

New Carbonate System Proxies: Foram Culturing and Pteropod Potentials

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Global climate change is one of the most pressing challenges our society is facing currently. Climate sensitivity due to atmospheric CO₂ doubling will most likely increase global temperatures by 2.0–4.5 °C (IPCC 2007). While some direct effects of increasing CO₂ are straightforward (e.g. ocean acidification, atmospheric temperature rise), the mid- and long-term impacts of increasing CO₂ levels are less easily predicted due to poorly qualified contribution from various potential positive and negative feedbacks in the climate system. Palaeoreconstructions combining temperature reconstructions and atmospheric paleo-CO₂ levels are necessary to validate models that aim at predicting future global temperature increases. Reconstructions of atmospheric CO₂ from ice-cores are confined to the last 800 ka (LÜTHI et al. 2008), while reconstruction of atmospheric pCO₂ on longer timescales rely largely on marine sedimentary archives (e.g. HÖNISCH et al. 2012). Within the latter, foraminifera play a central role, since the chemical and isotopic composition of their shells reflect the physicochemical properties of the seawater that these organisms grew in (EMILIANI 1955). Palaeo atmospheric CO₂ concentrations can be estimated from past seawater CO₂ (aq), which in turn can be reconstructed when two out of six parameters are known of the oceans carbonate system (“C-system”; CO₂, HCO₃⁻, CO₃²⁻, pH, DIC [dissolved inorganic carbon] and total alkalinity).

Currently established, foraminifera-based C system proxies include boron isotopes (pH), B/Ca (CO₃²⁻) or the reconstruction of total alkalinity *via* salinity variations (HEMMING and HANSON 1992, HÖNISCH and HEMMING 2005, HÖNISCH et al. 2009, SANYAL et al. 1995, YU et al. 2010). However, these proxies do not allow the reconstruction of the complete C system by themselves, due to various limitations and uncertainties associated with the different methods used (e.g. YU and ELDERFIELD 2007). Despite much recent progress in the field of paleoclimatology aiming at overcoming these limitations and uncertainties, accurate and precise reconstructions of past pCO₂ levels remains challenging. Here we present the potential of culturing studies with foraminifera and field studies using pteropods to establish new C system proxy relationships.

Culturing living foraminifera is a valuable tool to precisely calibrate new and existing proxies. In some species, asexual reproduction can be triggered in the laboratory, resulting in 50 to 300 one-chambered juveniles that can be placed into experiments under controlled conditions (e.g. various pH's, [DIC]s, TAs). After maintaining them at a range of environmental conditions until they have grown into maturity, the resulting isotope and element composition of their calcium carbonate can be measured and related to these environmental conditions.

Through careful selection of culturing conditions, where values can be tweaked far beyond to what is found in nature to get a good handle on the correlation between the seawater parameters and the proxy, it is thus possible to establish new proxy relationships. With respect to carbonate chemistry it is important to be able to know whether the proxy-carbonate system parameter correlation represents a causal relationship or solely an accidental regularity due to the covariation of the C system parameters. Experiments need therefore be constructed in a way that the individual parameters of the C system deconvolved and varied independently. The classical C system manipulation approaches are therefore inappropriate as parameters are changing simultaneously (e.g. SMITH and ROTH 1979). For example, changes in pH and carbonate ion concentration are correlated in classical C system manipulations, so that an observed effect cannot be traced back to an individual parameter and hence prevents separating the sole impact of e.g. pH on carbonate chemical composition.

To overcome this problem, we conducted C system culturing experiments on the benthic foraminifer *Ammonia* sp. (molecular type T6, HAYWARD et al. 2004) where the classical approach (covariation of parameters, e.g. pH and (CO_3^{2-})) is combined with a manipulation, where pH and (CO_3^{2-}) are varied independently (pH was kept constant, (CO_3^{2-}) was allowed to vary). The experimental setup used allows us hence to independently quantify effects of pH, (CO_3^{2-}) and DIC on foraminiferal calcite chemistry. Due to its shallow water habitat *Ammonia* sp. is not commonly used in palaeo-oceanographic studies, however, its abundance, good accessibility and tolerance of broad ranges of environmental parameters make it a suitable candidate when determining new potential proxy relationships and can thus serve as a model species.

1. Sr/Ca as a Proxy for DIC?

Sr/Ca is a widely measured parameter and has been used in a variety of organisms to reconstruct various parameters such as temperature in corals (SMITH and ROTH 1979). Foraminiferal Sr/Ca has been shown to be influenced by growth rates, temperature, salinity and pH (KISAKÜREK et al. 2008, LEA et al. 1999). With respect to the latter, it has been demonstrated by several studies that foraminiferal Sr/Ca varies with seawater carbonate chemistry (e.g. LEA et al. 1999, RAITZSCH et al. 2011, RUSSELL et al. 2004). However, due to the co-variation of the C system parameters in these studies, it remained inconclusive to isolate the impact of each parameter of the C system to incorporation of Sr in foraminiferal calcite. To solve this problem, we measured shell Sr/Ca using LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) on shells from C system manipulations, where the parameters were varied independently (see above, and also KEUL et al. 2013 for a full description of the experimental procedures). Linear regression analyses were performed to analyse the correlation between individual C system parameters and foraminiferal Sr/Ca. Since the carbonate system parameters covary differently in the two experimental approaches, it is possible to exclude certain parameters of the C system as (primary) causes for the observed changes in Sr/Ca, namely $p\text{CO}_2$, pH, (HCO_3^-) and (CO_3^{2-}) . This leaves TA and DIC as potential parameters that primarily affect Sr incorporation. The importance of TA on Sr/Ca is less likely, since it is an artificially constructed dimension, leaving DIC as the most likely parameter that determines foraminiferal Sr/Ca. The influence of DIC on Sr/Ca can be explained if one assumes that foraminifera need to keep Omega in the calcification environment stable (“Omega homeostasis”). The high DIC in our experiments (up to 3-times higher than normal oceanic levels)

leads to an influx of pCO₂ into the foraminiferal cell, since CO₂ in its gaseous form can easily diffuse across cell membranes. This CO₂ will be transformed into carbonate and bicarbonate ions both in the cell and in the calcification environment, which leads to an increase in Omega. To achieve Omega homeostasis, the foraminifera will need to adjust Ca. This decrease in Ca concentration would thusly cause an increase of the Sr/Ca concentration in the calcifying fluid and consequently also in the foraminiferal shell.

In the following paragraph we test whether this hypothesis fits published downcore records of Sr/Ca. MARTIN and colleagues (2000) have reported Sr/Ca oscillations in foraminiferal calcite over glacial-interglacial (G-IG) cycles, which seems to be a common phenomenon across species and ocean basins. It was demonstrated, that these oscillations cannot be explained by temperature effects or dissolution, also salinity and pH had to be ruled out since the magnitude of these changes was too small. While the authors have convincingly described how changes in the mean ocean Sr/Ca could be causing the oscillation in foraminiferal Sr/Ca over G-IG cycles, we will explore the potential role of DIC on foraminiferal Sr/Ca. In the above-mentioned C system manipulation experiments we found the following correlation between DIC and Sr/Ca:

$$\text{Sr/Ca} = 1.168\text{e-}04 \times \text{DIC} + 1.083 \quad (p < 0.001, R^2 = 0.65, \text{KEUL et al., in prep.}) \quad [1]$$

Assuming a G-IG change in DIC of 130 mmol/kg-sw, the resulting change in Sr/Ca would be 1.2%. While the direction of the change is correct, the magnitude is too small to account for the full oscillation (ca. 4%). ALLEN and co-authors (in prep.) have performed a similar calibration study with the planktonic species *G. sacculifer*, where the slope of the calibration was twice as steep. Applying this linear equation would lead to a change in Sr/Ca of 4.2%, which is in the order of the reported changes over G-IG cycles. The slope of a calibration is usually species-specific, so that it is likely that the absolute change in foraminiferal Sr/Ca as a response to the same environmental change will vary among species, which is shown here by the difference in slope of the *Ammonia* sp. calibration and that of *G. sacculifer*.

2. U/Ca as a Proxy for Carbonate Ion Concentration

The U/Ca ratio of benthic and planktonic foraminifera has been shown to correlate with carbonate system parameters ([CO₃²⁻] and pH; RAITZSCH et al. 2011, RUSSELL et al. 2004). In order to quantify the impact of each individual parameter (pH, [CO₃²⁻]) on foraminiferal U/Ca, LA-ICP-MS measurements were carried out on the foraminifera from the above mentioned culture experiments. The correlation of U/Ca and the carbonate system parameters were analysed by means of regression analysis. Since the carbonate system parameters co-vary differently in the two experimental approaches (see KEUL et al. 2013 for a detailed description of the experiments), it is possible to exclude certain parameters of the C system as causes for the observed changes in U/Ca. This approach points to [CO₃²⁻] as the sole parameter primarily affecting U/Ca ratios in *Ammonia* sp. The correlation between U/Ca and [CO₃²⁻] can be explained in terms of uranium speciation in seawater, as uranium easily complexes with carbonate ions (MARKICH 2002). Speciation depends strongly on [CO₃²⁻]: free uranium forms complexes with carbonate ions, consequently decreasing the amount of free uranium with increasing [CO₃²⁻]. It has been shown by MARKICH (2002) that free Uranium forms are taken up by algae cells. Our findings suggest that this might also be the case in *Ammonia*

sp., since similar to the content of free uranium in the seawater, the U/Ca content in the shell clearly decreases with increasing $[\text{CO}_3^{2-}]$:

$$\text{Log U/Ca} = 2.42 - 2.65 \times 10^{-3} \times [\text{CO}_3^{2-}] \quad (R^2=0.65, p>0.001; \text{KEUL et al. 2013}). \quad [2]$$

Fractionation against trace elements in foraminifera is species-specific, causing the U/Ca content to be different among foraminiferal species and underlines the necessity for species-specific calibrations when applying U/Ca to reconstruct past carbonate ion concentrations. Based on the described correlation we can infer that a glacial-interglacial decrease of 100 $\mu\text{mol/kg-sw}$ in carbonate ion concentration would result in a 54 % increase in foraminiferal U/Ca. With the great analytical precision associated to (LA-)ICP-MS, the glacial to interglacial changes can be resolved within 95 % confidence intervals.

3. Assessing the Proxy Potential of Pteropods

Another opportunity to establish new C system proxies is to examine the potential of pteropod shells. Pteropods are ideal candidates: they are abundant in all major ocean bodies (LALLI and GILMER 1989), and their physiology is known to be highly sensitive to climate change (Ocean Acidification and Ocean Warming; LISCHKA et al. 2011). Pteropods are pelagic molluscs, producing shells made out of aragonite, a metastable form of calcium carbonate, which is more soluble than calcite in seawater. This makes pteropods an interesting subject in the development of new proxies: since presence of pteropods in the underlying sediments is governed by the corrosiveness of the water column, pteropods can be used as a “double archive” as they offer the unique chance, to quantify both, the characteristics of the water column at the time of biomineralization (as imprinted in the trace elemental incorporation in the pteropod shell) and the corrosiveness of the water column (through their presence/absence/fragmentation in the sediment). It has been shown that pteropods are an excellent recorder of the aragonite saturation of bottom waters (MEKIK 2013). Through a combination of analyses on open-ocean, cultured and down core pteropods we are currently analysing the proxy potential of pteropods with a special regard on carbonate system proxies. Preliminary results will be presented. This includes a trace-elemental-calibration from a culturing study (under changing C system parameters and temperature) and the variability of trace elemental incorporation from a 10-year sediment trap study.

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