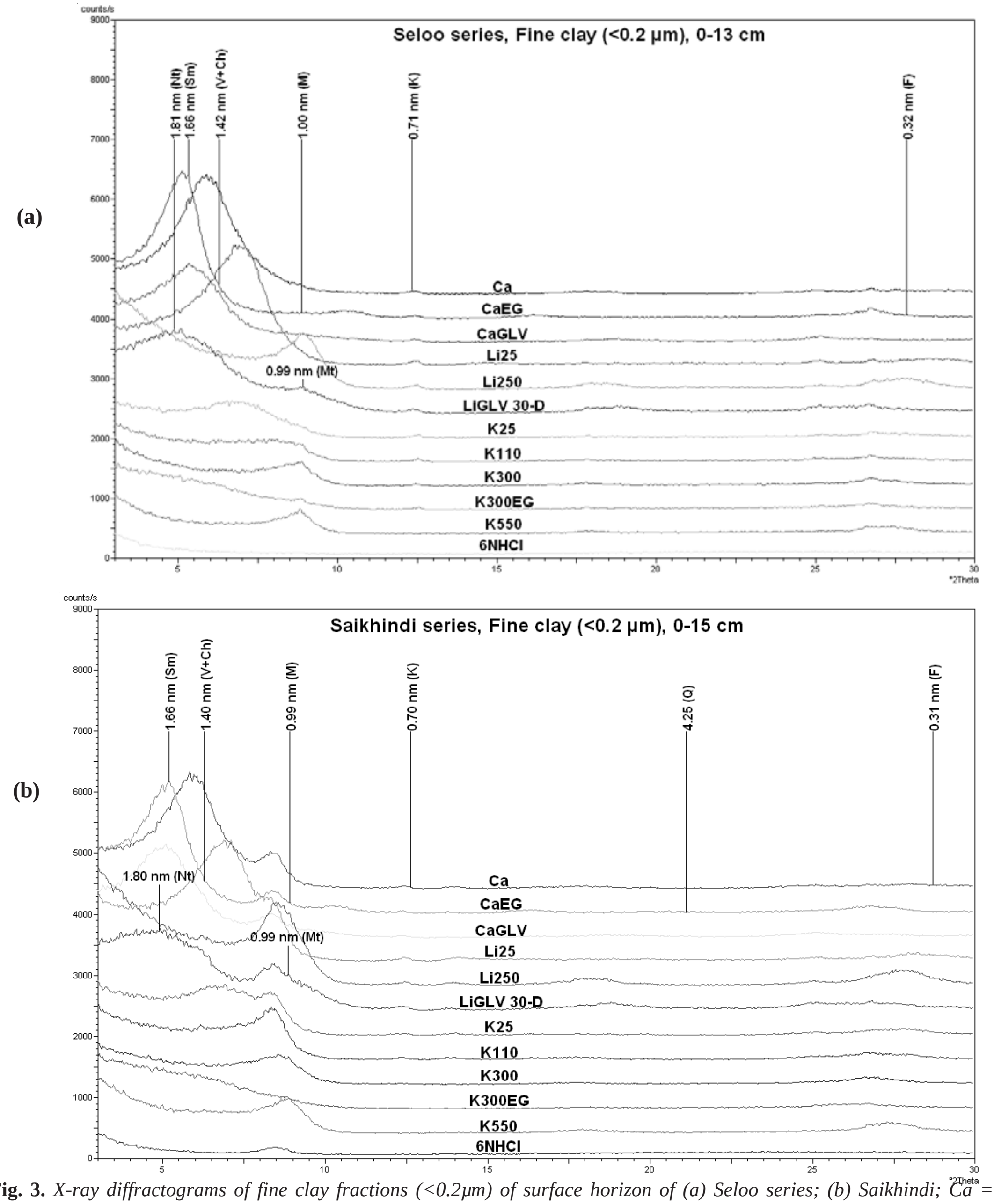
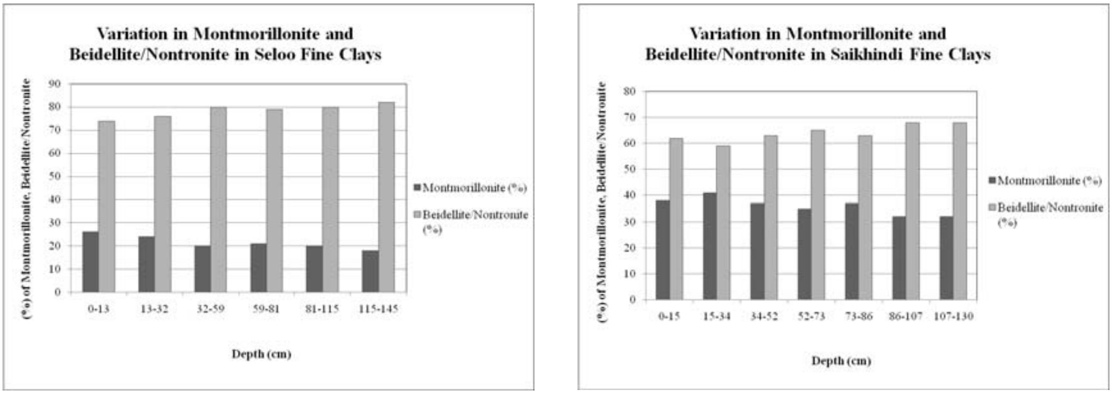


Fig. 3. *X-ray diffractograms of fine clay fractions (<0.2µm) of surface horizon of (a) Seloo series; (b) Saikhindi; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; CaGLV = Ca-saturated plus glycerol vapour treated; Li = Li-saturated and heated to 25°C, 250°C (16h), LiGLV 30-D = Li-saturated and heated at 250°C plus glycerol vapour treated and scanned after 30 days; K-saturated and heated to 25, 110, 300, 550°C. K300EG = K-saturated and heated to 300°C plus ethylene glycol vapour treated; 6NHCl = 6N HCl treated fine clays; Sm = Smectite, B/N = Beidellite/Nontronite; V + Ch = Vermiculite plus Chlorite; M = Mica; Mt = Montmorillonite; K = Kaolin; F = Feldspars.*



(a) **(b)**

Fig. 4. *Semi-quantitative estimates of Montmorillonite and Beidellite/Nontronite in (a) Seloo (b) Saikhindi fine clays.*

Seloo and Saikhindi fine clays are 0.472 and 0.431 mol(-)/ $(Si,Al)_4O_{10}(OH)_2$, respectively (Deshmukh, 2009). Moreover, the vermiculite content (6 to 8% in Seloo and 6 to 7% in Saikhindi) and amount of hydroxy-interlayering (Ray *et al*., 2008; Deshmukh, 2009) in both the soil fine clays are comparable and contributions towards higher charge due to these minerals would be almost identical. Therefore, higher tetrahedral substitution due to higher values of beidellite/ nontronite species in fine clay smectites of Seloo resulted in higher charge compared to Saikhindi (Deshmukh, 2009). This feature is generally repetitive for other soil fine clays (Thakare, 2008; Ray *et al*., 2008; Bhople, 2010).

Low charge dioctahedral smectites (beidellite/nontronite and montmorillonite, confirmed based on XRD with diagnostic analytical methods, Pal *et al*., 1987; Bhattacharyya *et al*., 1993) are known to be a direct weathering product of plagioclase feldspars (Pal and Deshpande, 1987) under humid tropical climate (Pal *et al*., 1989; Bhattacharyya *et al*., 1993). The difference in the amounts of beidellite/ nontronite species of smectites in the two soil fine clays of two distinct agro-ecoregions may be due to the differential loading of clay smectite during the erosion-deposition episodes of the weathering products of the Deccan basalt in the geological past (Pal and Deshpande, 1987). Due to their low charge these two smectite species may not have any implications in K adsorption of these soils (Pal *et al*., 2012) like those derived from micas (Singh and Heffernan, 2002). Thus the K adsorption by these soils is due to the presence of vermiculite as reported earlier (Pal *et al*., 2012).

Conclusions

Both the soil fine clays showed higher values of beidellite/nontronite compared to montmorillonite species of smectite. Larger amounts of beidellite/nontronite with relatively higher charge may apparently suggest their greater capacity to adsorb/ fix potassium compared to montmorillonite as reported often in the literature. This is in contrast with the established fact that low charge fine clay smectites do not show K-selectivity properties. This fact demands fresh research initiatives to find a probable answer for a consistent report of K response (through external K fertilizer addition) even though the soil test values showed high available K in the shrink-swell soils of the Peninsular India.

Acknowledgement

The authors are grateful to the Director, NBSS&LUP for providing the necessary facilities for the work. They are also thankful to Mr. S.P. Chivane for providing the Seloo soil samples and Ms. D.V. Balbuddhe and Mrs. W. Khandwe for word processing the manuscript.

References

Bhattacharyya, T., Pal, D.K. and Deshpande, S.B. 1993. Genesis and transformation of minerals in the formation of red (Alfisols) and black (Inceptisols & Vertisols) soils on Deccan basalt in the Western Ghats, India. *J. Soil Sci.*, **44**:159-171.

Bhattacharyya, T., Sarkar, D., Sehgal, J.L., Velayutham, M., Gajbhiye, K.S., Nagar, A.P. and Nimkhedkar, S.S. 2009. *Soil Taxonomic Database of India and the States (1:250,000 scale)*, NBSSLUP Publication 143, India, 266pp.

Bhople, B.S. 2011. Layer charge characteristics of some Vertisol clays of Maharashtra and its relationship with soil properties and management. PhD. Thesis (unpublished) submitted to Dr. Panjabrao Deshmukh Krishi Vidyapeeth , Akola, Maharashtra, India, pp.128.

Borchardt, G. 1989. Smectites. In: (J. B. Dixon and S. B. Weed, Eds.), *Minerals in Soil Environments*, Soil Science Society of America Book Series (No. 1), Soil Science Society of America Madison, Wisconsin, USA, pp. 675-727.

Deshmukh, V.V. 2009. Determination of layer charge after removal of hydroxy-interlayers in some shrink-swell soil clays of Maharashtra. MSc. Thesis (unpublished) submitted to Dr. Panjabrao Deshmukh Krishi Vidyapeeth, Akola, Maharashtra, India, pp.75.

Ghosh, S.K. and Kapoor, B.S. 1982. Clay minerals in Indian soils. In : *Review of Soil Research in India*. Trans 12th Inter. Congr. Soil Sci. New Delhi., **2**:703-710.

Gjems, O. 1967. Studies on clay minerals and clay minerals formation in soil profile in scandinavia. *Medd. Nor. Skagsforsuksves*. **21**:303-415.

Greene-Kelly, R. 1953. The identification of montmorillonoids in clays. *J. Soil Sci.*, **4**:233-237.

Greene-Kelly, R. 1955. Dehydration of the montmorillonite minerals. *Miner. Magazine*, **30**:604-615.

Hofmann, U. and Klemen, R.1950. Verlust der Austauschfahigkeit von Litiumionen and Bentonite durch *Erhitzung. Z. Anorg. Chem*. **262**: 95-99.

Harward, M.E., Carstea, D.D. and Sayegh, A.H. 1969. Properties of vermiculites and smectites : expansion and collapse. *Clays Clay Miner.*, **16**:437-447.

Jackson, M.L. 1979. Soil Chemical analysis-Advanced Cource. Published by author, Wisconsin, 2nd ed., published by the author, University of Wisconsin, Madison.

Kalbande, A.R., Pal, D.K. and Deshpande, S.B. 1992. *b*-fabric of some benchmark Vertisols in relation to their mineralogy. *J. Soil Sci.*, **43**:375-385.

Kapse, K.V. 2007. Charge characteristics of clays of some shrink-swell soils of Maharashtra. M.Sc. Thesis (unpublished) submitted to Dr. Panjabrao Deshmukh Krishi Vidyapeeth, Akola, Maharashtra, India, pp. 103.

Lagaly, G. 1994. Layer charge determination by alkylammonium ions. In: *Layer Charge characteristics of 2:1 silicate clay minerals* (A.P. Mermut, Ed.), pp.1-46, CMS Workshop lectures, Vol. 6, The Clay Minerals Society, Boulder, USA.

Lim, C.H. and Jackson, M.L. 1986. Expandible phyllosilicate reactions with lithium on heating. *Clays Clay Miner.*, **34**:346-352.

Mandal, C., Mandal, D. K., Jagdish Prasad., Dipak Sarkar., Chandran, P., Tiwary, P., Patil, N.G., Obireddy, G. P., Lokhande, M.A., Wadhai, K. N., Dongare, V.T., Sidhu, G. S., Sahoo, A.K., Nair, K. M., Singh, R.S., Pal, D.K., Ray, S.K. 2012. Revision of Black Soil Map of India for Sustainable Crop Production, In: (D.K. Prabhuraj, R. S. Reddy, T. R. Sreedhara Murthy, S. Vadivelu, K. Ashoka Reddy, B.P. Lakshmikantha, A. S. Rajashekar, Sanjana S Bakre, Prathima K, Eds), *Proceedings of National Seminar on Geospatial Solutions for Resource Conservation and Management*, Indian Institute of Science, Bengaluru , pp 36-44.

Pal, D.K. and Deshpande, S.B. 1987. Characteristics and genesis of minerals in some benchmark Vertisols of India. *Pedologie (Ghent)*, 7:259-275.

Pal, D.K., Bhattacharyya, T., Ray, S. K., Chandran, P., Srivastava, P., Durge, S. L., and Bhuse, S.R. 2006. 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., Deshpande, S.B., Venugopal, K.R. and Kalbande, A.R. 1989. Formation of di- and trioctahedral smectite as evidence for paleoclimatic changes in southern and central peninsular India. *Geoderma*, **45**:175-184.

Pal, D. K., Wani, S. P. and Sahrawat, K.L. 2012. Vertisols of tropical Indian environments: pedology and edaphology. *Geoderma*, **189-190**:28-49.

Ray, S.K., Chandran, P., Bhattacharyya, T., Pal, D.K. and Durge, S.L. 2008. *Determination of layer charge of 2;1 layer silicate minerals in soils of India*. Final Project Report, NBSS & LUP, Nagpur, p.111.

Sherman, G.D., Ikawa, H., Uehera, G. and Okazaki, E. 1962. Types of occurrence of nontronite and nontronite-like minerals in soils. *Pac. Sci.*, **16**:57-62.

Singh, B. and Heffernan, S. 2002. Layer charge characteristics of smectites from Vertosols (Vertisols) of New South Wales. *Aust. J. Soil Res.*, **40**:159-170.

Thakare, P.V. 2008. Layer charge of clay smectites in relation to soil properties of some benchmark Vertisols of Maharashtra. M.Sc. Thesis (unpublished) Dr. Panjabrao Deshmukh Krishi Vidyapeeth, Akola, Maharashtra, India, pp.81.

(Received June, 2012; Accepted November, 2012)