Middle-East Journal of Scientific Research 7 (2): 153-161, 2011
ISSN 1990-9233

Morphological, Physico-Chemical and Clay Mineralogy Investigation on Gypsiferous Soils in Southern of Tehran, Iran

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Abstract: In this study, based on topographic maps, satellite images and conducted several field visits, ten pedons studied in the area and for further study four representative pedons selected which occurring on two different landscapes (piedmont plain and hill). Occurrence of gypsum in studied soils related to weathering the parent material and climatic conditions. In all pedons were observed secondary gypsum in small crystalline with diameters of a few millimeters and in different forms. Gypsum content showed an increase with depth in middle of all pedons and then its content decrease in lower horizons. The XRD diffractograms indicate the presence of chlorite, smectite, illite, palygorskite and kaolinite as the major clay minerals in these soils. Chlorite, illite and kaolinite can be originated from parent material. The amount of smectite in the clay fraction increased with depth except in pedon 5 and as for smectite, palygorskite showed an increasing trend with depth in the pedons 2, 4. Probably inheritance and transformation from illite are the main ways for existence of smectite. Neoformation of palygorskite is believed to be the main mechanisms for the occurrence of this mineral in the studied soils.

Key words: Morphology · Clay mineralogy · Smectite · Palygorskite · Gypsum · Arid soils

INTRODUCTION

Gypsiferous soils comprise important land resources of arid and semiarid regions of the world [1]. Iran seems to have the largest area of gypsiferous soils [2]. These soils occupy the largest area within the Aridisols (Gypsids) of Iran [3]. Gypsum accumulation is a characteristic phenomenon in arid and semiarid soils. Gypsum in soils is found over a wide range of temperatures [4]. The behaviour of soils with gypsum is different from soils where silicate minerals prevail, when gypsum is the main component of the soil, it controls its behaviour. The presence of gypsum as a widespread soil component is due to its solubility. Gypsum can be dissolved and its ions translocated in the soil or from one place in the landscape to another [5]. Gypsiferous soils occur generally in level to hilly lands, or in depressions [6]. Sufficient quantities of gypsum ($CaSO_4$, $2H_2O$) can affect soil properties and causing physicochemical, fertility, plant growth and crop production problems.

There have been several studies on the morphology, mineralogy and genesis of gypsiferous soils in Iran. Mahmoodi and Haidari [1] studied the classification and physicochemical properties of gypsiferous soils in southwest Gilanegharb area. Khademi and Mermut [7] studied the mineralogy of gypsiferous soils in the Isfahan region of central Iran and reported palygorskite crystals as the dominant clay mineral. Toomanian *et al*. [8] studied the genesis of gypsiferous soils and processes of formation and alteration of gypsic horizons and their pedofeatures in central Iran.

Minerals are indicators of the amount of weathering that has taken place and the presence or absence of particular minerals gives information as to how soils formed [9]. The mineralogical composition of gypsiferous soils is neither uniform nor stable. Gypsiferous soils do not have particular clay mineralogy; thought the presence of palygorskyte has often been associated with the occurrence of gypsum. Because of the unstable chemical environment of gypsiferous soils, their mineralogy provides no sound criterion for differentiation and classification [6]. Environmental conditions are suggested to lead to smectite formation in Aridisols [10]. Palygorskite was found to be widespread in late Cenozoic sediments of arid and semi-arid regions of Iran [7, 11]. The objectives of the present study were:

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- To study the morphological, physicochemical and mineralogical characteristics of gypsiferous soils in arid environment.
- To explain the clay minerals distribution and its origin.

MATERIALS AND METHODS

Description of the Study Area: This study was conducted on the lands south of Tehran province, between 51° 11' to 51° 20' E longitude and 35° 33' to 35° 20' N latitude (Figure 1) and has 30 km long and 1 km width around Tehran-Qom Highway. The elevation of the area varies between 850 to 950 m above sea level and its Physiographic units consist of Piedmont alluvial Plains and hills.

In term of geological formations area is characterized mainly by Cenozoic age formation, namely: Clay flat (Quaternary) dominated by clay and silt; Mud flat (Quaternary) saline silty clay; Upper Red Formation (Miocene) red marl with Siltstone, Sandstone, shale, conglomerate and gypsum and Hezar -Darreh (Pliocene) conglomerate.

Climatic data indicates mean annual rainfall is about 177 mm, most of precipitation falls from December to April and minimum rain occurred in summer. Annual mean temperature is 17.4°C , the temperature range to be from 3.9 to 11.2°C during the winter and between 26.2 and 31.35°C during the summer. Mean annual Potential evapotranspiration (thornthwaite method) is about 1033 mm. The soil moisture and temperature regime in this area are Aridic and Thermic, respectively.

The native vegetation in the region is thinly scattered and consists of *Prosopis* sp. Gramineae, *Alhagi* sp. *Calligonum* sp. *Citrullus* sp. and annual grasses.

In this study, we studied topographic maps, satellite images and conducted several field visits, then according to observation, ten pedons studied which two pedons located in hill and the rest placed on Piedmont Plains. Between studied pedons, four representative pedons were considered for further study (Figure 1). Pedons 2, 4 and 5 located in Piedmont Plains and pedon 9 placed on hill. Selected pedons described morphologically (Table 1) and soils were sampled using standard techniques [12].

Laboratory Procedures: The particle-size distribution (PSD) was determined by the pipette method [13], when gypsum content was less than 5 percent the gypsum was washed out and on samples with higher gypsum content (greater than 5 percent), the gypsum was coated by barium chloride ($BaCl_2$) to decrease its solubility [14] and the particle size distribution was determined by conventional pipette method. Standard chemical properties; pH, EC, OC, $CaCO_3$ equivalent, cations and anions, gypsum (acetone method) were determined according to [12].

The CEC of soils was determined by Rhoades method [15] using Na-acetate and NaCl at pH 8.2 for saturating the soils and $Mg(NO_3)_2$ for displacement of Na ions. The preparation of XRD diffractograms following the method of Kittrick and Hope [16] for removal of cementing agents and treatments of clay sample for XRD analysis. X-ray diffraction (XRD) conducted by using a Siemens D-5000 instrument with CuKá radiation.

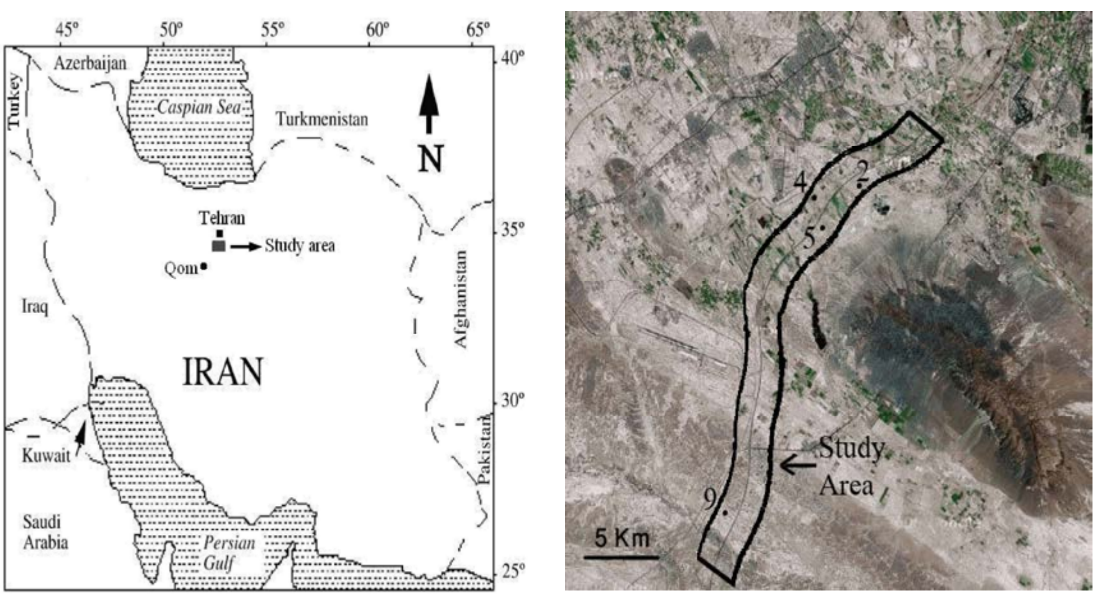

Fig. 1: Location of study area, southern of Tehran, Iran. (The dots and numbers indicate the position of study pedons)

Table 1: Classification and some of the morphological characteristics of the studied pedons.

Horizon	Depth(cm)	Boundary	Color (Moist)	Gypsum	Structure	Other components
Pedon 2- fine-gypseous, Hypergypsic, Thermic, Typic Calcigypsids						
Ap	0-28	aw	10YR5/3	-	Vf &f1gr	Common very fine roots,
$2By_1$	28-49	aw	10YR6/3	70% pendant 3f to ccs	m	few fine roots, %50-60 medium gravel
$3By_2$	49-90	aw	7.5YR5/4	3fcs	m	-
$4By_3$	90-150	-	7.5YR6/4	3fcs	m	-
Pedon 4- Loamy-skeletal, Gypsic, Thermic, shallow, Typic Petrogypsids						
Ap	0-10	as	2.5Y5/2	-	sg	%20 medium gravel
C	10-35	aw	2.5Y5/2	3f&mcs	sg	%70-80 fine & coarse gravel
2Bym	35-40	cw	10YR6/4	3f&mcs	m	-
2By	40-50	aw to as	10YR6/4	3fcs	Sg & 1vfabk	-
2Cr	50-60	cw	10YR6/4	2fcs	m	With rock structure (mudstone)
3C	60-75	as	10YR4/4	-	sg	Common fine and medium roots,
4Cr	75-98	as	10YR6/3	2fcs	m	With rock structure (siltstone)
5By	98-140	-	7.5YR5/4	2fcs	1fabk	-
Pedon5- Fine, Mixed, Semiactive, Thermic, Sodic Haplogypsids						
Ap1	0-10	aw	10YR6/4	-	1vfabk	Common very fine roots,
Ap2	10-23	cw	10YR5/4	-	m	Few very fine roots,
Bw1	23-45	cw	10YR4/4	-	1to 2fabk	Few fine roots,
Bw2	45-60	cw	10YR5/4	-	1vf &fabk	Few fine& medium roots,
Bg	60-90	cw	10YR6/4	-	1vfabk	Few fine& medium roots,
Bkyg1	90-105	as	10YR6/4	2fcs	2vf &fabk	Few fine& medium roots,
Bkyg2	105-115	as	2.5Y5/4	2fcs	m & sg	Few fine& medium roots,
2Bkyg3	115-150	-	10YR6/4	2fcs	2vf 7f abk	Few fine roots,
Pedon 9- Fragmental, Gypsic, Thermic, Typic Haplogypsids						
Ap	0-10	cw	10YR5/4	-	1vfgr & sg	-
Cy1	10-35	cw	10YR7/3	70- 80% pendant	-	%30 medium gravel & less than5% soil
Cy2	35-80	aw	10YR6/3	40-50% pendant	-	%60 coarse gravel & 5% soil
Cy3	80-110	aw	10YR5/3	20% pendant	-	%80 coarse gravel & stone & less than5% soil
2C	110-140	-	10YR6/4	<10% pendant	Sg &m	-

Symbols used according to abbreviation given in Soil Survey Manual, USDA.

Table 2: Physical and chemical properties of pedons in the studied region.

	Particle size distribution										
	Sand	Silt	Clay							CEC^S	CEC^C
Horizon	---------------------%----------------			SP	pH (paste)	EC(ds m^{-1})	OC %	CCE	Gypsum	--------(cmolc kg^{-1})-----	
Pedon 2											
A	55.7	18.6	25.7	51.82	7.55	3.2	0.48	11	37.02	10.98	42.72
$2By_1$	67.6	10.9	21.5	49.92	7.69	3.1	0.01	19.25	42.16	10.1	46.97
$3By_2$	49.8	14.4	35.8	57.87	7.52	3.05	0.01	3	67.22	16.01	44.72
$4By_3$	44.1	10.5	45.4	58.63	7.37	3.15	0.03	3.25	41.42	15.85	34.91
Pedon 4											
Ap	72	10.6	17.4	32.41	7.5	2.64	0.117	11.5	12.22	5.5	31.61
C	75.7	3.5	20.8	36.24	7.65	2.54	0.078	8	17.46	3.79	18.22
2Bym	53.3	18.1	28.6	46.65	7.81	3.02	0.088	12	51.6	5.44	19.02
2By	37.9	36.7	25.4	45.19	7.78	3.58	0.019	16	21.22	4.47	17.59
2Cr	24.1	44.1	31.8	46.15	8.02	6.3	0.136	16	12.82	7.32	23.01
3C	39.9	44.9	15.2	42.14	8.1	9.98	0.078	16.5	6.05	9.12	60
4Cr	10	51	39	54.09	8.17	14.37	0.039	19.5	14.88	12.49	32.02
5By	16.6	48	35.4	48.02	8.06	11.37	0.13	22	0.88	14.99	42.34
Pedon 5											
Ap1	31.6	47.2	21.2	36	7.89	7.17	0.575	17.5	0.5	12.87	60.70
Ap2	27.6	40.6	31.8	40.61	7.5	11.65	0.5	19.75	0	14.45	45.44
Bw1	29.6	35.6	34.8	41.6	7.79	10.82	0.3	19.25	0	13.27	38.13
Bw2	13.4	38.8	47.8	54.83	8.1	10.04	0.224	16	1.04	13.67	28.59
Bg	21	41.5	37.5	51.64	8.03	10.75	0.146	12.25	24.48	10.2	27.2
Bkyg1	17.1	36.7	46.2	51.11	8.18	14.2	0.136	14.25	9.28	14.15	30.63
Bkyg2	24.5	60.1	15.4	38.57	8.18	16.57	0.127	7.75	3.2	11.91	77.33
2Bkyg3	7	45	48	61.7	8.5	17.56	0.11	7	3.6	17.14	35.70
Pedon 9											
Ap	46.1	37.2	16.7	23.15	7.62	1.73	0.146	6.5	0.44	17.49	104.73
Cy1	71	7.3	21.7	41.13	7.9	2.63	0.048	1.5	29.32	13.31	61.33
Cy2	61.5	14.1	24.4	44.61	7.46	2.67	0.04	2.5	17.98	20.43	83.73
Cy3	80.3	9.4	10.3	41.18	7.43	3.13	0.01	0.5	6.02	20.75	---
2C	73.1	15.2	11.7	45.47	7.46	2.95	0.068	1.75	7.24	21.79	---

SP: Saturation Percentage. CCE: Calcium Carbonate Equivalent.
EC: Electrical Conductivity. CEC^S: Cation Exchange Capacity of soil.
OC: Organic Carbon. CEC^C: Cation Exchange Capacity of clay.

RESULTS AND DISCUSSION

Morphology and Physicochemical Characteristics: Table1 and 2 represent some important morphological, physical and chemical properties of the representative pedons, respectively.

Gypsum accumulation in soils is generally connected with the weathering of parent material which can be dissolved under the action of the penetrating water. Therefore, occurrence of gypsum in studied soils related to weathering the parent material and climatic conditions. Weathering and dissolution of gypsum in parent material and precipitation is considered the main mechanism for gypsum neoformation in the soils.

Stoops and Ilaiwi [17] explained the origin of gypsum in the gypsiferous soils of Syria which its originated from underlying or surrounding rock of Miocene age that are very rich in gypsum. The studied pedons contained measurable amounts of this mineral. Field observations, in all pedons were observed secondary gypsum in small crystalline with diameters of a few millimeters and in different forms such as pendant, lenticular, filament and irregular shapes which placed on groundmass. Stoops and Ilaiwi [17] noted the different types of gypsum crystals are without doubt related to specific environmental and pedogenetic factors, such as parent material, geomorphological position, climate, influence of the ground water, etc.

In pedons 2, 4 and 9 visible gypsum crystals were more than 20% (by volume) (Table 1) and the shapes of gypsum crystals in pedon 2 with increases depth lenticular and irregular form increased. In pedon 4 in upper horizons lenticular forms and in deeper horizons filament and irregular shapes were dominant. In pedon 5, gypsum crystals showed only in subsurface horizons (about 15% by volume) (Table 1) and the shapes of crystals in this pedon were irregular and lenticular forms. In pedon 9, in throughout the pedon pendant was dominant.

According to morphological and chemical analysis, gypsum content showed an increase with depth in middle of all pedons (between 30-80 cm) and then its content decrease in lower horizons. This suggests that during wetter and drier periods by leaching and capillary rise the gypsum was removed from soil surface and lower horizons, respectively and re-deposited in the middle pedons layers. The amounts of gypsum in studied area were between 0- 67.22 %. According to Soil Survey Staff 2010, pedons 2, 5, 9 had enough gypsum content in the soil to meet the requirements of the gypsic horizon and in pedon 4 meet the requirements of petrogypsic horizon. Pedon 2, 5 meet the requirements of the calcic horizon [18]. Therefore, coexistence of gypsic and calcic horizons in pedons 2 and 5, suggesting a two stages pedogenesis in these pedons.

The pH values of the studied soils range between 7.37-8.5 (Table 2). This parameter slightly increases with depth in pedons 4 and 5(slightly to moderately alkaline) and its nearly constant (slightly alkaline) in pedons 2 and 9. pH values of the surface layers are usually around 7.5. pH values in the studied soils confirmed the presence of salts, gypsum and calcium carbonate in the soils. The EC value of the soils is generally low to high (1.73-17.56 dS/m) (Table 2) but it shows an increase trend with depth, which is due to downward movement of more soluble salts. In pedons 4 and 5, probably, parent materials have influence on high EC.

The CEC of the soils is dependent on the amount and type of clay minerals, organic matter and gypsum content. Gypsum does not have electric charge therefore, with increasing gypsum in the soils CEC decreases. Soils exhibited CEC between 3.7 to 22 Cmol(+) kg^{-1} (Table 2). Boyadgiev and Verheye [6] indicated that CEC value in gypsiferous soils are generally between 6-22 Cmol(+) kg^{-1}. The CEC is often inversely correlated with the amount of gypsum in the soil [1, 6]. Low values of CEC in the soils are attributed to low organic matter, dominant clay minerals with low CEC and high amount of gypsum. The CEC of clay minerals in pedons 2, 4 and 5 are less than 60 Cmol(+)Kg^{-1} (Table 2) which indicate the clay minerals with low CEC are dominated, but in pedon 9 CEC of clay is high, that can be confirmed the exist of clay with high CEC.

The organic carbon (OC) content was low in the all studied pedons and generally decreases with depth. Higher organic carbon values were observed at surface horizons in pedons (Table 2). Deficiency of OC content showed limitation of water and excess of gypsum in the studied region. The OC content of gypsiferous soils is highly variable, although it is generally low and concentrated in the surface and decreases rapidly with depth in semiarid and arid environments [6].

The studied pedons according to the Soil Survey Staff [18], morphological, physicochemical and mineralogical data classified. pedons 2(fine-gypseous, Hypergypsic, Thermic, Typic calcigypsids), 4(Loamy-skeletal, Gypsic, Thermic, shallow, typic petrogypsids) and 5(Fine, Mixed, Semiactive, Thermic, Sodic Haplogypsids) which all of these pedons located on the piedmont plain and pedon 9(Fragmental, Gypsic, Thermic, Typic Haplogypsids) placed on the hill physiographic unit.

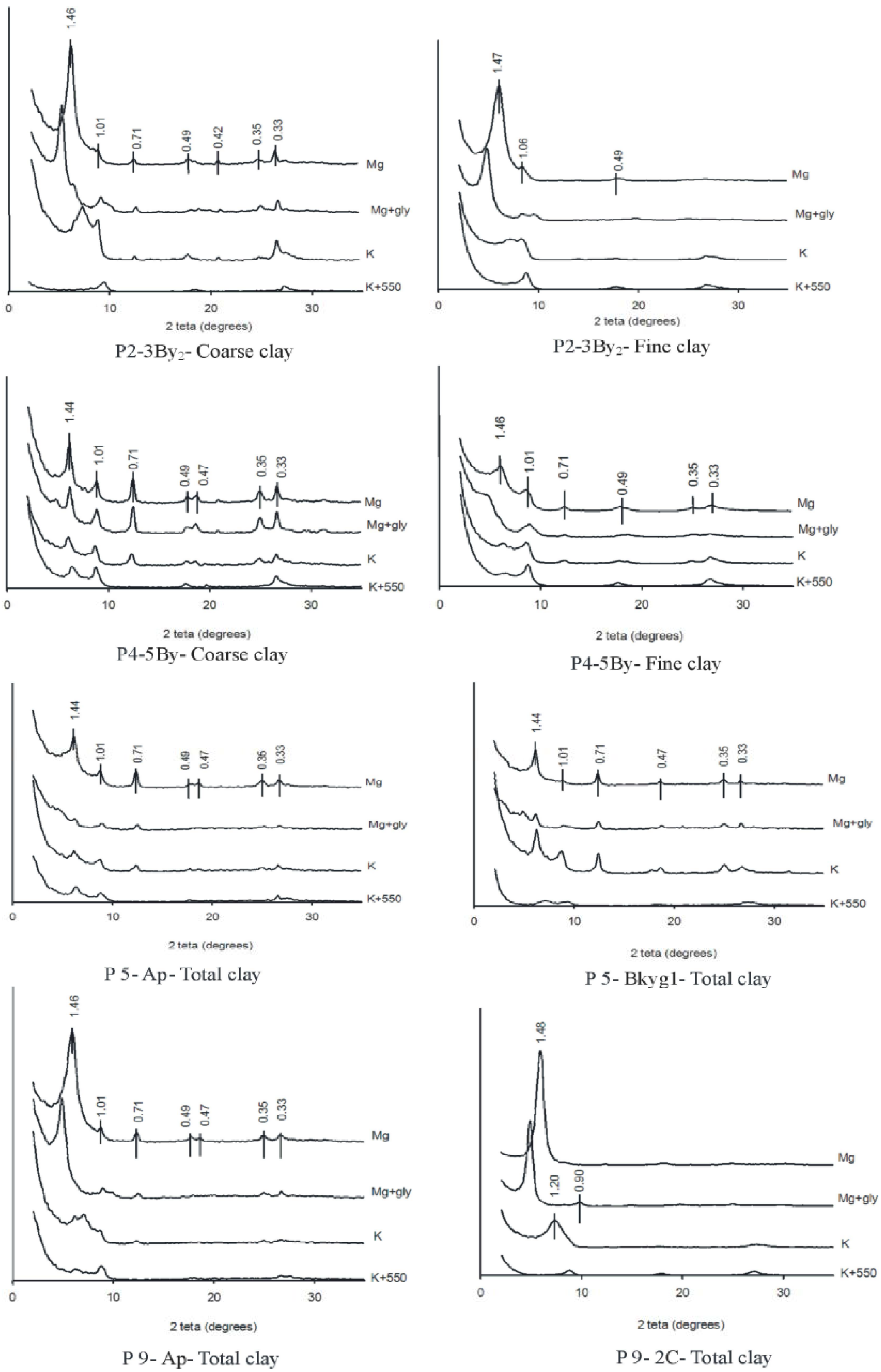

Fig. 2: XRD patterns of clay fractions (<0.002 mm) of the selected studied soil samples.

Clay Mineralogy of Soils: The XRD diffractograms indicate the presence of chlorite, smectite, illite, palygorskite, kaolinite and quartz as the major clay minerals in these soils (Figure 2). Large amount of chlorite and illite present at soils surface in pedons 2, 9. In contrast, low amount of those minerals exist in pedons 4 and 5, which distributed in regular manner. Smectite nearly observed in all pedons and increased with depth in pedons 2, 4, 9 and in pedon 5 contains almost homogenously distributed throughout the soil profile (Figure 2). As for Smectite, palygorskite showed an increasing trend with depth in the pedons 2 and 4.

The CEC of clay minerals in soils of pedons 2, 4 and 5 are less than 60 Cmol(+)Kg^{-1}(Table 2) which indicates that minerals with low CEC are dominant and confirmed the XRD results that showed dominated by Chlorite, illite, palygorskite and Kaolinite. The higher CEC values of the clay observed in soils of pedon 9 (Table 2), XRD results showing that they was dominated by smectite (Figure 2). Finally, the CEC values of clay minerals are in accordance with obtained data from clay mineralogy.

The presence of chlorite, illite and kaolinite can be originated from parent material, because conditions to form of these minerals did not exist in the studied region. Although mica (illite) in arid soils may form pedogenically as well, but only in special circumstances, mainly through K fixation of pre-existing smectite [19]. According to Jackson's weathering sequence, the evidence for the clay mineral weathering sequence is the depth distribution of the clay minerals. According to this sequence, the clay mica (illite) content should increase with depth. In contrast, the smectitic type of clay minerals should increase toward the surface [20]. However, our results showed an opposite trend in clay mineral distributions. The clay mica (illite) content of the surface horizon (in pedons 2, 4 and 9) was higher than the lower part of the solum. Several processes may account for this increase in the surface, such as aeolian deposition(dust fall) of this mineral [20], Enhanced physical weathering of biotite grains in the near-surface horizons due to large daily and seasonal fluctuations in temperature and moisture [10]. In the present study, this is probably due to the low clay mica content of the parent materials and with less probability simple transformation of illite to other clay minerals (mainly smectite) may play a major role in the decrease of illite content with depth. The calcareous and gypsiferous environment, high in Mg and Si mobility, may create favorable condition for the formation of smectite through transformation. Transformation of illite into smectite requires depotassification, dealumination and silication [21, 11]. In this study, the amount of smectite in the clay fraction increased with depth except in pedon 5. According to Buol [22], smectite content and the crystallinity increased with depth in semi-arid and arid regions. Allen and Hajek [23] have three possible explanations of the trend reported by Buol [22]: (1) synthesis of smectite in the lower part of the solum, (2) instability of smectite in the upper part of the solum and (3) preferential translocation of the smectite to the lower part of the solum.

Low-lying topography, poor drainage and base-rich parent material, favorable 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 [24]. Our results indicated that in all pedons were relatively well drained and lack the wetness conditions required for the neoformation of smectite. In the pedon 9 probably inheritance and detrital origin can be a major mechanism for occurrence of this mineral, because in XRD diffractograms the peak of smectite was height, sharp and did not has shoulder and in subsurface horizons other minerals were absent (Figure 2). In the other pedons probably transformation is the main way for existence of this mineral. Illite is a main precursor mineral for the formation of smectite in the soils.

The results indicated that, as for smectite, palygorskite showed an increasing trend with depth in the pedons 2, 4; probably due to more favorable conditions in the deeper horizons. Owliaie *et al*. [11] and Khormali and Abtahi [21] showed that there is a reverse correlation between palygorskite and smectite in arid and semiarid calcareous soils of southern Iran. In the studied pedons an inverse relation between smectite and palygorskite were not observed. Singer [25] noted that the frequent association of smectite and palygorskite is "a result of proximity in their stability field, but does not necessarily imply a solid-phase transformation of one into another."

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 [26]. Neoformation of palygorskite seems to need large activities of Si and Mg with a pH of about 2 [25]. Although both calcareous and gypsiferous soils can provide buffered alkaline media with necessary anions and cations for palygorskite crystallization but characteristics of the solution chemistry of the gypsiferous soils may result more favorable medium for this purpose. It is known that gypsum would increase the Mg/Ca ratio of the host water which could in turn encourage palygorskite formation [27]. Hence, this source of palygorskite can be a possible origin especially in arid region of the southern Tehran province.

The major pathways for the formation of clay minerals in arid regions for the studied pedons are: Chlorite, illite and kaolinite in soils are considered mainly of inherited origin from parent materials. Both inheritance (in pedon 9) and transformation from mica (illite) is believed to be the main mechanisms for the occurrence of smectite in the other studied pedons. Neoformation of palygorskite is the major mechanism for the occurrence of this clay mineral in the studied soils.

CONCLUSION

From a comprehensive study of the soils (field observations, physicochemical analyses and clay mineralogy), we draw the following conclusions:

- Weathering and dissolution of gypsum in parent material and precipitation is considered the main mechanism for gypsum neoformation in the soils. Gypsum content showed an increase with depth and reaches a maximum content at about (30-80 cm) in all pedons and again decreases in lower parts of the soils, this suggests that during wetter and drier periods by leaching and capillary rise the gypsum was removed from soil surface and lower horizons, respectively and re-deposited in the middle pedons layers.
- Chlorite, smectite, illite, palygorskite, kaolinite and quartz are the major clay minerals in the soils in decreasing order.
- Chlorite, illite and kaolinite can be originated from parent material.
- Probable due to the low clay mica content of the parent materials and with less probability simple transformation of illite to other clay minerals (mainly smectite) may play a major role in decrease of illite content with depth in the studied soils.
- All pedons were relatively well drained and lack the wetness conditions required for the neoformation of smectite. Therefore, inheritance and transformation are the main pathways for the occurrence of smectite in the soils studied.
- As for smectite, palygorskite shows an increasing trend with depth in pedons 2 and 4, probably due to more favorable conditions in the deeper horizons. Gypsum would favor the in situ formation of palygorkite from soil solution.

ACKNOWLEDGEMENT

The authors thank the department of soil science of Shahed and Tehran Universities for joint work in this study. We are also grateful to Dr. M.R. Miransari, Dr. A. Haidari, Mr. Mrs. Roushan and Mr. M.R. Azizi for their valuable help in this investigation.

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