

## Carbonate paleothermometry based on abundances of $^{13}\text{C}$ - $^{18}\text{O}$ bonds

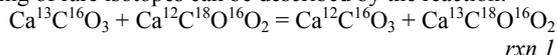
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Urey's carbonate oxygen isotope paleothermometer is a milestone of paleoclimate research but constrains temperature only if the oxygen isotope composition of water from which carbonate grew is known. Moreover, difficulty in recognizing diagenetic overprinting has confounded the interpretation of carbonate oxygen isotope compositions for much of the geological record. We present a carbonate paleothermometer based on the formation of bonds between  $^{13}\text{C}$  and  $^{18}\text{O}$ . This ordering of rare isotopes can be described by the reaction:



The equilibrium constant for rxn. 1 is temperature dependent and constrained by the isotopic composition of carbonate alone. Experiments on carbonate standards demonstrate that this equilibrium constant can be measured by phosphoric acid digestion and analysis of the proportion of  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$  in product  $\text{CO}_2$ .

Calcite inorganically precipitated from aqueous solution at 323-273 K has a 0.56-0.75 ‰ excess of  $\text{Ca}^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$  relative to the amount expected for a random distribution of isotopes, and this excess is positively correlated with  $1/T^2$ . These results are broadly consistent with theoretical models of the energetics of rxn. 1. Given the external precision of our measurements (ca. 0.01 ‰), it should be possible to use rxn. 1 to do paleothermometry with uncertainties as low as ca.  $\pm 1^\circ\text{C}$ .

Analyses of recent surface and deep-sea corals yield abundances of  $^{13}\text{C}$ - $^{18}\text{O}$  bonds that are consistent with their known growth temperatures, based on our experimental calibration of rxn. 1. These corals are aragonitic and have variable, sometimes large, 'vital effect' contributions to their  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. Thus, the success of our measurements suggests vital effects and structural differences between calcite and aragonite have small or negligible effects on the equilibrium constant of rxn. 1.

We will present the results of an application of the  $^{13}\text{C}$ - $^{18}\text{O}$  thermometer to late-preCambrian limestones and dolomites from Namibia and the Canadian Cordiera.

## Unraveling nutrient, growth rate, calcification, and diagenesis effects on the chemistry of coccolith calcite

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Coccoliths are the dominant biogenic carbonate in many deep sea sediment cores, and recent work to constrain the influence of vital effects on coccolith stable isotopic measurements, and to exploit vital effects on Sr/Ca ratios in coccoliths, have renewed interest in proxies from coccolith chemistry. Coccolith Sr/Ca ratios are correlated with productivity across upwelling gradients and in some transient blooms. To assess whether this response is triggered by cell growth and calcification or nutrient availability, and whether different responses among different genera reflect different ecological responses to these environmental gradients, we analyze Sr/Ca ratios of different coccolith fractions from a series of sediment traps in the northern and southern Bay of Bengal. In the northern trap series close to major river deltas, maximum coccolith fluxes occur during the southwest summer monsoon when productivity is highest, and correspond to elevated Sr/Ca ratios in several species. In some species, Sr/Ca ratios are more correlated to total productivity than to the export flux of coccoliths from that species, suggesting a link to an environmental variable like nutrients, or export response truncated by grazing. We further evaluate the nutrient influence on Sr/Ca with analysis of coccolith chemistry in N-limited and P-limited chemostat cultures of coccolithophorid *Emiliania huxleyi*.

New ion probe techniques for Sr/Ca measurements on individually picked coccoliths isolate the Sr/Ca variations in single species of fossil coccoliths from sediments. This approach reveals a large heterogeneity of Sr/Ca ratios among different genera of coccoliths. Such heterogeneity suggests that diagenesis has not homogenized the Sr/Ca ratios of coccoliths in many older (in this case Paleocene) sediments, an asset for paleoreconstructions. However, it indicates that the elemental variations in bulk carbonate may be influenced by changing nanofossil assemblages.