EPSL

High precision glacial–interglacial benthic foraminiferal Sr/Ca records from the eastern equatorial Atlantic Ocean and Caribbean Sea

Chuan-Chou Shen [a,b,*], David W. Hastings [c], Typhoon Lee [d], Chin-Hsin Chiu [d,e], Meng-Yang Lee [d,f], Kuo-Yen Wei [f], R. Lawrence Edwards [b]

[a] School of Oceanography, WB-10, University of Washington, Seattle, WA 98195, USA
[b] Minnesota Isotope Laboratory, Department of Geology and Geophysics, University of Minnesota, Minnesota, MN 55455, USA
[c] Galbraith Marine Science Laboratory, Eckerd College, St. Petersburg, FL 33711, USA
[d] Institute of Earth Sciences, Academia Sinica, P.O. Box 1-55, Nankang, Taipei, Taiwan
[e] Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan
[f] Institute of Geosciences, National Taiwan University, Taipei, Taiwan

Abstract

Glacial–interglacial variation in the marine Sr/Ca ratio has important implications for coral Sr thermometry [J.W. Beck et al., Science 257 (1992) 644–647]. A possible variation of 1–3% was proposed based on ocean models [H.M. Stoll and D.P. Schrag, Geochim. Cosmochim. Acta 62 (1998) 1107–1118]. Subsequently, studies have used fossil foraminifera to test this prediction [P.A. Martin et al., Geochem. Geophys. Geosyst. 1 (1999); H.M. Stoll et al., Geochim. Cosmochim. Acta 63 (1999) 3535–3547; H. Elderfield et al., Geochem. Geophys. Geosyst. 1 (2000)]. But whether some component of foraminiferal Sr/Ca variation can be uniquely ascribed to seawater Sr variation is still not clear. To address this question, we developed cleaning and analysis techniques and measured Sr/Ca ratios on individual shells of the modern benthic foraminifer *Cibicidoides wuellerstorfi*. We showed that different size shells have different Sr/Ca ratios; however, samples with shell sizes of 355–500 μm appear to have normally distributed Sr/Ca ratios ($1\sigma = 1.8\%$). For multi-shell measurements (with estimated errors of 0.12–0.39%), the ratio varied by as much as $7.2 \pm 0.5\%$ during the last glaciation for two Caribbean records at the same site and by $3.7 \pm 0.5\%$ over the past 40,000 yr for one record from the Sierra Leone Rise in the eastern equatorial Atlantic. The two Caribbean records are very similar indicating that the behavior of shell Sr uptake was identical locally and that the shell Sr/Ca ratio faithfully reflects the local environment. The Atlantic record differs from the Caribbean records by as much as several percent. Thus, the foraminiferal Sr/Ca changes cannot be solely due to changes in seawater Sr/Ca unless the glacial deep ocean had spatial variation in Sr/Ca well in excess of the modern ocean. Certain similarities between the three records do exist. Notably, the rate of change of Sr/Ca is similar between 9 and 0 ka (−0.25%/kyr) and between 25 and 16 ka (+0.16%/kyr). This

* Corresponding author. Present address: Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan.
E-mail addresses: shentwn@tc.umn.edu (C.-C. Shen), hastings@eckerd.edu (D.W. Hastings), typhoon@asiaa.sinica.edu.tw (T. Lee), chcstar@kimo.com.tw (C.-H. Chiu), monyoung@titan.seed.net.tw (M.-Y. Lee), weiky@ms.cc.ntu.edu.tw (K.-Y. Wei), edwar001@maroon.tc.umn.edu (R.L. Edwards).

suggests that during these intervals, benthic foraminiferal Sr/Ca was affected by similar large-scale variables. One of these variables may be the average marine Sr/Ca ratio; however, comparison with model predictions [H.M. Stoll and D.P. Schrag, Geochim. Cosmochim. Acta 62 (1998) 1107–1118] suggests other factors must also be considered. The discrepancies between the two sites may be related to the different water mass histories for the Caribbean and eastern Atlantic. Our results suggest that variation of the seawater Sr budget only partially contributed to *C. wuellerstorfi* Sr/Ca records, while other significant factors still need to be quantified. At present we cannot confidently determine past seawater Sr/Ca variation from our foraminiferal records. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Since Beck et al. [1] resurrected coral Sr/Ca thermometry using high precision isotope dilution mass spectrometry techniques, this proxy [2,3] has been applied to many important problems of climatic change [4–8]. Although coral Sr/Ca variations are dominated by Sr concentration changes [13], the thermometry is nevertheless based on the temperature-sensitive partition of Sr and Ca between coral and water [2,3]. In most work, the Sr/Ca ratio of the local sea surface water has been assumed not to vary over the time scales of the glacial–interglacial cycles [4–8]. This assumption is based on the several million year residence times for Sr and Ca in the ocean. Estimates suggest that the concentrations of Sr and Ca should not change significantly on time scales much shorter than 1 Myr [14]. However, careful measurements of Sr/Ca ratios in the modern oceans show spatial variation in the upper water column (Fig. 1) [2,15–17], as well as temporal variation in coastal settings such as Kenting, Taiwan [3].

Stoll and Schrag [9] considered possible variation in the seawater Sr/Ca ratio from 1 to 3% over the past 30 000 yr, corresponding to significant temperature changes (2–6°C) for the coral Sr/Ca thermometer. The proposed mechanism involved the addition of Sr dissolved from shelf aragonites that became exposed above receding sea levels and altered to calcites by fresh water during glaciation. Unfortunately, there is no direct check on the past cycling of seawater Sr and it is difficult to reconstruct paleo-oceanic Sr/Ca variations using geochemical proxies because for such a signal (on the order of 1% [9]) to be distinguishable from noise, the reproducibility of duplicate analyses should be less than 0.5%.

In the early 1980s, Cronblad and Malmgren [18] proposed that the planktonic foraminiferal Sr concentration might be valuable for reconstructing climatic change. The next question was: 'Can we use sedimentary foraminiferal Sr/Ca to accurately reconstruct variation in the paleo-oceanic Sr budget?' Martin et al. [10] first probed this question by measuring both planktonic and benthic foraminiferal Sr/Ca over the past 300,000 yr. Coherent glacial–interglacial Sr/Ca changes (5%) were revealed from diverse hydrographic settings [10]; however, amplitudes and fine patterns did not match well between records. Stoll et al. [11] showed that post-depositional dissolution effects could bias planktonic foraminiferal shell Sr/Ca in the sediments. Another difficulty involves environmental sensitivities for different foraminiferal species [12]. Even for the same planktonic species, inconsistencies of 1–3% between records from different locations (figure 3 of [11]) have been shown. These differences were caused either by environmental effects or different cleaning techniques. Using high precision analyses on individual shells, Shen [15] demonstrated that the within-species variation for the modern planktonic species *Globeriginoides sacculifer* (5%) is three times larger than that for the benthic species, *Cibicidoides wuellerstorfi*. The planktonic species live in environments characterized by large gradients in temperature, salinity, and Sr/Ca (Fig. 1). These factors, coupled with their migration behaviors and large seasonal changes in their surroundings, cause additional complications.

In general, water column Sr/Ca ratios increase from the surface value of 8.50–8.55 mmol/mol to 8.61 mmol/mol below 2000 m. Both Atlantic and Pacific oceans share deep water Sr/Ca ratios with
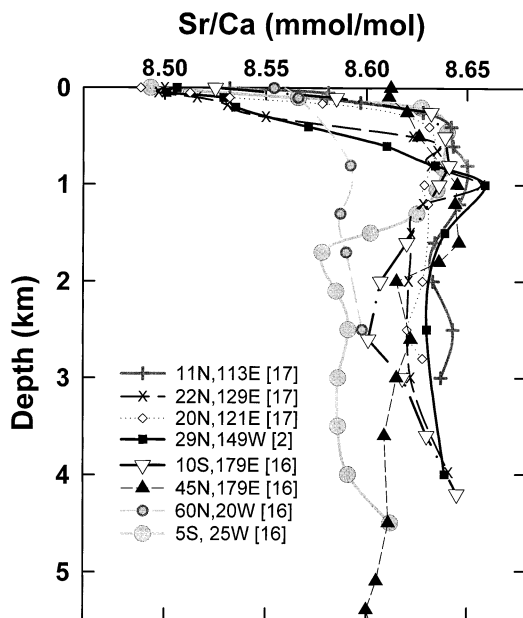
Fig. 1. Vertical profiles of Sr/Ca in the oceans. The locations for the two gray lines are at the Atlantic, the line with cross symbols at the South China Sea and others at the Pacific.

small variations of less than ±0.3% (Fig. 1). It has also been suggested that the distribution coefficient, D, for Sr in benthic foraminiferal calcite relative to seawater is insensitive to temperature [19,20]. Therefore, benthic foraminifera, which live in a relatively constant environment, offer potential to reconstruct the oceanic Sr history. Previous studies revealed large variations between D and water depth from specimen to specimen [19,20], although the mechanism of this 'pressure effect' is still unresolved [20]. Global data showed that only *C. wuellerstorfi* has a consistent relationship between D and water depth [19,20]. This species is an abundant epifaunal species, living at the sediment–seawater interface, and its dissolution-resistant shell is little influenced by pore water chemistry. Two *C. wuellerstorfi* Sr/Ca records from Pacific and Atlantic Oceans, measured by Martin et al. [10], showed a similar trend of glacial–interglacial variation. The collective evidence thus suggests that *C. wuellerstorfi* may be a good candidate for reconstructing the oceanic Sr record.

Some fundamental issues have yet to be solved. Early work showed that the D value is positively correlated with an increase in calcification rate for inorganic and organic calcite (e.g. [21,22]). This possible kinetically controlled biological effect (vital effect) is not yet quantified for *C. wuellerstorfi*. Due to the high precision required, we must understand this possible effect in advance. Moreover, different cleaning procedures could affect the accuracy of the data [10,11]. To address these issues, we developed the following strategy: (1) test the cleaning procedure, (2) test for possible kinetic effects and tracer variation among individual tests, and estimate appropriate sample size, (3) test for reproducibility of glacial–interglacial records from various locations, and (4) evaluate the role of environmental factors and whether or not the seawater Sr history is accurately reflected in the foraminiferal Sr/Ca records.

2. Materials and methods

2.1. Instrumental analyses

Sr/Ca measurements were made by the isotope dilution method using a ^{42}Ca–^{44}Ca–^{84}Sr triple spike [3] on a VG-354 thermal ionization mass spectrometer at the Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan. Analyses of four separately processed samples from a homogenized *C. wuellerstorfi* powder show that the reproducibilities (1σ) were 0.014% and 0.032% for [Ca] and [Sr], respectively, and only 0.028% for Sr/Ca due to no gravimetric uncertainty involved. Oxygen and carbon isotope measurements were performed on a Finnigan Delta Plus mass spectrometer with a 'Kiel' automated carbonate device at the Department of Geosciences, National Taiwan University. Results were reported with respect to the VPDB standard through calibration against a routinely analyzed reference material (NBS-19). The external precisions (1σ) are 0.10‰ for δ^{18}O and 0.06‰ for δ^{13}C. The error given in this paper is one standard deviation or one standard deviation of the mean unless otherwise noted.

2.2. Samples

Extensive testing of our experimental procedures was first performed on samples from the Caribbean (20–22 cm of core TT9108-1GC, 11°40′N, 79°36′W; 2540 m) and the Ontong Java Plateau (core-tops (0–2 cm) of MW0691-BC7 (2°11′S, 157°00′E; 1614 m), MW0619-BC13 (0°00′S, 158°55′E; 2301 m) and MW0691-BC24 (0°00′N, 160°26′E; 2965 m)) in the equatorial Pacific.

The benthic foraminifer *C. wuellerstorfi* was picked from two gravity cores, EN066-17GGC (5°22′N, 21°5′W) and TT9108-1GC, to establish the last glacial–interglacial records. EN066-17GGC core (Atlantic core hereafter) was taken from a water depth of 3050 m at the Sierra Leone Rise in the eastern equatorial Atlantic. The calcite lysocline is estimated to be 4800 m in that area [23]. For this Atlantic core, Holocene sedimentation rates averaged 1.4 cm/kyr compared to 2.7 cm/kyr during the last glacial period [24]. The TT9108-1GC core (Caribbean core) was taken from the southwestern Colombia Basin in the Caribbean with sedimentation rates of 2–3 cm/kyr in the Holocene and up to over 5 cm/kyr during glacial times [24]. The top 59 cm, covering Marine Isotope Stages (MISs) 1 and 2, was accidentally sampled twice during coring, with the gravity core penetrating the sediment and withdrawing briefly before repenetrating [24]. This event provided duplicate samples to reconstruct two glacial–interglacial Sr/Ca records in *C. wuellerstorfi* from the same site.

The eastern Atlantic and Caribbean have encountered different water mass histories and hydrological changes [25–28]. In the eastern Atlantic basin, North Atlantic Deep Water (NADW) with high δ^{13}C values shoaled and cold Southern Ocean Water (SOW) with low δ^{13}C values spread to the North Atlantic during glacial time [25–28]. The mixture of NADW and SOW is about 80:20 today and was 50:50 during the last glaciation [29,30]. Glacial sediments show more evidence for dissolution than those of interglacial age [29]. The source of deep Caribbean water is mostly North Atlantic Intermediate Water (NAIW), instead of NADW, because an 1800-m

sill separates the Caribbean basin from the Atlantic [25,27]. During the last glaciation, high salinity and high δ^{13}C glacial Mediterranean Overflow Water (MOW) was also an important source of water to the Caribbean [25,27]. Caribbean sediments reflect enhanced carbonate preservation during glacial time [31,32].

We analyzed the top 120 cm of the Atlantic core, covering MISs 1–3, and the top 120 cm of Caribbean core. Thus, one glacial–interglacial Sr/Ca record from the eastern Atlantic, and two records from one Caribbean site were obtained. A sample size of 20–200 individuals (355–500 μm) for each horizon (1.5–2.0 cm) was used for Sr/Ca analysis and five to eight individuals (>425 μm) for stable isotope analysis. Previous investigations of Mg/Ca [24], V/Ca [33] and U/Ca [34] ratios on planktonic foraminifera from the two cores indicate no obvious evidence of dissolution artifacts.

2.3. Chemistry

Various cleaning methods have been used for studies of foraminiferal trace elements (e.g. [9–12,19,24,33–35]). To identify the importance of variations caused by contaminants, we first tested our sample cleaning procedures on the 355–500 μm fraction at a depth of 20–22 cm in the Caribbean core. Our method was devised by modifying the procedures of previous workers [19,20,24,35]. Individual foraminifera were picked from the size fraction and leached sequentially in an ultrasonic bath using four reagents designed to remove physically attached particles, chemically exchangeable contaminants, organics, and hydrogenous metal oxides, respectively. The sequence of the four reagents (all at pH 8–8.5) was: (1) doubly distilled H_2O, (2) 1.0 M NH_4Cl, (3) 1% H_2O_2, and (4) 0.01 M NH_2OH, which was prepared from hydroxylamine-HCl.

After slightly leaching with 0.001 M HNO_3 for 3 min, the cleaned samples were dissolved completely in 0.5 M HNO_3. The removed particles and metal oxides, which have high Sr/Ca, can cause biases of 0.1% and 0.3%, respectively. These deviations were larger than our analytical uncertainty of 0.03% for Sr/Ca, which demonstrates the

importance of rigorous and methodical cleaning even for specimens already selected for their pristine appearance. We have also checked for internal heterogeneities in foraminifera by stepwise dissolution of cleaned specimens from core MW0619-BC13. The first 12 etching steps removed 55% of the total mass and the dissolutions affected the Sr/Ca ratio of the bulk sample by less than 0.03%. The final two steps removed 30% and 15% of the mass, respectively, and affected up to 0.13% of the bulk value. Therefore, only a slight internal heterogeneity for *C. wuellerstorfi* exists.

2.4. Individual foraminiferal Sr/Ca variation and sample size

We measured the Sr/Ca ratio of 54 cleaned individual shells from the top of the equatorial Pacific MW0691-BC7 core in order to determine variation of the Sr/Ca ratio in individual foraminiferal tests. Fig. 2 summarizes the mean and one standard deviation for the four size fractions in the individual foraminifer study. The Sr/Ca mean (1.316 mmol/mol) of the first size fraction (250–300 μm) is 8% lower than others (1.42–1.43 mmol/mol). This possible kinetic effect may explain why a lower Sr/Ca value of 1.36 ± 0.03 mmol/mol (for shell size > 150 μm) was obtained in an earlier study [36]. With increasing shell size, the standard deviations decrease from 0.042 to 0.025 mmol/mol. This trend is similar to that reported by Elderfield et al. [19].

We applied the Student *t*-test [37] to the data sets for the two largest size fractions (355–425 μm and 425–500 μm) and found that there is no significant difference between the two distributions at a 5% one-tailed probability level. We combined these two data sets consisting of 36 individual specimens. This data set appears to be independent of shell size and follows a normal distribution (normal probability plot at 5% probability level) [37] with a mean Sr/Ca of 1.430 mmol/mol. The standard deviation was 1.8%, much larger than the analytical uncertainty (0.03%). The Sr/Ca ratios of individual specimens exhibit too much variability to be used as a proxy for seawater Sr/Ca. Since the regional deep ocean has nearly constant temperature and dissolved

Sr/Ca values, there are apparently other factors affecting the Sr/Ca of individual specimens. Similar to the oxygen isotope stratigraphy using planktonic foraminifera [38,39], the mean Sr/Ca for a large number of individuals is less variable and thus a better proxy. The Sr/Ca data for *C. wuellerstorfi* with shell size between 355 and 500 μm follow a normal distribution. This suggests that the biological factors that affect the Sr uptake in the test vary randomly. The Central Limit Theorem applies and the standard deviation of the mean, σ_m, decreases by the $n^{-1/2}$ law [37], where n is the number of specimens. Twenty specimens is a reasonable choice for a minimum group size since the value of σ_m is only 0.39% and larger numbers of samples result in only minimal decreases. Because 20–200 individuals for each horizon were used, we estimated the uncertainty for these data to be ± 0.12–0.39%.

2.5. Relationship between foraminiferal Sr/Ca and water depth

One factor that could affect D is the hydrostatic pressure of the overlying water column. We measured Sr/Ca ratios of samples ($n = 40$–50, shell
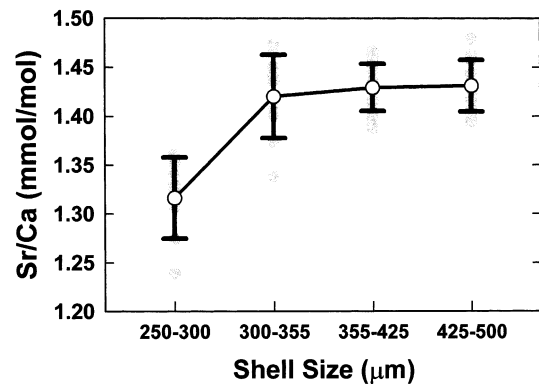

Fig. 2. Foraminiferal Sr/Ca data from 250–300 μm to 425–500 μm for *C. wuellerstorfi* from the MW0691-BC7 core-top: 1.316 ± 0.042 mmol/mol ($n = 8$) for the 250–300 μm group; 1.420 ± 0.043 mmol/mol ($n = 10$) for the 300–355 μm fraction; 1.429 ± 0.024 mmol/mol ($n = 17$) for the 355–425 μm fraction, and 1.431 ± 0.026 mmol/mol ($n = 19$) for the 425–500 μm fraction, where n is the number of shells used. Gray circles are individual Sr/Ca data and open circles are means for each shell size fraction. The vertical error bars are 1σ.

size: 425–500 μm) picked from the core-tops of three box cores, BC7 (1.430 ± 0.008 mmol/mol), BC13 (1.374 ± 0.010 mmol/mol), and BC24 (1.301 ± 0.010 mmol/mol), to determine a relationship between Sr/Ca and water depth. The data indicate that at water depths between 1500 m and 3200 m, the foraminiferal Sr/Ca sensitivity to depth is -9.54×10^{-3} mmol/mol per 100 m. These results, consistent with previous work [19,20], suggest that D of *C. wuellerstorfi* decreases with water depth at a rate of 0.75% per 100 m for sites deeper than 1500 m. A glacial–interglacial sea level change of 120 m would bring about a 0.9% change in D, which is significant in comparison to the possible seawater Sr variation of 1–3% [9]. We correct the D value for this effect based on sea level history [40].

3. Results and discussion

3.1. Eastern Atlantic core

Foraminiferal Sr/Ca data from the core-top to the depth of 60 cm for the Atlantic core are shown in Fig. 3 (and are listed in the **Background Dataset**[1]). The core-top value, 1.323 mmol/mol, is comparable with those (1.28–1.32 mmol/mol) from adjacent cores at similar depths reported by Rosenthal et al. [20]. The Sr/Ca ratio increased to a maximum of 1.367 mmol/mol at 15 cm, then decreased to a value of 1.320 mmol/mol at 60 cm. The overall amplitude of the observed Sr/Ca variation was 3.7% (−0.4% to +3.3% relative to the modern value). The $\delta^{18}O$ data varied from 2.5‰ in the Holocene to 4.0‰ at the last glacial maximum (LGM) (Fig. 3a) and the $\delta^{13}C$ data varied from 1.0 to 1.2‰ during the Holocene to ∼0.5‰ at the MIS 1/2 boundary (Fig. 3b). These data are consistent with the previous measurements [24–26]. The chronology is based on the $\delta^{18}O$ record and one ^{14}C age (16.4 ± 0.1 ka) on the planktonic foraminifer *G. sacculifer* at 23 cm. The MIS 1/2 boundary is at 17 cm and MIS 2/3 boundary is at 43 cm [24,33].
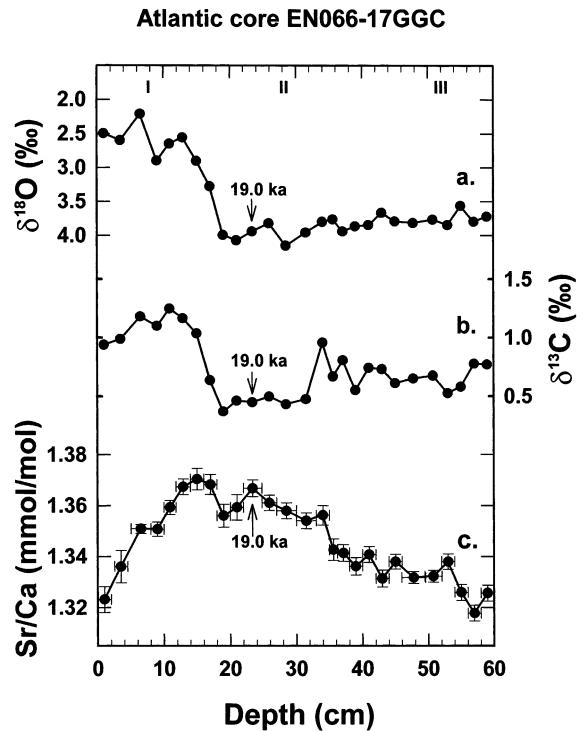
Fig. 3. Tracer data for *C. wuellerstorfi* in the eastern equatorial Atlantic core EN066-17GGC. (a) Oxygen isotope record. MISs are indicated on the top and separated by gray lines. (b) Carbon isotope record. (c) Sr/Ca record. The vertical error bars are $1\sigma_m$ and horizontal bars represent the time spans based on the depth intervals that correspond to the portion of core that was sampled for a particular measurement. One ^{14}C age (16.4 ± 0.1 ka) on the planktonic foraminifer *G. sacculifer* at 23 cm was measured and corrected to its calendar age of 19.0 ± 0.4 ka [41].

3.2. Caribbean core

Foraminiferal $\delta^{18}O$, $\delta^{13}C$ and Sr/Ca for the top 120 cm of Caribbean core are shown in Fig. 4 (and are listed in the **Background Dataset**[1]). Since this core penetrated the sediment twice, duplicate glacial–interglacial records (TT-A, 0–58 cm; TT-B, 60–120 cm) were obtained. Two similar glacial–interglacial Sr/Ca records for TT-A and TT-B ranged from 1.37 mmol/mol at present to a maximum of 1.47 mol/mol just after the MIS 1/2 boundary. Although the variations of two $\delta^{18}O$ records for TT-A and TT-B are very similar, the sediment thickness for MIS 1 in TT-B is only 20 cm, versus 34 cm in TT-A. The values of $\delta^{18}O$
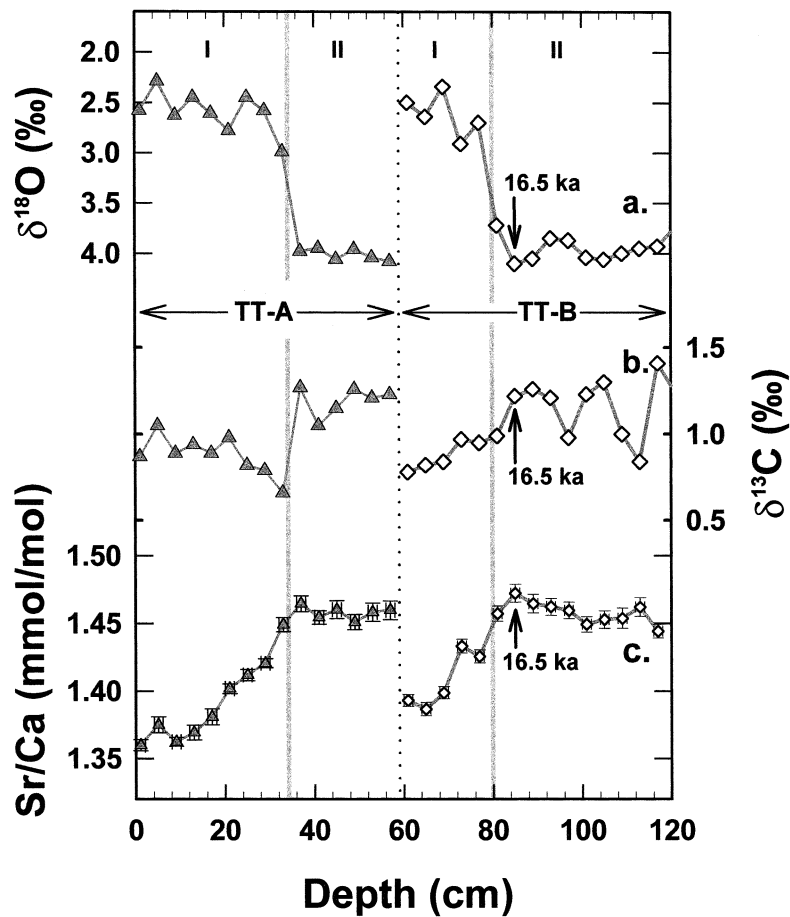
Fig. 4. Tracer data for *C. wuellerstorfi* in the Caribbean core TT9108-1GC. Since the top 58 cm was sampled twice, two sets of glacial–interglacial records (TT-A from 0–58 cm and TT-B from 60–120 cm) were obtained (separated by dotted line at 59 cm). Triangles are from TT-A and diamonds from TT-B. (a) Oxygen isotope records. MISs are indicated on the top and separated by gray lines. (b) Carbon isotope records. (c) Sr/Ca records. The vertical error bars are $1\sigma_m$ and horizontal bars represent the time spans based on sampled depth intervals. One ^{14}C age (14.1 ± 0.1 ka) on *G. sacculifer* at 84 cm was obtained and corrected to a calendar age of 16.5 ± 0.4 ka [41].

and $\delta^{13}C$ data of the top of TT-B (60–62 cm) are consistent with the ones at the core-top (0–2 cm of TT-A). This indicates that only minor mixing occurred at the interface between TT-A and TT-B during sampling. The Sr/Ca ratio of the top of TT-B is 1.39 mol/mol, similar to the values at 16–20 cm in TT-A. The rate of change of Sr/Ca at 60–84 cm is identical to the one at 20–38 cm. The observations strongly suggest that TT-B was not compressed and that the original top 12–16

cm of TT-B was lost when the gravity core contacted the sediment during repenetration.

The chronology was developed by assigning the MIS 1/2 boundary of TT-A to 33 cm, that of TT-B to 80 cm, and utilizing one ^{14}C age (14.1 ± 0.1 ka) at 84 cm (Fig. 4). With more $\delta^{18}O$ data at depth > 120 cm, not shown in Fig. 4a, the MIS 2/3 boundary of TT-B is estimated at 120 cm. We applied the sedimentation rate during MIS 1 of TT-A to the interval of 60–80 cm in TT-B and the
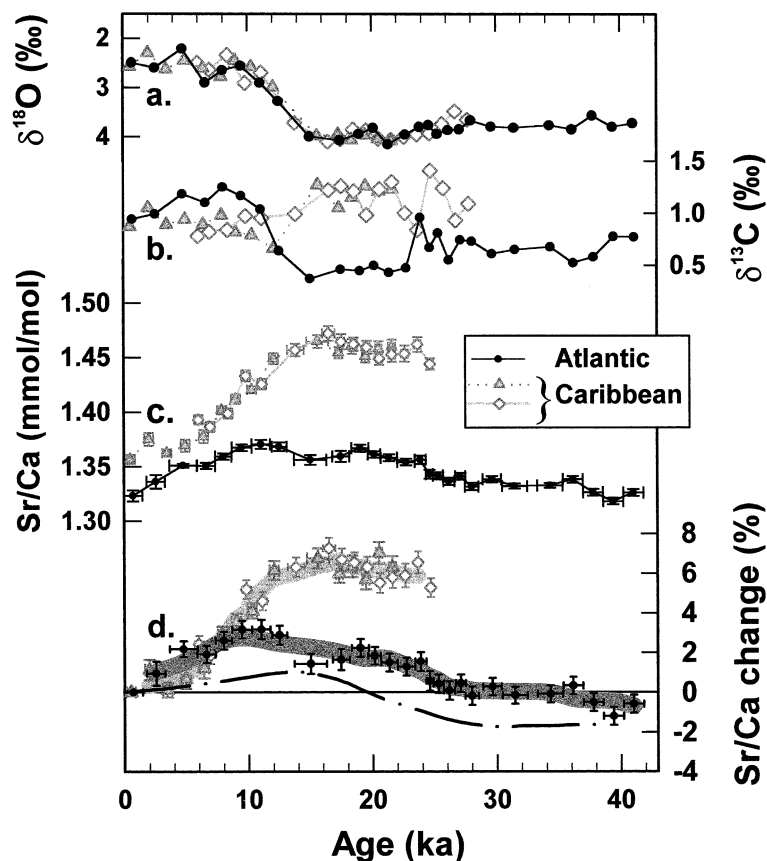
Fig. 5. Tracers versus age for the Atlantic and Caribbean cores. Ages are given in calendar years. The thin lines with circles are for Atlantic records, with triangles and diamonds for the Caribbean cores TT-A and TT-B, respectively. (a) Oxygen isotope records. (b) Carbon isotope records. (c) Benthic foraminiferal Sr/Ca records. The vertical error bars are $1\sigma_m$ and horizontal bars represent the time spans based on sampled depth intervals. (d) Adjusted foraminiferal Sr/Ca variation records (%) after correcting for pressure and indirect temperature effects. The rates of change of Sr/Ca are different between 16 and 9 ka for the Atlantic record (thick dark gray three-point-averaged line) and Caribbean records (thick gray three-point-smoothed line, including all Sr/Ca data from TT-A and TT-B). At both locations, the amplitudes of Sr/Ca variations are larger than the modeled simulation (dash-dot curve) [9].

rate during MIS 2 of TT-B to calculating ages between 33 cm and 58 cm in TT-A.

3.3. Sr/Ca records

The two Caribbean Sr/Ca records (TT-A and TT-B) are identical within error, varying from 1.37 mmol/mol at present to a maximum of 1.47 mmol/mol at 16 ka, then gradually decreasing to a value of 1.45 mmol/mol at 25 ka (Fig. 5). The duplicated results illustrate the same behavior of shell Sr uptake existed under the same local con-

ditions at one site. The Atlantic Sr/Ca record varies from 1.32 mmol/mol at present to a maximum of 1.37 mmol/mol at 11 ka, then decreases to 1.32 mmol/mol at 40 ka. Considering a possible bioturbation depth of ±5 cm, the foraminiferal Sr/Ca maxima were 11±4 ka for the Atlantic record and 16±2 ka for the Caribbean records. Whether the timing of maxima between the two sites is different or not should be further evaluated by tighter age constraints and/or analysis of nearby cores with higher sedimentation rates. However, the amplitudes are significantly different

($3.7 \pm 0.5\%$ in the Atlantic vs. $7.2 \pm 0.5\%$ in the Caribbean), indicating that foraminiferal carbonate Sr was strongly influenced by regional conditions.

An interesting observation is that the rates of change of Sr/Ca were similar between the Atlantic and Caribbean records during the periods of 9–0 ka (-0.25%/kyr) and of 25–16 ka ($+0.16\%$/kyr), when the stable isotopic compositions of deep seawater masses were steady [25–27]. The major offset between the two regions occurred between 16 and 9 ka, the glacial–interglacial transition zone. During this interval, the Caribbean Sr/Ca ratio decreased at a rate of 0.71%/kyr, but the Atlantic Sr/Ca ratio increased slightly at a rate of 0.18%/kyr.

3.4. Sr/Ca records adjusted for known environmental factors

From previous work, we know that the observed benthic foraminiferal Sr/Ca records shown in Fig. 5c cannot be attributed solely to changes in the seawater Sr/Ca ratio. Two known environmental factors are also involved: an indirect effect from deep sea temperature change and a direct pressure effect due to sea level change [20,42,43]. We subtracted the contribution of these two effects from the Sr/Ca records to aid further discussion.

D is dependent on the Mg content of the test [42], which in turn depends on temperature [20,43]. A 1°C cooling may indirectly cause an offset of -0.085% for foraminiferal Sr/Ca [42,43]. We followed Cutler's method [40] to separate the temperature component from the benthic foraminiferal oxygen isotope records. Since high salinity glacial MOW extended to the Caribbean [25], we estimated a LGM to present shift in deep seawater $\delta^{18}O$ ($\Delta\delta^{18}O$) of 1.10‰ for the Caribbean and a shift of 0.90‰ in the eastern Atlantic Ocean [44]. The present water temperatures at the locations are 2.6°C for the Atlantic core and 4.1°C for the Caribbean core [45] and the inferred glacial deep sea temperatures were 2–3°C and 1–2°C lower than present, respectively. We then subtract this effect from the Sr/Ca records. This is a minor effect, equivalent to less than

7% of the overall range of foraminiferal Sr/Ca variation in Atlantic record, and less than 2% in the Caribbean records.

The pressure effect was corrected for the Sr/Ca records based on the sea-level record of Cutler [40] and the foraminiferal Sr/Ca–depth relationship, -9.54×10^{-3} mmol/mol per 100 m, described in Section 2.5. The maximum effect, 1.1%, is equivalent to 30% of the Atlantic Sr/Ca record and 15% in the Caribbean records. After correcting the effects of pressure and indirect temperature, the amplitudes of the corrected Sr/Ca variations are $3.0 \pm 0.5\%$ for the Atlantic record and $6.4 \pm 0.5\%$ for the Caribbean records since the LGM (Fig. 5d).

The absolute values of the Sr/Ca records from the two sites can be directly compared after calibrating the values for different water depths. Applying the pressure correction, the core-top value of the Caribbean Sr/Ca records is 1.31 mmol/mol at the water depth of the Atlantic core. The inferred value is slightly lower than the core-top value, 1.32 mmol/mol, of the Atlantic record. This small discrepancy can be explained by the different Holocene sedimentation rates and water temperatures between two cores. However, the given glacial Caribbean Sr/Ca ratio is 1.40 mmol/mol, significantly different from the values of 1.35–1.37 mmol/mol for the glacial Atlantic foraminiferal Sr/Ca ratios (Fig. 5c). This larger discrepancy implies that other environmental factors besides water pressure are likely involved with the Sr/Ca values (see below).

3.5. Inconsistency between Atlantic and Caribbean Sr/Ca records

Although the overall patterns of adjusted Sr/Ca records at two sites are similar in that Holocene values are lower than glacial values, a substantial 4% offset in the deglacial trend is observed (Fig. 5d). During the interval from 16 to 9 ka, the Caribbean records decreased by 0.56%/kyr while the Atlantic record increased by only 0.14%/kyr. After 9 ka, the two rates were similar. The relation between the Atlantic and Caribbean records is coincident with the histories of water mass exchange at the two locations [25–27]; but the large

4% offset cannot be explained by different Sr/Ca ratios in the water masses. If the two adjusted records reflect deep seawater conditions, a 4% discrepancy of deep sea Sr/Ca ratios should have occurred by 16 ka. This discrepancy implies that Sr/Ca ratios of glacial NAIW and/or glacial MOW, the sources to the deep Caribbean, would be 4–6% higher than that of the water at the Sierra Leone Rise. However, depth gradients in modern seawater show < 2% variation from the surface to the deep sea (Fig. 1). The Sr/Ca ratio of deep Pacific water is on average 0.3% higher than that of NADW (Fig. 1). If these relations were similar during glacial time, deep sea Sr/Ca ratios in the eastern Atlantic should have been slightly higher (< 0.5%) than that in the Caribbean, when more SOW flowed into the eastern Atlantic basin. Therefore, the offset between Atlantic and Caribbean foraminiferal Sr/Ca records cannot be interpreted as different seawater Sr/Ca ratios. Questions that follow are (1) what factors caused the difference in the Sr/Ca records at different locations and (2) does either record represent past glacial–interglacial oceanic Sr/Ca changes?

When comparing the adjusted foraminiferal Sr/Ca records with Stoll and Schrag's model [9] (Fig. 5d), the amplitude of our total observed variation is larger than the maximum amplitude of their model (2.77%, run no. 17). Their model, using parameters varying within the range that they consider reasonable, cannot reproduce either of our curves. It would be particularly difficult to accommodate an increase as large as 3.1% since the LGM (Schrag, personal communication). As noted earlier, the Atlantic and Caribbean records have similar rates of change of Sr/Ca during two intervals. During the first interval (25–16 ka), the Sr/Ca ratio of the adjusted foraminiferal records increased by a rate of 0.14%/kyr, which is smaller than 0.17%/kyr in the maximum case for Stoll and Schrag's model (Fig. 5d). This implies that the foraminiferal Sr/Ca change rate during this interval might reflect the seawater Sr/Ca. However, during the second interval (9–0 ka), a rate of −0.25%/kyr is over three times larger than the modeled value. This rapid rate of change could be modeled only by using extreme and unrealistic parameter values that disagree with our current

understanding [11]. This suggests that during these intervals, benthic foraminiferal Sr/Ca ratios are controlled by additional factors besides seawater Sr/Ca.

3.6. Possible environmental effects

Possible environmental parameters that could control foraminiferal shell Sr uptake could include calcification temperature, salinity, and pH. Recent culture experiments using the planktonic foraminifera, *Orbulina universa* and *Globigerina bulloides*, indicate that shell Sr/Ca increases with increasing temperature, salinity and pH [46]. If temperature is a primary factor, temperature change would cause foraminiferal Sr/Ca ratios to be lower at glacial time than at present, in disagreement with the observed high glacial Sr/Ca values in the Atlantic and Caribbean records (Fig. 5). A global survey of core-top samples also indicates temperature is not a primary factor for *C. wuellerstorfi* [20]. Thus, the Sr/Ca records cannot be explained by different calcification temperatures.

Salinity is a possible factor, which increases shell Sr/Ca at $0.7 \pm 0.7\%$ per salinity unit (figure 5 of [46]). Because glacial sea level was 120 m lower than today [40], the glacial seawater salinity was about 3% higher and thus the glacial Sr/Ca values for *C. wuellerstorfi* would be expected to be $2 \pm 2\%$ higher than modern. Although the Atlantic record seems to match the expected value, the amplitude of $6.4 \pm 0.5\%$ shown in the Caribbean records is triple that value (Fig. 5d), and cannot be explained by salinity change alone. In addition, the glacial deep Caribbean might have had a higher salinity by $\sim 0.5\%$ from MOW than the glacial eastern equatorial Atlantic [25,27], which cannot satisfy the observed 4% Sr/Ca offset between the two sites by 16 ka.

Variation in carbonate ion concentration during glacial time may have affected the D value [11]. Culturing experiments indicate that changes in pH can contribute to Sr/Ca variations at 0.5–1.0% per 0.1 pH unit [46]. However, the amplitudes of the Atlantic and Caribbean records and the offset between records at the two sites cannot be interpreted by the pH effects alone. Moreover,

neither of our records is consistent with paleo-atmospheric pCO_2 curves [47].

Previous studies using planktonic foraminiferal tracers showed no evidence of dissolution artifacts for either of the two cores [24,33]. *C. wuellerstorfi* is a dissolution-resistance benthic species with little internal heterogeneity of shell Sr/Ca. Core-top data from a wide range of water depths indicate dissolution is not a primary factor in controlling sedimentary foraminiferal Sr/Ca [19,20] (see McCorkle et al. [36] for a different opinion). However, a possible effect related to diagenetic dissolution cannot be ruled out here. The study by Stoll et al. [11] reveals that planktonic foraminiferal records with large Sr/Ca variation (7–12%) bear a strong resemblance to dissolution histories, while those records with low variation (3–5%) show little correlation with indicators of dissolution intensity. Martin et al. [10] observed similarities between *C. wuellerstorfi* Sr/Ca and percent carbonate records and suggested that differential dissolution may account for high frequency Sr/Ca variations. These observations suggest that the dissolution effect can partially bias foraminiferal shell Sr/Ca ratios in the sediment. Carbonate dissolution cycles in the eastern Atlantic and Caribbean are out of phase [29,31,32]. Different amplitudes in synchronous Sr/Ca oscillations are illustrated in Fig. 5d, suggesting dissolution may be a minor factor controlling downcore *C. wuellerstorfi* Sr/Ca ratios. We speculate that the Sr-rich fraction of foraminiferal carbonate might have been slightly dissolved in the eastern Atlantic basin during glacial time, and that this dissolution caused the discrepancy in Sr/Ca records between the two sites (Fig. 5d). The influence of selective post-depositional dissolution on downcore Sr/Ca ratios is a process that remains to be quantified in future studies.

4. Conclusion

We quantify the variability of Sr uptake between individuals for the benthic foraminifer *C. wuellerstorfi*, the change in bulk foraminiferal Sr/Ca ratios with water depth, and present high precision foraminiferal Sr/Ca records from the eastern Atlantic basin and the Caribbean. The discrepancy of Sr/Ca records between the two sites cannot be explained by different seawater Sr/Ca ratios. Instead, the differences are likely attributable to different water mass histories during glacial time, and different environmental factors associated with the different water masses. In order to deconvolve the foraminiferal Sr/Ca records, we suggest that more culturing experiments are carried out to further understand Sr substitution in foraminiferal calcite, and to quantify factors such as temperature, salinity and pH. The influence of diagenetic dissolution should also be more closely evaluated. Analysis of modern samples and sedimentary cores from locations in different hydrological settings may shed light on the cryptic nature of glacial–interglacial Sr variations in benthic foraminifera.

References

[1] J.W. Beck, R.L. Edwards, E. Ito, F.W. Taylor, J. Recy, F. Rougerie, P. Joannot, C. Henin, Sea-surface temperature from coral skeletal strontium/calcium ratios, Science 257 (1992) 644–647.

[2] S. de Villiers, G.T. Shen, B.K. Nelson, Sr/Ca thermometry in corals: Method calibration and evaluation of (Sr/Ca)$_{seawater}$ and interspecies variability, Geochim. Cosmochim. Acta 58 (1994) 197–208.

[3] C.-C. Shen, T. Lee, C.-Y. Chen, C.-H. Wang, C.-F. Dai, L.-A. Li, The calibration of *D*[Sr/Ca] versus sea surface temperature relationship for *Porites* corals, Geochim. Cosmochim. Acta 60 (1996) 3849–3858.

[4] T.P. Guilderson, R.G. Fairbanks, J.L. Rubenstone, Tropical temperature variations since 20–000 years ago: Modulating interhemispheric climate change, Science 263 (1994) 663–665.

[5] M.T. McCulloch, G. Mortimer, T. Esat, X. Li, B. Pillans, J. Chappell, High resolution windows into early Holocene climate: Sr/Ca coral records from the Huon Peninsula, Earth Planet. Sci. Lett. 138 (1996) 168–178.

[6] J.W. Beck, J. Recy, F. Taylor, R.L. Edwards, G. Cabioch, Abrupt changes in the early Holocene tropical sea surface temperature derived from coral records, Nature 385 (1997) 705–707.

[7] M.K. Gagan, L.K. Ayliffe, D. Hopley, J.A. Cali, G.E. Mortimer, J. Chappell, M.T. McCulloch, M.J. Head, Temperature and surface-ocean water balance of the mid-Holocene tropical Western Pacific, Science 279 (1998) 1014–1018.

[8] M.T. McCulloch, A.W. Tudhope, M.T. Esat, G.E. Mortimer, J. Chappell, B. Pillans, A.R. Chivas, A. Omura, Coral record of equatorial sea-surface temperatures during the penultimate deglaciation at Huon Peninsula, Science 283 (1999) 202–204.

[9] H.M. Stoll, D.P. Schrag, Effects of Quaternary sea level cycles on strontium in seawater, Geochim. Cosmochim. Acta 62 (1998) 1107–1118.

[10] P.A. Martin, D.W. Lea, T.A. Mashiotta, T.P. Papenfuss, M. Sarnthein, Variation of foraminiferal Sr/Ca over Quaternary glacial–interglacial cycles: Evidence for changes in mean ocean Sr/Ca?, Geochem. Geophys. Geosyst. 1 (1999).

[11] H.M. Stoll, D.P. Schrag, S.C. Clemens, Are seawater Sr/Ca variations preserved in Quaternary foraminifera?, Geochim. Cosmochim. Acta 63 (1999) 3535–3547.

[12] H. Elderfield, M. Cooper, G. Ganssen, Sr/Ca in multiple species of planktonic foraminifera: Implications for reconstructions of seawater Sr/Ca, Geochem. Geophys. Geosyst. 1 (2000).

[13] M. Sun, C.-H. Chiu, C.-C. Shen, T. Lee, Sr thermometer for *Porites* corals: Little need to measure Ca?, Geochem. J. 33 (1999) 351–354.

[14] W.S. Broecker, T.-H. Peng, Tracers in the Sea, Columbia University Press, NY, 1982, 690 pp.

[15] C.-C. Shen, High Precision Analysis of Sr/Ca Ratio and its Environmental Application, Ph.D. Thesis, Tsing-Hua University, Taiwan, 1996, 187 pp.

[16] S. de Villiers, Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans, Earth Planet. Sci. Lett. 171 (1999) 623–634.

[17] C.-C. Shen, K.-Y. Wei, M.-Y. Lee, T. Lee, High precision seawater Sr/Ca variability in the western Pacific Ocean and South China Sea, in prep.

[18] H.G. Cronblad, B.A. Malmgren, Climatically controlled variation of strontium and magnesium in Quaternary planktonic foraminifera, Nature 291 (1981) 61–64.

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

[20] Y. Rosenthal, E.A. Boyle, N. Slowey, Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography, Geochim. Cosmochim. Acta 61 (1997) 3633–3643.

[21] R.B. Lorens, Sr, Cd, Mn, and Co distribution coefficients in calcite as a function of calcite precipitation rate, Geochim. Cosmochim. Acta 45 (1981) 553–561.

[22] J.W. Morse, M.L. Bender, Partition coefficients in calcite – Examination of factors influencing the validity of experimental results and their application to natural systems, Chem. Geol. 82 (1990) 265–277.

[23] R.C. Thunell, Carbonate dissolution and abyssal hydrography in the Atlantic Ocean, Mar. Geol. 47 (1982) 165–180.

[24] D.W. Hastings, A.D. Russell, S.R. Emerson, Foraminiferal magnesium in *Globeriginoides sacculifer* as a paleotemperature proxy, Paleoceanography 13 (1998) 161–169.

[25] D.W. Oppo, R.G. Fairbanks, Variability in the deep and intermediate water circulation of the Atlantic Ocean during the past 25 000 years: Northern Hemisphere modulation of the Southern Ocean, Earth Planet. Sci. Lett. 86 (1987) 1–15.

[26] W.B. Curry, J.C. Duplessy, L.D. Labeyrie, N.J. Shackleton, Changes in the distribution of $\delta^{13}C$ of deep water ΣCO_2 between the last glaciation and the Holocene, Paleoceanography 3 (1988) 317–341.

[27] J.C. Duplessy, N.J. Shackleton, R.G. Fairbanks, L.D. Labeyrie, D.W. Oppo, N. Kallel, Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation, Paleoceanography 3 (1988) 343–360.

[28] M. Sarnthein, K. Winn, S.J.A. Jung, J.C. Duplessy, H. Erlenkeuser, G. Gansen, Changes in the East Atlantic deep-water circulation over the last 30 000 years: Eight time-slice reconstructions, Paleoceanography 9 (1994) 209–267.

[29] W.B. Curry, G.P. Lohmann, Reconstructions past particle fluxes in the tropical Atlantic Ocean, Paleoceanography 5 (1990) 487–505.

[30] J.F. Adkins, H. Cheng, E.A. Boyle, E.R.M. Druffel, R.L. Edwards, Deep-sea coral evidence for rapid change in ventilation of the deep North Atlantic 15 400 years ago, Science 280 (1998) 725–728.

[31] C. Chen, Pleistocene pteropods in pelagic sediments, Nature 219 (1968) 1145–1149.

[32] G.A. Haddad, A.W. Droxler, Metastable $CaCO_3$ dissolution at intermediate water depth of the Caribbean and western North Atlantic: Implications for intermediate water circulation during the past 200 000 years, Paleoceanography 11 (1996) 701–716.

[33] D.W. Hastings, S.R. Emerson, A.C. Mix, Vanadium in foraminiferal calcite as a tracer for changes in the areal extent of reducing sediments, Paleoceanography 11 (1996) 665–678.

[34] A.D. Russell, S.R. Emerson, A.C. Mix, L.C. Peterson, The use of foraminiferal uranium/calcium ratios as an indicator of changes in seawater uranium content, Paleoceanography 11 (1996) 649–663.

[35] E.A. Boyle, Cadmium, zinc, copper and barium in foraminifera tests, Earth Planet. Sci. Lett. 53 (1981) 11–35.

[36] D.C. McCorkle, P.A. Martin, D.W. Lea, G.P. Klinkhammer, Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}C$, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau, Paleoceanography 10 (1995) 699–714.

[37] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, Ellis Horwood Press, NY, 1986, 202 pp.

[38] P. Schiffelbein, S. Hills, Direct assessment of stable isotope variability in planktonic foraminifera populations, Palaeogeogr. Palaeoclimatol. Palaeoecol. 48 (1984) 197–213.

[39] L.D. Stott, C.M. Tang, Reassessment of foraminiferal-based tropical sea surface $\delta^{18}O$ paleotemperatures, Paleoceanography 11 (1996) 37–56.

[40] K.B. Cutler, Carbon-14 Calibration and Sea-Level History from High-Precision Thorium-230 and Protactinium-231 Dating of Corals, Ph.D. Thesis, University of Minnesota, MN, 1999, 117 pp.

[41] M. Stuiver, P.J. Reimer, E. Bard, J.W. Beck, G.S. Burr, K.A. Hughen, B. Kromer, G. McCormac, J. Van der Plicht, M. Spurk, INTCAL98 radiocarbon age calibration, 24 000–0 cal BP, Radiocarbon 40 (1998) 1041–1083.

[42] S.J. Carpenter, K. Lohmann, Sr/Mg ratios of modern marine calcite: Empirical indicators of ocean chemistry and precipitation rate, Geochim. Cosmochim. Acta 56 (1992) 1837–1849.

[43] D. Nürnburg, J. Bijma, C. Hemleben, Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, Geochim. Cosmochim. Acta 60 (1996) 803–814.

[44] D.P. Schrag, G. Hampt, D.W. Murray, Pore fluid constraints on the temperature and oxygen isotopic composition of the glacial ocean, Science 272 (1996) 1930–1932.

[45] G. Wust, Stratification and Circulation of the Antillean-Caribbean Basins, Part 1, Columbia University Press, New York, 1964, 201 pp.

[46] D.W. Lea, T.A. Mashiotta, H.J. Spero, Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, Geochim. Cosmochim. Acta 63 (1999) 2369–2379.

[47] H. Fischer, M. Wahlen, J. Smith, D. Mastroianni, B. Deck, Ice core records of atmospheric CO_2 around the last three glacial terminations, Science 283 (1999) 1712–1714.