

## CONTEMPORARY PEDOGENIC FORMATION OF PALYGORSKITE IN IRRIGATION-INDUCED, SALINE-SODIC, SHRINK-SWELL SOILS OF MAHARASHTRA, INDIA

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**Abstract**—Increasing use of irrigation in India has exacerbated the problems of soil salinity and sodicity. The present study was undertaken on shrink-swell soils from Maharashtra State to determine if changes in soil chemistry due to irrigation have affected the clay mineralogy. Twenty six samples (15 locations) of irrigation-induced, saline-sodic, shrink-swell soils and 27 samples (22 locations) of normal un-irrigated (rain-fed) shrink-swell soils were studied using X-ray powder diffraction (XRPD), infrared spectroscopy (FTIR), and scanning and transmission electron microscopy (SEM, TEM). The XRPD analysis of the <0.2 μm fraction of rain-fed, shrink-swell soils indicates a predominance of dioctahedral smectite with minor to trace amounts of kaolinite and chlorite. Traces of palygorskite (1–4%) were detected in three samples. In contrast, palygorskite is a common component (1–20%) of the fine-clay fraction of saline-sodic soils. Quantitative analysis of palygorskite by XRPD in whole-soil (<2 mm) samples showed that saline-sodic soils contain up to 20 wt.% of palygorskite, whereas palygorskite was only detectable (1.5 wt.%) in one sample of the rain-fed set. The SEM, TEM, and FTIR confirm the presence of Fe-rich palygorskite in saline-sodic soils and demonstrate that the fibrous palygorskite crystals are exceedingly small (~0.5 μm long). Delicate palygorskite fibers radiate from the margins of smectite plates suggestive of a pedogenic origin and a close genetic relationship between smectite and palygorskite. The compositions of saturation-paste extracts display a shift from the stability field of smectite in rain-fed soils to that of palygorskite in saline-sodic soils. Thus the occurrence and formation of palygorskite appears to be related to the change in land management from rain-fed to irrigated agriculture. This change has occurred over a period of no more than 40–50 y, implying that palygorskite formation in the irrigated, saline-sodic soils has been an extremely rapid process.

**Key Words**—Beidellite, Irrigation, Montmorillonite, Palygorskite, Pedogenic, Shrink-swell, Soil, Smectite, Vertisol.

### INTRODUCTION

‘Shrink-swell soils’ is the name given to a group of typically ‘black’ soils which exhibit a range of morphological features related to cycles of shrinking and swelling. These soils are distributed extensively in many parts of world. In India they include Vertisols as well as vertic Inceptisols and Entisols and together cover an area of 76.4 million ha with the largest area (29.9 million ha) in Maharashtra State (Murthy, 1988) where they are derived almost entirely from the Eocene Deccan trap basalts (Roy and Chatterjee, 1998) and basaltic alluvium. The shrink-swell soils currently exist mainly under semi-arid climatic conditions (rainfall <750 mm) and occur predominantly in the topographically lowest areas of the landscape such as piedmont plains and river valleys. Not surprisingly, the main clay mineral in these shrink-swell soils is a dioctahedral smectite (Pal and Deshpande, 1987; Pharanade and Sonar, 1997; Pal *et al.*, 2000). According to

Pal *et al.* (2000), most smectite formation probably occurred by weathering of basaltic parent material under somewhat more humid conditions than those of the present day. Pal *et al.* (2000) also envisaged a major phase, or phases, of redistribution of smectite-rich weathering products to the topographically lowest areas. During redistribution, minor mineral components that cannot be derived from basalt, including quartz, K-feldspar, and muscovite, were incorporated.

Agriculture is central to the Indian economy and agriculturally these soils are very important. Cultivation is mainly under rain-fed conditions (85%) but their production potential is much greater (by a factor of three or four) under irrigated farming. Initially, when these soils are brought under irrigation they produced very high yields of different crops and this practice has contributed substantially to increases in the food, fodder, and fiber production of the State. However, over a period of four decades, irrigation for crop production has, in many areas, resulted in problems related to the development of saline-sodic conditions, water-logging (Jaglan and Qureshi, 1996), and a decline in productivity. Soil degradation due to sodicity is also a natural process (Balpande *et al.*, 1996; Srivastava *et al.*, 2002; Pal *et al.*, 2006) that may be accelerated by poor management. The problem is spreading gradually as

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ever-greater areas of these soils are brought under irrigation. The development of saline-sodic conditions and the resulting degradation of soil properties pose a clear threat to the sustainable use of the soil resource and ultimately agricultural production. Varade *et al.* (1985) reported that ~10% of irrigated shrink-swell soils in each irrigation project of Maharashtra is affected by increased salinity and sodicity. A more recent estimate reported by Challa *et al.* (1995) indicates that 0.6 million ha of soil in Maharashtra State is under the influence of salinity and sodicity.

Problems of salinity and sodicity in soils are well known and the chemical processes and degradation in physical properties that occur have been studied in detail by many authors, *e.g.* Naidu (1993). Also well known is that the inherent physical and chemical properties and biological fertility of soil are all strongly influenced by the kinds and quantities of clay minerals present in the soil (Mackenzie, 1990; Pal *et al.*, 2000). The present investigation was undertaken to determine if the development of salinity and sodicity, as a direct result of irrigation, had produced any detectable changes in the mineralogy, particularly the clay mineralogy, of the shrink-swell soils of Maharashtra. As shown below, clay mineralogy is substantially affected by salinity and sodicity in a manner that has not been recognized previously.

## MATERIALS AND METHODS

In total, 53 samples were collected from 37 locations across Maharashtra State (Figure 1, Table 1). At seven sites, samples were collected 'horizon-wise' from soil profiles, while at other sites, only representative surface samples (0–30 cm) were collected. The numbers of samples were sub-equally divided between sites cultivated solely under rain-fed conditions (22 sites, 27 samples) and sites where irrigation has been applied for periods of up to 40 y (15 sites, 26 samples).

For the rain-fed soils, samples were obtained from two representative pedons and from 19 surface (0–30 cm) sites all belonging to established and benchmarked soil series of different districts of Maharashtra (Table 1). Generally, these soils are deep to very deep with abundant shrink-swell features. They are very dark gray-brown (10YR3/2) in color and show the development of an ABC profile with a clayey texture throughout. All shrink-swell soils are moderate to strongly alkaline, calcareous, very base saturated, have a large cation exchange capacity (CEC), but contain little organic carbon (<1 wt.%). The Vertisols of Maharashtra were described in detail by Pharande and Sonar (1997). In addition, a sample of clay derived directly from an outcrop of spheroidally weathered Deccan basalt (1-ALP) was also included for study.

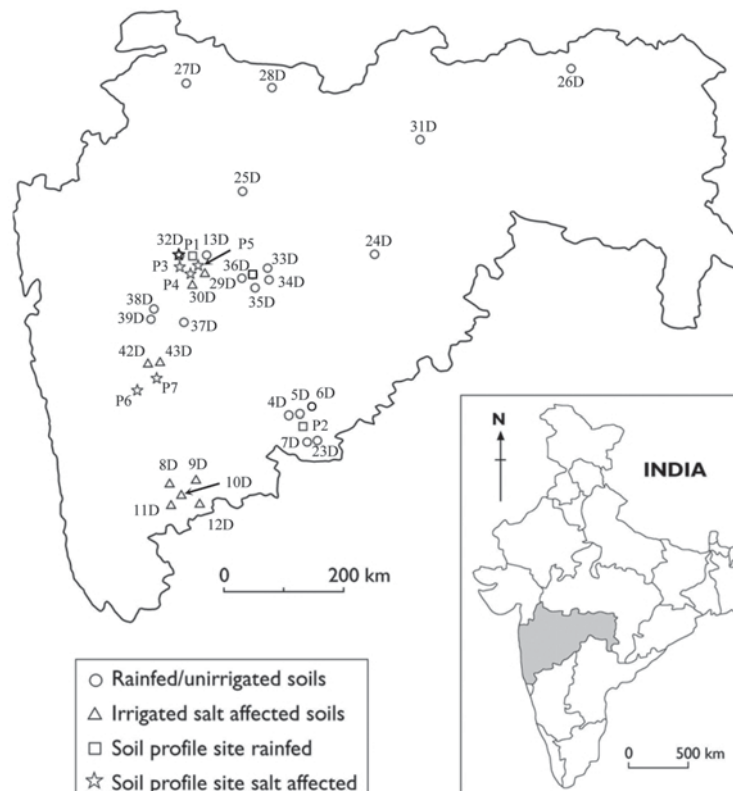


Figure 1. Sample and profile locations across the State of Maharashtra, India.

Table 1. Sample details and locations.

Status	Sample code	Horizon	Depth (cm)	Soil series	Soil classification	Location	District
"	2-ALP	Ap	0-15	Otur (Bench mark series)	Soil Pedon P1 (Typic Haplustert)	Rahuri	Ahmednagar
"	3-ALP	AB	15-35	"	"	Rahuri	"
"	4-ALP	Bss1	35-75	"	"	Rahuri	"
"	5-ALP	Bss2	75-110	"	"	Rahuri	"
"	1-D-ALP	Ap	0-30	Barshi (Bench mark series)	Soil Pedon P2 (Typic Haplustert)	Solapur	Solapur
"	2-D-ALP	AB	30-60	"	"	Solapur	"
"	3-D-ALP	Bss1	60-90	"	"	Solapur	"
"	4-D-ALP	Ap	0-30	Barshi (Bench mark series)	Surface soils (Typic Haplustert)	DFRS Solapur	"
"	5-D-ALP	Ap	0-30	"	"	ARS Solapur	"
"	6-D-ALP	Ap	0-30	Pather	Surface soils (Vertic Haplustepts)	Mohal	"
"	7-D-ALP	Ap	0-30	"	"	ARS Mohal	"
"	23-D-ALP	Ap	0-30	Barshi (Bench mark series)	Surface soils (Typic Haplustert)	Barshi	"
"	24-D-ALP	Ap	0-30	Tadpangari (Established)	"	Tadpangari	Parbhani
"	25-D-ALP	Ap	0-30	Ranjani (Established)	"	Ranjani	Aurangabad
"	27-D-ALP	Ap	0-30	Shendwade (Established)	"	Shendwade	Dhule
"	28-D-ALP	Ap	0-30	Hated (Identified)	"	Hated	Jalgaon
"	31-D-ALP	Ap	0-30	Jambha (Bench mark series)	"	Jambha	Akola
"	26-D-ALP	Ap	0-30	Kimapur (Established)	Surface soils (Entic chromustert)	Kimapur	Nagpur
"	33-D-ALP	Ap	0-30	Pather (Bench mark series)	Surface soils (Vertic Haplustepts)	Meeri-pathardi	Ahmednagar
"	34-D-ALP	Ap	0-30	"	"	Renukawadi	"
"	35-D-ALP	Ap	0-30	"	"	Sakegaon	"
"	36-D-ALP	Ap	0-30	"	"	Tisgaon	"
"	37-D-ALP	Ap	0-30	"	"	Pagori pimpalgaon	"
"	38-D-ALP	Ap	0-30	"	"	Chas	"
"	39-D-ALP	Ap	0-30	"	"	ARS Chas	"
"	13-D-ALP	Ap	0-30	Sawargaon (Bench mark)	Surface soil (Vertic Ustropept)	Sawargaon	"
"	1-ALP			Basalt weathered clay	"	Rahuri	"
Saline	6-ALP	Ap	0-13	Torkewadi (Established)	Soil Pedon P3 (Lithic Haplaquent)	Rahuri	Ahmednagar
"	7-ALP	Al2	13-33	"	"	"	"
Saline sodic	8-ALP	Ap	0-16	Nimone (Bench mark)	Soil Pedon P4 (Vertic Halaquent)	Rahuri	"
"	9-ALP	Bw1	16-28	"	"	"	"
"	10-ALP	Bw2	28-50	"	"	"	"
"	11-ALP	Bw3	50-77	"	"	"	"
"	12-ALP	Bw4	77-100	"	"	"	"
Sodic	17-ALP	Ap	0-30	Wadgaon Amla (Established)	Soil Pedon P5 (Sodic calcustert)	Rahuri	"
"	18-ALP	AB	25-45	"	"	"	"
"	19-ALP	Bss1	60-100	"	"	"	"
Saline sodic	13-ALP	Ap	0-25	Nimone (Bench mark)	Soil Pedon P6 (Udic Haplustert)	Padegaon	Pune
"	14-ALP	AB	25-45	"	"	"	"
"	15-ALP	Bss1	45-87	"	"	"	"
"	16-ALP	Bss2	87-120	"	"	"	"
Sodic	40-D-ALP	Ap	0-30	Pather (Bench mark series)	Soil Pedon P7 (Vertic Ustropept)	Baramati	Pune
"	41-D-ALP	Bw1	60-90	"	"	"	"

"												Ahmednagar
Saline sodic	30-D-ALP	Ap	0-30	Nimone (Bench mark)	Surface soils (Udic Chromustert)	Nimone	Otur	"	"	"	"	"
Naturally saline sodic	32-D-ALP	Ap	0-30	Otur	"	Wadgaon Aml		"	"	"	"	"
Saline sodic	29-D-ALP	Ap	0-30	Wadgaon Aml (Established)	"	Babhulgaon (Bench mark)		"	"	"	"	Sangli
"	8-D-ALP	Ap	0-30	"	"	"		"	"	"	"	"
"	9-D-ALP	Ap	0-30	"	"	"		"	"	"	"	"
"	10-D-ALP	Ap	0-30	"	"	"		"	"	"	"	"
"	11-D-ALP	Ap	0-30	"	"	"		"	"	"	"	"
"	12-D-ALP	Ap	0-30	Nimone (Bench mark)	"	"		"	"	"	"	Sangli
Sodic	42-D-ALP	Ap	0-30	"	"	"		"	"	"	"	"
Saline sodic	43-D-ALP	Ap	0-30	Targaon	Surface soil (Typic Haplustert)	"		"	"	"	"	Baramati tahsil
												"
												"

For the irrigated saline-sodic soils, samples were obtained from five representative pedons, three from Mula (Ahmednagar) and two from Nira (Pune) irrigation Command areas. Additionally, nine irrigation-induced, surface, saline-sodic, shrink-swell soils were collected, five from Krishna (Sangli) Command area, two from Mula Command area (Rahuri tahsil), and two from Nira Command area (Baramati tahsil) (Table 1). All of these soils have been cultivated intensively under irrigation, in some cases since about 1960. One naturally occurring saline-sodic soil (29D) from Ahmednagar district was also included in the study. In general, irrigation-induced, saline-sodic soils are strongly alkaline in reaction ( $\text{pH} > 8.5$ ), high in exchangeable Na ( $\text{ESP} > 10$ ) and in soluble salts ( $\text{EC} > 4.0 \text{ dSm}^{-1}$ ). Sodic soils have similar characters but contain only a small amount of soluble salt. These soils have a generally degraded and dispersive soil structure and often show salt effervescence and encrustation at the surface. The calcium carbonate content often increases with depth but the soils are highly calcareous throughout. The physical properties are poor with large bulk densities ( $> 1.5 \text{ Mg m}^{-3}$ ) and large values for Coefficient of Linear Extensibility (COLE), and very poor hydraulic conductivity. When these soils dry they become very hard and, when wet, very sticky, and not easily worked. Prior to the laboratory studies, all samples were air-dried and sieved to  $< 2 \text{ mm}$ . The details of soils series, classification, and locations for all samples are given in Table 1.

X-ray powder diffraction (XRPD) was the main technique employed to examine the mineralogy of the soils. All XRPD patterns were obtained using a Siemens D5000 instrument, with  $1^\circ$  divergence and antiscatter slits, and with  $\text{CoK}\alpha$  radiation selected by a diffracted-beam monochromator. Fine-clay fractions, coarse-clay fractions, fine silt, and bulk soil ( $< 2 \text{ mm}$ ) samples were examined. Fine clay ( $< 0.2 \mu\text{m}$ ) was separated by centrifugation following dispersion using de-ionized water and treatment for 45 min in an ultrasonic bath; when necessary, soluble salts were removed by repeated washing in de-ionized water. Samples were prepared as oriented mounts using the filter-peel transfer method and examined air-dried, after solvation with ethylene glycol overnight, and after heating to  $300^\circ\text{C}$  and  $550^\circ\text{C}$  for 2 h. Additionally, all fine clay samples were also examined after Mg saturation and K saturation. About half of the samples were also tested for expandability following Li saturation and heating to  $200^\circ\text{C}$  (Greene-Kelly, 1953) and for solubility in 6 M HCl, by boiling the clay for 30 min (Hayashi and Oinuma, 1964). For the Greene-Kelly test, samples were mounted on steel plates rather than glass slides to avoid the potential problem of sodium migration (Bystrom-Brusewitz, 1976). All clay fraction XRPD patterns were measured over the range  $2-45^\circ 2\theta$  in steps of  $0.02^\circ 2\theta$  and counting for 1 s per step. Quantitative analysis of the oriented fine clay

fraction was made using a reference intensity ratio method with intensity measured as peak areas. For the minerals smectite and kaolinite, intensity factors relative to illite (001) were calculated using the NEWMOD program (Reynolds, 1985) with parameters appropriate for the collimation of the D5000 device. For palygorskite, an intensity factor was determined from five different mixtures of a pure smectite separated as a 0.2  $\mu\text{m}$  size fraction from sample 4-ALP and palygorskite (Pal-24) from the Macaulay Institute mineral collection. The resulting reference intensity ratios (peak area) were 5.1 for ethylene-glycol smectite (001), 2.5 for kaolinite (001), and 1.7 for palygorskite (110). Coarse clay fractions (0.2–2  $\mu\text{m}$ ) were prepared and examined by identical procedures.

For bulk-soil samples, 1.5 g of soil plus 0.375 g of corundum (20 wt.%) were weighed accurately and then transferred to a McCrone mill to which ~15 mL of water was added before grinding for 12 min. Random powder samples were prepared by spray drying the resulting slurry directly from the mill, as described by Hillier (1999). Minerals present in the soils were identified by reference to patterns in the International Centre for Diffraction Data (ICDD) powder diffraction file (PDF) database. Reference intensity ratios were determined for each mineral identified using spray-dried mixtures of pure reference minerals and corundum. The minerals identified were then quantified using a reference intensity ratio method using 20 wt.% corundum as the internal standard, as described in detail by Hillier (2003).

For transmission electron microscopy (TEM) and analytical transmission electron microscopy (ATEM), suspensions of each clay fraction were diluted and agitated in an ultrasonic bath for several minutes. The

dispersed suspensions were then dried on carbon-covered, copper mesh sample grids (3.05 mm in diameter). Morphological and chemical data were collected using a JEOL 2000EX TEM equipped with a Link 10/85S Si(Li) energy dispersive X-ray spectrometer with electron diffraction capabilities. The microscope was operated at a beam voltage of 200 kV. X-ray emission spectra were processed quantitatively according to the ratio method of Cliff and Lorimer (1975). Spectra were collected at intervals of 100 s from electron beam spot sizes of <50 nm diameter. Background-corrected EDS counts were recalculated to wt.% oxides using experimentally determined calibration constants.

For scanning electron microscopy (SEM), bulk specimens were freshly fractured and mounted onto pin-type SEM stubs using colloidal carbon cement, and then sputter coated with a thin conductive layer of gold-palladium. The samples were examined in a Philips XL 20 SEM using the secondary electron imaging signal and a beam voltage of 20 kV.

Saturation-paste extracts using a 1:1.5 soil/water ratio were made in triplicate on three samples namely 4-ALP, 12-ALP, and 19-ALP. These samples were chosen as examples of normal, saline-sodic, and sodic soils, respectively. The extracts were analyzed for pH, electrical conductivity, various cations by inductively coupled plasma-optical emission spectroscopy (ICP-OES), and various anions by Dionex. The same three soil samples were also analyzed for exchangeable cations and cation exchange capacity by a standard 1 M  $\text{NH}_4\text{OAc}$  method at pH 8.5, followed by analysis by ICP.

Selected 0.2  $\mu\text{m}$  clay-fraction samples were analyzed by FTIR. Approximately 2 mg of each sample was incorporated in 13 mm KBr discs and spectra were

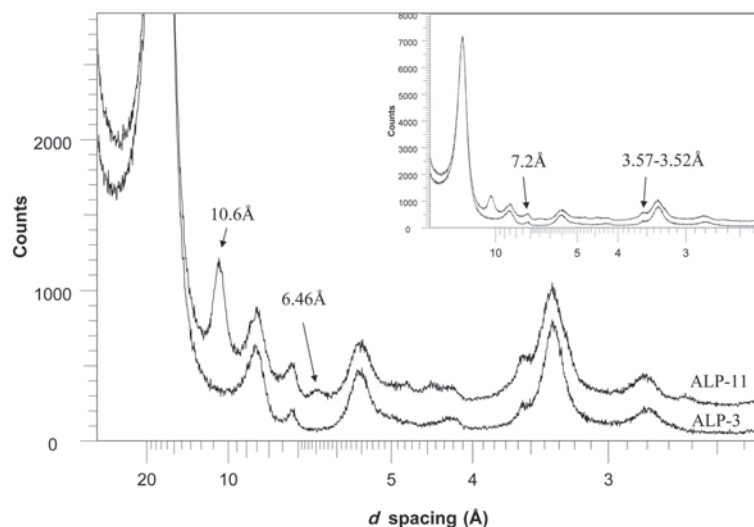


Figure 2. XRPD patterns of the glycolated fine clay fractions of sample 3-ALP (normal) and 11-ALP (salt-affected). Note the peaks due to palygorskite (10.6 Å, 6.46 Å) in 11-ALP. The insert shows a larger-scale trace of the smectite 001 reflection, including the locations of small peaks due to traces of kaolinite and/or chlorite.

recorded using a Nicolet Magna IR-550 FTIR spectrometer over the wavenumber range 340–4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . Spectra were recorded at room temperature and after heating the KBr discs to 150°C overnight to remove adsorbed water, each spectrum consisting of 400 co-added scans.

## RESULTS

### XRPD analysis

The XRPD patterns produced by air-dried, fine clays ( $N = 27$ ) of the normal un-irrigated (rain-fed) soils were dominated by a strong diffraction peak at  $\sim 15.2$ – $14.7$  Å which expanded on glycol solvation to 16.8–17.2 Å (Figure 2). In all but two cases, higher-order peaks of the ethylene glycol complex are clearly integral on the spacing of the main peak, confirming its identification as pure smectite. The two exceptions appear to have some 10 Å mixed-layering but are not illustrated or discussed further here. Small reflections at 7.2 Å and at 3.53–3.57 Å are also apparent in most samples. They

persist on heating up to 300°C but disappear on further heating to 550°C. This is consistent with the presence of minor kaolin. However, additional heating to 550°C produces a small but detectable peak at  $\sim 13.9$  Å in many samples, indicating the presence of trace amounts of chlorite in the fine clay fraction. Quantitative analysis of the fine clay fraction indicated >95% smectite for all samples, with the sole exception of the basalt clay sample (1-ALP) where a greater proportion of kaolin was found (Table 2).

Three of the fine-clay fractions of the rain-fed samples also showed the presence of minor amounts of palygorskite. In stark contrast, palygorskite was identified as a common component of the irrigated saline, and saline-sodic set of soils. The occurrence of palygorskite is indicated mainly by the appearance of peaks at  $\sim 10.6$  Å and 6.46 Å, (Figure 2) though in samples where it is most abundant, other peaks are also detectable. Quantitative analysis revealed that palygorskite may account for up to 20% or more of the fine-clay fraction of the irrigated soils (Table 2). In other respects the clay

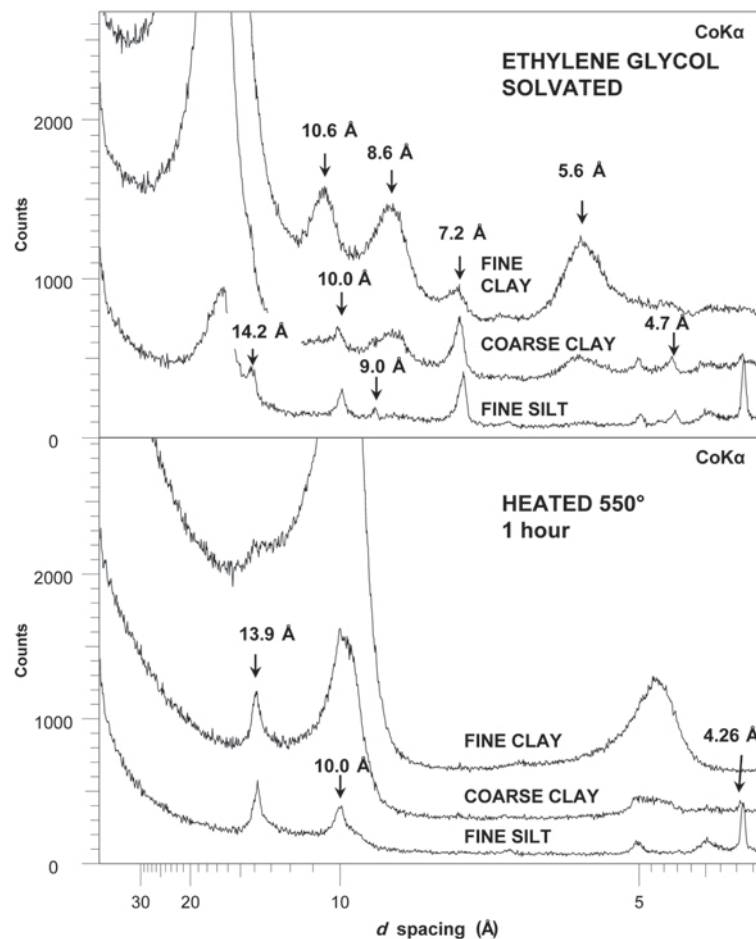


Figure 3. XRPD patterns of different size fractions of sample 15-ALP (ethylene glycol solvated and heated to 550°C), showing the changes in mineralogy as a function of grain size. Note the 10.6 Å peak for palygorskite in the trace of the fine clay fraction (glycolated).

mineralogy of the fine clay fraction of the irrigated soils is similar to the rain-fed soils, being dominated by smectite but also containing minor to trace amounts of kaolin and chlorite.

Analysis of coarse clay and fine silt fractions showed that palygorskite was generally less evident in these fractions compared to the fine clay. In addition, small amounts of illite, with a peak at 10.0 Å, are obvious in the coarse clay and fine silt, and chlorite is also clearly more abundant in these fractions relative to fine clay (Figure 3).

For the five soil pedons examined from the irrigated soils, palygorskite was detected at all depths, but no consistent trend in its abundance was observed, with abundance sometimes increasing with depth and sometimes decreasing (Table 2).

Application of the Greene-Kelly test to around half of the samples showed that the smectite could still be substantially expanded with both glycerol (17.8–18.2 Å) or ethylene glycol (16.8–17.2 Å) which is interpreted as evidence of an important beidellitic component. However, in many samples, enhanced diffraction in the region of 9.6 Å, corresponding to a collapsed smectite 2:1 layer spacing, suggests that the samples also contain a component that behaves like montmorillonite. In others, the relative intensity of the smectite 002 reflection is enhanced; this may be due to some sort of interstratification effect of collapsed and expanded layers (Figure 4), and yet others appear intermediate. To estimate the proportions of beidellite-like and montmorillonite-like components, it was assumed that the peak due to expanded layers diffracts with about five times the intensity of an equal weight of collapsed layers, as per the factors used for clay-mineral quantification. With this assumption, the behavior following the Greene-Kelly test indicates that the beidellitic component tends to dominate, although in some samples the amounts of beidellite-like and montmorillonite-like layers are sub-equal. Many of the fine-clay fractions were also tested for solubility in 6 M HCl. For the most part, the results showed that the smectite was readily soluble, presumably indicating an Fe-rich composition, although some samples did not dissolve completely. This indicates some degree of smectite heterogeneity, in accordance with the results of the Greene-Kelly test. A relatively Fe-rich average composition for the smectite is also indicated by the position of the 06 band, which is located at ~1.510 Å in the random powder diffraction patterns of the whole soil.

Analysis of the mineralogical composition of the bulk soils also showed a distinct difference between the two groups of soils with palygorskite detectable in only one of the rain-fed soils but detectable and quantifiable in 22 of the 26 salt-affected soils (85%). Quantitative analysis showed that palygorskite commonly accounts for at least 5 wt.% of the <2 mm bulk soil, and in two cases accounted for >20 wt.% (Table 2, Figure 5). Other

Table 2. Mineralogical compositions of the 0.2 µm clay fraction and corresponding bulk soil.

Sample Status	Sample code	0.2 µm clay fraction					Bulk soil							Total			
		Di-smec.	Kaolin	Paly.	Ill.	Chl.	Qtz	Plag.	Pyrox.	Cal.	Dol.	Illm.	Hem.		NaCl	Kaol.	Smec.
Rainfed	2-ALP	99.1	0.9	—	trace	11.3	1.0	2.1	0.9	1.1	1.2	1.2	—	3.0	79.2	—	99.8
"	2-ALP	98.9	1.1	—	trace	11.4	0.8	2.1	1.0	1.2	1.1	1.1	—	3.0	78.2	—	98.8
"	2-ALP	98.6	1.4	—	trace	10.7	0.5	1.8	2.5	0.9	1.1	1.1	—	3.7	78.9	—	100.1
"	2-ALP	94.2	1.5	4.3	trace	4.7	12.2	9.7	9.8	1.1	1.8	1.8	—	58.4	58.4	—	97.7
"	1-D-ALP	98.8	1.2	—	—	8.4	9.5	10.7	3.2	2.0	2.3	2.3	—	2.1	60.9	—	99.1
"	2-D-ALP	99.4	0.6	—	—	12.1	1.1	0.0	0.0	1.0	1.2	1.2	—	84.2	84.2	—	99.6
"	3-D-ALP	99.1	0.9	—	trace	10.9	1.8	—	0.0	0.6	1.1	1.1	—	1.9	81.9	—	98.2
"	4-D-ALP	99.4	0.6	—	—	11.1	1.9	3.7	1.4	1.4	1.8	1.8	—	2.5	74.4	—	98.2
"	5-D-ALP	98.6	1.4	—	—	11.1	1.1	1.2	1.9	1.0	1.5	1.5	—	1.6	83.0	—	102.4
"	6-D-ALP	99.0	1.0	—	trace	8.0	1.5	—	6.3	1.0	1.1	1.1	—	2.9	76.2	—	97.0
"	7-D-ALP	98.8	1.2	—	trace	8.1	2.9	—	7.0	1.2	1.2	1.2	—	2.3	79.6	—	102.3
"	23-D-ALP	99.0	1.0	—	—	7.0	4.3	—	3.8	1.3	1.4	1.4	—	2.0	79.4	—	99.2
"	24-D-ALP	98.5	1.5	—	trace	11.9	2.3	—	8.1	0.4	0.4	0.4	—	2.7	71.8	—	97.2
"	25-D-ALP	98.2	1.8	—	trace	15.9	1.4	—	9.3	0.3	0.6	0.6	—	3.7	68.3	—	99.5
"	27-D-ALP	98.5	1.5	—	trace	10.8	8.4	—	6.9	0.5	1.1	1.1	—	3.7	67.5	—	101.9
"	28-D-ALP	98.7	0.3	—	—	9.9	7.2	—	3.2	1.6	1.4	1.4	—	1.1	73.6	—	99.1

"	31-D-ALP	98.4	1.6	14.3	2.7	7.5	0.4	0.3	4.1	70.9	100.2
"	26-D-ALP	96.0	2.7	28.3	1.5	2.4		0.4	3.1	59.3	96.4
"	33-D-ALP	100.0		3.7	27.9	14.5	1.1	1.5	2.3	44.6	101.3
"	34-D-ALP	98.2	0.4	4.8	21.8	8.1	2.1	1.2	2.6	47.8	100.6
"	35-D-ALP	99.5	0.5	3.9	24.3	16.6	3.1	1.3	0.6	34.4	98.0
"	36-D-ALP	99.6	0.4	2.1	33.7	14.1	3.8	1.5		41.6	101.2
"	37-D-ALP	99.5	0.5	3.3	26.0	14.6	2.6	2.0	3.0	37.4	98.0
"	38-D-ALP	98.7	1.3	9.6	3.0	15.9	0.9	0.8	3.8	65.7	99.7
"	39-D-ALP	98.4	1.6	8.2	4.2	5.9	1.4	0.7	2.3	55.1	96.4
"	13-D-ALP	95.7	1.9	2.6	15.1	21.0	2.1	2.3	46.0	99.8	99.8
"	2-ALP	88.0	12.0	3.5	16.7	12.7	5.2	1.1	8.7	49.1	97.0
Saline	2-ALP	98.2	1.2	4.3	13.0	10.9	4.6	3.1	2.2	65.1	103.8
"	2-ALP	98.1	1.0	4.7	12.9	10.3	4.3	3.1	3.3	63.4	102.7
Saline sodic	2-ALP	93.2	2.0	4.5	21.8	13.1	10.8	3.8	1.8	38.0	4.8
"	2-ALP	90.3	1.6	4.5	14.7	9.9	10.8	4.0	3.8	46.2	5.2
"	10-ALP	85.9	2.4	6.0	15.8	9.3	11.0	5.6	2.6	42.7	9.8
"	11-ALP	84.8	2.4	6.2	11.1	3.9	13.4	6.8	2.2	41.1	11.4
"	12-ALP	75.6	1.1	23.3	17.3	3.2	11.8	6.5	2.3	40.2	11.0
Sodic	17-ALP	91.7	2.5	7.5	19.7	12.8	1.9	2.1	1.2	51.6	6.1
"	18-ALP	92.6	1.1	6.1	13.9	1.8	13.3	1.1	2.7	49.7	5.3
"	19-ALP	86.6	2.7	5.9	8.6	16.8	7.9	1.2	2.8	39.5	12.5
Saline sodic	13-ALP	89.7	1.8	6.1	7.2	25.2	0.4	1.3	2.1	52.4	10.2
"	14-ALP	88.8	2.6	6.5	11.0	16.7	0.6	1.6	2.3	51.6	7.8
"	15-ALP	87.7	2.5	6.1	17.2	8.1	0.9	2.4	1.0	58.2	4.1
"	16-ALP	92.3	2.1	5.7	18.6	8.9	1.1	2.4	1.4	62.4	2.8
Sodic	40-D-ALP	89.3	2.1	7.1	17.7	7.0	7.7	1.1	1.1	48.1	9.4
"	41-D-ALP	97.1	0.6	3.0	21.2	12.2	12.3	1.1	1.5	44.6	1.5
"	30-D-ALP	90.0	2.1	8.2	11.1	15.5	2.1	1.6	1.8	51.8	8.5
Saline sodic	32-D-ALP	75.3	2.1	8.9	5.8	15.5	0.5	1.2	3.9	48.2	14.3
Naturally saline sodic	29-D-ALP	96.1	1.8	4.7	23.0	9.9	12.1	0.8	1.9	42.1	2.3
Saline sodic	8-D-ALP	90.7	9.3	6.0	4.8	3.3	3.3	0.7	3.7	62.9	98.4
"	9-D-ALP	96.0	1.6	8.0	4.2	13.7	1.0	0.7	23.6	40.6	91.8
"	10-D-ALP	90.5	1.2	7.6	10.4	14.4	3.7	2.4	5.0	42.4	8.6
"	11-D-ALP	97.2	1.8	8.7	3.9	14.5	1.3	1.4	8.9	48.7	1.4
"	12-D-ALP	94.3	1.7	7.5	7.7	5.5	1.8	2.1	4.7	59.6	5.8
Sodic	42-D-ALP	83.8	0.9	6.0	9.0	12.9	0.4	1.8	4.1	51.4	20.1
Saline sodic	43-D-ALP	78.7	0.8	6.4	8.1	10.3	0.4	1.5	3.5	48.0	22.5

Cal.: calcite; Chl.: chlorite; Dol.: dolomite; Hem.: hematite; Ill.: illite; IIm.: ilmenite; Kaol.: kaolinite; Paly.: palygorskite; Plag.: plagioclase; Pyr.: pyroxene; Qtz: quartz; Smec.: smectite

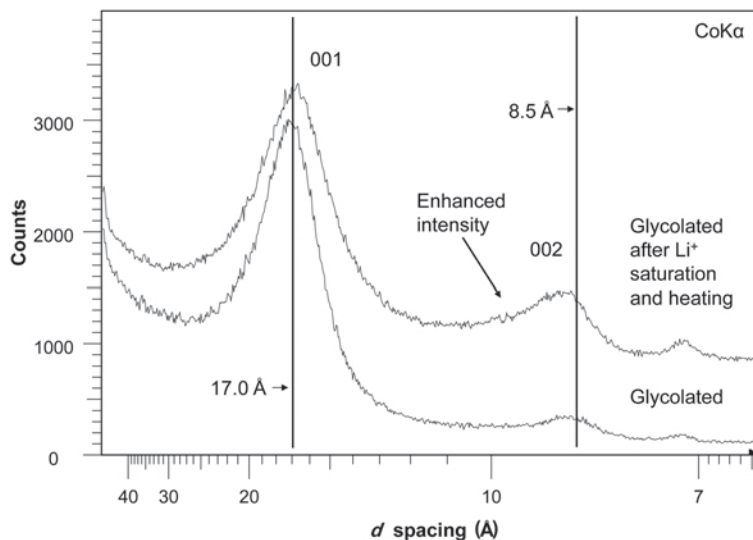


Figure 4. Comparison of XRD traces of sample 4-ALP (ethylene glycol-solvated), before and after the Greene-Kelly test.

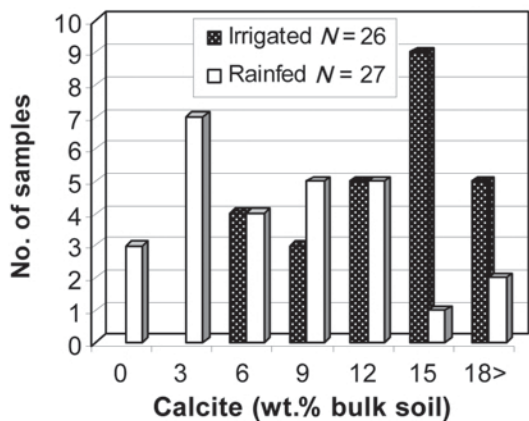
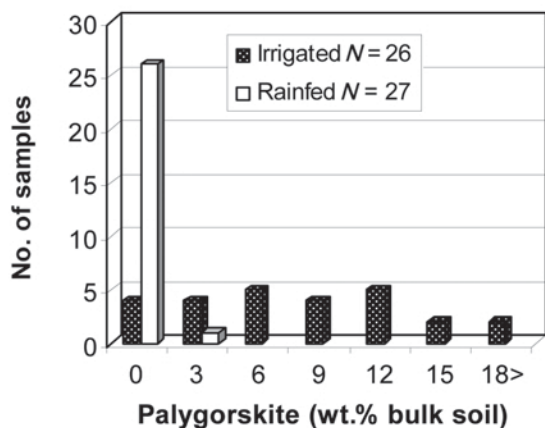


Figure 5. Histograms of palygorskite and calcite abundance in bulk-soil samples (<2 mm) for rain-fed and irrigated soils; actual data are given in Table 2.

minerals identified and quantified in the soil samples include quartz, plagioclase feldspar, pyroxene, calcite, dolomite, ilmenite, hematite, halite, kaolinite, and dioctahedral smectite. Examples of random powder XRPD patterns of two soils are shown in Figure 6. Apart from the obvious difference in terms of the presence and absence of palygorskite, the only other obvious mineralogical differences are the presence of halite and of dolomite in some of the irrigated soils. There is, however, also a tendency for a greater amount of calcite in the irrigated soils compared to the rain-fed soils (Figure 5, Table 2).

*IR spectroscopy*

The IR spectra of selected fine-clay fractions confirmed the identification of palygorskite in those samples where it had been detected by XRPD (Figure 7). The distinctive OH-stretching band at 3615 cm<sup>-1</sup> and bands due to coordinated water, e.g. at 3580 cm<sup>-1</sup> are clearly visible in the spectra, along with the high- and low-frequency Si–O stretching components at 1195 and 990 cm<sup>-1</sup>, which are characteristic of palygorskite (Russell and Fraser, 1994). The IR spectra also provide some information on the character of the smectite which has its OH-stretching band at 3622 cm<sup>-1</sup> while the position of the AlFe<sup>3+</sup>-OH deformation band at 875 cm<sup>-1</sup> indicates a relatively large Fe<sup>3+</sup> content.

*SEM and TEM studies*

Based on the XRPD results, three soils and their fine-clay fractions, from normal, un-irrigated (4-ALP), saline-sodic (12-ALP), and sodic soil (19-ALP) were used for SEM and TEM studies. The SEM of fractured surfaces of the normal un-irrigated soil showed the typical crinkly cornflake-like texture often observed for smectite (Figure 8). The edges of the flakes appeared

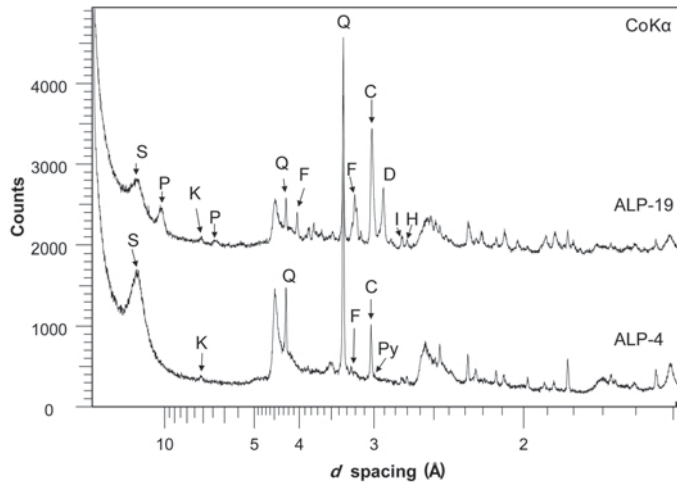


Figure 6. Random XRPD patterns (without added corundum) of samples 4-ALP and 19-ALP illustrating some of the main minerals identified. Some of the main peaks are labeled S = smectite, P = palygorskite, K = kaolin, Q = quartz, F = feldspar, C = calcite, D = dolomite, H = hematite, I = ilmenite, Py = pyroxene.

smooth, as well as slightly rounded, the latter possibly due to deposition of too much gold coating. In contrast, the saline-sodic and sodic soil revealed that, under high magnification, the edges of the clay flakes appear ragged. At the highest magnification, this ragged appearance can be seen to be due to bundles of fibers that seem to sprout from the edges of the more platy clay (Figure 8). Although the fibers appear somewhat rounded, this is again believed to be due to over-deposition of the gold coating and these fibers are reasonably assumed to be from the palygorskite identified by XRPD.

In the TEM, the occurrence of palygorskite in the saline-sodic and saline soils was very clear, as was its absence in the normal rain-fed soil (Figure 9). Indeed, the laths of palygorskite seemed to be far more obvious in the TEM images of samples 12-ALP and 19-ALP than one might have anticipated, given that XRPD analysis indicated mass fractions of ~20% and ~10% palygorskite, respectively, for these fine-clay fractions. This might be

due to the much poorer imaging characteristics of the very finely dispersed smectite. Measurements of the lath dimensions indicate an average length of 535 nm and width of 32 nm ( $N = 50$ ). These dimensions are comparable to those of the fibers observed on the ped surfaces in the SEM. Table 3 presents the elemental composition of six fibers (wt.% oxide) analyzed by ATEM, and the data cast as structural formulae assuming 21 oxygen equivalents. These data are similar to two Fe-rich palygorskite analyses listed by Weaver and Pollard (1973), reproduced in Table 3. The analysis presented by Siddiqui (1984) for palygorskite in lacustrine sediments formed from weathered Deccan basalts in an intertrappean sedimentary interval is also similar to data from the present study and is reproduced for comparison (Table 3). Other examples of palygorskite formed in association with basaltic or other basic igneous rocks also appear to be relatively Fe-rich (Rogers *et al.*, 1954; Long *et al.*, 1997). Weaver and Pollard (1973) pointed out that Fe-rich palygorskites tend to occur as 'short' fibers, <1  $\mu\text{m}$  long, an observation to which the current samples appear to conform.

#### Analysis of saturation-paste extract, and exchangeable cations

For the saturation-paste extracts (Table 4), three replicates were measured and the data were plotted in a smectite-palygorskite stability diagram (Figure 10), constructed as per the method used by Elprince *et al.* (1979). The results indicate that the saturation-paste extract composition of the normal soil plots within the stability field of smectite, whereas the sodic soil is close to, and the saline-sodic soil within, the field of palygorskite. The shift in the location of the points for the saline and saline-sodic soil relative to the normal rain-fed soil is due to increase in soil pH, and the activity of Mg and to some extent Si. The cation

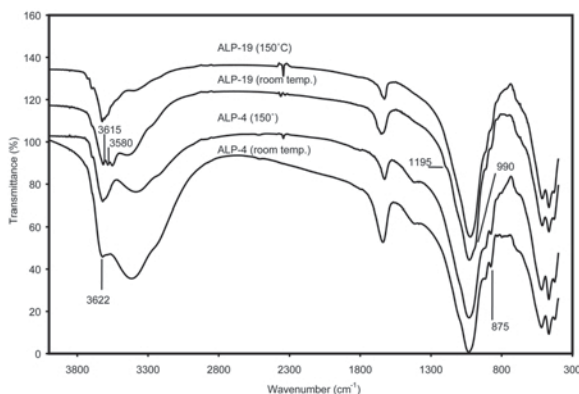


Figure 7. IR spectra of samples 4-ALP and 19-ALP, at room temperature and after heating to 150°C overnight.

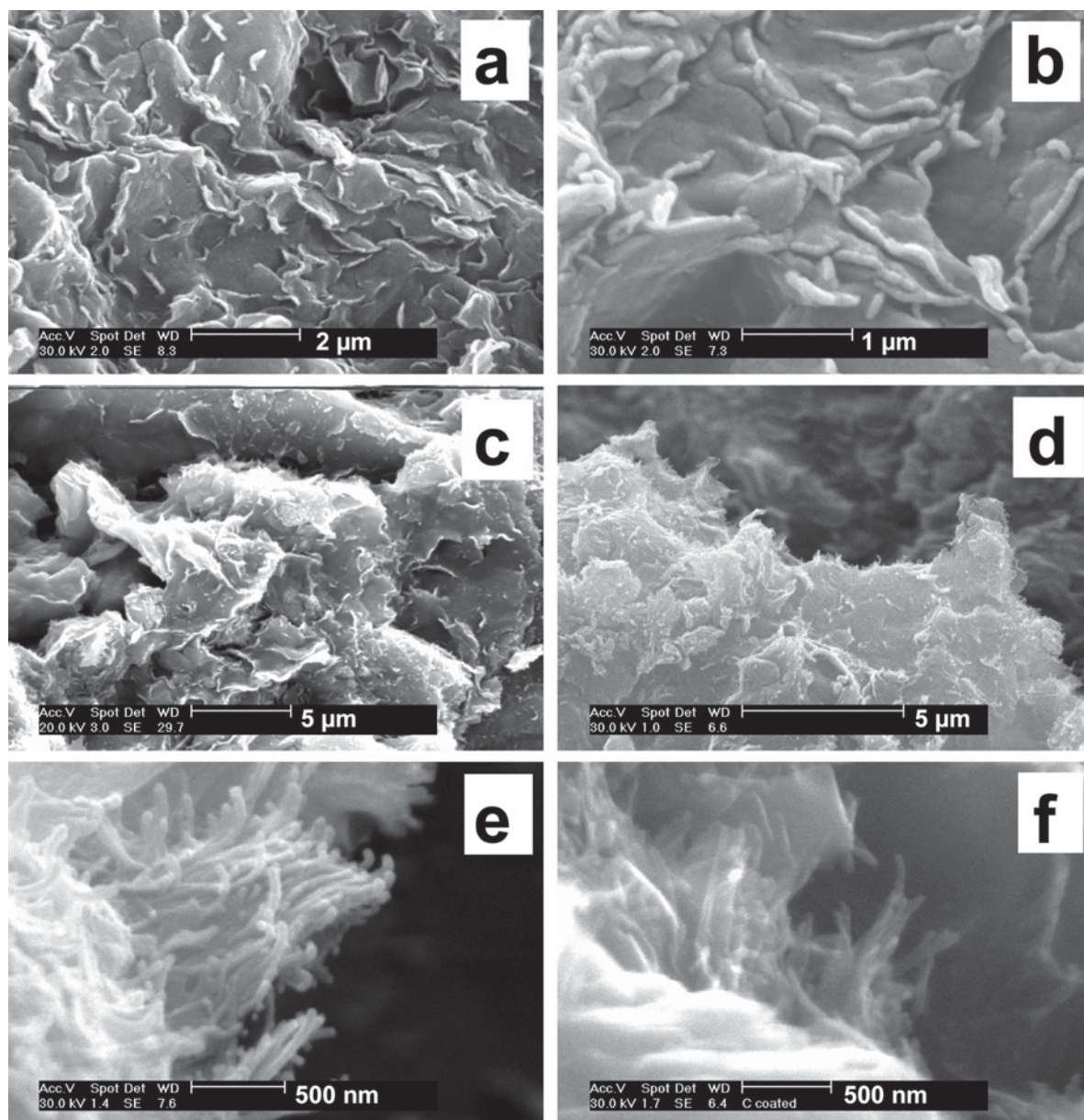


Figure 8. SEM images: (a,b) from sample 4-ALP, showing the smooth edges of smectite particles; the rounded appearance is due to over-deposition of gold coating; (c,d,e,f) from sample 12-ALP. At moderate magnification (c,d) the edges of smectite flakes appear much more ragged, and small fibrous protrusions are apparent. At high magnification (e,f) bundles of fibers, identified as palygorskite, are apparent. In (e), over-deposition of gold gives the fibers a rounded appearance; the image shown as in (f) is taken with a thin carbon coating for comparison.

exchange data (Table 5) show that the main exchangeable cations are Ca, Mg, and Na, and that the percentages of exchangeable Na and Mg both increase in the saline and sodic soil compared to the rain-fed soil. The change in the CEC may be related to the change in the kinds and amounts of clay minerals present in these three samples. Thus, assuming a typical CEC of 100 meq per 100g dry weight for smectite and assuming a CEC of 30 for palygorskite (Singer, 2002), the CEC values of the <2 mm soil would be predicted to be 78.9, 43.5, and

43.3, for samples 4-ALP, 12-ALP, and 19-ALP, respectively. These predictions, based on the whole-soil quantitative mineralogy, are in very good agreement with the measured values (Table 5).

## DISCUSSION

Previous studies of the shrink-swell soils of India have clearly demonstrated the predominance of smectite in these soils (Pal and Deshpande, 1987; Bhattacharya *et*

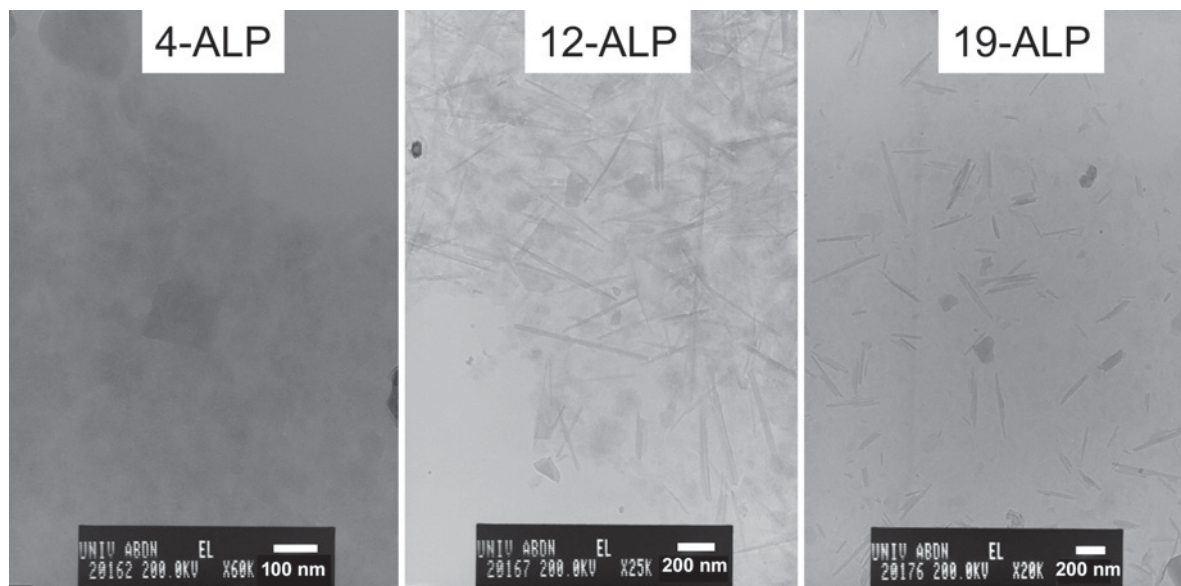


Figure 9. TEM images of fine clay fractions from samples 4-ALP, 12-ALP, and 19-ALP. Palygorskite fibers are very apparent in 12-ALP and 19-ALP, but not observed in 4-ALP.

*al.*, 1993, 1997; Pharande and Sonar, 1997; Shirsath *et al.*, 2000; Pal *et al.*, 2000). The smectite is believed to be inherited, derived from an alluvial redistribution of the weathering products of the Deccan trap basalts under a somewhat more humid climate than that of the present day (Pal and Deshpande, 1987; Pal *et al.*, 2000). In an early review of the mineralogy of the black soils of India, Gosh and Kapoor (1982) concluded that the smectites were predominantly mixtures of a beidellitic

and nontronitic nature, a conclusion based on chemical data. Pal and Deshpande (1987), however, found that a montmorillonite-like component with layer charge originating from the octahedral sheet was the dominant kind of smectite present, although it was admixed with a smaller amount of beidellite. This conclusion was based on the results of the response of the smectite to solvation with glycerol and also application of the Greene-Kelly test. In terms of its response to the Greene-Kelly test, our

Table 3. Wt.% oxide data and structural formulae of palygorskite laths analysed in the TEM, also shown for comparison are formulae for analyses 8 and 15 from Weaver and Pollard (1973) and that of an intertrappean palygorskite from Siddiqui (1984).

No	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	MnO	CaO	K <sub>2</sub> O
12FCT-A	66.1	0.2	16.0	12.0	0.0	4.7	0.0	0.0	1.0
12FCT-B	68.6	2.9	8.4	10.9	0.0	8.3	0.0	0.9	0.0
12FCT-C	70.9	0.5	10.9	9.5	0.0	7.7	0.0	0.4	0.0
19FCT-A	68.7	0.0	12.1	10.0	0.0	9.2	0.0	0.0	0.0
19FCT-B	63.8	0.0	17.1	6.8	0.0	11.7	0.0	0.6	0.0
19FCT-C	69.8	0.0	10.5	10.5	0.0	8.9	0.0	0.0	0.3
No	Si	Al(T)	Al(O)	Ti	Fe3	Mg	Sum(O)	Ca	K
12FCT-A	7.63	0.37	1.81	0.02	1.04	0.80	3.67	0.00	0.14
12FCT-B	7.91	0.09	1.06	0.25	0.94	1.44	3.69	0.11	0.00
12FCT-C	8.07	0.00	1.46	0.04	0.82	1.31	3.63	0.05	0.00
19FCT-A	7.86	0.14	1.48	0.00	0.85	1.56	3.90	0.00	0.01
19FCT-B	7.29	0.71	1.60	0.00	0.59	2.00	4.19	0.07	0.00
19FCT-C	7.99	0.01	1.40	0.00	0.91	1.52	3.83	0.00	0.04
W&P 8	7.31	0.69	1.34	—	0.81	1.66	3.81	0.04	-
W&P 15	7.64	0.36	1.73	—	0.63	1.45	3.81	0.20	-
Siddiqui*	7.80	0.20	1.13	—	0.87	1.83	3.83	0.14	0.23

\* includes 0.03 Na

Table 4. Saturation-paste extract and other data for three samples (three replicates); cation/anion concentrations are in mg L<sup>-1</sup>.

Parameters	4-ALP			Normal (Rainfed)			12-ALP			Saline sodic			19-ALP			Sodic		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
pH	7.58	7.73	7.65	8.00	8.11	8.00	8.29	8.00	8.25	8.29	8.00	8.25	8.00	8.25	8.25	8.00	8.25	8.25
EC dS m <sup>-1</sup>	0.27	0.31	0.32	3.29	4.16	4.22	0.4	0.4	0.39	0.4	0.4	0.39	0.4	0.4	0.39	0.4	0.4	0.39
Ca	46.56	47.95	48.02	31.62	33.52	32.85	6.40	6.51	6.17	6.40	6.51	6.17	6.40	6.51	6.17	6.40	6.51	6.17
Mg	8.19	8.41	8.45	28.30	30.18	29.66	9.38	9.52	8.81	9.38	9.52	8.81	9.38	9.52	8.81	9.38	9.52	8.81
Na	6.00	6.14	6.26	890.80	947.50	925.30	80.66	81.54	77.40	80.66	81.54	77.40	80.66	81.54	77.40	80.66	81.54	77.40
K	0.76	0.81	0.87	1.69	1.70	1.84	0.48	0.50	0.50	0.48	0.50	0.50	0.48	0.50	0.50	0.48	0.50	0.50
Fe	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Mn	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Al	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Si	3.50	3.75	3.75	5.40	5.82	5.92	3.67	3.80	3.52	3.67	3.80	3.52	3.67	3.80	3.52	3.67	3.80	3.52
F	0.47	0.31	0.55	1.51	1.59	1.61	4.26	4.23	3.91	4.26	4.23	3.91	4.26	4.23	3.91	4.26	4.23	3.91
Cl	38.3	39.1	38.9	864.7	903.4	896.6	13.9	13.8	13.6	13.9	13.8	13.6	13.9	13.8	13.6	13.9	13.8	13.6
SO <sub>4</sub>	2.91	2.89	2.87	240.3	249.2	248.8	7.18	7.21	6.77	7.18	7.21	6.77	7.18	7.21	6.77	7.18	7.21	6.77
HCO <sub>3</sub>	93	93	93	98	117	112	163	163	163	163	163	163	163	163	163	163	163	163
NO <sub>3</sub>	0.44	0.5	0.58	1.78	1.88	1.83	0.54	0.56	0.53	0.54	0.56	0.53	0.54	0.56	0.53	0.54	0.56	0.53

results are in general agreement with the findings of Pal and Deshpande (1987) that the smectite is a heterogeneous mixture of montmorillonite and beidellite. For the samples examined, however, the results of the Greene-Kelly test are interpreted to indicate that the beidellitic component is dominant, although it must be noted that interpretation of the results of the Greene-Kelly test is not necessarily straightforward (Wilson, 1987a; Moore and Reynolds, 1997). However, the IR spectra do not indicate the dominance of a beidellitic component. Pal and Deshpande (1987) also documented the ready solubility of the smectite in HCl, as was also observed in the current work. The smectite in the soils studied, although clearly heterogeneous, is, on the whole, best described as predominantly Fe-rich and with a notable component of beidellite character (Wilson, 1987b). The results of the quantitative analysis of the <2 mm soil show that smectite accounts for ~40–80 wt.% of the various soils, leaving no doubt about the origin of their Vertic properties (Bhattacharyya *et al.*, 1997).

In addition to smectite, small amounts of kaolinite, chlorite, and illite or mica are commonly reported in previous studies of these soils, as reviewed by Pal *et al.*

(2000). The present study, to the authors' knowledge, is the first report of the widespread occurrence of palygorskite in these soils, as initially reported by Pharande *et al.* (2000). The XRPD results show that palygorskite may account for as much as 20% of the fine clay fraction and up to 20 wt.% of the bulk soil. Infrared spectroscopy and electron microscopy confirm the identification of the palygorskite in these soils. Given the relatively Fe-rich nature of the palygorskite, the standard used for quantification by XRPD may not be entirely appropriate since its Fe content is not known. However, calculated XRPD patterns for palygorskite indicate that changing the total proportion of octahedral sites occupied by Fe from a nominal 0.1 to an Fe-rich 0.25 would increase the reference intensity ratio for palygorskite and reduce the reported palygorskite values by only 10% relative. Aside from the identification and the quantification, an even more interesting aspect, however, is the clear demarcation in the distribution of palygorskite between the normal rain-fed soils, where it is essentially absent, and the salt-affected irrigated soils, where it is of almost ubiquitous occurrence.

Palygorskite has been reported with increasing frequency in many soils from semi-arid regions of the

Table 5. Exchangable cations and cation exchange capacity data (meq/100 g dry weight) (NH<sub>4</sub>OAc [pH 8.5] method). Also given is CEC predicted from bulk-soil smectite and palygorskite contents.

Sample	Status	Exch. Ca	Exch. Mg	Exch. Na	Exch. K	ESP	EMP	CEC-Tot	CEC-Pred.
4-ALP	Normal rainfed	63.6	14.9	0.2	0.6	0.3	18.8	79.3	78.9
12-ALP	Saline sodic	16.1	14.0	14.7	0.4	32.5	30.9	45.1	43.5
19-ALP	Sodic	16.2	24.7	2.4	0.3	5.4	56.8	43.5	43.3

world. Reviews of these occurrences have been given by Singer (1984), Jones and Galán (1988), and more recently by Singer (2002). In some studies, the occurrence of palygorskite is attributed to inheritance from palygorskite-bearing rocks, which can be found among the parent materials from which the soils were derived (Khademi and Mermut, 1998). Potential clearly also exists for inheritance *via* aeolian transport, which may act over very long distances. In many other cases circumstantial evidence is good that the palygorskite is of a pedogenic origin (Singer and Norrish, 1974; Abtahi, 1977; Yaalon and Wieder, 1976; Elprince *et al.*, 1979; Singer, 1984; Monger and Daugherty, 1991; Ducloux *et al.*, 1995).

As mentioned above, the mineralogy of the shrink-swell, black soils of this region of India, especially the presence of minor amounts of minerals that cannot be derived from basalt (*e.g.* quartz, K-feldspar, mica), suggests a phase of transport in the formation of these soils (Pal *et al.*, 2000). Inheritance of palygorskite from rocks other than basalt is therefore a possibility that requires some discussion. Indeed, as a first approximation, the ubiquitous quartz content of the soils (Table 2) indicates that rocks other than basalt have contributed, in one way or another, up to 10% of the soil mass. In fact, sources of palygorskite are possibly associated with the Deccan-trap basalts (Ramaswamy and Rao, 1967; Siddiqui, 1967, 1984; Shrivastava, 2000) where they occur as intertrappean lacustrine clays; that described by Siddiqui (1984) is a commercially exploited deposit of palygorskite in the State of Andhra Pradesh, to the south of the study area. Here the palygorskite occurs as a bed of clay up to 3 m thick, beneath and between Deccan basalts, in association with cherty limestones. The palygorskite is believed to have formed in a lacustrine environment with weathered basalt providing the source of Mg and other ions.

Although some potential exists for intertrappean palygorskite deposits to have provided a source of palygorskite, the mechanism of inheritance cannot adequately explain the distribution of palygorskite between the rain-fed and the salt-affected soils. The various samples investigated are widely distributed across the study area (Figure 1) and no geographic pattern to the occurrence of palygorskite was observed. As such the argument would indeed be convoluted to suggest that the parent materials for the irrigated salt-affected soils contained inherited palygorskite, whereas the rain-fed set did not. Both groups of soils were formed from similar parent materials and by the action of similar soil-forming factors.

Singer (1984, 2002) provided a list of three situations that are associated with pedogenic palygorskite: (1) modern soils affected by fluctuating ground water; (2) soils with sharp textural transitions; and (3) soils with pedogenic features not necessarily associated at present with soils such as calcretes. In relation to ground water,

Singer and Norrish (1974) were among the first to indicate that temporary waterlogged conditions or frequent wetting of calcareous pedon conditions were suitable for the neof ormation of palygorskite. In terms of chemistry, palygorskite-bearing soils are invariably calcareous, mildly alkaline, and commonly saline (Singer, 2002). Field observations in the study area indicated that irrigation under semi-arid conditions has enhanced the processes of alkalization by altering the ustic moisture regime to udic and even aquic. Thus, the changes in chemistry and soil moisture regime as a result of irrigation, which have enhanced the problems of salinity and sodicity, appear ideally suited to have promoted the pedogenic formation of palygorskite in the soils.

In addition to the changes in clay mineralogy, the saline and saline-sodic soils are also more calcareous (Figure 5); indeed in some soils from this set, dolomite was also clearly identified by XRPD. According to Pal *et al.* (2000) and Srivastava *et al.* (2002), the Vertisols of Maharashtra contain both pedogenic and non-pedogenic carbonates. The enhanced calcite contents of the irrigated soils and the presence of dolomite only in the latter set, and therefore presumably pedogenic dolomite, suggests a greater accumulation of pedogenic carbonates in the latter. Regarding dolomite, Singer (2002) notes that where palygorskite coexists with secondary dolomite, soluble Mg concentrations have evidently been adequate for palygorskite formation. The association of palygorskite with pedogenic carbonate and calcretes is well known (Watts, 1980). In fact, a report of palygorskite in calcrete samples, consisting of >70% calcite from the Saswad-Nira area on the eastern flanks of the Western Ghats, Maharashtra, was made by Patil and Surana (1992). A number of other authors have also noted pedogenic palygorskites in association with pedogenic dolomite (*e.g.* Watts, 1980; Mashhady *et al.*, 1980; Botha and Hughes, 1992). Again this indicates that the changes in soil chemistry have resulted in conditions that ought to be conducive to the formation of palygorskite, and this appears to be confirmed by the saturation-paste extract data (Table 4, Figure 10).

The textural evidence obtained by electron microscopy of fine palygorskite fibers protruding into open pore space and appearing to emanate from smectite substrates suggests that palygorskite formation occurred by alteration or transformation of precursor smectite. Many authors, as reviewed by Singer (2002), have already suggested this as a pathway for pedogenic palygorskite formation, and TEM studies of specimens from other environments have provided some details (Tazaki, 1987; Chen *et al.*, 2004). In addition, good evidence was given for the transformation of palygorskite to smectite in some settings (Paquet and Millot, 1973; Bigham *et al.*, 1980; Paquet, 1983; Aydemir, 2001; Krekeler *et al.*, 2005). Given that the saturation-paste extract data fall very close to the phase boundary between palygorskite and smectite and that the composi-

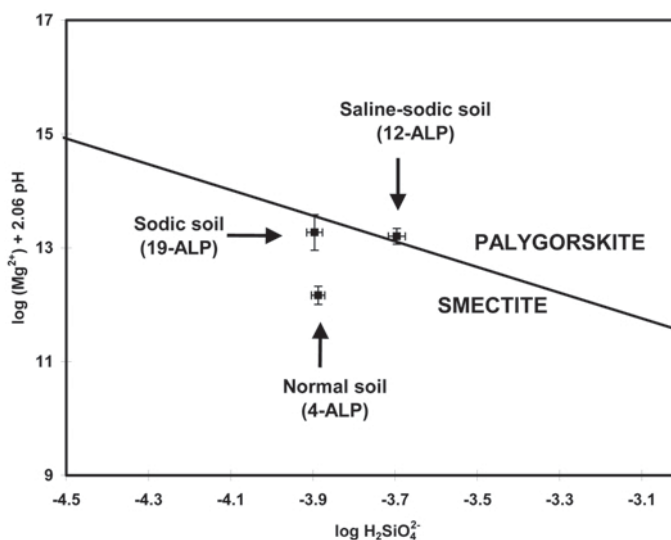


Figure 10. Saturation-paste extract data plotted in the smectite-palygorskite stability diagram as presented by Elprince *et al.* (1979).

tional fields of palygorskite and smectite overlap, the direction of reaction or transformation may be switched easily (Mackenzie *et al.*, 1984).

If the evidence for pedogenic formation of palygorskite in the studied soils is accepted as providing by far the most tangible explanation for palygorskite occurrence, then regardless of the precise mechanism of formation, the data on the distribution of palygorskite provide rather compelling circumstantial evidence that the rate of formation must have been exceedingly fast. Thus, palygorskite is abundant in those soils where irrigation has been implemented and only barely detected in those where rain-fed agriculture is practiced. This distribution implies that palygorskite formation is a result of the changes in chemistry and soil-moisture status brought about by irrigation. Since irrigation has only been introduced in the last 40–50 y, it follows that the formation of palygorskite must have occurred over this time period. Singer (2002) wrote that little is known about the time required for palygorskite formation and accumulation in soils and commented that the youngest soils commonly associated with pedogenic palygorskite are Holocene terrace or flood-plain soils. Essentially no information exists, however, as to the rate at which palygorskite formation can proceed. In the present investigation, apparently the rate would be effectively instantaneous from a geological perspective. At present, evidence for the rate of palygorskite formation is circumstantial and the possibility that those soils selected for irrigation have some other features in common that have predisposed them to pedogenic palygorskite formation over a longer period of time cannot be ruled out. Analysis of archived soils or archiving of soils prior to the expansion of irrigation into new areas are possible avenues for future research.

The feasibility of the formation of palygorskite from the evaporative concentration of irrigation waters was

demonstrated by Elprince (1985). The present investigation documents compelling circumstantial evidence that this is happening in the shrink-swell soils from Maharashtra State. Because trace amounts of palygorskite do occur in soils that have not been irrigated, these soils could have been poised on the boundary between smectite and palygorskite stability from a chemical point of view. As such, the chemical perturbations of salinity and sodicity and changes in ground-water regimes and water-logging brought about by irrigation must have been more than adequate to tip the balance in favor of the formation of palygorskite. Although clear evidence for such a rapid transformation of smectite to palygorskite in the soil environment has not been documented previously, Jacks *et al.* (2005), in a reference to an unpublished thesis by Arora (1991) stated "... in SW Punjab, in areas being waterlogged by the Indira Gandhi canal, newly formed sepiolite and palygorskite have been detected."

Palygorskite has also been reported in Vertisols from several other parts of the World, *e.g.* Jordan, Israel, Turkey, Cuba, and Iran (Khresat and Taimeh, 1998; Kapur *et al.*, 1997; Aydemir, 2001; Chizhikova, 2005; Heidari and Mahmoodi, 2006). Few studies have investigated the origin of palygorskite in other Vertisols, although Aydemir (2001) proposed the transformation of palygorskite to smectite in the Vertisols of the Harran plain in Turkey. Long *et al.* (1997) described an example of palygorskite formation from smectite in Miocene paleosols from China, which are believed to have been Vertisols and formed in association with basalts. The formation of palygorskite in the Indian soils described here may be an appropriate modern analog.

Neaman and Singer (2000) pointed out that nearly all palygorskite-containing soils are found in dry regions, where irrigation is indispensable for profitable agriculture. Concerned about the effects of irrigation on

palygorskite, Neaman and Singer (2000) investigated the release of Mg from palygorskite-bearing soils in a series of hydrolysis experiments. Singer (2002) highlighted the need for research about how palygorskite affects soil properties, particularly under sustained irrigation. Neaman and Singer (2004) reviewed the effects of palygorskite on the chemical and physio-chemical properties of soils. The results of the present investigation have shown that irrigation actually appears to have promoted the formation of pedogenic palygorskite which further highlights the need to understand how palygorskite may alter and affect soil properties. In the shrink-swell soils studied, the transformation of smectite to palygorskite has a clear effect on the CEC. Assuming the mass of palygorskite observed has replaced an equivalent mass of smectite, then the CEC may have been reduced by a third or more in many of the soils. Other important effects may be related to the possible preferential translocation of palygorskite in the soil profile (Neaman *et al.*, 1999; Kowsar, 2005), which, if it were to occur, may have undesirable effects on properties such as hydraulic conductivity.

#### CONCLUSIONS

The main clay mineral in the shrink-swell soils of Maharashtra is smectite, but where these soils have been irrigated, resulting in the accentuation of problems of salinity, sodicity, and water-logging, palygorskite is also present in the soils. Palygorskite may form as much as 20 wt.% of some soils, and is a short-fiber, Fe-rich variety. Textural evidence suggests the formation of palygorskite by transformation from smectite. All the soils examined, both irrigated and un-irrigated, are derived essentially from weathered basaltic material and the presence of palygorskite in the irrigated soils is believed to be a direct consequence of irrigation, and its effects on soil chemistry and moisture regime. This indicates that pedogenic palygorskite formation can be an extremely rapid process. The formation of palygorskite has decreased the CEC of the soils and may have an impact on other soil properties that are clearly undesirable from a soil-quality perspective.

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