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Late Pleistocene–Holocene environmental conditions in Lanzarote (Canary Islands) inferred from calcitic and aragonitic land snail shells and bird bones

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ABSTRACT

Aragonitic and calcitic land snails from carbonate-rich paleosols in northwestern Lanzarote (Canary Islands) were analyzed for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios to deduce the Pleistocene–Holocene transition in the westernmost Sahara zone. Modern, mid-late Holocene (~2.1–5.5 cal ka BP) and late Pleistocene (~23.3–24.0 cal ka BP) aragonitic shells exhibited respective values of -9.5 ± 1.6‰, -7.7 ± 1.5‰, and -2.3 ± 2.8‰ for $\delta^{13}C$; and $+0.3 \pm 0.3$‰, $+0.1 \pm 0.7$‰, and $+2.5 \pm 0.4$‰ for $\delta^{18}O$. Holocene and Pleistocene calcitic shells of the endemic slug *Cryptella canariensis* showed respective values of -0.7 ± 2.6‰ and -8.5 ± 2.5‰ for $\delta^{13}C$; and $+0.8 \pm 1.5$ and $+3.6 \pm 0.4$‰ for $\delta^{18}O$. Both aragonitic and calcitic shells showed equivalent temporal isotopic trends. Higher $\delta^{13}C$ values during ~23.3–24.0 cal ka BP suggest higher abundance of C_4 and/or CAM plants, likely associated with drier conditions and/or lower atmospheric CO_2 concentration. Maximum shell $\delta^{18}O$ values during ~23.3–24.0 cal ka BP opposes minimal values of Greenland ice cores and probably reflect the combined effects of (1) higher rain $\delta^{18}O$ values linked to higher glacial seawater $\delta^{18}O$ values and/or larger snail activity during summer seasons; (2) relative humidity values similar or slightly lower than at present; (3) higher evaporation rates; and (4) cooler temperatures. Bone remains of the extinct Dune Shearwater *Puffinus holeae* were only recovered from the Holocene bed. Collagen $\delta^{13}C$ and $\delta^{15}N$ values (-13.5 ± 0.2‰[PDB] and $+13.7 \pm 1.0$‰[air], respectively) match with the signature of a low trophic level Macaronesian seabird that fed upon local fish. Bone carbonate $\delta^{13}C$ (-7.4 ± 1.0‰[PDB]) and phosphate $\delta^{18}O$ ($+18.2 \pm 0.4$‰[SMOW]) values exhibited pristine signals denoting their potential value in future paleoenvironmental studies in the region. The age of *P. holeae* (~2.1–2.7 cal ka BP) supports that the aboriginal population possibly caused its extinction. In contrast, the extinction of the endemic helicid *Theba* sp. (~23.3–24.0 cal ka BP) was likely caused by environmental change.

1. Introduction

The great majority of land snails contain shells composed of aragonite, which is a thermodynamically unstable orthorhombic polymorph of calcium carbonate (e.g., Falini et al., 1996). Even so, aragonitic land snail shells are often well preserved in Quaternary paleontological and archeological sites, and therefore, they are suitable for paleoenvironmental studies (see reviews in Goodfriend, 1992, 1999). Some laboratory studies however have observed that crystals of calcite and occasionally vaterita can be deposited in scar repairs during land snail shell regeneration (Saleuddin and Wilbur, 1969). In exceptional cases, land snails contain shells that are entirely made of calcite, which is a more durable (less soluble in water) trigonal polymorph of calcium carbonate (e.g., Falini et al., 1996). In the eastern Canary Islands, the internal shell of slugs of the endemic genus *Cryptella* (Gastropoda: Parmacelidae) are constituted by calcite crystals. These calcitic shells of slugs have been preserved jointly with numerous aragonitic shells of many native land snail species in Quaternary eolian deposits of the easternmost islands of the Canary Archipelago. Hence, this material offers an exceptional opportunity to evaluate potential geochemical differences between calcitic and aragonitic sympatric land snail shells in deep time. The carbon and oxygen isotopic composition of land snail aragonitic shells has been increasingly investigated both in field and laboratory settings since the pioneer work of Yapp (1979). The carbon isotope composition ($\delta^{13}C$) of land snail shells is primarily influenced by the $\delta^{13}C$ values of the consumed and assimilated vegetation (Stott, 2002; Metref et al., 2003). The isotopic offset between shell and diet is about 14‰ (Stott, 2002; Metref et al., 2003; Yanes et al., 2008a). This offset may be larger if other potential factors like limestone ingestion contribute in the $\delta^{13}C$ values of the shell (e.g.,

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Yanes et al., 2008a). On the other hand, the stable oxygen isotope composition ($\delta^{18}O$) of land snail aragonitic shells is mainly influenced by the $\delta^{18}O$ values of the rainfall and water vapor, temperature and relative humidity (Yapp, 1979; Balakrishnan and Yapp, 2004; Balakrishnan et al., 2005a,b). The $\delta^{18}O$ values of the shell are several per mil higher than local rainwater, which reflects the effects of evaporation (e.g., Zaarur et al., 2011). The scale of the isotopic offset between rain and shell may be larger in arid locales in which evaporation processes are enhanced. Also, the isotopic scatter of shell $\delta^{18}O$ values of various contemporaneous individuals appears to be larger in drier environments (e.g., Yanes et al., 2009). To sum up, the oxygen isotopic composition of land snail shells is affected by multiple environmental factors operating jointly and may be difficult to understand. Despite inherent difficulties, aragonitic shells provide atmospheric information at the soil–air interface during snail active periods relevant for paleoclimatic studies. The majority of published paleoenvironmental studies using land snails have focused on aragonitic shells whereas well-preserved calcitic shells have received little attention. In the present study, several endemic species of aragonitic and calcitic shells of Quaternary land snails from Lanzarote (Canary Islands) were analyzed for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios (1) to evaluate potential isotopic differences between aragonitic and calcitic land snail shells, and (2) to explore late Pleistocene–Holocene paleoenvironmental conditions in the westernmost Sahara zone. Moreover, the bioclastic sediments in which shells were preserved were also analyzed for comparison with mollusk shells. Finally, the bone collagen, bone carbonate and bone phosphate of some vertebrate remains found in the same bed were also isotopically analyzed to further evaluate the environmental context of the studied time-intervals. Data are compared with published local snail studies and regional and global proxy data. The results from this study are relevant to paleontologists and archeologists interested on using continental shells to deduce past tropical–subtropical atmospheres.

2. Methods

2.1. Geographical and environmental setting

Lanzarote is the easternmost island of the Canary Archipelago, located at the latitude of 29°02′N and the longitude of 13°37′ W, about 125 km west from Moroccan coast (Fig. 1A). Lanzarote is a semiarid island with relatively low altitude (~670 m above sea level [a.s.l.]) that does not permit the formation of a moisture cloud sea as occur in central and western islands. Climate data for the recording period 1972–2000 from Arrecife Airport meteorological station (http://www.aemet.es) indicate that mean annual temperature is ~20 °C, annual precipitation is ~109 mm, and average relative humidity is ~71% (Fig. 2). Maximum relative humidity values are over 91% in the study area. The weighted $\delta^{18}O$ value of the rainfall in the Canary Islands is ~−3.5‰ (SMOW), on average (Yanes et al., 2008a, 2009, 2011). Lanzarote is dominated by vegetation adapted to arid conditions, which includes many native succulent-type plants and grasses that follow CAM and C_4 photosynthetic pathways, although C_3 plants largely dominate the landscape (Yanes et al., 2008a).

2.2. Study site and sampling protocol

In the Fuente de Gayo locality, at 460 m (a.s.l.) in northwestern Lanzarote (Fig. 1A), two newly discovered paleosols (Fig. 1B) containing abundant Quaternary fossils of land snail shells and some vertebrate remains were investigated. These paleosols likely contain a mixture of (1) marine and continental aragonite and calcite minerals, (2) clays, (3) minerals derived from weathering of local volcanic rocks, and (4) silt (e.g., quartz) coming from the nearby Sahara (e.g., Damnati et al., 1996; Williamson et al., 2004; Yanes et al., 2011). The upper (youngest) paleosol, named LGA-2 (Fig. 1B), is a brownish–yellowish ~100-cm-thick-paleosol with abundant endemic land snail shells and some bone remains. The lower (oldest) layer, LGA-1 (Fig. 1C), is a reddish

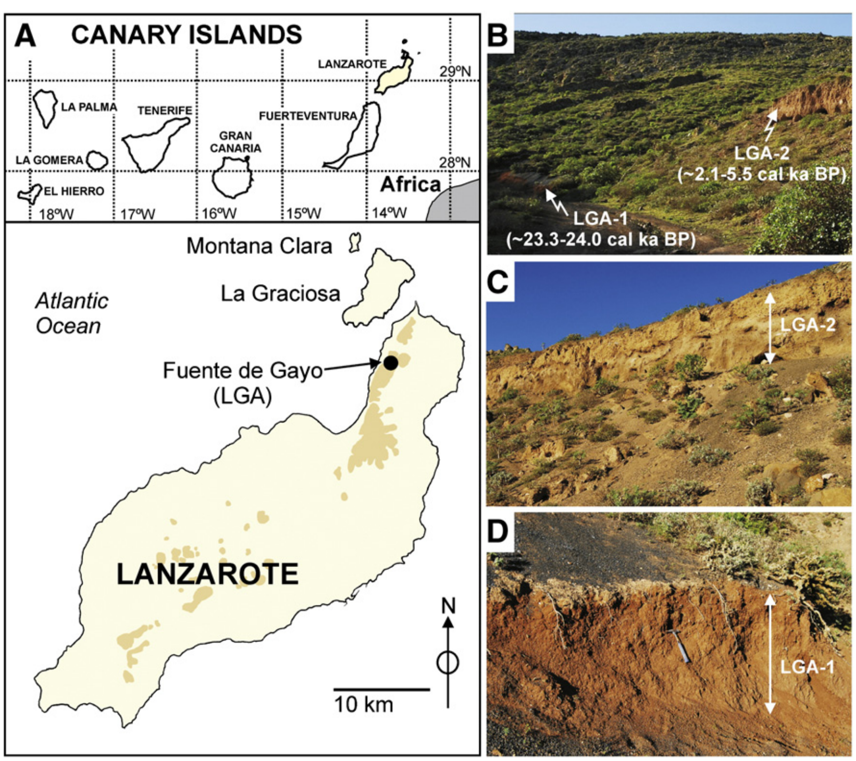

Fig. 1. Geographical location of the study site and field photographs. (A) Map of Lanzarote Island. (B) General view of the two studied paleosols from the Fuente de Gayo. (C) Close-up view of the youngest paleosol (LGA-2). (D). Close-up view of the oldest paleosol (LGA-1). Asterisks in panels C and D depict where samples were collected from each paleosol.

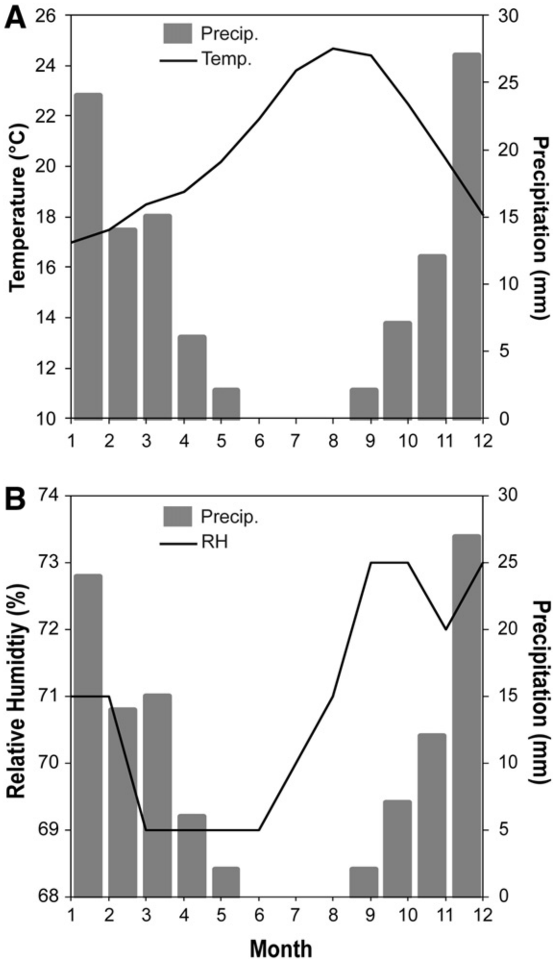

Fig. 2. Current climatic conditions in Lanzarote. Data was adapted from the meteorological station of Arrecife Airport (http://www.aemet.es) for the recording period from 1972 to 2000. (A) Mean monthly air temperature (solid line) and monthly precipitation (gray bars). (B) Mean monthly relative humidity (solid line) and monthly precipitation (gray bars).

~150-cm-paleosol containing numerous endemic land snail shells. These paleosols are not developed on the top of bioclastic dunes (Fig. 1B), as the eolian deposits studied by Yanes et al. (2011). Shelly assemblages are loosely packed and poorly sorted. Fossil shells were collected by dry-sieving sediments using a 1 mm mesh diameter. Shells from the outcrop surface were avoided to prevent from collecting reworked shell material. Vertebrate remains were only preserved in the upper paleosol LGA-2 whereas no bones were found in the lower paleosol LGA-1.

Nineteen entire shells (15 aragonitic and 4 calcitic) from LGA-2 and 20 entire shells (16 aragonitic and 4 calcitic) from LGA-1 were selected for isotopic analyses. Five endemic land snail species were studied: the helicids *Hemicycla flavistoma* Ibáñez & Alonso, 1991 (Fig. 3A), *Theba geminata* (Mousson, 1857) (Fig. 3B), and *Theba* sp. (Fig. 3C), the cochlicelid *Monilearia monilifera* (Webb & Berthelot, 1833) (Fig. 3D), and the parmacelid *Cryptella canariensis* Webb & Berthelot, 1833 (Fig. 3E). The first four species contain aragonitic shells whereas the later is a slug with an internal shell formed of calcite, confirmed by x-ray diffraction analyses of modern and fossil shells. All species live today in the region except *Theba* sp. (Fig. 3C), which is extinct. Modern specimens of dead organisms of the species *T. geminata* and *M. monilifera* from the same locality were also analyzed isotopically for comparison with local fossil material. In addition, bulk bioclastic sediments in which shells were preserved were analyzed for comparison with mollusk shells. Carbonate phases from these sediments are basically made of a mixture of marine and continental calcite and aragonite minerals (e.g., Damnati et al., 1996; Williamson et al., 2004; Yanes et al., 2011). Finally, three bones of the extinct Dune Shearwater *Puffinus holeae* Walker, Wragg & Harrison 1990 (J.C. Rando, personal communication, 2013) recovered from the upper paleosol (LGA-2) were studied to further explore the environmental context of this locale and age-interval.

2.3. Radiocarbon dating

Two fossil (buried) land snail shells of the small-size species *M. monilifera* and one bone sample of the fossil bird *P. holeae* were selected for radiocarbon analyses to estimate the age of the fossil material. The species *M. monilifera* (Fig. 3D) was chosen because it is a small species (smaller than 5 mm of shell length) and therefore, it is expected to incorporate less dead carbon into the shell than species with larger and thicker shells (Pigati et al., 2004, 2010). Nevertheless, the shell of one live-collected *M. monilifera* specimen was also radiocarbon dated to evaluate if the target species assimilated significant amounts of dead carbon. AMS radiocarbon analyses were conducted in the Poznan Radiocarbon Laboratory of Poland, using standard procedures. Radiocarbon data were calibrated using the *CALIB 6.1* (Stuiver and Reimer, 1993) program and the Marine09 calibration curve for the seabird bone, and IntCal09 for terrestrial shells. For the seabird sample, a local reservoir correction of $DR = 135 \pm 103$ obtained from samples between Portugal and Mauritania (above and below the Canary Archipelago) was additionally applied.

2.4. Stable isotope analyses

2.4.1. Mollusk shells

The sampling strategy in this study focused on the isotopic analysis of numerous entire shells recovered from each shell bed rather than on

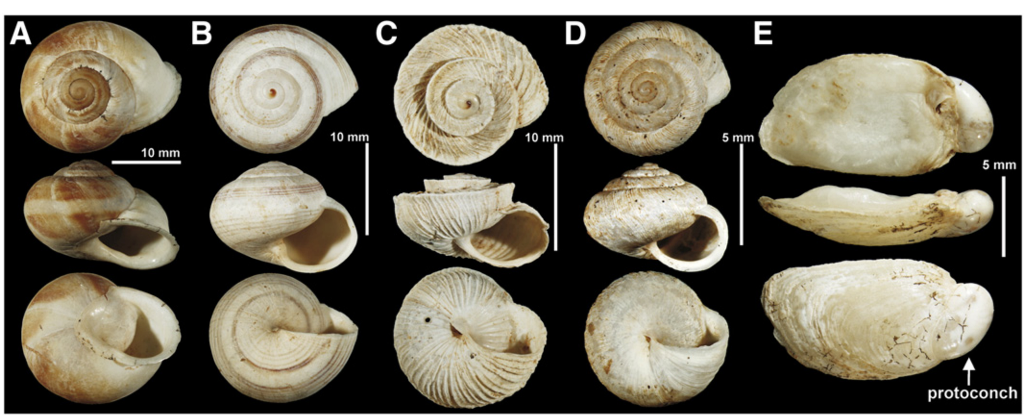

Fig. 3. Photographs of endemic land snail species analyzed isotopically. Aragonitic shells: (A) *Hemicycla flavistoma*. (B) *Theba geminata*. (C) The extinct *Theba* sp. (D) *Monilearia monilifera*. Calcitic shell: (E) *Cryptella canariensis*.

intra-shell analyses of a low number of individuals. The selected sampling approach is justified by several arguments. First, most species studied here are short-lived (annual to biannual), and therefore, the time averaging represented in the entire-shell analysis should be minimal. Second, the isotopic composition of mollusk shells may vary with ontogeny as a result of decreasing growth rates with increasing age (Goodwin et al., 2003; Schöne et al., 2003). Likewise, different contemporaneous specimens may differ in intrashell isotopic profiles (and in entire-shell values) as a consequence of differing ontogenetic stages. Specimens measured for this study were all mature adults, as revealed by the thickened lip in the aperture. Considering the short lifespan of the target species and the advanced ontogenetic stage of selected specimens, analyzed snails should represent reasonably comparable ontogenetic stages. Third, mollusks grow during seasons that are more favorable for them (e.g., Goodwin et al., 2003; Schöne et al., 2003). However, snails from Lanzarote currently live under a range of temperatures of 17–25 °C, and RH values always above 70% (Fig. 2) that allow them to be active almost year round, except slugs, which are difficult to find during the driest season (personal field observations, 2010–2012). Nonetheless, a rationally large number of specimens were measured per age interval to partially compensate potential seasonal and ontogenetic variations among contemporaneous specimens. Consequently, entire-shell analyses were preferred over intra-shell isotopic analyses along ontogeny for this study.

Samples were prepared and analyzed in the Instituto Andaluz de Ciencias de la Tierra (CSIC-Universidad de Granada). Shells were cleaned in deionized water and ultrasonication and subsequently oven-dried at 40 °C overnight. Entire shells were finely ground by hand using an agate mortar and pestle. About 5 mg of carbonate powder was placed in a 12 ml Exetainer vial that was subsequently flushed with helium. The carbonate was converted to CO_2 gas by adding 0.1 ml of 100% H_3PO_4 at 25 °C. The resulting CO_2 was analyzed after 24 h using the GasBench II connected to the Finnigan Delta^{PLUS} XP isotope ratio mass spectrometer (IRMS). Stable isotope results are reported in δ notation relative to the international standard Pee Dee Belemnite (PDB). The δ values are defined as:

$$\delta^{13}C \text{ or } \delta^{18}O \quad R_{sample}/R_{standard} - 1 \quad 1000 ‰$$

where R = $^{13}C/^{12}C$ or $^{18}O/^{16}O$. Analytical uncertainty was ±0.1‰ based on the repeated measurements of various in-house standards throughout each sequence (n = 20).

2.4.2. Bone samples

Three bird bone samples recovered from the paleosol LGA-2 were cleaned vigorously with deionized water, ultrasonication, and mechanical abrasion using brushes. After cleaning, samples were oven dried at 40 °C overnight. Each bone sample was ground by hand using an agate mortar and pestle. A small aliquot (~10 mg) was used for isotopic analyses of the bone carbonate and phosphate whereas the remaining sample was employed to extract bone collagen. Samples for bone carbonate analyses were measured as described above for land snail shells and sediments. About 2–3 mg of bone carbonate was weighted into a 6 ml Exetainer vial that was subsequently He-flushed. Bone carbonate was treated with 0.1 ml of 100% H_3PO_4 at 25 °C overnight to release CO_2 gas which was measured in the GasBench II connected to a Finnigan Delta^{PLUS} XP isotope ratio mass spectrometer. Oxygen from phosphates was precipitated as Ag_3PO_4 and analyzed in a TC/EA device coupled to a Finnigan Delta^{PLUS} XP isotope ratio mass spectrometer, following the procedure of Vennemann et al. (2002). Oxygen stable isotopes from bone carbonate and phosphate are expressed in δ notation relative to the international standard PDB and SMOW, respectively. Bone collagen was extracted following standard procedures (e.g., Arnay-de-la-Rosa et al., 2010). About 1 mg of bone collagen was weighed in a tin capsule and combusted in a Carlo Erba Elemental Analyzer (NA1500). The CO_2 and N_2 gases produced after combustion were analyzed using a Finnigan Delta^{PLUS} XP isotope ratio mass spectrometer. Results are expressed in δ notation, using the standard PDB for carbon and air for nitrogen. Analytical uncertainty was ±0.1‰ for oxygen and carbon isotopes from the carbonate, oxygen isotopes from the phosphate, and carbon and nitrogen isotopes from the collagen, based on the repeated measurements of in-house standards dispersed periodically throughout the run sequence.

2.5. Statistics

All statistical analyses were computed in *PAST 2.17b* software (Hammer et al., 2001) considering statistical significance at $\alpha = 0.05$. Mann–Whitney *U* test and Kruskal–Wallis test were used to evaluate potential differences in median values of groups of samples.

3. Results

3.1. Radiocarbon dating

The small shell of a live-collected *M. monilifera* specimen (LGA-3), with a shell length of ~5 mm, yielded a ^{14}C age of ~880 yr BP (Table 1). This value is considerably lower than that obtained by Ortiz et al. (2006) from a live-collected medium-size (length of ~15 mm) *T. geminata* individual in the study area, which yielded a ^{14}C age of ~2720 yr BP. This suggests that small land snail species appear to need lower limestone intake than medium-large size species in the Canary Islands. However, an important amount of dead carbon was incorporated in the small shell and therefore, this age anomaly (~880 yr BP) was used to correct the ages obtained from fossil *M. monilifera* shells (Table 1), assuming that fossil shells were affected by dead carbon in an equivalent manner than the live-collected specimen from the study area.

The corrected and calibrated radiocarbon results of fossil shells indicate that both studied paleosols are Quaternary in age (Table 1). The upper paleosol (LGA-2; Fig. 1B–C) was AMS radiocarbon dated with a bone collagen sample (~2.1–2.7 cal ka BP) and a small snail shell (~5.0–5.5 cal ka BP). An age offset of ~3 ka is observed between the bone and the shell both recovered from the same paleosol. Such age offset may reflect (1) a multi-millennial scale of age mixing of fossils within the same paleosol associated with the timespan of soil formation (see also Yanes et al., 2007), and/or (2) an age anomaly from shells even after correcting for the expected magnitude of dead carbon assimilation. Albeit age data from shells may exhibit an error of about 3 ka, these data are valid to roughly estimate the approximate age of the studied fossils. Thus, the upper paleosol LGA-2 seems to display an age of middle to late Holocene (~2.1–5.5 cal ka BP), representing an interglacial age-interval.

The lower paleosol (LGA-1; Fig. 1B–D) was dated using a small land snail shell by AMS radiocarbon dating as ~23.3–24.0 cal ka BP. Thus, this shell bed was likely deposited during the late Pleistocene, matching with the beginning of the Last Glacial Maximum (LGM) interval of the northern Hemisphere. Because no bones were preserved in this bed, only shells were available for radiocarbon dating. Even if shells from LGA-1 are ~3 ka anomaly older as may occur in LGA-2, this paleosol was clearly formed during the last glacial, around the LGM period. In this study we assume that these radiocarbon ages (Table 1) represent reasonably well the approximate age of all samples studied here.

3.2. Carbon isotopic composition of aragonitic and calcitic shells

The $\delta^{13}C$ values of modern land snail aragonitic shells ranged from −5.6‰ to −11.4‰ (Table 2), and averaged −9.5 ± 1.6‰ (n = 9). Both studied species, the medium size *T. geminata* and the small species

Table 1
Radiocarbon results.

Sample ID	Locality	Lab reference	Sample type	Species	^{14}C age (yr)	Corrected ^{14}C age (yr BP)	2-σ cal. age (cal yr BP)	2-σ cal. age DR = 135 ± 103* (cal year BP)
LGA-3	Fuente de Gayo, Lanzarote	Poz-50102	Live-collected land snail shell	*Monilearia monilifera*	880 ± 30	0	0	
LGA-2a	Fuente de Gayo, Lanzarote	Poz-47782	Fossil bird bone collagen	*Puffinus holeae*	2830 ± 30	2830 ± 30	2470–2700	2140–2700
LGA-2b	Fuente de Gayo, Lanzarote	Poz-47783	Fossil land snail shell	*M. monilifera*	5460 ± 35	4580 ± 35	5060–5450	
LGA-1	Fuente de Gayo, Lanzarote	Poz-47781	Fossil land snail shell	*M. monilifera*	20700 ± 110	19820 ± 110	23300–24040	

* Local mean marine reservoir value in the study area (average value between Portugal and Mauritania).

M. monilifera, did not differ significantly in δ^{13}C values (Fig. 4A). The δ^{13}C values of Holocene aragonitic shells ranged from −0.9‰ to +1.6‰ (Table 2), with an average value of +0.1 ± 0.7‰ (n =15). While *T. geminata* showed δ^{13}C values similar to those from *H. flavistoma* and *M. monilifera* (Fig. 4B), *M. monilifera* was significantly higher in δ^{13}C values than *H. flavistoma* (Mann–Whitney *U*-test, p = 0.020). The calcitic shells of the slug *C. canariensis* (n = 4) showed δ^{13}C values (from −11.0‰ to −5.2‰) that overlapped with those from all aragonitic shells (Fig. 4B). The δ^{13}C values of late Pleistocene aragonitic shells ranged from −6.4‰ to +1.7‰ (Table 2), and averaged −2.3 ± 2.8‰ (n = 16). The three studied late Pleistocene aragonitic species (Fig. 4C), *Theba* sp., *H. flavistoma* and *M. monilifera*, showed statistically equivalent δ^{13}C values (Kruskal–Wallis, p > 0.05). Calcitic shells of the slug *C. canariensis* ranged from −4.2‰ to +1.5‰ (n = 4) and overlapped with values of aragonitic shells (Fig. 4C).

3.3. Oxygen isotopic composition of aragonitic and calcitic shells

The δ^{18}O values of modern aragonitic shells ranged from −0.2‰ to +0.8‰ (Table 2), averaging +0.3 ± 0.3‰ (n = 9). Both snail species (*T. geminata* and *M. monilifera*) showed statistically similar δ^{18}O values (Fig. 4A). The δ^{18}O values of Holocene aragonitic shells ranged from −0.9‰ to +1.6‰ (Table 2), averaging +0.1 ± 0.7‰ (n = 15). All three aragonitic species, *T. geminata*, *H. flavistoma* and *M. monilifera* (Fig. 4B) showed similar δ^{18}O values (Kruskal–Wallis, p > 0.05). The δ^{18}O values of Holocene calcitic shells of *C. canariensis* ranged from −0.9‰ to +2.7‰ (Table 2), and averaged +0.8 ± 1.5‰ (n = 4). Holocene calcitic shells showed similar δ^{18}O values than aragonitic shells of all other species (Fig. 4B). Late Pleistocene aragonitic shells ranged in δ^{18}O values from +1.6‰ to +3.4‰ (Table 2), and averaged +2.5 ± 0.4‰ (n = 16). The three aragonitic species (*Theba* sp., *H. flavistoma* and *M. monilifera*) showed comparable δ^{18}O values among them (Fig. 4C). Finally, late Pleistocene calcitic shells showed δ^{18}O values that ranged from +3.0‰ to +4.1‰ (Table 2), and averaged +3.6 ± 0.4‰ (n = 4). Late Pleistocene calcitic shells were significantly higher in δ^{18}O values than late Pleistocene aragonitic shells of the three species (Fig. 4C; Kruskal–Wallis, p b 0.05).

3.4. Isotopic composition of sediments

Bulk carbonate-rich sediments (n = 3) on the modern soil surface (LGA-3) from the Fuente de Gayo showed an average δ^{13}C and δ^{18}O value of −10.5 ± 0.8‰ and −4.0 ± 0.8‰, respectively (Table 3). Holocene sediments (n = 3) displayed respective average δ^{13}C and δ^{18}O values of −9.3 ± 0.2‰ and −2.4 ± 0.5‰ (Table 3). Lastly, late Pleistocene δ^{13}C and δ^{18}O values of sediments (n = 3) showed average values of −8.2 ± 0.3‰ and −0.3 ± 1.0‰, respectively (Table 3). At all studied age-intervals, bulk carbonate-rich sediments showed a significantly different isotopic population than that of contemporaneous aragonitic and calcitic land snail shells (Fig. 5A–C).

Overall, the δ^{13}C and δ^{18}O values of all aragonitic (Fig. 6A, D) and calcitic (Fig. 6B, E) shells, as well as values of bulk carbonate-rich

Table 2
Carbon and oxygen stable isotope results of land snail shells.

Sample ID	Species	Carbonate type	~Age (cal ka BP)	δ^{18}O‰(PDB)	δ^{13}C‰(PDB)
LGA-3-1	*Theba geminata*	Aragonite	Modern	0.2	−5.6
LGA-3-2	*T. geminata*	Aragonite	Modern	0.5	−10.6
LGA-3-3	*T. geminata*	Aragonite	Modern	0.5	−10.5
LGA-3-4	*T. geminata*	Aragonite	Modern	0.2	−11.4
LGA-3-5	*Monilearia monilifera*	Aragonite	Modern	0.4	−9.2
LGA-3-6	*M. monilifera*	Aragonite	Modern	0.0	−9.6
LGA-3-7	*M. monilifera*	Aragonite	Modern	0.8	−10.0
LGA-3-8	*M. monilifera*	Aragonite	Modern	−0.2	−9.5
LGA-3-9	*M. monilifera*	Aragonite	Modern	0.6	−9.0
LGA-2-1	*Hemicycla flavistoma*	Aragonite	2.1–5.5	−0.6	−9.5
LGA-2-2	*H. flavistoma*	Aragonite	2.1–5.5	−0.7	−10.1
LGA-2-3	*H. flavistoma*	Aragonite	2.1–5.5	−0.9	−7.5
LGA-2-4	*H. flavistoma*	Aragonite	2.1–5.5	0.5	−8.7
LGA-2-5	*M. monilifera*	Aragonite	2.1–5.5	−0.5	−6.7
LGA-2-6	*M. monilifera*	Aragonite	2.1–5.5	−0.1	−6.8
LGA-2-7	*M. monilifera*	Aragonite	2.1–5.5	−0.4	−6.9
LGA-2-8	*M. monilifera*	Aragonite	2.1–5.5	0.9	−7.1
LGA-2-9	*M. monilifera*	Aragonite	2.1–5.5	0.8	−4.6
LGA-2-10	*T. geminata*	Aragonite	2.1–5.5	0.5	−7.9
LGA-2-11	*T. geminata*	Aragonite	2.1–5.5	0.1	−10.0
LGA-2-12	*T. geminata*	Aragonite	2.1–5.5	0.3	−7.2
LGA-2-13	*T. geminata*	Aragonite	2.1–5.5	−0.5	−7.0
LGA-2-14	*T. geminata*	Aragonite	2.1–5.5	0.5	−8.8
LGA-2-15	*T. geminata*	Aragonite	2.1–5.5	1.6	−6.3
LGA-2-16	*Cryptella canariensis*	Calcite	2.1–5.5	0.2	−11.0
LGA-2-17	*C. canariensis*	Calcite	2.1–5.5	−0.9	−8.2
LGA-2-18	*C. canariensis*	Calcite	2.1–5.5	2.7	−5.2
LGA-2-19	*C. canariensis*	Calcite	2.1–5.5	1.2	−9.5
LGA-1-1	*Theba sp.*	Aragonite	23.3–24.0	2.0	−5.8
LGA-1-2	*Theba sp.*	Aragonite	23.3–24.0	2.2	−6.4
LGA-1-3	*Theba sp.*	Aragonite	23.3–24.0	1.8	−1.6
LGA-1-4	*Theba sp.*	Aragonite	23.3–24.0	1.6	−0.2
LGA-1-5	*Theba sp.*	Aragonite	23.3–24.0	2.5	−0.3
LGA-1-6	*Theba sp.*	Aragonite	23.3–24.0	2.8	1.0
LGA-1-7	*Theba sp.*	Aragonite	23.3–24.0	2.7	−3.3
LGA-1-8	*Hemicycla flavistoma*	Aragonite	23.3–24.0	3.4	−0.9
LGA-1-9	*H. flavistoma*	aragonite	23.3–24.0	2.2	−2.0
LGA-1-10	*H. flavistoma*	Aragonite	23.3–24.0	2.7	−2.7
LGA-1-11	*H. flavistoma*	Aragonite	23.3–24.0	2.5	−1.7
LGA-1-12	*H. flavistoma*	Aragonite	23.3–24.0	2.5	−4.3
LGA-1-13	*M. monilifera*	Aragonite	23.3–24.0	2.5	−6.1
LGA-1-14	*M. monilifera*	Aragonite	23.3–24.0	2.6	1.5
LGA-1-15	*M. monilifera*	Aragonite	23.3–24.0	3.0	−6.4
LGA-1-16	*M. monilifera*	Aragonite	23.3–24.0	2.3	1.7
LGA-1-17	*C. canariensis*	Calcite	23.3–24.0	3.6	0.9
LGA-1-18	*C. canariensis*	Calcite	23.3–24.0	4.1	−1.0
LGA-1-19	*C. canariensis*	Calcite	23.3–24.0	3.5	1.5
LGA-1-20	*C. canariensis*	Calcite	23.3–24.0	3.0	−4.2

sediments (Fig. 6C, F), declined significantly from the late Pleistocene to the present.

3.5. Isotopic composition of bone tissues

Late Holocene (~2.1–2.7 cal ka BP) bone collagen samples ($n = 3$) from the extinct seabird *P. holeae* recovered from the paleosol LGA-2 (Fig. 1B–C) ranged from −13.7‰ to −13.3‰ in δ^{13}C; and from +14.8‰ to +13.1‰ in δ^{15}N (Table 4). The bone carbonate of the same samples varied from −7.7‰ to −6.9‰ in δ^{13}C; and from −1.0‰ to +0.6‰ in δ^{18}O (Table 4). Finally, bone phosphate δ^{18}O values ranged from +17.7‰ to +18.5‰ (Table 4).

4. Discussion

4.1. Sample preservation

4.1.1. Shells

Shell quality of Quaternary land snails preserved in carbonate-rich deposits from the Canary Islands has been studied in detail by Yanes et al. (2007, 2008b, 2011). A large number of x-ray diffraction analyses of cleaned and finely homogenized shells of multiple species recovered from different eolian deposits and paleosols reveal that Quaternary land snails from these islands have preserved their original mineralogical composition. New x-ray diffraction analyses of five aragonitic and one calcitic shells recovered from the two paleosols studied here further reinforced that hard-skeletons maintained their original composition. As appreciated in Fig. 3, shells used in this work even preserve original color patterns in their shells, what emphasizes their overall good preservation status. Moreover, several Quaternary shells from the Canary Islands have been studied by Yanes et al. (2011) using a Scanning Electronic Microscope (SEM). SEM micrographs further demonstrated that shells did not exhibit any evidence of recrystallization, also assuring the good preservation of shells. Finally, the range of oxygen and carbon isotope values here overlaps satisfactorily with expected values for well-preserved shells. Overall, previous and new data suggest that Quaternary land snail shells from this study are well preserved and appropriate for geochemical analyses and paleoenvironmental inferences.

4.1.2. Bones

The preservation of bone collagen can be evaluated by (1) the atomic C/N ratio and (2) the proportion of organic carbon and nitrogen yielded during collagen extraction (e.g., DeNiro, 1985; Ambrose, 1990; Bocherens et al., 1997; Klinken, 1999). The average atomic C/N ratio was 3.2 (Table 4), overlapping with values for well-preserved collagen. The percentage (by weight) of organic carbon (34%) and nitrogen (13%) agrees with values typical from well-preserved samples. Bone samples exhibited a carbon isotopic offset of ~5.7–6.1‰ between collagen and carbonate, pointing to a well-preserved δ^{13}C value from the bone carbonate (Lee-Throp et al., 1989; Clementz et al., 2009). The δ^{18}O offset between phosphate and carbonate (in SMOW scale) is usually constant in vertebrates because both precipitate in isotopic equilibrium with the oxygen isotopic composition of body waters (Iacumin et al., 1996). The δ^{18}O offset between phosphate and carbonate here (~12.1–12.9‰) exceeds the expected offset for well-preserved bone carbonate, suggesting hence some diagenetic alteration in the δ^{18}O values of the bone carbonate. Bone phosphates are more resistant to diagenetic alteration than carbonates (Clementz, 2012). The δ^{18}O values of apatite are more prone to alteration than the δ^{13}C values (Wang and Cerling, 1994). Thus, although the δ^{18}O values of bone carbonate here may be altered, the δ^{13}C values are probably pristine, as suggested by the δ^{13}C offset of ~6.1‰ (Table 4) between collagen and carbonate (Lee-Throp et al., 1989; Clementz et al., 2009). Accordingly, apart from bone carbonate δ^{18}O values, geochemical data from the studied bone samples here should be valid.

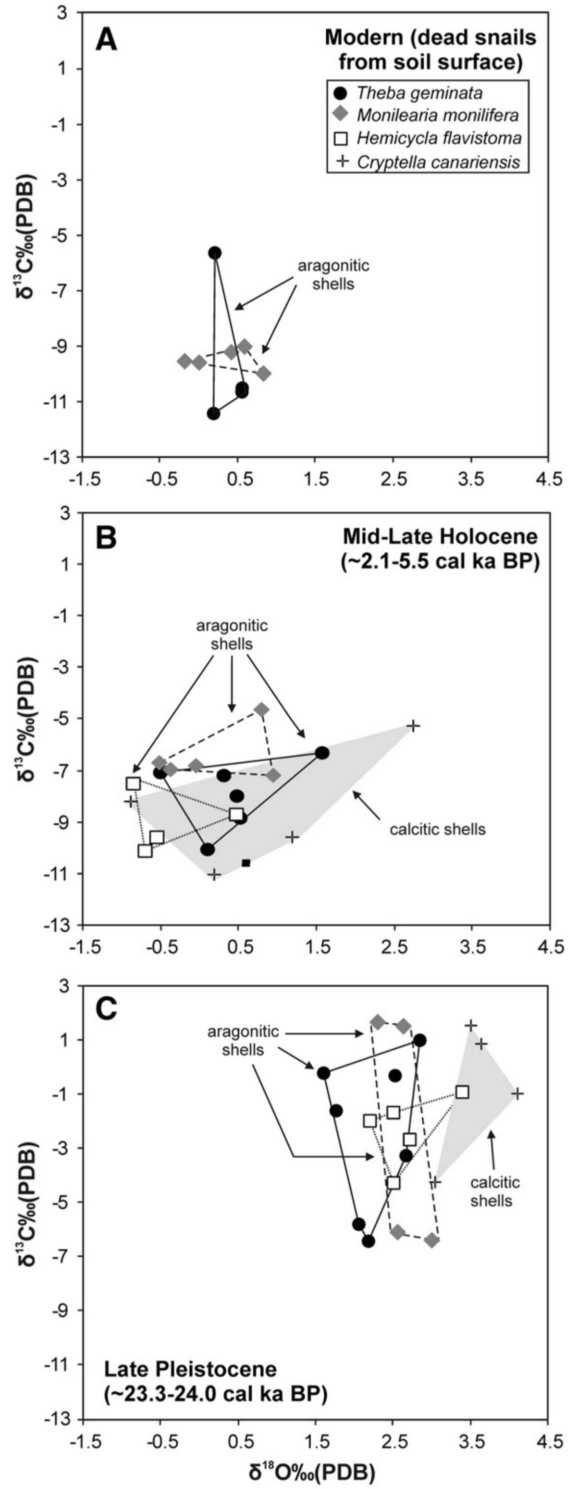

Fig. 4. Comparison of carbon and oxygen stable isotope values among land snail species from the Fuente de Gayo, Lanzarote. (A) Modern shells of recently dead snails collected from the soil surface. (B) Mid-late Holocene buried shells collected from LGA-2. (C) Late Pleistocene buried shells recovered from LGA-1.

4.2. Temporal variations in C_3/C_4-CAM plants

Current vegetation in the Fuente de Gayo includes C_3 and C_4/CAM photosynthetic pathways. C_4 and CAM plants in the study area are similar isotopically (Yanes et al., 2008a) and consequently, they are treated as a single group. The aragonitic shell δ^{13}C values of recently dead land snails ranged from −5.6‰ to −11.5‰, which reflects

Table 3
Carbon and oxygen stable isotope results of bioclastic sediments. It is assumed that sediments have similar age than fossils.

Sample	Carbonate type	~Age (cal ka BP)	$\delta^{18}O$‰(PDB)	$\delta^{13}C$‰(PDB)
LGA-3-Sed. 1	Aragonite/calcite mixture	Modern	−4.7	−11.4
LGA-3-Sed. 2	Aragonite/calcite mixture	Modern	−3.2	−10.2
LGA-3-Sed. 3	Aragonite/calcite mixture	Modern	−4.1	−9.8
LGA-2-Sed. 1	Aragonite/calcite mixture	2.1–5.5	−1.9	−9.4
LGA-2-Sed. 2	Aragonite/calcite mixture	2.1–5.5	−2.4	−9.2
LGA-2-Sed. 3	Aragonite/calcite mixture	2.1–5.5	−2.9	−9.4
LGA-1-Sed. 1	Aragonite/calcite mixture	23.3–24.0	0.1	−7.8
LGA-1-Sed. 2	Aragonite/calcite mixture	23.3–24.0	0.6	−8.3
LGA-1-Sed. 3	Aragonite/calcite mixture	23.3–24.0	−1.4	−8.4

that modern snails in this locale followed a varied diet which included variable amounts of C_3, C_4 and/or CAM plants, together with some carbonates from the surrounding sediment, as indicated in the ^{14}C age anomaly of a live-collected specimen (Table 1). Both modern land snail species (*T. geminata* and *M. monilifera*) showed comparable $\delta^{13}C$ values (Fig. 4A) and accordingly, they should have had similar feeding behavior and can be used jointly. Live-collected land snails from the Fuente de Gayo, with an average shell $\delta^{13}C$ value of −10.0‰ and an average body $\delta^{13}C$ value of −24.6‰ (n = 29), consumed about ~10% of CAM plants, on average (personal unpublished data). Snails analyzed here (n = 9) showed a shell $\delta^{13}C$ value of −9.5 ± 1.6‰, suggesting that measured specimens ingested a comparable proportion of CAM/C_4 plants than living specimens. Land snails from different coastal localities in the eastern Canary Islands (n = 17), which exhibit a notably drier microclimate than that of the Fuente de Gayo, showed an average shell $\delta^{13}C$ value of −5.2 ± 2.7‰ (Yanes et al., 2008a). This reveals that snails at coastal (drier) sites consumed higher amounts of C_4 and/or CAM plants than snails at higher (wetter) locales of the eastern Canary Islands. Thus, snails appear to track roughly the relative proportion of C_3 versus C_4 and/or CAM plants in the carbon isotope composition of the shell, even when carbonate-rich sediments ingested by snails may somewhat disguise the signature of the assimilated vegetation (Yanes et al., 2008a).

Mid-late Holocene aragonitic shells (~2.1–5.5 cal ka BP) showed a $\delta^{13}C$ value which was ~1.8‰ higher than modern snails (Fig. 6A). Moreover, late Pleistocene aragonitic shells (~23.3–24.0 cal ka BP) were up to ~7.2‰ higher in $\delta^{13}C$ values than modern individuals (Fig. 6A). This significant temporal variation in shell $\delta^{13}C$ values clearly reflects that the proportion of C_3/C_4-CAM plants in the same study site has fluctuated notably between glacial and interglacial times. Snails suggest that the proportion of C_4 and/or CAM plants was considerably higher in NW Lanzarote during the late Pleistocene (around the LGM) and from there, C_4 and/or CAM plants declined progressively their relative abundance reaching modern values in which C_3 plants manifestly dominate the landscape. The same pattern is appreciated in calcitic shells of slugs, that is, late Pleistocene shells were, on average, ~7.8‰ higher in $\delta^{13}C$ values than Holocene shells (Fig. 6B). Furthermore, $\delta^{13}C$ values of bulk carbonate-rich sediment samples displayed a subdued but equivalent temporal pattern (Fig. 6C). Thus, late Pleistocene sediments were ~2.3‰ higher in $\delta^{13}C$ values than modern sediments in the study site. This is also consistent with previous snail studies in the eastern Canary Islands (Fig. 7A) where Quaternary land snails and sediments from eolian deposits often showed higher $\delta^{13}C$ values during glacial rather than interglacial intervals (Yanes et al., 2011). The fact that bioclastic sediments showed similar temporal trends in $\delta^{13}C$ values than snail shells is explained because sediments are formed by a combination of pieces of land snail shells and pedogenic carbonates (which both should record the $\delta^{13}C$ values of the vegetation). However, since marine carbonates are probably present, the $\delta^{13}C$ trends in the sediments are subdued with respect to the shells. A similar situation applies for the $\delta^{18}O$ values of sediments presented below. Considering that carbon and oxygen isotope values of sediments are significantly different than those from shells

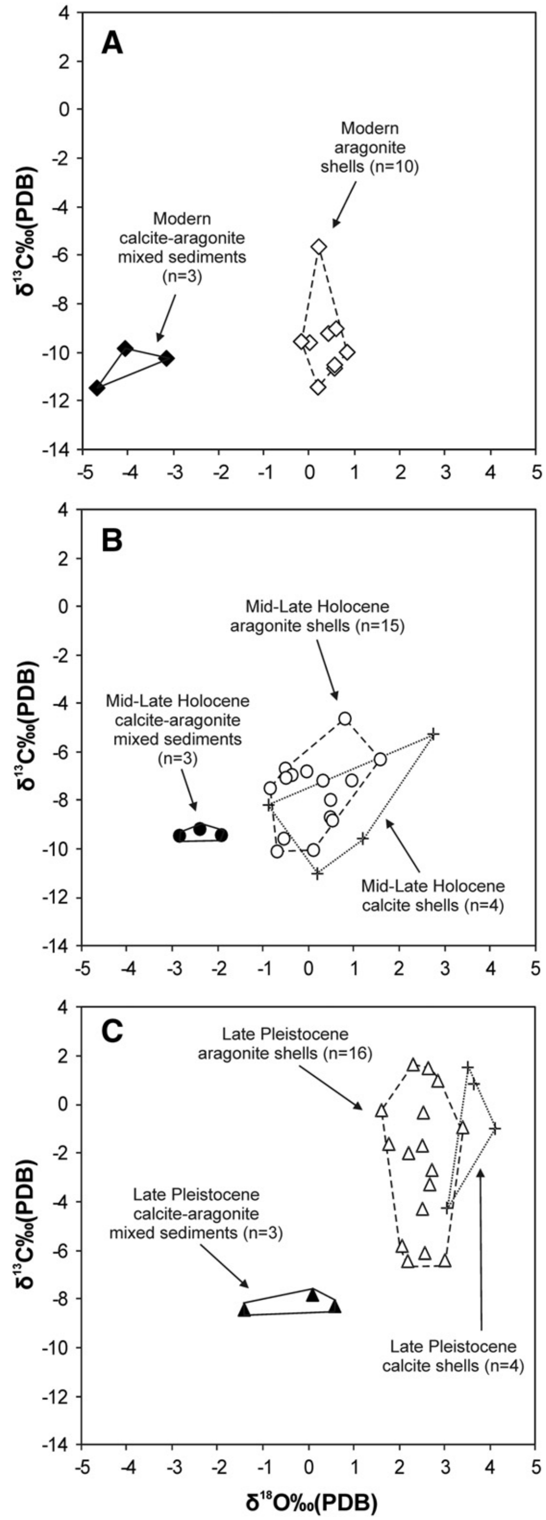

Fig. 5. Comparison of carbon and oxygen stable isotope values of land snail shells and bulk carbonate-rich sediments. (A) Modern shells and sediments. (B) Mid-late Holocene shells and sediments. (C) Late Pleistocene shells and sediments.

(Fig. 5), it is expected that analyzed shells were reasonably free of carbonates from the sediments (see also Yanes et al., 2011). All snail and sediment proxies presented here (Fig. 6A–C) suggest that C_4 and/or CAM plants were notably more abundant during the LGM and gradually declined their abundance to present values. This trend agrees with studies from nearby Africa (Gasse et al., 1990, 2008). Higher abundance of C_4 and/or CAM plants during the glacial interval may be explained by

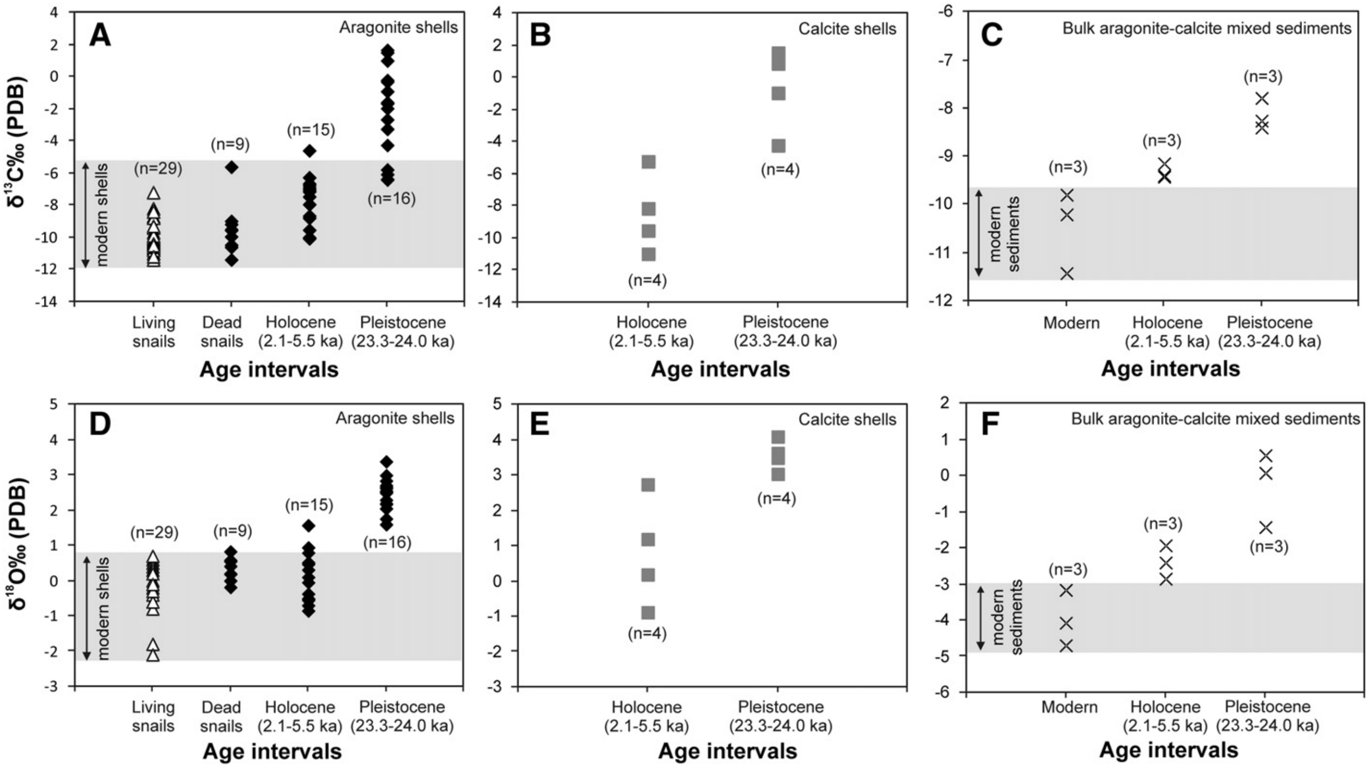

Fig. 6. Temporal variations in the isotopic composition of aragonitic and calcitic shells and bulk carbonate-rich sediments. (A–C) Carbon stable isotope values. (D–F) Oxygen stable isotope values. Open triangles in panels A and D depict data from live-collected *Theba geminata* individuals from the Fuente de Gayo (personal unpublished data). Gray bands represent the range of modern isotopic values in the study site. Numbers between brackets depict the number of samples analyzed per age-interval.

lower concentration of atmospheric CO_2 and/or somewhat drier conditions than today (e.g., Cole and Monger, 1994; Koch et al., 2004).

Overall, isotopic results from both calcitic and aragonitic snail shells illustrate that (1) several endemic species of snails from the Canary Islands follow comparable feeding strategies and therefore, can be used jointly as a paleovegetation proxy; (2) modern snail values indicate that NW Lanzarote, at 460 m a.s.l., exhibits a relatively low abundance (~10%) of C_4 and/or CAM plants, and (3) C_4 and/or CAM plants were considerably more abundant in the late Pleistocene, possibly linked to lower atmospheric CO_2 and/or drier conditions, and thereafter declined progressively to the present.

4.3. Temporal variations in atmospheric conditions

The $\delta^{18}O$ values of aragonitic shells of recently dead snails from the Fuente de Gayo averaged $+0.3 \pm 0.3$‰ ($n = 9$), which is similar to the value of -0.1 ± 0.6‰ ($n = 29$) observed in living specimens from the same locale (personal unpublished data) and with the value of $+0.8 \pm 0.8$‰ ($n = 17$) obtained from snails collected at various coastal locales of the eastern Canary Islands (Yanes et al., 2008a). This suggests that atmospheric conditions are reasonably homogeneous across localities of the eastern islands of the Canary Archipelago. Modern land snails of the eastern Canary Islands deposited aragonitic shell material under current average atmospheric conditions, i.e., air temperatures of ~19 °C, rain $\delta^{18}O$ values of ~ −3.5‰ (SMOW) and maximum relative humidity values of ~90–91% (Yanes et al., 2011). Aragonitic shells preserved in the mid-late Holocene paleosol (~2.1–5.5 cal ka BP) showed $\delta^{18}O$ values basically equivalent to the present (Fig. 6D). This points to comparable environmental conditions during the mid-late Holocene and today. In contrast, late Pleistocene aragonitic shells (~23.3–24.0 cal ka BP) were, on average, ~2.1‰ higher in $\delta^{18}O$ values than modern shells (Fig. 6D). Calcitic internal shells of slugs displayed a comparable trend, i.e., glacial shells were ~2.8‰ higher in $\delta^{18}O$ values than Holocene individuals (Fig. 6E). Interglacial calcitic shells of slugs exhibited statistically similar $\delta^{18}O$ values than other species with external aragonitic shells (Fig. 4B). Interestingly, late Pleistocene slugs were significantly higher in $\delta^{18}O$ values than late Pleistocene aragonitic shells (Mann–Whitney-*U* test, $p = 0.004$) (Fig. 4C). This may reflect that during glacial times, slugs possibly experienced more severe water stress than snails with external shells, which are better protected to prevent desiccation and water loss through evaporation. The $\delta^{18}O$ values of carbonate-rich sediments were notably higher during the late Pleistocene and thereafter, declined progressively to present values (Fig. 6F). Both snail and sediment data suggest that atmospheric conditions during the late Pleistocene were noticeably different to those from the Holocene. These results are in agreement with a previous snail study from the eastern Canary Islands (Fig. 7B), which documented significantly higher shell and sediment $\delta^{18}O$ values during the LGM than during the Holocene (Yanes et al., 2011).

Table 4
Stable isotope results of collagen, carbonate and phosphate tissues of three bone samples of the extinct Dune Shearwater *Puffinus holeae* (~2.1–2.7 cal ka BP) from the Fuente de Gayo, NW Lanzarote, Canary Islands.

	Bone collagen					Bone carbonate			Bone phosphate	
Sample ID	$\delta^{15}N_{coll}$‰ (air)	$\delta^{13}C_{coll}$‰ (PDB)	%N	%C	C/N	$\delta^{18}O_{carb}$‰ (PDB)	$\delta^{13}C_{carb}$‰ (PDB)	$\Delta^{13}C_{carb-coll}$ (PDB)	$\delta^{18}O_{phos}$‰ (SMOW)	$\Delta^{18}O_{carb-phos}$ (SMOW)
LGA-2-bone-1	+13.2	−13.3	0.14	0.37	3.2	+0.3	−7.7	5.7	+18.4	12.8
LGA-2-bone-2	+13.1	−13.4	0.13	0.34	3.2	+0.6	−6.9	6.5	+18.5	12.9
LGA-2-bone-3	+14.8	−13.7	0.12	0.31	3.2	−1.0	−7.6	6.1	+17.7	12.1

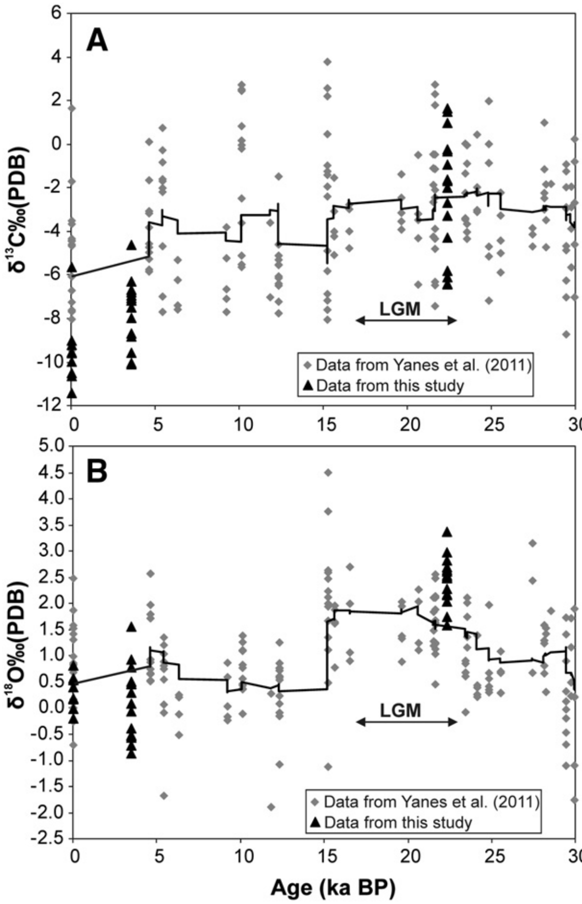

Fig. 7. Isotopic composition of Quaternary land snails from the Canary Islands. (A) Carbon stable isotope values of land snail aragonitic shells. (B) Oxygen stable isotope values of land snail aragonitic shells. Gray diamonds represent data from coastal eolian deposits published by Yanes et al. (2011) whereas black triangles depict data from this study. Solid lines depict 15-point running average of the data by Yanes et al. (2011). LGM = Last Glacial Maximum.

Calculations of the snail evaporative steady-state flux balance mixing model by Balakrishnan and Yapp (2004) suggest that snails from the late Pleistocene bed, with a shell $\delta^{18}O$ value of +2.5‰ deposited shell when maximum relative humidity (RH) was comparable to the present (~90%), if glacial rain $\delta^{18}O$ values were ~1‰ higher than today and temperature was ~4 °C cooler than the present (see Yanes et al., 2011 for further details). Alternatively, if glacial rain $\delta^{18}O$ values in Lanzarote were similar to present values, and holding other variables constant, then late Pleistocene shells may have precipitated at slightly drier conditions than today (RH of ~87%). Overall, RH during the LGM seems to have been similar or somewhat lower than at present in NW Lanzarote.

Snail proxies of aragonitic shells from many regions have often observed as high or higher shell $\delta^{18}O$ values during the late Pleistocene than today, including central European land snails (Kehrwald et al., 2010), snails from northern Iberian Peninsula (Yanes et al., 2012), and some snails from Italy (Colonese et al., 2010, 2011). Higher shell $\delta^{18}O$ values during glacial intervals probably reflect the combined effects of (1) higher $\delta^{18}O$ values of rainfall due to higher influence of ^{18}O-enriched summer precipitations and/or higher glacial seawater $\delta^{18}O$ values; (2) lower amount of precipitation; and/or (3) higher evaporation rates due to drier conditions. Moreover, several other proxies around the world (Yapp and Epstein, 1977; Plummer, 1993; Amundson et al., 1996; Mora and Pratt, 2001) have also observed higher $\delta^{18}O$ values of meteoric waters during the last glacial than at present. Interestingly, all these proxies (including snail data here) contradict the minimal $\delta^{18}O$ values observed in Greenland ice cores during the LGM (e.g., Dansgaard et al., 1993). While meteoric water $\delta^{18}O$ values from polar locales are strongly influenced by temperature (e.g., Dansgaard et al., 1993), other climatic variables besides temperature should have affected them in many ice-free locales (see also discussion in Yanes et al., 2011). For example, factors like increased summer precipitations, variations in relative humidity, and shifts in water vapor and seawater $\delta^{18}O$ values have been proposed as plausible hypotheses that may explain the higher meteoric water $\delta^{18}O$ values documented in several continental proxies during the last glacial interval (e.g., Yapp and Epstein, 1977; Plummer, 1993; Amundson et al., 1996; Mora and Pratt, 2001; Colonese et al., 2010; Kehrwald et al., 2010; Colonese et al., 2011; Yanes et al., 2011, 2012), including this study. The present and some previous studies suggest that the $\delta^{18}O$ values of meteoric waters are controlled by multiple environmental factors operating jointly that may result in opposite trends between polar and ice-free locales.

This work (1) reinforces previous local snail results by Yanes et al. (2011), (2) illustrates that the isotopic composition calcitic shells of land snails and bulk calcite–aragonite mixed sediment samples has the potential to track credible environmental information, and (3) shows that snail shells are useful continental proxies that record local and regional patterns of tropical glacial–interglacial atmospheres. Our results indicate that Quaternary environmental conditions have changed through time in NW Lanzarote. This climate change may have affected local snail communities. In fact, the species composition of the snail community preserved in the late Pleistocene paleosol is significantly different than that of the mid-late Holocene paleosol (personal unpublished data). Interestingly, while all snail species from these snail assemblages are extant in the region, the endemic helicid *Theba* sp. (Fig. 3C) went extinct. *Theba* sp. is, as far as we know, only preserved in this particular locale and time-interval. This species was considerably abundant during the late Pleistocene but it completely disappeared during the Holocene. In contrast, the remaining species survived from the late Pleistocene to the present. Although ecological factors (not studied here) may account for the extinction of *Theba* sp., it is plausible that this species was not able to adjust easily to the late Pleistocene–Holocene climate change in Lanzarote and therefore, eventually disappeared.

4.4. The extinct Dune Shearwater *Puffinus holeae*

As expected, bone collagen $\delta^{13}C$ (−13.5 ± 0.2‰) and $\delta^{15}N$ (+13.7 ± 1.0‰) values of *P. holeae* (n = 3) showed the signature typical of seabirds (Hobson et al., 1993). Tieszen et al. (1995) and Arnay-de-la-Rosa et al. (2010) measured the $\delta^{13}C$ and $\delta^{15}N$ values of organic tissues of several modern and prehistoric (= late Holocene) marine animals from the Canary Islands, including marine fish, sea urchin, sea crab and shellfish samples. These values are plotted jointly with bone collagen values of seabird bones to explore potential dietary items and trophic shifts of the studied individuals (Fig. 8A). Considering that bone collagen $\delta^{15}N$ values are offset by ~3.0–3.4‰ between consumer and prey (Hobson et al., 1993), the studied individuals likely fed upon local fish (Fig. 8A). This seems reasonable because most seabirds from the region mainly prey upon fish and squid (e.g., Hartog and Clarke, 1996; Jorge-Camacho et al., 2000; Roscales et al., 2011; Neves et al., 2012). Hence, *P. holeae* was a primary marine carnivore because secondary marine carnivores exhibit higher $\delta^{15}N$ values (Schoeninger and DeNiro, 1984). Bone collagen $\delta^{13}C$ values of *P. holeae* overlap with values of feathers of a modern Cory's Shearwater or a Barolo Shearwater from the Macaronesian region (e.g., Roscales et al., 2011; Neves et al., 2012). Considering that the bone collagen of predators are ~5–8‰ richer in ^{13}C than primary producers (e.g., Krueger and Sullivan, 1984; Lee-Throp et al., 1989), the $\delta^{13}C$ values of primary producers from the study area should vary from −18.5‰ to −21.5‰. These predicted values from bone collagen correspond with values of marine phytoplankton and local algae (personal unpublished data), which, in turn, fall between values of local terrestrial C_3 and C_4 plants (Yanes et al., 2008a).

The average values of bone carbonate $\delta^{13}C$ (−7.4 ± 0.4‰) and $\delta^{18}O$ (+0.0 ± 0.9‰) are compared to values of other carbonate samples recovered from the same paleosol LGA-2 (Fig. 8B). All bone carbonate, aragonitic and calcitic shell samples showed statistically equivalent $\delta^{13}C$ and $\delta^{18}O$ values (Kruskal–Wallis, $p > 0.05$). In contrast, bulk calcite–aragonite sediments represent a significantly different isotopic population, which also suggests that the studied bone samples here should be free of detritic contaminants (Fig. 8B). The $\delta^{13}C$ offset between bone collagen and bone carbonate reflects the trophic level, diet and physiology of mammals (e.g., Lee-Throp et al., 1989; Clementz et al., 2009). However, these kinds of studies are rare in birds. The studied samples show an average $\delta^{13}C$ offset between collagen and carbonate of ~6.1‰ (Table 4). This value falls on intermediate values between mammal herbivores and carnivores (e.g., Lee-Throp et al., 1989; Clementz et al., 2009). This difference may be explained by disparate physiology and metabolic rates between mammals and birds.

The environmental significance of the oxygen isotopic composition of bone phosphates in birds has been minimally investigated as well (Kohn, 1996; Amniot et al., 2008). A study on terrestrial (herbivorous) birds documented a relationship among the $\delta^{18}O$ values of surface waters, bone phosphate and relative humidity (Kohn, 1996). Because our samples belong to a seabird, phosphate $\delta^{18}O$ values here should be highly influenced by seawater $\delta^{18}O$ values, and therefore, meteoric water $\delta^{18}O$ values cannot be inferred. The studied bones showed phosphate $\delta^{18}O$ values of $+18.2 \pm 0.9$‰ and correlated positively with carbonate $\delta^{18}O$ values (Fig. 8C). Interestingly, that relationship is offset to the right from the curve obtained from mammals by Iacumin et al. (1996), possibly as a consequence of the diagenetic alteration of bone carbonate $\delta^{18}O$ values (Fig. 8C). Our study reveals that fossil bird bones from oceanic islands preserve useful information of the ecosystem in their isotope codes. Due to the limited number of bone samples, further environmental inferences are not possible. In future studies in the region it will be interesting to evaluate potential temporal variations in trophic levels and environmental conditions using fossil Macaronesian bird bones.

Four species of the genus *Puffinus* are breeders on the Canary Islands, two extant species, *P. puffinus* and *P. baroli*, and two extinct species, *P. olsoni* and *P. holeae* (Ramírez et al., 2010; Rando and Alcover, 2010). Rando and Alcover (2010) concluded that the aboriginal people that inhabited the archipelago probably caused the extinction of *P. holeae*, prior to the Europeans' arrival to these islands. Our age data from bone collagen (~2.1–2.7 cal ka BP) is the youngest published age for this species and further supports that *P. holeae* was still present during the initial aboriginal occupation of the archipelago (see detailed discussion in Rando and Alcover, 2010).

5. Conclusions

Both calcitic and aragonitic shells of contemporaneous land snails record comparable environmental information in their isotope codes. The $\delta^{13}C$ values of shells and bioclastic sediments were significantly higher during ~23.3–24.0 cal ka BP than during ~2.1–5.5 cal ka BP and today, reflecting higher abundance of C_4 and/or CAM plants at glacial rather than interglacial time-intervals. The $\delta^{18}O$ values of aragonitic and calcitic shells were ~2.1–2.8‰ higher during the late Pleistocene than during the mid-late Holocene and today. The $\delta^{18}O$ values of bioclastic sediments showed a subdued but equivalent trend than shells. This may reflect the transition from glacial (cooler) temperatures, higher rain $\delta^{18}O$ values and/or similar or slightly lower relative humidity values than today towards warmer temperatures and lower rain $\delta^{18}O$ values of the present. Aragonitic and calcitic snail shells and carbonate-rich sediment data from these paleosols displayed the same pattern than published data from local Quaternary eolian deposits. The inferred late Pleistocene–Holocene climate change here could have caused the extinction of the endemic helicid *Theba* sp. Several herbivorous land snail species from the same time-interval showed similar carbon and oxygen isotopic values in their hard skeletons suggesting that they followed comparable physiological and ethological mechanisms. Late Pleistocene slugs, however, likely underwent stronger water loss than other late Pleistocene species with

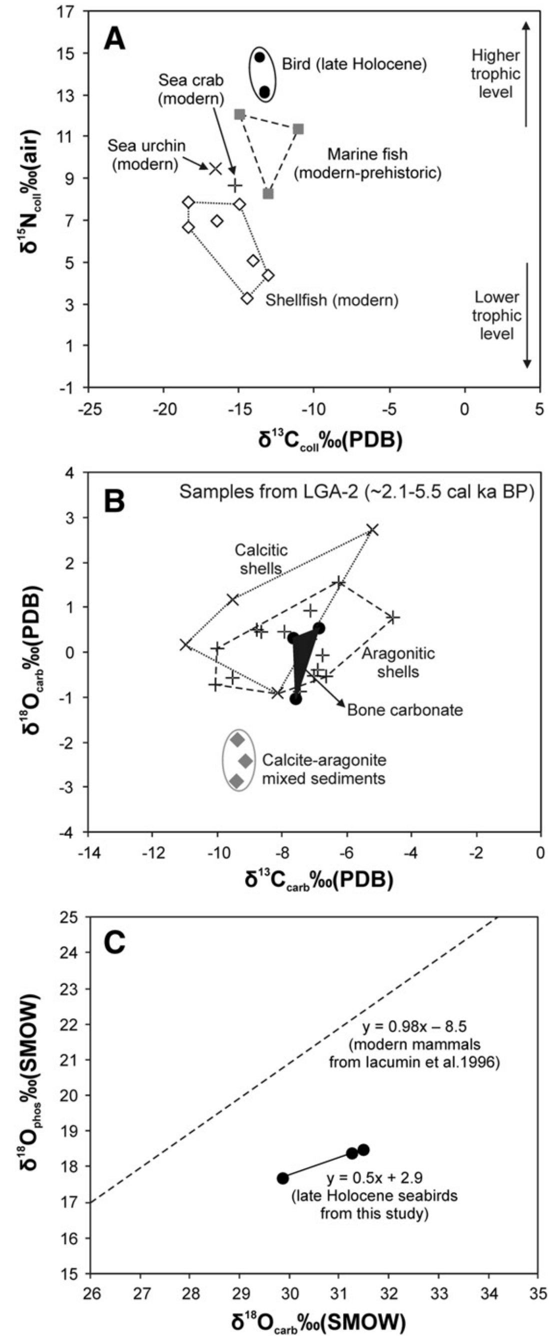

Fig. 8. Isotopic composition of the extinct Dune Shearwater *Puffinus holeae* (2.1–2.7 cal ka BP) from Lanzarote, Canary Islands. (A) Carbon and nitrogen stable isotope values of three samples of bone collagen of Holocene birds from this study (filled circles). Carbon and nitrogen stable isotope values of other organic matter samples from the Canary Islands (= modern and prehistoric marine animals) were adapted from Tieszen et al. (1995) and Arnay-de-la-Rosa et al. (2010) and plotted for comparison with bird samples. (B) Carbon and oxygen stable isotope values of three samples of bone carbonate of Holocene seabirds from this study (dark area). Carbon and oxygen isotope composition of sediments and land snail shells were also plotted for comparison. (C) Oxygen isotope composition of bone carbonate and bone phosphate of modern mammals (dashed line) by Iacumin et al. (1996) and seabird bones from the present study (continuous line).

external aragonitic shells, as expected due to their higher risk of desiccation during the last glacial interval. Late Holocene (~2.1–2.7 cal ka BP) bones ($n = 3$) of the extinct Dune Shearwater *P. holeae* exhibited bone collagen $\delta^{13}C$ and $\delta^{15}N$ values typical of a Macaronesian low trophic level seabird that prey upon local fish. Although the $\delta^{18}O$ values of bone carbonate were possibly altered, the $\delta^{13}C$ values of bone carbonate and the $\delta^{18}O$ values of bone phosphate showed pristine signatures useful for environmental inferences. In future studies it will be interesting to explore temporal and spatial variations in the environment and trophic level of extant and extinct Canarian birds using the isotopic composition of bone tissues. The radiocarbon age obtained from a bone of *P. holeae* reinforces previous published studies that suggested that this species existed during the initial period of aboriginal occupation in the archipelago.

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