# Calibration of Na partitioning in the calcitic foraminifer *Operculina ammonoides* under variable Ca concentration: Toward reconstructing past seawater composition

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## ARTICLE INFO

## ABSTRACT

Reconstructions of past changes in the seawater calcium concentration ($Ca_{sw}$) are critical for understanding the long-term changes in ocean chemistry, the carbon cycle and for accurate application of elemental proxies ($El/Ca_{CaCO_3}$) in foraminifera (e.g., Mg/Ca as proxy of temperature). Here we show that Na/Ca ratios in foraminiferal shells could be used for reconstructing $Ca_{sw}$ and Mg/Ca in the past oceans. Ca has a short residence time in the ocean ($\sim$1 My), whereas Na in seawater has a residence time of $\sim$100 My. Hence it may be reasonably assumed that $Na_{sw}$ is invariant over the Cenozoic, enabling variations in oceanic Ca to be deduced from foraminiferal Na/Ca ($Na/Ca_{shell}$) if Na incorporation into foraminiferal shells depends on Na/Ca in seawater. Furthermore, the paleo-concentrations of other major and minor elements may then be calculated relative to the Ca in the shells, provided that other environmental or biological factors do not present a further complication. To evaluate this hypothesis, we cultured the benthic foraminifer *Operculina ammonoides*, an extant relative of the Eocene *Nummulites*, under varying $Ca_{sw}$ and temperature. The foraminifera grew well under the experimental conditions and increased their weight by 40–90%. The newly grown calcite (identified using a $^{135}$Ba labeling in the experimental seawater) was analyzed by Laser-Ablation ICP-MS for Li, Na, Mg and Sr to Ca ratios. The relationship between Na/Ca and Mg/Ca in the shell and their ratio in the solution are best described as a power function, where the instantaneous distribution coefficient is the derivative of the power fit to the $El/Ca_{shell}$ versus $El/Ca_{sw}$. In contrast, $D_{Sr}$ and $D_{Li}$ are invariant with $El/Ca_{sw}$. The influence of temperature on Li, Na and Sr incorporation was smaller than the uncertainty of our measurements. We conclude that Na/Ca in foraminiferal shells can be used to calculate paleo-calcium concentrations in the oceans and also other elements that may change relative to calcium (e.g., Mg, Sr, Li and others).

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## 1. Introduction

### 1.1. Past changes in ocean chemistry

Evidence for large secular shifts in seawater chemistry are abundant throughout the geological record (e.g., Stanley and Hardie, 1998). Most of these studies have focused on oscillations in the magnesium to calcium ratio of seawater ($Mg/Ca_{sw}$), which indicate quasi-periodic shifts between 'calcite seas' and 'aragonite seas' (e.g., Hardie, 1996). For this reason, it has been proposed that $Mg/Ca_{sw}$ changes have also influenced the biomineralization and evolution of calcifying marine organisms (van Dijk et al., 2016). $Mg/Ca_{sw}$ may also be important in determining the differential response of calcite and aragonite producing organisms to past and future climatic perturbations (Katz et al., 2010). Elemental ratios in biogenic carbonates have played a major tool in paleoceanographic research (see review in Katz et al., 2010). Mg/Ca ratio is the most studied elemental proxy and is widely utilized as a paleothermometer due to temperature dependence of Mg incorporation. However, Mg incorporation in foraminifera also depends on the seawater Mg/Ca ratio (Evans et al., 2015; Hasiuk and Lohmann, 2010; Segev and Erez, 2006), which has

hampered the accuracy of these temperature reconstructions before the Pleistocene, when Mg/Ca$_{sw}$ cannot be assumed equal to that of today (Evans et al., 2016; Lear et al., 2010). Similarly, the use of other geochemical proxies, such as Sr/Ca (e.g., Sosdian et al., 2012) and Li/Ca (Delaney and Boyle, 1986; Lear et al., 2010) is also confounded by the effects of changing seawater chemistry on their partitioning in biogenic carbonates. Because of the relatively short residence time of Ca in the ocean ($\sim$1 My), on time scales of few million years, variations in foraminiferal El/Ca ratios are likely driven primarily by changes in seawater Ca. However, on longer time scales (Phanerozoic) the ratio (Mg/Ca) is influenced by changes in both elements.

Reconstruction of changes in the concentration of Ca$_{sw}$ is also important for understanding past variability in the processes that influence the ocean calcium cycle. Calcium is delivered to the ocean predominantly by weathering and is removed mainly by burial of CaCO$_3$ on carbonate platforms and the open ocean. However, dolomitization and the interaction of seawater with newly formed oceanic crust, also contribute to the long-term changes in seawater Mg/Ca. This implies that the concentration of these elements in seawater may be sensitive to both sea level and seafloor spreading rates (Berner, 2004). However, notwithstanding the important information derived from such seawater chemistry reconstructions, existing techniques are hampered by large uncertainties (e.g., Broecker, 2013).

Direct proxy reconstructions of Ca$_{sw}$ are available from the measurements and modeling of fluid inclusion data in marine halite (e.g., Horita et al., 2002) and from calcium isotope measurements of carbonate oozes and marine barite (e.g., Fantle and DePaolo, 2005). Fluid inclusions are known only from a handful of time intervals (e.g., Brennan et al., 2013), but because CaCO$_3$ and gypsum are the first minerals to precipitate, the remaining solution often does not contain Ca, rather, it can only be calculated by assuming a constant relationship between Ca and SO$_4$ concentrations (Brennan et al., 2013; Broecker, 2013). Hence, estimates of Ca concentrations are associated with large uncertainties (Horita et al., 2002). Likewise, data from Ca isotopes are difficult to interpret given that the isotopic composition of the sources of calcium to the ocean may have changed through time and pore-water sediment interaction must be accounted for (Fantle and DePaolo, 2005). In addition, there is relatively large fractionation of Ca isotopes in biogenic carbonates (Gussone et al., 2016) which may complicate this method. As a result, there is no proxy for Ca$_{sw}$ with an uncertainty suitable for examining the potential fine-scale changes in the calcium cycle through the Cenozoic.

Here we propose a new proxy, namely the Na/Ca ratio of foraminifera shells, as a direct method of reconstructing past changes in Ca$_{sw}$. Because Na has a residence time of $\sim$100 My in seawater (Broecker et al., 1982), we hypothesize that Cenozoic variations in foraminiferal Na/Ca should principally reflect changes in Ca$_{sw}$. Given the abundance of dated foraminifera in sediment cores, this presents the possibility of accurately reconstructing the Ca cycle, C cycle and other seawater cations at unprecedented temporal resolution. This hypothesis cannot be tested using field calibrations because the Na/Ca$_{sw}$ ratio in today's ocean is nearly constant. Therefore, we use culturing experiments of the benthic foraminifer *Operculina ammonoides* under a range of Ca$_{sw}$ and temperatures with the prime goal of calibrating the potential Na/Ca proxy in foraminifera. By simultaneously measuring the Li, Mg and Sr/Ca ratios in the same specimens, we also present our findings of the response of these trace element systems to varying Ca$_{sw}$.

### 1.2. Empirical determination of distribution coefficients

Distribution coefficients of elements (D$_{El}$) that are incorporated into the lattice of inorganic and biogenic carbonates (including foraminifera) can be determined only when the experimental solutions contain different El/Ca ratios. The distribution coefficient can thus be calculated as the change in the El/Ca ratio of the CaCO$_3$ mineral versus the change in the experimental solution i.e., the slope or derivative of the curve describing the El/Ca$_{CaCO_3}$ versus El/Ca$_{solution}$. To achieve this goal, one needs at least three data points and an intercept that goes through zero (Fig. 1A). A single point of El/Ca$_{CaCO_3}$ divided by El/Ca$_{solution}$ should be considered as an "apparent distribution coefficient" ("D$_{El}$") and not used to describe the distribution coefficient. The regression fit of El/Ca$_{CaCO_3}$ versus El/Ca$_{solution}$ is often not linear (Evans et al., 2015; Hasiuk and Lohmann, 2010; Segev and Erez, 2006). We therefore propose that a proper fit that goes through the origin should be an equation of the type:

$$y = a \cdot x^H \tag{1}$$

Where $y$ is El/Ca$_{CaCO_3}$, $x$ is El/Ca$_{solution}$ and $a$ and $H$ are constants that are obtained from the power curve fit of the set of values of $y$ versus $x$ and cannot be obtained from a single $y/x$ ratio (unless $H = 1$).

This approach is following Ries (2004), Segev and Erez (2006), De Choudens-Sanchez and Gonzalez (2009) and Hasiuk and Lohmann (2010) who used it for Mg in biogenic and inorganic calcite. The theoretical basis for such relations is derived originally from Langmuir (1917) adsorption curves as modified by Freundlich (1932), providing an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. This formulation of the equation describes integrated multi-layered adsorption as presented in Stumm and Morgan (1996, Chapter 9, Equation (14)). What has often been calculated in previous studies is a linear regression of the above variables with a non-zero intercept, which is physically impossible outside of the calibrated range. Therefore, the distribution coefficient should be calculated as the derivative of the power function (Fig. 1B):

$$D = y' = a \cdot H \cdot x^{(H-1)} \tag{2}$$

A classic example for this behavior is the inorganic experiments of Mucci and Morse (1983) for Mg as calculated from their data by De Choudens-Sanchez and Gonzalez (2009). Note however that the latter did not calculate the derivative properly but instead have plotted the "D$_{El}$" (i.e., El/Ca$_{calcite}$ divided by El/Ca$_{solution}$) as the distribution coefficient, and fitted a power regression through the data. Similar approach was exercised by other authors (e.g., Evans and Müller, 2012; Hasiuk and Lohmann, 2010; Morse and Bender, 1990; Mucci and Morse, 1983; Segev and Erez, 2006). In Fig. 1B we show that the distribution coefficient functions as calculated in Equation (2), does not fit the "D$_{El}$" both for the inorganic and biogenic calcites (Mucci and Morse, 1983 and Segev and Erez, 2006, respectively). Although these previous treatments are mathematically incorrect, in most cases a serious error is unlikely to have been propagated through to fossil reconstructions as these are typically based on a calibration between an El/Ca ratio to an environmental variable (e.g., temperature).

### 1.3. Prior foraminiferal Na/Ca studies

Investigations of the paleoceanographic utility of Na in biogenic calcites date back several decades. Early observations of major changes in the Na content of marine carbonates have led to