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Genesis of Associated Red and Black Shrink-swell Soils of Maharashtra

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Abstract : *Two associated shrink - swell soils (red and gray coloured) occurring in a catena in the Hingoli district of Maharashtra were taken for this study. Detailed study of the morphological, physical and chemical properties indicated that both the soils have Vertisol characteristics. The low hydraulic conductivity of red Vertisols is due to high Mg^{2+} and Na^{+} in the exchange complex. Mineralogical properties indicate that smectite is the dominant mineral in both the soils. The presence of kaolin in the gray Vertisols indicate that the transformation of smectite to kaolin in the past humid climate. The absence of kaolin in red Vertisol indicates that the parent material (red bole) was not exposed to the earlier humid climate. They have been formed from the red boles observed in the vicinity of the study area containing high amount of smectite along with palygorskite mineral. The presence of palygorskite mineral with smectite in red shrink-swell soils and its absence in other associated soils in a catena indicate that this mineral cannot be considered as an index mineral for arid climate. The release of Mg^{2+} from palygorskite mineral disperses the clay and clogs the pores resulting impeded drainage which adversely affected the crop production.*

Key words: Red shrink- swell soils, red boles, palygorskite mineral, soil management

Introduction

Shrink-swell soils (Vertisols and their intergrades) occupy an area of about 66 m ha in India (Bhattacharyya *et al*., 2009) and constitute about 35% of soils of Maharashtra. These soils are developed in the alluvium of weathering Deccan basalt that occur in central and Peninsular India. They are characterized by dark gray to black in colour (10 YR hue), high smectite-rich clay, neutral to alkaline in reaction, high cation exchange capacity with exchangeable position dominated by Ca^{2+}, Mg^{2+} and in sometimes by Na^{+}. The smectite clay mineral, in seasonally wet and dry climate are responsible for the swelling and shrinking that manifest many special characteristics of these soils (Borchardt, 1989).

There are many reports of the formation of red and black soil association in India (Gawande *et al.,* 1968; Murali *et al.,* 1978;

Pal and Deshpande 1987; Bhattacharyya *et al*., 1993). In most cases it was reported that the red soils are formed on higher topographic position with clay-enriched argillic horizon and presence of kaolin (smectite-kaolinite interstratified mineral) developed from smectite under more leaching environment and their associated Vertisols are formed in valleys on lower topographic position wherein the drainage is comparatively slow (Pal and Deshpande 1987; Kantor and Schwertmann 1974; Beckmann *et al.,* 1974). However, the present study discusses a unique red and black soil association in Hingoli district of Maharashtra developed in the alluvium and colluvium of basalt which resulted in the formation of Vertisols.

There are some reports that sequences of basalt flows commonly include spectacular red interflow strata widely known as bole beds, which serve as the marker of beds in between two basaltic flows. Bole horizons are weathered horizon (Paleosols) usually recognized in the field by their distinctive red colour suggesting processes of chemical weathering similar to what is observed in case of pedogenesis from basalt (Ghosh *et al*., 2006). In a few cases they are characterized by polygonal structures indicating shrinkage features developed after deposition (Sarkar *et al*., 2000). It is referred to as red Vertisol in view of its only contrasting colour features which differentiates it from other colour of Vertisols in the vicinity. Hence the present study was undertaken to understand the genesis of these soils and those of the associated gray coloured Vertisols.

Materials and Methods

The study area is located along a transect in Kesapur village of Hingoli District of Maharashtra at 450 to 500 m above mean sea level (msl) in the semi-arid climate (<700 mm annual rainfall). Here two soils are described, one at the higher elevation of the transect, namely the red Vertisol (pedon 1) and the other is a commonly seen gray Vertisol in the valley floor (pedon 2). These soils are developed in the basaltic alluvium and occur in close proximity to each other (Fig. 1). The morphological properties of the soils were studied as per Soil Survey Manual (Soil Survey Division Staff, 1995) and the soils were classified according to Soil Taxonomy

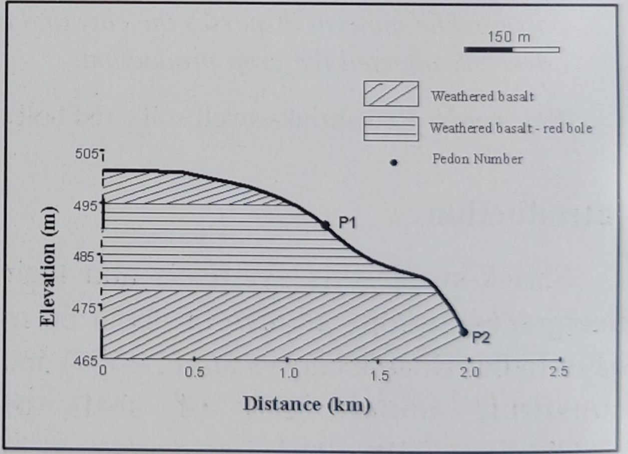

Fig. 1. *Schematic diagram showing the landscape representing the pedon sites in Hingoli district, Maharashtra (broken lines on Y axis indicate tentative thickness of basalt and red bole)*

(Soil Survey Staff, 2003). Horizon-wise samples were collected for laboratory analysis.

Physical and chemical properties of soils were determined as per standard procedures (Jackson, 1973). For mineralogical analysis, particle size fractions were separated as per size segregation procedure of Jackson (1979) after removal of $CaCO_3$, organic matter and free iron oxides. Silt and clay fractions were subjected to X-ray examination of the parallel oriented Ca/K saturated samples with a Philips diffractometer using a Ni-filtered Cu-Kα radiation and a scanning speed of $2°2\theta$ per minute. Semi-quantitative estimation of the clay minerals was based on the principles outlined by Gjems (1967).

Results and Discussion

Morphological properties indicate that the red shrink-swell soils are very deep with dark reddish brown colour (2.5YR 3/4 to 2.5YR 3/6) throughout the depth. These soils have 4-5 cm wide cracks at the surface which extends up to 50 cm. The associated shrink-swell soils (pedon 2) have an Ap horizon with very dark gray (10YR 3/2) colour. The B horizon up to a depth of 81 cm is very dark gray to dark grayish brown in colour (10YR 3/1 – 10YR 3/2) and below that up to 115 cm, the colour is very dark grayish brown to dark olive brown (2.5Y 3.5/3) (Table 1).

Particle size distribution indicates both the soils are clayey (Table 2) with very less amount of sand. This is common in Vertisols developed in the Deccan basalt areas (Pal 1988; Bhattacharyya *et al.*, 1993). Fine clay constitutes more than 50% of the total clay in almost all the horizons. The bulk density increased with depth in pedon 2, but no such trend was found in red Vertisols. The saturated hydraulic conductivity (sHC) in pedon 2 (black soils) varied from 1.85 to 3.85 cm h^{-1} and in red Vertisol it is very low (0.02 to 0.2 cm h^{-1}). Kadu *et al.*, (2003) observed that low sHC in soil is associated with high sodium or magnesium in exchange complex that disperse the clay to clog the soil pores.

Soils of pedon 1 are strongly to very strongly alkaline (pH 8.5 to 9.4) whereas pedon 2 is moderately alkaline (pH 8.1 to 8.3). Red Vertisol (pedon 1) showed higher amount of carbonate (11.6 to16.6 percent) than pedon 2 (5.82 to 7.1 per cent) (Table 3). CEC varied from 55.6 to 65.2 cmol (p+)kg^{-1} in these soils. Among the extractable cations calcium is dominant in the exchange complex in pedon 2, followed by Mg, Na, and K (Table 4). However in pedon 1, Mg is dominant followed by Ca, Na, and K. Exchangeable sodium percent (ESP) in pedon 1 is high and varied from 16.4 to 37.6 cmol(p+) kg^{-1}, whereas it is low (1.1 to 1.2) in pedon 2. This indicates that exchangeable sodium in pedon 1 affects the moisture retention and release behaviour in soils and can be considered as sodic according to Soil Taxonomy (Soil Survey Staff, 2003). Pal *et al.*, (2000) suggested

Table 1. *Morphological properties of soils.*

Horizon	Depth (cm)	Matrix colour (M)	Texture (1)	Coarse Fragments (%) (2)	Structure (3)			Effervescence dil. HCl (4)	Other features (5)
					(S)	(G)	(T)		
Pedon 1: Fine, smectitic, hyperthermic Sodic Haplusterts									
Ap	0-14	2.5YR3/4	c	3-5 (fg)	m	2	sbk	es	-
Bw1	14-29	2.5YR3/4	c	1-2(fg)1-2(cg)	m	1	sbk	es	-
Bw2	29-49	2.5YR3/4	c	1-2(fg),1-2 (cg)	m	1	sbk	es	PF
Bw3	49-71	2.5YR3/4	sic	1-2(fg),2-3(cg)	m	1	sbk	es	PF
Bss1	71-103	2.5YR3/4	sic	2-3(cg),1-2(fg)	m	1	abk	es	SS
Bss2	103-155+	2.5YR3/6	sic	2-3(cg),1-2(fg)	m	1	abk	es	SS
Pedon 2: Very fine, smectitic, hyperthermic, Typic Haplusterts									
Ap	0-15	10YR3/2	c	2-3 (fg)	m	1	sbk	e	-
Bw1	15-31	10YR3/2	c	1-2(fg)	m	2	sbk	e	PF
Bss1	31-49	10YR3/2	c	2-3(fg)	m	2	sbk/abk	e	PF
Bss2	49-81	10YR3/1	c	2-3(fg)	m	3	abk	e	SS
BCk	81-115	2.5Y3.5/3	cl	50-60(fg +cg)	f	1	gr/sbk	e	-

Abbreviations are according to Soil Survey Manual (Soil Survey Division Staff, 1995)

1. Texture: c- clay; sic-silty clay; cl- clay loam
2. Coarse fragments:fg-fine gravel; cg-coarse gravel; st- stony, b-boulders
3. Structure: S = size; m = medium; G = grade; 2 = moderate; 3 – strong; T=Type, sbk =subangular blocky, abk =angular blocky
4. e= slightly effervescence, es= strongly effervescence.
5. PF=Pressurefaces, SS=Slickensides

that increase in exchangeable magnesium percent (EMP) and ESP is related with relative decrease in Ca^{2+} ions in soil solution due to precipitation of Ca^{2+} ions as calcium carbonate. High ESP and EMP are also be related with low sHC of the soils of pedon 1.

XRD patterns of the silt, total clay and fine clay fraction of pedon 1 (Red Vertisol) are almost similar. For brevity the XRD of total clay of one horizon (Bss1) is given as fig. 3. The samples on Ca-saturation shows dominant peak at 1.48 and 1.05 nm. On glycolation 1.4 nm shifted entirely to 1.6 nm indicating the presence of smectite in the sample (Fig.2). Persistence of 1.05 nm peak on glycolation and heating up to 110°C indicate the presence of palygorskite mineral (though in small amount) in the sample. The expanding behaviour of 1.0 nm peak to 1.4 nm peak on glycolation after K-saturation and heating at 300°C indicates that the expanding lattice mineral is a low charge smectite. Interestingly the 0.7 nm peak of kaolin was not observed in these soils as generally expected in the

Table 2. *Physical properties of shrink –swell soils*

	Depth (cm)	Particle-size analysis (%)				Bulk density (Mg m^{-3})	sHC (cm h^{-1})*	COLE**
		Sand (2.0-0.05) mm	Silt (0.05-0.002) mm	Clay (0.002-0.0002) mm	Fine clay (<0.0002) mm			
	Pedon 1: Fine, smectitic, hyperthermic, Sodic Haplusterts							
Ap	0-14	2.0	32.3	65.7	45.8	1.47	0.08	0.26
Bw1	14-29	2.5	33.3	64.2	33.7	1.30	0.03	0.26
Bw2	29-49	1.4	39.5	59.1	32.7	1.35	0.04	0.30
Bw3	49-71	1.3	47.3	51.0	25.0	1.26	0.02	0.31
Bss1	71-103	0.5	47.2	52.6	29.0	1.30	0.04	0.30
Bss2	103-150	0.2	53.0	46.9	21.5	1.41	0.22	0.30
	Pedon 2: Very fine, smectitic, hyperthermic Typic Haplusterts							
Ap	0-15	1.2	35.6	63.1	27.2	1.06	1.77	0.32
Bw	15-31	1.0	31.1	67.8	37.3	1.26	2.68	0.30
Bss1	31-49	0.9	31.6	67.5	36.1	1.26	3.85	0.31
Bss2	49-81	1.0	27.4	71.5	44.5	1.40	2.18	0.31
BCk	81-115	39.6	21.7	38.6	29.2	1.49	1.17	0.23

*sHC : Saturated hydraulic conductivity

**COLE: Coefficient of linear extensibility

Table 3. *Chemical properties of soils*

Horizon	Depth (cm)	pH (1:2) H_2O	EC (1:2) (dS m^{-1})	Org. C. (%)	$CaCO_3$ equivalent (%)
	Pedon 1: Fine, smectitic, hyperthermic Sodic Haplusterts				
Ap	0-14	9.08	0.44	0.25	12.0
Bw1	14-29	9.15	0.66	0.13	11.8
Bw2	29-49	9.44	0.78	0.13	14.4
Bw3	49-71	9.3	0.88	0.13	16.6
Bss1	71-103	9.03	1.22	0.05	15.9
Bss2	103-150	8.54	1.00	0.05	10.7
	Pedon 2: Very fine, smectitic, hyperthermic Typic Haplusterts				
Ap	0-15	8.12	0.23	0.97	6.4
Bw	15-31	8.2	0.23	0.79	6.7
Bss1	31-49	8.16	0.19	0.79	5.8
Bss2	49-81	8.23	0.22	0.77	6.9
BCk	81-115	8.2	0.25	0.13	7.1

Table 4. *Exchange properties of soils*

Horizon	Depth (cm)	CEC	Extractable bases Ca^{++}	Mg^{++}	Na^{+}	K^{+}	BS (%)	ESP (%)	EMP (%)	ECP (%)
			... cmol (p^{+}) kg^{-1} ...							
Pedon 1: Fine, smectitic, hyperthermic Sodic Haplusterts										
Ap	0-14	55.65	28.61	23.39	9.13	0.22	110.2	16.4	42.0	51.4
Bw1	14-29	55.65	23.9	24.21	14.78	0.18	113.3	26.5	43.5	43
Bw2	29-49	60.00	21.4	25.97	18.26	0.16	109.6	30.4	43.3	35.7
Bw3	49-71	62.60	19.4	29.52	23.48	0.17	115.9	37.5	47.2	31
Bss1	71-103	62.60	19.89	28.9	23.48	0.20	115.7	37.5	46.2	31.8
Bss2	103-150	64.34	24.15	28.6	23.48	0.25	118.8	36.5	44.4	37.5
Pedon 2: Very fine, smectitic, hyperthermic Typic Haplusterts										
Ap	0-15	62.60	50.72	5.73	0.73	0.70	92.4	1.2	9.2	78.8
Bw1	15-31	64.34	53.36	5.19	0.69	0.35	92.6	1.1	8.1	85.2
Bss1	31-49	64.34	53.94	5.14	0.68	0.30	93.3	1.1	8	79.5
Bss2	49-81	62.60	49.71	5.91	0.75	0.27	90.4	1.2	9.4	77.3
BCk	81-115	65.21	49.61	7.57	0.75	0.18	89.1	1.2	11.6	77.1

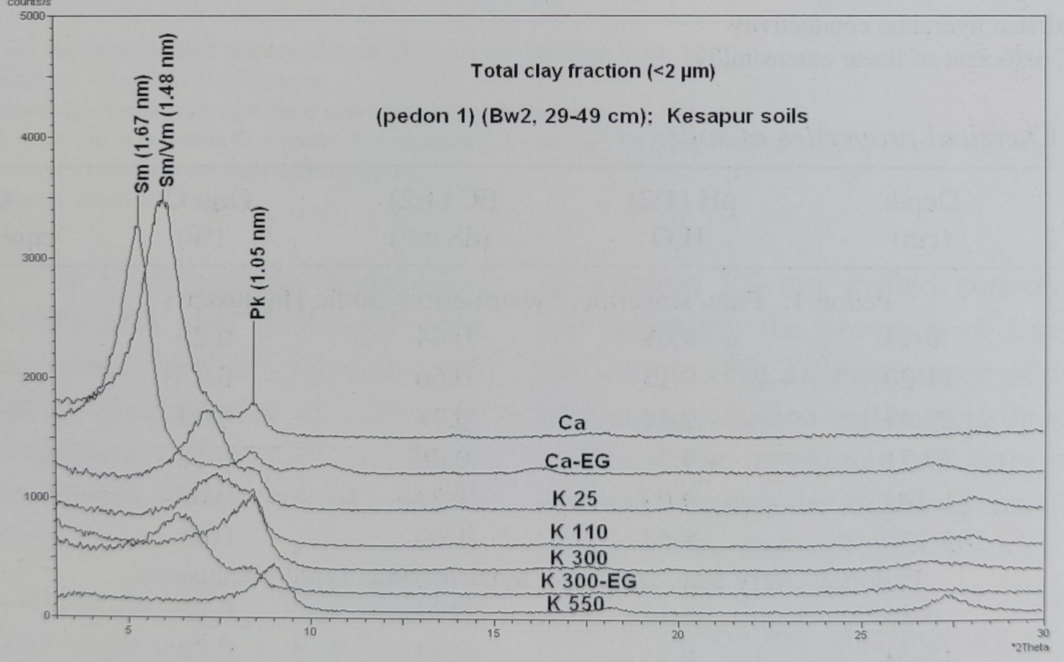

Fig. 2. *Representative X-ray diffractograms of total clay fractions of Pedon 1 (Sm=smectite, Sm/Vm=smectite or vermiculite, Pk=palygorskite, Ca = calcium saturated; CaEG = Ca-saturated and ethylene glycolated; K25°/K110°/K300°/K550° = K saturated and heated at 25, 110, 300 and 550°C. K300°EG= K saturated and heated at 300° and ethylene glycolated)*

associated ferruginous soils in a basaltic catena (Bhattacharyya *et al.*, 1993, Chandran *et al.*, 2000).

X-Ray diffraction patterns of the silt, total clay and fine clay of pedon 2 indicate that smectite is the dominant mineral in all the fractions and it was established by the basal reflection around 1.4 nm of Ca-saturated sample, which expanded to around 1.7 nm on glycolation (Fig. 3). The presence of kaolin was detected by the peak at 0.7 nm which persisted on K-treatment and heating at 300°C, but disappeared at 550°C.

Discussion

Genesis of soils

It has been established that the first weathering product of basalt under the humid tropical weathering is smectite (Pal and Deshpande, 1987). Under acid weathering conditions of the humid climate, the Al-hydroxy cations formed occupy the interlayer spaces of expanding minerals namely smectite (Pal *et al.*, 1989; Bhattacharyya *et al.*, 1999; Chandran *et al.*,

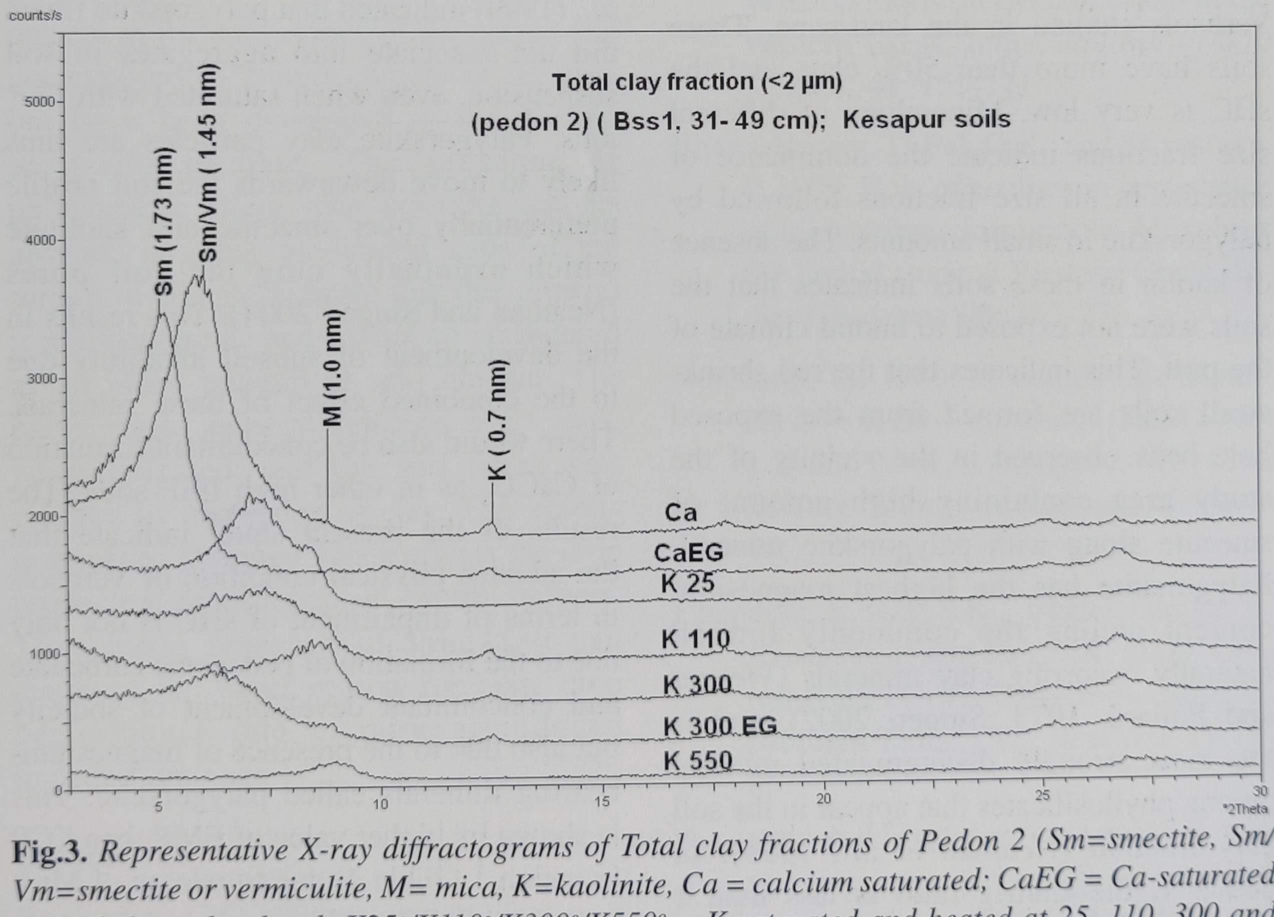

Fig.3. *Representative X-ray diffractograms of Total clay fractions of Pedon 2 (Sm=smectite, Sm/Vm=smectite or vermiculite, M= mica, K=kaolinite, Ca = calcium saturated; CaEG = Ca-saturated and ethylene glycolated; K25°/K110°/K300°/K550° = K saturated and heated at 25, 110, 300 and 550°C. K300°EG= K saturated and heated at 300° and ethylene glycolated)*

2000). The presence of large quantity of smectite and its transformation to kaolin in pedon 2 is possible only under humid climate which prevailed during the geological past. The deep weathering front of the humid climate due to erosion-deposition cycles of the past may have resulted in the formation of soils of the valley floor. This is confirmed by the small amounts of kaolin mineral present in the Vertisols of the valley (pedon 2).

Soils of the red Vertisols (pedon 1) are alkaline and the pH varies from 8.5 to 9.4 which is more than that of the other Vertisols studied in the landscape. These soils have more than 50% clay, and the sHC is very low. Mineralogy of different size fractions indicate the dominance of smectite in all size fractions followed by palygorskite in small amounts. The absence of kaolin in these soils indicates that the soils were not exposed to humid climate of the past. This indicates that the red shrink-swell soils are formed from the exposed bole beds observed in the vicinity of the study area containing high amount of smectite along with palygorskite mineral. Palygorskite has the highest magnesium content among the commonly formed naturally occurring clay minerals (Weaver and Pollard, 1973, Singer, 2002), and is the most strongly disaggregated mineral among phyllosilicates that appear in the soil clay fraction (Neaman *et al.*, 1999). In pedon 1, the Ca/Mg ratio is less than 1 indicating the dominance of Mg^{2+} in the exchange complex. Exchangeable Mg^{2+} in soils can influence soil properties by creating alkaline conditions and along with Na^{+} ions cause dispersion of clays compared to calcium dominant soils which tend to flocculate (Rahman and Rowell, 1979, Pal *et al.*, 2006). Magnesium is less efficient than calcium in flocculating soil colloids (Rengasamy *et a*l., 1986), and thus might have adversely affected the hydraulic properties of soils. Palaveyev and Penkov (1990) also reported negative effect of high exchangeable magnesium on physical condition of soils with strongly swelling and finely dispersed smectite. Neaman *et al.*, (1999) indicated that palygorskite fibers did not associate into aggregates in soil suspension, even when saturated with Ca^{2+} ions. Palygorskite clay particles are thus likely to move downwards the soil profile preferentially over smectite and kaolinite which eventually clog the soil pores (Neaman and Singer, 2004). This results in the development of subsoil alkalinity due to the combined effect of these minerals. There would also be concomitant formation of $CaCO_3$ as in other high ESP soils. The results of the present study indicate that the adverse physical condition of Vertisols in terms of impairment of sHC is not only due to the formation of pedogenic carbonate and concomitant development of sodicity but also due to the presence of magnesium-bearing minerals called palygorskite. This is shown by higher value of EMP than ECP in pedon 1 (Table 4) due to release of Mg^{2+} ions from palygorskite.

The ferruginous (red) shrink-swell soils were developed in the bole beds (red boles) which had not been exposed to humid climate of the past. These soils also contain palygorskite minerals which are rich in Mg^{2+} ions. Consequently there is an increase in exchangeable Mg which causes dispersibility of clay particles forming a 3D mesh in the soil matrix. Such soils on irrigation show drainage problem, a predicament for crop production.

Conclusion

The ferruginous shrink-swell soils are developed from bole beds which were present in the side slopes of the catena and not exposed to humid climate of the past but have been developed in the present semi-arid climate. The presence of palygorskite along with smectite and its absence in other associated soils of the semi-arid climate indicate that this mineral is non-pedogenic and cannot be considered as an index mineral of arid climate. The palygorskite mineral releases Mg^{2+} ions, when irrigated, and the soil pores gets clogged by dispersion of clay. This results in impeded drainage which affects the crop production as experienced by the farmers. Thus basic research of this kind can diagnose the exact reason for poor crop performance due to mineral induced impeded drainage.

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Variability of Lateritic Soil Development in Humid Tropical Environment

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Abstract: *West coast of peninsular India experience humid tropical climate: high rainfall and high temperature. Laterization –removal of bases and silica and residual enrichment of oxides of iron and aluminium-is the main soil forming process under the highly leaching environment. Though the overall climate is humid tropical, the pattern of annual rainfall distribution in the region results in subtle variations in the length of dry period and consequently duration of soil moisture deficit. This paper describes the variability in the properties of lateritic soils consequent to changes in period of soil dryness.*

Laterization in tropics leading to deeply weathered lateritic soils and petrologic end product laterite must be regarded as a geologic phenomenon may be 30 m thick as to a ferruginous or basaltic curass, which is 1 million years old. In laterization weathering tends to assist the accumulation of iron and alumina consequent to leaching of silica and bases (Mohr and Van Baren, 1954). The concept of kandic horizon was introduced in 1987 into diagnostic criteria used in soil taxonomy to overcome the deficiencies of the system when applied to low activity clays of tropics. Kandi soils may be presumed to be fairly widespread in some parts of India, where laterite and lateritic soils exist (Eswaran *et al.*, 1992). Highly weathered and leached low activity clay soils constitute approximately 30 per cent of soils of Kerala (Krishnan *et al.*, 1996). These soils generally occur in old geomorphic surfaces in the inter tropical areas intensively leached under humid climate with dominance of kaolinite and hydrous oxides of Fe and Al in the clay fraction resulting in low cation exchange capacity (Krishnan *et al.*, 2000).

In the present communication, an attempt has been made to reason out the depth of occurrence of hard laterite, plinthite or iron stone layer and presence of gravels, if any, in solum towards the dry period from less than 2 months to nearly 6 months from Neyyattinkara to Kasargod.

Materials and methods

Four pedons studied in locations of varying periods of soil moisture deficit were selected for the present study. The pedons are typical of soils in specified regions and have large spatial extent.

1. Neyyattinkara soils: Extensive south of Thiruruvananthapuram, Kerala. Rainfall is 1800 mm and length of dry period <2 months.
2. Panachikkad soils: Extensive in southern midlands of Kerala. Rainfall is 3000 mm and length of dry period 2-3 months.
3. Anakkayam soils: Extensive in central midlands of Kerala. Rainfall is around 3000 mm and length of dry period 3-4 months
4. Kasaragod soils: Extensive in northern midlands of Kerala. Rainfall is 3500 and length of dry period 5-6 months.

The climatic variability of the study area has been worked out using IMD data (IMD, 1999) following Thorthwaite and Mather (1955) at different probability levels of rainfall, its distribution and the ensuing expression of dry period. The morphology of the soils was described using standard terminology (AISLUS, 1970; Soil Survey Staff, 1993, 2004). Standard analytical procedures (USDA SCS, 1967; Sarma *et al.,* 1987) were used to characterize the soils in terms of physical and chemical properties. Soil classification was done according to Soil Taxonomy (Soil Survey Staff, 1999).

Results and Discussion

The significant properties of the soils are presented in Table 2.

Soils developed in south of Thiruvananthapuram (Neyyattinkara soils) are dark red (2.5YR/10R 3/6), very deep, well drained, slightly acid, non-gravelly clay (Table 2). The absence of gravel in the solum and plinthite layer distinguishes itself from laterite soils in other regions of the state. Climatic analysis revealed that Neyyattinkara soils have a dry period of less than 2 months (Nair *et al.*, 2011) and occur on gently sloping uplands cultivated to coconut, under khondalite landform. The soils have very low CEC and high BS. The dominant clay minerals of these soils, when put to rubber cultivation for a long while have been reported as kaolinite, gibbsite, sillimanite and hydroxy interlayered vermiculite (NBSS&LUP, 1999). Soils have been classified as fine kaolinltic family of Udic Kandiustalfs owing to a CEC less than 16 cmols per kg clay or an ECEC of less than 12 cmols and a base saturation of more than 35 per cent at a depth of 125 cm from the start of kandic horizon (Tables 3&4). The soils remain dry for less than 90 cumulative days.

Total rainfall of 1800 mm (Table 1) indicated a postulated silica sesquioxide ratio of more than 2.07, which in turn is congenial for the development of immature lateritic soils or non-lateritic red loams. Dry months of less than 2 months will not give considerable time for intense desiccation and followed by a not so heavy rainfall for the formation iron nodules or indurated layers (Mohr and Van Barren, 1954). Other

Table 1. *Monthly distribution of rainfall and dry period*

Station	Monthly Rainfall (mm)													Month <50 mm
	J	F	M	A	M	J	J	A	S	O	N	D	Total	
Neyyattinkara	41.6	13.0	20.2	59.3	169.4	229.1	261.1	191.5	113.9	246.1	303.7	147.8	1796-7	3
Kottayam	22.0	14.8	32.6	107.9	241.9	467.8	604.7	482.3	361.7	328.7	298.6	96.9	3059.9	3
Anakkayam	5.2	3.7	10.5	95.2	136.7	558.5	638.7	379.1	158.8	312.3	102.5	24.4	2425.6	4
Kasargod	5.3	3.3	14.7	49.3	186.7	992.6	1042.2	598.2	253.7	205.5	96.6	26.7	3477.8	5

pedogenic processes of leaching of bases and acidification are not so pronounced here. Rubrifaction is the active process here making very deep dark red subsoils. An XRD study conducted in a similar soil, Basavaraj and Sarma (1993) reported dominance of iron oxide minerals viz. lepidocrocite, haematite and goethite in the clay fraction. High proportion of dithionite soluble iron oxides over oxalate soluble indicated good drainage in soil profile and presence of Fe as a substitute ion for octahedral Al in kaolinite, apart from Fe being carried as mineral component by amorphous ferri-aluminosilicates.

Panchikkad soils are typical soils extensive in southern midlands of the state are deep, well drained, strongly acid and extremely gravelly clayey. Again, they have the plinthite layer starting at varying depths between 100-150 cm (Table 2). Total rainfall of 3000 mm (Table 1) with a dry period of nearly 3 months indicated a favourable silica sesqui oxide ratio of 1.33-2.00 for the development of laterite or red earth. Panchikad soils occur on gently to moderately sloping laterite mounds planted with rubber. Soils are very gravelly clayey, very strongly acid, rich in OC and low in CEC and base saturation. Soils have been classified as Clayey-skeletal kaolinitic family of Ustic Kanhaplohumults, owing to high OC status, BS of less than 35 per cent at 125 cm depth from the top of kandic horizon and a CEC and ECEC of less than 16 and 12 cmols per kg clay respectively and clay content decrease more than 20 per cent from highest towards lower depths (Tables 3 & 4).

Anakkayam soils are typical soils extensive in central midlands of the state are very deep, well drained, strongly acid and very gravelly clayey. Again, they have plinthite layer starting at varying depths between 150-200 cm (Table 2). A total rainfall of around 2500 mm (Table 1) favour a silica sesquioxide ratio of 1.33 to 2.07, which in turn assist the formation of laterite or red earth. A dry period of 4 months with high day temperature will help in intense desiccation and washing effect of good rainfall following dry season favour the formation of iron nodules (Table 2) and indurated layers. These soils occur on moderately sloping midland laterite hill side slopes formed under charnockite landform and occupied by cashew plantation. Soils are dark red, strongly acid, medium in organic carbon, low in cation exchange capacity and base saturation. Soils have been classified as Clayey-skeletal kaolinitic family of Typic Kandiustults, owing to medium organic carbon status, base saturation less than 35 per cent, and CEC and ECEC values less than 16 and 12 cmols per kg clay and no decrease of more than

Table 2. *Morphological properties of the soils*

Horizon/ Depth (cm)	Colour	Texture	Coarse Fragments (Vol %)	Structure	Consistence	Clay films	Iron concretions
1. Neyyattinkara soils: Fine, Kaolinitic, isohyperthermic Udic Kandiustalfs							
Ap: 0-14	5YR3/4	scl	Nil	1 Msbk	fr ss ps	-	-
Bt1: 52-87	2.5YR3/6	sc	Nil	2 Msbk	fr s p	T tn p	-
Bt6: 180-200	10R3/6	c	Nil	2 Msbk	fr s p	T tn p	-
2. Panachikkad soils: Clayey-skeletal, Kaolinitic, isohyperthermic Ustic Kanhaplohumults							
Ap: 0-15	5YR3/4	egc	65	2 Msbk	fi s p	-	-
Bt 15-99	5YR4/6	egc	65	2 Msbk	fr s p	T tn p	-
BC 99-136	10R4/6	gc	30	Massive	fr s p	T tn p	-
C: 136-150	Hard laterite						
3. Anakkayam soils: Clayey-skeletal, kaolinitic, isohyperthermic, Typic Kandiustults							
Ap: 0-10	5YR3/4	gscl	20	2 Msbk	sh fr ss ps	-	-
Bt1 10-100	5YR4/6	vgc	40	2 Msbk	fr s p	T tn p	f m p
Bt2: 100-165	10R4/6	gc	25	2 Msbk	fr vs vp	T tn p	f m p
C: 165-180	Hard laterite						
4. Kasaragod soils: Clayey, kaolinitic, isohyperthermic Petroferric Dystropepts							
A: 0-10	10YR4/4	gcl	15	1 Msbk	sh fr ss p0	-	f f&m p
Bw: 10-30	10YR4/4	gc	20	1 Msbk	l fr s p	-	m f&c p
C: 30-50	Iron stone (Extremely hard laterite)						

20 percent clay from highest towards lower layers of kandic horizon (Tables 3&4). Fluctuations in ground water triggered by long dry period and consequent heavy downpour also favour laterization by capillary movement and deposition of iron oxides and hydrous oxides on aggregate boundaries and pore spaces.

Kasaragod soils are typical of laterite plateaus of northern Kerala. It is rather a thin layer of soil on iron stone (irreversibly hardened laterite). At places, the ironstone is exposed on the surface. The uncultivated soils recorded high levels of organic carbon due to the presence of grasses. A total rainfall of around 3500 mm (Table 1). favour a silica sesquioxide ratio of 1.33 to 2.07 in soils, which in turn assist the formation of laterite or red earth. Dry period of 5-6 months and intense desiccation due to high day temperature and consequent very heavy rainfall favour the formation of iron nodules and indurated laterites or ironstone near surface. These soils occur on the summits of laterite mounds dominated with exposed iron stones with grass vegetation or cashew on deeper soils and side slopes. Soils are dark red (Table 2), gravelly clayey, strongly acid, rich in

Table 3. *Physical and chemical properties of the soils*

Horizon/ Depth (cm)	Particle size distribution (%)			Silt/ clay ratio	Gravel (%)	O.C. (%)	pH	CEC (cmol (+) kg^{-1} soil	B.S. (%)	CEC/ clay Ratio
	Sand	Silt	Clay							
1. Neyyattinkara soils: Fine, Kaolinitic, isohyperthermic Udic Kandiustalfs										
Ap: 0-14	75.4	1.2	23.4	0.05	Nil	0.93	6.4	4.3	98	0.18
Bt1: 14-100	54.9	4.5	50.1	0.09	Nil	0.57	6.5	3.3	88	0.07
Bt2 100-200	45.0	1.7	53.3	0.03	Nil	0.33	5.3	4.1	68	0.08
2. Panachikkad soils: Clayey-skeletal, Kaolinitic, isohyperthermic Ustic Kanhaplohumults										
Ap: 0-15	42.3	14.1	43.6	0.32	65	2.16	4.5	10.0	13	0.23
Bt: 15-99	33.3	8.4	58.3	0.14	65	1.24	4.8	5.8	23	0.09
BC: 99-136	30.4	12.2	57.4	0.21	30	0.89	4.9	3.8	35	0.07
C: 136-150	Plinthite									
3. Anakkayam soils: Clayey-skeletal, kaolinitic, isohyperthermic, Typic Kandiustults										
Ap: 0-10	56.6	15.8	27.6	0.57	20	0.97	5.1	4.6	34	0.23
Bt1: 10-77	43.0	14.4	42.6	0.34	40	0.69	5.4	4.2	49	0.10
Bt2: 77-165	38.4	9.6	47.2	0.20	25	0.34	5.8	4.7	52	0.10
C: 165-180	Plinthite									
4. Kasaragod soils: Clayey, mixed, isohyperthermic Petroferric Dystrustepts										
A: 0-10	25.7	36.6	37.7	0.97	15	4.78	5.2	15.0	8	0.40
Bw: 10-30	27.8	37.3	34.9	1.07	20	3.88	5.2	14.9	7	0.43
C: 30-50Iron stone (Extremely hard laterite)										

Table 4. *Cation exchange characteristics of the soils*

Horizon/ Depth (cm)	Exchangeable bases				Sum of bases	$BaCl_2$ TEA acidity	KCl extracable Al	ECEC	CEC by sum of cations	B.S. by sum of cations (%)	CEC cmol (p+) per kg clay
	Ca	Mg	Na	K							
	cmol (p+) kg^{-1}										
1. Neyyattinkara soils: Fine, Kaolinitic, isohyperthermic Udic Kandiustalfs											
Ap: 0-14	3.0	1.0	0.04	0.14	4.2	1.0	0.0	4.2	5.2	81	18
Bt1: 14-180	1.8	1.0	0.03	0.02	2.9	5.2	0.1	3.0	8.1	36	07
Bt2 180-200	1.9	0.9	0.03	0.01	2.8	7.3	0.1	2.9	10.1	28	08
2. Panachikkad soils: Clayey-skeletal, Kaolinitic, isohyperthermic Ustic Kanhaplohumults											
Ap: 0-15	0.7	0.3	0.05	0.22	1.3	17.6	2.1	3.4	18.9	07	23
Bt: 15-99	1.0	0.2	0.05	0.13	1.3	12.2	1.4	2.7	13.5	10	09
BC: 99-136	0.9	0.3	0.05	0.14	1.3	8.3	0.9	2.2	9.6	14	07
C: 136-150	Plinthite										
3. Anakkayam soils: Clayey-skeletal, kaolinitic, isohyperthermic, Typic Kandiustults											
Ap: 0-10	0.9	0.5	0.04	0.15	1.6	12.1	0.17	1.6	13.7	12	23
Bt1: 10-77	1.3	0.6	0.04	0.15	2.1	11.7	0.04	2.1	13.8	14	10
Bt2: 77-165	1.8	0.4	0.06	0.19	2.5	11.2	0.00	2.5	13.7	18	10
C: 165-180	Plinthite										
4. Kasaragod soils: Clayey, mixed, isohyperthermic Petroferric Dystrustepts											
A: 0-10	0.7	0.3	0.12	0.22	1.3	36.3	0.00	1.3	37.6	03	40
Bw: 10-30	0.6	0.2	0.10	0.17	1.0	35.1	0.00	1.0	36.1	03	43
C: 30-50	Iron stone (Extremely hard laterite)										

OC, low in CEC and very low in base saturation and hard laterite or iron stone occurs within 50 cm. Soils have been classified as Clayey, kaolinitic family of Petroferric Dystrustepts owing to very low base saturation below 60 per cent and hard petrroferric layer within 50 cm depth and a CEC per kg clay of less than 20 cmols (Tables 3&4).

Very low cation exchange capacity and low CEC/clay ratio qualifies the soils to be termed as low activity clay (LAC) soils. Many studies have shown the dominance of kaolinite and oxides of iron and aluminium in the clay fraction of the lateritic soils of Kerala (Basavaraj and Sarma, 1993). The description of laterites following the silica, alumina and iron oxide diagram (Lukens, 1964) can tell the dominant process like weak laterization and kaolinzation as in Neyyattinkara through Panachikkad towards strong laterization and kaolinization with iron enrichment as in Anakkayam and Kasargod. The process of laterization is influenced in general by humid tropical climate, rainfall, topography, ground water quality and movement and chemistry of different parent rocks (Raghu Nandan *et. al.,* 1993), but the most prominent is humid tropical climate, rainfall and duration of dry period. The near absence of gravel and plinthite in Neyyatinkara soils with very short dry period points to the need for dry conditions for development of gravel and plinthite. Plinthite and gravel formation was found to increase with increasing length of dry period. The iron stone formation is extensive in northern Kerala with dry period in the range of 4 to 6 months.

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Clay Mineralogy of Salt-affected Soils of Bhind District of Madhya Pradesh

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Abstract: *The salt-affected soils Chambal Command area of Bhind district of Madhya Pradesh were studied for their morphological, physico-chemical characteristics and clay mineralogical composition. The area lies between $25^0 50'$ and $26^0 50'$ N latitude and $78^0 10'$ and $79^0 08'$ N longitude and comprises typical wastelands of the district. Five typical pedons (Gohad-P2, Loharpura-P4, Chitora-P8, Tukeda-P10 and Parechha-P13) selected for the study were classified as Aeric Halaquepts (P2), Vertic Natragids (P4), Sodic Haplocalcids (P8), Typic Natrargids (P10) and Sodic Haplocambids (P13) based on sub-surface diagnostic horizons and soil moisture regimes. All the soils were high in ECe (5.0 to 31.0 dSm^{-1}) and ESP (17.8 to 61.5%) but somewhat low in pHs ranging from 7.5 to 8.8.*

The X-ray diffraction of clay fraction of the salt-affected soils of the area showed presence of illite, smectite, vermiculite, kaolinite and chlorite. Smectite was found to be the second dominant mineral after illite and present in appreciable amounts in all the salt-affected soils. Although transformation of illite to smectite could not be ascertained due to many pedogenic processes acting simultaneously however, it appears that some illite might have transformed to smectite under poor drainage condition and high salinity and sodicity in these soils. Illite, kaolinite and chlorite in these soils were probably inherited from parent material.

In India saline-sodic soils estimated to the extent of 9.8 M ha (Singh, 1992). A report of the Central Soil Salinity Research Institute, Karnal has cited a total about 6.73 M ha of salt-affected soil in India (Sharma *et al.*, 2007). The salt-affected soils in Madhya Pradesh is spread over 23 districts covering two physiographic landscapes, namely black soil region and the alluvial soil region of the Chambal. A total of about 2.5 lakh ha area in Madhya Pradesh is under salt-affected soils out of which around 2.0 lakh ha occur in Chambal Command (Anonymous, 2008). The problems of salt-affected soils are many folds with regard to their use for agriculture purpose. The property and behaviour of salt-affected soils changes clay content and with type of clay minerals (Chhabra, 1996). The problem of alkalinity is pronounced in clay soils than in loamy, silty or sandy soils. The clay soils containing montmorillonite or smectite are more subject to alkalinity problems than illite or kaolinite clay soils. Sharma (1979), while discussing the physiography and agricultural development, has described two soils groups of soil namely grey and brown soils having varied characteristics from lower Chambal valley. The information on the alluvial soils, particularly salt-affected soils of Bhind district of Madhya Pradesh is very scanty. In order to fill this gap and for better understanding and management, the salt-affected soils of Bhind district of Madhya Pradesh were studied for their physico-chemical characteristics and clay mineralogical composition.

Materials and Methods

The study area lies between 25^{0}50' and 26^{0}50' N latitude and 78^{0}10' and 79^{0}08' N longitude and comprises typical wastelands of Bhind district of Madhya Pradesh. The area comes under the Agro-ecological Region characterized by hot semiarid with alluvium-derived soils (N8D2). The area experiences annual precipitation of about 690 to 850 mm, 80% of which is received during the months of June to August. The characters of the area are hot summer and cold winter. The minimum and maximum temperatures are 8^{0}C and 48^{0}C respectively and the mean annual temperature is about 32 ^{0}C. The PET is 1400 to 1900 mm. The soil moisture control section remains moist for 90 cumulative days qualifying for *ustic* moisture regime and temperatures regime is hyperthemic. The soils have developed from the alluvium brought by the river Chambal and its tributaries, *viz.* Kali Sind, Kuwari and Pahuj. The detailed soil survey of the area was conducted as per procedure outlined in the Soil Survey Manual (Soil Survey Staff, 2004). Thirteen typical soils, seven in Gohad, five in Mehgaon and one in Lahar were selected in Gohad (7), Mehgaon (5) and Lahar (1) tehsils of Bhind district of Madhya Pradesh were identified. Geomorphologically, the soils are located distantly in the alluvial fan area. All the soil profiles were explosed for studying the morphological characteristics following the Soil Survey Manual (Soil Survey Staff, 2004). Horizon wise soil samples were collected and processed for various analysis. The soils were classified as per Soil Taxonomy (Soil Survey Staff, 1998). Five typical pedons (Gohad-P2, Loharpura-P4, Chitora-P8, Tukeda-P10 and Parechha-P13) were studied in detail for their morphological characterstics according to Soil survey staff (2004). Soil samples collected from each horizon were dried and sieved to obtain soil fraction (<2 mm) for analysis. Processed samples were analyzed for mechanical composition, pHs, ECe, CEC and exchangeable cations adopting the standard procedures. Saturation extracts of the soils were prepared and analyzed for pHs, ECe, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ (Richards, 1954). The soils were classified as per Soil Taxonomy

(Soil Survey Staff, 1998).

The soil samples from A and B-horizons of representative pedons P2 (Gohad), P4 (Luharpura), P8 (Chitora), P10 (Tukeda) and P13 (Parechha) were used for mineralogical investigations. The soil samples were treated with hydrogen peroxide and sodium acetate to destroy organic matter and carbonates and with sodium dithionite-citrate-bicarbonate to remove free oxides of iron and aluminum (Jackson, 1979). The clay fraction was separated by siphoning-off clay suspension after allowing requisite settling time (Piper, 1966). The potassium and Mg-saturated clays were prepared by treating clay samples with 1N KCl and 1N $MgCl_{2.}$ These clays were made salt free by repeatedly washing with distilled water. Basally-oriented clay specimens for X-ray diffraction were prepared by pouring the clay suspension on glass slide and then air-drying it. Potassium saturated clay samples were X-rayed after air-drying and after heating to 400°C for one hour whereas Mg-saturated samples were X-rayed at room temperature and after glycolation with ethylene glycol. The samples were run at a scanning speed of 2^0 2è per minute. The X-ray diffractograms for clay were obtained using a Philips PW1050 vertical goniometer, PW-1130 generator and PW-1370 recorder with Ni-filtered CuKα radiation. Semi quantitative estimation of the minerals was made by following the procedure given by Klages and Hopper (1982).

Results and Discussion

Morphological properties

The soils of the area have developed on alluvium deposited by Chambal river and its tributaries. The soils are deep, moderately drained and calcareous nature. The soils have hue of 10YR and value varying from 3 to 7. The color of the soils varies from light gray (10YR 7/1) to dark grayish brown (10YR 3/2) in moist condition. The soils have very low chroma probably due to reduced condition. The characteristics associated with wetness such as mottles and Fe-Mn concretions were observed in P2 soil. Usually few, fine faint yellowish brown (10YR 5/8) and few fine distinct strong brown (7.5 YR 5/6) mottles and few Fe-Mn concretions were recorded below 0.75 m in P2 soil signifying the presence of alternate oxidizing and reducing conditions. The texture varies from sandy loam to clay in different soils. The soil structure ranges from fine to moderate, medium and sub-angular blocky. Heterogeneity in parent material occurred in P2 soil as indicated by lithological break.

Physico-chemical properties

The physico-chemical characteristics of the studied soils are presented in Table 1. The soils are alkaline in nature having pH of saturation extract ranged from 7.5 to 8.8 in different horizons of the pedons. Highest pHs was observed in P13 soil and lowest in P8 soil. No definite trend in pHs with depth was noticed in different soils except in P13. Soil pHs appears to be related more

Table 1. *Physico-chemical characteristic of the studied soils*

Horizon	Depth (m)	pHs	ECe (dSm^{-1})	ESP	CaCO$_3$%	Clay %
Pedon 2 (Gohad) Loamy, mixed hyperthermic family of Aeric Halaquepts						
Ap	0.00-0.15	8.2	6.2	49.2	04.9	13.0
2B21	0.15-0.30	8.4	3.9	58.3	04.9	19.0
3B22	0.30-0.75	8.0	3.3	50.2	05.9	29.0
3Ck1	0.75-1.22	8.0	2.3	48.0	05.9	33.0
3Ck2	1.22-1.65	8.4	0.9	48.0	18.7	27.0
Pedon 4 (Luharpura) Fine, mixed, hyperthermic family of Vertic Natrargids						
Ap	0.00-0.15	8.1	6.1	35.5	05.9	32.5
B21w	0.15-0.38	8.0	6.1	37.0	02.9	42.5
B22w	0.38-0.80	8.1	4.3	28.5	02.9	44.5
B23w	0.80-1.25	8.2	1.9	25.5	02.9	48.5
B24w	1.25-1.70+	8.2	1.9	22.2	02.9	48.5
Pedon 8 (Chitora) Loamy, mixed, hyperthermic family of Sodic Haplocalcids						
Ap	0.00-0.15	7.7	3.4	25.8	03.9	18.5
B21t	0.15-0.35	7.7	2.9	24.3	03.9	16.5
B22t	0.35-0.52	7.5	2.2	20.9	05.8	28.5
B23tk	0.52-0.80	7.5	2.2	23.4	16.6	34.5
B24tk	0.80-1.25	7.6	1.6	19.3	16.6	40.5
B3	1.25-1.55	7.8	1.4	19.6	07.8	36.5
C	1.55+	7.7	1.2	18.1	07.8	32.5
Pedon10 (Tukeda) Fine, mixed, hyperthermic family of Typic Natrargids						
Ap	0.00-0.10	8.0	31.0	20.1	02.0	33.9
B21	0.10-0.23	8.3	18.0	17.8	05.9	29.9
2Bt22	0.23-0.46	8.0	18.0	32.3	03.9	41.9
2Bt23	0.46-0.65	8.0	15.0	32.9	11.8	39.9
2Bt24	0.65-0.99	8.3	12.0	29.3	11.8	39.9
Btk25	0.99-1.42	8.2	09.0	33.4	15.7	45.9
B3k	1.42+	8.2	05.0	27.7	15.7	41.9
Pedon 13 (Parechha) Loamy, mixed, hyperthermic family of Sodic Haplocambids						
Ap	0.00-0.06	8.8	9.2	61.5	11.0	17.2
B21	0.06-0.17	8.7	8.4	46.7	11.0	19.2
B22	0.17-0.37	8.5	7.2	54.5	07.4	17.2
B23	0.37-0.57	8.2	6.4	54.0	07.4	19.2
B24	0.57-1.16	8.0	3.6	40.0	09.2	21.2

with exchangeable sodium percentage. The soil P10 was highest in salt content with ECe varying from 5.0 to 31.0 dSm^{-1} followed by in P13 (ECe= 3.6 to 9.2 dSm^{-1}), P2 (ECe= 0.9 to 6.2 dSm^{-1}), P4 (ECe= 1.9 to 6.1 dSm^{-1}) and P8 (ECe= 1.2 to 3.4 dSm^{-1}). The salt content was highest in surface horizons and then gradually decreased with depth. The hot semiarid climate seems to be responsible for deposition of salts in surface horizon due to capillary rise of water and desiccation (Sharma, 1998). The salt-affected soils of Chambal area are more like that of salt-affected soils of Ganges delta where even at higher ESP the pHs was found to be low (Bandyopadhyay *et al.*, 1988). The Ca^{2+} and Mg^{2+} ions were the two dominant cations on the exchange complex of all the soils except in the some horizons of P2 and P13 soils where Na^+ was dominant over the others. Exchangeable sodium percentage ranged from 17.8 to 61.5 having highest in P13 and lowest in P8. Increased exchangeable sodium on clay complex has shown positive effect on soil reaction. The soils generally have more than 15 per cent clay suggesting loamy or clayey nature. The amount of clay has no effect on ESP of the soils. The soils P2 and P13 were characterized by imperfect drainage, high exchangeable sodium and pHs probably due to their low topographic position. The soils from Chitora are relatively lower in pHs, ECe and ESP compared to other soils. All the soils are saline-sodic except P8 which is sodic only. All the soils contain free calcium carbonate and it raged between 2.0 to 18.7 per cent. Carbonate accumulation is an important pedogenic feature of soils developed in arid or desert climate (Boul *et al.* 1997). Calcium carbonate followed different distribution trend in different soils. The highest content of calcium carbonate was observed in lower most horizons in P2 and P10 soils whereas in surface horizon in P4 and P13 soils. The P8 soil has shown accumulation of calcium carbonate in middle horizons suggesting effect of illuvial process.

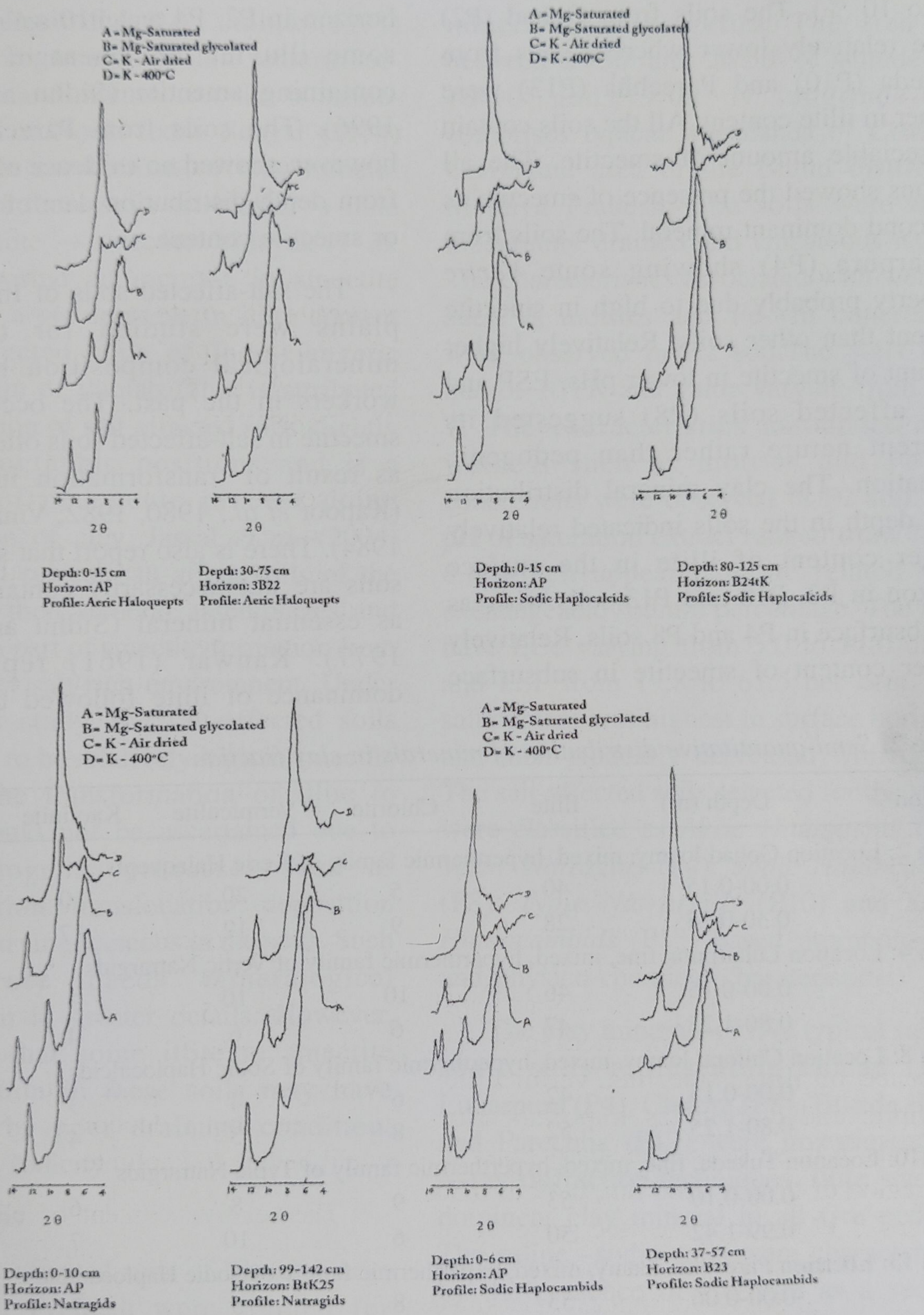
Taxonomical classification

The micro relief has played a vital role in the genesis of the salt-affected soils of this region. The relatively lower in topographic position associated with high ground water contributed to the salinization and alkalization of the soils. The increased clay accumulation in B horizon and also exchangeable sodium percentage more than 15, coupled with fine to moderate medium sub angular blocky structure, the P2, P4 and P10 soils indicated presence of nitric horizons. The darker color and little higher clay content in subsurface horizon than the undertaking C horizon, and structural development in P8, corroborates with criteria for cambic horizons. In areas around P2 soil, the water table was encountered at a depth of 100 cm and as such the soil remains water logged for quite a longer period. Thus P2 soil indicated mottling with chroma less than 3. These features lead to its classification as member of loamy, mixed hyperthermic family of *Aeric Halaquepts* (Soil Survey Staff, 1998). The characteristics of the pedon P4 revealed presence of 1 cm wide vertical cracks and slickensides that were tilted to 40° from the horizontal surface. Parellepipeds with shiny presence faces were also present. These features lead to the classification of this pedon into fine, smectitic, hyperthermic family of *Vertic Natrargids*. The soils P8 and P10 were classified based on their morphological features into fine loamy, mixed, hyperthermic family of *Sodic Haplocalcids* and fine, smectitic, hyperthermic family of *Typic Natrargids* respectively. The soil P13 was classified as a member of fine loamy, mixed, hyperthermic family of *Sodic Haplocoambids.*

Clay mineralogy

The X-ray diffractograms of clay fraction of the salt-affected soils are presented in figure 1 and the semi-quantitative distribution in Table 2. Interpretation of peaks appeared in the X-ray diffractograms obtained from Mg-saturated, Mg-glycolated, K-saturated and K-saturated and heated specimens indicated presence of illite, smectite, vermiculite, kaolinite and chlorite as important clay minerals in these soils. The sharp peaks in the region of 0.98 to 1.00 nm, 0.49 to 0.50 nm and 0.33 nm indicated the presence of illite in all the soils. The ratio of intensities of 0.5 and 1.0 nm peaks suggests that mica is dioctahedral in nature. In Mg-saturated clay samples, the asymmetric peak at 1.0 nm extends towards low angle and the tail is reduced considerably on K-saturation suggesting the loss of interlayer potassium due to weathering in illite or micas (Kapoor *et al.*, 1989). A sharp peak in in the region of 1.38 nm in Mg-saturated specimens indicated the presence of minerals like smectite, chlorite and vermiculite. On glycolation, a part of 1.38 shifted to 1.57 indicating the presence of smectite. The saturation of clay specimens with potassium has reduced the intensity of 1.38 nm peak with concurrent increase in the intensity of 1.0 nm peak, thus suggesting presence of vermiculite. At 500°C heating of K-saturated samples, the 1.38 nm peak remained persistent but reduced considerably in intensity, revealing the presence of chlorite. The weak 001 and 003 ordered reflections, and strong 002 reflections show that chlorite is rich in iron (Jassal *et al.*, 2000). The sharp peaks in the region of 0.70 to 0.73 and at 0.35 nm were observed in X-ray patterns of Mg-saturated clays in all the soils indicating the presence of kaolinite and chlorite. On heating upto 550°C, the intensity of this peak was reduced but remain present. The persistence of the peak could be attributed to chlorite, but reduction of peak intensity could be due to kaolinite.

The relative content of clay minerals in different soils (Table 2) showed the dominance of illite (28 to 53 %) followed by smectite (21 to 37 %), vermiculite (3 to 20 %), kaolinite (3 to 17 %) and chlorite



Depth: 0-15 cm
Horizon: AP
Profile: Aeric Haloquepts

Depth: 30-75 cm
Horizon: 3B22
Profile: Aeric Haloquepts

Depth: 0-15 cm
Horizon: AP
Profile: Sodic Haplocalcids

Depth: 80-125 cm
Horizon: B24tK
Profile: Sodic Haplocalcids

Depth: 0-10 cm
Horizon: AP
Profile: Natragids

Depth: 99-142 cm
Horizon: BtK25
Profile: Natragids

Depth: 0-6 cm
Horizon: AP
Profile: Sodic Haplocambids

Depth: 37-57 cm
Horizon: B23
Profile: Sodic Haplocambids

Fig. 1. *X-ray diffractograms of the total clay fraction of representative salt-affected soils*

(5 to 10 %). The soils from Gohad (P2) were relatively lower whereas soils from Tukeda (P10) and Parechha (P13) were higher in illite content. All the soils contain appreciable amount of smectite. The all pedons showed the presence of smectite as a second dominant mineral. The soils from Luharpura (P4) showing some *Vertic* property probably due to high in smectite content than other soils. Relatively higher amount of smectite in lower pHs, ESP and ECe affected soils (P8) suggested its inherent nature rather than pedogenic formation. The clay mineral distribution with depth in the soils indicated relatively higher content of illite in the surface horizon in P2, P10 and P13 soils whereas in subsurface in P4 and P8 soils. Relatively higher content of smectite in subsurface horizon in P2, P4 and P10 soils suggested some illuvial movement of fine clay containing smectite (Sidhu and Ghosh, 1996). The soils from Parechha (P13), however, showed no evidence of illuviation from depth distribution data of either clay or smectite content.

The salt-affected soils of Indogangetic plains were studied for their clay mineralogical composition by several workers in the past. The occurrence of smectite in salt-affected soils often regarded as result of transformation in the soils (Kapoor *et al.,* 1980, 1982; Vinayak *et al.,* 1984). There is also report that saline sodic soils are not necessarily contain smectite as essential mineral (Sidhu and Gilkes, 1977). Kanwar (1961) reported the dominance of illite followed by chlorite

Table 2. *Semi-quantitative distribution of minerals in clay fraction*

Horizon	Depth (m)	Illite	Chlorite	Vermiculite	Kaolinite	Smectite
Pedon 2: Location Gohad loamy, mixed, hyperthermic family of Aeric Halaquepts						
Ap	0.00-0.15	40	5	20	10	24
3B22	0.30-0.75	28	9	12	17	34
Pedon 4: Location Luharpura, fine, mixed, hyperthermic family of Vertic Natrargids						
Ap	0.00-0.15	46	10	10	3	31
B23w	0.80-1.25	47	6	6	4	37
Pedon 8: Location Chitora, loamy, mixed, hyperthermic family of Sodic Haplocalcids						
Ap	0.00-0.15	42	6	4	3	35
B24tk	0.80-1.25	52	8	3	4	33
Pedon10: Location Tukeda, fine, mixed, hyperthermic family of Typic Natrargids						
Ap	0.00-0.10	53	9	8	6	24
Btk25	0.99-1.42	50	6	10	7	27
Pedon 13: Location Parechha, loamy, mixed, hyperthermic family of Sodic Haplocambids						
Ap	0.00-0.06	53	8	5	7	27
B23	037-0.57	50	9	10	10	21

whereas Sehgal and De Coninck (1971) observed the presence of illite, chloritized-vermiculite and montmorillonite is saline-sodic soils of North India. Sehgal (1974) postulated a mechanism of clay mineral alteration in these soils as: biotite → illite → vermiculite → smectite. Vinayak *et al.* (1984) reported an increase in smectite content *vis* a *vis* decrease in illite content in salt affected soils of Indo-Gangetic alluvial plain of Punjab. This is attributed to the location of salt affected soils slightly lower topographic positions and is a resultant of pedogenic process doing sodimization of clay. Jassal *et al.* (2004) investigated typical salt-affect soils of the Punjab for their mineral assemblages and found that a part of smectite formation from biotite under salt-rich environment. Under the present study, the salt-affected soils were found to be relatively high in smectite content. The transformation of illite to smectite could not be ascertained due to many pedogenic processes such as transformation, translocation, deposition etc, going on simultaneous in the soils. Such as inference needs mineralogical investigation in greater details. However, it appears that some illite to smectite transformation in these soils may have facilitated by poor drainage condition, salinity and sodicity.

Conclusions

The salt-affected soils of Bhind district of Madhya Pradesh were studied for morphological, physical, chemical and mineralogical proprties. The area lies between 25^{0}50' and 26^{0}50' N latitude and 78^{0}10' and 79^{0}08' N longitude and comprises typical wastelands of Chambal Command area of the Bhind district of Madhya Pradesh. The soils were deep, moderately drained and calcareous nature. The characteristics associated with wetness such as mottles and Fe-Mn concretions were observed in P2 soil.The soils have hue of 10YR and value varying from 3 to 7. The characteristics associated with wetness such as mottles and Fe-Mn concretions were observed in P2 soil. The pH of saturation extract ranged from 7.5 to 8.8 which appeared to be related with exchangeable sodium percentage. The soils have ECe varying from 5.0 to 31.0 dSm^{-1} and ESP from 17.8 to 61.5 per cent. The salt content was highest in surface horizons and then gradually decreased with depth. The salt-affected soils selected for the study were classified as *Aeric Halaquepts* (P2), *Vertic Natragids* (P4), *Sodic Haplocalcids* (P8), *Typic Natrargids* (P10) and *Sodic Haplocambids* (P13) based morphological and physico-chemical charateristics.

The clay minerals of five typical saline-sodic soils representing Gohad (P2), Luharpura (P4), Chitora (P8), Tukeda (P10) and Parechha (P13) were investigated by X-ray diffraction techniques. Illite was the dominent clay mineral in all five pedons. The saline –sodic soils were characterized by the presence of smectite as a second dominant mineral. Minor amount of chlorite, vermiculite and kaolinite were present in all the soils. Illite, kaolinite and chlorite in these soils were probably inherited. The transformation of illite to smectite could not be ascertained due to many pedogenic processes going on simultaneous in the soils, and therefore it thought that some smectite may have developed by transformation from illite in these soils under poor drainage condition and high in saline and sodic condition.

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Studies on Morphological, Mineralogical and Physico-chemical Properties of Some Selected Soils of Different Agroclimatic Regions of West Bengal, India

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Abstract. *A study was undertaken to investigate the morphological, mineralogical and physico-chemical characteristics of some selected soils of four agroclimatic regions namely, Red and Lateritic Zone, Old Alluvial Zone, Coastal Saline and New Alluvial Zone of West Bengal. Undisturbed soil samples were taken from identifiable upper two horizons. The morphological parameters include horizon with depth, colour, texture, structure, consistency and boundary of the soils. The soils under study were both fine and coarse textured soils and the sub-surface layers contained higher amounts of clay than the surface layers. All these soils belonged to mixed mineralogy and hyperthermic temperature regime. The physico- chemical properties were found to vary with different agro-climatic regions. The mineralogical make-up and morphological characteristics of these soils seemed to influence the physico-chemical properties of the soils.*

Key words : Morphology, Mineralogy, Potassium X-ray diffraction, surface soils, sub-surface soils

Introduction

Soil morphology deals with the form and arrangement of soil features (Schoeneberger, 1998). The complex factors controlling soil development on multi-step terraces, the possibility of developing a soil chronosequence are examined through the variations in soil morphology. Soil morphological descriptions are commonly recorded and mostly used to aid classification purposes (Soil Survey Staff, 1998; FAO, 1998). Standard soil morphological descriptions have been

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quantified and combined in a soil profile development index for evaluating soil development (Meixner and Singer, 1981; Harden, 1982). In addition, McKenzie and Jacquier (1997) describe the use of soil morphological descriptions together with inexpensive field tests to derive soil hydraulic properties in low-surveyed regions. Last, soil color indices present a quantified approach for assigning drainage class to a soil (Megonigal *e. al.*, 1993; Thompson and Bell, 1996) and assessing the Fe$^-$ oxide mineralogy (Mokma, 1993). Another impotant aspect of soil morphology is that it includes local soil classification which is based on soil texture, ironstone, and soil color of the topsoil to tillage depth, and relates directly to land use and management (Gobin *et al.,* 2000). The mineralogy of the parent material has an impact on clay mineralogy of soil (Bronger *et. al.*, 1994 and Mehedi *et. al.*, 2000). As weathering proceeds, the clay content increases as a result of physical and chemical alteration of primary minerals. With further chemical changes, transformation may take place within the clay fraction of the soil. The type of clay minerals formed depends on the climatic conditions and the chemical environment within the soil (Mehedi *et. al.*, 2000). Srivastava *et. al.* (1998), studied the clay mineral assemblages of a soil chrono-association of Indo-Gangetic plain as an evidence to the climate change since Holocene age. This study shows that during the Holocene age the major pedogenesis of the soils of central Indo-Gangetic Plains and North-Central India have mainly involved clay illuviation and decalcification. Weathering of biotite was substantial at first making mixed layers with vermiculite and then vermiculite and smectite. The clay fractions of the ferruginous soils of India as well as in West Bengal have the dominance of kaolinite and smectite (Pal, 2003). Nayak and Sarkar (2005) studied the mineralogy of the poorly drained rice growing soils of West Bengal where they found that soils are dominated by mica (illite) (35 to 79%) followed by kaolinite (10 to 30%) and chlorite (2 to 19%). Ghosh *et. al.* (2006) reported the dominance of smectitic minerals in some arsenic affected alluvial soils of West Bengal. Pal *et. al.* (2006) also studied the Indian soils in respect of transformation of clay minerals with the climatic change. They used smectitie/kaolinite ratio to identify the change pattern of minerals over climatic change towards hotter and warmer conditions. The chemical and mineralogical compositions of soil have a particular influence on properties of soils. The cation exchange capacity increases with the contents of finer particles and 2:1 type minerals (Schulze, 1989). Besides, the mineralogical and morphological make-up of the soil also influences different physico-chemical properties of the soils. Present study was undertaken to study the morphological, mineralogical and physico-chemical properties of some soils of West Bengal.

Materials and Methods

Soil samples of surface and sub-surface layers (two horizons) from ten locations were collected from Old Alluvial Zone, New Alluvial Zone, Red & Lateritic Zone, Old Alluvial Zone and Coastal Saline agro-climatic zones of West Bengal. The study was conducted during 1992 to 1994. In Red & Lateritic zone the soils were collected from Abas (22°24'N & 87°20'E) & Rajrabundh (22°23'N & 87°10'E) of West Medinipur district. Barochowka (21°90'N & 87°38'E) and Kripanandapur (22°91'N & 87°38'E) soils of East Medinipur represent old alluvial zones of West Bengal whereas soils of Ramgangapur (21°45'N & 88°13'E) of South 24 Parganas represent coastal saline zone. Further, Enayatpur (23°5'N & 88°38'E), Kalyani (28°8'N & 88°38'E), Bansberia (23°24'N & 88°89'E) and Poragachha (23°24'N & 88°89'E) from Nadia district and Bhagalpur (26°25'N & 88°23'E) of North Dinajpur district comprise soils from alluvial zone. After studying the morphological characters in the field, soil samples were collected, labelled and packed for studies in the laboratory where further detailed physical, chemical and mineralogical analyses were performed.

The soil samples were air dried and ground to pass through 2 mm sieve by the usual method described by Piper (1966). The pH, electrical conductivity, available nitrogen, phosphate, organic carbon, exchangeable calcium, magnesium, sodium and potassium were determined through the standard methodology as outlined by Jackson (1967). However exchangeable iron and aluminium was determined through the method described by Black (1965) and cation exchange capacity was performed by following the method of Scollenberger and Simon (1945). Mechanical separation of sand, silt and clay was achieved through removal of cementing agents by treating the soils with sodium acetate-acetic acid buffer (pH 5.0), 30% H_2O_2 (Robinson, 1922) and sodium citrate, bicarbonate and dithionite (Mehra and Jackson, 1960) followed by Robinson's pippette method to separate different settling particles. Chemical analyses of clays were carried out by fusing 0.1g of clay in Na_2CO_3 and HF-$HClO_4$ digestion as described by Jackson (1967). For the semi-quantitative determination of different clay minerals potassium and magnesium-clay systems were prepared separately with 0.1N KCl and 0.1N $MgCl_2$ by repeated washing of H+ saturated clays which were prepared from repeated washing with 0.1N HCl. All the prepared slides of K^+ and Mg^{2+} saturated clay were dried and analysed by X-ray diffraction (Phillips PW1710) techniques using Ni filtered CuKα radiation produced at 35KV and 15mA with a scanning speed of 1.5°2θ per minute and a time constant of 4.0. X-ray diffractograms of the clays with the following treatments were recorded: (1) Mg-clay air dried, (2) Mg-clay glycerolated, (3) K- clay air dried, (4) K-clay heated to 550°C for two hours.

The estimation of minerals was performed through the procedure of Gjems (1967).

Finally the statistical procedures namely correlation coefficient (r) with the significance level at p = 0.05 and 0.01 was evaluated by the help of SPSS software version 10.

Results and Discussion

Soil Morphology

Table 1 reveals the specification of soils alongwith the morphological characteristics. Abas and Rajrabundh soils belonged to the Alfisol, Barochowka, Kripanandapur, Bansberia, Poragachha and Ramganganagar soils belonged to Inceptisols while the rests were Entisols. All the soils were developed under Hyperthermic condition. All the soils were alluvium derived but the origin of these alluvial soils were different. Abas and Rajrabundh soils originated from old alluvium, Barochowka and Kripanandapur from Bindhya alluvium, Enayatpur, Kalyani and Bhagalpur from weathered alluvium while the Ramgangapur soil was derived from deltaic and coastal alluvium. The Entisols doesn't have any B horizon while the Alfisols and Inceptisols doesn't have C horizons in the immediate layers of the soil surface. These two horizons were within 30-35 cms depth from the surface. The colour of Abas soil was greyish while subsurface soil was yellowish brown while the Rajrabundh soil has dark reddish colour in both the surface. The predominance of Fe and Al may be responsible for such colour. Similar soil colour reports for same type of soil were reported by Hassenzhad *et al.,* (2008) and Gobin *et. al.* (2000). The slluvial soils of Barochowka and Kripanandapur had very dark grey colour while the Poragachha and Bhagalpur surface soil had brown to dark brown colour.The surface soils of Kalyani and Enayatpur had light grey colour while the subsurface soil had light brownish to yellowish grey colour. The surface soils of Bansberia and Bhagalpur had yellowish brown to brown colour. The coastal alluvial soil, Ramganganagar had pinkish grey to reddish grey surface soil. Salt encrustation in these soils rendered the lighter nature of colour of this soil. The soils were having five textural types namely, clayey, silty loam, loam, clay loam and silty clay loam type soils. Regarding the soil structure the surface soils of Abas and Rajrabundh soil had weak, poorly formed indistinct peds with the form of block-like peds bounded by other peds whose rounded subangular faces formed the cast for the ped, finer in size and contrastingly the massive form of structure with subangular faces were found in subsurface horizons of these soils. The soils of Barochowka and Kripanandapur had strong grade fine sized massive angular blocky peds. Enayatpur, Kalyani and Bhagalpur soil had moderate grade massive peds while the surface soil of Bansberia had destructed ped under puddled condition. The subsurface horizon of Bansberia soil and Poragachha soil had strong graded subangular blocky peds. The soil of

Table 1. *Specification and Morphological characteristics of the experimental soils under study*

	Properties									
Name of the soil/ Taxonomic Description	Nature of Land	Parent material	Soil Type	Horizon	Depth/cm	Moist Colour	Texture	Structure	Consistency	Boundary
Abas (Fine loamy kaolinitic hyperthermic family of Typic Paleudalf)	Upland	OA*	Red	A_3	0-10	10 YR 5.5/4	l	1 fsbk	(wso/wpo) mvfr dsh	cs
				B_1	10-35	7.5 YR 5/6	scl	2 msbk	(wso/wpo) mvfr dsh	cs
Rajrabundh (Fine loamy kaolinitic hyperthermic family of Typic Paleustalf)	Sloping upland	OA	Red & Laterite	A_3	0-14	2.5 YR 3/6	sl	1 fsbk	(wso/wpo) mvfr dsh	gs
				B_{11}	14-34	2.5 YR 3/6	scl	1 msbk	(wso/wpo) mvfr dsh	gs
Baro Chowka (Very fine illitic hyperthermic family of Vertic Haplaquept)	Lowland	BA	Alluvial	A_1	0-12	10 YR 3/1	c	3 fmabk	(wvs/wvp) mvfi dch	gs
				B_1	12-31	10 YR 3/1	c	3 fmabk	(wvs/wvp) mvfi dch	gs
Kripanandapur (Fine illitic hyperthermic family of Vertic Haplaquept)	Lowland	BA	Alluvial	A_p	0-15	10 YR 3/1	c	3 fmabk	(wvs/wvp) mvfi dch	cs
Enayatpur (Coarse loamy montmorillonitic hyperthermic family of Typic Udifluvent)	Upland	WA	Alluvial	A_1	0-14	10 YR 7/2	sl	2 medium massive	(wps/wps) mfr dsh	cs
				C_1	14-30	10 YR 5/4	sl	2 medium massive	(wso/wpo) mfr dsh	gs
Kalyani (Fine loamy montmorillonitic hyperthermic family of Typic Udifluvent)	Upland	WA	Alluvial	A_1	0-13	10 YR 7/3	sl	2 medium massive	(wss/wps) mfr dsh	cs
				C_1	13-30	10 YR 6/2	sl	2 medium massive	(wss/wps) mfr dsh	cs
Bansberia (Coarse loamy illitic hyperthermic family of Dystric Eutrochrept)	Upland	GA	Alluvial	A_p	0-18	10 YR 5/4	sl	2 Puddled	(wss/wps) mfi dsh	cs
				B_2	18-39	10 YR 5/4	cl	3 sbk	(wss/wps) mvfi dh	cs
Poragachha (Fine illitic hyperthermic family of Vertic Eutrochrept)	Lowland	GA	Alluvial	A_p	0-18	10 YR 4/3	c	3 sbk	(wvs/wvp) mvfi deh	cs
				B_2	18-31	10 YR 4/3	c	3 sbk	(wvs/wvp) mvfi deh	cs

Table 1. *Continued*

				Properties						
Name of the soils/ Taxonomic Description	Nature of Land	Parent material	Soil Type	Horizon	Depth/cm	Moist Colour	Texture	Structure	Consistency	Boundary
Bhagalpur (Coarse loamy illitic hyperthermic family of Typic Udifluvent)	Upland	WA	Alluvial	A_p	0-14	10 YR 4/3	sl	2 medium massive	(wss/wps) mfi dsh	cs
				C_1	14-31	10 YR 3/2	sl	2 medium massive	(wss/wps) mfi dh	gs
Ramgangapur (Fine loamy illitic hyperthermic family of Udic Eutrochrept)	Upland	DCA	Coastal alluvial	A_p	0-10	5 Y 7/2	l	2 moderate medium platy	(wss/wps) mfr dsh	cw
				B_1	10-31	5 Y 5/2	l	2 moderate coarse sbk	(wss/wps) mfr dsh	gs

*OA = Old Alluvium, BA = Bindhya Alluvium, WA = Weathered Alluvium, GA = Gangetic Alluvium, DCA = Deltaic and Coastal Alluvium

Ramgangapur had moderate grade peds with massive form in surface and coarse subangular peds in the subsurface horizon. Except Barochowka, Rajrabundh and Ramgangapur soils all the other soils had clear 2-5 cm distinct boundary with smooth nearly plane topography. Barochowka, Rajrabundh and subsurface soil of Bhagalpur and Ramgangapur soil had 5-15 cm gradual boundary with smooth nearly plane topography. The surface soil of Ramgangapur had clear 2-5 cm distinct boundary with wavy topography. These observations were in conformity with the studies of Mehedi *et. al.* (2000).

Soil Minerology:

The process of establishing the mineral content from the various kinds of analytical data was done in such a way that the critical analytical evidence was taken into account which is known as "chemical allocation" (Jackson, 1979). Soil-clays of Abas and Rajrabundh soils showed 44.2 and 43.90% SiO_2, respectively as depicted in Table 2. it could be predicted that these soil-clays were dominated by 1:1 lattice layer minerals along with fair amount of 2:1 lattice minerals. Similar observations from the SiO_2/Al_2O_3 molecular ratios of the clay fraction were achieved by Mehedi *et. al.* (2000). The CEC values of these soil-clays were 22.5 and 23.5 cmol(p^+)kg^{-1} clay for Abas and Rajrabundh soils respectively. These were well in the vicinity of kaolinite-illite range of CEC. The presence of illite or micaceous minerals found support from

Table 2. *Chemical composition, molar ratios, CEC and Semi-quantitative estimation of soil clays (surface soil) from XRD (expressed as % of clay)*

Chemical composition, molar ratios, CEC, Mineralogy	Name of the soil									
	Abas	Rajrabundh	Baro Chowka	Kripanandapur	Enayatpur	Kalyani	Bansberia	Poragachha	Bhagalpur	Ramgangapur
SiO_2 (%)	44.2	43.9	50.8	47.3	47.9	50.8	46.1	47.5	48.0	48.5
Al_2O_3 (%)	34.2	30.8	22.4	27.3	26.4	25.4	24.5	25.8	26.2	26.9
Fe_2O_3 (%)	13.2	11.1	9.80	7.5	7.88	7.90	10.3	8.01	9.25	8.88
R_2O_3 (%)	47.4	41.9	32.2	35.81	34.3	33.3	34.8	33.8	35.5	35.8
CaO (%)	0.25	0.42	0.75	0.76	1.20	1.25	0.54	0.93	0.61	0.59
MgO (%)	0.70	0.32	3.15	3.10	3.20	2.80	0.85	2.65	1.72	2.03
K_2O (%)	0.82	0.97	2.78	3.42	3.18	2.80	2.10	3.80	3.32	2.50
CEC (cmol(p^+)kg^{-1})	22.5	23.5	56.3	52.0	46.7	46.2	39.1	42.0	49.7	47.2
Molar Ratio (SiO2/ Al_2O_3)	2.19	2.42	3.86	2.95	3.08	3.40	3.20	3.13	3.11	3.07
Molar Ratio (SiO2/ R_2O_3)	1.76	1.97	3.01	2.94	2.59	2.83	2.52	2.61	2.54	2.53
Kaolinite (%)	50	60	17	15	10	9	13	8	18	10
Illite (%)	31	18	47	33	33	28	42	44	37	32
Illite/Mica Intensity ratio	2.9	3.01	2.62	2.85	3.12	2.2	2.67	3.82	1.31	2.54
Montmorillonite (%)	-	-	11	12	34	34	12	21	6	27
Chlorite (%)	-	-	-	7	4	5	9	8	5	4
Vermicullite (%)	-	-	-	-	7	6	-	-	15	4
Mixed layer minerals (%)	17	20	24	33	7	9	21	19	16	15
Quartz (%)	2	2	-	-	2	4	3	-	1	4
Feldspar (%)	-	-	-	-	4	6	-	-	2	4

the K_2O% of these soil-clays (0.082 and 0.79% respectively in Abas and Rajrabundh soils). Another two soil-clays of East Medinipur namely, Kripanandapur and Baro Chowka showed SiO_2/Al_2O_3 molar ratios of 2.95 and 3.86%, K_2O of 3.42 and 2.78% and CEC of 52.0 and 56.3 cmol(p^+)kg^{-1} clay, respectively. These were quite different from those of the other two soil-clays isolated from Abas and Rajrabundh soils. The CEC values were quite indicative of the presence of large quantity of 2:1 layer lattice minerals and the K_2O% of the clays indicated the possible presence of K-bearing 2:1secondary minerals, i.e., illite. Reasonably high content of MgO and Fe_2O_3 of these soil-clays also suggested the presence of 2:1 type of minerals with sufficient octahedral substitution. Very high content of Fe_2O_3 in Abas and Rajrabundh soils (13.15 and 11.12% respectively) might be due to the free coating of oxides as was evident from their soil colour.

In the Kalyani, Enyatpur, Poragachha and Bansberia soil-clays, the content of

SiO_2 (%) were observed to vary from 46.08 in Bansberia to 50.81 in Kalyani soil-clay. The molar ratio of SiO_2/Al_2O_3 for these soil-clays varied from 3.08 to 3.40. These were indicative of the possible dominance of 2:1 lattice minerals along with some 1:1 lattice minerals in these soil-clays. The CEC values ranged from 39.1 to 46.7 cmol$(p^+)kg^{-1}$ clay which also supported the dominance of 2:1 lattice mineral. Higher Silica: alumina ratio indicates higher adsorptive capacity (Elsheikh *et al.,* 2009) and hence increases CEC of the soil. Comparing the percentage content of K_2O soil-clays (2.1 to 3.8) it could be predicted that 2:1 mineral component was illite along with some other minerals like smectite and/or vermiculite. The SiO_2/R_2O_3 molar ratio and Fe_2O_3 percentage of the clays clearly indicated octahedral substitution of Fe for Al in the structure. But the high values of Fe_2O_3 did not find support from the respective CEC values of the soil-clays. Therefore, a major portion of Fe_2O_3 in these soil-clays might be accounted for by the coating material over the crystalline component or a part of the amorphous ferri-aluminosilicate closely associated with the crystalline component of the soil-clays.

The CEC, SiO_2/Al_2O_3 and SiO_2/R_2O_3 molar ratios of Bhagalpur soil-clays were 49.7 cmol$(p^+)kg^{-1}$, 3.11 and 2.54 respectively. It could be predicted from these values that the Bhagalpur soil-clay was dominated by 2:1 lattice minerals with a fair amount of 1:1 lattice minerals. As the CEC value [49.7 cmol$(p^+)kg^{-1}$ clay] appeared to be a little higher than that of illite mineral range, it could be suggested that a good amount of 2:1 compound was smectite and/or vermiculite in the clay mixture. 3.32% K_2O was well indicative of the presence of affair amount of micaceous mineral as well. However, 1.72% MgO content of the clays supported the presence of 2:1 lattice minerals with fair degree of octahedral substitution. High content of Fe_2O_3 (9.25%) of this soil-clay also suggested the possibility of Fe-oxide coating around the crystalline clays.

The chemical composition and CEC values of Ramgangapur soil-clay with their molar ratios for SiO_2/Al_2O_3 and SiO_2/R_2O_3 are presented in Table 2. The SiO_2/Al_2O_3 and SiO_2/R_2O_3 molar ratios of this soil-clay were 3.07 and 2.53 respectively and the CEC was 47.2 cmol$(p^+)kg^{-1}$ clay. These data coupled with its K_2O content (2.5%) indicated the presence of good amount of illite in the Ramgangapur soil-clay. The MgO and CaO content (2.03 and 0.59%) indicated structural substitution in the octahedral layer. Thus, the information regarding chemical composition and CEC were suggestive of possible dominance of 2:1 lattice clay minerals along with some 1:1 lattice minerals.

Results of X-Ray diffraction studies to ascertain the semi quantification of clay mineralogy of the experimental soils are presented in Table 2. The diffractograms of Abas, Rajrabundh, Kripanandapur and

Barochowka of Midnapur and Poragachha, Bansberia of Nadia were taken from 3° to 3°2θ in Mg saturated samples and 3° to 15°2θ in glycerol solvated Mg-Clay, K-clay and K-clay heated to 550°C while those of Enayatpur and Kalyani of Nadia and Bhagalpur of North Dinajpur and Ramgangapur of South 24 Parganas were taken upto 30°2θ values in all treatments except Mg-saturated glycerol solvated samples (3° to 15°2θ only). The soils of Abas and Rajrabundh of Midnapur belonged to Typic Paleudalf and Paleustalf sub group respectively. The clay mineralogical composition of two soils as reflected in the diffractograms (Figs. 1a and 1b) were almost similar only differing in intensity of some peaks. The predominant mineral in clays was kaolinite as identified from the strong peaks at 7.17Å and 3.57 Å of Mg-saturated samples. The 7.17 Å peaks of both the soil-clays were retained in the glycerol treated and K-saturated samples, the said peaks disappeared on heating the K-saturated clay samples to 550°C. The next mineral in order of dominance was illite/mica identified from the strong peaks at 10.04/9.99 Å, 4.98 Å and 3.33 Å. A small peak at 4.26 Å was indicative of a small amount of quartz in the clay fraction. The possible presence of the mixed layer minerals were also evidenced in the clay fraction of both Abas and Rajrabundh soils as observed from the diffraction effects in the region of 19 Å, 24 Å and 10 to 14 Å of the diffractograms. As no distinct peaks were visible in the said regions, the minerals were expected to be irregularly inter-stratified minerals. The intensity of 10 Å peak increased on K-saturation and heating to 550°C which was indicative of presence of some 14 Å component (montmorillonite and /or vermiculite) other than chlorite in the soil-clays (Sahu *et. al.*, 1981). The extreme weathering under hot humid climatic conditions of these soils resulted in the dominance of kaolinitic clay minerals.

The Enayatpur (Typic Ustifluvent) and Kalyani (Typic Udifluvent) soil-clays of Nadia district were montmorillonite dominated as identified by a very strong peak at 18 Å in the Mg-saturated glycerolated samples (Figs.1e and 1f). These soils also contained illite/mica as reflected by 9.99 Å and 5.00 Å peak in the K-saturated and Mg-saturated samples, as the second dominant clay mineral in the soil-clays which were retained in the glycerolated and K-saturated samples and K-clays heated to 550°C. The same diffractograms (Figs. 1e and 1f) of K-clays subjected to 550°C heating showed that the 7.15 Å peaks of Mg-saturated and glycerolated samples disappeared confirming the presence of kaolinite. The presence of strong peaks at 14.2 Å along with its higher order at 4.73 Å in the two diffractograms of K-saturated Enayatpur and Kalyani soil-clays which did not change its position and/or intensity on glycerol solavation of Mg-saturated clays was possibly indicative of the presence of vermicullite and chlorite in clay fraction. Moreover, heating of K-clays to 550°C led to major reduction of intensity of 14.2 Å peak and subsequently increase in the intensity of 10 Å peak confirmed that most of the 14 Å minerals in these soil-clays were vermiculite and obviously, the rest was chlorite. This was further evidenced by the persistence of a small peak at 24 to 25 Å and 12 to 13 Å which did not change their position on glycerol salvation of Mg-clays suggested the possible presence of inter-stratification of 10 Å and 14 Å minerals. However, the first order (001) peak to be expected at 24 Å was not shifted to and merged with the 10 Å peak on heating the K-clay samples to 550°C. The 14 Å component of inter-stratification was of non-swelling type but had characteristics of collapsing on heating. So it might be chloritized vermiculite (Sahu *et. al.,*1981). The regularly inter-startified mineral might, therefore, be considered a mica-vermicullite one. Very weak peaks at 3.25 Å and 4.27 Å in the diffractograms of Enyatpur and Kalyani soil-clays suggested presence of feldspar and quartz.

The soil clays of Kripannadapur, Barochowka (Vertic Haplaquepts) of Midnapur, Poragachha (Vertic Eutrochrept) and Bansberia (Dystric Eutrochrept) of Nadia, Bhagalpur (Typic Udifluvent) of North Dinajpur and Ramgangapur (Udic Eutrochrept) of Noth 24 Parganas were mostly dominated by illite/mica as evident from very strong peaks at 10 Å of all the diffractograms (Figs. 1c to 1d, 1g to 1j). All these soil-clays showed a distinct peak at 17.8 Å peak of the Mg-saturated and glycerol solvated samples confirming the presence of montmorillonite in the clay fractions. Strong reflections at 7.1 Å and 3.6 Å, with different intensity which disappeared on heating the K-saturated samples to 550°C confirmed the presence of variable amount of kaolonite in these clays. The presence of peaks of medium to weak intensity at 14.2 Å along with its respective higher order peaks at 4.7 Å of the diffractograms might be due to the possible presence of chlorite and /or vermiculite in Barochowka, Poragachha, Bansberia, Bhagalpur and Ramgangapur soil clays. Out of these, in Bhagalpur and Ramgangapur soil clays these 14.2 Å reflections remained but with a reduced intensity on thermal treatment (550°C) of the K-saturated clays (Figs 1i and 1j) indicating the possible presence of vermiculite. Thus of the 14.2 Å components, Barochowka, Poragachha and Bnasberia soil-clays contained chlorite but Bhagalpur and Ramgangapur soil clays contained both chlorite and vermiculite. Mixed layer minerals were present fairly in high amount in these soil clays as was evident from the presence of a number of small peaks in the region of 19 Å to 24 Å and 10 Å to 14 Å. The peaks were not so distinct, but diffraction effect was clear enough to indicate that these mixed layer minerals were the result of interstratification of 14 Å and 10 Å components.

Furthermore, the presence of clay sized feldspar mineral in Bhagalpur and Ramgangapur soil-clays was indicated by very weak peaks at 3.25 Å and 3.15 Å. Small but relatively strong peaks at 4.27 Å of the diffractograms of Bhagalpur, Poragachha and Ramgangapur soil-clays suggested the presence of clay sized primary minerals quartz in these soils.

The semi-quantitative clay mineralogical composition of all the soil clays was calculated from the measurement of peak area above the base line and presented in Table 2. Kaolinite was the dominant clay mineral in Abas and Rajrabundh soil-clays (50-60% respectively). These soils were having red colour for which the predominance of kaolinite was observed. Such predominance of kaolinite in aged quarternary soils of Italy was reported by Constatini and Damiani (2004). The amount of mica/illite presence in Abas and Rajrabundh soil-clyas were 31 and 18%. The presence of 17 and 20% mixed layer minerals were observed in the soil-clays isolated from these soil-clays respectively. Very small amount of quartz and no feldsapar was observed in these soil clays. Montmorillonite and mica/illite were found to be the dominant clay minerals in Enayatpur and Kalyani soil-clays. As calculated from the diffractograms of these soil clays, it has been observed that about 34% montmorillonite and 33% mica/illite were present in Enayatpur soil-clay. Although the soil clays isolated from Kalyani soil had the same quantity of expanding clay but donot differ in mica/ content (28% only). Among other minerals Enayatpur soil-clay contained kaolinite (10%), vermiculite (7%), mixed layer minerals (7%), feldspar (4%) and quartz (2%). Kalyani soil-clay contained 9% each of kaolinite and mixed layer minerals, 6% each of vermiculite and feldspar, 5% chlorite and 4% quartz. The rest of the soil-clays under investigation viz., Kripanandapur, Barochowka, Poragachha, Bansberia, Bhagalpur and Ramganagapur were dominant in illite/mica containing 47, 33, 42, 44, 37 and 32% respectively. They also contained appreciable amount of inter-stratified minerals ranging from 15 to 33% and in particular 24, 33, 21, 19, 16 and 15% respectively in Kripanandapur, Barochowka, Poragachha, Bansberia, Bhagalpur and Ramganagapur soil-clays. The amount of kaolinite ranged from 8% in Bansberia to 18% in Bhagalpur soil-clay whereas montmorillonite content in these soil-clays ranged from only 6% in Bhagalpur to 27% in Ramgangapur soil-clay. Both Poragachha and Barochowka soil-clays contained 12% montmorillonite. This mineral is responsible for higher exchange of K in these soils. Similar reports were found from the observation of Saha and Inoue (1998).

The X-ray intensity ratios of peak heights of the 001 and 002 reflections of clay micas are presented in table 2. It appeared from the data that the intensity ratio was higher than unity indicating thereby apparently their muscovitic character. However, dioctahedral micas retain their K more strongly than their trioctahedral counterpart. In view of their present K release it is argued that this 001/002 ratio greater than unity indicated the presence of both muscovite and biotite than the former alone. If muscovite mica alone were present, this ratio should 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 10 Å reflection while contribution of biotite to the 5 Å reflection would be negligible, thus giving a higher value to this intensity ratio (Pal and Durge, 1993). The intensity ratio of the peak heights of Bhagalpur soil-clay was very close to unity (1.31) indicating the presence of biotite mica in this soil-clay. The intensity ratios of Bnasberia, Enyatpur and Rajrabundh soil clays were very high (3.82, 3.12 and 3.01 respectively) while the Abas, Barochowka, Poragachha, Kripanandapur, Ramgangapur and Kalyani soil-clays showed medium values (2.9,2.85,2.67,2.62,2.54 and 2.20 respectively). Thus, it may be concluded that all the soil-clays except that of Bhagalpur contained both muscovite and biotite micas.

The results obtained from the X-ray studies were in good agreement with the conclusions arrived at from the data of chemical analysis, molar ratios and CEC of soil clays. Thus, from the semi-quantitative estimation of clay minerals from the X-ray diffractograms coupled with the chemical composition, molar ratios and CEC of soil-clays it was inferred that the Abas and Rajrabundh soil-clays were dominantly kaolinitic with fair amount of illite; the Enyatpur and Kalyani soil-clays contained high amount of both montmorillonite and illite. Other soil-clays were dominantly illitic.

Correlation between mineralogy and chemical properties of soil clay:

Regarding correlation between the mineralogical properties and the chemical properties of the soil clay fraction, significant positive correlations were observed for kaolinite with Al_2O_3 (r = 0.800**), Fe_2O_3 (r =0.806**) and R_2O_3 (r = 0.873**); montmorillonite with feldspar (r = 0.802**), SiO_2 (r =0.646*), CaO (r =0.859**) and MgO (r= 0.670*); feldspar with quartz (r = 0.670*) and CaO (r = 0.640*); for SiO_2 with CaO (r = 0.701*), MgO (r = 0.801**), K_2O (r = 0.663*) and CEC (r = 0.860**); for Al_2O_3 with Fe_2O_3 (r = 0.644*) and R_2O_3 (r = 0.964**); Fe_2O_3 with R_2O_3 (r = 0.819**); CaO with MgO (r = 0.803**) and K_2O (r = 0.697*); MgO with K2O (r = 0.820**) and CEC (r = 0.835**); MgO with CEC (r = 0.835**) whereas significant negative correlations were observed for kaolinite with montmorillonite (r = -0.750*), chlorite (r = -0.692*), SiO2 (r =-0.760*), CaO (r = -0.693*), MgO (r = -0.746*), K_2O (r = -0.854**) and CEC (r = -0.833**); illite with Al_2O_3 (r = - 0.659*); montmorillonite with Fe_2O_3 (r = -0.740*) and R_2O_3 (r = -0.636*); mixed layer minerals with feldspar (r = -0.766*); SiO_2 with Al_2O_3 (r = -0.793*), Fe_2O_3 (r =-0.650*) andR_2O_3 (r = -0.818**); Al_2O_3 with K_2O (r = -0.700**) and CEC (r = -0.835**); Fe_2O_3 with CaO (r = -0.824**), MgO (r = -0.811**), K_2O (r= -0.889**) and CEC (r = -0.760*); R_2O_3 with CaO (r = -0.724*), MgO (r = -0.732*), K_2O (r = -0.821**) and CEC (r = -0.867**).

Physico-chemical Properties of soils:

Different physical, chemical and physico-chemical properties of soils are enumerated in Table 3. It is understood that the soils under study were both fine and course textured. The soils of surface layers contained higher amounts of clay than the sub-surface layers and so is the case of silt, except for Poragachha and Ramgangapur soils. The eluviation of finer particles like clays and silt from upper to lower horizon is the cause of higher percentage of these fractions in sub-surface layers of the soils. Expectedly the case is reverse in case of sand fractions, the percentage of which is higher in surface layers. The surface and subsurface soils of Baro chowka, Kripanandapur and Poragachha contained very high amounts of clay while same is least in Kalyani and Bhagalpur soils. The pH values showed wide ranging contrast between Bhagalpur soil (acidic having pH 4.5 in water) in one hand while Enayatpur and Ramgangapur soils on the other hand possessing alkaline soil pH (pH 11.9 and 9.5, respectively in water). All other soils were in slightly acidic to neutral range. Two soils of Midnapur West Red and Lateritic zone viz., Abas and Rajrabundh showed pH of 5.6 and 5.5 respectively. This was probably due to intense weathering and leaching of bases which was evident by the low content of exchangeable bases in these soils. In all the soils the sub-surface horizon showed higher pH than its surface counterpart which was because of leaching of bases to the deeper layers. This was similar to the findings of Onweremadu, 2007. The low pH of tropical soils due to leaching of bases was also reported by Seal *et.al.,* (2006). The data on electrical conductivity (EC) of soil solutions reveal that Enayatpur and Ramgangapur soils were having high salinity levels and the previous soil poses unsafe salt content (>4dSm^{-1}). Thus, from pH and EC data it appears that the two soils, viz., Enayatpur and Ramgangapur soils were problem soils (saline alkali). However, in other soils under investigation EC of soil solution was not a problem which ranged from a very low value of 0.9 dSm^{-1} in Abas soil to 3.1 dSm^{-1} in Kalyani soil. The percent oxidizable organic carbon values ranged from a minimum of 0.34 in Rajrabundh to a very high value of 1.89 in Kripanandapur soil. Soils of Bhagalpur, Barochowka and Poragachha also showed a very high value with 1.36, 1.14 and 0.73% organic carbon respectively. The same trend of distribution of percent total nitrogen was also evident and so was the case of C : N ratio. The

Table 3. *Physico-chemical properties of the soils*

Name of the soil	Horizon	Depth/ cm	Particle Size Distribution			pH		EC /dSm^{-1}	Organic carbon/ %	Org. matter/ %	Total N
			Sand %	Silt/%	Clay/%	H_2O	1(N)KCl				
Abas	A_3	0-10	58.5	23.5	18.0	5.6	5.0	0.9	0.48	0.85	0.04
	B_1	10-35	42.9	34.3	22.8	5.8	4.5	1.0	0.37	0.65	0.03
Rajrabundh	A_3	0-14	53.4	21.1	25.5	5.5	4.5	1.0	0.34	0.56	0.03
	B_{11}	14-34	47.0	22.6	30.4	5.9	5.1	1.0	0.27	0.48	0.02
Baro Chowka	A_1	0-12	3.6	31.7	64.7	6.9	5.0	2.9	1.14	2.01	0.10
	B_1	12-31	2.9	25.6	71.5	7.2	5.2	2.8	0.75	1.32	0.07
Kripanandapur	A_p	0-15	8.7	43.0	48.3	7.2	6.5	1.2	1.89	3.33	0.18
Enayatpur	A_1	0-14	52.5	31.3	16.2	11.9	11.2	4.2	0.54	0.93	0.05
	C_1	14-30	50.4	32.1	17.5	11.5	11.0	4.1	0.42	0.72	0.04
Kalyani	A_1	0-13	50.6	31.3	18.1	6.2	5.5	3.1	0.51	0.88	0.04
	C_1	13-30	49.7	30.9	19.4	6.5	5.6	3.1	0.40	0.52	0.03
Bansberia	A_p	0-18	62.6	22.1	15.3	7.5	6.1	1.4	0.48	0.84	0.04
	B_2	18-39	46.5	25.3	28.4	7.6	6.1	1.3	0.32	0.56	0.03
Poragachha	A_p	0-18	19.6	32.1	48.3	7.7	6.1	1.2	0.73	1.28	0.06
	B_2	18-31	16.3	23.7	60.0	7.9	6.3	1.2	0.49	0.86	0.04

Name of the soils	C : N Ratio	CEC/c mol (p$^+$) kg^{-1}	Available K mg kg^{-1} soil	Exchangeable cations /c mol (p$^+$) kg^{-1} soil				Available P_2O_5 (%)	Exch. Fe (%)	Exch. Al (%)	Base saturation
				Ca^{2+}	Mg^{2+}	K^+	Na^+				
Bhagalpur	A_p	0-14	49.9	33.6	15.5	4.5	4.2	1.8	1.36	2.32	0.11
	C_1	14-31	48.5	33.6	17.8	4.8	4.4	2.5	1.11	1.89	0.09
Ramgangapur	A_p	0-10	43.2	40.0	16.8	9.5	8.1	3.5	0.36	0.61	0.03
	B_1	10-31	43.9	37.3	18.8	9.7	8.5	3.6	0.18	0.31	0.02
Abas	12.63	9.5	78.2	1.91	0.64	0.16	0.35	0.0061	0.0173	0.0086	32.23
	11.93	15.0	88.3	1.75	0.45	0.21	0.44	0.0046	0.0168	0.0083	19.00
Rajrabundh	12.59	8.4	128.5	1.62	0.59	0.29	0.30	0.0068	0.0212	0.0056	33.31
	11.25	11.7	139.5	1.56	0.59	0.31	0.42	0.0052	0.0200	0.0056	24.61
Baro Chowka	11.06	36.8	763.5	11.72	7.15	1.62	1.56	0.0037	0.0067	Trace	59.90
	11.03	40.0	774.0	11.22	7.48	1.74	2.62	0.0042	0.0065	Trace	57.65

Table 3. *Continued..*

Name of the soils	C : N Ratio	CEC /c mol (p$^+$) kg^{-1}	Available K mg kg^{-1} soil	Exchangeable cations /c mol (p$^+$) kg^{-1} soil				Available P_2O_5 (%)	Exch. Fe (%)	Exch. Al (%)	Base saturation
				Ca^{2+}	Mg^{2+}	K$^+$	Na$^+$				
	11.03	40.0	774.0	11.22	7.48	1.74	2.62	0.0042	0.0065	Trace	57.65
Kripanandapur	10.68	32.1	605.3	12.64	9.57	1.44	0.55	0.0045	0.0073	Trace	75.39
Enayatpur	12.00	11.0	167.7	2.35	1.27	0.51	2.65	0.0008	0.0072	0.0029	61.65
	11.67	12.3	233.0	2.20	1.30	0.78	3.00	0.0007	0.0067	0.0033	59.16
Kalyani	12.75	10.4	166.3	2.20	1.31	0.66	2.19	0.0012	0.0068	0.0033	64.49
	12.00	9.50	195.3	2.21	1.24	0.50	2.19	0.0012	0.0066	0.0031	63.31
Bansberia	11.70	9.90	125.7	5.83	2.92	0.25	2.15	0.0132	0.0098	Trace	56.02
	11.03	17.1	159.8	4.85	1.32	0.33	2.41	0.0062	0.0095	Trace	52.09

C : N ratios were relatively higher for the surface horizon for all the soils indicating greater accumulation of undecomposed organic materials in the surface layers than in the respective sub-surface counterparts.

The cation exchange capacity values of soils presented in Table 1 showed that they ranged from 8.4 in Rajrabundh soil to 36.8 cmol(p$^+$) kg^{-1} in Barochowka soil. The low values of CEC in Abas [9.5 cmol(p$^+$)kg^{-1}] and Rajrabandh soils were due to lower clay content in addition to the dominance of kaolinite type minerals. The higher CEC values in the Kripanandapur and Poragachha soil may be attributed to the higher clay content in these soils. Among the exchangeable cations, Ca^{2+} occupied the major position. It was relatively high in Kripanandapur, Barochowka and Poragachha soils (12.64, 11.72 and 10.08 cmol(Ca$^+$) kg^{-1} respectively. Between the divalents, Mg^{2+} content was lower than the Ca^{2+}, and between the monovalents, Na$^+$ was always forerunner. All the soils, except those of Abas and Rajrabundh, had more than 50% base saturation. Bhagalpur and Kripanandapur soils showed 75% base saturation while Abas and Rajrabundh soils had only 32 to 33% base saturation. Low base saturation values of Abas and Rajrabundh soils were probably due to intense weathering and leaching of bases and concomitant accumulation of Fe and Al (Caracalla, 2006). Amount of available phosphate was very low in all the soils with somewhat higher values in Bansberia (0.0132%) and Poragachha (0.0132%) soils.

Since the clay content of the soil plays a vital role in transformation of nutrients, certain important parameters of the soil clays were also taken into consideration in the present study. The CEC values of the clay portion of the experimental soils varied from 22.5 cmol(p^+) kg^{-1} in Abas soil to 52.0 cmol(p^+) kg^{-1} in Kripanandapur soil. The molar ratios of SiO_2/R_2O_3 of these soils ranged from 1.76 to 3.01, where the lower ratio indicated the dominance of 1:1 type clay minerals while the higher values of the ratio indicates the dominance of 2:1 type clay minerals in comparison to 1:1 type minerals. The relationship of SiO_2/R_2O_3 and type of minerals was also reported by Tan and Troth, (1982).

Correlation between mineralogical and physico-chemical properties of soils

Simple correlation between the mineralogical properties and the physico-chemical properties of the soil revealed (Table 4) the significant positive correlations were observed for kaolinite with exchangeable Fe(r=0.976**) and Al (r=0.688*), Illite for calcium (r=0.661; montmorillonite with pH (r = 0.709*), EC (r =0.795**), K (r = 0.630*); for mixed layer minerals with clay (r=0.670*), org C(r = 0.657*), total N (r=0.690*), CEC (r =0.652*), available K (r =0.638*), calcium (r = 0.767*) and magnesium (r = 0.759*); for quartz with sand (r=0.727*); feldspar with EC (r = 0.781**) while the significant negative correlations were observed for kaolinte with K (r =-0.772*), illite with exchangeable Fe (r=-0.660*) and exchangeable Al (r =-0.658*); montmorillonite with exchangeable Fe (r= -0.693*); quartz with org C (r = -0.710*), total N (r= -0.704*), CEC (r =0.795**), calcium (r = -0.774*) and magnesium (r= -0.700*); feldspar with available phosphorus (r= -0.714*). Besides, significant positive and negative correlations were observed among the soil physico-chemical properties as reflected in Table 4. The results of these correlations indicate the chemical nature of clay minerals present in the soils to positive and negative responses towards the soil physico-chemical properties. Similar Correlation was observed by the findings of Igwe *et al.,* (1999). Interrelationship of the clay mineral fraction and soil organic carbon was reported by Ratnayeke *et al.,* (2011).

Conclusions

From the study it may be concluded that the experimental soils were mostly derived from the recent and old alluvium. Regarding the morphology of the soil, there is a wide variation in horizon, colour, texture, structure and boundary conditions among the soils. The clay component of these soils directly corroborates to the mineralogical characteristics of these soils. The origin (parent material) and clay mineralogy contributes to the contrasting physicochemical properties of these soils. Such contrasting characters are also statistically correlated with the mineralogical characteristics.

Table 4. *Correlation Coefficients (r) between clay mineralogy and different soil characteristics (n = 10)*

	Sand	Silt	Clay	pH	EC	Org C	Tot.N	CEC	Av.K	Ca	Mg	Na	K	Av.P	Ex.Fe	Ex.Al
Kao	0.324	-0.617	-0.136	-0.499	-0.545	-0.260	-.243	-.324	-.301	-.376	-.392	-.336	-.772*	.164	.976**	.688*
Ill	-0.483	0.192	0.493	0.146	0.066	0.332	.293	.607	.472	.661*	.551	.435	.487	.317	-.660*	-.658*
Mont	-0.017	0.426	-0.144	0.709*	0.795**	-0.221	-.207	-.042	.028	-.110	-.006	.021	.630*	-.430	-.693*	-.309
Chlor	-0.038	0.304	-0.077	0.219	-0.088	0.224	.217	.103	-.059	.319	.337	-.007	.526	.393	-.591	-.622
Vermi	0.316	0.247	-0.487	-0.062	0.395	0.157	.085	-.382	-.418	-.385	-.456	-.142	.610	-.555	-.283	.237
Mix	-0.628	0.226	0.655*	-0.325	-0.610	0.657*	.690*	.652*	.638*	.767	.759*	.569	-.537	.409	.066	-.428
Qrtz	0.727*	-0.205	-0.775	0.177	0.386	-0.710*	-.704*	-.795**	-.586	-.774*	-.700*	-.664*	.151	-.221	.128	.403
Felds	0.324	0.303	-0.506	0.360	0.781**	-0.299	-.312	-.443	-.300	-.533	-.454	-.203	.505	-.714*	-.384	.181
Sand	**1.000**	-0.601	-0.946**	-0.039	0.013	-0.671*	-.687*	-.972**	-.942**	-.894**	-.914**	-.895**	.088	.059	.479	.627
Silt	-0.601	**1.000**	0.311	0.297	0.357	0.611	.622	.463	.521	.435	.533	.530	.251	-.530	-.702*	-.350
Clay	-0.946**	0.311	**1.000**	-0.064	-0.155	0.544	.560	.968**	.912**	.887**	.873**	.848**	-.210	.145	-.285	-.606
pH	-0.039	0.297	-0.064	**1.000**	0.683*	-0.240	-.182	.014	.124	-.024	.080	-.042	.374	-.224	-.439	-.293
EC	0.013	0.357	-0.155	0.683*	**1.000**	-.0208	-.202	-.107	.106	-.237	-.191	.094	.532	-.715*	-.526	-.095
Org C	-0.671*	0.611	0.544	-0.240	-0.208	**1.000**	.994**	.661*	.589	.730*	.691*	.779*	-.089	-.126	-.370	-.434
Tot.N	-0.687*	0.622	0.560	-0.182	-0.202	.994**	**1.000**	.674*	.622	.743*	.722*	.791*	-.152	-.126	-.348	-.448
CEC	-0.972**	0.463	0.968**	0.014	-0.107	.661*	.674*	**1.000**	.918**	.952**	.941**	.883**	-.075	.115	-.466	-.692*
Av.K	-0.942**	0.521	0.912**	0.124	0.106	.589	.622	.918**	**1.000**	.852**	.870**	.912**	-.182	-.091	-.428	-.641*
Ca	-0.894**	0.435	0.887**	-0.024	-0.237	.730*	.743*	.952**	.852**	**1.000**	.974**	.835**	-.057	.292	-.477	-.795*
Mg	-0.914**	0.533	0.873**	0.080	-0.191	.691*	.722*	.941**	.870**	.974**	**1.000**	.814**	-.110	.226	-.489	-.776*
Na	-0.895**	0.530	0.848**	-0.042	0.094	.779**	.791*	.883**	.912**	.835**	.814**	**1.000**	-.107	-.198	-.465	-.629*
K	0.088	0.251	-0.210	0.374	0.532	-.089	-.152	-.075	-.182	-.057	-.110	-.107	**1.000**	-.127	-.729*	-.334
Av.P	0.059	-0.530	0.145	-0.224	-0.715*	-.126	-.126	.115	-.091	.292	.226	-.198	-.127	**1.000**	.231	-.312
Ex.Fe	0.479	-0.702*	-0.285	-0.439	-0.526	-.370	-.348	-.466	-.428	-.477	-.489	-.465	-.729	.231	**1.000**	.678*
Ex.Al	0.627	-0.350	-0.606	-0.293	-0.095	-.434	-.448	-.692*	-.641*	-.795	-.776	-.629	-.334	-.312	.678*	**1.000**

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

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An *ab initio* Approach to Construct Clay Mineral Structures : I. Kaolinite

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Abstract : *Ever since Linus Pauling proposed the structure of the clay minerals, interest in the subject magnified consistently with time. Essentially, experimental information guided the visualization, validation and refinement. However, in spite of numerous, rigorous, multi-approach, complimentary and supplementary experimentation, unknown areas and uncertainties remain. Certain parameters cannot be derived till today by any experimental means. Thus, an alternate theoretical approach based on an ab initio method, which does not require any experimental data, has been conceived of. Here, a quantum mechanical technique based on density functional theory (DFT) was utilized to develop a concept primarily based on a 1:1 type clay mineral, viz., kaolinite. Crystal structure was built up theoretically and crystal properties were derived there from. Literature information was used for verification. Positive outcome encourages the extension of this concept to other clay minerals.*

Quantum mechanics is now rapidly gaining ground in the field of mineralogy, silicates and ceramics, primarily for understanding phase transitions, structural disorders and surface reactivity (Sainz-Diaz *et al.*, 2005). In this work, we attempted to introduce a new approach to the study of clay minerals, involving *ab initio* derivation of the detailed crystal structure and ground state properties of layer lattice silicates, based on full-potential linearized augmented plane-wave method. The main objectives are : (i) To develop a method for deriving the crystal structure of clay minerals based initially on a 1:1 type mineral, viz., kaolinite. In this step, an optimized crystal structure is built up theoretically and crystal properties are derived by subsequent theoretical methods. (ii) To verify the results from available literature. (iii) To obtain parameters not yet determined by any experimental method. (iv) To open an avenue to extend this concept to other clay minerals.

Theory

An efficient and accurate scheme for solving the many-electron problem of a crystal (with nuclei at fixed positions) is the local spin density approximation

(LSDA) within density functional theory or DFT (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Therein, the key quantities are the spin densities $\rho_\sigma(r)$ in terms of which the total energy is

$$E_{tot}(\rho\uparrow, \rho\downarrow) = T_s(\rho\uparrow, \rho\downarrow) + E_{ee}(\rho\uparrow, \rho\downarrow) + E_{Ne}(\rho\uparrow, \rho\downarrow) + E_{xc}(\rho\uparrow, \rho\downarrow) + E_{NN}$$

with E_{NN} the repulsive Coulomb energy of the fixed nuclei and the electronic contributions, labeled conventionally as, respectively, the kinetic energy (of the non-interacting particles), the electron-electron repulsion, nuclear-electron attraction and exchange-correlation energies. Two approximations comprise the LSDA, (i) the assumption that E_{xc} can be written in terms of a local exchange-correlation energy density μ_{xc} times the total (spin-up plus spin-down) electron density as

$$E_{xc} = \int \mu_{xc}(\rho\uparrow, \rho\downarrow) \text{ x } [\rho\uparrow, \rho\downarrow] \, dr$$

and (ii) the particular form chosen for that μ_{xc}. Several forms exist in literature but the most accurate fit to the Monte-Carlo simulations of Ceperly and Alder are by Perdew and Wang (1992). The most effective way to minimize E_{tot} by means of the variational principle is to introduce orbitals χ_{ik}^{σ} constrained to construct the spin densities as $\rho_\sigma(r) = \Sigma\, \rho^{\sigma}_{ik} \left|\chi_{ik}^{\sigma}(r)\right|^2$

Here, ρ^{σ}_{ik} are occupation numbers such that $0 \leq \rho^{\sigma}_{ik} \leq 1/\omega_k$ where ω_k is the symmetry-required weight of point κ. Then variation of E_{tot} gives the Kohn-Sham equations (in Ry atomic units),

$$[-\Delta^2 + V_{Ne} + V_{ee} + V^{\sigma}_{xc}]\, \chi^{\sigma}_{\iota\kappa}(r) = \varepsilon^{\sigma}_{\iota\kappa}\, \chi^{\sigma}_{\iota\kappa}(r)$$

which must be solved and thus constitute the primary computational task. Kohn-Sham equations can be solved self-consistently in an iterative process, since finding the Kohn-Sham orbitals requires the knowledge of the potentials which themselves depend on the (spin-) density and thus on the orbitals again.

Methodology

A parallel computing system with 8-node cluster was installed. Each node was a Pentium IV of 3 GHz with 2GB RAM and gigabit LAN. The OS was Red Hat 9 and Beowulf architecture was followed for clustering. The clustering software used was Oscar 4.1. System partitioning and memory allocations were done with special regard to intensive memory usage. Several supporting softwares are needed for running the *ab initio* program. These include, fortran compilers and mathematical libraries. Intel Cluster MKL was installed for parallel data processing. *Ab initio* derivations were done using *Wien 2k* (Version 09) and structure visualization with *Xcrysden* (Varadachari and Bhowmick, 2009).

Wien2k performs electronic structure calculations of solids using DFT. It is based on the full-potential linearized augmented plane-wave (FP-LAPW) method (Blaha *et al.*, 2001). The FP-LAPW method is a procedure for solving the Kohn-Sham equations for the ground state density, total energy and eigenvalues (energy bands) of a many-electron system by introducing a basis set which is especially adapted to the problem (Martin, 2004). Kohn-Sham equations are solved self-consistently in an iterative process under the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional for the exchange-correlation energy subject to periodic lattice boundary condition. A dual basis set is used, consisting of a centrosymmetric set inside "muffin-tin" spheres surrounding individual atoms and a plane-wave set in the interstitial space between the "muffin-tin" spheres. Inside the "muffin-tin" radius, a linear combination of radial functions multiplied by spherical harmonics $Y_{im}(r)$ is used :

$$\phi_{k_n} = \sum_{lm}[A_{lm} u_l(r, E_l) + B_{lm} \dot{u}_l(r, E_l)]Y_{lm}(\hat{r})$$

where $\mu_l(r, E_l)$ is the regular solution of the radial Schroedinger equation energy E_l and the spherical part of the potential inside sphere *t*. The coefficients A_{lm} and B_{lm} are functions of $k_n = k + K_n$, the sum of the wave vector k inside the first Brillouin zone and the reciprocal lattice vector K_n. The basis function ϕ_{k_n} and its gradient are required to match the plane waves of the interstitial.

In the interstitial region, a plane wave expansion is used.

$$\Phi k_n = \frac{1}{\sqrt{\omega}} e^{ik_n r}$$

The solutions of the Kohn-Sham equations are expanded in this combined basis set of LAPWs and the coefficients are determined by the Rayleigh-Ritz variational principle. In its general form, the LAPW method expands the potential in the following form

$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r}) & \text{inside sphere} \\ \sum_{K} V_K e^{iKr} & \text{outside sphere} \end{cases}$$

A modified tetrahedron integration scheme is used to generate the k-mesh in the irreducible wedge of the Brillouin zone on a special point grid with total k-points (Blochl *et al.*, 1994).

Basic inputs for derivation

Derivation of optimized crystal structure was the critical step. Optimization of k-points followed by RK_{max} optimization was done before calculation of crystallographic parameters. The parameters for the required input were :

(i) Rmt : Atomic sphere radius (in Wien2k it is called muffin-tin radius). The spheres were chosen as large as possible to save computer time. The Rmt values used in this study were Rmt (Al) = 1.75 Å, Rmt (O) = 1.15 Å, Rmt (Si) = 1.50 Å, Rmt (H) =0.62 Å (in kaolinite Rmt values of both inner and interlayer hydrogens are the same).

(ii) RKmax (Rmt *kmax) : determines the number of basis functions (size of the matrices) where kmax is the plane wave cut-off, Rmt is the smallest of all atomic sphere radii and the optimized RKmax is 2.73.

(iii) KGEN : Program KGEN generates the k-mesh in the irreducible wedge of the Brillouin zone (IBZ). Here the optimized k-points = 8 was used and inversion was added.

(iv) Mixing factor = 0.10 (BROYD scheme).

(v) GGA (General Gradient Approximation) =13 [Perdew-Burke-Ernzerhof functional].

(vi) Cut-off energy : The energy cut-off between core and semicore was -9.0 Ry.

(vii) Emin : It is the minimum energy for which the output eigenvectors and eigenenergies will be printed is -9.0 Ry.

(viii) Emax: This is the maximum energy which in this case is 2.5 Ry.

Optimization of the cell structure

The internal atomic coordinates and the cell shape of kaolinite were systematically optimized by the following two consecutive steps, (i) force minimization and (ii) optimization of lattice constants.

The program "mini" in *Wien2k* (Blaha *et al.,* 2001) was used to determine the equilibrium positions of all individual atoms obeying the symmetry constraints of a P1 space group. The structure of kaolinite (before force minimization) (Bish, 1993) shows that the forces of this structure were high (1131.12 mRy/Bohr). Using "mini" program as stated above, force minimization was carried out and we got more relaxed structure with forces 37.62 mRy/Bohr (structure after force minimization).

For optimization of lattice constants (a,b,c), the following successive steps were executed using optimized RKmax and k-points (Cottenier, 2004) : (i) Optimization of b/a keeping c/a and volume constant, (ii) optimization of c/a keeping b/a and volume constant, and (iii) optimization of volume.

Theoretical XRD of the minerals were derived using Shape-software ATOMS63 (*version 6.3*) by supplying derived crystallographic inputs like optimized cell parameters, space group and optimized positions of the atoms.

Results and Discussion

The computed lattice parameters were in good agreement with the experimentally derived values (Bish, 1993) as seen in Table 1. The simulated a and b axis lengths were close to those observed experimentally. The derived d-spacing, 7.494 Å, was slightly larger than the experimental one (Bish, 1993). Calculated density, i.e., 2.568 g/cc was close to the experimental one, viz., 2.608 g/cc (Bish, 1993). The calculated Fermi-energy and binding energy was 0.15894 Ry and -14.28 kJ/mol respectively. The calculated total energy was -44759.39 kJ/mol. To the best of our knowledge, it is for the first time that the

Table 1. *Unit cell parameters of kaolinite*

Mineral Parameters	Calculated (ground state 0K)	Experimental (298K)
a axis length(Å)	5.191	5.160
b axis length(Å)	8.935	8.966
layer d spacing (Å)	7.494	7.131
density(g cc^{-1})	2.568	2.608
Fermi Energy (Ry)	0.15894	NA
Binding Energy (kJ/mol)	-14.28	NA
Total Energy (kJ/mol)	-44759.39	NA
Interstitial Charge (eV/atom)	4.41	NA
Charge of Al (eV)	2.48	NA
Charge of Si (eV)	3.32	NA
Charge of O (eV)	2.49	NA
Charge of H (eV)(inner)	0.809	NA
Charge of H (eV)(interlayer)	0.817	NA

NA=Not Available

total energy of a silicate mineral has been obtained.

The validation of the theoretically derived structure is evident from Tables 2 and 3. For structural comparison, the DFT calculations were performed on two structural subunits of kaolinite : (1) an Al atom hexacoordinated by OH, and (2) a tetrahedrally coordinated Si atom. Bonding trends for particular Al-O and O-H pairs were accurately reproduced. Al-O bond distances associated with interlayer OH groups, Al-O bonds involving the inner OH groups (adjacent to vacant octahedral sites) and the apical Al-O bonds joining the silica tetrahedral sheet; all had distinct bond lengths in the reported X-ray crystal structure refinements (Bish, 1993). From Table 2, it can be seen that this trend is replicated in the theoretically derived structure. Apical Al-O bonds (i.e., those which connect to Si-O bond) were observed to be longer than Al-O bonds involving OH groups whereas Al-O bonds that involve interlayer OH groups were shorter than Al-O bonds associated with the inner OH group. The calculated Si-O bond distances showed heterogeneity between the apical and basal Si-O bond. The apical Si-O bonds were shorter (~0.012 Å) than their basal counterparts.

Differences in O-H bond distances were found for the inner and interlayer OH groups (Table 2). These differences were in the order of ~0.005 Å. Significant differences of O-H bond distances from the experimental data were not observed. The orientations of OH groups in the derived structures were also similar to the experimental data (Table 3). In the present calculation, the three inner-surface OH groups (the interlayer OH groups) were found to form interlayer H-bonds with the basal O atoms of the opposing silica sheet. Two of the inner-surface OH groups were oriented nearly perpendicular to the layer (88.18° and 74.56°, respectively) with the third OH group oriented slightly more in the plane (66.53°). These predicted orientations were in agreement with the experimentally derived OH orientations noted using structural methods (Bish, 1993). It may be mentioned that the minor deviations in bond angles are due to the fact that our derivations are for the ground state (0 K) whereas experimental values are at room temperature and reflect the temperature effect on bond angles and bond lengths.

The charges of Al, Si and O (Table 1) are positive because of covalent nature of the bonds (electrons are contributed to the interstitial region). Intrinsic charge on interlayer H was higher than in the inner H due to the formation of H-bond with the basal O of silica of another layer. There was significant amount of electron density in the interlayer region which had an interstitial charge of 4.41 eV/atom. This evidences the extent of H-bonding between

Table 2: *Bond distances (Å) of kaolinite*

Bonds	Calculated (ground state 0K)	Experimental (298K)
Si-O (apical)	1.631	1.618
Si-O (basal)	1.643	1.616
Al-OH (interlayer)	1.864	1.880
Al-OH (inner)	1.946	1.926
Al-O (apical)	1.967	1.967
O-H (interlayer)	0.967	0.978
O-H (inner)	0.962	0.975

Table 3. *OH orientations and H-bond distances of kaolinite*

Atom	Calculated value of angle of OH with (001) plane in degree	Experimental value of angle of OH with (001) plane in degree	Hydrogen bond	Calculated bond distances (Å)	Experimentally determined bond distances (Å)
H1	0.60	0.46	H1-O1	2.638	2.577
H2	88.18	87.15	H2-O2	2.117	2.145
H3	74.56	74.33	H3-O3	2.009	2.039
H4	66.53	65.01	H4-O4	1.988	2.041

H1=inner; H2, H3, H4=interlayer

Table 4. *XRD analysis of kaolinite*

Plane (h k l)	d (theoretical) [Å]	d (experimental) [Å]
0 0 1	7.18	7.25
0 2 0	4.46	4.50
1-1 0	4.35	4.39
0 0 2	3.59	3.58
1 1 1	3.37	3.40
1-1 2	3.11	3.06

the unit layers which substantiates the experimental observation that the structure of kaolinite is quite stable and does not collapse easily.

The XRD bands as calculated solely on the basis of theoretically derived structure were in excellent agreement with the experimental data (Table 4).

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