

GEOCHEMISTRY OF A MEROMICTIC BRINE LAKE

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ABSTRACT

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A meromictic lake on the island of Gran Roque, Venezuela, is both thermally and chemically stratified. The density stratification is largely chlorine-controlled, but concentration of major cations is more variable. A statistical evaluation of chemical analyses serves to indicate that differences in concentration between a central depression and a seaward one suggest seepage of seawater into the latter. Additional cations are supplied by drainage, albeit small, from nearby hills composed of basic intrusives.

INTRODUCTION

The island of Gran Roque lies in the northeastern part of the Los Roques Archipelago, an atoll located about 150 km north of Caracas, Venezuela (Fig. 1). An average monthly rate of evaporation of about 187.5 mm (LEW, 1977) is counteracted by only about 150 mm of rainfall annually, mainly in late November, leaving a deficit in the annual water budget of the island in the neighbourhood of 2.1 m.

A series of lagoons on the east side of the roughly triangular island act as preconcentrators of sea water; in late fall, the Trade Winds and associated storms pile up the ocean waters into these lagoons. On the leeward side of the island lies a closed pond, Lago Pueblo, which then receives some of this preconcentrated ocean water as well as the surface runoff from the nearby hills.

Lago Pueblo is a shallow, roughly circular pond, 200-250 m in diameter, for the most part about 1 m deep in the rainy season, 10-30 cm deep in the summer. Towards the southeastern corner of the pond there are two deeper pools, the larger 4.6 m deep Lago Pueblo Deep near the center and the

smaller, 2.5 m deep Pinta Deep near the seaward edge. The pond is separated from the ocean by a 10-15 m wide road built of calcareous sand (Fig. 2) and has no apparent surface drainage.

The lake floor of Lago Pueblo is composed of mounds and polygons covered with framboidal and bladed gypsum crys-

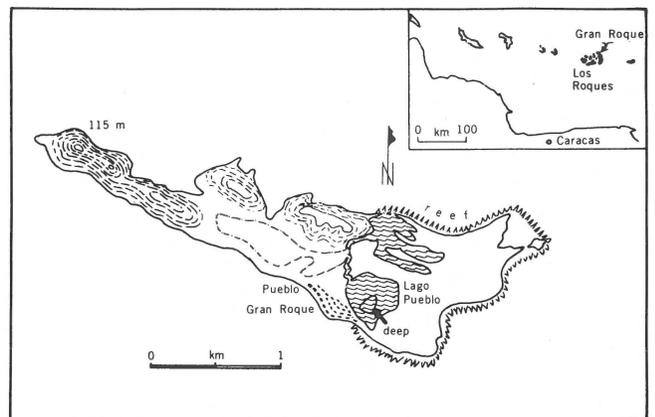


Fig. 1
Location map.

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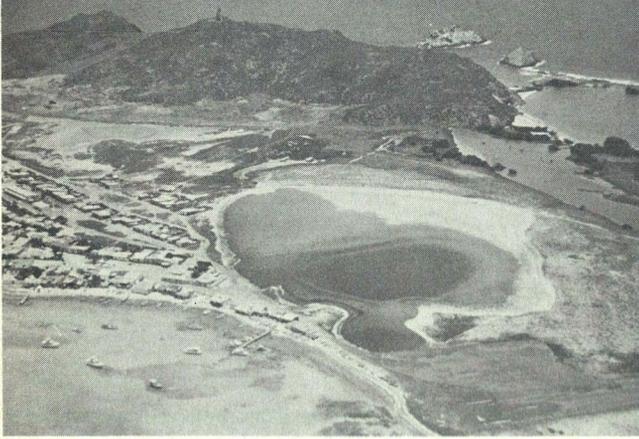


Fig. 2
Lago Pueblo showing Pinta Deep in the foreground and the larger Lago Pueblo Deep. Picture taken in the dry season (picture by M. Lew).

tals that are replacing a stromatolitic, calcareous algal mat (Fig. 3). Rows of gypsum-encrusted pinnacles also rise from the floor of the deeps to within 50 cm of the pond surface. On the north and on the east sides of the lake are two deltas formed by precipitated aragonite and calcite sand. Any clay derived from weathering of the nearby hills flocculates in the feeder streams and does not reach the pond.

The waters of Lago Pueblo are thermally stratified in the winter: the monimolimnion entraps solar radiation to convert the lake into a seasonally heliothermal lake or solar pond (HUDEC & SONNENFELD, 1974; SONNENFELD ET AL., 1977).

The thermal stratification corresponds to a density stratification and this in turn to a chemical stratification. During the rainy season and the concurrent influx of sea water, a very accentuated chemocline and pycnocline form between the epilimnion of density 1.086 - 1.128 and the monimolimnion of density 1.163 - 1.177; less pronounced interfaces occur at greater depths in the two deeps. After the epilimnion has evaporated in May, minor interfaces still appear to persist and bottom concentrations in Lago Pueblo Deep are about sevenfold those of adjacent open ocean water at a density of 1.1793.

Separate sets of water samples were collected by M. Lew at 50 cm intervals in both Lago Pueblo Deep and Pinta Deep in May, June, July, August and December 1976, by the writers in December 1973 and December 1975. They were then analyzed by a Varian-Techtron AA-5 atomic absorption spectrophotometer for the major cations Na, K, Mg and Ca, as well as for the predominant anion Cl.

Field tests proved SO_4 to be an insignificant component for most of the year as gypsum precipitation depletes the incoming supply contained in surface waters. Hydrogen sulfide is present only in traces at depth and in bottom sedi-



Fig. 3
Polygons of algal stromatolites replaced by gypsum crystals. Dry season halite harvesting (photo by M. Lew).

ments of the deeps. Samples of deeper waters precipitate significant quantities of gypsum as soon as sulfuric acid is added, which corroborates the observed lack of SO_4^{2-} even in subsequently aerated bottom water samples. CO_3^{2-} and HCO_3^- are entrapped by the life cycle of varicoloured bacteria and bluegreen algae, which are precipitating aragonite. These anions thus also become only minor components of the stratified waters. Because of the relative permanence of the stratification, overturning and oxygenation of lower brines does not take place.

INTERPRETATION OF ANALYSES

Chemical analyses of the brine samples taken from both the Lago Pueblo Deep and the Pinta Deep were grouped together for a statistical analysis. For this purpose, the samples taken from various depths and those taken at different times were considered as a single population. The linear correlation matrix of the results is given in Table I.

Most major cations and the Cl anion give a good correlation to each other, and to density and refractive indices, significant to the 99.5 percent level.

If individual variables are plotted and the statistical line of best fit is derived, the equation of the line can be used to learn something about the history of Lago Pueblo, and more specifically, about the source of the waters and the elements dissolved therein. Figure 4 shows the relationship between density and the chlorine content of the brine. An excellent correlation is seen, even between the brines isolated in the two deeps. Pinta Deep samples are given as solid squares, those of the Lago Pueblo Deep as crosses.

The good correlation indicates that the density is largely chlorine-controlled. This is further corroborated when the

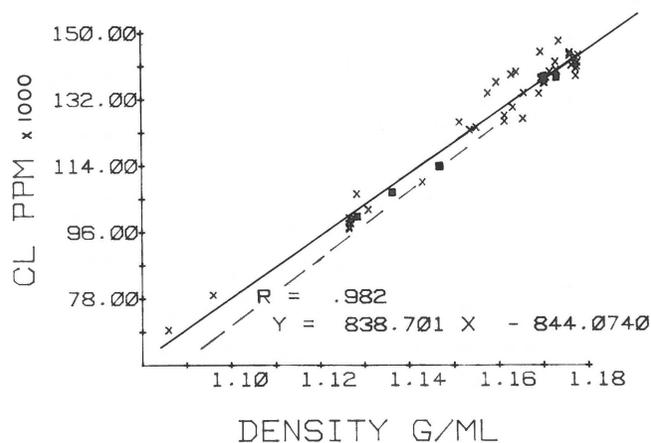


Fig. 4
Relationship of density to chlorine content. Squares: Pinta Deep; crosses: Lago Pueblo Deep; solid line: Lago Pueblo waters; dashed line: concentrated Los Roques sea-water.

correlation of density versus chlorinity of concentrated sea water is plotted on the same graph (dashed line). The slopes of the lines are subparallel; the lower intercept of the Lago Pueblo line simply indicates that other cations and/or anions also contribute to the density of the brine.

The density and refractive index also show good correspondence (Fig. 5). A line giving the same relationship for seawater is shown for comparison (dashed line). It again corroborates the observation that these are NaCl brines derived for the most part from sea water. The discrepancy between the two lines is again due to the presence of other cations and anions.

A much poorer relationship is seen between sodium content and density (Fig. 6). The scatter of points can be attributed to the addition of sodium from sources other than sea water. This is further illustrated by comparing the density-versus-sodium line for sea water (dashed line).

Table I
Correlation matrix, Lago Pueblo waters.

	Density	R.I.	Cl	Mg	Na	K
Density	1.0					
R.I.	0.99070	1.0				
Cl	0.98023	0.98986	1.0			
Mg	0.70180	0.68823	0.72018	1.0		
Na	0.79296	0.79387	0.82784	0.62729	1.0	
K	0.95414	0.95856	0.96841	0.67260	0.77373	1.0

No. of samples correlated 46

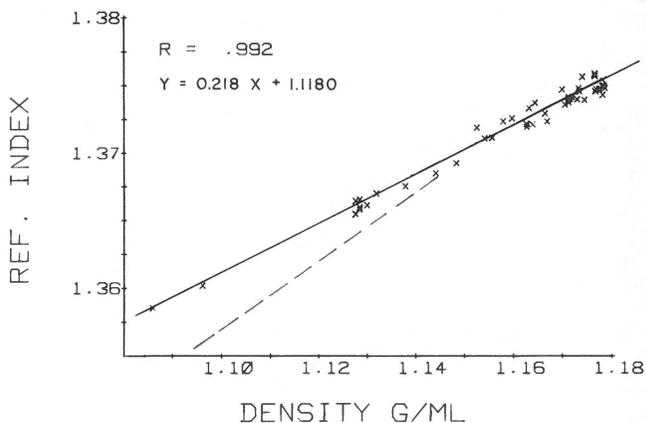


Fig. 5
Relationship of density to refractive index. Solid line: Lago Pueblo waters; dashed line: sodium chloride solution.

When we compare the relationship of combined major cations (Na, K, Mg, Ca) and dominant anion (Cl) to density (Fig. 7), the correlation is not so good, although still significant. The same can be seen in the relationship between refractive index and the sum of cations and anions (Fig. 8). The scatter of points is due to the variability in the cation concentration. Figure 9 gives the relationship between the conservative cations Mg, Na and K and density. As can be seen, the correlation is degraded further (i.e. the correlation coefficient is even lower). Figure 10 relates the major conservative cation content to the dominant anion. The results are represented separately for the large Lago Pueblo Deep (shown as crosses) and the smaller Pinta Deep (given as open squares). Although statistically there is no significant dif-

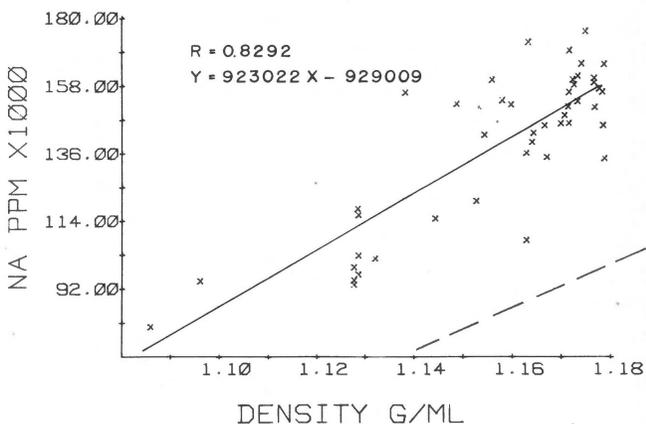


Fig. 6
Relationship of sodium content to density. Solid line: Lago Pueblo waters; dashed line: concentrated sea water.

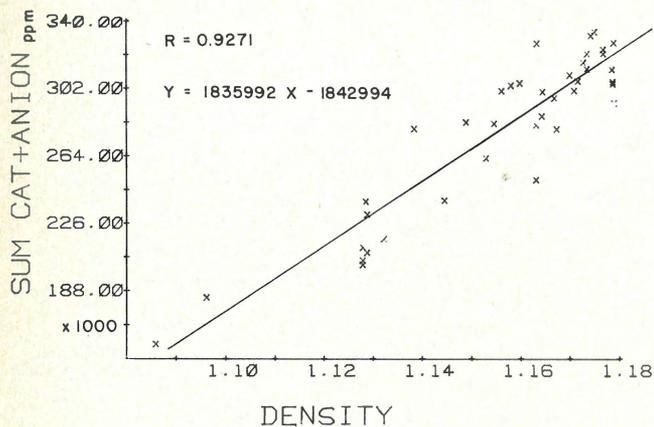


Fig. 7 Relationship of Na, K, Mg, Ca and Cl to density, Lago Pueblo waters.

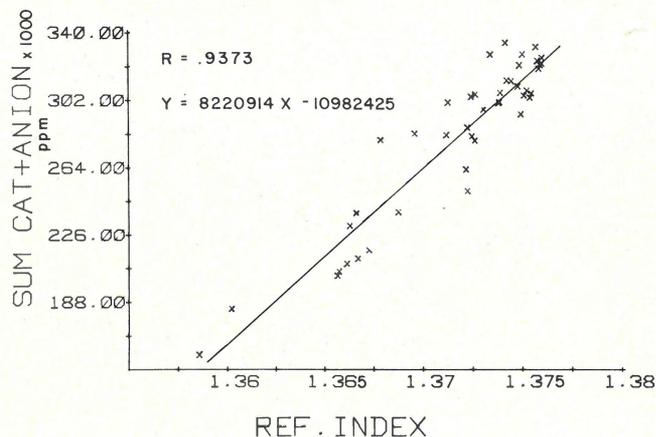


Fig. 8 Relationship of Na, K, Mg, Ca and Cl to refractive index, Lago Pueblo waters.

ference between the two lines, the graph nevertheless suggests that the Pinta Deep has a lower Cl content per given major cation content. This indicates that seepage of sea water into the Pinta Deep dilutes the abnormally high cation content.

Figure 11 shows the relationship between the Cl₁ and Na content of Lago Pueblo. A considerable scatter is seen, indicating either selective removal or addition of either of the variables. Comparing the line of best fit obtained to the line of best fit expected for normal concentration of Los Roques sea water (dashed line) it is evident that there is appreciable addition of sodium from other sources to the system.

SOURCE OF WATER AND OF MAJOR ELEMENTS

Sea water is clearly the major source of water for Lago Pueblo. However, analysis of the waters by 'unconcentrating' them indicates that the Lago Pueblo waters are enriched in the major cations relative to sea water. The 'unconcentration' is best accomplished by assigning the density and the chlorine content of normal sea water to the equation of the line of best fit, and determining the equivalent 'sea water values' for the cations in Lago Pueblo waters. Table II gives the results. The first column gives the assigned sea water

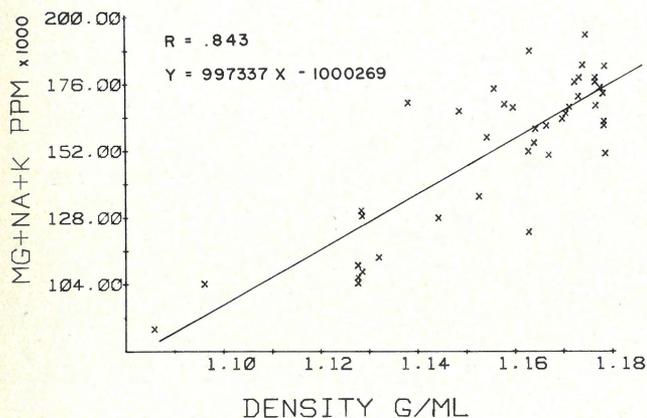


Fig. 9 Relationship between conservative elements Mg, Na, K and density, Lago Pueblo waters.

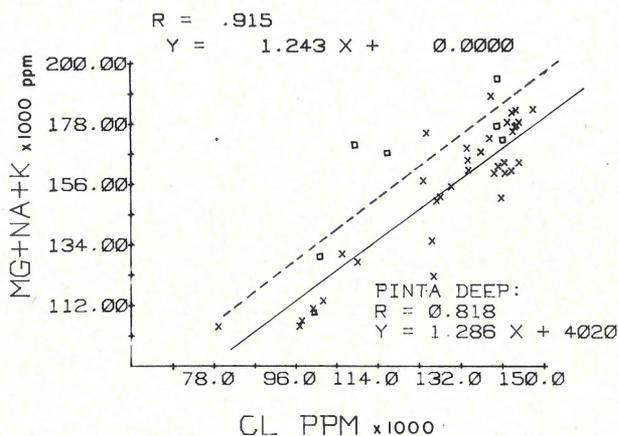


Fig. 10 Relationship between conservative elements Mg, Na, K and dominant anion Cl. Squares: Pinta Deep; crosses: Lago Pueblo Deep; solid line: Lago Pueblo waters; dashed line: concentrated sea water.

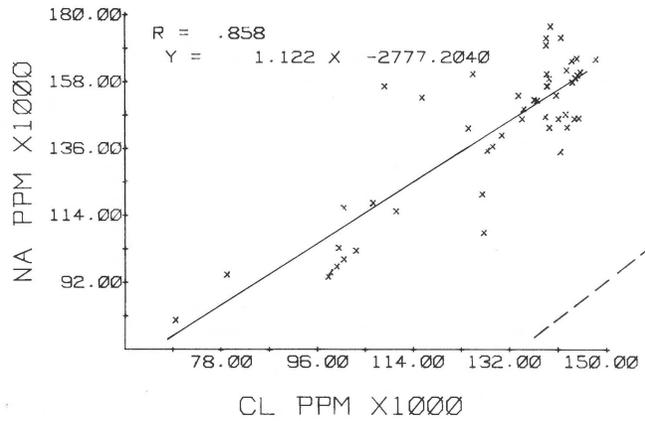


Fig. 11
Relationship between Na and Cl content. Solid line: Lago Pueblo waters; dashed line: concentrated sea water.

Table II
Comparison of Lago Pueblo water to sea water.

Variables	Seawater values	Equivalent calculated Lago Pueblo values
1. Density	1.0264	1.0307
Cl ppm	20,338	16,768
2. Density	1.0264	1.0224
Sum of Cations and Anions	34,190	41,468
3. Density	1.0264	1.0188
Na ppm	11,327	18,381
4. Density	1.0264	1.0164
Mg + Na + K	13,392	23,398
5. Cl ppm	20,338	12,570
Na ppm	11,327	20,042
6. Cl ppm	20,338	10,395
Mg + Na + K	13,392	25,393

values which were obtained by the analysis of sea water near Gran Roque island. The second column variable is the calculated 'unconcentrated' content. By comparing the calculated and the actual contents, it is possible to determine if the actual cation contents were derived from sea water alone, or were contributed from other sources.

Case 1 of Table II compares the original composition in respect to chlorine as a function of density. The calculated composition shows that some Cl has been removed from the Lago Pueblo waters. The removal can be accounted for by the annual harvesting of halite by the local inhabitants.

Comparing the total analyzed cation and anion content to density (case 2) shows that the cations are in excess of that expected by normal sea-water concentration. This is even better illustrated by cases 3 and 4: here it is seen that the cations are almost twice as abundant as in sea water. Cases 5 and 6 further corroborate this by indicating the concentration of cations almost twice as high for the equivalent chlorine content.

The above analysis clearly shows that the additional cations are derived from surface water and from groundwater runoff from the nearby hills. The bedrock there consists of metadiabase and metalamprophyre; their weathering products can be considered to be the supply of the additional cations.

CONCLUSION

A statistical analysis of water samples from the heliothermal pond Lago Pueblo on the island of Gran Roque shows that mere evaporative concentration of a surface sea-water inflow does not account for the ratios of cations dissolved in the hypersaline brine. A substantial amount is contributed by surface runoff from the nearby hills or through groundwater from the same source entering after the wet season near the northern delta. The Pinta Deep, on the other hand, suffers in the dry season from sea water incursion through porous strata separating it from the ocean. The Pinta Deep waters are thus slightly diluted in comparison to the Lago Pueblo Deep waters of corresponding depth.

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