Geochemistry of Trace Elements in Iraqi Marine Environment

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Abstract

Geochemistry of trace and some major element components were studied in Iraqi marine sediments. Two cores at profile depths of 10, 20, 30, and 40 cm (from profile A, B, C, to D respectively) of major elements (SiO_2, Al_2O_3, K_2O, MgO, CaO, MnO and Fe_2O_3) and trace elements (Cr, Mo, Ba, Pb, Th, Ga, Sr, Ni, Cu, Br, Zn, Zr ,V, Nb, As, and Rb) are investigated in 2018. The spatial distributions of element components showed the range of Al_2O_3 between 5.258-5.8%, when compared this result with alumina content in crustal content gave us data to mixed sediments between quartz and clay minerals. Mn and Fe consider as redox elements in marine sediments , and the spatial distribution for these elements showed high concentration within the uppermost part of the profiles, but with increase the depth it have undergoing some degree of depletion. Most of trace elements except Pb and As showed the same pattern of redox elements within the high concentration in upper surface and decrease steadily with increase the depth. It is clearly observable that the surface sediments are enriched with most of trace elements. These results may be considerable to adsorption the ions or ionic complex onto particle surfaces, such as clay minerals and organic matters. The negative relationship between organic matter with Pb and As elements may be attributed to liberate Pb and As during decomposition of organic matter. There is obvious positive relationship between $CaCO_3$ minerals with Pb and As. This relationship formed by the fact that calcite minerals supply regions of higher pH as well as nucleates centers of trace elements on the surface of carbonate. The relations between trace elements and Al are confirm these results. Enrichment factors in both cores for Cr, Sr, Ni, Br, and Ga elements often exhibited constantly high enrichment except at depth of 40 cm (profile D) for Sr , and at depth of 20 , 30 and 40 cm (profiles B, C and D) for Ga element. While enrichment factors for Mo, Pb, Zn, Zr, and Cu are commonly oscillate around more than 1 except the depleted elements at depth 40 cm (profile D) for Zr and depleted elements at depths of 20, 30, and 40 cm (profiles B, C, and D) for Cu . As is constantly enriched with the profiles C and D (30 cm and 40 cm).High concentrations of EF for some of trace elements in marine sediments are often attributed to anthropogenic sources.

Keywords: Iraqi marine, Enrichment, Trace elements, Pollution

1. Introduction

Marine sediments are the ultimate depository of many chemical compounds including trace metals from natural and anthropogenic sources (Forstner and Wittmann, 1979). A quantitative analysis of sediments can reflect upon the current features of marine system, whether the sediments behave as a sink or source of metals, depends on the dynamic of bio geochemical developments that occur at the sediments- water interface under oxic/anoxic conditions (Santschi et al., 1990). The different physiochemical properties of trace elements and their possible relation to the mineralogy of the sediments determine their biogeochemical behavior including biological uptake (Well et al., 1991), adsorption – desorption (Fuller and Davis, 1987). In the marine environment, trace elements distribution can be gave definite information about paleo climate and paleo environment (Müller, 2012 and Schnetger at el., 2000). Authors like François (1988), Morford and Emerson (1999), and Calvert and Pedersen, (1993) stated that trace elements in marine sediments have different behavior under oxic and anoxic conditions. Elements as Mn, Cr, Mo, Re, U, and V have highest solubility under oxic condition. Cu, Ni, Zn, and Cd are removed from solution in the presence of pyrite. While Mn, Co, Ni, and Cu associate with pyrite in sulfide sediments. The aim of this study is determine the distribution pattern of trace elements with depths in Iraqi marine sediments.

2. Location of study area
Study area is located in the Iraqi marine sediments , north and Northwest of Arabian Gulf between 29°46'36.75" N - 48°42'56.51" E for Core 1 , and 29°45'29.45" N - 48°38'2.87" E for Core 2 (Figure 1).

Figure 1: Map of study area

3. Analytical Methods

Two cores at depths of 40 cm are collected in Iraqi marine environment near to Basrah Oil Port by using Marine Sediments Core Sampler Device. The cores divided into four profiles A, B, C, and D at depths of 10, 20, 30, and 40 cm respectively (Figure 2). Total organic method (TOC) results are calculated by combustion at different temperature degrees. Calcium carbonate estimation by calcimeter device. Geochemical analysis for the major and trace elements calculated by inductively

coupled plasma – Atomic emission spectrometry (ICP-AES), and inductively coupled plasma – Mass spectrometry (ICP-MS) in the ALS Laboratory group in Spain.
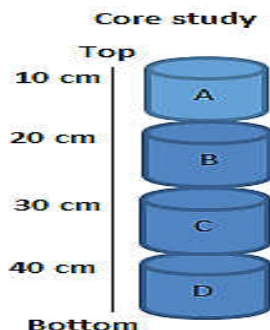

Figure 2: Division the core into profile parts

4. Results and discussion

Element composition of core sediments

In the marine sediments, the values of major and trace elements can be gave data about chemical, oceanographic, and sedimentary range, that controls on their supply to their distribution (Calvert and Pederson, 1993), such controls includes the chemical composition of detritus sedimentary that transported to the sea, the sharing of individual elements between solution and solid phases, the biogeochemical cycling to elements in the sea, and the manner in which they are transported to the sea floor. All samples in the marine sediments cores were chosen at interval depths 10, 20, 30, and 40 cm (profiles A, B, C, and D respectively) (Figure 2). The major elements composition of the core 1 and core 2 sediments expressed as SiO_2, Al_2O_3, K_2O, MgO, CaO, MnO and Fe_2O_3 are given in tables 1 and 2. The organic matter and calcium carbonate is included also in the same tables. The concentration profiles of the trace elements Cr, Mo, Ba, Pb, Th, Ga, Sr, Ni, Cu, Br, Zn, Zr ,V, Nb, As, and Rb are given in tables 3 and 4. Müller(2012) stated that fluctuation in concentrations of main elements like magnesium, aluminum, silicon and potassium in marine sediments are similar in their concentrations and that attributed to an external source such as fluvial and aeolian environments. Aluminum is characterized by not affected by biochemical and digenesis processes in marine environment (Bruland., 1983). Al^{+3} forms part of the structural component of most minerals introduced *via* fluvial and aeolian sources and, therefore, it seems to be the element of choice for quantifying the terrigenous-detrital fraction in marine environments. Another advantage of Al is its high concentration in alumosilicates and rather low abundance in seawater (Brumsack , 2006) . In this investigation, AI contents, expressed as Al_2O_3 were ranged from 5.258 to 5.8% (Tables 1and 2), in compared of crustal content of approximately 31% (Al_2O_3) (Guohui et al., 1988), this probably can be explained to mixed sediments between clay and quartz minerals. Redox elements (Fe and Mn) contents in the sediments of studied cores were high within the uppermost part of the profiles, but with increase the depth it have undergoing some degree of depletion (Tables 1 and 2), this result may be attributed to oxidation of Fe and Mn is very obviously in these sediments as a result of precipitation of iron and manganese - oxyhydroxides in the surface sediments as mentioned by Kahn et al (1992). The spatial distribution of trace elements were illustrated in tables 3 and 4, and figures 3 to 18. These figures showed the higher values of Sr, Ni, Ba, Br, Cu, and Ga in the uppermost part of the profiles (A profile) before undergoing to high degree of depletion towards the D profiles. Zr element showed the higher concentration in the surface part of the cores (profile A) before it shows the high degree of depletion towards the depth intervals especially from profiles C to D. V and Zn elements was enrichment in surface sediments of the cores (profile A) before it steadily decline towards the depth profiles (D profile). Most of trace elements in studied cores showed decrease with depth, this is a result of adsorption the ions or ionic complex onto particle surfaces, such as clay minerals and organic matters. Cr, Mo, Ba, Th, Ga, Sr, Ni, Cu, Sr ,Zn, Zr, V, Nb, and Rb showed the

same pattern of distribution of redox elements (Fe and Mn). As and Pb elements showed lower degree of concentration in the surface sediments and increased with depth intervals (Figures 6 and 18).

Table 1: Major element component with organic matter and CaCO₃ in core 1

Depth Profile	SiO₂	Al₂O₃	K₂O	MgO	CaO	MnO	Fe₂O₃	O.M	CaCO₃
A	25.93	5.577	1.052	4.297	27.43	0.0644	3.47	1.97	16.65
B	25.53	5.258	0.989	4.02	27.1	0.0663	3.43	1.72	20.22
C	26.26	5.473	0.998	3.73	27.56	0.065	3.42	1.71	29.34
D	23.97	5.8	0.88	3.22	33.22	0.063	3.40	1.52	33.70
Range	23.97-26.26	5.258-5.8	0.88-1.052	3.22-4.297	27.1-33.22	0.063-0.065	3.40-3.47	1.52-1.97	16.55-33.7
Mean	25.24	5.512	0.991	3.816	30.16	0.0646	3.43	1.73	24.97

**Table 2: Major element component with organic matter and CaCO₃ in core 2**

| Depth Profile	SiO₂	Al₂O₃	K₂O	MgO	CaO	MnO	Fe₂O₃	O.M	CaCO₃
A	25.81	5.542	1.04	4.1	27.52	0.0651	3.49	1.92	17.44
B	25.61	5.232	0.965	4.08	27.06	0.0662	3.43	1.75	21.4
C	26.33	5.5	0.973	3.4	27.32	0.067	3.42	1.73	27.2
D	23.82	5.7	0.82	3.31	33.32	0.0672	3.41	1.62	32.75
Range	23.82-26.33	5.232-5.7	0.82-1.04	3.31-4.1	27.06-33.32	0.0662-0.0672	3.41-3.49	1.62-1.92	17.44-32.75
Mean	25.39	5.49	0.94	3.722	28.8	0.0663	3.437	1.75	24.69

Table 3: Trace element component (in ppm) in core 1

| Depth Profile	Cr	Mo	Ba	Pb	Th	Ga	Sr	Ni	Cu	Br	Zn	Zr	V	Nb	As	Rb
A	153	6.6	163	8.3	4.2	75	496	91	21	40.7	62	101	41.7	3.36	1.49	17
B	169	4.5	146	8.2	3.8	19	479	84	18	31	58	103	34.5	2.58	1.54	16.6
C	130	4.9	116	8.7	3	10	517	87	17	32	54	105	33.6	2.48	1.72	16
D	93	4	77	8.83	2.1	8	99	85	15	30	50	45	31.8	1.68	3.08	15.7
Range	93-169	4-6.6	77-163	8.2-8.83	2.1 — 4.2	8-75	99-496	84-91	15-21	30-40.7	50-62	45-105	31.8-41.7	1.68-3.36	1.49-3.08	15.7-17
Mean	136	5	126	8.5	3.27	28	398	87	18	33	56	86	35.4	2.52	1.95	16.3

Table 4: Trace element component (in ppm) in core 2

Depth Profile	Cr	Mo	Ba	Pb	Th	Ga	Sr	Ni	Cu	Br	Zn	Zr	V	Nb	As	Rb
A	160	5.8	153	8.4	4.5	75	491	89	23	42	64	98	42.1	4.2	1.41	16
B	167	5.2	141	8.1	4.2	31	474	83	20	36	61	101	37.8	3.35	1.55	15.8
C	130	5	124	8.6	3.6	27	510	88	16	30	56	109	35.5	3.2	1.79	15.1
D	100	4.4	104	8.9	2.9	10	102	84	12	28	53	60	30.9	2.6	3.33	14.9
Range	100-167	4.4-5.8	104-153	8.1-8.9	2.9 — 4.5	10-75	102-510	84-89	12-23	28-42	53-64	60-109	30.9-42.1	2.6-4.2	1.41-3.33	14.9-16
Mean	139.5	5.1	130.5	8.5	3.8	35.7	394	86	17.7	34	57	92	36.5	3.3	2.02	15.6
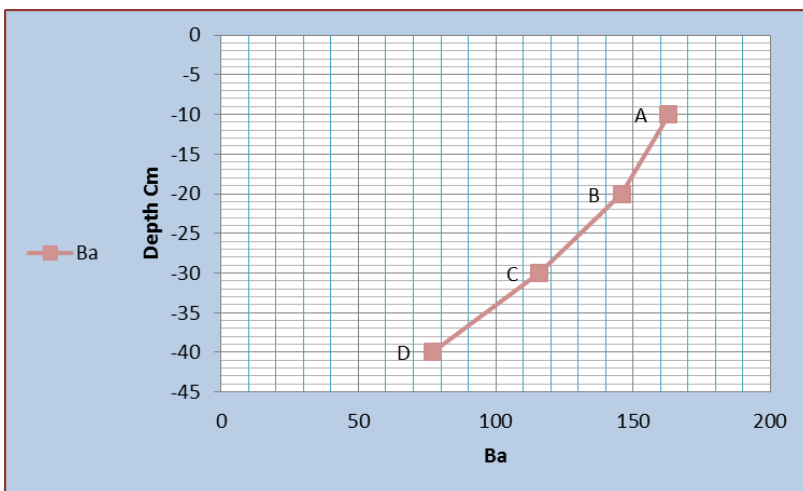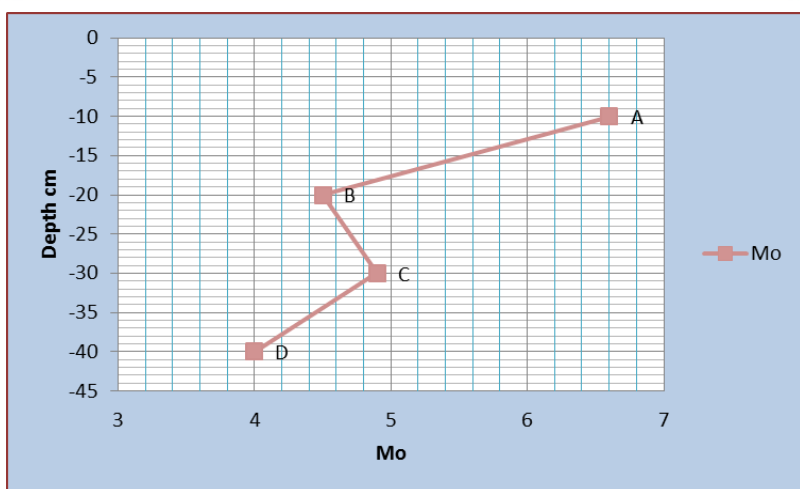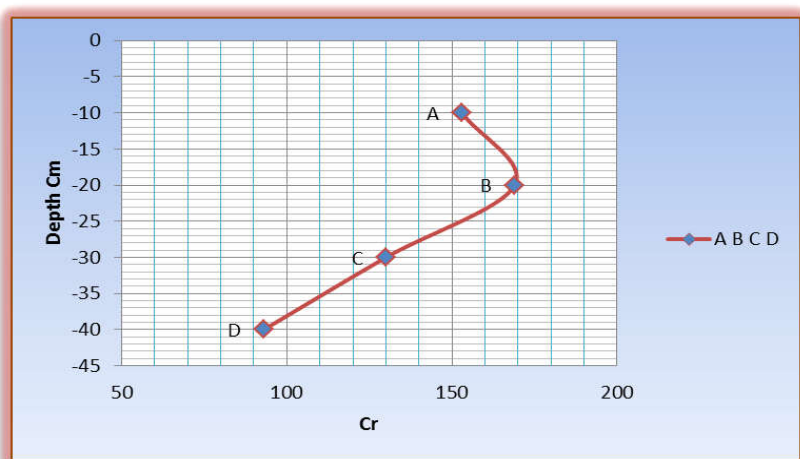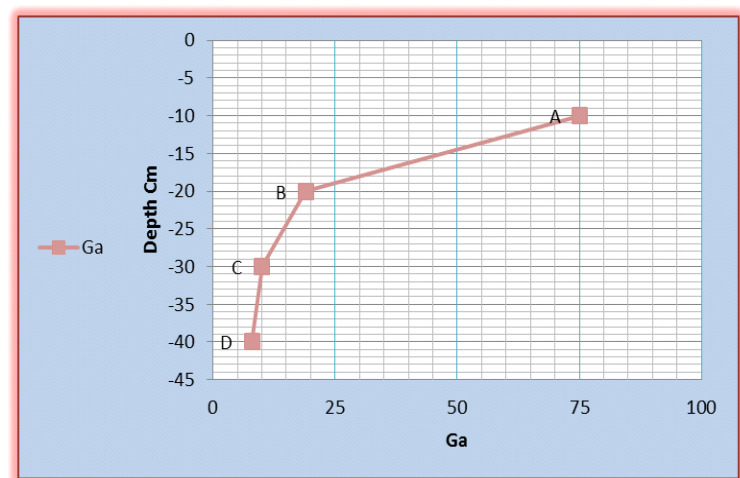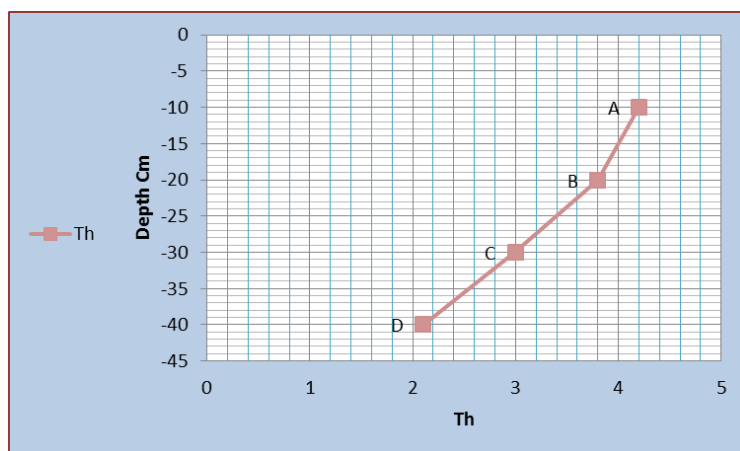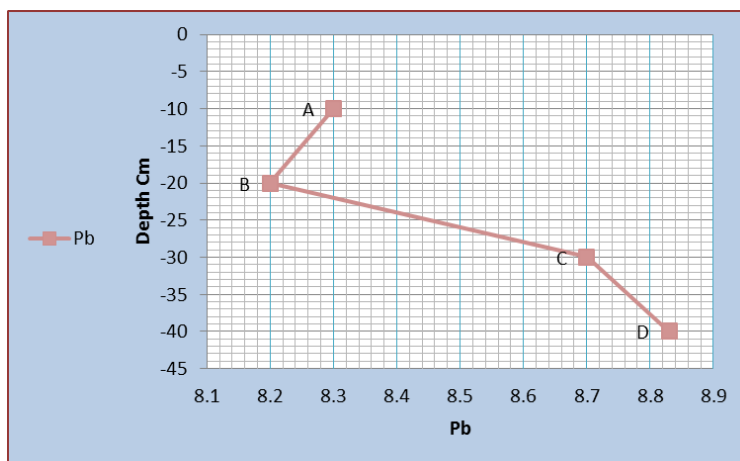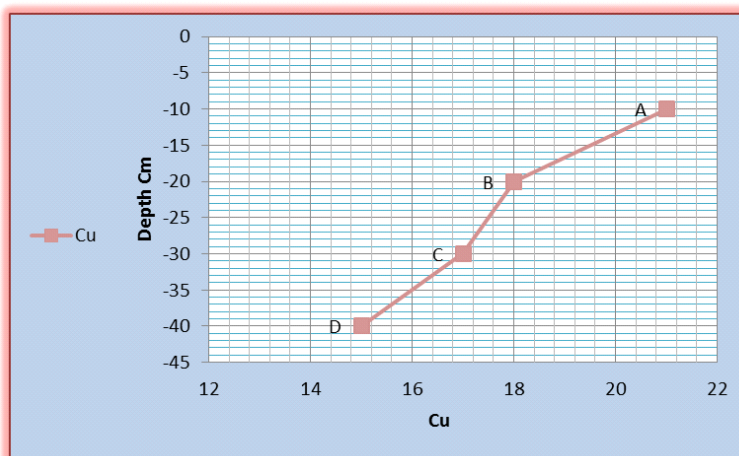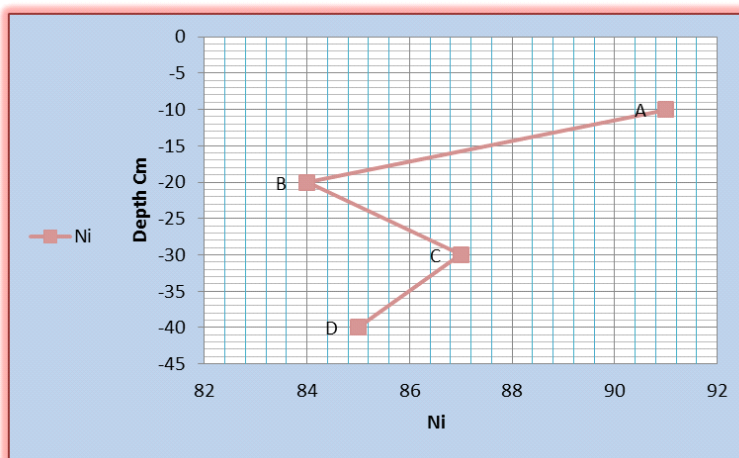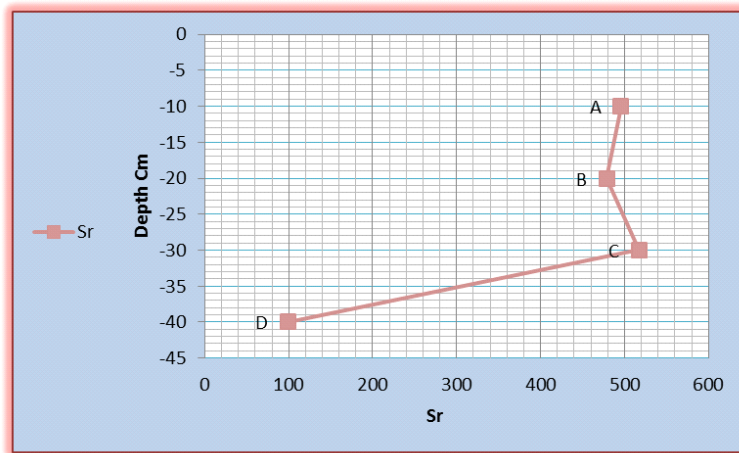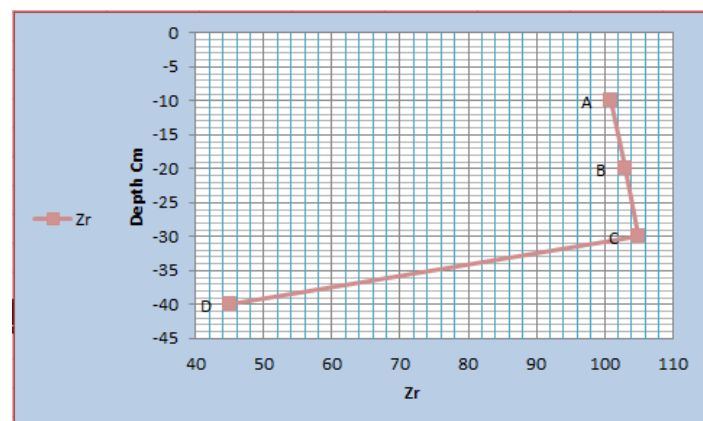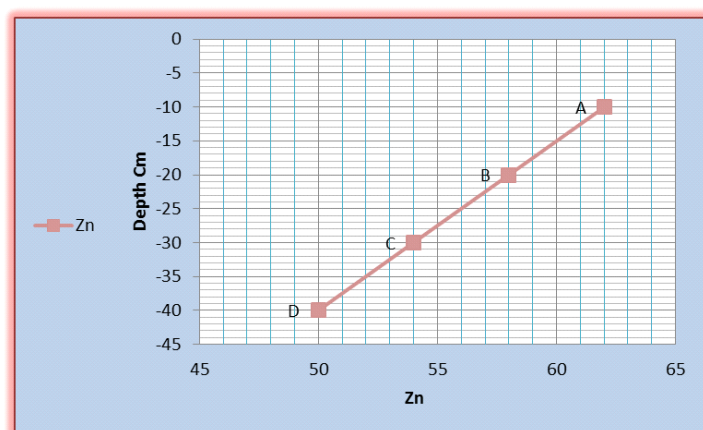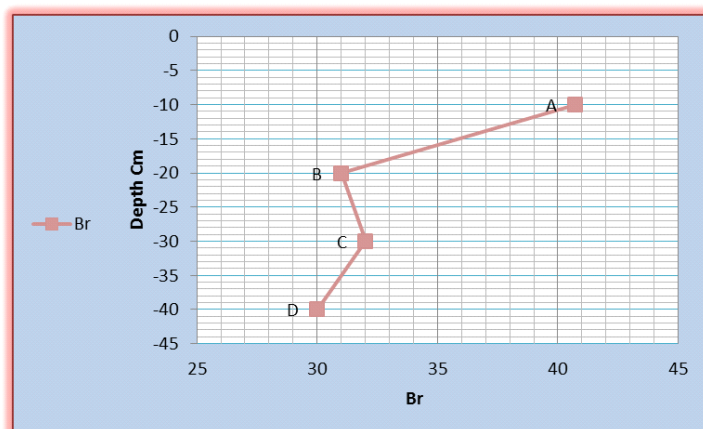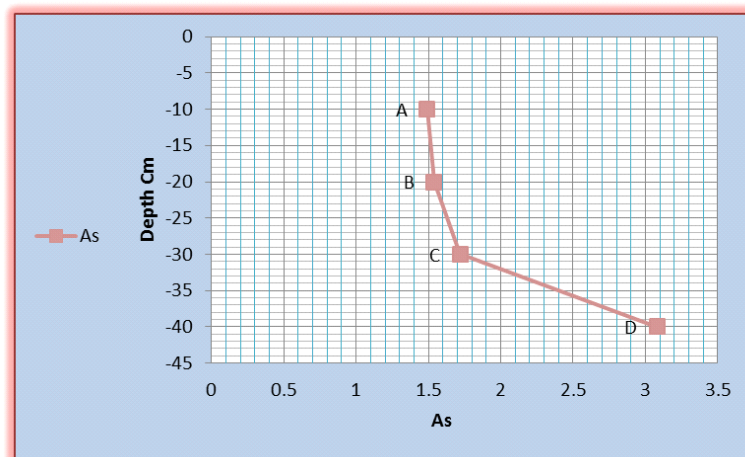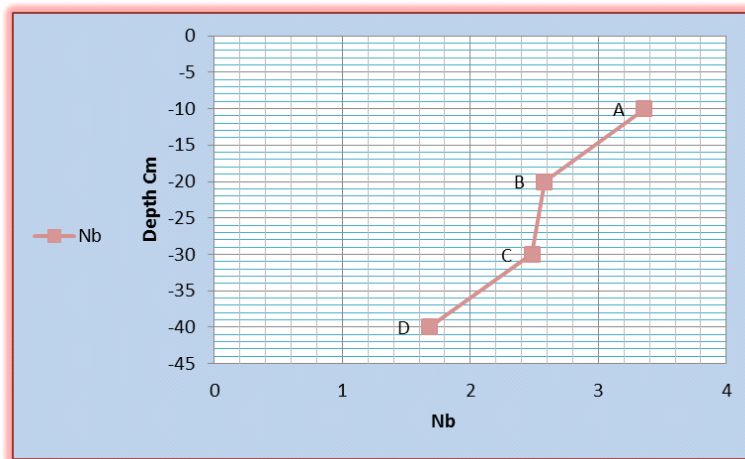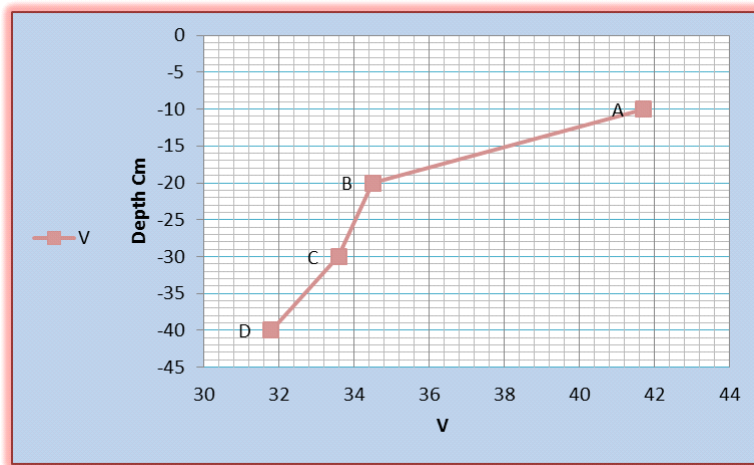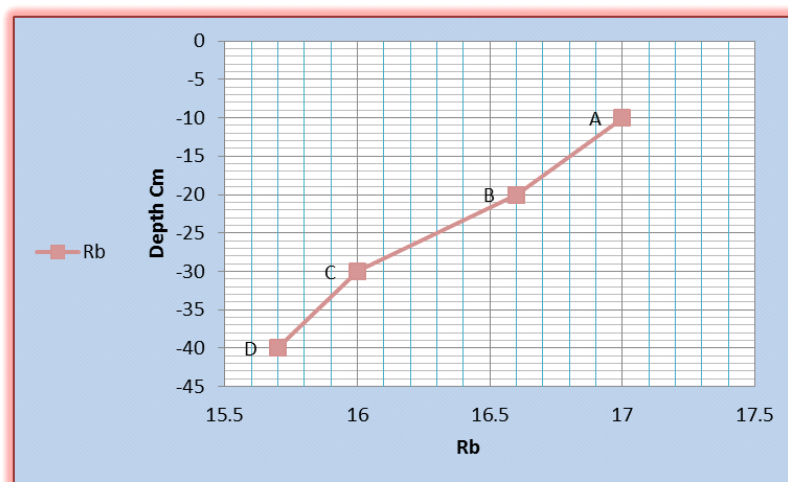
Figure 3-19:

Trace elements and Aluminum relationships

The relationships between trace elements and aluminum were shown in tables 5 and 6, and figures 3 to 19. Nb:Al. Mo:Al, and Th:Al ratios are almost equal in the surface core sediments of all depth stations, this indicate to same depositional processes of Nb, Mo, and Th from natural origin. Pb:Al and As:Al ratios fluctuated within the low concentrations in the upper part of the both profiles and increase steadily with increase of depth intervals. Br:Al and Zr:Al ratios show a little distinct peak in values within the whole profiles . Nb:Al and Sr:Al ratios belong to this group as well. Ga:Al, Zn:Al, Cu:Al and V:Al ratios showed the same pattern within the high concentration in upper surface and decrease steadily with increase the depths. It is clearly show that the surface sediments of studied cores are enriched with most of trace elements except Pb and As. Organic matter in the marine sediments decreased with increase depth profiles (Tables 1 and 2), and there are negative relationships between organic matter with Pb and As elements. This result may attribute to liberate Pb and As during decomposition of organic matter. This conclusion is agree with many of authors like Zurich (1991), Gerringa (1990) and Kahn et al (1992). The highest content of $CaCO_3$ with depths, the Pb and As. There are obvious positive relationships between $CaCO_3$ with Pb and As. Pruysers et al (1991) explained these relationships by the fact that calcite minerals supply regions of higher pH as well as nucleate centers of trace elements on the surface of carbonate. Most of trace elements in study area were found associate with clay minerals and organic matters as adsorption on the surface or inclusion in their crystal lattice.

Table 5: Relationship between trace elements and aluminum in core 1

Elements	Average Mud (Mclennan and Murray, 1999) ppm	Element/Al	Element Sample/ Al Sample	Element Sample/ Al Sample	Element Sample/ Al Sample	Element Sample/ Al Sample
		Mud	A	B	C	D
Al	39130					
Cr	100	0.0025	0.0106	0.011	0.0091	0.0066
Mo	1	2.5×10^{-4}	4.65×10^{-4}	3.13×10^{-4}	3.44×10^{-4}	2.8×10^{-4}
Ba	650	0.017	0.011	0.01	0.0081	0.0055
Pb	20	5.1×10^{-4}	5.37×10^{-4}	5.7×10^{-4}	6.11×10^{-4}	6.21×10^{-4}

Th	14.6	3.7×10^{-4}	2.9×10^{-4}	2.64×10^{-4}	2.1×10^{-4}	2.1×10^{-4}
Ga	20	0.00051	0.005	0.0013	0.0007	0.00057
Sr	200	0.0051	0.034	0.033	0.036	0.007
Ni	60	0.0051	0.0062	0.005	0.0061	0.006
Cu	50	0.0012	0.0014	0.0012	0.0011	0.001
Br	1.6	0.0004	0.0028	0.002	0.0022	0.002
Zn	85	0.0021	0.0042	0.004	0.0037	0.0035
Zr	210	0.0053	0.007	0.007	0.0073	0.0032
V	140	0.0035	0.0028	0.0024	0.0023	0.0022
Nb	19	3.3×10^{-4}	2.32×10^{-4}	1.79×10^{-4}	1.74×10^{-4}	1.2×10^{-4}
As	4.8	1.2×10^{-4}	1.02×10^{-4}	1.07×10^{-4}	1.28×10^{-4}	2.1×10^{-4}
Rb	160	0.0041	0.001	0.0011	0.0011	0.0011

Table 6: Relationship between trace elements and aluminum in core 2

Elements	Average Mud (Mclennan and Murray, 1999) ppm	Element/Al	Element Sample/ Al Sample	Element Sample/ Al Sample	Element Sample/ Al Sample	Element Sample/ Al Sample
		Mud	A	B	C	D
Al	39130					
Cr	100	0.0025	0.011	0.0122	0.009	0.0067
Mo	1	2.5×10^{-4}	4×10^{-4}	3.82×10^{-4}	3.49×10^{-4}	2.96×10^{-4}
Ba	650	0.019	0.0106	0.0103	0.0086	0.007
Pb	20	5.1×10^{-4}	5.82×10^{-4}	5.95×10^{-4}	6.01×10^{-4}	6×10^{-4}
Th	14.6	3.7×10^{-4}	3.12×10^{-4}	3.08×10^{-4}	2.5×10^{-4}	1.95×10^{-4}
Ga	20	0.00051	0.0052	0.0022	0.0018	0.00067
Sr	200	0.0051	0.034	0.0348	0.035	0.0068
Ni	60	0.0015	0.0061	0.0061	0.00615	0.0056
Cu	50	0.0012	0.0015	0.00147	0.002	0.0008
Br	1.6	0.0004	0.0029	0.0026	0.0025	0.0018
Zn	85	0.0021	0.0044	0.0044	0.0039	0.0035
Zr	210	0.00012	0.0068	0.0074	0.0076	0.004
V	140	0.0035	0.0029	0.0027	0.0024	0.002
Nb	19	3.3×10^{-4}	2.91×10^{-4}	2.46×10^{-4}	2.23×10^{-4}	1.75×10^{-4}
As	4.8	1.2×10^{-4}	9.7×10^{-5}	1.13×10^{-4}	1.25×10^{-4}	2.24×10^{-4}
Rb	160	0.0041	0.0011	0.0011	0.001	0.001

C-Enrichment Factor (EF)

Tables 5 and 6 presented the elements / Al ratio of average mud and Iraqi marine sediments in ppm and the correspond enrichment factors (EF) regarding Al in marine sediments. The enrichment factor is defined as follows: EF= (element /Al) samples / (element/Al) Mud, any relative enrichment expressed by an EF>1, whereas depleted elements have an EF<1.

The examination of the enrichment factors regarding the element/Al ratios of average mud compared to Iraqi marine sediments are showed in tables 7 and 8. In cores 1 and 2, Cr, Sr, Ni, Br, and Ga are often exhibit constantly high enrichment factors except at depth of 40 cm (profile D) for Sr , and at depths of 20 , 30 and 40 cm (profiles B, C and D) for Ga element . Mo, Pb, Zn, Zr, and Cu are commonly oscillate around enrichment factors more than 1 except the depleted elements at depth 40 cm (profile D) for Zr and depleted elements at depths of 20, 30, and 40 cm (profiles B, C, and D) for Cu . As is constantly enriched with the profiles C (30 cm) and D (40 cm). While the few measurement

of EF (depleted elements) for Ba, Th, V, Nb, and Rb. High concentration of Cr, Ga, Sr, Ni, and Br in marine sediments can be probably explained to anthropogenic sources. Forstner and Wittmann (1979) and Al-Dabbas and Al-Jaberi (2015) gave information about the higher concentration of trace elements in marine sediments are known to be effected by several natural and anthropogenic factors.

Table 7: Enrichment factor for trace elements in core 1

Elements	Enrichment Factor A	Enrichment Factor B	Enrichment Factor C	Enrichment Factor D
Al				
Cr	4.42	4.4	3.64	2.65
Mo	1.84	1.25	1.37	1.12
Ba	0.64	0.5	0.47	0.32
Pb	1.12	1.11	1.19	1.2
Th	0.78	0.71	0.56	0.56
Ga	10	2.5	1.37	1.11
Sr	6.6	6.47	7.05	1.37
Ni	4.18	3.3	4	4
Cu	1.2	1	0.91	0.83
Br	7.02	5	5.5	5
Zn	2	1.9	1.76	1.6
Zr	1.31	1.32	1.37	0.6
V	0.8	0.68	0.65	0.63
Nb	0.6	0.54	0.52	0.36
As	0.8	0.89	1.06	1.75
Rb	**0.24**	**0.25**	**0.26**	**0.26**

Table 8: Enrichment factor for trace elements in core 2

Elements	Enrichment Factor A	Enrichment Factor B	Enrichment Factor C	Enrichment Factor D
Al				
Cr	4.44	4.91	3.63	2.69
Mo	1.6	1.52	1.36	1.16
Ba	0.62	0.6	0.51	0.41
Pb	1.14	1.15	1.17	1.17
Th	0.84	0.83	0.67	0.52
Ga	10.2	4.46	3.7	1.32
Sr	6.68	6.83	6.99	1.34
Ni	4.11	4.06	4.1	3.77
Cu	1.33	1.22	0.93	0.67
Br	7.2	6.6	5.2	4.7
Zn	2.11	2.13	1.86	1.7
Zr	1.21	1.4	1.43	0.76
V	0.83	0.79	0.7	0.59
Nb	0.87	0.74	0.67	0.53
As	0.81	0.94	1.04	1.86
Rb	0.27	0.28	0.25	0.24

5. Conclusions

- The concentration of alumina and silica in the Iraqi marine sediments may be attributed to mixed sediments between sand and clay minerals.
- The oxidation of Fe and Mn in the sediments is very much and considered as redox elements, it

found in high concentration in the uppermost layers and decrease with increase depths.

- All the trace elements except Pb and As have the same pattern of redox elements.
- Associated of most trace elements with clay minerals and organic matter as adsorption or absorption.
- The positive relationship between Pb and As elements with calcium carbonate may explained that calcite minerals supply zones of higher pH as well as nucleate centers of these trace elements on the surface of carbonate.
- The negative relation between Pb , As and organic matter with depths may considered as the role of decomposition of organic matter and their effect by release of these elements.
- High concentration of EF for Cr, Ga, Sr, Ni, and Br elements in marine sediments as a result to anthropogenic sources.

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