Characterization of gypsiferous soils in the north of Urmia, Iran

L. Pashaei, Sh. Manafi[*]

Department of soil science, Faculty of agriculture and natural resources, Urmia University, Urmia, Iran

Abstract

Gypsiferous soils contain sufficient gypsum to influence soil physico-chemical, mineralogical, mechanical properties and geotechnical conditions and as a consequence, affect plant growth and crop production. So physico-chemical and mineralogical properties of 6 soil profiles located on the gypsiferous parent material with semi-arid climate in north of Urmia, West Azerbaijan province, Iran, were investigated. Based on standard methods, morphological, physico-chemical and mineralogical properties of these soils were determined. Soils with higher gypsum content had lighter color, lighter texture, lower values of organic carbon and cation exchange capacity and higher values of electrical conductivity. These parameters were reversely changed with decreasing gypsum content of soils. Semi-quantitative analysis of clay minerals indicated the presence of smectite, illite, chlorite, kaolinite and palygorskite were as major clay minerals with decreasing order from smectite to palygorskite. The origin of illite, chlorite and kaolinite were related to the inheritance from parent material. Smectite group of clay minerals has been resulted from three origins of inheritance from parent material, transformation of illite and palygorskite and neoformation, but the transformation and neoformation are the main pathways for its formation. Palygorskite has pedogenic origin and has been formed via neoformation. The comparison of clay mineralogy of soils with different gypsum values revealed the presence of higher smectites in soils with higher gypsum. Palygorskite was identified just in soils with higher gypsum. In soils with lower values of gypsum, illite and chlorite were the predominant clay minerals and palygorskite did not identified.

Keywords: Clay mineralogy, Gypsum, Neoformation, Palygorskite, Smectite, Transformation.

Introduction

Gypsiferous soils (soils with gypsum accumulations) extend over approximately 100 million ha in the world (Verheye and Boyadgiev, 1997). They are widespread in north, central and east Africa (51 million ha) and in south-central (21 million ha) and north-central Asia (16 million ha). Sometimes, they cover large parts of the national territory, e.g. in Syria (22%), Somalia (l6%), Iraq (11%) or Tunisia (9%) (Verheye and Boyadgiev, 1997; Al- Saoudi et al., 2013; Ahmed, 2013; Azeez and Rahimi, 2017; Owliaei et al., 2018). Estimates of the area under these soils in Iran are varied. Mashali (1996) has reported these soils to be distributed over 9.8 million ha. Based on Mahmoodi (1994), the extent of gypsiferous areas in Iran may be over 30 million ha. The optimal and sustainable use of these soils needs accurate recognition of their morphological, physical, chemical and mineralogical properties. A more adequate use of these soils might have a major impact on the economy and development potential of those countries with gypsiferous soils (Verheye and Boyadgiev, 1997; Al-Barrak and Rowell, 2006; Omran, 2012; Al- Saoudi et al., 2013; Kijjanapanich 2014).

---

[*] Corresponding author e-mail: sh.manafi@urmia.ac.ir

The mineralogical composition of gypsiferous soils is neither uniform nor stable (Al-Dabbas et al., 2010; Azizi et al., 2011; Owliaei et al., 2018). Gypsiferous soils do not have certain type of clay minerals; as for example the occurrence of palygorskite has often been associated with the presence of gypsum (Al-Dabbas et al., 2010; Buza et al., 2007; Hashemi et al., 2013; Owliaei et al., 2018; Bhattacharyya et al., (2018). Because of the unstable chemical environment of gypsiferous soils, their mineralogy provides no sound criterion for differentiation and classification (Azizi et al., 2011; Owliaei et al., 2018). Hashemi et al., (2013) revealed that playgorskite, chlorite, illite, and smectite are the major clay minerals in their studied gypsiferous soils along a toposequence. In a study of gypsiferous soils in southeastern Iran, Farpoor et al., (2005) reported palygorskite as one of the dominant clay minerals and stated that the amount and size of palygorskite bundles decrease moving down slope. Additionally, they reported that an increase in Mg/Ca ratio at the time of gypsum accumulation, accompanying high pH, and high soluble Si has led to palygorskite formation at the peripheries of interior lakes during Neogene. In gypsiferous soils of Samarra and Karbala areas in Iraq, Al-Dabbas et al., (2010) reported that chlorite, montmorillonite, kaolinite, illite and palygorskite were dominant clay minerals. They concluded that the dominant presence of palygorskite among the clay minerals reflects the arid and semiarid climatic conditions. Moreover, in a transect composed of different landforms including piedmont plain, alluvial fan, alluvial plain, river alluvial plain, and plateau on gypsifrous material, Owliaei et al., (2018) found smectite, illite, chlorite, palygorskite, kaolinite and quartz as major clay minerals in all landscape surfaces. They reported that a large amount of smectite is inherited from the marl formations, and related some of smectites to the product of transformation of illite and also palygorskite weathering, particularly at the surface horizons and in the soils with aquic moisture regime.

From the engineering view point, gypsiferous soils are one of the most complex materials that challenge the geotechnical engineers. These soils are usually characterized as collapsible soils, decreasing strength upon wetting, and dissolving in flowing water (Ahmed, 2013). The collapsibility of gypsiferous soils results from the direct contact of water. The dissolution of different types of salts contained inside the mass of gypsiferous soils will generate new pores inside the soil skeleton and loosen the cementing bonds between the particles. This process creates a metastable structure that facilitates the sliding of particles into a denser state (Al-Saoudi et al., 2013; Ahmed, 2013). The relatively moderate solubility of gypsum in water renders such susceptibility to sink-hole formation and caving (Al-Dabbas et al., 2010). Moreover, Golyeva et al., (2018) found almost pure gypsum within the cultural layer of soils in Late Bronze age in Ural Region (Russia), and stated that the presence of gypsum in this region is representing a consecutive series of houses built one after another at the same place. They concluded that the accumulation of large amounts of gypsum rocks within the ancient settlement site has been resulted to unusual/extreme gypsum content in the studied soils of this environment.

So, the correct and accurate identification and recognition of gypsum and gypsiferous soils are important for understanding potential uses and limitations of gypsiferous soils. Misidentification can lead to many problems including the misclassification of soils, improper land use, failure of engineered structures. Several researchers have studied gypsiferous soils from different parts of Iran (Khademi and Mermut, 1998; Farpoor et al., 2005; Azizi et al., 2011; Hashemi et al., 2013; Owliaei et al., 2018, among others). But all of these studies have been focused on central and southeast of Iran and gypsiferous soils in the north west of Iran have not yet been studied. The 1:1000000 soil map of Iran which is the only complete reference for the soils of Iran, contains no information about gypsiferous soils of northwest of Iran (due to its very small scale). So, the main objective of the present study was to

characterize the physico-chemical and mineralogical properties of gypsiferous soils in the north of Urmia region (northwest of Iran).

Materials and Methods

Description of Study Area

This study was conducted in the central part of West Azerbaijan province (north west of Iran), between 37° 44' to 37° 51' N latitude and 44° 59' to 45° 5' E longitude, 30 km north of Urmia (figure 1a). The elevation varies between 1338 to 1610 m above sea level. Physiographically, this area contains three physiographic units including hills, piedmont colluvial plains and piedmont non gravelly plains. According to Soltani Sisi (2005), geological formations of this area are characterized mainly by Cenozoic age formation, including: recent

Figure 1. a) Location of study area in West Azerbaijan Province, and b) map of the study area indicating representative pedons

Alluviums and some gravel fans (Quaternary) dominated by clay and silt; marl and argillaceous limestone with gypsum lenses (Qom formation, Oligocene) and in some parts metamorphosed rocks including gneiss, amphibolite, meta-diorite, schist and skarn (Precambrian). All of our studied profiles are located on parent material resulted from Qom formation, Oligocene. This formation contains gypsum to the extent that gypsum mining activities are concurrent in this area and in the surface of soils, one can see many gypseous rock fragments with different stages of weathering (figure 2).

Based on climatic data, mean annual rainfall of this area (1975-2015) is 345.3 mm and the most of precipitation falls from November to April and minimum rain falls during summer in July, August and September. Accordingly, mean annual temperature is 10.83°C, and mean monthly temperature ranges from 19.5 to 22.5°C during summer and from 0.7 to -2.2°C during winter and annual potential evapotranspiration (Thornthwaite method) is 679.7 mm. According to calculations of New Hall Program, the soil moisture and temperature regimes in this area are Dry Xeric and Mesic respectively.

Figure 2. Gypseous rock fragments with different stages of weathering

Field Sampling

The periphery of area with gypsiferous soils was determined based on topographic and geologic maps and several field survey and observations, and also the position of nine soil profiles were determined regarding topography and land use (table 1). These six soil profiles were dug, described and sampled using standard methods (Soil Survey staff, 2012) and were classified according to soil taxonomy (Soil Survey staff, 2014). Based on differences in topography and land use, six representative profiles were considered for further physico-chemical and mineralogical studies. Samples were taken from genetic horizons of soils for physico-chemical and mineralogical studies. Prior to laboratory analysis, soil samples were air dried, crashed and passed through a 2 mm sieve. The less than 2 mm fraction of soil samples was used for physico-chemical and mineralogical analysis.

Laboratory Methods

Particle size analyses were performed on samples from each horizon using the hydrometer method described by Gee and Bauder (1986). Regarding to the presence of different amounts of gypsum in these soils, 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 40 cm^3 of solution containing 50 g dm^{-3} barium chloride ($BaCl_2$) to decrease its solubility (Hesse, 1974) and the particle size distribution was determined by conventional pipette method. Chemical properties including pH, electrical conductivity (EC), organic carbon (OC), calcium carbonate equivalent (CCE), soluble cations and anions, and gypsum content (acetone method) were determined according to standard methods described by USDA (USDA-NRCS, 2004). Cation exchange capacity (CEC) was determined using sodium acetate 1 N at a pH of 8.2 (Sumner and Miller, 1996).

In order to do mineralogical analysis, selected samples were repeatedly washed out 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% H_2O_2. Iron oxides were removed from

the samples by the dithionate- citrate- bicarbonate (CBD) 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. Mg-saturated clay subsamples 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 4 hours) at 550°C. X-ray diffraction (XRD) patterns were obtained with SHIMADZU XRD 600 diffractometer, using Cukα radiation (30kV, 30mA).

Results and Discussion

A total of nine soil profiles were studied in this investigation. Among them, some morphological, physical and chemical properties of six representative pedons have been provided in tables 1 and 2. Presence of ochric, cambic, gypsic, hypergypsic and calcic diagnostic horizons were identified in field observations and were also confirmed by physicochemical properties of these soils (Table 1). Based on field observations, various forms of secondary gypsum accumulations were identified in all pedons including: wool-like masses, pendant, filament, blocky and irregular shapes which were placed in groundmass and on stones (Figure 3). These forms of gypsum are of the most common forms of gypsum accumulations in soils and have been reported by several researchers in all around the world (Shahid and Abdel Fattah, 2009; Azizi et al., 2011; Hashemi et al., 2013; Khechai and Daoud, 2016; Azeez and Rahimi, 2017; Owliaei et al., 2018, Golyeva et al., 2018, among others). As an example, Shahid and Abdel Fattah (2009) found 12 morphological forms of gypsum in desert soils of Abu Dhabi Emirate including lenticular, euhedral, rosettes, fibrous, tubular, fan, massive, exfoliated, honey comb or porous, powdery, bottlebrush, and rock outcrop. They stated these forms are developing different internal and external soil features.

The study of gypsum features using hand lenses revealed that most of these features have been formed in large pores and consequently formed more or less complete infillings. Golyeva et al., (2018) have been stated that due to the accumulation of gypsum infillings in pores, they are clearly pedogenic.

Table 1. Morphological and physical characteristics and classification (soil survey staff, 2014) of selected pedons

Horizon	Depth (cm)	Boundary	Color (moist)	structure	Particle size distribution (%)			Gypsum features	Coarse fragments (%)
					snad	silt	clay		
Pedon 1 (hills land type, seasonal pasture land use)- Fine-gypseous, Hypergypsic, mesic Gypsic Haploxerepts									
A	0-8	cs	10YR 4/4	1,2; m,c; gr	57.2	22.8	20	-	-
Byy	8-45	cs	10YR 5/6	2,3; m,c; abk	71.2	12.8	16	2fcs	< 5% fine gravel
Cyy	45-55	-	10YR 5/6	ma	54.2	20.8	25	2f&mcs	5-10% fine & medium gravel
Pedon 2 (hills land type, seasonal pasture land use)- Fine-gypseous, Hypergypsic, mesic Gypsic Haploxerepts									
A	0-10	cs	10YR 5/4	1,2; vf,f; gr	54.2	22.8	23	-	-
Cy1	10-35	ds	10YR 6/4	ma	57.2	17.8	25	2fcs	5-10% fine & medium gravel
Cy2	35-70	-	10YR 6/4	ma	62.2	15.8	22	2f&mcs	5-10% medium gravel
Pedon 3 (hills land type, seasonal pasture land use)- Fine-loamy, gypsic, mesic Gypsic Haploxerepts									
A	0-13	cs	10YR 5/4	1,2; f,m; gr	65.2	18.8	16	-	-
Cy1	13-55	ds	10YR 5/4	ma	57.2	18.8	24	2fcs; pendants 3%	5 gravel
Cy2	55-95	-	10YR 7/4	ma	66.2	13.8	20	2f&mcs; pendants 5%	5 medium gravel

Table 1 continued. Morphological and physical characteristics and classification (soil survey staff, 2014)

of selected pedons

Horizon	Depth (cm)	Boundary	Color (moist)	structure	Particle size distribution (%)			Gypsum features	Coarse fragments (%)
					snad	silt	clay		
Pedon 4 (piedmont plane land type, rain fed land use)- Fine-loamy, gypsic, mesic Gypsic Haploxerepts									
A	0-13	cs	10YR 5/6	1,2; vf,f; gr	57.2	19.8	23	-	-
Cy1	13-65	cs	10YR 5/6	Sg	67.2	13.8	19	2fcs; pendants 5%	10-20% fine & medium gravel
Cy2	65-100	ab	10YR 5/6	Sg	55.2	18.8	26	2fcs; pendants 10%	20-30% medium gravel
2Cy3	100-135	ds	10YR 6/6	ma	55.2	14.8	30	2fcs	5% fine gravel
3Cy4	135-155	-	10YR 5/4	ma	60.2	16.8	23	2fcs	5-10% fine & medium gravel
Pedon 5 (piedmont plane land type, orchard land use)- Fine-loamy, mixed, superactive mesic Typic Haploxerepts									
Ap	0-32	cs	10YR 4/3	2,3;m,c;gr 2; m; sbk	62	14	24	-	-
Bw	32-70	cs	10YR 4/3	2; m; abk	60	14	26	-	-
Cy1	70-110	ds	10YR 5/3	ma	59	18	23	2fcs	10% medium gravel
Cy2	110-155	-	10YR 6/3	ma	61	18	21	2fcs	15% medium gravel
Pedon 6 (piedmont plane land type, orchard land use)- Fine-loamy, mixed, superactive, mesic, Typic Calcixerepts									
Ap	0-31	cs	10YR 4/3	1; m; gr 1,2;f,m;abk	67	14	19	-	-
Bw	31-65	cs	10YR 5/6	2; m,c; abk	64	12	24	-	-
Bk	65-95	cs	10YR 5/4	2; m,c; abk	66	10	24	-	-
Bky	95-120	cs	10YR 5/4	2; m,c; abk	68	10	22	2fcs	< 5% fine gravel
Cy	120-150	cs	10YR 4/4	ma	62	17	21	2fcs	< 5% fine gravel
C	150-185	-	10YR 6/4	ma	64	12	24	-	10% fine gravel

Symbols adopted from: Soil Survey Staff, 2012. Field Book for Describing and Sampling Soils. National Soil Survey Center. Natural Resources Conservation Service. U.S. Department of Agriculture. Version 3.0, 315p.

**Table 2.** Chemical properties of selected pedons

Horizon	Depth (cm)	$pH_{(se)}$	EC (dSm^{-1})	OC (%)	CECs $(cmol_{(+)}kg^{-1})$	CCE (%)	Gypsum (%)	Dominant soluble cations and anions $(meql^{-1})$		
								Ca^{2+}	Mg^{2+}	SO_4^{2-}
Pedon 1- Fine-gypseous, Hypergypsic, mesic Gypsic Haploxerepts										
A	0-8	7.4	2.24	1.41	17.3	17.5	24.79	16.0	3.8	21.4
Byy	8-45	7.6	2.85	0.32	9.20	21.0	53.75	18.5	5.4	26.1
Cyy	45-55	7.6	3.60	0.20	7.20	18.0	62.91	22.8	6.2	30.5
Pedon 2- Fine-gypseous, Hypergypsic, mesic Gypsic Haploxerepts										
A	0-10	7.5	2.13	0.66	15.9	21.7	22.5	13.4	3.2	18.4
Cy1	10-35	7.7	2.66	0.64	13.7	26.0	39.1	18.6	4.8	23.8
Cy2	35-70	7.6	3.54	0.45	10.5	28.5	52.7	25.4	5.8	32.6
Pedon 3- Fine-loamy, gypsic, mesic Gypsic Haploxerepts										
A	0-13	7.6	1.43	1.62	17.35	20.1	19.96	8.8	2.3	11.5
Cy1	13-55	7.7	2.47	0.86	17.27	24	24.16	14.3	5.5	22.6
Cy2	55-95	7.4	3.29	0.39	14.6	27	29.79	22.2	5.6	30.7
Pedon 4- Fine-loamy, gypsic, mesic Gypsic Haploxerepts										
A	0-13	7.4	0.95	0.33	16.76	24.0	12.10	5.4	2.0	8.4
Cy1	13-65	7.5	2.25	0.30	14.14	26.5	19.37	11	5.6	21.1
Cy2	65-100	7.7	2.68	0.28	14.31	25.5	18.75	13	7.3	24.5
2Cy3	100-135	7.7	3.22	0.27	14.45	26.5	19.16	14.4	8.2	31.3
3Cy4	135-155	7.6	3.64	0.23	12.40	27.0	28.82	18.6	7.8	36.8

Table 2 continued. Chemical properties of selected pedons

Horizon	Depth (cm)	$pH_{(se)}$	EC (dSm^{-1})	OC (%)	CECs (cmol$_{(+)}$kg^{-1})	CCE (%)	Gypsum (%)	Dominant soluble cations and anions (meql^{-1})		
								Ca^{2+}	Mg^{2+}	SO_4^{2-}
Pedon 5- Fine-loamy, mixed, superactive mesic Typic Haploxerepts									
Ap	0-32	7.5	0.65	2.67	19.27	19.5	2.91	4.6	1.2	4.2
Bw	32-70	7.4	0.82	0.69	17.22	21.5	4.98	5.4	1.8	5.0
Cy1	70-110	7.7	1.12	0.51	14.42	14.0	9.91	7.1	2.4	7.2
Cy2	110-155	7.6	1.65	0.44	13.68	20.0	14.71	8.8	3.6	11.7
Pedon 6- Fine-loamy, mixed, superactive, mesic, Typic Calcixerepts									
Ap	0-31	7.4	0.57	2.07	18.16	13.5	3.12	3.1	1.8	3.8
Bw	31-65	7.4	0.65	0.36	15.55	14.5	3.12	3.8	1.2	4.4
Bk	65-95	7.6	0.75	0.23	13.8	21.5	7.77	4.6	1.8	4.6
Bky	95-120	7.5	0.85	0.23	11.42	19.5	11.7	5.1	1.9	5.5
Cy	120-150	7.7	1.10	0.21	10.91	23.0	14.7	6.7	2.8	7.4
C	150-185	7.7	1.46	0.21	11.52	18.5	8.47	7.2	3.4	11.5

$pH_{(se)}$: pH in saturated extract, EC: electrical conductivity, OC: organic carbon, CCE: calcium carbonate equivalent, CECs: cation exchange capacity of soil.

It seems the dissolution of gypsum in surface horizons and perdecendom movement of calcium and sulphate ions in percolating soil water creates the conditions for precipitation of gypsum in macropores and the formation of these pedofeatures. This is the most common mechanism for the formation of gypsum pedofeatures (Hashemi *et al.,* 2013; Khechai and Daoud, 2016; Azeez and Rahimi, 2017; Owliaei *et al.,* 2018, Golyeva *et al.,* 2018).
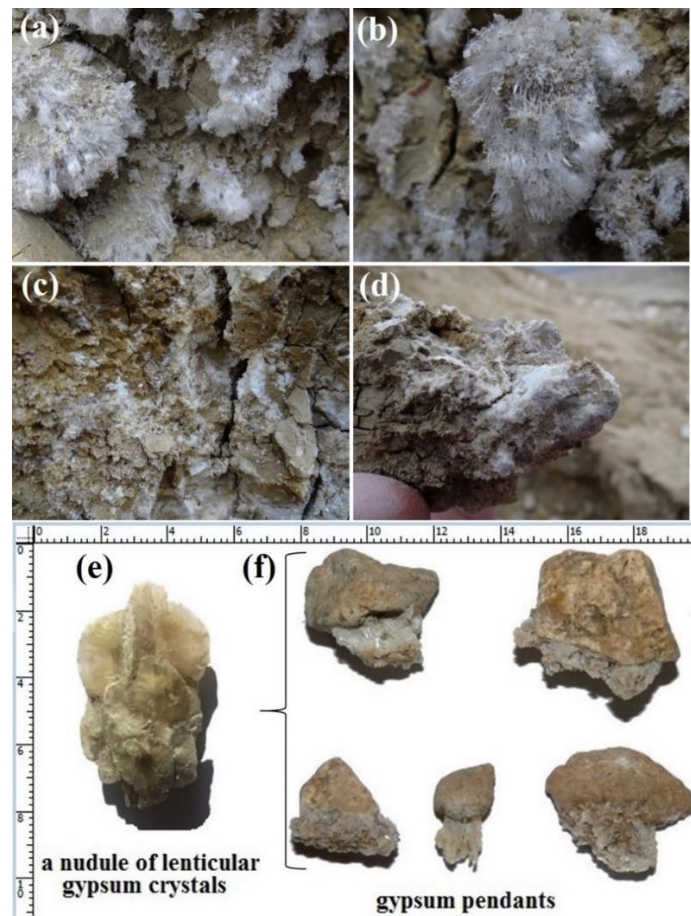
Figure 3. Various forms of gypsum accumulations in studied soils. a) and b) wool-like masses, c) and d) blocky microcrystals, e) lenticular crystals and f) pendants

One of the exciting forms of gypsum accumulations in theses soils is wool-like masses (Figure 3a and 3b) which was observed in truncated places and also walls of pedons as well as surfaces of peds and skeletal grains and formed wool-like structures and cranks of needle shape or fibrous structures with white colors (Figure 3). In order to test whether these structures are gypsum, some of them were dissolved in distilled water. Then acetone was added to this solution. The color of solution changed from colorless to white cloudy and white colored masses precipitates appeared which confirms the gyepseous origin of these structures. It seems these structures are the first products of evaporation of sulphate and calcium containing waters in contact with air and subsequently precipitation of gypsum in these shapes. Because these structures were observed only in places which have been exposed to the air and were absent in deeper places of pedons and in soil matrix as well.

All of the studied pedons were containing considerable amounts of gypsum (Table 2). Gypsum is a semi-soluble salt which is more soluble than calcite ($CaCO_3$) but much less soluble than other soluble salts like halite ($NaCl$) and thenardite (Na_2SO_4). Due to its solubility, dissolution of gypsiferous parent material is one of the possible origins for the presence of gypsum in soils. According to Soltani Sisi (2005), these pedons have been located on gypsiferous rocks of Miocene age. So, the occurrence of gypsum in these soils was related to the weathering of parent material and climatic conditions. Weathering and dissolution of gypsum in parent material and reprecipitation are considered the main mechanism for gypsum neoformation in these soils. In the same way, Owliaei et al., (2018) in South western, Iran, Azizi et al., (2011) in soils of Tehran, Iran, Farpoor et al., (2005) in southeast Iran and Abbaslou and Abtahi, (2007) in calcareous, gypsiferous, saline soils and sediments of Bakhtegan Lake Bank, Southern Iran were related the presence of gypsum to the weathering of parent material. In the same way, Buringh (1960) and Barzanji (1973) in Iraq, Stoops and Ilaiwi (1981) in Syria and Van Alphen and Romero (1971) in the Ebro Valley of Spain explained that the gypsum in their studied gypsiferous soils originated from underlying or surrounding rock that are very rich in gypsum. Khechai and Daoud (2016) in Algeria and Azeez and Rahimi (2017) in Iraq state that gypsum originates from the material in the catchment areas that has been eroded and re-deposited.

Gypsum content in all of the studied pedons was increased with depth, in which, its lower values were in A and Ap horizons and subsequently its higher content were in By, Byy, Cy and Cyy horizons (Table 2). The increasing trend of gypsum content with soil depth indicates that during wetter periods the gypsum was removed from soil surface by leaching and re-deposited in the lower horizons. Additionally, the presence of gypsum pendants in pedons 3 and 4 confirms that gypsum in these soils has been transported downward and gypsum pedofeatures (such as pendants) have been formed through perdescendom mode. The same results have been reported by Farpoor et al., (2005), Al-Barrak and Rowell (2006), Abbaslou and Abtahi (2007), Shahid and Abdel Fattah (2009), Azizi et al., (2011), Omran (2012), Al-Saoudi et al., (2013), Azeez and Rahimi (2017), and Owliaei et al., (2018) in gypsiferous soils of arid and semiarid regions in Middleast and Golyeva et al., (2018) in gypsiferous soils of Ural Region, Russia.

The amounts of gypsum in the studied area varied from 2.91% in Ap horizon of pedon 5 to 62.91% in Cyy horizon of pedon 1 (Table 2, Figure 3). According to Soil Survey Staff (2014), all of the studied pedons had enough gypsum content in the soil to meet the requirements of the gypsic horizon. The pedon 5 meets also the requirements of calcic horizon.

All of the studied soils were light textured and their clay content varies from 16% in Byy horizon of pedon 1 to 26% in Cy2 horizon of pedon 4 (Table 1). Van Alphen and Romero (1971), Abbaslou and Abtahi (2007), Azizi et al., (2011) and Azeez and Rahimi (2017) have also been reported the light texture of their studied gypsiferous soils. According to Van Alphen and Romero (1971), in the Ebro Valley, Spain, samples taken from the non gypsic

surface layer of gypsiferous soils showed the clay content to range from 2 to 40 %, and in the Euphrates Basin, Syria, from 2 to 35 %. The texture depends largely on the nature of the parent material from which the soil is derived and on their degree of interbedding in gypsum deposits.

These gypsiferous soils are calcareous too and their calcium carbonate content varies from 13.5% in Ap horizon of pedon 6 to 28.5% in Cy2 horizon of pedon 2 (Table 2). Calcium carbonate equivalent content of these soils increased with soil depth and secondary calcium carbonate accumulations were observed as soft masses and nodules in Bk and Bky horizons of pedon 6. This indicates the dissolution of calcium carbonate in surface horizons and its vertical translocation and subsequently reprecipitation at lower depths as stated by Van Alphen and Romero (1971), Abbaslou and Abtahi (2007), Azeez and Rahimi (2017) and Owliaei et al., (2018). The pH values of the studied soils ranged between 7.3-7.7 (Table 2) and in all pedons it increases slightly with depth (slightly to moderately alkaline). This parameter had the lower values in surface horizons (A and Ap horizons; Table 2). The semiarid climate of this area which restricts leaching of base cations and presence of relatively high values of calcium carbonate and its buffering capacity have restricted the variation of pH in these soils. In the same way, Azeez and Rahimi (2017) and Owliaei et al., (2018), have reported neutral to slightly alkaline pH values in gypsiferous soils and have related these pH values and its limited variations to the effect of calcareous parent material and type of climatic conditions. The EC value of the soils is generally low (0.57-3.64 dS/m) (Table 2) but it shows an increasing trend with depth, which is due to downward movement of more soluble salts. In pedons 1, 2, 3 and 4, probably, parent materials have influence on high EC. Profiles 5 and 6 with orchard land use have the lowest values of EC (Table 2) and it seems that irrigation in these agricultural soils has washed out soluble salts and gypsum out of soil profile. Additionally, the higher values of EC were observed in soils with higher values of gypsum especially in profiles 1, 2 and 3 (Table 2). This indicates contribution of gypsum in electrical conductivity of these soils (Al-Barrak and Rowell, 2006; Abbaslou and Abtahi, 2007; Azizi et al., 2011; Azeez and Rahimi, 2017).

The organic carbon (OC) content was relatively low in all the studied pedons and generally regularly decreases with depth, in which, the higher values of organic carbon were observed at surface horizons of all pedons (Table 2). This trend has also been reported by Al-Barrak and Rowell (2006), Abbaslou and Abtahi (2007), Azizi et al., (2011), Azeez and Rahimi (2017) and Owliaei et al., (2018). According to Van Alphen and Romero (1971), Verheye and Boyadgiev (1997) 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.

The CEC values of these gypsiferous soils were low and varies from 7.20 Cmol$_{(+)}$/kg in Cyy horizon of pedon 1 to 19.3 Cmol$_{(+)}$/kg in Ap horizon of pedon 5 (Table 2). The CEC of soils depends on the amount of organic matter, clay content, clay mineralogy and gypsum content of soils. In these soils higher values of CEC were observed in A and Ap horizons with higher values of organic carbon and lower content of gypsum (comparing with lower horizons in each profile) and the values of CEC were decreased with decreasing of organic carbon and increasing soil depth (Table 2). This trend of changes in organic matter content and values of CEC reflects direct effect of organic matter content on CEC of these soils. The same results have been reported by Farpoor et al., (2005), Abbaslou and Abtahi (2007), Al-Dabbas et al., (2010), Chiquoine (2012), Azizi et al., (2011), Hashemi et al., (2013), Azeez and Rahimi (2017) and Owliaei et al., (2018). Gypsum does not have negative electric charge. Therefore, with increasing gypsum in the soils, CEC decreases accordingly. Van Alphen and Romero (1971), Verheye and Boyadgiev (1997), Al-Barrak and Rowell (2006) and Owliaei et al., (2018) indicated that CEC values in gypsiferous soils are generally between 6-22 Cmol$_{(+)}$/kg

and the CEC is often inversely correlated with the amount of gypsum in the soil. Finally, low values of CEC in the soils were attributed to low organic matter, presence clay minerals with low CEC (discussed in the next section, table 3, figure 4) and high amount of gypsum.

Clay mineralogy of soils and parent material

X-ray diffractograms and semi quantitative abundance of clay minerals in the studied soils and related parent material are shown in Figure 4 and Table 3, respectively. The semi-quantitative contents of the clay minerals were estimated according to Johns et al., (1954). Semi-quantitative assessments make the identification of individual components in polymineralic samples much more valuable. Clay mineral investigation of parent material (C horizons; Figure 4a) revealed presence of illite, chlorite, kaolinite and miner values of smectite in the clay fraction of parent material. Additionally, smectite, illite, Chlorite, palygorskite and kaolinite were present in clay fraction of soils and smectite and illite were the major clay minerals in soil samples (Table 3; Figure 4). Kaolinite is present as a minor clay mineral in all studied soils and its abundance is nearly constant along pedons (Table 3). Thus the presence of kaolinite is related to the inheritance from parent material, because suitable conditions to the formation of this mineral do not exist in the studied region (Khademi and Mermut, 1998; Manafi, 2010; Al-Dabbas et al., 2010; Azizi et al., 2011; Hashemi et al., 2013; Owliaei et al., 2018). Moreover, the presence of similar amount of kaolinite in parent material to the soils also confirms this conclusion. According to the reports of Manafi (2010), Azizi et al., (2011), Hashemi et al., (2013) and Owliaei et al., (2018) in gypsiferous soils of arid and semiarid regions in Iran, almost constant values of kaolinite have been identified along soil profiles and these authors have the origin of kaolinite to the inheritance from parent material.

According to mineralogical results, illite and chlorite were two clay minerals in these soils (Table 3; Figure 4). Regarding the presence of considerable values of these minerals in parent material, their abundance in the soils is largely inherited from parent material. Manafi (2010) has reported that in semiarid soils of Rashakan region in the west of Urmia Lake, inheritance from parent material is the main source of illite and chlorite. Detrital origin of illite and chlorite in gypsiferous soils of arid and semiarid regions has been also reported by Grobler (2002), Farpoor et al., (2005), Abbaslou and Abtahi (2007), Al-Dabbas et al., (2010), Azizi et al., (2011), Hashemi et al., (2013) and Owliaei et al., (2018). According to Khademi and Mermut (1998) and Owliaei et al., (2018), where illite and chlorite are considered as the precursors for the pedogenic formation of other clay minerals.

Smectite is one of the major clay minerals in these soils and identified in all of studied samples. Higher smectite contents were observed in soils with higher gypsum (table 3; figure 4). Smectite in soils originates 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 (Borchardt, 1989; Wilson, 1999; Hashemi et al., 2013; and Owliaei et al., 2018). Regarding to the presence of little amounts of smectite in parent material of these soils (Figure 4a), an inheritance origin was considered for some of smectits. An overview of X-ray diffractograms reveals that the smectite content in soil samples is higher than that of parent material and inheritance from parent material can't be the only origin of smectite. So, other pathways for the presence of smectite such as transformation and neoformation must be considered. One of the main precursors for the formation of smectite in soils is illite, particularly at the surface horizons (Borchardt, 1989; Wilson, 1999; Manafi, 2010; Hashemi et al., 2013; and Owliaei et al., 2018). X-ray investigations revealed that nearly in all of these soils 1nm peaks are asymmetric and have a shoulder toward 1.4nm (figure 4). Moreover, there is a reverse correlation between illite and smectite in the studied

pedons (Table 3). These can be indicative of illite weathering and its transformation to other clay minerals such as smectite, as reported by Boettinger and Southard (1995), Abbaslou and Abtahi (2007), Al-Dabbas et al., (2010), Manafi (2010), Azizi et al., (2011) and Owliaei et al., (2018). The other clay minerals which can act as a precursor for the formation smectite in this area is Palygorskite (Buza et al., 2007; Galan and Singer, 2011; Hashemi et al., 2013). Our results revealed a reverse correlation between smectite and palygorskite in our studied pedons in which the highest content of palygorskite is observed in deeper horizons (Table 3). This can be indicative of weathering and transformation of palygorskite to smectite in surface horizons. According to Singer (2002) and Galan and Singer (2011), in areas with mean annual precipitation more than 300 mm, palygorskite weathers to smectite. Buza et al., (2007) stated that the stability of fibrous minerals is restricted to arid and semiarid regions and in wetter conditions these minerals weather to smectite. So, regarding to recent climate of this area with 345.3 mm annual precipitation, it seems that this amount of precipitation favors transformation of palygorskite to smectite in these soils where smaller quantities of palygorskite in surface horizons (Table 3) confirms this conclusion. The same results have been reported by Khademi and Mermut (1998), Buza et al., (2007), Hashemi et al., (2013), Owliaei et al., (2018) and Bhattacharyya et al., (2018) among others.
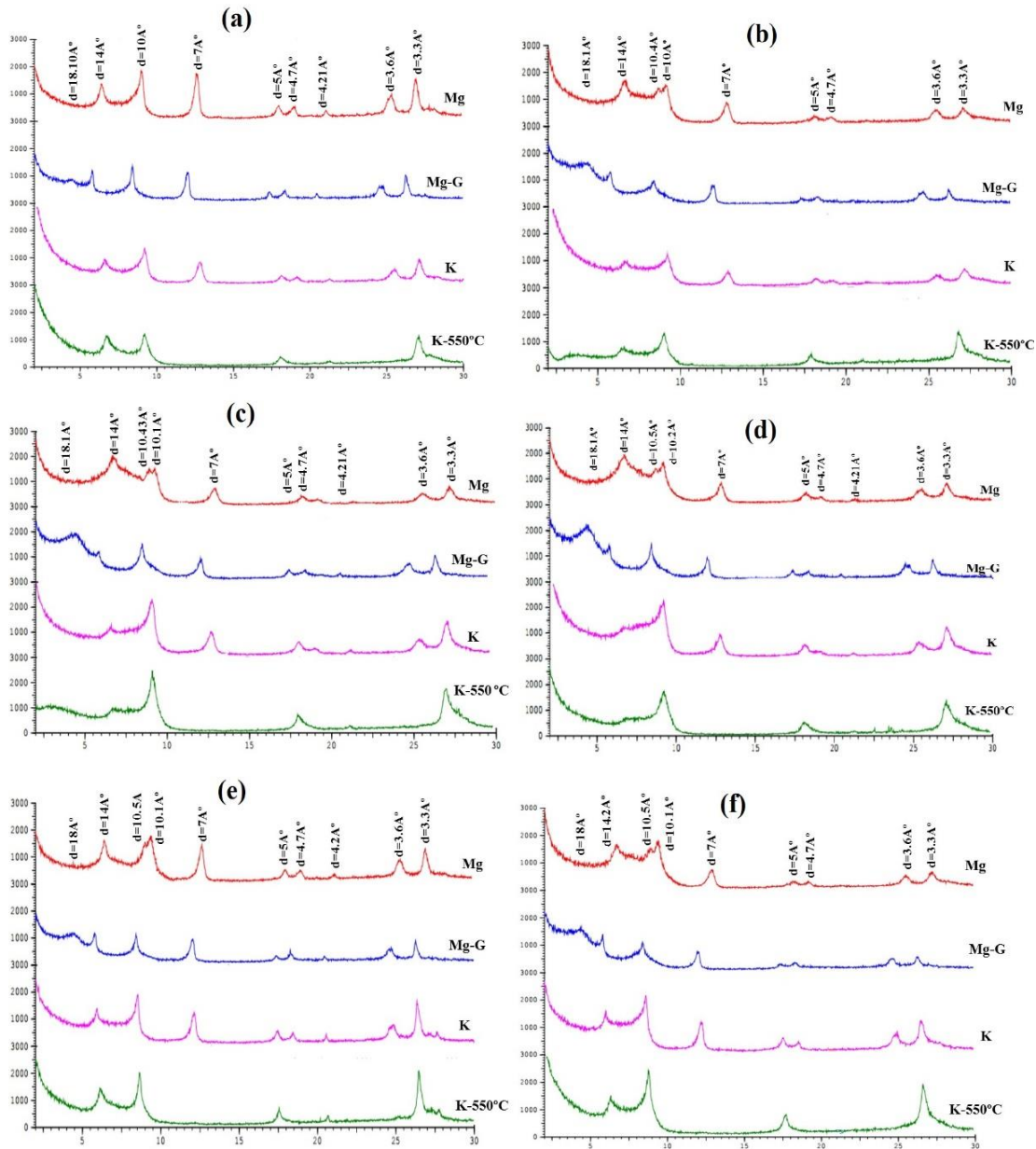
Figure 4. X-Ray diffractograms of the clay fraction in selected soils. a) C horizon of profile 6, b) Cyy horizon of profile 1, c) Cy2 horizon of profile 2, d) Cy2 horizon of profile 3, e) Bw horizon of profile 5 and f) Bky horizon of profile 6

Table 3. Semi quantitative values of clay minerals in the studied soils

Profile	Horizon	Clay minerals				
		Illite	Smectite	Chlorite	Kaolinite	Palygorskite
	A	++	++++	++	++	-
1	Byy	++	++	+	++	+
	Cyy	+++	+++	+	++	+++
	A	++	+++	++	+	-
2	Cy1	++	+++	++	++	+
	Cy2	+++	++++	++	++	++
	A	++	+++	+	++	-
3	Cy1	+++	++	++	++	+
	Cy2	+++	++++	+	+	+
	A	++	++	++	++	--
4	Cy1	+++	+++	++	++	--
	Cy2	++++	++	++	++	--

	Ap	++	+++	+	+	--
5	Bw	+++	+++	+	++	-
	Cy1	++++	++	++	++	-
	Cy2	++++	++	++	++	-
	Ap	++	++	+	++	--
	Bw	++	++	++	+	--
6	Bk	+++	+++	++	++	--
	Bky	+++	++++	++	++	-
	C	++++	++	++	+	--

-- < 1 % , - 1 % , + < 10% , ++ 10 -20 % , +++ 20-30% , ++++ 30-40% ,
+++++ > 50% (Wilson, 1999)

The other possible mechanism for the formation of smectite in these soils is neoformation. According to Borchardt (1989), Perkins (2002) and Churchman and Lowe (2012), neoformation of smectite from soil solution needs high pH, high silica activity, low activity Al and abundance of basic cations especially Mg. Moreover, Churchman and Lowe (2012) stated that, in soils with pH more than 7 (around 8) Si is highly soluble, whereas, in such pHs Al is insoluble. The pH values of these soils are more than 7.5 (Table 2) and it seems this conditions lead to solubility and high activity of Si as well as low activity of Al. So, it might that the abundance of basic cations (Ca and Mg, Table 2) along with high activity of Si and low activity of Al (as a consequence of high pH values) favor formation of smectite from soil solution. In addition, Churchman and Lowe (2012) have noted that in these conditions, high values of Mg which is present in calcareous materials can substitute Al in the mineral lattice and form smectite. These conditions are present in recent studied gypsiferous soils with high amounts of calcium carbonate (Table 2). Finally, all of these are clues of neoformation as a source of some of smectites in these gypsiferous soils, at least in lower horizons, where transformation of illite alone can't describe the presence of high values of smectites.

In these soils, palygorskite is present in lower depths and it is unidentifiable in surface horizon, as well as in parent material (Table 3, Figure 4). So, regarding the absence of palygorskite in parent material, a pedogenic origin for its presence was considered. Palygorskite requires alkaline conditions and high activities of Si and Mg and also appropriate input of Al in solution for stability (Singer, 2002; Galan and Singer, 2011). In these soils with alkaline conditions (Table 2), the highest values of palygorskite were identified in horizons with higher gypsum content and there was a positive correlation between palygorskite and gypsum content. This suggests that presence of gypsum favors the formation of palygorskite in these soils (Khademi and Mermut, 1998; Buza et al., 2007; Galan and Singer, 2011; Owliaei et al., 2018; Bhattacharyya et al., 2018). Precipitation and crystallization of gypsum decreases the content of calcium ions and reversely, increases magnesium content and so, Mg/Ca ratio in soil solution which provides suitable conditions for the neoformation of palygorskite. Khademi and Mermut (1998) have reported that increase of Mg/Ca ratio after gypsum crystallization in Tertiary followed by Miocene orogenic activities in arid lands of central Iran as the main formation factor of palygorskite. Neoformation of palygorskite has also been reported by Azizi et al., (2011), Hashemi et al., (2013) and Owliaei et al., (2018) in Iran, Buza et al., (2007) in Argentina, Al-Dabbas et al., (2010) in Iraq, and Bhattacharyya et al., (2018) in India.

Conclusion

The results of this study revealed the presence of different forms of secondary gypsum accumulations including wool-like masses, pendant, lenticular, filament, blocky, microcrystalline and irregular shapes which placed on groundmass. The dissolution of gypsum in surface horizons and perdecendom movement of calcium and sulphate ions via

percolating soil water and subsequent evaporation creates the condition for precipitation of gypsum in macropores and the formation of mentioned pedofeatures. The presence of gypsum pendants further, confirms this conclusion. The amounts of gypsum varied from 2.9% in Ap horizon of pedon 5 to 62.9% in Cyy horizon of pedon 1 which also indicates the dissolution of gypsum in soil surface. All of these soils were light textured and the electrical conductivity (EC) of these soils increased with increase in gypsum content, whereas, their organic carbon (OC) content and cation exchange capacity (CEC) decreased. Smectite, illite, Chlorite, palygorskite and kaolinite were present in the clay fraction of soils. The origin of illite, chlorite and kaolinite was related to the inheritance from parent material. Inheritance from parent material considered as origin of a part of smectites, but the main origin was transformation of illite and palygorskite (especially in surface horizons) and neoformation (in lower horizons) as well. Palygorskite in these soils is pedogenic and has been formed as a result of neoformation. Higher values of gypsum favor the formation of palygorskite and the highest values of palygorskite were identified in horizons with higher gypsum content.

References

Abbaslou H, Abtahi A. 2007. Origin and distribution of clay minerals in calcareous, gypsiferous, saline
   soils and sediments of Bakhtegan Lake Bank, Southern Iran. Iran Agricultural Research, 26(1-2): 71-
   86.
Ahmed KI. 2013. Effect of gypsum on the hydro-mechanical characteristics of partially saturated sandy
   soil. PhD thesis, College of Physical Sciences and Engineering Cardiff University, Cardiff, Australia,
   302p.
Al- Saoudi NKS, Al- Khafaji AN, Al- Mosawi MJ. 2013. Challenging Problems of Gypseous Soils
   in Iraq. In: Delage, P., J. Desrues, F. Roger, (Eds.). Challenges and innovations in geotechnics.
   Proceedings of the 18th International Conference on Soil Mechanics and Geotechnical Engineering,
   2-6 September, Paris. France. pp. 479-482.
Al-Barrak K, Rowell DL. 2006. The solubility of gypsum in calcareous soils. Geoderma, 136: 830–
   837.
Al-Dabbas MA, Schanz T, Yassen M.J. 2010. Comparison of gypsiferous soils in Samarra and Karbala
   areas, Iraq. Iraqi Bulletin of Geology and Mining, 6(2): 115- 126.
Azeez SN, Rahimi I. 2017. Distribution of gypsiferous soil using geoinformatics techniques for some
   aridisols in garmian, Kurdistan region-Iraq. Kurdistan Journal of Applied Research, 2(1): 57-64.
Azizi P, Mahmoodi Sh, Torabi H, Masihabadi M.H, Homaee M. 2011. Morphological, physico-
   chemical and clay mineralogy investigation on gypsiferous soils in southern of Tehran, Iran. Middle-
   East Journal of Scientific Research, 7 (2): 153-161.
Barzanji AF. 1973. Gypsiferous soils of Iraq. Ph.D. Thesis, University of Ghent, Ghent, Belgium.
Bhattacharyya T, Ray S.K, Chandran P, Karthikeyan K, Pal D.K. 2018. Soil quality and fibrous mineral
   in black soils of Maharashtra. Current science, 115(3): 482-492.
Boettinger JL, Southard R.J. 1995. Phyllosilicate distribution and origin in Aridisols on a granitic
   pediment, Western Mojave Desert. Soil Science Society of American Journal, 59: 1189-1198.
Borchardt G. 1989. Smectites. In: Dixon, J.B., S.B. Weed, (Eds.). 1989. Minerals in soil environment.
   2nd ed. Number I in the SSSA book series. Published by SSSA. Madison. Wisconsin. USA. pp. 675-
   729.
Bouza PJ, Simon MJ, Aguilar H, Rostagno M. 2007. Fibrous clay mineral formation and soil evolution
   in Aridisols of northeastern Patagonia, Argentina. Geoderma, 139: 38-50.

Buringh P. 1960. Soils and soil conditions in Iraq. Ministry of Agriculture, Iraq. 322p.

Chiquoine LP. 2012. Restoration of biological soil crust on disturbed gypsiferous soils in Lake Mead National Recreation area, eastern Mojave Desert. M.Sc. thesis, University of Nevada, Las Vegas, USA.

Churchman GJ, Lowe DJ. 2012. Alteration, formation, and occurrence of minerals in soils. In: Huang, P.M., Y. Li, M.E. Sumner, Handbook of Soil Science: Properties and Processes. CRC Press, Boca Raton, FL, USA; p. 1–72.

Farpoor MH, Khademi H, Eghbal MK. 2005. Genesis of selected gypsiferous soils in southeast Iran. In: Afyuni, M. (Ed.). Proceedings of international conference on human impacts on soil quality attributes. Sept. 12-16, 2005. Isfahan. Iran. pp. 126-131.

Galan E, Singer A. 2011. Developments in palygorskite- sepiolite research. A new outlook on these nanoparticles. Developments in clay science. Elsevier. 520p.

Gee GW, Bauder JW. 1986. Particle Size Analysis, Hydrometer Method. Part I. In: Klute, A. (Ed.). Methods of Soil Analysis. American Society of Agronomy, Madison, WI. pp. 404-408.

Golyeva A, Khokhlova O, Lebedeva M, Shcherbakov N, Shuteleva I. 2018. Micromorphological and chemical features of soils as evidence of Bronze Age ancient anthropogenic impact (late Bronze Age
muradymovo settlement, Ural Region, Russia). Geosciences, 8(9), 313: 1-12.

Grobler L. 2002. The nature of precipitated gypsum in a soil irrigated with gypsiferous water. M.Sc. thesis, Department of soil science, University of Pretoria, Pretoria, South Africa.

Hashemi SS, Baghernejad M, Najafi Ghiri M. 2013. Clay mineralogy of gypsiferous soils under different soil moisture regimes in Fars Province, Iran. Journal of Agricultural Science and Technology, 15: 1053-1068.Hesse, P.R., 1974. Methods of soil analysis- texture analysis of gypsic soils. The Euphrates pilot irrigation project, FAO. Report number 67, 522 p.

Jackson ML. 1975. Soil Chemical Analysis. Advanced Course University of Wisconsin, College of Agriculture, Department of Soils, Madison, WI. 894 pp.

Johns WD, Grim R.E, Bradley F. 1954. Quantitative estimation of clay minerals by diffraction methods.
Journal of Sedimentary Petrology, 24(4): 242-251.

Khademi H, Mermut AR. 1998. Source of palygorskite in gypsiferous Aridisols and associated sediments from central Iran. Clay Minerals, 33: 561-575.

Khechai S, Daoud Y. 2016. Characterization and origin of gypsum rhizoliths of Ziban Oases Soil- Algeria. World Applied Sciences Journal, 34 (7): 948-955.

Kijjanapanich P. 2014. Sulfate reduction for remediation of gypsiferous soils and solid wastes. Ph.D. Thesis, Erasmus Joint doctorate program in Environmental Technology for Contaminated Solids, Soils and Sediments (ETeCoS^3). 150p.

Kittrick JA, Hope EW. 1963. A procedure for the particle size separation of soils for X-Ray diffraction analysis. Soil Science Society of American Journal, 96: 312-325.

Mahmoodi Sh. 1994. Properties and management of gypsiferous soils. In: Jalalian, A. (Ed.). Proceedings
of 4th Soil Science Congress of Iran, Isfahan University of Technology, 29- 31 Aug. Isfahan, Iran. pp. 59-65.

Manafi Sh. 2010. Mineralogical Evidence of Climate Change in some Semiarid Soils of Southern Urmia,
Iran. Soil Science, Agrochemistry and Ecology, 4: 17-24.

Mashali AM. 1996. Soil management practice for gypsiferous soils. In: Poch, M. (Ed.). Proceedings of the International Symposium on Soil with Gypsum. Lleida, Catalonia, Spain. pp. 34-52.

Mehra OP, Jackson ML. 1960. Iron oxide removal from soils and clays by a dithionite citrate system with sodium bicarbonate. Clays and Clay Minerals, 7: 317-327.

Omran E. 2012. A neural network model for mapping and predicting unconventional soils at a regional
level. Applied Remote Sensing Journal, 2(2): 35-44.

Owliaie HR, Najafi Ghiri M, Shakeri S. 2018. Soil-landscape relationship as indicated by pedogenesis data on selected soils from Southwestern, Iran. Eurasian Journal of Soil Science, 7(2): 167–180.

Perkins D. 2002. Mineralogy. 2nd ed. Prentice Hall. New Jersey. 483p.

Shahid ShA, Abdel Fattah MA. 2009. Gypsum polymorphism in the desert environment of Abu Dhabi Emirate. European Journal of Scientific Research; 29(2): 237-248.

Singer A. 2002. Palygorskite and sepiolite. In: Dixon, J.B., D.G. Schulze, (Eds.). Soil Mineralogy with Environmental Applications, SSSA Book Series, Soil Science Society of America, Madison, WI, Vol. 7, pp. 555–583.

Soil Survey Staff, 2012. Field Book for Describing and Sampling Soils. National Soil Survey Center. Natural Resources Conservation Service. U.S. Department of Agriculture. Version 3.0, 315p.

Soil survey staff, 2014. Keys to soil taxonomy. 12th edition. USDA.NRCS. 346p.

Soltani Sisi G. 2005. Geological map of Iran, 1:100000 series, sheet No, 5065. Geological survey and mineral Exploration of Iran.

Stoops G, Ilaiwi M. 1981. Gypsum in arid soils morphology and genesis. In: Beinroth, F.H., A. Osman,

(Eds.). Proceeding of the third international soil classification workshop. Arab Center for the studies

of Arid Zones and Dry lands. Damascus, Syria. pp: 175-185.

Sumner ME, Miller WP. 1996. Cation Exchange Capacity and Exchange Coefficients. In: Sparks, D.L. (Ed.), Methods of Soil Analysis Part 3: Chemical Methods, SSSA Book Series 5, Soil Science Society

of America. Madison, Wisconsin. pp. 1201-1230.

USDA-NRCS, 2004. Soil Survey Laboratory Methods Manual. Soil survey investigations. Report No, 42. Version 3, 693p.

Van Alphen JG, Romero F. 1971. Gypsiferous soils. Notes on their characteristics and management. International Institute for Land Reclamation and Improvement. Bulletin number: 12. 44p.

Verheye WH, Boyadgiev TG. 1997. Evaluating the land use potential of gypsiferous soils from field pedogenic characteristics. Soil Use and Management, 13:97-103.

Wilson MJ. 1999. The origin and formation of clay minerals in soils: past, present and future perspectives. Clay Minerals, 34: 7-24.