

TRACE ELEMENT STUDY ON THE MIXED CARBONATE-PYROCLASTIC SEDIMENTS (LOWER MIOCENE, CENTRAL BASIN, IRAN)

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Abstract

Geochemical investigations have permitted the refinement of the environmental interpretation of the f-Member of the Qum formation, Central Basin, Iran, which has been established through detailed microfacies (MF) analysis. The analysis revealed that the f-Member carbonates consist of eight distinct microfacies designated by the letters A through H. On the basis of petrographic characteristics and environmental significance, the studied MF have been interpreted in terms of depositional environments as follows: MF-A (basin); MF-B (lower slope); MF-C (reef flank); MF-D (proximal talus), MF-E (organic reef); MF-F (lagoon); MF-G (restricted marine shoal), MF-H (restricted shelf). The concentrations of Ti, V, Fe, Co, Ni, Cu, Sr, Zr, U and Rb have been measured in limestones from outcrop samples of this formation. The analysis revealed a wide range of concentration both within and between different microfacies. A volcanic eruption in the nearby area located in the northeastern part of the sedimentary basin exerted an influence on trace element composition by supplying pyroclastic materials to carbonate sediments. In general, the basin microfacies is characterized by having the highest concentrations of Ti and Zr. The lower slope microfacies has the highest values of V, Fe, Ni, Cu, Sr, U and ratios of Ni/Co, Cu/Co and Ni/V, whereas the reef flank microfacies have only elevated concentrations of Co. All of these traces and elemental ratios are depressed in both proximal talus and reef microfacies. The restricted marine shoal microfacies possesses elevated Rb values and the restricted shelf microfacies is characterized by a high concentration of Sr and elevated Cu, U and Rb values and show a slight increase in the Ti, Fe, V, Co, Ni, Zr values.

Introduction

This study represents the first attempt to use trace

element data to examine depositional environments of the f-Member carbonates. The f-Member is the uppermost member of the oil-bearing Qum Formation. It consists of light coloured (whitish-yellow), porous; part chalky and part cemented limestone. The formations were subjected to numerous palaeontological, stratigraphic and structural

Keywords: Iran; Qum Formation; f-Member; Trace element; Mixed carbonate-pyroclastic; Lower Miocene

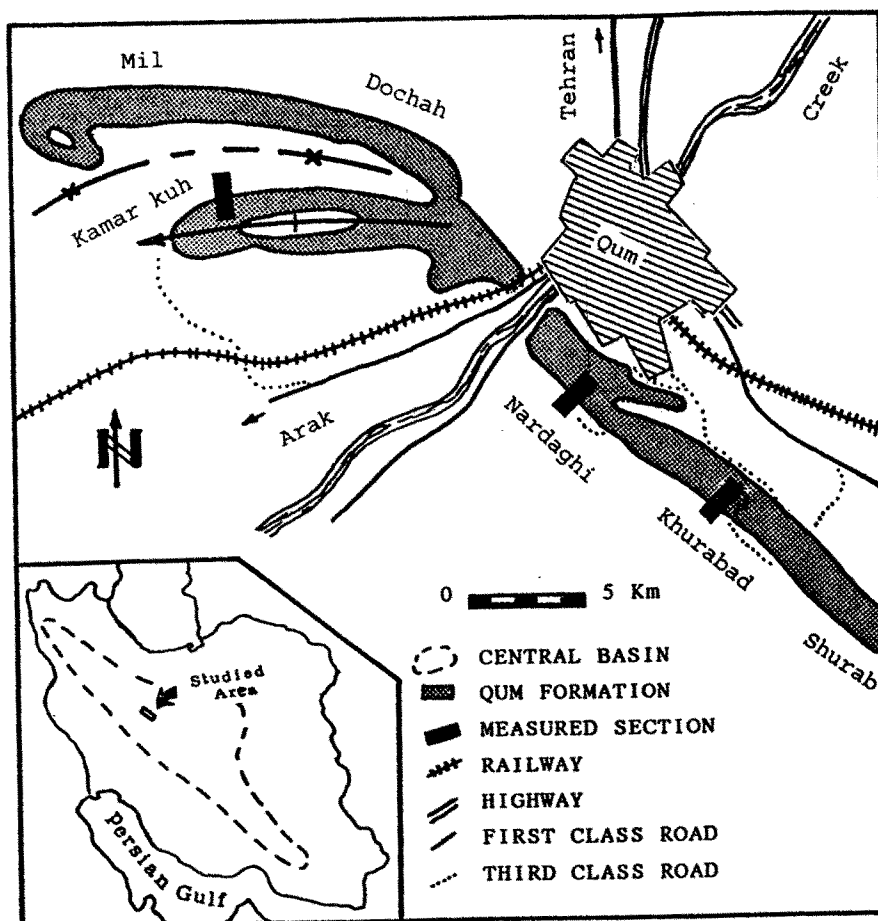


Figure 1. Location map

investigations [6, 13, 20, 2, 14]. A detailed account of the numerous works done on this subject previously is given by Amini [1], Okhravi and Amini [17].

This paper deals with geochemical studies of carbonate ramp microfacies previously investigated through microfacies analysis [17]. The study of trace elements of these carbonates may be particularly useful in revealing the chemical influence of pyroclastic material on carbonate systems. Relatively little work has been done on trace element composition of mixed carbonate-pyroclastic rocks.

Chester [4] pointed out that if there is significant variation in the content of a minor element when traced to certain types of environments, then that element could be useful as a geochemical indicator. He showed that differences exist in trace element contents of the reef and non-reef facies and concluded that in the sturgeon Lake reef area of Alberta, Canada a geochemical differentiation can be made between the carbonate of boreholes drilled in the reef facies and those of boreholes drilled in the non-reef facies.

Rao and Naqvi [19] pointed out that Sr and Na and their

respective molar ratios with Ca are the most important variables to consider in defining limestone depositional facies. They also concluded that Sr/Cr ratios vary according to facies. Buelter and Guillemette [3] discovered that in regard to the trace element concentrations in the back-reef, samples differ greatly from the reef complex sample. They also concluded that the concentration of Zn and Sr are generally higher in the back reef units, whereas concentrations of iron and manganese are much lower.

The objectives of this study are: (1) to determine and document trace elements of the f-Member carbonates, (2) to refine the depositional environment of the studied rocks previously established through microfacies analysis, and (3) to document the variations of trace elements in response to the influx of pyroclastic materials into the carbonate depositional environment.

Methods

Three stratigraphic sections (Fig. 1) of the f-Member of the Qum Formation were measured, described and sampled for microfacies analysis [17]. A total of 747 vertically

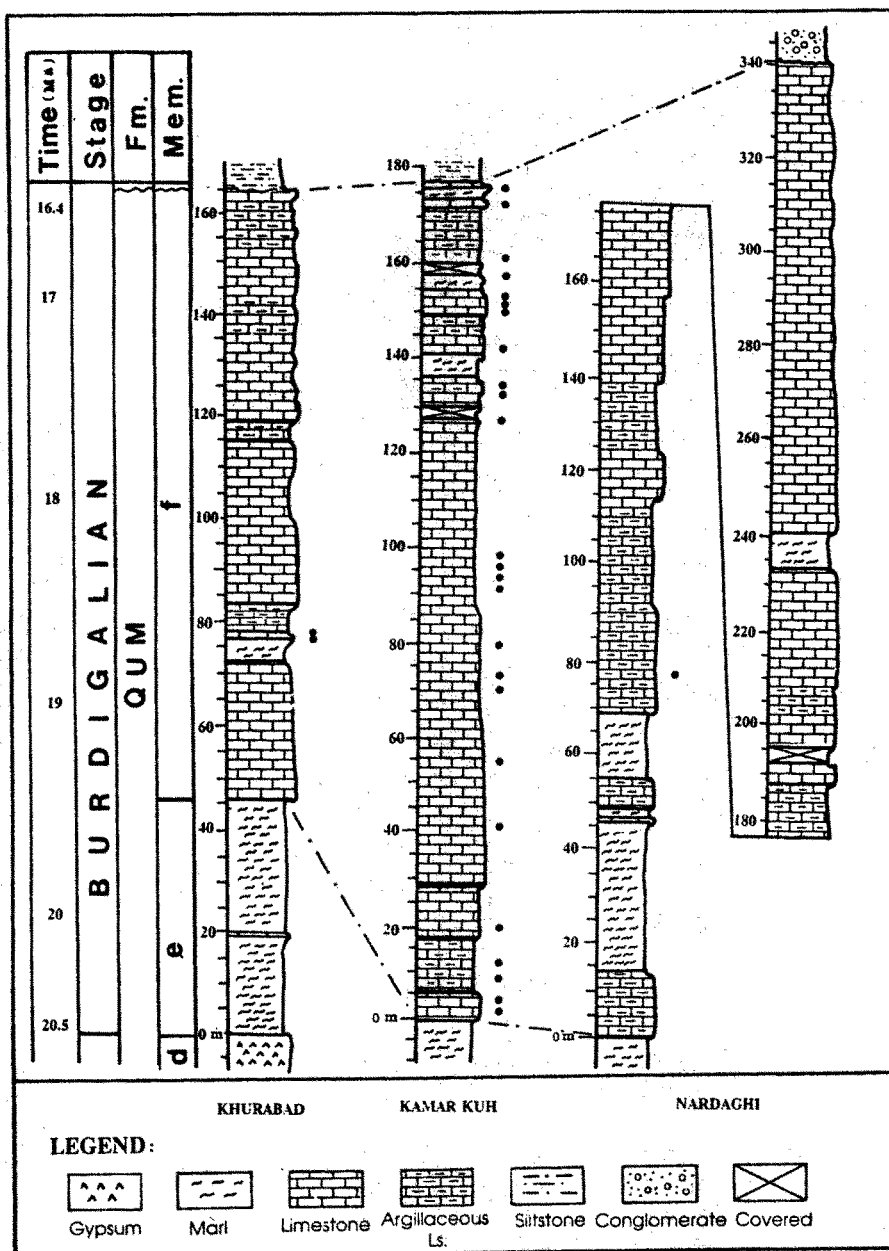


Figure 2. Measured section. Dots show sampling locations.

oriented hand specimens were collected and examined by hand lens. A total of 410 vertically oriented thin sections were prepared from the specimens and subjected to a detailed petrographic investigation. The depositional environments of the f-Member carbonates were established by Okhravi and Amini [17] using microfacies techniques [15, 16]. They defined the f-Member microfacies as follows: 1) MF-A as a bioturbated, bioclastic wackestone with planktonic foraminifers and fragments of coralline algae with an average diameter of 0.33 mm; 2) MF-B as a bioclastic wacke-to packstone with either micritic or

bioclastic calcisiltite matrix; 3) MF-C as a bioturbated, bioclastic packstone to grindstone with up to 8 percent clast size material. Euhedral volcanic quartz, feldspar and rock fragments are abundant in some samples which grade into tuffaceous limestone; 4) MF-D as a coarse-grained bioclastic packstone (with about 8 percent gravel size components) to floatstone. This microfacies mainly consists of reef-derived algal fragments with an average size of 1.5 mm, fragments of bryozoans and other reef building organisms with an average size of 5 mm and benthic foraminifers such as *Miogyopsina*, *Operculina* and

Dperculinoidea; 5) MF-E, as a coral-algal boundstone containing several genera of corals, many in life position together with red algae, bivalves, gastropods, echinoids and foraminifera. The coral growth forms are either domes, anduloses sheets or slender rods: The colony diameter is typically about 25 cm. This MF is characterized by the abundance of crustose coralline algae particularly Archaeolithothamnium, Lithothamnium and Mesophyllum; 5) MF-F as a bioclastic wackestone (whole fossil wackestone of Wilson, (1975); 7) MF-G as a bioclastic grainstone-rudstone. The important components of this microfacies are gastropods, brachiopods, pelecypods, miliolids, fragments of red algae, bryozoans, crinoids and worm tubes. Some samples of this microfacies contain significant amounts of volcanic quartz, feldspar, amphibole and volcanic rock fragments which grade into tuffaceous limestone; and 8) MF-H as a bioclastic packstone with matrix of either micrite or silt-sized particles. The abundance of volcanic ash grades some samples of this microfacies into tuffaceous limestone. The researched microfacies was interpreted [17] as follows: MF-A (basin); MF-B (lower

slope); MF-C (reef flank); MF-D (proximal talus), MF-E (organic reef); MF-F (shelf lagoon); MF-G (restricted marine shoal), MF-H (restricted shelf). Samples of each microfacies (a total of 28 samples) except MF-F, which occurs in a few samples, were chosen for trace element analysis in this study. Figure 2 shows the sampling points which are shown alongside the studied stratigraphic sections. The selected samples for geochemical analysis were examined by a hand lens and determined to be free of visible detrital particles. They were crushed, powdered and analyzed by XRF. The results of the trace element analysis are presented in Table 1 and Figures 3 and 4.

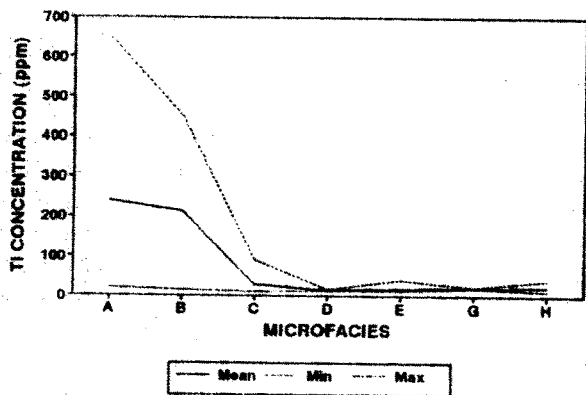
In order that the variations of the measured trace elements be compared to each other properly, their concentration values were standardized (coded) using the following formula [17]:

$$Z = (Y - \mu) / \sigma$$

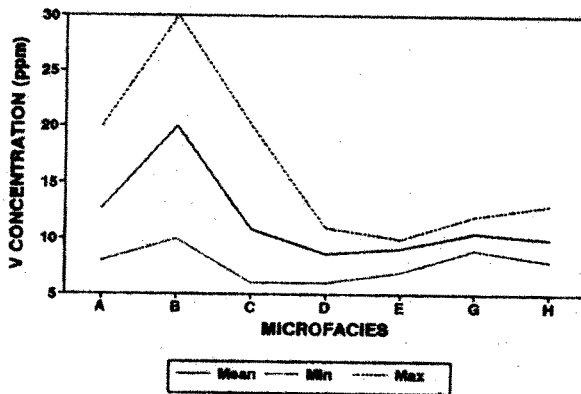
Z is a standardized average; Y is the average value for one element in one microfacies; μ is the average for that element using all samples; σ is the standard deviation of that element using all samples.

Table 1. Analytical results of the f-Member carbonates (ppm)

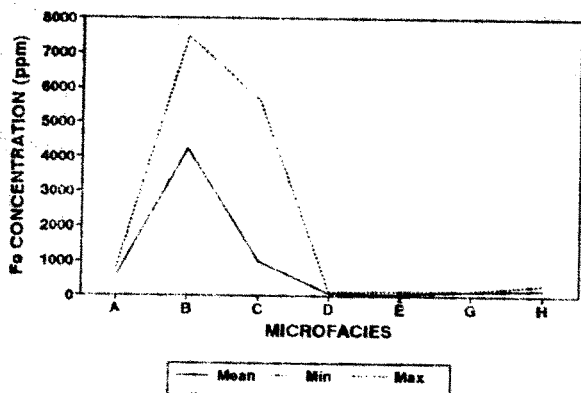
Sample	MF	Ti	V	Fe	Co	Ni	Cu	Sr	Zr	U	Rb
1	E	14	10	111	8	5	13	667	9	3	12
2	H	13	9	82	8	2	10	769	8	4	14
3	H	40	13	137	7	8	9	700	10	2	12
4	H	15	8	315	8	10	10	626	11	3	14
5	E	14	7	137	7	8	11	700	10	3	12
6	G	22	9	128	9	7	8	486	12	3	14
7	G	20	12	156	6	5	9	315	10	2	13
8	D	14	9	79	7	4	4	390	8	3	13
9	D	16	11	124	7	4	8	387	9	1	15
10	C	15	9	146	11	5	6	382	11	3	15
11	E	17	10	94	7	6	9	370	9	2	13
12	C	16	12	10	8	8	11	256	9	3	13
13	E	13	8	3	8	5	7	164	10	2	14
14	D	13	6	17	9	10	7	209	7	2	12
15	E	14	10	7	6	5	7	333	8	1	12
16	E	15	9	24	5	6	8	306	8	2	11
17	C	16	11	9	9	9	7	190	10	3	13
18	C	12	7	31	7	7	4	214	8	2	13
19	C	10	6	88	9	6	5	362	7	2	13
20	A	650	20	781	8	10	7	456	48	4	20
21	B	14	10	104	7	9	8	341	10	4	13
22	C	90	20	5650	11	10	12	1023	31	9	12
23	B	290	30	7490	8	7	27	674	13	5	13
24	E	40	10	50	8	3	3	195	1	2	4
25	A	50	10	240	7	5	15	226	4	1	5
26	B	450	20	6420	8	9	5	480	10	3	1
27	A	20	8	660	10	1	11	471	3	1	5
28	B	100	20	2940	7	12	11	849	2	5	13



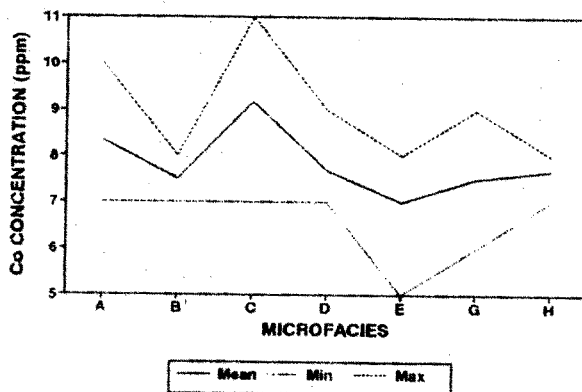
A. Concentration of Ti



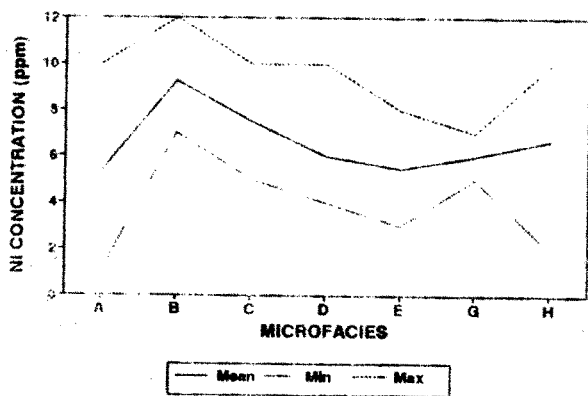
B. Concentration of V



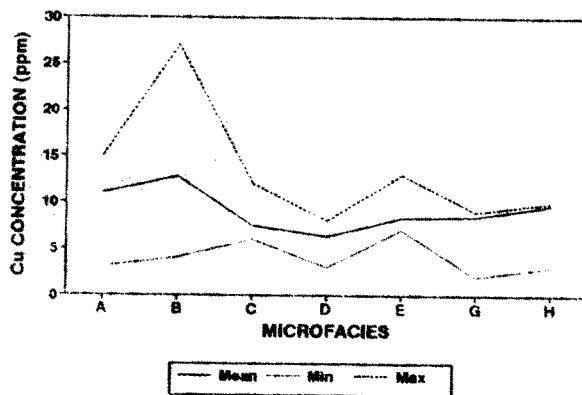
C. Concentration of Fe



D. Concentration of Co



E. Concentration of Ni

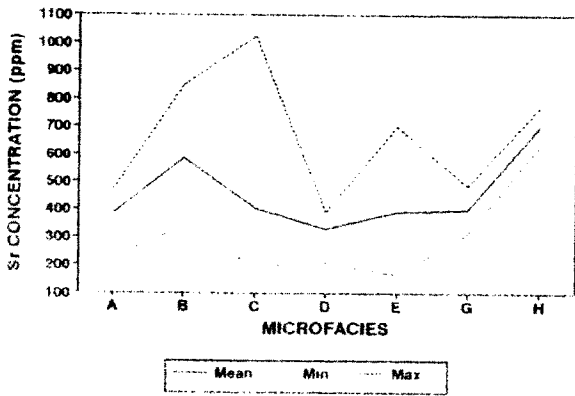


F. Concentration of Cu

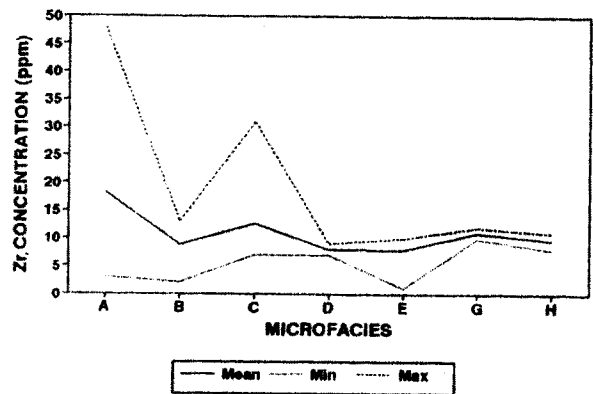
Figure 3. Variation of trace elements through microfacies

The advantage of coding data in this manner is that Z values for any component will have a mean of zero and a standard deviation of one. This facilitates graphic presentation of the data and allows for easy comparison of

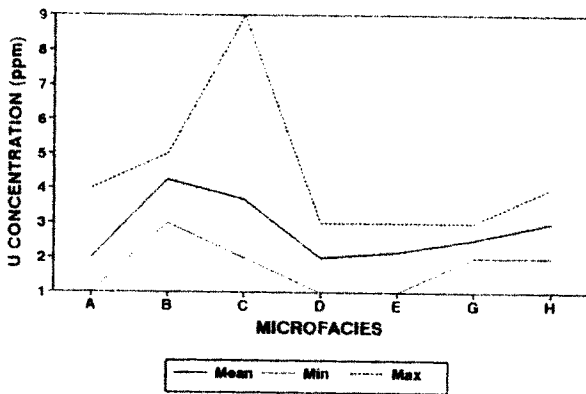
variations of the average values even though the uncoded average may vary greatly. The standard average value was of the measured parameters for each microfacies then calculated and the results are shown in Figure 5 (A-F).



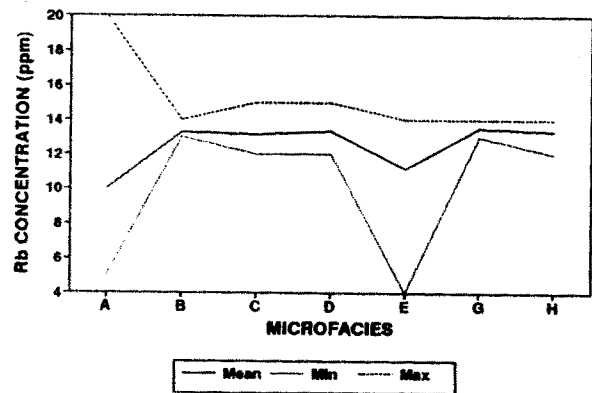
A. Concentration of Sr



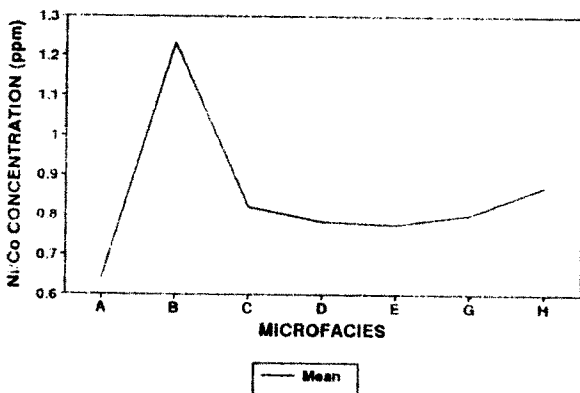
B. Concentration of Zr



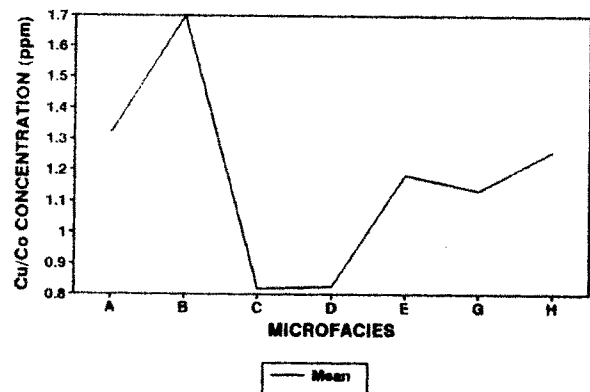
C. Concentration of U



D. Concentration of Rb



E. Concentration of Ni/Co



F. Concentration of Cu/Co

Figure 4. Variation of trace elements through microfacies

**Environmental Distribution of Elements-
Results**

Titanium

The average and maximum values for Ti start with rather larger values in basinal microfacies (MF-A), decrease rapidly towards MF-D and then increase very gradually

towards the land. However, the minimum values of Ti remain almost constant for all microfacies.

Vanadium

The average, maximum and minimum curves of V are at peak in the lower slope microfacies (MF-B), decreasing

rapidly towards MF-D and then very gradually increasing towards back-reef.

Iron

Iron is mostly concentrated at MF-B showing a progressive decrease towards facies (MF-D) where it declines to its minimum and then gradually increases towards MF-H. The values for maximum and minimum concentrations of these elements vary almost parallel to mean values. However, their values show more deviation from the mean in deeper waters.

Cobalt

The average values of concentration of Co display maximum value in MF-C, decreasing towards both MF-B and MF-E, then increasing both towards land and sea. This may be due to the fact that Co is mainly associated with clay minerals [10].

Nickel

The average value of Ni varies in a similar manner to Fe and V except that the average curve of the former reaches its minimum at reefal microfacies. Khawlie and Carozzi [10] showed that there is an increase in Ni concentration with more marine influenced environment.

Copper

Like iron, the average curve of copper displays its maximum value in MF-B and decreases gradually towards the reef where it reaches its minimum value. It then shows a gradual increase towards the land, reflecting minimum absorption by reef related organisms.

Strontium

The highest average value of Sr concentration occurs in MF-H and a lower peak in MF-B. The maximum value of Sr shows different variation, but the minimum curve varies somewhat parallel to the average value. The value of Sr concentration varies from 330 ppm in MF-D to 700 ppm in MF-H. The average value of Sr varies between 240-700 ppm. It shows values of 700 and 600 ppm in MF-H and MF-B respectively. It then decreases both basinward (MF-A) and toward MF-D, where it reaches its minimum.

In recent marine carbonates, the value of Sr concentration varies between 8000-11000 ppm [9]. Compared to recent carbonates, the f-Member limestones contain much less Sr (330 to 700 ppm), which implies a loss of about 54% during diagenetic alteration.

Zirconium

The average curve of Zr is at its peak in the basinal microfacies (MF-A), decreases to MF-B rapidly, and then remains almost constant with minor fluctuations.

Uranium

The U content of the f-Member of the Qum Formation varies between 1-9 ppm (Table 1, Fig. 4C). It reaches the maximum value within the lower slope and reef flank microfacies. The average U content varies between 2-4.3 ppm, which is higher than the average value of U in the ancient carbonates and its modern analogous. The average uranium content of marine organisms such as bryozoa, mollusca, red algae, foraminifera, echinodermata and arthropoda is less than 0.5 ppm [21].

Rubidium

Rb shows almost constant values in all microfacies except the reefal and basin MF which generally contain a lower amount of pyroclastic particles.

In conclusion, mean trace-element contents (ppm) of the f-Member carbonates are Ti = 71.89 (s= 145.52), V= 11.57, Fe= 929.75 (s= 2027.08), Co=7.86 (s= 1.36), Ni= 6.64 (s=2.64), Cu= 9.00 (s= 4.45), Sr= 610 (s= 219.32), Zr= 10.57 (s= 8.79), U= 2.86 (s=1.60) and Rb= 12.39 (s= 3.11). The concentrations of V, Cu, U and ratios of Ni/Co and Cu/Co vary similarly to Fe. (Figs. 3B, 3F, 4C, 4E and 4F)

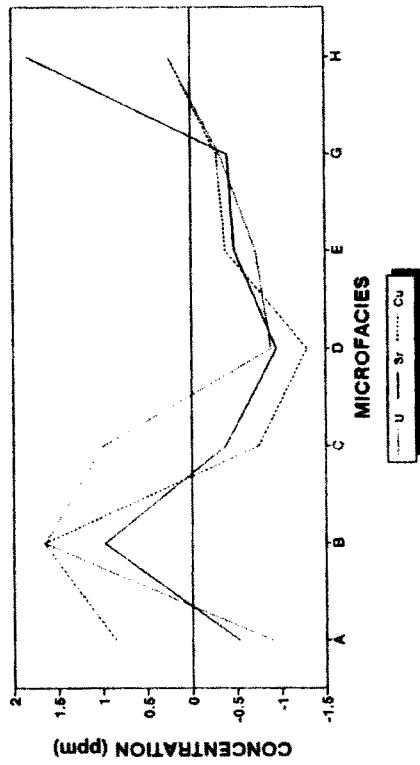
Discussion

The values of all measured trace elements except for Co decrease from the lower slope/basinal facies.

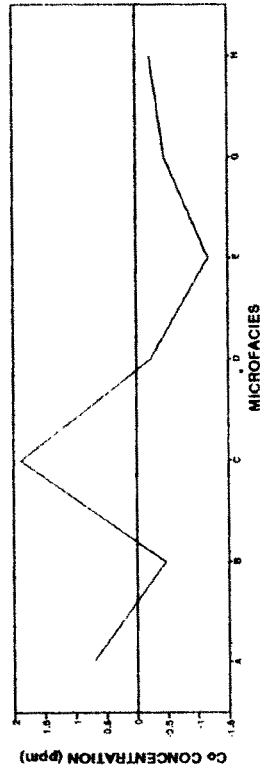
The average values of the trace elements show a bimodal distribution from basin to land. They generally begin to decrease towards either proximal talus or reefal microfacies and gradually increase towards the back-reef microfacies. The general trend of variation in the trace elements concentration varies in a manner similar to the variation of trace elements in reefal facies elsewhere [3, 12].

The coded average values of Ti, V, and Fe (Fig. 5A) correspond to each other satisfactorily except for MF-A, in which their coded values differ. These elements show an enrichment in fore-reef microfacies whereas it shows a depletion in reef and back-reef microfacies. The coded average for Ni (Fig. 5C) shows similar variations to those of Ti, V and Fe, but the former reaches its minimum value in the basin and reef microfacies. The coded average values for U, Sr and Cu (Fig. 5B) behave similarly. They show bimodal enrichment in fore-reef and back-reef, where they display depletion in reef microfacies. The variations of the coded average for Zr and Co are more or less similar (Fig. 4E and D). Finally, the coded average value for Rb (Fig. 4F) shows an almost leveled and above average value for all microfacies except for reef and basin microfacies.

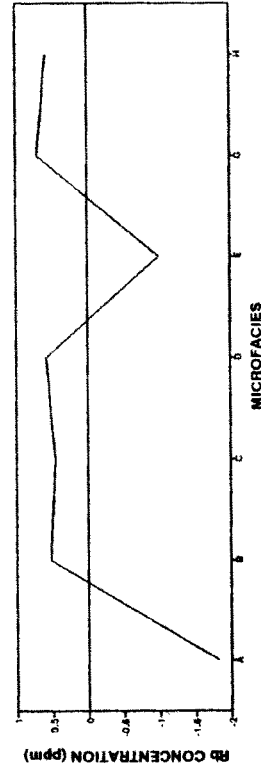
The concentration of U in different microfacies in many instances is considerably higher than the average concentration of carbonates. Swart and Hubbard [22]



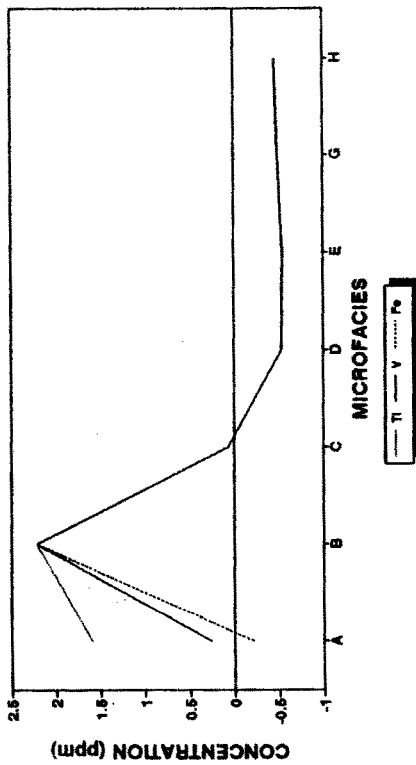
B. Concentration of U, Sr and Cu



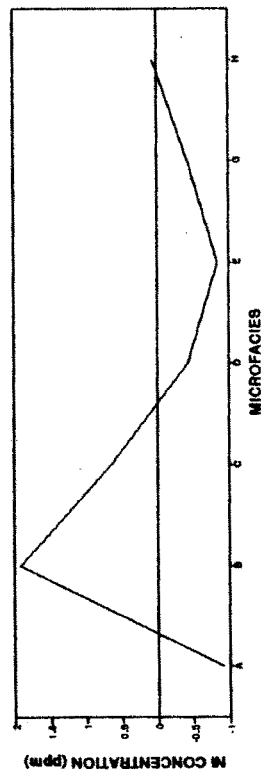
D. Concentration of Co



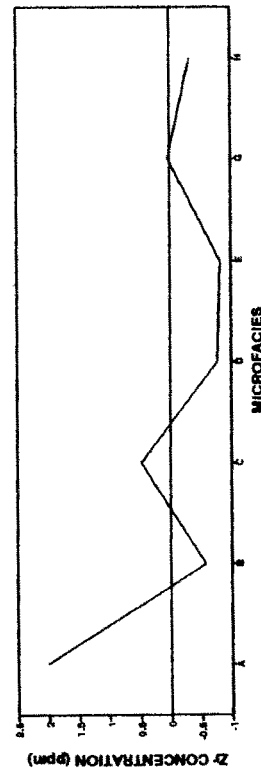
F. Concentration of Rb



A. Concentration of Ti, V and Fe



C. Concentration of Ni



E. Concentration of Zr

Figure 5. Variation of coded average value of trace elements through microfacies

concluded that in coral reefs, upon death, coral skeleton absorb U and increase in concentration from the normal level of 1.5-2 ppm to between 3-4 ppm. The average U content of micrite, Mg calcite cement and aragonite are 1.4, 2.5 and 3.5, respectively [22]. Hugland et al. [8] and Gvirtzman et al. [7] concluded that there was generally a decrease in the U concentration of carbonate rocks during freshwater diagenesis as metastable aragonite and high Mg Calcite (HMC) were dissolved and/or replaced by Low Mg Calcite. Early marine aragonite and HMC cements are not depleted in U and frequently contain comparable values to the original sedimentary components.

The high concentration of U in the rocks which were studied is surprising for several reasons. First, because the incorporation of higher radii elements such as U in large amounts in carbonate minerals is unlikely. Second, the concentration of U is several times higher than the average measured value for ancient carbonates (Table 2) and their modern analogues [21, 11, 5]. Third, there is generally a decrease in U concentration of carbonate rocks during freshwater diagenesis [8, 7, 21]. The petrographic investigation of the f-Member carbonates revealed that they have undergone extensive freshwater diagenesis [1, 17, 18]. One possible explanation for such high U concentrations in the studied rocks may lie in the fact that U had been mostly introduced to the sedimentary environment through volcanic activities. High Fe contents (> 4000 ppm) may also represent contribution from a pyroclastic source.

The data (Table 2) indicates that the studied rocks exhibit marked enrichment in Co, Cu, U and Rb over common carbonate rocks. These are mostly concentrated in the back reef microfacies when compared to other microfacies, presumably due to the abundance of volcanic ash. Enrichment of these trace elements was noted, indicating that these elements originated from volcanic ash.

Comparison of the trace element values of the studied rocks with average values of these elements in common carbonates and igneous rocks (Table 2) indicates that contributions from a magmatic (volcanic) source seems like a more reasonable explanation.

In general, the basin microfacies is characterized by having the highest concentration of Ti and Zr. The lower slope microfacies shows the highest values of V, Fe, Ni, Cu, Sr, U and ratios of Ni/Co, Cu/Co and Ni/V, whereas the reef flank microfacies shows only elevated Co values. All of these traces and elemental ratios are depressed in both proximal talus and reef microfacies. The restricted marine shoal microfacies possesses elevated Rb and the restricted shelf microfacies is characterized by its highest Sr values, elevated Cu, U and Rb and shows only a slight increase in Ti, Fe, V, Co, Ni and Zr values.

In order to find a model for the relationships between measured trace elements, Pearson correlation coefficient were calculated (Table 3). This table shows that the Ti contents of the f-Member carbonates strongly correlate with the Fe contents. The former also correlate well with both V and Zr. There are also positive correlations between U vs Sr and U vs Fe. These correlations may indicate that the distribution of these elements is probably controlled by a similar mechanism.

Conclusion

The concentration of all studied traces are above average in the fore-reef environments whereas all of them fall below average in reef microfacies. The average concentration of Sr, U, Cu and Rb display elevated values in the back-reef microfacies whereas the concentration of Ti, V, Fe, Ni, Co, and Zr fall below average.

Trace element concentrations in the f-Member carbonates show distinct differences between microfacies types. The basin and lower slope microfacies are enriched

Table 2. Abundance of the measured trace elements in f-Member, seawater, carbonates and igneous rocks*

Element	f-Member Carbonates	Seawater	Carbonate	Igneous Rocks
Ti	71.89 (s= 145.52)	1	400	4400
V	11.57 (s= 5.40)	2	20	135
Fe	929.75 (s= 2027.08)	3	3800	50000
Co	7.86 (s= 1.36)	0.4	0.1	25
Ni	6.64 (s=2.64)	7	20	75
Cu	9.00 (s=4.45)	3	4	55
Sr	448 (s=219.82)	0.008	610	375
Zr	10.57 (s=8.79)	0.03	19	165
U	2.86 (s=1.60)	3	2.2	2.7
Rb	12.39 (s=311)	0.012	3	90

* Sources: Mason & Moore, 1982; Faure, 1992

Table 3. Correlation of trace element concentration

Element	Ti	V	Fe	Co	Ni	Cu	Sr	Zr	U
V	0.70								
Fe	0.55	0.86							
Co	0.06	0.07	0.24						
Ni	0.36	0.39	0.34	0.05					
Cu	0.14	0.58	0.52	0.02	0.07				
Sr	0.17	0.48	0.51	0.22	0.27	0.45			
Zr	0.69	0.44	0.25	0.24	0.39	0.06	0.28		
U	0.29	0.61	0.63	0.40	0.51	0.33	0.70	0.53	
Rb	0.41	0.24	0.09	0.01	0.44	-0.10	0.17	0.59	0.30

in respect to trace elements whereas proximal talus and reefal microfacies show considerably reduced values and the back-reef microfacies again gradually become enriched.

The geochemical study of microfacies reveals that some elements like Fe and Sr show major variations whereas others like Co, Cu, Rb and Ni display minor variations. High concentrations of Fe, Co, Ni and in the studied microfacies compared to their concentration in normal sea water and their close relation with the average concentration of these traces in magmatic rocks indicate associations of the studied carbonates with the pyroclastic particles.

Compared to the average trace element values of ancient carbonate rocks, studied carbonates are enriched with respect to U, Co, Cu and Rb. It seems that the concentration of these elements both towards the shore and the basin of the reefs is due to their association with continental originated pyroclastic components and their accumulation in a marine environment. An increase in the values of these species of trace elements is brought on mainly by volcanic activity and indicates periods of pyroclastic influx.

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