# Soil quality and fibrous mineral in black soils of Maharashtra

# T. Bhattacharyya<sup>1,2,\*</sup>, S. K. Ray<sup>1</sup>, P. Chandran<sup>1</sup>, K. Karthikeyan<sup>1</sup> and D. K. Pal<sup>1</sup>

<sup>1</sup>Division of Soil Resources Studies, ICAR-National Bureau of Soil Survey and Land Use Planning, Amravati Road, Nagpur 440 010, India <sup>2</sup>Present address: Dr Balasaheb Sawant Konkan Krishi Vidyapeeth, Dapoli 415 712, India

There are many reports on soil parameters that have both yield-reducing and yield-favouring potential. However, only a few are available on the index soil properties of fibrous minerals containing soils on crop vields in the semi-arid tropical (SAT) regions. These minerals in soils are mostly palygorskite and sepiolite. In the present study, only the palygorskite mineral in black soils (cracking clay soils), its formation and probable influence on soil quality is addressed. The present study was also undertaken to indicate a possible genesis of palygorskite in Indian black soils with and without soil modifiers (Ca-zeolites and gypsum) supporting both rainfed and irrigated agriculture in SAT environments. Palygorskite is absent in aridic/gypsic/sodic intergrades of black soils (Haplusterts), which might indicate non-interference of soil modifiers in its formation. Palygorskite is present only in sodic black soils (Calciusterts) in Maharashtra and parts of central and western India that contain no soil modifiers, and are under both rainfed and irrigated agricultural systems. The severe impairment of hydraulic properties of palygorskite containing naturally degraded black soils warrants a new research initiative for soils containing fibrous minerals.

**Keywords.** Fibrous minerals, palygorskite, black soils, soil quality.

THE beneficial effects of clay minerals on human health include their use in pharmaceutical formulations, spas and aesthetic medicine. Their therapeutic action as active ingredients in pharmaceutical formulations is known. Although clay minerals have been found to be beneficial for plants and animals, there are cases where it has been proved otherwise. For example, fibrous minerals in soil clays can be hazardous to human health. Palygorskite, a type of fibrous mineral, is also an active agent of such hazards. Here we discuss the presence of palygorskite mineral that impairs soil physical properties to affect soil quality.

Among the fibrous minerals, structurally important element in palygorskite is the amphibole (double silica chain) oriented with its long direction parallel to the c-axis. The apexes of the tetrahedrons in successive chains point in opposite directions. Thus, palygorskite mineral is structurally distinct from the typical 1:1 and 2:1 layer structure and often found in soils of arid and semi-arid environments. It has fibrous morphology in contrast to the platy morphology of most other clay minerals. In an early review of the mineralogy of the Indian soils<sup>1</sup>, the presence of palygorskite in some western desert soils of India (Rajasthan) was reported. In recent years this mineral is identified in black soils developed in the alluvium of the weathering Deccan basalt in the central and western peninsular India in the states of Maharashtra<sup>2-4</sup> and Gujarat<sup>5</sup> under both rainfed and irrigated agriculture. This mineral is also found in Maharashtra and Gujarat<sup>2,5</sup> and also in materials derived from red clay boles in Maharashtra<sup>4</sup>.

Many reviews on the occurrence of palygorskite in soils from the semi-arid tropical (SAT) regions of the world are available<sup>6-8</sup>. Some authors have suggested that the soil palygorskite is pedogenic<sup>6,9,10</sup>, whereas others have reported this mineral as inherited from the soil parent materials<sup>11,12</sup>. In addition, marine geologic deposits (late Cretaceous and Tertiary) are reported as their parent materials<sup>13,14</sup>. Palygorskite is, on many occasions, found in association with smectite and its formation is often thought to be at the expense of the latter 15,16. Its formation is also suggested through an intense dissolution process of smectite that resulted in an increase in Al and Fe ions and Mg/Ca ratio favouring the formation 17,18 and an internal adjustment in the structure of smectite<sup>18</sup>. Studies in North Africa (Morocco, Tunisia, Libya and Egypt) and the Middle East (Syria, Lebanon, Iraq, Iran and Israel) indicate that under dry conditions pedological formation of palygorskite is common in the presence of calcium carbonate. The same holds good for Australia, Senegal and Kenya<sup>19</sup>. A recent study indicates its contemporary pedogenic formation in irrigation-induced saline-sodic black soils of western peninsular India in Maharashtra<sup>3</sup>.

Palygorskite is reported to be stable at very high Si and Mg level when the pH was approximately 6.0. Stable palygorskite can form at either low Mg or high Si concentrations or at high Mg and relatively low Si concentrations at pH  $\sim$ 9 (refs 14, 20). The enrichment of Ca<sup>2+</sup> ions both in the exchange and solution is likely to prevent the

<sup>\*</sup>For correspondence. (e-mail: tapas11156@yahoo.com)

development of higher Mg/Ca ratio required for the formation of palygorskite<sup>18</sup>.

Very little is known about the effect of palygorskite on soil properties, viz. hydraulic properties of black soils<sup>7</sup>. Palygorskite releases Mg<sup>2+</sup> ions when soils are irrigated, resulting in dispersion of fine particles rendering soils poorly drained<sup>21</sup>. This assumes importance in palygorskite-dominant soils of dry areas which require irrigation for growing crops. In view of its diverse genetic pathways, the present study was undertaken to follow the extent of presence of this mineral in Indian black soils with and without soil modifiers (Ca-zeolites and gypsum)<sup>22,23</sup> and also to suggest a possible pathway for the formation of palygorskite in SAT black soils. We also assessed the role of palygorskite minerals in influencing soil properties.

### Materials and methods

A total of seven benchmark black soils (cracking clay soils) from SAT environment (in sub-humid moist, semi-arid dry and arid dry bio-climates) of Maharashtra (P1, P5, and P6), Gujarat (P2, P7), Tamil Nadu (P3) and Andhra Pradesh (P4) were selected for the present study (Table 1). Among these highly smectitic soils, two are under rainfed agriculture systems (P3, P5) and the other five are under irrigated agriculture (P1, P2, P4, P6 and P7). Soils of P5 and P7 contain palygorskite mineral. Five black soils (P1, P2, P3, P5 and P6) contain Ca-zeolite but no palygorskite, although they have been under irrigated agriculture for the last 2–3 decades. Soils in P4 contain both Ca-zeolite and gypsum.

The majority of black soils in Maharashtra, Andhra Pradesh, Tamil Nadu and Gujarat occur in the lower physiographic positions, i.e. the lower piedmont plains or valleys or in micro depressions<sup>22,24,25</sup> and are developed in the same parent material, i.e. mainly in the alluvium of weathering Deccan basalt during the Holocene<sup>25,26</sup>. Macro-morphology of seven benchmark black soils was examined in the field following standard procedure<sup>27</sup>. The particle-size distribution was determined by the international pipette method after removal of organic matter, CaCO<sub>3</sub> and Fe-oxides. Sand (2000–50 µm), silt (50– 2  $\mu$ m), total clay (<2  $\mu$ m) and fine clay (<0.2  $\mu$ m) fractions were separated according to the size segregation procedure of Jackson<sup>28</sup>. CaCO<sub>3</sub> was determined by rapid titration<sup>29</sup>. After equilibrating the soil with distilled water in the ratio of 1:2 with occasional stirring for 30 min, pH of the soil suspension was measured<sup>30</sup>. Cation exchange capacity (CEC) was determined by saturating the soil with 1 N sodium acetate (pH 8.2) and exchanging the Na<sup>+</sup> ions in 1 N ammonium acetate (pH 7)<sup>30</sup>. The Na<sup>+</sup> ions were measured using an atomic absorption spectro-photometer to determine CEC. Exchangeable Ca and Mg were determined following the 1 N NaCl solution extraction method<sup>29</sup>. The saturated hydraulic conductivity (sHC) was determined using a constant head permeameter<sup>30</sup>. The electrical conductivity and soluble cations and anions of the saturation extract (ECe) were determined following the standard methods<sup>30</sup>. Mineralogy of the silt and clay fractions was carried out by X-ray diffraction (XRD) of oriented aggregates saturated with Ca and K using a Phillips diffractometer with Ni-filtered CuK $\alpha$  at a scanning speed of 1°2 $\theta$ /min. The minerals were identified using the diagnostic methods of Singer<sup>14</sup>, Jackson<sup>28</sup> and Brown<sup>31</sup>. Semi-quantitative estimates of clay minerals in the silt and clay fractions were carried out following the method of Gjems<sup>32</sup>.

Sand-sized particles were chosen after identification under a petrographic microscope. These sand particles were broken into two halves and mounted on an aluminum stud with the help of double-sided carbon tape (used to fix the samples on the stud) in such a way that the freshly broken side faced upwards. Then the image was viewed through a scanning electron microscope (SEM; FEI Inspect S model D8858, USA).

#### Results

The selected black soils are clayey (containing 30% to nearly 73% clay in <2 µm fractions), slightly (P4), moderately (P1, P2, P3, P6 and P7) and highly alkaline (P5) in reaction, and moderately (P2 and P4) to highly (P1, P3, P5, P6 and P7) calcareous. Soils have ECe < 4 dSm<sup>-1</sup>, indicating their non-saline character even though some soils are under irrigation for the last 1-2 decades (P1, P2, P4, P6 and P7). Some soils are sodic (P2, P3, P5 and P7) according to the criteria of the United States Salinity Laboratory<sup>30</sup> and some are non-sodic (P1 and P6). In Pahur (P2) soils, sodicity developed (pH > 8.5, exchangeable sodium percentage (ESP)  $\leq 15$  and ECe  $\leq 4$  dS m<sup>-1</sup>) due to the use of irrigation water but they were not salinesodic<sup>30</sup> unlike few black soils that have been reported to be saline-sodic in Maharashtra due to irrigation<sup>3</sup>. The soils have high (P1, P2, P6 and P7) to very high (P3, P4 and P5) CEC and high base saturation. Among the extractable bases, Ca and Mg dominate the exchange sites and Mg/Ca ratio (of P1-P5) is <1, except in two pedons (P6 and P7) where it gradually increased to >1.0 with depth (Table 2).

Black soils in Maharashtra, Andhra Pradesh, Tamil Nadu and Gujarat contain sand and silt-sized (2–0.05 mm, 0.05–0.002 mm) Ca-zeolites and gypsum (only in P4) as detected by XRD method and in micro-morphological thin section studies <sup>5</sup>. In the present study, some soils (P1, P2, P3, P4 and P6) contain silt-sized zeolites. The peak of Ca-zeolites gradually loses its intensity at 0.9 nm on heating to 110°C and 300°C and finally disappears at 550°C. This suggests that these zeolites belong to Si-poor heulandite type<sup>31</sup>. Similar zeolites have been reported earlier from Indian soils<sup>22,23</sup>.

Table 1. Soil site characteristics of the selected black soils in India

		1.0	TABLE 1. SOIL SILE CHAIACICH SILES OF LIFE SCIENCE DIACK SOILS III HILLIA	elected plack soms in mara		
	Soil series		Dorant motorial	Bioclimatic		Soil
Pedon no.	(district/state)	Geology	(physiography)	(MAR, MAT)	Land use	1:2) water
Zeolitic an	Zeolitic and/or gypsiferous soils					
P1	Nimone (Aridic Haplusterts;	Deccan basalt	Basaltic Alluvium (Upper	Arid, dry (520, 25.6)	Agriculture (cotton-wheat/chickpea,	8.4-8.5
	Ahmednagar, Maharashtra)		Maharashtra Deccan Plateau)		sugarcane)	
P2	Semla (Aridic Haplusterts;	Deccan basalt	Basaltic Alluvium (West	Semi-arid (dry)	Agriculture (groundnut/cotton, fodder	7.8 - 8.0
	Rajkot, Gujarat)		coast-Kathiawar Peninsula)	(635, 29.4)	jower, chickpea, wheat)	
P3	Kovilpatti (Gypsic	Deccan basalt/	Mixed Alluvium and granite	Semi-arid (dry)	Agriculture (sorghum/cotton: 2 year	7.4–8.0
	Haplusterts; Thoothokudi,	Peninsular	gneiss (riverine landform)	(660, 29.4)	rotation; sunflower, soyabean,	
	Tamil Nadu)	Gneiss			blackgram)	
P4	Sollapuram (Sodic	Deccan basalt/	Basaltic Alluvium (South	Semi-arid (dry)	Gram, sorghum, coriander	8.0 - 8.6
	Haplusterts; Ananthapur,	Peninsular	Deccan Plateau)	(583, 27.6)		
	Andhra Pradesh)	Gneiss				
P5	Pahur (sub-humid moist;	Deccan basalt	Basaltic Alluvium	Sub-humid (moist)	Cotton + pigeon pea, soybean, sugarcane	8.0-8.9
	Sodic Haplusterts;			(1134, 26.9)		
	Yeotmal, Maharashtra)					
P6	Kesapur (Sodic Haplusterts;	Deccan basalt	Basaltic Alluvium	Semi-arid (dry)	Agriculture (millets)	8.5-9.4
	Hingoli, Maharashtra)			(924, 26.3)		
Non-zeolit	Non-zeolitic and/or non-gypsiferous soils					
P7	Sokhda (Calcic Haplusterts;	Deccan basalt	Basaltic Alluvium	Arid, dry (533, 26.7)	Agriculture (cotton-bajra/linseed)	8.2-8.8
	(Rajkot, Gujarat)		(West Coast-Kathiawar			
			· curricata)			

\*Soil classification according to Soil Survey Staff<sup>63</sup> and Velayutham et al. <sup>54</sup>; MAR, Mean annual rainfall (mm); MAT, Mean annual temperature (°C).

Table 2. Selected properties of black soil

			ranie 2.		ned propert	selected properties of plack soft	1100						
			i							i		Mg/C	Mg/Ca ratio
Depth (cm)	Horizon	Total clay (<2 µm)	Fine clay (<0.2 µm)	pH (water)	ECe (dSm <sup>-1</sup> )	BD Mg m <sup>-3</sup>	sHC cm h <sup>-1</sup>	0C (%)	CaCO <sub>3</sub> (%)	Clay CEC cmol(+) kg <sup>-1</sup>	ESP	Extrac- table	Saturated extract
Zeolitized and/or gypsiferous soils													
Nimone, Aridic Haplusterts (P1)													
0-13	Ap	99	46	8.4	0.47	1.4	5.6	0.88	14	92	2	0.4	0.7
13–38	Bw1	89	49	8.4	0.53	1.4	2.0	89.0	14	72	2	9.4	0.5
38–55	Bw2	99	47	8.5	0.73	1.4	1.5	0.64	16	74	9	9.0	9.0
55–94	Bss1	69	50	85	1.74	1.3	1.5	0.63	14	70	6	9.0	1.0
94–128	Bss2	71	52	8.5	0.83	1.4	1.5	0.51	16	89	Ξ	0.7	6.0
128-150	BC	70	53	8.5	0.78	1.3	2.8	0.36	16	61	Π	0.5	6.0
Semla, Aridic Haplusterts (P2)													
0-17	Ap	35	16	7.8	0.4	1.4	2.3	0.83	15	141	-	0.4	1.2
17–42	Bw1	43	19	7.8	0.4	1.4	4.2	99.0	18	115	7	0.5	8.0
42–57	Bw2	50	25	7.9	1.4	1.4	2.1	89.0	19	106	5	0.7	1.4
57–86	Bss1	50	29	7.9	0.7	1.4	1.7	0.48	14	96	4	0.5	8.0
86–115	Bss2	49	24	7.9	1.0	1.7	3.2	0.61	17	106	9	0.7	1.0
115-144	Bsss3	48	28	7.9	1.2	1.5	6.0	0.54	18	86	3	9.0	6.0
144–155	BC	34	13	8.0	pu	1.5	1.2	0.23	23	111	8	1.0	pu
Kovilpatty, Gypsic Haplusterts (P3)													
9-0	Ap1	99	32	8.0	0.2	1:1	1.9	0.34	5	108	-	0.2	1.1
6-20	Ap2	62	44	8.0	0.3	1:1	2.2	0.37	4	92	-	0.3	0.3
20-41	Bw1	65	46	8.0	0.5	1.4	4.4	0.35	5	100	-	0.3	0.7
41–74	Bw2	99	50	8.0	0.4	1.4	3.0	0.35	∞	96	_	0.3	0.5
74–104	Bss1	29	51	7.9	0.2	1.4	3.7	0.30	12	107	П	0.2	9.0
104–128	Bss2	72	09	7.9	9.0	1.4	3.4	0.28	13	06	-	0.2	0.5
128-140	BC	70	55	7.4	2.7	1	3.2	0.28	16	77	1.8	0.2	1.2
140+	C	25	10	7.5	I	L	0.1	0.12	17	132	$\overline{\lor}$	0.2	pu
Sollapuram, Sodic Haplusterts (P4)													
0-14	Ap	65	41	8.4	0.44	1.4	0.5	0.61	18	91	8	0.3	1.1
14-40	Bw1	63	48	8.4	0.41	1.4	0.2	0.56	16	92	13	0.4	2.1
40–63	Bw2	64	55	9.8	0.05	1.3	0.1	0.49	16	102	14	0.4	8.0
63–102	Bss1	29	57	9.8	0.20	1.2	0.1	0.47	19	94	18	9.0	0.7
102-129	Bss2	72	63	8.2	3.78	1.4	0.2	0.42	18	91	22	0.5	0.7
129–150	Bk	72	61	7.9	6.70	1	0.3	0.29	23	96	22	0.4	6.0

Table 2. (Contd)

(came)													
		F	į							5		Mg/Ca ratio	ratio
Denth (cm)	Horizon		clay	pH (water)	ECe	BD Mg m <sup>-3</sup>	sHC	0C	CaCO <sub>3</sub>	CEC CEC $^{cmol(+)}$ $^{k}\sigma^{-1}$	п С	Extrac-	Saturated
Deptii (ciii)	110112011	(mm 7/)	(mm 2.0~)	(water)	( IIIch)	INI S III		(0/)	(0/)	CIIIOI(T) NB		table	callact
Pahur, Sodic Haplusterts (P5)													
0-19	Ap	09	30	8.0	0.52	1.5	1.0	6.0	5.1	80	1.6	0.5	0.7
19–40	Bw1	62	40	8.4	0.34	1.5	8.0	9.0	3.0	87	3.1	9.0	8.0
40–78	Bss1	61	42	9.8	0.35	1.6	0.3	9.0	2.4	98	10.0	0.5	1.0
78–122	Bss2	61	37	8.7	0.73	1.6	0.3	0.5	3.7	82	0.5	0.7	9.0
122-150	Bss3	29	47	8.9	0.75	1.6	3.0	9.0	2.3	84	0.5	9.0	9.0
Kesapur, Sodic Haplusterts (P6)													
0-14	Ap	99	46	9.1	0.44	1.5	80.0	0.2	12.0	84	16	8.0	pu
14–29	Bw1	64	34	9.1	99.0	1.3	0.03	0.1	11.8	87	26	1.0	pu
29–49	Bw2	59	33	9.4	0.78	1.3	0.04	0.1	14.4	102	30	1.2	pu
49–71	Bw3	51	25	9.3	0.88	1.3	0.02	0.1	16.6	124	37	1.6	pu
71–103	Bss1	53	29	0.6	1.22	1.3	0.04	0.05	15.9	119	37	1.5	pu
103-150	Bss2	47	21	8.5	1.00	1.4	0.22	0.05	10.7	136	36	1.2	pu
Non-zeolitized and/or non-gypsiferous soils													
Sokhda, Calcic Haplusterts (P7)													
0-11	Ap	31	13	8.2	0.4	1.4	3.2	0.48	22	88	4	0.5	9.0
11–37	Bw1	30	13	8.4	0.4	1.4	3.0	0.46	21	06	4	0.4	0.7
37–63	Bw2	40	18	8.7	0.5	1.5	1.5	0.45	21	71	6	0.7	1.0
63–98	Bss1	41	19	8.8	0.7	1.7	0.4	0.43	22	71	16	1.0	1.0
98–145	Bss2	43	20	9.8	4.2	1.6	0.2	0.25	22	71	28	1.2	0.2
145-160	BC	20	33	8.5	0.4	1.6	2.1	0.21	12	64	31	1.2	9.0

ECe, Electrical conductivity of saturation extract; BD, Bulk density; sHC, Saturated hydraulic conductivity; OC, Organic carbon; Clay CEC, Clay cation exchange capacity; nd, Not done.

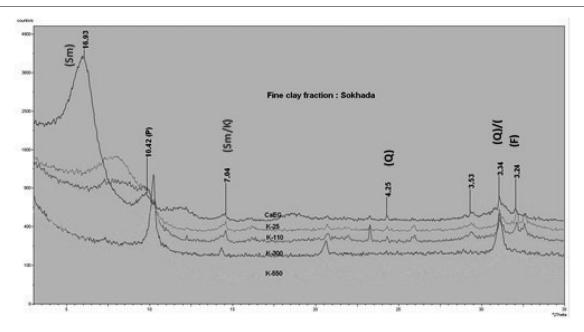
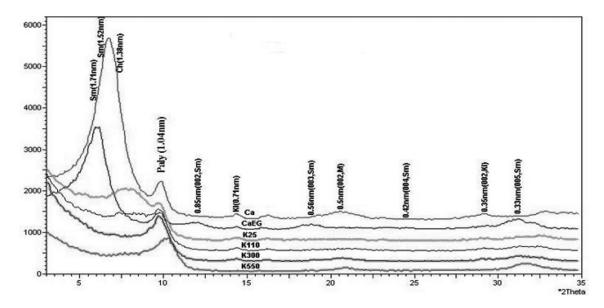


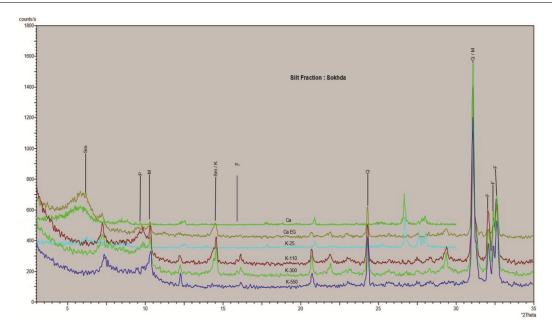
Figure 1. X-ray diffractograms of representative horizons of fine clay fractions (<0.2 μm) of Sokhda (P7) black soils (98–145 cm depth) (Sm, smectite; P, Palygorskite; Sm/K; Smectite–Kaolinite interstratified minerals; Q, Quartz; F, Feldspar).



**Figure 2.** Representative X-ray diffraction patterns of total clay fractions of Sokhda soils (P7) black soils of arid dry climate (98–145 cm depth); Ca, Ca-saturated; CaEG, Ca-saturated plus glycol vapour; K25/110/300/550, K-saturated and heated to 25°C, 110°C, 300°C and 550°C. Sm, Smectite; Ch, Chlorite; Paly, Palygorskite; Kl, Kaolin.

The fine clay fractions of these soils (P1, P2, P3, P4 and P6) contain low charge smectite (LCS) as dominant mineral (>90%) with very small amounts of mica and kaolin; no palygorskite was detected. In contrast, the non-zeolitic/non-gypsiferrous black soils (P5 and P7) contain silt and clay-sized palygorskite. Fine clay fractions also contain palygorskite along with dominant amount of LCS (Figure 1). Palygorskite peaks at 1.05, 0.637, 0.448 and 0.366 nm were identified. Although the heating of paly-

gorskite yields a loss of water and causes an initial decrease in the spacing of 011 reflections from 1.04 to 0.94 nm (ref. 33), we did not, however, observe such a peak shift. However, shifting of the palygorskite peak to 0.84 nm was observed at 300°C and 550°C (Figure 2). The major XRD reflection of palygorskite overlaps that of mica (1.0 nm) or hydrated halloysite. As proposed by Nathan<sup>34</sup>, heating the sample to 110°C showed a marked increase in the intensity of the 011 (1.05 nm) and 002



**Figure 3.** X-ray diffractograms of representative horizons of silt fractions (50–2 μm) from Sokhda (P7) black soils (98–145 cm depth) (Sm, Smectite; P, Palygorskite; M, Mica; Sm/K, Smectite–Kaolinite; Q, Quartz; F, Feldspar).

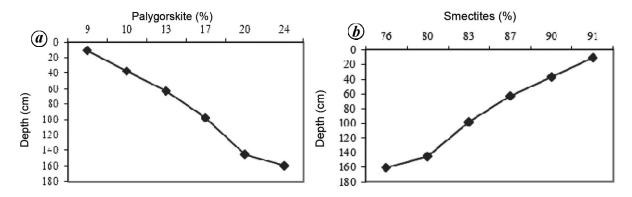


Figure 4. Distribution of (a) palygorskite and (b) smectite with depth in Sokhda (P7) black soils (98–145 cm depth).

(0.644 nm) reflections of palygorskite (Figure 3). Semiquantitative estimates of smectite and palygorskite in the fine clay fractions of black soils indicate an almost inverse relation between smectite and palygorskite, where the former decreases and the latter increases slightly with pedon depth. Such depth distribution of smectite and palygorskite clearly suggests that palygorskite is not formed at the expense of smectite (Figure 4a and b). In the event of formation of palygorskite from smectite, depth distribution of these two minerals would have showed a reverse trend, indicating more weathering of smectite, thus leaving less amount of the mineral on the surface. Similar depth distribution of smectite and palygorskite in a zeolitic/gypsiferrous black soil (P5) was observed in fine clay only and not in total clay. The depth distribution of these two clay minerals, as observed, indicates the preferential movement of fine clay palygorskite compared to smectite even in Ca<sup>2+</sup>-dominated systems<sup>21</sup>. Therefore, the presence of palygorskite in the black soils under study is of non-pedogenic origin and its formation at the expense of smectite may not be a common pedogenic event.

Until recently, the occurrence of palygorskite was hardly reported for soils of SAT. This is because normal clay mineralogical analysis is done after pre-treatment of the sample, whereby the acidification might destroy palygorskite <sup>19</sup>. Such difficulty was also experienced for deep black soils where only water was used to disperse soil clays (<2  $\mu$ m) for identification of palygorskite by XRD<sup>2</sup>. It is worth mentioning here that some zeolitic black soils (Typic Haplusterts) developed sodicity and associated sodic properties (ESP > 13 < 15, ECe < 4 dS<sup>-1</sup> m and low sHC) to qualify as sodic<sup>23</sup> due to prolonged irrigation (10–20 years) (Table 2). Palygorskite was, however, not

detected in these soils<sup>5</sup>, suggesting that irrigation may not be the only causative factor for the formation of this mineral. This contention is further supported by the presence of palygorskite only in P5 (Sodic Calciusterts) which is under both rainfed and irrigated systems. This is in contrast to reports of pedogenic formation of palygorskite in cracking clay soils of Maharashtra<sup>3</sup>.

The sHC of zeolitic black soils (P1 and P2) is >1.0, but < 3.0 cm h<sup>-1</sup> (weighted mean in the first 1 m of the profile), whereas gypsum containing black soils (P3) have sHC >3.0 cm h<sup>-1</sup> and sodic black soils (P4–P6) <<1.0 cm h<sup>-1</sup> (Table 2). In contrast, non-zeolitic/ gypsiferrous black soils (Calcic Haplusterts, P7) have sHC ranging from 0.2 to 3.2 mm h<sup>-1</sup> (Table 2). Similar impairment in sHC (<0.5 cm h<sup>-1</sup>) in non-zeolitic/ gypsiferrous soils (Typic Haplusterts) with palygorskite was also observed earlier by Zade<sup>2</sup>. Ca-zeolites improve the sHC of both non-sodic and sodic black soils<sup>5,23,26</sup>. Impairment of hydraulic properties in non-zeolitic/gypsic black soils (Typic Haplusterts) is thus primarily due to the presence of palygorskite. This (palygorskite) is the most disaggregated among clay minerals, and its fibres do not associate into aggregates in soils and suspensions even when the soils are saturated with Ca2+ ions. Black soils containing palygorskite (P6 and P7) have extractable Mg/Ca ratio from <1 at the surface to >1 in the subsurface (Table 2). Palygorskite particles thus move downward in the profile preferentially over smectite and eventually clog the soil pores<sup>21</sup>. Therefore, palygorskite containing black soils with high Mg ions on the exchange sites cause dispersion of the clay colloids that form a 3D mesh in the soil matrix. This interaction causes drainage problems when such soils are irrigated, presenting a predicament for crop production. Kadu et al.35 reported that an optimum yield of cotton in black soils of central India can be obtained when the soils are non-sodic and have sHC  $\geq$  2.0 cm h<sup>-1</sup>. They also reported 50% reduction in yield in the soils with sHC < 1.0 cm h<sup>-1</sup>. In view of the poor drainage conditions of these soils and loss of productivity, non-sodic and sodic black soils with palygorskite minerals should be considered naturally degraded soils, where soil drainage is impaired by the presence of palygorskite alone in non-sodic soils; in sodic soils such impairment is caused by both palygorskite and high ESP.

## Soil quality and fibrous minerals

Fibrous minerals, e.g. asbestos have been reported to be hazardous to human health. Palygorskite, one of the fibrous minerals, exists mainly in dry climate (arid and semi-arid); this demands a discussion on the advantages and disadvantages of this mineral in soils for dry land agriculture. Our limited datasets indicate that palygorskite might indirectly bring artefacts in soils leading to their poor physical condition. Thus, this mineral will have an

indirect effect on soil quality in crop production as explained below.

The role of palygorskite in impairing the drainage of black soils under both rainfed and irrigated agricultural systems is noteworthy. The ratio of extractable Mg/Ca > 1 in the lower depth of the profile indicates that palygorskite-containing black soils have a relatively high Mg-rich chemical environment (Table 2). However, this ratio is low in soils with gypsum and zeolites indicating better pedo-environment dominated by Ca-ions (Table 2). The pedo-chemical conditions necessary for the formation of palygorskite have been specified as the high activity of Mg and Si, some Al and pH of about 8 (ref. 14). It is often reported that calcite crystallization in SAT environment increases Mg in the soil solution, thus promoting dolomite and palygorskite formation<sup>3,18,36</sup>. However, extensive micro-morphological studies on CaCO3 of Indian black soils indicated the presence of only micritic and sparitic form of calcite and no crystals of dolomite<sup>23,25,37</sup>. Therefore, relatively more extractable Mg/Ca (<1) in the subsoils of P6 and P7 (Table 2) is due to rapid formation of CaCO3 in the SAT environment with concomitant development of subsoil sodicity<sup>23,25,38</sup>.

The parent material of Indian black soils is LCS, which formed in large amounts in an earlier humid climate in the source area as an alteration product of plagioclase<sup>22,26,39</sup>. LCS is partially hydroxy-interlayered as evidenced from the broadening at the low angle side of the 1.0 nm peak of the K-saturated and heated samples  $(550^{\circ}\text{C})^{24,25,40}$ . It is being preserved in the non-leaching environment of SAT<sup>25</sup>. Such hydroxy-interlayering occurs when positively charged hydroxy-interlayer materials enter into the interlayer spaces at moderately acidic pH  $(5.0-6.0)^{40}$ . Moderately acidic conditions are optimal for hydroxy-Al interlayering of smectite and the optimum pH for interlayering in smectite is 5.0–6.0, as small hydroxyl ions are most likely to be produced at a low pH<sup>40</sup>.

The pH of Indian black soils is slight to highly alkaline under which 2:1 layer silicates suffer congruent dissolution<sup>41</sup>, and partially remove the hydroxy-interlayer materials of the hydroxy-interlayered LCS, causing a decrease in layer charge of hydroxy-interlayered LCS<sup>42</sup>. In an alkaline environment, dissolution of primary and secondary minerals produces monomers of Si, Al and Fe in solution. However, these remain as poorly ordered silicates<sup>43</sup> and cannot form either tetrahedral or octahedral coordination until pH conditions become mildly acidic<sup>44</sup> or little above neutral<sup>14</sup>. According to some researchers, the transformation of smectite to palygorskite in solid state is unlikely because of the structural differences between the two minerals<sup>45,46</sup>. Extensive XRD analysis of the fine clay smectites of Indian black soils<sup>5,22,24,26</sup> does not indicate any intergrade minerals consisting of smectite and palygorskite as they are ubiquitous in fine clays of black soils as intergrade/interstratified minerals like 1.4-0.7 nm in humid or 1.0-1.4 nm in SAT climates<sup>22,26,40</sup>.

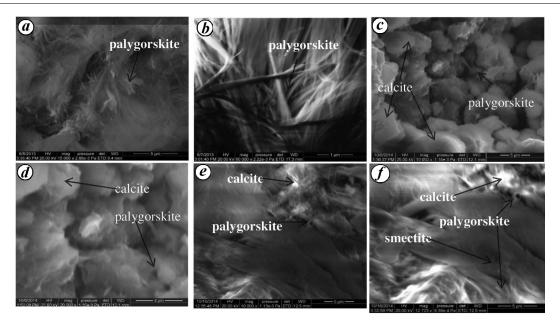


Figure 5. Representative scanning electron microscope images of Sokhda black soils (P7) and Bss1k horizon (63–98 cm depth). a, b, Typical palygorskite over calcretes; c, Palygorskite fibres embedded in calcite crystals. d, Magnified palygorskite (× 20,000) resembling cotton-like fibrous structures. e, f, Palygorskite fibres in close association with calcite crystals (e) and smectites (f).

In view of the various pathways discussed, formation of palygorskite at the expense of smectite or through neoformation in the presence of soluble carbonate and bicarbonate during the post-depositional period of LCS seems unlikely. In view of the absence of clay palygorskite in P2 and P5 under irrigated agricultural systems, it is realized that the hypothesis on the formation of palygorskite as envisaged<sup>3,18</sup> is inadequate to the genesis of palygorskite in sodic black soils under both rainfed and irrigated agriculture systems of India.

The possibility of inheritance of palygorskite from rocks other than the alluvium of the weathering Deccan basalt thus merits a study. The sources of palygorskite appear to be related to the intertrappean sediments sandwiched between the Deccan trap flows in Andhra Pradesh<sup>47</sup>, Karnataka and Gujarat<sup>48</sup> where palygorskite occurs in lacustrine sediments of high basicity under arid conditions induced and influenced by Deccan volcanism<sup>48</sup>. Such highly calcareous, palygorskitic and alkaline sediments are red in colour and often referred to as red bole, and at places in Maharashtra, red cracking clay soils are developed on such palygorskitic red bole clay materials<sup>49</sup> (P6, Table 1). Thus, the fine clay fractions of such red cracking clay soils do not contain kaolin as an evidence of transformation of smectite to 0.7 nm minerals, typical in humid climates, but may suggest the formation of calcareous and palygorskitic clay material in arid environments<sup>49</sup>. In contrast, the fine clay fractions of the closely associated Typic Haplusterts with the red cracking clay soils contain kaolin but not palygorskite<sup>49</sup>. This unique mineralogical composition of the fine clay fractions of the closely associated red (Sodic Calciusterts) and grey (Typic Haplusterts) black soils suggest that the formation of palygorskite is not pedogenic under the SAT environment. The prime pedogenic process in Indian SAT black soils is the dissolution of non-pedogenic CaCO3 to release Ca<sup>2+</sup> ions and their recrystallization as pedogenic CaCO<sub>3</sub> (PC)<sup>4,37,38</sup>. Formation of PC causes simultaneous development of sodicity, which impairs soil drainage. Such chemical natural degradation represents a regressive pedogenesis in soils of SAT environment<sup>50</sup>, which further supports the contention that the transformation of smectite to palygorskite as the progressive pedogenesis is not operative in SAT black soils at present. Thus palygorskite in these soils is a non-pedogenic entity even though palygorskite fibres are often observed closely associated with CaCO<sub>3</sub> crystals and smectites (Figure 5). Pal and Deshpande<sup>24</sup>, and Pal et al.<sup>26</sup> reported a major phase, or phases, of redistribution of smectite-rich alluvium of the weathering Deccan basalt in the lower physiographic positions, i.e. in the lower piedmont plains or valleys or in micro depressions. During such erosional and depositional episodes, minor minerals (quartz, K-feldspar, chlorite and micas)<sup>35</sup> that have no legacy to the Deccan basalt were incorporated due to the exhumation of other rock formations that underlie the Deccan basalt<sup>24</sup> which might have included the palvgorskite-rich clay sediments of the intertrappean. The presence of palygorskite mineral in P6 and P7 suggests its inheritance from the exhumed intertrappean clay sediments during the erosional and depositional episodes caused by extensive and massive denudation in the basaltic terrain in the past geological periods<sup>22,47,51,52</sup>.

Thus, the clay-sized palygorskite, mica and chlorite are the result of a physical comminution of their respective silt-sized forms.

#### Conclusion

The presence of both silt- and clay-sized palygorskite in some sodic black soils and its absence in spatially associated non-sodic soils (Typic Haplusterts) under SAT environment suggest that palygorskite clay mineral is inherited from the palygorskitic parent materials, and therefore its presence as an indicator mineral of arid climate is to be considered with caution. Palygorskite is responsible for impairing the hydraulic properties of these black soils which cause 50% reduction in crop yield. This dismal situation for drainage in palygorskitic black soils warrants an initiative to make an inventory on the occurrence of such soils and classify them properly keeping in view the soil quality parameters that at present do not support good agricultural land-use planning.

- Sarma, V. A. K. and Sidhu, P. S., Genesis and transformation of clay minerals. In 12th International Congress of Soil Science, New Delhi, 1982, pp. 718–724.
- Zade, S. P., Pedogenic studies of some deep shrink-swell soils of Marathwada Region of Maharashtra to develop a viable land use plan. Ph D thesis, Dr PDKV, Akola, Maharashtra, 2007.
- Hillier, S. and Pharande, A. L., Contemporary formation of palygorskite in irrigation induced saline–sodic, shrink–swell soils of Maharashtra, India. Clays Clay Miner., 2008, 56, 531–548.
- Kolhe, A. H., Characteristics and genesis of red swell-shrink soils of Hingoli District of Maharashtra, M Sc thesis submitted to Dr. PDKV, Akola, 2010, p. 91.
- Pal, D. K., Bhattacharyya, T., Ray, S. K. and Bhuse, S. R., Developing a model on the formation and resilience of naturally degraded black soils of the Peninsular India as a decision support system for better land use planning. NRDMS, DST Project Report, NBSS&LUP (ICAR), Nagpur, 2003, p. 144.
- Singer, A., Pedogenic palygorskite in the aid environment. In Palygorskite-Sepiolite Occurrences, Genesis and Uses (eds Singer, A. and Galan, E.), Elsevier, Amsterdam, The Netherlands, 1984, pp. 169–176.
- Singer, A., Palygorskite and sepiolite. In *Soil Mineralogy with Environmental Applications* (eds Dixon, J. B. and Schulze, D. G.), SSSA Book Series, Soil Science Society of America, Madison, WI, 2002, vol. 7, pp. 555–583.
- Jones, B. F. and Galan, E., Sepiolite and palygorskite. In *Hydrous Phyllosilicates. Reviews in Mineralogy, 19, Mineralogical Society of America* (ed. Bailey, S. W.), Washington DC, USA, 1988, pp. 631–674.
- Millot, G., Panquet, H. and Ruellan, A., Neoformation de l'attapulgite dans les sols a carapaces calcaires de la basse Moulouya (Maroc oriental). C.R. Academy of Sciences, Paris, 1969, 268, 2771–2774.
- Ducloux, J., Delhoume, J. P., Petit, S. and Decarreau, A., Clay differentiation in Aridisols of northern Mexico. Soil Sci. Soc. Am. J., 1995, 59, 269-276.
- Zelazny, L. W. and Calhoun, F. G., Palygorskite (attapulgite), sepiolite, talc, pyrophyllite and zeolites. In *Minerals in Soil Envi*ronment (eds Dixon, J. B. and Weed, S. B.), Soil Science Society of America, Madison, Wisconsin, USA, 1977, pp. 435–470.

- Heidari, A., Mahmoodi, Sh., Roozitalab, M. H. and Mermut, A. R., Diversity of clay minerals in the black soils of three different climatic regions in western Iran. J. Agric. Sci. Technol., 2008, 10, 269–284.
- 13. Callen, R. A., Clays of the palygorskite-sepiolite group: depositional environment, age and distribution. In *Palygorskite-Sepiolite Occurrences, Genesis and Uses* ((eds Singer, A. and Galan, E.), Elsevier, Amsterdam, The Netherlands, 1984, pp. 1–37.
- Singer, A., Palygorskite and sepiolite group minerals. In *Minerals in Soil Environments* (eds Dixon, J. B. and Weed, S. B.), SSSA Book Series No. 1, Madison, WI, USA, 1989, 2nd edn, pp. 830–873
- Bigham, J. M., Jaynes, W. F. and Allen, B. L., Pedogenic degradation of sepiolite and palygorskite on the Texas High Plains. Soil Sci. Soc. Am. J., 1980, 44, 159–165.
- Fassi, D., L'encroutement calcaire differencie. Approche analytique intergree d'un profil du Sais. Rev. Geogr. Moracaine, 1987, 10, 115-148.
- Kadir, S. and Eren, M., The occurrence and genesis of clay minerals associated with quaternary caliches in the Mersin area, southern Turkey. Clays Clay Min., 2008, 56, 244–258.
- Xie, Q. et al., Mechanism of palygorskite formation in the red clay formation on the Chinese Loess Plateau, northwest China. Geoderma, 2013, 192, 39–49.
- 19. Sombroek, W. G., The use of palygorskite as diagnostic criteria in soil classification. *Pedologie*, 1981, **31**, 121.
- Singer, A. and Norrish, K., Pedogenic palygorskite occurrence in Australia. Am. Mineral, 1974, 59, 508–517.
- 21. Neaman, A. and Singer, A., The effects of palygorskite on chemical and physico-chemical properties of soils: a review. *Geoderma*, 2004, **123**, 297–303.
- Bhattacharyya, T., Pal, D. K. and Deshpande, S. B., Genesis and transformation of minerals in the formation of red (Alfisols) and black (Inceptisols and black soils) soils on Deccan basalt. *J. Soil Sci.*, 1993, 44, 159–171.
- Pal, D. K., Bhattacharyya, T., Ray, S. K., Chandran, P., Srivastava, P., Durge, S. L. and Bhuse, S. R., Significance of soil modifiers (Ca-zeolites and gypsum) in naturally-degraded black soils of the Peninsular India in redefining the sodic soils. *Geoderma*, 2006, 136, 210–228.
- Pal, D. K. and Deshpande, S. B., Characteristics and genesis of minerals in some benchmark black soils of India. *Pedologie*, 1987, 37, 259–275.
- 25. Pal, D. K. *et al.*, Black soils (cracking clay soils) in a climosequence of Peninsular India: evidence for Holocene climate changes. *Quaternary Int.*, 2009, **209**, 6–21.
- Pal, D. K., Wani, S. P. and Sahrawat, K. L., Black soils of tropical Indian environments: pedology and edaphology. *Geoderma*, 2012, 189–190, 28–49.
- Bhattacharyya, T., Sarkar, D. and Pal, D. K. (eds), Soil Survey Manual, NBSS&LUP Publication No. 146, NBSS&LUP, Nagpur, 2009, p. 400.
- Jackson, M. L., Soil Chemical Analysis Advanced Course, University of Wisconsin, Madison, USA (Published by the author), 1979, 2nd edn.
- Piper, C. S., Soil and Plant Analysis, Hans Publishers, Bombay, 1966.
- Richards, L. A., Diagnosis and Improvement of Saline and Alkali Soils, USDA Agricultural Handbook, US Government Printing Office, Washington, DC, USA, 1954, vol. 60.
- Brown, G., Associated minerals. In Crystal Structures of Clay Minerals and their X-ray Identification (eds Brindley, G. W. and Brown, G. W.), Mineralogical Society, London, UK, 1984, pp. 361–410.
- Gjems, O., Studies on clay minerals and clay mineral formation of soil profiles in Scandinavia. *Medd. Nor. Inst. Skogforsok.*, 1967, 21, 303–415.

- 33. Van Scoyoc, G. E., Serna, C. J. and Ahlrichs, J. L., Structural changes in palygorskite during dehydration and dehydroxylation. *Am. Mineral.*, 1979, **64**, 215–223.
- Nathan, Y., An improved X-ray method for detecting small quantities of palygorskite in clay mineral mixtures. *Clays Clay Miner.*, 1970, 18, 363–365.
- 35. Kadu, P. R., Vaidya, P. H., Balpande, S. S., Satyavathi, P. L. A. and Pal, D. K., Use of hydraulic conductivity to evaluate the suitability of black soils for deep rooted crops in semi-arid parts of Central India. *Soil Use Manage.*, 2003, 19, 208–216.
- Owliaie, H. R., Abtahi, A. and Heck, R. J., Pedogenesis and clay mineralogical investigation of soils formed on gypsiferous and calcareous materials, on a transect, southwestern Iran. *Geoderma*, 2006. 134, 62–81.
- Srivastava, P., Bhattacharyya, T. and Pal, D. K., Significance of the formation of calcium carbonate minerals in the pedogenesis and management of cracking clay soils (black soils) of India. *Clays Clay Miner.*, 2002, 50, 110–125.
- Pal, D. K., Dasog, G. S., Vadivelu, S., Ahuja, R. L. and Bhattacharyya, T., Secondary calcium carbonate in soils of arid and semi-arid regions of India. In *Global Climate Change and Pedogenic Carbonates* (eds Lal, R. et al.), Lewis Publishers, Boca Raton, Florida, 2000, pp. 149–185.
- Pal, D. K., Deshpande, S. B., Venugopal, K. R. and Kabande, A. R., Formation of di and trioctahedral smectite as evidence for paleoclimatic changes of southern and central Peninsular India. *Geoderma*, 1989, 45, 175–184.
- Pal, D. K. et al., Clay minerals record from Late Quaternary drill cores of the Ganga Plains and their implications for provenance and climate change in the Himalayan Foreland. Palaeogeogr., Palaeoclimatol., Palaeoecol., 2012, 356–357, 27–37.
- 41. Pal, D. K., Potassium release from muscovite and biotite under alkaline conditions. *Pedologie*, 1985, **35**, 133–146.
- Thakare, P. V., Ray, S. K., Chandran, P., Bhattacharyya, T. and Pal, D. K., Does sodicity in Black soils affect the layer charge of smectites? *Clay Res.*, 2013, 32, 76–90.
- Rengasamy, P., Sarma, V. A. K., Murthy, R. S. and Krishna Murti,
  G. S. R., Mineralogy, genesis and classification of ferruginous soils of the eastern Mysore plateau. J. Soil Sci., 1978, 29, 431-445.
- De Kimpe, C., Gastuche, M. C. and Brindley, G. W., Ionic coordination in aluminosilicic gels in relation to clay mineral formation. *Am. Mineral.*, 1961, 46, 1370–1381.

- Singer, A., Palygorskite in sediments: detrital, diagenetic or neoformed – a critical review. *Geol. Rundsch.*, 1979, 68, 996–1008.
- Daoudi, L., Palygorskite in the uppermost Cretaceous–Eocene frocks from Marrakech High Atlas, Morocco. J. Afr. Earth Sci., 2004, 39, 353–358.
- Siddiqui, M. K. H., Palygorskite clays from Andhra Pradesh, India. Clay Min., 1967, 7, 120–123.
- Shrivastava, J. P., Salil, M. S, and Pattanayak, S. K., Clay mineralogy of Ir-bearing Anjar Intertrappeans, Kutch, Gujarat, India: inferences on paleoenvironment. *J. Geol. Soc. India*, 2000, 55, 197–206.
- Kolhe, A. H., Chandran P., Ray, S. K., Bhattacharyya, T., Pal, D.
  K. and Sarkar, D., Genesis of associated red and black shrink-swell soils of Maharashtra. *Clay Res.*, 2011, 30, 1–11.
- Pal, D. K., Sarkar, D., Bhattacharyya, T., Datta, S. C., Chandran,
  P. and Ray, S. K., Impact of climate change in soils of semi-arid tropics (SAT). In *Climate Change and Agriculture* (eds Bhattacharyya, T. et al.), Studium Press, New Delhi, 2013, pp. 113–121.
- Bhattacharyya, T., Pal, D. K. and Srivastava, P., Role of zeolites in persistence of high altitude ferruginous Alfisols of the Western Ghats, India. *Geoderma*, 1999, 90, 263–276.
- Bhattacharyya, T., Pal, D. K., Lal, S., Chandran, P. and Ray, S. K., Formation and persistence of Mollisols on zeolitic Deccan basalt of humid tropical India. *Geoderma*, 2006, 136, 609–620.
- 53. Soil Survey Staff, *Keys to Soil Taxonomy*, United States Department of Agriculture, Natural Resources Conservation Service, Washington, DC, USA, 10th edn, 2006.
- Velayutham M., Mandal D. K., Mandal, C. and Sehgal, J., Agro-ecological subregions of India for planning and development, NBSS&LUP Publ. No. 35, NBSSLUP, Nagpur, 1999, p. 372.

ACKNOWLEDGEMENTS. We thank the students, research fellows and research assistants at ICAR-NBSS&LUP, Nagpur for help. We also thank the Directors and Heads of the Research Divisions of ICAR-NBSS&LUP, Nagpur for providing the necessary facilities to carry out this work and Dr Balasaheb Sawant Konkan Krishi Vidyapeeth, Dapoli for help.

Received 29 July 2017; accepted 23 March 2018

doi: 10.18520/cs/v115/i3/482-492