Geochemical Fractionation of Trace Elements between Calcite and Dolomite Fractions Separated from Their Mixture in Some Egyptian Dolomitic Limestone Rocks

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Abstract: The present work is an attempt to separate calcite and dolomite fractions from dolomitic limestone samples. Fifty recognized dolomitic limestone samples were selected from several localities to cover most types of the Egyptian dolomitic limestone varieties. A series of experiments was carried out to determine the best conditions for the dissolution of calcite only and hence the chemical separation of calcite from dolomite in the dolomitic limestone samples. Calcite and dolomite were quantitatively differentiated from dolomitic limestone rocks by a method based on the quantitative dissolution of calcite in pH 4 buffer solution. The remaining dolomite is then dissolved in 1 N-HCl. The trace elements (Fe, Mn, Cd, Co, Ni, Zn, Pb, Sr & Ba) concentrations in both calcite and dolomite fractions were determined to through light on their distribution. Fe, Mn and Ni show a similar distribution being present in great amount in dolomite fraction than calcite fraction. Sr and Ba also are present to a great extent in dolomite fraction than calcite fraction. Cd, Co, Zn and Pb show distinctly different behavior to that of other elements, they rarely exceed 20 ppm in both calcite and dolomite fraction.

Key words: Trace elements, calcite, dolomite, Buffer solution.

INTRODUCTION

The process of separation of carbonate minerals from non-carbonate minerals in the sedimentary carbonate rocks is normally carried out chemically. The non- carbonate fraction in carbonate rocks is usually a mixture of quartz, clays, feldspars and to a lesser extent sulphides and phosphates. The common chemical method of separation involved digestion of the carbonate fraction with weak acid. The reaction of acids with non-carbonate minerals depends on the type of acid used, acid concentration and quantity, temperature, duration of reaction, particle size, solubility and crystallinity. El Hefnawi (1990), found that the best conditions for the separation of the non- carbonate constituents in carbonate rocks is by treating the powdered sample with 1 N-HCl for 30 minutes at 70° C. These conditions will ensure the complete dissolution of the carbonate fraction. The amount of acid used should be calculated according to the weight of sample (25 ml of 1 N-HCl for each gram of sample) under these conditions, the non- carbonate minerals are not affected.

On the other hand, the separation of the carbonate minerals from each other in their mixture represents a difficult problem. Petersen and Chesters (1966) started a method to differentiate quantitatively between calcite and dolomite in calcite – dolomite mixtures and limestones by a method based on the quantitative dissolution of calcite in pH 5.85 N citrate buffer. The acidity and chelating ability of citrate favored greatly the dissolution of calcite to that of dolomite, so, the use of buffered citrate solutions for the differential dissolution of calcite in the presence of dolomite was evaluated.

Most studies on the geochemistry of Egyptian carbonate rocks have been focused on the distribution of trace elements in whole rock samples (El Hinnawi and Loukina,1971& 1972, Kamel *et al* 1982, Mohammed *et al* 1987, Ismail and El Nozahy, 1987 and Loukina and El Hefnawi, 1997). These studies give a general idea on the concentration of the different trace elements in carbonate rocks as a whole. Some authors used selective chemical methods to determine the distribution of trace elements in specific fractions of carbonate rocks, Barber (1974) and Kelepertsis (1983) used 25% acetic acid, and Wagner *et al*., (1979) used HCl to separate the acid soluble fraction from the insoluble residue, and studied the distribution of trace elements in both fractions. Varnavas and Panages (1981) used acetic acid to separate the carbonate phase and adsorbed ions, followed by HCl to separate Fe oxide and other oxides adsorbed to clay minerals, and then fusion of the remaining insoluble residue.

Loukina and El Hefnawi (1997) used 1 N-HCl to separate the carbonate fraction from the insoluble residue fraction and then determined the trace elements in each fraction.

Recently, many authors studied in detail the origin and distribution of some trace elements in dolomite and calcite (Jones, 2007, Breesch *et al*., 2010, Immenhauser *et al*., 2010, Loyed and Corsetti, 2010 and Hertig, *et al*., 2011).

The present work is focused towards determining the best conditions for the dissolution of calcite only and hence its chemical separation from dolomite in the dolomitic limestone samples. The distribution of trace elements in both calcite and dolomite fractions was determined and discussed .

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Sampling:

50 recognized dolomitic limestone samples were selected from several localities to cover the most common dolomitic limestone varieties, (dolomitic micrite, dolomitic microsparite, dolosparite, calcitic dolosparite and dolomitic sandy- clayey microsparite). All the samples belong to the Cretaceous and Eocene ages (Table 1).

Experimental work:

In order to determine the most suitable conditions for treatment of carbonate rocks to differentiate between calcite and dolomite in their mixtures, a buffer solution is prepared using acetic acid buffered with sodium acetate to obtain different pH values as follows:

For pH 4: 80 ml of 0.2 N acetic acid is added to 20 ml of 0.2 N sodium acetate.

For pH 5: 30 ml of 0.2 N acetic acid is added to 70 ml of 0.2 N sodium acetate.

For pH 6: 5 ml of 0.2 N acetic acid is added to 95 ml of 0.2 N sodium acetate.

Table 1: Sample locations and rock type

Locality	Age	No.	Rock name
Hammam Faraun	Middle Eocene	1	Dolomitic limestone
		2	Dolomitic limestone
		3	Slightly calcitic dolomite
		4	Slightly calcitic dolomite
		5	Slightly calcitic dolomite
		6	Slightly calcitic dolomite
		7	Slightly calcitic dolomite
		8	Slightly calcitic dolomite
Gabal Ataqa	Middle Eocene	9	Dolosparite
		10	Dolosparite
		11	Calcitic arenaceous dolosparite
		12	Calcitic dolosparite
		13	Dolosparite
		14	Calcitic dolosparite
		15	Calcitic dolosparite
		16	Dolosparite
		17	Calcitic dolosparite
	Upper Cretaceous	18	Dolosparite
Abu Rawash	Turonian	19	Dolomitic microsparite
		20	Dolomitic microsparite
		21	Dolosparite
		22	Dolosparite
		23	Dolosparite
		24	Dolosparite
		25	Dolomitic micrite
		26	Fossiliferous dolomitic micrite
		27	Dolomitic micrite
		28	Dolomitic micrite
		29	Fossiliferous dolomitic sandy micrite
		30	Dolosparite
Darb El-Fayum	Upper Eocene	31	Dolosparite
		32	Dolosparite
		33	Dolosparite
Gabal Mokattam	Middle Eocene	34	Dolomitic microsparite
		35	Dolomitic microsparite
		36	Dolomitic microsparite
		37	Dolomitic microsparite
		38	Dolomitic microsparite
		39	Dolomitic microsparite
		40	Dolomitic microsparite
	Upper Eocene	41	Dolomitic microsparite
		42	Dolomitic sandy-clayey microsparite
		43	Dolomitic sandy-clayey limestone
		44	Dolomitic sandy-clayey limestone
		45	Dolomitic sandy-clayey limestone
Northern Galala	Middle Eocene	46	Dolomitic microsparite
		47	Dolomicrite
		48	Dolomicrite
	Early Eocene	49	Dolosparite
		50	Dolosparite

A series of experiments were carried out as follows: first a known weight (1 gm) of chemically pure calcium carbonate was treated with 150 ml buffer solution of different pH values (4, 5, and 6) for 30 minutes, the samples were then filtered and the calcium was determined in the filtrate using EDTA.

From the obtained data, it appears that the dissolution of calcium carbonate reach its maximum solubility by a buffer solution at pH 4. Then, the same experiment was carried out with a 200 ml buffer solution of pH 4 for 30 minutes, and then calcium carbonate was determined. The results of this series of experiments are given in Table (2).

Table 2: The results of the 4 series of experiments:

No. of experiments	pH	Buffer amount (ml)	Ca%	$CaCO_3$%
1	4	150	39.08	97.89
2	5	150	20.64	51.55
3	6	150	5.61	14.01
4	4	200	39.68	99.09

The data shows that, it is more suitable to use 200 ml buffer solution of pH 4 for 30 minutes to ensure the complete dissolution of calcium carbonate.

The experiments then were carried out using two dolomitic limestone samples of considerable percent of acid insoluble residue. One gram of each sample was treated with 200 ml of buffer solution of pH 4 for 30 minutes, and another gram was treated with 25 ml 1 N-HCl for 30 minutes to dissolve all the carbonates, then the solution in each case was filtered and the dissolved calcium and magnesium were determined by titration with EDTA. The $CaCO_3$ and $MgCO_3$ were then calculated. The data obtained are shown in Table (3).

Table 3: The content of $CaCO_3$ and $MgCO_3$:

Sample No.	Solvent	Ca%	Mg%	$CaCO_3$%	$MgCO_3$%	A.I.R	Total
1	Buffer	6.2	2.67	15.48	7.62	74.4	97.5
2	Buffer	25.45	1.58	63.56	4.50	79.4	97.46
1	1N-HCl	21.64	9.97	54.04	34.58	9.2	97.82
2	1N-HCl	30.06	2.19	75.07	7.59	15.7	98.36

The data suggest that calcite could be dissolved selectively and quantitatively from calcite- dolomite mixture in dolomitic carbonate rocks, and the contents of calcite can be calculated from the quantity of Ca soluble in the buffer.

The residue remaining after buffer treatment of carbonate rocks consists entirely of dolomite and acid insoluble residue.

Selective dissolution of calcite is evident from the X-ray diffractograms of dolomitic limestone samples before and after treatment with buffer solution (Fig. 1). We note the complete absence of calcite peaks after citrate treatment and the enhancement of dolomite and quartz peaks. The residue containing dolomite and quartz was treated with 1 N-HCl. After HCl treatment, dolomite was completely dissolved and only quartz remains, as shown in the XRD patterns which show only quartz peaks.

In the following next experiments, two dolomitic limestone samples were treated with 200 ml buffer solution for 30 minutes, then filtered and the residue was treated with 1 N-HCl and filtered again then calcium and magnesium were determined in each fraction using EDTA. Calcium carbonate and magnesium carbonate were then calculated. The data obtained are shown in tables (4 & 5).

Method:

One gram of dry powdered sample was weighed into a 250 ml beaker, 100 ml of distilled water at room temperature were added, and the mixture was occasionally stirred over a period of an hour. The sample was filtered and the solution is then transferred to a 250 ml volumetric flask. This stage separated the water soluble salts from the sample. The remaining sample on the filter paper was treated with 200 ml buffer solution to dissolve the calcite only, then the sample was washed with distilled water and the solution is transferred to a 250 ml volumetric flask. This stage separated the calcite fraction. The remaining dolomite and insoluble residue was treated with 25 ml 1 N-HCl to dissolve dolomite fraction. After dissolution of dolomite, the residue was washed with distilled water and the solution of dolomite fraction was transferred to 250 ml volumetric flask. The remaining residue was dried at 40°C and weighed. This residue represents the A.I.R.

The three obtained solutions (water soluble solution, calcite fraction solution and dolomite fraction solution) were analyzed for Ca and Mg by titration with EDTA, (Table 6). The trace elements (Fe, Mn, Cd, Co, Ni, Zn, Pb, Ba & Sr) in calcite fraction and dolomite fraction were determined using atomic absorption spectrometry; the results of the analysis are shown in (Tables 7&8)
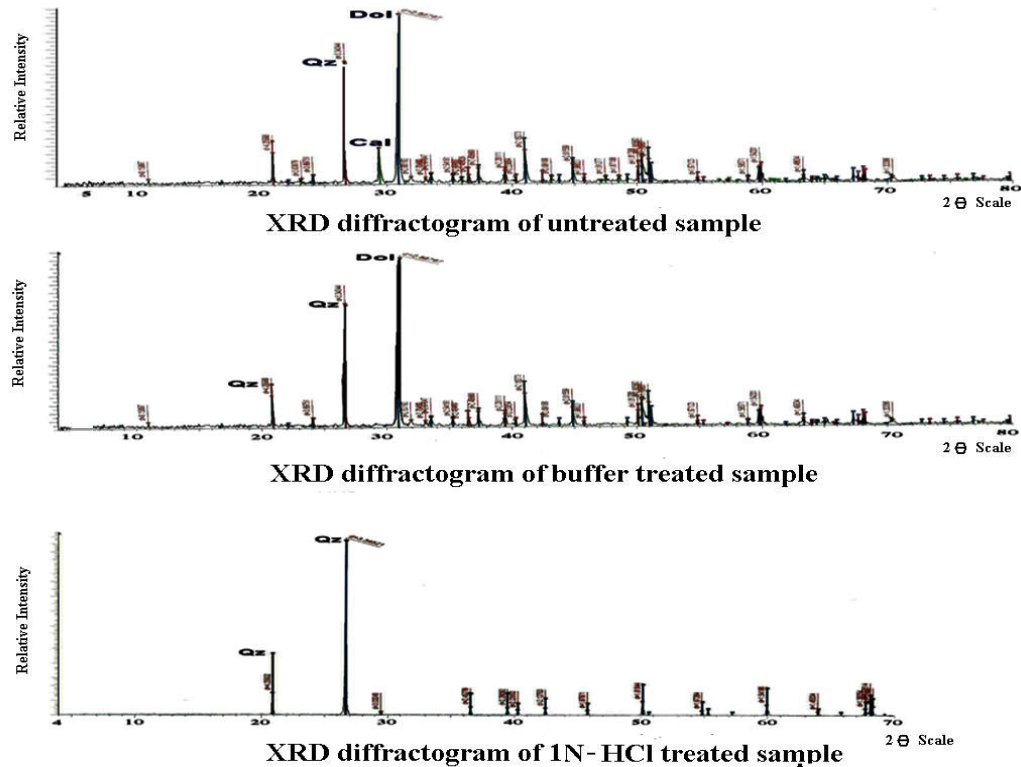
Fig 1: XRD diffractogram of the untreated sample, the buffer treated sample and the HCl treated sample

The content of $CaCO_3$ and $MgCO_3$ after treatment with buffer and with 1 N-HCl.

Tables 4:

Sample No.	Treatment with buffer					Treatment with 1 N-HCl				
	Ca%	Mg%	$CaCO_3$	$MgCO_3$	A.I.R	Ca%	Mg%	$CaCO_3$	$MgCO_3$	A.I.R
1	6.2	2.67	15.48	7.62	74.4	15.23	7.29	38.03	25.28	11.13
2	25.45	1.58	63.56	4.50	29.4	3.41	2.19	8.52	7.59	15.29

Table 5:

Sample No.	Treatment with buffer		Treatment with 1 N-HCl		A.I.R	Total
	$CaCO_3$%	$MgCO_3$%	$CaCO_3$%	$MgCO_3$%		
1	15.48	7.62	38.03	25.28	11.13	97.54
2	63.56	4.50	8.52	7.59	15.29	99.46

Discussion and conclusion:

The detailed study of the geochemistry of carbonate rocks requires the knowledge of the distribution of the different minor and trace elements in the various fractions constituting these rocks .The trace elements are associated with their constituents in a number of ways. They may be adsorbed on the surface or present as solid solution or both. The trace elements concentration in carbonate rocks are used to understand the depositional environment, diagenesis and dolomitization (Land 1980, Brand and Veizer, 1980 and Rao 1990).

Dolomite is a rhombohedral carbonate mineral consisting of alternating layers of carbonate anions and cations. In ideal dolomite, there are an equal number of Ca and Mg ions, and these are arranged in separate sheets with CO_3^{2-} planes.

Many, if not most, natural dolomites are not stoichiometric, and so they do not have the ideal molar ratio of $CaCO_3$ / $MgCO_3$ of 50:50 ($Ca_{0.5}$ $Mg_{0.5}$ CO_3). There is commonly an excess of Mg up Ca (Mg / Ca = 58 : 42) and less commonly an excess of Ca up Mg (Ca /Mg = 52 : 48). Also, other ions such as Fe^{2+}, Mn^{2+}, Na^+ and Sr^{2+} can substitute for the cations. Since Ca^{2+} ion is larger than Mg^{2+}, the lattice spacing increase as the effect of Ca substitution for Mg. Many dolomites are formed due to the replacement of pre-existing $CaCO_3$ and there is a wide range of replacement fabrics developed, dolomite also occur as a cement and filling voids in the same way as calcite spar.

The structure of dolomite is most simply pictured by substituting Mg ions into alternating Ca layers in the calcite structure. The substitution introduces a change in bond strength. This causes a displacement of atoms and results in dolomite possessing a lower degree of symmetry than calcite.

Table 6: Major chemical analyses data (weight %) of calcium and magnesium in different fractions:

No.	Calcium				Magnesium				CaCO$_3$ (%)	MgCO$_3$ (%)	A.I.R (%)
	Ca% in W.S.	Ca% in calcite fraction	Ca% in dolomite fraction	Total Ca %	Mg % in W.S.	Mg % in calcite fraction	Mg % in dolomite fraction	Total Mg %			
1	0.16	8.42	24.85	33.43	0.02	0.24	3.65	3.91	83.48	13.56	3.1
2	0.28	8.82	24.45	33.55	0.04	0.49	4.13	4.66	83.78	16.16	1.95
3	0.08	3.21	22.85	26.14	0.02	0.73	9.24	9.99	65.28	34.64	1.15
4	0.06	4.41	22.44	26.91	0.02	0.24	8.75	9.01	67.2	31.25	1.95
5	0.12	2.81	17.64	20.57	0.04	0.49	12.16	12.69	51.37	44.01	3.1
6	0.14	2.81	17.64	20.59	0.05	0.97	12.89	13.91	51.42	48.23	1.8
7	0.8	2.4	20.04	23.24	0.15	1.22	9.48	10.85	58.04	37.62	2.35
8	0.42	6.01	16.83	23.26	0.07	1.22	10.46	11.75	58.08	40.74	2.4
9	0.06	3.21	20.44	23.71	0.02	1.7	9.73	11.45	59.21	39.71	3.55
10	0.06	2.4	16.03	18.49	0.04	1.46	9.73	11.23	46.18	38.94	11.9
11	0.06	4.01	20.04	24.11	0.02	0.49	10.46	10.97	60.21	38.04	2.1
12	0.06	2.81	18.84	21.71	0.04	1.22	10.21	11.47	54.22	39.78	4.35
13	0.08	4.01	16.83	20.92	0.02	0.49	10.94	11.45	52.24	39.71	6.95
14	0.52	4.41	18.04	22.97	0.04	0.49	12.4	12.93	57.36	44.84	1.85
15	0.06	4.01	20.04	24.11	0.02	0.49	10.94	11.45	60.21	39.7	1.5
16	0.06	4.81	17.23	22.1	0.02	0.49	10.94	11.45	55.19	39.7	6.55
17	0.62	4.81	17.23	22.66	0.12	0.49	8.27	8.88	56.59	30.79	9.15
18	0.06	4.01	16.83	20.9	0.02	0.24	11.19	11.45	52.19	39.71	6.9
19	0.06	14.83	20.44	35.33	0.02	0.73	3.16	3.91	88.23	13.56	1.1
20	0.06	15.23	20.84	36.13	0.02	0.49	2.91	3.42	90.23	11.86	1.65
21	0.06	3.21	20.44	23.71	0.02	0.49	9.97	10.48	59.21	36.34	4
22	0.08	6.01	18.04	24.13	0.01	0.24	9.97	10.22	60.26	36.44	2.85
23	0.12	14.03	16.03	30.18	0.05	0.49	6.57	7.11	76.37	24.65	1.45
24	0.14	12.02	12.02	24.18	0.05	0.49	8.03	8.57	60.38	29.72	7.85
25	0.16	18.44	18.44	37.04	0.01	0.49	3.43	2.96	92.5	10.26	1.05
26	0.12	14.03	17.23	31.38	0.1	0.73	4.86	5.69	78.36	19.73	2.85
27	0.06	16.83	16.83	33.72	0.02	0.24	4.86	5.12	84.21	17.75	1.15
28	0.08	19.23	18.04	37.35	0.01	0.49	1.7	2.2	93.27	7.63	1.05
29	0.06	1.6	14.43	16.09	0.02	0.73	12.89	13.64	40.18	47.3	10.2
30	0.04	19.24	18.04	37.32	0.01	0.24	2.43	2.68	93.19	9.29	1.8
31	0.04	4.01	13.63	17.68	0.01	0.49	6.57	7.07	44.15	24.52	27.3
32	0.18	2.81	17.23	20.22	0.05	0.49	9.73	10.27	50.49	35.61	11.6
33	0.26	2.4	17.23	19.89	0.06	0.24	9.24	9.54	49.67	33.08	17.55
34	0.08	7.21	14.43	21.72	0.02	0.49	8.99	9.5	54.24	32.95	10.25
35	0.1	6.01	16.43	22.54	0.01	0.49	7.54	8.04	56.29	27.88	13.05
36	0.12	11.22	10.02	21.36	0.02	0.49	7.78	8.29	53.34	28.75	13.4
37	0.1	5.21	18.02	23.35	0.02	0.49	9.24	9.75	58.31	33.81	6.55
38	0.06	9.22	16.43	25.71	0.04	0.73	5.59	6.36	64.21	22.06	13.8
39	0.08	8.02	18.04	26.14	0.04	0.49	6.08	6.61	65.28	22.92	12.4
40	0.06	4.41	17.64	22.11	0.07	0.24	11.19	11.5	55.22	39.88	3.45
41	0.08	4.81	20.04	24.93	0.06	0.49	9.97	10.52	62.26	36.48	2.4
42	0.16	16.03	8.02	24.21	0.02	0.73	4.13	4.88	60.46	16.92	21.75
43	0.84	3.61	9.22	13.67	0.06	0.49	5.59	6.14	34.14	21.29	42.1
44	0.78	7.21	4.41	12.4	0.05	0.49	3.89	4.43	30.97	15.36	55.65
45	0.1	6.01	8.02	14.13	0.05	0.24	4.86	5.15	35.29	17.86	44.3
46	0.1	13.63	18.44	32.17	0.01	0.73	2.43	3.17	80.34	10.99	7.05
47	0.18	9.62	18.44	28.24	0.04	0.49	7.29	7.82	70.52	27.12	2.8
48	0.14	9.22	13.63	22.99	0.04	0.49	8.76	9.29	57.41	32.22	9
49	0.14	4.81	15.23	20.18	0.05	0.49	7.78	8.32	50.39	28.85	18.5
50	0.7	3.61	14.03	18.34	0.02	0.49	8.02	8.53	45.8	29.58	21.85

The finer size of dolomite crystals reflects an early stage of dolomitization process (dolomite and dolomicrosparite), this stage of dolomitization have taken place penecontemporaneously or soon after the deposition and after lithification and resulted in the development of the finer size dolomite. These finer size groups (dolomicrites and dolomicrosparite contain considerable amounts of trace elements in both calcite and dolomite fraction (Figs.2 a, b, c). Whereas, the coarser size dolomite belong to later phase of dolomitization that might have taken place after lithification, (Lee and Friedman, 1987). These coarse size groups of dolomite

(calcitic dolosparite, dolostone, slightly calcitic dolomite and dolomitic limestone) are characterized by higher concentration of trace elements in dolomite fraction than in calcite fraction, (Figs. 2 d, e, f, g).

Ca - rich dolomites are generally considered to have a near - surface origin, (Morrow, 1990), or produced in a rock-controlled, partly closed system under burial condition, (Hood *et al*. 2004, Kirmaci and Akdag 2005). Partly closed system is characterized by high content of Sr (Hood *et al* 2004). According to Hood *et al*. (op.cit) the Sr content ranges from 2500-3000 ppm which is higher than the results obtained in the present study. Sr content in dolomite fraction has a wide range (53-2469 ppm). According to Loukina and El Hefnawi (1997) Mg, Sr and to a lesser extent Pb occur replacing Ca in the calcite structure, so their values are high in dolomite fraction than in calcite fraction. The low concentration of Sr content in calcite fraction indicates that, the precursor limestone had undergone considerable diagenesis before the process of dolomitization which resulted in Sr depletion during diagenesis.

Table 7: Trace elements concentration in the calcite fraction.

Sample No.	Fe	Mn	Cd	Ni	Zn	Co	Pb	Sr	Ba
1	4	140	0	5	4	6	5	86	90
2	1	60	0	18	0	9	12	94	87
3	31	85	3	14	0	1	6	30	32
4	24	185	0	18	0	3	7	32	50
5	47	70	0	27	0	2	6	27	38
6	33	110	1	7	1	2	2	30	40
7	42	80	2	0	0	16	2	26	36
8	11	35	4	3	3	13	9	66	43
9	0	25	0	2	2	0	12	16	28
10	6	20	4	0	0	0	12	29	26
11	12	25	2	0	0	10	8	22	41
12	8	15	5	0	0	16	8	33	33
13	9	10	3	0	0l	8	12	24	38
14	17	20	0	16	2	3	22	78	43
15	19	30	0	11	0	0	15	42	37
16	6	35	4	24	0	0	16	32	53
17	125	45	4	35	0	0l	14	44	42
18	25	30	3	3	0	15	7	33	42
19	6	25	3	17	0	14	24	148	150
20	6	25	5	31	0	0	16	186	155
21	8	25	0	6	11	4	10	42	44
22	13	45	3	21	0	3	10	69	77
23	25	485	45	18	0	0	18	119	148
24	0	70	6	3	2	0	11	115	133
25	11	60	10	24	0	0	21	141	195
26	6	50	14	21	7	24	15	155	143
27	8	15	7	7	0	7	22	201	165
28	12	35	2	3	0	11	34	186	166
29	71	40	5	16	0	11	9	175	157
30	359	305	0	8	0	10	4	25	33
31	17	70	3	7	0	10	5	69	42
32	169	135	0	14	0	7	17	40	35
33	49	155	0	7	0l	2	6	35	24
34	26	40	2	7	0	10	15	241	72
35	6	15	2	12	0	16	17	306	66
36	14	40	5	8	1	4	25	1220	105
37	20	15	0	20	1	0	7	777	44
38	9	35	0	31	0	17	14	230	88
39	8	25	3	14	0	9	13	171	72
40	11	30	1	16	0	0	10	178	45
41	19	10	0	12	0	17	17	253	42
42	26	35	4	31	2	8	22	1162	140
43	280	90	2	13	0	5	23	72	36
44	648	55	0	19	0	0	7	41	37
45	708	180	0	40	0	0	19	91	62
46	31	20	2	22	0	15	21	76	131
47	6	20	1	25	0	17	9	84	84
48	5	15	4	26	0	8	15	91	97
49	6	25	0	16	0	19	15	73	48
50	75	35	0	18	0	13	6	105	42

Table 8: Trace elements concentration in the dolomite fraction.

Sample No.	Fe	Mn	d	Ni	Zn	Co	Pb	Sr	Ba
1	271	735	5	39	25	24	19	206	276
2	175	470	0	30	12	17	14	216	229
3	809	730	4	27	15	0	12	172	199
4	1260	700	2	32	17	18	9	164	199
5	1605	540	4	42	10	15	15	165	210
6	850	935	2	38	21	11	30	154	205
7	865	685	5	45	9	20	21	169	194
8	840	135	4	28	7	16	18	263	185
9	815	55	3	36	0	7	14	130	193
10	450	85	7	42	2	28	13	160	179
11	450	80	1	32	3	13	22	122	241
12	585	40	6	25	0	11	5	165	155
13	700	35	4	20	0	15	13	108	166
14	945	60	3	15	0	16	4	145	175
15	1075	40	1	25	0	28	4	153	192
16	270	45	2	31	3	32	6	103	179
17	2725	845	3	42	4	14	1	143	179
18	43	65	2	35	0	25	9	121	196
19	200	85	2	14	0	19	10	276	241
20	340	20	4	28	13	33	10	272	236
21	255	45	7	27	11	6	14	220	230
22	530	50	3	10	3	18	8	194	188
23	245	45	9	13	0	16	10	176	177
24	665	130	9	22	21	34	7	188	166
25	150	120	4	15	0	15	2	180	197
26	210	60	2	17	7	33	12	216	192
27	250	55	6	8	0	12	9	244	191
28	145	35	30	34	1	23	15	262	215
29	545	85	6	8	0	12	4	164	158
30	2320	2060	5	16	32	35	22	178	278
31	105	295	4	42	0	27	19	251	143
32	1050	825	4	12	15	19	6	178	172
33	1085	815	3	10	0	16	26	183	176
34	300	85	3	20	0	16	5	1158	168
35	370	20	4	12	0	11	12	1103	180
36	605	25	3	8	0	13	6	2469	182
37	375	30	4	11	0	10	8	2455	174
38	255	25	3	4	0	27	3	810	170
39	305	15	2	5	0	18	12	751	177
40	345	30	1	13	0	7	20	940	204
41	200	20	6	454	0	15	14	1238	178
42	1040	25	2	14	2	12	7	991	108
43	2525	290	1	3	0	0	7	105	104
44	2275	160	2	7	0	10	18	53	71
45	3825	325	5	15	0	11	12	94	101
46	260	15	8	26	2	12	20	144	174
47	385	25	3	9	4	9	12	156	197
48	340	25	4	5	0	13	21	102	147
49	505	30	1	13	0	12	15	159	165
50	690	30	2	11	2	16	13	142	162

Ba content ranges from 71-278 ppm which is the range of ancient marine to mixed marine- meteoric water dolomite (Land, 1980 and Wanas, 2002). Fe and Mn concentrations are low in seawater, whereas they occur in high concentration in meteoric water (Brand and Veizer, 1980). The calcite and dolomite fractions of the present study have high Fe and Mn contents. The high content of these trace elements suggest deposition of dolomite from fluids enriched in Fe and Mn under reducing conditions that influenced by meteoric water. The available source of Fe at the time of dolomitization may be the associated fine grained siliciclastic - rich sediments that supply valuable amounts of Fe. Also Fe may be provided from oxide coatings on clays and iron bound within clay mineral structure (Holail, *et al.*, 1988, Hood *et al.*, 2004), Therefore, the maximum value of iron in this study (2725 ppm) recorded in dolomitic sandy clayey limestone, (Fig.2 h). Cd, Co, Zn and Pb show distinctly different behavior to that of other elements, they rarely exceed 20 ppm in both calcite and dolomite fractions.
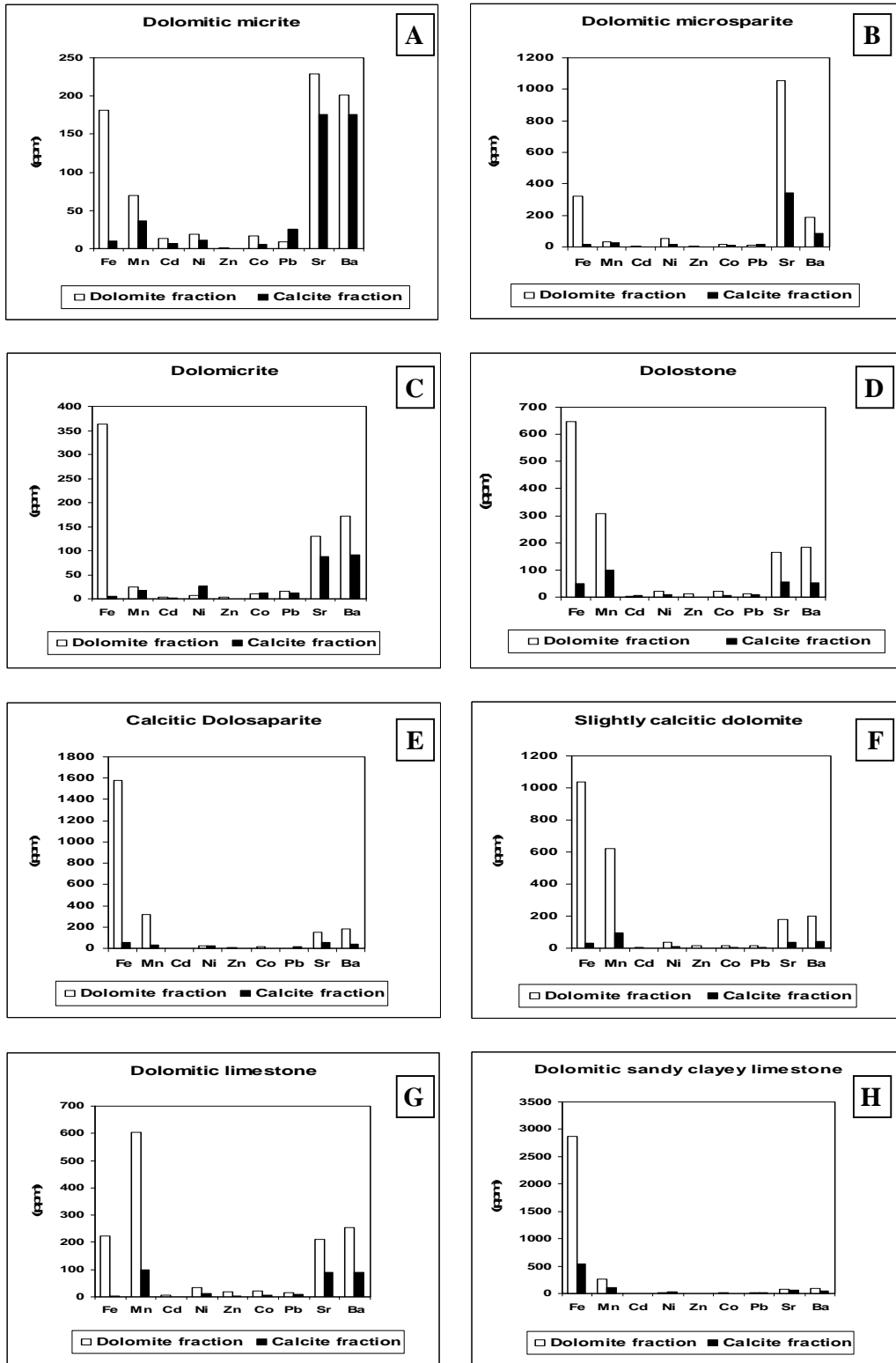
Fig. 2: Histograms showing the distribution of trace elements in both calcite and dolomite fractions for different types of dolomitic limestone.

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