

Zeolitic soils of the Deccan basalt areas in India: their pedology and edaphology

D. K. Pal*, S. P. Wani and K. L. Sahrawat

Resilient Dryland Systems, International Crops Research Institute for the Semi-Arid Tropics, Patancheru 502 324, India

Zeolites play an important role in modifying the chemistry, physics and biology of soils. Here we review the status of the pedology and edaphology of the zeolitic soils of the Deccan basalt areas of India. Research has been mainly conducted with clinoptilolite (a potassium-rich zeolite). However, some basic research has been conducted on zeolitic (heulandites, calcium-rich zeolites) soils of India developed from the Deccan basalts. The results of such research have added to basic understanding of the pedology of tropical soils; and have enhanced our understanding of edaphology related to the use of zeolitic sodic and non-sodic shrink-swell soils (Vertisols) for cultivating crops without causing any degradation in soil properties, but with an improvement in organic carbon status. Research is needed on the specific role of heulandites in the presence of K^+ and NH_4^+ fixing clay minerals in soil environments. Identification of soil zeolites by determining cation exchange capacity and extractable bases is possible when sophisticated instrumental facilities are not available. The need for future research on the pedology and chemistry of zeolitic soils for their sustainable use for agricultural production and environmental management is emphasized.

Keywords: Edaphology, heulandites, pedology, soil zeolites, tropical soils.

ZEOLITES have been known for over a century for their prominent role in cation exchange in the soils^{1,2}. The presence of zeolites in soils was established with the development of modern X-ray diffraction (XRD) methods³. During the last three decades, reports on zeolite minerals have been appearing with increasing frequency, as common constituents of Cenozoic volcanogenic sedimentary rocks and altered pyroclastic rocks⁴.

Zeolites are hydrated aluminosilicates of alkali and alkaline earth cations that possess a three-dimensional structure (i.e. tectosilicates). The negative charge created where Al^{3+} replaces Si^{4+} in the structural tetrahedra is counter-balanced by cations (e.g. Na^+ , K^+ , Ca^{2+} and Mg^{2+}). These charge sites are located in large structural channels and cavities throughout the structure and are referred to as cationic exchange sites. Small ions and molecules can pass through these channels, but large ones

are excluded. This ion selectivity, based on size, is known as ion sieving. Zeolites have high cation exchange capacity (CEC) (100–300 meq/100 g), depending upon the amount of Al^{3+} that replaces Si^{4+} in the structure.

Several reviews have been published on the occurrence and properties of zeolites in soils^{5–9}. Zeolites have also been reported as secondary minerals in the Deccan flood basalts of the Western Ghats in Maharashtra, India^{10,11}. Among the commonly occurring species of zeolites, heulandite is widely distributed both in time and space¹¹. Zeolites have the ability 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.

Over the past few decades, natural zeolites have been examined for a variety of agricultural and environmental applications, especially for their cation exchange, adsorption, and molecular sieving characteristics because of their abundance in near-surface, sedimentary deposits. Natural zeolites are being used as soil conditioners, slow-release fertilizers, carriers of insecticides and herbicides, remediation agents in contaminated soils, and dietary supplements in animal nutrition^{3,12–14}. These applications can result in direct or indirect incorporation of natural zeolites into soils. There are, however, very few studies on the role of zeolites in soil environments in expanding the basic knowledge in pedology and edaphology, except for some pioneering work reported from India. These pertain to (1) persistence of high-altitude Alfisols, Mollisols and Vertisols of the humid tropical Deccan basalt areas of the central and western peninsular India^{15–17}; (2) the role of zeolites in redefining the sodic soils¹⁸ and (3) mitigation of Holocene climate change by the zeolitic Sodic Haplusterts^{18–20}. However, no attempt has been made to establish a link between zeolite and adsorption and desorption behaviour of nutrients in soils. Because zeolites can be effective slow-release fertilizers and soil conditioners³, it would be useful to understand better the role of soil zeolites in nutrient availability and management. Hence, a review is in order to place recent research results which will provide a better understanding of soil characteristics influenced by zeolites. This review is aimed towards better management of zeolitic soils developed in the Deccan basalt areas in the central and western peninsular India and elsewhere for agricultural development.

*For correspondence. (e-mail: paldilip2001@yahoo.com)

Factors and processes in the formation of Mollisols, Alfisols and Vertisols in the humid tropics

Major part of the land area in India is between the Tropic of Cancer and Tropic of Capricorn, also known as the Torrid zone, and the soils therein may be defined as 'tropical soils'. Many, however, consider of tropical soils as the soils of the hot and humid tropics only, exemplified by deep red and highly weathered soils²¹. But, in the humid tropical (HT) climatic environments of India, occurrence of Mollisols, Alfisols and Vertisols is common. Therefore, factors and processes of formation and persistence of such soils in adverse HT climate need an explanation in the light of the existing conceptual models for tropical soil formation.

Red (Ferruginous Alfisols) and black soil (Vertisols) complex on zeolitic Deccan basalt of HT climate

Vertisols in micro-depressions are spatially associated with red ferruginous soils (Alfisols) and are seen as distinct entities under similar topographical conditions on the zeolitic Deccan basalt plateau in the HT climate¹⁵. The red ferruginous soils can be comprehended as having formed in the prevailing HT, but it is difficult to reconcile this hypothesis with the associated occurrence of Vertisols because smectite, which is mainly responsible for the formation of shrink-swell soils, is ephemeral in such environment. The Alfisols are mildly acidic and their clays are dominated by the 0.7 nm clay mineral (KI-HIS), which is an interstratified mineral of kaolin (KI) and hydroxy interlayered smectite (HIS). Additional minerals are HIS (in moderate amount) and mica. These soils are non-gibbsitic¹⁵ in spite of a prolonged weathering since the early Tertiary^{15,16}. The formation of HIS is accompanied at the expense of smectite and is an ephemeral stage in an acid weathering environment in HT climate. Transformation of HIS to kaolinite is inhibited because of continuous supply of bases from zeolites (heulandites), counteracting the impoverishment of bases by leaching in HT climate (Table 1). The enrichment of bases provides a chemical environment that prevents the formation of kaolinitic and/or oxidic clay minerals representing the advanced stages of weathering in soils, and fulfils the requirement of base saturation of soils (> 35%) dominated by KI-HIS even in the present-day HT climate.

The genesis of both red ferruginous soils (Typic Hapludalfs¹⁶ and Vertisols Typic Haplusterts²²) in adverse HT climate has been explained through the landscape-reduction process^{15,23}, as in similar soils elsewhere²⁴. In the initial stage of soil formation, smectite-rich products of weathering from the hills were deposited in micro-depressions, as evident from the general occurrence

of lithic/paralithic contacts of such Vertisols²⁰. Over time, these sites were gradually flattened and internal drainage dominated over surface run-offs. After peneplanation, the Alfisols on relatively stable surfaces continued to weather, forming KI-HIS. In contrast, the zeolite reserve stabilized the characteristic smectite mineral in the form of KI-HIS and HIS minerals and thus made possible the persistence of slightly acidic Vertisols in microdepressions (Table 1) even in a HT climate¹⁵ (Figure 1). Significance of zeolites in the formation and persistence of slightly acidic to acidic Vertisols (Typic Haplusterts) has been realized in the HT climatic environments not only in central and western India²², but elsewhere also²⁵.

Formation of Mollisols on zeolitic Deccan basalt of HT climate

In contrast to the general occurrence of non-acidic, calcareous and less weathered Mollisols in temperate semi-arid and humid climate, acidic, non-calcareous and fairly weathered Mollisols (Vertic Haplustoll and Vertic Argiustoll) on Deccan basalt are observed in hills of central (Satpura Range, Madhya Pradesh) and western (Western Ghats, Maharashtra) India under forest in the present HT climatic conditions¹⁷. The dominant clay mineral identified at 0.7 nm is not discreet kaolinite, but is KI-HIS associated with sub-dominant amount of HIS¹⁷. Such soil development has been due to the presence of zeolites (heulandites) in Deccan basalt, which as soil modifiers, provide bases to prevent complete transformation of smectite to kaolinite and maintain high base saturation level (> 50%) of these acidic Mollisols (Table 1). Favourable base status and greater water retention help in accumulation of organic carbon required for soils to qualify as Mollisols even under HT climate¹⁷.

Tropical soil formation

Mollisols, Alfisols and Vertisols are the members of Mollisol-Alfisol-Vertisol association^{17,22} on the zeolitic Deccan basalt areas. The associated Alfisols were formed in HT climate and are persisting since the early Tertiary¹⁶. The transformation of smectite (the first weathering product of the Deccan basalt)²⁶ to kaolin (KI-HIS) during HT weathering began at the end of the Cretaceous and continued during the Tertiary²⁷, and thus Alfisols date back to the Tertiary and Cretaceous²⁸. With a combination of high temperature and adequate moisture, the HT climate of the Western Ghats and Satpura Range provided a weathering environment that should have nullified the effect of parent rock composition in millions of years, resulting in kaolinitic and/or oxidic mineral assemblages consistent with either residua²⁹ or haplosoil³⁰ models of tropical soil formation like in Ultisols and Oxisols³¹.

Table 1. Selected properties of Mollisols, Alfisols and Vertisols of HT climate (adapted from Bhattacharyya *et al.*^{17,22})

Depth (cm)	Texture	pH (1 : 2)	Organic carbon (%)	Extractable bases				Cation exchange capacity	Base saturation (%)	Available K (kg ha ⁻¹)
				Ca	Mg	Na	K			
				cmol(+) kg ⁻¹						
Vertic Argiudolls										
0–15	Clay	5.7	2.0	9.2	2.5	0.4	0.5	18.6	68	429
15–40	Clay	5.7	1.2	10.3	2.7	0.4	0.4	18.5	75	343
40–70	Clay	5.7	0.7	10.3	2.8	0.4	0.2	18.7	73	172
74–108	Clay	6.1	0.4	12.0	3.0	0.4	0.2	18.6	85	172
108–146	Clay	6.1	0.3	12.0	4.6	0.5	0.2	18.7	92	72
Typic Haplustalfs										
0–9	Clay	5.7	1.3	6.7	3.0	0.6	0.4	8.4	127	343
9–31	Clay	5.3	1.2	7.1	1.5	0.5	0.3	9.8	96	257
31–60	Clay	5.3	1.0	6.8	1.6	0.4	0.3	9.8	93	257
60–107	Clay	5.6	0.91	9.1	3.3	0.3	0.3	8.6	151	260
Typic Haplusterts										
0–15	Clay	6.6	0.9	17.3	6.1	0.5	0.4	30.7	79	343
15–35	Clay	6.4	0.7	17.4	6.3	0.5	0.4	28.8	85	343
35–82	Clay	6.8	0.6	17.8	11.1	0.7	0.5	28.9	104	429
82–125	Clay	6.7	0.5	18.4	11.9	0.8	0.4	30.3	104	343

Instead, the soils of the zeolitic Deccan basalt have KI–HIS and represent Mollisols, Alfisols and Vertisols.

The models of Chesworth^{29,30} were based on the hypothesis that (a) the effect of parent rock will be overshadowed and nullified with time; (b) its effect will be evident only in younger or relatively immature soils and (c) time is the only independent variable of soil formation or any other process occurring spontaneously in nature. However, the formation of Mollisols, Alfisols and Vertisols and their pedogenic threshold at this time supports that steady state may exist in soils developed over a long period of time not spanning a few hundreds to thousands of years^{32–34}, but also millions of years^{15,16}. Therefore, the formation and persistence of Mollisols, Alfisols and Vertisols provides an example that in an open system such as soil, the existence of a steady state appears to be a more useful concept than equilibrium in a rigorous thermodynamic sense^{16,34}. Due to the presence of zeolites, the adverse effect of HT climate was overcome and thus the zeolitic Deccan basalt could produce Mollisols, Alfisols and Vertisols. The hypothesis of Chesworth^{29,30} on soil formation in HT climate cannot explain the persistence of these soils, because the stability of zeolites over time was not considered in his models. However, the models on the formation and persistence of Mollisols, Alfisols and Vertisols from zeolitic parent rock expand the basic knowledge on the formation of soils in HT climate. The knowledge gained on the role of zeolites in the persistence of soils not only provides a deductive check on the inductive reasoning on the formation of soil in the HT climate, but also throws light on the role of these minerals in preventing loss of soil productivity even in an intense

leaching environment. This indeed may be the reason why crops do not show response to liming in acid soils of the tropical Western Ghats³⁵.

Mitigation of adverse Holocene climate change in zeolitic Vertisols

Amidst neotectonics and the global warming, rising temperature and shrinking annual rainfall with erratic distribution pose threats to soil quality, not only for the Indian subcontinent but also to soils under similar climatic conditions elsewhere³⁶. In India, a change in climate has been recorded from humid to semi-arid in rainfed areas only during the Holocene period^{37,38}. It is observed that the major soil types of India under semi-arid tropical environments (SAT) are becoming calcareous with the concomitant increase of exchangeable sodium percentage (ESP) in the subsoils. This indicates a climatically controlled natural degradation³⁹. This type of degradation ultimately modifies the physical, biological and chemical properties of the soils. Such modifications resulting from regressive pedogenesis⁴⁰ restrict the entry of rain water and reduce the storage and release of soil water⁴¹. The lack of soil water impairs the possibility of growing both rainy and winter crops in a year, especially in vast areas under Vertisols of the SAT with mean annual rainfall (MAR) < 1000 mm (ref. 19). Not only the Vertisols with ESP > 15 (Sodic Haplusterts), but also the soils with ESP > 5 and < 15 (Aridic Haplusterts) cease to be sustainable for growing agricultural crops under the SAT environments^{19,36}. Many productive Vertisols (Typic Haplusterts) under rainfed conditions have been rendered unproductive

Table 2. Adverse effect of irrigation on zeolitic Typic Haplusters during sugarcane cultivation (adapted from Pal *et al.*⁵⁹)

Depth (cm)	pH (1 : 2)	ECe (dSm ⁻¹)	CaCO ₃ (<2 mm)%	ESP	sHC ^a (mmh ⁻¹)	Base saturation (%)	Available K (kg ha ⁻¹)
0–20	9.0	0.77	16.0	4.2	18	107	686
20–42	9.2	1.01	17.0	10.4	17	119	343
42–68	9.3	0.99	17.0	18.8	5	94	343
68–102	9.0	1.25	15.0	13.7	10	105	343
102–131	9.0	1.09	25.3	12.1	13	103	343
131–150	9.0	1.02	16.1	8.0	12	109	421

ECe, Electrical conductivity of the saturation extract; ESP, Exchangeable sodium percentage; sHC, Saturated hydraulic conductivity. ^a13 mm h⁻¹ is the weighted mean sHC in 0–100 cm depth of soil.

for agriculture under irrigated conditions in the longer term. However, some zeolitic Vertisols (Typic Haplusters) of the semi-arid moist parts of western India are under irrigated sugarcane production for the last 20 years. These soils lack salt efflorescence on the surface and are not waterlogged at present, suggesting that they are not degraded due to their better drainage. However, these soils are now Sodic Haplusters in view of their pH, ECe and ESP values, but their saturated hydraulic conductivity (sHC) is > 10 mm h⁻¹ (weighted mean in the 0–100 cm; ref. 19; Table 2). Continuous supply of Ca²⁺ ions from Ca-zeolites in these soils helps maintain a better drainage system. Because of such natural endowment with a soil modifier, no ill-effects of high ESP (> 15) in crop production in the Vertisols of Gezira in Sudan^{42,43} and in Tanzania⁴⁴ were observed. In addition, some Vertisols of the arid dry climate of western India are used to grow crops such as cotton under rainfed conditions comparable to those of the Typic Haplusters of the semi-arid moist climate of central India⁴⁵. The sHC (weighted mean, 0–100 cm) of these soils is > 15 mm h⁻¹, despite being Sodic Calcicusterts³⁸ (Table 2). In view of the present good agricultural practices, these soils show potentiality to mitigate the adverse effect of climate. However, the sustainability of crop productivity amidst the ill-effects of the pedogenic threshold of dry climates^{38,46} depends on the solubility and supply of Ca²⁺ ions from zeolites. Such situations are unique in nature; but predicting how long will it take for these soils to run out of zeolites is difficult, unless a new research initiative in this direction is taken up.

Zeolites in redefining sodic soils

Researchers^{47,48} envisaged that the threshold of ESP > 15 may need reconsideration because soil degradation can take place even at low ESP in dilute solutions. Northcote and Skene⁴⁹ reported serious structural degradation of some Australian soils at ESP as low as 6. Subsequently, many researchers in Australia^{50,51}, Italy⁵² and India⁵³ advocated that an ESP much lower than 15 should be used to denote the value above which a noticeable reduc-

tion in crop yields is observed as a result of deterioration of physical properties of soils. However, sodicity tolerance ratings of crops in loamy textured soils of the Indo-Gangetic Plains (IGP) indicate that 50% reduction in relative rice yields was observed when ESP was above 50; and for wheat it was around 40 (ref. 54). The reason for these apparently contrasting findings lay in the different values of solution concentration of the soils. Therefore, Sumner⁵⁰ opined that the establishment of a critical ESP threshold may be arbitrary because properties exhibited by the so-called classic sodic soils are simply the upper end of a continuum of behaviour that extends across the full range of sodium saturations. Sumner⁵⁰ made a strong case to develop criteria based on soil dispersibility to characterize and predict the behaviour of soils with respect to infiltration, hydraulic conductivity and hard setting, which indicates the mechanisms of swelling and dispersion^{47,48}. Dispersibility of soils is a result of the interactive effects of soil properties, such as clay content, nature of clay, cation suite, nature of soil solution composition and organic matter⁵¹. However, Gupta and Abrol⁵⁵ highlighted the importance and contribution of swelling and dispersion to hydraulic properties of soils in terms of clay mineralogy at the species level, the ESP of the soil, the electrolyte concentration and nature of electrolytes in the soil solution. Although soils containing all other clays swell with changes in moisture content, changes are particularly extreme in smectite-rich soils⁵⁶. The importance of smectite in impairing the hydraulic properties of soils through swelling and dispersion was also highlighted when Vertisols (ESP < 15, 491 g kg⁻¹ smectite in soil control section, SCS) and soils of the IGP (ESP 50, 46 g kg⁻¹ smectite in SCS) were compared for their agricultural productivity⁵⁷. Even low sodicity (ESP ≥ 5 and < 15) is enough to impair the hydraulic properties of the highly smectitic Vertisols. However, naturally occurring zeolites in some soils of sub-humid, semi-arid and arid climates showing high ESP (> 15) avoided a rise in pH, but favoured an increase in exchangeable Ca/Mg, and hydraulic properties¹⁸ (Tables 2 and 3). Therefore, fixing a lower limit of either ESP 5–15 (ref. 18) or ESP > 15 (ref. 31) for sodic shrink–swell soils may have no practical relevance to their use and management. In contrast, sodic

Table 3. Selected soil properties of zeolitic Chromic/Sodic Haplusterts cultivated to rice crops (adapted from Pal *et al.*⁵⁹)

Depth (cm)	pH (1 : 2)	ECe (dSm ⁻¹)	CaCO ₃ (< 2 mm)%	Organic carbon (%)	ESP	sHC ^a (mm h ⁻¹)	Base saturation (%)	Available K (kg ha ⁻¹)
Sakka soils – Chromic Haplusterts								
0–15	5.2	0.26	1.6	0.73	0.9	18	93	429
15–34	5.3	0.16	1.7	0.54	0.9	36	109	343
34–59	5.3	0.26	1.9	0.40	0.9	35	106	343
59–93	5.4	0.10	2.0	0.38	1.1	10	93	343
93–141	7.3	0.12	4.1	0.39	1.2	15	115	429
141–155	7.9	0.21	10.0	0.22	0.8	16	107	343
Teligi soils – Sodic Haplusterts								
0–10	7.9	0.4	10.5	1.55	1.5	62	103	515
10–25	8.0	0.3	10.7	0.81	1.7	27	113	343
25–44	8.0	0.4	12.2	0.76	1.8	29	109	343
44–69	7.8	0.4	10.3	0.73	4.0	21	117	257
69–97	7.6	0.3	5.9	0.69	3.4	11	108	515
97–123	8.6	0.4	15.1	0.50	16.8	3	110	257

^a23 mm h⁻¹ is the weighted mean sHC in 0–100 cm depth of Sakka soils and 24 mm h⁻¹ is the weighted mean sHC in 0–100 cm depth of Teligi soils.

Vertisols with zeolites as modifiers indicate that despite having high ESP, these soils support rainfed crops^{18,45}. Therefore, fixing a lower limit for sodic subgroup of Vertisols either at ESP 5–15 or at ESP > 15 may not reflect the impairment of drainage of soils. Characterizing such soils as sodic only on the basis of ESP may also mislead the end-users of these soils. In view of the pedogenetic processes that ultimately impair the drainage of soils, evaluation of Vertisols for deep-rooted crops on the basis of sHC alone⁴¹ showed that an optimum yield of cotton on Vertisols of the semi-arid part of central India can be obtained when the soils are non-sodic (ESP < 5) and have sHC ≥ 20 mm h⁻¹. These authors also reported 50% reduction in yield in the sodic (ESP > 5) soils with sHC < 10 mm h⁻¹. The study shows that sHC as a single parameter can indicate dispersibility, the most influencing factor of soil sodicity⁵⁰. Therefore, characterization of soil sodicity on the basis of sHC alone appears to be an incontrovertible parameter compared to ESP or SAR; and thus Pal *et al.*¹⁸ advocated a value of sHC < 10 mm h⁻¹ in distilled water (weighted mean in 0–100 cm depth of soil) for defining a sodic soil.

Zeolites sustain rice productivity in Vertisols

Vertisol use is not confined to a single production system. In India, major combinations of rainfed crops under semi-arid climatic environments are sorghum/pigeon pea, cotton/pigeon pea and cotton/sorghum/pigeon pea. Mixed cropping usually combines crops with different maturity lengths, drought-sensitive with drought-tolerant crops, cereals with legumes, and cash crops with food crops⁵⁸. In semi-arid western India (< 1000 mm MAR), sugarcane and rice are grown under irrigated conditions, whereas rice is grown under rainfed conditions in areas of sub-

humid moist climatic conditions of central India (with MAR > 1400 mm)^{19,59}. The sHC decreases rapidly with depth in Vertisols, but the decrease is sharper in non-zeolitic Sodic Haplusterts; and the weighted mean of sHC in 0–100 cm depth is < 10 mm h⁻¹. In non-zeolitic Typic Haplusterts, the sHC is > 10 mm h⁻¹. But in zeolitic Typic Haplusterts (Kheri soils at Jabalpur⁶⁰, and Sakka soils at Dindori, Madhya Pradesh⁵⁹) sHC is > 20 mm h⁻¹, and these soils are cultivated to rice as rainfed crop in areas with > 1400 mm MAR. Interestingly, zeolitic Sodic Haplusterts (Teligi soils in Bellary, Karnataka⁵⁹) in areas with < 700 mm MAR also have sHC > 20 mm h⁻¹; and rice is cultivated in these soils under canal irrigation. The enhanced sHC (> 20 mm h⁻¹) in zeolitic Vertisols due to the presence of zeolite appears to be just adequate for the period of submergence required for the rice crop, and post-rainy season crops are successfully grown with good yields. Morphological examination of such soils showed no sign of gleyed horizons and soil moisture regime does not reach aquic conditions. Such situations are unique in nature and pose a great challenge to the soil mappers to classify them according to the US Soil Taxonomy, as they have good productive potential despite being sodic in nature. Sustainability of rice cropping system in such soils will, however, depend on rate of dissolution of Ca-zeolite on a timescale, and a new research initiative on this topic is warranted.

Zeolites in adsorption and desorption of major soil nutrients

Several potential applications of natural zeolites have been examined as soil conditioners, slow-release fertilizers and many other uses^{3,13}. Among the zeolites, K-rich clinoptilolite has been the focus of most researchers

probably because of its widespread abundance in near-surface deposits³. But the report of its role as a modifier in natural soil environments has been rare, unlike that of heulandite (a Ca-rich zeolite)^{15–17,18–20}. Both clinoptilolite and heulandite are effective natural cation exchangers and have CECs that commonly range from 200 to 300 cmol_ckg⁻¹. The experimental results obtained with clinoptilolite as soil conditioner, efficient substrate for fertilizer use, to prevent nutrient leaching and slow-release fertilizers by several researchers (see ref. 3) provide hints about the possible role of heulandite in the adsorption and desorption of major nutrients in Vertisols containing smectite, vermiculite and micas.

Organic carbon

Zeolites improve hydraulic properties of soils by enriching soil exchange complex with Ca²⁺ ions in arid to HT climate^{18,38}. Long-term experiment on Vertisols at ICRISAT, Patancheru with improved management system⁶¹ indicates that the improvement of physical properties causes an enhanced soil water status for better vegetation and higher organic carbon sequestration¹⁹. The benefit of better physical properties caused by Ca²⁺ ions through dissolution of zeolites is realized with the formation of organic matter-rich, dark-coloured, soft, clayey, smectitic acidic Mollisols and Alfisols with 1–2% organic carbon (in the 0–30 cm depth) even in HT climate^{17,22} (Table 1). In order to follow the decomposition resistance of soil organic matter under high-temperature, experiments with Ca-zeolite and organic manure showed a slight increase in C/N ratio in soils of the Philippines, Paraguay and Japan. In addition, carbon accumulation in humic fractions as well as the degree of humification and aromaticity of humic acids increased⁶². In semi-arid dry region of India, zeolitic (heulandite) Vertisols (Teligi soils, Bellary, Karnataka; Jhalipura soils, Kota, Rajasthan; Jajapur, Mehboobnagar, Andhra Pradesh)⁵⁹, under wetland rice–rice/rice–wheat system showed wider C/N ratio (Table 4), indicating enough potential to sequester atmospheric carbon⁶³. This suggests that the presence of zeolites could be beneficial for soil organic matter conservation under global warming⁶².

Nitrogen

One of the forms of mineral nitrogen (N) is fixed NH₄-N, and several reports indicate that many tropical Vertisols are endowed with large amounts of fixed ammonium⁶⁴. Vermiculites, illites and smectites are often considered able to fix NH₄-N (ref. 65). Smectites have no selectivity for non-hydrated monovalent cations such as K⁺ because of their low-level charge⁶⁶. NH₄⁺ ion, also a non-hydrated monovalent cation with almost the same ionic radius as K, is not expected to be fixed in the interlayers of smec-

tites. It is equally difficult to understand the NH₄ ion-fixing capacity of illites, because they do not expand on being saturated with divalent cations⁶⁷. Earlier reports indicate that Vertisols developed in the basaltic alluvium of the Deccan basalt of Peninsular India, do not contain vermiculite^{68,69}. However, a recent report indicates that vermiculite content in such soils ranges from 2.0% to 3.5% in the silt, 3.5% to 10% in the coarse-clay and 5.0% to 9.5% in the fine-clay fractions⁷⁰. Zeolites are known to have pronounced selectivity for NH₄⁺-N over Ca²⁺, Mg²⁺ and Na⁺; and it is difficult to remove NH₄⁺ from zeolite exchange sites by these less selective cations. Therefore, NH₄⁺ is slowly released, however its rate of release from vermiculite and zeolite in a zeolitic Vertisols is not yet known. Thus, it would not be prudent to attribute the observed NH₄-N fixation in Vertisols⁶⁴ entirely to the presence of vermiculite only²⁰. A new research initiative in this direction is thus awaited. Zeolites have the ability to protect NH₄⁺ on zeolite exchange sites from microbial conversion of NH₄⁺ to NO₃⁻ because nitrifying bacteria are too large to fit into the channels and cages within zeolite structure where NH₄⁺ resides on exchange sites³. This way the protection of NH₄⁺ suggests that emission of N₂O from organic (farmyard manure) and inorganic N fertilizers would amount to a small fraction of the total world greenhouse gas emissions from zeolitic soils, because out of 500,000 km² Deccan basalt area in the Indian subcontinent⁷¹, zeolitic soil is expected to cover a considerable part⁵⁹. However, a map showing areas under zeolitic soils is awaited. Such basic understanding is essential to include fixed NH₄-N for assessing the potentiality of N available in zeolitic soils, especially as N₂O emission from Indian agricultural soils is a small fraction (about 1%) of the global warming caused by CO₂ emissions^{72,73}.

Phosphorus

It has been observed that the dissolution of apatite-rich phosphate rock is enhanced by the exchange of dissolved Ca²⁺ onto zeolite exchange sites. The addition of NH₄⁺, H⁺, or Na⁺-exchanged, clinoptilolite-rich tuff significantly increased solution P concentration when compared with phosphate rock without zeolite additions (see ref. 3). Soils occurring in the Deccan basalt areas under semi-arid and HT climate, contain heulandite [(Na, K)Ca₄(Al₉Si₂₇O₇₂)·24H₂O], which is rich in Ca²⁺ ions, and thus the soils are highly base-saturated. Therefore, the scope of P fertilization by dissolution and ion exchange with zeolite in such soils is expected to be limited. In smectitic Vertisols of the Deccan basalt areas, P adsorption is not a major problem and all the adsorbed P is easily exchangeable by P³² and a small amount is adsorbed in the non-exchangeable form^{74,75}. The rate of dissolution of Ca-P under the prevailing management system is adequate to meet the demand of crops²⁰.

Table 4. Selected properties in surface (0–30 cm) soil samples of zeolitic Vertisols under rice cultivation (adapted from Sahrawat *et al.*⁶³)

Benchmark soil series	District/state	Soil taxonomy ^a	pH (1 : 2)	Clay CEC	SOC (%)	Total N (%)	SOC : N
Jhalipura	Kota/Rajasthan	Typic Haplusterts	8.1	77	0.53	0.0443	12 : 1
Jajapur 1	Mehboobnagar/Andhra Pradesh	Sodic Haplusterts	8.5	62	0.88	0.082	11 : 1
Teligi	Bellary/Karnataka	Sodic Haplusterts	8.0	90	1.03	0.062	17 : 1
Teligi 1	Bellary/Karnataka	Sodic Haplusterts	7.8	99	0.88	0.0551	14 : 1

^aAdapted from Pal *et al.*⁵⁹.

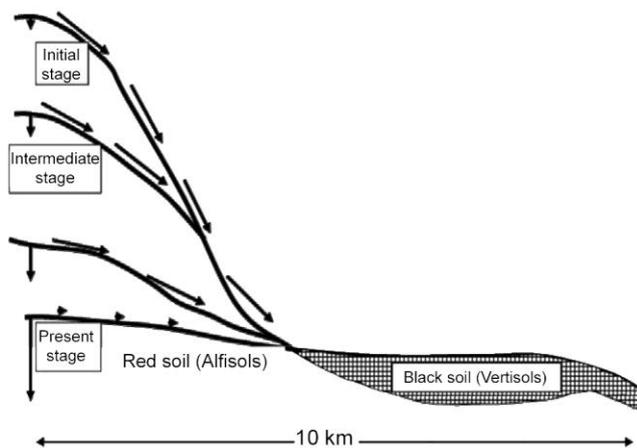


Figure 1. Schematic diagram of the pedon site of red soils (Alfisols) and black soils (Vertisols) showing the landscape reduction process explaining the formation of spatially associated red and black soils (adapted from Pal⁸¹).

Potassium

Soils (Mollisols, Alfisols and Vertisols) developed on the zeolitic Deccan basalt or in its alluvium, are stated to be adequately supplied with potassium (K), and therefore, responses to applied K are not generally obtained²⁰. These soils have high to very high available K status even in the subsurface (Tables 1–3). Potassium release in soils is primarily controlled by biotite mica, which constitutes approximately 1% in the < 2 mm fine earth fraction in Vertisols; and thus available K may not be sustainable over a longer term^{20,76}. The apparent incompatibility between medium to high available K status in surface horizons (≥ 250 kg K ha⁻¹; Tables 1–3) and low biotite mica in soils of the Deccan basalt areas, need further insight in view of pronounced selectivity of zeolites for K⁺ and NH₄⁺ ions. Contribution of zeolites to available K of soils is not uncommon^{77,78}.

Potassium adsorption/fixation in Vertisols does not appear to be sufficiently severe to conclude that K becomes unavailable to plants. The observed moderate amount of K adsorption in the Vertisol fine clays (25–30 mg K/100 g clay) has been attributed to the presence of vermiculite²⁰. However, in the presence of zeolites K adsorption should not be totally attributed to vermiculite as zeolites also have strong selectivity for K⁺ ion.

In view of the role of zeolites in adsorption and desorption of K⁺ and NH₄⁺ ions alongside vermiculite, a fresh research initiative is warranted to pinpoint the selective contribution of zeolite, biotite and vermiculite on a time-scale when they co-exist in soil environments.

Identification of zeolites in soils

Soil is a complex system. At times it is difficult to detect and identify small quantities of zeolite minerals in soils. Therefore, special care needs to be taken while preparing zeolitic soil samples for subsequent mineralogical analyses. Removal of cementing agents (e.g. carbonates, organic matter and iron oxides) to enhance dispersion of soil sample before particle-size fractionation and subsequent mineralogical analyses, chemical pre-treatments (1 N NaOAc buffered to pH 5 for CaCO₃, 30% H₂O₂ for organic matter, and dithionite-citrate-bicarbonate for free Fe₂O₃) are generally followed. Zeolites react differently when subjected to various pH solutions. Clinoptilolite can withstand acid treatments to a pH below 2 before structural degradation is detectable; however, analcime tends to dissolve during acidic treatments around and below a pH of 5. During such chemical pre-treatments some zeolite minerals may be destroyed³. Sand, silt and clay-sized zeolites can be conveniently identified by XRD technique and sand zeolites by scanning electron microscope (SEM), but only after ascertaining their optical characters under optical microscope^{15,16}.

The CEC procedure described by Ming and Dixon⁶ was developed to only quantify clinoptilolite. But the authors felt that the procedure needs further modification to quantify zeolites other than clinoptilolite, because there are more than 60 zeolites that occur in nature and each has unique crystal structures, ion-sieving properties, cation selectivity and cation-exchange capacity. As of now, there is no selective method to quantify the heulandite content in soils which carry other clay minerals. However, specific chemical methods were used by Bhattacharyya *et al.*¹⁶ to determine the CEC and extractable bases that provide indications for the possible presence of zeolites in soils. Bhattacharyya *et al.*¹⁶ determined the CEC of acidic and zeolitic soils using 1 N NaOAc (pH 7) for saturating the soils and 1 N NH₄OAc (pH 7) for exchanging the Na⁺ ions; and the CEC was determined by

estimating the adsorbed Na^+ ions⁷⁹. For calcareous, and slight to moderately alkaline Vertisols, determination of extractable Ca and Mg is done following 1 N NaCl solution extraction method⁸⁰ and for Na and K, 1 N NH_4OAc (pH 7) is used^{18,38,59}. Results indicate that base saturation exceeds more than 100 either throughout the pedon or in the subsoils, confirming the presence of heulandite. The base saturation in excess of 50 for acidic soils and 100 for calcareous and slightly to moderately alkaline Vertisols (Tables 1–3) provides an insight into the chemical environment of zeolitic soils even when facilities of XRD and SEM are not easily available or during difficulty in identifying the heulandite by XRD because of their small amounts⁵⁹, or if they are destroyed during the chemical pre-treatments.

Concluding remarks

The occurrence of acidic Mollisols, Alfisols and Vertisols in the Deccan basalt areas under HT climatic conditions, provides a unique example of tropical soil formation, which is not easily comprehensible unless the role of zeolites was highlighted by the Indian soil scientists during the last two decades. Persistence of these soils in HT climate for millions of years has provided a deductive check on the inductive reasoning of the conceptual models on the formation of soils in HT climate. Zeolitic Vertisols (both sodic and non-sodic by definition) are being used for cultivation of rice and sugarcane because they do not remain waterlogged for a longer time and they also support winter crops. At present these soils are mitigating the adverse effect of Holocene climate change to aridity and also sequestering carbon from the atmosphere. Experimental results obtained on the use of zeolites (other than heulandites) as soil conditioners and slow-release fertilizers provide important clues to address the possible role of soil heulandite in minimizing the conversion NH_4^+ ions to gaseous phases of N and adsorption and desorption of major nutrients in natural soil environments. Research is needed for delineating areas under zeolitic soils and also for understanding the selective role of zeolites in the adsorption and desorption reactions of N, P and K. Identification of soil zeolites is generally done by XRD and SEM. It also seems possible to identify zeolites by determining CEC and extractable bases when the base saturation exceeds 50% in acidic soils and more than 100% in calcareous and slight to moderate alkaline soils. We hope this review will help in developing management practices for an efficient use of zeolitic soils for enhancing agricultural productivity under wet and dry climatic conditions.

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