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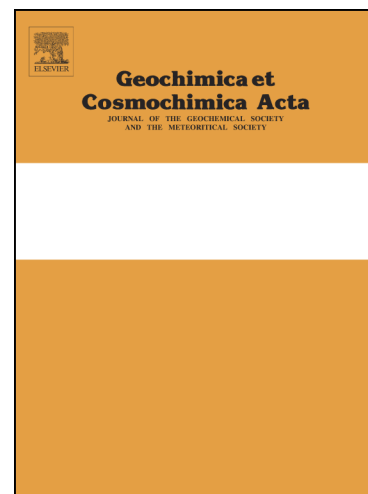
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Controls of extreme isotopic enrichment in modern microbialites and associated abiogenic carbonates

Scott R. Beeler^{1*}, Fernando J. Gomez², Alexander S. Bradley¹

¹Department of Earth and Planetary Science, Washington University in St. Louis, Saint Louis, Missouri, 63130, USA

²CICTERRA-CONICET, Facultad de Ciencias Exactas, Físicas, y Naturales, Universidad Nacional de Córdoba, Córdoba, X5000, Argentina

*corresponding author (beeler@wustl.edu)

Abstract

Microbialites and abiogenic carbonates of the closed-basin hypersaline lake Laguna Negra (Catamarca Province, Argentina) are highly enriched in both ^{13}C and ^{18}O . These carbonates precipitate in the zone of recharge where lake water mixes with groundwater. We examined the processes controlling the isotopic evolution of input waters in order to better interpret the isotopic compositions of the carbonates. Large enrichments of ^{13}C in dissolved inorganic carbon and ^{18}O in water occur as input groundwater chemically evolves. These enrichments can be explained through the abiotic processes of water-equilibration, evaporation, degassing, and carbonate precipitation. The ^{13}C and ^{18}O contents of lake carbonates are consistent with equilibrium precipitation from lake water indicating that the currently ongoing processes can explain the isotopic patterns observed in carbonates. Isotopic compositions of these microbialites are largely unrelated to the biological processes controlling microbialite formation – a pattern that may be generalizable to other settings. However, the isotopic compositions of these microbialites record information about their depositional environment.

1. Introduction

Microbialites are sedimentary structures arising from the interaction of microbial and geological processes that occur extensively throughout the rock record (Burne and Moore, 1987; Grotzinger and Knoll, 1999; Riding, 2000). These structures are among the oldest evidence of life on Earth and provide one of the best records of life, particularly in the Precambrian where a robust fossil record is lacking (Allwood et al., 2006; Schopf and Kudryavtsev, 2007; Nutman et al., 2016; Peters et al., 2017). Microbialites can provide insight into how life and the environment have co-evolved through geologic time. Microbialites have been proposed as a target in the search for extraterrestrial life because they provide geological evidence of life that can potentially be recognized at outcrop scale (Cady et al., 2003; Des Marais et al., 2008). However, structures that are morphologically similar to microbialites can be formed abiotically confounding their utility as a tool to detect and understand life on early Earth and potentially other planets (Grotzinger and Rothman, 1996). Even in cases where biogenicity is clear our ability to interpret the biogeochemical information potentially preserved in microbialites is incomplete (Grotzinger and Knoll, 1999; Bosak et al., 2013). Further lines of evidence in addition to morphology are therefore necessary to assess the biogenicity of microbialites and determine the biogeochemical information they may preserve.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonate minerals that comprise many microbialites are a compelling tool to understand the meaning of microbialites because they reflect environmental processes associated with their formation. If carbonate is precipitated in chemical equilibrium with dissolved inorganic carbon (DIC) and water, then the carbonate captures geochemical and hydrological processes. Microbial processes can also play a role, and the stable isotopic composition of carbon and oxygen of carbonate minerals have been analyzed to make inferences about the structure and function of microbial communities associated with microbialite formation (Andres et al., 2006; Brady et al., 2014; Birgel et al., 2015). Likewise, stable isotopic compositions have been suggested as a potential tool to assess the biogenicity of mineral structures on Mars (Banfield et al., 2001). The changes in isotopic values preserved in the laminated fabrics present in many microbialites have also been used as time series evidence of shifts in these processes (Nehza et al., 2009; Frantz et al., 2014; Petryshyn et al., 2016). At the broad scale, the isotopic composition of carbonate minerals are used as a tool to understand the evolution of biogeochemical cycles through geologic time (Kump and Arthur, 1999). Developing an understanding how isotopic signatures are generated and preserved in microbialites in modern environments can help to enhance our ability to interpret their meaning in ancient and potentially extraterrestrial examples.

The evaporative lake Laguna Negra (Catamarca Province, Argentina) contains microbialites and abiogenic carbonate structures with carbonate that is highly enriched in ^{13}C and ^{18}O . These isotopic compositions have been hypothesized to arise from the interactions of microbial, geochemical, and hydrological processes, and variability in isotopic compositions across sequential laminae within individual carbonate structures have been interpreted to reflect changes in environmental conditions temporally at the lake (Buongiorno et al., 2019). However, isotopic trends are also present in the overall dataset complicating our ability to interpret the meaning of the temporal variability in the isotopic compositions preserved within individual carbonate structures. Here we performed spatial analyses of isotopic and geochemical parameters in Laguna Negra waters to assess the degree and controls of isotopic variability at the lake over a single time interval. We then used this data to provide a framework for more robust interpretation of the overall dataset of isotopic values of carbon and oxygen from carbonate minerals at Laguna Negra and other comparable sites.

2. Field Area

Laguna Negra is a closed basin lake located in the Puna-Altiplano region of the Andes mountains (Figure 1). Lake waters are hypersaline (up to >300 ppt) reflecting the strongly negative water balance of the region (Risacher et al., 2003; Risacher and Fritz, 2009). The only identified inputs into Laguna Negra occur along its southeastern margin where more dilute groundwater and seasonal snowmelts enter into the lake in a zone referred to as the stromatolite belt (Gomez et al., 2014). These waters geochemically evolve from the input source into the lake body waters become progressively more saline and losing inorganic carbon (Gomez et al., 2014). Progressive precipitation of evaporitic minerals occurs across the stromatolite belt with no mineral precipitation near the water inputs transitioning to carbonate minerals and eventually salts nearest the lake body (Figure 2). Carbonate structures formed in the stromatolite belt include morphologies interpreted as microbialites and others interpreted as having formed without microbial influence (c.f. Gomez et al., 2014). Microbialitic morphologies found at Laguna Negra primarily occur as discrete spheroidal to discoidal laminated oncoids with less

frequent accretionary laminated stromatolites. In addition to microbialites, carbonates with morphologies interpreted to form abiogenically, based upon a high degree of inheritance among consecutive laminae and a lack of microfossils, are also observed across the lake edge primarily in the form of gravels and laminar crusts. The distribution of the different carbonate morphologies is spatially variable with microbialites primarily concentrated along the northeastern portion of the stromatolite belt while non-microbial carbonates occur in the central and western portions of the stromatolite belt. These variations in carbonate morphology are associated with changes in the occurrence and appearance of microbial mats. Petrographic evidence including changes in dominant microfabric type and the presence of microfossils between carbonate types of differing macroscopic morphologies is consistent with variable roles of biology in their formation (c.f. Gomez et al., 2014).

3. Materials and Methods

Waters were sampled in March 2017 from fifteen locations across the stromatolite belt to assess their geochemical and isotopic variability (Supplemental Figure 1). Two samples were taken from areas identified as potential sources of inlet waters: a groundwater fed pool and surface stream likely fed from snowmelt. The remaining thirteen samples were taken from locations across the zone of mixing. Water samples were taken from surface waters using a polypropylene syringe equipped with PTFE tubing. Prior to sample collection the syringe and tubing were each rinsed three times with water from the sample location. Basic geochemical parameters (Temperature, pH, and electrical conductivity) were measured *in situ* using a Myron L Ultrameter II handheld meter. Salinity (S) was calculated from electrical conductivity (EC) by the Ultrameter II algorithms with NaCl as the reference compound due to Na⁺ and Cl⁻ being previously determined to be the dominant ions in Laguna Negra waters (Gomez et al., 2014). Salinity conversions by the Ultrameter II have a maximum range of 200 ppt so values above this range were calculated using a conversion factor of $S=2*EC$, which is the maximum value used by the Ultrameter II algorithm. The conversion for these high conductivity samples likely represents an underestimation of salinity, but this underestimation does not affect the interpretations made from this data as the effect of error in salinity conversions on modelled values are more than an order of magnitude smaller than spatial variability in associated parameters. Samples were also collected for stable isotopic analysis of dissolved inorganic carbon (DIC) and oxygen and hydrogen of water. Samples for DIC analysis were collected by injecting waters into an evacuated 12 mL Exetainer vial filled with 1 mL of H₂SO₄ to evolve DIC into CO₂ for analysis. Additional water samples were also collected in 2 mL GC vials with no headspace for isotopic analyses of oxygen and hydrogen of water. Isotopic composition and concentrations of DIC were measured using GasBench II system interfaced to a Delta V Plus IRMS at the UC Davis Stable Isotope Facility. The long term standard deviation of isotopic values is 0.1‰ with lithium carbonate and deep seawater utilized as reference materials. Hydrogen and oxygen isotopic compositions of water were measured using a Laser Water Isotope Analyzer V2 at the UC Davis Stable Isotope Facility. The long term standard deviation for isotopic values was <0.3‰ for ¹⁸O and <2.0‰ for ²H with a range of reference waters calibrated against IAEA reference waters.

Speciation of the carbonate system and carbonate alkalinity was calculated using measured values of [DIC] and pH and the equilibrium constants of Sass and Ben-Yaakov (1977). The Sass and Ben-Yaakov constants were chosen because they are calibrated across a

high range of salinities (0 to 330 parts per thousand) unlike other equilibrium constants in the literature, which are only calibrated across a more narrow range of salinities (typically 0 to ~40 parts per thousand). One drawback of the Sass and Ben-Yaakov constants is that they were determined only at a temperature of 30°C, and do not account for the effect of changing temperatures on equilibrium constants. Measured lake water temperatures at Laguna Negra were all $\leq 22.0^\circ\text{C}$ and spatially variable, which may provide a source of error into speciation calculations performed using the Sass and Ben-Yaakov constants. To determine the importance of this error the speciation of the carbonate system of a solution was calculated accounting for temperature changes but not salinity changes using the equilibrium constants of Mehrbach et al. (1973) and compared to those calculated accounting for salinity but not temperature changes using the Sass and Ben-Yaakov constants (Supplemental Figure 2). The variability in the concentration of carbonate species accounting for salinity with the Sass and Ben-Yaakov constants was substantially larger than the variability accounting for temperature changes using the Mehrbach constants. This indicates that salinity effects have a larger influence than temperature effects on the equilibrium constants in this system supporting the use of the Sass and Ben Yaakov constants.

The stable carbon and oxygen isotopic values expected for calcite precipitated in equilibrium with Laguna Negra waters were calculated at each sampling location. Stable oxygen isotopic values of an equilibrium calcite mineral were calculated with the oxygen isotope fractionation factor from Kim and O'Neil (1997) using measured water temperature and oxygen isotope values. Stable carbon isotope values of an equilibrium calcite mineral were calculated using the calcite-bicarbonate fractionation factor of Rubinson and Clayton (1969). The isotopic composition of bicarbonate was calculated using the mass balance formula of Zeebe and Wolf-Gladrow (2001) using the fractionation factors of Mook (1986), measured $\delta^{13}\text{C}_{\text{DIC}}$ and DIC concentrations, and calculated concentrations of $\text{CO}_2(\text{aq})$, HCO_3^- , and CO_3^{2-} .

Geochemical and isotopic data were integrated into a geographic information system (GIS) data model in ArcMap (v.10.5.1). Interpolated maps of geochemical and isotopic parameters were generated using the Spline tool using a cell size of 3.6 m/pixel. Interpolated maps of modeled values for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of calcite were generated using the Raster Calculator tool in ArcMap to perform the above calculations with the interpolated raster maps of measured values.

4. Results

Basic geochemical parameters measured across the stromatolite belt at Laguna Negra displayed a high degree of spatial variability (Table 1, Figure 3). Inlet waters sourced from the groundwater pond (LN-003) were dilute (EC = 8.88 mS/m) and moderately alkaline (pH = 7.92). Waters measured from a surface stream (LN-015) were moderately alkaline (pH = 7.68) and substantially more saline (EC = 51.1 mS/m). In general, waters in the stromatolite belt became more saline and less alkaline moving away from the groundwater inlet source. The northeastern corner of the stromatolite belt contained the most saline (EC up to 176.5 mS/m) and acidic (pH = 6.76) waters. Temperature also varied across the stromatolite belt (3.1 to 22.0 °C), but the changes correlated with time of sampling indicating that ambient conditions likely control the temperature changes.

The stable oxygen and hydrogen isotopic composition of water were similarly variable. Input waters measured from the groundwater pool ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = -3.15\text{‰}$, and $\delta^2\text{H}_{\text{H}_2\text{O}} = -34.0\text{‰}$)

were depleted in heavy isotopes compared to other locations across the lake. Similar to the geochemical parameters, isotopic trends became more enriched in ^{18}O and ^2H moving away from the groundwater pool towards the lake ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$ up to +8.61‰ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ up to +21.0‰). Likewise, the concentration and isotopic composition of DIC was variable across the lake edge. The groundwater pool had the highest concentration ($[\text{DIC}] = 25.0 \text{ mM}$) and most depleted isotopic composition ($\delta^{13}\text{C}_{\text{DIC}} = +0.45\text{‰}$). These values are out of equilibrium with atmospheric values expected for T, S, and pH values for the ground water pool ($[\text{DIC}] = 1.34 \text{ mM}$ and $\delta^{13}\text{C}_{\text{DIC}} = +1\text{‰}$) calculated using the model of Zeebe and Wolf-Gladrow (2001). DIC concentrations decreased ($[\text{DIC}]$ as low as 1.6 mM) and became highly enriched isotopically ($\delta^{13}\text{C}_{\text{DIC}}$ up to +15.06‰) moving away from the groundwater pool towards the lake.

5. Discussion

5.1 Controls on the Isotopic and Geochemical Variability of Laguna Negra Waters

The isotopic and geochemical trends of waters as they evolve across the stromatolite belt can provide insight the processes driving their evolution. Input of water into the lake has previously been recognized to be primarily sourced from groundwater inlets with possible contribution from stream water inlets sourced from snowmelt (Gomez et al., 2014). While discharge rates for the groundwater springs and stream inlets are not known, our results are consistent with groundwater inlets being the primary source of water into the lake as there are clear geochemical and isotopic trends from the groundwater inlets outwards towards the lake body (Figure 3). In contrast, the influence of the stream water input on geochemical and isotopic compositions of waters in the stromatolite belt showed comparatively limited influence. Stream input waters were more saline, DIC rich, and isotopically enriched than expected for meteoric waters likely resulting from mixing with already evolved lake waters due to winds oriented upstream of the inlet source at the time of sampling. While this input may have local effects on the geochemical and isotopic compositions of waters near the input their overall effects on the trends observed across the stromatolite belt are limited compared to the influence of groundwater at least during the time of our sampling (late austral summer). Accordingly, the influence of these streams was assumed to be negligible in the following calculations and modelling, however it is recognized that it may be a more important influence seasonally.

The isotopic values of water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$) closer to the zone of groundwater recharge are relatively depleted and become progressively enriched moving outwards towards the lakes indicating progressive loss of the light isotope as input waters evolve across the stromatolite belt. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ strongly co-vary ($R^2 = 0.97$) across the lake edge along a trendline with a slope of 4.4 (Figure 4). These values are enriched relative to the isotopic compositions of meteoric waters in the region and project along trendline projects off of the local meteoric water line (Figure 4; Scheihing et al., 2017), which is characteristic of isotopic enrichment of waters driven by evaporation (Criss, 1999). This evaporative trend is also evident in the increase of electrical conductivity observed moving outwards into the lake, which covaries ($R^2 = 0.68$) with changes in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (Supplemental Figure 3).

The evaporative trend seen in water isotopes predicts an increase in DIC concentration from groundwater source outwards into the lake if evaporation is also the only control of DIC dynamics at Laguna Negra (i.e. only water is lost with no other associated processes such as

degassing occurring). Conversely, DIC concentrations decrease as water moves from the groundwater input into the lake. Thus, other processes must be responsible for carbon cycle dynamics at Laguna Negra in addition to evaporation. Degassing, carbonate precipitation, photosynthesis, and methanogenesis have all been observed or hypothesized to drive the loss of DIC at Laguna Negra and other similar hypersaline lakes (Valero-Garcés et al., 1999; Gomez et al., 2014; Birgel et al., 2015).

To determine the relative importance of these processes to DIC removal at Laguna Negra we developed a conceptual box model to probe the potential controls on the evolution of the carbonate system from the groundwater source to lake waters (Figure 5). In this model, groundwater is input into the lake and evolves to reach the lake water values through some combination of degassing, carbonate precipitation, and biological processes (photosynthesis and/or methanogenesis). Each of these processes drive associated changes in the [DIC], carbonate alkalinity, and $\delta^{13}\text{C}_{\text{DIC}}$ of lake waters as they evolve. To determine how these processes could combine to drive the evolution of groundwater inputs into lake body waters we compared the measured evolution of these parameters across the stromatolite belt with those expected from these various processes. Specifically, we sought to determine whether the observed trends can be explained abiotically or if they require a biological mechanism for their formation.

The concomitant changes in alkalinity associated with changes in DIC concentrations can be used to constrain the processes responsible for DIC removal at Laguna Negra. DIC and carbonate alkalinity strongly co-vary ($R^2 = 0.99$) along a line with a slope of 1.27 (Supplemental Figure 4; 95% CI [1.19, 1.34]). Degassing, photosynthesis, and methanogenesis each remove DIC without changing alkalinity while carbonate precipitation causes a decrease of two moles of alkalinity for each mole of DIC removed (Zeebe and Wolf-Gladrow, 2001). Therefore, the relative change in alkalinity vs. DIC can be used to determine the fraction of DIC removal by carbonate precipitation versus other processes. It should be noted that photosynthesis and methanogenesis cause a slight increase in alkalinity due to nutrient uptake, however given the large size of the DIC pool at Laguna Negra, the effect of this uptake on alkalinity is small and was not parameterized in this model (Zeebe and Wolf-Gladrow, 2001). Similarly, heterotrophic metabolisms may also increase DIC and alkalinity through remineralization of organic matter (Soetaert et al., 2007). However, the large decrease in DIC and alkalinity across the stromatolite belt indicates that processes removing DIC operate at substantially faster rates than these processes, thus heterotrophic processes are not included in our calculations. The fraction of DIC lost to carbonate precipitation (f_{cp}) necessary to explain the loss of alkalinity can be calculated following a method modified from that of Barkan et al. (2001). This can be calculated using the equation:

$$f_{\text{cp}} = \frac{\text{CA}_{\text{Exp}} - \text{CA}_{\text{Meas}}}{2(\text{DIC}_{\text{Exp}} - \text{DIC}_{\text{Meas}})}$$

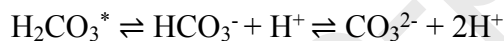
where CA_{meas} and DIC_{meas} are the measured concentrations of carbonate alkalinity and DIC for a water. CA_{Exp} and DIC_{Exp} are the concentrations of carbonate alkalinity and DIC expected for a water based on evaporation alone and are defined:

$$\text{CA}_{\text{Exp}} = \frac{\text{CA}_{\text{Initial}}}{(1 - f_{\text{Evap}})}$$

$$\text{DIC}_{\text{Exp}} = \frac{\text{DIC}_{\text{Initial}}}{(1 - f_{\text{Evap}})}$$

where $\text{CA}_{\text{Initial}}$ and $\text{DIC}_{\text{Initial}}$ are the concentrations of carbonate alkalinity and DIC of the initial groundwater input and f_{Evap} is the fraction of water removed due to evaporation.

Using this approach, we calculated f_{cp} across the stromatolite belt to assess the amount of DIC loss that can be attributed to carbonate precipitation. In this scenario, $\text{DIC}_{\text{Initial}}$ and $\text{CA}_{\text{Initial}}$ were defined as LN-003 (inlet water sample) and DIC_{Meas} and CA_{Meas} were defined as LN-011 (the sampling point with the lowest concentration of DIC). f_{Evap} was calculated for Laguna Negra as the percentage of water needed to evaporate to account for the change in salinity assuming evaporation is the only control on salinity yielding a value of 0.94 from ground water pool (LN-003) to lake water (LN-011). The calculated value of f_{Evap} is most likely an underestimation, because mineral precipitation is decreasing salinity by removing ions from solution. To account for any error in f_{Evap} values of 0.8 to 0.99 were utilized for our calculation of CA_{Exp} and DIC_{Exp} . Calculation of f_{cp} with these parameters yields a value of 0.61 (± 0.1 for different values of f_{Evap}) meaning that 61% $\pm 1\%$ of the DIC loss at Laguna Negra overall can be attributed to carbonate precipitation. DIC removal by carbonate precipitation also predicts a decrease in pH as the removal of CO_3^{2-} shifts the carbonate equilibrium towards CO_3^{2-} liberating H^+ :



Thus, DIC removal primarily through carbonate precipitation at Laguna Negra also accounts for the decrease in pH moving outwards towards the lake from the groundwater ponds.

Similarly, the fractionation factor associated with the isotopic evolution of DIC can provide insight into the processes driving its removal. The processes likely to be controlling the evolution of DIC at Laguna Negra, carbonate precipitation, degassing, photosynthesis, and methanogenesis each contain distinct fractionations allowing them to be used as a fingerprint for their respective process on the isotopic evolution of Laguna Negra waters (Zhang et al., 1995; Botz et al., 1996; Hayes, 2001). The total fractionation factor associated with DIC removal was calculated using a Rayleigh fractionation model for the evolution of DIC and $\delta^{13}\text{C}_{\text{DIC}}$ in this system. In the Rayleigh model, the fractionation of (ϵ) is approximately equal to the slope of the regression between the natural log of the fraction of DIC remaining in the system (f) versus the isotopic composition of the DIC. Ordinary least squares regression for values recorded at Laguna Negra yields a slope of 3.9 ($R^2=0.41$, 95% CI [-1.2, 6.6], $p = 0.007$; Figure 6). Therefore, for Laguna Negra waters as DIC is removed from the system the isotopic composition of the remaining pool increases with a fractionation factor (ϵ_{LN}) of $\sim 3.9\text{‰}$ (95% C.I. [-1.2‰, 6.6‰]).

Since the amount of DIC lost from calcite precipitation (f_{cp}) and its associated fractionation (ϵ_{cp}) are known (Romanek et al., 1992), the fractionation of DIC from processes other than calcite precipitation (ϵ_{other}) can be calculated using a mass balance approach using the equation:

$$\epsilon_{\text{other}} = \frac{\epsilon_{\text{LN}} - \epsilon_{\text{cp}} * f_{\text{cp}}}{1 - f_{\text{cp}}}$$

This approach yields a combined fractionation factor of 11.3‰ for processes other than calcite precipitation that remove DIC at Laguna Negra. This is higher than the equilibrium fractionation factor expected for degassing across the range of temperatures measured during our sampling is

8.2 to 10.2‰ (Zhang et al., 1995). However, fractionation factors of up to 19.4‰ have been obtained during evaporation of Dead Sea waters that have been attributed to non-equilibrium gas-transfer kinetic fractionations (Stiller et al., 1985). Given the high concentrations of DIC and degree of evaporation occurring it is reasonable to expect similar kinetic fractionations from degassing at Laguna Negra could be driving fractionations above the equilibrium value. Large fluxes of DIC from degassing are also consistent with DIC removal primarily through carbonate precipitation, because carbonate precipitation generates one mole of CO₂ for every mole of carbonate precipitated. Degassing driven through carbonate precipitation has been observed previously in the Dead Sea (Barkan et al., 2001; Golan et al., 2017). Therefore, the evolution of DIC at Laguna Negra can be explained through the abiotic processes of degassing and carbonate precipitation alone.

It should be noted that this observation does not rule out a role for biological processes in the removal and isotopic evolution of DIC at Laguna Negra. For instance, photosynthetic algae, which have been observed to be the dominant primary producers at Laguna Negra, can account for this change as they typically produce fractionations of ~17-30‰ (Fry, 1996). Methanogenesis also produces very large fractionations (up to ~80‰) and could also play a role in producing large carbon isotopic enrichments as has been suggested in similar systems (Talbot and Kelts, 1990; Botz et al., 1996; Birgel et al., 2015). However, it does demonstrate that the highly enriched carbon isotope values of waters at Laguna Negra do not require a biological mechanism for their formation.

5.2 Interpreting the Carbonate Isotopic Record at Laguna Negra

The processes controlling the isotopic evolution of Laguna Negra's waters provide a framework for interpreting the isotopic signals preserved in calcite structures at the lake. While the isotopic composition of carbon and oxygen in calcite largely reflect the isotopic composition of the water from which they precipitated additional fractionation also occurs during precipitation that can vary in magnitude due to physicochemical conditions (Zeebe and Wolf-Gladrow, 2001). To account for these fractionations and enable more direct comparison to values measured previously from oncoids and laminar crusts at Laguna Negra the isotopic values of carbon and oxygen were modeled for a calcite precipitated in equilibrium with waters measured in this study. The modeled isotopic values of carbon and oxygen of a theoretical calcite mineral ($\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{18}\text{O}_{\text{TC}}$) follow the same trends observed from the waters directly (Figure 7). This implies that the isotopic evolution of the lake's waters spatially should be preserved in the isotopic composition of calcite structures across the lake edge. The values of $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{18}\text{O}_{\text{TC}}$ co-vary ($R^2 = 0.76$) along a trendline with a slope of 1.15 (95% CI [0.87, 1.51]) by reduced major axis regression. This covariance is characteristic of closed-basin lakes and reflects the dual effects of physical and biological processes on the isotopic evolution of lake waters as described above (Talbot, 1990; Li and Ku, 1997).

Isotopic values measured from carbonate minerals at Laguna Negra ($\delta^{13}\text{C}_{\text{MC}}$ and $\delta^{18}\text{O}_{\text{MC}}$) by Buongiorno et al. (2018) display similar co-variant trends to those of the modeled values from lake water (Figure 8). Considering the complete isotopic dataset of all oncoids and laminar crusts together shows that the isotopic values co-vary along a trendline of the same slope ($m = 1.15$; 95% C.I. [1.05, 1.26]) by reduced major axis regression to that of the theoretical carbonate values, but their covariance is weaker ($R^2 = 0.50$). It should be noted that the range of isotopic compositions measured from carbonate minerals is more limited relative to the range of modeled

isotopic values. This disparity could be a result of the fact oncoids and laminar crusts are unevenly distributed spatially across the stromatolite belt, with laminar crusts occurring towards the northwestern corner of the stromatolite belt and oncoids located in the central to northeastern portion, which could restrict the possible range these structures may record (Gomez et al., 2014). Similarly, this disparity could be an artefact of the more limited spatial distribution of sample locations for carbonates in Buongiorno et al. (2018) compared to this study. In any case, the similar slope of the trendline for $\delta^{18}\text{O}_{\text{TC}}$ versus $\delta^{13}\text{C}_{\text{TC}}$ and $\delta^{18}\text{O}_{\text{MC}}$ versus $\delta^{13}\text{C}_{\text{MC}}$ suggests that the isotopic trends observed in the complete dataset of oncoids and laminar crusts preserve the trends of the isotopic evolution of lake waters spatially across the microbialite belt. Thus, the enrichment of ^{13}C and ^{18}O in carbonate minerals from Laguna Negra is also the result of the abiotic processes driving enrichment of the water.

The slope of the trendline of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ for individual structures is variable from the slope of the trend for theoretical calcite and the completed measured calcite dataset (Buongiorno et al., 2019). This implies that the isotopic variability within individual structures records localized changes in isotopic composition temporally rather than the overall spatial evolution trend seen in the theoretical and complete measured dataset. Therefore, individual structures should preserve a record of local environmental change, and supports the use of microbialites as time-series records of environmental evolution in Laguna Negra and other environments (Nehza et al., 2009; Frantz et al., 2014; Petryshyn et al., 2016). However, while the trends in the isotopic value record the temporal evolution of environmental conditions the absolute values rely primarily on the spatial evolution of lake waters. Analysis of values of the complete dataset alongside values from individual structures is necessary to correctly interpret the meaning of isotopic values in terms of both spatial and temporal dynamics.

The laminated nature of oncoids, which have previously been U/Th dated to an age of 2442 ± 252 years before present, preserve a time series of carbonate precipitation at the lake (Gomez et al., 2014). Therefore, the equivalence of slopes between measured carbonate isotopic values and those modeled for conditions during our study suggests that the environmental conditions observed in our study have persisted or at least recurred throughout this time. If the environmental conditions are not persistent and recur at specific time scales this could provide insight into the timescales at which carbonates precipitate. Additional work investigating the variability of lake conditions over different time scales (i.e. daily, seasonally, yearly) would enhance our ability to understand the isotopic record preserved in Laguna Negra carbonates.

5.3 Implications for Interpreting Microbialite Biogenicity

Microbialites constitute one of the oldest and most complete records of life on Earth making them valuable tools for understanding the co-evolution of life and the environment through geologic time (Riding, 2000; Peters et al., 2017). The identification of microbialites is commonly based upon morphological lines of evidence, however morphologically similar structures may also be formed through entirely abiotic processes complicating their interpretation (Buick et al., 1981; Grotzinger and Rothman, 1996). Distinguishing microbialites from these abiotic mimics is crucial for our ability use microbialites as biosignatures in the geologic record. This is particularly significant for the most ancient examples which are among the oldest evidence of life on Earth, but whose biological origin is controversial (Allwood et al., 2006; Nutman et al., 2016; Allwood et al., 2018). Likewise, being able to assess the biogenicity of alleged microbialites is critical for their use as a target in astrobiological investigations (Cady et

al., 2003; Des Marais et al., 2008). Identifying additional lines of evidence of biological activity associated with the formation of a potential microbialites is thus necessary to enable more confident assessment of its biogenicity (Grotzinger and Knoll, 1999).

Enriched carbon isotopic signatures in carbonate minerals may be generated as result of microbial processes, and the presence of these enrichments have been used as evidence of microbial activity, and even specific metabolisms, in both ancient and modern microbialites (Brady et al., 2010; Birgel et al., 2015; Nutman et al., 2016). However, the carbon isotopic signatures generated through biological activity are non-unique and may also be generated through abiotic processes (Clark and Lauriol, 1992; Sumner, 2001; L veill  et al., 2007). The results of this study demonstrate this point as the highly enriched carbon isotopic compositions occurring in Laguna Negra's carbonates formed through abiotic processes. The isotopic enrichments observed in Laguna Negra are unique from those found in other settings because while the enrichments are abiotic in origin they occur within microbialites of demonstrable biogenicity (Gomez et al., 2014). Therefore, similarly large fractionations associated with possible microbialites should not necessarily be taken as evidence of biological activity, particularly if there is evidence for formation in an evaporative setting or the depositional setting is ambiguous.

5.4 Implications for the Geologic Carbon Isotopic Record

The carbon isotopic composition of carbonate minerals preserved in the geologic record is frequently utilized as a tool to understand variability in the global carbon cycle through Earth's history (Kump and Arthur, 1999; Bartley and Kah, 2004). However, these isotopic compositions may also reflect local environmental conditions complicating their interpretation (Melezhik et al., 1999). Developing a more robust understanding of the processes that drive localized enrichment in carbon isotopes in modern settings is necessary in order to better interpret local versus global effects in the geologic record. Our results show that at Laguna Negra degassing driven by evaporation and precipitation of carbonate minerals drives isotopic enrichments of $\delta^{13}\text{C}_{\text{DIC}}$ up to $\sim +15\%$, and that these enrichments are in turn recorded in the carbonate minerals precipitated from the lake. Additionally, the degree of isotopic enrichment increases across the stromatolite belt in relation to the distance from the source, which as the lake evolves through time could be preserved as a stratigraphic isotope excursion. While the spatiotemporal extent of carbonate precipitation at Laguna Negra is limited, larger scale and longer lived evaporative basins are common throughout the geologic record where similar processes were operating and could in principle drive isotopic enrichments (Schreiber et al., 2007).

The magnitude of the carbon isotopic enrichments found at Laguna Negra are particularly noteworthy because they are comparable to the most highly enriched values found in the geologic record, the Paleoproterozoic Lomagundi carbon isotopic excursions (Schidlowski et al., 1976; Bekker, 2014). The Lomagundi isotopic excursions are observed globally and have thus been interpreted to reflect global scale changes in biogeochemical processes, however the excursions have also been suggested to have been generated or enhanced due to isotopic enrichment driven by local and/or diagenetic processes (Melezhik and Fallick, 1996; Hayes and Waldbauer, 2006; Planavsky et al., 2012). Many of the geologic units containing the Lomagundi excursion were deposited in restricted basins and contain stromatolites, and environmental processes such as evaporation or biological activity have been suggested as possible drivers of localized isotopic enrichment (Melezhik et al., 1999; Melezhik et al., 2005). Laguna Negra

provides a comparable modern analog to study how these processes may combine to drive positive carbon isotopic excursions, and our results are consistent with the possibility of a local origin or enhancement of the Lomagundi excursion. Our work indicates that even the most extreme isotopic enrichments observed in the geologic record can be generated through a combination of the abiotic processes of evaporation, degassing, and carbonate precipitation. Despite the occurrence of these isotopic enrichments within microbialites and associated facies these signatures can be explained without a biological origin. Thus, the occurrence of the Lomagundi excursion within microbialites does not necessarily imply a biological role in the formation of the carbon isotope enrichments. These results emphasize that local physicochemical processes should be considered when interpreting the meaning of enriched carbon isotopic compositions in carbonates from the geologic record, particularly when there is evidence for deposition in an evaporative basin. Additionally, our work suggests that the information that can be gained from isotopic studies of carbonates is dependent upon the sampling technique employed (i.e. lateral versus stratigraphic sampling). Analysis of the isotopic composition of carbonate minerals across a stratigraphic section may provide insight into the temporal evolution of environmental, ecological, or hydrological conditions through time at that location. In addition, investigation of the isotopic variability laterally between contemporaneously deposited facies allows us to provide insight into spatially variable processes within the depositional environment. The difference in information gained between sampling techniques highlights the need for measurement of lateral variability in isotopes of a single bed in addition to measurements vertically along a stratigraphic column (e.g. da Silva and Boulvain, 2008; Metzger and Fike, 2013; Kläbe et al., 2018). Together this data will enable a more complete understanding of the spatial and temporal evolution of the processes that control the isotopic signatures and ensure that isotopic trends are more properly interpreted.

6. Conclusions

The isotopic composition of dissolved inorganic carbon and oxygen in water can record information about microbial, geochemical, and hydrological processes, which can in turn be recorded in carbonate minerals precipitating from the water. We analyzed the spatial variability in the isotopic composition of lake waters at Laguna Negra and their relationship to the isotopic values preserved in carbonate minerals from the lake. Our results demonstrate that in Laguna Negra's carbonates oxygen isotopic enrichment is due solely to evaporation, while carbon isotopic enrichment results can be explained by the combined effects of carbonate precipitation and degassing. Therefore, despite their association with microbialites the isotopic signatures preserved at Laguna Negra can be explained without a biological mechanism. Additionally, agreement between previously measured carbonate isotopic values and those modelled for carbonates formed under the conditions of this study suggest that the environmental conditions found at the lake today have been persistent, or at least recurrent, over the history of carbonate deposition at the lake.

These results imply that similarly large fractionations found in the rock record or on other planets associated with possible microbialites should therefore not necessarily be interpreted as biological in origin and should not be used as evidence for biogenicity of the structures. Constraining the depositional environment and analyzing several contemporaneously deposited facies within a microbialite forming environment is necessary to fully understand the processes responsible for the isotopic values preserved in microbialites and associated abiogenic

carbonates. Placing the isotopic values measured in microbialites in the rock record in the proper context of their depositional environment may be able to provide spatiotemporal information about the evolution of the system in which they were formed and enable more robust interpretation of their meaning.

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Declarations of interest: None

Figure Captions

Figure 1: Aerial view of Laguna Negra indicating location of the microbialite belt where carbonate formation including microbialites and abiogenic carbonates form in a zone of input of more dilute water. Base image from ArcGIS World Imagery.

Figure 2: Generalized schematic cross section of changes in the depositional environment from the groundwater input to hypersaline lake body at Laguna Negra.

Figure 3: Spatial variability of geochemical and isotopic parameters across the stromatolite belt at Laguna Negra. Values are interpolated for the entire belt from measurements taken across the lake edge (black dots). In general, waters become more saline, acidic, DIC poor, and isotopically enriched moving away from the groundwater input source.

Figure 4: Measured isotopic values of oxygen and hydrogen from Laguna Negra water (grey points). Isotopic values follow a linear trend (grey dashed line) from the local meteoric water line (black line; Scheibling et al. 2017) implying evaporation is the primary control of the isotopic evolution of oxygen and hydrogen in water.

Figure 5: Box model used to investigate the processes that controlling the carbonate system at Laguna Negra. Groundwater is input into the lake and evolves into lake water through a combination of evaporation, degassing, biological processes, and carbonate precipitation. Outputs are described in terms of their effects on DIC concentration, carbonate alkalinity, and the isotopic composition as either increasing (\uparrow), decreasing (\downarrow), or no change (-)

Figure 6: Regression of $\ln(f)$ (the natural log of the fraction of DIC remaining) vs. $\delta^{13}\text{C}_{\text{DIC}}$ for measured lake waters used to calculate the fractionation factors of lake waters (ϵ_{LN}). Black line is OLS regression with grey bars representing the 95% confidence interval. The slope of the regression is 3.9 ($R^2=0.41$, 95% CI [1.2, 6.6], $p = 0.007$).

Figure 7: Spatial variability of modeled $\delta^{13}\text{C}_{\text{Calcite}}$ and $\delta^{18}\text{O}_{\text{Calcite}}$ formed in equilibrium with water measured in this study. Maps are interpolated from measured values (black dots).

Figure 8: Comparison of modeled values for carbon and oxygen isotope values from a calcite formed in equilibrium with water measured in this study (closed squares) to those measured previously from oncoids and laminar crusts in Buongiorno et al. (2018).

Supplemental Figure 1: Locations sampled for geochemical and isotopic compositions in the stromatolite belt. Base image from ArcMap World Imagery.

Supplemental Figure 2: Variability in speciation of the carbonate system calculated using the equilibrium constants of Mehrbach et al. (1973), which accounts for temperature changes but not salinity changes, compared to those calculated using the Sass and Ben-Yaakov constants, which accounts for salinity but not temperature changes across the range of pH at Laguna Negra. These results indicate that salinity effects are substantially larger than temperature effects and supports use of the Sass and Ben-Yaakov constants to calculate carbonate speciation.

Supplemental Figure 3: Relationship between electrical conductivity and $\delta^{18}\text{O}$ across the stromatolite belt. Values co-vary ($R^2 = 0.68$) consistent with evaporation driving isotopic enrichment at Laguna Negra.

Supplemental Figure 4: Relationship between [DIC] and carbonate alkalinity at Laguna Negra. Values co-vary ($R^2 = 0.99$) along line with a slope of 1.27.

Table 1: Geochemical parameters measured across the stromatolite belt. Dashes indicate locations where data was not collected for that location.

Sample	pH	Temperature (°Celsius)	Conductivity (mS/m)	Salinity (ppt)	[DIC] (mM)	Carbonate Alkalinity (meq/L)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰, V-PDB)	$\delta^2\text{H}_{\text{H}_2\text{O}}$ (‰, V-SMOW)	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰, V-SMOW)	Water Depth (mm)
LN-003	7.92	19.2	17.2	15.8	25.0	30.6	0.45	-34.0	-3.15	150
LN-004	8.12	20.7	19.0	17.7	19.8	26.4	5.55	-22.5	-0.86	9
LN-005	8.15	17.9	13.7	12.3	17.5	23.2	4.29	-30.3	-2.47	5
LN-006	7.93	16.5	31.6	32.5	8.8	11.3	11.6	-9.5	1.72	16
LN-007	7.72	16.7	43.1	47.1	6.6	8.2	10.9	-13.6	0.43	12
LN-007b	7.82	17.7	45.7	50.4	5.1	6.6	9.73	-15.7	-0.12	12
LN-008	7.43	13.8	35.2	37.5	-	-	-	-43.9	-5.64	30
LN-008b	7.39	18.1	34.7	36.3	4.7	5.1	3.43	-42.9	-5.35	15
LN-009	7.14	3.1	115.4	236	3.6	6.3	3.79	-26.3	-1.18	5
LN-010	7.04	10.1	169.0	338	3.2	6.2	13.9	10.8	7.11	1
LN-011	7.18	16.7	157.6	315	1.6	3.1	15.1	10.9	7.02	18
LN-011b	6.99	21.5	176.5	353	-	-	-	21.0	8.61	11
LN-012	7.62	15.9	71.6	92.7	5.9	8.2	10.4	-14.2	0.56	10
LN-013	7.93	16.6	28.9	29.2	8.1	10.3	4.21	-41.6	-4.64	8
LN-014	7.35	20.0	90.1	133	16.5	23.1	7.59	-17.5	0.53	5
LN-015	7.68	21.7	51.1	57.0	7.0	8.8	2.62	-29.3	-1.18	30
LN-016	7.87	17.8	61.5	75.1	-	-	-	-	-	5
LN-017	7.92	18.4	39.6	42.7	5.7	7.6	13.5	3.0	4.28	5
LN-018	6.76	22.0	189.9	380	2.0	3.9	15.1	7.6	8.21	4

Supplemental Table 1: Metadata for locations sampled across the stromatolite belt

Sample	Location Tyoe	Easting	Northing	Date	Time
LN-003	Groundwater Input	545083	6961624	March 6, 2017	15:37
LN-004	Stromatolite Belt	544944	6941652	March 6, 2017	16:15
LN-005	Stromatolite Belt	544867	6941619	March 6, 2017	16:50
LN-006	Stromatolite Belt	544832	6941691	March 6, 2017	17:14
LN-007	Stromatolite Belt	544846	6941787	March 6, 2017	17:40
LN-007b	Stromatolite Belt	544846	6941787	March 7, 2017	13:25
LN-008	Stromatolite Belt	544963	6941722	March 6, 2017	18:05
LN-008b	Stromatolite Belt	544963	6941722	March 7, 2017	13:15
LN-009	Stromatolite Belt	545113	6942057	March 7, 2017	9:10
LN-010	Stromatolite Belt	545074	6942051	March 7, 2017	9:45

LN-011	Stromatolite Belt	545067	6941984	March 7, 2017	11:12
LN-011b	Stromatolite Belt	545067	6941984	March 7, 2017	16:11
LN-012	Stromatolite Belt	545021	6941910	March 7, 2017	11:45
LN-013	Stromatolite Belt	545042	6941830	March 7, 2017	12:12
LN-014	Stromatolite Belt	545109	6941921	March 7, 2017	13:48
LN-015	Stream Inlet	543761	6941186	March 7, 2017	14:55
LN-016	Stromatolite Belt	544085	6941239	March 7, 2017	15:14
LN-017	Stromatolite Belt	544076	6941435	March 7, 2017	15:30
LN-018	Stromatolite Belt	545142	6942074	March 7, 2017	15:56

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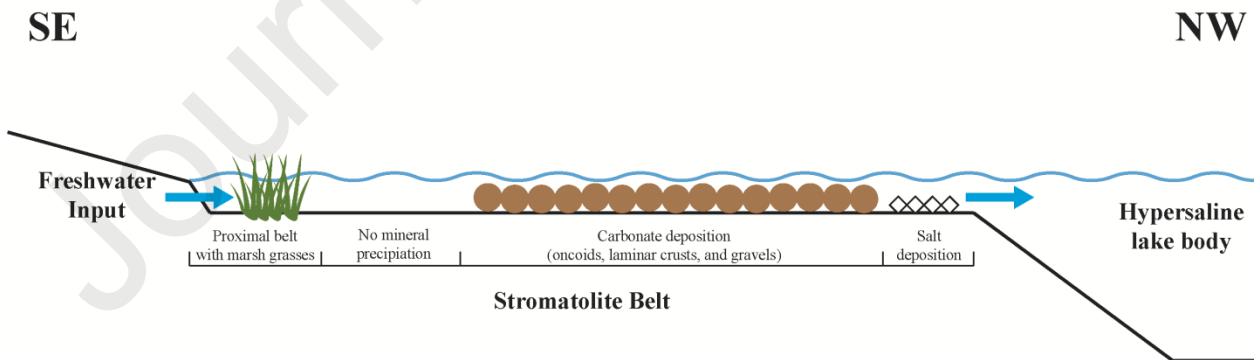
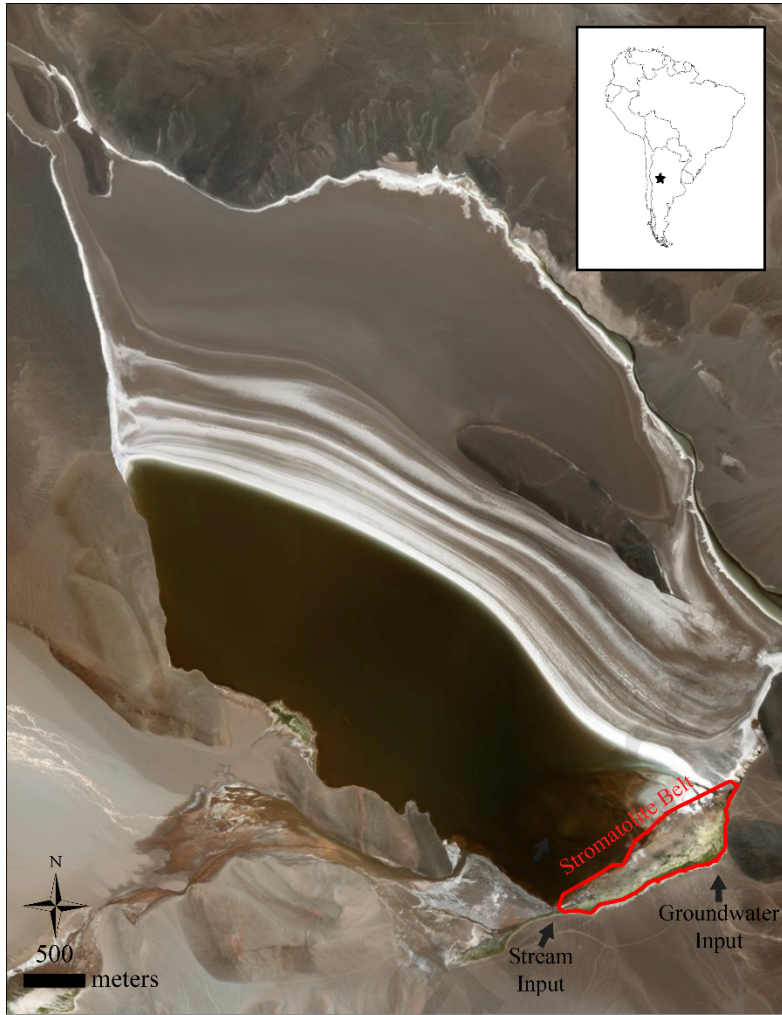
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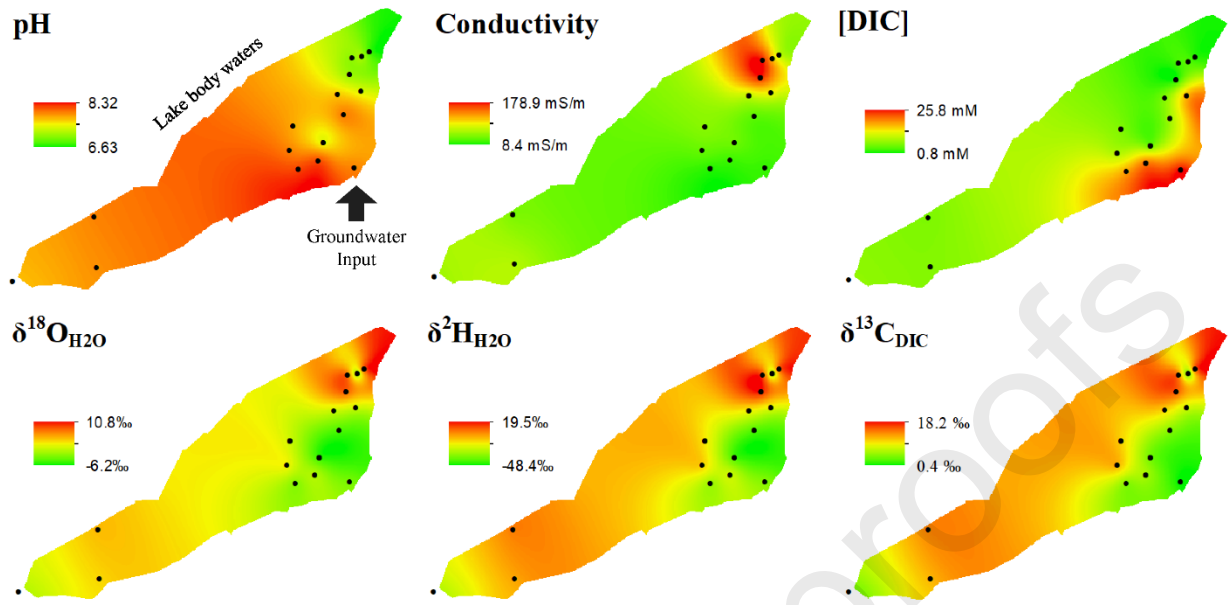
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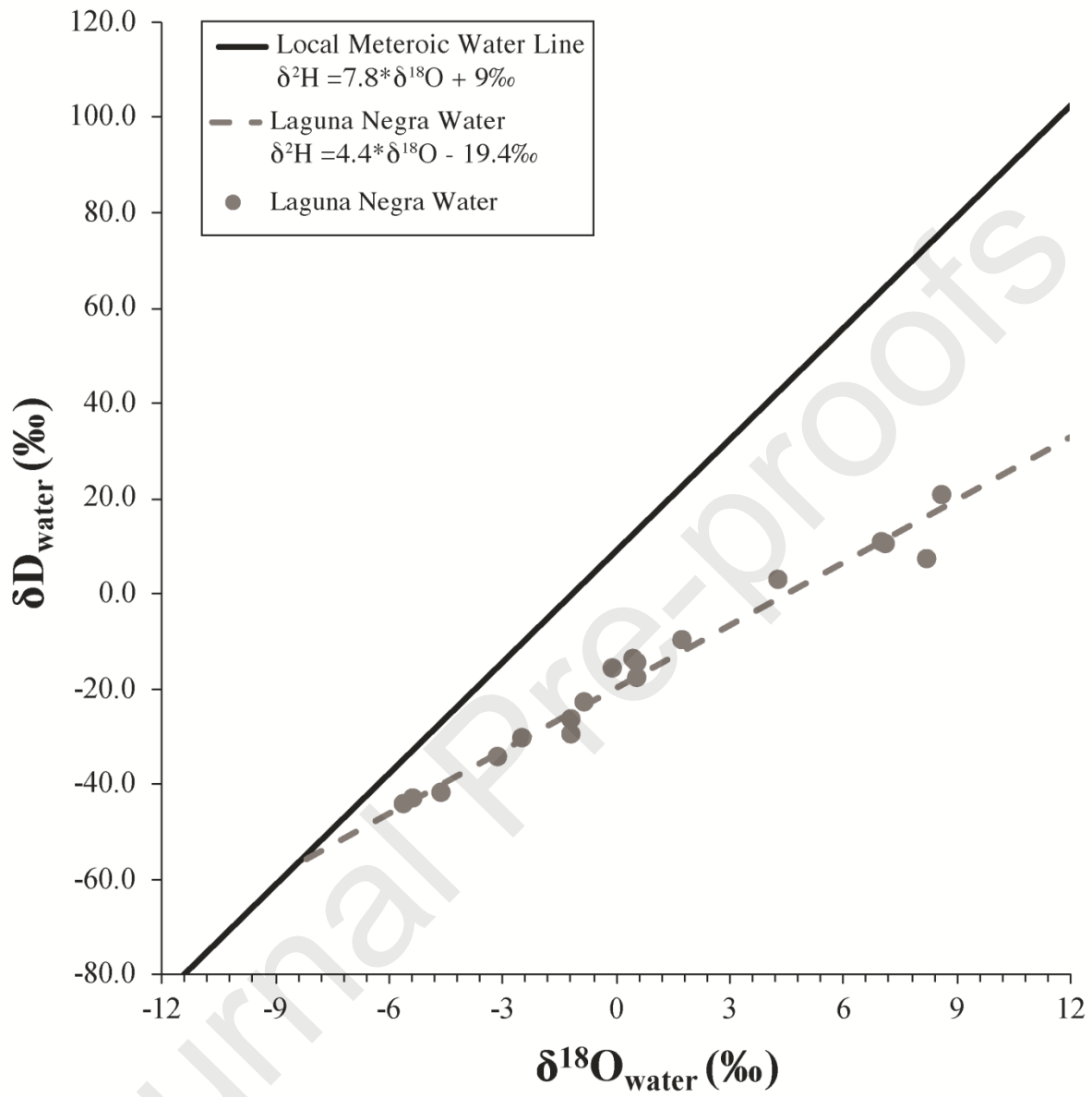
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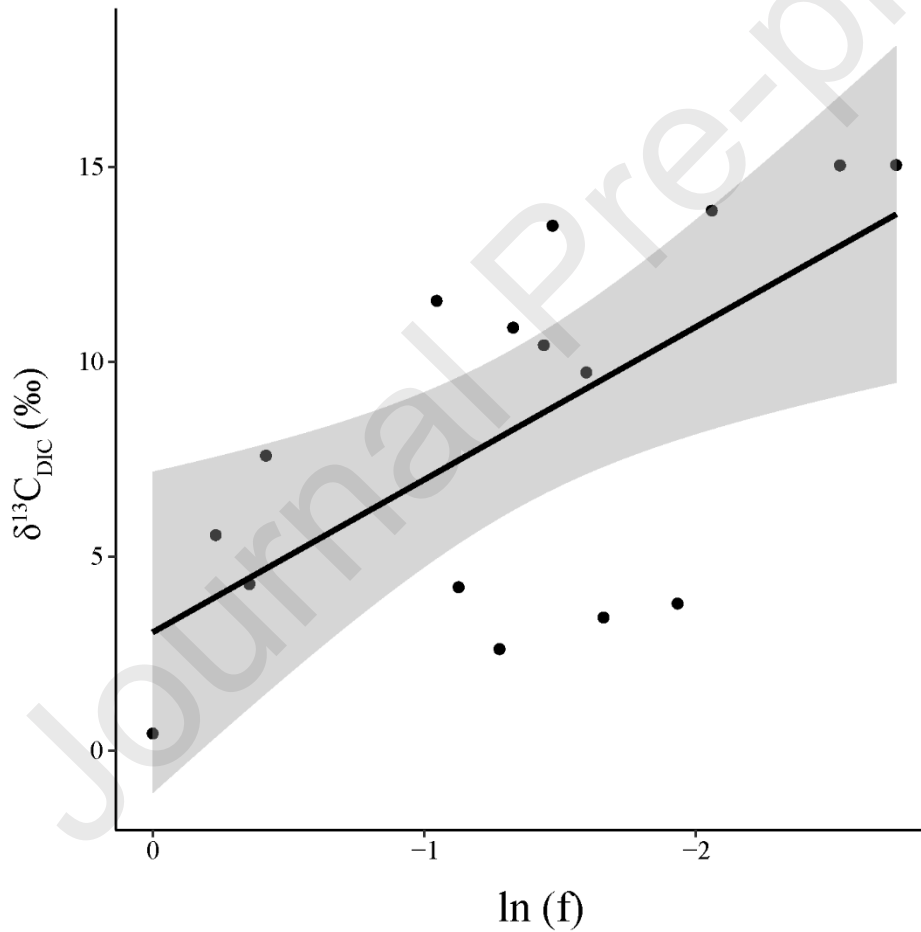
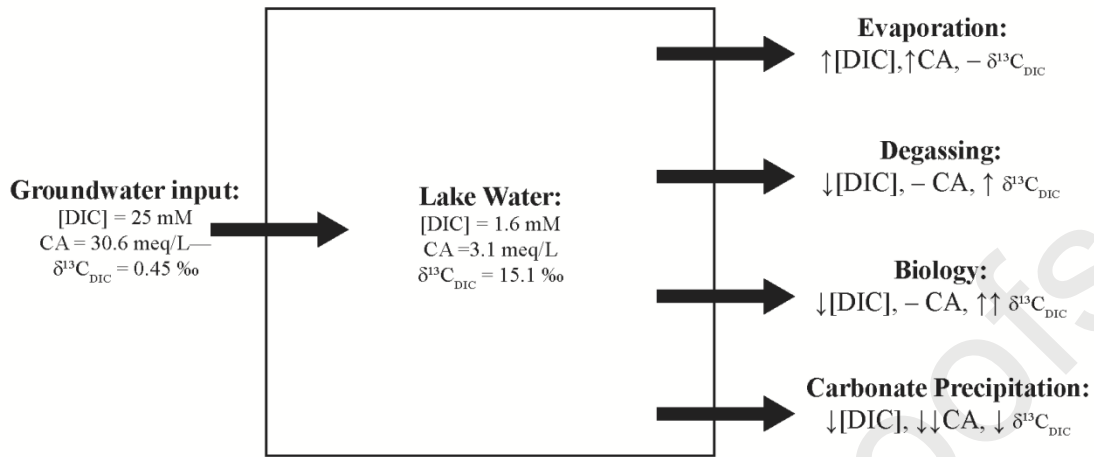
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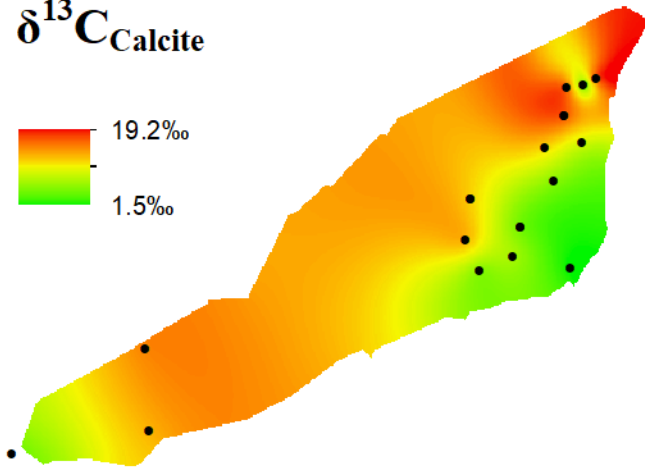
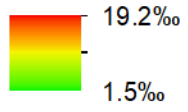
Journal Pre-proofs









$\delta^{13}\text{C}_{\text{Calcite}}$  $\delta^{18}\text{O}_{\text{Calcite}}$ 