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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By
Joji Uchikawa

Dissertation Committee:

Richard E. Zeebe, Chairperson
Brian N. Popp
Yuan–Hui Li
Jane E. Schoonmaker
Gregory E. Ravizza

Abtract

Ocean pH affects marine $CaCO_3$ cycling and the oxygen isotope ($\delta^{18}O$) values of biogenic $CaCO_3$. 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 $\delta^{18}O$ values of biogenic $CaCO_3$.

For a release of 5,000 Pg of carbon in 500 years, the surface ocean pH and atmospheric CO_2 will rise to 7.4 and 1,900 ppmv. Eventually anthropogenic CO_2 will be sequestered via continental weathering followed by $CaCO_3$ burial in sediments. But these processes will not effectively mitigate the predicted carbon–cycle perturbations on centennial timescales.

Studying the impact of CO_2–forcing on global temperatures from past climate events is crucial for predicting future global warming. But paleotemperature reconstructions using $\delta^{18}O$ values of biogenic $CaCO_3$ can be hampered by past changes in seawater pH. For example, planktonic foraminiferal $\delta^{18}O$ 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 $\delta^{18}O$ values of biogenic $CaCO_3$ [*Zeebe*, 1999, 2007] assumes ^{18}O equilibrium in the CO_2–H_2O system in the calcification microenvironments and that equilibrium fractionation between dissolved CO_2 species and H_2O by *Beck et al*. [2005] holds in seawater. These assumptions were evaluated by quantitative $BaCO_3$ 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_2O system.

CA accelerates ^{18}O equilibration in the CO_2–H_2O 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_2O system. These outcomes contribute to fundamental understanding of vital effects on $\delta^{18}O$ values of biogenic $CaCO_3$.