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Role of zeolites in persistence of high altitude ferruginous Alfisols of the humid tropical Western Ghats, India

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Abstract

The high altitude ferruginous Alfisols associated spatially with shrink-swell soils on the Deccan basalt plateau and dissected table lands in the Western Ghats of India were analysed for their morphological, chemical and mineralogical properties with a view to comprehend their formation and persistence in the tropical humid climate prevailing since the early Tertiary. The study indicates that despite their acidic pH the soils have high bases and their clay fractions are dominated by interstratified smectite-kaolin. The persistence of these non-kaolinitic and/or non-oxidic Alfisols has been possible due to the presence of base-rich zeolites of amygdoloidal basalt. It suggests that for an open system such as soil, the existence of steady state is a more meaningful concept than thermodynamic equilibrium. The knowledge gained on the role of zeolites in soils provides a check on the reasoning of models on the formation of soils in tropical humid climate. The study also indicates that the supply of bases from zeolites can prevent the soils from losing their productivity even in intense leaching environment. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last 3 decades zeolite minerals have been recognised with increasing regularity as common constituents of Cenozoic volcanogenic sedi-

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mentary rocks and altered pyroclastic rocks (Ming and Mumpton, 1989). Zeolites have also been reported as secondary minerals in the Deccan flood basalt of the Western Ghats in the state of Maharashtra, India (Jefferv et al., 1988: Sabale and Vishwakarma, 1996). The compound flows comprising the lower lithostratigraphic formations of the Deccan Volcanic Province are extensively zeolitised and are mostly confined to the western and northern parts of Western Maharashtra (Sabale and Vishwakarma, 1996). An account of zeolites and other cavity minerals in Deccan volcanics has been given by Phadke and Kshirsagar (1981). In the vesicular or amygdular top of the compound flows, some of the amygdules are partly filled while some are completely filled. Among the commonly occurring species of zeolites, heulandite has a wide occurrence both in time and space (Sabale and Vishwakarma, 1996). Though the occurrence of zeolites is maximum in the upper amygdular part of a compound flow (Phadke and Kshirsagar, 1981), larger cavities occur at the base of the highly amygdular part of the flow units, with quartz being common in the central massive part. Zeolites have abilities to hydrate and dehydrate reversibly and to exchange some of their constituent cations and thus can influence the pedochemical environment during the formation of soils. Significance of these zeolites has recently been realised in the formation of shrink-swell soils (Vertic Eutropepts). It has been shown that zeolites can provide sufficient bases to prevent the transformation of smectite to kaolinite and thus making the formation of shrink-swell soils possible in microdepressions even in a humid tropical climate of the Western Ghats (Bhattacharvva et al., 1993).

Spatially associated red (Alfisols) and black (Vertic Inceptisols) soils as distinct entities with similar topographical conditions occur on the Bhimashankar plateau (1100 m above mean sea level) of the Western Ghats. There are several table lands with similar altitudes in and around the Western Ghats where ferruginous Alfisols also occur (Fig. 1). These soils are often referred to as laterites (Sahasrabudhe and Deshmukh, 1981). Since the terms 'red' and 'laterite' have led to controversial opinions the associated laterite and red soils (Alfisols) of the Western Ghats are referred to here, as ferruginous soils (Rengasamy et al., 1978). Contrary to general belief that such soils are difficult on which to grow crops (Aleva, 1994), the ferruginous soils of the Western Ghats are cultivated profitably to various agricultural and horticultural crops besides forestry with appropriate conservation measures (Bhattacharyya et al., 1992; Challa et al., 1995).

Fig. 1. (a) A part of the Western Ghats in Maharashtra, India showing different rainfall zones, (b) High altitude laterite areas on the Western Ghats (Sahasrabudhe and Deshmukh, 1981; Schmidt et al., 1983; Bhattacharyya et al., 1993), (c) Soil map of the study area (Bhattacharyya et al., 1992), (d) Representative profiles of high altitude ferruginous Alfisols on the Western Ghats showing soil-site characteristics (m1/2sbk: moderate weak/medium subangular blocky structure; Cl/C: clay loam/clay texture).



Judging by the tropical humid climate in the Western Ghats it is generally expected that base-poor ferruginous soils representing soil orders of Ultisols and/or Oxisols should form on these high altitude plateau surfaces in the present day climate. The presence of base rich Alfisols, on the contrary, can possibly be understood by studying the zeolites and their role in maintaining the chemistry of the pedoenvironment of soils.

2. Geomorphic and climatic history of the Western Ghats

The Arabian sea currently confronts the Western Ghats which rise precipitously across to an average height of 1200 m. The result is an orographic rainfall being heavy all along the West Coast. The lee-side towards the east receives less than 1000 mm of rainfall and is typically rain-shadowed (Rajaguru and Korisettar, 1987). Occurrence of numerous ferruginous soils capping the detached plateaus at an average elevation of about 1100 m above msl with an annual rainfall of more than 5000 mm (Anonymous, 1984), along the Western Ghats, suggests that an extensive peneplaned surface with gentle southerly slopes and moderate relief existed earlier in this part (Sahasrabudhe and Deshmukh, 1981).

The formation of ferruginous soils on Bhimashankar plateau was earlier explained in terms of a progressive landscape reduction process (Bhattacharyya et al., 1993). In the initial stage of soil formation, weathered material from the hills charged with montmorillonite as the first weathering product of Deccan basalt (Pal and Deshpande, 1987) was deposited in the microdepressions of the extended hills. With time, these sites on the hills gradually flattened and thus internal drainage dominated over the surface run off. After the peneplanation the ferruginous soils on a relatively stable surface continued to weather to form clay minerals of an advanced stage of weathering. The transformation of montmorillonite to clay minerals of advanced stage of weathering during laterization began at the end of the Cretaceous and continued during the Tertiary (Kumar, 1986; Tardy et al., 1991). In the dominantly erosional landscape of the north-western Deccan upland (Kale and Rajaguru, 1987) the existence of mesa, buttes and inselbergs in the study area has been described as the results of different erosional cycles (Subramanyan, 1981). The similarity in the relative elevations of the table lands and other conical hills in the study area and its surroundings indicate that these features were not independent as they are today; they were once a part of a single plateau. Due to truncation, in upper soil layers, both the total and fine clay presently show their very high contents and argillans almost immediately below the thin A horizon (Table 1). Gravel sized basaltic lithorelicts (≥ 2.5 cm in size) increase from 5 to 20% with depth within the solum and upto 40% (2.5–7.5 cm in size) in the C-horizon. Petrographic examination of primary minerals in the sand fractions of the soils indicate that quartz (cryptocrystalline) and zeolites are subangular to angular in shape (Fig. 2)

Table 1Selected data of a representative ferruginous soil—Pedon 4 of Fig. 1

Hori- zon	Depth (cm)	Particle size distribution of $< 2 \text{ mm soil } (\text{g kg}^{-1})$					pH	Extractable bases					CEC	Clay CEC	Clay CEC	Base
		Sand (2000– 50 μm)	Silt (50– 2 μm)	Clay			$\frac{(1:2)}{\text{Soil}}$	$\frac{(\text{cmol}(+) \text{kg}^{-1})}{C_{2} \text{ Ma Na } K}$				Cum	$\frac{(\text{cmol}(+))}{(+)}$	$(\operatorname{cmol}(+))$ $k\sigma^{-1}$	Soil Control Section (cmol	saturation
				Coarse (2.0– 0.2 µm)	Fine (< 0.2 μm)	Total (< 2 μm)	H ₂ O	Ca	wig	INA	К	Suili		Kg)	(+) kg ⁻¹)	()0)
Al	0-14	110	260	220	410	630	5.5	7.0	3.0	0.4	0.7	11.1	17.0	25		65
Bt21	14-60	70	280	240	410	650	5.2	7.0	2.5	0.4	0.4	10.3	17.0	26		61
Bt22	60-97	50	230	250	470	720	5.5	7.0	3.0	0.4	0.4	10.8	16.0	23	24	67
Bt23	97-151	170	210	220	420	640	5.7	6.5	3.5	0.4	0.3	10.7	15.0	24		71
С	151+	250	200	170	380	550	5.7	8.0	4.0	0.5	0.5	13.0	12.0	22		108



Fig. 2. Representative scanning electron microscopic photographs of (a) sand sized quartz particle of Bt21 horizon of Pedon 4, (b–e) zeolites in Al, Bt21, Bt22 and Bt23 horizons of Pedon 4, (f) zeolites of 2B26 horizon of Pokhri soils, and (g) zeolites of 2C2 horizon of associated black soils of semi-arid part of the Western Ghats (Bhattacharyya et al., 1993).

indicating that they are not transported over long distance and deposited. These data indicate that the ferruginous soils under study are residuum over weathered

basalt. In reality many of these high altitude ferruginous soils have been dated back to the Tertiary and Cretaceous (Idnurm and Schmidt, 1986). Earlier Schmidt et al. (1983) also found that the oldest and highest laterites on high altitude plateaus date back to the Cretaceous–Tertiary boundary. In other words, they were formed almost as soon as the Deccan basalt had been erupted (Ollier, 1995). This suggests that although these soils are formed in humid tropical climate for several millions of years they have not reached the advanced stage of weathering represented by Ultisols and Oxisols in Soil Taxonomy (Soil Survey Staff, 1994). Instead, they represent soils of the Alfisol order.

3. Materials and methods

From a reconnaissance survey the study area representing the table lands and plateau surfaces (Fig. 1) was mapped as the association of Pokhri (Vertic Eutropepts), Dhakevadi (Typic Hapludalfs) and Jambori (Typic Hapludalfs) soil series (Bhattacharyya et al., 1992, 1993, 1997). The Jambori soils are deep to very deep (120–155 cm) whereas Dhakevadi soils are shallow to moderately deep (32–55 cm). Other table lands of the study area were mapped as a single series namely Jambori soils. These deep and ferruginous soils were hitherto referred to as high altitude laterites (Sahasrabudhe and Deshmukh, 1981). Several soil samples were collected from these high altitude plateaus and table lands. The soil and site characteristics of four representative Jambori pedons (P1, P2, P3 and P4) are schematically presented in Fig. 1d. Jambori series thus represent the benchmark soil of the study area in the Western Ghats due to their characteristics and geographical extent (Bhattacharyya et al., 1992; Challa et al., 1995). The analytical data of P4 is presented in this paper as a representative of the high altitude ferruginous soils of the Western Ghats.

Sand (2000–50 µm), silt (50–2 µm), total clay (<2 µm) and fine clay (<0.2 µm) fractions were separated from the samples after dispersion according to the size segregation procedure of Jackson (1979). Cation exchange capacity (CEC) was determined following the method of Richards (1954), using neutral normal NaOAc because the soils are noncalcareous. The KCl extractable H⁺ and Al³⁺ and NH₄OAc (pH 7) extractable bases were determined following the methods of Jackson (1973). Oriented Ca and K saturated clay samples were subjected to X-ray diffraction (XRD) analysis using a Philips diffractometer and Ni-filtered CuK_α radiation at a scanning speed of 1°2θ per minute and also of 2°2θ per minute. The analysis of powder specimens of the sand fractions were also carried out. After identification under the petrographic microscope the sand sized zeolites were picked up, ground and X-rayed. A few zeolite crystals were fixed on aluminium stub with LEIT-C conductive carbon cement, coated with gold and examined under Philips SEM.

4. Results and discussion

The soils represented by P4 are very deep (> 150 cm) and acidic (5.2–5.7) with subangular blocky structure and reddish brown to dark reddish brown colour. They show evidence of translocation and accumulation of clay forming diagnostic argillic horizons in the form of clay skins identified by $10 \times$ hand lens (Soil Survey Staff, 1994). The CEC ranges from 12 to 17 cmol(+) kg⁻¹ with Ca as dominant cation. Despite their acidic nature these soils show high base saturation (> 60%) in the solum and more than 100% in the C-horizon (Table 1). They classify as Alfisols (Soil Survey Staff, 1994). High base saturation suggests the presence of base contributing minerals which had earlier been identified as zeolites (heulandites) in the associated black soils (Pokhri series) on these plateaus (Bhattacharyya et al., 1993).

Zeolites were identified in considerable proportion in the field by their typical morphology. The content of zeolites increases with depth in moderately deep to deep black soils (Vertisols and their intergrades) in the adjoining semi-arid part of the study area (Bhattacharyya et al., 1993). Zeolites constitute almost 50% of the total mass of the weathered basalt of the C-horizons of Vertisols and their intergrades. Identification of the altered zeolites in the field in high altitude ferruginous soils was difficult due to coating of iron. Petrographic examination of sand fractions (> 50 μ m) indicated the presence of both altered and unaltered zeolites constituting 5-10% of the sand fractions. The altered zeolites are thinly coated with iron oxides whereas the unaltered ones are colourless and have relatively smooth surfaces. Both the altered and unaltered zeolites are elongated and angular in shape. XRD analysis also supported the presence of zeolites in the sand fractions of Jambori and Pokhri soils. The intensity of the zeolite peak indicates that zeolite content varies from little to moderate amount in these soils (Fig. 3a and b). This is in contrast to strong peaks of well crystallized heulandites in almost all size fractions of moderately deep to deep black soils (Fig. 3c) of adjoining eastern part of the Western Ghats.

The XRD analysis indicated a strong peak at 0.90 nm of zeolites with other accessory minerals such as mica, feldspars, quartz and anatase (Fig. 3c). Changes of phases of zeolites on thermal treatments as indicated by shifting of 0.90 nm peak to 0.86 nm and 0.83 nm at 300°C and its disappearance at 450°C suggest that these zeolites belong to Si-poor heulandite type (Brown, 1984; Ming and Dixon, 1986). Presence of such crystalline zeolites, having CECs of

Fig. 3. Representative XRD diagrams of the powdered sand fractions $(2000-50 \ \mu m)$ of (a) all the horizons of Pedon 4 and (b) Pokhri soils, (c) the 2C2 horizon of the associated black soils in semi-arid part of the Western Ghats heated to (i) 25°C, (ii) 210°C, (iii) 300°C, (iv) 400°C, and (v) 550°C. All thermal treatments were given for 2 h.



200 to 300 cmol(+) kg⁻¹ (Ming and Mumpton, 1989), is expected to increase the CEC of soils. Low CEC values of ferruginous soils, on the contrary, might be due to small amounts of zeolites and/or error in the analytical method followed for CEC measurement. In this method, NaOAc (pH 7) was used for saturating the soils and NH OAc (pH 7) for exchanging the Na⁺ ions; and the CEC was determined by estimating the adsorbed Na⁺ ions. During saturation the exchange between Na^+ ions and Ca/Mg ions of zeolites is expected to be negligible because zeolites have less selectivity for Na⁺ ion (Ming and Mumpton, 1989). Conversely during the determination of extractable bases by NH OAc, zeolites can contribute Ca and Mg ions by NH₄-Ca/Mg exchange since zeolites have higher selectivity for NH_{4}^{+} ions (Ming and Mumpton, 1989). This is the reason for high base saturation in spite of low CEC of these acidic ferruginous soils. The morphology of zeolite crystals indicates that the zeolites are more weathered in spatially associated ferruginous and black soils of the humid study area than the black soils of semi-arid part of the Western Ghats (Fig. 2). Due to intense weathering the zeolites in the ferruginous soils are now confined to sand (> 50 μ m) size fractions. Despite their low contents these base-rich heulanditic zeolites are still maintaining high base status of these soils. This might be the reason why crops do not show response to liming (Mandal et al., 1975; Kadrekar, 1979) in these high altitude Alfisols on the Western Ghats.

The first weathering product of Deccan basalt is smectite and it is nearer to montmorillonite in the montmorillonite-nontronite series (Pal and Deshpande, 1987). As the smectite is ephemeral in humid tropical climate (Pal et al., 1989) it transforms to kaolin. During such transformation smectite /kaolin interstratification appears to be an important ephemeral stage under an acid weathering environment in a humid tropical climate with plenty of Al in the system (Herbillon et al., 1981). The clay ($< 2 \mu m$) mineralogy of the ferruginous soils showed that kaolin (0.72 nm) and mica (1.0 nm) are the dominant minerals with chloritized smectite and quartz in minor amounts (Fig. 4). A slight shift and tailing of the 0.72 nm peak on glycolation and gradual reinforcement of the 1.0 nm peak with a corresponding decrease in the 0.72 nm peak intensity on K-saturation and subsequent heating $(110-550^{\circ}C)$ suggests that these kaolins are to some extent interstratified with chloritized smectites (Sm/K) (Fig. 4) and are not true kaolins. This is in contrast to commonly reported kaolinitic and/or oxidic mineralogy of ferruginous soils of India (Gowaikar, 1972; Rengasamy et al., 1978; Sahasrabudhe and Deshmukh, 1981; Sahu and Krishnamurti, 1984; Chitale and Gueven, 1989; Varghese and Byju, 1993) and elsewhere (Mohr et al., 1972; Aleva, 1994). The fine clays of these soils are dominated by interstratified smectite-kaolin (Sm/K) with minor amounts of chloritized smectite and mica (Fig. 4). The proportion of smectite and kaolin in Sm/K could not be calculated by peak shift analysis (Wilson, 1987) because of restricted shifting of the 0.72 nm peak towards lower angles on glycolation due to partial chloritization of smectite interlayers (Fig. 4). The CEC of the clays of ferrugi-



Fig. 4. Representative XRD diagrams of (a) total clay ($< 2 \mu m$) and (b) fine clay ($< 0.2 \mu m$) fractions of the Bt23 horizon of Pedon 4. Ca = Ca-saturated; Ca-Eg = Ca-saturated and glyco lated; K25°/110°/300°/550°C = K-saturated and heated; M = mica; Sm/K = smectite-kaolin interstratified minerals; Sm = chloritized smectite.

nous soils ranges from 23 to 26 and measures 24 in the control section indicating their mineralogy more towards kaolinitic class (Smith, 1986).

With a combination of high temperature and adequate moisture the humid tropical climate of the Western Ghats provided a weathering environment that should have nullified the effect of parent rock composition by resulting in kaolinitic and/or oxidic mineral assemblages consistent with either residua (Chesworth, 1973) or haplosoil model of soil formation (Chesworth, 1980). These models are based on the hypothesis that (a) the effect of parent rock will be (i) overshadowed, and (ii) ultimately nullified with time; (b) its effect will be evident only in younger or relatively immature soils, and (c) the time is the only

independent variable of soil formation or any other process occurring spontaneously in nature. In the ferruginous soils, on the contrary, dominance of Sm/Kin the fine clay fractions indicates that in spite of a prolonged weathering since early Tertiary (Sahasrabudhe and Deshmukh, 1981; Schmidt et al., 1983; Idnurm and Schmidt, 1986; Ollier, 1995) the weathered products of Deccan basalt have not yet reached the kaolinitic and/or oxidic mineralogy due to the following reasons.

The presence of zeolites even in the present day climate indicates that these minerals are still persisting in the Deccan basalt. The loss of bases during leaching of soils has thus been continuously replenished by the steady supply of bases from these zeolites. This provides a chemical environment that prevents the formation of kaolinitic and/or oxidic clay minerals representing the advanced stages of weathering in soils. On the other hand it fulfils the requirement of base saturation (> 35%) dominated by Sm/K interstratified minerals even in the present day humid tropical climate. Therefore, the formation of these Alfisols and their persistence supports the supposition that steady state may exist in soils developed over long periods of time not only a few hundreds to thousands of years (Yaalon, 1971, 1975; Smeck et al., 1983) but also millions of years. The hypothesis of Chesworth for soil formation in humid tropics cannot explain the persistence of these high altitude ferruginous Alfisols on the Western Ghats because the stability of zeolites over time was not considered in his model.

It is thus proposed that the formation and persistence of Alfisols on the Western Ghats for millions of years provide an unique example that in an open system such as soil, the existence of a steady state appears to be a more meaningful concept than equilibrium in a rigorous thermodynamic sense (Smeck et al., 1983). The knowledge gained on the role of zeolites in the persistence of Alfisols not only provides a deductive check on the inductive reasoning on the formation of soil in humid tropical climate (Chesworth, 1973, 1980) but also enlightens us about the role of these minerals in preventing loss of soil productivity even in an intense leaching environment.

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