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Mineralogy of Some Benchmark soils of the Coastal Plain, West Bengal

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Abstract : *Mineralogical studies of sand, silt and clay fractions of four benchmark soils (Ballartop, Chandipur, Narayanpur and Patibunia) occurring on coastal plain, West Bengal were conducted to identify the minerals present in these fractions and also to understand their transformation in this ecosystem. Ballartop, Chandipur and Narayanpur soils were developed on very gently sloping to nearly level plain with poor drainage whereas Patibunia soil was developed on degraded mangrove with imperfectly drainage condition. The soils were dark grayish brown to dark gray in colour except Narayanpur soils which was gray to dark gray throughout the profile with olive brown to dark brown mottles and the texture of the soils varied from silt loam to silty clay. The soils were neutral to moderately saline (pH 6.7 to 8.1) except the soil of Ballartop (pH 4.7- 8.2). The EC value ranged from 0.72 to 8.3 dSm^{-1} and the clay content varied from 19.8 to 51.9%. The CEC of the soils was low to high and ESP of these soils ranges from 6.1 to 33.5.*

The mineralogical study revealed that in the heavy sand fraction, the minerals were present in the order: opaque > limonite > biotite > phlogopite > hornblende > pyroxene > goethite > kyanite and the other minerals are in trace. In the light sand fraction, quartz was the dominant mineral (43-89%), followed by muscovite (6-48%), potash feldspar (1-14%) and plagioclase feldspar (1-11%). The minerals in silt fraction followed the order: mica (42-67%) > kaolinite (9-24%) > chlorite (6-16%) > vermiculite (5-15%) smectite (1-10%) > K- plagioclase > feldspar feldspar with minor to trace amount of 10-14Å mixed layer mineral and 8Å smectite/kaolinite (sm/k). In clay fraction, mica was the dominant mineral followed by kaolinite and varying amount of smectite, chlorite and vermiculite. Significant amount of smectite (26-33%) was present in Narayanpur soils and in some horizons of Chandipur soils. The mineralogy of Ballartop, Chandipur and Patibunia soils was "illitic" and that of Narayanpur soils was "mixed". The higher peak intensity ratio of 001/002 mica reflection of silt and clay fractions indicated the dominance of tri-octahedral mica which have significant amount of reserve potash.

Key words : Coastal plain, mineralogy, clay fraction, mica, mixed layer mineral, reserve potash.

The knowledge of the mineralogical make up of soils (sand, silt and clay fractions) helps to understand their genesis, physical, chemical and nutrient holding capacity for proper soil management. Some information on clay mineralogical composition of different soils mainly alluvial, red & lateritic and Darjiling soils of the state were reported earlier (Adhikari, 1957, Ghosh and Dutta, 1974, Sahu and Ghosh, 1982). Very little database is generated for mineralogical composition of coastal soils of West Bengal. The coastal areas of West Bengal comprises of the major part of (South) 24-Parganas, southern part of (North) 24-Parganas, and south-eastern part of Purba Medinipur districts. It occupies an area of 0.68 m ha representing 7.6 percent of total geographical area of the state (Haldar *et al.*, 1992).

Materials and Methods

Four representative Benchmark soils viz. Ballartop, Chandipur, Narayanpur and Patibunia were collected from different landforms under varying land use systems. The detail of the site characteristics was given in table 1. The soil moisture regime of the area was 'ustic' and 'aquic' and the soil temperature regime was 'hyperthermic'. The morphological characteristics of the different horizons of the profiles were studied (Soil Survey Staff, 1951). The soil samples (horizon wise) were collected, air dried and processed for

Table 1. *Site Characteristics of the Benchmark soils under study*

Series Name	Location	Lat. & Long.	Depth (cm)	Landform	Drainage	Surface feature	Land Use
Ballartop	Vill-Ballartop Block-Basanti 24-Parganas(s)	22°12'30" N 88°43'30" E	0-150	Very gently sloping plain	Poorly drained	Slight erosion	Cultivated (monocropped)
Chandipur	Vill-Chandipur Block-Kulpi 24-Parganas(S)	22°07'30" N 88°15'30" E	0-150	Nearly level plain	Poorly drained	Small to medium cracks	Cultivated (monocropped)
Narayanpur	Vill-Narayanpur Block-Kakdwip 24-Parganas(S)	21°44' N 88°17' E	0-140	Nearly level plain	Very poorly drained	Moderate cracking	Mostly cultivated and partly forested
Patibunia	Vill-Patibunia Block-Namkhana 24-Parganas(S)	21°36'15" N 88°13'55" E	0-156	Lower delta plain	Imperfectly drained	Slight to moderate erosion	Degraded mangrove forest

laboratory analysis. The physical and chemical properties were determined by standard procedures (Page *et al.*, 1982; Jackson, 1979). The mineralogy of sand fraction was done using Laborlux-12 Petrographic microscope. Very fine sands of selected horizons were fractionated into heavy and light fractions using bromoform (sp.gr.2.85). These minerals were than mounted on slides with Canada balsam and mineral species were identified by microscope. Silt (50-2 µm) and clay (<2 µm) fractions were analysed by X-ray diffraction of parallel oriented aggregates on glass slides saturated with Ca and K using Philips diffractometer with Ni-filtered CoKα radiation at a scanning speed of 2°2θ/ minute. The Ca saturated samples were glycolated and K treated samples were heated to 25°C, 110°C, 300°C and 550°C to identify the minerals present. Minerals were identified by the method of Wilson (1987) and estimated semi-quantitatively (Gjems, 1967). Structural characteristics of mica were determined by measuring X-ray intensity ratio of its (001) and (002) reflections (peak height).

Results and Discussion

Morphological characteristics

Soils of the coastal plain are developed over the sediment brought down by the river Ganga and deposited on the mouth of Bay of Bengal in the form of Delta. The landforms are very gently sloping to nearly level land and drained towards south and south-eastern direction. The soils are very deep, poorly to imperfectly drained and have moderately fine to fine texture (silt loam to silty clay), moderate to strong, medium to very coarse sub-angular blocky structure. The surface soils are dark grayish brown (2.5Y4/2 M) to brown (10YR 5/3M) and subsurface and subsoils are grayish brown (10YR 5/3 & 2.5Y 5/2M) to dark gray (5Y 4/1M) in colour due to water logging and improper drainage.

Physical and chemical characteristics

The surface soils are neutral to moderately alkaline (pH 6.7 to 8.0) except Ballartop soils (pH 4.7) and it increases downwards in most soils, The electrical conductivity is normal for Ballartop and Chandipur soils and it is injurious to crops for Narayanpur and Patibunia soils ranging from 4.3 to 8.34 dSm^{-1} (Table 2). Organic carbon content of surface soils varies from 5.1 to 1.8 gkg^{-1} and it decreases with depth. Clay content of the soils ranges from 19.8 to 51.9 and high amount of silt is present in all profiles (41.4 to 80.0%). CEC is medium (9.8 to 20.2 cmol(p$^+$) kg^{-1}) except Narayanpur soils which shows higher value (32.9-37.2 cmol) kg^{-1} with high base saturation (80-99%). High ESP (14.0 to 33.5%) is observed for Ballartop, Narayanpur and Patibunia soils due to high exchangeable Na [2.5 to 6.0 cmol(p$^+$) kg^{-1}].

Mineralogical Properties of very fine sand fraction

Mineral composition of sand fraction

Table 2. *Physical and Chemical Characteristics of the soils*

Horizon	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Texture	$pH_{(H2O)}$	$pH_{(KCl)}$	EC (dS/m)	Org.C (g kg^{-1})	CEC	B.S. (%)	ESP	CEC/ Clay
Ballartop series: Fine, illitic, hyperthermic family of Typic Endoaquepts													
Ap	0-11	1.0	51.1	47.9	sic	4.7	3.9	0.80	18.0	19.9	91	15.1	0.34
AB	11-37	0.8	53.3	45.9	sic	6.3	5.2	0.82	3.6	20.2	97	16.3	0.33
Bw1	37-63	1.4	46.7	51.9	sic	7.0	6.0	0.87	2.9	17.5	98	16.5	0.32
Bw2	63-90	1.4	56.7	41.9	sic	7.5	6.2	0.82	2.9	16.9	94	16.6	0.33
Bw3	90-120	-	57.1	42.9	sic	7.6	6.4	0.75	0.7	17.0	86	14.7	0.32
Bw4	120-150	-	56.1	43.9	sic	8.2	6.7	0.72	0.7	18.0	92	16.6	0.31
Chandipur series: Fine, illitic, hyperthermic family of Aeric Endoaquepts													
Ap	0-12	7.8	64.6	27.6	sicl	6.7	5.5	1.06	7.1	9.8	80	6.1	0.35
BA	12-26	2.0	62.4	35.6	sicl	7.2	6.0	0.84	2.5	15.2	84	6.6	0.43
Bw1	26-62	4.8	60.6	34.6	sicl	7.5	6.2	0.95	1.1	15.0	88	9.3	0.43
Bw2	62-98	3.8	60.6	35.6	sicl	7.7	6.2	0.96	1.1	14.8	91	14.9	0.41
Bw3	98-118	2.2	59.2	38.6	sicl	7.7	6.3	0.97	0.8	15.5	90	19.3	0.40
Bw4	118-150	1.6	56.8	41.6	sicl	7.6	6.2	0.95	0.5	18.6	88	7.2	0.45
Narayanpur series: Fine, mixed, hyperthermic family of Vertic Endoaquepts													
Ap	0-15	12.0	41.4	46.6	sic	7.7	7.2	8.34	5.1	37.2	86	14.5	0.80
BA	15-45	20.0	41.4	38.6	sicl	7.8	7.2	7.14	3.5	34.6	88	16.2	0.89
Bw1	45-72	28.0	43.4	28.6	sicl	7.8	7.3	4.79	3.5	32.9	88	14.0	1.15
Bw2	72-96	20.0	49.4	30.6	sicl	7.8	7.3	6.38	3.1	33.4	88	16.2	1.09
Bw3	96-140	6.5	48.9	44.6	sic	7.6	7.3	4.34	4.7	34.7	85	17.3	0.78
Patibunia series: Fine-loamy, illitic, hyperthermic family of Fluventic Endoaquepts													
Ap	0-13	0.2	80.0	19.8	sil	8.0	7.5	4.3	5.7	16.3	99	25.7	0.82
BA	13-37	0.4	60.4	39.2	sicl	8.1	7.4	5.1	4.0	14.5	94	31.0	0.37
Bwg	37-69	0.4	59.0	40.6	sic	8.0	7.4	4.9	3.2	15.0	98	33.3	0.37
BCg	69-97	0.4	66.9	32.7	sicl	7.9	7.2	6.1	3.2	14.6	95	32.2	0.45
C1g	97-129	0.9	72.3	26.8	sicl	7.8	7.3	6.3	3.6	15.1	91	30.0	0.56
2C2g	129-156	0.6	62.0	37.4	sicl	7.6	6.9	6.6	5.5	16.7	95	33.5	0.45

(Table 3) indicates that in the heavy sand fraction, the minerals were present in the order: opaque > limonite > biotite > phlogopite > hornblende > pyroxene > goethite > kyanite and the other minerals are in trace, whereas in the light sand fraction, quartz was the dominant mineral (43-89%), followed by muscovite (6-48%), potash feldspar (1-14%) and plagioclase feldspar (1-11%). Primary hydrous mineral of iron (goethite) which may be the derivatives of hornblende/pyroxene has been completely altered/changed to limonite or opaque (hematite/magnetite). Surfaces of pyroxene and hornblende are etched and showing iron leaching of goethite/limonite material. Low abundance of these minerals indicates that they have been dissolved rapidly by solution after their deposition. Minor amount of boron bearing mineral, tourmaline is present, which may be the source of boron to these soils. K-feldspar (a potash bearing mineral) are present in adequate amount in Patibunia soils whereas in other soils it is present in minor to trace amount. Most of this feldspar in finer forms (silt fraction) changes to secondary mineral but when it comes to clay size particle, it is totally disappeared indicating its complete dissolution/ transformation. Higher abundance of biotite and phlogopite in the sand fraction indicate that they are responsible for K-release in the soil. These minerals in their finer forms break down and form illite mica rich in biotite which can be observed by 001/002 intensity ratio of 10Å mica with >2 value in both silt and clay fraction.

Mineralogy of silt fraction

Mineralogical investigation of silt fraction of the soils showed the abundance of minerals in the following order: mica > kaolinite > chlorite > smectite > K-feldspar > plagioclase feldspar with minor to trace amount of 10 – 14 Å mixed layer mineral and 8Å smectite/kaolinite (sm/k) as well as vermiculite (Table 4). Presence of nearly half amount of K-feldspar (1-4%) and plagioclase feldspar (1-5%) in silt fraction in comparison to sand fraction in Patibunia soils indicates that weathering and transformation is continuing. Increase in the intensity of 14Å peak during heat treatment from 25 to 550°C indicate the presence of chlorite in Patibunia soils (Fig.4) whereas reduction in 14 Å with heat treatment points the interlayering of chlorite with Hydroxy Interlayered vermiculite in Ballartop and Narayanpur soils (Fig.1 and 3). In some soils lowering of 14Å peak and their disappearance after heat treatment from 110 to 300°C indicates the presence of vermiculite in Ballartop and Chandipur soils (Figs. 1 and 2). Interstratifications of 14Å between smectite and chlorite (Fig. 3 and 4) and smectite with vermiculite (Fig.2) can also be observed. The XRD curve of Ballartop soils (Fig.1), indicate that mica has been transformed to vermiculite and smectite via 10-12Å mixed layer minerals. These above observations reveals that interlayering and mixing is very common phenomenon in these soils which may be

Table 3. *Mineral abundance in sand fraction (in percent)*

Depth (cm)	Horizon	Texture	Heavy sand fraction														Light sand fraction							
			Moderately unstable mineral				K bear-ing		Moderately stable Al and Fe bearing mineral			Ultra stable mineral			P bearing mineral		Fe bearing mineral			Rock frag-ment	qu-artz	Na-Ca mine-ral	K bearing mineral	
			Fe-Al bearing																					
			hb	px	gt	e	b	ph	ky	sil	st	z	t	r	a	mo	g	lm	op	rf	q	pf	kf	mu
Ballartop series																								
0-11	Ap	sic	11	5	tr	1	13	tr	3	2	tr	tr	3	tr	tr	tr	5	18	37	2	89	3	2	6
37-63	Bw1	sic	9	2	tr	tr	10	3	-	2	tr	tr	7	tr	tr	tr	7	20	39	2	87	2	5	6
90-120	Bw3	sic	8	6	tr	2	3	5	2	2	tr	tr	3	tr	tr	tr	12	13	40	4	78	2	5	15
Chandipur series																								
0-12	Ap	sicl	4	4	tr	tr	15	10	5	2	1	tr	11	tr	tr	tr	3	3	42	tr	58	1	3	38
26-62	Bw1	sicl	3	2	tr	tr	11	9	3	tr	2	tr	13	tr	tr	tr	2	4	51	tr	51	2	3	44
118-150	Bw4g	sic	2	3	tr	tr	15	7	5	tr	1	tr	8	tr	tr	tr	2	3	54	tr	43	4	5	48
Narayanpur series																								
0-15	Ap	sic	5	9	tr	1	12	10	5	1	2	tr	5	tr	tr	tr	2	3	43	2	63	1	1	35
45-72	Bw1	sicl	7	8	tr	tr	21	8	3	tr	3	tr	3	tr	tr	tr	3	4	40	1	65	2	1	32
72-96	Bw2	sicl	8	4	tr	tr	18	10	4	tr	2	tr	6	tr	tr	tr	2	6	37	3	61	4	5	30
Patibunia series																								
0-13	Ap	sil	7	5	1	3	14	7	3	1	-	tr	4	tr	tr	tr	2	11	40	2	48	5	12	35
37-69	Bwg	Sic	5	4	tr	2	22	9	2	tr	2	tr	3	tr	tr	tr	1	15	34	2	45	11	14	30
97-129	C1g	Sicl	12	7	tr	2	20	-	1	1	-	tr	5	tr	tr	tr	2	12	38	tr	50	7	11	32

hb - hornblende, px - pyroxene, gt - garnet, e - epidote, b - biotite, ph - phlogopite, ky - kyanite, sil - sillimanite, st - staurolite, z - zircon, t - tourmaline, r - rutile, a- apatite, mo - monazite, g - goethite, lm - limonite, op-opaque, rf - rock fragment, q - quartz, pf - plagioclase feldspar, kf - potash feldspar, mu – muscovite.

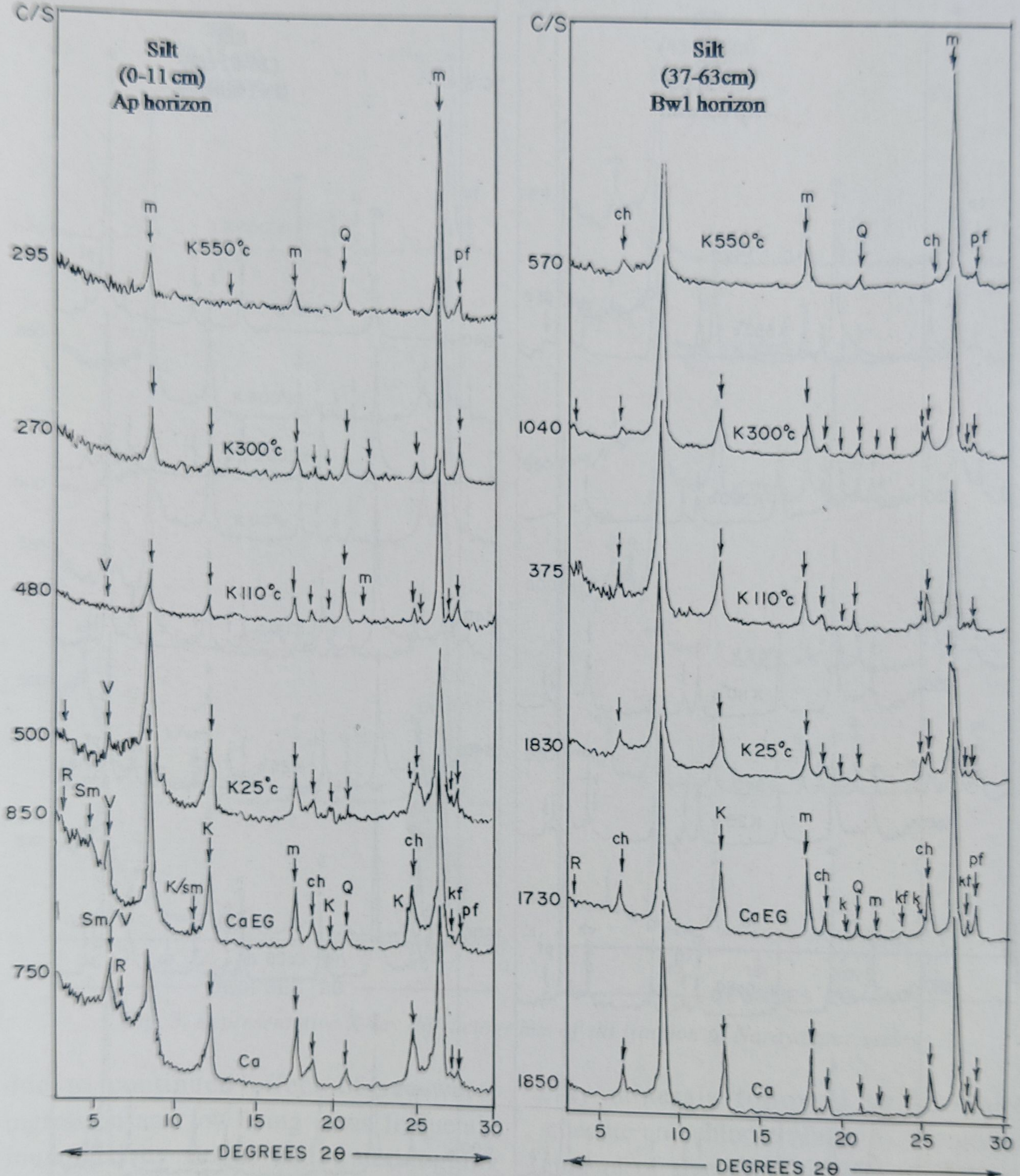
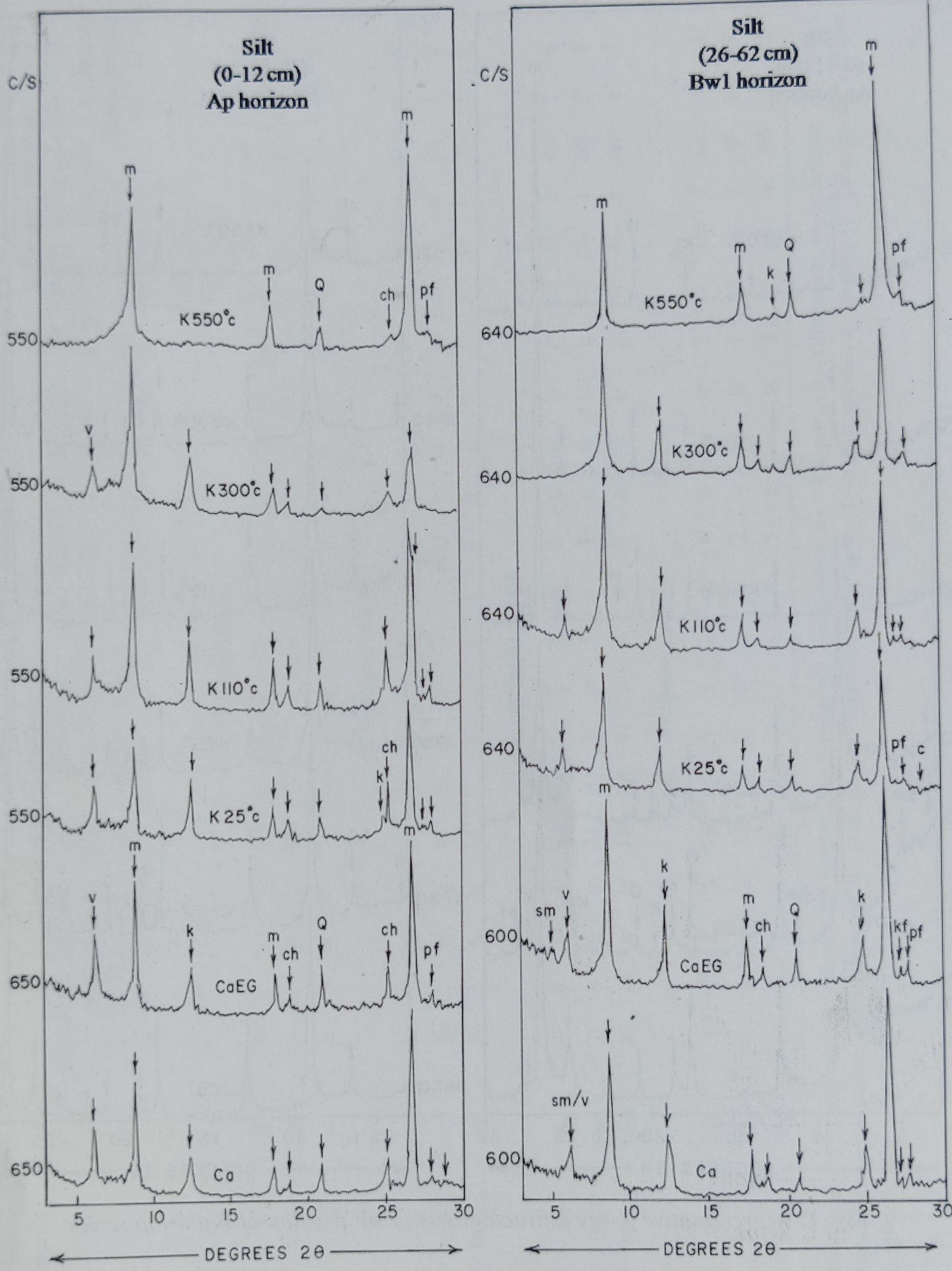


Fig. 1. *Representative X-ray diffractograms of silt fraction of Ballartop series*



Silt (0-12 cm) Ap horizon

Silt (26-62 cm) Bw1 horizon

Fig. 2. *Representative X-ray diffractograms of silt fraction of Chandipur series*

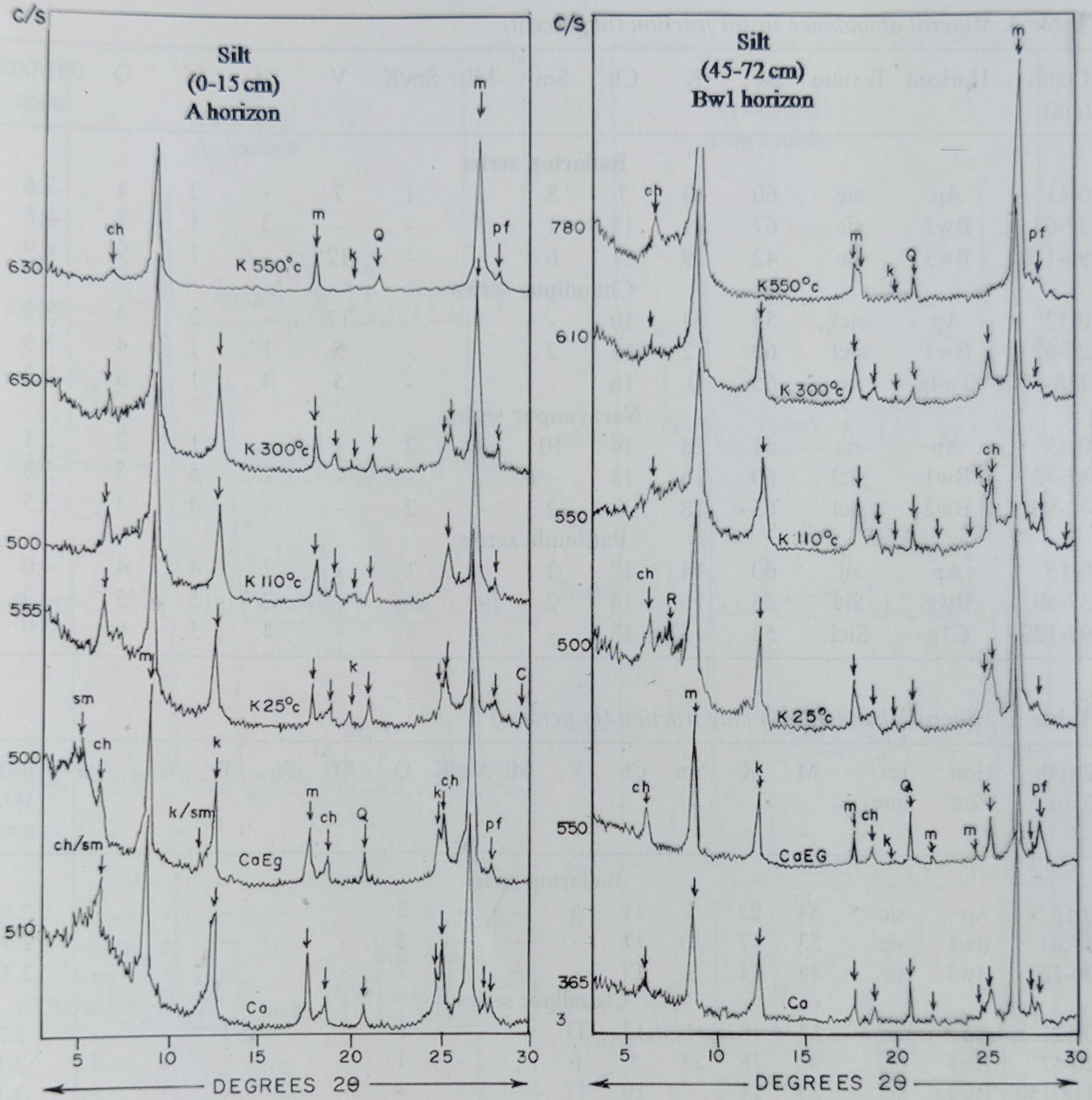


Fig. 3. *Representative X-ray diffractograms of silt fraction of Narayanpur series*

due to continued effect of sea-water ingression and low lying areas frequently inundated by floods and water logging during rainy season.

Mineralogy of clay fraction

In most soils, mica was the dominant clay minerals followed by kaolinite, smectite and chlorite (Table 5). Significant amount of smectite (26-33%) was present in Narayanpur soils which qualifies the soils for "Vertic" subgroup (Shirsath *et al*., 2000) and in some horizons of Chandipur soils. The clay fraction of these soils shows the

Table 4. *Mineral abundance in silt fraction (in percent)*

Depth (cm)	Horizon	Texture	M	K	Ch	Sm	MI	Sm/K	V	Kf	Pf	Q	001/002 mica
						Ballartop series							
0-11	Ap	sic	60	13	7	8	1	1	7	-	2	1	2.6
37-63	Bw1	sic	67	11	15	1	1	-	-	3	1	1	2.8
90-120	Bw3	sic	42	19	11	6	-	-	12	-	1	9	4.9
						Chandipur series							
0-12	Ap	sicl	53	24	10	-	-	-	17	-	2	4	3.2
26-62	Bw1	sicl	60	12	15	2	-	-	5	1	1	4	3.9
118-150	Bw4g	sic	65	9	16	-	-	-	5	4	1	3	3.3
						Narayanpur series							
0-15	Ap	sic	51	18	14	10	3	2	-	-	1	2	3.1
45-72	Bw1	sicl	60	16	13	-	-	-	-	2	5	5	3.8
72-96	Bw2	sicl	65	18	6	2	-	2	-	-	4	3	3.5
						Patibunia series							
0-13	Ap	sil	60	14	12	2	-	1	-	2	4	4	4.0
37-69	Bwg	Sic	56	15	14	2	-	-	-	3	5	5	4.3
97-129	C1g	Sicl	58	13	13	-	-	-	-	4	5	6	3.9

Table 5. *Mineral abundance in clay fraction (in percent)*

Depth (cm)	Hori Zon	Tex- ture	M	K	Sm	Ch	V	Ml	Sm/K	Q	Kf	Pf	T	C	Am	001/ 002 mica
							Ballartop series									
0-11	Ap	sic	54	22	5	11	6	-	-	2	-	-	-	-	-	2.50
37-63	Bw1	sic	53	17	10	17	-	-	-	2	-	-	-	-	-	2.48
90-120	Bw3	sic	48	21	9	19	-	-	-	2	-	-	-	-	-	2.35
							Chandipur series									
0-12	Ap	sicl	52	18	4	13	11	-	-	1	-	-	1	-	-	3.2
26-62	Bw1	sicl	38	16	33	5	6	-	-	1	-	-	-	1	1	3.1
118-150	Bw4g	sic	53	14	-	10	17	-	-	4	-	2	-	-	-	3.1
							Narayanpur series									
0-15	Ap	sic	40	17	26	14	-	-	-	1	-	-	2	-	-	3.5
45-72	Bw1	sicl	38	14	30	14	-	-	-	1	-	-	3	-	-	3.2
72-96	Bw2	sicl	35	16	29	14	-	3	-	2	1	1	2	-	-	3.0
							Patibunia series									
0-13	Ap	sil	61	18	5	11	3	-	-	1	-	-	1	-	-	2.6
37-69	Bwg	Sic	58	20	6	9	3	-	-	2	-	-	-	2	-	2.8
97-129	C1g	Sicl	61	19	6	8	4	-	-	2	-	-	-	-	-	2.7

M-Mica (illite), K- Kaolinite, Sm- Smectite, Ch-Chlorite, V-Vermiculite, MI - Mixed layer mineral, sm/k- smectite/kaolinite, Q- Quartz, Kf -Potash feldspar, Pf- Plagioclase feldspar, t - talc, c-calcite, am-ambhibole.

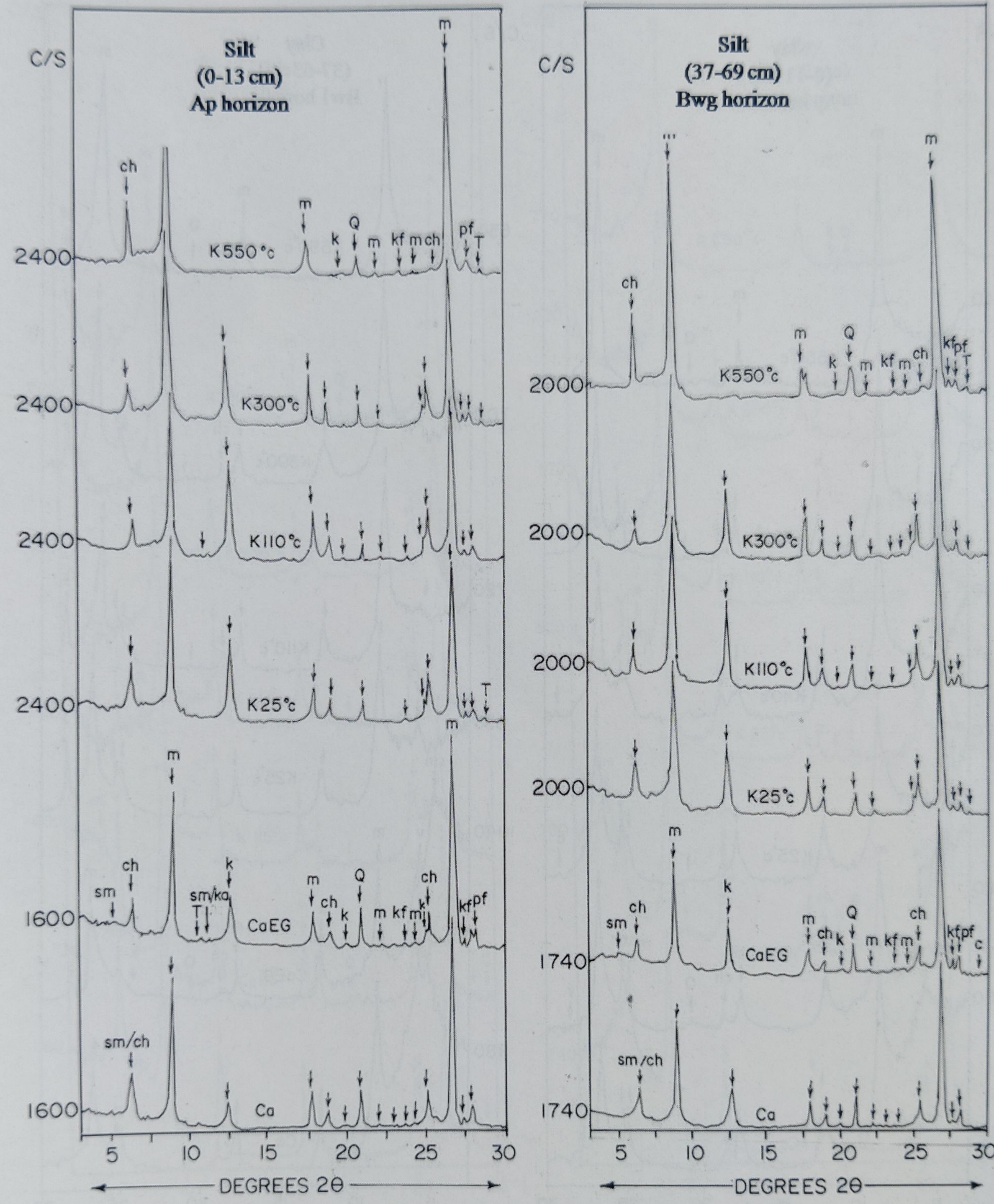


Fig. 4. *Representative X-ray diffractograms of silt fraction of Patibunia series*

Fig. 5. *Representative X-ray diffractograms of clay fraction of Ballartop series*

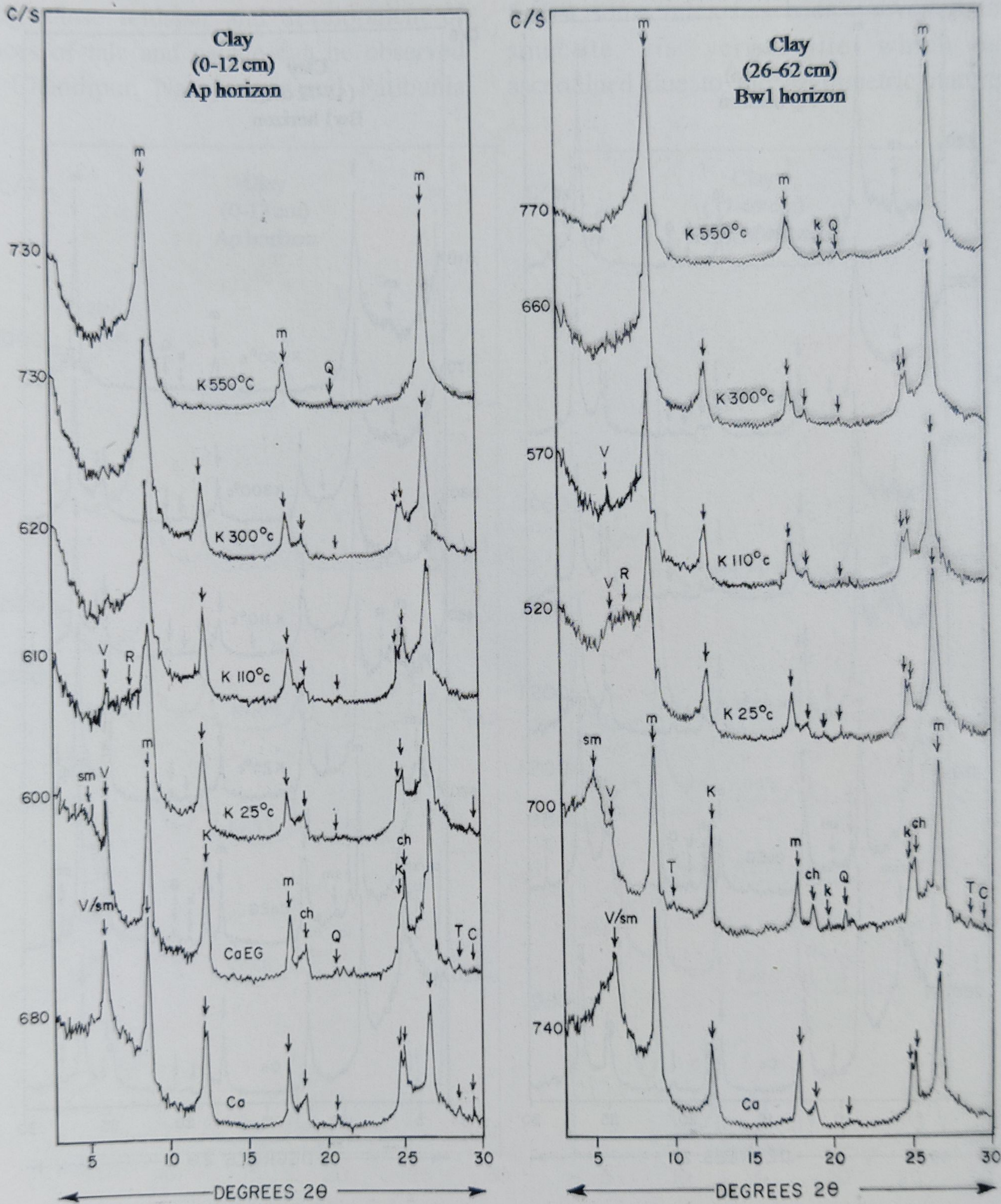


Fig. 6. *Representative X-ray diffractograms of clay fraction of Chandipur series*

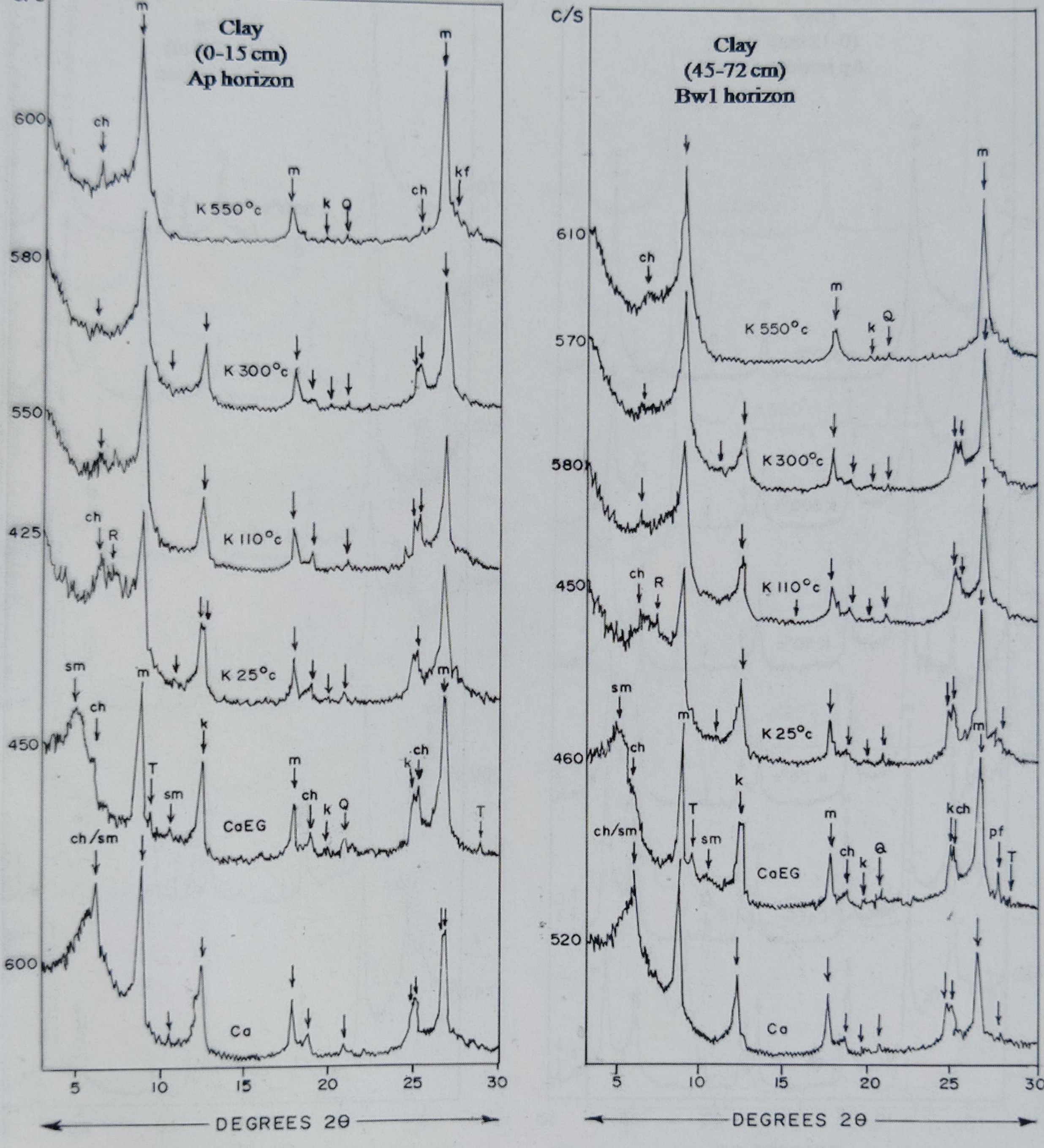


Fig. 7. *Representative X-ray diffractograms of clay fraction of Narayanpur series*

complete transformation of K-feldspars and plagioclase feldspar and development of traces of talc and calcite can be observed in Chandipur, Narayanpur and Patibunia soils. It is observed from the data of table 5 that some mica has been converted to smectite via vermiculite which is ascertained due to the asymmetric nature

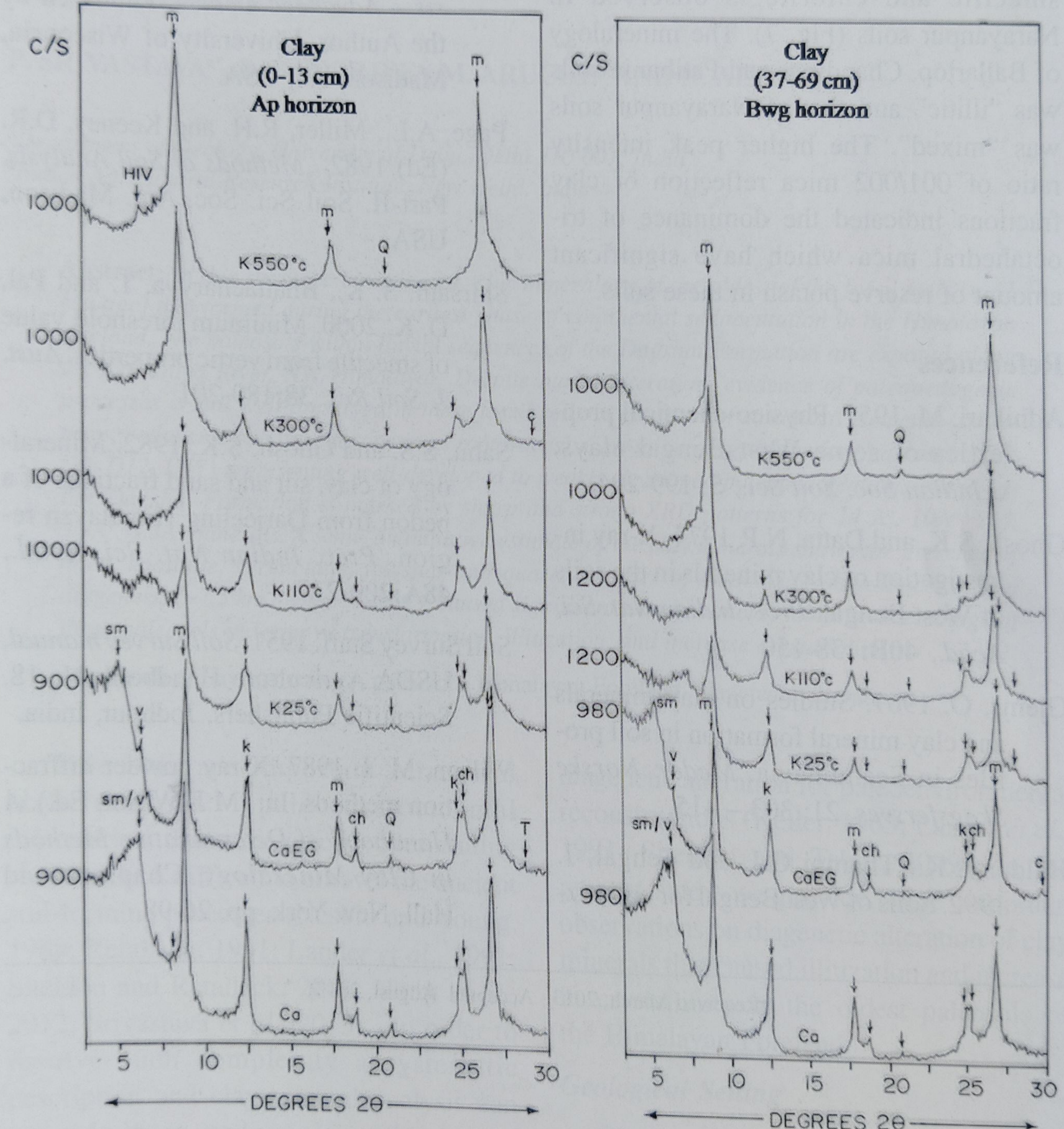


Fig. 8. *Representative X-ray diffractograms of clay fraction of Patibunia series*

of 10 Å mica towards higher'd' value (Figs.5,6,8). An appreciable amount of chlorite is present in the clay fractions of all soils and the interstratifications between smectite and chlorite is observed in Narayanpur soils (Fig. 7). The mineralogy of Ballartop, Chandipur and Patibunia soils was "illitic" and that of Narayanpur soils was "mixed". The higher peak intensity ratio of 001/002 mica reflection of clay fractions indicated the dominance of tri-octahedral mica which have significant amount of reserve potash in these soils.

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Clay Mineralogy of the Oldest Paleosols from the Himalayan Foreland: Implications of Diagenetic Overprinting and Paleoenvironments

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Abstract: *In this study we investigated clay mineralogy of the oldest of the fossil soils (~ 31 Ma age) that formed during the earliest phase of continental sedimentation in the Himalayan foreland. The paleosols within fluvial sequences of the Dagshai Formation are exposed along the Koshaliya River, NW Himalaya. Despite burial alteration, evidence of paleopedogenic processes is still well-preserved in these fossil soils in the form of structural elements (structures, pedogenic calcite, clay coatings, root traces). Clay mineralogy of the four paleosols (D5, D9, D12, D17) representing well-developed to weakly-developed paleopedofeatures of the entire Dagshai Formation is marked by sharp and strong XRD patterns for 14 A°, 10A°, 7A°, 3.5A°, 3.3A° minerals. A semi- quantitative estimate of the clay minerals shows the presence of mica, kaolinite, vermiculite, feldspar and quartz in order of decreasing abundance. Burial diagenesis (~7.5 km depth, ~140°C) caused significant changes in clay mineral assemblage of these paleosols in terms of transformation, illitization, and increase crystallinity.*

Key words : Clay mineralogy, paleosols, Himalayan Foreland, diagenetic alterations

Paleosols are important terrestrial archives of paleoenvironmental information. But diagenetic overprinting could make it difficult to unravel the ancient soil-forming processes (Nesbitt and Young, 1989; Retallack, 1991; Lander *et al.*, 1991; Sheldon and Retallack, 2001; Nordt *et al.*, 2012, Srivastava *et al.*, 2013). In order to resolve such complexity a systematic description and clay mineral analysis can provide post pedogenic pathways of diagenetic alteration for paleoenvironmental reconstructions (Keller, 1963; Lander *et al.*, 1991; Sheldon and Tabor, 2009). In the present study we provide some important observations on diagenetic alteration of clay minerals that caused illitization and increase in crystallinity in the oldest paleosols of the Himalayan Foreland.

Geological Setting

The Himalayan Foreland (Fig. 1)

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resulted from thrust loading and subsidence with synorogenic sedimentation from the hinterland (Raiverman *et a*l., 1983; Burbank *et al*., 1996). The terrestrial sedimentary record of this tectonically active basin is related to exhumation history of the hinterland, southward propagation of the thrust sheets, and progressive shift of the provenance (Ravikant *et al*., 2011). The marine Subathu Formation in the basal part of the foreland is overlain by continental Dagshai Formation consisting of red mudstone and white/gray sandstone deposited by meandering rivers (Bhatia and Bhargava, 2006; Najman, 2006; Bera *et al*., 2008; Ravikant *et al*., 2011). The depositional age of the lowermost and uppermost parts of the Dagshai formation have been dated to 31.6 ± 3.9 Ma and 30.3± 3.9 Ma, respectively, by detrital-zircon fission-track (ZFT) analysis (Jain *et al*., 2009). The Dagshai Formation sediments experienced burial by 7.0-7.5 km thick sediments during the deposition of the Kasauli Formation and Siwalik Group, followed by thrusting along the Main Boundary Fault during Neogene (Karunakaran and Rao, 1976). Based on a geothermal gradient of ~20°C km^{-1} for the Siwalik basin, this corresponds to a minimum temperature of ~140 °C after the burial of the Dagshai Formation (Mugnier *et al*., 1995).

Methods

Four sections (D5, D9, D12, and D17) exposed along the Koshaliya River (Fig. 1C) close to the Kalka-Simla highway comprising the entire fluvial succession of the Dagshai Formation were described for field characteristics of the paleosols (Soil Survey Staff, 1999). The degree of pedogenic development was assessed on the basis of maturity of the paleopedogenic features following criteria established for macro-and micro-morphological features (Birkeland, 1999; Bullock *et al.,* 1985). We used decompaction equation established by Sheldon and Retallack (2001) to reconstruct the pre-burial thickness of the fossil soils. The guidelines of Nesbitt and Young (1989) and Retallack (1991) were used to distinguish paleopedological features overprinted by burial diagenesis.

Particle size distribution was carried out by International Pipette method (Jackson, 1979). Total clay (<2 μm) and fine clay (<0.2 μm) fractions were separated after dispersion according to the size segregation procedure of Jackson (1979). Clay fractions were analysed for qualitative mineralogy by X-ray diffraction (XRD) technique of oriented aggregates that were Ca- and K-saturated, glycolated, heated at 25, 110, 300 and 550°C, using a Philips diffractometer with Ni-filtered CuKα radiation and a scanning speed of 2°2θ per minute. The identification of minerals was done following the criteria of Jackson (1979) and Wilson (1987). Information about the structure of the clay fraction, fine clay in particular, was obtained from the 060

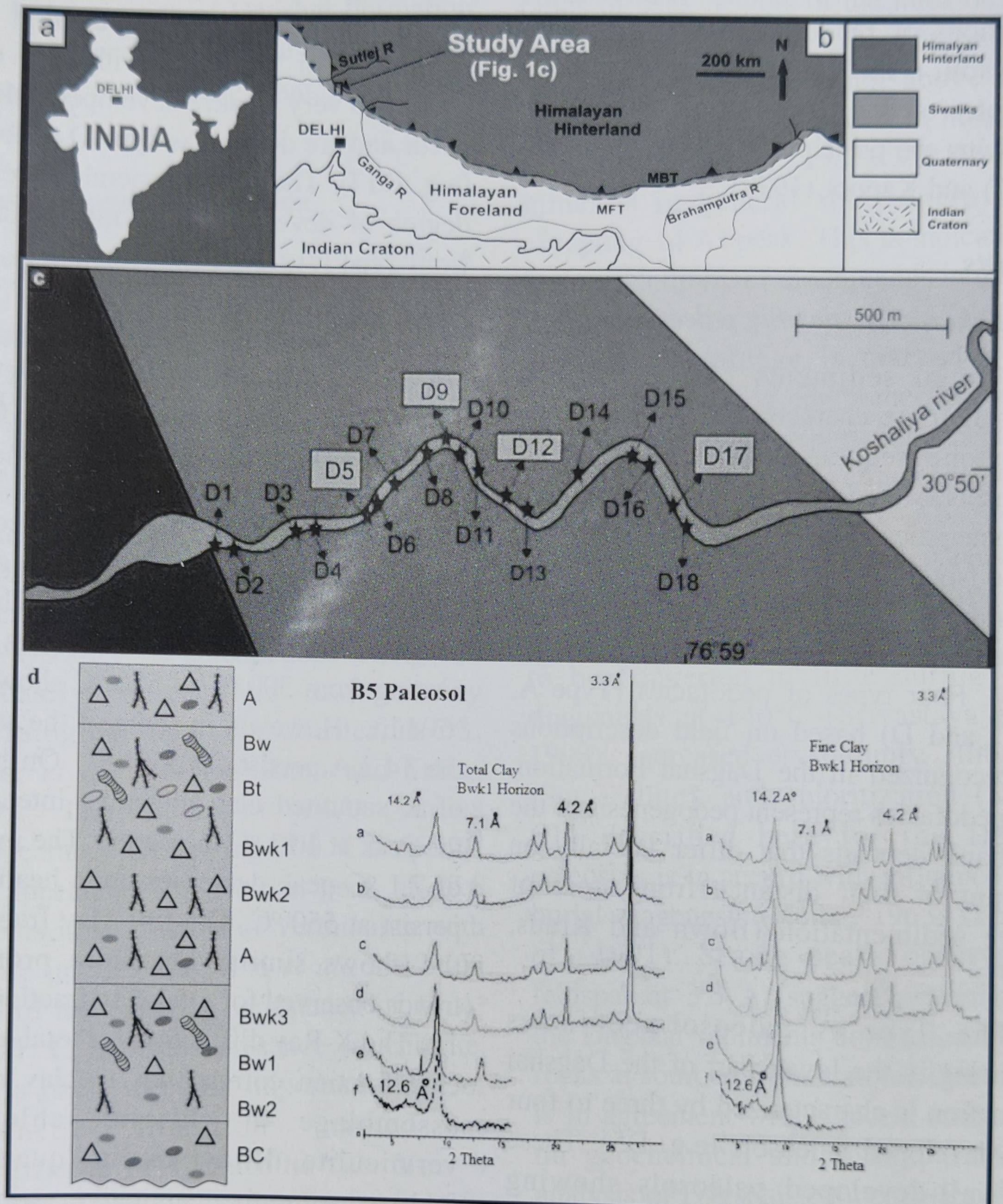

Fig. 1. **(a)** *Location of India,* **(b)** *Location of study area (Subathu basin) in the Himalayan foreland (after Gansser, 1964).* **(c)** *Location of the measured litho-sections (D5, D9, D12, D17) from Dagshai Formation along the Koshaliya River, NW Himalaya,* **(d)** *A summarised account of the key pedofeatures of the paleosols representing Pedofacies-A (D5 paleosols) after Srivastava et al., (2013), X-Ray diffraction of total clay and fine clay of Bwk1 horizon of the D5 paleosol (a: Ca saturated, b: Ca saturated and glycolated, c: K saturated at 25°C, d: K saturated and heated to 110°C, d: K saturated and heated to 300°C, e: K saturated and heated to 550°C).*

reflections of randomly oriented samples (Jackson, 1979). Semi-quantitative estimates of the clay minerals were made following the principles outlined by Gjems (1967) and Kapoor (1972).

Results

Field characteristics the paleosols

Fluvial sediments of the Dagshai Formation are characterized by mudstone-sandstone sequences with ferruginous paleosols. Macro- and micro-morphological characteristics, bulk rock geochemistry, and stable isotope geochemistry of these fossil soils have been described elsewhere (Srivastava *et al.,* 2013; Srivastava Saur, 2013). Four types of pedofacies (Type A, B, C, and D) based on field descriptions are recognized in the Dagshai Formation. The pedofacies represent pedogenesis of the overbank deposits that differ laterally on account of their distance from areas of active sedimentation (Bown and Kraus, 1987).

The Type A paleosol-pedofacies occurring in the lower part of the Dagshai Formation is characterized by three to four well-developed paleosols (e.g. D5). These are well-developed paleosols showing dusky-red color, silty texture and numerous root traces (Fig. 1d). Type B paleosol-pedofacies occurring mainly in the middle parts show one to two well-developed paleosols (e.g. D12). Further upwards only moderately developed paleosols (e.g. D9) occur that are defined as Type C paleosol-pedofacies. In the uppermost part dominance of sediments with only a few weakly to very weakly developed paleosols occur and are defined as Type D pedofacies (e.g. D17). There is a general decrease in degree of development in these paleosols from Type A to Type D paleosols.

Clay mineralogy of the paleosols

The X-Ray diffraction (XRD) of the total clay fraction (<2μm) for D5, D9, D12, D17 paleosols shows strong and sharp peaks for 14.2 A°, 10.1 A°, 7.1 A°, 3.5 A°, 3.3A° minerals (Fig. 1d). On glycolation there is broadening of the 14.2 A° in general without any distinct shift to 17 A°. The 14.2 °C peak in K-saturated samples upon heating from 300 °C to 550 °C shows 12.6 °C shift. However, in some of the samples the 14.2 A persists at 550 °C. On heating of K saturated clay minerals, intensity of the peak at 10.1 °C increases. The intensity of 7.1 °C peak decreases upon heating but persist at 550 °C. The fine clay fraction of the shows similar but more prominent trends observed for total clay fraction. (Fig. 1d) The X-Ray diffraction for total and fine clay fraction corresponds to clay mineral assemblage of chlorite, chloritised vermiculite, Illite, kaolin, quartz and feldspar. A semi- quantitative estimate of the clay minerals based on intensity and area in XRD show mica, kaolinite, chloritised vermiculite, vermiculite, feldspar and quartz in order of decreasing abundance. A depth distribution of different clay minerals present in paleosols from upper to basal parts of Dagshai Formation shows a general increase of kaolin and a decrease of vermiculite content in these paleosols.

Discussion and conclusions

Burial diagenesis (~7.5 km depth of burial, ~140°C) of these paleosols suggests differential compaction ranging from 54% to 78% of the pre-burial thickness (Sheldon and Retallack, 2001). Despite the severe compaction estimated for the Dagshai paleosols, most of the paleopedogenic characteristics are still well-preserved, although overprinted by additional diagenetic features. The diagenetic pathways after the paleopedogenesis could be easily determined using clay mineralogical analysis (Keller, 1963; Lander *et al.,* 1991; Sheldon and Tabor, 2009). The peak at 14A° shows disappearance on heating 300 °C - 550 °C with appearance of a broad peak at 12.6 A°. This is suggestive of vermiculite with chlorite interlayering (Pal *et al*., 2012). In some of the paleosol persistence of 14 A° at 550 °C indicates presence of chlorite. This is likely to be an important phase of diagenetic alteration marked as chloritization of vermiculite (i.e. Vm → Ch). Other minerals present in clay fraction include mica, kaolin, quart and feldspar. The increase in intensity of mica/illite indicates that the vermiculite changes to illite/ mica on heating. The decrease in the intensity of the kaolinite peak on heating confirms its conversion to mica/ illite. The ratios of peak heights of the mica 001 and 002 reflections in the total clay and fine clay fraction remain much above unity, suggesting the presence of both muscovite and biotite (Pal *et al*., 1987). All the above minerals in general show sharp peaks excepting 14 A° peak. This is indicative of high crystallinity of the minerals in the clay fraction. In the present study, the clay mineral assemblage is marked by the absence of swelling clay (smectite), which is in contrast with reports of smectite in Dagshai Sediments (Raiverman and Suresh, 1997; Raiverman, 2002). Absence of swelling clays from Dagshai paleosols is possibly due to burial diagenesis of ~7 km of Dagshai sediments. The smectite is likely to be converted to Illite during burial diagenesis at 140°C (Srivastava *et al.,* 1998). Increased crystallinity, illitization (Sm à Illite), and chloritization (Vm → Ch) described here for the Dagshai paleosols is in accord with influence of the burial diagenesis (Keller, 1963; Lander *et al*., 1991). Strong peaks observed for feldspar at 3.3 A° suggest provenance of the Dagshai sediments dominated by basic rocks at sourced from cratonic areas, which is in agreement with a recent study recent on geochemical and fission track (FT) analysis of Dagshai sediments (Ravikant *et al.,* 2011). The post paleopedogenic pathways of clay mineral changes described form the present study provides an important addition and also in agreement with whole rock geochemistry, stable isotope geochemistry, pedogenic carbonate alteration, and micromorphological evidences of diagenetic overprinting (Srivastava *et al.,* 2013; Srivastava and Saur, 2013).

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Soil Boron and Its Fractions in Agro-Climatic Zones of Karnataka

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Abstract : *The study was conducted to evaluate the distribution of native soil B fractions and to investigate their relationships to soil properties. 12 soils of surface as well as subsurface of 10 agro climatic zones of Karnataka with diverse properties were studied. The extraction scheme proposed here partitioned B into five pools, (i) readily soluble, (ii) specifically adsorbed, (iii) oxide bound, (iv) organically bound, and (v) residual boron, respectively extracted with 0.01 M* $CaCl_2$*, 0.05 M* KH_2PO_4*, 0.175 M* NH_4*-oxalate (pH 3.25), 0.5 M NaOH, and HF +* H_2SO_4 *+* $HClO_4$*. Among the fractions, residual boron contributed around 98 per cent and ranged from 125 in central dry zone to 567 mg* kg^{-1} *in northern dry zone followed by oxide bound boron that ranged from 2.15 in coastal zone to 8.21 mg* kg^{-1}*in eastern dry zone and the least amount was readily soluble boronthat ranged from 0.03 mg* kg^{-1} *in southern transition zone to 0.78 mg*kg^{-1} *in northern dry zone. Total boron was in highest amount in northern dry zone (582.3mg* kg^{-1}*). Residual boron has minimum effect on available boron, whereas readily soluble boron, specifically adsorbed boron, oxide bound boron and organically bound boron contribute towards boron nutrition in all the agro climatic zones. Relationships of individual B fractions with physical and chemical properties of the experimental soils confirmed the general validity of the proposed fractionation scheme,which is satisfactory in terms of sensitivity and position for soil boron.*

Key words : Soil boron, various fractions, Karnataka soils

Boron is an essential micronutrient required for normal growth of most plants and is distributed in various soil components, soil solution, organic constituents and mineral matter. Boron in soil solution is readily available for the plant uptake, but this pool constitutes less than 3 per cent of total soil boron (Jin *et al.*, 1987; Tsalidas *et al.*, 1994; Datta *et al.* (1998). To assess the agricultural and environmental impacts of boron, it is necessary to understand and quantify the different forms of boron in soil and sediments. These fractions include readily

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soluble, specifically adsorbed, oxide bound, organically bound and residual boron. The objectives of this research were to study the distribution of native soil boron fractions and to establish their relationships to soil properties.

Materials and Methods

Soil samples from surface as well as subsurface were drawn from 12 soil profiles representing major soils of Karnataka covering all 10 agro-climatic zones. Soil texture was determined by international pipette method, organic carbon by the Walkley and Black method (Jackson. 1973), while soil pH was measured in a 1:2.5 soil water suspension and available boron by Azomethine H method. Separate extraction of soil boron fractions were based on the sequential fractionation procedures (Fig.1) of Jin *et al*. (1987) and Datta *et al*. (2002).

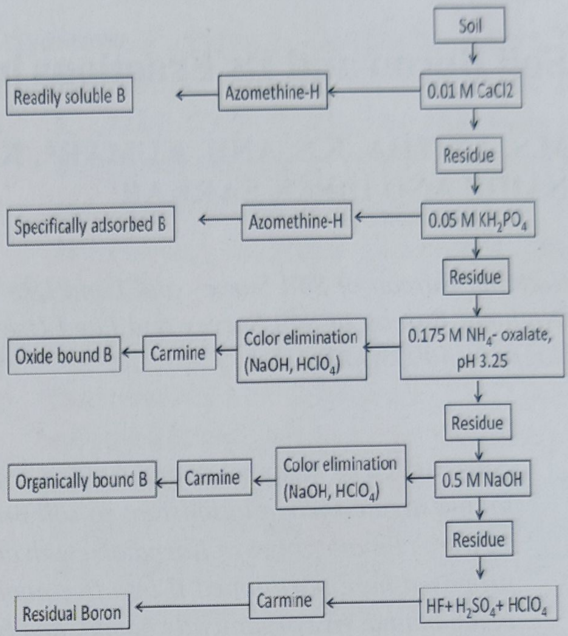

Fig 1. *Flow diagram for the fractionation scheme of boron in soils (Modified method from Datta, et al. 2002)*

Results and Discussion

The physical and chemical properties of soils studied are given in table 1. Total soil boron (Table 2) varied from 134.82 to 582.25 mg kg^{-1}, which is well in the reported range (7-630 mg kg^{-1}) of total boron for Indian soils (Kanwar and Randhawa, 1974). Readily soluble boron, specifically adsorbed boron, oxide bound boron, organically bound boron constituted only 0.03 to 8.21 mg kg^{-1} of the total boron. Plant available boron of surface and subsurface soils were analyzed and mapped (Fig.2), indicating that hilly and coastal soils are deficient in B.

The mean proportion of extractable boron for surface soil was 0.10 per cent as readily soluble forms, 0.14 per cent as specifically adsorbed forms, 1.53 per cent associated with oxide bound form, 0.91 per cent as organically bound forms and the major portion of boron in soils existed as residual or occluded forms which accounted for 96.9 to 98.7 per cent.

Relationship between and among surface soil boron fractions

For surface soils, readily soluble boron represented in small proportion of total boron and was low in Southern Transitional zone (Arakalgudu) and high content in

Table 1. *Physical and chemical properties of soils*

Soil	Location	Agroclimatic zones	Soils	Textural class	pH	Organic carbon	Clay (%)	Available B	CEC
1	Belwataki, Dharwad	Northern dry zone	Surface soil	c	7.9	0.58	66.4	0.72	63.8
			Subsoil	c	8.2	0.21	63.9	0.76	64.9
2	Siriguppa, Bellary		Surface soil	c	8.7	0.51	62.6	0.79	64.5
			Subsoil	c	8.7	0.44	67.0	0.93	63.0
3	Tiptur, Tumkur	Central dry zone	Surface soil	sc	7.8	0.34	44.8	0.67	10.4
			Subsoil	sc	7.5	0.33	42.1	0.69	8.8
4	Sira, Tumkur		Surface soil	gscl	8.1	0.52	21.5	0.65	16.9
			Subsoil	vgsc	7.8	0.39	35.3	0.57	18.9
5	Tumkur	Eastern dry zone	Surface soil	scl	8.2	0.45	31.0	0.77	9.2
			Subsoil	sc	7.9	0.36	39.0	0.73	9.5
6	Maddur, Mandya	Southern dry zone	Surface soil	gsl	8.2	0.94	17.2	0.77	11.9
			Subsoil	scl	8.1	0.77	21.7	0.75	15.0
7	Kollegal, Chamarajanagar		Surface soil	ls	6.6	0.36	14.6	0.36	6.9
			Subsoil	ls	6.5	0.30	12.8	0.59	6.8
8	Arakalgudu, Hassan	Southern transition zone	Surface soil	sl	4.5	0.91	17.4	0.17	4.7
			Subsoil	scl	5.7	0.60	24.3	0.35	7.0
9	Shimoga		Surface soil	scl	5.6	0.91	21.0	0.21	6.3
			Subsoil	gsc	6.1	0.81	35.7	0.45	9.0
10	Harapanahalli, Davangere	Northern transition zone	Surface soil	sl	8.3	0.32	18.4	0.79	9.6
			Subsoil	scl	8.4	0.43	25.5	0.80	12.8
11	Chethalli N.Kodagu	Hilly zone	Surface soil	scl	5.5	1.88	34.0	0.18	12.6
			Subsoil	sc	5.7	1.94	38.8	0.42	14.4
12	Udupi, Dakshina Kannada	Coastal zone	Surface soil	gscl	5.8	1.28	32.3	0.19	5.5
			Subsoil	gc	5.7	1.08	44.8	0.29	4.4

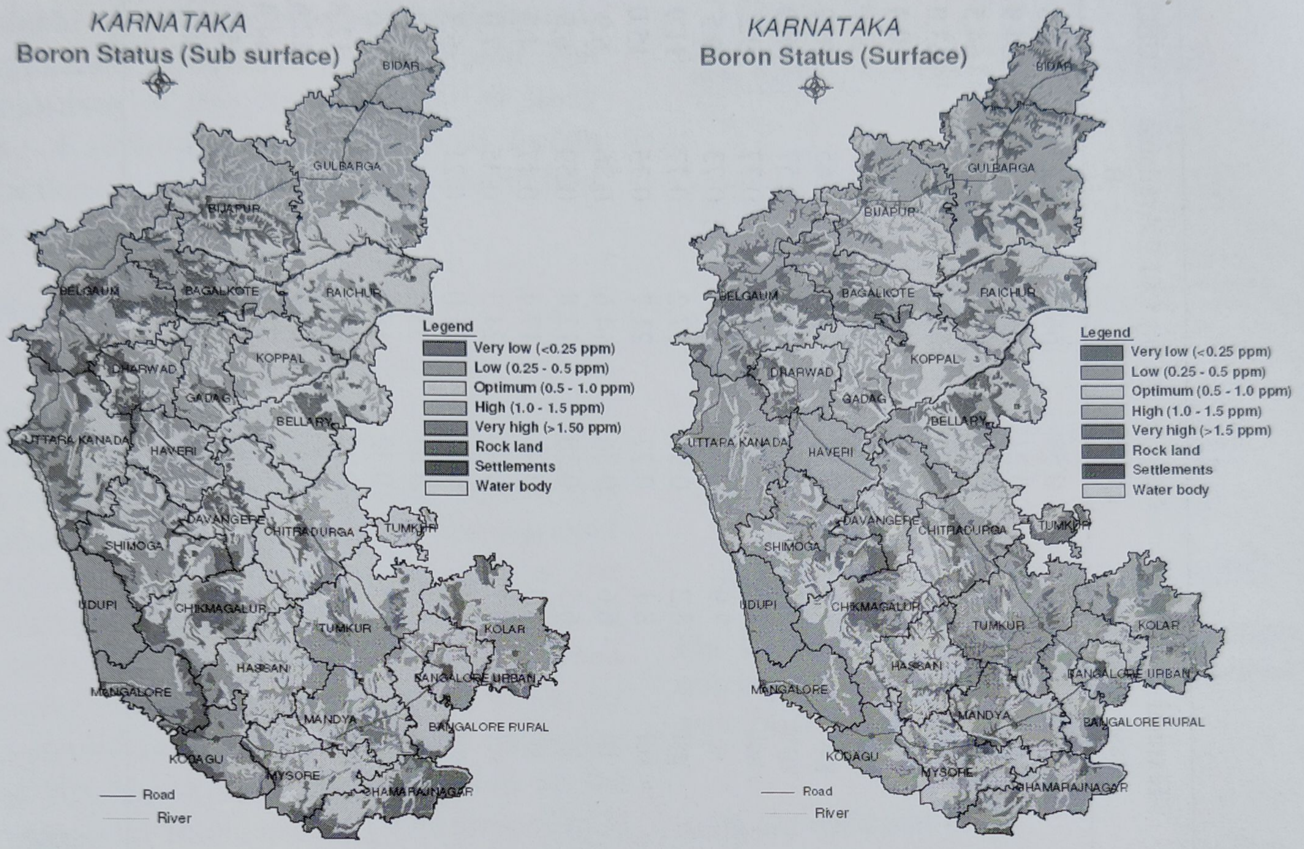

Fig. 2. *Available Boron in surface and sub surface soils of Karnataka*

Northern dry zone (Siruguppa, Bellary) and ranged from 0.03 to 0.78 mg kg^{-1}. In specifically adsorbed boron, was low in Southern Transitional zone (Arakalgudu) and high in Northern Transitional zone (Harapanahalli) and ranged from 0.06 to 0.84 mg kg^{-1}. In oxide bound boron, low in Coastal zone (Udupi) and high in Eastern dry zone (Tumkur) and ranged from 2.15 to 8.21 mg kg^{-1}. In Organically bound boron, low in Central dry zone (Tiptur) and high in Northern Transitional zone (Harapanahalli) and ranged from 2.05 to 4.23 mg kg^{-1}. The total boron and its fractions in surface, except oxide and organic bound ones correlated positively with soil reaction and OC and have no significant correlation with clay content (Table 3).

The available boron content has a significant and positive correlation with readily soluble (r = 0.887**), specifically adsorbed boron (r = 0.959**) and oxide bound boron (r = 0.584*) (Table 5). Such relationships suggest that the extractants used were reasonably selective in the fractions extracted and the oxide bound boron fraction includes tightly bound boron

Table 2. *Boron cont in different soil fractions of Karnataka.*

Soil	Location	Agroclimatic zones	Soils	Readily soluble B	Specifically adsorbed B	Oxide bound B	Organically bound B	Residual B	Total B
					←	mg/kg		→	
1	Belwataki, Dharwad	Northern dry zone	Surface soil	0.67 (0.136)	0.67 (0.14)	7.32 (1.48)	3.03 (0.61)	481.62 (97.6)	493.31
			Subsoil	1.13 (0.24)	3.54 (0.77)	4.28 (0.93)	3.43 (0.75)	446.70 (97.3)	459.08
2	Siriguppa, Bellary		Surface soil	0.78 (0.15)	0.72 (0.14)	7.45 (1.41)	3.56 (0.67)	516.43 (97.6)	528.94
			Subsoil	1.78 (0.31)	3.87 (0.77)	5.67 (0.97)	3.78 (0.65)	567.15 (97.4)	582.25
3	Tiptur, Tumkur	Central dry zone	Surface soil	0.23 (0.15)	0.42 (0.27)	3.56 (2.27)	2.05 (0.13)	150.34 (96)	156.6
			Subsoil	0.96 (0.71)	2.79 (2.1)	3.01 (2.23)	2.78 (0.21)	125.28 (92.9)	134.82
4	Sira, Tumkur		Surface soil	0.21 (0.06)	0.51 (0.14)	5.76 (1.57)	3.08 (0.84)	356.35 (97.4)	365.91
			Subsoil	1.87 (0.56)	2.18 (0.56)	3.18 (0.82)	4.19 (1.08)	378.32 (97.1)	389.74
5	Tumkur	Eastern dry zone	Surface soil	0.56 (0.17)	0.68 (0.04)	8.21 (2.46)	2.67 (0.8)	321.54 (96.4)	333.66
			Subsoil	1.08 (0.23)	1.12 (0.3)	3.28 (0.69)	3.12 (0.66)	467.70 (98.2)	476.3
6	Maddur, Mandya	Southern dry zone	Surface soil	0.57 (0.15)	0.72 (0.19)	6.45 (1.66)	3.81 (0.98)	377.22 (97)	388.77
			Subsoil	1.34 (0.38)	1.45 (0.41)	4.41 (1.25)	4.12 (1.16)	342.42 (96.8)	353.74
7	Kollegal, Chamarajanagar		Surface soil	0.12 (0.04)	0.42 (0.14)	2.99 (0.97)	3.87 (1.26)	300.66 (97.6)	308.06
			Subsoil	0.86 (0.21)	2.49 (0.62)	3.92 (0.97)	3.92 (0.97)	391.14 (97.2)	402.33
8	Arakalgudu, Hassan	Southern transition zone	Surface soil	0.03 (0.012)	0.06 (0.2)	4.89 (1.99)	2.31 (0.94)	237.90 (97)	245.19
			Subsoil	0.45 (0.12)	0.95 (0.24)	2.67 (0.69)	1.56 (0.4)	384.00 (98.6)	389.63
9	Shimoga		Surface soil	0.05 (0.02)	0.11 (0.14)	4.12 (1.68)	2.76 (1.13)	238.02 (97.1)	245.06
			Subsoil	0.43 (0.13)	1.05 (0.66)	5.67 (1.65)	2.04 (0.59)	335.46 (97.3)	344.65
10	Harapanahalli, Davangere	Northern transition zone	Surface soil	0.76 (0.29)	0.84 (0.32)	2.87 (1.1)	4.23 (1.62)	251.94 (96.7)	260.64
			Subsoil	1.62 (0.43)	4.01 (1.07)	5.28 (1.41)	4.89 (1.31)	358.67 (95.8)	374.47
11	Chethalli N. Kodagu	Hilly zone	Surface soil	0.04 (0.01)	0.12 (0.03)	3.89 (0.87)	1.56 (0.35)	439.80 (98.7)	445.41
			Subsoil	0.12 (0.21)	0.67 (0.12)	3.17 (0.57)	1.91 (0.34)	551.10 (98.9)	556.97
12	Udupi, Dakshina kannada	Coastal zone	Surface soil	0.06 (0.03)	0.09 (0.04)	2.15 (0.93)	3.76 (1.63)	224.11 (97.4)	230.17
			Subsoil	0.08 (0.03)	0.67 (0.24)	6.11 (2.2)	2.50 (0.89)	270.19 (96.7)	279.55

(Values in paranthesis show per cent of total) at the mineral surface as well as boron that has been replaced by Al or Fe through isomormous substitution within the octahedral sheet of the minerals (Hou *et al*., 1994). A non-significant but positive relationship exists between available boron and other boron fractions. Readily soluble boron has a correlated significant and positive correlation with specifically adsorbed boron (r = 0.929**) and oxide bound boron (r = 0.580*). The oxide bound boron fraction includes tightly bound boron at the mineral surface as well as boron that has been replaced by Al or Fe through isomorphous subst within the octahedral sheet of the minerals (Hou *et al*., 1994). Specifically adsorbed boron has non-significant but positive correlation with other fractions of boron. Whereas oxide bound boron correlated significantly and positively with residual boron (r = 0.646*) and total boron (r = 0.657*). Organically bound boron shows a non-significant but positively correlation with residual and total boron. A significant and positive correlation was observed between residual boron and total boron (r = 0.999**), suggesting that the sequential extraction procedure was satisfactory in terms of precision.

Relationship between and among sub-surface soil boron fractions

The mean proportion of extractable boron for subsurface soil was 0.28 per cent as readily soluble forms, 0.61 per cent as specifically adsorbed form, 1.20 per cent associated with oxide bound form, 0.75 per cent as organically bound form and the major portion of boron in soils existed as residual or occluded form which accounted for 92.92 to 98.95 per cent for subsurface soils.

Readily soluble boron content was low in soils of Coastal zone (Udupi) and high in Central dry zone (Sira) and ranged from 0.08 to 1.87 mg kg$^{-1.}$ Specifically adsorbed boron, was low in soils of Hilly zone (Chetahalli) and high in Northern Transitional zone (Harapanahalli) and ranged from 0.67 to 4.01 mg kg^{-1}. Oxide

Table 3. *Coefficient of correlation (between boron fractions and physical and -chemical properties of surface soil.*

Fractions of B	pH	OC	Clay
Rs boron	0.841**	-0.0095	0.443
Sp. Boron	0.943**	-0.269	0.254
Oxide bound B	0.529	0.195	0.444
Org bound B	0.397	-0.263	-0.183
Res boron	0.365	0.656*	0.539
Total	0.377	0.648*	0.540

* and ** are significant at 0.05 and 0.01 probability levels respectively.

bound boron was low in soils of Southern transitional zone (Arakalgudu) and high in Coastal zone (Udupi) and ranged from 2.67 to 6.11 mg kg^{-1}. Organically bound boron was low in soils of Southern transitional zone (Arakalgudu) and high in Northern Transitional zone (Harapanahalli) and ranged from 1.56 to 4.89 mg kg^{-1}. The total boron and its fractions in subsurface, except oxide and organic bound ones has positive correlation with soil reaction and OC and have no significant correlation with clay content (Table 4).

The available boron content correlated (Table 6) significantly and positively with readily soluble (r = 0.904**), specifically adsorbed boron (r = 0.797**) and organically bound boron (r = 0.782*). Such relationships suggest that the extractants used were reasonably selective in the fractions extracted and a non-significant, but positive relationship was observed between available boron and other boron fractions. Readily soluble boron correlated significantly and positively with specifically adsorbed boron (r = 0.734**) and

Table 4. *Coefficient of correlation between boron fractions and physical and -chemical properties of subsoils.*

Fractions of B	pH	OC	clay
Rs boron	0.907**	-0.326	0.144
Sp. Boron	0.749**	-0.125	0.335
Oxide bound B	-0.041	0.257	0.289
Org bound B	0.736**	-0.348	-0.091
Res boron	0.204	0.578*	0.297
Total	0.222	0.580*	0.303

* and ** are significant at 0.05 and 0.01 probability levels respectively.

Table 5. *Coefficient of Correlation between available boron and boron fractions and among fractions in surface soils.*

Fractions	available boron	Rs boron	Sp. Boron	Oxide boron	Org bound boron	Res boron	Total
Available B	1						
Rs boron	0.887**	1					
Sp. Boron	0.959**	0.929**	1				
Oxide B	0.584*	0.580*	0.523	1			
Org bound B	0.363	0.4739	0.518	-0.089	1		
Res boron	0.322	0.488	0.395	0.646*	0.051	1	
Total	0.335	0.4995	0.407	0.657*	0.0583	0.999**	1

* and ** are significant at 0.05 and 0.01 probability levels respectively

Table 6. *Coefficient of correlation between available B and boron fractions in Sub-surface soils.*

Fractions	Available B	Rs boron	Sp. boron	Oxide B	Org bound B	Res boron	Total
Available B	1						
Rs boron	0.904**	1					
Sp. Boron	0.797**	0.734**	1				
Oxide B	0.067	0.022	0.210	1			
Org bound B	0.782**	0.845**	0.699*	0.221	1		
Res boron	0.2201	0.146	0.0666	0.0074	0.0449	1	
Total	0.2401	0.166	0.0889	0.0217	0.0675	0.999**	1

* and ** are significant at 0.05 and 0.01 probability levels respectively.

organically bound boron (r = 0.845**). This is due to high amount of organically bound boron, suggesting that organic substances are very important potential pools of plant available boron. Specifically adsorbed boron correlated significantly and positively with organically bound boron (r = 0.699*), whereas oxide bound boron correlated non-significantly but positively with organically bound boron, residual boron and total boron. Organically bound boron has a non-significant but positive correlation with residual and total boron. A significant and positive correlation was observed between residual boron and total boron (r = 0.999**), suggesting that the sequential extraction procedure for sub soils was also satisfactory in terms of precision.

Conclusion

The fractionation scheme developed for soil B proved to be satisfactory in terms of sensitivity and position of soil boron. The methodology should be useful in determining the effects of soil management practices on soil boron status and in monitoring changes in boron distribution with time due to the various soil practices. It also helps in better understanding of the chemistry of B in soils and in developing an improved soil test method for available B, since, this procedure is compatible with colorimetry. Furthermore this is useful for gaining a better understanding of the chemistry of soil boron and in developing an improved soil boron extraction procedure.

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Mineralogical Transformation in Benchmark Soils of Prakasam District, Andhra Pradesh as Influenced by Weathering and Pedogenic processes

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Abstract : *The mineralogical analysis of fine sand, silt and clay fraction at different physiographic division of soils of Prakasam district was undertaken to identify the dominant minerals present in the sand, silt and clay fractions and also for understanding the rate of weathering in different soil orders developed over quartzite, sandstone and shale landscapes. The area lie between 15° 30' to 16° 00' N latitudes and 78° 45' to 79° 30' E longitudes and represented by five major physiographic divisions. The soils of hill side slope and undulating pediments are shallow, developed over quartzite and sandstone and are classified as Typic Ustorthents. Soils of upper pediplains, lower pediplains and stream bank are moderately deep to very deep, developed over quartzite, sandstone and shale landscapes and are classified as Typic Haplustepts, Typic Natrustalfs and Typic Haplusterts. Mineralogical analysis of clay fraction indicates that soils developed over quartzite and sandstone are mostly dominated by mica and kaolinite group of minerals whereas soils developed over shale are dominated by smectite group of minerals. Weathering Index clearly indicates that the rate of weathering in Vertisols was higher than Entisols, Inceptisols and Alfisols. Interestingly, the rate of weathering in Alfisols was lower than Entisols and Inceptisols. It was due to presence of exchangeable cations as it reduces the rate of weathering. The sand and silt fractions among soils orders were mostly dominated by quartz, mica, K, Na and Ca-feldspars and trace amount of heavy minerals respectively.*

Key words : Mineralogy, soil morphology, genesis, physiography, hill side, undulating pediments, upper pediplains, lower pediplains and stream bank.

Introduction

Soil clay minerals are naturally occurring inorganic materials (usually crystalline) found in soils and other earthy

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deposits (Brady, 1996). It is the product of disintegration and decomposition of parent rocks and other silicate minerals at the earth's surface. They reflect successive stages of mineralogical evolution depending on the various environmental conditions that have prevailed during soil formation (Wilson, 2004; Turpault *et al.,* 2008). Soil minerals act as "chemical sponges" which play a vital role in soil fertility since mineral surfaces serve as potential sites for nutrient storage. The physico-chemical properties of soils primarily governed and dictated by the nature of clay minerals, including a profound effect on the nature, size and stability of the aggregates, in addition, these naturally occurring clays are good cation exchanger and play a very important role in plant nutrition (Leelavathi *et al.*, 2010; Bloem, 1992; Stern, 1990). However, different types of clay minerals hold and retain differing amounts of nutrients as well as the mineralogical transformation of these clay minerals are governed by the chemical weathering, pedogenic processes and nature and properties of parent materials. Weathering is the process of disintegration and decomposition of rocks and minerals by various physical and chemical changes resulting formation of secondary products. Weathering can be studied on the basis of the development of the mineralogy and (or) chemistry from fresh rock (Weijden and Pacheco, 2003). Likewise, Pedogenesis is the process of soil formation from the unconsolidated rocks with the combined effect of soil forming factors such as climate; living organisms; parent material; topography; and time (Jenny, 1941) which exhibit their effects on the clay mineralogy (Joshi and Tambe, 2008).

Comprehensive reviews on the nature and distribution of clay minerals in Indian soils were published earlier by Mukherjee *et al.* (1971) and Ghosh and Raychaudhuri (1974). The methods of their identification and quantification were reviewed by Raman and Ghosh (1974). Later, detailed study on mineralogy of Indian soils was carried out by various workers. Ghosh and Ghosh, (1977) reported that the soils from different places in Karnataka and Kerala were dominance of kaolinite, varying from 50 to 90 per cent, with occasional presence of other minerals such as mica, smectite, vermiculite and mixed-layer minerals. Ghosh *et al.* (1974; 1976a) revealed the dominance of smectite, mica and kaolinite with occasional presence of mixed-layer minerals in alluvial soils of Bankura and Midnapore in West Bengal. Chatterjee and Dalai (1976) also reported dominance of illite together with kaolinite and halloysite and a little quartz in the red ferralitic soils of Purulia district of West Bengal. Yadav and Gupta (1974) reported that the illite (mica), smectite, chlorite and kaolinite were dominant clay minerals in the fine clay fractions of some semi-arid soils of Eastern Rajasthan and Western Uttar Pradesh. Similarly, most of the workers from the various part of the country also reported that the smectite was dominant clay minerals in black soils developed on basalt in Malwa plateau (Krishna Murti and Satyanarayana, 1970); smectite, with small amounts of illite, in the black soils of Kalahandi region in Orissa (Sahu and Nanda, 1974); smectite and kaolinite in Mandsaur district of Madhya Pradesh (Singh and Krishna Murti, 1974) and kaolinite and illite in red and yellow soil of Tripura (Ghosh, 1973). Bhattacharyya *et al., (*1993) concluded that the, smectite clay minerals are ephemeral in the humid tropical climate and they transform to kaolin.

Most of the previous workers did not studied the physiography wise variation of clay minerals differing in same locality and also effect of weathering and pedogenic processes on mineralogical transformation, hence, it was necessary to understand how clay mineralogy relates to geological and chemical weathering conditions while assessing the inherent soil fertility for appropriate large scale land management. Keeping above fact in mind, the aim of the present study was undertaken to identify the mineralogical transformation of soils as influenced by pedogenesis at different physiographic divisions in selected mandals of Prakasam district of Andhra Pradesh, India as well as to understand the rate of chemical weathering in different soil orders.

Materials and methods

General description of the area

The mineralogical analysis of fine sand, silt and clay fraction at different physiographic division of soils of Prakasam district was undertaken. The Prakasam district of Andhra Pradesh lies between 14° 55' to 16° 20' N latitudes and 78° 45' to 80° 30' E longitudes spread over an area of 2.0 million ha, however the study area i.e. Markapur, Kambham, Giddalur and Komarulu mandals of Prakasam district lies between 15° 30' to 16° 00' N latitudes and 78° 45' to 79° 30' E longitudes with total geographical area of 3, 52,185 ha. Location map of study area is given in Fig. 1.

General description of the pedons

General descriptions of pedons are given in table 1 and landscape-soil

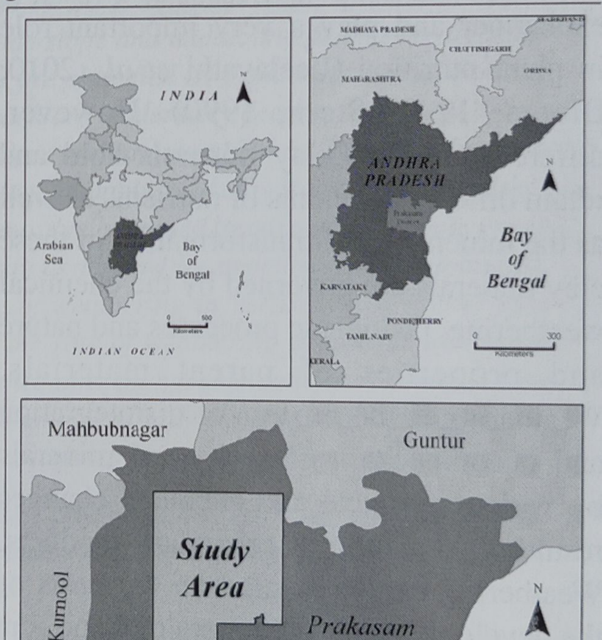


Fig. 1: *Location map of study area*

Table 1. *General descriptions of pedons*

Pedon No.	Toposheet No.	Latitude/ Longitude	Village Name	Mandal	Elevation (m)	Physiography	Slope (%)	Land Use	Drainage	Erosion	Parent material
1	57 M/2	15° 33' 23" N 79° 04' 52" E	Devanagaram	Kambham	260	Hill side	25-50	Forest	Excessively drained	Severe	Quartzite & Sandstone
2	57 M/3	15° 15' 17" N 79° 00' 26" E	Komarulu	Komarulu	240	Undulating pediments	3-10	Rainfed	Well drained	Moderate	Quartzite & Sandstone
3	57 I/14	15° 31' 01" N 79° 16' 47" E	Chollavidu	Giddalur	230	Stream bank	3-5	Waste land	Mod. well drained	Moderate to severe	Complex geology quartzite, sandstone and shale
4	57 M/2	15° 32' 05" N 79° 08' 27" E	Kalagotla	Kambham	180	Stream bank	1-5	Waste land	Well drained	Moderate to severe	Alluvium
5	57 M/2	15° 35'57"N 79° 12'11" E	Gollapalle	Markapur	180	Upper pediplains	1-3	Fallow	Mod. well drained	Slight to moderate	Quartzite & Sandstone
6	57 I/16	15° 12' 35" N 78°54' 55" E	Uyyalavada	Giddalur	160	Upper pediplains	1-3	Rainfed	Mod. well drained	Slight to moderate	Shale
7	57 I/15	15° 46' 21" N 79° 19' 19" E	Nikarampalle	Markapur	140	Lower pediplains	0-3	Rainfed	Mod. well drained	Slight to moderate	Shale

*Latitude and longitude based on Toposheet and not on GPS scale.

relationship curve in fig. 2. Alluvium, quartzite, sandstone and shale are main geologic formation in the survey area. Physiographically, the area has been divided into hill side, undulating pediments, pediplains and stream bank. The hill side slope are steep to very steep (25-50% slope) and occur at an altitude between 260 to 871 m above MSL whereas most of the area surrounding hills represents very gently to moderate sloping (1-10% slopes) of undulating pediments, upper pediplains, lower pediplains and stream bank and occur at an altitude between 120 to 240 m above MSL respectively. The study area is directly drained by river Gundlakamma and its tributaries and the drainage pattern is sub-parallel to parallel with moderate to severe

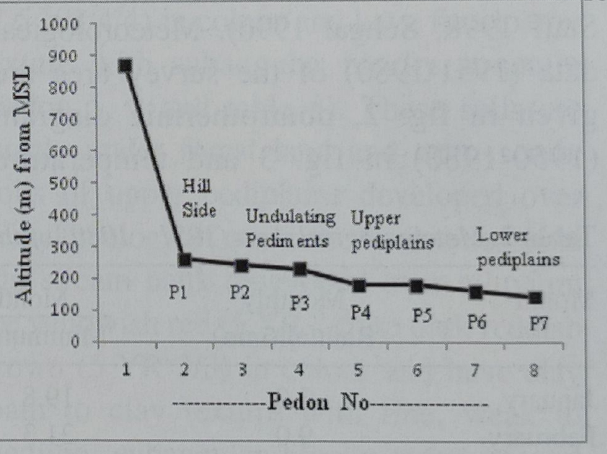


Fig. 2. *Landscape-Soil relationship curve*

Soil pedons were studied in different physiographic units i.e. hill side slope (pedon 1), undulating pediments (pedon 2), stream bank (pedon 3 and 4), upper pediplains (pedon 5 and 6) and lower pediplains (pedon 7). Details of general description of pedons are given in table 2 and fig. 4. Horizon wise sample were collected from typical pedons and analyzed and classified with standard procedure (Soil Survey Staff 1998; Black, 1985; Jackson, 1979).

Climate

The mean annual precipitation (1950-1980) of the survey area was 874 mm, of which 78.7 percent occurs between July to November. The climate is semi-arid type and mean annual temperature is 28.9 °C whereas mean summer soil temperature and mean winter soil temperature is 29.1°C and 28.1°C respectively. The soil moisture regime is *'ustic'* and soil temperature regime is *'isohyperthermic'* (Soil Survey Staff 1998; Sehgal 1996). Meteorological data (1951-1980) of the survey area are given in fig. 2, obmrothermic diagram (1950-1980) in fig. 3 and temperature curves (1950-1980) in fig. 4.

Petrographic analysis of fine sand:

The fine sand was separated in the granulometric analysis which is further separated into light and heavy mineral fractions using bromoform, sp. gr. 2.81 (Jackson, 1979), however, the permanent

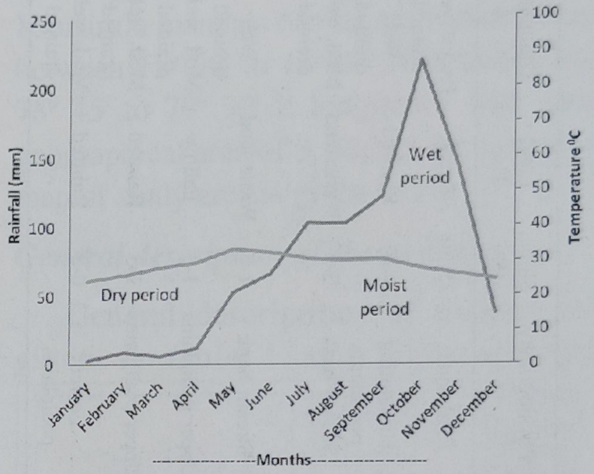


Fig. 3. *Obmrothermic diagram (1950-1980) of temperature and rainfall showing dry, moist and wet period of Prakasam district.*

Table 2. *Meteorological data (1951 - 1980) of the survey area*

Month	Monthly Rainfall(mm)	Monthly Temperature °C		Mean Monthly Temperature °C
		Minimum	Maximum	
January	3.0	19.8	29.3	24.6
February	9.0	21.3	31.0	26.2
March	6.0	23.3	33.5	28.4
April	12.0	26.1	33.5	29.8
May	53.0	28.1	39.2	33.7
June	66	28.1	37.5	32.8
July	103	26.8	34.8	30.8
August	102	26.4	34.4	30.4
September	121	26.9	34.3	30.6
October	219	24.7	31.3	28.0
November	143	22.3	30.2	26.3
December	37	20.1	29.1	24.6

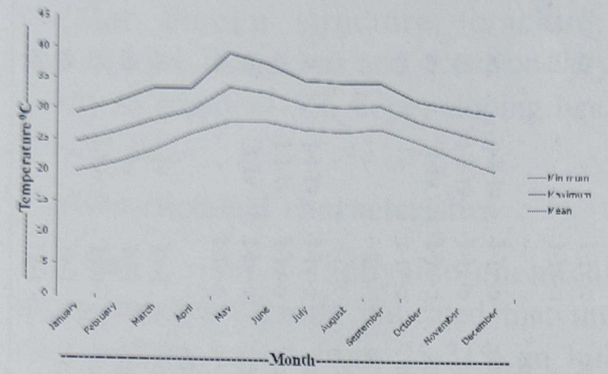


Fig. 4. *Temperature curves (1950-1980) showing mean, maximum and minimum temperature of Prakasam district.*

slides of the light and heavy mineral fractions were prepared by using Canada balsam as binding agent (Cady, 1965). The permanent slides prepared followed the procedure stated above was studied under Leitz Panphot Polarizing (Petrographic) Microscope (Cady, 1965).

X-ray diffraction analysis of fine sand, silt and clay fraction

The powdered samples of sand and silt was also mounted separately in Philips powdered sample holders (Wilson, 1987). The surface sample was smoothened using a glass slide and run on X-ray diffractometer with Ni-filtered CoKα radiation at a scanning speed of $2^0 2\theta$ per minute. The clay obtained by sedimentation technique in granulometric analysis was saturated with potassium and magnesium for x-ray diffraction analysis. The excess electrolyte was removed as per Jackson (1956). The Interpretation of x-ray diffractograms was carryout according to Brown (1961) and (Gjems, 1967) where as the semi quantitative estimation of the minerals present in soil clay sample was carried out according to procedure of (Gjems, 1967) with some modification suggested by Ghosh and Datta (1974). Weathering index of clay minerals has been calculated based on the peak area and the Jackson's (1964) weathering sequence of soil minerals.

Result

Soil Morphology

The soils of hill side slope and pediments are shallow to moderately deep, well drained and rapidly permeable. They are brown (7.5 YR 3/4) to reddish brown (7.5 YR 4/4) in colour and have fine loamy texture with subangular blocky structure (pedon 1, 2 and table 3). These soils are mostly under forest land and open scrub. Soils of upper pediplains developed over mixed geology of quartzite, sandstone, shale and stream bank developed over alluvium are yellowish red (5 YR 4/6) to dark reddish brown (5 YR 3/3) in colour and have clay loam to clay texture with fine, weak to medium, subangular blocky structure and occur on very gently to gently sloping (1-5% slope) land (pedon 3, 4, 5 and 6). These soils are mostly under rainfed cultivation in pediplains and waste land in stream bank. Soils of lower pediplains developed over shale are very dark brown (10 YR 3/2) in colour and have clay texture with fine, medium to strong, subangular blocky to

Table 3. *Morphological properties of soils**

Horizon	Depth (m)	Colour (moist)	Texture	Structure	Gravel (%)	—Consistence—			Cutans/ Slickensides/ cracks (cm)	Boun- dary	Pores	Roots	Effer- vescence
						Dry	Moist	Wet					
Pedon 1 (Hill Side): Loamy skeletal, mixed, isohyperthermic, Typic Ustorthents													
AC	0-23	7.5YR 3/4	Scl	m2sbk	36	dsh	mfr	wss wps	-	cs	f-f	f-f	-
Cr	23-55	Weathered quartzite and sandstone											
Pedon 2 (Undulating pediments): Fine loamy, mixed, isohyperthermic, Typic Ustorthents													
Ap	0-15	5 YR 4/4	Scl	m1sbk	20	dsh	mfr	ws wp	-	cs	c-vf-f	vf-f-f	es
AC	15-29	5 YR 4/4	Scl	m1sbk	25	dh	mfr	ws wp	-	gs	c-vf-f	vf-f	
Cr	29-63	Weathered quartzite and sandstone											
Pedon 3: Fine loamy, mixed, isohyperthermic, Typic Haplustepts													
Ap	0-18	7.5YR 5/4	Scl	sbk-1-m	12	dsh	mfr	ws wp	-	cs	f-vf	vf	es
Bwk1	18-42	7.5YR 4/4	Scl	sbk-2-m	25	dsh	mfr	ws wp	-	cs	f-vf	vf	es
Bwk2	42-65	5 YR 4/4	Cl	sbk-2-m	8	dh	mfr	ws wp	-	gs	f-vf	vf	ev
Bwk3	65-1.05	5 YR 4/4	Cl	sbk-2-m	8	dh	mfr	ws wp	-	-	f-vf	-	ev
Pedon 4 (Stream bank): Fine loamy, mixed, isohyperthermic, Typic Haplustepts													
Ap	0-13	7.5YR 4/6	Scl	m1sbk	20	dsh	mfr	ws wp	-	cs	c-vf-f	vf-f-p	ev
A12	13-33	5 YR 4/6	Scl	m2sbk	10	dh	mfr	ws wp	-	cs	c-vf-f	vf-f-f	ev
Bwk1	33-58	5 YR 4/6	Cl	m2sbk	10	dh	mfr	ws wp	-	gs	c-vf-f	vf-f	ev
Bwk2	58-85	5 YR 4/6	Cl	m2sbk	8	dh	mfr	ws wp	-	gs	c-vf-f	-	ev
Bwk3	85-1.10	5 YR 4/6	Scl	m2sbk	10	dh	mfr	ws wp	-	-	c-vf-f	-	ev
Pedon 5 (Upper pediplains): Fine loamy, mixed, isohyperthermic, Typic Haplustepts													
Ap	0 -15	5 YR 3/4	Scl	m2sbk	-	dh	mfr	ws wp	-	cs	c-vf-f	vf-f-p	es
Bw1	15 -40	5 YR 3/3	Scl	m2sbk	-	dh	mfi	ws wp	-	cs	c-vf-f	vf-f-f	es
Bw2	40 -60	5 YR 3/3	Sc	m2sbk	8	dh	mfi	ws wp	-	gs	c-vf-f	vf-f	es
BC	60 -86	5 YR 3/3	Sc	m2sbk	30	dh	mfi	ws wp	-	cs	c-vf-f	-	ev
Cr	86-1.10	Weathered quartzite and sandstone											
Pedon 6(Upper pediplains): Fine, smectitic, isohyperthermic, Typic Natrustalfs													
Ap	0 -15	10 YR 4/3	Cl	m2sbk	-	dsh	mfr	ws wp	-	cs	c-vf-f	vf-f-f	e
Bt1	15 -42	10 YR 4/3	C	m2sbk	-	dh	mfi	ws wp	tn-py	cs	c-vf-f	vf-f-f	es
Bt2	42 -75	10 YR 4/4	C	m2sbk	-	dh	mfi	ws wp	tk-py	gs	c-vf-f	vf-f	es
Bt3	75 -1.10	10 YR 4/4	C	m2sbk	-	dh	mfi	ws wp	tk-py	-	c-vf-f	-	es
Pedon 7 (Lower pediplains): Very fine, smectitic, isohyperthermic, Typic Haplusterts													
Ap	0-15	10 YR 3/2	C	m2sbk	-	dh	mfi	ws wp	2-5	cs	f-vf	vf	es
Bw1	15-35	10 YR 3/2	C	m2sbk	-	dh	mfi	ws wp	2-3	gs	f-vf	vf	es
Bwssk1	35-65	10 YR 3/2	C	m2sbk	-	dvh	mfi	wvs wvp	pf	cs	f-vf	vf	ev
Bwssk2	65-90	10 YR 3/2	C	m2abk	-	dvh	mvfi	wvs wvp	ss	cw	f-vf	-	ev
Bwssk3	90-1.20	10 YR 3/2	C	m2abk	-	dvh	mvfi	wvs wvp	ss	-	f-vf	-	ev

*Symbols used according to Soil Survey manual, (Soil Survey Staff, 2000 and AIS & LUS, 1970) angular blocky structure, cracking, slickensides, calcareous and occur on very gently to gently (1-5% slope) sloping land (pedon 7).

Physico-chemical characteristics

Data of physico-chemical characteristics of soils indicated that the clay content varied from 25-31% in hill side slope and undulating pediments and 24-53% in upper pediplains, lower pediplains and stream bank respectively (table 4). The Sand and silt content in all the pedons ranged from 33-63% and 11-25% respectively. Sand content in soils of higher altitude was higher and decreased with increasing depth whereas silt content in all the pedons have irregular trend with the depth. The textural class among the pedons ranged from fine loamy to fine. The pH in soils of hill side and undulating pediments ranged from 6.4 to 8.1 and 7.6 to 10.0 in upper pediplains, lower pediplains and stream bank respectively. Electrical conductivity of soils was in the range of 0.20 to 2.1 dS m^{-1}. The electrical conductivity significantly correlates with soil pH. Organic carbon content of soils ranged from 0.08 to 0.52% which decreased with depth. Organic carbon content was low to medium throughout the pedons. The $CaCO_3$ content ranged from 0.5 to 11.0% which noticed higher in stream bank and pediplains. The CEC of the soils varied from 11.2 to 46.8 cmol (p^+) kg^{-1} which corresponds to clay content in the horizons. Exchangeable bases in all the pedons irrespective of landforms were almost in the order: $Ca^{2+} \geq Mg2^{+} > Na^{+} > K^{+}$ and base saturation varied from 63.6 to 87.9%. Bulk density and particle density of the soils ranged from 1.51 to 1.85 Mg m^{-3} and from 2.48 to 2.61 Mg m^{-3} respectively among all the physiographic divisions.

Mineralogy of fine sand fraction

The minerals dominant in the fine sand fraction was identified by the petrographic and x-ray diffraction analysis method. Mineralogical analysis of fine sand fraction indicates that the strong diffraction peak at 4.34 Å identified the presence of quartz high whereas the small diffraction peak at 3.76 Å, 3.36 Å, 3.96 Å, 3.92 Å and 3.01 Å indicates presence of feldspars, K-feldspars, Na and Ca feldspars and plagioclase feldspars. Likewise, the small diffraction peak at 10.28 Å detected the presence of smectite collapsed whereas presence of Kaolinite at 7.13 Å, quartz low/ goethite at 4.23 Å, pyroxenes at 3.23 Å and 2.60 Å, amphibole at 2.74 Å and 2.73 Å also observed by small diffraction peak in both surface and sub-surface horizons among pedons (Table 5; Fig. 5(a-j) and fig. 6). Mineralogical analysis of fine sand fraction also indicates that the surface horizon (pedon 1 and 2; Typic Ustorthents) developed over hill side slope and undulating pediments was mostly dominated by Quartz high, K-feldspars, plagioclase feldspars, vermiculite, smectite collapsed and kaolinite group of clay minerals whereas the pedon 5 (Typic

Table 4. *Physico-Chemical properties of soil*

Depth (m)	Sand	Silt (%)	Clay	Texture	pH (1:2)	EC (dsm-¹)	OC (%)	$CaCO_3$ (%)	Exchangeable Bases [cmol (p^+) kg^{-1}]						ESP	BS (%)	BD	PD	Porosity (%)
									Ca	Mg	Na	K	Sum	CEC			(Mg m^{-3})		
Pedon 1 (Hill Side): Loamy skeletal, mixed, isohyperthermic, Typic Ustorthents																			
0.00-0.23	57	14	29	Scl	6.4	0.2	0.52	0.8	5.1	1.8	0.1	0.2	7.1	11.2	0.6	63.6	1.74	2.59	33
Pedon 2 (Undulating pediments): Fine loamy, mixed, isohyperthermic, Typic Ustorthents																			
0.00-0.15	57	18	25	Scl	7.8	0.3	0.39	0.8	10.5	3.6	0.2	0.3	14.6	19.7	1.2	74.2	1.68	2.59	35
0.15-0.29	49	20	31	Scl	8.1	0.3	0.33	0.5	13.8	4.2	0.2	0.4	18.6	25.2	1.0	73.8	1.72	2.56	33
Pedon 3 (Stream Bank): Fine loamy, mixed, isohyperthermic, Typic Haplustepts																			
0.00-0.18	59	17	24	Scl	9.9	1.36	0.11	4.8	12.3	9.9	12.0	0.5	34.7	44.4	27.1	78.1	1.65	2.52	35
0.18-0.42	53	18	29	Scl	9.8	1.33	0.12	11.0	11.7	11.1	13.0	0.6	36.4	46.2	28.1	78.8	1.62	2.48	35
0.42-0.65	44	25	31	Cl	10	1.53	0.17	9.0	13.8	8.7	13.3	0.5	36.3	46.3	28.7	78.5	1.59	2.48	36
0.65-1.05	45	23	32	Cl	10	2.0	0.17	3.3	11.1	9.0	11.7	0.5	32.4	40.1	29.3	80.7	1.63	2.50	35
Pedon 4 (Stream bank): Fine loamy, mixed, isohyperthermic, Typic Haplustepts																			
0.00-0.13	63	12	25	Scl	9.1	1.1	0.22	9.0	10.8	10.5	7.2	0.6	29.1	36.1	19.9	80.7	1.75	2.61	33
0.13-0.33	52	17	31	Scl	8.5	1.6	0.27	7.3	11.1	9.6	11.8	0.7	33.2	39.1	30.2	84.8	1.73	2.55	32
0.33-0.58	45	18	37	Cl	9.1	1.6	0.15	5.5	11.1	10.8	13.3	0.6	35.8	42.6	31.3	84.1	1.69	2.53	33
0.58-0.85	43	19	38	Cl	9.4	2.1	0.10	6.3	12.3	12.3	12.9	0.6	38.1	46.5	27.8	81.9	1.68	2.52	33
0.85-1.10	44	18	38	Scl	9.6	1.9	0.08	6.8	12.3	12.9	13.2	0.4	38.8	46.8	28.2	82.9	1.68	2.52	33
Pedon 5(Upper pediplains): Fine loamy, mixed, isohyperthermic, Typic Haplustepts																			
0.00 -0.15	59	16	25	Scl	7.6	0.3	0.50	0.8	10.5	9.6	0.1	0.3	20.5	27.1	0.2	75.6	1.55	2.56	39
0.15 -0.40	55	14	31	Scl	7.8	0.2	0.47	1.2	12.9	9.0	0.2	0.4	22.5	30.1	0.6	74.7	1.58	2.56	38
0.40 -0.60	53	11	36	Sc	8.2	0.3	0.38	4.0	12.3	6.9	0.2	0.3	19.8	26.4	0.8	74.9	1.58	2.53	38
0.60 -0.86	53	12	35	Sc	8.2	0.2	0.20	5.3	12.0	8.1	0.3	0.3	20.7	26.4	1.1	78.5	1.59	2.51	37
Pedon 6 (Upper pediplains): Fine, smectitic, isohyperthermic, Typic Natrustalfs																			
0.00 -.15	48	19	33	Cl	8.2	0.5	0.29	1.8	11.1	9.0	4.9	0.6	25.6	35.2	13.9	72.6	1.52	2.52	40
0.15 -0.42	43	18	39	Cl	9.0	0.7	0.24	1.8	12.9	8.1	5.6	0.6	27.2	35.6	15.7	76.3	1.55	2.52	38
0.42 -0.75	45	15	40	C	9.1	1.0	0.24	2.5	12.3	7.8	9.7	0.3	30.1	35.9	26.9	83.8	1.51	2.48	39
0.75 -1.10	44	16	40	C	9.0	1.5	0.20	2.3	9.3	8.4	8.2	0.3	26.2	35.1	23.3	74.7	1.53	2.46	38
Pedon 7 (Lower pediplains): Very fine, smectitic, isohyperthermic, Typic Haplusterts																			
0.00-0.15	41	12	47	C	8.1	0.31	0.41	5.3	10.8	8.7	0.7	0.9	21.0	27.6	2.4	76.2	1.78	2.58	31
0.15-0.35	37	12	51	C	8.6	0.33	0.39	6.0	12.9	8.1	4.0	0.9	25.9	31.0	12.8	83.5	1.85	2.52	27
0.35-0.65	33	14	53	C	8.7	0.34	0.36	6.5	13.8	8.1	5.7	0.4	28.1	34.1	16.8	82.3	1.75	2.51	30
0.65-0.90	33	18	49	C	8.8	0.58	0.36	6.5	12.3	9.0	6.9	0.5	28.8	36.6	18.9	78.6	1.78	2.55	30
0.90-1.20	34	15	51	C	8.9	0.72	0.33	6.5	9.9	10.2	9.5	0.5	30.1	34.3	27.8	87.9	1.67	2.60	36

Natrustalfs) and pedon 6 (Typic Haplustepts) developed over upper pediplains was dominated by Quartz high, smectite collapsed, feldspars, K-feldspars, plagioclase feldspars and amphibole group of minerals respectively. The minerals dominated in the surface and sub-surface horizons of pedon 7 (Typic Haplusterts) developed over lower pediplains and pedon 3 and pedon 4 (Typic Haplustepts) developed over stream bank are quartz high, feldspars, K-feldspars, Na & Ca Feldspars, smectite collapsed and plagioclase feldspars respectively.

Mineralogy of silt fraction

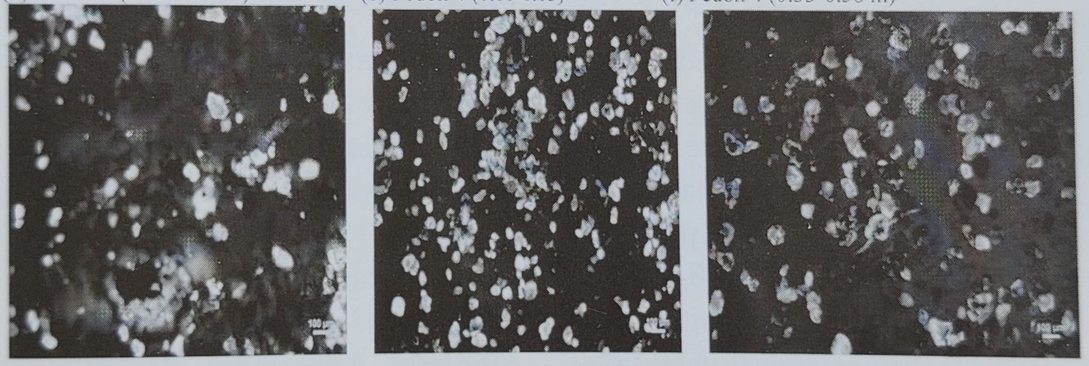
Based on relative peaks, the minerals like quartz low/goethite observed at 4.23 Å, k-feldspars at 3.32 Å, anatase at 3.52 Å, pyroxenes at 3.23 Å, plagioclase at 3.01, margarite at 3.18 Å, crystobalite at 3.15 Å and microcline at 2.97 Å respectively identified in surface and sub-surface horizons of silt fractions among pedons (table 5; fig. 7). Mineralogical analysis of silt fraction indicates that the surface horizon (pedon 1 and 2; Typic Ustorthents) developed over hill side slope and undulating pediments was mostly dominated by margonite, quartz low/goethite, K-feldspars, margarite, plagioclase feldspars, kaolinite, chlorite, anatase and pyroxenes group of minerals whereas the pedon 6 (Typic Natrustalfs) and pedon 7 (Typic Haplustepts) developed over upper pediplains was dominated by Margonite, Quartz high, K-feldspars, Plagioclase feldspars, smectite collapsed, quartz low/goethite, pyroxenes, margarite and amphibole group of minerals respectively. The minerals in the surface and sub-surface horizons of pedon 7 of Typic Haplusterts developed over lower pediplains and pedon 3 and pedon 4 of Typic Haplustepts developed over stream bank was also dominated by Margonite, Quartz high, K-feldspars, Plagioclase feldspars, smectite collapsed, quartz low/goethite, pyroxenes, margarite and amphibole group of minerals respectively. The variation in the minerals within the physiographic divisions was almost similar.

Mineralogy of clay fraction

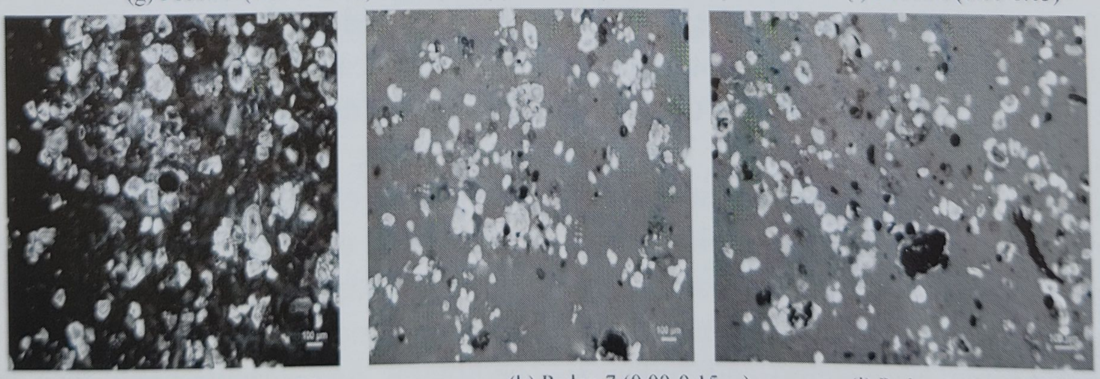
The semi-quantitative estimation based on relative peak intensities Mg-glycerol saturated clay observed in XRD pattern that the mica was dominating clay minerals at 10.28 Å, 10.20 Å and 9.40 Å whereas smectite was dominating clay minerals at peak 21.03 Å, 19.63 Å and 18.34 Å. Similarly, dominating clay minerals like Kaolinite identified by its Mg-glycerol saturated peak at 7.25 Å and 7.13 Å and these peaks disappeared on heating at 550°C (table 5; fig. 8). Further, the mineralogical analysis of clay fraction indicates that the surface and sub-surface horizons of all the pedons (except pedon 7) developed over hill side slope, undulating pediments, upper pediplains and stream bank was mostly dominated by mica and kaolinite group of minerals followed by smectite in less amount whereas the surface and sub-surface

a) Pedon 1(0.00-0.23 m) (b) Pedon 2 (0.00-0.15 m) (c) Pedon 3 (0.00-0.18 m)

(d) Pedon 3 (0.42-0.65 m) (e) Pedon 4 (0.00-0.13) (f) Pedon 4 (0.33-0.58 m)



(g) Pedon 5 (0.00-0.15 m) (h) Pedon 5 (0.40 -0.60 m) (i) Pedon 6 (0.00-0.15)



(j) Pedon 6 (0.42-0.75) (k) Pedon 7 (0.00-0.15 m) (l) Pedon 7 (0.35-0.65 m)

Fig. 5(1-I): *Mineralogy of fine sand fraction by Petrographic method*

Table 5. *Mineralogy of fine sand, silt and clay fraction.*

Pedon	Physiography	Soil order at	Name of minerals Sand		Silt	Clay		
No		family level	Surface horizon	Sub-surface horizon	Surface	Sub-surface	Surface	Sub-surface
Pedon 1	Hill Side	Loamy skeletal, mixed, isohyperthermic, Typic Ustorthents	Vermiculite Smectite collapsed Quartz high K-feldspars Pyroxenes Plagioclase feldspars Amphibole Pyroxene	NH*	Margonite Quartz low/Goethite K-feldspars Margarite Plagioclase feldspars Kaolinite	NH*	Smectite Mica Kaolinite	Smectite Mica Kaolinite
Pedon 2	Undulating pediments	Fine loamy, mixed, isohyperthermic, Typic Ustorthents	Quartz high Feldspars K-feldspars	NH*	Chlorite Margonite Kaolinite Quartz low/Goethite Anatase K-feldspars Pyroxenes Plagioclase feldspars	NH*	Smectite Mica Kaolinite	Smectite Mica Kaolinite
Pedon 3	Stream bank	Fine loamy, mixed, isohyperthermic, Typic Haplustepts	Quartz high K-feldspars Plagioclase feldspars	Quartz high Feldspars K-feldspars	Quartz low/Goethite K-feldspars Margarite	Quartz low/ Goethite K-feldspars	Smectite Mica Kaolinite	Smectite Mica Kaolinite
Pedon 4	Stream bank	Fine loamy, mixed, isohyperthermic, Typic Haplustepts	Quartz high Feldspars K-feldspars Plagioclase feldspars	Smectite collapsed K-feldspars	Quartz low/ Goethite K-feldspars Margarite Plagioclase feldspars	K-feldspars	Smectite Mica Kaolinite	Smectite Mica Kaolinite
Pedon 5	Upper pediplains	Fine loamy, mixed, isohyperthermic, Typic Haplustepts	Smectite collapsed Quartz high Feldspars K-feldspars Plagioclase feldspars	Smectite collapsed Quartz low/ Goethite K-feldspars	Margonite Quartz high K-feldspars Plagioclase feldspars Amphibole	Smectite collapsed Quartz low/ Goethite K-feldspars Margarite Plagioclase feldspars Pyroxenes Amphibole	Smectite Mica Kaolinite	Smectite Mica Kaolinite

Table 5. *Continued....*

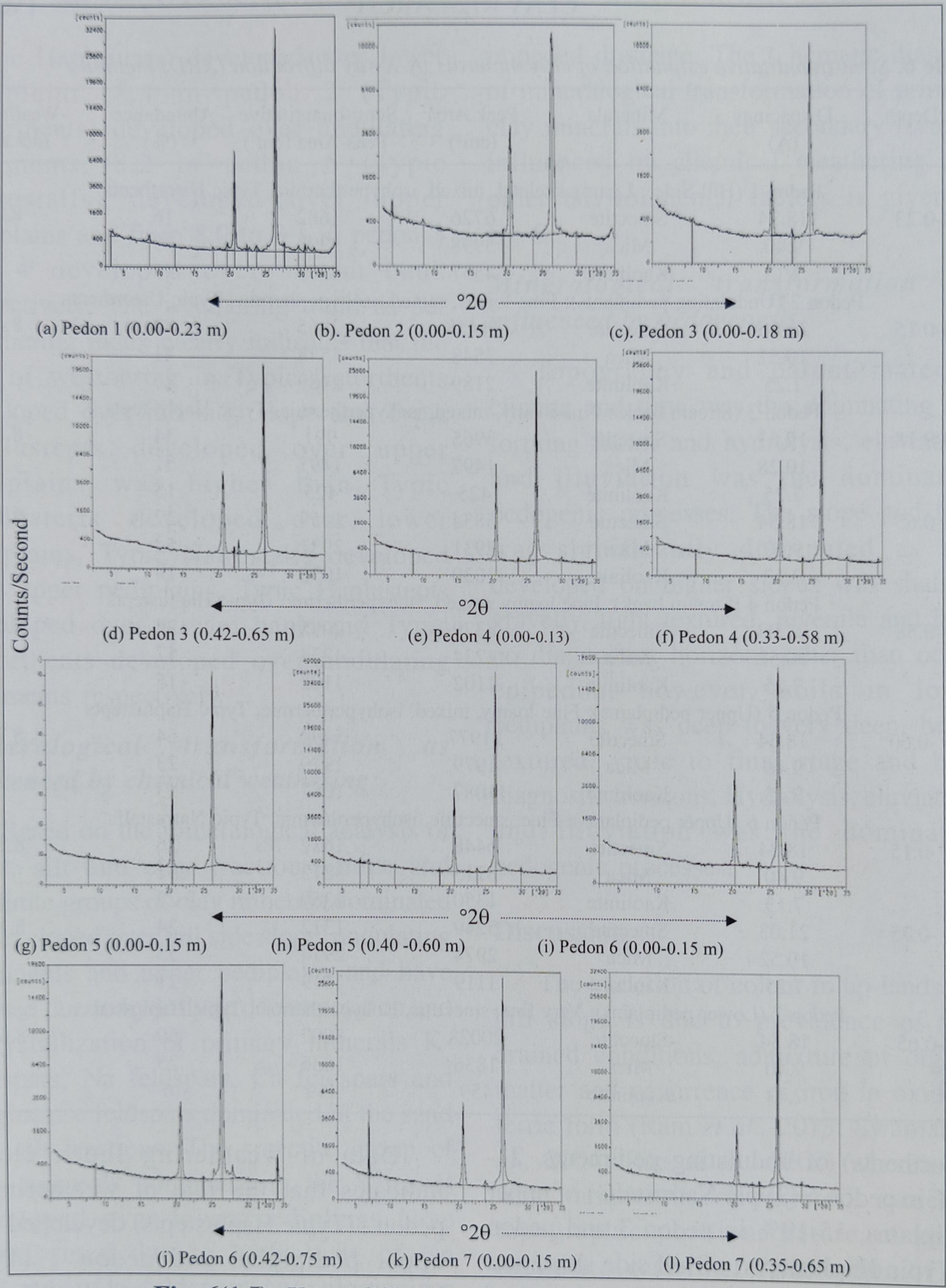
Pedon No	Physiography	Soil order at family level	Name of minerals Sand		Silt	Clay		
			Surface horizon	Sub-surface horizon	Surface	Sub-surface	Surface	Sub-surface
Pedon 6	Upper pediplains	Fine, smectitic, isohyperthermic, Typic Natrustalfs	Smectite collapsed Quartz high Feldspars K-feldspars Amphibole	Smectite collapsed Quartz high Feldspars K-feldspars	Quartz low/ Goethite K-feldspars	Quartz low/ Goethite K-feldspars Margarite	Smectite Mica Kaolinite	Smectite Mica Kaolinite
Pedon 7	Lower pediplains	Very fine, smectitic, isohyperthermic, Typic Haplusterts	Quartz high Feldspars K-feldspars	Smectite collapsed Quartz high Na-Feldspars Ca-Feldspars K-feldspars Plagioclase feldspars	Quartz low/ Goethite K-feldspars Ca- feldspars Margarite Crystobalite	Quartz low/ Goethite K-feldspars Margarite	Smectite Mica Kaolinite	Smectite Mica Kaolinite

NH*=No sub-surface horizon

horizons of pedon 7 of Typic Haplusterts developed over lower pediplains indicates that the smectite group of minerals such as montmorrilonite was dominant and it was just reverse to rest of the soil order.

Weathering Index in relation to clay minerals and soil order:

The weathering index in relation to clay minerals and soil order is given in Table 6. The semi-quantitative estimation of clay minerals based on relative peak intensities in XRD pattern observed that the smectite was dominant clay minerals in pedon 7 (Typic Haplusterts) of lower pediplains, constituting about 69% followed by 64% in pedon 5 (Typic Haplustepts) of upper pediplains, 27-34% in pedon 3 and pedon 4 (Typic Haplustepts) of stream bank, 33% in pedon 2 (Typic Ustorthents) of undulating pediments and 16% in pedon 1 (Typic Ustorthents) of hill side slope respectively. The mica was dominant clay minerals in pedon 3 and pedon 4 (Typic Haplustepts) of stream bank, constituting about 51-57% followed by 52% in pedon 6 (Typic Natrustalfs) of upper pediplains, 41% in pedon 2 (Typic Ustorthents) of undulating pediments, 39% in pedon 1 (Typic Ustorthents) of hill side slope, 25% in pedon 7 (Typic Haplusterts) of lower pediplains and 23% in pedon 5 (Typic Haplustepts) of upper pediplains respectively. Kaolinite was dominant clay minerals in pedon 1 (Typic Ustorthents) of hill side slope, constituting about 45% followed by 25% in pedon 2 (Typic



(a) Pedon 1 (0.00-0.23 m) (b). Pedon 2 (0.00-0.15 m) (c). Pedon 3 (0.00-0.18 m)

(d) Pedon 3 (0.42-0.65 m) (e) Pedon 4 (0.00-0.13) (f) Pedon 4 (0.33-0.58 m)

(g) Pedon 5 (0.00-0.15 m) (h) Pedon 5 (0.40 -0.60 m) (i) Pedon 6 (0.00-0.15 m)

(j) Pedon 6 (0.42-0.75 m) (k) Pedon 7 (0.00-0.15 m) (l) Pedon 7 (0.35-0.65 m)

Fig. 6(1-I): *X ray diffraction analysis of fine sand fraction*

Table 6. *Semi-quantitative estimation of clay minerals by X-ray diffraction (XRD) method*

Soil Depth (m)	D spacings (Å)	Minerals	Peak Area (cm^2)	Semi-quantitative Peak Area (cm^2)	Abundance (%)	Weathering Index (%)
Pedon 1 (Hill Side): Loamy skeletal, mixed, isohyperthermic, Typic Ustorthents						
0.00-0.23	18.34	Smectite	6726	1682	16	8.7
	9.40	Mica	3998	3998	39	
	7.13	Kaolinite	4557	4557	45	
Pedon 2 (Undulating pediments): Fine loamy, mixed, isohyperthermic, Typic Ustorthents						
0.00-0.15	21.03	Smectite	11458	2865	33	8.4
	10.52	Mica	3548	3548	41	
	7.25	Kaolinite	2189	2189	25	
Pedon 3 (Stream bank): Fine loamy, mixed, isohyperthermic, Typic Haplustepts						
0.00-0.18	19.63	Smectite	3965	991	34	8.1
	10.28	Mica	1497	1497	51	
	7.25	Kaolinite	425	425	15	
0.42-0.65	18.34	Smectite	5834	1459	27	8.1
	9.40	Mica	2931	2931	54	
	7.13	Kaolinite	1030	1030	19	
Pedon 4 (Stream bank): Fine loamy, mixed, isohyperthermic, Typic Haplustepts						
0.33-0.58	21.03	Smectite	8379	2095	28	8.0
	10.52	Mica	4234	4234	57	
	7.25	Kaolinite	1102	1102	15	
Pedon 5 (Upper pediplains): Fine loamy, mixed, isohyperthermic, Typic Haplustepts						
0.40 -0.60	18.34	Smectite	21977	5494	64	8.7
	9.40	Mica	1979	1979	23	
	7.13	Kaolinite	1087	1087	13	
Pedon 6 (Upper pediplains): Fine, smectitic, isohyperthermic, Typic Natrustalfs						
0.00 -0.15	18.34	Smectite	6448	1612	26	8.2
	9.40	Mica	3213	3213	52	
	7.13	Kaolinite	1350	1350	22	
0.42 -0.75	21.03	Smectite	5249	1312	24	8.1
	10.52	Mica	2974	2974	55	
	7.25	Kaolinite	1119	1119	21	
Pedon 7 (Lower pediplains): Very fine, smectitic, isohyperthermic, Typic Haplusterts						
0.35-0.65	18.34	Smectite	20028	5007	69	8.6
	9.40	Mica	1836	1836	25	
	7.13	Kaolinite	459	459	6	

Ustorthents) of undulating pediments, 21-22% in pedon 6 (Typic Natrustalfs) of upper pediplains, 15-19% in pedon 3 and pedon 4 (Typic Haplustepts) of hill side slope and only 6% in pedon 7 (Typic Haplusterts) of lower pediplains respectively.

Data of weathering Index clearly indicates that the rate of weathering in pedon 5(Typic Haplustepts) developed over upper pediplains and pedon 1 (Typic Ustorthents) developed over hill side slope was 8.7 whereas it was 8.6 in pedon 7

(Typic Haplusterts) developed over lower pediplains, 8.4 in pedon 2 (Typic Ustorthents) developed over undulating pediments, 8.2 in pedon 6 (Typic Natrustalfs) developed over upper pediplains and from 8.0 to 8.1 in pedon 3 and 4 developed over stream bank respectively. The weathering trend as per weathering index clearly indicates that the rate of weathering in Typic Ustorthents developed over hill side slope and Typic Haplustepts developed over upper pediplains was higher than Typic Haplusterts developed over lower pediplains, Typic Natrustalfs developed over upper pediplains, Typic Haplustepts developed over stream bank and Typic Ustorthents developed over undulating pediments respectively.

Mineralogical transformation as influenced by chemical weathering:

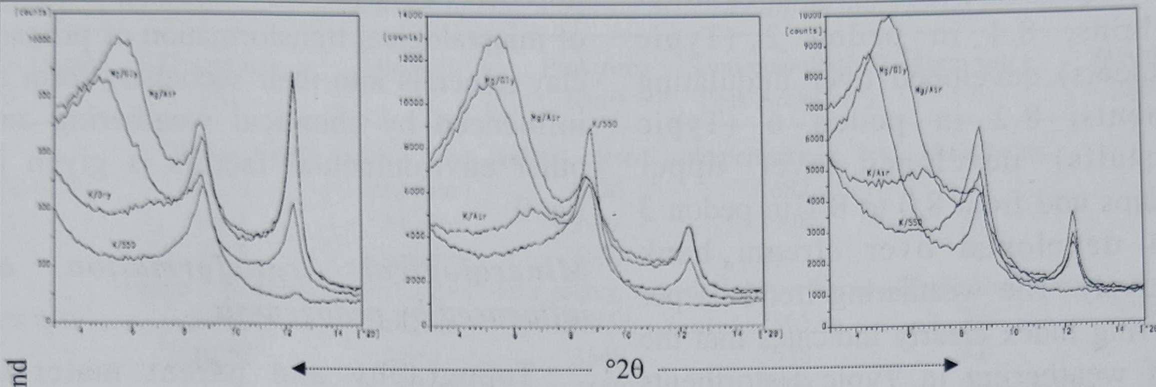
Based on the mineralogical analysis of sand, silt and clay fractions, mica and kaolinite groups of clay minerals dominated in developed over hill side slope, undulating pediments and upper pediplains and have formed due to hydrolytic decomposition and recrystallization of primary minerals K-feldspars, Na feldspars, Ca feldspars and plagioclase feldspars dominated in the sand and silt fractions. The smectite group of clay minerals dominated in the Vertisols developed over lower pediplains have transformed due to hydrolysis of Na feldspars, Ca feldspars and plagioclase feldspars in alkaline environment and impeded drainage. The schematic diagram of mineralogical transformation of primary clay minerals into their secondary form as influenced by chemical weathering and other environmental factors is given in fig. 9.

Mineralogical transformation as influenced by pedogenesis

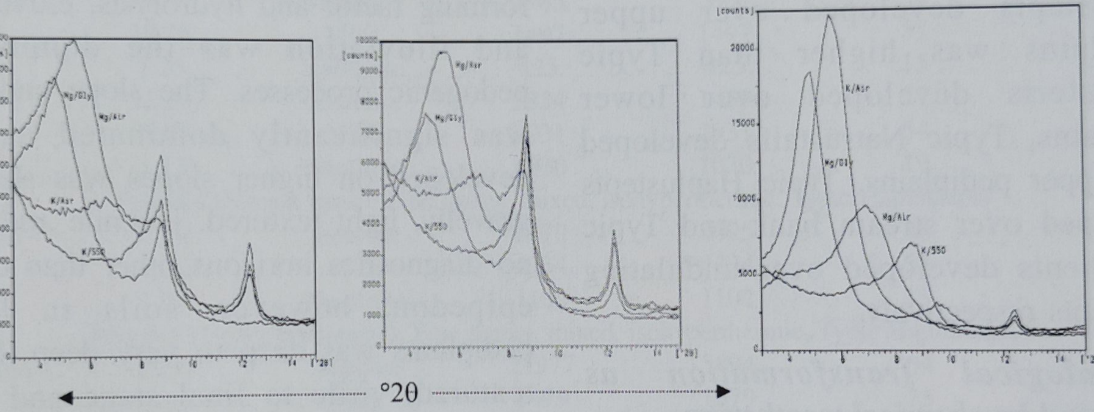
Topography and parent material, climate and time was the dominating soil forming factor and hydrolysis, eluviations and illuviation was the dominating pedogenic processes. The slope and time was significantly dominated as soil developed on higher slopes was shallow, gravelly, light textured, juvenile and have no diagnostics horizons other than ochric epipedon, however, soils in lower pediplains was deep to very deep, heavy textured, virile to final stage and have diagnostic horizons. Hydrolysis, eluviations and illuviation was the dominating pedogenic processes.

Discussion

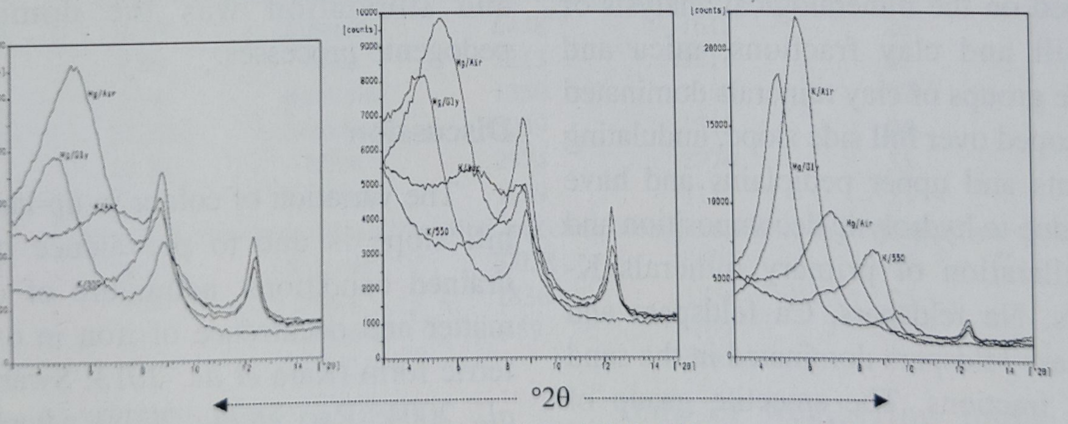
The variation of colour in up-lands and hill slope is due to prevalence of well drained conditions, admixture of organic matter and occurrence of iron in oxidized ferric form (Ram *et al.,* 2013; Swarnam *et al.,* 2004; Rao *et al.,* 2008) whereas the wide variation in soil texture is caused by topographic position, nature of parent material, weathering, translocation of clay and age of soils (Nayak *et al.,* 2002). The variation in soil structure is a reflection of



(a) Pedon 1 (0.00-0.23 m) (b) Pedon 2 (0.00-0.15 m) (c) Pedon 3 (0.00-0.18 m)

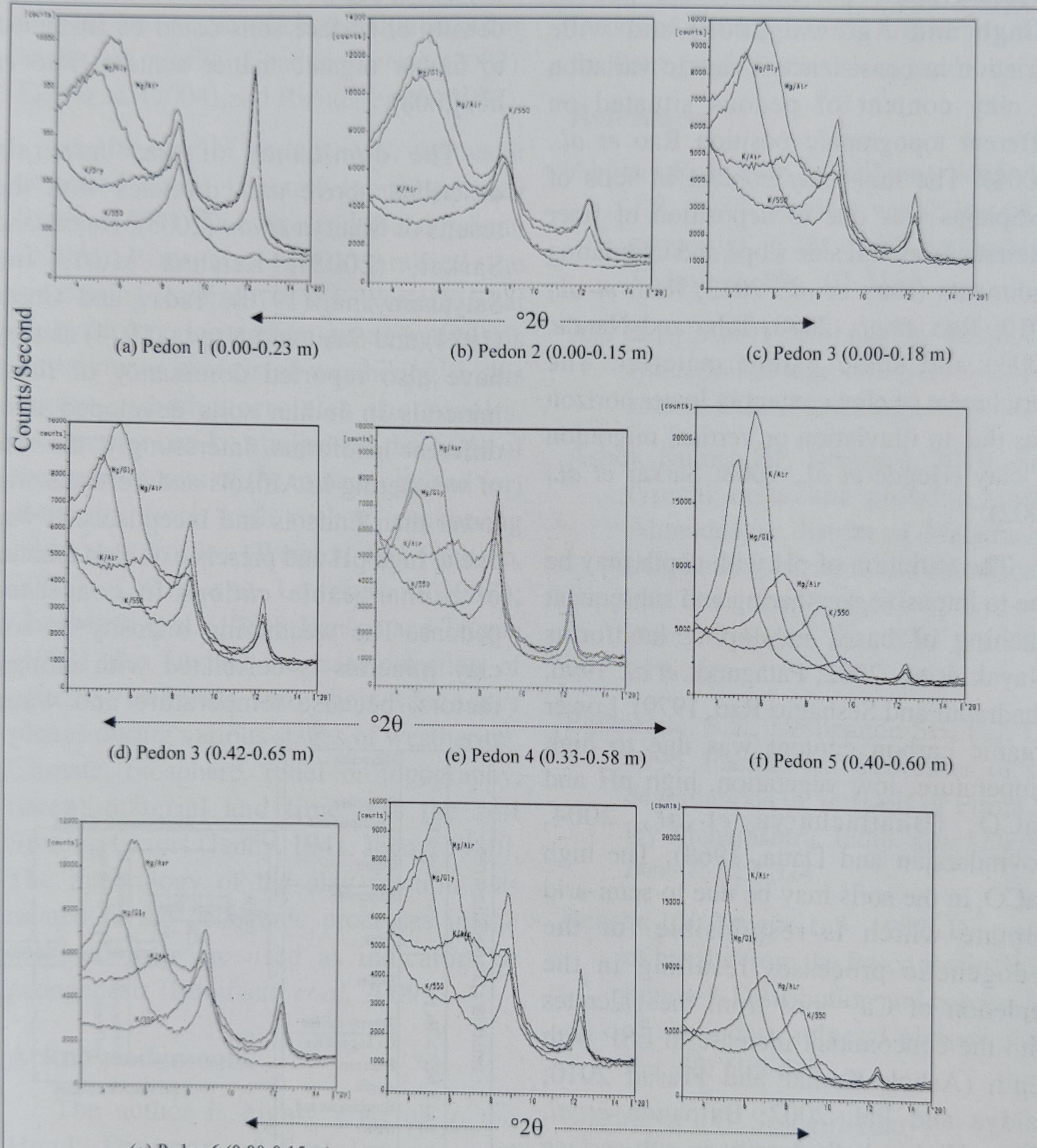


(d) Pedon 3 (0.42-0.65 m) (e) Pedon 4 (0.33-0.58 m) (f) Pedon 5 (0.40-0.60 m)



(g) Pedon 6 (0.00-0.15 m) (h) Pedon 6 (0.42 -0.75 m) (i) Pedon 7 (0.35-0.65 m)

Fig. 7. (a-j): *X-ray diffraction analysis of silt fraction*



(a) Pedon 1 (0.00-0.23 m)

(b) Pedon 2 (0.00-0.15 m)

(c) Pedon 3 (0.00-0.18 m)

(d) Pedon 3 (0.42-0.65 m)

(e) Pedon 4 (0.33-0.58 m)

(f) Pedon 5 (0.40-0.60 m)

(g) Pedon 6 (0.00-0.15 m)

(h) Pedon 6 (0.42 -0.75 m)

(i) Pedon 7 (0.35-0.65 m)

Fig. 8. (a-j): *X-ray diffraction analysis of clay fraction*

physio-graphic position of the pedons (Singh and Agrawal 2003) and wide variation in consistence is due to variation in clay content of pedons situated on different topographic position Rao *et al.,* (2008). The high clay content in soils of pediplains was due to deposition of finer fractions from hill side slope and undulating pediments (Ram *et al.,* 2013; Ram *et al.,* 2010; Rao *et al.,* 2008, Taha and Nanda, 2003) and shale parent material. The enrichment of clay content in lower horizon was due to illuviation or vertical migration of clay (Hegde *et al.,* 2008; Sarkar *et al.,* 2002).

The variation of pH with depth may be due to intensive weathering and subsequent leaching of bases in sloping landforms (Nayak *et al.,* 2002; Patagundi *et al.* 1996, Bhadrapur and Seshagiri Rao, 1979). Lower organic carbon content was due to high temperature, low vegetation, high pH and $CaCO_3$ (Bhattacharya *et al.,* 2004, Govindarajan and Datta, 1968). The high $CaCO_3$ in the soils may be due to semi-arid climate which is responsible for the pedogenetic processes resulting in the depletion of Ca^{2+} ions from the calcretes with the concomitant increase in ESP with depth (Ashok Kumar and Prasad 2010; Vaidya and Pal, 2002; Balpande *et al.* 1996). Higher bulk density in sub-surface horizons was observed which may be due to high clay content, greater compaction in swelling clay soils and organic carbon. (Ashok Kumar and Prasad, 2010; Ahuja *et al.,* 1988; Jewitt *et al.,* 1979). Lower bulk density of surface soils could be attributed to higher organic matter content (Rao *et al.,* 2008).

The dominancy of clay minerals described above are correlates with the results of Maurya *et al.,* (2005); Nayak and Sarkar, (2005); Krishna Murti and Satyanarayana, (1970); Yadav and Gupta (1974) and Sahu and Nanda (1974) as they have also reported dominancy of these minerals in Indian soils developed over different landforms. Interestingly, the rate of weathering in Alfisols and Vertisols was lower than Entisols and Inceptisols. It was due to high pH and presence of high amount of exchangeable cations in concerned pedons. The weathering intensity of soil clay minerals is correlated with climate factors, because temperature and water

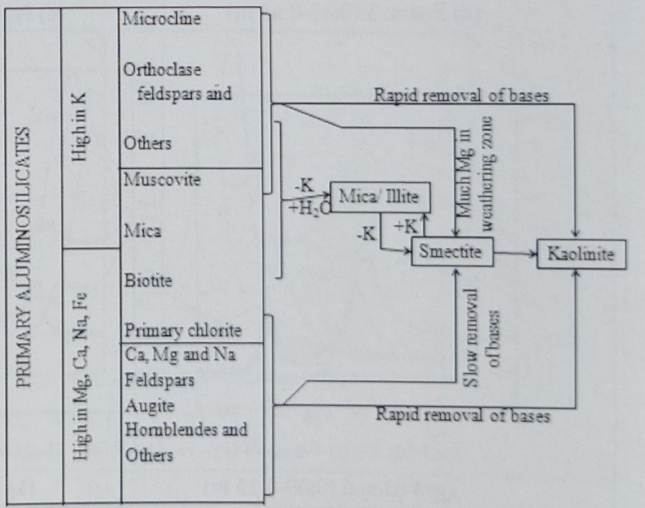


Fig. 9. *Schematic diagram of mineralogical transformation of primary clay minerals into their secondary form as influenced by chemical weathering.*

availability in soils strongly affect the amount and extent of chemical weathering in the soil profile (Chadwick *et al.* (2003); Egli *et al.* (2004) and Richter *et al.* (2007).

In the case of pedogenesis, the result as stated above is totally correlate with Brady (1996). Deepthy and Balakrishnan (2005); Bourgeon (2001) studied the weathering patterns in the Western Ghat (Sahyadri) region and proposed hydrolysis as the major process of weathering in this region, which correlates the results. Weathering can be studied on the basis of the development of the mineralogy and (or) chemistry from fresh rock to weathering rinds and profiles (Weijden and Pacheco, 2003). Craig and Loughnan (1964); Chesworth et al. (1981); Benson and Teague (1982) also studied the transformation of primary minerals into their secondary phases during various stages of weathering. Climate, biosphere, relief or topography, parent material and time was the soil forming factors (Jenny, 1941, Jenny, 1980), The mineralogy of the clay fraction was related to the pedogenic processes in the soil and they are used as indicators of pedogenesis (Bonifacio *et al.* 2009).

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Weathering of Silicate Minerals by Humic Acids : I. Nature of Cation Solubilisation from Olivine and Tourmaline and Characteristics of the Residual Products

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Abstract : *An attempt has been made here to understand the effect of HAs (extracted from Entisol, Alfisol and Mollisol) on the differential release of cations from the silicates, viz., olivine (neso) and tourmaline (cyclo), their relative order of stabilities, the kinetics of solubilisation processes and nature of the residual products on weathering. The kinetics curves of dissolution of both the minerals are unique in consisting of a series of recurring peaks and troughs signifying a cycle of alternate dissolution and reprecipitation. The release of cations from the structure being dependent on its respective position in the crystal lattice which in turn determines the access of HA to it; in addition, the stability of the chelate formed between HA and that particular cation is a determinant. Study of the residues of mineral-HA reaction showed that not only the easily weatherable olivine but also the resistant tourmaline has undergone significant changes including reduction in* $Fe^{2+/3+}$ *and* Si^{4+} *and enrichment in* Al^{3+} *and* Mg^{2+} *(olivine only). Emergence of new crystalline phases are evident from the XRD data while IR studies point out the deposition of HA on mineral surface probably after complexation with ionic constituents in the minerals.*

Key words **:** Weathering, silicates, olivine, tourmaline, humic acids, cation, solubilisation.

The mechanisms controlling silicate dissolution have always been a point to debate. The propounders of the diffusion theory assert the formation of an altered surface enriched in highly polymerized Si and Al (Weissbart and Rimstidt, 2000; Benzerara *et al.*, 2005) or formed due to interfacial dissolution-reprecipitation (Hellmann *et al.*, 2003) controlling further diffusion of cations while those favouring the surface-controlled process (Blum and Lasaga, 1988; Hansley and Briggs, 1994) emphasize the formation of activated complex and subsequent detachment of silica and alumina species through decomposition of these surface complexes when they are in the activated state (Stumm and Wieland, 1990) after initial rapid release of alkalis for protons. Overall, the crystallo-chemical structure of the primary

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minerals especially their lattice imperfections influences the actual mechanism of dissolution (Wehrli *et al.*, 1990; Hamer *et al.*, 2003). The dissolution of olivine in acidic solutions, is initially incongruent but dissolve congruently thereafter (Seyama *et al.*, 1996; Pokrovsky and Schott, 2000a). The activated complex for forsterite dissolution involves a hydronium ion for proton-promoted, and H^+ ion and a ligand for ligand-promoted (Drever and Vance, 1994), adsorbed on to the bridging oxygen atoms of Si-O-Mg on the forsterite surface which dissociates to form H-O-Si bonds as water molecules move from the solution to co-ordinate Mg atoms as $[Mg(H_2O)_6]^{2+}$ which is the rate-controlling step for dissolution (Rosso and Rimstidt, 2000; Pokrovsky and Schott, 2000b). The rate determining step for the overall dissolution process is the release of silica (as H_4SiO_4) from the surface (Liu *et al.*, 2006). Olivine exhibit an extremely fragmented surface while tourmaline presents etching of the grain surface and dissolution of the ultrafine particles present in the grain surface after being treated by organic acids (Varadachari *et al.*, 1994), with the emergence of new crystalline phases in both the cases. Dissolution in the presence of organic ligands including humic acids (HAs) is surface-controlled (Song and Huang, 1988; Ochs *et al.*, 1993). Organic acids are known to enhance mineral dissolution (Drever and Stillings, 1997; Welch *et al.*, 1999) either directly by a proton- or a ligand-mediated mechanism (Furrer and Stumm, 1986; Stumm and Wieland, 1990) or indirectly by the formation of complexes in solution (Tan, 1993; Strobel, 2001). The ligand-mediated mechanism is dependent on the structure and concentration of the ligand and the accessibility of the ligand ions to the cations and the extent to which the removal of one ion affects the neighbouring ions (Holdren and Speyer, 1985; Barman *et al.*, 1992). HAs are more effective in enhancing dissolution than organic acids (Schnitzer and Kodama, 1976; Tan, 1980) in their ability to exert both acidic and interaction effects.

After a thorough literature survey, it came to light that studies pertaining to weathering of silicates by organic acids are confined to mainly olivine and feldspars with low molecular weight organic acids. Therefore, the weathering reactions of silicates by HAs call for further research. The present study aimed at understanding the implications of primary silicate mineral weathering by HAs in relation to pedogenesis and nutrient release and the transformations brought about in the residues. The study included the kinetics of dissolution of the primary minerals by HAs at varying pH and analysis of the residues formed due to the interaction of primary minerals with HAs. The current study did not limit its focus to olivine rather extended it to include one cyclosilicate, viz., tourmaline.

Materials and Methods

Characterisation of minerals

The minerals used in this study are olivine (nesosilicate) and tourmaline (cyclosilicate) provided by the Geological Survey of India, Kolkata. The minerals were powdered and dry-sieved to the 80-150 mesh B.S. size fraction, washed and dried at 80^{0}C. X-ray diffraction (XRD) of the minerals as well as their weathered products was recorded on a Philips PW 1140 x-ray diffractometer using Ni-filtered CuKα radiation at a scanning speed of 1^{0}2θ/min and IR spectra on a Perkin Elmer model FTIR RX1 spectrometer within a scanning range of 4000 to 400 cm^{-1} using pellets containing KBr as matrix.

Chemical analysis of the samples was done according to a combined scheme of (1) Shapiro and Brannock and (2) Riley (Maxwell, 1968; Jeffery, 1970). A portion of the sample fused with NaOH was analysed for Si^{4+} as the molybdenum blue complex (Maxwell, 1968). Another portion of the sample, digested with HF-$HClO_4$ mixture, was analysed for $Fe^{2+/3+}$ as the o-phenanthroline complex (Maxwell, 1968), Al^{3+} as the calcium aluminium alizarin-red S complex (pH adjusted to 4-5), Ti^{4+} as the H_2O_2 complex (Jeffery *et al.*, 1991) and B^{3+} as the 1-1' dianthrimide complex in H_2SO_4 medium (Snell and Snell, 1959), Ca^{2+} and Mg^{2+} by AAS and Na^+ and K^+ by flame photometry (Jackson, 1973). Adsorbed water (H_2O^-) and water lost by heating to 1000^{0}C (H_2O^+) were also determined.

Extraction and characterisation of humic acids

The HAs were extracted from the surface soil (0-15 cm) of an Entisol (Aeric Fluvaquent; deltaic new alluvium; Baruipur, W. Bengal), Alfisol (Ultic Paleustalf; ferruginous soil; Vishnupur, W. Bengal) and Mollisol (Typic Hapludoll; mountain soil; Auli, Uttarakhand). The method of extraction, fractionation, purification and characterisation of HAs was carried out broadly as suggested by Schnitzer and Khan (1972), Chen *et al.* (1977) and Ahmed *et al.* (2002). The HAs were characterised for their C, H and N contents, E_4/E_6 ratio, NaOH titratable acidity and total acidity (Varadachari *et al.*, 1992). Concentrations of Si^{4+}, $Fe^{2+/3+}$, $Al^{3+}$and Mg^{2+} present in HA were determined. Si^{4+} was determined as the silico-molybdate complex (Maxwell, 1968) after fusing with NaOH. The determination of $Fe^{2+/3+}$ was done as the o-phenanthroline complex, Al^{3+} as the calcium-aluminium-alizarin-red S complex (Maxwell, 1968) and Mg^{2+} by AAS following the digestion of HA by perchloric acid .

Elimination of interference by humic acids in the chemical analysis of cations

The standard methods for the determination of cations solubilised had to be slightly modified as the presence of the HAs cause interference in colour development procedures. For this purpose, 2 ml conc. $HClO_4$ (70%) was added to mineral-HA interacted solutions, heated until almost dry, cooled and made to volume. The process was previously standardized using standard Fe^{3+}, standard Al^{3+}, standard Fe^{3+} + HA, standard Al^{3+} + HA and blank HA solutions taken separately. From the $HClO_4$ digested solution, $Fe^{2+/3+}$, Al^{3+} and Mg^{2+} were determined as stated above. The amount of each cation present in HA was subtracted from the estimated value for mineral extracted solutions to give the actual amount extracted from the minerals.

In the determination of Si^{4+} as silico-molybdate complex (Maxwell, 1968), the inhibitory effect of HA was overcome by adding an excess of the molybdate reagent (four times the recommended amount) and the amount of HA that will not interfere with Si^{4+} analyses with this amount of molybdate were ascertained to be 0-4.8 ppm for Entisol HA, 0-8 ppm for Alfisol HA and 0-20 ppm for Mollisol HA. The amount of each cation present in HA was taken care of, as mentioned above.

Kinetics studies

Rates of release of cations from the silicates by HAs were studied in the following manner. To 200 mg of mineral sample in plastic bottles, 20 ml of 1000 ppm HA was pipetted in at a pH varying from 6-9. These were shaken intermittently (8h/day) for 7 days. At the end of the reaction period, which was 7, 14, 21, 28, 35, 42 and 49 days, the solutions were filtered, washed and made to volume and analysed for the major cations.

Studies on residual products

Weathered products of reaction were prepared in the following manner. To 2 g mineral sample in a plastic bottle, 50 ml of 1000 ppm HA was added and the solutions agitated on a shaker intermittently (5h/day) for three consecutive months. The residues were then filtered and dried in an oven at 80°C. These were analysed for the major cations in a manner similar to that of the untreated minerals.

Results and Discussion

It may be inferred that the neosilicate, olivine (Tables 1, 4) is closer to the forsterite group. The cyclosilicate mineral tourmaline (Tables 1, 4) belongs to the subgroup schorl, as also confirmed by its black colour.

Table 1. *Chemical composition of the silicate minerals*

% Oxide	Olivine	Tourmaline
SiO_2	40.45	40.98
$FeO+Fe_2O_3$	7.08	11.45
Al_2O_3	0.24	33.81
TiO_2	0.32	0.18
MnO_2	N.D.	N.D.
CaO	3.26	0.34
MgO	47.67	0.43
Na_2O	N.D.	1.35
K_2O	N.D.	0.21
B_2O_3	-	8.59
H_2O^-	0.07	0.01
H_2O^+	0.50	2.90

The elemental analysis data of HAs on dry ash-free basis were 55.20% C, 5.05% H, 4.36% N and 35.39% O for Entisol HA, 54.90% C, 6.51% H, 5.64% N and 32.95% O for Alfisol HA, 57.47 % C, 5.91% H, 4.83% N and 31.79% O for Mollisol HA; all of which are in the normal range. The E_4/E_6 ratios of the HA samples were recorded as 4.29, 3.27 and 4.23 for Entisol, Alfisol and Mollisol HAs respectively. It appears from the data that aromaticity (Kononova, 1966) or paticle size (Chen *et al.*, 1977) follows the order Alfisol HA > Mollisol HA > Entisol HA. The NaOH titratable acidity values were 2.50, 2.60 and 3.50 meq/g. As pH-metric titration estimates only about half of the actual acidity values, conductometric titrations of the HAs were also carried out to determine the total acidity of the HAs; the values are 5.90, 6.66 and 8.50 meq/g for Entisol, Alfisol and Mollisol HAs respectively. The IR spectrum of HAs show absorptions at 3750, 3400, 2900 2370, 1600, 1200, 1000, 660 cm^{-1} that are in conformity with the literature (Schnitzer and Khan, 1972).

Order of cation solubilisation from the minerals

The ion that is most solubilised from olivine (Fig. 1) is $Fe^{2+/3+}$ irrespective of the HA used with the % release from Entisol HA and Alfisol HA being comparable while that from Mollisol HA being much lower. The kinetics curves present a succession of peaks and troughs. No significant effect of pH is observed. Mg^{2+} is released in small amount while the release of Si^{4+} is negligible with all the three HAs.

The higher solubility of Fe^{2+} over Mg^{2+}, though both these cations occupy similar positions (link between isolated silica tetrahedra) (Deer *et al.*, 1985), is due to the high affinity of organic acids for Fe^{2+} which forms strong complexes with them (Schnitzer and Kodama, 1976; Barman *et al.*, 1992). The very slow release of Si^{4+} was due to the great stability of Si-O bonds (Oelkers, 2001) (energy of formation 3110-3142 Kcal/mol) compared to that of the Fe-O (919 Kcal/mol) and Mg-O (912 Kcal/mol) bonds (Keller, 1954).

The kinetics curves of tourmaline (Fig. 1) of $Fe^{2+/3+}$ release show alternate rise and drops; generally $Fe^{2+/3+}$ release at any pH being much greater than Al^{3+} and Si^{4+}. The release of Al^{3+} with Entisol HA deviates from the general pattern with a slowly decreasing trend. Al^{3+} release curves with the other two HAs are typified by distinct peaks and troughs. The solubility of Si^{4+} is very poor and the curves are mostly linear.

Relative stabilities of the minerals

Olivine possess discrete silica tetrahedra interlinked by Mg^{2+} and/or Fe^{2+}ions which are highly susceptible to attack as being unprotected by the tetrahedra (Deer *et al.*, 1985). Moreover, ionic type linkages, in addition to the high ratio of divalent cations to silicon (2:1) and the looser packing of oxygen, render its further chemical instability. These cations are readily leached from the exposed surfaces (Welch and Banfield, 2002) thereby releasing the Si tetrahedra.

In sharp contrast to olivine, tourmaline has a complex structure with abundance of Si-O linkages imparting it high chemical stability. The linkages in tourmaline are predominantly covalent. Corresponding to each hexasilicate ring, with Fe^{2+} and Na^{+} occupying the space within the ring in the structure, there is another ring containing three Mg^{2+} atoms and three B^{3+} atoms, with the individual units being linked laterally by octahedrally coordinated Al^{3+} lying between the rings (Deer *et al.*, 1985). The cations like Mg^{2+}, Na^{+} or Fe^{2+} serve as the weakest spots in the crystal. HA can be visualised as boring its way into the structure and bringing out the inner ring of composition $R_3(OH)_4Si_6O_{27}$ after complexation where R is predominantly Fe^{2+} as the mineral is a schorl. As the entire inner ring is brought out by HA, Si^{4+} which is part of the chain is released leaving behind the relatively loosely held Al^{3+} between the rings.

Congruency of dissolution

Both olivine and tourmaline show incongruent dissolution behaviour which points to a rather complex mechanism of dissolution. The $Fe^{2+/3+}$/ Si^{4+} mole ratios (Table 2) are much greater than 1 for both the minerals with all the HAs, indicating that $Fe^{2+/3+}$ ions are more readily solubilised than Si^{4+} signifying depletion of $Fe^{2+/3+}$ and enrichment in Si^{4+} in the residue. The Al^{3+}/ Si^{4+} mole ratios (Table 2) with tourmaline with all the HAs are generally greater than 1 (much lower than $Fe^{2+/3+}$/ Si^{4+}) implying that Al^{3+} is released in preference to Si^{4+} but not so rapidly as that of $Fe^{2+/3+}$. Variations from the general pattern do occur at times with the Al^{3+}/ Si^{4+} mole ratios being less than 1 indicating that at this stage, $Si^{4+}$is being preferentially released over Al^{3+}. This incongruency in Al^{3+} dissolution points to a rather complex mechanism. The mole ratios of Mg^{2+}/ Si^{4+} (Table 2) also indicate that Mg^{2+} release is preferred to that of Si^{4+} from olivine with all the HAs, the highest with Mollisol HA.

Kinetics of dissolution

The rate curves representing the dissolution pathways of minerals in HA (Fig. 1) are unique in terms of their complexity and are being very different from the dissolution patterns in inorganic, aqueous or low-molecular weight organic acids (Berner and Holdren, 1979; Zutic and Stumm, 1984; Song and Huang, 1988).

The absence of linear kinetics implies that fresh surfaces of minerals are not exposed to attack at a rate at which cations are being removed from the surface (Barman *et al.*, 1992) giving an indication of precipitation of the metal ions on the surface of the mineral. The precipitated surface layer, however, does not hinder the normal movement of ions and, therefore, not rate inhibiting. The alternate peaks and troughs actually signify that the reaction pathway varies between dissolution and

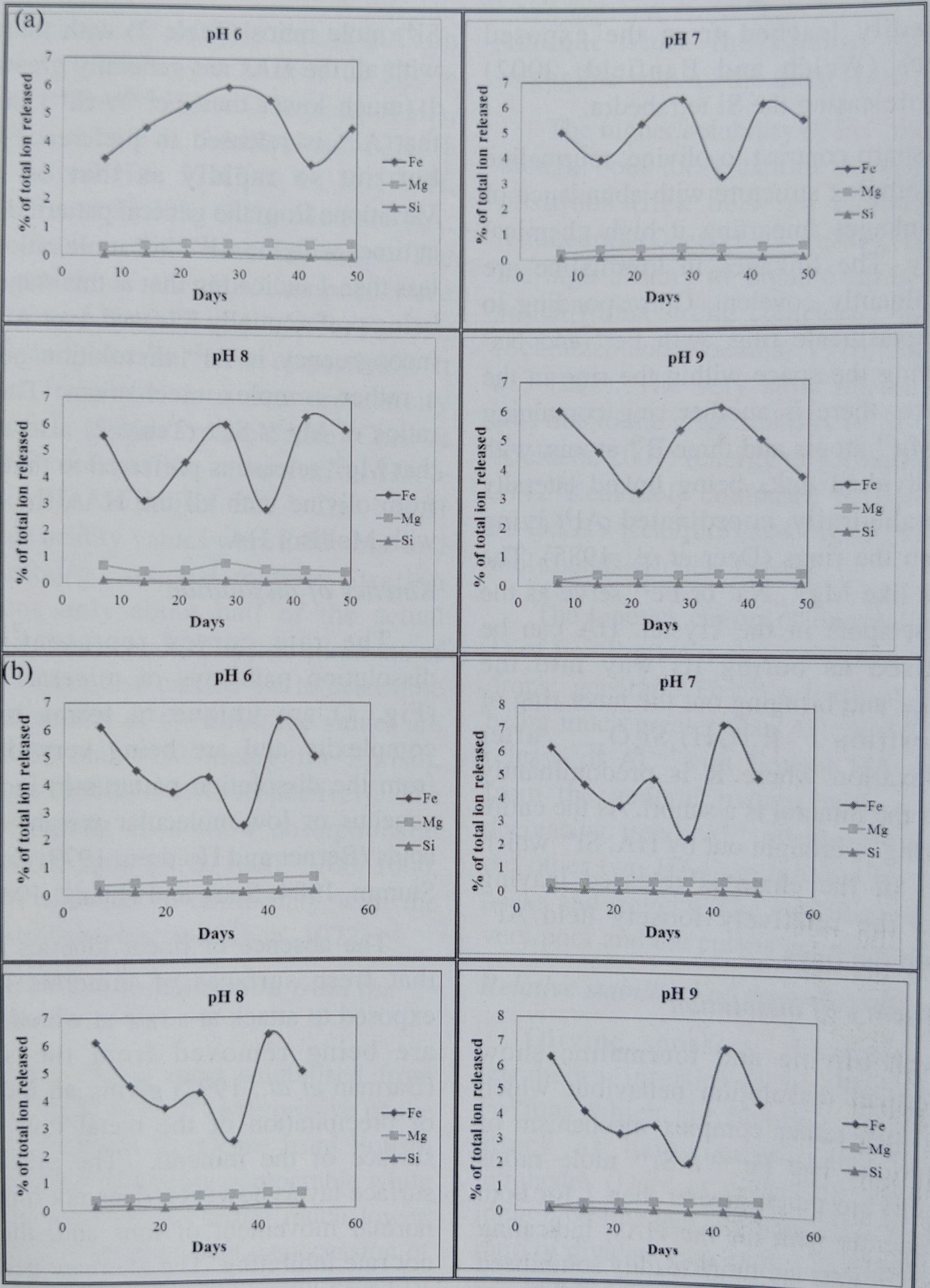

Fig. 1. (A) Release of cations from (a) olivine by Entisol HA and (b) olivine by Alfisol HA

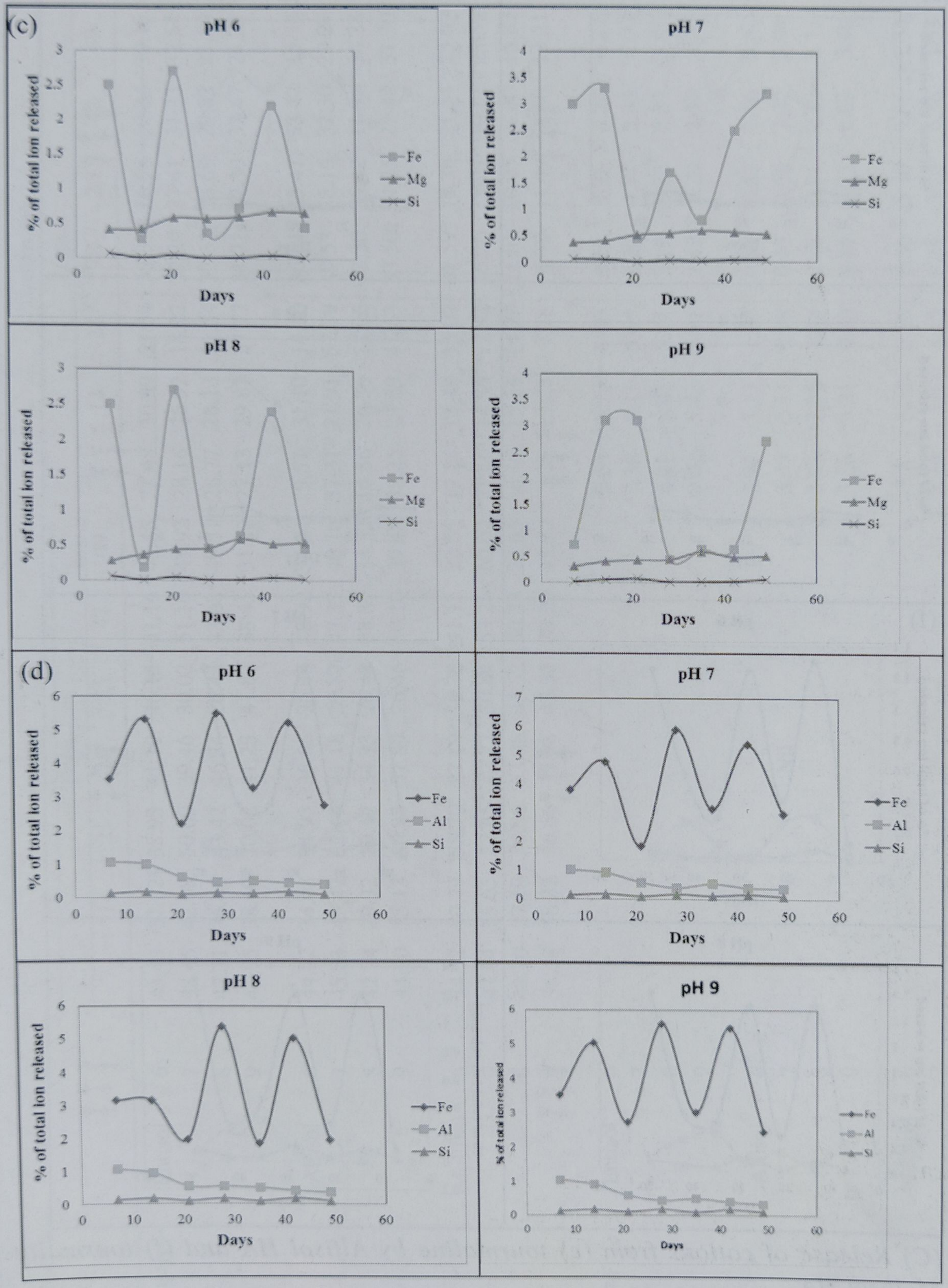

Fig. 1. *(B) Release of cations from (c) olivine by Mollisoll HA and (d) tourmaline by Entisol HA*

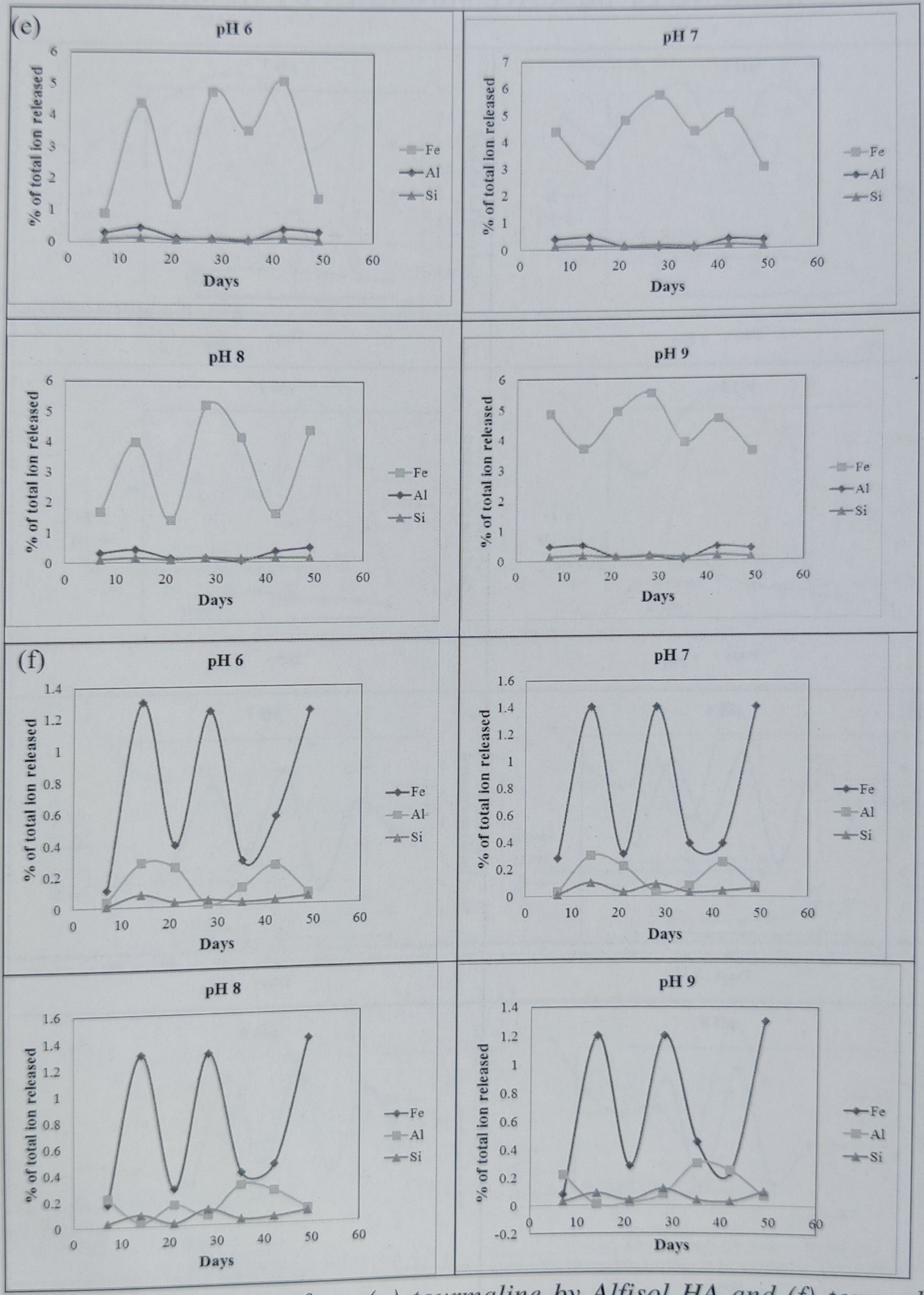

Fig. 1. *(C) Release of cations from (e) tourmaline by Alfisol HA and (f) tourmaline by Mollisol HA*

Table 2. *Mole ratio of $Fe^{2+/3+}$/ Si^{4+}, Al^{3+}/Si^{4+} and Mg^{2+}/ Si^{4+} solubilised from minerals by HAs*

Mole ratio	HA	pH	Olivine							Tourmaline						
			Days							Days						
			7	14	21	28	35	42	49	7	14	21	28	35	42	49
Fe^{2}/Si^{4+}	Entisol	6	43.43	37.82	38.93	41.19	46.15	41.16	48.55	28.48	30.99	21.54	38.37	26.58	30.34	30.15
		7	38.45	42.08	50.60	39.46	30.02	51.10	41.92	28.16	26.92	18.22	32.20	27.41	31.33	32.57
		8	42.31	36.46	43.42	46.84	26.43	43.68	49.51	26.77	28.13	21.54	32.82	23.69	29.82	21.54
		9	41.95	38.60	30.02	41.23	41.82	38.45	31.27	27.13	29.82	27.77	31.21	32.30	32.47	24.29
	Alfisol	6	44.22	34.68	34.93	36.65	26.43	48.92	34.94	9.57	31.10	14.10	36.61	33.47	33.47	15.38
		7	45.53	43.42	32.49	41.18	29.87	47.33	40.16	37.31	21.91	57.79	49.53	38.16	32.30	29.07
		8	42.74	29.32	29.17	34.33	26.43	38.89	34.32	16.56	26.36	14.96	32.30	35.42	11.36	34.28
		9	44.30	35.13	30.88	37.89	26.46	50.10	39.48	38.25	23.59	41.63	33.50	34.25	27.48	31.30
	Mollisol	6	34.32	40.79	58.70	27.19	36.74	41.15	22.65	17.24	15.48	15.07	31.59	14.36	21.54	23.69
		7	41.04	55.65	22.65	42.77	30.84	53.26	60.02	21.66	14.36	12.92	15.20	15.07	10.05	25.59
		8	42.70	27.19	50.96	33.98	45.32	50.33	22.65	6.46	15.24	14.29	11.01	10.05	8.60	15.83
		9	36.59	58.32	46.66	33.98	45.32	30.20	45.30	3.23	13.23	7.18	9.98	11.49	8.60	13.21
Al^{3}/ Si^{4+}	Entisol	6								8.63	5.77	6.00	3.15	3.98	2.53	4.22
		7								7.36	5.11	5.65	2.20	4.71	2.33	4.00
		8								8.91	5.83	5.74	3.19	6.23	2.37	3.82
		9								8.02	5.43	5.91	2.42	5.20	2.37	3.26
	Alfisol	6								2.97	3.17	1.67	0.88	0.67	2.76	3.67
		7				Nil				3.35	3.11	0.98	0.45	0.53	2.32	2.94
		8								3.02	2.76	1.48	0.86	0.31	2.33	3.71
		9								3.56	3.21	0.90	0.85	0.22	2.63	3.40
	Mollisol	6								5.5	3.34	9.56	0.36	5.70	9.56	1.34
		7								2.14	3.0	8.55	0.31	3.23	6.38	1.53
		8								8.55	0.33	0.86	0.71	7.56	4.78	1.25
		9								8.55	0.15	7.56	0.68	7.55	9.50	0.71

Table 2. *Continued* ....

Mole ratio	HA	pH	Olivine							Tourmaline						
			Days							Days						
			7	14	21	28	35	42	49	7	14	21	28	35	42	49
Mg^{2}/Si^{4+}	Entisol	6	4.03	3.43	3.46	3.43	4.70	6.29	6.04	Nil						
		7	2.08	4.21	4.06	2.89	4.15	3.99	3.77							
		8	5.23	5.42	4.81	6.00	5.46	3.43	4.11							
		9	1.54	3.10	3.68	3.00	3.02	3.27	3.69							
	Alfisol	6	2.59	3.14	4.33	4.38	5.39	4.45	4.09							
		7	2.59	3.49	4.03	4.12	6.67	3.65	4.64							
		8	2.66	3.15	4.63	4.64	6.04	3.64	4.09							
		9	1.28	3.00	3.53	4.63	5.38	3.83	4.96							
	Mollisol	6	5.63	63.71	12.44	42.90	30.08	12.56	32.87							
		7	5.09	6.82	26.02	13.65	22.41	12.25	9.92							
		8	4.68	54.97	8.28	34.87	44.64	13.12	27.26							
		9	15.32	20.03	6.39	33.27	44.19	24.31	8.53							

precipitation suggesting that precipitation of the reaction products is reversible (Helgeson, 1971).

The pathway of mineral-HA interaction could be envisaged to consist of initial complexation of the cation by HA upto a critical point of solubilisation which also serves as the threshold of precipitation. Again, the limiting value of precipitation acts as the threshold of redissolution. For every particular ion in every particular mineral being reacted with a particular HA, there is a definite threshold of dissolution and precipitation which may be partially influenced by pH changes. The cycle of dissolution-precipitation repeats itself a number of times in a definite period of experimentation.

Chelation appears to be the dominant factor of cation release from minerals by HA (Tan, 1980) with specific adsorption of HA onto the mineral surfaces (Stumm and Furrer, 1987; Stumm and Wieland, 1990) also playing a part.

Study of Residues

Chemical analysis

Marginal change in pH after reaction of minerals and HAs suggests that the cations dissolved by HA are not in solution and precipitation must have occurred as suggested by kinetics curves.

Olivine residue weathered by all the three HAs (Table 3) shows a relative reduction in Si^{4+} and $Fe^{2+/3+}$ and a relative enrichment in Al^{3+} and Mg^{2+} due to reduction in total ionic content and precipitation of Mg-HA and Al-HA complex on olivine surface.. Composition of the residue suggests a magnesium silicate. The highest degree of change is brought about by Alfisol HA. The preferential release of $Fe^{2+/3+}$ stems from its stronger complexation with HA.

There has been reduction in Si^{4+} and $Fe^{2+/3+}$ and enrichment in Al^{3+} in tourmaline with all the three HAs (Table 3). The decrease in Si^{4+} was highest with Mollisol HA and $Fe^{2+/3+}$ with Alfisol HA.

Another observable feature has been the increase in both adsorbed and structural water with the minerals which could be attributed to the precipitation of the HAs onto the mineral surface after complexation with the ionic constituents present in the mineral.

XRD studies

Olivine (Table 4) revealed a drastic change on weathering with all the three HAs with the major diffraction line of olivine being either very weak or absent indicating a total breakdown of structure. Many other bands have increased in intensity after weathering by Entisol HA but have mostly decreased in intensity with Alfisol HA and Mollisol HA weathered residues. Appearance of new phases with all the three HAs corroborate to the presence of magnesium silicate hydrate and magnesium iron carbonate hydroxide hydrate with Entisol HA, and magnesium silicate hydroxide, magnesium carbonate hydroxide hydrate, magnesium carbonate hydroxy hydrate (JCPDS, 1972, 1980, 1983) with both Alfisol HA and Mollisol HA. This also finds support from chemical analysis data.

Even tourmaline, which is hard to weather (Table 4) revealed many changes. The main band of tourmaline is either absent from the diffraction spectra of all the weathered residues or is present in a

Table 3. *Percent change in ionic constituents on weathering*

Humic acid	Mineral		%Si	% change	% Fe	% change	% Al	% change	% Mg	% change	H_2O-	H_2O+
	Olivine	O	18.88		5.50		0.13		28.75		0.07	0.50
Entisol		W	17.75	-6.0	4.50	-18.2	0.05	-60.0	30.00	+4.4	1.02	1.85
Alfisol		W	15.25	-19.2	2.97	-46.1	0.26	+110.0	34.38	+19:6	0.50	2.15
Mollisol		W	17.75	-6.0	5.00	-9.1	0.13	0.0	31.25	+8.7	0.45	1.70
	Tourmaline	O	19.13		8.90		17.9				0.01	2.90
Entisol		W	17.00	-11.1	8.00	-10.1	19.4	+8.4	-	-	0.55	3.20
Alfisol		W	17.50	-8.5	7.50	-15.7	19.4	+8.4	-	-	1.00	4.20
Mollisol		W	15.50	-19.0	8.20	-7.9	19.7	+10.1	-	-	1.30	4.40

O : Original mineral W : Weathered mineral % Change (-) : indicates deposition

Table 4. *XRD data of olivine and tourmaline and its residues*

Olivine								Tourmaline							
Original		Weathered by Entisol HA		Weathered by Alfisol HA		Weathered by Mollisol HA		Original		Weathered by Entisol HA		Weathered by Alfisol HA		Weathered by Mollisol HA	
d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I	d (A^0)	I
7.33	36	11.93	26	7.43	7	5.6	4	6.35	100	8.14	3	7.32	8	9.7	7
6.47	2	5.14	26	5.7	3	3.93	14	4.98	1	6..44	10	4.85	8	4.67	15
5.12	17	4.71	37	4.6	3	3.67	4	4.62	36	6.02	4	4.58	8	3.71	5
4.59	8	3.67	52	4.23	3	3.53	14	4.23	50	4.33	8	3.18	6	3.51	10
3.95	14	3.18	18	3.95	6	3.14	3	3.47	38	3.95	3	3.03	8	2.87	2
3.91	100	3.09	30	3.66	6	2.92	3	3.18	5	3.75	3	2.64	5	2.34	56
3.75	36	2.98	30	3.15	3	2.75	3	2.95	59	3.2	4	2.35	31	2.24	2
3.66	22	2.79	40	3.03	14	2.42	6	2.9	2	2.89	3	2.16	3	2.09	9
3.51	25	2.5	26	2.79	100	2.35	9	2.83	1	2.6	3	2.03	67	2.03	100
2.77	50	2.34	40	2.71	2	2.3	4	2.73	1	2.55	2	1.93	100	2.0	2
2.75	38	2.25	11	2.55	5	2.14	3	2.58	2	2.35	7	1.78	49	1.8	5
2.51	18	2.03	100	2.47	5	2.09	3	2.45	1	2.19	2	1.73	3	9.7	7
2.47	16	1.89	11	2.35	14	2.04	91	2.35	12	2.13	4	1.66	47		
2.35	22	1.62	22	2.25	2	2.03	100	2.31	23	2.03	52	1.6	10		
2.27	13			2.2	2	1.83	6	2.19	5	2.0	15				
2.16	67			2.18	3	1.75	9	2.12	74	1.6	100				
2.1	15			2.12	3	1.74	12	2.03	24						
2.04	63			2.03	34			1.99	1						
2.03	57			1.89	3			1.92	5						
1.94	4			1.82	9			1.87	62						
1.91	2			1.76	69			1.81	5						
1.86	6			1.74	3			1.73	1						
1.79	7			1.68	3			1.66	1						
1.74	24			1.64	3			1.59	81						
1.7	11			1.6	3			1.58	43						
1.67	15			1.58	6										
1.64	4														
1.61	2														
1.57	6														

much subdued form while some other diffractions have either increased in intensity or decreased or have vanished from the spectra of the weathered residues. New phases have come up in all the three HA-treated residues to which the probable compound assigned is aluminium carbonate hydroxide (Scarbroite) (JCPDS, 1972) which points to the precipitation of aluminium on the surface of the treated residues. Chemical analysis data corroborates the inference.

IR spectroscopic studies

All the weathered residues of olivine retain the major features of the original mineral with some alterations. The disappearence of the band at 770 cm^{-1} (Si-O-Si) and presence of absorptions at around 3400, 2930, 2390 and 1600 cm^{-1} indicate deposition of HA on the surface of olivine (Schnitzer and Khan, 1972).

Ample changes are manifested in all the weathered residues of tourmaline which share only two absorptions in common to that of the unweathered mineral featuring the absence of one prominent absorption at 1000 cm^{-1} (due to Si-O-Si) which is explicable considering the low penetrating power of IR radiation and the inaccessibility of the Si-O groups covered by HA deposits (Varadachari *et al.*, 1994). The absorptions around 3550 cm^{-1} present in untreated tourmaline as attributed to H-bonded –OH has been much more intensified with weathered residues due to the presence of phenolic and carboxylic groups of HA. The absorptions at 3700-3400 cm^{-1} and 2360 cm^{-1} signify the precipitation of HA on the surface of the mineral after complexation with most probably aluminium of tourmaline. The inference finds support from chemical analysis and XRD studies.

Conclusions

Cation solubilisation from silicates by HA is quite different from aqueous weathering or by low molecular weight organic acids. The kinetics curves represent alternate crests and troughs signifying dissolution and precipitation respectively. No noticeable variation with pH is perceived. The broad pattern of dissolution with different HAs remain the same while some differences in the amount of cation release is noticed.

For olivine and tourmaline, $Fe^{2+/3+}$ is most readily solubilised due to the high affinity of HAs for chelation with $Fe^{2+/3+}$, followed by Mg^{2+} in olivine and Al^{3+} in tourmaline; Si^{4+} is released in trace amounts. The pattern of dissolution of both the minerals is incongruent. Alfisol and Entisol HAs are found to be more effective weathering agents.

Olivine and tourmaline residues, formed after treatment with HAs, show a relative reduction in Si^{4+} and $Fe^{2+/3+}$ and a relative enrichment in Al^{3+}. In addition, olivine is also enriched in Mg^{2+}. The major XRD bands of both the minerals are either very weak or absent. New phases indicating the presence of Mg^{2+} in olivine and Al^{3+} in tourmaline have also emerged. However, the IR spectra of olivine and tourmaline primarily provide evidence regarding the deposition of HA on mineral surface.

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Does Sodicity in Vertisols Affect the Layer Charge of Smectites?

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Abstract : Sodicity in smectite dominant shrink-swell soils (Vertisols and vertic intergrade) is common in the semi-arid region. It is not known whether long-term sodicity in soils changes the layer charge of smectites as layer charge is an important fundamental property of smectite-dominated soils and most of the soil properties depends upon the layer charge. Understanding the importance of layer charge of soil clay smectites, two benchmark Vertisols, one Paral soils (sodic) and the other Boripani soils (non-sodic) from Akola and Nagpur districts of Maharashtra were chosen for the study. The study intended to show whether long-term sodicity causes hydroxy-interlayering in smectites which result in an increase in layer charge. The soils had high clay and smectite content and the smectite charge was distributed in both tetrahedral and octahedral layers. The layer charge of both the soil fine clays are the lowest reported till date for Indian smectites and varied from 0.307 to 0.353 and 0.328 to 0.360 mol(-)/{Si, Al)$_4$O$_{10}$(OH)$_2$} in a soil profile for Paral and Boripani soils respectively. Hydroxy-interlayering in smectites was also negligible. The study discussed that sodicity may not be responsible for the formation of hydroxy-interlayering in smectites and thus not likely to increase the layer charge.

Shrink-swell soils of the Upper Peninsular India are mainly formed from the weathering of Deccan basalt, rich in plagioclase feldspars and yield dioctahedral smectite as the first weathering product (Pal and Deshpande, 1987; Bhattacharyya *et al.*, 1993). These smectites are dominated by beidellite-nontronite type of minerals (Ghosh and Kapoor, 1982). It was later confirmed by diagnostic methods that smectites of Indian shrink-swell soils are nearer to montmorillonite of the montmorillonite-nontronite series (Pal and Deshpande, 1987).

To characterize the shrink-swell soils which contain dominant proportions of smectites, determination of their layer charge is fundamental to all physical and chemical properties of soils. The properties include soil structure, drainage, aeration, water retention (Laird *et al.*, 1987), cation exchange reactions, specific surface area and degree of hydration (Bailey, 1980; Wilding and Tessier, 1988). The layer

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charge also determines the properties of soil clay minerals and indicates a mineral's capacity to retain cations and adsorb water and other polar organic molecules (Lagaly and Weiss, 1969; Malla and Douglas, 1987). It is also known that different swelling properties of clays with identical interlayer cations are mainly due to differences in layer charge densities (Weiss *et al.*, 1955).

Shrink-swell soils (Vertisols and vertic intergrades) of India contain smectites which are quite often hydroxy-interlayered (HI). It is reported that HI in smectites occurred due to the intrusion of positively charged HI materials into the smectite interlayers at much lower pH than the present day conditions (Deshmukh, 2009; Pal *et al.*, 2012) and presence of HI indicated their formation in humid climate (Pal *et al.*, 2012). Earlier studies indicated that in soils that have pH higher than 7, HI formation could be a possibility . Therefore, sodic shrink-swell soils in the semi-arid tract of Peninsular India may also be prone to form hydroxy-interlayering in smectites and may result increase in layer charge of smectites (Ray *et al.*, 2008; Deshmukh, 2009; Bhople, 2010). The Peninsular India, particularly Maharashtra state has large tract of sodic soils. One such area is the Purna valley in Maharashtra (Pal *et al.,* 2000). Therefore, the present work was formulated based on the hypothesis whether long-term sodic environment in Vertisols would increase their layer charge as such increase is likely to reflect in the bulk soil properties.

Materials and Methods

Two benchmark soil series were selected for present study. One of these is Paral (P1) (Sodic Haplusterts) in Akola district which is a sodic soil, agriculturally important, widely distributed and intensively cultivated soils grown for cotton, sorghum, pigeonpea, etc. The other one is Boripani (P2) (Leptic Haplusterts) which is non-sodic supporting reserve forest in Nagpur district of Maharashtra was taken for comparison. Horizon-wise soil samples were collected for laboratory characterization. Some characteristics of the soils are shown in table 1. Silt varies from 21.8 to 37.6% and clay values ranged from 61.2 to 75.8%. Fine clay values are quite high which ranged from 42.6 to 59.4%. Fine clays being the dominant fraction in these soils were used for the determination of layer charge of fine clay smectites. High COLE values (> 0.10) are almost similar in both the soils. Available water capacity (AWC) is higher in Paral soils due to higher pH and exchangeable Na^+ content. Paral soils are strongly alkaline whereas Boripani soils are neutral to mildly alkaline. Organic carbon, CEC and base saturation are higher in Boripani soils, whereas $CaCO_3$ and ESP are higher in Paral soils.

Fine clays were separated from soil by size segregation method of Jackson (1979) following the removal of cementing agents. The fine clay (<0.2 μm) fractions of each horizon of the two pedons were analyzed for qualitative mineralogy by X-ray

Table 1. *Some properties of the soils given in ranges as they vary in a soil profile*

Sl. No.	Soil property	Paral (P1)	Boripani (P2)
1.	Sand (%)	0.6 – 1.1	1.3 – 2.2
2.	Silt (%)	31.1 – 37.6	21.8 – 32.5
3.	Clay (%)	61.2 – 68.2	65.5 – 75.8
4.	Fine clay (%)	42.6 – 51.7	47.8 – 59.4
5.	COLE[1]	0.17 – 0.25	0.17 – 0.26
6.	AWC[2] (%)	16.8 – 27.0	16.9 – 20.2
7.	pH	8.5 – 8.9	7.4 – 7.7
8.	Organic carbon (%)	0.51 – 0.65	0.14 – 1.00
9.	$CaCO_3$ equivalent (%)	9.5 – 11.2	3.8 – 7.9
10.	CEC {cmol(p+)kg^{-1}}	50.4 – 61.0	59.8 – 74.8
11.	Clay CEC {cmol(p+)kg^{-1}}	75.6 – 94.1	88.4 – 99.0
12.	Base saturation (%)	80.0 – 83.0	94.0 – 99.0
13.	ESP[3]	2.3 – 16.3	0.5 – 2.0

[1] COLE – coefficient of linear extensibility, [2] AWC – available water capacity, [3] ESP – exchangeable sodium percentage

diffraction (XRD) techniques. For identification of clay minerals, the fine clay fractions were subjected to XRD of the parallel oriented samples using a Philips X' Pert Pro diffractometer with Ni filtered Cu-Kα radiation at a scanning speed of 2°2θ/min. Different thermal pre-treatments of the K-saturated samples were given to distinguish and confirm the type of mineral present. Greene-Kelley (1953) test was also performed on these fine clays to distinguish between montmorillonite and beidellite / nontronite.

Characterization of layer charge

Alkylamines with carbon atoms 6, 7, 8, 9, 10, 11, 12, 13, 14, 16 and 18 were taken and their chloride salts were made (Lagaly, 1994; Ray *et al.*, 2003, 2008) by first dissolving the required amount of respective amines in small amount of ethanol and then titrating it with HCl up to a pH of about 6.5 to 7. After preparing the various alkylammonium hydrochlorides, concentrations of various alkylamines were made as follows : 2M for chain lengths 6 and 7, 0.5 M for chain lengths 8, 9 and 10, 0.1 M for chain lengths 12, 13 and 14 and 0.05 M for chain lengths 16 and 18. Clay suspensions were pipetted containing 25-30 mg of Na-saturated clay. 10 ml of each alkylamine was added and kept at 65°C for 24 h. Another 10 ml of alkylamine was added after decanting the previously added amine and again kept at 65°C for 24 h. The excess alkylamine was washed first with 1:1 ethanol: water mixture and then with pure ethanol to remove excess salt. The alkylammonium-clay complexes formed were subsequently prepared as oriented aggregates on glass slides. The alkylammonium treated samples were dried under vacuum in a dessicator at 65°C for 24 h before XRD analysis.

Calculation of Layer Charge

It has been observed by Lagaly and Weiss (1969, 1976) that short chain alkylammonium-smectite derivatives have basal spacings of about 13.6 Å, reflecting a monolayer of interlayer alkylammonium cations. Long chain alkylammonium-smectite derivatives have basal spacings of about 17.6 Å indicating a bilayer of interlayer alkylammonium cations and also at about 22 Å indicating a pseudotrimolecular layer of alkylammonium cations. The layer charge density was calculated by using the following equation:

$\xi = 23.25/(5.67nc + 14)$ for dioctahedral clays, where ξ is the layer charge density and n_c is the number of carbon atoms in the alkylammonium chain

Results and Discussion

Mineralogy of the fine clay fractions (<0.2 µm)

The fine clay fractions are mostly composed of smectite with small amounts of vermiculite and traces of chloritized smectites, mica, kaolin, quartz and feldspar (Table 2, Fig. 1). On glycolation the 1.4 nm peak expanded to about 1.7 nm indicating the presence of smectites. On K-saturation at 25°C the smectite peak shifted from 1.1 to 1.2 nm, which is characteristic of smectite (Pal and Deshpande, 1987). The shifting of the 1.0 nm peak of K-saturated and heated (300°C)

Table 2. *Semi-quantitative estimates of minerals in fine clay fraction of soils*

Horizon	Depth (cm)	Clay Minerals (%)						
		Smectite	Vermiculite	Chlorite	Kaolin*	Mica	Quartz	Feldspar
Paral soils								
Ap	0-9	76	12	2	2	3	2	3
Bw1	9-35	75	13	1	1	3	3	4
Bssk1	35-69	81	10	2	1	3	1	2
Bssk2	69-105	78	10	1	1	3	3	4
Bssk3	105-132	80	7	3	1	3	2	4
Bssk4	132-150+	80	5	5	1	3	2	4
Boripani soils								
A1	0-16	77	7	7	1	3	3	2
Bw1	16-44	86	4	5	2	1	1	1
Bss1	44-57	88	4	4	1	1	1	1
Ck1	57-94+	91	3	2	1	1	1	1

*Interstratified smectite – Kaolinite mineral.

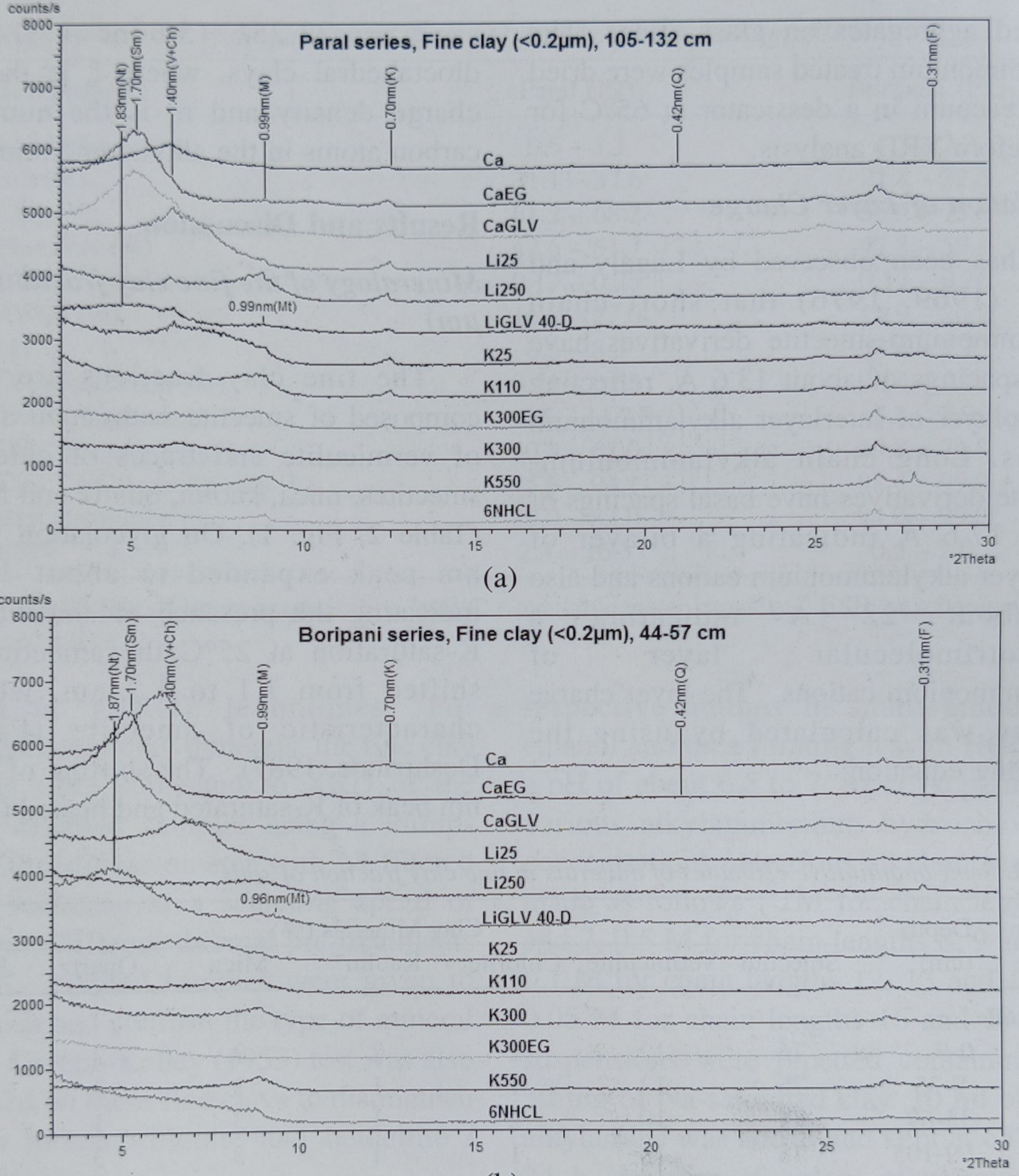


Fig. 1. *X-ray diffractograms of representative fine clay fractions (<0.2μm) for (a) Paral series and (b) Boripani series; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; CaGLV = Ca-saturated plus glycerol vapour treated; Li = Li-saturated and heated to 25°C, 250°C (16h), LiGLV 40-D = Li-saturated and heated at 250°C plus glycerol vapour treated and scanned after 40 days; K-saturated and heated to 25, 110, 300, 550°C. K300EG = K-saturated and heated to 300°C plus ethylene glycol vapour treated; 6NHCl = 6N HCl treated fine clays; Sm = Smectite, B/N = beidellite/nontronite; V+Ch = vermiculite plus chlorite; M = mica; Mt = montmorillonite; K = Kaolinite; F = Feldspars*

sample on glycolation to 1.4 nm indicates its low charge density (Bhattacharyya *et al.*, 1993).

The presence of 0.70 and 0.35 nm peaks in Ca-saturated and glycolated sample and 0.72 nm peak in K-saturated and heated (300°C) sample and its disappearance at 550°C and reappearance of the peak at 0.70 nm after treating with HCl indicates the presence of kaolin. The smectite was little chloritzed as evidenced by the broadening towards the low angle side of 1.0 nm peak in K-saturated sample after subsequent heating to 550°C. Such chloritization is common in black soils (Pal and Deshpande, 1987a; Pal and Durge, 1989; Balpande, 1993; Kadu, 1997; Pal *et al.*, 2000). On K-saturation and subsequent heating at 110°C, the 1.0 nm peak of mica was reinforced which indicates the presence of vermiculite. A weak peak of 0.97 nm followed by 0.48 nm peaks indicates the presence of small amount of mica in these fine clay fractions of the soils.

Ca-treated and glycerol solvated samples gave distinct peak at around 1.8 nm showing the presence of montmorillonite (Borchardt, 1989). The Li-treated samples at 25°C showed a broad peak around 1.4 nm. However, the Li-treated clays on heating at 250°C for 16 h (Lim and Jackson, 1986) gave a broad peak around 1.0 nm and another at about 1.4 nm. The same sample when glycerol solvated, gave a strong peak around 1.4 nm and another at around 0.95-1.0 nm. There is only a small hump at around 1.8 nm. This hump developed into a mature peak after about 40 days of glycerol solvation. This indicates that the fine clays consist of both montmorillonite and beidellite/nontronite. As these samples are unstable in 6*N*HCl, they are closer to nontronite. Thus, charge of smectites is distributed in both octahedral and tetrahedral layers (Bhattacharyya *et al.*, 1993; Kapse, 2007; Ray *et al.*, 2008; Kapse *et al.*, 2010; Bhople *et al.*, 2011; Deshmukh *et al.*, 2012).

Alkylammonium treatment of clays

The X-ray diffraction patterns of the representative fine clay samples of Paral and Boripani soils treated with alkylammonium hydrochlorides are presented in figure 2. The alkylamines treated with lower chain lengths (containing carbon atoms C6 to C8) generally gave peak at around 1.42 nm. A hump at around 1.34 nm was also observed. For the alkylamines with chain lengths of C9 to C11, sharp peaks were obtained at about 1.79 nm to 1.92 nm with the exception of C10 which sometimes gave abruptly higher values. With increase in chain length from dodecylamine to octadecylamine (C12 to C18), the d-values increased proportionately from around 2.0 nm to 3.2 nm. All these values primarily showed the presence of smectites (Ray *et al.*, 2003). The alkylamines occupy the interlayers of smectites and replace the cations therein in a fashion similar to a Lewis acid (Jaynes

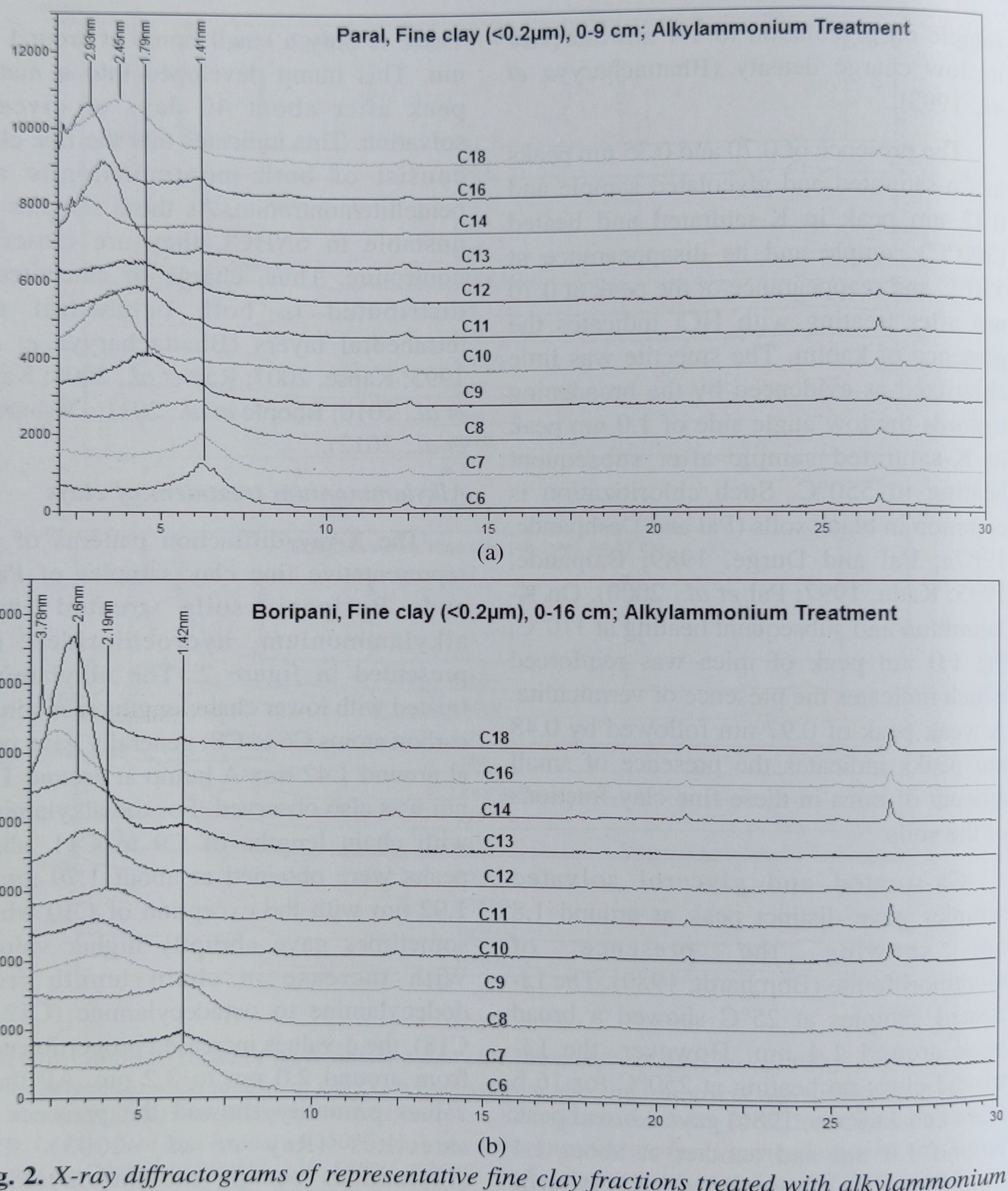
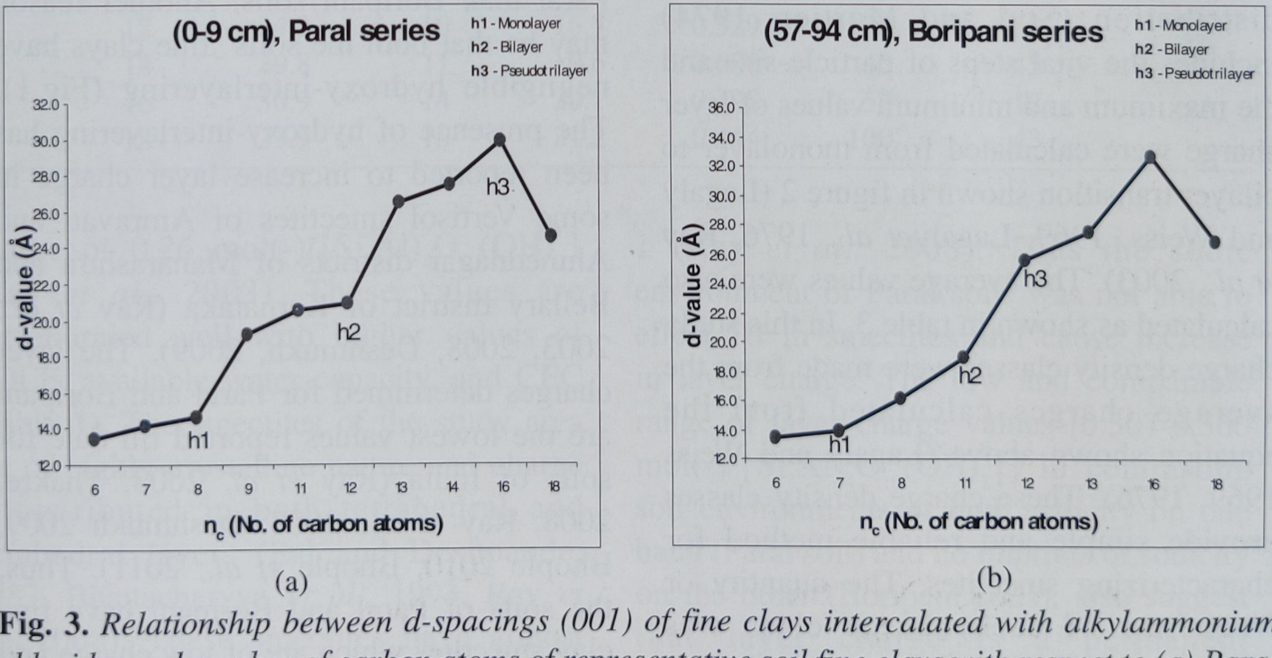


Fig. 2. *X-ray diffractograms of representative fine clay fractions treated with alkylammonium chlorides having number of carbon atoms C6, C7, C8, C9*, C10, C11, C12, C13*, C14, C16, C18 with respect to (a) Paralsoils and (b) Boripani soils*

and Bigham, 1987).

The lower chain alkylamines usually form a monolayer of alkylamines in the interlayer and the resultant d-values are in the order of 1.36 nm (Lagaly, 1994; Ray *et al.*, 2003). Further increase in chain length resulted in bilayers (above 1.76 nm), pseudotrilayer (2.2 nm) and paraffin type 22Å to ∞ (Lagaly and Weiss, 1969, 1976). The mainly monolayer to bilayer transition indicates that these fine clays are of low charge smectites (Lagaly and Weiss, 1969; Malla and Douglas 1987; Laird *et al.,* 1987; Jaynes and Bigham, 1987). For the fine clay smectites under the study the integral monolayer and bilayer spacings were actually not obtained, indicating that the smectites are not homogeneous but non-integral and heterogeneous in nature with respect to lower carbon chain lengths. However, non-integrality is more conspicuous in case of higher chain lengths of carbon atoms from C12 to C18 compared to that showed by alkylamines with lower carbon chain length. This also suggests that the monolayers and bilayers succeed each other in a random manner (Lagaly, 1969; Ray *et al.,* 2003). The point where non-integrality ends in bilayer is the lower limit of charge density (Fig. 3). The point h1 in the figure where non-integrality begins in a monolayer is the upper limit of charge density. This non-integrality disappears as the d-spacing approaches 1.76 nm. The graphs in figure 3 show S-type curves where they depict transition from one layer to other. It is more homogeneous and integral if the curves are sharper in nature



(a) (b)

Fig. 3. *Relationship between d-spacings (001) of fine clays intercalated with alkylammonium chlorides and number of carbon atoms of representative soil fine clays with respect to (a) Paral series and (b) Boripani series*

and vice-versa. It is interesting to note in the figures that for Paral fine clays the transition from monolayers to bilayers is sharper compared to Boripani, where more gradual. This may indicate that the Boripani soils may be slightly hydroxy-interlayered as compared to Paral fine clays (Lagaly *et al.*, 1976; Ray *et al.*, 2006).

Determination of layer charge of soil clays

Charge densities were calculated according to the above equations. For both monolayer and bilayer transition the charges are shown in table 3. The fine clay fractions (<0.2 μm) were used for the study to correct the error due to particle-size fraction. This error in calculation may occur due to the displacement of alkylammonium ions out of the interlayer space (Lagaly, 1994; Ray *et al.*, 2003). The calculation for frequency distribution (Stul and Mortier, 1974) includes the vital steps of particle-size and the maximum and minimum values of layer charge were calculated from monolayer to bilayer transition shown in figure 2 (Lagaly and Weiss, 1969, Lagaly*et al.*, 1976, Ray *et al.*, 2003). The average values were also calculated as shown in table 3. In this study charge density classes were made from the average charges calculated from the equation shown above (Lagaly and Weiss 1969, 1976). These charge density classes provide simple and reliable method for characterizing smectites. The quantity or frequency of each charge class was calculated (Table 3) and charge distribution diagrams were constructed (Fig. 3) (Stul and Mortier, 1974; Lagaly and Weiss, 1976, Ray *et al.*, 2003, 2008). For the sake of brevity, details of the method of calculation is provided only for two depths in table 3 (Ray *et al.*, 2003). Peak migration curve analysis deduced by McEwan *et al.* (1961) and Ruiz Amil *et al.* (1967) was utilized here to calculate the frequency distribution of charge.

The average layer charge density varies from 0.307 to 0.353 mol(-)/$\{Si,Al)_4O_{10}(OH)_2\}$ for Paral fine clays and 0.328 to 0.360 mol(-)/$\{Si,Al)_4O_{10}(OH)_2\}$ for Boripani fine clays. In both soils, the layer charge decreases down the depth which may be due to the increase in smectite content with concomitant decrease in vermiculite and chlorite content (Ray *et al.*, 2006). This decrease is relatively more in Paral than Boripani soils. Another reason may be that both the soils' fine clays have negligible hydroxy-interlayering (Fig.1). The presence of hydroxy-interlayering has been reported to increase layer charge in some Vertisol smectites of Amravati and Ahmednagar districts of Maharashtra and Bellary district of Karnataka (Ray *et al.*, 2003, 2008, Deshmukh, 2009). The layer charges determined for Paral and Boripani are the lowest values reported till date for soils of India (Ray *et al,* 2003, Thakre, 2008, Ray *et al.*, 2008, Deshmukh 2009, Bhople 2010, Bhople *et al.*, 2011). Thus, the soils of Paral and Boripani have fine clay smectites which are of low charge and nearer to the bentonite (Wyoming) layer

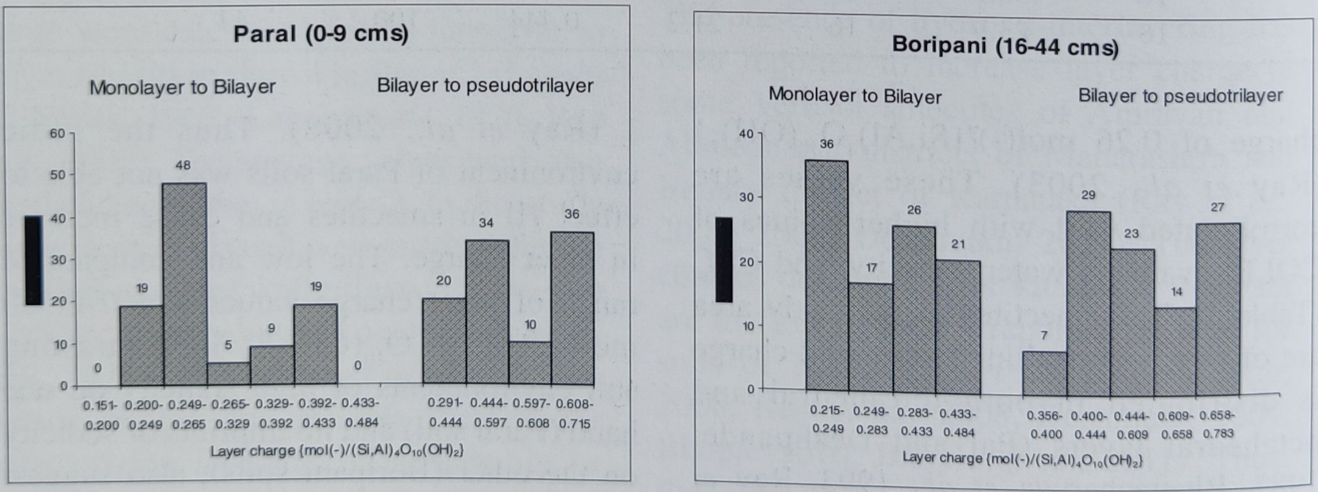
Table 3. *Frequency distribution of various charge densities in fine clays of the soils of Paral*

Depth cm	No. of C-atoms	Act. D-value (Å)	Rearr-anged no. of C-atoms	Modi. D-value (Å)	Charge density {mol(-)/ $(Si,Al)_4O_{10}(OH)_2$}	Bilayers/ Trilayers (%)	Freq. (%)	Avg. charge {mol(-)/ $(Si,Al)_4O_{10}(OH)_2$}
0-9	6	13.4	6	13.4	0.484	0	0	0.353
	7	14.2	7	14.2	0.433	19	19	
	8	14.6	8	14.6	0.392	29	10	
	9	19.2	10	14.8	0.329	33	5	
	10	24.5	18	14.8	0.200	33	0	
	11	20.5	13	16.8	0.265	81	48	
	12	20.9	14	17.7	0.249	100	19	
	13	26.5	9	19.2	0.715	36*	36	
	14	27.4	16	20.1	0.444	56	20	
	16	29.8	11	20.5	0.608	66	10	
	18	24.5	12	20.9	0.597	100	34	
9-35	6	14.9	18	14.2	0.200	19	10	0.342
	7	15.3	8	14.3	0.392	21	2	
	8	14.3	12	14.6	0.283	29	7	
	10	26.4	6	14.9	0.484	36	8	
	11	19.6	7	15.3	0.433	45	9	
	12	24.3	10	16.7	0.329	100	55	
	14	29.8	11	19.6	0.608	45	45	
	16	30.9	14	20.1	0.498	57	12	
	18	23.9	16	21.2	0.444	100	43	

charge of 0.26 mol(-)/{$(Si,Al)_4O_{10}(OH)_2$} (Ray *et al.,* 2003). These values are corroborated well with higher values of COLE, available water capacity, and CEC (Table 1). The smectites of the study area are of highly crystalline nature and charge is distributed in both tetrahedral and octahedral layers (Pal and Deshpande, 1987, Bhattacharyya *et al.,* 1993, Ray *et al.,* 2008). These smectites have almost negligible HI as envisaged from Ca, CaEG and K treated XRD graphs shown in figure 1 (Ray *et al.,* 2008). Thus the sodic environment of Paral soils was not able to effect HI in smectites and cause increase in layer charge. The low and comparable range of layer charge values [0.307-0.360 mol(-)/{$(Si,Al)_4O_{10}(OH)_2$}] in contrasting soil environments of high sodicity on one hand (Paral soil) and no imprints of sodicity on the other (Boripani soils), also suggest that layer charge is a permanent characteristic of layer silicate minerals which is unlikely to change even under long-term sodic environment. The presence of HI which has been reported to increase the layer charge in some other soil clay minerals was not necessarily due to sodicity but acquired from sources primarily from high rainfall regions where acidic conditions prevailed (Pal *et al.*, 2012, Deshmukh *et al.*, 2012). On the other hand, alkaline conditions in soils are likely to remove the HI in smectites, especially the aluminium hydroxy-polymers (AHP) as Al is amphoteric in nature. The AHPs are usually in six fold co-ordination state, $[Al(OH)_x(H_2O)_y]^{(3-x)+}$ where x+y = 6. The process of removal of AHP with normal sodium citrate (pH 7.3) from acid soils has been described by Tamura (1958). For soils dominated with smectites, HI was effectively removed by sodium salt of ethylene diamine tetraacetic acid (Ray *et al.*, 2008; Deshmukh, 2009; Khuspure, 2012). However, in the context of smectite dominated soils, the HI materials are dominated by hydroxy-polymers of Fe and Mg with moderate amounts of AHP (Ray *et al.*, 2008; Deshmukh, 2009). Therefore, it appears that sodic environment in smectitic soils are not likely to increase

Table 4. *Layer charge of Paral and Boripani soil fine clays.*

Depth (cm)	Avg. charge{mol(-) / $\{(Si,Al)_4O_{10}(OH)_2\}$
Paral soil	
0-9	0.353
9-35	0.342
35-69	0.342
69-103	0.317
103-132	0.317
132-150	0.307
Boripani soil	
0-16	0.360
16-44	0.348
44-57	0.341
57-94	0.328



(a) (b)

Fig. 4. *Frequency distribution of charge density of representative soil fine clays for (a) Paral series and (b) Boripani series*

the layer charge, but on the other hand may partially remove the HI from smectite interlayers and decrease the layer charge.

Conclusions

The layer charge densities determined for Paral and Boripani soils are the lowest values reported till date for smectitic soils of India. Paral and Boripani soils have low charged fine clay smectites nearer to the layer charge of bentonite (Wyoming) having 0.26 mol(-)/$\{Si,Al)_4O_{10}(OH)_2\}$. In spite of the fact that Paral soils are sodic in nature, it did not lead to hydroxy-interlayering in the smectite interlayers and thus did not result in an increase in layer charge.

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Clay Research

Vol. 32 **June 2013** **No. 1**

CONTENTS

Mineralogy of Some Benchmark Soils of the Coastal Plain, West Bengal
D.C. Nayak and Dipak Sarkar .. 1

Clay Mineralogy of the Oldest Paleosols from the Himalayan Foreland: Implications of Diagenetic Overprinting and Paleoenvironments
P. Srivastava, B. Banerjee, M. Aruche and N. Ahmed .. 17

Soil Boron and Its Fractions in Agro-Climatic Zones of Karnataka
M.S. Anitha, K.S. Anil Kumar, K.M. Nair, C.R. Shivaprasad, L.G.K. Naidu and Dipak Sarkar 25

Mineralogical Transformation in Benchmark Soils of Prakasam District, Andhra Pradesh as Influenced by Weathering and Pedogenic processes
R.L. Ram, P.K. Sharma, N. Ahmed, S.S. Datta and R.K. Sharma .. 34

Weathering of Silicate Minerals by Humic Acids : I. Nature of Cation Solubilisation from Olivine and Tourmaline and Characteristics of the Residual Products
Sruti Das, Kunal Ghosh and Chandrika Varadachari .. 58

Does Sodicity in Vertisols Affect the Layer Charge of Smectites?
P.V. Thakare, S.K. Ray, P. Chandran, T. Bhattacharyya and D.K. Pal .. 76

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