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Water geochemistry of shallow lakes from the southeastern Pampa plain, Argentina and their implications on mollusk shells preservation

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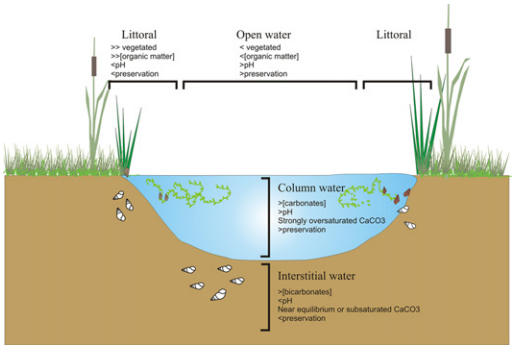
HIGHLIGHTS

- Littoral (LIT) areas have less favorable physico-chemical conditions for shell preservation than open waters (OW).
- In sediments, aragonite and calcite indices are in equilibrium or slightly subsaturated in both LIT and OW settings.
- Mollusk shells within sediments would be subject to dissolution.
- The water column in is strongly oversaturated with regard to carbonates.
- Mollusk shells in contact with the column water are not likely to be dissolved.

GRAPHICAL ABSTRACT



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ABSTRACT

A seasonal sampling of sediments, column and interstitial water for physico-chemical analysis were performed in littoral and open water areas in three freshwater shallow lakes (Nahuel Rucá, Las Mostazas and Los Carpinchos) from Southeastern Pampa plain, Argentina. The main objective of the present study is to evaluate how the characteristics of the depositional environments could be affecting mollusk shell preservation. These lakes are very shallow (2 m) and are characterized by an extensive littoral area, dominated by the emergent macrophyte *Schoenoplectus californicus*, which forms a complete ring around the lake, and an open water area, in general free of vegetation. Five samples of sediments in each compartment were extracted for analysis of pH, moisture, organic matter and carbonates content using a gravity corer, while five samples from column and interstitial water were extracted for chemical analysis (pH, conductivity, major ions, minor ions and hardness). Besides, calcite and aragonite saturation indices and the redox potential were calculated for each lake. The results show the significant impact of water chemistry and redox conditions on the preservation potential of freshwater mollusk and consequently in the quality of paleonvironmental reconstruction based on the biological record from the study region. The higher concentration of organic matter and lower pH registered in the littoral area, mainly during warm months (autumn and summer), suggest worst environments for mollusk preservation, compared to open waters. Moreover, water geochemistry analysis showed aragonite and calcite indices near equilibrium or slightly subsaturated in interstitial water associated with more acid pHs, while column water is strongly

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oversaturated related to alkaline pHs. These results suggest that carbonate remains within sediments will be subject to dissolution affecting negatively their preservation potential. However, mollusk shells in contact with the column water are not expected to be dissolved.

1. Introduction

In aquatic environments, most taphonomic loss is thought to occur at and below (first centimeters) the sediment–water interface, a zone known as the Taphonomically Active Zone (TAZ; Davies et al., 1989). Dissolution appears to be the main factor affecting preservation within the TAZ, owing to the metabolic activity of organisms, mainly by bacterial decomposition of organic matter, which regulate the state of redox within sediments and affect the saturation state of calcium carbonate (Aller, 1982; Walker and Goldstein, 1999; Best et al., 2007; Cherns et al., 2008). The microbial zone and the saturation state of the pore waters with respect to calcium carbonate will be the most important aspects of any taphonomic study that examines post-burial preservation of skeletal hard parts (Walker and Goldstein, 1999).

In marine settings different redox environments have been recognized in the sedimentary milieu (Berner, 1981) in relation to increasing reducing conditions, which can be identified through the species that reduces during the organic matter oxidation. On one hand, in the aerobic zone bioturbation produces acidity through respiration (because of the increment of CO_2) and sulfide oxidation. On the other hand, as long as we go deeper into the anoxic sediments, alkalinity increases due to sulfate reduction which adds HCO_3^- and H_2S. These sulfides may react with iron minerals to produce iron sulfide phases avoiding potential acid conditions. Below the sulfate reduction milieu, there is a zone of methane production which diminish pH, but do not produce carbonate subsaturation unless little alkalinity accumulate during sulfate reduction (Canfield and Raiswell, 1991; Cherns et al., 2011). In freshwater sediments, the decomposition of organic matter follows the same pattern, but with the important difference that sulfate reduction is much less significant due to its lower concentration in these environments. Large organic matter concentrations can be degraded by methanogenesis, which releases CO_2 and sediments can quickly subsaturate with respect to $CaCO_3$. Although sulfate reduction is much less significant than in marine environments, it produces large amounts of iron oxides which are available to be reduced, directly generating alkalinity due to production of HCO_3^-. This process tends to neutralize the acid CO_2 formed by methanogenesis. Since bacterial activity is higher during warmer months, preservation would be affected by seasonality (Walker, 2001). Thus, preservation potential of calcium carbonate hard parts is highly variable, depending on the initial composition of water and the relative importance of methanogenesis and iron reduction, and to a less degree to sulfate reduction (Canfield and Raiswell, 1991).

At present studies that integrate taphonomic analysis and water chemistry composition are scarce in freshwater environments (Cummins, 1994; Nielsen et al., 2008). In particular, it is unknown how pH, organic matter, carbonates, and water chemistry composition affect mollusks preservation below the sediment-water interface in freshwater shallow lakes from the Pampa region. Specifically, the freshwater malacofauna of the region is characterized by low taxonomic diversity (richness vary between 1 and 11) and is dominated by epifaunal gastropods, mainly *Heleobia parchappii* and *Biomphalaria peregrina*. Most of the species represented in the area display a wide range of ecological tolerance, i.e., most species are found in different kinds of water bodies (for details see Tietze and de Francesco, 2010, 2012), and have been widely used for paleoecological and paleoenvironmetal reconstruction of the area (Prieto et al., 2004; de Francesco et al., 2013; Steffan et al., 2014; Pisano et al., 2015; as examples). However, the fossil record formation depends not only on ecological processes that affect life assemblages but also on taphonomic processes which modify death assemblages during and after their deposition (Beherensmeyer et al., 2000). Therefore, the knowledge about the dynamic and processes occurring within modern depositional environments will have a significant impact in the improvement of paleoenvironmental reconstruction quality based on the biological record.

The aim of the present work is to analyze the chemical composition of sediments, column and interstitial water in shallow lakes from the Pampa plain in order to highlight their relative influence on mollusk shells preservation. Results are compared with previous taphonomic studies carried out in the same study region (Cristini and De Francesco, 2012; Cristini, 2016; Tietze and de Francesco, 2012, 2014, 2017). In particular, the present contribution aims to compare (a) patterns between different compartments of the lakes (littoral versus open water) and (b) calcium carbonate saturation indices with respect to aragonite and calcite between column and interstitial water as well as to estimate potential redox from sediments.

2. Materials and methods

2.1. Study area

The region is a vast grassy plain that covers the central area of Argentina, which is characterized by a quite uniform relief, except for the presence of two mountains ranges (Tandilia and Ventania) towards the southeast (Diovisalvi et al., 2014) (Fig. 1). Soils of the area are generally fertile with a high content of nutrients, composed mainly of loess and with a marked capacity for cationic interchange, predominantly involving calcium (Rodrigues Capítulo et al., 2010). The climate is temperate humid or sub-humid with a mean annual temperature of 15 °C and a mean annual precipitation of 1100 mm (Feijoó and Lombardo, 2007). Precipitation patterns also display large variability, both geographically and inter-annually. This large interannual variability in combination with poorly developed drainage systems results in recurrent and extensive floods, alternating with drought periods (Fig. 2). All these processes affect the lake water residence time, the water content of soils, and the depth of the water table (Diovisalvi et al., 2014).

The gently slope of the landscape promotes the development of numerous permanent and temporary shallow lakes, which are very shallow (2 m) without thermal stratification except for short periods of time (Quirós and Drago, 1999; Fernández Cirelli and Miretzky, 2004). These lakes are characterized by an extensive littoral area, dominated by the emergent macrophyte *Schoenoplectus californicus* (C. A. Mey) Soják, which forms a complete ring around the lake, and an open water area, in general free of vegetation except for the submerged macrophytes *Myriophyllum elatinoides* and *Ceratophyllum demersum* (Stutz et al., 2010, 2012). These general characteristics are common for the three studies lakes. They have several environmental functions, among them charge and discharge of aquifers, flood control, water provision, climate regulation, recreational use, sportive fishing, and waste disposal (Fernández Cirelli and Miretzky, 2004), being naturally eutrophic or hypertrophic with most of them turbid due to the high amount of algae, while few are clear macrophyte-dominated lakes (Quirós et al., 2002; Quirós et al., 2006). Their degree of salinity is varied, ranging from