$\delta^{13}C$ and Mg/Ca dripwater response to environmental conditions in the Ortigosa caves (La Rioja, Spain)

La respuesta de $\delta^{13}C$ y Mg/Ca del agua de goteo a las condiciones ambientales en las cuevas de Ortigosa (La Rioja, España)

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ABSTRACT

Rainfall on Ortigosa de Cameros (La Rioja), dripping rate and drip water $\delta^{13}C$, and Mg/Ca from the caves, as well as $\delta^{13}C$ and Mg/Ca from a close river and spring, were monitored during a hydrological year. Dripping rate follows local rainfall, excepting for an autumn delay, due to the drying of the epikarst after summer. The general more slowly response of La Viña Cave is likely due to the thicker vadose zone above the cave. $\delta^{13}C$ and Mg/Ca patterns are consistent with the dripping rate, showing the dripping autumn delay, related to the water decrease in the epikarst during summer and the subsequent decline of the biological activity. The spring $\delta^{13}C$ and Mg/Ca minimum values correspond to the rainfall maximum and dripping resume after winter, and are linked to the spring biological activity surge. $\delta^{13}C$, similar in dripping caves, river and spring, reflects clearly the general spring humidity and the accompanying biological activity, whereas Mg/Ca values are more variable and more sensitive to the summer drought, delayed to autumn.

Key-words: *Cave monitoring, hydrological response, dripwater geochemistry, seasonality, Ortigosa Caves.*

RESUMEN

Durante un año hidrológico se han monitorizado, en Ortigosa de Cameros, la lluvia, la tasa de goteo y sus valores de $\delta^{13}C$ y Mg/Ca de dos cuevas, junto con los de un río y un manantial próximos. La tasa de goteo concuerda con la lluvia, excepto por un retraso en otoño, debido a que el epikarst se seca en verano. En general, la cueva de La Viña responde más lentamente, debido al mayor espesor de roca que la cubre. Las evoluciones de $\delta^{13}C$ y Mg/Ca del agua de goteo son paralelas a la de la tasa de goteo, observándose el mismo retraso en otoño, relacionado con la pérdida de agua del epikarst en verano. El mínimo de $\delta^{13}C$ y Mg/Ca en primavera se corresponde con el máximo de lluvia y la reanudación del goteo tras el invierno, así como al aumento de la actividad biológica en primavera. Los valores de $\delta^{13}C$, semejantes en las cuevas, el río y el manantial, reflejan claramente la mayor humedad en primavera, junto con la actividad biológica asociada, mientras que la relación Mg/Ca es más variable y más sensible a la sequía de verano, diferida al otoño.

Palabras clave: *Monitorización, respuesta hidrológica, geoquímica del agua de goteo, estacionalidad, Cuevas de Ortigosa.*

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Introducción

Combined speleothem $\delta^{13}C$ and Mg/Ca are used as indicators of palaeoenvironmental humid/arid conditions (Fairchild and Treble, 2009; Meyer *et al.*, 2014). However, their interpretation is hampered by the diversity of processes involved. $\delta^{13}C$ reflects changes in the vegetation cover, biological soil activity, cave ventilation and temperature. In turn, Mg/Ca is related to effective rainfall controlled by evapotranspiration and the previous calcite precipitation (PCP) process in the epikarst. Monitoring $\delta^{13}C$ and Mg/Ca values of dripwaters can help to understand the factors controlling the $\delta^{13}C$ and Mg/Ca behavior in a specific karst system (McDermott, 2004; Frisia *et al.*, 2011; Cruz *et al.*, 2015).

Speleothemic dynamics in the Ortigosa de Cameros (La Rioja) cave system was previously established (Muñoz *et al.*, 2009; Osácar at al., 2014 and references therein). In this work the dripping behaviour and its $\delta^{13}C$ and Mg/Ca signatures are monitored for a hydrological year (September 2010 to August 2011) to understand the hydrological response of the caves and the differential signal of the two parameters. Additional data of local rainfall, river water and underground discharge are also considered.

Geological setting

The endokarstic system of Ortigosa de Cameros (Iberian Ranges, Northern Iberia) is developed in a karstic massif made of Jurassic, marine limestones, dipping to the S-SE (Fig.1). This massif, at about 1000 m a.s.l., is covered by poorly developed calcareous soils (rendzina) and a mesophytic forest of *Quercus*. The cave system is com-

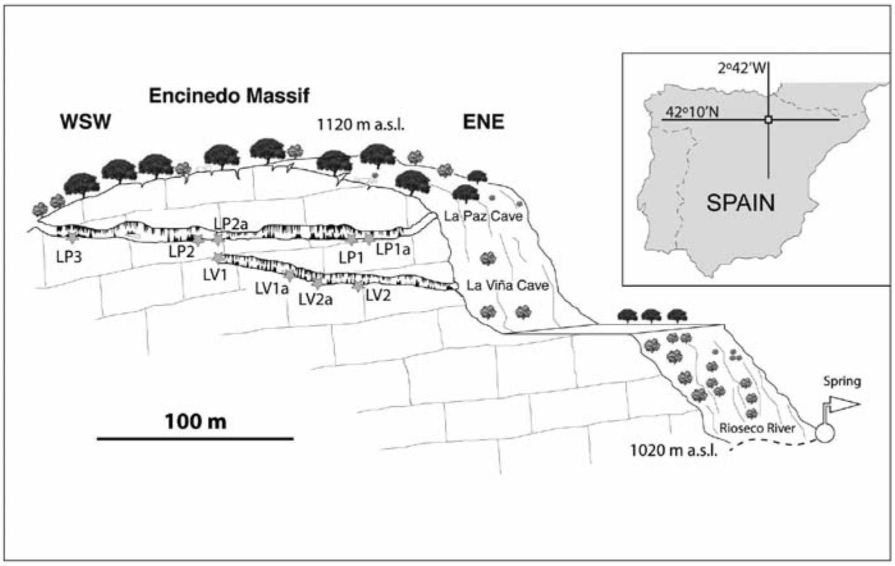

Fig. 1.- Geographical setting and outline of the Ortigosa de Cameros caves.

Fig. 1.- Situación geográfica y esquema de las cuevas de Ortigosa de Cameros.

posed of two linear, horizontal, single-conduit passages: La Paz Cave, 236 m long, open on both ends, and La Viña Cave, 114 m long and with an only entrance. La Paz Cave is topographically above La Viña Cave, but one cave does not overlay the other. They are open to public visits from March to October.

Methods

Dripping rate was measured continuously at one site in each cave (sites LV1 and LP2 in figure 1) by means of two sensors HOBO® Data Logging Rain Gauge of ONSET Model nº RG2. Another identical sensor, installed out of the caves, recorded the precipitation.

Dripping water of the two caves has been sampled monthly in several sites in each cave: up to 5 sites in La Paz Cave (LP1, LP1a, LP2, LP2a and LP3) and up to 4 sites in La Viña Cave (LV1, LV1a, LV2, LV2a) (Fig.1). In the dry periods some of the sites dried up and were not sampled. River and spring water have also been sampled every month.

Water samples for $\delta^{13}C$ were poisoned with a solution of $HgCl_2$ before the analysis, which was carried out at the J. Stefan Institute in Ljubljana (Slovenia). The results are expressed as $\delta^{13}C$‰ V-PDB.

For Ca and Mg analysis, a 65% HNO_3 solution was added to the water samples. The analyses were carried out at the University of the Basque Country (Spain), by ICP-MS.

Results

Precipitation and dripping rate

Local precipitation concentrates in autumn and spring, although there are also some stormy events in summer (Fig. 2). Cave dripping records also two main activity periods, after the autumn and spring rainfalls (Fig. 2); the rest of the year dripping reduces and even some of the monitored sites dried up. After the dry summer, in La Paz Cave dripping resumes in November, following previous rainfall events, whereas in La Viña Cave, dripping resumes at the end of December. From middle February to April dripping declines, and the sparse dripping in La Paz Cave coincides with the rain events.

In April, about one month after an important March rainfall event, dripping resumes in both caves. From that moment onwards, the dripping rate of the two caves follows the rainfall events, although in La Viña Cave dripping is always weaker. In June rainfall reduces except for some heavy rainfall events in summer that are shadowed by dripping.

Water $\delta^{13}C$ signature

Dripping water $\delta^{13}C$ values from the various cave sites display similar patterns (Fig. 3), whose means are also broadly parallel in both caves (Fig. 2). Nevertheless, the April minimum, obvious in both caves, is more distinct in La Paz Cave (-15.3‰). From September to February in La Paz Cave and to January in La Viña Cave (Fig. 3), values are more dispersed. LP2 is the only dripping site remaining for sampling from September to November (Fig. 3) and is responsible for the November maximum (-6.4‰) of mean water $\delta^{13}C$ in La Paz Cave (Fig. 2). La Viña Cave shows another relative maximum in February (-8.1‰). After the April minimum, $\delta^{13}C$ increases during late spring and summer. July and August also show certain variability, especially in La Viña Cave (Fig. 3).

Water $\delta^{13}C$ from river and spring shows the same April minimum than the drip waters, and two maxima: in June, as La Paz Cave dripping, and close to spring (in February in the spring water and in March in the river water, Fig. 2). From the April minimum to August the spring and river water values are higher than the cave waters.

Mg/Ca

Mg/Ca conforms broadly to $\delta^{13}C$ in both caves, although Mg/Ca variations are softened with respect to $\delta^{13}C$ (Fig. 2). The water Mg/Ca values of individual dripping sites are generally higher in La Viña Cave (x=0.02; s=0.008) than in La Paz Cave (x=0.01; s=0.005) (Fig. 3), where they are more homogeneous, excepting for LP2, which shows higher values than the other sites until February. The decreasing trend of the mean Mg/Ca value of La Paz Cave from November to April (Fig. 2) is greatly induced by the decreasing Mg/Ca of LP2 from December to May (Fig. 2). In La Viña Cave, in relation with the highly dispersed values (Fig. 3), Mg/Ca mean is steady around 0.017 and the April minimum is less conspicuous (Fig. 2).

The spring values are slightly higher than the river values and they show little variability (Fig. 2). Both, river and spring Mg/Ca values, are one order of magnitude higher than the caves dripping water (x=0.18 in the spring waters, x= 0.15 in the river waters, 0.014 in the caves) and there is no parallelism with the dripping water Mg/Ca.

Discussion

Hydrological response in the caves

Dripping follows the rainfall events, although with some delay, especially after the autumn rainfalls, which are larger in La Viña. Thus, dripping pattern can vary according to the rainfall pattern (Muñoz *et al.*, 2009). Nevertheless, a similar delay has been explained by the time needed for the water to reach the caves after summer, when the epikarst probably dried (Osácar *et al.*, 2014). Therefore, the water of the first autumn precipitations would have been stored in the epikarst, before reaching the cave, for longer than the spring rainfalls. The response of La Viña Cave seems also be slower than La Paz Cave. The thicker vadose zone above La Viña Cave may be the reason for the larger delay, because of the longer flow-paths.

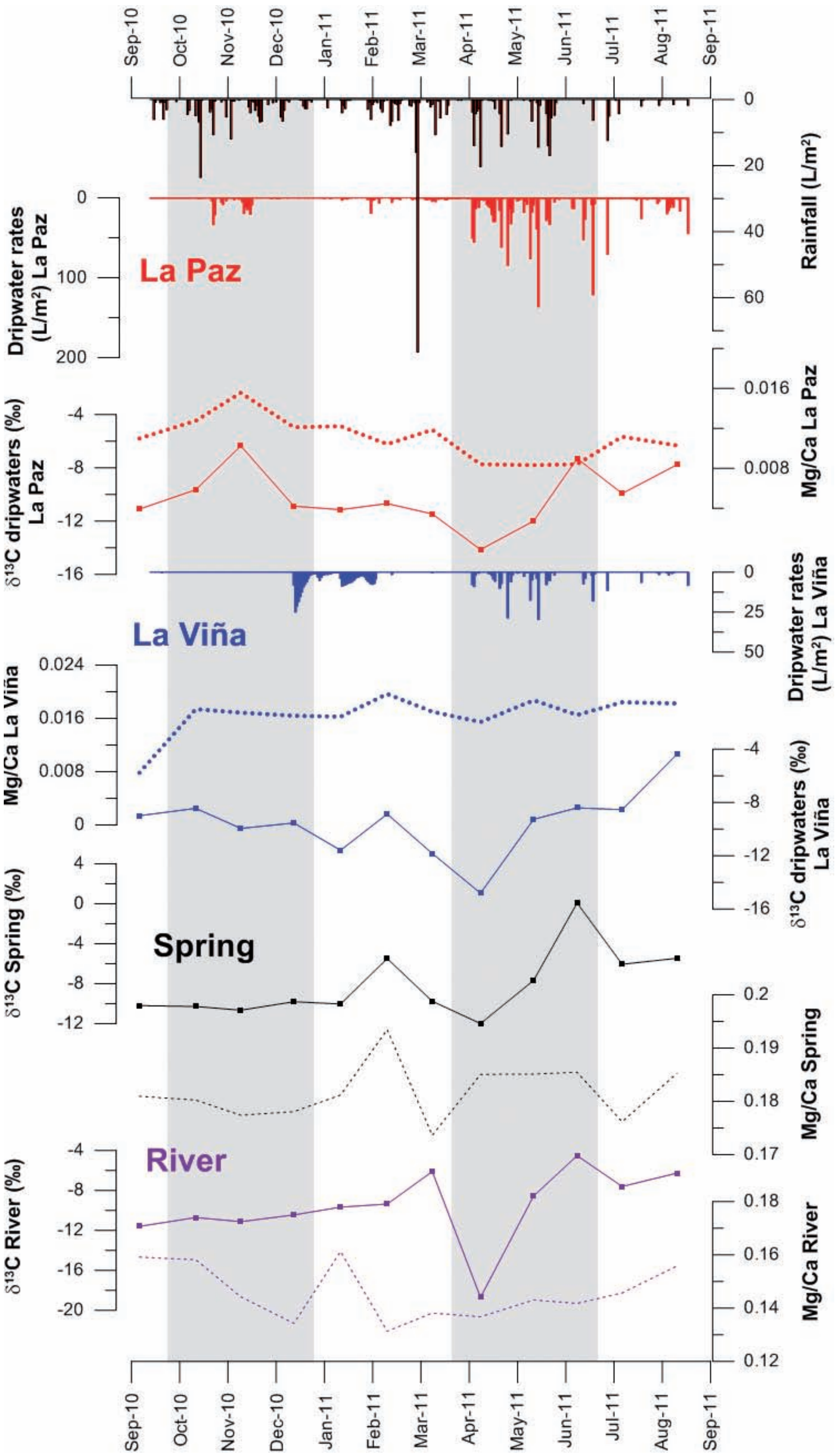

Fig. 2.- Daily precipitation in the caves area, daily dripping rates of both caves, mean values of $\delta^{13}C$ and Mg/Ca in both caves and in the river and the spring nearby of the Ortigosa de Cameros caves. Autumn and spring are shown in grey.

Fig. 2.- Precipitación diaria en la zona de las cuevas, tasa de goteo diaria en ambas cuevas, valores medios de $\delta^{13}C$ y Mg/Ca en ambas cuevas, en el río y el manantial próximos a las cuevas de Ortigosa de Cameros. El otoño y la primavera aparecen en gris.

$\delta^{13}C$ and Mg/Ca in dripping, spring and river

$\delta^{13}C$ and Mg/Ca roughly follow the cave dripping pattern. In autumn, because of the dripping delay from rainfall, the water from the first precipitations is stored in the epikarst and, through PCP, it becomes enriched in Mg (Fairchild and Treble, 2009; Cruz *et al.*, 2015). When the epikarst becomes wetted, a flushing mechanism would pump into the caves this Mg-rich water (Orland *et al.*, 2014). As the autumn water reaches the cave, the water Mg/Ca content decreases noticeably in LP2 in La Paz Cave, while the other dripping sites resume dripping with low Mg/Ca water (Fig. 3). In La Viña Cave the autumn maximum occurs in February, accordingly to the more slowly response of la Viña Cave (Fig. 2).

The heavy $\delta^{13}C$ signal in autumn is likely due to the decline of the biological activity linked to the water decrease in summer (Fig. 2). Additionally, the drying of the epikarst (LP2 is the only remaining dripping site in La Paz Cave) can contribute to water ^{12}C depletion by degassing in the voids of the dry epikarst. The longer stay of water in the vadose zone might also increase the input of ^{13}C-enriched to the water by limestone dissolution (Dreybodt and Scholz, 2011) and the degassing linked to PCP can also yield higher $\delta^{13}C$ (Fairchild and Treble, 2009). However, the similarity between the $\delta^{13}C$ values from both caves and the river and the spring (Fig. 2) suggests that this signal is not substantially altered in its way through the vadose zone. On the contrary, Mg/Ca increases slightly from La Paz Cave to La Viña Cave and is much higher in the spring and the river, which denotes the relevance of the path-flow length along the vadose zone. Also, the diversity of the Mg/Ca signal in La Viña Cave (Fig. 3) may be related to the differential pathways of the various dripping sites in this cave.

The spring rainfall water, shortly stored in the epikarst, reaches both caves simultaneously, likely because the epikarst is not as dry as in summer, and yields the April Mg/Ca minimum, probably prompted by the March heavy rainfall event. The synchronous (caves, spring and river) $\delta^{13}C$ April minimum is likely caused by the input of biogenic light carbon related to the spring biological activity surge (Dreybrodt and Scholz, 2011), arising from the warmer temperatures and the larger water availability. The rainfall signal is transmitted with a small delay, due to the time required for water to reach the caves, after the winter, as it is shown by the dripping rate. Subsequently, through the $\delta^{13}C$ increase of late spring and

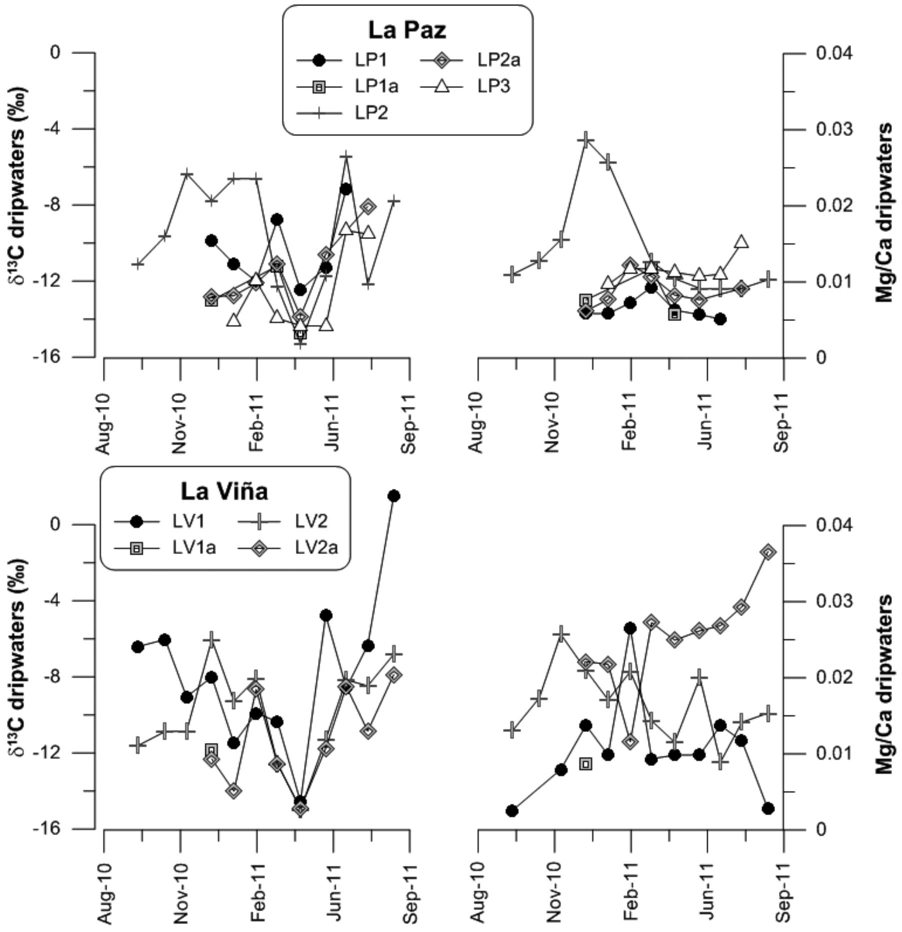

Fig. 3.- Single values of $\delta^{13}C$ and Mg/Ca of the various dripping sites in both caves

Fig. 3.- Valores individuales de $\delta^{13}C$ y Mg/Ca en los distintos puntos de goteo de ambas cuevas.

summer, there is a July minimum, more distinct in La Paz Cave, which follows an increase of dripping, synchronous woth some summer rainfall events. This may represent the decrease of biogenic carbon input, after this first biological burst. Only a water availability increment likely triggers the biological activity again, causing a $\delta^{13}C$ decrease. The spring and summer rise of spring and river water $\delta^{13}C$ may be due to the increase in the residence time of water in the epikarst.

$\delta^{13}C$ vs Mg/Ca as seasonality proxies

Although both proxies answer to the seasonal water availability, the different acting mechanism introduces disparities in the respective patterns. On one hand, the dripwater $\delta^{13}C$ reflects the local water signal of both spring and river, that is, groundwater, which, in turn, responds to seasonal oscillations linked to precipitation and temperature; it reflects especially clearly the spring humidity and the increase of the soil biological activity.

On the other hand, Mg/Ca shows significant differences between caves and between sites in a cave (Tremaine and Froelich, 2013). Although Mg/Ca is less sensitive to the spring event than $\delta^{13}C$, in autumn, with less biological activity, the summer delayed water shortage is more noticeable in Mg/Ca than in $\delta^{13}C$.

Conclusions

One year monitoring of the Ortigosa endokarstic system evidences that dripping rate, $\delta^{13}C$ and Mg/Ca of dripwater respond to environmental conditions.

- Cave dripping shows a delay from rainfall in autumn, probably linked to the epikarst becoming almost dry after summer. This delay is also transmitted to the water $\delta^{13}C$ and Mg/Ca signatures. Delays are generally larger in La Viña Cave, likely due to the thicker vadose zone above the cave.
- Dripping water $\delta^{13}C$ shows the wet and warm seasonality more precisely, due to the influence of the biological activity,
- By contrast, dripping water Mg/Ca, more variable than $\delta^{13}C$, reveals better the summer-autumn water availability and it is affected by processes acting along the flow-path.

Additional studies, including more parameters, and a longer monitoring period, are needed to validate these interpretations.

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