Chapter 19

The carbonate system in hypersaline lakes: the Laguna Negra case (Puna of Catamarca, Argentina)

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19.1 Abstract

Carbonate precipitation in hypersaline lakes is controlled by a combination of physicochemical as well as microbiological processes. These processes are recorded, at least partially, in the textural and chemical signatures preserved in the resulting carbonates. Unravelling these controls is important to have a better understanding of environmental (e.g. climate, local hydrology and sedimentology) and biogeochemical (e.g. carbon cycling, microbe-mineral interactions) signatures there preserved, and helps to improve our understanding of environmental evolution preserved in recent and ancient sedimentary carbonates.

Here a review of data about the carbonate system in the Laguna Negra is done. The Laguna Negra is a hypersaline lake in the Altiplano-Puna region of northwest Argentina, where an extensive and active microbialites system has developed for at least $\sim 2442 \pm 252$ years. Some first-order controls in carbonate precipitation are discussed and some comparisons with available data of other lakes in the region are made.

19.2 Introduction

Lacustrine sedimentary carbonates are an excellent record of environmental and climate conditions during carbonate deposition (Alonzo-Zarza and Tanner, 2010a and 2010b; Frantz et al., 2014; Petryshyn et al., 2016). Physico-chemical processes as well as microbiological activity can trigger carbonate precipitation and dissolution by controlling pH, alkalinity and the availability of ions and carbon species (for example Ca^{+2} and CO_3^{-2}) (Visscher and Stolz, 2005; Arp et al., 2001) and that have impact on calcite and aragonite chemical equilibrium (Morse et al., 2007). In addition, extreme changes in environmental factors, like salinity and temperature, which are particularly important in the Laguna Negra and other systems in the Puna region, have a significant influence by controlling the equilibrium constants involved in the equilibrium reactions of the carbonate system (Saas and Ben Yaakov, 1970; Weiss, 1974, for a review see Zeebe and Wolf-Gladrow, 2001; Mucci, 1983). Here available hydrochemical data of the Laguna Negra (from Gomez et al., 2014) are compiled as well as of other lakes in the Chile, Bolivia and Argentina region to make some comparisons. The compiled data and references can be seen in Table 1, which is a file presented as a supporting online material in GitHub, <https://github.com/FernandoJGomez/Gomez-et-al.-2019-Elsevier-Book-Puna>), together with the **Jupyter notebooks** that make most plots of this contribution.

The Laguna Negra is a shallow (≤ 2 m) hypersaline lake located at 4200 meters above sea-level. The high-altitude, hot and dry climate (with a strongly negative water balance) combine to favor the precipitation of evaporites (halite, gypsum, calcite, etc) and produce

favorable conditions for the development of microbial mats where abundant carbonate precipitation takes place, particularly in the mixing zone between groundwater springs and the main lake waters. For details about microbial biodiversity as well as textural and geochemical aspects of these carbonates see Gomez et al., (2014, 2018); Mlewski et al., (2018); Buongiorno et al., (2018); Shalygyn et al., (2018), Boidi et al., (2019, this volume). Beeler et al (in press) provide further details regarding the Laguna Negra hydrochemistry and water isotope signature. Here we focus on discussing some relevant aspect regarding the carbonate system in the Laguna Negra and similar lakes in the region.

The carbonate system parameters are calculated by using published information of these hypersaline systems. References that provide the necessary data to calculate the carbonate system parameters (cf. Zeebe and Wolf-Gladrow, 2001) and calcite-aragonite solubility (Mucci, 1983) were selected. Given that some data recorded either salinity or conductivity, to estimate salinity from available conductivity data a polynomy was fitted to those data where both salinity and conductivity were known. Then used this, to calculate salinity when only conductivity was known. Weiss (1974) was used for the Henry's constant K_H . Given that the experimental determinations of the acidity constants K_1 and K_2 , as published by Roy et al., (1994), were focused on seawater and are not parameterized for high salinity, Saas and Ben-Yaakov (1974) was used, because these were determined for salinities up to ~300 ppt (see also Beeler et al., in press). It worth mentioning that, most of the compiled studies (Table 1) did not publish a full water chemistry that would allow to use a more proper speciation model to calculate cation and anion activities (for example Pitzer, 1971) and mineral saturation states (Harvie et al., 1984). Our approach here seems reasonable given our main goal, which is just to make some general comparisons of the carbonate system in the Laguna Negra with other lakes in the region. Besides, the effect of high ionic strength on activities of the carbonate system ions is implicit in Saas and Ben-Yaakov (1974) experimental determination for K_1 and K_2 . Solubility product constant for calcite and aragonite (K_{spc} and K_{spa} respectively) were calculated by using the data from Mucci, (1983) although it is necessary to be aware that these were parameterized only for salinities up to 45 ppt (almost an order of magnitude lower). The Python Jupyter notebooks that perform the calculations and plots can be downloaded from the GitHub website together with Table 1, https://github.com/FernandoJGomez/Gomez-et-al.-2019_Elsevier_Book_Puna.

19.3 The Laguna Negra carbonate system: comparison with other lakes in the Puna

Figure 19.1 show DIC (dissolved inorganic carbon) and Alkalinity data from Gomez et al., (2014), recalculated by using Saas and Ben-Yaakov (1974) and Mucci (1983). As expected, alkalinity and DIC (dissolved inorganic carbon) show a strong positive covariation and these variables also positively correlate with salinity (Figure 19.1) (see also Beeler et al., in press for additional data and a deeper analysis by using DIC stable isotopes). Fitting a trend line to a scatter plot of Laguna Negra data shows that the Alk:DIC ratio is of 1.12:1. Calcium carbonate precipitation consumes alkalinity and DIC in a 2:1 ratio (Zeebe and Wolf-Gladrow, 2001). The Laguna Negra Alk:DIC ratio of 1.12:1 suggests that, besides carbonate precipitation, more DIC is also lost due to other processes (a smaller slope in the trend line). Most probably this is due to CO_2 degassing which is also consuming DIC, and strong degassing has been suggested to explain co-variation and extreme enrichments in carbon and oxygen stable isotopes (Gomez et al., 2014, Buongiorno et al., 2018, Beeler et al., in press). Beeler et al., (in press) did a more detailed work, which also recorded a similar Alk:DIC ratio value (1.27:1) and showed, by mass-balance carbon isotope modeling, that 60% of DIC loss

was due to carbonate precipitation and the remaining by other processes, where CO₂ degassing was suggested (Beeler et al., in press).

Figure 19.1 Scatter plot of alkalinity and DIC values of the Laguna Negra (recalculated from Gomez et al., 2014). The color bar also shows how salinity correlated with these variables.

As observed in Figure 19.2, most DIC and alkalinity values for the lakes are ≤ 0.025 moles/L and ≤ 0.05 moles/L respectively, with a median below 0.01 moles/L. The same is observed for the Laguna Negra. Both (DIC and alkalinity) are enriched (~ 1 order of magnitude higher) when compared to seawater (typically 0.0021 for DIC and 0.00236 moles/L, Zeebe and Wolf-Gladrow, 2001). It is also higher than some hypersaline systems like the Dead Sea (Barkan et al., 2001). When compared to the Laguna Negra, the median values of DIC and alkalinity between Laguna Negra and all lakes are similar (Figure 19.2). Given that many of these lakes are also enriched in calcium (Ca²⁺, Table 1), it is expected that many of these are also saturated in carbonate minerals (Figure 19.7).

Figure 19.2 Histograms and box plots of the compiled alkalinity and DIC data of lakes in the Puna-Altiplano region, including the Laguna Negra. The panel at the right shows the box plots after some outliers were removed to better compare Laguna Negra data (Alk_{LN} and DIC_{LN}) with the whole dataset (Alk_{all}, DIC_{all}).

19.4 pH and Salinity of some Puna-Altiplano lakes

When analyzing saline lakes of the Puna-Altiplano region it can be seen that pH has a bimodal distribution, with pH around 5.5-6 and 7.5-8, with just a few alkaline lakes with pH above 9.5 (Figure 19.3). Salinity is also highly variable, due to net balance between evaporation, mineral precipitation and freshwater input, with some lakes reaching 400 ppt (Figure 19.4). Laguna Negra shows lower pH in the main lake (pH=5.6) and higher pH in the

inlet as well as mixing zone waters (pH up to 7.8). Salinity is also variable in the Laguna Negra, where inlet waters (9 ppt) and main lake waters (325 ppt) are the two end-members (Table 1). Even when relatively low pH has been recorded in the main lake, it has shown to be variable, since pH above 7 have been also recorded (data not shown and Beeler et al., in press). These changes in the pH could be related to increased CO₂ input into the main lake area or also due to carbonate precipitation events, which can also increase CO₂ (Barkan et al., 2001, Golan et al., 2017) and thus lowering the pH through the following reaction:

By the *Le Châtellier* principle, when degassing occurs reaction (1) proceeds to the right to restore the equilibrium and carbonate precipitation takes place, also producing CO₂. Even when for each mole of carbonate precipitated, CO₂ should increase in 1 mole as well, it does not actually happen due to buffering, since CO₂ is transformed into bicarbonate (HCO₃⁻) (Zeebe and Wolf-Gladrow, 2001).

Figure 19.3 Compiled pH data of the Puna-Altiplano lakes.

Figure 19.4 Compiled salinity data of the Puna-Altiplano lakes.

19.5 CO₂ degassing and pH

Measured pH and calculated CO₂ (by using pH and alkalinity) covariates in a non-linear way and a decreasing logarithmic function can be fitted to these data (Figure 19.5). Salinity also shows a trend with these variables, as salinity increases, CO₂ and pH decrease (Figure 19.5). When CO₂ is lost through degassing to the atmosphere (or consumed by photosynthesis and other metabolic processes) pH increases, increasing carbonate ion concentration (CO₃⁻²) and, if enough calcium (Ca⁺²) is available to overcome carbonates saturation, this triggers carbonate precipitation according to calcite equilibrium (Equation 1 and 2).

If equilibrium with calcite is assumed, it can be seen how pH may change as CO₂ degassing occurs (Figure 19.5). This can be shown by modeling pH versus CO₂ in equilibrium with calcite (through equations 3 and 4, from Kano, 2019; see derivation in the supporting online material). The model follows the same trend as the data (Figure 19.5) and the differences in pH may be because, even when CO₂ degassing increases the pH, carbonates precipitation also produces CO₂ and lowers the pH. Thus, the net balance of these driving processes will define the final pH and CO₂ concentration during the degassing-precipitation trend (Figure 19.5).

$$\text{H}^+ = (\text{K}_2^{1/3}(\text{K}_\text{H}\text{K}_1)^{2/3}/2\text{K}_\text{sp}^{1/3}) p\text{CO}_2^{2/3} \quad (3)$$

$$\text{pH} = -\log[\text{H}^+] \quad (4)$$

Figure 19.5 CO₂ versus pH data for the Laguna Negra (colored dots according to salinity). The red dashed trend-line represents a fitted exponential function to the data and the blue continuous line are the calculated values according equation 3 and 4.

19.6 Calcite and Aragonite saturation and processes triggering carbonate precipitation

The main problem when calculating carbonate minerals saturation state in hypersaline lakes is the lack of experimental data for the solubility product (K_sp) of calcite and aragonite at high ionic strength and salinities. The classic work of Mucci (1983) has been focused on seawater and for salinities up to 45 ppt. Saas and Ben-Yaakov (1977) determined K_1 and K_2 for salinities up to 309 ppt (at 30 Celsius degrees) and suggested a value for K_sp for calcite of $6.7 \cdot 10^{-4}$. This is about 1000 times higher than typical values for seawater (Saas and Ben-Yaakov, 1977) and this would lower saturation state for carbonate minerals. In these lower values for K_sp and saturation state of calcite is implicit that, at high ionic strength, activities of carbonate and calcium ions will be lower, given ion interactions and pairing that decrease ion activities. With the aim of illustrating the effect of salinity and using available data, Figure 19.6 shows saturation states for calcite (Ω_cal) versus DIC and salinity to show how, as salinity increases, saturation state decreases (using K_1 and K_2 from Saas and Ben-Yaakov, 1974; and K_sp of calcite from Mucci, 1983). As a reference, the white dot on Figure 19.6 represents a sample of the groundwater springs with salinity = 9.1 and DIC = .0173 moles/L (sample IW-7 of Laguna Negra, Gomez et al., 2014), which is oversaturated.

Figure 19.6 Omega versus DIC and Salinity for a pH=7.84 and Ca= 0.0115 moles, using K_1 and K_2 from Saas and Ben-Yaakov (1974) and K_{spc} (calcite) of Mucci (1983). Note that for constant DIC and pH, when salinity increases, Ω_{cal} decreases. The vertical blue dotted line shows the salinity range up to which Mucci (1983) K_{spc} is valid.

As observed in Figure 19.7, Saturation index ($SI = \log(\Omega)$, where $SI > 0$ and $SI < 0$ indicates over and undersaturation of carbonate minerals respectively) suggests that Laguna Negra lake waters are undersaturated (given the relatively low pH=5.7) and most mixing zone and inlet waters are oversaturated in calcite. When calculating saturation state with a pH of 7, as it has also been observed (Beeler et al., in press), the main lake waters became slightly oversaturated, so the main lake may fluctuate between oversaturated and undersaturated states.

Strong evaporation, as observed in the Laguna Negra, increases saturation state and CO_2 degassing, also increasing pH thus triggering carbonate precipitation. As salinity increases, carbonate precipitation takes place and thus pH gets lower as well as the saturation index (Figure 19.7). Beeler et al., (in press) documented that pH and DIC spatially changes from the groundwater springs, to the mixing zones and reaching the main lake and it has been interpreted as related to calcite precipitation. It is the net balance of these complex interacting processes that controls saturation state and mineral precipitation in the Laguna Negra.

As shown in Figure 19.7 (left panel), most lakes are oversaturated in calcite and aragonite and although variable, the Laguna Negra samples shows similar degrees of saturation when compared with other lakes (Figure 19.7, right panel).

Figure 19.7 Saturation index (S.I.) histograms and box plots for calcite and aragonite for the whole data set (including Laguna Negra) and the Laguna Negra itself. The vertical red and blue dotted lines show the equilibrium line where S.I.=0.

19.7 The Mg/Ca molar ratio of Laguna Negra and other Puna-Altiplano lakes

The Mg/Ca molar ratio for the Laguna Negra waters fluctuates between ~0.08 and ~2, like more than half (62%, Figure 19.8) of the Lakes in the Chilean-Argentinian-Bolivian Puna-Altiplano area. Given that, as shown by experimental and thermodynamic models (Sun et al., 2015 and references therein), Mg/Ca ratios below 2 are considered important for calcite precipitation, it is expected that calcite should be the predominant calcium carbonate mineral species (if oversaturation is reached). The other 39% is above this boundary (Figure 14.20) and even some of them show Mg/Ca molar ratios extremely high (between 25-35), such as for example the Diamante lake (Argentina), Chaxa (Chile) and the Tebenquiche (Chile, here gypsum and halite predominate, and aragonite is subordinated). Thus, aragonite is expected to be the main carbonate mineral in these lakes. Even when mineralogy data is scarce, it has been observed that in the Diamante and La Brava lakes aragonite precipitation prevails (Farias comm. pers.). In hypersaline lakes, the Mg/Ca molar ratio will be controlled by the local geology (weathering of available rocks and minerals), hydrothermal input (in some cases) and the evolution of the lake during evaporation, so this ratio, as opposed to seawater, is expected to be highly variable and thus carbonate mineralogy as well. Further studies integrating hydrochemistry, evaporite mineralogy and local geology would be necessary to have a better understanding of the main controls on calcium carbonate mineralogy in hypersaline lakes.

Figure 19.8 Mg/Ca molar ratio of lakes in the Puna-Altiplano region.

It worth mentioning that the aragonite/calcite ratio is not only controlled by the Mg/Ca molar ratio but also by many other processes like precipitation rate, temperature, salinity and solution composition (see for Morse et al., 2007, Jones, 2017, a recent review). In the Laguna Negra, only two samples were close to the value where aragonite should precipitate, one coming from the groundwater and other from the mixing zone. In the Laguna Negra calcite is the predominant mineral, as observed in the main lake, mixing zones sediments, in the oncoids (Gomez et al., 2014, Buongiorno et al., 2018) and within the microbial mats (Boidi et al., in review). It worth mentioning that aragonite traces have been recorded within some laminae in the oncoids (Buongiorno et al., 2018). More interestingly aragonite have been currently recorded during local diatom blooms event (Gomez et al., 2018) and associated to cyanobacteria like Rivularia (Mlewski et al., 2018), in areas where the Mg/Ca ratio is clearly below 2 suggesting other controls in carbonate polymorph selection, probably related to the kinetic influence of microbial metabolisms, in this case photosynthesis given the direct

association with cyanobacteria and diatoms (Gomez et al., 2018; Boidi et al., 2019). In addition, Rivularia has been observed to concentrate calcium on the cells surface (Mlewski et al 2018) and could be locally modifying the Mg/Ca ratio on the sheaths and thus controlling carbonate polymorph selection.

19.8 Concluding remarks

In hypersaline environments, alkalinity and DIC changes are strongly controlled by a set of physico-chemical processes like evaporation and strong CO₂ degassing. In the Laguna Negra, CO₂ degassing as well as carbonate precipitation have shown to be a main control on pH, alkalinity and DIC evolution of lake waters. In addition, water mixing also contribute to changes these variables, and can be particularly important to increase saturation states, thus promoting carbonate precipitation as observed in the mixing zone in the Laguna Negra. By changing chemical equilibrium, microbial activity can also modify alkalinity and DIC. Photosynthesis consume CO₂, lowering DIC and thus changing pH consequently triggering carbonate precipitation. Anoxic degradation of organic matter increases alkalinity also promoting oversaturation of carbonate minerals. Exopolimeric substances and other organic matrixes can also serve as nucleation sites for mineral precipitation. Thus, the net balance of these combined microbiological and physico-chemical processes will define the textural and chemical signatures preserved in these sedimentary carbonates.

Mg/Ca molar ratio is known to influence the carbonate polymorph that may precipitate, and this has been observed in several lakes in the Puna-Altiplano area, where a high Mg/Ca molar ratio favored aragonite precipitation. For example, in the Diamante lake (Argentina) and the Tebenquiche and Chaxa (Chile), where abundant aragonite has been recorded. Although the prevalence of aragonite at high Mg/Ca ratios is supported by thermodynamics, several processes control carbonate polymorph selection. For example, aragonite precipitation has been observed in the Laguna Negra, where the Mg/Ca molar ratio is low, and related to the photosynthetic activity of diatoms and cyanobacteria, suggesting a kinetic control on mineral polymorphism.

There is a need to have a better understanding of the carbonate system in hypersaline lakes, particularly given that some of the parameters and equilibrium constants useful to calculate carbon species concentrations, have not been determined for high-ionic strength solutions like typically observed in the Puna-Altiplano region. Improving this can help to better understand geomicrobiological aspects and the environmental record of carbonates precipitated in modern and ancient hypersaline systems.

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