Mn Distribution in the Carbonate Fraction of Shallow Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)

Rana Abbas Ali

Dept of Geology,College of Science,University of Baghdad,P.O. Box:47138,Baghdad,Iraq

Postal address:Iraq-Baghdad-Aljaderia-Baghdad University post office-P.O.

Abstract

Chemical determinations of Mn on (48) samples of carbonate rocks from Cenozoic Euphrates sequence of Wadi Fuhaimi and Anah town (Western Iraq) have been carried out. From the relationships between Mn content on one hand, the mineralogy and depositional environments on the other, the following conclusions can be drawn: (1) Mn appears to be mainly associated with carbonate fraction. (2) The low Mn content of the shallow water formation reflects the original carbonate phase, mainly aragonite; sharply higher Mn content has been found in deeper sea formation, in origin essentially calcitic. (3) Preferential substitution of manganese for calcium in the rhombohedral structure of calcite. (4) Diagenetic processes, particularly dolomitization, do not appear to have seriously modified the original Mn content. (5) The relatively high Mn content in some stratigraphic levels could be related to periods of intensive weathering and /or to a larger availability of Mn^{+2}, due to more reducing sea water conditions.

Key words: Manganese, Carbonate fraction, Euphrates formation, marine lithofacies, Western Iraq.

المستخلص

تم حساب تركيز المنغنيز ل(48) أنموذجا" للصخور الكاربونايتية من تتابع الفرات (العصر الحديث) لوادي الفحيمي ومدينة عنه (غرب العراق). من خلال العلاقات بين محتوى المنغنيز من جهة، مع المعدنية والبيئات الترسيبية من جهة أخرى، تم استنتاج ما يأتي: (1) يظهر المنغنيز بشكل رئيسي متحدا" مع الجزء الكاربونايتي. (2) المحتوى القليل للمنغنيز

Mn Distribution in the Carbonate Fraction of Shallow

Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)

Rana Abbas Ali

في المناطق الضحلة من التكوين يعكس أصل الصخور الكاربونايتية، معظمه اراكونايت، المحتوى الأعلى للمنغنيز يتواجد في المناطق العميقة من التكوين، وأصله متكون من الكالسايت بشكل رئيسي. (3) الإحلال الأنسب للمنغنيز محل الكالسيوم في الكالسايت ذي التركيب المعيني القائم. (4) العمليات التحويرية، الدلمتة الجزئية، لا توجد عمليات تحويرية مؤثرة على محتوى المنغنيز. (5) محتوى المنغنيز العالي نسبيا"في بعض المستويات الطباقية له علاقة بمراحل التجوية الشديدة و/ أو يرجع هذا المحتوى العالي لحالات الاختزال في ظروف مياه البحر.

كلمات مفتاحية: منغنيز، الجزء الكاربونايتي، تكوين الفرات، سحنات بحرية ، غرب العراق.

Introduction

The present work is an attempt to clarify the behavior and distribution of Mn in carbonate rocks from shallow (shelf) marine lithofacies of lower Miocene age in western Iraq. It represents also an extension of geochemical researches (minor elements analysis) on the Cenozoic carbonate formation. Finally it is meant to be the background for further regional studies aiming at paleoenvironmental reconstructions.

The Euphrates Limestone Formation is the most typical and most widespread representative of the Euphrates group which comprises Ghar, Euphrates, Serkagni and Dhiban Formations of Lower Miocene age. The type section near Wadi Fuhaimi, SE Anah town, consists of 8m of chalky, shelly, recrystallized limestone, a maximum thickness of 100m was reported elsewhere in surface and subsurface sections (1). The formation is of great lithological variability as fully recognized by the various geological parts through the years 1960 – 1973. This fact led many geologists to attempt dividing the formation into units or members. The formation was divided by (2) , into three members, these are from bottom to top: (a) Cavernous and conglomeratic limestone (represents the described type section), (b) Shelly limestone, (c) Marly and chalky limestones. According to field surveys by (3), (4), and (5); the formation was divided into the following units: (a) Basal conglomeratic limestone, (b) Chalky limestone, (c) Silicified limestone, (d) White chalky and recrystallized limestone, (e) Complex upper member.(6) described the Euphrates rocks at Wadi Fuhaimi and Anah sections in terms of their calcite and dolomite content. The limestone rocks are restricted to the lower part of Anah section. They are composed of micritic skeletal limestone and micritic

detrital limestone. The middle and upper parts of Anah and Fuhaimi sections are both composed of fine grain dolomites alternating with calcareous dolomites.

The lower contact of the formation is unconformable with the underlying Anah and Sheikh Alas Formations; then become conformable with the Serikagni Formation with which the Euphrates Formation interfinger towards the center of basin. The Jeribe Limestone Formation unconformably overlies the Euphrates Limestone Formation in areas where the Dhiban Anhydrite is absent ,(7).

In the present study samples were taken from two sections, the first Wadi Fuhaimi section (8m), Fuhaimi area lies 70 km distance from SE Anah town, the second Anah section (80m), this section represent core of Anah Anticline (Fig.1).

Materials and Methods

Acid-soluble Mn was obtained treating all the samples with HCL, (8) . To check the possibility of Mn associated with clay minerals a few samples were attacked with CH_3COOH ,(9) . Whole rock Mn on 10 samples was determined after digestion in HF and $HCLO_4$.

Mn Distribution in the Carbonate Fraction of Shallow

Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)

Rana Abbas Ali
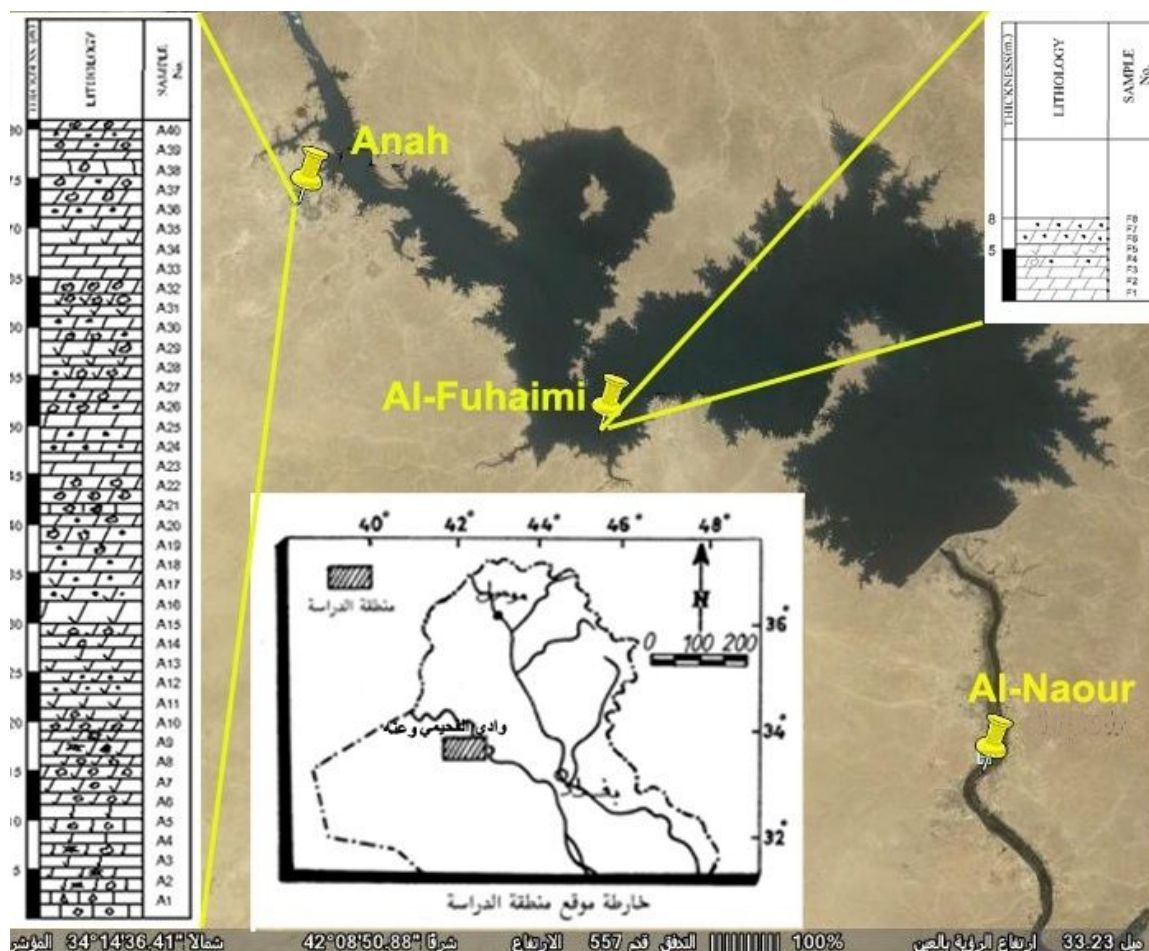
Fig. 1: Space image shows study area and stratigraphic sections.

The procedure of the attack is as follow:

HCL- soluble Mn:- Weight 200mg of powdered sample into a 50ml beaker. Add gently 30ml of 3N HCL and heat at 50-60 C° for half an hour. Filter the warm solution and then dilute it to 100ml with deionized water.

CH_3COOH- soluble Mn:- The above described procedure is followed, but N CH_3COOH is used instead of 3N HCL.

Whole rock Mn:- Weight 200mg of powdered sample into a 30ml crucible. Add about 1ml of deionized water and mix to moisten sample. Add, in order: 10 drops of $HCLO_4$ (very gently to avoid loss by splattering), and 10ml HF. Heat on a hot plate at 130-150 C° until dry. Add

2ml of concentrated HCL and then evaporate slowly to dryness. Cool and dissolve the residue in 5ml of concentrated HCL. Dilute to 100ml with deionized water.

Mn was analyzed using a perkin-Elmer atomic absorption spectrophotometer, equipped with automatic null recorder readout in College of Science,University of Baghdad.Instrument settings were taken from the Perkin- Elmer analytical methods book (1971),the method previously was used from (10).

The amount of acid (HCL or CH$_3$COOH) in the Mn standard solutions was set to be nearly the same as that contained in the analyzed sample solutions.

Precision of analysis was $\pm$ 5% ,where it is agreement of values among frequent readings for particular content from the sample. The accepted value was specified in confidence level measurement at(95%),equation (1) according to (11).The precision is the confidence level at (63%) according to (12),equation (2) .

P%=2SD/X*100 ......(95% confidence).....(11)........(1).

P%=SD/X *100 ....(63% confidence)......(12).........(2).

Where: $\mathbf{SD} = \sqrt{(x_1 - x)^2 + (x_2 - x)^2 + (x_3 - x)^2 / N}$

x_1, x_2, x_3....are the actual readings of analyses of the same sample.

N:the number of readings(number of analyses**).**

X:the average of readings for each element.

SD:standard deviation.

Accuracy: It is the closeness of the results to reality,using international standards,these standard materials are to be used for estimating the accuracy of the analysis of the varios elements.

The problem of Mn determination and results

Geochemical studies show that manganese in limestones is almost totally restricted to the acid-soluble carbonate fraction (13) and that manganese does not appear to undergo significant changes during diagenesis (10; 14; 15). If so, manganese could be used as an

indicator of original carbonate mineralogy and associated depositional and early diagenetic environments.

Table 1: Comparative analysis of acid-soluble and whole rock **Mn**, Ca, Mg, and insoluble residue data in four samples.

Sample No.	Ca %	Mg %	Insoluble residue %	Acid - soluble portion		
				Whole rock HCL	CH_3COOH	
F_3	51.97	0.92	5.8	35	25	35
F_8	45.65	1.36	4.88	48	93	124
A_1	46.41	2.70	1.55	37	30	53
A_{14}	40.43	1.65	2.28	70	55	69

Analytical data of acid-soluble and whole rock Mn content as well as Ca, Mg, and insoluble residue percentages after HCL acid are given for four samples in table 1.

Differences between HCL-soluble and whole rock Mn contents are negligeable, considering precision of analysis. In the case of F_3 and A_{14} samples the CH_3COOH-soluble Mn content appears somewhat lower than the HCL-soluble and whole rock Mn contents.

Using the above mentioned differential attacks it is not always possible to separate the Mn portion associated with the carbonate fraction from that associated with clay minerals. The average Mn content of clay minerals is as follows: 2550 ppm for chlorite, 1700 ppm for vermiculite, 770 ppm for montmorillonite and illite. No Mn is present in Kaolinite ,(16) .

In the case of Wadi Fuhaimi and Anah sections it is not possible to evaluate the Mn contributed by the clay minerals. The insoluble residue (consisting of Quartz, Feldspars, Palygorskite, Montmorillonite and Kaolinite) is approximately 5% , Fig.2(a,b) . If all of the insoluble residue were clay minerals, 50% of which being clay minerals (as is the case of all samples considered in the present study), the average Mn content contributed by the insoluble
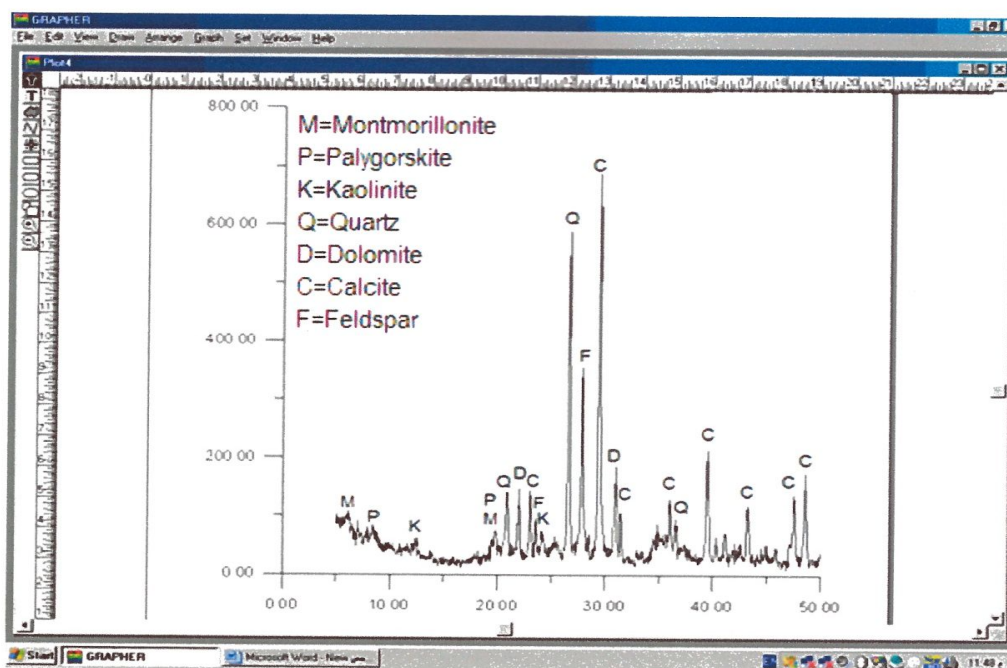
DIYALA JOURNAL FOR PURE SCIENCES

Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)
Rana Abbas Ali

residue should be estimated around 10 ppm. Considering the precision of analysis such a value becomes meaningless. Nevertheless, no significant differences result among whole rock Mn, HCL-soluble Mn and CH_3COOH-soluble Mn (Tables 1 and 2). Since according to(8) and (17) the HCL-treatment is not intense enough to attack most clay minerals to any appreciable degree, it can be suggested that no appreciable Mn is contained in the crystal structure of clay minerals. Mn is likely to be adsorbed on clay minerals, but this being the case, also a weak attack as the acetic one should be enough to remove it (18).

We therefore conclude that Mn in the analyzed samples is largely contributed by the carbonates. Similar results were found by (19) in sedimentary rocks of the Paris basin, and by(20) in carbonate rocks from Himalaya (India).
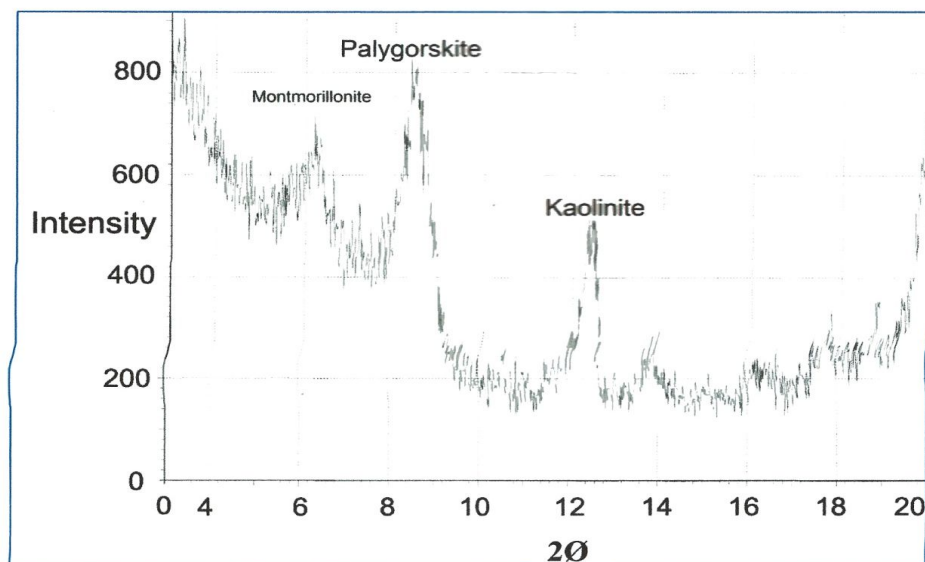
The results of HCL-soluble Mn determinations for all the studied samples are reported in Table 2.

Fig.2-a: X- ray diffractograph for Euphrates Formation sample no. F₅.

Fig.2-b:X-ray diffractograph for clay fraction of Euphrates Formation sample no.A$_{34}$

Manganese Distribution

The relationship between Mn content and stratigraphy is shown in Fig. 2. Wadi Fuhaimi and Anah sections show by far the lowest values of Mn content.

Because of a general increase of terrigenous clay from shallow to deep marine lithofacies, the possibility exists that manganese values for the acid- soluble fraction may have been influenced by the insoluble residue of shallow marine lithofacies. Statistical analyses of shallow marine samples (r = 0.22, Fig.3) show that there is no significant correlation between Mn value and insoluble residue at the 99% confidence level. The value of r, however, measures only the strength of linear relationships between two variables and does not necessarily imply a cause-effect relationship (21). Assuming a cause-effect relationship exists between Mn and insoluble residue, the real effect of X (insoluble residue) on Y (Mn) should be inferred from $100.r^2$ in percent (21). Accordingly, only 5% of Mn in shallow marine lithofacies is likely to be controlled by insoluble residue. This may include dissolved Mn oxides, Mn stripped away from clay and Mn in the carbonate lattice.

Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)
Rana Abbas Ali

During acid attack, it is not uncommon to strip away some adsorbed ions (18) like Mn from associated clay minerals. Insoluble residue of our samples contain predominantly Quartz, Feldspar and Pyrite with only traces of Palygorskite and Montmorillonite. Even if we assume 10% of total insoluble residue is composed of clay minerals with an average Mn content of 2000 ppm (a high value for sedimentary clay minerals), estimated Mn values range from 4 to 160 ppm. This suggests that clay-mineral contribution of Mn in our samples is negligible. Furthermore, cation-exchange analysis indicates that the clay minerals present are not rich in manganese (22). Therefore, most Mn is clearly not derived from the insoluble residue, but from the carbonates.

Table 2: Mn content in the Cenozoic carbonate rocks from Wadi Fuhaimi and Anah sections. Arithmetic mean $\bar{X}$, standard deviation S, and coefficient of variation in percent C%, are given for each section.

Wadi Fuhaimi section

Sample No.	Concentration Mn ppm	I.R.%	Sample No.	Concentration Mn ppm	I.R.%
F_1	35	1.46	A_{23}	80	3.48
F_2	85	3.78	A_{24}	90	1.26
F_3	35	5.8	A_{25}	90	2.83
F_4	35	3.24	A_{26}	70	2.79
F_5	55	5.59	A_{27}	40	3.48
F_6	35	3.75	A_{28}	40	2.18
F_7	35	3.74	A_{29}	40	2.83
F_8	48		A_{30}	80	

Sample No.	Concentration Mn ppm	I.R.
		4.88
	$\bar{X} = 45.375$	
	$S = 36.68$	
	$C\% = 80.837$	
	Anah section	
A_1	37	1.55
A_2	36	1.79
A_3	35	3.18
A_4	35	4.29
A_5	60	3.72
A_6	35	2.83
A_7	60	3.36
A_8	60	3.47
A_9	35	2.31
A_{10}	35	3.81
A_{11}	65	3.72
A_{12}	65	5.30
A_{13}	65	5.16
A_{14}	70	2.28
		2.79
A_{31}	80	3.68
A_{32}	30	6.65
A_{33}	40	3.34
A_{34}	50	6.65
A_{35}	80	5.72
A_{36}	40	3.46
A_{37}	85	3.57
A_{38}	140	4.88
A_{39}	130	2.31
A_{40}	150	4.91

$\bar{X} = 60.7$

$S = 140.12$

$C\% = 230.84$

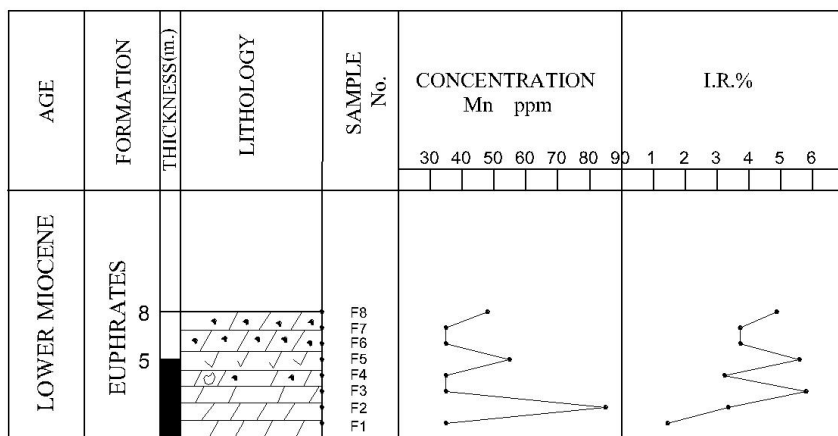I.R.: Insoluble residue

Diyala Journal For Pure Sciences

**Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)**

Rana Abbas Ali

|		
A_{15}	35	
4.18		
A_{16}	65	
3.21		
A_{17}	35	
2.53		
A_{18}	60	
5.18		
A_{19}	30	
2.35		
A_{20}	50	
6.72		
A_{21}	35	
3.35		
A_{22}	70	
4.98		

(a)

Mn Distribution in the Carbonate Fraction of Shallow

Marine Lithofacies, Lower Miocene, Wadi Fuhaimi and Anah town (Western Iraq)

Rana Abbas Ali

Fig.3.(a,b) : Distribution of manganese in Wadi Fuhaimi and Anah sections.

DIYALA JOURNAL FOR PURE SCIENCES

**Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)
Rana Abbas Ali**
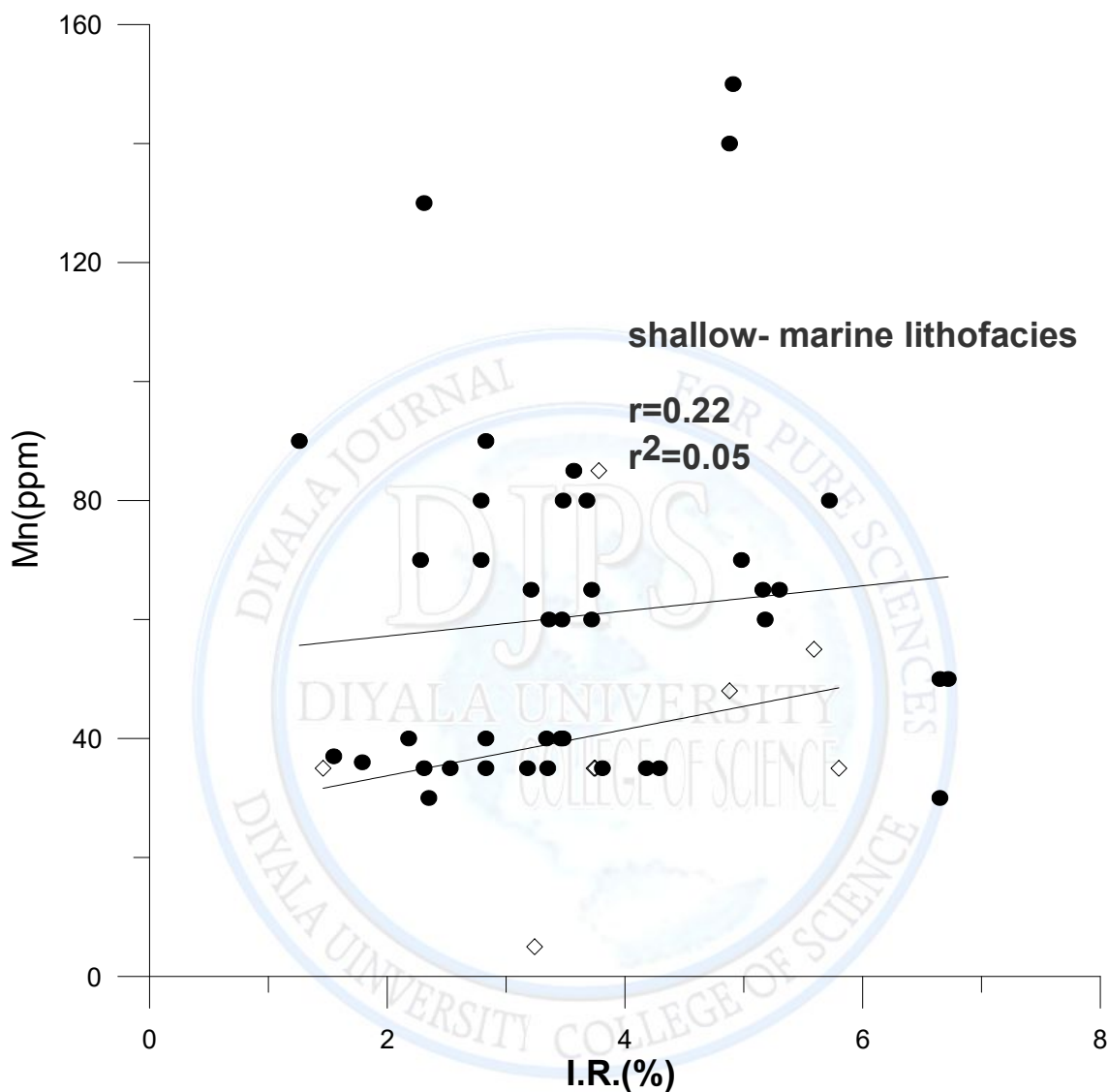
Fig.4: Correlation of insoluble residue (I.R.)and Mn in shallow marine lithofacies ;
r=coefficient of correlation.

Adistinct increase in manganese content from bottom to top marine lithofacies exists in
Anah section (Fig.3.b) corresponding the Insoluble residue is the same level in both sections
(Fig.3.a),that refers most Mn is clearly not derived from the Insoluble residue,but from the
carbonates.

DIYALA JOURNAL FOR PURE SCIENCES

**Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)
Rana Abbas Ali**

Controlling Factors

Structural chemistry

Modern carbonate sediments are mainly composed of aragonite in shallow marine environments and calcite in deep marine environments (23; 24; 25). A clear understanding of crystal structure of calcite and aragonite is critical in explaining the substitution of manganese in this sequence.

Calcite and aragonite are polymorphs of $CaCo_3$. The coordination of calcium is six in calcite and nine in aragonite; therefore, manganese has the proper ionic radius (0.80 A°) and charge (+2) to substitute for calcium (0.99 A°; +2) only in the calcite structure. Furthermore, considering that calcite rather than aragonite forms in the presence of Mn (26), it is apparent that geometrical rather than chemical considerations are an important factor in governing genesis of Mn-rich carbonate sediments.

Another important consideration in trace-element behavior is electronegativity (27; 28; 29). The electro negativity of Mn^{+2} and Ca^{+2} is 1.4and 1.0, respectively.

Because of its higher electro negativity, Mn^{+2} tends to pull electrons closer to its nucleus. A significant result of this behavior is a reduction of the atomic radius (30). The small size and absence of distorted outer electron shells are features that promote the low polarizability of Mn^{+2} (31). The substitution of Mn^{+2} for Ca^{+2}, therefore, occurs without distortion of the calcite lattice.

Small ionic radius, high electronegativity and low polarizability of Mn^{+2} favor its substitution for Ca^{+2} in calcite and its exclusion from aragonite. Manganese-bearing calcites are known to have up to 42 mole % $MnCO_3$ (32). In modern marine carbonates, Mn content in calcite is an order of magnitude higher than in aragonite (Table 3). The concentration factors (33)of Mn within calcitic carbonates (1-130) are quite high when compared to Mn within aragonitic carbonates (0.4-28).

Table 3: Distribution of Mn in modern marine carbonate constituents (compiled from several sources, 33); tr = trace

Carbonate constituent	Dominant mineralogy	Mn (ppm)
Pelletoid	Aragonite	10-80
Oolite	Aragonite	3-7
Aggregate	Aragonite	4-7
Green algae	Aragonite	8
Codiaceae	Aragonite	16-18
Dasycladacea	Aragonite	2-14
Coral (Zoantharia)	Aragonite	2-16
Cephalopoda	Aragonite	2-14
Pteropod	Aragonite	tr-150
Pelecypod	Aragonite	tr-150
Gastropod	Mixed (Aragonite and Mg calcite)	tr-130
Polychaete annelid		
Coralline algae	Mg calcite	11-392
Corallineae	Mg calcite	7-94
Melobesia	Mg calcite	2-80
Foraminifera (benthonic)	Mg calcite	10
Sponge (sclerites)	Mg calcite	4-7
Coral (Octocorallia)	Mg calcite	6-100
Arthropoda (Decapoda)	Mg calcite	6-94
Echinoderm (Echinoidea)		
Coccolith ooze	Calcite	245-280
Atlantic	Calcite	290-930
Pacific	Calcite	950-2000
Indian	Calcite	9-13
Foraminifera (planktonic)	Calcite	3-438
Pelecypod	Calcite	2-1900 (brackish)
Arthropoda (Cirripedia)		

Paleobathymetry and Mineralogy

Aragonite survives only in shallow shelf areas of high carbonate productivity whereas calcite can survive even in deep-sea environments, (24).(25), ascribed the abundance of aragonite in shallow waters (less than 200m) to biological control and the abundance of calcite in deep waters to inorganic precipitation.

Because substitution of Mn for Ca occurs more readily in the calcite structure, shallow-water aragonitic carbonate sediments do not show significant amounts of Mn, whereas the high Mn content in deep-water lithofacies reflects the original calcite mineralogy. A similar relationship between bathymetry and manganese content occurs in the Mesozoic carbonate rocks from Lima Valley in the Northern Apennines, (10).

For reasons discussed above, Mn^{+2} in its reduced state is a favorable substitute for Ca^{+2} in the calcite structure. Because manganese goes into solution under reducing conditions (34; 35; 36), oxygen-deficient environments promote production of Mn-enriched calcite. Under oxygenated conditions manganese would form oxides and hydroxides and be unavailable for incorporation into the calcite structure, (37).

Diagenesis

Different views exist on the effect of carbonate diagenesis on manganese. (10), (14) and (15) argue that manganese distribution is not significantly affected during diagenesis. (38) suggests that manganese tends to increase due to diagenetic autoenrichment.

Because the partition coefficient of Mn ($K_{calcite}$=15) between calcite and solution is greater than unity (38), a diagenetic enrichment of Mn during aragonite/calcite transformation and calcite/calcite reaction is likely to result. This is because the crystals growing from a solution become enriched in trace components with respect to the solution, (39). Solution/reprecipitation and inversion processes, however, are considered to be less common during the Paleozoic than in the Cenozoic due to higher atmospheric CO_2 levels during the pre-Carboniferous (40; 41).

Such a vast difference in manganese content reflects the original distribution of manganese controlled by the initial mineralogy in the shallow-and deep-water environments. The original difference in manganese between lithofacies was so distinct that this difference has remained through time during diagenesis. It is conceivable that some of the Mn could be due to a late generation calcite cement. Cathodoluminescence study shows that the deep marine lithofacies do not contain Mn-rich void filling calcite cement of late diagenetic origin. In contrast, shallow marine lithofacies (Wadi Fuhaimi and Anah sections) show Mn-rich void filling calcite cement of early diagenetic origin. However, levels of Mn detected by electron microprobe analyses of the manganiferous zones are insufficient to obscure the trend observed in the sequence. Mn content in the total carbonate fraction of shallow marine lithofacies are two orders of magnitude smaller than the deep marine lithofacies. Thus late diagenesis is not a major controlling factor of Mn distribution in the shallow and deep marine lithofacies.

Discussion of Results

In this section attemting to evaluate the Mn content as related to:

1. Mineralogy of the original sediments.
2. Physicochemical conditions of sea water in the depositional environment and contribution by weathering on continental areas.
3. Diagenetic processes.

The low Mn content in Wadi Fuhaimi and Anah sections seems to be related to the shallow water depositional environment. The original sediments of this formation were likely to be mainly aragonite, in agreement with the composition of Recent shallow water carbonate sediments (23; 42). In the aragonite structure, Mn does not appear to substitute appreciably for Ca((43); according to (44), and (18), pure marine aragonite contains less than 20 ppm Mn), whereas much more Mn can substitute for Ca in calcite structure (natural Mn-rich calcites can contain up to several percent $MnCO_3$, according to data reported by(43). With reference to this fact, the computation of correlation coefficient r between aragonite and Mn

DIYALA JOURNAL FOR PURE SCIENCES

**Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)
Rana Abbas Ali**

contents of Recent carbonate sediments from Florida (data from 23) gave rise to a highly significant negative correlation.

Low Mn contents similar to the ones observed in Wadi Fuhaimi and Anah sections have been found in Recent mainly aragonitic shallow water sediments by (23); (44); (45) and (46); in Pliocene-Recent reef limestone by (47); in reef and subreef rocks of Upper Jurassic age by(48).

Since an open system was likely to be operative in the studied sequence, as it can be dedticed from the occurrence of dolomitization processes in the shallow water formation, a postdepositional change of Mn content could be suggested. However, as within formation the Mn values from dolomitized samples fall in the same range as those from non- dolomitized ones, it must be concluded that the dolomitization itself did not produce significant changes in Mn content. The original differences in Mn content between shallow water and deeper sea formations, should have been maintained:-

1. The change in mineralogy (aragonite or calcite) of the original sediments, which allows Mn content to be the screening factor between shallow water and deeper sea formations.

2. The variation of paleobathymetry. Mn shows a general tendency to be concentrated in deep-sea sediments (49; 17; 50), wheremore reducing conditions would allow a larger amount of Mn^{+2} to enter the crystal structure of calcite.

3. The variation of Mn supply due to the weathering conditions on continental areas (or may be, in some case, to submarine volcanic activity).

It should be further pointed out that in the studied sequence Mn would be by far prcierable to Sr as a paleoenvironmental indicator. Mn does not appear to have undergone serious changes during diagenesis, especially during the aragonite -----› calcite inversion. The generalization of the conclusion about sharp differences in Mn content attributable to differences in the original mineralogy of carbonate sediments, requires further studies to be carried out particularly on ancient carbonate sequence including shallow water and deep-sea formations.

Conclusions

From the study of Mn content in the Cenozoic carbonate sequence of Wadi Fuhaimi and Anah sections the following conclusions can be drawn:

1. Mn appears to be mainly associated with carbonate fraction.

2. The original aragonite mineralogy of the shallow marine environments and calcite mineralogy of the deep marine environments were a major controlling factor for Mn distribution.

3. Mn tends to concentrate in calcite because the substituting cation (Mn) prefers the rhombohedral structure of calcite to the orthorhombic structure of aragonite.

4. Diagenetic processes, particularly dolomitization, do not appear to have seriously modified the original Mn content: original differences are maintained.

5. The relatively high Mn content in some stertigraphic levels is likely to be related to periods of intensive weathering on continental areas (possibly, also to submarine volcanic activity) and/or to a larger availability of Mn^{+2} (substituting for Ca in calcite) due to more reducing sea water conditions.

Mn Distribution in the Carbonate Fraction of Shallow

Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)

Rana Abbas Ali

References

1. Buday, T., 1980: The regional geology of Iraq, Vol.1, stratigraphy and paleontology, 445pp. Khassab, I.I.M. And Jassim, S.Z. (edts) S.O.M., Baghdad.

2. Antonets, V.B., Podgornov, V.M. and Pasekov, Y.M., 1963:Report on the prospecting and geophysical surveying of the phosphate raw material in the western desert and SW Iraq in 1962 No.299 SOM Library Baghdad.

3. Al-Mubarak, M., 1971: Final geological report of the Euphrates Vally. NIMCO Report, SOM Library, Baghdad.

4. Al-Jumaily, R., 1974: Report on the regional geological mapping of the area of the Iraqi-Syrian border-T1 pumping station, Western Desert. NIMCO Report, SOM Library, Baghdad.

5. Prazak, J., 1974: Stratigraphy and paleontology of the Miocene of the Western Desert, Western Iraq. NIMCO Report, SOM Library, Baghdad.

6. Banat, K.M. and Al-Dyni, N.K., 1981: Petrology and mineralogy of selected sections from the Euphrates and Jeribe Formations (Miocene) Iraq.J.Geol.Soc.Iraq 14,1-14.

7. Bellen, R.C. Van, Dunnington, H.V., Wetzel, R. and Morton, D.,1959: Lexique stratigraphique international. Asie, Fasc 10a Iraq.Paris.

8. Bisque, R.E., 1961:Analysis of carbonate rocks for calcium, magnesium, iron, and aluminum with EDTA: Jour. Sed. Petrology, V.31,P.113-122.

9. Renard, M., and P. Blanc, 1972: Influence des conditions de mise en solution (choix de L'acide, temperature, durée d'attaque) dans le dosage des elements en traces des roches carbonatées: Comptes Rendus Acad. Sci, Parid, Série D, V.274, P.632-635.

10. Bencini, A. and Turi, A.,1974: Mn distribution in the Mesozoic carbonate rocks from LimaValley, northern Apennines, J. Sediment. Petrol., 44:773-782.

11. Maxwell, J. A., 1968:Rock and mineral analyses .John Wiley and Sons. New York. 584p.

12. Stanton, R. E.,1966: Rapid methods of trace elements for geochemical applications, Edward Annold pub. London,96p.

13. Barber, C., 1974: Major and trace elements associations in limestones and dolomites. Chem. Geol., 14: 273-280.

DIYALA JOURNAL FOR PURE SCIENCES

Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)
Rana Abbas Ali

14. Rao, C.P. and Naqvi, I.H., 1977: Petrography, geochemistry and factor analysis of a Lower Ordovician subsurface, Tasmania, Australia. J. Sediment. Petrol., 47: 1036-1055.

15. Robinson, P.,1980: Determination of calcium, magnesium, manganese, strontium, sodium and iron in the carbonate fraction of limestones and dolomites. Chem. Geol., 28:135-146.

16. Deer, W.A., R.A., Howie, and J.Zussman, 1962a: Rock-forming minerals, V.3, Longmans, London, 270P.

17. Muller, G., 1967, The HCL-soluble iron, manganese, and copper contents of Recent Indian Ocean sediments off the eastern coast of Somalia: Mineralium Deposita, V.2, P.54-61.

18. Thompson, G.,1972: A geochemical study of some lithified carbonate sediments from the deep sea. Geochim. Cosmochim. Acta,36:1237-1253.

19. Bienner, F.,B. De Jekhowsky, R. Pelet, and B. Tissot, 1968: Abondance et repartition de certains éléments dans les formations sédimentaires du Bassin de Paris: in Ahrens, L.H. (ed.), Origin and distribution of the elements, Pergamon Press, Oxford, P.1039-1063.

20. Awasthi, N., 1970: Some aspects of the Krol Formation of the Himalaya, India: Contr. Mineralogy and Petrology, V.28, P.192-220.

21. Freund, J.E., 1967: Modern elementary statistics (3rd ed.) . Prentice Hall, Englewood Cliffs, N.J., 432PP.

22. Benedict III, G.L., 1983: The establishment and evolution of the Western Margin of the Sevier Basin, Middle Ordovician, Southern Appalachians. Ph.D. Diss., University of Tennessee Knoxville, Tenn. (in prep.).

23. Stehli, F.G., and J.. Hower,1961: Mineralogy and early diagenesis of carbonate sediments: Jour. Sed. Petrology, V.31, P.358-371.

24. Friedman, G.M., 1965: Occurrence and stability relationship of aragonite, high-magnesian calcite, and low- magnesian calcite under deep-sea conditions. Geol. Soc. Am. Bull., 76: 1191-1196.

25. Milliman, J.D., and Miller, J., 1977: Characteristics and genesis of shallow-water and deep-sea limestones. In: N.R. Anderson and A. Malahoff (Editors), The Fate of Fossil Fuel CO_2 in the Oceans. Plenum Press, New York, N.Y., PP. 655-672.

26. Fonda, G.R., 1940: The preparation of fluorescent calcite.J.Phys.Chem.,44,P.435.

27. Pauling, L., 1940: The nature of the chemical bond, Cornell Univ. Press, Ithaca, N.Y., 450PP.

28. Ringwood, A.E.,1955: The principles governing trace element distribution during magmatic crystallization, part1: the influence of electronegativity. Geochim. Cosmochim. Acta, 7:189-202.

29. Ahrens, L.H.,1964: The significance of the chemical bond for controlling the geochemical distribution of the elements-Part1.In: L.H. Ahrens, F. Press and S.K. Runcorn (Editors), Physics and Chemistry of the Earth. Mac Millan, New York, N.Y.,PP.4-54.

30. Sanderson, R.T.,1973: Electronegativity. In: C.A. Hampel and G.G. Hawley (Editors), The Encyclopedia of Chemistry (3rd ed.). Nostr and Reinhold, New York, N.Y.,1198PP.

31. Basolo, F. and Pearson, R.G., 1967: Mechanisms of Inorganic Reactions (2nd ed.) Wiley, New York, N.Y., 701PP.

32. Deer, W.A., Howie, R.A. and Zussman, J., 1978: An Introduction of the Rock-forming minerals. Longmans, London, 528PP.

33. Milliman, J.D., 1974: Marine Carbonates, Part I. Springer, New York, N.Y., 375PP.

34. Lynn, D.C. and Bonatti, E., 1965: Mobility of manganese in diagenesis of deep-sea sediments. Mar. Geol.,3: 457-476.

35. Eaton, A., 1979: The impact of anoxia on Mn fluxes in the Chesapeake Bay. Geochim. Acta, 43: 429-432.

36. Davison, W.,1981: Supply of iron and manganese to an anoxic lake basin. Nature, 290: 241-243.

37. Oglesby, T.W., 1976: Amodel for the distribution of manganese iron and magnesium in authigenic calcite and dolomite cements in the upper Smackover Formation in Eastern Mississippi. M.S. Thesis. Univ. of Missouri, Columbia, Mo., 122PP.

DIYALA JOURNAL FOR PURE SCIENCES

Mn Distribution in the Carbonate Fraction of Shallow
Marine Lithofacies, Lower Miocene,Wadi Fuhaimi and Anah town (Western Iraq)
Rana Abbas Ali

38. Pingitore, N.E., 1978: The behavior of Zn^{+2} and Mn^{+2} during carbonate diagenesis: theory and applications. J. Sediment. Petrol., 48: 799-814.

39. McIntire, W.L., 1963: Trace element partition coefficients-a review of theory and apphcations to geology. Geochim. Cosmochim. Acta, 27: 1209-1264.

40. Pigott, J., Schoonmaker, J. and Mackenzie, F.T., 1980: Phanerozoic carbonate diagenesis: a new model. Bull. Am. Assoc. Pet, Geol., 64: 764-765.

41. Mackenzie, F.T. and Pigott, J.D.,1981: Tectonic controls of Phanerozoic sedimentary rocks cycling. J. Geol. Soc. London, 138: 183-196.

42. Cloud, P.E., 1962: Environment of calcium carbonate deposition west of Andros Island, Bahamas: U.S. Geol. Survey Prof. Paper 350, p.1-138.

43. Deer, W.A., R.A., Howie, and J.Zussman, 1962b: Rock-forming minerals, V.5, Longmans, London, 371P.

44. Friedman, G.M., 1968: Geology and geochemistry of reef, carbonate sediments, and waters, Gulf of Aqaba (Elat), Red Sea: Jour. Sed. Petrology, V.38, P.895-919.

45. Pilkey, O.H., B.W. Black welder, L.J. Doyle, E.Estes, and P.M. Terlechy, 1969, Aspects of carbonate sedimentation on the Atlantic continental shelf off the southern United States: Jour. Sed. Petrology, V.39, P.744-768.

46. Angino, E.E.,W.R. Bryant, and J.L. Harding, 1972: Trace elements geochemistry of carbonate sediments, Yucatan Shelf, Mexico: in Geological oceanography of Gulf of Mexico, Gulf Publishing Company, P.281-290.

47. Honjo, S., and H. Tabuchi, 1970: Distribution of some minor elements in carbonate rocks,1: in Minato, M.,M.Gorai, K.Ichikawa, and M.Omori (eds.), Pacific Geology, V.2, Tsukiji Shokan Publishing Company, Tokyo, P.41-79.

48. Davies, P.J.,1972, Trace element distribution in reef and subreef rocks of Jurassic age in Britain and Switzer land : Jour. Sed. Petrology, V.42, P.183-194.

49. Kraus Koph,K.B.,1967 :Introduction to geochemistry,McGraw-Hill Company,New York,N.Y.,721P.

50. Elder field, H., 1972: Compositional variations in the manganese oxide component of marine sediments: Nature Phys. Sci., V.237, P.110-112.