



Sr/Ca-ratios in coccoliths and carbon isotopic composition of C₃₇ alkenones in particulate matter: testing a new *p*CO₂ reconstruction strategy

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Earth climate has undergone major changes over geologic time-scales. Observations from trapped air bubbles in glacier ice cores revealed that changes in atmospheric CO₂ levels over the last 420,000 years co-vary with Quaternary climate. Predictions of future changes of climate on Earth are difficult since the relationship between atmospheric CO₂ and long-term climatic cycles is complex and poorly understood. To define better the mechanisms by which oceanic and atmospheric levels of CO₂ have changed over geological time scales, palaeoceanic sources and sinks of CO₂ must be delineated. This requires accurate palaeo-indicators (proxies) for past CO₂ concentrations in the surface oceans.

The carbon isotopic fractionation (ϵ_p ; expressed in ‰) of C₃₇-alkenones was used to reconstruct past atmospheric CO₂ concentrations (Jasper and Hayes 1990). ϵ_p is mainly a function of the growth rate, the factors influencing the growth rate (e.g. nutrients) and the ambient CO₂(aq) concentration. Consequently, precise reconstructions of CO₂(aq) based on ϵ_p of alkenones require a correction for the influence of growth rate and factors influencing the growth rate, respectively. Based on surface sediment studies Stoll and Schrag (1999) suggested the Sr/Ca ratio in coccolithophorid calcite to be an independent proxy of coccolithophorid growth rate. Indeed, culture experiments confirmed the growth rate dependence of Sr incorporation during coccolith calcification. Thus, it was suggested to combine coccolith Sr/Ca ratios with the carbon isotopic fractionation of C₃₇alkenones in order to improve palaeo-CO₂ estimates.

In the present study we determined, for the first time, paired data of the partition coefficient of strontium (D_{sr}) into coccolith calcite and the isotopic fractionation (ε_p) of C_{37} alkenones in particulate matter from oceanic surface waters of the Caribbean Sea. Consistently for sediment-based and culture studies, a positive relationship is observed between D_{sr} and surface water phosphate concentration ($[PO_4^{3-}]$) suggesting a growth rate-depending control on D_{sr} . In contrast to laboratory studies no temperature dependence of D_{sr} was observed. The obtained relationships between ε_p and surface water concentrations of phosphate and carbon dioxide ($[CO_2(aq)]$) imply that ε_p is mainly influenced by two factors, the growth rate and the ambient $CO_2(aq)$ concentration. Following the approach of Stoll and Schrag (1999), in a further step we used the observed relation between $[PO_4^{3-}]$ and D_{sr} to correct ε_p for the growth rate influence. The resulting corrected values (ε_p -corrected) show a significant negative correlation ($R=0.93$) with the inverse of the carbon dioxide concentration $[CO_2(aq)]$ as expected from model calculations. Apparently, coccolith Sr/Ca ratios in combination with the carbon isotopic fractionation of C_{37} alkenones permits more reliable calculation of past dissolved CO_2 in the surface ocean.