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Biological and ecological insights into Ca isotopes in planktic foraminifers as a palaeotemperature proxy

Simone A. Kasemann [a,*], Daniela N. Schmidt [b,1], Paul N. Pearson [c,2], Chris J. Hawkesworth [b,3]

[a] School of Geosciences, Grant Institute of Earth Science, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JW, UK
[b] Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, Bristol BS8 1RJ, UK
[c] School of Earth Sciences, University of Cardiff, Main Building, PO Box 914, Cardiff CF10 3YE, UK

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ABSTRACT

Sea surface temperature (SST) is a critical variable in the Earth's climate system since it influences atmospheric circulation, the hydrological cycle and, via ocean surface density, drives ocean circulation. A detailed reconstruction of past SST's is therefore a central goal of palaeoceanographic studies. Although calcium isotopes in foraminiferal carbonate have been introduced as a new proxy for SST reconstruction, there is considerable debate about their robustness and general applicability. To resolve some of these questions, we have investigated the extent to which other environmental parameters e.g. the calcification temperature, depth stratification, growth rates and/or environmental adaptation may influence the δ^{44}Ca values of planktic foraminifers in modern and Eocene samples. Geographically distributed data sets are affected by the exchange of cryptic species, *i.e.* morphologically similar but genetically distinct species, and by a mixing of optimal versus less optimal adaptation. Thus, we have compared species within individual samples to evaluate whether the well documented depth stratification of foraminifers is reflected in their calcium isotopes. The Eocene data set shows a general agreement between δ^{44}Ca and δ^{18}O-derived calcification temperatures which supports a temperature effect on Ca isotope incorporation. The vertical temperature gradient using the different depth habitats of several foraminiferal species indicates a δ^{44}Ca temperature dependence of ~0.034‰ °C^{-1} similar to inorganic calcite (0.015‰ °C^{-1}) and cultured *O. universa* (0.019‰ °C^{-1}). The gradient resembles the global sediment δ^{44}Ca compilation, but it is significantly smaller than the temperature calibration of 0.22±0.02‰ °C^{-1} for cultured *G. sacculifer*. The modern data set shows a general correlation between δ^{44}Ca and depth habitat reflecting a similar temperature gradient to the Eocene sample set. In contrast, the lower absolute δ^{44}Ca values for the Eocene foraminifers suggest a lower seawater isotope composition. *In situ* analyses of individual calcite layers reveal large isotopic differences between the different calcite layers of the foraminifers highlighting the strong biological control on δ^{44}Ca in foraminiferal calcite that may overprint a potential T-relationship.

1. Introduction

The ocean's temperature influences atmospheric circulation through heat exchange and evaporation as well as through ocean circulation in response to density differences. Therefore, assessing past temperatures and the related climate change provides valuable information for future climate change predictions. Direct knowledge of past climates is restricted to the instrumental record which just reaches back to the last century. Longer records rely on proxy data for past temperatures. The precision of the temperature data will constrain climate models and hence determine the predictability of future climate projections.

Several temperature proxies rely on the chemical analysis of marine carbonates, e.g. δ^{18}O (e.g. Emiliani, 1955; Shackleton, 1967), Sr/Ca ratios in corals (Beck et al., 1992), Mg/Ca ratios in foraminifers (Elderfield and Ganssen, 2000; Nürnberg et al., 1996) and most recently δ^{44}Ca (Nägler et al., 2000). However, all of these proxies are controlled by more than one environmental parameter (e.g. Spero et al., 1997; Meland et al., 2006) and can be modified by the carrier that incorporates the palaeotemperature signal (Allison et al., 2005; Schmidt et al., in press). Planktic foraminifers are arguably one of the most important carriers for palaeoclimate information and they have been extensively used to reconstruct past temperatures (see Henderson, 2002 for a review).

The multitude of influences on the proxy, especially in regions such as high latitudes and upwelling areas (Kucera et al., 2005), make it necessary to combine a suite of proxies to carefully constrain past climate change. The shortfalls of traditional proxies, e.g. in high

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* Corresponding author. Tel.: +44 131 6508525; fax: +44 131 6683184.
E-mail addresses: Simone.Kasemann@ed.ac.uk (S.A. Kasemann), d.schmidt@bristol.ac.uk (D.N. Schmidt), Paul.Pearson@earth.cf.ac.uk (P.N. Pearson), C.J.Hawkesworth@bristol.ac.uk (C.J. Hawkesworth).
[1] Tel.: +44 117 9545414; fax: +44 117 9253385.
[2] Tel.: +44 29 20874579.
[3] Tel.: +44 117 9545425.

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latitudes δ^{18}O is strongly influenced by meltwater input altering the salinity and the Mg/Ca temperature response is very small, make the potential application of δ^{44}Ca in foraminiferal calcite as a temperature proxy very attractive. Initial studies suggested a temperature control on δ^{44}Ca in foraminifers (Skulan et al., 1997; Zhu and Macdougall, 1998; De La Rocha and DePaolo, 2000) leading to the determination of a temperature dependent isotope fractionation in culture and core-top studies of *Globigerinoides sacculifer* (Nägler et al., 2000). Subsequent work on the closely related foraminiferal species *Orbulina universa* and *G. sacculifer* (Gussone et al., 2003; Hippler et al., 2006) revealed considerable species-dependent differences in their temperature sensitivity on calcium isotope fractionation (0.019‰ °C^{-1} for *O. universa* compared to 0.24‰ °C^{-1} for *G. sacculifer*). Gussone et al. (2003) attributed these differences to different calcification mechanisms in both species. They suggested diffusion of a high mass Ca^{2+}-aquacomplex in *O. universa*, which is less affected by temperature variations, while in *G. sacculifer* Ca^{2+}-ions are actively dehydrated and there is temperature controlled transport of the dehydrated Ca^{2+}-ion to the calcification site. However, this interpretation is disputed (DePaolo, 2004), and other explanations, such as differences in calcium ion bond strength or in the biomineralisation processes, have been suggested (e.g. Marriott et al., 2004). To address the intriguing nature of the δ^{44}Ca–SST relationships in an ecological context, Sime et al. (2005) analysed foraminiferal species from core-top sediments covering large environmental gradients and different ocean basins, but found no significant correlation between the estimated sea surface temperature and δ^{44}Ca values of these species. They suggest that the culture-based temperature calibrations could have been obscured by so far un-quantified metabolic and/or physiological processes in natural habitats.

Generally, the δ^{44}Ca values in foraminiferal carbonate are significantly lower than the seawater value and more variable than in inorganic calcite indicating a strong control by the organism on Ca isotope incorporation. This opens the potential for a wide range of factors other than temperature, e.g. ecology, precipitation/growth rates and/or metabolic processes, to influence foraminiferal δ^{44}Ca values. Furthermore, foraminiferal tests are composed of several calcite layers termed ontogenetic and gametogenic calcite (Fig. 1) which formed at different times during their life cycle (ontogeny). Foraminifers additionally vary their habitat depth during their ontogeny, which, depending on the species, can be several hundreds of meters (Hemleben et al., 1989). Consequently, carbonate layers are formed at different water depth and potentially have different Ca isotope ratios.

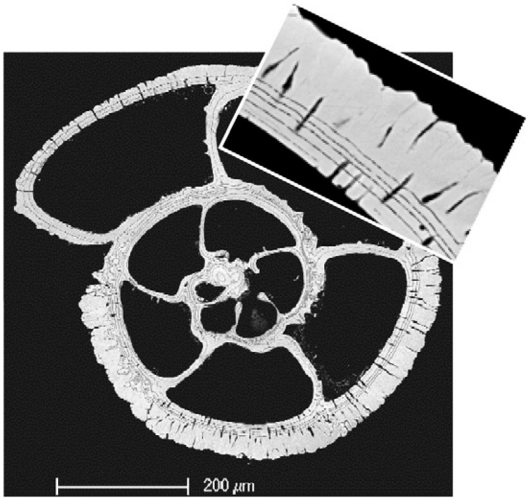

Fig. 1. Back scattered electron image of a *G. truncatulinoides*. The inset shows a detail of the same specimen, clearly highlighting the layered structure of the foraminiferal test and emphasising the thick gametogenic calcite at the outside covering the thinner ontogenetic layers. The black lines represent the former position of the organic layers.

Other well studied isotope systems show biological influences on isotope fractionation. For example, the respiration and photosynthesis of foraminiferal symbionts (Spero and DeNiro, 1987) has been shown to alter the carbonate ion concentration and they influence the boron, carbon and oxygen isotope composition of tests (e.g. Spero et al., 1997; Spero and DeNiro, 1987; Zeebe, 1999; Zeebe et al., 2003). In contrast, the current understanding of biological influences on calcium isotope fractionation is still in its infancy and, more fundamentally, the magnitude of the isotope fractionation and the factors governing it are still debated for inorganic carbonates (Gussone et al., 2003; Marriott et al., 2004; Skulan and DePaolo, 1999). Post-depositional, diagenetic processes in sediments can also alter the original signal via exchange with pore waters (Fantle and DePaolo, 2007) and the spatial heterogeneity of Ca isotopes in the foraminiferal layers may lead to changes in the bulk composition during dissolution.

Before Ca isotopes in planktic foraminifers can be applied as a palaeotemperature proxy, the relationship between Ca isotope fractionation and temperature has to be verified and secondary biological and ecological factors that may influence the fractionation factor have to be quantified. Until now, all approaches have focussed on either laboratory cultures or samples from different sites to investigate the temperature dependency of calcium isotope fractionation. Although a wide geographical range offers a broad temperature range, and hence improves the signal to noise ratio, this approach also combines cryptic, *i.e.* genetically distinct but morphologically very similar, foraminiferal species which have subtly different environmental adaptation (e.g. Darling et al., 2003; Kucera and Darling, 2002) or biology (Huber et al., 1997). Furthermore, this approach compares specimens growing under optimal environment conditions, and hence high growth rates, with specimens which were exposed to environmental stress and hence have low growth rates (Schmidt et al., in press; Schmidt et al., 2004; Schmidt et al., 2006). To avoid these problems, we have chosen to make use of the well established depth stratification of the habitat of planktic foraminifers to investigate if δ^{44}Ca displays similar trends to those shown by plankton tow studies and δ^{18}O.

We analysed the calcium, oxygen and carbon isotope composition in planktic foraminifers from a Holocene sample set from the western equatorial Pacific and well-preserved Eocene specimens from coastal outcrops in Tanzania. We then place our multi-species data set in the context of all published Ca isotope data on modern and Holocene planktic foraminifers, to assess the influence of biology and ecology on Ca isotopes in planktic foraminifers.

2. Materials and methods

2.1. Samples

The Holocene foraminifer sample set was collected from the top 1–2 cm of box core ERDC-92 in the western equatorial Pacific (2°13.5′S, 156°59.9′E, 1598 m) (Berger et al., 1978). We analysed the shallow-dwelling symbiont bearing species *Globigerinoides conglobatus*, *Globigerinoides ruber*, *G. sacculifer*, *Globigerinella siphonifera* and *O. universa*, the intermediate dwelling species *Sphaeroidinella dehiscens*, *Globorotalia menardii*, *Pulleniatina obliquiloculata*, and the thermocline dweller *Globorotalia tumida*. The selected foraminifera tests showed no overgrowth or infilling of diagenetic calcite.

The well-preserved middle Eocene (RAS 99-17 from Ras Mtama, Lindi, Tanzania, 9°57′07″S, 39°42′52″E) samples are from coastal outcrops in Tanzania (Pearson et al., 2001; Nicholas et al., 2006). The clay-rich sediments were not affected by significant burial and they effectively protected the embedded foraminifers against diagenesis and recrystallisation (Sexton et al., 2006; Van Dongen et al., 2006). We have analysed the symbiont bearing mixed layer species *Acarinina bullbrooki*, *Acarinina praetopilensis*, *Igorina broedermanni*, *Morozovella aragonensis*, *Morozovelloides crassatus*, and non-symbiont bearing