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Stable isotopes of gypsum hydration water in recent playa-lake sediments: implications for paleoclimate reconstructions

Isótopos estables del agua de hidratación del yeso en sedimentos lacustres recientes: implicaciones para reconstrucciones paleoclimáticas.

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ABSTRACT

We investigate the oxygen and hydrogen stable isotopes of hydration water in gypsum ($CaSO_4 \cdot 2H_2O$) from surface sediment of Laguna de la Ratosa playa-lake (northern Málaga Province, Spain). We aim to enhance the understanding of how lacustrine gypsum from playa-lakes can be used for paleoclimate reconstruction. Gypsum samples were collected at 30-meter intervals along a transect from the shore to the depocenter of the lake. Comparison of $\delta^{18}O$ and δ^2H values of gypsum hydration water with the modern seasonal isotope variability of lake water points to gypsum formation in spring and early summer, before complete desiccation of the lake. An increasing trend in the $\delta^{18}O$ and δ^2H values of gypsum hydration water, by ~1,5 and ~15‰, respectively, is observed from the shore to the depocenter. This indicates that coeval gypsum formed in different parts of the lakebed record slightly different isotopic values of the lake water during precipitation. This spatial variability should be considered when interpreting stable isotope series of gypsum hydration water from ephemeral lake sediments.

Keywords: *gypsum, stable isotopes, playa-lake, gypsum hydration water, modern lake sediments.*

RESUMEN

En este trabajo se han investigado los isótopos estables de oxígeno e hidrógeno del agua de hidratación en el yeso ($CaSO_4 \cdot 2H_2O$) de los sedimentos superficiales de la Laguna de la Ratosa (norte de la provincia de Málaga, España). El objetivo es mejorar nuestro conocimiento sobre cómo el yeso de lagunas salinas efímeras puede utilizarse para la reconstrucción paleoclimática. Se tomaron muestras cada 30 metros a lo largo de un transecto desde el centro hasta la orilla del lago. Los valores de $\delta^{18}O$ y δ^2H del agua del lago se compararon con los del agua de hidratación del yeso. El yeso registra la composición isotópica del lago en primavera y principios del verano, antes de que la laguna se seque. Los valores de $\delta^{18}O$ y δ^2H del agua de hidratación del yeso aumenta desde la orilla hasta el depocentro, aproximadamente en ~1,5 y ~15‰, respectivamente. Esto indica que yesos formados simultáneamente, pero en diferentes partes del lago, pueden presentar composiciones isotópicas ligeramente distintas. Esta variabilidad espacial debe tenerse en cuenta a la hora de interpretar los resultados de isótopos estables del yeso en sedimentos de lagunas salinas efímeras.

Palabras clave: *yeso, isótopos estables, lagunas efímeras, agua de hidratación del yeso, sedimentos lacustres recientes.*

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Introduction

Playa-lakes are shallow, ephemeral water bodies located in arid and semi-arid areas where evaporation exceeds precipitation, resulting in a water deficit. In the Andalusian lowlands, and other Mediterranean regions, they commonly occupy the lower areas of endorheic basins (Rodríguez-Rodríguez, 2007). In most cases, the water depth rarely exceeds one meter and the hydroperiod extends from winter to early summer, but prolonged drought periods can lead to the desiccation of the playa-lake, lasting several years (Rodríguez-Rodríguez *et al*., 2015).

Playa-lakes provide sedimentary sequences that can contain useful indicators for paleoclimate studies (Dixit *et al*., 2018; Martegani *et al*., 2022). They undergo cycles of drying and filling over the years, which are recorded in their sediments through mineralogical and/or geochemical proxies (García-Alix *et al*., 2022). Gypsum ($CaSO_4 \cdot 2H_2O$) is one of the most common evaporitic minerals in the sedimentary record of Andalusian lakes and is preserved in lake sedimentary sequences due to its relatively low solubility compared to halite and other evaporites (Escavy *et al*., 2012). It precipitates in lakes due to increased concentration of calcium and sulfate by evaporation. In Andalusian playa-lakes, calcium and sulfate ions are commonly derived from dissolution of ancient gypsum deposits (e.g., Triassic or Miocene deposits).

Gypsum captures water molecules during crystallization, recording the isotopic composition of the liquid water (Gázquez *et al*., 2017). Therefore, stable isotopes of gypsum hydration water (GHW) can be used as paleoenvironmental indicators, serving as a paleo-humidi-

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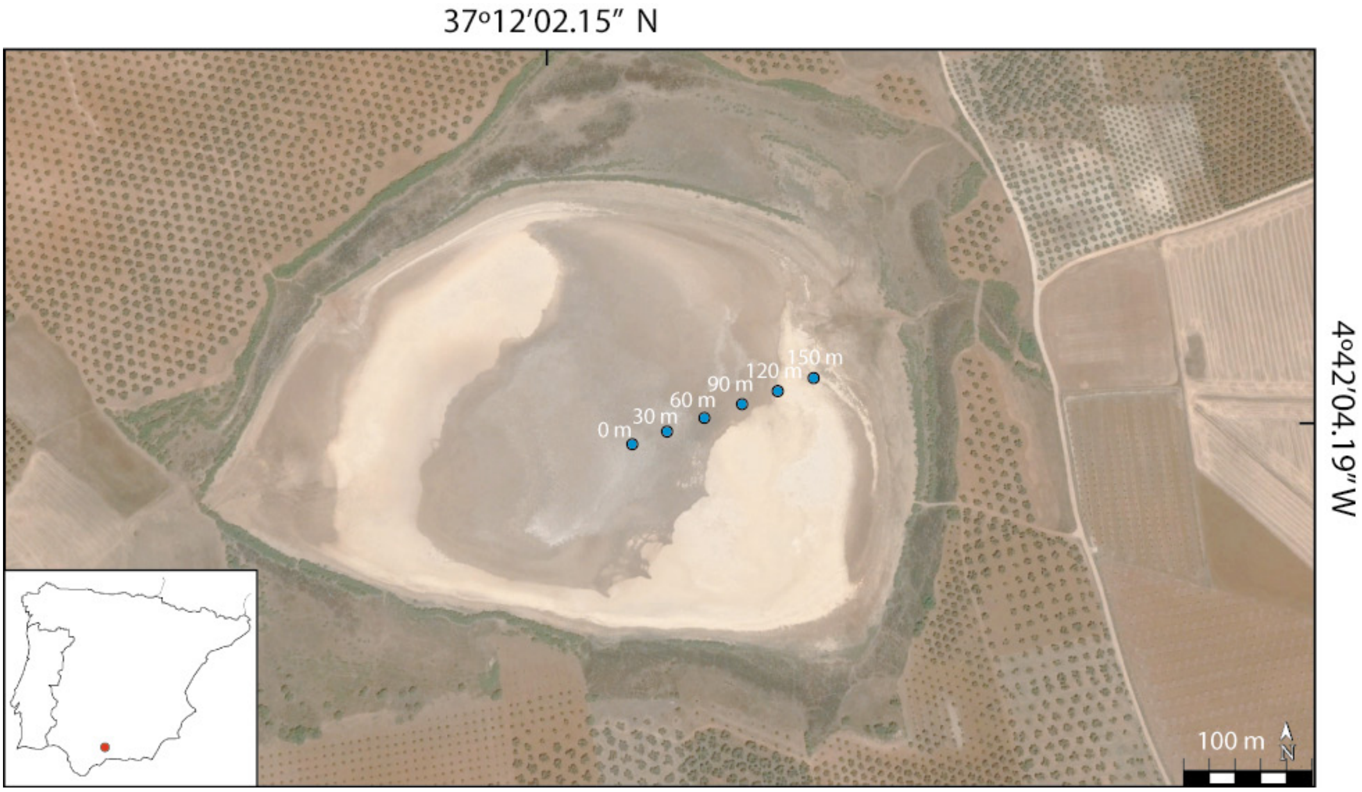

Fig. 1. Location and aerial photograph of the Laguna de la Ratosa. The blue dots indicate the sites where surface gypsum samples were taken.

Fig. 1. Localización y fotografía aérea de la Laguna de la Ratosa. Los puntos azules indican los lugares dónde se tomaron las muestras de yeso superficial.

ty/paleo-aridity proxy (Hodell *et al*., 2012; Dixit *et al*., 2018; Martegani *et al*., 2022; Gázquez *et al*., 2018; 2023), and enabling quantitative paleoclimate reconstructions (Hodell *et al*., 2012; Evans *et al*., 2018; Gázquez *et al*., 2018; 2023).

This study focuses on the analysis of oxygen and hydrogen stable isotopes of GHW in surface gypsum from Laguna de la Ratosa, a playa-lake whose sedimentary sequence is being studied for paleoclimate reconstructions. We investigate the relationship between the present lake water (02/2022-06/2023) and the isotopic composition of GHW of surface gypsum, which likely precipitated from the lake water in recent years. The spatial variability of GHW within the lake is also investigated. Understanding how the isotopic composition of the lake water is recorded by GHW at present will help to accurately interpret the data from lake sediment cores.

Geological and climate setting

Laguna de la Ratosa playa-lake (37º12'02.15"N 4º42'04.19"W) is located northwest of the Sierra de la Camorra, in the northern region of the province of Málaga (Fig. 1). The climate in this area is semi-continental dry-subhumid Mediterranean, with average annual temperatures ranging from 15°C to 18°C. The mean annual precipitation is 435 mm (Gómez-Zotano *et al*., 2015).

The predominant surface deposits in the playa-lake catchment are clastic-eva-

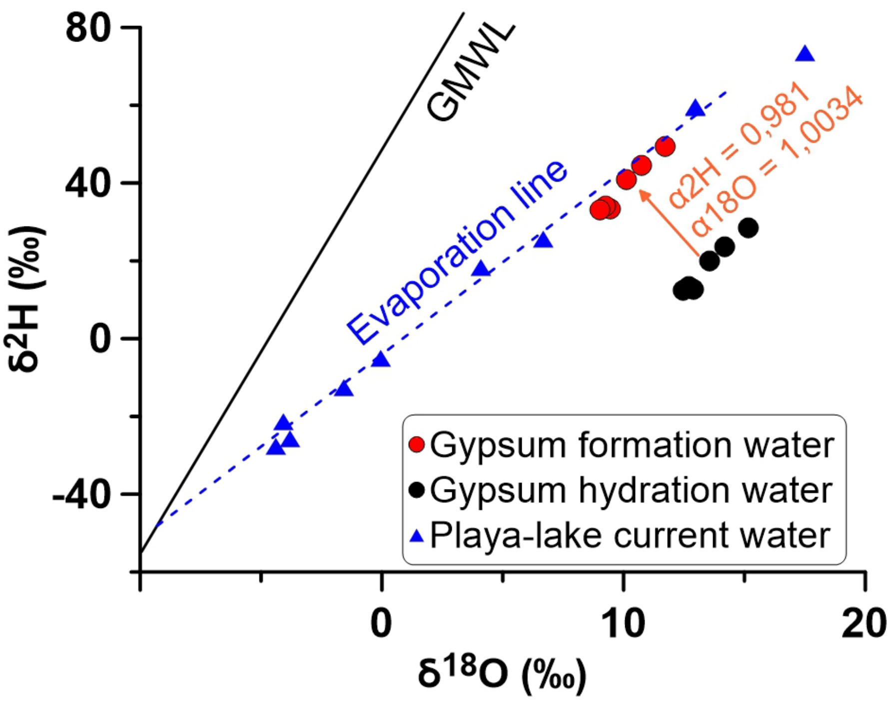

Fig. 2. Isotopic composition of the water from which gypsum precipitated in Laguna de la Ratosa, reconstructed from GHW. The δ^{18}Olake and δ^{2}Hlake values align along an evaporation line intersecting the GMWL (Global Meteoric Water Line) at -8‰ for δ^{18}O and -45‰ for δ^{2}H. See color figure in the web.

Fig. 2. Composición isotópica del agua a partir de la cual precipitó el yeso en la Laguna de la Ratosa reconstruida a partir del agua de hidratación del yeso. Los valores de δ^{18}Olago y δ^{2}Hlago se alinean con los de las aguas actuales del lago en una línea de evaporación que corta a la GMWL (línea meteórica del agua global) a -8‰ para el δ^{18}O y a -45‰ para el δ^{2}H. Ver figura en color en la web.

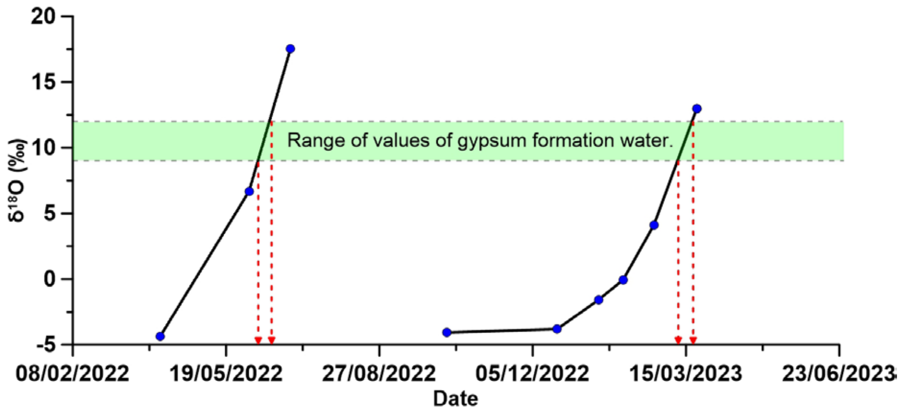

Fig. 3. $\delta^{18}O$ values of lake waters in Laguna de la Ratosa from February, 2022, to June, 2023. The green-colored band represents the range of $\delta^{18}O_{lake}$ values recorded by surface gypsum.

Fig. 3. Valores del $\delta^{18}O$ de las aguas de la Laguna de la Ratosa entre febrero de 2022 y junio de 2023. La franja de color verde representa el rango de valores de $\delta^{18}O_{lago}$ registrados por el yeso superficial.

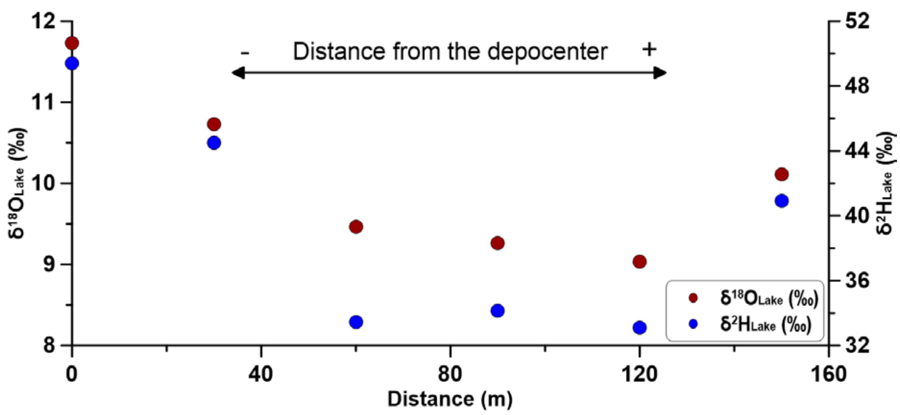

Fig. 4. $\delta^{18}O_{Lake}$ and $\delta^{2}H_{Lake}$ values from surface gypsum samples taken at 30-meter intervals from the center of Laguna de la Ratosa. See color figure in the web.

Fig. 4. Valores del $\delta^{18}O_{Lago}$ y $\delta^{2}H_{Lago}$ de las muestras de yeso superficial tomadas a intervalos de 30 metros desde el centro de la Laguna de la Ratosa. Ver figura en color en la web.

poritic materials, characterized by low permeability, including clays and marls (Benavente *et al*., 2000; Rodríguez-Rodríguez, 2007). According to recent investigations, its deposits are saline-alkali sediments (Halmos *et al*., 2022). These are Quaternary materials that overlay Triassic rocks, such as calcarenite outcrops and interbedded evaporites, including gypsum, from the Upper Miocene. The formation of this playa-lake is linked to the karstification of the evaporites of the Triassic substrate (Benavente *et al*., 2000).

Material and methods

Six samples of gypsum-rich sediment were taken in summer 2022 when the lake dried up, along a transect of 150 m, at regular intervals of 30 m from the lake center to the shore. Water samples were collected on a monthly basis during the flooded period (winter to early summer) from February 2022 to June 2023. Gypsum, which appeared as mm-sized crystals, was manually separated from clays under the microscope.

GHW was extracted from gypsum (~200 mg) off-line by heating the samples under vacuum using the method described in Gázquez et al. (2015). Subsequently, the $\delta^{18}O$ and $\delta^{2}H$ of GHW was analyzed using a CRDS (Cavity Ringdown Spectroscopy) laser spectrometer Picarro® L2140-i at the Laboratory of Stable Isotopes of the University of Almería, Spain. The results are standardized with respect to the international reference material V-SMOW (Vienna-Standard Mean Ocean Water) and normalized to V-SMOW – V-SLAP (Vienna-Standard Light Antarctic Precipitation) scale. The external precision (1σ) of the method is better than 0.2‰ and 1‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively, based on the repeated analysis of an internal gypsum standard along with the samples.

The isotopic composition of GHW is then used to calculate the isotopic values of the lake water from which gypsum formed, by applying known isotope fractionation factors at 25°C. We used $\alpha^{18}O_{GHW\text{-}Lake}$ of 1.0034±0.0001 and $\alpha^{2}H_{GHW\text{-}Lake}$ of 0.981±0.001 (Gázquez *et al*., 2017). Importantly, these fractionation factors are largely independent of temperature (from 0 to 30ºC) and salinity (<150 g/l) (Gázquez *et al*., 2017). These limits are unlikely to have been exceeded during gypsum precipitation in Laguna de la Ratosa.

Results

The isotopic composition of GHW ranged from 12.5‰ to 15.2‰ for $\delta^{18}O_{GHW}$ and from 12.5‰ to 18.4‰ for $\delta^{2}H_{GHW}$ (Fig. 2). This variability is significant, but considerably smaller than in preliminary analyses of $\delta^{18}O_{GHW}$ and $\delta^{2}H_{GHW}$ in Holocene sediment cores extracted from Laguna de la Ratosa (e.g., 0 to 10‰ for $\delta^{18}O$; unpublished data). After applying fractionation coefficients, we found that the isotopic composition of the water at the time of gypsum precipitation varied from 9.0‰ to 11.7‰ for $\delta^{18}O_{Lake}$ and from 33.1‰ to 49.4‰ for $\delta^{2}H_{Lake}$ (Fig. 2).

The modern isotopic composition of the water in Laguna de la Ratosa changes considerably throughout the year, from $\delta^{18}O$ and $\delta^{2}H$ values similar to rainwater (-8‰ and -45‰, respectively) in winter-spring to isotopically enriched water (17,5‰ for $\delta^{18}O$ and 73,6‰ for $\delta^{2}H$) by the beginning of summer. These values align with the $\delta^{18}O_{lake}$ and $\delta^{2}H_{lake}$ values reconstructed from GHW, along an evaporation line that intersects the Global Meteoric Water Line (GMWL) at -8‰ and -45‰, which is within the range of modern rainwaters in this region (Gázquez *et al*., 2023).

Discussion

The $\delta^{18}O_{lake}$ values estimated from surface gypsum in Laguna de la Ratosa are within the range of values of lake water in late spring and early summer (Fig. 3). This shows that GHW does not record the mean isotopic composition of the lake throughout the year, but rather represents the spring-summer conditions. The fact that the isotopic composition recorded by GHW resembles that of evaporated lake water instead of isotopically depleted water (e.g. rainwater) indicates that the effect of any post-depositional isotopic exchange between GHW and lake water (Gázquez *et al*., 2022) and gypsum recrystallization (Pierre, 2018) are negligible.

The lower isotopic ratios of GHW observed near the shore reflect the isotopic composition of the lake at high water level when the water is barely evaporated (Fig. 4), except for the sample taken 150 meters from the playa-lake's depocenter, which presents slightly higher isotopic value. One possible explanation is that during the playa-lake's desiccation, there were isolated flooded areas disconnected from the main body of water (as observed in satellite images) due to the topographic heterogeneity of the basin, evaporating independently and thus, recording higher isotopic values. As the lake evaporates, the flooded area shrinks and water gets enriched in heavier isotopes (i.e. ^{18}O and ^{2}H). Gypsum samples from areas closer to the depocenter record this terminal evaporation stage. This finding suggests that the location of gypsum deposits in relation to the extension of the flooding area in playa-lakes can cause isotopic variability in GHW and should be considered when interpreting the isotopic composition of GHW in sediment cores for paleoclimate reconstructions.

Conclusions

The results presented in this study allow us to draw several conclusions:

(1) Our dataset confirms that GHW can be a powerful tool for studying paleoclimate and past environmental conditions from playa-lake sediments.

(2) We conclude that the isotopic composition of GHW varies slightly with the position of the sample with respect to the lake depocenter. This variability is significant, but considerably smaller than that observed in preliminary analyses of δ^{18}O and δ^{2}H in GHW of sediment cores from Laguna de la Ratosa (i.e. from 0 to 10‰ for δ^{18}O; unpublished data). Therefore, the migration of the lake depocenter over time alone cannot account for the observed variability in the sedimentary sequence, but it is more likely associated with hydroclimate changes.

(3) GHW records the isotopic composition of the playa-lake water during a specific period, between spring and early summer at present. Therefore, this has to be taken into account when interpreting the isotopic composition of GHW in sediment cores.

Author contributions

J.C.P carried out the analyses of gypsum. F.G. developed the analytical method and obtained funds to conduct this study. L.M., F.G. A.G.A, G.J.M and M.R.R. carried out the sampling of gypsum. C.V. and L.M. sampled the lake water. J.C.P wrote the draft of the manuscript and all the co-authors contributed to the final version.

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