



Interaction of temperature, salinity and extracellular polymeric substances controls trace element incorporation into tufa calcite

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Abstract

The influence of extracellular polymeric substances on carbonate mineral growth in natural settings remains one of the most poorly understood contributors to the growth of non-marine carbonate sediments. The influences of these materials are complicated by their association with living cells creating local microenvironments via metabolism and enzyme production, and by our uncertainty about the extracellular polymeric substances materials themselves. Different mixtures of extracellular polymeric substance molecules may behave in different ways, and differences in the local physical environment may alter how the mixtures influence mineral formation, and even result in different patterns of polymerization. Here, the influence of extracellular polymeric substances on calcite precipitation rate and Mg/Ca_{calcite} in the absence of cells is investigated using extracts of extracellular polymeric substances from temperate fluvial tufa biofilm. The influence is complex, with the concentration of extracellular polymeric substances in solution altering deposition rate and trace element incorporation. Moreover, the results show interaction of the presence/absence of extracellular polymeric substances and both temperature and salinity. However, despite extracting extracellular polymeric substances from the same parent sample, a uniform influence was not found in these experiments, implying that the mixture is sufficiently variable within a sample for microenvironments within the biofilm to either promote or inhibit mineralization. As sedimentologists, we can no longer take the view that extracellular polymeric substances are a bystander material, or that they have a single set of coherent and predictable or intuitive influences. Rather, the emphasis must be on investigating the specific mixtures present in nature, and their complex and dynamic interaction with both mineral surfaces and hydrochemical conditions.

1 | INTRODUCTION

The growth of calcite crystals can be manipulated by the addition of a range of organic additives (Meldrum & Cölfen, 2008), permitting specific growth forms to be created (Meldrum & Ludwigs, 2007), and a range of materials to be

incorporated into the lattice, including fully tuneable fluorescence (Green et al., 2016). This concept has been successful in explaining biomineralization and skeletal growth, to the extent that it has been proposed that hydrogel scaffolds could be used to grow artificial bone grafts in humans (Kurian et al., 2019). The structure and trace element composition

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of carbonate skeletons (Allemand et al., 2004) and tests (De Nooijer et al., 2014) depends on similar organic-calcite interaction. It has long been established that similar processes occurred in freshwater limestones (tufa) (Braissant et al., 2003). Increasingly, it is recognised that organic-calcite interactions are the primary control determining the trigger for precipitation of tufa (Pedley et al., 2009), its structure (Mercedes-Martin et al., 2017) and trace element incorporation (Saunders et al., 2014). As tufa precipitates are generally considered bio-influenced rather than biomediated (Dupraz & Visscher, 2005), there is less control on the sites of mineral nucleation in tufa than in comparable sites in coral skeleton growth. Consequently, the chemistry of fluids at these sites is far more able to vary, and little is known about how local conditions will alter the properties of the mineral formed. This paper takes the first steps towards establishing the joint control of organic influence and local environment, by investigating the combined impact of naturally occurring organic additives, salinity and temperature on calcite precipitation in the absence of metabolic processes.

1.1 | Extracellular polymeric substances and their role in tufa formation

The precipitation of calcite in karstic streams generally occurs in the presence of microbial biofilms. It is well accepted that microorganisms have some influence on calcite precipitation through varying mechanisms such as metabolic processes (Bissett et al., 2008; Merz-Preiss & Riding, 1999; Shiraishi et al., 2010) and acting as nucleation sites to enhance precipitation rates (Bosak & Newman, 2003). Nucleation happens on the surface of cells (Brasier et al., 2018), but also on hydrogels of extracellular polymeric substances (EPS). These materials generally account for between 50% and 90% of the total organic matter of a biofilm (Wingender et al., 1999), so an understanding of its role is a crucial step in the quest to discover the full role of biofilms in calcite precipitation. It has been reported that the chelation of Ca^{2+} ions to EPS is initially an inhibiting factor in carbonate mineral precipitation in seawater (Kawaguchi & Decho, 2002), however, in vitro experiments have shown this may not be the case in a freshwater setting (Pedley et al., 2009; Rogerson et al., 2008) and the presence of anionic functional groups on EPS molecules may help initiate calcite precipitation through the unidentate bonding of Ca^{2+} to the anionic groups (Decho, 2010). Furthermore, the binding of Ca^{2+} to EPS molecules can reduce the activation energy barrier which usually limits spontaneous precipitation (Dittrich & Sibbler, 2010), indicating that the presence of EPS may result in greater precipitation rates. The ability of isolated EPS molecules to precipitate calcite in the absence of the microbial processes of the associated organisms has been observed experimentally (Dittrich &

Sibbler, 2010; Ercole et al., 2007; Kawaguchi & Decho, 2002; Tournay & Ngwenya, 2009). These processes likely operate via electrochemical influences operating between dissolved or hydrated EPS molecules and ions within ambient water, and consequently are sensitive to the ionic strength of the solution (Rogerson et al., 2014).

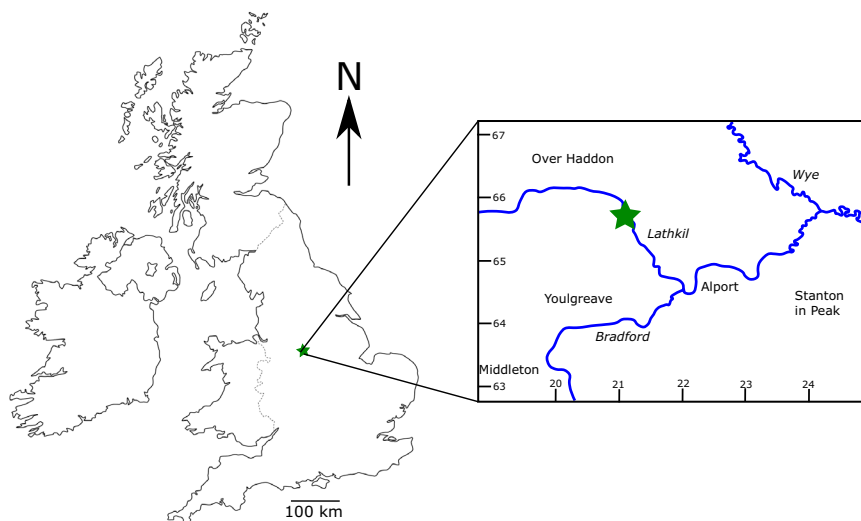
1.2 | Trace element incorporation into tufa carbonate

Incorporation of trace elements into carbonates frequently provides critically important information about past environments, from ocean surface conditions in foraminiferal tests (Allen et al., 2016) and coral skeletons (Fowell et al., 2016) to recharge processes overlying speleothems (Rossi & Lozano, 2016). Similar ratios of trace elements to calcium have been used in tufa geochemistry studies over the last 20 years (Dabkowski et al., 2019; Garnett et al., 2004; Ihlenfeld et al., 2003; Sironić et al., 2017; Wróblewski et al., 2017), but use of these proxies is complicated by the organic-calcite interactions described above (Saunders et al., 2014). Clearly, full development of these proxies will require effective biomineralization models comparable to those that have been found to be necessary in foraminifera (Evans et al., 2018) and corals (Marchitto et al., 2018). Understanding how the organic components in the tufa system cause trace element incorporation to deviate from the inorganic thermodynamic equilibrium will be a key step toward this. As there is a continuum of depositional contexts from strictly freshwater 'tufa' to geothermal 'travertine' and even marine biofilm deposition, this investigation centres on the roles played in controlling carbonate Mg/Ca from temperature, concentration of EPS and salinity.

2 | METHODS

Tufa biofilm was collected from artificial substrates put into the River Lathkill (Derbyshire, UK grid reference SK 225 645; Figure 1) for >2 years. These substrates had accumulated substantial carbonate growth associated with a diverse diatom-cyanobacterial biofilm, similar to that used in previous experiments (Pedley et al., 2009; Rogerson et al., 2008). From this material, an aliquot of 10 ± 0.2 g was removed for extraction of organic components following the heat extraction approach of Barranguet et al. (2004). To this, 24 ml of ultrapure water (18 M Ω) was added in a 50 ml conical flask. The mixture was shaken vigorously to ensure mixing and then placed in a preheated oven at 130°C for 2 h (Barranguet et al., 2004). The solution was gently shaken every 20 min while in the oven. After heating, the solution was allowed to cool before being centrifuged at 3300 rpm for 15 min.

FIGURE 1 Location of biofilm sampling site. Numbers in inset indicate UK National Grid reference within the SK block



The supernatant was filtered through 11 μm filter papers and then through 0.2 μm filter papers into sterilised sterilin tubes to ensure the EPS solution was free from cells. This yielded an EPS solution with a dissolved organic component of 0.925 ± 0.025 mg/L.

Experimental treatments were created by adding volumes of EPS solution (or no solution) to 25 mL of natural-analogue water supersaturated with respect to calcium carbonate. Experiments investigating the influence of temperature were conducted in clear conical flasks mounted on a Stuart SF1 flask shaker (Bibby Scientific Limited) which was set to 100 oscillations per minute, with temperature controlled via a water bath using the approach of Saunders et al. (2014). Otherwise, experiments were conducted in clear plastic Petri dishes to reduce sample volumes. In both cases, each contained two frosted glass microscope slides. The flasks, dishes and slides were sterilised with pure ethanol. Where the ionic strength of the solution was manipulated, this was done by adding heat sterilised $\text{NaCl}_{(s)}$ directly to the mixed solution. Lids were placed on each dish, which were sealed by applying a thin coating of clear silicone gel to ensure no infection occurred during the experiment. The dishes were then covered to exclude light and left under controlled conditions for 27 days within an air-conditioned laboratory at 16°C . The standard deviation of temperature variability through all experiments was $<0.5^\circ\text{C}$.

At the end of the experiment, the lids were carefully removed and a sample of the dish solution was taken from each dish and immediately acidified by dilution with 5% ultrapure HNO_3 for determination of Ca^{2+} and Mg^{2+} concentrations by inductively coupled plasma-atomic emission spectroscopy (ICP-OES). The slides were gently rinsed with ultra-high quality water and returned to new Petri dishes and placed in an oven at 60°C to dry. The washing of the slides was done to ensure no further precipitation could take place during the drying process. Ultrapure 10% HNO_3 was gravimetrically added to each dried dish to dissolve the precipitates on the

slides. Each dish was left for 2 h and shaken gently every 20 min to aid dissolution.

Experimental water was collected from a spring sourced by a Cretaceous chalk aquifer at Welton Beck, East Yorkshire (UK grid reference SE 965 275). It was analysed for its Ca^{2+} and Mg^{2+} concentrations by ICP – OES. Acetates of calcium ($\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$) and magnesium ($\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$) (Alfa Aesar) were added to the spring water to bring the concentrations of Mg^{2+} and Ca^{2+} to a constant 51 ± 1.8 and $1,544 \pm 19.8$ mg/L respectively, giving a Mg/Ca molar ratio of 0.054 ± 0.002 . Using a natural water provides a more suitable matrix in which to perform these experiments than a solution based on UltraPure water, which would lack the range of minor ions present in nature. In addition, using a stock water already rich in Ca and Mg achieves a constant concentration and ratio of these metals, while adding a minimum concentration of counter-ions. The saturation state of the experimental solution was determined using the aqueous geochemical modelling software PHREEQC. The saturation index for the experimental solution was 1.64 at 16°C . In the case of flask experiments, 50 ml solution was used and in the case of Petri dishes 25 ml solution was used.

The analyses were carried out on a Perkin Elmer Optima 5300DV ICP-OES instrument at the University of Hull. The selection of the analytical lines used in the results was based on the Perkin Elmer recommendations for the Optima 5300 DV spectrometer, 393.366 nm for calcium and 280.271 nm for magnesium. Calibration standards were prepared using 1,000 ppm standard stock solutions (99.9% pure or greater, PrimAg, Xtra, Romil) of calcium and magnesium. Mixed standards of calcium and magnesium were prepared through dilution with 2% ultrapure HNO_3 to give calibration standards of 1, 2, 3, 4 and 5 ppm for calcium and 0.1, 0.2, 0.3, 0.4 and 0.5 ppm for magnesium. Samples for analysis were diluted with 5% ultrapure HNO_3 to bring the expected concentrations to within or very near the linear calibration of the standards.

3 | RESULTS

3.1 | Influence of the presence of EPS

For this experiment, Petri dishes were used to house the solution. Four replicates were run for each treatment, and for a control with no EPS addition. Figure 2A shows the influence of EPS on the Mg/Ca of calcite, and Figure 2B shows the precipitation rate, calculated from the loss of calcium from the parent solution. It is probably a small mass of calcium and magnesium is chelated to EPS during these experiments in addition to that deposited as calcite, but masses released during slide washing were minor compared to mineral

accumulation. These data reveal a simultaneous reduction in calcite precipitation and rise in the Mg/Ca of the mineral precipitated. Both trends appear to be quasi-linear across the range investigated in these experiments. Figure 2C shows the interaction between the controls, emphasising that addition of EPS tends to result in slower precipitation, and higher Mg/Ca in the precipitate.

3.2 | Influence of salinity

For this experiment, Petri dishes were used to house the solution. Two replicates were run for each treatment for control (no EPS)

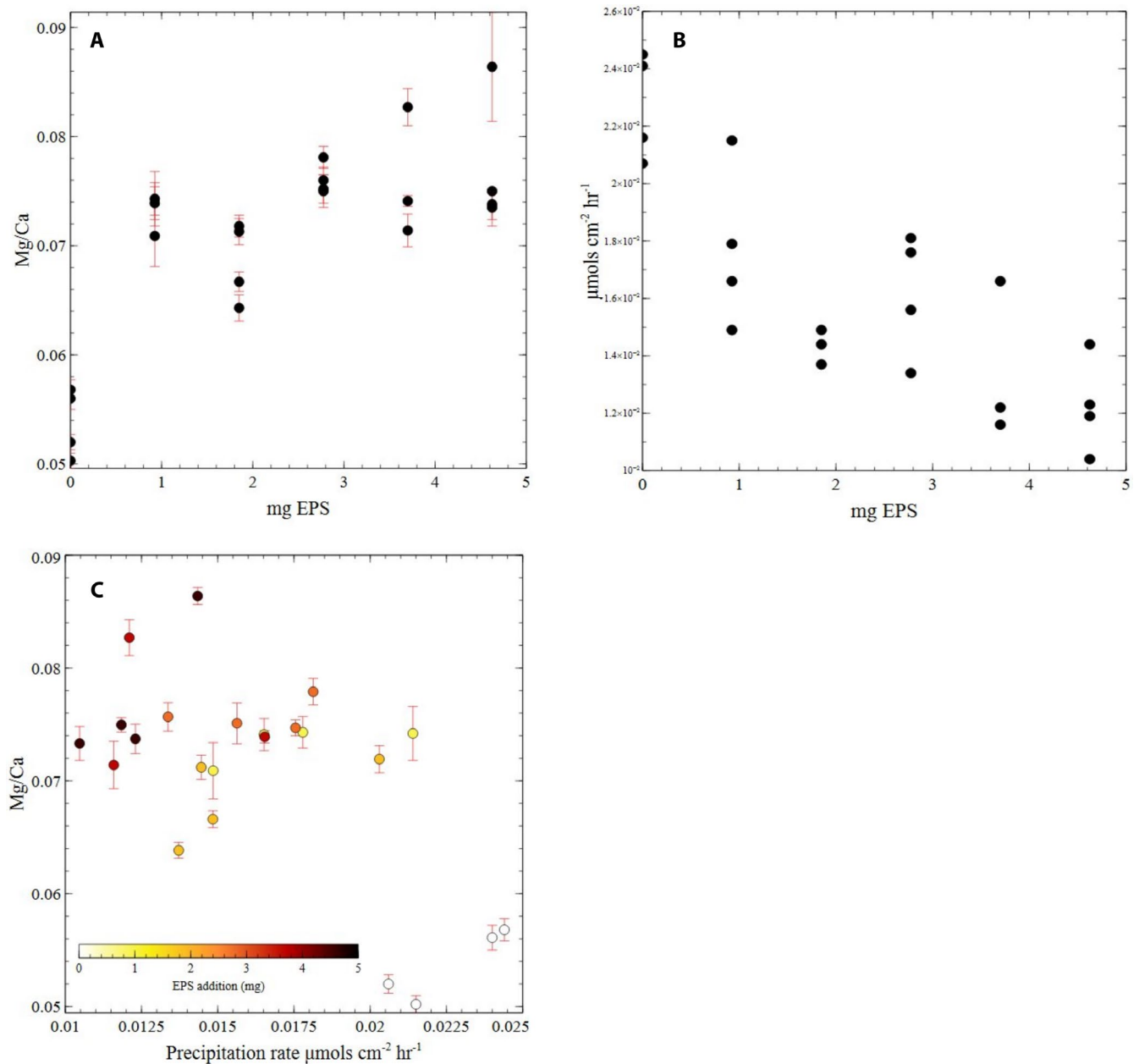


FIGURE 2 (A) Relationship of Mg/Ca and addition of EPS. Error bars are measurement uncertainty. (B) Relationship of precipitation rate and addition of EPS. (C) Interaction of EPS addition, precipitation rate and Mg/Ca. Error bars are measurement uncertainty

and treatment (3 ml EPS solution, forming a 0.05 mg/L concentration of EPS) respectively. A concentration of 0.05 mg/L EPS was selected for this experiment, as this placed it in the middle of the range used for the previous experiment, helping integration of results. Figure 3A shows the Mg/Ca of control and treatment experiments respectively, and Figure 3B shows the precipitation rate for the two experiments. No systematic change in Mg/Ca and only a slight reduction in precipitation rate is found in the absence of EPS, but both change significantly with rising salinity with EPS present. Precipitation was also higher in most experiments where EPS was present, with the gain over control reducing as salinity increased. Figure 3C shows the increasing Mg/Ca with falling precipitation for EPS-treated solutions, and the overall control from salinity. With EPS present, Mg/Ca rises as precipitation rate falls in a similar manner to that seen in the concentration experiment (Figure 2C), meaning that high salinity tends to lead to raised Mg/Ca.

3.3 | Influence of temperature

For this experiment, flasks were used to house the solution, so that a controlled temperature different to the ambient laboratory (16°C) could be maintained. Both control (no EPS) and treatments (3 ml EPS solution, forming a 0.05 mg/L concentration of EPS which lies at the middle of the range of conditions used for the variable EPS concentration experiment) were run, with two replicates at 12.1 ± 0.5, 14.3 ± 0.2, 16.3 ± 0.2, 18.3 ± 0.3 and 20.5 ± 0.5°C. Figure 4A shows Mg/Ca for both control and EPS treated solutions, and Figure 4B shows precipitation rate for EPS treated samples. From 12 to 18°C, precipitation rate falls and Mg/Ca rises with temperature, and there is little difference between control and EPS treated flasks. However, at 20°C, there is a dramatic change, with an order of magnitude increase in precipitation rate and a matching decrease in Mg/Ca. Figure 4C shows the relationship between precipitation rate and Mg/Ca for the EPS-treated samples, showing the same tendency to a non-linear inverse relationship. The fit shown in Figure 4C has the form $\text{Mg/Ca} = 0.00069 \times \text{precipitation rate}^{-0.804}$, which is very comparable to the value previously published for living biofilms in similar experiments (Saunders et al., 2014).

4 | DISCUSSION

4.1 | Control of calcite precipitation rate by EPS

The results shown in Figures 2 and 3 provide further evidence that the presence of dissolved organic matter at sites of precipitation will influence carbonate precipitation kinetics, even in the absence of metabolism from living cells. This has been

established both for laboratory systems where manufactured molecules are provided to the precipitation solution (Meldrum & Cölfen, 2008) and for natural extracts of organic matter from biofilms (Dittrich & Sibling, 2010; Kawaguchi & Decho, 2002). However, the presented data are ambiguous whether the presence of EPS will enhance or impede precipitation, with different extracts from the original biofilm sometimes raising precipitation rate (Figure 3B) and sometimes reducing it (Figure 2B). It is worth considering that the EPS concentration used in the zero ppm salinity experiment (Figure 3B) is in the middle of the range used in the EPS concentration experiment (Figure 2B). All of these extracts were from a single parent sample from the River Lathkill, and extracted in the same way. Clearly, the parent material is heterogeneous, and the specific characteristics of the EPS extracted have widely different consequences for carbonate precipitation.

These EPS mixtures are challenging to characterise. They comprise a mixture of polar and non-polar organic components, each assembled from a relatively limited range of carbon chain and functional group components (Dittrich & Sibling, 2010). However, the way in which the molecule is assembled can alter its behaviour considerably, even to the level of the chirality (i.e. symmetry) of the molecule potentially changing its behaviour. They may also change their behaviour depending on the state of the solution (Decho et al., 2005), making this an especially difficult problem to solve. The most likely active agents in the organic-carbonate system are polar, as these components are most able to bind either onto dissolved ions or onto the growing surface of the crystal (Meldrum & Cölfen, 2008). The functional groups providing polar characteristics to these molecules are generally polysaccharides such as amino or fatty acids and glycoconjugates with reactive functional groups including carboxylic, phosphoric, sulphhydryl, amin-phenolic and hydroxyl bonds (Dittrich & Sibling, 2010). Indeed, the balance of amino and hydroxyl groups in otherwise similar EPS has been shown to strongly influence precipitation rate in a manner analogous to the findings reported here (Li et al., 2017; Shiraishi et al., 2017).

The different extractions made differed in composition, revealing that the precipitation environment within the biofilm itself is highly heterogeneous. Assuming that the probably cause of differences in these experiments arises from change in the functional group ratio (cf. Li et al., 2017), it is possible to conclude that the influence of the organic component of biofilms varies on a millimetre scale and is independent of influences arising from metabolism. Research needs to move on from the established perspective of sedimentologists to consider 'how EPS influences precipitation', or to explicitly link precipitation processes to organism metabolisms. A dedicated survey of the composition, variance and influence of the mixtures of EPS arising in nature are urgently needed.

The changing influence of EPS as the salinity (Figure 3) and temperature (Figure 4) of the solution is altered

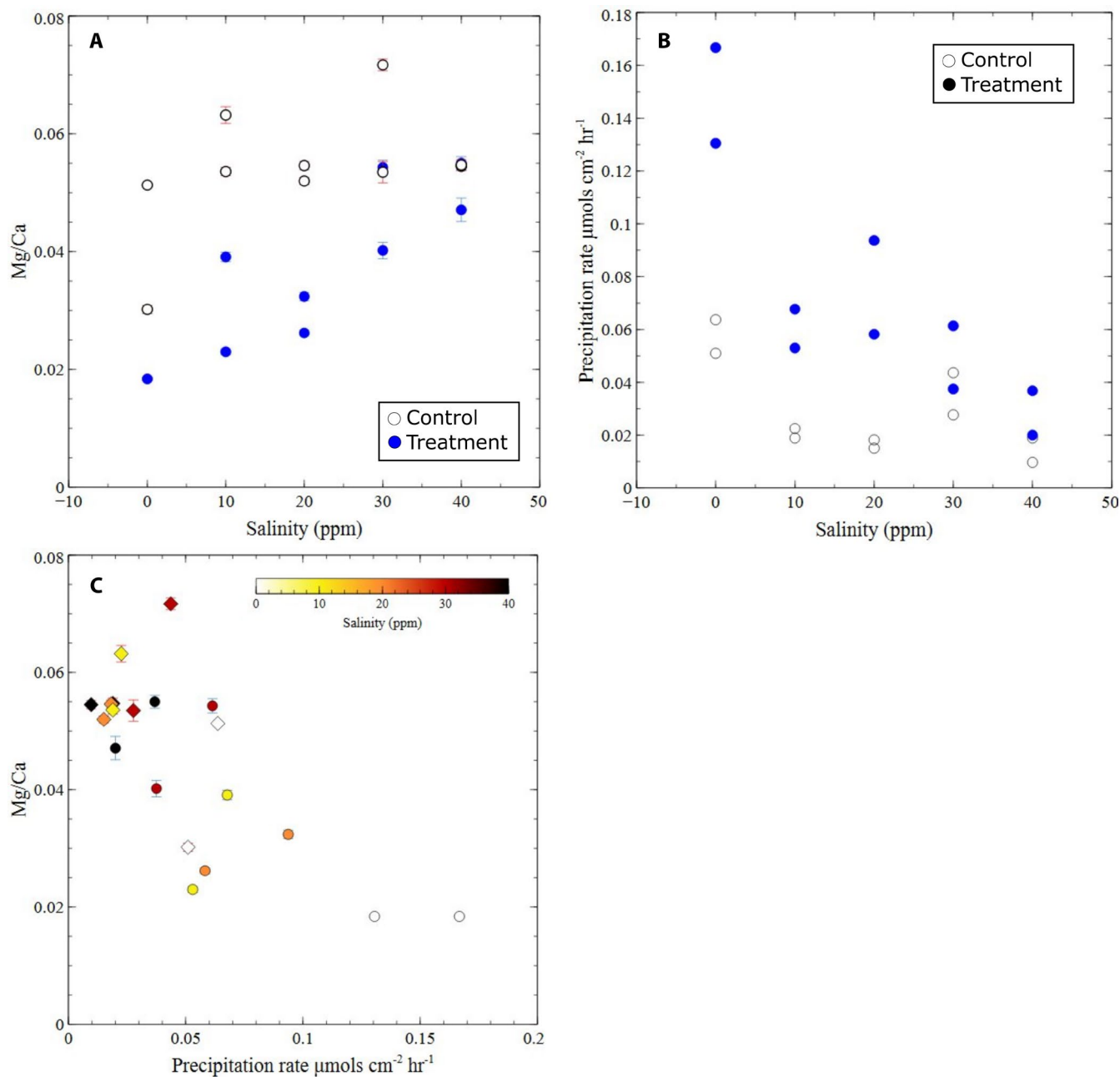


FIGURE 3 (A) Relationship of Mg/Ca and salinity. Filled circles are in the presence of EPS, and open circles are in its absence. Error bars are measurement uncertainty. (B) Relationship of precipitation rate and salinity. Filled circles are in the presence of EPS, and open circles are in its absence. (C) Interaction of salinity, precipitation rate and Mg/Ca in the presence (circles) and absence (diamonds) of EPS. Error bars are measurement uncertainty

demonstrates that there is important interaction between the organic and inorganic components of the solution. The abrupt and spectacular change in the system behaviour at the highest temperature investigated (20°C , Figure 4) may reflect a protein thermally denaturing, and a consequent change in the behaviour of one or more components of the EPS present in this experiment. It is interesting that the EPS extracted in this experiment has ‘cooked’ at a temperature low enough to be within the envelope of natural environmental variance. This limit on the stability of the EPS components may reflect the

natural variability of water temperature in their habitat, as 20°C represents the most extreme warm days recorded in monitoring efforts of adjacent catchments in Derbyshire UK (Dove and Manifold) (Toone et al., 2011). However, monitoring reveals that water average temperature in English rivers is rising by *ca* $0.03^{\circ}\text{C}/\text{year}$ (Orr et al., 2015). It is thus possible that riverine tufa formation may be vulnerable to contemporary and future climate change, and further investigation of EPS composition will also be needed to elucidate this possibility. Regardless, temperatures $>20^{\circ}\text{C}$ will certainly

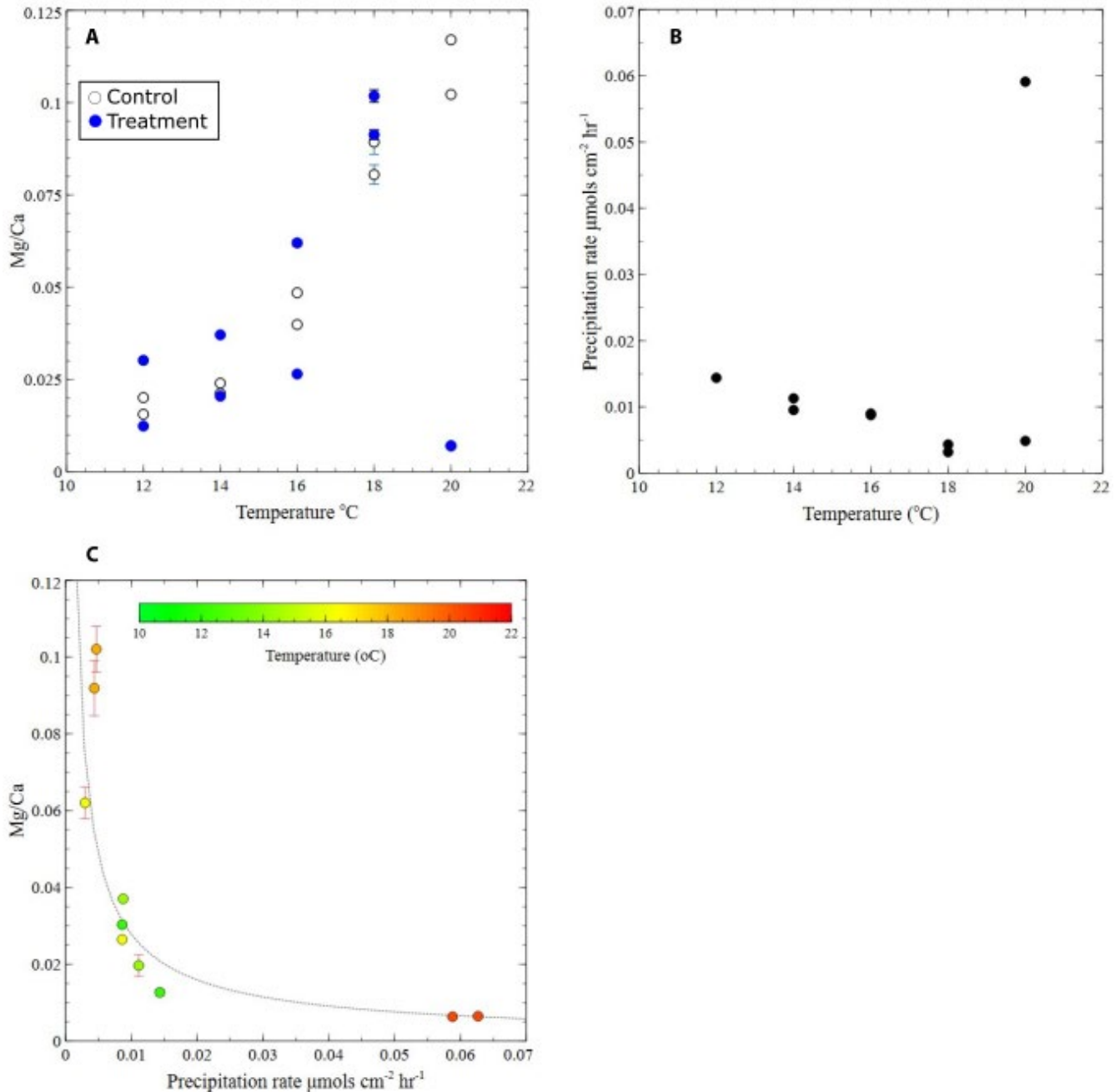


FIGURE 4 (A) Relationship of Mg/Ca and temperature. Filled circles are in the presence of EPS, and open circles are in its absence. Error bars are measurement uncertainty. (B) Relationship of precipitation rate and temperature. (C) Interaction of salinity, precipitation rate and Mg/Ca in the presence of EPS. Error bars are measurement uncertainty. Line shows fit with regression $0.00069 * x^{-0.804}$

be routinely achieved on hot days in shallow/still pools and river margins, so transient changes in EPS-calcite interaction may be a generic feature of tufa systems which has yet to be investigated.

4.2 | Influence of isolated EPS on Mg/Ca

The results presented here show that, generally, the Mg/Ca of calcite precipitated is enhanced in the presence of EPS

(Figures 2A and 3A). This is consistent with previous experiments, which have demonstrated that polar EPS molecules bind metal ions, and that ions with low charge density are selectively bound (Rogerson et al., 2008). The consequence of this binding can be that calcite precipitation is favoured due to immobilisation of calcium ions (Zippel & Neu, 2011) or impeded by reduction of calcium concentration in solution (Decho et al., 2005). Here, the emphasis is on the latter (Figures 2A and 3A) and the rise in $Mg/Ca_{(calcite)}$ can be considered a direct consequence of the rise in $Mg/Ca_{(solution)}$ caused by calcium

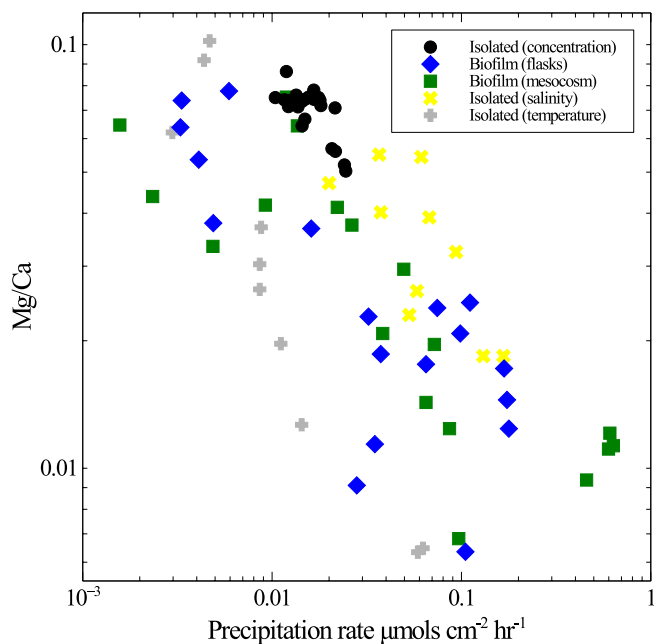


FIGURE 5 Precipitation rate against Mg/Ca for isolated EPS and experiments with living biofilm. Note logarithmic axes

chelation by EPS locally at sites of precipitation. The observation that Mg/Ca increases with falling precipitation rate gives further support that this is the primary control, as generally incorporation of the less abundant ion would increase with precipitation rate if this was a kinetic fractionation.

Combining the results of the isolated EPS experiments presented here with previously published experiments with living biofilms (Saunders et al., 2014) show similar behaviour, although with some scatter arising from the different conditions of the experiment (Figure 5). The link between low precipitation rate (i.e. high influence of EPS-bound calcium) and high Mg/Ca is persistent between these experiments, demonstrating that this is a metabolism-independent process comparable to what is found in metazoans (Pérez-Huerta et al., 2008).

5 | CONCLUSIONS

Extracellular polymeric substances regulate the rate of precipitation and trace element incorporation into tufa calcite, even in the absence of living cells. The control on trace element incorporation into tufa calcite, including Mg/Ca, largely arises from organic-metal interaction before precipitation, overcoming inorganic thermodynamic and metabolic controls. However, the impact will be highly context dependent. Where there is a net production of EPS molecules, it is probably that precipitation will have increased Mg/Ca as calcium is bound to the organic components and becomes unavailable for precipitation. Where there is a net consumption of EPS, the release of bound calcium is probably to cause decreased Mg/Ca.

However, the specific impact depends on the composition of the EPS at the site of mineral formation. This composition is variable at millimetre scale, to the extent that different microsites within a biofilm may exhibit opposite tendencies. Clearly, the assumptions that (a) EPS is essentially a ‘bystander’ to processes which are either inorganic or metabolically forced and (b) that the impact of EPS can be established as a single, homogenous feature of tufa sedimentology is false. Process-based understanding of these systems will require detailed and wide-ranging assessment of the organic geochemistry of the materials which make up this complex material. Moreover, the observed interaction with environmental conditions (e.g. salinity) which may be non-linear (e.g. high-temperature ‘cooking’ EPS molecules) indicate that even where the local recipe for EPS is known, its sedimentological impact may still vary between and within sites, and at different times at the same site.

We need more knowledge of the polysaccharides present at sites of tufa carbonate formation, their functional groups and the stability of those functional groups to environmental variance. The possibility that where a biofilm material is taken beyond its normal envelope of conditions (e.g. ‘high’ temperature, in this case $\geq 20^{\circ}\text{C}$) it may substantially change its influence on calcite formation implies that tufa formation may be significantly altered by contemporary climate change. This adds urgency to the need to close the gap in our knowledge addressed by this study.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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