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Chemical and Mineralogical Characteristics of Ferruginous Soils of Goa

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Abstract: Physical, chemical and mineralogical properties of two Benchmark soils of Goa are reported. The soils are acidic and DpH is negative. KCl extractable acidity is low but total acidity of $BaCl_2$ -Tea is remarkably high indicating hydroxy-interlayering in clay minerals. CEC is medium to low but base saturation is >35% and thus classified as Alfisols.

Kaolin is the dominant mineral both in silt and clay fractions alongwith gibbsite, mica, vermiculite and chlorite. The kaolins are interstratified with 1.4 nm minerals. The 1.4 nm minerals are hydroxy-interlayered. Gibbsite is formed in an earlier alkaline pedo-environment and hence its presence should not be considered as an index of weathering. The persistence of good amount of organic matter in these soils are due to their linkage with weatherable clay minerals and other polyvalent cations which helps to improve the soils properties. The detailed information of minerals and their weathering stages helps in understanding the potential of the so-called highly weathered ferruginous soils of this part of tropical India.

It is well recognized that ferruginous soils are formed under humid tropical climate due to leaching of bases and release of iron and its coating on soil surfaces. Although ferruginous soils of India are formed under humid tropical conditions for millions of years, they vary in their physical, chemical and mineralogical characteristics. They are classified as Ultisols, Alfisols and even Inceptisols. Ferruginous soils of southern and western part of the country are fairly well characterized, but the detailed information on soils of Goa are very few except on their physical and chemical characteristics (Raghu Mohan *et al.*, 1971; Govindarajan *et al.*, 1974, Singh *et al.*, 1988). The ferruginous soils in general, have low fertility status, but they support good vegetation. This prompted the

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authors to study the soils of Goa in detail to understand the process of soil formation and it is hoped that it will enhance our knowledge on genesis of ferruginous soils of tropical India in general and that of Goa in particular.

Materials and Methods

The state of Goa is located in the south-western part of India. The National Bureau of Soil Survey and Land Use Planning (ICAR) during its soil survey programme of the country, surveyed the state of Goa on 1:50,000 scale and the soils are mapped at the level of soil series association (Harindranath *et al.*, 1999).

Two representative benchmark pedons widely occurring in the State have been selected for the present study. The soils are developed from Goa group of Archeans consisting of schists and ferruginous quartzite. The climate of the state is warm tropical with an annual rainfall of 2600 mm and average temperature of 26°C. The moisture regime is ustic. The difference between mean summer and winter temperature is <6°Cand thus qualifies for iso-hyperthermic temperature regime.

Morphological properties of the two soils were studied and described as per Soil Survey Manual (Soil Survey Division Staff, 1995) and the soils are Alfisols. (Soil Survey Staff, 1999).

Physical and chemical properties of soils were determined as per standard procedures (Jackson, 1973). Sand (2000-50 mm), silt (50-2 mm), clay (<2 mm) and fine clay (<0.2 mm) fractions were separated as per size segregation procedure of Jackson (1979) after removal of CaCO₃, organic carbon and free iron oxides. Oriented silt and clay fractions were subjected to X-ray diffraction (XRD) analysis in a Philips diffractometer with Ni-filtered, Cu-Ka radiation at a scanning speed of 2020/min. Samples were saturated with (1) Ca and solvated with ethylene glycol and (2) K-saturated and heated to 25, 110, 300 and 550°C and X-rayed. Identification of clay minerals in different fractions was done following the criteria laid down by Jackson (1979).

Results

Brief morphological properties of the soils are given in table 1. It indicates that the soils are moderately deep to very deep, brown to red in colour (7.5YR to 2.5YR hue) and are excessively drained. Clay content is substantially high in subsoil of Pedon 1 but the soils of Pedon 2 (Darbhandora soils) have high clay content (>35%) throughout its depth (Table 2).

Both the soils are acidic (pH 5.1-5.5), noncalcareous and KCl pH is less than water pH. The high negative Δ pH (-0.8 to

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Lab. No	Horizon	Depth (m)	Colour (moist)	Texture	Structure	Con	sistence
Pedon-1		Madgaon seri	es			moist	Wet
2904 2905 2906 2907	Ap Bw1 Bt1 Bt2	0-0.18 0.18-0.46 0.46-0.73 0.73-1.07	5YR3/4 5YR4/4 2.5YR4.5/6 5YR5/6	sl sl si cl sic	flsbk flsbk mlsbk mlsbk	fr vfr fr fr	ss p0 ssp0 sp sp
Pedon-2		Darbhando	ora seris				•
2908 2909 2910 2911	A A2 Bt1 Bt2 Cr	0-0.08 0.08-0.19 0.19-0.51 0.51-0.89 0.89+	7.5 YR3/3 5YR3/4 5YR3/4 2.5YR3/4 weat	sic sic sic sic hered later	m1sbk m1sbk m2sbk m2sbk rized material	fr fr fr fr	ss ps ss ps sp sp

Table 1. Morphological properties of soils

Note: The abbreviations are as per USDA Soil Survey Manual (Soil Survey Staff, 1951)

Table 2. Physical and chemical characteristics of soils

Lab. No	Sand <	Silt Clay	FC		рН		Org. C
		(73)		H ₂ O	KCI	ΔрΗ	(g kg ^{-r})
Pedon-1							
2904 2905 2906 2907 <i>Pedan-2</i>	78.2 77.0 41.0 14.4	10.511.611.511.531.327.742.043.6	7.8 7.0 10.7 10.5	5.1 5.5 5.5 5.4	4.1 4.3 4.5 4.5	-1.0 -0.8 -1.0 -0.9	18.7 8.4 7.9 2.5
2908 2909 2910 2911	20.7 9.1 7.0 8.8	33.146.228.762.235.757.226.065.2	18.1 33.7 29.5 35.5	5.4 5.3 5.2 5.2	4.6 4.4 4.4 4.4	-0.8 -0.9 -0.8 -0.8	50.4 25.2 20.1 14.7

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-1.0) indicates that these soils contain appreciable amount of clay minerals with relatively constant surface charge (Blecker and Sageman, 1990). Darbandora soils have higher organic carbon than Madgaon soils (Table 2). CEC and ECEC of the soils of Madgaon series are lower compared to the Darbandora soils due to their low organic carbon and clay content (Table 2). Though the extractable acidity by 1 NKCl is low, the same obtained by BaCl₂-TEA is remarkably high (Table 3). Bhattacharyya et al. (1994) also observed low to nil KCl extractable Al⁺³ in ferruginous soils of Manipur and Meghalaya when the pH of the soils exceeded 5. Though the soils are acidic, the base saturation is more than 35%. Calcium dominates the exchange complex of the soils followed by Mg. CEC of the soils is low to medium (6-19 cmol(p⁺) kg⁻¹) as commonly observed in ferruginous soils of India (Chandran et al., 2000; Bhattacharyya et al., 2000).

The BaCl₂-TEA extractable acidity is several times more than KCl acidity. High amount of BaCl₂-TEA extractable acidity indicates that large amount of Al⁺³ released during humid tropical weathering are trapped in the interlayer of clay minerals and are not easily extractable by KCl. This suggests that most of the fairly high BaCl₂-TEA extractable acidity of

these soils can be attributed to the Al⁺³ in the Al-hydroxy components that are held tenaciously on the exchange complex (DeAlwis and Pluth, 1976). Elemental composition of soils (Table 4) indicates silica as a dominant component followed by Al_2O_3 and Fe_2O_3 . Molar ratio of silica: sesquioxide is more than 2.5 indicating siliceous nature of these soils and incomplete desilication process. The tropical ferruginous soils of India, thou they are considered as laterites are reported to have high SiO₂/Al₂O₃ and SiO₂/R₂O₃ ratio (Varghese and Byju, 1993). Though it is presumed that the process of laterization is active in humid tropical area with high rainfall and high temperature, the ideal pH condition for the primary process of silica solubilisation is possible at a pH of ~9 (Millot, 1970) which is not prevalent in most of the tropical ferruginous soils. Therefore the process of laterization began at the end of Cretaceous (Kum'ar, 1986; Tardy et , 1991) and ceased to operate further when the pH of the system became neutral and then acidic.

Mineralogy of Soils

Mineralogy of sand: XRD of sand fraction (Fig. 1) indicate the presence of gibbsite (0.48 nm peak), kaolin (0.72 nm) and quartz, along with some feldspar. The presence of gibbsite in all size fractions questions the probability of its formation

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l ab No	- 	Extrac (cmc	ctable ol(P ⁺)k	bases (g ⁻¹)		Total	Ex (cmc	. Acidit I (P ⁺) K	у (g-)	(cm	CEC ol (P ⁺) K _i	g-)	B	S
L'aU.IVO	Ca ²⁺	Mg ^{2:}	+	Va⁺	\mathbf{K}^{\star}		H ⁺	Al ³⁺	BaCl ₂ - TEA	AmAc 2	Cations	ECEC	AmAc 2	Cations
Pedon-1			K											
2904	1.8	5 0.6	3	0.44	0.08	3.01	0.12	0.19	3.29	6.42	6.30	3.2	46.68	47.78
2905	1.9.	3 0.6	8	0.44	0.06	3.11	0.10	0.08	4.1	9.73	7.20	3.19	31.96	43.15
2906	2.9(0.8	5	0.36	0.09	4.17	0.04	00.00	5.76	6.31	9.93	4.17	66.07	41.59
2907	3.45	5 1.3	1 (0.44	0.08	5.28	0.05	0.02	4.11	6.64	9.39	5.30	79.2	56.26
Pedon-2										. 8				
2908	4.56	1.6	7 (.57	0.80	7.6	0.17	0.05	18.89	18.99	26.49	7.65	40.02	28.69
2909	3.94	1.6	5 ().63	0.23	6.45	0.19	0.37	19.65	15.75	26.10	6.82	40.95	24.71
2910	3.59	1.8	3 (.57	0.23	6.22	0.21	0.41	18.03	16.16	24.25	6.63	38.45	25.65
2911	3.51	2.1:	3).66	0.23	6.53	0.22	0.38	16.46	14.33	22.99	6.91	45.57	28.40

Table 3. Exchange characteristi

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* AmAc = ammonium acetate.

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olar ratios	$\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	7.4 6.6 3.9 3.2	3.9 3.6 3.6
W	SiO R ₂ C	4.0 2.7 2.8	2.3 3.0 2.9 2.9
K ₂ O		0.50 0.55 0.83 0.64	1.34 1.55 1.63 1.70
Na ₂ O		0.87 0.78 0.61 0.35	0.61 0.68 0.66 0.60
MgO		0.76 0.73 0.56 0.52	1.10 1.02 0.93 1.03
CaO		0.86 0.82 0.77 0.78	0.96 0.48 0.43 0.45
R ₂ O ₃		29.9 30.4 35.2 32.1	33.9 30.1 32.3 31.4
TiO2		2.2 1.74 1.66 1.71	1.46 1.62 1.64 1.66
Fe ₂ O ₃	*	15.7 14.2 13.9 6.4	15.9 6.80 11.1 7.4
Al ₂ O ₃		12.0 14.5 19.7 24.6	16.5 21.7 19.6 22.3
SiO ₂		53.5 55.0 44.9 46.0	37.7 45.8 45.0 47.2
roi Loi		12.6 10.7 16.0 17.4	23.4 19.3 17.5 16.7
Lab.No	Pedon-1	2904 2905 2906 2907 Pedon-2	2908 2909 2910 2911

Table 4. Elemental composition of soils

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Fig. 1. Representative X-ray diffractogram of sand fraction. G = gibbsite, K = kaolin, Q = quartz, F = feldspars

from the layer silicates alone. Similar conclusions were made earlier by Bhattacharyya *et al.*(2000) for soils of NE, India and Chandran *et al.* (2003, 2004) for the Ultisols of southern India.

Mineralogy of silt: XRD pattern of both the samples (Fig. 2) are similar. Casaturated and EG treated samples show characteristic peaks at 1.4 nm, 1.02 nm, 0.72 nm, 0.48 nm along with small peaks for quartz and feldspars. The K-saturation and subsequent heating resulted in the partial shifting of the 1.4 nm peak towards 1.0 nm but reappeared at K550^oC. This indicates that a part of the 1.4 nm minerals are hydroxy-interlayered and

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Fig. 2. Representative XRD diagrams of silt fractions : Ca =Ca-saturated, Ca-Eg = Ca saturated and glycolated, K25/110/300/550/ = K saturated and heated to 25° C, 110° C, 300° C, 550° C, HIV = hydroxy-interlayered vermiculite, M = mica, G = gibbsite, K = kaolin, Q = quartz, F = feldspars

part is fully chloritized. The presence of gibbsite in the sample was confirmed by a peak at 0.48 nm on Ca-saturation and its disappearance on K treatment and heating at 300° C. The sharpness of the peak suggests its high degree of crystallization. The 0.72 nm peak of

kaolin has a broad base indicating probable interstratification with 1.4 nm minerals. Therefore, the co-existence of both gibbsite and 2:1 minerals appears to be a common phenomenon in tropical ferruginous soils (Wada and Kakuto, 1983; de Brito Galvao and Schulze, 1996;

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Bhattacharyya *et al.*, 2000; Chandran *et al.*, 2004) and podzols (Wilke and Schwertmann, 1977) thus questioning antigibbsite hypothesis (Jackson, 1963; 1964).

Mineralogy of clay : The XRD pattern of clay fraction (Fig. 3) exhibits well defined XRD maxima indicating the presence of hydroxy-interlayered vermiculite, mica, kaolin and gibbsite and small peaks for quartz and feldspars. The 1.4 nm mineral did not change its position or intensity on glycol treatment indicating that it is of non-expanding type. On heating the K⁺ saturated samples from 110 to 300°C, the 1.4 nm peak partially collapsed reinforcing the 1.0 nm peak. However, when this sample was heated to 550°C, the partially hydroxy-interlayered vermiculite collapsed to 1.0 nm and at the same time the 1.4 nm peak of fully hydroxy-interlayered portion (chlorite) reinforced. This indicated that a portion of 1.4 nm peak is due to the presence of chlorite. The 0.7 nm peak of kaolin was confirmed by its characteristics high intensity peak and its disappearance on heating with K at 550°C. However, the 0.7 nm peak has a broad base tailing towards the low angle side indicating that these are not true kaolinites but interstratified with 2:1 minerals. This is more common in tropical soils of India than reported earlier (Bhattacharyya et al.,

2000; Chandran et al., 2001).

Mineralogy of fine clay: The fine clay fraction of Ca-saturated and glycolated samples (Fig. 4) shows dominant peaks at 0.72 nm. and 0.48 nm indicating the presence of kaolin and gibbsite The characteristics 0.72 nm peak of kaolin has a broad base tailing towards the low angle region. On heating the K-saturated samples at 550°C the 0.72 nm peak disappeared reinforcing the 1.0 nm regions indicating the interstratifications of 2:1 mineral with the 1:1 mineral, probably a KI-HIV mineral. A sharp peak at 0.48 nm and its disappearance on K treatment and heating at 300°C confirmed the presence of gibbsite. The decrease in intensity of 0.48 nm peak with the decrease in size fraction indicated that gibbsite might not have formed from the secondary minerals, as otherwise it might have accumulated in the finer fractions.

Discussion

Chemical and mineralogical data of the soils of Goa indicate that these soils are siliceous and contain considerable amount of weatherable minerals. This is a common feature in ferruginous soils of India (Satyanarayana and Thomas, 1962; Varghese and Byju, 1993; Chandran *et al.*, 2003; 2005). High amount of total extractable acidity indicate that Al⁺³ released during humid tropical weathering



Fig. 3. Representative XRD diagrams of total clay fractions : Ca = Ca-saturated, Ca-Eg = Ca saturated and glycolated, $K25^{0}/110^{0}/300^{0}/550^{0} = K$ saturated and heated to $25^{\circ}C$, $110^{\circ}C$ $300^{\circ}C$, $550^{\circ}C$, HIV hydroxy-interlayered vermiculite, M = mica, K = kaolin, G = gibbsite, Q = quartz, F = feldspars





Fig. 4. Representative XRD diagrams of fine clay fraction : Ca = Ca-saturated, Ca-Eg = Ca saturated and glycolated, K25/110/300/550 = K saturated and heated to $25^{\circ}C,110^{\circ}C$ $300^{\circ}C$, $550^{\circ}C$, HIV = hydroxy-interlayered vermiculite, M = mica, K = kaolin, Q = quartz, F = feldspars

are trapped in the interlayers of 2:1 minerals to form hydroxy-interlayered mineral. The vermiculite acts as a sink for aluminium and thus protects the biota from aluminium toxicity. These Al^{+3} ions are not easily extractable by 1 N KCl. Thus the vermiculites are formed from mica during the present humid tropical weathering conditions and are therefore considered as the products of contemporary pedogenesis.

The CEC and base saturation of these soils are high when compared with the soils of the humid tropical soils of Kerala (Chandran *et al.*, 2004) and humid subtropical Meghalaya state of the NE Region of India (Bhattacharyya *et al.*, 2000). Therefore they are grouped under Alfisols order of Soil Taxonomy (Soil Survey Staff, 1996). This high CEC may be due to the presence of large amount of weatherable minerals and high organic matter. Kaolin in these soils is still in an intermediate weathering stage of KI-HIV and it also helps in retention of organic matter.

The presence of HIV and KI-HIV and feldspars in this ferruginous soil indicate that in spite of tropical weathering conditions for millions of years, the soils of Goa are still Alfisols with > 35% base saturation. Thus they are less weathered than the soils of Kerala (Chandran and Bhattacharyya, 2003). With the

continuation of the tropical climate, the soils of Goa may become Ultisols due to leaching of bases and may become more acidic. But the acidic condition already prevailing in these soils may prevent further desilication to transform these soils into Oxisols.

The presence of M, HIV, KI-HIV and feldspar in both silt and clay fractions confirm the existence of good amount of weatherable minerals in the soils. Persistence of high organic matter in these soils is an indication of organic matter linkage with these minerals and other polyvalent cations. The organic matter retention in these ferruginous soils helps in improving soil properties which in turn support good crop growth. Thus the detailed information of minerals and their weathering stages helps in understanding the potential of the so called highly weathered soils of tropical areas.

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