

Polyhalite Replacement After Gypsum at Ojo de Liebre Lagoon (Baja California, Mexico): An Early Diagenesis by Mixing of Marine Brines and Continental Waters

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ABSTRACT

The presence of polyhalite in the supratidal evaporite flats around the Ojo de Liebre lagoon was first discovered by Holser (1966), who attributed its origin to the diagenesis of gypsum by interstitial marine brines. A large part of this area is now occupied by artificial salt ponds. However, some remnants of the ancient evaporite flats are still accessible, for example, on the southeast coast of the evaporitic complex, where sedimentological, chemical and isotopic investigations were performed on evaporitic sediments and interstitial solutions. In May 1979, the evaporitic succession was mainly composed of gypsum; a few centimeters below the surface, polyhalite was present in the form of small nodules that were partially replacing former gypsum crystals. In May 1980, this evaporitic succession was drastically modified, since gypsum sediments lying below the water table were totally replaced by polyhalite. We have thus an exact timing for the mineral transformation, which clearly points to some chemical evolution of the solutions permeating the sediments.

During this one-year period, ionic concentrations of in-

terstitial brines have increased from $\times 1.3$ to $\times 18$ with respect to seawater concentrations. Besides, chemical data indicate that SO_4^{2-} concentrations of interstitial solutions are higher than in normal marine brines and progressively increase in a landward direction, thus suggesting gypsum dissolution by groundwaters. That both water and aqueous sulphate of the solutions in this basin have a mixed marine and continental origin is also supported by isotopic analysis (^{18}O and ^2H of water, ^{18}O and ^{34}S of SO_4^{2-}). Thus, it appears that sulphate ions are provided for one part by marine brines, and for the other part by continental waters which have dissolved Pleistocene gypsum present at depth. The replacement of gypsum by polyhalite requires not only high Mg^{2+} and K^+ , but also high SO_4^{2-} concentrations in the solutions (Braitsch, 1971).

These results illustrate a peculiar case where the gypsum diagenesis into polyhalite is promoted by the mixing of concentrated marine brines and sulfate ion-bearing continental waters.

INTRODUCTION

Natural polyhalite ($\text{Ca}_2\text{MgK}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) was first discovered by Holser (1966) in the southeastern part of the evaporite flats around the Ojo de Liebre lagoon (Figure 1). It occurred as either a hard white layer just under the water table or dispersed in the underlying sands. Petrographic observations indicate that it formed by replacement of former gypsum in those sediments permeated with Mg^{2+} and K^+ rich brines (Holser, 1966; Holser *et al.*, 1981).

As described by Holser (1981), the typical evaporitic succession is represented by a surficial halite crust (up to 2 metres in thickness) interbedded with a few layers of gypsum sand and of polyhalite, and alternating layers of black silts and banded gypsum sands up to about 2 metres

thick. These deposits overlie brown silts and sands which contain some marine shells. In these detrital sediments, gypsum is also present, generally at a depth between 4 and 7 metres more rarely near the surface, as large (up to 10 cm) lenticular poikilitic crystals, enclosing sand grains, and commonly concretionary. Such a gypsum crystal habit, similar to the "sand-rose" facies, is also encountered in the southern part of the complex, outcropping as discontinuous layers at the margins of the evaporite flats. Their formation is obviously related to an evaporitic episode, or several episodes, which are tentatively attributed to a low sea level stage at the end of the Pleistocene (i.e., late Sangamonian) (Ortlieb, 1978, 1979a, 1979b; Ortlieb and Pierre, in prep.; Pierre, 1982).

Since 1957, a large part of the natural evaporite flats has been progressively transformed into artificial salt

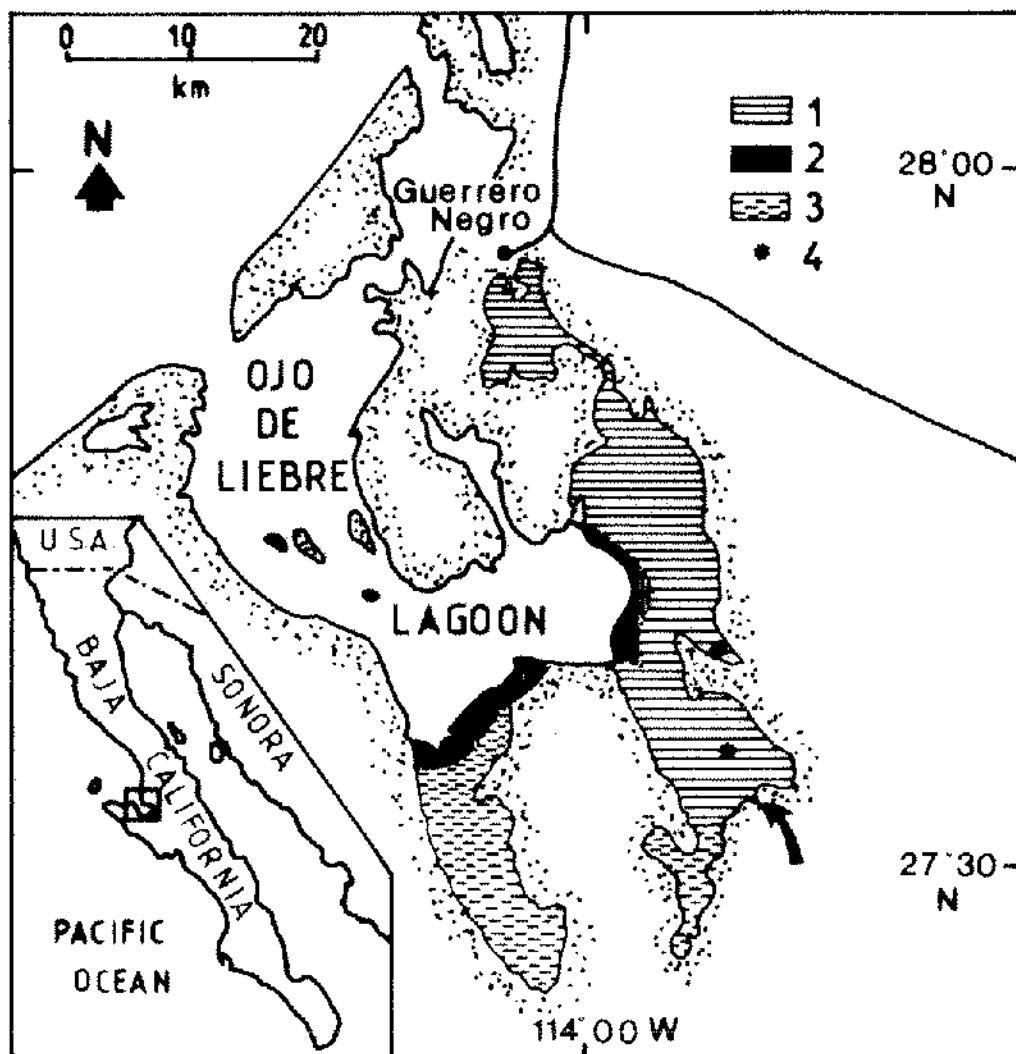


Figure 1. Schematic map of the Ojo de Libre evaporitic complex in Baja California (N.W. Mexico). Present day situation: (1) artificial salt pans; (2) natural algal flats; (3) residual natural evaporite flats; (4) location of the sites of polyhalite occurrence found by Holser in 1960–1961; arrow: location of the site of the newly formed polyhalite.

pans for extensive halite production. As a result, most of the area previously studied by Holser is now flooded, except some remnants of the natural evaporite flats along the eastern and southern margins which are isolated by artificial dikes from the adjacent concentrating ponds (Figure 1).

During a search for polyhalite at Ojo de Libre in 1979, it was finally found in a small salt pond of nearly 1.5 km length and 300 m wide, at the southeastern margin of the evaporitic complex (Figure 1). This basin is surrounded by sand dunes 3 to 5 metres high; it is rimmed along the northwest by a five-metre-high artificial dike, such that marine brines from the nearby concentrating area can only seep laterally through the sediments toward the basin. As a result, the brine level in the main salt pan controls the

water table depth in the connected basin. This explains why the water table in the small pond dropped a few centimetres after the main salt pan dried up between the two sampling periods of May 1979 and May 1980.

Samples of sediments and interstitial brines were collected in small hand dug pits during May 1979, May 1980 and April 1981. As will be discussed below, the sedimentary succession in the central part of the basin was drastically modified between May 1979 and May 1980, because polyhalite partly replaced former gypsum deposits. Chemical and isotopic analyses were therefore conducted on interstitial brines in order to determine the origin of water and ionic species and to follow the geochemical evolution of the solutions that cause the diagenesis of sulphate minerals.

THE SEDIMENTARY SUCCESSION

In May 1979, the evaporitic succession in the central part of the basin was mainly composed of gypsum sediments, with a maximum thickness of 30 cm, overlain by a millimetre-thick halite crust (Figure 2). A few centimetres below the surface, a discontinuous clayey-sandy layer was invaded by millimetre-size gypsum crystals more or less replaced by polyhalite; there, polyhalite appeared to be millimetre-size white nodules, sometimes containing relicts of former gypsum crystals in their core. At depth, in the underlying gypsum sediments, the lenticular gypsum crystals range up to a few centimetres in size. Other minor evaporitic minerals were locally associated with gypsum: glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) occurs as white crystals pseudomorphing gypsum crystals; millimetric white nodules of celestite (SrSO_4) were scattered within the sediment.

The following year, in May 1980, gypsum sediments lying just below the water table in the centre of the pond

were totally replaced by polyhalite. This mineralogical transformation is accompanied by a large volume increase. Standard state molar volumes for gypsum and polyhalite are, respectively, 74.32 cm^3 and 216.54 cm^3 (Berner, 1971). In the case of an equimolar replacement of gypsum by polyhalite, the variation of volume is thus $+190\%$. In this way the detrital sedimentary matrix is expelled; whereas formerly pore spaces existed between gypsum crystals, these pores are largely filled by polyhalite. As a result, this polyhalite layer appears as a homogeneous white soft paste, with locally hard concretions.

During the third visit, in April 1981, the massive polyhalite bed was more hardened and the upper nodular polyhalite layer was thicker than before, reaching nearly 10 cm.

These field observations confirm Holser's conclusions for the diagenetic origin of polyhalite after gypsum. Furthermore, this diagenesis appears very rapid and is obviously related to the chemistry of interstitial solutions.

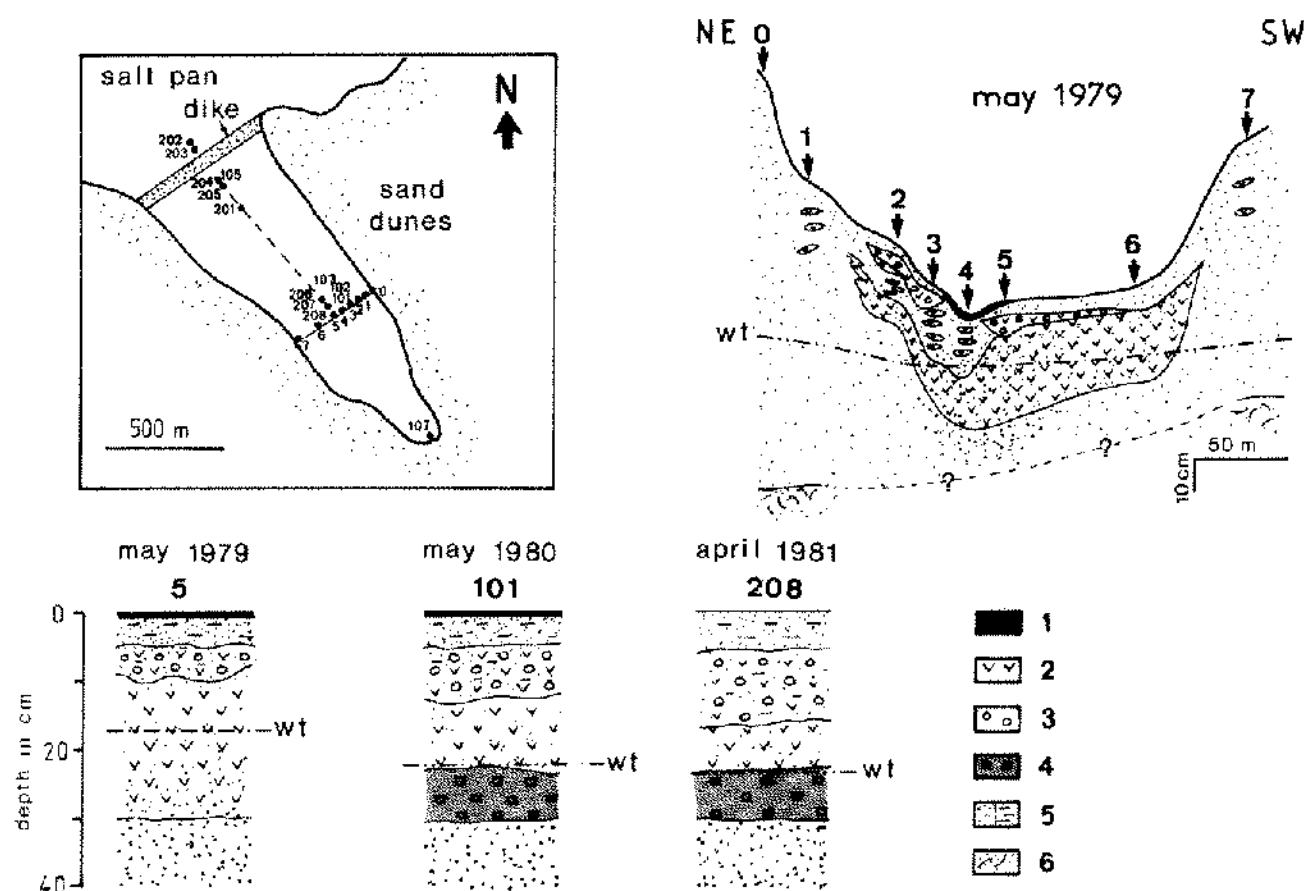


Figure 2. Schematic map of the salt pond located at the southeastern margin of the Ojo de Liebre evaporitic complex, and location of the samples collected in May 1979 (0 to 7), in May 1980 (101 to 107) and in April 1981 (201 to 208). Schematic cross-section of the salt pond along its transverse axis, showing the sedimentary succession in May 1979. Evolution of the evaporitic succession in the central part of the salt pond during May 1979, May 1980 and April 1981. 1: halite crust; 2: gypsum sediments; 3: nodular polyhalite; 4: massive polyhalite; 5: sands and clays; 6: sands with marine shells; w.t.: water table.

THE INTERSTITIAL SOLUTIONS

Chemical Data

Density measurements and variations in ionic concentrations document how brine chemistry affects the early diagenetic patterns.

In the centre of the pond, the density of interstitial solutions was 1.218 in May 1979, 1.226 in May 1980 and 1.229 in April 1981 (Table 1). The concentration factor of these solutions relative to seawater (evaluated from Li^+ concentrations, using $\text{Li}^+ = 28.10^{-6} \text{ m.kg}^{-1}$ water for mean seawater concentration) increased from $\times 13$ in May 1979 to $\times 18$ in May 1980 and to $\times 23$ in April 1981, thus clearly demonstrating that the increase of brines concentration is due to an evaporation effect and not to the dissolution of any salt phase.

The evolution toward higher salt concentration in these solutions is related to the higher degree of evaporation of the inflowing brines from the adjacent main salt pan as a result of its desiccation.

Physico-chemical parameters (density, temperature, pH, EH) were measured *in situ* (Table 1). From the centre toward the edges of the pond, densities decrease rapidly, thus arguing for dilution of the brines by continental waters. The pH values ($6.2 < \text{pH} < 7.8$) increase due to increasing water activities. Temperatures are quite constant ($t = 24 \pm 2^\circ\text{C}$). High redox potential values ($+210 < \text{EH mV} < +410$) indicate strictly oxidizing conditions in the overall interstitial environment in the small pond, while reducing conditions ($\text{EH} = -160 \text{ mV}$) prevail locally in sediments of the main salt pan.

Ionic concentrations of the solutions collected in the small pond are very different from those of marine derived brines. This is well depicted in the triangular plots (Figure 3) where the relative concentrations in $\text{Cl}^- - \text{Mg}^{2+} - \text{SO}_4^{2-}$, $\text{Mg}^{2+} - \text{SO}_4^{2-} - \text{K}^+$, and $\text{Ca}^{2+} - \text{SO}_4^{2-} - \text{Mg}^{2+}$ of the solutions are compared with chemical data for evaporating seawater up to halite saturation (Hermann *et al.*, 1973).

Ionic ratios for the solutions sampled in the main salt pan and at the entrance of the small pond (i.e., just behind the dike) are very similar to those of marine brines saturated with respect to halite.

Traversing the small pond and toward its margins, the interstitial solutions become progressively richer in Cl^- , SO_4^{2-} and Ca^{2+} ions; it thus follows that the observed excesses in the solutions for these ionic species derive from halite and gypsum and dissolution by continental waters s.l. (i.e., mainly groundwaters in such an arid region, although dissolution of the halite crust is due to meteoric waters).

These results show the double origin of ionic species in the solutions of the small pond, which are supplied both by marine brines seeping laterally from the adjacent salt

pan and by continental waters that have dissolved gypsum and halite.

Isotopic Data

Oxygen and hydrogen isotope composition of water. $\delta^{18}\text{O}$ values of water of the interstitial solutions decrease progressively from the centre of the pond to the margins where they become negative ($\delta^{18}\text{O} = -1.2\%$), thus confirming the dilution of the brines by groundwaters inflowing toward the basin. This dilution effect is also detected in the solutions of the adjacent salt pan (Table 1).

The same conclusions follow from $\delta^{18}\text{O} - \delta^2\text{H}$ values of water of these solutions when compared with the isotopic behaviour of seawater during evaporation in the Ojo de Liebre salt pans (Figure 4). This is well depicted in the $\delta^{18}\text{O} - \delta^2\text{H}$ diagram showing, on one hand, that the solutions result from mixing between marine brines and the local meteoric waters and, on the other hand, that these solutions are subject to capillary evaporation in the basin.

Furthermore, oxygen isotopic composition of water of solutions collected in May 1979, May 1980 and April 1981 are rather similar, showing only a slight increase in their degree of evaporation, as indicated by their increase in salt concentrations.

Oxygen and sulphur isotope composition of aqueous sulphate. The $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of aqueous sulphate of the solutions exhibit a wide range of variations throughout the basin ($+8.2 < \delta^{18}\text{O} < +11.7$; $+17.3 < \delta^{34}\text{S} < +19.1$) and diverge considerably from those of normal seawater sulphate ($\delta^{18}\text{O} = +9.5$, Longinelli and Craig, 1967, Lloyd, 1967, 1968; $\delta^{34}\text{S} = +20.0$, Thode *et al.*, 1961).

Because oxidizing conditions in this environment preclude any bacterial sulphate reduction (except in the adjacent salt pan), these isotopic variations may only be related to inorganic processes such as dissolution or crystallization effects.

The δ values of aqueous sulphate were the same in the centre of the basin for both May 1979 (sampling site 5) and May 1980 (sampling site 101). This means that the gypsum-polyhalite transformation does not affect the isotopic composition of the aqueous sulphate pool (i.e., the aqueous-solid sulphate pools have evolved under closed system conditions). It may thus be inferred that the isotopic fractionations during gypsum and polyhalite crystallization are identical and that all the gypsum used by the reaction has been replaced by polyhalite.

The $\delta^{18}\text{O} - \delta^{34}\text{S}$ data plot between two poles is shown in Figure 5. The first with low $\delta^{18}\text{O} - \text{high } \delta^{34}\text{S}$ values, represents the entrance of the basin; the second, with high $\delta^{18}\text{O} - \text{low } \delta^{34}\text{S}$ values, represents the margins of the basin. The distribution within the basin corresponds to a mixing zone between these two different aqueous sulphate pools, one being of marine origin, the other one continental.

TABLE I

Chemical and isotopic data on interstitial solutions collected at the southeastern edge of the Ojo de Liebre evaporitic complex.

Ionic concentrations are expressed as molalities (mole/kg water). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of water which are not in brackets are expressed on an activity scale; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of water which are in brackets 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 ⁻⁶ m	m Na ⁺ /m Cl ⁻	Water		Aqueous SO ₄ ²⁻	
																δ ¹⁸ O SMOW	δ ² H SMOW	δ ¹⁸ O SMOW	δ ² H C.D.
May 1979																			
0	—	1,110	—	—	76	3.0	47.8	17.5	16.9	232.8	7,401	2,806	2.8	32	1.17	892	-0.2 (-0.2)	+11.3	+18.5
1	23.5	1,126	7.5	+210	92	3.0	50.9	27.3	16.1	272.5	2,800	3,202	2.6	33	1.14	928	+0.5 (+0.5)	+10.2	+18.1
2	25	1,160	7.3	+370	102	5.6	66.0	36.0	13.0	350.4	3,643	4,215	2.1	28	1.15	647	+0.9 (+1.0)	+10.1	+17.3
3	26	1,182	7.2	+360	127	4.6	80.7	38.2	11.0	386.5	4,336	4,853	2.0	24	1.12	942	+0.9 (+1.0)	+10.5	+18.3
4	26	1,200	6.7	+370	207	13.8	542.1	147.6	8.8	391.0	4,817	4,458	2.2	17	0.92	348	+0.4 (+1.0)	+9.5	+18.1
5	25.5	1,218	6.2	+410	385	16.2	824.3	230.8	7.5	483.6	5,340	4,335	1.7	14	0.81	329	-0.1 (+0.8)	+10.0	+19.0
6	26.5	1,157	7.1	+330	141	4.9	168.1	55.8	13.6	341.7	3,662	4,005	2.2	25	1.09	747	+0.1 (+0.3)	+9.5	+17.8
7	23	1,100	7.2	+390	106	4.4	105.8	36.3	22.3	189.8	2,225	2,376	2.3	33	1.06	509	-0.6 (-0.6)	+9.7	+17.4
May 1980																			
101 (=5)	23	1,226	6.4	+340	469	18.7	1210.2	284.1	8.2	519.3	5,521	4,382	6.3	36	0.79	285	+0.2 (+1.5)	+10.0	+19.0
102	23.5	1,220	6.5	+285	506	17.6	1072.4	270.1	8.5	475.5	5,529	4,537	6.3	26	0.82	315	+0.1 (+1.3)	+9.1	+19.1
103	23	1,224	6.6	+280	428	17.4	724.5	253.7	8.2	471.1	5,322	3,687	6.1	56	0.69	305	+0.1 (+0.9)	+9.5	+18.9
104 (=0)	23	1,111	8.0	+340	—	2.8	53.8	42.9	17.8	221.7	2,389	2,322	6.7	215	0.97	856	+0.6 (+0.7)	+10.3	+18.1
105	24	1,240	6.3	+400	741	22.3	1973.9	319.0	6.3	571.8	6,231	3,529	10.0	26	0.56	279	-1.1 (+1.0)	+8.2	+19.0
107	24	1,095	7.8	+390	—	3.7	34.9	12.6	12.8	209.0	2,162	2,173	7.1	209	1.00	500	-1.2 (-1.2)	+11.7	+18.3
April 1981																			
208 (=103)	23.5	1,229	6.6	+360	641	19.4	1189.6	250.6	7.4	484.7	5,948	4,508	6.4	51	0.76	307	+0.4 (+1.7)	—	—
207 (=102)	23	1,229	6.6	+380	557	18.9	1167.7	261.8	7.7	479.9	5,772	4,609	6.3	67	0.81	305	-8.4 (-16.8)	—	—
206 (=103)	23	1,226	6.6	+400	637	20.7	1200.9	266.7	7.3	499.4	5,583	4,430	6.3	50	0.79	269	+0.4 (+1.7)	—	—
201	21.5	1,218	6.8	+300	344	18.2	757.4	182.6	9.2	362.3	5,777	5,217	5.2	168	0.90	318	+0.1 (+0.9)	+9.6	+18.4
205 (=106)	24	1,241	6.2	+355	835	24.6	1868.4	290.9	5.5	598.0	6,093	3,458	8.2	26	0.56	247	-0.7 (+1.3)	+10.3	+18.8
204 (=105)	24	1,245	6.2	+405	887	29.6	—	—	—	—	—	—	—	—	—	—	15.9 (-27.5)	—	—
203	23	1,230	6.7	+160	552	19.5	1260.4	269.8	7.3	430.3	5,568	4,410	17.1	176	0.79	286	+1.6 (+2.9)	+11.3	+19.6
202	23	1,239	7.3	+355	640	—	1593.7	344.5	6.5	540.8	6,115	3,991	18.7	144	0.65	—	+1.9 (+3.6)	+12.9	+19.8

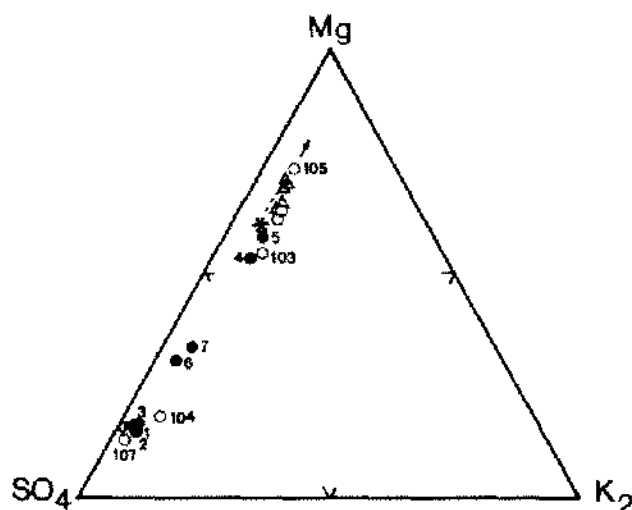
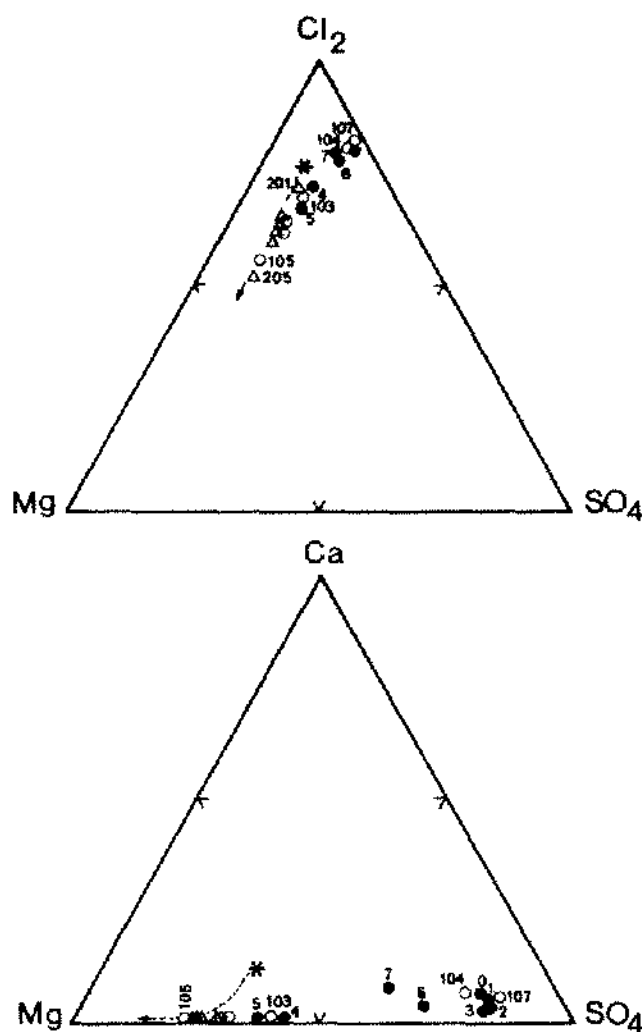


Figure 3. (continued)

Figure 3. Plots of relative ionic concentrations ($\Sigma \text{Cl}_2 + \text{Mg} + \text{SO}_4 = 100$; $\Sigma \text{Ca} + \text{Mg} + \text{SO}_4 = 100$; $\Sigma \text{Mg} + \text{SO}_4 + \text{K}_2 = 100$) of interstitial solutions collected in May 1979 (filled circle), May 1980 (open circle), and April 1981 (triangle). Dotted line gives evolution of seawater (star) during evaporation up to halite saturation as calculated from data of Hermann *et al.* (1973).

These results fit well with the evolution within the basin for both SO_4^{2-} concentrations and $\delta^{18}\text{O}$ values of water of interstitial brines.

For the solutions from the adjacent salt pan, $\delta^{34}\text{S}$ values of the dissolved sulphate account for a single marine origin ($+19.6 < \delta^{34}\text{S} < +19.8$). The $\delta^{18}\text{O}$ enrichment ($+11.3 < \delta^{18}\text{O} < +12.9$) relative to the mean seawater sulphate implies that aqueous sulphur compounds and water are submitted to oxygen isotope transfer during bacterial oxydo-reduction reactions, according to a steady-state mechanism similar to that described in the salt pans of South of France (Fontes and Pierre, 1978; Pierre, 1982; Pierre and Fontes, 1983).

Furthermore, when crossing in the small pond, these solutions are progressively diluted by more and more con-

tinental waters containing allochthonous aqueous sulphate from gypsum dissolution. These SO_4^{2-} ions provided by groundwaters are characterized by $\delta^{34}\text{S}$ values lower than $+17\%$.

Such values were measured for the large poikilitic gypsum crystals attributed to Sangamonian sediments, which were sampled in outcrops at the southern margin of the evaporite flats. Oxygen and sulphur isotope compositions of these gypsum deposits ($+12.0 < \delta^{18}\text{O} < +13.7$; $+15.4 < \delta^{34}\text{S} < +16.4$) are not consistent with a marine origin because $\delta^{34}\text{S}$ values are lower by nearly 5% than Cenozoic marine gypsum (Thode and Monster, 1965; Holser and Kaplan, 1966; Claypool *et al.*, 1980). The strontium content ($250 < \text{Sr ppm} < 380$) is about ten times lower than in gypsum that crystallizes from marine brines (Holser *et al.*, 1981). Therefore, according to the facies "sand-rose," the sparse distribution in the sediments, the ^{34}S and Sr contents, it may be concluded that this gypsum does not have a marine origin but represents typically pedo-genetic products (i.e., gypscrites) developed in a continental environment.

The "sand-rose" gypsum was commonly encountered as part of the artificial dike fill, which implies that this type of gypsum occurs at a shallow depth in the sediments of the basin. The dissolution of these deposits by groundwaters would provide SO_4^{2-} ions, which would explain variations in the *in situ* ^{18}O and ^{34}S of aqueous sulphate of the solutions toward inland margins.

CONCLUSIONS

At the landward edge of the Ojo de Liebre evaporitic complex, the polyhalite replacement after gypsum was observed to occur within a one-year period in a small evaporite pond.

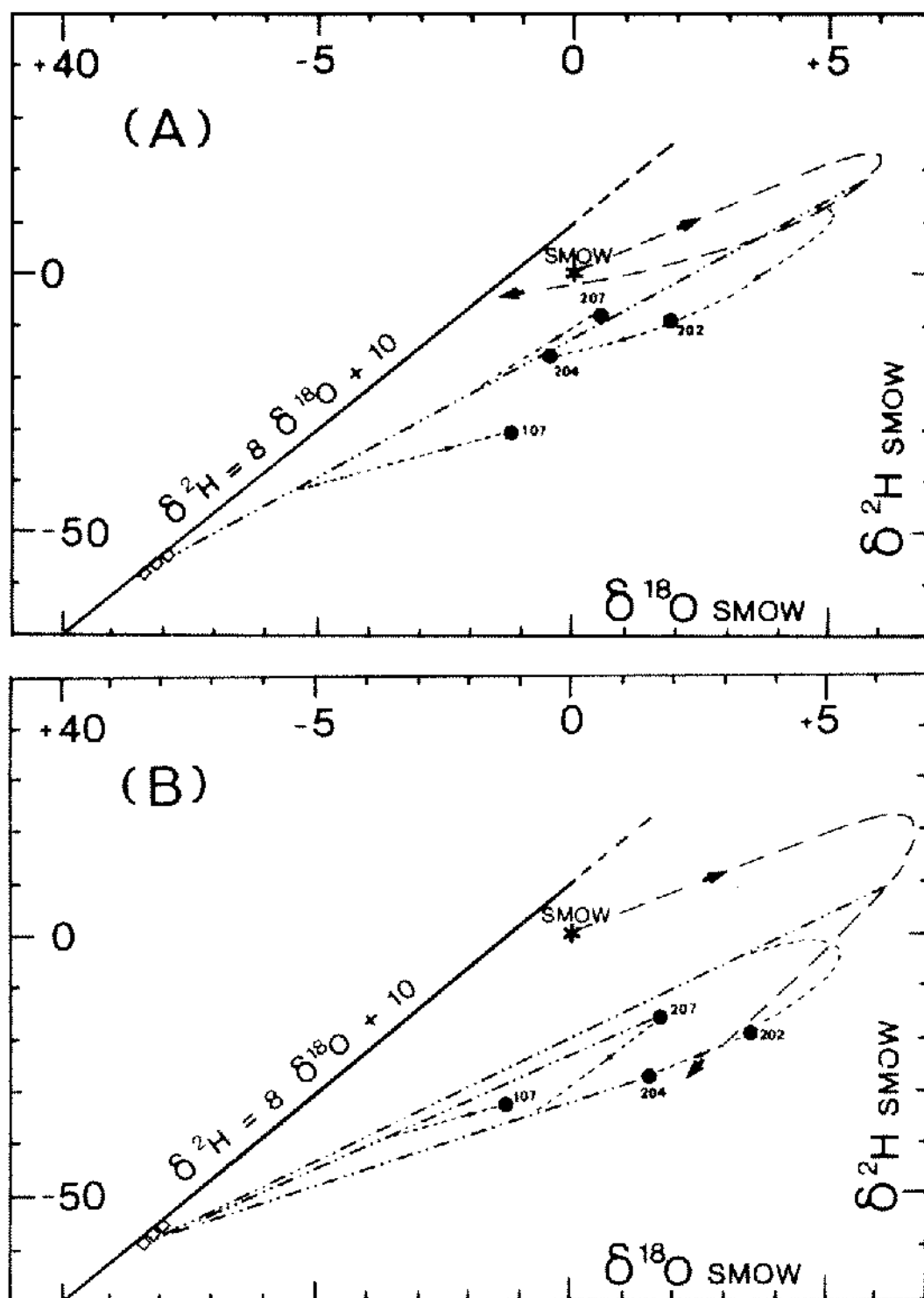


Figure 4. Relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of water of some interstitial solutions collected at the southeastern margin of the Ojo de Liebre evaporitic complex. Diagrams give the δ values expressed on an active scale (A), or a concentration scale (B) following Sofer and Gat corrections for saline solutions (1972, 1975). S.M.O.W. corresponds to the Standard Mean Ocean Water. The large-peaked curve represents the isotopic behavior of seawater during evaporation as measured in marine brines collected in the salt pans of the Ojo de Liebre evaporitic complex (Pierre, 1982). The local meteoric waters (open rhomb), collected in wells about 20 km inland, are located on the general meteoric water line ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$). Effects of evaporation and dilution by meteoric waters in the interstitial solutions are respectively represented by the small-peaked lines and curves and by the dotted-peaked lines.

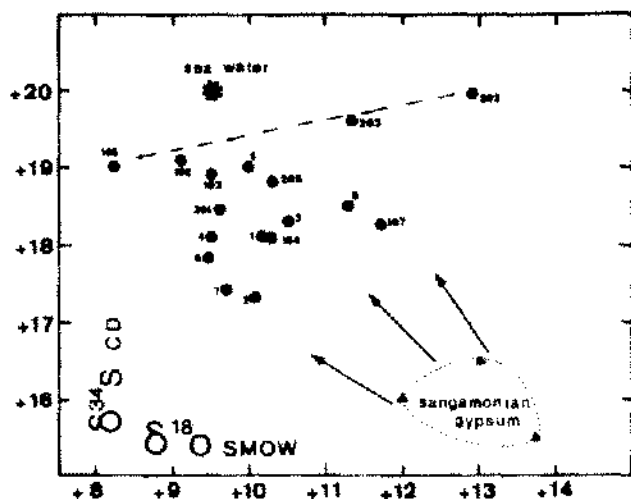


Figure 5. Oxygen and sulphur isotope composition of aqueous sulphate of interstitial solutions collected in the salt pond at the southeastern margin of the Ojo de Liebre evaporitic complex. The δ values of Sangamonian gypsum were measured on samples collected about 6 km southerly at the margin of the evaporite flats. The mean δ values of the seawater aqueous sulphate are reported by comparison.

The geochemical evolution in space and time of the aqueous solution-mineral system was deduced from chemical and isotopic data on interstitial brines. The mixing of $Mg^{2+} - K^{+}$ -rich marine brines with SO_4^{2-} -bearing groundwaters has caused this diagenesis of sulphate minerals in those sediments permeated with the solutions, after a slight modification in the chemistry of inflowing marine brines.

With respect to the phenomenological aspects, these field observations and analytical results are consistent with the theoretical predictions of evaporitic mineral paragenesis based on thermodynamic equilibria between solutions and solid phases at sedimentary temperatures (Braitsch, 1971; Eugster *et al.*, 1980; Harvie and Weare, 1980; Harvie *et al.*, 1980).

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