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Christophe Lécuyer, Antonio Sanchez Marco, Alejandro Lomoschitz, Juan-Francisco Betancort, François Fourel, et al..  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of diagenetic land snail shells from the Pliocene (Zanclean) of Lanzarote, Canary Archipelago: Do they still record some climatic parameters?. *Journal of African Earth Sciences*, 2020, 162, pp.103702. 10.1016/j.jafrearsci.2019.103702 . hal-02991811

**HAL Id: hal-02991811**

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Submitted on 17 Nov 2020

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## $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of diagenetic land snail shells from the Pliocene (Zanclean) of Lanzarote, Canary Archipelago: Do they still record some climatic parameters?

Christophe Lécuyer<sup>a,\*</sup>, Antonio Sanchez Marco<sup>b</sup>, Alejandro Lomoschitz<sup>c</sup>, Juan-Francisco Betancort<sup>d</sup>, François Fourel<sup>e</sup>, Romain Amiot<sup>a</sup>, Thibault Clauzel<sup>a</sup>, Jean-Pierre Flandrois<sup>f</sup>, Joaquín Meco<sup>d</sup>

<sup>a</sup> Laboratoire de Géologie de Lyon, CNRS UMR 5276, Université Claude Bernard Lyon 1, France

<sup>b</sup> Institut Català de Paleontologia Miquel Crusafont, Barcelona, Spain

<sup>c</sup> Instituto de Oceanografía y Cambio Global, IOCAG – Unidad Asociada de I+D+i al CSIC, Universidad de Las Palmas de Gran Canaria, ULPGC, 35017 Las Palmas de Gran Canaria, Canary Islands, Spain

<sup>d</sup> Departamento de Biología, Universidad de Las Palmas de Gran Canaria (ULPGC), 35017 Las Palmas de Gran Canaria, Canary Islands, Spain

<sup>e</sup> Laboratoire d'Ecologie des Hydrosystèmes Naturels et Anthropisés, CNRS UMR 5023, Université Claude Bernard Lyon 1, France

<sup>f</sup> Laboratoire de Biométrie et Biologie Évolutive, CNRS UMR 5558, Université Claude Bernard Lyon 1, France

### ARTICLE INFO

#### Keywords

Pliocene  
Climate  
Canary Archipelago  
Stable isotope  
Gastropod  
Giant bird

### ABSTRACT

Fossiliferous bioclastic calcarenites of fluvial-aeolian origin were deposited between  $4.3 \pm 0.7$  Ma and  $3.78 \pm 0.71$  Ma in Lanzarote, Canary Archipelago. Climate was characterized by warm and steppic conditions. The fossil assemblage contains land snail shells that recrystallized into calcite as revealed by Raman spectroscopy. Carbon and oxygen isotope measurements were performed to understand whether or not these isotopic compositions may still reflect some climatic conditions contemporaneous with shell fossilisation and burial. Interpretations have been performed assuming two working hypotheses 1) isotopic compositions still record climatic conditions at the time of snails were living despite diagenesis and 2) isotopic compositions reflect both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of soil water as well as soil temperature. Positive correlations are observed between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of fossil land snail shells, which are not observed within populations of modern aragonitic land snail shells. This pattern could reflect shell  $\text{CaCO}_3$  recrystallisation from a  $\text{CO}_2$ -rich aqueous solution that suffered varying rates of evaporation. For the present investigated case, we propose that stable isotope compositions of these diagenetic land snail shells mimic those expected for unaltered snail shells that would still record original climatic conditions. Indeed,  $\delta^{13}\text{C}$  values could result from soil plant decay, which were not significantly different from the  $\delta^{13}\text{C}$  of snail diet mainly based on fresh leaves, even though a bias may result from diet preferences while soil organic matter averages the composition of the vegetation. Oxygen isotope ratios of shells result from a combination of evaporated soil water inherited from meteoric waters and soil temperatures that are closely related to mean air temperatures.

### 1. Introduction

Lanzarote, the most northeastern island of the Canary Archipelago, is located in the Eastern Central Atlantic Ocean characterized by a semi-arid subtropical climate. The oldest volcanic rocks dated so far erupted 15 My ago (Coello et al., 1992). Valle Grande, Valle Chico and Fuente de Gusa are the three main paleontological sites of Early Pliocene (Zanclean) age. The fossiliferous bioclastic calcarenites of fluvial-aeolian origin were deposited between  $4.3 \pm 0.7$  Ma and  $3.78 \pm 0.71$  Ma on the basis of K/Ar dating of underlying and overlying basaltic lava flows (Lomoschitz et al., 2016). Those sediments were deposited on a flat plain, extended over at least  $16\text{ km}^2$ , where aeolian sands moved freely under prevailing NNE-WSW winds. Cli-

matic conditions have been estimated as mainly dry with some rainy episodes (Lomoschitz et al., 2016). All the sedimentary beds of Zanclean age contain the same fossil assemblage consisting of insect egg pods, land snails, tortoises and avian eggshells. These avian eggshells have been assigned to a flightless giant bird that could have been related to the group of ratites (Rothe, 1964; Sauer and Rothe, 1972; Sanchez Marco, 2010). Lazzzerini et al. (2016) analyzed the stable carbon and oxygen isotope compositions of eggshell fragments and concluded that they were laid by a bird whose diet was mainly based on C3 plants and freshwater with a  $\delta^{18}\text{O}$  of  $\sim -3 \pm 2\text{‰}$  (VSMOW) typical of a tropical dry climatic environment (Craig, 1961). Land snail shell  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are also known to record climatic parameters and vegetation (Yapp,

\* Corresponding author. 2 rue Dubois, Campus de la Doua, Institut Universitaire de France, University of Lyon, 69622, Villeurbanne, France.

E-mail address: [Christophe.Lecuyer@univ-lyon1.fr](mailto:Christophe.Lecuyer@univ-lyon1.fr) (C. Lécuyer)

1979; Magaritz et al., 1981; Abell and Williams, 1989; Goodfriend et al., 1989; Balakrishnan and Yapp, 2004; Yanes et al., 2008, 2009; Yanes, 2015). Indeed, several authors have shown that the oxygen isotope composition of the shell of land snails is related to the composition of rainfall even though the relationship is complicated by other factors such as the relative humidity and the ambient water vapour (Yapp, 1979; Magaritz et al., 1981; Goodfriend et al., 1989; Balakrishnan and Yapp, 2004; Balakrishnan et al., 2005; Yanes et al., 2008, 2009). In the case of carbon isotopes, several studies performed in a natural or laboratory-controlled context led their authors to conclude that the  $\delta^{13}\text{C}$  of land snail shells mainly reflect their diet, sometimes scrambled by the minor consumption of pedogenic carbonates that constitutes a source of calcium for their shells (e.g. Goodfriend, 1987; Stott, 2002; Metref et al., 2003; McConnaughey and Gillikin, 2008; Yanes et al., 2008; Yanes et al., 2013).

In this study, we investigated the stable carbon and oxygen isotope compositions of the land snail shells collected from the Zanclean terrestrial deposits that crop out in northern Lanzarote, Canary Islands. The isotopic analyses have been performed to understand whether or not these isotopic compositions may still reflect some climatic conditions contemporaneous of shell fossilisation and burial.

## 2. Geological, paleontological and paleoclimatic context

### 2.1. Geological setting

The Canary Islands volcanism is the result of Neogene and Quaternary magmatic activity. Their origin has been the subject of several interpretations. Anguita and Hernáiz (2000) proposed a unifying model considering a wide sub-lithosphere thermal anomaly, as a general layer beneath the Canary Islands, the Atlas mountain range and their surrounding areas. This thermal anomaly corresponds to an old residual mantle plume that has been active during the opening of the Atlantic Ocean starting in the Triassic and could be in its terminal stage now. Carracedo et al. (2002) considered the oldest dated rocks for each island and showed that the oldest islands are also those closest to the African coast: Fuerteventura (20.6 Ma), Lanzarote (15.5 Ma), Gran Canaria (14.5 Ma) and Tenerife (11.6 Ma). However, a significant erosional gap and period of volcanic quiescence are apparent in each of these islands, lasting millions of years, though the gaps did not occur simultaneously. Erosional gaps appeared first in Fuerteventura and Lanzarote and later in Gran Canaria and then in Tenerife, while La Gomera Island is still in this stage (Carracedo et al., 2002). These erosional gaps were followed by late stage or rejuvenated volcanism during the Mio-Pliocene in Lanzarote, Pliocene in Fuerteventura, Mio-Pliocene in Gran Canaria and Pleistocene in Tenerife. The westernmost Canary Islands underwent Pleistocene (La Palma and El Hierro) or Mio-Pliocene (La Gomera) volcanism, but do not exhibit an intermediate erosional gap. It is significant that the Quaternary and historic volcanism of the Canary Islands bears no relation to the interrelated geographical position of the youngest volcanic eruptions.

Van Den Bogaard (2013) considered the Canary Island Seamount Province (CISP) as a whole, comprising more than 100 islands and seamounts that formed parallel to the NW African continental margin. His  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of these isolated volcanic structures on the seafloor ranges from 142 to 0.2 Ma, suggesting as an alternative interpretation, a broad, shallow mantle upwelling beneath the Atlantic Ocean basin and off the edge of the NW African continental lithosphere, which produced recurrent melting and seamounts from the Late Jurassic to recent. Van Den Bogaard (2013) considered the CISP to be the oldest hotspot in the Atlantic Ocean and the most long-lived mantle anomaly on Earth.

### 2.2. Pliocene deposits of the Canary Islands

Pliocene sedimentary deposits of the Canaries consist of marine conglomerates, sandstones and aeolian calcarenites (Meco et al., 2007, 2015; Lomoschitz et al., 2016). Pioneering studies devoted to the Pliocene marine deposits of Gran Canaria and Fuerteventura date as far back as the 19th century (Buch, 1825; Hartung, 1857; Lyell, 1865; Rothpletz and Simonelli, 1890). These deposits have been subsequently related to the volcanic history of both islands (Bourcart and Jérémme, 1937; Bravo, 1960; Vuagnat, 1960; Navarro et al., 1969; Schneider et al., 2004), radiometrically dated (Lietz and Schmincke, 1975; Guillou et al., 2004) and then correlated to the other Canary Islands (Meco and Stearns, 1981; Meco et al., 2007).

The island of Lanzarote is one of the seven main volcanic islands that constitute the Canary Archipelago (Fig. 1A). This NE-SW oriented island is located on the 29th parallel north at about 300 km off the Moroccan Sahara Desert, Africa. Lanzarote was generated by volcanism that produced both the Famara and Los Ajaches edifices whose ages range from ca. 15.5 to 12.3 Ma and from ca. 10.2 to 3.8 Ma, respectively.

The presence of Pliocene marine deposits in Lanzarote, however, could only be demonstrated by fossils recovered from the southeast of the island, which also occur in the Early Pliocene of Fuerteventura and Gran Canaria (Meco et al., 2007). All other sedimentary deposits in Lanzarote are of Tortonian age. On the western coast (Salinas de Janubio) of Lanzarote, marine deposits containing *Nerita emiliana* occur beneath lava flows dated using the K/Ar method at 6.6 Ma (Coello et al., 1992) and ~8.9 Ma (Meco et al., 2007).

For the purpose of this study, the most interesting Pliocene deposits are those of terrestrial origin located in the north of the island, named the Famara edifice. Its fauna was first studied in the second half of the twentieth century (Rothe, 1964; Sauer and Rothe, 1972; Gittenberger and Ripken, 1985), and revisited in the current century (Meco et al., 2005; Sánchez Marco, 2010; Lomoschitz et al., 2016; Lazzerini et al., 2016).

### 2.3. Paleontological sites

The Pliocene terrestrial sedimentary deposits of Lanzarote crop out in Valle Grande, Valle Chico and Fuente de Gusa (Fig. 1B) in the form of sedimentary beds. The land snail shells analyzed in this work were collected from these sedimentary beds mainly composed of bioclastic calcarenites of aeolian origin (sand sheet deposits) and coarse bioclastic calcarenite with volcanic fragments of fluvial-aeolian origin (mainly stream deposits). Remarkably, all the beds contain the same fossils (insect egg pods, land snails, avian eggshells and tortoise eggshells). The paleontological sites are close to each other (1–1.5 km) and their calcarenite beds have been geologically correlated and dated between ca. 4.3 and 3.78 Ma (Lomoschitz et al., 2016).

#### 2.3.1. Valle Grande

The representative section of the Valle Grande site is composed of three sedimentary beds with a total thickness of 4.2 m, which are intercalated between two piles of basaltic and pyroclastic lava flows. The most common fossils are insect egg pods, land snails, avian and tortoise eggshells.

#### 2.3.2. Valle Chico

The representative section of the Valle Chico site is composed of three sedimentary beds with a total thickness of 6.2 m, which are intercalated between two piles of basaltic and pyroclastic lava flows.

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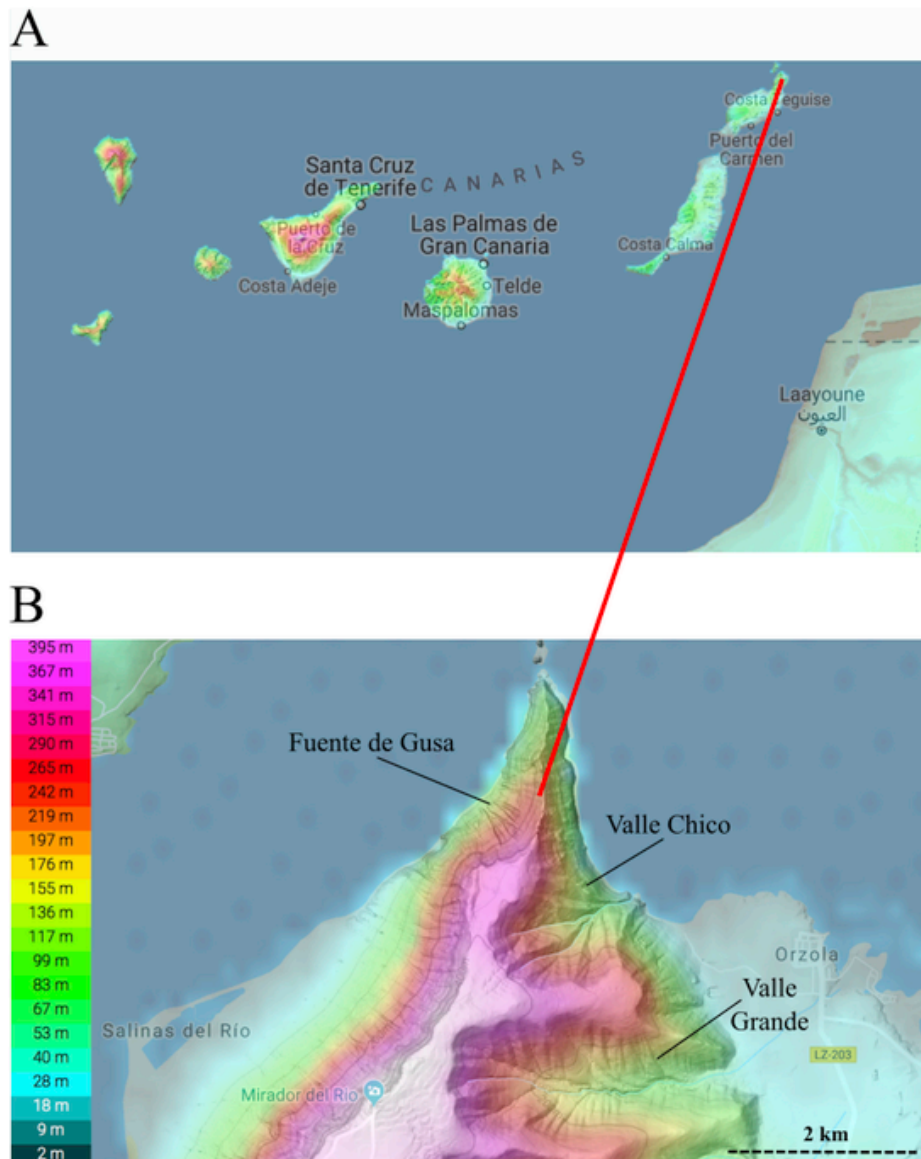


Fig. 1. A) Canary Archipelago in the eastern Central Atlantic Ocean with the location of Lanzarote, the northeasternmost island of the Archipelago and the closest one to the African coast. B) Geographic locations of the three Zanclean sedimentary deposits where the land snail shells were sampled near Orzola, northern Lanzarote.

Documented fossils include land snails, insect egg pods, and avian and tortoise eggshells. The insect egg pods are highly abundant and are presumably similar to those studied by Meco et al. (2011).

### 2.3.3. Fuente de Gusa

The reference sedimentary sequence for the Fuente de Gusa site corresponds to the area characterized by the highest fossil abundance and which crops out on the coastal cliff at a height of about 22m. It is composed of two sedimentary beds with a total thickness of 1.1 m, which are intercalated between basaltic lava flows. The observed fossils include insect egg pods, land snails, and avian and tortoise eggshells.

### 2.4. Early Pliocene Canary paleoclimate

The Canary climate was influenced by two main processes in the Pliocene: the growth of the ice sheet in the Arctic Ocean and the spatial expansion of deserts in Africa. Consequently, two groups of effects took place: (a) the cold Canary Current origin, followed by a

falling of the sea level; and (b) desert dust arrivals as well as Acrididae infestations favored by humid periods and the eventual initiation of differentiated climatic seasons. As a result, geological changes took place including the sedimentation of large amounts of bioclastic aeolian sands and of some interbedded paleosol horizons according to these processes.

Huge amounts of bioclastic sands, later transformed into calcarenite, originated from extensive marine deposits occurring along many low Canary coasts in the Early Pliocene. In addition, dated lava flows from Gran Canaria and Fuerteventura indicate that the biocalcarenite beds, intercalated between the lava-flows, were formed after ca. 4.2Ma and before ca. 2.9Ma (Meco et al., 2015). Moreover, in a global context, the original sand deposits would be exposed to the air due to a general sea-level fall produced when the North Hemisphere Ice-sheet and the West Antarctic Ice-sheet were formed between 4.6 and 3.1 Ma (Zachos et al., 2001). Nevertheless, 4.2Ma ago, the Canary marine deposits still had warm tropical fauna (Meco et al., 2015). At this time, the cold Canary Current had not yet fully developed, but would have gradually formed soon after. Its

appearance may have coincided with a progressive sea level fall that has been documented by a rapid increase in the  $\delta^{18}\text{O}$  values of benthic foraminifera from 3‰ at the beginning of the Early Pliocene to 3.6‰ at its end according to Zachos et al. (2001).

The first arrival of Acrididae plagues to the Canary Islands from Africa took place near the end of the Early Pliocene before 3Ma ago as recorded in palaeosols containing African dust and innumerable relicts of egg pods built by temperate-region locusts (Meco et al., 2011). These egg pods had a protection function for the Acrididae individuals against adverse climate conditions (Meco et al., 2015) and we consider their presence as evidence of differentiated climate seasons. Indeed, Lanzarote may have been already suffering arid conditions at least at the seasonal scale. This hypothesis is compatible with the climate and vegetation reconstructions inferred from the use of a hybrid method combining data and output calculations from model BIOME4 (Dowsett et al., 2009) as well as the synthesis of geochemical proxies of sea surface temperature (SST) performed in the eastern Central Atlantic Ocean, close to the Canary Archipelago (Fedorov et al., 2013). Indeed, Dowsett et al. (2009) proposed SST and mean annual temperature (MAT) higher by about 3°C and 2°C than today (MAT = 19.2°C–22.3°C (mean = 20.8°C) from 1959 to 2013 in Lanzarote; National Center for Atmospheric Research), respectively, and a moisture balance equivalent to present-days or even slightly positive. Fedorov et al. (2013) estimated that SST were 4°C–5°C higher than today, a conclusion inferred from geochemical data obtained from samples recovered from ODP site 958A located along the North African margin. As the mean minimal and maximal temperatures recorded in Lanzarote during the last ten years have been  $17 \pm 1^\circ\text{C}$  in January and  $26 \pm 1^\circ\text{C}$  in August (National Center for Atmospheric Research), we can estimate that Zanclean MAT were comprised between 21–22°C and 30–31°C assuming a comparable seasonality.

## 2.5. Terrestrial gastropods and giant birds

### 2.5.1. Terrestrial giant birds

The identity of the birds that laid the eggs unearthed from the Neogene outcrops of northern Lanzarote has been a controversial issue. The first studies devoted to this subject (Rothe, 1964; Sauer, 1972; Sauer and Rothe, 1972), which were based on the egg shape and thickness as well as the arrangement of the pores for gas exchange located on the outer surface allowed Sauer (1972) to propose they belong to two ratite species. Indeed, the pore pattern is very similar to that of the extinct elephant bird *Aepyornis* from Madagascar and another one is similar, although with some differences, to the most widespread subspecies of the extant African ostrich *Struthio camelus camelus*. Sauer and Sauer (1978) identified both morphotypes, Struthionid and Aepyornithoid, from the Neogene deposits of Ouarzazate, Morocco. The Struthionid eggshells from Lanzarote and Ouarzazate received the denomination of *Struthilithus saueri* (Mikhailov, 1997). Casañas (1990) reexamined this issue with the study of new eggshells and the finding of a bone fragment, and tentatively attributed all the remains to an odontopterygiform (= Pelagornithidae), which is an extinct group of marine birds. Their work has the crucial flaw of ignoring the eggshells traits and relied exclusively on the alleged avian affinities of one bone fragment, which could supposedly belong to a pelagornithid. Even doubts have been expressed about whether the referred bone fragment should be assigned to a bird (Sánchez Marco, 2010).

### 2.5.2. Land snails and study material

Fifty land snail shells (Table 1) have been collected from the sedimentary layers cropping out at Valle Grande, Valle Chico and Fuente de Gusa (Fig. 1B). To be representative of the three main

**Table 1**

Stable carbon and oxygen isotope compositions of early Pliocene (Zanclean) land snail shells from northern Lanzarote, Canary Archipelago (Fig. 1).

Sample	Taxon	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
		‰ VPDB	‰ VPDB
<b>Fuente de Gusa</b>			
FG1	<i>Leptaxis orzolae</i>	−5.78	−4.8
FG2	<i>Zootecus insularis</i>	−5.75	−4.0
FG3	<i>Theba orzolae</i>	−5.69	−2.3
FG4	<i>Leptaxis orzolae</i>	−5.24	−3.9
FG5	<i>Zootecus insularis</i>	−6.56	−4.0
FG6	<i>Zootecus insularis</i>	−5.78	−4.8
FG7	<i>Leptaxis orzolae</i>	−5.21	−1.5
FG8	<i>Theba orzolae</i>	−6.03	−2.1
FG9	<i>Zootecus insularis</i>	−6.73	−5.0
FG10	<i>Leptaxis orzolae</i>	−5.73	−3.8
FG15	<i>Leptaxis orzolae</i>	−4.24	−2.8
FG16	<i>Leptaxis orzolae</i>	−3.98	−3.0
FG18A	<i>Leptaxis orzolae</i>	−4.69	−1.5
FG18B	<i>Zootecus insularis</i>	−4.17	−3.8
FG19	<i>Zootecus insularis</i>	−5.79	−4.4
<b>Valle Grande Este</b>			
VGE2A	<i>Leptaxis orzolae</i>	−5.77	−1.1
VGE2B	<i>Leptaxis orzolae</i>	−7.58	−3.5
VGE4B	<i>Leptaxis orzolae</i>	−6.39	−3.2
VGE5A	<i>Leptaxis orzolae</i>	−7.57	−4.2
VGE5B	<i>Leptaxis orzolae</i>	−7.29	−4.3
VGE6	<i>Theba orzolae</i>	−4.55	−0.4
VGE7	<i>Theba orzolae</i>	−5.72	−1.2
VGE8	<i>Theba orzolae</i>	−5.24	−2.4
VGE9	<i>Theba orzolae</i>	−5.27	−2.5
VGE10	<i>Theba orzolae</i>	−5.96	−2.3
VGE11	<i>Zootecus insularis</i>	−7.77	−3.8
VGE12	<i>Zootecus insularis</i>	−7.84	−3.2
VGE13	<i>Zootecus insularis</i>	−7.43	−3.3
VGE14	<i>Zootecus insularis</i>	−6.37	−4.3
<b>Valle Chico</b>			
VCS2	non identified	−5.92	−1.5
VCS2-5	non identified	−4.89	−2.9
VCS2-7	non identified	−3.30	−1.9
VCS2-8	non identified	−6.10	−0.9
VCS2-10	non identified	−4.93	−2.5
VCS4-1	<i>Theba orzolae</i>	−6.85	−3.7
VCS4-3	<i>Leptaxis orzolae</i>	−6.58	−4.4
VCS4-4	<i>Leptaxis orzolae</i>	−5.93	−3.1
VCS4-5	<i>Leptaxis orzolae</i>	−7.97	−4.3
VCS4-6	<i>Leptaxis orzolae</i>	−6.03	−3.2
VCS4-8	<i>Leptaxis orzolae</i>	−5.26	−2.4
VCS4-9	<i>Leptaxis orzolae</i>	−6.31	−2.3
VCS4-10	<i>Theba orzolae</i>	−5.68	−2.2
VCG1	non identified	−5.50	−1.6
VCG2	non identified	−4.95	−3.4
VCG3	non identified	−5.29	−2.1
VCG4	non identified	−5.51	−3.0
VCG5	non identified	−5.91	−1.4
VCG6	non identified	−4.70	−1.0
VCG7	non identified	−6.20	−2.2
VCG8	non identified	−5.07	−1.5

stratigraphic sections, they have been sampled all along with the calcarenite beds. Three main species (Fig. 2) have been assigned to *Theba orzolae* (Gittenberger and Ripken, 1985), *Leptaxis orzolae* (Gittenberger and Ripken, 1985) and *Zootecus insularis* (Ehrenberg, 1831). Raman spectroscopy revealed that these fossil shells consist of calcite (Fig. 3).



Fig. 2. Photomicrographs of the three most common land snail species recovered from the early Pliocene of northern Lanzarote: *Theba orzolae*, *Leptaxis orzolae* and *Zootecus insularis*.

*Theba orzolae* and *Leptaxis orzolae* are extinct endemic species from Lanzarote, Canary Islands (Gittenberger and Ripken, 1985). *Z. insularis* currently lives from the Atlantic Sahara to Egypt, and in Arabia and India. However, nowadays, *Z. insularis* is notoriously absent from the Canary Islands and from the rest of Atlantic archipelagos. It could indicate better dispersion conditions in the past between Lanzarote Island and the African coasts.

### 3. Physiology and ecology of modern land snails

Land snails are active when the relative air humidity (Rh) is comprised between 75% and 95% (Sacchi, 1955, 1958). Their shell growth is optimal between 7°C and 27°C according to Sacchi (1958) and their activity is mostly nocturnal, a life trait being potentially responsible for a bias in the record of daily temperatures. Life expectancy of land snails is comprised between 2 and 7 years in average (Heller, 1990), however, the duration of shell growth is about a few months, which means a seasonal scale record in terms of paleoclimatic reconstructions (Benbellil-Tafoughalt and Koene, 2015). According to Benbellil-Tafoughalt and Koene (2015), if we consider a seasonal growing temperature (SGT) close to 20°C, which is close to the present-day mean annual air temperature in Lanzarote, land snails born in autumn need 15 weeks ( $\approx 4$  months) to

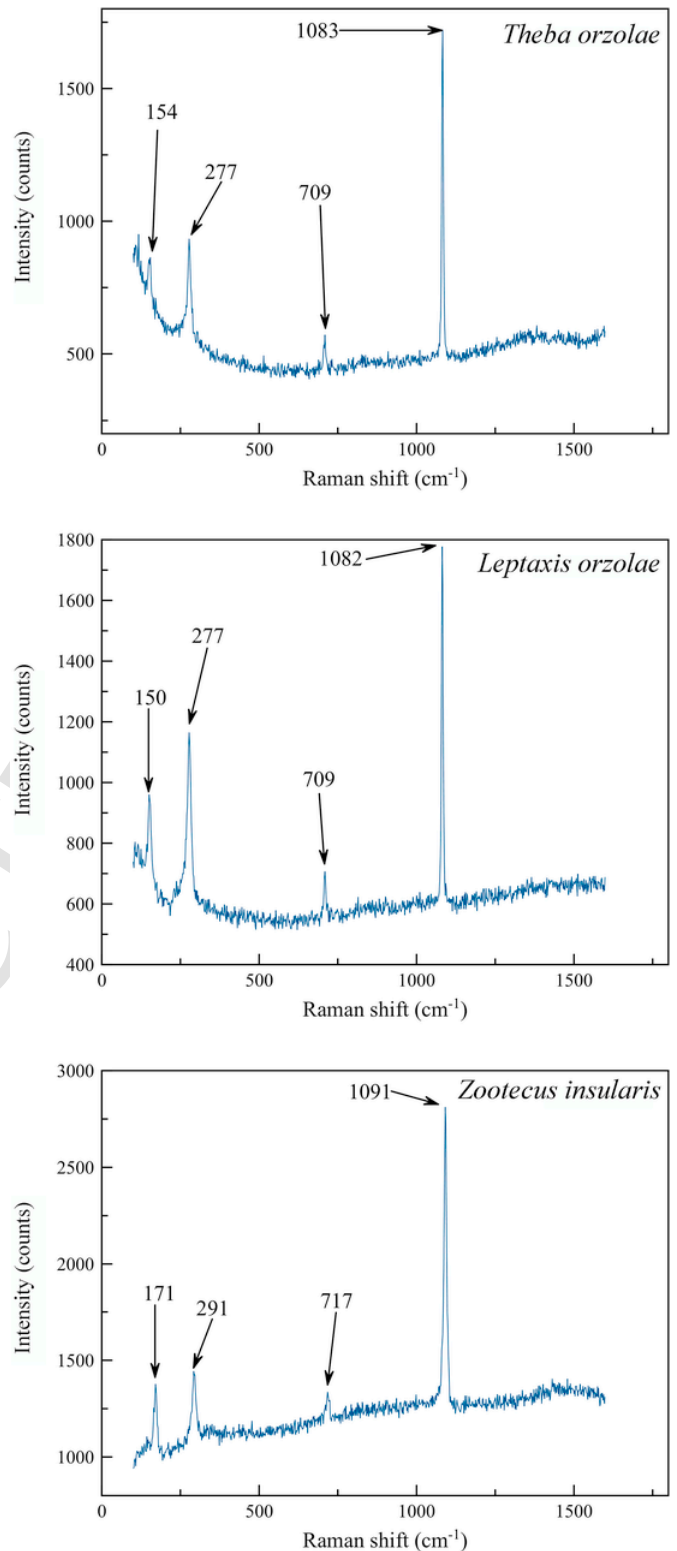


Fig. 3. Raman spectra of land snail shells *Theba orzolae*, *Leptaxis orzolae* and *Zootecus insularis* from Fig. 2. All these shells are made of calcite that is characterized by the presence of relative intense peaks in the 150–290  $\text{cm}^{-1}$  range for lattice modes, and 709–717  $\text{cm}^{-1}$  for the bending mode of the carbonate group. The peak located close to 1080–1090  $\text{cm}^{-1}$  is characteristic of the carbonate group stretching mode.

reach about 90% of their final body weights while for those born in spring only 12 weeks ( $\approx 3$  months) are necessary.

#### 4. Analytical techniques

##### 4.1. Raman spectroscopy

We used Raman spectroscopy in order to characterize the mineralogy of all the studied skeletal carbonates. The two polymorphs of  $\text{CaCO}_3$  are readily identified from the low frequency part of the spectra, and especially from the position and splitting of the symmetric bending mode which occurs as a single peak at  $712\text{ cm}^{-1}$  in calcite and as a doublet at  $701\text{--}704\text{ cm}^{-1}$  in aragonite (Unvros et al., 1991; Gillet et al., 1993). The Raman Spectrometer X'plora, hosted by the Laboratoire de Géologie de Lyon at the University Claude Bernard Lyon 1, has been operated by using an objective x 1000, an optical network of 1800 lines per mm, a monochromatic laser (wavelength of  $532\text{ nm}$ ) filtered by 10% with two acquisitions (60 s per acquisition) performed between 100 and  $1600\text{ cm}^{-1}$ .

##### 4.2. Carbon and oxygen isotope analysis of land snail shells

Only complete land snail shells have been selected for the stable isotope analysis. Shells were cleaned within an ultrasonic bath to remove sediment matrix. After washing with deionized water, samples (i.e. one complete shell) were dried at ambient temperature and crushed in an agate mortar until a fine powder was obtained. Stable isotope ratios were determined by using an auto sampler MultiPrep™ system coupled to a dual-inlet GV Isoprime™ isotope ratio mass spectrometer (IRMS). Aliquot size was about  $300\text{ }\mu\text{g}$  of calcium carbonate. All aliquots were reacted with anhydrous oversaturated phosphoric acid at  $90\text{ }^\circ\text{C}$  during 20 min. Oxygen isotope ratios of calcium carbonate are computed assuming an acid fractionation factor  $1000\ln\alpha(\text{CO}_2\text{--CaCO}_3)$  of 8.1 between carbon dioxide and calcite (Swart et al., 1991). All sample measurements were duplicated and adjusted to the international references NIST NBS18 ( $\delta^{18}\text{O}_{\text{VPDB}} = -23.2\text{ ‰}$ ;  $\delta^{13}\text{C}_{\text{VPDB}} = -5.01\text{ ‰}$ ) and NBS19 ( $\delta^{18}\text{O}_{\text{VPDB}} = -2.20\text{ ‰}$ ;  $\delta^{13}\text{C}_{\text{VPDB}} = +1.95\text{ ‰}$ ). External reproducibility is close to  $\pm 0.1\text{ ‰}$  for  $\delta^{18}\text{O}$  and  $\pm 0.05$  for  $\delta^{13}\text{C}$  ( $2\sigma$ ).

In the case of oxygen isotope ratios, a correction of  $-0.27\text{ ‰}$  was applied to convert the assumed  $\delta^{18}\text{O}$  of water from the VSMOW to VPDB scales according to Hut (1987). This correction is necessary to compare measured  $\delta^{18}\text{O}$  of  $\text{CO}_2$  produced by the reaction of the carbonate with  $\text{H}_3\text{PO}_4$  and the  $\text{CO}_2$  equilibrated with  $\text{H}_2\text{O}$ . It applied to the empirically-determined oxygen isotope fractionation equations established between aragonite and water or calcite and water (e.g. Anderson and Arthur, 1983; Grossman and Ku, 1986; Brand et al., 2013), not to those that have been experimentally-determined in the laboratory (e.g. O'Neil et al., 1969; Kim and O'Neil, 1997; Kim et al., 2007).

#### 5. Results

Zanclean land snail shells collected from three sites in northern Lanzarote display large ranges in both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (Table 1; Fig. 4). As a whole,  $\delta^{13}\text{C}$  are comprised between  $-7.97$  and  $-3.30$  (‰ VPDB) while  $\delta^{18}\text{O}$  vary from  $-5.02$  to  $-0.42$  (‰ VPDB). Calculated mean isotopic compositions of land snail shells from Fuente de Gusa ( $\delta^{13}\text{C} = -5.42 \pm 0.83$  and  $\delta^{18}\text{O} = -3.44 \pm 1.17$ ;  $n = 15$ ), Valle Grande Este ( $\delta^{13}\text{C} = -6.48 \pm 1.10$  and  $\delta^{18}\text{O} = -2.85 \pm 1.26$ ;  $n = 14$ ) and Valle Chico ( $\delta^{13}\text{C} = -5.66 \pm 0.94$  and  $\delta^{18}\text{O} = -2.45 \pm 0.98$ ;  $n = 21$ ) have a probability to be equal (Welch two sample t-test) that ranges from 0.0075 to 0.43 depending on either the sampling site or isotopic system is considered (Table 2). These land snail shells are characterized by significant  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  positive Pearson linear correlations; the highest correlation ( $r = 0.78$ ) is observed at the site of

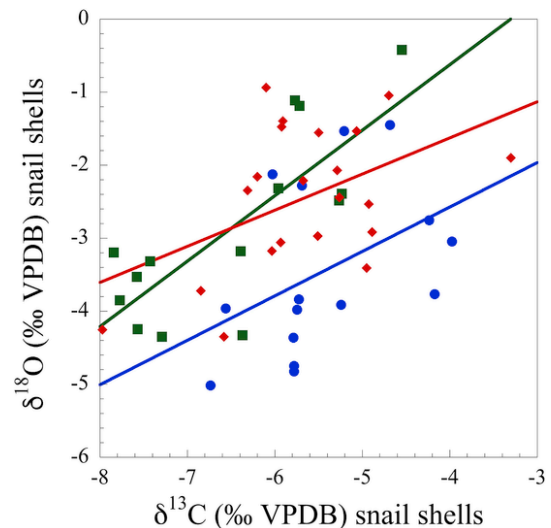


Fig. 4. Bivariate plot and linear correlations between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values (‰ VPDB) of early Pliocene land snail shells sampled from the three sampling sites in northern Lanzarote: Valle Grande ( $\delta^{18}\text{O} = 0.896\delta^{13}\text{C} + 2.958$ ;  $R^2 = 0.61$ ; green squares), Valle Chico ( $\delta^{18}\text{O} = 0.495\delta^{13}\text{C} + 0.353$ ;  $R^2 = 0.22$ ; red diamonds) and Fuente de Gusa ( $\delta^{18}\text{O} = 0.609\delta^{13}\text{C} - 0.137$ ;  $R^2 = 0.19$ ; blue circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Welch two sample t-test calculating the probability  $p$  of the null hypothesis: means are equal between the paired  $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$  values (Table 1) of land snail shells from the three sampling sites in northern Lanzarote: Valle Grande, Valle Chico and Fuente de Gusa (Fig. 1B).

Welch two sample t-test:	
Valle Grande & Valle Chico snail samples:	
	probability $p$ of equal means
$\delta^{13}\text{C}$	0.030
$\delta^{18}\text{O}$	0.327
Valle Grande & Fuente de Gusa snail samples:	
	probability $p$ of equal means
$\delta^{13}\text{C}$	0.008
$\delta^{18}\text{O}$	0.204
Valle Chico & Fuente de Gusa snail samples:	
	probability $p$ of equal means
$\delta^{13}\text{C}$	0.430
$\delta^{18}\text{O}$	0.013

Valle Grande while weaker correlations are obtained for samples coming from Fuente de Gusa and Valle Chico with  $r = 0.43$  and  $r = 0.47$ ; respectively (Fig. 4). A Fisher test revealed that those coefficients of correlation have a very low ( $p = 0.080$ ) to significant probability (0.446) to have no significant difference between them; depending on paired sampling sites (Table 3).

#### 6. Basic principles

##### 6.1. The record of air temperatures in land snail shell $\delta^{18}\text{O}$

###### 6.1.1. The case of unaltered aragonitic land snail shells

Several authors proposed that the oxygen isotope compositions of land snail shells ( $\delta^{18}\text{O}_{\text{sh}}$ ) record climatic parameters of their living environment such as air temperature, amount of precipitation and air humidity (e.g. Yapp, 1979; Magaritz et al., 1981; Abell and Williams, 1989; Goodfriend et al., 1989; Balakrishnan and Yapp, 2004; Yanes et al., 2008, 2009; 2015, 2018). On the contrary to aquatic skeletal carbonate-secreting invertebrates, their ter-

**Table 3**

Fisher test calculating the probability  $p$  of the null hypothesis: correlation coefficients 'r' are equal between the paired  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  values (Table 1) of land snail shells from the three sampling sites in northern Lanzarote: Valle Grande, Valle Chico and Fuente de Gusa (Fig. 1B).

Fisher test:	
Valle Grande & Valle Chico snail samples:	
z	probability $p$ of equal correlations
1.399	0.081
Valle Grande & Fuente de Gusa snail samples:	
z	probability $p$ of equal correlations
1.403	0.080
Valle Chico & Fuente de Gusa snail samples:	
z	probability $p$ of equal correlations
0.135	0.446

restrial ecology makes more complex the interpretation of their shell oxygen isotope ratio ( $\delta^{18}\text{O}_{\text{sh}}$ ) as their body water composition ( $\delta^{18}\text{O}_{\text{bw}}$ ) may differ from that of the water they ingest through their diet mainly based on fresh plant leaves of which water derives from rainfall ( $\delta^{18}\text{O}_{\text{mw}}$ ). On the basis of flux balance models and empirical observations (Yapp, 1979; Magaritz et al., 1981; Goodfriend et al., 1989; Balakrishnan and Yapp, 2004), the magnitude of the body water  $^{18}\text{O}$ -enrichment appears to strongly depend on ambient temperature, relative humidity, isotopic composition of atmospheric vapour water and metabolic activity of the snail. This  $^{18}\text{O}$ -enrichment of land snail body water relative to meteoric water may reach up to 6‰ (Balakrishnan and Yapp, 2004; Zaarur et al., 2011) because of evaporation that prevailed in arid and hot environments while it is commonly comprised between 1‰ and 4‰ in subtropical and relative dry environments such as the eastern islands (Lanzarote, Tenerife) of the Canary Archipelago (Yanes et al., 2008, 2009). Theoretically, ambient air temperature of the growing season of land snails can be estimated by solving the isotopic fractionation between biogenic aragonite and water that was either empirically determined by Grossman and Ku (1986) or experimentally by Kim et al. (2007). Both oxygen isotope fractionation equations provide comparable outputs with differences in calculated water  $\delta^{18}\text{O}$  values lower than 0.5‰ and differences in air temperature ranging from 0.5 °C to 2 °C in the temperature range 20 °C–30 °C. The use of those equations implies to be able to estimate  $\delta^{18}\text{O}_{\text{bw}}$  being related to  $\delta^{18}\text{O}_{\text{mw}}$  by adding an offset value that requires to be determined. It is worthy to note that this issue can be potentially solved by using the clumped-isotope thermometer as already addressed by Zaarur et al. (2011) and Wang et al. (2016) for example.

Under middle to high latitudes, mean air temperatures are generally well linearly correlated to the oxygen isotope composition of meteoric waters (Dansgaard, 1964; Craig and Gordon, 1965; Yurtsever and Gat, 1981; Rozanski et al., 1993; Gat, 1996; Fricke and O'Neil, 1999). In this case, we have two available equations that relate MAT to  $\delta^{18}\text{O}_{\text{sh}}$ ,  $\delta^{18}\text{O}_{\text{bw}}$  and  $\delta^{18}\text{O}_{\text{mw}}$ :

$$\text{MAT} = 20.6 - 4.34(\delta^{18}\text{O}_{\text{sh}} - \delta^{18}\text{O}_{\text{bw}}) \quad (\text{adapted from Grossman and Ku, 1986}) \quad (1)$$

$$\text{MAT} = A\delta^{18}\text{O}_{\text{mw}} + B \quad (2)$$

Let also consider that  $\delta^{18}\text{O}_{\text{bw}}$  is related to  $\delta^{18}\text{O}_{\text{mw}}$  as follows:

$$\delta^{18}\text{O}_{\text{bw}} = \delta^{18}\text{O}_{\text{mw}} + C \quad \text{with } C \text{ being a constant} \geq 0 \quad (3)$$

Hence, we set equations (1) and (2) equal to each other, which implies the assumption that snail body temperature is equivalent to the seasonal growing temperature (SGT), and  $\delta^{18}\text{O}_{\text{mw}}$  can be solved as follows:

$$\delta^{18}\text{O}_{\text{mw}} = (4.34\delta^{18}\text{O}_{\text{sh}} + B - 4.34C - 20.6)/(4.34 - A) \quad (4)$$

with SGT finally obtained by substituting equation (4) into equation (2):

$$\text{SGT} = A * [(4.34\delta^{18}\text{O}_{\text{sh}} + B - 4.34C - 20.6)/(4.34 - A)] + B \quad (5)$$

### 6.1.2. The case of land snail shells made of diagenetic calcite

Here, we assume that diagenesis takes place in soils where water  $\delta^{18}\text{O}$  is comparable to that of meteoric waters and soil temperature in °C is related to that of mean air temperature as follows:

$$T_{\text{soil}} = [20.6 - 4.34(\delta^{18}\text{O}_{\text{sh}} - \delta^{18}\text{O}_{\text{mw}})] \quad (\text{adapted from Grossman and Ku, 1986}) \quad (6)$$

Combined to:

$$T_{\text{air}} = A\delta^{18}\text{O}_{\text{mw}} + B \quad (7)$$

$$\text{with } T_{\text{soil}} = T_{\text{air}} + C' = A\delta^{18}\text{O}_{\text{mw}} + B + C' \quad (8)$$

Setting equations (6) and (8) equal to each other,  $\delta^{18}\text{O}_{\text{mw}}$  can be solved as follows;

$$\delta^{18}\text{O}_{\text{mw}} = (4.34\delta^{18}\text{O}_{\text{sh}} - 20.6 + B + C')/(4.34 - A) \quad (9)$$

$T_{\text{air}}$  (°C) is finally obtained from equation (7). As the aragonite of land snail shell has been converted into calcite, the isotopic fractionation between aragonite and calcite needs to be taken into account. This isotopic fractionation has been experimentally determined at 25 °C ( $\Delta_{\text{aragonite-calcite}} = +0.6\text{‰}$ ) by Tarutani et al. (1969) and further documented ( $\Delta_{\text{aragonite-calcite}} = +0.6 \pm 0.3\text{‰}$ ) by Grossman and Ku (1986) who compared its biogenic aragonite dataset to the experimental calcite curve determined by O'Neil et al. (1969). Here, we emphasize that the slopes of these equations are near identical; which means that the  $\Delta$  value is not temperature-sensitive. Consequently, temperatures inferred from Grossman and Ku (1986) equation need to be corrected by an offset of  $\approx +3$  °C that corresponds to the slope value of 4.34 multiplied by the  $\Delta_{\text{aragonite-calcite}}$  value of 0.6‰. Here we emphasize that the use of calcite-water isotopic fractionation equations determined either by O'Neil et al. (1969) or Kim and O'Neil (1997) provide comparable estimates in water  $\delta^{18}\text{O}$  values of temperatures in the same order of magnitude as analytical uncertainties.

## 6.2. The record of vegetation in land snail shell $\delta^{13}\text{C}$

### 6.2.1. The case of unaltered aragonitic land snail shells

The  $\delta^{13}\text{C}$  of shell carbonate from land snails is primarily composed of respiratory  $\text{CO}_2$  derived from the consumption of plants as it operates for all terrestrial molluscs (McConnaughey et al., 1997; McConnaughey and Gillikin, 2008), therefore recording the proportions of C3–C4–CAM plants in their diet. Even though some researchers (Goodfriend, 1987, 1999; Ortiz et al., 2006) have shown that additional factors may influence  $\delta^{13}\text{C}$  shell values such as the ingestion of soil carbonates, plant diet seems to be the main source of carbon for the precipitation of shell carbonate. The magnitude of  $^{13}\text{C}$ -enrichment that takes place between the calcium carbonate and diet is also sensitive to two other main environmental factors. Indeed, an increasing rate of insolation tends to decrease the  $\delta^{13}\text{C}$  of plants while an increasing water stress causes an increase of their  $^{13}\text{C}/^{12}\text{C}$  ratios (Farquhar et al., 1989). In the latter case, it becomes possible that the  $\delta^{13}\text{C}$  of some C3 plants mimics those of CAM plants.

$\delta^{13}\text{C}$  shell values are much higher than the carbon derived from the diet ( $\Delta^{13}\text{C}_{\text{shell-diet}}$ ) because of isotope exchange between respiratory  $\text{CO}_2$  and  $\text{HCO}_3^-$  from which the shell aragonite is precipitated



(McConnaughey and Gillikin, 2008). This  $\Delta^{13}\text{C}_{\text{shell-diet}}$  most commonly lies between 12 and 14‰ (Stott, 2002; Metref et al., 2003; Liu et al., 2007). Plant  $\delta^{13}\text{C}$  values may also directly depend on other chemical factors such as the carbon isotope ratio of carbon dioxide and its atmospheric partial pressure (e.g. Schubert and Jahren, 2012). However, those chemical effects most likely had a restricted impact on the early Pliocene vegetation because both atmospheric  $\delta^{13}\text{C}$  values of carbon dioxide ( $-7 < \delta^{13}\text{C}(\text{CO}_2) < -6.5\text{‰}$  VPDB; Tipple et al., 2010) and its partial pressure ( $300 \text{ ppm} < p\text{CO}_2 < 500 \text{ ppm}$ ; Zhang et al., 2013) were close to those analyzed during these last decades ( $350 \text{ ppm} < p\text{CO}_2 < 400 \text{ ppm}$  and  $\delta^{13}\text{C}(\text{CO}_2) \approx -7.5\text{‰}$ ; Francey et al., 1999). Moreover, those differences, which never exceeded a few tenths of ‰, remain negligible regarding the large isotopic differences that distinguish the two plant groups represented by C3 and C4-CAM plants. While C4 plants developed an adaptive ecology to warm and monsoonal climates, CAM plants generally occur in water-stressed habitats as summarized by (Ehleringer and Monson, 1993).

### 6.2.2. The case of land snail shells made of diagenetic calcite

If we consider recrystallisation of shell aragonite into calcite in open-system conditions, the source of carbonate may directly derive from soil  $\text{CO}_2$  which results from organic matter decay as follows:



In presence of water  $\text{CO}_2$  reacts to form carbonic acid:



At pH of soils close to 7 or 8, carbonic acid dissociates to form bicarbonate ions  $\text{HCO}_3^-$  that may combine with  $\text{Ca}^{2+}$  to precipitate calcite. As measured by Cerling and Quade (1993), the carbon isotope fractionation that takes place between soil carbonate and soil  $\text{CO}_2$  ( $\Delta^{13}\text{C}_{\text{carbonate-carbon dioxide}}$ ) ranges from 13.5 to 16.5. A linear regression was performed between  $\Delta^{13}\text{C}_{\text{carbonate-organic matter}}$  and MAT on the basis of data compiled into Table 1 provided by Cerling and Quade (1993). The carbon isotope fractionation between soil carbonate and organic matter tends to decrease with increasing mean air temperatures according to the following equation:

$$\Delta_{\text{carbonate-organic matter}} = 16.04(\pm 0.33) - 0.076(\pm 0.027)\text{MAT} \quad (12)$$

(R = 0.45)

As demonstrated by Cerling and Quade (1993), the  $\delta^{13}\text{C}$  of soil carbonate is ultimately controlled by the  $\delta^{13}\text{C}$  of vegetation and the diffusional mass transport of soil gases. According to their model, the carbon isotope composition of soil carbonate should become steady below 25 cm in depth. Therefore, Cerling and Quade (1993) concluded that “if significant variation in the isotopic composition of pedogenic carbonate is apparent from a single soil, then a complex vegetation history is implied”.

In addition, in dry environments or at least in geographic areas that suffer one dry season in the year, variations in evaporation rates of soil  $\text{CO}_2$ -rich aqueous solutions are able to produce isotopic enrichments in both heavy isotopes  $^{18}\text{O}$  and  $^{13}\text{C}$  that are recorded in precipitated soil carbonates (e.g. Bojar et al., 2010; Quade et al., 2007; Horton et al., 2016). Indeed, it can be observed that soil carbonates that developed in arid or hyper-arid environments are both  $^{18}\text{O}$ - and  $^{13}\text{C}$ -enriched relative to those documented in humid to semi-arid environments (Horton et al., 2016).

## 7. Discussion

### 7.1. Hypothesis 1: calcitic land snail shells preserved climatic parameters of their living environment

#### 7.1.1. Oxygen isotope ratios and air temperatures

SGT values are calculated by combining equations (1) and (2). In this case, temperatures inferred from Grossman and Ku (1986) equation need to be corrected by an offset of about  $+3\text{ °C}$  (see section 6.1.2) as the studied land snail shells have a calcitic composition instead of the expected original aragonite. Concerning the parameters A and B in equation (2), we can consider for example, the European continent (IAEA stations around the Mediterranean Basin excluded) for which A and B are equal to 1.41 and 22.02, respectively, according to the equation computed by Lécuyer et al. (2018). We underline that this equation was computed using the IAEA stations of the European continent excluding those located around the Mediterranean Sea. Indeed, The Mediterranean basin is characterized by a specific  $\delta^{18}\text{O}$ -T relationship compared to the rest of Europe as shown, for example, by Gat and Carmi (1970) and Lécuyer et al. (2018). This area is characterized by specific patterns of atmospheric circulation with dry and cold continental air masses that interact with a marine basin characterized by high evaporation rates and relative high sea surface temperatures ( $\approx 20\text{ °C}$ ). Such air-sea interactions generate important sites of cyclogenesis, especially in the eastern part of the Mediterranean Sea. Thus, applying equation (5) to our set of oxygen isotope data obtained for Lanzarote Pliocene land snail shells, the range of inferred air temperatures is unrealistic ( $9\text{ °C} < T < 25\text{ °C}$ ) for a range of  $\Delta_{\text{bw-mw}}$  ( $= \delta^{18}\text{O}_{\text{bw}} - \delta^{18}\text{O}_{\text{mw}}$ ) comprised between 0 and  $+3\text{‰}$ . Indeed, such relationships cannot be used worldwide (Fricke and O’Neil, 1999). At low latitudes, where mean annual temperatures  $\geq 20\text{ °C}$  prevail along with low seasonality variations, changes in  $\delta^{18}\text{O}_{\text{mw}}$  present a negative linear correlation (Dansgaard, 1964; Yapp, 1982; Cole et al., 1999) with the amount P (mm) of precipitation. In dry and warm environments, common climatic modes are BWh (arid-desert-hot) and BSh (arid-steppe-hot) according to the Köppen-Geiger classification updated by Kottke et al. (2006), such as those prevailing today in the Canary Archipelago. The range of  $\delta^{18}\text{O}_{\text{mw}}$  is restricted and negatively correlated to the monthly precipitations (Fig. 5A) while no significant correlation is observed with monthly temperatures (IAEA/WMO data, Santa Cruz de Tenerife; Fig. 5B).

In present-day Lanzarote, monthly  $\delta^{18}\text{O}_{\text{mw}}$  values range from  $-2.6$  to  $+4.3\text{‰}$  with a mean value of  $-0.4 \pm 2.5$  (Yanes et al., 2008) where modern shells have  $\delta^{18}\text{O}_{\text{sh}}$  comprised between  $-0.3$  and  $2.5\text{‰}$  with a mean value of  $0.97 \pm 0.79\text{‰}$  (Yanes et al., 2008). These present-day  $\delta^{18}\text{O}_{\text{sh}}$  ranges are significantly higher than those measured in our Lanzarote fossil land snail shells (from  $-5.03$  to  $-0.94\text{‰}$  with a mean value of  $-2.86 \pm 1.18\text{‰}$ ), suggesting that the mean  $\delta^{18}\text{O}_{\text{mw}}$  was most likely lower in Lanzarote during the early Pliocene. Indeed, a  $\delta^{18}\text{O}_{\text{mw}}$  value of  $\approx -3 \pm 2\text{‰}$  has been estimated for the early Pliocene meteoric waters in Lanzarote on the basis of oxygen isotope compositions of calcite eggshell remains (Lazzerini et al., 2016) assigned to a giant terrestrial bird most likely belonging to the family of ratites (Rothe, 1964; Sauer and Rothe, 1972; Sanchez Marco, 2010). This isotopic value could correspond to the “humid season” that preceded a dry and warm period favourable to the reproduction of ratites as observed nowadays for wild ostriches (Sebei et al., 2009).

Considering the estimated  $\delta^{18}\text{O}$  value of  $-3 \pm 2\text{‰}$  for early Pliocene meteoric waters in Lanzarote, we can assume a Pliocene monthly  $\delta^{18}\text{O}_{\text{mw}}$  range most likely comprised between  $-5$  and  $-1\text{‰}$  (SMOW), which is a common amplitude of meteoric water  $\delta^{18}\text{O}$  values in subtropical oceanic island environments (Jouzel et al.,

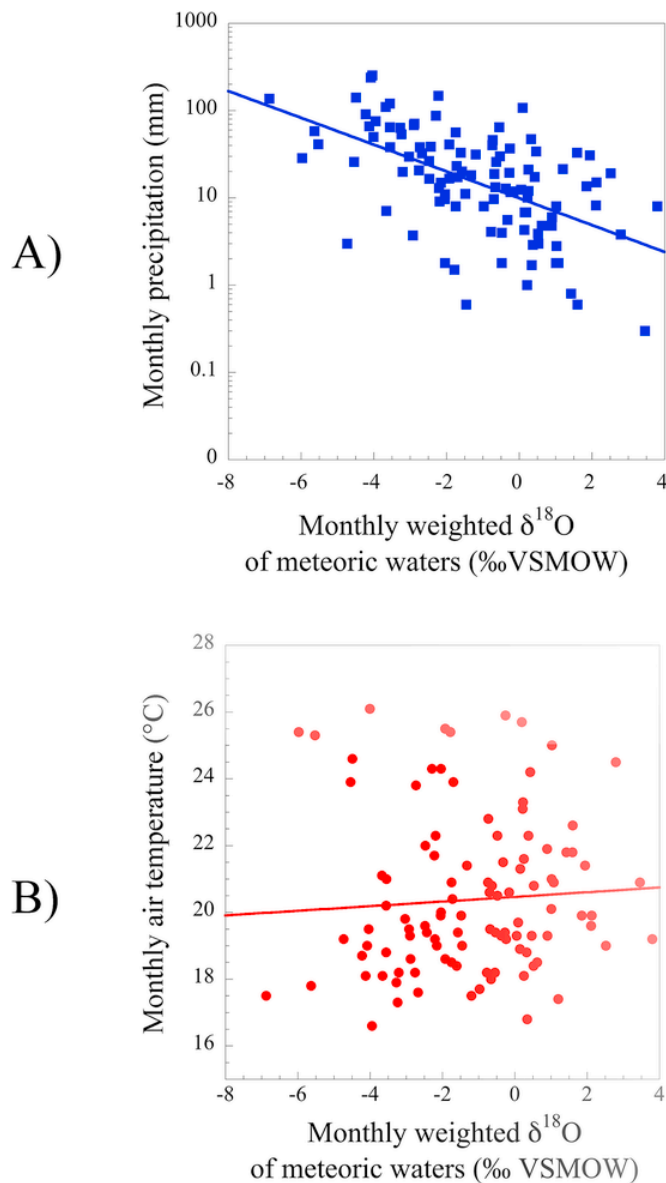


Fig. 5. Bivariate plot and correlations between A) monthly precipitation 'P' (mm) and monthly weighted  $\delta^{18}\text{O}$  values (‰ VSMOW) of meteoric waters ( $P = \exp^{-0.35378180} + 9.89$ ;  $R^2 = 0.25$ ) and B) monthly air temperature 'MAT' (°C) and monthly weighted  $\delta^{18}\text{O}$  values (‰ VSMOW) of meteoric waters ( $\text{MAT} = \exp^{0.00348180} + 20.46$ ;  $R^2 = 2.10^{-3}$ ).

1987). Using equation (1), it can be deduced from Fig. 6 that the  $\delta^{18}\text{O}$  range of measured Pliocene land snail shells (Table 1) is compatible with  $\Delta_{\text{bw-mw}}$  values higher than 0 and lower than +3 along with SGT comprised between 21 °C and 31 °C. We emphasize that these calculated temperatures should only indicate temperatures of shell growth which are roughly compatible with those favourable to snail activity and reproduction.

#### 7.1.2. Carbon isotope ratios and the vegetation cover

At Tenerife, modern shells have  $\delta^{13}\text{C}$  ranging from  $-13.8$  to  $-0.6$ ‰ while at Lanzarote and Fuerteventura,  $\delta^{13}\text{C}$  range from  $-9.4$  to  $+1.7$ ‰ (Yanes et al., 2008). High  $\delta^{13}\text{C}$  values of those shells, especially recorded in the warm and dry easternmost islands of the Archipelago, were interpreted as reflecting the contribution from CAM, C4 or water-stressed C3 plants (Yanes et al., 2008). These results are in line with the documentation of abundant CAM/C4 plants

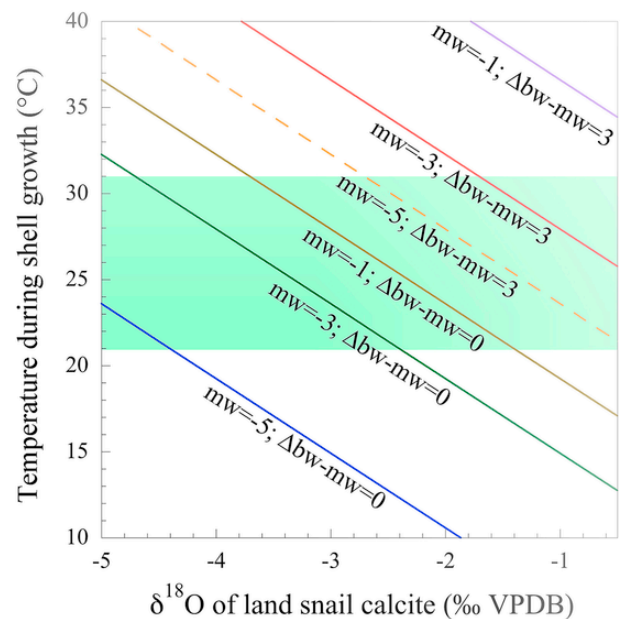


Fig. 6. 2D-space defined by the ambient temperature (°C) during land snail shell growth reported as a function of  $\delta^{18}\text{O}$  values of land snail shell calcite (‰ VPDB). Calculated abacuses define a temperature range in which snails most likely built their shells in a range of meteoric water  $\delta^{18}\text{O}$  values (mw) comprised between  $-5$  and  $-1$ ‰ and a range of body water  $^{18}\text{O}$ -enrichment ( $\Delta_{\text{bw-mw}}$ ) comprised between 0 and +3 (‰ VSMOW). The green area covers the estimated seasonal range of Zanclean air temperatures (Cf § 2.4). Calculations were performed using equation (1), Cf § 7.1.1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

occurring in the Canary Archipelago according to the database established by Méndez (2001). Contrasting with these patterns, early Pliocene Lanzarote fossil snail shells display a more restricted  $\delta^{13}\text{C}$  range from  $-7.97$  to  $-3.30$ ‰, reflecting either a more homogeneous snail diet or vegetation cover. The highest  $\delta^{13}\text{C}$  value of  $-3.30$ ‰ is much lower than the highest ones recorded in present-day Tenerife, Lanzarote and Fuerteventura. Consequently, Pliocene  $\delta^{13}\text{C}$  values could reflect less abundant CAM-C4 plants or water-stressed C3 plants resulting from more humid climatic conditions.

The C4-CAM vs C3 plant proportions into the snail diet may be estimated by using a simple mass balance calculation even though the varying impact of water stress on the  $\delta^{13}\text{C}$  of plants cannot be taken into account in this first-order approach. We can therefore compare these plant proportions between present-day and early Pliocene snail shells assuming comparable carbon isotope ratios for the two plant  $\delta^{13}\text{C}$  end-members. At Tenerife, the  $\delta^{13}\text{C}$  plant values range from  $-32.2$  to  $-11.6$ ‰ (V-PDB) (Yanes et al., 2009). The majority of the plant species were classified as C3 plant types with  $\delta^{13}\text{C}$  values ranging from  $-32.2$  to  $-23.1$ ‰ and averaging  $-27.1$ ‰. CAM plants have  $\delta^{13}\text{C}$  from  $-22.2$  to  $-11.6$ ‰ and one C4 plant has a  $\delta^{13}\text{C}$  of  $-13.5$ ‰; the average  $\delta^{13}\text{C}$  value is  $-17.3$ ‰ (Yanes et al., 2009). At La Graciosa Islet, northern Lanzarote, plant  $\delta^{13}\text{C}$  values range from  $-29$  to  $-13$ ‰ (Yanes et al., 2008); their high variability being also interpreted as reflecting extensive water stress. The mean  $\delta^{13}\text{C}$  values of C3 and CAM-C4 plants in Lanzarote are  $-25.3$ ‰ and  $-16.9$ ‰; respectively (Yanes et al., 2008). Consequently, we consider that the two mean present-day plant  $\delta^{13}\text{C}$  end-members are  $-25 \pm 2$ ‰ and  $-17 \pm 2$ ‰ (V-PDB) according to data obtained from Lanzarote plants. The mean  $\delta^{13}\text{C}$  value of snail shells is  $-5.8$ ‰ and, using for example the  $\Delta^{13}\text{C}_{\text{shell-diet}}$  of  $+13.7$  determined by Metref et al. (2003), the calculated mean plant  $\delta^{13}\text{C}$  value is  $-19.5$ ‰ (V-PDB). According to the mass balance equation

(13):

$$M = X\delta^{13}\text{C}_{(C4)} + Y\delta^{13}\text{C}_{(C3)} \quad (13)$$

with  $X + Y = 1$  to respect mass conservation;  $M$  being the  $\delta^{13}\text{C}$  of the snail diet;  $X$  and  $Y$  being the mass fractions of  $C4$  and  $C3$  plants in the snail diet, respectively. The fraction of  $C4$  plants in the diet of snails is expressed as follows according to equation (14):

$$X = \{M - \delta^{13}\text{C}_{(C3)}\} / \{\delta^{13}\text{C}_{(C4)} - \delta^{13}\text{C}_{(C3)}\} \quad (14)$$

Thus, we obtain  $69 \pm 25\%$  of CAM- $C4$  plants in the diet of Pliocene land snails. This rough estimate proportion of CAM- $C4$  plants, most likely  $\geq 50\%$ , does not really reflect the structure of the vegetation cover as  $C4$ -CAM plants could have been preferentially consumed by the land snails. Indeed, Yanes et al. (2008) underlined that “dense populations of land snails occur in direct associations with xerophytic plants”. Therefore, according to this hypothesis, we could consider that the  $\delta^{13}\text{C}$  values of Zanclean land snail shells only reveal the sizable presence of  $C4$ -CAM plants, confirming that their climatic environment was already characterized by steppic (subtropical or Mediterranean-like climate) landscapes.

## 7.2. Hypothesis 2: calcitic land snail shells record parameters of their burial environment

### 7.2.1. Soil and air temperatures

Following this hypothesis, the calculation of air temperature above the soil is obtained by substituting equation (9) into equation (7). According to Rodriguez et al. (2010), the mean soil temperature at 50 cm depth and at low altitudes in Tenerife Island is about  $5^\circ\text{C}$  higher than air temperature ( $C' = 5$  in equation (8)), which is a typical feature of hyperthermic regimes. We assume a similar relationship for Lanzarote Island. We consider again the European continent to solve equation (7). Thus, applying equation (9) to our set of oxygen isotope data obtained for Lanzarote Pliocene land snail shells, the range of inferred air temperatures ( $17^\circ\text{C} < T < 27^\circ\text{C}$ ) is comparable to present-days and seems too low considering our current knowledge of the early Pliocene climate. Keeping in mind that Zanclean MAT were most likely comprised between  $21\text{--}22^\circ\text{C}$  and  $30\text{--}31^\circ\text{C}$ . Using equation (6), it can be deduced from Fig. 7 that the  $\delta^{18}\text{O}$  range of measured Pliocene land snail shells is compatible with  $\delta^{18}\text{O}_{\text{mw}}$  values comprised between  $-4\text{‰}$  and  $+2\text{‰}$ . The snail shells that have the highest  $\delta^{18}\text{O}$  values correspond to the most evaporated soil waters. Therefore, soil waters that react with aragonitic shells to produce calcite suffered significant rates of evaporation that most likely took place during the warm and dry season. It is worthy to note that the calculated  $\delta^{18}\text{O}$  value ( $-3 \pm 2\text{‰}$  V-SMOW) of water drunk by the contemporaneous terrestrial giant bird of Lanzarote (Lazzerini et al., 2016) is compatible with our calculated range of soil water  $\delta^{18}\text{O}$  values (from  $-4$  to  $+2\text{‰}$ ).

### 7.2.2. Carbon isotope ratios of soil organic matter

According to equation (12), in the range  $25^\circ\text{C}\text{--}35^\circ\text{C}$  that roughly corresponds to the mean soil temperatures during the Zanclean, the  $\Delta_{\text{carbonate-organic matter}}$  value equals  $13.8 \pm 0.4$ . It means that the  $\delta^{13}\text{C}$  of organic matter ranges from  $-21.8$  to  $-17.1$  according to the range of land snail shell  $\delta^{13}\text{C}$  values (Table 1). Here we emphasize that the  $\Delta_{\text{carbonate-organic matter}}$  value inferred from the data published by Cerling and Quade (1993) is not distinguishable from the  $\Delta^{13}\text{C}_{\text{shell-diet}}$  of  $+13.7$  determined by Metref et al. (2003). In conclusion, a similar proportion of CAM- $C4$  plants ( $69 \pm 25\%$ ) is calculated for the composition of the vegetation cover that produced the soil organic matter. Carbon isotope ratios of well-preserved eggshell calcite fragments from the contemporaneous giant terrestrial bird (Lazzerini et al., 2016) reflect a diet closer to a  $C3$  plant end-mem-

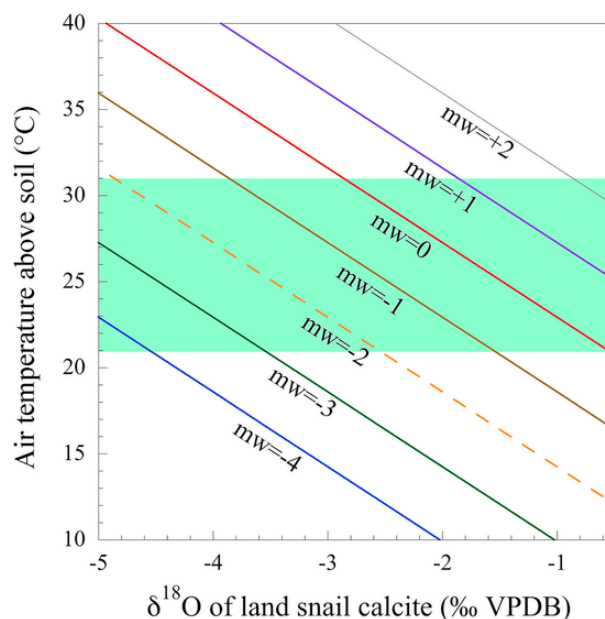


Fig. 7. 2D-space defined by the mean air temperature ( $^\circ\text{C}$ ) above the soil reported as a function of  $\delta^{18}\text{O}$  values of land snail shell calcite ( $\text{‰VPDB}$ ). Calculated abacuses define a temperature range in which snail shells recrystallized in the soil from aragonite to calcite for a range of meteoric water  $\delta^{18}\text{O}$  values ( $\text{mw}$ ) ranging from  $-4$  to  $+2$  ( $\text{‰VSMOW}$ ). The green area covers the estimated seasonal range of Zanclean air temperatures (Cf § 2.4). Calculations were performed using equations (7) and (9), Cf § 7.2.1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

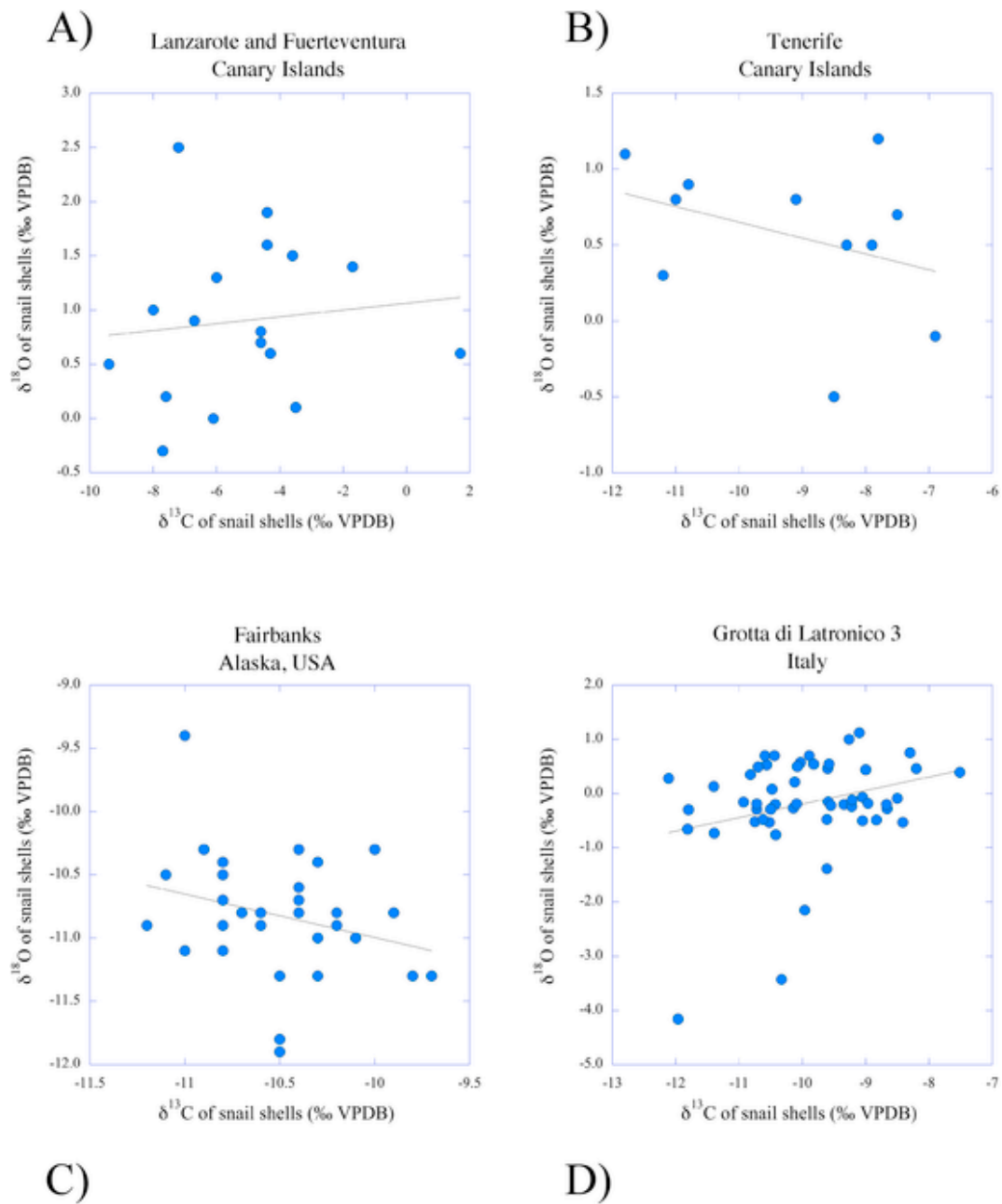
ber ( $\approx -23\text{‰}$  V-PDB) in comparison to the lower  $\delta^{13}\text{C}$  of the organic matter consumed by the land snail shells, most likely indicating a difference in dietary preferences between the gastropods and the birds.

### 7.3. $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ patterns in modern and fossil land snail shells

In this study, we emphasize that the stable isotope compositions of the diagenetic land snail shells from the early Pliocene of Lanzarote mimic those expected for unaltered snail shells that would still record original climatic conditions. Indeed,  $\delta^{13}\text{C}$  values could result from soil organic matter decay, which were not really different from the  $\delta^{13}\text{C}$  of snail diet, even though a bias may result from diet preferences between  $C3$  and  $C4$  plants while soil organic matter averages the composition of the vegetation cover.

Oxygen isotope ratios of shells result from a combination of more or less evaporated soil water that are inherited from meteoric waters and soil temperatures that are themselves closely related to mean air temperatures under tropical latitudes. This mechanism was responsible for the range of shell  $\delta^{18}\text{O}$  values that have been measured and that could be also explained by variable  $^{18}\text{O}$ -enriched snail body water in response to water stress in the case where snails would have preserved their pristine aragonitic shells.

Beyond the mineralogical transformation into calcite of investigated land snail shells that revealed a diagenetic alteration of the pristine aragonite, a geochemical diagnosis is the observation of positive correlations between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , which are not observed within populations of modern unaltered aragonitic land snail shells. Indeed, a selection of data compiled from the literature shows that  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of modern aragonitic shells from Canary Islands (Yanes et al., 2008, 2009), Alaska (Yanes, 2015) and from the early-middle Holocene of Italy (Colonese et al., 2010) are poorly correlated (Fig. 8) while Late Pleistocene-Holocene shells from Lanzarote (Yanes et al., 2013) show a strong positive correla-



**Fig. 8.** Bivariate plots between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (‰ VPDB) of a selection of present-days and archaeological land snail shell aragonite. A) Lanzarote and Fuerteventura, Canary Islands (Yanes et al., 2008);  $R^2 = 0.013$ ,  $n = 17$ . B) Tenerife, Canary Islands (Yanes et al., 2009);  $R^2 = 0.12$ ,  $n = 11$ . C) Fairbanks, Alaska, USA (Yanes, 2015);  $R^2 = 0.08$ ,  $n = 35$ . D) Early-middle Holocene archaeological deposits of Grotta di Latronico 3, southern Italy (Colonese et al., 2010);  $R^2 = 0.08$ ;  $n = 49$ . Note that the coefficients of determination are weak in all cases while slopes of regression lines are either slightly positive or negative.

tion (Fig. 9) as observed in our study (Fig. 4). Such isotopic correlations could reflect shell  $\text{CaCO}_3$  recrystallisation from a  $\text{CO}_2$ -rich aqueous solution that suffered varying rates of evaporation throughout seasons (Quade et al., 2007; Horton et al., 2016).

## 8. Conclusions

We have collected land snail shells from the early Pliocene paleosol deposits of northern Lanzarote, Canary Archipelago, which suffered physico-chemical processes of early diagenesis as evidenced by their recrystallisation into calcite. The analysis of the  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios of their shells allowed us to propose several lines of evidence concerning their usefulness to reconstruct some aspects of their paleoenvironments:

- $\delta^{13}\text{C}$  values could result from soil organic matter decay, which were not really different from the  $\delta^{13}\text{C}$  of snail diet, even though a bias may result from diet preferences between C3 and C4 plants while soil organic matter averages the composition of the vegetation cover.
- the  $\delta^{18}\text{O}$  range of measured Pliocene land snail shells is compatible with  $\delta^{18}\text{O}_{\text{mw}}$  values comprised between  $-4\text{‰}$  and  $+1\text{‰}$ . Soil waters that reacted with aragonitic shells to produce calcite suffered significant rates of evaporation during the warm and dry periods of the year. Therefore, the snail shells that have the highest  $\delta^{18}\text{O}$  values correspond to the most evaporated soil waters. This isotopic enrichment mimics the *in vivo* process of  $^{18}\text{O}$ -enrichment

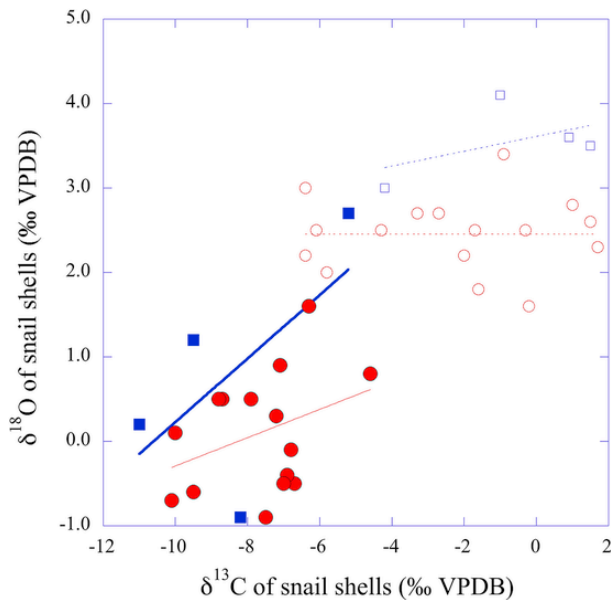


Fig. 9. Bivariate plot between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (‰ VPDB) of Late Pleistocene (23.3–24.0 ka BP) and Holocene (2.1–5.5 ka BP) land snail shells (made either of aragonite or calcite) from Lanzarote, Canary Islands (Yanes et al., 2013, Table 2). Filled blue squares: Holocene calcite ( $n = 4$ ;  $R^2 = 0.37$ ); open blue squares: Late Pleistocene calcite ( $n = 4$ ;  $R^2 = 0.25$ ); filled red circles: Holocene aragonite ( $n = 15$ ;  $R^2 = 0.13$ ); open red circles: Late Pleistocene aragonite ( $n = 16$ ;  $R^2 = 1.2 \times 10^{-6}$ ). Note that both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  variables are significantly correlated for land snail shell calcite. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of snail body water in response to water stress that has been documented for snails living in subtropical environments.

- Positive linear correlations between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of Lanzarote land snail shells, which are not observed in the case of unaltered aragonitic specimens, could reflect shell  $\text{CaCO}_3$  recrystallisation from a  $\text{CO}_2$ -rich aqueous solution that suffered varying rates of evaporation throughout seasons.
- Both carbon and oxygen isotope compositions of early Pliocene land snail shells from Lanzarote reflect a pedogenesis that took place under warm and dry conditions with a vegetation cover already dominated by C4-CAM plants.

Therefore, we show that the stable isotope compositions of diagenetic land snail shells from the Zanclean of Lanzarote mimic those expected for unaltered snail shells that would still record original climatic conditions. Applying the appropriate equations to those isotopic data, warm and dry conditions are inferred from these diagenetic land snail shells that recrystallized into calcite within the paleosols.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was granted by CNRS and IUF (CL).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jafrearsci.2019.103702>.

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