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Influences on the fractionation of calcium isotopes in planktonic foraminifera

Elizabeth M. Griffith [a,*], Adina Paytan [b], Reinhard Kozdon [c], Anton Eisenhauer [c], A. Christina Ravelo [b]

[a] *Department of Geological & Environmental Sciences, Stanford University, Building 320, Room 118, Stanford, CA 94305-2115, USA*
[b] *Ocean Sciences Department, University of California, Santa Cruz, CA 95064, USA*
[c] *Leibniz-Institut für Meereswissenschaften IFM-GEOMAR, Wischhofsraße 1-3, D-24148 Kiel, Germany*

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Abstract

For paleoceanographic studies, it is important to understand the processes that influence the calcium (Ca) isotopic composition of foraminiferal calcite tests preserved in the sediment record. Seven species of planktonic foraminifera from coretop sediments collectively exhibited a Ca temperature dependent fractionation of 0.013‰ per °C. This is in agreement with previously published estimates for most species of planktonic foraminifera as well as biogenic and inorganic calcite and aragonite. Four species of planktonic foraminifera collected from a sediment trap showed a considerable amount of scatter and no consistent temperature dependent fractionation. Analyzed size fractions of coretop samples show no significant relationship with $\delta^{44/40}$Ca. However, preliminary results suggest that the symbiotic and spinose foraminifera *Globigerinoides sacculifer* might exhibit a relationship between test size and $\delta^{44/40}$Ca. A one-box model in which Ca isotopes are allowed to fractionate by Rayleigh distillation from a biomineralization reservoir (internal pool) was used to constrain the isotopic composition of the original biomineralization Ca reservoir, assuming around 85% of the Ca reservoir is precipitated and the fractionation factor during precipitation is $0.9985+0.00002(T\,°C)$. To explain the foraminiferal Ca isotope data, this model indicates that the Ca isotopic composition of the biomineralization reservoir is offset from seawater (approximately −0.8‰).

Keywords: calcium isotopes; planktonic foraminifera; paleotemperature; biomineralization; isotopic fractionation

1. Introduction

Foraminiferal Ca isotope ratios have been suggested as a new paleotemperature proxy (Zhu and Macdougall, 1998; Nägler et al., 2000; Gussone et al., 2004; Hippler et al., 2006). This proxy is potentially more robust to diagenetic alteration than Mg/Ca since Ca is the major cation in calcite (Henderson, 2002) and is not thought to fractionate during dissolution (Hönisch, 2002; Fantle and DePaolo, 2007). It is also insensitive to parameters that influence other paleotemperature proxies such as global ice volume, evaporation, and freshwater input (Skulan et al., 1997; Sime et al., 2005; Hippler et al., 2006). However, development of Ca isotopes as a paleotemperature tool is ongoing, and results-to-date indicate a range of possible sensitivities of foraminiferal Ca isotopes to temperature. More work needs to be done to assess various controls on the temperature dependence of Ca isotopic fractionation in planktonic foraminifera before this proxy can be applied and downcore Ca isotope records can be interpreted. Changes in the Ca isotopic composition of seawater also need to be determined in order to use this proxy over timescales longer than 1 million years, the approximate Ca oceanic residence time (De La Rocha and DePaolo, 2000).

1.1. Calcium isotope fractionation

Calcium has six stable isotopes (^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca, and ^{48}Ca) and because of the large spread in isotopic

* Corresponding author. Tel.: +1 650 736 0655; fax: +1 650 725 0979.
E-mail addresses: emgriffith@stanford.edu (E.M. Griffith), apaytan@ucsc.edu (A. Paytan), rkozdon@ifm-geomar.de (R. Kozdon), aeisenhauer@ifm-geomar.de (A. Eisenhauer), acr@ucsc.edu (A.C. Ravelo).

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masses, potential exists for significant mass-dependent isotopic fractionation. However, studies of natural samples (from Earth) have revealed relatively small variations in $^{44}Ca/^{40}Ca$ ratio, only up to ~5‰ (Russell et al., 1978; Skulan et al., 1997; Zhu and Macdougall, 1998). Ca isotope ratios are reported in $\delta^{44/40}Ca$ notation in permil relative to a seawater standard (Eisenhauer et al., 2004):

$$\delta^{44/40}\mathrm{Ca} = \left[\left(^{44}\mathrm{Ca}/^{40}\mathrm{Ca}_{\mathrm{sample}} - ^{44}\mathrm{Ca}/^{40}\mathrm{Ca}_{\mathrm{standard}}\right)/^{44}\mathrm{Ca}/^{40}\mathrm{Ca}_{\mathrm{standard}}\right] \times 1000 \quad (1)$$

It is thought that equilibrium isotope dynamics control discrimination against heavy Ca isotopes in calcite and aragonite, two polymorphs of calcium carbonate, $CaCO_3$ (Bullen et al., 2003; Marriott et al., 2004; Gussone et al., 2005). This asserts the assumption that bonding of Ca in a carbonate mineral structure is weak relative to bonding of Ca in an aquocomplex. Heavier isotopes are energetically preferred in stronger bonds, explaining observed ^{44}Ca depletion in solid carbonates (with weaker bonds). Systematic differences of ~0.5‰ between the Ca isotope composition of inorganic calcite and aragonite have been explained by differences in thermodynamic crystal properties associated with crystal lattice structure and coordination of Ca with oxygen (Gussone et al., 2005; Schauble, 2005).

1.2. Temperature dependent fractionation

Existing data on temperature dependence of Ca isotope ratios in foraminifera are inconsistent, resulting in conflicting interpretations. Skulan et al. (1997) suggested that temperature dependence of Ca isotopic fractionation within foraminifer species is very small (~0.02‰ per °C), which was later confirmed with cultured results of planktonic foraminifera *Orbulina universa* (Gussone et al., 2003) and inorganically precipitated calcite (Marriott et al., 2004) and aragonite (Gussone et al., 2003). In contrast, Zhu and Macdougall (1998) observed a large difference (0.6‰) in $\delta^{44/40}Ca$ between the Holocene and Last Glacial Maximum for planktonic foraminifera *Globigerinoides sacculifer*, which was interpreted as reflecting changes in sea surface temperatures (SSTs) of 4–6 °C (~0.1‰ per °C). Nägler et al. (2000) corroborated this strong temperature dependence with cultured specimens of *G. sacculifer* exhibiting a fractionation of 0.24‰ per °C, which was recently supported by results from plankton tow samples (Hippler et al., 2006). This is in contrast to the study of Sime et al. (2005) that analyzed twelve species of planktonic foraminifera from coretop samples, including *G. sacculifer*, and found negligible temperature dependence for all twelve species. Not surprisingly, there is no consensus on mechanisms that control temperature dependent fractionation of Ca in biogenic carbonate formed by foraminifers.

Temperature dependence for most species appears to be similar to that published for inorganic precipitates, however, an extrapolation of these inorganic studies to foraminifera can be misleading because precipitation rates might be much lower and precipitation mechanisms much different in foraminifera (Erez, 2003; Marriott et al., 2004). Lemarchand et al. (2004) proposed an alterative explanation of variations in temperature dependence during $CaCO_3$ precipitation. They suggested that equilibrium isotope fractionation of Ca in $CaCO_3$ is overprinted by incorporation of unequilibrated Ca into the crystal, i.e. kinetic fractionation. This process increases with increasing precipitation rate and saturation state, which is related to the temperature dependence of dissociation constants of carbonate species (Lemarchand et al., 2004). Therefore, measured temperature dependent Ca isotope fractionation is ultimately controlled by kinetic effects related to the precipitation environment (Lemarchand et al., 2004).

Based on controlled culture experiments of planktonic foraminifera *O. universa*, Gussone et al. (2005) found that Ca isotope fractionation does not depend on ambient carbonate concentrations. The small temperature dependent isotopic fractionation observed (similar to that of inorganic calcite and aragonite) was attributed to biological controls on carbonate chemistry in calcifying vesicles (Gussone et al., 2005). However, this does not preclude the idea that kinetic fractionation of Ca isotopes might be related to precipitation rates and ultimately, ambient temperature, as suggested by Lemarchand et al. (2004); instead it makes the distinction that biogenic calcification draws on fluid in calcifying vesicles rather than ambient seawater directly. In addition, reaction pathways and stages that an organism uses to precipitate $CaCO_3$ could influence its fractionation of Ca and its sensitivity to temperature (Lemarchand et al., 2004; Böhm et al., 2006; Gussone et al., 2006). Important new insights on biomineralization pathways and reactions may be revealed through careful study of systematic variations in Ca isotopes in foraminifera and other organisms.

1.3. Biomineralization in foraminifera

The degree of active biologic control on Ca (and its isotopes) in foraminifera during the biomineralization process is highly debated (Kuile et al., 1989; Erez, 2003; Sadekov et al., 2005; Bentov and Erez, 2006). Two major factors potentially influence the Ca isotopic composition of calcite tests and their trace metal content. These are (1) the chemistry of the parent solution (Ca pool) and (2) the process by which Ca is precipitated from this pool. An internal Ca pool, used for calcification, was first noted by Anderson and Faber (1984) in planktonic foraminifera *G. sacculifer*. However, Lea et al. (1995) claimed to have found no indication of a Ca pool in another planktonic species *O. universa* from ^{48}Ca uptake experiments. Erez (2003) instead suggests that their data shows a lag time similar to that found by Anderson and Faber (1984) and inferred that a Ca pool was present. It is likely though that not only the presence of a Ca pool but also the process(es) of biomineralization from this pool influence Ca isotopic fractionation in foraminifera.

Chamber formation and thus the process of biomineralization in foraminifera appear to be a discontinuous process (Elderfield et al., 1996). The internal reservoir from which calcite is formed could fill between or during precipitation of new chambers and run down over time (Elderfield et al., 1996). If the reservoir acts as an open system (i.e. the reservoir is replenished during calcification), the fluid chemistry composition remains more or

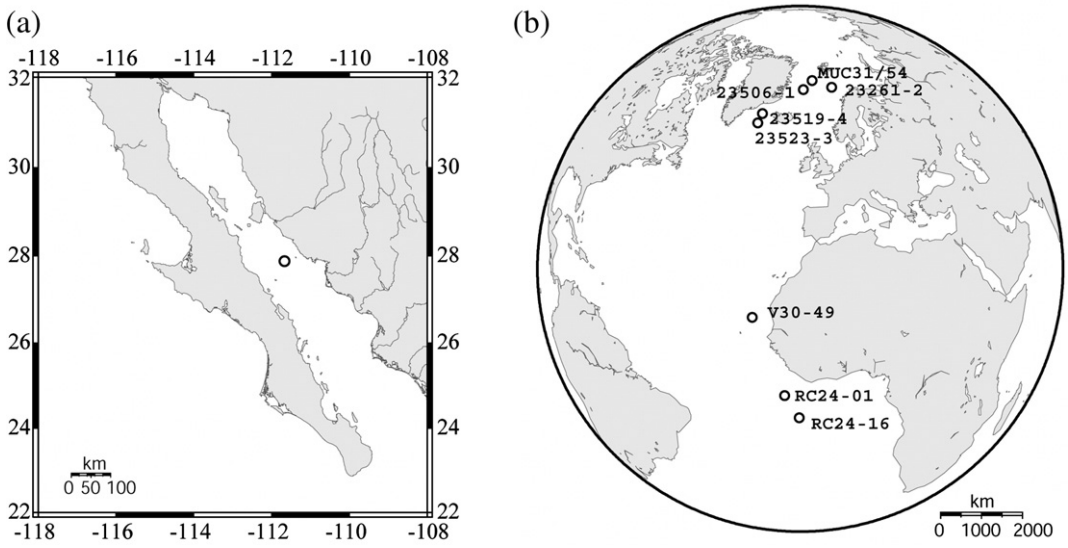

Fig. 1. Locations of sediment trap (a) and cores (b). Maps were created using Online Map Creation with the Generic Mapping Tools (http://www.aquarius.geomar.de/omc/).

less the same throughout calcification. If it acts as a closed system, the reservoir changes during calcification.

Previously, it has been assumed that the parent solution for calcification is close in chemical composition to seawater (Elderfield et al., 1996). Seawater appears to be internalized by the cell into large intracellular vacuoles which undergo some modification during the calcification process (Erez, 2003). Alkalization, possibly water removal, and other processes modify seawater in the vacuoles. The vacuoles are then introduced to the extracellular space where calcification occurs from this modified solution (Erez, 2003).

This study aims to explain the variable temperature dependence of Ca isotope fractionation in several species of planktonic foraminifera. Coretop sediments from subarctic, subtropical, and tropical Atlantic and a sediment trap time series in Guaymas Basin, Gulf of California were used to determine the sensitivity of $\delta^{44/40}$Ca in foraminifera to calcification temperature. A model of biomineralization in planktonic foraminifera is applied to provide constraints on parent solution chemistry (internal Ca pool) and possible fractionation processes (e.g. Rayleigh distillation) during biomineralization. Attempts are made to (1) account for the fact that temperature dependent fractionation cannot explain all of the variability between and within planktonic foraminiferal species from different sample collections; (2) identify processes that contribute to the partitioning of Ca isotopes in foraminifera; and (3) highlight gaps in the current understanding of biomineralization in foraminifera and in Ca isotopic fractionation during biogenic $CaCO_3$ precipitation.

2. Methodology and materials

2.1. Sediment trap series

The Guaymas Basin, Gulf of California, sediment trap was located at 27° 53′ N, 111° 40′ W (Fig. 1a) and positioned at approximately 485 m water depth, about 200 m above seafloor (Thunell et al., 1999) (Table 1). The automated sediment trap collected two-week long samples continuously from January 1992 until October 1997. Four species of planktonic foraminifera were identified and analyzed: *Globigerina bulloides*, *Globigerinoides ruber* (white), *G. sacculifer*, and *Neogloboquadrina dutertrei* (Table 2). Results from 29 samples from January 1994 to July 1997 (capturing maximum seasonal temperature variability) are presented. Samples were well preserved with intact spines and no visible dissolution. Gametogenic calcite did not appear to be prevalent in these samples (McConnell and Thunell, 2005). Foraminifera were picked from one of three different size fractions: 212–300 μm, 300–355 μm, and 212–355 μm. Not all species were present in each sample due to individual species' environmental preferences and life cycle (Pride, 1997). Occurrence of *G. sacculifer* is rare, and it was found only in small numbers in June–September. *G. sacculifer* with and without the sac-like final chamber were combined and analyzed together due to limited numbers of this species.

Table 1
Sample locations for this study

Site	Longitude	Latitude	Depth (mbsl)	Average annual salinity	Average annual SST (°C)
Coretop sediments					
RC24-01	−13.35	0.57	3850	35.5	26.3
RC24-16	−10.2	−5.03	3543	35.7	25.5
V30-49	−21.08	18.43	3093	36.2	22.9
MUC31/54	0.1	75	3760	34.6	0.6
23506-1	−7.600	72.39	2670	34.3	0.8
23261-2	13.11	72.18	2224	35	6.4
23523-3	−30.22	62.25	2156	35.1	7.8
23519-4	−29.6	64.8	1903	34.7	6.2
Sediment trap					
Guaymas Basin	−111.67	27.88	485	35.3	22.7

Salinity and sea surface temperatures (SST) are annual averages for the upper 10 m from World Ocean Atlas 1998 (Conkright et al., 1998).

Table 2
Guaymas Basin sediment trap foraminifer results

Trap	Date	Size fraction (μm)	Satellite SST (°C)	$\delta^{18}O$	$\delta^{18}O$ temp (°C)	Average $\delta^{44/40}Ca$	n	$2\sigma_{mean}$ [a]
Globigerina bulliodes:								
Guay 11-12	3/10/1996	355–212	18.3	−0.35 [b]	15.3	−1.75	2	0.49
Guay 9-8	1/15/1995	355–212	18.2	−0.61 [b]	16.6	−1.16	1	–
Guay 7-7	1/1/1994	355–212	18.6	−0.67 [b]	16.9	−1.34	2	0.18
Guay 9-4	11/20/1994	355–212	23.4	−1.40 [b]	20.5	−1.34	3	0.21
Duplicate	11/20/1994	355–212	23.4	−1.40 [b]	20.5	−1.43	3	0.31
Guay 8-4	5/22/1994	355–212	24.3	−1.21 [b]	19.6	−1.26	2	0.02
Guay 10-13	9/24/1995	355–212	31.2	−2.40 [b]	25.4	−1.38	3	0.24
Guay 8-10	8/14/1994	250–212	31.4	−2.74 [b]	27.1	−1.28	3	0.12
Globigerinoides ruber (white):								
Guay 12-3	5/8/1996	355–212	24.4	−1.63 [c]	23.2	−0.98	2	0.03
Guay 12-5	6/5/1996	355–300	28.3	−1.97 [c]	24.8	−1.23	2	0.01
Guay 13-3	10/27/1996	300–212	26.8	−2.05 [c]	25.2	−1.13	3	0.34
Guay 11-3	11/5/1995	355–212	25.7	−2.23 [b]	26	−1.43	1	–
Guay 13-2	10/13/1996	355–300	30.3	−2.96 [c]	29.5	−1.28	2	0.01
Guay 14-8	7/13/1997	355–212	30.8	−3.02 [c]	29.8	−1.58	2	0.08
Guay 14-7	6/29/1997	355–212	30.4	−3.02 [c]	29.8	−1.41	2	0.04
Guay 14-9	7/27/1997	355–212	31.1	−3.30 [c]	31.2	−1.32	2	0.34
Duplicate	7/27/1997	355–212	31.1	−3.30 [c]	31.2	−1.44	1	–
Globigerinoides sacculifer:								
Guay 14-6	6/15/1997	355–250	27.8			−0.98	2	0.08
Guay 12-6	6/19/1996	355–250	28.8			−1.02	2	0.19
Guay 10-11	8/27/1995	355–250	30.4			−0.81	1	–
Guay 14-8	7/13/1997	355–250	30.8			−1.16	3	0.13
Guay 10-12	9/10/1995	355–250	31.1			−1.64	2	0.06
Duplicate	9/10/1995	355–250	31.1	−3.30 [d]	31.2	−1.12	2	0.44
Neogloboquadrina dutertrei:								
Guay 11-12	3/10/1996	355–212	18.3	−0.11 [b]	14.2	−1.3	3	0.03
Guay 11-9	1/28/1996	355–212	18.6	−0.18 [b]	14.5	−1.37	3	0.25
Guay 14-1	4/6/1997	355–212	20.6	−0.35 [c]	15.4	−1.37	3	0.3
Guay 12-1	4/10/1996	355–212	21.3			−1.52	4	0.32
Guay 14-5	6/1/1997	355–212	27.3	−0.36 [c]	15.4	−1.43	3	0.12
Guay 12-5	6/5/1996	355–212	28.8			−1.24	3	0.35

$\delta^{18}O$ temperatures were derived as described in Section 2.1.
[a] $2\sigma_{mean} = 2\sigma/n^{0.5}$ calculated from repeated TIMS measurements of an individual sample.
[b] Source: Pride (1997).
[c] Source: McConnell and Thunell (2005).
[d] Source: this study.

For all species in this study, with the exception of *G. sacculifer*, we use $\delta^{18}O$ based calcification temperature estimates as described by McConnell and Thunell (2005) using measured foraminiferal $\delta^{18}O$ data, the paleotemperature equation derived by Bemis et al. (1998), and seawater $\delta^{18}O$ estimated using the relationship determined by Fairbanks et al. (1982). Due to limited number of *G. sacculifer* tests, calcification temperatures of *G. sacculifer* samples were estimated using SSTs calculated from Advanced Very High Resolution Radiometer data (Pride, 1997; Thunell et al., 1999; McConnell and Thunell, 2005) that were found to agree with temperature estimates from $\delta^{18}O$ of *G. ruber* (McConnell and Thunell, 2005) (Table 2).

2.2. Coretop samples

Seven planktonic foraminiferal species were obtained from coretop samples: *G. ruber* (white and pink), *G. sacculifer* (with or without the final sac-like chamber), *G. bulloides*, *Globorotalia inflata*, *Globorotalia tumida*, *Globorotalia truncatulinoides*, and *N. dutertrei* (Table 3). Samples were collected in subarctic, subtropical, and tropical Atlantic to represent a range of calcification temperatures (Fig. 1b). Ages of samples determined using radiocarbon dating were found to be within the Holocene (Mix and Ruddiman, 1985; Ravelo and Andreason, 1999; Simstich, 1999; Simstich et al., 2003). The calcification temperature range of each species varies according to its environmental preferences (Table 3). In general, non-globorotaliid species inhabit the photic zone and bear symbionts (except for *G. bulloides*), while globorotaliid species dwell deeper in the water column and do not bear symbionts.

$\delta^{18}O$ derived calcification temperatures were obtained for all samples on crushed homogenized sample splits, except for subarctic samples. Isotopic analyses were made in the stable isotope laboratory at University of California Santa Cruz using a

Table 3
Coretop foraminifer results

Core	Size fraction (μm)	δ^{18}	δ^{18}O temp (°C)	Average $\delta^{44/40}$Ca	n	$2\sigma_{mean}$ [a]
Globigerinoides ruber (pink):						
RC24-01	425–355	−1.36	26.6	−1.14	2	0.13
RC24-01	355–250	−1.5	27.2	−1.16	2	0.05
V30-49	355–250	−1.59	27.7	−1.02	2	0.06
RC24-16	425–355	−1.71	28.3	−1.04	2+(1)	0.02
V30-49	425–355	−1.76	28.5	−1.19	2	0.1
RC24-16	355–250	−1.85	28.9	−1.24	2	0.17
Globigerinoides ruber (white):						
V30-49	355–250	−1.2	25.8	−1.21	1	–
RC24-16	425–355	−1.23	25.9	−1.14	2	0.18
RC24-01	425–355	−1.27	26.1	−1.15	2+(1)	0.16
RC24-01	355–250	−1.41	26.8	−1.21	2	0.1
RC24-16	355–250	−1.44	26.9	−1.08	2+(1)	0.18
V30-49	425–355	−1.47	27.1	−1.08	2	0.05
Globigerinoides sacculifer (without sac):						
RC24-01	425–355	−0.01	20.1	−1.08	2+(3)	0.08
V30-49	425–355	−0.82	23.9	−1.15	2+(1)	0.11
RC24-16	425–335	−0.82	24	−1.18	2+(1)	0.08
V30-49	355–250	−1.01	24.9	−0.98	(1)	–
RC24-16	600–425	−1.11	25.3	−1.30	2	0.1
Globigerinoides sacculifer (with sac):						
RC24-01	355–250	0.31	18.6	−1.13	2	0.12
V30-49	355–250	−0.76	23.7	−1.00	5	0.12
RC24-01	425–355	−0.84	24.1	−0.97	(1)	–
V30-49	425–355	−0.89	24.3	−0.92	(1)	–
RC24-16	355–250	−0.95	24.6	−1.25	3	0.35
Globorotalia inflate:						
RC24-01	355–250	1.32	15.3	−1.28	2	0.04
V30-49	355–250	0.15	20.9	−1.21	1	–
V30-49	425–355	0.11	21.1	−1.04	3	0.09
Globorotalia truncatulinoides:						
RC24-16	355–250	2.22	11	−1.51	(1)	–
RC24-01	425–355	1.9	12.5	−0.92	2	0.09
RC24-01	355–250	1.52	14.4	−1.56	(1)	–
RC24-16	425–355	−1.34	14.8	−1.42	2+(1)	0.08
V30-49	425–355	0.67	18.4	−1.16	2	0.09
Globorotalia tumida:						
RC24-01	425–355	1.51	14.4	−1.21	2+(2)	0.28
RC24-16	355–250	0.97	17	−1.25	3	0.18
V30-49	425–355	0.72	18.2	−1.34	2+(1)	0.15
RC24-16	425–355	−1	26.4	−1.28	2	0.07
RC24-16	600–425			−1.30	2	0.19
RC24-16	250–150			−1.29	2	0.06
Neogloboquadrina dutertrei:						
RC24-01	355–250	0.45	19.5	−1.21	2	0.06
RC24-16	355–250	0.34	20	−1.34	2+(1)	0.16
RC24-01	425–355	0.32	20.1	−1.2	(1)	–
RC24-16	425–335	0.05	21.4	−1.22	2+(1)	0.02
V30-49	425–335	−0.04	21.8	−1.19	2+(1)	0.04
Globigerina bulliodes:						
23506-1	250–125		2.3 [b]	−1.39	2	0.22
MUC 31/54	250–125		2.8 [b]	−1.56	2	0.23
23261-2	250–125		7.3 [b]	−1.47	2	0.09

Table 3 (*continued*)

Core	Size fraction (μm)	δ^{18}	δ^{18}O temp (°C)	Average $\delta^{44/40}$Ca	n	$2\sigma_{mean}$ [a]
23519-4	250–125		7.3 [b]	−1.3	2	0.3
23523-3	250–125		8.9 [b]	−1.34	2	0.11

Sample runs in parentheses were analyzed at the U.S. Geological Survey, Menlo Park by Thomas D. Bullen.
[a] $2\sigma_{mean}=2\sigma/n^{0.5}$ calculated from repeated TIMS measurements of an individual sample.
[b] Temperatures calculated from World Ocean Atlas 2001 (Conkright et al., 2001) as described in Section 2.2.

Fisons Prism dual inlet gas source ratio mass spectrometer. Precision of NBS-19 and an in-house standard were better than 0.08‰ (1σ) for δ^{18}O. Measurements of δ^{18}O are reported relative to Vienna Pee Dee Belemnite (V-PDB). Paleotemperature equations (Bemis et al., 1998) were used to estimate calcification temperature: low light equation for all surface dwelling, spinose species and high light equation for all others. Temperature estimates assume a seawater δ^{18}O value of 0.8‰ (Schmidt et al., 1999).

Calcification temperature estimates for subarctic Atlantic coretop samples were based on averaged summer temperatures (July–September) in 0–50 m water depth from World Ocean Atlas 2001 (Conkright et al., 2001). The main planktonic bloom in the Nordic Seas culminates in these 3 months, and it has been shown that δ^{18}O of *G. bulloides* from this region points toward a population reflecting a water depth of about 60 m (Schiebel et al., 1997).

2.3. Sample preparation

The number of individuals used for each sample varied depending on availability (1–20 tests). Foraminiferal samples were first gently crushed using glass plates to open chambers and then homogenized to minimize potential error arising from sample heterogeneity. Crushed tests where then cleaned with ethyl alcohol and rinsed several times with Milli-Q ultra-pure water to remove clays. Cleaned samples were dissolved with 2% trace metal clean nitric acid in acid-cleaned centrifuge tubes.

To determine if organic matter impurities have any effect on the Ca isotopic analysis, two samples were split and one fraction was cleaned using the method described above while a second fraction was treated with an additional NaOH–H_2O_2 step prior to Ca isotopic analysis (Gussone et al., 2004; Hippler et al., 2006). No significant difference was found between Ca isotopic analyses of the two splits with different preparations. Any analytical effect associated with organics has been shown to be small, i.e. shift mean values ~0.1‰ (Böhm et al., 2006), and does not contribute significantly to trends seen in our data. *G. sacculifer* sediment trap and *G. bulloides* coretop samples were prepared using the additional NaOH–H_2O_2 step.

2.4. Ca isotopic measurements

Ca isotope ratios were determined by Thermal Ionization Mass Spectrometry (TIMS) on the Finnigan TRITON using a double-spike technique at IFM-GEOMAR research center in Kiel, Germany (Heuser et al., 2002). Samples were analyzed for Ca isotope ratios on the TIMS using an internal standard of ^{43}Ca–^{48}Ca enriched solution (double-spike) of a precisely known Ca isotopic ratio to correct for isotopic fractionation occurring during the course of analysis.

Prior to adding the double-spike, Ca concentration in the solution was determined from an aliquot of dissolved sample using an inductively coupled plasma atomic-emission spectrometer in Stanford University's Environmental Measurements Lab. An aliquot of 300 ng of sample Ca was then spiked and dried. The residue was dissolved in 2 μL of 2.5 N HCl. This solution was then loaded with a Ta_2O_5-activator solution onto an outgassed single zone refined rhenium filament using the "sandwich-technique" (activator–sample–activator) (Birck, 1986). After evaporating to dryness, the filament was briefly glowed. Most samples were run in replicate to improve the statistical significance of a single $\delta^{44/40}$Ca measurement. All samples were measured at least twice, except twelve samples that were analyzed only once due to small sample size. Total Ca blanks were less than 3% of the sample. Three foraminifera samples were split and prepared in duplicate and showed an average variability of 0.24‰ between replicates (Table 2). Two samples repeated within 0.15‰ (similar to the average $2\sigma_{mean}$ uncertainty), however a third sample did not reproduce well, giving an error of 0.52‰.

The sample's Ca isotopic composition is expressed as the deviation from a standard solution value, using δ-notation according to Eq. (1). Standard measurements of $CaCO_3$ standard NIST SRM915a and an in-house CaF_2 standard were performed throughout the analysis period. The mean of these measurements was used for normalization for samples run on the same turret. Forty measurements of NIST SRM915a during this investigation gave an average $\delta^{44/40}$Ca of −1.87‰ (2σ=0.26; $2\sigma_{mean}$=0.04) relative to seawater. NIST SRM915a was defined as −1.88‰ (Schmitt et al., 2001). Complete details of the TIMS analytical method are outlined in Heuser et al. (2002). All sample ratios fell on the correct mass-dependent fractionation line on a three isotope plot.

Several samples were also run on a Finnigan MAT 261 adjustable collector instrument using the double-spike technique at U.S. Geological Survey at Menlo Park, California as indicated in Table 3. No systematic difference between the two instruments was found.

3. Results

3.1. Interspecies variation of $\delta^{44/40}$Ca

The average Ca isotopic composition of all planktonic foraminiferal calcite analyzed in this study is −1.24‰ (75 samples, 172 analyses). Individual values range from −1.75‰

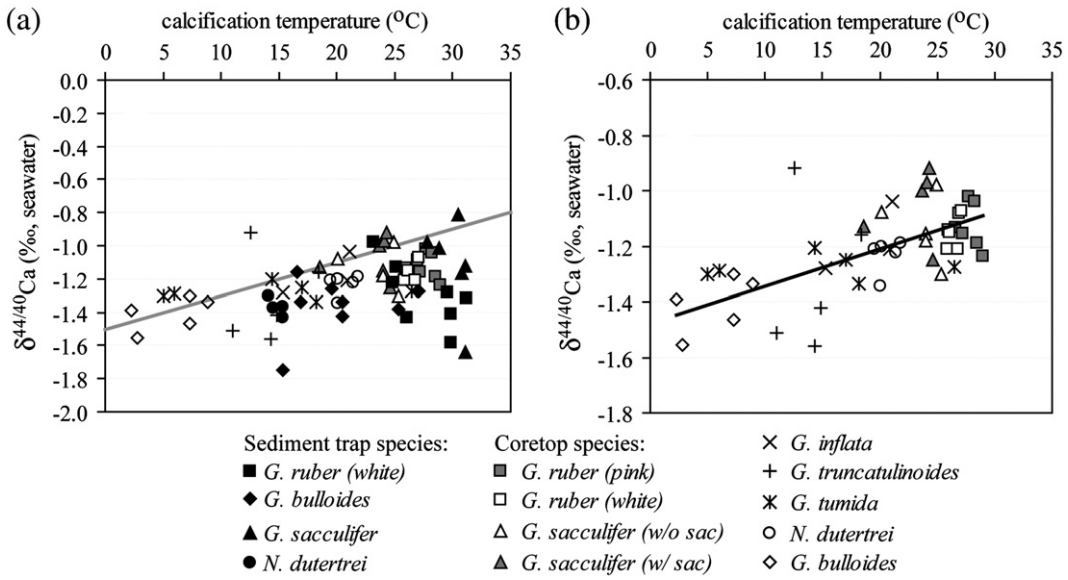

Fig. 2. Ca isotope ratio versus calcification temperature. (a) All samples (sediment trap in filled black symbols, coretop samples in open or gray symbols). (b) Coretop samples only. Solid gray line is the investigated inorganic fractionation factor, $\alpha(T)=0.9985+0.00002(T\,°C)$. Solid black line is the temperature dependent Ca isotopic fractionation for the coretop samples, $\delta^{44/40}Ca=0.013(T)-1.48$ ($n=44$, $R^2=0.37$).

to −0.81‰ with both extreme values measured in sediment trap samples. It is not possible to construct statistically significant temperature relationships for each individual species because ranges in calcification temperature are too narrow relative to the scatter in Ca isotope values (Tables 2 and 3). Overall, temperature sensitivity of the entire set of samples measured, independent of individual species, is most similar to the small temperature dependence of 0.02‰ per °C (Fig. 2a) first suggested for foraminifera (Skulan et al., 1997) and inorganically precipitated calcite (Marriott et al., 2004) and aragonite (Gussone et al., 2003). In particular, coretop samples (Fig. 2b) collectively exhibit a statistically significant temperature dependent fractionation of 0.013‰ per °C ($r^2=0.37$, $n=44$) within the 95% confidence interval. However, sediment trap data exhibit a considerable amount of scatter in their isotopic signatures relative to the inferred calcification temperature and thus exhibit no significant temperature dependent fractionation. Specifically, deviations in sediment trap data from the coretop temperature dependent fractionation are largest at high temperatures (>27 °C) for *G. ruber* and *G. sacculifer*. Because all data cannot be explained by a simple empirical temperature relationship, we explore in the discussion below one widely used model of biomineralization in foraminifera (Elderfield et al., 1996) to investigate potential mechanisms (environmental and physiological) for deviations from this relationship.

3.2. Intraspecies variation of $\delta^{44/40}Ca$

The only species which was examined in both sediment trap and coretop samples in overlapping temperature ranges was *G. ruber*. There appear to be significant differences in this species' Ca isotopic signature between these two types of samples at similar calcification temperatures (both calculated from measured $\delta^{18}O$). For this reason, combining these two sets of samples does not result in a coherent temperature dependent relationship between $\delta^{44/40}Ca$ and calcification temperature.

3.3. Ontogenetic variations in $\delta^{44/40}Ca$

From each coretop sample at RC24-10, RC24-16, and V30-49, two size fractions (425–355 and 355–250 μm) of most species were analyzed in order to determine whether test size correlated to its Ca isotopic composition (Fig. 3). Test size is thought to be indicative of growth stage, age, growth rate, and/or conditions during growth of the foraminifer. No significant difference can be seen for *G. ruber* (6 pairs), *G. sacculifer* (3 pairs), *G. inflata* (1 pair), *G. tumida* (1 pair), and *N. dutertrei* (2 pairs). Samples of *G. truncatulinoides* included one pair that fell on the 1:1 relationship and one outlier pair. The outlier includes the 425–355 μm sample from RC24-01 whose $\delta^{44/40}Ca$ value falls off the temperature–$\delta^{44/40}Ca$ relationship for all

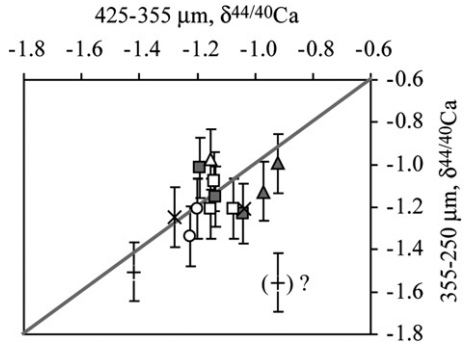

Fig. 3. Coretop foraminifer Ca isotope ratio comparison of larger size fraction (425–355 μm) versus smaller size fraction (355–250 μm) from the same coretop sample. Same legend as Fig. 2. Solid gray line indicates 1:1 relationship (425–355 μm size fraction=355–250 μm size fraction). Error bars are the average $2\sigma_{mean}=0.14‰$.

foraminifera species (Fig. 2b) in a positive direction that cannot be easily explained by the model presented in the discussion section below.

Two species were further tested by analyzing additional size fractions from coretop samples (Fig. 4). Asymbiotic and nonspinose foraminifera *G. tumida* showed no relationship with test size (Fig. 4a) in the size fractions analyzed (250–150, 355–250, 425–355, 600–425 μm). However, symbiotic and spinose foraminifera *G. sacculifer* (without the final sac-like chamber) potentially exhibits a size dependent isotopic fractionation (Fig. 4c). Three size fractions were analyzed (355–250, 425–355, 600–425 μm) at similar calcification temperatures (20–25 °C). They appear to exhibit decreasing isotopic values with increasing test size. However, these preliminary results require further testing of more samples in more size fractions from single coretops at multiple sites.

When compared to *G. sacculifer* tests with the final sac-like chamber (Fig. 4b), any size dependent fractionation is masked by spread in δ^{44}Ca within a single size fraction. The range of calcification temperatures for all coretop *G. sacculifer* samples (with and without final sac-like chamber) is about 5 °C (19–25 °C), theoretically equivalent to a maximum difference in temperature dependent fractionation of only 0.1‰ between samples (assuming temperature dependent fractionation of 0.02‰ per °C). This temperature dependent fractionation could add to uncertainty in comparing different sized tests whose calcification temperatures differ, but in this study it appears to be a minor influence on isotopic differences between the measured size fractions.

4. Discussion

4.1. Fractionation during biomineralization

The simplest observation is that, in general, the foraminiferal calcite appears to precipitate with a constant fractionation from seawater of 0.9985 with a temperature dependence equal to that of inorganic calcite, 0.00002(T °C) (Lemarchand et al., 2004; Marriott et al., 2004). It is interesting to note that a fractionation factor of 0.9985 (at 0 °C in our study) is equal to the equilibrium fractionation factor for calcite precipitated from an experimental solution at 21 °C (Lemarchand et al., 2004) and to the fractionation factor calculated for cultured *O. universa* at 0 °C (Gussone et al., 2003). Perhaps this suggests that a universal mechanism, possibly governed by isotopic equilibrium, is controlling Ca isotope fractionation in $CaCO_3$. However, this observation cannot explain why some samples deviate from this empirical relationship with temperature or why the sediment trap samples collectively do not show a consistent trend with temperature. It also cannot explain the difference between the large temperature dependence previously published for culture and plankton tow samples of *G. sacculifer* (Nägler et al., 2000; Hippler et al., 2006) and the small temperature sensitivity seen in coretop samples for the same species. In order to investigate potential mechanisms for these differences, we test one model for biomineralization in foraminifera (Elderfield et al., 1996) with our data and explore the implications and insight it lends to potential isotopic fractionation processes which might explain these observations. The model results that follow rely on the accuracy of the model and our assumptions which are further examined in the discussion that follows.

4.2. Conceptual model of a dynamic Ca pool

The purpose of the model presented here is to characterize a dynamic internal biomineralization reservoir of Ca, which evolves during calcification (Elderfield et al., 1996), in order to quantify the initial isotopic composition of the internal Ca pool and its potential influence on the final Ca isotopic composition of the foraminiferal calcite test. The notion that differences in measured sensitivity of Ca isotope fractionation in foraminiferal calcite to temperature is ultimately due to the presence (or absence) of an internal reservoir of Ca has been previously suggested (Gussone et al., 2003; Chang et al., 2004; Marriott et al., 2004; Sime et al., 2005). A set of different associated assumptions were made in each of these studies, however, none presented a quantitative model to explain the isotope data. Under the assumptions outlined below, a variation of the model presented originally by Elderfield et al. (1996) is used to illustrate how the concept of an internal Ca pool could manifest itself in measured Ca isotopic signatures of whole foraminiferal calcite tests.

In this model, we assume that (1) Ca isotopes are extracted during calcite precipitation from the biomineralization reservoir with a fractionation factor (α) that is dependent on temperature (T), and (2) the fraction of Ca (f) in the biomineralization reservoir, which remains after the formation of foraminiferal

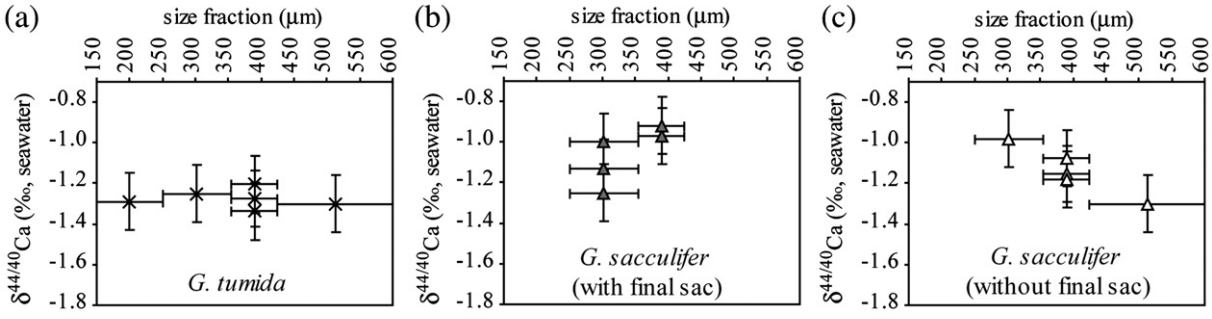

Fig. 4. Coretop foraminifer Ca isotope ratio comparison of several size fractions from subtropical to tropical Atlantic coretop samples. (a) *Globorotalia tumida* (nonspinose, symbiant barren). (b) *Globigerinoides sacculifer* (spinose, symbiant bearing) with final sac-like chamber and (c) without final sac-like chamber. *Y* error bars are the average $2\sigma_{mean}$=0.14‰ and *X* error bars indicate the total range of the measured size fraction.

calcite, is less than or equal to 1 (Elderfield et al., 1996). Based on the assumptions of the model, the isotopic composition of foraminiferal calcite changes as a function of the fraction of the Ca remaining in the biomineralization reservoir following Rayleigh fractionation behavior. Using an estimate from the literature of the fraction of Ca (f) remaining in the biomineralization reservoir after precipitation of the whole test, the Ca isotopic composition of the initial biomineralization reservoir can be calculated from measured Ca isotope ratios of foraminiferal calcite tests assuming a known fractionation factor $\alpha(T)$ during precipitation. The sensitivity of this result to assumed values of parameters f and $\alpha(T)$ can then be evaluated.

4.3. Model equations

The Rayleigh fractionation equation for the modeled system is:

$$\left[{}^{44}Ca/{}^{40}Ca\right]_{\text{reservoir}} / \left[{}^{44}Ca/{}^{40}Ca\right]_{\text{initial reservoir}} = f^{\alpha(T)-1} \quad (2)$$

where f = fraction of Ca remaining in the biomineralization reservoir and $\alpha(T)$ = fractionation factor for precipitation of $CaCO_3$ from the reservoir with a given dependence on temperature (T). Combining this with the mass balance expression:

$$\left[{}^{44}Ca/{}^{40}Ca\right]_{\text{initial reservoir}} = f\left[{}^{44}Ca/{}^{40}Ca\right]_{\text{reservoir}} + (1-f)\left[{}^{44}Ca/{}^{40}Ca\right]_{\text{foram}} \quad (3)$$

gives:

$$\varepsilon = \left[{}^{44}Ca/{}^{40}Ca\right]_{\text{foram}} / \left[{}^{44}Ca/{}^{40}Ca\right]_{\text{initial reservoir}} = \left(1 - f^{\alpha(T)}\right)/(1-f) \quad (4)$$

which shows how ε, the empirical fractionation factor (or enrichment factor), changes as a function of the proportion of Ca (f) in the biomineralization reservoir that remains after formation of foraminiferal $CaCO_3$ (Fig. 5). For the end member situation in which $f=0$ results in $\varepsilon=1$ (Eq.(4)) and all Ca in the original biomineralization reservoir is used up to make calcite, consequently $[{}^{44}Ca/{}^{40}Ca]_{\text{foram}}$ is equal to $[{}^{44}Ca/{}^{40}Ca]_{\text{initial reservoir}}$ (or $\delta^{44/40}Ca_{\text{foram}} = \delta^{44/40}Ca_{\text{initial reservoir}}$). When $f=1$, bulk calcite $[{}^{44}Ca/{}^{40}Ca]_{\text{foram}}$ or $\delta^{44/40}Ca_{\text{foram}}$ is determined by the fractionation factor $\alpha(T)$ associated with precipitation of calcite from the initial reservoir, $\varepsilon=\alpha(T)$. Therefore, ε must be between $\alpha(T)$ and 1.

4.4. Determining $\delta^{44/40}Ca_{initial\ reservoir}$

Using the empirical fractionation factor that defines the upper boundary of our data, $\alpha(T)$ is defined as $0.9985+0.00002$ (T °C). Given the additional constraint from trace element data that most (~85%) of the Ca^{2+} in the calcification reservoir is precipitated ($f=0.15$) in planktonic foraminifera species (Elderfield et al., 1996; Erez, 2003), we solved for the initial isotopic composition of the biomineralization reservoir using the model

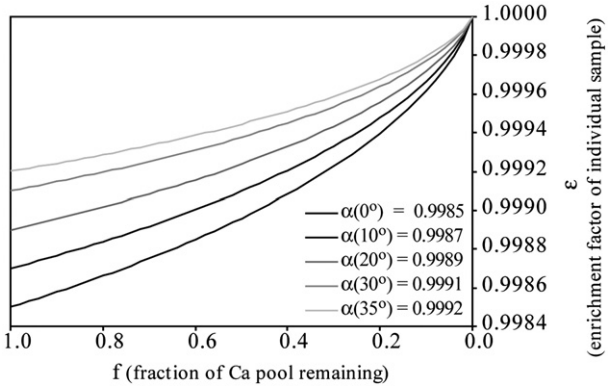

Fig. 5. Model curves of the relationship between the enrichment factor (ε) of a measured foraminiferal calcite test and the calculated f (fraction of Ca remaining in the reservoir) for a range of α.

(Eq. (4)). The average initial Ca reservoir, obtained based on this calculation and constrained by coretop planktonic foraminifera $\delta^{44/40}Ca$ measured in this study, is −0.84‰ (Fig. 6). The average calculated from sediment trap samples is −0.95‰ with a larger range of calculated individual values. This indicates that the initial Ca reservoir is depleted in ^{44}Ca relative to seawater and suggests that Ca isotopes are fractionated as Ca is channeled into the biomineralization reservoir from seawater vacuoles (e.g. via Ca-channels or Ca-ATPase pumps) (Erez, 2003).

Kinetic isotope effects due to different rates of diffusion or active transport for each isotope result in a lower $^{44}Ca/^{40}Ca$ ratio of the fluid in the calcification reservoir compared to that of seawater. Alternatively, if Ca is stored as an amorphous calcium carbonate (ACC) phase or cytoplasmic granules (Erez, 2003; Bentov and Erez, 2006) and is dissolved in the calcifying fluid pool to be used as the primary source of Ca for precipitation of foraminiferal calcite (Sadekov et al., 2005), this Ca reservoir might be isotopically depleted in ^{44}Ca relative to seawater. This could be due to kinetic or equilibrium fractionation processes associated with precipitation of the ACC phase (where bonding of Ca is not as strong as in the Ca-aqueous complex and/or ^{40}Ca is preferentially used in ACC formation).

Another possibility is that the $\alpha(T)$ assumed for this model ($0.9985+0.00002(T)$) is not correct. Measured $\delta^{44/40}Ca$ foraminiferal values, which are consistently lower than ambient seawater, could be explained using this model by more extreme fractionation ($\alpha(T) \ll 0.9985+0.00002(T)$). In this case, the calculated $\delta^{44/40}Ca_{\text{initial reservoir}}$ could be much more similar to seawater ($\gg -0.84$‰). It follows that instead of an initial isotopically light biomineralization reservoir more extreme fractionation during precipitation could explain measured foraminiferal calcite values. More work is needed to determine whether more extreme fractionation during precipitation of calcite is actually plausible.

4.5. Further model applications

There is quite a bit of variability from species to species that cannot be explained by first-order correlation between $\delta^{44/40}Ca_{\text{foram}}$ and calcification temperature. This variability could be

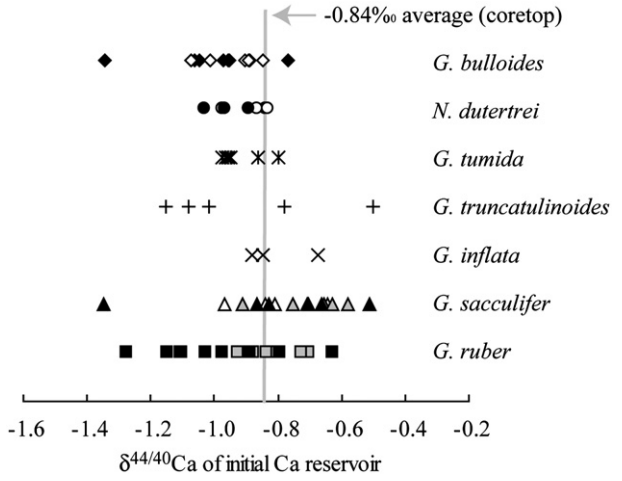

Fig. 6. Results for $\delta^{44/40}Ca_{initial\ reservoir}$ calculated from the measured $\delta^{44/40}Ca_{foram}$ from this study assuming $f=0.15$ and $\alpha(T)=0.9985+0.00002(T)$. Legend same as in Fig. 2.

explained simply by differences in the initial isotopic composition of the Ca reservoir, which range from −1.35 to −0.50‰ assuming $f=0.15$. Alternatively, perhaps the fraction of Ca remaining (f) varies from species to species or within a species depending on environmental and physiological conditions. Again, species specific measured values can be used to calculate the fraction of Ca used (f) given an initial isotopic composition of the Ca reservoir (Eq. (4)). As discussed above, if the initial Ca reservoir is assumed to be isotopically equal to seawater ($\delta^{44/40}Ca_{\ initial\ reservoir}=0$‰), then even at the limit of $f=1$, the fractionation factor must be much less than $0.9985+0.00002(T)$. If instead we assume that our previous assumption was correct ($\alpha(T)=0.9985+0.00002(T)$) and that the initial isotopic composition of the Ca reservoir for all foraminifera is −0.84‰, then the calculated range in f values is 0.02 to 0.59. Our data, combined with this simple model, are not sufficient to constrain unique species specific values of f or $\delta^{44/40}Ca_{\ initial\ reservoir}$, which may in reality vary within species.

In sum, this modeling exercise demonstrates that coretop samples, specifically relatively low $\delta^{44/40}$Ca foraminiferal values compared to seawater, are on average consistent with the estimate of $f=0.15$ (Elderfield et al., 1996) and with a small temperature dependent fractionation (Lemarchand et al., 2004) when the initial Ca isotopic composition of the internal pool is around −0.84‰ (Fig. 6). Only if f were much closer to 1, combined with a fractionation factor significantly lower than published estimates, would we expect the internal Ca pool to be isotopically similar to seawater. Combined with the fact that coretop $\delta^{44/40}$Ca foraminiferal values correlate with calcification temperature, in general agreement with previously published work (Skulan et al., 1997; Gussone et al., 2003; Lemarchand et al., 2004; Marriott et al., 2004), these results indicate that the closed system model is a generally appropriate representation of calcification processes and Ca isotopic fractionation in foraminifera. Yet, there is quite a bit of variability from one sample to another that cannot be explained by temperature dependent fractionation. In the closed system model that we have used, this variability could be explained by small differences in ε, $\delta^{44/40}$Ca initial reservoir, and/or f as explained above.

Another way to explain this sample-to-sample variability is to consider that the closed system model that we used above is not completely appropriate, but rather, turnover of the internal Ca pool will also impact the test's Ca isotopic composition. As such, the range of possible values for $\delta^{44/40}Ca_{initial\ reservoir}$, and/or f in our closed system model, and the resulting ε, could actually be indicative of a fully or partially open system with: (a) differences in flushing time of the internal Ca pool; (b) associated differences in calcification rates; and (c) differences in size of the biomineralization reservoir (Elderfield et al., 1996). The potential influence of each of these factors on ε and f between and within individual species is described below.

Flushing time could be controlled independently by foraminifera (species or individual) such that a longer flushing time would result in a more open Ca pool (larger f, smaller ε). The size of the Ca pool may also play a role into how 'open' the reservoir appears isotopically. Some species may have a larger Ca pool relative to other species and therefore be less affected by precipitation rate, thus appearing more open (i.e. will have a larger f and smaller ε).

It also appears that under conditions of faster calcification (for benthic foraminifera), the biomineralization reservoir is flushed at a higher rate (Elderfield et al., 1996). This likely indicates that the reservoir is more open when the calcification rate is higher (larger f, smaller ε). Another way to interpret this observation is that enrichment factors (ε) which are closest to one (smallest f values) are equated with slow foraminiferal calcification rates. If this is true for planktonic species, the smallest size fraction, which includes the youngest, fastest-growing individuals, should exhibit the largest fractionation due to higher flushing rates (large f, small ε). However, the measured fractionation cannot be more than the assumed fractionation factor, i.e. at $f=1$, $\varepsilon=\alpha(T)$. f should also decrease with increasing test size since it is thought that foraminiferal growth is fast initially and slows to maturity. Our results (Section 3.3) indicate that this effect might exhibit itself differently for different species (e.g. *G. sacculifer* vs. *G. tumida*) and therefore might contribute to interspecies differences in Ca isotopic fractionation.

There are many complexities that might exhibit themselves in planktonic foraminifera that are not considered as independent variables in this model. These include different biomineralization models including addition of secondary and gametogenic calcite (Bé, 1980; Lohmann, 1995; Bentov and Erez, 2006) and interactions of various environmental parameters on different species such as those associated with optimum growth conditions (Delaney et al., 1985; de Villiers, 2004). These additional factors might change the initial isotopic composition of the biomineralization reservoir, the fraction of Ca used (f), or the assumed fractionation factor, $\alpha(T)$, thereby influencing our interpretations. In other words, these parameters could be dependent on ontogeny and/or ecology of each species, and the Rayleigh fractionation model alone cannot fully capture all processes that influence the Ca isotopic composition of foraminifera. This is particularly evident when our results are compared to previously published results.

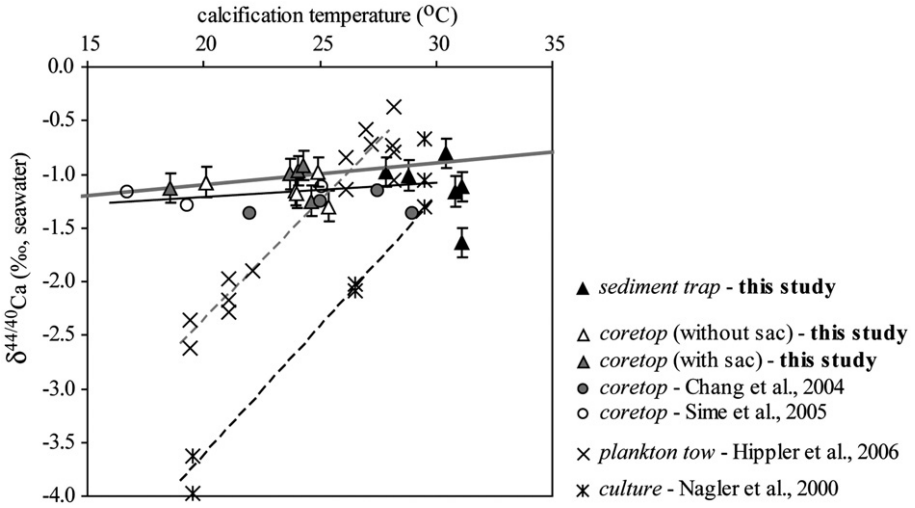

Fig. 7. Comparison of coretop data for *Globigerinoides sacculifer* (Chang et al., 2004; Sime et al., 2005, this study) and sediment trap (this study), plankton tow (Hippler et al., 2006), and culture samples (Nägler et al., 2000). Solid gray line is the investigated inorganic fractionation factor, $\alpha(T)=0.9985+0.00002(T)$. Solid black line is the temperature dependent Ca isotopic fractionation for the coretop samples, $\delta^{44/40}\mathrm{Ca}=0.013(T)-1.48$ ($n=44$, $R^2=0.37$). Dashed gray and black lines are empirical Ca isotope–temperature relationships from Hippler et al. (2006) and Nägler et al. (2000) respectively. Error bars are the average $2\sigma_{\mathrm{mean}}=0.14‰$ for this study only.

Results of *G. sacculifer* from plankton tow and culture indicate that this species has a large temperature dependent fractionation; however, coretop samples do not exhibit this same large temperature dependent fractionation, Fig. 7. Our model (and associated assumptions) cannot account for differences between plankton tow samples of *G. sacculifer* because at high temperatures the calculated ε is greater than 1 for these samples. It is not possible for bulk foraminiferal calcite to be more enriched in ^{44}Ca than the original biomineralization reservoir (ε must be ≤ 1). For this reason, the model cannot explain Ca isotope ratios from plankton tow samples that fall above the assumed $\alpha(T)$. It is possible that differences between these types of samples are due to fractionation processes associated with different modes of calcification (e.g. ontogenetic and gametogenic calcification (Bé, 1980)). Because coretop samples in deep water are dominated by tests that have undergone gametogenesis (Rosenthal et al., 2000), their Ca isotopic signature could be quite different from pre-gametogenic tests dwelling in the water column if the two modes of calcification result in different isotopic fractionations.

In order to test this hypothesis, plankton tow samples of *G. sacculifer* and coretop samples explicitly identified as pre- or post-gametogenic should be compared from the same location (and same temperature range). The sediment trap samples should theoretically also have been useful to test this hypothesis since gametogenic calcite was not prevalent in these samples (McConnell and Thunell, 2005). However, temperature ranges of our samples only overlap coretop data at high temperatures for *G. ruber* (Fig. 2a). Above the overlapping temperature range, sediment trap data deviates from the trend pointing to possibly additional processes that fractionate Ca isotopes at high temperatures that are much higher than the optimal growth temperature range for *G. ruber* (Schmidt et al., 2006). Culture experiments at high temperatures (~30 °C) could be used to test this observation.

5. Conclusions

It is important to distinguish between temperature calibrations of Ca isotopes from culture, plankton tow, sediment trap, and coretop samples of foraminiferal calcite as each yields different important information on biomineralization and other processes that control its elemental and isotopic signature. For paleoceanographic studies, it is important to understand what processes influence the isotopic signature of preserved foraminiferal calcite tests in the sediment record. In this study, coretop planktonic foraminifera samples (representing the potential archive for paleoceanographic work) collectively exhibited a temperature dependent fractionation of 0.013‰ per °C in agreement with previously published estimates for most species of planktonic foraminifera obtained from core tops as well as biogenic and inorganic calcite and aragonite. This indicates that foraminiferal calcite $\delta^{44/40}$Ca is not a sensitive paleothermometer. Sediment trap data showed a considerable amount of scatter resulting in no consistent temperature dependent fractionation. It is likely that factors other than temperature influence fractionation of Ca isotopes in planktonic foraminifera samples collected at shallow depths in the water column.

An internal pool (one-box) model in which Ca isotopes are fractionated by Rayleigh distillation from a biomineralization reservoir was used to evaluate the impact of this mechanism on Ca isotope signatures assuming that ~85% of the Ca pool is precipitated (Elderfield et al., 1996). Results from this model indicate that the Ca biomineralization pool must be very different from seawater in its Ca isotopic signature assuming the inorganic fractionation factor is $\alpha(T)=0.9985+0.00002(T\ °\mathrm{C})$. Moreover, the initial isotopic composition of the biomineralization reservoir and/or the fraction of Ca remaining in the reservoir (f) could be variable and depend on species or life stage of the foraminifera. Complications involved in modeling additional potential fractionation steps (other than those associated with Ca precipitation

from the internal pool) are difficult to resolve given our current understanding of the biomineralization process in planktonic foraminifera. Transfer mechanisms and isotopic fractionation of Ca into the foraminiferal biomineralization Ca pool, residence time of Ca within the internal pool, differences in calcification rate between species and during different life stages within a species, and influences of different modes of biomineralization on Ca fractionation during precipitation should be studied further in order to constrain biologic and biomineralization pathways of Ca in foraminifera and their influence on Ca isotopic fractionation in foraminifera. Previous attempts to interpret $\delta^{44/40}$Ca as a quantitative temperature proxy in foraminifera should be reexamined to identify alternative influences on $\delta^{44/40}$Ca including physiological processes and environmental factors other than temperature.

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References

Anderson, O.R., Faber, W.W.J., 1984. An estimation of calcium carbonate deposition rate in a planktonic foraminifer *Globigerinoides sacculifer* using ^{45}Ca as a tracer: a recommended procedure for improved accuracy. J. Foraminiferal Res. 14, 303–308.

Bé, A.W.H., 1980. Gametogenic calcification in a spinose planktonic foraminifer, *Globigerinoides sacculifer* (Brady). Mar. Micropaleontol. 5, 283–310.

Bemis, B.E., Spero, H.J., Bijma, J., Lea, D.W., 1998. Reevaluation of the oxygen isotopic composition of planktonic foraminifera: experimental results and revised paleotemperature equations. Paleoceanography 13, 150–160.

Bentov, S., Erez, J., 2006. Impact of biomineralization processes on the Mg content of foraminiferal shells: a biological perspective. Geochem. Geophys. Geosyst. 7.

Birck, J.L., 1986. Precision K–Rb–Sr isotopic analysis: application to Rb–Sr chronology. Chem. Geol. 56, 73–83.

Böhm, F., Gussone, N., Eisenhauer, A., Dullo, W.C., Reynaud, S., Paytan, A., 2006. Calcium isotope fractionation in modern scleractinian corals. Geochim. Cosmochim. Acta 70, 4452–4462.

Bullen, T.D., Kim, S.T., Paytan, A., 2003. Ca isotope fractionation during Ca-carbonate precipitation: there's more to it than temperature. Goldschmidt Conference Abstracts, p. A49.

Chang, V.T.C., Williams, R.J.P., Makishima, A., Belshaw, N.S., O'nions, R.K., 2004. Mg and Ca fractionation during $CaCO_3$ biomineralisation. Biochem. Biophys. Res. Commun. 323, 79–85.

Conkright, M.E., Levitus, S., O'Brien, T., Boyer, T.P., Antonov, J.I., Stephens, C., 1998. World Ocean Atlas 1998 CD-ROM Data Set Documentation. Tech. Rep., vol. 15, p. 16. NODC Internal Report, Silver Spring, MD.

Conkright, M.E., Locarnini, R.A., Garcia, H.E., O'Brien, T.D., Boyer, T.P., Stephens, C., Antonov, J.I., 2002. World Ocean Atlas 2001: Objective Analyses, Data Statistics, and Figures, CD-ROM Documentation. National Oceanographic Data Center, Silver Spring, MD, p. 17.

De La Rocha, C.L., DePaolo, D.J., 2000. Isotopic evidence for variations in the marine calcium cycle over the Cenozoic. Science 289, 1176–1178.

de Villiers, S., 2004. Optimum growth conditions as opposed to calcite saturation as a control on the calcification rate and shell-weight of marine foraminifera. Mar. Biol. 144, 45–49.

Delaney, M.L., Bé, A.W.H., Boyle, E.A., 1985. Li, Sr, Mg, and Na in foraminiferal calcite shells from laboratory culture, sediment traps, and sediment cores. Geochim. Cosmochim. Acta 49, 1327–1341.

Eisenhauer, A., Nägler, T.F., Stille, P., Karmers, J., Gussone, N., Bock, B., Fietzke, J., Hippler, D., Schmitt, A.D., 2004. Proposal for international agreement on Ca notation resulting from discussion at workshops on stable isotope measurements held in Dayos (Goldschmidt 2002) and Nice (EGS-AGU-EGU 2003). Geostand. Geoanal. Res. 28, 149–151.

Elderfield, H., Bertram, C.J., Erez, J., 1996. A biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate. Earth Planet. Sci. Lett. 142, 409–423.

Erez, J., 2003. The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies, Biomineralization. Rev. Mineral. Geochem. 54, 115–149.

Fairbanks, R.G., Sverdlove, M., Free, R., Wiebe, P.H., Bé, A.W.H., 1982. Vertical-distribution and isotopic fractionation of living planktonic-foraminifera from the Panama Basin. Nature 298, 841–844.

Fantle, M.S., DePaolo, D.J., 2007. Ca isotopes in carbonate sediment and pore fluid from ODP Site 807A: the Ca^{2+}(aq)-calcite equilibrium fractionation factor and calcite recrystallization rates in Pleistocene sediments. Geochim. Cosmochim. Acta 71, 2524–2546.

Gussone, N., Eisenhauer, A., Heuser, A., Dietzel, M., Bock, B., Böhm, F., Spero, H.J., Lea, D.W., Bijma, J., Nägler, T.F., 2003. Model for kinetic effects on calcium isotope fractionation (δ^{44}Ca) in organic aragonite and cultured planktonic foraminifera. Geochim. Cosmochim. Acta 67, 1375–1382.

Gussone, N., Eisenhauer, A., Tiedemann, R., Haug, G.H., Heuser, A., Bock, B., Nägler, T.F., Müller, A., 2004. Reconstruction of Caribbean sea surface temperature and salinity fluctuations in response to the Pliocene closure of the Central American Gateway and radiative forcing, using $\delta^{44/40}$Ca, δ^{18}O and Mg/Ca ratios. Earth Planet. Sci. Lett. 227, 201–214.

Gussone, N., Böhm, F., Eisenhauer, A., Dietzel, M., Heuser, A., Teichert, B.M.A., Reitner, J., Worheide, G., Dullo, W.C., 2005. Calcium isotope fractionation in calcite and aragonite. Geochim. Cosmochim. Acta 69, 4485–4494.

Gussone, N., Langer, G., Thorns, S., Nehrke, G., Eisenhauer, A., Riebessell, U., Wefer, G., 2006. Cellular calcium pathways and isotope fractionation in Emiliania huxleyi. Geology 34, 625–628.

Henderson, G.M., 2002. New oceanic proxies for paleoclimate. Earth Planet. Sci. Lett. 203, 1–13.

Heuser, A., Eisenhauer, A., Gussone, N., Bock, B., Hansen, B.T., Nägler, T.F., 2002. Measurement of calcium isotopes (δ^{44}Ca) using a multicollector TIMS technique. Int. J. Mass Spectrom. 220, 385–397.

Hippler, D., Eisenhauer, A., Nägler, T.F., 2006. Tropical Atlantic SST history inferred from Ca isotope thermometry over the last 140 ka. Geochim. Cosmochim. Acta 70, 90–100.

Hönisch, B., 2002. Stable Isotope and Trace Element Composition of Foraminiferal Calcite — from Incorporation to Dissolution. University of Bremen.

Kuile, B., Erez, J., Padan, E., 1989. Mechanisms for the uptake of inorganic carbon by two species of symbiont-bearing foraminifera. Mar. Biol. 103, 241–251.

Lea, D.W., Martin, P.A., Chan, D.A., Spero, H.J., 1995. Calcium-uptake and calcification rate in the planktonic foraminifer *Orbulina universa*. J. Foraminiferal Res. 25, 4–23.

Lemarchand, D., Wasserburg, G.J., Papanstassiou, D.A., 2004. Rate-controlled calcium isotope fractionation in synthetic calcite. Geochim. Cosmochim. Acta 68, 4665–4678.

Lohmann, G.P., 1995. A model for variation in the chemistry of planktonic foraminifera due to secondary calcification and selective dissolution. Paleoceanography 10, 445–458.

Marriott, C.S., Henderson, G.M., Belshaw, N.S., Tudhope, A.W., 2004. Temperature dependence of δ^7Li, δ^{44}Ca, and Li/Ca during growth of calcium carbonate. Earth Planet. Sci. Lett. 222, 615–624.

McConnell, M.C., Thunell, R.C., 2005. Calibration of the planktonic foraminiferal Mg/Ca paleothermometer: sediment trap results from the Guaymas Basin, Gulf of California. Paleoceanography 20.

Mix, A.C., Ruddiman, W.F., 1985. Structure and timing of the last deglaciation: oxygen isotope evidence. Quat. Sci. Rev. 4, 59–108.

Nägler, T.F., Eisenhauer, A., Müller, A., Hembleben, C., Kramers, J., 2000. The δ^{44}Ca–temperature calibration on fossil and cultured *Globigerinoides sacculifer*: new tools for reconstruction of past sea surface temperatures. Geochem. Geophys. Geosyst. 1.

Pride, C., 1997. An evaluation and application of paleoceanographic proxies in the Gulf of California. PhD. Dissertation, University of South Carolina, 197 pp.

Ravelo, A.C., Andreason, D.H., 1999. Using planktonic foraminifera as monitors of the tropical surface ocean. In: Mix, A.a. (Ed.), Reconstructing Ocean History: a Window into the Future. Kluwer Academic/ Plenum Publishers, New York, pp. 217–243.

Rosenthal, Y., Lohmann, G.P., Lohmann, K.C., Sherrell, R.M., 2000. Incorporation and preservation of Mg in *Globigerinoides sacculifer*: implications for reconstructing the temperature and O-18/O-16 of seawater. Paleoceanography 15, 135–145.

Russell, W.A., Papanastassiou, D.A., Tombrello, T.A., 1978. Ca isotope fractionation on the Earth and other solar system materials. Geochim. Cosmochim. Acta 42, 1075–1090.

Sadekov, A.Y., Eggins, S.M., De Deckker, P., 2005. Characterization of Mg/Ca distributions in planktonic foraminifera species by electron microprobe mapping. Geochem. Geophys. Geosyst. 6.

Schauble, E.A., 2005. Modeling stable isotope fractionation in crystals. Geochim. Cosmochim. Acta 69, A209 (Supplement 1).

Schiebel, R., Bijma, J., Hemleben, C., 1997. Population dynamics of the planktic foraminifer *Globigerina bulloides* from the eastern North Atlantic. Deep-Sea Res., Part 1, Oceanogr. Res. Pap. 44, 1701–1713.

Schmidt, G.A., Bigg, G.R., Rohling, E.J., 1999. Global seawater oxygen-18 data base, website.

Schmidt, D.N., Lazarus, D., Young, J.R., Kucera, M., 2006. Biogeography and evolution of body size in marine plankton. Earth-Sci. Rev. 78, 239–266.

Schmitt, A.D., Bracke, G., Stille, P., Kiefel, B., 2001. The calcium isotope composition of modern seawater determined by thermal ionisation mass spectrometry. Geostan. Newslet. 25, 1–9.

Sime, N.G., De La Rocha, C.L., Galy, A., 2005. Negligible temperature dependence of calcium isotope fractionation in 12 species of planktonic foraminifera. Earth Planet. Sci. Lett. 232, 51–66.

Simstich, J., 1999. Die ozeanische Deckschicht des Europäischen Nordmeers im Abbild stabiler Isotope von Kalkgehäusen unterschiedlicher Planktonforaminiferenarten. . Berichte-Reports, vol. 2. Christian-Albrechts-Universität.

Simstich, J., Sarnthein, M., Erlenkeuser, H., 2003. Paired δ^{18}O signals of *Neogloboquadrina pachyderma* (s) and *Turborotalita quinqueloba* show thermal stratification structure in Nordic Seas. Mar. Micropaleontol. 48, 107–125.

Skulan, J., DePaolo, D.J., Owens, T.L., 1997. Biological control of calcium isotopic abundances in the global calcium cycle. Geochim. Cosmochim. Acta 61, 2505–2510.

Thunell, R.C., Tappa, E., Pride, C., Kincaid, E., 1999. Sea-surface anomalies associated with the 1997–1998 El Nino recorded in the oxygen isotope composition of planktonic foraminifera. Geology 27, 843–846.

Zhu, P., Macdougall, J.D., 1998. Calcium isotopes in the marine environment and the oceanic calcium cycle. Geochim. Cosmochim. Acta 62, 1691–1698.