Chemistry of Benthic Foraminiferal Shells for Recording Ocean Environments: Cd/Ca, δ^{13}C and Mg/Ca

Kazuyo T<small>ACHIKAWA</small>[1] and Henry E<small>LDERFIELD</small>[2]

[1]*CEREGE, Europole de l'Arbois BP 80, 13545 Aix en Provence, France*
[2]*Department of Earth Sciences, University of Cambridge,
Downing St., Cambridge CB2 3EQ, England, U.K.*

Abstract. Cd/Ca, δ^{13}C and Mg/Ca of six species of benthic foraminifera with different microhabitat were analysed from throughout the sediment mixed layer at three well-characterised sites in the Northeastern Atlantic: *Cibicidoides wuellerstorfi*, *Uvigerina peregrina*, *Cibicides bradyi*, *Melonis barleeanum*, *Bulimina striata* and *Hoeglundina elegans*. Reductive cleaning decreased Mn/Ca and Cd/Ca of *C. wuellerstorfi* but did not significantly influence Mg/Ca and Sr/Ca values. A comparison of δ^{13}C in foraminifera with bottom water and pore waters has been used to estimate average calcification depths within the sediment for each species and thereby determine D_{Cd} based on the Cd concentrations at these depths. Pore waters are 2 to 4 times more enriched in Cd than bottom waters; consequently, D_{Cd} values are different from estimates based on bottom water Cd. Results give D_{Cd} of ~1 for all the infaunal species, with no significant water depth dependence. D_{Cd} for *C. wuellerstorfi* based on bottom water Cd are 3.2 ± 1.1 at 3600 m water depth and 3.9 ± 1.3 at 1900 m water depth, being consistent with D_{Cd} estimated from culture experiments. Based on this approach, equations are presented that link oxygen utilization to differences in δ^{13}C and Cd/Ca between epifaunal and infaunal species. The method shows good agreement with microelectrode profiles of porewater O_2 at the sites.

Keywords: benthic foraminifera, microhabitat, Cd/Ca, Mg/Ca, carbon isotopes, oxygen utilization

1. INTRODUCTION

Calcareous benthic foraminifera secrete calcium carbonate shells which preserve environmental information on the properties of sea waters in which they calcify. In particular, Cd/Ca, δ^{13}C and Mg/Ca recorded in benthic foraminiferal shells have been used as proxies of dissolved phosphate, carbon, and temperature in the deep ocean, respectively (Boyle, 1988, 1992; Duplessy *et al*., 1988; Charles and Fairbanks, 1990; Rosenthal *et al*., 1997; Lear *et al*., 2000, 2002; Martin *et al*., 2002). Recent studies, however, have revealed some complications related to i) different cleaning methods applied to foraminiferal shells to remove contaminating phases (Martin and Lea, 2002), ii) partial dissolution of shells on seafloor and within the sediments (McCorkle *et al*., 1995) and iii) microhabitat

effects (pore water influence) on benthic foraminiferal shell chemistry (McCorkle *et al.*, 1990; Tachikawa and Elderfield, 2002). This review discusses these points with special attention to the microhabitat effect.

Phosphorus and carbon are tightly linked during biological uptake and decomposition of organic matter. Therefore, a correlation between variations of Cd/Ca and $\delta^{13}C$ is expected unless factors other than the biological pump are involved. However, significant discrepancies in palaeochemical interpretations between those based on foraminiferal Cd/Ca and on $\delta^{13}C$ have been observed in certain oceanic regions, including the Southern Ocean which is a key zone for changing pCO_2 (Sarmiento and Toggweiler, 1984). One of the key issues is that of the effects of microhabitat on shell chemistry. Benthic foraminiferal $\delta^{13}C$ clearly shows the influence of pore waters (McCorkle *et al.*, 1990) whereas Cd/Ca of the selected epifaunal (living at the sediment-water interface) and shallow infaunal species (living within the sediments) are not significantly different from each other (Boyle, 1992).

In this work, we document Cd/Ca and $\delta^{13}C$ of six species of benthic foraminifera (*Cibicidoides wuellerstorfi*, *Uvigerina peregrina*, *Cibicides bradyi*, *Melonis barleeanum*, *Bulimina striata* and *Hoeglundina elegans*) to examine the influence of pore waters on foraminiferal Cd/Ca and $\delta^{13}C$. We consider how differences in Cd/Ca and $\delta^{13}C$ between epifaunal and infaunal species might be exploited in paleoceanography. Additionally, the influence of different cleaning methods on Mg/Ca was studied using *C. wuellerstorfi* and *U. peregrina*.

2. SAMPLES AND ANALYTICAL PROCEDURES

2.1 Foraminifera and water samples

Multicore samples were collected at three sites in the Northeastern Atlantic during the NERC BENthic BOundary layer processes (BENBO) programme in August 1996, May 1997 and August 1997 (Fig. 1). Organic flux is higher at the shallower sites (sites B and C) than at the deeper site (site A) (Thomson *et al.*, 2000). At site A, only the top 12 cm of the sediment is Holocene and <10 ky; the early Holocene and the glacial/interglacial sediments have been lost, probably from downslope erosion (Thomson *et al.*, 2000). All dead and living specimens were collected from the top 10 cm of the sediments, except for *C. wuellerstorfi* for the cleaning tests where the 10–30 cm section was used (this corresponds to a sediment age of 3000 to 6000 years; Thomson *et al.*, 2000). ^{210}Pb and ^{14}C indicate that the top 10 cm sediment layer consists of well bioturbated homogeneous Holocene sediments (Thomson *et al.*, 2000). Dead specimens were picked from the 300 to 350 μm fraction at sites A and C, and from the 250 to 300 μm fraction at site B. Stained specimens were picked from the >150 μm fraction. Bottom water samples were filtered using 0.4 μm filters. Pore water was extracted from sliced sediment cores by centrifugation under a N_2 atmosphere followed by filtration of the supernatant water through a 0.4 μm filter.

We classified six species of benthic foraminifera by microhabitat, according to the distribution of living specimens (Corliss and Chen, 1988; Corliss and
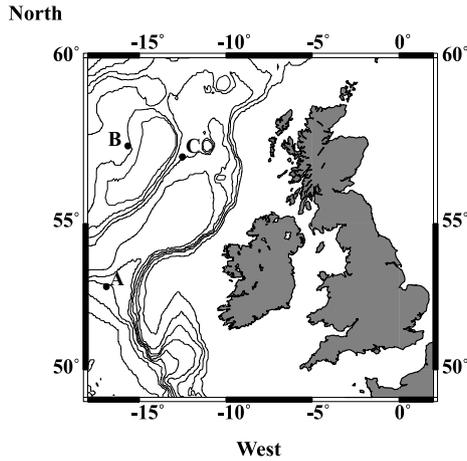
North

West

Fig. 1. Map showing the three BENBO sites in the Northeastern Atlantic. Site A (52°92′ N, 16°92′ W, water depth 3600 m), site B (57°43′ N, 15°68′ W, water depth 1100 m) and site C (57°91′ N, 12°52′ W, water depth 1900 m).

Emerson, 1990; McCorkle *et al*., 1990; Jorissen *et al*., 1998; van der Zwaan *et al*., 1999): *C. wuellerstorfi* and *H. elegans* are epifaunal (E); *C. bradyi*, *B. striata* and *U. peregrina* are shallow infaunal (SI) and *M. barleeanum* is intermediate infaunal (II). We have used these terms to indicate the relative calcification depth in the order of E ≤ SI ≤ II.

2.2 Cleaning methods of foraminiferal shells and instrumental analysis

Foraminifera shells contain contaminating phases which should be removed prior to chemical analysis. These phases are clay minerals, organic matter, Mn oxide coating and all the elements adsorbed on the shell surface (Boyle, 1981). To remove all the contaminants, we applied the multi-step cleaning method described by Boyle and Keigwin (1985/1986) then modified by Boyle and Rosenthal (1996) to Cd analyses. There has been discussion over the absolute necessity of the reductive cleaning to remove Mn oxide coating for Mg/Ca analysis (Brown and Elderfield, 1996; Martin and Lea, 2002; Lear *et al*., 2003). To investigate the influence of reductive cleaning on benthic foraminiferal Mg/Ca, we carried out a simple experiment where we compared samples cleaned as described above ("full cleaned") with those where the reductive cleaning step was omitted ("short cleaned"). This test was applied to *C. wuellerstorfi* (site C) and *U. peregrina* (site B). In addition to Mg/Ca, Sr/Ca was analysed to monitor potential dissolution of shells during the cleaning.

The detailed analytical procedures were described in Tachikawa and Elderfield (2002). Briefly, Cd was analysed by ID-TIMS (Rickaby *et al*., 2000) whereas as Ca, Mg, Sr and Mn concentrations were determined by ICP-AES (Varian Vista).

The analytical uncertainties estimated from replicate analyses are 2% for Ca measurement, 1% for Cd analysis and 2% for Mg/Ca. Total Cd blank is <0.5 pg and Ca and Mg blank is below detection limit.

3. INFLUENCE OF REDUCTIVE CLEANING TO BENTHIC FORAMINIFERAL Mg/Ca

We selected *C. wuellerstorfi* at site C (1900 m) from 10 to 30 cm in sediments where pore water data showed Mn^{2+} mobilisation and the presence of a Mn carbonate overgrowth on the "short-cleaned" specimens beneath 10 cm (Fig. 2a). "Short-cleaned" samples show smoothly increasing Mn/Ca with sediment depth, to ~80 μmol/mol at 15 cm and >120 μmol/mol at the basd of the core. Reductive cleaning did not affect Mn/Ca until 15 cm depth but, beneath this, reduced all Mn/Ca to less than 100 μmol/mol. Foraminiferal shells with Mn/Ca less than 100 μmol/mol are considered to be "successfully cleaned" (Boyle, 1983). Cd/Ca of the "full-cleaned" samples is lower and less scattered than that of "short-cleaned" samples, indicating the importance of reductive cleaning for Cd/Ca analysis (Fig. 2b). Mg/Ca of the "full-cleaned" and "short-cleaned" samples are 1.099 ± 0.111 ($n = 9$) and 1.254 ± 0.098 ($n = 9$), respectively (Fig. 2c). These values are, within error, the same as above 10 cm (Mg/Ca = 1.182 ± 0.068 mmol/mol, $n = 11$, Table 1). These results suggest that the effect of reductive cleaning on Mg/Ca is negligible comparing to chemical heterogeneity between different specimens. Our result is consistent with the observation for down core records by Lear *et al.* (2003). Sr/Ca of *C. wuellerstorfi* is not different between cleaning methods (Fig. 2d). Applying the Mg/Ca calibration for *C. wuellerstorfi* (Mg/Ca = 0.867exp(0.109T); Lear *et al.*, 2002) to the BENBO data (0–10 cm), we estimated a bottom water temperature (BWT) at site C at $2.8 \pm 0.5°C$. This estimate is in
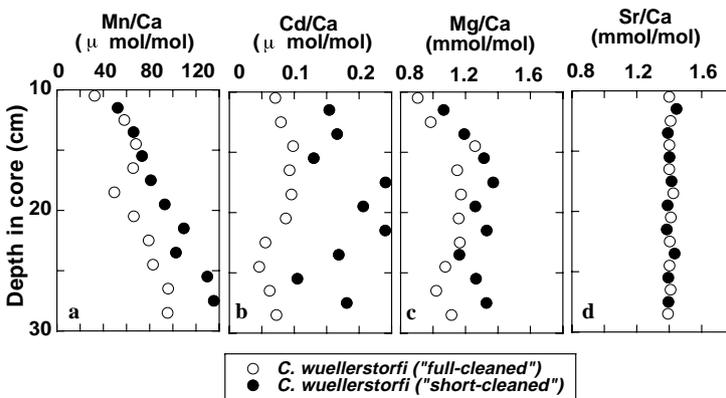

Fig. 2. Comparison of Mn/Ca (a), Cd/Ca (b), Mg/Ca (c) and Sr/Ca (d) in foraminifera with and without reductive cleaning to remove Mn-rich coatings. *C. wuellerstorfi* at site C (1900 m) from 10 to 30 cm within the sediments.

good agreement with *in situ* BWT of 3.0–3.1°C (Turley and Dixon, 2002).

We also compared "full-cleaned" and "short-cleaned" *U. peregrina* at site B (1100 m) within the upper 10 cm (Figs. 3a, 3b, 3c and 3d). Mn/Ca for "full-cleaned" and "short-cleaned" samples are both lower than 40 μmol/mol, suggesting that Mn oxide coating did not develop on the surface of this species (Fig. 3a). Cd/Ca and Sr/Ca do not show any significant difference between the cleaning methods (Figs. 3b and 3d). However, Mg/Ca of the "full-cleaned" samples (Mg/Ca = 1.280 ± 0.084, n = 13) is lower than that of the "short-cleaned" samples (Mg/Ca = 1.462 ± 0.084, n = 11, Fig. 3c). As Mn/Ca did not vary between the cleaning methods, the difference in Mg/Ca cannot be related to Mn oxide coating phase. It is probably due either to the presence of contaminating phases such as clay minerals or to partial dissolution of shells (Barker *et al.*, 2003). Applying the Mg/Ca calibration for *Uvigerina* spp. (Mg/Ca = 0.924exp(0.061T); Lear *et al.*, 2002) to the "full-cleaned" and "short-cleaned" samples, we obtained BWT at site B of 5.3 ± 1.0 and 7.5 ± 1.0°C, respectively (*in situ* BWT is 5.0 to 6.3°C; Turley and Dixon, 2002). It is worth noting that temperature-dependency of *U. peregrina* Mg/Ca is weaker than that of *C. wuellerstorfi* (Lear *et al.*, 2002). It is therefore possible that other environmental factors influence Mg/Ca of *U. peregrina*.

Table 1 compiles Mg/Ca of six species from the top 10 cm of the sediments, together with *in situ* BWT data (Turley and Dixon, 2002). There is no significant down core variability in Mg/Ca, suggesting the early diagenesis did not influence benthic foraminiferal Mg/Ca at the studied sites. Because of the narrow BWT range at the studied sites (2–6°C) and the difficulty to obtain the same species at all the sites, we are unable to establish Mg/Ca calibration at the BENBO sites.

Table 1. Mean values and the standard deviation *s* of Mg/Ca (mmol/mol) of dead foraminifera from the top 10 cm of the sediments.

	Site B	Site C	Site A
Water depth (m)	1100	1900	3600
Species			
C. wuellerstorfi	n.d.	1.182 ± 0.068 (n = 11)	1.149 ± 0.091 (n = 12)
U. peregrina	1.280 ± 0.084 (n = 13)	1.185 ± 0.051 (n = 4)	1.073 ± 0.079 (n = 8)
M. barleeanum	1.483 ± 0.094 (n = 12)	n.d.	1.259 ± 0.034 (n = 11)
B. striata	1.746 ± 0.129 (n = 7)	1.306 ± 0.120 (n = 12)	n.d.
C. bradyi	1.506 ± 0.073 (n = 11)	n.d.	n.d.
H. elegans[1]	n.d.	n.d.	0.305 ± 0.124 (n = 11)
BWT (°C)[2]	5.0–6.3	3.0–3.1	2.0–2.5

n.d. = not determined due to lack of specimens.

1. Mg/Ca of *H. elegans* is much lower than the data based on LA-ICP-MS technique (Reichart *et al.*, 2003). We are uncertain as to the reason for the discrepancy. One possibility is that, as *H. elegans* is an aragonite species, artificial dissolution of shells during the chemical cleaning could significantly lower Mg/Ca compared with calcitic benthic species.
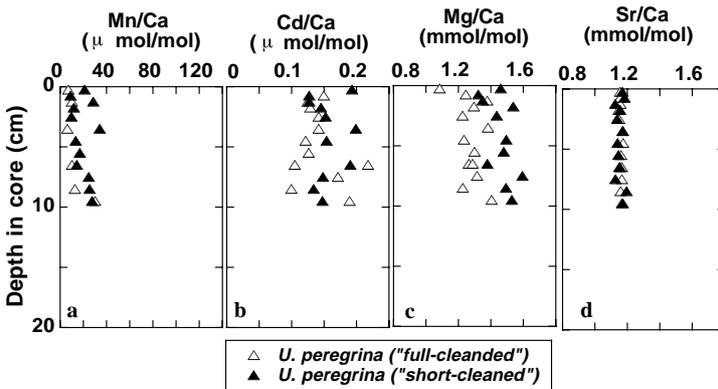
2. Turley and Dixon (2002).

Fig. 3. Comparison of Mn/Ca (a), Cd/Ca (b), Mg/Ca (c) and Sr/Ca (d) in foraminifera with and without reductive cleaning to remove Mn-rich coatings. *U. peregrine* at site B (1100 m) from 0 to 10 cm within the sediments.

However, as well as *C. wuellerstorfi* and *U. peregrina*, *M. barleeanum* shows a Mg/Ca temperature dependency consistent with the calibration by Lear *et al.* (2002).

4. PARTITION COEFFICIENT (D_{Cd}) TAKING INTO ACCOUNT MICROHABITAT

Cd/Ca in individual species of dead foraminifera are reasonably constant throughout down core (Fig. 4). Stained foraminiferal Cd/Ca (*U. peregrina* and *M. barleeanum* at site B) are the same as or slightly lower than that of dead specimens and show no down core depth dependency (see Tachikawa and Elderfield, 2002 for the detail of comparison between dead and stained specimens). The vertical lines in Fig. 4 show predicted $(Cd/Ca)_{foram}$ values defined from the equation $D_{Cd} = (Cd/Ca)_{foram}/(Cd/Ca)_{water}$ using bottom water Cd concentrations together with D_{Cd} proposed by Boyle (1992) and Boyle *et al.* (1995): D_{Cd} = 2.9 at site A, 1.3 at site B and 2.0 at site C for calcite species and D_{Cd} = 1.0 for *H. elegans*. Measured Cd/Ca of four sets of samples, *C. wuellerstorfi*, *U. peregrina* and *H. elegans* at site A, and *B. striata* at site C, are in good agreement with predicted $(Cd/Ca)_{foram}$ values. Cd/Ca of the other seven sets are higher than predicted $(Cd/Ca)_{foram}$ values. Because Cd concentrations in the pore waters are higher than in bottom waters, a pore water influence on shell chemistry is a potential (and obvious) explanation for the high foraminiferal Cd/Ca values. In the following, we determine D_{Cd} of each species taking into account their microhabitat.

Firstly, it is necessary to estimate calcification depths of each species. The vertical distribution of the stained foraminifera suggests that *U. peregrina* lives mainly within 0.5–1 cm whereas *M. barleeanum* lives deeper, principally 1.5–3 cm at site B (Tachikawa and Elderfield, 2002). To provide an alternative method which can be applied to all the analysed species, we have used $\delta^{13}C$ data. Provided
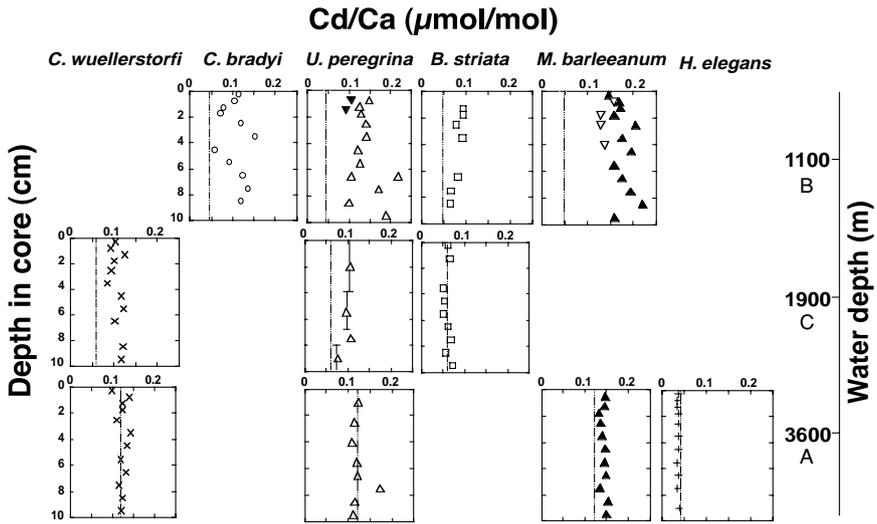
Cd/Ca (µmol/mol)

Fig. 4. Foraminiferal Cd/Ca versus depth in sediments. Right scale shows water depths of the sites: site B at 1100 m, site C at 1900 m and site A at 3600 m. Stained *U. peregrina* and *M. barleeanum* from site B are indicated with solid triangles and open triangles, respectively. Vertical lines show Cd/Ca of foraminifera estimated from bottom water Cd concentrations and D_{Cd} proposed by Boyle (1992) and Boyle *et al*. (1995). D_{Cd} = 2.9 at site A, 1.3 at site B and 2.0 at site C for calcite species and D_{Cd} = 1.0 for *H. elegans*.

vital effects on foraminiferal δ^{13}C are negligible, calcification depths may be estimated from δ^{13}C in the pore waters. Mean foraminiferal δ^{13}C of each species (Table 2) have been placed on pore water δ^{13}C model curves (Fig. 5) and the calcification depths of each species calculated from the equations of the model curves. According to this δ^{13}C comparison method, all the species examined calcified within the top 2 cm of the sediments (Table 2). For *U. peregrina* and *M. barleeanum* we can compare calcification depths based on the distribution of stained foraminifera and the δ^{13}C method. The two estimates for *U. peregrina* is in good agreement, suggesting that vital effect is negligible for this species. In contrast, the δ^{13}C method gives significantly shallower depth for *M. barleeanum* (Table 2), suggesting that the vital effect is not negligible for this species. However, the pore water Cd concentration is almost constant within this depth range (Table 2). Thus, vital effects give only minor influence on D_{Cd} estimates for this species. A detailed discussion on vital effects on D_{Cd} is given in Tachikawa and Elderfield (2002). Because δ^{13}C of *H. elegans* is higher than calcitic species, we cannot apply the δ^{13}C method and have simply assumed that the species is epifaunal.

Next we determine pore water Cd concentrations at the calcification depths by interpolating measured Cd concentrations to the calcification depths derived from δ^{13}C (Table 2). Pore water Ca was assumed to be 10 mmol/kg and

Table 2. Foraminiferal Cd/Ca and $\delta^{13}C$, estimated calcification depths, dissolved Cd concentrations at calcification depths and consequent D_{Cd}.

Species	Water depth (m)	Foraminiferal Cd/Ca (μmol/mol)	Foraminiferal $\delta^{13}C$ (VPDB)	Calcification depth (cm)*	Cd concentration (nmol/kg)	D_{Cd}
Epifaunal						
C. wuellerstorfi	1900	0.107 ± 0.014	1.09 ± 0.24	−0.2–0.2	0.3 ± 0.2	3.9 ± 1.3
C. wuellerstorfi	3600	0.125 ± 0.013	0.82 ± 0.18	−0.1–0.1	0.4 ± 0.2	3.2 ± 1.1
H. elegans	3600	0.036 ± 0.001	2.59 ± 0.16	0	0.4 ± 0.2	0.9 ± 0.3
Infaunal						
U. peregrina	1100	0.143 ± 0.035	−0.31 ± 0.15	0.1–0.5	1.2 ± 0.2	1.2 ± 0.2
U. peregrina#	1100	0.100 ± 0.009	−0.62 ± 0.14	0.2–0.9 (0.5~1.0)	1.2 ± 0.2	0.8 ± 0.1
U. peregrina	1900	0.097 ± 0.014	0.11 ± 0.17	0.1–0.7	1.0 ± 0.4	1.1 ± 0.3
U. peregrina	3600	0.123 ± 0.021	−0.52 ± 0.19	0.3~1.0	1.4 ± 0.2	0.9 ± 0.1
M. barleeanum	1100	0.177 ± 0.022	−0.53 ± 0.10	0.1–0.7	1.2 ± 0.2	1.4 ± 0.2
M. barleeanum#	1100	0.138 ± 0.013	−0.89 ± 0.19	0.3–1.7 (1.5~3)	1.5 ± 0.6	1.0 ± 0.3
M. barleeanum	3600	0.143 ± 0.007	−0.47 ± 0.42	0.2–1.2	1.4 ± 0.2	1.0 ± 0.1
B. striata	1100	0.081 ± 0.013	0.11 ± 0.28	0–0.3	1.2 ± 0.1	0.7 ± 0.1
B. striata	1900	0.061 ± 0.007	0.28 ± 0.20	0–0.6	1.0 ± 0.4	0.7 ± 0.2
C. bradyi	1100	0.108 ± 0.029	0.31 ± 0.13	0–0.2	1.2 ± 0.1	0.9 ± 0.1
Corrected for vital effect						
M. barleeanum	1100	0.177 ± 0.022		0.4–1.5	1.5 ± 0.6	1.2 ± 0.3
M. barleeanum#	1100	0.138 ± 0.013		0.9–3.8	1.5 ± 0.6	1.0 ± 0.2
M. barleeanum	3600	0.143 ± 0.007		0.5–2.2	1.4 ± 0.1	1.1 ± 0.1

#Stained specimens.

*Depth in core. Negative depth corresponds to bottom water. Range between brackets indicates calcification depth estimated based on stained specimen distribution.
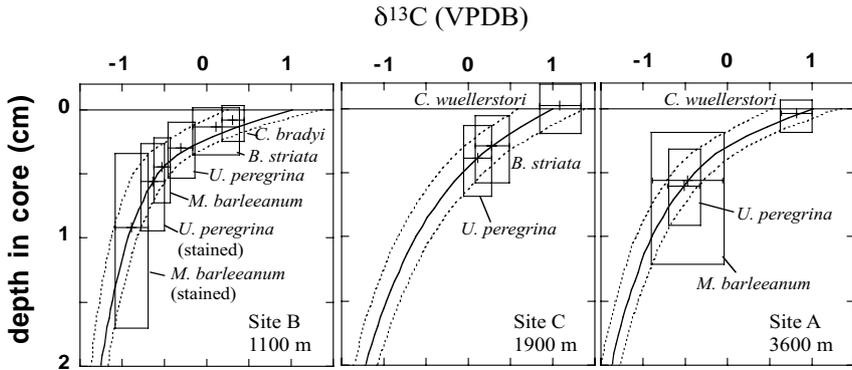
$$\delta^{13}C \text{ (VPDB)}$$

Fig. 5. Comparison of pore water and foraminiferal $\delta^{13}C$ showing inferred calcification depth of foraminiferal species (rectangles). Mean foraminiferal $\delta^{13}C$ (Table 2) are fitted to the modelled $\delta^{13}C$ curve of pore water: $\delta^{13}C = 3.30(z + 0.23)^{-0.29} - 4$ ($R = 0.91$) at site A; $\delta^{13}C = 3.10(z + 0.06)^{-0.17} - 4$ ($R = 0.92$) at site B; $\delta^{13}C = 4.08(z + 0.60)^{-0.40} - 4$ ($R = 0.95$) at site C. Bottom water $\delta^{13}C$ is assumed to be +1‰ at the three sites based on data at GEOSECS station 23 (60°40′ N, 18°62′ W). The quoted uncertainties in estimated calcification depths are based on the standard deviations of foraminiferal $\delta^{13}C$ from the top 10 cm of the sediments and depth intervals of pore water sampling (0.5 cm for the top 2 cm of sediments). Pore water $\delta^{13}C$ data are from H. Kennedy and S. Papadimitriou (pers. comm.). See Tachikawa and Elderfield (2002) for detail.

foraminiferal Cd/Ca values were the means from the top 10 cm of the sediments. D_{Cd} estimates obtained in this manner (Table 2) are clearly different from water depth-dependent D_{Cd} values (Boyle, 1992). Estimated D_{Cd} for all the analysed SI and II species (*U. peregrina*, *C. bradyi*, *M. barleeanum*, *B. striata*) is ~1 with no significant depth dependence. D_{Cd} for *H. elegans* (E) is 0.9 ± 0.3, being in good agreement with Boyle *et al.* (1995). D_{Cd} for *C. wuellerstorfi* are 3.9 ± 1.3 at 1900 m (site C) and 3.2 ± 1.1 at 3600 m (site A). D_{Cd} at site C is significantly higher than Boyle's depth-dependent D_{Cd} (2.0). The reason for this offset has not been totally clarified. Recently, Havach *et al.* (2001) reported D_{Cd} for another *Cibicidoides species* (*C. pachyderma*) based on culture experiments. Their D_{Cd} (4 ± 2) is in good agreement with our D_{Cd}.

5. ESTIMATION OF OXYGEN UTILIZATION USING FORAMINIFERAL $\delta^{13}C$ AND Cd/Ca

McCorkle *et al.* (1990) suggested that the difference in $\delta^{13}C$ between epifaunal and deep infaunal species occupying extremely low O_2 environments might be used to estimate bottom water dissolved oxygen concentrations. In the following, we calculate pore water oxygen concentration from foraminiferal shell chemistry and compare it with values determined from microelectrode measurements (Black *et al.*, 2001).

The mass balance equations for the C system (ignoring $CaCO_3$ dissolution) are

$$[TCO_2]_{\text{porewater}} = [TCO_2]_{\text{bottomwater}} + [\Delta TCO_2]$$

$$[TCO_2]_{\text{porewater}} \delta^{13}C_{\text{infaunal}} = [TCO_2]_{\text{bottomwater}} \delta^{13}C_{\text{epifaunal}} + [\Delta TCO_2] \delta^{13}C_{\text{organic}}$$

where $[\Delta TCO_2]$ is the increase in total inorganic carbon resulting from organic diagenesis and $\delta^{13}C_{\text{organic}}$ is the $\delta^{13}C$ of organic matter.

The equivalent equation for dissolved oxygen is

$$[\Delta O_2] = [O_2]_{\text{bottomwater}} - [O_2]_{\text{porewater}}$$

(note, we have subtracted porewater from bottomwater $[O_2]$ to make $[\Delta O_2]$ positive). $[\Delta O_2]$ corresponds to oxygen utilization. We need to correct for diffusion, and assuming Redfield stoichiometry.

$$\frac{\text{Flux}[O_2]}{\text{Flux}[TCO_2]} = \frac{138}{106} = \frac{D_{O_2}[\Delta O_2]}{D_{TCO_2}[\Delta TCO_2]}$$

where D_{O_2} and D_{CO_2} are diffusion coefficients for O_2 and TCO_2, respectively. This gives

$$[\Delta O_2] = [TCO_2]_{\text{bottomwater}} \frac{D_{TO_2}}{D_{O_2}} \frac{138}{106} \left\{ \frac{\delta^{13}C_{\text{epifaunal}} - \delta^{13}C_{\text{infaunal}}}{\delta^{13}C_{\text{infaunal}} - \delta^{13}C_{\text{organic}}} \right\}. \qquad (1)$$

Equation (1) is simplified through assuming that variations in $\delta^{13}C_{\text{infaunal}}$ are small relative to the $\delta^{13}C_{\text{organic}}$

$$[\Delta O_2] = \frac{[TCO_2]_{\text{bottomwater}}}{-\delta^{13}C_{\text{organic}}} \frac{D_{TCO_2}}{D_{O_2}} \frac{138}{106} \left\{ \delta^{13}C_{\text{epifaunal}} - \delta^{13}C_{\text{infaunal}} \right\}$$

or

$$[O_2]_{\text{porewater}} = \frac{[TCO_2]_{\text{bottomwater}}}{\delta^{13}C_{\text{organic}}} \frac{D_{TCO_2}}{D_{O_2}} \frac{138}{106} \Delta\delta^{13}C_{\text{foram}} + [O_2]_{\text{bottomwater}}. \qquad (2)$$

The gradient of $\Delta\delta^{13}C_{\text{foram}}$ ($\delta^{13}C_{\text{epifaunal}} - \delta^{13}C_{\text{infaunal}}$) versus $[O_2]_{\text{porewater}}$ in Eq. (2) is about $-20/2200 \times 1.23/0.61 \times 106/138 = -0.014‰/\mu\text{mol/kg}$ ($[O_2]_{\text{porewater}}/\Delta\delta^{13}C_{\text{foram}} = -71\ \mu\text{mol/kg/‰}$); diffusion coefficients ($10^{-10}\ \text{m}^2\text{s}^{-1}$) from Schulz (2000).
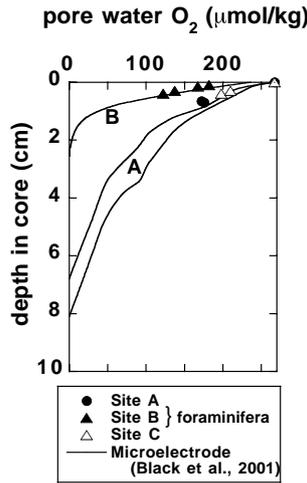
Fig. 6. Pore water O_2 concentrations calculated from benthic foraminiferal $\delta^{13}C$ using Eq. (2) compared with measured values (Black *et al.*, 2001). At site B, $\Delta\delta^{13}C_{foram}$ was calculated from infaunal $\delta^{13}C$ and bottom water $\delta^{13}C$ because epifaunal $\delta^{13}C$ is not available.

We have used Eq. (2) to estimate pore water O_2 concentrations versus depth within the sediment, using bottom water O_2. The obtained O_2 concentrations are compared with values determined from microelectrode measurements at sites A and B (Fig. 6). The field data show that the O_2 penetration depths, about 7 cm (Black *et al.*, 2001), are significantly below the calcification depths (<1 cm). Considering the uncertainties in estimation of foraminiferal habitat depths (Fig. 5) and temporal variability in O_2 profiles, the agreement is excellent.

This method may be applied also to Cd/Ca under the condition that the stoichiometry of Cd/P is maintained in pore water. Although CdS precipitation evokes de-coupling of Cd from P (McCorkle and Klinkhammer, 1991), all the analysed foraminifera are expected to calcify at the top 1 cm of the sediments where pore water oxygen is not exhausted (Fig. 6).

For Cd, we write the additional expressions

$$[Cd]_{diagenesis} = [Cd]_{porewater} - [Cd]_{bottomwater} = [\Delta Cd]$$

$$[\Delta Cd] = [Ca]\{(Cd/Ca)_{porewater} - (Cd/Ca)_{bottomwater}\}$$

$$\frac{Flux[O_2]}{Flux[Cd]} = \frac{138}{[Cd/P]} = \frac{D_{O_2}[\Delta O_2]}{D'_{Cd}[\Delta Cd]}.$$
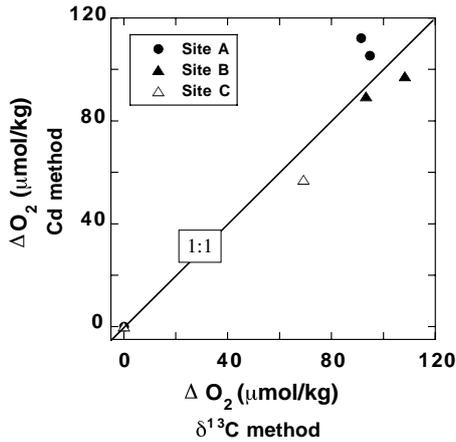
Fig. 7. O_2 utilization calculated from benthic foraminiferal $\delta^{13}C$ using Eq. (2) compared with utilization calculated from benthic foraminiferal Cd/Ca using Eq. (3). The results of three benthic foraminifera frequently used for palaeoceanographic studies are indicated: *C. wuellerstorfi*, *U. peregrina* and *M. barleeanum*. As epifaunal foraminiferal Cd/Ca is not available at site B, the bottom water Cd/Ca was used instead of $(Cd/Ca)_{epifaunal}/D_{Cd}$.

This gives

$$[\Delta O_2] = \frac{138}{[Cd/P]} \frac{D'_{Cd}}{D_{O_2}} [Ca] \left\{ \left[\frac{Cd/Ca}{D_{Cd}} \right]_{infaunal} - \left[\frac{Cd/Ca}{D_{Cd}} \right]_{epifaunal} \right\}. \qquad (3)$$

Note that D'_{Cd} is a diffusion coefficient ($D'_{Cd} = 0.385 \times 10^{-10} \, m^2 s^{-1}$; Schulz, 2000) and D_{Cd} is a partition coefficient (Table 2). Although Cd/P ratio in fresh organic matter is variable, we apply seawater dissolved Cd/P of 4×10^{-4} mol/mol for the first approximation. The estimates of O_2 utilization obtained using Cd/Ca are similar to the values based on $\delta^{13}C$ (Fig. 7). This is, in part, a consequence of the tight coupling between the two tracers in the estimation of calcification depths and Cd partition coefficients. Building on the work of McCorkle *et al.* (1990), it cannot be assumed that the deepest infaunal species examined will always reflect very low O_2 conditions. Therefore, this method will not allow estimation of bottom water oxygen concentrations unless some assumption is made as to the O_2 utilization regime. Nevertheless, the method would be valuable to address estimation of organic matter rain rates in the paleoceanographic record through the measure of O_2 utilization.

6. SUMMARY AND CONCLUSIONS

Cd/Ca, $\delta^{13}C$ and Mg/Ca of six species of benthic foraminifera with different microhabitat were analysed for Holocene sediments from three well characterised

sites in the Northeastern Atlantic. To investigate the influence of the reductive cleaning on foraminiferal Mg/Ca, "full-cleaning" and "short-cleaning" (where the reductive cleaning step was omitted) were applied to the species frequently used for palaeoceanographic studies. The reductive cleaning decreased Mn/Ca and Cd/Ca of *Cibicidoides wuellerstorfi* but did not influence significantly Mg/Ca and Sr/Ca values.

Cd/Ca ratios of some species of infaunal foraminifera are higher than (Cd/Ca)$_{foram}$ predicted from bottom water Cd and the depth-dependent D$_{Cd}$ values, suggesting that the shell chemistry is influenced by pore water composition. We propose a D$_{Cd}$ of ~1 for all the infaunal species, with no significant water depth dependence and D$_{Cd}$ for *C. wuellerstorfi* of 3.2 ± 1.1 at 3600 m water depth and 3.9 ± 1.3 at 1900 m water depth. Differences in δ^{13}C and Cd/Ca between epifaunal and infaunal species have been used to estimate O$_2$ utilization and show good agreement with O$_2$ microelectrode measurements.

REFERENCES

Barker S., M. Greaves and H. Elderfield (2003) A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochem. Geophys. Geosyst.* **4** (No. 9, 8407), doi:10.1029/2003GC000559.

Black K. S., G. R. Fones, O. C. Peppe, H. A. Kennedy and I. Bentaleb (2001) An autonomous benthic lander: preliminary observation from the UK BENBO thematic programme. *Continental Shelf Res.* **21**, 859–877.

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

Boyle E. A. (1983) Manganese carbonate overgrowths on foraminiferal tests. *Geochim. Cosmochim. Acta* **47**, 1815–1819.

Boyle E. A. (1988) Cadmium: chemical tracer of deepwater paleoceanography. *Paleoceanography* **3**, 471–489.

Boyle E. A. (1992) Cadmium and δ^{13}C paleochemical ocean distributions during the stage 2 glacial maximum. *Annu. Rev. Earth Planet. Sci.* **20**, 245–287.

Boyle E. A. and L. D. Keigwin (1985/1986) Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories. *Earth Planet. Sci. Lett.* **76**, 135–150.

Boyle E. A. and Y. Rosenthal (1996) Chemical hydrography of the South Atlantic during the last glacial maximum: δ^{13}C vs. Cd. In *The South Atlantic: Present and Past Circulation* (ed. G. Wefer, W. H. Berger, G. Siedler and D. Webb), pp. 423–443. Springer-Verlag.

Boyle E. A., L. Labeyrie and J.-C. Duplessy (1995) Calcitic foraminiferal data confirmed by cadmium in aragonite *Hoeglundina*: Application to the last glacial maximum in the northern Indian Ocean. *Paleoceanography* **10**, 881–900.

Brown S. J. and H. Elderfield (1996) Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: Evidence of shallow Mg-dependent dissolution. *Paleoceanography* **11**, 543–551.

Charles C. D. and R. G. Fairbanks (1990) Glacial to interglacial changes in the isotopic gradients of southern ocean surface water. In *Geological History of the Polar Oceans: Arctic Versus Antarctic* (ed. U. Bleil and J. Thiede), pp. 519–538. Kluwer Academic, Boston, Mass.

Corliss B. H. and C. Chen (1988) Morphotype patterns of Norwegian Sea deep-sea benthic foraminifera and ecological implications. *Geology* **16**, 716–719.

Corliss B. H. and S. Emerson (1990) Distribution of Rose Bengal stained deep-sea benthic foraminifera from the Nova Scotian continental margin and Gulf of Maine. *Deep-Sea Res*. **37**, 381–400.

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

Havach S. M., G. T. Chandler, A. Wilson-Finelli and T. J. Shaw (2001) Experimental determination of trace element partition coefficients in cultured benthic foraminifera. *Geochim. Cosmochim. Acta* **65**, 1277–1283.

Jorissen F. J., I. Wittling, J. P. Peypouquet, C. Rabouille and J. C. Relexans (1998) Live benthic foraminiferal faunas off Cape Blanc, NW-Africa: community structure and microhabitats. *Deep-Sea Res*. **45**, 2157–2188.

Lear C. H., H. Elderfield and P. A. Wilson (2000) Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* **287**, 269–272.

Lear C. H., Y. Rosenthal and N. Slowey (2002) Benthic foraminiferal Mg/Ca-paleothermometry: A revised core-top calibration. *Geochim. Cosmochim. Acta* **66**(19), 3375–3387.

Lear C. H., Y. Rosenthal and J. D. Wright (2003) The closing of a seaway: ocean water masses and global climate change. *Earth Planet. Sci. Lett*. **210**, 425–436.

Martin P. A. and D. W. Lea (2002) A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca. *Geochem. Geophys. Geosyst*. **3**(10), 8401, doi:10.1029/2001GC000280.

Martin P. A., D. W. Lea, Y. Rosenthal, N. J. Shackleton, M. Sarnthein and T. Papenfuss (2002) Quaternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca. *Earth Planet. Sci. Lett*. **198**, 193–209.

McCorkle D. C. and G. P. Klinkhammer (1991) Porewater cadmium geochemistry and the porewater cadmium: δ^{13}C relationship. *Geochim. Cosmochim. Acta* **55**, 161–168.

McCorkle D. C., L. D. Keigwin, B. H. Corliss and S. R. Emerson (1990) The influence of microhabitats on the carbon isotopic composition of deep-sea benthic foraminifera. *Paleoceanography* **5**(2), 161–185.

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

Reichart G.-J., F. Jorissen, P. Anschutz and P. R. D. Mason (2003) Single foraminiferal test chemistry records the marine environment. *Geology* **31**, 355–358.

Rickaby R. E. M., M. J. Greaves and H. Elderfield (2000) Cd in planktonic and benthic foraminiferal shells determined by thermal ionisation mass spectrometry. *Geochim. Cosmochim. Acta* **64**, 1229–1236.

Rosenthal Y., E. A. Boyle and N. Slowey (1997) 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**, 3633–3643.

Sarmiento J. L. and J. R. Toggweiler (1984) A new model for the role of the ocean in determining atmospheric pCO$_2$. *Nature* **308**, 621–624.

Schulz H. D. (2000) Quantification of early diagenesis: dissolved constituents in marine pore water. In *Marine Geochemistry* (ed. H. D. Schultz and M. Zabel), pp. 87–128. Springer-Verlag.

Tachikawa K. and H. Elderfield (2002) Microhabitat Effects on Cd/Ca and Carbon Isotopes of Benthic Foraminiferal Shells. *Earth Planet. Sci. Lett*. **202**, 607–624.

Thomson J., L. Brown, S. Nixon, G. T. Cook and A. B. MacKenzie (2000) Bioturbation and Holocene sediment accumulation fluxes in the north-east Atlantic Ocean (Benthic Boundary Layer Experiment sites). *Mar. Geol*. **169**, 21–39.

Turley C. M. and J. L. Dixon (2002) Bacterial numbers and growth in surficial deep-sea sediments and phytodetritus in the NE Atlantic: Relationships with particulate organic carbon and total nitrogen. *Deep-Sea Res. I* **49**, 815–826.

van der Zwaan G. J., I. A. P. Duijnstee, M. den Dulk, S. R. Ernst, N. T. Jannink and T. J. Kouwenhoven (1999) Benthic foraminifers: proxies or problem? A review of paleoecological concepts. *Earth-Sci. Rev*. **46**, 213–236.

K. Tachikawa (e-mail: kazuyo@cerege.fr) and H. Elderfield