TEMPORAL DISTRIBUTION OF SELECTED ELEMENTS IN CARBONATE ROCKS OF MIDDLE JURASSIC JAISALMER FORMATION, RAJASTHAN, INDIA

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ABSTRACT

The distribution and vertical variation patterns of Ca, Mg, Fe, Mn, Sr, K, Na, Pb, Zn, Ni and IR (Insoluble Residue) from carbonate rocks of Jaisalmer Formation suggest a change in the depositional conditions of the basin through time from a normal marine to hypersaline depositional environment. The R-mode factor analysis of the chemical data reveal the significance of three common factors contributing about 72% of total variance. These three factors have been interpreted as related to gross mineralogy, colloidal precipitation of secondary minerals and the effect of diagenesis. Based on the present study, a shallow, near normal to less marine condition of the deposition has been interpreted for the lower four members (viz. Hamira, Joyan, Fort, and Badabag) and a hypersaline, lagoonal environment suggested for the topmost Kuldhar member of the Jaisalmer Formation.

INTRODUCTION

It has been well established through the study of ancient carbonate rocks that the distribution of both major and trace elements associated with carbonate lattice are essentially controlled by the depositional facies (Veizer and Demovic, 1974, Veizer, 1977). The chemistry of fossiliferous Phanerozoic carbonates provide information to delineate different depositional environments and facies and also to confirm the previously observed mineralogical, petrological and palaeontological attributes for the facies interpretation of the rocks. Further, the understanding of the variations in elemental composition will aid in quantitative reconstruction of the diagenetic history.

The Jaisalmer Formation, a Middle Jurassic sequence exposed in western Rajasthan, is known for a variety of carbonates belonging to depositional facies varying form hypersaline to normal marine in origin (Dasgupta, 1975). The Jaisalmer Formation rich in fossils has been studied extensively for its palaeontology and stratigraphy (Narayanan, 1964; Dasgupta, 1975; Kachhara and Jodhawat 1982; Kalia and Chowdhury 1983). The sedimentologic nature of coarse clastics has been given in (Mahender and Banerjee, 1989). However, a proper understanding of chemical character of carbonates including vertical variation of trace and minor element concentrations has not received proper attention. Therefore, the present study has been undertaken with the following objectives:

(a) to understand the distribution of various minor and trace elements in the carbonates,

(b) to evolve interrelationships between various elements using statistical analysis, and

(c) to interpret the depositional conditions of the Jaisalmer Formation in the light of the chemical parameters.

GEOLOGY OF THE AREA

The Jaisalmer Formation forms a major part of Jurassic of western Rajasthan and is exposed around Jaisalmer town in a rectangular area limited within Lat. 26^0 45' to 27^0 10' N and Long. 70^0 45' to 71^0 10' E (Fig. 1). The Jaisalmer Formation showing a gradual intertonguing relationship with the underlying sandy Lathi Formation and an unconformable contact with the overlying shaly Baisakhi Formation, is represented by a variety of lithological units with variable skeletal and non-skeletal particles. Generally these beds strike NE-SW with a gentle dip of less than 5^0 towards NW and NNW. The area is covered in many places by windblown Recent sands, which are usually arranged in the form of linear dunes with high degree of parallelism.

The lithology of the formation comprises mainly the carbonates including limestone and a few dolomites, followed by sandstone and clays in order of abundance. The carbonates are generally oolitic and sandy in nature and show a continuous gradation from sandy limestone to calcareous sandstone. These limestones are generally hard, massive, orange yellow to brown in colour. The sandstones are brownish to grey in colour, fine to medium grained, massive to flaggy in nature. The sandstones and sandy limestones often exhibit cross-bedding structures.

The Jaisalmer Formation has been divided into five members, in an ascending order. These are, the Hamira, the Joyan, the Fort, the Badabag and the Kuldhar members. The general stratigraphic succession of the study area is presented in Table 1.

TABLE 1

LITHOLOGICAL UNITS OF JAISALMER FORMATION (MAHENDER, 1986)

| Formation	Member	Lithology	Typical Sections	Age
BAISAKHI		Intercalated fine, argillaceous sandstone and grey gypseous clays, siltstone		Kimmeridgian
		----- Unconformity -----		
	KULDHAR	Argillaceous, ferruginous, silty and oolitic limestone-type; oolitic shale, gypsiferous clays sandstone	Kuldhar nala section	Middle Callovian to Oxfordian
	BADABAG	Cross-bedded calcareous sandstone, dolomitised sandy limestone, intraformational conglomerate and sandstone	Badabag hill scarp section	Lower Callovian to Middle Callovian
JASALMER	FORT	Coarse, sandy, fossiliferrous, oolitic limestone cross-bedded sandy limestone, fine to medium grained sandstone	Fort escarpment section	Bathonian to Lower Callovian
FORMATION				
	JOYAN	Coquinoidal limestone, gritty sandstone, ferruginous sandstone.	Jaisalmer-Thiat Road sections	? Bajocian
	HAMIRA	Sandy limestone, calcareous sandstone and marl bands	Thiat scarp, and Hamira village sections	? Bajocian
		----- Graded contact -----		
LATHI		Calcareous sandstone, variegated calcareous sandy siltstone and conglomerate and fossil wood		Lias
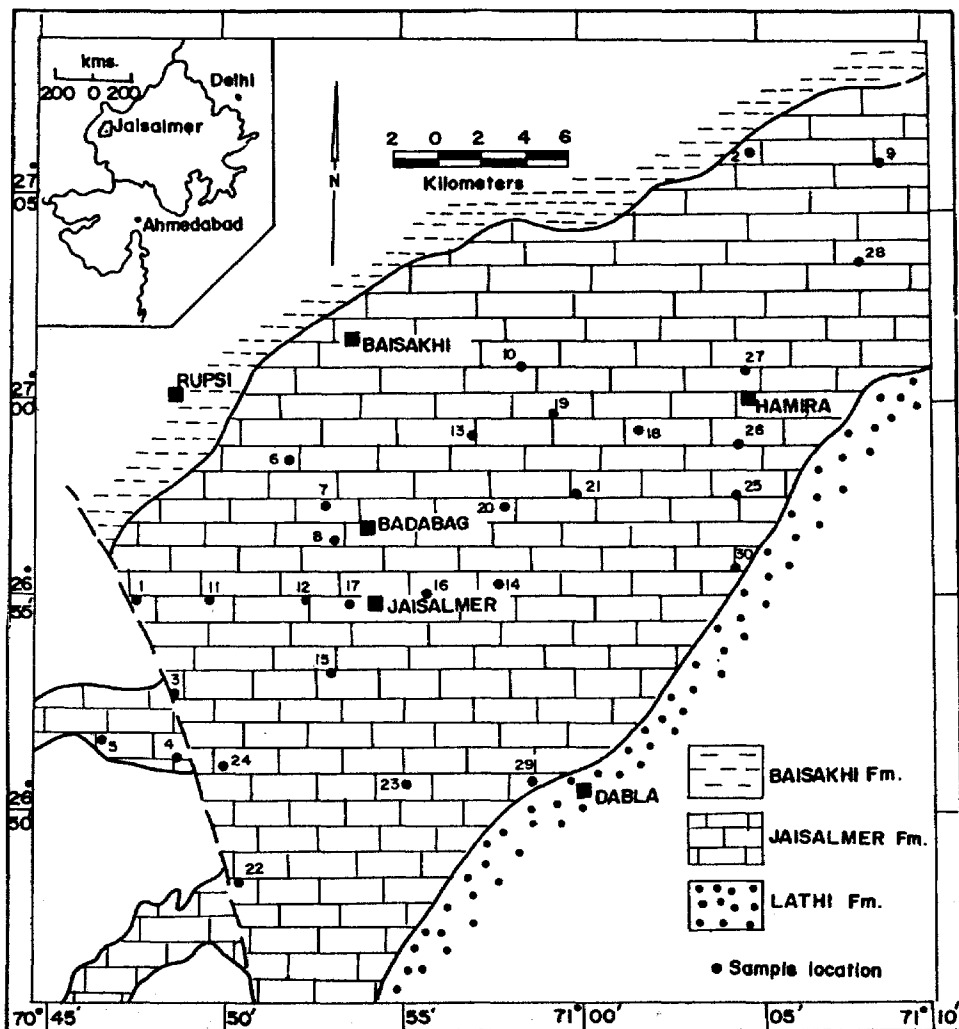
Fig. 1   Geological map of Jaisalmer showing sample locations.

ANALYTICAL PROCEDURES AND RESULTS

For the present, analytical study, the carbonate rock samples have been collected systematically along a set of three traverses covering almost the entire exposed patch of the Jaisalmer Formation (Fig. 1).

The method of dissolution and analyses of carbonate sediments used for the present study has been described as follows:

The major elements such as Ca and Mg were determined by EDTA titration procedure, by digesting the samples in 1N HCl and titrating against 0.2M EDTA solution in the presence of NaOH with Murieoxide as indicator for Ca and in the presence of Buffer solution with Erichrome Black T as indicator for Mg. The solutions to analyse the trace and minor elements were prepared by dissolving the powdered sample in $HF + HNO_3 + HClO_4$ acid solution for complete dissolution and the salts formed after evaporation of the acid were made used to prepare sample aliquots. These aliquots were analysed by Atomic Absorption Spectrometer (Varian Techtron AAS-6R) at the Regional Sophisticated Instrumentation Center, I.I.T., Bombay for the determination of Fe, Mn, Sr, Na, K, Pb, Zn and Ni elements. The IR was determined gravimetrically by ashing the filter paper at 600^0 C for 1hr. The analytical data is presented in Table 2 and the distribution of elements is shown by histograms (Fig. 2) both of which show wide variation in elemental values. These variations have been interpreted by statistical analyses using R-mode factor analysis. The methodology of R-mode factor analysis is given in Harman (1976) and Davis (1973). The present study included eleven variables viz. Ca, Mg, Fe, Na, K, Mn, Sr, Pb, Zn, Ni, and IR for interpretation. The various computational steps involved were as follows:

1. computation of correlation coefficients* on the measured variables.
2. Extraction of eigen values or the initial factors and selection of number of factors.
3. An initial matrix of factor loadings defining the principle uncorrelated components of the system.
4. Varimax rotation of the initial matrix to obtain the final rotated matrix of factor loadings.

The correlation coefficient matrix and the matrix of varimax rotated factor loadings are presented in Table 3 and Table 5 respectively.

For the present study the Pearson Correlation Coeffient (r) defined in Krumbein et al (1967) has been used

$$ r = \frac{\sum_{i=1}^{N} x_i y_i - (\sum_{i=1}^{N} x_i)(\sum_{i=1}^{N} y_i)/N}{\sqrt{(\sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2/N)(\sum_{i=1}^{N} y_i^2 - (\sum_{i=1}^{N} y_i)^2/N)}} $$

where x, y are two variables and N is number of observations

INTRAFORMATIONAL VARIATIONS

The vertical distibution of various elements in different members is presented in fig. 3. It is apparent from Fig. 3, that the distribution of Ca shows somewhat an opposite trend compared to that of other elements. A relative enrichment of most of the elements except Ca and Fe is clearly seen in the topmost Kuldhar Member. A continuous decrease in Fe, Mn and Sr contents up to the Badabag and thereafter sudden increase in their values in Kuldhar Member is indicative of different depositional conditions for the Kuldhar Member. A relatively higher values of Na and Sr in Hamira and Kuldhar members is due to the presence of clays. In the lower four members the concentrations of Pb, Zn and Ni remain almost constant, wher as slightly higher values for the elements are however noted in Kuldhar.

TABLE 2

DISTRIBUTION OF VARIOUS ELEMENTS IN JAISALMER CARBONATES (IN PPM)

| Member	Variable	Ca	Mg	Fe	Mn	IR	Sr	Na	K	Pb	Zn	Ni
	Range	175361-308436	2770-12140	9760-37256	209-1193	23600-376274	450-1271	75-4980	590-7120	52-105	18-244	24-85
KULDHAR	Mean	234829.33	7141.33	42448.33	843.83	205062.0	643.83	250	1603.33	74.17	100.5	57.83
	Std.Dev	51775.93	3910.13	48250.97	427.42	11305	182.01	150.01	793.34	27.75	97.20	26.09
	Range	187460-36852	1475-3288	5940-14268	280-606	30225-138500	235-760	69-170	160-2010	50-100	13-102	28-69
BADABAG	Mean	290153.67	2075.17	9755	434	68099.67	475.5	115.33	740	65.67	44.83	35.50
	Std.Dev	67178.10	622.24	1800.04	141.13	38053.44	180.04	41.08	692.07	19.51	39.29	16.98
	Range	274128-384582	1682-2190	9098-17164	290-631	21893-356800	390-638	52-280	130-1190	41-96	13-118	15-46
FORT	Mean	337313.0	1903.33	11771.44	456.33	55430.75	518.78	137.67	414.22	72.78	65	34.89
	Std.Dev	40855.93	173.57	3748.55	113.04	49132.16	104.33	63.21	371.57	20.14	31.40	11.79
	Range	200286-368521	2338-6042	5234-12304	112-776	39941-678200	310-1102	160-320	450-3010	44-94	59-68	38-44
JOYAN	Mean	288369	3826	8472	477.33	255547	456	230	313.67	75.67	65	41.33
	Std.Dev	84397.44	1956.37	3572.23	333.67	366053	179.21	81.85	130.46	27.58	5.20	3.06
	Range	102790-298316	1624-27820	6204-22550	60-1222	49300-585200	360-788	120-580	190-2540	45-77	30-71	23-42
HAMIRA	Mean	248019.33	6907.17	11444.17	811.67	178920.17	528	271.67	'855.83	57	54.16	31.17
	Std.Dev	76050.32	10383.81	5900.40	404.79	208979.97	153.26	175.77	957.14	12.30	13.57	6.79
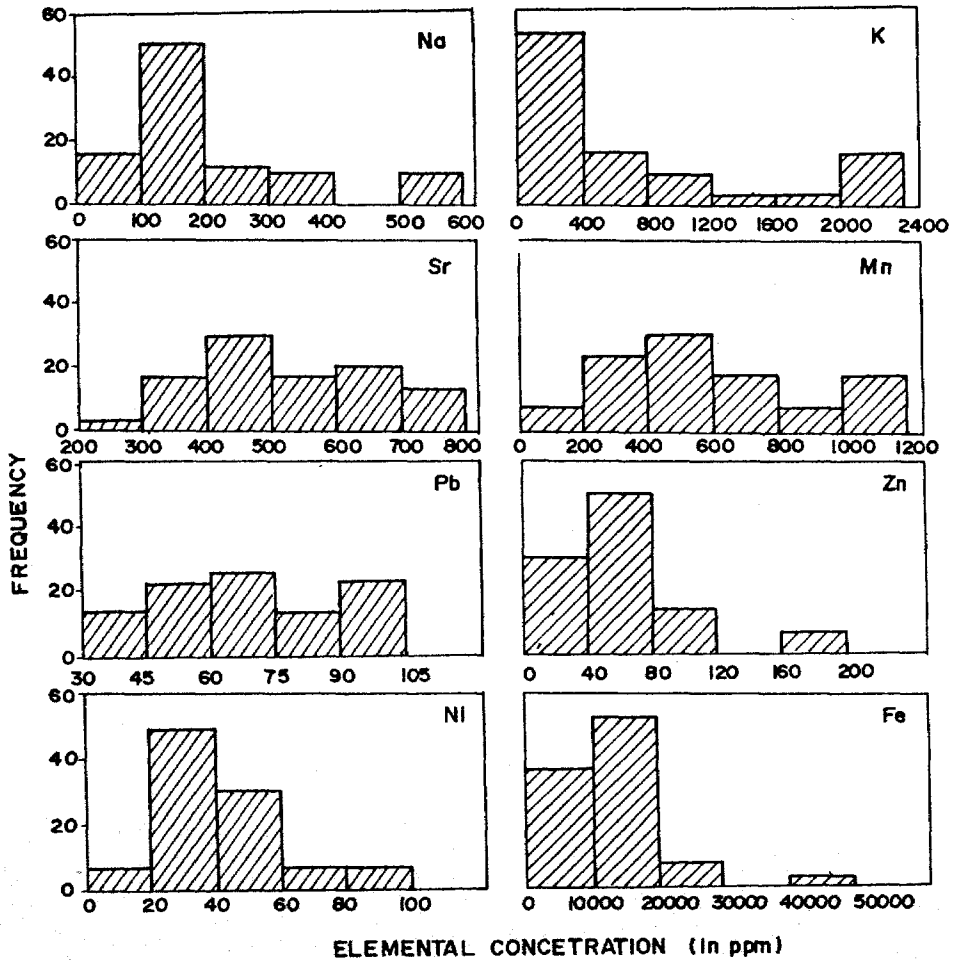
Fig. 2 Histograms showing elemental distribution in carbonate samples of Jaisalmer Formation.
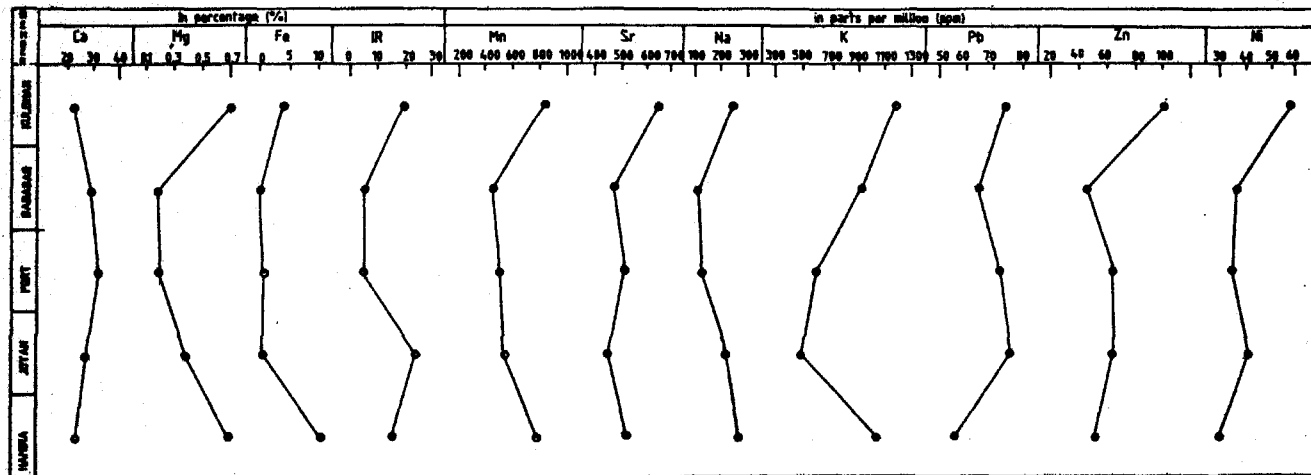
Fig. 3 Vertical variations in mean elemental concentration in carbonate rock samples of Jaisalmer Formation.

DATA INTERPRETATION

CALCIUM, MAGNESIUM AND INSOLUBLE RESIDUE

The negative correlation of Ca with Mg and positive correlation of IR with Mg (Fig. 4a & b) are attributed to the selective leaching effect of Ca by the primary solution resulting in a relative enrichment of IR and Mg in the limestones. The IR may act as a barrier (or membrane) preferentially concentrating Mg in the interstitial solutions which are squeezed out during diagenesis. The IR in these carbonates comprises mainly quartz and clays.

IRON AND MANGANESE

The iron in limestones occur as coatings of iron oxides on various carbonate particles and clays. Both calcite and dolomite can accommodate appreciable ferrous ions in their structures; the ability of dolomite to do so is enhanced by more ready substitution of Fe for Mg than Ca (Veizer, 1978). The positive correlation of Fe with Mg (r=0.3927, Table 3) and in absence of a well defined correlation of Fe with Ca (r=-0.2926, Table 3) are indicative of the capacity of dolomites to accommodate more iron than that of limestones. This is also corroborated by the data presented in Table4, where samples affected by dolomitisation display, within each member, a tendency to have higher Fe contents compared to the nondolomitised samples. Fig. 4e shows a positive correlation of Mn with Fe (r=0.4595, Table3); this could suggest a common source for the two elements. The Fe content decidedly increase with increase of clay fraction. No relation is observed between Mn and IR.

SODIUM AND POTASSIUM

The alkali contents of limestones have been generally ascribed to the presence of non-carbonate minerals, and solid impurities. The positive correlation of Na and K with IR (Fig. 4d & 4c) confirms this. The negative correlation of Na with Ca (r=-0.4622, Table 3) and positive correlation with Mg (r=0.4979, Table 3) suggest enrichment of Na with the process of dolomitisation. The general Na level shown by Jaisalmer samples could be interpreted in the light of White's (1977) experiments as pointing to their formation from an equilibration with solutions whose salinities were somewhat more dilute than sea water. The approximate division between normal to hypersaline environment can be placed at 230 ppm (Veizer *et al*, 1977). The present samples with abundant fauna of gastropod, pelecypod, echinoid and algae show values of Na ranging from 50 to 580 ppm, with highest frequency ranging in 130-360 ppm, indicating a more or less normal marine environment.

The general stratigraphic trend of K content is similar to that shown by Na values, showing a positive correlation (r=0.5433, Table 3). The observed K trend also closely resembles the trends of IR and Mg, in accordance with the high correlation coefficients for K, IR and Mg (Table 3). The K trend may result either from (a) a higher K content in the samples from hypersaline environments or (b) due to leaching out of K from IR during laboratory treatment, with samples from hypersaline environments containing more detrital clays, or (c) due to a combination of both the processes.

STRONTIUM

Sedimentary geochemists use Sr as a tool for facies analysis and petroleum geochemists use Sr for identification of oil basins associated with carbonates. Generally, Sr concentration is more in sea water than in fresh water, and therefore, it reflects the nature of ancient basinal water. The positive correlation of Sr with Na (r=0.4430, Table 3, Fig. 4f) is indicative of the marine nature of strontium. The overall concentration depends on the fractions of aragonite and high-Mg-calcite replacement, and the
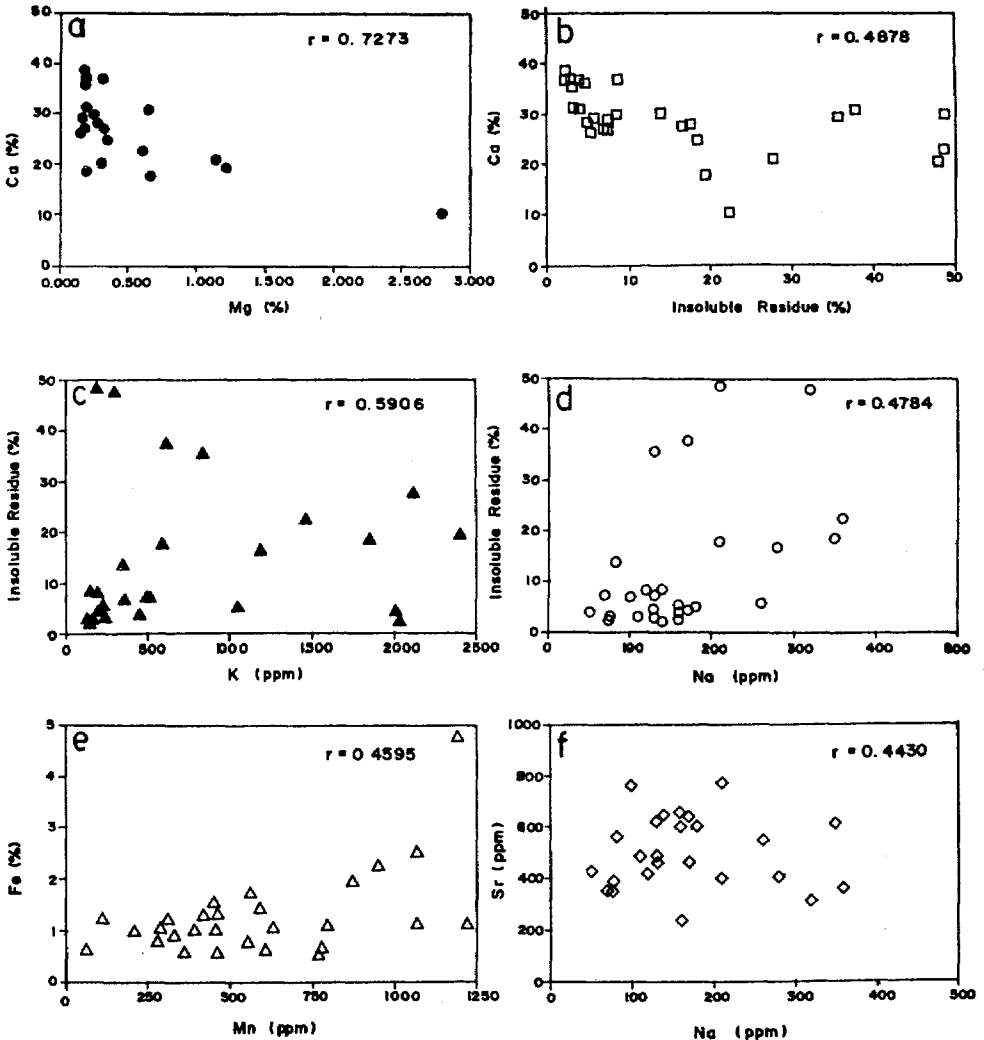
Fig. 4 Scatter diagrams of selected elements

a) Ca Vs Mg
b) Ca Vs. insoluble residue
c) Insoluble residue Vs K

d) Insoluble residue Vs Na
e) Fe Vs Mn
f) Sr. Vs Na.

TABLE 3

CORRELATION COEFFICIENT MATRIX OF NORMALISED CHEMICAL PARAMETERS OF JAISALMER CARBONATE SAMPLES (N = 30)

	Ca	Mg	Fe	Mn	IR	Sr	Na	K	Pb	Zn	Ni
Ca	1.0000										
Mg	—0.7273**	1.0000									
Fe	—0.2906	0.3927*	1.0000								
Mn	0.0588	—0.0879	0.4595**	1.0000							
IR	—0.4876**	0.4924**	0.2111	—0.0122	1.0000						
Sr	0.1971	0.1311	—0.0122	0.0426	0.1816	1.0000					
Na	—0.4622**	0.4979**	0.3807*	0.0185	0.4784**	0.4430*	1.0000				
K	—0.8044**	0.7994**	0.2662	—0.1920	0.5906**	—0.0793	0.5433**	1.0000			
Pb	—0.2516	0.1741	0.6934	0.3105 *	0.1219	0.1337	0.4060	0.1866	1.0000		
Zn	0.3209*	—0.1101	0.3943	0.2447	—0.0882	—0.2135	0.2542	—0.2731	0.2526	1.0000	
Ni	—0.2568	0.2794	0.5733**	0.2447	0.5057**	0.0390	0.3636*	0.3443*	0.4855**	0.0597	1.0000

* Significant at 99% confidence level   * Significant at 95% confidence level

TABLE 4

COMPARISION BETWEEN CONTENTS OF Mn AND Fe IN THE DOLOMITISED AND NON DOLOMITIZED SAMPLES FROM JAISALMER FORMATION

		Mn ppm.	Fe ppm
Non-dolomitised samples	Range	112-631	5640-17164
	x	438	11046
	N		16
Dolomitised samples	Range	209-1222	5234-47562
	x	790	16750
	N		14

rate of movement of the pore fluid through the rocks (Harris and Mathews, 1968). Kinsman (1969) has interpreted the values of Sr in calcite as a result of the passage of large volume of fluid through the sediment. In his study he found the average Sr content in calcite to be 418 ppm, and he concluded that the process of diagenesis was in a less saline environment, in an open system. Present values of Sr content in Jaisalmer carbonates, when correlated with Kinsman's theory, indicate a less-saline condition of palaeo-sea in western India.

LEAD, ZINC AND NICKEL

Lead is considerably larger in its ionic size than Ca and the diadochy should obviously be very limited. The present samples are characterised by uniform presence of Pb. The positive co-relation of Pb with Fe, Na and Ni (Table 3) indicated an external source. Limestones and dolomites are in general, low in Pb content. The distribution coefficients for Zn between calcite and precipitated fluid is greater than unity, such that the element (i) will be present at very low levels in precipitated marine carbonates which have diagenetically unaltered, and (ii) will be largely lost to solution during diagenesis (Morrow and Meyer, 1978). Most of Zn liberated by the dissolution of aragonite during early diagenesis will be incorporated into the subsequently formed calcite. Wedepohl noted that additional Zn can enter both limestone and dolomite fractions with increasing diagenesis. The positive relation of Zn with Ca (r=0.3209, Table 3) supports the above inference. The lower concentration of Zn and positive correlation of Zn with Fe (r=0.3943, Table 3) is attributed to a shallow water phase and an external source, respectively.

Nickel is very stable in aqueous solutions and capable of migration over long distance. The weathering of ultrabasic rocks gives rise to Fe, Ni and silica. As the aqueous solution sinks Fe oxidises and precipitates as ferric hydroxides, and then loses water ultimately to form goethite and hematite in which small amounts of Ni ions are trapped. In the Jaisalmer samples the presence of iron oxide coating on various particles and presence of goethite (x-ray analysis data, Mahender, 1986), can be related to the consistent presence of Ni. Generally, deep sea sediments show a higher concentration of Ni, upto 1000 ppm, whereas shallow water sediments show low concentrations. Speaking alternatively, the lower values of Ni in the samples are related to a shallow water phase. The significant positive correlation of Ni (i) with Fe and IR (Table 3) is marked as an evidence of external source of Ni, and (ii) with Na, K and Pb (Table 3) indicates that a part of Ni is present in clays.

TABLE 5

FACTOR LOADINGS FOR THE FIRST THREE FACTORS AFTER VARIMAX ROTATION (N=30)

Variables	Factors 1	2	3	Communality
Ca	-0.8807	—	0.2686	0.8650
Mg	0.8362	—	—	0.7189
Fe	0.2519	0.8863	—	0.8520
Mn	-0.2809	0.7065	—	0.5845
IR	0.7356	—	0.2536	0.6055
Sr	—	—	0.8775	0.7737
Na	0.6033	0.2633	0.5809	0.7707
K	0.9503	—	—	0.9180
Pb	—	0.7710	—	0.6930
Zn	-0.3159	0.4504	0.5420	0.5965
Ni	0.3965	0.6132	—	0.5369
Percent of Total variance	33.83	23.34	14.40	
Cumulative percent variance	33.83	57.17	71.57	
Eigen values	3.7181	2.5655	1.5875	7.8711

IR = Insoluble Residue

Loadings <0.2 are omitted.

FACTOR MODEL FOR JAISALMER CARBONATES

A 11 X 11 correlation matrix from the standardised variable data has been computed giving factors contributing 100% variance. Three common factors have been retained for varimax rotation and interpretation. The three factors together explain about 72 percent of total variance, and have been explained as follows:

FACTOR-1

The first factor depicts strong influence of Ca-Mg-IR-K and Na and explains almost 34% of total variance. Mg, IR, K and Na are positively linked with the first factor, whereas Ca is negatively related (Table 5). Thus the factor can be jointly explained by two sources. The strong loadings on Ca, Mg, and IR is taken as a source related to gross mineralogy of Jaisalmer carbonates. The variable K may be due to the influence of alkalies (mainly clay mineral viz., illite etc) on gross lithology. The negative relation of Ca with Mg and IR indicates that the Ca is primary and is replaced by Mg, due to which there is the additional IR. A part of the IR is also caused by Na and K contents present in the non-carbonate clay fraction.

FACTOR-2

The second factor, accounting for some 23% of the total variation shows strong loadings on Mn, Fe, Ni and Pb indicates the colloidal precipitation of goethite and hematite along with the entrapped Pb and Ni ions. A common external source is also suggested for Mn and Fe.

FACTOR-3

The third factor explaining about 14% of total variance is strongly loaded on Sr, Na and Zn, and indicates diagenetic solution activity during which most of the Zn and Sr were liberated by the dissolution of aragonite during early diagenesis. The elements Zn and Sr got incorporated into the subsequently formed calcite.

CONCLUSION

The distributional study of selected elements in Jaisalmer carbonates is made to reveal various similarities and dissimilarities in mineral and chemical components. The bar diagrams for Na, Sr, Zn, Ni and Fe show a unimodal distribution and the alkalies (Na and K) and Mn show a bimodal population. The variation in the elemental concentration (Na, Sr and Zn) of Jaisalmer carbonates suggest normal to less marine shallow water environment for the lower four members (including the Hamira, the Joyan, the Fort and the Badabag Members) and a hypersaline marine environment for the topmost Kuldhar Member. This is also further confirmed from the vertical distribution of elemental concentration (Fig. 2). The positive correlation of Fe and Mn suggests a common source for the two elements. Presence of alkalies and Sr contents in appropriate amount indicate normal to less marine condition of paleo-sea. A slightly higher values of K of Kuldhar Member are related to hypersaline environment of deposition for Kuldhar Member. The relatively low content of Zn and Ni can be ascribed to a shallow water phase of the depositional basin. The abundant presence of quartz and clays in the insoluble residue is indicative of poor sorting values and could suggest a depositional environment proximate to the shore and rapid sedimentation (Macquown and Bloxam, 1972). The other evidences supporting the above inference include the presence of some of the well preserved fossil fragments together with the cross-bedding structures.

The factor analysis of Jaisalmer chemical data of carbonates shows the significance of three factors contributing about 72% of total variation.

As a whole, the depositional environment of Jaisalmer carbonates show a normal to less marine conditions of the basin during which the lower four member were deposited and the uppermost Kuldhar Member was deposited in a hypersaline facies, which marks the close of Jaisalmer sedimentation.

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"*A human being is a part of the whole, called by us Universe. He experiences himself, his thoughts and feelings as something separate from the rest - a kind of optical delusion of his consciousness. This delusion is a kind of prison for us, restricting us to our personal desires and to affection for a few people nearest to us.*

— *Einstein*

"*To know what is right and not to do it is the worst cowardice.*"

— **Confucius**