EFFECT OF SEAWATER pH, Mg$^{2+}$ AND CARBONIC ANHYDRASE ON MARINE BIOGENIC CARBONATES AND THEIR $\delta^{18}$O VALUES: FUTURE AND PALEO APPLICATIONS

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Abstract

Ocean pH affects marine CaCO₃ cycling and the oxygen isotope (δ¹⁸O) values of biogenic CaCO₃. Based on a carbon–cycle model and laboratory experiments, this study explores future perspectives of ocean acidification and characterizes the mechanism and paleoclimatic implications of the pH effect on δ¹⁸O values of biogenic CaCO₃.

For a release of 5,000 Pg of carbon in 500 years, the surface ocean pH and atmospheric CO₂ will rise to 7.4 and 1,900 ppmv. Eventually anthropogenic CO₂ will be sequestered via continental weathering followed by CaCO₃ burial in sediments. But these processes will not effectively mitigate the predicted carbon–cycle perturbations on centennial timescales.

Studying the impact of CO₂-forcing on global temperatures from past climate events is crucial for predicting future global warming. But paleotemperature reconstructions using δ¹⁸O values of biogenic CaCO₃ can be hampered by past changes in seawater pH. For example, planktonic foraminiferal δ¹⁸O values could have been biased by +0.4‰ at maximum (up to 2 °C of underestimated temperature) due to pH decline during the Paleocene–Eocene Thermal Maximum (~56 Ma).

A proposed explanation for the pH effect on δ¹⁸O values of biogenic CaCO₃ [Zeebe, 1999, 2007] assumes ¹⁸O equilibrium in the CO₂–H₂O system in the calcification microenvironments and that equilibrium fractionation between dissolved CO₂ species and H₂O by Beck et al. [2005] holds in seawater. These assumptions were evaluated by quantitative BaCO₃ precipitation experiments.
focusing on the effect of carbonic anhydrase (CA) and Mg$^{2+}$ on the kinetics and equilibrium of $^{18}$O partitioning in the CO$_2$–H$_2$O system.

CA accelerates $^{18}$O equilibration in the CO$_2$–H$_2$O system by catalyzing CO$_2$ hydration. Calculations suggest that $^{18}$O equilibration within the timescales of calcification is possible with $10^{-8}$ to $10^{-7}$ M of CA. Mg$^{2+}$ is the most important cation for complex formation with CO$_3^{2-}$ in seawater. Although the MgCO$_3^0$ abundance in the total dissolved CO$_2$ was varied up to 30% in the experiments, the results revealed no discernible influence on equilibrium $^{18}$O fractionation in the CO$_2$–H$_2$O system. These outcomes contribute to fundamental understanding of vital effects on $\delta^{18}$O values of biogenic CaCO$_3$. 

vi