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THERMAL ANALYSIS (TGA), DIFFRACTION THERMAL ANALYSIS (DTA), INFRARED AND X-RAYS ANALYSIS FOR SEDIMENT SAMPLES OF TOUBROUK CITY (LIBYA) COAST

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ABSTRACT

Thermal analysis (TGA & DTA), Infrared (I.R) and X-ray measurements for sediment samples collected from near shore locations at Tobrouk city (Libya) coast were used to identification of the chemical structure of sediments. The results showed that all sediments have the similar peaks of TGA and DTA curves are composed mainly one major peaks, the high decomposition was occurred in the temperature range of (700-900^{o}C) with loss weights at the above temperature decomposition ranged between (33.10-38.55%), also the DTA curves show one high peaks ranged between (786.79821.25^{o}C). These peaks mainly attributed to the presence of the calcite $CaCO_3$ and / or magnesium calcite Ma $CaCO_3$. The microscope (X-ray) analysis also give high contents of calcium in all the studied samples in the presence of minor minerals as calcium and magnesium, this is agreement with the TGA & DTA measurement. The I.R. curves of all samples are very similar indicating that the constituents are almost the same, where high broad peaks feature in the range of (1400-1449 cm^{-1}) characteristic for carbonate radical. Also the M-O bands were appeared at the range of (702-715 cm^{-1}).

Key words: Tobrouk coast sediment, Thermal analysis, I.R., X-ray.

INTRODUCTION

Thermal analysis plays an important role in the environmental studies[1]. Sediments mineral analysis is essential and usually requires the use of two or more supplementary analytical techniques for establishing the nature of minerals present[2]. If the kinetic mechanism is known, calculation can be made to demonstrate quantitatively the effect of procedure variables, such as sample mass and heating rate on the appearance of an experimental thermal analysis curve[3].

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Tobrouk region lies at the eastern north of Libya. The beaches of Tobrouk are covered with well-sorted sands mixed with shell fragments of various marine organisms. This work aims to characterize some Tobrouk coast sediments using thermal (TGA & DTA) and structural (IR and X-ray) studies.

EXPERIMENTAL

Materials and methods

Surface sediment samples were collected from five different locations on Tobrouk city coast (Fig. 1).

Sampling was performed during Spring (2013) from near shore of the investigated area. The samples were kept in polyethylene bags, and washed with distilled water and dried at 85^{o}C in an oven, then grinded in mortar. Thermal analysis (TGA) and (DTA) were carried out using a Shimadzu DTA/TGA-50 instrument located at central laboratory of Doky Center Cairo, X-ray powder microscope were recorded by Pentaler link ISIS. Sediment samples were analysis scanining microscope spectra were taken in the range of 1-8 Kev and I.R. curves were recorded by infrared Perkin-Elmer 1430, Ratio recording spectrophotometer.

Fig. 1: The area of study

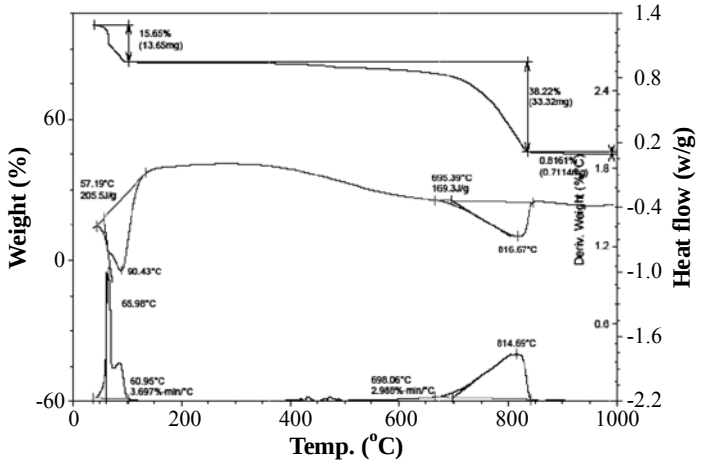
RESULTS AND DISCUSSION

Thermal analysis

The quantitative estimation of calcite fraction can be achieved based on thermal analysis technique. The loss in mass in the temperature range 50-150^{o}C is considered due to dehydroxylation of clay, while that in the range of 786.79-821.25^{o}C is due to calcite decomposition with the evolution of CO_2 gas[4]. However, it is difficult to calculate the molecular weight of each clay minerals, because of the many possibilities of substitution inside the lattice[5], but only the estimation of relative values is possible.

The thermo gravimetric analysis curves of the sediment samples are composed mainly of one peak (Figs. 2). However, these samples are mainly calcite mixed with magnesium calcite minerals as reported[6]. One can say that the reported data of the southern of coast of Mediterranean sea is mainly consisting of calcareous organisms such as algae, mollusks, echinoids, protozoa and carbonate peteoids with amorphous silica[7]. The mass losses obtained from the TG (Figs. 2), are very useful to estimate directly the presence of gases (H_2O and/or CO_2) evolved from all samples[4].

The TG curves calculations of the all sediment samples under study (Figs. 2), indicated that the decomposition of calcite occurred at a lower temperature than reported[4] (750-1000^{o}C), i.e. < 750. The decomposition of carbonate minerals in these samples may be associated to the ease of reversibility of calcite decomposition. Whereas, the decarbonation temperature is affected by the amount of CO_2 gas present during firing[8] and the presence of magnesium calcite. The thermal data are in harmony with the reported records[4] for the mineral composition of southern category of coast of Mediterranean sea.



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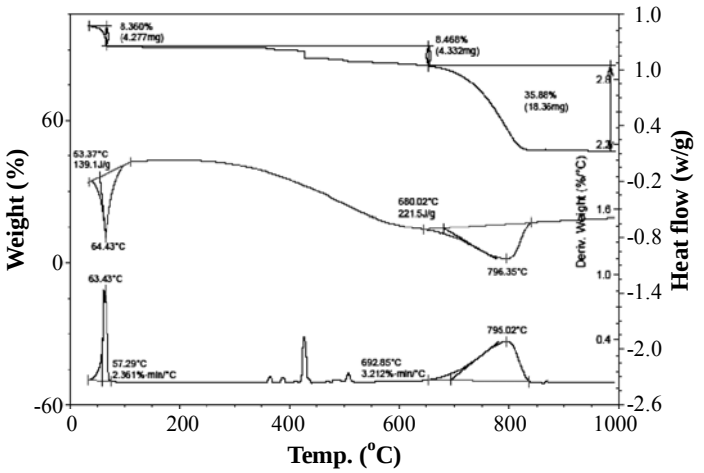
8.360%
(4.277mg)
8.468%
(4.332mg)
35.88%
(18.36mg)
63.37°C
139.1J/g
64.43°C
680.02°C
221.5J/g
796.35°C
63.43°C
57.29°C
2.361%-min/°C
692.85°C
3.212%-min/°C
795.02°C
Weight (%)
Heat flow (w/g)
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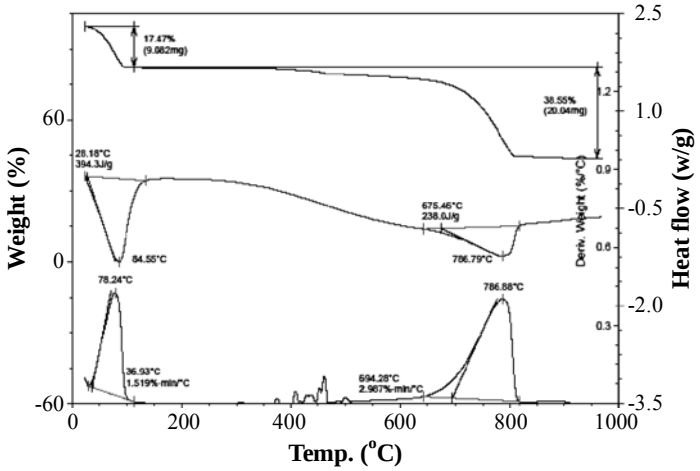
17.47%
(9.082mg)
38.55%
(20.04mg)
28.18°C
394.3J/g
84.55°C
675.46°C
238.6J/g
786.79°C
78.24°C
36.93°C
1.519%-min/°C
694.28°C
2.967%-min/°C
786.88°C
Weight (%)
Heat flow (w/g)
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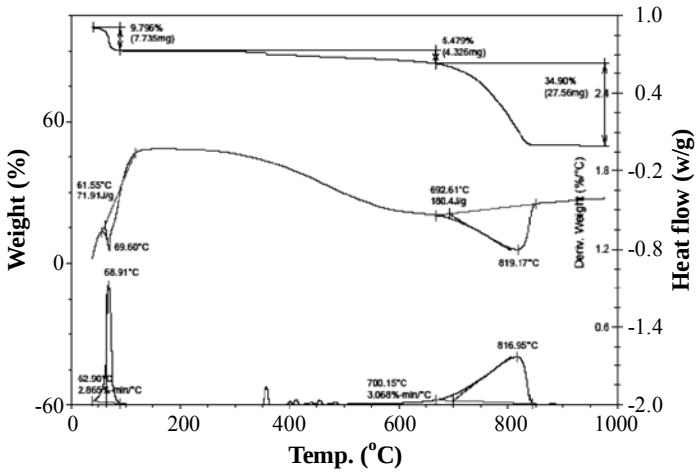
Temp. (°C)


9.796%
(7.735mg)
5.479%
(4.326mg)
34.90%
(27.56mg)
61.55°C
71.91J/g
69.60°C
692.61°C
180.4J/g
819.17°C
68.91°C
62.90°C
2.865%-min/°C
700.15°C
3.068%-min/°C
816.55°C
Weight (%)
Heat flow (w/g)
Deriv. Weight (%/°C)
Temp. (°C)

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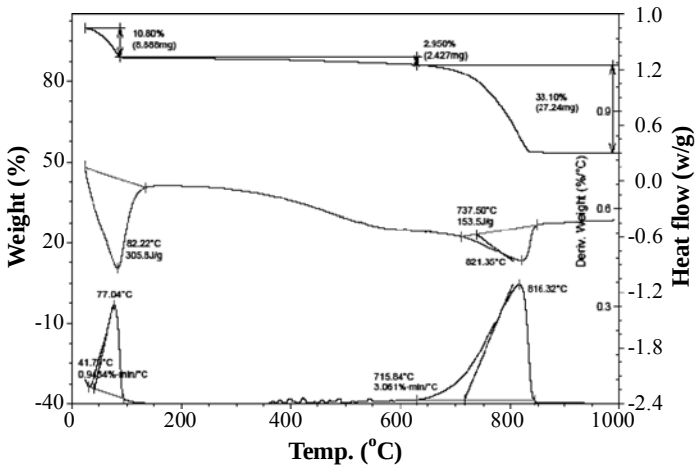


Fig. 2: Thermo gravimetric analysis (TGA and DTA) for sediment samples

The small losses in mass in the temperature range of 50-150°C is considered to the dehydration of grain boundary water[9]. However, the amount of water adsorbed on clay minerals evidently depends on the relative humidity of the external atmosphere, the nature of cations occupying exchange sites between the layers of the structure skeleton, the grain diameter distribution of the sample and the concentration of structure defects[10].

Kinetic study of TGA

The thermo gravimetric data are used to evaluate the kinetic parameters of solid state reactions involving weight loss (or gain) are of wide spreading[11]. However, it was stated some of the advantages of this method over conventional isothermal studies.

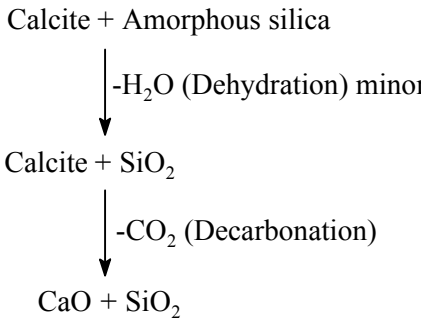
Many models have been developed for decomposition mechanism and methods have been worked out for solving the differential equation to represent solids determined under isothermal and non-isothermal conditions. The retrieval of kinetic parameters from weight loss versus temperature data can be done using several techniques[12].

The decomposition fraction g (α) as a function of temperature for all the TGA curves belongs to the sediment samples seems to be linear using the following equation.

$$\mathrm{Log}\left[\frac{g(\alpha)}{T^2}\right] = \mathrm{Log}\left[\frac{AR}{\phi E_a}\right] - \frac{E_a}{2.3RT} = \mathrm{Log}\left[\frac{AR}{\phi E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.3RT}$$

where, A (Arrhenius frequency factor) and ϕ (heating rate) have the usual meanings.

The thermal decomposition equation of sediment samples is given as follows:



However, decarbonation of calcite seems to be at 625-782.48, 630-78.82 and 651-782.59^{o}C, for samples, respectively. This can be considered as the second step. It was stated that raw calcite decarbonated at the temperature range of 500-900^{o}C[13].

Table 1: Kinetic values for the sediment samples

Sediment sample	Temp. (^{o}C)	Weight %	E_a KJ/mole	A(S^{-1})
Station (1)	700-800	38.20%	155.76	0.37
Station (2)	650-750	35.88%	172.32	0.24
Station (3)	700-780	38.55%	135.94	0.21
Station (4)	625-800	34.90%	143.89	0.43
Station (5)	610-800	33.10%	122.5	0.19

The steps are due to decarbonation.

DTA analysis

The DTA curves of the sediments samples of the investigated area (Fig. 2), gave one large endo-exothermic peaks (Table 2). The samples are generally characterized by presence large peak in the temperature range of due to evaluations of CO_2 gas (788.79-821.35^{o}C) in harmony with the the previously TGA curves. The lower temperature range of carbonate decomposition than the reported for pure calcite (750-1000^{o}C) may be attributed due to the presence of small impurtes contents within the carbonate[4]. The small peaks observed at temperature range (64.43-93.43^{o}C) indicated the presence of small contents of quartz (SiO_2). This may explain the presence of Si peak in X-ray analysis.

Table 2: Endo and exothermic peaks for the sediments samples

Station	Start temp. (^oC)	Final temp. (^oC)	Peak
1	57.19	848	816.67
2	53.37	840	798.35
3	28.18	825	788.79
4	61.55	820	819.17
5	20	825	821.35

Infrared spectra

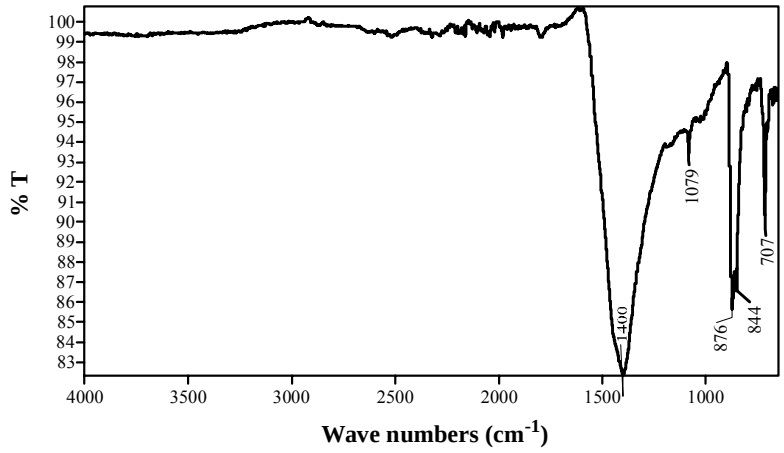
Infrared spectra are normally used in mineralogy for quantitative analysis and identification of different minerals, even complex mixtures. It is based on positions and shapes of absorption bands[14].

Spectra of all sediment samples are very nearly similar indicating that the constituents are almost the same. The main features of the sediment absorption spectra are: (1) the hydrogen bonding of the structural OH groups (2) M-O vibrations in the tetrahedral, octahedral sub-layers and other associated oxide mineral[15].

Sediments of the area under investigation (Table 3 and Fig. 4), showed a broad band at 3453 cm^{-1} assigned for O-H stretching vibration of H_2O which readily lost upon heating[16]. These regions are mainly composed of calcareous sediment containing amorphous silica. A weak band at 2529 cm^{-1} is characteristic for absorption of carbonate minerals (calcite and magnesium calcite). Furthermore, the spectra of all samples showed strong broad feature at 1445 cm^{-1} characteristic for carbonate radical (Table 3 and Fig. 3).

Table 3: Fundamental infrared bands (cm^{-1}) of sediment samples from different locations of Tobrouk coast (Libya)

Infrared bands (cm^{-1})	Assignment
3667-3689	ν OH
1788-1810	δ H_2O water deformation
1440-1449	ν CO_3 coordinated
1082-1159	O-H in plan vibration
868-876	δ AlOH or MgAlOH in plane vibration
704-715	ν M-CO_3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Wave numbers (cm-1)
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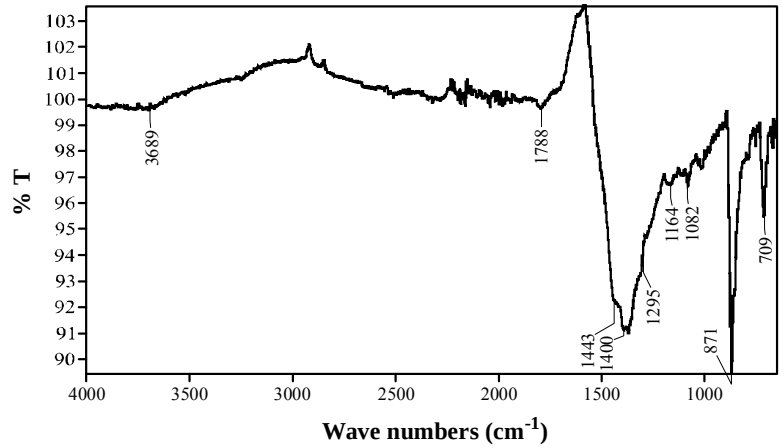
1079
876
844
707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1082
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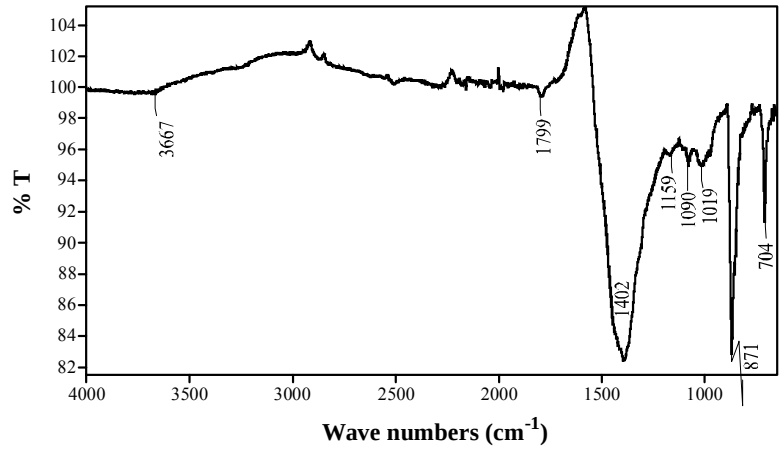
709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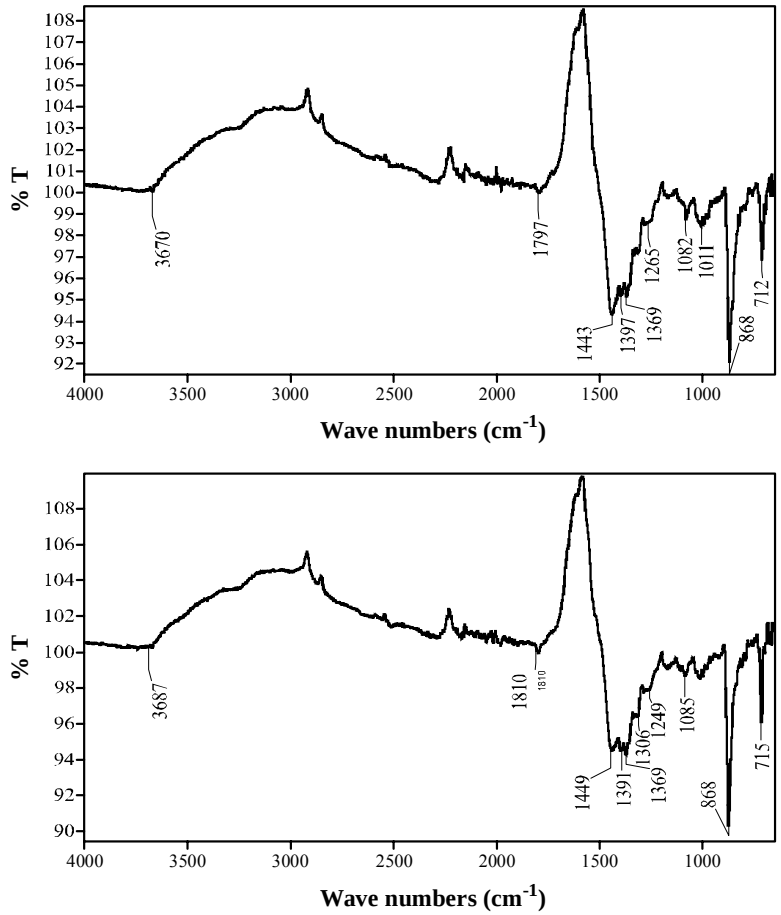


Fig. 3: The infrared analysis for the sample of stations (1, 2, 3, 4 and 5, respectively)

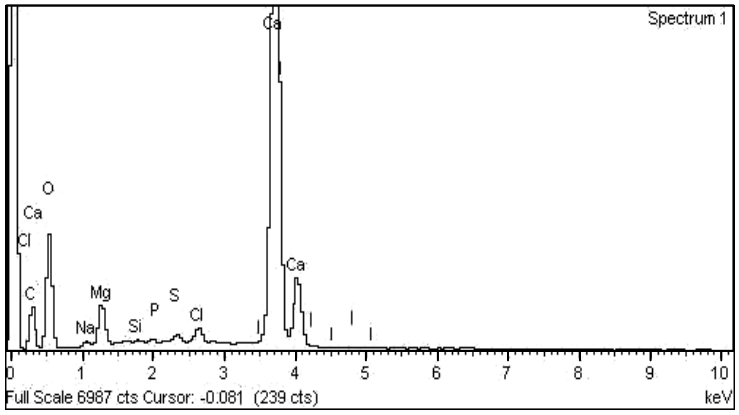
It was reported that the band characteristic for pure calcite appears at 1400 cm^{-1}. The in plane bending vibration band at 1080 cm^{-1} for O-H in the sediment samples appears in all regions. However, the bands at 863 cm^{-1} represent the bending in plane vibration band of O-H groups for δ MgAlOH[16].

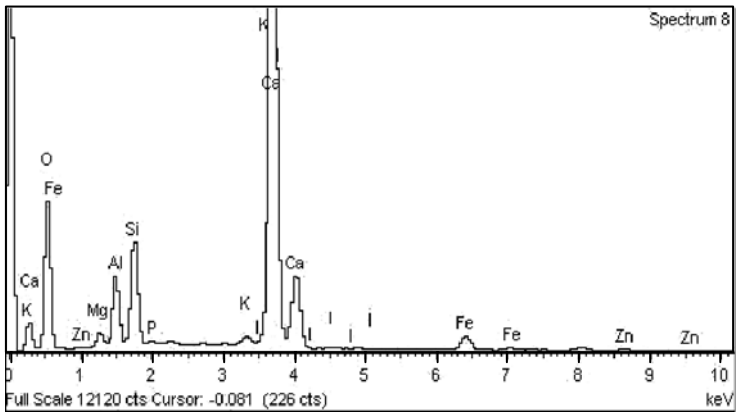
Carbonate minerals in all sediments are identified by the wave number of M-CO_3 stretching band at 715 cm^{-1}. The symmetric Si-O-Si stretching appeared as a weak bands at 450 cm^{-1} (Fig. 3 and Table 3).[17]

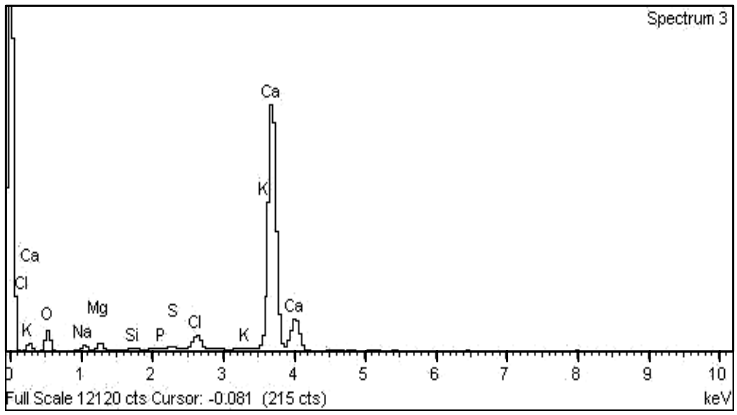
X-ray analysis

The X-ray analysis showed that, all samples containing very high contents of calcite. Fig. 4 indicates that the structure of these samples is mainly calcite ($CaCO_3$). The data are in

harmony with the TG and DTA and IR spectral findings. The variation of Si contents were due to the presence of SiO_2 (quartz).







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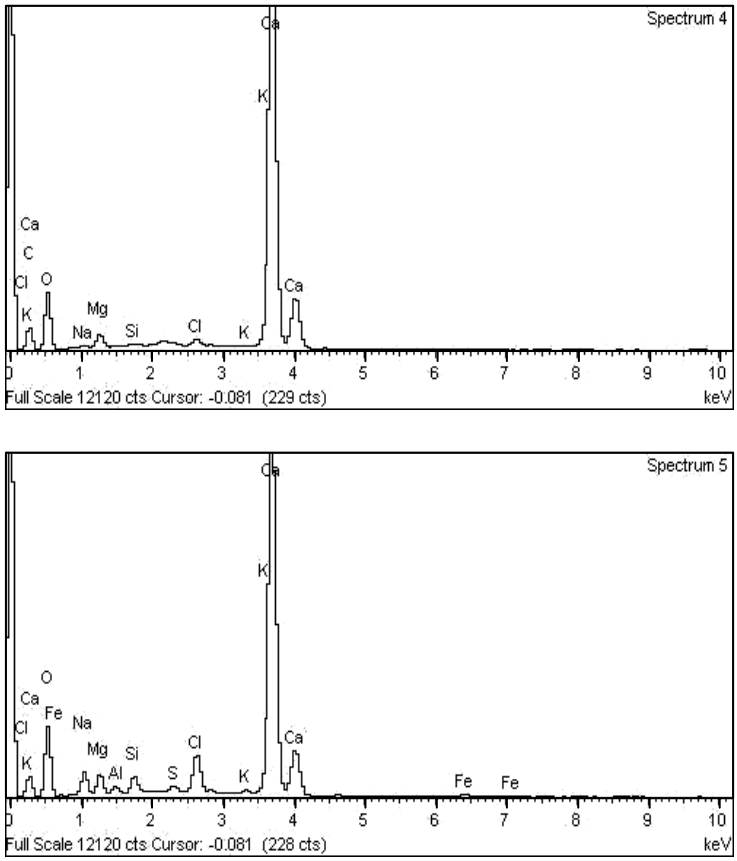

Fig. 4: X-ray analysis

CONCLUSION

According to the thermal analysis (TGA, DTA, IR and X-ray microscope scanning) the sediment samples were mainly composed of calcite and Mg-calcite. The I.R. spectra of the all sediment samples are similar indicating that the constituents are almost the same. This is in accordance with X-ray analysis, which indicated the presence of calcite and Mg-calcite in the collected sediment samples. The TGA and DTA analysis curves were composed mainly of one peak and indicated that the decomposition of calcite occurred at temperature rang (700-1000^{o}C).

Comparison of the thermal analysis for the present work with those of neighboring coastal area (Egypt) suggests that the Egyptian coast sediment containing another minerals such as quarts and feldspar[1].

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