

Stable isotope composition of *Littoridina australis* from the coast of Buenos Aires province, Argentina, during Holocene climatic fluctuations

Composition des isotopes stables (^{13}C , ^{18}O) de *Littoridina australis* du secteur côtier de la Province de Buenos Aires, Argentine, pendant les fluctuations climatiques de l'Holocène

Composición de isótopos estables (^{13}C , ^{18}O) de *Littoridina australis* del sector costero de la Provincia de Buenos Aires, Argentina, durante fluctuaciones climáticas del holoceno

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Abstract

Stable isotope (carbon and oxygen) analyses were performed on *Littoridina australis* shells collected from molluscan concentrations within Holocene littoral deposits along the Bonaerensian coastal area of Argentina (south-western Atlantic). Isotope data allow us to define two very different areas: the Samborombon Bay, where isotope composition of shells was mainly governed by mixing between marine and freshwater, and the Mar Chiquita lagoon, where the original brackish environment was dominated by evaporation of water that originated high isotope shell values. In both areas some isotope profiles show short and quite large oscillations in $\delta^{18}\text{O}$. Their origin may be tentatively explained as due to the changes in moisture regime that control freshwater supply. The results suggest that these deposits can represent natural archives potentially useful for palaeoclimate reconstruction. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Résumé

Ont été effectuées des analyses d'isotopes stables (carbone et oxygène) sur des coquilles de *L. australis* qui proviennent de concentrations coquillières des dépôts littoraux holocènes de la région côtière de Bonaerense en Argentine (Atlantique sudoccidentale). Les données isotopiques permettent de définir deux régions bien différentes: la zone du Bahía Samborombón, où la composition isotopique des coquilles a été contrôlée par le mélange entre eau marine et eau continentale, et la zone de la lagune de Mar Chiquita, où l'environnement original a été dominé par des eaux saumâtres en régime évaporitique. Quelques sections échantillonnées dans différents niveaux se caractérisent par des oscillations courtes mais de relative grande amplitude en $\delta^{18}\text{O}$. Leur origine est peut être liée aux changements de régime d'humidité qui contrôlait l'apport de l'eau douce et suggère que les sections étudiées représentent des archives naturelles potentiellement utiles à des fins paléoclimatiques. © 2002 Éditions scientifiques et médicales Elsevier SAS. Tous droits réservés.

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Resumen

Se efectuaron análisis de isótopos estables (carbono y oxígeno) en conchillas de *Littoridina australis* recolectadas en concentraciones conchiles de depósitos litorales holocenos a lo largo del área costera bonaerense en Argentina (Atlántico sudoccidental). Los datos isotópicos permiten definir dos áreas bien diferentes: el área de Bahía Samborombón, donde la composición isotópica de las conchillas estuvo controlada por la mezcla entre agua marina y continental, y el área de la laguna Mar Chiquita, donde el ambiente original estuvo dominado por evaporación de agua que originó altos valores isotópicos en las conchillas. Algunas de las secciones muestreadas en diferentes niveles se caracterizan por oscilaciones cortas y bastante grandes de $\delta^{18}\text{O}$. Su origen puede ser ligado tentativamente a cambios en el régimen de humedad que controla el aporte de agua dulce, lo cual apoya la hipótesis de trabajo y sugiere que las secciones estudiadas representan archivos naturales potencialmente útiles para fines paleoclimáticos. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Stable isotopes; *Littoridina australis*; Molluscs; Holocene; Palaeoenvironments; Argentina

Mots clés: Isotopes stables; *Littoridina australis*; Mollusques; Holocène; Palaéoenvironnements; Argentine

Palabras claves: Isótopos estables; *Littoridina australis*; Moluscos; Holoceno; Paleoambientes; Argentina

1. Introduction

During the Holocene, the Bonaerensean region (Buenos Aires Province, Central Argentina) (Fig. 1) experienced significant variations in rainfall regime (e.g. Bonadonna et al., 1999; Iriondo and Garcia, 1993). The position of sea surface currents along the Atlantic coast also experienced changes that probably affected inland climate (e.g. Aguirre, 1993, 1996). However, land and sea data are not fully coincident and further study is needed to correlate land–sea stratigraphy and palaeoclimatic records.

The Bonaerensean coast, from Punta Indio to Bahía Blanca, preserves several marginal marine deposits of Holocene age (e.g. Aguirre and Whatley, 1995) potentially useful for investigating the changes in hydrology of the area, since marginal marine environments are sensitive to changes in freshwater supply. Waters of continental and marine origin usually have large different isotopic signatures, the same is true for the isotope composition of the dissolved inorganic carbon (DIC). Therefore, carbon and oxygen stable isotope composition of mollusc shells living in marginal marine environments can record the mixing between continental and marine waters (e.g. Mook and Vogel, 1968; Eisma et al., 1976; Ingram et al., 1996).

In the simplest case, at a given temperature, isotopic compositions of shells will describe a linear mixing trend between two end members corresponding to marine and continental environments when plotted in a $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ diagram. Several studies have used this approach to reconstruct palaeosalinity (e.g. Dodd and Stanton, 1975; Hudson et al., 1995) and changes in river discharge (e.g. Ingram et al., 1996) in ancient marginal marine deposits. However, local factors such as evaporation, increase in the equilibration with atmospheric CO_2 reservoir, in situ decay of organic matter, and strong local biological activity, may

alter drastically the model (e.g. Lloyd, 1964; Hendry and Kalin, 1997).

The role of freshwater supply in fossil molluscan assemblages found in the Bonaerensean region has been previously shown by palaeontological studies (e.g. Aguirre, 1993, 1996) and isotope data (C, O and Sr) from *Maetra isabellana* shells (Aguirre et al., 1998). In this work we discuss the stable isotope results obtained from the euryhaline mollusc *Littoridina australis* (D'Orbigny, 1835; Hydrobiidae, Mesogastropoda) and their palaeoenvironmental implications with the main aim of inferring the changes of freshwater supply during the Holocene. Moreover, analyses performed on living *L. australis* and marine shells contribute to a better understanding of the isotope composition of shells now inhabiting in well defined environments.

2. Regional setting

The deposits studied are located between Punta Indio and Mar Chiquita (Fig. 1) and are formed mainly by regressive shell ridges, while a few belong to coastal lagoon or estuarine facies and tidal flats (Aguirre and Whatley, 1995; Codignotto and Aguirre, 1993). The most widespread deposits belong to the Las Escobas Formation (ca. 7.5–1.4 ka BP, Aguirre and Whatley, 1995).

The modern Bonaerensean oceanic littoral belongs to an ecotone known as the Argentine Zoogeographic Province. It is determined by the Subtropical Convergence of the South Atlantic (between 29°S and 47°S in winter and 34°S and 49°S in summer), a zone where mixing of the subtropical and subantarctic shallow water masses takes place (Olson et al., 1988; Garzoli and Giulivi, 1993). It forms by the influence and extension of the Brazilian shallow warm current, which flows southwards off coast, with little influence on the coastal area at present, and by the cool

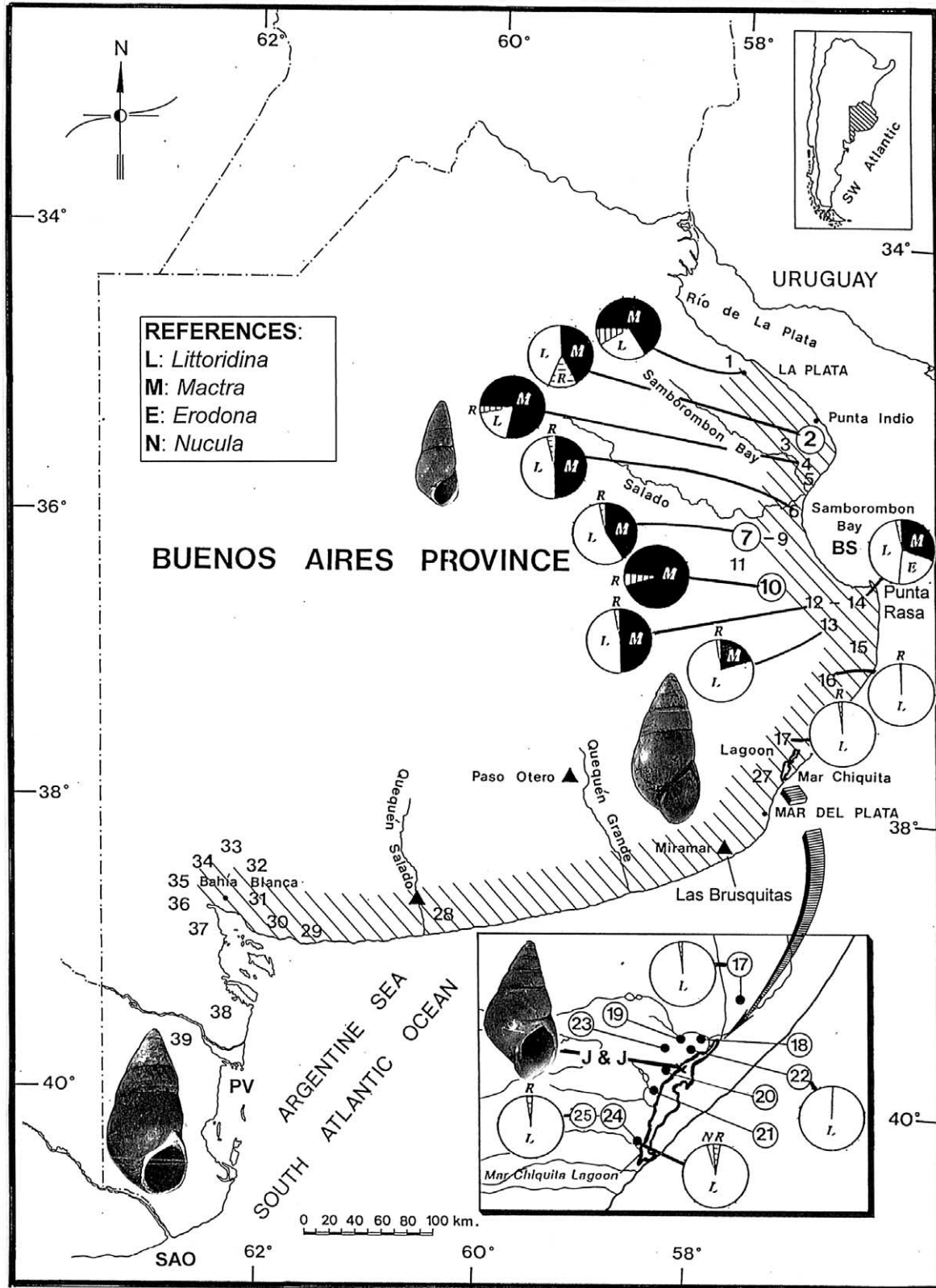


Fig. 1. Location map showing the localities discussed in the text. Area of study along the Bonaerensian coastal area: 1–39, Holocene deposits of collection of *L. australis* for palaeoecological studies; encircled numbers refer to localities selected for stable isotope analyses (see Table 1). SB, J&J, PV, SAO refer to living samples. Different size and shape of *L. australis* respond to different environmental conditions.
 Plan des localités mentionnées dans le texte. Localités étudiées sur la côte de la région de Buenos Aires (1–39) avec les coupes stratigraphiques de l’holocène utilisées pour des études de paléocologie; les nombres avec les cercles sont les localités utilisées pour les études isotopiques ($\delta^{13}\text{C}$ et $\delta^{18}\text{O}$). SB, J&J, PV, SAO indiquent les localités d’échantillonnage de *L. australis* vivant. Sa dimension et sa forme indiquent différents milieux.

Table 1

Isotope data of the Holocene *L. australis*. The table also shows the ^{14}C ages available. (1) ^{14}C new data. Complete source of information and references on dates in Aguirre and Whatley (1995) and Aguirre and Farinati (2000). Asterisks indicate different samples from the same level.

Le tableau montre les compositions isotopiques des échantillons des fossiles holocènes de *L. australis*. Le tableau indique aussi les données du ^{14}C . Le nombre (1) indique les données nouvelles reportées ici pour la première fois. Toutes les informations relatives aux données du ^{14}C et à la bibliographie figurent dans Aguirre and Whatley (1995) et Aguirre and Farinati (2000). L'astérisque indique de distinctes données du ^{14}C provenant du même niveau

Fossil shells Locality	Sample	$\delta^{13}\text{C} \text{ ‰}$	$\delta^{18}\text{O} \text{ ‰}$	^{14}C yr BP
2 Punta Indio	115	-0.46	-0.63	5760 ± 60 (1)
	117	-0.02	-0.89	
7 Samborombon Bay	19	0.67	-0.82	4440 ± 110–3490 ± 80 5500 ± 80–5150 ± 70
	20	0.32	-0.94	
	21	0.3	-0.45	
	24	0.34	-0.23	
	25	0.72	-0.35	
	26	-0.26	-0.69	
	27	0	0.14	
	28	-0.11	-0.49	
	29	0.44	-1.16	
	30	0.4	-0.63	
	31	0.49	-0.63	
10 Samborombon Bay	82bis	0.54	1.52	4550 ± 110 4510 ± 110–4220 ± 110
	83bis*	0.34	1.02	
	83bis*	0.48	1.09	
	84bis	0.16	1.1	
	85bis	0.23	0.88	
	86bis	0.04	1.43	
	87bis	0.19	0.29	
	88bis	0.21	0.81	
	89bis	0.55	0.99	
	90bis	0.1	0.47	
17 Mar Chiquita	156	1.87	2	3850 ± 60–3110 ± 80
18 ‘	135	-0.4	1.55	2880 ± 90–2820 ± 80 3330 ± 70 (1)
19 ‘	157	-0.13	1.16	
20 ‘	158	0.32	1.57	
21 ‘	159	0.11	1.94	
22 ‘	108	0.69	1.24	
‘	109	-0.33	1.2	
‘	110	-0.27	1.04	
‘	111	-0.11	1.13	
‘	112	-1.25	0.46	3230 ± 70 (1)
23 Mar Chiquita	136	0.84	1.48	3690 ± 70 (1)
	137	0.94	1.34	3280 ± 70 (1) 4830 ± 70 (1)
	138	0.52	1.41	
	139	0.06	1.72	
100	1.86	1.81		
24 Mar Chiquita	101	1.68	1.53	4960 ± 60–4430 ± 45 (3) 3520 ± 60 (3) 2920 ± 80–2700 ± 50
	102	1.64	1.36	
	103	1.68	1.72	
	104	1.32	1.54	
	106	0.92	1.84	
	134	-0.8	0.9	
	134*	0.31	0.45	
25 Mar Chiquita	134*	0.52	0.5	

Malvinas current, which flows between the continent and the Brazilian Current. Two very different salinity conditions at present characterise the area of study. The Río de La Plata influences the northern area (Punta Indio-Samborombon Bay) of mainly freshwater character, whereas marine waters of the South Atlantic influence the southern sector (Punta Rasa-Mar Chiquita).

In the northern area, off Punta Indio-Samborombón Bay, water in the littoral environment corresponds to the mixohaline zone (salinity 8–18‰). The southern sector around Mar Chiquita corresponds to the modern oceanic littoral

(salinity ~35‰) but inside the coastal lagoon (Fig. 1) there is a horizontal zonation as described by Olivier et al. (1968): mixo-oligohaline (~2–3‰), an inner zone where creeks and small rivers flow into the lagoon, a mixo-polyhaline (~22‰) in the middle, and an euhaline area (~34‰) near the mouth.

3. Samples and species studied

Littoridina australis was chosen for the stable isotope analyses because of its ubiquity, dominance, and excellent

preservation all over the area. Fourteen localities from two different areas (Samborombon Bay and Mar Chiquita lagoon) were selected for sampling and subsequent stable isotope analyses (Fig. 1). For this study some new radiocarbon dates (conventional and AMS) were achieved for shells of *L. australis* and *Macra isabelleana* which represent the dominant molluscan species in these deposits (Table 1). Living shells of *L. australis* were collected at Samborombon Bay, Mar Chiquita, Península Verde, and San Antonio Oeste (Fig. 1). Marine species were collected in Patagonia at Rada Tilly and Bahía Langara (Table 1), both of which are areas where mixing with continental water is negligible.

From a palaeontological point of view *L. australis* is thought to represent an autochthonous component of the original benthic communities in the area (Brandt, 1989). *L. australis* is an epifaunal, mobile, species living from the supralittoral down to the upper infralittoral. It feeds on vegetation particles and bacteria (microphagous) and is occasionally detritivorous so it can be considered an opportunistic species (Cadeé, 1984). It occurs in major densities and with maximum sizes in mixohaline (brackish) environments which can be considered the species optimum, although it can tolerate salinity variations from mixo-oligohaline (3‰) to polyeuhaline (18–35‰) gradients where it occurs with considerably less abundance and smaller sizes. Its growth pattern is still unknown but it most probably has an annual cycle (S. Martín, pers. com.) like *Littoridina parchappii*, a similar and very close freshwater species. Detailed taxonomic, distributional, palaeoecological and taphonomic aspects of *L. australis* have been published elsewhere (Aguirre and Farinati, 2000).

4. Materials and methods

Autochthony and the same age of the shells are assumed by their dominance, excellent preservation, and AMS and conventional radiocarbon ages (Table 1). Three to seven whole and well preserved shells of *L. australis* were selected, cleaned in an ultrasonic bath, dried and finally powdered. Carbon dioxide for isotope analysis was produced by reacting the powder with 100% phosphoric acid at 90°C using a VG Isocarb automated carbonate device attached to a VG PRISM2 mass spectrometer. Oxygen and carbon isotopic ratios are expressed in the well known $\delta\%$ notation relative to V-PDB standard. Mean reproducibility of carbonate shells based on replicate analyses was of $\pm 0.08\%$ and $\pm 0.04\%$ for oxygen and carbon respectively. Two separate samples were analysed to check the variation within stratigraphic levels from two beds at localities 10 and 25. The differences found ($\leq 0.2\%$ for carbon and $\leq 0.05\%$ for oxygen; Table 1) confirm that reworking is largely absent and different generations with somewhat different ecological circumstances can be disregarded. Previous to stable isotope analyses living shells

were treated with an oxygen plasma for 2 h to remove organic contaminant.

5. Stable isotope results

The isotope values of fossil *L. australis* shells range from -1.16 to $+1.94\%$ for the oxygen and -1.25 to $+1.87\%$ for the carbon (Fig. 2a, b; Table 1). Living marine shells of different species range from $+0.6$ to $+1.67\%$ for the oxygen and from $+0.6$ to $+2.56\%$ for the carbon: shells of living *L. australis* show lower isotope values (Fig. 2a; Table 2). Even though the isotope values are fairly continuous within their range, the $\delta^{18}\text{O}$ values of fossil *L. australis* allow us to separate two sets of samples: a set characterised by ^{18}O -depleted values (from -1.16 to -0.23%) and a set with higher $\delta^{18}\text{O}$ values (from $+0.14$ to $+2\%$). In both sets there are samples with ^{13}C -depleted values (Fig. 2b). The shell samples with high $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are mostly dated between about 5000 and 4000 years BP (Table 1), and include most samples from Mar Chiquita area (localities 17, 20, 21, 23, 24, 25) which show the highest $\delta^{18}\text{O}$ values and a set of samples from locality 10 in central Samborombon Bay (~ 4500 years BP). The faunal composition suggests original mixo- to polyeuhaline (Mar Chiquita) and polyhaline (Samborombon Bay) salinity conditions, respectively. The shells with high $\delta^{18}\text{O}$ and relatively low $\delta^{13}\text{C}$ values include Mar Chiquita samples from localities 18, 19, 22 and 25, mostly younger than ca. 4000 years BP, which belong to assemblages indicative of brackish (mixohaline) environments.

The shells with lowest $\delta^{18}\text{O}$ are chronologically placed between ca. 6000 and 3500 years BP. This group includes samples from the locality 2 at Punta Indio and from locality 7 at central Samborombon Bay. Those samples slightly depleted in ^{13}C (115 and 117 from locality 2 and 26 and 28, from locality 7, Table 1) are characterized by molluscan assemblages which differ from the remaining samples, including thermally anomalous taxa indicative of warmer waters than present (Aguirre, 1993).

Five of the localities provide longer sections which allowed extensive sampling at different levels (Fig. 3): two from Samborombon Bay (localities 7 and 10) and three from Mar Chiquita lagoon (localities 22, 23 and 24). Locality 7 is at the side of Salado river with *L. australis* representing 50% of the whole molluscan content and a majority of euryhaline associated taxa. This indicates a polyhaline (mixopolyhaline?) environment. The largest variation in $\delta^{18}\text{O}$ with a depletion in $\delta^{18}\text{O}$ of about 1% is observed between the sample 27 and 29. This depletion is followed by an increase of about 0.5% . Locality 10, in central Samborombon Bay, shows that *L. australis* is nearly absent ($< 1\%$) (Fig. 1) while *Macra isabelleana* is dominant ($\sim 90\%$), an indication of a polyhaline to polyeuhaline environment. Like in locality 7, $\delta^{18}\text{O}$ of locality 10 is characterized by a large and rapid oscillation and the largest

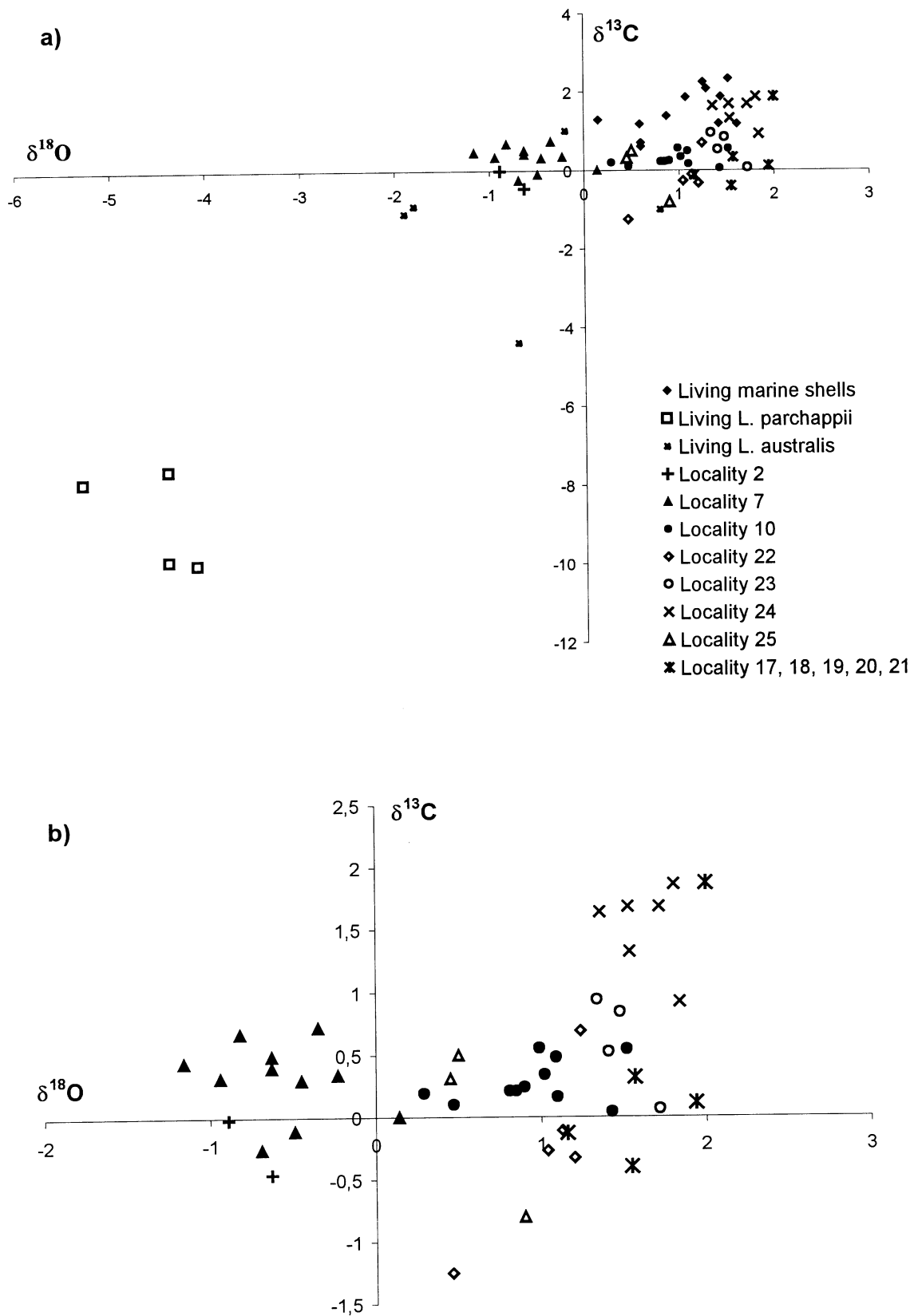


Fig. 2. a. The full $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ data set of the Holocene *Littoridina australis* and modern *Littoridina parchappii*, *Littoridina australis* and marine molluscs samples. b. The $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ data set of Holocene *Littoridina australis*.

a. Diagramme de $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ de tous les échantillons analysés de *Littoridina australis* de l'Holocène et de *Littoridina parchappii*, *Littoridina australis* et des mollusques marins vivants. b. Diagramme de $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$: exclusivement les échantillons des fossiles de l'Holocène de *Littoridina australis*.

Table 2
Isotope data of modern *L. parchappii*, *L. australis* and marine molluscs sampled. Marine shells come from an area where great freshwater input can be neglected excluding the samples of *M. isabellana* from Punta Rasa at the mouth of La Plata river. Isotope data of *M. isabellana* from Aguirre et al. (1998); isotope data of *L. parchappii* from Bonadonna et al. (1999).

Le tableau présente les données des compositions isotopiques des échantillons modernes de *Littoridina parchappii*, *Littoridina australis* et des mollusques marins. Les mollusques marins proviennent d'une zone où le mélange avec les eaux douces a eu un effet négligeable, à l'exception de *M. isabellana* espèce échantillonnée près de la rivière La Plata (Punta Rasa). Les données de la composition isotopique du *M. isabellana* sont de Aguirre et al. (1998) tandis que celles de la composition isotopique du *L. parchappii* sont de Bonadonna et al. (1999)

Living shells	Species	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰
Euryhaline			
Samborombon Bay (BS)	<i>Littoridina australis</i>	-0.94	-1.78
Samborombon Bay (BS)	'	-1.09	-1.89
LV1 Mar Chiquita (J&J)	'	-4.38	-0.67
LV3 Península Verde (PV)	'	0.10	-0.25
LV4 S. Antonio Oeste (SAO)	'	-1.03	0.76
Punta Rasa	<i>Mactra isabellana</i>	1.28	0.15
Mar del Plata	'	1.17	0.59
Freshwater			
Quequén Salado	<i>Littoridina parchappii</i>	-7.6	-4.4
Quequén Salado	'	-7.9	-5.3
Quequén Grande	'	-10.0	-4.1
Quequén Grande	'	-9.9	-4.4
Marine			
MAP2 Rada Tilly	<i>Protothaca antiqua</i>	0.7	0.6
'	<i>Protothaca antiqua</i>	0.6	0.6
'	<i>Brachidontes purpuratus</i>	1.85	1.07
'	<i>Brachidontes purpuratus</i>	2.07	1.29
'	<i>Patinigera magellanica</i>	2.56	1.67
'	<i>Patinigera magellanica</i>	1.38	0.87
'	<i>Buccinanops globulosus</i>	1.19	1.42
'	<i>Buccinanops globulosus</i>	1.17	1.61
MAP6 Bahía Lángara	<i>Patinigera magellanica</i>	1.86	1.44
'	<i>Patinigera magellanica</i>	2.24	1.25
'	'	2.32	1.52

$\delta^{18}\text{O}$ (of about 1‰) is observed between samples 86bis and 87bis, followed by a rise in $\delta^{18}\text{O}$ of about 0.7‰. Locality 24 is placed near the mouth of Mar Chiquita lagoon, with high percentages (~94%) of *L. australis* and occurrence of associated stenohaline marine molluscan taxa suggesting a poly- to mixopolyhaline environment. Carbon shows a progressive ^{13}C -depletion from the base to the top of the section. $\delta^{18}\text{O}$ values are very high and show oscillations of which the largest, of about 0.4‰, is observed from the base (sample 100) to sample 102. The radiocarbon ages indicate that part of the series roughly correlates with localities 7 and 10 in Samborombon Bay. Locality 22 is placed inside Mar Chiquita lagoon, showing maximum percentages (~99%) of *L. australis* for the whole area of study, suggesting a mixohaline environment. $\delta^{18}\text{O}$ values are quite constant, except for the sample 112 at the top of the section. $\delta^{13}\text{C}$ shows a trend towards a progressive depletion from the base to the top of the section, reaching minimum values in sample 112. Locality 23 also contains high percentages (~98%) of *L. australis*, $\delta^{18}\text{O}$ values are quite constant, increasing to the top, and $\delta^{13}\text{C}$ values show a similar progressive decreasing trend from the base to the top of the section. In all sections studied no covariance between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ was observed.

6. Discussion and conclusion

Fig. 2 shows the whole data set together with the isotope analyses from living *L. parchappii* [data from Bonadonna et al. (1999)], the freshwater counterpart of *L. australis*, collected in some Bonaerensean rivers. Living shells of *L. parchappii*, *L. australis* and marine samples outline a broad region in the $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ diagram that would show the mixing trend between fresh and marine waters. Several samples of the fossil *L. australis* shells plot in this region. The broad spectrum of the fossil isotope values may depend on local differences in the isotopic composition between the marine and continental waters. As a matter of fact today marine waters off the Bonaerensean coast have $\delta^{18}\text{O}$ values around -0.5‰ (Schmid et al., 1999) whereas rainwater shows values of about -5‰ (e.g. Rozanski et al., 1993). However, rivers can show a ^{18}O -enrichment due to evaporation (Bonadonna et al., 1999). In this area the DIC of freshwater is probably in the range of -7 to -10‰ (Bonadonna et al., 1999) whereas marine water off the coast has about 1–2‰ (e.g. Kroopnick, 1980). However, these values are only indicative because several local factors can concur in complicating the isotopic composition of mixed waters. Nevertheless, high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ suggest the prevailing

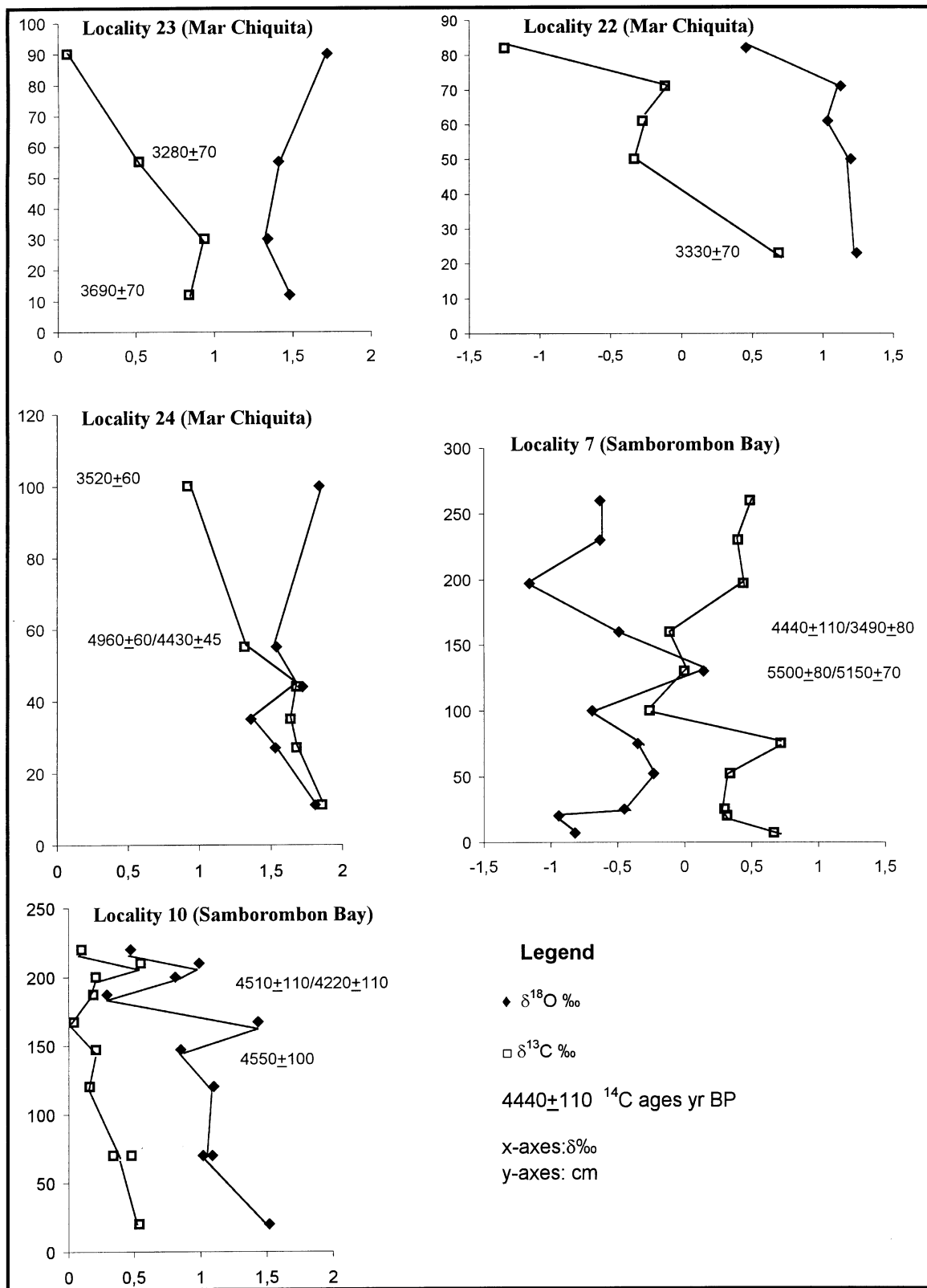


Fig. 3. Oxygen isotope composition vs depth of localities 7 and 10 (Samborombon Bay) and localities 22, 23 and 24 (Mar Chiquita lagoon). In the y-axis 0 cm refers to the base of the stratigraphic section.

Les compositions isotopiques vs la profondeur des coupes stratigraphiques 7 et 10 (Baie de Samborombon) et 22, 23, 24 (Lagune de Mar Chiquita). La base de la coupe stratigraphique est indiquée par 0 cm dans l'axe-y.

marine water component whereas ^{18}O and/or ^{13}C -depleted values can indicate a greater mixing with continental water.

In Punta Indio–Samborombon Bay area (i.e. localities 2 and 7) low $\delta^{18}\text{O}$ values indicate the importance of freshwater input through the Rio de La Plata and Samborombon and Salado rivers. This is especially shown by the Punta Indio samples with lower $\delta^{13}\text{C}$ and two samples from locality 7. These levels have a characteristic molluscan assemblage rich in warm-water taxa of Brazilian (warm water) affinity. These lower $\delta^{13}\text{C}$ values, respect to the shells from the same area, may hypothetically correspond to episodes characterized by supply of lower carbon isotope composition of the DIC of continental origin, generated by large vegetation development in the catchment area of the river during warmer phases. Samples from locality 10 are closer to the isotope values of marine shells, suggesting a stronger influence of marine water. It is interesting to note that, although samples from locality 7 show lower $\delta^{18}\text{O}$ values, the range of carbon is quite similar to that of locality 10. Low DIC concentration and/or progressive re-equilibration with atmospheric CO_2 of the freshwater member acting on locality 7 may each explain the observed trend.

Several samples from Mar Chiquita have both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ close to marine shells isotope values and should indicate salinity near the marine condition (i.e. $\sim 35\text{‰}$). However, this interpretation appears too simplistic when palaeoecological data are considered. Indeed, in the Mar Chiquita area *L. australis* prevails in the fossil assemblages indicating a typical salinity range of brackish environments, whereas assemblages from Samborombon Bay indicate higher salinity conditions. According to the mixing model, we expect lower isotopic values in Mar Chiquita than Samborombon Bay. Consequently, we suggest that high $\delta^{18}\text{O}$ values for the shells in Mar Chiquita originated in an environment fed by freshwater with low degree of mixing with marine water which experienced a moderate enrichment in H_2^{18}O caused by evaporation. Overall, the body of water did not reach elevate salinity as suggested by the faunal assemblages (dominance of *L. australis*; Fig. 1). The high $\delta^{13}\text{C}$ values can be explained in several ways. Progressive equilibration with atmospheric CO_2 can produce high $\delta^{13}\text{C}$ values (e.g. Turner et al. 1982). On the other hand, significant evaporation enhances CO_2 outgassing from a restricted body of water increasing the $^{13}\text{C}/^{12}\text{C}$ ratio in the DIC (Talbot, 1990). Moreover, biological activity and different recycling of organic matter during burial can also play a role in increasing $\delta^{13}\text{C}$ in local carbon budget (e.g. Keith and Parker, 1965; Hendry and Kalin, 1997).

This interpretation is also supported by the geological data that show Mar Chiquita palaeolagoon with an open connection to the Atlantic at ca. 5–4 ka, afterwards being progressively closed through the formation of barrier spits (e.g. Codignotto and Aguirre, 1993; Fasano et al., 1982). The progressive ^{13}C -depletion, from the base of the sections to the top, observable in the localities 22, 23 and 24 (Fig. 3) could be linked to an increase of local decay of organic

matter or an increase in the supply of DIC of continental origin in an environment that was becoming more and more enclosed. However, isotope differences among the different sections with comparable ages indicate (Fig. 3) the presence of several microenvironments. This situation is also recognizable at localities 10 and 7 in Samborombon Bay. However, in this case, the oscillations of $\delta^{18}\text{O}$ are quite large and according to the ^{14}C ages, quite rapid indicating rapid shift in the isotopic composition of the host waters. This may suggest that some external factors influence both localities. These oxygen isotope trends could have been driven by a change in freshwater input. During a period of greater rainfall an increase of river discharge, which would have locally diluted marine waters, led to lower $\delta^{18}\text{O}$ in the shells, whereas periods of decreasing rainfall would likely have generated higher $\delta^{18}\text{O}$ values in the shells owing to a greater influence of marine waters. Further, during a period of climatic optimum there was an intensified and southward displaced anticyclonic center in the south-western Atlantic (Irondo and García, 1993). The ‘amount effect’ in the rain due to the increased rainfall (Bonadonna et al., 1999) might have produced rainwater depleted in heavy isotope, so that the effect on the mixed water was amplified.

These data would suggest that, in the Bonaerensean region, some periods within the Holocene have been punctuated by short climatic phases characterized by a change in hydrological conditions. They are probably better recorded in areas where the original body of water is less influenced by evaporative phenomena that can buffer the effect of change in freshwater input. At the moment, this represents only a preliminary working hypothesis but our data suggest that careful selection of sites and more precise dating and sampling can give a record of changing freshwater discharge during the Holocene. Probably the most sensitive area would be located in Samborombon Bay, due to the presence of larger rivers.

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of *L. australis* (intertidal to upper infralittoral free epifaunal) are in general terms within the range observed from *Macra isabellana* (upper infralittoral moderately deep burrowing bivalve) from the same localities (Aguirre et al., 1998) and in agreement with other palaeontological and palaeobiogeographical evidence.

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References

- Aguirre, M.-L., 1993. Palaeobiogeography of the Holocene fauna from Northeastern Buenos Aires Province, Argentina: its relation to coastal evolution and sea level changes. *Palaeogeography, Palaeoclimatology, Palaeoecology* 102, 1–26.
- Aguirre, M.-L., 1996. Cambios ambientales y climáticos en la región costera bonaerense durante el Cuaternario tardío. Evidencias malacológicas. *Actas 1, IV Jornadas Geológicas y Geofísicas Bonaerenses (Junín)*, 35–45.
- Aguirre, M.-L., Farinati, E.-A., 2000. Aspectos sistemáticos, de distribución y paleoambientales de *Littoridina australis* (D'Orbigny, 1835) (Mesogastropoda) en el Cuaternario marino de Argentina (Sudamérica). *Geobios* 33 (5), 569–597.
- Aguirre, M.L., Whatley, R.C., 1995. Late Quaternary marginal marine deposits and palaeoenvironments from Northeastern Buenos Aires Province, Argentina: a review. *Quaternary Science Reviews* 14, 223–254.
- Aguirre, M.-L., Leng, M.-J., Spiro, B., 1998. Variation in isotopic composition (C, O and Sr) of Holocene *Macra isabelleana* (Bivalvia) from the coast of Buenos Aires Province, Argentina. *The Holocene* 8 (5), 613–621.
- Bonadonna, F.P., Leone, G., Zanchetta, G., 1999. Stable isotope analyses on the last 30 ka molluscan fauna from Pampa grassland, Bonaerense region, Argentina. *Palaeogeography, Palaeoclimatology, Palaeoecology* 153, 289–308.
- Brandt, D.S., 1989. Taphonomic grades as classification for fossiliferous assemblages and implications for paleoecology. *Palaios* 4, 303–309.
- Cadeé, G., 1984. 'Opportunistic feeding': a serious pitfall in trophic structure analysis of (paleo) faunas. *Lethaia* 17, 289–292.
- Codignotto, J.O., Aguirre, M.L., 1993. Coastal evolution, changes in relative sea level and molluscan fauna in northeastern Argentina during the Late Quaternary. *Marine Geology* 110, 163–175.
- Dodd, J.R., Stanton, R.J., 1975. Palaeosalinities within a Pliocene Bay. Kettleman Hills, California: A case study of the resolving power of isotopic and faunal techniques. *Geological Society of America Bulletin* 86, 51–64.
- Eisma, D., Mook, W.-G., Das, H.-A., 1976. Shell characteristics, isotopic composition and trace element contents of some euryhaline molluscs as indicators of salinity. *Palaeogeography, Palaeoclimatology, Palaeoecology* 19, 39–62.
- Fasano, J., Hernández, M., Isla, F., Schnack, E., 1982. Aspectos evolutivos y ambientales de la Laguna Mar Chiquita (Provincia de Buenos Aires, Argentina). *Acta Oceanológica SP*, 285–292.
- Garzoli, S.L., Giulivi, C., 1993. What forces the variability of the southwestern Atlantic boundary currents. *Deep-Sea Research* 41 (10), 1527–1550.
- Hendry, J.P., Kalin, R.M., 1997. Are oxygen isotopes of mollusc shells reliable palaeosalinity indicators in marginal marine environments? A case study from the Middle Jurassic of England. *Journal of the Geological Society*. London 154, 321–333.
- Hudson, J.D., Clements, R.G., Riding, J.B., Wakefield, M.I., Walton, W., 1995. Jurassic paleosalinities and brackish-water communities – a case study. *Palaios* 10, 392–407.
- Ingram, B.L., Ingle, J.C., Conrad, M.E., 1996. Stable isotope record of late Holocene salinity and river discharge in San Francisco Bay. *California. Earth and Planetary Science Letters* 141, 237–247.
- Iriondo, M., Garcia, O., 1993. Climatic variations in the Argentine plains during the last 18,000 years. *Palaeogeography, Palaeoclimatology, Palaeoecology* 101, 209–220.
- Keith, M.L., Parker, R.H., 1965. Local variation of ^{13}C and ^{18}O content of mollusk shells and the relatively minor temperature effect in marginal marine environments. *Marine Geology* 3, 115–129.
- Kroopnick, P., 1980. The distribution of ^{13}C in the Atlantic ocean. *Earth and Planetary Science Letters* 49, 469–484.
- Lloyd, R.-M., 1964. Variations in the oxygen and carbon isotope ratios of Florida Bay molluscs and their environmental significance. *Journal of Geology* 72, 84–111.
- Mook, W.G., Vogel, J.C., 1968. Isotopic equilibrium between shells and their environment. *Science* 159, 874–875.
- Olivier, R., Escofet, A., Penchaszadeh, P., Orensanz, J., 1968. Estudios Ecológicos De La Región Estuarial De Mar Chiquita (Buenos Aires, Argentina). I. Las Comunidades Bentónicas. *Anales Sociedad Científica Argentina* 193, 237–261.
- Olson, D.B., Podesta, G.P., Evans, R.H., Brown, O.B., 1988. Temporal variations in the separation of Brazil and Malvinas Currents. *Deep-Sea Research* 35 (12), 1971–1990.
- Rozanski, K., Araguás-Araguás, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Swart, P.-K., Lohmann, K.-C., McKenzie, J.-A., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records Geophysical Monograph* 78. pp. 1–36.
- Schmidt, G.-A., Bigg, G.-R., Rohling, E.-J. Global Seawater Oxygen-18 Database. <http://www.giss.nasa.gov/data/o18/data/> (1999). <http://www.giss.nasa.gov/data/o18/data/>
- Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chemical Geology* 80, 261–279.
- Turner, J.-V., Fritz, P., Karrow, P.-F., Warner, B.-G., 1982. Isotopic and geochemical composition of marl lake waters and implications for radiocarbon dating of marl lake sediments. *Canadian Journal of Earth Science* 20, 599–615.