

The relevance of pelagic calcification in the global carbon budget of lakes and reservoirs

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ABSTRACT

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Calcite precipitation acts as a carbon sink in the sediments and a short-term source of carbon dioxide (CO₂) to the atmosphere, as widely acknowledged in marine studies. However, pelagic calcite precipitation has received limited attention in lakes. Here we use the relationship between lake water alkalinity and reported calcification rates to provide the first global estimate of pelagic calcification in lakes. Global gross calcification rates amount to 0.03 Pg C yr⁻¹ (0.01 – 0.07) comparable to rates of organic carbon burial, whereas its related CO₂ release is largely buffered by the carbonate equilibria. Calcification occurs at water alkalinity above 1 meq/L corresponding to 57 % of global lake and reservoir surface area. Pelagic calcification therefore is a prevalent process in lakes and reservoirs at the global scale, with a potentially relevant role as a sedimentary inorganic carbon sink, comparable in magnitude to the total calcite accumulation rates in ocean sediments.

Key words: calcite precipitation, pelagic calcification, carbon cycle, lake carbon budget, carbon fluxes, carbon sink

RESUMEN

La relevancia de la calcificación pelágica en el balance global de carbono de lagos y embalses

La precipitación de calcita actúa como un sumidero de carbono en sedimentos y una fuente a corto plazo de dióxido de carbono (CO₂) a la atmósfera, como es ampliamente reconocido en sistemas marinos. Sin embargo, la precipitación pelágica de calcita ha recibido una atención limitada en lagos. Aquí utilizamos la relación entre la alcalinidad del agua y tasas reportadas de calcificación para proporcionar una primera estima global de calcificación pelágica en lagos. Las tasas de calcificación bruta global ascienden a 0.03 Pg C año⁻¹ (0.01 - 0.07) comparables a las tasas de enterramiento de carbono orgánico, mientras que la consecuente liberación de CO₂ está en gran medida amortiguada por los equilibrios de sistema de carbono inorgánico disuelto. La calcificación se produce a alcalinidad superior a 1 meq/L, que corresponde al 57 % de la superficie global de lagos y embalses. Por lo tanto, la calcificación pelágica es un proceso frecuente en lagos y embalses a escala global, con un rol potencialmente relevante como sumidero de carbono inorgánico sedimentario, comparable en magnitud a las tasas de acumulación total de calcita en los sedimentos oceánicos.

Palabras clave: precipitación de calcita, calcificación pelágica, ciclo del carbono, balances de carbono en lagos, flujos de carbono, sumidero de carbono

INTRODUCTION

Lakes and reservoirs are important components of the continental carbon (C) cycle due to large emissions of methane and CO₂ to the atmosphere and burial of organic carbon (OC) in their sediments (Cole *et al.*, 2007; Mendonça *et al.*, 2017; Raymond *et al.*, 2013). OC production, decomposition and burial have been described as the main drivers of C fluxes (Duarte & Prairie, 2005). Most studies relating C fluxes to OC metabolism in lakes have been conducted in systems with low water alkalinity (i.e. less than 1 meq/L) and high dissolved OC concentrations (McDonald *et al.*, 2013). However, increasing evidence suggests that inorganic carbon (IC) may be equally relevant in lakes of higher alkalinity (Marcé & Obrador, 2019), comprising 57 % of world's lakes area (Marcé *et al.*, 2015; McDonald *et al.*, 2013). While the role of benthic calcification is acknowledged in such systems, calcification in the pelagic zone is assumed to be negligible due to the rarity of planktonic organisms that produce calcareous shells in freshwaters (Kelts & Hsü, 1978). However, recent evidences stress the important role of pelagic calcite precipitation in lakes as an alkalinity sink and CO₂ source (Müller *et al.*, 2016). This double-edged role is widely acknowledged and quantified in marine studies (Frankignoulle *et al.*, 1994; Ridgwell & Zeebe, 2005), but its relevance in lakes has been assumed to apply only to saline systems. Evidence suggests that calcification contributes to the large CO₂ emissions found in saline lakes, yet those systems represent only a fifth of the Earth's lake surface (Duarte *et al.*, 2008). The biogeochemistry of carbon in saline lakes usually differs from those of freshwater lakes, because of the large carbon pools supporting high CO₂ exchange rates and chemical enhancement processes that are usually less relevant in freshwater systems (Duarte *et al.*, 2008). It is therefore necessary to study pelagic calcification in freshwater lakes separately to assess the relevance of this process in these systems representing the vast majority of the Earth's lake surface. Moreover, the majority of freshwater lakes are above the alkalinity threshold of 1 meq/L where calcification is likely to occur (Khan *et al.*, 2020; Marcé *et al.*, 2015; McConnaughey & Whelan,

1997). While the occurrence of pelagic calcification in freshwater lakes has often been reported, it has never been quantified at a global scale, nor has its derived CO₂ emissions.

High rates of calcite precipitation are often found during the summer season of lakes when calcite saturation peaks due to enhanced primary production that rises the pH by depleting CO₂ concentrations, thereby shifting the carbonic acid equilibrium towards oversaturation of carbonates (Müller *et al.*, 2016). Yet, spontaneous calcification is unlikely to occur, rather it is biologically mediated by picocyanobacteria that provide ideal nucleation sites that further facilitate calcite precipitation in the pelagic zones of lakes (Obst *et al.*, 2009). Calcite precipitation in lakes has been presented as a natural process that can reduce summer eutrophication (Rodrigo *et al.*, 1993). Because of this seasonal association and its occurrence during high primary production, most studies that have quantified calcite precipitation in lakes have focused on the summer season. Using summer pelagic calcification rates from the literature ($n = 26$, Supplementary information, available at <http://www.limnetica.net/en/limnetica>), here we identify a clear association with water alkalinity. Using water alkalinity as the driver variable with obvious mechanistic links with calcification, we provide a first gross global estimate of calcification rates and its derived CO₂ emissions. We intentionally excluded rates measured in other seasons than summer or averaged over the year, rates for benthic calcification caused by calcifying macrophytes, rates in brackish systems and saline lakes.

METHODS

Data on pelagic calcite precipitation was obtained from published literature reporting areal or volumetric rates from either sediment traps, sediment cores, C or Ca²⁺ mass balances, incubations, or modelling (Supplementary information, available at <http://www.limnetica.net/en/limnetica>). Most rates found in the literature are average rates covering only the summer season, therefore we excluded mean annual rates from this analysis. When reported per unit area, areal rates were divided by the mixed layer depth (Z_{mix}) to obtain

rates per unit volume, assuming that most pelagic calcification occurs in the epilimnion (Hartley et al., 1995; Obst et al., 2009). If Z_{mix} of a specific lake was not specified in the literature, it was calculated using FLAKE Global model (Kirillin et al., 2011). The strong relationship found between alkalinity and calcification rates was used in the upscaling to global rates, using the 5 %, 50 % and 95 % quantiles to obtain a range of uncertainty. The volumetric rates obtained from this relationship were converted to areal rates by multiplying the volumetric rates with an average Z_{mix} value of 6.72. The average Z_{mix} was calculated from a dataset of 628 lakes (Woolway & Merchant, 2019), using a hyperbolic function between Z_{mix} and lake fetch (Lewis, 2011). The areal rates by alkalinity level were multiplied by the global surface area of lakes corresponding to each level of alkalinity

(alkalinity intervals of 0.05 meq/L) (Marcé et al., 2015). The sum of these rates was multiplied by the average number of days of measurements (94 days) from which each reported daily rate in the literature was averaged. These calculations are presented in the supplementary Data file.

For upscaling CO_2 emissions, the 5 %, 50 % and 95 % quantiles of the relationship between alkalinity and calcification was used to build a model that simulates the resulting range of lake CO_2 partial pressure (pCO_2) increase at different daily calcification rates that are dependent on the initial alkalinity value. The model is based on the chemical dissolved inorganic carbon (DIC) equilibria whereby 1 mole of calcite that precipitates results in a loss of 1 mole of DIC (because 2 moles of HCO_3^{2-} are lost in the reaction and 1 mole of CO_2 is released) and a loss of 2 equiva-

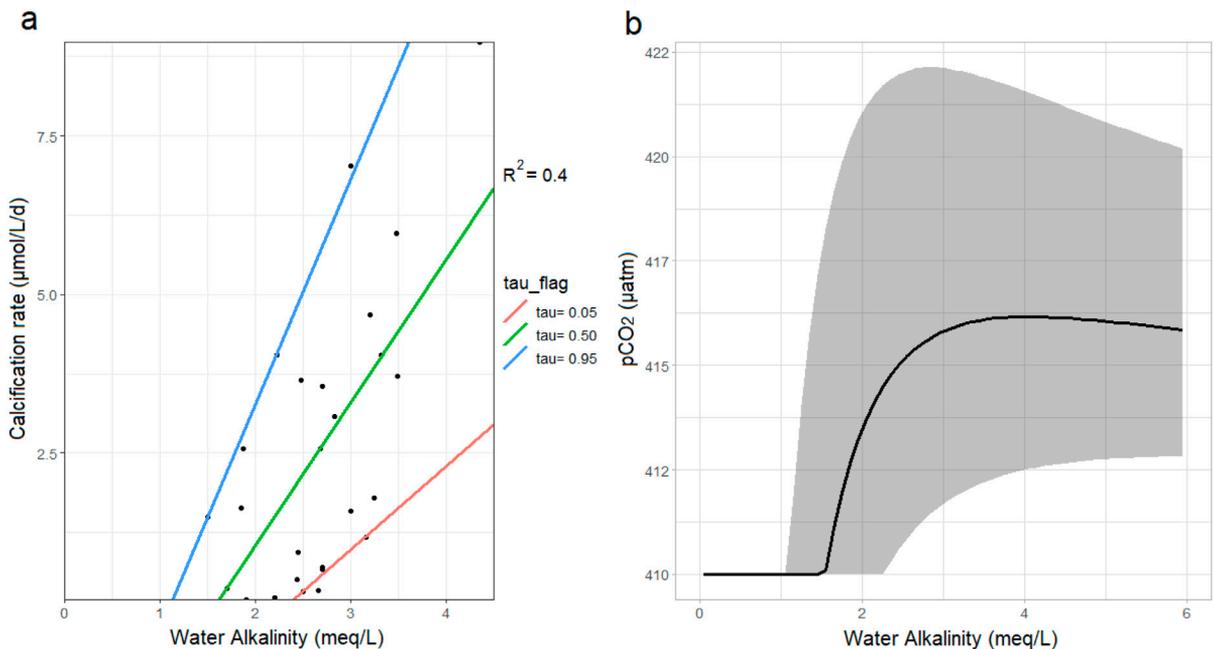


Figure 1. Effects of alkalinity on calcification rates. (a) relationship between alkalinity and calcification rates reported in the literature for global lakes. Lines corresponds to quantile regressions at the 95 % quantile (blue), 50 % (green), and 5 % (red). (b) Daily effect of calcite precipitation on pCO_2 at different alkalinity levels. Initial pCO_2 value is at atmospheric equilibrium. The solid line represents the 50 % quantile. The shaded area corresponds to the range of calcification found at a given alkalinity level using the 5% and 95% quantiles. *Efectos de la alcalinidad sobre las tasas de calcificación. (a) relación entre alcalinidad y tasas de calcificación reportadas en la bibliografía para lagos. Las líneas corresponden a regresiones de cuantiles al cuantil 95 % (azul), 50 % (verde) y 5 % (rojo). (b) Efecto diario de la precipitación de calcita sobre la pCO_2 a diferentes niveles de alcalinidad. El valor inicial de pCO_2 está en equilibrio atmosférico. La línea sólida representa el cuantil 50 %. El área sombreada corresponde al rango de calcificación encontrado a un nivel dado de alcalinidad usando los cuantiles del 5 % y 95 %.*

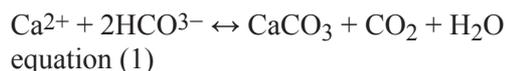
lents of alkalinity. The fate of the CO₂ released by calcification and its interaction with the DIC equilibria is therefore taken into account in this model. The initial pCO₂ value was set at the atmospheric equilibrium value of 410 ppm. The model is freely available online in the following link (<http://hdl.handle.net/2445/172489>). The global upscaling was done similarly to the upscaling of calcification rates, using existing data of the global surface area of lakes per alkalinity levels (Marcé *et al.*, 2015). CO₂ flux was calculated using Fick's Law of gas diffusion (Millero, 1979) using the global average Piston velocity (k_{600}) value of 1 m/d with an uncertainty range between 0.74 and 1.33 (Raymond *et al.*, 2013). The sum of the fluxes correspond to the global annual CO₂ emissions caused by planktonic calcification. It is a first estimate of the CO₂ emissions related to calcification and should therefore be understood as an approximate estimation that can be further refined by research, rather than an ultimate value. All calculations are available in the Supplementary Data File.

RESULTS AND DISCUSSION

A significant positive linear relationship ($R^2 = 0.4$, $n = 26$, $p < 0.001$) was found between water alkalinity and calcite precipitation rates, suggesting that the importance of this process is significantly higher with increasing alkalinity (Fig. 1a). No significant effect of chlorophyll-*a* and total phosphorus on calcification rates was found and including these variables with alkalinity in a multiple linear regression only decreased the strength of the model ($R^2 = 0.34$, $p < 0.05$). However, in lakes, spontaneous calcification is unlikely to occur. Rather, it is mediated by picoplankton that promote the chemical environment necessary for calcification by increasing the pH and by offering ideal nucleation sites (Obst *et al.*, 2009). The absence of any significant effect of chlorophyll-*a* and total phosphorus concentrations could be due to the fact that calcite saturation is more determined by alkalinity than by production of the system. The strength of primary production to promote calcification likely depends on the level of calcite saturation which is directly related to water alkalinity. A quantile regression using the

95 % quantile suggests an alkalinity threshold for calcification at ~1 meq/L (Fig. 1a), below which calcification is unlikely to occur. This is consistent with the threshold of 1 meq/L reported in previous studies (Marcé *et al.*, 2015; McConnaughey & Whelan, 1997). Considering that 57 % of the global area occupied by lakes and reservoirs have alkalinity values above 1 meq/L (Marcé *et al.*, 2015), pelagic calcite precipitation is likely to occur in most lakes and reservoirs around the globe. In addition, the 5 % quantile regression indicates that virtually all lakes with alkalinity beyond 2.5 meq/L will show summer pelagic calcification (Fig. 1a).

Calcite precipitation and dissolution reactions imply changes on both alkalinity and the relative abundance of (DIC) species (Ridgwell & Zeebe, 2005) (1).



Whereby calcite precipitation releases one mole of CO₂ per mole of calcite precipitated, increasing pCO₂. Because of the higher calcification rates found in lakes of higher alkalinity, one would expect the increase in pCO₂ caused by calcification to be stronger in such systems. However, the ratio between calcite precipitation and CO₂ release (commonly referred to as Ψ) depends on the capacity to buffer changes in pCO₂ (Frankignoulle *et al.*, 1994; Smith & MacKenzie, 2016). As a result, the buffering capacity of high alkalinity lakes mitigate pCO₂ increase preventing most of the released CO₂ to escape to the atmosphere (Fig. 1b). Therefore, the potential change in pCO₂ caused by calcite precipitation on a daily time scale is minimal (Fig. 1b).

We used the alkalinity – calcification rates relationship together with the global distribution of lakes and reservoirs per alkalinity level (Marcé *et al.*, 2015) for upscaling calcite precipitation rates to the entire globe. The resulting annual global rate of calcite precipitation of 0.03 Pg C yr⁻¹ (range 0.01 – 0.07 Pg C yr⁻¹) is comparable in magnitude to global annual rates of OC burial of 0.15 Pg C yr⁻¹ (range 0.06 – 0.25 Pg C yr⁻¹, (Mendonça *et al.*, 2017), Fig. 2a). Global calcite precipitation would thus be of the same order of

magnitude as OC burial, making them both similarly relevant as main drivers of C cycling in lakes. As a comparison, the average areal calcification rates in lakes (13.8 g C m⁻² yr⁻¹, range: 5.4 – 28, Supplementary Data File) correspond to 37 % (14 % - 75 %) of areal rates of pelagic calcification in oceans (37 g C m⁻² yr⁻¹) (Smith & Mackenzie, 2016).

The net role of pelagic calcification as a sedimentary inorganic carbon sink depends on calcite dissolution during sedimentation and in the sediments. In open oceans 80 % of all carbonate that precipitates dissolves within the water column or in the sediments (Ridgwell & Zeebe, 2005). Although some studies have reported calcite dissolution in some lakes (Ohlendorf & Sturm, 2001; Ramisch et al., 1999), others report no dissolution during settling of calcite crystals (Stabel, 1986). A study on 13 lakes revealed that calcite dissolution in lakes and reservoirs is minor compared to calcite precipitation because rather than dissolving in the hypolimnion, calcite tends to accumulate in the sediments (Müller et al., 2016), thereby acting as a long-term C sink. These results are in agreement with another study on 5 lakes that reports calcite precipitation with no evidence of calcite dissolution (Lenz et al., 2018). Yet, high rates of calcite dissolution are reported in deeper stratified systems rich in OC where decomposition of organic matter promotes anoxic conditions and low pH in the hypolimnion (Ohlendorf & Sturm, 2001) and where calcite crystals may partly dissolve in the water column during sedimentation (Ramisch et al., 1999). The global calcification rate provided in this study is a gross estimate to be further built upon. The role of calcite dissolution needs to be assessed at a global scale to determine the net burial flux, which is beyond the scope of this study. Considering calcification alone, the total export of calcite to the sediments would represent between 10 % and 70 % of the total net oceanic sink for pelagic calcification (0.1 Pg C yr⁻¹) (Sabine & Tanhua, 2010). So long as calcite dissolution hasn't been estimated at a global scale, these values remain hypothetical. This is even more uncertain in the context of global change which is likely to increase the frequency of anoxic conditions in the hypolimnion of stratified systems (Jankowski et al., 2006;

Schwefel et al., 2016) which could promote ideal conditions for calcite dissolution. Nevertheless, these values highlight the disproportionately important role of calcite precipitation in lakes and reservoirs as a potential carbon sink despite the relatively small area that these water bodies occupy on the globe.

The gross estimate of global CO₂ emissions caused by calcification is 0.0002 Pg C yr⁻¹ (range: 0.00005 – 0.0007 Pg C yr⁻¹). This is an irrelevant fraction of the total CO₂ emissions from lakes and reservoirs (< 0.5 %, Fig. 2b). Our results contrasts with those of saline lakes where calcite precipitation is expected to contribute significantly to CO₂ emissions (Duarte et al., 2008). The low contribution of calcification-derived CO₂ emissions is because higher rates of calcite precipitation are found in lakes of higher alkalinity (Fig. 1) that have a stronger capacity to buffer changes in pCO₂. Recent studies found that inorganic processes including DIC loading from chemical weathering and calcite precipitation are important drivers of CO₂ emissions in lakes and reservoirs (Marcé et al., 2015; McDonald et al., 2013). Our results suggest that pelagic calcite precipitation represents a minor share of emissions caused by inorganic sources (Fig. 2b).

It is important to mention that pelagic calcification rates reported here are probably only a share of total calcification in lakes and reservoirs. Benthic primary production can account for a large fraction of the overall metabolism of lakes (Cremona et al., 2016), and benthic habitats dominated by calcifying macrophytes can promote daily losses of up to 0.57 meq/L of alkalinity due to intense calcification (Andersen et al., 2017). In the absence of a global estimate of lake benthic calcification we can only speculate about its relevance, but considering potentially high calcification rates from benthic macrophytes (McConnaughey & Whelan, 1997) and their prevalence in lakes, we posit benthic calcification could be even higher than pelagic. Furthermore, our global estimate only accounts for calcification during the summer season assuming that this represents the largest part within a year. While calcification usually occurs mainly in the summer season, it is variable in time and the possibility of its occurrence in other seasons cannot be excluded (Trapote

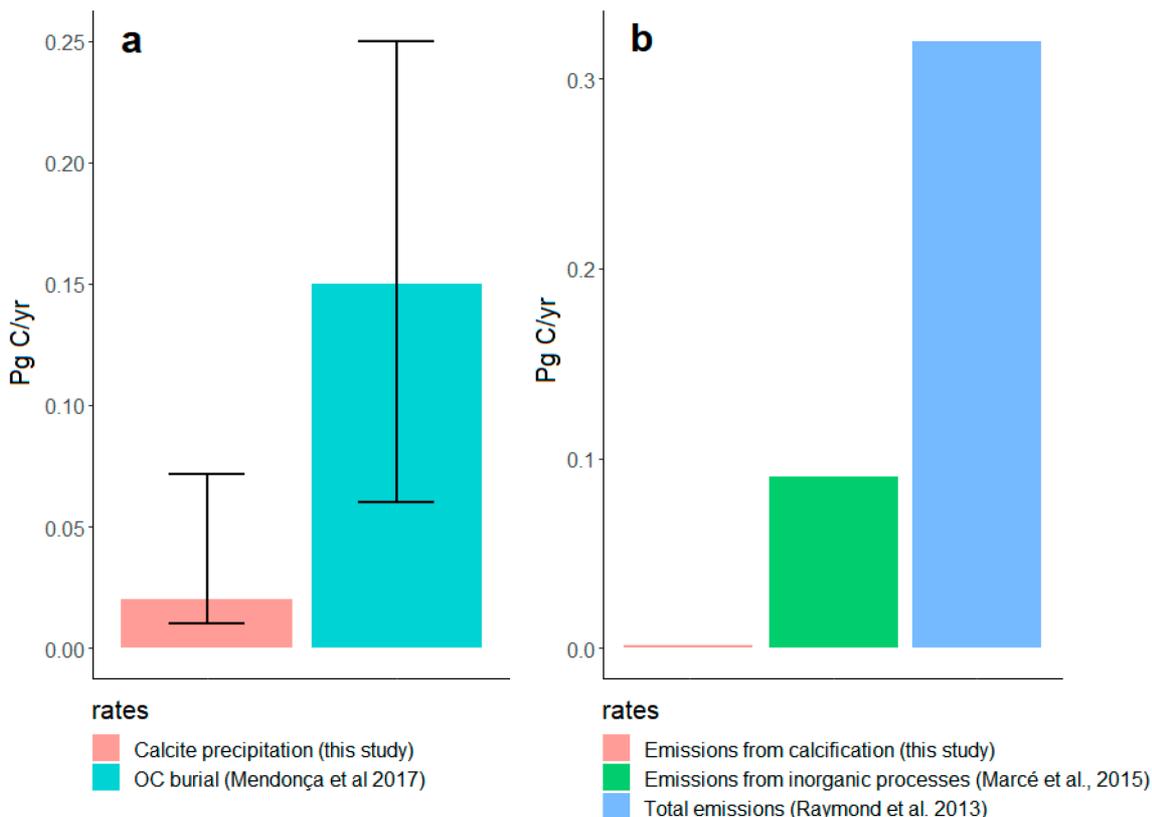


Figure 2. Global rates of calcification and CO₂ emissions. (a) Global annual rates of calcite precipitation (this study) and OC burial (Mendonça et al., 2017) in lakes and reservoirs. The error bars represent the range. (b) Global rates of CO₂ emissions from calcification (this study), inorganic processes (Marcé et al., 2015) and total emissions (Raymond et al., 2013). *Tasas globales de calcificación y emisiones asociadas de CO₂. (a) Tasas globales anuales de precipitación de calcita y enterramiento de carbono orgánico en lagos y embalses. Las barras de error representan el rango. (b) Tasas globales de emisiones de CO₂ en lagos asociadas a la calcificación (este estudio), procesos inorgánicos (Marcé et al., 2015) y emisiones totales (Raymond et al., 2013).*

et al., 2018). The seasonality of calcification is likely to be directly related to the seasonality of primary production since calcification in lakes is a biologically mediated process that is enhanced during peaks of primary production (Obst et al., 2009). Arriving at a mechanistic understanding of how primary production promotes calcification within the physicochemical context of a lake, including its alkalinity level, is a next step to predict calcification events in lakes and further refine its global estimation by integrating seasonality at a finer scale.

While CO₂ emissions caused by calcite precipitation is minor at a global scale, CO₂ release during summer calcification can have significant

implications on C dynamics at a local scale, resulting in imbalances between metabolic rates and C concentrations (Khan et al., 2020). Such imbalances can reach a point where lakes are simultaneously in an autotrophic state, yet they emit CO₂ to the atmosphere, as is likely the case in approximately one third of lakes in the boreal region and in the contiguous United States (Bogard & Giorgio, 2016; McDonald et al., 2013). Accounting for the role of calcite precipitation on C dynamics at a local scale is necessary to improve the reliability and predictability of lake models that are currently unable to explain the reported imbalances between metabolism and C fluxes (Lu et al., 2018).

To conclude, the rates provided here highlight the role of pelagic calcite precipitation as an important component of the C cycle in lakes and reservoirs and the need to account for it in global C budgets (Marcé & Obrador, 2019). Research should aim at quantifying the ratios between production and calcification rates as well as between calcite precipitation and CO₂ release along alkalinity gradients in order to account for this process in models of inland water C processing. Temporal patterns of calcite precipitation and environmental conditions for its occurrence need to be investigated for predicting this process at short and longer temporal scales. Finally, calcite precipitation and dissolution in lakes and reservoirs need to be understood in the context of climate change predictions in order to assess their role as potential C sinks or C sources in a changing climate.

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DATA AVAILABILITY STATEMENT

All calcification rates collected from the literature are compiled in the Supplementary Data Excel file, available at <http://www.limnetica.net/en/limnetica>. The calculations for the global upscaling of calcification rates and its associated CO₂ emissions are presented in this same data Excel file. The code that was used for calculating the effect of calcification on CO₂ partial pressure is available online (<http://hdl.handle.net/2445/172489>).

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