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# The use of foraminiferal uranium/calcium ratios as an indicator of changes in seawater uranium content

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**Abstract.** We examine the utility of the uranium (U) content of planktonic foraminifera tests as an indicator of past changes in seawater U content. The U/Ca ratio in foraminifera from Atlantic and Caribbean cores is constant in the Holocene and decreases by ~25% during the last glacial period. Magnesium/calcium (Mg/Ca) ratios of the same samples show similar trends. While the timing of the U/Ca changes appears to be associated with glacial-interglacial changes, the magnitude of the change is too large to be caused by variations in the extent of anoxic or suboxic sediments or by changes in riverine input. We assume that the same process produced changes in both U/Ca and Mg/Ca ratios because of a strong correlation between the two ratios. Partial dissolution of the calcite is ruled out, because we observe the same changes in well-preserved cores from basins with opposite dissolution histories. We also reject exchange between foraminiferal and pore water U because of the oxic depositional environment of both cores and because of the consistency in the U/Ca trends from cores in different parts of the ocean. We suggest that the observed foraminiferal U/Ca and Mg/Ca trends may be the result of a temperature effect on the incorporation of these metals. If this is true, it introduces the possibility of a new paleotemperature indicator but complicates the use of U/Ca ratios in planktonic foraminifera tests as an indicator of past seawater U changes.

## Introduction

Changes in the cycling of organic and inorganic carbon in the ocean have been proposed as mechanisms leading to glacial-interglacial changes in atmospheric carbon dioxide measured in ice cores. In spite of the ocean's acknowledged importance in controlling atmospheric carbon dioxide concentrations, however, the roles of chemical and physical processes governing carbon transfers between the ocean and atmosphere are still poorly understood. Based on the observation that nutrient levels in the high-latitude surface ocean today are not depleted, several early models [*Knox and McElroy,* 1984; *Sarmiento and Orr*, 1991; *Sarmiento and Toggwieler*, 1984; *Siegenthaler and Wenk*, 1984] attributed glacial-interglacial changes in atmospheric $CO_2$ to a higher efficiency of biological transfer of carbon to the deep sea at high latitudes during glacial times. These models produced lower atmospheric $CO_2$ levels but required widespread anoxia in deep and intermediate waters where organic carbon respiration occurs. A more detailed three-dimensional nutrient model lowered atmospheric $CO_2$ levels with only localized anoxia in the southern Indian Ocean [*Sarmiento and Orr*, 1991]. Alternatively, atmospheric $CO_2$ changes could have resulted from variations in global ocean alkalinity, driven by shallow-carbonate precipitation and dissolution cycles [*Opdyke and Walker*, 1992] or by changes in the intensity of respiration-driven carbonate dissolution in deep-sea sediments [*Archer and Maier-Reimer*, 1994], without any change in deep water oxygen levels.

Since models of atmospheric $CO_2$ change vary significantly in their predictions for deep ocean oxygen concentration, an indicator of changes in the extent of anoxic conditions in the ocean would provide an important constraint on the marine processes controlling atmospheric carbon dioxide. Valuable information about the availability of oxygen can be obtained from sedimentary indicators such as the presence or absence of benthic fauna and sediment laminations, the distribution of foraminiferal species that are tolerant of low-oxygen conditions in today's ocean [*Streeter and Shackleton*, 1979], and the presence of enriched solid-phase concentrations of trace metals (e.g., chromium, molybdenum, rhenium, uranium, and vanadium) which are concentrated in anoxic sediments [*Calvert and Pedersen*, 1993; *Emerson and Huested*, 1991]. However, sedimentary indicators of anoxia or low oxygen levels require extensive coring to characterize ocean basin condi-

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**Table 1.** Summary of U Mass Balance for the Ocean

| Sources | Rate, $10^7$ mol/yr | |
|---|---|---|
| River inflow | 4.5±1.5[a] | |
| Amazon shelf sediments | 0.6[b] | |
| Total sources | 5.1±1.5 | |
| Sinks | Rate, $10^7$ mol/yr | Percent of Inflow |
| Sediments | | |
| Oxic, deep-sea | 0.34[c] | 7 |
| Organic-rich anoxic | 0.6[d]-1.1[e] | 12-22 |
| Continental margin | 1.1[d]-2.8[f] | 22-55 |
| Corals and molluscs | 0.34[c] | 7 |
| Crustal alteration | | |
| Ridge-crest hydrothermal | 0.03 to 0.16±0.04 (high T) | <1-3 |
| | 3.1±0.8 (low T)[g] | 61 |
| Metalliferous sediments | 0.59[h] | 12 |
| Low-temperature basalt weathering | 1.5-5.0[h] | 29-98 |
| Total sinks | 4.5-13.3 | 88-261 |

modified from *Cochran* [1992]
[a] *Palmer and Edmond* [1993]
[b] *McKee et al.* [1987]
[c] *Cochran* [1982]
[d] *Barnes and Cochran* [1990]
[e] *Emerson and Huested* [1991]
[f] *Klinkhammer and Palmer* [1991]
[g] *Edmond et al.* [1979]
[h] *Bloch* [1980]

tions and may be subject to physical erosion or alteration by changing oxidation-reduction conditions within the sediments after they are deposited.

A record of changes in the U content of seawater could provide an indicator of global changes in the extent of sediments overlain by anoxic or low-oxygen bottom waters. U is concentrated in reducing sediments by reduction and subsequent immobilization by adsorption or by precipitation of insoluble minerals [*Anderson et al.*, 1989a; *Anderson et al.*, 1989b; *Barnes and Cochran*, 1990; *Cochran*, 1992]. Removal into anoxic and low-oxygen sediments together represent the largest sink in the marine U mass balance (Table 1) capable of changing its magnitude over 10 to 100-kyr timescales. Fluctuations in the extent of such sediments therefore should lead to changes in the concentration of U in seawater. The long residence time of U in seawater with respect to riverine inflow (~300-600 kyr) relative to the ocean mixing time means that changes in seawater U concentration are global and also suggests that the tracer would be most suitable for determining changes over ~100-kyr timescales.

During glacial times, the amount of U taken up into sediments overlain by anoxic and low-oxygen waters could have changed due to changes in sea level, ocean productivity, and bottom-water oxygen concentration. U removal by anoxic marginal basin sediments would have been affected by sea level lowering of 121±5 m [*Fairbanks*, 1989], which completely isolated the Black Sea and the Sea of Azov (sill depth 40 m) and the Baltic Sea (sill depth 20 m). Today, these basins represent two thirds of the area of sediments overlain by anoxic bottom waters (0.3% of the sea floor), and their isolation would decrease the size of the anoxic sediment sink during glacial times. However, lowered sea levels also restricted circulation into the Japan Sea (sill depth 130 m) and the Red Sea (sill depth 100 m), which together account for 0.4% of the sea floor. If sediments in these basins contained little or no oxygen during glacial periods, U removal into anoxic sediments of marginal basins could have been the same or even greater than it is today [*Almogi-Labin et al.*, 1986; *Halicz and Reiss*, 1981; *Luz and Reiss*, 1983; *Oba et al.*, 1991; *Piper and Isaacs*, 1995].

An increase in glacial productivity and/or a decrease in bottom-water oxygen would cause the oxygen penetration depth in continental margin sediments to shoal [*Emerson et al.*, 1985], enhancing the diffusive flux of U to sediments. High authigenic U concentrations have been detected in glacial-age sediments from the southeast Arabian Sea [*Sarkar et al.*, 1993], the southeast Indian Ocean [*McCorkle et al.*, 1994], the equatorial Atlantic [*Mangini*, 1978; *Thomson et al.*, 1990], the Panama Basin [*Yang et al.*, 1995], and the Atlantic and Indian sectors of the Southern Ocean [*Kumar et al.*, 1995; *Rosenthal et al.*, 1995a]. U enrichment in these sediments has been attributed to higher glacial organic carbon flux to the sea floor and/or lower glacial bottom-water oxygen concentrations, although the possibility that U enrichment is active today cannot be eliminated without pore water data [*Thomson et al.*, 1990].

The history of seawater U concentrations has been based on analyses of U in corals [*Bard et al.*, 1990; *Broecker et al.*, 1968; *Edwards*, 1988] which have remained constant within 20% over the last 30 kyr [*Bard et al.*, 1990]. The coral record is inadequate for developing continuous records of seawater U concentration over longer periods because of large gaps in the availability of unaltered corals. Recent work indicates that U incorporation by corals is strongly dependent on temperature

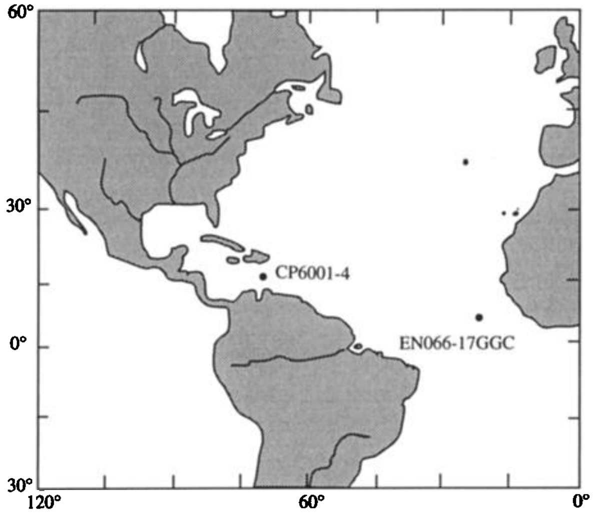

**Figure 1.** Locations of cores used in this study.

and may be related to changes in seawater alkalinity and salinity as well [*Min et al.*, 1995; *Shen and Dunbar*, 1995].

Shells of foraminifera have the potential to provide a continuous record of changes in seawater U concentration. Using cleaning techniques developed for other trace metals in foraminiferal calcite, *Delaney and Boyle* [1983] determined that the U content of a clay-free sample was 0.023 ppm, confirming *Ku*'s [1965] results. In a previous study, we presented culture experiment results demonstrating that U incorporation into foraminiferal calcite occurs in proportion to seawater concentration and showed that partial dissolution lowers U/Ca in foraminifera tests [*Russell et al.*, 1994b].

In this paper, we examine the utility of foraminiferal U/Ca as a tracer of seawater U concentrations by measuring U/Ca ratios in foraminifera over the last 30-70 kyr from two deep-sea cores from the Atlantic Ocean and the Caribbean Sea. These locations were chosen because calcium carbonate preservation in the deep Atlantic Ocean is inversely correlated with preservation in the Caribbean basins [*Haddad and Droxler*, 1991; *Peterson*, 1990]. If similar U/Ca changes are measured in Atlantic and Caribbean cores, the U/Ca trend cannot be attributed to a partial dissolution artifact. In addition, the cores were selected from locations above both the present and the glacial calcite lysocline. Mg/Ca ratios in foraminifera were measured as an index of dissolution, based on the observation from the core-top transects that Mg/Ca decreases with increasing water depth [*Rosenthal and Boyle*, 1993; *Russell et al.*, 1994b] and on the observation that dissolution-susceptible species contain higher Mg/Ca than dissolution-resistant species [*Kilbourne and Gupta*, 1973].

## Methods

### Core Description

EN066-17GGC (5° 22' N, 21° 5' W, water depth 3050 m) is from the Sierra Leone Rise (Figure 1), which is blanketed by carbonate-rich sediments between 2800 and 4700 m. EN066-17GGC is located about 1.5 km above the present-day regional lysocline [*Curry and Lohmann*, 1990]. Profiles of foraminiferal fragmentation from the Sierra Leone Rise indicate that the lysocline has been at or below 3750 m during the last interglacial-glacial cycle [*Curry and Lohmann*, 1986]. In EN066-17GGC, the fraction of foraminiferal fragments relative to whole tests was low and virtually constant between stages 1 and 2 (6 and 7%), suggesting that effects of varying dissolution should be minimal over this time period.

The chronology for EN066-17GGC is based on stable oxygen isotope measurements from *Cibicidoides wuellerstorfi*, percent carbonate, and the occurrence of *Globorotalia menardii* [*Curry and Lohmann*, 1986]. The depths of the isotope stage boundaries were identified by *Curry and Lohmann* [1986]. Sample ages were determined by assigning SPECMAP ages [*Imbrie et al.*, 1984] to these stage boundary depths, correcting for the effects of the $^{14}$C-calendar year offset [*Bard et al.*, 1990] and assuming constant sedimentation rates through each stage.

The Caribbean core (CP6001-4; 14° 55' N, 71° 50' W; 3645 m) was raised from the Beata Ridge, which separates the Colombia and Venezuela Basins. The top of the piston core was missing, so the U/Ca and Mg/Ca records are a composite of samples from the trigger weight core and the piston core. The amount lost from the piston core top was estimated to be 25 cm by overlapping U/Ca and Mg/Ca profiles from the trigger weight core and the piston core. Excellent preservation in CP6001-4 through the Holocene is indicated by low foraminiferal fragmentation (<10%) (L. Peterson, unpublished data, 1993), by the abundance of dissolution-susceptible species (*Globigerinoides ruber*, *Glogiberinoides sacculifer*, and *Orbulina universa*) and by the presence of *G. ruber* and *G. sacculifer* tests with spines. Abundant pteropods in isotope stage 2 indicate a deepening of the aragonite compensation depth during this time; thus effects of partial calcite dissolution should be minimal.

The chronology for CP6001-4 is based on the presence of *G. menardii* and on stable oxygen isotopes from *G. sacculifer* and *G. ruber* (performed by L. Peterson). The depth of the isotope stage 1-2 transition is approximately 33-36 cm, based on the presence of *G. menardii*. Sample ages were estimated by assigning an age of 12 kyr to the depth at which *G. menardii* appears (35 cm) and assuming a constant sedimentation rate (2.9 cm/kyr) through stage 1. Since there is no age control for the samples immediately overlying the turbidite, the stage 2 sedimentation rate was assumed to be 10% higher (3.2 cm/kyr), based on *Prell*'s [1978] observation that glacial sedimentation rates for pelagic cores from the adjacent Colombia Basin were ~10% higher than interglacial rates.

### Cleaning Procedure

Cleaning procedures based on those described by *Boyle and Keigwin* [1985/86] were developed for removing organic material and metallic coatings from samples prior to analysis. The procedure reported below was the one that yielded the lowest U/Ca ratios. Bulk sediments were washed in a solution of sodium hexametaphosphate with *p*H adjusted to be greater than 7 with NaOH, and were then dried and sieved. Samples of *G. sacculifer* (EN066-17GGC and CP6001-4) and *G. ruber* (EN066-17GGC) were picked from the bulk foraminifera, crushed with an agate mortar and pestle, split into replicates, and transferred to clean microcentrifuge tubes for cleaning. Samples weighed 2-7 mg before cleaning. The cleaning procedure consists of (1) at least three water rinses with vortexing and sonication to remove fine-grained material; (2) a 30-min bath in buffered oxidizing solution (250 µL $H_2O_2$ + 0.2 g NaOH into 50 mL $H_2O$) at 80°-90°C with sonication for 2 min every 10 min while heating; (3) three distilled water rinses with vortexing and sonication; (4) two 30-min baths in hot reducing solution (15 mL $NH_4OH$, 3 mL 0.6 *N* citric acid, and 2 mL $NH_2NH_2$) with a distilled water rinse between baths; (5) two distilled water rinses with vortexing and sonication; (6) two 10-min baths in hot distilled water followed by a distilled water rinse with vortexing and sonication; (7) transfer to a clean microcentrifuge tube; and (8) a rinse with 0.001 *N* $HNO_3$, with brief sonication, followed by a final distilled water rinse. The effectiveness of the cleaning procedure in removing manganese (Mn) oxyhydroxide coatings on core samples was evaluated by monitoring the Mn/Ca of each sample [*Boyle*, 1981; *Boyle and Keigwin*, 1985/86]. Typical Mn/Ca ratios in sediment trap and core-top foraminifera samples are less than 20 µmol/mol; higher Mn/Ca ratios in downcore samples indicates that manganese oxide or manganese carbonate phases are present.

### Analytical Techniques

U analyses were performed by isotope dilution mass spectrometry, using the VG PlasmaQuad $2^+$ inductively coupled plasma mass spectrometer (ICP-MS) at the University of California at Santa Barbara for samples from the Atlantic core (EN066-17GGC) and the Perkin Elmer/Sciex Elan 5000 ICP-MS at the University of Washington for samples from the Caribbean core (CP6001-4). Samples were dissolved in ~2 *N* $HNO_3$, spiked, and diluted until the final calcium concentration was less than 30 mM for introduction via Meinhardt nebulizer. The final sample volume was 750 µL, and the sample flow rate into the plasma was 1 mL/min. Background counts for $^{238}U$ on a solution of deionized distilled water were consistently <10 counts per second on both the PlasmaQuad $2^+$ and the Elan 5000.

Mass fractionation was corrected by repeated analysis of NIST U500 ($^{235}U/^{238}U = 0.999698$). A mass fractionation correction factor $\alpha$ was calculated using the ratio of measured to known $^{238}U/^{235}U$ in NIST U500 and the following definition

$$\alpha = \frac{\left(R_m/R_a - 1\right)}{\Delta m} x100,$$

where $R_m$ is the measured ratio, $Ra$ is the actual ratio, and $\Delta m$ is the mass difference between isotopes 235 and 238. Average daily fractionation factors varied from -0.16 to 1.44% per amu over a period of 1 year. Daily average fractionation factors were used to estimate actual $^{235}U/^{238}U$ ratios from measured ratios. If a linear trend in $\alpha$ was evident over the period of analysis, $\alpha$ was calculated for each sample by interpolating between measurements of $^{235}U/^{238}U$ ratios in U500 solution.

Calcium and magnesium analyses were performed using a Perkin Elmer Model 5000 flame atomic absorption spectrophotometer. Samples and standards for Ca were prepared in a solution of 1 mM $La_2O_3$, dissolved in 0.048 *N* HCl, to suppress interferences from phosphine in the acetylene. Mn analyses were performed by graphite furnace atomic absorption spectrophotometry using a Hitachi Z-9000 instrument and a pyrocoated graphite tube. The temperature program was optimized at an atomization temperature of 2100°C. Mn and Mg standards were added to a solution of 3.2 mM Ca prepared with trace-metal clean calcium carbonate (Johnson Matthey Specialty Products; total impurities < 1 ppt by weight) to approximate the sample matrix.

Analytical precision for U and calcium was estimated by repeated measurements of a solution of dissolved bulk foraminifera. Daily analytical precision was ±2-4% for the U analysis and ±1-3% for the calcium analysis. Between February 1991 and October 1993, the mean U concentration of the standard foraminiferal (SF) solution was 1.002±0.054 nM ($1\sigma$ = 5%; $N$=130); the mean Ca concentration was 70.92±4.30 mM ($1\sigma$ = 6%; $N$=122). For every ten samples, at least two analyses of SF solution were made. The ratio of the daily mean SF U/Ca measurement to a constant value of 13.7 nmol/mol was used to correct sample U/Ca for interrun analytical variability. External precision was evaluated by running at least two (and normally three or more) replicates from each interval. Replicates were split after crushing and processed separately thereafter. The average $1\sigma$ of replicate downcore samples was 5%.

## Results

Results of downcore U/Ca, Mg/Ca, and Mn/Ca analyses from each core are given in Table 2a (EN066-17GGC; *G. sacculifer*), Table 2b (EN066-17GGC; *G. ruber*), and Table 3 (CP6001-4; *G. sacculifer*). Within a given depth interval, replicate samples were excluded from means and figures (but not from tables) if the U/Ca was more than $2\sigma$ different from the interval mean U/Ca. U/Ca ratios are positively correlated with Mn/Ca ratios in samples with Mn/Ca > 60 µmol/mol (Figure 2a), suggesting addition of U by association with a manganous carbonate phase. In samples with Mn/Ca < 60 µmol/mol (Figure 2b), the inverse relationship between U/Ca and Mn/Ca ratios is most likely due to the fact that U/Ca decreases with depth in the upper portion of the core while Mn/Ca increases with depth, and is not an indication of diagenetic alteration. Only samples with Mn/Ca ratios lower than 60 µmol/mol are included in the discussion of downcore trends in U/Ca and Mg/Ca.

### Core-top U/Ca and Mg/Ca

In EN066-17GGC, the core-top value of U/Ca for *G. sacculifer* was 9.4±0.3 nmol/mol, within $2\sigma$ of the mean of 11 other shallow Atlantic and Pacific core tops (11.0±1.2 nmol/mol) [*Russell et al.*, 1994b]. Mean Mg/Ca for *G. sacculifer* in the EN066-17GGC core top was 4.0±0.1 mmol/mol; this value is within $1\sigma$ of the mean Mg/Ca in *G. sacculifer* from shallow core tops (4.1±0.3 mmol/mol). U/Ca in core-top samples of *G. ruber* from EN066-17GGC averaged 12.7±0.2 nmol/mol, within $2\sigma$ of the mean based on 3 shallow Ceará Rise core tops (11.4±0.7 nmol/mol) [*Russell et al.*, 1994b]. In contrast, both U/Ca (8.0±0.6 nmol/mol) and Mg/Ca (3.5±0.2 mmol/mol) in core-top samples of *G. sacculifer* from the Caribbean core CP6001-4 (trigger core) were significantly lower than the means reported above (95% confidence level).

**Table 2a.** U/Ca, Mg/Ca, and Mn/Ca in *G. sacculifer* (355-425 μm) From Eastern Equatorial Atlantic Core EN066-17GGC

| Depth, cm | Age, kyr | U/Ca, nmol/mol | Mg/Ca, mmol/mol | Mn/Ca, μmol/mol |
|---|---|---|---|---|
| | | *Stage 1* | | |
| 0-2 | 0.7 | 9.8 | (7.27) | <10 |
| 0-2 | | 9.4 | 4.45 | <10 |
| 0-2 | | 9.1 | 4.25 | <10 |
| 3-4 | 2.5 | 8.9 | 4.41 | 13 |
| 3-4 | | 8.4 | 4.26 | <10 |
| 3-4 | | 9.1 | 4.26 | 11 |
| 9-10 | 6.7 | 9.6 | 4.30 | 12 |
| 9-10 | | 9.6 | 4.31 | 11 |
| | | *Stage 2* | | |
| 19-20 | 13.4 | 8.5 | 4.01 | 18 |
| 19-20 | | 8.5 | 4.72 | 20 |
| 19-20 | | 8.4 | 4.05 | 19 |
| 23-24 | 15.6 | 7.6 | 3.59 | 25 |
| 23-24 | | 7.5 | 3.65 | 24 |
| 23-24 | | 7.8 | 3.77 | 25 |
| 29-30 | 18.8 | 7.4 | 3.54 | 29 |
| 29-30 | | 7.6 | 3.60 | 27 |
| 29-30 | | 7.4 | 3.73 | 28 |
| 36-37 | 22.7 | 7.3 | 3.78 | 35 |
| 36-37 | | 6.4 | 4.21 | 33 |
| | | *Stage 3* | | |
| 49-50 | 31.0 | 7.1 | 3.70 | 41 |
| 49-50 | | 7.7 | 3.64 | 40 |
| 49-50 | | 6.7 | 4.05 | 38 |
| 69-70 | 44.2 | 6.8 | 3.56 | 49 |
| 69-70 | | 6.3 | 2.95 | 40 |
| 69-70 | | 6.6 | 3.05 | 45 |

Mg/Ca in parentheses indicates value omitted from means and figures.

**Table 2b.** U/Ca, Mg/Ca, and Mn/Ca in *G. ruber* (355-425 μm) From Eastern Equatorial Atlantic Core EN066-17GGC

| Depth, cm | Age, kyr | U/Ca, nmol/mol | Mg/Ca, mmol/mol | Mn/Ca, μmol/mol |
|---|---|---|---|---|
| | | *Stage 1* | | |
| 0-2 | 0.7 | 12.8 | NA | <10 |
| 0-2 | | - | 3.20 | <10 |
| 3-4 | 2.5 | 12.4 | NA | <10 |
| 3-4 | | 12.8 | NA | <10 |
| 9-10 | 6.7 | 14.0 | 3.35 | <10 |
| 9-10 | | 14.1 | NA | <10 |
| 9-10 | | 13.6 | NA | <10 |
| | | *Stage 2* | | |
| 19-20 | 13.4 | 11.7 | NA | <10 |
| 19-20 | | 12.5 | NA | <10 |
| 19-20 | | 13.0 | NA | <10 |
| 23-24 | 15.6 | 13.1 | 3.12 | <10 |
| 23-24 | | 13.0 | NA | <10 |
| 23-24 | | 12.6 | NA | <10 |
| 29-30 | 18.8 | 11.6 | 2.95 | <10 |
| 29-30 | | 11.4 | NA | <10 |
| 36-37 | 22.7 | 10.4 | 2.73 | <10 |
| 36-37 | | 9.9 | NA | <10 |
| | | *Stage 3* | | |
| 49-50 | 31.0 | 10.3 | 2.81 | 17 |
| 69-70 | 44.2 | 9.6 | NA | 17 |
| 69-70 | | (15.3) | 2.52 | 14 |
| 89-90 | 57.4 | 10.3 | 2.76 | 18 |
| 89-90 | | 10.4 | NA | 20 |

U/Ca in parentheses indicates value omitted from means and from figures. NA indicates not analyzed.

**Table 3.** U/Ca, Mg/Ca, and Mn/Ca in *G. sacculifer* (355-425 µm) From Caribbean Core CP6001-4

| Depth, cm | Age, kyr | U/Ca, nmol/mol | Mg/Ca, mmol/mol | Mn/Ca, µmol/mol |
|---|---|---|---|---|
| | | *Stage 1* | | |
| TW 0-2 | 0.3 | 8.7 | 3.65 | <10 |
| TW 0-2 | | 7.7 | 3.42 | <10 |
| TW 0-2 | | 7.6 | 3.33 | 12 |
| TW 6-8 | 2.4 | 8.7 | 4.11 | <10 |
| TW 6-8 | | 8.8 | 4.22 | <10 |
| TW 6-8 | | 9.0 | 4.14 | <10 |
| TW 12-14 | 4.5 | 8.5 | 4.06 | <10 |
| TW 12-14 | | 8.3 | 4.05 | <10 |
| TW 12-14 | | 7.3 | 3.78 | <10 |
| TW 21-23 | 7.6 | 8.0 | 3.95 | 17 |
| TW 21-23 | | 8.0 | 4.09 | 19 |
| TW 21-23 | | 7.5 | 3.81 | 19 |
| PC 5-6 (30-31) | 10.5 | 7.9 | 3.63 | 20 |
| PC 5-6 (30-31) | | 8.2 | 3.79 | 22 |
| PC 5-6 (30-31) | | 8.2 | 3.85 | 18 |
| TW 31-33 | 11.0 | 6.4 | 3.59 | 19 |
| TW 31-33 | | 5.9 | 3.38 | 18 |
| TW 31-33 | | 6.9 | 3.65 | 17 |
| | | *Stage 2* | | |
| TW 40-42 | 13.9 | 5.8 | 3.13 | 15 |
| TW 40-42 | | 6.0 | 3.41 | 20 |
| TW 40-42 | | 5.8 | 3.00 | 18 |
| TW 51-53 | 17.3 | 5.9 | 3.12 | 22 |
| TW 51-53 | | (3.3) | 3.24 | 18 |
| TW 51-53 | | 5.6 | 3.08 | 20 |
| TW 61-63 | 20.4 | 7.3 | 3.40 | 26 |
| TW 61-63 | | 7.8 | 3.43 | 34 |
| TW 61-63 | | 7.6 | 3.75 | 28 |
| PC 11-12 (36-38) | 12.8 | 5.7 | 3.08 | 26 |
| PC 11-12 (36-38) | | 5.8 | 3.14 | 22 |
| PC 11-12 (36-38) | | 6.2 | 3.37 | 29 |
| PC 21-23 (46-49) | 15.9 | 5.1 | 3.24 | 26 |
| PC 21-23 (46-49) | | 5.5 | 3.39 | 22 |
| PC 21-23 (46-49) | | 5.3 | 3.27 | 26 |
| PC 31-33 (56-58) | 18.9 | 5.5 | 3.41 | 21 |
| PC 31-33 (56-58) | | 5.5 | 3.27 | 20 |
| PC 31-33 (56-58) | | 5.6 | 3.03 | 36 |
| PC 41-43 (66-68) | 22.0 | 6.4 | 3.36 | 20 |
| PC 41-43 (66-68) | | 5.6 | 3.10 | 27 |
| PC 41-43 (66-68) | | 5.8 | 3.16 | 27 |
| PC 51-53 (76-78) | 25.1 | 6.1 | 3.60 | 18 |
| PC 51-53 (76-78) | | 5.6 | 3.44 | 38 |
| PC 51-53 (76-78) | | 6.4 | 3.48 | 18 |

TW indicates trigger weight core samples and PC indicates piston core samples. Depths in parentheses in piston core samples are relative to the top of the trigger core, with offset of 25 cm added (see text). U/Ca in parentheses indicates value omitted from means and figures.

The core-top Mg/Ca from CP6001-4 is suspect because it deviates markedly from the trend observed in deeper Holocene samples. Such a low Mg/Ca could result from mixing with deeper glacial samples with lower Mg/Ca, via bioturbation or winnowing from shallower sediments on the Beata Ridge. However, the presence of *G. menardii* indicates that the core top is Holocene. Mixing with glacial sediments would produce an isotopically enriched core-top $\delta^{18}O$ and a lower core-top U/Ca ratio compared with deeper Holocene samples, and this was not observed. Partial dissolution could also lower foraminiferal Mg/Ca ratios, but the presence of foraminiferal spines and the lack of a similar trend in U/Ca rule out dissolution as a cause of the low core-top Mg/Ca. It is unlikely that the low core-top Mg/Ca reflects oceanographic conditions, so we assume that the actual core-top Mg/Ca ratio is similar to the ratio from the 6 to 8-cm interval (4.2±0.1 mmol/mol). This value is close to the mean Mg/Ca for other Atlantic and Pacific core tops.

One possible explanation for the relatively low core-top U/Ca ratio in CP6001-4 is that *G. sacculifer* in the Caribbean calcify during the rainy season (June-November), when *Wüst* [1964] shows surface salinities in the region are ~1‰ lower than in the dry season. Lower June-November surface salinities are due in part to higher runoff during this season from the Magdalena, Orinoco, and Amazon Rivers, combined with lower excess evaporation over precipitation [*Wüst*, 1964]. Assuming that the U content of discharge from these rivers is negligible and using the U/salinity relationship ($9.34\pm10^{-8}$

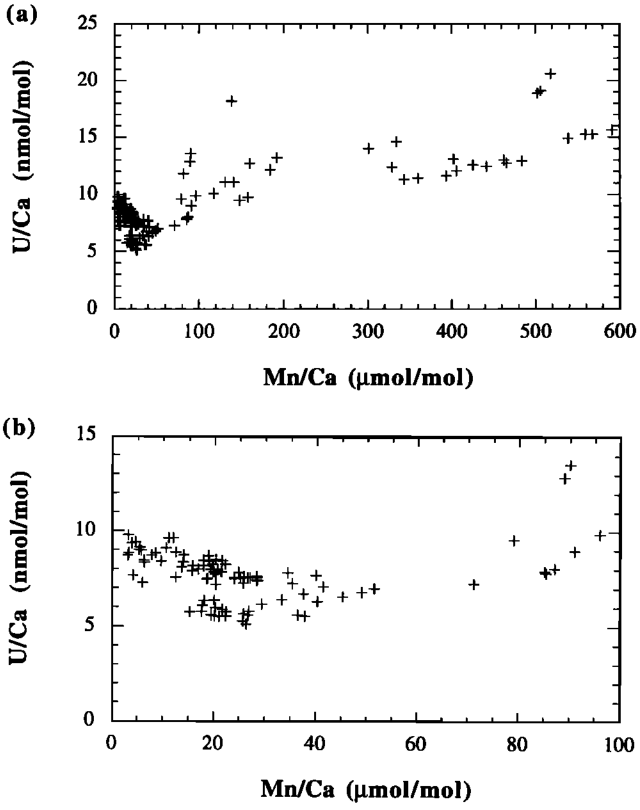

**Figure 2.** U/Ca versus Mn/Ca in *G. sacculifer* from downcore samples: (a) all data ($R^2 = 0.66$) and (b) Mn/Ca < 60 μmol/mol ($R^2 = 0.32$). Data are from EN066-17GGC, CP6001-4, and V25-56 (not discussed in this paper because of high Mn/Ca ratios).

g/g) from *Ku et al.* [1977], a salinity decrease of 1‰ would lower the seawater U concentration by only 3%, explaining only 10% of the observed difference between the Caribbean core-top U/Ca and the mean Atlantic-Pacific core-top U/Ca. Thus the salinity change observed by Wüst is insufficient to explain the low core-top U/Ca in the Caribbean core. Nor can Atlantic-Caribbean differences in surface-water temperature explain the lower Caribbean core-top U/Ca ratio, since seasonal average surface temperatures for the Caribbean are the same as those for the equatorial Atlantic within the variability of the data set (~0.8°-1°C) [*Levitus*, 1982]. At this time, we are unable to explain the low core-top U/Ca in the Caribbean core.

### Downcore U/Ca and Mg/Ca

In both the Atlantic and Caribbean cores, mean U/Ca in Holocene (stage 1) foraminifera is ~25% higher than mean U/Ca from glacial (stage 2) foraminifera, and Mg/Ca trends parallel U/Ca trends. In EN066-17GGC, U/Ca from *G. sacculifer* and *G. ruber* is constant during isotope stage 3 but increases during stage 2 to a maximum value during stage 1 (Figure 3). U/Ca and Mg/Ca in *G. sacculifer* from CP6001-4 also increase from stage 2 to stage 1 (Figure 4). The offset in U/Ca from EN066-17GGC observed in the core top is maintained at depth in the core. U/Ca ratios from both cores are plotted against age in Figure 5. The correlation of interval mean U/Ca and Mg/Ca in downcore samples of *G. sacculifer* shows a strong positive linear relationship between U/Ca and Mg/Ca in samples from both cores, and the U/Mg ratios from these cores are parallel within error (Figure 6). Average U/Ca and Mg/Ca from EN066-17GGC and CP6001-4 for isotope stages 1-3 are summarized in Table 4.

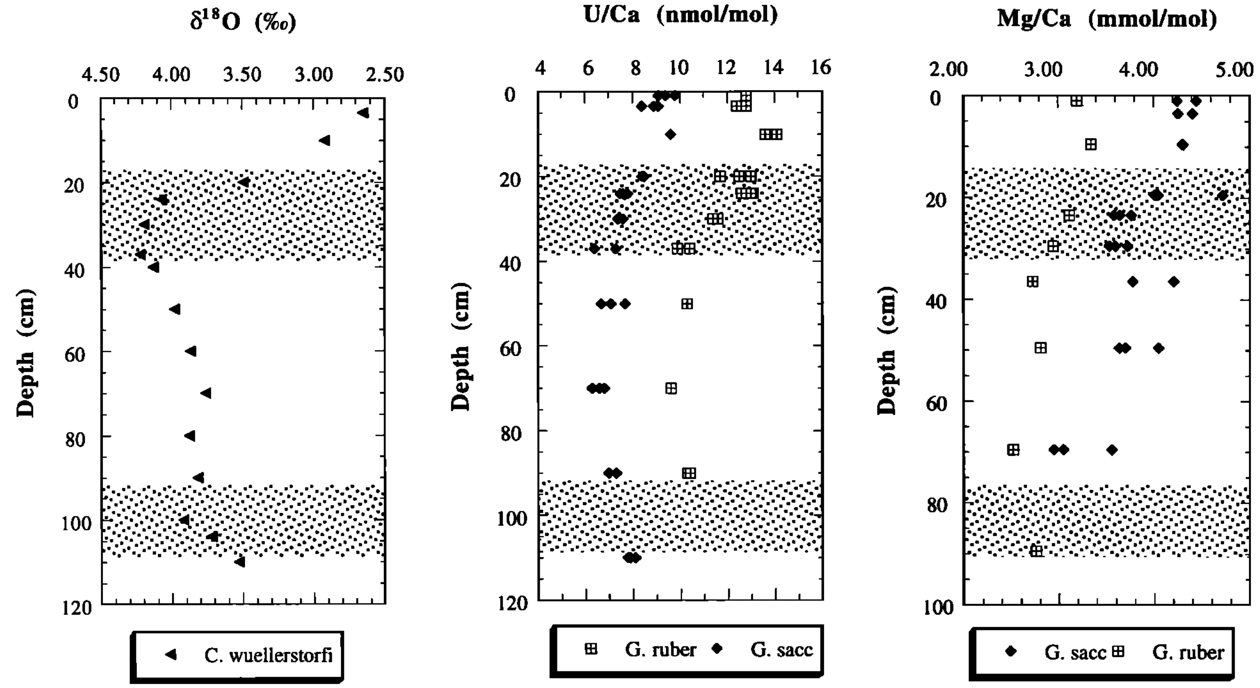

**Figure 3.** Values of $\delta^{18}O$ from *C. wuellerstorfi* (from W. Curry, WHOI) and U/Ca and Mg/Ca in *G. sacculifer* and *G. ruber* (355-425 μm) from eastern equatorial Atlantic core EN066-17GGC. Isotope stage numbers are shown on the $\delta^{18}O$ plot; stippled area indicates glacial stages 2 and 4.

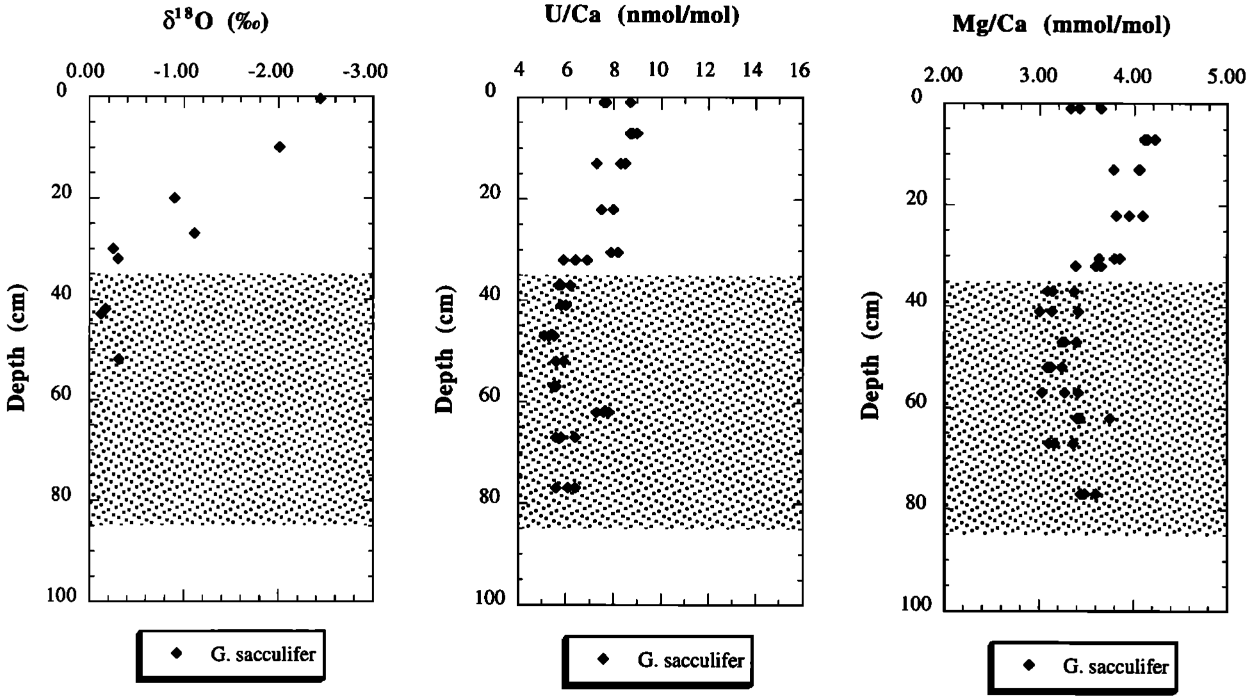

**Figure 4.** Values of $\delta^{18}O$ from *G. sacculifer* (L. Peterson, University of Miami) and U/Ca and Mg/Ca in *G. saculifer* (355-425 μm) from Caribbean core CP6001-4. Isotope stage numbers are shown on the $\delta^{18}O$ plot; stippled area indicates glacial stage 2 as identified by the absence of *G. menardii.*

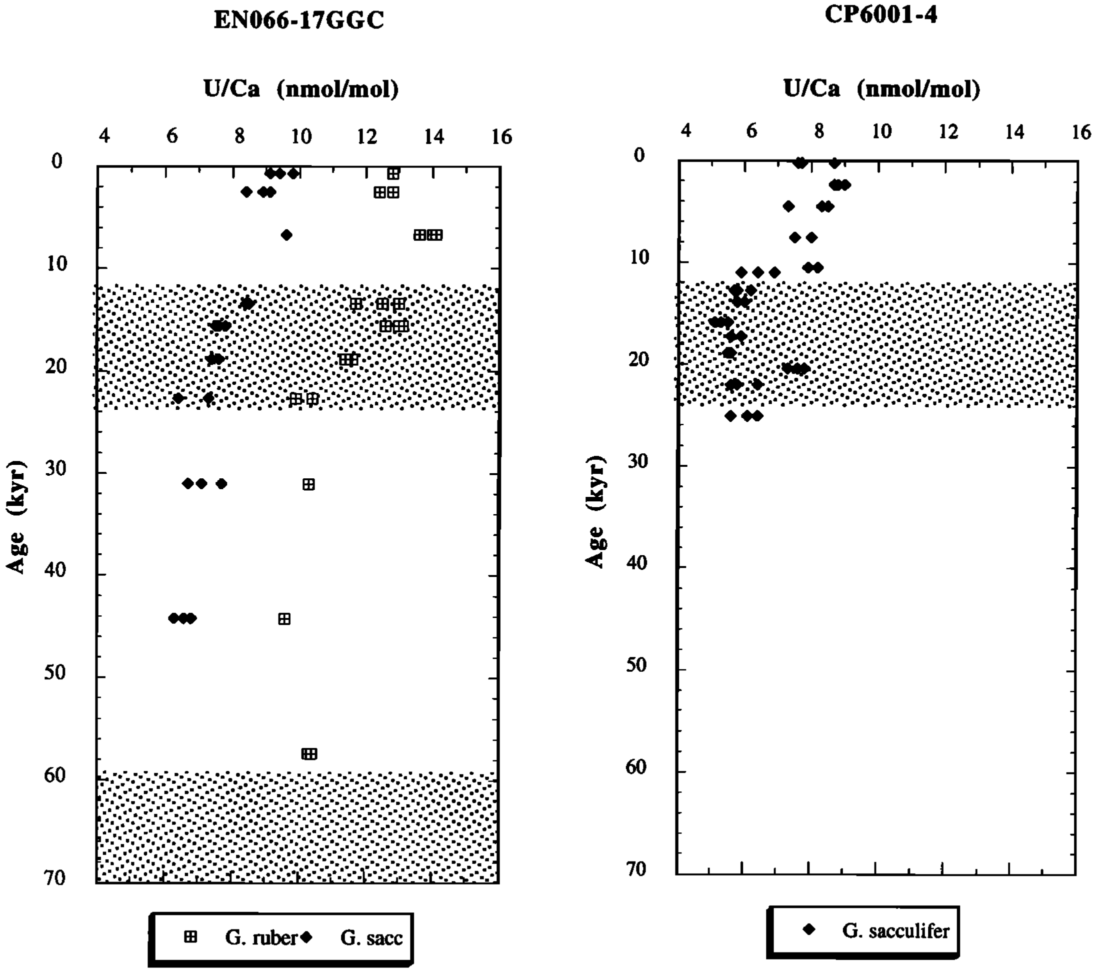

**Figure 5.** U/Ca versus age for EN066-17GGC (Atlantic) and CP6001-4 (Caribbean) cores.

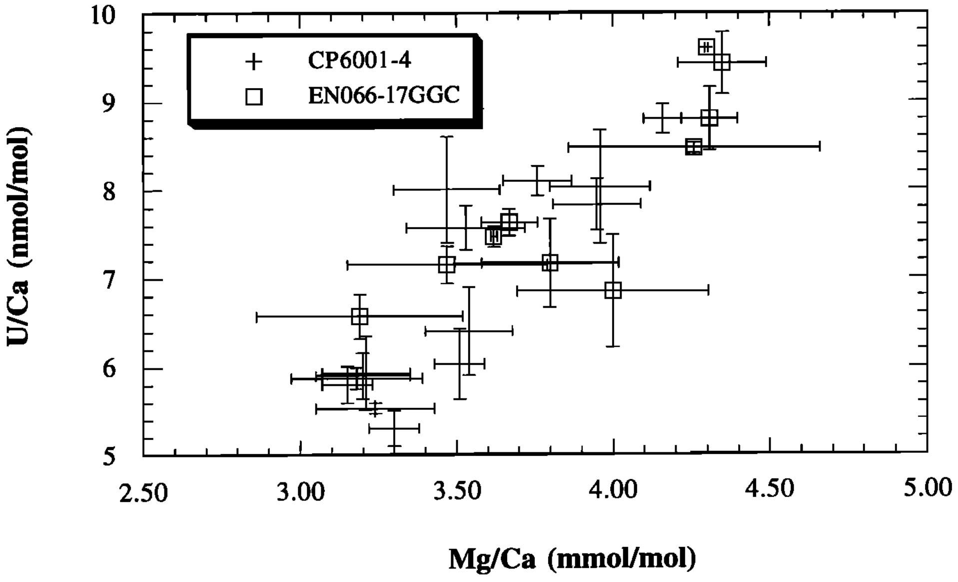

**Figure 6.** Correlation between U/Ca and Mg/Ca ratios in downcore samples of *G. sacculifer* from Atlantic and Caribbean cores, showing a strong positive linear relationship between U/Ca and Mg/Ca in samples from CP6001-4 ($R^2$=0.76) and from EN066-17GGC ($R^2$=0.71). The U/Mg ratios from these cores (equal to the slopes of the regression lines) are parallel within error (for CP6001-4, U/Mg = 3.1±0.5 nmol/mmol; for EN066-17GGC, U/Mg = 2.2±0.5 nmol/mmol).

## Discussion

U/Ca ratios in both cores increase significantly between the last glacial maximum and the Holocene. Downcore variations in U/Ca ratios could be caused by changes in the composition of seawater, by changes in the factors controlling incorporation of U in calcite, or by diagenetic alteration after burial. In this section, we explore several possible explanations for the observed trends in U/Ca and Mg/Ca ratios.

### Glacial-Interglacial Variations in the Composition of Seawater

**Changes in U content of seawater.** If glacial-Holocene changes in foraminiferal U/Ca reflect actual changes in seawater U content, the inventory of seawater U increased by at least 25% between the last glacial maximum and the present. Such a rapid increase in U inventory could be achieved only by increasing U inputs to seawater during interglacial periods and not simply by decreasing the sink size. This can be illustrated using a one-box mass balance model in which loss of $^{238}$U by radioactive decay is assumed to be neglible (parameter values are given in Table 5):

$$\frac{dU_8}{dt} = \mathrm{U}_{8,\mathrm{in}} - \mathrm{k}_{\mathrm{out}} U_8$$

where $U_8$ is the ocean inventory of U (moles), $\mathrm{U}_{8,\mathrm{in}}$ is the U inflow into the ocean (moles/yr), and $\mathrm{k}_{\mathrm{out}}$ is the time constant for U removal from seawater (1/yr). With the initial condition that $U_8(0)=\mathrm{U}_{8,0}$ at $t$=0, the solution is

$$U_8(t) = \mathrm{U}_{8,0} \exp(-\mathrm{k}_{\mathrm{out}} t) + \frac{\mathrm{U}_{8,\mathrm{in}}}{\mathrm{k}_{\mathrm{out}}}\left[1 - \exp(-\mathrm{k}_{\mathrm{out}} t)\right] \quad (1)$$

Assuming long-term steady state and that today's inflow and inventory are at the long-term steady state levels, $\mathrm{U}_{8,\mathrm{in}}=\mathrm{k}_{\mathrm{out}}\mathrm{U}_{8,0}$ and $\mathrm{k}_{\mathrm{out}}=\mathrm{U}_{8,\mathrm{in}}/\mathrm{U}_{8,0}$. After a doubling of the sink for 50 kyr, the ocean U inventory drops by almost 12% to $1.68\times10^{13}$ moles. If there is no change in U inflow into the ocean, after 20 kyr the ocean inventory recovers less than 1% of the original U inventory. The source must increase sixfold in order to produce a 25% increase in U inventory over 20 kyr.

Changes in the global U flux from continental weathering can be constrained using $^{234}$U/$^{238}$U of dated corals and a mass balance model for $^{234}$U and $^{238}$U in seawater. $^{234}$U in rocks is more easily mobilized than $^{238}$U because of alpha recoil damage to the rock matrix; as a result, $^{234}$U/$^{238}$U in most rivers lies between 1.2 and 1.3 [*Cochran*, 1982]. The modern seawater $^{234}$U/$^{238}$U ratio is 1.144±0.002 (2σ; *Chen et al.* [1986]). Initial $^{234}$U/$^{238}$U activity ratios in corals formed over the last 30 kyr average 1.144±0.008 (2σ; *Bard et al.*, [1990]), in agreement with the modern seawater value, and are assumed to record variations in the seawater ratio. We used the mass balance model for $^{238}$U given above coupled with the following mass balance for $^{234}$U (parameter values given in Table 5) to determine how much riverine U could have changed over 30 kyr without driving the seawater ratio away from the modern value by more than the uncertainty of the coral record. For $^{234}$U,

$$\frac{dU_4}{dt} = \mathrm{R}_{\mathrm{in}}\mathrm{U}_{8,\mathrm{in}} + \lambda_8 U_8(t) - (\mathrm{k}_{\mathrm{out}} + \lambda_4)U_4$$

where $U_4$ is the inventory of $^{234}$U in seawater, $\mathrm{R}_{\mathrm{in}}$ is the $^{234}$U/$^{238}$U ratio of U input to seawater, $\lambda_8$ is the $^{238}$U decay constant, $\mathrm{k}_{\mathrm{out}}$ is the time constant for U removal from seawater (the same as for $^{238}$U), and $\lambda_4$ is the $^{234}$U decay constant. With the initial condition $U_4(0)=\mathrm{U}_{4,0}=\mathrm{R}_{\mathrm{sw}}\mathrm{U}_{8,0}$ at $t$=0 (where

**Table 4.** Summary of Mean U/Ca and Mg/Ca From Isotope Stages 1-3

| | | Stage 1 | | Stage 2 | | Stage 3 | |
|---|---|---|---|---|---|---|---|
| Core | Species | U/Ca | Mg/Ca | U/Ca | Mg/Ca | U/Ca | Mg/Ca |
| EN066-17GGC | *G. sacculifer* | 9.3±0.4 | 4.3±0.1 | 7.7±0.6 | 3.9±0.4 | 6.9±0.4 | 3.5±0.4 |
| EN066-17GGC | *G. ruber* | 13.4±0.7 | 3.3±0 | 11.9±1.1 | 2.9±0.2 | 10.2±0.4 | 2.7±0.2 |
| CP6001-4 | *G. sacculifer* | 7.9±0.8 | 3.8±0.3 | 6.0±0.7 | 3.3±0.2 | - | - |

$R_{sw}$ is today's seawater $^{234}U/^{238}U$ ratio), the solution is

$$U_4(t) = R_{sw}U_{8,0}\exp\left[-\left(k_{out}+\lambda_4\right)t\right]$$

$$+\frac{R_{in}U_{8,in}+\lambda_8 U_8(t)}{k_{out}+\lambda_4}\left\{1-\exp\left[-\left(k_{out}+\lambda_4\right)t\right]\right\} \quad (2)$$

At each time *t*, $U_8(t)$ was calculated using equation (1), and the result was used in equation (2) to calculate $U_4(t)$ for the same value of *t*. The results showed that a sixfold increase in river inflow of U would raise the seawater activity ratio by 0.04 after 30 kyr, a change that is well outside the observed variation of coral $^{234}U/^{238}U$ ratios. River inflow could increase by no more than a factor of 2 (assuming constant input ratio) without violating the coral $^{234}U/^{238}U$ constraint. To increase river inflow sixfold without changing the seawater $^{234}U/^{238}U$, input $^{234}U/^{238}U$ would have to decrease by at least 0.10 for the 30-kyr period. This would require a significant reorganization of current weathering patterns, with a greater contribution of U inflow from rivers with near-equilibrium $^{234}U/^{238}U$ ratios, such as the highland streams of the Ganga-Brahmaputra system ($^{234}U/^{238}U \sim 1.05$), which flow through sedimentary rocks that have already lost much of their easily mobilized $^{234}U$ [*Sarin et al.*, 1990].

Other workers constrain glacial-interglacial weathering changes to ±50% or less. Periodic variations in river U inflow on the order of ±50% would produce maximum changes in the seawater $^{234}U/^{238}U$ activity ratio of less than 0.01 for forcing periods of 100 kyr or less [*Richter and Turekian*, 1993], while high-precision Sr isotope measurements in corals over the last 400 kyr limit glacial-interglacial variations in Sr input to within ±30% [*Henderson et al.*, 1994]. Thus our estimate of a doubling of river U input as the largest glacial-interglacial change consistent with coral $^{234}U/^{238}U$ is most likely a maximum estimate, unless significant changes in the river input ratio occurred simultaneously, which we consider unlikely.

**Table 5.** Input Parameters For Mass Balance Model

| Parameter | Value |
|---|---|
| $U_8$ | $1.9\times10^{13}$ moles |
| $U_{8,in}$ | $5.1\times10^{7}$ moles/yr |
| $R_{sw}$ | $6.260\times10^{-5}$ mole/mole<br>(activity ratio 1.144) |
| $R_{in}$ | $6.949\times10^{-5}$ mole/mole<br>(activity ratio 1.27) |
| $\lambda_8$ | $1.551\times10^{-10}$ 1/yr |
| $\lambda_4$ | $2.835\times10^{-6}$ 1/yr |
| $k_{out}$ | $k_{out} = U_{in} / U_0$ |

from *Emerson and Huested* [1991], *Chen et al.* [1986.]; *Richter and Turekian* [1993], and *Edwards et al.* [1986/87].

Low sea levels during glacial periods exposed shallow-water carbonates and organic-rich continental shelf sediments to erosion. However, both of these potential sources would increase glacial, not interglacial seawater U concentrations. A maximum U flux from shallow carbonate deposits to the glacial ocean can be estimated using *Opdyke and Walker*'s [1992] estimate for the glacial maximum bicarbonate flux ($8.0\times10^{12}$ mol/yr) and the $U/CO_3^{2-}$ ratio in corals ($U/CO_3^{2-}$ =1.3 µmol/mol, assuming 3 ppm U). The glacial U flux from carbonates would thus be $1.0\times10^{7}$ mol/yr, or 20% of today's average U transport from rivers ($4.5\times10^{7}$ mol/yr). If the glacial flux were maintained over half a glacial cycle (50 kyr), the seawater U inventory would increase by 3%.

We estimated the contribution of U to glacial seawater from oxidation of sedimentary organic carbon from continental shelves to be 2.5% of today's seawater U inventory, assuming that all of the glacial-interglacial difference in $\delta^{13}C$ of marine carbonates can be attributed to oxidation of shelf carbon and that the U/C ratio of this source is 10 µmol/mol (U/C in reducing sediments from the California margin is 6 µmol/mol [*Huh et al.*, 1987; *Klinkhammer and Palmer*, 1991]). Thus shallow carbonates and organic-rich shelf sediments together could have raised glacial seawater U by ~6% relative to the Holocene. Since our data would suggest that glacial seawater U was ~25% lower than Holocene levels, U from these two sources would if anything mask an even larger change in continental weathering, which has been ruled out based on the U isotopic constraint discussed above.

Reducing sediments could become a source of U to seawater if they are exposed to oxygenated bottom waters. The tendency for U sequestered in reducing sediments to go into solution when sediments are exposed to oxygen is well documented. Simply exposing reducing sediments to air for a few minutes increased pore water U concentrations by a factor of 6 [*Anderson et al.*, 1989b]. In the Chesapeake Bay, seasonal changes in water-column U concentration indicate a U flux into anoxic sediments in summer followed by a flux out of the sediments when bottom waters became reoxygenated in winter [*Shaw et al.*, 1994]. Further evidence that U is remobilized when reducing sediments are exposed to oxygen comes from solid-phase U profiles through organic-rich turbidites in the Madeira abyssal plain, which show U depletion in the oxidized portion of the turbidite and a peak in U concentrations just below the color change indicating the boundary between reduced and oxidized sediments [*Colley et al.*, 1984; *Rosenthal et al.*, 1995b].

The amount of U potentially added to seawater from formerly anoxic sediments depends on the area of anoxic sediments, the sediment U concentration, and the total penetration depth of oxidants (the sum of the biological mixing depth and the depth of $O_2$ diffusion from bottom waters). Mixed-layer depths vary from ~8 cm in pelagic environments to 10-15 cm on continental slopes, reaching 30-140 cm on the continental shelf [*Aller*, 1982; *Kershaw*, 1986]. A reasonable estimate of the average mixed-layer depth of sediments from which U could be remobilized is 15 cm, which is at the high end of the range for continental slope sediments. *Colley et al.* [1984] modeled oxygen penetration into an organic-rich turbidite overlain by slowly accumulating clays as a function of time since the turbidite emplacement into an oxygen-rich environment. Their model suggested that the depth of oxygen penetration after 20 kyr is 15-21 cm. The total depth from which U could be remobilized by biological stirring combined with oxygen diffusion would thus be 30-35 cm. If the area of anoxic sediments expanded by a factor of 10 during glacial periods and these sediments contained 25 ppm U, the amount of U that could be added to seawater at the end of an anoxic episode would be only $2.55 \times 10^{11}$ moles, or 1.3% of today's seawater inventory. Continental margin sediments overlain by low-oxygen bottom waters cannot provide a significant source of U to seawater because the amount of U stored in such sediments today is less than 1% of the U inventory (assuming that these sediments cover 10% of the sea floor, contain 5 ppm U, and can return U to seawater from a depth of 30 cm).

Finally, the correlation of U/Ca with Mg/Ca in downcore samples suggests that at least part of the U/Ca trend is due to changes in metal incorporation and/or preservation. It is unlikely that glacial-interglacial fluctuations in a common source or sink produced the observed downcore changes in foraminiferal U/Ca and Mg/Ca. The mass balance of Mg is controlled by river inflow and by removal via hydrothermal circulation (balancing ~45% of river inflow) and via incorporation into carbonates, clays, and interstitial waters. The residence time of Mg in seawater (with respect to river inflow) is 12-22 million years [*Chester*, 1990], compared with the U residence time of ~375 kyr. Even if seawater concentrations of both elements were affected by the same forcing, the Mg response should be strongly attenuated relative to the U response because of the large difference in residence times, whereas the observed downcore changes in U/Ca and Mg/Ca are of similar magnitude. These arguments lead us to believe that the observed change in foraminiferal U/Ca between the last glacial maximum and the present is unlikely to be the result of changes in the U content of seawater.

### Postdepositional Alteration

**Partial dissolution.** Glacial-interglacial changes in dissolution intensity can be ruled out as the main control on U/Ca and Mg/Ca in downcore samples, since both Atlantic and Caribbean cores show decreased U/Ca and Mg/Ca in glacial samples. If dissolution controlled the trace metal content of foraminiferal calcite in these cores, U/Ca and Mg/Ca would be expected to be higher in glacial than in Holocene samples from the Caribbean.

**Exchange with U in pore waters.** Evidence that $^{234}U/^{238}U$ ratios in foraminiferal calcite increase with sample age has raised the suggestion that foraminiferal U concentrations may be open to exchange with pore water U [*Henderson and O'Nions*, 1995]. Equilibration with pore water U is unlikely to explain our downcore trends in foraminiferal U/Ca because both cores are located in oxic environments in which U is most likely reduced and removed from solution at depths much greater than the depths of the U/Ca minima in these cores (35-40 cm). U reduction and removal from pore waters occurs at about the depth of sulfate reduction, well beneath the depth of $O_2$ penetration into pore waters [*Klinkhammer and Palmer*, 1991]. Bottom-water oxygen concentrations in the vicinities of these cores are 242 μmol/kg (Sierra Leone Rise; 3000 m) and 210 μmol/kg at 3500 m (Beata Ridge; 3500 m) [*Levitus*, 1982]. At the Sierra Leone Rise (core EN066-38GGC; water depth 2931 m) the organic carbon (OC) concentration averages 0.3% from 0 to 30 kyr (approximately 60 cm) [*Curry and Lohmann*, 1990]. At the Ceará Rise (water depth 3271 m; OC = 0.2-0.5% [*Curry and Lohmann*, 1990]; bottom-water $O_2$ = 260 μmol/kg [*Bainbridge*, 1981]), pore water U concentrations from in situ samples average 3.46±0.13 ppb ($2\sigma$) and show a slight increase with depth over the bottom-water U concentration (3.20 ppb) from 5 to 60 cm [*Russell et al.*, 1994a]. This profile, which we expect to be similar to the pore water U profile at our Sierra Leone Rise core because both are oxic, organic carbon-poor environments, is markedly different from the foraminiferal U/Ca trend which decreases monotonically with depth into the sediment to ~40 cm. While no sedimentary OC data are available for the Caribbean core, we expect pore water U profiles in the region of this core to be similar to the Ceará Rise profile because of the oxic depositional environment at the Beata Ridge. Furthermore, it is unlikely that equilibration with pore water U in two cores from different parts of the ocean could produce such similar trends in foraminiferal U/Ca. The observed trends in foraminiferal U/Ca are thus unlikely to be controlled by exchange with pore water U.

An alternate explanation for *Henderson and O'Nions*' [1995] results, which accounts for the increase in foraminiferal $^{234}U/^{238}U$ without a corresponding increase in total U concentration, is that $^{234}U$ is enriched on the foraminiferal calcite surface by decay of adsorbed $^{234}Th$ ejected into pore waters during decay of sedimentary $^{238}U$ (G. Henderson, personal communication, 1996). Exchange with pore water U is a less plausible mechanism since it does not account for the constancy of foraminiferal total U with age.

### Effects on Incorporation of U into Foraminiferal Calcite

The large, rapid glacial-interglacial changes in foraminiferal U/Ca observed in our downcore profiles, coupled with similar changes in Mg/Ca, suggest that changes in factors affecting the incorporation of U and Mg into foraminiferal calcite control the profiles of both ratios.

**Effect of changes in the carbonate ion content of seawater.** The observation that U in saline lakes correlates well with $CO_3^{2-}$ concentration led *Broecker and Peng* [1982] to hypothesize that U in corals could be used as a tracer of changes in ocean $CO_3^{2-}$. Based on the strong tendency of U to form carbonate complexes, *Swart and Hubbard* [1982] suggested that U is incorporated into coralline aragonite by substituting $UO_2(CO_3)_2^{2-}$ for $CO_3^{2-}$ in the calcium carbonate lattice via the reaction

$$CaCO_3 + UO_2(CO_3)_2^{2-} \Leftrightarrow CaUO_2(CO_3)_2 + CO_3^{2-}$$

making U incorporation into corals dependent on seawater $CO_3^{2-}$. Seasonal variations in coralline U/Ca can be explained by changes in the abundance of $UO_2(CO_3)_2^{2-}$ associated with upwelling and nonupwelling conditions [*Shen and Dunbar*, 1995]. Since foraminiferal U/Ca in our cores was lower during the last glacial maximum than during the Holocene, whereas glacial surface-water $CO_3^{2-}$ concentrations were higher than interglacial levels [*Archer and Maier-Reimer*, 1994; *Sanyal et al.*, 1995], foraminiferal U/Ca is apparently not directly correlated to surface-water $CO_3^{2-}$. However, changes in surface-water $CO_3^{2-}$ concentrations would change the speciation of U in seawater and thus, if foraminifera are selective in the U-carbonyl species incorporated into calcite, may change the amount of U available for incorporation. Higher glacial carbonate ion concentrations would drive the equilibrium reactions

$$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3^{\circ}$$

$$UO_2^{2+} + 2CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$$

$$UO_2^{2+} + 3CO_3^{2-} \Leftrightarrow UO_2(CO_3^{2-})_3^{4-}$$

toward formation of U-carbonyl species, decreasing the abundance of free $UO_2^{2+}$. Thus, if foraminiferal U incorporation is sensitive to $CO_3^{2-}$, the inverse relationship between glacial-interglacial foraminiferal U/Ca trends and surface-water $CO_3^{2-}$ would suggest that foraminifera incorporate U as $UO_2^{2+}$.

Existing data on core-top U/Ca in planktonic foraminifera are inadequate to test the sensitivity of U/Ca to changes in carbonate ion concentration, because these samples come from the equatorial Atlantic and Pacific Oceans [*Russell et al.*, 1994b], and cover a small range in $CO_3^{2-}$. However, U/Ca in Atlantic and Pacific core-top benthic foraminifera (*C. wuellerstorfi*) did not differ significantly (within 13%) in spite of a carbonate ion concentration difference of ~20% (from 80 to 110 μmol/kg; this $CO_3^{2-}$ difference should have produced $(U/Ca)_P/(U/Ca)_A$ ~1.8-2.5, depending on the U-$CO_3^{2-}$ species substituted [*Russell et al.*, 1994b]). The relationship between carbonate ion concentration and planktonic foraminiferal U/Ca remains to be investigated and may contribute to observed glacial-interglacial changes in foraminiferal U/Ca. However, downcore changes in Mg/Ca are less likely to be related to changes in carbonate ion content, since in seawater Mg exists primarily as free $Mg^{2+}$ ion, with only a small fraction present as $MgCO_3$ [*Millero and Sohn*, 1992]. Also, $Mg^{2+}$ (radius 0.65 Å) is considered to substitute for $Ca^{2+}$ (radius 0.9 Å) in the calcite lattice [*Mucci and Morse*, 1983]; its incorporation into calcite is expected to be independent of $CO_3^{2-}$.

**Temperature effects.** Temperature effects on incorporation of U and Mg into foraminiferal calcite may explain glacial-interglacial changes in both U/Ca and Mg/Ca. Seasonal variations in U/Ca from corals are strongly anticorrelated with measured seawater temperature [*Min et al.*, 1995] and are in phase with the temperature proxies $\delta^{18}O$ [*Shen and Dunbar*, 1995] and Sr/Ca [*Min et al.*, 1995]. Both studies showed an apparent temperature sensitivity of +4% change in U/Ca per 1°C cooling of seawater. The only existing data on the temperature dependence of U incorporation into foraminiferal calcite are from U/Ca ratios in shallow core-top *Globorotalia tumida* (a deep-dwelling, cold-water species) and *G. sacculifer* (a surface-dwelling, warm-water species). U/Ca in these species are the same within error over $\delta^{18}O$-derived calcification temperatures from 21°C to 27°C, suggesting no significant temperature dependence [*Russell*, 1994]. This apparent lack of a U/Ca-T relationship could be due to interspecies differences in the extent of biological control over U incorporation. If intraspecies foraminiferal U/Ca is indeed sensitive to temperature, our downcore data suggest a direct (rather than an inverse) correlation. Culture experiments to test the temperature dependence of U incorporation into planktonic species are important to establish temperature effects on records used for paleoceanographic interpretation.

The temperature dependence of Mg incorporation in both abiotic and biogenic calcite has raised great interest over the last several decades. The distribution coefficient of Mg in abiotic calcite shows a strong dependence on temperature [*Katz*, 1973; *Mucci*, 1987; *Oomori et al.*, 1987]. Early work on the temperature dependence of Mg/Ca in foraminiferal calcite was somewhat inconclusive. Across several species of planktonic foraminifera collected from South Pacific core tops, *Savin and Douglas* [1973] found a general correlation between calcification temperature (determined from stable oxygen isotopes) and magnesium content when data from all species were considered together, but within a single species (*G. sacculifer*), no correlation between temperature and magnesium content was found [*Bender et al.*, 1975; *Savin and Douglas*, 1973]. Mg in *Globigerina bulloides* and *Globorotalia inflata* from deep-sea sediment cores showed fluctuations in phase with oscillations in paleoclimatic indices [*Cronblad and Malmgren*, 1981], but culture experiments to determine the temperature effect on Mg incorporation into *G. sacculifer* and *O. universa* gave inconsistent results between experiments [*Delaney et al.*, 1985]. Recently, a study of Mg in *Neogloboquadrina pachyderma* (sinistral) in modern core tops showed that Mg covaried with surface water temperature [*Nürnberg*, 1995], and culture experiments using *G. sacculifer* showed a 130% increase of Mg for each 10°C change in water temperature [*Nürnberg et al.*, 1996]. A detailed interpretation of Mg/Ca trends in these cores as indicators of changes in sea surface temperature will be published in a forthcoming paper (D. Hastings et al., manuscript in preparation, 1996). We believe that recent work cited above establishes Mg in foraminiferal calcite as a paleothermometer in the absence of partial dissolution and we suggest as a working hypothesis that changes in temperature control both U/Ca and Mg/Ca profiles in these cores.

## Summary and Conclusions

We developed records of U/Ca in single-species samples of foraminiferal calcite from cores in the eastern equatorial Atlantic Ocean (EN066-17GGC) and the Caribbean Sea (CP6001-4) in order to evaluate the utility of U in foraminifera as an indicator of changes in seawater U concentration. U/Ca in both cores increased by ~25% between isotope stages 2 and 3 and the Holocene, and Mg/Ca trends paralleled U/Ca trends. A 25% increase in seawater U over 20 kyr would require a six-fold increase in U input since the last glacial maximum. Such a large increase in U input is inconsistent with the constancy of the seawater $^{234}U/^{238}U$ over this timescale without compensating changes in the isotopic composition of the input. The amount of U contained in anoxic and suboxic sediments is also insufficient to produce a 25% increase in seawater U. For these reasons, we believe that the observed changes in foraminiferal U/Ca are not due to a change in the seawater U concentration.

The correlation of U/Ca with Mg/Ca in downcore samples suggests that at least part of the U/Ca trend is due to changes in metal incorporation and/or preservation. Dissolution can be excluded as a controlling factor because trends are the same in the Atlantic and in the Caribbean. We believe that temperature effects on the incorporation of U and Mg may control both profiles. Mg incorporation into abiotic and foraminiferal calcite shows a strong direct dependence on temperature, so lower glacial Mg/Ca ratios could be due to cooler glacial calcification temperatures. Insufficient data are available to establish the temperature dependence of U incorporation into foraminifera; culture experiments to determine this dependence are a high priority in order to interpret downcore records of U/Ca in foraminifera.

These results suggest that at least over ~50-kyr timescales, variations in foraminiferal U/Ca due to changes in factors controlling U incorporation are significantly larger than variations due to changes in the extent of anoxic or suboxic sediments. Future research should be directed toward understanding the mode of U incorporation into foraminiferal calcite, particularly the effects of temperature and ambient carbonate ion concentration on foraminiferal U content.

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