## Experimental investigation of factors controlling aragonite crystallization

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Ocean acidification reduces seawater pH, shifts the dissolved inorganic carbon (DIC) equilibrium (increasing  $[HCO_3^{-1}]$  and decreasing  $[CO_3^{2^-}]$ ) and reduces the calcification rates of many calcareous marine organisms. Aragonite and calcite precipitation rates are determined by the seawater saturation state,  $\Omega$  (reflecting the availability of  $CO_3^{2^-}$  and  $Ca^{2^+}$  for incorporation in the CaCO<sub>3</sub> precipitate). However, both aqueous HCO<sub>3</sub><sup>-</sup> and  $CO_3^{2^-}$  are inferred to attach to growing calcite crystal surfaces [1] and HCO<sub>3</sub><sup>-</sup> is observed in both coral and synthetic aragonite [2]. Understanding the roles of both HCO<sub>3</sub><sup>-</sup> and  $CO_3^{2^-}$  in CaCO<sub>3</sub> precipitation is key to predicting the responses of calcareous organisms to ocean acidification.

We are conducting experiments to study aragonite precipitation at a constant saturation state ( $\Omega = 4, 7, 10, 13$  or 18) over varying seawater pH levels (pH= 8.337, 8.545 and 8.727). These changes in pH were accompanied by changes in [DIC] (850-7800 µmol kg<sup>-1</sup>) and, subsequently, [HCO<sub>3</sub><sup>-</sup>] but [CO<sub>3</sub><sup>2-</sup>] remains essentially unchanged. All experiments were conducted at T = 25±0.1°C, salinity = 34 and using an aragonite seed. We correlated aragonite precipitation rates with concentrations of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ions. Our results show that the precipitation rate of aragonite reflects the CO<sub>3</sub><sup>2-</sup> ion concentrations (fig 1) while HCO<sub>3</sub><sup>-</sup> ion concentrations has a negligible effect on precipitation rate (fig 2). This implies HCO<sub>3</sub><sup>-</sup> is not a substrate for aragonite formation and has important implications on the interpretation of O isotope proxies.



Figure 1 shows the precipitation rate of aragonite as a function of carbonate ion concentration. Different saturation states are denoted by different symbols: yellow diamonds show  $\Omega = 4$ , blue squares  $\Omega = 7$ , purple triangles  $\Omega = 10$ , green squares  $\Omega = 13$  and orange circles  $\Omega = 18$ 



Figure 2 shows the precipitation rate of aragonite as a function of bicarbonate ion concentration. Different saturation states are denoted by different symbols: yellow diamonds show  $\Omega = 4$ , blue squares  $\Omega = 7$ , purple triangles  $\Omega = 10$ , green squares  $\Omega = 13$  and orange circles  $\Omega = 18$