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Vanadium in foraminiferal calcite: Evaluation of a method to determine paleo-seawater vanadium concentrations

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Abstract—We assess the potential of using foraminiferal calcite as a paleoceanographic indicator of seawater V concentrations. Laboratory culture experiments show that living benthic and planktonic foraminifera incorporate V into their test in direct proportion to seawater concentrations. Distribution coefficients relative to the culture solution are $D = 2.1 \times 10^{-3}$ and 2.8×10^{-3} for *G. calida* and *A. lobifera*, respectively. We use a cleaning procedure that effectively removes most V-rich contaminant phases from foraminiferal calcite preserved in the fossil record including organic matter and Mn-Fe oxyhydroxides. MnCO₃ overgrowths cannot be eliminated. Since V is conservative in the ocean, foraminiferal calcite recently accreted and found in surface sediment samples should have the same V content if this tracer accurately reflects seawater concentrations. V/Ca values for the same species of foraminifera are constant for core-top samples collected above the foraminiferal lysocline in different ocean basins. The mean distribution coefficients relative to seawater are $D = 5.8 (\pm 1.0) \times 10^{-3}$, $10.3 (\pm 0.7) \times 10^{-3}$ and $32 (\pm 2.5) \times 10^{-3}$ for *G. sacculifer*, *G. tumida*, and *C. wuellerstorfi*, respectively. These differences suggest that V incorporation is species dependent. Core-top analyses along two submarine rises in the Equatorial Atlantic and Pacific oceans indicate significant dissolution effects. With increasing depth of deposition, and thus more extensive partial dissolution of the test, V/Ca decreases by a factor of three in *G. tumida*, increases by up to a factor of four in *G. sacculifer*, and increases by a factor of two in *C. wuellerstorfi*. No exchange between foraminiferal V and detrital V in sediments is observed over an interval of 200 kyr.

1. INTRODUCTION

The V concentration in the modern ocean deviates slightly from conservative behavior, with an average deep water value of 36 nM and a surface depletion of about 4 nM (Collier, 1984; Hastings and Emerson, 1995). The oceanic residence time of V with respect to riverine input is approximately 100 kyr (Shiller and Boyle, 1987). Sediment and porewater measurements indicate that the flux of V between sediments and seawater is sensitive to the redox chemistry of surface porewaters, which is determined mainly by the particulate rain rate of organic carbon and bottom water oxygen concentration. Anoxic sediments, which are a known sink for V, account for 8 (± 5)% of the riverine input (Emerson and Husted, 1991). Sediments overlain by oxygen-depleted bottom water may be a major source of V to the ocean, based on porewater profiles and bulk sediment analyses (Seralathan and Hartmann, 1986; Emerson and Husted, 1991; Hastings, 1994). If other terms in the oceanic V cycle have been constant over the past glacial cycle, temporal changes in $[V]_{sw}$ should be a reflection of global changes in the boundary conditions that control the redox state of the surface sediments.

Several of the ocean-atmosphere models developed to explain the reduced atmospheric CO₂ observed during glacial periods invoke a more efficient “biological pump” at high

latitudes (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984). These models require a significant depletion of deep-water oxygen levels of 144 $\mu\text{mol/kg O}_2$ and lead to the prediction of deep ocean anoxia during glacial periods. Similar nutrient depletion scenarios that employ more sophisticated three dimensional global circulation models (Sarmiento and Orr, 1991) call on less drastic but nonetheless significant deep-water oxygen reductions of about 40 $\mu\text{mol/kg O}_2$ during the last glacial period. Other models of the Quaternary CO₂ history based on the organic carbon-driven dissolution of carbonate sediments (Archer and Maier-Reimer, 1994) or proposed changes in high-latitude alkalinity (Broecker and Peng, 1989) predict less or no glacial deep-water anoxia. Given our present estimates of benthic flux values from reducing sediments (Hastings, 1994), an increase in the extent of sediments overlain by anoxic bottom water from the present-day value of 0.3% to 3% would be predicted to decrease the V concentration of seawater by 34% after 50,000 yr, or half a glacial cycle. Doubling the area of suboxic sediments would result in an increase of about 30% in $[V]_{sw}$ after 50 ky, both of which are significant and detectable changes.

This work assesses the viability of V incorporation in foraminifera and corals as a paleoceanographic indicator of the V content of the ocean. Such data potentially provide a means to constrain ocean models of glacial-interglacial change and increase our understanding of the glacial ocean. The success of the method requires that the V content of calcite tests be related to the V concentration of the seawater

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in which it is grown, that surficial contaminant phases can be removed, and that the V/Ca ratio does not change after the CaCO_3 is formed. This study involved experiments with living planktonic and benthic foraminifera cultured in the laboratory to determine the distribution coefficient, evaluation of the effectiveness of the cleaning method to remove contaminant phases, and investigation of postdepositional alterations including dissolution and association with V-rich contaminant phases that could significantly alter the original V content of the foraminiferal calcite. The potential of coralline aragonite deposited up to 19 kyr BP as a recorder of seawater V levels was explored by analyzing ancient corals drilled off Barbados.

2. METHODS

2.1. Collection and Culture of Live Foraminifera

2.1.1. Planktonic foraminifera

Planktonic foraminifera were collected 2–4 km offshore from the H. Steinitz Marine Biology Laboratory, Eilat, Israel, in the northern Gulf of Eilat in February and March 1992. Drift tows were made using a 200 μm plankton net for a duration of 10 min at 5–10 m depth. Living plankton samples were brought back to the laboratory immediately after collection where individual foraminifera were picked from the bulk plankton with a Pasteur pipette under a dissecting microscope. *Globigerinella calida*, a spinose, nonsymbiotic species, was cultured. They were placed in glass culture dishes with fresh seawater to recover for at least 24 hours (see Erez and Luz, 1983; Hemleben et al., 1989). Following recovery, healthy foraminifera, as indicated by long spines, were isolated in small petri dishes, measured with a micrometer ($\pm 20 \mu\text{m}$) and fed one newly hatched brine shrimp (*Artemia* nauplius). Typical sizes ranged from 150–300 μm diameter and skeletal weight of 2–6 μg . Surface seawater was collected in acid rinsed polyethylene carboys at the same stations, brought back to the laboratory, and filtered through a 0.45- μm filter for use in the culture experiments.

Healthy foraminifera of similar initial sizes were grouped together in 250 mL covered Pyrex culture dishes filled with filtered seawater. The temperature of the culture solutions was maintained in a thermostated water bath at 23°C (± 0.3), the average ambient surface temperature in the Gulf of Eilat at the time of collection. Light levels were controlled with a water-cooled halogen light at approximately 250 $\mu\text{Einsteins}/\text{m}^2/\text{s}$ on a 12 h on/off cycle. Evaporation was controlled by covering culture dishes with an inverted glass petri dish and sealing with parafilm. Salinities were monitored by a hand-held refractometer to check for losses due to evaporation. No detectable changes in salinity were found.

Solutions of different vanadium concentrations were prepared by spiking filtered seawater with an ammonium vanadate standard solution to yield 1, 2, and 4 times natural seawater V concentration. Change in alkalinity due to addition of this standard was 24 $\mu\text{eq}/\text{kg}$ or about 1%; change in pH was less than 0.05 pH units and thus considered negligible. Radioactive V-49 ($t_{1/2} = 331$ days) was added as a tracer in correspondingly increasing activities. V-49 was isolated from an irradiated zinc oxide target by the Medical Radioisotope Research Program at Los Alamos National Laboratory.

Each foraminifer was fed daily with one larval brine shrimp (*Artemia* nauplius) for the first four or five days of culture but less often during subsequent days. Aliquots of culture solution (40 μL) were sampled regularly to monitor potential losses of V including adsorption onto the glass walls. Each experiment lasted 12 days during which time 75–90% of the foraminifera went through gametogenesis. Gametogenesis occurs at the end of the life cycle in planktonic individuals and involves the expulsion of thousands of individual gametes from the shell leaving behind an empty, white test (Bé et al., 1977; Hemleben et al., 1989), which is similar to the shells found in sediments.

At the end of each experiment, the tests were rinsed briefly five times in distilled, deionized (DDI) H_2O to remove excess V and

sea salts, cleaned with hot alkaline H_2O_2 (10% H_2O_2 in 0.1 N NaOH) at 80°C for 20 min with one minute sonication every 5 min to remove organic material, rinsed 3 \times in DDI H_2O again, dried and stored in plastic micropaleontological slides to be weighed later. Foraminifera were subsequently dissolved in 0.5 mL 1% H_3PO_4 . Both dissolved foraminifera and specific activity samples were added to 10 mL fluor (Insta-gel II) and counted on a Packard 1900 CA liquid scintillation analyzer. A quench correction of 1.18 was included to compensate for the dissolved Ca added to the fluor.

Two control experiments were carried out to test for potential artifacts related to adsorption effects and the thoroughness of the rinsing and cleaning procedure. A dead control was made by placing fourteen dead foraminifera in seawater spiked with V-49 for the duration of the live uptake experiment. Foraminifera were killed by immersion in 4% buffered formalin solution for 30 min. In the live control, fourteen living foraminifera were placed in V-49 spiked seawater for 30 min, rinsed, and cleaned as previously described.

Vanadium incorporation into the foraminiferal test was corrected for the presence of initial calcite not grown in culture by subtracting the estimated initial weight from the final measured weight to obtain a value for the new calcite. The initial amount of calcite present in an experimental group prior to culture cannot be determined directly. We developed a size-weight relationship for *G. calida* by measuring foraminifera not used for culturing with a micrometer then rinsing, drying, and weighing them on a Cahn Model 4700 electrobalance. With length and mass expressed in micrometers and micrograms respectively, the relationship is

$$\text{length} = 253 \times \log(\text{mass}) + 151; \quad r^2 = 0.98.$$

Measurement errors were $\pm 20 \mu\text{m}$ for length and $\pm 0.3 \mu\text{g}$ for weight. The initial weight of calcite present in an experimental group was estimated using this relationship and the length measured before individuals were put into culture.

2.1.2. Benthic foraminifera

Benthic foraminifera were also used in culture experiments using natural V. The principal advantages of the benthics are that they are easy to collect in large quantities, require little maintenance during culture, and will grow for many months as long as the seawater is changed regularly. These benefits offset the disadvantage of a slow growth rate of approximately 1%/day compared to about 25%/day for healthy planktonic species and the fact that they are shallow water dwelling species.

Shallow water benthic foraminifera (*Amphistegina lobifera*) attached to sea grass (*Halophila* sp.) were collected by SCUBA at 15 m depth 2 km south of the Interuniversity Institute for Marine Science, Eilat, Israel, in March 1992. The *Halophila* sp. plants were brought back to the laboratory, where, within one hour of collection, the foraminifera were separated from the leaves and sediment by vigorous rinsing with seawater under a plastic colander. The foraminifera were transferred to glass jars in the laboratory where their viability was checked by observing upward mobility on glass slides inserted into the jars. Those organisms that climbed the glass slides and walls of the jar were sieved into separate size fractions and further divided into two groups. One control group was rinsed, dried, counted, and weighed to obtain a value for the average initial weight per individual (32.8 μg) and initial V/Ca value (13 nmol V/mol Ca).

A. lobifera were isolated and cultured in solutions with varying V concentrations for eight months. The culture seawater solutions were replaced every 2–3 weeks with filtered seawater spiked with V. Aliquots of the spiked seawater were subsampled each time the water was changed and combined to obtain an integrated value for the V concentration of the culture water for the duration of the experiment. The V concentration of each solution was analyzed by isotope dilution inductively coupled plasma–mass spectrometry with electrothermal vaporization (ICP–MS–ETV) (Hastings et al., 1996b). Calcium concentrations were determined by flame atomic absorption spectroscopy to yield final V/Ca values. The cleaning procedure for fresh benthic foraminifera was essentially the same as for preserved tests (see below), except that a 10% hot alkaline peroxide oxidation step was used and repeated twice to ensure that

Table 1. Locations and depths of core tops used in this study

Core	Latitude	Longitude	Water depth (m)
Pacific Ocean			
MW91-9 1 BC 3	2° 14.158' S	156° 59.865' E	1616
MW91-9 2BC 13	0° 00.48' S	158° 54.772' E	2301
MW91-9 2.5BC 37	0° 00.276' N	159° 29.028' E	2445
MW91-9 3BC 24	0° 00.467' N	160° 25.516' E	2965
MW91-9 4BC 51	0° 01.413' S	161° 00.987' E	3411
MW91-9 5BC 54	0° 00.804' S	161° 46.205' E	4025
TT-154 10 BC	10° 20' S	111° 20' W	3225
W8402A-14GC	0° 57.2' N	138° 57.3' W	4287
Atlantic Ocean			
KNR110-84BC	4° 21.69' N	43° 30.64' W	2947
KNR110-86BC	4° 26.57' N	43° 29.04' W	3320
KNR110-90BC	4° 42.8' N	43° 25.3' W	3654
KNR110-92BC	4° 46.37' N	43° 16.53' W	3882
KNR110-94BC	4° 52.51' N	43° 04.81' W	4107
KNR110-96BC	4° 52.10' N	42° 58.80' W	4427
KNR110-99BC	5° 09.08' N	42° 44.23' W	4643
ENO66-17GGC	5° 22' N	21° 5' W	3050
Caribbean and Red Sea			
CP6001-4	14° 55' N	71° 50' W	3645
TT9108-1PC	11° 39.83' N	79° 35.52' W	2540
TT9108-1TC	11° 39.83' N	79° 35.52' W	2540
Red Sea	29° 20' N	34° 85' E	400

all the organic material was removed. Final V/Ca ratios reported were corrected for the presence of initial calcite not grown in culture.

2.2. Core-Top Foraminifera and Coral Samples

Core-tops used in this study were chosen because of their geographical and oceanographic diversity (Table 1). Two planktonic species *Globigerinoides sacculifer* and *Globorotalia tumida* and benthic species *Cibicides wuellerstorfi* were chosen for analysis because of their relatively high abundance in the sediments of interest. *G. sacculifer* is a spinose foraminifer with symbiotic dinoflagellates attached to the spines that calcifies in the top 50 m of the water column. *G. tumida* is a nonsymbiotic bearing, nonspinose species that calcifies predominantly below the euphotic zone (Hemleben et al., 1989; Lee et al., 1991).

Core-tops from transects down two submarine rises in the Pacific and Atlantic oceans were chosen to evaluate any effects related to depth of deposition, especially those arising from partial dissolution. A bathymetric transect of "Soutar" box cores from the Ontong Java Plateau in the Eastern Equatorial Pacific was collected in July 1991 on cruise 91-9 of R/V *Moana Wave*. The stations along this transect are within 500 km of each other, yet range in depth from 1600 m to 4440 m. The foraminiferal lysocline in this region, defined as the water depth below which dissolution effects are easily recognized (Berger, 1971), is estimated to lie between 3200 m and 3400 m, as indicated by percent fragmentation, dissolution, and scanning electron microscopy (Berger and Killingley, 1977; Bonneau et al., 1980; Berger et al., 1982). Core-tops of "Soutar" box cores from the Ceará Rise in the Western Equatorial Atlantic were also sampled. The lysocline here is estimated to be 4000–4300 m (Curry and Lohmann, 1986). Two cores in the Caribbean, TT 9108-1GC (11°39.83' N, 79°35.52' W; 2540 m) in the western region of the Columbia Basin and CP 6001-4 (14°55' N, 71°50' W; 3645 m) from the Beata Ridge separating the Columbia and Venezuela Basin were also sampled and analyzed. The top 5 cm from a grab sample of surface sediments from the Gulf of Eilat in the Red Sea were collected in March 1992.

To evaluate whether coralline aragonite could be used as a recorder of the V composition of paleo-seawater we obtained samples from the Caribbean reef-crest coral *Acropora palmata* drilled off the

south coast of Barbados (Fairbanks, 1989; Fairbanks, 1990). These samples are unusual in that they date back to 18,000 year BP, and have an existing chronology based both on ¹⁴C and U/Th dating.

2.3. Sample Preparation and Cleaning Method

2.3.1. Foraminiferal calcite

Sedimentary foraminifera were obtained by washing and sieving (>63 μm) bulk ocean sediment several times in 5% sodium hexametaphosphate buffered to pH 8 with NaOH to remove clays and fines, dried under a laminar flow hood, and sieved into five different size fractions (<250 μm, 250–355 μm, 355–425 μm; 425–495 μm; >495 μm) using stainless steel sieves (Newark Wire Cloth Co.). Single species of foraminifera were hand-picked from the washed, dried, and size-fractionated sample. Those individuals visibly contaminated by black surficial specks, assumed to be ferromanganese oxyhydroxides, were not used. After the picking process, all operations were performed using trace-metal clean techniques in a HEPA laminar flow hood.

Vanadium-rich contaminant phases associated with foraminifera that must be removed from the foraminiferal calcite prior to analysis include detrital clays, organic matter, and trace-metal-rich surficial ferromanganese oxyhydroxide coatings which are deposited during diagenesis. We developed a modified cleaning procedure to eliminate these phases based on the method described for foraminiferal Cd (Boyle, 1981; Boyle and Keigwin, 1985/86). Foraminifera were first gently crushed between two glass plates or in an agate mortar and pestle to open the individual chambers. Duplicate samples were transferred to acid-leached 1.5 mL polypropylene microcentrifuge tubes. Multiple rinses with distilled, deionized water using ultrasonication and vortexing were employed at the beginning and between all steps to remove detrital clays and other fine-grained material. Following each step the supernatant was removed by carefully siphoning off the overlying liquid. The cleaning procedure relied on a highly reducing mixture of hot 16 M NH₄OH, 0.25 M citric acid and 1 M NH₂NH₂·H₂O to remove the FeMn oxide coating.[†] One mL of freshly prepared solution was added to each sample, capped, and heated in a hot (90°C) water bath for 30 min with brief ultrasonication every 2 min. An oxidation step with hot 0.15% H₂O₂ in 0.1 N NaOH with sonication for 1 min every 10 min for a total of 30 min was used to remove organic material. After this procedure a second reducing step identical to the first was carried out followed by two hot distilled water rinses for 10 min each and a room temperature rinse in DDI H₂O. Samples were transferred to 6 mL Teflon® beakers, rinsed once with 0.005 N HNO₃ to remove remaining adsorbed metals, and dissolved in 600 μl HNO₃. Following dissolution, 500 μL of each sample was transferred to another set of 6 mL Teflon® beakers for V analysis, gravimetrically spiked with an enriched ⁵⁰V isotope tracer, and taken to dryness to ensure isotopic equilibration. The remainder of the sample was used for Ca, Mg, and Mn analysis. Dried samples were redissolved, eluted through cation exchange resin (Biorad AG50 × 8 100–200 mesh) to remove Ca⁺ and other elements causing isobaric interferences, and analyzed for V by isotope dilution thermal ionization mass spectrometry or ICP-MS-ETV (Hastings et al., 1996b). Analyses with anomalously high isobaric interferences at m/z 50 that interfere with the isotope dilution measurement are not included in the calculated mean values nor shown in the figures. This problem occurred in 5% of the samples. Sample loss during the cleaning process ranged from 30–50% due primarily to loss of fines generated during the crushing step.

The efficacy of this cleaning procedure was evaluated by cleaning 8 mg core-top samples of single species foraminifera (*G. sacculifer*; 355–425 μm) from the Ontong Java Plateau in the Eastern Equatorial Pacific with sequentially more rigorous cleaning methods. Re-

[†] Extra precaution should be taken with hydrazine as it is extremely toxic, and explodes on contact with oxidants (Mitchell et al., 1980).

Table 2. Results of cleaning experiment on foraminifera *G. sacculifer*, 355-425 μm .

sample ID	Cleaning process	V/Ca (nmol/mol)	Mn/Ca ($\mu\text{mol/mol}$)	Mg/Ca (mmol/mol)
A	Washed, sieved forams	533.1	40.2	4.83
B	Multiple distilled water rinses with sonication	506.0	40.4	5.03
C	Water rinses followed by oxidation with alkaline peroxide	41.5	7.2	4.21
D	Same as C, followed by reducing step with hydrazine	32.2	6.6	4.23
E	Same as C, followed by two reducing steps with hydrazine	21.3	7.2	4.20
F	Same as E but order changed: reducing step, oxidizing step then another reducing step	19.1	5.7	4.32
G	Same as F, followed by one dilute acid rinse (0.005N)	21.5	5.7	4.18
H	Same as F, followed by three dilute acid rinses (0.005N)	27.0	7.2	4.47

sults of these experiments are given in Table 2 and shown in Fig. 1. Sample A reflects the V and Mn content of untreated foraminiferal tests. The hot alkaline peroxide in sample C removes over 90% and 80% of the V and Mn-rich contaminant phases compared to the sample B which was treated only with distilled water rinses and ultrasonication. Two reducing steps with hot hydrazine reagent (sample E) are more effective than one (sample D) and lower the V content by an additional factor of two. The relative order of these cleaning steps was investigated by starting with the reducing step, followed by the alkaline peroxide and then another reducing step, as illustrated by sample F. In foraminiferal samples from reducing sediments, it has been demonstrated that starting with the reducing step results in a significantly lower Cd/Ca value (Boyle and Rosenthal, 1995). The relative order does not appear to be significant within the measurement error for foraminiferal V in this sample. Nonetheless, the mean V/Ca value is about 10% lower when the

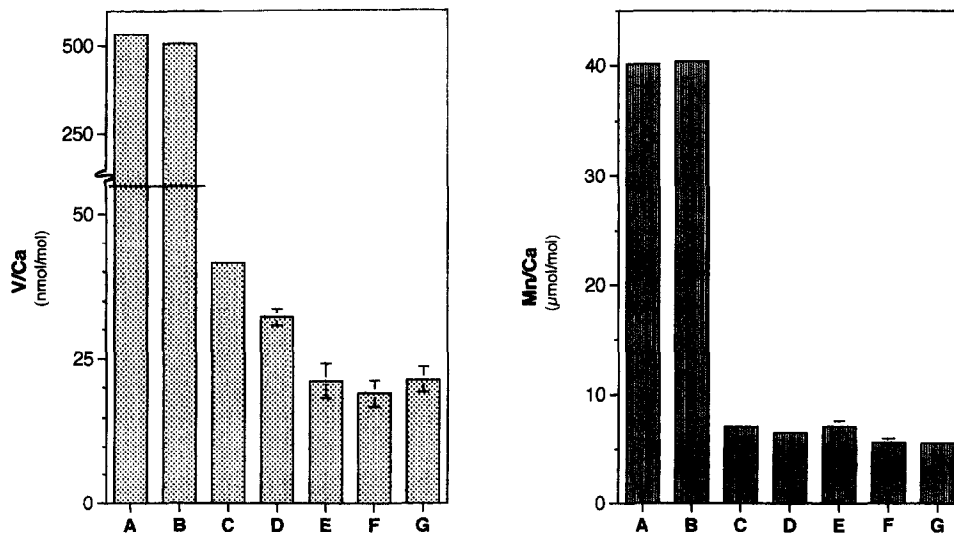


FIG. 1. Results of cleaning experiment using sequentially more rigorous cleaning methods. Note the break in the scale for V/Ca values. Errors less than $\pm 4\%$ are not shown. Cleaning steps used for each sample, detailed in the text, are summarized as follows: A: Washed, sieved, and picked foraminifera with no chemical cleaning; B: Multiple distilled water rinses with sonication; C: Distilled water rinses followed by oxidation with hot alkaline H_2O_2 ; D: Same as C, followed by a reducing step with hot hydrazine; E: Same as C, followed by two reducing steps with hot hydrazine; F: Same as E, but order of steps is changed: hydrazine followed by alkaline H_2O_2 , then another reducing step with hydrazine; G: Same as F, followed by one dilute acid rinse.

oxidation step is between the two reducing steps; this order was used for all samples.

The dilute 0.005 N HNO_3 rinse (step G) does not appear to significantly affect the V/Ca value. For samples with a MnCO_3 overgrowth coating the acid rinse does lower the V/Ca ratio since the vanadium-rich MnCO_3 phase is somewhat more dissolution-susceptible than calcite (Boyle, 1983). For this core-top sample, with little or none of this contaminant phase, acid rinses do not lower the V or Mn content of the test. Three dilute acid rinses increased the V/Ca value by 25% (Table 2). The oxidizing reagent in step C significantly lowers the Mg/Ca ratio, but foraminiferal Mg remains relatively constant following the subsequent chemical cleaning methods (Table 2).

2.3.2. Major and minor element analysis

Magnesium, calcium, and manganese were measured simultaneously by ICP-MS on 25 μL subsamples of the dissolved sample diluted into 2 mL of 0.1 N HNO_3 . Samples were introduced into the plasma via a Meinhardt® glass nebulizer with a Perkin-Elmer® AS-90 autosampler. Dwell times of 400 ms at m/z 24, 43, 55, and 45 for a total measurement time of 50 s were used. The ion optics were optimized for Mg and Mn at m/z 24 and 55 to give equal response for those two elements. To normalize for both short-term variability and long-term drift in the mass spectrometer, samples and standards were spiked with a Sc internal standard (Vanhaecke et al., 1992). 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 using a Perkin Elmer® model 5000. 50 μL subsamples of the dissolved sample were diluted into 25 mL of La solution (400 ppm La in 0.05 N HCl and 0.002 N HNO_3 ; La_2O_3 from Baker Chemicals). The La eliminates suppression of the Ca signal due to phosphine in the acetylene.

2.3.2. Coralline aragonite

Coral subsamples from the samples collected off Barbados (Fairbanks, 1989, 1990) were cut with a diamond saw and a stainless steel blade in Dr. Richard Fairbanks' laboratory. The cleaning proce-

cedure for vanadium analysis was adapted from the method for trace metal analysis in corals (Shen and Boyle, 1988). This method involves an initial 10 min DDI H₂O rinse, a 3 min acid leach in 0.16 N HNO₃ to remove metals adsorbed from the cutting process, followed by 20 min in hot 15% H₂O₂, 0.2 N NaOH. The coral sample was then crushed with an agate mortar and pestle, and sieved with an acid leached polypropylene sieve to remove fines smaller than 63 μ m. Samples (40–45 mg) were cleaned as described above for foraminiferal calcite. The cleaning procedure was modified by using 15% H₂O₂ to remove organic material, and 0.08 N HNO₃ was used for the initial and final acid rinses.

3. RESULTS AND DISCUSSION

3.1. Culture Experiment Results

In order to use foraminiferal V as a reliable proxy for vanadium in seawater, it is first necessary to demonstrate that incorporation into the calcitic test is proportional to $[V]_{sw}$. By determining metal/Ca ratios in foraminifera collected in different oceanic regimes with different metal concentrations, it has been shown that elements such as Cd and Ba are incorporated in proportion to seawater concentrations (Boyle, 1981; Hester and Boyle, 1982; Lea and Boyle, 1989). In contrast, V is nearly conservative in the ocean so the incorporation into foraminiferal calcite must be demonstrated empirically in the laboratory, using living foraminifera cultured in experimental solutions with varying V levels. This has been proven to be a successful method to assess trace element incorporation in foraminifera for Cd, Ba, and U (Delaney et al., 1985; Lea and Spero, 1994; Russell et al., 1994). Since planktonic species are relatively difficult to culture in quantities necessary for natural V analysis, and because only a small amount of V is incorporated into foraminiferal calcite, we relied on a radioactive tracer to study the incorporation of V into the skeletal calcite.

Evaluation of V incorporation in living foraminifera and the distribution coefficient for V in calcite were determined by culturing foraminifera at different V concentrations. Both the "dead" and "live" control runs for the radioactive experiment yielded only background levels of radioactivity. This indicates that the cleaning procedure is adequate to remove V adsorbed to the test. No significant changes in dissolved V-49 were detected over the course of the radioactive experiment, indicating that V was not adsorbed onto the surfaces of the culture dish.

Results shown in Fig. 2 and summarized in Table 3 indicate that incorporation of V into both planktonic and benthic species is directly proportional to seawater concentrations. The apparent distribution coefficient, D , relates the concentration of V in the solid phase normalized to Ca to the V/Ca ratio in solution, which in this case is the seawater the organisms are grown in:

$$D = \frac{(V/Ca)_{\text{foram}}}{(V/Ca)_{\text{seawater}}}$$

The distribution coefficient for each species is equivalent to the slope of the line in each experiment. We have chosen to force the line through the intercept since foraminifera grown in seawater with no V would be expected to have no V incorporated in the tests. The distribution coefficient for *G. calida* determined from Fig. 2 is $D = 2.1 (\pm 0.3) \times 10^{-3}$

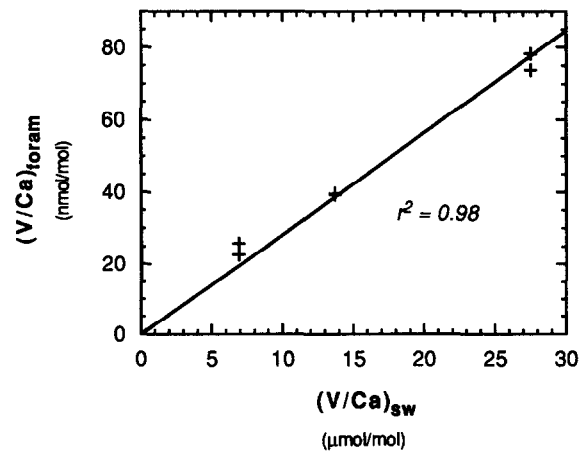
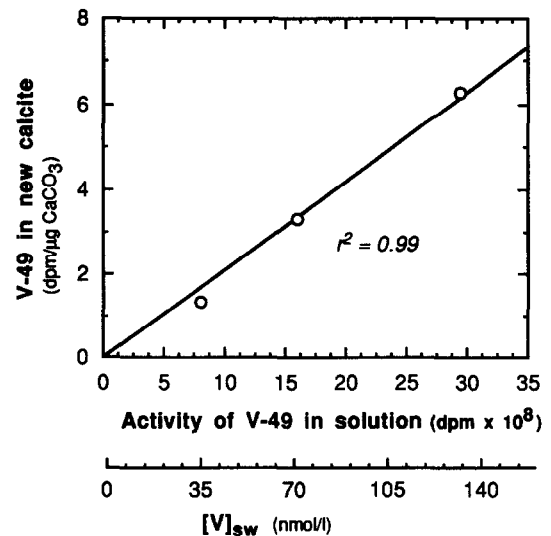


FIG. 2. Foraminiferal V, corrected for initial calcite, as a function of V in culture solution. (a) Planktonic species *G. calida* cultured in solutions spiked with radioactive V-49 which is increased in proportion to $[V]_{sw}$. When forced through the intercept, the slope of the line is $2.1 (\pm 0.2) \times 10^{-3}$ (95% confidence interval) and gives an apparent distribution coefficient for *G. calida* of $D = 0.0021$. (b) Benthic species *A. lobifera* cultured in 2 \times , 4 \times , 8 \times $[V]_{sw}$ seawater solutions. The slope of the line forced through the intercept is $2.8 (\pm 0.2) \times 10^{-3}$ (95% confidence interval) or $D = 0.0028$.

(95% confidence interval) and for the benthic species *A. lobifera* is $D = 2.8 (\pm 0.2) \times 10^{-3}$ (95% confidence interval).

3.2. Incorporation Mechanism

The metals that have been most widely used as paleoceanographic indicators (e.g., Cd, Sr, and Ba) are characterized by an ionic charge and radius similar to Ca and are assumed to substitute for Ca²⁺ in the calcite lattice (e.g., Boyle, 1988; Pingitore et al., 1992). There are three possible explanations for the incorporation of V into foraminiferal calcite: (1) the divalent metavanadate ion HVO_2^- may replace the carbonate

Table 3. Results of planktonic and benthic foraminifera culture experiments

A. Planktonic foraminifera experiments using *G. calida* and radioactive V-49

Expt	[V]sw	n	Total for foraminifera				V-49 in culture sol'n	V incorporated into new calcite
			initial wt (a)	final wt	new calcite added	V-49 final (b)		
	(nM)	(#forams)	(μg)	(μg)	(μg)	(cpm)	($\times 10^{-8}$ dpm/l)	(cpm/ μg)
1x V	35	11	41.1	137.6	96.5	127.5	8.0	1.32
2x V	70	9	24.9	63.0	38.1	126.0	16.0	3.30
4x V	140	13	78.6	141.5	62.9	394.4	29.4	6.27

^a Initial weight estimated from length of tests and empirical relationship between length and weight.

^b Activity of V-49 incorporated in calcite tests after completion of experiment.

B. Benthic foraminifera experiments using *Amphistegina lobifera*

Expt	n	avg initial	avg final	(V/Ca)soln	(V/Ca)init	(V/Ca)foram	(V/Ca)expt
		weight	weight	(a)	(b)	(c)	(d)
	#forams	($\mu\text{g}/\text{ind}$)	($\mu\text{g}/\text{ind}$)	($\mu\text{mol}/\text{mol}$)	(nmol/mol)	(nmol/mol)	(nmol/mol)
2x V	57	32.8	140	6.86	13	29.8	25.8
	58	32.8	132		13	27.0	22.7
4x V	51	32.8	161	13.7	13	43.0	39.7
	81	32.8	117		13	44.3	39.2
8x V	72	32.8	135	27.5	13	78.0	73.8
	44	32.8	162		13	81.5	78.2

^a V/Ca concentration ratio in the culture solution.

^b V/Ca content of foram shell before culture.

^c Measured V/Ca content of foram shell after culture.

^d Vanadium content of new calcite grown in experimental solution.

ion in CaCO_3 ; (2) the reduced oxocation VO^{2+} could substitute for Ca^{2+} ; or (3) random processes such as interstitial substitution between planes or at the edges of calcite domains, or substitution at vacant lattice positions might also lead to the incorporation of V (McIntire, 1963; Veizer, 1990).

Based on equilibrium thermodynamic arguments, V is predicted to be an oxyanion in seawater (Turner et al., 1981; Wehrli, 1987; Sadiq, 1988). The divalent metavanadate ion HVO_4^{2-} may substitute for the carbonate ion in CaCO_3 since both have the same charge. Supporting evidence for this mechanism is that other divalent anions, SO_4^{2-} and SeO_4^{2-} , replace CO_3^{2-} in synthetic and natural carbonates (Busenberg and Plummer, 1985; Takano, 1985; Staudt et al., 1994). However, the longest dimension of the vanadate ion along the equatorial axis is approximately 3.4–3.6 Å which is almost twice that of the carbonate ion, estimated to be 1.95 Å (Shannon and Calvo, 1973; Shannon, 1976).

It is probable that foraminiferal calcification is regulated by biological systems in which simple thermodynamic equilibria are not the controlling parameters. Biological control is important for parameters such as crystal texture (Berman et al., 1993). Manganese, magnesium, and strontium distributions in calcite grown in the laboratory violate equilibrium partitioning and are controlled by the surface structure as well as external conditions (Paquette and Reeder, 1995). Since V is an essential trace element for even prokaryotic organisms (Rehder, 1991), the incorporation of V into foraminiferal calcite might be subject to biological control and not the equilibrium processes that geochemists typically consider.

miniferal calcite might be subject to biological control and not the equilibrium processes that geochemists typically consider.

Although V is predicted to be an oxyanion in seawater, the actual speciation has not been determined and kinetic arguments suggest the possibility of a role for VO^{2+} incorporation. The vanadyl cation is extremely stable, as demonstrated by its long oxidation half-life (Wehrli and Stumm, 1989) and the very strong $\text{V}=\text{O}$ bond (Selbin, 1966). Thus, the potential exists for the presence of the reduced divalent cation VO^{2+} which could substitute for Ca^{2+} in the calcite matrix. This would involve direct incorporation of VO^{2+} from seawater or intracellular reduction of V within the living organism. A reducing intracellular "pool" could alter the speciation of V by reducing the vanadate to vanadyl and subsequently serve as the source of the V incorporated into the test. Such internal control of C and Ca incorporation has been demonstrated for perforate species of foraminifera (Anderson and Faber, 1984; ter Kuile and Erez, 1987, 1988). The vanadyl ion is characterized by an ionic radius of 1.6 Å (Selbin, 1966), comparable to that of Ca^{2+} , which has an effective ionic radius of 1.00 Å (Shannon, 1976).

3.3. Core-Top Study

Core-top (sea floor) values for V/Ca, Mg/Ca, and Mn/Ca determined in this study are listed in Table 4. The locations represent a range of surface salinities, temperatures and de-

Table 4 (a): V/Ca, Mg/Ca and Mn/Ca values for foraminifera from core-tops in the Pacific Ocean.

station	depth (m)	V/Ca (nmol/mol)	Mg/Ca (mmol/mol)	Mn/Ca (μ mol/mol)	V/Ca (nmol/mol)	Mg/Ca (mmol/mol)	Mn/Ca (μ mol/mol)
<i>G. sacculifer</i>				<i>G. tumida</i>			
MW 91-9 1 BC 3	1616	(195.8)	4.97	2.3	(90.0)	2.42	<10
	1616	(265.3)	4.80	2.6	(64.0)	2.40	<10
MW91-9 2 BC 13	2301	18.8	4.37	2.1	40.4	2.01	<10
	2301	24.8	4.42	2.6	42.8	1.89	<10
MW91-9 2.5 BC 37	2445	47.0	4.62	3.7			
	2445	61.0	10.84	18.7			
MW91-9 3 BC 24	2965	77.4	4.49	1.9	39.0	1.87	<10
	2965	(43.0)	4.57	2.5	37.0	1.95	<10
MW91-9 4 BC 51	3411	100.4	4.80	4.3			
	3411	108.2	4.63	0.7			
MW91-9 5 BC 54	4041				17.0	2.15	<10
	4041				15.0	1.62	<10
W84 02 14 GC	4287				16.2		<10
					19.7		<10

Table 4 (b): V/Ca, Mg/Ca and Mn/Ca values for foraminifera from core-tops in the Atlantic Ocean, Caribbean Sea, and the Red Sea (Gulf of Eilat).

station	depth (m)	V/Ca (nmol/mol)	Mg/Ca (mmol/mol)	Mn/Ca (μ mol/mol)	V/Ca (nmol/mol)	Mg/Ca (mmol/mol)	Mn/Ca (μ mol/mol)	V/Ca (nmol/mol)	Mg/Ca (mmol/mol)	Mn/Ca (μ mol/mol)
<i>G. sacculifer</i>				<i>G. tumida</i>			<i>C. wuellerstorfi</i>			
KNR110 84 BC	2947	19.6	3.78	3.4	35.3	2.06	10.6	--	1.44	15.2
		21.8	3.81	2.9	39.2	1.95	9.3			
KNR110 86 BC	3320	22.3	3.78	7.5	36.8	2.02	9.9			
KNR110 90 BC	3654	24.3	3.93	1.7	29.2	1.87	9.0	115	1.68	38.6
		22.7	3.87	2.3	28.0	1.89	9.0			
KNR110 92 BC	3882	35.7	3.75	2.6						
		37.3	3.53	4.0						
KNR110 94 BC	4107	33.1	3.43	3.0	31.7	1.62	8.4	102	1.22	12.5
		27.0	3.42	1.7	31.1	1.63	8.7			
KNR110 96 BC	4427	36.5	3.33	1.7				213	0.82	9.8
		53.3	3.24	1.8						
KNR110 99 BC	4643	70.7	3.14	6.9	17.1	1.28	6.0	247	0.91	30.0
		59.7	2.98	8.3	16.8	1.28	5.9			
EN06617GGC	3050	19.7	3.66	2.3				119	1.40	11.1
		(28.8)	3.74	2.3				110	1.46	14.8
		19.1	3.66	8.0						
		17.6	3.73	8.9						
Red Sea	560	21.7	4.79	29.4						
		(56.0)	4.81	29.2						
CP-6001 4 TC	3645	25.0	4.32	310.9						
		16.4	3.71	10.2						
TT 9108 1 PC	2540	31.0	3.98	6.8						
		20.5	3.87	4.6						

positional environments. All core-top samples are from the top 0–5 cm interval. The mean V/Ca value for those planktonic samples collected at depth of 2300 m or above in the Pacific Ocean and above 3400 m in the Atlantic Ocean (to avoid dissolution artifacts; Rosenthal and Boyle, 1993; Russell, 1994; McCorkle et al., 1995) is 21.7 (± 3.6) nmol V/mol Ca for *G. sacculifer* and 38.6 (± 2.5) nmol V/mol Ca for *G. tumida* (Fig. 3a,b). This corresponds to a distribution coefficient of $D = 6.2 (\pm 1.0) \times 10^{-3}$ and 11.0 (± 0.7) $\times 10^{-3}$ for *G. sacculifer* and *G. tumida*, respectively (Table 5). Out of fifty-six planktonic samples, all but three have Mn/Ca values less than 15 μ mol/mol and 90% less than 10 μ mol/mol indicating that Mn-rich contaminant phases in core-top samples were absent or eliminated in the cleaning process. No significant correlation between V/Ca values and

either Mg/Ca or Mn/Ca exists, indicating that neither selective dissolution, which affects foraminiferal Mg, nor Mn-rich phases are controlling the V content of these cleaned tests. The mean V/Ca value for *C. wuellerstorfi* collected above 4100 m in the Atlantic is 112 (± 9) nmol V/mol Ca; $D = 32 (\pm 2.5) \times 10^{-3}$. There is no obvious factor such as the presence of symbionts, spines, or planktonic habitat, for example, to account for the different distribution coefficient for the various species.

3.4. Postdepositional Alteration

3.4.1. Dissolution artifacts

The effects of dissolution on the V content of foraminifera were studied by analyzing core-top samples from two tran-

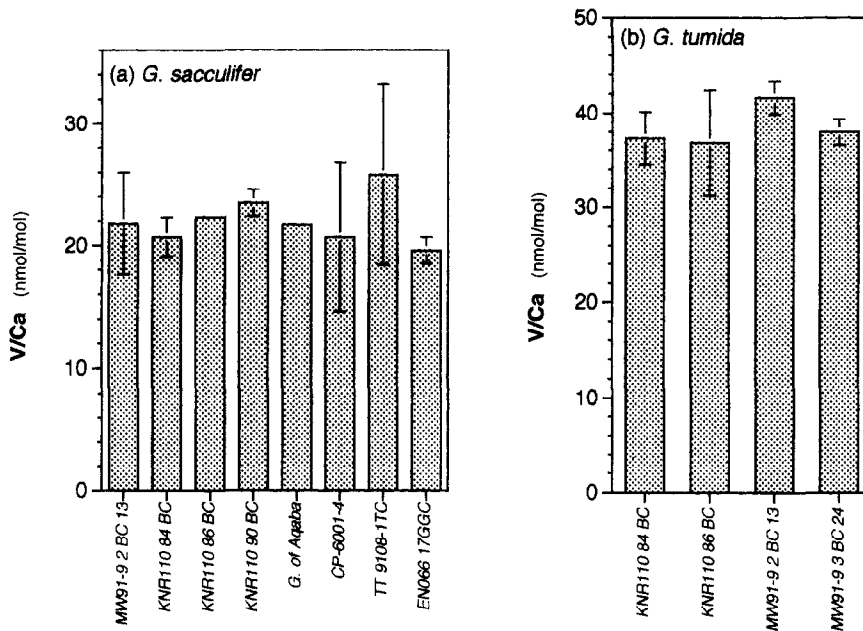


FIG. 3. (a) Average V/Ca values for *G. sacculifer* for core tops from various locations in the Pacific, Atlantic, Caribbean, and Red Sea above the depth where selective dissolution affects the V content (see text). Mean value is V/Ca = 21.7 (± 3.6) nmol/mol. (b) Average V/Ca values for *G. tumida* for core tops from various locations in the Pacific and Atlantic above the depth where selective dissolution affects the V content (see text). Mean value is V/Ca = 38.6 (± 2.5) nmol/mol.

sects that cross the foraminiferal lysocline on submarine rises in the Equatorial Pacific and Atlantic oceans. V/Ca data for the different species in both ocean basins show a strong dependence on water depth. The V/Ca values for *G. tumida* decrease by over 50% from 37.2 (± 2.8) nmol/mol at 2.9 km to 16.9 (± 0.2) nmol/mol at the deepest station (4 km) in the Ceará Rise (Fig. 4a). Mg/Ca ratios show a corresponding decrease from 2.0 to 1.3 mmol/mol. This behavior is also observed in the Ontong Java plateau samples where V/Ca values decrease from a core-top value of 41.6 (± 1.7) nmol/mol at 2.3 km to 16 (± 1.4) nmol/mol in the deepest

sample (4.6 km) with Mg/Ca values decreasing from 2.0 mmol/mol to 1.5 mmol/mol (Fig. 4b). Depth dependencies found for other tracers in foraminiferal calcite all reflect decreasing metal/calcium ratio with increasing water depth, including U (Russell et al., 1994), Sr (McCorkle et al., 1995), Mg (Lorens et al., 1977; Rosenthal and Boyle, 1993), and F (Rosenthal and Boyle, 1993). It might be possible to use Sr/Ca ratios, for example, as a quantitative index to estimate the dissolution loss of trace elements Cd and Ba (McCorkle et al., 1995). Partial dissolution of foraminiferal tests has been shown to increase ^{18}O (Savin and Douglas, 1973; Berger and Killingley, 1977; Bonneau et al., 1980).

Vanadium in *G. sacculifer* responds in the opposite sense to changes in depth of deposition. In the Ceará Rise transect shown in Fig. 5a, the V/Ca values increase by a factor of three from 20.7 (± 1.6) nmol/mol at the shallowest station to 65.0 (± 7.1) nmol/mol at 4.6 km. Mg/Ca values decrease from 3.8 to 3.1 mmol/mol in the same samples. The Ontong Java samples corroborate these findings for *G. sacculifer* with V/Ca values increasing from 21.8 (± 4.2) nmol/mol at 2.3 km to 104.3 (± 5.5) nmol/mol at 3.4 km (Fig. 5b). There is no clear monotonic trend in the Mg/Ca values for these latter samples. The V content of benthic species *C. wuellerstorfi* also reflects a large change with depth, increasing from a value of about 110 nmol V/mol Ca above the foraminiferal lysocline to values of almost 250 nmol/mol at 4643 m depth in the Ceará Rise (Fig. 6).

These observations cannot be a result of variable seawater V concentrations because V in the ocean is nearly conservative (Collier, 1984; Hastings and Emerson, 1995). It is implausible that the distribution coefficient would change by

Table 5. Comparison of mean core-top V/Ca values and apparent distribution coefficients in several ocean basins for (a) *G. sacculifer*, (b) *G. tumida*, and (c) *C. wuellerstorfi*. Only those samples collected at water depths where dissolution effects are not significant are included.

Ocean basin	V/Ca nmol/mol	D_{app} $\times 10^3$	n
(a) <i>G. sacculifer</i>			
Atlantic	20.9 (2.2)	5.6 (0.6)	8
Pacific	21.8 (4.2)	5.8 (1.1)	2
Red Sea	21.7	5.8	1
Caribbean	23.2 (6.3)	6.2 (1.7)	4
mean	21.7 (3.6)	5.8 (1.0)	15
(b) <i>G. tumida</i>			
Atlantic	37.1 (2.0)	9.9 (0.5)	3
Pacific	39.8 (2.4)	10.6 (0.6)	4
mean	38.6 (2.5)	10.3 (0.7)	7
(c) <i>C. wuellerstorfi</i>			
Atlantic	112 (9.0)	32.0 (2.5)	3

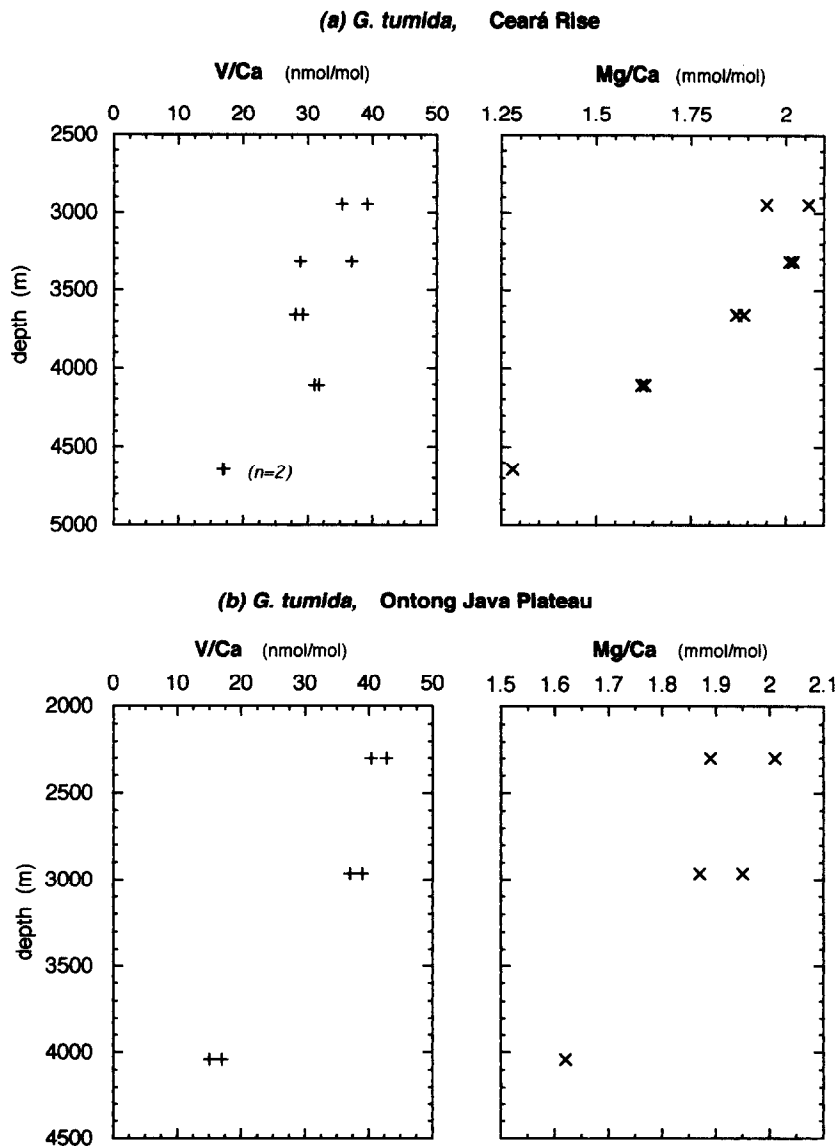


FIG. 4. Foraminiferal V and Mg in *G. tumida* in core tops from (a) Ceará Rise in the Western Equatorial Atlantic and (b) Ontong Java plateau in the Western Equatorial Pacific plotted vs. water depth.

over 50% for the same species since the planktonic foraminifera are accreting their tests under virtually identical conditions irrespective of the final depth of deposition. The geographical range covered by the two transects is relatively small, less than 500 km and 200 km for the Ontong Java plateau and Ceará Rise, respectively; so possibly important oceanographic parameters, such as surface temperature, salinity, or productivity, are unlikely to have varied significantly.

The changes are most likely due to postdepositional modifications of the tests on the sea floor in response to different bottom water or sediment conditions. Two such modifications are (1) leaching of V from the test or (2) preferential dissolution of V-enriched (*G. tumida*) or V-depleted (*G. sacculifer* and *C. wuellerstorfi*) calcite in increasingly deeper and more corrosive water. The first possibility implies that V is not lattice bound, but is incorporated in a noncarbonate

phase such as an organic component of the test. Sulfate, for example, is highly concentrated in interlamellar boundaries of benthic foraminifera (Szafronek and Erez, 1993). A down-core profile of V/Ca from site C in the Equatorial Pacific (Hastings, 1994) indicates that the ratio varies in concert with glacial-interglacial dissolution cycles in the Pacific. Since the leaching process would be expected to be a one-way process, this is evidence against this mechanism as an explanation for the observed trends.

Selective dissolution of different calcite parts or phases with varying trace element contents is a process that can explain the observed trends in the core-top data. This implies that distribution of V within the test is inhomogeneous and that various parts of the calcite shell have different V concentrations. According to this explanation the most dissolution resistant part of the *G. sacculifer* test is enriched in V by at least a factor of four compared to the undissolved core-top

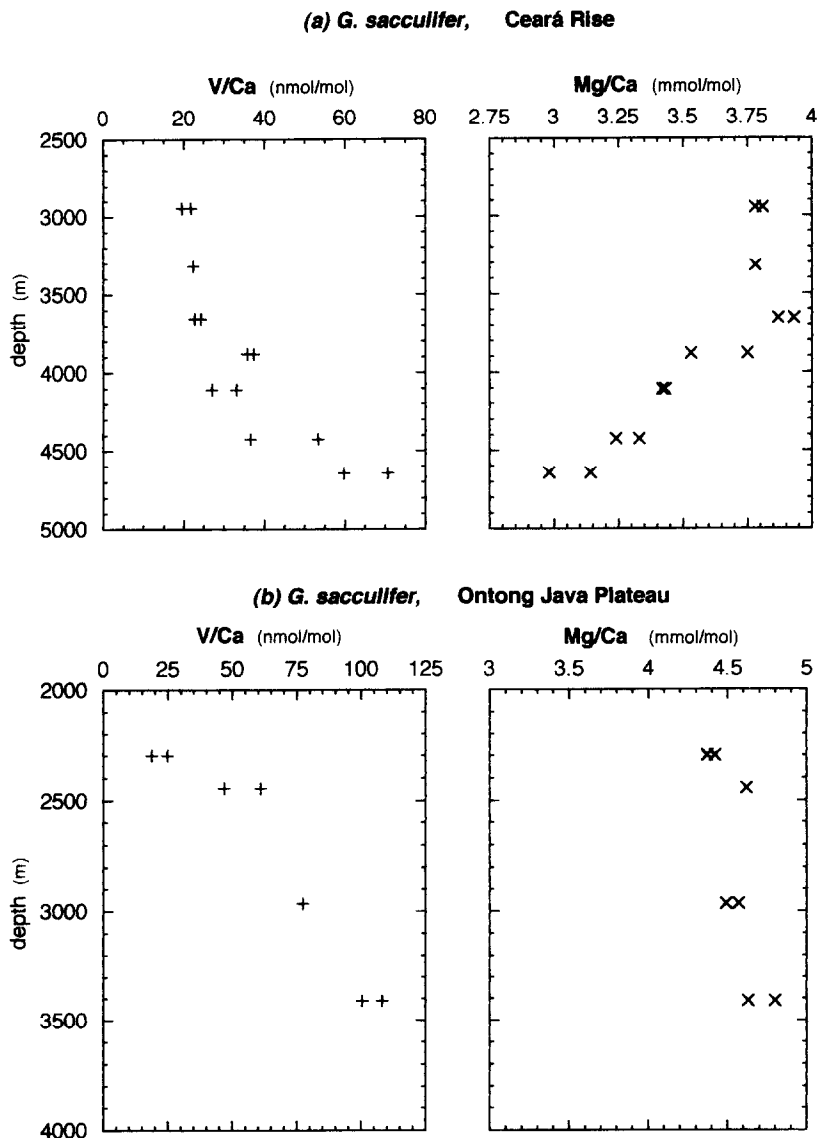


FIG. 5. Foraminiferal V and Mg in *G. sacculifer* in core tops from (a) Ceará Rise in the Western Equatorial Atlantic and (b) Ontong Java plateau in the Western Equatorial Pacific plotted vs. water depth.

value. These variations could apply to the average V/Ca value of the entire assemblage of a single species within a limited size fraction or, they could be due to the complete dissolution of less robust shells, resulting in a modified assemblage. The present data set does not distinguish between selective dissolution of a distinct group of individuals in the assemblage (for example thin shelled tests) and the dissolution of different phases within individual tests.

A unified explanation for the observed changes in V/Ca and Mg/Ca for the two different species relies on an understanding of three basic processes: (1) the biomineralization of primary (e.g., "chamber") and secondary ("crust") calcite for each species; (2) how trace elements are incorporated into these different parts; (3) how diagenetic influences, in particular partial dissolution, affect each phase and consequently the trace element content.

The different behavior of V in different phases can be

explained by a model for trace metal incorporation in calcite (Elderfield et al., 1996). A fundamental point in this model is that elements are incorporated into skeletal calcite from a biomineralization reservoir within the foraminifera, and not directly from seawater (Anderson and Faber, 1984; ter Kuile, 1991). As the reservoir is depleted, the apparent, or empirical, distribution coefficient (D) approaches the inorganic D since the trace elements are extracted from the internal pool by Raleigh distillation. For elements such as V with a solid/liquid partition coefficient in foraminifera less than the inorganic value, the end result is that the apparent D increases as the pool is depleted.

An additional consideration in this model is that the reservoir can be closed or progressively more open with respect to exchange with the surrounding seawater. As the calcification rate increases, the reservoir is predicted to be flushed more quickly, is thus more open with respect to seawater,

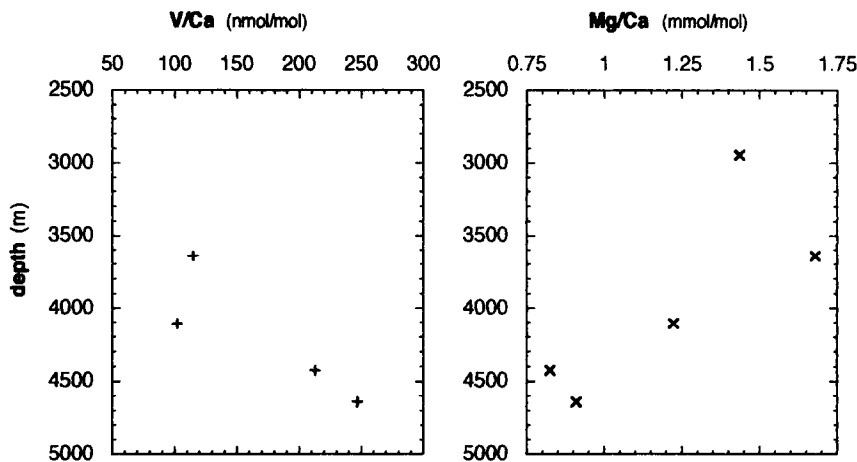
C. wuellerstorfi, Ceará Rise

FIG. 6. Foraminiferal V and Mg in *C. wuellerstorfi* in core tops from the Ceará Rise in the Western Equatorial Atlantic plotted vs. water depth.

and hence has a D more similar to the inorganic value compared to slower calcification. For V, this implies that higher calcification rates and a more open biomineralization reservoir will result in greater values for the apparent distribution coefficient. Based on this model, those phases that are calcified more quickly would be expected to be characterized by a greater D compared to those phases that are calcified slowly. Experimental observations using the planktonic foraminifer *O. universa*, which calcifies a single, large, spherical chamber, are not consistent with the existence of an internal reservoir which lead Lea et al. (1995) to question if such a pool could have a significant impact on shell chemistry.

G. tumida is characterized by a dissolution-resistant secondary calcite that is precipitated slowly in deep, cold waters (Mélières, 1977; Hemleben et al., 1989, p. 211). This "blocky" calcite crust and keel are typically the last parts of the test remaining in a partially dissolved sample (Hecht et al., 1975; Bonneau et al., 1980). As predicted, electron microprobe studies show that this secondary calcite is depleted in Mg relative to the primary calcite for both *G. tumida* (Brown and Elderfield, 1996) and *G. truncatulinoides* (Duckworth, 1977). Thus, V/Ca ratios are lower in *G. tumida* samples affected by partial dissolution where the keel and the blocky crust make up much of the mass of each test (Fig. 4).

G. sacculifer, on the other hand, precipitates an outer secondary calcite, which is expected to occur rapidly compared to the primary or chamber calcite (Bé, 1980; Hemleben et al., 1989) and would thus be expected to have high V/Ca values according to the model described above. According to a model for the variation in the chemistry of foraminifera due to selective dissolution, this secondary calcite is more dissolution resistant compared to the primary calcite (Lohmann, 1995). This explains the downslope increase in V/Ca values shown in Fig. 5; the dissolution resistant secondary crust of *G. sacculifer* is calcified quickly and characterized by a high V/Ca ratio resulting in higher V/Ca values in samples from deeper, more corrosive waters.

Magnesium and vanadium in *G. sacculifer* respond differently to changes in the depth of deposition and degree of dissolution intensity in the Ceará Rise core top samples. While the behavior of V can be explained by different dissolution responses of two different phases there must be at least one additional phase to explain the Mg/Ca trends. During the last stage in the life cycle of *G. sacculifer*, gametogenic calcite is added to the shell which typically adds 28% to the total mass of the test (Bé, 1980). Electron microprobe studies have shown that this gametogenic calcite is enriched in magnesium compared to primary calcite by at least a factor of three and possibly by as much as an order of magnitude (Nürnberg et al., 1996). Thus, foraminiferal Mg in *G. sacculifer* is controlled by the relative abundance of gametogenic calcite in these progressively more dissolved samples. The lack of significant downslope variation in Mg/Ca from the Ontong Java Plateau *G. sacculifer* samples (Fig. 5b) can be explained by the fact that all the gametogenic calcite has dissolved at even the shallowest depths.

The decrease with depth of Mg/Ca values for both species is consistent with earlier research on the effect of Mg on the solubility and stability of calcite. Magnesian calcite solubility increases with increasing Mg content both in abiotic and biogenic calcites (Mucci and Morse, 1990). Savin and Douglas (1973) noted a positive correlation between solution susceptibility and Mg/Ca values in foraminifera, suggesting that increased Mg in the test makes the shell more prone to dissolution. Other studies have also shown that foraminiferal Mg decreases with increasing depth of deposition (Bender et al., 1975; Lorens et al., 1977; Rosenthal and Boyle, 1993; Brown and Elderfield, 1996).

3.4.2. Manganese carbonate overgrowth

A mixed Mn-Ca-Mg carbonate has been identified in many reducing environments (Lynn and Bonatti, 1965; Pedersen and Price, 1982; Shimmield and Price, 1986; Calvert and Pedersen, 1993) and has been suggested to control pore-

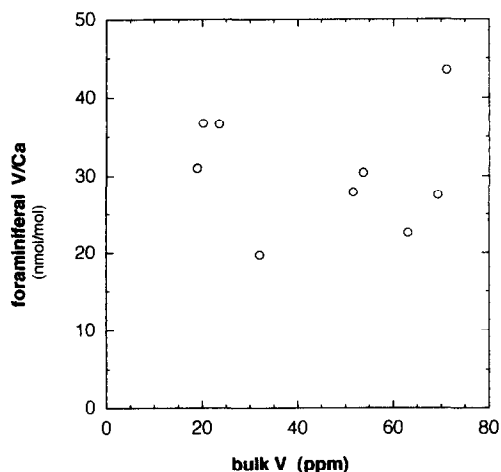


FIG. 7. Bulk sedimentary V in Equatorial Pacific core W8402A-14GC (MANOP site C) plotted vs. the foraminiferal V/Ca values. Lack of correlation between the foraminiferal and sediment V values is consistent with no exchange between the lattice bound and detrital V.

water Mn (Middelburg et al., 1987). Such Mn carbonate coatings are highly enriched in trace elements including Ba and Cd (Boyle, 1983). Vanadium is enriched in other Mn phases including Mn nodules (590 ppm, Cronan, 1976) and Mn-rich metalliferous sediments (1300 ppm, Hastings, 1994). Based on the related geochemistries of Mn and V and the enrichment of other trace metals in MnCO_3 , this overgrowth should also be enriched in V. Since this phase cannot be completely eliminated in the cleaning procedure, samples with a significant Mn carbonate overgrowth, as indicated by Mn/Ca levels over $50 \mu\text{mol/mol}$ or that co-vary with V/Ca values, cannot be used as a proxy for seawater V levels. A more comprehensive evaluation of this postdepositional artifact, as illustrated by several downcore sediment records from the Caribbean Sea and Atlantic Ocean, is given elsewhere (Hastings, 1994; Hastings et al., 1996a).

3.4.3. Sediment-shell V exchange

The concentration of V in sediments ($\sim 150 \text{ ppm}$) is four orders of magnitude higher than that in foraminiferal calcite (10 ppb). The potential exists for exchange between the two phases if foraminiferal vanadium is not lattice bound. In sediments from Pacific core W8402A-14GC which span a wide V concentration range, the bulk V content in the sediment is not correlated with foraminiferal V (Fig. 7). This is consistent with the argument that V in foraminiferal calcite is a closed system with respect to bulk sedimentary V within the 200 ky time interval represented by this core.

3.5. Coralline Aragonite

Trace metal incorporation in corals has been used as a paleoceanographic tool for several metals including Ba, Cd, Cu, Mn, Sr, and U for timescales of decades to several hundred years (Shen et al., 1987; Shen and Boyle, 1987; Lea et al., 1989; Linn et al., 1990; de Villiers et al., 1995; Shen and Dunbar, 1995). The distribution coefficient for V

in corals has been determined to be $D = 0.027$ (Shen and Boyle, 1988). Larger sample size, higher distribution coefficient for V, and consequent ease of analysis make coralline aragonite a desirable matrix to assess the V concentration of seawater. With the recent use of off-shore drilling rigs to recover ancient corals, much older samples spanning longer time scales are now available to reconstruct the compositional history of seawater.

V/Ca values in Barbados corals between 18.7 and 9.1 kyr range from 95 to 154 nmol V/mol Ca in agreement with the previously determined distribution coefficient (Shen and Boyle, 1988). While the average precision of duplicate measurements is good ($\pm 6\%$; 1σ) these results do not indicate any consistent or monotonic trend over the time period studied (Fig. 8). Seasonal measurements of V/Ca in a living Barbados coral (*Montastrea annularis*) indicate that V concentration in corals can vary by as much as 100% (from 70 to 130 nmol V/mol Ca; G. Shen, unpubl. data) over one annual cycle. It was not possible to differentiate seasonal growth in the ancient Barbados corals, which could explain the scatter in the data.

4. CONCLUSIONS

We have investigated the potential of using foraminiferal calcite as an indicator of seawater V concentration. Laboratory experiments indicate that planktonic and benthic foraminifera incorporate V into their tests in direct proportion to the seawater concentrations in which they are cultured. Calculated distribution coefficients are 2.1×10^{-3} and 2.8×10^{-3} for *G. calida* and *A. lobifera*, respectively. The incorporation mechanism cannot be specified due to the paucity of relevant thermodynamic data and the unknown role of biological controls of biomineralization and trace element incorporation into skeletal material. Possible mechanisms include VO^{2+} replacement for Ca^{2+} , HVO_4^{2-} substituting for carbonate, or interstitial incorporation of V at vacant lattice

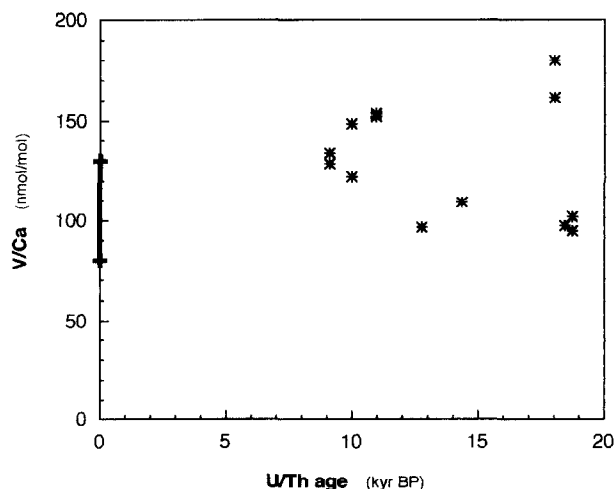


FIG. 8. Coralline V/Ca values from ancient Barbados corals *A. palmata* as a function of age of deposition. The bar at 0 ky indicates the annual range of V/Ca for modern Barbados coral *Montastrea annularis*.

sites, defects, or at the edge of calcite domains. It may be possible to test these different mechanisms by culturing foraminifera in solutions with differing $[Ca^{2+}]_{sw}$ and constant $[V]_{sw}$ to obtain varying V/Ca ratios in the culture media.

Preserved foraminifera must be rigorously cleaned to remove V-rich contaminant phases including detrital clays, FeMn oxides, organic material, and adsorbed ions. Data from experiments using sequentially harsher cleaning treatments indicate that two reducing steps with 5% hydrazine and oxidation with alkaline peroxide are effective in eliminating the V not originally incorporated into the biogenic test. Core-top data indicates that for the two planktonic species analyzed, *G. sacculifer* and *G. tumida*, V/Ca ratios are constant over the world ocean with mean distribution coefficients of $5.8 (\pm 1.0) \times 10^{-3}$ and $10.3 (\pm 0.7) \times 10^{-3}$, respectively. Significant differences between *G. sacculifer* and *G. tumida* as well as the culture results suggests that V incorporation is species dependent. In an Equatorial Pacific core spanning the past 200 ky there is no correlation between V in bulk sediment and foraminiferal calcite, indicating that V in foraminiferal calcite is a closed-system.

Postdepositional alteration was evaluated by analyzing core-top samples down depth transects on submarine rises. The V/Ca ratios changed by a factor of three with increasing water depth across the foraminiferal lysocline in both Pacific and Atlantic oceans. The V content of *G. tumida* decreased with increasing water depth whereas foraminiferal V increased with depth in *G. sacculifer* and *C. wuellerstorfi*. This suggests that V is distributed heterogeneously in different phases of the two species. The data are consistent with a model in which elements are extracted by Raleigh distillation from a biomineralization reservoir. Foraminiferal samples with an appreciable $MnCO_3$ overgrowth which is enriched in V cannot be used. The effect of postdepositional diagenetic alteration appears to be significant, but can be minimized in many cases by careful choice of study material from depths shallow enough to avoid significant calcite dissolution.

Since V is conservative in the ocean, a single sediment record of foraminiferal V that is unaffected by postdepositional alteration would provide a global record of seawater V changes. Since the oceanic mass balance of V is sensitive to variations in the expanse of reducing sediments, determining changes in V/Ca ratios of foraminifera has the potential to provide valuable information regarding changes in the areal extent of reducing sediments over glacial-interglacial time scales.

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