



Computing the carbonate chemistry of the coral calcifying medium and its response to ocean acidification



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ARTICLE INFO

Article history:

Received 4 July 2016

Revised 25 April 2017

Accepted 28 April 2017

Available online 3 May 2017

Keywords:

Scleractinian corals

Calcification

Calcifying fluid

Aragonite saturation state

Ocean acidification

ABSTRACT

Critical to determining vulnerability or resilience of reef corals to Ocean Acidification (OA) is a clearer understanding of the extent to which corals can control carbonate chemistry in their Extracellular Calcifying Medium (ECM) where the CaCO₃ skeleton is produced. Here, we employ a mathematical framework to calculate ECM aragonite saturation state ($\Omega_{\text{arag, (ECM)}}$) and carbonate system ion concentration using measurements of calcification rate, seawater characteristics (temperature, salinity and pH) and ECM pH ($\text{pH}_{\text{(ECM)}}$). Our calculations of ECM carbonate chemistry at current-day seawater pH, indicate that $\Omega_{\text{arag, (ECM)}}$ ranges from ~10 to 38 (mean 20.41), i.e. about 5 to 6-fold higher than seawater. Accordingly, Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) were calculated to be around 3 times higher in the ECM than in seawater. We also assessed the effects of acidification on ECM chemical properties of the coral *Stylophora pistillata*. At reduced seawater pH our calculations indicate that $\Omega_{\text{arag, (ECM)}}$ remains almost constant. DIC_(ECM) and TA_(ECM) gradually increase as seawater pH declines, reaching values about 5 to 6-fold higher than in seawater, respectively for DIC and TA. We propose that these ECM characteristics buffer the effect of acidification and explain why certain corals continue to produce CaCO₃ even when seawater chemistry is less favourable.

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1. Introduction

Calcification by scleractinian corals is responsible for the world's most prominent biomineral constructions, coral reefs. Although coral reefs cover less than 0.2% of the world's ocean (Spalding et al., 2001), they offer a habitat for approximately one third of known marine species (Porter and Tougas, 2001) and provide an estimated US\$30 billion annually in ecosystem goods and services (Moberg and Folke, 1999). Currently, coral reefs are faced with many anthropogenic threats, both at global scales (e.g. Ocean Acidification (OA) and warming) and regional scales (e.g. pollution, habitat destruction, over-fishing, eutrophication).

Corals precipitate calcium carbonate (as the polymorph of aragonite) to form their skeletons, a process which is sensitive to OA. Although the response of different coral species may vary and

many aspects of how coral reefs respond to OA remain poorly understood, meta-analysis of published data indicates that generally ocean acidification has a deleterious effect on coral calcification rates (Chan and Connolly, 2013). Coral skeletons do not grow in direct contact with the surrounding seawater, however, but actually under the coral tissue in an Extracellular Calcifying Medium (ECM), located at the interface between the calcifying cells and the underlying skeleton surface. Knowledge of the chemical composition of the ECM at this interface is crucial to understanding how changes in the chemical properties of the external seawater drive changes in coral calcification. However, available information about the coral ECM remains limited, partly because it is difficult to access under several overlying cell layers and because its thickness varies from just a few nanometers to a few micrometers (Tambutté et al., 2011). Only a few studies concern either direct (Al-Horani et al., 2003; Cai et al., 2016; Kühl et al., 1995; Ries, 2011; Venn et al., 2011; Venn et al., 2013) or indirect (Dissard et al., 2012; Holcomb et al., 2014; Hönisch et al., 2004; Krief et al., 2010; McCulloch et al., 2012a; Reynaud et al., 2004; Trotter et al., 2011) measurements of chemical parameters in the ECM and

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results show that ECM composition differs from seawater, suggesting a biological control by corals. Whereas most of the above studies focused on assessing ECM pH, only two gave values of calcium (Al-Horani et al., 2003) and carbonate (Cai et al., 2016) concentrations. Carbonate ion concentrations together with pH inside corals have been recently measured for the first time using microelectrodes on three scleractinian coral species (Cai et al., 2016). However, due to experimental difficulties to reach the ECM, measurements of two parameters of the carbonate system remains scarce. This knowledge gap precludes a clear understanding of the effect of OA on calcification.

Two methods of indirect assessment of ECM chemical composition have therefore been proposed in the literature (Allison et al., 2014; McCulloch et al., 2012a). McCulloch and colleagues used a modelling approach (IpHRAC model) which is based on the assumption that $[DIC]_{(ECM)} = 2 \times [DIC]_{(SW)}$, where SW refers to seawater (McCulloch et al., 2012a). Aragonite saturation state in the ECM ($\Omega_{arag,(ECM)}$) is then calculated from $[DIC]_{(ECM)}$, $pH_{(ECM)}$ and $[Ca^{2+}]_{(ECM)}$ and coral calcification rate is therefore deduced from $\Omega_{arag,(ECM)}$. In the study of Allison and colleagues, ECM composition was assessed from skeletal boron geochemistry (Allison et al., 2014). As it is unclear if both bicarbonate and carbonate are utilised during aragonite precipitation, they used $B(OH)_4^-/CO_3^{2-}$, $B(OH)_4^-/HCO_3^-$ and $B(OH)_4^-/(CO_3^{2-} + HCO_3^-)$ aragonite partition coefficients from $\delta^{11}B$ and $pH_{(ECM)}$ to estimate all the other parameters in the ECM DIC system.

Here we present a novel, alternative means of indirectly assessing ECM carbonate chemistry using coral calcification rates, seawater characteristics (temperature, salinity and pH) and pH measurements of the ECM ($pH_{(ECM)}$). The robustness of this approach relies on the fact that our series of calculations is not based on an assumption of $[DIC]_{(ECM)}$, but rather on empirical data. Furthermore, our approach has the advantage of using calcification rate, which is among the most widely used and easily measured physiological parameter for corals, and for which a large reservoir of data is available in the literature on which to base our calculations.

Only two carbonate chemistry variables are needed to calculate concentrations of the other ions in the carbonate system. Here we used species-specific estimations of $pH_{(ECM)}$ (derived from seawater pH) and $[CO_3^{2-}]_{(ECM)}$ (determined from calcification rate) to calculate all the other parameters of the carbonate system. As there are few measurements of $pH_{(ECM)}$ relative to calcification measurements available in the literature, we first present a species-specific method to calculate $pH_{(ECM)}$ from seawater pH when it has not been experimentally measured. Secondly, we use coral calcification rates to calculate $\Omega_{arag,(ECM)}$ and $[CO_3^{2-}]_{(ECM)}$. Thirdly, we used $pH_{(ECM)}$ and $[CO_3^{2-}]_{(ECM)}$ to calculate the ionic concentration of the other chemical species of the carbonate system in the ECM. A comprehensive scheme summarising the different steps of our approach is given in Fig. 1.

We applied this series of calculations on 29 calcification rates retrieved from the literature (from cold-water corals to tropical species) in order to evaluate the range of chemical conditions under which coral skeletons are formed under current environmental seawater conditions. Additionally, we go on to evaluate how partial-pressure CO_2 -driven seawater acidification influences ECM characteristics. Insight into the extent to which corals modify their ECM composition in response to OA will help inform models of coral calcification (Hohn and Merico, 2012; Nakamura et al., 2013) and improve biogeochemical models (Alekseenko et al., 2014; Gehlen et al., 2014; Raybaud et al., 2011) in making predictions for the fate of coral reefs in the 21st century and beyond.

2. Methods

2.1. Origin of extracellular calcifying medium pH data and statistical analysis

We compiled $pH_{(ECM)}$ data from six studies on 5 different species in the literature that have measured $pH_{(ECM)}$ at several different levels of seawater pH. As these studies include $pH_{(ECM)}$ data over a range of seawater pH values, we considered that these studies were the most informative for assessing the $pH_{(ECM)}$ and seawater pH relationship. Using these studies, we calculated species-specific linear regressions between seawater pH and $pH_{(ECM)}$ for: *Desmophyllum dianthus*, *Cladocora caespitosa*, *Porites* spp., *Acropora* spp. and *Stylophora pistillata*. The data include $pH_{(ECM)}$ measurements derived from boron isotope analysis and direct $pH_{(ECM)}$ measurements by confocal microscopy. $pH_{(ECM)}$ data for *S. pistillata* were more widely spread than the other species. We conducted two regressions for the *S. pistillata* data, one for the boron isotope measurements of $pH_{(ECM)}$ and one for the confocal measurements of $pH_{(ECM)}$.

We used these relationships between seawater pH and $pH_{(ECM)}$ in the rest of the manuscript to determine $pH_{(ECM)}$ in studies listed in Supplementary Table S1 with the aim to calculate the corresponding ECM chemical composition. This analysis included the use of both $pH_{(ECM)}$ regressions generated for *S. pistillata*. $pH_{(ECM)}$ data were transformed to $[H^+]_{(ECM)}$ according to the formula:

$$[H^+]_{(ECM)} = 10^{-pH_{(ECM)}} \quad (1)$$

All pH values are expressed in total scale. When pH measurements were given on NBS scale, we converted pH data to total scale using VB-scripts 'pH_nbs2total' provided by MBARI (available at: <http://www.mbari.org/products/research-software/visual-basic-for-excel-oceanographic-calculations/>).

2.2. Origin of the calcification rates

We compiled 29 coral calcification rates (normalized to the corals' surface area) and seawater characteristics (temperature, salinity, pH) from 20 peer-reviewed publications (listed in Supplementary Table S1) to calculate the corresponding values of $\Omega_{arag,(ECM)}$ and the carbonate chemistry composition of the ECM. We restricted our data compilation to studies for which species-specific linear regressions between seawater pH and $pH_{(ECM)}$ has been established (see paragraph 2.1). We considered only laboratory experiments under controlled environmental conditions, i.e. no field studies. We retrieved only the calcification rates of control treatment (i.e. optimal light and food) or present-day conditions (current seawater pH, pCO_2 and $\Omega_{(sw)}$) with the aim to calculate the composition of the calcifying fluid corresponding to optimal or current conditions. When full carbonate chemistry was not available directly from the publications or when variables were reported in different units, we calculated carbonate chemistry using the relevant data deposited for the respective publication in the OA-ICC (Ocean Acidification International Coordination Centre; <http://www.iaea.org/ocean-acidification/page.php?page=2195>) database (Nisumaa et al., 2010). Although our list of coral calcification rates normalized to surface area is not exhaustive, the high number of values (N=29) enabled us to evaluate the range of ECM compositions on a wide range of corals, from cold-water species (which have a slow growth rate) to tropical corals (which grow faster).

Since the 29 calcification rates used here were measured using two different experimental techniques (total alkalinity anomaly and buoyant weight), we verified the adequacy between measurements before using them. A graphical representation of mean and standard deviation of calcification rates measured using the

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