

## MINERALOGY AND GEOCHEMISTRY IMPACT ON MIDDLE AND LATE EOCENE CARBONATE ROCKS., EAST HELWAN AREA, EGYPT

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### ABSTRACT

*The present study deals with Geochemistry and Mineralogical impact on Middle and Late Eocene rocks exposed at East Helwan area -Egypt. The studied area lies between Latitudes 29° 47' 30" and 29° 53 ' 00" N. and longitudes 31° 21' 04" and 31° 28' 45" E.*

*Middle and Late Eocene sediments are subdivided into five rock units from base to top: Middle Eocene (Gebel Houf and Observatory Formations); Late Eocene (EL-Qurn, Wadi Garawi and Wadi Houf Formations).*

*Mineral composition was done on nineteen carbonate samples (using x-ray diffraction method. The study reveals the presence of a number of carbonate minerals; calcite, dolomite, and non-carbonate minerals name Gypsum, Anhydrite, Halite, and quartz in variable amounts.*

*Chemical composition of the carbonate rocks for fifty four samples (major and trace elements) represent Middle and Late Eocene carbonates were done. The data reveal that Middle and Late Eocene carbonates were deposited under shallow, alkaline and oxidizing environmental conditions.*

### INTRODUCTION

The study area lies between Latitudes 29° 47' 30" and 29° 53 ' 00" N. and longitudes 31° 21' 04" and 31° 28' 45" E. (Fig. 1 and 2). Middle and Late Eocene outcrops in the examined localities range from Lutetian to Priabonian in age.

Middle and Late Eocene sediments are subdivided into five rock units Eocene (Gebel Houf and Observatory Formations); Late Eocene (EL-Qurn, Wadi Garawi and Wadi Houf Formations).

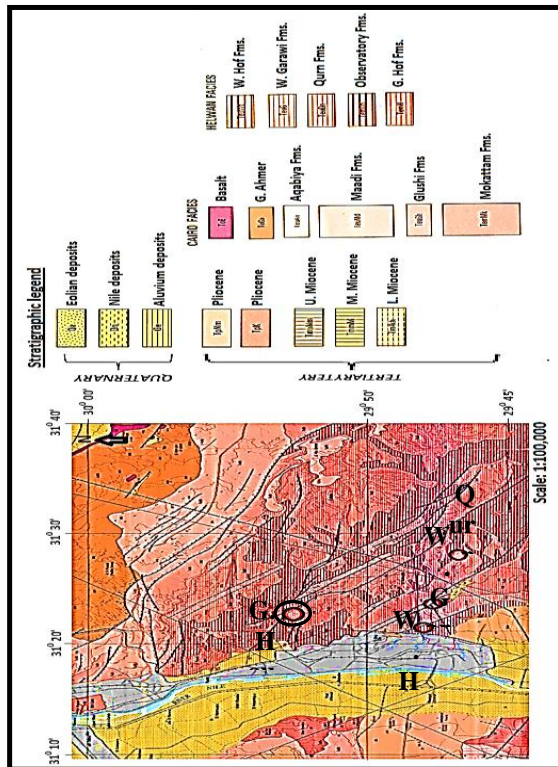


Fig. (1): Geological map of the study area (geological survey of Egypt, 1983).

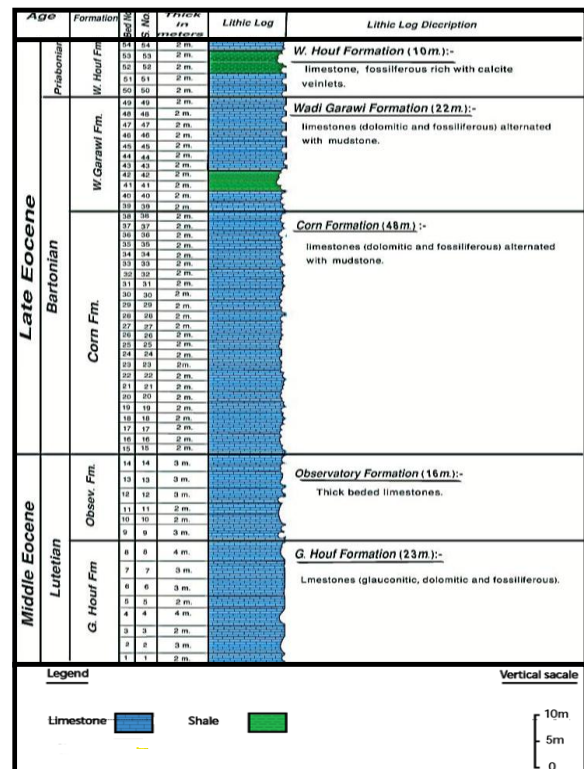


Fig. (2): Idealized composite columnar lithological section of Middle and Late Eocene rock units (East Helwan area).

## MATERIALS AND METHODS OF STUDY

Nineteen carbonate samples were analyzed, using x-ray diffraction method. The samples were selected in order to represent the carbonates of various ages, whereas samples were ground to 200 meshes and analyzed without any chemical treatment (bulk sample).

The x-ray diffraction analysis was carried out at (Egyptian Mineral Authority Labs) using the Philips X-ray diffraction (Monochromatic, X'Pert PRO type) with Ni-filter Cu-radiation, ( $\lambda = 1.542\text{\AA}$ ) at 50 K.V., 40 M.A. and a normal scanning speed of 0.02 $\theta$ /sec. was used. The x-ray diffraction analysis of the bulk limestone samples (e).

Forty six samples analyzed; at Lafarge Cement Company Labs; representing, Middle and Late Eocene carbonates distributed as follows: - Middle Eocene (Lutetian) G. Houf Fm., (8 samples) and Observatory Fm., (6 samples). Late Eocene (Bartonian) Qurn Fm., (21 samples) and W. Garawi Fm., (8 samples). Late Eocene (Priabonian) W. Houf Fm. (3 samples) for major elements (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, Cl, L.O.I and soluble chlorides Cl-) and trace elements namely (Ti, Mn, Ni, Ba, Cu and Sr) were quantitatively estimated using the atomic absorption method.

### *Mineral composition*

The present study was done aiming to determine the variations and differences in the mineralogical composition of the different *Middle and Late Eocene* carbonate sediments represented in the study area and its significance in the environmental interpretations. The x-ray diffraction analysis of the bulk limestone samples (Table 1) detected the presence of a number of carbonate minerals; calcite, dolomite, and non-carbonate minerals namely gypsum, Halite, in addition to quartz in variable amounts. Generally, *Middle and Late Eocene* environments of deposition were shallow, alkaline and oxidizing environment, whereas marine basin close to the landmass that supplied the basin by evaporates, and quartz minerals.

### *Chemical composition:- Weathering indices*

Weathering means the approach to equilibrium of a system involving rocks, air and water, and the agents of chemical weathering namely moisture, free oxygen, carbon dioxide, organic acids and nitrogen acids (Krauskopf, 1979). The indices are based on the principle that the ratio between concentrations of mobile and immobile elements should decrease over time as leaching progresses. In the present study, weathering index proposed by Ibrahim *et al.*, (2017) (modified after Krauskopf 1979) was used to classify Middle and Late Eocene limestone's and to correlate facies changes.

**Weathering index =**

$$\frac{\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{TiO}_2 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}$$

The computed weathering index for Middle and Late Eocene carbonates are shown in Table (2). The weathering index values are high fraction (except for Late Eocene (W. Garawi and W. Houf Fms.) carbonates suggesting that the studied rocks are slightly affected by the agents of weathering.

The low value for Late Eocene (W. Garawi and W. Houf Fms.) carbonates is mostly due to the predominate clastic materials rich in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

### *Abundance and distribution of major components:*

#### *Oxides forming silicates:*

The chemical composition, range and the average contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O of the different rock units are shown in Tables (3-8) and Figures (3-8). *Middle Eocene*, Lutetian, (G. Houf and observatory Fms) oxides forming silicate minerals are considerably low. However, regarding to the values of Al<sub>2</sub> O<sub>3</sub> relative to those of SiO<sub>2</sub>, Middle Eocene limestone are characterized by the presence of free quartz, *Late Eocene* Bartonian (Qurn and W. Garawi Fms.) limestone's are characterized by abundant of free quartz. However, Late Eocene Priabonian (W. Houf Fms.) contain a considerable amount of free quartz. Generally it was noticed that

there is an increase in the oxides forming silicate minerals from Middle Eocene, Lutetian, (observatory Fm) to Late Eocene Bartonian (Qurn and W. Garawi Fms.) towards Late Eocene Priabonian (W. Houf Fm.) Limestone. The inconsistent distribution of  $Al_2O_3$  and  $Na_2O$  and occasionally  $K_2O$  suggests their presence don't in the form of alumina-silicate minerals.

### Silicon dioxide:

The distribution of the silica content during Middle and Late Eocene times limestone reveals that there is an increasing (from Middle Eocene, observatory Fm., towards Late Eocene, W. Houf Fm., ) with decreasing in age of the limestone. The presence of free quartz suggests shallow marine conditions. The higher silica

Table (1): X-ray diffraction data of of Middle and Late Eocene carbonate samples.

Age	Fms.	Sample NO.	Mineral detected	2 $\theta$	I/I <sub>0</sub>	dA <sup>0</sup>	2 $\theta$	I/I <sub>0</sub>	dA <sup>0</sup>	2 $\theta$	I/I <sub>0</sub>	dA <sup>0</sup>	
Late Eocene	Priabonian	54	Quartz	26.86	81.65	3.31	39.68	13.80	2.27	23.29	6.26	3.81	
			Calcite	29.66	100	3.01	39.68	13.80	2.27	43.42	12.99	2.08	
			Albite	39.68	13.08	2.27	43.42	12.99	2.08	48.78	11.84	1.86	
		51	Calcite	29.57	100	3.02	39.60	12.51	2.27	48.69	12.40	1.87	
			Quartz	39.60	12.51	2.27	26.77	8.78	3.32	20.98	6.93	4.23	
			Albite	39.60	12.51	2.27	48.69	12.40	1.87	43.34	11.29	2.08	
		49	Calcite	29.65	100	3.01	39.65	15.38	2.27	47.77	14.11	1.90	
			Clinoptilolite	29.65	100	3.01	43.39	13.97	2.08	14.95	8.86	5.92	
			Halite	32.04	8.27	2.79	56.82	2.20	1.62	45.63	1.05	1.98	
	Bartonian	Wadi Garawi	44	Calcite	29.59	100	3.01	39.58	14.76	2.27	47.69	13.88	1.90
				Halite	31.80	5.72	2.81	45.60	2.42	1.98	57.62	7.50	1.60
				Kaolinite	9.98	29.10	8.85	39.58	14.76	2.27	47.69	13.88	1.90
		39	Calcite	29.56	100	3.02	39.58	12.94	2.27	47.73	12.15	1.90	
			Clinoptilolite	29.56	100	3.02	39.58	12.94	2.27	31.82	12.08	2.81	
			Halite	31.82	12.08	2.81	45.55	3.09	1.99	56.65	1.08	1.62	
	Bartonian	Qurn	36	Gypsum	29.31	18.73	3.04	23.58	11.61	3.77	31.31	10.81	2.85
				Quartz	11.82	100	7.48	50.51	1.67	1.80	39.61	0.74	2.27
				Calcite	29.31	18.73	3.04	29.63	4.52	3.01	43.49	2.70	2.08
			31	Calcite	29.57	100	3.02	39.58	14.12	2.27	43.31	13.29	2.08
				Calcite	29.60	100	3.01	43.33	15.35	2.08	48.69	14.06	1.86
				Calcite	29.61	100	3.01	39.62	13.11	2.27	48.73	11.45	1.86
			26	Quartz	39.62	13.11	2.27	26.81	5.07	3.32	57.62	4.89	1.59
				Dolomite	30.86	3.15	2.89	48.73	11.45	1.86	57.62	4.89	1.59
				Calcite	29.60	100	3.01	48.70	12.14	1.86	43.35	11.21	2.08
			24	Halite	29.60	100	3.01	39.58	13.06	2.27	56.76	1.79	1.62
				Quartz	26.81	8.91	3.32	31.86	6.12	2.80	57.57	4.49	1.60
				Albite	39.58	13.06	2.27	48.70	12.14	1.86	43.35	11.21	2.08
				Dolomite	28.05	1.13	3.18	30.98	2.91	2.88	48.70	12.14	1.86
			21	Calcite	29.57	100	3.02	39.57	13.55	2.27	43.30	12.60	2.08
				Halite	45.60	0.75	1.98	31.59	1.65	2.83	45.60	0.75	1.99
				Calcite	29.60	100	3.01	48.72	17.50	1.86	39.61	16.91	2.27
			20	Halite	31.85	9.94	2.80	45.58	7.31	1.98	56.71	2.36	1.62
				Quartz	39.61	16.91	2.27	26.78	7.52	3.32	57.63	4.84	1.59
				Calcite	29.58	100	3.01	39.57	14.20	2.27	48.68	13.92	1.87
			19	Calcite	29.60	100	3.01	39.61	13.15	2.27	43.35	12.26	2.08
				Quartz	39.61	13.15	2.27	57.60	4.33	1.60	26.80	2.80	3.32
Dolomite				30.89	6.05	2.89	48.70	9.57	1.86	56.82	1.96	1.62	
Dolomite				30.88	100	2.89	41.05	12.28	2.19	44.84	8.33	2.02	
Quartz				50.83	7.32	1.79	50.22	5.78	1.81	26.76	3.28	3.33	
Calcite	29.58	100		3.02	36.13	10.33	2.48	47.27	12.45	1.90			
Middle Eocene	Lutetian	Observatory	Gypsum	39.56	13.86	2.27	43.33	12.33	2.08	48.63	12.32	1.87	
			Calcite	29.56	100	39.56	13.86	2.27	43.31	13.08	2.08		
			Calcite	29.65	100	3.01	36.26	11.47	2.47	39.68	14.91	2.27	
	G. Houf	3	Halite	31.95	4.52	2.80	56.86	2.31	1.61	57.68	4.35	1.59	
			Dolomite	30.99	1.85	2.88	48.74	9.92	1.86	57.68	4.35	1.59	
			Calcite	23.22	7.73	3.82	29.58	100	3.01	39.61	1.96	2.82	
		1	Calcite	23.22	7.73	3.82	29.58	100	3.01	39.61	1.96	2.82	
			Gypsum	11.77	4.81	7.51	20.79	0.53	4.27	43.35	11.27	2.08	

Table (2): Weathering index values of Middle and Late Eocene Carbonates.

Age	Fms.	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Weathering Index ratio	
Late Eocene	Priabonian	W. Houf	45.25	0.71	0.10	0.09	11.89	1.85	1.07	0.11	0.76
	Bartonian	W. Garawi	42.69	1.54	0.20	0.02	10.25	2.23	0.97	0.11	0.77
		Qurn	48.26	1.18	0.77	0.09	3.91	1.51	0.55	0.08	0.89
Middle Eocene	Lutetian	Observatory	50.35	3.33	0.07	0.01	0.90	0.46	0.03	0.01	0.97
		G. Houf	50.98	1.13	0.73	0.03	1.74	0.81	0.27	0.03	0.94

Table (3): chemical analyses (Major components in Wt. %) of Middle Eocene (Lutetian , G. Houf Fm.) limestone's.

AGE	Formation	S.No	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	Cl %	SO <sub>3</sub> %	L.O.I %	
Middle Eocene	Lutetian	G. Houf	H8	1.45	0.71	0.13	50.71	1.13	0.03	0.01	0.11	2.43	43.32
			H7	1.05	0.72	0.11	51.17	0.71	0.91	0.03	0.10	3.06	42.13
			H6	1.21	0.85	0.16	52.33	0.49	0.04	0.01	1.71	0.46	43.07
			H5	1.52	0.55	0.19	52.03	1.71	0.39	0.03	0.20	0.45	42.05
			H4	1.95	0.71	0.25	49.23	1.54	0.61	0.03	1.48	1.31	43.20
			H3	1.97	0.70	0.25	50.39	1.55	0.59	0.03	0.83	1.31	42.91
			H2	1.93	0.82	0.39	55.21	0.84	0.22	0.02	0.02	0.33	40.47
			H1	2.81	1.44	0.69	46.78	1.06	3.08	0.07	0.05	1.72	41.90
			Average	1.74	0.81	0.27	50.98	1.13	0.73	0.03	0.56	1.38	42.38

content than those given by Pettijohn (1975) 0.7 to 7.91 %, can be attributed to the presence of SiO<sub>2</sub> in the form of quartz grains which were microscopically identified.

Corbel (1959) proved that there is an increase in SiO<sub>2</sub> content towards the warmer climatic zone while Dekimpe et al. (1961) noted that with increasing pH there is a decrease in the silica content.

Accordingly Middle and Late Eocene limestone were mostly deposited under relatively warm alkaline conditions. However the pH degree of alkalinity during Middle Eocene, G. Houf Fm. (Less in SiO<sub>2</sub> content) was higher than that prevailed during Middle and Late Eocene time.

**Table (4): chemical analyses(Major components in Wt. %) of Middle Eocene (Lutetian , observatory Fm.) limestone's**

AGE	Formation	S.No	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	Cl% %	SO <sub>3</sub> %	L.O.I %
Middle Eocene	Lutetian observatory	H-14	0.51	0.42	0.01	56.39	0.59	0.03	0.01	0.06	2.07	40.69
		H-13	0.71	0.31	0.02	50.63	0.45	0.04	0.02	0.04	5.31	42.76
		H-12	1.94	0.16	0.05	36.22	17.76	0.16	0.01	0.06	0.75	42.76
		H-11	0.72	0.55	0.05	49.48	0.32	0.05	0.02	0.08	2.18	45.76
		H-10	0.71	0.74	0.03	54.77	0.39	0.06	0.01	0.31	0.80	42.45
		H-9	0.81	0.55	0.04	54.62	0.44	0.06	0.01	0.12	0.58	43.10
		Average	0.90	0.46	0.03	50.35	3.33	0.07	0.01	0.11	1.95	42.92

**Table (5):- chemical analyses(Major components in Wt. %) of Late Eocene (Bartonian , Qurn Fm.)limestone's**

AGE	Formation	S.No	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	Na <sub>2</sub> O %	K <sub>2</sub> O% %	Cl %	SO <sub>3</sub> %	L.O.I %
Late Eocene	Bartonian Qurn	Q-35	1.38	0.84	0.10	52.02	1.81	0.25	0.03	0.21	0.43	42.96
		Q-34	<b>1.28</b>	<b>0.37</b>	0.28	53.75	0.43	<b>0.04</b>	0.02	1.35	0.73	41.99
		Q-33	1.45	0.66	0.18	52.41	0.43	0.38	0.03	0.55	3.89	40.23
		Q-32	4.64	1.08	0.46	<b>40.01</b>	0.55	1.55	0.11	2.40	<b>25.70</b>	<b>23.26</b>
		Q-31	1.88	0.56	0.12	54.02	0.49	0.17	0.02	0.58	0.32	42.46
		Q-30	1.38	0.56	<b>0.07</b>	53.09	<b>0.40</b>	0.12	0.01	0.59	0.11	<b>43.33</b>
		Q-29	2.18	0.43	0.08	53.81	0.41	0.09	0.03	<b>0.12</b>	0.06	42.96
		Q-28	1.72	0.81	0.17	<b>53.83</b>	0.48	0.11	<b>0.02</b>	0.25	0.03	43.27
		Q-27	3.60	1.47	0.42	50.46	0.70	0.36	0.04	0.79	0.26	41.97
		Q-26	4.14	1.66	0.50	48.37	<b>2.22</b>	0.31	0.03	0.88	0.16	41.88
		Q-25	8.18	1.78	0.65	45.94	0.65	1.26	0.20	2.17	<b>0.09</b>	39.29
		Q-24	<b>10.08</b>	2.07	0.85	42.66	1.23	0.88	0.28	1.47	0.13	39.80
		Q-23	3.78	2.38	1.05	46.31	2.08	1.02	<b>0.33</b>	1.75	0.13	41.17
		Q-22	3.35	2.68	0.91	44.08	2.16	1.40	0.12	3.64	0.20	41.46
		Q-21	3.37	<b>3.53</b>	<b>1.33</b>	40.31	1.01	<b>4.75</b>	0.23	<b>7.44</b>	0.99	37.04
		Q-20	9.68	3.07	1.01	41.60	1.36	1.93	0.11	3.86	0.17	37.57
		Q-19	2.03	0.81	0.20	50.71	0.54	0.24	0.02	1.51	0.32	42.49
		Q-18	6.06	1.01	0.51	48.62	1.25	0.21	0.02	0.78	0.29	40.98
Q-17	3.60	2.48	0.82	47.03	1.56	0.25	0.03	1.67	0.11	42.44		
Q-16	3.98	3.06	1.31	45.56	2.97	0.54	0.09	0.91	0.16	41.42		
Q-15	4.40	0.95	0.64	48.83	2.12	0.29	0.03	0.87	0.21	41.91		
Average	<b>3.91</b>	<b>1.51</b>	<b>0.55</b>	<b>48.26</b>	<b>1.18</b>	<b>0.77</b>	<b>0.09</b>	<b>1.61</b>	<b>1.64</b>	<b>40.47</b>		

**Table (6):-chemical analyses(Major components in Wt. %) of Late Eocene (Bartonian ,W. Garawi Fm.)limestone's**

AGE	Formation	S.No	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	Cl %	SO <sub>3</sub> %	L.O.I %
Late Eocene	Bartonian W. Garawi	W.G- 49	3.77	<b>1.21</b>	0.46	<b>46.65</b>	1.20	<b>0.41</b>	<b>0.04</b>	<b>1.07</b>	<b>9.91</b>	<b>35.40</b>
		W.G- 48	6.83	1.69	0.73	45.85	1.97	0.10	<b>0.01</b>	1.25	0.94	41.22
		W.G- 47	10.62	2.12	0.98	41.17	<b>2.67</b>	0.09	0.02	2.41	0.15	41.55
		W.G- 46	<b>6.15</b>	1.33	<b>0.59</b>	46.51	1.83	<b>0.02</b>	0.01	2.01	<b>0.03</b>	<b>42.43</b>
		W.G- 45	6.52	1.69	0.58	45.81	2.12	0.03	0.01	1.34	0.14	42.26
		W.G- 44	<b>20.55</b>	4.02	1.78	35.53	1.12	0.60	0.05	2.00	0.85	34.69
		W.G- 43	18.07	<b>4.15</b>	<b>1.92</b>	<b>37.07</b>	<b>1.00</b>	0.26	0.03	1.87	0.19	36.38
		W.G- 39	9.50	1.63	0.68	42.90	2.25	0.08	0.01	<b>3.83</b>	0.17	41.59
Average	<b>10.25</b>	<b>2.23</b>	<b>0.97</b>	<b>42.69</b>	<b>1.54</b>	<b>0.20</b>	<b>0.02</b>	<b>1.97</b>	<b>1.55</b>	<b>39.32</b>		

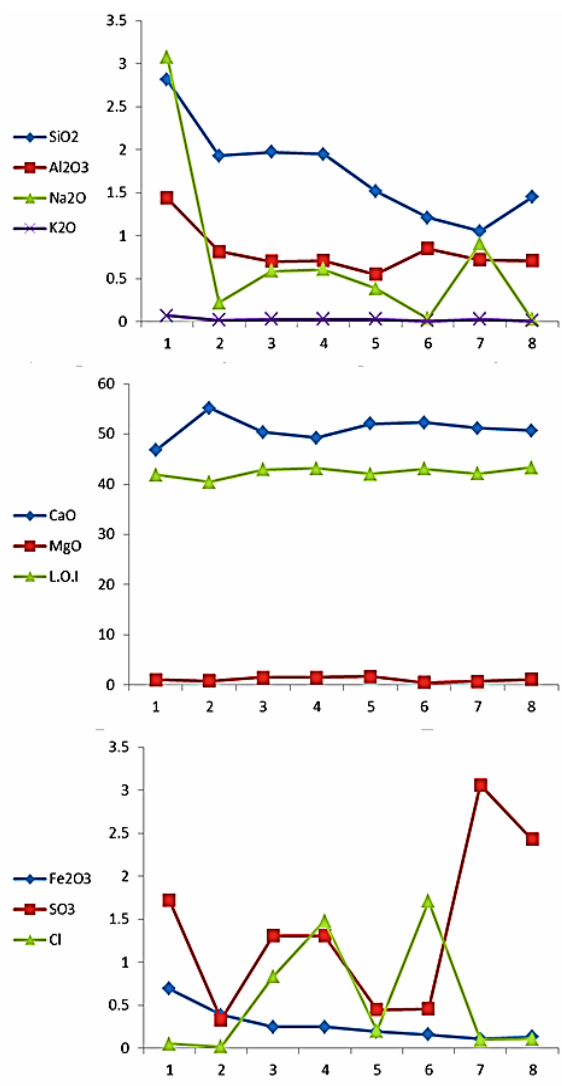
**Table (7): Chemical composition (Major components in Wt. %) of LateEocene (Priabonian, Wadi Houf Fm.)limestone's**

AGE	Fms	S.No	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO%	MgO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	Cl %	SO <sub>3</sub> %	L.O.I %
LateEocene	Priabon	W.H 54	17.00	2.36	1.26	41.70	0.74	0.12	0.10	0.75	0.02	36.17
		W.H 51	12.13	1.74	0.87	45.56	0.71	0.11	0.12	0.19	0.09	38.27
		W.H 50	6.55	1.45	1.09	48.48	0.67	0.06	0.04	0.63	0.13	41.31
		Average	11.89	1.85	1.07	45.25	0.71	0.10	0.09	0.52	0.08	38.58

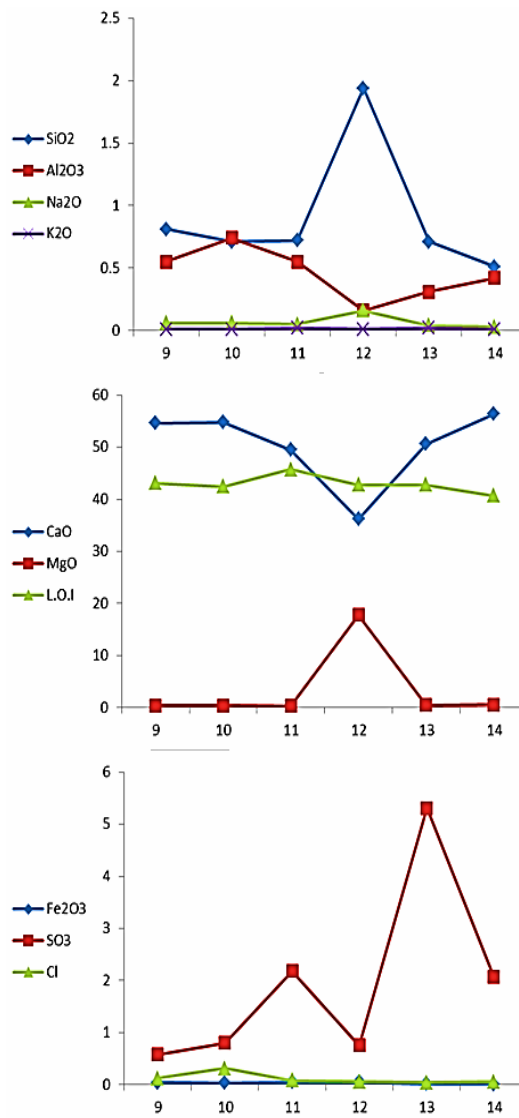
**Aluminum Oxide:**

According to Krauskopf (1956) and Wey (1961), Al<sub>2</sub>O<sub>3</sub> is more soluble in acidic medium than SiO<sub>2</sub> and in neutral medium (5-6 pH) Al<sub>2</sub>O<sub>3</sub> is insoluble whereas SiO<sub>2</sub> retains its solubility. In alkaline medium the two solubility's meet and increase together (pH over

9). The consistent distribution of both Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>favoured their contemporaneous deposition suggesting that the pH of the medium was 7.8 to 8.



**Figure (3): Distribution curves of chemical components (%) of Middle Eocene( G. Houf Fm.) limestone**



**Figure (4): Distribution curves of chemical components (in wt. %) of Middle Eocene (observatory Fm.) limestone.**





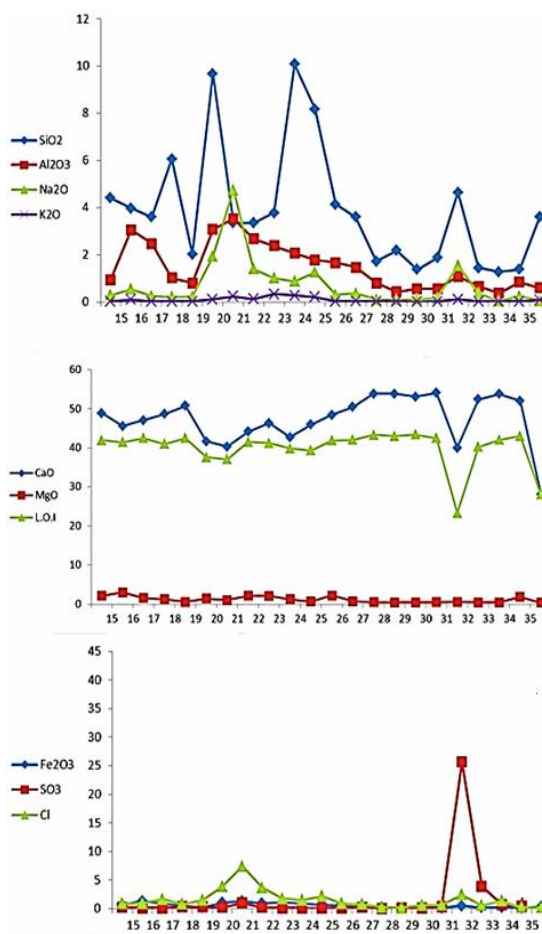
**Iron oxides:**

The distribution of ferric oxide in Middle and Late Eocene carbonates (Table 4) shows to a great extent consistent distribution with those of both SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> suggesting the presence of Fe<sub>2</sub>O<sub>3</sub> connected with silt or clay fractions in The variation in Fe<sub>2</sub>O<sub>3</sub> concentration among Middle and Late Eocene carbonates (Table 4 and fig.3) can be attributed agreement with Martens (1939). Millot (1970) stated that "during diagenesis iron has a great tendency to re-enter silicate structure. Castano and Garrels (1950) stated that" the residence time for iron and alumina in sea in years is very short. Hence it should expect that iron oxides, silica and alumina are to be concentrated in continental and near-shore marine environments". to variation in the environment of deposition. However the pH degree of alkalinity during Middle Eocene, W.Houf Fm.(Less in Fe<sub>2</sub>O<sub>3</sub>

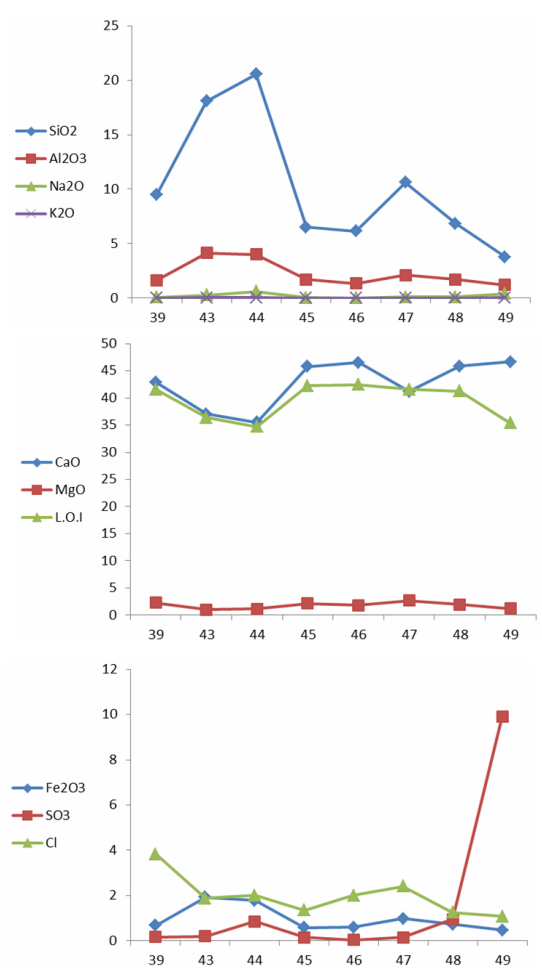
was lower than that prevailed during Middle and Late Eocene time.

**Oxides forming carbonate  
Calcium Oxide:**

The distribution of CaO in limestones reveals that there's a decrease inCaO content with time from Middle Eocenetowards Late Eocene contrary to the silica distribution . However Trask (1939) mentioned that" the higher the salinity, the greater the content of CaCO<sub>3</sub>, this relationship is connected with higher temperature and greaterorganic production". In addition Kukal (1971) stated that" the content of natural salts and increase in temperature decrease the CaCO<sub>3</sub> solubility and also the increased content of Ca<sup>2+</sup> ions from other sources cause the decreased solubility of CaCO<sub>3</sub>.. Nevertheless the higher CaCO<sub>3</sub> content at Middle Eocene, G. and Houf Fms.) limestone seems to be due to the fact that the depth of water during deposition was not deep



**Figure (5):- Distribution curves of chemical components (in wt. %) of Late Eocene ( W. Garawi Fm.) limestone.**



**Figure (6):- Distribution curves of chemical components (in wt. %) of Late Eocene (Qurn Fm.) limestone**



enough to cause a great variation in temperature and to increase the solubility of  $\text{CaCO}_3$  or the amounts of the argillaceous materials derived to the site of deposition were un-considerable, leading to the relative increase in the  $\text{CaCO}_3$  at the expense of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents.

**Magnesium oxide:**

The distribution of MgO in Middle Eocene and Late Eocene reveals that MgO follow CaO in its manner of distribution. This can be attributed to variations in the ecological and paleontological parameters of the environments under which the studied limestones were

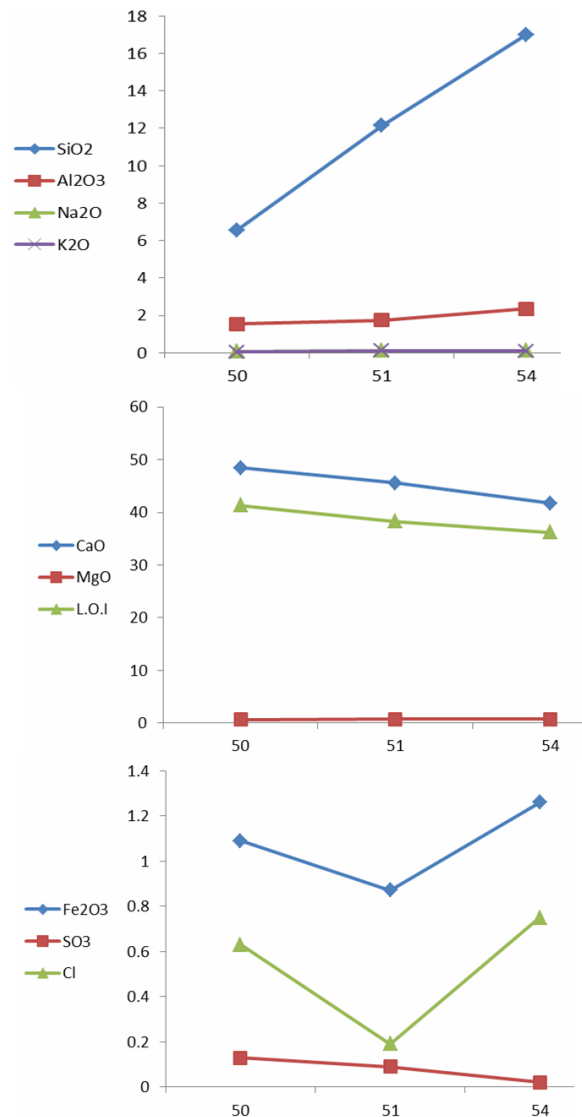


Figure (7): Distribution curves of chemical components (in wt. %) of Middle and Late Eocene limestone

deposited. Chave (1954) suggested that there is a direct relation between the content of MgO and temperature.

Chilingar (1963) stated that "the MgO content increases with salinity but is simultaneously affected by so many other factors that it cannot serve as an adequate indicator". He also noted that in carbonate sediments the Ca/ Mg ratio increases sea wards with depth. Chilingar (1967) stated that " in as muchas shallow near-shore waters are systematically warmer as arule than deep off-shore waters; the gross Ca/Mg ratio reflects temperature-depth-distance from shore."

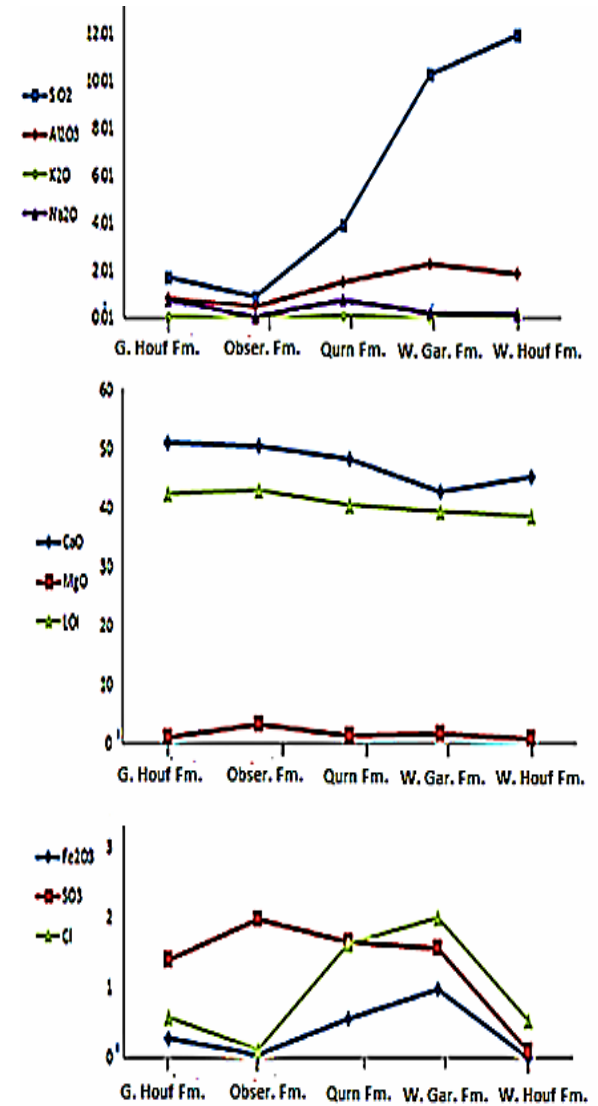
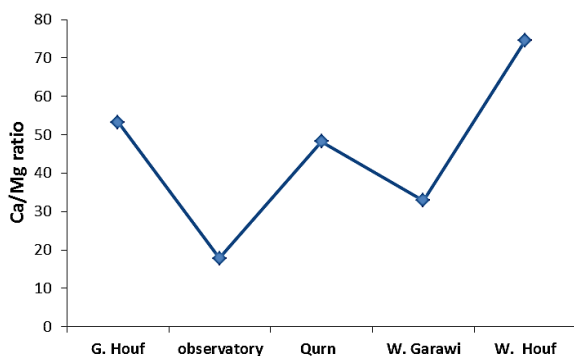


Figure (8): Distribution curves of chemical components (in wt. %) of Late Eocene (Wadi Houf Fm.) limestone

The gross Ca/Mg ratio is represented by table (10) and figure (9), suggest that there is no particular trend for the distribution of Ca/Mg average ratio and this can be attributed to the selective adsorption of  $Mg^{2+}$  by illite clays Chilingar (op.cit) so, the gross ratio reflects the illite content or perhaps the degree of diagenesis of Middle and Late Eocene limestone.



**Fig. (9): Average Ca/Mg in Middle and Late Eocene limestone**

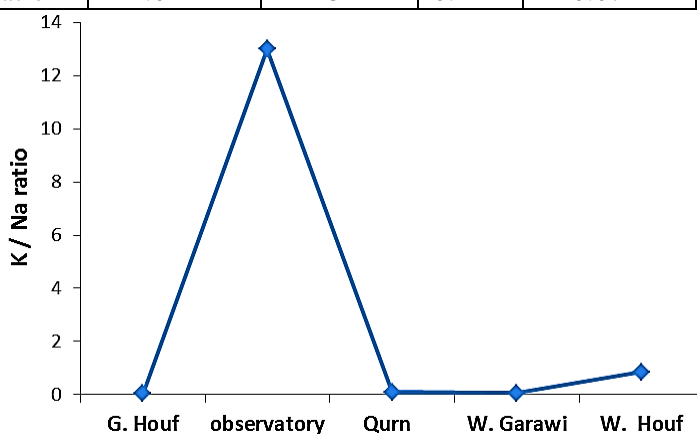
**Sodium and Potassium oxides:**

From table (10) and figure (10) it is obvious that  $Na_2O$  predominates  $K_2O$  in Middle Eocene, Lutetian, (G. Houf Fm) and Late Eocene limestones except for those of Middle Eocene, ( observatory Fm.). The outstanding characteristics of  $K_2O$  in comparison with that

of  $Na_2O$  has been noted for a long time in a way like that described by(Noll, 1931 ; Urbain, 1933; Goldschmidt, 1937; Harvey, 1949 and Millot 1949). Milot (1949) stated that "one sees that in the course of continental weathering sodium turns out to be much more mobile than potassium and dominates the latter in natural water. Potassium is sorted up and conserved in a preferential way". Again Millot (1970) mentioned that "if one considers the behaviour of K ions in solution, one sees that they are preferentially adsorbed by the fine-grained particles of the sediments". Consequently the slight predominance of  $K_2O$  contents over  $Na_2O$  contents in Middle Eocene, (observatory Fm.) limestones could be understood according to Garrels and Christ (1965) and Weaver (1967), the K/Na ratio is very important, where low ratio favour the formation of montmorillonite materials and high ratio leads to the formation of illite. It seems that clays in the form of illite predominate over montmorillonite clays in Middle Eocene, (observatory Fm.) and montmorillonite predominate over illite in Middle Eocene, Lutetian, (G. Houf Fm) and Late Eocene Formations limestones.

**Table (10): Average K / Na Ratio in Middle and Late Eocene limestone**

Age	Middle Eocene		Late Eocene		
	G. Houf	observatory	Qurn	W. Garawi	W. Houf
K	0.02	0.65	0.06	0.01	0.06
Na	0.54	0.05	0.57	0.15	0.07
K / Na Ratio	.04	13	0.11	0.07	0.85



**Fig. (10): Average K / Na Ratio in Middle and Late Eocene limestone.**

**Soluble chlorides:**

The soluble chlorides contents of Middle and Late Eocene limestones are relatively higher than that given by (Turckian and Wedepohl, 1961) (0.015%), indicating the prevalence of warm climate as well as relatively shallow occasionally restricted medium.

**Abundance and distribution of trace elements:**

The major features of the distribution of trace elements in sedimentary rocks can be related to ionic size charge and bond character, Most of the trace elements are more abundant in fine-grained detrital sediments than in sandstones or carbonate rocks. notable concentrations of trace elements formed by sedimentary processes alone are not common (Krauskopf, 1979). Since the elements behave differently in their migration and deposition so, the abundance and behavior of each element in Middle and Late Eocene carbonate sediments will be considered.

**Titanium:**

Titanium is the most abundant trace element recorded in Middle and Late Eocene limestones. Since the average concentration of titanium in carbonates, given by Turekian and Wedepohl (1961) is 400 ppm, The lower average titanium contents were recorded in the limestone's of Middle Eocene Lutetian (observatory and G. Houf Fms.), and the heights contents in Late Eocene, Bartonian, (Qurn and W. Garawi Fms.) and in Late Eocene, Priabonian, (W. Houf Fm.) limestone's (table12). The distribution of titanium in Middle and Late Eocene limestones does not show any particular trend for distribution and this can be attributed to the different rates of sedimentation (Arrhenius, 1954).The high Ti content values recorded in Late Eocene limestones can be attributed to the amounts of terrigenous materials brought to the site deposition (Isayeva, 1977).

**Table (11): chemical analyses(trace elements in Wt. %) of Middle Eocene (Lutetian , G. Houf Fm.) limestone's**

Age		Formation	S.No	TiO2	P2O5	MnO	SrO	Cr2O3	ZnO
Middle Eocene	Lutetian	G. Houf	H8	0.01	0.03	0.00	0.09	0.00	0.00
			H7	0.02	0.04	0.00	0.12	0.00	0.00
			H6	0.02	0.05	0.01	0.08	0.00	0.01
			H5	0.03	0.10	0.01	0.12	0.00	0.01
			H4	0.04	0.14	0.01	0.14	0.00	0.02
			H3	0.04	0.14	0.01	0.14	0.00	0.01
			H2	0.04	0.13	0.02	0.15	0.00	0.01
			H1	0.05	0.12	0.05	0.11	0.00	0.00
Average			0.03	0.09	0.02	0.12	n.d	0.01	

**Table (12): chemical analyses(trace elements in Wt. %) of Middle Eocene (Lutetian , observatory Fm.) limestone's**

AGE	Fms	S.No	TiO2	P2O5	MnO	SrO	Cr2O3	ZnO	
Middle Eocene	Lutetian	observatory	H-14	0.01	0.02	0.01	0.07	0.00	0.00
			H-13	0.01	0.03	0.00	0.13	0.00	0.00
			H-12	0.01	0.03	0.01	0.16	0.00	0.00
			H-11	0.01	0.03	0.01	0.06	0.00	0.01
			H-10	0.01	0.03	0.00	0.08	0.00	0.00
			H-9	0.01	0.03	0.01	0.08	0.00	0.00
			Average		0.01	0.03	0.01	0.10	n.d

**Table (13):- chemical analyses(trace elements in Wt. %) of Late Eocene (Bartonian , Qurn Fm.)limestone's**

AGE		Formation	S.No	TiO2	P2O5	MnO	SrO	Cr2O3	ZnO
Late Eocene	Bartonian	Qurn	Q-38	0.04	0.03	0.00	0.40	0.01	0.00
			Q-37	0.06	0.03	0.01	0.29	0.00	0.00
			Q-36	0.06	0.03	0.01	0.36	0.00	0.00
			Q-35	0.02	0.05	0.01	0.17	0.00	0.00
			Q-34	0.02	0.04	0.03	0.15	0.00	0.00
			Q-33	0.02	0.03	0.01	0.15	0.00	0.00
			Q-32	0.07	0.06	0.01	0.25	0.00	0.00
			Q-31	0.01	0.03	0.01	0.11	0.00	0.01
			Q-30	0.01	0.03	0.01	0.11	0.00	0.01
			Q-29	0.02	0.05	0.01	0.11	0.01	0.00
			Q-28	0.02	0.07	0.01	0.14	0.00	0.01
			Q-27	0.05	0.07	0.01	0.22	0.01	0.01
			Q-26	0.07	0.21	0.01	0.23	0.01	0.02
			Q-25	0.10	0.07	0.01	0.18	0.01	0.01
			Q-24	0.12	0.07	0.01	0.21	0.01	0.02
			Q-23	0.16	0.08	0.02	0.22	0.01	0.03
			Q-22	0.12	0.09	0.01	0.19	0.01	0.01
			Q-21	0.19	0.41	0.01	0.09	0.01	0.00
			Q-20	0.13	0.16	0.01	0.11	0.01	0.01
			Q-19	0.03	0.08	0.01	0.10	0.01	0.01
Q-18	0.07	0.08	0.01	0.25	0.00	0.02			
Q-17	0.11	0.11	0.01	0.13	0.01	0.03			
Q-16	0.16	0.17	0.01	0.17	0.01	0.03			
Q-15	0.08	0.10	0.02	0.25	0.01	0.02			
Average			<b>0.08</b>	<b>0.10</b>	<b>0.01</b>	<b>0.17</b>	<b>0.01</b>	<b>0.02</b>	

**Table (14):-chemical analyses(Major components in Wt. %) of Late Eocene (Bartonian ,W. Garawi Fm.)limestone's**

AGE		Formation	S.No	TiO2	P2O5	MnO	SrO	Cr2O3	ZnO
Late Eocene	Bartonian	W. Garawi	W.G- 49	0.06	0.08	0.00	0.43	0.01	0.00
			W.G- 48	0.08	0.11	0.00	0.33	0.01	0.00
			W.G- 47	0.11	0.13	0.00	0.29	0.01	0.00
			W.G- 46	0.07	0.09	0.01	0.31	0.00	0.00
			W.G-45	0.07	0.11	0.00	0.31	0.00	0.00
			W.G- 44	0.19	0.11	0.03	0.24	0.01	0.00
			W.G- 43	0.20	0.10	0.04	0.24	0.01	0.00
			W.G- 39	0.07	0.08	0.01	0.34	0.01	0.00
Average			0.11	0.10	0.02	0.31	0.01	n.d	

Again titanium has an intermediate ionic potential, hence it is precipitated by hydrolysis in the form of hydroxides at still low alkaline pH values. It seems that Late Eocene limestones were deposited under alkaline conditions that permit Ti to be concentrated in Late Eocene Limestones.

#### **Phosphates:**

The distribution averages of P<sub>2</sub>O<sub>5</sub> show that there is no particular trend for distribution with time.

The lower average P<sub>2</sub>O<sub>5</sub> average contents were recorded in the limestones of Middle

Eocene Lutetian (observatory and G. Fms.) (table 16), and the high contents in Late Eocene, Bartonian, (Qurn and W. Garawi Fms.) and Priabonian, (W. Houf Fm.) limestones (table 16) than the average given by Turekian and Wedepohl (op.cit) (0.04 %) reveals that Late Eocene limestones were deposited under reduced slightly alkaline conditions (Kukal, 1971) that permit P<sub>2</sub>O<sub>5</sub> to be concentrated in Late Eocene limestones.

#### **Manganese Oxide:**

The averages of manganese in Middle and Late Eocene limestones show that it is present in subordinate concentrations in comparison with that given by Turekian and Wedepohl, 1961, (1100 ppm). The subordinate manganese

concentration can be attributed to the fact that manganese is less mobile under oxidizing conditions and it will be mobilized in a reducing environment and precipitated as divalent ion in carbonates (Manheim, 1961; Wedepohl, 1964 and Hartmann, 1964). It seems that Middle and Late Eocene limestones were deposited under relatively reduced alkaline conditions that permit Mn to be mobilized.

#### **Strontium Oxide:**

The distribution of Strontium in Middle and Late Eocene limestones does not show any particular trend. Chilingar (1967) stated that "Strontium increases towards shore-wards, where warm waters". Kukal (1971), Kitano and Kawasaki (1958) and Bathurst (1968) suggested that the SrO content is affected mainly

**Table (15): Chemical composition (trace elements in Wt. % of Late Eocene (Priabonian, Wadi Houf Fm.) limestone's.**

AGE	Fms	S.No	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Sr O	Cr <sub>2</sub> O <sub>3</sub>	ZnO	
Late Eocene	Priabonia	Wadi Houf	W.H 54	0.17	0.14	0.01	0.23	0.00	0.00
			W.H 51	0.09	0.12	0.01	0.23	0.00	0.00
			W.H 50	0.08	0.09	0.00	0.18	0.00	0.00
			Average	0.11	0.11	0.01	0.21	n.d	n.d

**Table (16): Average Chemical composition (Major components in Wt. %) Of Middle Eocene limestone**

AGE	Fms	Range	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	SrO O	Cr <sub>2</sub> O <sub>3</sub>	ZnO	
Late Eocene	Priabonian	W. Houf	Min.	0.08	0.09	0.01	0.18	n.d	n.d
			Max.	0.17	0.14	0.01	0.23	n.d	n.d
			Average	0.11	0.11	0.01	0.21	n.d	n.d
	Bartonian	W. Garawi	Min.	0.06	0.08	0.01	0.24	0.01	n.d
			Max.	0.20	0.13	0.04	0.43	0.01	n.d
			Average	0.11	0.10	0.02	0.31	0.01	n.d
		Qurn	Min.	0.01	0.03	0.01	0.09	0.01	0.01
			Max.	0.19	0.41	0.03	0.25	0.01	0.03
			Average	0.08	0.10	0.01	0.17	0.01	0.02
Middle Eocene	Lutetian	observatory	Min.	0.01	0.02	0.01	0.06	n.d	0.01
			Max.	0.01	0.03	0.01	0.16	n.d	0.01
			Average	0.01	0.03	0.01	0.10	n.d	0.01
	G. Houf	Min.	0.01	0.09	0.01	0.08	n.d	0.01	
		Max.	0.05	0.14	0.05	0.15	n.d	0.02	
		Average	0.03	0.09	0.02	0.12	n.d	0.01	

by the aragonite content and SrO content in carbonate sediments appear to be a reliable indicator of the salinity and temperature.

Pilkey and Godell (1963) record that differences in salinity cause greater changes in shell composition than differences in temperature. Accordingly, the high strontium content in the studied carbonates than the average given by Turekian and Wedepohl, (1961) (610ppm) suggests that the salinity and temperature of the environment was high saline and to certain extent high temperature.

#### **Chromium oxide:**

Chromium oxide did not detected in Late Eocene, Priabonian, (W.Houf Fm.) rock unit. Chromium oxide contents in Late Eocene, Bartonian, (Qurn and W. Garawi Fms.), carbonates rock units is higher than that given by Turekian and Wedepohl, (1961) (11ppm). It seems that Late Eocene, Bartonian, (Qurn and W. Garawi Fms.), carbonates rock units were deposited under more alkaline conditions that permit  $\text{Cr}_2\text{O}_3$  to be concentrated.

#### **Zinc Oxide:**

Late Eocene Bartonian (W. Garawi Fm) and Priabonian (W. Houf Fm.) rock units, the Zinc oxide is not detected (Tables 12- 17, Figs 11- 16 ). The detected Zinc Oxide contents in Middle Eocene, Lutetian, (G. Houf and observatory Fms) and Late Eocene, Bartonian, (Qurn Fm.) is higher than that given by Turekian and Wedepohl, (1961) (20 ppm) reveal formation under relatively reduced alkaline conditions that permit zinc oxide to be concentrated.

### **Physiochemical Parameters**

#### **1- Temperature:**

The values of the Ca/Mg, ratio during Middle and Late Eocene rocks carbonates suggest that they are limestones relatively rich by magnesium reflecting prevalence of warm marine conditions with an occasional increase in the temperature causing the increase in the magnesium content of the precipitated calcium carbonates, since the values of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , indicate that the amount of clay minerals is practically negligible.

#### **2- Salinity:**

The soluble chlorides contents during

Middle and Late Eocene times are relatively higher than that given by (Turekian and Wedepohl, 1961) (0.015%), indicating the prevalence of warm climate as well as relatively shallow occasionally restricted medium.

#### **3- The Acidity and Alkalinity (pH):**

Middle and Late Eocene sediments consists of proper limestone beds as well as highly calcareous beds with an oscillation in the oxygen and  $\text{CO}_2$  contents at time intervals suggesting the prevalence of alkaline conditions.

#### **4- Recrystallization and dolomitization:**

Recrystallization according to Bausch (1968) or aggrading neomorphism is restricted to limestones with less than 2% clays. Generally, Middle and Late Eocene times carbonate sediments, according to Tucker's classification (1981), are clustered mainly as limestones (Less than 10 %  $\text{MgCO}_3$ ). The classification of Middle and Late Eocene carbonate sediments as limestones supports the assumption of local dolomitization and local source of magnesium ions.

### **CONCLUSIONS**

Middle and Late Eocene sediments are subdivided into five rock units from base to top: Middle Eocene (Gebel Houf and Observatory Formations); Late Eocene (EL-Qurn, Wadi Garawi and Wadi Houf Formations). Mineral composition was done on nineteen carbonate samples (using x-ray diffraction method. The study reveals the presence of a number of carbonate minerals; calcite, dolomite, and non-carbonate minerals name Gypsum, Anhydrite, Halite, and quartz in variable amounts. Chemical composition of the carbonate rocks for fifty four samples (major and trace elements) represent Middle and Late Eocene carbonates were done. The data reveal that Middle and Late Eocene carbonates were deposited undershallow, alkaline and oxidizing environmental conditions.

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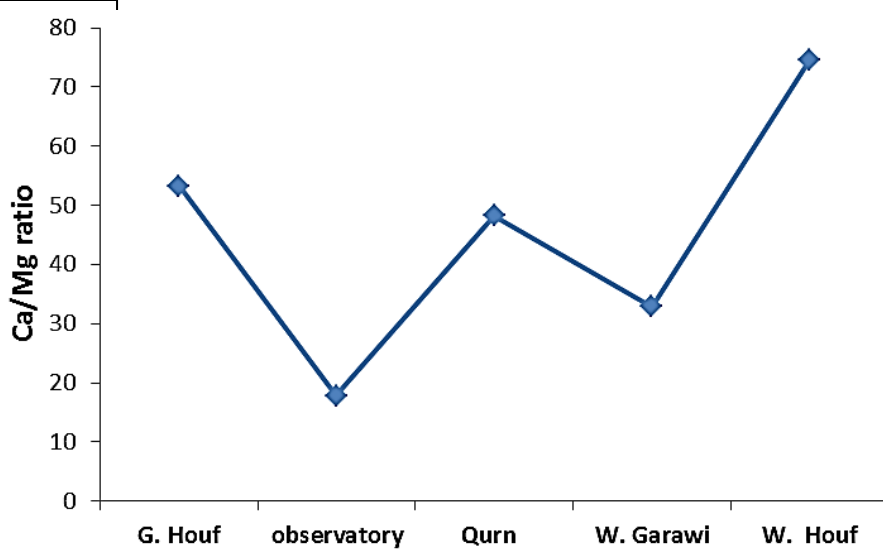


Fig. (9): Average Ca/Mg in Middle and Late Eocene limestone

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