

Clay Mineralogy of Gypsiferous Soils under Different Soil Moisture Regimes in Fars Province, Iran

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ABSTRACT

This study investigated the relationship between clay minerals and different soil moisture regimes in gypsiferous soils of Fars Province in southern Iran. The overall climate of the Province is arid and semi-arid and, under this condition, parent material is the most important factor affecting clay minerals distribution. Beside this factor, climate conditions have determining role too. Palygorskite, smectite, chlorite, illite, and kaolinite were identified as the main clay minerals in gypsiferous soils, using XRD, TEM and SEM analyses. Chlorite and illite were inherited largely from parent rocks and their abundance in soils with different moisture regimes was generally uniform. The presence of gypsum and saline and alkaline ground water in some pedons has favoured the neoformation of palygorskite from soil solution. Palygorskite shows an increasing trend with depth that may be related to its authigenic formation in the presence of gypsum. The correlation between palygorskite percentage and gypsum content was estimated ($R^2 = 0.56$). The highest amount of palygorskite was observed in soils with aridic moisture regimes, and its lowest amount was estimated in soils with xeric moisture regimes. Notably, with increasing moisture, the length of palygorskite fiber decreased. High soil moisture and rainfall and low evaporation are reasons for instability of palygorskite relative to smectite in xeric moisture regime. Large amounts of well-bundled and elongated palygorskite in soils of piedmont plain are related to their authigenic formation; while presence of slight amounts of short palygorskite fibres in lowlands suggest their transformation to smectite. Results of soil and rock samples analyses showed that some palygorskite in all moisture regimes originated from parent materials. Also, results indicated that the smectite/(illite+chlorite) ratio increased with increase in moisture and the largest value (equal to 2.12) was observed in soils with xeric moisture regime.

Keywords: Clay minerals, Land forms, Palygorskite, Smectite.

INTRODUCTION

Palygorskite is a clay mineral characterized by a microfibrillar morphology, low surface charge, high magnesium content, and high specific surface area. Palygorskite-containing soils can be cultivated profitably especially when using irrigation water. According to Paquet and Millot (1973), palygorskite weathers to smectite when the mean annual rainfall exceeds 300 mm. Palygorskite is stable only at relatively high Si

and Mg activities and alkaline pH (Singer and Norrish, 1974). This mineral is the most magnesium-rich among the common clay minerals (Singer, 2002). It can be formed in flood plains and alluvial fan soils affected by fluctuations of water table (Abtahi, 1977; Pimentel, 2002), by alteration or transformation of Mg-rich smectite (Yaalon and Wieder, 1976), or by neoformation from the soil solution (Singer and Norrish 1974; Monger and Daugherty, 1991).

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Bouza *et al.* (2007) suggested that the carbonate was mainly low-Mg calcite and, during its precipitation, the Mg^{2+} activity must have increased in the soil solution, favoring the smectite to palygorskite transformation. Henderson and Robertson (1958) and Burnett *et al.* (1972) were the first to report palygorskite in sediments and soils from Iran. Several researchers have suggested that palygorskite is formed pedogenically in the soils of Iran (Abtahi, 1977; Abtahi, 1980; Mahjoory, 1979; Gharaee and Mahjoori, 1984; Khademi and Mermut, 1999).

In arid regions, the pedogenic formation of palygorskite and sepiolite is closely associated with the calcic horizon and calcrete development. Watts (1980) indicated that the pedogenesis of palygorskite and sepiolite might be related to the release of Mg^{2+} by high-Mg to low-Mg calcite transformation at high pH values.

The presence of palygorskite, mainly around quartz grains, in micropores or associated with secondary products such as gypsum, support the idea that palygorskite precipitates after calcrete formation and constitutes a late diagenetic product occurring in an appropriate environment such as the alkaline medium of limecrusts (Verrecchia and Le Coustumer, 1996).

The presence of gypsum in soils provides favorable conditions for the formation of palygorskite. Eswaran and Barzanji (1974) have shown that the palygorskite fibers coat gypsum and hornblende crystals. The association of large amounts of palygorskite bundles with gypsum in the gypsiferous soils studied supports the hypothesis that palygorskite was probably formed after the initial precipitation of gypsum, that created a high pH and Mg/Ca ratio (Khademi and Mermut, 1998). Khormali and Abtahi (2003) concluded that the percentage of palygorskite in soils is related to the gypsum content and ratio of mean annual precipitation to mean annual reference crop evapotranspiration (P/ET).

The studies reported so far have not developed any relationship between palygorskite and soil moisture regimes. Therefore, our objective was to compare the amounts of palygorskite in soils of the following five soil moisture regimes in Fars Province of Iran: (1) xeric moisture regime with the moisture control section, in normal years, being dry in all parts for 45 or more

consecutive days in four months and a mean annual temperature lower than 22°C; (2) ustic moisture regime, which is similar to xeric regime regarding the rainfall, but its mean annual temperature is higher than 22°C; (3) aridic-ustic transitional regime; (4) xeric-aridic transitional regime, and (5) aridic moisture regime.

MATERIALS AND METHODS

Area Description

The study sites are located in an area of about 132,000 km² in Fars Province, southern Iran (Figure 1). According to Banaei (1998), the area has different soil moisture and temperature regimes (xeric, ustic, and aridic soil moisture and mesic, thermic, and hyperthermic soil temperature regimes). Precipitation ranges from 200 mm in the arid areas in the north, south, and the southeast to 800 mm in the mountainous region of the northwestern area. However, a large part of the study area receives 200-300 mm. Annual evaporation ranges from 1100 mm in the east (Sarvestan plain) with a mesic temperature regime to 1900 mm in the arid area with a hyperthermic temperature regime.

Fars Province, a part of the Zagros range, has been the site of more or less continuous sedimentation from Triassic to Pleistocene era. Regional disconformities occur at the top of Aptian, Cenomanian-Turonian, Cretaceous and Eocene (James and Wynd, 1965).

The study area is a part of the post-Tethyan sea environment where sediments are rich in soluble salts and gypsum in most of the southern and southeastern parts (Zahedi, 1976). The results of the sulfur isotope geochemistry of gypsiferous aridisols of central Iran strongly support the hypothesis that such areas were cut off from the Tethys Seaway at the end of the Mesozoic era. As a result, the lower Cretaceous sulfate has controlled the sulfur geochemistry of the younger sediments (Khademi and Mermut, 1998).

The main geological units containing gypsum include Hormoz formation, Sachun formation, Gachsaran and Razak formation (Table 1). In the north and northeastern parts, aridic moisture regime is dominant. The temperature regime varies from mesic and thermic in north and northeast, hyperthermic in the southern and the

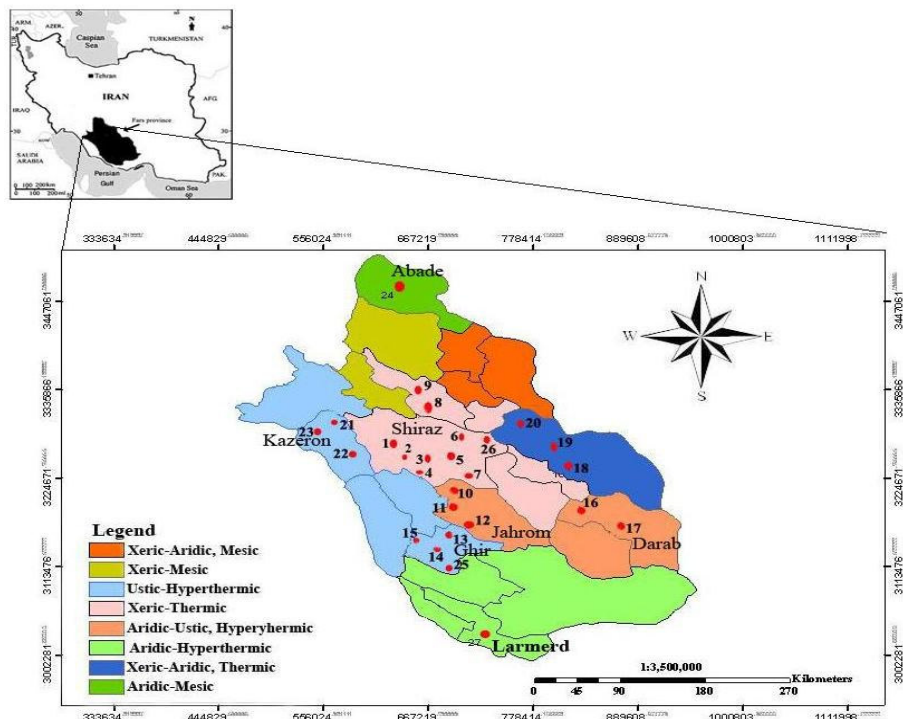


Figure 1. Soil moisture regimes and location of soil pedons in the study area.

ustic and ustic-aridic prevail in the western and south-central parts. Xeric moisture regimes prevail in the northwest. Soil temperature regimes vary from mesic in the higher elevations to thermic in the center of the Province (Figure 1).

Gypsum-enriched soils in Fars Province occur mainly in alluvial plains, flood plain, and piedmont plains and are rarely found in lowlands.

Field Sampling

Based on the previous soil survey and remote sensing reports, there are seven major soil series in the study area, out of which only four are gypsiferous. Based on soil moisture regimes, 27 pedons were investigated. Sixteen representative pedons were considered for further mineralogical study. In addition, five rock samples from the

Table 1. Geological properties of the formation of the study area (James and Wynd, 1965).

Geological units	Formation	Geological period
Hormoz formation	Mainly of salt, anhydrite, crusted dolomites, basic igneous rocks, and red siltstones	Cambrian
Sachun formation	Cherts marls, marlstones and silt, off-white limestones that it followed by gypsum and dolomites which are overlain by off-white and brown-ochre marlstones and dolomites	Mid-Upper Cretaceous
Gachsaran formation	Consists of red, grey and green silt marls, interbedded with subordinate silt limestone and minor sandstone ribs	Tertiary
Razak formation	One of the evaporitic sediments, showing thick-bedded alternating layers of anhydrite and marl	Tertiary



dominant geological strata from parent material were collected for mineralogical study. Among the distinguished Inceptisols, Aridisols, Entisols and Vertisols of the studied area, 16 pedons were selected. Most of the pedons were located in flood plains, piedmont plains, colluvial fans and plateau. Samples were taken from the genetic horizons of the soils for macro- and micro-morphological studies. Pedons were described and classified according to the Soil Survey Manual (Soil Survey Staff, 2003) and Keys to Soil Taxonomy (Soil Survey Staff, 2010).

Laboratory Methods

Chemical and Physical Characterization

Due to the high content of gypsum, the laboratory analyses of gypsiferous soil present some special problems (e.g. soil texture measuring and separation of clay fraction). Particle size analyses were performed on samples from each horizon in the 16 soil profiles using the hydrometer method described by Gee and Bauder (1986). Organic carbon was measured by wet oxidation with chromic acid and back titration with ferrous ammonium sulfate (Nelson and Summers, 1996). Calcium carbonate equivalent (CCE) was measured by acid neutralization (Loppert and Suarez, 1996).

Soil pH was measured with a glass electrode in a saturated paste (mixture of water and soil) (Thomas, 1996). Electrical conductivity (EC) was measured in the saturation extract (Rhoades, 1996). Cation exchange capacity (CEC) was determined using sodium acetate at a pH of 8.2 (Sumner and Miller, 1996).

Gypsum was quantified with the revised acetone method (Loppert and Suarez, 1996) and corrected for hydration water. This procedure involved changing soil/water ratio from 1/5 to 1/500, increasing the first shaking period from 0.5 to 24 hours and increasing the sedimentation period from 0.5 to 2 hours after adding acetone (Toomanian et al. 2001).

Mineralogical Analysis

Prior to mineralogical analysis, samples were repeatedly washed to remove gypsum and soluble salts. Carbonates were removed using 1N

sodium acetate, buffered at pH 5. This reaction was performed in a water bath at 80°C. Organic matter was oxidized by treating the carbonate-free soils with 30% H₂O₂. Iron oxides were removed from the samples by the dithionate-citrate-bicarbonate method (Mehra and Jackson, 1960).

Separation of clay fractions was carried out according to the methods of Kittrick and Hope (1963) and Jackson (1975). Separate subsamples of clay were weighed (40 mg) and saturated with Mg and K; Vortex and ultrasound agitators were used to homogenize the suspensions. Mg-saturated clay samples were solvated by ethylene glycol vapors in a desiccator over a period of 48 hours. The K-saturated clay samples were studied both after air-drying and heating (for 2 hours) at 550°C. X-ray diffraction (XRD) patterns were obtained with Philips D500 diffractometer, using Ni-filtered CuK α radiation (40kV, 30mA).

Electron Microscopy Studies

Ten dried clay samples from soils of five different moisture regimes were selected. Samples were mounted on Al stubs using double-sided tape and carbon paste, and then sputter coated with Au and examined using LEO SEM. Identification of the chemical composition of minerals was carried out by using EDX analysis. For TEM study, droplets of diluted suspensions of selected clay samples fractions dried on 200-mesh form var-coated Cu grids under a heat lamp for 25 minutes and examined using a LEQ 906E transmission electron microscope (TEM).

RESULTS

Physico-chemical Properties

Selected properties of pedons including parent material, physiographic unit, location and soil moisture regimes are presented in Table 2 and physicochemical properties are depicted in Table 3. Since the parent material of the study area contains gypsum, the soils are also highly gypsiferous. Alluvial soils (Entisols) and moderately developed soils with gypsic and

Table 2. General characteristics of pedons studied.

Pedon. No	Location	landform	Longitude and latitude	Moisture-temperature regimes	Parent material
3	Gharehbagh	Flood plain	645958 E 3265850 N	Xeric-thermic	Calcareous and Gypsiferous alluvium
5	Sarvestan	Piedmont plain	689110 E 3245730 N	Xeric-thermic	Calcareous and Gypsiferous alluvium
7	Sarvestan	Flood plain	698905 E 3237529 N	Xeric-thermic	Calcareous and Gypsiferous alluvium
8	Marvdasht	Flood plain	679787 E 3322268 N	Xeric-Thermic	Calcareous and Gypsiferous alluvium
10	Jahrom	Alluvial plain	756814 E 3166782 N	Aridic-ustic, Hyperthermic	Calcareous and Gypsiferous alluvium
11	Jahrom	Flood plain	764039 E 3165386 N	Aridic-ustic, Hyperthermic	Calcareous and Gypsiferous alluvium
12	Jahrom	Flood plain	764040 E 3165381 N	Aridic-ustic, Hyperthermic	Calcareous and Gypsiferous alluvium
13	Ghyr	Plateau	706511 E 3145205 N	Aridic-ustic, Hyperthermic	Calcareous and Gypsiferous alluvium
16	Darab	Piedmont plain	244863 E 3183400 N	Aridic-ustic, Hyperthermic	Calcareous and Gypsiferous alluvium
17	Darab	Alluvial plain	249467 E 3148813 N	Aridic-ustic, Hyperthermic	Calcareous and Gypsiferous alluvium
18	Nyriz	Flood plain	231437 E 3239239 N	Xeric-aridic, Thermic	Coarse gypsiferous alluvium
20	Nyriz	Low land	223591 E 3239511 N	Xeric-aridic, Thermic	Coarse gypsiferous alluvium
22	Kazeron	Low land	572658 E 3263923 N	Ustic-hyperthermic	Calcareous and Gypsiferous alluvium
24	Abadeh	Piedmont plain	6694939 E 3428321 N	Aridic-mesic	Gravelly sediment alluvium
25	Ghyr	Piedmont plain	715352 E 3140912 N	Aridic-ustic, Hyperthermic	Calcareous and Gypsiferous alluvium
26	Sarvestan	Plateau	712805 E 3228449 N	Xeric-thermic	Calcareous and Gypsiferous alluvium

cambic horizons (Inceptisols and Aridisols), comprise about 95% of soils in the area. The soils rich in gypsum cover a large area in the flood and piedmont plains. These soils are under aridic and ustic moisture regimes in the southern, northwestern, and eastern parts with annual precipitation less than 300 mm, and high evapotranspiration. They also occur in the vicinity of saline and alkaline lakes and are classified as Typic Haplogypsis, Typic Calcigypsis, Gypsic Haplustepts and Gypsic Haplosalids. Gypsiferous and saline soils are mainly bare or under pasture.

Mineralogical Studies

Semi-quantitative estimates of different clay minerals in the clay fraction of the samples are given in Table 4. The percentages of the clay minerals were estimated according to Johns et al. (1954). In this method, the major clay minerals ratio of X-ray peak areas in the glycol-treated samples is considered a semi-quantitative measure of their occurrences.

Palygorskite, smectite, chlorite, illite, and kaolinite were the main clay minerals in



Table 3. Physico-chemical properties of pedons studied.

Horizon	Sand (%)	Silt (%)	Clay (%)	pH	EC dS m ⁻¹	CEC (Cmol _c kg ⁻¹)	CCCE	Gypsum (%)	OM (%)
3. Aquic Haploxerept (Gharehbagh)									
A	5.5	43.5	51	7.7	1.1	17.4	19	0.3	0.04
Byss1	15.3	31.4	53.3	8.2	2.7	14.6	25	13.4	0.4
Byss2	5.3	30.7	64	8.2	0.8	17	37	9.4	0.5
Byg1	13.3	19.4	67.3	8.1	5.2	19	39	6.4	0.6
Cg	11.3	15.4	73.3	7.9	0.5	20	39	0.3	0.7
5. Typic Calcixerept (Sarvestan)									
A	47.3	51.4	1.3	8.0	0.2	4.2	34	3.2	0.21
Byk	63.3	35.4	1.3	8.1	0.3	4.2	40	45.5	0.3
By	63.3	35.4	1.3	8.3	0.6	2.1	36	54.3	0.2
C	69.4	30.6	-	7.9	0.8	5.2	36	45.5	0.3
7. Gypsic Haploxerept (Sarvestan)									
Ay	58.2	38	3.8	7.7	0.2	7.3	9	80	1
By1	60.2	38	1.8	8.1	0.4	7.3	12	80	0.2
By2	50.2	48	1.8	8.1	0.4	8.3	10	81	0.6
By3	50.2	48	1.8	8.0	0.5	9.4	15	79	0.1
C	48.1	51.3	.6	7.9	0.5	13.2	14	72	0.3
8. Typic Calcixerept (Marvdasht)									
A	26.1	46	27.9	7.7	0.06	16.7	48	3.6	0.7
Bw	12.7	32	55.3	7.8	0.07	21.4	18	2.7	0.6
Byk	20.7	38	41.3	7.8	0.15	14	50	6.7	0.4
C	22.7	36	41.3	7.7	0.06	14.5	33	2.3	0.6
10. Gypsic Haploxerept (Jahrom)									
A	44.7	42	13.3	7.5	0.2	8.4	49	1	0.6
By1	68.7	24	7.3	7.5	0.8	7.2	28	44	0.07
By2	29.4	24	46.6	8.4	0.8	12.4	27	16	0.2
11. Gypsic Haploxerept (Jahrom)									
Ay	54.1	35.3	10.6	7.3	0.15	12.5	48	5.8	0.56
By1	88.1	1.3	10.6	7.7	0.16	4	29	53.6	0.3
By2	85.4	14	0.6	7.6	0.22	6.4	39	37.5	0.2
C	13.4	64	22.6	7.7	0.38	12	45	2.3	0.2
12. Aridic ustorthent (Jahrom)									
Ay	48.7	40.7	10.6	7.5	0.18	11.6	46	1.3	1
C1	68.8	30.7	0.6	6.9	0.16	2.8	24	64	0.07
C2	88.7	10.7	0.6	8	0.17	2.6	23	71	0.03
13. Gypsic Calcixerept (Ghyr)									
Ay	54.7	32.7	12.6	7.9	0.5	13	51	14.7	0.4
Byk1	44.9	42.7	12.6	7.9	0.3	9.5	49	31	0.5
Byk2	32.7	50.7	16.6	8.7	1.7	11.5	48	40.3	0.2
C	17.1	44.2	38.7	7.9	0.3	12.5	27	64	0.3
16. Gypsic Calcixerept (Darab)									
A	43.4	55.3	1.3	7.9	3.0	13.2	34	3.5	0.58
Bw	27.4	71.3	1.3	8.3	1.4	7.2	34	3.6	0.2
Byk	39.4	59.3	1.3	8.4	0.6	6.5	38	15.6	0.22
C	9.4	89.3	1.3	8.2	0.6	4.5	45	3.6	0.05
17. Sodic Haploxypsid (Darab)									
A	30.7	67.3	2	8.2	5.0	9.4	34	0.6	.05
By1	54.7	43.3	2	8.4	2.5	8.3	29	8.7	0.6
Bw	26.7	71.3	2	8.5	2.6	6.3	33	1.5	0.5
By2	18.7	79.3	2	8.4	2.2	10.4	32	5	0.78
By3	46.7	51.3	2	8.3	2.0	12.5	33	12.7	0.45
C	44.7	53.3	2	8.5	1.6	10.4	35	32	0.38
18. Choromic Gypsitorret (Nyriz)									
Ap	8.7	60	31.3	7.6	0.5	17.4	36	0.9	1.8
Bss	7.5	42	50.5	7.7	1.5	18	41	1.4	1.28
Byss	0.8	43.2	56.0	7.4	1.5	18.1	35	19.7	0.45
20. Gypsic Aquisolid (Nyriz)									
Azg	52	37.2	10.8	7.9	37.8	14.6	35	2.3	0.35
Byzg1	20	73.2	6.8	8.1	38	14.6	24	21.4	0.45
Byzg2	36	59.2	4.8	7.9	38	15.3	15	9.7	0.28
Bg	39	58.2	2.8	8.0	8	13.2	31	3.7	0.21
22. Gypsic Haploxerept (Kazeron)									
Ayz	46.7	32.7	20.6	8.9	51.3	14.6	19	5.6	2.5
Bw	28.7	28.7	42.6	8.6	14	12.5	35	1.5	0.65
By	11.3	66.7	22.0	8.6	17.6	9.4	40	16.4	0.4
24. Calcic petrogypsid (Abadeh)									
AP	39	46	15	7.4	1.8	11	49	0.2	0.96
BK1	37	48	15	7.6	0.7	7	56	0.3	0.64
BK2	34	43	23	7.5	1.8	8	54	9.1	0.41
Bym1	53	30	17	7.6	1.4	12	43	18.7	0.35
Bym2	71	23	6	7.4	1.9	7	48	20.8	0.54
25. Gypsic Calcixerept (Ghyr)									
Ay	19	72	9	7.8	1.87	14	43	4.6	1.7
Byk	29	58	13	7.7	2.2	12	44	15.5	0.7
Bykm	25	54	21	7.5	2.2	15	33	33.5	0.5
26. Calcic Haploxerept (Sarvestan)									
Ap	53	40	7	7.2	2.2	9	33	2	1.6
By	79	18	3	7.4	2	5	10	72	3
Bym	75	22	3	7.4	2.2	3	1	91	2

Table 4. Relative abundance of silicate minerals in the clay fraction of the samples studied ^a.

Pedon. No.	Horizon	Chlorite	Illite	Smectite	Vermiculite	Palygorskite	Kaolinite	Quartz	Mix
3	Ap	+	++	++++	+	++	-	tr	+
3	Byss1	++	++	++++	+	+++	-	+	+
3	Byss2	++	+++	++++	+	+	-	tr	+
3	Cg	++	++	++++	+	++	-	+	tr
5	A	+++	+++	tr	-	+++	-	tr	+
5	Byk	+++	+++	+	-	++++	-	+	+
5	C	++	++	++	-	+++	-	+	+
7	Ay	++	++	+++	-	++	-	+	+
7	By2	++	+++	+	-	++++	-	+	+
7	C	+++	++	-	-	++++	-	tr	tr
8	Bw	++	++	+++	+	+++	-	+	+
8	Byk	++	++	+++	+	++	-	+	tr
8	C	++	+++	++	+	+++	-	+	tr
10	A	+	++	+++	-	+++	-	+	+
10	By1	++	++	++	-	+++	-	++	+
11	Ay	++	++	+++	-	++	-	+	+
11	By2	++	++	+++	-	++	-	+	+
11	C	++	+++	++	-	+++	-	++	+
12	Ay	++	++	+++	-	+++	-	+	+
12	C2	+++	+++	+	-	+++	-	+	+
13	Ay	++	++	+	+	+++	-	+	+
13	Byk2	++	+++	tr	tr	+++	-	+	+
13	C	+++	+++	-	-	++++	-	+	+
16	A	+	++	++++	+	++	-	+	+
16	Byk	+	++	++++	+	+	-	++	+
16	C	++	++	+++	+	+	-	+	+
17	A	++	+++	tr	-	+++	-	+	+
17	By1	+++	+++	tr	+	+++	-	++	+
17	Bw	+++	+++	-	-	+++	-	+	tr
17	By3	+++	+++	-	-	+++	-	+	+
17	C	+++	++++	++	-	++	-	+	+
18	Ap	+	++	+++	tr	+++	-	+	+
18	Bss	++	++	++++	tr	++	-	tr	+
18	Byss	+	++	+++	tr	++	-	+	+
20	Azg	+	++	++++	tr	+	-	+	+
20	Byzg1	+++	+++	++	-	+	-	+	+
20	Byzg2	+++	+++	++	-	+	-	+	+
20	Bg	+++	+++	+	-	+	-	+	+
22	Ayz	++	tr	++++	tr	+++	-	+	+
22	By	++	+++	tr	-	++++	-	+	tr
24	Ap	++	++	+++	-	++++	+	++	+
24	Bk2	++	+++	++	-	+++	+	++	+
24	Bym1	++	+++	+	-	+++	+	++	+
24	Bym2	++	+++	++	-	+++	+	++	+
25	Ay	++	++	tr	-	+++	-	++	+
25	Byk	+++	+++	tr	-	++++	-	+	+
25	Bykm	++	++	++	-	++++	-	++	+
26	Ap	++	++	-	++	++++	+	+	+
26	By	++	++	tr	++	++++	+	+	+
26	Bym	++	++	tr	++	++++	+	+	+

^a (tr)< 5%; (+) 5-10%; (++) 10-25%; (+++) 25-40%, (++++) 40-60%.

gypsiferous soils, using XRD, TEM, and SEM analyses.

Chemical analysis indicated an inverse relationship between soil CEC and the content of palygorskite (Figure 2). The results of mineralogical analysis indicated that with increase in palygorskite content in the clay fraction, the CEC was reduced. A negative

significant relationship was observed between palygorskite and CEC ($R^2=0.44$) (Figure 2).

In the gypsiferous soils, soil texture is predominantly coarse; however, cation exchangeable capacity is not realistic. The CEC values ranged from 3 to 23 Cmolckg^{-1} .

In arid and semiarid soils, mineralogy is sometimes controlled by parent materials.

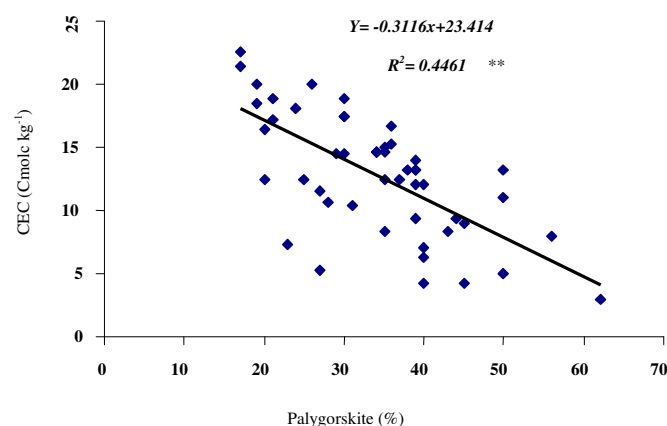


Figure 2. The relation between soil CEC (Cation exchange capacity) content and palygorskite percentage.

Chlorite and illite are inherited largely from parent rocks (all pedons). Smectite in the gypsiferous soils originated from two sources: (1) inheritance from parent materials; and (2) pedogenic formation through neoformation or transformation of 2:1 minerals, especially of illite. The origin of palygorskite is neoformation, but a lot of it is probably formed through the authigenesis (pedon 26) (Table 5).

Xeric Moisture Regime

Soils with a xeric moisture regime exist in four landforms: flood plain, piedmont plain, plateau and alluvial fan. Results showed that Bym horizon of pedon 26 and Ap horizon of pedon 3 contained the highest and the lowest amount of palygorskite, respectively. In the flood plain (pedon 3), smectite was the most abundant silicate clay mineral in the subsurface layers. These findings suggested the transformation of palygorskite to smectite.

Palygorskite occurred as short and broken fibres. Although abundance of palygorskite was less than smectite, its content increased with depth increase.

Palygorskite dominates the clay fractions in the alluvial fans. In the plateau, palygorskite abundance was high (pedon 26), because this pedon formed near saline and alkaline lakes (e.g, Maharlo) that favoured the authigenic palygorskite formation (Figure 3-g). SEM images showed that palygorskite in this area had formed in situ (Figure 5-a).

In piedmont plain (pedon 5) in Sarvestan area with annual rainfall of 1,100 mm, palygorskite decreased with depth, but its abundance was more than the other minerals. Comparison within soil and rock samples showed that palygorskite in this pedon was inherited.

TEM observations showed that palygorskite bundles in the piedmont plain soils were long (Figure 3-c), but, in the plateau, were short and broken (Figure 3-g).

Table 5. The origin of clay minerals in the soils studied (Khormali and Abtahi, 2003).

Clay minerals	Neoformation	Inheritance	Diagenetic
Illite	— ^d	***	—
Chlorite	—	***	—
Smectite	** ^b	* ^a	***
Palygorskite	*** ^c	**	**
Kaolinite	—	***	—

^a low abundance, ^b moderately abundance, ^c high abundance, ^d without abundance

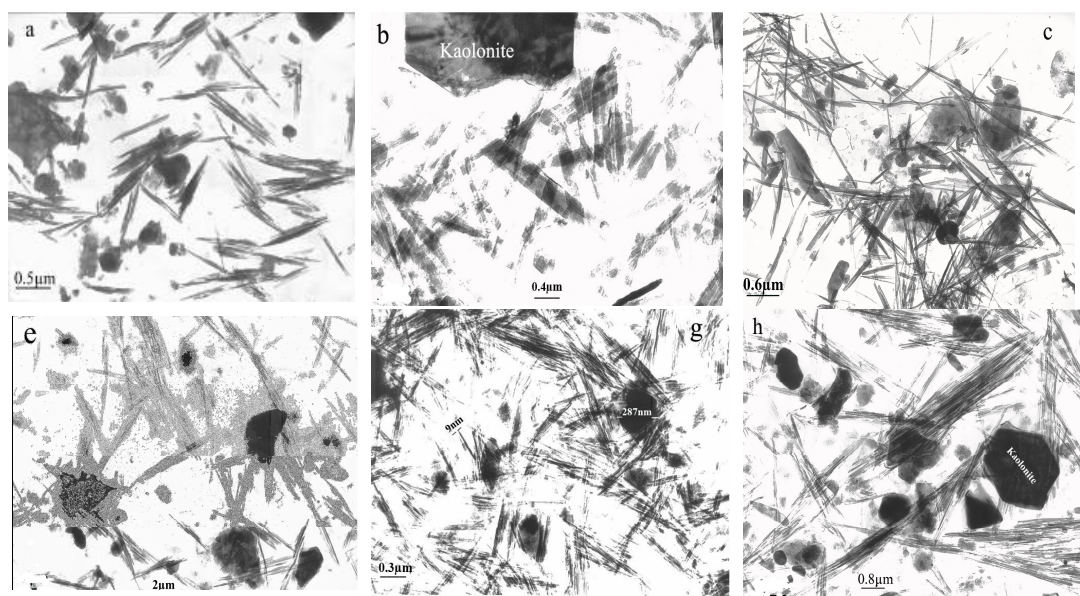


Figure 3. (a) Short fibrous of palygorskite in with xeric-aridic moisture regime (pedon 20); (b) Thickness and long fibrous of palygorskite with aridic-ustic moisture regime (in pedon 17); (c) Thin and long fibrous palygorskite with xeric moisture regime (pedon no. 7); (d) Longer fibrous of Bym horizon pedon 25 in Ghyr plain; (e) Broken fibrous of palygorskite in plateau (pedon 26), and (f) Long fibrous of palygorskite and kaolinite clay in the aridic moisture regime in Sormagh plain (pedon 24).

Xeric-aridic Moisture Regime

Two pedons (18, 20) were studied in two landscapes. In the lowlands (pedon 20), smectite was dominant. Poor drainage and high water table level are important factors for transfer of palygorskite to smectite. In the Azy horizon, smectite was the most abundant clay mineral, but it decreased with depth.

Comparison of clay mineral in xeric moisture regime (pedon 3) and xeric-aridic moisture regime (pedon 18) indicated that palygorskite content in xeric-aridic regime was more than that of xeric regime. Both Pedons 3 and 18 were Vertisols located in flood plain, but, pedon 3 had xeric moisture and pedon 18 had a xeric-aridic regime, however, increase in aridity leads to increase in the abundance of palygorskite (Table 4). Palygorskite crystals in these soils were short and broken (Figure 3-a).

Ustic Moisture Regime

Unfortunately, only one pedon was investigated for mineralogical studies.

Mineralogical studies in soil with ustic moisture regime (pedon 22) indicated that palygorskite content in this soil was more than that with xeric-aridic moisture regime. Pedons 20 and 22 are located in lowland position; palygorskite in the pedon 22 was greater than that in pedon 20 (Table 4). The amount of palygorskite increased with depth, but decreased with smectite amount increase in the surface horizons. In the Ayz horizon, the amount of illite was very low and smectite amount was very high, but in the deeper soils, content of smectite was reduced, such that, in the By horizon, it decreased to less than 5%.

Aridic-ustic Moisture Regime

Mineralogical studies in aridic-ustic regime were carried out in four physiographic units. In subsurface horizons of pedons 10 and 12, palygorskite was dominant, but in the surface horizon, smectite was dominant. In the surface soil, palygorskite was weathered and transformed to smectite. Comparison of XRD peaks of palygorskite in this moisture regime indicated that its abundance in this moisture regime was more than those of other minerals.

Thickness and length of fibers of palygorskite were observed (Figure 3-b) in the by horizon of the pedon in the Darab area (pedon 17).

In the piedmont plain (pedon 25) with gypsic and petrogypsic horizons, palygorskite was the main clay, but its amount did not change with depth. The presence of petrogypsic horizon in pedon 25 in the Ghir area induced increase in peak intensity of palygorskite and TEM analysis showed longer fibrous of palygorskite (Figure 3-e).

Aridic Moisture Regime

Soils with aridic moisture regime had the highest content of palygorskite in the subsurface horizon. In piedmont plain (pedon, 24), the presence of a petrogypsic horizon may be the main reason for large content of palygorskite. X-ray diffraction results showed that peak intensity in Bk2 sample was more than that in Bym1 and Bym2 samples (Figure 4).

In Ap horizon of pedon 25, palygorskite was abundant. But, in the xeric regime, peak intensity of palygorskite is very low, favoring its transformation to smectite. Due to leaching in flood plain, palygorskite is not detrital, but is inherited from the parent rock. In two pedons (24 and 25) illite and chlorite content increased with depth.

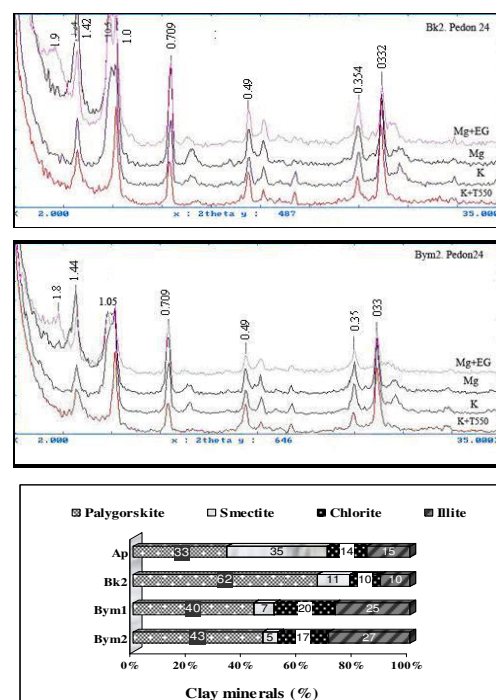


Figure 4. Comparison peak intensity (1.05 Å) in two horizons of pedon 24, and diagram of clay minerals percentage in the horizons of the 24 pedon.

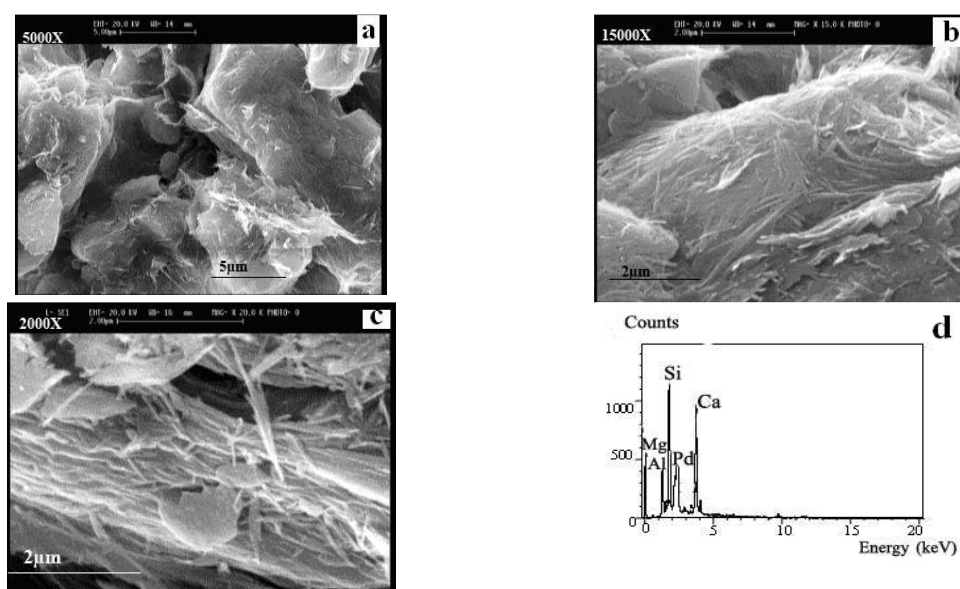


Figure 5. (a) SEM image of pedogenic gypsum coated by palygorskite in the Sarvestan plain (pedon 26); (b and c) SEM images of palygorskite of clay fraction, and (d) EDX curve of image a.

DISCUSSION

Xeric Moisture Regime

The presence of gypsum and saline and alkaline groundwater in some pedons has favoured the neoformation of palygorskite from soil solution (such as pedon 26). The occurrence of palygorskite in soils corresponds to an area once covered by the post-Tethyan intermountain shallow lagoons, during the Tertiary era.

Khademi and Mermut (1998) concluded that the major portion of the palygorskite in colluvial and plateau soils was probably formed authigenically when central Iran was covered by the post Tethyan shallow and hyper-saline lagoons.

In the xeric soil moisture regime, presence of seasonal soil moisture and high seasonal rainfall are the main reasons for transformation of palygorskite to smectite. However, with high water table level and poor drainage of the location, it is possible to have a transformation of palygorskite to smectite. The lower amount of palygorskite in the surface horizon is likely due to the transformation of palygorskite to smectite. Presence of high soil moisture and rainfall and low evapotranspiration are reasons for instability of palygorskite over smectite in this soil moisture regime.

Xeric-aridic Moisture Regime

Palygorskite crystals in this regime are short and broken (Figure 3-a). Comparison of clay mineral in xeric moisture regime (pedon 3) with xeric-aridic moisture regime (pedon 18) indicated that palygorskite content in xeric-aridic regime was more than that in xeric regime. Increase in aridity leads to increase in the abundance of palygorskite (Table 4, Figure 6). Also, poor drainage affects mineral formation, especially smectite. There are two sources of smectite in these soils: Neoformation from the soil solution and transformation from other clay minerals (palygorskite and illite). In calcareous and gypsiferous soils and sediments, decrease in

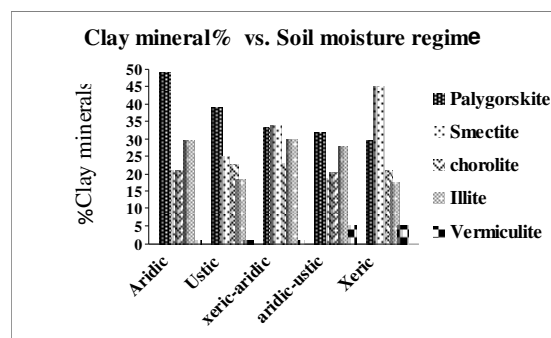


Figure 6. Dispersive clay minerals under different moisture regimes.

moisture leads to lower calcium ion in soil solution, however, Mg/Ca ratio increases and, as a result, these conditions are suitable for formation of palygorskite. But poor drainage induce palygorskite transformation to smectite, therefore, smectite was assumed the abundant clay in pedon 18. Illite and chlorite in these pedons (18 and 20) increased with increase in depth, however, it was shown that these minerals were inherited from parent material.

Ustic Moisture Regime

In this regime, evaporation is very high; therefore, leaching is not a reason for increase in palygorskite content in the deeper horizon. The high moisture likely favours the formation of pedogenic palygorskite, thus, increase in moisture in the lower depth induces pedogenic palygorskite formation. Also, it is possible that the observed amount of palygorskite in the area was inherited from parent material. the content of palygorskite in this regime is more than other moisture regimes. Figure 6). Heidari *et al.* (2008) investigated the role of climate on the formation of vertisols in this area with ustic moisture regime. They showed that palygorskite and illite were the dominant clay minerals in this area.

Aridic-ustic Moisture Regime

The content of palygorskite in this regime is very high and the intensity of aridity accentuates



this factor, but landscape has the most important role in the clay mineral variety. Seven pedons in this regime have studied. In all pedons, with increasing depth, the palygorskite content increased. The observed surface pedons smectite content was more than other minerals and we can conclude that palygorskite and illite weathered to smectite on the soils surface. The presence of salic and gypsic horizons, too, is a factor for increasing the amount of palygorskite. Chlorite increased with increase in depth, showing inheritance from parent materials.

Aridic Moisture Regime

The presence of carbonates of pedogenic origin in the Bk2 horizon of pedon 24 decreased the migration of palygorskite, without significant effect on migration of smectite (Figure 4). Peak intensity in the Bk2, Bym1, and Bym2 horizon samples indicated that Bk2 had the highest palygorskite content. Probably, carbonates in the Bk2 induced entrapment of palygorskite in these horizons and inhibited its transfer toward subsurface horizons.

Neaman and Singer (2004) also reported that entrapment of palygorskite by carbonates of lacustrine origin occurred in the subsoil horizons.

Long fibbers of palygorskite and hexagonal forms of kaolinite crystals were observed in Sormagh soil in this regime (Figure 3-h). The presence of kaolinite in this area is due to its inheritance from the surrounding kaolinite-bearing Cretaceous rocks. Studies of Khormali and Abtahi (2003) in soils of Fars Province, Iran, indicated that kaolinite was the main mineral in Cretaceous sediments, mainly due to its detritus origin.

General Discussion

In some pedons, lower contents of illite may be due to the transformation to smectite. The content of illite is greater in the aridic and aridic-ustitic moisture regime and is the lowest in the xeric moisture regime.

Quartz in all samples was inherited from the parent material (Table 4). The presence of kaolinite in the arid and semi arid soils (pedons

24 and 17) is also due to inheritance from parent rocks (Figures 3-b and -h).

Smectite in gypsiferous soils originated from two sources: (1) inheritance from parent materials; and (2) pedogenic formation through neoformation or transformation of 2:1 minerals, especially of illite and palygorskite.

Low-lying topography, poor drainage and parent materials rich in bases, favourable chemical condition characterized by high pH, high silica activity and an abundance of basic cations are factors that strongly influence the presence and distribution of smectite in pedons 3 and 20 (Borchardt, 1989). The content of this mineral appears to be greater in the surface than in deeper horizons of moist soils. But in pedon 16, it was observed that smectite in the subsurface horizons was inherited from the parent material.

The presence of palygorskite in the piedmont plains and plateau originated from detrital materials. Large amounts of well-bundled and elongated palygorskite in soils of piedmont plain are related to their authigenic formation, while the lower amount of short palygorskite fibres in lowlands suggest their transformation to smectite. Results of soil and rock samples analyses showed that some palygorskite in all regimes originated from parent materials. However, two sources of palygorskite in the gypsiferous soils have been proposed: (1) Inheritance from the parent rock, and (2) alteration of pre-existing phyllosilicate minerals such as mica or smectite and, then, transformation to palygorskite.

All SEM images in all moisture regimes are similar with respect to the palygorskite form, except in Sarvestan plain (pedon 26), which is near the Maharlo lake (Figure 5-a). In fact, palygorskite in this location is residual. These soils contain high gypsum in their subsurface horizons, the highest intensity of palygorskite peak observed in this area. But, recent studies (Khormali *et al.*, 2003) have indicated that parent rocks in this area contain low palygorskite. The presence of palygorskite in this area could be related to their authigenic formation in the presence of gypsum. Palygorskite forms in SEM image do not show dendrite form, but coats the pedogenic gypsum (Figure 5-a). The presence of shallow, saline and alkaline groundwater has

also favoured the neoformation of palygorskite from the soil solution.

TEM images showed that reducing the moisture increased fiber length of palygorskite both in surface and sub surface horizons (Table 6).

Of course, beside this factor, landscape type should not be ignored since it induced diversity in palygorskite forms. Hashemi *et al.* (2011) have shown that gypsum mineral forms also vary in different moisture regimes in the study area. Near the aridic regimes, more crystals grow length-wise with limited thickness (such as columnar, fibrous, perpendicular, blade and needle forms), while with increasing rainfall, like in xeric regime, more crystals grow in width with higher thickness (such as lenticular, globular, tabular and rosette-like forms).

The highest and lowest amounts of palygorskite were observed in soils of aridic and xeric soil moisture regimes, respectively (Figure 6). The high moisture led to instability of palygorskite and its transformation to smectite. Khormali *et al.* (2003) showed that there was a reverse correlation between palygorskite and smectite in arid and semi-arid calcareous soils of this area. Abundance of clay minerals in different soil moisture regimes is shown in Figure 6. Illite and chlorite abundance in soils with different moisture regimes are mainly uniform.

Palygorskite content in the lowland soils is the lowest and its maximum content was observed in the plateau soil. Palygorskite shows an increasing trend with depth that may be related to its authigenic formation in the presence of gypsum. Increase in gypsum content with depth was similar to palygorskite. The relationship of palygorskite content with gypsum content was statistically significant ($R^2 = 0.56$) (Figure 7).

In clay mineralogical investigation, Owliaie *et al.* (2006) concluded that soils formed from gypsiferous and calcareous materials in southwestern Iran have more pedogenic palygorskite as compared to calcareous soils.

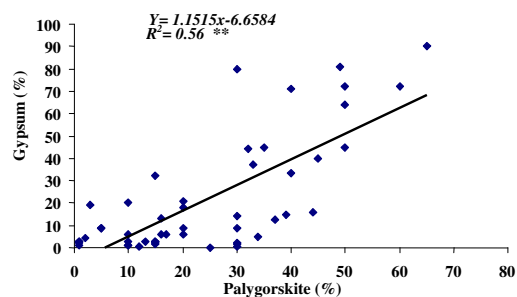


Figure 7. Relationship between palygorskite percentage and gypsum percentage in soils.

Their results showed that neoformation of palygorskite, as a result of calcite and gypsum precipitation, seems to be a major pathway for the occurrence of this mineral, especially on plateau soils, although inheritance has less importance.

In this study, the presence of gypsum demonstrates the high salinity of the soil solutions and the evaporative conditions that favour the neoformation of palygorskite. Regardless of the particular mechanism, the solution chemistry with respect to Mg, Si, Al and pH will control the crystallization (Birosoy, 2000). Both gypsiferous and calcareous soils can provide buffered alkaline media with necessary anions and cations for palygorskite formation, but the solution chemistry of the gypsiferous soils may result in more favourable condition. We can say that the diversity of parent materials in these plains offers a suitable environment to study the origin and distribution pattern of clay minerals in arid and semi-arid region.

The ratio of smectite/illite+chlorite assessment in all moisture regimes and the mean of ratio are equal to 1.26 in the xeric moisture regime and 0.38 in aridic moisture regime. This ratio can help us to determine soil evolution. In pedon 3 with xeric moisture regime, the ratio reaches 2.12. The sequence of smectite content is:

Table 6. The relationship between soil moisture regime and palygorskite fibrous length.

Soil moisture regime	Xeric Pedon 3,7	Xeric-Aridic Pedon 3,7	Aridic-ustic Pedon 13	Aridic Pedon 24
Palygorskite crystal length	8-10 μm	20-40 μm	50-70 μm	80-100 μm



Xeric> Xeric-aridic> Aridic moisture regime.

CONCLUSIONS

We concluded that: Playgorskite, chlorite, illite, and smectite are the major clay minerals in the gypsiferous soils. Illite, chlorite, and kaolinite are inherited from parent material and their contents in the different moisture regimes are almost constant. The highest amount of smectite was observed in the xeric moisture regime that originated from illite and palygorskite transformation or, rarely, inheritance. The highest content of palygorskite (> 50%) in the clay fraction in the gypsiferous soils was observed in: (1) the aridic moisture regimes, (2) the upper part of toposequence such as alluvial fans and piedmont plain and in plateau, and (3) the materials with high contents of gypsum and carbonate, such as Bk, By and Bym horizons. Not only the amount of palygorskite but also its morphology is different in soils with different soil moisture regimes. Transmission electron micrographs indicated that with increasing aridity, palygorskite bundles contained longer and thinner fibers. Results showed that smectite/(illite+chlorite) ratio increased with the increase in moisture and the highest ratio was found in the xeric moisture regime.

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کانی‌شناسی رس در خاکهای گچی با رژیمهای رطوبتی متفاوت در استان فارس جنوب ایران

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چکیده

این مطالعه ارتباط بین کانیهای رس با رژیمهای رطوبتی متفاوت در خاکهای گچی استان فارس را بررسی کرده است. آب و هوای کلی استان خشک و نیمه خشک و تحت این شرایط، مواد مادری مهمترین عامل موثر در توزیع کانیهای رس می باشد. در کنار این عامل هم چنین شرایط اقلیمی نیز نقش تعیین کننده ای دارد. پالی گورسکایت، اسمکتیت، کلریت، ایلایت و کائولینیت کانیهای اصلی خاکهای گچی با آنالیزهای XRD، TEM و SEM شناخته شده اند. کلریت و ایلایت به ارث رسیده از مواد مادری هستند و فراوانی آنها در خاکهای با رژیم رطوبتی متفاوت به طور کل یکنواخت بوده است. حضور گچ، نمک و سفره آب زیرزمینی قلیائی در برخی پدونها برای نوتشکیلی پالی گورسکایت از محلول خاک مطلوب بوده است. افزایش پالی گورسکایت همراه با افزایش عمق خاک ممکن است مربوط به تشکیل اتوژنیک آن در حضور گچ باشد. همبستگی بین درصد پالی گورسکایت و محتوی گچ تخمین زده شده است ($R^2=0/56$). بیشترین مقدار پالی گورسکایت در خاکهای با رژیم رطوبتی اریدیک و کمترین مقدار آنها در خاکهای با رژیم رطوبتی زریک برآورد شده و با افزایش رطوبت طول فیبرهای پالی گورسکایت کاهش می یابد. حضور رطوبت خاک و بارندگی زیاد و تبخیر کم دلایلی برای ناپایداری پالی گورسکایت نسبت به اسمکتیت در رژیم رطوبتی زریک می باشد. مقادیر زیاد پالی گورسکایت طویل و سوزنی در دشتهای دامنه ای مربوط به تشکیل اتوژنیک آنها و فیبرهای کوتاه پالی گورسکایت نشان دهنده تبدیل آن به اسمکتیت در اراضی پست است. نتایج نمونه های سنگ و خاک نشان می دهد که پالی گورسکایت در تمامی رژیمها منشاء گرفته از مواد مادری است. هم چنین نتایج نشان داده که نسبت اسمکتیت به (ایلایت+کلریت) با افزایش رطوبت افزایش می یابد و بیشترین مقدار این نسبت در رژیم رطوبتی زریک (برابر ۲/۱۲) مشاهده شده است.