

# Vanadium isotope data from globally representative sediments that have a range of bottom water oxygen conditions

**Website:** <https://www.bco-dmo.org/dataset/820063>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2020-08-04

## Project

» [Fingerprinting and Calibrating Low Oxygen Conditions Using Vanadium Isotopes](#) (Vanadium Isotopes)

Contributors	Affiliation	Role
<a href="#">Owens, Jeremy D.</a>	Florida State University (FSU)	Principal Investigator
<a href="#">Nielsen, Sune G.</a>	Woods Hole Oceanographic Institution (WHOI)	Co-Principal Investigator
<a href="#">Rauch, Shannon</a>	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

## Abstract

This dataset includes the first vanadium isotope data from globally representative sediments that have a range of bottom water oxygen conditions.

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## Coverage

**Spatial Extent:** N:53.525 E:170.387 S:-39.491 W:-120.03

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## Dataset Description

This dataset includes the first vanadium isotope data from globally representative sediments that have a range of bottom water oxygen conditions.

**Note:** Data other than V isotopes were obtained in previous studies and references for this work can be found in the published work of Wu et al., 2020. Cells with "nd" indicate that data was not available or obtained.

## Methods & Sampling

### Methodology:

This work analyzed V isotope composition of previously collected sediments from a global network that have a range of bottom water oxygen conditions. Below is a description of the methods used for the samples collected by various cruises.

Twenty-two pelagic sediment samples from various localities around the globe were investigated in this study. A total of thirteen samples were analyzed from the Pacific Ocean at water depths of 3500–5800 m, four samples were analyzed from the Indian Ocean at water depths of 4400–5200 m, four samples were analyzed

from the Atlantic Ocean at water depths of 3300–6000 m, and one sample was analyzed from the Arctic Ocean at water depths of 4041 m. All the samples are distal from any known marine hydrothermal vent field and thus should not include a hydrothermal signature. Sediment lithologies consist predominantly of oxidized fine-grained pelagic clay ranging from light to dark brown or greenish-gray in color, with various carbonate and calcareous ooze contents. Dried sediments were collected from cores housed in the sediment repository of Woods Hole Oceanographic Institution (WHOI) and from the U.S. GEOTRACES East Pacific Zonal Transect (EPZT GP16). These samples are bulk powders from the top portions (0–10 cm) of cores.

Sediment samples from the continental margin off Namibia in the eastern South Atlantic were collected as part of the RV Meteor expeditions M57/2. The core samples were collected on a continental slope transect with water depths between 605 and 2470 m. The bottom water oxygen contents of the sample locations are from 150 to 220  $\mu\text{M}$ . The sediments in the Eastern Cape Basin are characterized by low input of terrigenous matter and high biogenic contents. The high amounts of organic matter (up to 9% for the analyzed V isotope sites) in the sediments are due to high water column primary production on the shelf and lateral transport of organic carbon from the shelf to the slope. The sediments off Namibia analyzed here are all core top sediments from 0 to 5 cm.

Sediment samples from the Argentine Basin in the western South Atlantic were collected during R/V Meteor expedition M78/3. The predominantly terrigenous material in this region is delivered from the numerous fluvial tributaries along the coast of Argentina and Uruguay and transported further downslope via gravity-controlled mass flows. The core samples were collected east of the Rio de la Plata mouth from water depths between 58 m and 4273 m, forming a transect from shelf to deep basin. The sediments from the Argentine Basin analysis here are from core depths between 5 to 45 cm.

Samples from the Peruvian Margin in this study were mostly from a transect along 11°S during the RV Meteor cruise M77-1 in November 2008. In addition, some Peruvian Margin sediment samples were collected during the U.S. GEOTRACES East Pacific Zonal Transect (EPZT GP16) and R/V Moana Wave cruise 87 leg 08. High oxygen demand within the water column leads to a perennial oxygen minimum zone (OMZ) that impinges on the continental shelf/ slope between 50 and 500 m water depth. Thirteen sediment cores were analyzed from the continental shelf to deep slope at water depths between 85 and 2025 m, which transects from the reducing OMZ to the deeper oxic seafloor with bottom water oxygen contents from 1.5 mM to 93.4  $\mu\text{M}$ . The Peruvian Margin samples analyzed were from core depths between 0 to 35 cm.

Sediment samples from the deepest portion (594 m water depth) of the Santa Barbara Basin were collected in 2001 as part of the CALMEX cruise (R/V New Horizon in November 2001). The Santa Barbara Basin is a shallow, near-shore basin off southern California with a sill depth of approximately 475 m. Below the basin sill depth of 475 m, the water column is characterized by limited exchange with waters outside of the basin, thus the circulation within the basin is restricted resulting in low bottom water oxygen concentrations, typically < 5  $\mu\text{M}$ , though the concentration can vary on seasonal timescales. The core samples were collected at the center of the basin with bottom water oxygen contents near-zero (1  $\mu\text{M}$ ). The Santa Barbara Basin samples analyzed here include the core top sediment (0–3 cm) to shallow depths (10–11 cm).

Sediment samples from the Cariaco Basin were collected in 1990 as part of the PLUME Leg 7 Cruise (R/V Thomas Washington). The Cariaco Basin is the second-largest euxinic (anoxic and sulfidic water column) marine basin in the modern ocean. Below 300 m water depth, the basin is euxinic due to a combination of limited deepwater renewal and high surface productivity supplying organic matter that promotes microbial respiration, oxygen depletion, and the accumulation of hydrogen sulfide. Seven separate box core top samples (0–1 cm) from around the Cariaco basin including both sub-basins were collected. All of the Cariaco sediment samples measured in this study were collected below the permanent chemocline (sulfidic portion) at water depths between 400 and 1350 m.

### **Sampling and analytical procedures:**

#### **Sample dissolution:**

Samples were dissolved using bulk digestion and leaching methods. Both methods were carried out to ensure that the V isotope analyses captured the authigenic values, especially given the limited enrichment for some of the samples (e.g. differences between the bulk and leach methods). For the bulk digestion, sediment samples for V isotope analysis were ashed overnight at 600°C to remove organic phases. Ashed sediment powders were then completely digested with a multi-acid HF–HNO<sub>3</sub>–HCl procedure using trace metal clean acids. All materials were completely dissolved in 0.8 N HNO<sub>3</sub> prior to purification using ion exchange column chemistry.

The leach technique was applied to extract authigenic V. For the organic carbon-rich sediments, splits of sediment were leached in a Teflon Savillex vial with 3 mL of 3 N HNO<sub>3</sub> for 12–16 hours at room temperature with constant agitation using a shaking table. These samples were then centrifuged, and the supernatant was collected and placed in a new clean Savillex vial and dried. During the collection of the supernatant, care was

taken to avoid the solid phase siliciclastic materials; additionally, HF was avoided to ensure the limited dissolution of siliciclastic minerals. Several high-purity acid treatments (aqua regia, conc. HNO<sub>3</sub>) were added to each vial to completely oxidize any organic matter that might have been present. Samples were then dissolved with 0.8 N HNO<sub>3</sub> prior to ion exchange column chemistry. To validate this leaching method, the leaching method was performed on United States Geological Survey (USGS) shale standards SCo-1 and SDO-1 with 1 N HNO<sub>3</sub> concentrations. Splits of the leach solution were also taken for elemental analysis.

For the oxic pelagic sediments, we applied the well-established extraction technique for oxide dissolution to obtain the isotopic analysis of the authigenic V. One aliquot of the pelagic sediments was reacted in 10 mL 25% acetic acid + 1 N hydroxylamine hydrochloride solution at 90°C for three hours, and each sample was agitated every 30 minutes. The supernatant was removed from the detrital particles, treated with 8 N HNO<sub>3</sub> and then dissolved with 0.8 N HNO<sub>3</sub> prior to ion exchange column chemistry.

#### Vanadium Purification:

The purification of V was conducted with a four-step ion exchange procedure by coupling cation- and anion-exchange columns. Briefly, samples were first loaded on a cation resin AG50W-X12 (200–400 mesh) and major cations Al, Ti, and Na were eluted with 0.8 N HNO<sub>3</sub> + 0.1 N HF and 0.8 N HNO<sub>3</sub>. V was then eluted and collected with 1.2 N HNO<sub>3</sub>. The major cations Fe, Mg and Ca do not leave the resin by the time all of the V is eluted, thus the procedure separates all major cations except for K. The anion exchange resin AG1-X8 (200–400 mesh) was subsequently applied to remove all the residual matrix elements from V as described in Nielsen et al. (2011). The anion column was performed twice in order to quantitatively remove any residual Ti and Cr. In-between each column, samples were evaporated and refluxed in aqua regia overnight at 135°C to remove potential organic material leached from the resin, evaporated again, and redissolved in the next solution. The yield of the entire V column chemistry procedure is within error of 100%. Samples were re-dissolved in 1 mL 2% HNO<sub>3</sub> prior to elemental and isotopic analysis. Total procedural blanks (from sample dissolution/leach to instrumental analysis) were < 2 ng, which is negligible compared with the amount of V extracted from each sample (2–6 mg).

#### Instrumental Configuration:

Instrument measurements were performed at the National High Magnetic Field Laboratory at Florida State University (FSU) using a Thermo Scientific Neptune Multicollector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS). Measurements were performed on the flat-topped shoulder on the lower mass side of the overlapping V and molecular interference peaks in medium-resolution mode (resolution > 4000) to resolve all interfering molecular species representing combinations of C, N, O, S, Ar and Cl (such as <sup>36</sup>Ar<sup>14</sup>N+, <sup>36</sup>Ar<sup>16</sup>O+, and <sup>38</sup>Ar<sup>14</sup>N+). To obtain the highest possible V transmission efficiency, solutions were introduced with a desolvating nebulizer system (Aridus II) and Jet sample and Ni X-skimmer cones were also applied. The typical sensitivity of <sup>51</sup>V under such configuration was 1.5–2.5 nA/ppm.

## Data Processing Description

### Data processing:

Sample analysis protocols follow standard-sample bracketing procedures. The 10<sup>10</sup>Ω resistor is applied to monitor <sup>51</sup>V, while other concerned isotopes (<sup>49</sup>Ti, <sup>50</sup>V, <sup>52</sup>Cr, <sup>53</sup>Cr) are monitored with conventional 10<sup>11</sup>Ω resistors to accommodate the large natural isotope abundance differences of V (<sup>51</sup>V/<sup>50</sup>V = 400). While the chemical purification nearly quantitatively separates Ti and Cr from V, minor amounts of <sup>50</sup>Ti and <sup>50</sup>Cr remain in solution which can dramatically affect the analysis on <sup>51</sup>V/<sup>50</sup>V ratio, especially for low V concentration measurements. Therefore, analysis of the <sup>49</sup>Ti/<sup>51</sup>V and <sup>53</sup>Cr/<sup>51</sup>V ratios are needed and should be less than 0.00005 to properly correct for interferences of <sup>50</sup>Cr and <sup>50</sup>Ti. Here we use the procedure described by Nielsen et al. (2011) and Wu et al. (2016) to correct the raw data for any potential interferences. Briefly, 50 ng/g Cr and 50 ng/g Ti standard solutions were analyzed every time the mass spectrometer was tuned to calculate the mass bias coefficients. The obtained mass bias coefficients were then used to calculate the true <sup>50</sup>Ti and <sup>50</sup>Cr ion beam that was subtracted from the total signal on mass 50.

Vanadium isotopic data are reported in conventional δ notation in permil relative to AA ( $\delta^{51}\text{V} = ((^{51}\text{V}/^{50}\text{V})_{\text{sample}} / ^{51}\text{V}/^{50}\text{V})_{\text{AA}} - 1) \times 1,000$ ). Each data analysis was run with 40 cycles of 4.194 s integrations for each cycle and baseline calibration was run before each analysis. Each sample was bracketed by measurements of the AA solution to obtain an average value and stability of the instrument for the highest quality control. After the evaluation of two samples, a solution standard, BDH, was measured to ensure the performance and stability of the analysis on the MC-ICP-MS. The in-house isotope BDH standard was a 1000 μg/g V standard solution, which has an isotope composition of  $\delta^{51}\text{V} = -1.2\text{‰}$  based on analyses in several different labs worldwide. The errors for V isotope results of each sample are reported in two standard deviations relative to the average

value (2SD). Measurements of BDH in this study gave an average  $\delta^{51}\text{V} = -1.19 \pm 0.10\text{‰}$  (2sd, n = 121). The USGS igneous rocks reference materials BCR-2, BIR-1, and AGV-2 were processed through the same ion-exchange procedures and  $\delta^{51}\text{V}$  values are in agreement with literature values. The uncertainties of  $\delta^{51}\text{V}$  for reference materials are better than  $\pm 0.12\text{‰}$  (2SD), representing the long-term external reproducibility of the data in this study.

#### **BCO-DMO Processing:**

- moved site names into a column;
- modified parameter names;
- replaced 'NA' with 'nd' (no data);
- converted latitude and longitude to decimal degrees.

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## **Data Files**

<b>File</b>
<b>Sed_V_signatures.csv</b> (Comma Separated Values (.csv), 9.63 KB) MD5:652019cf59450da93cd62e87b1636faa
Primary data file for dataset ID 820063

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## **Related Publications**

Wu, F., Owens, J. D., Huang, T., Sarafian, A., Huang, K.-F., Sen, I. S., ... Nielsen, S. G. (2019). Vanadium isotope composition of seawater. *Geochimica et Cosmochimica Acta*, 244, 403–415. doi:[10.1016/j.gca.2018.10.010](https://doi.org/10.1016/j.gca.2018.10.010)  
*Methods*

Wu, F., Owens, J. D., Scholz, F., Huang, L., Li, S., Riedinger, N., ... Nielsen, S. G. (2020). Sedimentary vanadium isotope signatures in low oxygen marine conditions. *Geochimica et Cosmochimica Acta*, 284, 134–155. doi:[10.1016/j.gca.2020.06.013](https://doi.org/10.1016/j.gca.2020.06.013)  
*Methods*

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## **Parameters**

<b>Parameter</b>	<b>Description</b>	<b>Units</b>
Site	Site name	unitless
Location_Name	Location name	unitless
Latitude	Latitude	decimal degrees North
Longitude	Longitude	decimal degrees East
Water_Depth	Water depth to the sediment where the sample was collected	meters (m)
Bottom_Water_O2	Measured and published bottom water oxygen in micromoles	micromolar (uM)

Sediment_Depth	Sediment sample depth below the seafloor (BSF)	centimeters
d51VBulk	Measured bulk V isotope value	per mil (‰)
two_sd_d51VBulk	2 standard deviation error from all analyses of d51VBulk	per mil (‰)
n_d51VBulk	Number of isotope analyses for d51VBulk	unitless
TOC_pcnt	Quantified bulk total organic carbon in weight percent	weight percent
Bulk_Al_pcnt	Quantified bulk aluminum concentration in weight percent	weight percent
Bulk_Fe_pcnt	Quantified bulk iron concentration in weight percent	weight percent
Bulk_Mn_pcnt	Quantified bulk manganese concentration in weight percent	weight percent
Bulk_Ti_ppm	Quantified bulk titanium concentration in parts per million	parts per million (ppm)
Bulk_V_ppm	Quantified bulk vanadium concentration in parts per million	parts per million (ppm)
d51VLeach	Measured leach V isotope value	per mil (‰)
two_sd_d51VLeach	2 standard deviation error from all analysis of d51VLeach	per mil (‰)
n_d51VLeach	Number of isotope analysis for d51VLeach	unitless
Leach_Al_pcnt	Quantified leached aluminum concentration in weight percent	weight percent
Leach_Ti_ppm	Quantified leached titanium concentration in parts per million	parts per million (ppm)
Leach_V_ppm	Quantified leached vanadium concentration in parts per million	parts per million (ppm)

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## Instruments

<b>Dataset-specific Instrument Name</b>	Thermo Neptune multi-collector ICP-MS
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Generic Instrument Description</b>	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

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## Project Information

### Fingerprinting and Calibrating Low Oxygen Conditions Using Vanadium Isotopes (Vanadium Isotopes)

#### *NSF Award Abstract:*

Discovering, testing, and developing chemical proxies (relic materials) in marine sediments that reveal how strongly or weakly oxidizing near-surface environmental conditions were in the Earth's geological past are immensely important for understanding interactions between ocean chemistry, biological evolution and extinctions, and climate. To date scientists do not have a proxy for low but non-zero oxygen conditions -- the sort of conditions that are likely to have dominated in biologically important periods of Earth history. In this project, researchers will study the relationship between bottom water oxygen concentration and the isotopes of the trace metal vanadium (V) in a range of oxygen conditions in the modern ocean. Based on pilot data, theoretical calculations and dissolved seawater V concentrations they believe that stable V isotope ratios of core top sediments will correlate systematically over a range of bottom water oxygen conditions. By analyzing these materials, the research team expects to establish the relationship between V isotopes and bottom water oxygen concentrations. Given the importance of chemical proxies to quantify past climate change, the results of this study will be of great importance to the modern and paleoceanographic community, as well as for modelers to better understand a broad range of oxygen variability in Earth history.

Although recent investigations have provided a wealth of information about the redox conditions of the ancient oceans, there is a significant gap in understanding low oxygen conditions throughout Earth history. Therefore, it is important to develop new paleoredox proxies that can provide additional and complementary knowledge about ocean redox conditions during these important periods of Earth history. In this study, scientists will analyze bulk sediments and their organic and ferromanganese mineral fractions to investigate the V isotopic variability within the various sedimentary components. (These samples comprise organic rich to ferromanganese rich sediments due to a range in bottom water oxygen concentrations.) Reconstructing marine low oxygen conditions using vanadium isotopes would fill a void in the paleoredox proxy toolbox. Developing, calibrating, and fingerprinting the V isotopic variability in modern sediments is required to be able to apply vanadium isotopes as an accurate paleoredox proxy.

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1434785</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1624895</a>

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