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SIGNIFICANCE OF THE FORMATION OF CALCIUM CARBONATE MINERALS IN THE PEDOGENESIS AND MANAGEMENT OF CRACKING CLAY SOILS (VERTISOLS) OF INDIA

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Abstract—Micromorphological studies were performed in order to understand the factors and processes involved in the formation of calcium carbonate ($CaCO_3$) in twenty three soil series of Vertisols representing sub-humid, semi-arid and arid climatic regions of Peninsular India. The study indicates that Vertisols contain both pedogenic calcium carbonate (PC) and non-pedogenic calcium carbonate (NPC) irrespective of the ecosystems to which they belong. The NPCs are part of the parent material of Vertisols. Dissolution of NPCs and recrystallization of dissolved Ca^{2+} ions are responsible for the formation of PCs. Vertisols of arid and semi-arid climates contain more PC in their soil control section (SCS) than those of sub-humid climates. Formation of PC is the prime chemical reaction responsible for the increase in pH, the decrease in the Ca/Mg ratio of exchange site with depth and in the development of subsoil sodicity. Petrographic and scanning electron microscopic (SEM) examination of quartz, feldspars and micas indicate little or no alteration, discounting the possibile formation of smectite during Vertisol formation. X-ray diffraction (XRD) analysis of clays indicates that smectites of Vertisols are fairly well crystallized and do not show any sign of transformation except for hydroxy interlayering. The preservation of the crystallinity of smectite and the lack of transformation of primary minerals thus validate the hypothesis of positive entropy change during the formation of Vertisols.

The precise cause-effect relationship between $CaCO_3$ of pedogenic and non-pedogenic origin, and exchangeable Mg, Na and Ca percentages (EMP, ESP and ECP) has been established in the study. This indicates that impoverishment of Ca^{2+} ions on the exchange sites of Vertisols needs to be controlled by rehabilitation methods that can replenish Ca^{2+} ions, and thus the study provides relevant information for future land resource management programmes not only on Vertisols of India but also on similar soils occurring elsewhere.

Key Words—Calcium Carbonates, Mineral Alteration, Pedogenesis, Soil Micromorphology, Vertisols.

INTRODUCTION

Calcium carbonate is a very common mineral in soils of dry (sub-humid to arid) regions all over the world. Arid and semi-arid climates cover 54% of the total geographical area of India and the soils of these regions are calcareous. The estimated area of calcareous soils is 228.8×10^6 hectares which covers 69.4% of the total geographical area of the country. The occurrence of calcareous soils in different agro-ecological subregions (Velayutham *et al.*, 1999) indicates that $CaCO_3$ is present not only in soils of arid and semi-arid regions but also in soils of humid and perhumid regions. However, its presence in the latter climatic regions is considered to be inherited in soils developed either in strongly calcareous parent material or in young geomorphic surfaces (Pal *et al.*, 2000a).

The global distribution (except in Antarctica) of Vertisols and Vertic intergrades indicates that ~30% of the area of 257×10^6 hectares, confined between the 45°N and 45°S latitudes, is to be found in India (Dudal, 1965). The arid and semi-arid regions of India (8°45′ to 26°0′ N latitudes and 68°0′ to 83°45′ E longitude) are also dominated by Vertisols and their intergrades. The majority of these Vertisols in India occur in the lower piedmont plains or valleys or in microdepressions, and are developed in the alluvium of weathering Deccan basalt (Pal and Deshpande, 1987a).

Petrographic examination of Deccan basalt indicates that plagioclase is by far the most dominant mineral (Deshmukh, 1980). The first weathering product of plagioclase-rich Deccan basalt is a dioctahedral smectite in arid to humid climates (Tardy *et al.*, 1973; Pal and Deshpande, 1987a; Pal *et al.*, 1989; Bhattacharyya *et al.*, 1993). Formation of Vertisols reflects a positive entropy change because weathering of primary minerals contributes very little towards the formation of smectite (Smeck *et al.*, 1983). It is thus difficult to reconcile the formation of large amounts of smectite in Vertisols with the current arid and semi-arid climates. Recent studies, however, indicate that smectite was formed in an earlier humid climate and preserved in the non-leaching environment of arid and semi-arid climates (Pal *et al.*, 2000b, 2001).

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There is a need to identify the Ca-bearing minerals, other than plagioclase feldspars, that must have provided a sufficient amount of Ca^{2+} ions in soil solution for the formation of $CaCO_3$ in Vertisols of sub-humid to arid climates. The present study was undertaken to follow the formation and distribution of $CaCO_3$ at various depths of Vertisols on the basis of existing micromorphological data held by the Soil Resource Studies Division (Pal *et al.*, 2000a,b, 2001) supplemented by new data. It is hoped that this study will provide further insight into the development and management of Vertisols with special reference to agriculture.

MATERIALS AND METHODS

Twenty three Vertisols were selected from sub-humid, semi-arid and arid climates with mean annual rainfall (MAR) of 1100–1300 mm, 700–1060 mm and 500–663 mm, respectively, for detailed micromorphological study of the $CaCO_3$. The majority of these soils are developed in the alluvium of weathered Deccan basalt. However, a few soils occurring in the lower piedmont plains or valleys or in microdepressions are formed in the alluvium of other rock formations rich in plagioclase feldspars and ferromagnesian minerals (Figure 1, Table 1).

The characteristics of each pedon and its individual horizons were described following the procedure of the soil survey manual (Soil Survey Staff, 1951). Both sphenoids and slickensides observed in the field confirm the presence of slickensided B horizons (Bss) (Soil Survey Staff, 1999). Undisturbed soil blocks (8 cm long, 6 cm wide and 5 cm thick) were collected from soil horizons, and thin-sections were prepared using the methods of Jongerius and Heintzberger (1975). They were described according to the nomenclature of Bullock *et al.* (1985). The amounts of minerals and the carbonates were determined by the frequency distribution chart of Bullock *et* al. (1985). After identification using a petrographic microscope, sand-sized plagioclase and mica grains were hand-picked and fixed on aluminum stubs with LEIT-C conductive carbon cement, coated with gold and examined under a Philips SEM.

The particle-size distribution was determined by the international pipette method after removal of organic matter, $CaCO_3$ and free Fe oxide. Sand (2000–50 μm), silt (50–2 μm), total clay (<2 μm) and fine clay (<0.2 μm) fractions were separated according to the procedure of Jackson (1979). The $CaCO_3$, pH, cation exchange capacity (CEC) and exchangeable Na and K were determined on the total fine earth (<2 mm) by standard methods (Richards, 1954). Exchangeable Ca

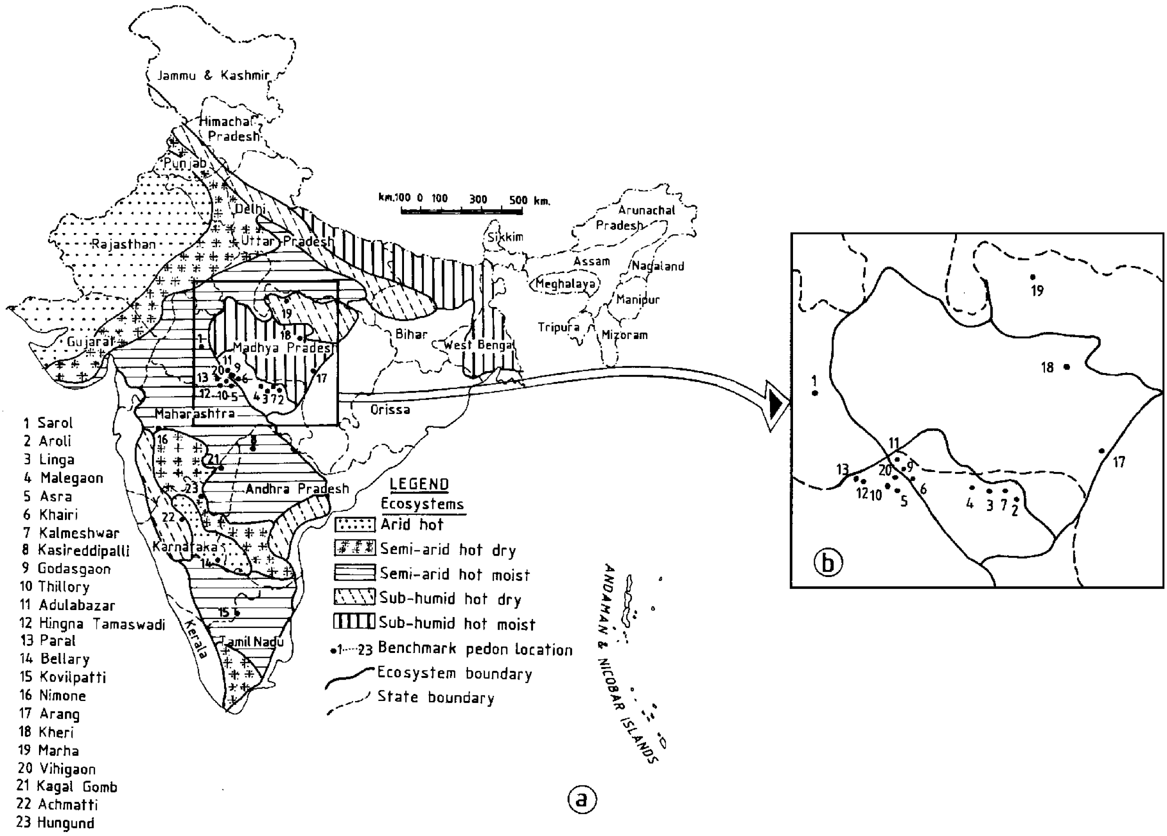

Figure 1. Vertisols in different climatic regions in India. (a) Sub-humid, semi-arid and arid climatic regions of India and location of Vertisol pedons. (b) Closer view of the location of Vertisol pedons in central India.

and Mg were determined following the 1 N NaCl solution extraction method (Piper, 1966). The saturated hydraulic conductivity (HC) was determined using a constant head permeameter (Richards, 1954). The electrical conductivity and soluble cations and anions in saturated extracts were determined by the method of Richards (1954). Sand and silt fractions (500–2 μm) were digested with HF-$HClO_4$ in order to determine the Ca and Na.

The clay fractions were analyzed mineralogically by XRD of oriented aggregates saturated with either Ca or K, using a Philips diffractometer with Ni-filtered CuKα radiation at a scanning speed of $2°2\theta$ min^{-1}. The minerals were identified using Jackson's (1979) method.

RESULTS

General properties of the soils

The soils under study are Vertisols (Soil Survey Staff, 1999) and their detailed morphological, physical and chemical properties are described in several previous publications (Pal and Deshpande, 1987a,b; Kalbande *et al.*, 1992; Balpande *et al.*, 1996, 1997; Pacharne *et al.*, 1996; Paranjape *et al.*, 1997; Pal *et al.*, 2000a,b, 2001; Shirsath *et al.*, 2000). However, data of interest to the present study are presented here.

The soils are grayish brown to dark brown in color, fine textured and generally >100 cm deep. The surface horizons had a subangular blocky structure (Table 1) and were hard to very hard (dry), with a friable consistency (moist). The slickensides present in the Bss horizon are sufficiently close to intersect, and are characterized by strong, coarse angular blocky structure. Intersecting slickensides forming parallelepipeds, with their long axes tilted to 30–45° from the horizontal, were prominent in the Bss horizons (Table 1). This structure breaks into strong, coarse angular blocks with shiny pressure faces and firm (moist) consistency (Table 1). In most soils cracks penetrate to >50 cm depth and gradually terminate at the slickenside zones, which is most strongly expressed at or just below the depth of cracking. However, cracks >1 cm wide cut through the slickensided zones in many soils of low rainfall (<900 mm mean annual rainfall) of arid and semi-arid regions (Pal *et al.*, 2000b, 2001).

The soils are clayey, and fine clay (<0.2 μm) constitutes >50% of the total clay fraction. The soils are, in general, neutral to slightly alkaline and strongly alkaline when they occur in semi-arid and arid environments (<900 mm MAR). The pH and $CaCO_3$ generally increase as the rainfall decreases from sub-humid to arid climates. The soils are impoverished with respect to organic carbon (<1%, Velayutham *et al.*, 2000) and Ca^{2+} is the dominant exchangeable cation, followed by Mg^{2+}, Na^{+} and K^{+} in almost all soils. However, in soils of semi-arid and arid climates, the Mg^{2+} ion tends to dominate the exchange sites (Table 2).

Micromorphology of $CaCO_3$

The formation of $CaCO_3$ in soils is an important pedogenic process in many arid and semi-arid parts of the world. Vertisols and Vertic intergrades of arid and semi-arid parts of India are calcareous. It is difficult, however, to consider that the $CaCO_3$ in these soils is entirely of pedogenic origin because many of these soils may have non-pedogenic $CaCO_3$ due to their polygenesis (Pal *et al.*, 2000b, 2001). All calcite nodules of soils may not be of pedogenic origin. To resolve the difficulty in the identification of PC and NPC, their respective petrographic features, as detailed elsewhere (Pal *et al.*, 2000a), were considered for categorization.

The Vertisols under study exhibit the presence of both PC and NPC (Table 3). Some $CaCO_3$ glaebules are sub-rounded to rounded nodules coated with Fe-Mn oxides and have sharp boundaries with the soil matrix, and these are considered to be NPC (Brewer, 1976; Wright, 1990; Levine and Hendricks, 1990). The other glaebules that are fine textured with irregular shapes and diffuse boundaries and without Fe-Mn coatings, are considered to be PC (Sehgal and Stoops, 1972; Wieder and Yaalon, 1974; Rabenhorst *et al.*, 1984; West *et al.*, 1988; Kalbande *et al.*, 1992). The PCs and NPCs were observed in Vertisols in all three climatic regions, namely, sub-humid, semi-arid and arid (Table 3). The distribution of the NPCs indicates that they are present throughout the soil irrespective of climatic region. However, the PCs are present at ⩾70 cm in soils of sub-humid climate with higher rainfall (MAR = 1300 mm), at ⩾50 cm in sub-humid climate with low rainfall (MAR = 1100 mm), ⩾30 cm in semi-arid climate with higher rainfall (MAR = 1000 mm) and throughout the soil depth in semi-arid (MAR = 700 mm) and arid climate (MAR = 500 mm) (Figure 2).

$CaCO_3$ in Vertisols of sub-humid climate. In this climatic region (1100–1300 mm MAR) Vertisols (Arang, Tables 1 and 3) did not contain PC down to 70 cm of soil depth. No PC at all was observed in the Kheri soils. As determined by the frequency distribution chart of Bullock *et al.* (1985), the PC constitutes 2–3% of the total volume (Table 3, Figure 3a). The NPCs were observed throughout the depth of both the Arang and Kheri soils and constitute 1–3% of the total volume. However, they are marked by dissolution features (Figure 3b) and consist of sparite and microsparite crystals. In the lower rainfall zone of sub-humid climates (~1100 mm), 1–3% PCs were observed below 50 cm depth in the Aroli and Marha soils. They occur as dull white-colored diffuse nodules and dense micrite crystals in the groundmass (Figure 3c). The Linga soils contain even fewer PCs. About 3–10% NPCs occur throughout the depth of soils. These carbonates consist mainly of sparite and microsparite crystals and are marked by extensive dissolution features (Figure 3d).

Table 1. General properties of the Vertisols in sub-humid, semi-arid and arid ecosystems in India.

Soil Series (Soil taxonomy) (State)	Parent material(s)	MAR[5] MRw MRd mm	MAT[6] MTw MTd °C	Structure/lime nodules[7]	Soil Reaction (pH 1:2) water	Cracks (width, depth) Slickensides (depth)[8] Values in cm Effervescence[9] (with dilute HCl)
Subhumid (MAR: 1100–1300 mm)						
Arang[1] (Typic Haplusterts) (Madhya Pradesh)	Basaltic alluvium	1300 1163 137	28 30 23	Coarse subangular blocky in the Ap horizon and medium angular blocky in the Bss horizons/fine, few lime nodules	8.2–8.6	2–3, 40; 41 e–ev
Kheri[1] (Typic Chromusterts) (Madhya Pradesh)	Basaltic alluvium	1300 1163 137	28 30 23	Medium prismatic peds breaking into coarse angular blocky and parallelepipeds in the Bss horizons/ fine, few lime nodules	7.5–8.0	3–4, 60; 37 e–es
Linga[1] (Udic Haplusterts) (Maharashtra)	Basaltic alluvium	1100 790 310	29 29 26	Coarse subangular blocky in the Ap and coarse parallelepipeds in the Bss horizons/fine, few lime nodules	8.1–8.3	3–5, 90–100; 17 e–es
Marha[1] (Entic Haplusterts) (Madhya Pradesh)	Basaltic alluvium and Bundelkhand Gneiss	1100 980 120	28 29 23	Medium moderate subangular blocky in the Ap and coarse strong angular blocky in the Bss horizons/ fine, few lime nodules	8.0–8.1	2–4, 120; 70 e–es
Aroli[1] (Typic Chromusterts) (Maharashtra)	Basaltic alluvium	1100 790 310	29 29 26	Coarse prismatic and subangular blocky in the Ap horizon and coarse angular blocky in the Bss horizons/fine, few to common lime nodules	7.9–8.3	3–5, 100; 42 e–ev
Semi-arid (MAR: 700–1060 mm)						
Sarol[1] (Typic Chromusterts) (Madhya Pradesh)	Basaltic alluvium	1050 950 100	27 27 23	Coarse prismatic in the Ap breaking into coarse subangular blocky and angular blocky in the Bss horizons/medium to coarse, common lime nodules	7.7–8.1	4–5, 120; 51 e–es
Asra[2] (Aridic Haplusterts) (Maharashtra)	Basaltic alluvium	975 830 145	30 28 27	Medium subangular blocky in the Ap grading to coarse angular blocky in the Bss horizons/fine to medium, common lime nodules	8.2–8.3	2–3, 27; 27 es–ev
Malegaon[3] (Typic Haplusterts) (Maharashtra)	Basaltic alluvium	903 766 137	30 27 30	Medium subangular blocky and coarse angular blocky in the lower horizons/fine, few lime nodules	7.6–8.5	2–3, 84; 30 es
Hingna Tamaswadi[2] (Aridic Haplusterts) (Maharashtra)	Basaltic alluvium	875 755 120	30 28 26	Medium subangular blocky in the Ap grading to coarse angular blocky in the lower horizons/fine, few to common lime nodules	8.3–8.6	4–5, 110; 57 ev
Paral[2] (Sodic Haplusterts) (Maharashtra)	Basaltic alluvium	875 755 120	30 28 26	Medium subangular blocky in the Ap grading to coarse angular blocky in the Bss horizons/fine, few to common lime nodules	8.5–9.0	4–5, 142; 69 ev
Khairi[2] (Aridic Haplusterts) (Maharashtra)	Basaltic alluvium	975 830 145	30 28 27	Medium subangular blocky in the Ap horizon and medium angular blocky in the Bss horizons/fine, few to medium lime nodules	8.2–8.6	2, 52; 85 es
Kalmeshwar[1] (Typic Haplusterts) (Maharashtra)	Basaltic alluvium	1060 770 290	29 29 26	Fine subangular blocky in the Ap horizon and medium angular blocky in the Bss horizons/fine, few to medium lime nodules	8.0–8.2	2–2.5, 60; 50 e–es
Vihigaon[4] (Aridic Haplusterts) (Maharashtra)	Basaltic alluvium	876 756 290	30 28 26	Medium subangular blocky in the Ap horizon grading to medium angular blocky in the Bss horizons/ fine, few lime nodules	8.1–8.4	2–2.5, 53; 53 e–es

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Table 1. (*contd*.)

Soil Series (Soil taxonomy) (State)	Parent material(s)	MAR[5] MRw MRd mm	MAT[6] MTw MTd °C	Structure/lime nodules[7]	Soil Reaction (pH 1:2) water	Cracks (width, depth) Slickensides (depth)[8] Values in cm Effervescence[9] (with dilute HCl)
Godasgaon[2] (Sodic Haplusterts) (Maharashtra)	Basaltic alluvium	976 830 146	30 28 27	Coarse subangular blocky and coarse angular blocky in the Bss horizons/fine, common lime nodules	8.5–8.9	4–5, 98; 32 e–es
Thillory[2] (Sodic Haplusterts) (Maharashtra)	Basaltic alluvium	976 830 146	30 28 27	Medium subangular blocky in the Ap horizon and coarse angular blocky in the Bss horizons/fine, common lime nodules	8.2–9.1	2–2.5, 100; 87 es–ev
Adulabazar[2] (Sodic Haplusterts) (Maharashtra)	Basaltic alluvium	876 755 121	30 28 26	Medium subangular blocky in the Ap horizon and coarse angular blocky in the Bss horizons/fine, few lime nodules	8.4–8.7	4–5, 100; 57 ev
Kasireddipalli[1] (Typic Pellusterts) (Andhra Pradesh)	Basaltic alluvium	760 582 178	28 27 25	Medium subangular blocky in the Ap horizon and coarse angular blocky and parallelepipeds in the Bss horizons/fine to medium, common lime nodules	8.6–9.4	2–3, 60; 40 es
Kagal Gomb[1] (Typic Chromusterts) (Karnataka)	Precambrian metamorphic rocks/sedimentary alluvium	762 579 183	24 24 27	Fine subangular blocky to granular in the Ap horizon and coarse wedge shaped sphenoids and angular blocky in the Bss horizons/fine, few to many lime nodules	8.5–9.3	5–7, 75; 50 e–es
Nimone[1] (Typic Chromusterts) (Maharashtra)	Basaltic alluvium	677 503 174	28 25 25	Coarse subangular blocky in the Ap horizon and coarse angular blocky in the Bss horizons/fine to coarse, few to many lime nodules	8.4–9.8	3–4, 60; 38 es–ev
Arid (MAR: 500–663 mm)						
Bellary[1] (Typic Pellusterts) (Karnataka)	Peninsular gneiss	518 501 17	30 28 27	Coarse subangular blocky in the Ap horizon and coarse angular blocky in the Bss horizons/fine to medium, few to many lime nodules	8.7–9.0	2–3, 100; 55 e–ev
Kovilpatti[1] (Typic Chromusterts) (Tamil Nadu)	Peninsular gneiss	659 464 195	28 28 28	Coarse subangular blocky in the Ap horizon and coarse angular blocky in the Bss horizons/fine to coarse, many lime nodules	7.6–8.0	3–4, 90; 52 e–ev
Achmatti[1] (Typic Pellusterts) (Karnataka)	Alluvium of Precambrian metamorphic rocks	663 430 233	26 24 28	Fine granular in the Ap horizon and coarse angular blocky and wedge shaped sphenoids in the Bss horizons/medium to coarse, common lime nodules	8.4–8.9	3, 100; 22 es–ev
Hungund[1] (Udic Chromusterts) (Karnataka)	Precambrian chlorite-schist	663 430 233	26 24 28	Fine granular in the Ap horizon and coarse angular blocky and wedge shaped sphenoids in the Bss horizons/medium to coarse, common to medium lime nodules	8.7–9.9	2–6.5, 80; 30 es–ev

Sources:
[1] Lal *et al.* (1994)
[2] Balpande *et al.* (1996)
[3] Gabhane (1996)
[4] Kadu (1997)
[5] Mandal *et al.* (1999), MAR: mean annual rainfall; MRw = mean rainfall wet months; MRd: mean rainfall, dry months
Wet months: June, July, August and September, except for Bellary (July, August, September and October) and Kovilpatti (April, September, October, November)
[6] MAT = mean annual temperature; MTw = mean temperature wet months; MTd = mean temperature dry months
[7] Described according to the Soil Survey Staff (1951)
[8] Indicates the depth of the first occurrence of slickensides
[9] e = slight; es = strong; ev = violent effervescence.

Table 2. Selected physical and chemical properties of Vertisols in subhumid, semi-arid and arid climates in India.

Horizon	Depth (cm)	pH (1:2) water	$CaCO_3$ <2 mm (% fine earth basis)	Carbonate clay <2 mm (% fine earth basis)	Particle-size distribution of <2 mm soil (% fine earth basis) Sand 2000–50 μm	Silt (50–2 μm)	Total clay (<2 μm)	Fine clay (<0.2 μm)	Exchangeable cations cmol (+) kg^{-1} Ca	Mg	Na	K	CEC cmol (+) kg^{-1}	Exch. Ca/Mg	ECP	EMP	ESP	HC mm/h
17* Arang soil: representative of Vertisols of subhumid, hot moist (MAR: 1300 mm)																		
Ap	0–17	8.2	Trace	Nil	6	41	53	28	23.2	9.6	0.6	0.3	37.4	2.42	62	26	2	6.0
A	17–41	8.3	Trace	Nil	6	40	54	27	21.2	11.4	0.6	0.3	39.1	1.86	54	29	2	6.0
Bw	41–65	8.4	Trace	Nil	5	45	50	33	20.0	15.0	0.7	0.3	37.4	1.33	53	40	2	5.0
Bss1	65–94	8.5	Trace	Tr	5	41	54	37	20.2	13.4	0.9	0.3	34.8	1.51	58	38	3	5.0
Bss2	94–123	8.6	0.5	1.8	6	43	51	38	20.2	12.6	1.2	0.3	34.8	1.60	58	36	3	4.0
Bss3	123–146	8.6	1.2	2.0	6	46	48	39	17.6	12.4	1.6	0.4	33.5	1.42	52	38	5	2.0
2: Aroli soil: representative of Vertisols of subhumid, hot dry (MAR: 1100 mm)																		
Ap	0–15	7.9	0.8	0.5	3	34	63	47	31.2	12.8	0.9	0.6	55.4	2.43	56	23	2	8.0
Bw1	15–30	8.1	0.7	0.8	3	35	62	47	33.2	15.0	0.9	0.6	55.1	2.21	60	27	2	6.0
Bw2	30–55	8.1	0.9	1.0	2	35	62	48	28.0	17.4	1.0	0.5	57.6	1.61	49	30	2	5.0
Bss1	55–80	8.2	1.3	0.9	2	35	63	45	25.4	19.6	1.3	0.6	57.1	1.29	44	34	2	4.0
Bss2	80–98	8.3	7.1	0.9	1	38	61	48	21.4	16.4	1.4	0.5	51.1	1.30	42	32	3	3.0
Bss3	98–116	8.7	7.5	0.6	1	33	66	38	24.4	14.0	3.5	0.6	50.0	1.74	49	29	7	1.0
Bss4	116–144	8.8	8.4	0.7	1	32	67	43	17.6	21.6	4.9	0.7	51.1	0.81	34	42	10	0.5
12: Hingna-Tamaswadi soil: representative of Vertisols of semi-arid, hot moist (MAR: 875 mm)																		
Ap	0–22	8.3	4.7	3.6	5	29	66	31	31.3	15.1	0.4	1.9	53.9	2.1	58	28	1	4.4
B	22–57	8.4	4.9	3.8	7	28	65	30	31.0	15.5	0.8	1.4	56.5	2.0	48	27	1	4.0
Bss1	57–75	8.4	4.3	4.2	6	25	69	34	14.6	24.5	1.3	1.2	53.9	0.6	27	45	2	4.2
Bss2	75–155	8.5	4.7	3.0	6	25	69	36	17.6	25.2	2.4	1.1	57.0	0.7	30	44	4	1.7
Bss3	155–162	8.6	4.3	3.5	7	25	68	37	13.3	32.4	3.6	1.2	53.9	0.4	25	60	7	0.8
8: Kasireddipalli soil: representative of Vertisols of semi-arid, hot moist (MAR: 760 mm)																		
Ap	0–20	8.6	5.3	2.7	21	25	54	37	30.0	10.0	1.0	0.5	54.0	3.00	55	18	2	4.0
Bw1	20–42	8.8	7.4	3.8	19	25	56	39	31.6	11.6	1.7	0.5	55.0	2.72	57	21	3	3.0
Bw2	42–65	9.0	7.0	3.2	15	22	63	44	26.6	12.6	5.2	0.6	56.5	2.11	47	22	9	0.7
Bss1	65–95	9.1	6.3	9.1	15	24	61	44	24.2	13.4	6.3	0.6	57.0	1.80	42	23	11	0.6
Bss2	95–132	9.2	6.2	6.0	9	19	72	52	21.0	15.8	9.4	0.7	56.6	1.33	37	28	17	0.3
Bss3	132–190	9.3	7.5	4.8	9	24	67	48	20.8	15.0	10.9	0.7	57.6	1.39	36	26	19	0.2
Bss4	190–210	9.4	8.0	4.3	11	24	65	48	19.4	14.8	10.7	0.6	57.6	1.31	34	26	19	0.1
14: Bellary soil: representative of Vertisols of arid, hot (MAR: 518 mm)																		
Ap	0–17	8.7	2.8	5.8	8	28	64	48	37.0	10.6	8.3	0.9	62.0	3.50	60	17	13	2.0
Bw1	17–55	8.8	2.0	5.5	9	17	74	56	32.6	9.8	9.8	0.7	67.4	3.33	48	14	14	0.8
Bss1	55–107	8.7	5.0	8.4	5	21	74	53	30.6	10.6	9.4	0.6	69.0	2.89	44	15	14	0.5
Bss2	107–141	9.0	12.0	14.8	4	12	84	64	37.8	11.4	16.7	0.8	65.2	3.31	58	17	26	0.5
BC	141–160	9.0	8.4	10.2	5	17	78	54	38.8	10.0	16.5	0.8	63.3	3.88	61	16	26	0.5

* Numbers indicate location of the soils in Figure 1.
ECP: exchangeable calcium percentage; EMP: exchangeable magnesium percentage; ESP: exchangeable sodium percentage
HC: hydraulic conductivity

$CaCO_3$ in Vertisols of semi-arid climate. Vertisols of this climatic region (700–1060 mm MAR) contained PC in all parts of the Kalmeshwar, Asra, Sarol, Hingna-Tamaswadi, Vihigaon, Godasgaon and Malegaon soils. The PC content varied however; it was up to 10% in Kalmeshwar soil and present in trace levels in the Khairi and Sarol soils. In all other soils it ranged from 1 to 4%. The PCs were dull white diffuse nodules of micrite crystals (Figure 3e) and found in close association with NPC. In general, they showed an increase with depth. In the Asra soils, 15–20% of the groundmass consisted of the accumulation of dense micrite crystals below 120 cm depth.

The NPCs occur throughout the soils as sub-rounded nodules coated with Fe-Mn oxides showing sharp boundaries with the matrix (Figure 3f) and range from 1 to 6%. These NPCs also showed features of dissolution although the extent was much less than for those of the sub-humid climatic region.

The PCs occur as diffuse dull white nodules of micrite in the Paral, Hingna-Tamaswadi and Kasireddipalli soils (Figure 3g) in areas of low rainfall of semi-arid climate (⩾700 mm) and their amount ranged from 3 to 4%. About 5–6% of NPCs occur throughout the depth of the Paral and Hingna-Tamaswadi soils but in the Kasireddipalli soils, the amount ranges from 10 to 20%. They share a sharp boundary with the matrix, are Fe-Mn coated and made up of dense sparite and microsparite (Figure 3h).

$CaCO_3$ in Vertisols of arid climate. In soils of arid climate (500–663 mm MAR), PCs occur as diffuse dull white nodules of micrite throughout the Bellary, Kovilpatti and Nimone soils (Figure 3i) and were found very close to NPC in their SCSs. The PC content is 2–3% at the surface which increases to 10–15% with depth in the Nimone soils.

The NPCs are found as sub-rounded nodules of microsparite crystals and range between 3 and 4%. These are coated with Fe and Mn and show very few dissolution features (Figure 3j) except in the Bellary soils where their amounts decrease from 10–15% in the surface horizons to 2–3% below 100 cm depth.

DISCUSSION

Factors in and processes of $CaCO_3$ formation in Vertisols

Vertisols of central, western and southern peninsular India contain both PC and NPC and the PCs are generally observed in close proximity to the NPCs. Our observations indicate that the distance could be ⩽3 μm. However, in soils of sub-humid climate (MAR = 1300 mm), the PC was generally not present in their SCSs, but was observed in abundance in the SCSs of semi-arid and arid climates. Dissolution of NPC was substantial in soils of sub-humid climate. In arid and semi-arid climates both NPC and PC show very little dissolution. The Vertisols of this part of the country have been reported to be polygenetic in nature and in the later phase of soil development, the rate of dissolution of minerals has been found to be minimal (Pal *et al.*, 2000b, 2001). The NPCs are generally coarse textured qualifying as microsparitic to sparitic in nature, whereas the PCs are mainly fine textured, *i.e.* micritic in nature. Sparitic NPCs are Fe-Mn coated, sub-rounded in shape and are in sharp contrast with the matrix. The PCs are dull white in color and have diffuse boundaries with the matrix.

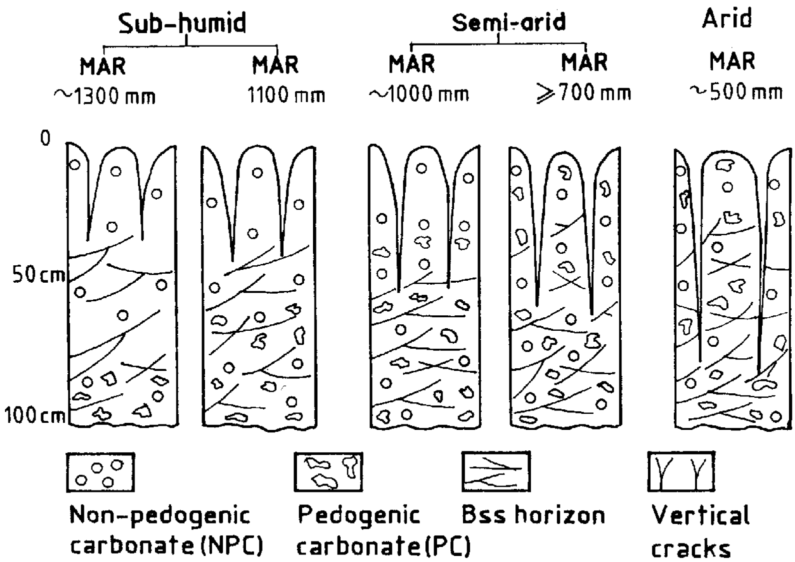

Figure 2. Schematic diagram showing the distribution of pedogenic carbonate (PC) and non-pedogenic carbonate (NPC) in Vertisols of different climatic regions; MAR: mean annual rainfall.

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Table 3. Mineral weathering and micromorphological properties of calcium carbonate.

Soil series	Skeletal grains (primary minerals of >20 µm size)	$CaCO_3$ Pedogenic (PC)	$CaCO_3$ Non-pedogenic (NPC)
1	2	3	4
Arang	Quartz (50–500 µm) Amount: 5–10% 1–2% polycrystalline showing fractures and linear striations of rod-shaped zircons	Nil up to 70 cm soil depth Beyond 70 cm PC in the groundmass as dense micritic crystals and as diffuse nodules Amount: 2–3% (Figure 3a)	Subrounded nodules of microsparite Amount: 1–3% Coated with Fe/Mn Large scale dissolution (Figure 3b)
Kheri	Quartz and feldspars Amount: 3–4% Feldspars: <1% Microcline (300–400 µm) Fresh/weakly altered Plagioclase (50–100 µm) Unaltered	Nil	Subrounded nodules of microsparite Amount: <1% Show dissolution features
Linga	Quartz, feldspars and basaltic rock fragments Amount: 4–5% Plagioclase Amount: <1% Unaltered	Diffuse dull white micrite nodules Amount: <1%	Fe/Mn coated nodules of microsparite and sparite Amount: 3–4% Show dissolution features
Marha	Quartz, feldspars and opaques Amount: 10–15% Feldspars: 1–2% Microcline Fresh/poorly weathered Plagioclase Weak alteration	Diffuse dull white nodules Micrite coatings on concretions Amount: 1–3%	Subrounded nodules of micrite and microsparite Amount: 5–10% Coated with Fe/Mn
Aroli	Quartz, feldspars and basaltic fragments Amount: 5–6% Plagioclase Amount: <1% Fresh/weakly altered	Nil up to 50 cm soil depth Amount: 1–2% Beyond 50 cm depth Diffuse nodules of micrite (Figure 3c)	Subrounded nodules of microsparite and sparite Amount: 5–10% (Figure 3d) Coated with Fe/Mn
Sarol	Quartz and feldspars (>50 µm) Amount: 10–15 % Plagioclase Amount: <1% Unaltered	Diffuse dull white nodules of micrite Amount: <1% below 100 cm soil depth	Subrounded nodules of micrite and microsparite Amount: 4–5% Coated with Fe/Mn
Asra	Quartz, rock fragments and opaques (>50 µm) Amount: 8–10 % Plagioclase Amount: <1% Unaltered	Up to 120 cm soil depth Diffuse dull white nodules of micrite Amount: 1–2% Beyond 120 cm soil depth Micritic groundmass Amount: 15–20%	Subrounded nodules of micrite and microsparite Amount: 5–6% Coated with Fe/Mn
Malegaon	Quartz (20–50 µm), plagioclase, heavy minerals and rock fragments Amount: 10–15% Plagioclase Amount: <1% Unaltered	Dull white diffuse nodules of micrite Amount: 1–2% (upper horizons) Amount: 3–4% (lower horizons) Dissolution features	Subrounded nodules of sparite and microsparite Amount: 1–2% Fe/Mn coatings Dissolution features
Hingna Tamaswadi	Quartz, feldspars, rock fragments and opaques Amount: 5–6% Plagioclase Amount: <1 % Unaltered	Soft dull white diffuse nodules of micrite Amount: 1–2%	Subrounded nodules of sparite and microsparite Amount: 5–10% Fe/Mn coatings
Paral	Quartz, feldspars, rock fragments and opaques Amount: 10–12% Plagioclase Amount: <15% Unaltered	Diffuse nodules of micrite Amount: 1–2%	Subrounded nodules Amount: 3–4% Fe/Mn coatings

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Table 3 (*contd*.)

Soil series	Skeletal grains (primary minerals of >20 µm size)	$CaCO_3$ Pedogenic (PC)	Non-pedogenic (NPC)
1	2	3	4
Khairi	Quartz, feldspars, rock fragments and opaques Amount: 10–15% Plagioclase Amount: 1–2% Fresh/weakly altered	Groundmass highly calcareous with dense micrite crystals Up to 100 cm Amount: <1% Below 145 cm Amount: 50%	Subrounded nodules Amount: 5–10% Fe/Mn coatings Dissolution features
Kalmeshwar	Quartz, rock fragments, plagioclase and opaques Amount: 15–20% Plagioclase in basaltic lithorelicts and in groundmass Amount: 1–2% Unaltered	Soft dull white diffuse nodules of micrite Amount: 8–10%	Subrounded nodules of sparite and microsparite Amount: 10–15%
Vihigaon	Quartz, feldspars, rock fragments and opaques Amount: 8–10% Plagioclase Amount: ~1% Unaltered	Diffuse dull white nodules of micrite Amount: 1–2%	Subrounded nodules of sparite and microsparite Amount: 3–4%
Godasgaon	Quartz, feldspars, rock fragments, and opaques Amount: 10–15% Plagioclase in rock fragments and groundmass Amount: 1–2% Unaltered	Groundmass highly calcareous due to dense micrite Up to 100 cm depth Amount: 1–2% Below 120 cm depth Amount: 50–60%	Large subrounded nodules of sparite and microsparite Amount: 5–6% Dissolution features
Thillory	Quartz, feldspars, basaltic rock fragments, and opaques Amount: 10–15% Plagioclase grains Amount: <1% Unaltered	Groundmass highly calcareous due to dense micrite Up to 100 cm depth Amount: 1–2% Below 120 cm depth Amount: 40–50%	Subrounded Fe/Mn coated nodules Amount: 5–6% Dissolution features
Adulabazar	Quartz, feldspars, basaltic rock fragments, and opaques Amount: 8–10% Plagioclase Amount: <1% Unaltered	Soft dull white diffuse nodules of micrite Up to 100 cm depth Amount: 1–2% Below 100 cm depth Amount: 5–6%	Sharp nodules of sparite and microsparite Amount: 3–4% Fe-Mn coated
Kasireddipalli	Quartz (fractured, mono and poly-crystalline), feldspars and opaques Amount: 15–20% K-feldspars (microcline) Amount: 2–3% Fresh to weakly weathered Plagioclase Amount: <1% Fresh to very weakly weathered	Dull white diffuse nodules of micrite Up to 60 cm depth Amount: traces Below 60 cm depth Amount: 3–4% (Figure 3g).	Subrounded sharp nodules (upper horizons) Amount: 15–20%
Kagal Gomb	Quartz, feldspars and opaques Amount: 2–5% Plagioclase Amount: <1% (40–50 µm) Fresh/weakly altered	Dull white diffuse nodules of micrite Amount: 10–15% Increase with depth	Dark subrounded nodules of sparite and microsparite Amount: 2–3%
Nimone	Quartz, feldspars, pyroxenes and opaques Plagioclase Amount: 3–4% Fresh/very weakly altered	Dense micrite groundmass Upper horizon Amount: 5–6% Lower horizon Amount: 10–15%	Subrounded nodules of microsparite Upper horizon Amount: 5–6% Lower horizon Amount: 2–3%
Bellary	Quartz (polycrystalline, mono-crystalline) Amount: 2–3% Plagioclase: 1–2% Weakly/moderately altered	Diffuse nodules of micrite Up to 100 cm depth Amount: 1–2% Below 100 cm depth Amount: 3–4%	Subrounded nodules of sparite and microsparite Amount: 5–6%

Table 3 (*contd.*)

Soil series 1	Skeletal grains (primary minerals of >20 µm size) 2	$CaCO_3$ Pedogenic (PC) 3	$CaCO_3$ Non-pedogenic (NPC) 4
Kovilpatti	Quartz and feldspars Amount: 4–5% Plagioclase Amount: 1–2% Weakly/moderately altered	Dull white diffuse nodules of micrite Amount: 1–2% Increases with depth	Subrounded sharp nodules of microsparite Upper horizon Amount: 5–6% Below 100 cm Amount: 3–4%
Achmatti	Quartz and feldspars Amount: 2–3% Plagioclase Amount: <1% Fresh/weakly altered	Dull white diffuse nodules of micrite Amount: 2–3% Increase with depth	Sharp subrounded nodules Amount: 3–4%
Hungund	Quartz (50–200 µm) (monocrystalline, polycrystalline) Amount: 8–10% Plagioclase: 1–2% Fresh/weakly altered	Dull white micritic nodules and groundmass Amount: 50%	Sharp subrounded nodules of sparite and microsparite Amount: 8–10%

The observed depth distribution of PC in Vertisols of sub-humid to arid climates supports the water loss through evapotranspiration and/or lowering of pCO_2 as the primary mechanism in the precipitation of PC (Arkley, 1963; Scholz, 1971; Rabenhorst *et al.*, 1984). Temperature as an additional factor plays an important role in controlling the water flow in the soil profile (Arkley, 1963).

The NPCs are common in Indian Vertisols (Pal *et al.*, 2000a). According to Brewer (1976), the observed forms of NPC are pedorelict features, formed elsewhere and then transported and deposited. Mermut and Dasog (1986) concluded that black soils with Fe-Mn-coated glaebules are older than those with white carbonate glaebules. Pal *et al.* (2000a,b, 2001) suggested that the Fe-Mn-coated glaebules were formed in a climate much wetter than the present one and are an integral part of the parent material of Vertisols and their intergrades. Petrographic examination showed 5–10% coarse fractions (>20 µm) wherein quartz and feldspars constitute 3–4% and 1–2%, respectively. Quartz and feldspar particles are angular to subangular in shape (Figure 4a). This suggests that the smectite-rich parent material for Vertisols was derived from basaltic rocks close to the site of deposition (Pal and Deshpande, 1987a).

The Ca^{2+} ions required for subsurface precipitation of PCs (as $CaCO_3$) might have emanated from the NPCs as shown by their dissolution features (Figure 3b). When

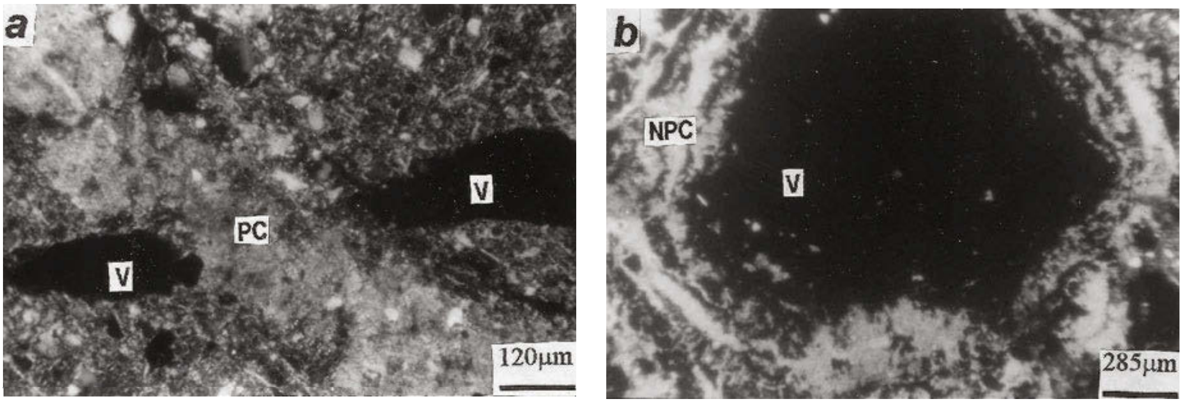
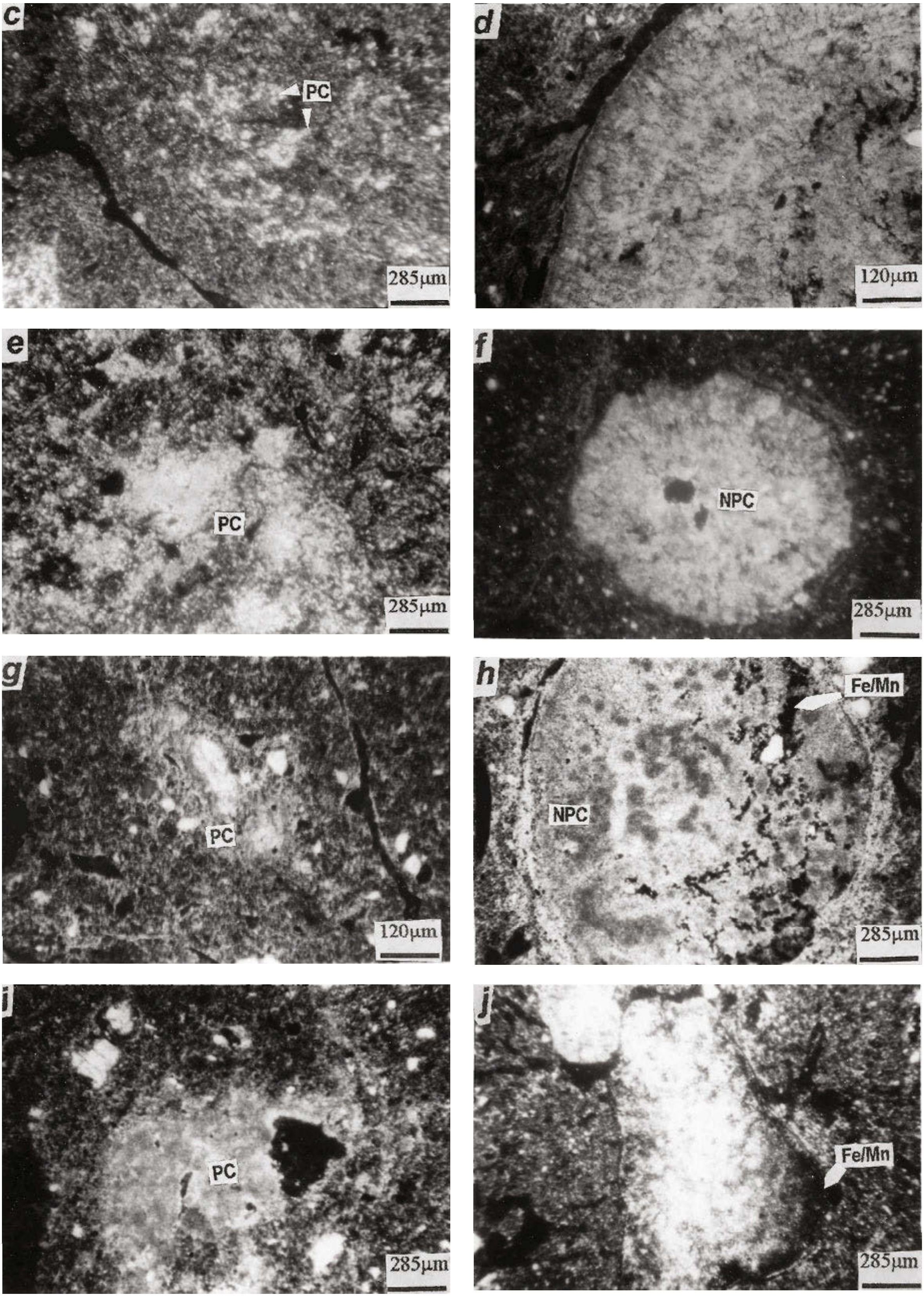


Figure 3 (a, b *above*, c–j *opposite*). Micromorphological features of $CaCO_3$ in the Vertisols, in cross-polarized light. (a) PC as diffuse nodules and dense aggregates of micrite crystals in the groundmass, Arang soils, 44–59 cm. (b) NPC showing dissolution and removal of $CaCO_3$ from the nodule, Arang soils, 44–59 cm. (c) PC occurring as diffuse aggregates of micrite and micro-sparite crystals in the groundmass, Aroli soils, 120–135 cm. (d) NPC showing coarsening of fabric due to recrystallization, Aroli soils, 120–135 cm. (e) PC as diffuse nodules of micrite, Kalmeshwar soils, 51–59 cm. (f) NPC as a rounded nodule with sharp boundary, Kalmeshwar soils, 51–59 cm. (g) PC as diffuse nodules and as micrite crystals in the groundmass, Kasireddipalli soils, 65–95 cm. (h) NPC showing dissolution, Kasireddipalli soils, 15–30 cm. (i) PC as a diffuse nodule of micrite and as coating along void, Bellary soils, 20–50 cm. (j) NPC showing sharp boundary and Fe-Mn coating, Bellary soils, 20–50 cm. V = Void, PC = pedogenic carbonates, NPC = non-pedogenic carbonates, Fe/Mn = Fe-Mn coatings.



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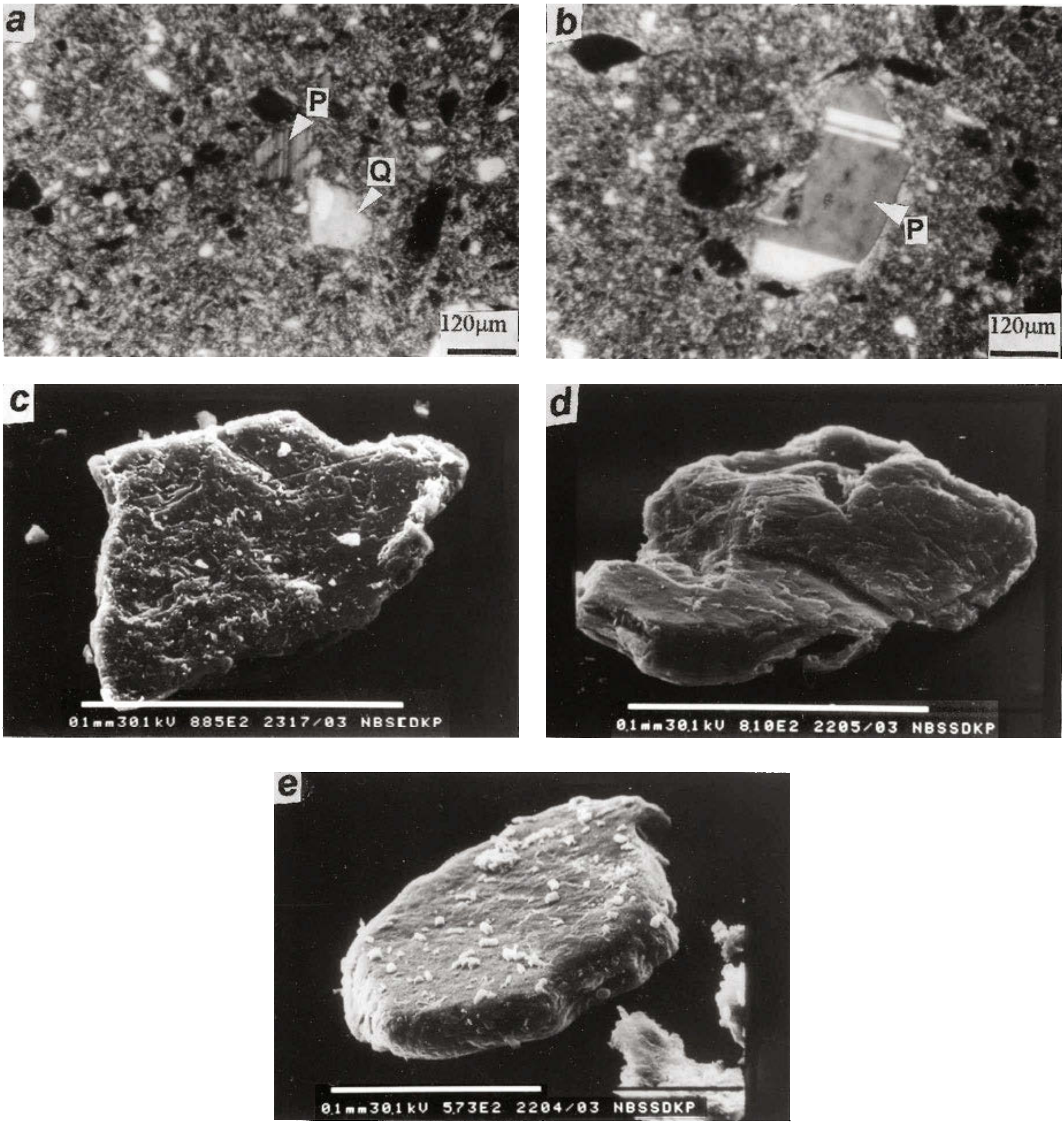

Figure 4. Weathering features of different minerals: (a) subangular quartz (Q) and plagioclase (P) grains in the groundmass. Plagioclase grains do not show substantial alteration, Kheri soils, 94–109 cm. (b) Fresh to very weakly-altered plagioclase grain with few etch pits on the surface, Linga soils, 40–67 cm. (c) SEM photograph showing weakly-altered plagioclase marked by etch pits on the surface, Khairi soils, 13–32 cm. (d) SEM photograph showing unaltered biotite mica, Khairi soils, 32–53 cm. (e) SEM photograph showing unweathered muscovite mica, Khairi soils, 32–53 cm.

the Ca^{2+} ions could not be transferred further down the soil profile due to lack of moisture (aridity/semi-aridity), the fabric of the NPC became coarser due to recrystallization *in situ* (Figure 3d). This suggests that the NPCs may be a major source of Ca^{2+} ions in soil solution. Petrographic and SEM examinations of plagioclase and micas indicated that both the minerals are only slightly altered and lack etch pits and/or dissolution pits (Table 3; Figure 4a–e). The plagioclase feldspars are, thus, not the primary source of Ca^{2+} ions in soil solution. Almost uniform depth distribution of the CaO and Na_2O contents of the sand and silt fractions of representative sodic and non-sodic Vertisols (Figure 5) further supports this observation. It seems, therefore, that chemical weathering of primary minerals has not been substantial during the Vertisol formation. This could also be the reason for less transformation of smectites in Vertisols of sub-humid climate. The fine clay smectite of Vertisols

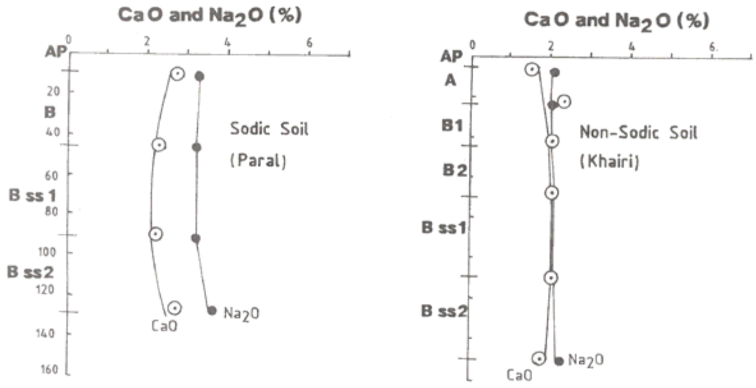

Figure 5. CaO and Na_2O contents of sand and silt (500–2 μm) fractions of representative sodic and non-sodic Vertisols.

under study is generally reasonably well crystallized as it yields a sharp basal reflection on glycolation and shows a regular series of higher-order reflections, though these are short and broad (Figure 6). However, hydroxy interlayering in smectite interlayers was observed in soil clays of Bellary, Kovilpatti and Nimone due to high pH conditions (Jackson, 1963). The preservation of smectite and its crystallinity could be achieved due to aggradation processes which took place in a nearly non-leaching environment of sub-humid to arid climates.

Vertisols of sub-humid climate are dominated by Ca^{2+} ions on their exchange complex throughout the depth. However, in subsoils of Vertisols of arid and semi-arid climates, the Mg^{2+} ion dominates in the exchange complex. These are more calcareous than the former soils and are sodic (ESP $\geqslant 5$, Balpande *et al.*,

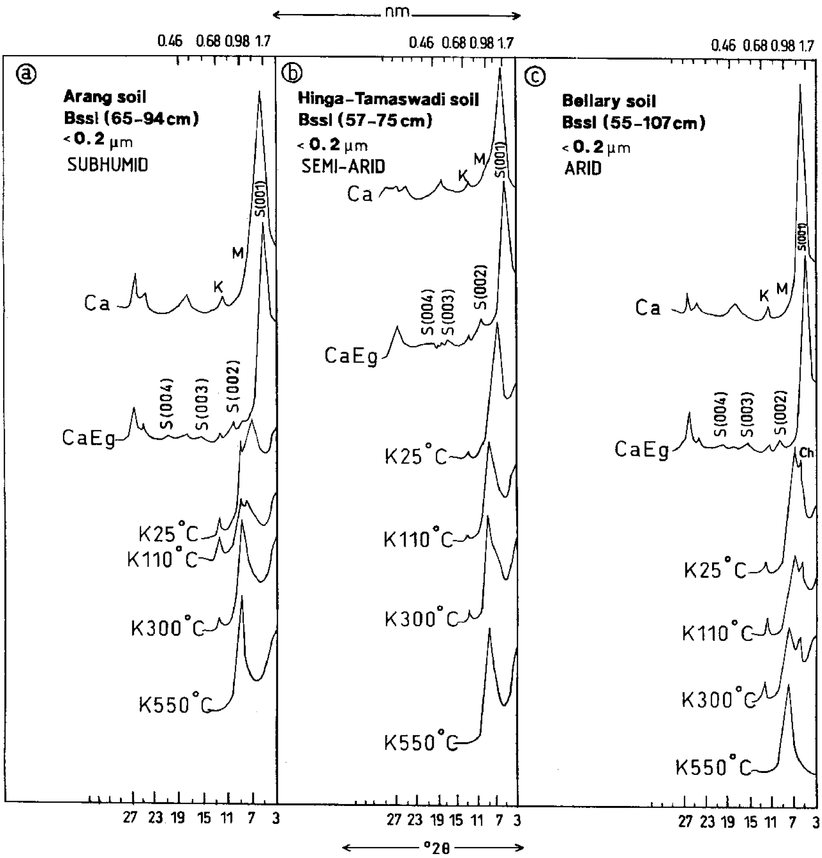

Figure 6. Representative XRD patterns of fine clay fractions of Vertisols from sub-humid, semi-arid and arid climates of Peninsular India. S = smectite; M = mica; K = kaolin; Ch = chlorite; Ca = Ca-saturated; Ca-Eg = Ca-saturated and glycolated; K25/100/300/500 = K saturated and heated to 25, 110, 300 or 550°C.

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1996) in the subsoil (Table 2). It appears that maintenance of the higher Ca/Mg ratio (~2, Pal *et al*., 2000a) in the soil solution and on the exchange site becomes difficult because Ca^{2+} ions are precipitated as $CaCO_3$ during high evaporative demands for soil water. This results in an increase in EMP and ESP and concomitant decrease in ECP down the profile (Table 2).

More rainfall and better drainage cause downward movement of soluble bicarbonates which become precipitated as carbonates in the subsurface horizons. This observation is supported by the overall increase of clay carbonate (on a fine earth basis) with depth (Table 2). More rainfall (MAR = 1100–1300 mm) must have resulted in greater dissolution of NPC causing an increase in Ca^{2+} ion concentration in soil solution and on exchange sites, thus improving the hydraulic properties of soils (Table 2). Due to the better hydraulic properties (HC $\geqslant$5 mm/h), the Vertisols of sub-humid climates do not generally contain PC. In soils of arid and semi-arid climates, due to the accelerated rate of formation and accumulation of PC, the subsoils become sodic and thus their hydraulic properties are impaired (Table 2). The initial impairment of the percolative moisture regime in the subsoils results eventually in a soil system where gains exceed losses, and this self-terminating process (Yaalon, 1983) subsequently leads to the development of sodic soils where ESP decreases with depth (Figure 7). This has been demonstrated through the formation of the Natrustalfs of the Indo-Gangetic alluvial plains (Pal *et al*., 2000a). The formation of PC can, therefore, be considered as a basic and natural process of soil degradation for the development of calcareous sodic soils (Pal *et al*., 2000a).

It is now understood that the chemical properties of Vertisols are governed mainly by the dissolution of NPC. This dissolution process maintains a ready supply of Ca^{2+} ions which are precipitated as $CaCO_3$ (PC) to modify further the physical properties of these soils. This clearly indicates that the weathering of primary minerals contributes very little not only towards the formation of smectites but also in terms of the chemical and physical processes of their formation. In thermodynamics parlance, such Vertisols may serve as an example of positive entropy change in the field of naturally occurring soil systems (Smeck *et al*., 1983).

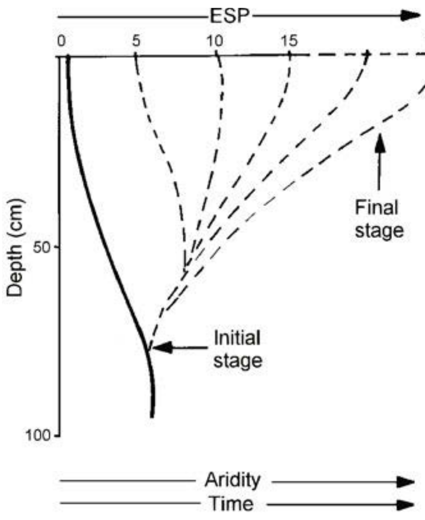

Figure 7. A projected view of the progressive development of sodicity in Vertisols with depth in aridic soil environment.

Management of calcareous Vertisols

Both rainy- and post-rainy-season crops perform better in Vertisols of the sub-humid climate compared to their performance in the arid and semi-arid ecosystems (NBSS&LUP-ICRISAT, 1991). This has been possible because the SCSs of Vertisols of the sub-humid climate are, in general, free from PC and sodicity. Additionally, due to dissolution of NPC, the soils are enriched with Ca^{2+} ions. This ensures better drainage and available soil water content during cropping seasons. The poor crop performance in Vertisols of arid and semi-arid climates is a continuation of the natural degradation process in terms of the formation of PC and the concomitant development of subsoil sodicity (Balpande *et al*., 1997; Pal *et al*., 2000a,b, 2001). Due to the large amount of smectite (491 g kg^{-1} soil) in SCS of the Vertisols under study, an ESP of 5 causes sufficient reduction in hydraulic conductivity to impair drainage and soil-water storage for crop growth (Pal *et al*., 2000b, 2001). Displacement of exchangeable Na^+ ions by Ca^{2+} ions from PC is not feasible at pH >8.0 (Pal *et al*., 2000a). However, it can be effected indirectly by surface application of gypsum (Gupta and Abrol, 1990) as stated below.

Calcium ions released through the dissolution of gypsum prevent clay dispersion and hydraulic conductivity decline, both at the surface and within the soil profile (Shainberg *et al*., 1989; Gupta and Abrol, 1990). Further, cultivation of crops may create an environment for the dissolution of both NPC and PC by dissolved CO_2 after the establishment of crops. The improvement in physical properties of soils may thus restore the productivity of calcareous sodic Vertisols of arid and semi-arid climates.

CONCLUSIONS

The results of the present study indicate that the NPC is an integral component of the parent material of Vertisols. The dissolution of the NPC to release Ca^{2+} ions and their recrystallization as $CaCO_3$ (PC) is the prime chemical reaction of the pedogenesis of these Vertisols. This reaction modifies pH, exchangeable Ca and Mg, and induces soil sodicity and hydroxy interlayering in the smectite interlayers. The observed petrographic features of $CaCO_3$ and lack of alteration in plagioclase and micas validate the hypothesis that the formation of Vertisols reflects a positive entropy change (Smeck *et al.*, 1983).

The established cause-effect relationship between the process of formation of $CaCO_3$ of pedogenic and non-pedogenic origin, and the change in pedoenvironment with respect to the exchangeable cations (Ca, Mg and Na) is likely to help provide suitable methods to rehabilitate sodic Vertisols and also to maintain the productivity of non-sodic Vertisols of India as well as for similar soils occurring elsewhere.

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