

# Sedimentology and geochemistry of carbonates from lacustrine sequences in the Madrid Basin, central Spain

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## Abstract

Lacustrine and alluvial carbonate facies have been investigated in Middle Miocene successions of the western side of the Madrid Basin in order to evaluate paleoenvironments in which carbonates formed. Carbonate facies are varied and include: (1) calcrete and dolocrete; (2) pond deposits; (3) lake margin dolostone; (4) mudflat carbonate; and (5) open-lake carbonate facies. The dominant mineralogy of these is dolomite and/or low-Mg calcite. No high-Mg calcite or aragonite have been detected in any sample.  $\delta^{18}\text{O}$ - and  $\delta^{13}\text{C}$ -values range from -8.20 to -1.80‰ PDB and -10.25 to -0.70‰ PDB, respectively. More negative  $\delta^{18}\text{O}$ - and  $\delta^{13}\text{C}$ -values correspond to predominantly calcite calcretes and to carbonate deposited in ponds at the foot of arkosic alluvium. Higher  $\delta^{18}\text{O}$ -values are from both lacustrine carbonate and dolocrete. This latter lithofacies has strong geochemical similarities to dolostones deposited in a lake margin environment. Mudflat carbonate, deposited on shallow platforms subject to lake water oscillation, shows great heterogeneity in both stable isotope value and trace-element content. The mineralogy of these carbonates is dominated by calcite and the limestones contain molds of gypsum. Occurrence of calcitized dolomite textures in these facies suggests the influence of fresher water during expanding lacustrine cycles or further interaction with less saline groundwater. Trace-element contents are considered to be potential indicators of the different carbonate facies types, thus aiding the paleoenvironmental interpretation. However, discrimination among carbonate facies on the basis of trace-element contents appears to be dependent on the statistical method utilized for treatment of data. More information is needed to ascertain their use as paleoenvironmental indicators.

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## 1. Introduction

Sedimentological research on carbonate deposits from ancient lacustrine sequences deposited under a variety of geological and paleoclimatic conditions have contributed to establishing sedimentological models (Eugster and Kelts, 1983; Allen and Collinson, 1986; Tucker and Wright, 1990; Platt and Wright, 1991) which constitute the current basis for the interpretation

of lacustrine deposits. The chemical composition of carbonate deposits in lacustrine sequences has been used to characterize the hydrogeochemistry of the paleolake basin and, in a few cases, has also been used to deduce paleoclimatic changes (Molenaar and DeFeyter, 1985; Gasse et al., 1987; Janaway and Parnell, 1989; Bellanca et al., 1992). Isotope geochemistry in particular is increasingly used to obtain paleoenvironmental information, including paleohydrology, paleoclimate and the role of photosynthetic activity in the precipitation of lake carbonate (Fritz and Fontes, 1986;



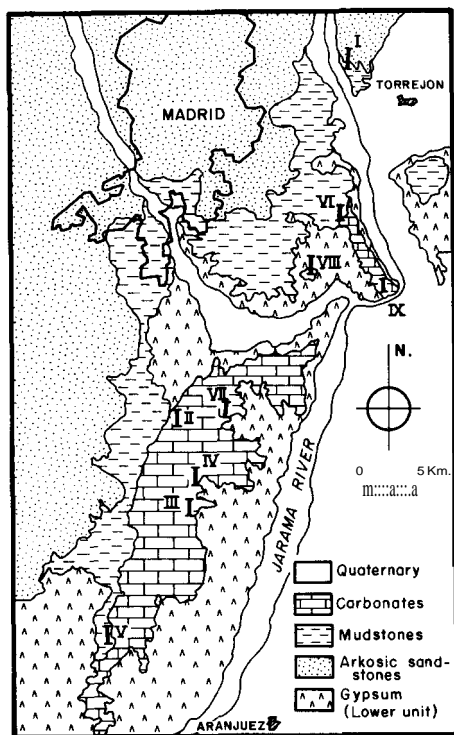


Fig. 2. Geologic map of the study area with bars showing the location of the lithostratigraphic logs (I-IX) presented in Fig. 3.

ments (see Fig. 4) (Calvo et al., 1989). Carbonate samples from these localities were supplemented by samples from isolated outcrops in the area.

Fig. 3 shows the correlation of the selected lithostratigraphic logs. Section I (Paracuellos de Jarama area) contains distal facies of arkosic alluvium from the northwestern margin of the basin, and consists of an alternation of fine arkosic deposits, sandy mudstones, dolocretes and calcretes that prograded over marginal lake deposits (lowermost part of the section). Sections II-V correspond to marginal and mudflat carbonate facies that were variably influenced by influx of medium- to coarse-grained terrigenous deposits. Sections VI, VIII and IX are formed in the basal part of the mudflat facies, characterized by the alternation of carbonate and laminated mudstone. These deposits are overlain by more continuous and thicker carbonate beds representative of open-lake facies. Mudstones decrease both in frequency and thickness from the lake margin to the open lake.

Cyclicity recognized in most of the sections suggests repeated fluctuations in lake level. In addition, a pro-

gressive lake expansion is indicated towards the top of the Intermediate Unit. This episode is marked by the development of carbonate deposits in sections VII-IX, and has been studied in some detail by Bellanca et al. (1992). The uppermost deposits in these sections display features related to a widespread episode of karstification during the Vallesian (Calvo et al., 1984; Ordóñez et al., 1985; Cafiaveras et al., 1995).

Ninety-one samples of carbonate (both limestone and dolostone) were collected for mineralogical and chemical analysis (Tables 1 and 2). The samples were chosen to represent specific carbonate layers, covering most representative carbonate facies in the area. Sampling points from lithologic sections are depicted in Fig. 3 whereas the remaining samples were collected from discontinuous outcrops. From this set of samples, only 32 were selected for isotopic analyses (Table 2) as they were considered to be quite representative of the different carbonate facies. Samples 82-90 were collected in a second phase of the work in order to investigate a specific carbonate type (calcrete) in more detail. Gypsum was not detected in significant amounts in any of the samples. Only very small traces of gypsum occur in carbonates containing lenticular molds. The samples were analyzed for mineralogical composition using a Philips® X-ray diffraction (XRD) system operated at 40 kV and 30 mA, and a monochromated  $\text{Cu-K}\alpha$  radiation. The Mg content in calcite was determined according to the method proposed by Goldsmith and Graf (1958). With pure quartz as an internal standard, the reflections used were (104) for calcite and (101) for quartz. Mg contents (mole%) were <5% in all samples.

Subsamples (1 g) of the limestone and dolostone powders were treated with 50 ml of 4% (v/v) hydrochloric acid for 4 and 24 hr, respectively, at room temperature. Under these conditions, the alteration of the non-carbonate fraction (clays, sand-sized minerals) is minimal. The insoluble residues were collected on filter paper to determine percentage insoluble residue by gravimetric methods.

All solutions were analyzed by atomic absorption spectrophotometry for determination of Li, Na, K, Fe, Mn and Sr. The analytical results are given as concentrations recalculated on a pure carbonate (insoluble residue-free) basis (Table 1).

For stable isotopic analysis, all samples were ground to pass through a 100-mesh sieve; the 250-mesh frac-



ronments (Calvo et al., 1984, 1989; Lomoschitz et al., 1985; Alonso et al., 1986; Alonso Zarza et al., 1992). Such environments represent the transition from distal alluvial fan zones and adjoining lake margin settings to mudflat and open-lake areas. Five carbonate facies have been distinguished: (1) calcrete and dolocrete; (2) carbonate pond facies; (3) lake margin dolostone; (4) mudflat carbonate; and (5) open-lake carbonate facies.

#### 4.1. *Calcretes and dolocretes*

Calcrete profiles consist of nodular, prismatic and platy facies (Esteban and Klappa, 1983) and locally show small root traces. Single calcrete profiles range from 0.4 to 1.8 m in thickness and occur as beds separated by arkosic sandstone and/or sandy mudstone, or are locally amalgamated ("composite paleosols" of Wright, 1989). Some differences concerning paleogeographic location of the calcretes can be outlined. Thus, a set of calcretes is located in the medial zone of arkosic alluvium (samples 82-90, see Table 2); herein, the calcrete is characterized by both broad development of alveolar-septa structures (Klappa, 1980) that disrupt former clay cutans and massive replacement of pedologic clay textures by low-Mg micrite. All these features suggest that calcrete developed on a previous soil.

Other calcretes (samples 7-18) formed on distal alluvial zones. In this setting, carbonate in the lower part of the calcrete profiles consists of cracked micrite and abundant clay aggregates. These clays are mostly dioctahedral smectites, although sepiolite has also been recognized. Carbonate content increases toward the upper parts of profiles where textures consist of dense to clotted micrite displaying alveolar features, desiccation cracks, and lumpy to pelloidal fabrics (Calvet and Julia, 1983). This calcrete type is mostly composed of low-Mg calcite.

Finally, a third type of paleosol comprises dolocretes (in the sense of Netterberg, 1980) that developed close to the lake margin facies (described below). This carbonate (several samples listed in Table 1) contains typical calcrete textures such as irregular spar-filled cracks, floating detrital grains, dense crystalline matrices and etched silicate grains (Alonso Zarza et al., 1992). Dolomite occurs as contorted dolomicrite veins, coated by fine to medium crystalline dolomite cement,

separating areas of locally strongly orientated clays. The presence of analcime, averaging 5-10% of the total rock, has been often determined from the dolocrete profiles.

#### 4.2. *Carbonate pond facies*

Carbonate pond facies occur locally at the foot of arkosic alluvium between distal fan and lake margin facies (Fig. 4). Good examples of this facies have been observed in locations close to section I of Fig. 3. Ponds fed by relatively fresh, silica-bearing surface or groundwater were sites for the accumulation of bedded nodular carbonate and cream to whitish sepiolitic clay (Calvo et al., 1986; Doval et al., 1986). The total thickness of the deposits averages 4 m. Carbonates are predominantly calcite as homogeneous dense micrite with alveolar root textures, fenestral voids, isolated clay aggregates, and scarce fragments of gastropods and ostracods. Contact between clay and carbonate in alternating beds is usually transitional.

#### 4.3. *Lake margin dolostones*

Lake margin dolomite occurs interbedded with green clay in monotonous 2-4-m vertical successions wherein Mg-rich smectites grade upward into pink clay to dolostone. Doval et al. (1986) and Martfn de Vidales et al. (1989) indicate that pink clay is kerolite-stevensite mixed-layer material.

Tabular dolostone beds exhibit characteristic nodular or concretionary structures and consist of micrite to microsparite with abundant desiccation cracks. Dolomites lack fossils but occasionally contain bioturbation traces of worms or roots. Dolomites also contain dispersed micrite lumps or clay aggregates.

#### 4.4. *Mudflat carbonates*

Mudflat carbonate occurs between lake margin dolostone and open-lake carbonate that extends toward central parts of the basin (Fig. 4). Mudflat carbonate can be traced laterally some 2-3 km in width, while the abundance of interbedded mudstone decreases toward open lacustrine areas. These beds form characteristically the upper part of upward shoaling cycles that represent the transition from high to low stands of the lake.

Table I  
Trace-element composition and mineralogy of carbonates

Sample	Na	K	Li	Fe	Mn	Sr	I.R.	Calcite	Dolomite	Carbonate facies	Number of facies	1'Na, Li, Fe, Mn, Sr	Sr	Na	I:Li, Fe, Mn
2	728	894	27	943	640	63	32.6	0	100	lake margin dolostones		2,401	2.62	30.32	67.06
5	3,947	422	33	775	697	58	16.4	10	90	dolocretes	6	5,510	1.05	71.63	27.31
6	125	91	3	211	80	232	20.9	0	100	calcretes	2	651	35.64	19.20	45.16
7	73	83		178	84	163	0.4	100	0	calcretes	2	501	32.53	14.57	52.89
ii	246	206	4	220	88	442	17.5	100	0	calcretes	2	1,000	44.20	24.60	31.20
9	159	458	13	459	80	80	33	100	0	calcretes	2	791	10.11	20.10	69.79
JO	98	260	6	311	48	139	20.9	100	0	calcretes	2	602	23.09	16.28	60.63
II	73	283	3	178	84	163	0.4	100	0	calcretes	2	501	32.53	14.57	52.89
12	98	260	6	311	48	139	20.9	100	0	calcretes	2	602	23.09	16.28	60.63
13	366	225	13	189	182	169	18.1	100	0	calcretes	2	919	18.39	39.83	41.78
15	81	70	2	86	35	165	4.5	100	0	calcretes	2	369	44.72	21.95	33.33
16	103	202		175	76	116	16.7	100	0	calcretes	2	475	24.42	21.68	53.89
17	204	353	20	318	49	219	25.3	100	0	calcretes	2	810	27.04	25.19	47.78
iii	355	274	27	510	138	37	22.4	100	0	calcretes	2	1,067	3.47	33.27	63.26
23	311	318	18	III	34	295	37.7	100	0	calcretes	2	769	38.36	40.44	21.20
25	331	669	40	132	457	107	21.1	0	100	lake margin dolostones		1,067	10.03	31.02	58.95
26	258	434	22	590	264	101	11.7	0	100	lake margin dolostones		1,235	8.18	20.89	70.93
27	265	162	19	285	1,808	38	14.1	0	100	dolocretes	6	2,415	1.57	10.97	87.45
29	4,555	618	35	1,083	540	118	22.3	0	100	dolocretes	6	6,331	1.86	71.95	26.19
30	1,260	841	18	434	796	141	9.5	0	100	dolocretes	6	2,649	5.32	47.57	47.11
32	697	230	2	183	64	137	21.5	100	0	carbonate ponds		1,083	12.65	64.36	22.99
33	372	72	2	87	28	181	5.7	100	0	carbonate ponds		670	27.01	55.52	17.46
34	130	86		114	80	170	8.5	100	0	carbonate ponds	3	497	34.21	26.16	39.64
35	III	525	14	1,101	116	3,002	17.2	100	0	mudflat carbonates	4	4,344	69.11	2.56	28.34
36	405	117	35	295	218	152	4.8	0	100	lake margin dolostones		1,105	13.76	36.65	49.59
37	96	161	11	430	68	3,519	5.1	100	0	mudflat carbonates	4	4,124	85.33	2.33	12.34
38	66	124	7	250	75	2,738	7.4	100	0	mudflat carbonates	4	3,136	87.31	2.10	10.59
39	296	214	27	1,354	172	149	7.1	0	100	mudflat carbonates	4	1,998	7.46	14.81	77.73
40	768	64		351	155	138	3.4	0	100	mudflat carbonates	4	1,420	9.72	54.08	36.20
41	335	170	24	396	76	161	15.4	0	100	open-lake carbonates	5	992	16.23	33.77	50.00
42	493	84	18	428	223	202	3.2	0	100	open-lake carbonates		1,364	14.81	36.14	49.05
44	155	268	13	854	190	394	14.6	100	0	mudflat carbonates	4	1,606	24.53	9.65	65.82
45	88	188		510	54	1,160	9.1	100	0	mudflat carbonates	4	1,820	63.74	4.84	31.43
46	214	226	8	1,302	328	1,034	11.1	30	70	mudflat carbonates	4	2,886	35.83	7.42	56.76
47	236	384	25	1,886	785	629	19	0	100	mudflat carbonates	4	3,561	17.66	6.63	75.71
411	231	104	48	573	504	958	6.6	0	100	lake margin dolostones		2,314	41.40	9.98	48.62
49	196	126	14	1,200	275	138	2.5	65	35	mudflat carbonates	4	1,823	7.57	10.75	81.68
50	498	127	16	1,334	333	135		0	100	mudflat carbonates	4	2,316	5.83	21.50	72.67

Table I (continued)

Sample	Na	K	Li	Fe	Mn	Sr	I.R.	Calcite	Dolomite	Carbonate facies	Number of facies	∑Na, Li, Fe, Mn, Sr	Sr	Na	∑Li, Fe, Mn
51	429	363	10	613	70	134	8.7	25	75	open-lake carbonates	5	1,256	10.67	34.16	55.18
52	264	85	2	215	149	241	5.2	100	0	mudflat carbonates	4	871	27.67	30.31	42.02
53	75	155	9	606	91	712	5.7	100	0	mudflat carbonates	4	1,493	47.69	5.02	47.29
54	245	185	5	476	140	79	1.8	40	60	mudflat carbonates	4	945	8.36	25.93	65.71
55	1,055	73	3	241	54	123	1.6	80	20	mudflat carbonates	4	1,476	8.33	71.48	20.19
56	422	37		179	109	165	0.8	75	25	open-lake carbonates	5	878	18.79	48.06	33.14
58	904	105	11	428	120	203	8.8	0	100	dolocretes	6	1,666	12.18	54.26	33.55
60	106	106	13	435	898	45	6	0	100	dolocretes	6	1,497	3.01	7.08	89.91
62	77	141	5	256	25	93	6	100	0	calcretes	2	456	20.39	16.89	62.72
63	252	176	45	1,429	1,799	72	21	0	100	lake margin dolostones		3,597	2.00	7.01	90.99
64	164	139	36	1,678	1,349	52	9.9	100	0	lake margin dolostones		3,279	1.59	5.00	93.41
65	64	139	2	584	416	456	4.8	100	0	mudflat carbonates	4	1,522	29.96	4.20	65.83
66	78	97	9	371	88	420	6.3	100	0	mudflat carbonates	4	966	43.48	8.07	48.45
67	69	89	10	353	316	304	5.8	100	0	mudflat carbonates	4	1,052	28.90	6.56	64.54
68	100	331		580	425	233	10.3	100	0	mudflat carbonates	4	1,341	17.38	7.46	75.17
69	142	135	10	539	143	336	6.6	80	20	mudflat carbonates	4	1,170	28.72	12.14	59.15
70a	320	354	27	1,488	1,424	69	21.9	0	100	lake margin dolostones		3,328	2.07	9.62	88.31
70b	363	110	35	615	1,190	139	10.8	0	100	lake margin dolostones		2,342	5.94	15.50	78.57
71	387	147	25	663	470	74	14.3	0	100	lake margin dolostones		1,619	4.57	23.90	71.53
72	139	253	7	704	354	245	9.3	100	0	mudflat carbonates	4	1,449	16.91	9.59	73.50
73	633	83	10	435	125	110	39.3	0	100	open-lake carbonates	5	1,313	8.38	48.21	43.41
74	544	63	6	211	246	151	1.7	0	100	open-lake carbonates	5	1,158	13.04	46.98	39.98
75	74	48	2	173	118	117	2.6	90	10	open-lake carbonates	5	484	24.17	15.29	60.54
76	926	98	11	331	123	223	6.9	0	100	open-lake carbonates	5	1,614	13.82	57.37	28.81
77	155	123	5	735	958	283	7.2	100	0	mudflat carbonates	4	2,136	13.25	7.26	79.49
78	139	322	4	674	797	220	15.5	90	10	mudflat carbonates	4	1,834	12.00	7.58	80.43
79	189	245		459	601	260	7.2	100	0	mudflat carbonates	4	1,512	17.20	12.50	70.30
80	129	182	4	765	339	377	5.2	100	0	mudflat carbonates	4	1,614	23.36	7.99	68.65
81	905	187	14	409	302	164	11.5	0	100	mudflat carbonates	4	1,794	9.14	50.45	40.41

Trace elements contents of the carbonate (insoluble residue-free) fraction expressed in ppm. I.R. insoluble residues (%). Mineralogy in %.

Table 2

## Oxygen and carbon isotopic composition of carbonate

Sample	Mineralogy	$\delta^{18}\text{O}$ (‰ vs. PDB)	$\delta^{13}\text{C}$ (‰ vs. PDB)	Carbonate facies
3	dolomite	-6.65	-2.75	dolocretes
5	dolomite	-7.90	-4.75	dolocretes
7	calcite	-0.70	-3.95	calcretes
JO	calcite	-9.95	-7.95	calcretes
II	calcite	-9.65	-7.85	calcretes
12	calcite	-10.15	-8.15	calcretes
23	calcite	-9.50	-6.75	calcretes
25	dolomite	-7.45	-4.05	lake margin dolostones
26	dolomite	-6.45	-4.40	lake margin dolostones
30	dolomite	-6.85	-4.10	dolocretes
32	calcite	-10.25	-8.10	carbonate ponds
34	calcite	-9.95	-7.95	carbonate ponds
36	dolomite	-4.95	-4.20	lake margin dolostones
37	calcite	-4.70	-3.95	mudflat carbonates
38	calcite	-4.45	-5.65	mudflat carbonates
40	dolomite	-4.30	-3.05	mudflat carbonates
44	calcite	-2.75	-5.25	mudflat carbonates
45	calcite	-3.45	-5.15	mudflat carbonates
46	dolomite	-0.60	-6.90	mudflat carbonates
46	calcite	-0.90	-3.25	mudflat carbonates
48	dolomite	-3.25	-5.10	lake margin dolostones
51	calcite	-9.25	-7.50	open-lake carbonates
53	calcite	-4.70	-6.10	mudflat carbonates
54	dolomite	-4.50	-1.75	mudflat carbonates
54	calcite	-10.05	-7.00	mudflat carbonates
R2	calcite	-10.90	-8.00	calcretes
83	calcite	-10.30	-7.65	calcretes
84	calcite	-9.90	-7.20	calcretes
85	calcite	-10.10	-7.60	calcretes
R6	calcite	-10.10	-7.45	calcretes
87	calcite	-10.20	-7.55	carbonate ponds
88	calcite	-10.15	-7.55	carbonate ponds
R9	calcite	-10.50	-7.90	carbonate ponds
90	calcite	-10.90	-8.00	calcretes

Several different carbonate facies are included in this group. The most abundant facies is thinly bedded (2-4 cm thick), evenly laminated dolostone or limestone exhibiting a tabular geometry. These carbonates contain abundant molds of lenticular gypsum. Locally this type of carbonate exhibits gently domed, stromatolite-like shapes that are disrupted by desiccation cracks or tepee structures. The texture of the carbonate is varied, but is mostly composed of unimodal microsparite mosaics in which single crystals exhibit planar boundaries (Sibley and Gregg, 1987). Many of the crystals have rhombohedral shapes characteristic of dolomite. These crystals are commonly red-stained and the bulk composition of the rock is calcite, as determined by XRD, which suggests that calcitization was a generalized process affecting precursor dolomite deposits. Transformation of dolomite to calcite could be related to periodic shoaling accompanied by influx of meteoric water over the previously deposited sediments.

The thinly bedded carbonate alternates with more massive carbonate and clays in vertical sequences. The massive carbonates are decimetre-thick beds made of poorly indurated dolostone. The dolostone consists of homogeneous, rather porous mosaics of subhedral to rhombohedral, 20-45- $\mu\text{m}$ -sized crystals. These carbonates do not show definite features of subaerial exposure and are located in the lower part of the sequences. Thus, the transition from massive dolostones to clay and thinly bedded carbonates upward in the sequence suggests a progressive shoaling of the lake.

#### 4.5. Open-lake carbonate facies

This group of carbonates extends into the central area of the basin forming rather monotonous, well-bedded sequences intercalated with thin beds of mudstone (sections VII-IX of Fig. 3). Bed thickness ranges from 10 to 100 cm. The beds are internally massive and consist mostly of dolomite, although calcite is present at the top of the sections. The uppermost deposits were affected by karstification at the beginning of the Late Miocene. Karst-related features are represented by irregular-shaped, large voids ranging a few centimetres to several decimetres in diameter with drusy calcite veneers. Karsting resulted in the calcitization of the uppermost beds of the lacustrine sections.

The open-lake carbonates are weakly indurated and consist of porous aggregates of  $\mu\text{m}$ -size dolomite crys-



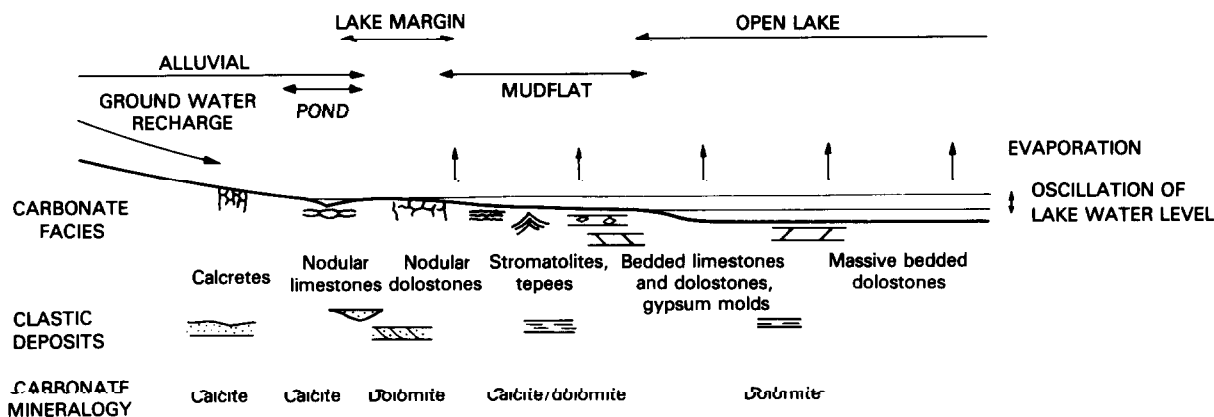


Fig. 4. Idealized sketch of carbonate sedimentary environments in the western side of the Madrid Basin with indication of main carbonate and clastic facies as well as carbonate mineralogy. Graphic not to scale.

tals. Dispersed fragments of ostracods, gastropods and algal filaments are present but rare.

The paleogeographical distribution of the carbonate facies is sketched in Fig. 4. The shallow nature of the lake is inferred from the sedimentological characteristics of the deposits, particularly from the architecture of the elastic strata (Calvo et al., 1989), as well as from the lateral arrangement of the facies belts. The sedimentary model corresponds to a shallow lake in which water level fluctuated periodically (Calvo et al., 1984). Oxic conditions prevailed throughout the water column in the most open-lake areas.

Lake carbonates are nearly devoid of fossils, suggesting that hydrochemistry of the lake restricted the development of floral and fauna communities. Only plants, represented by rhizoliths and rare carbonaceous debris, have been recognized in the carbonates. Some poorly preserved remains of gastropods and ostracods have been observed in the open-lake facies. The scarcity of fossils along with the mineralogical and petrographical characteristics of the carbonates suggest that the latter were probably precipitated inorganically. By contrast, organic fabrics are clearly recognized in calcretes, which suggests that plants contributed significantly to carbonate accumulation in this type of facies. No conclusive evidence has been found to support a primary precipitate or secondary replacement origin for the dolomite facies, although the latter mechanism is thought to be more plausible in view of the isotopic results discussed below.

General climatic conditions during the period of lake sedimentation are inferred from paleoecological data

furnished by mammal faunas (Lopez Martinez et al., 1987). These faunas are indicative of warm, semi-arid, seasonally-contrasted climatic regimes, probably similar to those found in present-day tropical savanna environments.

## 5. Geochemistry

### 5.1. Trace elements

Na, Mn, Fe and Sr were selected for analysis because of their significance in carbonate sedimentation and diagenesis. Particularly, Sr content may be a helpful tool for understanding the origin and diagenesis of carbonates (Kinsman, 1969; Veizer et al., 1971; Veizer and Demovic, 1974; Al-Hashimi, 1976; Veizer, 1983). Li and K contents were analyzed because of their common occurrence in clays in the Madrid Basin. Other elements, such as Zn, Ba and Pb, were also measured, but the contents of these elements did not show significant differences between the various carbonate groups.

Data obtained by trace-element analysis are listed in Table I. The mean values and standard deviations calculated for all elements are presented with respect to the main carbonate facies (Fig. 5). Calcretes, dolocretes, pond deposits, lake margin dolostones and open-lake carbonates show a similar range of Sr content. Mudflat carbonate facies are characterized by higher mean Sr content (Table 3), although Sr contents in this facies are more variable than in the other carbonate types (Fig. 5). This is mainly due to anomalous sam-

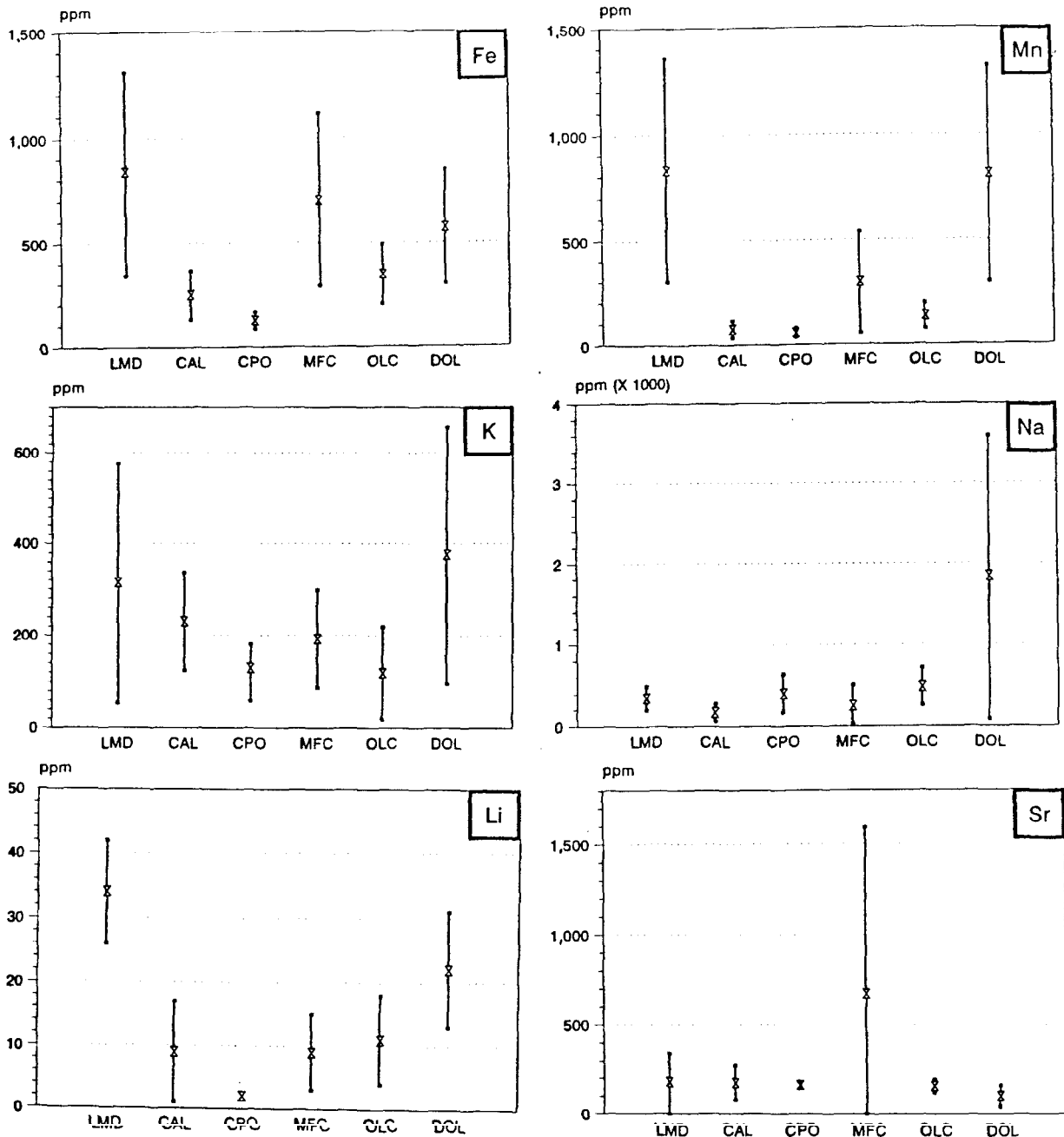


Fig. 5. Graphic representation of mean values (double triangle) and one standard deviation (bars) for the analyzed elements related to the carbonate facies. LMD = lake margin dolostone; CAL = calcrite; CPO = carbonate pond; MFC = mudflat carbonate; OLC = open-lake carbonate; DOL = dolocrete.

pies (35, 37, 38) which consist of calcite microspar mosaics with abundant gypsum molds. Excluding these samples, the mean value of Sr content in the mudflat

carbonates is 370 ppm, still higher than in the other facies. In general, the dolomite samples contain less Sr than the calcite samples. This behaviour agrees with

Table 3

Mean and standard deviation values (ppm) for trace-element content in the different carbonate facies

Carbonate facies	Fe		K		Li		Mn		Na		Sr	
	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.
Lake margin dolostones	841	499	314	261	34	8	832	529	343	147	179	262
Calcretes	251	117	230	106	9	8	75	41	169	104	175	97
Carbonate ponds	128	40	129	71	2	0	57	22	400	232	163	19
Mudflat carbonates	703	411	193	105	9	6	297	241	249	259	673	916
Open-lake carbonates	346	143	118	100	11	7	136	60	482	229	158	37
Dolocrete	573	272	376	280	22	9	810	511	1,839	1,756	101	60

S.D. = standard deviation.

the findings of others that Sr substitutes for Ca rather than Mg in the dolomite lattice (Behrens and Land, 1972; Kretz, 1982) and that the distribution coefficients for Sr in dolomite (K<sub>Sr</sub>) are much lower than unity (Katz and Matthews, 1977; Jacobson and Usdowski, 1976).

Mn and Fe contents show similar trends in the different facies. The calcites have relatively low Fe and Mn contents and the dolomites higher values, except for dolostones deposited in open-lake environments. The similar trend shown by Fe and Mn may be explained by the geochemical affinity of this pair of elements.

Li and K have similar distributions in the different carbonate facies, with a maximum for the lake margin dolostones. The lack of reliable data for distribution coefficients of this pair of elements (Veizer, 1983) makes it difficult to be conclusive about their mutual

Table 4

Factor analysis. Eigenvalues, total variance and weightings for the variables for each factor

	II	III	IV	
Eigenvalues	2.55	1.26	1.08	0.83
Total variance (%)	36.4	18.1	15.6	11.8
Total variance (cumulative %)	36.4	54.5	70.1	81.9
Fe	0.807	0.065	0.051	0.209
K	0.1	0.05	0.06	0.07
Li	0.719	0.294	0.279	-0.053
Mn	0.856	0.028	-0.038	-0.237
Na	0.098	0.126	0.958	-0.098
Sr	-0.033	-0.023	-0.088	0.967
I.R.	0.072	0.919	-0.044	-0.121

I.R. = insoluble residues.

geochemical behaviour. Finally, Na contents of the limestones are quite similar to values obtained for dolomites in all facies. Only Na content in dolocrete shows higher values, up to 4555 ppm, which is probably due to the presence of analcime in some of the samples, especially samples 29, 30 and 58 (Table 1). Excluding these samples, the mean value of Na in dolocrete is  $169 \pm 104$  ppm, lower than the mean values obtained for the other facies types.

Trace-element contents determined in the carbonate samples were subjected to factor analysis. The analysis reveals the existence of four factors which explain 82% of the total variance of our data (Table 4). The first factor, which accounts for 36% of the total variance is related to Mn, Fe and Li. The second factor, representing 18% of the total variance, is related to insoluble residue and potassium. The third and fourth factor components, accounting for 16% and 12% of the total variance, are related to Na and Sr, respectively. Because insoluble residue and K content are considered to be closely associated with the clay fraction of the samples, we selected the other three factor components for plotting trace-element data from carbonates in a triangular diagram (Fig. 6). In this representation, fields from the different carbonate facies are only partially discriminated. A discriminant function analysis was carried out using the trace-element data as well as trace-element

and stable isotope contents combined. As aforementioned, this latter attempt did not lead to significant results, which is probably due to the reduced number of isotopic data. By analyzing trace-element content alone, two discriminant functions are defined that represent percentages of 60% and 21.6%, and canonical correlations of 0.87 and 0.73, respectively. Standard-

ized discriminant function coefficients for both functions are given in Table 5. The variable "facies" was used as the classification factor in the analysis. The two main discriminant functions obtained allow plotting of the samples according to their trace-element contents ( Fig. 7 ). By this method, fields corresponding to the different facies are well discriminated except for mud-flat and open-Jake carbonates. However, the discrimination of carbonate types obtained graphically is only partially in agreement with the classification rates determined from the discriminant function analysis. As deduced from the results shown in Table 6, lake margin dolostones and carbonate ponds are best classified whereas calcretes show the lower classification rates.

### 5.2. Isotope geochemistry

Isotopic analysis were carried out on 32 carbonate samples in order to aid in environmental interpretations as well as to establish geochemical similarities or differences among the carbonate facies. Oxygen and carbon isotopic ratios, expressed as  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , are listed in Table 2.

Only two samples ( 46, 54 ) contained sufficient amounts of both calcite and dolomite for both to be analyzed; all other analyses were for only one mineral. Dolomite in sample 46 is significantly enriched in  $^{13}\text{C}$

Table 5  
Standardized discriminant function coefficients

	Discriminant function	
	1	2
Fe	-0.487	-0.206
K	0.407	-0.112
Li	0.874	0.663
Mn	0.757	-0.497
Na	0.141	-0.945
Sr	-0.049	-0.421
I.R.	-0.397	0.494

Discriminant functions: 1 (60% percentile), 2 (21.6% percentile).  
I.R. = insoluble residues.

and depleted in  $^{18}\text{O}$  relative to calcite. In sample 54, the dolomite is significantly enriched ( by 5-6% ) in both  $^{13}\text{C}$  and  $^{18}\text{O}$  relative to the calcite. In both cases the relative values of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in dolomite and calcite are outside of the usual ranges for coexisting authigenic dolomite and calcite in some recent environments ( Northrop and Clayton, 1966; Khoury et al., 1982 ).

The isotopic values obtained for different carbonate deposits have been represented in a cross-plotted  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  diagram ( Fig. 8 ). In this representation the carbonates are distributed in two broad groups, probably

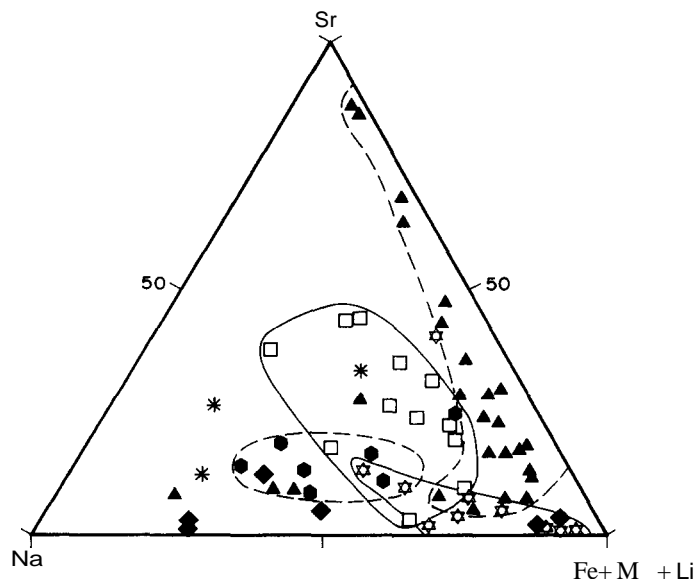


Fig. 6. Sr-Na-(Fe + Mn + Li) ternary plot of all study samples. The enclosing circles define fields where the several carbonate types are more densely plotted on the diagram.

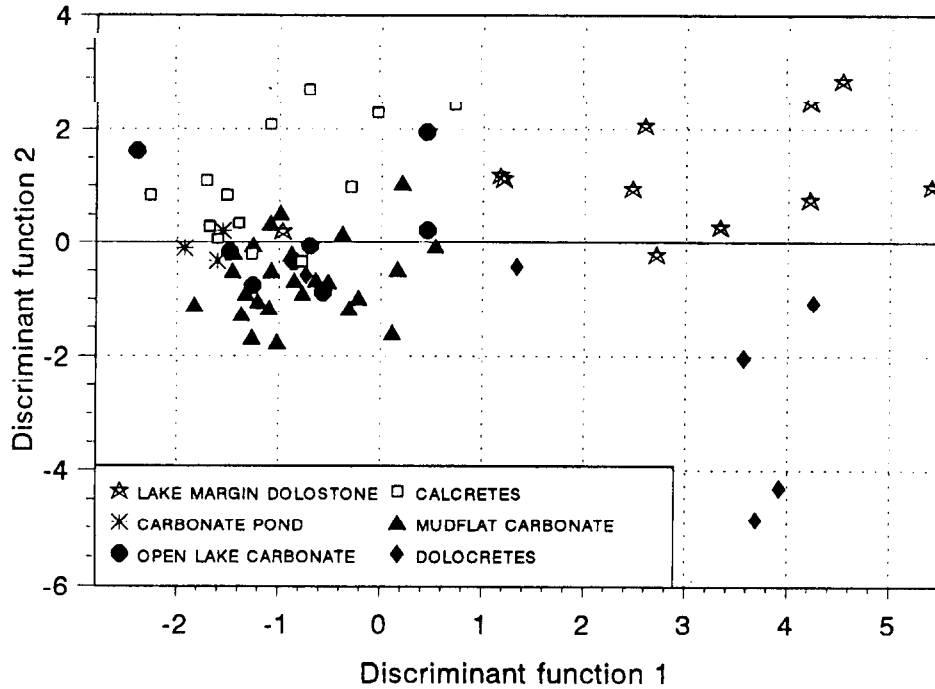


Fig. 7. Discrimination of carbonate facies types.

reflecting different paleoenvironmental conditions of carbonate formation. Calcretes show the most negative values. Carbonate accumulated in ponds is isotopically depleted, similar to calcretes. This confirms the close relationship of paleohydrologic conditions where both types of carbonates were deposited. In contrast, dolocretes show considerably less negative values of both  $8^{18}O$  and  $8^{13}C$ . Differences between  $8^{18}O$ -values of dolocrete and calcrete suggest that these two types of pedogenic carbonate formed in sedimentary subenvi-

ronments characterized by distinct hydrochemistry. Thus, isotopic contents of dolocretes show a similarity with those of lake margin dolostones and mudflat carbonate (Fig. 8) which would reflect the influence of the saline lake on the formation of dolocretes.

Carbonate minerals of mudflat facies show more varied isotopic values and, in general, are enriched relative to calcretes and are perhaps slightly enriched in  $^{13}C$  relative to margin dolostones. The variability of isotope compositions within the mudflat carbonate deposits would reflect different subenvironments of carbonate deposition (differences of subaerial exposure ratios, periods of low or high stand in the lake, etc.; Eugster and Kelts, 1983). The dolomite samples, at least samples 46 and 54, seem to be slightly enriched relative to the calcites, but given the small number of samples, the data are not sufficient to conclude a definite trend.

The single open-lake carbonate analyzed (51) is not truly representative of this facies type. Sample 51 was collected from carbonate beds that were strongly affected by karstification at the top of the lacustrine sequences. The interaction of karst-related meteoric water with the lacustrine carbonates could explain the

Table 6  
Classification rates obtained from discriminant function analysis (%)

	Function analysis (%)					
	LMD	CAL	CPO	MFC	OLC	DOL
Lake margin dolostone (LMD)	100	0	0	0	0	0
Calcretes (CAL)	0	57	21	7	14	0
Carbonate pond (CPO)	0	0	100	0	0	0
Mudflat carbonate (MFC)	0	0	7	77	15	0
Open-lake carbonate (OLC)	0	12	0	12	76	0
Dolocretes (DOL)	0	0	0	0	33	67

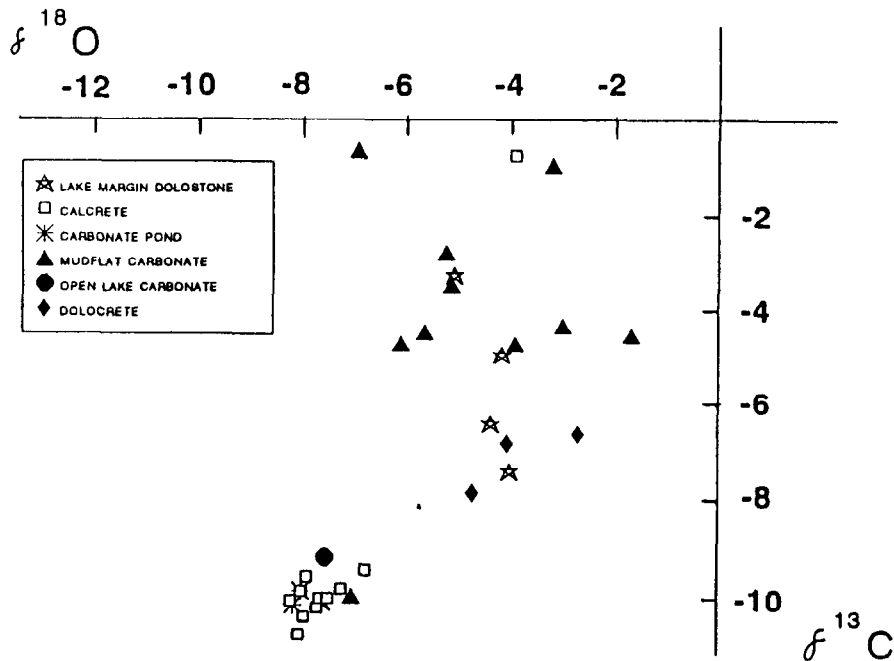


Fig. 8.  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  cross-plot of some of the investigated samples. A set of samples comprising calcrete and carbonate pond facies are well differentiated from those samples corresponding to carbonates formed under the influence of the saline lake. The sample from open-lake carbonate is anomalous (see explanation in text).

very negative isotopic values measured in this type of carbonate.

## 6. Discussion

One of the aims of this paper is to search the correlation between facies types and trace-element and isotope contents of carbonates deposited in lacustrine and related alluvial facies of the western side of the Madrid Basin. Our results show that, in this context, both sets of data may be considered potential discriminators of paleoenvironments of carbonate deposition. This approach to the use of geochemical data as a tool for interpreting paleoenvironmental conditions of lacustrine carbonate deposition follows those performed by Spencer (1982), Molenaar and De Feyter (1985), Janaway and Parnell (1989), and Cojan et al. (1992), amongst others.

The lacustrine and alluvial related carbonates show a distribution pattern consistent with the preliminary sedimentary model proposed by Calvo et al. (1984, 1989). This sedimentary model, sketched in Fig. 4,

reflects the geographical distribution of the different alluvial and lake subenvironments, each characterized by distinct hydrological conditions. Because of the lack of carbonate source areas northwest of the basin and the lack of petrographic evidence for detrital carbonate grains, it is assumed that the carbonates are mostly authigenic. Their mineralogical and geochemical characteristics were closely controlled by the parent solution. Organic influence and early or later meteoric diagenetic processes have also affected the primary deposit. Most of the carbonate facies analyzed display textural features indicative of diagenetic transformation. In spite of these changes, the carbonates retain some of the original geochemical imprints so that they may be used to discriminate among different conditions of carbonate formation (e.g., Molenaar and De Feyter, 1985; Platt, 1992).

The morphological features, such as prismatic structure, rhizocretions and clay cutans, displayed by both calcretes of the medial and distal zones of the alluvium and dolocrete are indicative of a pedogenic origin. In all cases, precipitation of carbonate within the soil horizon is thought to have been mainly controlled by the

combined effect of evaporation and biological activity. In fact, micromorphological features related to roots (alveolar fabrics) are widely recognized within both calcretes and dolocretes. The common pedogenic features recognized in these dolocretes make them different from those formed in phreatic conditions. This latter origin has been suggested as the most frequent mechanism of dolocrete formation (Wright and Tucker, 1991; Spolt and Wright, 1992).

$^{818}\text{O}$ -values determined in most of the calcretes, whether developed on previous soils of medial zones or on distal alluvial fan clays, are clearly negative and would indicate a strong meteoric influence, quite compatible with the pedogenic origin suggested for these deposits (Alonso et al., 1986). The low Sr contents measured in the calcretes corroborate this assumption. Similarly, the negative  $\text{O}^{13}\text{C}$ -values may be related to biogenic production of  $\text{CO}_2$  in the soil zone (Cerling and Hay, 1986). Dolocretes have less negative  $^{818}\text{O}$ - and  $\text{O}^{13}\text{C}$ -values than calcretes. This could be explained by two factors: (1) the commonly observed  $^{818}\text{O}$  enrichment in dolomite compared to calcite due to equilibrium isotopic fractionation (Northrop and Clayton, 1966; Molenaar and De Feyter, 1985); and (2) higher evaporation rates in the area where the dolocretes developed (Wright and Alonso Zarza, 1992). In both cases, it is assumed that the formation of dolomite in this facies took place under the influence of more saline waters of the adjacent lake.

The presence of analcime in some dolocrete samples requires comment. The occurrence of zeolites formed authigenically in calcareous paleosols has been described from Quaternary arid and semi-arid environments (Hay, 1978; Watts, 1980; Renaut, 1993) similar to those of the Madrid Basin during the Aragonian. In these settings, zeolites, in particular analcime forms at and close to the land surface mainly through evapotranspiration of shallow lake margin groundwaters. Analcime was probably formed by reaction of alkaline, sodic pore waters with poorly crystalline clays, though other silicates like plagioclase could also contribute (Renaut, 1993).

The similarity between carbonate deposited in ponds and calcretes is better illustrated by isotopic values than by trace-element content.  $^{818}\text{O}$ -values for pond carbonates also indicate derivation from meteoric waters.  $\text{O}^{13}\text{C}$ -values are quite similar and are in agreement with the textural evidence suggesting a contribution of

plants to these deposits. Although the sepiolite interbedded with pond carbonate has not been analyzed for isotopic composition, the clearly negative isotopic values for the carbonate seem to corroborate previous statements (Khoury et al., 1982; Hay et al., 1986; Jones, 1986) on the precipitation of sepiolite without the requirement of extensive evaporative concentration.

The close isotopic relationship between dolocretes and lake margin dolostones (Fig. 8) supports the hypothesis that the formation of dolomite in the former facies took place under the influence of the adjacent saline lake. A similar situation has been pointed out by Hay et al. (1986) in carbonate deposits of the Amargosa Desert in the western U.S.A. Dolocretes and lake margin dolostones also show striking similarities with regard to trace-element compositions (see Figs. 5 and 6). The common dolomitic nature of both facies accounts for their low Sr contents and concomitant high Fe and Mn contents.

Dolostones constitute the most common carbonate facies in lake margin and open-lake environments, whereas limestones are widely found in the mudflat belt. Dolomite is present in both recent and ancient Jake environments (Muller et al., 1972; Jones and Bowser, 1978; Eugster and Kelts, 1983; DeDeckker and Last, 1989; Last, 1990). Dolostones in our study area fit in the category of penecontemporaneous dolomite sediments which were formed under saline conditions involving concentration of Mg-rich waters. We have no conclusive data to postulate a primary or early diagenetic origin of the dolomite. Some geochemical data suggest the latter mechanism is more probable, as discussed below.

The sedimentological analysis of the lake margin dolostones provides evidence that the dolomite deposits were formed during stages of less water inflow to the lake, accompanied by minor elastic input. Under these conditions, the lake water became progressively concentrated by evaporation, producing enrichment in  $^{18}\text{O}$  (Fig. 8). The formation of dolomite could be favored by the presence of Li (Gaines, 1980) which is abundant in the clays that underlie dolomite beds in the lake margin sequences (Ribes et al., 1985). Na and Sr contents are low in this type of dolostone (Fig. 5). The low contents could be related to the early diagenetic origin of these dolostones, linked to the low distribution coefficient values of Na and Sr for the dolomite. The

high Mn and Fe contents in these facies can be explained by the combined effect of fixation by plants and lack of further leaching in the dolomite beds. The role of plants is also indicated by the relatively negative  $\text{O}^{13}\text{C}$ -values obtained for the lake margin dolostone. In addition, some samples from this facies (Fig. 8) show  $\text{O}^{13}\text{C}$ -values similar to dolocretes in which plant contribution is clearly recognized.

Mudflat carbonate facies are very different from either the calcite found in carbonates that occur in alluvial settings and the dolomite found in central Jake environments. The carbonate deposits included in this group show the highest variability in terms of both isotopic values and trace-element contents. This can be related to the variety of carbonate subtypes that form this major facies group. Petrographic analysis of the mudflat carbonates reveals that many of the calcite mosaics recognized in limestones actually consist of previous dolomite textures that are now calcitized. In some cases, calcitization took place almost simultaneously with the deposition of the primary carbonate, as is indicated by the alternation of thin dolomite and calcite laminae. However, this alternation is not a general feature and calcite is the predominant mineral of many carbonate beds. Calcite is especially prevalent in the carbonate beds that form the upper levels of the lacustrine cycles, which suggests that calcitization could be related to rather short-term periods of exposure.

Finally, the isotopic contents of open-Jake carbonate facies have not been studied in detail. One sample from this facies falls in the field of calcrete and carbonate pond facies (Fig. 8) which is explained by the fact that the analyzed material corresponds to open-Jake carbonate that underwent karstification, that is, modification by meteoric fresh water. On the other hand, discrimination of open-lake carbonate from other facies on the basis of trace-element contents is not unequivocal and depends on the method of statistical analysis. Thus, open-lake facies is fairly well discriminated from mudflat carbonate in a triangular Sr-Na-(Fe + Mn + Li) representation but the two facies types plot together on a bi-axial diagram derived from discriminant analysis. Accordingly, the use of trace-element contents for recognizing differences seen sedimentologically must be carried out with caution.

## 7. Conclusions

Stable isotope and trace-element analyses appear to be useful for differentiating among the various carbonate types and help in paleoenvironmental interpretation of lacustrine and alluvially-related carbonate facies deposited during the Middle Miocene on the western side of the Madrid Basin. Specifically,  $\delta^{18}\text{O}$ -values provide evidence of the different hydrologic conditions, in terms of evaporative concentration and influence of meteoric waters, in which carbonate deposits were formed. Depleted  $\delta^{18}\text{O}$ -values correspond to calcretes and carbonates that were deposited in ponds at the foot of alluvial fans. The intimate association of sepiolite with these deposits indicates that saline conditions were not required for precipitation of this clay mineral. In the same way,  $\delta^{18}\text{O}$ -values clearly identify carbonate facies that were deposited in brackish or saline lacustrine environments, although some erratic values, particularly in mudflats may indicate that other factors, such as the interplay with groundwaters could control the geochemistry and mineralogy of this group of carbonates.

$\text{O}^{13}\text{C}$ -values are sensitive to the contribution of biogenic  $\text{CO}_2$ , whether in the paleosol profiles or in very shallow lake environments. The commonly observed negative  $\text{O}^{13}\text{C}$ -values both in calcretes and carbonate ponds agree well with the textural evidence of root-related fabrics in these deposits. The relatively higher  $\text{O}^{13}\text{C}$ -values in lacustrine carbonates or in paleosols (dolocretes) formed under the influence of the saline lake may be interpreted as resulting from higher organic productivity of the moderately alkaline lake waters.

Trace-element contents do not allow so conclusive results as indicators of the different carbonate facies types, but aid the paleoenvironmental interpretation. In fact, fitness in using trace elements as discriminators of the study carbonates appears to be somewhat dependent on the chosen multivariate statistical method. This is particularly clear for the discrimination between mudflat and open-lake carbonates. Some anomalies, such as those detected for Na in dolocretes or for Sr in mudflat carbonates, could be related to early diagenetic products (zeolites, gypsum) or indicative of diagenetic, groundwater-related processes affecting the previous carbonates. Sr contents are clearly discriminated according to the carbonate mineralogy (calcite or dolomite) of the deposits. High Mn contents



seem to have been more directly related to dolomites but more information is needed to establish the relevance of this element in paleoenvironmental interpretation.

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