

## Real reactions of seawater and mineral matter: coral reef ecology

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We need to elucidate which marine calcifying organisms can carry out the actual fixation of atmospheric carbon dioxide or not. The carbon dioxide species dissolved into seawaters are starting material of reversible reaction between calcification and decalcification. In our bottom-up research the real enhanced skeleton formation was actually observed from individual primary corals to each tubular colony. The proton transfer in coral reef-building seawaters controls all reversible acid/base dissociation reactions (Chem. Eur. J. 2014, 20, 13656-13661\*). After the true real reactions among different chemical species in seawaters were identified on the basis of material energetics and biology of marine calcifying organisms, a reasonable overall reaction should be estimated as material balance. From our data of base/acid titration (Chem. Eur. J. 2007, 13, 10176-10181\*\*), light microscope observation and culture experiment\*) it was become clear that the enhanced skeleton production of each coral polyp skeleton and each colony is controlled by reversible reaction between calcification and decalcification,  $\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{H}^+$ . Here solubility product  $[\text{Ca}^{2+}][\text{HCO}_3^-]$  is much larger than  $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$  for reversible equation  $\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3$ . Our idea\*) of proton dynamics demonstrated the increase of  $[\text{Ca}^{2+}]$ , and the decrease of major  $[\text{HCO}_3^-]$  and minor  $[\text{CO}_3^{2-}]$  with decreasing pH at a given  $P_{\text{CO}_2}$  and  $\sim 7.8 < \text{pH} < \sim 8.4$ . Thus stable variation of seawater pH over geological and laboratory timescales is actually real in reef-building seawaters under no anthropogenic influence on atmospheric carbon dioxide. \*) Suwa, Hatta and Ichikawa. \*\*) Ichikawa.

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