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Preliminary interpretation of the stable-isotope composition in lacustrine stromatolites of the Sierra de Alcubierre (Miocene, Ebro Basin, Spain)

Interpretación preliminar de la composición de isótopos estables en estromatolitos lacustres de la Sierra de Alcubierre (Mioceno, Cuenca del Ebro, España)

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ABSTRACT

The stable isotope composition of the laminae in two stromatolites of the Middle Miocene lacustrine record in the Sierra de Alcubierre (unit T6, Ebro Basin) reveals cyclic variations between laminae with different texture and distinct evolution of the isotopic composition through time. Light, porous (micrite-microspar) laminae (0.65 mm to 6 mm thick) and dark, dense (micrite) laminae (0.5 mm to 2 mm thick) alternate through time. Most of these laminae are composite. The significant correlation between $\delta^{13}C$ and $\delta^{18}O$ suggests that the precipitation/evaporation ratio (P/E) mainly controlled the short-term isotopic evolution of the saline carbonate closed-lake environment of unit T6 in the Ebro Basin. The dark laminae have higher $\delta^{13}C$ and $\delta^{18}O$ than the light laminae, which represents cyclic changes (seasonal to interannual) in the P/E ratio. The decrease in both $\delta^{13}C$ and $\delta^{18}O$ composition and in $\delta^{13}C$ vs. $\delta^{18}O$ correlation coefficient values between the studied stromatolites indicate a trend toward higher P/E ratio through time.

Key-words: *Stable isotopes, lacustrine stromatolites, Miocene, Ebro Basin, Spain.*

RESUMEN

La composición de isótopos estables de las láminas de dos estromatolitos lacustres del Mioceno medio de la Sierra de Alcubierre (unidad T6, Cuenca del Ebro) revela variaciones cíclicas entre láminas con diferente textura y clara evolución de la composición isotópica a lo largo del tiempo. Consisten en una alternancia de láminas claras, porosas (micrita-microesparita, de 0.65 mm a 6 mm de espesor) y láminas oscuras, densas (micrita, 0.5 mm a 2 mm de espesor). La mayoría de estas láminas son compuestas. La significativa correlación entre $\delta^{13}C$ y $\delta^{18}O$ sugiere que la relación precitación/evaporación (P/E) controló en gran medida la evolución isotópica a corto plazo del ambiente lacustre salino de la unidad T6 en la Cuenca del Ebro. Las láminas oscuras tienen valores mayores de $\delta^{13}C$ y $\delta^{18}O$ que las claras, lo cual representa cambios cíclicos (estacionales a plurianuales) en la relación P/E. El decrecimiento en $\delta^{13}C$ y $\delta^{18}O$ y en el coeficiente de correlación ($\delta^{13}C$ vs. $\delta^{18}O$) entre los estromatolitos estudiados indica una tendencia hacia una mayor relación P/E a lo largo del tiempo.

Palabras clave: *Isótopos estables, estromatolitos lacustres, Mioceno, Cuenca del Ebro, España.*

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Introducción

Stromatolites are laminated microbialites that develop from cyanobacterial mats, which grow attached to substrates in marine and aqueous continental areas in several environmental conditions. Commonly, coupled textural and geochemical analyses in laminated microbialites are used to infer palaeoenvironmental conditions on different time scales. In general, the temporal duration of the laminae is unknown. The stable-isotope composition shows that laminated microbialites are high-resolution records of short climatic and hydrological changes, e.g. seasonal and interannual (Chafetz *et al.*, 1991; Andrews and Brasier, 2005; Osácar *et al.*, 2013; Dabkowski *et al.*, 2015).

The Miocene lacustrine record of the Ebro Basin (NE Spain) encompasses stromatolite exposures that are particularly abundant in the Sierra de Alcubierre (Fig. 1). This work focuses on the environmental significance of the stable-isotope variations ($\delta^{13}C$ and $\delta^{18}O$) across lamination in several stromatolite samples of the Middle Miocene lacustrine record of the Sierra de Alcubierre, with emphasis on 1) the isotopic variations between laminae with different texture and 2) the evolution of the isotopic composition through time.

Stratigraphic and sedimentologic context

The Early and Middle Miocene record of the central part of the Ebro Basin, north of the Ebro River, consists of an approximately

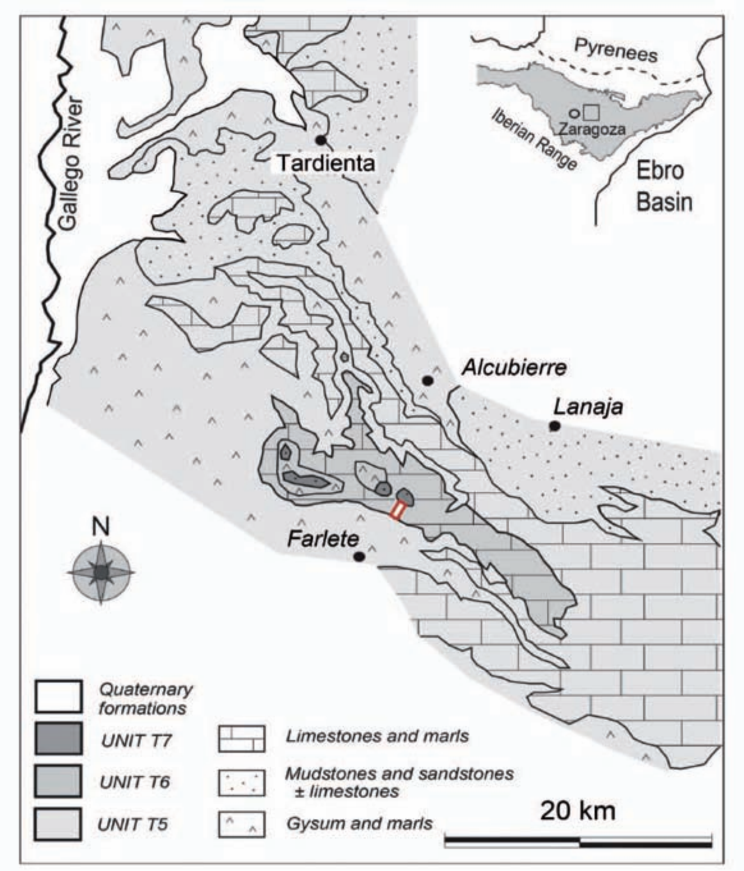

Fig. 1.- Geologic map with tectosedimentary units and main lithofacies in the Sierra de Alcubierre (Arenas and Pardo, 1999). The bar indicates the section where SC-31 and SC-141 samples were taken.

Fig. 1.- Mapa geológico con las unidades tectosedimentarias y principales litofacies de la Sierra de Alcubierre (Arenas y Pardo, 1999). La línea señala la sección donde se cogieron las muestras SC-31 y SC-141.

630 m thick succession that has been divided into three allostratigraphic units, named T5, T6 and T7 (Arenas, 1993; Arenas *et al.*, 2007). In this central part, the units are made of sulphate and carbonate lacustrine deposits (limestones, dolostones, gypsum and marls) and distal alluvial deposits (sandstones and mudstones) of Pyrenean provenance (Fig. 1).

In the lacustrine facies model proposed for the Miocene units in the central sector of the Ebro Basin, two distinct lacustrine environments alternated through time (Arenas and Pardo, 1999): 1) carbonate depositional environments in freshwater systems that correspond to high lake levels, in which massive and bioturbated limestones and marls formed, and 2) sulphate depositional environments that occurred during low lake levels, in which sulphate facies formed. Stromatolitic and laminated limestones, at places dolostones, developed at intermediate situations, during oscillations from situations 1 to 2 and vice versa, and represent saline carbonate lake conditions. This is corroborated by the bulk isotopic composition of stromatolites ($\delta^{13}C$=-1.7±1.2; $\delta^{18}O$=-3.2±2.6‰ PDB; N= 59) and laminated limestones ($\delta^{13}C$=1.9±0.9; $\delta^{18}O$=-2.9±2.7‰ PDB; N=47) (Arenas *et al.*, 1997). Increased $\delta^{18}O$, compared with the other facies (massive limestones, with $\delta^{13}C$=-2.6±2.6 and $\delta^{18}O$=-6.1±1.2‰ PDB, N= 10; and bioturbated limestones, with $\delta^{13}C$=-3.1±1.4 and $\delta^{18}O$=-6.1±0.9‰ PDB; N=17), indicates that these facies formed with intense evaporative conditions, (Arenas *et al.* 1997).

Stromatolites occur at two main positions in the vertical associations of facies: 1) at the base of deposits that represent a deepening process/sequence (e.g., over bioturbated facies), and 2) through and at the top of deposits that represent a shallowing process/sequence (i.e., alternating with or at the top of laminated limestones) (Arenas and Pardo, 1999; Martín-Bello *et al.*, 2016).

Materials and methods

Two samples of stromatolites of unit T6 in the San Caprasio stratigraphic section (Fig. 1) were selected for a lamina normal profile stable isotope analysis: sample SC-31 (Fig. 2A), 7 cm thick planar body from the lower part of the unit, and sample SC-141, 20 cm thick, vertically discontinuous bioherm, from the middle-upper part of the unit. A portion of the base and another of the top were selected in SC-141 for isotopic analyses (b and t).

Texture was studied in thin sections obtained from the same sections used for isotopic analyses. Polished slabs were used for powder sampling of successive dark and light laminae with a microdrill. The total number of samples is 36: 15 from SC-31; 9 from SC-141b and 12 from SC-141t.

The mineralogy of these samples was determined by X-Ray Diffraction at the Servicio de Apoyo a la investigación (SAI) of the University of Zaragoza. Samples consist of calcite with very small amounts (<1%) of quartz and clay minerals. The $\delta^{13}C$ and $\delta^{18}O$ analyses were performed in a Thermo Finnigan MAT-252 mass spectrometer in the Serveis científico-tècnics of the University of Barcelona, following standard procedures. The results are expressed in δ‰ units and reported against the V-PDB standard.

Results

Sample SC-31 corresponds to a mammillary planar body at the base of a deepening cycle. The body lies on intensely bioturbated limestones of the underlying shallowing sequence (Fig. 2A). Sample SC-141 is a vertically discontinuous bioherm, within a shallowing cycle. The stromatolite alternates with cm-thick layers of laminated limestones that show wave cross-stratification.

In thin sections, the stromatolite laminae are always smooth, with variable degree of lateral continuity, and are arranged in domes and cumulate growth forms. The structure shows a common pattern: alternating light (porous micrite and microspar) and dark laminae (dense micrite). Both the light and dark laminae show disperse micrite filamentous bodies that are set subperpendicular to perpendicular to lamination and that are attributed to cyanobacteria. The thickness of the light laminae in SC-31 ranges from 0.65 mm to 2 mm, exceptionally up to 6.4 mm (Fig. 2B). The thickness of the light laminae in SC-141 ranges from 1 to 2 mm. Usually the light laminae wedges down the domes. The thickness of the dark laminae ranges from 0.5 mm to 2 mm in SC-31 and from 1 to 2 mm in SC-141. Most

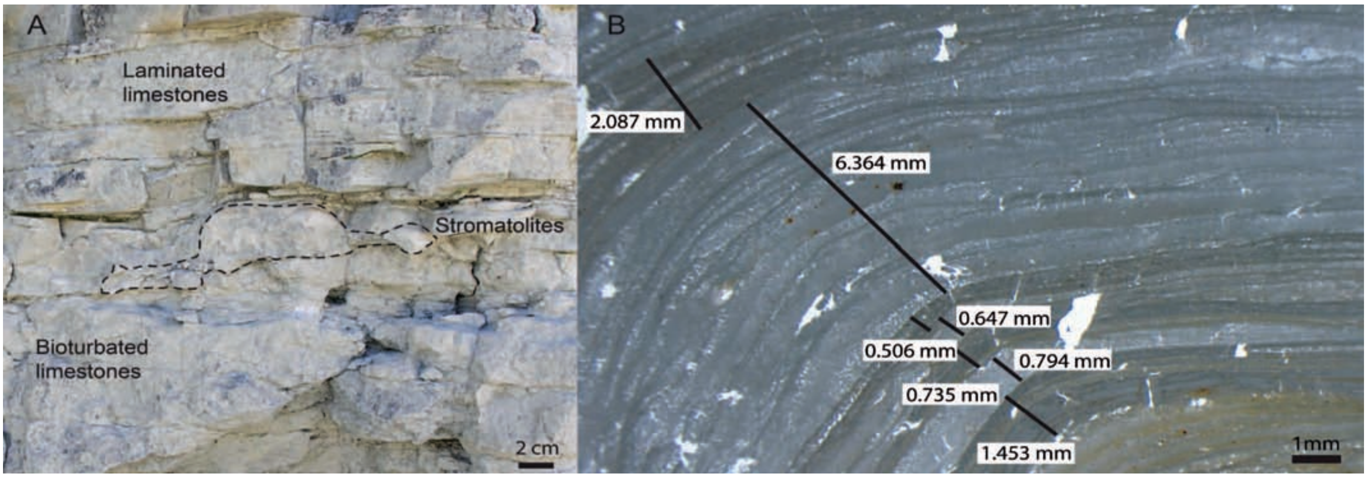

Fig. 2.- SC-31 sample in outcrop (A) and optical microscope view (B). In (B), stromatolite lamination with thickness of the light (porous) and dark (dense) laminae.

Fig. 2.- Imágenes de afloramiento (A) y microscopio óptico (B) de la muestra SC-31. Están representados los espesores de las láminas claras (porosas) y oscuras (densas)

of these laminae correspond to composite laminae in which either the light or the dark single laminae dominate, and can alternate through time. In most cases, these groups of single laminae can be distinguished with the unaided eye (Fig. 3A). Dark laminae in hand sample correspond to dense micrite in optical microscope (Figs. 2B and 3A).

The isotopic composition of the two samples (Table I) covers a narrow range of negative $\delta^{18}O$ and $\delta^{13}C$ values (-5,33 < $\delta^{18}O$ <-3,62‰ V-PDB and -2,14 < $\delta^{13}C$ <-0,53‰ V-PDB). Mean $\delta^{13}C$ (‰ V-PDB) varies from -0.7 in SC-31, to -1.8 in SC-141b, to -1.7 in SC-141t. Mean $\delta^{18}O$ (‰ V-PDB) varies from -3.9 in SC-31, to -4.6 in SC-141b, to -4.8 in SC-141t. The correlation coefficient between $\delta^{13}C$ and $\delta^{18}O$ decreases from SC-31 to SC-141t. In all samples, mean $\delta^{18}O$ and $\delta^{13}C$ values are lower in the light laminae than in the dark laminae (Table I).

Discussion

There is not a regular pattern in thickness variation of the light and dark laminae. The light laminae contain more microbial filamentous bodies associated with larger crystal texture than the dark laminae. The cyclic variations in texture (alternating light and dark laminae) can be related to short time (seasonal to interannual) variations in microbial development associated with climatic parameters (Casanova, 1994; Arenas *et al*., 2015).

The $\delta^{13}C$ and $\delta^{18}O$ values of the studied samples (Table I) are within the range of values obtained in other closed lake systems subject to variable evaporation and without intense development of soils (Andrews *et al*., 1993; Casanova, 1994). Given the residence time effect in closed lake systems, the $\delta^{18}O$ values reflect the influence of both temperature and evaporation. Accordingly, the textural variations between light and dark laminae record the different development of the microbial populations related to seasonal and/or interanual variations in water supply (precipitation/evaporation ratio, P/E ratio) and temperature.

However, the influence of water temperature on oxygen fractionation is difficult to untangle if strong evaporation occurs. In mid latitude regions, the higher temperatures in the warm seasons commonly coincide with the drier conditions. Assuming that this was the case in the studied lacustrine area, temperature and evaporation would produce opposite effects on $\delta^{18}O$, thus yielding a smoothed cyclic $\delta^{18}O$ variation through time (Fig. 3). The significant correlation between $\delta^{13}C$ and $\delta^{18}O$ (Table I) suggests that the P/E ratio greatly controlled the short-term isotopic evolution of the saline carbonate closed-lake environment of unit T6 in the Ebro Basin, which is consistent with the long residence time of water in closed lake basins (e.g., as shown by López-Blanco *et al*., 2016).

The differences between the light and dark laminae can then be referred primarily to changes in the P/E ratio. The higher values of $\delta^{13}C$ and $\delta^{18}O$ in the dark laminae compared to those of the light laminae (differences of mean $\delta^{13}C$= 0.23‰ and $\delta^{18}O$= 0.4‰) may reflect the increased CO_2 loss and increase ^{18}O enrichment due to higher evaporation. Although the $\delta^{13}C$ values in these stromatolites are dominated by strong residence time effects, the low $\delta^{13}C$ values in the light laminae may record the input of light CO_2 produced by organic matter decay or development of soils, which occurs preferably in higher P/E ratio conditions.

The cyclic pattern of both isotopes through time might correspond to seasonal and/or interannual changes in the above mentioned factors: the light laminae would represent wetter conditions and the dark laminae drier conditions.

The decrease in the correlation coefficient through the studied stromatolites may represent a slight increase in the P/E ratio,

	δ13C ‰ V-PDB		δ18O ‰ V-PDB		r (δ13C-δ18O)
SAMPLES	Light laminae	Dark laminae	Light laminae	Dark laminae	
SC-141t (N=12)	-1.8 ± 0.2	-1.5 ± 0.2	-5.0 ± 0.4	-4.6 ± 0.4	0.60
SC-141b (N=9)	-1.9 ± 0.2	-1.7 ± 0.2	-4.8 ± 0.4	-4.4 ± 0.5	0.71
SC-31 (N=15)	-0.8 ± 0.1	-0.6 ± 0.1	-4.1 ± 0.3	-3.7 ± 0.2	0.83
Mean	-1.51	-1.28	-4.62	-4.22	

Table I.- Average isotopic composition in dark and light laminae in the studied samples. "r" is the correlation coefficient of Pearson.

Tabla I.- Composición isotópica media de las láminas claras y oscuras en las muestras estudiadas. "r" es el coeficiente de correlación de Pearson.

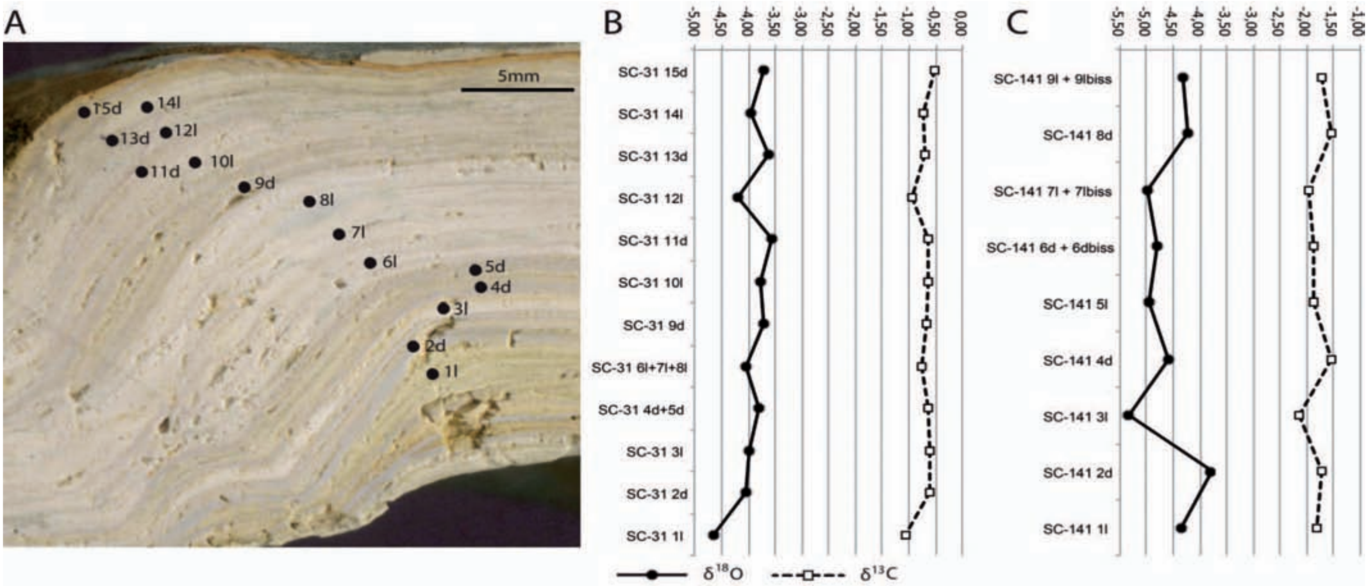

Fig. 3.- A) Cross section of sample SC-31 with sampling microboreholes. B) Stable isotope profile in sample SC-31. C) Stable isotope profile in sample SC-141b. In some cases, one value represents the average of several samples. l: light laminae; d: dark laminae.

Fig. 3.- A) Sección de la muestra SC-31 con microsondeos. B) Perfil isotópico de la muestra SC-31. C) Perfil isotópico de la muestra SC-141b. En algunos casos, un punto representa la media de los valores de varias muestras. l: light laminae; d: dark laminae.

which is consistent with 1) the lower $\delta^{18}O$ and $\delta^{13}C$ values of the SC-141 sample respect to those of SC-31, and 2) the general trend toward wetter conditions through unit T6 (e.g., as stated by Arenas *et al*., 1997).

Conclusions

The stable-isotope composition ($\delta^{13}C$ and $\delta^{18}O$) across lamination in two stromatolite samples of the Middle Miocene lacustrine record (unit T6) of the Sierra de Alcubierre (Ebro Basin), allowed preliminary environmental interpretation of 1) isotopic variations between laminae with different texture and 2) evolution of the isotopic composition through time.

Lamination consists of alternating light, porous composite laminae and dark, dense composite laminae. Light laminae have lower $\delta^{13}C$ and $\delta^{18}O$ values than the dark laminae The cyclic variations in texture parallel cyclic variations in $\delta^{13}C$ and $\delta^{18}O$.

The significant correlation between $\delta^{13}C$ and $\delta^{18}O$ suggests that the precipitation/evaporation ratio (P/E ratio) greatly controlled the short-term isotopic evolution of the saline carbonate closed-lake environment of unit T6 in the Ebro Basin.

The cyclic variations in texture can be related to short time (seasonal to interannual) variations in the microbial development associated with changes in P/E ratio. Primarily, light laminae represent wetter conditions and dark laminae drier conditions. The low $\delta^{13}C$ values in the light laminae may also record the input of light CO_2.

The decrease in the correlation coefficient between $\delta^{13}C$ and $\delta^{18}O$ through the studied stromatolites of unit T6 is consistent with the general climatic evolution in the study zone that suggests a slight increase in the P/E ratio. However, the study of more samples will help confirm the correlation coefficient evolution.

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