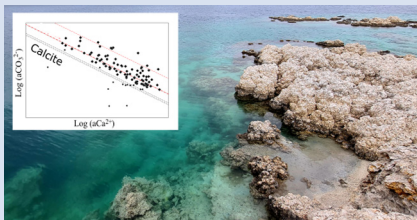# The chemical conditions necessary for the formation of microbialites

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Abstract

Whether biological and/or physico-chemical variations may have changed the abundance of microbialites over geological times remains debated. This calls for a better appraisal of the conditions necessary for the formation of modern microbialites. Here, we compiled datasets from 140 aqueous environments where modern microbialites have been reported, including their respective physico-chemical parameters. By analysing this database, we find that solutions where microbialites form have a relatively high saturation with calcite, the chemical activities of Ca^{2+} and CO_3^{2-} being controlled by the solubility of amorphous calcium carbonate (ACC) or monohydrocalcite (MHC) in most of these localities. Further statistical analyses of two databases listing ∼8000 continental aqueous systems show that only a few of them display saturation with ACC/MHC, appearing as candidates for the detection of overlooked microbialites.

Introduction

Microbialites are organosedimentary deposits formed by benthic microbial communities that mediate authigenic mineral precipitation (Burne and Moore, 1987). They are found throughout the geological record up to 3.43 billion years ago and are considered as among the oldest traces of life on Earth (Allwood *et al.*, 2007). It has been argued that the diversity of microbialites has varied over geological time with an overall decline at the end of the Proterozoic (*e.g.*, Awramik, 1971). The causes of these fluctuations have fed debates opposing two major models: (i) one involving biotic causes suggests that grazing by Metazoans induced the decline of microbialites (Walter and Heys, 1985), and (ii) a second "abiotic" model proposes that changes in the chemical composition of the ocean were responsible for microbialite decline (Fischer, 1965; Kempe and Kaźmierczak, 1994; Peters *et al.*, 2017).

While this debate is difficult to directly tackle, it emphasises that we still do not understand the conditions necessary for microbialites to form. Modern microbialites have been described in diverse environments (*e.g.*, marine, freshwater, hypersaline) and in the presence of very diverse microbial communities (*e.g.*, Iniesto *et al.*, 2021). Presently, there are many reports in the literature characterising the aqueous geochemistry of single sites where modern microbialites form. However, only a few meta-analyses gathering some of these data provide a broader, statistical overview (*e.g.*, Zeyen *et al.*, 2021). Here, we achieve an unprecedented compilation of datasets from 140 locations where modern microbialites form, spanning freshwater, brackish, saline and hypersaline environments (Table S-1).

We analyse the variability of the chemical parameters of microbialite-hosting environments and look for possible invariants. Moreover, in order to assess the rareness/commonness of conditions encountered in microbialite-hosting environments, we compare our database with two databases of continental aqueous systems.

Results

Physico-chemical parameters of microbialite-hosting environments. The compilation was achieved by systematically searching the terms "stromatolite", "thrombolite" or "microbialite" in the literature (see Supplementary Information). The 140 compiled modern microbialite-hosting systems occur on all continents (Fig. S-1) in a diversity of climates and geological contexts. Most of the environments were freshwater, but 34 were marine. The database includes emblematic microbialites, such as those of Shark Bay, Lagoa Vermelha or the Bahamas, that have received much attention as modern analogues of ancient microbialites. Dissolved Ca^{2+} and Mg^{2+} concentrations were measured in a majority (∼90 %) of the corresponding aqueous solutions and ranged from 0.001 to 643 mM and 0.001 to 1325 mM, respectively. Concentrations of other major chemical species (Na^+, Cl^-, K^+, SO_4^{2-}) were also generally well documented (∼88 % of systems on average). Measurements of the dissolved inorganic carbon (DIC) concentrations ranged between 0.022 and 6236 mM. These measurements were less documented (∼76 % of systems) in the database, despite their importance in carbonate-rich environments. In seven lakes, alkalinity values

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were available and assumed to be equal to DIC (Dickson *et al.*, 1981; Fig. S-2).

Overall, microbialite-forming waters in our database span a high diversity of water chemical types as defined by Boros and Kolpakova (2018), which were: saline (53 % of the occurrences), soda-saline (23 % of the occurrences) and soda (24 % of occurrences) (Fig. S-3). Principal component analyses (PCA) were conducted on 10 chemical variables measured on 545 samples of microbialite-hosting environments in order to find the variables contributing to most of the dataset variability. It showed that most of the variance (~62 %) in the dataset was explained by (i) salinity (logarithms of Na, Cl, K activities) (35.22 %), and (ii) the logarithm of CO_3^{2-} activity anticorrelated with the logarithm of Ca^{2+} activity (26.32 %) (Fig. S-4).

Assessment of the saturation index of waters in which modern microbialites form. The anticorrelation between Ca^{2+} and CO_3^{2-} activities was further analysed by plotting their logarithms against each other. This plot also allows us to assess the saturation index (defined as $SI = \log(IAP/K_s)$, where IAP is the ion activity product and K_s is the solubility constant) of solutions with various $CaCO_3$ phases such as anhydrous crystalline phases and amorphous phases (ACC). Four hundred and sixteen chemical measurements performed on 102 microbialite-forming environments that were available in the database. The mean value was considered for the environments for which several measurements were available (Fig. 1). Conclusions were similar when using the median.

A large majority (89 %) of aqueous environments were highly supersaturated with respect to calcite and aragonite and aligned between the solubility lines of vaterite and an ACC phase (ACC2) as determined by Brečević and Nielsen (1989) (Fig. 1).

Diverse ACC phases exist with $\log K_s$ varying between −7.63 and −6.04. Here, many points align close to the solubility lines of MHC and ACC1 phase (another ACC phase as determined by Kellermeier *et al.*, 2014).

A few environments ($n = 5$) appeared significantly undersaturated with calcite. However, three of them harboured microbialites that were siliceous (*e.g.*, Great Obsidian Pool, Mound Spring; Table S-1) or formed by pure trapping and binding of clays (*e.g.*, Lake Untersee, Antarctica; Table S-1). In two others (Kauai caves, Hawaii), microbialites formed on cave walls in freshwater seeping out of basalts and may experience significant chemical variations by evaporation and CO_2 degassing (Léveillé *et al.*, 2007).

Finally, some environments hosting carbonate microbialites were on average supersaturated with anhydrous carbonates but undersaturated with ACC and vaterite ($n = 9$; Figs. 1, S-5). Only one single analysis was available for Ciocaia drill (Romania). However, several ones were available for the other locations. For Pavilion Lake, solution geochemistry varied over time, reaching saturation with ACC at certain periods (Fig. S-5). For Lake Kelly, none of the several available measurements were saturated with ACC but it was reported that microbialites may no longer actively form (Lim *et al.*, 2009). Last, at least four other environments showed spatial chemical heterogeneities. They were undersaturated with ACC on average but supersaturated with ACC at certain locations. For example, Lakes Joyce and Hoare (Antarctica) have chemically stratified waters, and microbialites form at depths where DIC water content rises (Mackey *et al.*, 2018). Pastos Grandes (Bolivia) harbours groundwater outflows chemically evolving by evaporation along their travel away from the source. Microbialites form when water reaches saturation with ACC (Muller *et al.*, 2022). Overall, 98 % of aqueous
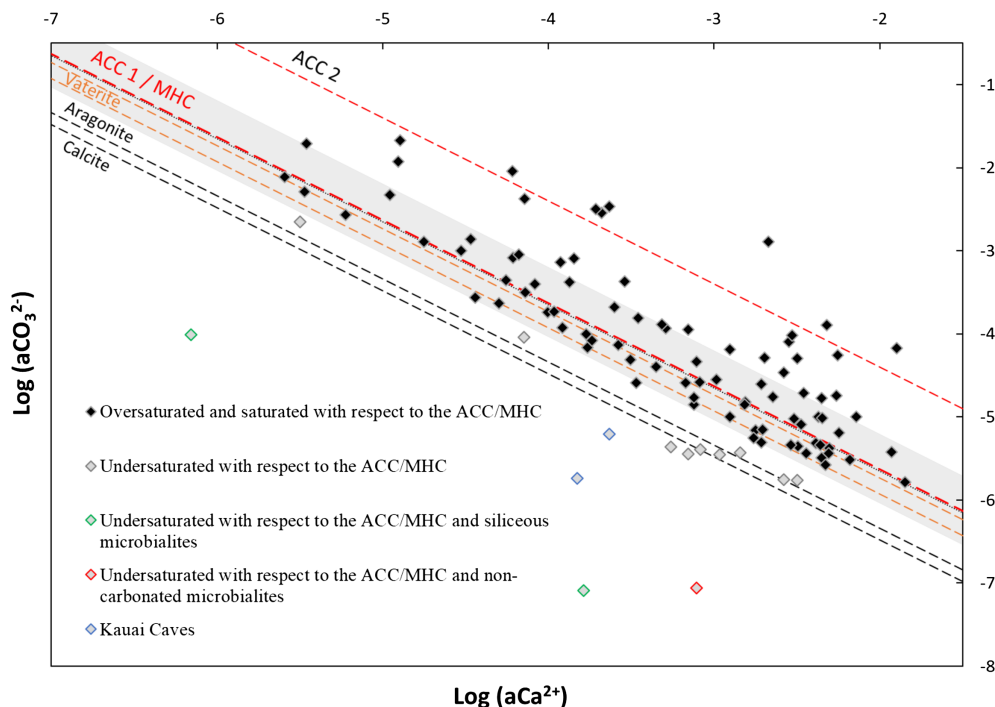

Figure 1 Plot of the log of the activities of CO_3^{2-} *vs.* Ca^{2+} for 102 microbialite-hosting environments. Solubility lines (dashed lines) are reported for calcite ($\log K_s = -8.48$), aragonite ($\log K_s = -8.34$), monohydrocalcite (MHC; $\log K_s = -7.6$), vaterite (De Visscher and Vanderdeelen, 2003), ACC1 as reported by Kellermeier *et al.* (2014; $\log K_s = -7.63$) and ACC2 as reported by Brečević and Nielsen (1989; $\log K_s = -6.39$). Only mean values are provided for each environment by a diamond. Green diamonds correspond to siliceous microbialites; red diamond corresponds to a clayey microbialite. Black diamonds correspond to environments saturated and oversaturated with ACC1 and/or vaterite; grey diamonds correspond to environments undersaturated with vaterite. The grey shaded zone highlights a 95 % confidence interval on the saturation values of microbialite-hosting environments with respect to ACC1/MHC.

environments hosting modern microbialites were saturated with ACC at least part of the time.

Comparison of the chemistry of modern microbialite-hosting aqueous solutions with two global freshwater databases. The chemical compositions of carbonate microbialite-hosting environments were compared with many aqueous environments listed in two general databases, in order to assess how unique the former might be. The Global Lake Ecological Observatory Network (GLEON) database compiles 105,678 samples from 6422 North European lakes with only temperature, pH, DIC and Ca^{2+} concentrations as physico-chemical parameters (Weyhenmeyer *et al.*, 2019; see Supplementary Information). The Environmental Data Initiative (EDI) groups 28,455 samples from 1547 North American lakes with several additional

parameters (Supplementary Information). Some of the lakes compiled in the EDI and GLEON databases possibly harbour microbialites but if this is the case, they have not been described in the literature and therefore are not in our microbialites database. The comparison showed that pH, DIC and calcium concentrations in the carbonate microbialite database were significantly higher on average than in lakes from the GLEON and EDI databases (Wilcoxon comparison tests of means; threshold of 0.05 and p values of 0, 2.1×10^{-210} and 3.8×10^{-175}, respectively) (Figs. 2a–c, 3 and S-6). A principal component analyses on the physico-chemical parameters from EDI and microbialite-hosting environments databases outlined that ~88 % of the variance of all these aqueous environments is explained by the activity of Cl^- or Ca^{2+} (70.2 % of the variability) and DIC (17.9 %) (Fig. 2d). The EDI lakes spread as
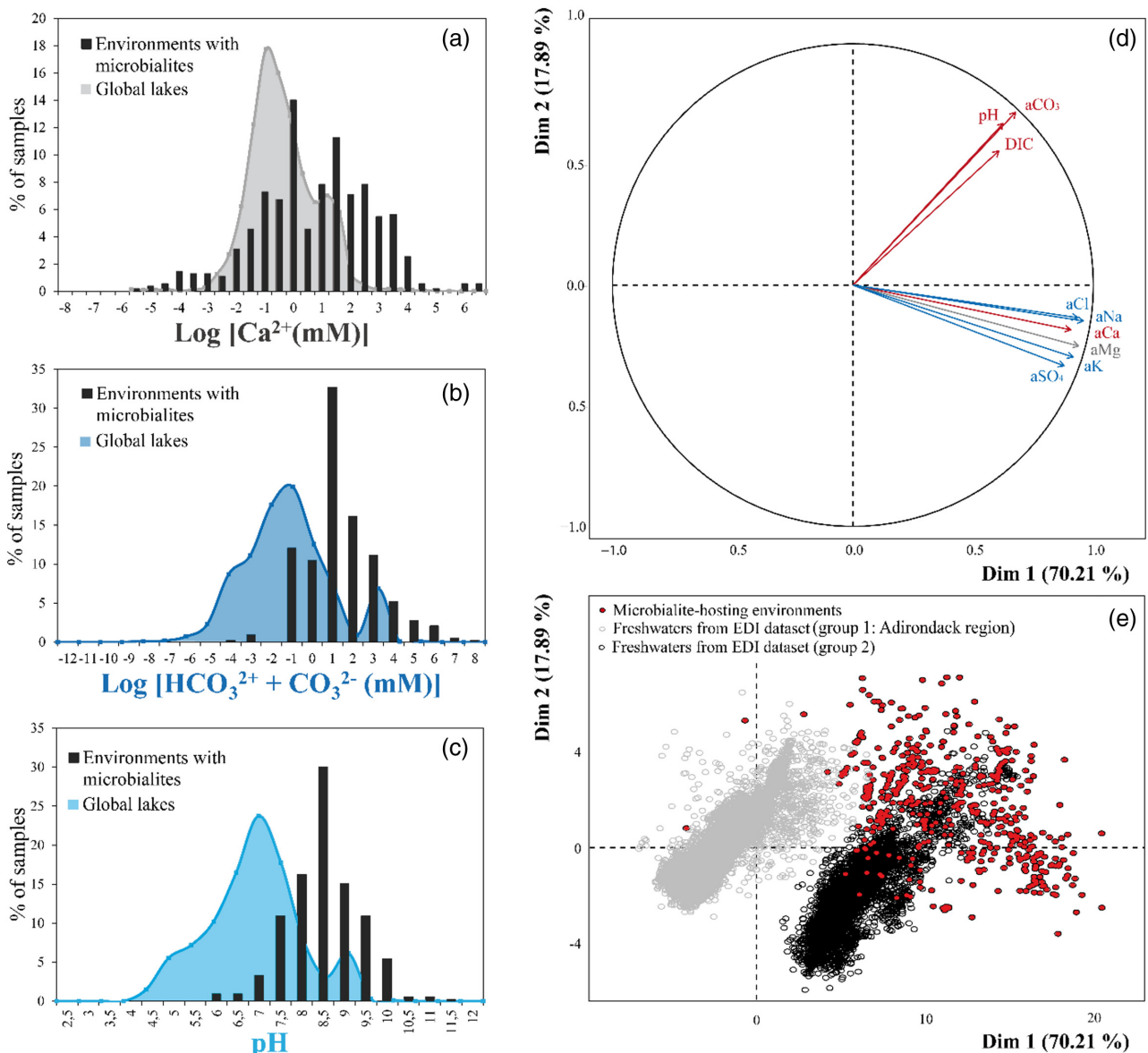

Figure 2 Comparison of the microbialite-hosting environments and lakes in the EDI and GLEON databases. Compared distributions are **(a)** the log [Ca^{2+}(mM)], **(b)** the log [$HCO_3^- + CO_3^{2-}$ (mM)] and **(c)** the pH of the microbialite-hosting environments (black bars) and the EDI and GLEON databases (grey or blue surface). Ca^{2+} activities were calculated using all major ion concentrations in the EDI database, whereas they were approximated to concentrations in the GLEON database. Errors due to this approximation are estimated to be minor (Fig. S-7). **(d)** Correlation circle from the global PCA of the physico-chemical parameters of EDI lakes and microbialite solutions. The logarithms of the activities and DIC were used. The colours correspond to those used to differentiate the principal components on the microbialite-hosting environments PCA (Fig. S-4). **(e)** Plot of all aqueous environments hosting microbialites (red dots) and from the EDI database (black and grey dots) along the two main dimensions of the ACP.
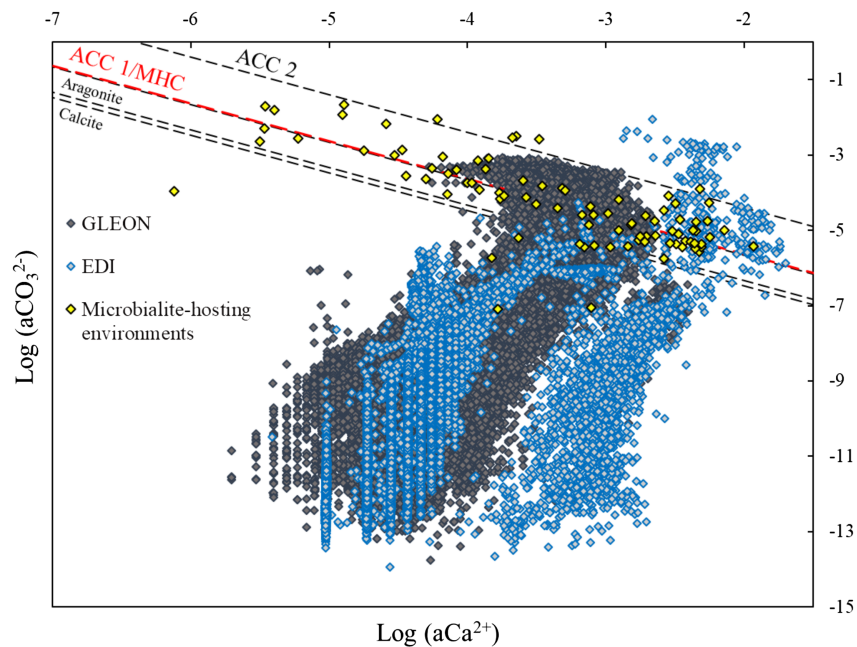
Figure 3 Plot of the activity of CO_3^{2-} vs. Ca^{2+} for all lakes from the EDI (blue diamonds), GLEON (grey diamonds) and microbialite-hosting environments (yellow diamonds) datasets. Solubility lines of aragonite, calcite, monohydrocalcite and ACC are the same as in Figure 1.

two groups in the plot of the two PCA dimensions. One group contains Adirondack region lakes (USA), including Mirror Lake, New York, whereas the second group is composed of all other more saline lakes. In this plot, microbialite-forming solutions mostly plot separately and stretch orthogonally to the freshwaters from the EDI database (Fig. 2e). GLEON data were not included in this PCA analysis, because too many parameters were missing.

Finally, by plotting the EDI and GLEON environments in the $CaCO_3$ solubility diagram, less than 5 % of them show saturation with ACC/MHC (Fig. 3).

Discussion

Saturation with vaterite/ACC/MHC as a necessary condition for the formation of microbialites. The need for a relatively high apparent critical saturation of the solutions so that microbialites form is suggested by the analysis of the compiled database. Arp *et al.* (2001) argued that a SI of ~1 relative to calcite was required for biofilm calcification to occur, based on the study of modern non-marine calcifying cyanobacterial biofilms. Such a value approximately corresponds to the solubilities of vaterite, ACC1 or MHC. Moreover, Fukushi *et al.* (2020) observed that several alkaline lakes were saturated with MHC and suggested this phase as a precursor of anhydrous carbonates. Accordingly, many microbialite-hosting environments in our database are alkaline. More recently, the same observation was done by Zeyen *et al.* (2021) in microbialite-hosting lakes in Mexico, who suggested ACC as an alternative precursor. In order to explain these observations, they proposed that ACC may precipitate first, before transforming to the less soluble MHC, then anhydrous carbonate phases, including vaterite. Here, based on a new database of 140 microbialite-bearing systems, encompassing freshwater, saline and hypersaline conditions, we generalise this observation to all environments where microbialites form, suggesting that saturation with ACC1/MHC or with vaterite appears as a necessary condition for the formation of modern microbialites. This model may be further adjusted in the future.

The ACC1 solubility line reported in Figure 1 is a lower bound for ACC. Indeed, the solubility of ACC increases with the Mg content (Mergelsberg *et al.*, 2020). According to Blue and Dove (2015), the partition coefficient K_d of Mg *vs.* Ca in ACC is constant (0.047) for pH below 9.5. Based on this, the Mg/Ca ratio in ACC possibly formed in microbialite-bearing systems ranges between 0.012 and 225, which may correspond to a variation in solubility by ~1 log unit.

Several conditions may allow the achievement of relatively high SI values with $CaCO_3$ as observed in microbialite-hosting environments. Aqueous alkaline environments are fed by fluxes of Ca^{2+} and HCO_3^- ions, *e.g.*, from water-rock interactions, and/or atmospheric inputs (Pulido-Villena *et al.*, 2006). This generally does not directly create high saturation conditions, except when locally, *e.g.*, Ca^{2+}-rich groundwater outflows in high DIC lakes such as in Lake Van (Shapley *et al.*, 2005). In many cases, evaporation is a major driver for concentrating solutions and achieving high saturation with $CaCO_3$ (Pecoraino *et al.*, 2015). This is consistent with the abundance of microbialites in saline environments. The SI values of aqueous solutions are not controlled by the precipitation of crystalline anhydrous $CaCO_3$, which are the least soluble $CaCO_3$ phases. Instead, SI values are higher. Recently, Pietzsch *et al.* (2022), suggested that in some alkaline lakes, orthophosphate concentrations are high and inhibit crystalline anhydrous $CaCO_3$ precipitation, allowing the onset of saturation levels as high as the solubility of ACC. Unfortunately, this cannot be further tested here since dissolved PO_4^{2-} concentrations are only reported in eleven microbialite-forming environments of our database. Similarly, the role of exopolymeric substances (EPS) in locally controlling SI values could be questioned. Whether this inhibition may be a major process in all reported microbialite-hosting environments will require further data acquisition. Once Ca^{2+} and CO_3^{2-} activities reach values high enough so that MHC/ACC solubility is attained, we hypothesise that any further input of Ca^{2+} and/or DIC to the system can contribute to the accumulation of carbonates, partly as microbialites, helping to control their overall abundance in the aqueous system.

Another outcome of the present analyses is that they may help in finding localities where modern microbialites have been potentially overlooked so far, by screening aqueous environments based on their SI with $CaCO_3$ (Fig. 3). Some environments listed in the GLEON and EDI databases are saturated with ACC/MHC. However, we presently do not know if they host microbialites. Two options are possible: (i) all these environments host microbialites, which would imply that saturation with ACC/MHC is a necessary and sufficient condition for microbialite formation; and (ii) some of these environments do not contain microbialites, which means that some other conditions may be necessary in addition to saturation with ACC/MHC to form microbialites.

Presently, it may be speculated that changes in seawater chemistry, possibly at the end of the Proterozoic, from ACC-saturated to ACC-undersaturated seawater, may have caused the decline of microbialite abundances (Fig. S-8). However, to be validated, this speculation will need further constraints on the value of SI_{ACC} in past oceans.

Finally, a control of water chemistry by MHC/ACC precipitation as a necessary condition for the growth of microbialites does not mean that microbial communities or any biological parameter have no impact at all in the formation of microbialites. Instead, it suggests that in order for them to participate in authigenic microbialite formation, at least some specific physico-chemical environmental conditions, *i.e.* saturation with ACC/MHC, must be met.

Acknowledgements

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2311.

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