Lack of a significant temperature influence on the incorporation of Cd into benthic foraminiferal tests

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[1] Benthic foraminiferal Cd/Ca is an important proxy for seawater paleonutrient concentrations and therefore deep ocean paleocirculation. Although previous work suggests that the incorporation of Cd into benthic foraminiferal calcite is insensitive to temperature, at least one species of planktonic foraminifer appears to be strongly influenced. The present study provides a closer look at the relationship between benthic Cd partition coefficients and temperature, using new and previously published data from the Bahama Banks. Neither calcitic taxa nor the aragonitic Hoeglundina elegans exhibits any consistent changes in partition coefficients over the range 4 to 18°C.

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1. Introduction

[2] Cd/Ca ratios in the tests of benthic foraminifera from modern sediments are strongly correlated with seawater dissolved Cd concentrations [Hester and Boyle, 1982; Boyle, 1988]. Since the distribution of seawater Cd closely resembles that of the nutrient PO₄ [Boyle et al., 1976; Boyle, 1988], benthic foraminiferal Cd/Ca has been used to infer nutrient concentrations and water mass reorganizations during the past [e.g., Boyle and Keigwin, 1982, 1985/1986, 1987; Boyle, 1992; Beveridge et al., 1995; Marchitto et al., 1998, 2002; Zahn and Stuber, 2002]. Boyle [1992] showed that the incorporation of Cd into benthic foraminiferal calcite, represented by the empirical partition coefficient \( D_{\text{Cd}} \),

\[
D_{\text{Cd}} = (\text{Cd/Ca})_{\text{foram}} / (\text{Cd/Ca})_{\text{seawater}},
\]

varies with water depth:

\[
D_{\text{Cd}} = 1.3 \text{ for } < 1150 \text{ m},
\]

\[
D_{\text{Cd}} = 1.3 + (\text{depth} - 1150)(1.6/1850) \text{ for } 1150 - 3000 \text{ m},
\]

\[
D_{\text{Cd}} = 2.9 \text{ for } > 3000 \text{ m}.
\]
In contrast, $D_{\text{Cd}}$ for the aragonitic benthic foraminifer *Hoeglundina elegans* appears to be independent of water depth, with a value of 1 [Boyle et al., 1995]. Limited data suggested that water temperature was not an important influence on $D_{\text{Cd}}$ but Boyle [1992] acknowledged that he could not confidently rule it out. Rosenthal et al. [1997] analyzed several taxa from a range of relatively shallow water depths (301–1585 m) and warm temperatures (4–18$^\circ$C) on Little Bahama Bank. Although no explicit comparison was made between $D_{\text{Cd}}$ and temperature, Rosenthal et al. [1997] concluded that temperature must not exert a significant influence because their measured Cd/Ca values were close to predictions using the depth-dependent $D_{\text{Cd}}$ of Boyle [1992].

[1] Rickaby and Elderfield [1999] subsequently measured Cd/Ca in the planktonic foraminifer *Globigerinoides bulloides* from a latitudinal transect of core tops in the North Atlantic. Inferred partition coefficients were found to increase sharply with temperature ($\sim$15% per $^\circ$C over the range 8–15$^\circ$C):

$$D_{\text{Cd}} = 0.637 \cdot e^{0.15T}. \quad (5)$$

Although *G. bulloides* partition coefficients determined from laboratory culturing experiments at 22$^\circ$C ($D_{\text{Cd}} = 1.9 \pm 0.2$ [Mashiotta et al., 1997]) and 28–30$^\circ$C ($D_{\text{Cd}} \approx 2–4$ [Delaney, 1989]) are much lower than those predicted by Rickaby and Elderfield’s [1999] observations, the core top data are compelling.

[2] Should we therefore expect Cd/Ca in benthic taxa to be similarly influenced by temperature? Mg/Ca is strongly temperature dependent in both planktonic and benthic foraminifera, though clear differences in sensitivity exist [e.g., Lea et al., 1999; Lear et al., 2002]. There are also indications that benthic Mg/Ca responds more linearly to temperature than planktonic Mg/Ca [Toyofuku et al., 2000; Marchitto and deMenocal, 2003]. Sr/Ca increases slightly with temperature in planktonic foraminifera (with large inter-genus differences) [Lea et al., 1999; Elderfield et al., 2000], but no temperature effect has yet been demonstrated for benthic taxa, possibly because it is masked by the decrease of Sr/Ca with water depth [Elderfield et al., 1996; Rosenthal et al., 1997]. On the basis of these observations it is unclear whether or not benthic foraminiferal Cd/Ca should behave similarly to *G. bulloides* Cd/Ca. A reexamination of the relationship between benthic foraminiferal Cd partition coefficients and temperature is therefore warranted.

2. Materials and Methods

[5] Seven taxa of benthic foraminifera (*Cibicidoides kullenbergi*, *C. pachyderma* (cf. *floridanus*), *C. wuellerstorfi*, *Hoeglundina elegans*, *Planulina ariminensis*, *P. foveolata*, and *Uvigerina* spp.) were picked from 14 core tops and two grab samples from Little and Great Bahama Banks (Table 1). These sites span a range of 334–1477 m water depth and 4.2–17.7$^\circ$C (based on CTD station 84C from Slowey and Curry [1995]). Previous downcore work on the gravity and piston cores established that these surface sediments are late Holocene in age, with sedimentation rates of $\sim$5–20 cm kyr$^{-1}$ during the Holocene [Slowey and Curry, 1995]. Core top benthic foraminiferal $^{18}$O measurements are in excellent agreement with predictions based on modern seawater temperatures and $^{18}$O [Slowey and Curry, 1995; Lynch-Stieglitz et al., 1999]. Although 12 of the cores used here were collected on the same cruise (R/V Oceanus 205-2) as those used by Boyle et al. [1995] and Rosenthal et al. [1997], only one core from each study was reanalyzed.

[6] Bottom water Cd concentrations were estimated from dissolved PO$_4$ measurements made on samples collected during SSV Westward cruise 120A [Marchitto et al., 1998], using the “global” Cd:PO$_4$ relationship of Boyle [1988]. Seawater Ca was taken to be uniform at 0.01 mol kg$^{-1}$ [Boyle, 1992]. Cd partition coefficients were then calculated from foraminiferal Cd/Ca using equation (1), assuming that all species calcify from bottom waters (not pore waters). This is a good assumption for epifaunal species, and thus for all taxa measured here except the shallow infaunal *Uvigerina* [Tachikawa and Elderfield, 2002].

[7] Each foraminiferal sample typically consisted of $\sim$5–20 individuals (>250 $\mu$m) and was reductively and oxidatively cleaned following the methods of Boyle and Keigwin [1985/1986] as modified by Boyle and Rosenthal [1996]. Some replicates were split after crushing, while others represent separate picks from the same samples, which results in significantly worse reproducibility [Boyle, 1995]. Cd and Mn (used to monitor the
probability of contamination by Mn-carbonate overgrowths (Boyle, 1983) were measured by graphite furnace atomic absorption spectrophotometry (AAS) and Ca was measured by flame AAS, all on a Hitachi Z-8200. Analytical precision is ±3–5% for Cd/Ca and ±8–9% for Mn/Ca, on the basis of frequent analyses of three gravimetric consistency standards that simulate typical foraminiferal chemistry. Cross-calibration with E. Boyle, using both gravimetric standards and benthic foraminferal samples, revealed no significant analytical offset between the two labs.

3. Results and Discussion

3.1. Cd/Ca in Calcitic Taxa

A total of 61 Cd/Ca measurements were made on calcitic benthic foraminifera from 15 sites (Figure 1 and Table 2). Only three of these measurements are omitted (not shown in Figure 1) because of obvious contamination (Cd/Ca values much higher than replicates). Mn/Ca ratios are mostly below 20 μmol mol⁻¹ and all are below 50 μmol mol⁻¹, suggesting that Mn-carbonate overgrowths are not a significant source of contamination. The vertical profile of Cd/Ca is generally in good agreement with predictions based on seawater Cd estimates and the depth-dependent partition coefficients of Boyle [1992]. Overall agreement with Rosenthal et al. [1997] is also good, though their means in deeper waters (below ~800 m) tend to be slightly higher (Figure 1b).

3.2. Cd/Ca in Hoeglundina elegans

Results for the aragonitic species H. elegans were presented by Marchitto et al. [1998] and are reproduced here. A total of 54 H. elegans Cd/Ca measurements were made at 15 sites, with two measurements excluded because of apparent contamination (Figure 2 and Table 2). Negligible Mn/Ca ratios, all below the detection limit of 3 μmol mol⁻¹, reflect the apparent immunity of H. elegans to Mn-carbonate overgrowths [Boyle et al., 1995]. The vertical profile of Cd/Ca is again in good agreement with predicted values using a partition coefficient of 1 [Boyle et al., 1995]. Boyle et al. [1995] measured H. elegans Cd/Ca in the same Little Bahama Bank cores used by Rosenthal et al. [1997] and found values generally lower than those presented here (Figure 2b). Although our interlaboratory calibra-

Table 1. Sediment Cores and Grab Samples, With Estimated Bottom Water Temperatures and Cd Concentrations

<table>
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<tr>
<th>Core</th>
<th>Latitude, °N</th>
<th>Longitude, °W</th>
<th>Depth, m</th>
<th>Temp., °C</th>
<th>Cd, nmol/kg</th>
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<tr>
<td>W120A-15SG</td>
<td>26.570</td>
<td>77.968</td>
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aBC, Box Core; GGC, Giant Gravity Core; JPC, Jumbo Piston Core; SG, Shipek Grab Sample.
tion revealed no significant offset between the two labs, a slight analytical difference could exist at the very low Cd concentrations of these samples. Note that although the offset is systematic, it is smaller than the average reproducibility of replicate picks from the same foraminiferal sample (±0.023 μmol mol⁻¹) [Boyle, 1995].

3.3. Cd Partition Coefficients and Temperature

[11] Inferred partition coefficients for individual species are plotted versus water depth in Figure 3, along with the local temperature profile (red line) and the partition coefficients predicted by those temperatures if benthic foraminifera behaved like Rickaby and Elderfield’s [1999] G. bulloides (black line). Also shown are Boyle’s predicted D_Cd values for H. elegans (dotted line) [Boyle et al., 1995] and calcitic taxa (dashed line) [Boyle, 1992]. Overall, the Bahama Banks data suggest no significant increase of benthic D_Cd with water temperature.

[12] Partition coefficients for individual species are plotted versus temperature in Figure 4a and fitted using exponential equations of the form

\[ D_{\text{Cd}} = ae^{bT}, \]

with parameters (a and b) and statistics listed in Table 3. Only two of these regressions are significant at the 5% level: C. pachyderma (r² = 0.22, P = 0.02, n = 25) and P. foveolata (r² = 0.74, P = 0.03, n = 6). However, removing just one measurement from each regression (the highest C. pachyderma at 16.1°C and the single P. foveolata at 17.7°C) renders them insignificant (r² = 0.14, P = 0.07, and r² = 0.00, P = 0.98, respectively). Although these two suspect data are not anomalously high in terms of Cd/Ca (see two shallowest cores in Figure 1a), their D_Cd values are necessarily uncertain because of error magnification in shallow, low-Cd waters. None of the other taxa are significantly related to temperature, and there is no consistent response overall. In all cases, linear fits were statistically very similar to the exponential fits (r² within 0.03, P within 0.02).

3.4. Thermodynamic Considerations

[13] It has been suggested that inorganic thermodynamics play an important role in the incorporation of Mg into foraminiferal CaCO₃ [e.g., Rosenthal et al., 1997; Mashiotta et al., 1999] despite the complications of biogenic calcification [Morse and Bender, 1990; Elderfield et al., 1996]. Assuming thermodynamic equilibrium, the Gibbs-Helmholtz equation may be used to derive an expression for the temperature dependence of D_Cd:

\[ D_T = D_0 \exp\left(-\frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right), \]

where D_T and D_0 are the Cd partition coefficients at absolute temperatures T and T₀, respectively;
Table 2. Individual Cd/Ca Measurements for Bahama Banks Benthic Foraminifera

<table>
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<tr>
<th>Core</th>
<th>C. kullenbergi</th>
<th>C. pachyderma</th>
<th>C. wuellerstorfi</th>
<th>P. ariminensis</th>
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−ΔH° is the standard enthalpy of the exchange reaction:

\[
\text{CaCO}_3(s) + \text{Cd}^{2+}(aq) \rightarrow \text{CdCO}_3(s) + \text{Ca}^{2+}(aq);
\]

and R is the gas constant. Since equation (8) is exothermic (\(\Delta H^\circ = -10.2 \text{ kJ mol}^{-1}\) for calcite, \(-10.1 \text{ kJ mol}^{-1}\) for aragonite [Robie et al., 1978]), \(D_{\text{Cd}}\) is predicted to decrease slightly with increasing temperature (Figure 4b). Given the low slope of this relationship, a thermodynamic influence on the Bahama Banks data cannot be ruled out. It is clear, however, that the strong relationship observed for \(G. \text{ bulloides}\) [Rickaby and Elderfield, 1999] is not explained by simple thermodynamics. It must be kept in mind that foraminiferal \(D_{\text{Cd}}\) values are much lower than both inorganic experimental measurements (20–1510) [Rimstidt et al., 1998] and thermodynamic regression analyses of those experiments (190–330) [Rimstidt et al., 1998; Wang and Xu, 2001], so biology likely plays an important role.

### 3.5. Cd Partition Coefficients and Water Depth

[14] Most of the Bahama Banks calcitic \(D_{\text{Cd}}\) values (including those from Rosenthal et al. [1997]) are marginally higher than predicted by Boyle [1992], whose globally distributed data set contained 8 cores shallower than 1500 m. If the Bahamas data are representative of the global ocean, then the true upper ocean calcitic \(D_{\text{Cd}}\) might be closer to 1.7 than 1.3. This result requires that there is no sizable

![Figure 2](image-url)
systematic error in estimating seawater Cd concentrations from PO4 at Bahama Banks: increasing seawater Cd by 30% would reduce the mean $D_{Cd}$ to ~1.3. Note that using the alternative Atlantic Cd:PO4 equation of Elderfield and Rickaby [2000] would decrease Bahamas seawater Cd by ~13%, making inferred $D_{Cd}$ values even slightly higher (though this would also complicate any direct

Figure 3. Mean Cd partition coefficients for individual species, based on data in Figures 1a and 2a (symbols, ±1σ). Error bars do not account for uncertainty in the estimation of seawater Cd concentrations. Dotted and dashed lines show predicted partition coefficients for the aragonitic H. elegans [Boyle et al., 1995] and for calcitic taxa [Boyle, 1992], respectively. For comparison, solid black line is the temperature-dependent relationship for G. bulloides [Rickaby and Elderfield, 1999], calculated using temperatures from a nearby CTD profile (red line).

Figure 4. (a) Individual Cd partition coefficients based on data in Figures 1a and 2a, plotted versus water temperature (symbols as in previous Figures). Curves show significant exponential fits for two species, though each is rendered insignificant by removing a single measurement (Table 2). (b) Mean Cd partition coefficients for individual species, based on data in Figure 4a (±1σ). Error bars do not account for uncertainty in the estimation of seawater Cd concentrations. Solid curve is the G. bulloides exponential equation from Rickaby and Elderfield [1999]. Also shown is the theoretical thermodynamic equilibrium behavior of calcitic partition coefficients as a function of temperature (dotted lines, equation (7)) (aragonitic curves are virtually identical). For each curve, number refers to the partition coefficient $D_0$ at $T_0 = 0^\circ$C.
Table 3. Individual Species Fits for the Equation $D_{\text{Cd}} = ae^{bT}$

<table>
<thead>
<tr>
<th>Species</th>
<th>n</th>
<th>r²</th>
<th>P</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. kullenbergi</td>
<td>13</td>
<td>0.11</td>
<td>0.27</td>
<td>1.11</td>
<td>0.038</td>
</tr>
<tr>
<td>C. pachyderma</td>
<td>25</td>
<td>0.22</td>
<td>0.02¹</td>
<td>0.90</td>
<td>0.073</td>
</tr>
<tr>
<td>C. vuellerstorfi</td>
<td>9</td>
<td>0.03</td>
<td>0.65</td>
<td>2.96</td>
<td>−0.105</td>
</tr>
<tr>
<td>P. foveolata</td>
<td>6</td>
<td>0.74</td>
<td>0.03²</td>
<td>0.01</td>
<td>0.328</td>
</tr>
<tr>
<td>Uvigerina</td>
<td>4</td>
<td>0.24</td>
<td>0.51</td>
<td>2.28</td>
<td>−0.021</td>
</tr>
<tr>
<td>H. elegans</td>
<td>52</td>
<td>0.04</td>
<td>0.14</td>
<td>1.13</td>
<td>0.023</td>
</tr>
</tbody>
</table>

¹Increases to 0.07 after removing one suspect point.
²Increases to 0.98 after removing one suspect point.

comparison to Boyle’s [1992] results). In agreement with Boyle [1992], there is no strong depth influence on cacitic $D_{\text{Cd}}$ within the upper ocean, leaving the $D_{\text{Cd}}$ gradient to mid depths (~1150–3000 m according to Boyle [1992]).

[15] Most of the new H. elegans $D_{\text{Cd}}$ values are similarly slightly higher than predicted by Boyle et al. [1995]. However, this discrepancy could be due to the apparent analytical offset from that study. There is a hint of a minor increase of $D_{\text{Cd}}$ with water depth, from ~1 at 300 m to ~1.4 at 1500 m. Boyle et al. [1995] noted a considerably smaller increase with depth (~8% per km) which they deemed insignificant given uncertainties in estimating seawater Cd. The present data appear to support a slight depth dependence for H. elegans, but its magnitude is within the range of the analytical offset and is therefore questionable. Alternatively, the apparent $D_{\text{Cd}}$ increase with depth could be due to decreasing water temperatures, following simple thermodynamics (Figure 4b).

3.6. Carbonate Ion Influence

[16] Carbonate ion concentration and temperature are often strongly correlated in the upper ocean. Nearby measurements from the Florida Straits indicate a $\Delta CO_3^{2−}$ increase from ~100 to 220 µmol kg$^{-1}$ over the temperature range 6–20°C, equivalent to a $\Delta CO_3^{2−}$ (calcite) increase from ~50 to 170 µmol kg$^{-1}$ (D. McCorkle and T. Marchitto, unpublished data). Benthic foraminifera from the deep ocean (>3000 m) suggest that $D_{\text{Cd}}$ increases with $\Delta CO_3^{2−}$ in strongly undersaturated waters, but there is no discernable relationship in supersaturated waters [McCorkle et al., 1995; Marchitto et al., 2004]. If there were a positive $\Delta CO_3^{2−}$ influence on $D_{\text{Cd}}$ in supersaturated waters, it would compound any positive $D_{\text{Cd}}$; temperature relationship in Figure 4. Hence any $D_{\text{Cd}}$ increase due to temperature cannot be masked by $\Delta CO_3^{2−}$ in these samples.

4. Conclusions

[17] Seven taxa of benthic foraminifera from the Bahama Banks exhibit $D_{\text{Cd}}$ values close to those predicted by Boyle [1992] and Boyle et al. [1995]. Slight differences between these studies may be within the uncertainties of measuring Cd/Ca and estimating seawater Cd. While previous observations suggest that Cd/Ca in the planktonic G. bulloides is strongly influenced by temperature [Rickaby and Elderfield, 1999], there is no indication of a similar influence on benthic species. A slight decrease of benthic $D_{\text{Cd}}$ with rising temperature, as predicted by simple thermodynamics, cannot be ruled out.

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