Authigenic uranium in foraminiferal coatings: A proxy for ocean redox chemistry

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[1] The rate of uranium accumulation in oceanic sediments from seawater is controlled by bottom water oxygen concentrations and organic carbon fluxes—two parameters that are linked to deep ocean storage of CO_2. To investigate glacial-interglacial changes in what is known as authigenic U, we have developed a rapid method for its determination as a simple addition to a procedure for foraminiferal trace element analysis. Foraminiferal calcite acts as a low U substrate (U/Ca < 15 nmol/mol) upon which authigenic U accumulates in reducing sediments. We measured a downcore record of foraminiferal U/Ca from ODP Site 1090 in the South Atlantic and found that U/Ca ratios increase by 70–320 nmol/mol during glacial intervals. There is a significant correlation between U/Ca records of benthic and planktonic foraminiferal species and between U/Ca and bulk sediment authigenic U. These results indicate that elevated U/Ca ratios are attributable to the accumulation of authigenic U coatings in sediments. Foraminiferal Mn/Ca ratios were lower during the glacial intervals, suggesting that the observed U accumulation on the shells is not directly linked to U incorporation into secondary manganese phases. Thus, foraminiferal U/Ca ratios may provide useful information on past changes in sediment redox conditions.

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1. Introduction

[2] Uranium accumulation in sediments is often used as a proxy for deep water oxygen concentrations or organic matter fluxes in the past [e.g., *Chase et al.*, 2001; *Kumar et al.*, 1995; *Rosenthal et al.*, 1995; *Francois et al.*, 1997; *Frank et al.*, 2000; *McManus et al.*, 2005]. The principle of this methodology lies in the speciation and redox chemistry of uranium in seawater and pore waters. Uranium behaves conservatively in oxygenated seawater as highly soluble uranyl carbonate (U(VI)) complexes with a long oceanic residence time of >400 ka [*Dunk et al.*, 2002]. In contrast, uranium is removed from pore waters of marine sediments where organic matter is consumed by iron or sulfate reduction [*Cochran et al.*, 1986]; U(VI) is reduced to insoluble U(IV) and precipitates from pore waters. U added to sediments by this process is referred to as authigenic U. Its enrichment in sediments is typically limited by the diffusive flux of U from overlying bottom waters to the redox boundary below the oxygen penetration depth. This depth is determined by overlying deep ocean oxygen concentrations and the supply of organic carbon to the sediment

[*Anderson*, 1982; *Barnes and Cochran*, 1990; *Klinkhammer and Palmer*, 1991; *Francois et al.*, 1993].

[3] In practice, a correction has to be applied to measured U concentrations. This is because U exists in marine sediments in two other phases upon which authigenic U is superimposed; as U contained within lithogenic and organic materials. In most cases, authigenic U concentrations have been measured as the difference between the total U content of the bulk sediments and an estimate of lithogenic U based on the product of the total ^{232}Th content, which is assumed to be completely lithogenic, and a U/^{232}Th ratio that is typical for aluminosilicates. However, U/Th ratios can vary by over 40% in detrital minerals [*Anderson*, 1982; *Wedepohl*, 1995]. The authigenic U method does not distinguish between authigenic uranium and uranium associated with organic particles, which may be as high as 2–3 μg/g in sediments with high organic matter fluxes and can lead to overestimations of authigenic U [*Zheng et al.*, 2002a, 2002b].

[4] The above review demonstrates that the authigenic U method in principle provides a very useful means of investigating changes in ocean redox chemistry but with practical uncertainties related to contamination of authigenic uranium by other sedimentary phases. In this paper, we describe an alternative approach that circumvents some of the issues described above. We describe a novel rapid method for measuring authigenic U by analyzing the coatings of foraminiferal calcite shells. Foraminiferal shells buried in marine sediments accumulate secondary U under reducing conditions [*Henderson and O'Nions*, 1995; *Lea et al.*, 2005]. Concentrations of U reach U/Ca of 300 nmol/mol, much higher than lattice-bound U. Foraminiferal calcite has very low concentrations of lattice-bound uranium, with U/Ca ratios

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ranging from 1 to 15 nmol/mol [*Delaney and Boyle*, 1983; *Russell et al.*, 1994, 1996, 2004; *Yu et al.*, 2008; *Raitzsch et al.*, 2011]. Measuring authigenic U in this way avoids the need to correct for non-authigenic sources of sedimentary U. A bonus of the method is that U/Ca measurements can easily be added to existing foraminiferal trace element methods. Thus, foraminiferal U/Ca values may provide a simple means of evaluating redox changes in sediments where bulk sediment U data is unavailable or unreliable.

2. Methods

2.1. Site Location

[5] Foraminiferal U/Ca ratios were measured from sediment cores at ODP Site 1090 located in the subtropical zone of the Cape Basin in the South Atlantic. A continuous record was created by splicing together records from the top of piston core TTN057-6-PC4 (42° 53′S, 8° 58′E, 3751m depth) with ODP Site 1090 (42° 55′S, 8° 54′E, 3702 m depth) at 420 ka. The age model was constructed by tuning benthic foraminiferal $\delta^{18}O$ from *Cibicidoides wuellerstorfi* [*Hodell et al.*, 2001, 2003; *Venz and Hodell*, 2002] to the LR04 benthic stack of *Lisiecki and Raymo* [2005]. Previous measurements of U from bulk sediments at ODP Site 1090 have demonstrated that authigenic U is consistently enriched during glacial intervals [*Martínez-Garcia et al.*, 2009], making it an ideal region to compare intervals of high and low authigenic U accumulation recorded by foraminifera shell U/Ca ratios.

2.2. Element/Ca Measurements

[6] Element/Ca ratios were measured on shells of one benthic (*Uvigerina* spp.) and two planktonic species (*Globigerina bulloides* and *Globigerina inflata*) from sediment samples spanning 200 to 600 ka (6–18 m composite depth, mcd). Approximately 8–15 benthic shells (250–355 μm fraction) or 15–20 planktonic shells (300–355 μm fraction) were picked, crushed, and cleaned by the "Mg-cleaning" method of *Barker et al.* [2003] routine in our laboratory. Briefly, clays were removed by washing with water and methanol. Samples were then oxidatively cleaned to remove organic matter and coarse aluminosilicate grains were removed by hand before a final dilute acid leach to remove contaminants that may have adsorbed to the shell during cleaning. The cleaned samples were dissolved in 0.1M HNO_3 and diluted to 100 ppm Ca prior to analysis by ICP-MS [*Yu et al.*, 2005].

[7] The uncertainty of the U/Ca ratios reflects both analytical error and natural variability between samples. In this study, the calibration was extrapolated to measure U/Ca ratios as high as 450 nmol/mol. Twenty samples with U/Ca ratios between 7 and 335 nmol/mol were re-analyzed using separate instrument calibrations and showed reproducibility within 7%. Accuracy of extrapolation was confirmed by cross calibration with independent standard solutions, where agreement between U/Ca determined from extrapolated instrument calibrations and the standard solutions was 8–10% over the range 65 to 325 nmol/mol U/Ca.

[8] To assess natural variability in U/Ca ratios, four replicate samples of *G. bulloidies* and/or *G. inflata* from three different sediment intervals were picked, cleaned and analyzed. Variability was low ($1\sigma = 2$–8%) among replicates with U/Ca < 15 nmol/mol. There was more variability among replicates with U/Ca > 100 nmol/mol ($1\sigma = 8$–27%).

Potential sources of natural variability are discussed in section 3.3. All data presented in this paper are available in the auxiliary material.[1]

2.3. Effect of Chemical Cleaning on Foraminiferal U/Ca

[9] Methods for foraminiferal trace element analysis often include chemical cleaning treatments to remove organic matter, iron-manganese oxide coatings, or adsorbed contaminants from the carbonate shell. We tested the effects of five cleaning procedures on U/Ca values of planktonic foraminifera *G. bulloides* and *G. inflata* from three different samples with low, medium, and high levels of secondary U accumulation (depths 8.65 mcd, 13.11 mcd, and 13.31 mcd respectively).

[10] For each test, samples of 20 foraminiferal shells were washed to remove clays and then subjected to one of five cleaning procedures: (1) no further cleaning (2) oxidative cleaning (3) acid leach (4) oxidative cleaning and acid leach (5) reductive cleaning, oxidative cleaning, and acid leach. Oxidative cleaning and acid leach steps were carried out as described above. Reductive treatment followed the method of *Rosenthal et al.* [1997]. Coarse aluminosilicate grains were removed prior to dissolution and dilution for ICP-MS analysis. Each test was replicated up to four times to evaluate the reproducibility of these measurements, and all samples were measured in one batch with a single calibration curve. Six samples with Al/Ca ratios greater than 50 μmol/mol were considered contaminated with aluminosilicates and were discarded from the data set. Due to the low number of *G. inflata* shells in these sediments, fewer samples were analyzed for this species.

[11] In samples with little U enrichment (U/Ca < 15 nmol/mol), oxidative cleaning and acid leaching steps do not affect the U/Ca ratios of *G. bulloides* or *G. inflata* shells, suggesting that organic matter and adsorbed contaminants are not significant sources of uranium in this sediment interval (Figure 1a). The reductive cleaning step lowered U/Ca ratios in *G. inflata* by $\sim$30%, which is consistent with the findings of *Yu et al.* [2007] and may be due to partial dissolution of U-rich calcite during this step.

[12] In sediments containing elevated U/Ca ratios, oxidative cleaning alone reduces U/Ca values of *G. bulloides* by $\sim$12–16% (Figures 1b and 1c). The dilute acid leach appears to redissolve authigenic U, resulting in a 14–17% decrease in U/Ca. Oxidative treatment followed by acid leaching has an additive effect on U/Ca values, resulting in a total decrease of 26–33% in *G. bulloides* and $\sim$44% in *G. inflata*. When reductive treatment is added to the cleaning procedure, U/Ca values fall to $\sim$15% of their original value. Since the cleaning procedures have a significantly greater effect on foraminifera with elevated U/Ca ratios, these data suggest that most U is present in a labile form coating shells rather than being lattice bound.

3. Results and Discussion

3.1. U/Ca Variability Between Species

[13] Previous measurements of foraminiferal U/Ca ratios have used reductive cleaning steps to remove secondary


[1]Auxiliary materials are available in the HTML. doi:10.1029/2012PA002335.
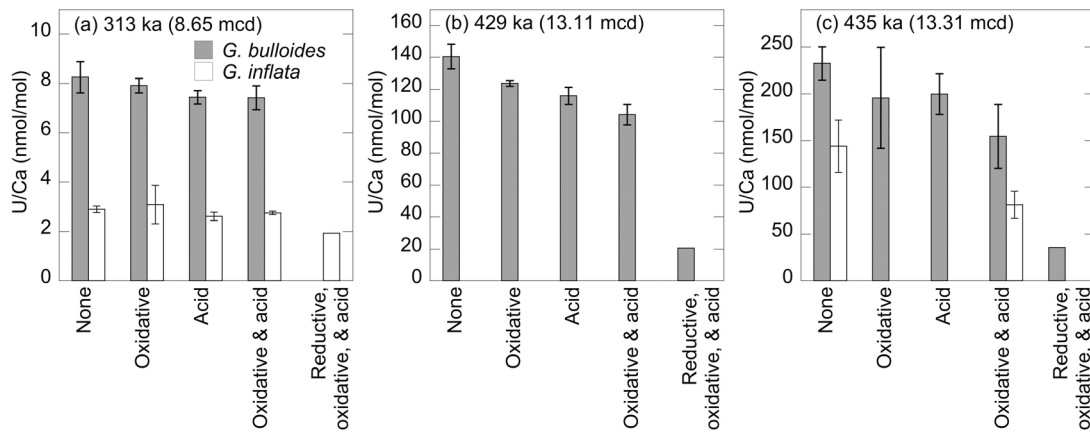
Figure 1. (a–c) The effect of five cleaning procedures on the average U/Ca values of *G. bulloides* (gray bars) and *G. inflata* (white bars) from three sediment intervals of ODP Site 1090. Foraminifera were cleaned with (1) no chemical treatment, (2) oxidative treatment, (3) acid treatment, (4) oxidative and acid treatment, or (5) reductive, oxidative, and acid treatment. Error bars represent 1 standard deviation. Values without error bars are based on single measurements.

phases and reveal calcite lattice-bound uranium values, which typically range from 1 to 15 nmol/mol [e.g., *Russell et al.*, 1994, 1996, 2004; *Yu et al.*, 2008]. In this study, the reductive cleaning step was eliminated in order to preserve the foraminiferal coatings. Thus, the elevated U/Ca values reported here (up to 334 nmol/mol) appear to be caused by a secondary process involving accumulation of U onto foraminiferal shells.

[14] In all three records of two planktonic and one benthic species of foraminifera from ODP Site 1090, there is a clear contrast between low U/Ca values under 10 nmol/mol during interglacial periods and high values between 50 and 340 nmol/mol during glacial intervals (Figure 2a). These patterns cannot be of lattice-bound U. The sensitivity of foraminiferal U/Ca to changes in temperature and pH is far too small to explain the 5–34 fold changes in U/Ca observed
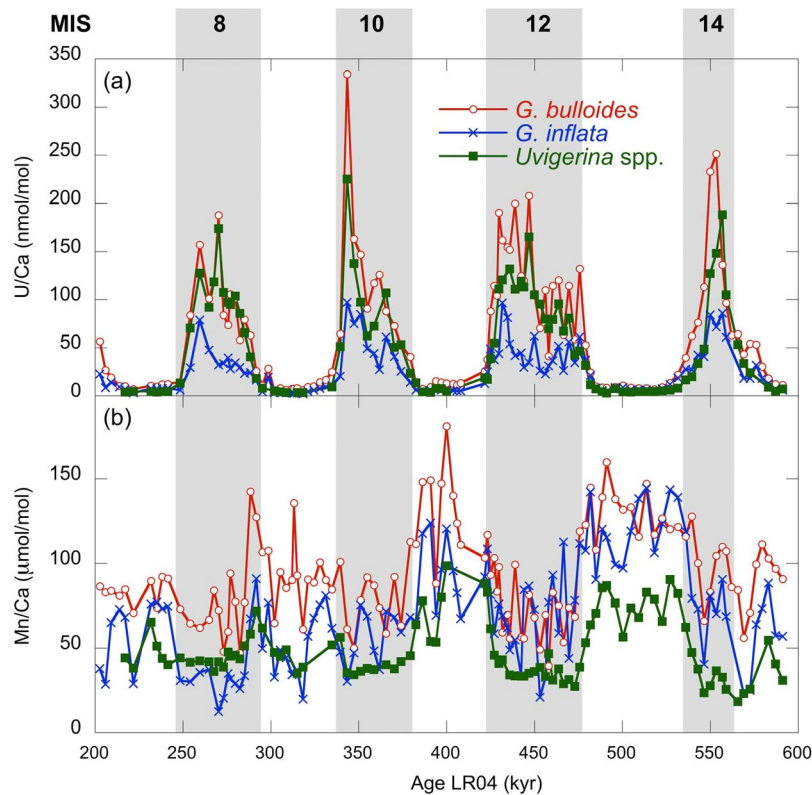
Figure 2. Age profiles of foraminiferal (a) U/Ca ratios and (b) Mn/Ca ratios from ODP Site 1090. Glacial Marine Isotope Stages (MIS) are highlighted in gray.
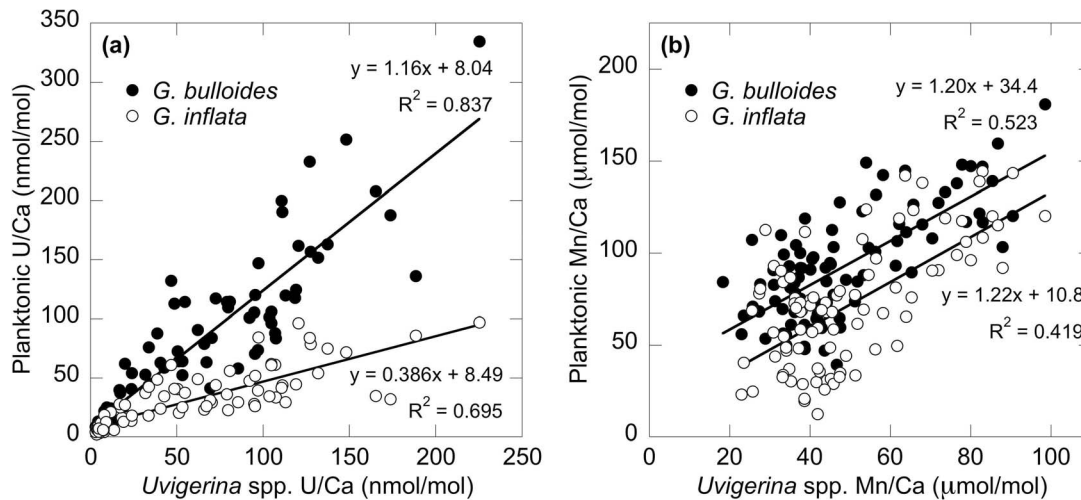
Figure 3. Crossplot of benthic versus planktonic (a) U/Ca and (b) Mn/Ca ratios from ODP Site 1090 sediment intervals.

in these records. Raising temperatures by 1°C results in a 4–21% increase in lattice-bound U/Ca, while lowering pH by 0.1 causes an increase of 12–16% [*Russell et al.*, 2004]. Moreover, colder sea surface temperatures and higher pH are expected in Southern Ocean surface waters during glacial periods, which would both have a decreasing effect on lattice-bound U/Ca. Therefore, the changes in U/Ca between interglacial and glacial periods reflect changes in the accumulation of diagenetically precipitated U rather than changes in lattice-bound U/Ca.

[15] Further evidence that the data reflect the accumulation of secondary U on glacial-age shells is the correlation between planktonic and infaunal benthic foraminiferal U/Ca ratios from ODP Site 1090. Measurements of U/Ca from *Uvigerina* spp. correlate with U/Ca from *G. bulloides* ($R^2 = 0.84$) and *G. inflata* ($R^2 = 0.69$) measured on the same sediment intervals (Figure 3a). The data are not consistent with U being incorporated in the lattice of planktonic foraminifera in surface and subsurface waters. They are consistent with U enrichment occurring after the planktonic and benthic foraminifera shells were buried together in the sediment.

[16] The amount of uranium that accumulates on foraminiferal shells appears to vary with species. U/Ca ratios of *G. bulloides* are similar to those of *Uvigerina* spp. picked from the same sediment interval (ratio ∼ 1.2), while U/Ca ratios of *G. inflata* are considerably lower (ratio ∼ 0.4) (Figure 3a). As discussed earlier, we do not attribute these differences to changes in lattice-bound U. They may results from variations in the morphology or surface chemistry of different foraminiferal species. Since authigenic uranium is deposited as a coating on the surface of sediments, foraminiferal shells that have a larger surface area to mass ratio or rougher surface texture may have higher authigenic U/Ca values. Consequently, *G. inflata* shells, which have smooth glossy surfaces and thick walls, likely accumulate less uranium per mass unit than *G. bulloides* and *Uvigerina* spp. shells, which have pitted and creviced surfaces.

3.2. Mn/Ca Ratios

[17] In order to use foraminiferal U/Ca ratios as a measure of authigenic U, it is important that the accumulation of U on the shell surface is not associated with the formation of Mn oxides and Mn carbonate coatings. Under oxic sedimentary conditions, dissolved Mn in pore waters precipitates as Mn(IV) oxides [*Burdige*, 1993; *Calvert and Pedersen*, 1996]. Reductive dissolution below the oxic-anoxic boundary can redissolve these oxide coatings [*Froelich et al.*, 1979], and the Mn(II) remobilized by this process may be taken up by carbonates or may diffuse up to the Mn redox boundary and be reoxidized [*Klinkhammer*, 1980; *Pedersen and Price*, 1982; *Thomson et al.*, 1986]. To investigate the relation between Mn and U in foraminiferal coatings, we compared changes in foraminiferal Mn/Ca and U/Ca ratios. As with U, the background concentration of calcite-bound Mn in foraminiferal shells is low (Mn/Ca < 20 μmol/mol) compared to the diagenetic accumulation of Mn oxides and Mn carbonate coatings [*Boyle*, 1983; *Pena et al.*, 2005, 2008]. The downcore Mn/Ca profiles at ODP 1090 (Figure 2b) show that Mn/Ca ratios vary between 30 and ∼150 μmol/mol in all three species analyzed. The chemical cleaning procedure used in this study reduces Mn/Ca ratios by 15–22%.

[18] There is a pattern of elevated Mn/Ca ratios during interglacial intervals that correspond to low U/Ca levels (Figure 2b). The lack of correlation between U/Ca and Mn/Ca indicates that foraminiferal U enrichment is not associated with the accumulation of Mn coatings. Instead, the data suggest that Mn accumulation increases during interglacial periods when the sediments are more oxic, while reduced U precipitates or adsorb onto the foraminiferal shell during glacial intervals when the oxygen penetration depth is shallower. Similar patterns of glacial/interglacial changes in Mn and U have been observed in bulk sediments [*Finney et al.*, 1988; *Burdige*, 1993; *Mangini et al.*, 2001] and attributed to changes in the depth of the sedimentary redox boundaries for these elements.
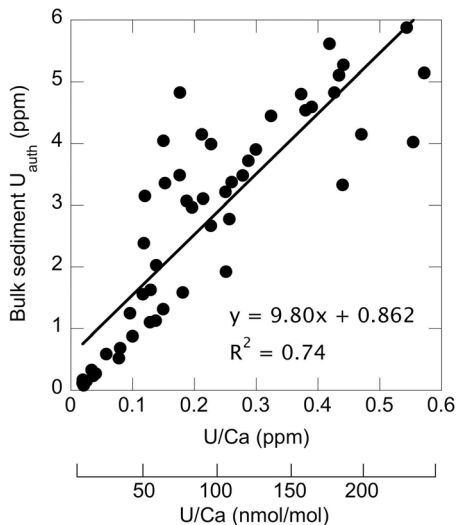
Figure 4. Crossplot of foraminiferal U/Ca (*G. bulloides*) (lower abscissa scale) versus bulk sediment authigenic U (U$_{auth}$) (ordinate scale) from *Martínez-Garcia et al.* [2009]. U/Ca values for each depth were estimated by linearly interpolating between measured points. U/Ca data have been converted to ppm (μg/g) units (upper abscissa scale) to allow comparison with bulk sediment data (1 nmol/mol = 0.00238 ppm U/Ca).

[19] There is a weaker correlation between the Mn/Ca ratios of the species measured at ODP Site 1090 than there is for U/Ca ratios (Figure 3). In addition, the ratio of Mn/U accumulation on foraminiferal shells is different for each species. For example, *G. inflata* shells accumulate more Mn but less U than *Uvigerina* spp. shells from the same sediment interval. Why do shells that are buried together in the same sediment layer appear to accumulate diagenetic phases of U and Mn in different proportions? *Uvigerina* spp. may have lower Mn/Ca ratios than the planktonic foraminifera since it grows below the sediment surface and therefore spends less time in the upper oxic layer of the sediments where Mn oxides form. Another possible explanation is that shell morphology has a different effect on Mn accumulation than it does on U accumulation. *Pena et al.* [2008] found that species had a significant effect on the distribution of diagenetic Mn phases. They observed that secondary Mn phases form a continuous thin layer in the inner part of the chambers of *Neogloboquadrina dutertrei*, whereas *Globigerinoides ruber* shells from the same sediments had Mn phases localized in patches around pores. While such variations may account for the differences between Mn and U enrichment on foraminiferal surfaces, further work is needed to better characterize the mineral phases into which Mn and U are incorporated and to determine their spatial distribution on the shell for each species.

3.3. Comparison With Bulk Sediment Authigenic U Measurements

[20] We compared foraminiferal U/Ca values to previously published bulk sediment measurements of authigenic U for ODP Site 1090 [*Martínez-Garcia et al.*, 2009]. Since different sediment intervals were analyzed with each method, foraminiferal U/Ca ratios were linearly interpolated to estimate

values at each depth where bulk sediment authigenic U data was available. Samples younger than 419 ka were excluded from the comparison because this portion of the bulk sediment record was measured by *Martínez-Garcia et al.* [2009] from a different core (PS2489–2) with slight differences in age model and diagenetic history.

[21] Bulk sediment authigenic U values correlate with interpolated U/Ca values from the same depth interval (Figure 4). However, authigenic U values measured from bulk sediment are ~10 times higher than U/Ca values of *G. bulloides* at ODP 1090. This finding suggests that most authigenic U accumulates on the fine sediment fraction, which has a much greater surface area to mass ratio than intact foraminiferal shells. It may also reflect the underestimation of foraminiferal U/Ca due to the partial removal of the uranium coating during cleaning and the overestimation of bulk sediment measurements, which include organic-associated uranium in the estimate of authigenic U.

[22] There are different sources of uncertainty associated with the bulk sediment method of estimating authigenic U and the method described here. In the bulk sediment method, over/undercompensating for the fraction of lithogenic or organic U can give rise to artifacts in the U data attributed to changes in the flux or composition of detrital and organic material. Other factors may complicate the use of U/Ca ratios as measurement of total sedimentary authigenic U accumulation. Changes in sediment composition may vary the fraction of authigenic U that is incorporated into foraminifera coatings. For example, if the grain size of the sediments changes to finer particles with greater surface areas or to materials with a greater affinity for authigenic U phases, then less uranium may be deposited on the surface of intact foraminiferal shells. In addition, dissolution or a change in shell morphology may also affect foraminiferal U/Ca ratios by changing the shell's surface area to mass ratio. Finally, variations in calcite lattice-bound U/Ca ratios may result in up to 15 nmol/mol changes in foraminiferal U/Ca. While these factors can influence the partitioning of sedimentary U onto foraminiferal shells, the correlation between foraminiferal U/Ca and bulk sediment authigenic U measurements suggests that their effect on foraminiferal U/Ca is small.

[23] Our results demonstrate that the foraminiferal U/Ca ratios obtained by the method described here provide semi-quantitative information about sediment redox chemistry and have the bonus that the method can be easily added to procedures for foraminiferal trace element analysis. The uncertainty of these measurements can be reduced with several improvements to the method. The oxidative and acid leach treatments should be avoided if possible, since they remove authigenic uranium. Second, analyzing a greater number of shells per sample and picking from a narrower size fraction may reduce the variability caused by differences in shell surface area to mass ratios.

3.4. Glacial-Interglacial U/Ca Variability

[24] The downcore variability in foraminiferal U/Ca at ODP Site 1090 demonstrates the use of this proxy for investigating changes in Southern Ocean sediment redox conditions that are linked to carbon cycling. The Southern Ocean is thought to play a central role in regulating glacial-interglacial atmospheric CO_2 cycles [e.g., *Toggweiler et al.*, 2006; *Anderson et al.*, 2009; *Sigman and Boyle*, 2000;
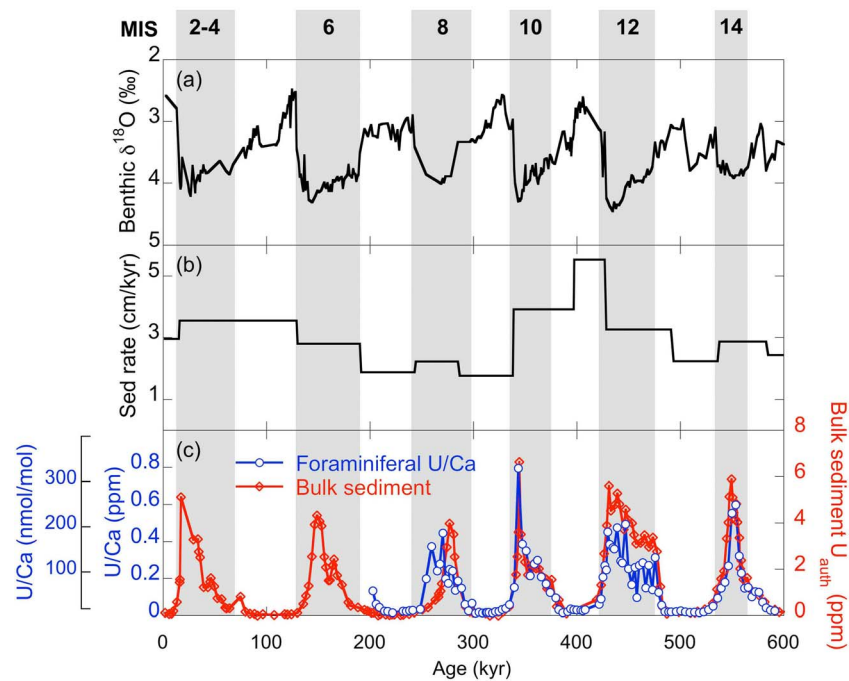
Figure 5. (a) Benthic oxygen isotope ratios of *C. wuellerstorfi* [*Hodell et al.*, 2003]. (b) Sedimentation rates based on the age model tuned to the LR04 benthic oxygen isotope stack [*Lisiecki and Raymo*, 2005]. (c) Foraminiferal U/Ca ratios of *G. bulloides* (this study) also shown converted to ppm units (blue) and bulk sediment authigenic U [*Martínez-Garcia et al.*, 2009] from ODP Site 1090 (red).

Sigman et al., 2010]. Today, it is the region where most of the ocean's CO_2 and nutrient rich deep water makes its first contact with the sea surface [*Primeau*, 2005]. A glacial decrease in upwelling due to Antarctic ice cover or altered wind patterns may have trapped remineralized carbon and reduced O_2 replenishment in the deep ocean [*Watson and Naveira Garabato*, 2006; *Toggweiler et al.*, 2006; *Anderson et al.*, 2009]. Furthermore, iron fertilization or a change in biological community structure may have enhanced export production during glacial stages [*Anderson et al.*, 2002; *Kohfeld et al.*, 2005]. Since these processes increase U enrichment in glacial age sediments, authigenic U profiles can potentially provide useful information on the sequestration of CO_2 in the deep ocean during glacial periods.

[25] The bulk sediment authigenic U and U/Ca records from ODP Site 1090 both show a consistent pattern of authigenic U enrichment in sediments during glacial periods over the past 600 ka (Figure 5). Our ability to independently produce a similar record using foraminiferal U/Ca addresses two major concerns about the reliability of the bulk sediment authigenic U record. *Martínez-Garcia et al.* [2009] demonstrated that the lithogenic and organic carbon content of ODP Site 1090 sediments were significantly greater during glacial periods when estimates of bulk sediment authigenic U are higher. These two factors are possible sources of error that may contribute to the apparent increase in bulk sediment authigenic U. In contrast, foraminiferal U/Ca values are not affected by changes in the lithogenic or organic U content of the sediments. Thus, the good agreement between the U/Ca and bulk sediment records indicates that the error from lithogenic and organic U is minor and supports the claim that these sediments were more reducing during glacial periods.

From 200 to 300 ka, there are some discrepancies between the two records. These may be primarily due to differences in the age models or diagenetic histories of the cores that were sampled to generate the foraminiferal U/Ca (TTN057–6) and bulk sediment (PS2489–2) records after 419 ka.

[26] U accumulation in reducing sediments is a function of three factors: sedimentation rate, organic carbon flux (including vertical export production and horizontal sediment focusing), and bottom water oxygen content. Lower sedimentation rates can increase the amount of time that a sediment interval spends in the redox zone where U precipitation occurs. However, sedimentation rate can be ruled out as an important factor for the observed changes in U enrichment since it does not co-vary with U/Ca or bulk sediment authigenic U (Figure 5b). Furthermore, estimates of sediment focusing based on excess [230]Th as a constant flux proxy measured by *Martínez-Garcia et al.* [2009] indicate that sediment focusing was relatively low at ODP Site 1090. Thus, a shoaling of the oxygen penetration depth due to increased export production or reduced bottom water oxygen concentrations appears to drive the recurring pattern of authigenic U enrichment in glacial-aged sediments at ODP 1090. These results are consistent with the hypothesis that the deep South Atlantic played an important role in glacial CO_2 storage [*Anderson et al.*, 2009; *Skinner et al.*, 2010].

4. Conclusions

[27] This study demonstrates the use of foraminiferal U/Ca ratios as a novel approach for measuring the authigenic U content of sediments. Under reducing conditions within pore waters, authigenic U accumulates on foraminiferal shells in

quantities that are an order of magnitude greater than U/Ca ratios of foraminiferal calcite. We have shown a significant correlation between benthic and planktonic foraminiferal species (Figure 3) and between U/Ca and bulk sediment authigenic U (Figure 4) that extend over paleoceanographic records. A down core profile of foraminiferal U/Ca from the Southern Ocean shows a recurring pattern of higher U/Ca during glacial periods, interpreted as higher export production or reduced bottom water oxygen concentrations. These results demonstrate the feasibility of using foraminiferal U/Ca to infer past sedimentary redox changes.

[28]   A large number of paleo-productivity proxies are used in the literature, including burial rates of organic carbon and opal, excess Ba, radionuclide fluxes of ^{231}Pa and ^{10}Be, and isotopes of N and Si [*Frank et al.*, 2000; *Chase et al.*, 2001; *Kohfeld et al.*, 2005]. It is difficult to separate the effects of productivity and deep-water oxygen concentrations, even in today's ocean, since they often occur together. Used with paleo-water mass tracers, it is possible that the proportions of each factor may be estimated by comparing foraminiferal U/Ca from cores with broad geographic and depth coverage. The method described here provides a tool for obtaining such information with existing procedures for routine foraminiferal trace element analysis.

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