

## IR Spectroscopic Investigation, X-Ray Fluorescence scanning, and Flam photometer analysis for sediments and rock Samples of Al Gabal Al –Akhder Coast region (Libya)

Fatimah A. Abdulsayid<sup>1</sup>, Hamad M. Adress Hasan<sup>2</sup>, Huda A. Egoil<sup>3</sup>

<sup>1</sup>Chemistry Department, Faculty of Science, Benghazi University, Alkufra-Libya.

<sup>2,3</sup>Chemistry Department, Faculty of Science, Omar Al–Mukhtar University, Albaydha- Libya.

---

### Abstract

The methods which applied in this study to estimate the chemical composition, especially XRF – and IR , showed that: The samples under studied (Sediments and Rocks ) contain high levels of calcium and the IR spectra shows presence one major peak which gave indicate that the main composition is  $\text{CaCO}_3$  mixed with small amounts of  $\text{CaO}$ . Also, the X –Ray analysis recorded Al and Si metals in most samples, this is mainly attributed to presence other ores as feldspar or silica, the presence of magnesium in the most is concern to magnesium – calcite carbonate (Dolomite). Generally, this study concluded that the sediment and rocks of Al – Gabal Al –Akhder (Libya) coast mainly composed by calcite with minor contents with other oxides.

**Keywords:** Sediments and Rocks, XRF, IR, Ras AL-hilal, Susah, Easterner coast, Libya.

---

Date of Submission: 10-04-2021

Date of Acceptance: 26-04-2021

---

### I. Introduction

Coastal sediments usually serve as sinks for river-borne metals released in terrestrial ecosystems by weathering and human activities<sup>[1][2][3]</sup>. Mineral analysis offers an immediate area of study as well as an important method on an economic scale. Thin section study, X-ray diffraction (XRD), and FT-IR spectroscopy are some of the approaches used to classify minerals using standard techniques. Because of its significance in determining environmental change, the mineral composition of coastal and marine sediments is of great interest. A number of studies on the mineral distribution of the coastal environment have been performed, and it has been discovered that the morphology of the mineral distribution in the marine environment is an indicator of the sediment source and sea level<sup>[4][5]</sup>. Anthropogenic activities can affect and alter the mineral composition of marine sediments. Mineral composition, sediment texture, adsorption, desorption processes, and various physical-chemical characteristics all influence metal aggregation and distribution<sup>[6]</sup>. Metal concentrations in sediments are commonly found near industrialized harbors and coastal regions in the marine environment<sup>[7]</sup>. Similar research has been conducted in South Africa.<sup>[8][9][10][11]</sup> Materials derived from rock, soil, and anthropogenic sources make up sediment particles. The basic structural units of inorganic sediments are silicate and aluminosilicate<sup>[5][12][13]</sup>.

This study was carried out on sediments and rocks samples collected from different sectors around Easterner coast for Al Gabal Al -Akhder ( Libya), The aims of study can be summarized in the following: (1) Determining the forms of chemical composition of sediments and rocks using one of Nanotechnology's techniques (X-Ray Fluorescence). (2) Description of the key functional community in the analyzed rocks and sediments samples using infrared spectra (I.R). (3) Measure the metal content of the rocks and sediments in the investigation region based on their chemical compositions.

### Experimental

#### Sampling:

Six sediments and rock samples were collected from different three locations distributed at Easterner coast of Al Gabal Al -Akhder region (Libya). Sediments and Rock samples were collected during winter 2015. The samples were selected from East Ras AL-hilal, to West Susah, and Easterner coast, at each section Sediments and Rock soil samples. The collected samples were kept in polyethylene bags and transferred to central unit of chemical analysis, Faculty of Science, Omar El–Mukhtar University.

#### Sample preparation:

The samples were washed with distilled water then grinded in mortar then garbled. **Samples analysis:**  
The samples were analyzed using XRF and I.R and Flam photometer.

#### **X-Ray Fluorescence scanning (XRF):**

The X- Ray micro scanning of the samples were carried out by using X-ray scanning at the central lab (X- Ray unit) of Alexandria University, Faculty of science.

#### **Infrared Red spectra ( I.R ):**

The infrared analysis of the samples were measured by using (I.R instrument Type perklen at Faculty of Science, Omar El –Mukthar University.

#### **Carbonate content:**

The carbonate content was measured by titration with 0.1 M HCl by Ph. Ph (indicator) method.

#### **Major elements:**

0.5 gram of sample was designed with 5ml of concentrate HCl, the samples filtered then transferred into 100 ml measuring flask by distilled water (Sodium, Potassium and Calcium) were measured by Flam phoetmetr, Magnesium was determined by titration method with EDTA in presence of E.B.T. indicator.

## **II. Results And Discussion:**

#### **Carbonate:**

The total carbonate content is certainly the most important environmental factor and of the equilibrium system in the marine environmental. It plays an important role in constructing the shells in all species<sup>[14]</sup>.  $\text{CaCO}_3$  precipitation is controlled by photosynthesis<sup>[15]</sup>. Although many calcite rich sediments may have largely allergenic source of carbonate, many other lacustrine carbonate sediments are truly androgenic. Their principal constituents have been precipitated directly from the water column. In this study the carbonate contents were fluctuated in the following ranges of (54 – 57.6 %) and (44.1 – 49.70 %) in sediment and rock samples, respectively. It was reported that the concentration of carbonate in the sediments is attributed to the aquatic plants and phytoplankton applied to extra  $\text{CO}_2$  and thus promote precipitation of carbonate with the increase of  $\text{p}^{\text{H}}$ .

#### **Major Cations**

##### **Calcium:**

The values of calcium concentrations in sediment and Rock samples and the area under study, (Tables 1,2) and (Figures 1-6), were ranged between (40–43 %) and (40.2 – 49.10 %) in sediment and rock samples. The high values may be due to biogenic origin, where organisms living in the water readily abstract calcium to form their skeletal framework. So, when these organisms died, their skeletons begin to decay<sup>[16]</sup>. Generally, the change in calcium content, may be attributed to several factors such as the biodetrital mixture of mollusks, coralline, algae, echinoids, formation tests, carbonate petetiods and the precipitation of  $\text{CaCO}_3$  from the water column.

##### **Magnesium:**

The values of magnesium concentration in sediment in the studied area.(Tables 1,2 and Figures 1-6), were ranged between 2.20 at Ras AL-hilal region and 1.40 mg/g at Easterner coast, and Rock sample ranged between 6.15 mg/g at Ras AL-hilal and Easterner coast 1.20 mg/g probably due to precipitation of  $\text{Mg}^{+2}$  as carbonate.

##### **Sodium:**

The levels of sodium concentration in the sediment and Rock of studied area (Table 1, 2 and Figures 1-6) were ranged between 0.40 at Ras AL-hilal and 0.28 mg/g at Easterner coast, and 0.15 mg/g at Susah, 0.40 mg/g at Easterner coast in rock sample. The slight variation in the concentrations of sodium can be attributed to minor changes in mineralogy or grain size of sediments. The high sodium contents in marine sediment may be attributed to the ability of certain organisms to concentrate sodium.

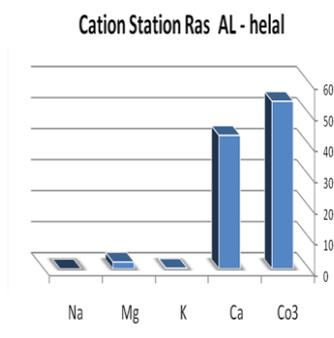
##### **Potassium:**

The values of  $\text{K}^+$  concentrations in sediment and rock samples (Tables 1, 2) assigned ranges between 0.18 and 0.22 mg/g at Susah and Easterner coast respectively, and 0.35 mg/g at Easterner coast and 0.10 mg/g for Susah. In general, the order of major cations concentrations in the sediments of the investigated area are given in the following order :

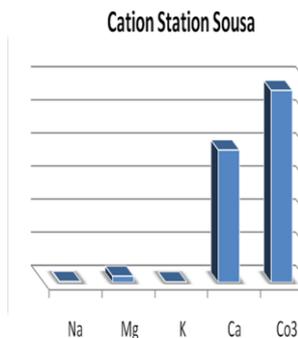


**Table (1):** Concentrations of major cations Ca% (Mg , Na and K) (mg/g) in Sediment during winter (2015).

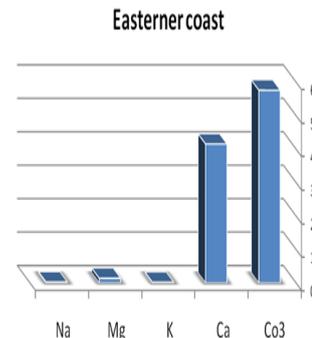
Location	Parameter				
	CO <sub>3</sub> %	Ca%	Mg (mg/g)	Na(mg/g)	K(mg/g)
Ras AL-hilal	54	43	2.20	0.40	0.22
Susah	58	40	1.92	0.30	0.18
Easterner coast	57.6	41.5	1.40	0.28	0.20



**Figure (1):** The carbonate and minerals concentrations in sediment at location Ras AL-hilal



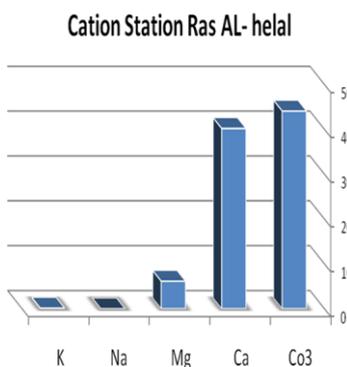
**Figure (2):** The carbonate and minerals concentrations in sediment at location Susah



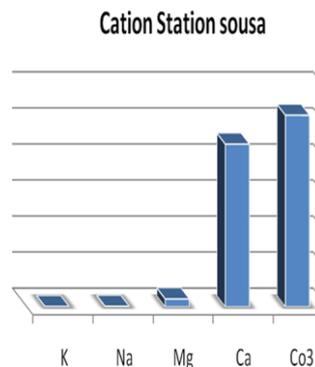
**Figure (3):** The carbonate and minerals concentrations in sediment at location Easterner coast.

**Table (2):** Concentrations of major cations Ca% (Mg , Na and K) (mg/g) in Rocks during winter (2015).

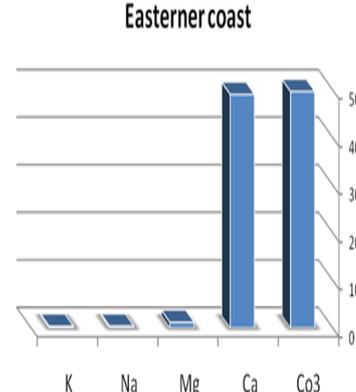
Location	Parameter				
	CO <sub>3</sub> %	Ca%	Mg (mg/g)	Na (mg/g)	K(mg/g)
Ras AL-hilal	44.1	40.20	6.15	0.30	0.15
Susah	53.12	45.13	2.20	0.15	0.10
Easterner coast	49.70	49.10	1.20	0.40	0.35



**Figure (4):** The carbonate and minerals concentrations in rock at location Ras AL-hilal.



**Figure (5):** The carbonate and minerals concentrations in rock at location Susah.



**Figure (6):** The carbonate and minerals concentrations in rock at location Easterner coast.

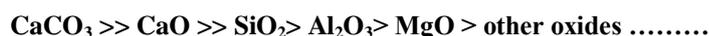
**X-ray Fluorescence (XRF).**

The contents of the elements oxides of the studied samples are shown in Figures (7-9) and curves (10-15) and represented in Table (3). The results showed that the concentration contents of metal oxides in sediments and rocks samples at location Ras AL-hilal were contain high levels for calcium carbonate (CaCO<sub>3</sub> ). While the metal oxides in sediments and rocks of sample Ras AL-hilal recorded (NaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SO<sub>3</sub>,

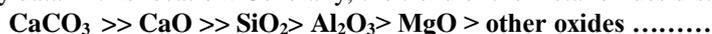
CaO, CuO, ZnO, and Fe<sub>2</sub>O<sub>3</sub>) are extant rate lower at location Ras AL-hilal in comparison with carbonate in both sediments and rocks samples. The trend distribution of oxides at this location is in order of:



in both Sediments and Rocks samples. These results which recorded by X –Ray analysis are agreement with the chemical analysis which recorded high levels of calcium and carbonate. Meanwhile, the metal and carbonate contents at the location Susah, of the metal oxides were in Table (3) and (Figure 8). The results showed high levels of calcium carbonate in rocks and sediments samples at this location are also the Al<sub>2</sub>O<sub>3</sub> oxide content in Rocks sample at location Ras Al-hilal are higher than those reported at location Susah, this mainly due to presence on of silicon ores as silica of feldspar, where aluminum oxide also recorded at this location. In all sediments and rocks samples, the distribution of metal oxides follows the following pattern:



On the other side the contents of the metal oxides at the location Easterner coast, are presented in Table (3) and Figure (9). The results at this location not recorded zinc oxide (ZnO) in Sediments and rocks samples. As the other locations the carbonate group exhibit very high content comparing with metal of oxides which appearance in X- Ray data in this location. Generally, the trend of the metal oxides distribution is as the following order:



in both Sediments and Rocks samples, the presence or absence of some rare metals at some locations mainly due to presence different or other types of ores which may contain metals, but the major component of the samples under studied is Ca, and recorded high levels as CaCO<sub>3</sub> with CaO.

**Table (3) :**The values of the metal oxides % in Sediments and Rocks samples of locations (Ras AL-hilal, Susah and Easterner coast).

Metal	Samples					
	Ras AL-hilal		Susah		Easterner coast	
	Sediments	Rocks	Sediments	Rocks	Sediments	Rocks
NaO	0.2	0.1	0.1	0.3	0.1	0.1
MgO	0.7	2.3	1.0	2.2	1.0	1.6
Al <sub>2</sub> O <sub>3</sub>	1.6	1.2	1.9	0.0	1.3	0.3
SiO <sub>2</sub>	0.2	2.7	3.1	1.4	0.9	0.1
SO <sub>3</sub>	0.6	0.6	0.4	0.4	0.7	0.4
CaO	11.1	10.5	10.3	10.6	10.7	11.6
CaCO <sub>3</sub>	83.0	79.7	80.5	81.4	83.8	84.7
Fe <sub>2</sub> O <sub>3</sub>	0.1	0.5	0.4	0.4	0.2	0.3
CuO	0.3	0.6	0.6	0.8	0.1	0.5
ZnO	0.2	0.4	0.5	0.5	-	-

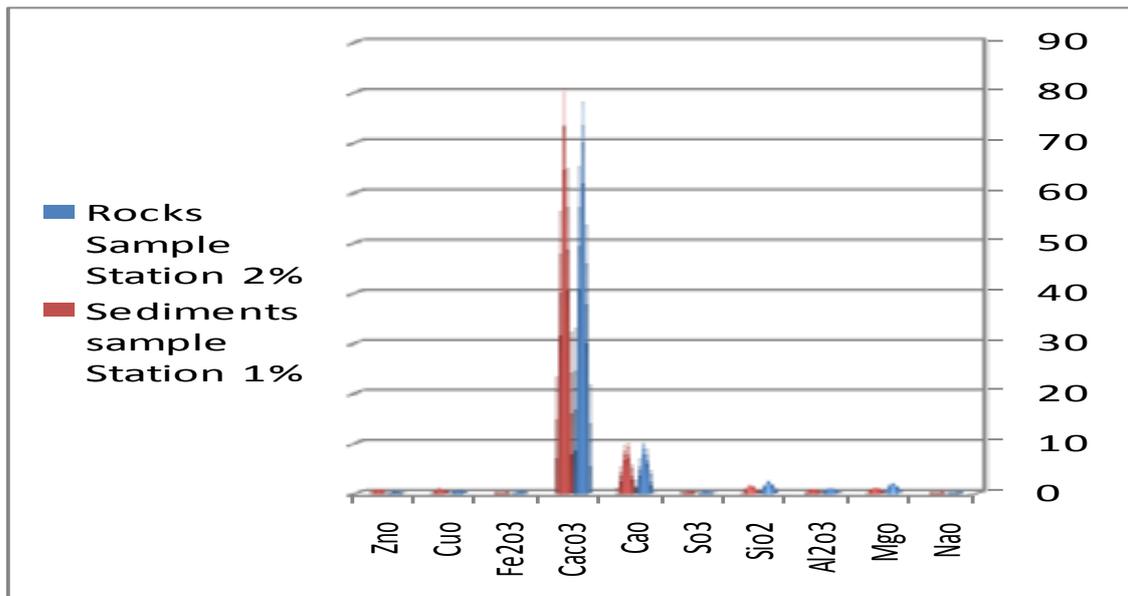


Figure (7): The oxides contents at location Ras AL-hilal.

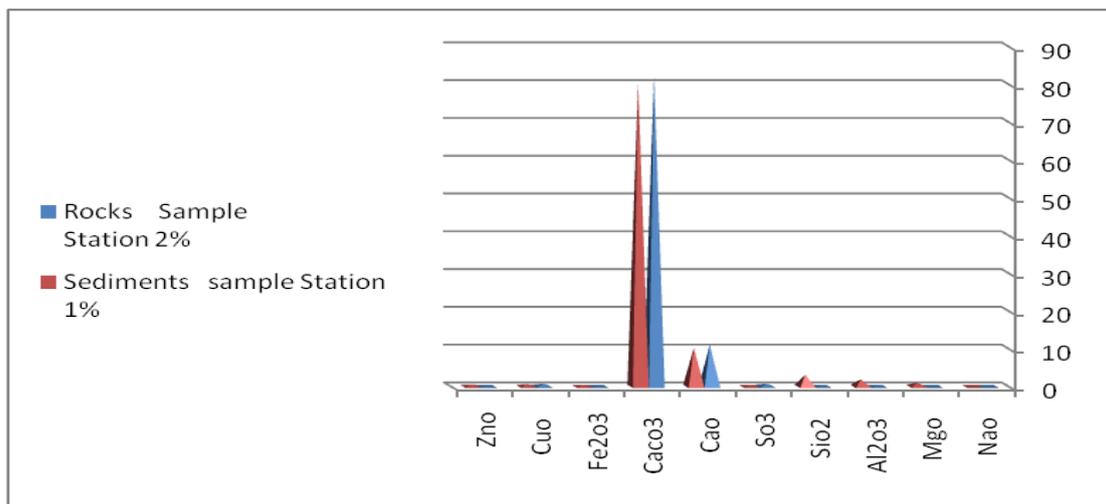


Figure (8): The oxides contents at location Susah.

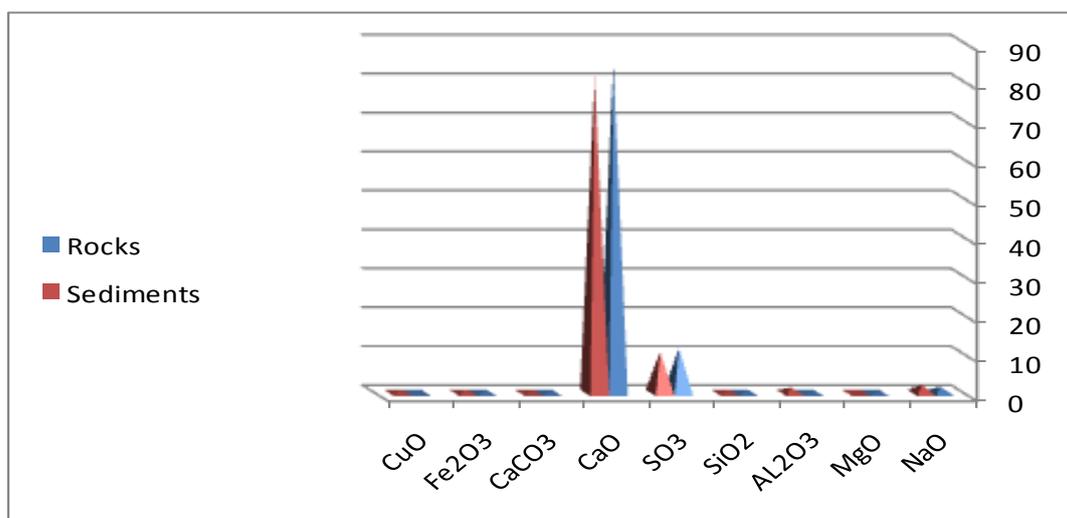
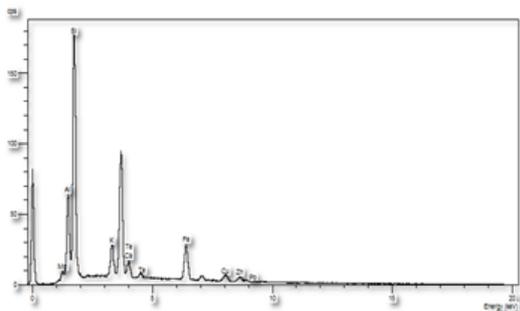
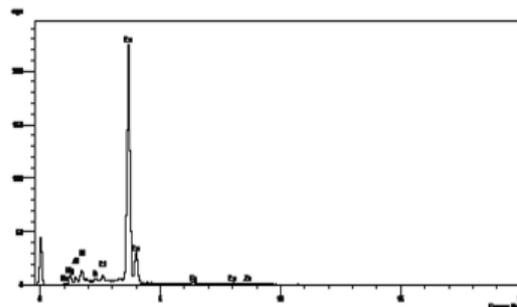


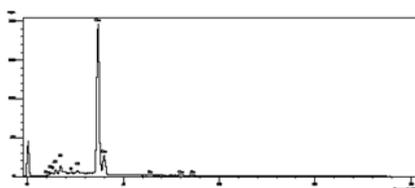
Figure (9) : The oxides contents at location Easterner coast.



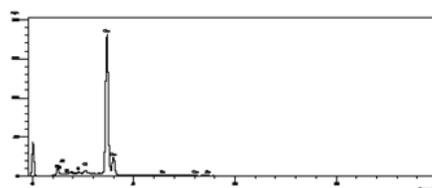
**Figure (10):** XRF curve of Sediments sample Ras Al-hilal.



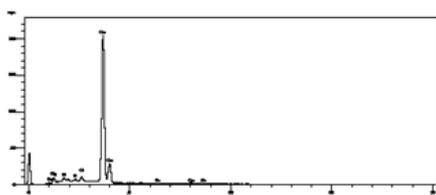
**Figure (11):** XRF curve of Rocks sample Ras Al-hilal.



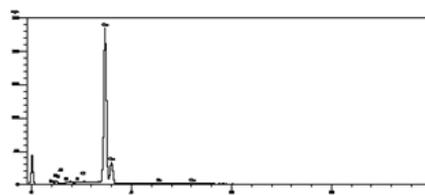
**Figure (12):** XRF curve of Sediments sample Susah.



**Figure (13):** XRF curve of Rocks sample Susah.



**Figure (14):** XRF curve of Sediments sample Easterner coast.



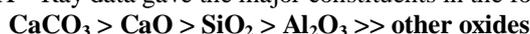
**Figure (15):** XRF curve of Rocks sample Easterner coast.

### III. Discussion of XRF results:

The concentration levels of the metal oxides that determined by XRF in Tables (3). showed relatively high levels of  $\text{SiO}_2$  at location Ras AL-hilal sediments and rocks are (0.2-2.7%), respectively. whereas, the lowest concentration  $\text{SiO}_2$  was observed at location Easterner coast in rocks in sediments with value of 0.1%. On the other side the lowest concentration for  $\text{Al}_2\text{O}_3$  was observed at location Easterner coast in rocks with 0.3%, and not extant observed at location Easterner coast in sample sediments. The relatively high levels that recorded at location Ras AL-hilal for  $\text{MgO}$  in rocks with value 2.3%, and relatively lowest concentration for  $\text{MgO}$  observed at location Ras AL-hilal in sediments with 0.7 %, while lowest concentration for  $\text{SO}_3$  observed at location Susah in sediments and rock are (0.4 - 0.4 %), respectively. The low levels for  $\text{CaO}$  observed at location Ras AL-hilal in rocks, and location Susah in marine sediments are (10.5 and 10.3%), respectively. Generally, Calcite is a carbonate mineral of calcium  $\text{CaCO}_3$  in all the samples is increases to maximum at all locations their high levels observed at location Easterner coast in sediments and rocks are of ranges (83.8 and 84.7%), respectively. While lowest levels for  $\text{CaCO}_3$  observed at location Susah in sediments. The concentration of  $\text{ZnO}$  was generally lower than that observed of  $\text{CuO}$  at all locations. While was high levels for  $\text{ZnO}$  that observed at location Susah in marine sediment and rock ranges (0.5 and 0.5 %), respectively, absence at location Easterner coast.

The presence of Al and Si of the samples are mainly due to  $\text{SiO}_2$  (Quartz), and the presence of Al in all the X-ray spectra is probably due to the clay minerals as potash feldspar ( $\text{KAlSiO}_8$ ) and / or Kaolininte ( $\text{Al}_2\text{Si}_2\text{O}_5$ ). The few contents of Mg may be due to the presence of small amounts of dolomite. The small

variations between location to another in the metal contents mainly due to presence the above ores in different concentrations. In general, the X – Ray data gave the major constituents in the following order:



**Infrared analysis(I.R):**

The spectra of infrared spectra are shown in Figures (16 - 21) and the fundamental bands are given in Table (4). Infrared spectra are normally used in mineralogy for quantitative analysis and identification of different minerals, even complex mixtures. It is based on positions and shapes of absorption bands<sup>[17]</sup>. Spectra of all samples under investigations are very nearly similar indicating that the constituents are almost the same. The main features of the soils absorption spectra are: (1) the hydrogen bonding of the structural OH<sup>-</sup> groups and (2), M-O vibrations in the tetrahedral, octahedral sub-layers and other associated oxide mineral<sup>[18]</sup>. The samples of the area under investigation showed a broad band at 3616 - 3696 cm<sup>-1</sup>) assigned for O-H stretching vibration of H<sub>2</sub>O which readily lost upon heating. These regions are mainly composed of calcareous soils containing amorphous silica. A weak bands at 2529 cm<sup>-1</sup> is characteristic for absorption of carbonate minerals (calcite and magnesium calcite).

Furthermore, the spectra of all samples showed strong broad feature at (2500 cm<sup>-1</sup>) characteristic for carbonate radical. It was reported that the band characteristic for pure calcite appears at 1400 cm<sup>-1</sup>. The in plane bending vibration band at 1080 cm<sup>-1</sup> for O-H in the sediment samples appears in all regions. However, the bands at 863 cm<sup>-1</sup> represent the bending in plane vibration band of O-H groups for MgAlOH. Carbonate minerals in all sediments are identified by the wave number of M-CO<sub>3</sub> stretching band at 715 cm<sup>-1</sup>. The symmetric Si O-Si stretching appeared as a weak bands at 450 cm<sup>-1</sup> and the bands between (500-650 cm<sup>-1</sup>) are assigned to the metal oxides. Generally, the I.R spectra are in harmony with the XRF analysis in presence of silicon and calcite or calcium oxide, in addition to presence of different peaks which could be related to metal oxides<sup>[19]</sup>.

**Table (4):** Fundamental infrared bands (cm<sup>-1</sup>) of soils samples.

Infrared bands (cm <sup>-1</sup> )	Assignment
3619 - 3696	v OH
3424 - 3442	v SiO <sub>4</sub>
2500	CO3 Minerals
1797 - 1798	δ H <sub>2</sub> O water deformation
1629 – 1938.2	v CO <sub>3</sub> coordinated
1030 - 1033.6	O-H in plan vibration
873.1 – 876.7	δ Al OH or Mg Al OH in plane vibration
694.53 – 796.11	v M-CO <sub>3</sub>
470.87 - 535	M – O

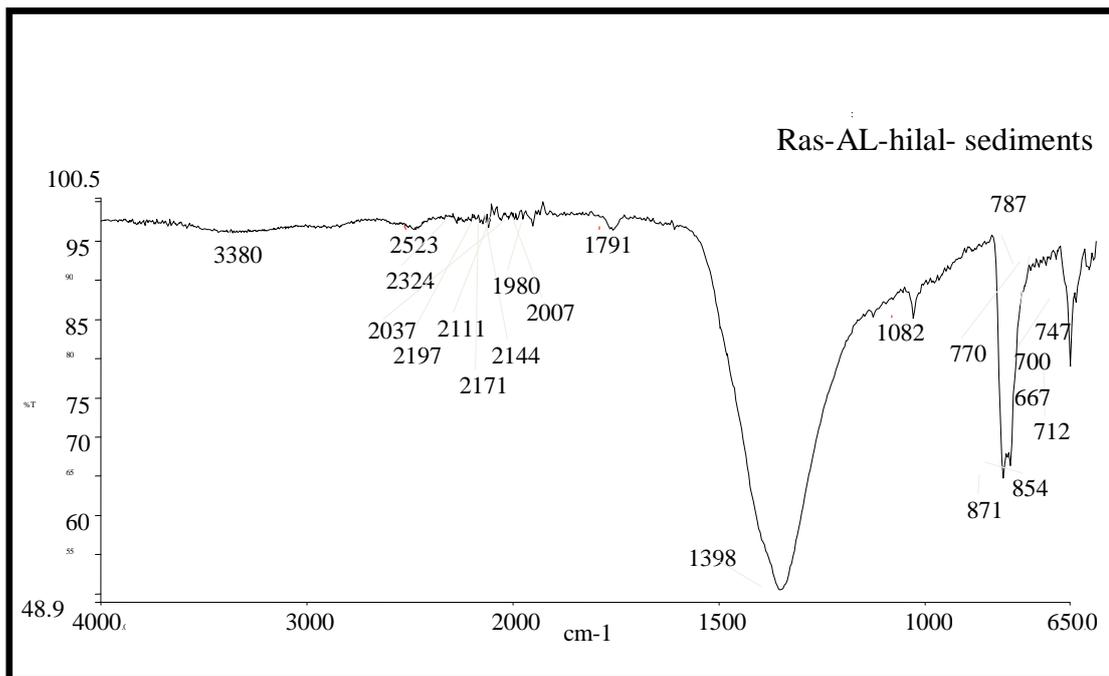


Figure (16): IR analysis for Ras AL-hilal sediments.

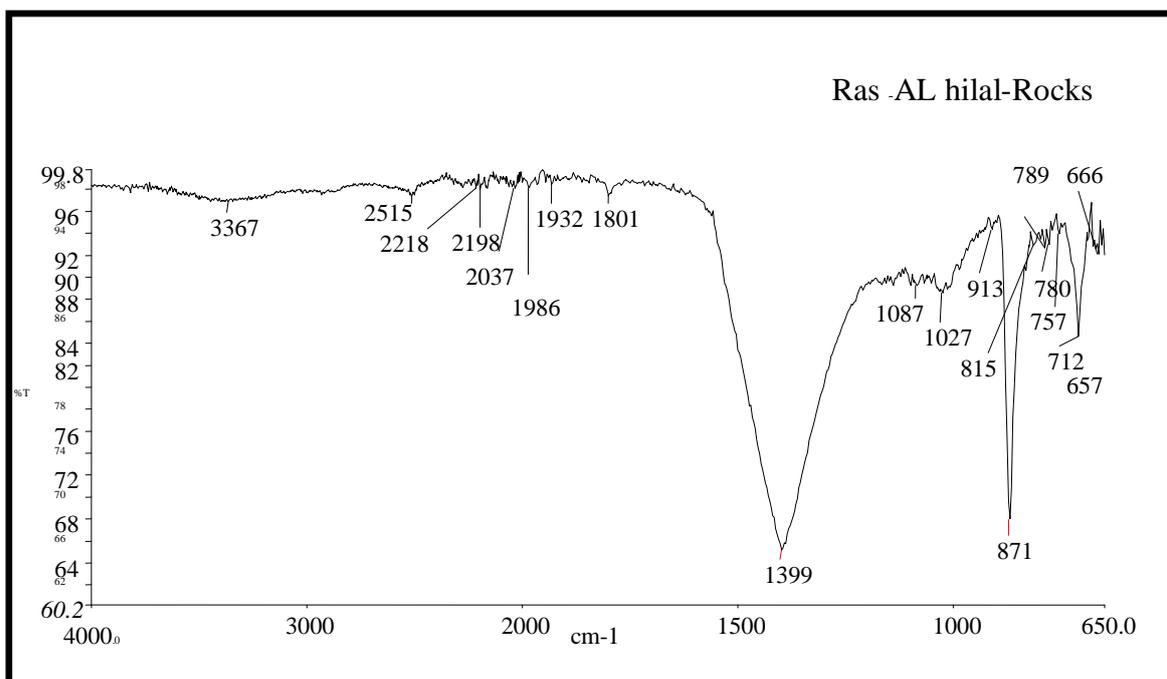


Figure (17): IR analysis for Ras AL-hilal Rocks.

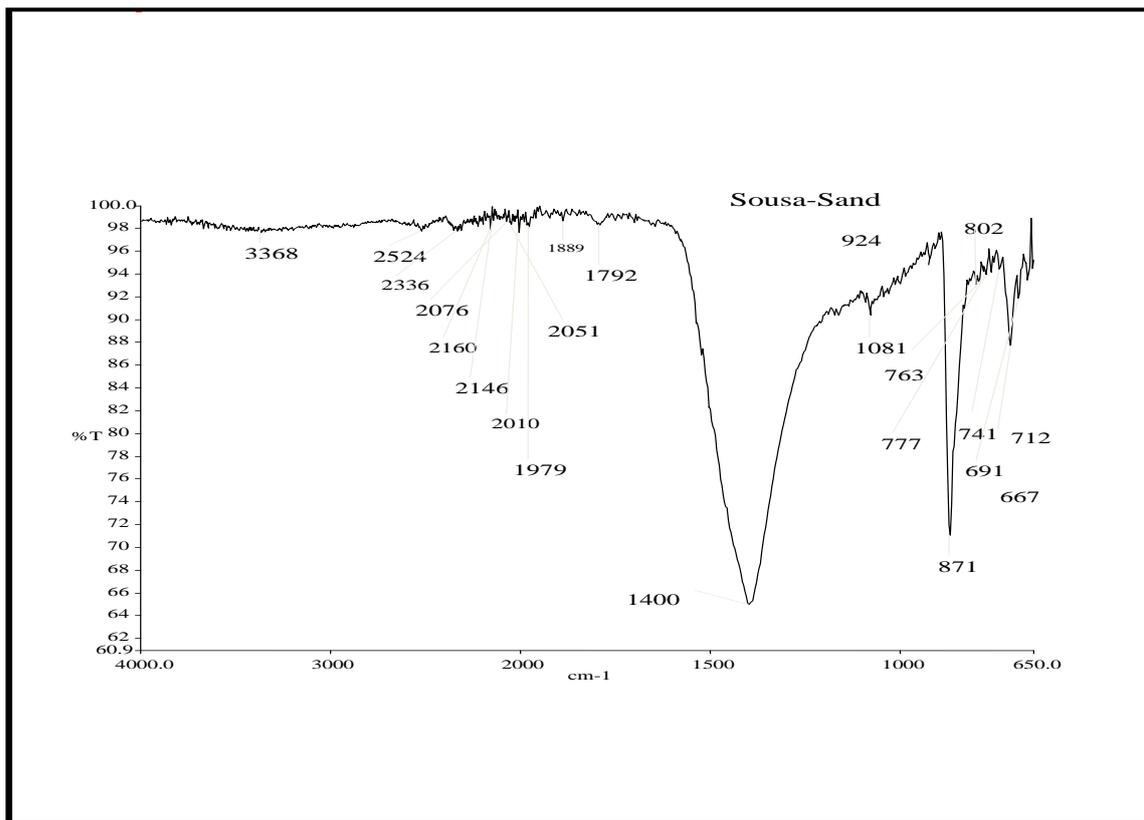


Figure (18): IR analysis for Susah sediments.

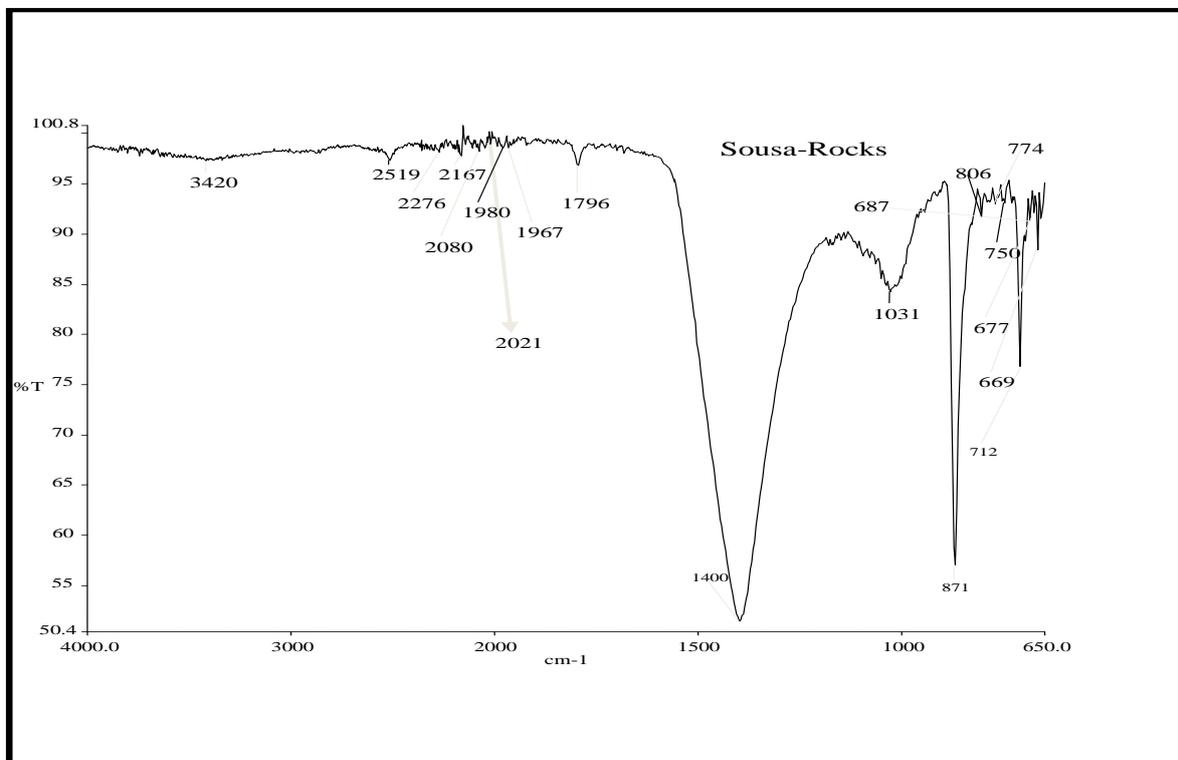


Figure (19): IR analysis for Susah Rocks.

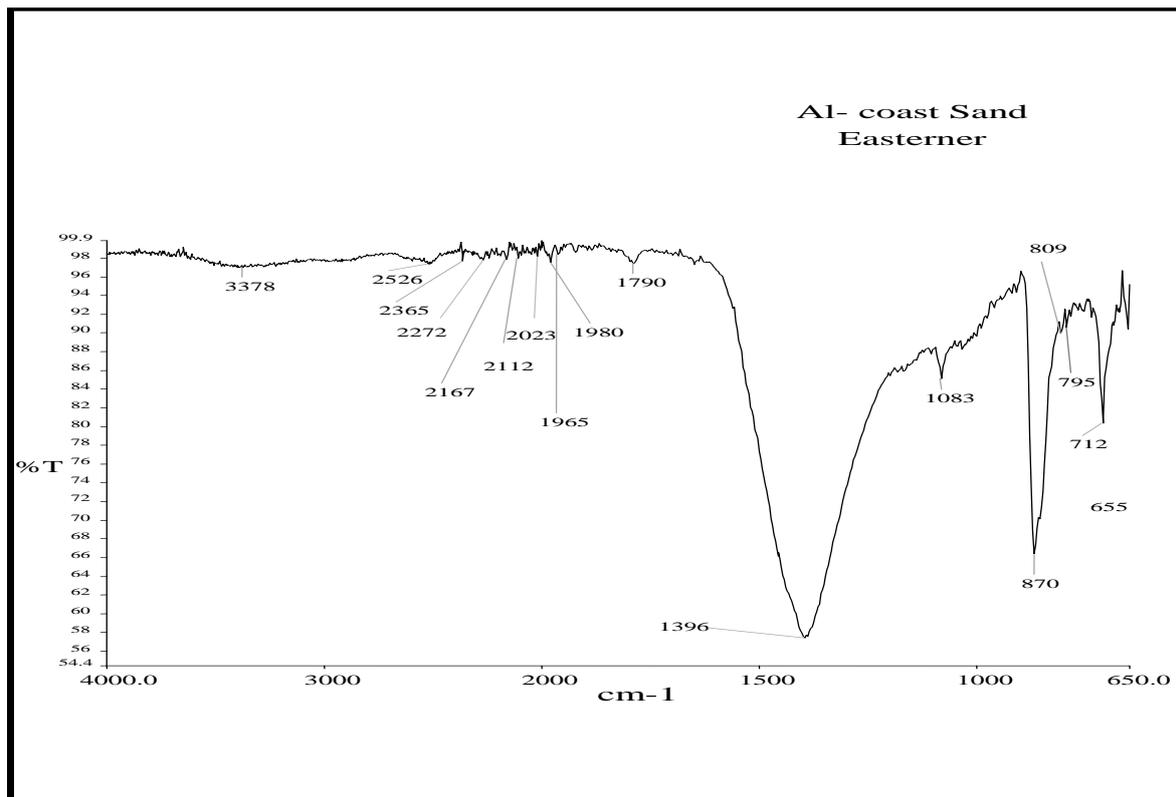


Figure (20): IR analysis for Easterner coast Sediments.

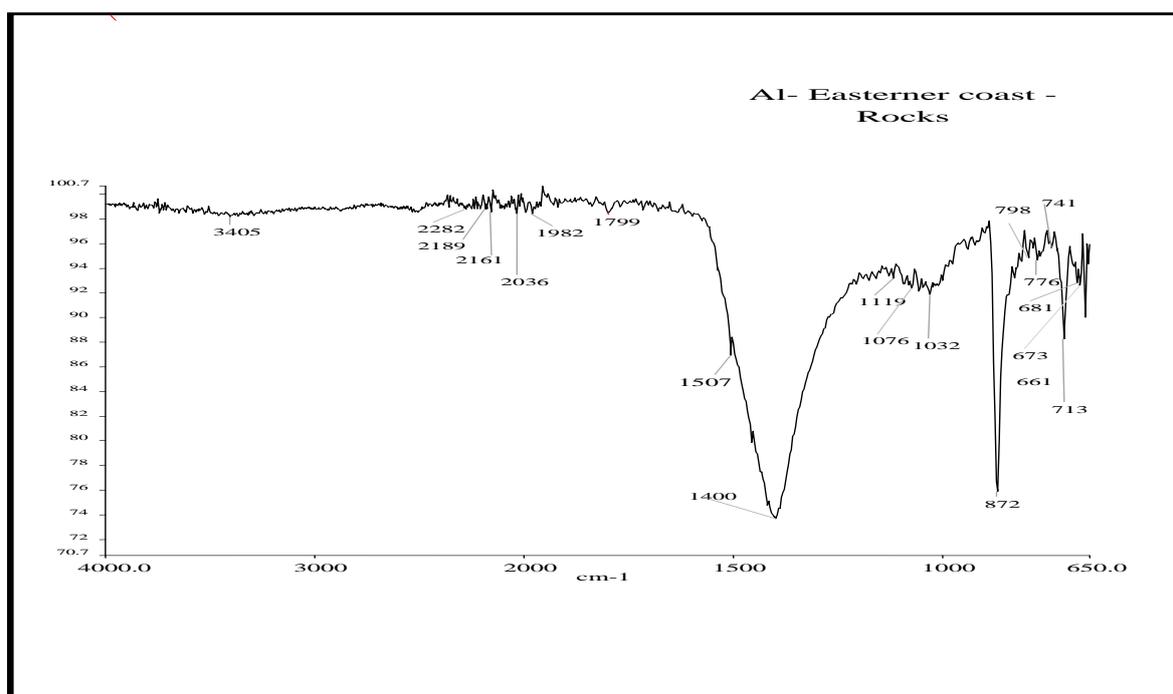


Figure (21): IR analysis for Easterner coast Rocks.

### References

- [1]. Ravisankar R. (2009) Application of Spectroscopic techniques for the identification of minerals from beach rocks of Tamilnadu. *EARFAM*. 19:272.
- [2]. Farmer VC. (1974 )The IR Spectra of Minerals. Mineralogical Society. London. 1974:182.
- [3]. Pichard C, Frohlich F. (1986) Quantitative IR analysis of sediments, Example of Quartz and Calcite determination. *Revue de I InstitutFrancais du Petrol*.;41:6.
- [4]. Mattesson, A. and Herron, M. M. (1993) .Studied the Geochemical Assessment of sediment in Cape Town Harbour, South Africa 9308 presented at the Society of Core Analysis Annual Meeting, August 9-11.
- [5]. Wang, Z.; Chen, Z.; Tao, J. J. Coastal Res. 2006,studied geochemical Assessment of sediment in cape town harbour, south Africa.
- [6]. Zahra, A., Hashmi, M. Z., Malik, R. N. and Ahmed, Z.(2014). Enrichment and geo-accumulation of heavy metalsand risk assessment of sediments of the Kurang Nallah Feeding tributary of the Rawal Lake Reservoir, Pakistan .*Science of the Total Environment*, 470–471, 925933.
- [7]. Wang, X. C., Feng, H., Ma, H.Q. 2007. Assessment of Metal Contamination in Surface Sediments of Jiaozhou Bay, Qingdao, China. *Clean*, 35 (1), 62–70.
- [8]. Binning, K.; Baird, D.( 2001) Studied the Geochemical Assessment of sediment in Cape Town Harbour , south Africa *Water SA* 27, 461.
- [9]. Fatoki, O.S.; Awofolu, R.O. J. (2003) Studied the Geochemical Assessment of sediment in Cape Town Harbour , south Africa *Chromatogr*. 98,225.
- [10]. Shuping, L.S.; Snyman, R.G and Odendaal, J.P and Ndakidemi, P.A. (2011) *Water Air Soil Pollut.*, 216,319.
- [11]. Fatoki, O. S.; Okoro, H. K.; Adekola, F. A.; Ximba, B. J.; Synman, R.G.(2012). Studied the Geochemical Assessment of sediment in Cape Town Harbour , South Africa *The Environmentalist* 32,48.
- [12]. Fatoki, O. S.; Awofolu, R. O. J. (2003) Studied the Geochemical Assessment of sediment in Cape Town Harbour , south Africa *Chromatogr*. 98,225.
- [13]. Kovac, I.; Hugh, S. C.; Neill, O.; Hermann. J and Hauri, E. H.(2010), Studied the Geochemical Assessment of sediment in Cape Town Harbour , South Africa *American Mineralogists* 95, 292.
- [14]. Serruya, C. (1970). Problems of sedimentation in lake of Geneva. *Vert.Int. Limnol*.
- [15]. Lermman ,A.(1978). *Lakes, Chemistry .Geology, Physics, Spiger voltage* ,New York ,356 pp.
- [16]. Honisch ,B, A. Ridgwell, D.N. Schmidt, E. Thomas, and S. J. Gibbs (2012)*The Geological record of ocean acidification*, *Science* 335 ,1058.
- [17]. Vagenas N. V., A. Gatsouli, C. G. Kontoyannis, Quantitative analysis of synthetic calcicum carbonate polymorphs using FTIR spectroscopy, *Talanta* 59 (2003) 831–836.
- [18]. Chandrasekaran A. A., A. Rajalakshmi a, R. Ravisankar b, S. Kalarasai (2015), Analysis of beach rock samples of Andaman Island, India by spectroscopic techniques.
- [19]. Sivakumar R , Ravisankar R, A. Chandrasekaran3 and J. Prince Prakash Jebakumar (2013), FT-IR Spectroscopic Studies on Coastal Sediment Samples from Nagapattinum District, Tamilnadu, India.

Fatimah A. Abdulsayid, et. al. "IR Spectroscopic Investigation, X-Ray Fluorescence scanning, and Flam photometer analysis for sediments and rock Samples of Al Gabal Al –Akhder Coast region (Libya) ." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 14(4), (2021): pp 20-30.