Seasonal and decadal stable isotope evolution recorded by recent tufa deposited on artificial substrates in the Monasterio de Piedra Natural Park (NE Spain)

Evolución estacional y decenal de isótopos estables registrada en tobas recientes depositadas en substratos artificiales en el Parque del Monasterio de Piedra (NE España)

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ABSTRACT

Identification of six-month intervals in carbonate deposits formed on tablets installed in several fluvial subenvironments of the Monasterio de Piedra Natural Park, from 1999 to 2009, allowed six-monthly stable-isotope analysis of such records. Slight differences in $\delta^{13}C$ and $\delta^{18}O$ exist between stromatolites (fast-flowing water areas) and moss-bearing deposits (cascades). Sediment $\delta^{13}C$ values did not show clear regular variations through time. A chiefly cyclic pattern of sediment $\delta^{18}O$ values reflected the seasonal variations in temperature. The calculated water temperature values were consistent with measured air and water temperature values. The increasing tendency of air temperature is closely reflected by the estimated temperature tendencies. The isotopic results stress the validity of the seasonal variation pattern detected through thickness measures, and underscore the environmental significance of tufas, which accounts for the use of this type of analysis in climate interpretation from ancient tufa records.

Key-words: *Modern tufas, experimental six-month deposits, stable isotopes, air and water temperature variations.*

RESUMEN

La identificación de intervalos semestrales en depósitos carbonatados formados sobre losetas instaladas en diversos subambientes fluviales del Parque Natural del Monasterio de Piedra, desde 1999 hasta 2009, ha permitido el análisis semestral de isótopos estables de dichos registros. Existen pequeñas diferencias en $\delta^{13}C$ y $\delta^{18}O$ entre las facies estromatolíticas (áreas de flujo rápido) y las ricas en musgos (cascadas). Los valores de $\delta^{13}C$ no muestran variaciones temporales regulares. Los valores de $\delta^{18}O$ presentan una pauta cíclica que refleja las variaciones estacionales de temperatura. Los valores calculados de la temperatura estacional del agua son acordes con las temperaturas medidas de aire y agua. La tendencia creciente de la temperatura del aire se refleja en las tendencias de temperatura estimadas. Estos resultados refuerzan la validez del patrón estacional detectado mediante la medida de espesores de los depósitos, y confirman la utilidad de este tipo de análisis en la interpretación climática de tobas antiguas.

Palabras clave: *Tobas actuales, depósitos semestrales experimentales, isótopos estables, variaciones de temperatura del aire y del agua.*

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Introduction

The use of tufas as palaeoenvironmental records requires the understanding of the relationships between tufa formation and environmental parameters. Monitoring of present tufa formation has been proved a useful tool to disclose these relationships (Vázquez-Urbez *et al*., 2010 and references therein).

Measurement of tufa deposition rates and analysis of sediment, including stable isotope composition (carbon and oxygen), are among the most important parameters to decipher the factors that control the tufa formation process (Chafetz *et al*., 1991; Matsuoka *et al*., 2001; Andrews and Brasier, 2005; Andrews, 2006; Arenas *et al*., 2010).

This contribution is part of a wider tufa study that comprised six-month monitoring of properties and parameters of water and sediment in several rivers in the Iberian Range. Periodic monitoring of tufa thickness and related physical, chemical and biological parameters of the River Piedra within the Monasterio de Piedra Natural Park (Fig. 1) showed high tufa sedimentation rates and a distinctive six-month deposition pattern (Arenas *et al*., 2010; Vázquez-Urbez *et al.*, 2010), which enabled sedimentological and geochemical analysis of the seasonal deposits.

The purpose of this contribution was to analyse the climatic significance of variations in stable isotope composition recorded by tufa deposited on artificial substrates installed in two different fluvial subenvironments in the Monasterio de Piedra Natural

Park, from August 1999 to September 2009.

General context

The Monasterio de Piedra Natural Park is located along the lower reach of the River Piedra, in the central Iberian Range, NE Spain (Fig. 1). Most water is provided by upstream springs fed by the Mesozoic carbonate-rock aquifer. Mean annual discharge of the River Piedra is 1.05 m^3/s (data from *Confederación Hidrográfica del Ebro*).

In the Park, a stepped river profile with waterfalls, pools and caves exists. The river water is of HCO_3-(SO_4)-Ca type, with mean pH of 8.12 (for the studied period), and is permanently saturated with respect to calcite (Vázquez-Urbez *et al.*, 2011).

Climate is of continental Mediterranean type, with strong seasonal contrasts in air and water temperature. Most precipitation occurs in spring and autumn.

Methods

Sediment characteristics (texture, $\delta^{13}C$ and $\delta^{18}O$) and sedimentation rates were obtained from sediment deposited on limestone tablets (25x15x2 cm) installed in different riverine subenvironments in the Park. Details of the procedure are provided by Vázquez-Urbez *et al.* (2010). The tablets were removed from the river at the end of each six-month period for measurements of sediment accumulation and then were returned to their original position until the following semester. The differences in sediment height between consecutive six-month measuring times represented the six-monthly sedimentation rates at each site. The six-month periods, referred hereafter as warm period and cool period, correspond roughly to spring + summer and autumn + winter respectively.

During the 10-year monitoring, each group of tablets was replaced with new ones after 3–4 years as a result of thick accumulation. Once removed, the tablets were cut perpendicular to the accumulation surface, and the six-month intervals were identified on the cross-sections by plotting the successive measurements of the raw corresponding to the section. Then, samples were collected in each six-month interval for diverse types of analysis. Water samples were collected at the tablet sites at the end of June and December, and water temperature was recorded simultaneously. Water $\delta^{18}O$ and sediment $\delta^{18}O$ and $\delta^{13}C$ analyses were made at the Stable Isotope Analysis Laboratory of the University of Salamanca (Spain). The analytical precision was better than 0.1‰. The results are expressed in δ notation relative to the V-SMOW and V-PDB scales. The sediment $\delta^{18}O$ values were used to estimate the water temperature through the formula of O'Brien *et al.* (2006), using the mean water $\delta^{18}O$ values of warm and cool periods from Osácar *et al.* (2013).

Air temperature data of the studied area were obtained from the *Agencia Estatal de Meteorología* (La Tranquera station, Fig. 1)

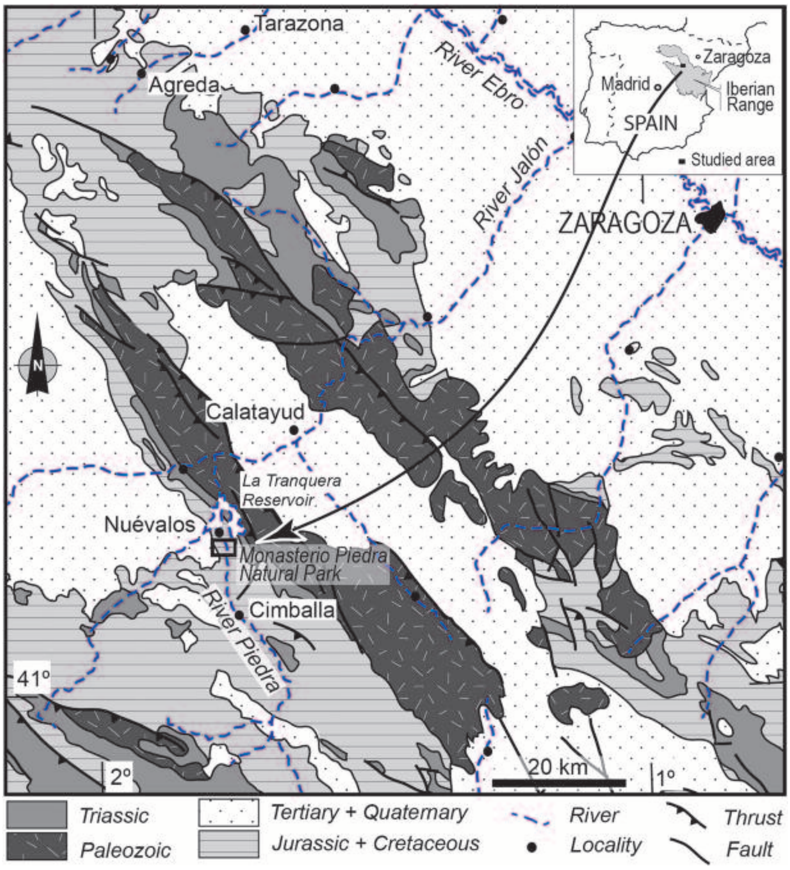

Fig.1.- Location of the studied site.

Fig.1.- Localización del área estudiada

Tufa sedimentation

Six main subenvironments, mostly defined by bed morphology, physical flow attributes and flora associations, were distinguished in the Park, with distinct facies formed in each one (Vázquez-Urbez *et al.*, 2010). The sedimentation rates of the tablets in the Park showed highly variable values depending on the depositional environmental conditions (Vázquez-Urbez *et al.*, 2010, 2011). From 1999 to 2009, the highest rates (from 13.4 to 17.0 mm/year) corresponded to gentle- to moderate-slope sites devoid of macrophytes with fast-flowing water, in which laminated tufa (stromatolites; Fig. 2A) formed. Tablets installed in stepped waterfalls with mosses, filamentous algae and cyanobacterial mats (Fig. 2B) recorded lower and highly variable rates (7.6 to 13.2 mm/y), with common features of erosion detected in the six-month intervals. Environmental differences in tufa rates are mostly linked to mechanical CO_2 outgassing. In all subenvironments sedimentation rates were higher in warm periods (mean: 6.1 mm) than in cool periods (mean: 2.8 mm), suggesting that temperature was the primary factor governing seasonal rates (Arenas *et al.*, 2013). Laminated deposits and moss-bearing deposits (Fig. 2) were selected for this contribution, due to their higher sedimentation rate, which enabled the interval identification.

Stable isotopes: results and discussion

The stable isotope composition of all sampled six-month intervals did not yield

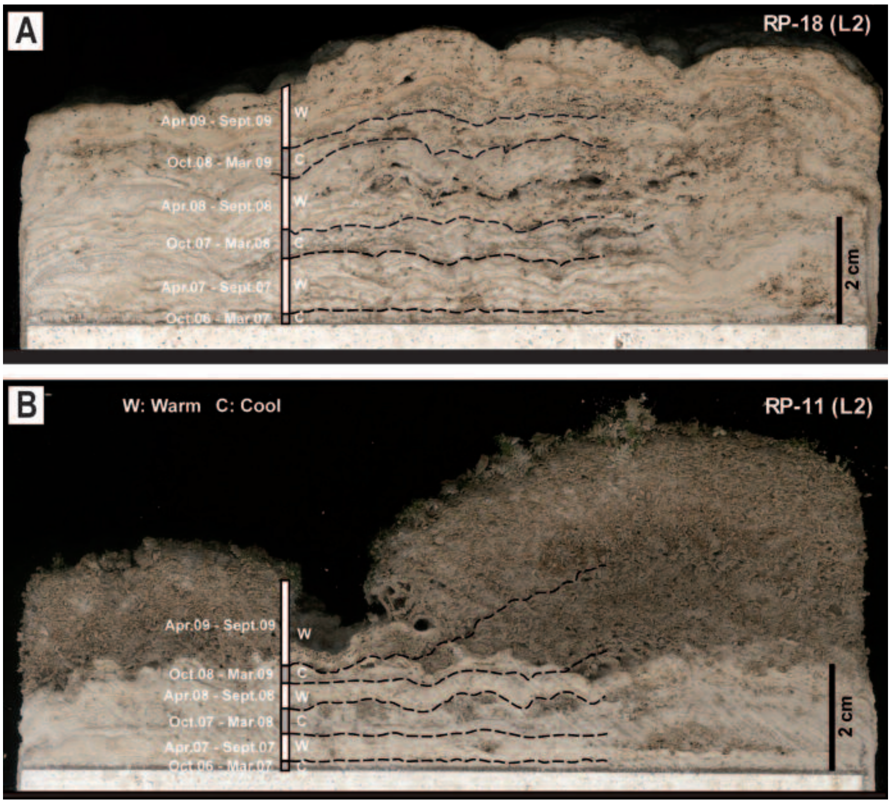

Fig. 2.- Deposits formed from October 2006 to September 2009, with indication of six-month intervals. A: Cross-section of tablet RP-18; stromatolitic deposits formed in a fast-flowing water area of gentle slope devoid of macrophytes. B: Cross-section of tablet RP-11; boundstone of mosses, filamentous algae and stromatolites formed in a cascade.

Fig. 2.- Depósitos formados desde octubre 2006 a septiembre 2009, con indicación de los intervalos semestrales. A: Corte transversal de la loseta RP-18; depósitos estromatolíticos formados en un área de flujo rápido, de poca pendiente, desprovista de macrofitas. B: Corte transversal de la loseta RP-11; boundstone de musgos, algas filamentosas y estromatolitos formados en un cascada.

important differences among depositional subenvironments, although slight variations exist (Table I). For the two subenvironments represented by tablets RP-18 and RP-11 (Figs. 2 and 3), slightly lower $\delta^{13}C$ and $\delta^{18}O$ values were recorded by moss-bearing deposits (RP-11) compared to stromatolitic deposits (RP-18) (Table I). These results might indicate greater soil-derived CO_2 contribution in stepped, moss-bearing cascades (RP-11), leading to lower $\delta^{13}C$, and more intense CO_2-loss in fast flowing areas devoid of macrophytes (RP-18), leading to higher $\delta^{18}O$; nevertheless, further work is needed to validate this assumption.

Sediment $\delta^{13}C$ values did not show a clear pattern in any of the two studied cases (Fig. 3A), which is likely related to the variety of carbon sources and processes involved. A decreasing tendency of $\delta^{13}C$ values was recorded by tablets in both subenvironments (Fig. 3A), but the reason for this trend is still unclear

Sediment $\delta^{18}O$ values showed a cyclic variation with lower values in warm periods and higher values in cool periods (Fig. 3B), which is coherent with the oxygen fractionation dependence on temperature. This pattern was altered only in a few cool periods, which were not the same for both tablets. Thus, these alterations might be linked either to local processes or even to the sampling process. Water $\delta^{18}O$ values also showed seasonal variations, although without a distinct pattern.

	Total average	Warm periods average	Cool periods average	Maximum	Minimum
RP-11					
$\delta^{13}C$‰	-7.8	-8.0	-7.7	-7.1	-8.4
$\delta^{18}O$‰	-8.2	-8.5	-7.9	-7.5	-9.0
RP-18					
$\delta^{13}C$‰	-7.6	-7.6	-7.5	-7.0	-8.3
$\delta^{18}O$‰	-8.0	-8.4	-7.6	-7.2	-8.7

Table I.- Averages and ranges of $\delta^{18}O$ and $\delta^{13}C$ values (V-PDB) of deposits on tablets.

Tabla I.- Promedios y rangos de los valores de $\delta^{18}O$ y $\delta^{13}C$ (V-PDB) de depósitos de tabletas.

Water temperatures estimated from the sediment $\delta^{18}O$ values (see Methods) are represented in Figure 3C, along with measured water temperatures and air temperature averages. Water temperatures measured at the sampling moment and average air temperatures display similar seasonal patterns (Fig. 3C). Estimated water temperatures display a clear seasonal pattern, with no significant differences between RP-11 and RP-18. Their range of variation is smaller than that of measured temperatures (both of water and air); that is, estimated water temperatures for warm periods are always cooler than measured air and water temperatures, and estimated temperatures for cool periods are always warmer. These differences are not uncommon in tufas (Brasier *et al.*, 2010). In the studied case, air temperatures are always more extreme than water temperatures. Measured water temperatures correspond to the water sampling moment, whereas estimated temperatures derive from tufa calcite deposited during a longer time period. Anyhow, the estimated water temperature pattern is consistent with the measured air temperature pattern (Fig. 3C).

Despite the differences between the estimated water temperatures and the air temperatures, the tendency lines of both water and air temperatures are very close. In both cases temperature increases through the 10-year interval, with differences of around 1ºC through time (Fig. 3D). Therefore, the temperature tendency was recorded more precisely than the temperature. These isotopic results reinforce the use of tufas as archives of reliable temperature tendencies on a decadal scale.

Conclusions

The stable isotope analysis of six-month intervals (warm periods: spring+summer; cool periods: autumn+winter), identified in tufa deposits recorded on tablets installed in two subenvironments (1: fast-flowing water areas of gentle slope, stromatolitic facies and 2: stepped-cascades, with boundstones of mosses, filamentous algae and stromatolitic facies) in the Monasterio de Piedra Natural Park, from 1999 to 2009, allowed some preliminary remarks:

1. The sediment $\delta^{13}C$ composition does not show a clear pattern, probably linked to the diversity of carbon sources and processes involved.

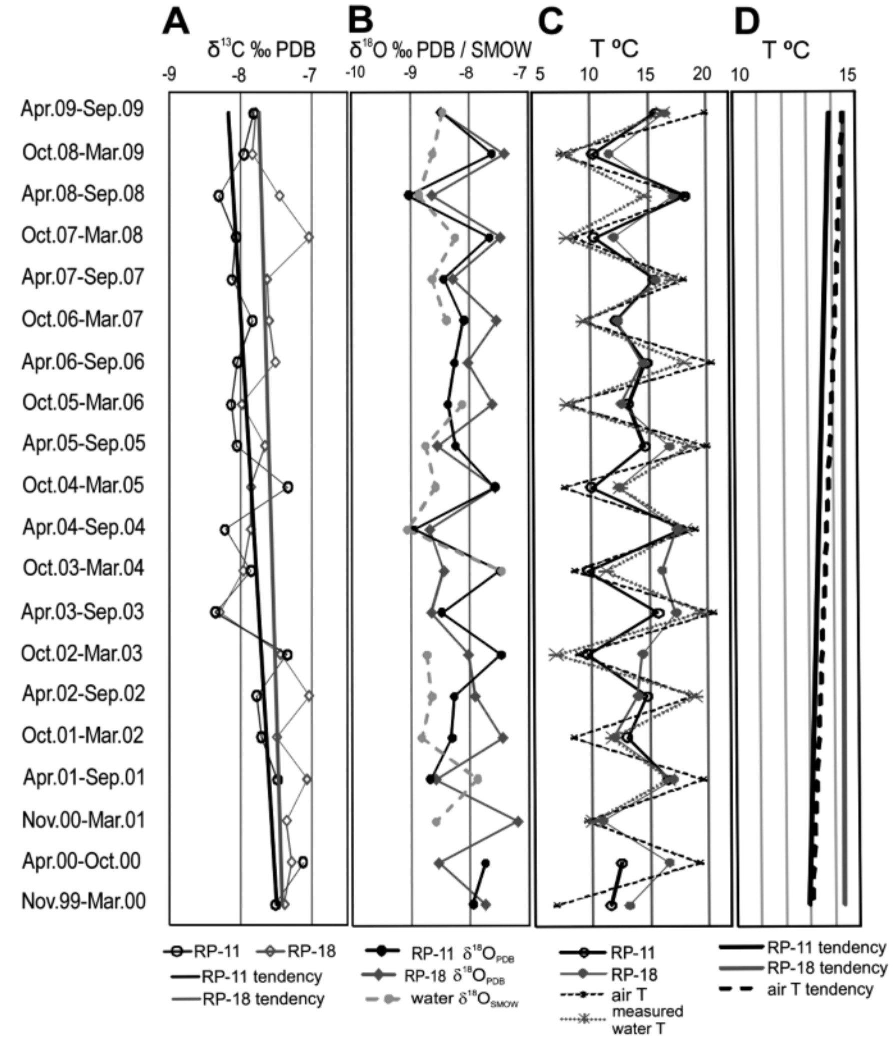

Fig. 3.- Stable isotope composition and water temperature estimate from deposits of tablets RP-11 and RP-18 over the 10-year study (1999-2009). A) $\delta^{13}C$ composition and tendencies. B) $\delta^{18}O$ composition of tufa calcite and water. C) Estimated water temperatures, water temperatures measured at the sampling moment, and average six-month air temperatures. D) Tendencies of air temperature and estimated water temperatures. Air temperature data from *Agencia Estatal de Meteorología*.

Fig. 3.- Isótopos estables y temperatura del agua calculada para las losetas RP-11y RP-18, a lo largo de los 10 años del estudio (1999-2009). A) Composición y tendencias del $\delta^{13}C$. B) Composición de $\delta^{18}O$ de la calcita tobácea y del agua. C) Temperatura del agua calculada, temperatura del agua medida durante el muestreo y promedio semestral de la temperatura del aire. D) Tendencias de la temperatura del aire y de las temperaturas calculadas para el agua. Datos de temperatura del aire de la Agencia Estatal de Meteorología.

2. The sediment $\delta^{18}O$ composition records the seasonal variability of temperature in both subenvironments. The calculated water temperature values are consistent with the mean air temperature values for each six-month period. Moreover, the estimated water temperature tendencies fit closely the increasing trend of the air temperatures. Temperature variations can therefore be detected through stable isotope composition at the scale of seasonal and decadal periods.

These results stress the validity of the seasonal pattern detected through thickness measurements and assess the environmental significance of tufas as high-resolution tools.

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