V isotope composition of previously collected seawater samples

Website: https://www.bco-dmo.org/dataset/819946
Data Type: Cruise Results
Version: 1
Version Date: 2020-08-03

Project
» Fingerprinting and Calibrating Low Oxygen Conditions Using Vanadium Isotopes (Vanadium Isotopes)

Contributors	Affiliation	Role
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Abstract
This dataset includes the validation of the seawater column chemistry method and seawater analysis.

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Coverage

Spatial Extent: **N**:44.052 **E**:-64.518 **S**:22.75 **W**:-158

Dataset Description

This dataset includes the validation of the seawater column chemistry method and seawater analysis.

Methods & Sampling

Methodology:
This work analyzed V isotope composition of previously collected seawater samples. Below is a description of the methods used for the samples collected by various cruises. Six seawater samples were anlalyzed in this study, several using multiple methods and replicate analysis. The studied samples include the North Atlantic Surface Seawater (NASS-6) reference material distributed by National Research Council of Canada (NRC - CNRC), three samples from the Bermuda Atlantic Time-series Study (BATS), one from the Gulf of Mexico, and one from the Pacific Ocean. NASS-6 is a seawater reference material collected from surface water at Sandy Cove, Nova Scotia (44°03.10'N, 64°42.20'W) in March 2007. The certified concentrations of some metals, including vanadium, are available from NRC/CNRC (https://www.nrc-cnrc.gc.ca/eng/solutions/advisory/crm/certificates/nass_6.html). Three BATS samples were collected with Go-Flo samplers mounted on a rosette equipped with a CTD instrument on R/V Atlantic Explorer from Bermuda Institute of Ocean Sciences (BIOS), Cruise AE0908 on September 2009 (32°18.50'N 64°31.10'W). These unfiltered BATS samples are sampled at depths of 150 m, 650 m, and 750 m and acidified to pH <2 with concentrated HCl and

then stored in acid-washed 10 L polypropylene cubitainers for transporting to the laboratory. Surface seawater (~2–3 m) from the Gulf of Mexico (26°60'N, 85°200'W) was collected in 2015 using a trace metal-clean towed 'fish', filtered during collection at sea using an acid-washed Acropak-200 capsule filter (0.2 mm pore size), and stored unacidified in an acid-washed cubitainer until subsampled for analyses. Samples were then acidified to 0.024 M HCl (ultrahigh purity, distilled) and allowed to sit at least three days before column chemistry. Deepwater from the North Pacific Ocean was collected at 3500 m at Station ALOHA (A Long-term Oligotrophic Habitat Assessment; ~22°450'N, 15°8'W, here denoted as S9) during the 2002 Intergovernmental Oceanographic Commission (IOC) cruise using trace metal-clean 30-L Go-Flo samplers, filtered shipboard using acid-cleaned 142-mm Nuclepore PCTE filters (0.4 mm pore size), and stored acidified (0.012 M HCl, Optima) in acid-washed 500 ml HDPE bottles since 2002. All acids were trace metal grade (e.g., Aristar) or higher, and all water was purified using a Milli-Q deionization system to ≥18.2 MΩ per cm^2.

Sampling and analytical procedures:
Instrumental Configuration: Instrument measurements were performed at both Woods Hole Oceanographic Institution (WHOI) and the National High Magnetic Field Laboratory at Florida State University (FSU) with similar configurations at both institutions 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 $^{36}Ar^{14}N+$, $^{36}Ar^{16}O+$, and $^{38}Ar^{14}N+$). Jet sample and Ni X-skimmer cones were used to obtain the highest possible V transmission efficiency. In addition, the amplifiers with $10^{10}\Omega$ and $10^{11}\Omega$ resistor were applied to monitor ^{51}V and ^{50}V signal, respectively. We applied dry plasma inlet system with Aridus II desolvator (CETAC Technologies). The typical sensitivity under such configuration was ~150–250 volts/ppm. The configuration requires 400 ng of V for at least one V isotope measurement.

Vanadium Purification:
WHOI Method: Four columns were used to separate vanadium from matrix elements. The first two columns consist of a large quartz column, stem of 10 cm in length and 0.6 cm in diameter, with quartz wool inserted as a porous barrier to retain the resins. The first column pre-concentrates V (and other metals) from the salt matrix of seawater and used 1.5 mL of Nobias PA-1 chelating resin (Hitachi High-Technologies, 45–90 lm mesh size) at pH ~ 6. For the chemical procedures described below, prior to adding new or more solution the previous volume was completely discharged. Nobias resin was first activated and cleaned using 3 mL methanol. Then 1 ml of 3 M HNO_3 was added and completely drained prior to another addition of 4.5 mL 3 M HNO_3 (documented as 1 + 4.5 mL hereafter) in sequence and then 1 + 4.5 mL H2O was added to wash out the acid. Before load on seawater, the resin was preconditioned with 1 + 6 mL of ammonia acetate buffer solution (pH ~ 6), which was made by mixing ammonium hydroxide, acetic acid and de-ionized water. Approximately 250 mL of seawater, which was first adjusted to pH of 6 ± 0.1 using the ammonia acetate buffer solution, was loaded onto the column. Under these conditions trace metals were adsorbed onto the resin while the major seawater salt matrixes (Na, K, Mg, Ca) were eluted. Subsequently, V and other retained metals were then eluted and collected with 1 + 15 mL of 3 M HNO_3. The eluted solution was dried down, and re-dissolved into 0.01 M HCl with 1% (volume/volume) H_2O_2. Further purification of V was achieved through exchange columns with AG 1-X8 200–400 mesh anion resins (Bio-Rad Laboratories). The anion resins were repeatedly soaked and cleaned with 6 M HCl and H2O successively for several times before use. In the second column, 1 mL of AG 1-X8 200–400 mesh anion exchange resin was loaded in the quartz columns and cleaned with 5 mL 1 M HCl. Then the resin was pre-conditioned with 3 + 3 mL 0.01 M HCl + 1% (volume/volume) H_2O_2. In this solution pentavalent V forms anionic complexes with H_2O_2 that are strongly adsorbed onto the resin. Because of its rapid dissociation, hydrogen peroxide should be added immediately prior to loading the sample onto the column. After loading the samples onto the resin bed, another 2 + 10 mL 0.01 M HCl + 1% (volume/volume) H_2O_2 was loaded to elute off the residual matrix compounds including Cr. Vanadium was subsequently eluted and collected with 1 + 5 mL 1 M HCl. The AG 1-X8 anion exchange resin was used for only once and throwing away after use. The solution was dried down, and re-dissolved into 0.5 mL 2 M HF. The final two columns were employed to ensure quantitative removal of residual Ti and Cr. They were minicolumns with 0.1 mL resin volume using AG 1-X8 200–400 mesh resin. The resin was cleaned and pre-conditioned with 1 + 1 mL of 1 M HCl and 0.5 + 0.5 mL of 2 M HF, respectively. Sample solutions were loaded on to the column, and the eluent was immediately collected. Another 0.5 mL of 2 M HF and then 0.1 + 1.3 mL of 0.5 M HCl + 0.5 M HF were also added and collected together with the sample load. The last mini-column was identical to the second column except that all volumes were scaled down by a factor of 10, which is applied to further eliminate Cr. In between each column procedure, samples were refluxed in aqua regia for at least four hours to break down minor amounts of organic resin material that had eluted together with V. The final purified V sample was dissolved in 2% (volume/volume) HNO_3 before isotope analysis.

FSU Method: Four columns were applied to separate vanadium from matrix elements and interferences. The first column was identical to that used in the WHOI method. The second column used the same general

procedure as the WHOI method, while relied on different column dimensions and resin and reagent volumes. In addition, we found that Ti could also be eluted with Cr if we use 0.1 M HCl + 2% (volume/volume) H_2O_2 rather than 0.01 M HCl + 1% (volume/volume) H_2O_2 for the anion column. Thus, we further modified the anion column step at FSU. The procedure was performed in a pre-cleaned BioRad Poly-Prep chromatography column (9 cm high and 2 mL bed volume) loaded with 2 mL of AG 1-X8 200–400 mesh resin. The AG 1-X8 resin was first cleaned and preconditioned using 15 mL of 6 M HCl, 10 mL of H2O, and 4 + 4 mL of 0.01 M HCl with 2% (volume/volume) H_2O_2, respectively. The sample that had been dissolved in 10 mL of 0.1 M HCl + 2% (volume/volume) H_2O_2 was then loaded on the column. Another 1 + 14 mL of 0.01 M HCl and 2% (volume/volume) H2O2 was added to remove residual matrix elements including Cr. The V portion was subsequently eluted and collected with 14 mL of 6 M HCl + 10 mL of 2 M HNO_3. The solution was then dried down, and re-dissolved into 1 mL 0.01 M HCl with 2% (volume/volume) H_2O_2. Similar mini-columns to those used in the WHOI method with 0.1 mL AG 1-X8 200–400 mesh resin were also used in the FSU method to remove minor amounts of residual Ti and Cr. However, the columns that utilize HF were omitted from the FSU method. For the third column procedure, resin loaded onto the columns were cleaned and pre-conditioned with 1 mL 6 M HCl, 1 mL H2O, and 0.75 + 0.75 ml 0.01 M HCl with 2% (volume/volume) H_2O_2, respectively. Samples in 1 mL of 0.01 M HCl with 2% (volume/volume) H_2O_2 were then loaded and matrix elements were eluted with 0.3 mL of 0.1 M HCl with 2% (volume/volume) H_2O_2 and 1.5 mL of 0.01 M HCl with 2% (volume/volume) H_2O_2 successively. The additional step using 0.1 M HCl was found to be efficient at removing Ti. The V was subsequently eluted and collected with 1.5 mL of 6 M HCl + 1.5 mL of 2 M HNO_3. The fourth column was a repeat of the third and was employed to ensure complete removal of Cr and Ti. As described for the WHOI method, samples were refluxed in aqua regia in between all columns and dissolved in 2% (volume/volume) HNO_3 for isotopic analysis.

Data Processing Description

Data processing:
While the chemical purification quantitatively separates Ti and Cr from V, minor amounts of Ti and Cr in solution can dramatically affect the isotopic value especially for low V concentration measurements. Therefore, analysis of the $^{49}Ti/^{51}V$ and $^{53}Cr/^{51}V$ ratios are needed and should be less than 0.00005 to properly correct for interferences of ^{50}Cr and ^{50}Ti. We used the procedure described by Nielsen et al. (2011) and Wu et al. (2016) to correct the raw data for any potential interferences. Briefly, 100 ppb Cr and 100 ppb Ti standard solutions were analyzed before each sequence analysis. These were used to correct for the instrumental mass bias factor (β) for Cr and Ti which are calculated with the assumption of the natural abundances of ^{49}Ti, ^{50}Ti, ^{50}Cr and ^{53}Cr in the standard solutions (de Laeter et al., 2003). The ion beam intensities of ^{50}Ti and ^{50}Cr were then subtracted from the signal mass 50 from the measured ^{49}Ti and ^{53}Cr ion beams for each sample with the calculated b values. Samples were measured using sample-standard bracketing. All V isotope measurements from different labs mentioned in this study used the aliquots of the Alfa Aesar (AA) V standard primary made and distributed by Nielsen et al. (2011) and Prytulak et al. (2011) as the bracketing solution, and V isotopic data are reported in standard d notation in per mil relative to AA($\delta^{51}V = ((^{51}V/^{50}V)sample / ^{51}V/^{50}V)AA - 1) \times 1{,}000$). The AA V standard solution is defined as $\delta^{51}V = 0‰$ (Nielsen et al., 2011). Each sample analysis consists of 40 cycles of 4.194 s integrations and was bracketed by double measurements of AA solution on each side to obtain an average value and stability of the instrument for the highest quality control. After 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 1,000 ppm V standard solution originally bought from BDH Chemicals (Nielsen et al., 2011). Analyses of the BDH standard for this work have an overall average $\delta^{51}V$ of -1.19 ± 0.15‰ (2SD), with average $\delta^{51}V$ of -1.19 ± 0.17‰ (2SD, n = 96) run at WHOI and -1.19 ± 0.10‰ (2SD, n = 55) run at FSU. The average and uncertainty is in agreement within previously reported values (-1.19 ± 0.17‰, 2SD). All sample measurements were performed with ^{51}V ion beam intensities greater than ~1 nA for optimal measurements.

BCO-DMO Processing:
- modified parameter names;
- replaced empty values with 'nd' (no data);
- moved 'V Spiked Sample' note to the Notes column;
- converted latitude and longitude from degrees and decimal minutes to decimal degrees.

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Data Files

File
V_isotopes_seawater.csv (Comma Separated Values (.csv), 1.95 KB) MD5:c41fc3133cd8e38adc5560ab86340881 Primary data file for dataset ID 819946

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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
Methods

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Parameters

Parameter	Description	Units
Location_Name	Location name	unitless
Latitude	Latitude	decimal degrees North
Longitude	Longitude	decimal degrees East
d51V	Measured V isotope value	per mil (‰)
two_sd	2 standard deviation error from all analysis	per mil (‰)
n	Number of analyses	unitless
Recovery_pcnt	The percetnage of V recovered after all column purification which is compared with previously reported values or spiked concentrations	unitless (percent)
Spiked_AA	The amount of V recovered after all column purification which is compared with previously reported values or spiked concentrations	micrograms (ug)
Volume	Amount of seawater analyzed for spiked samples	milliliters (mL)
Lab	Analytical institution	unitless
Notes	Notes and methods used to remove potential organic	unitless

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Instruments

Dataset-specific Instrument Name	Go-Flo samplers
Generic Instrument Name	GO-FLO Bottle
Generic Instrument Description	GO-FLO bottle cast used to collect water samples for pigment, nutrient, plankton, etc. The GO-FLO sampling bottle is specially designed to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

Dataset-specific Instrument Name	Thermo Neptune multi-collector ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	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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Deployments

BATS_cruises

Website	https://www.bco-dmo.org/deployment/58883
Platform	Unknown Platform
Report	http://bats.bios.edu/bats-data/
Start Date	1988-10-20
Description	Bermuda Institute of Ocean Science established the Bermuda Atlantic Time-series Study with the objective of acquiring diverse and detailed time-series data. BATS makes monthly measurements of important hydrographic, biological and chemical parameters throughout the water column at the BATS Study Site, located at 31 40N, 64 10W.

HOT_cruises

Website	https://www.bco-dmo.org/deployment/58879
Platform	Unknown Platform
Report	http://hahana.soest.hawaii.edu/hot/
Start Date	1988-10-31
Description	Since October 1988, the Hawaii Ocean Time-series (HOT) program has investigated temporal dynamics in biology, physics, and chemistry at Stn. ALOHA (22°45' N, 158°W), a deep ocean field site in the oligotrophic North Pacific Subtropical Gyre (NPSG). HOT conducts near monthly ship-based sampling and makes continuous observations from moored instruments to document and study NPSG climate and ecosystem variability over semi-diurnal to decadal time scales.

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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
NSF Division of Ocean Sciences (NSF OCE)	OCE-1434785
NSF Division of Ocean Sciences (NSF OCE)	OCE-1624895

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