Sr/Ca-ratios in coccoliths and carbon isotopic composition of C\textsubscript{37} alkenones in particulate matter: testing a new pCO\textsubscript{2} 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 CO\textsubscript{2} 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 CO\textsubscript{2} and long-term climatic cycles is complex and poorly understood. To define better the mechanisms by which oceanic and atmospheric levels of CO\textsubscript{2} have changed over geological time scales, palaeoceanic sources and sinks of CO\textsubscript{2} must be delineated. This requires accurate palaeo-indicators (proxies) for past CO\textsubscript{2} concentrations in the surface oceans.

The carbon isotopic fractionation ($\varepsilon_p$; expressed in $\%$) of C\textsubscript{37}-alkenones was used to reconstruct past atmospheric CO\textsubscript{2} concentrations (Jasper and Hayes 1990). $\varepsilon_p$ is mainly a function of the growth rate, the factors influencing the growth rate (e.g. nutrients) and the ambient CO\textsubscript{2}(aq) concentration. Consequently, precise reconstructions of CO\textsubscript{2}(aq) based on $\varepsilon_p$ 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 C\textsubscript{37} alkenones in order to improve palaeo-CO\textsubscript{2} 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 ($\epsilon_p$) 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 $\epsilon_p$ and surface water concentrations of phosphate and carbon dioxide ([CO$_2$(aq)]) imply that $\epsilon_p$ 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 $\epsilon_p$ for the growth rate influence. The resulting corrected values ($\epsilon_p$-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.