MAJOR AND TRACE ELEMENTS DISTRIBUTION IN STREAM SEDIMENTS OF THE LESSER ZAB RIVER AT NORTHEASTERN IRAQ: IMPLICATIONS TO WEATHERING AND TRANSPORTATION

Abbas R. Ali[1]

Received: 23/ 8/ 2011, Accepted: 5/ 4/ 2012
Key words: Lesser Zab River, Northeastern Iraq, Weathering and transport, Sediment chemistry, Elemental mobility

ABSTRACT

Fifteen samples of stream sediments were collected from the Lesser Zab River (LZR), which represent one of three major tributaries of the Tigris River at northeastern Iraq. The sediment samples were subjected to laboratory studies including chemical analyses (using polarized energy dispersive XRF) for major (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, TiO_2 and MnO, in weight %) and trace (Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr and Zn in ppm) elements. These results have been used to characterize chemical weathering and transportation in the catchments area, to assess relative mobility of elements during weathering and to understand trace element associations. Correlation coefficients being significant for most of the major elements among themselves which suggests that concentrations of these elements are significantly controlled by Ferro manganese oxides-hydroxides, clay and carbonate mineral abundances during weathering and transported of Lesser Zab river sediments. Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW) and Index of Compositional Variation (ICV) for LZR sediments averages at (46%, 50% and 2.25 respectively), indicating that weathering in the basin is of moderate intensity. Comparison of the chemistry of sediments with the composition of source rocks and average Upper Continental Crust (UCC) suggests significant loss of most major elements from source rocks during weathering, the degree of loss being more for Na_2O and K_2O. Available results seem to indicate that Sr and Ba are effectively more mobile than other metals, which is thought to be a combined effect of higher solubility of Sr and Ba. Trace elements show higher concentrations in the river sediments and significant positive correlation with themselves (exception Cr) and with Al_2O_3, Fe_2O_3 and MnO. These observations suggest that trace element concentrations are also controlled mainly by clay mineral abundances and those of Fe-Mn oxides. Cr shows significant positive correlation with SiO_2 which indicates to diffusion of Cr from chromite margin toward the silicate matrix during alteration of chromites and metamorphism, resulted in the development of ferrit-chromite and chlorite. Observed higher Al_2O_3 concentrations and its strong association with trace elements in LZR sediments would indicate to preponderance of clay minerals over K-bearing minerals such as K-feldspars and micas. Hence, the sediments of the LZR are mainly enriched in clays in comparison with rock forming minerals. Enrichment factor and geo-accumulation index calculated for trace elements in LZR sediments suggest that they are mainly of natural origin and that anthropogenic activities exert little influence on their abundances.

---

[1] Department of Applied Geology, Faculty of Science, University of Kirkuk, Iraq
e-mail: arkervanci@yahoo.com

توزيع العناصر الرئيسية والأثرية في رواسب المجرى
لنهر الزاب الأسفل – شمال شرق العراق: نتائج مترتبة عن التجوية والنقل

عباس رشيد علي

المستخلص

جمعت خمسة عشرة نموذجا من الرواسب الحديثة لنهر الزاب الأسفل والتي تعتبر واحدة من الروافد الثلاثة الرئيسية لنهر دجلة، شمال شرق العراق. أخضعت هذه النماذج الى دراسة مختبريه تضمنت التحليل الكيميائي (باستخدام جهاز تشتت الطاقة المستقطبة XRF) للعناصر الرئيسية (TiO_2، P_2O_5، K_2O، Na_2O، MgO، CaO، Fe_2O_3، Al_2O_3، SiO_2 و MnO) والعناصر الأثرية (Sr، Rb، Pb، Ni، Cu، Cr، Co، Ba و Zn)، واستخدمت هذه النتائج لتحديد خصائص التجوية الكيميائية والنقل في حوض التصريف وذلك لتقييم الحركة النسبية للعناصر خلال التجوية ولفهم تجمعات العناصر الأثرية.

تؤشر معاملات الترابط لمعظم العناصر الرئيسية على تحكم أكاسيد وهيدروكسيدات الحديد المنغنيزية ووفرة المعادن الطينية والكاربوناتية في أغناء رواسب نهر الزاب الأسفل بهذه العناصر خلال عمليات التجوية والنقل. إن متوسط قيم المعامل الكيميائي للتحلل (CIA) والمعامل الكيميائي للتجوية (CIW) ومعامل تغاير في المكونات (ICV) (46%، 50% و 2.25 على التوالي) يشير الى الشدة المتوسطة للتجوية في حوض التصريف.

تبين من خلال أجراء مقارنة للتركيب الكيميائي لهذه الرواسب مع مكونات الصخور المصدرية ومعدل القشرة القارية العليا (UCC) الى فقدان رئيسي لمعظم العناصر الرئيسية وبدرجة كبيرة لـ (K_2O و Na_2O) من الصخور المصدرية خلال عمليات التجوية. وكذلك أظهرت النتائج المتاحة الحركة النسبية العالية لعنصري Sr و Ba مقارنة بالعناصر الأخرى. تواجد العناصر الأثرية بتراكيز عالية في رواسب قيد الدراسة وارتباطها بمعاملات ربط موجبة قوية مع بعضها البعض (باستثناء عنصر الـ Cr) ومع Fe_2O_3، Al_2O_3 و MnO. إن هذه الملاحظات تشير الى التحكم الرئيسي للمعادن الطينية وأكاسيد الحديد والمنغنيز أيضاً في إغناء رواسب النهر بالعناصر الأثرية.

يرتبط عنصر الكروم (Cr) بمعاملات ربط موجبة قوية مع SiO_2 مم يدل على تحرر عنصر الكروم من نطاق معادن الكرومايت باتجاه الأرضية السليكاتية خلال التحلل الكيميائي لمعادن الكرومايت وعمليات التحول الذي يؤدي الى تطور في نمو المعادن الكرومايت الغنية بالحديد والكلورايت. يشير التراكيز العالية الملاحظة لـ Al_2O_3 وارتباطه بشكل قوي مع العناصر الأثرية الى رجحان وفرة المعادن الطينية على المعادن البوتاسية مثل معادن الفلدسبار البوتاسي والمايكا، وبالتالي أغناء هذه الرواسب وبشكل رئيسي بالمعادن الطينية مقارنة بالمعادن المكونة للصخور. لقد أوضح عامل الإغناء ودليل التراكم الأرضي المحسوبة للعناصر الأثرية في رواسب نهر الزاب الأسفل أساساً الى الأصل الطبيعي والتأثير النسبي القليل للأنشطة البشرية في وفرة هذه العناصر في الرواسب.

INTRODUCTION

Investigations of the chemical composition of stream and river sediments have been used as a prospecting tool for mineral deposits (Levinson, 1974; Rose *et al.*, 1979 and Plant and Hale, 1994) but the same principles and techniques can be extended to more environmentally-related studies (Howarth and Thornton, 1983; Förstner, 1983 and Förstner *et al.*, 1991). The geochemistry of river sediments has been receiving much attention as it reflects the source, natural processes and human activities in the watershed and studies of the major and trace element distribution in these sediments contribute to a better understanding of these processes (Zhang and Wang, 2001).

In general, the chemical composition of stream sediments depends on several factors, such as the lithology, morphology and structural setting of the catchment basin, and on the effect of climate, which controls weathering rates and hydrological features as well as the density and type of vegetation cover (e.g., Salomons and Förstner, 1984 and Dinelli *et al.*, 2005).

Stream sediment is derived from the erosion and transport of soil and rock debris and other materials within the catchment basin upstream of the sampling site. It is, thus, representative of the geochemistry of materials from the upstream drainage basin. The stream sediments are generally composed of weathering products introduced into the stream. The interpretation of the elements content within these stream sediments must take into account the fact that the data are frequently related to a number of geochemical populations, each of which represents geochemical features in the environment (Morsy, 2000). Erosion and weathering of the rocks and minerals plays an important role in providing the river sediments with a variety of elements since many phases of clay and heavy minerals are the main holder for these elements. Study of the geochemical element distributions from the clastic sediments and their content of heavy and clay minerals are among the numerous processes the earth scientists adopts in understanding depositional environments, transportation processes and the physiochemical activities releasing these heavy and clay minerals (Al-Juboury, 2009).

The Lesser Zab River (LZR) drains parts of the folded zone in the northeastern parts of Iraq where exposures of Eocene, Oligocene and Miocene sediments are observed (Fig.1). The recent sediments of LZR consist major deposits of pebbles in upstream areas and mainly of loose to fairly well-indurate deposits of sands, silts and mud (Ali, 2006). The most significant mineralogical constituents of the Lesser Zab sand are quartz, rock fragments (sedimentary, igneous and metamorphic origin) predominantly sedimentary, feldspars, heavy minerals (opaque minerals, epidote, amphibole, pyroxene) and micas.

A reconnaissance study of stream sediment geochemistry, source and distribution of major and trace elements including heavy metals were carried out in a 120 Km segment of the Lesser Zab River, Northeast Iraq. The Lesser Zab River is one of three major tributaries of the Tigris River. Includes the Greater Zab, Lesser Zab and Diyala Rivers, all drain from the Foothills and Zagros Mountain. In addition, the Lesser Zab drains from the Nappe zone. It travels from the northeastern parts of Zagros Mountains to the southwest. The Lesser Zab River cuts through a variety of geological formations range in age from Jurassic (Qulqula Series) to Pliocene (Mukdadiyah and Bi-Hassan formations) (Fig.1).

GEOLOGICAL BACKGROUND

The study area extends from highly Folded Zone of the Foreland Basin into the foreland and related basins, as well as the platform region of the Arabian Plate (Fig.2).

The Zagros Thrust Zone of northeastern Iraq consists of parallel ridges of folded Upper Paleozoic and Mesozoic limestones, and a nappe of metamorphosed Lower Paleozoic rocks present along the Iranian border (Figs.1 and 2). The Foothill Zone consists mainly of Upper Miocene and Pliocene coarse detrital sediments, which are gently folded along the NW – SE axis parallel to the structural trend of the Zagros Mountains (Berry *et al*., 1970).

Iraq is located at the contact between the major Phanerozoic units of the Middle East, i.e. the Arabian part of the African Platform (Nubio-Arabian) and the Asian branches of the Alpine tectonic belt. The platform part of the Iraqi territory is divided into two main units, i.e., stable and unstable shelves. The stable shelf is characterized by a relatively thin sedimentary cover, which shows little evidence of significant folding. In contrast, the unstable shelf comprises a thick, folded sedimentary cover, where the intensity of the folding increases toward the northeast (Buday, 1980 and Jassim and Goff, 2006). Structurally, the studied area (Lesser Zab River) lies in the Foothill and High Folded zones of the platform foreland of Iraq as shown in Figure (2) (Numan, 2001).

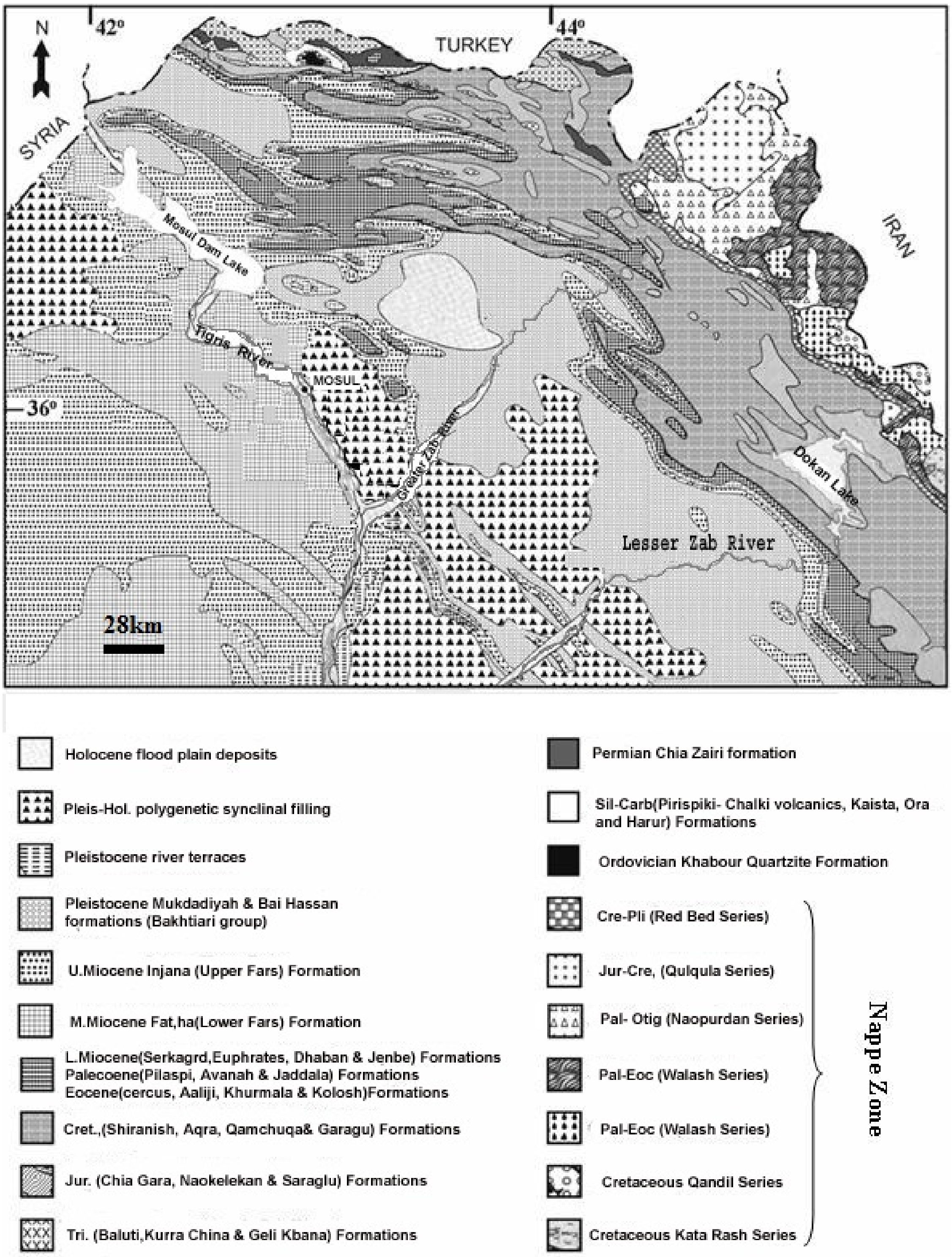

Fig.1: Geological map of northern Iraq showing the geologic formations of the Ordovician to recent (after Jassim *et al*., 1986)

The main sediment Formations which appear as outcrops range in age from Jurassic to Quaternary (Fig.1). This zone has undergone widespread igneous activity including the intrusion of dolerite, gabbros and granite, and the extrusion of andesite and basalt (Buday, 1980) as well as explosive pyroclastics and tuff. Rocks in this zone show low grade of metamorphism (e.g. slates, phyllites, schist and spilites).

The Lesser Zab River (LZR) travels a distance of 400 Km until its junction with the Tigris River at 35 Km southwest Sharqat city and its catchment covers an area of 22250 Km^2 (Fig.3). River collect it's water from the northeast drainage area. Lesser Zab River has risen from NE Nappe Zone (i.e. across the Mawat-Chuwarta Ophiolite Complex area). The Nappe Zone includes the area of north and northeast Iraq, forming the high and tectonically complex Zagros Mountains, which trend northwest – southeast. The headwaters of a number of rivers which drain southwestward to the Tigris River occur in this area.

METHODOLOGY

Fifteen recent sediment samples were collected from the Lesser Zab Main stream (Fig.3) located in to the northeastern of Iraq during April 2009. The sediments were sampled manually especially which were in contact with running water using a metal bucket of the dimensions 26 × 8 × 3 cm. Sampling was performed at distance from the river banks to avoid possible contamination from the bank material. About 2 – 4 Kg of sediments was collected from the main stream to provide enough material in plastic bags for geochemical analysis. Details of the analysis techniques are given in Timothy and La (1989) and Johnson *et al.* (1999).

The samples were sun-dried and then ground into fine powder in an agate mortar. The samples were sieved to pass through 200 μm sieve, and then pressed into thick pellets of 32 mm diameter using wax as blinder. USGS standards, GEOL, GBW 7109 and GBW-7309 sediment equally pressed into pellets in a similar manner as the samples, and these used for quality assurance (Timothy and La, 1989 and Johnson *et al.*, 1999).

Multi-element concentration was determined by using polarized energy dispersive XRF. The PEDXRF analysis carried out at the Earth Sciences Research and Application Center of Ankara University, TURKEY. The instrument model used in this study was Spectro XLAB 2000 PEDXRF spectrometer, which was equipped with a Rh anode X-ray tube, 0.5 mm Be side window. The detector of spectrometer is Si (Li) by liquid N_2 cooled with resolution of < 150 eV at Mn Kα, 5000 cps. Total analysis time for each addition element was 30 min. The sample measurements by PEDXRF mainly done by three types of targets (Stephens and Calder, 2004):

i. Light element targets of high density designed for efficient scattering and polarization of polychromatic source radiation. This target is suitable for the excitation of elements with Z > 22 and this target named as Barkla target.

ii. The second target is oriented crystal target, mosaic and single crystals; this will generate very intense source radiation of more specific energies. This target is suitable for light elements up to Z = 22 and can be named as Bragg targets.

iii. The last target is pure metal target, generate very intense near monochromatic X-ray sources, include unpolarized and polarized radiation scattered from the X-ray tube. This target is suitable for specific elements or small groups of adjacent elements. In addition, this target is useful for generating Compton scatter peaks, which can be used for matrix correction.

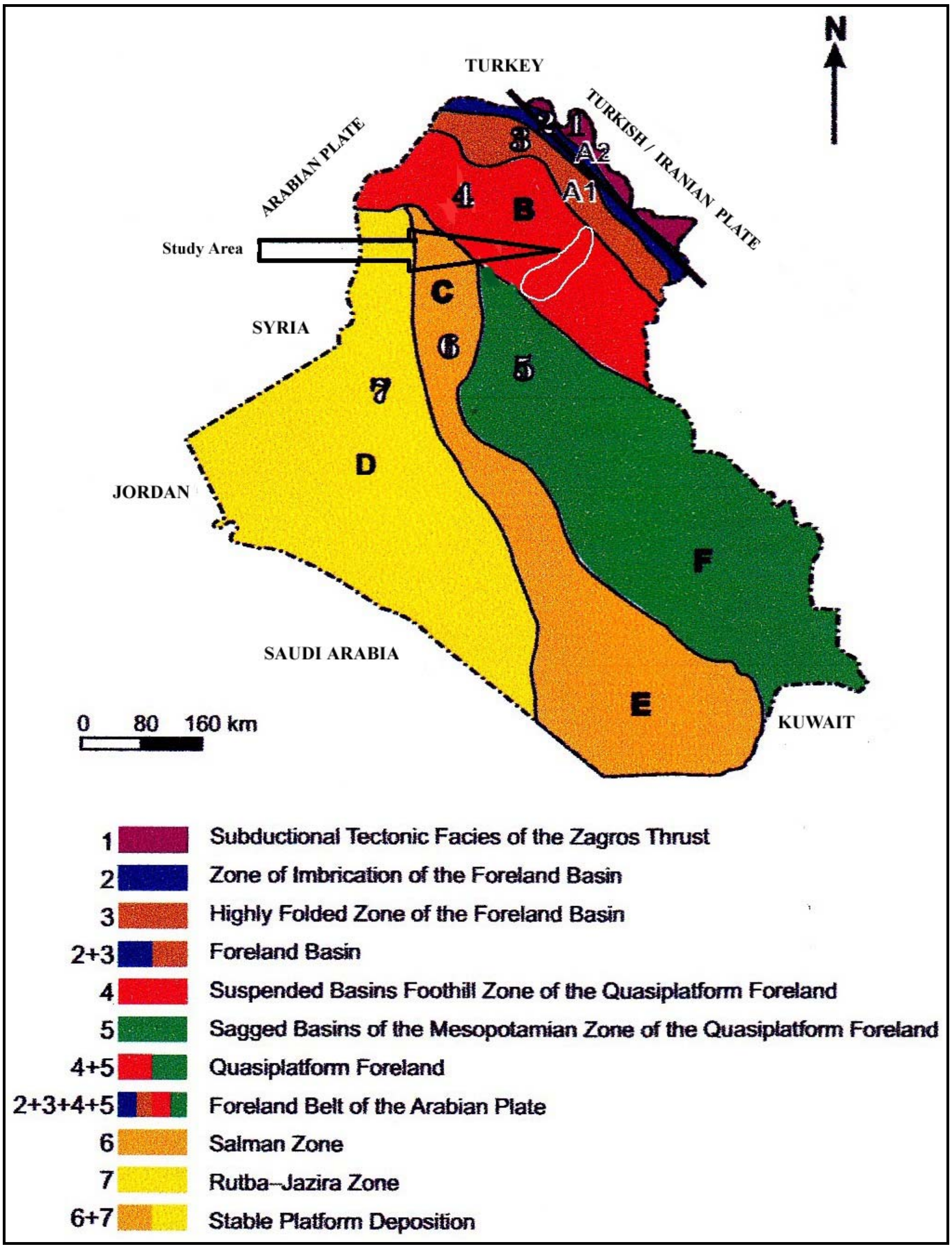

Fig.2: Tectonic division (modified from Numan, 2001) and the physiographic provinces of Iraq. Provinces are: Zagros Mountains (**A1**, folded zone; **A2**, nappe zone), Foothills (**B**), Jezira (**C**), Northern (**D**) and Southern (**E**) deserts and the Mesopotamian Plain (**F**) (after Berry *et al*. 1970)

RESULTS AND DISCUSSION

The concentrations of major elements (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, TiO_2 and MnO, in weight%); trace elements (Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr and Zn in ppm) are presented in Table (1), range and mean are presented in Table (2). In order to observe general variability in the sediment chemistry of the LZR, statistical parameters of the data (arithmetic mean, maximum and minimum value, standard deviation and coefficient of variation) were calculated (Table 2).

The concentrations of major and trace elements generally vary by 3 to 32% for the LZR; with exception of Cr, which is, vary by 54%. Coefficient of variation (C.V.) is Maximum (26 – 32%) for Co and Cu, 20 – 25% for Rb, Zn, Ni and Pb, and is within < 20% for other elements (Table 2).

▪ Major elements

In order to determine interrelation among the major and trace elements, multiple regression analysis carried out and the results are given in Table (3).

Among major elements, MgO, Fe_2O_3, MnO, TiO_2 and K_2O show positive correlation with Al_2O_3; correlation coefficient being the highest for the MnO – Al_2O_3 and Fe_2O_3 – Al_2O_3 (0.73, 0.67 respectively) (Table 3). CaO show weak positive correlation with Al_2O_3. These trends suggest that concentrations of MgO, Fe_2O_3, MnO, TiO_2 and K_2O of LZR sediments were significantly controlled by Ferro manganese oxides-hydroxides, clay and carbonate mineral abundances that are progressively diluted by quartz content. Due to mechanical transport and hydrodynamic sorting, many of the major and trace elements are known to be associated with clay and fine silt fractions of sediments and suspended particulates of rivers, whereas quartz is usually abundant in the sand fractions (Tebbens *et al.*, 2000). TiO_2 combined with some of the fine particles of heavy minerals like (rutile and ilmenite) into the sedimentary rocks. Because of the high resistance of heavy minerals to the weathering coefficients, therefore they were fixed into the sediments, and caused to enrichement weathering residual with TiO_2 (Rankama and Sahama, 1950 and Goldschmidt, 1962). Also (Ti) perecent with clay minerals as replaced with (Fe^{+3}) and (Al^{+3}) in to the crystal lattice of clay minerals or forms small particles of Rutile (Hirst, 1962 and Wright, 1974). Therefore, many phases of clay and heavy minerals are the main holder for these elements.

SiO_2 shows significant negative correlation with most of trace elements and has no significant positive correlation with most of the major elements or with any trace element exception Cr (Table 3). However, this behavior could be attributed to the extraction method applied to this research. The positive correlation between SiO_2 and Cr indicates to association of chlorite with altered chromites and they support the idea of genetic linkage. Chromite is expected to be the only mineral which could contribute Al, Mg, Cr for chlorite during alteration of chromites {Diffusion or expulsion of these elements (Cr) from chromite to surrounded silicate minerals cause reaction with silicate minerals and formation of chlorite} also the altered chromites are enriched in Si which are transferred from silicate to chromites (Al-Chalabi, 2004). On the other hand, the considerable number of trace elements (e.g. Cr, Ni, V, Pb) and Fe would be incorporated within the lattice of the micaceous (Chlorite, Muscovite and Biotite) constituents (Al-Juboury, 2009).

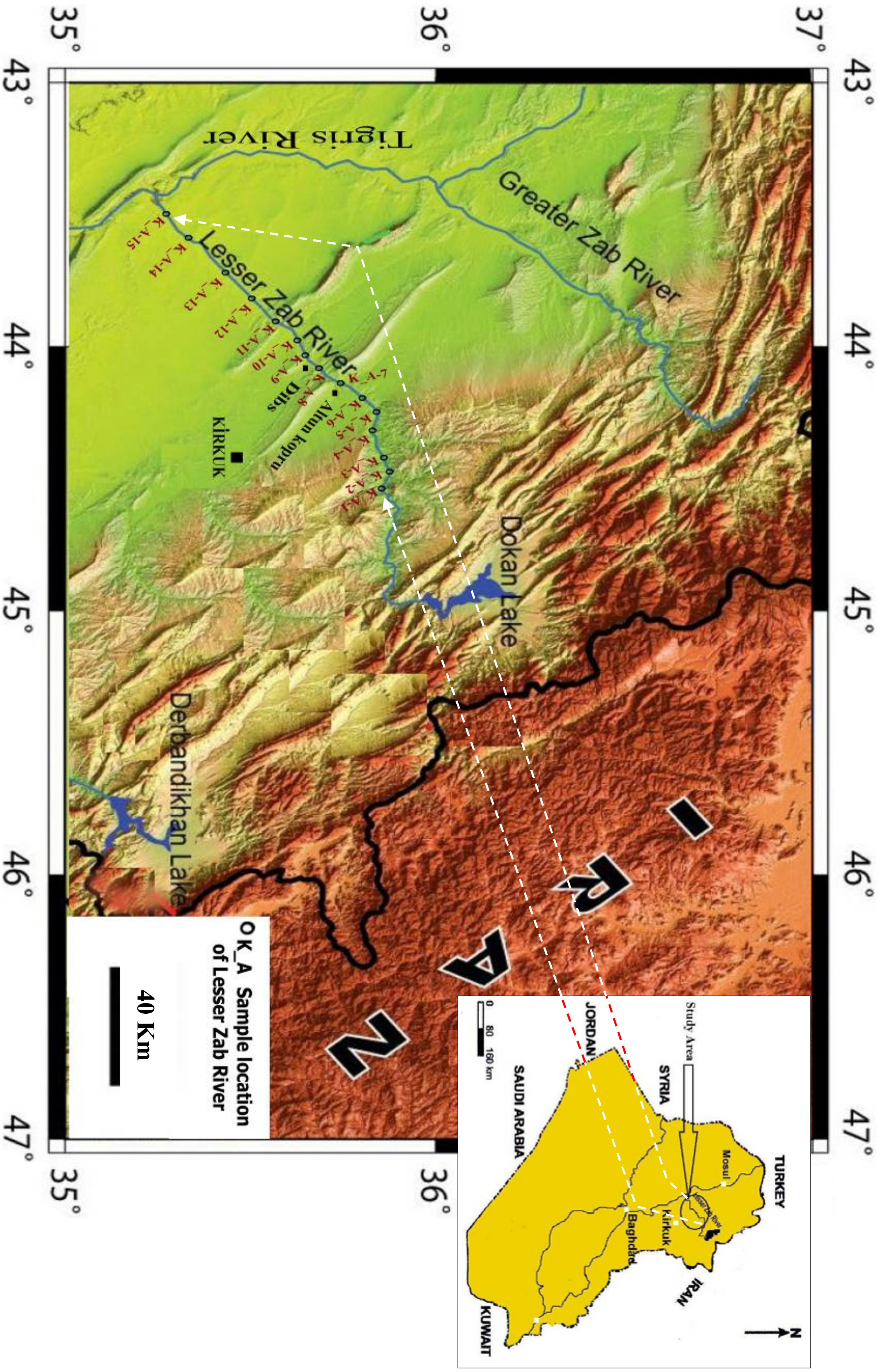

Fig.3: Map showing sediment sampling locations in the Lesser Zab River

Table 1: Major and trace element concentrations of LZR sediments

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	LOI	Cr	Co	Ni	Cu	Zn	Rb	Sr	Ba	Pb
	(wt%)											(ppm)								
K_A-1	0.074	2.869	6.237	41.91	0.1311	1.382	17.01	0.4442	0.0564	3.435	26.32	309	16.7	100.7	20.2	41.7	30.7	155.1	255.8	6.8
K_A-2	0.071	2.986	6.453	42.83	0.1015	1.065	17.99	0.4522	0.0748	3.445	24.35	318	18.2	71.7	16.3	38.7	33.7	157.1	258.8	6.4
K_A-3	0.073	3.959	8.817	42.35	0.1205	1.555	18.04	0.668	0.1009	5.086	19.21	300	17.6	71.1	29.8	44.8	46.7	201.9	255.1	12.5
K_A-4	0.075	5.049	9.181	40.77	0.1298	1.667	18.88	0.699	0.1087	4.995	18.54	322	34.8	134.3	29.5	52.1	52.3	235.5	261.2	11.5
K_A-5	0.074	4.959	9.817	42.35	0.1305	1.534	18.95	0.6297	0.1139	5.174	16.38	295	44.6	142.1	29.4	64.8	57.3	245.9	274.8	12.5
K_A-6	0.076	4.7	9.271	41.57	0.1227	1.446	16.78	0.5901	0.1087	4.978	20.39	327	24	140.3	26.3	59.1	53.3	237.5	271.2	11.5
K_A-7	0.078	4.111	10.025	40.79	0.11	1.351	17.52	0.5505	0.1035	4.782	20.65	189	24.4	138.1	23.7	53.2	49.1	243.1	270.6	9.9
K_A-8	0.07	4.002	11.179	40.01	0.1021	1.47	17.26	0.6109	0.0983	4.286	20.88	211	30.2	136.3	20.6	77.7	45.5	240.7	264	14.5
K_A-9	0.072	5.123	11.033	40.11	0.0993	1.182	18.98	0.5013	0.0931	4.39	18.58	312	37.8	150.9	17	52	41.3	250.1	260.4	12.1
K_A-10	0.077	5.664	9.087	39.01	0.0915	1.794	18.95	0.4317	0.0879	4.194	20.65	302	32.4	152.1	19.9	60.3	55.4	249.9	256.8	11.5
K_A-11	0.074	5.405	8.541	40.67	0.0837	1.726	18.96	0.3921	0.0827	5.098	18.98	205	40	155.3	20.8	70.6	60.3	255.5	253.2	13.5
K_A-12	0.075	5.271	11.08	40.12	0.1232	1.807	18.98	0.6386	0.1062	6.096	15.87	168.3	42.4	160.3	35.9	78	70.6	255.8	294.8	15.5
K_A-13	0.077	5.137	11.11	39.27	0.1127	1.78	18.5	0.599	0.098	6.067	17.36	131.6	44.2	156.7	33.9	76.4	67.9	256.1	287.4	13.8
K_A-14	0.076	5.403	10.196	39.16	0.1022	1.69	17.4	0.567	0.101	6.092	19.23	94.9	42.8	160	34.7	74.8	65.7	256.4	292	14.1
K_A-15	0.079	5.406	10.196	39.19	0.1025	1.72	17.43	0.57	0.104	6.095	19.09	95	43.3	163	35.2	75.01	66.3	256.7	292	14.4

Table 2: Variability in major (wt%) and trace element (ppm) concentrations in the LZR Sediments

Major Oxides (%)	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**P_2O_5**	**TiO_2**	**MnO**	**LOI**
Min.	39.01	6.24	3.44	16.78	2.87	0.07	1.07	0.08	0.39	0.06	15.87
Max.	42.83	11.18	6.10	18.98	5.66	0.08	1.81	0.13	0.70	0.11	26.32
Mean.	40.67	9.48	4.95	18.11	4.67	0.075	1.55	0.11	0.56	0.10	19.77
S.D.	1.28	1.54	0.89	0.82	0.89	0.003	0.23	0.02	0.09	0.02	2.73
C.V. (%)	3.15	16.25	18.07	4.53	18.95	3.41	14.76	13.42	16.66	15.75	13.80
Trace Elements (ppm)	**Ba**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Rb**	**Sr**	**Zn**		
Min.	253.20	16.71	94.90	16.31	71.10	6.40	30.70	155.10	38.70		
Max.	294.81	44.60	327.00	35.90	163.00	15.50	70.61	256.70	78.01		
Mean.	269.87	32.89	159.10	26.21	135.53	12.03	53.07	233.15	61.28		
S.D.	14.93	10.39	86.36	6.90	30.27	2.65	12.15	34.22	13.77		
C.V. (%)	5.53	31.58	54.28	26.31	22.34	22.01	22.89	14.68	22.47		

S.D. = Standard deviation, C.V. = Coefficient of variation

The results obtained for LZR sediments, as discussed above, thus underscore the importance of transport processes in regulating the elemental abundances of river sediments. positive correlation of Al_2O_3 with MgO and CaO, and also positive correlation of LOI with CaO and MgO may be caused by contributions from detrital carbonates. MnO shows significant positive correlation with Fe_2O_3, which is suggestive of Mn-Fe association in oxide and hydroxide phase (Table 3). Mn characterized by high mobility, therefore it was easily leached and transported by the water solutions during weathering process (Vinogradov, 1959).

The Lesser Zab River and its tributaries, as mentioned earlier, have major part of their drainage basins (Altunkopri drainage basins) in the main catchment areas of the northern Iraq. The LZR recent sediments generally are classified as litharenite that composed principally of rock fragments followed in amounts by quartz, feldspars and heavy minerals (Ali, 2006). Comparison of element abundances in the LZR sediments with those in the Quaternary River Terraces, Late Miocene Injana Formation (sandstone and mudstone) and Middle Miocene Fatha Formation (sandstone and mudstone) from northern Iraq (Table 4) (Al-Jouboury, 2009), suggesting that the Na, K, Ca and Mg have been lost from outcrops of these rocks during weathering. Thus, the chemical analysis of the stream sediments of the LZR indicates that sediment features reflect the mineralogical and chemical composition of the rocks in the drainage basin. To measures the difference between the concentrations of the mobile cations (Na_2O, K_2O and CaO) in weathered recent sediments of LZR and those in originally fresh source rocks (Injana and Fatha formations) Mobiles index (I_{mob}) were calculated and analyzed (Irfan, 1996). (I_{mob}) (mole-ratio) expressed as:

$$I_{mob} = \frac{(K_2O + Na_2O + CaO)\text{ source rocks} - (K_2O + Na_2O + CaO)\text{ LZR sediments}}{(K_2O + Na_2O + CaO)\text{ source rocks}} \quad \textbf{....(1)}$$

Table 3: Co-variation matrix for major and trace element concentration of Lesser Zab River sediments

Elements	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**LOI**	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**Sr**	**Ba**	**Pb**	**Rb**
Na_2O	1																			
MgO	0.46	1																		
Al_2O_3	0.17	0.65	1																	
SiO_2	-0.49	-0.69	-0.65	1																
P_2O_5	0.03	-0.31	-0.11	0.48	1															
K_2O	0.55	0.71	0.38	-0.60	-0.03	1														
CaO	0.03	0.59	0.25	-0.21	-0.15	0.36	1													
TiO_2	0.05	0.13	0.50	0.05	0.64	0.25	-0.01	1												
MnO	0.27	0.56	0.73	-0.17	0.23	0.33	0.20	0.78	1											
Fe_2O_3	0.56	0.70	0.67	-0.51	0.05	0.71	0.25	0.54	0.68	1										
LOI	-0.25	0.43	0.33	0.36	-0.06	-0.57	0.67*	-0.56	-0.81	-0.79	1									
Cr	-0.48	-0.41	-0.53	0.66	0.31	-0.52	0.04	-0.11	-0.25	-0.74	0.358	1								
Co	0.24	0.84	0.68	-0.64	-0.20	0.61	0.50*	0.18	0.49	0.74	-0.79	-0.59	1							
Ni	0.52	0.84	0.71	-0.79	-0.27	0.58	0.32	0.02	0.42	0.62	-0.60	-0.57	0.84	1						
Cu	0.55	0.47	0.47	-0.33	0.38	0.68	0.09	0.68	0.63	0.91	-0.64	-0.62	0.54	0.38	1					
Zn	0.29	0.67	0.74	-0.71	-0.26	0.69	0.17	0.22	0.47	0.74	-0.63	-0.77	0.80	0.80	0.56	1				
Sr	0.45	0.91	0.86	-0.72	-0.11	0.61	0.41	0.26	0.69	0.73	-0.81	-0.53	0.81	0.89	0.46	0.79	1			
Ba	0.53	0.45	0.59	-0.49	-0.31	0.45	-0.01	0.44	0.52	0.81	-0.51	-0.77	0.64	0.58	0.82	0.69	0.51	1		
Pb	0.20	0.76	0.84	-0.62	0.15	0.70	0.25	0.45	0.65	0.81	-0.82	-0.61	0.75	0.69	0.63	0.87	0.84	0.57	1	
Rb	0.61	0.83	0.64	-0.62	-0.18	0.84	0.29	0.33	0.62	0.93	-0.79	-0.71	0.81	0.75	0.79	0.83	0.81	0.76	0.82	1

The value of mobiles index (I_{mob}) is 0.45 and 0.65 for Injana Formation (for sandstone and mudstone respectively) with 0.373 and 0.48 for Fatha Formation (for sandstone and mudstone respectively). Hence, it indicates the composition changes in rocks during weathering. The higher the index, the bigger the difference in the amount of mobile cations presence in the weathered Lesser Zab River sediments and fresh rocks; and hence the more intense weathering is.

Since river sediments are composite of weathering products of all the lithologies in the catchments area (Fig.4), major element concentrations of sediments were normalized with those of the average Upper Continental Crust (McLennan, 1995). Normalization of elemental concentration of river sediments with those of the UCC is a common approach to assess the elemental mobility during weathering and transport (Taylor and McLennan, 1985). In LZR sediments, the UCC normalized ratio for most of the major elements is < 1 (Fig.5). This would suggest their loss from source rocks during weathering and transport. Exceptions to this trend are MgO and CaO, which have UCC normalized ratios > 1 (1.05 and 2.84 respectively). This observation seems to support the idea that MgO and CaO are derived in addition to the carbonate rich sandstone of Injana and upper unit of Fatha Formations, from nearest supplied outcrops source rocks represented by Cretaceous and Tertiary age carbonate rocks formations in the catchment areas (Ali, 2006) (Fig.1). Wide occurrence of limestone and dolomite in the basin, together with the observed co-variation of CaO and MgO (Table 3) and large abundance of MgO and CaO in the LZR sediments in comparison with those in UCC, support the idea that the carbonates in LZR sediments are mainly of detrital origin with little contribution from calcite precipitation (Dalai *et al.*, 2004 and Haweiz, 2003).

Table 4: Mean percent values of the major and trace elements analyses of the recent sediments of the Lesser Zab River (A, study samples) and of the Quaternary River Terraces (B); Late Miocene Injana Formation (C, sandstone; D, mudstone); Middle Miocene Fatha Formation (E, sandstone; F, mudstone) from northern Iraq. Data for B, C, D, E and F from (Al-Juboury, 2009)

Major Oxides (%)	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**P_2O_5**	**TiO_2**	**MnO**	**LOI**
A	40.67	9.48	4.95	18.11	4.67	0.075	1.54	0.11	0.56	0.10	19.77
B	45.86	9.4	10.71	13.08	4.65	1.62	1.1	0.19	0.99	0.09	11.06
C	48.37	8.28	3.49	16.72	3.61	1.66	1.51	0.07	0.54	0.1	14.81
D	29.59	7.28	4.38	29.16	4.35	0.42	1.76	0.08	0.45	0.08	18.33
E	42.51	10.06	8.23	14.8	6.04	0.38	2.22	0.10	0.69	0.15	14.11
F	38.46	9.3	6.64	18.44	5.69	0.39	2.12	0.10	0.63	0.13	18.03
Trace Elements (ppm)	**Ba**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Rb**	**Sr**	**Zn**		
A	269.87	32.89	238.65	26.21	135.53	12.033	53.07	233.15	61.28		
B	244.3	30	666.7	20.6	144.7	33.6	38.4	260.5	39.7		
C	309.3	25.4	790.3	16.5	183.6	19.6	44.1	308.1	37.7		
D	207.1	11.7	146.3	7.8	73.2	13.7	41.3	226.4	27.6		
E	208.3	28.5	330.1	17.8	118.3	8.3	55.7	235.9	82.8		
F	259.8	28.7	368.3	16.3	131.8	8.3	57.6	489.2	72.9		

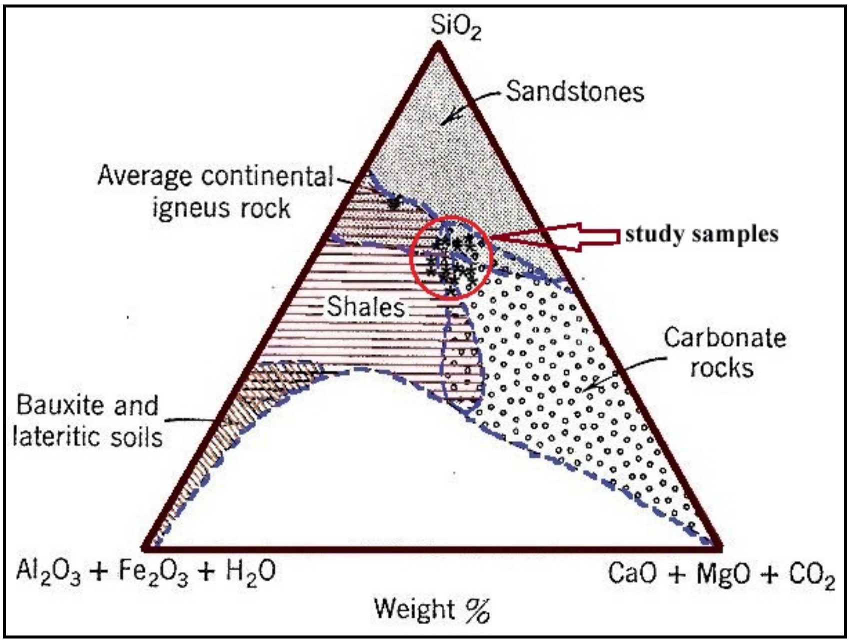

Fig.4: Triangular plot of compositional variations of common sediments and studied sediment samples (after Mason and Moore, 1982)

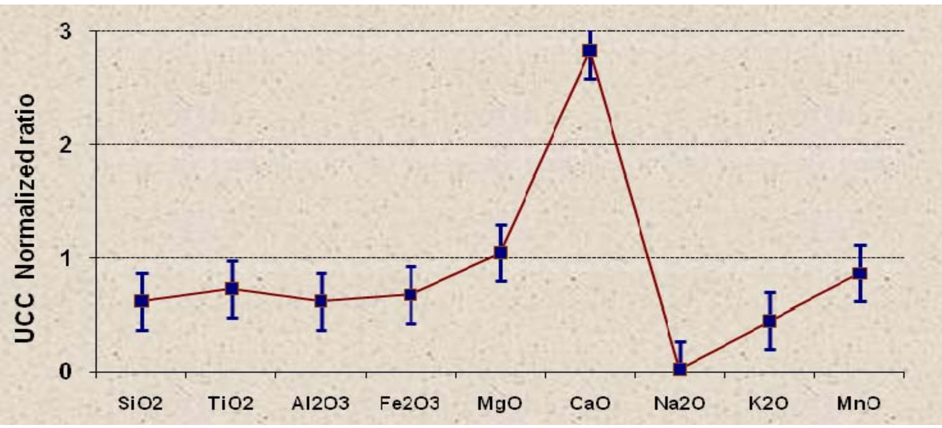

Fig.5: Upper Continental Crust (UCC) normalized ratios (concentrations of the river sediment/ concentration of the UCC) for major elements in LZR sediments

Average Al_2O_3 content of Lesser Zab River sediments (9.48 weight %) is much higher than that in the universality average (average sandstones = 4.72%) (Turekian and Wedepohl, 1961). Higher variation in the Al_2O_3 proportions produce by larger differences in mineral composition bearing aluminum in the recent sediments (Ali, 1996). Influence weathering in river basins yields high clay content and Al concentration in the river particulates and sediments. (Nesbitt and Young, 1982) illustrated that Higher Al_2O_3 concentration would also indicate that chemical weathering in the river bed sediments is so intense, although this might have been partly caused by mineral sorting. Chemical index of alteration (CIA) and Chemical index of weathering (CIW) of LZR sediments provides a semi-quantitative measure of the degree of silicate weathering in the river catchments. CIA (Nesbitt and Young, 1982 and Okunlola and Okoroafor, 2009) and CIW (Nyakairu and Koeberl, 2001) are given by:

$$\mathrm{CIA} = [(Al_2O_3)/ (Al_2O_3 + CaO^* + Na_2O + K_2O)] \cdot 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(2)}$$
$$\mathrm{CIW} = [Al_2O_3/ (Al_2O_3 + CaO^* + Na_2O)] \cdot 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(3)}$$

Where CaO^* represents CaO of the silicate fraction (Nesbitt and Young, 1982 and Okunlola and Okoroafor, 2009). The results of CIA and CIW reveal average values of (46% and 50%, respectively) for the LZR sediments. These values indicate that chemical weathering of the source rocks in the basin is of moderate intensity. During chemical weathering of silicates, more soluble cations, i.e., Ca and Na released to solution, leaving Al in the residual products such as clay. High intensity weathering results in high abundances of clay and consequently high Al in sediments (Nesbitt and Young, 1982). However, the average CIA in LZR sediments is lower than that in average shale, 70 – 75 (Nesbitt and Young, 1982) this indicates that chemical weathering of silicates in the LZR basin is relatively intense. Therefore, the values of CIA in the LZR sediments infer also that erosion and physical weathering regulate sediment chemistry of the LZR and the Major element compositions of the analyzed river sediment samples are controlled mainly by clay minerals rather than the non-clay silicate phases (Moosavirad *et al*., 2010). Clay minerals and non-clay silicate minerals are characterized by very different proportions of alumina. This trend also can be illustrated from the values of the Index of Compositional Variation (ICV) (Cox *et al*., 1995) where:

$$\mathrm{ICV} = (Fe_2O_3 + K_2O + Na_2O + CaO^* + MgO + MnO)/ Al_2O_3 \quad \ldots\ldots\ldots\ldots\ldots \mathbf{(4)}$$

It measures the abundance of alumina relative to the other major cations in a rock fragment or mineral contents into the river sediments. Silica is excluded to eliminate problems of quartz dilution. Non-clay silicates contain a Lower proportion of Al_2O_3 than clay minerals, relative to other constituents; therefore, they have a higher ICV. In addition, there is a compositional gradient within the non-clay silicates: the ICV tends to be highest in minerals high in the weathering sequence of (Cox *et al*., 1995), such as the pyroxenes and amphiboles and decreases in more stable minerals such as the alkali feldspars. The ICV decreases further in the montmorillonite group clay minerals and is lowest in the kaolinite group (Cox *et al*., 1995). ICV values of the river sediments of the present study are low and vary from 1.8 to 2.5 (average = 2.25). Hence, the river sediments of the present study are mainly enriched in clays in comparison with rock forming minerals. These values also indicate preponderance of clay minerals over K-bearing minerals such as K-feldspars and micas (Cox *et al*., 1995).

▪ Trace elements

Trace elements concentration in sediments is mainly driven by the weathering of bedrocks and catchments area (Yang and Rose, 2005). Alkaline earth metals such as Sr and Ba are known to be relatively mobile in natural oxic and aqueous environments (Dupre *et al*., 1996 and Gaillardet *et al*., 1999). Sr concentration of LZR sediments ranges from 155.1 to 256.7 ppm with mean: 233.15 ppm (Table 2) and shows no definite downstream trend. This mean is lower than those in the Quaternary River Terraces, Late Miocene carbonate rich sandstones from the Injana Formation and Middle Miocene carbonate rich sandstones from the Fatha Formation in the catchments area (Table 4) (Al-Juboury, 2009). The Upper Continental Crust (UCC) normalized ratio for Sr in LZR sediments averages at 0.695 (Fig.6). It is borne out from all these comparisons, that Sr was removed from source rocks during weathering. In LZR sediments, Sr shows significant positive correlation with Ca and Mg (Table 3) suggesting that it is associated mainly with plagioclase and carbonate minerals. (Hirst, 1962) mentioned that Sr also associated with clay minerals where it is transported in to the depositional basin largely stracturally combined in the lattice of clay minerals. (Goldschmidt, 1962) explained that Sr substitute in to the clay minerals by base ionic exchange, consequently in the LZR sediments, significant positive correlation of Sr with most of trace elements underscores coexistence Sr into the clay minerals.

Ba concentration of LZR sediments ranges from 253.2 to 294.8 ppm with mean: 269.87 ppm (Table 2) shows no distinct downstream trend. The UCC normalized ratio for Ba in LZR sediments averages at 0.459 (Fig.6). It is tempting to infer from this ratio that there is overall loss of Ba during weathering of bedrocks. If source rocks in LZR basin have a wide range in Ba concentrations, the above interpretation may seem over simplified. Ba shows positive correlation with Co, Ni, Cu, Zn, Rb and Pb, which indicates that the affinity of Ba to be adsorbed conjugate with trace elements onto solid phase like clay particles.

In LZR sediments, most of trace elements (Co, Ni, Cu, Zn, Rb and Pb), except for Cr, are show positive correlations among themselves (Table 3) suggesting that a common mechanism regulates their abundance. This, coupled with the observation that these elements also show co-variations with Al_2O_3 (Table 3), leads to infer that occurrence of Al-rich phases such as clay minerals exert significant control on abundances of metals. These mineral phases were abundant in the mineralogical constituents of the recent LZR as well as older sediments (Ali, 2006 and Al-Juboury, 2009). Strong association of trace elements with Al-rich phase demonstrates the role of sediment transport and mineral sorting in influencing the distribution of metal abundances of LZR sediments. Trace element concentrations of LZR sediments likewise show significant positive correlation with Fe_2O_3, MgO and MnO (Table 3) suggest that these elements concentrations are controlled mainly by clay mineral abundances and Fe-Mg, Fe-Mn oxides. As mentioned above Cr show significant positive correlation with SiO_2 (Table 3), during alteration of chromites and metamorphism resulted in the development of ferrit-chromite and chlorite, led to diffusion of Cr from chromite margin toward the silicate matrix.

The relative higher concentrations of these trace elements in to the recent LZR sediments than those of main source rock compositions around the LZR (Table 4) suggest the effect of difference in stability of various minerals subjected to weathering and hence to differences in mobility of the chemical elements during the weathering processes. Many trace elements (e.g. Rb) may incorporate in the structure of clay minerals. Cu like Co and Ni, probably entered the basin of deposition largely structurally combined in the lattice of clay minerals. Zn probably incorporated within ferromagnesian heavy minerals (amphiboles, pyroxenes, and biotite) as well as combination in the lattice structure of montmorillonite (Goldschmidt, 1964). All these mineral phases were abundant in the mineralogical constituents of the recent LZR as well as older sediments (Ali, 2006 and Al-Juboury, 2009). Lead (Pb) adsorbed generally within iron oxide minerals in addition to its association with Rb in the lattice structure of feldspars and mica (Goldschmidt, 1964). Rb also associates with Ba within feldspars and biotite (Mason, 1966).

Among the trace elements, UCC normalized ratios for Rb, Zn and Pb are < 1 (Fig.6). This can be because of loss of these metals from bedrocks during weathering and/ or less abundance of clay (and Al) in bed sediments compared to that in UCC. For Cu and Co, UCC normalized values are indistinguishable from 1 within errors. However, normalized ratio for Ni and Cr are higher than 1 (this will be valid even after accounting for over estimation of Ni and Cr suggesting that it is supplied to sediments from non-lithogenic source(s).

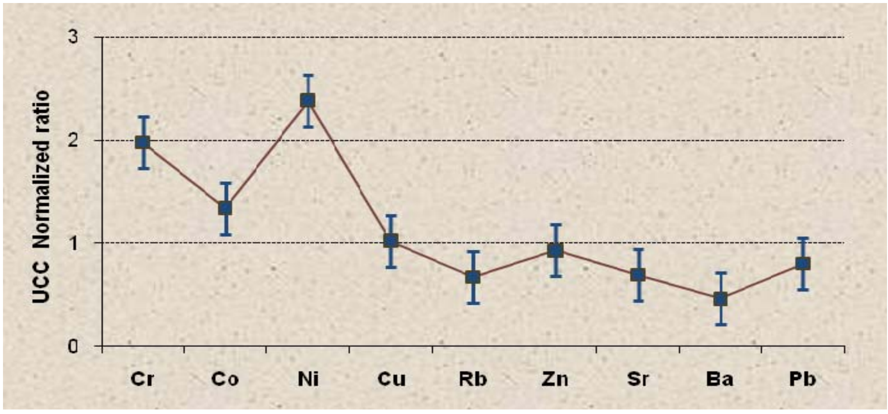

Fig.6: Upper Continental Crust (UCC) normalized ratios (concentrations of the river sediment/concentration of the UCC) for trace elements in LZR sediments

- **Evaluation of trace element pollution**

Element concentrations in river sediments is a net result of variability in source rock composition, sediment texture, redox reactions, adsorption/ desorption, sediment transport, mineral sorting and anthropogenic activity. Contributions of elements to sediments from non-lithogenic sources can be gauged by calculating their enrichment factors (EF). EF is given by:

$$EF = (X/Al)_{sample} / (X/Al)_{shale} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(5)}$$

Such estimation minimizes dilution effects caused by matrix variables such as quartz. For calculation of EF, we have used the composition of Shale (Turkian and Wedepohl, 1961). Distribution of EF for trace elements is shown in figure (7). It can be seen that Cr, Ni and Co are enriched in LZR sediments relative to Shale whereas other metals do not show clear enrichment. A value of EF ≤ 2 can be considered to be of lithogenic origin for element whereas EF > 2 is suggestive of sources such as biogenic and anthropogenic (Grousset *et al.*, 1995). Elements analyzed in this study, except Cr, have EF ≤ 2 suggesting that they are mainly of natural origin. It has already been mentioned that Cr may have been over estimated in this study by about 30%. If higher EF for Cr in LZR sediments is indeed real, it may be supplied to sediments by non-lithogenic source(s).

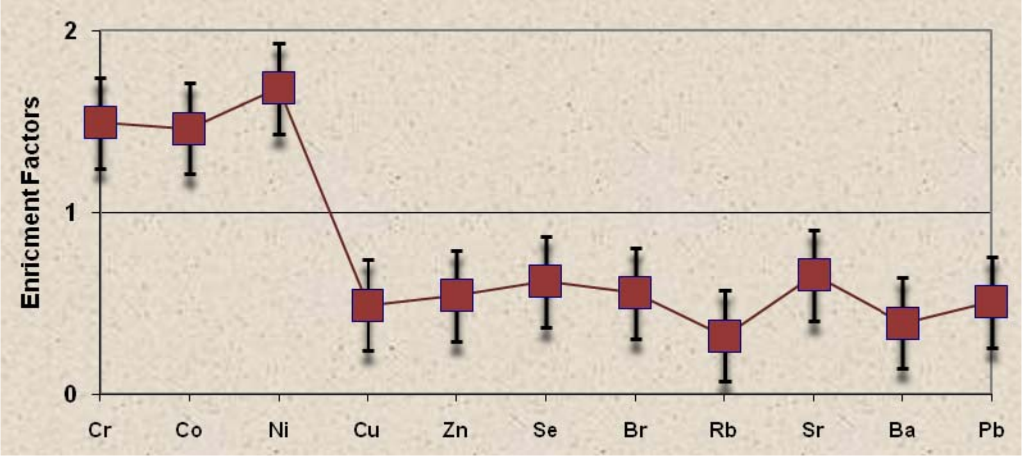

Fig.7: Scatter plot of enrichment factors for trace elements in LZR Sediments (See text for calculation of enrichment factor)

Another approach of quantitative assessment of element pollution in sediments is to determine geo-accumulation index (I_{geo}) of metals as proposed originally by Müller (1979). Igeo is expressed as:

$$I_{geo} = \log_2 [(X_n)/ 1.5(Y_n)] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(6)}$$

where X_n and Y_n are the measured and background concentrations of the element n respectively; and 1.5 is the correction factor used to account for possible variability in the background data due to lithological variation. Element concentrations of average shale (Turkian and Wedepohl, 1961) are used as the background concentrations for elements. Calculation using Eq. (6) showed that I_{geo} values for elements of LZR sediments are between 0.0 and 0.5. Such values indicate that LZR sediments are unpolluted for the elements analyzed in this study.

SUMMARY AND CONCLUSIONS

The essential aim of this study has been to characterize weathering and transportation in the Lesser Zab River basin in the northeastern Iraq and to understand relationships between major and trace element and their association in river sediments. This has been achieved through measurements of major and trace elements of recent stream sediments of the Lesser Zab River. Results obtained in this study, in conjunction with data available for source rocks of the drainage basin, have led to the following conclusions.

1. Elemental variations observed for the LZR sediments are compared to those for source rocks such as the Quaternary River Terraces, Late Miocene Injana Formation and Middle Miocene Fatha Formation from northern Iraq, suggesting that the river sediments are composite weathering products of all the lithologies in the catchments and Na, K, Ca and Mg have been removed from outcrops of these rocks during weathering. Thus, the chemical analysis of the stream sediments of the Lesser Zab River indicates that sediment features reflect the mineralogical and chemical composition of the rocks in the drainage basin. Mobiles index (I_{mob}) measures the difference between the concentrations of the mobile cations (Na_2O, K_2O and CaO) in weathered recent sediments of LZR and those in originally fresh source rocks (Injana and Fatha formations). Hence, it indicates the composition changes in rocks during weathering. The higher the index, the bigger the difference in the amount of mobile cations presence in the weathered LZR sediments and fresh rocks and hence the more intense weathering.
2. Among major elements, MgO, Fe_2O_3, MnO, TiO_2 and K_2O show positive correlation with Al_2O_3; correlation coefficient being significant for the MnO-Al_2O_3 and Fe_2O_3-Al_2O_3. CaO show weak positive correlation with Al_2O_3. These trends suggest that concentrations of MgO, Fe_2O_3, MnO, TiO_2 and K_2O of LZR sediments are significantly controlled by Ferro manganese oxides-hydroxides and clay mineral abundances. TiO_2 combined with some of the fine particles of heavy minerals like rutile and ilmenite in to the sedimentary rocks. Because of the high resistance of heavy minerals to the weathering conditions, therefore they were fixed into the sediments and caused to enrichment weathering residual with TiO_2.
3. SiO_2 show significant negative correlation with most of trace elements and has no significant positive correlation with most of the major element or with any trace element except Cr. The significant positive correlation between SiO_2 and Cr indicates to association of Chlorite with altered chromites and they support idea of genetic linkage. During alteration of chromites and metamorphism resulted in the development of ferrit-chromite and chlorite, led to diffusion of Cr from chromite margin toward the silicate matrix.

4. In LZR sediments, the Upper Continental Crust (UCC) normalized ratio for most of the major elements is < 1. This would suggest their loss from source rocks during weathering and transport. Exceptions to this trend are MgO and CaO, which have UCC normalized ratios > 1. This observation seems to support the idea that MgO and CaO are derived in addition to the carbonate rich sandstone of Injana and upper unit of Fatha Formations, but also from nearest supplied outcrops source rocks represented by Cretaceous and Tertiary age carbonate rocks formations in the catchment areas. Wide occurrence of limestone and dolomite in the basin, together with the observed co-variation of CaO and MgO and large abundance of MgO and CaO in the LZR sediments comparison with those in UCC, support the idea that the carbonates in LZR sediments are mainly of detrital origin with little contribution from calcite precipitation.
5. Chemical index of alteration (CIA), Chemical index of weathering (CIW) and Index of compositional variation (ICV) for LZR sediments averages at (46%, 50% and 2.25 respectively), indicating that weathering in the basin is of moderate intensity. Therefore, the values of CIA in the LZR sediments infer also that erosion and physical weathering regulate sediment chemistry of the Lesser Zab River and the Major element compositions of the analyzed river sediment samples are controlled mainly by clay minerals rather than the non-clay silicate phases.
6. In LZR sediments, Higher Al_2O_3 concentration than that in the universality average (average sandstones) would indicate that chemical weathering in river basin is so intense, although this might have been partly caused by mineral sorting. Influence weathering in river basins yields high clay content and Al concentration in the river particulates and sediments.
7. Lower concentrations of the UCC normalized ratio for Alkaline earth metals such as Sr and Ba in LZR sediments is < 1 suggesting that there are overall loss of Sr and Ba during weathering of source rocks and indicates to trace element concentration in sediments is mainly driven by the weathering of bedrock and catchment area.
8. In LZR sediments, most of trace elements, except for Cr, are show positive correlations among themselves, suggesting that a common mechanism regulates their abundance. This coupled with the observation that these elements also show co-variations with Al_2O_3, leads to infer that occurrence of Al-rich phases such as clay minerals exert significant control on abundances of metals. These mineral phases were abundant in the mineralogical constituents of the recent Lesser Zab River as well as older sediments. Strong association of trace elements with Al-rich phase demonstrates the role of sediment transport and mineral sorting in influencing the distribution of metal abundances of LZR sediments. Trace element concentrations of LZR sediments likewise show Significant positive correlation with Fe_2O_3, MgO and MnO suggest that these element concentrations are controlled mainly by clay mineral abundances and Fe-Mg, Fe-Mn oxides.
9. The relative higher concentrations of trace elements in to the recent LZR sediments than those of main source rock compositions (Injana and Fatha Formation) around the Lesser Zab River suggest the effect of difference in stability of various minerals subjected to weathering and hence to differences in mobility of the chemical elements during the weathering processes.
10. Among the trace elements, UCC normalized ratios for Rb, Zn and Pb are < 1. This can be because of loss of these metals from bedrocks during weathering and/or less abundance of clay (and Al) in bed sediments compared to that in UCC. For Cu and Co, UCC normalized values are indistinguishable from 1 within errors. However, normalized ratio for Ni and Cr are higher than 1 (this will be valid even after accounting for over estimation of Ni and Cr suggesting that it is supplied to sediments from non-lithogenic source(s).

11. Enrichment factor and geo-accumulation index of metals indicate that they are mainly of natural origin and LZR sediments are unpolluted for metals analyzed in this study.

ACKNOWLEDGMENTS

The author would like to thank Prof. Dr. Yusuf K. Kadioğlu for his help during laboratory analysis that was carried out at the Earth Sciences Research and Application Center of Ankara University, Turkey. Also would like to thank Mr. Mohammed Jamil of Kirkuk University for his help during sample collection. Thanks also are due to Prof. Dr. Salim Al-Dabbagh of Mosul University for the many valuable remarks about the scientific content, as well as proof reading the manuscript.

REFERENCES

Al-Chalabi, S.N.A., 2004. Mineralogy and origin of Chromate in Qalander area Northern Iraq. M.Sc. Thesis, Salahaddin University – Erbil, Iraq. 104pp.

Ali, A.R., 1996. Minerology and geochemistry of stream sediments, Adhaim river basin, Eastern Iraq. M.Sc. Thesis.

Ali, A.S., 2006. Variations in heavy minerals as indicators provenance of the recent sediments from the Lesser Zab River, North Iraq. Journal of Kirkuk University, scientific research, Vol.1, p. 37 – 50.

Al-Juboury, A.I., 2009. Natural Pollution by Some Heavy Metals in the Tigris River, Northern Iraq. Int. J. Environ. Res., 3(2), p. 189 – 198.

Cox, R., Lowe, D.R. and Cullers, R.L., 1995. The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States. Geochim. Cosmochim. Acta 59, p. 2919 – 2940.

Berry, R.W., Brophy, G.P. and Naqash, A., 1970. Mineralogy of the suspended sediments in the Tigris, Euphrates and Shatt Al-Arab Rivers of Iraq and the recent history of the Mesopotamian plain. Jour. Sed. Petrology. 40, p. 131 – 139.

Buday, T., 1980. The Regional Geology of Iraq. Stratigraphy and Palaeogeography, State Organization for Minerals, Baghdad, Iraq.

Dalai, T.K., Rengarajan, R. and Patel, P.P., 2004. Sediment geochemistry of the Yamuna River System in the Himalaya: Implications to weathering and transport. Geochemical Journal, Vol.38, p. 441 – 453.

Dinelli, E., Cortecci, G., Lucchini, F. and Zantedeschi, E., 2005. Sources of major and trace elements in the stream sediments of the Arno river catchment, northern Tuscany, Italy. Geochemical Journal, Vol.39, p. 531 – 545.

Dupre, B., Gaillardet, J., Rousseau, D. and Allegre, C.J., 1996. Major and trace element of river-born material: the Congo basin. Geochim. Cosmochim. Acta 60, p. 1301 – 1321.

Förstner, U., 1983. Assessment of metal pollution in rivers and estuaries. Applied environmental Geochemistry (Thornton, I., Ed.), p. 395 – 423, Academic Press.

Förstner, U., Ahlf, W., Calmano, W. and Kersten, M., 1991. Sediment criteria development. Sediments and Environmental Geochemistry (Heling, D., Rothe, P., Förstner, U. and Stoffers, p., eds.), p. 312 – 338, Springer-Verlag.

Gaillardet, J., Dupre, B. and Allegre, C.J., 1999. Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. Chem. Geol. 159, p. 3 – 30.

Geological Map of Iraq, 1986. Series scale 1: 1 000 000. Directorate General of Geological survey and Mineral Investigation, Baghdad, Iraq.

Goldschmidt, V.M. (1962), Geochemistry, London, Oxford univer., press, 730pp.

Goldschmidt, V.M. (1964). Geochemistry, Clarendon, Oxford.

Grousset, F.E., Quetel, Q.E., Thomas, B., Donard, O.F.X., Lambert, C.E., Guillard, F. and Monaco, A., 1995. Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Medierranean Sea. Mar. Chem. 48, p. 291 – 310.

Haweiz, A.K.R., 2003. Mineralogy and Geochemistry of recent sediments of Greater Zab River – Northeastern Iraq. M.Sc. Thesis, Salahaddin University – Erbil, Iraq.

Hirst, B.M., 1962. The geochemistry of modern sediments from the Gulf of Paria – I. Ther relationship between mineralogy and the distribution of major elements. Geochim. Cosmochim Acta, Vol.26, p. 309 – 334.

Howarth, R.J. and Thornton, I., 1983. Regional geochemical mapping and its application to environmental studies. Applied Environmental Geochemistry (Thornton, I., Ed.), p. 41 – 73, Academic Press.

Irfan, T.Y., (1996).Mineralogy, fabric properties and classification of weathered granite in Hong Kong. Quarterly Journal of Engineering Geology, Vol.29, p. 5 – 35.

Jassim, S.Z. and Goff, J.C., 2006. Geology of Iraq. 1st edition, Dolin. Prague and Moravian Museum, Brno, p. 1 – 345.

Jassim, S.Z., Hagopian, D.H. and Al-Hashimi, H.A., 1986. Geological Map of Iraq, scale 1: 1 000 000, 1nd edit. GEOSURV, Baghdad, Iraq.

Johnson, D.M., Hooper, P.R. and Conrey, R.M., 1999. XRF Analysis of Rocks and Minerals for Major and Trace Elements on a Single Low Dilution Li-tetraborate Fused Bead, International Centre for Diffraction Data, p. 843 – 867.

Levinson, A.A., 1974. Introduction to Exploration Geochemistry. Applied Publ. Co., Calgary, 612pp.

Mason, B., 1966. Principles of Geochemistry, 3rd edition, John Wiley and Sons Inc.

Mason, B. and Moore, C.B., 1982. Principles of Geochemistry, 4th ed. John Wiley and Sons, New York.

McLennan, S.C., 1995. Sediments and soils: Chemistry and abundances. Rock Physics and Phase Relations, A Handbook of Physical Constants, AGU Reference Shelf 3, 8 – 19, American Geophysical Union.

Moosavirad, S.M., Janardhana, M.R., Sethumadhav, M.S., Moghadam, M.R. and Shankara, M., 2010. Geochemistry of lower Jurassic shales of the Shemshak Formation, Kerman Province, Central Iran: Provenance, source weathering and tectonic setting. Chemie der Erde. CHEMER-25162; p. 1 – 10.

Morsy, M.A., 2000. Application of multivariate statistics to study stream sediment data from the vicinity of lead-zinc occurrences at Gabal-Rusas area, eastern desert, Egypt. Introductional Archives of Photogrammetry and Remote Sensing. Vol. XXXIII, Part B7. Amsterdam.

Müller, G., 1979. Schwermetalle in den sedimenten des Rheins-Veranderungen seit 1971. Umschau 79, p. 778 – 783.

Nesbitt, H.W. and Young, G.M., 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature 299, p. 715 – 717.

Numan, N.M.S., 2001. Cretaceous and Tertiary Alpine subductional history in Northern Iraq. Iraqi J. Earth Sci 1: p. 5 – 74.

Nyakairu, G.W. A. and Koeberl C., 2001. Mineralogical and chemical composition and distribution of rare earth elements in clay-rich sediments from central Uganda. Geochemical Journal, Vol.35, p. 13 – 28.

Okunlola, O.A. and Okoroafor, R.E., 2009. Geochemical and petrogenetic features of schistose rocks of the Okemesi fold belt, Southwestern Nigeria. RMZ – Materials and Geoenvironment, Vol.56, No.2, p. 148 – 162.

Plant, J. and Hale, M., 1994. Drainage geochemistry. Hand book of Exploration Geochemistry, Vol.6 (gowett, G.J.S., ed.), Elsevier, 792pp.

Rankama, K. and Sahama, T.G., 1950. Geochemistry, University of Chicago, Chicago. 911pp.

Rose, A.W., Hawkes, M.E. and Webb, J.S., 1979. Geochemistry in Mineral Exploration. 2nd (Eds.), Academic Press, 657pp.

Salomons, W. and Förstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag.

Stephens, W.E. and Calder, A., 2004. Analysis of non-organic elements in plant foliage using polarised X-ray fluorescence spectrometry. Anal Chim Acta 527, p. 89 – 96.

Taylor, S.R. and McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Oxford, 312pp.

Tebbens, L.A., Veldkamp, A. and Kroonenberg, S.B., 2000. Natural compositional variation of the river Meuse (Maas) suspended load: a 13 ka bulk geochemical record from the upper Kreftenheye and Betuwe Formations in northern Limburg. Netherlands J. of Geosciences 79, p. 391– 409.

Timothy, E., La, T., 1989. Analysis of Rocks using X-Ray Fluorescence Spectrometry, The Rigaku Journal, 6/1, p. 3 – 9.

Turkian, K.K. and Wedepohl, K.H., 1961. Distribution of the elements in some major units of the Earth's crust. Geol.soc.Amer.Bull., 72: p. 175 – 192.

Vinogradov, A.P., 1959. The geochemistry of rare and dispersed chemistry elements in soils, 2nd (Eds.), Consultants Bureau New York. 209pp.

Wright, P.L., 1974. The chemistry and mineralogy of clay fractions of sediments from the Southern Barents Sea. Chem. Geol., Vol.13, p .197 – 216.

Yang, H. and N., Rose, 2005. Trace element pollution records in some UK lake sediments, their history, influence factor and regional difference. Environ. Int., 31: p. 63 – 75. DOI: 10.1016/j.envint. 2004.06.010.

Zhang, C. and L., Wang, 2001. Multi-element geochemistry of sediment from the Pearl River system, China. Applied Geochem., 19: p. 1251 – 1259. DOI: 10.1016/S 0883-2927(01)00007-5.