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STABLE ISOTOPE COMPOSITION OF FRESHWATER MOLLUSK SHELLS FROM CENTRAL-WESTERN ARGENTINA

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ABSTRACT – The variability in $\delta^{18}O$ and $\delta^{13}C$ composition of modern and fossil mollusk shells in central-western Argentina was assessed in order to contribute to a better understanding of their value as paleoclimatic indicators. Living mollusks were collected from 17 sites distributed along a latitudinal/altitudinal gradient in Mendoza Province. Quaternary mollusks were obtained from five alluvial successions outcropping in river margins from the same area. Results indicated that $\boldsymbol{\delta}^{18}O_{shell}$ reflects the isotope composition of ambient water. For rivers, mollusks reflect the highly depleted isotopic values recorded in the catchment areas (glaciers). Mollusks inhabiting brackish lakes exhibited the maximum enrichment isotope values in coincidence with high evaporation. Variations in $\boldsymbol{\delta}^{13}C_{shell}$ were consistent with regional variations in productivity. No differences in $\delta^{18}O$ and $\delta^{13}C$ values were recorded among different species coexisting at the same site, suggesting that mollusks exhibit minor, if any, physiological fractionation effects. The high $\delta^{18}O$ values obtained in Late Pleistocene shells suggest an increased evaporation rate for this moment, in coincidence with the development of damp areas characterized by an increase of ice melting in a warmer phase. An ^{18}O enrichment together with a ^{13}C depletion was recorded during the Holocene, suggesting less productive paleoenvironments, probably due to the incidence of more arid conditions than present.

Key words: oxygen and carbon isotopes, semiarid, paleoenvironmental reconstruction, South America, Late Quaternary, Andean piedmont.

RESUMO – Variações de $\delta^{18}O$ e $\delta^{13}C$ em conchas de moluscos fósseis e atuais do centro-oeste da Argentina foram avaliadas a fim de se contribuir para a melhor compreensão do valor desses elementos como indicadores paleoclimáticos. Moluscos vivos foram coletados en 17 locais distribuídos ao longo de um gradiente latitudinal/altitudinal na Província de Mendoza. Moluscos quaternários foram obtidos em cinco depósitos aluviais aflorantes nas margens do rios desta região. Os resultados indicaram que os valores de $\delta^{18}O_{concha}$ refletem a composição isotópica da água do ambiente. Nos rios, os moluscos refletiram os valores isotópicos altamente empobrecidos, registrados nas áreas de captação (geleiras). Em lagos de água salobra, os moluscos apresentaram os valores máximos de enriquecimento de isótopos, que refletiram a alta taxa de evaporação. Variações nos valores de $\delta^{13}C_{concha}$ foram consistentes com variações regionais de produtividade. Diferenças nos valores de $\delta^{18}O$ e $\delta^{13}C$ não foram registradas entre espécies diferentes convivendo nos mesmos locais, sugerindo que moluscos exibem pouco ou nenhum efeito fisiológico ao fracionamento. Os altos valores de $\delta^{18}O$ obtidos em conchas do Pleistoceno Superior sugerem que uma taxa de evaporação mais elevada deve ter ocorrido neste intervalo de tempo, concomitantemente ao desenvolvimento de áreas úmidas e ao aumento no degelo que ocorreram em fase de temperatura mais quente. Um enriquecimento de ^{18}O, acompanhado por uma depleção de ^{13}C, foi registrado durante o Holoceno, sugerindo a existência de paleoambientes menos produtivos, provavelmente devido à incidência de condições mais secas do que no presente.

Palavras-chave: isótopos de oxigênio e carbono, semi-árido, reconstrução paleoambiental, América do Sul, Quaternário Superior, piemonte andino.

INTRODUCTION

The oxygen and carbon stable-isotope values of freshwater mollusk-shell carbonate ($\delta^{18}O$, $\delta^{13}C$) generally reflect the isotopic composition of ambient water (Fritz & Poplawski, 1974; Leng *et al*., 1999) and, therefore, constitute a powerful tool for palaeoenvironmental reconstruction. In particular, oxygen isotopes provide useful estimates of environmental temperature change by indicating the effect of temperature on evaporation. Relatively high $\delta^{18}O$ values are interpreted as indicating high evaporation/precipitation ratios, which are considered to reflect relatively warm, dry conditions, while relatively low values indicate cooler and moister times (Stuiver, 1968). Carbon isotopes, on the other hand, mainly reflect dissolved inorganic carbon (DIC) (Fritz & Poplawski, 1974; McConnaughey & Gillikin, 2008; Shanahan *et al*., 2005). This is partly because aquatic CO_2/O_2 ratios tend to be higher than those in air, causing aquatic animals to exchange away more of their respired CO_2 for environmental CO_2 during respiratory gas exchange. As the DIC pool is often changed by biological productivity within the water body, mainly by preferential take up of ^{12}C by aquatic plants and diatoms during photosynthesis, variations in $\delta^{13}C$ have been used as proxies of photosynthesis, respiration, decay, and paleoproductivity (see Miller & Tevesz, 2001 and references therein). Yet, in some lung-breathing snails and bivalves, shell carbonate is built mainly from respired CO_2 (Dettman *et al.*, 1999; Wurster & Patterson, 2001; Geist *et al.*, 2005), limiting the wide use of $\delta^{13}C_{shell}$ as environmental recorder. This led McConnaughey & Gillikin (2008) to conclude that the proper interpretation of carbon isotope records depends on context.

Besides the limitations stated above, stable oxygen and carbon isotope compositions of freshwater mollusk shells have been extensively used for reconstructing past environmental and climatic conditions in a variety of locations around the world (*e.g.* Abell & Williams, 1989; Abell & Hoelzmann, 2000; Tevesz *et al*., 1998; Leng *et al*., 1999; Zanchetta *et al*., 1999; Jones *et al.*, 2002; Baroni *et al.*, 2006; Wu *et al*., 2007; Hassan *et al*., 2012). In all cases, paleoenvironmental inferences were based on local data, because both oxygen and carbon isotope ratios vary geographically as consequence of fractionation in the precipitation which falls in different catchment basins. For oxygen isotope ratios, the latitude at which the rain falls (providing the host body of water for gastropods) together with the altitude at which precipitation occurs are probably the most important factors in determining the oxygen isotope ratios in freshwater gastropod shells (Abell & Williams, 1989).

Numerous deposits containing freshwater Quaternary mollusk shells are exposed in the margins of several rivers and streams in central Argentina, constituting valuable natural archives for understanding past environmental changes (*e.g.* Prieto *et al*., 2004; De Francesco *et al*., 2007; De Francesco & Hassan, 2009). Many of these deposits occur at different hydrological settings along gradients of aridity and altitude, and possess abundant mollusk shells whose stable isotope compositions remain nearly unknown. In fact, the only regional isotopic study conducted on Quaternary freshwater mollusk shells has been carried out in the humid Pampa plain (Bonadonna *et al*., 1999). This study supported the usefulness of isotope compositions as palaeoclimatic and palaeoenvironmental indicators in the area, by recognizing a change from dry to wet climate at about 9 ka BP as well as short climatic fluctuations caused by local circumstances.

In the present contribution, we report the first regional isotope study of modern and fossil freshwater mollusk shells from the semiarid region of central-western Argentina, between latitudes 32° and 36°S. The aim is to establish the paleoecological significance of the variability of oxygen and carbon isotopes in these shells to serve as a basis for palaeoclimatic and palaeohydrologic reconstructions for this region. The study area is particularly interesting from a paleoclimatic standpoint because covers a gradient of decreasing altitude from north to south of the Andes Cordillera, which constitutes the catchment area for precipitation. The area is included in the South American Arid Diagonal (Bruniard, 1982), a north-south climatic belt that registers the lowest humidity contribution from Atlantic and Pacific anticyclones. During the Late Quaternary, displacements and/or intensity variations of the circulation systems have triggered the extent and aridity of the Arid Diagonal, with great impact on the evolution of the regional vegetation cover (Abraham de Vazquez *et al*., 2000). In addition, climatic variations have also affected the dynamics of fluvial systems (Tripaldi *et al*., 2011), but their magnitude and temporal extent remain unknown.

STUDY AREA

The study area comprises the Mendoza Province and the western part of San Luis Province (Figure 1). The area is close to the Andes Cordillera, which shows a relative decrease in height from north (3500-4000 m at *circa* 33ºS) to south (3000 m at *circa* 37ºS). The climate is semiarid with a mean annual precipitation (rain and snow) of 240-250 mm. Precipitations are higher from late fall to early spring (snow) due to the much stronger influence of western (Pacific) conditions at high elevation sites (Masiokas *et al*., 2006; Garreaud *et al*., 2009). In southern Mendoza there are also short and intense rains during summer (Ostera & Dapeña, 2003). The mean annual temperature is 15.4ºC in the north (Mendoza city) and decreases to 12.5ºC in the south mainly due to the higher influence of the Pacific winds, as consequence of the lower height of the cordillera (Llancanelo region; Ostera & Dapeña, 2003; Capitanelli, 2005).

The area is cut across by several fluvial systems (Mendoza, Tunuyán, Diamante, Atuel, and Malargüe rivers) with their headwaters located in the high Andes Cordillera. The water discharges of these rivers depend mainly on glacial melting with a November to February (late spring-early summer) snowmelt peak that represents about 57% of the annual discharge (Masiokas *et al*., 2006). As snow comes from colder polar precipitation of Pacific origin (which has lower δ values) river waters exhibit lower $\delta^{18}O$ values in sites close to their headwaters (Andes Cordillera), and turn into higher values by evaporation in successive dams (Panarello & Dapeña, 1996).

MATERIAL AND METHODS

Both living and fossil (Quaternary) shells of the different species present in the area were analyzed for oxygen and carbon isotope composition. Sampling was intended to represent the maximum heterogeneity of aquatic environments in the area, that is, the whole range of variation in morphology, substrate, and flow (*e.g.* streams, rivers, springs, shallow lakes, ponds, dams, canals). The species were selected according to their natural abundance in each site.

Living mollusks

Living mollusks were collected from 17 sites distributed along a latitudinal/altitudinal (N to S) gradient (Figure 1): (i) northwestern Mendoza (sites 1-6, located in streams of the Río Tunuyán basin; (ii) central-eastern Mendoza (sites 7-8, located on the Río Diamante basin); and (iii) southern Mendoza (sites 9-16) located within the Río Atuel and Río Malargüe basins; the Llancanelo saline lake is included here). Additionally, we sampled a shallow brackish stream (Arroyo Bebedero, site 17) in San Luis Province to compare

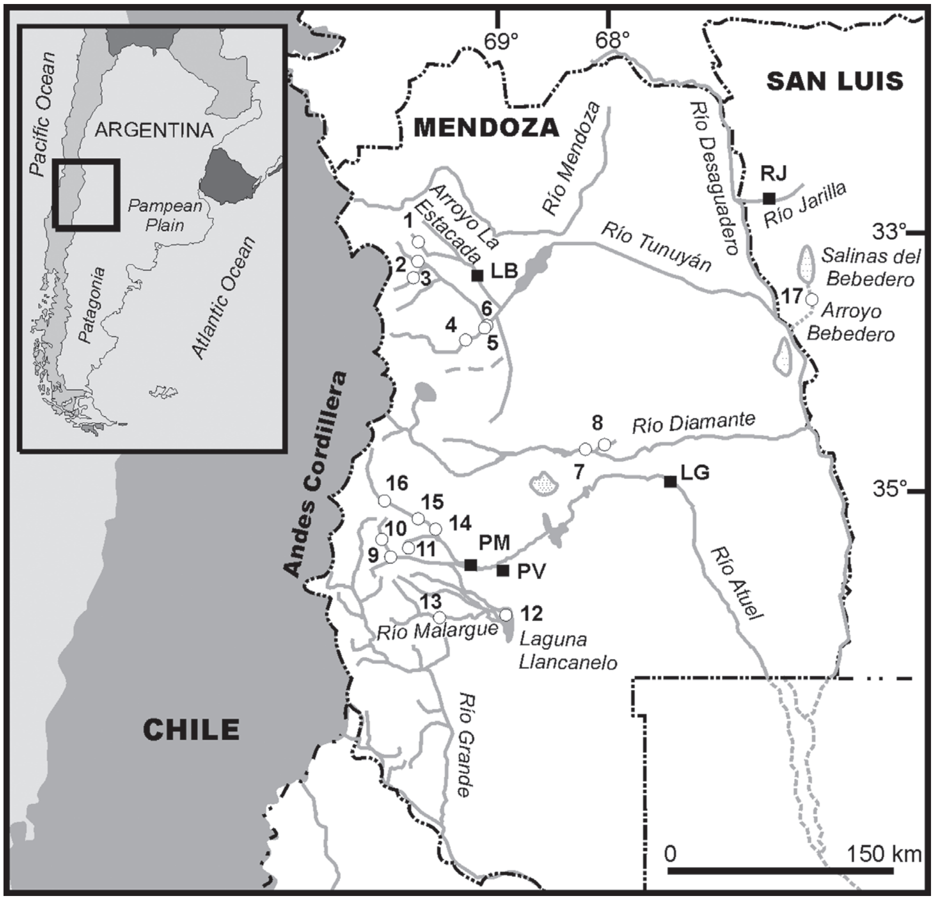

Figure 1. Location map of modern (white circles) and Quaternary (black squares) study sites in central-western Argentina. **Abbreviations: LB,** La Bomba; **LG**, La Guevarina; **PM**, Puesto Moya; **PV**, Puesto Vicencio; **RJ**, Río Jarilla.

isotopic values in highly evaporated systems of semiarid regions located eastwards.

Mollusks were collected both by hand and with the aid of sieves (0.5 mm). Both gill-breathing and lung-breathing mollusks were collected according to their abundance in the field. Gill-breathing aquatic mollusks represented in central-western Argentina corresponded to the hydrobioids *Heleobia hatcheri* (Pilsbry, 1911), *H. kuesteri* (Ströbel, 1874), *H. parchappii* (d'Orbigny, 1835) and the bivalve *Pisidium chiquitanum* Ituarte, 2001. In general, *Heleobia* snails are highly adaptive and particularly sensitive to their environment, being found in a wide variety of aquatic environments such as springs, streams and shallow lakes. The two former snail species (*H. hatcheri* and *H. kuesteri*) together with *P. chiquitanum* are strictly freshwater species (conductivities of 0.5-1.2 mS cm^{-1}) inhabiting streams and springs (De Francesco & Hassan, 2009). *Heleobia hatcheri* is a typical Patagonian species, Mendoza being its northernmost natural limit. On the other hand, *H. parchappii* appears to be adapted to extreme conditions such as brackish waters (8-16 mS cm^{-1}) in Laguna Llancanelo and Arroyo Bebedero (De Francesco & Hassan, 2009). Three pulmonate species *Chilina mendozana* Strobel, 1874, *Lymnaea viator* d'Orbigny, 1835 and *Physa acuta* Draparnaud, 1805 are common in freshwater lotic and lentic environments from central-western Argentina. *C. mendozana* and *P. chiquitanum* occur in lotic habitats (streams and rivers) where a directional water flow exists, while *L. viator* and *P. acuta* are more common in lentic habitats (shallow lakes) or calm backwaters (pools) within lotic systems such as streams and rivers (De Francesco & Hassan, 2009).

In order to assess the environmental significance of isotopic data, at each site, current velocity, depth, water temperature, pH, conductivity, aquatic vegetation cover (estimated visually and quantified as a nominal variable as 0=no vegetation, 1=low vegetation cover, and 2=high vegetation cover), organic content (estimated using the loss-on-ignition method, LOI; Heiri *et al*., 2001), and chemical variables (NO_3^-, SO_4^{2-}, Cl^-, F^-, PO_4^{3-}, HCO_3^-, Mg^{2+}, Ca^{2+}, SiO_2, and hardness) were measured (Table 1). The isotopic composition ($\delta^{18}O$ ratios) of water in the area was obtained from previously published works (Vogel *et al*., 1975; Panarello & Dapeña, 1996; Ostera & Dapeña, 2003).

Fossil mollusks

Fossil mollusks were obtained from five Quaternary alluvial successions outcropping in the same area covered by modern samples (Figure 1): La Bomba (**LB**), Puesto Vicencio (**PV**), La Guevarina (**LG**), Puesto Moya (**PM**), and Río Jarilla (**RJ**).

Table 1. Values obtained for environmental variables in the modern sampling sites. **Abbreviations: Cond**, conductivity (mS cm^{-1}); **Temp**, water temperature (°C), Depth (cm); **Cur**, current velocity (m s^{-1}); **Veg**, vegetation cover; **Hard**, hardness (mg l^{-1} of CaCO3); **LOI**, organic content (%). Concentrations of ions are expressed in mg l^{-1} (modified from De Francesco & Hassan, 2009).

Site	Cond	pH	Temp	Depth	Cur	Veg	Hard	LOI
1-Arroyo Guajardino	0.33	8.25	13.5	6	0.00	2	184.0	7.87
2-Río Las Tunas	0.64	8.06	18.2	40	1.00	2	373.0	5.00
3-Arroyo del Medio	0.75	8.05	17.1	150	0.27	2	321.0	5.31
4-Arroyo Vista Flores	1.21	7.87	16.0	6	0.10	1	451.0	7.81
5-Arroyo Guiñazu	0.74	8.10	16.5	49	0.43	2	240.0	4.27
6-Arroyo Caroca	0.81	7.88	17.0	75	1.00	2	420.0	3.53
7-Presa del Tigre	0.71	7.71	19.0	20	0.38	2	314.0	1.00
8-Arroyo Gaby	0.76	8.17	19.3	85	0.16	2	333.0	3.95
9-Lag. Los Molles	0.79	7.81	21.6	26	0.00	2	323.0	4.32
10-Vertiente Molles	0.62	7.47	14.5	3	1.00	0	338.0	1.21
11-Lag. Niña Encantada	0.76	7.72	11.7	55	0.67	2	337.0	3.33
12-Lag. Llancanelo	8.68	7.87	19.9	25	0.00	0	598.0	2.95
13-Vertiente Malargüe	0.72	7.93	16.0	5	0.10	2	248.0	2.23
14-Arroyo Sosneado	0.79	8.11	14.3	14	0.17	2	415.0	2.38
15-Vertiente Sosneado	0.80	8.24	19.3	7	0.17	2	343.6	1.69
16-Lag. Sosneado	0.22	9.40	22.3	20	0.10	2	144.4	5.58
17-Arroyo Bebedero	16.00	7.66	20.6	20	0.00	0	3764.0	5.44

Table 1. Cont.

Site	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	F^-	HCO^{3-}	SiO_2	Ca^{2+}	Mg^{2+}
1-Arroyo Guajardino	13.1	123.0	6.80	0.01	1.45	123.6	10.7	10.0	38.1
2-Río Las Tunas	26.3	280.0	0.50	0.00	1.76	231.7	48.0	34.9	68.5
3-Arroyo del Medio	39.5	286.0	5.35	0.22	1.24	239.4	56.3	22.0	63.8
4-Arroyo Vista Flores	145.0	525.0	0.50	0.21	0.70	409.4	61.4	33.8	88.0
5-Arroyo Guiñazu	26.3	324.0	0.00	2.54	1.54	301.2	48.7	23.2	43.6
6-Arroyo Caroca	59.3	204.5	0.50	0.00	2.38	224.0	54.6	28.2	83.8
7-Presa del Tigre	85.7	315.0	0.00	0.17	1.62	131.3	12.7	20.5	63.1
8-Arroyo Gaby	98.9	117.0	11.70	0.00	1.17	168.0	11.6	35.1	58.8
9-Lag. Los Molles	115.4	68.8	4.97	0.00	1.55	594.0	34.5	31.8	58.4
10-Vertiente Molles	214.0	11.2	0.96	0.00	0.64	610.0	16.5	62.4	43.6
11-Lag. Niña Encantada	26.3	392.0	12.80	0.00	0.70	231.0	28.5	133.0	1.1
12-Lag. Llancanelo	427.4	1670.0	1.41	0.00	2.42	139.0	5.6	90.0	89.7
13-Vertiente Malargüe	27.0	124.0	0.00	0.00	1.30	278.0	38.0	13.3	51.5
14-Arroyo Sosneado	39.5	256.0	0.00	0.00	0.69	160.0	34.4	27.2	83.2
15-Vertiente Sosneado	26.3	342.0	0.00	0.08	1.45	226.0	50.7	36.5	60.5
16-Lag. Sosneado	46.1	79.5	0.00	0.13	0.50	58.6	43.7	17.2	24.3
17-Arroyo Bebedero	7717.0	2140.0	0.00	0.02	1.39	150.8	72.7	345.0	695.0

The LB succession (33°28′S, 69°03’W), which records the interval between circa 35 ^{14}C ka BP and 31 ^{14}C ka BP (Table 2), crops out on the right margin of Arroyo La Estacada, a tributary of Río Tunuyán (in the area of modern sites 1-6; Figure 1). The succession, which is 3 m high, was analyzed in detail by De Francesco *et al*. (2007). In that article, the $\delta^{18}O$ and $\delta^{13}C$ shell composition of the freshwater snail *Lymnaea viator* was analyzed in 14 discrete levels (LB1-LB14) located in the lowest 2 m of the profile. Additional new data on $\delta^{18}O$ and $\delta^{13}C$ composition of the freshwater planorbid *Biomphalaria peregrina* (d'Orbigny, 1835) and the land microsnail Vargas-Almonacid, 2000 *Radiodiscus quillajicola* were also analyzed here in order to assess interspecies variability.

The PV, LG and PM successions, which testimony the Late Glacial, early Holocene and Late Holocene, respectively (Table 2), crop out on the right margin of Río Atuel in southern Mendoza (Figure 1). Freshwater mollusks are very scarce and restricted to a few sedimentary

Table 2. Radiocarbon dates from the five successions analyzed in central-western Argentina.

Sample no.	Depth (m)	Lab no.	^{14}C age BP ± SD	Material dated	Source
La Bomba (LB)					
LB1	0.10	AA61397	31,570±440	*Succinea meridionalis* (d'Orbigny, 1835)	De Francesco *et al*. (2007)
LB7	1.85	AA61398	31,520±520	*Lymnaea viator*	De Francesco *et al*. (2007)
LB9	2.20	AA61399	35,460±740	*Succinea meridionalis*	De Francesco *et al*. (2007)
LB12	2.65	AA61400	35,170±670	*Lymnaea viator*	De Francesco *et al*. (2007)
Puesto Vicencio (PV)					
PV4	1.85	AA73236	12,148±34	*Chilina mendozana*	this work
PV14	3.25	AA73235	6575±73	organic sediments	this work
La Guevarina (LG)					
LG18	8.30	AA58288	8420±60	organic sediments	Paez et al. (2010)
LG30	11.25	Beta-215660	9190±40	organic sediments	Paez et al. (2010)
Puesto Moya (PM)					
PM10	0.45	AA73237	904±33	organic sediments	Hassan *et al.* (2013)
PM6	0.82	AA73238	1238±33	organic sediments	Hassan *et al.* (2013)
PM4	1.00	AA73233	1727±34	*Lymnaea viator*	Hassan *et al.* (2013)
PM3	1.10	AA73239	2890±32	organic sediments	Hassan *et al.* (2013)
Río Jarilla (RJ)					
RJ19	1.80	LP1173	9280±80	*Chilina mendozana* + *Heleobia parchappii*	Chiesa *et al*. (2010)

levels, characterized by the presence of abundant partially decayed vegetation matter. The PV succession (35°13′S, 69°06′W), which has a total height of 7.84 m, only recorded abundant shell material in a sedimentary layer located at approximately 1.85 m in depth (De Francesco & Dieguez, 2006). Shells of the species *Chilina mendozana* (dated in 12,148±34 ^{14}C years BP) and *Heleobia kuesteri* from that level were analyzed here. The LG succession (34°44′S, 68°02′W), which represents the interval between 9190±40 and 8420±60 ^{14}C years BP (Paez *et al*., 2010), has a total height of approximately 15 m, with mollusks recorded at 8.30 m (De Francesco, 2010). Five levels containing *H. parchappii* and *C. mendozana* were analyzed here. The PM succession (35°15′S, 69°14′W) has a total height of 4.67 m, and is composed of eight sedimentary levels, of which only one dated in 1727±34 ^{14}C years BP (located at 1 m) contained shells of the pulmonate *Lymnaea viator* (De Francesco & Dieguez, 2006) and was analyzed in the present contribution.

The RJ succession is located on the right margin of Río Jarilla, close to its opening into Río Desaguadero in San Luis Province (Figure 1). We analyzed a single level containing shells of *H. parchappii* and *C. mendozana*, dated in 9280±80 years ^{14}C BP (Chiesa *et al*., 2010; Table 2).

Isotope analysis

Isotope analysis (δ^{18}O and δ^{13}C) of modern mollusk shells (24 samples) were carried out at the Laboratorio de Isótopos Estables, INGEIS (Buenos Aires, Argentina). Different species (the gill-breathing snails *Heleobia kuesteri*, *H. parchappii*, and *H. hatcheri*, the gill-breathing bivalve *P. chiquitanum* and the lung-breathing snails *Chilina mendozana* and *Lymnaea viator*) were analyzed in order to examine the variability in shell chemistry of different taxa living in the same environment, caused by different physiological effects or growth periods. Fossil mollusk shells (*H. kuesteri*, *H. parchappii*, *C. mendozana*, *L. viator*, *Biomphalaria peregrina*, and the land snail *Radiodiscus quillajicola*) from PM, PV, and RJ (five samples) were also carried out at the INGEIS, while those from LB (15 samples) and LG (five samples) were carried out at the INSTAAR Stable Isotope Laboratory, University of Colorado (USA).

In all cases, isotopic analyses were performed on a number of 5-10 individuals for each sample (in order to reach the minimum sample size required by the laboratories). Shell samples were washed in deionized water and hand-brushed. The washed shells were then individually crushed to a fine powder in mortar and pestle and sent to the laboratories for isotopic analyses. The standard deviation was ±0.06 for ^{13}C and ±0.1 for ^{18}O at INSTAAR, and ±0.1 for both ^{13}C and ^{18}O at INGEIS. Isotope values (δ^{18}O and δ^{13}C) are reported as per mil (‰) deviations of the isotope ratios (^{18}O/^{16}O, ^{13}C/^{12}C) from standards (VPDB).

Data analysis

Differences in δ^{18}O and δ^{13}C values among northern, central and southern Mendoza as well as among species were evaluated with one-way ANOVAs. When assumptions of normality and homoscedasticity were not met, data were analyzed with the Kruskal-Wallis test. In order to search for latitudinal differences, a Principal Component Analysis (PCA) based on the environmental variables measured, was performed. Environmental data were log transformed, as log (x+1). All analyses were carried out with the computer program PAST v 1.81 (Hammer *et al*., 2008).

RESULTS

$\delta^{18}O$ and $\delta^{13}C$ values of modern shells from central-western Argentina

$\delta^{18}O$ values varied between −15.9‰ and +2.4‰ (Table 3; Figure 2A). In most samples (22 out of 24) values ranged between −15.9‰ and −11‰ (all corresponding to species inhabiting oligohaline habitats). The other two values, which showed the highest isotope values of the dataset (-0.8‰ and +2.4‰), corresponded to shells of the hydrobioid snail *H. parchappii* collected alive from two brackish environments (8-16 mS cm^{-1}) subject to high evaporation (Laguna Llancanelo and Arroyo Bebedero). Excluding these two brackish sites, the comparison of $\delta^{18}O$ values among basins indicated the existence of significant differences (Kruskal-Wallis, H=12.3; p=0.002). In fact, the $\delta^{18}O$ values of shells from southern Mendoza were higher (mean=-13.2‰) than those obtained from northwestern Mendoza and central-western Mendoza (mean=-15.5 to -14.8‰), which did not differed between them. These results agreed with the differences observed in $\delta^{18}O_{water}$ among these same areas (Table 4), suggesting that $\delta^{18}O_{shell}$ is reflecting $\delta^{18}O_{water}$. Similarly, $\delta^{13}C$ varied from -14.4‰ to -2.1‰ (Table 3) showing differences among basins (ANOVA, F=54.05; p< 0.0001). In this case, shells from northwestern Mendoza had the lowest $\delta^{13}C$ values, which ranged from -14.4‰ to -10.8‰ (mean=-12.3±1.2‰), followed by those from southern Mendoza, which varied between -13.2‰ and -7.4‰ (mean=-9.5±1.9‰). On the other hand, the shells from central-eastern Mendoza displayed the highest $\delta^{13}C$ values (-4.2‰ to -3‰; mean=-3.6±0.5‰).

The first two components of the PCA ordination (Figure 3) accounted for 47.6% of the variation in the data. The first component explained 32.3% of the total variation and exhibited a strong positive correlation with conductivity and hardness (r=0.41). In addition, this component was negatively correlated with vegetation cover (r=-0.32) and, to a lesser extent, with pH (r=-0.21). The second component, which explained 15.3% of total variation, was positively correlated with HCO_3^- (r=0.34), and negatively with LOI (r=-0.37), temperature (r=-0.35), pH (r=-0.35), SO_4^{2-}, depth, PO_4^{2-}, F^-, and vegetation cover (r=-0.20 to -0.30).

In the PC1×PC2 plot (Figure 3), sites from northwestern Mendoza were placed towards the left bottom corner, indicating that they are characterized by higher vegetation cover, pH, and PO_4^{2-} compared to southern sites, which were mostly located towards the left top corner. The only exception was site 16 that corresponded to a highly vegetated shallow lake. Sites 7 and 8 were located in the middle of the plot. The brackish sites 12 and 17 were displaced towards the right of the diagram, as they were characterized by higher hardness and conductivities.

Except for *Heleobia parchappii*, we did not find substantial interspecies differences in the $\delta^{18}O$ values of mollusk shells (ANOVA, F=2.13; p=0.14; Figure 4). Average $\delta^{18}O$ values for *Heleobia hatcheri*, *H. kuesteri*, *Chilina mendozana*, *Lymnaea viator*, and *Pisidium chiquitanum* varied between -15.3‰ and -13.1‰. Similarly, no interspecies differences were found in the $\delta^{13}C$ values of mollusk shells (ANOVA, F=2.24; p=0.12), suggesting that $\delta^{13}C$ may be also controlled by environmental variables. This is evident in the convergent isotopic values recorded in those sites where different species coexist (*i. e.* in site 7 the species *C. mendozana*, *H. hatcheri*, and *H. kuesteri* displayed $\delta^{18}O$ values of -15.3‰, -15.4‰, and -15.6‰, and $\delta^{13}C$ values of -3.5‰, -4.2‰ and -3.0‰, respectively; Table 3).

Table 3. Isotopic composition of modern shells from central-western Argentina. **Abbreviations: chi**, *Chilina mendozana*; **hat**, *Heleobia hatcheri*; **kue**, *Heleobia kuesteri*; **par**, *Heleobia parchappii*; **lym**, *Lymnaea viator*; **pis**, *Pisidium chiquitanum*. For reference on site numbers see Figure 1.

Sample no.	$\delta^{13}C$	$\delta^{18}O$
1-lym	-14.4	-15.0
2-kue	-12.7	-14.7
3-hat	-12.1	-15.6
3-kue	-12.0	-15.4
4-chi	-11.5	-15.4
4-pis	-13.1	-15.9
5-lym	-13.4	-11.5
6-hat	-11.0	-14.5
6-kue	-10.8	-15.3
7-chi	-3.5	-15.3
7-hat	-4.2	-15.4
7-kue	-3.0	-15.6
8-chi	-3.5	-15.7
9-lym	-13.2	-13.2
10-hat	-9.9	-13.6
11-chi	-7.8	-12.9
11-lym	-9.9	-13.1
12-par	-3.9	-0.8
13-hat	-9.8	-11.0
14-chi	-7.8	-14.1
14-hat	-7.4	-14.3
15-pis	-10.7	-12.3
16-lym	-9.5	-11.8
17-par	-2.1	2.4

Table 4. Average $\delta^{18}O$ isotopic composition (‰) of water and modern shells from central-western Argentina. **Abbreviations:** [a]Panarello and Dapeña (1996); [b]Vogel et al. (1975); [c]Ostera and Dapeña (2003).

Sample no.	$\delta^{18}O_{water}$	$\delta^{18}O_{shell}$
Northwestern Mendoza (Tunuyán River)	-16.7[a]	-14.8
Central-eastern Mendoza (Diamante and Atuel Rivers)	-17.3[b]	-15.5
Southern Mendoza (Atuel and Malargue Rivers)	-15.4[c]	-13.2
Llancanelo Lake	+0.5[c]	-0.8

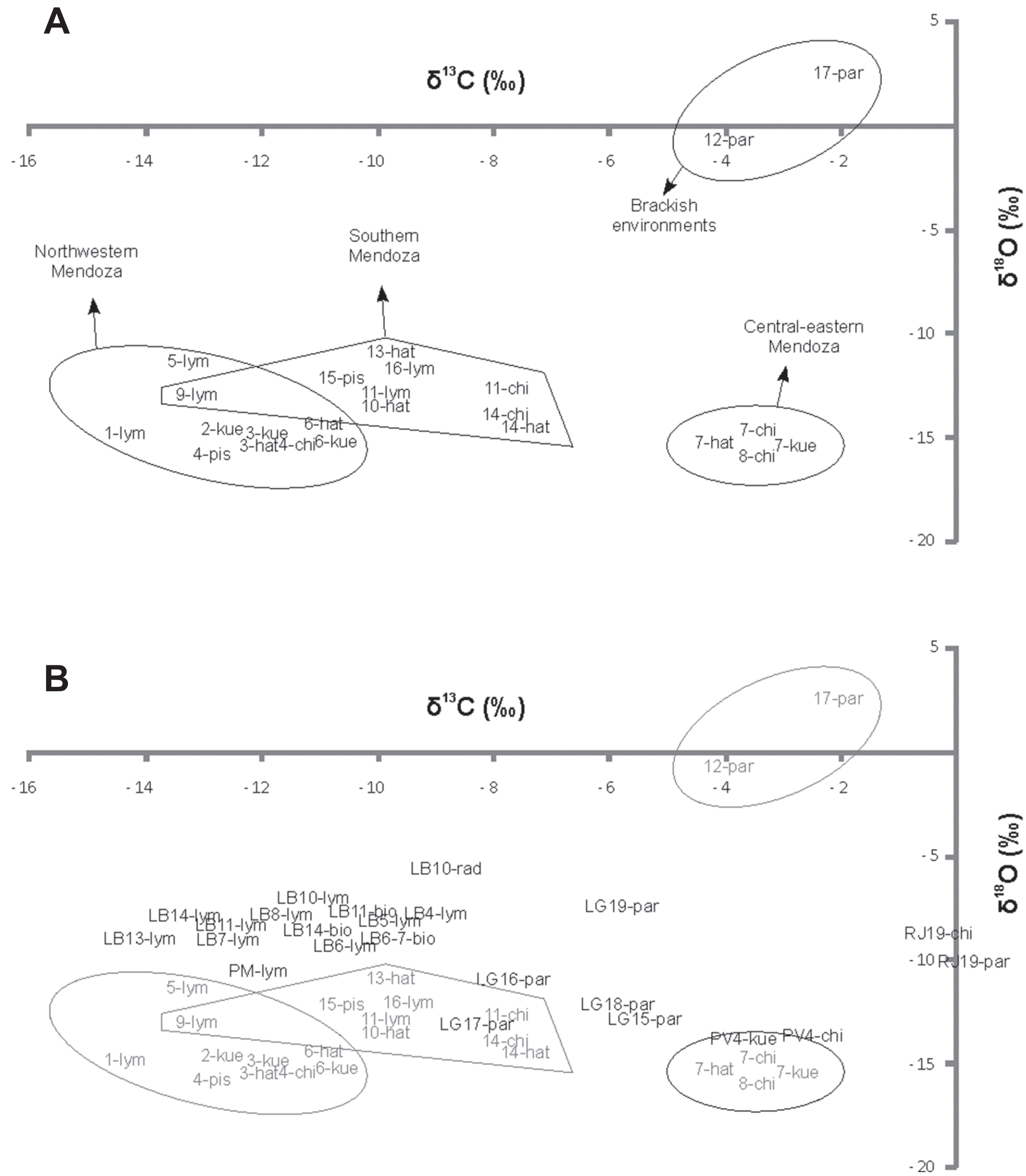

Figure 2. δ18O versus δ13C for shell carbonate from central-western Argentina. **A**, modern samples. **B**, fossil samples. **bio**, *Biomphalaria peregrina*; **chi**, *Chilina mendozana*; **hat**, *Heleobia hatcheri*; **kue**, *Heleobia kuesteri*; **lym**, *Lymnaea viator*; **par**, *Heleobia parchappii*; **pis**, *Pisidium chiquitanum*; **rad**, *Radiodiscus quillajicola*.

δ^{18}O and δ^{13}C values of fossil shells from central-western Argentina

Overall, δ^{18}O values of shells varied between −14.0‰ and −5.8‰ (Table 5; Figure 2b) being within the range of modern shells. The lowest values corresponded to the successions outcropping on the margins of Río Atuel (PV, LG, PM) in southern Mendoza. On the other hand, most levels from LB and RJ exhibited higher values. δ^{13}C varied from -14.1‰ to +0.4‰. The highest values were recorded at PV and RJ successions, while LG, PM and LB displayed lower values.

When fossil levels are plotted together with modern sites (Figure 2b) no exact correspondence is observed. Most fossil shells had relatively higher δ^{18}O values than modern ones. The only exception was PV, which appeared plotted relatively close to modern sites 7 and 8 (Río Diamante). In this succession, different species (the gill-breathing *H. kuesteri* and the pulmonate *C. mendozana*) coincided in their isotope values. Similarly, the LG succession showed δ^{18}O values similar to those of PV only in some levels, but values were significantly higher for the lowermost LG19 level.

On the other hand, the fossil successions were clearly separated along the δ^{13}C axis. LB and PM showed the lowest values and were located towards the left half, close to modern sites from Río Tunuyán and southern Mendoza, while RJ exhibited the highest values, that were outside the range of modern shells (between -0.3‰ and +0.4‰). LG and PV showed intermediate positions along this axis.

The δ^{18}O isotopic composition of the samples analyzed in LB ranged from −8.9‰ to −7.1‰ while the δ^{13}C values varied between −14.1‰ and −8.7‰ (Figure 5; Table 5).

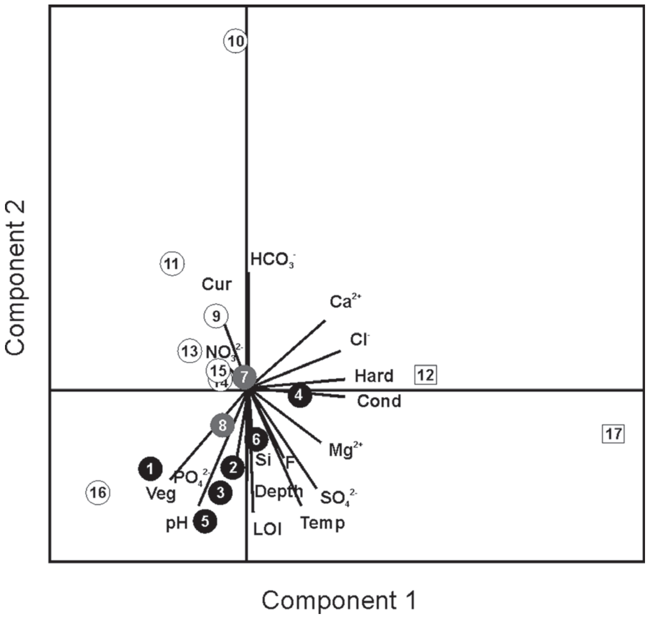

Figure 3. Principal Component Analysis (PCA) ordination plot showing the relationship between sampling sites (circles and squares) and environmental variables (arrows). Black circles: sites from northwestern Mendoza; grey circles: sites from central-eastern Mendoza; white circles: sites from southern Mendoza; white squares: brackish sites (Laguna Llancanelo and Arroyo Bebedero). **Abbreviations: Cond**, conductivity; **cur**, current velocity; **hard**, hardness; **veg**, vegetation cover; **temp**, temperature. For site numbers see Figure 1.

A subtle increase in δ^{13}C was observed from the bottom to the top of the analyzed section (*ca.* 31 ka). As mentioned above these δ^{13}C values were similar to the modern values recorded in modern shells from the same area (Tunuyán basin).

A gradual increase in δ^{18}O values from the oldest (PV; mean= -13.8‰) to the youngest alluvial succession (PM; -10.6‰) was recorded along the Río Atuel sites. On the other hand, a decrease in δ^{13}C values (from -3.1‰ to -12.0‰) was exhibited in this same direction (Figure 5).

The unique level analyzed in RJ (Desaguadero Basin) showed similar values for the two species sampled. δ^{18}O values were between -9.7‰ and -8.8‰. δ^{13}C values were relatively high, close to zero (Table 5). This level showed the highest δ^{13}C values of all sequences.

DISCUSSION

δ^{18}O and δ^{13}C values of modern shells from central-western Argentina

Modern shells from Mendoza Province exhibited a latitudinal increase in δ^{18}O values from north (mean=-15.5 to -14.8‰) to south (mean=-13.2‰). These differences coincided with previous results obtained for the isotopic composition of running waters in these two areas (Table 4) and reflect the relative decrease in height of the Andes Cordillera. In fact, δ^{18}O values from Tunuyán River (Andes Cordillera = 3500-4000 m) are lower (from -17.8‰ in winter to -15.6‰ in summer; Panarello & Dapeña, 1996) than those from Malargüe River (-14.9‰ to -14.4‰; Ostera & Dapeña, 1996) where the Andes Cordillera is approximately 3000 m high. Vogel *et al.* (1975) pointed out that the ^{18}O contents of the Andean rivers clearly reflect the altitude of the catchment areas, the extreme values being δ^{18}O =-19.2‰ for Río Mendoza which drains the highest part of the Central Andes (see Figure 1) and δ^{18}O = -11.4‰ for Río Negro which originates from the less elevated Patagonian Andes (at ~40° S). Between 2000 and 4000 m the decrease in ^{18}O is about 0.3‰ per 100 m (Vogel *et al.*, 1975). Consequently, the δ^{18}O of freshwater mollusk shells faithfully reflect the δ^{18}O of ambient water and, therefore, constitute good paleoenvironmental indicators.

High δ^{18}O values (close to zero or higher) appear to be indicators of brackish water conditions, as can be seen in the results obtained in *Heleobia parchappii* shells from Laguna Llancanelo and Arroyo Bebedero. The former is a saline water body situated at a mean altitude of 1300 m in southern Mendoza, and constitutes the most important lentic environment in the region. The lake waters have the maximum enrichment isotope values of the area (*δ*^{18}O=+0.5‰; Ostera & Dapeña, 2003). Although we do not have at present information on the isotope composition of waters from Arroyo Bebedero,

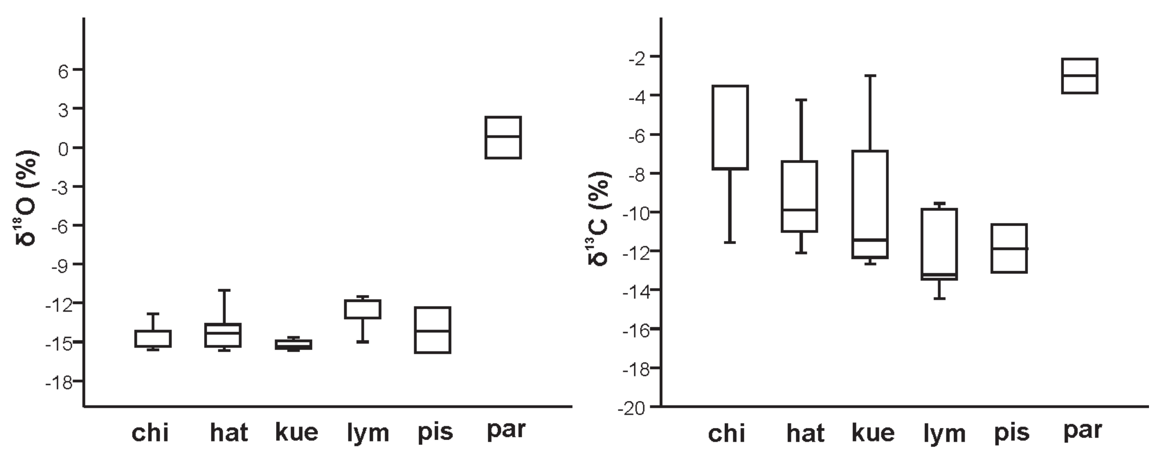

Figure 4. Box plot comparisons of isotopic data (δ^{18}O and δ^{13}C) among species. The upper and lower margins of the box indicate the 25-75 percent quartiles. The line through box indicates the median. **Abbreviations: chi**, *Chilina mendozana*; **hat**, *Heleobia hatcheri*; **kue**, *Heleobia kuesteri*; **lym**, *Lymnaea viator*; **pis**, *Pisidium chiquitanum*; **par**, *Heleobia parchappii*.

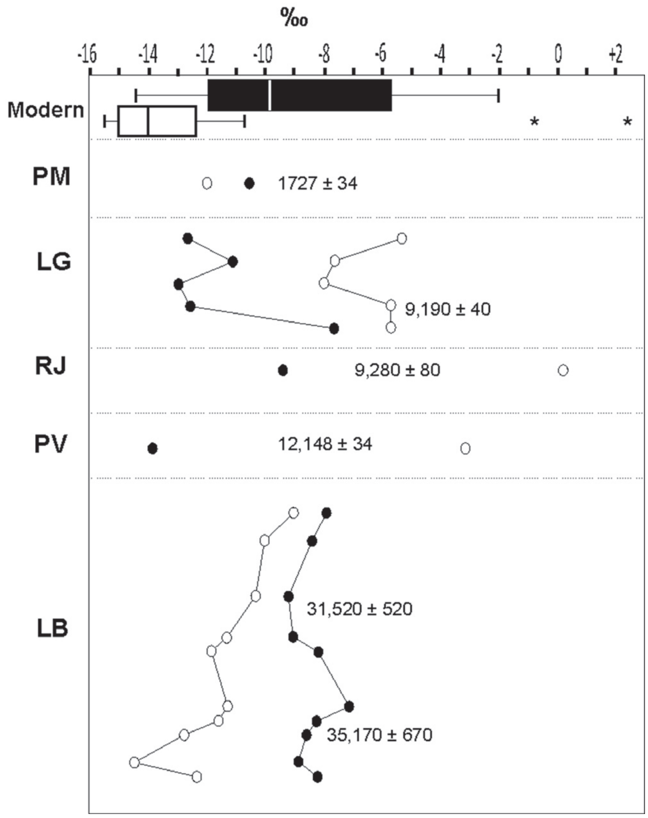

Figure 5. Changes in δ18O (black) and δ13C (white) through time in mollusk shells from central-western Argentina. Asterisks indicate outliers. **Abbreviations: LB**, La Bomba; **PV**, Puesto Vicencio; **LG**, La Guevarina; **PM**, Puesto Moya; **RJ**, Río Jarilla.

the observed high conductivity (16 mS/cm) combined with its shallow depth (20 cm) suggest a similar behavior to that of Llancanelo. High $\delta^{18}O_{water}$ values in these aquatic systems are consequence of the high evaporation that takes place in these systems, and constitute a common feature in semiarid areas. In a previous contribution, De Francesco (2010) pointed out that fossiliferous levels composed exclusively of *H. parchappii* shells (the unique species that inhabits brackish water bodies in the region) may be indicating the development of brackish water conditions in the past. According to the results obtained here, we conclude that those fossil shells should also exhibit relatively high $\delta^{18}O$ values, bringing an additional support to the previous interpretation based solely on ecological aspects.

The $\delta^{13}C$ composition of modern shells showed a regional pattern of variation with shells from northwestern Mendoza having the lowest values (mean=-12.3‰), followed by those from southern Mendoza (mean=-9.6‰) and central-eastern Mendoza (mean=-3.5‰). As water bodies from northwestern Mendoza are highly productive (the PCA indicated that sites from this area were characterized by higher vegetation cover, LOI and PO_4^{2-}) the low $\delta^{13}C$ values obtained here may be consequence of organic matter oxidation (which is enriched in ^{12}C). In fact, this process can lead to very low $\delta^{13}C_{DIC}$ in the water due to release of ^{12}C from dead plants (Leng & Marshall, 2004). On the other hand, the higher $\delta^{13}C$ values obtained in shells from central and southern Mendoza, and also the brackish waterbodies of Laguna Llancanelo and Arroyo Bebedero may be responding to a lower effect of organic matter oxidation in a less productive environment. An additional increase in ^{13}C concentration may also occur in the water body as consequence of preferential evaporative loss of the ^{12}C (lighter isotope).

The quite homogeneous values (for both $\delta^{18}O$ and $\delta^{13}C$) recorded by different species in the same environment supports the idea that freshwater mollusks exhibit minor, if any, physiological fractionation (vital) effect. This is advantageous to paleontologists because allows combining isotopic information gathered from different species without affecting the interpretation. This is particularly useful in Quaternary freshwater successions, where different species usually succeeded each other or eventually are represented in some levels and absent in others. The similarity in isotope composition values showed by aquatic species in the fossil record (*e.g.* the gill-breathing *Heleobia kuesteri* and the pulmonate *Chilina mendozana* from PV) reinforces this previous conclusion. Although in the present study we did not sample living terrestrial snails it can be noted from fossil data (level LB10) that $\delta^{18}O$ values of the terrestrial microsnail *Radiodiscus quillajicola* appear to be higher than those from aquatic snails. This is consistent with the fact that land snails do not inhabit running waters with $\delta^{18}O$ values resembling those of the catchment areas in the high Andes cordillera, but land microhabitats subject to different humidity and temperature because of the influence of local precipitation. The $\delta^{18}O$ composition of land snail shell carbonate is closely related to the isotopic composition of rain plus the temperature-dependent fractionation between aragonite and water (Goodfriend & Ellis, 2002).

$\delta^{18}O$ and $\delta^{13}C$ values of fossil shells from central-western Argentina

The LB succession showed higher $\delta^{18}O$ values (mean= -8.4±0.6‰) than modern samples (mean=-14.8±1.3‰) and $\delta^{13}C$ values (mean=-11.3±1.5‰) relatively similar to those of modern samples (mean=-12.3±1.2‰) from the same area. The higher $\delta^{18}O$ values in these fossil shells can be accounted for by a temperature rise, which, in turn, is associated with ^{18}O enriched meteoric precipitation. This is based on their ^{14}C ages, which fall between 34 and 31 ka, and clearly prove this series was deposited during an interstadial (Marine isotope stage 3) of the last glacial cycle with wetter and warmer climatic conditions than the present time (De Francesco *et al.*, 2007; Tripaldi *et al.*, 2011). In such scenery, water bodies would have been subjected to intense evaporation. Oxidation of organic matter in the water body would have played an important role in lowering $\delta^{13}C$ values. The most important changes in $\delta^{13}C$ along the section appear associated with changes in the $\delta^{18}O$ record, which again suggest an indirect climatic control. In fact, the most negative values were recorded at the bottom of the section (*ca.* 35 ka) with an increasing trend towards the top (*ca.* 31 ka), probably related with an increase in evaporation as consequence of higher temperatures. This is also supported by diatom analyses,

Table 5. Isotopic composition of fossil shells from central-western Argentina. **Abbreviations: bio**, *Biomphalaria peregrina*, **chi**, *Chilina mendozana*; **kue**, *Heleobia kuesteri*; **par**, *Heleobia parchappii*; **lym**, *Lymnaea viator*; **rad**, *Radiodiscus quillajicola*; **LB**, La Bomba; **LG**, La Guevarina; **PM**, Puesto Moya; **PV**, Puesto Vicencio; **RJ**, Río Jarilla.

Sample no.	$\delta^{13}C$	$\delta^{18}O$	Sample no.	$\delta^{13}C$	$\delta^{18}O$
LB04 lym	-9.0	-7.9	LG15 chi	-5.4	-12.6
LB05 lym	-9.9	-8.4	LG16 chi	-7.7	-11.0
LB06 lym	-10.5	-9.3	LG17 chi	-8.1	-12.9
LB06 bio	-9.9	-9.1	LG18 par	-5.8	-12.5
LB07 lym	-12.5	-8.9	LG19 par	-5.8	-7.6
LB07 bio	-9.8	-9.1			
LB08 lym	-11.6	-8.2	PV4 chi	-2.5	-13.7
LB10 lym	-11.1	-7.1	PV4 kue	-3.7	-14.0
LB10 rad	-8.7	-5.8			
LB11 lym	-12.6	-8.5	PM2 lym	-12.0	-10.6
LB11 bio	-10.2	-8.0			
LB12 lym	-12.5	-8.5	RJ19 chi	-0.3	-8.8
LB13 lym	-14.1	-8.9	RJ19 par	0.4	-9.7
LB14 lym	-13.2	-8.1			
LB14 bio	-11.0	-8.3			

which showed a tendency for increasing ionic strength and temperature towards the top of the section (Hassan *et al*., 2013). These findings are consistent with the development of a swamp environment, probably a very shallow and ephemeral water body subject to occasional submersions within a semi-temporary regime.

The three Holocene successions outcropping on the right margin of Río Atuel (PV, LG and PM) showed an inverse trend in $\delta^{18}O$ and $\delta^{13}C$ values. The gradual increase in $\delta^{18}O$ from the oldest (LB) to the youngest (PM) alluvial succession suggests an increase in evaporation, while the decrease in $\delta^{13}C$ may indicate a gradual increase in the productivity of water bodies. Both interpretations are consistent with a gradual increase in regional temperature, which may have favored both evaporation and development of vegetation in shallow swampy environments. There is evidence that the climate was windier and more arid during the last glacial maximum (*ca.* 24-12 ka) (Tripaldi *et al*., 2011) leading to the development of less productive and stressful environments. The poor preservation exhibited by shells (De Francesco & Hassan, 2009) is in agreement with this interpretation. Moreover, it is highly probable that these shells represent reworked concentrations (from older successions) that were redeposited in PV through episodic flood events, as suggested by the inverted ages obtained in this succession (Table 2). In LG (ca. 9 ka), *Chilina mendozana* shells are also present but accompanied by *Heleobia parchappii* and *Biomphalaria peregrina* shells. Although $\delta^{18}O$ values did not vary substantially along the section $\delta^{13}C$ values showed a subtle decrease in this direction, suggesting a temporal increase in productivity. In PM (*ca.* 1.7 ka) $\delta^{13}C$ values decreased while $\delta^{18}O$ increased in correspondence with a relatively increase in paleoproductivity probably related to an increase in temperature. This interpretation agrees well with the presence of *Lymnaea viator* in PM that suggests a vegetated shallow lake within the floodplain not connected to the main fluvial system (De Francesco & Hassan, 2009).

RJ (9280±80 years ^{14}C BP) exhibited high $\delta^{18}O$ values (mean=-9.2‰) in coincidence with a relatively high evaporation rate, but not as high as present-day conditions of Arroyo Bebedero. This suggests that the waterbodies developed in RJ during the early Holocene would have exhibited lower conductivities than modern ones, due to the higher availability of fresh water in the basin. The provenance of this water may be related to the overflow waters of Río Desaguadero, which nowadays is a large collector of ice-melt water from the Cordillera de los Andes, between 28°S and 33°S (García, 1999). The glacial growth in the Andes under global cold conditions led to a large amount of seasonal meltwater through the Desaguadero River, partially flowing into the Salinas del Bebedero basin by the Arroyo Bebedero stream. This inflow generated high Late Pleistocene lacustrine stages, whose ages agree with other evidence of glacial advances on the Andes (González & Maidana, 1998). According to the high $\delta^{13}C$ values obtained here (which were outside the range of modern shells) water bodies would have been poorly vegetated, supporting the previous idea of adverse conditions related to the cold climate associated to the early Holocene.

CONCLUSIONS

The $\delta^{18}O$ composition of Quaternary mollusk shells from central-western Argentina provides information concerning general climatic conditions prevailing at the time the mollusk lived, as fluvial shells faithfully reflects the highly depleted isotopic values recorded in the catchment areas (glaciers from the Andes Cordillera). Consequently, this constitutes an indirect potential method to infer paleoprecipitation and related changes in atmospheric circulation patterns. On the other hand, enriched isotope values recorded in closed basins (lakes) appear to be indicative of evaporative processes. This becomes a very useful tool in semiarid regions where most environmental changes are related to variations in precipitation-evaporation (P-E) rates. In addition, the magnitude of the $\delta^{18}O$ values recorded in shells from lakes (usually *Heleobia parchappii*) provides indication of the paleosalinity of the water body.

The interpretation of the isotope composition of Quaternary mollusk shells from the area, based on the modern results obtained here, coincides with previous explanations carried out on the basis of paleoecological and sedimentological studies (De Francesco *et al*., 2007; De Francesco & Hassan, 2009) bringing additional support to the validity of isotope data for paleoenvironmental and paleoclimatic inferences. This work suggests that isotope composition of freshwater mollusk shells brings valuable information for discussing past changes in large-scale atmospheric circulation patterns during the Late Pleistocene and the Holocene. Further study should be aimed to investigate temporal variations in isotope composition of mollusk shells along more complete sedimentary successions of closed-basin origin (such as Laguna Llancanelo).

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