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Geochemical Study for the Upper Shale Member - Zubair Formation in Rumaila Oilfield, South Iraq

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Abstract: *Zubair is the most important formation in Lower Cretaceous deposition cycle in Iraq. It consists mainly of inter bedded Sand stone, Shale, Siltstone and sometimes thin beds of Carbonate. This Formation has five members in Iraq; the Upper Shale is one of these members. Geochemical analysis of Upper Shale member consists mainly of SiO_2 with little have of Al_2O_3, CaO, Fe_2O_3, MgO, K_2O, TiO_2 and SO3. Also the trace element funded in Upper Shale rocks consists of (Cs, Ba, Pb, Y, Co, Zn, Cu, Zr, Nb, Ni, Ga, V, U, Sr, Cr, Mn and P). Clay minerals composition is more in north of Rumaila than the south.*

Keywords: *Geochemical; Zubair Formation; Rumaila Oilfield*

1. INTRODUCTION

Geochemical study considered as Important means to solve some mystery which accompanied sedimentation process through distribution study major element content as well secondary element distribution whereas those element reflect affecting environmental conditions in type of original sediments, sedimentation speed and digenetic process that occur on sediments after compaction , so attempt of find relation between the geochemical datum relationship with digenetic process it possible to reflect depositional conditions.

Classic sediments chemical composition is the net results of a number of geological factors, these comprise , source rocks, the rate of sediments supply, the intensity of their chemical weathering and sorting (both textural and mineralogical) through transportation and deposition. This is first geochemical study of Zubair formation- Upper shale member in Rumaila oilfield. Ten subsurface samples were collected from two wells in south and north Rumaila oilfield at depth (3145-3281) m. These samples were distribution for five samples in south Rumaila (RS) and five samples in north Rumaila oilfield(RN) covered almost Upper shale member from (USM20 to USM65).

The main aim of this study is to understand the geochemical nature of the sediment by determine the major oxides for the sediments (Al_2O_3, SiO_2, CaO, Fe_2O_3, MgO, K_2O, TiO_2 and SO3), with special focus to the chemical behaviour of the trace elements (Ba, Cs, Pb, Y , Co, Zn, Cu, Zr, Nb, Ni, Ga, V, U, Sr, Cr, Mn and P).

1.1. Study Area

The Rumaila oilfield is located of about 50 km to the northeast of North Luhais oilfield in the Basrah city, southern Iraq. The field lies approximately between (47º, 14\` 47 –º, 19\`) Latitude and (30º, 13\` – 30º, 24\`) Longitude (Figures. 1). Rumaila oilfield is located 50 km to the west of Basra covering an area of 1800 km2. The Rumaila is the biggest oilfield in Iraq that was discovered in 1953 and in 1972 started in operation; it is a 6th globally, with oil reserves of about 17 billion barrels.

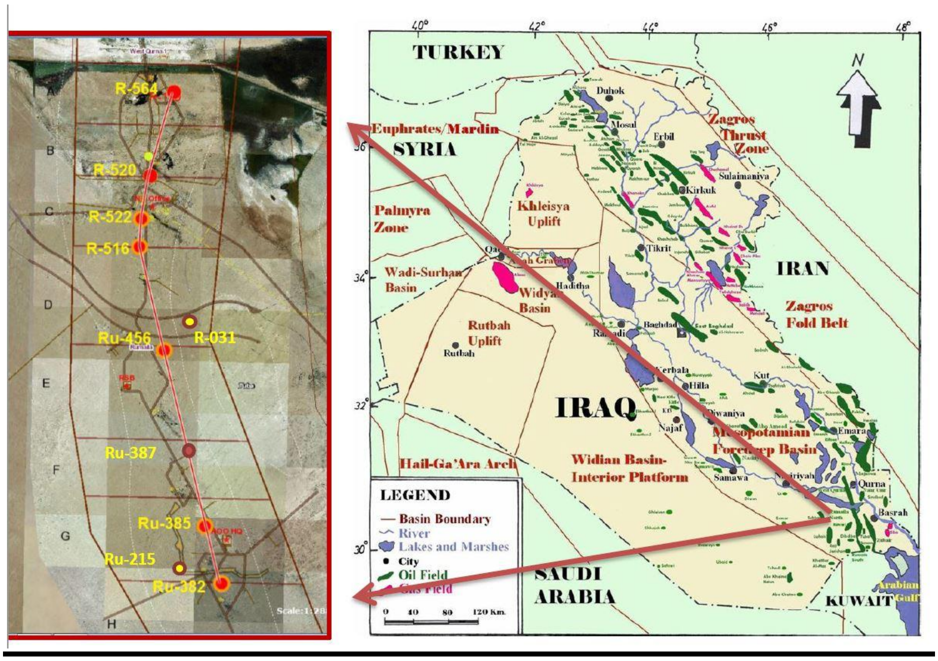

Figure1. *Location map shows the Rumaila oilfield*

2. Geochemical Of Major Oxides

2.1. Silica (SiO_2)

Silica has been characterized by the highest percentage from major oxides to all rocks Zubair formation - Upper Shale member. Most of present silica oxides in the Upper shale rocks represented by quartz minerals compared to clay minerals, and that observe in the negative correlation of silica with Al_2O_3 such as Figures (4and 5) also correlation of silica with each of Fe_2O_3 presented by Figure (6), the negative correlation of silica with Iron may be attributed to difference in geochemical behaviour between both of these elements as a result to increase of silica movement in basic solution, while increase of iron movement in acidic Solution (Salmenhaara, 2016). The mean of silica in south of Rumaila was 88.32%, while in north of Rumaila was 68.83% as showed in Tables (1, 2) and Figures (2, 3).

Table1. *Ranges and averages values of major oxides to the USMs in the study area*

Sample No		SiO2%	Al2O3%	Fe2O3%	CaO%	MgO%	K2O%	TiO2%	SO3
RS	Min.	80.36	0.559	0.2236	0.2538	0.0034	0.0024	0.228	0.6798
	Max.	96.29	6.629	1.316	0.906	0.2006	0.6315	1.355	1.518
	Mean	88.325	3.594	0.7698	0.5799	0.102	0.31695	0.7915	1.0989
	S.D	11.26421	4.292138	0.772443	0.461175	0.139441	0.444841	0.796909	0.592697
RN	Min.	59.88	7.889	1.221	0.3119	0.4372	0.8538	1.057	0.9907
	Max.	77.78	28	6.022	1.429	1.038	2.203	2.697	2.66
	Mean	68.83	17.9445	3.6215	0.87045	0.7376	1.5284	1.877	1.82535
	S.D	12.65721	14.22062	3.39482	0.789909	0.42483	0.954028	1.159655	1.180373

Table2. *Ranges values of major oxides to the USMs in the study area*

Sample No		SiO2%	Al2O3%	Fe2O3%	CaO%	MgO%	K2O%	TiO2%	SO3
RS	USM20	93.48	0.559	0.2788	0.906	0.0068	0.0024	0.6734	1.08
	USM30	80.36	6.629	0.5832	0.208	0.0034	0.1667	1.355	1.194
	USM50	96.29	1.013	0.2236	0.3267	0.0034	0.0313	0.228	0.6798
	USM60	87.76	5.42	1.316	0.2538	0.2006	0.6315	1.238	1.518
	S.D	7.035829	3.070059	0.502588	0.325277	0.098046	0.291291	0.523263	0.346044
RN	USM20	77.78	7.889	2.954	2.237	0.5095	0.1944	0.9118	2.66
	USM30	59.88	28	6.022	0.3866	1.038	2.203	2.697	1.598
	USM50	77.4	11.14	1.221	0.3119	0.4372	1.166	2.329	1.456
	USM60	67.07	12.8	5.779	1.429	0.871	0.8538	1.057	0.9907
	S.D	8.663207	8.931193	2.314457	0.918465	0.287555	0.836982	0.897194	0.705307

Table3. *Major oxides correlation coefficient in Rumaila oilfield*

	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	K_2O%	TiO_2%	So3
SiO_2%	1							
Al_2O_3%	-.934-	1						
Fe_2O_3%	-.464-	0.692	1					
CaO%	0.514	-.727-	-.482-	1				
MgO%	-.157-	0.429	0.947	-.333-	1			
K_2O%	-.387-	0.644	.994**	-.510-	.967*	1		
TiO_2%	-.925-	0.913	0.71	-.391-	0.462	0.634	1	
So3	-.618-	0.693	0.886	-.178-	0.774	0.832	0.87	1

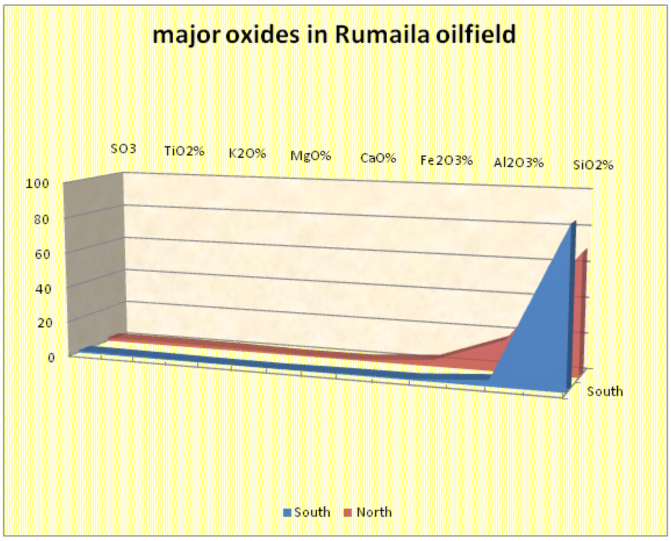

Figure2. *Major oxides in Rumaila oilfield*

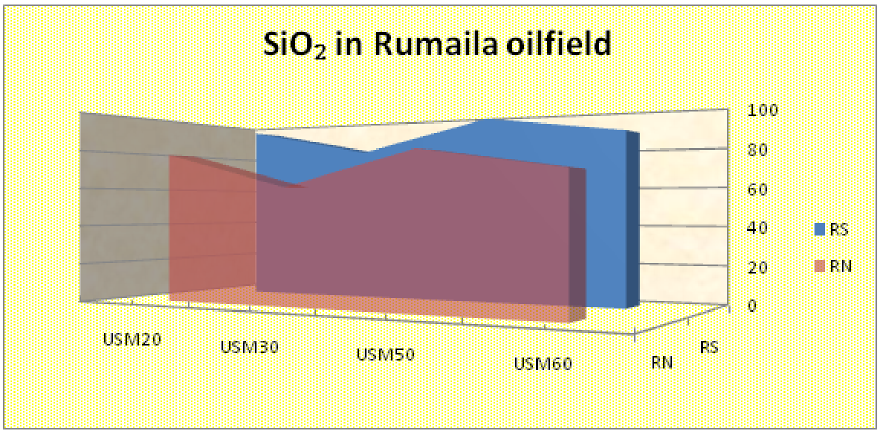

Figure3. *SiO2concentrationsin Rumaila oilfield*

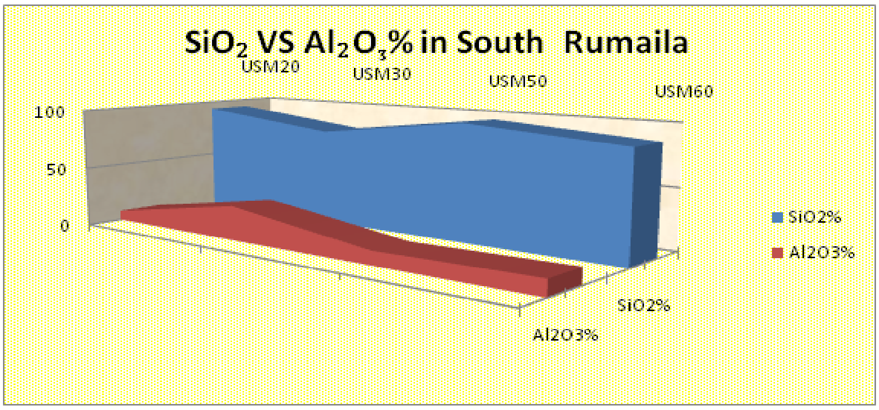

Figure4. *Correlation of silica with Al2O3 in South Rumaila*

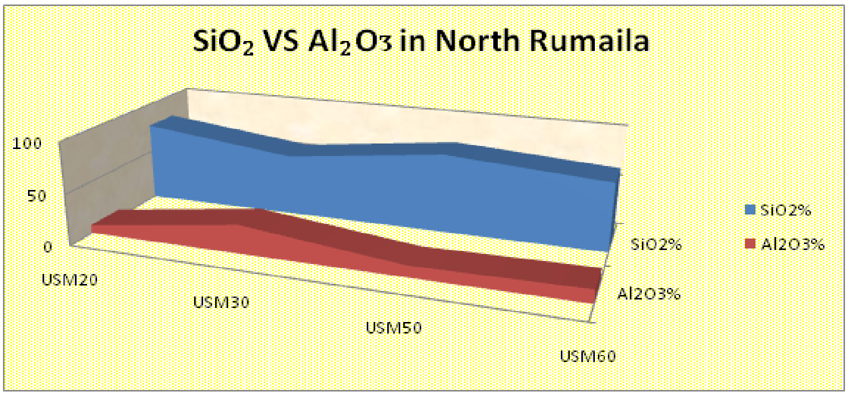

Figure5. *Correlation of silica with Al2O3 in North Rumaila*

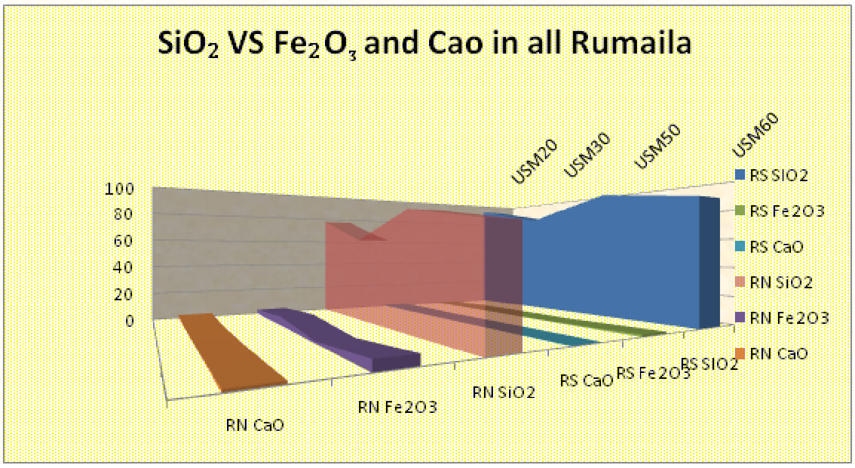

Figure6. *Correlation of silica with Fe2O3 and Cao in Rumaila oilfield*

2.2. Alumina (Al_2O_3)

The percentage of Al_2O_3 ranged in south of Rumaila between (0.559- 7.889%) with average 4.224%, while in the North between (6.629-28%) with range 17.3145%, as showed in Table (1). The reason for increase Alumina ratio in north of Rumaila due to being the main component of crystalline construction for clay minerals (Weaver and Pollard, (1974; (Jenne 1968), Aluminium ion (Al^{+3}) is a conservative element and a main component of clay minerals (Rubio *et al*., 2000) (Figure7). On the other hand, the Alumina is reduced by increasing silica in the study area as showed in Figures (4 and 5).

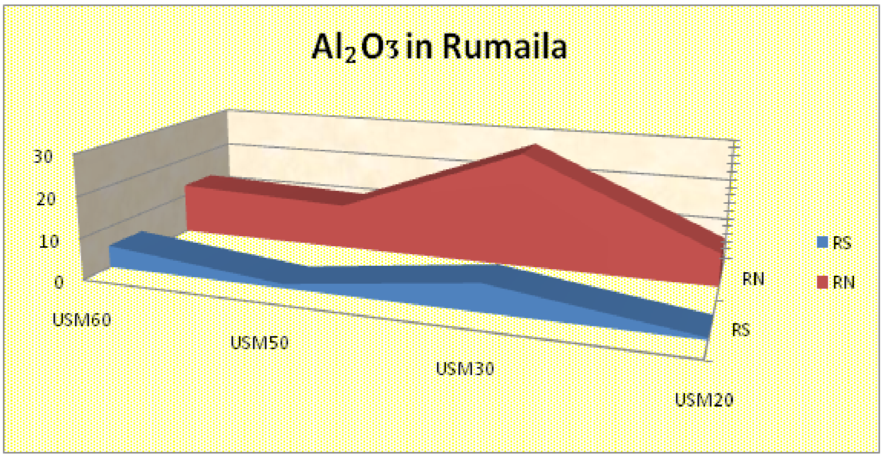

Figure7. *Al_2O_3 concentration in Rumaila oilfield*

2.3. Iron Fe_2O_3

The ratio of Iron concertation ranged in south of Rumaila between (0.2236-2.954%) with average 1.5888%, while in the North between (0.5832-6.022%) with range3.3026 %,(Table1 and Figure8).This result may back to iron adsorbed on clay minerals surface (Goldshmidt, 1970), Or combined with minerals that bearing of titanium accompanied by result of weathering represented by kaolinite (Weaver and Pollard, 1974).

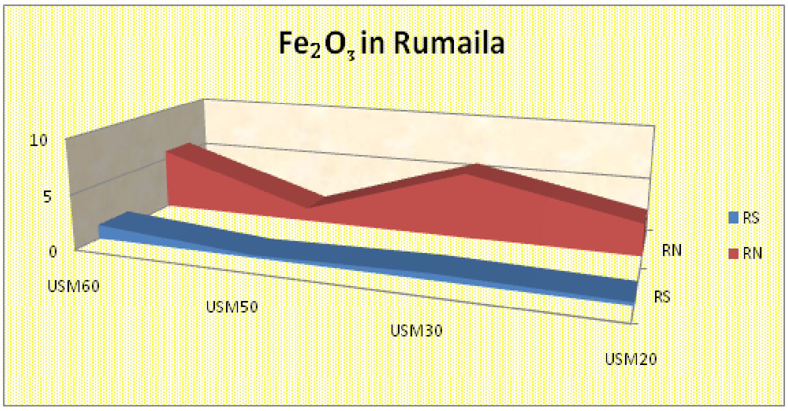

Figure8. *Fe_2O_3 concentration in Rumaila oilfield*

2.4. Titanium (TiO_2)

The percentage of Titanium ranged in south of Rumaila between (0.228-1.238%) with average 0.733%, while in the North between (1.057-2.697%) with range 1.877%as cleared in table (1) and Figure(9). The reason for increase of Titanium oxide may in the north of Rumaila attribute to replacement of (Ti^{+4}) with (Al^{+3}) in the crystalline construction of clay minerals due to similar of ionic radius, also replacement of (Fe^{+3}) and (Mg^{+2}) within octahedral for Palygorskite mineral that is found in study area for same reason (Velde, 1992).

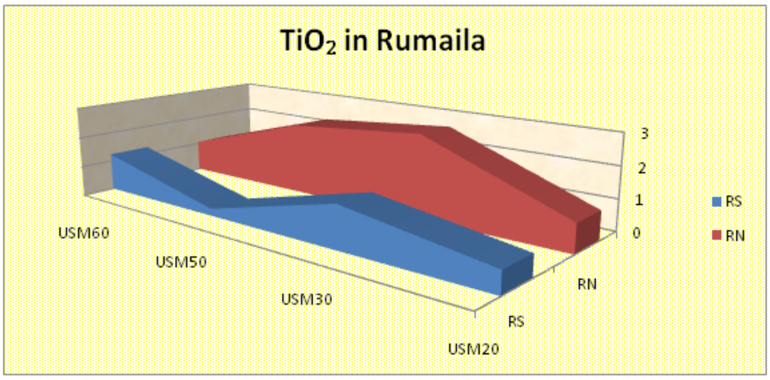

Figure9. *Ti2concentration in in Rumaila oilfield*

2.5. Calcium (CaO)

The ratio of Calcium concertation ranged in south of Rumaila between (0.2538-2.237%) with average 1.2454%, while in the North between (0.208-1.429%) with range 0.8185% (Table 1 and Figure10). CaO had positive relationship withSiO_2; the negative correlation of CaO with $Fe_2O_3$and Al_2O_3 (Table 3), this result suggests that the great content of CaO in the sediments is caused by a high concentration of calcium carbonate from biogenic shelly.

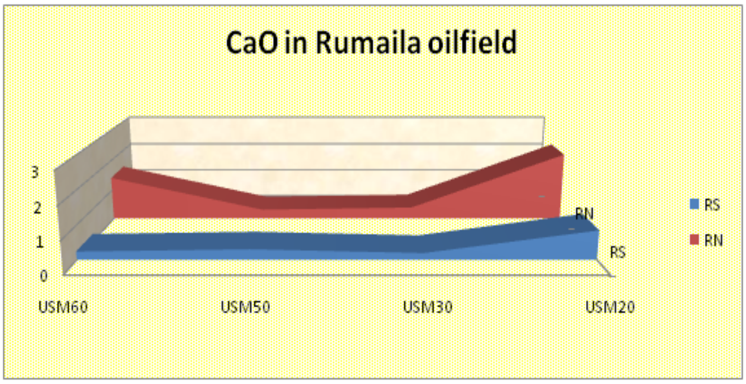

Figure10. *CaO concentration in Rumaila oilfield*

2.6. Magnesium MgO

The percentage of Magnesium ranged in south of Rumaila between (0.0034, 0.5095) % with average 0.25645 %, while in the North between (0.0034, 1.038) % with range 0.5207 %, (Table 1) and Figure (11), it has positive relations with Al_2O_3 and CaO, these relations may due to presence of magnesium ions in the clay minerals. Negative relations of MgO with each of K_2O, MnO, Sr and Cr (Table 3 and 6), may be that the Magnesium is not an important constituent of any minerals of silicate rock. However, it can substitute for Fe^{+2} orCa^{+2} in the structures of silicate (Hem 1989).Furthermore, concentrations of soil-solution forMg^{+2} increase accordingly of this displacement from exchange sites by Fe^{+2}displacement from exchange sites may also partly account for the increase in the soil-solution concentration of cationic trace elements (Ponnamperuma, 1972 in Hamon, 2006).

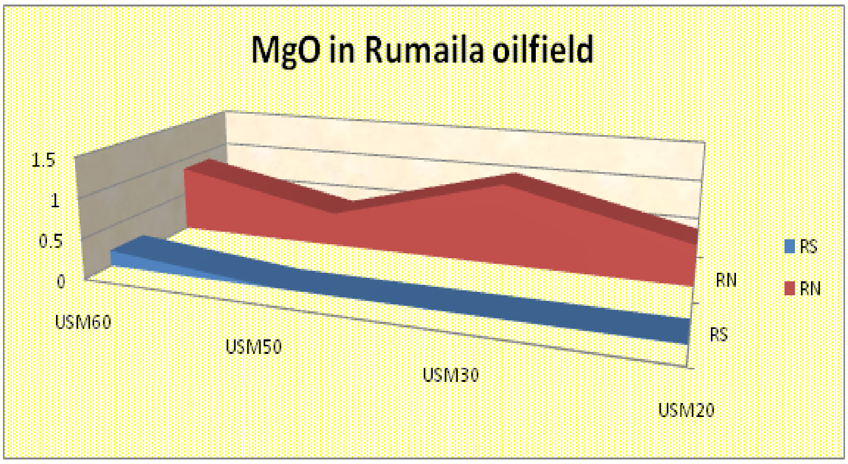

Figure11. *MgO concentration in Rumaila oilfield*

2.7. Potassium (K_2O)

The ratio of Potassium concertation ranged in south of Rumaila between (0.0034-0.5095%) with average 0.25645%, while in the North between (0.0034-1.038%) with range 0.5207%, as showed in table (1) and Figure(12).Potassium is associated with the presence of clay minerals, where it enters as one of mutual ions in Illite or may agglutinate on clay mineral Figures (Goldshmidt, 1970).

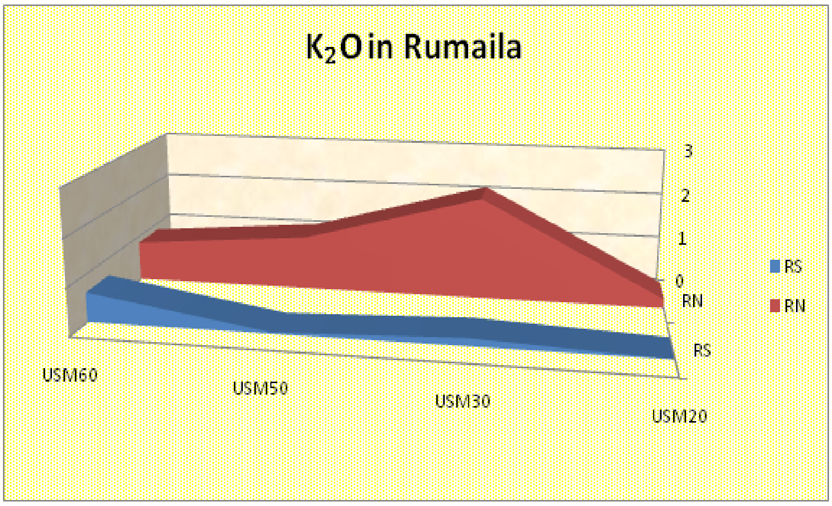

Figure12. *K_2O concentration in in Rumaila oilfield*

2.8. Sulphates (SO_3)

The percentage of Sulphates ranged in south of Rumaila between (0.6798-2.66%) with average 1.6699 %, while in the North between (0.9907-1.598%) with range 1.29435 %, as showed in (Table 1) and (Figure 13).Sulphur is found in the oil extracted, which is acidic oil containing H_2S gas(Amosa and Yaro, 2010), Sulphur is also found in combination with many metals, composed of sulphidesthe most common is: pyrite iron FeS_2 and pyrite iron and copper it is known as Chalkopirate, $CuFeS_2$, Galena PbS and sphaleriteZnS (Javadi, 2015).

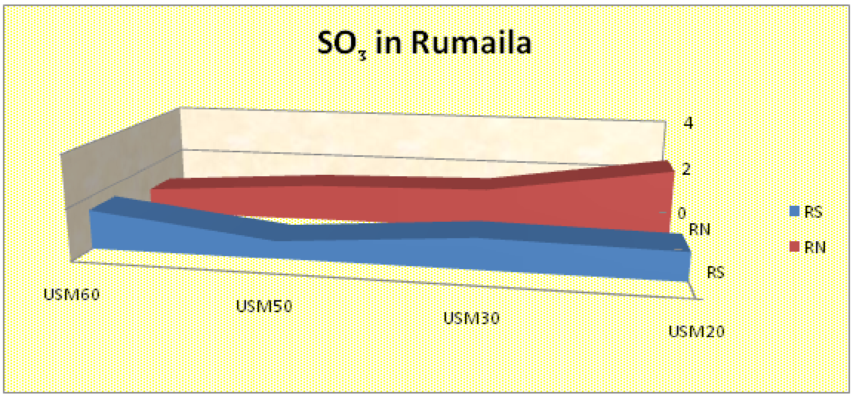

Figure13. *SO₃ concentration in Rumaila oilfield*

3. TRACE ELEMENTS

Definition by W. M. White (1982) of trace elements, constitute only a minor fraction of the system of concern, trace elements are that elements that are not stoichiometric constituents of phases in the system of interest, they provide geological and geochemical information out of proportion to their abundance. There are numerous causes for this. First, variations in the concentrations of many trace elements are much higher than variations in the concentrations of major components, usually by many orders of magnitude. Second, in any system there are by far more trace elements compared to major elements, in most geochemical systems, around10 or fewer major components those together accounts for 99% or more of the system. This leaves 80 trace elements, the sedimentary environment of trace elements may occur as:

- adsorbed on solids
- precipitated and co-precipitated on solids
- Incorporated on solid biologic materials and incorporated in crystal structures (Forstner and Wittman, 1983 in Liaghati, 2004).

Trace elements occurrence in rock forming minerals is based on the type of crystallographic structure. The behaviour of trace elements is complex during sedimentary processes by several factors such as weathering, sorting, adsorption, origin, processes and transformation processes.

4. GEOCHEMICAL OF TRACE ELEMENTS

4.1. Zinc (Zn)

Zinc element is present in the sphalerite and Galina minerals (Fairbrige, 1972). Also abundance in the ultra-mafic rocks and in the sedimentary rocks. The average concentrations of Zn in the Upper shale rocksof south Rumaila are 21.2-181.4 ppm with range of101.3 ppm while it averaged between 26.28-161.9 ppm with range of94.1 ppm in the north as showed in (Tables 4 and5) and Figure(14), it has positive relations with each of Al_2O_3 and Fe_2O_3 (Table 6), these relations may be attribute to zinc adsorbed on the surface of clay, iron minerals, and this may be interpret the positive relation of zinc with each of V, Cu, Ga, Nb, Ni, Rb, , Th, and Y.

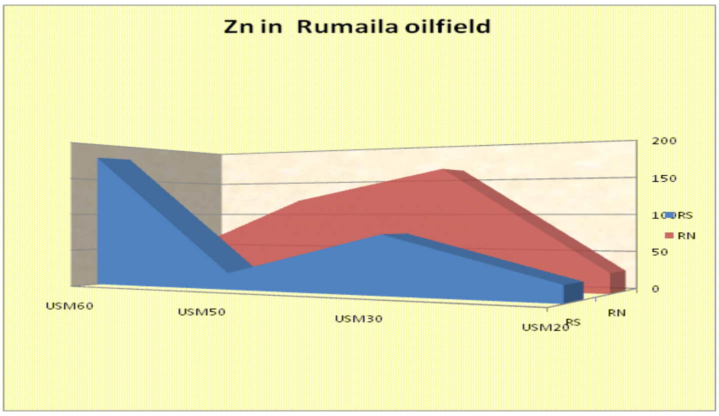

Figure14. *Zn concentration in Rumaila oilfield*

Table4. *Ttrace element concentration in the sediment of study area*

	Sample No	Cl	V	Co	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr	Nb	Ba	Hf	Ta	W	Pb	Th	Cr	Mn	P
RS	USM20	1743	0.481395	3.0085714	11.2	12.854054	21.236842	5.3	0.44	3.7	0.8121951	37.83478	9.1	533.5	1.9827869	484.4	8.2	27.904839	3.0204082	51.66	3.3	1	24.84848	1651.5
	USM30	510	3.476744	11.957143	15.47778	9.2486486	75.631579	7.2	0.66	7.9	2.3914634	44.85652	25.6	1029.2857	12.938525	120.4	22	35.440323	403.67755	20.773333	9.7	7.3	16.59091	211.7143
	USM50	303.3	4.011628	63.334286	13.37778	6.6621622	22.105263	0.5	0.953333	2	1.3085366	23.37826	5.1	179.5	17.441803	114.1	4.3	38.658602	1101.6939	2.9155556	1.6	0.5	5.681818	290.1429
	USM60	5408	18.72093	26.768571	13.53333	13.559459	181.42105	8.6	1.1	3.2	5.9109756	36.67826	42.9	3124.2857	17.37459	48.3	43.8	34.223656	629.52857	8.2	14.7	24.9	33.40909	171.2143
	S.D	2364.9584	8.181026	26.582963	1.748847	3.2233753	75.308545	3.5355339	0.295616	2.5677487	2.3000027	8.966247	17.27008	1318.6551	7.2794213	197.77282	17.846078	4.5079628	458.37553	21.839744	6.0279211	11.410923	11.83038	715.2772
RN	USM20	857.1	10.96512	25.842857	21.15556	8.8567568	26.289474	6.4	1.173333	5.8	3.0231707	47.99565	22	738.57143	9.8467213	87.3	16.5	35.518817	428.67143	18.313333	6	11.1	463.5606	244.9286
	USM30	1325	97.61628	25.92	59.65556	42.245946	161.92105	45.3	6.16	7.9	28.246341	210.2391	51	444.57143	18.517213	191.3	1	32.732258	23.483673	44.006667	27.2	55.733333	131.2121	428.3571
	USM50	2745	62.31395	25.071429	19.52222	14.735135	120	16	2.823333	42	11.1	113.587	48.6	1232.1429	15.089344	123.5	16.2	31.083871	258.2449	12.664444	13.7	30.433333	29.31818	387.2143
	USM60	24230	69.80233	20.442857	28.46667	9.4837838	35.763158	9.9	5.133333	28.9	8.2573171	72.69565	38.2	910.71429	9.1409836	87.1	20.2	35.204839	220.94286	10.477778	8.3	34.566667	434.9242	1196.357
	S.D	11322.309	36.15118	2.6125322	18.71231	15.831317	65.851078	17.716471	2.250823	17.377859	10.918176	71.39515	13.19331	329.21069	4.4554045	49.079799	8.5132739	2.1084246	166.2999	15.450879	9.4984209	18.3071	217.3672	428.6934

Table5. *Ranges values of trace element on the sediments of study area*

	Sample No	Cl	V	Co	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr	Nb	Ba	Hf	Ta	W	Pb	Th	Cr	Mn	P
RS	Min.	303.3	0.481395	3.0085714	11.2	6.6621622	21.236842	0.5	0.44	2	0.8121951	23.37826	5.1	179.5	1.9827869	48.3	4.3	27.904839	3.0204082	2.9155556	1.6	0.5	5.681818	171.2143
	Max.	5408	18.72093	63.334286	15.47778	13.559459	181.42105	8.6	1.1	7.9	5.9109756	44.85652	42.9	3124.2857	17.441803	484.4	43.8	38.658602	1101.6939	51.66	14.7	24.9	33.40909	1651.5
	Mean	2855.65	9.601163	33.171429	13.33889	10.110811	101.32895	4.55	0.77	4.95	3.3615854	34.11739	24	1651.8929	9.7122951	266.35	24.05	33.28172	552.35714	27.287778	8.15	12.7	19.54545	911.3571
	S.D	3609.568	12.8973	42.656722	3.004846	4.8771257	113.26734	5.7275649	0.46669	4.17193	3.6053823	15.18742	26.72864	2082.2779	10.931175	308.36927	27.930718	7.6040591	776.87946	34.467527	9.2630988	17.253405	19.60614	1046.72
RN	Min.	857.1	10.96512	20.442857	19.52222	8.8567568	26.289474	6.4	1.173333	42	3.0231707	47.99565	22	444.57143	9.1409836	87.1	1	31.083871	23.483673	10.477778	6	11.1	29.31818	244.9286
	Max.	24230	97.61628	25.92	59.65556	42.245946	161.92105	45.3	6.16	28.9	28.246341	210.2391	51	1232.1429	18.517213	191.3	20.2	35.518817	428.67143	44.006667	27.2	55.733333	463.5606	1196.357
	Mean	12543.55	54.2907	23.181429	39.58889	25.551351	94.105263	25.85	3.666667	35.45	15.634756	129.1174	36.5	838.35714	13.829098	139.2	10.6	33.301344	226.07755	27.242222	16.6	33.416667	246.4394	720.6429
	S.D	16527.136	61.27162	3.8729249	28.37855	23.609722	95.906009	27.506454	3.526106	9.2630988	17.835475	114.7235	20.5061	556.8971	6.6299955	73.680527	13.57645	3.1359806	286.51101	23.708505	14.990664	31.560533	307.0558	672.7616

Table6. *Trace elemnts correlation coefficient in Rumaila oilfield*

	SiO2%	Al2O3 %	Cl	V	Co	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr	Nb	Ba	Hf	Ta	WO	Pb	Th	Cr	Mn	P
SiO2%	1																								
Al2O3 %	-.934-	1																							
Cl	-.097-	0.315	1																						
V	-.200-	0.504	0.895	1																					
Co	0.515	-.276-	-.180-	0.149	1																				
Ni	-.762-	0.825	-.164-	0.201	0.148	1																			
Cu	-.155-	0.155	0.796	0.461	-.691-	-.431-	1																		
Zn	-.481-	0.715	0.871	0.949	-.111-	0.342	0.551	1																	
Ga	-.746-	0.745	0.66	0.535	-.722-	0.242	0.764	0.759	1																
As	-.949-	0.832	0.507	0.811	0.688	0.347	-.119-	0.645	-.002-	1															
Br	-.904-	0.702	-.278-	-.237-	-.602-	0.646	-.017-	0.068	0.525	-.428-	1														
Rb	-.407-	0.669	0.873	.975*	-.009-	0.329	0.501	.994**	0.686	0.72	-.020-	1													
Sr	-.848-	0.665	0.158	0.01	-.891-	0.313	0.506	0.319	0.839	-.459-	0.853	0.217	1												
Y	-.646-	0.823	0.798	0.861	-.267-	0.431	0.565	.978*	0.86	0.506	0.271	.951*	0.504	1											
Zr	0.693	-.690-	0.932	0.945	-.180-	0.201	0.662	.988*	0.781	0.586	0.002	.980*	0.323	.959*	1										
Nb	-.135-	0.438	0.199	0.612	0.73	0.644	-.417-	0.5	-.088-	0.92	-.158-	0.567	-.381-	0.412	0.392	1									
Ba	0.369	-.640-	-.232-	-.640-	-.554-	-.780-	0.333	-.603-	-.113-	-.857-	-.063-	-.647-	0.148	-.558-	-.485-	-.971-*	1								
Hf	0.679	-.916-	0.851	0.902	-.228-	0.359	0.596	.992**	0.834	0.548	0.175	.973*	0.437	.995**	.983*	0.419	-.547-	1							
Ta	-.065-	0.272	-.241-	0.212	0.818	0.69	-.765-	0.104	-.395-	0.695	-.060-	0.171	-.470-	0.043	-.029-	0.903	-.853-	0.029	1						
W	0.286	-.018-	-.094-	0.297	.966*	0.373	-.671-	0.083	-.547-	0.8	-.442-	0.177	-.748-	-.051-	-.011-	0.879	-.750-	-.026-	0.922	1					
Pb	-.711-	0.902	-.132-	-.551-	-.796-	-.604-	0.486	-.416-	0.191	-.910-	0.216	-.490-	0.466	-.317-	-.307-	-0.995	0.944	-.328-	-.929-	-.924-	1				
Th	-.703-	0.859	0.756	0.821	-.310-	0.471	0.55	.959*	0.881	0.459	0.345	0.926	0.561	.997**	0.936	0.388	-.548-	.984*	0.036	-.087-	-.291-	1			
Cr	-.422-	0.663	0.904	.961*	-.106-	0.273	0.587	.997**	0.746	0.648	0.006	.994**	0.285	.964*	.995**	0.477	-.567-	.985*	0.067	0.074	-.395-	0.941	1		
Mn	-.281-	0.335	0.88	0.622	-.623-	-.252-	.976*	0.719	0.848	0.054	0.034	0.673	0.53	0.731	0.807	-.224-	0.121	0.758	-.614-	-.552-	0.305	0.716	0.746	1	
P	0.422	-.663-	-.124-	-.547-	-.536-	-.845-	0.411	-.532-	-.087-	-.790-	-.155-	-.571-	0.108	-.507-	-.404-	-.951-*	.992**	-.485-	-.879-	-.737-	0.926	-.506-	-.489-	0.202	1

4.2. Copper (Cu)

Copper is most common elements in the sediments and rocks, it has high mobility in the acidic conditions (Hawkes and Web, 1962). Depending on the organic matter, clay concentration, source rocks and pH value (Aubert and Pinta, 1977). The average concentrations of Cu in the Upper shale rocks of south Rumaila are 6.66-13.55 ppm with range of 10.11 ppm while it averaged between8.85-42.2 ppm with range of25.5 ppm in the north as presented in tables (4 and5) and Figure(15), Cu in North Rumaila is more than the south because of the Cu element had positive relations with Al_2O_3(Table 6), this relation may be attribute to copper adsorbed on the surface of clay minerals.

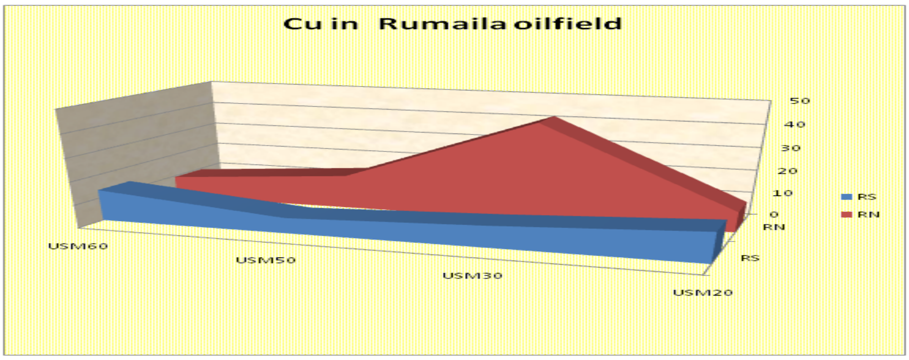

Figure15. *Cu concentration in Rumaila oilfield*

4.3. Cobalt (Co)

Cobalt is present in the most of ultra basic mafic rocks, and less in the acidic and sedimentary rocks (Aubert and Pinta, 1977).The average concentrations of Co in the Upper shale rocks of south Rumaila are3.0-63.3 ppm with ranged of 33.17 ppm while it averaged between20.4-25.9 ppm with range of23.18 ppm in the north as shown in (Tables3and 4) and Figure (16). The high concentration of Coelement in south of Rumaila may be due to attributed to adsorbed on Quarts minerals due to it has positive relationship with SiO_2 (Table 6). In addition Co has present in north of Rumaila but in little ratio. The cobalt is flowed Iron especially in Kaolinite due to convergence of the ionic radius (Krauskopf,)1967

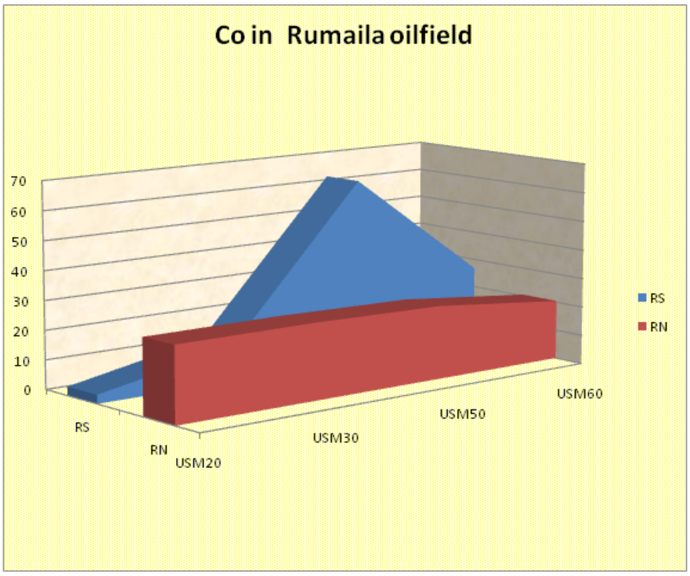

Figure16. *Co concentration in Rumaila oilfield*

4.4. Nickel (Ni)

Nickel is present in the ultra-mafic igneous rocks such as dionite and peridotite (Venugopal and Luckey, 1978). Nickel has wide changes in the sediments, and their concentrations depend on the abundance of clay minerals and organic matter (Aubert and Pinta, 1977).The average concentrations of Ni in the Upper shale rocks of south Rumaila are 11.2-15.5 ppm with ranged of13.3 ppm while it averaged between19.5-59.65 ppm with range of 39.59 ppm in the north as showed in tables (3and 4) and Figure(17). Nickel abundance increase in north of Rumaila may due to adsorbs on clay minerals due to it has positive relationship with Al_2O_3 (Table 6).

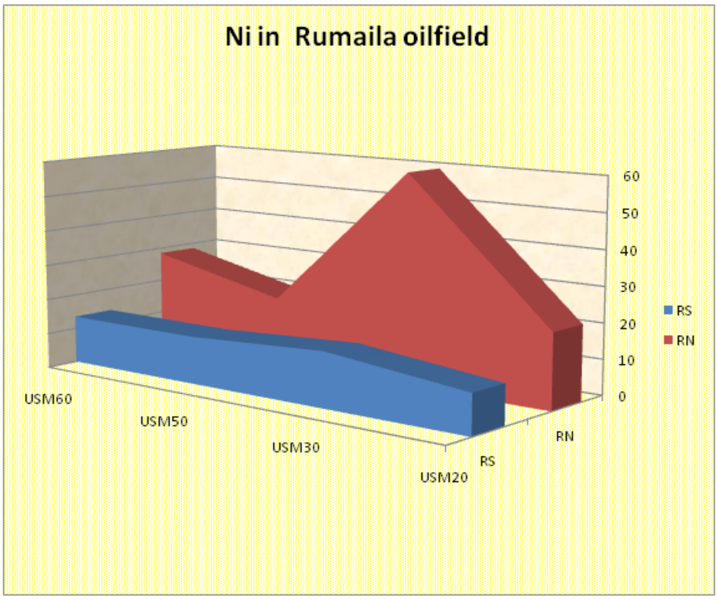

Figure17. *Ni concentration in Rumaila oilfield*

4.5. Chromium (Cr)

Chrome of the remaining elements of non-transitional during weathering process and through processes of transformation (Hassan, 2012; Rose et al., 1979) The average concentrations of Chromium in the Upper shale rocks of south Rumaila are0.5-24.9 ppm with range of12.7 ppm while it averaged between 11.1-55.7 ppm with range of 33.4 ppm in the north (Tables1and2) and Figure (18).It had positive relation with each of Sr, and Al_2O_3 (Table 6). This may be a main reason to increase this element in north compared to south, and that may be attributed to present of these element in Clay minerals especially Illite.

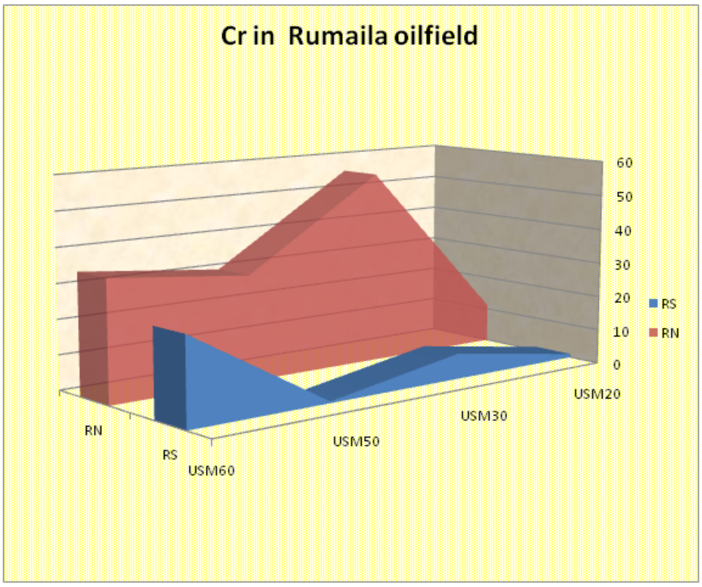

Figure18. *Cr concentration in Rumaila oilfield*

4.6. Phosphor (P)

The average concentrations of Pin the Upper shale rocks of south Rumaila are 171.21-1651.5ppm with range of 911.357 ppm while it averaged between 244.928-1196.357ppm with range of720.642 ppm in the north(Tables1and2) and Figure(19).The positive relation with SiO_2 (Table 6), may be due to adsorbed of phosphor on the surface of the Quartz mineral.

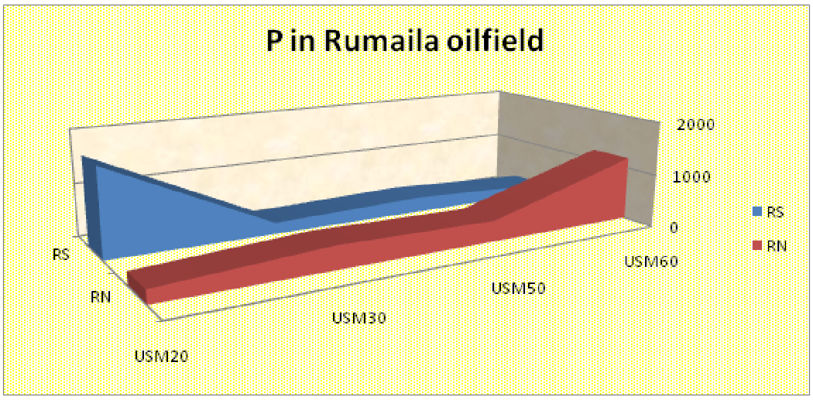

Figure19. *P concentration in Rumaila oilfield*

4.7. Strontium (Sr)

The wide variation of Strontium concentration is characteristic of its movement during transformation (Hassan, 2012). Being of medium transitional elements that are washed during chemical weathering processes(Short,1961).High concentration for Sr is associated with the presence of sulphate, which indicates the presence of Salastite metal and enhances the microscopy mineral study done by Somani(2011) which mentioned to existence of this metal clearly, that is explains strong positive relationship correlation with the sulphate. It may be adsorbed on the surfaces of clay minerals or inside its composition, especially in montmorilonite (Hirrst, 1962). The only strong positive relationship correlation with trace elements is represented of barium element (Table 6), in addition the

Sr has indicator for digenetic process (Roddaz *et al*., 2006). The average concentrations of Sr in the Upper shale rocks of south Rumaila are 23.37-44.85ppmwith range of34.117 ppm while it average between 47.995-210.239ppm with range of129.117 ppm in the north as showed in Tables (3and 4) and Figure (20). The negative relation with SiO_2 and positive relations with Al_2O_3 (Table 6), may be due to presence of this element with clay and lack in quartz minerals.

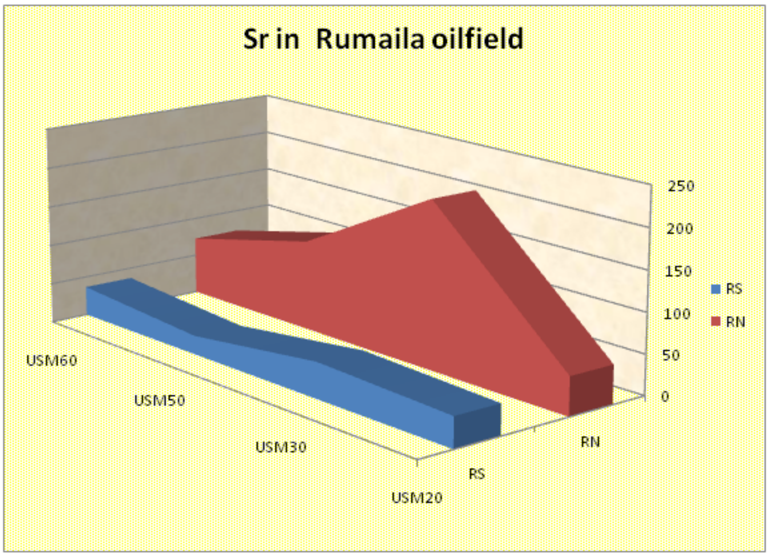

Figure20. *Sr concentration in Rumaila oilfield*

4.8. Lead (Pb)

The average concentrations of Pb in the Upper shale rocks of south Rumaila are 2.915-51.66ppmwith ranged of27.287 ppm and 10.4-44 ppm with range of27.24ppm in the north as showed in Tables (3and 4) and Figure (21), it positive relation with Al_2O_3 (Table 6), this relation may be interpret to lead adsorbed on the surface of clay and iron minerals, and the negative relations with SiO_2 (Table 6), as indicator to lack present of lead on quartz. The reason of adsorbed Pb on clay minerals surface that is replacement Pb^{+2} with K^{+1} by Capturing process due to have similar of ionic radius and convergent in charge.

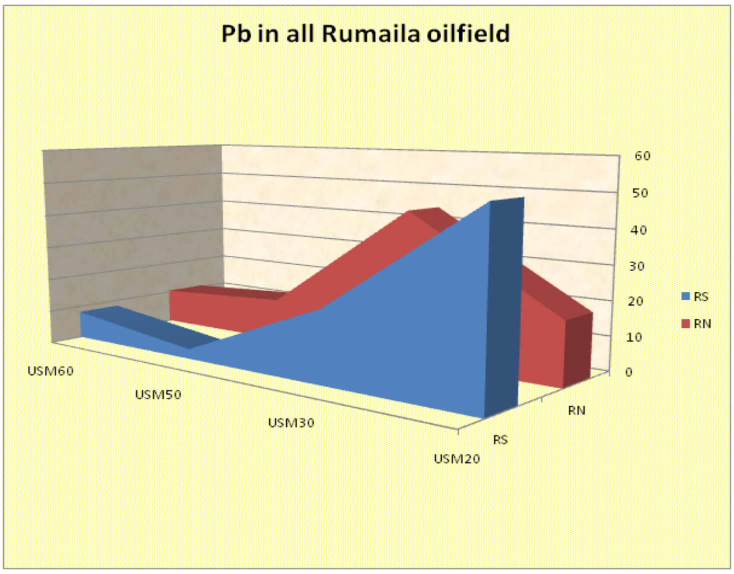

Figure21. *Pb concentration in Rumaila oilfield*

4.9. Vanadium (V)

Vanadium is a crucial element for numerous marine phytoplankton species (Moore *et al*., 1996), macro algae (Nalewajko *et al*., 1995), and further organisms (Taylor et al., 1997).Steven et al (1991) showed that vanadium could enter in the clay minerals as well as in the iron and calcite minerals, which reflect by positive relation with Al_2O_3 as indicator to Clay minerals and negative relations with

SiO_2 (Table 6), may be reflecting the lack present of vanadium in the Quartz minerals. In addition could be replacement Fe^{+3} with V^{+3}due to thy have similar of ionic radius and convergent in charge.The average concentrations of V in the Upper shale rocks of south Rumaila are0.48-18.72ppmwith range of9.60ppm while in the north Rumaila the average between10.96-97.61ppmwith range of54.29 ppm (Tables 3and 4) and Figure (22), This reflected high V element in north Rumaila comparison with south Rumaila.

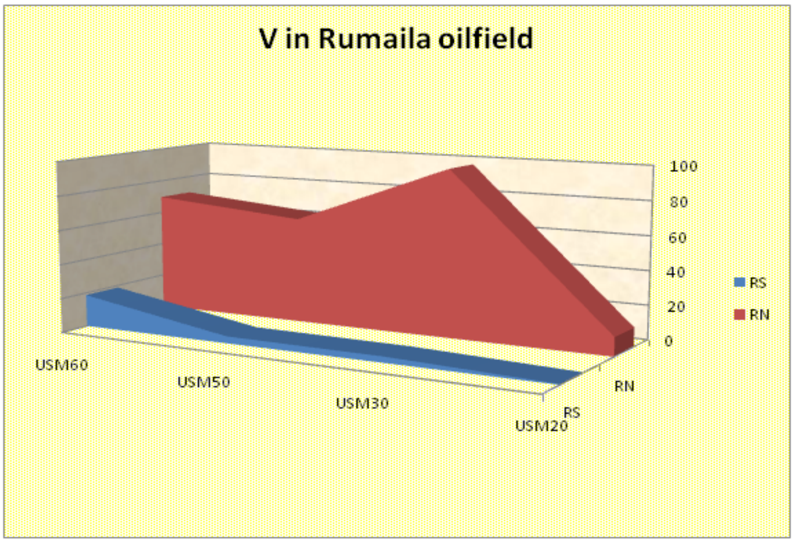

Figure22. *V concentration in Rumaila Field*

4.10. Zirconium (Zr)

Zirconium is a heavy and low mobility element and that cause to abundance in the detrital sediments (Freidman and Sanders, 1978), Zirconium is a non-transitional element that is resistant to chemical and physical weathering (Rose *et al*., 1979). .The average concentrations of Zr in the Upper shale rocks in south of Rumaila are 179.5-3124.28 ppm with range of 1651.89ppm while in the north Rumaila the average between 444.57-1232.14ppmwith range of 838.35 ppm as showed in Tables (3and 4) and Figure (23).It has positive relations with SiO_2 as a result to Zr adsorbed on the surface of Quartz minerals, which interpreted the higher concentration of Zr element in south of Rumaila comparison to north of Rumaila.

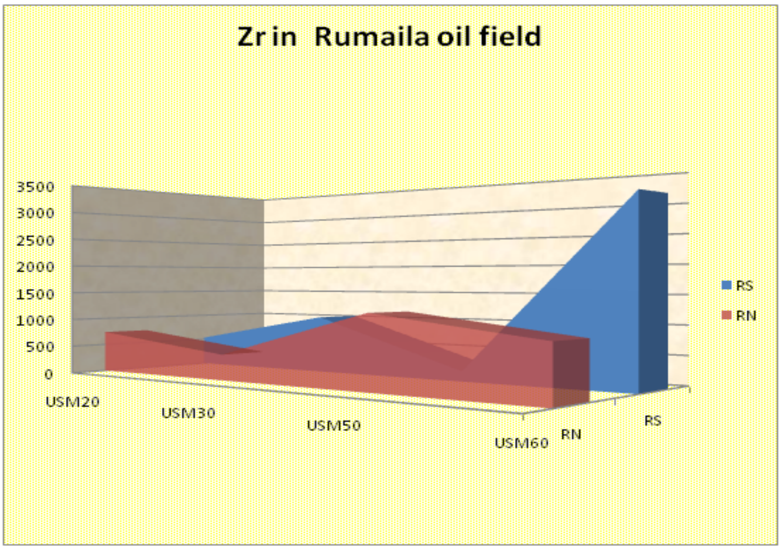

Figure23. *Zr concentration in Rumaila Field*

4.11. Rubidium (Rb)

The range concentrations of Rb in the Upper shale rocks of south rumaila are 0.81-5.91 ppm with rang of3.36 ppm while in the north Rumaila the average3-28.2 ppm with rang of 15.6 ppm (Tables 3and 4) and Figure (24). It positive relation with Al_2O_3 (Table 6), this relation may be attribute to the possibility of adsorption for Rubidium on the clay mineral surface especially in Illite due to replacement Rb^{+1} with K^{+1} by (Admission) process due to large of ionic radiusas cleared by Goldshmidt (1970) and this may concluded to increase of Rb elements in the north of Rumaila comparison with south of Rumaila.

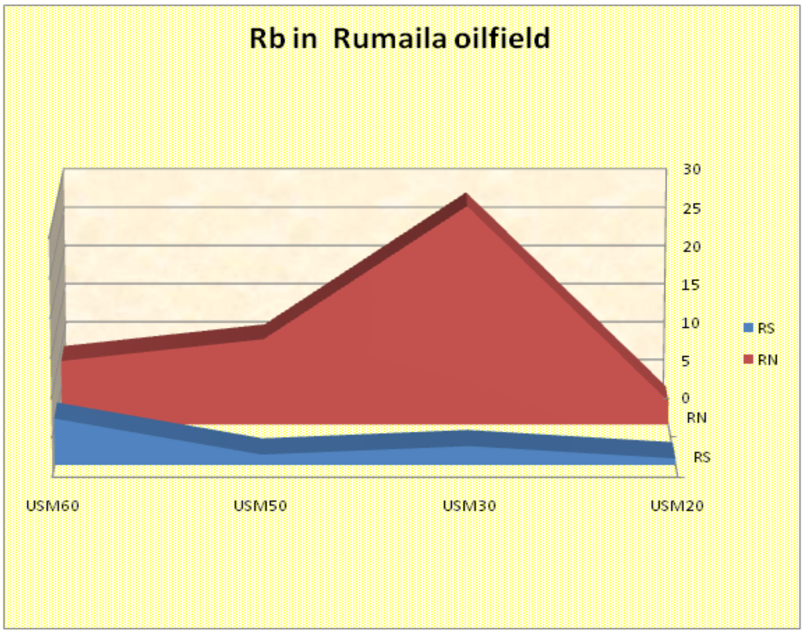

Figure24. *Rb concentration in Rumaila Field*

4.12. Niobium (Nb)

The range concentrations of Nb in the Upper shale rocks in south Rumaila are 1.98-17.44ppmwith range of 9.71ppmwhile in the north Rumaila the average 9.14-18.51 ppm with rang of13.82 ppm (Tables 3and 4) and Figure(25),it has positive relations with Al_2O_3 (Table 6), this relation may be due to adsorption of Nb on the surface of clay andiron minerals. The negative relations with SiO_2 (Table 6), may due to lack presence of Nb in the quartz.

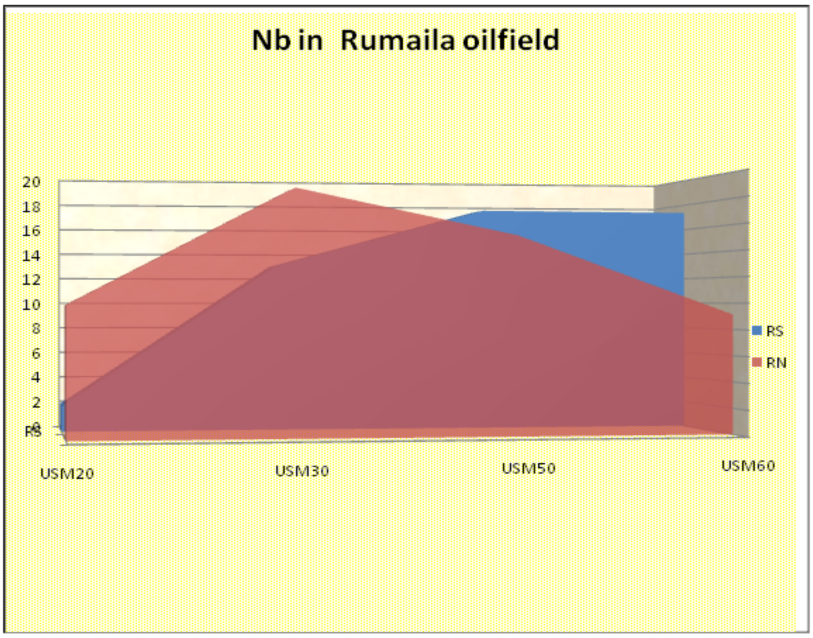

Figure25. *Nb concentration in Rumaila Field*

4.13. Hafnium (Hf)

The range concentrations of Hf in the Upper shale rocks of south Rumaila are 4.3-43.8ppmwith range of24.05ppmwhile in the north Rumaila the average1-20.2 ppm with range of10.6 ppm (Table 3and 4) and Figure(26), it has positive relations with SiO_2 (Table 6)a result to adsorption on the surface of quartz mineral. The negative relation with Al_2O_3 may reflect the lack presence of Hf in the clay minerals.

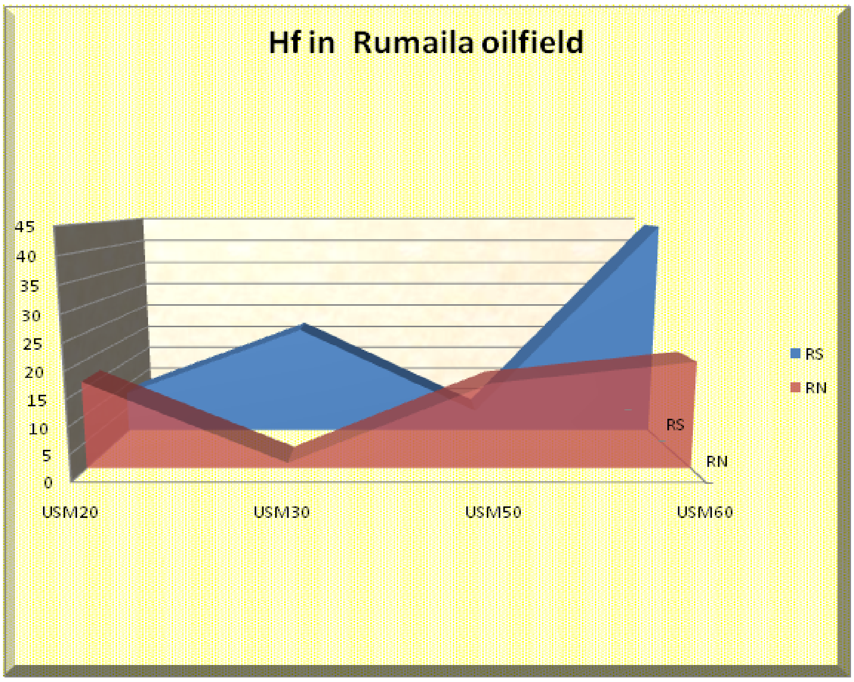

Figure26. *Hf concentration in Rumaila Field*

4.14. Gallium (Ga)

Gallium is a transitional element, the range concentrations of Ga in the Upper shale rocks of south Rumaila are 0.5-8.6 ppm with ranged 4.55ppmwhile in the north Rumaila the average was6.4-45.3 ppm with range of 25.85 ppm (Tables3and 4) and Figure(27), it has positive relations with Al_2O_3, this relation is attribute to the presence of gallium in the Clay minerals. The negative correlations with SiO_2 may be due to the lack of this element presence in the Quartz minerals.

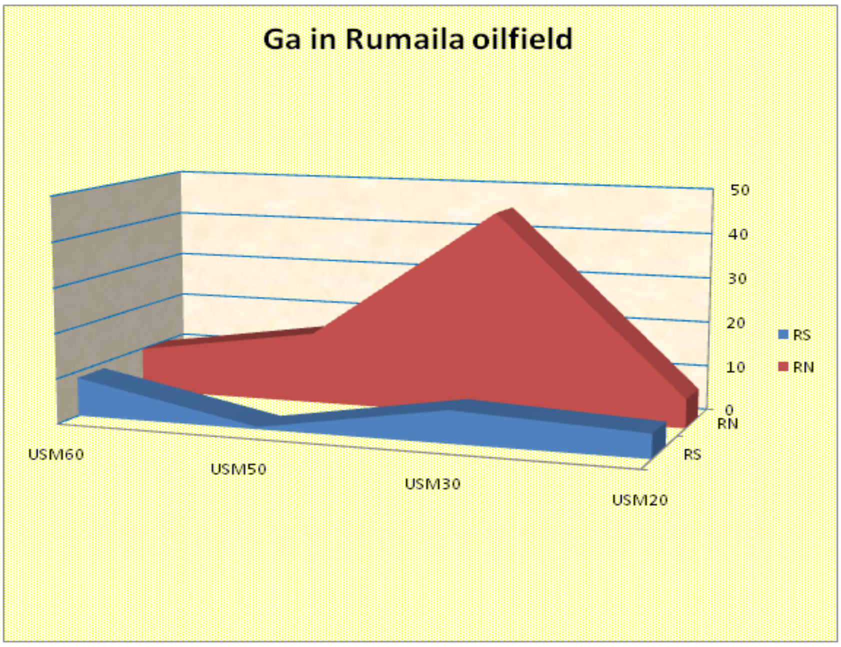

Figure27. *Ga concentration in Rumaila Field*

4.15. Thorium (Th)

Thorium adsorbs on Clay minerals surface and Iron oxide (Ullah, 2009). The range concentrations of Th in the Upper shale rocks of south Rumaila are1.6-14.7 ppm with ranged8.15 ppm while in the north Rumaila the average was 6-27.2 ppm with range of16.6 ppm as shown in tables(3and4) and

Figure(28). It has positive relations with Al_2O_3 (Table 5-6); this relation is due to present of Th with most of trace elements on the surface of clay and Iron minerals.

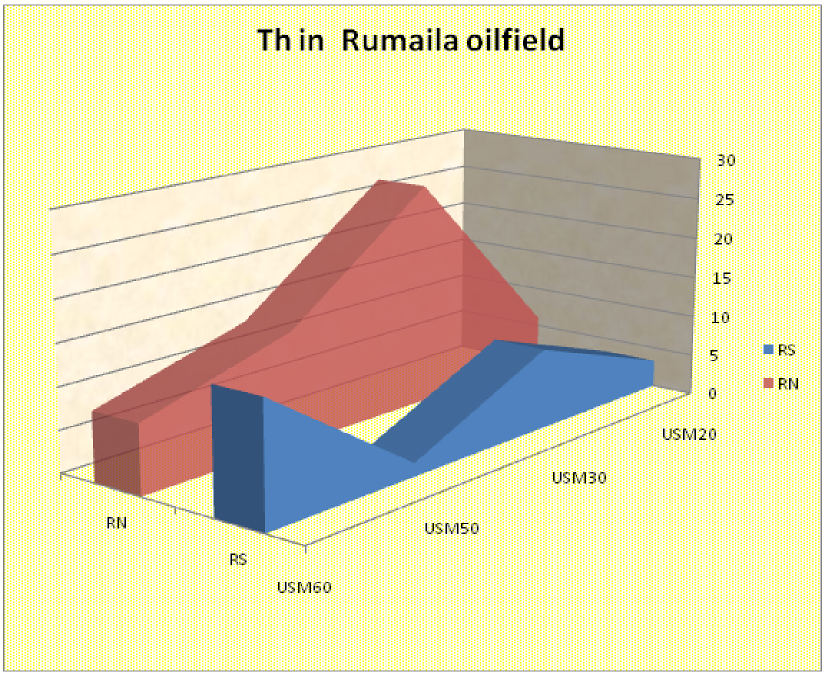

Figure28. *Th concentration in Rumaila Field*

4.16. Yttrium (Y)

The range concentrations of Yttrium in the Upper shale rocks of south Rumaila are 5.1-42.9 with ranged 24 ppm while in the north Rumaila the average was 22-51 ppm with range of36.5ppm as showed in tables(3and 4) and Figure(29).It has positive correlation with Al_2O_3 (Table 6) as a result to the similarities in their geochemical characteristics and to low solubility of these elements, this result may be back to being of Yttrium and Aluminium are compatible to the chemical weathering processes that cause to enrichment of these elements together in the sediments. The positive correlation with each of Fe_2O_3, Ni, and V (Table 6) may back to similarities of geochemical behaviour.

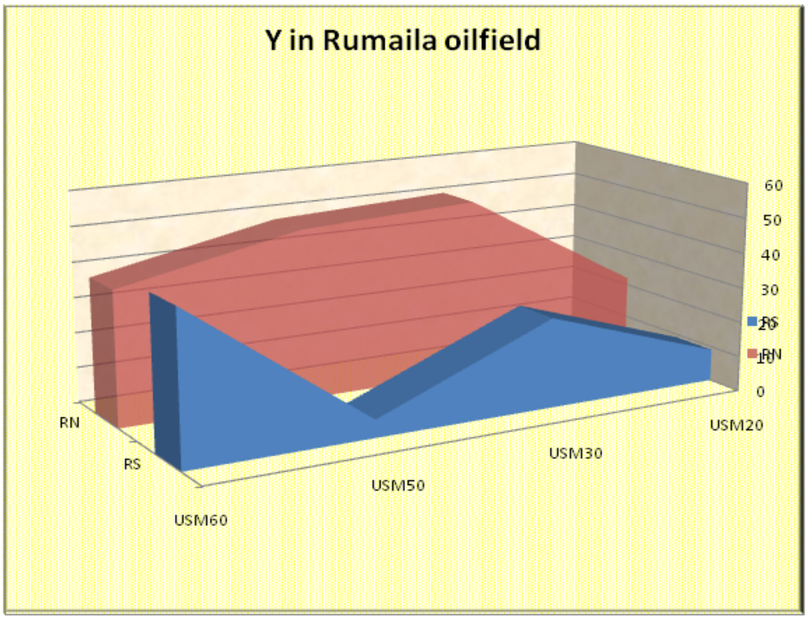

Figure29. *Y concentration in Rumaila Field*

4.17. Barium (Ba)

Barium is one of the elements moving during secondary processes. The average concentrations of Ba in the Upper shale rocks of south Rumaila are 48.3-484.4 ppm with ranged 266.35 ppm while in the north Rumaila the average was 87.1-191.3ppm with range of139.2 ppm as showed in tables(3and 4) and Figure(30). It has positive correlation with SiO_2 (Table 6) as a result of increase Ba in south Rumaila due to absorb on Quartz particulars.

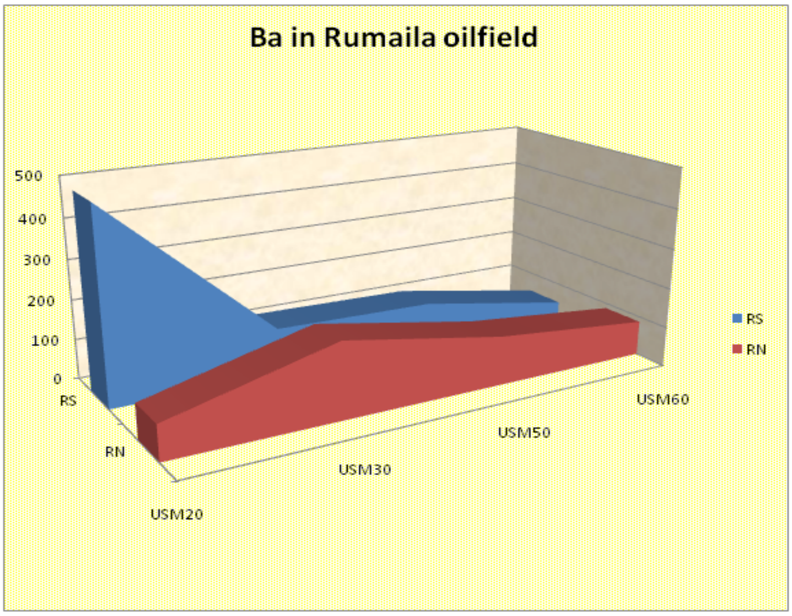

Figure30. *Ba concentration in Rumaila filed*

4.18. Chlorine (Cl)

Chlorine can be found in the Carnallite minerals (Magnesium Potassium Chloride) and Sylvite (Potassium Chloride).The range concentrations of Cl in the Upper shale rocks of south Rumaila are 303.3-5408 ppm with ranged 2855.65ppm while in north Rumaila the average is857.1-24230 ppm with range of12543.55ppm as presented in tables(3and 4)and Figure(31).It has positive relations with Al_2O_3 (Table6); this relation may be due to present of Cl with most of trace elements on the surface of Clay and Iron minerals. The negative correlation with SiO_2 (Table6), can be due to lack presence of this element in the Quartz minerals.

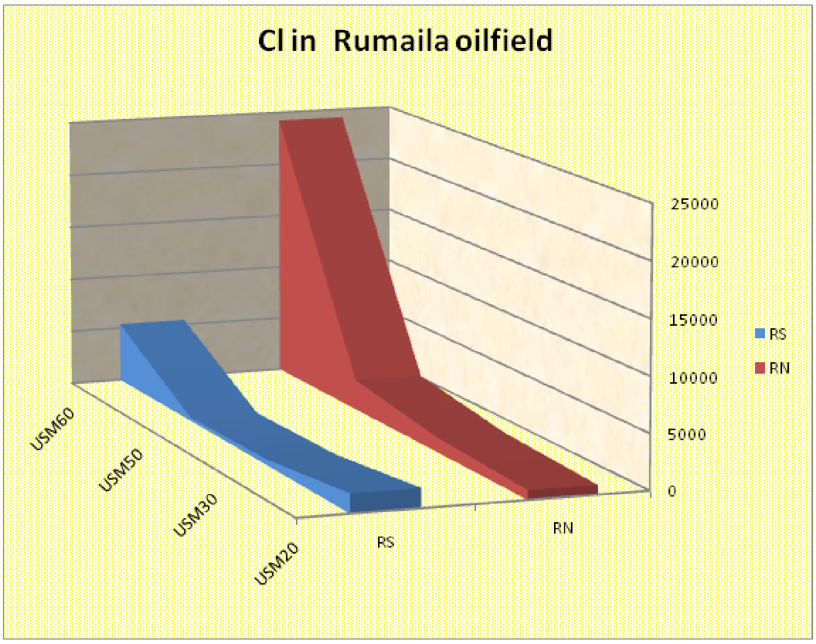

Figure31. *Cl concentration in Rumaila Field*

4.19. Arsenic (As)

The range concentrations of Asin the Upper shale rocks of south Rumaila are 0.44-1.1 with ranged of0.77 ppm while in north Rumaila it averaged 1.17-6.16 ppm with range of3.66 ppm as showed in tables(3and 4)and Figure(32). It has positive relation with Al_2O_3 (Table 6); this relation may be due to present of Arsenic with most of trace elements on the surface of Clay and Iron minerals. The negative correlations with SiO_2 (Table 6) can be due to lack presence of this element in the Quartz minerals.

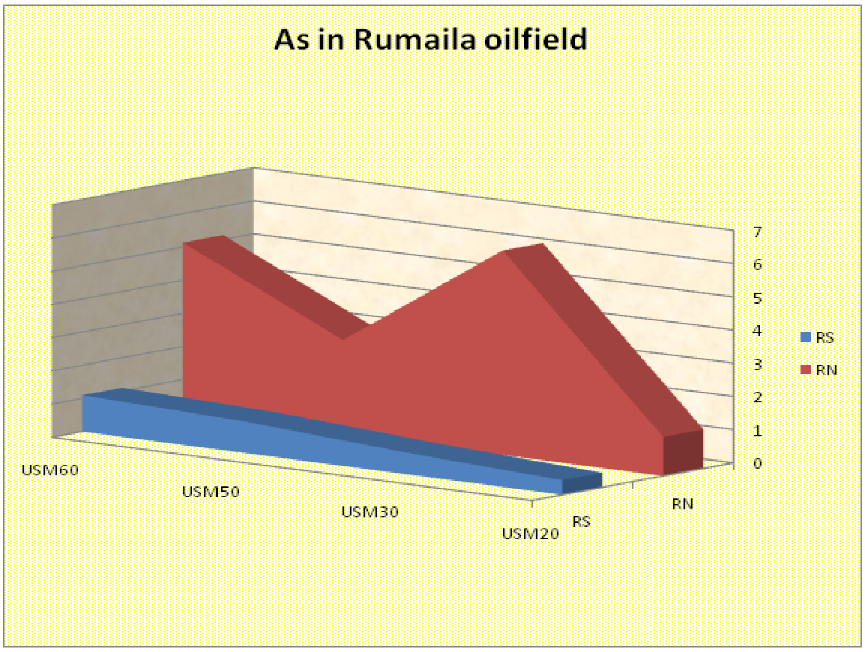

Figure32. *As concentration in Rumaila Field*

4.20. Bromine (Br)

The average concentrations of Br in the Upper shale rocks of south Rumaila are2-7.9 ppm with ranged of4.95 ppm while in north Rumaila it averaged between 28.9-42 ppm with range of 35.45ppm as showed in tables (3and 4) and Figure (33).It has positive relation with Al_2O_3 (Table 6); this relation is due to present of Br with most of trace elements on the surface of clay minerals.

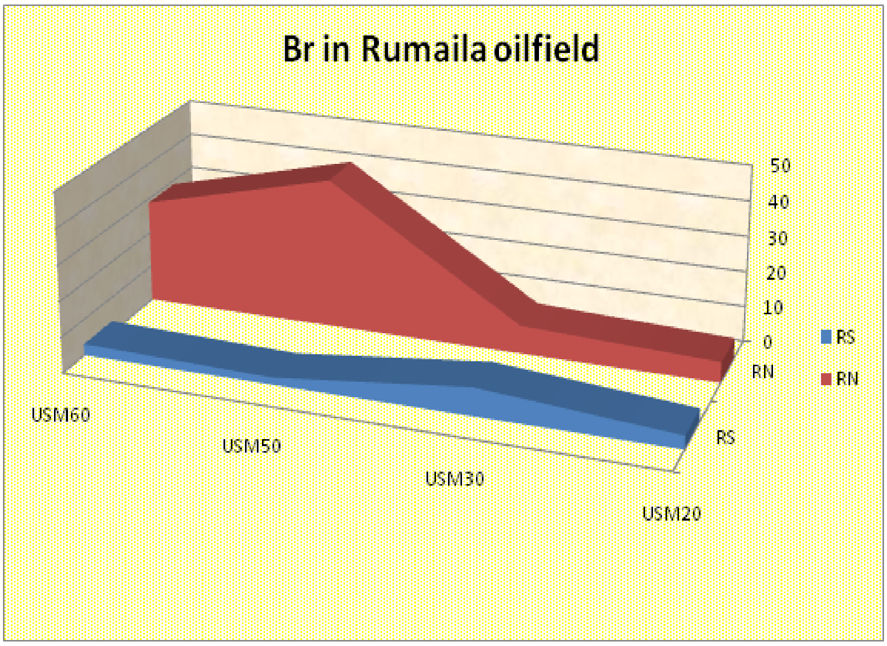

Figure33. *Br concentration in Rumaila Field*

4.21. Manganese (Mn)

The range concentrations of Mn in the Upper shale rocks of south Rumaila are 5.7-33.4 ppm with range of19.5 ppm while in north Rumaila it averaged between 29.3-463.5 ppm with range of246.4 ppm as shown in Table (3and4) and Figure (34).It has positive relation with Al_2O_3 (Table 6); this relation is due to present of Mn with most of trace elements on the surface of Clay minerals.

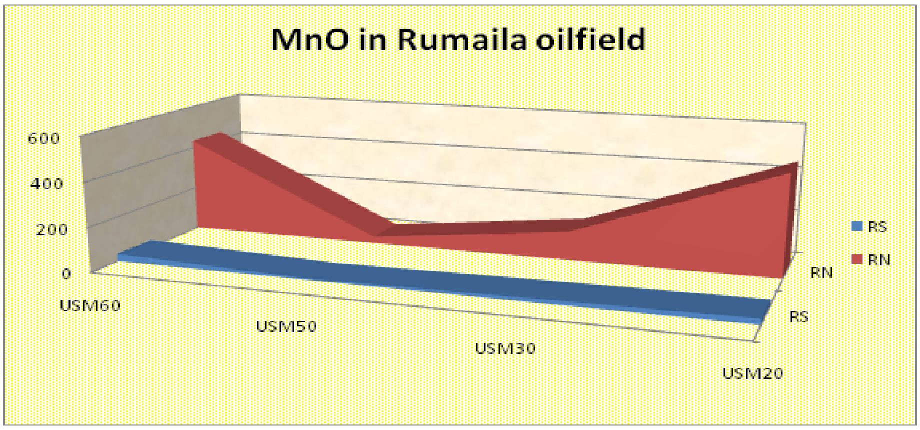

Figure34. *Mn concentration in Rumaila Field*

4.22. Tungsten (W)

The range concentrations of W in the Upper shale rocks of south Rumaila are 3-1101 ppm with range of 552ppmwhile in north Rumaila it averaged between 23- 443 ppm with range of226ppm as presented in tables (3and 4) and (Figure35).It has positive correlation with SiO2 (Table 6) as a result the increase of W in south Rumaila was due to absorb on Quartz particulars.

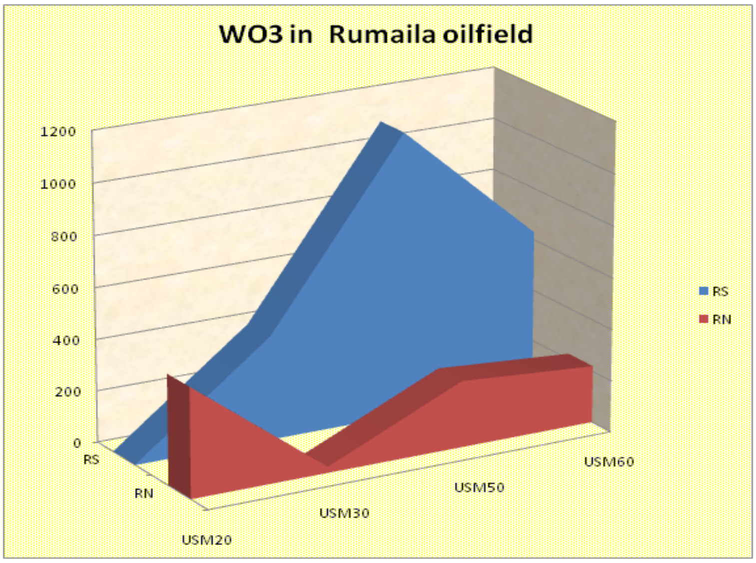

Figure35. *W concentration in Rumaila Field*

5. Discussion

Silica, Alumina, Iron, Calcium, Magnesium, Potassium, Sulphates and Titanium oxides are the major oxides in the sediments of the study area (Tables 1and 2). Silica oxides in the south of Rumaila are more than in north of Rumaila, and that correspond with the mineralogical study. Increase of the silica elements in these rocks offset by a lack of some basic elements such as alumina, iron, calcium and magnesium as a result to decrease of clay with increase of quartz minerals. On the other hand the alumina has been increased in north Rumaila as result to increase clay minerals (Kaolinite and Illite) and siltstone.

The major oxides (Al_2O_3, Fe_2O_3, K_2O and MgO) increase in north of Rumaila due positive relationship with Clay minerals specially Kaolinite and Illite, which increase in matrix of Upper shale rocks in north of Rumaila, while the SiO_2 had dominated in Upper shale rocks of south Rumaila due to degreased of Clay minerals in Upper shale matrix rocks.

Ba, Cs, Pb, Y, Co, Zn, Cu, Zr, Nb, Ni, Ga, V, U, Sr, Cr, Mn and Pare most of trace element in the sediment of study area.

The Trace elements can be divided into two parts: some of them had adsorbed on Quartz in south of Rumaila specially Co, Zr, Ba, Hf, W and P. While the other in north Rumaila adsorbed on the surface of Clay minerals or replacement with basic components of Clay minerals at the convergence of the charge or ionic radius and those elements are Pb, Y, Co, Zn, Rb, Ta,Cu, Nb, Ni, Br,Ga, V, U, Sr, Cr,As, Th, Mn and P.

6. CONCLUSIONS

- In south of Rumaila increased of SiO_2 and CaO that give indicator that the sand is dominated in south of Rumaila, while in north of Rumaila increase of major oxides (Al_2O_3, MgO, K_2O, TiO and SO_3) as a result present of clay minerals (kaolinite and Illite).
- Trace elements (Co, Zr, Ba, Hf, W and P) has been increasing in south Rumaila due to positive relations with Sio2, while other trace elements (Ci, V, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Nb, Ta, Pb, Th, Cr and Mn) are increasing in north of Rumaila due to positive relations with Al_2O_3.

REFERENCES

[1] Alsamani, Jasimjabar, Mineralogy and geochemical of Sandston for Miqdadia formation in selected areas north east of Missan, Msc. Thesis unpublished in University of Basra, 100 page.(in Arabic)

[2] Amosa, M. K., Mohammed, I. A., &Yaro, S. A. (2010).Sulphide scavengers in oil and gas industry–A review.Nafta, 61(2), 85-98.

[3] Aubert, H. and Pinta, M., 1977.Trace elements in soils, Developments in soil science, Elsevier scientific publishing Co., Amsterdam, p395.

[4] Fairbridge, R.W., 1972. Encyclopedia of geochemistry and environmental science.Encyclopedia of earth science seriese ,Newyork, V.IVA, 1321P.

[5] Friedman, G.M., and Sanders, F.E., 1978.Prnciples of sedimentology., Wiley, New York .792p.

[6] Friedman, G.M., and Sanders, F.E., 1978.Prnciples of sedimentology., Wiley, New York .792p.

[7] Goldshmidt, V.M., 1970. Geochemistry, Oxford university press, London, 730p.

[8] Hamon, R., McLaughlin, M., &Lombi, E. (Eds.).(2006). Natural attenuation of trace element availability in soils.CRC Press.

[9] Hassan, D.K., 2012. Petrology, Geochemistry and Ptrogenesis of amphibolite rocks from the Penjween Area, NE Iraq. Unpublished.MSc. Thesis, University of Baghdad, 115p.

[10] Hawks,H.E., and Webb, J.S.,1962.Geochemical in mineral exportation. Harper and Row Co.377pp.

[11] Hem JD (1989) Study and interpretation of the chemical characteristics of natural water, U.S. Geological Survey, Water Supply Paper 2254. pp 263

[12] Hirrst, D.M., 1962. The geochemistry of modern sediments from the Gulf of paria, The location and distribution of trace elements, Geoch. Et. Cosmoch.Acta,V. 26,pp. 1147-1187.

[13] Hofmann, A. W., & White, W. M. (1982). Mantle plumes from ancient oceanic crust. Earth and Planetary Science Letters, 57(2), 421-436.

[14] Javadi, A. (2015). Sulphide Minerals: Surface Oxidation and Selectivity in Complex Sulphide Ore Flotation (Doctoral dissertation, Luleåtekniskauniversitet).

[15] Jenne, E.A. ,1968. Controls on Mn, Fe, Co, Ni, Cu and Zn.Concentration in soils and water; the significant rols of hydrous Mn& Fe Oxides. In: Trace inorganics in water. Adf. Chem. ser. V.67, pp. 337-387.

[16] Krauskopf, K.B., 1967. Introduction to Geochemistry, Mc-Graw-Hill Book Company, New York, 721p.

[17] Moore, R.M.; Webb, R.; Tokarczyk, R., Wever; R., 1996.Bromoperoxidase and iodoperoxidase enzymes and production of halogenated methanes in marine, diatom cultures. J. Geophys. V.101, pp.20899–20908.

[18] Nalewajko, G.; Lee, K.; Jack, T.R., 1995.Effects of vanadium on freshwater phytoplankton photosynthesis.Water Air Soil Poll.V.81, pp.93–105.

[19] Roddaz, M., Viers, J., Brusset, S., Baby, B., Boucayrand, C. and Herail, G., 2006. Controls on weathering and provenance in the Amazonian foreland basin, Insights from major and trace element geochemistry of Neogene Amazonian sediments, Chem. Geol., 226, pp. 31-65.

[20] Rose, A.W., Hawkes, H.E. and Webb, J.S.,1979. Geochemistry in mineral exploration, 2nd ed., 657p.

[21] Rose, A.W., Hawkes, H.E. and Webb, J.S.,1979. Geochemistry in mineral exploration, 2nd ed., 657p.

[22] Rubio, B.; M. Nombela ,A.; Vilags ,F., 2000.Geochemistry of Major and Trace Elements in Sediments of the RiadeVigo (NW Spain): an Assessment of Metal Pollution. Marine Pollution Bulletin V. 40, No. 11, pp. 968-980.

[23] Salmenhaara, O. (2016). Separation of ions from acid solutions by nanofiltration.

[24] Short, N. M. (1961).Geochemical variations in four residual soils. The Journal of Geology, 69(5), 534-571.

[25] Steven R. and Sarah S. , 1991. Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. Elsevier Science Publishers B.V., Amsterdam , Marine Chemistry, V.34 ,pp.177-196 .

[26] Venugopal, B. , and Lucky, T.D.,1978. Metal toxicity in mammals, V.2, Toxicity of metals and metalloids, New York, Plenum Press, 380P.

[27] Weaver ,C.E., and Pollard, L., 1974. The Chemistry of Clay Minerals, Elseiver Scientific Publication Co., New York, 213p.

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