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Geochemistry of some ferruginous soils of Kerala, India

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Abstract: The four representative ferruginous soils on lateritic cover developed over Precambrian rocks in parts of Kottayam of Kerala were studied to understand the weathering pattern and genesis through geochemistry. These soils are strongly to moderately acidic, reddish brown with low Cation exchange capacity CEC and base saturation having SiO_2 - 33 to 57%, Al_2O_3 - 16-31%, Fe_2O_3 - 8 to 15% and TiO_2 -0.7 to 1.4%. Kanjirapalli (P3) and Athirampuzha (P4) soil series were more intensely weathered as compared to the Kinalur (P1) and Chingavanam series (P2) with silica to alumina-iron ratio less than 2 and had a significant negative relationship with Chemical index of alteration CIA (-0.75**), Harnois index (-0.678**), Richie index (-0.953**) and Plagioclase Index of Weathering (-0.705**). The trace elemental concentration ranges were above the values of world soils having an enrichment index more than 1 in Kanjirapalli series (P3) and Ni contamination in genetic horizons (Ni > 200$\mu g g^{-1}$). The cluster analysis showed similar major oxide concentration pattern in Group -1 and Group - 2 but varied in trace elemental pattern with Cr > Ba > Cu in Group - 1 and Cu > Cr > Ba in Group - 2 soils whereas Zr > Ni > Mn in Group - 3 to Ni > Mn > Zr in Group - 4 soils. The study further showed that differential rate of weathering in soils under tropical climate was further accelerated due to anthropogenic activities such as improper land use practices and deforestation on sleep slopes.

Keywords: Chemical index of weathering, Enrichment index, Index of laterization, Kerala, Trace elements

INTRODUCTION

Chemical weathering is one of the most important processes that change the chemical composition of soils and distribution of elements in weathering products that differ from parent rocks (Nesbitt and Markovics, 1997). Chemical compositions of soils have been used effectively to evaluate weathering and soil formation conditions, to trace the provenance of soils (Nesbitt *et al.,* 1996) and to reconstruct paleoclimate records (Zabel *et al*., 2001; Wei *et al.,* 2004). Thus, quite a number of studies have been carried out in the past several decades to investigate chemical weathering (Price *et al.,* 1991; Little and Aeolus Lee, 2006). Previous studies show elements that are conserved in temperate zone, such as Ti and Zr, are mobile during extreme chemical weathering in tropical regions (Cornu *et al.,* 1999). Probing into element behaviour during weathering is pivotal to understanding element mobilization and redistribution during chemical weathering. In addition, laterites, the products of extreme weathering, account for over 85% of the present world soil cover (Nahon, 2003).
Quantitative characterization of weathering in soils is made through development of weathering indices (Price and Velbel, 2003; Abbaslou *et al.*, 2013 and Yousefifard *et al.,* 2014). The chemical index of alteration (CIA, Nesbitt and Young, 1982), chemical index of alteration (CIW, Harnois, 1988) and plagioclase index of alteration (Fedo *et al.*, 1995) serve as examples of the decomposition of unstable minerals. According to the principles of soil genesis, alkali and alkaline earth elements move through soil horizons prior to silicon as weathering progresses (Souri *et al.,* 2006). Laterite and lateritic soils are formations peculiar to India and some other tropical countries with intermittently moist climate. In India they cover a total area of about 248,000 sq. Kilometres in the states of Deccan, Karnataka, Kerala, Madhya Pradesh, Eastern Ghat regions of Orissa, Maharashtra, Malabar and parts of Assam (Raychaudhuri, 1980) but cover one-fourth of the total geographical area of 329 millon ha on the basis of soil resource inventory (Sehgal, 1998 and Bhattacharyya *et al.*, 2009).
The general characteristics of laterite associated soils in Kerala were reported by Satyanarayana and Thomas (1962) and of Nellore district in Andhra Pradesh by Bhaskar and Subbaih (1995).The geochemical trends in lateritic profiles of Kerala were reported by Narayanaswamy (1992) indicating the depletion of silica and enrichment of sesquioxides and TiO_2 during the process of weathering. Later , Ramahashay *et al.*(1987)

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reported the occurrence of halloysite in association with kaolinite , goethite, gibbsite and quartz in these soils possessing high plasticity and cation exchange capacity. Silica as invariant was used to work out geochemical mass balance sheet of laterite associated soils of Somasila project (Bhaskar *et al.,* 1999). The distinguishing feature of these laterite soils is development of strong chroma and redder hue accumulation of clay, and relatively minor accumulation of Fe and Al sesquioxides in the B horizons where in silica to sesiquioxide ratio is less than 2 (Chandran *et al.,* 2005).

The recent review on pedology of red ferruginous soils of India was made by Pal *et al* (2014) describing several pedological and edaphological aspects of alfisols, mollisols and ultisols mainly of humid tropical climate but little emphasis was made on geochemical records of these soils. .The lateritic soils are dominant in Southern mid land zone (SMZ) mostly used for rubber (Hevea *brasiliensis*) under terraced hill slopes from Tiruvananthapuram to Kottayam. The intensive monsoon climate in the region is strongly interlinked with strong chemical weathering of lateritic soils and occurrence of devastating land slides. Among various geo-environmental factors, slope plays vital role for many land use associations and cautious towards necessity of adopting land use control. In India, therefore, comprehensive understanding of the behaviour of elements during extreme weathering in the tropical laterite profile may aid in our understanding of the mechanisms of weathering and for drawing meaningful geotechnical measures in the region. There is scanty of literature on geochemical interpretations of lateritic soils dealing with elemental organizations as controlled by geology in Kerala. Hence in the present study, an attempt has been made for geochemical characterization of lateritic soils from parts of Kottayam, Kerala (India) to decipher the pedogenic association and interrelationships of these soils with geology and bioclimatic conditions.

MATERIALS AND METHODS

Details of study area: The study area is part of southern midland zone of Kerala and confined to the parts of Kottayam, Ernakulam and Kozhikode where Precambrian rocks like charnockites with narrow bands of pyroxene granulites and magnetite-quartz rocks are dominant (Damodaran, 1955). In Nilambur Valley, Kozhikode district, magnetite - quartzite, pyroxene and hornblende granulites and charnockite gneiss constitute the charnockite group (Sawarkar, 1980). Broadly, the soils of this region have been categorized as red sandy or sandy clay loams (Kamath, 1985) or more specifically by Bourgeon (1989) as mainly ferrallitics (French soil taxonomy) or subgroups of Ultisols, Alfisols and Inceptisols as per USDA soil taxonomy (USDA, NRCS, 2008). Kerala has substantial portion of laterites (around 60 percentage of the exposed surface area Krishnan *et al.,* 1996 and Haridranath *et al*., 1999) developed over rocks of different composition and age. South midland zone of Kerala receives mean annual rainfall of 3265 mm from early June to late September. The soil moisture regime is u*stic* with soil temperature regime of *Isohyperthermic* (Eswaran *et al.,* 1990) with a length of growing period of 210 to 270 days (Sehgal *et al*., 1992). The dominant natural vegetation comprises of *Canarium strictum, Mesa ferrea, Dipterocarpus spps., Callophylum elatum, Cullinia excels, Palaquium ellipticum, Tectonia grandis, Terminalia tomentosa, Dalbergia latifosa, Xylia xylocarpa, Pterocarpus marsupium, Santalum album, Avecinnia spps., Rhizophora spps*., etc. Patches of scrub vegetation with other xerophytic plants are found in association with tropical fruit trees like jack fruit and cashew.

The soil profiles under study in the midlands (≤ 300m) of Kerela (Fig. 1) were as follows.

P1: Kinalur series ($11^0$28'00"N latitude and $75^0$50'00"E longitude) is a member of clayey, kaolinitic, Ustic Kanhaplohumults. These soils are very deep, well drained, dark red, gravelly sandy clay loam surface and red to reddish brown gravelly sandy clay sub soils with argillic horizon occurring on uplands and mounds.

P2: Chingavaram series ($9^0$44'00"N latitude and $76^0$51'48"E longitude) is a member of loamy skeletal, kaolinitic, family of Typic Kandiustults . These soils are deep, well drained dark red surface horizons and red argillic Bt horizons with sandy clay loam texture. These soils occur on midlands having >15 per cent slopes.

P3: Kanjirapalli series($9^0$33'00"N latitude and $76^0$47'00"E longitude) is a member of clayey-skeletal, kaolinitic, Ustic Kandihumults. These soils are very deep, well drained formed on charnokite with dark reddish brown gravelly sandy clay loam surface and red to reddish brown gravelly sandy clay sub soils with argillic horizon occurring on uplands mounds and hills having more than 30 % slopes.

P4: Athirampuza series ($9^0$39'34"N latitude and $76^0$31'35"E longitude) is a member of clayey-skeletal, kaolinitic, Ustic Kanhaplohumults. These soils are deep, well drained formed on laterized rocks (charnokites) with yellowish red gravelly clay surface and red to yellowish red gravelly argillic clay subsoils. This soil occurs on uplands, mounds and hills having slopes more than 30 per cent. This is a competing series of Arur series (Harindranath *et al.,* 1999).

Laboratory analysis: Horizon wise soil samples for each soil series were collected and passed through 2mm sieve after air drying. The fine earth fraction was used for laboratory analysis for particle size distribution (International pipette method), pH (1:2.5), organic carbon (OC, Walkley Black), cation exchange capacity (CEC) and exchangeable bases (ammonium acteate) and percent base saturation was estimated as sum of bases/CEC*100. The ECEC (Effective cation exchange capacity) was derived as summation of ex-

Table 1. Summary of weathering indices formula.

Index	Formula	References
Chemical index of alteration (CIA)	CIA= $Al_2O_3/Al_2O_3+Na_2O+CaO=K_2O*100$	Nesbit and Young (1989)
WIP	$(2*Na_2O / (0.35) + (MgO / 0.90) + (2*K_2O)0.25) + (CaO/0.70)*100$	Parker (1970)
Si/Al		Birkeland (1999)
Bases/Alumina		
Bases/R2O3		
Reiche product index (RPI)	$100* (SiO_2) / (SiO_2+R_2O_3)$	Reiche (1943)
Vogt ratio	$Al_2O_3 + K_2O / MgO + CaO + Na_2O$	Vogt (1927)
Weathering Ratio (WR)	$(CaO + MgO + Na_2O) / TiO_2$	Chittleborough(1991)
Weathering Index -1	$(CaO + SiO_2) / (Fe_2O_3 + TiO_2)$	Darmody (2005)
Weathering Index -2	$(CaO + SiO_2) / (Al_2O_3 + Fe_2O_3 + TiO_2)$	
Ignition loss index	H_2O*	Jayawardena (1994)

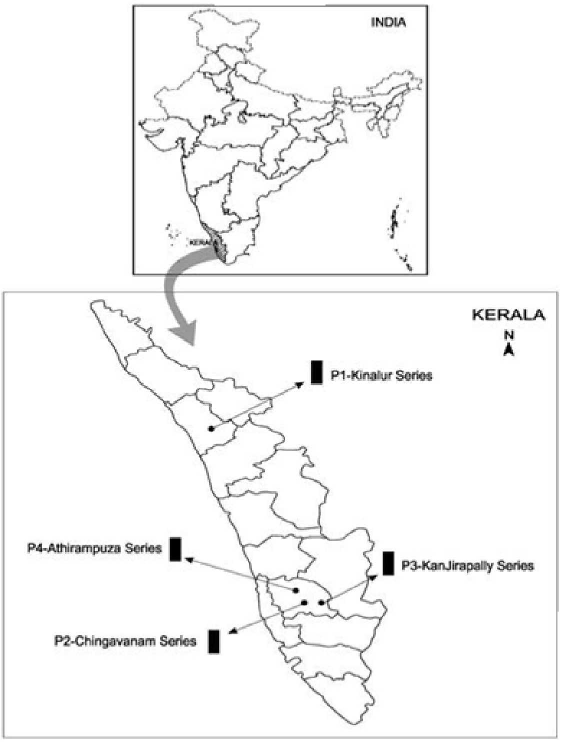

Fig. 1. *Location map of soil profiles under study in Kerala.*

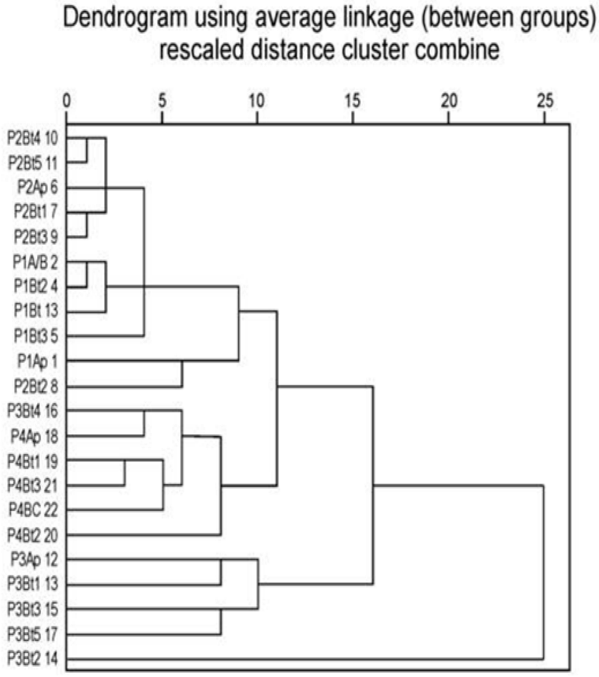

Fig. 2. *Soil grouping based on geochemical data.*

changeable aluminium and exchangeable bases. 1M KCl extractable aluminium was determined titrimetricaly, apparent CEC and ECEC was estimated as CEC/ clay*100 and ECEC/clay*100 (Sarma *et al.,* 1987; Jackson, 1975).

Elemental analysis was carried out using 1mm soil fraction by acid digestion (HF) for all elements except silica. Silica was estimated separately by sodium carbonate fusion using platinum crucibles (Page *et al.,* 2002). Molar concentrations were estimated by dividing the elemental concentrations with atomic weight of the elements. The weathering indices were calculated by various methods as listed in table 1.

RESULTS AND DISCUSSION

Soil characteristics: The characteristics red and lateritic soils of Kerala developed over granite (P1), laterite (P2 and P3) and charnokite (P4) are listed as below and presented in table 2. Kinalur series (P1) have 10cm thick, dark brown, very strongly acid (pH < 4.5) A horizons and have 70cm thick kandic dark reddish (5YR3/4) to reddish brown(5YR4/4) or red (2.5YR/6) strongly acid (pH of 5.1 -5.5) with more than 30% clay and base saturation less than 35% to classify than under the subgroup of Ultisols. The kandic horizon has an apparent CEC less than 16 cmol/kg clay and an apparent ECEC less than 12 cmol/kg within 100cm to further classify Kanhaplic Haplustults. The very strongly acid Chingavanam series (P2) have 15 cm thick, dark red (2.5YR3/6) Ap horizons and red (2.5YR4/6) to reddish brown (2.5YR4/4) clay rich kandic horizons (30 to 36% clay) with base saturation less than 35%, to classify as Typic Kandiustults.

The very strongly acid Kanjiraplli series (P3) and Athiram puzha series (P4) are classified as Ustic Kandihumults because these soils have an organic carbon more than 0.9 per cent in upper 15 cm of kandic horiozon with low base saturation. These soils have reddish brown Ap horizons (5YR3/3 to 3/4) and dark

Table 2. Selected morphological, physical and chemical properties of soils of Kerala .

Depth (cm)	Horizon	Matrix colour	Texture	Particle size distribution (%) sand	silt	clay	pH	OC g/kg	CEC	ECEC	CEC/ C*100	ECEC/ C*100	Base saturation (%)
									cmol(P+)kg^{-1}				
P1-Kinalur series, Kozhikode, Kerala: Fine loamy, isohyperthermic family of Kaolinitic, Kanhaplic Haplustults (Granite Gneiss) - 11^{0}28'N latitude - 75^{0}50'E longitude													
0-10	Ap1	7.5YR 3/4	SCl	47.2	21.2	31.6	4.5	31.9	7.4	2.3	23.41	7.27	12.5
10-36	AB	5 YR 3/4	SCl	48.7	18.7	32.6	5.1	22.2	5.4	1.8	16.56	5.52	9.0
36-48	Bt1	5 YR 4/4	SCl	48.5	19.3	32.2	5.3	14.8	6.1	1.6	18.94	4.96	9.2
48-66	Bt2	5 YR 4/4	SCl	47.1	19.5	33.4	5.2	12.0	5.4	1.4	16.16	4.19	10.8
66-80	Bt3	2.5YR 4/6	SCl	50.7	19.2	30.1	5.1	6.1	5.1	1.6	16.94	5.31	13.7
P2-Chingavanam series, Kottayam, Kerala:Loamy skeletal, Kaolinitic family of Typic Kandiustults (Laterite) - 9^0 44''N latitude - 76^{0}51'E longitude													
0-15	Ap	2.5YR 3/6	SCl	50.2	16.3	33.5	4.5	8.7	4.5	2.4	13.43	7.16	44.2
15-41	AB	2.5 YR 4/6	SCl	52.2	17.9	29.9	4.7	3.5	3.1	0.9	10.36	3.01	19.7
41-66	Bt1	2.5 YR 4/6	SCl	47.4	22.1	30.5	4.7	2.3	3.0	1.3	9.83	4.26	23.3
66-99	Bt2	2.5 YR 4/4	SCl	46.9	20.4	32.7	4.9	3.1	3.6	1.3	11.00	3.97	19.2
99-140	Bt3	2.5 YR 4/4	SCl	39.5	24.3	36.2	4.8	3.9	3.5	1.9	9.66	5.24	37.1
140-176	Bt4	2.5 YR 4/4	SCl	45.2	22.8	32.0	5.0	3.1	3.5	1.7	10.93	5.31	
P3-Kanjirapally series, Kottayam, Kerala: Loamy skeletal, Kaolinitic family of Ustic Kandihumults (Charnokite) - 9^{0}39'N latitude – 76^{0}31'E longitude													
0-13	Ap	5YR 3/3	SCl	69.9	9.0	21.2	4.8	23.5	4.5	1.6	21.22	7.54	21.7
13-32	Bt1	5 YR 3/4	SCl	56.1	12.5	31.3	4.4	18.6	3.5	1.1	11.18	3.51	17.1
32-56	Bt2	2.5 YR 3/6	SCl	59.9	11.1	28.9	4.5	15.0	3.7	0.8	12.80	2.76	14.0
56-83	Bt3	2.5 YR 3/6	SCl	62.8	11.4	25.7	4.5	9.0	4.1	0.7	15.95	2.72	13.2
83-112	Bt4	2.5YR 4/6	SCl	57.1	11.3	28.5	4.4	11.1	3.9	0.6	13.68	2.10	13.2
122-150	Bt5	2.5YR 4/6	SCl	62.6	13.4	24.0	4.7	12.2	4.0	0.7	16.66	2.91	16.8
P4.Athirampuza series, Ernakulam, Kerala:Clayey skeletal, Kaolinitic family of Ustic Kandihumults (Laterite) - 9^{0}33'N latitude – 76^{0}47'E longitude													
0-16	Ap	5 YR 4/4	SC	51.7	11.0	37.3	4.0	23.6	9.0	2.6	24.12	6.97	6.3
16-42	Bt1	5 YR 4/6	C	39.7	8.0	52.3	3.8	12.6	8.1	3.4	15.48	6.50	5.7
42-66	Bt2	5 YR 4/6	C	33.3	6.7	60.0	4.1	9.9	7.3	3.3	12.16	5.5	5.1
66-89	Bt3	2.5 YR 4/6	C	34.6	11.8	53.6	4.3	6.7	6.4	3.1	11.94	5.78	6.7
89-105	BC	2.5 YR 4/6	C	30.3	16.3	53.4	4.1	6.3	7.0	2.4	13.10	4.49	14.0

Table 3. Elemental composition of selected soil of Kerala.

Depth (cm)	Horizon	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Cu	Zn	Mn	Ni	Cr	Cd	Zr	Ba	Sr	LOI (%)	Enrichment Index (EI)
		(%)								μg/g										
P1-Kinalur series																				
0-10	Ap1	55.80	17.40	1.20	0.80	1.59	0.68	1.97	1.08	304	142	324	60	48	8	14	33	40	16.91	0.66
10-36	Ap2	54.40	16.40	8.10	0.70	2.13	0.71	2.46	1	47	156	311	56	82	9	13	68	34	14.02	0.33
36-48	Bt1	56.30	17.80	3.70	1.00	1.59	1.15	3.09	1.17	43	234	359	33	89	8	15	54	36	14.17	0.32
48-66	Bt2	57.20	17.00	3.90	0.80	1.39	0.65	2.74	0.98	42	204	275	49	94	9	15	40	33	13.26	0.34
66-80	Bt3	50.30	17.80	13.20	0.70	1.05	0.77	1.87	1.05	43	327	250	49	72	8	13	60	31	13.05	0.38
P2-Chingavanam series																				
0-15	Ap	45.10	22.00	8.20	1.70	1.46	0.41	2.67	0.42	64	172	221	38	105	10	17	90	28	16.1	0.33
15-41	Bt1	43.70	21.20	13.50	1.80	1.10	0.41	2.79	0.45	67	274	192	18	74	11	16	76	23	14.52	0.87
41-66	Bt2	44.30	20.60	15.90	1.40	1.43	0.33	3.33	0.42	450	184	180	22	107	11	19	59	23	12.37	0.29
66-99	Bt3	40.10	20.40	16.30	1.30	1.05	0.4	4.13	0.48	55	213	199	18	81	14	16	64	24	16.53	0.33
99-140	Bt4	45.50	20.60	13.80	1.20	1.19	0.44	3.44	0.49	70	151	160	26	110	11	16	69	25	12.97	0.30
140-176	Bt5	46.70	22.00	11.80	1.30	1.23	0.39	3.05	0.46	74	145	172	5	122	10	17	78	25	11.9	1.41
P3-Kanjirapally series																				
0-13	Ap	45.40	26.10	6.40	1.10	0.74	0.54	0.2	0.52	17	151	535	624	127	0	371	38.64	17	18.18	0.94
13-32	Bt1	37.90	27.30	12.70	1.10	0.46	0.49	0.17	0.51	34	140	707	384	99	0	350	36.21	16	19.59	2.13
32-56	Bt2	37.30	30.90	11.60	1.00	0.54	0.67	0.17	0.53	20	126	784	990	167	26	261	30.45	14	18.93	1.33
56-83	Bt3	36.10	27.60	14.90	1.10	0.57	0.48	0.19	0.63	251	137	484	416	121	67	513	32.3	14	18.52	0.53
83-112	Bt4	33.70	30.00	14.90	1.20	0.52	0.31	0.13	0.65	59	117	299	175	62	0	221	52.4	11	18.96	1.54
112-150	Bt5	33.00	31.30	12.70	1.20	0.42	0.29	0.15	0.5	316	109	357	507	69	0	256	19.74	12	20.39	0.78
P4.Athirampuza series																				
0-16	Ap	46.80	24.60	8.30	1.90	0.44	0.43	0.22	0.79	15	185	360	296	116	0	220	25.91	21	16.56	0.61
16-42	Bt1	43.70	29.20	8.10	1.50	0.33	0.43	0.17	0.62	9	164	268	233	81	0	360	24.5	25	16.22	0.69
42-66	Bt2	39.20	30.40	12.50	1.40	0.55	0.41	0.17	0.69	162	148	169	156	91	65	473	42.81	25	15.12	0.76
66-89	Bt3	40.70	30.60	10.20	1.40	0.36	0.41	0.2	0.69	18	200	182	286	104	13	376	31.91	22	15.94	0.95
89-105	BC	41.60	31.80	7.80	1.40	0.33	0.45	0.17	0.71	18	145	188	415	67	13	269	26.67	22	15.41	2.84

Table 4. Geochemical grouping based on elemental affinity in soils of Kerala.

Clusters	Horizon sequences	Major elements	Trace elements
Group -1	P2Bt4- P2Bt5- P2Ap-P2Bt3	Si>Al>Fe>Na>Ti>Ca>K>Mg	Mn>Zn>Cr>Ba>Cu>Sr>Ni>Zr
Group-2	P1Bt3-P1Bt4-P1A/B-P1Bt2-P1Bt1-P1Ap-P2Bt2		Mn>Zn>Cu>Cr>Ba>Ni>Sr>Zr
Group-3	P3Bt4-P4Ap-P4Bt1-P4Bt3-P4BC-P4Bt2	Si>Al>Fe>Ti>K>Ca>Mg>Na	Zr>Ni>Mn>Zn>Cr>Cu>Ba>Sr
Gropu-4	P3Ap-P3Bt1-P3Bt3-P3Bt5-P3Bt2		Ni>Mn>Zr >Zn>Cr>Cu>Ba>Sr

reddish brown (5YR3/4, P5) to reddish brown(5YR4/6, P4) but changed to red (2.5YR4/6) in lower kandic horizons. The texture is uniformly sandy clay loam in Kanjirapalli series (P3) but of clay in case of Athirampuzha series (P4). The apparent CEC and ECEC are similar to that of kandic horizons reported elsewhere in India (Bhaskar *et al.,* 2005; Bhattacharyya *et al*., 2006). The occurrence of kandic gentic horizons in ferruginous soils of rubber growing areas in Kerala and Tamil nadu were reported (Krishnan *et al.,* 1996). The kandic horizons have set of properties resembling ferralic horizon with low CEC (<4 cmol/kg in sub horizons of B) and apparent effective cation exchange capacity <12cmol$_c$kg-1clay and cation exchange capacity <16cmol$_c$kg-1clay with thickness more than 30cm (FAO, 2006). It is interesting to mention here that the top soils of these profiles meet the criteria to define as modic that display characteristics like incompletely mineralized OM (intensive rubber growing area and frequent additions of leaf) and an OC content of >0.6 percent, blackish brownish in the hue of 5YR with base saturation < 10 per cent and pH <5.0 (FAO, 1998). The occurrence of modic topsoils in ferruginous soils of Shillong plateau were reported and proposed to use modic at subgroup level for Sombrihumults in Shillong plateau (Bhaskar *et al.,* 2009). The difficulties in identifying the clay skins in argillic horizons in soils of Kerala and in Northen states was very well expressed in review of red ferruginous soils of India by Pal *et al*., 2014 and places some soils in the subgroups of Dystrudepts.

Elemental composition: The elemental composition of four lateritic and associated soils of Kerala is presented in table 3. Among major elemental oxide, SiO_2 is dominant with it gradational decrease in concentrations to less than 40 per cent in kandic horizons of Kanjirapalli series(P3) but 40 to 50% with irregular trends in Chingavanam series (P2) and Athirampuzha series(P4) and exceeding 50 per cent in Kinalur series (P2). Next to SiO_2, Al_2O_3 concentration is 25 to 31 per cent with irregular depth trends in Kanjirapalli (P3) and of increasing trends in Athirampuzha series (P4). The Chingavanam series (P2) have Al_2O_3 concentration of 20 to 22 per cent with fairly uniform depth distribution but less than 20 per cent in Kinalur (P1, irregular trends). The Fe_2O_3 content is 3.7 per cent in kandic B horizons (P1) and reached to a maximum of 16.3 per cent in Bt3 horizon of P4. These soils have 1.1 to 2.2 per cent of TiO_2 with high concentration of 1.9% in P4 but decrease its concentrations in Bt horizons. The concentration of alkali and alkaline earth elements are less than 1 per cent in majority of soil horizons with the exceptions in soils where CaO and Na_2O exceed 1% (P1/P2).

Trace elements: Trace elements concentration in the lateritic profiles is mainly driven by weathering of bedrocks .Trace elements are defined as those elements that are present at concentrations below 1000 mgkg^{-1} or 0.1% (Rollinson, 1993). The distribution of trace elements with depth varies according element and to the different soil profiles due to variations in mobility characteristics, oxidation or intense leaching, effects of organic carbon contents and iron/ manganese co - precipitation under humid climate. The concentration range of these elements is as follows: Cu – 9 – 450 µgg^{-1}, Zn – 109-327 µgg^{-1}, Mn – 117-1571 µgg^{-1}, Cr – 48-281 µgg^{-1} , Ni – 5 - 990 µgg^{-1}, Ba – 19.7 -94 µgg^{-1}, Sr – 11.2 – 40 µgg^{-1}, and Zr – 13-513 µgg^{-1}. The Cu content is 304 µgg^{-1} in Ap horizon but decreases to 42 to 43 µgg^{-1} in genetic Bt horizons(P1) while in Chingavanam series (P2), the Cu content is 64 µgg^{-1} in Ap horizon but reached to 450 µgg^{-1} in Bt2 layer with its concentrations varying from 55 to 74 µgg^{-1} . In Kanjirapalli series (P3), the Cu content is 17 µgg^{-1} in Ap horizon but varying from 20 to 59 µgg^{-1} in genetic layers with maximum value of 251 (Bt3) to 316 µgg^{-1} (Bt5) . The Cu content in Athirampuza (P4) is 15 µgg^{-1} in Ap layer, 9 to 18 µgg^{-1} in B horizon with 162 µgg^{-1} in Bt2 layer (Table 3). The Cu anamolies are well expressed due to greater dispersion of Cu in iron rich lateritic soils. The Zn contents are more than 200 µgg^{-1} in genetic horizons of P1 and P2 as compared to P3 and P4. The mean Zn concentration is 180 µgg^{-1} which is three times more than world average for soils (90 mg/kg, Bowen, 1979). The surface enrichment of Mn contents (268 to 535 µgg^{-1}) in A horizons of all soils with decreasing values in Bt horizons except in P3 where its concentration reached to more than 700 µgg^{-1} In Bt1 and Bt2 layers .The Ni contents are less than 100 µgg^{-1} in P1 and P2 but reached to a maxima of 990 µgg^{-1} in Bt2 horizon of P3 and 415 µgg^{-1} in BC horizon of P4. The mean Ni content is 220 µgg^{-1} which is almost four times higher than world average for soils (60 mg/kg, given by Bowen, 1979). Comparing the Ni contents (> 200 µgg^{-1}) with the Great London Council (2001), these soils are registered as contaminated . The strong negative relation of Ni with SiO_2 (r = - 0.51**, significant at 1% level) indicating its decrease with

Table 5. Weathering indices and ratios in soils of Kerala.

Depth	Horizon	mSi/mAl	mSi/mR_2O_3	VR	CIA %	RPI*100	WIP*100	WR	WI-1	WI-2	Fe:Al	Base:Al	Base: R_2O_3	CIW	Si:Ti	PIA	Al:Ti
P1-Kinalur series																	
0-10	Ap1	5.44	4.94	1.11	68.15	18.82	39.77	7.69	54.59	5.09	123.60	0.61	0.56	73.94	80.48	71.52	14.79
10-36	Ap2	5.63	4.11	1.37	62.67	22.03	44.59	10.87	15.86	4.28	17.86	0.77	0.56	67.44	81.16	64.75	14.41
36-48	Bt1	5.37	4.46	1.20	63.71	21.03	52.70	8.53	27.05	4.59	40.44	0.70	0.59	69.06	79.49	66.24	14.81
48-66	Bt2	5.71	4.73	1.21	65.77	20.12	44.82	8.50	28.37	4.86	38.99	0.53	0.44	70.73	80.95	68.34	14.17
66-80	Bt3	4.80	3.15	1.52	71.98	26.60	37.28	7.76	9.37	3.22	10.13	0.57	0.38	78.12	79.45	76.08	16.57
ώ (weighted mean)		5.43	4.23	1.30	65.83	21.84	43.97	9.24	24.06	4.37	0.24	0.61	0.48	-	-	-	-
P2-Chingavanam series																	
0-15	Ap	3.48	2.60	1.34	73.77	28.84	35.57	3.73	10.70	2.70	14.62	0.41	0.31	75.74	72.15	75.07	20.77
15-41	Bt1	3.50	2.31	1.52	74.07	31.50	36.19	3.32	6.98	2.37	8.61	0.44	0.29	76.29	71.72	75.55	20.50
41-66	Bt2	3.65	2.31	1.58	69.94	31.91	41.36	4.99	6.52	2.39	7.41	0.53	0.34	71.83	73.49	71.05	20.14
66-99	Bt3	3.34	2.10	1.59	68.02	31.84	48.83	5.86	5.80	2.15	6.54	0.46	0.29	70.09	72.40	69.15	21.71
99-140	Bt4	3.75	2.50	1.50	70.24	30.35	43.08	5.834	7.68	2.56	8.76	0.45	0.30	72.48	74.56	71.57	19.89
140-176	Bt5	3.61	2.54	1.43	73.08	30.60	39.00	4.97	8.87	2.61	10.52	0.21	0.14	75.20	73.91	74.46	20.52
ώ		3.57	2.38	1.50	71.23	30.94	41.42	4.99	7.56	3.56	0.42	0.41	0.27	-	-	-	-
P3-Kanjirapally series																	
0-13	Ap	2.95	2.44	1.21	90.82	30.98	12.77	2.17	14.28	2.45	18.86	0.15	0.13	93.97	78.81	93.75	24.32
13-32	Bt1	2.36	1.75	1.35	92.98	36.11	11.49	1.68	6.85	1.77	7.93	0.12	0.09	96.07	67.76	95.94	28.76
32-56	Bt2	2.05	1.60	1.28	93.23	38.82	12.49	2.316	7.40	1.62	8.55	0.13	0.10	96.07	65.38	95.95	31.92
56-83	Bt3	2.22	1.60	1.40	91.65	37.78	13.67	1.83	5.71	1.62	6.44	0.13	0.09	95.35	66.61	95.14	30.01
83-112	Bt4	1.91	1.40	1.38	92.70	40.26	12.81	1.27	5.27	1.42	6.01	0.11	0.08	96.28	63.47	96.12	33.29
122-150	Bt5	1.79	1.37	1.31	94.18	40.15	10.51	1.14	5.89	1.39	6.91	0.09	0.07	96.87	62.19	96.78	34.76
ώ		2.10	1.59	1.33	92.84	38.23	12.16	1.63	6.83	1.62	0.28	0.11	0.09	-	-	-	-
P4-Athirampuzha series																	
0-16	Ap	3.23	2.46	1.31	90.36	31.70	15.81	0.93	10.39	2.48	14.99	0.15	0.11	95.49	71.01	95.21	21.99
16-42	Bt1	2.54	2.04	1.24	93.51	35.59	12.60	1.03	10.55	2.06	14.34	0.11	0.09	97.08	68.53	96.95	26.98
42-66	Bt2	2.19	1.66	1.32	92.24	39.40	14.12	1.30	6.91	1.68	8.34	0.12	0.09	95.96	65.97	95.79	30.15
66-89	Bt3	2.26	1.78	1.27	93.12	38.15	13.91	1.13	8.40	1.79	10.61	0.11	0.08	96.88	66.60	96.75	29.51
89-105	BC	2.23	1.83	1.21	93.55	37.83	13.96	1.13	10.52	1.85	14.18	0.10	0.08	97.31	66.37	97.19	29.89
ώ		2.67	2.10	1.39	92.57	40.37	15.26	1.22	7.62	3.33	0.22	0.12	0.09	-	-	--	-

increase of SiO_2 but has a strong relation with Al_2O_3 (r = 0.67**) suggesting the occurrence of Al rich phases such as clay minerals excert significant control on abundance of Ni (Al Chalabi, 2004). The Cr contents varied from 48 to 167 μgg^{-1} with mean of 94.9 μgg^{-1} which is more than average of world soil (68 μgg^{-1}, Callender, 2004). The mean strontium content is 23.62 μgg^{-1} with strong positive relation with SiO_2 (r = 0.48**) and MgO (r = 0.78**) suggesting its strong association with plagioclase feldspars. The source of Sr is andesine and presence of Zr in these soils can be explained by presence of plagioclase feldspars. It was reported by Brantley *et al*. (1999) that Sr releases from feldspar at pH 3.0 where bytownite releases Sr by factor of 60 to 400 times than anorthite and microcline respectively. The Ba content is 47.84 μgg^{-1} with strong positive correlation with CaO (r = 0.67**) and K_2O (r = 0.77**). Alkalis and alkaline earth elements, such as K, Na and Sr, are the most active elements and easily removed from the profile during chemical weathering (Nesbitt *et al.*, 1980). This can be inferred from the major and trace element records that these soils are intensively weathered under tropical monsoon climate with an annual precipitation more than 2000 mm and the consecutively trapping Sr by clay minerals.

Soil grouping: The horizon wise major and trace elemental concentrations in these soils are grouped into four clusters (Fig.2) that displayed different patterns of dominance of these elements as shown below.

The major element concentration pattern in Group-1 and 2 is similar with an order of Si > Al > Fe > Na > Ti > Ca > K > Mg with Cr > Ba > Cu in Group-1 and Cu > Cr > Ba in Group-2 soils whereas Si > Al > Fe > Ti > K > Ca > Mg >Na with Zr > Ni > Mn in Group-3 to Ni > Mn > Zr in Group-4 soils (Table 4). In all soils ferric iron oxide is enriched in the lower and intermediate horizons while enrichment of titanium in Group-3 and Group-4 is controlled by the original mafic lithology that bears remarkable high percentages of titaniferous pyroxenes and Fe-Ti oxide minerals (Moufti, 2010).

Weathering indices: Chemical weathering indices are commonly used for characterizing weathering intensity of four lateritic profiles of Kerala by incorporating bulk major elemental oxide chemistry in a single metric (Table 5). The indicies are based on the principle that the ratio between concentrations of mobile (such as SiO_2, CaO, MgO, and Na_2O) and immobile elements (Al_2O_3, Fe_2O_3, TiO_2) should decrease over time as leaching progresses (Souri *et al.,* 2006). The ratio's of more active elements to that of more stable elements, like the molecular ratio of Si to Al or Si to (Al+Fe), have been used in soil genesis studies for a long time to judge soil weathering degree and as criteria in soil genetic classification systems.

The molar ratio of Si to Al (Ruxton, 1968), used to evaluate loss of SiO_2 with weathering that shows less than 2 in kandic horizons of Kanjirapalli series (P3) indicating presence of kaolinite and Al chlorite with more weathering. The wider ratio's (> 3) in P1 is an indication of persistence of primary minerals such as quartz and muscovite and the values in between 2 and 3 in other soils is an indication of moderate weathering. This observation is further confirmed with silica to sesquioxide ratio (SiO_2 / R_2O_3). The classification is possible on the basis of geochemistry of this ratio (Gidigasu, 1976). The ratio is in between 1.33 to 2.0 in kandic horizons of P3 and P4 to define as lateritic (Raychaudhuri, 1980, Burke *et al*., 2006) whereas in other soils this ratio is above 2 to define as non lateritic tropical soils. The Kanjirapalli (P3) and Athirampuzha (P4) soils are subjected to intensive continuous weathering with hydrolysis of silicates, processes of argillation (mobilization and accumulation of clay particles due to sudden wetting of dry soils under extreme acid condition) and rubification (transformation of ferric oxide to bright red hematite). It was recognized that Fe and Al are retained preferentially because of the precipitation of poorly crystalline soild phases (e.g, ferrihydrite) from supersaturated solutions (Chadwick *et al*., 2003). These ferrallitic soils are characterized by low silica to sesiquioxide ratio and base saturation. The other soils are fersiallitic soils with this ratio more than 2. These soils are further divided based on base saturation less than 35 (P3 and P4) and moderate to high (Kalpage, 1974).

Vogt residual index values in these soils vary from 1.21 to 2.07 showing slight variations with depth and are less than 1.4 in majority of kandic horizons. The low vogt ratio corresponds to pH values between 3.8 to 5.3and found to be less effective in capturing weathering trends in lateritic profiles. The chemical index of alteration (CIA), Harnois chemical weathering index (CIW) and plagioclase index of weathering (PIA) are more than 90 in P3 and P4 indicating high degree of weathering as reported in lateritic profiles of Kerala (Sanjinkumar *et al.,* 2011). The rationale of the CIA is to give a quantitative measure of feldspar weathering by relating Al to Na, Ca and K, which should be removed from a soil profile in the course of plagioclase and K-feldspar weathering (Nesbitt and Young, 1982). The CIA values more than 90 in P3 and P4 indicates intense chemical weathering correspond to pH values less than 4.5 whereas CIA values less than 75 in P1and P2 indicates less intensely weathered with a corresponding pH more than 4.7. The assumption that Ca, Na and K decrease as weathering intensity increases and that Al stays mostly immobile (Kirkwood and Nesbitt, 1991) is valid here. These results are in accordance with observations in other weathering studies and theoretical considerations of the element behavior, suggesting that K release is small compared to the Na release. This is due to stronger weathering resistance of K phases such as K-feldspar and due to the fixation of K on clay minerals (Yang *et al*., 2004 and Reeder *et al*., 2006). Moreover, high CIA values, suggest derivation from a stable terrain (autochthonous in nature) of SMZ of Kerala (Hossain *et al*., 2010). The high PIA values (P3 and P4) further indicate that the plagioclases in parent rock displayed increasing chemical weathering with steadily decreasing contents of plagioclases and enriched in secondary aluminous clay minerals (Roy *et al*., 2008).These indices illustrate the relative loss of Ca, K and Na very rapidly in humid tropical environments and are perhaps more suitable for the study of early stages of rock weathering rather than for well-developed tropical soils. Given the formulations of weathering indices such as molar ratio of Si to Ti, Parker index and weathering ratio shows decreasing values signifying greater weathering in P3 and P4 as compared to the other soils under study. The parker index values less than 15 in P3/P4 and more than 40 in P1/P2. The kind variations in parker index were reported in highly weathered soils by Eswaran and Raghu Mohan (1973). The similar trends of weathering ratio's are recorded with its values of less than 2 in P3/P4, 9.24 in P3 and 4.99 in P2. The indices CIA and CIW are perhaps more suitable for the study of early stages of rock weathering rather than for well-developed tropical soils The serious loss of bases in these soils is evident with bases to alumina and sesiquioxide ratios (<0.5). The molar ratio of Al to Ti do not show any trends with respect to soils but its values vary from 9.67 to 34.76. The ratio is more than 20 in P2, P3 and P4. In general, the values of WPI, PI, Si-Al, Wp and MWPI decrease as the weathering grade or density increases. This is in accordance with findings from Jayawardena and Izawa (1994) and Gupta and Rao (2001). Decreasing values of WPI, MWPI and Wp indicated decreasing mobile cations and increasing hydroxyl water with increasing weathering. Decreasing PI, Si-Al and Si-Ti values are indicative of a decreasing silica content. It can be seen that there was a sharp decrease in these particular weathering indices from the highly weathered granite to granite saprolite state and this confirms the field observations of the abrupt change between the weathered rock and saprolite. Alternatively, CIA, CIW and loss on ignition showed a continuous increase with increasing degree of weathering. This can be attributed to the loss of mobile cations and alteration of the crystal structure, hence the increase in hydroxyl water.

It is interesting to note that high degree of weathering in P3/P4 profiles is reflected by low SiO_2/R_2O_3 ratios and high CIA, PIA and CIW (Ranger, 2002). The triangular plots of SiO_2-Al_2O_3-Fe_2O_3 clearly shows that these soils are subjected to weak laterization in P1, moderate in case of P2 to strong laterization process in P3/P4 (Schellmann, 1981). The differential rates of weathering in other profiles is due to prevalence of tropical monsoonic climate triggering the mechanism of chemical weathering and also by anthropogenic activities such as improper land use practises on sleep slopes (Topioca and banana cultivation) and deforestation further accelerating chemical weathering in the region (Sanjinkumar *et al.,* 2011). It is further reported that the nature of clay minerals formed due to weather differs with intensity and duration of rainfall. The weathering profiles under high rainfall (300 cm) have clays, aluminium hydroxides and Fe-Al Oxides but in rain shadow zones (< 200cm) have complex clay mineralogy and absence of or low Fe-Al oxides in the clay fraction (Deepthy and Balakrishnan, 2005).

The applicability of the various weathering indices to different material types and weathering conditions has long been a source of debate. Parker (1970) stated that the Silica-Alumina Ratio was restricted as to its use because the amount of sesquioxides must remain approximately constant during weathering and there must preferably be no formation of smectites or vermiculites as initial weathering products. Harnois (1988) reported that the use of K_2O as a mobile component in the CIA, WPI and MWPI limits their application to soils in which potassium has been leached, as potassium, through its high exchange capacity can be adsorbed onto other clays in the weathering profile, thus masking its mobility. The Vogt ratio uses K_2O as an immobile component which contradicts the evidence that potassium is commonly leached. The common point made by all of these authors is that for chemical weathering indices to be effective, an understanding of the geochemical composition and nature of geochemical processes and trends of the particular material of interest is required for the successful application of any weathering index.

Conclusion

The geochemical properties of four representative ferruginous soils of Kerala showed strong laterization in Kanjirapalli (P3) and Athirampuzha (P4), weak laterization in Kinalur (P1) and moderate laterization in case of Chingavanam series (P2). These soils have Vogt residual index values less than 1.4 in majority of kandic horizons with chemical index of alteration (CIA), chemical weathering index (CIW) and plagioclase index of weathering (PIA) more than 90 in P3 and P4 indicating high degree of weathering. The enrichment index values more than 1 in majority of soil horizons of Kanjirapalli series (P3) in BC layers of Athirampuzha series (P4) and in Bt5 horizon of Chingavanam series (P2) indicated the high concentration of Ni and Sr thatassociation with SiO_2 ,Al_2O_3 and MgO suggestthe occurrence of Al rich phases such as clay minerals which exert significant control on abundance of Ni and strontium content. The kandic horizons with set of properties of ferralic horizon and mollic top soil properties (intensive rubber growing area and frequent additions of leaf) with pH <5.0 must be considered to be placed at subgroup level of Ultisols.

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