



Trace element proxies for surface ocean conditions: A synthesis of culture calibrations with planktic foraminifera

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Abstract

The trace element composition of planktic foraminiferal calcite provides a useful means of determining past surface ocean conditions. We have assembled the results of culture experiments for three species of symbiont-bearing planktic foraminifera, *Globigerinoides ruber*, *Globigerinoides sacculifer*, and *Orbulina universa*, and one symbiont-barren species, *Globigerina bulloides*, to evaluate their responses to temperature, salinity, pH, carbonate ion, and dissolved inorganic carbon (DIC) growth conditions. Trace element ratios (Li/Ca, B/Ca, Mg/Ca, Sr/Ca, Mn/Ca, Cd/Ca, Ba/Ca, Na/Ca, and U/Ca) were measured simultaneously on samples grown with the same culture techniques, which provides robust, reliable calibrations that may be used together in multi-proxy paleoceanographic studies. Our data confirm that temperature is the dominant control on foraminiferal Mg/Ca under the ranges of conditions studied and that the potential effects of salinity and CO_3^{2-} on Mg/Ca of these tropical species across late Pleistocene glacial cycles are relatively small. Carbonate system experiments suggest that Sr/Ca may be useful for reconstructing large DIC changes. Na/Ca increases with salinity in *G. ruber* (pink), but not in *G. sacculifer*. As these emerging proxy relationships become more firmly established, the synthesis of multiple trace element ratios may help paleoceanographers isolate the effects of different environmental parameters in paleo records. Calcification rates ($\mu\text{g}/\text{day}$) vary among species and do not respond consistently to any experimental parameter. Comparison of our calcification rates with those observed in inorganic calcite precipitation experiments suggest that foraminifera calcify $\sim 100\times$ more slowly than inorganic calcites grown in similar solutions. We suggest that calcification rate does not typically exert a dominant control on trace element partitioning in planktic foraminiferal calcite, though it may play a role for some elements under certain circumstances. Differences in average growth rate cannot explain composition differences among species, pointing to alternative controls that may be biological in origin.

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1. INTRODUCTION

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Shells (tests) of foraminifera preserved on the sea floor constitute an important archive for paleoceanographers, and much has been done in recent decades to quantify

and understand relationships between the composition of foraminiferal calcite and the environmental conditions in which foraminifera have grown. The shell of modern planktic foraminifera is composed of calcite, the trigonal polymorph of CaCO_3 . Calcite's flexible corner-sharing structure allows it to accommodate a wide range of trace elements (Reeder, 1983), but the total contribution of trace elements to foraminiferal calcite is typically less than 2% (moles of trace elements/moles calcium \times 100), including Li, B, F, Na, Mg, P, V, Mn, Fe, Cu, Zn, Sr, Cd, Ba, Nd, and U (Lea, 1999). Laboratory and field studies have shown that changes in environmental conditions such as temperature and seawater carbonate ion concentration ($[\text{CO}_3^{2-}]$) can produce predictable variations in the trace element composition of foraminiferal calcite (e.g., Lea et al., 1999; Anand et al., 2003; Russell et al., 2004). Assuming that fossil foraminifera behaved similarly to these modern specimens, the calibration of these variations can be used to infer past environmental changes.

In this study we report the chemical composition of calcite precipitated in culture experiments by planktic foraminifera, specifically the ratios of lithium, magnesium, strontium, manganese, cadmium, sodium, and uranium to calcium (Li/Ca, B/Ca, Na/Ca, Mg/Ca, Sr/Ca, Mn/Ca, Cd/Ca, Ba/Ca, and U/Ca). In previous studies, these ratios have often been considered separately, and one of our goals is to consider a wide variety of trace elements to gain new insight into these proxies. Some models of trace element incorporation predict different partitioning behavior for different elements due to variations in chemical properties (e.g., ionic radius, charge). Therefore a holistic approach that includes a wide range of elements enables testing of these predictions. For example, Elderfield et al. (1996) analyzed a suite of trace element ratios to test the idea that Rayleigh distillation from an internal pool or reservoir could explain trace element partitioning during foraminiferal calcification. Their results provided some support for this model in benthic foraminifera, but not in planktics. Later studies built on the pioneering work of Elderfield et al. by considering the distribution of multiple elements within single shells (e.g., Hathorne et al., 2009), which confirmed the earlier studies' findings regarding the lack of Rayleigh-distillation behavior in planktics and also provided a detailed picture of micro-scale trace element distribution patterns.

Here, we synthesize a suite of trace element and calcification rate data to assess controls on the composition of foraminiferal calcite. We aim to assess whether some recent models for trace element incorporation in inorganic carbonates may apply to foraminifera as well. According to one growth-entrapment model of trace element incorporation (DePaolo, 2011), as mineral growth rates increase, incorporation of cations larger than Ca^{2+} (hereafter "large" ions) should increase while incorporation of cations smaller than Ca^{2+} ("small" ions) should decrease. The underlying idea is that larger ions are easier to dehydrate, which might lead to greater rates of incorporation compared to smaller, more strongly hydrated ions at higher growth rates. Another growth-entrapment model is based on the idea that trace element incorporation is determined by the com-

peting effects of crystal growth rate and diffusivity of ions in the near-surface region of a growing crystal (Watson, 1996, 2004). These two models invoke different mechanisms but produce similar predictions regarding trace metal inclusion in calcite. If such growth-rate effects exerted a dominant influence on foraminifera, we should see an inverse relationship between concentrations of large cations (Sr^{2+} , Ba^{2+}) and small cations (Mg^{2+} , Mn^{2+} , Cd^{2+}) in foraminiferal calcite. Our large suite of trace element data measured on the same samples allows this kind of hypothesis to be tested.

First, to provide context for our new results, we summarize existing knowledge and observations from both field-based studies and laboratory-based culture experiments.

1.1. Large divalent cations

1.1.1. Sr/Ca

Both culture and field studies demonstrate Sr/Ca of planktonic foraminiferal calcite is not influenced strongly by temperature or salinity (e.g., Lea et al., 1999), but do suggest increases with shell calcification rate (Lea et al., 1999; Elderfield et al., 2002; Kısakürek et al., 2008; Dueñas-Bohórquez et al., 2009). This is consistent with observations of increased Sr incorporation in calcite at higher precipitation rates in inorganic precipitation studies (Lorens, 1981; Paquette and Reeder, 1995; Gabitov and Watson, 2006), and suggests observed increases with temperature and salinity in planktic foraminifer shells may be an indirect effect of enhanced calcification rate (Dueñas-Bohórquez et al., 2009). Systematic variations in planktic foraminifer shell Sr/Ca in the geologic record have been attributed to changes in seawater Sr/Ca, and also to $[\text{CO}_3^{2-}]$ and nutrient availability (Martin et al., 1999; Stoll et al., 1999; Billups et al., 2004). As with temperature and salinity, these latter factors might be linked to their influence on foraminifer calcification rates. Sr/Ca varies little within single shells (Hathorne et al., 2009).

1.1.2. Ba/Ca

Previous culture studies have demonstrated that Ba/Ca of foraminiferal calcite exhibits no detectable response to salinity, temperature, or carbonate system parameters; rather, it increases linearly with Ba/Ca of seawater (Lea and Spero, 1994; Hönisch et al., 2011). Empirical evidence for the influence of growth rate on Ba/Ca of inorganic calcite is mixed, with some experiments suggesting an increase in Ba incorporation with growth rate (Tesoriero and Pankow, 1996) and others suggesting Ba incorporation is independent of growth rate (Pingitore and Eastman, 1984). As a result of its strong dependence on Ba/Ca of seawater, Ba/Ca of foraminiferal calcite has been used to track ocean processes that involve changes in seawater Ba/Ca, such as freshwater runoff (which has much higher [Ba] than seawater) and remineralization of Ba-rich biogenic particles in the deep ocean (e.g., Hall and Chan, 2004). Since results of our culture experiments have been thoroughly discussed in Hönisch et al. (2011), we only discuss them here in the context of the trace element suite.

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