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Ca-zeolites as Transitory Eco-System Engineers: Hydro-Pedological Evidence in Cracking Clay Soils (Vertisols) of Semi-Arid Marathwada Region, Maharashtra

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Abstract– *Out of the area under cracking clay soils (Vertisols) in Peninsular India, nearly 5.6 % is occupied by Vertisols in the state of Maharashtra. Research endeavors on the genesis and management of Vertisols of semi-arid tropical (SAT) climate was accomplished during the last few decades for major regions of Maharashtra except Marathwada. But such effort needs to be extended to this region as precise information on the physical and chemical characteristics associated with the hydro-pedology of Vertisols developed in the alluvium of the Deccan trap basalt of the Marathwada region is not adequate enough to suggest appropriate management protocols to enhance their productivity. Majority of the Marathwada region support rain-fed agriculture with low productivity. Therefore, systematic studies on the SAT Vertisols of Marathwada region are warranted to know the extent of regressive pedogenetic processes that are operative in SAT Vertisols of this region and also to develop cause-effect relationship of natural soil degradation (if any) in presence of soil modifiers or ecosystem engineers like Ca-zeolites. Ten SAT Vertisols were selected in the districts of Buldhana, Parbhani, Osmanabad, Beed, Jalna and Aurangabad of Maharashtra state. These Vertisols contain Ca-zeolites in their basaltic parent materials. Ca- zeolites are considered as prolonged ecosystem engineers in supporting the successful enterprise for forestry, horticultural and cereal crops, and spices in non-calcareous and acidic Vertisols, Alfisols and Mollisols developed on the Deccan basalt or in its alluvium under the humid tropical climate of the Western Ghats and Satpura Regions for the several millions of years. In contrast, SAT Vertisols of Marathwada showed contrasting physical and chemical characteristics so much that their US Soil Taxonomic classes are Typic Haplusterts and Sodic Haplusterts. Due to the dominant pedogenetic processes like the formation of pedogenic* $CaCO_3$ *(PC) and illuviation of Na-saturated fine clays, some Typic Haplusterts showed more exchangeable Mg percentage (EMP) than exchangeable Ca percentage (ECP) in their Bss horizons, which caused lowering of saturated hydraulic conductivity (sHC) at a value little over 10 mm* hr^{-1}*, preventing strong swelling of plasmic fabric and rise of pH near to 8.2 and above. Zeolites could not prevent the lowering of exchangeable Ca/Mg ratio < 1.5 almost throughout depth, rise in pH, exchangeable Na percentage (ESP) and EMP, weak swelling of plasmic fabric and reducing the sHC << 10 mm* hr^{-1} *in Sodic Haplusterts. This anomalous chemical environment in SAT Vertisols appears to be related to zeolite reserve and the rate of Ca ions release from zeolites amidst the formation of PC as the major pedogenetic process. Selective analytical method to quantify the amount of soil Ca-zeolites is still not available and in its absence the anomalous situation will continue to baffle the researchers. The rate of formation of PC must have been much higher than the rate of release of Ca ions from zeolites in SAT environments as evidenced from the impaired soils' hydraulic properties. This kind of hydro-pedological process would not support the irrigationpractice to raise agricultural crops including sugarcane in the Marathwada region of Maharashtra. Ca-zeolites have proved their worthiness as prolonged ecosystem engineers while supporting successful enterprise for various land uses in the Deccan basalt derived non-calcareous and acidic soils of the humid tropical (HT) climate. Since Ca-zeolites losetheir significance in the*

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contemporary dominant hydro-pedological processes (regressive pedogenesis) theywould remain as transitory ecosystemengineers in SAT Vertisols of the Peninsular India in general and Marathwada region in particular.

Key words: SAT Vertisols, Marathwada, Maharashtra, Zeolites as eco-system engineers, Hydro-pedological evidence, Regressive pedogenesis, Natural soil degradation

Cracking clay soils (Vertisols) occupy 26.62% of the total geographical area of Peninsular India, andMaharashtra has a share of 5.6% of this area (Pal *et al*., 2012a). Extensive research on the genesis and management of Vertisols of SAT climate has been made during the last two and a half decades (Pal, 2017) for major regions of Maharashtra except in the Marathwada region. Precise information on the physical and chemical characteristics associated with pedogenetic processes of Vertisols developed in the alluvium of the Deccan trap basalt of the Marathwada region is scanty. Adequate knowledge in this regard forms the basic necessity forplanning better use and management of SAT soils because in the present SAT climate, Ca^{2+} ions are removed from exchangeable complex and get precipitated as pedogenic carbonates (PC) due to reduced pCO_2 in the soil system (Pal *et al*., 2000, Pal *et al*., 2001, Srivastava *et al*., 2002). This has resulted in the increase in ESP and EMP with depth, which cause dispersion of fine clay smectites, and thus pose problem of blocking macro- and micro pores and poor drainage. Such unfavorable physical and chemical environments make SAT Vertisols less productive for agricultural crops. However, due to the improvement in hydraulic properties caused by the occasional presence of natural modifiers like Ca-zeolites (as constituents of the basaltic parent material), many agricultural crops often grow well in these soils under both rain-fed and irrigation conditions. Ca-zeolites provide enough of Ca^{2+} ions in soil solution and improve the hydraulic properties of the soils even in high ESP (>5) and also in preventing the enhancement of pH and ESP or EMP (Pal *et al*., 2003a).

Majority of the SAT Vertisols of Marathwada region support rain-fed agriculture with low productivity and there are several challenges in improvingthe livelihoods of the rural poor. Therefore, systematic studies on the SAT Vertisols of Marathwada region are warranted to develop cause-effect relationship of natural soil degradation (if any) in probable presence of Ca-zeolites. It is also not known yet how long Ca-zeolites can act as ecosystem engineers in improving hydraulic properties that can help in better movement of rain water in the soil profile, and storing in the subsoils and releasing the stored soil water for crops between the rains. Obviously, this knowledge base is likely to help in making proper management interventions to improve their soil properties conducive for better agricultural land uses.

Materials and Methods

Ten SAT Vertisols were selected in the districts of Buldhana, Parbhani, Osmanabad, Beed, Jalna and Aurangabad, representing the major districts of Marathwada region (Table 1) that are developed in the alluvium of the Deccan basalt. The characteristics of each pedon and its individual horizons were described following the standard procedure (Soil Survey Division Staff, 1993). Particle size distribution was determined by the international pipette method after the removal of organic matter, $CaCO_3$ and free Fe oxides. Sand (2000-50 μm), silt (50-2 ìm) and clay fractions (<2 μm and <0.2 ìm)were separated using the size segregation procedure of Jackson (1979). Soil saturated soil paste was made and the saturation extracts were prepared as per procedure outlined by Richards (1954). The EC of the saturation extract were (ECe) determined by using conductivity bridge. Saturation extract were analyzed for their ionic composition as described by Richards (1954).

The $CaCO_3$, pH, cation exchange capacity (CEC), exchangeable Na and K were determined on total fine earth (<2mm) by standard methods (Richards, 1954). Carbonate clay (Shields and Meyer, 1964) was determined by gravimetric loss of carbon dioxide using Collin's calcimeter. Exchangeable calcium and magnesium were determined from <2 mm sieved samples by leaching with 1N NaCl solution (Piper, 1950) and titrating the leachate against saturated EDTA solution as per the method of Richards (1954).The saturated hydraulic conductivity (sHC) was determined by constant head method as describedby Richards (1954). For identification of clay minerals, the silt and clay fractions were subjected to X-ray examinations of the parallel oriented samples saturated with Ca and K, using a Philips diffractometer with Ni filtered CuKα radiation at a scanning speed of 2 degree 2ε/min. Glycolation and different thermal pretreatments as required were given to distinguish and confirm the type of minerals present (Jackson, 1979). Undisturbed soil blocks (8cm long, 6cm wide and 5cm thick) were collected from soil horizons, and thin sections were prepared by the methods of Jongerius and Heintzberger (1975). They were described according to the nomenclature of Bullock *et al.* (1985).

Results

Morphological Properties

Vertisols under study are deep to very deep (100 to more than 150 cm), very darkgray to dark yellowish brown (10YR 3/1.5 to 10YR 4/4), moderately to highly calcareous throughout the depth and have peds that broke into small sub angular blocky to angular blocky peds.Both sphenoids and slickensides observed in the field confirm the presence of slickensided B horizons (Bss) (Soil Survey Staff, 1999), which also occur beyond 100cm (Table 1). Typical cracks of Vertisols were 2 to 5 cm wide at the surface and extended upto a depth to 60 cm and beyond.Such deep cracklings are generally seen when subsoils are alkaline and have impaired drainage (Pal, 2017). Detailed morphological descriptions are available elsewhere (Zade, 2007; Zade *et al*., 2017).

Physical Properties

These soils contain very small amount of sand (<5%) but are highly clayey containing < 40 % to as high as 75% < 2µm clay fractions. The fine clay fractions (< 0. 2µm) constitute from 30% to 76 % of the < 2µm clay (Table 2). The total clay content shows more than 8% clay in the Bss horizons than in the Ap horizons. The ratio of fine clay to total clay (FC/TC) in the Bss horizons is greater than 1.2 times than the ratio in the Ap horizon. Depth distribution of total and fine clays suggests the clay illuviation process which enriched the Bss horizons (Soil Survey Staff, 2003).The fine clays are low charge di-octahedral smectites and nearer to montmorillonite in the montmorillonite-nontronite series (Zade *et al*., 2017).This suggests that any management protocol to enhance the hydrological properties of these SAT soils requires due attention to the presence of this type of smectite with very high co-efficient oflinear expansion (COLE) (0.2-0.3, Zade, 2007), especially when soils may have unfavorable cations like Mg and Na on their exchange complex (Pal, 2017).

The saturated hydraulic conductivity (sHC) of soils varies enormously within and among the ten Vertisols(Table 2). It decreases gradually with depthin soils at Chandaj of Parbhani district (Pedon 1), Satgaon of Buldhana district (Pedon 2), Adgaon of Jalna district (Pedon 4), Patrud of Beed district (Pedon 12), Raurgaon of Beed district (Pedon 13) and its weighted mean (WM) value within first 1m soil depth ranges from 17

Table 1: *General properties of the Vertisols selected from different districts and their mean annual rainfall (MAR)*

Pedon No.	Soil Series (Soil Taxonomy) (District)	Parent Material	Latitude	Longitude	*MAR (mm)
1	Chandaj (Typic Haplusterts) (Parbhani)	Basaltic alluvium with zeolites	19°32’42" N	76°42’20" E	957
2	Satgaon (Typic Haplusterts) (Buldhana)	Basaltic alluvium with zeolites	20°23’53" N	76°13’45" E	899
3	Kalegaon (Sodic Haplusterts) (Jalna)	Basaltic alluvium with zeolites	19°49’15" N	75°59’57" E	840
4	Adgaon (Typic Haplusterts) (Jalna)	Basaltic alluvium with zeolites	20°27’32" N	75°49’20" E	840
5	Khasgaon (Sodic Haplusterts) (Osmanabad)	Basaltic alluvium	18°14’59" N	75°29’31" E	809
6	Nali Wadgaon (Sodic Haplusterts) (Osmanabad)	Basaltic alluvium with zeolites	18°35’58" N	75°30’29" E	809
10	Bhalgaon (Sodic Haplusterts) (Aurangabad)	Basaltic alluvium with zeolites	19°49’38" N	75°28’42" E	792
11	Babhulgaon (Sodic Haplusterts) (Aurangabad)	Basaltic alluvium with zeolites	20°02’40" N	74°58’03" E	792
12	Patrud (Typic Haplusterts) (Beed)	Basaltic alluvium with zeolites	19°04’15" N	76°12’10" E	685
13	Raurgaon (Typic Haplusterts) (Beed)	Basaltic alluvium with zeolites	18°45’43" N	75°42’20" E	685

*MAR – Mean Annual Rainfall

to 44mm hr^{-1} (Table 2). On the contrary, the decrease of sHC is very sharp in soils at Kalegaon of Jalna district (Pedon 3), Khasgaon of Osmanabad district (Pedon 5), at Nali Wadgaon of Osmanabad district (Pedon 6), at Bhalgaon of Aurangabad district (Pedon 10) and Babhulgaon of Aurangabad district (Pedon 11). Its WM value ranges from< 1 to 9 mm hr^{-1}. Pal *et al*. (2006) brought out a fact that an optimum yield of cotton in Vertisols of SAT 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 and with sHC<10mm h$^{”1}$,and this study also permitted to advocate a value of sHC<10mm h$^{–1}$ in distilled water(weighted mean in 0–1m depth of soil) to define a sodic soil. The differential hydraulic properties of Vertisols under study clearly indicate that both physical and chemical environments are not similar even though these Vertisols are developed in SAT environment. It is expected that the possible presence of Ca-zeolites might have modified soil properties (Pal *et al*., 2006).

Chemical Properties

Vertisols under study contain around 1% organic carbon (OC) in their surface horizons (Zade, 2007) and are mildly to strongly alkaline in reaction.Soils those are strongly alkaline in nature (pH > 8.5), show very low sHC (< 10 mm hr^{-1}), and their exchangeable sodium percentage (ESP) ranges from > 5 to > 15. And soils those are moderately alkaline (pH ≤ 8.5), have sHC >> 10 and their ESP values are < 5. Soils are not saline as their ECe values are much less than 4 dS m^{-1} (Tables 2 and 3). Although all soils are calcareous, soils with pH > 8.5, contain more $CaCO_3$ (< mm) than soils those have pH < 8.5, and their clays (< 2µm) also contain $CaCO_3$ (Table 3). The CO_3 clay constitutes as high as 31% of the total soil $CaCO_3$ content, suggesting that the calcification is the major pedogenetic process. It is interesting to note that although

Table 2: *Some physical and sodicity related chemical properties of soils*

Depth (cm)	Exch. Ca/Mg	ECP	EMP	ESP	sHC mm hr^{-1}	< 2µm clay fraction %	< 0.2µm clay fraction %	< 0,2µm clay /< 2µm clay %
Pedon 1 : Chandaj (Parbhani) –Typic Haplusterts								
Ap(0-13)	4.8	80	17	0.8	30	64	19	30
Bw1(13-28)	5.8	83	14	0.5	49	69	25	36
Bw2(28-45)	5.2(4.6)*	82	16	0.5	56(44)**	70	42	60
Bss1(45-75)	4.5	80	18	0.4	42	70	45	64
Bss2(75-108)	3.7	77	21	0.6	42	70	47	67
Pedon 2 : Satgaon (Buldhana) - Typic Haplusterts								
Ap(0-6)	3.1	73	23	1.3	15	65	31	48
Bw1(6-19)	2.9	73	25	1.2	84	64	33	51
Bw2(19-35)	2.9(2.1)*	73	25	1.6	40(43)**	66	34	51
BC(35-51)	2.2	67	31	1.7	50	66	37	56
Bss(51-118)	1.5	58	39	1.6	34	74	46	62
Crk(118-130+)	1.3	53	42	3.7	9	60	22	37
Pedon 3 : Kalegaon (Jalna) – Sodic Haplusterts								
Ap(0-14)	2.0	65	32	1.4	10	42	13	31
Bw1(14-36)	1.6	57	36	4.8	12	46	15	33
Bw2(36-57)	1.3(1.2)*	51	39	7.9	4(5)**	47	16	34
Bss1(57-87)	0.8	37	48	12.5	.0..3	49	20	41
Bss2(87-114)	0.7	34	47	17.9	0.3	44	16	36
C(114-130+)	0.8	38	44	17.7	1	13	9	69
Pedon 4 : Adgaon (Jalna) Typic Haplusterts								
Ap(0-12)	2.9	71	24	1.0	17	49	13	26
Bw1(12-33)	1.9	63	33	1.1	32	53	24	45
Bw2(33-49)	1.4(1.5)*	56	40	1.6	33(32)**	67	34	51
Bss1(49-82)	0.9	46	51	1.9	41	77	31	40
Bss2(82-105)	1.1	50	46	2.5	24	78	32	41
C(105-129+)	1.1	51	45	2.4	25	45	13	29
Pedon 5 : Khasgaon (Osmanabad)- Sodic Haplusterts								
Ap (0-14)	2.0	64	32	3.2	08	59	38	64
Bw1(14-30)	1.8	61	33	4.5	10	58	39	67
Bw2(30-53)	2.6(2.4)*	68	26	6.1	12(9)**	62	44	71
Bss1 (53-77)	2.9	68	27	7.2	10	63	48	76
Bss2(77-102)	2.3	64	28	7.6	9	60	44	73
Bw1 (102-150)	1.5	56	36	5.9	9	56	33	59
Pedon 6 : Nali Wadgaon (Osmanabad) – Sodic Haplusterts								
Ap (0-13)	1.4	56	40	3.0	12	50	35	70
Bw1 (13-33)	1.0	48	46	4.1	11	52	15	29
Bw2 (33-53)	0.8(0.76)*	41	53	5.7	9(9)**	57	43	75
Bss1 (53-82)	0.5	31	63	4.6	8	62	47	76
Bss2(82-99)	0.5	33	61	5.2	5	61	46	75
Bss3 (99-150)	0.6	34	60	4.7	4	67	48	72
Pedon 10 : Bhalgaon (Aurangabad)- Sodic Haplusterts								
Ap (0-12)	1.4	48	35	12.9	2	30	8	27
Bw1 (12-33)	0.9	38	43	14.8	0.1	37	12	32
Bw2 (33-62)	0.8(0.83)*	33	41	22.6	0.8(<1)**	39	14	36
Bss1 (62-88)	0.8	31	39	25.4	0.8.	42	16	38

Table 2. *Continued*

Depth (cm)	Exch. Ca/Mg	ECP	EMP	ESP	sHC mm hr^{-1}	< 2µm clay fraction %	< 0.2µm clay fraction %	< 0,2µm clay /< 2µm clay %
Bss2(88-123)	0.5	24	44	29.1	0.1	51	18	35
Bss3 (123-150)	0.5	20	40	37.3	0.1	46	17	37
Pedon 11 : Babhulgaon (Aurangabad) - Sodic Haplusterts								
Ap (0-15)	1.1	48	45	2.4	5	33	11	33
Bw1 (15-34)	0.8	41	49	4.0	.5	32	13	40
Bw2 (34-72)	0.5(0.62)*	27	58	11.1	1(2)**	38	16	42
Bss1(72-97)	0.4	21	60	15.8	1	39	18	46
Bw3 (97-130)	0.3	22	65	9.7	1	29	13	49
Bw4 (130-160)	0.4	22	63	12.5	1	26	13	50
Pedon 12 : Patrud (Beed)- Typic Haplusterts								
Ap (0-13)	4.6	79	17	1.1	7	43	14	32
Bw1 (13-36)	3.2	75	23	0.7	14	49	17	35
Bw2(36-61)	2.8(2.8)*	72	25	0.3	14(26)**	48	16	33
Bss1 (61-104)	2.1	65	31	0.9	27	49	16	33
Bss2 (104-140)	1.5	60	39	0.2	42	51	16	31
Bss3 (140-160)	1.7	61	35	0.9	34	59	24	41
Pedon 13 : Raurgaon (Beed) - Typic Haplusterts								
Ap (0-14)	3.1	73	24	0.5	31	69	24	35
Bw1 (14-28)	2.1	66	32	0.9	29	71	30	42
Bw2 (28-43)	1.7(1.5)*	62	35	1.5	19(17)**	72	35	49
Bss1 (43-85)	1.1	50	46	1.8	10	72	35	49
Bss2 (85-130)	0.6	38	59	1.4	8	75	38	51
Bss3 (130-150)	0.5	33	63	2.8	6	58	21	36

*Weighted mean value of exchangeable Ca/Mg in the 0-1m depth of soil
**Weighted mean value of sHC in the 0-1m depth of soil

sodification of SAT Vertisols under study is observed but it is restricted in soils of Jalna (Pedon 3), Osmanabad (Pedon 5 and Pedon 6) and Aurangabad (Pedons 10 and 11) districts, and the soils of Parbhani (Pedon1), Buldhana (Pedon2), Jalna (Pedon 4) and Beed (Pedon 12 and Pedon 13) are free from sodicity. Judging by their pH, ECe and sHC, soils of pedons 3, 5, 6, 10 and 11 qualify as Sodic Haplusterts, and the soils of pedons 1, 2, 4, 12 and 13 as Typic Haplusterts on the basis of observations made by Pal *et al*. (2006) who advocated a value of sHC<10mm h^{-1} (as weighted mean in the first 1m of soil) instead of ESP or sodium adsorption ratio (SAR) to define a sodic soil. Their study reaffirms a fact that the decisive feature of soil classification must be evidently the crop performance because it indicates the nature of soil much more explicitly than any other arbitrary definition and nomenclature possibly can claim to do.

Zeolites and their Implication in sHC

Several reviews have been published about the occurrence and properties of zeolites in soils (Pal *et al*., 2013a; Bhattacharyya *et al*., 2015). Among the commonly occurring species of zeolites, Si-poor Ca -rich heulandite is widely distributedin cracking clay soils developed in the alluvium of the weathering Deccan basalts (Bhattacharyya *et al*., 2015). Zeolites have the ability to hydrate and dehydrate reversibly and to exchange some of their constituent cations and thus, can influence the pedo-chemical and hydro-pedological environments during the formation of soils.

It is a fact that there is no selective method to quantify the heulandite in soils which have other clay minerals. But the qualitative presence of heulandite in soils developed in Deccan basalt alluvium could be made by a simple method (Bhattacharyya *et al*., 1999). These researchers determined the CEC and extractable bases that provide indications for the possible presence of zeolites in soils. They determined the CEC of acidic and zeolitic soils using 1 N NaOAc (pH 7) for saturating the soils, and 1 N NH_4OAc (pH 7) for exchanging the Na^+ ions; and the CEC was determined by estimating the adsorbed Na^+ ions (Richards 1954). But for the calcareous, and slight to moderately alkaline Vertisols, determination of extractable Ca and Mg is done following 1 N NaCl solution extraction method (Piper 1966) and for Na and K, 1 N NH_4OAc (pH 7) (Pal *et al*., 2006) is used. The base saturation (BS) calculated using CEC and extractable bases exceeds ≥ 100 either throughout the pedon depth or in the sub-soils. Vertisols under study have BS ≥ 100 (Table 3), confirming the presence of zeolites in general and heulandite in particular. Presence of zeolites in the silt and coarse clay fractions along with other clay and primary minerals, was further confirmed by the XRD technique (Figs. 1 and 2)as demonstrated by Bhattacharyya *et al*.(1993,1999). Micro morphological soil thin sections studies also indicated the presence of zeolites (Fig. 3).

It is well known that many productive Vertisols under rainfed conditions have been rendered unproductive for agriculture when they are irrigated in thelonger-term. However, some zeolitic SAT Vertisols at Pahur and Loni of Yavatmal district, and at Vasmat of Hingoli district (Pal *et al*., 2003a) have been irrigated through canals for the last twenty years toproduce sugarcane. These soils lack salt-efflorescence on the surface unlike the sodic soils of the NW parts of the Indo-Gangetic Alluvial Plains, and are not waterlogged at present. This may apparently suggest that these soils are notdegraded due to their better drainage even these soils are nowSodic Haplusterts in view of their pH, ECe and ESP values. Interestingly, theyhave sHC>10 mm hr^{-1}. A constant supply of Ca^{2+} ions from

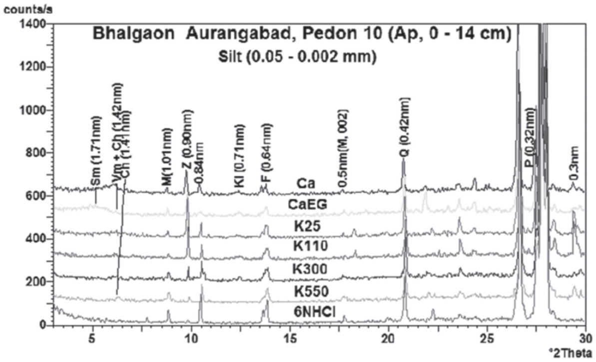

Fig. 1. *XRD patterns of the silt fraction as representative of Typic and Sodic Haplusterts. Ca=Ca saturated, CaEG=Ca saturated plus glycol vapour, 25/110/300/550°C=K saturated and heated to 25°C, 110°C, 300°C and 550°C, 6NHCl= HCl treated silt, Sm=Smectite, Vm=Vermiculite, Ch=Chlorite, M=Mica, Kl=Kaolin, F=Feldspar, Q=Quartz, Z=Zeolite, P=Plagioclase*

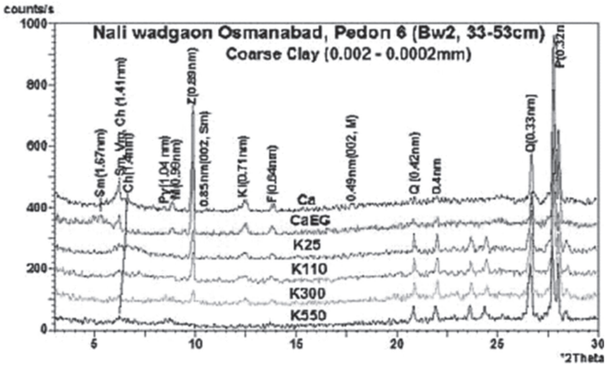

Fig. 2. *XRD patterns of the coarse clay fractions as representative of Typic and Sodic Haplusterts. Ca = Ca-saturated, CaEG = Ca-saturated plus glycol vapour, K25/110/300/550°C = K-saturated and heated to 25°C, 110°C, 300°C and 550°C, K300EG= K-saturated plus ethylene glycol vapour and heated at 300°C, Sm= smectite, Vm=vermiculite, Ch=chlorite, Py=palygorskite, M=mica, Z=zeolite, Kl=kaolin, Q = quartz, F=feldspars, P=plagioclase.*

Table 3. *Chemical properties of soils*

Hori-zon	Depth (cm)	pH (1:2) H_2O	ECe dS m^{-1}	O. C. %	Calcium carbonate equivalent as $CaCO_3$ <2 mm (%)	Carbonate clay % on fine earth basis	Extractable bases				Sum of cations	CEC cmol(p+) kg^{-1}	Base saturation %
							Ca	Mg	Na	K			
							←— cmol(p+)kg^{-1} —→						
Pedon 1 : Chandaj (Parbhani)-Typic Haplusterts													
Ap	0-13	8.2	1.2	0.9	6.7	2.5	52.3	10.9	0.5	1.9	65.6	61.8	106.1
Bw1	13-28	8.3	0.3	0.8	6.3	2.7	55.9	9.7	0.3	1.3	67.3	59.1	113.9
Bw2	28-45	8.3	0.4	0.8	6.5	2.7	54.9	10.6	0.3	1.1	67.0	57.5	116.6
Bss1	45-75	8.2	0.3	0.8	6.8	2.8	54.2	12.1	0.3	1.0	67.7	50.6	133.7
Bss2	75-108	8.3	0.3	0.7	6.7	2.9	51.9	14.1	0.4	1.2	67.6	56.8	119.1
Pedon 2 : Satgaon (Buldhana)-Typic Haplusterts													
Ap	0-6	8.5	0.4	1.1	6.0	2.4	47.11	15.0	0.9	1.3	64.3	68.6	93.7
Bw1	6-19	8.5	0.5	1.2	7.8	2.6	46.6	16.0	0.8	0.8	64.2	72.3	88.7
Bw2	19-35	8.5	0.5	0.9	9.5	2.9	39.8	13.7	0.8	0.3	54.5	60.4	90.3
BC	35-51	8.5	0.6	0.7	14.8	3.4	32.9	15.0	0.8	0.2	48.9	51.7	94.7
Bss	51-118	8.5	0.5	0.8	16.7	3.8	36.5	24.8	1.0	0.9	63.3	66.6	95.1
Crk	118-130+	8.6	0.7	0.2	24.9	3.2	20.6	16.3	1.4	0.5	38.8	38.4	100.9
Pedon 3 : Kalegaon (Jalna)- Sodic Haplusterts													
Ap	0-14	8.8	0.5	0.7	15.0	2.0	36.7	18.1	0.8	1.2	56.9	51.7	109.9
Bw1	14-36	8.9	0.15	0.6	14.2	2.3	32.9	21.1	2.8	0.9	57.7	54.3	106.2
Bw2	36-57	9.3	0.4	0.6	14.4	2.4	29.5	22.4	4.5	0.8	57.2	53.3	107.2
Bss1	57-87	9.3	0.7	0.6	15.5	2.6	21.1	27.3	7.2	1.4	56.9	54.4	104.7
Bss2	87-114	9.2	1.1	0.5	17.0	2.3	18.5	25.9	9.9	0.8	55.1	50.9	108.2
C	114-130+	9.6	0.30	0.1	24.4	0.7	12.6	14.7	5.6	0.08	33.3	21.8	152.7
Pedon 4 : Adgaon (Jalna) - Typic Haplusterts													
Ap	0-12	8.3	0.6	1.1	13.2	2.1	33.7	11.6	0.5	1.8	47.7	48.6	98.1
Bw1	12-33	8.7	0.4	1.0	11.7	2.1	30.8	16.2	0.5	1.0	48.6	47.4	102.4
Bw2	33-49	8.6	0.5	0.8	14.6	3.4	31.2	22.3	0.9	0.8	55.1	51.2	107.7
Bss	49-82	8.7	0.6	0.7	20.5	3.9	25.8	28.5	1.1	0.5	55.9	49.9	111.9
Bss2	82-105	8.7	0.6	0.7	21.0	4.1	29.9	27.2	1.5	0.7	59.3	54.2	109.3
C	105-129+	8.6	0.5	0.3	24.5	1.8	20.1	17.7	0.9	0.5	39.2	33.9	115.7
Pedon 5 : Khasgaon (Osmanabad) — Sodic Haplusterts													
Ap	0-14	8.4	0.5	1.0	8.6	1.9	37.8	18.9	1.9	0.6	59.2	65.4	90.6
Bw1	14-30	8.4	0.5	0.9	9.8	2.4	37.7	20.8	2.8	0.7	62.1	70.8	87.7
Bw2	30-53	8.3	0.9	0.8	10.1	2.5	42.0	15.9	3.6	0.4	62.0	64.7	95.9
Bss1	53-77	8.2	1.3	0.8	9.9	2.6	40.8	13.9	4.3	0.6	59.6	64.7	92.3
Bss2	77-102	8.6	1.6	0.7	11.4	2.5	37.8	16.4	4.5	0.5	59.2	59.3	99.8
Bw1	102-150	8.9	1.8	0.7	15.5	2.2	31.1	20.3	3.3	0.9	55.6	56.7	98.0

Table 3. *Contined ...*

Hori-zon	Depth (cm)	pH (1:2) H_2O	ECe dS m^{-1}	O. C. %	Calcium carbonate equivalent as $CaCO_3$ <2 mm (%)	Carbonate clay % on fine earth basis	Extractable bases				Sum of cations	CEC cmol(p+) kg^{-1}	Base saturation %
							Ca	Mg	Na	K			
							←————— cmol(p+)kg^{-1}				—————→		
Pedon 6 : Nali Wadgaon (Osmanabad) - Sodic Haplusterts													
Ap	0-13	8.5	0.6	0.8	12.7	1.7	25.2	18.1	1.4	0.7	45.3	45.4	99.8
Bw1	13-33	8.6	0.5	0.6	13.5	1.7	23.1	22.1	1.9	0.4	47.6	47.1	100.9
Bw2	33-53	8.9	0.9	0.6	13.6	2.4	21.0	27.3	2.9	0.4	51.7	51.7	99.9
Bss1	53-82	9.1	0.5	0.6	13.8	2.7	17.0	34.1	2.5	0.6	54.2	56.5	96.0
Bss2	82-99	9.2	0.6	0.6	13.5	2.8	19.4	35.6	3.1	0.4	58.5	58.4	100.1
Bss3	99-150	8.9	0.4	0.6	18.9	3.0	20.3	35.8	2.8	0.7	59.6	55.8	106.9
Pedon 10 : Bhalgaon (Aurangabad) - Sodic Haplusterts													
Ap	0-12	8.8	1.0	0.5	12.3	1.4	20.1	14.6	5.4	1.9	42.0	34.0	123.6
Bw1	12-33	9.1	1.2	0.3	13.5	2.0	15.3	17.0	5.9	1.5	39.7	37.1	107.0
Bw2	33-62	9.1	1.3	0.3	14.2	2.1	13.4	16.6	9.2	1.5	40.6	41.6	97.5
Bss1	62-88	9.0	1.3	0.3	14.7	2.3	14.2	17.8	11.5	1.8	45.5	40.8	111.5
Bss2	88-123	8.8	1.4	0.2	11.7	2.9	12.3	22.0	14.7	1.4	50.4	44.4	113.5
Bss3	12-150	8.9	2.4	0.2	12.8	2.7	11.2	23.0	21.3	1.5	57.0	40.9	139.1
Pedon 11 : Babhulgaon (Aurangabad) - Sodic Haplusterts													
Ap	0-15	8.5	1.0	0.8	17.3	1.5	17.9	16.7	0.9	1.9	37.5	33.4	112.1
Bw1	15-34	8.5	0.7	0.8	18.5	1.6	15.2	18.3	1.5	2.2	37.2	31.5	117.8
Bw2	34-72	8.8	0.8	0.6	17.0	1.9	11.4	24.0	4.6	1.4	41.6	35.2	117.9
Bss1	72-97	9.1	0.9	0.4	17.2	2.0	8.8	24.5	6.5	1.0	40.8	35.0	116.3
Bw3	97-130	9.3	1.1	0.2	20.1	1.5	7.3	21.4	3.2	0.8	32.7	25.9	126.5
Bw4	130-160	9.3	1.0	0.2	20.2	1.2	7.3	20.7	4.1	0.8	32.9	30.5	107.6
Pedon 12 : Patrud (Beed)- Typic Haplusterts													
Ap	0-13	8.7	0.2	0.8	12.7	1.9	47.8	10.4	0.7	1.7	60.7	55.1	110.2
Bw1	13-36	8.8	0.3	0.7	13.9	2.1	44.1	13.7	0.4	0.9	59.1	54.5	108.5
Bw2	36-61	8.7	0.2	0.6	13.3	2.2	45.4	15.9	0.2	1.3	62.8	62.7	100.0
Bss1	61-104	8.5	0.4	0.5	12.6	2.4	39.1	18.7	0.5	1.6	59.9	56.6	105.9
Bss2	104-140	8.9	0.3	0.3	13.9	2.2	36.2	23.5	0.1	0.8	60.6	52.6	115.2
Bss3	140-160	8.5	0.4	0.3	11.8	2.4	37.8	21.6	0.6	1.9	61.9	60.4	102.5
Pedon 13 : Raurgaon (Beed) - Typic Haplusterts													
Ap	0-14	8.5	0.4	0.9	11.8	2.3	46.4	15.1	0.3	1.6	63.3	64.6	98.0
Bw1	14-28	8.5	0.3	0.8	12.2	2.8	43.0	20.8	0.6	1.0	65.4	65.4	100.1
Bw2	28-43	8.5	0.3	0.7	10.2	2.9	42.4	24.0	1.0	1.0	68.4	68.3	100.2
Bss1	43-85	8.6	0.4	0.7	9.9	3.1	34.5	31.6	1.2	1.0	68.3	68.5	99.6
Bss2	85-130	8.5	0.4	0.4	11.8	3.2	26.1	40.7	1.0	1.1	68.9	69.0	99.8
Bss3	130-150	8.5	0.6	0.4	1.02	2.3	22.9	44.3	2.0	1.1	70.3	67.1	104.7

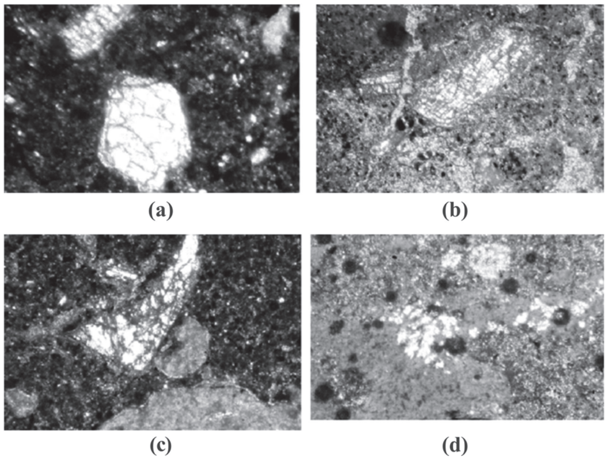

Fig. 3. *Representative photograph of zeolite minerals in cross polarized light : (a) Typic Haplusterts (Pedon 1, 88-93cm), (b) Sodic Haplusterts (Pedon 3, 110-118), (c) Sodic Haplusterts (Pedon 10, 48-56 cm), (d) Typic Haplusterts (Pedon 12, 34-66cm).*

Ca-zeolites in these soils most likely helps maintain a better drainage system. However it is be noted that the five zeolitic Vertisols (Sodic Haplusterts) under study (Pedons 3, 5, 6, 10 and 11) have sHC $\leq$ 10 mmhr^{-1} (Table 2) whereas the rest of the zeolitic Vertisols (Pedons 1, 2, 4, 12 and 13) which are Typic Haplusterts and have sHC >> 10 (Table 2). Sodic Haplusterts under study obviously are no more vibrant substrate for good agricultural land use plans because of poor hydraulic properties unlike similar soils of Yavatmal and Hingoli district.It is to be noted here that Vertisols developed in SAT climate in the zeolitic basalt alluvial material belong to two kinds of subgroups; one is Typic Haplusterts and the other is Sodic Haplusterts. In addition, Sodic Haplusterts under study though zeolitic are,however, notcomparable in terms of their hydraulic properties to those of Yavatmal and Hingoli district. This is a paradoxical situation and needs to be explained.

Plasmic fabric, sHC and Shrink-Swell phenomena

Shrinking and swelling result in a very dense groundmass exhibiting porostriated, parallel-striated, reticulate striated, granostriated,stipple-speckled, mosaic speckled and crystallitic plasmic fabric, which are observed in Vertisols of HT and SAT climatic conditions (Pal *et al.*, 2006, 2009). Vertisols of semi-arid moist (SAM) and dry(SAD) climate under study (Pedons 1, 2, 12 and 13 - Typic Haplusterts) show moderately strong plasma separation with reticulateand granostriated plasmic fabrics (Fig. 4a,b) whereas soils of semi-arid dry (SAD) climate (Pedons 3, 5, 6,10- Sodic Haplusterts) showed moderateto weakplasma separation with mosaic-speckled, stipple-speckled and crystallitic plasmic fabric (Fig.4c,d,e). Despite a high degree of clay activity, and shrink–swell process (as evidenced in high COLE values 0.2 – 0.3, Zade, 2007), the plasmic fabric is not uniform among the Vertisols of SAM and SAD bio-climates because of the difference in hydraulic properties in Typic and Sodic Haplusterts. Zeolites in Sodic Haplusterts under study could not help in improving the sHC like those of Yavatmal and Hingoli districts (Pal *et al.*, 2003a). This suggests that the release of Ca^{+2} ions from Ca-zeolite was not enough in improving the sHC, and preventing the rise in pH and ESP and EMP in the subsoils of Sodic Haplusterts under study. Because of poor sHC, free entry of rain water was prevented in to the Vertisols when they are sodic, and this situation does not provide adequate soil water in the subsoils for greater shrink-swell process to create strong plasma separation while Typic Haplusterts with a relatively better sHC could remainwith enoughsoil water to cause greater shrink-swell activity to causemoderately strong plasma separation.

Discussions

The results of the present study indicates that the SAT Vertisols of Marathwada region of Maharashtra state are calcareous and the soils with mean annual rainfall (MAR) < 1000 mm are mild to strongly alkaline and are of both

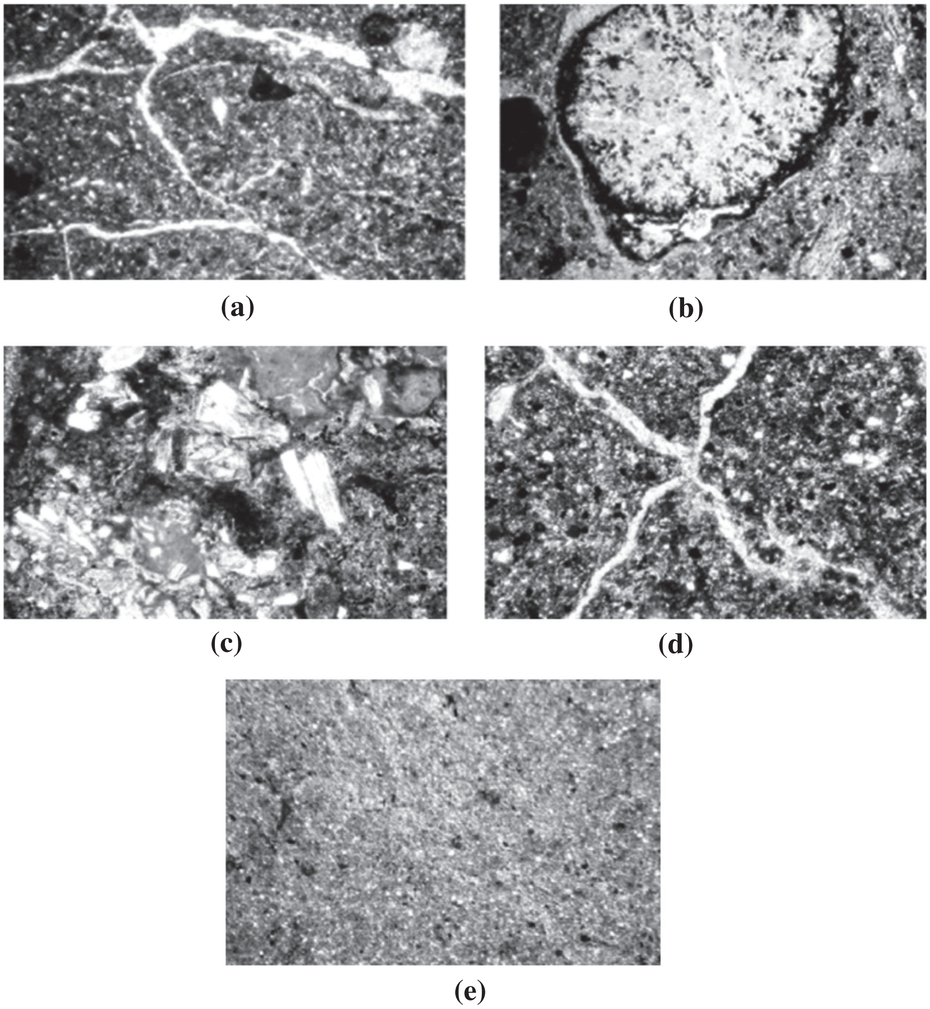

Fig. 4. *Representative photograph of plasmic fabric in cross polarized light. (a) Reticulate b-fabric of Typic Haplusterts (Pedon2, 83-91cm), (b) Granostriated b-fabric of Typic Haplusterts (Pedon 12, 97-105 cm), (c) Stipple-speckled b-fabric of Sodic Haplusterts (Pedon 3, 110-118cm), (d) Crystallitic b-fabric of Sodic Haplusterts (Pedon, 5, 66-74 cm), (e) Mosaic-speckled b-fabric of Sodic Haplusterts (Pedon 10, 91-99 cm).*

sodic and non-sodic in nature, and thus they are classed as Typic Haplusterts and Sodic Haplusterts. Calcareousness of soils is due to the presence of both pedogenic and non-pedogenic $CaCO_3$, but the pedogenic formation of $CaCO_3$ (PC) is not a favourable chemical reaction for soil health because this impairs sHC, causes high pH with concomitant enrichment of both Na and Mg ions on the soil exchange complex (Pal *et al*., 2000; Balpande *et al*., 1996; Bhattacharyya *et al*., 2004). The presence of pedogenic PC that is distinguished from the pedorelict $CaCO_3$ (NPC) by the soil thin section studies (Pal *et al.,* 2000), is very common in SAT Vertisols.

The enrichment of Na ions on soil exchange complex in turn cause dispersion of the fine clay particles. The dispersed fine clays translocate as the formation of PC creates a Na $^+$ - enriched chemical environment conducive for the deflocculation of clay particles and their subsequent movement downward. The formation of PC and the clay illuviation are thustwo concurrent and contemporary pedogenetic events, which result in an increase in relative proportion of sodium and magnesium, causing increased

ESP, EMP, pH values and a decrease in sHC and exchangeable Ca/Mg ratio with depth (Table 2). These pedogenetic processes represent a pedogenic threshold during the dry climates of the Holocene (Pal *et al*., 2003b, 2012a, 2014,2016; Srivastava *et al*., 2015), and clearly suggest that the formation of PC is a basic natural chemical degradation process (Pal *et al*., 2000, 2016), which exhibits the regressive pedogenesis (Pal *et al*., 2013b, 2016); and it also immobilizes soil carbon in unavailable form.

Vertisols under study contain Ca-zeolites in their silt and clay fractions; however their contents are not as high as are observed from their XRD intensity of the Western Ghats Vertisols of HT climate (Bhattacharyya *et al*., 1993, 1999). Zeolites are known as effective soil modifiers as they improve sHC (Pal *et al*., 2003a, 2006). It is however paradoxical that even in presence of Ca-zeolites, SAT Vertisols under study is not Typic Haplusterts. Even zeolites could not prevent the formation of ill drained Sodic Haplusterts with sHC << 10mmhr^{-1}. This queer scenario needs however an explanation.

It is observed that although the soils belong to Typic Haplusterts, their pH values are often close to or little over 8.5 (Table 3), indicating that the formation of PC has been an active pedogenetic process. Active calcification as PC caused greater exchangeable Mg in the Bss horizons of some Typic Haplusterts (Pedons 4, 12 and 13) and the exchangeable Mg was very close or greater than exchangeable Ca when exchangeable Ca/Mg ratio reaches a value around 1.5 or less (Table 2). In the sub soils, especially in the Bss horizons of the Sodic Haplusterts, exchangeable Ca /Mg ratio often reaches a ratio much less than 1.5 when exchangeable Mg was greater than exchangeable Ca (Table 2). It is now understood that the endowment of soil modifier like Ca-zeolites did help maintain sHC >> 10 mmhr^{-1} and moderately strong plasma separation butfailed to maintain the pH below 8.5. However, Ca-zeolites could succeed maintain in general,the exchangeable Ca/Mg ratio at 1.5 and above in Typic Haplusterts. In Sodic Haplusterts, Ca-zeolites could not improve the sHC beyond 10 mmhr^{-1}, resulting in poorplasma separation. This is however in contrast to the scenario in Hingolidistricts of Marathwada region where zeolitic Typic Haplusterts with sHC >> 10 mm hr^{-1} became Sodic Haplusterts under decade long irrigated agriculture but their hydraulic property was not impaired as it still maintains at sHC > 10 mm hr^{-1}. However, a contrasting result was observed in Yavatmal district where better drained Typic Haplusterts after irrigation turned out to be Sodic Haplusterts, which showed sHC << 10 mm hr^{-1} (Pal *et al*., 2003a). This anomalous scenario indicates the necessity to gain knowledge on the reserve of Ca-zeolites in soil system in different bio-climates where Vertisols occur in Peninsular India (Bhattacharyya *et al*., 2015). However, fresh research initiative is warranted to follow the dynamics on the rate of Ca ion release from zeolites in diverse soil types. At this moment it appears that Ca-zeolites actonly as transitory ecosystem engineers in making SAT Vertisols sustainable for long term productive agriculture under irrigation.

At presentit isdifficult to detect and identify small quantities of zeolite minerals in soils by the XRD method (Pal *et al*., 2013a). The CEC procedure described by Ming and Dixon (1987) was developed to only quantify zeolite like clinoptilolite. But the authors felt that the procedure needs further modification to quantify zeolites other than clinoptilolite. Therefore, as of now, there is no selective method to quantify the heulandite (Ca-rich zeolite) content in soils which carry other clay minerals (Pal *et al*., 2013a). Bhattacharyya *et al*. (1999) advocated specific chemical protocol to determine the CEC and extractable bases that provide indications for the possible presence of zeolites in soils. Authors demonstrated when the base saturation in excess of 50 for acidic soils and 100 for calcareous and slight to moderate alkaline Vertisols provides an evidence of the presence of zeolite. According to this criterion, Vertisols under study have BS ≥ 100.

Bhattacharyya *et al*. (1993, 1999, and 2006) highlighted the unique role of Ca-rich zeolites as ecosystem engineers in the formation and persistence of non-calcareous and acidic Vertisols, Alfisols and Mollisols in the Deccan basalt area under HT Western Ghats (WG) and Satpura Regions (SR). Natural endowment of Ca-zeolites in these soils helped in the enrichment of organic carbon(OC), adequate moisture, high base saturation(BS) and more exchangeable Ca than Mg on soil exchange complex, and moderately smectite rich clays and also a better soil drainage since the several millions years. In reality, these soils support the successful enterprise forforestry, horticultural and cereal crops, and spices. Now the question arises how long zeolites would help sustain such varied land uses? One can, however, envisage that such necessity would arise when the stocks of zeolites is depleted completely under continuing HT climate, acidic Vertisols, Alfisols and Mollisols would phase towards the base poor and OC rich Ultisols (Pal *et al.*, 2012a, 2014; Pal, 2017). In view of their weathering since the several millions years, the stock of Ca-zeolites is still not exhausted in HT soils of the WG and SR, suggesting a constant supply of Ca ions in soils. The BS >50% in general of the soils suggest that WG and SR areat present non-calcareous and acid soils,and far away from phasing towards Ultisols, which justifies the existence of Ca-zeolites in these soils as prolonged ecosystem engineers.

The present rate of formation of PC in SAT Vertisols is estimated to be around 37.5 kg ha^{-1} yr^{-1} (Pal *et al*., 2000). Thus, it can be safely presumed that the rate of formation of PC is much faster than the rate release of Ca ions from zeolites as evident in the enrichment of exchangeable Mg more than the exchangeable Ca on the soil exchange complex in the Bss horizons of some of Typic Haplusterts, and in Sodic Haplusterts exchangeable Mg is more than exchangeable Ca in the Bw to the Bss horizons (Table 3). It is envisaged that with time and under the SAT climatic environments, the present day Typic Haplusterts would phase towards ill drained and agriculturally unproductive Sodic Haplusterts. Such phasing would be facilitated if such soils are irrigated for raising crops especially the sugarcane. Therefore, Ca-zeolites qualify to be transitory ecosystem engineers in managing and sustaining the productivity of SAT Vertisols of Marathwada region of Maharashtra. Suitable management protocols to enhance the productivity of such SAT Vertisols in rain-fed conditions needs to be followed to make them a sustaining productive system (Pal *et al*., 2012b; Pal 2017)

Conclusions

The results of the present study indicate some interesting information on the impairment of hydraulic properties of SAT Vertisols of Marathwada region of Maharashtra even though they are endowed with Ca-zeolites. Among the major pedogenetic processes typical in SAT soils, the formation of PC mainlycaused the impairment of sHC even in the Bss horizon of the Typic Haplusterts by enriching with exchangeable Mg, and throughout depth of Sodic Haplusterts by enriching both exchangeable Mg and Na. Ca-zeolites could not prevent the rise of pH and exchangeable Mg in Typic Haplusterts and very poor sHC in Sodic Haplusterts. The rate of formation of PC must have been much higher than the rate of release of Ca ions from zeolites in SAT environments, which is not likely to support the practice of irrigation in raising agricultural crops especially the sugarcane in the Marathwada region of Maharashtra. While the Ca-zeolites can act as prolonged ecosystem engineers in supporting successful enterprise for various land uses in non-calcareous and acidic soils of the HT climate, they however will remain as transitory ecosystem engineers in SAT Vertisols of the Peninsular India in general and Marathwada region in particular.

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