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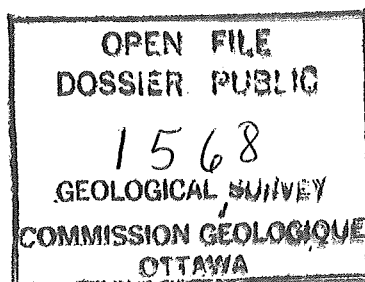
**PRELIMINARY REPORT ON PALEO-CHEMISTRY OF BENTHIC
FORAMINIFERAL TESTS FROM FOUR GEOGRAPHICAL AREAS:
ARCTIC, LABRADOR SLOPE, SCOTIAN RISE, AND BERMUDA RISE**

by

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Introduction

The possibility of using the trace element chemistry of benthic foraminifera as an indicator of past oceanic nutrient concentrations and ocean circulation patterns has been investigated. Experimenters (Delaney, 1983; Graham et al., 1982; Hester and Boyle, 1982) have drawn parallels between nutrient levels and metal profiles in foraminifera tests to answer questions about paleo-geochemistry. Boyle (1980, 1985) noted a similarity between nutrient levels and the trace metal Cd in foraminifera tests. However, paleoceanographic studies of nutrient levels and circulation patterns using carbon and oxygen isotope ratios in foraminifera tests have not been free of problems, and such similar comparisons using trace element ratios in foram tests may also arise. Bender (1975) investigated concentrations of the major cations Na, Mg, and Sr, in foraminifera. They concluded that ratios of the major cations to calcium concentrations in foraminifera decreased with average growth depth of each species but did not vary with temperature.

Boyle (1980) found that planktonic foraminiferal tests show a variation in zinc and cadmium concentrations that mimic growth habitats, or calcification environments, for three planktonic foraminifera, *G. conglobatus*, *G. tumida*, and *G. truncatulinoides*. Although Boyle did note an interspecific and geographical difference in metal contents, the lack of larger samples prevented an investigation of size-specific difference.

Palmer (1985) evaluated the possibility of using the chemistry of rare earth elements (REE) as paleonutrient indicators, because the distribution of dissolved heavy REE in the water column is similar to that of silicates. A further study by Palmer and Elderfield (1985) concluded that in foraminifera, one cannot assume that isotope ratios of neodymium (Nd) reflect the Nd isotope composition of the seawater where calcification occurred. The measured Nd is attributed to Fe/Mn rich coatings, invariably found adsorbed to foraminifera tests, originating from sediment pore waters or, less likely, bottom waters. (These samples were not homogeneous, being composed of various species and sizes.)

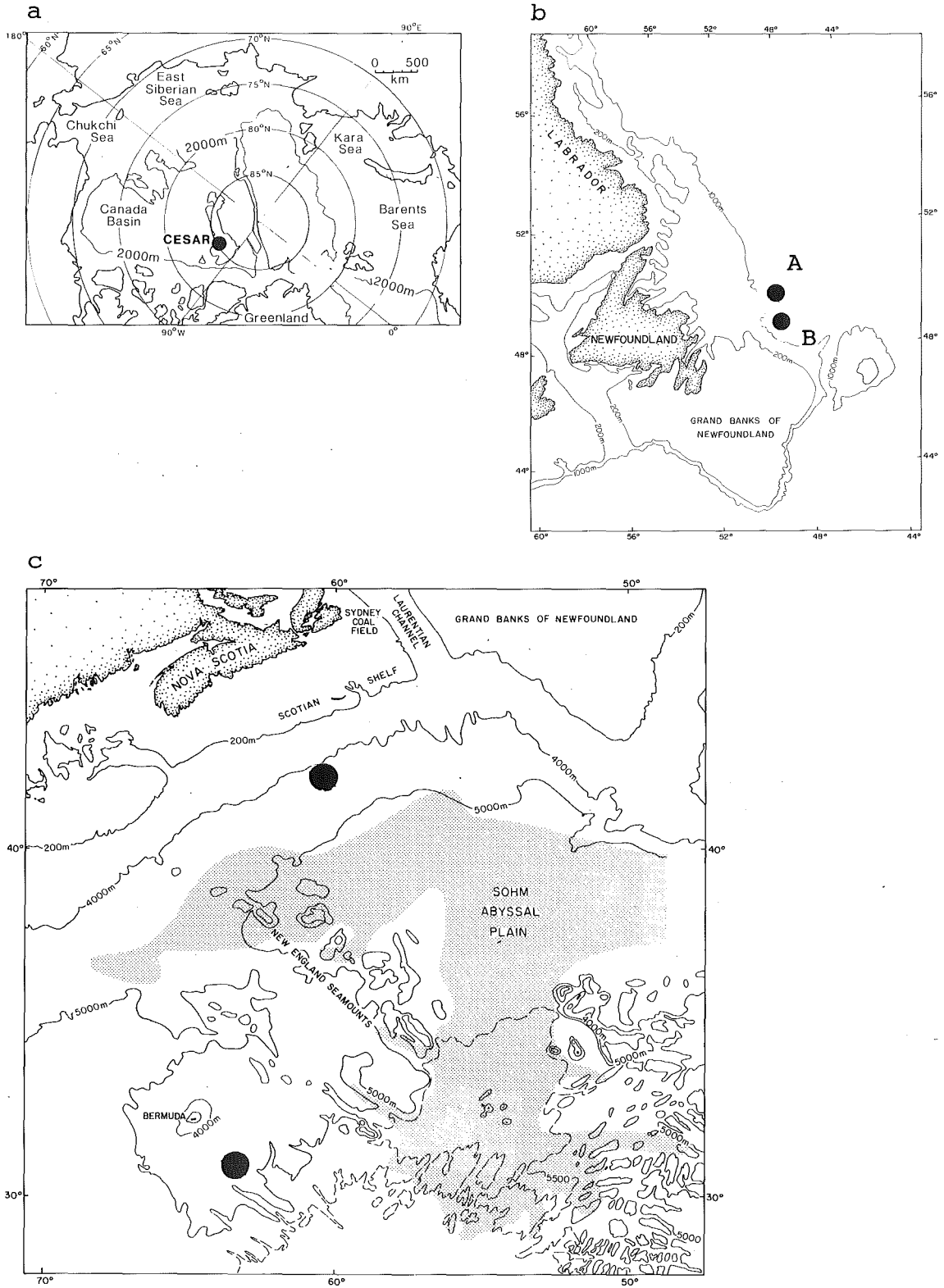


Figure 1. Areas of foraminiferal tests investigation: (a) Arctic (CESAR), (b) Labrador Slope A and B, and (c) Scotian Rise and Bermuda Rise.

In this study we have taken foraminiferal samples from five different locations (Fig. 1, Table 1). Within these areas, sufficient sample could be obtained to investigate both size-specific and inter-specific differences in metal concentrations. Two species of benthic foraminifera were chosen and split into two classes: *Planulina wuellerstorfi* (250 μm - 800 μm , and greater than 800 μm) and *Abicidoides kullenbergi* (250 μm - 1000 μm , and greater than 1000 μm).

It was noted that one group of samples from the Bermuda Rise appeared to be more transparent than the majority of chalk-like foraminifera.

Laboratory Methods

Sample Preparation

The weights (1-5 mg) of samples containing between 7 and 100 foraminiferal tests were determined on a Mettler microgram-atic balance (accuracy = 2.9%; precision = \pm 0.31%). The foram tests were crushed between quartz slides and transferred with a dry brush to 2 ml polyethylene sample cups. The samples were then exposed to 1 ml of a basic cleaning solution composed of 40% ammonium hydroxide (NH_4OH), 5% hydroxylamine hydrochloride ($\text{NH}_2\text{OH.HCL}$), and 5% citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$). This solution was brought to volume with 5% sodium dithonite ($\text{Na}_2\text{S}_2\text{O}_4$) and the samples were kept at 80°C (Boyle, 1980) for 45 minutes to remove Fe/Mn oxides and other adsorbed contaminants. The foram tests were agitated on a Vortex-genie for 15 seconds every five minutes during the 45 minute heating period to ensure complete circulation of the cleaning solution.

Analytical Procedures

Elemental concentrations in the lattice structure of foraminifera tests were determined by dissolving about 1 mg of sample in 1 ml of 1.0 N HNO_3 until test fragments were no longer visible under a binocular microscope. The original weight of each sample was determined by measuring the concentration of calcium dissolved in the acid solution. The

Table 1
Mean Cd/Ca

| | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------|--------------|--------------|--------------|-------------------|--------------------|----------------|
| | CESAR | SCOTIAN RISE | BERMUDA RISE | LABRADOR A | LABRADOR B | ALL AREAS |
| LATITUDE | 85°50'24.7" | 41°58'51" | 31°45'0" | 49°29'8" | 49°27.6'0" | _____ |
| LONGITUDE | 249°55'45.1" | 60°41'91" | 64°18'40" | 49°0'8" | 47°03'05" | _____ |
| DEPTH | 1650 m | 4050 m | 4290 m | 2758 m | 2560 m | _____ |
| | Pw | Pw | Pw | PW | PW | PW 2.82 ± 5.58 |
| | .065 ± .026 | 0.325 ± .325 | 1.33 ± 1.15 | .716 ± .320 n = 6 | 5.72 ± 8.21 n = 5 | N = 11 |
| | n = 6 | n = 5 | n = 5 | pw | pw | pw 4.95 ± 9.43 |
| | | | | 4.48 ± 7.89 n = 6 | 9.15 ± 14.37 n = 4 | n = 10 |
| | | | | CW | CW | CW 0.66 ± 0.64 |
| | | | | .248 ± .158 n = 6 | .912 ± .737 n = 11 | n = 17 |
| | | | | cw | cw | cw 0.35 ± 0.29 |
| | | | | | | n = 11 |
| | | | | | | Pw 0.56 ± 0.81 |
| | | | | | | n = 16 |

Note: PW = Planulina wuellerstorfi > 800 µm
pw = Planulina wuellerstorfi 250-800 µm
CW = Cibicidoides kullenbergi > 1000 µm
cw = Cibicidoides kullenbergi 250-1000 µm
Pw = Planulina wuellerstorfi 0-2000 µm

total Cd, Cu, Cr, and Co concentrations in 1 ml of the foram test solution (1 ml 1.0 N HNO₃) was determined by direct flameless atomic absorption spectrophotometry. Aqueous samples at pH = 1.5 were injected directly into the atomization chamber of a Varian 975 equipped with a GTA 95 graphite furnace. Calibration standards were prepared in an acidified calcite solution identical to the chemical matrix of the foram test solutions and were analyzed in the same manner as the samples. Instrumental parameters were as recommended by the manufacturer. Total Cd concentration is reported as μ mole L⁻¹ and the precision and accuracy was determined to be \pm 9% at the 0.008 μ mole L⁻¹ level. Based on 20 μ L injection volumes, the absolute detection limit for Cd was 1.2×10^{-3} μ mole L⁻¹, Cu = 5.4×10^{-3} μ mole L⁻¹; Cr = 3.0 μ mole L⁻¹; Co = 3.0 μ mole L⁻¹. Total Ca was determined in the foram test solutions by flame atomic absorption spectroscopy (FAAS) following aqueous sample dilution. Total Ca is reported in m mole L⁻¹. Precision was \pm 1%. Furnace parameters and flame characteristics are given in Table 2.

Distilled de-ionized water (Millipore Super-Q) was used for all blanks and standards, prepared from Fisher atomic absorption primary standards, Fisher certified ACS grade anhydrous CaCO₃, and Baker Instra-analyzed acids. Chemicals used for the cleaning solution were all analytical reagent grade. All laboratory ware was soaked in 6N HNO₃ for 24 hours and rinsed several times with de-ionized water. Standards and blank solutions were stored in teflon bottles.

Results and Discussion

The cadmium/calcium ratios are given for each area and species investigated in Table 1. A range of parameters (final sample weight, moles Cd, moles Ca, weight of CaCO₃, etc) was included in our analysis to investigate possible correlations. We found a correlation between the concentration of calcium analyzed by FAAS and the final weight (mg) of sample, prior to dissolution, for the large size class of *cibicidoides kullenbergi* from the Labrador sites (Fig. 2). At a correlation of 0.973, with less than 0.000005 risk factor, we can be confident that

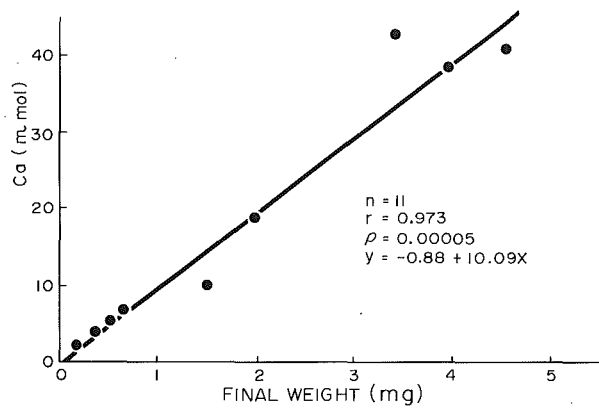


Figure 2. Millimoles of calcium versus final weights of the crushed and washed tests of *C. kullenbergi* (>1000 μ) from the Labrador sites.

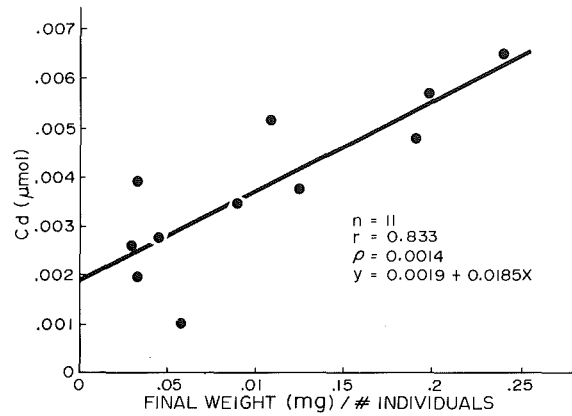


Figure 3. Micromoles of cadmium versus the final average weight of individual crushed and washed tests of *C. kullenbergi* (>1000 μ) from the Labrador sites.

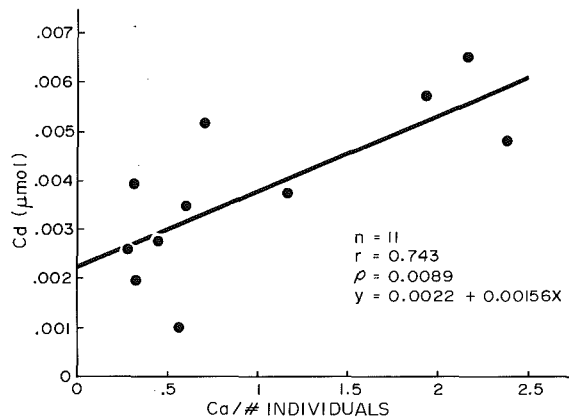


Figure 4. Micromoles of cadmium versus average millimoles calcium of individual crushed and washed tests of *C. kullenbergi* (>1000 μ) from the Labrador sites.

the analytical measurement of calcium is an accurate representation of the mass of calcium carbonate available for trace metal incorporation. This should be true for all the foraminiferal classes studies, but perhaps the smaller size-classes prevent this relationship from being shown.

The same sample group demonstrated an increase in cadmium as the individual average weight of a test increases (Fig. 3). Since a similar relationship was not found in the other sample groups, perhaps adverse conditions at this sample location (Fig. 1) have caused the foraminifera to thicken their shell rather than increase the chamber number. At the time of shell thickening, essential nutrients could perhaps come from terrestrial environments, which are typically higher in cadmium. In this sample group, we also found an increase in cadmium with an increase in moles of calcium (Fig. 4).

When both size classes of *C. kullenbergi* are combined, the previous relationships do not hold. The analytical precision rises from less than 20% in the previous situation, to over 40% in some cases. The two size classes chosen for our study may not be appropriate. Where we used 250 μm as the lower end of our small size class, Bender et al. (1975) chose samples greater than 250 microns and referred to them as being "particularly large".

From the limited data available, we did not find in all samples, a statistically significant relationship between cadmium and calcium values to exhibit species or site-specific differences in Cd/Ca ratios of the two benthic foraminifera, *Cibicidoides kullenbergi* and *Planulina wuellerstorfi*. No significant relationships were observed for Cu, Cr and Co with Ca. Also, there were no significant differences for the Cu, Cr and Co ratios with Ca between the two benthic foraminifera or the different sampling sites.

As was mentioned previously, foram samples from the Bermuda Rise (Fig. 1, Table 1) were more transparent than the chalk-white forams from other sites. No statistical relationship was found here.

Future in-depth studies should include: 1) refining of sample preparation techniques including cleaning methods; 2) evaluation of other size classes and benthic species;

Table 2

Analytical conditions for Cd, Co, Cu analysis

| Element | λ (nm) | Slit (nm) | Comments | Atomization Temp. | Gas Flow (during atomization) |
|---------|----------------|-----------|--|-------------------|-------------------------------|
| Cd | 228.8 | 0.5 | background correction (deuterium lamp) | 1800°C | 0 |
| Co | 240.7 | 0.2 | " | 2300°C | 0 |
| Cu | 324.8 | 0.5 | " | 2300°C | 0 |

Note: Four-point standard curves were run prior to and following each group of samples. Blank and deionized water values were below the detection limit of the instrument. Drying time was adjusted to accommodate the increase in sample volume to 20 μ l.

To prevent losses due to the volatile nature of cadmium, we employed a low char temperature of 200°C and analyzed for Cd in an acidified matrix.

3) examination of the interaction between transition-alkali metals and foram tests; and 4) include SEM-EDS studies to aid in preliminary screening and classification of benthic foraminifera tests.

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