SUPRATIDAL EVAPORITIC DOLOMITE AT OJO DE LIEBRE LAGOON: MINERALOGICAL AND ISOTOPIC ARGUMENTS FOR PRIMARY CRYSTALLIZATION[1]

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ABSTRACT: This paper deals with a new site of dolomite formation in supratidal evaporite flats, at the southernmost edge of the Ojo de Liebre evaporitic complex (Baja California, Mexico).

The sedimentary context is mostly siliciclastic, except for calcareous outcrops around the flats. Both chemical and isotopic data on the interstitial solutions demonstrate a mixing between Mg^{2+}-rich marine-derived brines and calcium bicarbonate-bearing continental waters, which are subjected to concentration by capillary evaporation. The lack of any in situ solid $CaCO_3$ in the sedimentary matrix argues for direct crystallization of dolomite from aqueous solutions. This is documented by the oxygen isotope compositions of the dolomite which are consistent with deposition under equilibrium conditions of ambient temperature and $\delta^{18}O$ of water of the interstitial solutions.

Furthermore, the low $\delta^{13}C$ values of the dolomites and the absence of living plants or organisms in the basin indicate that a fraction of the total dissolved inorganic carbon reservoir is biogenic and is mostly provided by continental groundwaters. Therefore, crystallization of dolomite occurs within the sands infiltrated by solutions whose state of saturation relative to dolomite is mainly governed by the chemistry of continental groundwaters mixing with the inflowing marine brines.

INTRODUCTION

The formation of dolomite at the low temperatures and pressures of the earth's surface requires drastic chemical conditions which are rarely found in sedimentary environments, either marine or continental. High alkalinities and low ionic concentrations of calcium (relative to magnesium) and of sulfate in the solutions are often considered as critical factors which control the formation of sedimentary dolomites (Lippmann 1973). The first condition may be realized by inorganic or biogenic processes such as dissolution of carbonates; hydrolysis of silicates by CO_2-bearing waters; bacterial oxidation of organic matter, or intense photosynthetic activity. Low calcium and sulfate concentrations require either a previous and massive crystallization of calcium minerals (carbonates, sulfates) in order to depress the Ca^{2+} and SO_4^{2-} concentrations in the solutions, and/or a bacterial sulfate reduction by which the SO_4^{2-} concentration is lowered and alkalinities are elevated.

These chemical considerations explain why present-day sedimentary dolomites mostly occur as an in situ replacement product of calcium carbonate sediments, particularly in evaporitic sites where sulfate minerals crystallize extensively. The direct crystallization of dolomite from aqueous solutions, however, has been suggested in ephemeral alkaline lakes, such as the Coorong area in Australia and the intramountainous basin of Deep Spring Lake in California (Alderman and Skinner 1957; Alderman and Von der Borch 1960, 1961, 1963; Clayton et al. 1968; Peterson et al. 1963, 1966; Skinner 1963; Von der Borch 1965, 1976).

This study deals with the discovery of do-

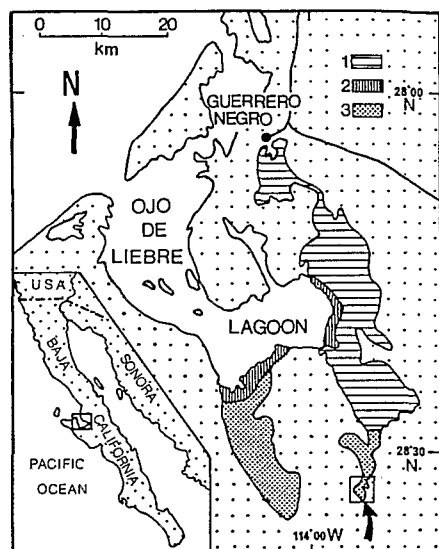[1] Manuscript received 19 October 1983; revised 26 January 1984.

FIG. 1.—Schematic map of the Ojo de Liebre evaporitic complex in Baja California (NW Mexico). Situation of the area until 1981: 1) artificial salt pans; 2) natural algal flats; 3) residual natural evaporite flats; arrow: location of the site of dolomite formation, detailed in Figure 2.

lomite formation in Baja California (Mexico), occurring in a siliciclastic environment. In this area, it can be inferred that dolomite precipitated directly in the sediment from interstitial solutions (Pierre et al. 1981, 1982; Pierre 1982). Petrographic and mineralogic studies of the sediments and chemical and stable isotope analysis of interstitial solutions and carbonate sediments, were performed to determine a) the origin and the evolution of the water and the ionic species of the solutions, and b) the state of chemical and isotopic equilibria between the solutions and the carbonate minerals.

SITE DESCRIPTION

The Ojo de Liebre lagoon is located on the western coast of the Baja California peninsula, in northwestern Mexico, between lat. 28°00′N and lat. 27°30′N (Fig. 1). In this area, the climate is arid, but it is tempered by the influence of the Pacific Ocean. It is characterized by a low rainfall ($\simeq$ 35 mm year^{-1}),

a high evaporation rate ($\simeq$ 1,500 mm year^{-1}), and by quite constant and strong west to west-northwest winds. The mean monthly maximum and minimum temperatures range between 20–29°C and 8–20°C (Phleger and Ewing 1962).

The Ojo de Liebre lagoon is bordered by extensive supratidal flats which have been progressively transformed since 1957 into artificial saline ponds for industrial salt production. At the southern part of this evaporitic complex, remnants of the natural evaporitic supratidal flats extend up to 15 km inland. They are surrounded by sand dunes, and by a plateau about 30 m high composed of Mesozoic sandstones and Mio-Pliocene limestones which are capped by a thick calcrete. On the northeastern edge of the evaporite flats, some levees about 3 m high are covered by shell beds and discontinuous gypsum deposits of late Pleistocene age (probably Sangamonian). Except for these calcareous outcrops, the sediments where authigenic minerals are developing are sands containing mainly quartz, feldspar, and hornblende. The nonauthigenic carbonate fraction of these sands (less than 1% of total dry weight of sediment) consists of tiny, highly corroded shell fragments.

A 250-m-long south-north transect was made at the southern edge of the evaporite flat. In addition, a few other sites were selected up to 3 km to the north (Fig. 2). A collection of brines from immediately below the water table, and sediments at different depths were taken in a series of hand-dug pits in May 1979 and April 1981.

THE SEDIMENTARY SEQUENCE

The sedimentary sequence appears quite different in the northern part and at the southern margin of the evaporite flat (Fig. 2). In the northern part of the flat, evaporitic deposits consist of a thin halite crust, and locally of scattered gypsum crystals in the sand. Southerly, in the central part of the pan, the halite crust thickens up to 30 cm. Gypsum deposits, with a maximal thickness of 35 cm, are located along the basin edge and at a few centimeters depth. The lenticular habit of the gypsum crystals and the abundance of sand grains within the gypsum crystals indicate diagenetic growth within the host detrital sediment. At the inland edge of the basin, the
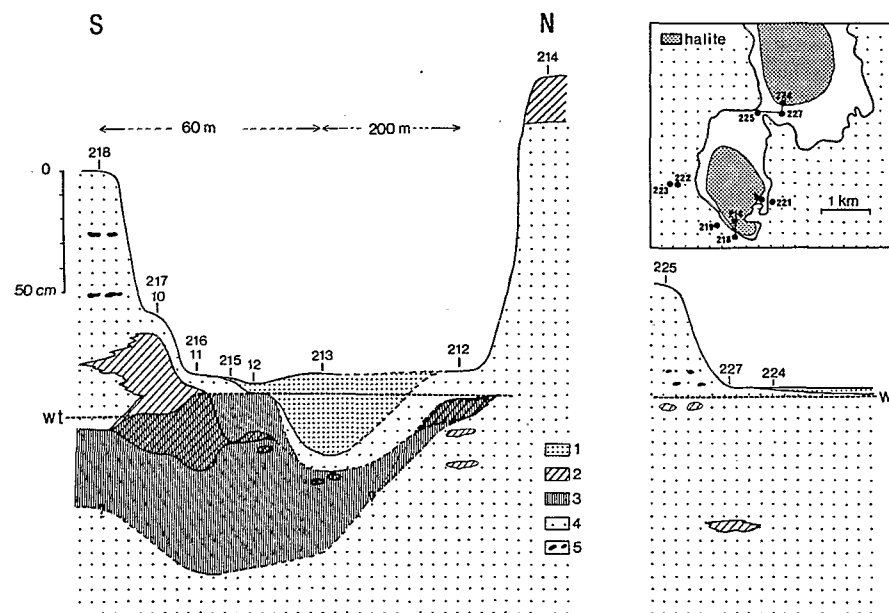

FIG. 2.—Schematic cross-sections showing the sedimentary succession at the southern edge of the Ojo de Liebre evaporitic complex, and location of the collected samples. (1) halite; (2) gypsum; (3) dolomite; (4) sand; (5) concretions of calcite; w.t. = water table.

upper layers of gypsum are most probably reworked and accumulated by wind, as evidenced by rough layering of sedimentary elements and corrosion features of the gypsum crystals.

The sedimentary matrix of gypsum sediments, occurring above the water table contains only minor amounts of calcium carbonate as small shell fragments or concretions, while below the water table, gypsum is associated with dolomite (Fig. 2). These halite and gypsum deposits are underlain by a layer of grayish-green massive mud, up to 40 cm of maximum thickness; this mud, which includes variable amounts of dolomicrite (1 to 50% dry weight; Table 2), locally contains some large, lenticular crystals of gypsum.

PETROGRAPHY AND MINERALOGY OF THE DOLOMITIC SEDIMENTS

Mineralogical compositions of the bulk samples were determined by X-ray diffraction. The dolomites are well-ordered with all

superstructure reflections present and well-developed, except for the (015) peak which is weakened (Fig. 3).

The chemical composition of these dolomites was estimated by measuring the displacement of the (104) reflection peak (Goldsmith and Graf 1958; Goldsmith and Heard 1961). These are calcian dolomites with a compositional range of $Ca_{54.5-51.5}Mg_{45.5-48.5}$.

Optical microscope and SEM observations of the dolomitic sediments show that the dolomite crystals are of three types. The most common crystals are small (less than 5 μm) and exhibit an elongated subhexagonal habit; these are occasionally twinned (Fig. 4A, B). The second type consists of larger, subrhombohedral crystals measuring up to 15 μm (Pierre 1982; plate 4). The third facies, found in millimeter-size concretions, corresponds to aggregates of small, subhexagonal crystals (Fig. 4). Besides, dolomitized shell fragments were rarely observed in the <160 μm fraction of some washed dolomitic sediments (LV 1235, L 218 b).
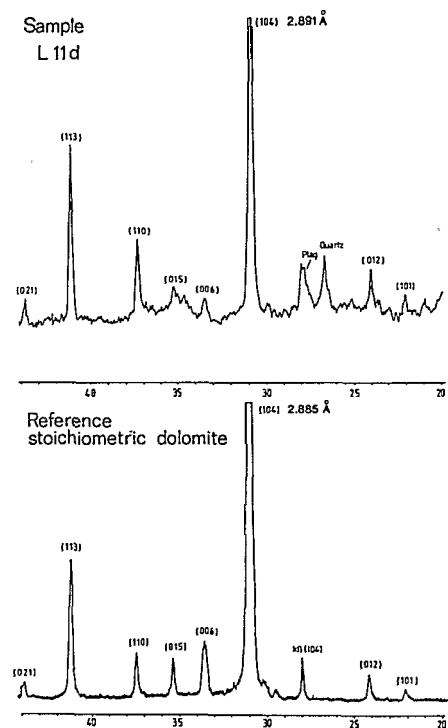
FIG. 3.—X-ray diffraction (Cu Kα) diagrams of the sample L 11d and of reference stoichiometric dolomite (secondary sedimentary dolomite of Jurassic age from Montpellier-le-Vieux, Aveyron, France).

ANALYTICAL PROCEDURES

Chemical Analyses

Immediately after collection in the field, the solutions were filtered on paper, and 1/10 diluted with distilled water to avoid further crystallization of salts.

Ionic concentrations were measured by classical methods: colorimetry for major anions (Cl^- and SO_4^{2-}); atomic absorption spectrophotometry for Ca^{2+}, Mg^{2+}, Sr^{2+}, Li^+; flame emission photometry for K^+ and Na^+; iodinometry with potentiometric indication of the equivalence point for Br^-.

The analytical results are given with an ionic balance generally lower than 5%.

Isotopic Analyses

Isotopic measurements were realized on a double-collector mass spectrometer (VG Micromass 602). Appropriate correction factors were applied (Craig (1957) for CO_2 gas, Hulston (1962) for SO_2 gas) on results expressed in δ units.

The oxygen isotopic composition of water was determined by the classical method of CO_2-H_2O equilibration at 25°C (Epstein and Mayeda 1953); however, the duration of equilibration was extended to one week for these highly concentrated solutions.

Deuterium analyses of water were performed on hydrogen produced through water reduction on uranium at 800°C (Friedman and Hardcastle 1970).

Before isotopic preparation, the aqueous sulfate was precipitated as $BaSO_4$ (Longinelli and Craig 1967). The oxygen isotope ratio of sulfate was then measured on CO_2 gas produced using the method described by Longinelli and Craig (1967). The sulfur isotope ratio of sulfate was measured on SO_2 gas prepared by burning Ag_2S in pure oxygen (Filly et al. 1975).

For carbonate isotopic analyses, about 100 to 200 mg of the bulk sample were previously treated during several hours with a sodium hypochlorite solution to remove any organic material. After careful washing with distilled water, and drying, 10 to 50 mg of the sample were reacted with 100% phosphoric acid at 25°C (McCrea 1950). The $\delta^{18}O$ values of dolomite were corrected by −0.8‰ to compare with calcite $\delta^{18}O$ values, to account for the differential fractionation factor introduced during the acid extraction of CO_2 from dolomite and calcite (Sharma and Clayton 1965).

CHEMICAL AND ISOTOPIC DATA ON THE INTERSTITIAL SOLUTIONS

Chemical Data

Physicochemical parameters (temperature, density, pH, EH) of the interstitial solutions were measured in situ at the time of sampling. Importantly, results for the analysis of solutions collected in May 1979 and April 1981 are quite similar (Fig. 5, Table 1).

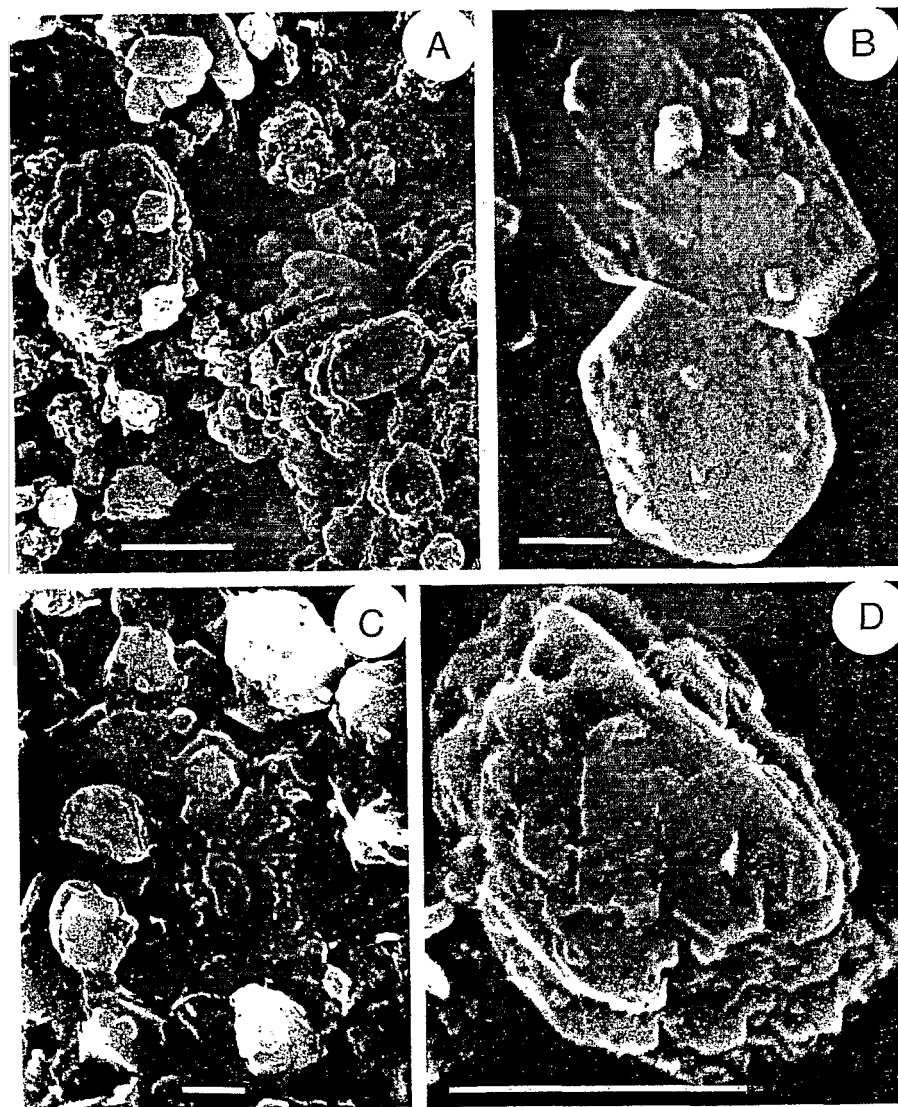The density of the solutions ranges from 1.217 in the center of the pan to 1.091 toward

FIG. 4.—SEM micrographs showing different facies of dolomite crystals in selected dolomitic samples from the southern edge of the Ojo de Liebre evaporitic complex. A) Sample L 218a: small, elongated subhexagonal dolomite crystals associated with larger subrhombohedral dolomite crystals (scale bar = 5 μm). B) Fine fraction (< 2 μm) of sample L 11d: twinned dolomite crystals with subhexagonal habit (scale bar = 0.5 μm). C) Millimeter-sized dolomitic concretion from the coarse fraction (> 160 μm) of sample L 11d: small dolomitic crystals with badly defined rhombohedral shape (scale bar = 1 μm). D) Sample L 11d: twinned dolomitic crystal composed by inframicron-sized crystal units.
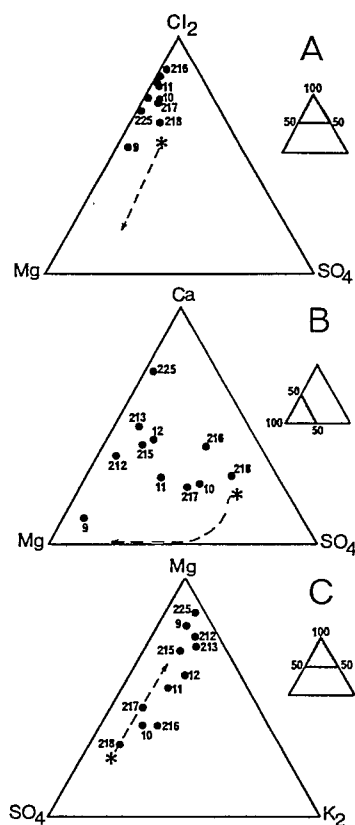
FIG. 5.—Triangular plots of ionic concentrations of the interstitial solutions collected at the southern edge of the Ojo de Liebre evaporitic complex. The dashed lines give the sea water (symbol = star) evolution during evaporation as deduced from Hermann et al. (1973) data. (A) Σ Cl$_2$ + Mg + SO$_4$ = 100; (B) Σ Ca + Mg + SO$_4$ = 100; (C) Σ Mg + SO$_4$ + K$_2$ = 100.

the basin edge. This suggests a progressive dilution of inflowing brines by continental fresh waters at the basin margins. Temperatures of the solutions were roughly constant, ranging between 18°C and 23.5°C. The lowest pH values (pH = 6.1) were measured in the most concentrated solutions for which the activity of water was also the lowest. EH values were very positive ($+330 <$ EH mV $< +460$) and indicate strictly oxidizing conditions in the interstitital environment; how-

ever, a trend towards more reducing conditions in the center of the basin is indicated by EH values sharply decreasing by more than 200 mV.

Ionic concentrations of the solutions appear very different when compared to normal marine brines[2] (Fig. 5). The K$^+$/Li$^+$ molar ratio of these solutions ranges between 130 and 390. These values are intermediate between the one which is calculated by using Wedepohl's data (1970) for the mean sea water (K$^+$/Li$^+$ = 10.10^{-3}/26.10^{-6} = 384), and the one which is measured in the continental waters of the local aquifer (K$^+$/Li$^+ \cong$ 50). This suggests that these brines have a mixed marine and continental origin.

The most important chemical features of the solutions are the large excess in Ca^{2+} and Sr^{2+} ions, and the deficit in SO$_4{}^{2-}$ ions relative to marine-derived brines (Fig. 5). The high Ca^{2+} and Sr^{2+} concentrations strongly suggest a dissolution from components containing both these ionic species, like marine skeletal aragonites and calcites, calcrete or other carbonates outcropping around the basin margins. Because carbonate minerals are nearly absent in the sedimentary sequence, the Ca^{2+} and Sr^{2+} ions are most probably supplied into the basin by continental waters which have dissolved surrounding carbonate sediments during their subterranean transit.

At the southern edge of the basin, the excess input of Ca^{2+} ions is balanced by the uptake of Ca^{2+} during the crystallization of dolomite and gypsum. Such authigenic mineral precipitation may account for the large variations observed in Mg^{2+}/Ca^{2+} and Sr^{2+}/Ca^{2+} molar ratios ranging from 1.7 to 5.5 and 0.95 10^{-2} to 3.14 10^{-2}, respectively, which were documented in the interstitial solutions.

In the northern part of the basin, the brines possess very low SO$_4{}^{2-}$ concentrations. This is probably due to the extensive precipitation of gypsum in the northern supratidal flats through which inflowing marine brines must transit from the Ojo de Liebre evaporitic complex.

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[2] Ionic concentrations are expressed in molalities (i.e., moles per kg of pure water). Comparisons were established with Hermann et al. (1973) chemical data on evaporated marine brines from the artificial salt pans of Secovlje (Yugoslavia).

TABLE 1.—Chemical and isotopic data on interstitial solutions collected in May 1979 and April 1981 in the southernmost supratidal evaporite flats around the Ojo de Liebre evaporitic complex. Ionic concentrations are expressed in molalities (i.e., moles kg^{-1} of pure water). The $\delta^{18}O$ and δ^2H values of the water which are not in parentheses are expressed on an activity scale; the $\delta^{18}O$ and δ^2H values of water which are in parentheses are expressed on a concentration scale (Sofer and Gat 1972, 1975)

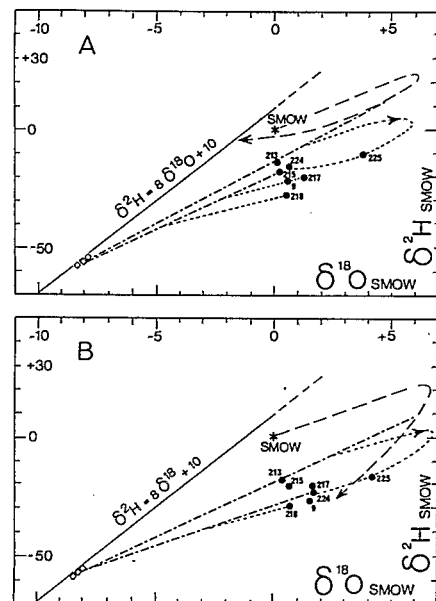| Sample	t°C	Density	pH	EH mV	Li$^+$ 10^{-6} m	Br$^-$ 10^{-3} m	Mg^{2+} 10^{-3} m	K$^+$ 10^{-3} m	Ca^{2+} 10^{-3} m	SO$_4{}^{2-}$ 10^{-3} m	Cl$^-$ m	Na$^+$ m	HCO$_3^-$ 10^{-3} m	Sr^{2+} 10^{-4} m	m Na$^+$/m Cl$^-$	m Cl$^-$/m Br$^-$	$\delta^{18}O$ SMOW	δ^2H SMOW	$\delta^{18}O$ SMOW	$\delta^{34}S$ CD
May 1979																				
10	22.5	1.136	6.8	+460	156	2.0	222.7	45.7	43.2	76.4	3.790	3.464	0.9	618	0.91	1,864	+1.3 (+1.5)	—	+7.9	+12.5
11	23	1.186	6.6	+440	176	2.3	258.1	59.7	52.6	48.8	5.371	4.806	1.0	681	0.89	2,274	0.0 (+0.3)	—	+6.1	+12.8
12	22	1.195	6.3	+200	162	—	234.2	63.2	75.6	29.5	5.863	5.196	0.7	880	0.88	—	−0.2 (+0.1)	—	+9.3	+13.3
9	—	1.215	—	—	445	10.1	861.0	93.2	43.3	48.5	6.062	4.105	0.8	692	0.68	600	+0.7 (+1.7)	−20.9 (−27.4)	+4.4	+9.5
April 1981																				
218	22	1.091	7.1	+340	196	1.4	170.2	25.1	42.0	79.3	2.330	2.293	1.5	1,162	0.98	1,651	+0.5 (+0.7)	−27.8 (−29.9)	+9.5	+12.8
217	23.5	1.138	7.0	+385	247	1.5	239.1	37.6	43.4	71.6	3.833	3.685	0.8	1,364	0.96	2,632	+1.3 (+1.6)	−19.7 (−22.7)	—	—
216	23.5	1.188	6.8	+285	340	7.5	157.3	46.0	51.9	49.6	5.709	5.257	4.3	550	0.92	763	+0.5 (+0.7)	—	—	—
215	20.5	1.197	6.5	+295	230	5.9	285.9	48.3	82.7	29.7	6.290	5.667	4.8	806	0.90	1,080	+0.2 (+0.6)	−17.6 (−21.9)	—	—
213	19	1.202	6.6	+150	279	5.9	304.0	64.2	105.1	19.5	6.268	5.697	4.5	997	0.91	1,060	0.0 (+0.3)	−14.2 (−18.8)	—	—
212	18	1.204	6.4	+275	361	5.9	414.8	71.5	96.7	22.8	6.351	5.577	5.2	1,009	0.88	1,078	+1.0 (+1.5)	—	—	—
225	23	1.196	6.2	+330	271	3.3	475.1	59.6	276.0	9.4	5.469	4.576	5.7	3,035	0.83	1,650	+3.7 (+4.2)	−11.3 (−17.4)	+10.6	+14.6
224	20.5	1.217	6.1	+370	447	9.4	—	—	—	—	—	—	—	—	—	—	+0.6 (+1.6)	−16.7 (−22.8)	—	—

FIG. 6.—Relationship between $\delta^{18}O$ and δ^2H values of water of the interstitial solutions collected at the southern edge of the Ojo de Liebre evaporitic complex. The two diagrams give the δ values expressed either on an activity scale (A) or on a concentration scale (B), following Sofer and Gat (1972, 1975) corrections for saline solutions. The large-dashed curve represents the isotopic behavior of sea water during evaporation as measured in the marine brines collected in the salt pans of the Ojo de Liebre evaporitic complex (Pierre 1982). The local meteoric waters (symbol = open squares) sampled in wells about 20 km east of the site, are located on the general meteoric water line $\delta^2H = 8 \delta^{18}O + 10$). The effects of evaporation and of dilution by meteoric waters in the interstitial solutions are respectively represented by the small-dashed lines and curves and by the dotted-dashed lines.

Farther toward the southern edge of the basin, the solutions are progressively enriched in SO_4^{2-} ions, which are therefore allochtonous. This nonmarine source of SO_4^{2-} ions must be searched for in the vicinity of the site, and most probably comes from the dissolution by continental waters of Pleistocene gypsum deposits which locally crop out along the basin edge.

Oxygen and Hydrogen Isotope Composition of Water of the Solutions

From a general point of view, the isotopic ratios of the oceanic water reservoir are constant, and give the SMOW reference for oxygen and hydrogen isotopic compositions of waters in such a way that the δ values of the mean sea water are equal to zero on the SMOW scale (Craig 1961b). Because of fractionation phenomena between light and heavy isotope species of water, induced by evaporation and condensation processes, meteoric waters are depleted in heavy isotopes while evaporated marine waters are enriched in heavy isotopes relative to sea water (Craig 1961a; Craig et al. 1963; Craig and Gordon 1965; Sofer and Gat 1972, 1975; Fontes 1976). The isotopic composition of water of solution which thus constitutes an accurate marker of the water origin, was measured in the Ojo de Liebre interstitial brines in order to follow their isotopic evolution throughout the basin.

The oxygen and hydrogen isotope ratios of water of these solutions are significantly depleted relative to normal marine brines (Fig. 6). When plotted in the same diagram, $\delta^{18}O$ and δ^2H values of water of the solutions define curves which are related to two effects: dilution of marine brines with the local meteoric water and capillary evaporation of the resultant solutions.
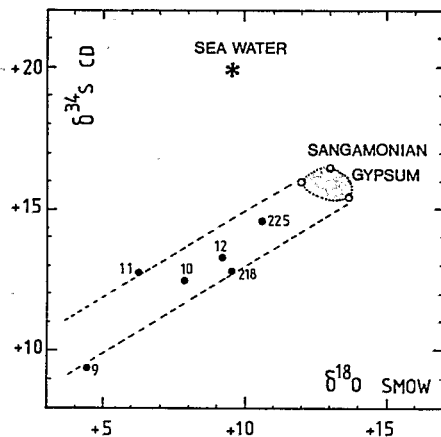

FIG. 7.—Oxygen and sulfur isotope compositions of aqueous sulfate of interstitial solutions collected at the southern edge of the Ojo de Liebre evaporitic complex. The δ values of sulfate of Sangamonian gypsum were measured on samples of nearby outcrops. The mean δ value of sea-water aqueous sulfate (Longinelli and Craig 1967; Lloyd 1967, 1968; Thode et al. 1961) is reported by comparison.

TABLE 2.—*Mineralogy and isotopic composition of carbonates (calcite and dolomite) collected at the southern edge of the supratidal evaporite flats around the Ojo de Liebre evaporitic complex. The $\delta^{18}O$ values of dolomites are corrected by -0.8‰ for the acid-extraction fractionation effect to allow comparison between them and $\delta^{18}O$ values of calcites (Sharma and Clayton 1965)*

Sample (Subbottom Depth)	Nature of the Sediment and Mineralogy of Carbonate	Carbonate Weight % of Total Dry Sediment	$\delta^{18}O$ PDB	$\delta^{13}C$ PDB	$\alpha^{18}O_{carb-water}$ (Measured)
L 218e (25 cm)	concretion of calcite	<1	−2.3	−2.4	1.0278
L 218d (50 cm)	concretion of calcite	14	−3.5	−4.1	1.0265
L 218a (110 cm)	dolomite $Ca_{53.5} Mg_{46.5}$	10	+5.1	−4.3	1.0351
L 218b (125 cm)	dolomite $Ca_{53} Mg_{47}$	—	+3.3	−3.8	1.0333
L 217b (38 cm)	calcite	<1	+3.0	−2.3	1.0323
L 217a (67 cm)	dolomite $Ca_{54.5} Mg_{45.5}$	6	+4.8	−3.6	1.0340
L 216b (15 cm)	calcite	<1	−1.4	−1.2	1.0286
L 216a (46 cm)	dolomite	15	+3.8	−3.2	1.0328
LV 1235 (80 cm)	dolomite $Ca_{54} Mg_{46}$	—	+2.3	−3.7	
L 11a (10 cm)	gypsum and dolomite	—	+3.1	−2.5	1.0337
L 11c (30 cm)	gypsum and dolomite $Ca_{53} Mg_{47}$	—	+3.8	−2.4	1.0343
L 11d (41 cm)	dolomite $Ca_{51.5} Mg_{48.5}$	49	+3.4	−3.7	1.0339
L 215c (3 cm)	calcite	<1	−0.6	−0.9	1.0296
L 215a (23 cm)	dolomite $Ca_{54} Mg_{46}$	1	+2.4	−2.5	1.0326
L 215b (27 cm)	dolomite $Ca_{53.5} Mg_{46.5}$	27	+5.1	−3.6	1.0354
L 12b (21 cm)	gypsum and dolomite $Ca_{53} Mg_{47}$	—	+3.0	−2.6	1.0336
L 12c (23 cm)	dolomite $Ca_{53} Mg_{47}$ with isolated gypsum crystals	25	+3.0	−5.3	1.0336
L 213a (41 cm)	dolomite $Ca_{52} Mg_{48}$	19	+3.2	−2.7	1.0336
L 212a (14 cm)	gypsum and dolomite $Ca_{53} Mg_{47}$	6	+4.6	−3.2	1.0346
L 212b (20 cm)	gypsum and dolomite $Ca_{52} Mg_{48}$	4	+4.7	−3.8	1.0347
L 9c (20 cm)	gypsum and dolomite $Ca_{52} Mg_{48}$	1	+4.1	−4.1	
L 225a (50 cm)	concretion of calcite	8	−1.7	−1.2	1.0250
L 226 (100 cm)	concretion of calcite	—	−2.5	−1.5	
L 220b	fragments of Sangamonian shells	—	+0.4	−1.6	
L 221	calcrete	—	−3.0	−3.6	
L 219	calcrete	—	−5.7	−3.7	
L 223a	calcrete	—	−2.0	−3.5	
L 223b	calcrete	—	+1.1	−1.1	

These results confirm that the interstitial solutions consist of a progressive mixing between marine brines and continental waters.

Oxygen and Sulfur Isotope Composition of Aqueous Sulfate of the Solutions

The $\delta^{18}O$ and $\delta^{34}S$ values of aqueous sulfate of the solutions ($+4.5 < \delta^{18}O < +10.6$; $+9.4 < \delta^{34}S < +14.6$) are distinct from the δ values of the sea water aqueous sulfate (Fig. 7). In a $\delta^{18}O - \delta^{34}S$ plot, the points corresponding to the δ pairs of the aqueous sulfate of the solutions are distributed within a narrow belt which connects the group of δ values measured for Pleistocene gypsum sampled near the site (Fig. 7); these results confirm that SO_4^{2-} ions in these solutions are not of

marine origin but come exclusively from the dissolution of Pleistocene gypsum. Furthermore, the simultaneous variations of $\delta^{18}O$ and $\delta^{34}S$ values, in a ratio which is close to that of the isotopic enrichment factors between gypsum and aqueous sulphate ($\epsilon^{18}O/\epsilon^{34}S = 3.5/1.65$), clearly describe a "reservoir" effect due to the progressive crystallization of gypsum in a system closed relative to the SO_4^{2-} ions source (Pierre 1982).

ISOTOPIC DATA ON THE CARBONATE SEDIMENTS

Oxygen and carbon isotope analyses were performed on the dolomitic sediments, on the calcium carbonate fraction of the surficial sediments, and on the calcrete and Sangamonian shells in carbonates cropping out around the basin (Table 2; Fig. 8).
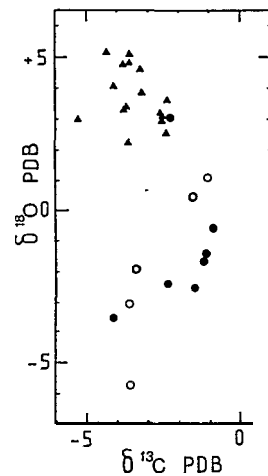
FIG. 8.—Oxygen and carbon isotope compositions of calcite (symbols = full circles) and dolomite (symbols = full triangles) from sediments collected at the southern edge of the Ojo de Liebre evaporitic complex. The δ values of carbonates from surrounding outcrops (calcrete and shells of Sangamonian age; symbols = open circles) are also reported on this figure.

Dolomites

The δ values of dolomites range from +2.3 to +5.1 for ^{18}O, and from −5.3 to −2.4 for ^{13}C.

The low carbon isotope ratios of dolomites point to a contribution of biogenic CO_2 to the total dissolved inorganic carbon (TDIC) reservoir. Because living organisms such as plants are practically absent in the basin, this biogenic carbon must be of terrestrial origin, supplied perhaps by continental waters as bicarbonate ions, and by wind as plant fragments. Furthermore, the $\delta^{13}C$ values of dolomites show a rough trend to increase upwards (Table 2). This may be due to a greater degassing of CO_2 from the interstitial solutions in the upper levels of the sedimentary section by capillary evaporation, when the TDIC reservoir is closed or semiclosed; by such an effect, the removal of CO_2, depleted in ^{13}C relative to the TDIC reservoir, tends to enrich in ^{13}C the remaining TDIC by mass-balance effect (Deines et al. 1974).

The measured values for the oxygen isotope fractionation factor $\alpha^{18}O$ between do-

lomite and water[3] range between 1.0326 and 1.0354, with a mean value of 1.0336. These values are very close to the theoretical ones (1.0321 to 1.0369) which are calculated for the same temperature range (from 18°C to 23.5°C) using the experimental equations of Fritz and Smith (1970), Matthews and Katz (1977), Friedman and O'Neil (1977). These results suggest that dolomite and water are in isotopic equilibrium for ^{18}O and are compatible with dolomite precipitation directly from the interstitial solutions.

Calcium Carbonate

The oxygen and carbon isotope ratios of the calcium carbonate fraction from the sands located above the water table exhibit a large range of values ($−3.5 < \delta^{18}O < +3.0$; $−4.1 < \delta^{13}C < −0.9$).

As previously mentioned, this $CaCO_3$ fraction may come either from small shell fragments and/or from an authigenic phase which consists of magnesian calcite cementing the sand grains. This difference of origin, as well as possible differences in the chemistry of the calcium carbonate, most probably explains the large dispersion observed in the $\delta^{18}O$ and $\delta^{13}C$ values.

The lowest $\delta^{18}O$ and $\delta^{13}C$ values are obtained in the carbonate concretions which are scattered in the sands at the southern basin edge; for these samples, the measured oxygen isotope fractionation factor between calcite and the underlying water ($1.0250 < \alpha^{18}O < 1.0278$), is distinctly lower than the theoretical one $\alpha^{18}O = 1.0292$ to 1.0295 calculated for the same temperature using the O'Neil et al. (1969) equation. In this case, the authigenic calcite has crystallized either under nonequilibrium conditions with the water, or more probably, with water more depleted in ^{18}O (i.e., less evaporated) than in the underlying saturated zone.

DISCUSSION AND CONCLUSIONS

The sedimentary environment of the southern supratidal evaporite flats surrounding the Ojo de Liebre lagoon is mostly silic-

[3] $\alpha^{18}O_{carbonate\ water} = \dfrac{\delta^{18}O_{carbonate/SMOW}+1,000}{\delta^{18}O_{water/SMOW}+1,000}$

iclastic, and only sparse carbonate deposits (such as calcrete and marine shells of Pleistocene age) crop out at a short distance from the flats.

At the southernmost edge of the evaporite flats, gypsum and dolomite crystallize in sands which are infiltrated with the interstitial solutions. Above the water table the carbonate fraction of the sands and of the gypsum sediments is not dolomite but calcium carbonate. The coincidence of the upper range of dolomitic sediments with the water table clearly points to a genetic relationship between the solutions and dolomitic formation. In these sediments, calcian dolomite is the only carbonate phase present. Furthermore, no conspicuous solid calcium carbonate precursor for dolomite is evidenced in the sediments. It seems unlikely that the rare dolomitized shell fragments, which are too scarcely distributed in the sediment, correspond to such an in situ precursor for dolomite.

The chemical and stable isotope compositions of the interstitial solutions and of the dolomite lead to some major conclusions about the origin and the evolution of the water and ionic species of the brines and about the state of isotopic equilibrium between the solutions and the dolomite:

(1) The interstitital solutions result from the mixing of marine-derived brines with continental waters, as deduced from their ionic concentrations and the $\delta^{18}O$ and δ^2H values of water.
(2) The marine brines, which have seeped laterally at least 15 km from the Ojo de Liebre salt ponds towards the southern supratidal flats, have been strongly modified during their subterranean migration. They have markedly lost SO_4^{2-} ions as a result of extensive gypsum crystallization, and gained Ca^{2+} and Sr^{2+} ions presumably from calcium carbonate dissolution by CO_2-bearing continental waters. Farther to the south, the SO_4^{2-} concentration increases in the interstitial solutions; it is suggested by oxygen and sulfur isotope ratios of aqueous sulfate that SO_4^{2-} was derived from the local dissolution of outcropping Pleistocene gypsum by fresh waters.

As a result, all the ionic species (i.e., Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-) which are involved in the gypsum-dolomite formation, are provided by marine-derived brines and continental waters. Among the chemical factors which control the dolomite authigenesis, the low SO_4^{2-} concentrations of the solutions are probably determinant, as emphasized by some authors (Lippmann, 1973; Baker and Kastner 1981). However, this condition is not sufficient for dolomite formation. Another requirement seems to be the lowering of Ca^{2+} concentration below some critical level (here it is close to 100 millimoles kg^{-1}) by gypsum crystallization so that the solutions have Mg^{2+}/Ca^{2+} molar ratios higher than 3.

Furthermore, the oxygen isotope compositions of the dolomite represent the isotopic equilibrium values for the true environmental conditions (i.e., temperature and $\delta^{18}O$ of water): this argues for the direct crystallization of dolomite from the interstitial solutions.

The relatively low $\delta^{13}C$ values of the dolomite indicate that part of the total dissolved inorganic carbon reservoir of the interstitial solutions is biogenic: it is land-derived and must be provided by groundwaters since few living organisms are present in the evaporite flat itself.

In summary, this example illustrates dolomite precipitation at low temperature within quartz-feldspar sands from saturated interstitial solutions. Dolomite precipitation is governed by the mixing of two solutions of different chemical facies, Mg^{2+}-rich, marine-derived brines and calcium bicarbonate continental waters, further modified by capillary evaporation.

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