

2017

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10.1002/lol2.10052

Macreadie, P. I., Serrano, O., Maher, D. T., Duarte, C. M., & Beardall, J. (2017). Addressing calcium carbonate cycling in blue carbon accounting. *Limnology and Oceanography Letters*, 2(6), 195-201.

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## ESSAY

## Addressing calcium carbonate cycling in blue carbon accounting

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### Scientific Significance Statement

There is considerable interest in measuring the capacity of the world's ecosystems to trap and store excess atmospheric carbon dioxide to mitigate human-induced climate change. Blue carbon describes the carbon storage potential of vegetated coastal ecosystems including tidal marshes, mangroves, and seagrasses. Efforts are now underway to include blue carbon in global carbon offset schemes by managing these ecosystems to enhance carbon sequestration by focusing on their effect on organic carbon processing. However, it is unclear what role inorganic carbon processing in blue carbon ecosystems plays in their overall carbon sequestration. Here, we argue that there are key uncertainties that will need to be addressed before we can account for this important process to more accurately estimate carbon offsets in blue carbon ecosystems.

### The white elephant in the blue carbon room

The capacity of the world's ecosystems to sequester carbon dioxide (CO<sub>2</sub>) is a major focus of research guiding conservation and restoration of these natural sinks to help mitigate climate change. Seven years ago the term “blue carbon” was coined to describe the disproportionately large organic carbon storage potential of coastal vegetated ecosystems (Nellemann et al. 2009). Efforts are now underway to include blue carbon ecosystems (tidal marshes, mangrove forests, and seagrass meadows) into global carbon offset schemes, focused on their optimal management to enhance CO<sub>2</sub> sequestration as well as minimize CO<sub>2</sub> emissions that result from disturbance (Macreadie et al. 2017).

However, the focus on organic carbon (IPCC 2007; Nellemann et al. 2009) in blue carbon ecosystems has left the globally significant process of calcium carbonate (CaCO<sub>3</sub>)

production and dissolution unaccounted for, despite calcium carbonate cycling having been key drivers of changes in climate over Earth's history (Falkowski et al. 2000). Calcium carbonate production runs counter (i.e., an atmospheric CO<sub>2</sub> source) to the effects of organic carbon production (CO<sub>2</sub> sink through photosynthesis), because in the oceans calcification increases *p*CO<sub>2</sub> (by depleting CO<sub>3</sub><sup>2-</sup> and therefore reducing total alkalinity, “TA”), which facilitates the return of CO<sub>2</sub> to the atmosphere (Frankignoulle et al. 1994; Zeebe and Wolf-Gladrow 2001). Specifically, for every mole of CaCO<sub>3</sub> precipitated, two moles of TA and one mole of DIC are consumed, resulting in increased *p*CO<sub>2</sub> and potential flux to the atmosphere (Fig. 1).

Hence, calcium carbonate production could represent a process that—depending on the timescale (Archer et al. 1998)—exacerbates climate change and/or fuels ocean acidification, whereas calcium carbonate dissolution would act as a CO<sub>2</sub> sink. Timescales are important to bear in mind; overall climate impacts resulting from such changes are predicted to be minor over the new few centuries, especially when compared to the influence of anthropogenic CO<sub>2</sub> emissions; however, the effects are expected to be significant in the long-term (Tyrrell 2008). Of immediate relevance, however, is how calcium carbonate cycling (i.e., precipitation and dissolution) is treated in national and global blue carbon

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**Author Contribution Statement:** All authors contributed extensively to the work presented in this paper.

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**Table 1.** “Back-of-the-envelope” estimates of C fluxes in seagrass ecosystems based on the balance between their organic carbon accumulation (CO<sub>2</sub> sink) and inorganic carbon accumulation (CO<sub>2</sub> source) rates.

	Mean	SD	Max	Min	References
PIC accumulation (g C m <sup>-2</sup> yr <sup>-1</sup> )	126.3	31.5	157.8	94.8	Mazarrasa et al. (2015)
POC accumulation (g C m <sup>-2</sup> yr <sup>-1</sup> )	138.0	38.0	176.0	100	McLeod et al. (2011)
Net CO <sub>2</sub> sequestration (g C m <sup>-2</sup> yr <sup>-1</sup> )	58.4		116.3	0.59	This study*
Global seagrass area (m <sup>2</sup> )	3.9E+11		6.0E+11	1.8E+11	McLeod et al. (2011)
Global net CO <sub>2</sub> sequestration (Tg C yr <sup>-1</sup> )	22.6		69.8	0.1	This study†

\* Calculated by multiplying the PIC accumulation rate by 0.63 to meet the assumption that 0.63 moles of CO<sub>2</sub> is released per mole of CaCO<sub>3</sub> precipitated, then deducting this adjusted PIC value from the POC accumulation rates to get net CO<sub>2</sub> sequestration.

† Calculated by multiplying net CO<sub>2</sub> sequestration by global seagrass area.

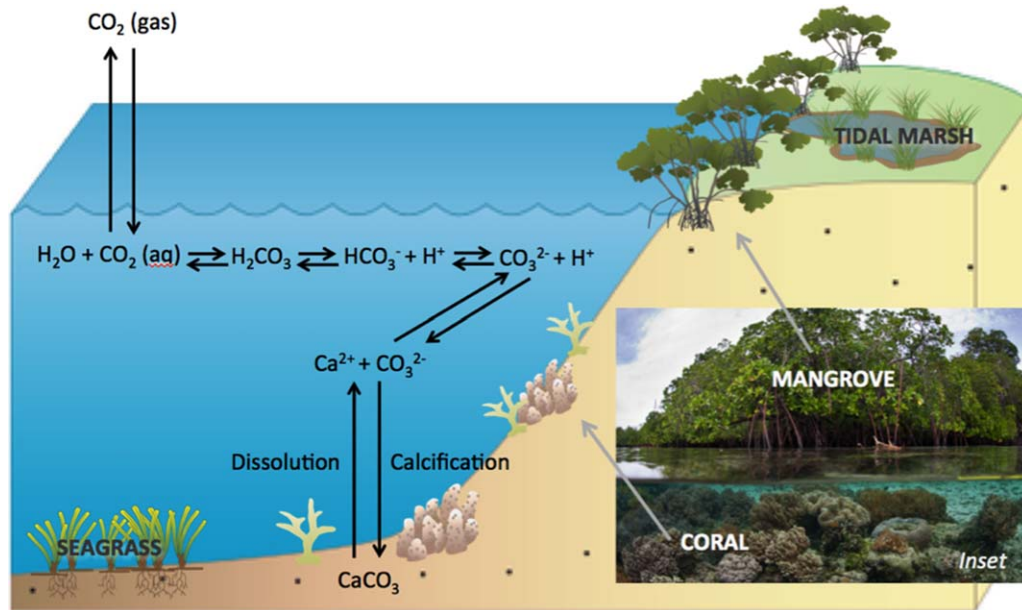
**Table 2.** Uncertainties in the dynamics of calcium carbonate and organic carbon cycling within blue carbon ecosystems and research questions that will need to be addressed in order to account for those uncertainties.

	Uncertainties	Research questions	References
1	Stoichiometry and fate of CO <sub>2</sub> fluxes during calcium carbonate cycling are unknown for blue carbon ecosystems	Is CO <sub>2</sub> release during calcification buffered by metabolic processes (i.e., photosynthesis) and physical processes (e.g., tides, waves)?	Frankignoulle et al. (1994), Russell et al. (2013), Cox et al. (2016)
2	Varying temporal scales for preservation of organic carbon and calcium carbonate	What are the decay rates of calcium carbonate and organic carbon pools, and at what depth/age should organic carbon accumulation be considered a long-term sink?	Mazarrasa, et al. (2015), Burdige (2007), Maher et al. (2017)
3	The presence of geogenic calcium carbonates could lead to an overestimation of calcification rates	What proportions of the calcium carbonate pool are made up of geogenic calcium carbonate (fossil) and biogenic calcium carbonate (recent)?	Zamanian et al. (2016)
4	Calcium carbonate production may enhance sediment accumulation, organic carbon deposition, and preservation	Are there positive feedbacks between the accumulation of calcium carbonates and organic carbon?	McLeod et al. (2011), Le Quere, et al. (2016), Gattuso et al. (1998)
5	The net impacts of climate change on calcium carbonate precipitation/dissolution are not known	How will future climate change scenarios (ocean acidification, rising temperatures, and sea level rise) affect organic carbon and calcium carbonate cycling?	Gattuso et al. (1998)

accounting, and in quantifying the importance blue carbon ecosystems in climate change mitigation.

Current blue carbon offset schemes focus solely on organic carbon, ignoring calcium carbonate cycling. Further, there has been a rapid expansion of scientific literature on blue carbon, with minimal attention paid to the importance of calcium carbonate precipitation and burial. Yet some blue carbon ecosystems, particularly tropical seagrass meadows, are hotspots for calcium carbonate production owing to their provision of 3D habitat for calcifying organisms (Mazarrasa et al. 2015) (Fig. 2). Indeed, coastal sediments can hold

enormous quantities of calcium carbonate accumulated over geological time scales (e.g., the White Cliffs of Dover). The burning question is how accounting for the balance between calcium carbonate production and dissolution, i.e., net calcium carbonate production, in blue carbon ecosystems affects estimates of their CO<sub>2</sub> sink capacity based on organic carbon sequestration? And, importantly, how will the balance of calcium carbonate production and dissolution and its effects on blue carbon budgets change in the future as oceans warm and absorb anthropogenic CO<sub>2</sub> emissions? It has been demonstrated already that shallow-water oceans are



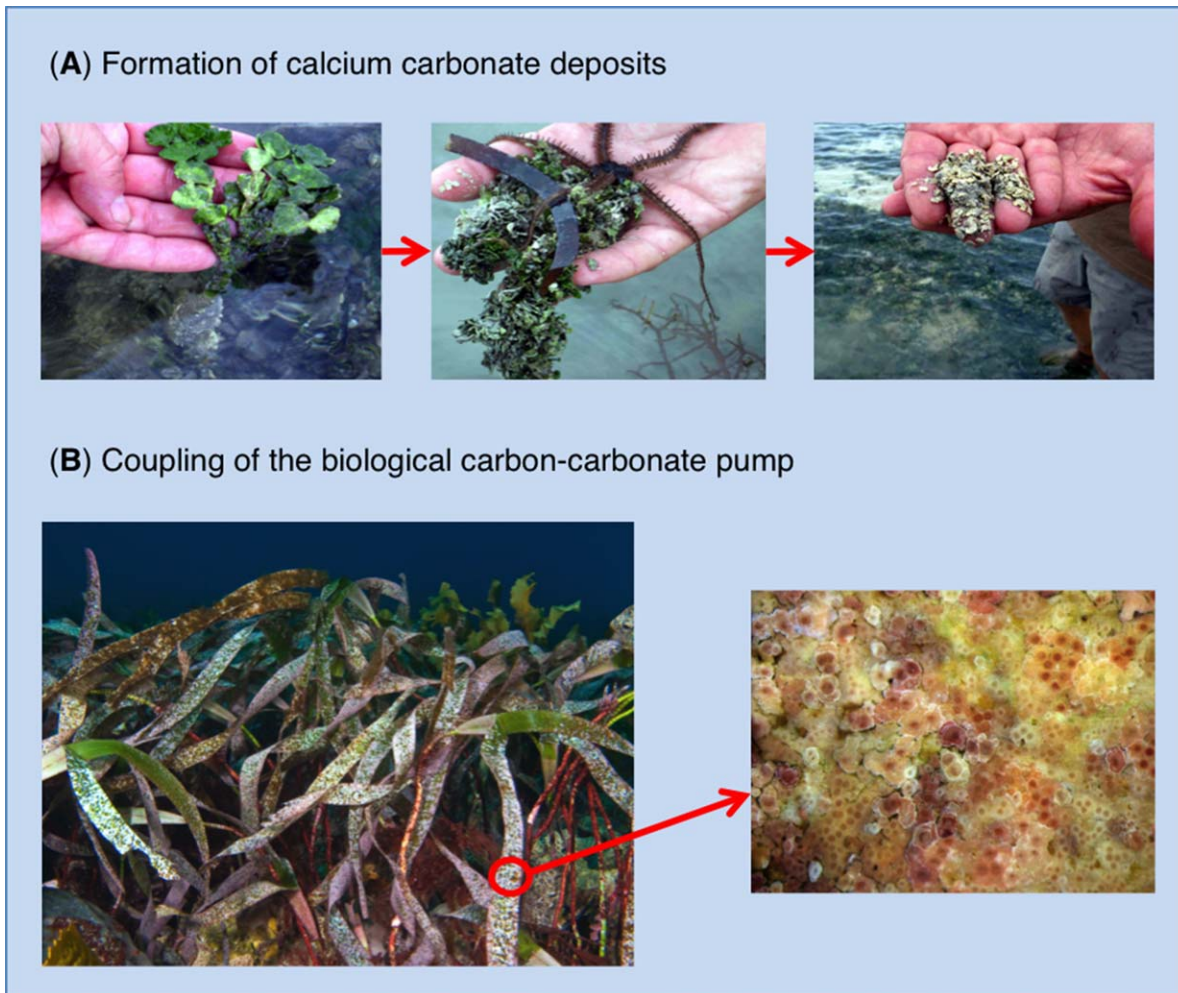
**Fig. 1.** Conceptual diagram showing the chemical reactions involved in  $\text{CO}_2$  exchange between the air and coastal ocean, including the production (calcification) and dissolution of calcium carbonate ( $\text{CaCO}_3$ ). Blue carbon ecosystems (seagrasses, mangroves, and tidal marshes) often occur in close proximity to sites with high rates of calcium carbonate cycling (e.g., coral reefs – see inset), resulting in interactions between the organic (blue) and inorganic (carbonate) cycles. Inset photo credit: Ethan Daniels/Shutterstock. Conceptual diagram produced using the Integration and Application Network (IAN), University of Maryland, Center for Environmental Science, Cambridge, Maryland.

particularly dynamic and can switch between acting as an atmospheric  $\text{CO}_2$  source or sink depending on human activities (Andersson and Mackenzie 2004). Biogenic production of calcium carbonate is expected to decrease by 42% by 2100 due to declining carbonate saturation states of surface ocean waters (Andersson et al. 2003, 2005). The overall influence of the latter on climate will be relatively minor compared to anthropogenic emissions, but nevertheless should be taken into account in carbon budgets now, and into the future.

Taking sinks of seagrass soil organic carbon burial into account (ranging between 100 and 176 g C organic  $\text{m}^{-2} \text{yr}^{-1}$ ; McLeod et al. 2011) and sources of non-organic carbon (net calcium carbonate deposition; ranging between 95 and 158 Tg C inorganic  $\text{yr}^{-1}$ ; Mazarrasa et al. 2015), seagrass meadows seem to constitute a net sink of  $\text{CO}_2$  (ranging from 0.59 g C  $\text{m}^{-2} \text{yr}^{-1}$  to 116 g C  $\text{m}^{-2} \text{yr}^{-1}$ ) (Table 1). After accounting for release of  $\text{CO}_2$  after calcification, our estimates suggest that seagrass meadows worldwide accumulate  $\text{CO}_2$  at a mean rate of 22.6 Tg C  $\text{yr}^{-1}$ , which is about half of the accumulation potential accounting for organic carbon alone. It is important to note that the net drawdown of  $\text{CO}_2$  by seagrasses and other blue carbon ecosystems will only offset a small fraction of anthropogenic  $\text{CO}_2$  emissions ( $\sim 0.23\%$  based on  $\sim 10$  Pg C emitted per year; Le Quere et al. 2016), regardless of whether calcium carbonate cycling is taken into account. This is not to say that blue carbon should be ignored in climate change mitigation efforts, but that it should be considered as one of many strategies

necessary to limit temperature increase, which must involve an important reduction of emissions. This includes avoided emissions from destruction of blue carbon ecosystems, which is estimated to release about 0.04–0.28 Pg C per year (0.42–2.83% of global emissions) (Pendleton et al. 2012).

The wide range of values reported above and in Table 1 highlight the large uncertainty associated with current estimates of organic carbon burial, calcium carbonate burial, and even seagrass area. Therefore, caution should be exercised when interpreting these results. For example, the values reported by Mazarrasa et al. (2015) assumed that all calcium carbonate present in seagrass soils was biogenic, thereby ignoring the presence of calcium carbonate within the mineral matrix. Indeed, whereas organic carbon density drops substantially in sediments outside seagrass meadows, calcium carbonate density remains elevated, suggesting that calcium carbonate loads in sediments are not the sole result of calcification processes in seagrass meadows (Mazarrasa et al. 2015). Currently, these estimates can be useful to highlight the potential importance of calcium carbonate cycling within blue carbon ecosystems for carbon accounting and crediting, but are susceptible to large changes as the uncertainties pointed out are yet to be clarified. Determining calcification rates for a given blue carbon ecosystems using DIC and TA measurements, as well as actual rates of net community calcification, will help to determine the relative importance of the organic to inorganic carbon cycle, while also avoiding erroneous calcification estimates based on geogenic



**Fig. 2.** (A) The calcifying green alga *Halimeda* showing various stages of thallus deterioration, from a healthy algae (left), through dead and partially disintegrated thalli (center) to the calcium carbonated tissues giving rise to gravel and sand in some tropical ecosystems (right); and (B) coupling of the biological carbon-carbonate pump. Here, carbonate-forming algae growing on seagrass *Thalassodendron pachyrhizum*, increase pCO<sub>2</sub> through calcification which may then enhance seagrass photosynthesis resulting in a positive feedback that could potentially avoid an atmospheric fate of the CO<sub>2</sub> released during calcification. Photos by Sven Beer (top row) and John Huisman (bottom row).

carbonates. On the other hand, however, translating short-term calcification rates into long-term calcium carbonate burial would be prone to error due to the potential for dissolution and temporal variability in calcification.

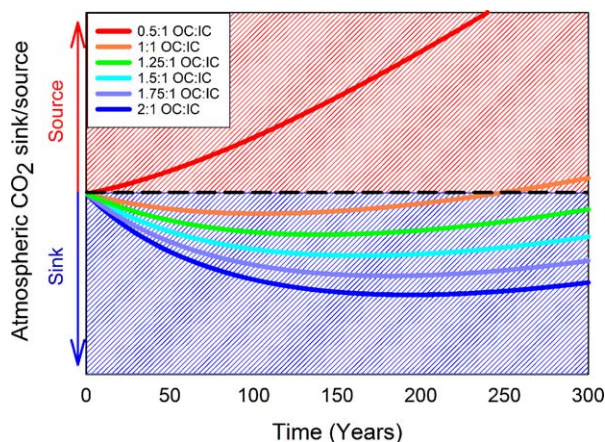
**How should we deal with calcium carbonates in blue carbon science?**

We maintain that calcium carbonate production should be accounted when estimating carbon sequestration potential of blue carbon ecosystems. But how? If calcium carbonate production is a net source of CO<sub>2</sub>, then the release of CO<sub>2</sub> from calcium carbonate production should be subtracted from organic matter sequestration. For example, simply accounting for the ratio of OC : IC burial, the stoichiometry associated with the buffering of the CO<sub>2</sub> released during calcification (i.e., the assumption that 0.63 moles of CO<sub>2</sub> are released per

mole of CaCO<sub>3</sub> precipitated) and the decay of buried OC over time is a good starting point (Fig. 3). While seemingly simple, this accounting approach relies on complex assumptions that need be resolved.

In Table 2, we summarize five key uncertainties and questions that need be resolved in order to properly account for calcium carbonate cycling in blue carbon ecosystems. These range from equilibrium assumptions about CO<sub>2</sub> exchange between the land and sea (Smith 2013), to the extent to which blue carbon ecosystems utilize the higher CO<sub>2</sub> concentrations as a result of calcium carbonate production offsetting atmospheric CO<sub>2</sub> release (McConnaughey and Whelan 1997; Invers et al. 2001; Schneider and Erez 2006; Semesi et al. 2009).

The stoichiometry of the calcification reaction (Fig. 1) in coastal environments is complicated due to the buffering



**Fig. 3.** Model of net atmospheric  $\text{CO}_2$  sink associated with different ratios of organic carbon : inorganic carbon (OC : IC) burial. The model assumes a decay rate for OC of  $0.0056 \text{ yr}^{-1}$  (Serrano et al., 2016), no dissolution of calcium carbonates, and assumption of 0.63 moles of  $\text{CO}_2$  released per mole of calcium carbonate precipitated.

effect in seawater (Frankignoulle et al. 1995), leading to less than 1 mole of  $\text{CO}_2$  being released to seawater due to the reaction of  $\text{CO}_2$  with bases in the water. This ratio has been estimated as  $\sim 0.63$  under current atmospheric  $\text{CO}_2$  concentrations (i.e., net emission of 0.63 mole  $\text{CO}_2$  for every mole of  $\text{CaCO}_3$  precipitated), and oceanic DIC and TA concentrations and is predicted to increase with increasing atmospheric  $\text{CO}_2$  concentrations. Indeed, the natural variability in calcium carbonate dynamics (i.e.,  $\text{CO}_2$  emissions related to calcification) in blue carbon systems is largely driven by tidal, seasonal, and diurnal metabolic processes. Moreover, there is uncertainty in the fate of  $\text{CO}_2$  released after calcification, which could determine whether calcification in blue carbon ecosystems constitutes a  $\text{CO}_2$  source (e.g., in the form of atmospheric  $\text{CO}_2$  release) or sink (e.g., through enhancement of organic matter production and burial rates).

Over long time-scales it is assumed that  $\text{CO}_2$  in the form of dissolved inorganic carbon (DIC) will remain in the oceans until  $\text{CO}_2$  concentrations in the water body exceed those in the atmosphere. However, this equilibrium assumption, which applies for the global ocean (Smith 2013; Smith and Mackenzie 2016), may not apply in blue carbon ecosystems and over short time scales where fluxes can be influenced by weather (e.g., wind speeds, temperature) and metabolic processes (e.g., calcification, primary productivity, and respiration). For example, in the case of seagrasses,  $\text{CO}_2$  produced through calcium carbonate formation can be rapidly utilized (through photosynthesis) by epiphytes and nearby plants, potentially offsetting rises in  $\text{CO}_2$  (McConnaughey and Whelan 1997; Invers et al. 2001; Schneider and Erez 2006; Semesi et al. 2009), leading to greater productivity and higher rates of blue carbon sequestration (Russell et al. 2013). Conversely, photosynthetic activity within blue

carbon ecosystems could increase pH and enhance calcification of nearby calcareous organisms (De Beer and Larkum 2001).

Another key uncertainty relies on the fact that the organic carbon pool (i.e., organic matter) is more labile compared to the inorganic carbon pool (i.e., calcium carbonates), and it is therefore important to consider the temporal scale when accounting for the  $\text{CO}_2$  sequestration capacity of blue carbon ecosystems. Indeed, the presence of geogenic calcium carbonates in blue carbon ecosystems could lead to an over-estimation of calcification rates. Therefore, there is a need to differentiate between geogenic and biogenic calcium carbonates within blue carbon soils in order to properly assess the role of carbon cycling in blue carbon accounting. Moreover, simple calculations also assume that calcium carbonate and organic carbon cycling in blue carbon ecosystems are independent processes. However, available evidence suggests that calcium carbonate and organic carbon cycling in blue carbon ecosystems are unlikely to be independent processes. For example, primary production is conducive to conditions that facilitate calcification, whereas respiration favors carbonate dissolution. In addition, calcium carbonate production can increase the burial efficiency of organic carbon, by interfering with microbial access to organic carbon in close physical association with calcium carbonate minerals (Mayer 1994; Ingalls et al. 2004). Calcium carbonates also support much of the sediment accretion rate in many seagrass meadows (Mazarrasa et al. 2015), a major component of the capacity of vegetated coastal ecosystems to preserve organic carbon and help adapt to sea level rise (Duarte et al. 2013). Further, respiration of organic matter produced in blue carbon ecosystems can fuel calcium carbonate dissolution, thereby resulting in no net effect of calcification on atmospheric  $\text{CO}_2$  (Burdige et al. 2008). Addressing the key uncertainties arising from complexities of calcium carbonate cycling in blue carbon ecosystems, and resolving the key questions that currently preclude proper accounting for net calcium carbonate production in blue carbon ecosystems requires a concerted research effort.

In summary, calcium carbonate cycling makes an important contribution to global carbon budgets over geological timescales, yet the magnitude and direction of its influence on  $\text{CO}_2$  sinks within blue carbon is unclear and currently unaccounted for. Considering the rapid rise of interest in blue carbon as a climate change mitigation and adaptation strategies, we argue that calcium carbonate cycling needs to be included when assessing the importance of these globally significant carbon stores as  $\text{CO}_2$  sinks. Addressing calcium carbonate cycling in blue carbon accounting is timely given that anthropogenic activities and climate change may alter calcium carbonate cycling within coastal ecosystems with unknown feedbacks for climate change. For example, with increasing atmospheric  $\text{CO}_2$  and ocean acidification, the ratio of released  $\text{CO}_2$  to precipitated calcium carbonate is

expected to rise (Frankignoulle et al. 1995). Yet increased calcium carbonate dissolution (Fig. 1), and decreased calcification rates are also coupled to higher atmospheric CO<sub>2</sub>, with both processes lowering the rate of CO<sub>2</sub> fluxed to the atmosphere. Moreover, partial dissolution of the large calcium carbonate stock deposited in blue carbon ecosystems may provide a buffer to ocean acidification while acting as a CO<sub>2</sub> sink. Clearly accounting for calcium carbonates in blue carbon systems is a tricky business.

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### Acknowledgments

We thank Patricia A. Soranno, Stephen V. Smith, and an anonymous reviewer for their advice in revising this paper. PM was supported by an Australian Research Council DECRA Fellowship (DE130101084) and a Linkage Project (LP160100242). OS was supported by the CSIRO Flagship Marine and Coastal Carbon Biogeochemical Cluster and an ARC DECRA (DE170101524). DM was supported by an ARC DECRA Fellowship (DE150100581). CMD was supported by baseline funding from KAUST.

Submitted 22 February 2017

Revised 26 May 2017; 25 July 2017

Accepted 25 September 2017