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Research Paper

Effect of weathering and mineralogy on the distribution of major and trace elements (Hormozgan province, Southern Iran)

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Abstract: Geochemistry composition and mineralogy distribution of different bulk soil and rock samples from Hormozgan province were investigated in order to address element distribution of soils in the context of their weathering, soil forming process and geology to describe impacts of parent material and soil evolution on the soil characteristics. For this reason, major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, and Zr) as metal oxides and mineralogy composition of bulk soil and rocks were analyzed. Total content of some trace elements (Cr, Ni, Cu, Zn, Cd, Sn, and Pb) were measured in bulk soil samples as well. The studied area is part of arid region in southern Iran with predominant sedimentary rocks and evaporite/evaporate formations. Coefficients between the elements of each subgroup are positive and significant ($p < 0.05$), indicating that their presence can be accounted for by similar reasons. Most samples and most elements controlled by the geochemical composition of parent material, this may be attributed to the weak soil development and lack of soil contamination in the studied pedons. Calcium correlated positively with loss on ignition (LOI) and negatively with Major elements; it does not indicate the anthropogenic origin of Ca. In general, soils developed on metamorphic and igneous parent rocks rather than evaporates indicated distinct accumulation of Si, Al, Fe, Mn, K, Ti, and Zr in different particles. Indices based on soil macro elements, such as CIA, CIW, PWI, WIP could express the variations in unweathered materials and rate of weathering and can be taken as an index of soil development. In addition to high contents of alkali and alkali earth elements of the sand and silt rich soils, both the Chemical Index of Alteration values (4.61 to 67.40), Chemical Index of Weathering values (4.82 to 71.73) and also high Product of Weathering Index (PWI) and Weathering Index of Parker (WIP) contents, suggests a relatively mild weathering source area.

Keywords: Soil geochemistry, pedogenesis, sedimentary rocks, enrichment factor, arid climate

Introduction

The wide range of elements concentrations observed in soils is the result of interaction between various factors affecting geological weathering and soil forming processes. During early pedogenesis, the chemical composition of a soil are generally controlled by the lithology of soil parent material, whereas the elemental distribution of mature soils strongly reflects the effects of weathering environment and pedological processes responsible for the formation of soils, in particular climate (Mitchell, 1964; Thanachit, et al. 2006; Nael et al. 2009; Acosta et al. 2011; Scarciglia et al. 2011; Achyuthan et al. 2012).

The influence of lithogenic factors and soil-forming processes on the content and mobilization of elements vary strongly among elements and soil profiles. Nael et al. (2009) studied the forest soils of western Alborz, Iran and showed that different elements exhibited very different enrichment/depletion patterns in a given pedon. Moreover, depth distribution patterns differed also for a given element among soils with different parent material and even showed considerable variation among soils with similar lithology. Trace element concentrations in the soils of western Alborz were related primarily to the parent material type while pedogenic processes appear to have played a minor role.

Soils are characterized by an intrinsic variability through time and space at different scales of observation and are often affected by morphodynamic processes strictly interacting with pedogenesis, under changing (paleo) environmental/climatic conditions. Therefore, an overall increasing degree of soil evolution with age appears from the values of the weathering indices, as well as from the detailed analysis of element distribution, although rejuvenation or aging of the pedogenetic front is often recorded by these features (Scarciglia, et al. 2011). The geochemistry and mineralogy are influenced primarily by the composition of the soil parent material, but climate (i.e., average annual precipitation) also is a major factor as pointed out by Smith et al. 2011 and Woodruff et al. (2009).

A holistic understanding of the environmental behavior of ME and TE in the soil should not be limited to total element contents in bulk soils but must also include their concentrations in different solid phases in a soil (Hardy and Cornu, 2006).

The effect of both physical and chemical processes on the parental materials prior to and during transport will influence particle size ranges and therefore accessory mineral and clay content, which in turn control many aspects of element chemistry (Castillo et al. 2008).

Accompanying studies of soil mineralogy and geochemistry will be identified here are useful not only for understanding the development of pedology in future areas of research and providing a frame of reference from which pedologists can evaluate potential scientific contributions to a rapidly changing world, but also for sustainable management of land and resources. However, the distribution of metals in soil in regard with soil evolution have not been well studied, in particular in arid soils which are in initial stages of development and/or current arid soils that have been influenced by paleoclimate (wetter climate). Therefore, the objective of this research were: (1) to quantify the geochemical composition of the soil (2) to assess the influence of inherited lithogenic factors on the content of major elements and their fate during weathering and pedogenesis in arid soils.

Materials and Methods

Study area

The study area is located in Hormozgan province (between 24° 25' to 57° 28' N latitude and 41° 52' to 15° 59' E longitudes) in the southern Iran and northern Persian Gulf and Oman Sea (Figure 1). The study area is situated in a desert to a semi-desert like region with a warm (hot) and dry climate that the mean annual precipitation and temperature of the region are 185 mm and 25°C, respectively. Aridic and Ustic soil moisture regimes were obtained for the whole Hormozgan province. The soil temperature regime is hyperthermic but some rare north and coastal areas have thermic and isothermic regime, respectively (Van Wambeke, 2000). Geologically, this province is a junction of three important structural zones of Iran: "Zagros", "Makran" and "Central Iran". The study area dominated with diverse lithostratigraphic units from Late Precambrian to Cenozoic sequences and covered by Carbonatic sequence of Jurassic-Cretaceous evaporates formations of Eocene-Pliocene, and Quaternary deposits (Figure 1). Stable subsidence and the unique landscape-climatic conditions favored the accumulation of a very thick sedimentary lens of carbonate rocks and evaporates (Aghanabati, 2004).

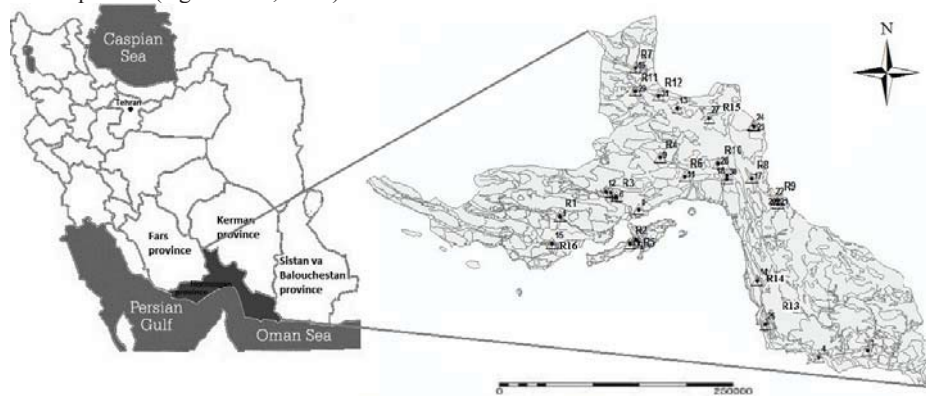


Figure 1. Location of the study area and sampling points(R: rock samples, numbers: Soil samples)

Sample collection and preparation

Pedogenic and lithogenic horizons of 28 soil pedons (41 soil sample) and associated rock samples (10 samples) were selected for laboratory analyses. Samples for laboratory analysis were air dried, crushed with a roller, and sieved through a 2mm sieve. For chemical composition and mineralogical composition: sieved samples, rocks, and different soil particle sizes were oven dried, ground to a fine powder in a twin swinging motorized mill with agate mortar and balls.

Physicochemical analysis

General soil characterization analysis followed standard procedures for soils in Arid and Semi-Arid Regions (Bashour and Sayeegh, 2007). In summary: particle size distribution by dispersion with NaOH and Hydrometer method; calcium carbonate equivalent (CCE) using acid neutralization; percentage of gypsum by using precipitation with acetone; organic matter (OM) by wet oxidation with 0.4 N K₂Cr₂O₇; cation exchange capacity (CEC) by sodium acetate 1N at pH 8.2; electrical conductivity (EC) in saturated paste extracted; pH with a glass electrode in saturated paste.

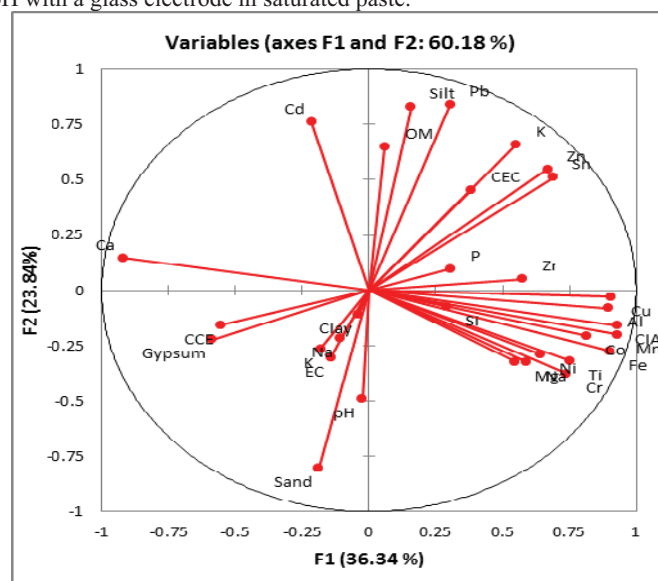


Figure 2. Biplot based on principle component analyses of soil characteristics

Mineralogical analyses

Chemical cementing agents were removed and clay fractions separated according to Mehra and Jackson (1960), Kittrick and Hope (1963) and Jackson (1975).

Next, certain soil particle size fractions were isolated for mineralogical analyses. The oriented clay fraction slides were prepared for the treatments, heating to 550°C; solvation with Glycerol; solvation with Dimethyl Sulfoxide (Moore and Reynolds, 1997). The prepared samples were scanned using an X-ray diffractometer (Philips PW-1710 CuK α radiation) and X-ray diffraction patterns were obtained for air-dried grinded rock, soil, silt, and sand samples according to Azaroff and Buerger method (1958).

Geochemical analysis

Total elemental composition of grounded bulk soil and rocks were determined for the contents of SiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, Zr, and LOI by X-ray fluorescence in a Philips (PW-2440) apparatus. Trace elements for bulk soils were determined after digestion in a microwave oven using nitric, hydrofluoric and boric acids (US EPA, 1996). The digest was analyzed for the contents of Cr, Ni, Cu, Zn, Co, Pb, Cd, and Sn by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a PE SCIEX ELAN-500A spectrophotometer.

Soil statistical analysis

Descriptive statistics (maximum, minimum, mean, and standard deviation) of metals were calculated. We used the ANOVA test for significant differences ($p < 0.05$) among soils develop from different parent materials. The relationships between elemental compositions were determined using correlation and principal component analysis (PCA). PCA is useful tools to identify relationships that are not readily evident from simple correlation analysis. Statistical analysis was performed with the MS Excel application XLstat, and SPSS 19.0.

-Element transfer from rock to soil and accumulation in particles size fractions

We estimated the enrichment/depletion of soil using an enrichment factor (EF) (Sutherland et al. 2000) give in Eq. (1),

$$EF = (C_n/C_{ref}) / (B_n/B_{ref}) \quad (1)$$

Where C_n is the content of the examined element, C_{ref} is the content of the reference element, B_n is the background value of the examined element and B_{ref} is the background value of the reference element. In this study, Zr was used as the reference element. Values > 1.0 indicate accumulation of metals in soils due to soil forming processes while values of 1.0 and < 1.0 show that enrichment of metals is not detectable and loss of metals due to pedogenic processes. An EF value of approximately 1 for any element implies a present concentration equal to the lithogenic input, whereas $EF > 1$ indicate enrichment of metals in soils due to soil forming processes and EF of 1 and < 1 show that enrichment of metals is not detectable and loss of metals due to pedogenic processes (depletion).

Weathering Indices

Assessing the geochemical component and weathering indices can improve our understanding of soil formation and process. Among the indices proposed by the researchers, we used CIA, CIW, PWI, and WIP as commonly used calculated indices (Table 1).

Table 1. Summary of weathering indices

Index	Formula	Optimum Value	Fresh	Optimum Weathered Value	Reference
CIA	$[(Al_2O_3 / Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$	≤ 50		100	Nesbit and Young (1982)
CIW	$[(Al_2O_3 / Al_2O_3 + CaO + Na_2O)] \times 100$	≤ 50		100	Harnois and moore (1988)
WIP	$[(2Na_2O/0.35) + (MgO/0.9) + (2K_2O/0.25) + (CaO/0.7)]$	> 100		0	Parker (1970)
PWI	$[SiO_2 / (TiO_2 + Fe_2O_3 + SiO_2 + Al_2O_3)] \times 100$	> 50		0	Souri et al. (2006)

Results

Soil characteristics

The maximum, minimum, mean, and standard deviation of soil physicochemical characteristics of the studied soil samples are given in Table 2. Physiographically, soils locate in lowlands, flood plains, flood basins, plateau, alluvial plains, fans, and piedmont plains, being the most dominant physiographies in the study area alluvial plains and flood plains.

Table 2. Selected physicochemical properties of the studied soils (n=41)

Statistics	Sand	Silt	Clay	pH	EC (dS m ⁻¹)	SAR	CEC (cmol _c kg ⁻¹)	CCE	Gypsum	OM
	%							%		
Minimum	12.5	8	1	7.1	0.02	0.01	2.15	21.1	0.08	0.2
Maximum	90	82	18	8.7	45	14.36	19	81.53	29.03	1.8
Average	53.58	41.02	5.68	7.85	9.87	1.34	7.91	47.92	7.08	0.7
Standard Deviation	20.27	18.71	4.11	0.37	12.79	2.3	3.5	16.48	9.18	0.37

The soils pH ranged from 7.1 to 8.7 with an average of 7.85 (Table 2). Possibly due to the soils developed on highly carbonatic and gypsic bedrocks, the pH are within the normal range for these type of soils. The high values could also be a result of impression by salt formations and irrigation water contain significant quantities of calcium, magnesium, or sodium in certain regions and soils generally occur in areas where precipitation is too low to leach the minerals from the soils.

The EC and SAR values of the soils are generally in a broad range, 0.02 -45 dS m⁻¹ and 0.01 -14.36 (Table 2), respectively. The high values of EC in soils are related to saline ground water, saline irrigation water, and parent materials containing saline composition and uplifting of salt diapirs (Hormoz formation).

Soils exhibited CEC between 2.15 to 19 cmol_c kg⁻¹. The CEC of the soils depends 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. Low values of CEC in the soils are attributed to low organic matter, low clay minerals with low CEC and presence of gypsum in notable amount in most soil samples. The maximum organic matter was 1.8 % with an average of 0.7% (Table 2).

In term of particle size, soil samples are classified according to frequency as sandy loam, silt loam, loamy sand, silt, sand, loam, and silty clay loam with a low clay size fraction. The average value for clay, silt and sand size fraction was 5.68, 41.02, and 53.68 % (Table 2), respectively. The most dominant fractions are sand and silt. Gypsum (7.08 ± 9.18) and CCE (46.92 ± 16.45) percentage were variable and often high in most soils (Table 2). Soils were classified as Aridisols, Entisols and Inceptisols with calcic, gypsic, salic, cambic, argilic horizons and ochric epipedons (Soil survey staff, 2010).

Statistical relationships

The PCA (Figure 2) was used to discriminate soil profiles and horizons, to assess the dominant component in the different parameters and to make a synthesis of the relationship between chemical and physical parameters.

This analysis was performed on selected trace and major elements, particle size distribution (clay, silt and sand), CCE, gypsum, OM, CEC, pH, EC, and CIA. The first principal component (PC1) shows a positive correlation with CIA index and the total amount of Al, Fe, Mn, Mg, Ti, Cu, Co, Cr, Ni components and negatively with the total Ca content, CCE and gypsum percentage (Figure 2). The second principal component (PC2) correlates positively Sn, Zn, Pb, Cd, K, OM, Silt, and CEC whereas it correlates negatively with pH and Sand. Around 60 % of the total variability was explained by these two components with a much smaller amount being explained by the subsequent principal component (12.5% for PC3).

Results of correlation analysis for bulk soil samples (Table 3) showed that Al was positively significantly correlated with Fe, Mn, Na, K, Ti, P, and Zr and negatively with Ca and LOI, but did not show any correlation with Mg. Silicon was not correlated with elements and no relationship was observed for Si with other ME (Table 3). Calcium showed a negative correlation with all major elements that correlations were significant for Al, Fe, Mn, Mg, Na, K, Ti, Zr. Loss on Ignition (LOI) negatively correlated with Al, Fe, Mn, Na, Ti and positively correlated with Ca content.

Major and trace elements in soil

The bulk soil maximum, minimum, mean, median, standard deviations of major elements were reported as metal oxides in Table 4. The bulk soil concentrations of Zr, Cr, Co, Ni, Cu, Zn, Cd, and Sn are reported as mg kg⁻¹ soil. Major and trace elements contents in bulk soil and rocks elements such as Si, Ca, Al, Fe, and Mg ranged from 10,000 – 60,000 mg kg⁻¹ soil while Na, K, Ti, Mn were present in less quantities (i.e., <3000 mg kg⁻¹). Zircon, P and trace elements (Cr, Ni, Zn, Cu, Co, Sn, Pb, and Cd) were present in minor contents of major and trace elements in parent rocks were less than soils except for Si, Ca, and Mg which were dominant.

Table 3. Correlations of major elements in bulk soils

	Si	Al	Fe	Mn	Mg	Ca	Na	K	Ti	P	Zr	LOI
Si	1											
Al	0.373	1										
Fe	0.275	0.893**	1									
Mn	0.246	0.800**	0.894**	1								
Mg	0.081	0.348	0.574**	0.577**	1							
Ca	-0.421	-	-	-	-	1						
Na	0.405	0.961**	0.911**	0.884**	0.462**	-	1					
K	0.154	0.761**	0.658**	0.586**	0.075	0.760**	-	1				
Ti	0.211	0.595**	0.301	0.300	-0.005	0.505**	0.211	1				
P	0.124	0.869**	0.879**	0.746**	0.354	0.860**	0.818**	0.284	1			
Zr	0.184	0.514**	0.385	0.250	-0.221	-0.383	0.436**	0.426	0.483**	1		
LOI	-0.361	0.469**	0.353	0.376	0.023	-	0.313	0.393	0.422	0.388	1	
		0.914**	0.892**	-0.853**	-0.418	0.461**	0.961**	-	-	-0.346	-0.377	1
						0.961**	0.831**	-0.369	0.894**			

** . Correlation is significant at the 0.01 level (2-tailed).

The highest values of Cr, Co, Ni, Zn, Cu, Cd, Pb, and Sn were developed in soils on north and eastern north parts. Maximum Calcium and magnesium were found in western and southern parts and Si in east and eastern north, while Al, Fe, Ti, and Mn in eastern north parts. High amounts of P were found in agricultural lands of eastern and north eastern parts (Table 4).

Mineral identification and distribution

The soils contained an important average amount of calcite (29%), dolomite (19.5%), alkali-feldspars (19 %), mica (muscovite or biotite) (15.6 %), quartz (14.3 %), gypsum (13%), 14 A°-phyllosilicates (11.6 %), plagioclase (6.6 %), and halite (<1%). Carbonates, including calcite and dolomite were also predominant in the fine fraction. All soil samples and also around 90 percent of soil samples contained high values of calcite and gypsum, respectively (Figure 3).

Carbonates, gypsum, quartz, chlorite, mica (biotite/muscovite), amphiboles, feldspars, and apatite were identified as major rock minerals, whereas halite, rutile, zircon, apatite, and sepiolite as less quantity were detected according to X-ray diffraction studies.

The total sand fractions of all horizons were dominated by quartz, Alkali feldspars, and contained lesser amounts of 14A phyllosilicates, plagioclase, mica, and dolomite (Figure 4). Gypsum and Calcite was observed in the silt fraction of two and one samples, though not in any horizons described in the field as containing carbonate nodules or masses.

Table 4. Summary statistics (min, max, mean, median, and standard deviation) of major/minor elements, LOI, and weathering indices of bulk soil samples (n=41).

Element	Unit	Min	Max	Mean	Med	S.D. ^b	World soil Mean ^a
SiO ₂	%	0.66	59.40	30.12	32.54	19.18	59.90
Al ₂ O ₃	%	1.48	13.67	8.17	8.76	3.32	15.10
Fe ₂ O ₃	%	1.19	7.97	4.60	4.51	1.82	5.00
MnO	%	0.03	0.16	0.09	0.10	0.04	0.07
MgO	%	2.39	10.50	5.64	5.25	2.13	1.49
CaO	%	4.49	46.10	19.98	15.42	10.85	1.96
Na ₂ O	%	<LLD	2.76	1.07	0.88	0.76	1.35
K ₂ O	%	0.39	2.68	1.37	1.21	0.62	1.69
TiO ₂	%	0.05	1.23	0.51	0.49	0.26	0.67
P ₂ O ₅	%	0.07	0.19	0.13	0.14	0.03	0.17
Zr	mg kg ⁻¹	8.40	178.90	100.10	104.80	37.95	230
Cr	mg kg ⁻¹	24.27	487.18	144.73	98.55	110.17	80
Co	mg kg ⁻¹	2.53	47.62	15.85	13.69	9.62	10
Ni	mg kg ⁻¹	21.24	419.83	142.76	101.66	112.19	20
Cu	mg kg ⁻¹	5.06	72.80	25.42	21.38	15.22	30
Zn	mg kg ⁻¹	17.13	165.55	63.79	57.87	33.61	70
Cd	mg kg ⁻¹	0.14	0.38	0.24	0.23	0.07	0.53
Pb	mg kg ⁻¹	5.26	33.71	13.55	10.86	6.50	17
Sn	mg kg ⁻¹	8.28	32.18	17.36	17.00	5.13	4
LOI	%	2.89	37.29	18.26	17.17	8.38	-
PWI	%	14.00	80.00	61.55	73.86	25.30	-
WIP	-	33.24	54.00	41.33	40.84	5.67	-
CIW	%	4.82	71.73	38.75	41.92	16.30	-
CIA	%	4.61	67.40	35.17	38.17	15.00	-

^a Reimann et al. (2000), Adriano (2001), Kabata-Pendias and Pendias (2001)

^b S.D.: Standard Deviation

However, the silt fraction of the soils was characterized by a rather high amount of quartz, alkali-feldspars, mica, 14 A- phyllosilicates, plagioclase, dolomite, a very rare amount of calcite. Quartz, alkali-feldspar, 14 A- phyllosilicates, dolomite, and mica were existed in all silt fractions of analyzed samples (Figure 5). Gypsum was not observed in any silt or clay despite being observed in the field in many pedons.

In regard with minerals associated with clay fraction, most soil pedons contain greater quantities of chlorite, palygorskite, illite, only few amounts of smectite, interstratified minerals, and very trace amounts of kaolinites and no vermiculite (Figure 6). In contrast, in more developed soils the amount of smectite increased and illite or/and chlorite decreased.

Discussion

Soil properties and classification

Parent materials greatly influence soil development and the distribution of soils on the southern Iran which are generally alkaline in nature and high in soluble salts and calcium contents. Characteristically these soils are very low in organic matter/humus and most of the elements reserve is present in un-weathered mineral forms.

The soils on fans and piedmonts are shallow to medium deep, excessively drained, sandy-skeletal to loamy skeletal, highly calcareous and severely eroded with low organic carbon and available water capacity. In general, soils with continuous sedimentation, medium texture, and high salinity are settled in flood plains and lowlands. Moderate sub angular blocky to angular blocky and massive structures are common; however some horizons have platy, prismatic or columnar structures. Prismatic and columnar structures which are a common structure type in sodic soils (Soil Survey Staff, 2010).

In the modern US Soil Taxonomy (soil taxonomy, 2010), the presence of less developed diagnostic horizons (cambic, ochric) and the absence of well-developed ones (temporary argillic, oxic, etc.) in soils are considered to be the result of the limiting influence of climatic (Aridisols), lithological or chronological factors (Inceptisols, Entisols). Within these orders relatively more developed soils occur at the levels of suborders and soil great groups reflecting the total results of the "opposition" of this or that soil-forming factor to the principal factor limiting soil development. However, the nature of the bedrock (calcareous and gypsiferous) appeared to determine the additional presence of certain characteristic taxonomic units which may suggest the presence of locally adapted groups.

In regard with the most regions have aridic soil moisture regimes, a variety of soils classified as Aridisols and Entisols. The Inceptisols with calcic horizons were only reported in north and east northern parts of Hormozgan province. Gypsiferous soils have increased as we move toward the western section and in comparison soils with a calcic horizon have increased toward the northern sector. Occurrence of an argillic horizon in calcareous parent material of an arid climate could point to a palaeoprocess in stable geomorphologic conditions (as plateau) (Khormali et al. 2003).

Distribution of trace and major elements

Elevated amounts of Al, Fe, Mn, Mg, Cr, Ni, Co, Cu were observed in northern and eastern north parts. Silicon was known to be related mainly to quartz and sand soil particles. Na-feldspars were resistant to weathering and thus occur in quartz-sand (Reimann et al. 2003), so the positive correlation of Si with Al and Na might be interpreted as a sandy factor.

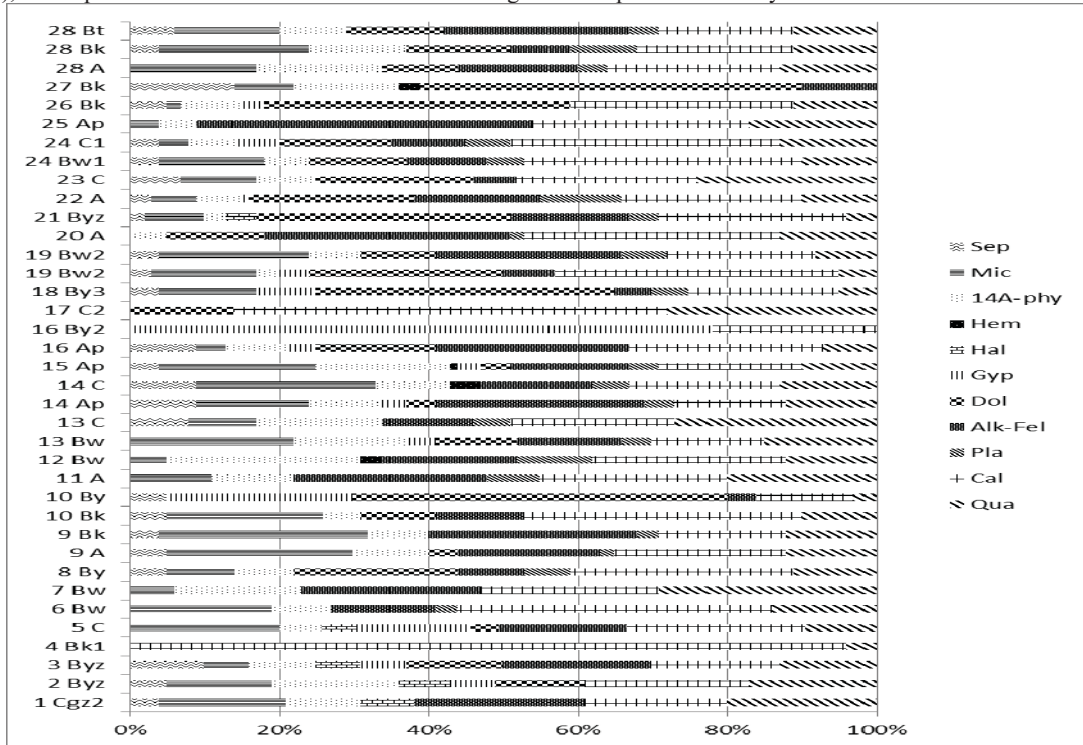


Figure 3. Relative distribution of soil minerals in different soil horizons

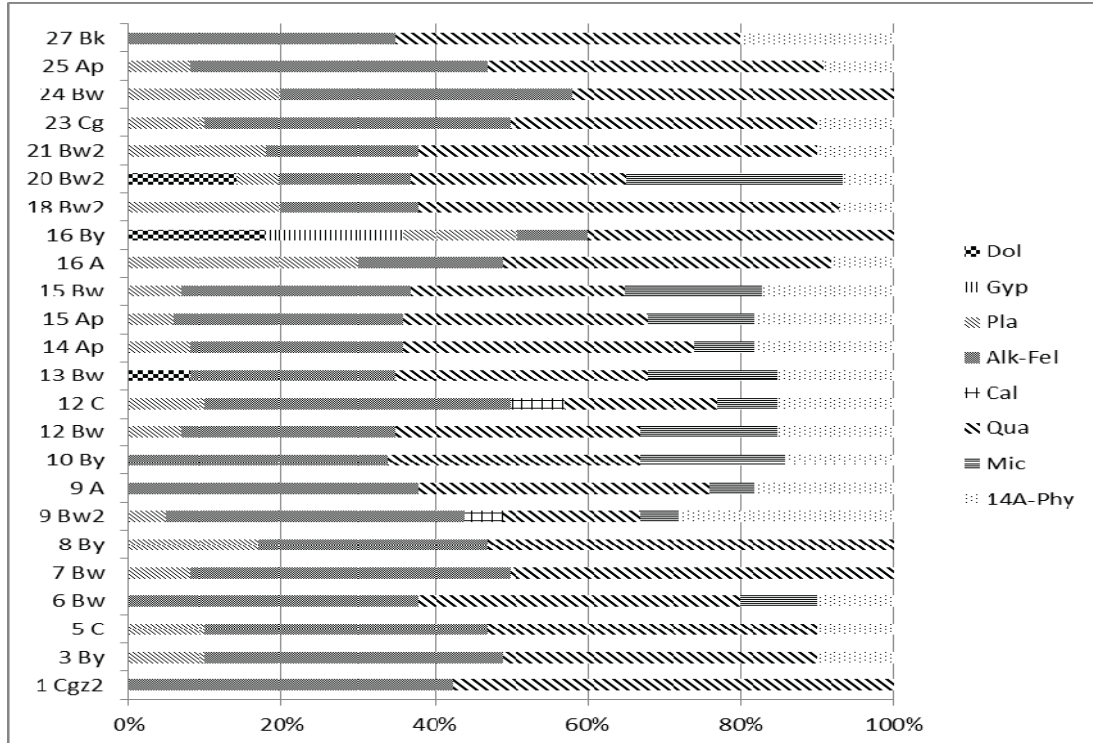


Figure 4. Relative distribution of sand minerals in different soil horizons

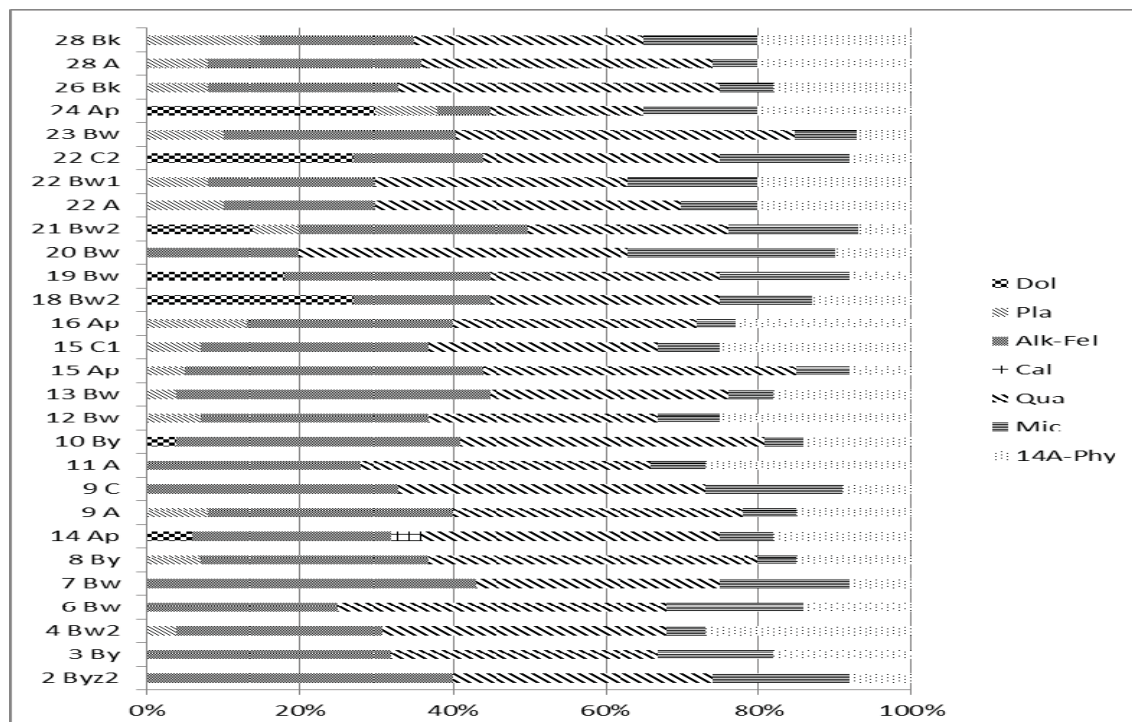


Figure 5. Relative distribution of silt minerals in different soil horizons

The Cr, Ni, Co, Mg, Cu, Mn, Fe, Al, Ti were positively loaded with PCA 1 that suggesting their common origin i.e., terrigenous and Ca was negatively loaded, emphasizing their inverse geochemical behavior. There was significant ($p < 0.05$) positive correlation of six trace elements (Cr, Co, Ni, Cu, Zn, Sn) with Al, Fe, Mn, Mg, Na, Ti, Zr. The color differences were reflected in the Fe content, which was higher in the redder soils in north and eastern north sub-regions. In general soils derived from central Iran and Zagros fold belt zone had $> 5\%$ Fe_2O_3 , while the other soils (Makran and High zagros zone) had $< 3\%$ Fe_2O_3 .

The average TiO_2 content of most of the soils in the data set was approximately 3.0 g kg^{-1} with an average of $5.1 \pm 2.6 \text{ g kg}^{-1}$. The soils derived mostly from igneous and metamorphic rocks (soils 12, 28, 15) had $> 6\text{--}12.2 \text{ g kg}^{-1}$ TiO_2 . Besides Ti and Fe, soils developed on igneous (Basaltic) are also rich in P (Marques et al., 2004). Iron, Ti, and P contents were positively correlated. The total P contents tend to be slightly higher in the surface horizons of agricultural soils because of P cycling by plants. The mean P_2O_5 content for our study was 0.13, whereas the mean P_2O_5 content for world soils was 0.17%. The average amounts of Zr were $100.1 \pm 38.0 \text{ mg kg}^{-1}$ with a maximum of 179.0 mg kg^{-1} .

In most of the soils, the Si content was higher than Al and Fe contents. Soils from pairs of very similar soils all on the north and eastern north parts of Hormozgan Province showed the same trends. Sedimentary rocks have even great ranges of quartz content that are controlled by chemical weathering and physical sorting of material during transport to a depositional environment (Pettijohn, 1975). Soils show a huge span of Si contents ranging from $< 1 \text{ wt.-% Si}$ in Histosols (Steinmann and Shotyky, 1997) up to 45 wt.-% Si in very old Podzols developed in quartzitic sands (Skjemstad et al., 1992). In study soil samples Si amounts ranged from 0.35 to 28% Si with an average of 13.7%.

The median values of CaO, MgO, K₂O, and Na₂O of world soils are 1.96, 1.49, 1.3, and 1.97%, respectively (Koljonen, 1992). In this research total soils revealed much higher values of CaO ($20 \pm 10.9\%$) and Mg ($5.6 \pm 2.1\%$), while K (1.4 ± 0.62) and Na (1.1 ± 0.74) showed approximately same trend with world soils. Significant negative correlations were found in horizons between calcium content and the concentrations of all elements examined except for P (Table 3). After element concentrations were transformed to a calcium cement-free basis (clay particles) only negative correlations of Mg and Na changed to non-significant correlations and Si changed to significant negative correlations.

Significant negative correlations between soil horizon calcium content and concentrations of elements examined demonstrate the influence calcium can have upon soil chemistry. The negative correlations might be a direct effect of calcium dilution. In samples with greater calcium content, calcium has displaced other minerals and materials that contain the elements listed. The range of R² values show that the dilution effect appears to control concentrations of certain elements (e.g. Al and Fe) more strongly than others. However, none of the elements examined appears to be completely exempt.

Soil sampled and classified as Gypsic Haplosalids, Typic Endoaquents contained maximum values of Na₂O. Elements exhibit varying mobility in soil, which translates into different vulnerability to leaching. The base cations Na, Ca and Mg all exhibit high degrees of mobility that cause them to be lost from leached soils, with soil water concentrations often influenced by mineral dissolution and cation exchange (McBride, 1994). Aluminium and Fe generally exhibit intermediate mobility, with significant fractions retained in secondary phases and soil water concentrations influenced by pH, chelation and redox (McBride, 1994). Based upon mobility differences, it is surprising to find several strong positive correlations between unadjusted concentrations of the base cations and Fe and Al (Table 2, Figure. 3). Since the climate was arid and precipitation is scarce; so, the positive correlations between different elements might not be unusual. As the soils were highly calcareous and the effect described above, the caution will be warranted in their interpretation.

Significant contents of Ca, Mg, K, and Na for profiles suggested a considerable content of primary and weatherable minerals. The high Na, K, and Mg contents occurred in both the surface and subsurface horizons; even though there both were obvious morphological evidence for additions in the subsurface horizon and also parent materials were rich in carbonate and feldspar minerals.

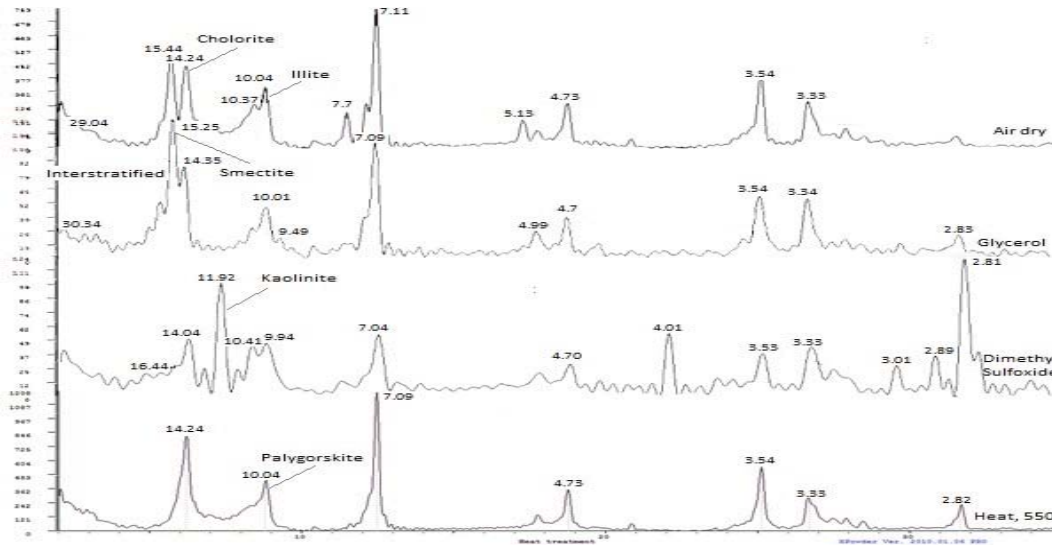


Figure 6. X-ray diffractograms of the clay fraction (Bw2).

The loss on ignition was reported as part of an elemental or oxide analysis of a mineral. The volatile materials lost usually consist of "combined water" (hydrates and labile hydroxy-compounds) and carbon dioxide from carbonates. Marques et al (2004) found that the clayey soils have LOI, as high as 20-30% and loss on ignition varies with clay content because hydroxyl-rich secondary mineral trend to occur in the clay fraction.

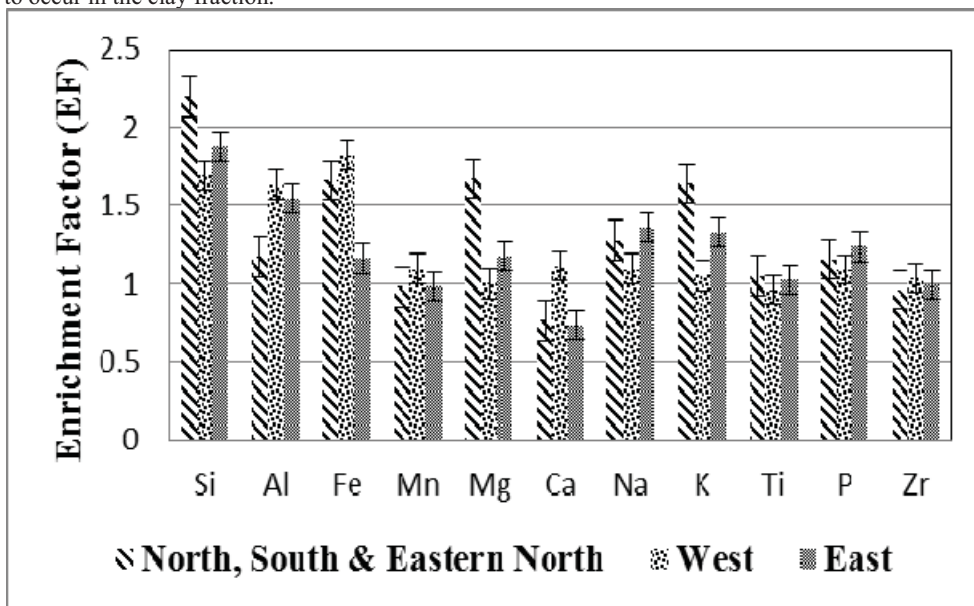


Figure 7. Enrichment factor (mean and standard error) for major elements in soils.

Total organic matter content is no more than ~ 0.5-2% and clay varies from 1 to 18 % (Table 2) for studied soil samples. In general Ca and LOI to some extent follow the same trend and inverse other major elements. Subsurface and calcic horizons indicated the highest CaO (46%) contents. Therefore most of the soil mass of Hormozgan soils are attributable to the loss of carbonates rather than structural hydroxyls consistent with the clay mineralogy or volatilized constituents of organic matter.

Enrichment and depletion patterns

As can be seen in Figure 7 the enrichment of ME in soils highly depended on the parent rocks and soil development. Different elements can show completely different enrichment/depletion patterns. Most soils for most ME had enrichment factor values ≤ 1 especially for Zr, Ti, Ca, and Mn. Aluminum, Si, Fe, Na, and K showed enrichment factor mean > 1 for all sub-region. The EF values for Ti, Zr and Mn signified that its concentration controlled by lithogenic input (EF~1). As most parent materials are carbonatic and sedimentary rocks rich in carbonate, the lithogenic Ca values are much more than pedogenic Ca values; so, most soils indicated depletion of Ca. In soils developed in wetter area with further evolution (north and eastern north regions) had more Ca depletion in comparison to western parts. On the contrary, Si, Al, Fe, Mg, K, and Na were enriched in the soil solum; with slightly higher values in sub-regions north and eastern north sub-regions. In general the depletion was least for Fe, Si, Al; intermediate for K, Na, Mg, and P and strong for Ca. Aluminum, Fe, Ti, and K showed enrichment trend in ustepts parallel to the development of more evolved B hoeizons.

Relation between geochemical composition and mineralogy

Investigating the variability and evolution of soil mineral and geochemical composition during pedogenesis was crucial for modeling the development of soils over time, and thus understanding the state of soils today.

Presence of high quantities of quartzite and carbonatic minerals showed that the importance of Ca and Si as determining major elements for soil evolution in study area. In regard with soils are calcareous and Ca is dominant, it can be concluded that presence of carbonates is most effective factor in element transformation, redistribution, leaching, neof ormation and consequently soil evolution.

The high correlation of Na with Al, Fe, Mn, and Ti suggest that these elements are associated with Na-bearing minerals (like Albite) which were common in studied samples. The positive significant correlations among Mg, Fe, and Mn were suggesting that Fe and Mn were associated with Mg bearing minerals such as chlorite and biotite.

Soil had the diverse contents of total Ca, Mg, Na, K reflecting the fact that this soil still contains primary minerals, probably feldspars and evaporates, inherited from the parent rock. Despite the high Ca and Mg contents, the K and Na content of soil are not high, from which we conclude that plagioclase feldspars and alkali feldspars were virtually less frequent than carbonates in the parent rocks.

Mg content showed a correlation with dolomite and gypsum and horizons with a calcic horizon and also calcareous pedons indicated the highest values of Ca. Potassium increased with increasing plagioclase and Na almost increased with increasing salinity. To some extent K showed a better correlation with in moister climate and more developed pedons (north and northeastern parts).

Calcite, Gypsum, and feldspar are present as major minerals, it is expected that the weathering process induces the high quantities of metals into soil solution, however aridity (low rainfall) and too much weatherable minerals in soils indicated high amounts of elements will be released to soil solution parallel to soil development. Also quartzite where both the main mineral was resistant to weathering existed in higher amounts in most soils.

Weathering Indices

Chemical weathering indices useful in pedogenesis or other geological applications are commonly used for characterizing weathering profiles by incorporating bulk major element oxide chemistry into a single metric for each sample. Weathering information and investigate stage of soil evolution is as well important for agricultural and environmental researches.

Among the weathering indices that monitor the decomposition of an unstable mineral include the Chemical Index of Alteration (CIA; Nesbitt and Young, 1982), the Chemical Index of Weathering (CIW; Harnois, 1988). Given that the CIA index logically predicts the extent of conversion of feldspar minerals and that feldspars are the most abundant rock-forming mineral group in the Earth's crust, this index has been widely employed in studies (Fiantis et al., 2010; Mourier et al., 2008; Zhang et al., 2007; Price and Velbel, 2003; Nyakairu and Koeberl, 2001). The indices CIA and CIW are perhaps more suitable for the study of early stages of rock weathering rather than for well-developed tropical soils (Zhang et al. 2007).

Weathering index of Parker (WIP) and product of weathering index (PWI) according to Souri et al. (2006) can be used to identify the initial and lateral products of weathering which can be tracked at the same time. WIP is a suitable index to investigate the mobility of alkaline and alkaline-earth metals (Price and Velbel, 2003), while PWI is proper to track movements of less mobile elements. Based on the principle of WIP and PWI, as the values of the indices get smaller, the samples are more weathered and assumed to be elder (Fiantis et al. 2010).

Although the soils of Hormozgan province were situated and developed in an arid region, the evaluation of the weathering indices was performed with the objective of showing the soil condition at the early stage of weathering. Chemical alterations are dependent on the climate or specifically accelerated by the rainfall (Fiantis et al., 2010). Nanzyo et al. (2007) reported that the value of weathering indices of four types of volcanic ash in Japan increase with an advance in weathering through enrichment of Al and depletion of some alkaline and alkaline-earth elements.

The minimum values of CIA and CIW were belonged to By horizon of a gypsiferous soil. Gypsiferous and saline soils showed a CIA and CIW around 10 -25, while soils of northern and east northern parts indicated from 35 to 55. The highest value was reported in a Bw horizon of Calciustepts developed on basic igneous parent material in north of Hormozgan province. CIA and CIW can be used to measure the extent of feldspar conversion to clays (Price and Velbel, 2003; Fiantis et al. 2010).

The CIA actually is identical to the CIW, except that CIW eliminates K₂O from the equation. Values of CIA (4.61 to 67.40) and CIW (4.82 to 71.73) indicated the slight difference between indices. It can be concluded that Alkali feldspars are more dominant than plagioclase, though the mineralogy data has confirmed it. The CIA and CIW are both lower than those of average soils, suggesting relatively gentle source area weathering. The low CIA and CIW values in the arid soils probably reflect the presence of high detrital feldspars and few clay minerals. The PWI mean values (73.86±25.30) were bigger than of WIP values (40.84±5.67), however the minimum of WIP was 33.24. These data suggested that Si were high in studied soils and also alkaline and alkaline earth elements present in almost high quantities in soils and were not removed from soil pedons.

Relationship between element contents in the soils and parent materials

The elemental composition of a soil will be inherited from the parent material and will gradually change as a result of the influence of the predominating pedogenic processes. However the rate of accumulation depends on susceptibility of rocks to weathering or constituent minerals, climate and human activities. The most important human activity was irrigation by saline water that led to accumulation of soluble cations specially sodium. Salinization, a process that concentrates soluble salts, can be expected to alter the chemical composition of a soil. Moreover, physical weathering is of major importance in the overall soil development in such a context. Variations in the element chemistry of arid soils from southern Iran are controlled dominantly by bedrock geology, physical weathering and salinization.

The parent material in particular is a key influence, with desert sands and silts commonly retaining a signature of their source area bedrock geology at considerable distances from their origin (Moreno et al., 2005; Muhs et al., 2003; Pease and Tchakerian, 2002; Zimelman and Williams, 2002). Thus our samples are dominated by geological rock-forming minerals (silicates, oxides and carbonates), but the finer grain size fractions were more phyllosilicate-rich and contain higher concentrations of Al, Na, Mg, and Fe.

From the Early to the early Late Pleistocene, the main pedogenic processes were the leaching of carbonates, weathering, illuviation and rubification, but the degree of development of the Bt horizons varied over time. Ortiz et al. (2002) studied the evolution of surface and buried soils over the Quaternary period in a Mediterranean climate (SE Spain) and concluded the difference in the Fet+Al/ Sit ratio between the Bt horizons and C horizons should increase with greater weathering and leaching and similarity in all of the soils, indicating an equivalent degree of weathering and development. The minor differences in the indices of these soils could be attributed to parent-material differences or to waterlogging in some profiles.

Weathering of primary silicates leads to the formation of secondary clay minerals (Duchaufour, 1972; Sposito, 1989). Because of their trivalent state, the adsorption onto clays is stronger for REEs than for alkali metals and alkaline earths (Roaldset, 1975) and kinetically fast (Aja, 1998; Coppin, 2002), whereas at alkaline pH they adsorb as inner-sphere complexes onto amphoteric sites at the edges of the particles (strong chemisorption, variable pH-dependent charge). Since silt and sand are common particles in soils, clay minerals and clay particles are rare in studied soils and adsorption could not be so high though soils had a high pH.

Some of the leading pedologists of today lay great stress on the distinction between weathering processes and soil-forming processes. Weathering includes solution, hydrolysis, carbonization, oxidation, reduction, and clay formation.

Among the soil-forming processes, the following are listed: calcification, podsolization, laterization, salinization, desalinization, alkalization and dealkalization, formation of peat and poorly drained soils, including gleization (Isaak and Gershill, 1935). All weathering processes are possible but the rates of reactions were different. Salinization, calcification, and alkalization were important soil-forming processes in studied arid soils. Weathering and soil formation leave characteristic imprints in the chemical composition of soils.

Conclusion

Besides salinization and continuous sedimentation, sultry weather and physical weathering enable the breakdown of minerals and releasing to soil, but lack of enough water for moving down elements and removing out of soil pedon, has caused soil remained in initial state of development in most of soils and observing high concentration of TEs and MEs especially alkaline earth elements.

In any case the ME (Al, Fe, Mn, and Mg) may be called anthropogenic factor. This statement is proved by the fact that most of TE except of Cd and Pb are also significantly ($p < 0.05$) correlated with major elements. On the contrary, the Ca is of natural origin, because there are many significant negative correlation coefficients between trace elements and other ME. This is essentially true for Si, Na, and Al indicating the poor sorption capacity of sandy soil.

The same distribution of almost most elemental contents in soils and rocks are indicative that ME and TE in soils were to inherited. Silicon, Fe, Mn, Cr, Co showed the higher affinity to parent material. The different degree of similarity to soils to rocks can be due to differential resistance of rocks to weathering, leaching processes, formation of clay minerals, new sedimentation, and human activities.

The maximum chemical index of alteration (CIA) values (67.4), chemical index of weathering (CIW) values (71.73) and high contents of the alkali and alkali earth elements of the silt-rich sediments suggest a slightly weathering source area.

The parent material and climate are influential parameters in soil development, distribution of elements in soils and particle sizes.

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