Response: Commentary: Evaluating the Role of Seagrass in Cenozoic CO₂ Variations

Marco Brandano 1,2*, Luis Pomar 3, Guillem Mateu-Vicens 3,4, Marco Cuffaro 2, Giovanni Gaglianone 1, Patrizio Petricca 1 and Vincenzo Stagno 1

1 Dipartimento Scienze della Terra, Università Roma La Sapienza, Rome, Italy, 2 Istituto di Geologia Ambientale e Geoingegneria (CNR), sez. Sapienza, Dipartimento Scienze della Terra, Università Roma La Sapienza, Rome, Italy, 3 Cátedra Guillem Colom Casasnoves, Universitat de les Illes Balears, Palma de Mallorca, Spain, 4 Laboratorio de Zoología, Departament de Biologia, Universitat de les Illes Balears, Palma de Mallorca, Spain

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A commentary on

Commentary: Evaluating the Role of Seagrass in Cenozoic CO₂ Variations

by Macreadie, P. I., Serrano, O., Duarte, C. M., Beardall, J., and Maher, D. (2017). Front. Environ. Sci. 5:55. doi: 10.3389/fenvs.2017.00055

We would like to acknowledge Macreadie et al. (2017) for their interest in clarifying some key points on the processes involved in the balance of CO₂ exerted by the seagrass ecosystems during the Cenozoic. However, their criticisms seem to be based on some misunderstandings regarding the biocalcification processes. So we take this opportunity to make clear some concepts on this topic.

Macreadie et al. (2017) criticize Brandano et al. (2016) when considering the epiphytic carbonate production to result in net CO₂ sequestration, in addition to the CO₂ sequestration by the growth of the seagrasses. In fact, they assert "the authors have not accounted for the fact that calcification increases pCO₂ (by depleting CO₃³⁻ and therefore reducing alkalinity), which facilitates the return of CO₂ to the atmosphere. Specifically, for every mole of CaCO₃ precipitated as carbonate, the process also consumes 2 moles of HCO₃⁻ and releases 1 mole of CO₂".

This criticism is clearly questionable and contradicts themselves (Macreadie et al., 2014) when considered the C to be stored by the seagrass system not only in the organic tissues (leaves, roots and rhizomes) but also in the inorganic skeletons (carbonates). In fact they wrote "... carbonates – even though they are inorganic, and carbonate formation releases net CO₂ – should be included as part of the C stock because they consist of bound C that is locked away, and might otherwise end up as CO₂ in the atmosphere."

The seagrass ecosystem uses the CO₂ in two main processes: in the photosynthetic production of the organic tissues –leaves, roots and steams, as well as the organic parts of all associated organisms that live in this ecosystem, and in the carbonate precipitation forming skeletons of the epiphytic biotas. In both processes, the DIC (CO₂ and HCO₃⁻) is used. The organic matter is only a temporary sink of the CO₂ because after death and decay the CO₂ returns to the atmosphere.

It is well-known that photosynthetic prokaryotes since the Archean, prokaryotes and eukaryotes during the Proterozoic, and more evolved forms of photosynthetic life also during the Phanerozoic have been using the CO₂ derived from the Earth Mantle outgassing. Nevertheless, following the Great Oxidation Event, around 2000 Ma ago, the oxygen started to accumulate in the atmosphere and dissolved in the oceans. This reverted the reaction and the organic matter that was not buried (isolated from the oxidizing environments) became oxidized and the carbon returned to
the atmosphere in the form of CO$_2$ (1). But, if organic matter is buried, it is isolated from oxidizing processes and becomes a real sink of C, as represented by are the hydrocarbon and coal deposits.

\[ \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{CH}_3\text{O} + \text{O}_2 \quad (1) \]

In alkaline waters, bicarbonate is the most abundant DIC species, but it is inaccessible without a source of protons (2). Diffusion from ambient waters can supply protons that are consumed during photosynthesis. But as diffusion is slow, the CO$_2$ becomes depleted, photosynthesis is inhibited and the photosynthetic organisms are bathed in an alkaline microenvironment. By discharging the protons from calcification into their boundary layers (2) and Figure 1, photosynthetic organisms can maintain or even elevate CO$_2$ concentrations despite photosynthetic CO$_2$ uptake (3). This enhances carboxylation efficiencies (McConnaughey and Whelan, 1997; Pomar and Hallock, 2008).

\[ \text{Ca}^{++} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}^+ \quad (2) \]

\[ \text{H}^+ + \text{HCO}_3^- \rightarrow \text{CH}_3\text{O} + \text{O}_2 \quad (3) \]

Adding reactions (2) and (3) one obtains a 1:1 ratio of calcification to photosynthesis in which both calcification and organic matter are part of the same system.

**FIGURE 1 |**“Cis” and “trans” calcification mechanisms. Photosynthetic alcalinization of the water causes cis calcification, while enzyme Ca$^{++}$/ATPase drives the Ca$^{++}$/H$^+$ exchange in the trans calcification (redrawn from McConnaughey and Whelan, 1997). Cis calcification occurs on the same side of the photosynthetic carbon uptake, whereas trans calcification occurs away of the site of carbon uptake.
\[
\text{Ca}^{++} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{O}_2 \quad (4)
\]

The CaCO_3 accumulates in the lithosphere, being the limestones and dolostones a permanent storage form of CO_2. The same applies to the skeletons of calcifying organisms. The only process releasing the CO_2 trapped in the carbonate rocks is the recycling of the lithosphere in the subduction zones and the associated volcanism.

When Macreadie et al. (2017) use the reaction (5) to illustrate calcification as a source of CO_2, they ignore the stoichiometry of the complete system (6):

\[
\begin{align*}
\text{Ca}^{++} + 2\text{HCO}_3^- & \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \\
2\text{CO}_2 + 2\text{H}_2\text{O} & \leftrightarrow 2\text{H}_2\text{CO}_3 < \rightarrow 2\text{H}^+ + 2\text{HCO}_3^-
\end{align*}
\]

As it is obvious, to release one CO_2 from carbonate precipitation (5), two CO_2 are needed to produce the two required bicarbonates (6). So, the balance of the carbonate precipitation is a net CO_2 sink. This is well illustrated in the different calcification processes (Figure 1).

Macreadie et al. (2017) opinion that calcification represents a global CO_2 source to the atmosphere, and therefore seagrass meadows could represent a significant net CO_2 source is just the vision of one half of the processes, and cannot be sustained when looking at the entire carbon cycle.

As result of these biased misconceptions, the authors enter in continuous contradictions. Their estimations from Mediterranean case histories made them to conclude that calcification in P. oceanica meadows could be responsible for the emission of 0.7 to 4.2 Tg C yr\(^{-1}\) to the atmosphere (Mateo and Serrano, 2012). So why are people promoting to restore and protect P. oceanica meadows, in order to fulfill their key role in carbon cycle and storage by adopting efficient regulation of human pressures such as fishing? Some of the coauthors of the Macreadie et al. (2017) commentary (e.g., Fourqurean et al., 2012) state that the rapid loss of seagrasses resulted in a substantial decrease in C sequestration by seagrass ecosystems of 6 to 24 Tg C yr\(^{-1}\). So the authors of the Macreadie et al. (2017) paper have to take a decision: are seagrasses a sink or a source of CO_2? If they conclude seagrasses are a source, then we should review the entire evolution of Earth and Life.

**AUTHOR CONTRIBUTIONS**

MB, LP, and GM led the paper. All authors contributed to the discussion.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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