PEDOGENIC CARBONATE δ^{13}C AND ENVIRONMENTAL PRECIPITATION CONDITIONS

δ^{13}C DES CARBONATES PEDOGENETIQUES ET CONDITIONS ENVIRONNEMENTALES DE PRECIPITATION

δ^{13}C DEI CARBONATI PEDOGENETICI E CONDIZIONI AMBIENTALI DI PRECIPITAZIONE

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Summary

Carbon isotopic analysis is a useful tool for investigating paleoenvironments, as the pedogenic carbonate δ^{13}C is related to δ$^{13}C_{SOM}$ and to the proportions of C_3/C_4 plants. In this work we interpreted the paleoenvironmental conditions at the time of carbonate precipitation in soils formed under different climates and during different geological ages. Samples were taken from a Bk (PR1, Holocene) and from two Bkm horizons (PR2 and PR3, Pleistocene). When the mean δ^{13}C plant values and the most plausible paleotemperatures were used in the evaluation, PR1 showed a lower percentage of C_4 plants (48%) than Pleistocene soils (~53%), in agreement with paleoclimate changes. When instead the δ^{13}C values of current plants were used for PR1, C_4 plants ranged from 59 (12°C) to 66% (18°C), suggesting two possible interpretations: either plant species changed during the Holocene, or the plant mean values normally used in the literature are not suitable for Pleistocene reconstructions.
Keywords: *stable C isotopes; C_3-C_4 vegetation; paleoenvironment.*

Résumé

L'analyse des isotopes du C peut aider à l'évaluation des paléo-environnements puisque les δ^{13}C des carbonates pédogénétiques sont liés au δ$^{13}C_{SOM}$ et au rapport entre plantes C_3 et C_4. Avec cette technique on a déterminé les conditions paléo-environnementales dans des sols d'âges et sous climats différents, en utilisant un horizon Bk (PR1, Holocène) et deux Bkm (PR2 et PR3, Pléistocène). En effectuant l'évaluation avec les δ^{13}C moyens des plantes et les paléo-températures les plus plausibles, PR1 montrait une proportion des plantes C_4 (48%) inférieure à celle des sols du Pléistocène (~ 53%), en accord avec les changements paléo-climatiques. Les plantes C_4, cependant, variaient de 59 (12°C) à 66% (18°C) lorsqu'on utilisait pour PR1 le δ^{13}C des plantes actuelles. Ces résultats conduisent à deux interprétations possibles, soit que les espèces ont changé au cours de l'Holocène,

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soit que les $\delta^{13}C$ moyens normalement utilisés dans la littérature ne sont pas appropriés pour la reconstitution du Pléistocène.
Mots-clés: *isotopes stables de C, végétation C_3-C_4; paléoenvironnement.*

Riassunto

L'analisi degli isotopi del C è un utile strumento per la valutazione dei paleoambienti poiché i $\delta^{13}C$ dei carbonati pedogenetici sono relazionati ai $\delta^{13}C_{SOM}$ e al rapporto tra piante C_3 e C_4. Con questa tecnica sono interpretate le condizioni paleoambieantali al tempo di precipitazione dei carbonati in suoli formati in climi ed ere geologiche differenti, utilizzando un orizzonte Bk (PR1, Olocene) e due Bkm (PR2 e PR3, Pleistocene). Considerando i $\delta^{13}C$ medi delle piante e le più plausibili paleotemperature, PR1 mostrava una più bassa proporzione di piante C_4 (48%) rispetto i suoli pleistocenici (~53%), in accordo con i cambiamenti paleoambientali. Le piante C_4, invece, variavano da 59 (12°C) a 66% (18°C) usando per PR1 i $\delta^{13}C$ delle piante attuali. I risultati portano a due possibili interpretazioni: o le specie sono cambiate durante l'Olocene, oppure i $\delta^{13}C$ medi delle piante normalmente utilizzati in letteratura non sono adeguati per le ricostruzioni pleistoceniche.
Parole chiave: *isotopi stabili del C; vegetazione C_3-C_4; paleoambiente.*

Introduction

Through the geologic ages there have been important variations in the proportion of C_3 and C_4 plants (Rao *et al.*, 2007) mainly because of the climatic changes that have occurred, especially between Pleistocene (from 11.7 ky BP to 2.58 My BP) and Holocene (11.7-0 ky BP). In particular, the Southwest of the United States of America was characterized by important climate variations, from pluvial conditions during the glacial periods to aridity connected to the interglacial phases (Hawley, 2005). In this region, during the last glacial maximum (~20 ky BP) the temperatures were probably 5–7°C cooler than present (Phillips *et al.*, 1986), while around 7-5 ky ago, during Holocene, the paleoclimate was relatively arid and hot, and this condition was maintained up to nowadays (Antevs, 1955). In terms of vegetation, paleoenvironmental reconstructions can be performed using the relation between $\delta^{13}C$ values of the pedogenic calcite and the coexisting organic matter (Nordt *et al.*, 1998). Indeed, pedogenic carbonate $\delta^{13}C$ value is closely related with the soil CO_2 present at the time of calcite precipitation, and the soil CO_2 isotopic composition reflects that of organic matter ($\delta^{13}C_{SOM}$) and plant respiration. In soil profiles, therefore, calcite precipitation may proceeds through several geological times, with specific morphological features that keep the memory of paleoenvironmental conditions. The sequence of morphological characteristics has been described by Gile et al. (1966) with a sequence of stages of progressive carbonate accumulation. Their model is still the most used in studies dealing with calcic horizons genesis. In this context it is particularly important to distinguish among the different stages of carbonate accumulation in soils, because, although

the rates of accumulation vary from region to region, Gile *at al.* (1966)'s stages are correlated to surface age (Schaetzl and Anderson, 2005).
The $\delta^{13}C_{SOM}$ at the time of calcite accumulation can be estimated with the relationship (Nordt *et al.*, 1998):

$$\delta^{13}C_{SOM} = \delta^{13}C_{pedogenic\ carbonate} - (\Delta CO_{2\ diffusion} + \Delta CO_2 - CaCO_3) \qquad [1]$$

where $\delta^{13}C_{pedogenic\ carbonate}$ is measured from the carbonate in the calcic horizon, $\Delta CO_{2\ diffusion}$ represents the isotopic fractionation of CO_2 purely linked to gas movements (+4.4‰) and $\Delta CO_2\text{-}CaCO_3$ is the isotopic fractionation during the precipitation process. This last factor is highly influenced by temperature as the transformation from CO_2 to $CaCO_3$ involves shifts in physical states; if the temperature is higher, the heaviest ^{13}C isotope is more retained in the solid phase during carbonate precipitation (Deines *et al.*, 1974). The temperature-driven fractionation is for instance +12.4‰ at 0°C and +9.8‰ at 25°C (Cerling *et al.*, 1989). The $\delta^{13}C_{SOM}$ is in turn controlled by the biomass contributions from C_3 and C_4 plants. C_3 plants typically show an isotopic signature varying between –20 and –35‰, while the values for C_4 plants are much higher, between –10 and –14‰ (Cerling, 1999). The relative contribution of C_3 and C_4 plants to the formation of the isotopic composition of the soil organic matter, present during the precipitation of the pedogenic carbonate, can be therefore evaluated according to the equation (Morgun *et al.*, 2008):

$$C_4\ plants\ (\%) = \frac{\delta^{13}C_{SOM} - \delta^{13}C_{C_3}}{\delta^{13}C_{C_4} - \delta^{13}C_{C_3}} x100 \qquad [2]$$

where the values normally used for $\delta^{13}C$ of C_3 and C_4 plants are the means of –27 and –12‰ respectively given by Cerlin and Quade, 1993.
The aim of this work was the interpretation of paleoenvironmental conditions at the time of calcite precipitation in soils which sharply differ in age, thus have formed in different climates, using the C isotopic method.

Materials and methods

The soils were selected in the northern Chihuahua Desert, near Las Cruces (New Mexico, USA, Figure 1). The region has a mean annual temperature of 16°C and mean annual precipitation of 230 mm (Gile and Grossman, 1979); the present soil temperature regime is aridic. The evaluation was done at three sites, where soil profiles were described and sampled (PR1, PR2 and PR3, Figure 1) and a vegetation survey was performed. The current vegetation was the same at all sites and included both C_3 and C_4 plants; the dominant species, creosotebush (*Larrea tridentata* (DC) Coville, a C_3 plant) and grama grass (*Bouteloua spp.,* C_4 plants), were collected. The PR1 and PR2 profiles evolved on alluvium terraces derived from rhyolite, while PR3 consisted of an alluvial fan surface derived from gray limestone, with very minor amounts of calcareous sandstone and rhyolite. The first profile was located on a Holocene surface; the others (PR2 and PR3) were older,

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dating from Late Pleistocene. According to Soil Taxonomy (Soil Survey Staff, 2010) the soils were a Typic Calciargid (PR1), an Argic Petrocalcid (PR2) and a Calcic Petrocalcid (PR3).

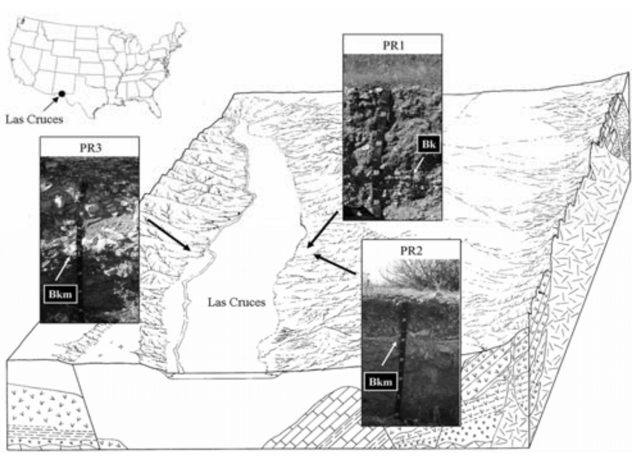

Figure 1

Location and sketch of the study areas and images of PR1, PR2 and PR3 profiles. Arrows indicate the horizon of maximum carbonate accumulation

Samples were taken from the horizon of maximum carbonate expression. This corresponded to stage I of the Gile *et al.* (1966)'s sequence (Bk horizon) in Holocene soil (PR1) at a depth from 60 to 80 cm, while the soils evolved on Late Pleistocene surfaces (PR2 and PR3) showed a petrocalcic horizon (Bkm), which was identify as stage IV (Gile *at al.*, 1966), at a depth of 40 to 70 cm.
Samples collected from each profile were air-dried; pedogenic carbonates were scraped off rock fragments with a steel spatula from the bulk soil and finely ground by hand in an agate mortar. Plant samples were accurately washed with 1 M HCl to eliminate potential calcium carbonate residues and rinsed with deionized water, dried in oven at 40°C and finely milled. Plant and pedogenic carbonate samples were then analysed for the carbon isotope signature using a Eurovector elemental analyser (Eurovector, Milan, Italy) coupled to a Micromass Isoprime mass spectrometer (Micromass, Manchester, UK). Stable isotope ratios were reported in δ‰ units versus PDB standard (Craig, 1957). Carbonate $\delta^{13}C$ were used to estimate the $\delta^{13}C_{SOM}$ using the equation [1]. To take into account the effect of climatic variations of geological past, the mean average temperatures reported in literature for all the profiles (Phillips *et al.*, 1986; Antevs, 1955), as well as their maximum swings of ±3°C for the Holocene profile (Smith and Betancourt, 2003). The proportions of C_3–C_4 plants at the time of calcite precipitation were calculated with the equation [2] for both $\delta^{13}C$ plant mean values reported in bibliography and the actual values measured.

Results and discussion

The pedogenic carbonate isotopic ratios were similar and did not depend from the parent material from which the soil formed. This is in agreement with the results obtained in other soils of the area (Kraimer and Monger, 2009). The $\delta^{13}C$ was –4.5‰ for the $CaCO_3$ from Bk horizon (PR1) and –3.1 and –3.7‰ for the older carbonates of PR2 and PR3 (Bkm horizons), respectively. From these values, the $\delta^{13}C_{SOM}$ at the time of precipitation for four different temperatures were obtained (Table 1).

Profile	**Temperature**			
	10°C	**12°C**	**15°C**	**18°C**
PR1	-20.3	-20.1	-19.7	-19.4
PR2	-18.8	-18.6	-18.3	-17.9
PR3	-19.5	-19.2	-18.9	-18.6

Table 1

$\delta^{13}C_{SOM}$ (‰) calculated values for PR1, PR2 and PR3 10, 15 and 20°C

The $\delta^{13}C_{SOM}$ data on the average showed the lowest values at the lowest temperature, as a consequence of the laws that the fractionation processes follow. Among the profiles, PR1 showed always lower $\delta^{13}C_{SOM}$ than PR2 and PR3, which instead had values more similar each other. This indicated that during Holocene, soil organic matter was more enriched in the lighter carbon isotope than during Pleistocene. The $\delta^{13}C_{SOM}$ values were used to calculate the percentages of C_3 and C_4 plants at the time of carbonate precipitation for all profiles (Fig. 2).

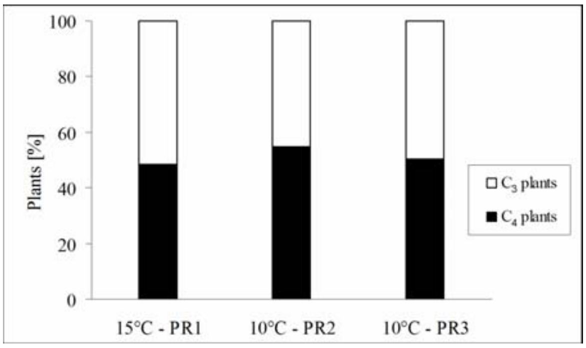

Figure 2

Estimate of C_3/C_4 plants in PR1, PR2, PR3 calculated by taking into account the most probable Holocene and Pleistocene temperatures and the average isotopic signatures for C_3 and C_4 plants.

The most plausible mean temperature during the Late Pleistocene was 10°C (Phillips *et al.*, 1986), while during the Holocene the most probable temperature was assumed to be similar to the actual one (15°C). Following the normal interpretation of isotope data for the purpose of obtaining the proportions of plants with different types of photosynthesis, the mean $\delta^{13}C$ plants values were used (Morgun *et al.*, 2008). The floristic composition during the Holocene at a temperature of 15°C was of 48 and 52% for C_4 and C_3 plants respectively, while during the Late Pleistocene at 10°C the C_4 plants were more abundant (+2–7%).

Despite the common interpretation that a shift from C_3 to C_4 results from increased aridity, there are particular cases in which it is possible to observe the opposite trend (e.g. Schulze *et al.*, 1996), especially since many desert shrubs are C_3 plants (Monger *at al.*, 2009). In some extremely arid environments, other strategies become more important than the high water–use efficiency of C_4 plants, such as root distribution or leaves orientation (Whitford, 2002). This is reflected by the dominance of C_3 shrubs, as *Larrea spp.*, in many hot deserts (Nellessen, 2004), including the Chihuahuan Desert. Therefore, the decrease of C_4 plants observed

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from PR2 and PR3 to PR1 is in agreement with paleoenvironmental changes as it confirms the significant increase in aridity during the Holocene with respect to the Pleistocene in New Mexico. To obtain further indications about the possible species variations during geologic ages, the $\delta^{13}C$ of C_3 and C_4 of actual plants were measured (Fig. 3).

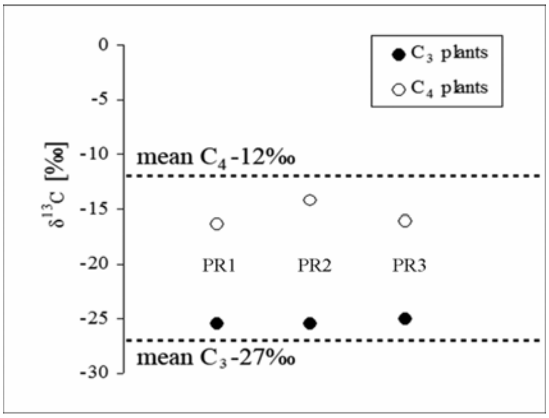

Figure 3

$\delta^{13}C$ C_3 and C_4 plants values at PR1, PR2 and PR3 sites. Dotted lines indicate the mean values reported in literature.

The isotopic signature of C_4 plants was slightly enriched in the lighter C isotope with respect to the values normally reported (Cerlin and Quade, 1993), and the opposite occurred for C_3 plants. All values fell, however, within the range described by Cerling (1999) with mean variations of +1.7‰ for C_3 and –3.5‰ for C_4 plants. During the last 10 ky, the maximum temperature swings have been of ±3°C (Smith and Betancourt, 2003), thus Holocene climate changes have probably not induced major variations in plant species with respect to current vegetation. Therefore, nowadays vegetation should be a proxy for that present during $CaCO_3$ precipitation in PR1 (Breecker *et al.*, 2009). The isotopic values of present days vegetation were used to calculated the proportion of C_3 and C_4 plants at the average actual temperature of 15°C (Figure 4). To take into account Holocene temperature swings, the same estimate was carried out also at 12 and 18°C (Fig. 4).

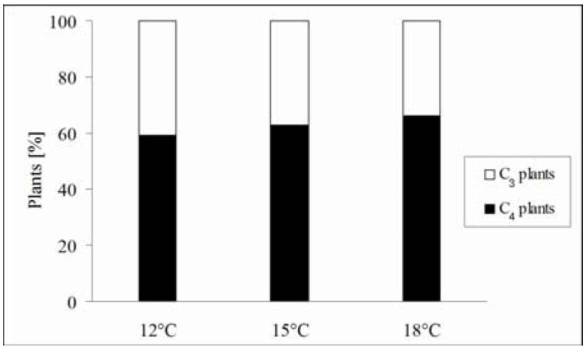

Figure 4

Estimate of C_3/C_4 plants in PR1 taking into account Holocene temperature swings and isotopic signatures of actual plants.

The percentage of C_4 plants obtained from PR1 carbonates at 15°C was 63%, and varied from 59 to 66% with changes in temperature. Consequently, all temperatures considered, including the actual one, indicated a higher proportion of C_4 plants than those found with the most probable scenario for PR2 and PR3 (Fig. 2). A higher proportion of C_4 plants during Holocene than Late Pleistocene is not in agreement with paleoclimatic data, suggesting that current species do not reflect those that influenced the most Holocene carbonate precipitation. On the other hand it is also possible that the average $\delta^{13}C$ data used in Figure 2 for PR2 and PR3, although widely used, do not correspond to those of Pleistocene vegetation. The isotopic signature of Late Pleistocene plants should in fact give a proportion of C_4 plants for that period higher than the Holocene one (i.e. >66% C_4), which was the conclusion of similar isotopic studies of both alluvial (Monger et al., 1998) and eolian (Buck and Monger, 2000) paleosols in the Chihuahuan Desert.

Conclusions

In general, when the pedogenic carbonates are present along the profile, the isotopic method is an important tool for investigating paleoenvironmental conditions if coupled with a good knowledge of studied soils. This allows hypothesizing the past terrestrial ecology.

From the results obtained in this study, two possible paleovironmental interpretations were obtained. One hypothesis involves a change in dominant plant species during the last 10 ky, with consequent variations in their isotopic signatures; the other hypothesis is more related to methodological issues. The average values of plant isotopic ratios normally used may be not suitable for Pleistocene reconstructions in the Chihuahuan Desert, especially in the case where younger generations of carbonate crystals are overprinted on older generations in relict paleosols (Deutz *et al.*, 2002).

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