Stable-isotope changes in tufa stromatolites of the Quaternary Añamaza fluvial system (Iberian Ranges, Spain)

Los variaciones en los isótopos estables de estromatolitos tobáceos cuaternarios del sistema fluvial del Añamaza (Cordillera Ibérica, España)

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ABSTRACT

The stable isotope composition ($\delta^{13}C$ and $\delta^{18}O$) of the laminae in three Quaternary, calcitic, tufa stromatolites of different ages (MIS6, MIS5 and MIS1) in the Añamaza valley are studied and compared with the modern tufa in the Añamaza river. The cyclic textural variations represent thick cyanobacterial growth in the light laminae and thin or absent cyanobacterial growth in the dark laminae. The textural cyclicity is parallel to $\delta^{18}O$ changes: Each light-dark couplet corresponds to one year in which the light lamina (lower $\delta^{18}O$ values) represents warmer water temperatures ($T_w$) than the dark lamina (higher $\delta^{18}O$ values). This is consistent with the fact that the large crystals composing the dark laminae correspond to precipitation in the absence of microbial films and likely represent the coldest conditions. The $\delta^{18}O_{calcita}$ derived $T_w$ from MIS5 stromatolite is higher than the MIS6 and MIS1 samples, which agrees with the commonly admitted climatic conditions during MIS5 in NE Iberia. Moreover, $\delta^{18}O_{calcita}$ from MIS6 suggests a wider yearly $T_w$ range than the two other samples. The higher and more disperse $\delta^{13}C$ values of the MIS1 stromatolite are consistent with the peculiarities of the vegetal cover and the decreased water availability in the Holocene.

Key-words: Stromatolite texture, stable isotopes, fluvial tufa, Pleistocene, Holocene

Introducción

Tufa stromatolites are considered suitable records to study high frequency environmental changes based on the stable isotope composition ($\delta^{13}C$ and $\delta^{18}O$) of the successive laminae (Andrews, 2006 and references therein). These analyses are especially useful in the study of the Quaternary climatic changes in the Mediterranean domain. However, the interpretation of the past climatic conditions based on the isotopic record is hampered by the lack of information on the isotopic composition of water and the diversity of factors that condition the isotope signature (Matsuoka et al., 2001).

Monitoring of the modern tufa formation process provides useful information that helps interpret variations of the isotopic composition on different temporal scales in the geological record (Osácar et al., 2013).

The purpose of this work is to interpret, in terms of environmental (mainly climatic) parameters, the isotopic variations 1) between light and dark laminae and 2) through time of Quaternary tufa stromatolites of different ages in the Añamaza tufa system, with the help of the results of the modern tufa monitoring in the present system.

Geological context: Stratigraphy and Sedimentology

The Añamaza valley, in the Northwestern Iberian Range (NE Spain, Fig. 1A), exhibits Mid-Late Pleistocene and Holocene tufas and associated detrital facies forming...
stepped buildups, a few meters up to 70 m thick, along the valley. These Quaternary deposits lie over Mesozoic and Cenozoic rocks through an angular unconformity (Fig. 1B) (Arenas et al., 2014). Several stages of tufa development in the Pleistocene (marine isotope stages, MIS9, 6 and 5) and Holocene (MIS1) have been distinguished by means of absolute datings (Arenas et al., 2010; Sancho et al., 2015). The deposits consist of dominant carbonates (tufa and related facies) lying over less abundant detrital deposits formed by conglomerates and, occasionally, mudstones. The carbonate facies include: stromatolites, phytoherms, tufa, bryophyte boundstone, phytoclastic and intraclastic limestones, bioclastic sands and silts, massive marls and speleothems (Arenas et al., 2014).

Within the general stepped carbonate fluvial context, two conceptual sedimentary models are clearly defined in the Añamaza valley (Arenas et al., 2014). The moderate-slope model includes extensive standing water areas; abundant stem phytoherms, phytoclastic and intraclastic limestones, bioclastic sands and silts, massive marls and speleothems (Arenas et al., 2014). The standing water areas; abundant stem phytoherms account for extensive palustrine areas. The high-slope model consists of smaller dammed areas between close-up cascades and barrage-cascades, which were composed primarily of moss phytoherms, stromatolites and phytoclastic tufas. For each model, the depositional bodies consist, respectively, of large and small wedges that open downstream. The sedimentological and hydrological differences between the Pleistocene and Holocene fluvial systems in the Añamaza valley can be referred, respectively, to the high-slope and moderate-slope models, but the models can coexist in a single sedimentary system (Arenas et al., 2014). The Pleistocene stromatolite samples studied here (164.4±1.8 ka and 111.7±1.7 ka, MIS6 and MIS5 respectively; Sancho et al., 2015) form part of a stepped cascade developed at the downstream part of a small wedge that was deposited in a high-slope area of the valley (low aggradation/progradation ratio, Arenas et al., 2014). The Holocene stromatolites studied here (7.7±3.8 ka, MIS1; Sancho et al., 2015) formed at the downstream part of a large wedge, in a moderate slope area of the valley that included small barrages and cascades and wide palustrine zones (Arenas et al., 2014).

Materials and methods

Three samples of stromatolites were selected for stable-isotope analyses. Two samples from the Pleistocene (A, MIS6 and B, MIS5) and one sample from the Holocene (C, MIS1), spanning approximately 12 cm thick in total. Successive light and dark laminae were sampled with a microdrill (Fig. 2). In a few light laminae two samples were obtained vertically. A total of 42 powder samples from light laminae (13 in A, 15 in B and 14 in C) and 37 from dark laminae (13 in A, 15 in B and 9 in C) were obtained. According to the X-Ray Diffraction analyses, carried out at the University of Zaragoza, samples consist almost entirely of calcite. Texture was studied in thin sections through optical microscope and in scanning electron microscope (SEM) in the University of Zaragoza. Thin sections were prepared by the Servicio de Preparación de Rocas y Materiales Duros of the University of Zaragoza. The δ13C and δ18O analyses were performed in a Thermo Finnigan MAT-252 mass spectrometer in the Serveis científicos-tècnics of the University of Barcelona, following standard procedures.

Results

Structure and texture of stromatolites

The Pleistocene samples were taken from multi-convex meter-thick bodies in which stromatolite (5-20 cm thick), phytoclastic tufa and bryophyte boundstone layers alternate, and the Holocene sample from a slightly undulate, 4 cm-thick body that lies over a phytoclast tufa and stem boundstone layer.

The three studied samples consist of flat to slightly undulate, locally domed, laminae (Fig. 2). Lamination is defined by an alternation of light laminae (1 to 3.5 mm thick) and dark laminae (0.2 to 1 mm thick). The light laminae correspond to micrite and spar calcite with abundant cyanobacterial fila-

Fig. 1.- Location of the Añamaza valley and geological mapping, with Quaternary outcrops and position of the studied stromatolite samples. Modified from Arenas et al. (2014) and Sancho et al. (2015).

Fig. 2.- Detail of sample B (MIS5) showing alternating light and dark laminae. Microperforaciones correspond to sampling.
δ13C values range from -3.96 to -6.45‰ V-PDB. Means and standard deviations of δ18O for each sample are shown in Table I and figure 4. Differences between the light and dark laminae are 0.94, 0.51 and 0.21‰ in A, B and C, respectively. In all cases, the dark laminae have significantly less negative values than the light laminae.

The correlation between δ13C and δ18O is absent or very poor (r = 0.23, 0.06 and 0.30, for A, B and C, respectively).

Discussion

The textural variations are cyclic and represent thick cyanobacterial growth in the light laminae and thin or absent cyanobacterial growth in the dark laminae (Fig. 3). The large crystals of the dark laminae are primary precipitates and likely correspond to precipitation in the absence of microbial films (cf., Arp et al., 2010). The textural cyclicity can be, thus, interpreted as a function of seasonal variations in microbial growth associated with climate parameters. The oscillation of δ18O, with lower values in the light laminae and higher values in the dark laminae, represents seasonal changes in water temperature (Tw). Following the temperature dependence of the oxygen fractionation, the thinner, dark laminae formed with lower Tw, and the thicker, light laminae with higher Tw. All together, these facts suggest that every light-dark couplet likely represents a year, whose Tw oscillation is reflected in the δ18O values of each light and dark couplet. Nevertheless, it cannot be inferred that the two types of laminae represent similar time spans, but intervals with dominant warm and cold conditions.

Assuming each couplet represents a year, the Holocene sample (C, MIS1) represents 9 years and the Pleistocene samples represent 15 years (B, MIS5) and 13 years (A, MIS6). Sedimentation rates for the three intervals with dominant warm and cold conditions.

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The respective MIS6 and MISS δ¹⁸O values of light and dark laminae reflect also different temperature range: the difference between dark and light laminae would correspond to ca. 4°C in MIS6 sample, and 2.1°C in the MISS sample. The MIS1 sample temperature range is even smaller, 0.9°C. However, the actual Tw range through the year might be larger, taking into account the influence of the seasonal changes in water δ¹⁸O signature. Sedimentation monitoring of the Añamaza River (from 2007 to 2010) showed a significant difference between the present water δ¹⁸O of the warm and cool seasons (ca. 0.5‰). This seasonal water δ¹⁸O difference may cause a narrowing in the calcite δ¹⁸O range of these deposits that formed at very different Tw. In the Añamaza modern tufa, with a mean difference of 0.1‰ between calcite δ¹⁸O of the warm and cool seasons, the calculated Tw difference was ca. 6°C (Auqué et al., 2014).

The dispersion of δ¹³C values in the MIS1 sample is larger than in the MIS6 and MISS samples (Fig. 4), which is difficult to interpret, due to the diversity of processes involved in the calcite δ¹³C signature.

**Conclusions**

Textural features of lamination and stable-isotope composition of Pleistocene (MIS and MISS) and Holocene (MIS1) tufa stromatolites of the Añamaza valley indicate the development of a biannual lamination pattern, with light laminae mostly reflecting the warm interval and dark laminae the cold interval.

Lamination is controlled by seasonal variations in the cyanobacterial growth that are parallel to oscillations of δ¹⁸O values, reflecting biannual changes in water temperature. According to calcite δ¹⁸O, the MISS stromatolite corresponds to higher temperature than the MIS6 and MIS1 samples; moreover, MIS6 sample suggests a higher yearly temperature range than the two other samples. As it has been observed in the recent tufas, the seasonal variability of the water δ¹⁸O must be taken into account to interpret the actual temperature range, which can be larger than the directly inferred from the calcite δ¹⁸O range.

δ¹³C values for the Holocene tufa are higher and more disperse than those measured in the Pleistocene samples. This difference may be associated with peculiarities in the vegetal cover and with the decreased water availability in the Holocene relative to the Late Pleistocene.

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**References**


