LIMNOLOGY AND OCEANOGRAPHY
Letters

ASLO
Open Access

Limnology and Oceanography Letters 2024

doi: 10.1002/lol2.10452

SYNTHESIS

Calcium carbonate and phosphorus interactions in inland waters

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Scientific Significance Statement

In many lakes, rivers, wetlands, and streams, calcium carbonate may deposit, forming permanent or temporary features like travertine dams, suspended particles ("whiting events"), or layered microbial structures. When $CaCO_3$ forms, it may sequester phosphorus, a nutrient necessary for all life. However, much remains unknown about the ecological implications of this feedback and the extent to which it is ubiquitous across aquatic ecosystem types. This paper provides a comprehensive review of how the formation and dissolution of $CaCO_3$ impacts phosphorus cycling across inland water ecosystems, highlighting open research areas.

Abstract

Phosphorus, an element essential to all life, is impacted by calcium carbonate ($CaCO_3$) co-precipitation and dissolution dynamics across aquatic ecosystems. Changes to climate, hydrology, and eutrophication, coupled with differences in terminology related to naming $CaCO_3$-producing ecosystems (i.e., chalk, carbonate, karst, travertine), point to the urgency and challenges in understanding this portion of the phosphorus cycle. Forms of $CaCO_3$ vary across inland aquatic ecosystems, from "whiting events" in open waters to massive travertine or tufa formations to cemented layers on basal resources. And, across lakes, streams, and wetlands, periphyton mats and microbialites may form in photic regions. These biogenic carbonate structures beg the question: if aerobic photosynthesis promotes $CaCO_3$ precipitation, but $CaCO_3$ precipitation sequesters P, is this a challenge or opportunity for organisms? This review considers that question and others to better characterize this unexpectedly dynamic and influential portion of a major biogeochemical cycle.

Phosphorus (P) is an essential element in all life. It makes up the backbone of DNA and cell walls, and is used in energy transfer reactions in cells. The availability of P in the environment is often one of the extremes—there may not be enough and it limits growth (e.g., Elser et al. 2007) or there is an excessive amount and it causes "too much" growth, as in the case of eutrophication (e.g., Carpenter et al. 1998; Smith and Schindler 2009). A single P atom may be recycled numerous times in an aquatic ecosystem, supporting higher rates of primary production than otherwise would be expected (e.g., in

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Associate editor: Peter R Leavitt

Author Contribution Statement: JC conceived and designed the study, collected and analyzed the data, and wrote the paper.

Data Availability Statement: Data are available in the Dryad repository at http://datadryad.org/stash/share/KUZ8zXRRhSPh7wguKTLr2rR7oDhVZE1ENa_ISC2REqM.

Additional Supporting Information may be found in the online version of this article.

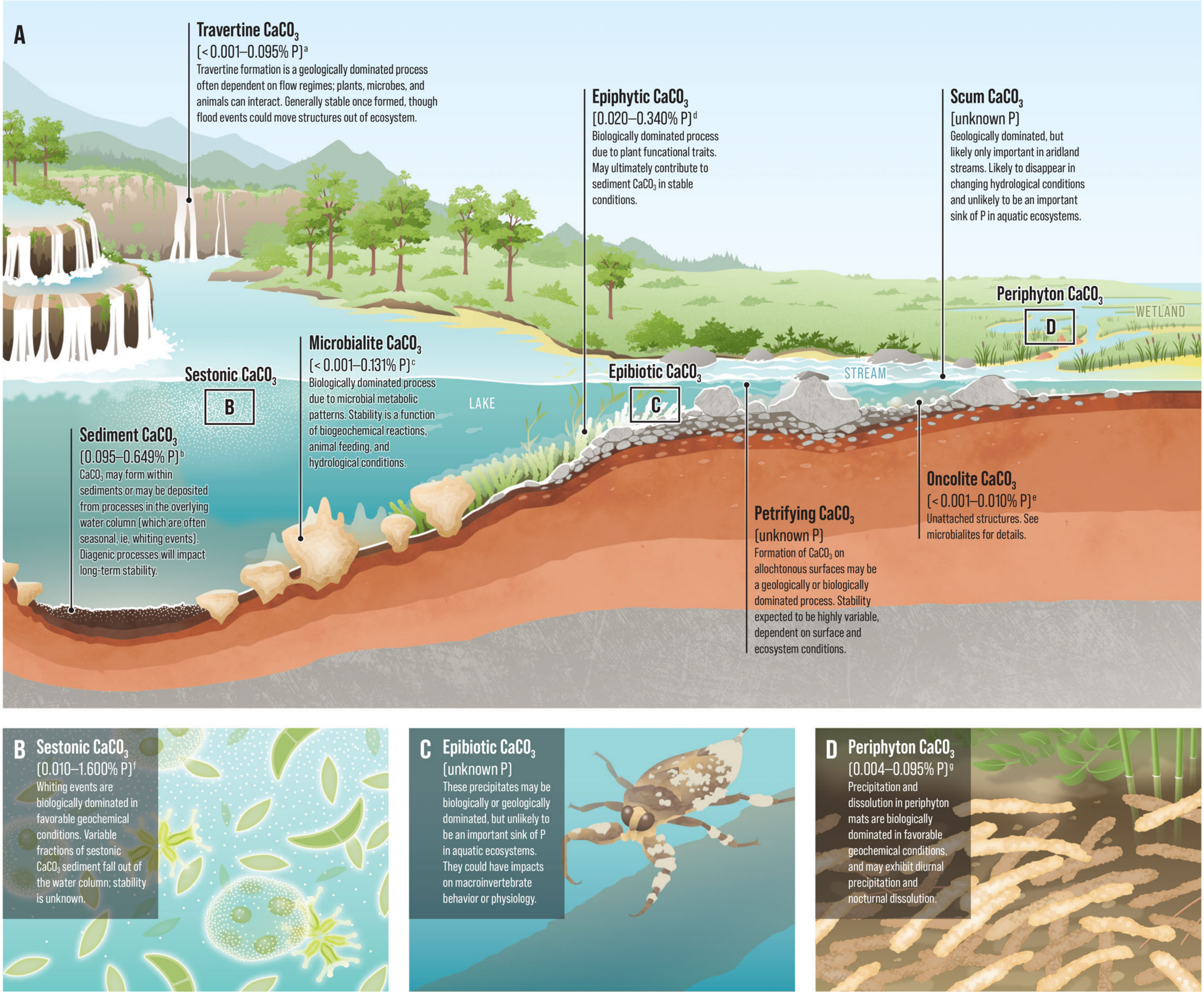
the ocean, 90% of gross primary production is supported by local recycling of organic phosphorus, Karl 2014), particularly in oligotrophic ecosystems (Cotner and Biddanda 2002; Ptacnik et al. 2010). Hence, understanding it is fundamental to understanding many ecosystem processes. Yet, phosphorus cycling is not often reported on or studied at the same intensity as its biogeochemical counterparts, carbon (C), and nitrogen (N) (Jaisi and Blake 2010). While P cycling is simpler than C or N cycling in that P has only a negligible gas phase and its redox state is primarily unchanged, unlike C and N, P cycling may be made bewilderingly complex by its multitude of mineral interactions (Williams and Mayer 1972; Pettersson et al. 1988; Moore and Reddy 1994; Orihel et al. 2017). Indeed, one aspect of P cycling that has received particularly little attention, and the focus of this paper, is that related to co-precipitation dynamics with calcium carbonate ($CaCO_3$). Other sources review phosphorus biogeochemistry more broadly (e.g., Reddy et al. 1999; Canfield et al. 2005; Diaz et al. 2008; Karl 2014; Duhamel et al. 2021).

Co-precipitation of P with $CaCO_3$ can impact ecosystem dynamics across inland aquatic ecosystems, primarily by temporarily or permanently sequestering bioavailable phosphorus (Fig. 1). Of particular interest to biologists and ecologists is that one of the main processes resulting in $CaCO_3$ supersaturation and precipitation—photosynthesis—is a process that itself is influenced by P availability (Elser et al. 2007). Thus, a central research question is to understand when photosynthetically induced $CaCO_3$ co-precipitation of P leads to negative consequences for photoautotrophs. Additionally, there is still much to learn in terms of how this interaction may impact aquatic ecosystem management in a changing climate, present food-web or other ecological constraints, or, given the importance of carbonate microbialite communities throughout much of Earth's history (Arp et al. 2001; Allwood et al. 2006), have influenced evolution of early earth (Toner and Catling 2020).

In this review, I first briefly describe the importance of studying $CaCO_3$-producing ecosystems and the chemistry of $CaCO_3$ deposition and P co-precipitation. This section, and much of the paper, is focused on the impacts of P sequestration via production of $CaCO_3$, though the reverse process, release of co-precipitated P due to $CaCO_3$ dissolution, is equally important. Far fewer studies on this release process exist and the reader is encouraged to keep $CaCO_3$ equilibrium (or lack thereof!) in mind. Next, the review describes our understanding of ecological feedbacks related to $CaCO_3$ deposition, organized by ecosystem type and the process driving $CaCO_3$ formation. I begin with lakes, where this process was first described in the pelagic zone (i.e., "whiting" events), but has been considered in the benthos, as well (e.g., in association with charophytes). Then, I move to wetlands, where $CaCO_3$ deposits are associated with cyanobacterial and periphyton mats. Finally, I discuss streams, where $CaCO_3$ deposits range from primarily abiotically driven (e.g., travertine terraces or dams) to biotically driven (e.g., microbialites and epilithic encrustations). The reader should remember that the types of $CaCO_3$ deposits described in each section are not necessarily unique to those ecosystems—while microbialites are discussed primarily in streams and wetlands, they are also found in lakes (e.g., Pavilion Lake, Canada, Omelon et al. 2013; Lake Alchichica, Mexico, Gérard et al. 2013; Great Salt Lake, USA, Pace et al. 2016). And while whiting events of suspended $CaCO_3$ precipitates are most commonly associated with lakes, $CaCO_3$ precipitation can also occur in the water column of rivers (e.g., Ichetucknee River, Florida, USA, Cohen et al. 2013; Colorado River, Arizona, USA, Suarez 1983). Thus, a reader new to the subject would best be served by reviewing all sections and considering how the structure of their ecosystem(s) of interest may influence the type of $CaCO_3$ deposits and, ultimately, how these different forms and the stability of those forms might influence P cycling (Figs. 1, 2). A discussion of terms used to describe $CaCO_3$-rich structures and ecosystems is included in Table 1 (Text Box 1). Finally, the review ends with a synthesis of research questions related to the topic.

Why study carbonate-phosphorus dynamics in inland aquatic ecosystems?

Understanding the ecological and biogeochemical consequences of co-precipitation of P with $CaCO_3$ within ecosystems is important because the process is globally ubiquitous, is culturally and industrially relevant, and may be impacted by global environmental change. Inland water carbonate-rich ecosystems occur on every continent (Pentecost 2005), including Antarctica (Parker et al. 1981; Mackey et al. 2018). Alkaline waters that could potentially precipitate $CaCO_3$ are abundant worldwide (Marcé et al. 2015), though alkalinity alone does not mean precipitation will occur (Müller et al. 2016). While studies of carbonate-rich inland aquatic ecosystems have occurred across the globe (Fig. 3; Corman 2024), many ecosystems remain unexplored. Global maps of carbonate rocks (Goldscheider et al. 2020) or carbonate-rich soils (Batjes 2016; Gallagher and Breecker 2020) may help identify regions more likely to have $CaCO_3$ precipitation/dissolution dynamics (Pentecost 2005). Carbonate-rich or "calcifying" ecosystems are often culturally relevant sites (reviewed in Li et al. 2020). What would Jiuzhaigou Valley National Park (Sichuan, China), Plitvice Lakes National Park (Croatia), Mammoth Springs in Yellowstone National Park (USA), or Cascadas de Agua Azul (Chiapas, Mexico) be without their iconic carbonate structures? Understanding $CaCO_3$-P interactions is also important to industrial processes. In biotechnological applications, $CaCO_3$ precipitation may be suitable for metal remediation, carbon sequestration, oil recovery, and construction recovery (Zhu and Dittrich 2016). Similarly, precipitation of calcium-phosphorus minerals is used in wastewater treatment to recover P (Moutin et al. 1992). Insights from aquatic ecosystems may help make



Travertine $CaCO_3$
[<0.001–0.095% P][a]
Travertine formation is a geologically dominated process often dependent on flow regimes; plants, microbes, and animals can interact. Generally stable once formed, though flood events could move structures out of ecosystem.

Epiphytic $CaCO_3$
[0.020–0.340% P][d]
Biologically dominated process due to plant funcational traits. May ultimately contribute to sediment $CaCO_3$ in stable conditions.

Scum $CaCO_3$
[unknown P]
Geologically dominated, but likely only important in aridland streams. Likely to disappear in changing hydrological conditions and unlikely to be an important sink of P in aquatic ecosystems.

Periphyton $CaCO_3$

Microbialite $CaCO_3$
[<0.001–0.131% P][c]
Biologically dominated process due to microbial metabolic patterns. Stability is a function of biogeochemical reactions, animal feeding, and hydrological conditions.

Sestonic $CaCO_3$

Epibiotic $CaCO_3$

Sediment $CaCO_3$
[0.095–0.649% P][b]
$CaCO_3$ may form within sediments or may be deposited from processes in the overlying water column (which are often seasonal, ie, whiting events). Diagenic processes will impact long-term stability.

Oncolite $CaCO_3$
[<0.001–0.010% P][e]
Unattached structures. See microbialites for details.

Petrifying $CaCO_3$
[unknown P]
Formation of $CaCO_3$ on allochtonous surfaces may be a geologically or biologically dominated process. Stability expected to be highly variable, dependent on surface and ecosystem conditions.

B Sestonic $CaCO_3$
[0.010–1.600% P][f]
Whiting events are biologically dominated in favorable geochemical conditions. Variable fractions of sestonic $CaCO_3$ sediment fall out of the water column; stability is unknown.

C Epibiotic $CaCO_3$
[unknown P]
These precipitates may be biologically or geologically dominated, but unlikely to be an important sink of P in aquatic ecosystems. They could have impacts on macroinvertebrate behavior or physiology.

D Periphyton $CaCO_3$
[0.004–0.095% P][g]
Precipitation and dissolution in periphyton mats are biologically dominated in favorable geochemical conditions, and may exhibit diurnal precipitation and nocturnal dissolution.

Fig. 1. Calcium carbonate ($CaCO_3$) precipitation or deposition may occur in different forms and across inland aquatic ecosystem types. Each of these forms could represent a pool of phosphorus, estimates as % dry mass are in the parenthesis. [a](Pentecost 2005), [b](Boström et al. 1988; Dittrich et al. 2013); [c](Borovec et al. 2010; Büttner et al. 2021), [d](Rossknecht 1980; Siong and Asaeda 2006; Kufel et al. 2016; Liu et al. 2016), [e](Corman et al. 2016b), [f](Rossknecht 1980; Schernewski et al. 1994; Hamilton et al. 2009; Walsh et al. 2019), [g](Gaiser et al. 2004; Borovec et al. 2010). Artwork by Fiona Martin.

these industrial applications more sustainable (Bueso and Tangney 2017).

Adding urgency to studies of $CaCO_3$-P co-precipitation is environmental change. Many of the hydrological or physicochemical conditions that influence $CaCO_3$ equilibrium are changing. For example, in some streams, where travertine deposition rates are related to flow (Chen et al. 2004; Pentecost and Coletta 2007; Brusa and Cerabolini 2009), changing drought frequency has shifted flow regimes such that travertine deposition has ceased (e.g., Bogan and Lytle 2011). And in some watersheds, soil acidification caused by and recovery from acid precipitation, reductions in atmospheric calcium input, and/or calcium losses from forest biomass harvesting has decreased calcium concentrations in receiving waters (Jeziorski et al. 2008; Weyhenmeyer et al. 2019). In other watersheds, atmospheric deposition (Ballantyne et al. 2011) and processes related to urbanization (Effler et al. 2012; Wu et al. 2018) have caused calcium

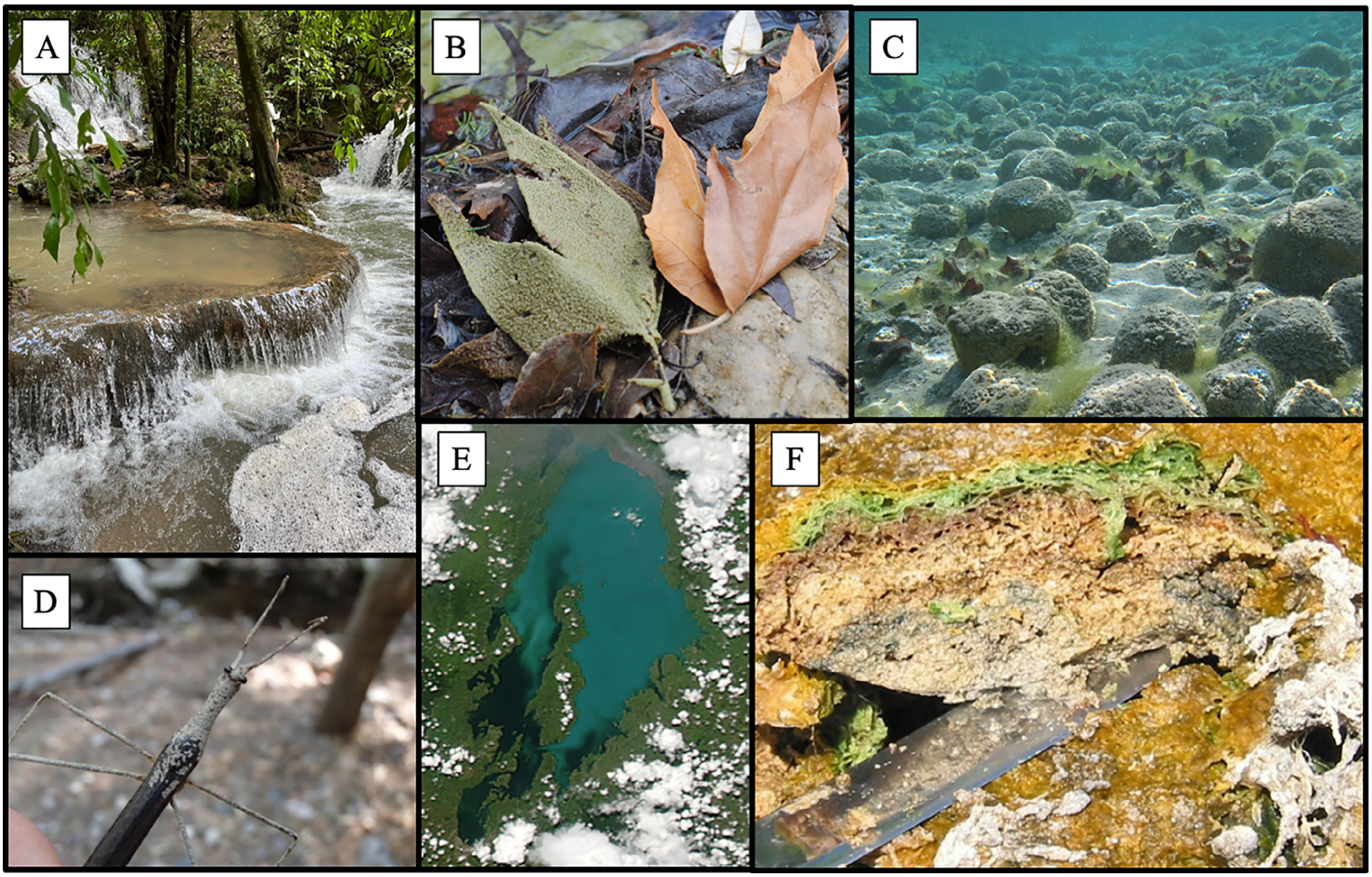


Fig. 2. Examples of calcium carbonate formations in aquatic ecosystems include (**A**) travertine dams or terraces (stream in Mato Grasso, Brazil), (**B**) deposition on allochthonous material (a comparison of leaves with and without deposits), (**C**) biogenic carbonate structures (microbialites, Cuatro Ciénegas, Mexico), (**D**) deposition on living organisms (*Ranatra quadridentate* [Nepidae]), (**E**) lake "whiting" events (Lake Kivu, Rwanda, Democratic Republic of the Congo), and (**F**) benthic microbial mats (vertical cross-section of a benthic cyanobacterial mat with the bottom yellow-gray layer being marl sediment; Belize). Photographs in panels A and C by Jessica Corman; B and D by Eric Moody; E by Jeff Schmaltz, NASA; and F by Eliška Rejmánková.

concentrations to increase. Inorganic carbon fluxes, which often covary with calcium fluxes, may be increasing in some aquatic ecosystems (Szramek and Walter 2004; Raymond and Hamilton 2018), as well. Hence, ecosystems that previously supported $CaCO_3$ deposition may no longer and others that never did now may.

A brief review of carbonate—Phosphate chemistry

Calcium carbonate needs favorable thermodynamic conditions to form (Eq. 1). These conditions include higher calcium concentrations, an alkaline pH, higher temperature, and the presence of nucleation sites. The metric used to describe the likelihood of mineral precipitation based on thermodynamic factors is the mineral "saturation index" or SI; a $SI < 0$ indicates that mineral is more likely to dissolve while a $SI > 0$ indicates that mineral will more likely precipitate (expressed on a logarithmic scale; Stumm and Morgan 1996). In natural environments, chemical equilibrium alone does not indicate precipitation: Merz-Preiß and Riding (1999) find $SI_{CaCO_3} > 0.8$ indicates when $CaCO_3$ precipitation is most likely, reflecting the complex interactions that can impact mineral formation in lakes, wetlands, and rivers, as discussed further below.

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O \tag{1}$$

In inland water ecosystems, the presence of $CaCO_3$ is often because that ecosystem's source water passed through a carbonate aquifer (or, simply, came to equilibrium with carbonate minerals along groundwater flow paths). As water travels through soils, it typically becomes enriched with carbon dioxide (CO_2) which exists in equilibrium with carbonic acid (H_2CO_3), due to interaction with soil and microbial respiration and/or regional geothermal activity (Stumm and Morgan 1996; Pentecost 2005). Upon flowing through the aquifer, the acid reacts with calcareous minerals, increasing the concentration of dissolved Ca^{2+} and HCO_3^-. By the time the

Text Box 1. What is $CaCO_3$? A brief etymology

Throughout this paper, I will refer to any number of structures or mineral composed primarily of calcium carbonate ($CaCO_3$) as “calcium carbonate” (Fig. 2). This choice is deliberate—there are many terms to describe these structures or minerals and these terms are not mutually exclusive (Table 1). For instance, rivers capable of supporting $CaCO_3$-deposition in the UK and Europe are often referred to as “chalk” rivers (e.g., Itchen River, UK), while similar streams in the US may be referred to as “travertine” rivers (e.g., Little Colorado River, AZ). Here, the difference is related to the type of limestone in the source aquifers, but that distinction is less relevant to naming the actively depositing $CaCO_3$ within the stream. Similarly, the $CaCO_3$-depositing biofilms themselves may be stromatolites, biological felt, or tufa in streams, or marl, reef, or Seekreide, in lakes. An emphasis on process vs. nomenclature invites the discovery of generalizations across ecosystem types.

groundwaters reach the surface, the waters will be supersaturated with CO_2. Outgassing or biological uptake of CO_2 will occur, raising the pH and causing $CaCO_3$ to become super saturated in the water. $CaCO_3$ can form either in the water column or on underwater surfaces (Table 1; Fig. 2). Cell surface nucleation sites, such as those provided by some photoautotrophs, may be necessary for $CaCO_3$ precipitation to occur (i.e., Dittrich et al. 2004; Dittrich and Obst 2004). When $CaCO_3$ precipitates on surfaces, it may form as loose, unattached materials (e.g., microbialites, Fig. 2C), deposits on plant materials (e.g., charophytes), or thick or thin benthic coverings on bedrock or sediments (e.g., travertine dams or terraces; Fig. 2A; Pentecost 2005). The review by Morse et al. (2007) provides an excellent, detailed synopsis of the considerations of $CaCO_3$ formation and dissolution in natural environments, though the focus is on marine systems.

Other dissolved chemical compounds may interact with $CaCO_3$. Of particular concern to this review is phosphorus, in the form of orthophosphate (hereafter, “phosphate”; Fig. 1). $CaCO_3$ co-precipitates phosphate ions by adsorbing those ions via surface complexation and/or forming a calcium phosphate mineral. The former, adsorption, is thought to be the primary process of phosphate removal by carbonates and the latter, incorporation into the primary carbonate crystal structure, is thought to only account for a small fraction of the co-precipitated phosphate (Avnimelech 1980; Douglas et al. 2004). Phosphate adsorption to calcite, as well as vaterite, a polymorph of calcite, appears to be a multi-step process (Freeman and Rowell 1981; Sawada et al. 1992; Millero et al. 2001). Up to 80% of the initially adsorbed phosphate may be released within a day (Millero et al. 2001) with decreasing exchangeability through time (Freeman and Rowell 1981). In this review, I refer to the absorption or binding of phosphate with $CaCO_3$ precipitation and or formation of calcium phosphate minerals collectively as “co-precipitation.”

The kinetics of phosphate co-precipitation with $CaCO_3$ have been studied under a variety of conditions using artificial and natural solutions (Kitano et al. 1978; Freeman and Rowell 1981; Ishikawa and Ichikuni 1981; House and Donaldson 1986; Suzuki et al. 1986; House 1990), including in sewage waste water (e.g., Plant and House 2002). Adsorption tends

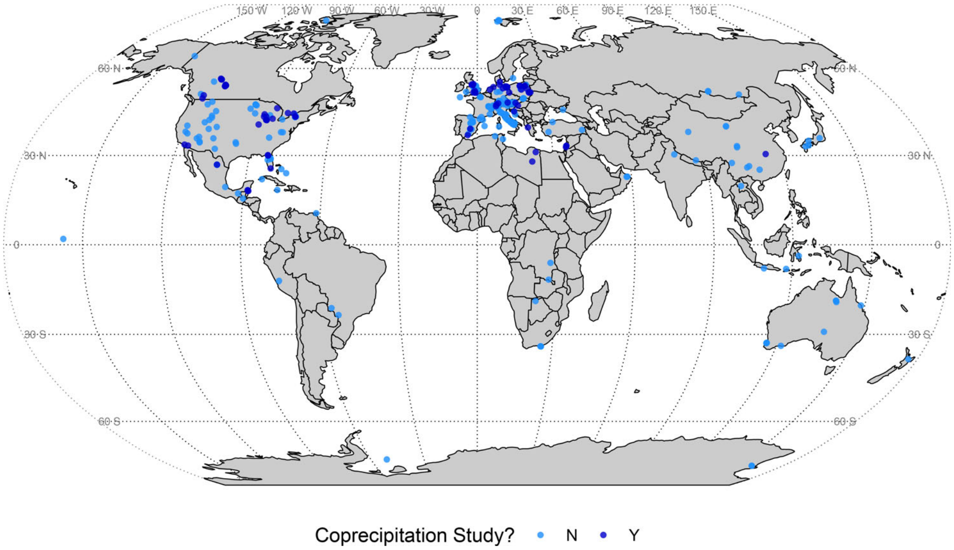


Fig. 3. Map denoting studies of $CaCO_3$-depositing aquatic ecosystems, with colors indicating where phosphorus co-precipitation studies have occurred. Site information is available in the Supporting Information; further information on tufa sites in Europe is available through the Natura 2000 network.

Table 1. Review of terms used to describe $CaCO_3$ deposits or the ecosystems depositing them.

Term	Definition(s)	Citation(s)
$CaCO_3$-type structures		
Biological felt (feutre biologique)	Benthic, biogenic carbonate structure (French term)	Freytet and Plet 1996
Balcite, aragonatie, vaterite	Mineral composed of calcium carbonate	
Chalk*	Limestone composed mainly of fossil foraminifer shells	
Marl (lake)	Deposits in lake beds usually resulting from biologically induced $CaCO_3$ precipitation (via photosynthesis)	Pentecost 2005
Microbialite	Benthic microbial deposit† due to trapping and binding detrital sediment and/or microbially directed mineral precipitation, may be laminated or unlaminated	Riding 1999; Burne and Moore 1987
Oncolite; oncoid	Unattached spherical form of calcareous stromatolites; rounded, laminated travertine deposits	Hagele et al. 2006; Riding 2000
Ooid (marine)	Spherical or ovoidal, laminated carbonate grains, mostly marine and predominately abiotically formed	Diaz and Eberli 2019
Reef (lake)	Calcareous formation along lake margins due to coagulation of fine planktonic particles and/or other carbonate particles	Pentecost 2005
Seekreide	Benthic, calcareous mud (German term)	Kempe and Emeis 1985
Stromatolite	Laminated, benthic microbial deposit†	Riding 1999
Thrombolite	Weakly laminated microbial deposit†	Riding 2011; Aitken 1967
Travertine*	Terrestrial limestone formed via chemical precipitation, mostly around seepages, springs and along streams and rivers, but occasionally in lakes; sometimes defined as arising only from warm waters (Riding 1991)	Pentecost 2005, Riding 1999
Tufa* (algal tufa, calcareous tufa)	Dominantly low-magnesium deposit which developed under ambient temperatures by biomedicine and/or physicochemical processes; can also be analogous with the term travertine (Trobej et al. 2017)	Pedley et al. 2003; Pentecost 2005
$CaCO_3$-type ecosystems		
Alkaline	Having a pH > 7	
Calcareous	Containing calcium carbonate; term can describe aquatic ecosystems that actively form calcium carbonate	
Carbonate or carbonate-rich	Containing carbonates	
Karst	Region underlain by limestone which has been eroded by dissolution; term can describe aquatic ecosystems originating from these landscapes	
Petrifying springs (or, limestone-precipitating springs)	Springs which can precipitation tufa or travertine deposits	Grootjans et al. 2021; Cantonati et al. 2016
Terms describing $CaCO_3$ formation		
Calcification	The formation of calcite; can be further distinguished between "environmental" or "inorganic" calcification and "biological" calcification	Krumbein 1979; Burne and Moore 1987
Deposition†	The accumulation or formation of minerals or sediments typically on benthic or low-lying surfaces	

(Continues)

Table 1. Continued

Term	Definition(s)	Citation(s)
(Microbial) Lithification†	The net precipitation of minerals by microbial communities through trapping and binding of sediments and/or metabolic microbial activities	Dupraz and Visscher 2005
Precipitation†	The formation of a mineral (or solid) coming out of solution	

*Terms that can also be used as adjectives to describe a $CaCO_3$-producing ecosystem.

†Terms do not necessarily indicate $CaCO_3$ minerals are present or dominant. For example, deposits may also be composed of silicates, high magnesium calcites, halites, etc. (e.g., Chagas et al. 2016; Zeyen et al. 2021; Vignale et al. 2022).

to increase with greater ionic activity of Ca^{2+} (Suzuki et al. 1986; Sø et al. 2011), more basic pH (in the range of 7–9.5), higher temperature (in the range of 5–35°C; House and Donaldson 1986), and decreasing salinity (Millero et al. 2001). Based on these laboratory studies, House and co-authors proposed a geochemical model for the rate of surficial absorption capacity at 0.2 μmol m^{-2} (House and Donaldson 1986; House 1990). However, interdependencies among calcite, water, dissolved inorganic carbon equilibrium, and phosphate render unexpected interactions in natural environments (House 2003; Sø et al. 2011; Bańkowska-Sobczak et al. 2020). For instance, at higher phosphate concentrations, $CaCO_3$ precipitation may be impeded (Dove and Hochella 1993; Reddy et al. 1999; Lin and Singer 2006) or calcium phosphate minerals, rather than $CaCO_3$, may be thermodynamically favored (Moutin et al. 1992; Plant and House 2002). Some microbial communities have a tendency to form Ca phosphates in addition to $CaCO_3$, though the reason is not well understood (Büttner et al. 2021). The aggregation of dissolved organic matter or colloidal and particulate phosphorus species with calcite may also account for the association of phosphorus with $CaCO_3$ (Chave 1965; Küchler-Krischun and Kleiner 1990; Koschel 1997), though these processes are likely less important than the aforementioned co-precipitation dynamics. The reader is directed to the excellent review in Bańkowska-Sobczak et al. (2020) for more information on the chemistry of co-precipitation.

Carbonate—Phosphate chemistry and ecological feedbacks

In the water column—Mostly lakes, sometimes streams, and wetlands

Calcium carbonate precipitation in lakes has long been of interest to limnologists (Minder 1929; Küchler-Krischun and Kleiner 1990; Fig. 2E). Much of the initial interest was related to describing lake metabolism (Ohle 1952; Hutchinson 1957) and inquiries into carbon cycling continue today (e.g., Stets et al. 2009; Khan et al. 2020; Escoffier et al. 2023). Oddly, and certainly to the detriment of our understanding of P cycling, many scientists working on soft water lakes discounted the role of $CaCO_3$ in P cycling, instead focusing on iron and sulfur as primary drivers (Boström et al. 1988; Orihel et al. 2017). Fortunately, this view has changed. Recent work has provided insights into $CaCO_3$ controls on eutrophication (e.g., Bańkowska-Sobczak et al. 2020), evolution of life on Earth (e.g., Toner and Catling 2020), and the complex balance of geochemical and hydrologic controls on biogeochemical processes (e.g., Alvarez Cobelas and Sánchez Carrillo 2016).

Planktonic microbes

In lakes, many phytoplankton are associated with $CaCO_3$ precipitation (Heath et al. 1995; Hartley et al. 1997). There are two major mechanisms by which these organisms can promote precipitation: (1) the generation of an alkaline environment near the cell when photoautotrophs use HCO_3^- in photosynthesis and, therefore, must exchange the hydroxyl ion (OH^-) produced in HCO_3^- fixation (Thompson and Ferris 1990) and (2) the cell surface (or extracellular compounds) can act as a nucleation site (Stabel 1986; Dittrich et al. 2004). The latter may be a particularly important role of autotrophic picoplankton in lakes (Dittrich and Obst 2004). Indeed, *Synechococcus* can be continually entombed within growing calcite crystals (Thompson and Ferris 1990). In a study of the Plitvice Lakes, phytoplankton living in low-nitrogen environments excreted mucopolysaccharides as a waste product, creating a “glue” that may promote carbonate deposition (Kempe and Emeis 1985). However, extracellular polymeric secretions (EPS) may not always promote deposition; this role is dependent on its chemical characteristics (Dittrich and Obst 2004).

Whiting events/pelagic precipitation

A closer look into lake ecosystems presents one of the best-studied examples of $CaCO_3$ precipitation and P dynamics: “whiting” events (Fig. 2E). Whiting events, named for the resultant milky appearance of the water column, happen due to shifts in temperature, primary production, and the phytoplankton community that promote calcite formation (Hodell et al. 1998). In large lakes like the Laurentian Great Lakes (Lake Michigan, Erie, and Ontario) or Lake Constance, the whiting events may be dramatic enough to be seen by satellites (Strong and Eadie 1978; Pulvermüller et al. 1995). In an early study of whiting events and the co-precipitation mechanism in lake water, Otsuki and Wetzel (1972) demonstrated that phosphate concentrations could decrease by as much as 80% when $CaCO_3$ precipitation is induced in lake water. Since then, co-precipitation of phosphate with $CaCO_3$ has been described in a number of lakes (eg., Nagawika Lake, Robertson et al. 2007; Lake Wallersee, Jäger and Röhrs 1990; Lake Constance, Kleiner 1988; Onondaga Lake, Effler 1996; Black Lake, Murphy et al. 1983; Lake Kinneret, Avnimelech 1983; Lake Belau, Schernewski et al. 1994). And, even when $CaCO_3$ precipitation is not enough to be considered a whiting event, it may still precipitate and lead to absorption of phosphate on seston (Gunatilaka 1982).

How effective is co-precipitation in removing P from a water column in a lake? Answering this question is related to understanding (1) when $CaCO_3$ precipitation occurs, (2) how much P is absorbed, and (3) the stability of the precipitate. Understanding the seasonality and temporality of $CaCO_3$ production is necessary for predicting its impacts on P availability. Whiting events are episodic. While some lakes, like Lake Constance, show a trimodal pattern concomitant with multiple peaks of phytoplankton growth (e.g., late spring, summer, and fall; Stabel 1986), other lakes show a single annual whiting event (e.g., late spring in Fayetteville Green Lakes, NY; Thompson and Ferris 1990). When finer timescales are considered, lakes may also show a diel pattern, with $CaCO_3$ production occurring during daylight when photosynthesis is occurring (e.g., Cicerone et al. 1999). On the other hand, $CaCO_3$ production related to EPS production may not show a diel signal (i.e., as in the Plitvice Lakes, Kempe and Emeis 1985), but more research is needed to test this hypothesis.

The incorporation of P into $CaCO_3$ seston varies, with percentages ranging from 0.01% to 1.0% P (Rossknecht 1980; Schernewski et al. 1994; Fig. 1). The variability is primarily related to the grain size of $CaCO_3$ (Avnimelech 1980; Douglas et al. 2004). Grain size determines the area available for surface complexation of phosphate. Larger grain sizes will have relatively less surface area available; hence, smaller grain sizes can lead to greater co-precipitation rates. In a lake, conditions that support $CaCO_3$ supersaturation may lead to increased grain size, faster precipitation, and less co-precipitation (Niessen and Sturm 1987; Stabel and Chondrogianni 1988; Lotter et al. 1997). Phosphorus co-precipitation rates are also related to P concentrations. There is an unimodal relationship between P concentrations and co-precipitation rates, with incorporation of P into $CaCO_3$ being more efficient at higher P concentrations (Danen-Louwerse et al. 1995), but only to a point, as a strong decrease in efficiency at higher trophic states has been identified (Koschel 1990; Gonsiorczyk et al. 1995). The attenuation of $CaCO_3$ precipitation at higher P concentrations may lead to situations where $CaCO_3$ precipitation relies on seasonal or semi-permanent reductions of P, that is, biological uptake during the growing season (Lotter et al. 1997) or watershed remediation efforts (Walsh et al. 2019), respectively.

As phosphate co-precipitation can lower P concentrations in the photic zone, it has been of great interest to understand in relation to its potential as a negative feedback on primary production, aka the "self-cleaning mechanism" (Rossknecht 1980; Avnimelech 1983; Koschel et al. 1983; Murphy et al. 1983; Kleiner 1988; Robertson et al. 2007). While $CaCO_3$ precipitation can substantially lower dissolved inorganic P concentrations (as phosphate; Otsuki and Wetzel 1972; Murphy et al. 1983; House 1990), it may also lead to decreases of other forms of P in the water column. In an experimental induction of a whiting event, Hamilton et al. (2009) found a 47% reduction of TP in the water column, about half of which was explained directly by phosphate co-precipitation of $CaCO_3$ (with organic P accounting for the remainder). In some lakes, this reduction is high enough to buffer against excessive phosphorus inputs (e.g., Robertson et al. 2007). Yet, this reduction is conditional on $CaCO_3$-P stability in lake sediments, a topic discussed in the next section. Most studies that have investigated $CaCO_3$ precipitation as a possible in-lake mitigation strategy for improving water quality stress that the mitigation will only be effective in the long-term if external nutrient sources are reduced or diverted (Babin et al. 1994; Prepas et al. 2001; Walpersdorf et al. 2004; Koschel et al. 2006).

In the aphotic benthos—Mostly lakes. A sink or source of P?

$CaCO_3$ and P interactions in sediments

Internal release of P from lake sediments has long been recognized as a source of P fueling primary production. The traditional view has been that this release is controlled by redox chemistry and Fe and S cycling. In hardwater lakes, this is likely not the case (Boström et al. 1988; Golterman 2001; Orihel et al. 2017). And, even in soft water lakes, the presence of Fe and S may make it difficult to distinguish carbonate—phosphorus interactions (Kinsman-Costello et al. 2016). Therefore, understanding $CaCO_3$-P dynamics in lake sediments, including the scales at which diagenesis leads to long-term P sequestration, may be key to understanding long-term controls on the lake trophic state.

Across many lake types, $CaCO_3$-P minerals are found in lake sediments (e.g., Dorioz et al. 1989; de Vicente et al. 2006). While this observation supports the importance of $CaCO_3$ precipitation on P cycling (Boström et al. 1988; Golterman 2001), it begs the question: how stable is $CaCO_3$-bound P in lake sediments? $CaCO_3$-bound P can be immobile in some sediments (e.g., Lake Arreskov, Denmark; Andersen and Ring 1999), but contribute to internal P loading in others (e.g., Lake Simcoe, Ontario, Canada (Dittrich et al. 2013); Lake Mendota, USA (Wentz and Lee 1969)). The stability of $CaCO_3$-P in sediments likely reflects the complex interactions between phosphorus source (Penn and Auer 1997), lake trophic status (Müller et al. 2006), sediment stability (Andersen and Ring 1999), and timescale considered

(Dittrich et al. 2013). In terms of lake trophic status, one might predict that in more eutrophic lakes, $CaCO_3$-P minerals would be less stable, as changes in sediment pore water chemistry due to higher respiration rates would likely drive down pH and promote $CaCO_3$ dissolution and, therefore, P release. However, this is not always the case (e.g., Andersen and Ring 1999; Müller et al. 2006). In a comparison of oligotrophic and eutrophic lake sediment diffusion rates, calcite dissolution was twice as great in the oligotrophic lake, despite lower pH values in the eutrophic lake (Müller et al. 2006). The authors suggest that this unexpected result is because, in the oligotrophic lake, organic matter residence time is higher, penetration of oxygen in the sediment pore water is deeper, and the $CaCO_3$ crystal size is smaller (Müller et al. 2006).

It is important to note that the adsorption or incorporation process of phosphate into $CaCO_3$ minerals may take place in either the water column (i.e., due to a whiting event, as described above), and then settle into the sediments (e.g., Penn and Auer 1997), or in the sediments, if $CaCO_3$ minerals are actively forming there. In a study of Salton Sea sediments, sulfate reduction—which generates bicarbonate ions and therefore increases alkalinity and induces $CaCO_3$ precipitation (Visscher and Stolz 2005)—removed 82–100% of the dissolved P in the pore waters (Rodriguez et al. 2008). It is unknown whether one process would lead to longer-term stability of sequestered P than the other. Given the role of internal P cycling in lake trophic status, and the attention it has in lake management practices, it is imperative to better disentangle water column vs. sediment $CaCO_3$ precipitation (Orihel et al. 2017; Markovic et al. 2019).

In the littoral zone—Plants and epiphytic carbonates

Macroalgae and vascular plants

Submerged vascular plants (e.g., *Potamogeton*) and macroscropic algae of the class Charophyceae are commonly responsible for carbonate deposition in hardwater lakes (McConnaughey and Whelan 1997). Due to their calcite encrustations, charophytes are commonly known as "stoneworts" or "brittleworts." In the process of photosynthesis, charophytes build a calcite encrustation around their thalli, an accumulation that may reach more than 70% of their dry mass (Raven and Giordano 2009; Kufel et al. 2013; Pełechaty et al. 2013). Charophytes and some vascular plant species like *Utricularia gibba* and *Utricularia subulata* may also support the growth of filamentous cyanobacteria that are known to promote calcite precipitation (Gaiser et al. 2011). The reader is directed toward the review by McConnaughey and Whelan (1997) for a more detailed review of the mechanisms of $CaCO_3$ precipitation on underwater surfaces of macroalgae and vascular plants.

Carbonate precipitation associated with macrophytes may be consequential to lake P cycling. Characterization of $CaCO_3$ precipitates on *Potamogeton* confirms the presence of $CaCO_3$ co-precipitated-P (Liu et al. 2016). In a comparison of different charophyte species, $CaCO_3$ co-precipitated-P accounted for 21–26% of the TP on the plant material (Kufel et al. 2013). Further work suggests that the encrustations are redox-insensitive and not readily bioavailable (Siong and Asaeda 2006, 2009). Hence, these macrophyte-induced carbonates could lead to stable sequestration of P in sediments (Kufel and Kufel 2002; Pukacz et al. 2016), but this contribution has yet to be quantified.

Moss

Another type of non-vascular plant, moss, may interact with $CaCO_3$, generally by acting as a support for the growth of $CaCO_3$-precipitating microbial communities (Freytet and Verrecchia 1995; Pitois et al. 2003). In a study of bare limestone pavements, moss cushions increased phosphorus availability to vascular plants (Sand-Jensen and Hammer 2012). The authors suggest that this P is derived from limestone-bound P. It is unknown whether or not a similar mechanism of P-liberation occurs in $CaCO_3$-producing waters.

In the photic benthos—Wetlands, streams, and, sometimes, lakes

Benthic, biogenic carbonate structures

Benthic microbial activity may result in complex, layered lithified structures (e.g., stromatolites or microbialites, Fig. 2C, or microbial mats, Fig. 2F; *see* Table 1 for a definition of terms) or encrusted periphyton mats (e.g., calcareous periphyton). Lithifying microbes are perhaps the best-studied group of organisms in relation to carbonate structures. The reader is directed to the many excellent reviews of microbial precipitation (e.g., Burne and Moore 1987; Riding 1991; Chagas et al. 2016), including with respect to the earliest known microbial community fossils (Allwood et al. 2006). The focus of this section will be on the ecological implications of $CaCO_3$ precipitation in photic, benthic regions, drawing primarily from wetland ecosystems, though benthic precipitation is often important in alkaline streams and lake littoral zones (e.g., Chagas et al. 2016; Zeyen et al. 2021).

While photosynthetic activity generally promotes $CaCO_3$ formation, cyanobacteria (and bacteria) can promote precipitation extracellularly through several mechanisms (*see* Benzerara et al. 2014 for a discussion of intracellular precipitation). In cyanobacterial filamentous sheaths, photosynthesis and/or the carbon concentrating mechanism may locally increase pH and $CaCO_3$ supersaturation (Kah and Riding 2007; Shiraishi et al. 2008). Microbes living in conditions where calcite supersaturation already occurs may also promote precipitation by providing a nucleating site for crystal formation (Merz-Preiß and Riding 1999). In microbial mats, $CaCO_3$ precipitation in mats (often referred to more generally in the context of "lithification"; Table 1) may be supported by several microbial metabolisms, including aerobic photosynthesis or anaerobic sulfate reduction (Dupraz et al. 2009; Sun et al. 2020), or through exo-polymeric substance (EPS) binding of calcium (Braissant et al. 2007; Sun et al. 2020). $CaCO_3$ precipitation in microbial mats can occur even when calcite has a low saturation index (SI_{CaCO_3} of 0.2–0.3) in the surrounding water column (Merz 1992; Merz-Preiß and Riding 1999).

In a study of calcite precipitates in a tufa fluvial barrage-lacustrine system (Ruidera Lakes, Spain), authors suggest that cyanobacteria-mediated precipitation is more likely to cause $Ca\text{-}PO_4$ precipitates while eukaryotic-mediated precipitation (from algae or mosses) is more likely to cause calcite precipitates (Souza-Egipsy et al. 2006), leading to the formation of either phosphorus-rich or phosphorus-poor tufa deposits, or, more simply, higher or lower P sequestration rates. It is unknown whether the form in which the precipitates occur influences dissolution and diagenesis.

$CaCO_3$ precipitation in microbial mats—A way to get more P?

Much of what is known about $CaCO_3$ co-precipitation of P and benthic microbes comes from work done in the Everglades, a carbonate-precipitating sub-tropical wetland ecosystem. The periphyton in this region is known to rapidly take up available P, leading to very low water column concentrations of P (Noe et al. 2003; Gaiser et al. 2004). However, the P cycling in the periphyton represents a complex exchange between biotic and $CaCO_3$-associated forms. First, there is a diurnal signal related to the rates of photosynthesis and respiration: in the day, $CaCO_3$ precipitates and at night, it dissolves. This diurnal signal is reflected in periphyton P cycling. Initially, much of the P is associated with the mineral fraction (Noe et al. 2003). However, within a day, much of it turns over into the organic pool, suggesting night time dissolution may release P and render it available for biological uptake (Gleason and Spackman 1974; Noe et al. 2003). Some of the Ca-P fraction is eventually incorporated into the sediment matrix (Reddy et al. 1993; Scinto and Reddy 2003; Gaiser et al. 2004). Phosphorus cycling in periphyton is also related to hydrologic events. The Everglades are subjected to wetting and drying cycles; $CaCO_3$ co-precipitated P is released upon these re-wetting events (Gottlieb et al. 2005). One of the $CaCO_3$-precipitating cyanobacteria found in the Everglades, *Scytonema*, is tolerant of P scarcity and desiccation (Marazzi et al. 2017), suggesting that at least some microbes here may take advantage of this release of co-precipitated P. Microbial communities beyond those in the Everglades may also benefit from the paradoxical increase in P availability associated with $CaCO_3$ deposition. While this hypothesis remains to be tested, several lines of evidence support it.

First, some microbes prefer to colonize or grow on carbonate substrates over other surfaces (Kock et al. 2006; Álvarez and Pardo 2007; Pentecost and Whitton 2012; Trobej et al. 2017). The reason for this association may be in part due to nutrient availability: in a comparison of biofilm growth across different rock and mineral surfaces, biofilm biomass was more than 5X greater on the carbonate rocks (limestone and dolostone) than pure calcite, suggesting microbes were able to access nutrients in the rocks (Jones and Bennett 2014). Hence, microbes may be able to "mine" nutrients, including phosphorus, available in mineral or rock substrates, rendering those microbes a competitive advantage compared to those not able to access those nutrients.

Second, microbes in actively calcifying mats take advantage of loosely bound P on EPS or $CaCO_3$ (Gleason and Spackman 1974), similar to the aforementioned observations in the Everglades periphyton (Noe et al. 2003). In a study of cyanobacterial mats in Belize, Borovec and co-authors (2010) observed very little bioavailable P in the lower layers of the mat. And, in the surficial layers, they observed a diurnal increase of reactive, exchangeable P and of organic P, suggesting microbial uptake of P is occurring at night when pH lowers due to respiration (Borovec et al. 2010).

Third, biogenic carbonate substrates, whether stromatolites or not, tend to form in low phosphorus environments (e.g., Hägele et al. 2006; Corman et al. 2015; Rishworth et al. 2017). The author of this review is currently unaware of these substrates forming in high P environments. Whether through direct manipulation of phosphorus concentrations and responses in microbial growth and metabolism (e.g., Corman et al. 2015), detection of alkaline phosphatase activity or observations of high N:P ratios (Valdespino-Castillo et al. 2014), or high TN : TP ratios (Rosen et al. 1996; Hägele et al. 2006; Lim 2009), environmental conditions in carbonate-depositing ecosystems suggest organismal growth may be phosphorus-limited. The access to some co-precipitated P, but not enough, may be the very thing that allows these communities to persist (Daoust and Childers 2004; Gaiser et al. 2004, 2006, 2011; Rejmánková et al. 2008; Smith et al. 2010).

However, some lines of evidence contradict the aforementioned hypothesis. First, various advantages of benthic $CaCO_3$ precipitation to microbes have been suggested, including protection against high light intensities (Merz 1992), buffer against pH changes (Merz 1992), and protection against uncontrolled, and hence detrimental, calcite nucleation (Obst et al. 2009). Further, researchers studying oncoids from the River Alz (Germany) suggest that P-deplete conditions primarily limit the growth of macrophytes in the region, allowing the cyanobacterial communities to thrive (Hägele et al. 2006). This viewpoint echoes earlier positions taken by Wetzel and others that co-precipitation of P is an indirect density-dependent control on both phytoplankton and macrophyte populations (Otsuki and Wetzel 1972). Clearly, more work is needed.

$CaCO_3$ in flowing waters

A continuum of $CaCO_3$ forms in lotic ecosystems

Stunning examples of $CaCO_3$ formations in lotic ecosystems include the massive travertine dams, step-pool systems, or perched springline paludal tufa formations (Chafetz and Folk 1984; Pedley et al. 2003; Fuller et al. 2011; Fig. 2A) of

Plitvice National Lakes (Croatia), Jiuzhaigou Valley National Park (Sichuan, China), or Mammoth Hot Springs (Yellowstone, USA). In lotic waters, $CaCO_3$ formation spans a gradient of predominantly abiotically driven, through the process of CO_2 degassing in waters supersaturated with $CaCO_3$ (e.g., Herman and Lorah 1987; Drysdale 2001; Malusa et al. 2003), to predominantly biotically driven, through the metabolic uptake of CO_2 and/or nucleation of $CaCO_3$ to form biogenic microbial carbonate structures (e.g., microbialites in River Alz, Germany, Hägele et al. 2006; Cuatro Cienegas, Winsborough et al. 1994; and Burgundy, France, Freytet and Plet 1996; bryoherms, Freytet and Verrecchia 1995; or calcareous crusts Pitois et al. 2003); the latter is described in the previous section. Even animals may be involved (Text Box 2). As the relative contribution of abiotic and biotic processes can vary through space and time due to changing environmental conditions (Merz-Preiß and Riding 1999), the forms can be distinguished based on their morphology. In a carbonate-producing stream in Oklahoma, USA, Stewart (1988) describes three main forms of $CaCO_3$: loose, flocculent material; off-white surficial material attached to surfaces (e.g., on microscopic plants and stones; Fig. 2B); and surficial "scum" of fine white, crystalline carbonates on the water surface (Stewart 1988). Surficial scum is likely driven by evaporitic processes and, while not a massive form of $CaCO_3$ in streams, is thought to be more common in arid, stream ecosystems (Stewart 1988). While precipitation in the water column of flowing aquatic ecosystems is possible (Neal 2001), that which occurs in the benthos is likely more important (Jarvie et al. 2002).

$CaCO_3$ and P cycling in streams: Benthic processes

Like lakes, stream and river sediments may have a high capacity for P adsorption (Mc Callister and Logan 1978; House 2003). If the overlying water has more inorganic P than the sediment porewater, that P will be retained by mineral interactions with the sediment, of which carbonates may be important (Reddy et al. 1999). However, in high-P scenarios, the impact of P adsorption and co-precipitation may be overall negligible to the P budget of the river system (Bedore et al. 2008). And, at low soluble P concentrations, it is expected that co-precipitated P on $CaCO_3$ would be released back into the water column (Green et al. 1978). Furthermore, the continuously moving nature of water in streams means that the stability of phosphorus in stream bed sediments is not just a function of the chemical composition of the overlying water (and sediment), but also a consequence of the water's sediment load. As water flows increase, sediment loads increase. If those sediments are composed of $CaCO_3$ and phosphorus, there may be a high net export of P (even if the ecosystem storage is low). Note that these processes are not

Text Box 2. A bit about animals

Across all aquatic ecosystems, animals can interact with $CaCO_3$, both creating and destroying $CaCO_3$ forms. One of the main mechanisms of creation is termed "biologically controlled calcification." Biologically controlled calcification is defined herein as the process by which organisms completely control the process of $CaCO_3$ deposition like the building of snail shells or skeletal material (Burne and Moore 1987). Indeed, bone, made up of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is well recognized to be an important sink of calcium-associated P in vertebrate organisms (Sterner and Elser 2002). Readers are directed to the aforementioned studies and others (e.g., Moody et al. 2016; Brodie and McIntyre 2019) for further review of the potential impacts of biologically controlled calcification on P cycling. Of note is the opportunity for skeletal-P to be a terrestrial subsidy to aquatic ecosystems (e.g., Parmenter and Lamarra 1991; Subalusky et al. 2020). Animals are also known to graze on $CaCO_3$ formations (e.g., snails on stromatolites, Garcia-Pichel et al. 2004; Elser et al. 2006; parrotfish on corals, Mumby et al. 2006). Could $CaCO_3$ grazing liberate P into the foodweb, similar to the shunt of $CaCO_3$-derived P by calcite-dissolving moss?

Animals may also indirectly promote calcification by acting as a nucleating site for $CaCO_3$ deposition or by hosting epibiotic communities, either on their bodies (e.g., turtles, Neil and Allen 1954; Fig. 2D) or their casings (e.g., caddisflies, Mooney et al. 2014; snails, Lukens et al. 2017), which may host microbes who influence $CaCO_3$ deposition via the mechanisms described above. Calcareous deposits have been documented on numerous aquatic macro invertebrates including dragonfly larvae, damselfly larvae, giant water bugs, caddisflies, riffle beetles, amphipods, fly larvae, stoneflies, water scorpions, snails, and aquatic mites (Krüper 1930; Edwards and Heywood 1960; Minckley 1963; Durrenfeldt 1978; Ruff and Maier 2000; Moody et al. 2016; Brown 1972). While several studies have considered the implications of epibiota to ecosystem processes (e.g., Mooney et al. 2014; Lukens et al. 2017), the impacts of animal-$CaCO_3$ deposits to P cycling via impacts on P-coprecipitation are currently unknown. Additionally, through the process of constructing silken nets, hydropsychid caddisflies may promote deposition of $CaCO_3$ by providing a nucleating surface for crystal formation (Drysdale 1999; Paprocki et al. 2003). Larval caddisflies of *Cheumatopysche* also build nets and retreats that promote tufa development. These deposits are well preserved in the fossil record (Drysdale et al. 2003), suggesting that this animal-induced $CaCO_3$ deposition may be quite stable.

necessarily specific to $CaCO_3$-P interactions. However, there is still much evidence to suggest that $CaCO_3$ co-precipitation of P in streams is important both to P flows through the ecosystem and to biological processes within the ecosystem.

Despite the ubiquity of large $CaCO_3$ structures in different stream and river ecosystems, there are still many unknowns about how $CaCO_3$ influences P cycling in streams. Much of the evidence for $CaCO_3$ controlling P concentrations is given by trends in P concentrations in $CaCO_3$-precipitating streams (Kempe and Emeis 1985; Hägele et al. 2006; Katsaounos et al. 2007; Matoničkin Kepčija et al. 2011) or geochemical modeling (Salingar et al. 1993; Cohen et al. 2013). Indeed, the ability of periphyton to promote the formation of Ca-phosphate minerals or co-precipitated P due to localized increases in pH from photosynthesis is often considered a given in stream ecosystems (Woodruff et al. 1999; Neal 2001; Dodds 2003)—a very different paradigm than in lakes where $CaCO_3$-P can settle out of the epilimnion and thus be unavailable for that stratification period. However, as seen in lake and wetland ecosystems, $CaCO_3$ deposition in streams may be reduced under high P concentrations (Pentecost 2018). Threshold values vary (Neal 2001): concentrations as low as 10 μM P reduced $CaCO_3$ precipitation in the Tartare Springs (Italy) by ~40% (Bono et al. 2001). Dampening of $CaCO_3$ deposition due to increased P has been particularly of concern in culturally relevant sites, where increased tourist activity can increase P inputs into the ecosystem and diminish the growth of the very ecosystem attributes those tourists are visiting.

Several studies have considered the impacts of co-precipitation on stream ecosystems. When $CaCO_3$ deposition rates were experimentally reduced in a travertine stream in southern Arizona, researchers found a reduction in P uptake rates in the stream and an increase in periphyton %P, yet no change in water column concentrations (Corman et al. 2016a). Similar results of increased biomass, biomass % P, and primary production were found during experimental reductions of $CaCO_3$ precipitation in microbialites from a stream in northern Mexico (Corman et al. 2016b). Further, $CaCO_3$ deposition is associated with N:P ratios of the primary producers that are well above 16:1 (Hägele et al. 2006; Corman et al. 2016b), and P limitation of primary production may be typical of most regions of streams with active $CaCO_3$ deposition (Matoničkin Kepčija et al. 2011; Corman et al. 2016a).

Conclusions

Given the common occurrence of $CaCO_3$ precipitation and dissolution across inland water ecosystems, phosphorus absorption/release dynamics with $CaCO_3$ may—and already have been shown to—play a critical role in phosphorus cycling and ecosystem processes. Yet, there are distinct geographic gaps in our knowledge. While many studies of microbialites and other biogenic carbonate structures in tropical aquatic ecosystems exist, far fewer exist about tropical or sub-tropical whiting events or macrophyte precipitation (Fig. 3; Tapia Grimaldo et al. 2017). Many questions also remain in understanding the ecological and evolutionary consequences of $CaCO_3$ co-precipitation of P. $CaCO_3$ can take many forms and the variation of P within these forms can equally vary (Fig. 1). How do these different forms influence the stability or bioavailability of co-precipitated P? On what timescales is co-precipitated P a permanent or temporary sink of P, and how does this vary by $CaCO_3$ forms? Given the biotic role in many $CaCO_3$-forming processes, how does the interaction between the organisms' need for P mitigate $CaCO_3$ deposition? Do evolutionary feedbacks exist, and how do these vary among different organismal types (i.e., microbes, macrophytes, and animals)? Further, few studies consider explicitly the mechanisms by which P co-precipitation occurs (though *see* Rodriguez et al. 2008). Answering this question could help determine how sediment processes interact with P sequestration and how it varies between different forms of co-precipitated P. Studying these questions may help uncover new insights into biology and ecology, and help manage the numerous, important ecosystems with $CaCO_3$ deposition.

References

Aitken, J. D. 1967. Classification and environmental significance of cryptalgal limestones and dolomites, with illustrations from the cambrian and ordovician of Southwestern Alberta. SEPM J. Sediment. Res. **37**. doi:10.1306/74D7185C-2B21-11D7-8648000102C1865D

Allwood, A. C., M. R. Walter, B. S. Kamber, C. P. Marshall, and I. W. Burch. 2006. Stromatolite reef from the Early Archaean era of Australia. Nature **441**: 714–718. doi:10.1038/nature04764

Álvarez, M., and I. Pardo. 2007. Factors controlling epilithon biomass in a temporary, karstic stream: The interaction between substratum and grazing. J. N. Am. Benthol. Soc. **26**: 207–220 doi:10.1899/0887-3593(2007)26[207:FCEBIA]2.0.CO;2.

Alvarez Cobelas, M., and S. Sánchez Carrillo. 2016. Short-term nutrient fluxes of a groundwater-fed, flow-through lake. Limnetica. **35**: 143–158. doi:10.23818/limn.35.12

Andersen, F. Ø., and P. Ring. 1999. Comparison of phosphorus release from littoral and profundal sediments in a shallow, eutrophic lake, p. 175–183. *In* N. Walz and B. Nixdorf [eds.], *Shallow Lakes'98*. Springer.

Arp, G., A. Reimer, and J. Reitner. 2001. Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans. Science **292**: 1701–1704. doi:10.1126/science.1057204

Avnimelech, Y. 1980. Calcium-carbonate–phosphate surface complex in calcareous systems. Nature **288**: 255–257. doi:10.1038/288255a0

Avnimelech, Y. 1983. Phosphorus and calcium carbonate solubilities in Lake Kinneret. Limnol. Oceanogr. **28**: 640–645. doi:10.4319/lo.1983.28.4.0640

Büttner, S. H., E. W. Isemonger, M. Isaacs, D. Van Niekerk, R. E. Sipler, and R. A. Dorrington. 2021. Living phosphatic stromatolites in a low-phosphorus environment: Implications for the use of phosphorus as a proxy for phosphate levels in paleo-systems. Geobiology **19**: 35–47. doi:10.1111/gbi.12415

Bańkowska-Sobczak, A., A. Blazejczyk, E. Eiche, U. Fischer, and Z. Popek. 2020. Phosphorus inactivation in Lake sediments using calcite materials and controlled resuspension—mechanism and efficiency. Minerals **10**: 223. doi:10.3390/min10030223

Babin, J., E. E. Prepas, T. P. Murphy, M. Serediak, P. J. Curtis, Y. Zhang, and P. A. Chambers. 1994. Impact of lime on sediment phosphorus release in hard water lakes: The case of hypereutrophic Halfmoon Lake, Alberta. Lake Reserv. Manag. **8**: 131–142. doi:10.1080/07438149409354465

Ballantyne, A. P., J. Brahney, D. Fernandez, C. L. Lawrence, J. Saros, and J. C. Neff. 2011. Biogeochemical response of alpine lakes to a recent increase in dust deposition in the Southwestern, US. Biogeosciences **8**: 2689–2706. doi:10.5194/bg-8-2689-2011

Batjes, N. H. 2016. Harmonized soil property values for broad-scale modelling (WISE30sec) with estimates of global soil carbon stocks. Geoderma **269**: 61–68. doi:10.1016/j.geoderma.2016.01.034

Bedore, P. D., M. B. David, and J. W. Stucki. 2008. Mechanisms of phosphorus control in urban streams receiving sewage effluent. Water Air Soil Pollut. **191**: 217–229. doi:10.1007/s11270-008-9619-x

Benzerara, K., and others. 2014. Intracellular Ca-carbonate biomineralization is widespread in cyanobacteria. Proc. Natl. Acad. Sci. U. S. A. **111**: 10933–10938. doi:10.1073/pnas.1403510111

Bogan, M. T., and D. A. Lytle. 2011. Severe drought drives novel community trajectories in desert stream pools: Drought causes community regime shifts. Freshw. Biol. **56**: 2070–2081. doi:10.1111/j.1365-2427.2011.02638.x

Bono, P., W. Dreybrodt, S. Ercole, C. Percopo, and K. Vosbeck. 2001. Inorganic calcite precipitation in tartare karstic spring (Lazio, central Italy): Field measurements and theoretical prediction on depositional rates. Environ. Geol. **41**: 305–313. doi:10.1007/s002540100375

Borovec, J., D. Sirová, P. Mošnerová, E. Rejmánková, and J. Vrba. 2010. Spatial and temporal changes in phosphorus partitioning within a freshwater cyanobacterial mat community. Biogeochemistry **101**: 323–333. doi:10.1007/s10533-010-9488-4

Boström, B., J. M. Andersen, S. Fleischer, and M. Jansson. 1988. Exchange of phosphorus across the sediment–water interface. Hydrobiologia **170**: 229–244. doi:10.1007/BF00024907

Braissant, O., A. W. Decho, C. Dupraz, C. Glunk, K. M. Przekop, and P. T. Visscher. 2007. Exopolymeric substances of sulfate-reducing bacteria: Interactions with calcium at alkaline pH and implication for formation of carbonate minerals. Geobiology **5**: 401–411. doi:10.1111/j.1472-4669.2007.00117.x

Brodie, J. F., and P. B. McIntyre. 2019. Bushmeat biogeochemistry: hunting tropical mammals alters ecosystem phosphorus budgets. Proc. R. Soc. B Biol. Sci. **286**: 20190966. doi:10.1098/rspb.2019.0966

Brown, H. P. 1972. Trials and tribulations of a riffle beetle buff (or why didn't I stick with the Protozoa?). Bios **43**: 51–60.

Brusa, G., and B. E. L. Cerabolini. 2009. Ecological factors affecting plant species and travertine deposition in petrifying springs from an Italian 'Natura 2000' site. Bot. Helv. **119**: 113–123. doi:10.1007/s00035-009-0064-2

Burne, R. V., and L. S. Moore. 1987. Microbialites: Organosedimentary deposits of benthic microbial communities. PALAIOS **2**: 241. doi:10.2307/3514674

Canfield, D. E., E. Kristensen, and B. Thamdrup. 2005. The phosphorus cycle, p. 419–440. *In Advances in marine biology*. Elsevier.>

Cantonati, M., and others. 2016. A global review on ambient limestone-precipitating springs (LPS): Hydrogeological setting, ecology, and conservation. Sci. Total Environ. **568**: 624–637. doi:10.1016/j.scitotenv.2016.02.105

Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. **8**: 559–568 doi:10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2.

Chafetz, H. S., and R. L. Folk. 1984. Travertines: Depositional morphology and the bacterially constructed constituents. SEPM JSR **54**: 0289–0316. doi:10.1306/212F8404-2B24-11D7-8648000102C1865D

Chagas, A. A. P., G. E. Webb, R. V. Burne, and G. Southam. 2016. Modern lacustrine microbialites: Towards a synthesis of aqueous and carbonate geochemistry and mineralogy. Earth Sci. Rev. **162**: 338–363. doi:10.1016/j.earscirev.2016.09.012

Chave, K. E. 1965. Carbonates: Association with organic matter in surface seawater. Science **148**: 1723–1724. doi:10.1126/science.148.3678.1723

Chen, J., D. D. Zhang, S. Wang, T. Xiao, and R. Huang. 2004. Factors controlling tufa deposition in natural waters at waterfall sites. Sediment. Geol. **166**: 353–366. doi:10.1016/j.sedgeo.2004.02.003

Cicerone, D. S., A. J. Stewart, and Y. Roh. 1999. Diel cycles in calcite production and dissolution in a eutrophic basin. Environ. Toxic Chem. **18**: 2169–2177. doi:10.1002/etc.5620181008

Cohen, M. J., M. J. Kurz, J. B. Heffernan, J. B. Martin, R. L. Douglass, C. R. Foster, and R. G. Thomas. 2013. Diel phosphorus variation and the stoichiometry of ecosystem metabolism in a large spring-fed river. Ecological monographs **83**: 155–176. doi:10.1890/12-1497.1

Corman, J. R. 2024. *Distribution of studies on calcium carbonate in inland waters* [Dataset accessed 10/09/2024]. Dryad. doi: 10.5061/dryad.5qfttdzgr

Corman, J. R., A. T. Poret-Peterson, A. Uchitel, and J. J. Elser. 2016*b*. Interaction between lithification and resource availability in the microbialites of Río Mesquites, Cuatro Ciénegas, México. Geobiology **14**: 176–189. doi:10.1111/gbi.12168

Corman, J. R., E. K. Moody, and J. J. Elser. 2015. Stoichiometric impact of calcium carbonate deposition on nitrogen and phosphorus supplies in three montane streams. Biogeochemistry **126**: 285–300. doi:10.1007/s10533-015-0156-6

Corman, J. R., E. K. Moody, and J. J. Elser. 2016*a*. Calcium carbonate deposition drives nutrient cycling in a calcareous headwater stream. Ecol. Monogr. **86**: 448–461. doi:10.1002/ecm.1229

Cotner, J. B., and B. A. Biddanda. 2002. Small players, large role: Microbial influence on biogeochemical processes in pelagic aquatic ecosystems. Ecosystems **5**: 105–121. doi:10.1007/s10021-001-0059-3

Danen-Louwerse, H. J., L. Lijklema, and M. Coenraats. 1995. Coprecipitation of phosphate with calcium carbonate in Lake Veluwe. Water Res. **29**: 1781–1785. doi:10.1016/0043-1354(94)00301-M

Daoust, R. J., and D. L. Childers. 2004. Ecological effects of low-level phosphorus additions on two plant communities in a neotropical freshwater wetland ecosystem. Oecologia **141**: 672–686. doi:10.1007/s00442-004-1675-3

de Vicente, I., K. Cattaneo, L. Cruz-Pizarro, A. Brauer, and P. Guilizzoni. 2006. Sedimentary phosphate fractions related to calcite precipitation in an eutrophic Hardwater Lake (Lake Alserio, northern Italy). J. Paleolimnol. **35**: 55–64. doi:10.1007/s10933-005-6786-2

Diaz, M. R., and G. P. Eberli. 2019. Decoding the mechanism of formation in marine ooids: A review. Earth-Sci. Rev. **190**: 536–556. doi:10.1016/j.earscirev.2018.12.016

Diaz, J., E. Ingall, C. Benitez-Nelson, D. Paterson, M. D. De Jonge, I. McNulty, and J. A. Brandes. 2008. Marine polyphosphate: A key player in geologic phosphorus sequestration. Science **320**: 652–655. doi:10.1126/science.1151751

Dittrich, M., P. Kurz, and B. Wehrli. 2004. The role of autotrophic picocyanobacteria in calcite precipitation in an oligotrophic Lake. Geomicrobiol. J. **21**: 45–53. doi:10.1080/01490450490253455

Dittrich, M., and M. Obst. 2004. Are picoplankton responsible for calcite precipitation in lakes? Ambio **33**: 559–564. doi: 10.1579/0044-7447-33.8.559

Dittrich, M., and others. 2013. Phosphorus retention in a mesotrophic lake under transient loading conditions: Insights from a sediment phosphorus binding form study. Water Res. **47**: 1433–1447. doi:10.1016/j.watres.2012.12.006

Dodds, W. K. 2003. The role of periphyton in phosphorus retention in shallow freshwater aquatic systems. J. Phycol. **39**: 840–849. doi:10.1046/j.1529-8817.2003.02081.x

Dorioz, J. M., E. Pilleboue, and A. Ferhi. 1989. Dynamique du phosphore dans les bassins versants: Importance des phenomenes de retention dans les sediments. Water Res. **23**: 147–158. doi:10.1016/0043-1354(89)90038-9

Douglas, G. B., M. S. Robb, D. N. Coad, and P. W. Ford. 2004. A review of solid phase adsorbents for the removal of phosphorus from natural and waste waters, p. 291–320. *In Phosphorus in environmental technology: Principles and applications*. IWA Publishing.

Dove, P. M., and M. F. Hochella. 1993. Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by scanning force microscopy. Geochim. Cosmochim. Acta **57**: 705–714. doi:10.1016/0016-7037(93)90381-6

Drysdale, R. N. 1999. The sedimentological significance of hydropsychid caddis-fly larvae (order; Trichoptera) in a travertine-depositing stream; Louie Creek, Northwest Queensland. Australia. J. Sediment. Res. **69**: 145–150. doi: 10.2110/jsr.69.145

Drysdale, R. N., K. D. Carthew, and M. P. Taylor. 2003. Larval caddis-fly nets and retreats: A unique biosedimentary paleocurrent indicator for fossil tufa deposits. Sediment. Geol. **161**: 207–215. doi:10.1016/S0037-0738(03)00114-3

Drysdale, R. N. 2001. Factors controlling the hydrochemistry of Louie Creek, a travertine-depositing stream in the seasonally wet tropics of northern Australia. Mar. Freshw. Res. **52**: 793. doi:10.1071/MF00117

Duhamel, S., J. M. Diaz, J. C. Adams, K. Djaoudi, V. Steck, and E. M. Waggoner. 2021. Phosphorus as an integral component of global marine biogeochemistry. Nat. Geosci. **14**: 359–368. doi:10.1038/s41561-021-00755-8

Dupraz, C., and P. T. Visscher. 2005. Microbial lithification in marine stromatolites and hypersaline mats. Trends Microbiol. **13**: 429–438. doi:10.1016/j.tim.2005.07.008

Dupraz, C., R. P. Reid, O. Braissant, A. W. Decho, R. S. Norman, and P. T. Visscher. 2009. Processes of carbonate precipitation in modern microbial mats. Earth Sci. Rev. **96**: 141–162. doi:10.1016/j.earscirev.2008.10.005

Durrenfeldt, A. 1978. Untersuchungen zur Besiedlungsbiologie von Kalktuff faunistosche, okologische, und elektronenmikroskopische Befunde. Arch. Für Hydrobiol. **54**: 1–79.

Edwards, R. W., and J. Heywood. 1960. Effect of a sewage effluent discharge on the deposition of calcium carbonate on shells of the Snail Potamopyrgus jenkinsi (Smith). Nature **186**: 492–493. doi:10.1038/186492a0

Effler, S. W., A. R. Prestigiacomo, D. A. Matthews, and F. Peng. 2012. Sources and sinks of phosphorus for a perturbed stream and the effects of mineral deposits. J. Am. Water Resour. Assoc. **48**: 321–335. doi:10.1111/j.1752-1688.2011.00617.x

Effler, S. W. [ed.]. 1996. *Limnological and engineering analysis of polluted urban Lake*. Springer.

Elser, J. J., J. Watts, J. H. Schampel, and J. Farmer. 2006. Early Cambrian food webs on a trophic knife-edge? A hypothesis and preliminary data from a modern stromatolite-based ecosystem. Ecol. Lett. **9**: 295–303. doi:10.1111/j.1461-0248.2005.00873.x

Elser, J. J., and others. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. Ecol. Lett. **10**: 1135–1142. doi:10.1111/j.1461-0248.2007.01113.x

Escoffier, N., P. Perolo, G. Many, N. T. Pasche, and M.-E. Perga. 2023. Fine-scale dynamics of calcite precipitation in a large hardwater lake. Sci. Total Environ. **864**: 160699. doi:10.1016/j.scitotenv.2022.160699

Flores Bueso, Y., and M. Tangney. 2017. Synthetic biology in the driving seat of the bioeconomy. Trends Biotechnol. **35**: 373–378. doi:10.1016/j.tibtech.2017.02.002

Freeman, J. S., and D. L. Rowell. 1981. The adsorption and precipitation of phosphate onto calcite. J. Soil Sci. **32**: 75–84. doi:10.1111/j.1365-2389.1981.tb01687.x

Freytet, P., and A. Plet. 1996. Modern freshwater microbial carbonates: the *Phormidium stromatolites* (tufa-travertine) of southeastern Burgundy (Paris Basin, France). Facies **34**: 219–237. doi:10.1007/BF02546166

Freytet, P., and E. Verrecchia. 1995. Discovery of Ca oxalate crystals associated with fungi in moss travertines (Bryoherms, freshwater heterogeneous stromatolites). Geomicrobiol. J. **13**: 117–127. doi:10.1080/01490459509378010

Fuller, B. M., L. S. Sklar, Z. G. Compson, K. J. Adams, J. C. Marks, and A. C. Wilcox. 2011. Ecogeomorphic feedbacks in regrowth of travertine step-pool morphology after dam decommissioning, Fossil Creek, Arizona. Geomorphology **126**: 314–332. doi:10.1016/j.geomorph.2010.05.010

Gérard, E., B. Ménez, E. Couradeau, D. Moreira, K. Benzerara, R. Tavera, and P. López-García. 2013. Specific carbonate–microbe interactions in the modern microbialites of Lake Alchichica (Mexico). ISME J. **7**: 1997–2009. doi:10.1038/ismej.2013.81

Gaiser, E. E., D. L. Childers, R. D. Jones, J. H. Richards, L. J. Scinto, and J. C. Trexler. 2006. Periphyton responses to eutrophication in the Florida Everglades: Cross-system patterns of structural and compositional change. Limnol. Oceanogr. **51**: 617–630. doi:10.4319/lo.2006.51.1_part_2.0617

Gaiser, E. E., L. J. Scinto, J. H. Richards, K. Jayachandran, D. L. Childers, J. C. Trexler, and R. D. Jones. 2004. Phosphorus in periphyton mats provides the best metric for detecting low-level P enrichment in an oligotrophic wetland. Water Res. **38**: 507–516. doi:10.1016/j.watres.2003.10.020

Gaiser, E. E., P. V. McCormick, S. E. Hagerthey, and A. D. Gottlieb. 2011. Landscape patterns of Periphyton in the Florida Everglades. Crit. Rev. Environ. Sci. Technol. **41**: 92–120. doi:10.1080/10643389.2010.531192

Gallagher, T. M., and D. O. Breecker. 2020. The obscuring effects of calcite dissolution and formation on quantifying soil respiration. Global Biogeochem. Cycles **34**: e2020GB006584. doi:10.1029/2020GB006584

Garcia-Pichel, F., F. A. Al-Horani, J. D. Farmer, R. Ludwig, and B. D. Wade. 2004. Balance between microbial calcification and metazoan bioerosion in modern stromatolitic oncolites. Geobiology **2**: 49–57. doi:10.1111/j.1472-4669.2004.00017.x

Gleason, P. J., and W. Spackman. 1974. Calcareous periphyton and water chemistry in the Everglades, p. 146–181. *In Environments of South Florida: Present and past*. Miami Geological Society.

Goldscheider, N., and others. 2020. Global distribution of carbonate rocks and karst water resources. Hydrgeol. J. **28**: 1661–1677. doi:10.1007/s10040-020-02139-5

Golterman, H. L. 2001. *Phosphate release from anoxic sediments or 'What did Mortimer really write?'*. Hydrobiologia **450**: 99–106. doi:10.1023/A:1017559903404

Gonsiorczyk, T., P. Casper, and R. Koschel. 1995. Sedimentuntsuchungen zum Kohlenstoff- und Phosphorgehalt in baltischen Seen. Limnologica **25**: 365–379.

Gottlieb, A., J. Richards, and E. Gaiser. 2005. Effects of desiccation duration on the community structure and nutrient retention of short and long-hydroperiod Everglades periphyton mats. Aquat. Bot. **82**: 99–112. doi:10.1016/j.aquabot.2005.02.012

Green, D. B., T. J. Logan, and N. E. Smeck. 1978. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River basin of Ohio. J. Environ. Qual. **7**: 208–212. doi:10.2134/jeq1978.00472425000700020011x

Grootjans, A. P., L. Wołejko, H. de Mars, A. J. P. Smolders, and G. van Dijk. 2021. On the hydrological relationship between petrifying-springs, alkaline-fens, and Calcareous-spring-mires in the lowlands of North–West and Central Europe; consequences for restoration. Mires Peat **27**: 1–18. doi:10.19189/MaP.2020.OMB.StA.2134

Gunatilaka, A. 1982. Phosphate adsorption kinetics of resuspended sediments in a shallow lake, Neusiedlersee, Austria. Hydrobiologia **91–92**: 293–298. doi:10.1007/BF02391946

Hägele, D., R. Leinfelder, J. Grau, E.-G. Burmeister, and U. Struck. 2006. Oncoids from the river Alz (southern Germany): Tiny ecosystems in a phosphorus-limited environment. Palaeogeogr. Palaeoclimatol. Palaeoecol. **237**: 378–395. doi:10.1016/j.palaeo.2005.12.016

Hägele, D., R. Leinfelder, J. Grau, E.-G. Burmeister, and U. Struck. 2006. Oncoids from the river Alz (southern Germany): Tiny ecosystems in a phosphorus-limited environment. Palaeogeogr. Palaeoclimatol. Palaeoecol. **237**: 378–395. doi:10.1016/j.palaeo.2005.12.016

Hamilton, S. K., D. A. Bruesewitz, G. P. Horst, D. B. Weed, and O. Sarnelle. 2009. Biogenic calcite–phosphorus precipitation as a negative feedback to lake eutrophication. Can. J. Fish. Aquat. Sci. **66**: 343–350. doi:10.1139/F09-003

Hartley, A. M., W. A. House, M. E. Callow, and B. S. C. Leadbeater. 1997. Coprecipitation of phosphate with calcite in the presence of photosynthesizing green algae. Water Res. **31**: 2261–2268. doi:10.1016/S0043-1354(97)00103-6

Heath, C. R., B. C. S. Leadbeater, and M. E. Callow. 1995. Effect of inhibitors on calcium carbonate deposition mediated by freshwater algae. J. Appl. Phycol. **7**: 367–380. doi:10.1007/BF00003794

Herman, J. S., and M. M. Lorah. 1987. CO_2 outgassing and calcite precipitation in Falling Spring Creek, Virginia, U.S.A. Chem. Geol. **62**: 251–262. doi:10.1016/0009-2541(87)90090-8

Hodell, D. A., C. L. Schelske, G. L. Fahnenstiel, and L. L. Robbins. 1998. Biologically induced calcite and its isotopic composition in Lake Ontario. Limnol. Oceanogr. **43**: 187–199. doi:10.4319/lo.1998.43.2.0187

House, W. A. 1990. The prediction of phosphate coprecipitation with calcite in freshwaters. Water Res. **24**: 1017–1023. doi:10.1016/0043-1354(90)90124-O

House, W. A. 2003. Geochemical cycling of phosphorus in rivers. Appl. Geochem. **18**: 739–748. doi:10.1016/S0883-2927(02)00158-0

House, W. A., and L. Donaldson. 1986. Adsorption and coprecipitation of phosphate on calcite. J. Colloid Interface Sci. **112**: 309–324. doi:10.1016/0021-9797(86)90101-3

Hutchinson, G. E. 1957. *A treatise on limnology*, v. **1**. Wiley.

Ishikawa, M., and M. Ichikuni. 1981. Coprecipitation of phosphate with calcite. Geochem. J. **15**: 283–288. doi:10.2343/geochemj.15.283

Jäger, P., and J. Röhrs. 1990. Phosphorfällung über Calciumcarbonat im eutrophen Wallersee (Salzburger Alpenvorland, Österreich). Coprecipitation of phosphorus with calcite in the eutrophic Wallersee (Alpine Foreland of Salzburg, Austria). Int. Rev. Hydrobiol. **75**: 153–173. doi:10.1002/iroh.19900750204

Jaisi, D. P., and R. E. Blake. 2010. Tracing sources and cycling of phosphorus in Peru Margin sediments using oxygen isotopes in authigenic and detrital phosphates. Geochim. Cosmochim. Acta **74**: 3199–3212. doi:10.1016/j.gca.2010.02.030

Jarvie, H. P., C. Neal, A. Warwick, J. White, M. Neal, H. D. Wickham, L. K. Hill, and M. C. Andrews. 2002. Phosphorus uptake into algal biofilms in a lowland chalk river. Sci. Total Environ. **282–283**: 353–373. doi:10.1016/S0048-9697(01)00924-X

Jeziorski, A., and others. 2008. The widespread threat of calcium decline in fresh waters. Science **322**: 1374–1377. doi:10.1126/science.1164949

Jones, A. A., and P. C. Bennett. 2014. Mineral microniches control the diversity of subsurface microbial populations. Geomicrobiol. J. **31**: 246–261. doi:10.1080/01490451.2013.809174

Küchler-Krischun, J., and J. Kleiner. 1990. Heterogeneously nucleated calcite precipitation in Lake Constance. A short time resolution study. Aquat. Sci. **52**: 176–197. doi:10.1007/BF00902379

Kah, L. C., and R. Riding. 2007. Mesoproterozoic carbon dioxide levels inferred from calcified cyanobacteria. Geol **35**: 799. doi:10.1130/G23680A.1

Karl, D. M. 2014. Microbially mediated transformations of phosphorus in the sea: New views of an old cycle. Ann. Rev. Mar. Sci. **6**: 279–337. doi:10.1146/annurev-marine-010213-135046

Katsaounos, C. Z., D. L. Giokas, A. G. Vlessidis, and M. I. Karayannis. 2007. Identification of longitudinal and temporal patterns of phosphorus fractionation in river sediments by non-parametric statistics and pattern recognition techniques. Desalination **213**: 311–333. doi:10.1016/j.desal.2006.04.090

Kempe, S., and K. Emeis. 1985. Carbonate chemistry and the formation of Plitvice Lakes, p. 351–383. *In Transport of carbon and minerals in major world Rivers, Pt. 1*. SCOPE/UNEP Sonderband.

Khan, H., A. Laas, R. Marcé, and B. Obrador. 2020. Major effects of alkalinity on the relationship between metabolism and dissolved inorganic carbon dynamics in lakes. Ecosystems **23**: 1566–1580. doi:10.1007/s10021-020-00488-6

Kinsman-Costello, L. E., S. K. Hamilton, J. M. O'Brien, and J. T. Lennon. 2016. Phosphorus release from the drying and reflooding of diverse shallow sediments. Biogeochemistry **130**: 159–176. doi:10.1007/s10533-016-0250-4

Kitano, Y., M. Okumura, and M. Idogaki. 1978. Uptake of phosphate ions by calcium carbonate. Geochem. J. **12**: 29–37. doi:10.2343/geochemj.12.29

Kleiner, J. 1988. Coprecipitation of phosphate with calcite in lake water: A laboratory experiment modelling phosphorus removal with calcite in Lake Constance. Water Res. **22**: 1259–1265. doi:10.1016/0043-1354(88)90113-3

Kock, C., A. Meyer, B. Spänhoff, and E. I. Meyer. 2006. Tufa deposition in karst streams can enhance the food supply of the grazing caddisfly *Melampophylax mucoreus* (Limnephilidae). Int. Rev. Hydrobiol. **91**: 242–249. doi:10.1002/iroh.200510839

Koschel, R. 1990. Pelagic calcite precipitation and trophic state of hardwater lakes. Arch. Hydrobiol. **33**: 713–722.

Koschel, R., J. Benndorf, G. Proft, and F. Recknagel. 1983. Calcite precipitation as a natural control mechanism of eutrophication. Arch. Hydrobiol. **98**: 380–408.

Koschel, R., P. Casper, T. Gonsiorczyk, R. Roßberg, and G. Wauer. 2006. Hypolimnetic Al and $CaCO_3$ treatments and aeration for restoration of a stratified eutrophic hardwater lake in Germany. SIL Proc. **1922–2010**: 2165–2171. doi:10.1080/03680770.2006.11903075

Koschel, R. H. 1997. Structure and function of pelagic calcite precipitation in lake ecosystems. SIL Proc. **1922–2010**: 343–349. doi:10.1080/03680770.1995.11900731

Krüper, F. 1930. Über Verkalkungserscheinungen bei Dipteren-Larven und ihre Ursachen. Arch. Für Hydrobiol. **22**: 185–219.

Krumbein, W. E. 1979. Photolithotropic and chemoorganotrophic activity of bacteria and algae as related to beachrock formation and degradation (gulf of Aqaba, Sinai). Geomicrobiol. J. **1**: 139–203. doi:10.1080/01490457909377729

Kufel, L., E. Biardzka, and M. Strzałek. 2013. Calcium carbonate incrustation and phosphorus fractions in five charophyte species. Aquat. Bot. **109**: 54–57. doi:10.1016/j.aquabot.2013.04.002

Kufel, L., M. Strzałek, and E. Biardzka. 2016. Site- and species-specific contribution of charophytes to calcium and phosphorus cycling in lakes. Hydrobiologia **767**: 185–195. doi:10.1007/s10750-015-2498-4

Kufel, L., and I. Kufel. 2002. Chara beds acting as nutrient sinks in shallow lakes—A review. Aquat. Bot. **72**: 249–260. doi:10.1016/S0304-3770(01)00204-2

Li, X., M. Zhang, W. Xiao, J. Du, M. Sheng, D. Zhu, A. Plenković-Moraj, and G. Sun. 2020. The color formation mechanism of the blue Karst Lakes in Jiuzhaigou nature reserve, Sichuan, China. Water **12**: 771. doi:10.3390/w12030771

Lim, D. S. S. L. 2009. Limnology of Pavilion Lake, B. C., Canada—characterization of a microbialite forming environment. Arch. Hydrobiol. **173**: 329–351. doi:10.1127/1863-9135/2009/0173-0329

Lin, Y.-P., and P. C. Singer. 2006. Inhibition of calcite precipitation by orthophosphate: Speciation and thermodynamic considerations. Geochim. Cosmochim. Acta **70**: 2530–2539. doi:10.1016/j.gca.2006.03.002

Liu, G., W. Guo, S. Yuan, H. Zhu, T. Yang, Y. Zhou, and D. Zhu. 2016. Occurrence and characterization of $CaCO_3$-P coprecipitation on the leaf surface of *Potamogeton crispus* in water. Environ. Sci. Pollut. Res. **23**: 23308–23315. doi:10.1007/s11356-016-7844-1

Lotter, A. F., M. Sturm, J. L. Teranes, and B. Wehrli. 1997. Varve formation since 1885 and high-resolution varve analyses in hypertrophic Baldeggersee (Switzerland). Aquat. Sci. **59**: 304–325.

Lukens, N. R., B. M. Kraemer, V. Constant, E. J. Hamann, E. Michel, A. M. Socci, Y. Vadeboncoeur, and P. B. McIntyre. 2017. Animals and their epibiota as net autotrophs: size scaling of epibiotic metabolism on snail shells. Freshw. Sci. **36**: 307–315. doi:10.1086/691438

Müller, B., J. S. Meyer, and R. Gächter. 2016. Alkalinity regulation in calcium carbonate-buffered lakes: Alkalinity regulation in calcium carbonate-buffered lakes. Limnol. Oceanogr. **61**: 341–352. doi:10.1002/lno.10213

Müller, B., Y. Wang, and B. Wehrli. 2006. Cycling of calcite in hard water lakes of different trophic states. Limnol. Oceanogr. **51**: 1678–1688. doi:10.4319/lo.2006.51.4.1678

Mackey, T. J., D. Y. Sumner, I. Hawes, S. Z. Leidman, D. T. Andersen, and A. D. Jungblut. 2018. Stromatolite records of environmental change in perennially ice-covered Lake Joyce, McMurdo Dry Valleys, Antarctica. Biogeochemistry **137**: 73–92. doi:10.1007/s10533-017-0402-1

Malusa, J., S. T. Overby, and R. A. Parnell. 2003. Potential for travertine formation. Appl. Geochem. **18**: 1081–1093. doi:10.1016/S0883-2927(02)00241-X

Marazzi, L., E. E. Gaiser, and F. A. C. Tobias. 2017. Phosphorus scarcity and desiccation stress increase the occurrence of dominant taxa in wetland benthic primary producer communities. Aquat. Ecol. **51**: 571–589. doi:10.1007/s10452-017-9637-0

Marcé, R., B. Obrador, J.-A. Morguí, J. Lluís Riera, P. López, and J. Armengol. 2015. Carbonate weathering as a driver of CO_2 supersaturation in lakes. Nat. Geosci. **8**: 107–111. doi:10.1038/ngeo2341

Markovic, S., A. Liang, S. B. Watson, J. Guo, S. Mugalingam, G. Arhonditsis, A. Morley, and M. Dittrich. 2019. Biogeochemical mechanisms controlling phosphorus diagenesis and internal loading in a remediated hard water eutrophic embayment. Chem. Geol. **514**: 122–137. doi:10.1016/j.chemgeo.2019.03.031

Matoničkin Kepčija, R., M. Miliša, M. Sertić Perić, M. Matijić Cvjetović, and B. Primc-Habdija. 2011. Response of periphyton to nutrient addition in a tufa-depositing environment. Aquat. Microb. Ecol. **65**: 183–195. doi:10.3354/ame01545

Mc Callister, D. L., and T. J. Logan. 1978. Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio. J. Environ. Qual. **7**: 87–92. doi:10.2134/jeq1978.00472425000700010018x

McConnaughey, T. A., and J. F. Whelan. 1997. Calcification generates protons for nutrient and bicarbonate uptake. Earth Sci. Rev. **42**: 95–117. doi:10.1016/S0012-8252(96)00036-0

Merz-Preiß, M., and R. Riding. 1999. Cyanobacterial tufa calcification in two freshwater streams: Ambient environment, chemical thresholds and biological processes. Sediment. Geol. **126**: 103–124. doi:10.1016/S0037-0738(99)00035-4

Merz, M. 1992. The biology of carbonate precipitation by cyanobacteria. Facies **26**: 81–102. doi:10.1007/BF02539795

Millero, F., F. Huang, X. Zhu, X. Liu, and J.-Z. Zhang. 2001. *Adsorption and desorption of phosphate on calcite and aragonite in seawater*. Aquatic Geochemistry. **7**: 33–56. doi:10.1023/A:1011344117092

Minckley, W. L. 1963. The Ecology of a Spring Stream Doe Run, Meade County. Kentucky. Wildl. Monogr. **11**: 3–124.

Minder, L. 1929. Chemische Untersuchungen am Stausee Wäggital. Weiterer Beitrag zur Abklärung des Stoffhaushaltes im See. SIL Proc. 1922–2010 **4**: 454–461. doi:10.1080/03680770.1929.11898421

Moody, E. K., J. R. Corman, and M. T. Bogan. 2016. Caught between a rock and a hard mineral encrustation: Long-lived aquatic insects accumulate calcium carbonate deposits in a montane desert stream. West. North Am. Nat. **76**: 172–179. doi:10.3398/064.076.0204

Mooney, R. J., E. A. Strauss, and R. J. Haro. 2014. Nutrient recycling by caddisflies alleviates phosphorus limitation in case periphyton. Freshw. Sci. **33**: 1086–1092. doi:10.1086/677806

Moore, P. A., and K. R. Reddy. 1994. Role of Eh and pH and phosphorus geochemistry in sediments of Lake Okeechobee, Florida. J. Environ. Qual. **23**: 955–964. doi:10.2134/jeq1994.00472425002300050016x

Morse, J. W., R. S. Arvidson, and A. Lüttge. 2007. Calcium carbonate formation and dissolution. Chem. Rev. **107**: 342–381. doi:10.1021/cr050358j

Moutin, T., J. Y. Gal, H. El Halouani, B. Picot, and J. Bontoux. 1992. Decrease of phosphate concentration in a high rate pond by precipitation of calcium phosphate: Theoretical and experimental results. Water Res. **26**: 1445–1450. doi:10.1016/0043-1354(92)90063-A

Mumby, P. J., and others. 2006. Fishing, trophic cascades, and the process of grazing on coral reefs. Science **311**: 98–101. doi:10.1126/science.1121129

Murphy, T. P., K. J. Hall, and I. Yesaki. 1983. Coprecipitation of phosphate with calcite in a naturally eutrophic lake. Limnol. Oceanogr. **28**: 58–69. doi:10.4319/lo.1983.28.1.0058

Neal, C. 2001. The potential for phosphorus pollution remediation by calcite precipitation in UK freshwaters. Hydrol. Earth Syst. Sci. **5**: 119–131. doi:10.5194/hess-5-119-2001

Neil, W. T., and E. R. Allen. 1954. Algae on turtles: some additional considerations. Ecology **35**: 581–584. doi:10.2307/1931051

Niessen, V. F., and M. Sturm. 1987. Die Sedimente des Baldeggersees (Schweiz)—Ablagerungsraum und Eutrophierungsentwicklung wahrend der letzten 100 Jahre. Arch. Hydrobiol. **108**: 365–383. doi:10.1127/archiv-hydrobiol/108/1987/365

Noe, G. B., L. J. Scinto, J. Taylor, D. L. Childers, and R. D. Jones. 2003. Phosphorus cycling and partitioning in an oligotrophic Everglades wetland ecosystem: A radioisotope tracing study. Freshw. Biol. **48**: 1993–2008. doi:10.1046/j.1365-2427.2003.01143.x

Obst, M., and others. 2009. Precipitation of amorphous $CaCO_3$ (aragonite-like) by cyanobacteria: A STXM study of the influence of EPS on the nucleation process. Geochim. Cosmochim. Acta **73**: 4180–4198. doi:10.1016/j.gca.2009.04.013

Ohle, W. 1952. Die hypolimnische Kohlendioxyd-Akkumulation als produktionsbiologischer Indikator. Arch. Hydrobiol. **46**: 153–285.

Omelon, C. R., A. L. Brady, G. F. Slater, B. Laval, D. S. S. Lim, and G. Southam. 2013. Microstructure variability in freshwater microbialites, Pavilion Lake. Canada. Palaeogeogr. Palaeoclimatol. Palaeoecol. **392**: 62–70. doi:10.1016/j.palaeo.2013.08.017

Orihel, D. M., H. M. Baulch, N. J. Casson, R. L. North, C. T. Parsons, D. C. M. Seckar, and J. J. Venkiteswaran. 2017. Internal phosphorus loading in Canadian fresh waters: A critical review and data analysis. Can. J. Fish. Aquat. Sci. **74**: 2005–2029. doi:10.1139/cjfas-2016-0500

Otsuki, A., and R. G. Wetzel. 1972. Coprecipitation of phosphate with carbonates in a marl lake. Limnol. Oceanogr. **17**: 763–767. doi:10.4319/lo.1972.17.5.0763

Pace, A., and others. 2016. Microbial and diagenetic steps leading to the mineralisation of Great Salt Lake microbialites. Sci. Rep. **6**: 31495. doi:10.1038/srep31495

Paprocki, H., R. W. Holzenthal, and C. Cressa. 2003. A new species of Smicridea McLachlan (Trichoptera: Hydropsychidae) from venezuela and its role in travertine biogenesis. J. North Am. Benthol. Soc. **22**: 401–409. doi:10.2307/1468270

Parker, B. C., G. M. Simmons, F. G. Love, R. A. Wharton, and K. G. Seaburg. 1981. Modern stromatolites in antarctic dry valley lakes. Bioscience **31**: 656–661. doi:10.2307/1308639

Parmenter, R. R., and V. A. Lamarra. 1991. Nutrient cycling in a freshwater marsh: The decomposition of fish and waterfowl carrion. Limnol. Oceanogr. **36**: 976–987. doi:10.4319/lo.1991.36.5.0976

Pełechaty, M., A. Pukacz, K. Apolinarska, A. Pełechata, and M. Siepak. 2013. The significance of *Chara* vegetation in the precipitation of lacustrine calcium carbonate G.D. Porta [ed.]. Sedimentology **60**: 1017–1035. doi:10.1111/sed.12020

Pedley, M., J. A. G. Martín, S. O. Delgado, and M. García Del Cura. 2003. Sedimentology of quaternary perched springline and paludal tufas: Criteria for recognition, with examples from Guadalajara Province, Spain. Sedimentology **50**: 23–44. doi:10.1046/j.1365-3091.2003.00502.x

Penn, M. R., and M. T. Auer. 1997. Seasonal variability in phosphorus speciation and deposition in a calcareous, eutrophic lake. Mar. Geol. **139**: 47–59. doi:10.1016/S0025-3227(96)00097-7

Pentecost, A. 2005. *Travertine*. Springer.

Pentecost, A. 2018. Cyanobacteria–phosphate–calcite interactions in limestone (hardwater) streams of England. Hydrobiologia **811**: 49–60. doi:10.1007/s10750-017-3280-6

Pentecost, A., and B. A. Whitton. 2012. Subaerial cyanobacteria, p. 291–316. *In* B. A. Whitton [ed.], *Ecology of cyanobacteria II*. Springer.

Pentecost, A., and P. Coletta. 2007. The role of photosynthesis and CO_2 evasion in travertine formation: A quantitative investigation at an important travertine-depositing hot spring, Le Zitelle, Lazio, Italy. JGS **164**: 843–853. doi:10.1144/0016-76492006-037

Pettersson, K., B. Boström, and O.-S. Jacobsen. 1988. Phosphorus in sediments—speciation and analysis. Hydrobiologia **170**: 91–101. doi:10.1007/BF00024900

Pitois, F. D. R., A. Jigorel, and G. Bertru. 2003. *Development of cyanobacterial build-up and evolution of river bed morphology* *in the chalk stream Eaulne (Upper-Normandy, France)*. Biodiversity and Conservation. **12**: 621–636. doi:10.1023/A:1022412211915

Plant, L. J., and W. A. House. 2002. Precipitation of calcite in the presence of inorganic phosphate. Colloids Surf. A Physicochem. Eng. Asp. **203**: 143–153. doi:10.1016/S0927-7757(01)01089-5

Prepas, E. E., J. Babin, T. P. Murphy, P. A. Chambers, G. J. Sandland, A. Ghadouani, and M. Serediak. 2001. Long-term effects of successive $Ca(OH)_2$ and $CaCO_3$ treatments on the water quality of two eutrophic hardwater lakes. Freshw. Biol. **46**: 1089–1103. doi:10.1046/j.1365-2427.2001.00792.x

Ptacnik, R., T. Andersen, and T. Tamminen. 2010. Performance of the Redfield ratio and a family of nutrient limitation indicators as thresholds for phytoplankton N vs. P limitation. Ecosystems **13**: 1201–1214. doi:10.1007/s10021-010-9380-z

Pukacz, A., M. Pełechaty, and M. Frankowski. 2016. Depth-dependence and monthly variability of charophyte biomass production: Consequences for the precipitation of calcium carbonate in a shallow Chara-lake. Environ. Sci. Pollut. Res. **23**: 22433–22442. doi:10.1007/s11356-016-7420-8

Pulvermüller, A. G., J. Kleiner, and W. Mauser. 1995. Calcite patchiness in Lake Constance as viewed by LANDSAT-TM. Aquat. Sci. **57**: 338–349. doi:10.1007/BF00878397

Raven, J. A., and M. Giordano. 2009. Biomineralization by photosynthetic organisms: Evidence of coevolution of the organisms and their environment? Geobiology **7**: 140–154. doi:10.1111/j.1472-4669.2008.00181.x

Raymond, P. A., and S. K. Hamilton. 2018. Anthropogenic influences on riverine fluxes of dissolved inorganic carbon to the oceans. Limnol. Oceanogr. Lett. **3**: 143–155. doi:10.1002/lol2.10069

Reddy, K. R., R. H. Kadlec, E. Flaig, and P. M. Gale. 1999. Phosphorus retention in streams and wetlands: A review. Crit. Rev. Environ. Sci. Technol. **29**: 83–146. doi:10.1080/10643389991259182

Reddy, K. R., W. F. DeBusk, R. D. DeLaune, and M. S. Koch. 1993. Long-term nutrient accumulation rates in the Everglades. Soil Sci. Soc Am. J. **57**: 1147–1155. doi:10.2136/sssaj1993.03615995005700040044x

Rejmánková, E., P. Macek, and K. Epps. 2008. Wetland ecosystem changes after three years of phosphorus addition. Wetlands **28**: 914–927. doi:10.1672/07-150.1

Riding, R. 1999. The term stromatolite: towards an essential definition. Lethaia **32**: 321–330. doi:10.1111/j.1502-3931.1999.tb00550.x

Riding, R. 2000. Microbial carbonates: the geological record of calcified bacterial–algal mats and biofilms. Sedimentology **47**: 179–214. doi:10.1046/j.1365-3091.2000.00003.x

Riding, R. 2011. Microbialites, stromatolies, and thrombolites, p. 635–654. *In*, *Encyclopedia of geobiology*. Springer.

Riding, R. [ed.]. 1991. *Calcareous algae and stromatolites*. Springer.

Rishworth, G. M., R. Perissinotto, T. G. Bornman, and D. A. Lemley. 2017. Peritidal stromatolites at the convergence of groundwater seepage and marine incursion: Patterns of salinity, temperature and nutrient variability. J. Mar. Syst. **167**: 68–77. doi:10.1016/j.jmarsys.2016.11.010

Robertson, D. M., H. S. Garn, and W. J. Rose. 2007. Response of calcareous Nagawicka Lake, Wisconsin, to changes in phosphorus loading. Lake Reserv. Manag. **23**: 298–312. doi:10.1080/07438140709354018

Rodriguez, I. R., C. Amrhein, and M. A. Anderson. 2008. Laboratory studies on the coprecipitation of phosphate with calcium carbonate in the Salton Sea, California. Hydrobiologia **604**: 45–55. doi:10.1007/s10750-008-9310-7

Rosen, M. R., L. Coshell, J. V. Turner, and R. J. Woodbury. 1996. Hydrochemistry and nutrient cycling in Yalgorup National Park, Western Australia. J. Hydrol. **185**: 241–274. doi:10.1016/0022-1694(95)02981-8

Rossknecht, V. H. 1980. Phosphatelimination durch autochthone Calcitfallung im Bodensee-Obersee. Arch.Hydrobiol. **88**: 328–344.

Ruff, H., and G. Maier. 2000. Calcium carbonate deposits reduce predation pressure on Gammarus fossarum from salamander larvae: Calcium carbonate deposits on Gammarus. Freshw. Biol. **43**: 99–105. doi:10.1046/j.1365-2427.2000.00527.x

Sø, H. U., D. Postma, R. Jakobsen, and F. Larsen. 2011. Sorption of phosphate onto calcite; results from batch experiments and surface complexation modeling. Geochim. Cosmochim. Acta **75**: 2911–2923. doi:10.1016/j.gca.2011.02.031

Salingar, Y., Y. Geifman, and M. Aronowich. 1993. Orthophosphate and calcium carbonate solubilities in the upper Jordan Watershed Basin. J. Environ. Qual. **22**: 672–677. doi:10.2134/jeq1993.00472425002200040006x

Sand-Jensen, K., and K. J. Hammer. 2012. Moss cushions facilitate water and nutrient supply for plant species on bare limestone pavements. Oecologia **170**: 305–312. doi:10.1007/s00442-012-2314-z

Sawada, K., S. Yoshida, and T. Suzuki. 1992. Adsorption of phosphate on vaterite. Faraday Trans. **88**: 2227. doi:10.1039/ft9928802227

Schernewski, G., L. Theesen, and K. E. Kerger. 1994. Modelling thermal stratification and calcite precipitation of Lake Belau (northern Germany). Ecol. Model. **75–76**: 421–433. doi:10.1016/0304-3800(94)90037-X

Scinto, L. J., and K. R. Reddy. 2003. Biotic and abiotic uptake of phosphorus by periphyton in a subtropical freshwater wetland. Aquat. Bot. **77**: 203–222. doi:10.1016/S0304-3770(03)00106-2

Shiraishi, F., A. Bissett, D. de Beer, A. Reimer, and G. Arp. 2008. Photosynthesis, respiration and exopolymer calcium-binding in biofilm calcification (Westerhöfer and

Deinschwanger Creek, Germany). Geomicrobiol. J. **25**: 83–94. doi:10.1080/01490450801934888

Siong, K., and T. Asaeda. 2006. Does calcite encrustation in *Chara* provide a phosphorus nutrient sink? J. Environ. Qual. **35**: 490–494. doi:10.2134/jeq2005.0276

Siong, K., and T. Asaeda. 2009. Effect of magnesium on charophytes calcification: Implications for phosphorus speciation stored in biomass and sediment in Myall Lake (Australia). Hydrobiologia **632**: 247–259. doi:10.1007/s10750-009-9846-1

Smith, M. D., S. E. Goater, E. S. Reichwaldt, B. Knott, and A. Ghadouani. 2010. Effects of recent increases in salinity and nutrient concentrations on the microbialite community of Lake Clifton (Western Australia): Are the thrombolites at risk? Hydrobiologia **649**: 207–216. doi:10.1007/s10750-010-0246-3

Smith, V. H., and D. W. Schindler. 2009. Eutrophication science: Where do we go from here? Trends Ecol. Evol. **24**: 201–207. doi:10.1016/j.tree.2008.11.009

Souza-Egipsy, V., M. A. García Del Cura, C. Ascaso, A. De Los Ríos, J. Wierzchos, and J. A. González-Martín. 2006. Interaction between calcite and phosphorus in biomineralization processes in tufa carbonates. Int. Rev. Hydrobiol. **91**: 222–241. doi:10.1002/iroh.200510845

Stabel, H.-H. 1986. Calcite precipitation in Lake Constance: Chemical equilibrium, sedimentation, and nucleation by algae1. Limnol. Oceanogr. **31**: 1081–1094. doi:10.4319/lo.1986.31.5.1081

Stabel, H., and C. Chondrogianni. 1988. Seasonal shifts in the grain size of settling particles in lake constance. Water Res. **22**: 251–255. doi:10.1016/0043-1354(88)90086-3

Sterner, R. W., and J. J. Elser. 2002. *Ecological stoichiometry: The biology of elements from molecules to the biosphere*. Princeton Univ. Press.

Stets, E. G., R. G. Striegl, G. R. Aiken, D. O. Rosenberry, and T. C. Winter. 2009. Hydrologic support of carbon dioxide flux revealed by whole-lake carbon budgets. J. Geophys. Res. **114**: 2008JG000783. doi:10.1029/2008JG000783

Stewart, A. J. 1988. Alkalinity dynamics in a hard-water prairie-margin stream. Arch. Hydrobiol. **112**: 335–350. doi:10.1127/archiv-hydrobiol/112/1988/335

Strong, A. E., and B. J. Eadie. 1978. Satellite observations of calcium carbonate precipitations in the Great Lakes. Limnol. Oceanogr. **23**: 877–887. doi:10.4319/lo.1978.23.5.0877

Stumm, W., and J. J. Morgan. 1996. *Aquatic chemistry: Chemical equilibria and rates in natural waters*, 3rd Edition. Wiley.

Suarez, D. L. 1983. Calcite supersaturation and precipitation kinetics in the lower Colorado River, All-American Canal and East Highline Canal. Water Resour. Res. **19**: 653–661. doi:10.1029/WR019i003p00653

Subalusky, A. L., C. L. Dutton, E. J. Rosi, L. M. Puth, and D. M. Post. 2020. A river of bones: wildebeest skeletons leave a legacy of mass mortality in the Mara River. Kenya. Front. Ecol. Evol. **8**: 31. doi:10.3389/fevo.2020.00031

Sun, B., H. Zhao, Y. Zhao, M. Tucker, Z. Han, and H. Yan. 2020. Bio-precipitation of carbonate and phosphate minerals induced by the bacterium Citrobacter freundii ZW123 in an anaerobic environment. Minerals **10**: 65. doi:10.3390/min10010065

Suzuki, T., S. Inomata, and K. Sawada. 1986. Adsorption of phosphate on calcite. J. Chem. Soc. Faraday Trans. 1 **82**: 1733. doi:10.1039/f19868201733

Szramek, K., and L. M. Walter. 2004. Impact of carbonate precipitation on riverine inorganic carbon mass transport from a mid-continent, forested watershed. Aquatic Geochemistry **10**: 99–137. doi:10.1023/B:AQUA.0000038960.63501.5b

Tapia Grimaldo, J., and others. 2017. Environmental drivers of freshwater macrophyte diversity and community composition in calcareous warm-water rivers of America and Africa. Freshw. Biol. **62**: 1511–1527. doi:10.1111/fwb.12962

Thompson, J. B., and F. G. Ferris. 1990. Cyanobacterial precipitation of gypsum, calcite, and magnesite from natural alkaline lake water. Geol **18**: 995. doi:10.1130/0091-7613(1990)018<0995:CPOGCA>2.3.CO;2

Toner, J. D., and D. C. Catling. 2020. A carbonate-rich lake solution to the phosphate problem of the origin of life. Proc. Natl. Acad. Sci. U. S. A. **117**: 883–888. doi:10.1073/pnas.1916109117

Trobej, M., J. Bednar, J. Waringer, and M. Schagerl. 2017. Algal communities of spring-associated limestone habitats. Aquat. Microb. Ecol. **80**: 61–75. doi:10.3354/ame01836

Valdespino-Castillo, P. M., R. J. Alcántara-Hernández, J. Alcocer, M. Merino-Ibarra, M. Macek, and L. I. Falcón. 2014. Alkaline phosphatases in microbialites and bacterioplankton from Alchichica soda lake, Mexico. FEMS Microbiol. Ecol. **90**: 504–519. doi:10.1111/1574-6941.12411

Vignale, F. A., and others. 2022. Lithifying and non-lithifying microbial ecosystems in the wetlands and salt flats of the Central Andes. Microb. Ecol. **83**: 1–17. doi:10.1007/s00248-021-01725-8

Visscher, P. T., and J. F. Stolz. 2005. Microbial mats as bioreactors: Populations, processes, and products. Palaeogeogr. Palaeoclimatol. Palaeoecol. **219**: 87–100. doi:10.1016/j.palaeo.2004.10.016

Walpersdorf, E., T. Neumann, and D. Stüben. 2004. Efficiency of natural calcite precipitation compared to lake marl application used for water quality improvement in an eutrophic lake. Appl. Geochem. **19**: 1687–1698. doi:10.1016/j.apgeochem.2004.04.007

Walsh, J. R., J. R. Corman, and S. E. Munoz. 2019. Coupled long-term limnological data and sedimentary records reveal new control on water quality in a eutrophic lake. Limnol. Oceanogr. **64**: S34–S48. doi:10.1002/lno.11083

Wentz, D. A., and G. F. Lee. 1969. Sedimentary phosphorus in lake cores; observations on depositional pattern in Lake Mendota. Environ. Sci. Technol. **3**: 754–759. doi:10.1021/es60031a001

Weyhenmeyer, G. A., and others. 2019. Widespread diminishing anthropogenic effects on calcium in freshwaters. Sci. Rep. **9**: 10450. doi:10.1038/s41598-019-46838-w

Williams, J. D., and T. Mayer. 1972. Effects of sediment diagenesis and regeneration of phosphorus with special reference to lakes Erie and Ontario, p. 281–315. *In Nutrients in natural waters*. Wiley-Interscience.

Winsborough, B. M., J.-S. Seeler, S. Golubic, R. L. Folk, and B. Maguire. 1994. Recent fresh-water lacustrine stromatolites, stromatolitic mats and oncoids from Northeastern Mexico, p. 71–100. *In* J. Bertrand-Sarfati and C. Monty [eds.], *Phanerozoic Stromatolites II*. Springer.

Woodruff, S. L., W. A. House, M. E. Callow, and B. S. C. Leadbeater. 1999. The effects of biofilms on chemical processes in surficial sediments. Freshw. Biol. **41**: 73–89. doi:10.1046/j.1365-2427.1999.00387.x

Wu, P., A. Yin, M. Fan, J. Wu, X. Yang, H. Zhang, and C. Gao. 2018. Phosphorus dynamics influenced by anthropogenic calcium in an urban stream flowing along an increasing urbanization gradient. Landsc. Urban Plan. **177**: 1–9. doi:10.1016/j.landurbplan.2018.04.005

Zeyen, N., and others. 2021. Integrative analysis of the mineralogical and chemical composition of modern microbialites from ten Mexican lakes: What do we learn about their formation? Geochim. Cosmochim. Acta **305**: 148–184. doi:10.1016/j.gca.2021.04.030

Zhu, T., and M. Dittrich. 2016. Carbonate precipitation through microbial activities in natural environment, and their potential in biotechnology: A review. Front. Bioeng. Biotechnol. **4**. doi:10.3389/fbioe.2016.00004

Acknowledgments

The author thanks Matthew Cohen and Tracy Frank for friendly reviews, two anonymous reviewers, and numerous conversations with lab members and colleagues including Eric Moody, Steve Thomas, and Kauan Fonseca. JRC was supported by NSF grant OIA-2019596.

Conflict of Interest

None declared.

Submitted 30 January 2024
Revised 21 October 2024
Accepted 02 November 2024