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## Geochemical conditions allowing the formation of modern lacustrine microbialites

Nina Zeyen<sup>a\*1</sup>, Damien Daval<sup>b</sup>, Purification Lopez-Garcia<sup>c</sup>, David Moreira<sup>c</sup>, Jérôme Gaillardet<sup>d</sup>, Karim Benzerara<sup>a</sup>

<sup>a</sup>IMPMC, Sorbonne Universités, UMR Centre National de la Recherche Scientifique 7590, UPMC, MNHN, IRD, 75252 Paris, France

<sup>b</sup>Lab Hydrol & Geochim Strasbourg, Univ Strasbourg, EOST CNRS UMR 7517, 67084 Strasbourg, France

<sup>c</sup>Unité d'Ecologie, Systématique et Evolution, Centre National de la Recherche Scientifique UMR 8079, Université Paris-Sud, Orsay, France

<sup>d</sup>IPGP, Sorbonne Paris Cité, UMR 7154, Université Paris Diderot, Centre National de la Recherche Scientifique, Paris, France

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### Abstract

Interpreting the environmental conditions of ancient microbialites rely on comparisons with modern analogues. Yet, we lack a detailed reference framework relating the chemical and mineralogical composition of modern lacustrine microbialites with the physical and chemical parameters prevailing in the lakes where they form. Here we performed geochemical analyses of water solutions and mineralogical analyses of microbialites in 12 Mexican crater lakes. We found a large diversity of microbialites in terms of mineralogical composition, with occurrence of diverse carbonate phases such as magnesian calcite, monohydrocalcite, aragonite, hydromagnesite, and dolomite as well as authigenic magnesium silicate phases. In parallel, the chemical compositions of the lakes differed particularly by their alkalinity, their concentration of ortho-silicic acid ( $\text{H}_4\text{SiO}_4$ ) and their Mg/Ca ratio. From this study, we infer a minimum alkalinity value for the formation of lacustrine microbialites, as well as several constraints given by the presence of mineral phases on the chemical composition of the lakes in which microbialites formed. Finally, we observe a general correlation between the alkalinity and the sodium content of the lakes. This may relate to variations in evaporation intensity and provide a historical model for lacustrine microbialite formation: microbialite start forming only when the lake is sufficiently old/evaporated.

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**Keywords:** microbialites; carbonates; Mg-silicates; paleoenvironments.

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### 1. Introduction

Microbialites are organo-sedimentary rocks formed in close association with microorganisms. These structures are abundant in the ancient fossil record and are generally considered as being among the oldest life remains on the Earth<sup>1</sup>. Marine and lacustrine microbialites have been found in the geological record<sup>2,3</sup>. Inference of

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\* Corresponding author. Tel.: +33-144274510; E-mail address: [nina.zeyen@impmc.upmc.fr](mailto:nina.zeyen@impmc.upmc.fr)

the diversity of biotic and abiotic processes involved in the formation of ancient microbialites requires a solid knowledge of modern analogues. However, while many studies have focused on lacustrine microbialites from one single locality/lake, there is no global overview linking precisely the chemical conditions prevailing in lakes and the size and mineralogical composition of microbialites. Here we studied twelve Mexican crater lakes located in the Miocene to Holocene trans Mexican volcanic belt (TMVB)<sup>4</sup>. These lakes are relatively diverse in terms of their geochemical composition and the microbialites they harbor have various mineralogical composition and size. First, we aim to define the chemical parameters controlling the formation and mineralogical composition of modern lacustrine microbialites. Then we propose some hypothesis explaining the chemical variations observed for the different lakes.

## 2. Materials and Methods

Investigated crater lakes belong to the TMVB. The lakes are located at an elevation between 1690 m (Rincon de Parangueo) and 2380 m (Tecuítlapa). Lake Zirahuén is deprived of microbialites, while the Rincon de Parangueo crater contained fossil microbialites but shows an almost total evaporation of the lake. Except for these lakes and for Lake Joya de Yuriria, which contained fossil microbialites, the nine other lakes are populated by living microbialites. Microbialites are more or less developed ranging from calcified crusts measuring few millimeters in thickness around basaltic rocks to meter-sized mounds with various morphologies. The main field campaign was conducted in May 2014, complementing previous campaigns in June 2007 and January 2012. Surface water samples were collected from the shore of the lakes at <1 m away from the sampled microbialites. Samples from the center (Atx-M) and the northern shore (Atx-N) of Lake Atexcac as well as samples from the center (AL-M) and the western shore (AL-W) of Lake Alchichica were collected. The total alkalinity was determined by titration using hydrochloric acid. Ortho-silicic acid concentrations ( $\text{H}_4\text{SiO}_4$ ) were measured by continuous flow colorimetry. Anionic species concentrations (fluorides, chlorides, bromines, nitrates, phosphates and sulfates) were measured by ion chromatography. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine major and minor cation concentrations. Activities of anions, cations and ortho-silicic acid as well as saturation indices of the surface water solutions were calculated using the Visual MINTEQ software. The bulk mineralogical composition of microbialites was determined by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). XRD measurements were performed using a Panalytical X'Pert diffractometer equipped with a cobalt anode (Co-K $\alpha$ ). Data were recorded at 45 kV and 35 mA in the continuous-scan mode between 4 and 120° (2 $\theta$ ) with a step of 0.0084° and a total counting time of around 4 h. For FTIR analyses, transmission spectra were recorded between 400 and 4000  $\text{cm}^{-1}$ , using a Nicolet 6700 FTIR spectrometer. Finally, scanning electron microscopy (SEM) analyses were performed on polished sections to observe the spatial distribution of mineral phases within microbialites.

Table 1. Mineralogical composition of microbialites in Mexican lakes. A: aragonite; H: hydromagnesite; MgC: magnesian calcite; MC: monohydrocalcite; D: dolomite; MgSi: magnesium silicate phase. The Ø symbol stands for the absence of microbialites in the Lake Zirahuén

Lake	Description	Main mineral phases
Zirahuén (Z)	No microbialites	Ø
La Alberca (Alb)	Basalts finely encrusted by living microbialites	MgC – MgSi
Quechulac (Q)	Living microbialites	A – MgSi
Alberca Los Espinos (AE)	Living microbialites	MgC – MC – MgSi
Patzcuaro (P)	Living microbialites	MgC – A – MgSi
Aljojuca (Alj)	Basalts largely encrusted by living microbialites	MC – MgC – A
La Preciosa (LP)	Well-developed living microbialites	A – MgSi
Joya de Yuriria (Jo)	Basalts largely encrusted by fossil microbialites	MgC – MgSi
Tecuítlapa (T)	Basalts largely encrusted by living microbialites	MgC – MC – A – MgSi
Atexcac (Atx-N & Atx-M)	Well-developed living microbialites	A – MgSi – D
Alchichica (AL-W & AL-M)	Well-developed living microbialites	A – H
Rincon de Parangueo (R)	Fossil microbialites	H – A – MgSi

### 3. Results and Discussion

Microbialites from the studied lakes have different bulk mineralogical composition as summarized in Table 1. Geochemical analyses of water solutions reveal ionic balances better than 4% supporting the consistency of ICP-AES, continuous flow colorimetry and ion chromatography measurements. The studied lakes have a similar pH around 9. Reported water temperatures range between 19°C for Lake La Preciosa and 29°C for Lake Patzcuaro. These lakes have various chemical compositions. Several earlier studies have monitored the chemical composition of surface water in some of these lakes at different periods during the year<sup>5,6,7</sup>. Comparison with present data suggests that the solution chemistry of these lakes does not vary significantly seasonally. The lakes show a large range of alkalinities (here almost identical to  $[\text{HCO}_3^-]$ ) from 1.23 mM (Lake Zirahuen) to 50 mM (Lake Tecuítlapa). All lakes, except Lake Zirahuen, harbor microbialites suggesting that a minimum alkalinity of 1.23 mM may be required for microbialite formation to occur. Saturation indices of the surface waters with several mineral phases were calculated. All lakes were supersaturated with different Ca-carbonates (calcite, vaterite, and aragonite) as well as dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). Lake Alchichica is also supersaturated with hydromagnesite. Consistently, diverse carbonates compose the microbialites of the different lakes: magnesian calcite, monohydrocalcite, aragonite and dolomite. Hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) is a major phase only in Alchichica and Rincon de Parangueo microbialites. The identity of the major carbonate phase composing microbialites in particular the presence of calcite and/or aragonite is controlled by the Mg/Ca ratio of lakes which varies here from 1 (Lake Zirahuen) to 90 (Lake Alchichica, Fig. 1). Microbialites mainly composed of calcite (Mg-calcite and/or monohydrocalcite) are formed in lakes with a Mg/Ca ratio less than 10. Aragonite appears at a Mg/Ca value of 3 in Lake Patzcuaro. For a Mg/Ca interval between 3 to 6, microbialites are mainly composed of calcite and contain minor amounts of aragonite (Lake Patzcuaro, Tecuítlapa and Aljojuca). Finally, microbialites are exclusively composed of aragonite (Quechulac, La Preciosa, Atexcac and Alchichica) for water with a Mg/Ca ratio above 10.3. These limits differ substantially from those inferred for marine conditions. Indeed, experiments conducted on biofilms cultured under different seawater conditions, showed that at a Mg/Ca of 1.5, biofilms produced exclusively Mg-calcite (as observed in our study); at a Mg/Ca ratio of 2.5, biofilms produced mainly Mg-calcite (85%) and lesser amount of aragonite (15%) and for a modern seawater Mg/Ca ratio (5.2), biofilms were calcified by both aragonite and Mg-calcite<sup>8</sup>.

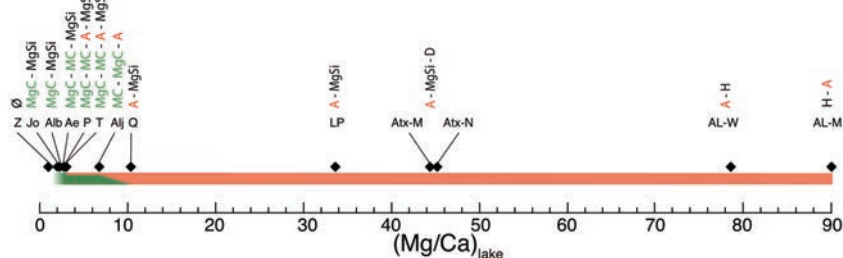


Fig. 1. A correlation between the calcium carbonate mineralogy and the Mg/Ca ratio of lake water solutions. Black diamonds correspond to Mg/Ca ratios of each lake. Magnesian-calcite and monohydrocalcite are in green and aragonite in red.

Moreover, all lakes harboring microbialites are supersaturated with Mg-silicates. Consistently, authigenic magnesium silicates are systematically observed except for microbialites from lakes Aljojuca and Alchichica. These silicates were previously characterized as poorly crystalline hydrated talc phases, similar to kerolite, and showed a high potential for fossilizing microbial structures<sup>9</sup>. As mentioned, the saturation index of kerolite is higher for Lake Aljojuca (SI kerolite = 4.9) than for lake Quechulac (SI kerolite = 4.3) for example. However, microbialites in Lake Aljojuca do not contain authigenic magnesium silicates, while microbialites in Lake Quechulac contain minor amounts of magnesium silicates. Therefore, it seems that the concentration of ortho-silicic acid ( $\text{H}_4\text{SiO}_4$ ) in these lacustrine systems is a better parameter predicting where precipitation of magnesium silicate occurs. More precisely, a concentration of ortho-silicic acid in the surface waters higher than 0.56 mM is a good indicator of the abundant presence of magnesium silicate phase in the microbialites (lakes La Preciosa, Tecuítlapa, Joya de Yuriria, Alberca los Espinos, Atexcac, La Alberca). Microbialites from Lake Quechulac and Patzcuaro contain minor amounts of magnesium silicate phases, with ortho-silicic acid concentrations in the lakes of 0.23 and 0.37 mM respectively. Lakes with concentrations of ortho-silicic acid less than to 0.16 mM do not show authigenic magnesium silicate

phases associated with microbialites (Alchichica, Aljojuca). The reason why silica concentration might be a better indicator in these systems than supersaturation with kerolite is that there is a competition for Mg between Mg-silicates and Mg-carbonates. This may also explain why no correlation is observed between the concentration of magnesium in the lakes and the presence of magnesium silicates within microbialites.

Finally, a positive correlation is observed between the logarithm of alkalinity and the logarithm of sodium concentration, which varies widely between 0.4 (Lake Zirahuen) and 103 mM (Lake Alchichica) (Fig. 2). Here, we test the hypothesis that the studied lakes form an evolutionary series with increasing evaporation and/or increasing degree of weathering of the silicates composing the craters. As a result, microbialites appear once a sufficient alkalinity is reached, which occurs at a certain stage of this series of evaporation/weathering. The chemical composition of the lake continues then to evolve and the mineral composition of the microbialites evolves accordingly following the relationships provided above. The general rules exposed here will need to be checked on the numerous other occurrences of known modern microbialites and will offer a solid framework for better interpreting the paleoenvironmental conditions under which ancient lacustrine microbialites formed.

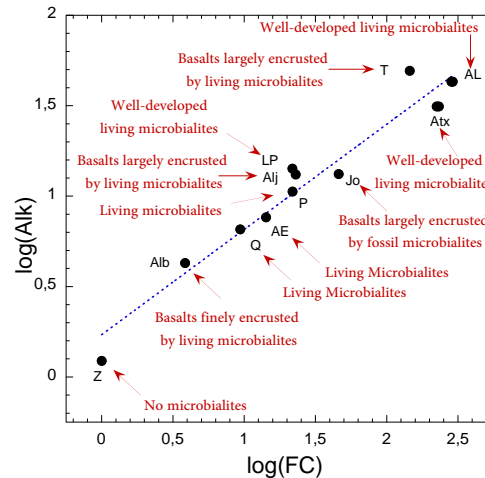


Fig. 2. A positive correlation between the log of alkalinity and the log of the concentration factor. The concentration factor is calculated as the sodium concentration of a given lake normalized by the sodium concentration of Lake Zirahuen.

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