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Coral reef calcification: carbonate, bicarbonate and proton flux under conditions of increasing ocean acidification

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Data on calcification rate of coral and crustose coralline algae were used to test the proton flux model of calcification. There was a significant correlation between calcification (G) and the ratio of dissolved inorganic carbon (DIC) to proton concentration ([DIC] : [H^+] ratio). The ratio is tightly correlated with [CO_3^{2-}] and with aragonite saturation state (Ω_a). An argument is presented that correlation does not prove cause and effect, and that Ω_a and [CO_3^{2-}] have no basic physiological meaning on coral reefs other than a correlation with [DIC] : [H^+] ratio, which is the driver of G.

Comment

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Most previous reports conclude that CO_3^{2-} is the primary substrate for calcification in corals and crustose coralline algae (CCA), and assume that under increasing conditions of ocean acidification (OA) the effect of declining [CO_3^{2-}] is the primary factor responsible for the observed decline in calcification rate (G). Nearly every scientific report concerning the effects of OA on coral reefs describes changes in G as a function of [CO_3^{2-}] or its surrogate aragonite saturation state (Ω_a). The recent report by Comeau *et al*. [1] challenges this paradigm by demonstrating that both HCO_3^- and CO_3^{2-} are involved in calcification of the reef coral *Porites rus* and the crustose coralline algae (CCA) *Hydrolithon onkodes*. The effect of changes in aqueous CO_2, which is the third component of total dissolved inorganic carbon (DIC), was not tested in these experiments. Their data analysis can be taken a step further by investigating the possible importance of seawater hydrogen ion concentration [H^+] and [DIC] on the calcification process. These data were derived from incubation experiments, and thus describe net material flux between the calcifying organism and the water column. These data do not tell us what is actually happening within the 'black box' of the calcifier. Correlation of G with bulk seawater [CO_3^{2-}] does not prove that [CO_3^{2-}] controls G. In all their growth experiments, [HCO_3^-] was by far the highest potential source of inorganic carbon. Without showing active transport and use of CO_3^{2-} from the seawater pool, the relationship of [CO_3^{2-}] to G has no clear physiological meaning. The efflux of H^+ from the calcifying organism influences speciation of bulk water [CO_3^{2-}]. Also, net calcification rate as reported in these experiments does not disentangle the relative contributions of gross calcification and dissolution rates [2]. Measurement of gross calcification is difficult, but might offer an explanation for differences in calcification response of various taxa to OA [3]. Advanced physiological techniques [4] are presently providing insights into processes within coral tissue and in the calcifying space between the skeleton and coral tissues. The various forms of inorganic carbon in seawater rapidly interconvert. DIC is the sum of CO_3^{2-}, HCO_3^- and aqueous CO_2 concentration. The ratio [DIC] divided by [H^+] as presented by Jokiel [5,6] can be viewed as the relative availability of reactant (inorganic carbon) in relation to concentration of inhibitory calcification waste product (protons) in the bulk water surrounding the calcifier. Analysis of existing data suggests that a mechanism influencing the net calcification rate is diffusion limitation of excess H^+ from the coral into the water

Table 1. Data from Comeau *et al*. [1] used in the calculations.

CO_3^{2-} conditions	HCO_3^- conditions	$[HCO_3^-]$ (μmol kg^{-1})	$[CO_3^{2-}]$ (μmol kg^{-1})	$[CO_2]$ (μmol kg^{-1})	pCO_2 (μatm)	Ω_a	T (°C)	A_T (μmol kg^{-1})	pH_T
low CO_3^{2-}	high HCO_3^-	2243	75	56	2108	1.2	28	2424	7.44
	med HCO_3^-	1695	85	27	1047	1.4	28	1910	7.62
	low HCO_3^-	1025	82	13	503	1.3	28	1258	7.8
medium CO_3^{2-}	high HCO_3^-	2287	223	19	733	3.6	28	2814	7.91
	med HCO_3^-	1731	227	11	401	3.7	28	2289	8.04
	low HCO_3^-	1069	203	5	188	3.3	28	1612	8.19
high CO_3^{2-}	high HCO_3^-	2334	384	11	435	6.2	28	3224	8.13
	med HCO_3^-	1802	381	7	257	6.1	27	2712	8.25
	low HCO_3^-	1195	365	3	120	5.8	28	2114	8.41

Table 2. Calcification data from Comeau *et al*. [1] and calculated values for the $[DIC] : [H^+]$ ratio.

conditions	[DIC] (μmol kg^{-1})	$[H^+]$ (nmol kg^{-1})	$[DIC] : [H^+]$ ratio $([DIC] \times [H^+]^{-1}) \times 10^3$	mean coral G (mg $CaCO_3$ d^{-1} cm^{-2})	mean CCA G (mg $CaCO_3$ d^{-1} cm^{-2})	coral G (light) (μg $CaCO_3$ h^{-1} cm^{-2})	coral G (dark) (μg $CaCO_3$ h^{-1} cm^{-2})	CCA G (light) (μg $CaCO_3$ h^{-1} cm^{-2})	CCA G (dark) (μg $CaCO_3$ h^{-1} cm^{-2})
low CO_3^{2-}	2374	36.31	65	0.8	0.1	33	12	−9	−70
	1807	23.99	75	1.1	0.4	35	0	−65	−30
	1120	15.85	71	0.68	−0.2	−2	−4	−48	−143
medium CO_3^{2-}	2529	12.30	206	1.5	0.8	65	36	70	43
	1969	9.12	216	1.9	1.7	48	12	8	−30
	1277	6.46	198	1.4	0.2	18	13	−25	−83
high CO_3^{2-}	2729	7.41	368	2.1	2.1	112	50	118	115
	2190	5.62	389	1	0.9	70	47	60	58
	1563	3.89	402	1.5	2.1	43	48	26	11

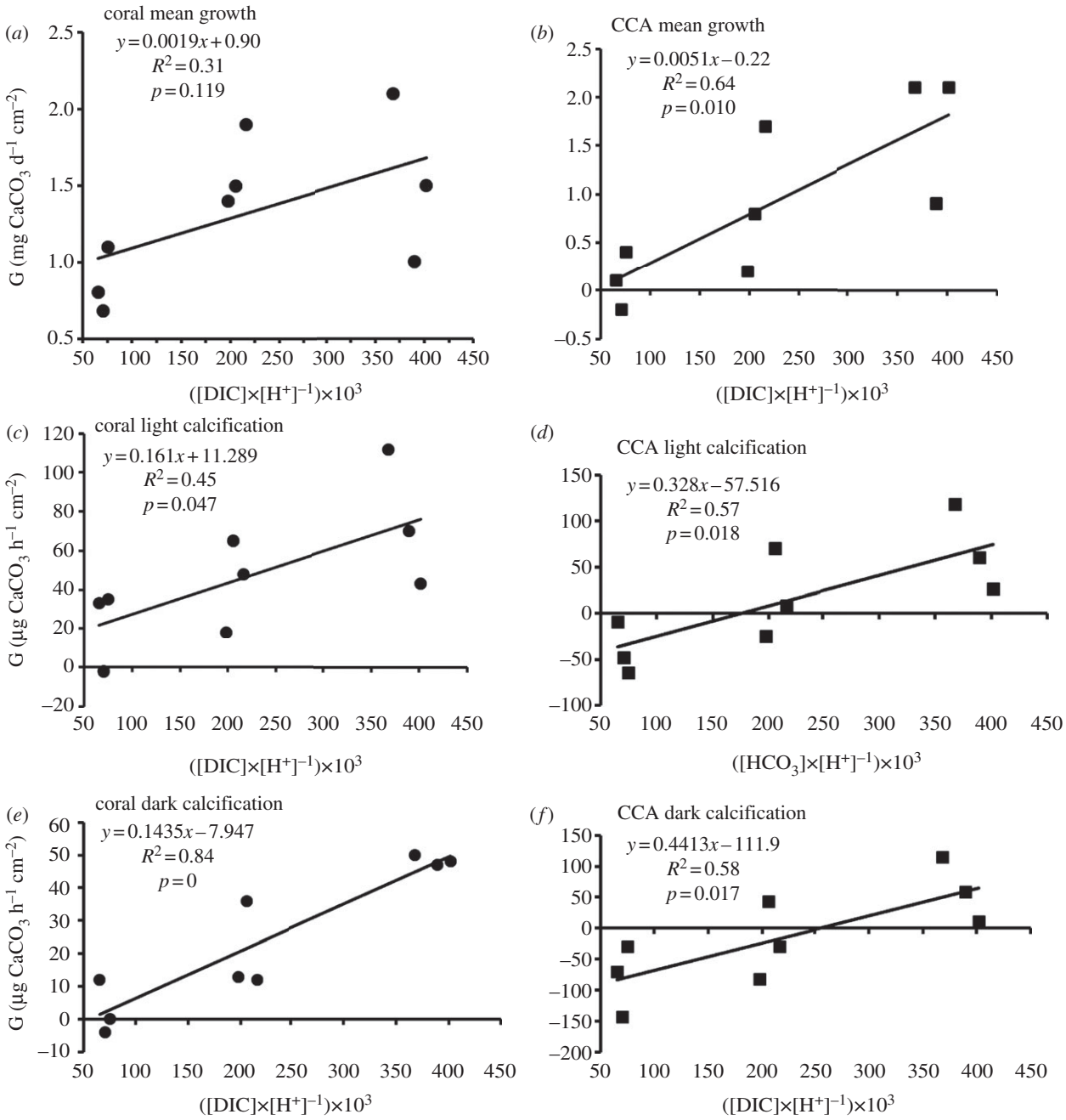

Figure 1. Plots of [DIC] to [H^+] ratio versus calcification rate (G) for (*a*,*c*,*e*) the coral *Porites rus* and (*b*,*d*,*f*) the crustose coralline algae (CCA) *Hydrolithon onkodes* using data from Comeau *et al*. [1]. (*a*,*b*) Net calcification measured by buoyant weight over two-week incubations; (*c*,*d*) net hourly calcification in the light measured by the alkalinity anomaly technique; (*e*,*f*) net hourly calcification in the dark measured by the alkalinity anomaly technique.

column. The resulting 'proton flux model' states that the lowered calcification rate observed in corals under increasing conditions of OA can be attributed to higher [H^+] in the seawater, with consequent decrease in the efflux of waste H^+ from calcifiers through the boundary layer.

In order to test these hypotheses, the data from Comeau *et al*. [1] were used to calculate [DIC], [H^+] and the ratio of [DIC] to [H^+] (tables 1 and 2). Calcification rate (G) was plotted against the [DIC] : [H^+] ratio for each of their six incubation experiments (figure 1). Coral and CCA hourly light and dark calcification rates (figure 1*c*–*f*) showed a significant relationship to the [DIC] : [H^+] ratio. Mean growth over a two-week period showed a significant trend for CCA (figure 1*b*), but this trend was not significant for mean coral growth (figure 1*a*). The same pattern was found by Comeau *et al*. [1] in relation to [CO_3^{2-}] and [HCO_3^-]. The results are consistent with the concept that calcification (G) is controlled by the [DIC] : [H^+] ratio. The relatively weak correlation during rapid coral calcification in the light (figure 1*c*) outweighed the high correlation for the coral in the dark (figure 1*e*) to produce a non-significant relationship with mean coral growth measured over the integrated two-week period (figure 1*a*). These data emphasize the important role played by HCO_3^- and H^+ in daylight when corals are undergoing rapid photosynthesis as well as rapid calcification [6].

Plotting the data for the [DIC] : [H^+] ratio against either CO_3^{2-} or Ω_a provides another useful insight (figure 2). It is apparent that [CO_3^{2-}] is correlated with the ratio of [DIC] to [H^+], which explains its correlation with G. Likewise, Ω_a is essentially a function of [CO_3^{2-}], and therefore will also correlate with G. The physical chemist's concept of Ω_a has been essential to our understanding of global changes in the

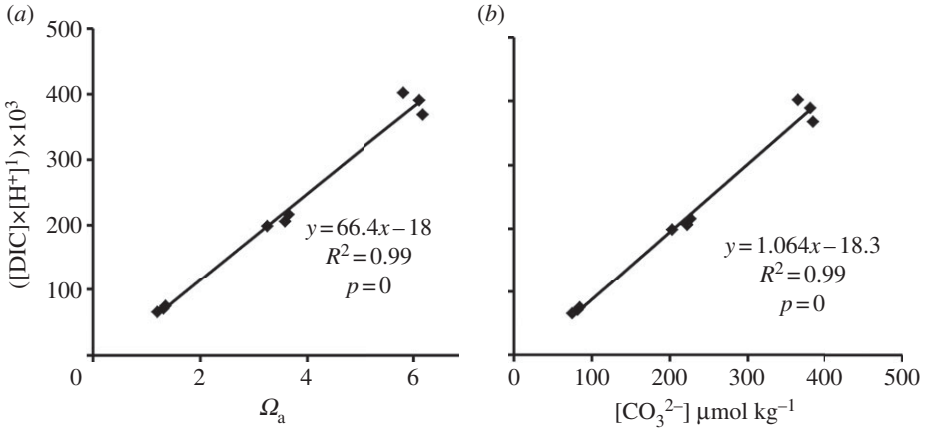

Figure 2. Relationship between (*a*) Ω_a and [DIC] : [H^+], and (*b*) [CO_3^{2-}] and [DIC] : [H^+], using data from Comeau *et al*. [1].

carbonate chemistry of the sea. The vertical and horizontal distribution of Ω_a in the past, present and future will continue to be the subject of extensive research. Originally, the correlation between Ω_a and G along with the expansion of OA research led biologists away from the classic physiological concepts [7], with acceptance of a physical chemistry concept that has no intrinsic relationship to coral metabolites. Biologists involved in OA studies have widely used Ω_a as the independent variable related to coral calcification, based on this empirical correlation. The use of the [DIC] : [H^+] ratio is based on measurement of the most important materials involved in calcification and thus is relevant to understanding basic physiology. Therefore, the [DIC] : [H^+] ratio is conceptually preferable to the physical chemistry concept of Ω_a in describing G. This is especially important if we wish to draw conclusions about G from cases where Ω_a is decoupled from [H^+] as occurs in the palaeo-ocean over timescales greater than 10 000 years [8]. The practice of plotting G versus Ω_a will probably continue because it is convenient to relate a primary biological response of corals (G) to the primary physical chemistry measurement describing ocean chemistry (Ω_a), especially in modelling the future changes on coral reefs. The nature of seawater carbonate chemistry is that some of the parameters are strongly correlated with each other and some correlate with calcification rate. However, correlation does not prove cause and effect, and we must keep in mind the fact that parameters such as Ω_a and [CO_3^{2-}] have no basic physiological meaning on coral reefs other than a correlation with [DIC] : [H^+] ratio, which is the driver of G. Certain tropical calcifying species such as the coral *Pocillopora damicornis* and calcified alga *Halimeda macroloba* appear to be insensitive to OA, whereas others show dramatic changes in calcification rate [9]. With increasing OA, the decrease in [CO_3^{2-}] is accompanied by a large increase in [HCO_3^-] and [H^+], so organisms with effective morphological and metabolic means of dissipating H^+ while increasing uptake of HCO_3^- [6] can maintain high rates of G as the [DIC] : [H^+] ratio of seawater decreases.

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