Vanadium concentrations and isotope compositions of seawater samples collected from the South Atlantic Ocean (2010 UK GEOTRACES cruise GA10/D357 Leg 1) and the Black Sea (2013 MedBlack GEOTRACES cruise leg 2, 64PE373, R/V Pelagia)

Website: https://www.bco-dmo.org/dataset/957165
Data Type: Cruise Results
Version: 1
Version Date: 2025-04-01

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

Contributors	Affiliation	Role
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Abstract

These data include vanadium concentrations and isotope compositions of seawater samples from the South Atlantic Ocean (collected during the UK GEOTRACES cruise GA10/D357 Leg 1) and the shallow water columns in the Black Sea (collected during the leg 2 of the MedBlack GEOTRACES cruises, 64PE373, R/V Pelagia). The resin column chromatography method is utilized to purify vanadium. The vanadium concentrations were measured with the Agilent 7500ce Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Thermo Element 2 ICP-MS, and the isotope compositions were measured with the Neptune Multi-collector-ICP-MS. These data assess the cycling of vanadium isotopes in seawater and were collected by Dr. Siqi Li at Florida State University.

Table of Contents

Coverage

Spatial Extent: **N**:42.52 **E**:31.4 **S**:-39.99 **W**:0.92
Temporal Extent: 2010-10 - 2013-07

Methods & Sampling

Collection protocols for the South Atlantic Ocean seawater samples (Owens et al., 2017): a "trace metal-clean" titanium rosette with a PTFE-coated CTD system was used and deployed using a plasma rope to collect the seawater samples. Seawater samples were filtered through 0.2-micrometer (µm) filter capsules and transferred into 1-liter (L) HDPE bottles in a trace metal clean container. Then seawater samples were acidified at WHOI (Woods Hole Oceanographic Institution) to pH ~2 using concentrated distilled HCl.

Collection protocols for the Black Sea seawater samples (Cruise Report 64PE373 on RV Pelagia): an ultra-clean titanium CTD system was deployed to collect the seawater samples. The collected seawater was filtered with 0.2 µm Sartobran 300 filter cartridges (Sartorius) and acidified on board to pH ~2 with Baseline grade Seastar HCl. (See: https://www.geotraces.org/ga04-2/)

Here we describe the general protocols for chemical procedures. The in-lab column chromatography procedures to pre-concentrate and purify seawater vanadium (V) for concentration and isotope composition measurement are described in detail in Li et al. (under review). The chemical reagents utilized were trace-metal clean.

For seawater V concentration measurement, the column chromatography utilizing Bio-rad AG 50W-X12 cation resin was used to pre-concentrate V (Li et al., under review). The acidified seawater samples (pH ~2) were doped with H2O2 solution to contain 2% H2O2 before being loaded onto the resin column. Vanadium was yielded with weakly acidic H2O2 solution (0.01 M HCl + 2% H2O2) with the matrix metal elements being retained on the resin.

For seawater V isotope composition measurement, a four-column chromatography (Wu et al., 2019) was used to pre-concentrate and purify seawater V. Details of further improvements on this column chromatography method have been described in Li et al. (under review). The pre-cleaned Hitachi Nobias Chelate PA-1 resin and Bio-rad AG1-X8 anion resin were utilized to pre-concentrate and purify seawater V. The first column utilized Nobias Chelate PA-1 resin. Seawater samples were buffered to pH at 6.0 ± 0.1 with acetic acid and ammonia solutions before being loaded onto the column. Then V was yielded with 3 M HNO3. The following three columns utilized Bio-rad AG1-X8 anion resin to further purify seawater V, and the yielded V from the previous column was redissolved in 0.01 M HCl + 2% H2O2 solution before being loaded onto the column. Then, clean the resin column after the complete dripping of the sample solution using 0.01M HCl + 2% H2O2. Finally, V was yielded with 6M HCl and 2M HNO3.

The artificial seawater standards SW Matrix-AA and SW Matrix-BDH were made as in-lab standards for isotope composition measurement. The matrix elutes of two seawater samples were yielded after the first Nobias resin column and were separately doped with pure V solution standards, ~900 nanograms (ng) AA-V (SW Matrix-AA) and ~900 ng BDH V (SW Matrix-BDH). The two artificial seawater standards were processed parallelly with seawater samples with the same chemical procedures.

BCO-DMO Processing Description

- Imported original file "Seawater vanadium concentrations and isotope compositions_Update.xlsx" into the BCO-DMO system.
- Flagged "N/A" as a missing data value (missing data are empty/blank in the final CSV file).
- Renamed fields to comply with BCO-DMo naming conventions.
- Made the south latitude values negative.
- Saved the final file as "957165_v1_vanadium_concentrations_and_isotope_compositions.csv".
- Saved the "NASS-6 V concentration" sheet as a PDF and attached as a Supplemental File.
- Saved the "Seawater standards" sheet as a PDF and attached as a Supplemental File.

[table of contents | back to top]

Data Files

File
957165_v1_vanadium_concentrations_and_isotope_compositions.csv (Comma Separated Values (.csv), 3.23 KB) MD5:2f8d342855f38928e2ac26af06a5dd35 Primary data file for dataset ID 957165, version 1

[table of contents | back to top]

Supplemental Files

File
NASS-6_V_Concentrations.pdf (Portable Document Format (.pdf), 103.13 KB) MD5:55379f445ae9ea3997797ebbbf4ea808 Supplemental file for dataset ID 957165, version 1. Column Descriptions: [V]measured, "measured seawater vanadium concentration", ng/g [V]average, "the average seawater vanadium concentration calculated from duplicate and replicate measurement", ng/g [V]certified, "the certified vanadium concentration for the NASS-6 seawater standard", ng/g
Seawater_Standards.pdf (Portable Document Format (.pdf), 362.67 KB) MD5:59d2d07ffedfc09eb79c42f30c2c135f Supplemental file for dataset ID 957165, version 1. Column descriptions: V doped, "amount of V doped to the in-lab seawater matrix", ng V yielded, "yielded amount of V from the column chromatography method", ng δ51V, "vanadium isotope composition", ‰ per mil 2SD , "2 standard deviation", ‰ per mil N, "duplicate measurement", unitless

[table of contents | back to top]

Related Publications

Brophy, C., Clancy, V., Willie, S., & Yang, L. (2012). NASS-6: Seawater reference material for trace metals (Version 1). National Research Council of Canada. https://doi.org/10.4224/CRM.2012.NASS-6
Methods

Conway, T. M., John, S. G., & Lacan, F. (2016). Intercomparison of dissolved iron isotope profiles from reoccupation of three GEOTRACES stations in the Atlantic Ocean. Marine Chemistry, 183, 50–61. doi:10.1016/j.marchem.2016.04.007
Methods

Horner, T. J., Kinsley, C. W., & Nielsen, S. G. (2015). Barium-isotopic fractionation in seawater mediated by barite cycling and oceanic circulation. Earth and Planetary Science Letters, 430, 511–522. doi:10.1016/j.epsl.2015.07.027
Methods

Li, S., Nielsen, S.G, & Owens, J.D. (under review, 2025) Global cycling of vanadium isotopes from multiple ocean water masses and a restricted euxinic basin.
Results

Nielsen, S. G., Owens, J. D., & Horner, T. J. (2016). Analysis of high-precision vanadium isotope ratios by

medium resolution MC-ICP-MS. Journal of Analytical Atomic Spectrometry, 31(2), 531–536. doi:10.1039/c5ja00397k https://doi.org/10.1039/C5JA00397K
Methods

Owens, J. D., Nielsen, S. G., Horner, T. J., Ostrander, C. M., & Peterson, L. C. (2017). Thallium-isotopic compositions of euxinic sediments as a proxy for global manganese-oxide burial. Geochimica et Cosmochimica Acta, 213, 291–307. https://doi.org/10.1016/j.gca.2017.06.041
Methods

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

[table of contents | back to top]

Parameters

Parameter	Description	Units
Cruise_ID	Cruise identifier	unitless
Location	Location description	unitless
Station	Station number	unitless
Sample_ID	Sample ID number. The "dup" and the number in the bracket indicate the re-dilution and remeasurement of the same solution.	unitless
Longitude	Longitude of collection location	degrees East
Latitude	Latitude of collection location; negative values = South	degrees North
Date	Year and month of sample collection	unitless
Depth	Depth below the sea surface	meters (m)
Salinity	Salinity (The salinity data are from Conway et al. (2016) and Horner et al. (2015).)	PSU
Seawater_V_ng_g	Seawater vanadium concentration in ng/g	nanograms per gram (ng/g)
Seawater_V_nmol_kg	Seawater vanadium concentration in nmol/kg. The seawater V concentration is averaged with duplicate measurements. The uncertainty 1RSD is calculated with duplicate measurements, otherwise the instrumental measurement precision with 1RSD better than 5% is assigned.	nanomoles per kilogram (nmol/kg)

one_RSD	One relative standard deviation	percent (%)
Seawater_V_normalized_nmol_kg	The seawater V concentration is normalized to salinity = 35‰.	nanomoles per kilogram (nmol/kg)
Yielded_V	Yielded vanadium after column chromatography	nanograms per gram
Yielding_rate	Yielding rate	percent (%)
d51V	delta 51V; Vanadium isotope composition	per mil (‰)
two_SD	Two standard deviations	per mil (‰)
number_duplicates	Number of duplicate measurements	unitless

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	Agilent 7500ce Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
Generic Instrument Name	Agilent 7500ce inductively coupled plasma mass spectrometer
Dataset-specific Description	The vanadium concentrations were measured with the Agilent 7500ce Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Thermo Element 2 ICP-MS.
Generic Instrument Description	The Agilent 7500ce is a laboratory benchtop inductively coupled plasma mass spectrometer (ICP-MS) for metal analysis. The instrument comprises a sample introduction system (micromist glass concentric nebuliser, quartz Scott-type spray chamber, peristaltic pump), an interface of nickel cones and dual on-axis extraction lenses, a vacuum system, mass flow controllers (plasma, auxiliary, makeup, and carrier gas and two Octopole Reaction System (ORS) reaction gas lines), a shieldtorch system (STS), an all-solid state digitally-driven 27 MHz RF generator and an off-axis Omega lens. The octopole cell of the ORS can be used with no gas, operated in collision mode using pure He cell gas or used in H2 reaction mode for ultra-trace Se analysis and semiconductor applications. All three of these modes come as standard in the 7500ce model. The instrument has been discontinued.

Dataset-specific Instrument Name	CTD
Generic Instrument Name	CTD - profiler
Dataset-specific Description	Seawater samples were collected with a "trace metal-clean" titanium rosette with a PTFE-coated CTD system in the South Atlantic and an ultra-clean titanium CTD system in the Black Sea.
Generic Instrument Description	The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see https://www.bco-dmo.org/instrument/869934.

Dataset-specific Instrument Name	Neptune Multi-collector-ICP-MS
Generic Instrument Name	Thermo Finnigan Neptune inductively coupled plasma mass spectrometer
Dataset-specific Description	The vanadium isotope compositions were measured with the Neptune Multi-collector-ICP-MS.
Generic Instrument Description	A laboratory high mass resolution inductively coupled plasma mass spectrometer (ICP-MS) designed for elemental and isotopic analysis. The instrument is based on a multicollector platform, comprising eight moveable collector supports and one fixed center channel equipped with a Faraday cup and, optionally, an ion counter with or without a retardation lens. The Faraday cup is connected to a current amplifier, whose signal is digitized by a high linearity voltage to frequency converter. The instrument was originally manufactured by Thermo Finnigan, which has since been replaced by Thermo Scientific (part of Thermo Fisher Scientific). This model is no longer in production.

Dataset-specific Instrument Name	Thermo Element 2 ICP-MS
Generic Instrument Name	Thermo Fisher Scientific ELEMENT 2 inductively coupled plasma mass spectrometer
Dataset-specific Description	The vanadium concentrations were measured with the Agilent 7500ce Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Thermo Element 2 ICP-MS.
Generic Instrument Description	The Thermo Scientific Element 2 ICP-MS is a double-focussing magnetic-sector-field Inductively Coupled Plasma Mass Spectrometer equipped with a discrete dynode detector system, linear over nine orders of magnitude - from ppq to ppm concentrations. Other features include: Sensitivity (Concentric Nebuliser) greater than 1 x 10^9 counts per second (cps)/ppm In; Dark noise less than 0.2 cps; Mass resolution 300, 4,000, 10,000 (10 percent valley, equivalent to 5 percent height), 600, 8,000, 2,000 (FWHM); Signal stability better than 1 percent RSD over 10 minutes or 2 percent RSD over 1 hour; Mass stability: 25 ppm / 8 hours; Magnetic scan speed: m/z 7 to 240 to 7 in less than 150 ms, Electronic scan speed: 1 ms/jump, independent of mass range.

[table of contents | back to top]

Deployments

D357

Website	https://www.bco-dmo.org/deployment/637790
Platform	RRS Discovery
Report	http://dmoserv3.bco-dmo.org/data_docs/GEOTRACES/UK_GT/D357_cruise_report.pdf
Start Date	2010-10-18
End Date	2010-11-22
Description	UK GEOTRACES cruise

64PE373

Website	https://www.bco-dmo.org/deployment/957201
Platform	R/V Pelagia
Report	https://www.bodc.ac.uk/resources/inventories/cruise_inventory/reports/pe373.pdf
Start Date	2013-07-13
End Date	2013-07-25
Description	GEOTRACES Section Cruise GA04N

[table of contents | back to top]

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.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1434785
NSF Division of Ocean Sciences (NSF OCE)	OCE-1624895
National Aeronautics & Space Administration (NASA)	Exobiology Grant NNX16AJ60G
Alfred P. Sloan Foundation (Sloan)	FG-2020-13552

[table of contents | back to top]