Origin and distribution of clay minerals in calcareous arid and semi-arid soils of Fars Province, southern Iran

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ABSTRACT: The clay mineralogy of soils and of the main calcareous sedimentary parent rocks of southern Iran were investigated to determine their origin and factors controlling their distribution pattern in soils. The results revealed that the soil-available moisture plays the major role in the distribution pattern of palygorskite and smectite clay minerals in the arid and semi-arid areas studied. There is an inverse correlation between palygorskite and smectite with regard to the soil-available moisture as expressed by P/ET° (ratio of mean annual precipitation to mean annual reference crop evapotranspiration). At P/ET° values >0.4 palygorskite transforms to smectite. Smectite is thought to be mainly of 'transformed' origin. It is detected in trace amounts in soils of more arid areas and increases in soils having greater available moisture. The general decrease in illite content with depth is related mainly to its transformation to smectite under favourable moisture conditions of the deeper horizons. Palygorskite is considered to be inherited in plateau soils of the arid regions whereas in saline and alkaline soils and soils with high gypsum, it is mainly of authigenic origin. The P/ET° and gypsum content show a significant correlation with the palygorskite content. The occurrence of kaolinite in some soils is due to its inheritance from the surrounding kaolinite-bearing Cretaceous rocks. Illite and chlorite abundance in soils is also largely related to their presence in parent rocks. The rare occurrence of vermiculite in the studied calcareous soils is mainly related to its lower stability under high pH, low Al activity and the presence of large amounts of Si and Mg in soils.

KEYWORDS: clay mineralogy, palygorskite, smectite, P/ET°, gypsum, arid and semi-arid climate, clay pedogenesis.

Palygorskite, smectite, chlorite, illite, kaolinite and vermiculite are the main clay minerals occurring in arid and semi-arid regions. Chlorite and illite (micaceous minerals) are commonly believed to be inherited largely from parent rocks (Wilson, 1999). However, there is some evidence that mica in arid soils may form pedogenically as well, but only in special circumstances, mainly through K fixation of pre-existing smectite (Nettleton *et al.*, 1973; Mahjoory, 1975; Niederbudde & Kussmaul, 1978; Sanguesa *et al.*, 2000). Bronger *et al.* (1998)

found illite and vermiculite to be the two main pedogenically formed clay minerals in the B or Bt horizons of Holocene soils in Tadjikistan.

Environmental conditions are suggested to lead to smectite formation in Aridisols (Dregne, 1976; Boettinger & Southard, 1995). Smectite in arid soils has been noted in Iraq (Al Ravi *et al.*, 1969), Iran (Abtahi, 1977) and Saudi Arabia (Aba Huseyn *et al.*, 1980). Nettleton & Peterson (1983) considered smectite in argillic horizons of the Argid suborder as Pleistocene relics related to a more moist climate and to illuvial deposition to the soil.

Neoformation of smectite was reported by Gharaee & Mahjoory (1984) and by Givi &

Abtahi (1985) under saline and alkaline conditions with high concentrations of Si, Mg and Al in southern Iran. Abtahi & Khormali (2001) found smectite as a major clay mineral in poorly drained Calciaquolls of southern Iran. The relative abundance of smectite increases in the deeper horizons indicating that its weathering is accelerated in the surface soil (Ducloux et al., 1998).

Minor amounts of smectite were present in Oligo-Miocene parent rocks of central Iran (Khademi & Mermut, 1998), but no smectite was present in Cretaceous rocks of that region. Chlorite and illite were reported as the major clay minerals of Entisols of alluvial and colluvial fans of the southern Iran (Abtahi, 1977; Khormali & Abtahi, 2001).

Palygorskite in arid soils has been stated to originate from two main sources: (1) inheritance from parent materials; and (2) pedogenic formation through neoformation or transformation of 2:1 minerals. The presence of gypsum (Eswaran & Barzanji, 1974), calcrete or caliche (Roads et al., 1994; Singer et al., 1995; Lopez et al., 1996), in saline and alkaline groundwater (Abtahi, 1977) would favour the in situ formation of palygorskite from the soil solution. The occurrence of palygorskite in the soils and sediments of the Middle East generally corresponds to the area once covered by the post-Tethyan intermontane shallow lagoons during the Tertiary (Callen, 1984). Khademi & Mermut (1998) found palygorskite and sepiolite and appreciable amounts of mica and smectite in the clay fraction of the Oligo-Miocene limestone, but only traces of palygorskite in Cretaceous limestone. This indicates that the sedimentary environment of the study region during the Tertiary was suitable for the formation of palygorskite and sepiolite.

In arid regions of southern Iran, palygorskite is the major mineral in well drained Mollisols, while smectite is the major mineral in poorly drained Mollisols (Abtahi & Khormali, 2001). Singer (1989) noted that the frequent association of smectite and palygorskite is a result of the proximity in their stability fields. Paquet & Millot (1972) showed that palygorskite is not stable and transforms to smectite when annual precipitation is $\geqslant 300$ mm. Sanchez & Galán (1995) concluded that palygorskite forms as transformation products of smectite and illite. Sepiolite is rarely detected in soils by XRD, mainly because of its dissolution under NaOAC treatment in pH of 4.5 for the removal of carbonate (Abtahi, 1977, 1985). Under acidic conditions, sepiolite is destroyed more rapidly than palygorskite because of its magnesic composition and the larger size of its structural microchannels (Myriam, 1998). Moreover, sepiolite has a lower stability under the presence of high Al in soil which provides favourable conditions for the formation of palygorskite rather than sepiolite. Very few occurrences of vermiculite have been reported in soils of arid and semi-arid regions (Abtahi, 1977; Khademi & Mermut, 1998; Khormali & Abtahi, 2001).

Fars province, the study area, is one of the most important agricultural regions in Iran. Its wide range of climate, including xeric, aridic and ustic soil-moisture regimes and mesic, thermic and hyperthermic soil-temperature regimes, provides a suitable area to study the origin and distribution pattern of clay minerals. Therefore, the main objectives of this study were: (1) to investigate the origin of clay minerals in the calcareous arid and semi-arid regions of southern Iran; and (2) to determine the distribution patterns of clay minerals under different soil-available moisture regimes.

MATERIALS AND METHODS

Site description

Fars Province, the study area, is located in the southern part of Iran, ($50°30'-55°38'E$, $27°03'-31°42'N$, with a land area of 13.2 million ha (Fig. 1a).

Geology

Fars Province is part of the Zagros orogenic area (Fig. 1b). The Zagros mountain ranges, with a northwest to southeast direction, are extended towards the central parts of the province. Elevation varies from 500 m above sea level in the southern parts to ~4000 m above sea level in the northern areas. According to Zahedi (1976), the Zagros area underwent a relatively moderate orogenic phase (attenuated Laramian phase) near the end of the Cretaceous and the beginning of the Eocene, characterized by folding, emergence and erosion. The Laramian movements were succeeded by a shallow marine transgression. A later regression of the sea eastward resulted in the formation of intermontane lakes in the Middle Tertiary, which may have produced an environment conducive to the formation of fibrous clay minerals.
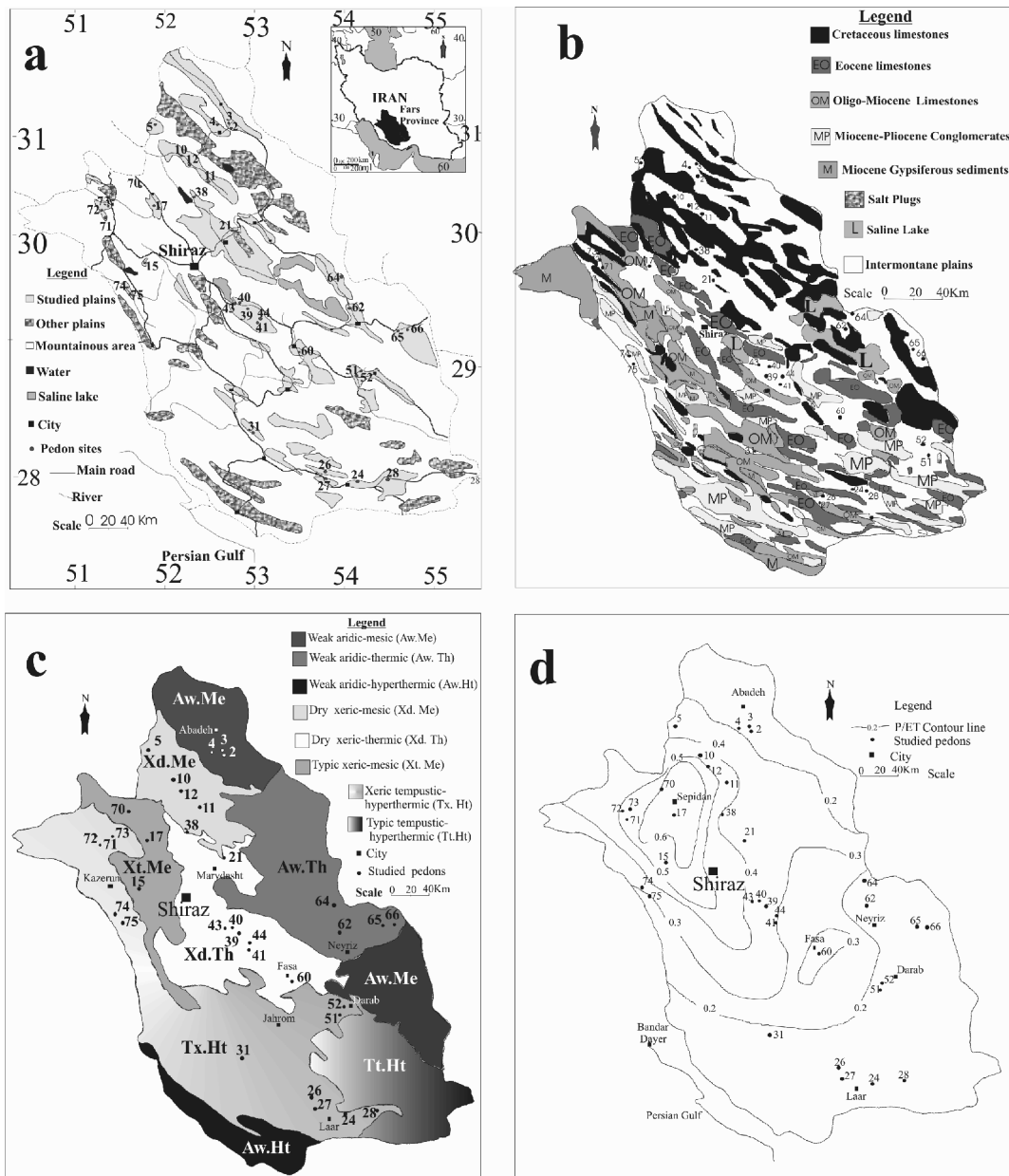
FIG. 1. (a) Location map and the sites of the different studied pedons, (b) geological map, (c) soil moisture and temperature regimes map and (d) average annual Iso-(P/ET°) lines for Fars Province.

The study area is therefore a part of the Post-Tethyan Sea environment rich in the evaporites (salts and gypsum) in most of the southern and southeastern parts.

Climate

Due to the geographical location of the Zagros mountain range, a major part of the rain-producing

air masses enter the region from the west and the northwest, with relatively large amounts of precipitation for those areas (600–900 mm, Table 1). Towards the south and southeast, a reduction of rainfall is observed. Furthermore, winter precipitation in the northwest area is in the form of snowfall, but for the other areas it is mostly in the form of rainfall. The mean annual precipitation for the province ranges from 50 to 1000 mm (MPB, 1994) (Fig. 1c,d).

Fars Province comprises xeric, ustic and aridic soil-moisture regimes along with mesic, thermic

and hyperthermic soil-temperature regimes according to the 'Soil Moisture and Temperature Regime Map of Iran' (Banaei, 1998). As shown in Fig. 1c, in mountainous areas of the northwest, the xeric moisture regime prevails. In the northern, northeastern and southern parts, the aridic moisture regime is dominant. The ustic moisture regime prevails in the western and south-central parts.

The agroclimatological index (P/ET°) was calculated for the Fars Province (Sadeghi *et al.*, 2002) and the ISO-(P/ET°) lines were plotted on the map of the province for area identification (Fig. 1d). The index is an important agricultural and biological criterion for crop growth in arid and semi-arid regions as well as a reliable weathering index based mainly on climatic factors for soil development and mineral weathering and transformation. The index varies (Fig. 1d) from <0.2 in arid areas of the north, east and south to >0.6 in mountainous regions of the northwest. This variation is in accordance with the soil moisture and temperature regime map of Fars Province.

TABLE 1. Climatological data of the studied pedons*.

Pedon	P (mm)**	T (°c)**	ET° (mm)[†]	P/ET°
2	149	13.58	1500	0.1
3	149	13.58	1500	0.1
4	149	13.58	1500	0.1
5	341.6	12.1	1000	0.35
10	346.8	12.3	800	0.45
11	346.8	12.3	800	0.45
12	346.8	12.3	800	0.45
15	698	12.5	1300	0.5
17	609	12.4	1000	0.6
21	328.2	15.89	1300	0.3
24	224	23.3	3000	0.1
26	224	23.3	3000	0.1
27	224	23.3	3000	0.1
28	224	23.3	3000	0.1
31	251	23.2	1900	0.13
38	338	14.8	900	0.4
39	288	18	1100	0.3
40	288	18	1100	0.3
41	288	18	1100	0.3
43	288	18	1100	0.3
44	288	18	1100	0.3
51	257	21.5	1900	0.14
52	257	21.5	1900	0.14
60	300	19.4	1100	0.3
62	224	15.85	1350	0.2
64	224	15.85	1350	0.2
65	173	16.7	1500	0.1
66	173	16.7	1500	0.1
70	856	10.4	900	>0.7
71	600	21	1300	0.5
72	600	21	1300	0.5
73	600	21	1300	0.5
74	400	22.2	1600	0.3
75	400	22.2	1600	0.3

* from Sadeghi *et al.* (2002)
** mean annual
[†] ET°; mean annual reference crop evapotranspiration

Fieldwork

Thirty intermontane plains were selected for this study (Fig. 1a). The total number of 75 soil series was selected on the soil survey maps, and pits were dug, described and classified, according to the Soil Survey Manual (Soil Survey Staff, 1993) and Keys to Soil Taxonomy (Soil Survey Staff, 1998), respectively. Thirty four representative pedons were considered for further mineralogical study. In addition, eight rock samples from the dominant geological strata were collected for mineralogical study.

Physicochemical analyses

Air-dried soil samples were crushed and passed through a 2 mm sieve. Particle-size distribution was determined after dissolution of $CaCO_3$ with 2 N HCl and organic matter was destroyed with 30% H_2O_2. After repeated washing for removal of salts, samples were dispersed using sodium hexametaphosphate for determination of sand, silt and clay fractions by the pipette method (Day, 1965). Alkaline-earth carbonate (lime) was measured by acid neutralization (Salinity Laboratory Staff, 1954).

Organic carbon was measured by wet oxidation with chromic acid and back titrated with ferrous

ammonium sulphate according to Nelson (1982). Gypsum ($CaSO_4.2H_2O$) was determined by precipitation with acetone (Salinity Laboratory Staff, 1954). Soil pH was measured with a glass electrode in a saturated paste. Electrical conductivity (total soluble salts) was determined in the saturation extract (Salinity Laboratory Staff, 1954). Cation exchange capacity (CEC) was determined using sodium acetate (NaOAc) at a pH of 8.2 (Chapman, 1965).

Mineralogical analyses

Removal of chemical cementing agents and separation of clay fractions was carried out according to Mehra & Jackson (1960), Kittrick & Hope (1963) and Jackson (1975). After repeated washing for removal of salts (including gypsum), the carbonates were removed using 1 N sodium acetate buffered at pH 5. The addition of 1 N sodium acetate was continued until no effervescence was observed with 1 N HCl (Jackson, 1975). The reaction was performed in a water bath at 80ºC. Organic matter was oxidized by treating the carbonate-free soils with 30% H_2O_2, and digestion in a water bath. This treatment also dissolved MnO_2. Iron oxides were removed from the samples by the dithionate citrate bicarbonate method (Mehra & Jackson, 1960) and iron was determined in the filtrated solution by atomic absorption spectroscopy.

The iron oxide-free samples were centrifuged at 750 rpm for 5.4 min (RCF = 157 g, International IEC Centrifuge) and clay separates were removed. Additionally, for removal of fine clay (particles <0.2 µm), clay separates were centrifuged at 2700 rpm for 40 min according to Kittrick & Hope (1963). X-ray diffraction (XRD) studies were carried out using a Philips diffractometer on both fine and coarse clay fractions, while equal concentrations of clay suspensions were used for all samples in order to allow for a more reliable comparison between relative peak intensities for different samples.

The (00*l*) reflections were obtained following Mg saturation, ethylene glycol solvation and K saturation. The K-saturated samples were studied both after drying and heating at 330 and 550ºC for 4 h. To identify kaolinite in the presence of trioctahedral chlorite, samples were also treated with 1 N HCl at 80ºC, overnight. The percentages of the clay minerals were estimated according to Johns *et al.*

(1954). Rock samples were ground and also treated with sodium acetate (pH 5) to remove carbonates and the clay fractions were separated using the centrifuge technique discussed above. A total number of 81 clay samples from soils and parent rocks were studied using XRD.

Electron microscopy studies

Small soil aggregates (~1 cm^3) were studied by scanning electron microscopy (SEM). Dried samples were mounted on Al stubs using double-sided tape and carbon paste, then coated with Au and examined using a LEO SEM. For TEM studies, suspensions of 1:500 (g dry clay/ml water) were prepared from dried soil and rock clay particles and 100 µl of the suspension were dried on 200-mesh formvar-coated Cu grids under a heat lamp for 25 min and examined using a LEO 906E transmission electron microscope (TEM).

RESULTS AND DISCUSSION

Physicochemical properties of the soils

The parent material of southern Iran is mainly limestone, and most of the soils are highly calcareous throughout. The electrical conductivities (EC) of the well drained soils are low, but in imperfectly drained soils which are mostly saline, it reaches a maximum of 240 dS/m (pedon 62). The total gypsum content of soils ranges from trace amounts in most pedons to ~30% in the By horizon of pedon 66. Only a few pedons have a high enough organic carbon content in their surface layers to meet the requirements of the mollic epipedon (pedons 51, 70 and 72). The pH range in the studied pedons is 7–8.5. The CEC of the soils which is dependent on the amount and the type of clay minerals, ranges from 3–4 cmole (+) kg^{-1} in coarse-textured pedon 52 to a maximum of 32 cmole (+) kg^{-1} in Bt horizon of pedon 70 (Table 2).

Clay mineralogy of soils and rocks

The semiquantitative analysis of clay minerals, in the studied rocks and soils are shown in Table 3. Chlorite, illite, smectite, palygorskite and kaolinite are the major clay minerals of both the parent rocks and soils. Studies by XRD and TEM of the sedimentary rocks in the study area revealed that

TABLE 2. Range, mean and median of some selected physicochemical properties of the studied pedons.

	Sand	Silt	Clay	OC*	Gypsum	CCE*	pH	EC* dS m⁻¹	CEC* cmol kg⁻¹
				%					
Range	31.7–76.4	7–69.2	7–54	0–2.8	0–30.6	9–74	7–8.6	0.2–240	3–32.1
Mean	31.7	38.1	30.3	0.4	3.9	43	7.9	11.8	14.6
Median	29.3	40	29.9	0.2	0.2	43	7.8	1.0	14.7

OC: organic carbon
EC: electrical conductivity
CCE: calcium carbonate equivalent
CEC: cation exchange capacity

TABLE 3. Relative abundance of clay minerals, CEC of the clay fraction, and Fe$_{DCB}$ of the studied soils and parent rocks.

Pedon	Horizon	Clay size*	Chl⁺ %	Ill⁺ %	Sme⁺ %	Pal⁺ %	Kao⁺ %	Ver⁺ %	Mixed layer %	CEC of clay cmol kg⁻¹	Fe$_{DCB}$ %
2	Ap	c	30	30	–	40	–	–	–	35	0.51
2	By2	c	20	20	–	60	–	–	–	35	0.33
3	Bk	c	20	30	<10	40	<10	–	–	36.5	0.83
4	Bky	c	20	25	15	40	–	–	–	42.5	0.62
4	By11	c	20	20	15	45	–	–	–	42.5	0.48
5	Ap	cc	30	35	25	–	10	–	–	45.5	0.99
5	Ap	fc	10	15	40	15	10	10	–	60	
5	Btk2	cc	30	25	30	–	15	–	–	47	0.58
5	Btk2	fc	10	20	35	15	10	10	–	57.5	
10	Ap	cc	25	35	25	–	15	–	–	44.5	1.02
10	Ap	fc	20	30	30	10	10	–	–	45	
10	Btk1	cc	35	30	25	–	<10	–	–	45	0.57
10	Btk1	fc	20	20	45	10	<10	–	–	56.5	
11	Bt2	cc	25	35	30	–	10	–	–	48	0.74
11	Bt2	fc	15	20	30	20	<10	10	–	56	
12	Ap	c	20	30	30	20	–	–	–	50	0.41
12	Bss2	c	15	15	40	20	<10	–	–	52.5	0.08
15	C	c	30	40	15	15	–	–	–	42.5	0.45
17	Ap	c	25	25	30	–	<10	10	–	53	0.74
17	Bk	c	15	20	35	–	20	10	–	55.5	0.73
21	Ap	cc	30	50	<10	–	<10	–	–	33.5	0.45
21	Ap	fc	15	20	20	30	<10	–	15% ill–sme	41	
21	Bt2	cc	30	50	<10	–	<10	–	–	33.5	0.4
21	Bt2	fc	20	25	20	35	–	–	–	45	
24	Cyz2	c	25	20	<10	45	–	–	–	36	0.12
26	Ap	cc	20	20	20	40	–	–	–	45	0.52
26	Ap	fc	15	10	<10	65	–	–	–	36	
26	Btk	cc	20	20	<10	50	–	–	–	36	0.39
26	Btk	fc	<15	–	–	85	–	–	–	35	
27	C	c	20	20	–	50	<10	–	–	31	0.26
28	Bk2	c	20	25	–	55	–	–	–	35	0.36
31	Ap	c	20	30	–	50	–	–	–	35	0.26
31	By2	c	15	30	–	55	–	–	–	35	0.26
38	Ap	cc	40	40	20	–	–	–	–	45	0.41
38	Ap	fc	20	15	35	20	<10	–	–	48.5	
38	Btk3	cc	40	30	20	–	<10	–	–	42.5	0.72

TABLE 3. (*contd.*)

Pedon	Horizon	Clay size*	Chl[+] %	Ill[+] %	Sme[+] %	Pal[+] %	Kao[+] %	Ver[+] %	Mixed layer %	CEC of clay cmol kg^{-1}	Fe$_{DCB}$ %
38	Btk3	fc	20	15	35	20	<10	–	–	50	
39	Bk1	c	30	25	10	30	<10	–	–	40.5	0.5
40	Btny	cc	20	20	25	35	–	–	–	47.5	0.43
40	Btny	fc	15	10	15	50	<10	–	–	40	
41	Ap	cc	20	20	20	20	–	–	20% ill–sme	39	0.6
41	Ap	fc	10	15	40	25	–	10	–	62	
41	Bty1	cc	20	20	25	35	–	–	–	47.5	0.5
41	Bty1	fc	20	10	10	60	–	–	–	40	
43	Cy1	c	20	10	10	50	<15	–	–	37.5	0.43
44	Ap	cc	20	30	10	40	–	–	–	40	0.56
44	Ap	fc	15	15	15	55	–	–	–	45.5	
44	Btk	cc	25	25	15	30	<10	–	–	41.5	0.6
44	Btk	fc	15	15	10	50	–	–	10% ill–sme	37	
44	By	cc	20	15	20	45	–	–	–	45	0.35
44	By	fc	15	10	15	60	–	–	–	42.5	
51	Apg	c	25	20	25	30	–	–	–	47.5	0.05
51	Bkg2	c	10	10	50	20	<10	–	–	57.5	0.09
52	Cz2	c	20	60	20	–	–	–	–	35	0.2
60	Ap	c	20	20	10	50	–	–	–	40	0.3
60	Bk1	c	10	25	15	50	–	–	–	42.5	0.32
62	Az	c	30	40	20	10	–	–	–	45	0.61
62	By2	c	30	30	–	40	–	–	–	35	0.38
64	Bk2	c	35	30	15	20	–	–	–	42.5	0.53
65	C	c	25	20	–	55	–	–	–	35	0.63
66	Btk	c	20	20	20	40	–	–	–	45	0.63
66	By	c	20	20	10	40	<10	–	–	37.5	0.55
70	A	cc	10	30	40	–	20	–	–	59	0.98
70	A	fc	10	15	30	<10	25	10	–	49	
70	Bt	cc	30	15	25	–	30	–	–	41.5	0.85
70	Bt	fc	15	15	40	<10	20	10	–	59.5	
71	Bk1	c	20	20	20	25	<10	–	10% chl–sme	41	0.42
72	Ap	c	30	30	20	10	10	–	–	43	0.64
72	Btk	c	20	20	20	30	10	–	–	39	0.54
73	C1	c	20	20	30	20	<10	10	–	61.5	0.62
74	Ap	c	25	35	–	40	–	–	–	35	0.31
74	By2	c	20	25	–	55	–	–	–	35	0.23
75	Bky	c	15	15	<10	60	<10	–	–	36.5	0.33
R1**	–	c	10	15	–	–	75	–	–	17	0.02
R2		c	25	20	25	30	–	–	–	22	0.28
R3	–	c	15	15	25	–	45	–	–	25	0.03
R4	–	c	–	5	–	–	95	–	–	12	0.24
R5	–	c	20	25	15	40	–	–	–	27	0.03
R6	–	c	20	20	20	–	40	–	–	26	0.01
R7	–	c	40	20	20	10	–	–	10% ill–sme	32	0.01
R8	–	c	15	10	10	65	–	–	–	25	0.02

* c: clay <2 μm; cc: coarse clay 2–0.2 μm; fc: fine clay <0.2 μm
[+] chl: chlorite, Ill: illite, Sme: smectite, Pal: palygorskite, Kao: kaolinite, Ver: vermiculite, ill–sme: illite–smectite chl–sme: chlorite–smectite
**: Rock samples

kaolinite is the dominant clay mineral in the Cretaceous rock samples (R1, R3, R4 and R6). In Oligo-Miocene and Pliocene samples, palygorskite is dominant (R2, R5 and R8). However, there is no palygorskite observed in the Cretaceous rocks. Chlorite and illite are present in all samples. Smectite is less abundant in two of the Cretaceous samples (R3 and R6), but is present in other, younger sediments (R2, R5, R7 and R8).

Both fine and coarse clay fractions were analysed by XRD in soils with argillic horizons to study their development and process of clay illuviation. Chlorite, illite, smectite, palygorskite and kaolinite are the main minerals in the total clay fraction. In the fine clay fraction, palygorskite is dominant in pedons 21, 44, 26, 72 and 66 and smectite in pedons 38, 5, 10, 70 and 11. Almost all the soils studied contain illite and chlorite as the major part of the coarse clay fraction. Kaolinite occurs in small amounts in many of the soils studied.

Palygorskite is the dominant clay mineral of pedons 2, 3, 4, 24, 27, 28, 31, 40, 41, 43, 44, 60, 62, 65, 74 and 75 (Table 3). These soils are mainly from more arid areas (Fig. 1). Smectite is the dominant clay mineral in soils with vertic properties (pedons 11 and 12) and in poorly drained Aquolls (pedon 51). Illite-smectite is the main interstratified clay mineral occurring in small amounts in some of the pedons. Mixed-layer chlorite-smectite is only present in small amounts in pedon 71. Vermiculite was only detected in small amounts in the fine clay fraction of pedons 5, 11, 17, 41, 70 and 73.

Table 3 also presents the CEC of the clay fraction and Fe_{DCB} of the studied soils and rocks. The CEC values range from 31 cmole/kg in pedon 27 to as high as 62 in the fine clay fraction of pedon 41. The CECs of coarse clays are consistently less than those of fine clay fractions. The higher CEC values of the fine clay in northwestern soils are in accordance with XRD results showing that they are dominated by smectite. The CEC values are in accordance with the clay mineralogical data. The Fe_{DCB} content of the soils ranges from <0.1% in pedon 51 to 1% in pedon 10. The Fe_{DCB} content of the rocks is very low.

Origin and distribution of clay minerals in soils

Illite and chlorite. Illite and chlorite are two commonly observed clay minerals occurring mainly in areas of steep relief where active mechanical erosion limits soil formation (Fanning *et al.*, 1989; Wilson, 1999). Their abundance in soils is largly due to their presence in parent rocks. They are the dominant clay minerals of the coarse clay fraction (Table 3). As presented in Table 3, the illite content of most of the soils of northwestern areas decreases with depth. Several processes may account for this decrease, such as aeolian deposition of this mineral (McFadden *et al.*, 1986), enhanced physical weathering of biotite grains in the near-surface horizons due to large daily and seasonal fluctuations in temperature and moisture and to limited lessivage in the aridic climate (Boettinger & Southard, 1995). In the present study, simple transformation of illite to other clay minerals (mainly smectite) may play a major role in the decrease in illite content with depth, especially in soils of the northwestern regions where the soil-available moisture increases, and provides a relative leaching environment for the release of K^+ from micaceous minerals and mainly illite. Moreover, the calcareous environment high in Mg and Si mobility might provide favourable conditions for the formation of smectite through transformation at the soil surface, and its subsequent lessivage results in greater accumulations of it in the deeper horizons.

As stated earlier, there is some evidence that mica may form pedogenically from K fixation in pre-existing smectites because of the hot and dry soil conditions (Mahjoori, 1975). However, illite (mica) constitutes the main part of all studied parent rocks, and its presence in soils is mainly of detrital origin. Chlorite is also inherited in the studied soils, as well as illite, but it does not show any regular pattern with increasing depth (Table 3). Chlorite and illite were reported as the major clay minerals of Entisols of alluvial and colluvial fans of the southern Iran (Abtahi, 1977; Khormali & Abtahi, 2001).

Kaolinite. Precipitation of kaolinite from solution requires acid conditions with moderate silica activity and small amounts of base cations. This clay mineral forms mainly from feldspars and mica alteration, in conditions of low K^+ activity and high H^+ activity (Curtis, 1983; Dixon, 1989). These conditions occur in warm and humid tropical and subtropical climates.

In the study area, kaolinite is mainly detected in the clay fraction of pedons located near the Cretaceous outcrops (Table 3, Fig. 2, mainly in pedons 5, 10, 11, 17, 70, 72, and in trace amounts in some other pedons). Thus it can be concluded
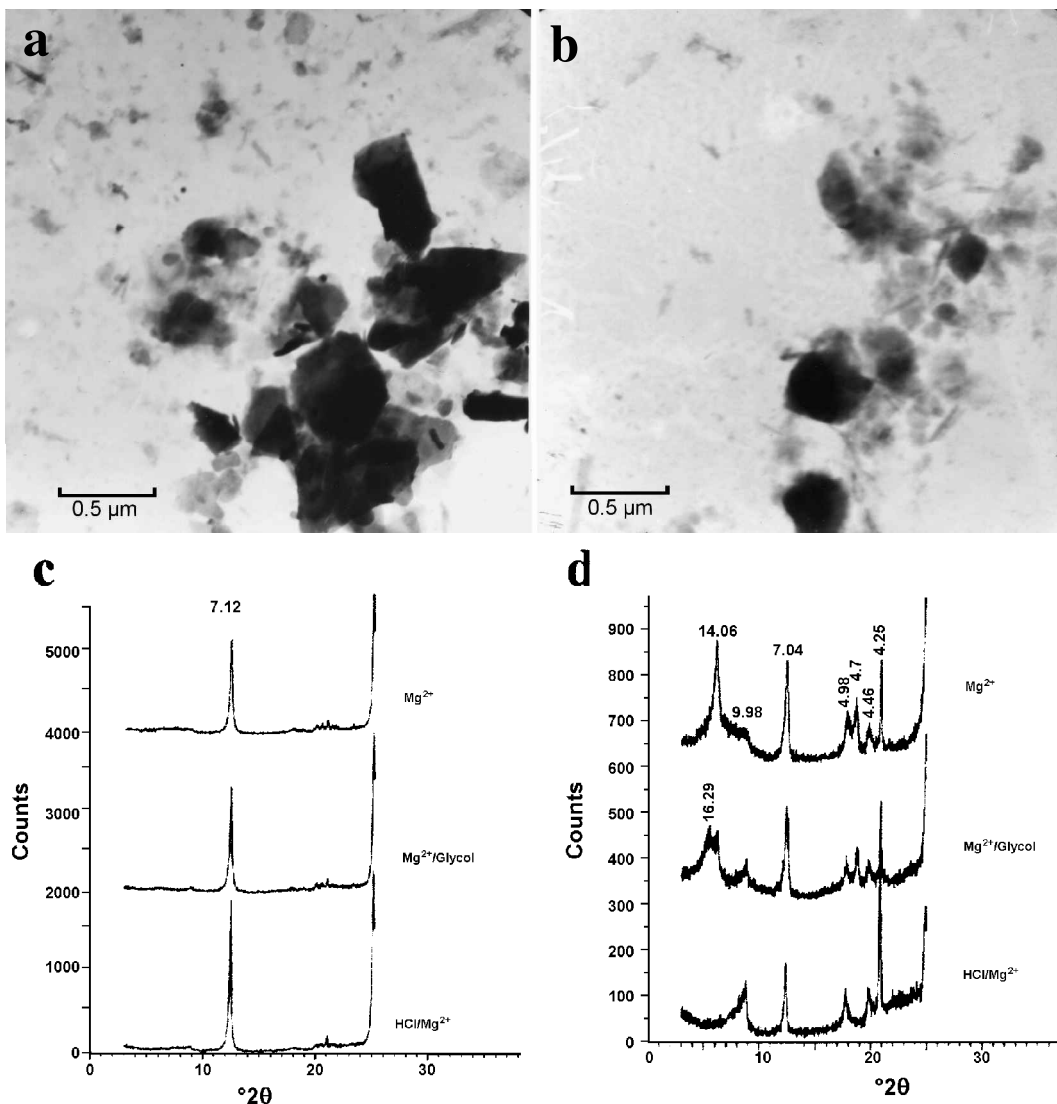
FIG. 2. TEM image of clay in Cretaceous rock (a) and in the Bt horizon of pedon 70 (b), showing hexagonal kaolinite and a few short palygorskite fibres. (c) and (d) are XRD patterns of clay in Cretaceous rock (a) and in the Bt horizon of pedon 70 (b), respectively.

that the presence of this clay mineral in the studied soils of arid and semi-arid regions is due to its inheritance from surrounding parent rocks. As shown in Fig. 2, the greater occurrence of kaolinite in pedon 70 is mainly related to the presence of kaolinite-bearing Cretaceous outcrops and high precipitation. There is no (or only traces of) kaolinite in the southern parts of the study area which are formed on or near geological formations which are younger than the Cretaceous sediments.

Smectite and palygorskite. As presented in Table 3, smectite constitutes the major portion of the clay minerals in the well drained Alfisols (pedons, 5, 10, 11, 21, 38, 41, 44, 70 and 72), some poorly-drained Mollisols (pedon 52), and Calcixerepts with high precipitation (pedon 17). It is detected in trace amounts in arid soils of the southern, southeastern, southwestern and northern parts. Figure 3 shows the distribution of smectite in soils of the study area. It can be concluded that in
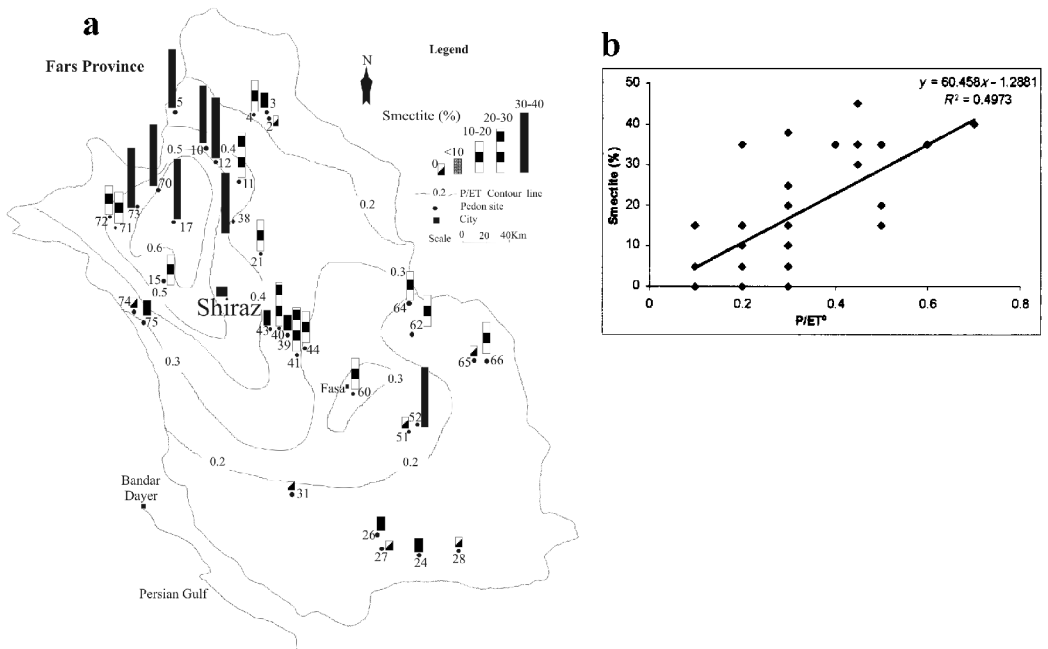
Fig. 3. (a) Distribution of smectite in different climatic regions of Fars Province; (b) smectite percentage (as an average for the soil profile) *vs.* P/ET°. $R^2 = 0.497$.

well-drained soils, with increasing soil-available moisture (as expressed in P/ET°), smectite shows an increasing trend.

There are three main sources of smectite in soils: (1) neoformation from soil solution; (2) detrital origin or inheritance; and (3) transformation of other clay minerals. Low-lying topography, poor drainage and base-rich parent material, favourable chemical conditions characterized by high pH, high silica activity and an abundance of basic cations are the factors strongly influencing the origin and distribution of smectite in soils (Borchardt, 1989; Aoudjit *et al.*, 1995). The presence of large amounts of this mineral in poorly drained pedon 52 (as discussed by Abtahi & Khormali, 2001) suggests a neoformational origin of this mineral under favourable soil solution conditions. Neoformation of smectite was also reported by Givi & Abtahi (1985) and Gharaee & Mahjoory (1984) under saline and alkaline conditions with high concentrations of Si, Mg and Al in southern Iran. However, neoformation can not solely explain the general increasing trend of this mineral with increasing soil-available moisture in relatively well-drained soils of the northwestern parts (Fig. 3).

Increasing soil-available moisture towards the northwest, and consequently a relatively more leaching environment for the release of K^+ from micaceous minerals and mainly illite, in the calcareous environment with high Mg^{++} and high Si mobility might provide favourable conditions for the formation of smectite through transformation. As discussed, earlier illite content decreases with increasing depth, unlike smectite which shows an increasing trend (Table 3). The presence of inter-stratified illite-smectite in some pedons could be an indication of an intermediate stage of illite transformation into smectite. Transformation of chlorite into smectite has rarely been reported, in contrast to many reports about illite to smectite transformation which seems rather more likely.

Palygorskite is the other possible precursor mineral for smectite in arid and semi-arid environments. Singer (1989) noted that the frequent association of smectite and palygorskite is a result of the proximity of their stability fields. Paquet & Millot (1972) showed that palygorskite is not stable at precipitation levels above 300 mm and transforms to smectite. Figure 4 shows that there is a reverse correlation between palygorskite and
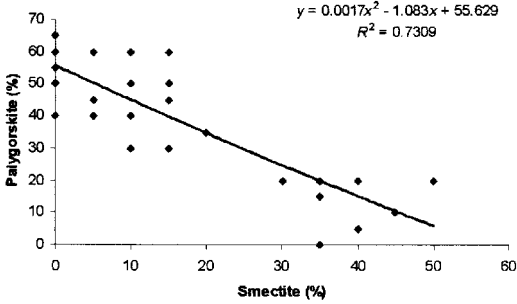
FIG. 4. Palygorskite (%) *vs.* smectite (%) in the studied pedons ($R^2 = 0.731$).

smectite in the soils studied. Smectite forms the dominant clay mineral of the argillic horizons when P/ET° is >~0.4 (Fig. 3, pedons 5, 10, 11, 38 and 70). However, in the argillic horizons of the arid regions (mainly pedons 26 and 66), palygorskite is the dominant clay mineral.

As discussed earlier smectite is also present in sedimentary rocks of late Cretaceous and younger deposits. Thus detrital origin must also be considered. However, this process is not a dominant source of smectite in soils, since there is no uniform distribution of smectite in soils near the smectite-bearing outcrops. In contrast to kaolinite, this correlation is not evident for smectite. Therefore, transformation seems to be the dominant factor for the formation and distribution of smectite in well-drained soils of the arid and semi-arid soils studied. Climate or soil-available moisture has a strong influence on the distribution and formation of smectite in the different parts of the study area. Smectite in less weathered C horizons of some soils is most probably of detrital origin (Pedons 15, 43 and 73, as reported also by Wilson, 1993).

In argillic horizons of arid regions (Pedons 26, 66) most evidence suggests that these minerals are Pleistocene relics related to a moister climate and to eluvial deposition in the soil (Nettleton & Peterson, 1983). The relative abundance of smectite in deeper horizons indicates that its weathering is accelerated in the surface soil. Moreover it is dominant in the fine clay portion. Therefore, it can also be concluded that smectite is the major illuviated clay mineral of the smectitic argillic horizons.

In contrast to smectite, palygorskite shows a decreasing trend with increasing soil-available moisture or decreasing aridity. Figure 5 shows the distribution of palygorskite in the studied soils of the Fars Province. The greatest occurrence of this
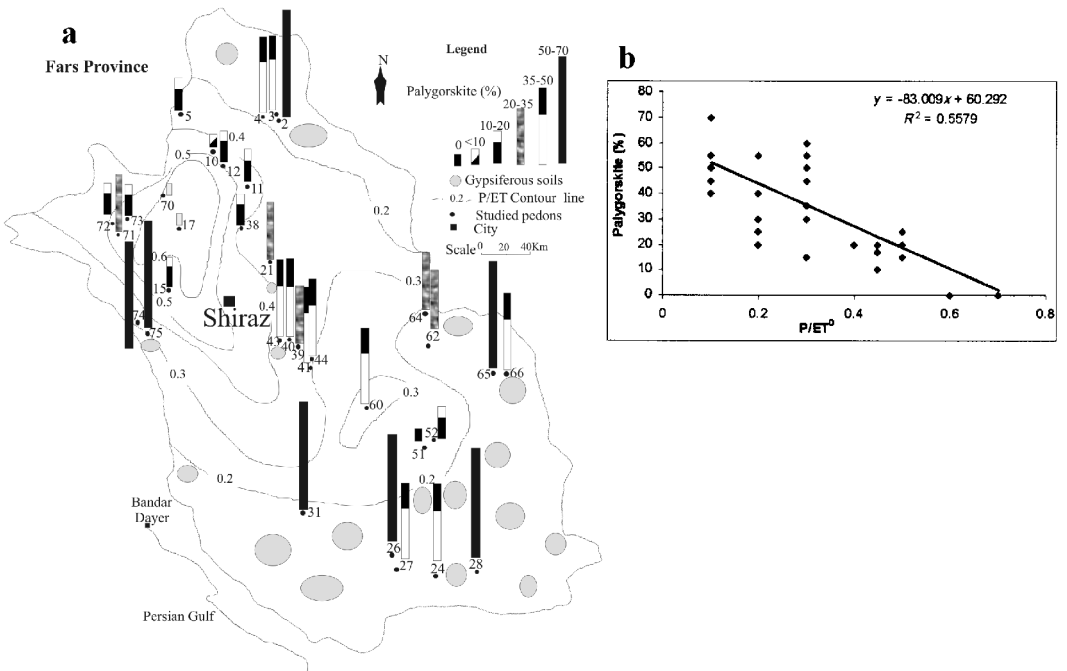

FIG. 5. (a) Distribution of palygorskite in different climatic regions of Fars Province; (b) palygorskite percentage (as an average for the soil profile) *vs.* P/ET°. $R^2 = 0.558$.

fibrous mineral is in the more arid areas of the south, southeast and north, and it occurs in small amounts or is even absent in soils of the north-western parts where there is more soil-available moisture (P/ET° >0.4).

Henderson & Robertson (1958) and Burnett *et al.* (1972) were the first to report traces of palygorskite in sediments and soils from Iran. Several researchers consider that palygorskite formed pedogenically in the soils of Iran (Abtahi, 1977, 1980; Mahjoory, 1979; Gharaee & Mahjoory, 1984; Khademi & Mermut, 1998, 1999).

An environment rich in Si and Mg with high pH but poor in Al and Fe is favourable for the formation of palygorskite and sepiolite (Singer, 1989). Palygorskite in arid soils has been stated to have two main origins: (1) inheritance from parent materials; and (2) pedogenic formation through neoformation or transformation of 2:1 minerals. The transformation of 2:1 clay minerals mainly illite or smectite to palygorskite in solutions high in Si and Mg and low in Al and K is a possible mechanism reported by many researchers (Suarez, 1994). As stated earlier, parent sedimentary rocks of Tertiary age and younger, contain considerable amounts of palygorskite which can be inherited by the adjacent soils. Therefore, this source of palygorskite can be a possible origin especially in more arid parts of the southern Fars province. Well preserved, long palygorskite bundles of plateau soils of southern arid regions (e.g. Pedon 26) formed directly on the late Tertiary sedimentary rocks (R5) containing a lot of palygorskite, are probably of inherited origin (Fig. 6). This was also indicated by Khademi & Mermut (1998) in plateau soils of central Iran. In pedon 26, palygorskite constitutes the majority of the fine clay especially in the argillic horizon. The presence of palygorskite in alluvial or colluvial soils (e.g. pedon 27) could also be related to inheritace from the parent rocks (detrital).

As mentioned ealier, gypsum would favour the *in situ* formation of palygorkite from soil solution. The distribution of gypsiferous soils in Fars Province is shown in Fig. 5. Gypsum, like other evaporite minerals, has been precipitated after drying the shallow saline and alkaline lakes present in the Tertiary. Due to the arid climate this soluble mineral is stable in those areas. As for palygorskite, gypsiferous soils also occur in more arid parts of the Fars Province.

The relationship of palygorskite with gypsum can be deduced from the SEM images (Fig. 7): this fibrous mineral is enmeshed with gypsum crystals and sprouts from their surfaces, which suggests their authigenic origin, consistent with the earlier observations of Khademi & Mermut (1998), Ingles & Anadon (1991), Singer *et al.* (1995) and Pletsch *et al.* (1996). It is known that gypsum would increase the Mg/Ca ratio of the host water which could in turn encourage palygorskite formation (Hassouba & Shaw, 1980). The relationship of palygorskite percentage to gypsum content of the soils and soil-available moisture (P/ET°) for the studied pedons is presented as the following equation:

Palygorskite (%) = 53.4 +
$$0.47 \text{ Gypsum } (\%) - 67.7 \text{ P/ET}°$$
$R^2 = 0.56, n = 34$

The percentage of palygorskite in soils is significantly related to the gypsum content and P/ET° of the soils. An increase in gypsum or decrease in P/ET° (or increase in aridity) would lead to higher levels of palygorskite in soils. As for smectite, palygorskite shows an increasing trend with depth, probably due to more favourable conditions in the deeper horizons mainly containing gypsum in arid regions (Table 3).

There is considerable palygorskite in soils of the Sarvestan area (Pedons, 39, 40, 41, 43 and 44), which were affected by the nearby saline and alkaline lake (Maharlu). These soils contain gypsum in their subsurface horizons. The presence of large
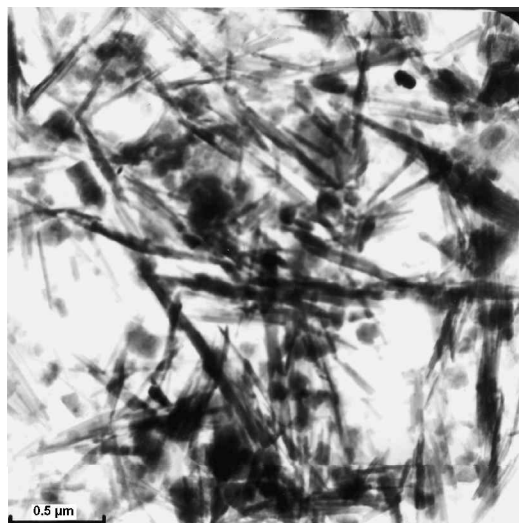

FIG. 6. TEM image of pedon 26, showing well preserved long palygorskite bundles.
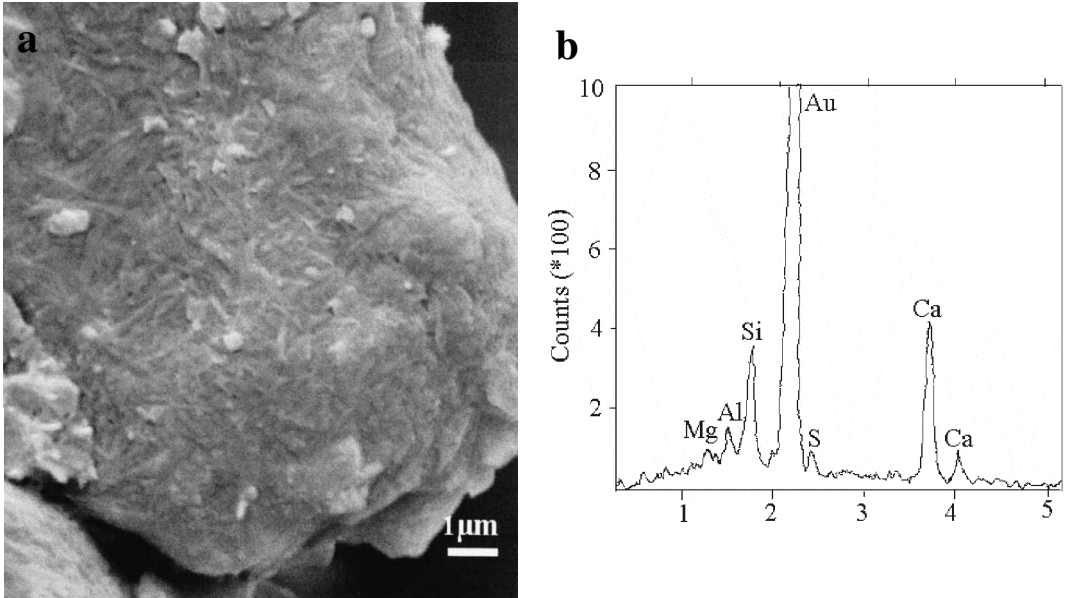
FIG. 7. (a) SEM image of pedogenic gypsum coated with palygorskite (pedon 74, By3); (b) elemental analysis of palygorskite fibres on gypsum crystals (SEM-EDX).

amounts of well bundled and elongated palygorskite in soils of this area with parent sedimentary rock containing little palygorskite (R7) could be related to their authigenic formation in the presence of gypsum (Fig. 8a). The presence of shallow saline and alkaline groundwater (pedons, 43, 62 and 24), could also have favoured the neoformation of palygorskite from soil solution. Under such conditions palygorskite may also form from smectite (Singer, 1989).

Towards the northwest, palygorskite decreases, whereas the smectite content of the soils increases. Figure 8b shows a few short palygorskite fibres in pedon 10, indicating their gradual disappearance
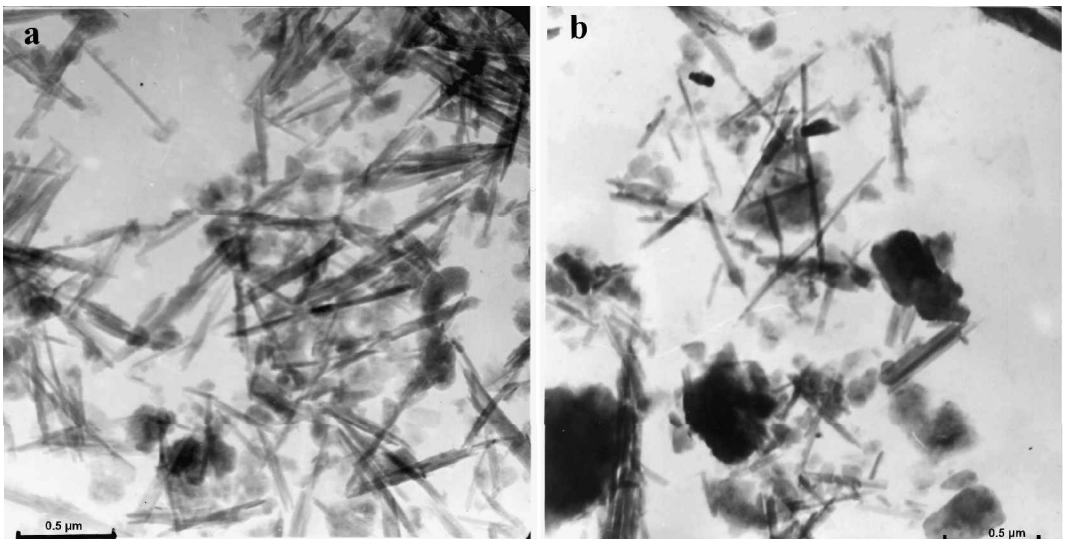

FIG. 8. TEM images of fine clay in the By horizon of pedon 44 (a), and the Btk1 horizon of pedon 10 (b).

and possible transformation into smectite. Therefore, it can be concluded that the critical available moisture as expressed by P/ETº is ~0.4, above which palygorskite is highly unstable and transforms mainly to smectite. Sepiolite is rarely detected in soils by XRD, mainly because of its dissolution under NaOAC treatment at pH 4.5 for the removal of carbonate (Abtahi, 1985).

Vermiculite. The occurrence and stability of vermiculite in calcareous and silica-rich soils has not been well documented (Boettinger & Southard, 1995). It is also reported in trace amounts in calcareous soils of southern or central Iran (Khademi & Mermut, 1998; Khormali & Abtahi, 2001). In the present study only rare occurrences of this clay mineral were detected, mainly in north-western parts (Table 3, pedons, 5, 11, 17, 70 and 73) where there is more available moisture in the soils (P/ETº >0.4). According to the literature, mica in Aridisols can weather to vermiculite via direct simple transformation (Douglas, 1989). However, this cannot explain the rare occurrence of this mineral in the highly calcareous soils of southern and/or central Iran.

Mica can transform into smectite in the following way:

$$\text{mica} \xrightarrow{+\text{Si}, +\text{Ca}, +\text{Mg}, -\text{Al}, -\text{K}} \text{smectite} + \text{Al} + \text{K}$$
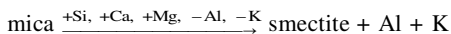
This transformation requires depotassification, dealumination and silication. In other words, temperature and pressure must be low enough to destabilize [Al] in the mineral structure. Low activity of K^+ and Al^{3+} and high $Si(OH)_4$ activity are other requirements. At ~pH >6 (as is the case for the studied soils), Al is insoluble, and in contrast Si is highly soluble, especially at pH of ~8 (as in calcareous soils of the Fars Province). Therefore, the large amount of Mg present in calcareous materials can substitute for Al in the lattice and form smectite. Moreover, in the north-western regions, there is enough precipitation to allow the process of depotassification. At pH <6, the activity of Al increases and vermiculite can form. In the case of very low pH and a highly leaching environment, kaolinite may even form from vermiculite. This explanation is proposed for the rare occurrence of vermiculite in highly calcareous soils of the study area. Those pedons with traces of vermiculite in their fine clay hold more available moisture in contrast to other pedons. The longer periods of moisture availability for chemical weathering and dampened temperature

fluctuations relative to other areas may have favoured the stability of vermiculite in those areas as discussed previously for smectite (Boettinger & Southard, 1995).

Figure 9 presents the major pathways for the formation of clay minerals in arid and semi-arid regions for the studied pedons. Vermiculite as discussed earlier is considered to be unstable under the present conditions of the studied area and its occurrence is of little importance. Kaolinite, chlorite and illite in soils are considered mainly of inherited origin from parent rocks. Neoformation is the main mechanism for the occurrence of palygorskite and formation of smectite could be mainly related to transformation of illite and/or palygorskite.

CONCLUSIONS

The presence of some kaolinite in northwestern parts of Fars province is due to its inheritance from the surrounding kaolinite-bearing Cretaceous rocks. Illite and chlorite are two commonly observed clay minerals and their abundance in the soils is largely due to their presence in parent rocks. Simple transformation of illite to other clay minerals (mainly smectite) may play a role in its relative decrease with depth.

Smectite constitutes the major portion of the clay minerals in well drained Alfisols, somewhat poorly drained Mollisols, and Calcixerepts with high precipitation. It is detected in trace amounts in soils of more arid areas. Therefore, it can be concluded that in well drained soils, with increasing soil-available moisture (as expressed in P/ETº), smectite increases. Increase in soil available moisture, and consequently a relatively leaching environment for the release of K^+ from micaceous minerals and mainly illite, in the calcareous environment with high Mg^{++} and high Si mobility, might provide favourable conditions for the formation of smectite through transformation.

There is an inverse correlation between paly-gorskite and smectite with regard to the soil available moisture. Palygorskite is scarce when P/ETº is >0.4. This indicates that the critical available moisture as expressed by P/ETº is ~0.4, above which palygorskite is highly unstable and weathers mainly to smectite. Palygorskite is considered to be inherited in plateau soils of the arid regions whereas its occurrence in saline and alkaline soils and soils high in gypsum is mainly of
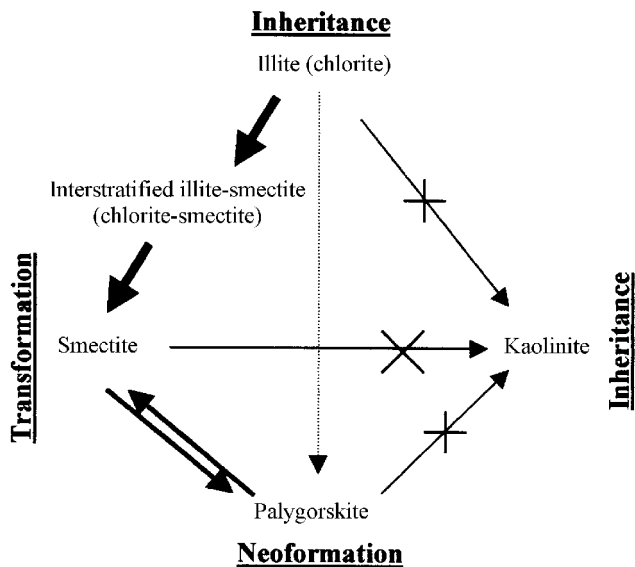
FIG. 9. Pathways for the formation of clay minerals in the studied soils. Note that kaolinite formation through transformation of other minerals is not possible under the current climate of the study area (designated with crosses). Palygorskite is considered mainly to form as a result of neoformation and smectite forms mainly through transformation of illite and/or palygorskite. The thickness of the arrows indicates the importance of the pathway. The parentheses indicate lesser importance.

authigenic origin. The rare occurrence of vermiculite in the calcareous soils studied is proposed to be related to its instability under high pH, low Al activity, high Si and Mg. These conditions are favourable for smectite formation.

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