

## Vanadium in foraminiferal calcite as a tracer for changes in the areal extent of reducing sediments

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**Abstract.** We have used the vanadium concentration in cleaned foraminiferal calcite as a tracer of seawater V changes in the past. Since the benthic flux of vanadium is sensitive to the redox potential of sediments, changes in the vanadium concentration of seawater should be a reflection of changes that control the redox state of sediments. V/Ca in *G. sacculifer* from an eastern equatorial Atlantic core (ENO66-17GGC) is 21.6 ( $\pm 2.8$ ) nmol V/mol Ca. This value does not change over 35 kyr, indicating that there was no measurable change in seawater vanadium levels over this period. Potential artifacts from partial dissolution are not significant based on low, constant values for foraminiferal fragmentation (6-7%) in the top 50 cm of the core. A minor correction to account for vanadium associated with Mn carbonate overgrowths, estimated from two Caribbean cores where this mixed phase dominates the deeper V/Ca values, has been applied. Changes in the areal extent of anoxic and suboxic sediments are thus constrained by this constant value and the standard deviation of the measurement,  $\pm 12\%$ . Based on a mass balance for vanadium where suboxic sediments are a source and anoxic sediments are a sink to the ocean, suboxic sediments are predicted to have changed by no more than 0.5–1.5 times the current value, assuming no change in the areal extent of anoxic sediments. This corresponds to 1.3–3.5% of total ocean sediments. Given a constant area of suboxic sediments, the areal extent of anoxic sediments did not increase by more than fivefold, or 1.5% of the ocean floor over the past 35 kyr. The significant reductions in deep water oxygen levels and consequent changes in sediment redox conditions required by polar nutrient depletion scenarios are not reflected in the foraminiferal vanadium data over the past 35 kyr. This suggests that models which call on less or no changes in deep water oxygen are more likely alternatives.

### Introduction

One class of coupled ocean-atmosphere geochemical models developed to explain the reduced glacial age atmospheric  $p\text{CO}_2$  [Barnola *et al.*, 1987; Jouzel *et al.*, 1993] relies on more efficient utilization of nutrients in high-latitude surface waters [Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Martin *et al.*, 1990]. A consequence of these models is that the increased export of organic matter to the deep ocean and subsequent remineralization results in a large depletion in deep water oxygen during glacial periods. A three-dimensional ocean circulation model of the carbon cycle [Sarmiento and Orr, 1991] predicts a decrease in average deep water oxygen by 40  $\mu\text{M}$ , with bottom water anoxia resulting in the southwestern Indian Ocean. Other modeling efforts to explain reduced  $p\text{CO}_2$  during the last glacial age are based on alkalinity changes in the ocean [Broecker and Peng, 1989; Opdyke and Walker, 1992; Archer and Maier-

Reimer, 1994] which predict less or no oxygen depletion during glacial times. The diverse modeling efforts therefore predict different deep water oxygen levels during the last glacial maximum. Which approach is valid?

Several proxies exist to assess changes in sediment redox conditions in order to evaluate and constrain these different models. The most unambiguous indicator for bottom water anoxia is the existence of laminated sediments and the absence of benthic foraminifera. Based on the existence of benthic fauna in most sediment cores, it is safe to rule out vast areas of ocean anoxia for at least the last ten or twenty thousand years. Evidence of decreased bottom water oxygen has been evaluated by determination of trace metal enrichment in sediments [e.g., Dean, 1989; Calvert and Pedersen, 1993; Sarkar *et al.*, 1993; Colodner *et al.*, 1994; Piper and Issacs, 1995; Rosenthal *et al.*, 1995; Yang *et al.*, 1995; Crusius *et al.*, 1996] and faunal indices such as the number of fecal pellets and size and abundance of benthic foraminifera [Pedersen *et al.*, 1988]. These indicators are limited in that they reflect local depositional conditions primarily in equatorial upwelling areas. The record can easily be disturbed by physical erosion, chemical alteration, and bioturbation if overlain by oxygenated sediments [Thomson *et al.*, 1995]. Using these approaches, it would be necessary to sample ocean sediments comprehensively in order to evaluate global changes in the extent of sediments

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overlain by anoxic bottom water. Since the areal extent of anoxic sediments is presently very small, about 0.3% of the ocean floor, an order of magnitude increase would be only 3% of the sediment surface. Such an increase would be difficult to detect. Another approach which reflects global changes is based on the difference between  $\delta^{18}\text{O}$  of atmospheric oxygen and seawater (the Dole effect) as recorded in the Vostok ice core over the past 130 kyr [Bender, 1994]. Since the Dole effect is nearly unchanged on a glacial-interglacial timescale, the authors conclude that there cannot have been major changes in global marine productivity and hence minimal excursions in oxic versus suboxic or anoxic sedimentation.

In this work we develop a new paleoceanographic tracer for changes in sediment redox conditions on a global scale using vanadium incorporation in foraminiferal calcite as an indicator of past V concentrations in the ocean. The potential of using foraminiferal vanadium as a paleoceanographic proxy for seawater vanadium concentrations has recently been demonstrated [Hastings et al., 1996a]. Laboratory culture experiments show that living planktonic and shallow water benthic foraminifera incorporate vanadium into their tests in direct proportion to seawater concentrations. V/Ca values for the same species of foraminifera in different ocean basins are constant for core-top samples collected above the foraminiferal lysocline in different ocean basins. The mean core-top values are  $21.7 (\pm 3.6; n=15)$  and  $112 (\pm 9; n=3)$  nmol V/mol Ca for *Globigerinoides sacculifer* and *Cibicidoides wuellerstorfi*, respectively. Core-top analyses along two submarine rises across the foraminiferal lysocline indicate a significant effect related to partial dissolution of the tests. With increasing depth of deposition, more corrosive bottom waters, and thus more extensive partial dissolution of the test, V/Ca increases by up to a factor of 4 in *G. sacculifer* and by a factor of 2 in *C. wuellerstorfi*. This dissolution effect can be minimized by careful choice of study material from depths shallow enough to avoid significant calcite dissolution. By demonstrating that incorporation of vanadium in cultured foraminifera is directly proportional to seawater concentrations and that global core-top V/Ca values above the foraminiferal lysocline are constant, we have shown that foraminiferal vanadium is a valuable tool to reveal past changes in the vanadium levels in seawater. In this paper we examine the downcore V/Ca record to constrain changes in seawater V over the past 35 kyr, which in turn provides information regarding changes in the redox state of marine sediments.

## The Marine Vanadium Cycle

Vanadium is a useful tracer because the flux to and from ocean sediments is sensitive to the redox state of bottom water. Since the vanadium concentration is nearly conservative throughout the world ocean [Collier, 1984], a single paleoceanographic record is sufficient to provide a global estimate of changes in the areal extent of reducing sediments. The major source of dissolved vanadium to the ocean is riverine input, which accounts for a global flux of  $5 \times 10^8$  mol V yr<sup>-1</sup> [Shiller and Boyle, 1987]. It is well established that anoxic sediments, defined here as those overlain by anoxic bottom water, are a known sink for vanadium [Holland, 1984; Breit and Wanty, 1991] responsible for removing  $8 \pm 5\%$  of the riverine input [Emerson and Husted, 1991]. Hydrothermally

derived Fe oxyhydroxides are highly efficient scavengers of oxyanions such as vanadium and can account for removing  $60 \pm 30\%$  of the riverine input [Trefry and Metz, 1989; Kadko, 1993; Rudnicki and Elderfield, 1993]. The residence time of V with respect to riverine input is 100 kyr [Shiller and Boyle, 1987].

Especially relevant to this work is that several data sets from reducing sediments off the coast of northwest Africa suggest that there is a significant benthic flux of vanadium out of suboxic sediments, where Mn is also diffusing into overlying bottom waters [Serlathan and Hartmann, 1986; Legeleux et al., 1994; Hastings and Emerson, 1995]. This is consistent with the observation that in hemipelagic sediments, V is tightly coupled with the redox cycle of Mn. In suboxic sediments, operationally defined in this work as those where pore water oxygen is depleted within the upper 1-3 cm, and where no surficial enrichment of Mn oxides is observed, lower bulk V concentrations imply a diffusive flux of vanadium into the overlying bottom waters of about  $6 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ . The areal extent of these suboxic sediments is estimated to be 2.5% of ocean sediments based on sediments that have an overlying productivity greater than  $200 \text{ g C m}^{-2} \text{ yr}^{-1}$  at depths not exceeding 1500 m. The depth and productivity criteria are based on those sediments where there is a diffusive flux of V out of the sediments. Other estimates of suboxic sediments are higher, ranging from 8 to 13% [Klinkhammer and Palmer, 1991; Reimers et al., 1992], but are evaluated using different criteria. Based on the estimate that such suboxic sediments account for 2.5% of ocean sediments, the V flux is estimated to be equivalent to 45% of the riverine input. An in-depth examination of the marine mass balance for vanadium and associated data sets is given elsewhere [D. Hastings et al., manuscript in preparation, 1996]. Assuming that other terms in the oceanic V cycle are constant over the past glacial period, changes in the vanadium concentration in seawater should reflect changes in the redox state of the surface sediments.

## Methods

Foraminifera were obtained by washing and sieving ( $>63 \mu\text{m}$ ) bulk ocean sediment several times in 5% ( $\text{NaPO}_3$ )<sub>6</sub> buffered to pH 8 with NaOH to remove clays and fines. After drying, the sediment was sieved into five size fractions ( $<250$ , 250-355, 355-425, 425-495, and  $>495 \mu\text{m}$ ), and single species of foraminifera were hand-picked under a dissecting microscope from the 355 to 425  $\mu\text{m}$  fraction. Those individuals visibly contaminated by black specks, assumed to be ferromanganese oxide, were not used. Foraminifera were gently crushed to open the individual chambers and rigorously cleaned using a method modified from Boyle and Keigwin [1985/86] to eliminate these phases. Two reductive cleaning steps before and after the oxidative step were used. Following the cleaning procedure, all sample handling was performed in a HEPA laminar flow hood in a class 100 clean room. A complete description of the cleaning procedure is given by Hastings et al. [1996a].

Cleaned samples were dissolved, gravimetrically spiked with an <sup>50</sup>V isotope spike enriched to 44 atom %, and taken to dryness. Dried samples were redissolved, eluted through cation exchange resin to remove Ca and isobaric interferences, and analyzed for V by isotope dilution thermal ionization mass

spectrometry (TIMS) or by isotope dilution electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) [Hastings *et al.*, 1996b]. Drying the sample in the ETV unit before analysis quantitatively eliminates the  $\text{ClO}^+$  isobaric interference with V at mass 51, which is a significant problem for V determination by ICP-MS. Analyses with anomalously high isobaric interferences at mass 50 ( $^{50}\text{Cr}$  and  $^{50}\text{Ti}$ ) that interfere with the isotope dilution measurement are not included in the calculated mean values or shown in the figures. This problem occurred in 5% of the samples.

Measurement precision on the same sample of a dissolved  $\text{CaCO}_3$  standard, equivalent to 2.5 mg calcite after cleaning, was  $\pm 3\%$  ( $1\sigma$ ;  $n=10$ ) over the course of one ICP-MS run and  $\pm 7\%$  ( $1\sigma$ ;  $n=9$ ) by TIMS. Using 5 to 15-mg foraminiferal samples that have been cleaned individually reduces the average precision on duplicate samples to  $\pm 8\%$  ( $1\sigma$ ) by ICP-MS and  $\pm 9\%$  ( $1\sigma$ ) by TIMS. This reflects some of the natural variability in actual samples and is also an indication of how effective the cleaning procedure is in removing contaminant phases. The procedural blank value, determined by nonisotope dilution method, was 0.27 pg V. The detection limit for ETV-ICP-MS, defined as 3 times the standard deviation of the blank at mass 51, was 0.3 pg V without the isotope spike and 6 pg V using isotope dilution. The isobaric interferences at mass 50 from Cr and Ti significantly affect the value for the detection limit. A detailed explanation of the analytical method is given elsewhere [Hastings *et al.*, 1996b].

Magnesium, calcium, and manganese were measured simultaneously by inductively coupled plasma mass spectrometry (ICP-MS) on 25- $\mu\text{L}$  subsamples of the dissolved sample diluted into 2 mL of 0.1 N  $\text{HNO}_3$  [Hastings *et al.*, 1996a]. These values were used for Mg/Ca and Mn/Ca determinations. Calcium analyses used to calculate V/Ca ratios were performed by flame atomic absorption spectrophotometry. Fifty- $\mu\text{L}$  sub-

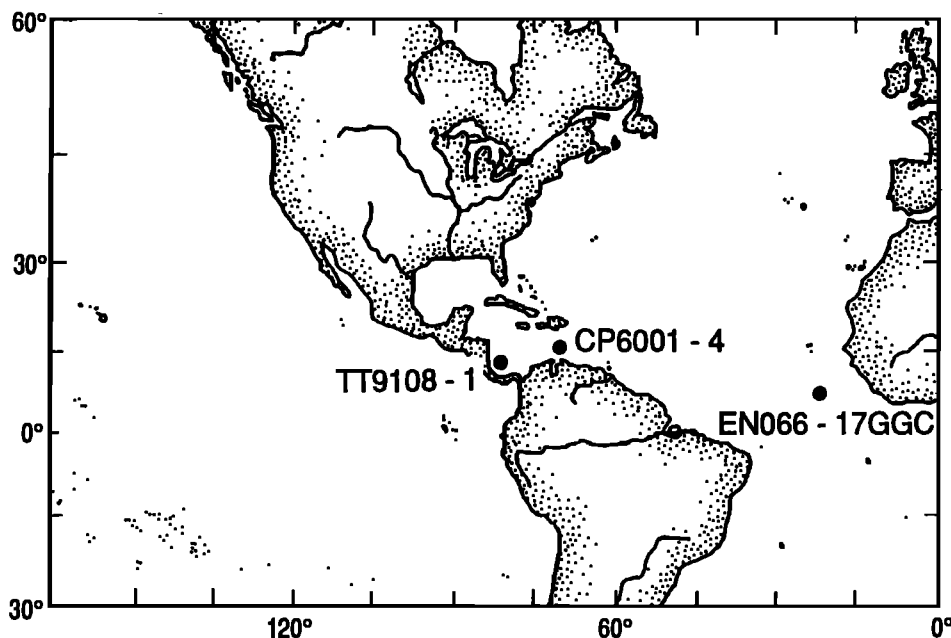
samples of the dissolved sample were diluted into 25 mL of La solution (400 ppm La in 0.05 N HCl and 0.002 N  $\text{HNO}_3$ ). The bulk metal content of marine sediments was determined by digesting dried sediments in strong acids (2 mL concentrated  $\text{HNO}_3$ , 3 mL concentrated HF, and 1 mL concentrated  $\text{HClO}_4$ ) and subsequent analysis by ICP-MS [McLaren *et al.*, 1987; Longerich *et al.*, 1990]. Details on the procedure are given by Hastings [1994].

## Site Description and Chronology

### Caribbean Sea

Two relatively shallow cores were selected in the Caribbean Sea. TT9108-1GC (11°39.83'N, 79°35.52'W; 2540 m) is located in the western region of the Columbia Basin (Figure 1). Measurements of  $\delta^{18}\text{O}$  on *C. wuellerstorfi* and the visual description of the core indicate that the top 50 cm of the sediment was sampled twice. The gravity core probably penetrated the sediment, withdrew briefly, and then reentered. These additional 50 cm are not included in data shown for this core. Core CP 6001-4 (14°55'N, 71° 50'W; 3645 m) is from the Beata Ridge that separates the Columbia and Venezuela Basins. The average sedimentation rate was 4.2 cm/kyr. Since the top 25 cm of the piston core are missing, the data shown are a composite of the trigger weight core and the piston core. The changes in  $\delta^{18}\text{O}$ , V/Ca, and Mg/Ca in the top 50 cm were used to estimate the extent of the core top missing from the piston core.

The 1800-m sill separating the Caribbean Sea from the Atlantic Ocean blocks the inflow of North Atlantic Deep Water. Deep Caribbean waters therefore reflect the chemistry of Atlantic intermediate waters, and sediments from the Caribbean reflect dissolution cycles that are opposite in sense



**Figure 1.** Location of cores used in this study. Specific locations and water depths for these cores are EN066-17GGC, 5°22'N, 21°5'W, 3050 m; CP6001-4PC, 14°55'N, 71°50'W, 3645 m; and TT9108-1GC, 11°39.83'N, 79°35.52'W, 2540 m.

to the dissolution cycles of the deep Atlantic [Peterson, 1990; see also Imbrie *et al.*, 1992]. In contrast to Atlantic sediments, glacial Caribbean sediments reflect enhanced carbonate preservation.

### Eastern Equatorial Atlantic

Core EN066-17GGC (5°22'N, 21°5'W) is a 278-cm gravity core raised from 3050 m water depth on the Sierra Leone Rise. The chronology is based on isotope stage boundaries estimated from oxygen isotope changes measured on *C. wuellerstorfi* and on changes in percent carbonate [Curry and Lohmann, 1986]. Ages associated with these stage boundaries are from Imbrie *et al.* [1984] and incorporate the effects of the <sup>14</sup>C-U year differences now observed [Bard *et al.*, 1990]. The multilinear algorithm [Keigwin and Jones, 1994] based on the original linear equation [Bard *et al.*, 1993] was used to make the corrections to calendar years. Carbonate content decreases downcore from Holocene values of 75% to glacial values of approximately 50% CaCO<sub>3</sub> [Curry and Lohmann, 1986, 1990]. This relatively shallow core in the eastern Atlantic was chosen to avoid dissolution of calcite. Deep waters in this basin are less corrosive than those in the western basin due to the relatively low amount of corrosive Antarctic Bottom Water (AABW) that enters the basin [Warren, 1981]. Thunell [1982] estimated the lysocline to be 4800 m in the eastern basin compared with 4000-4300 m in the western Atlantic. Foraminiferal fragmentation and fraction of dissolution-resistant species increase sharply at 4600 m, suggesting increasing levels of dissolution below that depth [Dubois and Prell, 1988]. Fragmentation and carbonate accumulation data in the eastern basin indicate a shoaling of the lysocline by 1000 m during glacial stages [Curry and Lohmann, 1986], which implies that the foraminiferal lysocline was at about 3700 m during the last glacial period.

## Results

### Caribbean Sea

Relatively shallow cores collected above the foraminiferal lysocline were sampled in order to avoid the effect related to partial dissolution. Foraminiferal fragmentation for core CP 6001-4 (3645 m) is less than 10% throughout the core to stage 5, reflecting good preservation (L. Peterson, personal communication, 1993). Sediments from core TT 9108-1, which is 1100 m shallower than CP 6001-4, should also be well preserved. Thus partial dissolution of tests should not be a significant effect. In core TT 9108-1, V/Ca ratios in *G. sacculifer* (355-425 μm) increase linearly with depth from a core-top value of 20 nmol V/mol Ca to values greater than 500 nmol/mol at 140 cm (Table 1). Mn/Ca values also increase from a value of less than 8 μmol Mn/mol Ca at the top of the core to 270 μmol/mol at 140 cm. In core CP6001-4, V/Ca ratios in *G. sacculifer* (355-425 μm) increase monotonically with depth from a mean core-top value of 20.5 nmol V/mol Ca to a value of 312 nmol/mol at stage 5e (Table 2). Mn/Ca ratios also increase from a core-top value of about 10 μmol Mn/mol Ca to 500 μmol/mol at 482 cm, stage 5e.

In these two Caribbean cores, the foraminiferal V values at depth are 15-25 times greater than the core-top value, while the Mn/Ca values are 35-50 times higher. The correlation

**Table 1.** V/Ca, Mn/Ca, and Mg/Ca Values for *G. sacculifer* From Core TT9108-1GC

Corrected Depth, <sup>1</sup> cm	V/Ca, nmol/mol	Mn/Ca, μmol/mol	Mg/Ca, mmol/mol
1	20.5	4.6	3.87
1	31.0	6.8	3.98
10	26.6	7.4	3.75
10	27.2	3.8	3.56
20	62.4	21.5	3.66
20	36.9	23.8	3.58
30	96.2	49.4	3.41
30	89.0	51.7	3.47
40	146	58.4	3.27
40	137	59.4	3.25
60	261	116	3.07
60	261	132	3.26
80	814	152	3.10
80	307	166	3.07
100	400	229	3.11
100	398	216	3.07
120	487	220	3.37
120	469	231	3.32
140	552	359	3.50
140	552	272	3.34

<sup>1</sup> Depths at and below 10 cm have been corrected for the apparent double penetration of the gravity core by subtracting 50 cm from the original depths.

between V/Ca and Mn/Ca values is significant, with a regression coefficient of  $r^2 = 0.98$  for TT9108-1GC and  $r^2 = 0.80$  for CP 6001-4 (Figures 2a and 2b). Living foraminifera incorporate very little Mn into their tests (<15 μmol Mn/mol Ca), as shown by core-top values in this study and previous measurements of sediment trap samples [Boyle, 1983]. These data suggest that a Mn-rich phase, accreted after deposition, controls both the Mn and V contents of foraminiferal calcite in these sediments. It is not likely to be a FeMn oxyhydroxide coating since the reductive cleaning step used to clean the foraminiferal tests effectively removes these oxyhydroxides [Boyle and Keigwin, 1985/86; Hastings *et al.*, 1996a]. Recrystallization and subsequent incorporation of authigenic Mn in the foraminiferal test is not plausible since the stable isotopic composition of foraminifera accurately records the chemistry of the water in which they grew. The most likely explanation is a mixed Mn, Ca carbonate overgrowth on the tests that is deposited in the reducing sediments during diagenesis [Boyle, 1983]. A mixed Mn-Ca-Mg carbonate has been identified in many reducing environments [Lynn and Bonatti, 1965; Pedersen and Price, 1982; Shimmiel and Price, 1986] and has been suggested to control pore water Mn concentrations [Middelburg *et al.*, 1987]. Such manganoan carbonate coatings are highly enriched in trace elements, including Ba, Cd, and U [Boyle, 1983; Russell *et al.*, 1994, 1996]. Vanadium is enriched in other Mn phases, including manganese nodules [Cronan, 1976] and Mn-rich metalliferous sed-

**Table 2.** V/Ca, Mn/Ca, and Mg/Ca Values for *G. sacculifer* Samples From Caribbean Core CP6001-4 (3654 m)

Corrected Depth, <sup>1</sup> cm	V/Ca, nmol/mol	Mn/Ca, μmol/mol	Mg/Ca, mmol/mol
<i>Trigger Weight Core</i>			
1	25.0	(311)	4.32
1	16.4	10.2	3.71
7	15.6	8.4	3.84
7	28.8	8.7	3.87
22	60.2	57.7	3.63
22	52.6	55.3	3.66
41	97.0	47.9	3.12
41	111	47.8	3.09
<i>Piston Core</i>			
25.5	71.3	39.7	3.67
31.5	139	76.0	2.96
42	129	67.4	3.17
52	45.2	63.7	3.10
52	146	62.9	3.24
72	125	51.7	3.24
162	105	79.1	3.07
162	102	78.9	3.15
202	123	113	3.17
202	110	114	3.18
242	184	154	3.36
242	179	159	3.45
542	304	484	3.86
542	320	506	3.91
662	96.0	160	3.16
662	95.2	150	3.12

<sup>1</sup> Piston core depths have been corrected by adding 25 cm to account for loss of core top.

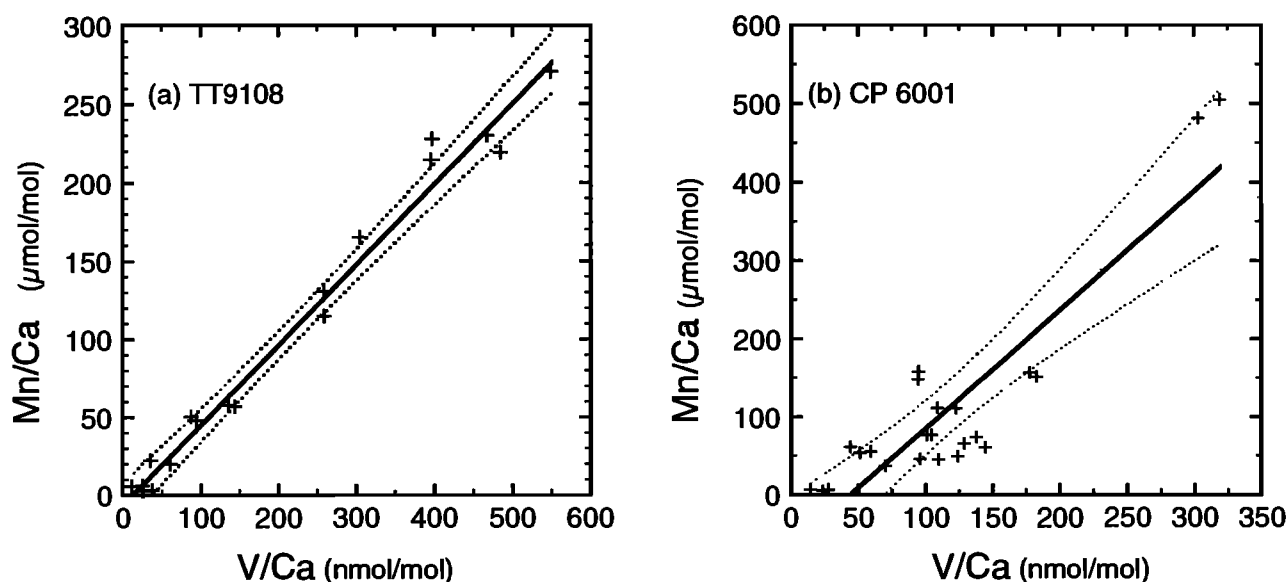
iments [Piper, 1973]. Based on the related geochemistries of Mn and V and the enrichment of other trace metals in Mn carbonate, the Mn carbonate overgrowth would also be predicted to be enriched in vanadium.

To obtain reliable foraminiferal V, it is essential to monitor Mn levels. Samples with Mn/Ca > 50 μmol/mol and with foraminiferal V values that are linearly correlated with Mn/Ca, such as those from the Caribbean cores, cannot be interpreted as indices of paleo-seawater vanadium levels. However, based on measured Mn/Ca values from a given sample and the correlation observed in the Caribbean cores where the Mn carbonate phase controls the V content, we can quantitatively estimate the fraction of V from the Mn carbonate phase. The estimated V content of the Mn carbonate is 0.2 and 0.06 molar percent for cores TT 9108-1GC and CP 6001-4, respectively, based on the slope of the regression lines shown in Figure 2. Although leaching briefly with acid (0.1 N HNO<sub>3</sub>) does appear to preferentially dissolve the Mn carbonate phase relative to the calcite, removal of the Mn carbonate is incomplete, and losses associated with this modified cleaning procedure are unacceptably high given the required sample size.

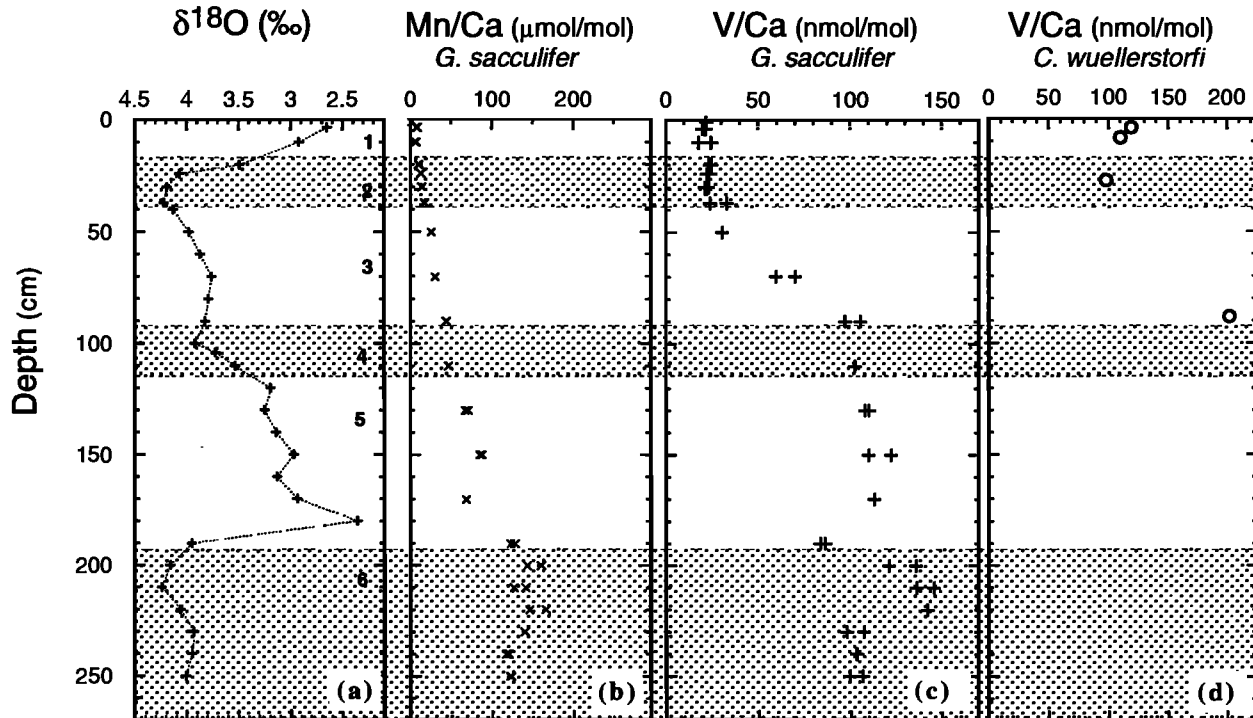
#### Eastern Equatorial Atlantic

Foraminiferal V/Ca values in *G. sacculifer* (355-425 μm) from core ENO66-17GGC are relatively constant in the uppermost 50 cm (Figure 3; Table 3) and are consistent with the global core-top data set [Hastings et al., 1996a]. In the 50 to 90-cm interval, V/Ca increases dramatically to 105 nmol/mol, a value 5 times greater than the core-top value, and then does not change significantly. Mn/Ca ratios increase linearly with depth to values of approximately 200 μmol/mol at 200 cm. Although both Mn/Ca and V/Ca increase with depth, the changes are asynchronous (Figure 4).

The dramatic increase in foraminiferal vanadium from 50 to 90 cm is due to partial dissolution of foraminiferal tests fol-



**Figure 2.** V/Ca plotted versus Mn/Ca for Caribbean cores TT9108-1 and CP 6001-4. Calculated regressions are indicated by the heavy lines and 99% confidence intervals are shown by the dotted lines. (a) Core TT9108-1: calculated slope = 0.513, y intercept = -4.5,  $r^2=0.98$ , and  $n = 18$ . (b) Core CP 6001-4: calculated slope = 1.52, y intercept = -62.9,  $r^2=0.81$ , and  $n = 23$ .



**Figure 3.** Eastern equatorial Atlantic core EN066-17GGC at 3050 m. (a)  $\delta^{18}\text{O}$  from *C. wuellerstorfi*; glacial stages 1-6 are indicated on the right side of the  $\delta^{18}\text{O}$  depth profile and separated by dashed lines. (b) Mn/Ca and (c) V/Ca variations with depth in cleaned *G. sacculifer*. (d) V/Ca in cleaned benthic species *C. wuellerstorfi* from select intervals.

lowing deposition. In this core, mean V/Ca values for each isotope stage show a clear dependence on the relative extent of dissolution, as estimated by the fragmentation data (Figure 5). Foraminiferal fragmentation in the  $>250\text{-}\mu\text{m}$  fraction, a reliable indicator of dissolution, is 6-7% for stage 1 and glacial stage 2, increases to 13% and 23% for stages 3 and 4, respectively, and decreases to 10% for interglacial stage 5 [Curry and Lohmann, 1986]. Based on this index, the greatest dissolution would be expected in stage 4, consistent with fragmentation data from adjacent cores at the Sierra Leone Rise. Individual foraminifera of a given species in the 85 to 90-cm interval are visibly more dissolved than those at or above 50 cm when viewed at 40x magnification, lending qualitative support to this conclusion. In the following sections, only the 0 to 50-cm interval is considered from this core because this is the only section largely free of postdepositional artifacts related to partial dissolution of foraminifera tests.

Since a Mn-rich phase has been inferred to affect significantly the vanadium content of foraminifera even at Mn/Ca ratios below  $100\ \mu\text{mol/mol}$ , the V/Ca values from core EN066-17GGC have been corrected for the amount of vanadium expected to be in the contaminant phase. Based on the slope of the regression shown in Figure 2b between Mn/Ca and V/Ca in the Caribbean core CP 6001-4, 0.06 molar percent V is predicted to be in the Mn carbonate phase. Sediments from CP 6001-4 are more representative of the pelagic conditions encountered at the Sierra Leone Rise in the equatorial Atlantic; the shallower water depth and higher productivity of overlying water suggest that sediments from TT9108-1GC are more

reducing with higher pore water [Mn] than those from either CP 6001-4 located in the middle of the Caribbean Sea or the equatorial Atlantic. The correction for Mn carbonate assumes that some Mn is incorporated into the foraminiferal test when it is originally formed. Based on the average Mn/Ca value of  $15\ \mu\text{mol/mol}$  for reductively cleaned planktonic foraminifera collected in sediment traps [Boyle, 1983] and the range of core-top Mn values determined in this work ( $5\text{-}10\ \mu\text{mol/mol}$ ), an average value of Mn/Ca =  $10\ \mu\text{mol/mol}$  has been chosen for lattice-bound Mn. The Mn carbonate overgrowth correction for V/Ca is

$$(\text{V/Ca})_{\text{corr}} = (\text{V/Ca})_{\text{m}} - ((\text{Mn/Ca})_{\text{m}} - 10) \times 0.6 \quad (1)$$

where  $(\text{V/Ca})_{\text{m}}$  and  $(\text{Mn/Ca})_{\text{m}}$  refer to measured ratios in the cleaned foraminiferal calcite in units of nmol V/mol Ca and  $\mu\text{mol Mn/mol Ca}$ , respectively. Corrections are small: less than 15% of the initial values, except for the 50-cm interval, which is corrected by 30%. Unless stated otherwise, all V/Ca data presented in the following sections are corrected values. The mean corrected V/Ca value of  $21.6 (\pm 2.8; n=14)$  nmol/mol for this 35-kyr period (Figure 6) compares well with the mean global core-top value of  $\text{V/Ca} = 21.7 (\pm 3.6)$  for *G. sacculifer* [Hastings et al., 1996a].

The trends in the vanadium measurements for benthic species *C. wuellerstorfi* (250-425  $\mu\text{m}$ ) are similar to the planktonic profile, with a constant V/Ca value of  $109\ \text{nmol/mol}$  ( $\pm 10\%$ ) in the top 30 cm and a significant increase at 90 cm (Figure 3d; Table 4). The existing benthic measurements confirm the trend obtained from the planktonic species.

**Table 3.** V/Ca, Mn/Ca, and Mg/Ca Values for *G. sacculifer* From Eastern Equatorial Atlantic Core EN066-17GGC

Depth, cm	Age, ka	V/Ca, nmol/mol	(V/Ca) <sub>corr</sub> , <sup>1</sup> nmol/mol	Mn/Ca, μmol/mol	Mg/Ca, mmol/mol
1	0.8	22.1	22.1	2.3	3.74
1	0.8	(31.0)	(31.0)	2.3	3.66
3.5	2.9	21.6	21.6	8.0	3.66
3.5	2.9	20.0	20.0	8.9	3.73
10	8.3	24.8	24.8	6.4	3.82
10	8.3	17.8	17.8	7.5	3.64
20	16.0	24.0	23.3	11.1	3.37
20	16.0	24.9	24.7	10.3	3.48
24	18.5	22.4	20.3	13.6	3.11
24	18.5	23.0	21.1	13.1	3.10
30	22.4	21.2	18.5	14.5	3.22
30	22.4	22.8	19.9	14.8	3.12
37	26.9	24.1	19.4	17.9	2.93
37	26.9	33.1	28.2	18.2	2.99
50	34.8	30.5	20.9	26.0	2.91
70	46.7	69.8	51.5	30.8	3.03
70	46.7	59.5	41.3	30.6	3.00
90	58.6	105	76.6	44.7	3.09
90	58.6	97.1	68.9	43.9	3.21
110	69.0	103	71.8	47.3	3.51
130	82.7	108	62.2	67.1	3.49
130	82.7	110	61.8	70.6	3.48
150	97.3	122	62.7	85.3	3.70
150	97.3	110	48.5	87.9	3.76
170	111.9	113	66.1	68.4	3.75
190	126.5	86.0	-2.0	123	3.73
190	126.5	83.5	-8.5	128	3.93
200	133.4	135	32.3	143	3.88
200	133.4	121	4.6	160	3.52
210	140.2	145	43.4	141	3.38
210	140.2	136	44.9	127	3.57
220	147.0	199	93.5	146	3.44
220	147.0	142	21.0	166	3.45
230	153.8	107	6.1	140	3.73
230	153.8	98.0	--	(347)	3.64
240	160.6	103	17.2	120	3.66
240	160.6	103	19.6	117	3.68
250	167.6	106	19.1	122	3.66
250	167.6	99.5	11.4	123	3.78

Foraminiferal V values below 50 cm are not reliable due to partial dissolution of tests.

$$^1 (V/Ca)_{\text{corr}} = (V/Ca)_{\text{measured}} - ((Mn/Ca) - 10) \times 0.6 \text{ (see text).}$$

Since the concentration of V in sediments is 4 orders of magnitude higher than that in foraminiferal calcite, the potential exists for exchange between the two phases if foraminiferal vanadium is not lattice bound. In sediments from core EN066-17GGC, the bulk V content is relatively constant with depth (Table 5) and shows no correlation with foraminiferal vanadium (Figure 7), which varies considerably downcore. This suggests that the vanadium in foraminiferal calcite is a closed system with respect to bulk sedimentary V and does not exchange over the 160-kyr period represented by the core.

### Sensitivity Analysis

A simple time-dependent model based on the marine mass balance for vanadium is used to evaluate the sensitivity of dissolved V to changes in the areal extent of anoxic and suboxic sediments over time, as well as the other important source and sink terms.

$$V_o \frac{\partial C}{\partial t} = J_R + A_{so} F_{so} - A_o F_o - A_a F_a - J_H \quad (2)$$

where  $V_o$  is the ocean volume;  $C$  is the concentration of vana-

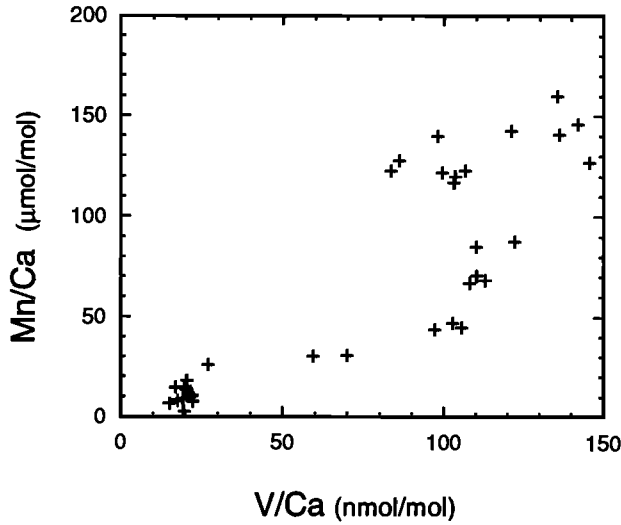


Figure 4. Foraminiferal V/Ca versus Mn/Ca for eastern equatorial Atlantic core EN066-17GGC.

dium in seawater;  $F_o$ ,  $F_a$ , and  $F_{so}$  are equal to the vanadium flux from oxic, anoxic and suboxic sediments, respectively;  $A_o$ ,  $A_a$ , and  $A_{so}$  are equal to the areal extent of oxic, anoxic, and suboxic sediments;  $J_R$  is the riverine flux of vanadium; and  $J_H$  is removal by hydrothermally produced Fe oxides. An instantaneous change is assumed at  $t = 0$  using the present seawater value of 36 nM. Removal to anoxic and oxic sediments and by hydrothermally derived Fe oxyhydroxides is modeled as a first-

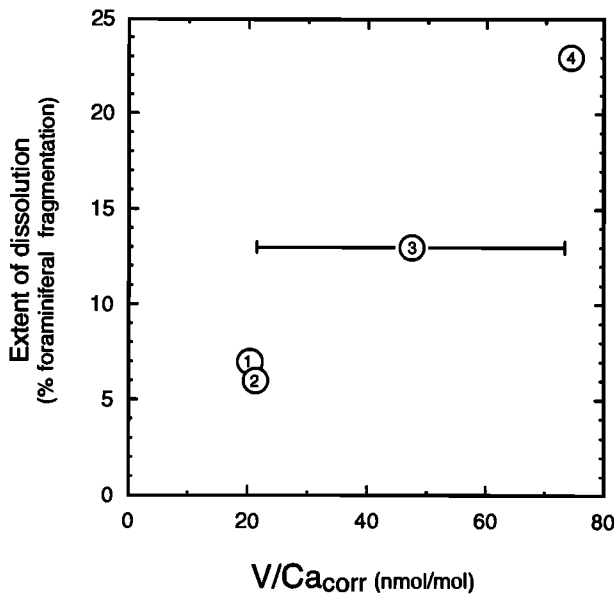


Figure 5. Mean corrected V/Ca for isotope stages 1, 2, 3, and 4 shown as a function of foraminiferal fragmentation in eastern equatorial Atlantic core EN066-17GGC. Each isotope stage is indicated by the corresponding number inside the open circle. Error bar for stage 3 indicates the actual range of foraminiferal V/Ca values for that interval. Increasing V/Ca with increasing fragmentation is consistent with earlier data, indicating that foraminiferal V is sensitive to partial dissolution of tests.

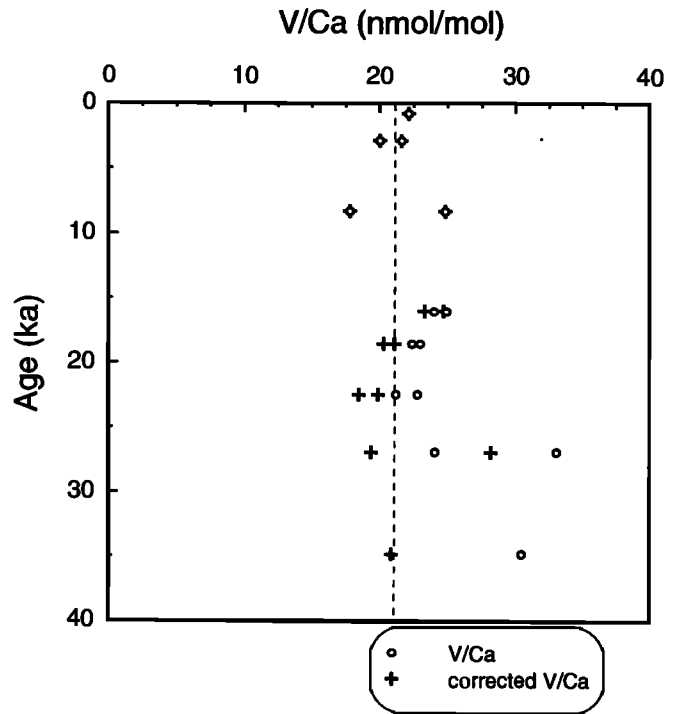


Figure 6. V/Ca values corrected for vanadium in the Mn carbonate phase plotted versus calendar age in the uppermost 50 cm of eastern equatorial Atlantic core EN066-17GGC. Corrected V/Ca values (see text) are indicated by plus signs, and uncorrected values are indicated by open circles, for comparison. Vertical dashed line indicates the global mean core-top value of 21.7 nmol/mol determined earlier [Hastings *et al.*, 1996b].

order reaction. A complete description of the model is presented in the appendix.

The sensitivity of  $[V]_{sw}$  to changes in source and sink terms is illustrated in Figure 8. Increasing  $A_a$ , the areal extent of anoxic sediments, by a factor of 10 from 0.3% to 3% of ocean sediments results in a 12-nM or 32% decrease in vanadium concentration after 50 kyr, or about half a glacial cycle. Increasing  $A_{so}$ , the area of suboxic sediments, by a factor of 5 from the current estimated value of 2.5% to 12.5% of the ocean bottom results in a corresponding increase of 22 nM or 62% after 50 kyr.

Table 4. V/Ca and Mn/Ca Values for *C. wuellerstorfi* from Eastern Equatorial Atlantic Core EN066-17GGC

Sample Depth, cm	V/Ca, nmol/mol	Mn/Ca, µmol/mol
2-6	119	11.1
6-11	110	14.8
25-30	98	32.0
30-35	(243)	104
86-90	202	57.8



**Table 5.** Bulk Metal Concentrations for Equatorial Atlantic Core EN066-17GGC

Depth, cm	CaCO <sub>3</sub> , <sup>1</sup> %	Mn, ppm	Fe, %	V, ppm	Al, %
10	75	516	0.86	34.6	2.11
40	53	546	2.34	77.0	4.44
70	58	411	2.06	61.7	4.27
100	36	299	1.30	43.8	3.05
130	67	276	3.14	89.5	5.33
160	56	370	--	70.0	--
190	58	317	1.77	54.2	3.47
220	45	287	2.16	76.1	4.60
250	38	342	--	86.5	--

<sup>1</sup> Percent carbonate data from *Curry and Lohmann* [1986].

Because the riverine input and hydrothermal activity are major terms in the marine vanadium cycle, possible temporal variability in these processes must also be considered. Changes in chemical erosion and riverine input over glacial-interglacial cycles are not well constrained. Recent calculations based on changes in global bicarbonate fluxes estimate that chemical erosion at 18 ka B.P. was only 20% greater than present-day values [*Gibbs and Kump*, 1994]. A 20% increase in chemical erosion would increase  $[V]_{sw}$  by only 2 nM, or 6%, relative to present conditions. Doubling the riverine input, as predicted by *Froelich et al.* [1992], would result in a 35% increase in V (12.5 nM) over 50 kyr, clearly a significant change (Figure 8). Riverine flux is assumed to be constant in the interpretation of the foraminiferal data.

Change in the rate of seafloor spreading is one indicator of variations in metalliferous sediment production at hydrothermal spreading centers. Precise estimates of seafloor spreading rates indicate that plate motions have been nearly constant ( $\pm 3\%$ ) over the past 5 million years [*Wilson*, 1993]. Plate velocities averaged over shorter timescales of several to a dozen years agree within  $\pm 5\%$  to those over the past 3 Myr [*Gordon*, 1993]. Consequently, removal by hydrothermally produced Fe and Mn rich oxides is assumed to be constant.

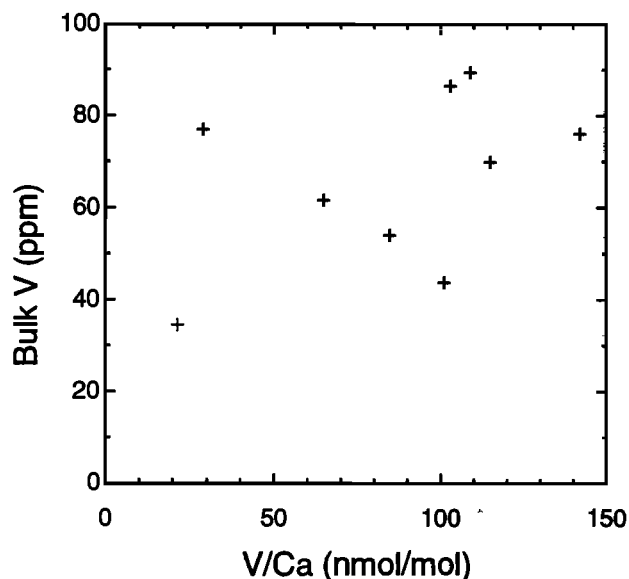
## Discussion

To interpret the foraminiferal data, the model and V mass balance presented earlier are used to constrain changes in the area of reducing sediments. The change in the vanadium concentration of seawater that would be predicted 35 kyr after an instantaneous change in the areal extent of anoxic and suboxic sediments is illustrated in Figure 9. Since the changes in suboxic and anoxic sediments are likely to be correlated, different combinations of changes are shown. The modern value at  $x=1$ ,  $y=1$  is indicated by a solid square. Using the modern values estimated for the extent of anoxic and suboxic sediments of 0.3% and 2.5%, respectively, the percent changes in seawater V concentration are given in this contour plot. For example, if the area of anoxic sediments increased tenfold from the current

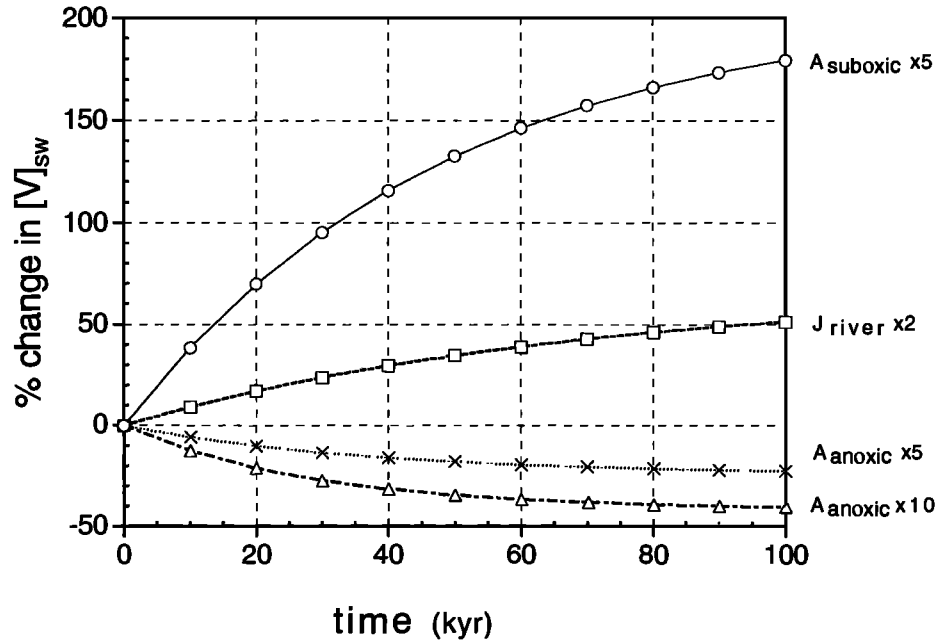
value of 0.3% to 3% (relative change = 10) and the extent of suboxic sediments did not change (relative change = 1), the vanadium concentration of seawater would be expected to decrease by 30% over 35 kyr, as indicated by the asterisk in Figure 9.

From 35 kyr B.P. to the present, corrected V/Ca values are constant in equatorial Atlantic core EN066-17GGC. Analysis of benthic species *C. wuellerstorfi* confirms the result of no measurable change within this interval. Postdepositional alterations including partial dissolution and Mn carbonate overgrowth are not important in this interval, as reflected in the foraminiferal fragmentation data, which indicate no change in dissolution intensity. Mn/Ca levels are low ( $<30 \mu\text{mol/mol}$ ), and correlation between foraminiferal Mn and uncorrected V is poor over this period ( $r^2 = 0.4$ ; Figure 4), demonstrating that a Mn carbonate overgrowth phase is not important. Foraminiferal vanadium data indicate that there was no measurable change in  $[V]_{sw}$ . Consequently, the changes in the extent of reducing sediments predicted by the model are constrained by the standard deviation of the measurement,  $\pm 12\%$ , which is indicated by the stippled region in Figure 9. The model results indicate that assuming no change in the area of suboxic sediments, the areal extent of anoxic sediments did not increase by more than fivefold, or 1.5% of the ocean floor, over the past 35 kyr. This is shown by the annotated arrows at  $y = 1$  and  $x = 5$ . Alternatively, given a constant area of anoxic sediments, suboxic sediments are predicted not to have decreased by more than 0.5 times or enlarged by more than 1.5 times the current value. Assuming a current value of 2.5% [*Hastings and Emerson*, 1995] this corresponds to 1.3-3.5% of total ocean sediments. Simultaneous increases in both variables might be expected. For example, a fivefold increase in the area of anoxic sediments constrains the change in suboxic sediments from approximately 1 to 2 times the current value.

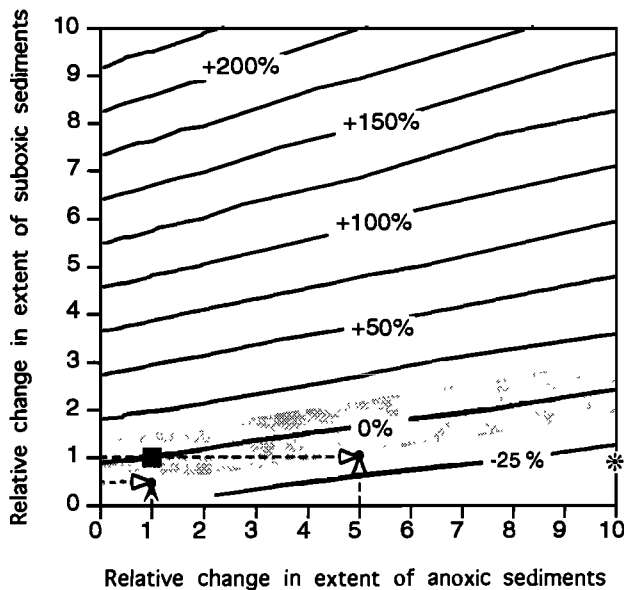
Since real-world changes in the areal extent of reducing sediments are not likely to be instantaneous, another model was



**Figure 7.** Solid phase vanadium versus foraminiferal vanadium in eastern equatorial Atlantic core EN066-17GGC.



**Figure 8.** Percent change in the vanadium concentration in seawater as a function of time after an instantaneous fivefold (crosses) and tenfold (triangles) increase in the areal extent of anoxic sediments, a fivefold increase in suboxic sediments (circles), and a doubling of riverine input (squares).

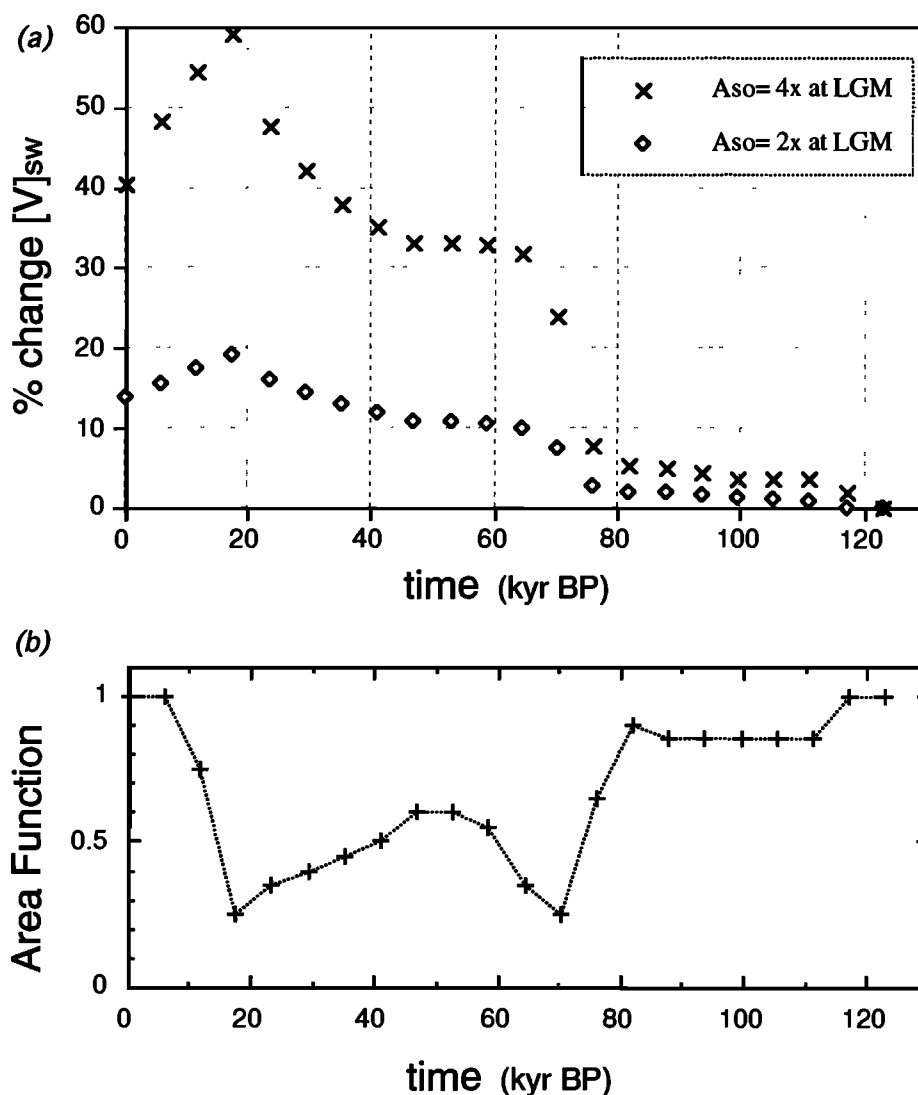


**Figure 9.** Percent change in the vanadium concentration of seawater predicted 35 kyr after an instantaneous change in the areal extent of anoxic and suboxic sediments. Units for the  $x$  and  $y$  axes are changes in their areal extent compared with the modern values of 0.3% and 2.5% respectively. The modern value at  $x=1$ ,  $y=1$  is indicated by the solid square. The stippled region corresponds to the precision of the V/Ca measurement ( $\pm 12\%$ ), which is used as a proxy for  $[V]_{sw}$ . Changes in the areal extent of reducing sediments over the past 35 kyr are constrained to this stippled gray region.

created using a variable input. This model is presented to illustrate the effect of gradual changes in the areal extent of suboxic sediments. Since changes in the areal extent of anoxic sediments result in relatively minor changes in  $[V]_{sw}$  compared with suboxic sediments,  $A_a$  is assumed to be constant. Changes in the area of suboxic sediments are proportional to observed changes in the stacked  $\delta^{18}O$  SPECMAP record [Martinson *et al.*, 1987]. Two different solutions are presented, given an increase in the areal extent of suboxic sediments by a factor of  $2x$  and  $4x$  during the last glacial maximum (LGM) (Figure 10a). The value for  $A_{SO}$  at other times is scaled to the curve shown in Figure 10b. Concentrations of vanadium in seawater were calculated by stepping forward in time using the model described earlier but reassigning the initial condition every 6 kyr.

Foraminiferal V/Ca values limit the changes of  $[V]_{sw}$  within the last 35 kyr to less than  $\pm 12\%$ , or about  $\pm 4$  nM, equivalent to a maximum glacial-interglacial difference of 24%. For the scenario in which suboxic sediments are doubled, the variability reflected in model-derived  $[V]_{sw}$  is 3 nM (8%), which is within this margin of error. For the case where  $A_{SO}$  is expanded by a factor of 4, model-derived  $[V]_{sw}$  changes by 9 nM, or 25%, during the last 35 kyr, which is larger than the measurement error. Given a variable input for  $A_{SO}$  based on changes in  $\delta^{18}O$ , the foraminiferal V data constrain the increase in the areal extent of suboxic sediments to no more than a factor of 4, equivalent to 10% of total ocean sediments.

Previous reconstructions of sediment redox conditions differ in their conclusions. Based on enrichments of Cd and U in glacial Subantarctic sediments, Rosenthal *et al.* [1995] suggest that higher glacial productivity might have increased the areal extent of reducing sediments to 16% during the last glacial maximum, twice the current value of 8%. Other records from the Sea of Japan [Piper and Issacs, 1995] and the south-



**Figure 10.** (a) Percent change in  $[V]_{sw}$  relative to 36 nM, given gradual changes for the areal extent of suboxic sediments.  $A_{so}$  is increased by a factor of 2 (crosses) and 4 (squares) at the last glacial maximum and is scaled to the oxygen isotope stratigraphy for the other times using the function plotted in Figure 10b.

eastern Indian Ocean [McCorkle *et al.*, 1994] also suggest more reducing conditions in glacial sediments. The observed increase in export production in the glacial Southern Ocean, based on several radionuclide proxies and coincident with an increase in lithogenic iron input from wind-blown dust [Kumar *et al.*, 1995], would be expected to drive glacial sediments to more reducing conditions. By contrast, the existence of a Mn spike in Panama basin sediments coincident with a pulse in organic carbon is evidence that overlying waters in the eastern equatorial Pacific could not be suboxic and must have been oxic [Yang *et al.*, 1995] since the mechanism to preserve the Mn spike requires an oxic cap [Calvert and Pederson, 1996]. These eastern equatorial Pacific sediments are particularly sensitive to potential changes since a pulse in organic carbon related to higher productivity seen during the last glacial would be expected to drive them to a more reduced state. These estimates of sediment redox conditions are typically qualitative, restricted to local environments, and subject to possible phys-

ical and chemical alteration of the tracers used to make the estimates.

The foraminiferal vanadium data indicate that over the past 35 kyr, global changes in the areal extent of suboxic sediments and sediments overlain by anoxic bottom water were minimal. If our understanding and assumptions about the V mass balance are correct, this excludes the polar nutrient models as described by simple box model simulations [Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984] as a viable explanation for reduced atmospheric  $pCO_2$  during the last glacial period. The nutrient depletion model using a three-dimensional global circulation model is also not viable, as it results in bottom water oxygen depletion of  $40 \mu M O_2$  [Sarmiento and Orr, 1991], leading to anoxic sediments in the southwestern Indian Ocean. Although difficult to quantify, an increase in the areal extent of suboxic sediments would be expected to accompany an expansion in anoxic sediments. Both of these changes are large

enough to be reflected in the vanadium foraminiferal record, yet there is no detectable change in the V/Ca values.

Other mechanisms to explain lowered  $p\text{CO}_2$  during the last glacial maximum rely on alkalinity changes in the ocean. The polar alkalinity hypothesis [Broecker and Peng, 1989] increases the alkalinity of glacial age Circumpolar Deep Water, which results in an alkalinity increase in Antarctic surface waters and consequently reduced atmospheric  $p\text{CO}_2$ . An increase in the organic carbon/ $\text{CaCO}_3$  ratio of material reaching the sediments would increase organic-carbon-driven dissolution and drive up the  $[\text{CO}_3^{2-}]$  with a corresponding decrease in atmospheric  $p\text{CO}_2$  [Archer and Maier-Reimer, 1994]. The coral reef hypothesis [Opdyke and Walker, 1992] relies on decreased coral growth in shallow surface waters during glacial times with a corresponding shift of  $\text{CaCO}_3$  deposition to the deep sea. These models require less or no deep water oxygen reduction, no additional anoxic sediments, and no significant increases in the areal extent of suboxic sediments. The foraminiferal vanadium data presented in this work support explanations that require minimal excursions in the areal extent of anoxic or suboxic sediments over the past 35 kyr.

## Conclusions

Downcore profiles of foraminiferal vanadium in the Caribbean and Atlantic basins reveal the utility of V/Ca ratios as a paleotracer of seawater vanadium. Postdepositional effects, including partial dissolution and precipitation of an inferred Mn carbonate overgrowth phase, can significantly alter the original V/Ca values. Such effects must be considered in all efforts to interpret the data. The advantage of examining a conservative tracer such as vanadium is that only one acceptable core is required to yield a global record of changes in vanadium concentrations. The top 50 cm (representing 35 kyr) of such a core in the eastern equatorial Atlantic yields such a record.

Using foraminiferal V data from the Caribbean where the Mn carbonate phase controls the V content of the tests, a minor correction was applied to the top 50 cm of the eastern equatorial Atlantic V measurements to compensate for the V in this contaminant phase. The corrected V/Ca profile for this interval reveals no change, indicating that within the error of the measurement ( $\pm 12\%$ ), seawater vanadium levels have not changed over the past 35 kyr. Applying an oceanic mass balance for vanadium and a time-dependent model, this constant value constrains the changes in the areal extent of anoxic and suboxic sediments. Assuming no change in the area of anoxic sediments, the area of suboxic sediments is predicted not to have changed by more than 0.5 to 1.5 times the current value, which corresponds to 1.3–3.5% of the total area of ocean sediments. This is the first effort to quantify the global change in suboxic sediments over late Pleistocene climate cycles. Alternatively, assuming a constant area of suboxic sediments, the areal extent of anoxic sediments did not increase by more than five-fold, or 1.5% of the ocean floor over the past 35 kyr. Using a numerical model where changes in the extent of suboxic sediments are proportional to changes in  $\delta^{18}\text{O}$ , the increase in suboxic sediments is constrained to no more than a factor of 4, equivalent to 10% of total ocean sediments.

Model simulations presented to explain changes in atmospheric  $p\text{CO}_2$  during the glacial period differ in their predicted

changes in deep water oxygen levels and can be constrained by the data set presented here. Polar nutrient depletion scenarios require significant oxygen reductions in bottom waters that would have led to an increase in the areal extent of anoxic sediments and suboxic sediments in parts of the world ocean. The foraminiferal vanadium data indicate such changes have not occurred over the past 35 kyr. Those scenarios based on alkalinity changes in the global ocean, which require little or no change in deep water oxygen, are consistent with the constant V/Ca values observed in this study.

## Appendix

The model for sensitivity of the vanadium concentration in seawater to changes in the redox state of sediments is based on the oceanic mass balance for vanadium.

$$V_o \frac{\partial C}{\partial t} = J_R + A_{so} F_{so} - A_o F_o - A_a F_a - J_H$$

where  $V_o$  is the ocean volume;  $C$  is the concentration of dissolved vanadium in seawater;  $F_o$ ,  $F_a$ , and  $F_{so}$  are the vanadium flux from oxic, anoxic and suboxic sediments, respectively;  $A_o$ ,  $A_a$ , and  $A_{so}$  are equal to the areal extent of oxic, anoxic, and suboxic sediments;  $J_R$  is the riverine flux of vanadium; and  $J_H$  is removal by hydrothermally produced iron oxides.

Sinks are proportional to vanadium concentration ( $C$ ):

$F_o = \beta C$ ;  $F_a = \alpha C$ ;  $J_h = \epsilon C$ . Here,  $\beta$ ,  $\alpha$ , and  $\epsilon$  are solved for using present-day values,  $C_{t=0} = 36$  nM. Constants are  $V_o = 1.37 \times 10^{24}$  cm<sup>3</sup>;  $A = 3.61 \times 10^{18}$  cm<sup>2</sup>;  $J_r = 5.4 \times 10^8$  mol yr<sup>-1</sup>; and  $F_o = 0.12$  nmol cm<sup>-2</sup> yr<sup>-1</sup>. Assumed present day values are  $A_{so} = 2.5\% A$  and  $A_a = 0.3\% A$ .

Solution is

$$C = \frac{\lambda}{\gamma} + X \exp(-\gamma t)$$

where

$$\lambda = \frac{R + A_{so} F_{so}}{V_o}; \quad \gamma = \frac{A_o \beta + A_a \alpha + \epsilon}{V_o}; \quad X = C_{t=0} - \frac{\lambda}{\gamma}$$

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