

# Determination of Picogram Quantities of Vanadium in Calcite and Seawater by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry with Electrothermal Vaporization

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**We developed a method to measure picogram quantities of vanadium in calcite and seawater by isotope dilution (ID) inductively coupled plasma mass spectrometry using electrothermal vaporization (ETV) to introduce the sample into the plasma. A  $^{50}\text{V}$  isotope spike enriched to 44 atom % was equilibrated with samples, followed by chemical purification by cation exchange chromatography. Samples were introduced into the ETV unit with a Pd modifier and heated to 1000 °C. This quantitatively eliminates the  $\text{ClO}^+$  isobaric interference with V at  $m/z$  51 for solutions up to 0.5 N HCl. The procedural blank was 0.27 pg of V. Corrections for  $^{50}\text{Ti}$  and  $^{50}\text{Cr}$ , which interfere with the  $^{50}\text{V}$  signal, were made by measurement of  $^{49}\text{Ti}$  and  $^{53}\text{Cr}$ . These isobaric interferences and variable ArC levels were the limiting sources of error in the ID measurement and diminished the detection limit to 6 pg of V. The detection limit for nonisotope dilution applications was 0.3 pg of V. Measurement precision on the same sample of dissolved calcite over the course of one run was  $\pm 3\%$  ( $1\sigma$ ). Accuracy was confirmed by determination of V standards in  $\text{CaCO}_3$  and by comparative measurement with ID thermal ionization mass spectrometry and graphite furnace atomic absorption spectroscopy.**

Calcitic shells of foraminifera, unicellular marine animals that grow in surface waters and in ocean sediments, have concentrations of certain elements that are determined by the seawater concentration of the water in which the shell was formed. The determination of trace elements such as Cd, Ba, and Li in foraminiferal calcite has proven to be a powerful tool to deduce the history of ocean circulation patterns, nutrient concentrations, and oceanic inputs.<sup>1–4</sup> The development of new foraminiferal tracers including B, F, U, Mg, and V is an active area of oceanographic research which has shed new light on paleoclimatology and variations in the global carbon cycle.<sup>5–8</sup>

Recent interest in the geochemistry of vanadium has arisen from its unique redox behavior<sup>9,10</sup> and the observation of enriched concentrations in anoxic sediments, black shale, and crude oil.<sup>11,12</sup> Because V deposition is redox sensitive, its concentration in seawater is most likely sensitive to the oxidation state of sediments. The calcitic shells of foraminifera accurately record seawater concentrations of V,<sup>13</sup> so the V content of the fossil shells of these microscopic oceanic organisms potentially can serve as an indicator of changes in past ocean anoxia.<sup>14</sup>

A typical 5 mg hand-picked sample of these microscopic shells yields only 50–200 pg of vanadium. Existing analytical methods for the determination of vanadium at such low levels are inadequate because of poor sensitivity, calcium matrix effects, and isobaric interferences. Table 1 summarizes methods to determine the concentration of V in seawater and other low-level environmental samples. The most common methods use either instrumental neutron activation analysis (INAA) or graphite furnace atomic absorption spectrometry (GFAAS). A preconcentration step is used, which typically involves coprecipitation with ferric hydroxide,<sup>15</sup> cobalt APDC,<sup>16</sup> or APDC and activated carbon.<sup>17</sup> Addition of coprecipitants necessarily increases the procedural blank. Potential variability in the recovery for the preconcentration results in inaccurate determinations for several of these methods. As a result, significant variations have been obtained for surface seawater samples.<sup>18,19</sup>

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Table 1. Comparison of Methods for the Determination of Vanadium in Seawater and Other Environmental Samples

method	ref	detectn limit	precision (%)	recovery (%)	comments
FeOH INAA	15	10 ng	25%	100 ± 10	reported [V] <sub>sw</sub> is 30% low
Co-APDC GFAAS	16	500 pg	5	80	seawater analysis
ID-TIMS	36	90 pg	12		biological samples
ID-TIMS	a	18 pg	5	93	calcite, seawater analysis
ID-ICPMS-ETV	a	6 pg	3%	93	calcite, seawater analysis
ICPMS-ETV	a	0.18 pg	8%		blank determination

<sup>a</sup> This work.

Determination of vanadium by inductively coupled plasma mass spectrometry (ICPMS) is complicated by the presence of <sup>35</sup>Cl<sup>16</sup>O<sup>+</sup> in the plasma. In samples with even small amounts of chlorine (0.01%), these polyatomic ions overlap the spectra of the elements of interest. A wide variety of methods have been developed to correct or reduce the ClO interference. One of the simplest is to determine the <sup>35</sup>ClO concentration by using the known isotope ratio of <sup>35</sup>Cl/<sup>37</sup>Cl and monitoring the <sup>37</sup>ClO peak at *m/z* 53.<sup>20</sup> This is feasible only if Cr levels in the sample are low and if relatively low levels of Cl (<1%) are present. Alternative sample preparation methods which eliminate the use of HCl<sup>21,22</sup> are a first-order solution to reducing some polyatomic interferences. On-line separation methods to remove Cl species which cause spectral interferences have been successfully employed.<sup>23</sup> Cryogenic desolvation has been found to be effective in reducing the levels of interfering oxides and chlorides by removing the water and HCl in the sample.<sup>24</sup> Anodic stripping voltammetry interfaced with ICPMS eliminates the ClO<sup>+</sup> interference, but only at levels up to 0.1% chloride.<sup>25</sup>

A variety of mixed gas plasmas has been used to attenuate polyatomic interferences; for example, N<sub>2</sub> in the outer (coolant or plasma) gas<sup>26, 27</sup> and N<sub>2</sub>, Xe, O<sub>2</sub>, or CH<sub>4</sub>, mixed with Ar in the aerosol (nebulizer) gas.<sup>28–30</sup> High-resolution mass spectrometry to resolve the spectral interferences is an effective yet costly technique,<sup>31</sup> since a resolution of 30 000 is necessary to resolve ClO<sup>+</sup> at *m/z* 50.964 and V<sup>+</sup> at *m/z* = 50.944. The wide variety of approaches used in resolving or attenuating interferences in ICPMS are included in a comprehensive review.<sup>32</sup>

In this paper, we describe a method to determine vanadium in calcite and in seawater by isotope dilution (ID) ICPMS using electrothermal vaporization to eliminate the volatile chlorine species. In addition to removing the isobaric polyatomic ions, ETV dramatically increases the efficiency of analyte transport into the plasma compared to conventional nebulization, from <2% to

60–80%.<sup>33</sup> This improves the detection limit by at least an order of magnitude. Use of isotope dilution and no chemical preconcentration results in highly reliable determinations and low procedural blank.

## EXPERIMENTAL SECTION

**Standards and Solutions.** Solutions were prepared using distilled, deionized (DDI) water. Reagent grade HNO<sub>3</sub> and HCl were doubly distilled in a quartz still. For ultratrace applications, acids and water were purified further by triple and quadruple distillation in Teflon (FEP) sub-boiling stills and stored in acid-leached Teflon bottles. Ultrapure H<sub>2</sub>O<sub>2</sub> (Ultrex, J. T. Baker) was stored in the dark at 4 °C. Ten parts-per-million Pd solution was prepared by dissolving 99.9% Pd(NO<sub>3</sub>)<sub>2</sub> (Aesar/Johnson Matthey, Ward Hill, MA) in sub-boiled HNO<sub>3</sub>. Teflon (PFA) beakers (Savillex Corp., Minnetonka, MN) were boiled in 8 N HNO<sub>3</sub>, rinsed in DDI H<sub>2</sub>O, and refluxed for 24 h on a heated clean table with 1 N doubly distilled HCl, followed by refluxing for 24 h with 2× sub-boiled water. All plasticware was leached in 1 N HCl at 50 °C for at least 12 h; polypropylene autosampler cups were immersed in hot 1 N HNO<sub>3</sub> for a minimum of 3 days and then rinsed with DDI water and dried immediately before use.

*Enriched vanadium-50 isotope spike* was obtained as V<sub>2</sub>O<sub>5</sub> from the National Institute of Standards and Technology, originally prepared at Oak Ridge National Laboratories (ORNL). Approximately 0.5 mg of V<sub>2</sub>O<sub>5</sub> was dissolved in ultrapure HNO<sub>3</sub> and diluted with 0.1 N HNO<sub>3</sub> to meet the requirements of the measurement. Original isotopic analysis performed at ORNL was stated as 44.1% <sup>50</sup>V (±0.1), 55.9% <sup>51</sup>V (±0.1), or a ratio of <sup>50</sup>V/<sup>51</sup>V = 0.789. The isotope ratio of the spike was determined in this laboratory by thermal ionization mass spectrometry (TIMS) and by ETV-ICPMS. The V concentration of the spike solution was determined by isotope dilution TIMS by comparison to a gravimetrically prepared V single-element ICP standard accurate to within ± 0.3%.

*Vanadium standard* for vanadium analysis in calcite was prepared by cleaning 5 g of bulk foraminiferal calcite, dissolving this in concentrated HNO<sub>3</sub>, and diluting to ~150 mL with DDI H<sub>2</sub>O. This standard was analyzed to determine the relative accuracy and precision of both the TIMS and ICPMS analyses; the standard was analyzed every nine samples. Replicate measurements of the standard were analyzed to determine the relative precision of the measurement. A CaCO<sub>3</sub> standard prepared from ultrapure CaCO<sub>3</sub> (99.9965% Puratronic grade, Aesar/Johnson Matthey) and spiked with a known amount of the V single-element ICP standard was also used to determine the accuracy of each method.

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**Sample Preparation.** The overall chemical preparation scheme involves picking single species of foraminifera from a ocean sediment core, removing contaminant phases via chemical and physical cleaning methods, and dissolving the cleaned foraminiferal calcite. This solution was then spiked with the enriched isotope tracer, and major cations ( $\text{Ca}^{2+}$  or  $\text{Na}^+$ ) and some isobaric interferences (Cr and Ti) were removed by cation exchange chromatography. The sample was then dried and taken up in a small volume of dilute nitric acid for injection into the ETV-ICPMS.

**Cleaning Procedure.** Foraminifera were obtained by washing and sieving bulk ocean sediment several times to remove clays and fines. Single species of foraminifera were hand-picked from the washed, dried, size-fractionated sample. Several V-rich contaminant phases associated with foraminifera must be removed from the foraminiferal calcite prior to analysis. Foraminifera were gently crushed to open the individual chambers and rigorously cleaned using a method modified from Boyle<sup>34</sup> to eliminate these phases. Following the cleaning procedure, all sample handling was performed in a HEPA laminar flow hood in a class 100 clean room. For a complete description of the cleaning procedure, see ref 13.

Cleaned samples were transferred to 6 mL Teflon beakers, subjected to a final 0.005 N  $\text{HNO}_3$  rinse to remove remaining adsorbed metals, and dissolved in 600  $\mu\text{L}$  of 6 N  $\text{HNO}_3$ . Following dissolution, 500  $\mu\text{L}$  of each sample was transferred to another set of 6 mL Teflon beakers for V analysis, gravimetrically spiked with the enriched  $^{50}\text{V}$  isotope tracer, and taken to dryness to ensure isotopic equilibration. The remainder of the sample was used for Ca, Mg, and Mn analyses. Dried samples were redissolved in 500  $\mu\text{L}$  of 0.01 N HCl and 0.3%  $\text{H}_2\text{O}_2$  and loaded onto prepared ion exchange chromatography columns.

**Ion Exchange Chromatography.** The cation exchange resin (AG50W-X8, 100–200 mesh,  $\text{H}^+$  form; Bio-Rad Laboratories, Hercules, CA) was batch cleaned prior to use by soaking 150 g of resin in 750 mL of 6 N HCl for at least 1 h. This treatment was repeated six times and followed by repeated rinses with DDI water until  $\text{pH} \geq 4$  and stored in DDI water for at least 2 weeks prior to use. For 3–10 mg samples, 1.5 mL of hydrated resin slurry was poured into precleaned 10 mL polypropylene columns (Bio-Rad). The resin was cleaned in situ with one column volume of 1 N HCl and 0.6%  $\text{H}_2\text{O}_2$ , followed by three column volumes of 0.01 N HCl and 0.3%  $\text{H}_2\text{O}_2$ . The final column conditioning rinse was prepared with the cleanest acids and water available.

Cleaned, dissolved, and spiked samples were loaded onto the resin, eluted with 4 mL of 0.01 N HCl and 0.3%  $\text{H}_2\text{O}_2$ , and collected in 6 mL Teflon beakers. A vanadium(V) peroxide complex forms which was eluted quantitatively while  $\text{Ca}^{2+}$  was retained on the column.<sup>35</sup> Any reduced vanadyl should be oxidized to vanadate by the peroxide and eluted from the column. High titanium and chromium levels in the final sample will severely compromise both the accuracy and the precision of the vanadium measurement by isotope dilution. Both have isotopes at  $m/z$  50 which are isobaric with  $^{50}\text{V}$ , so it is essential to eliminate or reduce their concentration in the final sample. Titanium forms a complex with  $\text{H}_2\text{O}_2$  that is strongly retained by the cation exchange resin at the low acid strengths used; final  $^{50}\text{Ti}$  levels were typically  $<2$  pg. Cr(III) is

preferentially eluted at higher acid strengths (3 M HCl), but Cr(VI) is eluted even at 0.01 N HCl;  $^{50}\text{Cr}$  was usually  $<6$  pg in the final sample. Following the ion exchange step, samples were taken to dryness and redissolved in 0.16 N  $\text{HNO}_3$ . Processing for analysis by ICPMS and TIMS was identical except that sample size was substantially larger for the TIMS measurement (30–40 mg compared to 3–10 mg of calcite), so the resin volume was increased to 4 mL.

Chemical yields for the ion exchange step were determined by spiking the standard foraminifera mixture with the enriched isotope spike following the column chromatography. The calculated value was compared with the value determined by spiking the sample beforehand. Recovery of V from the ion exchange step varied from 89 to 95%, with an average recovery of 93%. It should be noted that, assuming isotopic equilibration between spike and sample before any sample processing, variability in recoveries will not affect the final result.

**Seawater samples** (0.1–1 g) were processed in the same way as calcitic samples. After acidification to pH 2, they were spiked with the enriched  $^{50}\text{V}$  isotope tracer, taken to dryness and dissolved in 500  $\mu\text{L}$  of 0.01 N HCl and 0.3%  $\text{H}_2\text{O}_2$ . Elution through the cation exchange resin eliminates the matrix interferences from the high sodium concentration and removes some of the trace Ti and Cr.

**Thermal Ionization Mass Spectrometry.** Vanadium was analyzed on a VG Sector thermal ionization mass spectrometer equipped with a Daly detector for signal amplification. Samples were dried down to a 2–3  $\mu\text{L}$  drop, loaded onto a zone-refined, outgassed Re filament with a colloidal graphite suspension, and gradually heated to 1400–1450  $^\circ\text{C}$ .<sup>36</sup> To reduce contamination, the graphite was leached twice in 6 N HCl, rinsed with DDI  $\text{H}_2\text{O}$ , and resuspended in 4 $\times$  sub-boiled water prior to use. The signals at  $m/z$  49.5, 49, and 52 were monitored in order to correct for background and isobaric interferences.  $^{50}\text{Ti}$  and  $^{50}\text{Cr}$  were estimated by measuring  $^{49}\text{Ti}$  and  $^{52}\text{Cr}$  and using the natural isotopic abundance ratios  $^{50}\text{Ti}/^{49}\text{Ti} = 0.954$  and  $^{50}\text{Cr}/^{52}\text{Cr} = 0.05186$  to determine the appropriate correction factor.<sup>37</sup> Two blocks of data with 10 individual ratio measurements of 5 s integration were taken for each sample. Total time to run each sample was  $\sim 50$  min. Minimum sample size was 150 pg of V, or about 30 mg of calcite before cleaning. Typical observed ion currents were  $1 \times 10^{-15}$ – $4 \times 10^{-15}$  A on  $^{51}\text{V}$ .

**Inductively Coupled Plasma Mass Spectrometry.** A Perkin Elmer Sciex ELAN 5000 ICPMS with a Perkin Elmer HGA-600MS electrothermal vaporization (ETV) unit and an AS-60 autosampler was used. The conventional detector (channel electron multiplier) was replaced with a discrete dynode electron multiplier (ETP Scientific, Auburn, MA). The ICP operation conditions and ETV temperature program are given in Table 2. Ion optics, nebulizer flow, and torch position were optimized for maximum sensitivity and minimum noise for vanadium  $m/z$  51 while the conventional pneumatic nebulizer was in place. Doubly charged ions and oxide levels, as represented by  $\text{Ba}^{2+}/\text{Ba}^+$  and  $\text{CeO}/\text{Ce}$ , were monitored in the optimization process and kept below 2 and 3%, respectively. No readjustment of operating conditions was necessary after attaching the ETV unit. Signals were collected in peak height mode. Pyrolytically coated graphite tubes were used. To remove

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Table 2. Operating Conditions for ELAN 5000 ICPMS-ETV

Inductively Coupled Plasma					
Ar outer flow	15 L min <sup>-1</sup>				
Ar nebulizer flow	1.015 L min <sup>-1</sup>				
Ar auxiliary flow	0.85 L min <sup>-1</sup>				
forward power	1.1 kW				
detector voltage	3.8 kV				
Mass Spectrometer					
lenses	tune to V at <i>m/z</i> 51				
sampling position	9 mm from load coil				
sampler cone	Pt, 1.1 mm diameter orifice				
skimmer cone	Pt, 0.9 mm diameter orifice				
dwelt time	15 ms				
measurement time	675 ms				
resolution mode	normal (0.7 amu at 10% peak height)				
scanning mode	peak hop transient, 1 pt/peak				
signal profile	maximum (peak height)				
signal profile smoothing	11 point running average				
sample volume	30–35 μL (in duplicate)				
modifier	200 ng of Pd as PdNO <sub>3</sub>				
Temperature Cycle for ETV					
stage	temp (°C)	ramp (s)	hold (s)	argon flow (mL/min)	
				internal	carrier
1, dry	100	2	10	300	0
2, dry <sup>a</sup>	120	10	5	300	0
3, pyrolysis	1000	5	15	300	0
4, vaporization	2400	0	5	0	1000
5, cool	20	1	5	0	1000
6, clean	2650	1	5	0	1000
7, cool	20	1	10	0	1000

<sup>a</sup> Drying steps 1 and 2 are carried out following addition of both Pd modifier and sample.

residual vanadium before sample analysis, graphite tubes were conditioned by heating to 2650 °C for 10 s repeatedly until tube blanks did not decrease significantly and were below 700 counts/s at *m/z* 51. The sample passes from the graphite furnace to the torch via a 63 mm long, 6.4 mm i.d. Teflon tube.

**Palladium Nitrate.** Addition of a carrier is essential to assure that the analyte does not condense on surfaces following vaporization in the graphite furnace. We used 20 μL of a 10 ppm PdNO<sub>3</sub> solution. By acting as a physical carrier of the vaporized analyte, the Pd assured adequate transport efficiency from the graphite tube into the plasma.<sup>38,39</sup> Two hundred nanograms of Pd was determined to be the optimal amount for vanadium determination. The intensity decreases with lesser amounts, while additions larger than 200 ng of Pd do not significantly improve the signal. We explored several other modifiers including dilute seawater, lanthanum oxide, and the CaCO<sub>3</sub> present in the original sample. Ten microliter aliquots of seawater diluted 1:1000, which contains ~350 ng of Na and is intrinsically low in transition metals, was used.<sup>40,41</sup> While the seawater modifier increased the intensity relative to no added carrier, 200 ng of PdNO<sub>3</sub> gave 30% more counts in peak height mode. Signal intensities for V standards using a La modifier were also inferior to those for Pd. The CaCO<sub>3</sub>

in the original sample, typically 2 mg, was not a useful modifier; calcium suppressed the signal by 90%.

**ETV Temperature Program.** The Pd modifier was introduced into the graphite tube and heated gradually to 120 °C. After the tube was cooled briefly, 35 μL of sample was introduced and slowly dried. The sample was charred at 1000 °C for 20 s to eliminate Cl and vaporized at 2400 °C to introduce it into the plasma. Maximum power heating was used in this step, with a heating rate of ~2000 °C s<sup>-1</sup>. An optimal vaporization temperature of 2400 °C was chosen on the basis of obtaining the highest signal while prolonging tube life. At 2600 °C, the vanadium signal was 15% greater, but the tube life was significantly shortened. Three seconds before and during the vaporization step, the sample introduction hole in the graphite tube was closed with a graphite rod to prevent sample loss. During this period, the argon flow passes through the graphite tube, down the Teflon tubing and into the ICP torch, instead of being directed from the ends of the tube out of the sample introduction hole, as it was during the preceding dry and pyrolysis steps. Vanadium is a refractory metal and forms refractory carbides in the graphite furnace,<sup>42</sup> resulting in peak tailing and carryover of V from one sample to the next. To reduce this effect, a high-temperature cleaning step (2650 °C) was used following the vaporization step.

Intensity at *m/z* 49, 50, 51, 52, and 53 was measured with 15 ms dwell times in peak hop transient mode at normal resolution (Table 2). Background levels were determined at the beginning of the run by monitoring those masses for the Pd modifier only. Each sample was analyzed in duplicate. Total time for each duplicate analysis, including addition of Pd modifier and sample, drying, charring, vaporization, and cleaning, was <6 min.

**Isotope Dilution Calculations.** Isotope dilution allows highly accurate and precise determinations in elemental determination. Any variable sample loss following spike equilibration (e.g., during ion exchange chromatography, sample processing, or in the ETV) will not affect the final value. The concentration of vanadium in the sample spiked with the enriched <sup>50</sup>V tracer was determined from the isotopic ratio, *R<sub>m</sub>*, measured by mass spectrometry and calculated according to the following equation:

$$C_x = \frac{C_s W_s}{W_x} \frac{{}^{50}\text{V}_s - R_m {}^{51}\text{V}_s}{{}^{51}\text{V}_x - R_m {}^{50}\text{V}_x}$$

where *C<sub>x</sub>* and *C<sub>s</sub>* are the concentrations of V in the sample and spike, respectively; *W<sub>x</sub>* and *W<sub>s</sub>* are the weights of the sample and spike; <sup>50</sup>V<sub>x</sub> and <sup>50</sup>V<sub>s</sub> are the atom fractions of the enriched isotope <sup>50</sup>V in the sample and spike, respectively; <sup>51</sup>V<sub>x</sub> and <sup>51</sup>V<sub>s</sub> are the atom fractions of <sup>51</sup>V in the sample and spike, respectively; and *R<sub>m</sub>* is the measured <sup>50</sup>V / <sup>51</sup>V ratio of the spiked sample. <sup>50</sup>V<sub>x</sub> = 0.0024 and <sup>51</sup>V<sub>x</sub> = 0.9976 are taken from the natural abundances of the isotopes. <sup>50</sup>V<sub>s</sub> = 0.444 and <sup>51</sup>V<sub>s</sub> = 0.556 are taken from repeated measurements of the spike by TIMS. These values agree to within ±0.3% of the original isotopic analysis performed at ORNL.

In isotope dilution calculations, the precision of the analysis depends to some extent on the value of the measured ratio, *R<sub>m</sub>*. An optimal ratio equal to the geometric mean of the spike and sample ratios, *R<sub>opt</sub>* = 0.002, will theoretically minimize the error introduced by the propagation of errors in the above isotope dilution equation.<sup>43</sup> However, the uncertainty decreases with

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increasing total counts for both isotopes, which results in a greater optimal ratio.<sup>44</sup> A target spiking ratio of  $R_{\text{opt}} = 0.1-0.3$  was chosen.

**Mass Bias.** Error introduced by instrumental and matrix-induced mass discrimination is an important consideration in mass spectrometry and must be evaluated before these methods can be relied on to produce reliable and accurate results. Unfortunately, there is no good isotopic standard for vanadium. Since the abundance of  $^{50}\text{V}$  is extremely low in natural samples (0.24%), it is not possible to accurately measure the natural isotopic ratio by TIMS or ICPMS. Therefore, mass bias effects must be estimated. In TIMS, the greatest source of mass fractionation is Raleigh distillation as the sample is ionized from the heated filament. Results from K and Rb in our laboratory indicate that mass fractionation was rarely  $>0.1\%$   $\text{amu}^{-1}$  in the relevant mass range. The isotope ratio of the spike, as measured by TIMS in our laboratory and corrected for isobaric interferences  $^{50}\text{Cr}$  and  $^{50}\text{Ti}$ , was  $0.799 (\pm 0.001; 1\sigma)$ . This value did not change within the measurement error over a period of 4 years. It agrees with the ratio measured at ORNL to within  $\pm 0.3\%$ , suggesting that mass fractionation by TIMS was consistently reproducible.

While such fractionation at the ion source does not occur in plasma mass spectrometry, significant mass bias effects are possible in the lens stack and within the quadrupole mass spectrometer. Instrumental mass discrimination has been measured at  $1-2\%$   $\text{amu}^{-1}$  for Os isotopes<sup>45</sup> and as large as  $5-7\%$  for  $^{10}\text{B}/^{11}\text{B}$  ratios.<sup>46,47</sup> Mass fractionation in the ELAN 5000 was estimated by comparing the isotopic composition of the vanadium spike as determined by TIMS with those measured by ICPMS. The enriched isotope spike was analyzed by ICPMS frequently over the course of several runs to assess the relative degree of mass bias within each run and between runs. The  $^{50}\text{V}/^{51}\text{V}$  ratio of this standard did not vary by more than  $\pm 0.5\%$   $\text{amu}^{-1}$  during any single run, indicating that machine drift was not a significant concern. However, the isotopic ratio of the spike determined by ETV-ICPMS was up to 5% lower than the value determined by TIMS. A mass fractionation correction factor,  $\alpha$ , is included in the calculation to determine the vanadium content and provide consistency with TIMS analysis:  $\alpha = (R_m/R_{\text{spike}} - 1)/\Delta m$ , where  $R_m$  is the measured ratio,  $R_{\text{spike}}$  is the ratio determined by TIMS, and  $\Delta m = 1$  is the mass difference between the two isotopes  $^{50}\text{V}$  and  $^{51}\text{V}$ . Given a mass bias of 3%, the final calculated concentration for a 200 pg V sample using a 0.1 g spike was 5% higher using this correction factor. An alternative method to treat mass bias concerns would be to make the isotope spike calibration measurements by ID-ETV-ICPMS instead of by ID-TIMS, and use this value in the calculations. Since, to first order, spike calibrations should exhibit the same mass discrimination as samples, any bias is canceled in concentration measurements, and no correction would need to be made.

## RESULTS AND DISCUSSION

**Blanks.** Low-level vanadium analyses are possible only if reagent, water, and procedural blanks are consistently at extremely

Table 3. Vanadium Content of Water, Reagent, and Process Blanks

reagents	V concn (pg/mL)	amount used <sup>a</sup> (mL)	V total (pg)
H <sub>2</sub> O	0.05	4.0	0.20
H <sub>2</sub> O <sub>2</sub>	5.62	0.01	0.06
HCl	0.13	0.04	0.01
total known sources of blank			0.27
measured process blank			0.27
unknown sources of blank (by difference) <sup>b</sup>			<DL

<sup>a</sup> Four milliliters of 0.01 N HCl/0.3% H<sub>2</sub>O<sub>2</sub> used for each sample.  
<sup>b</sup> Resin, containers, airborne contamination, etc.

Table 4. Isotope Abundances of Elements and Interfering Polyatomic Ions in the Relevant Mass Range for Vanadium Determination by Isotope Dilution

	<i>m/z</i>							
	47	48	49	50	51	52	53	54
V				0.24	99.76			
Ti	7.28	73.94	5.51	5.34				
Cr				4.31		83.76	9.55	2.38
Fe								5.82
other	PO <sup>+</sup>	<sup>48</sup> Ca <sup>+</sup>			ClO <sup>+</sup>	Ar <sup>12</sup> C <sup>+</sup>	Ar <sup>13</sup> C <sup>+</sup>	Ar <sup>14</sup> N <sup>+</sup>

low levels. To avoid contamination, sample processing was kept at an absolute minimum, and reagent volumes were as low as possible without sacrificing sample recovery.

Blank levels for each of the reagents and the water were quantified by comparing the vanadium intensity at  $m/z$  51 with those of known standards. Sample volumes of 20–30 mL were used in order to obtain a true blank value significantly above the limit of detection (DL), even though less volume was used in practice. The V content of one, two, and four combined procedural blanks was determined to obtain an accurate value for the blank. A regression of the V content versus the number of procedural blanks results in a slope of 0.27 pg of V per blank ( $r^2 = 0.97$ ). Variability of this blank value was primarily dependent on the quality of the water used, although contaminated batches of resin occasionally contributed to a high blank. Abnormally high levels of chromium were also found in some resin batches. In these cases of higher V or Cr, the resin was recleaned by soaking in HCl, as described earlier. The total known sources of blank from the reagents and the measured procedural blank were equal (Table 3), which indicates that unknown sources of blank including V from the resin, containers, and environmental contamination were negligible.

**Isobaric Interferences.** Ionization suppression due to matrix effects was essentially eliminated by removing major cations (e.g., Ca<sup>2+</sup>, Na<sup>+</sup>) with the ion exchange column chromatography. However, isotopes of chromium and titanium as well as interfering polyatomic ions ClO<sup>+</sup>, ArC<sup>+</sup>, and PO<sup>+</sup> make the determination of V by isotope dilution especially complex (Table 4).

**Elimination of ClO<sup>+</sup> Interference.** The ClO<sup>+</sup> ion at  $m/z$  51 is the primary interference in vanadium-51 measurement by ICPMS and prevents accurate determination in matrices with Cl levels as low as 0.01%. Sample introduction with ETV effectively eliminates the ClO<sup>+</sup> isobaric interference in solutions of 0.01–0.5 N HCl (Table 5). By preheating the sample in a graphite furnace before addition to the plasma, the volatile Cl is removed

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Table 5. Evaluation of the Importance of the  $\text{ClO}^+$  Interference at  $m/z$  51 as a Function of HCl Concentration Using Standard Pneumatic Nebulization Compared with Electrothermal Vaporization To Introduce the Sample<sup>a</sup>

HCl concn (N)	pneumatic nebulization at $m/z$ 51 (counts/s)	ETV at $m/z$ 51 <sup>b</sup> (counts/s)
0	777	121
0.01	42 000	95
0.1	410 000	170
0.5	830 000	86

<sup>a</sup> Volatilization of Cl in the graphite furnace before analysis eliminates the background due to  $\text{ClO}^+$ , even at high concentrations of Cl.  
<sup>b</sup> Blank corrected values.

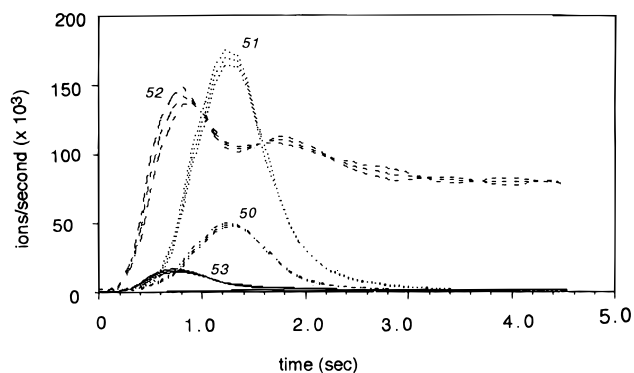


Figure 1. ICPMS-ETV signal profile of a typical spiked sample of foraminiferal calcite following cleaning and ion exchange. Shown are profiles of intensity at  $m/z$  50, 51, 52, and 53. Peak intensity for  $m/z$  49 is typically 1000 counts/s at 1.4 s and is at baseline in this figure. Note the high Cr-52 and  $^{40}\text{Ar}^{12}\text{C}$  peaks at 0.8 and 1.7 s, respectively, at  $m/z$ . Duplicate analyses and the averaged profile are shown.

and the  $\text{ClO}^+$  interference eliminated. The pyrolysis temperature and time were optimized for complete removal of Cl with no loss of V. Based on these criteria, the optimum pyrolysis condition was found to be 1000 °C for 20 s. Even at only 200 °C for 5 s, 90% of the Cl was removed.

**Titanium and Chromium-50 Correction.** Since both Ti and Cr have isotopes at  $m/z$  50 (relative abundances of 5.31 and 4.31%, respectively), they interfere with the  $^{50}\text{V}$  measurement (Table 4). While efforts were made to separate these elements during the ion exchange process, measurable quantities of both were still present.  $^{49}\text{Ti}$  (5.51%) was used to correct for the  $^{50}\text{Ti}$ . Titanium isotopes at mass 48 and 46 were avoided due to the potential interference with calcium;  $^{47}\text{Ti}$  has a higher and more variable background due to the  $\text{PO}^+$  ion.  $^{50}\text{Ti}$  accounts for 2–4% of the  $^{50}\text{V}$  signal. The correction for the interference due to  $^{50}\text{Cr}$  was more complex since isobaric elements exist at all the other chromium isotopes:  $^{52}\text{Cr}$  (83.76%),  $^{53}\text{Cr}$  (9.55%), and  $^{54}\text{Cr}$  (2.38%).  $^{54}\text{Cr}$  was not a viable alternative because of the high background from  $^{40}\text{Ar}^{14}\text{N}$  and the isobaric overlap with  $^{54}\text{Fe}$ , which is not easily corrected. Polyatomic ions resulting from carbon argides at  $m/z$  52 ( $^{40}\text{Ar}^{12}\text{C}$ ) and 53 ( $^{40}\text{Ar}^{13}\text{C}$ ) overlap with  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$ . They are difficult to correct for due to their very broad signal pulse, which is especially prominent at  $m/z$  52 in Figure 1. Peak height measurements rather than integrated signals were used for the determination of Cr, which significantly reduces the background counts due to these carbon argides.<sup>38</sup> Measurement of  $^{53}\text{Cr}$  was used to estimate  $^{50}\text{Cr}$  because the intensity of the  $^{40}\text{Ar}^{13}\text{C}$  peak is 2 orders of magnitude lower than the  $^{40}\text{Ar}^{12}\text{C}$  peak ( $^{13}\text{C} = 0.011^{12}\text{C}$ ).

A value of 400–800 counts/s for  $^{40}\text{Ar}^{13}\text{C}$  based on 1.1% of the  $^{40}\text{Ar}^{12}\text{C}$  peak was subtracted from the total counts at  $m/z$  53. The  $^{50}\text{Cr}$  content was calculated from the resulting  $^{53}\text{Cr}$  and used to correct the  $^{50}\text{V}$ . Since Cr is vaporized off the graphite tube more readily than vanadium (0.8 s vs 1.3 s; Figure 1), and because peak height measurements are used, the Cr intensity is reduced to 60% of its maximum value at the vanadium peak. Thus, only 0.60 times the intensity of  $^{50}\text{Cr}$  was used in the final correction. The equation used for the complete correction is given by

$$\begin{aligned}
 ^{50}\text{V} &= m/z\ 50 - 0.6(^{50}\text{Cr}) - (^{50}\text{Ti}) \\
 &= m/z\ 50 - 0.6(4.31/9.55)(m/z\ 53 - ^{40}\text{Ar}^{13}\text{C}) - \\
 &\quad (5.34/5.51)(^{49}\text{Ti})
 \end{aligned}$$

$^{50}\text{Cr}$  levels typically ranged from 5 to 15% of the total signal at  $m/z$  50. Figure 1 is a characteristic signal profile that illustrates the relative magnitude of vanadium isotope signals and interferences of a typical spiked sample. This sample contained an estimated 60 pg of natural vanadium and was spiked with 20 pg of  $^{50}\text{V}$  and 25 pg of  $^{51}\text{V}$ .

**Detection Limit.** The detection limit for vanadium by ETV-ICPMS without the isotope spike was 0.3 pg of V, based on the mass of vanadium that gives a response equivalent to 3 times the standard deviation of the blank at  $m/z$  51. In this case, the blank was the response obtained from the vaporization of 33  $\mu\text{L}$  of 0.1 N  $\text{HNO}_3$  and 20  $\mu\text{L}$  of the Pd modifier ( $n = 15$ ).

Using isotope dilution, the isobaric interferences at  $m/z$  50 from the chromium and titanium result in a detection limit which is significantly higher. This was determined by treating the enriched isotope spike as a blank and measuring the V concentration on 0.1 mL aliquots. By definition, the vanadium concentration of the spike with no added sample, determined by isotope dilution, should be zero. The detection limit, defined as 3 times the standard deviation of the calculated value of the spike, was 6 pg of V. This higher value is due to the variability of the Cr and Ti levels, occasional ArC peaks from the graphite tube much higher than average, and the uncertainty in the correction for these isobaric interferences.

#### Sensitivity, Precision, and Accuracy of Sample Analysis.

**Sensitivity** varied from run to run, depending on the condition of the cones, Ar flow, tuning of ion lenses, and other instrument conditions. Over a 1 year period, response at  $m/z$  51 averaged 2500 counts  $\text{s}^{-1}$   $\text{pg}^{-1}$  of V ( $\pm 25\%$ ). An important matrix effect was observed that resulted in significant signal suppression above 1 mM  $\text{Ca}^{2+}$ . At 10 mM Ca, the vanadium intensity was 65% lower than that for a Ca-free matrix; at 100 mM Ca, signal suppression was 90%. The levels of  $\text{Ca}^{2+}$  in an untreated sample were  $\sim 0.5$  M. Similar suppression was observed for a seawater matrix, necessitating the ion exchange to remove major cations, including  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , from the sample. Following this separation step,  $\text{Ca}^{2+}$  levels in the dissolved calcite samples were  $< 10$  nmol/L as determined by ICPMS at  $m/z$  43.

**Precision.** Using 0.1 g of the dissolved foraminiferal standard, or the equivalent of about 2.5 mg of calcite after cleaning, the precision of the vanadium determination by ETV-ICPMS within one run was  $\pm 3\%$  ( $1\sigma$ ;  $n = 10$ ).

**Accuracy.** We assessed the accuracy of the analysis by two independent tests: standard addition and comparison to other methods for V determination. The first check was performed by

Table 6. Intercomparison of Methods for Determination of V in Calcite

method	V (pg of V/g of CaCO <sub>3</sub> )	amount used (mg of CaCO <sub>3</sub> )	precision (%)
ID-ICPMS-ETV	370	2.5	±3
ID-TIMS	360	25	±5
APDC GFAAS	339	300	±4

adding 10–1000 pg of vanadium to 250  $\mu$ L aliquots of the ultrapure CaCO<sub>3</sub> standard, which is equivalent to 7.5 mg of CaCO<sub>3</sub> or a typical foraminifera sample. These standards were processed according to the described method and analyzed by ID-ETV-ICPMS. Final values were corrected for background levels of V in the CaCO<sub>3</sub> standard, which was independently quantified by isotope dilution to be 14 pg of V/250  $\mu$ L aliquot. A comparison of 10–1000 pg of V standard added to calcite versus vanadium of these samples, as determined by ID-ETV-ICPMS, resulted in a near perfect correlation. Vanadium added compared to the values as calculated by this method resulted in a linear correlation with a slope of 0.998 and  $r^2 = 1.000$ , which demonstrates that the method is accurate and linear over this range of values. Based on the instrument characteristics of the ICPMS, the method should be linear to levels at least 5 times greater, or 5000 pg.

Another indication of the accuracy of the measurement is to analyze the vanadium concentration of the standard foraminifera mixture by several different and independent methods: ID-ETV-ICPMS, ID-TIMS, and coprecipitation with APDC and graphite furnace atomic absorption spectrophotometry. As the results shown in Table 6 indicate, the two isotope dilution methods agree to within the precision of the measurement. The value for the

GFAAS determination was 10% lower than that obtained with the other methods, possibly due to incomplete recovery of V by the APDC.

## CONCLUSIONS

Isotope dilution inductively coupled plasma mass spectrometry using electrothermal vaporization to remove isobaric interference at  $m/z$  51 provides an extremely sensitive tool for the determination of V at picogram levels. This technique is sufficiently sensitive to allow the measurement of V in foraminiferal calcite, which has the potential to quantify changes in the redox state of the deep ocean over glacial–interglacial cycles. This method can be directly applied to the determination of V in other calcareous biogenic phases, including coralline aragonite and pteropods. Assuming that these living organisms incorporate vanadium into their skeleton in proportion to the vanadium concentration of seawater, foraminifera could also be useful paleoceanographic tools over different time scales and in different depositional environments. The technique is useful for the determination of V in seawater where sample volumes are limited, such as in benthic chamber experiments and porewater studies. The use of <sup>50</sup>V as an isotope tracer eliminates any inaccuracy due to variable recoveries during sample processing. Analysis of other environmental and biological samples characterized by ultralow levels of vanadium could also be facilitated by this method.

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