

Assessing Past Environmental Changes through Sediment Records in a Hypersaline Lagoon*

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Carbon and oxygen isotopes, organic matter elemental composition, and mineralogy of carbonates were used as proxies to investigate environmental changes recorded in the carbonate-rich sediment of the hypersaline lagoon "Vermelha", Rio de Janeiro. Isotopic and other data suggest that two striking shifts in environmental conditions occurred about 1900 and 3200 years ago. Carbonates $\delta(^{18}\text{O})$ and $\delta(^{13}\text{C})$ were found in the range of +1.5 ‰ to +4.5 ‰ (PDB), and –2 ‰ to –11 ‰ (PDB), respectively. In organic matter, $\delta(^{13}\text{C})$ ranged from –22 ‰ to –15 ‰ (PDB). Calcites and dolomites are present in the studied core; their relative abundance seems to be related to the observed changes. Calcites are enriched up 38 % in MgCO_3 (mole fraction, x). As distinct from calcites with lower magnesium contents, Mg-calcite with $x(\text{Mg}) > 20$ % shows an additional peak at 0.2929 nm in the X-ray diffractogram. Samples that contain Mg-calcite or 100 % dolomite show similar $\delta(^{13}\text{C})$ values. There are strong indications for an early formation of dolomite already in the microbial mat region. ^{18}O and ^2H determinations in lagoon water confirm evaporation as the water balance controlling process.

Keywords
carbon isotopes
oxygen isotopes
climate change
Southeastern Brazil
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INTRODUCTION

Carbon and oxygen stable isotopes and elemental composition of organic matter have been frequently used as environmental proxies.^{1–6} Sedimentary records of $\delta(^{18}\text{O})$ in lakes are usually associated with changes in the temperature or precipitation/evaporation ratio while those in carbon have been applied to demonstrate changes in carbon, nutrient cycling and productivity.¹

Hypersaline environments are found in various parts of the world, usually in tropical arid or semi-arid climates. They are associated with conditions such as a low precipitation/evaporation ratio and the presence of abun-

dant carbonate precipitation. Extensive studies have been performed by several authors in some of these environments concerning the deposition and diagenesis of carbonate minerals.^{7–11} A number of factors may determine the occurrence of different carbonate polymorphs. For instance, Mg-calcite/dolomite mixtures in sediments from Coorong (Australia) were probably formed during periods of high evaporation, while aragonite precipitation would occur over periods of lower salinity.¹² The mechanism of dolomite formation at room temperature is still unclear and, although apparently most dolomites have been identified as diagenetic,¹³ some authors have suggested that primary precipitation of dolomite may

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have taken place.¹⁴ Environments with decaying organic matter, generally rich in CO₂, ammonia and H₂S, seem to favour dolomite formation of possibly primary origin.¹⁵ As a result of the variety of dolomites existing in nature, the various occurrences cannot be explained by a single model. Studies of recent dolomite in hypersaline environments elucidate some aspects of dolomitization; however, even in these cases the individual chemical characteristics of aquatic systems do not allow generalizations. It has been proposed that sulphate-reducing bacteria can mediate dolomite nucleation, playing an active role in the formation of this mineral in nature.¹⁶

Carbon and oxygen isotopic composition of carbonates have been used as an important tool in the search for understanding the processes that led to the deposition or predominance of a particular carbonate mineral. In addition, the isotopic record gives information on the changes occurring in the environment over the geological time, which may be associated with climatic and/or biogeochemical changes.

Epstein *et al.*¹⁷ using the ¹⁸O fractionation factors given by Sharma and Clayton¹⁸ for well ordered dolomites observed that dolomites precipitated from aqueous environments should be enriched in ¹⁸O (+6 ‰ to +10 ‰ PDB) compared to cogenetic calcite and aragonites. Studying recent calcites and dolomites from various localities, O'Neil and Epstein¹⁹ observed no significant differences in their δ(¹⁸O) values. Degens²⁰ concluded from this and other data that all sedimentary dolomites, regardless of age, environment and pathway of formation, result from the metasomatism of calcite, and that aragonite should be transformed into calcite before dolomitization.

Extrapolating to 35 °C precipitation results obtained at high temperature, Matthews and Katz²¹ found δ(¹⁸O) differences of 2.8 ‰. For dolomites from Sabkhas, Mckenzie²² found maximal δ(¹⁸O) differences of 3.2 ‰.

¹⁸O data also provide information on the climatic conditions under which a certain carbonate deposit was formed. Positive δ(¹⁸O) values are associated with carbonates precipitated from evaporated water bodies. Carbonate δ(¹⁸O) data may also contain information on the degree of re-crystallization of the mineral.²³ There are evidences that isotopic records may be influenced by interlinked environmental processes rather than by a single factor.¹

Primary carbonates deposited under marine conditions as well as secondary carbonates formed by re-crystallization of primary inorganic carbonate minerals have δ(¹³C) between +4 ‰ and -4 ‰.²⁴ However, in stagnant environments precipitation can proceed under the influence of biogenic CO₂, which is depleted in ¹³C (δ(¹³C) -10 ‰ to -55 ‰).^{11,25} During diagenesis, marine carbonate can progressively become lighter due to exchange with CO₂.^{1,26}

In the present work, chemical, mineralogical and isotopic compositions recorded in Lagoa Vermelha sediments are used to understand the mechanisms of carbonate precipitation in this hypersaline lagoon and to obtain information on possibly interlinked environmental changes.

Physical quantities used in the paper are defined as usual. Isotope enrichment of an isotope, $\delta(^yE) = (R_s(^yE) / R_{ref}(^yE)) - 1$; isotope ratio, $R(^yE) = N(^yE) / N(^xE)$, where $y > x$. R_s denotes isotope ratio of the sample, R_{ref} that of the reference material (PDB, Pee Dee Belemnite standard; SMOW, standard mean ocean water).

Deposition Environment

The site examined, named "Lagoa Vermelha" (Red Lagoon), is a hypersaline water body located east of the city of Rio de Janeiro (Figure 1). Lagoa Vermelha is part of a lagoon system formed over the last 4500 years.²⁷ The lagoon has an area of 2.4 km² and a maximum water depth of about 1.5 m. It is separated from the Atlantic Ocean by a 350 m wide sand bar which is 4 m above sea level. The scarce vegetation in the area is typical of dunes.

The average air temperature in the region varies from 19 to 31 °C and the annual rainfall (mean) is close to 900 mm while evaporation reaches 1400 mm.²⁸ The northeast winds prevailing in this region with an average speed of 6 m/s are in part responsible for the occurrence of seasonal coastal upwelling and for the observed semi-arid climate.

Concentrations of major ions in the lagoon waters are very close to those of the local coastal waters (waters

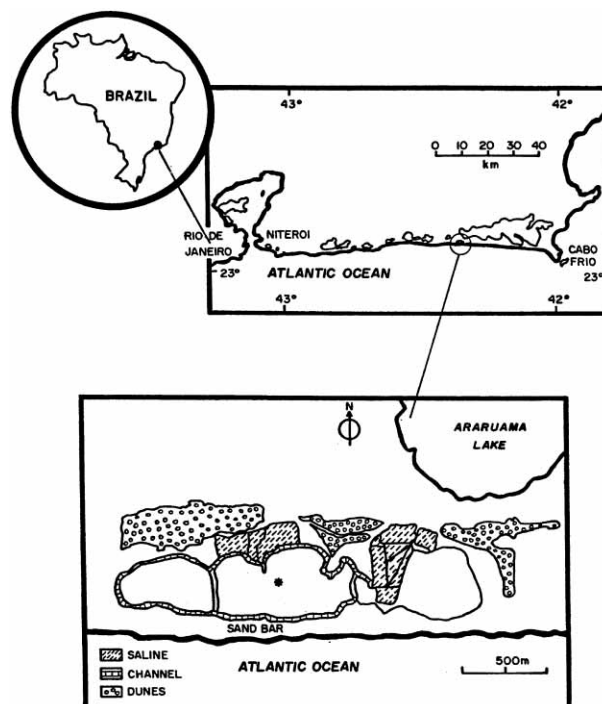


Figure 1. Localization and topography of Lagoa Vermelha. (* represents the sampling site).

from the Brazil Current or, during upwelling events, a mixture of these warm water with colder and less saline central waters from the South Atlantic); however, some depletion of calcium is apparent.^{29,30}

The bottom of the lagoon is covered by a 2 to 8 cm thick laminated microbial mat. Primary production is restricted to the mat because the overlying waters are very poor in nutrients. The mat is composed of three layers of microorganisms: a dark green layer with the predominance of *Aphanotheca* sp., a whitish layer where *Oscillatoria* sp., prevails, and a dark red layer composed of *Microcoleus* sp., *Lyngbya* sp., *Beggiatoa* sp., and *Chromatium* sp.³⁰ During dry periods, due to excess evaporation, the water volume in the lagoon is reduced, exposing to the air a strip of algae mat up to 6 m wide at the rim of the lagoon.

Sediments below the mat are rich in carbonates and laminated.³¹ pH and E_h of interstitial waters are around 6.5 and -0.1 V, respectively, while bacterial reduction causes a remarkable drop in sulphate/chlorinity ratio (40 to 50 %) below the sediment surface.^{29,30}

EXPERIMENTAL

A 1 m sediment drill-core was extracted from the central location shown in Figure 1 by intruding a PVC tube of 8.0 cm diameter into the sediment and pressing it down into the ground as deep as possible. Subsequently, the sediment core was divided into segments of about 2 cm each after discarding the fluid surface layer composed of decaying microbial mat material. Special care was taken not to mix individual layers during the core segmentation.

Mineralogical Analysis

Sediment water content was obtained by the weight difference after drying the samples at 70 °C.

Samples were pulverized and homogenized in an agate ball mill up to the grain size smaller than 100 mesh and thereafter analyzed in a Philips PW 1320/00 X-ray diffractometer. The instrumental parameters were: Cu tube with monochromator, flow counter detector, goniometer rate 0.5°, 2 θ /min., and 2 θ interval 25 to 50°.

The relative mineralogical composition of the samples (as shown in Table II), was obtained by measuring the heights of the more intensive reflection peaks of carbonates. The content of magnesium in the carbonates was evaluated from the shift of the most intensive calcite peak ($d_{104} = 0.3036$ nm, $2\theta = 29.4$).³²

Chemical Analysis

The following chemical determinations were performed on all sediment samples as well as on samples from the microbial mat: organic carbon and nitrogen, calcium and magnesium, total phosphate and carbonate concentrations.

Organic carbon was determined by combustion using a WR-12 LECO instrument after eliminating the carbonates

by treatment with HCl. For the content of organic nitrogen, a CHN analyzer 240 Perkin Elmer was used.

Calcium and magnesium were determined by titration with EDTA (Titriplex III, Merck) after extraction from the sediments with hot HCl (vol. ratio, $\Psi_{\text{HCl,H}_2\text{O}} = 1:3$) for one hour.

Total phosphorus was measured spectrophotometrically using molybdenum blue and the flow-injection system. For this analysis, dried samples were calcinated at 500 °C and then heated to dryness in Teflon crucibles with H₂O₂, HF and HClO₄ and dissolved in 1 M HCl.

The "Karbonat-Bombe" was utilized to determine the carbonate content.³³

All chemicals so far used in the analytical procedures cited above were of Merck *p.a.* grade.

Isotopic Analyses

The following isotopic analyses were performed: the D/H ratio in surface waters (local coastal waters, lagoon water and brackish water from small pools spread around the inland margin of the lagoon), ¹⁸O/¹⁶O in surface waters (the same samples as for D/H determination), ¹⁸O/¹⁶O and ¹³C/¹²C in carbonates and ¹³C/¹²C in organic matter.

For the D/H determination, the procedure was basically that described by Friedman,³⁴ and a Varian Mat-GD-150 spectrometer was used.

The methodology applied for oxygen isotopic analysis in water was that developed by Epstein and Mayeda,³⁵ with some modifications recommended by Matsui.³⁶ A Finnigan Mat Delta E spectrometer was utilized for all oxygen and carbon isotopic determinations. For water, all $\delta(^2\text{H})$ and $\delta(^{18}\text{O})$ results are given in reference to SMOW (Standard Mean Ocean Water).

The $\delta(^{18}\text{O})$ determinations in the carbonates followed the procedures of McCrea.³⁷ Samples were treated with 100 % phosphoric acid and released CO₂ was collected, as described by Epstein *et al.*¹⁷ after 1 hour and 72 hours of reaction, respectively. The values of ¹⁸O obtained for the 72 hours reaction were not corrected for different fractionation factors following the arguments presented by Land.⁹

The ¹³C content in carbonates was determined using the same procedure as described above for oxygen. The $\delta(^{13}\text{C})$ in the organic matter was obtained after eliminating the carbonates with diluted HCl. The $\delta(^{18}\text{O})$ and $\delta(^{13}\text{C})$ results for carbonate and organic matter are referred to PDB. In all cases, analytical precision was at least 0.01 ‰. Isotopic data are reported using the conventional notation.

RESULTS AND DISCUSSION

The results obtained are shown in Tables I and II and in Figures 2 through 9.

Mineralogical Composition

The macroscopic description of the core is displayed in Figure 2. The first 5 cm of sediment below the microbial

mat contain abundant shells of various sizes. Peloidal layers are intercalated by laminated layers of different thickness. Below 40 cm appears an interlayer bedding lenses predominantly containing dark organic material, followed by 4 cm of massive carbonate concretions. In a deeper portion of the core, an interlayer with concretions is again dominant. In general, from the surface to a 50-cm depth, sediments contain abundant relics of ostracods. Yellow crystals found in the lower core segment were identified as orthorhombic sulphur. Sediments are very fine grained with absolute predominance of micritic material.

Mineralogical analysis of the sediments revealed a change in the mineral assembly that coincides with pronounced changes in isotopic shifts. Figures 3 and 4 show the X-ray diffractograms for some samples. Mg-calcites, which were encountered in the majority of the segments, are extremely rich in magnesium and are characterized by two distinct reflections.

Two "classes" of magnesium rich calcite were detected. In general, magnesium fractions ranged from 7 to 38 % (mole fraction, x). For all samples with $x(\text{Mg})$ higher than 20 % an additional peak at 0.2929 nm shows up, which is completely missing for Mg-calcite, with Mg fraction below 20 %.

In further discussions, calcite with $x(\text{Mg}) \leq 20\%$ is referred to as HMgC_1 and with $x(\text{Mg}) > 20\%$ as HMgC_2 . HMgC_2 is not a dolomite phase. It differs from dolomites because the main reflection appears in the range given

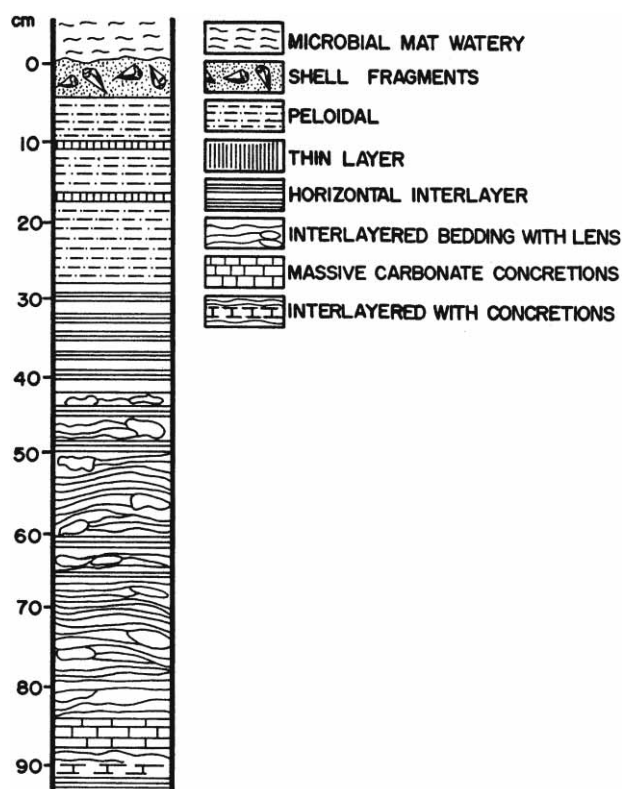


Figure 2. Macroscopic description of the core.

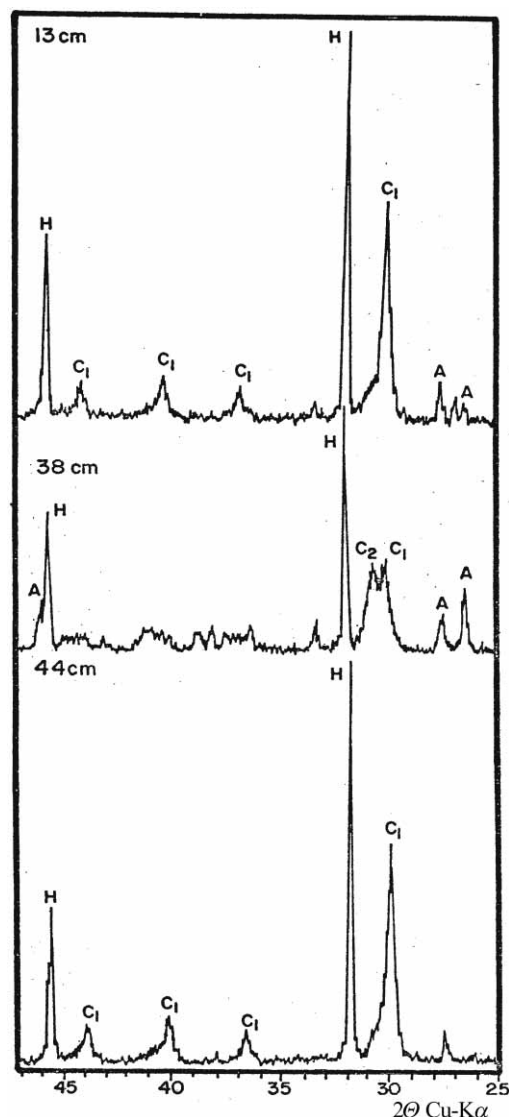


Figure 3. X-ray diffractograms for samples from 13, 38, and 44 cm depths. A = aragonite; H = halite (internal standard); C_1 = HMgC_1 (MgCO_3 mole fraction, $x < 20\%$)

above, and it does not show a defined 210 peak or any of the other dolomite reflections, but an asymmetric band in the range of 0.2252 and 0.2199 nm. The minerals that produced the 210 reflection will be referred to as dolomite.

Dolomite enriched in calcium ($x(\text{CaCO}_3) < 60\%$) was observed at 5 cm depth and in all samples below 56 cm depth. Those of higher ordering degree are at 5 and 90 cm (0.45), while for others the ordering degree (defined by Goldsmith and Graaf)³⁸ varies between 0.22 and 0.36 and is not related to the sediment depth (or age).

Aragonite is present in the samples from 13 to 42 cm depths. The observation of the samples under the microscope demonstrates abundant micritic aragonite needles, probably formed via chemical precipitation directly from the water column or at the sediment/water interface. The XRD from the 13-cm depth sample showed

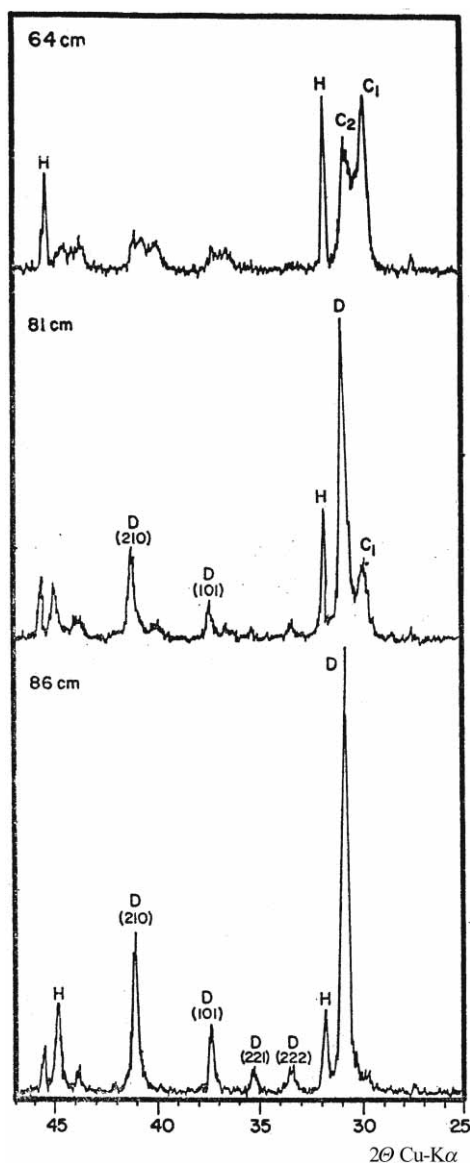


Figure 4. X-ray diffractograms for samples from 64, 81, and 86 cm depths. A = aragonite; H = halite (internal standard); C₁ = HMgC₁; C₂ = HMgC₂; D = dolomite.

that poorly crystallized aragonite, most probably derived from shells (*e.g.*, gastropods), was also present.

Below 56 cm depth the content of HMgC₁ as well as MgCO₃ fraction decreases, while dolomite appears with increasing frequency. There are two ways in which the observed change in mineralogy may have occurred: (i) the more stable solid dolomite was formed from the less stable HMgC₂ and perhaps from HMgC₁, and (ii) different environmental conditions at the time of deposition favoured the predominant precipitation of a certain mineral. Electron microscope scanning of some samples shows evidence of HMgC₁₋₂ dissolution and continuation of the recrystallization process. The present aragonite crystals apparently were not subjected to dissolution and represent the original precipitation form, while HMgC₂ and to some extent HMgC₁ underwent dolomitization.

A thin layer of a wet white-yellowish material deposited at the margin of the lagoon was sampled and analyzed for mineralogical composition. Dolomite with an ordering degree of 0.29 and HMgC₂ ($x = 22\%$) were detected. Both minerals in this recent material must have been formed due to extensive evaporation in these shallow areas, and in this case dolomite may have been precipitated directly from solution.

Isotopic Records

$\delta(^2\text{H})$ and $\delta(^{18}\text{O})$ data obtained for surface waters ($\delta(^{18}\text{O})$: small ponds = +0.41 ‰, coastal waters = +0.38 ‰, lagoon water = +3.5 ‰; $\delta(\text{D})$: small ponds = -0.41 ‰, coastal waters = +0.38 ‰, lagoon water = +0.21 ‰) indicated a linear isotopic enrichment leading to the expression:

$$\delta(^2\text{H}) = 4.7 \delta(^{18}\text{O}) + 4.4 \quad (1)$$

The slope of 4.7 that indicates evaporation as the dominant process controlling the isotope fractionation in the lagoon is in good agreement with the value reported by Gonfiantini *et al.*³⁹ and Lloyd.⁴⁰

All sediment samples produced CO₂ after 1 hour and 72 hours of reaction, despite differences in their mineralogical compositions. The obtained $\Delta\delta(^{13}\text{C})$ and $\Delta\delta(^{18}\text{O})$ values (difference between the values for 1 and 72 hours extraction) are small compared to the total shift along the core and to the $\Delta\delta$ values reported in the literature (average $\Delta\delta(^{13}\text{C}) = 0.32 \pm 1.14\%$ and $\Delta\delta(^{18}\text{O}) = 0.8 \pm 0.6\%$). Exceptions are the $\Delta\delta(^{13}\text{C})$ and $\Delta\delta(^{18}\text{O})$ equal to -4.2 ‰ and 1.7 ‰, respectively, found for the sample from 5 cm depth. These results show that CO₂ sampling at several reaction times yielded no information on the possible differences between carbonate minerals. The information obtained from stepwise CO₂ extraction has to be considered as resulting from simultaneous dissolution. A good example to the point is given in the work by Walters *et al.*⁴¹ showing that the collected CO₂ (from calcite as well as from dolomite) becomes progressively enriched in ¹⁸O as the reaction progresses, independently of the grain size, mineral or chemical composition. Indeed, the $\delta(^{18}\text{O})$ values obtained in the present work are higher for the 72 hours leaching. This behaviour is well understandable as a Rayleigh fractionation of isotopes occurring at the liquid/solid interface during the process of dissolution. Dissolution is a slow process compared to the establishment of the two-phase equilibrium necessary for the Rayleigh fractionation. Any interpretation of the genesis of carbonate minerals based on data derived from the stepwise CO₂ extraction has to be taken carefully since grain size may critically affect the intended separation.¹

The results obtained from the 1 hour or 72 hour leaching show no significant differences. The slopes of the isotopic shifts along the core (calculated by linear regres-

sion) are: (i) for 10–93 cm depth: 0.034 ‰ cm^{-1} , $\delta(^{18}\text{O})_{1\text{h}}$ and 0.033 ‰ cm^{-1} , $\delta(^{18}\text{O})_{72\text{h}}$; (ii) for 10–44 cm depth: 0.031 ‰ cm^{-1} , $\delta(^{13}\text{C})_{1\text{h}}$ and 0.031 ‰ cm^{-1} , $\delta(^{13}\text{C})_{72\text{h}}$; (iii) 46–93 cm depth: 0.0060 ‰ cm^{-1} , $\delta(^{13}\text{C})_{1\text{h}}$ and 0.0055 ‰ cm^{-1} , $\delta(^{13}\text{C})_{72\text{h}}$. Identical conclusions on environmental processes can be obtained using data from either 1 hour or 72 hour leaching.

Oxygen Isotopic Record

The $\delta(^{18}\text{O})$ values found in the carbonates are characteristic of carbonates precipitated from a hypersaline environment. These $\delta(^{18}\text{O})$ values as well as the chlorinity of interstitial water³⁰ indicate that sediments in the lagoon have not been in contact with significant amounts of fresh water.

As Figure 5 shows, there is an increasing trend in $\delta(^{18}\text{O})$ from 44 to 93 cm depth. This tendency does not exist in the upper layers, where periodic ^{18}O oscillations are more evident. The observed isotopic shift (increase in ^{18}O content) with increasing depth results in part from the increasing dolomite content of the samples. But, also calcite and aragonite at the depth of 62–64 cm are considerably richer in ^{18}O than in all the layers above. Dolomite is known to have a higher ^{18}O content than calcite or aragonite.⁹ Rosen *et al.*¹¹ report a strong positive correlation between isotopic composition and the amount of dolomite in samples from a hypersaline lake.

To analyze the above observations in more detail, the following procedure was adopted:

A. – $\delta(^{18}\text{O})$ values for the single phases (a) aragonite/calcite and (b) dolomite were determined and then the overall composition of mixed samples was evaluated.

The average isotopic composition of a carbonate sample was determined using the isotopic mass balance:

$$\delta(^{18}\text{O})_{\text{crystalline sample}} = (V_{1\text{h}} / V) \cdot \delta(^{18}\text{O})_{1\text{h}} + (V_{72\text{h}} / V) \cdot \delta(^{18}\text{O})_{72\text{h}} \quad (2)$$

where V is the total volume of released CO_2 , (V_1 / V) and (V_{72} / V) are fractions of V released after 1 hour and between 1 and 72 hours, respectively. This procedure was applied to all samples of single phases which included:

(a) The 12 samples from 11 to 46 cm depth which consisted only of aragonite and/or calcite, but did not contain dolomite. It turned out that the $\delta(^{18}\text{O})$ of these aragonite/calcite samples equals $2.58 \pm 0.12 \text{ ‰}$. The $\delta(^{18}\text{O})$ value found in the two pure aragonite/calcite samples at 62 and 64 cm was considerably higher, $3.30 \pm 0.08 \text{ ‰}$. Calcite and aragonite do not show a significant trend in their ^{18}O content in the range of 10–54 cm, and fluctuations in isotopic composition are not related to the relative aragonite/calcite content.

(b) The 4 samples from 86 to 93 cm depth containing only dolomite. In this case, $\delta(^{18}\text{O})$ was $4.46 \pm 0.34 \text{ ‰}$.

B. – The above data and Eq. (2) were used to calculate the expectable $\delta(^{18}\text{O})$ value of samples composed of aragonite/calcite and dolomite and to compare the result with the observed value.

(a) For the uppermost sample taken from 5 cm depth that contains 58 % calcite and 42 % dolomite, the calculated $\delta(^{18}\text{O})$ was $3.33 \pm 0.24 \text{ ‰}$. The observed value is 2.31 ‰ , *i.e.*, more than 4 standard deviations below the above value calculated using the ^{18}O content of dolomite from the lower end of the core.

(b) For samples taken at 60 cm (41 % HMgC_1 , 59 % dolomite), the calculated $\delta(^{18}\text{O})$ was $3.66 \pm 0.27 \text{ ‰}$, while the observed value was 2.62 ‰ .

(c) For the sample taken at 68 cm (33 % HMgC_1 , 67 % dolomite), the calculated $\delta(^{18}\text{O})$ was $3.82 \pm 0.29 \text{ ‰}$, while the observed $\delta(^{18}\text{O})$ was 2.80 ‰ .

(d) For samples taken at 81 cm (20 % HMgC_1 , 80 % dolomite), the calculated $\delta(^{18}\text{O})$ was $4.07 \pm 0.31 \text{ ‰}$, while the observed value was 3.15 ‰ .

In all cases, $\delta(^{18}\text{O})$ of samples from 5 to 81 cm depth (composed of aragonite/calcite and dolomite), calculated using the $\delta(^{18}\text{O})$ values found in single phases of aragonite/calcite and of dolomite (86 and 93 cm depths) are significantly higher than the measured $\delta(^{18}\text{O})$ values. This means that the $\delta(^{18}\text{O})$ values used in the calculations for the single phases are too high. In other words, dolomite at around 90 cm depth has a higher ^{18}O content than dolomite encountered at lower depths.

The increase in ^{18}O content with depth is gradual below *ca.* 50 cm, as can be demonstrated qualitatively. Unfortunately, quantitative separation of all mineral phases in the samples of mixed carbonates, needed to determine the ^{18}O content directly, was not feasible. Therefore, in order to demonstrate the gradual increase in ^{18}O content in dolomite at least qualitatively, the variable ^{18}O content, found in aragonite/calcite as a function of depth, was used to calculate the hypothetical $\delta(^{18}\text{O})$ values that the dolomite phase in the mixed samples should have to explain the observed overall composition of each sample. Results are given in Table I.

The hypothetical $\delta(^{18}\text{O})$ of dolomite increases with depth.

The core covers a period of about 4000 years,²⁷ during which the $\delta(^{18}\text{O})$ value in the mineral forming water

Table I. Hypothetical $\delta(^{18}\text{O})$ values in the dolomite phase of mixed samples

Depth / cm	$\delta(^{18}\text{O})_{\text{hypothetical}}$
05	2.03
60	2.70
68	2.94
81	3.31
86–93	4.46 (observed)

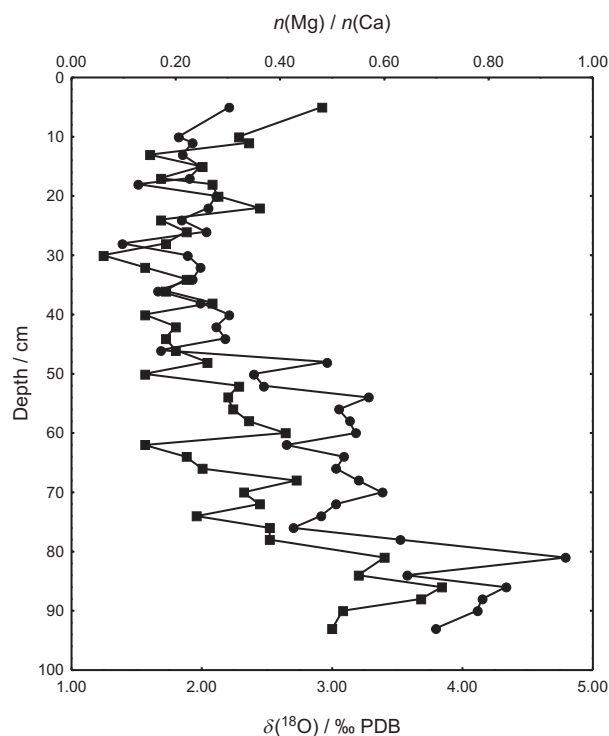


Figure 5. $\delta(^{18}\text{O}_{\text{carb}})$ and Mg/Ca (mole ratio) variations as a function of sediment depth. Dots – $\delta(^{18}\text{O})$; Squares – Mg/Ca. Values in the microbial mat: Mg/Ca = 0.44.

body gradually decreased by 2 ‰ to the actual value, reflecting a change from a more arid to a less arid climate. The average climatic conditions have evidently been constant during the period registered between 10 and 50 cm. The intrinsic difference in $\delta(^{18}\text{O})$ between aragonite/calcite and dolomite may be close to the value observed in the uppermost layer at 5 cm, *i.e.*, around 1 ‰.

The $\delta(^{18}\text{O})$ record is characteristic in three different periods – (i) 93–81 cm: 4.12 ± 0.42 ‰; (ii) 78–48 cm: 3.00 ± 0.31 ‰; (iii) 46–05 cm: 1.92 ± 0.22 ‰.

These two transitions most probably indicate a decrease of the evaporation/precipitation ratio (E/P). Lakes in which water loss is mainly due to evaporation show large fluctuations in isotopic composition as the ratio E/P changes with climate.¹ As large variations of temperature in this region certainly did not occur, the transitions must be due to changes in the climate-controlling parameter which, in this area, is mainly the northeast wind. The precise dating of these two events of pronounced changes has still to be done. However, an estimate can be made by assuming a constant sedimentation rate. Then, with 4000 years for the precipitation of 100 cm of sediments, the change at 47 cm refers to 1900 years ago, and that at 80 cm depth to about 3200 years ago. This excludes correlation with the climatic changes in South America during the »Little Ice Age« as recorded in ice cores from Peru.⁴² Large variations in temperature did certainly not occur in this region during the

last 4000 years or so, and to explain the observed changes in ^{18}O content of the carbonates as an effect of temperature would lead to the assumption of temperatures below 0 °C for the oldest layers. The explanation must therefore be considered in terms of the climate-controlling parameter which, in this area, is the northeast wind that causes upwelling off the coast and semi-arid conditions. The northeast wind is responsible for the semi-arid conditions and also promotes the upwelling off the coast of Cabo Frio. It should be pointed out that the sea level along the Brazilian coast dropped over the last 4000 years.⁴³ This eliminates the possibility that the observed effect was caused by an increasing inflow of less saline ocean water. A possible decrease of water volume in the lagoon due to the sea regression would have inverted the trend of the $\delta(^{18}\text{O})$ values, contrary to the observed trend.

It has been suggested that drier periods than the present occurred during the Holocene in South America.^{44,45} Servant *et al.*⁴⁶ report a drought period in South American lowlands during the middle Holocene but no association can be proved between this generally accepted climatic event and the present observations in a different region. Martinelli *et al.*⁴⁷ concluded from the isotopic analysis of soils from south-eastern Brazil that those regions must have also experienced a similar paleoclimatic change. There are, therefore, other indications that a drastic climatic change of at least continental scope took place around the period where the first ^{18}O shift was recorded in Lagoa Vermelha. However, information is lacking on other more recent events that may explain the second observed ^{18}O shift and the regular bands appearing after that. These $\delta(^{18}\text{O})$ oscillations, which are more evident between 10 and 44 cm depths, suggest periodic climate alterations with subsequent changes in the evaporation/precipitation ratio and, consequently, in the intensity and frequency of the upwelling phenomenon.

Carbon Isotopic Record

$\delta(^{13}\text{C}_c)$ and $\delta(^{13}\text{C}_{\text{org}})$ values are shown in Table II and Figure 7. The plot of $\delta(^{13}\text{C}_c)$ versus $\delta(^{18}\text{O})$ (see Figure 6) demonstrates the existence of two groups of carbonates with different isotopic signatures, probably derived from the changes in environmental conditions. Consequently, the two groups of data will be interpreted separately as given below.

A. – $\delta(^{13}\text{C}_c)$ values in the interval from 5 to 42 cm

Interpretation of data from this interval is based on the assumption that the sediment contains material from two different sources:

Source 1: material originating in the water column or at the sediment-water interface. This should be the relics of calcareous organisms and aragonite crystals, which are present in the sediments only above the con-

TABLE II. Isotopic shifts (PDB standard) and mineralogical composition^(a)

Depth cm	$\delta(^{13}\text{C}_c)$	$\delta(^{13}\text{C}_o)$	$\delta(^{13}\text{C}_c)_{72\text{h}}$	$\delta(^{18}\text{O})$	$\delta(^{18}\text{O})_{72\text{h}}$	$w(\text{H}_2\text{O})$	Mineralogical composition, <i>w</i> / %			
	‰	‰	‰	‰	‰	%	A	HMgC ₁	HMgC ₂	Dol
5	-4.59	-19.02	-8.78	2.21	3.95	65.16		58		42
10	-3.97	20.40	-4.97	1.82	2.59	61.42		88	12	
11	-3.70	-21.57	-3.83	1.93	2.65	63.60		100		
13	-4.66	-19.82	-5.18	1.85	2.34	69.85	8	92		
15	-3.97	-19.78	-4.52	1.99	2.57	63.42	6	81	13	
17	-3.45	-19.21	-4.20	1.90	2.33	71.31	7	77	16	
18	-4.43	-19.62	-4.73	1.51	2.55	67.00	6	78	16	
20	-5.21	-18.23	-5.73	2.11	2.87	67.78	14	63	23	
22	-4.70	-18.75	-5.67	2.05	2.75	67.44	17	13		
24	-3.34	-20.35	-5.98	1.84	2.75	62.57	47	53		
26	-3.33	-21.85	-3.84	2.03	2.46	59.26	52	48		
28	-3.03	-22.03	-3.90	1.39	2.46	62.03	57	43		
30	-2.80	n.d.	-3.91	1.89	2.61	59.59	72	28		
32	-3.85	-21.07	-4.81	1.99	2.68	63.29	55	45		
34	-3.77	-21.14	-4.83	1.93	2.24	64.04	64	36		
36	-1.94	-21.96	-3.55	1.66	2.19	62.78	63	37		
38	-5.26	-20.36	n.d.	1.99	n.d.	67.23	26	38	36	
40	-6.18	-19.16	-5.98	2.21	2.42	66.59	25	50	25	
42	-6.18	-19.57	n.d.	2.11	n.d.	57.76	24	76		
44	-5.85	-17.72	-7.42	2.18	2.60	69.27		100		
46	-9.73	-16.91	-8.52	1.68	2.37	66.92		100		
48	-11.15	17.79	-10.31	2.96	3.26	55.91		57	43	
50	-9.99	-17.50	-9.62	2.40	2.69	65.46		100		
52	-10.27	-17.36	-10.05	2.47	2.64	64.67		100		
54	-10.26	n.d.	-9.50	3.28	3.06	66.71		68	32	
56	10.59	-17.24	-10.57	3.05	3.09	64.88		39		61
58	-10.56	-17.02	-10.35	3.13	3.58	64.44		57		43
60	-10.34	-17.15	-10.02	3.18	3.96	61.67		41		59
62	-10.71	-17.87	-9.91	2.65	3.25	65.55		71	29	
64	-11.06	-17.21	-10.58	3.09	3.36	66.87		57	43	
66	-10.96	-16.27	-9.92	3.03	3.82	66.09		56		44
68	-10.69	-16.95	-10.24	3.20	4.04	57.61		33		67
70	-10.68	-16.62	-9.80	3.38	4.58	58.00		34		66
72	-10.72	-17.38	-9.67	3.03	4.34	60.32		55		45
74	-10.60	-16.57	-9.98	2.91	3.81	59.07		53		47
76	-9.97	-15.50	-9.52	2.70	3.58	66.34		54		46
78	-9.74	-15.46	-9.38	3.52	3.62	57.74		26		74
81	-9.34	-15.92	-8.81	4.79	6.32	53.76		20		80
84	-10.23	-18.95	-9.08	3.57	6.15	59.85		21		79
86	-10.47	-19.60	-9.87	4.33	4.48	35.28				100
88	-10.53	-19.29	-9.69	4.15	4.99	42.63				100
90	-10.19	-19.56	-9.93	4.11	4.78	68.67				100
93	-10.21	-17.14	-9.90	3.79	4.13	69.93				100

^(a) A = aragonite; Dol = dolomite; subscript 72h stands for 72 h reaction products; subscripts c and o stand for carbonate and organic matter, respectively; HMgC₁ = calcite with *x*(Mg) ≤ 20 %; HMgC₂ = calcite with *x*(Mg) > 20 %.

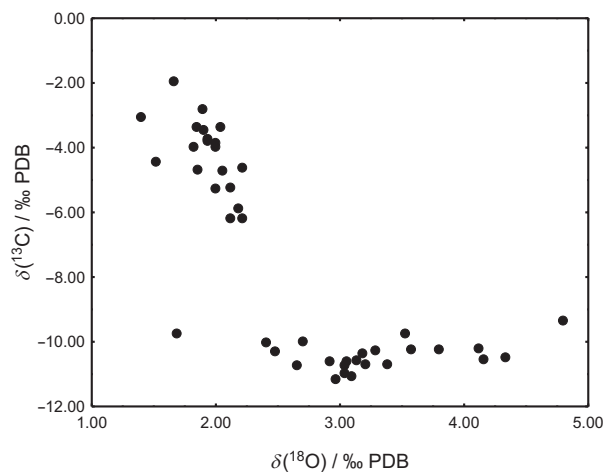


Figure 6. $\delta(^{13}\text{C}_{\text{carb}})$ plotted versus $\delta(^{18}\text{O}_{\text{carb}})$ values. Dots in the upper left part of the plot stand for samples from 5 to 44 cm depths.

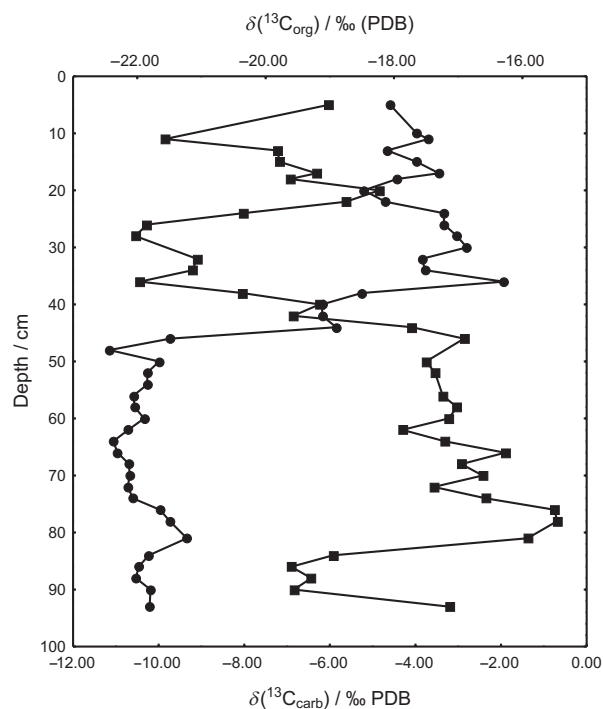


Figure 7. Depth profiles of $\delta(^{13}\text{C}_{\text{carb}})$ and $\delta(^{13}\text{C}_{\text{org}})$. Squares – $\delta(^{13}\text{C}_{\text{carb}})$; Dots – $\delta(^{13}\text{C}_{\text{org}})$. Values in the microbial mat: $\delta(^{13}\text{C}_{\text{carb}}) = -2.53$ ‰ and $\delta(^{13}\text{C}_{\text{org}}) = -14.22$ ‰.

sidered interval. Calcareous organisms are aerobic and could only have grown at the surface of the sediments or in the water column itself. The isotopic composition of such materials should be: $\delta(^{13}\text{C}_c) = +2$ ‰.

This value turns out from the fractionation factor for the reaction $^{13}\text{CO}_2 \leftrightarrow \text{H}^{13}\text{CO}_3^-$ (9.1 ‰)⁴² combined to the value for atmospheric CO_2 (-7 ‰).

Source 2: authigenic carbonate (HMgC and dolomite) precipitation in the sedimentary environment rich in CO_2 derived from decomposing organic matter: $^{13}\text{C}_{(\text{org. mat.})} \leftrightarrow ^{13}\text{CO}_2$ with an unknown fractionation fac-

tor. This CO_2 then reacts with water forming bicarbonate: $^{13}\text{CO}_2 \leftrightarrow ^{13}\text{CO}_2(\text{aq.}) \leftrightarrow \text{H}^{13}\text{CO}_3^-$ with a fractionation factor at 25 °C of +9.1 ‰.⁴⁸ The isotope fractionation factor for the first reaction can be calculated from the correlation between the observed trends of (i) concentration of organic carbon *vs.* depth (Figure 9), and (ii) $\delta(^{13}\text{C}_{\text{org}})$ *vs.* depth (Figure 7).

These trends are well defined for the interval between 50 and 76 cm, but they are poorly evident in the upper layers due to the larger scatter of the individual values. The decrease in organic matter content with depth is followed up by an increase in $\delta(^{13}\text{C}_{\text{org}})$ and is interpreted as resulting from degradation processes.

The co-variation of organic matter content and ^{13}C suggests a Rayleigh fractionation:

$$\gamma / \gamma_0 = (v_0/v)^{\alpha-1} \quad (3)$$

The fractionation factor (α) can be calculated from equation (3), where γ , γ_0 , v_0 and v are taken at the interval given before (calculated from the linear regression of all data in the interval): (i) γ_0 (50 cm) = 1 - 17.22 ‰ = 0.9828, (ii) γ (78 cm) = 1 - 16.09 ‰ = 0.9839, (iii) v_0 (50 cm) = 4.52 % $\text{C}_{(\text{org.})}$, (iv) v (78 cm) = 3.28 % $\text{C}_{(\text{org.})}$.

This gives $\alpha = 1.0051$.

The isotopic composition of the original material was estimated from the $\delta(^{13}\text{C}_{\text{org}})$ values detected between 5 and 42 cm as -20.23 ‰.

Combining the data obtained above, the isotopic carbonate composition of the sediments between 5 and 42 cm was calculated as: $\delta(^{13}\text{C}_c) = -20.23 - 5.1 + 9.1 = -16.23$ ‰.

The observed average isotopic content of carbonate for the given interval is $\delta(^{13}\text{C}_c) = -4.1$ ‰ with lower and upper limits of -1.98 ‰ and -6.18 ‰, respectively. This value indicates that 66.5 % of the carbonate originated from source 1 material, while 33.5 % would have been authigenic. In fact, such a result is in good agreement with the macro- and microscopic observations of the core. Shells, foraminifera remains and aragonite crystals are very abundant between 5 and 42 cm, while rare in the lower part of the core.

B. - $\delta(^{13}\text{C}_c)$ values in the interval from 50 to 78 cm

Over this interval the average isotopic composition of the organic carbon is $\delta(^{13}\text{C}_{\text{org}}) = -16.86$ ‰.

When applying the same procedure as before, the carbonate deposited under the influence of CO_2 derived from this material is obtained by: $\delta(^{13}\text{C}_c) = -16.86 - 5.1 + 9.1 = -12.86$ ‰

The actual average $\delta(^{13}\text{C}_c)$ value for this interval is -10.48 ‰. In this case, there should have been an addition of about 16 % from source 1 material.

A possible third source of material in the form of ^{13}C reach carbonate resulting from methanogenesis was

discarded. Its contribution could only be marginal because all carbonates considered are ^{13}C depleted. The content of total phosphorus (Figure 8) in the sediments increased from surface to bottom as the following averages show – (i) 05–45 cm: 0.13 ± 0.01 % P (mass fraction, w), (ii) 50–75 cm: 0.21 ± 0.03 % P (w).

McKenzie demonstrated that the content of phosphorus in the sediments is related to primary production and to the $\delta(^{13}\text{C})$ of carbonates.⁴⁹ In addition, in the case of Vermelha Lagoon where there is a very limited source of terrestrial organic carbon, $\delta(^{13}\text{C}_{\text{org}})$ can be a reliable proxy for paleoproductivity. These sets of results point to an increase in primary production during periods of high evaporation. There is a good correlation between $\delta(^{18}\text{O})$ values and total phosphorus (linear correlation coefficient, $r = 0.779$) as well as between $\delta(^{13}\text{C}_c)$ values and P (linear correlation coefficient, $r = -0.858$). These relations can be understood assuming that an increase in productivity results in the generation of larger amounts of organic matter, which in turn stimulates the growth of bacteria. As a consequence of increased bacterial activity (both aerobic and sulphate reducing), a growth in the light CO_2 pool and precipitation of carbonates enriched in ^{12}C should be expected. Refractory organic matter that remains in the sediments under such conditions will be enriched in ^{13}C . This argumentation is also supported by the good correlation found between total phosphorus and $\delta(^{13}\text{C}_{\text{org}})$ (linear correlation coefficient, $r = 0.758$).

The C/N amount ratio can be used to help define the source of organic matter (values <10 and 12 are usual for lacustrine algae and >20 for terrestrial plants, and between 10 and 20 for mixed sources).¹ This ratio decreases continuously below 42 cm depth (Figure 8). At approximately 44 cm, a pronounced shift in C/N values occurs, resembling the sudden change in $\delta(^{13}\text{C})$ already discussed. The correlation between C/N values and other variables such as total phosphorus, $\delta(^{18}\text{O})$ and $\delta(^{13}\text{C})$ is only regular; however, in spite of this, the shift in C/N is certainly related to environmental and biomass changes. For instance, the tendency of increasing the C/N values between 93 and 50 cm could have resulted from the transition of the predominance of cyanobacteria to a mixture with other algal species, like diatoms. A contribution from terrestrial material driven into the lagoon by wind action cannot be ruled out under more humid conditions.

CONCLUSIONS

Results obtained for the Lagoa Vermelha sediments strongly indicate that the observed shifts in $\delta(^{13}\text{C}_c)$ and $\delta(^{13}\text{C}_{\text{org}})$ are due to a sequence of closely interrelated events. In the past, climatic changes (as inferred from the $\delta(^{18}\text{O})$ data) resulted in salinity decrease, which in turn caused profound alterations in the existing biota and

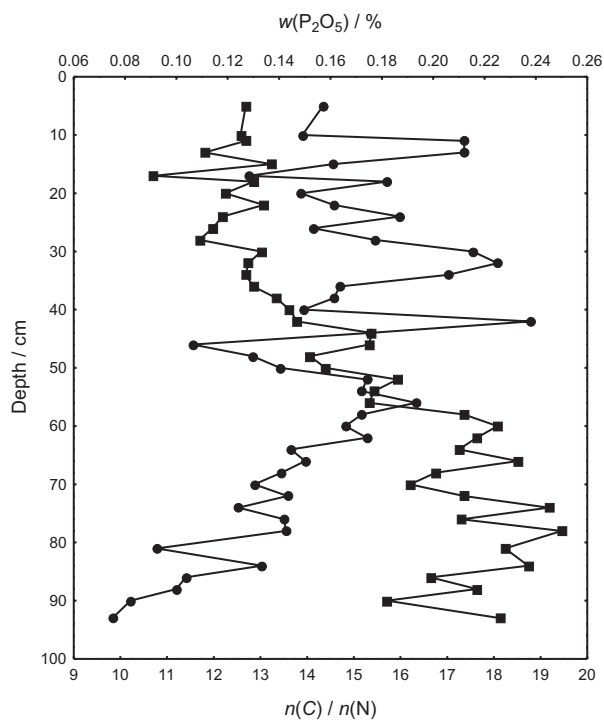


Figure 8. C/N mole ratio and P_2O_5 mass fraction (w) variations as a function of sediment depth. Dots – C/N; Squares – $w(\text{P}_2\text{O}_5)$. Values in the microbial mat material: C/N = 15.90 and $w(\text{P}_2\text{O}_5) = 0.11$ %.

in mineralogy. The isotopic data, the C/N ratio, and the phosphorus content variability provide evidence of the changes in primary production, taxonomy and microbial activity. By lowering the salinity, primary production and microbial activity declined and, at a certain critical salinity, conditions became favourable for the growth of shell organisms and diversification of algal species. The change in salinity also affected the mineralogical assemblage, allowing precipitation of aragonite and the predominance of this polymorph over a certain sedimentary interval.

The intimate relation between climatic conditions and the observed mineralogy is confirmed here, among other factors, by the similarities in $\delta(^{18}\text{O})$ and Mg/Ca trends (Figure 5). In addition, the isotopic data together with observing the sediments under the microscope indicate that aragonite is formed in the water column, while HMgC and dolomite are deposited in the benthic environment.

An interesting finding was the identification of HMgC_2 as a distinct phase. This identification was based on the appearance of XRD reflections, which were different from those for HMgC_1 and dolomite.

Precipitation of high magnesium calcite seems to be occurring at the boundary between the oxidizing and reducing zones of the microbial mat. Carbonate precipitation can be induced by photosynthesis and bacterial respiration. In the latter case, precipitation proceeds in the

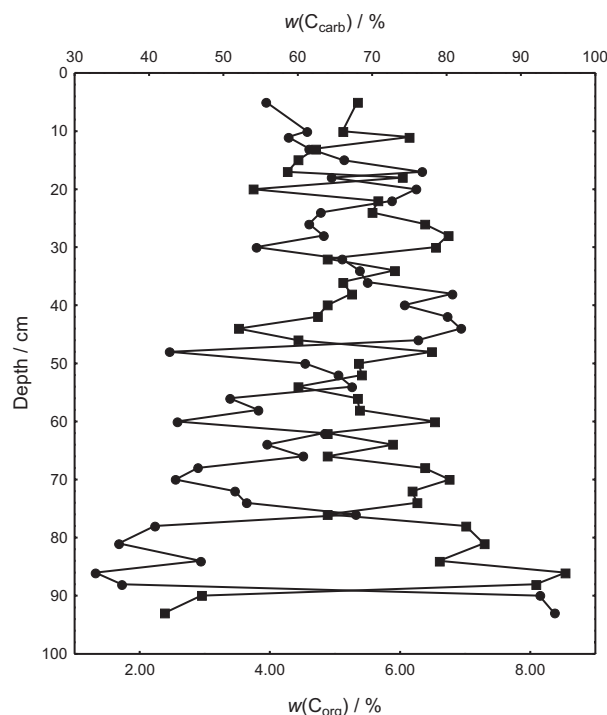


Figure 9. Organic carbon and carbonate contents as a function of sediment depth. Squares – carbonates; Dots – organic carbon. Values in the microbial mat: mass fraction, $w(C_{carb}) = 44.4\%$ and $w(C_{org}) = 5.94\%$.

presence of CO_2 and additional Mg ions originating from the decomposition of organic material. The inverse relationship between the carbonate and organic carbon contents, as shown in Figure 9, provides evidence for the linkage between decomposition of organic material and carbonate precipitation. The values of $\delta(^{13}C_{org.}) = -14.22\%$ and $\delta(^{13}C_c) = -2.53\%$, encountered for material from the microbial mat, demonstrate that the bulk of the degradation process and isotopic exchange occurs already in the mat. As the dolomites present in the sediments show isotopic composition similar to that of calcite, they must have been preferably formed in the mat.

In the range of depth where $\delta(^{13}C_c)$ varies very little (50–93 cm), sample mineralogy shifts from 100 % $HMgC_1$ to 100 % dolomite. Other evidence that dolomitization occurs in the mat and that the isotopic composition of the dolomites to a large extent represents the original mat environment, is the good correlation between $\delta(^{18}O)$, $\delta(^{13}C)$ and parameters like P content and C/N amount ratio, intimately bound to the biological and environmental characteristics of the mat.

The occurrence of recrystallization observed by scanning electron microscopy³⁰ does not exclude the formation of dolomite in the mat and does not invalidate the proposed model for the observed carbonate isotopic shift. This is true because low permeability of the microbial mat²⁹ and of the organic material in the sediments as well as the presence of concretions in the bottom of the core

impede vertical fluxes. In this way, precipitation and dissolution proceed in closed systems where the isotopic composition of the original solid is preserved.

There are also indications that dolomite deposition would be favoured during extremely dry periods when water depth is drastically reduced. The presence of concretions and sediment cracks, which coincide with the appearance of dolomite in deeper layers of the core, suggest that at certain times the lagoon may have lost all of its water.

As far as the water balance in the lagoon is concerned, no significant underground influx of either fresh or sea water existed. The whole balance appears to be occurring through the surface with inputs of fresh water from rain events. Seawater influx and reflux of lagoon water is controlled by the high/low tidal periods via the permeable sandbar. This seawater is the source of Mg and other ions for the lagoon. The ratios of ion concentrations of the lagoon water are very close to those of seawater ($[SO_4^{2-}] / [Cl^-] = 0.052$; $[Ca^{2+}] / [Cl^-] = 0.019$; $[Mg^{2+}] / [Cl^-] = 0.096$), indicating that the loss of Ca and Mg to the sediments is greatly compensated by seawater input. This water exchange and the removal of Mg ions via precipitation of very high magnesium calcite and perhaps of primary dolomite are responsible for the observed ionic ratio.

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SAŽETAK

Procjena prošlih promjena u okolišu proučavanjem sedimenata u hiperslanoj laguni

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U radu je opisana uporaba izotopa ugljika i kisika, elementnog sastava organske tvari i mineralogije karbonata kao faktora u istraživanju promjena na okolišu utvrđenih u karbonatom bogatim sedimentima hiperslane lagune "Vermelha" kod Rio de Janeira u Brazilu. Izotopski i drugi podaci ukazuju na dvije značajne promjene okolišnih uvjeta, koje su se dogodile prije 1900 odnosno 3200 godina. U karbonatima, vrijednosti $\delta(^{18}\text{O})$ i $\delta(^{13}\text{C})$

izmjerene su u rasponu od +1,5 ‰ do +4,5 ‰, odnosno od –2 ‰ do –11 ‰ (standard Pee Dee Belemnite – PDB). Kod organske tvari, vrijednost $\delta(^{13}\text{C})$ varira u rasponu od –22 ‰ do –15 ‰ (PDB). U istraživanoj su sedimentnoj jezgri utvrđeni kalcit i dolomit, a njihova relativna zastupljenost povezana je s utvrđenim okolišnim promjenama. Kalciti sadrže do 38 % MgCO_3 (molni udjeli, x). Za razliku od kalcita s nižim sadržajem magnezija, magnezijev kalcit ($x(\text{Mg}) > 20\%$) pokazuje dodatnu liniju na rendgenskom difraktogramu kod 2929 nm. Uzorci koji sadrže magnezijev kalcit ili čisti dolomit pokazuju slične vrijednosti $\delta(^{13}\text{C})$. Postoje snažne indicije za stvaranje dolomita već u području mikrobnih pokrova. Vrijednosti ^{18}O i ^2H u vodi lagune ukazuju na to da je isparavanje proces koji kontrolira bilancu vode u sustavu.