

A direct proxy for palaeo-pCO₂ is the δ¹³C of organic matter (δ¹³C_{org}). The fractionation of carbon isotopes during photosynthesis by phytoplankton is controlled by the concentration of carbon dioxide in the surface waters outside the cell (CO₂(aq)) and the metabolic uptake of carbon during photosynthesis (μ) (e.g. Laws et al., 1995). Past studies using this approach to reconstruct palaeo-pCO₂ (e.g. Freeman and Hayes, 1992; Pagani et al., 1999) have assumed that μ remained constant. Since there is considerable evidence to suggest that oceanic productivity has varied considerably throughout geological history, δ¹³C_{org} must be corrected by an independent measure of μ in order to reconstruct accurately surface water carbon dioxide concentrations. The positive correlation between the Sr/Ca of calcite and the rate of precipitation observed in inorganic experiments provides a basis for investigating Sr/Ca in biogenic calcites as a measure of phytoplankton growth rate (Lorens et al., 1981). Indeed, preliminary studies suggest that this relationship may be extended to the Sr/Ca of the rapidly precipitating calcite coccoliths of the modern ocean [Stoll and Schrag, 2000]. We present new results from a culture experiment which was undertaken with *Emiliani huxleyi* under controlled conditions of temperature, light and nutrients but in two tanks with differing levels of pCO₂. Growth rate during the culture experiment was estimated from the increase in number of cells (μ_i), particulate organic carbon (μPOC), particulate inorganic carbon (μPIC) and corrected in each case for respiration during the dark hours of the 16:8 light:dark daily cycle. The Sr/Ca of the coccoliths was determined on an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Schrag, 1999).

In each tank the Sr/Ca of the coccoliths was relatively high (0.25 mmol/mol) during the exponential phase of cell division. As the culture slowed towards the stationary phase, the Sr/Ca also decreased and approached a value of 0.05 mmol/mol. Therefore, at high growth rates the partition coefficient for Sr into calcite (D_{Sr}) is five times higher than low growth rates when D_{Sr} tends towards an equilibrium value. There is a remarkable correlation between the Sr/Ca of coccoliths with all the experimental estimates of growth rate (r > 0.8), but the best correlation exists with μPIC (r = 0.97). Although all the estimates of growth rate are interrelated and linked to metabolic carbon utilisation, in reality the most accurate measure of μ for the culture experiments will be ε_p provided pCO₂ is maintained at a constant level. The data from Tank 2, where pCO₂ was maintained at approximately 500 ppmV, confirm that there is an impressive correlation between ε_p and the Sr/Ca of coccoliths (Figure 1).

Stoll and Schrag (2000) suggested that the Sr/Ca covariation with growth rate reflects a calcification rate dependence, as has been demonstrated by inorganic precipitation experiments

(Lorens, 1981). Our results suggest a strong correlation between μPIC and carbon uptake as well as with Sr/Ca. This could be interpreted as supporting the inorganic calcification rate dependence on Sr/Ca provided there is a close metabolic relationship between crystal growth rate and photosynthesis. Alternatively, as calcification in coccolithophorids occurs in vesicles within the cell, the analogy to inorganic precipitation of calcite may not be applicable. Instead, there may be a direct control of Ca in the cell tied to carbon metabolism. Regardless of the biological mechanism linking these three factors, a quantitative relationship exists between the Sr/Ca of *E. huxleyi*, ε_p, and pCO₂. This relationship, defined by the culture data, has been tested on the palaeoceanographic record by comparing down-core analyses of Sr/Ca and δ¹³C_{org} from a subtropical core with the Vostok record of pCO₂.

Figure 1: Sr/Ca measured in *E. huxleyi* versus ε_p for the culture experiment in Tank 2 with an approximately constant pCO₂ of 500 ppmV.

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