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TRENDS IN THE BROAD CHEMICAL COMPOSITION OF CARBONATES – A STUDY OF THE SELECTED CARBONATE SEQUENCE USING DISCRIMINANT ANALYSIS *

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Abstract

Basic processes of carbonate sedimentation result in certain predictable facies frame-work that recur in a variety of tectonic settings and reconstruction of the same can be made with the use of petrographic and geochemical data. In the present paper, three different carbonate groups viz., Precambrian, Jurassic and Pleistocene have been analyzed for their characterization and classification. Similar trends in the broad chemical components have been observed in all the three groups. Multivariate Discriminant Analysis of these carbonate groups provided a clear separation between these three different groups with about 90 percent samples correctly grouped into respective categories. The predictions are better for Younger (Pleistocene) group (Group 3) than either of the other groups (Precambrian and Jurassic) and emphasize the separation between the younger and older.

Keywords : Carbonate rocks, Petrography, Classification, Discriminant analysis.

1. Introduction

Evaluation of the evolutionary and cyclic properties of carbonate rocks and other lithologies is necessary for both sedimentary geologists and geochemists. For the geologist, knowledge of the secular or cyclic variation of the initial composition of marine carbonate precipitates with geologic age is prerequisite for interpretation of path ways of diagenesis. For the geochemist, knowledge of the trend in dolostone/limestone ratios with geologic age may help in constituting models of atmospheric-ocean evolution. The basic processes of carbonate sedimentation result in certain predictable facies frame-work that recur in a variety of tectonic settings and reconstruction of the same can be made with the use of petrographic and geochemical data. Thus, trends in sedimentary rock properties with geologic age can be used as the basis for understanding the long term geochemical cycling behavior of carbonates.

A number of authors have studied secular variations in the chemistry and mineralogy of sedimentary carbonate rocks (Vinogradov and Ronov, 1956; Veizer et al., 1980; Wilkinson, 1982; Schmoker and Hester, 1986). Most of the earlier studies focused on the Ca/Mg ratio or dolomite/calcite ratio of these rocks. It has been concluded that in sedimentary carbonates the "Primary" phenomena are responsible for the observed secular compositional trends although secondary processes (diagenesis, recycling, etc.,) play some role.

In the present study, a comparison of carbonate rocks from three geological time periods has been taken up with an objective of understanding the long term behavior of carbonates. The paper, while discussing the trends in chemical properties of carbonates, throws light on similarities and dissimilarities in the character of carbonates with geologic age. Discriminant Analysis of chemical data of the carbonates helps in classification and characterization and differentiating the carbonate rocks of different time periods.

2. Methodology

In this study, the carbonate samples belonging to three different rock sequences of India viz., Precambrian, Jurassic and Pleistocene, formed by different processes have been subjected to detailed petrographic and chemical analysis. In all, a total of 75 samples have been included for the present study out of which fifteen were from the Precambrian Limestone Formation, North Goa; thirty from the Jurassic Jaisalmer Formation, W. Rajasthan; and thirty from the Pleistocene Miliolitic

* *Poster Presentation*

Limestone. The sedimentological, petrogrpahic and geochemical details of the three sequences are given in Mahender and Banerji (1990); Mahender (1994, 1996). The chief distinguishing features of the three groups are presented in Table 1. The chemical data (Table 2), as determined by the standard procedures, has been subjected to Discriminant Analyses to know inter and intra-group variations in these chemical parameters. SPSS computer software (Statistical Package for Social Sciences) has been used to carry out Discriminant Analysis. The best predictor variables have been selected from the linear combination of all data variables using principal component analysis. The major chemical parameters (viz., Ca, Mg, Insoluble Residue, Ca/Mg and Mg/Ca) of carbonate samples are observed as the best predictor variables and the same have been used for Discriminant Analysis. Fig. 1(a-c) portrays the mutual relationships between the major chemical parameters in the form of bivariate plots. Fig. 2 displays the variation in the rare earth element composition amongst the three groups of carbonates rocks.

3. Discriminant Analysis

Discriminant Analysis seems particularly appropriate among various multiple-regression techniques for the purpose of characterization and classification (Snedecor and Cochran, 1967). It permits to classify and assign samples mathematically or to manipulate the various chemical parameters into a two-dimensional function plot so that the data and results can be presented and discussed graphically. Multi-group discriminant analysis combines a rationale similar to that of analysis of variance with computational procedures related to those of factor analysis.

If only two groups of data are to be analyzed the discrimination is simple because it involves easy solutions of simultaneous equations. The situation is more complicated when more than two groups are being analyzed and three or more variables are involved. With three groups Multivariate Discriminant Analysis yields two discriminant functions. The first of these discriminant function is defined to make the maximum differentiation among the groups using all the information. The second of the discriminant function uses the residual information, which is independent of the first discriminant function, to make further distinction amongst the groups, if possible. Fig. 3 shows the steps involved in the conventional scheme to determine classification functions. A detailed summary of the Multivariate

Table 1. General Lithological Characters of the limestone groups

	Group 1	Group 2	Group 3
Formation Name	Precambrian Limestone	Jaisalmer Formation	Miliolitic Limestone
Location	North Goa, Goa	Jaisalmer, Rajasthan	Saurashtra, Gujarat
Geological Age	Precambrian	Middle Jurassic	Mid-Late Pleistocene
Lithology	Limestone, Dolomitic Limestone	Limestone, calcareous sandstone, sandy limestone	Limestone
Mineral constituents	Calcite, Dolomite, quartz, micas, chert & chalcedony.	Fossils, oolites, pellets, intraclasts, quartz, clay minerals cemented in calcitic, dolomitic & aragonitic cements.	Skeletal allochems, pellets, quartz, clay minerals cemented in calcite, aragonite,
Petrography	Crystalline Limestone	Mudstone-Grainstone	Packstone-Grainstone
Diagenesis	Late Diagenetic Dolomitization, Silicification	Early to Late and burial diagenetic fabric characteristic of shallow marine/marine phreatic environment.	Early stage cements and diagenetic fabric characteristic of vadose zone.
Depositional Process	Chemical	Mechanical & Bioclastic Biochemical / Organic	Mechanical/bioclastic

Table 2. Chemical Data of Carbonates.

	Precambrian Limestone(Group -1, n=15)					Jaisalmer Formation (Group -2, n=30)					Miliolitic Limetsone (Group -3, n=30)				
S.No	Ca	Mg	IR	Ca/Mg	Mg/Ca	Ca	Mg	IR	Ca/Mg	Mg/Ca	Ca	Mg	IR	Ca/Mg	Mg/Ca
1	24.00	7.56	11.50	2.4339	0.4109	20.76	1.14	27.68	13.9617	0.0716	33.08	0.37	16.59	69.3171	0.0144
2	26.00	6.21	8.25	3.2100	0.3115	30.84	0.65	37.63	36.3763	0.0275	31.28	0.30	19.95	79.2305	0.0126
3	27.40	6.49	1.03	3.2369	0.3089	24.59	0.34	18.36	55.4494	0.0180	32.50	0.33	14.79	74.9300	0.0133
4	22.90	7.84	11.80	2.2394	0.4465	27.82	0.28	17.63	76.1757	0.0131	29.89	0.30	22.36	77.4329	0.0129
5	23.90	7.92	9.32	2.2362	0.4472	17.54	0.67	19.38	20.0711	0.0498	29.24	0.38	22.00	58.4663	0.0171
6	23.19	7.84	12.01	2.3372	0.4279	19.35	1.21	2.36	12.2606	0.0816	29.94	0.99	16.13	23.1199	0.0433
7	29.19	2.21	14.08	10.1265	0.0988	18.75	0.19	4.35	-75.6598	0.0132	33.42	0.24	9.50	107.4019	0.0093
8	27.60	3.64	10.07	5.8133	0.1720	26.20	0.15	5.36	133.9144	0.0075	34.69	0.24	9.79	111.7541	0.0089
9	30.49	1.61	12.70	14.5194	0.0689	26.85	0.33	6.89	62.3803	0.0160	33.05	0.23	9.77	112.2152	0.0089
10	24.57	6.41	10.80	2.9388	0.3403	35.65	0.19	3.02	143.8544	0.0070	33.49	0.26	9.62	99.5101	0.0100
11	24.20	7.01	5.63	2.6464	0.3778	30.03	0.20	13.85	115.1178	0.0087	33.28	0.22	9.28	113.6505	0.0088
12	23.99	7.29	11.20	2.5230	0.3964	26.61	0.19	7.39	107.3763	0.0093	34.41	0.28	10.95	95.7981	0.0104
13	22.35	8.31	5.88	2.0620	0.4850	31.24	0.19	3.29	126.0592	0.0079	33.74	0.23	9.59	110.9261	0.0090
14	21.34	9.62	4.16	1.7007	0.5880	36.85	0.18	2.79	156.9576	0.0064	34.64	0.25	8.80	106.8717	0.0094
15	25.04	7.67	10.81	2.5030	0.3995	38.45	0.18	2.31	163.7726	0.0061	33.48	0.47	9.94	54.8936	0.0182
16						36.85	0.21	2.19	134.5351	0.0074	34.93	0.24	7.51	110.7146	0.0090
17						36.05	0.17	4.60	162.5824	0.0062	35.22	0.28	7.52	97.9778	0.0102
18						27.41	0.17	16.57	123.6168	0.0081	34.95	0.36	9.01	75.2812	0.0133
19						30.84	0.19	3.95	124.4452	0.0080	33.59	0.28	11.38	92.0461	0.0109
20						26.85	0.21	8.63	98.0262	0.0102	34.97	0.21	8.50	130.2025	0.0077
21						29.03	0.22	35.68	101.1677	0.0990	31.41	0.41	18.64	58.8082	0.0170
22						36.85	0.31	3.99	91.1367	0.0110	33.93	0.23	9.41	112.3567	0.0089
23						29.63	0.23	48.50	98.7691	0.0101	34.63	0.38	7.08	69.5875	0.0144
24						20.03	0.30	37.82	51.1890	0.0195	30.03	0.70	14.67	33.0694	0.0302
25						29.03	0.16	5.85	139.1055	0.0072	30.42	0.98	20.45	23.8188	0.0420
26						28.23	0.18	4.93	120.2419	0.0083	33.74	0.41	27.62	63.5061	0.0157
27						29.83	0.25	8.39	91.4809	0.0109	34.50	0.28	6.97	93.9312	0.0106
28						29.03	0.16	7.38	139.1055	0.0072	34.95	0.26	9.24	104.9711	0.0095
29						20.28	1.78	22.27	5.5929	0.0828	32.35	0.33	12.69	74.6192	0.0134
30						22.43	0.60	38.52	28.6613	0.0349	33.32	0.38	14.15	67.6955	0.0148
Mean	25.08	6.51	9.08	4.0400	0.3500	28.13	0.37	14.05	93.6300	0.0200	33.10	0.36	12.80	83.4700	0.0100
S.D	2.58	2.28	3.40	3.5900	0.1400	5.88	0.38	13.50	47.8900	0.0300	1.76	0.20	5.40	27.8800	0.0100
Min.	21.34	1.61	1.03	1.7007	0.0689	17.54	0.15	2.19	5.5900	0.0061	29.24	0.21	6.97	23.1200	0.0077
Max.	30.49	9.62	12.70	14.5194	0.5880	38.45	1.78	48.50	163.7700	0.0990	35.22	0.99	27.62	130.2000	0.0433

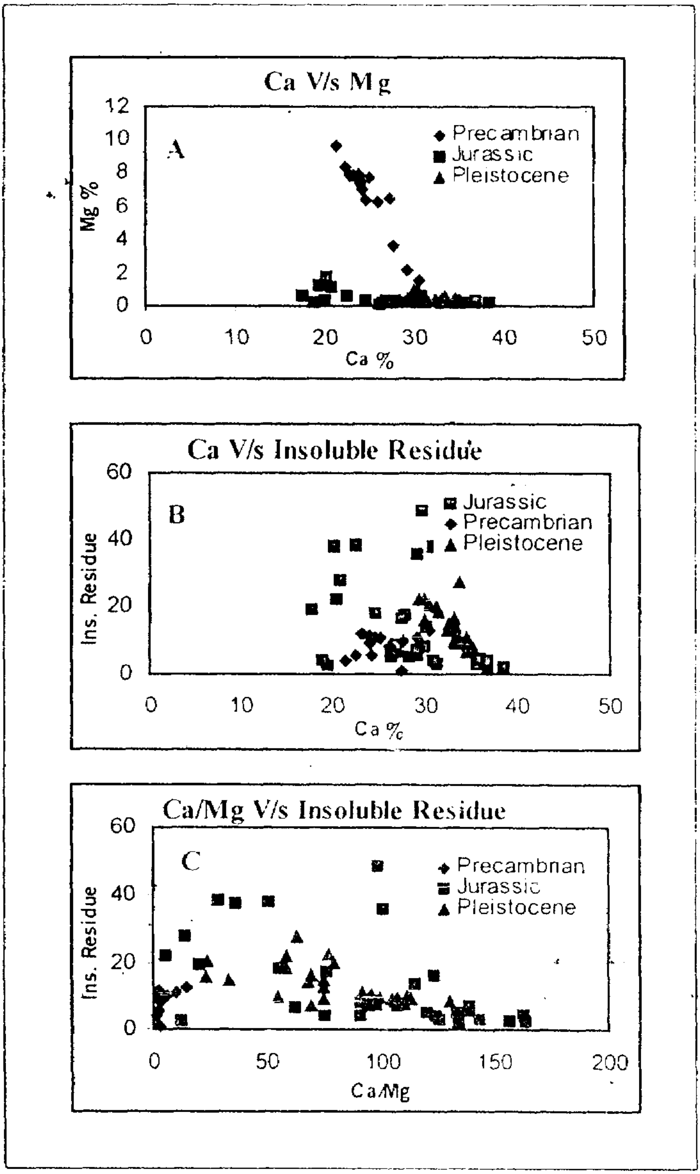

Fig. 1. Scatter plots of the broad chemical parameters.

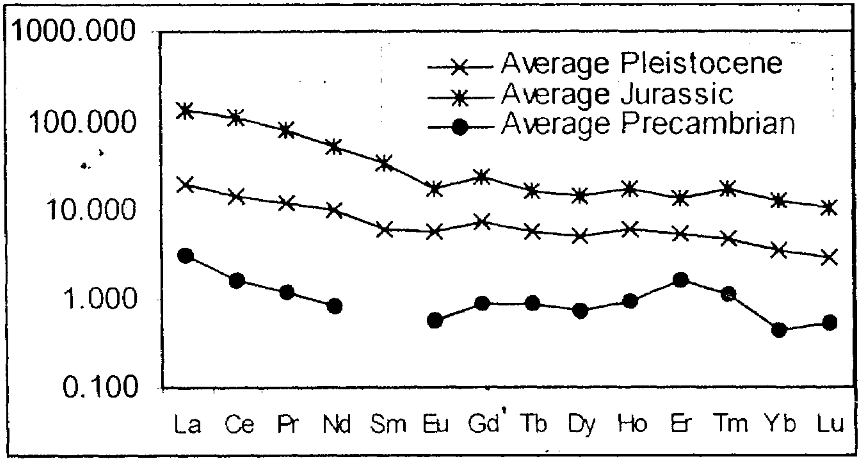

Fig. 2. REE pattern of the three carbonate groups

Discriminant Analysis can be found in Davis (1973) and Swan and Sandilands (1995). The important steps involved are described as follows:

3.1 Discriminant Function

Discriminant functions are useful for determining if several groups presumed to be different are distinct. The distinctness of the three limestone groups selected for the present study is clearly observable from Tables 1 and 2. To compute multiple discriminant function, first a determinant containing within group (w) sums of squares and sums of products and the between group (b) sums of squares and sums of products for the data matrix (Table 3) has been constructed following the procedures laid down in Cooley and Lohnes (1971). The resulting functions provide the greatest group separation while maintaining the least group inflation.

If the elements of these vectors are applied to the original determinants, a score for each sample is obtained. These scores can be used in characterizing the limestone groups analyzed. The distance between the means of the two groups is termed the Mahalanobis' distance. Half of this distance can be used as cut-off point for assigning unknowns. In the present study, since there are only three groups, the discrimination requires two discriminant functions and corresponding discriminant scores. The complete analytical results are given in Table 3.

3.2 Classification Function

Classification function coefficients for the three limestone groups (listed at Table 3G) are generated from discriminant-function scores (Nie et al., 1975). These functions permit not only the characterization of the limestone but also allows classify the unknowns. Assigning these classification functions to the original variables, it is possible to predict their group membership. The results of this prediction are listed in Table 3J.

In an ideal example, 100 percent of the samples should be assigned to their original group, but as shown in Table 3J, there are exceptions. Two samples from Precambrian and six samples from Jurassic are classified as Pleistocene. These samples have been identified to have similar chemical characteristics with those of Pleistocene and the deviation could be related to the effectiveness of the set of variables used.

4. Canonical Analysis of Discriminance

Canonical analysis of discriminance

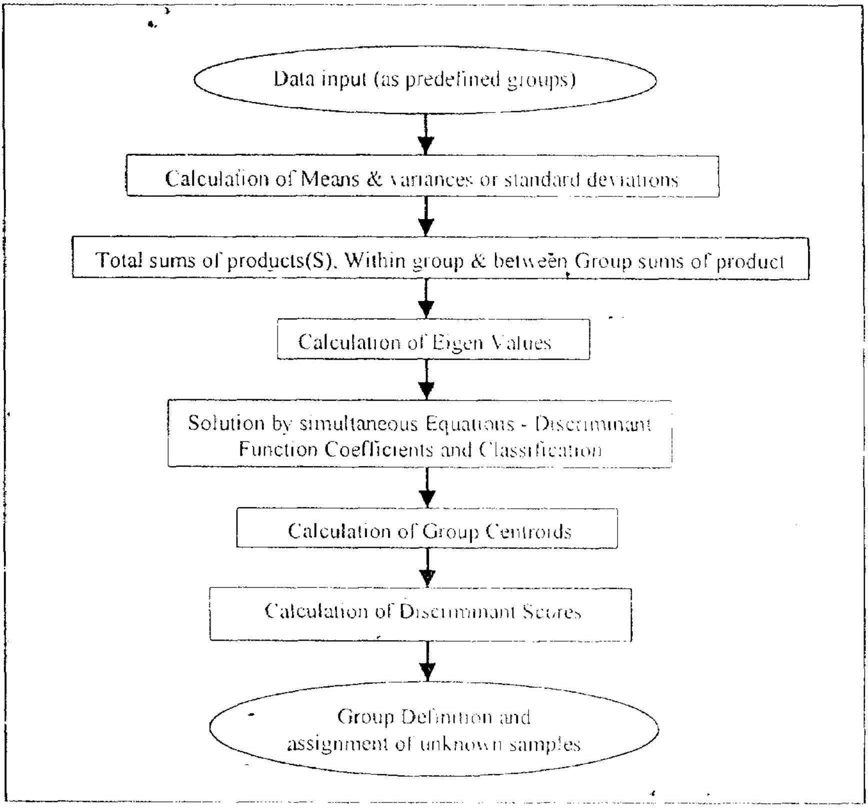

Fig 3 Flowchart for Discriminant Analysis

Table 3. Computational Results of the Disrciminant Analysis.

A. Group Means | B. Group Standard deviations

Group	Ca	Mg	IR	Ca/Mg	Mg/Ca	Ca	Mg	IR	Ca/Mg	Mg/Ca
1	25.0773	6.5087	9.0827	4.0351	0.3520	2.581	2.280	3.405	3.591	0.143
2	28.1300	0.3743	14.0520	93.6348	0.0225	5.882	0.378	13.503	47.888	0.027
3	33.1022	0.3598	12.7972	83.4701	0.0145	1.764	0.197	5.399	27.879	0.009
Total	29.5083	1.5954	12.5562	71.6490	0.0852	5.101	2.678	9.405	48.837	0.149

C. Pooled within-groups covariance matrix with 72 degrees of freedom

Variable	Ca	Mg	IR	Ca/Mg	Mg/Ca
Ca	16.482				
Mg	-1.655	1.081			
IR	-14.299	0.238	87.431		
Ca/Mg	104.495	-9.102	-173.368	1239.235	
Mg/Ca	-0.107	0.066	0.037	-0.517	-0.001

D. Pooled within-groups correlation matrix

Variable	Ca	Mg	IR	Ca/Mg	Mg/Ca
Ca	1.000				
Mg	-0.392	1.000			
IR	-0.377	0.025	1.000		
Ca/Mg	0.731	-0.249	-0.527	1.000	
Mg/Ca	-0.402	0.975	0.061	-0.224	1.000

E. Classification function coefficients (Fisher's linear discriminant functions)

Variable	Group-1 Precambrian	Group-2 Jurassic	Group-3 Pleistocene
Ca	4.310	3.164	4.003
Mg	17.551	1.524	1.703
IR	.356	.464	.424
Ca/Mg	-.229	-.096	-.177
Mg/Ca	-113.090	44.796	51.703
Constant	-94.015	-44.942	-63.180

F. Canonical Discriminant Functions

Fcn	Eigen Value	% var.	Cum %	Can. corr	After Fcn	Wilks' Lambda	Chi-square	df	sig.
					0	0.058	199.460	10	0.001
1*	8.1950	90.31	90.31	0.944	1	0.532	44.154	4	0.001
2*	0.8791	9.69	100.00	0.684					

* Marks the 2 canonical discriminant functions remaining in the analysis

G. Standardized canonical discriminant function coefficients | H. Unstandardized canonical discriminant function coefficients | I. Canonical discriminant functions evaluated at group means (Group Centroids)

Variables	Func 1	Group	Func 1	Func 2	Group	Func 1	Func 2
Ca	0.496	1	5.5485	-0.2706	1	5.549	-0.271
Mg	2.342	2	-1.8490	-0.9482	2	-1.849	-0.948
IR	-0.125	3	-0.9252	1.0835	3	-0.925	1.084
Ca/Mg	-0.524	-1.154	-0.015	-0.033			
Mg/Ca	-1.479	0.895	-22.596	13.673			
Constant			-4.041	-7.702			

J. Classification results

Actual Group	No. of Cases	Predicted Group Membership 1	2	3
Group 1	15	13 (86.70%)	0	2 (13.30%)
Group 2	30	0	24 (80.00%)	6 (20.00%)
Group 3	30	0	0	30 (100.00%)

Percent of "grouped" cases correctly classified : 89.33%

provides a graphical form of presenting multidimensional data (Morrison, 1967). It determines the linear combination of two sets of variables, one is the classification functions and the other is an artificially created set portraying the membership of the data from one of the three groups. The coefficients of the first canonical variate are obtained through line fitting to the group means distributed in a multidimensional space. The next successive variates are lines mutually orthogonal. There will be g-1 vectors of canonical coefficients if the group number is less than the variable number 'p' (in the present case it is two because there are 3 groups).

The scatter plot of the two canonical discriminant functions (Fig.4) clearly shows how samples from each limestone group distribute around their group mean. This has happened because canonical analysis has forced the original data ellipsoid into sphere. Mathematically, this is equivalent to bringing the within-samples variances and their corresponding standard deviation to a fixed number and using the latter as the radius for corresponding sphere. The plot also shows how samples from different limestone units, originally polarized in a multidimensional space defined by chemical data, can be transformed and presented in a two-dimensional surface. The transformation makes it possible to group limestones and to identify unknowns graphically in a measurable manner.

5. Conclusions

Multivariate Discriminant Analysis of chemical data of carbonates seems to be significant in differentiating the three groups. Although the trends in chemical composition with special reference to REE composition of the carbonate rocks is sufficient enough to differentiate the carbonate rocks belonging to different time periods, the present statistical analysis gives a quantitative separation between the various groups. The study provides an insight into the statistical classificatory techniques in identifying the group to which they belong based on the major chemical parameters. In the present study, 90% of the samples have been correctly classified into their respective groups suggesting

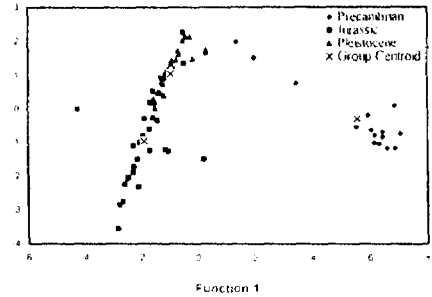

Fig. 4. Canonical Discriminant Function Plot.

the success of the analysis. The predictions are better for Pleistocene (Group 3) than either of the groups emphasizing the separation between the "younger" carbonates (group 3) and the "older carbonates" (Groups 1&2).

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