

# Vanadium isotope and elemental concentration analyses of numerous ferromanganese crusts and nodule samples

**Website:** <https://www.bco-dmo.org/dataset/819983>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2020-08-03

## Project

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

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## Abstract

This vanadium isotope and elemental concentration dataset analyzes numerous ferromanganese crusts and nodule samples.

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## Coverage

**Spatial Extent:** N:31.033 E:155 S:9 W:-154

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## Dataset Description

This vanadium isotope and elemental concentration dataset analyzes numerous ferromanganese crusts and nodule samples.

## Methods & Sampling

### Methodology:

Various types of iron (Fe) and manganese (Mn) material, crusts and nodules, were analyzed to determine the fractionation from the starting seawater value to better understand the oxic sink of vanadium. The Fe-Mn crusts and nodules studied here were collected at 2013 from three seamounts or guyots at the West Pacific Ocean using the Chinese manned submersible Jiaolong during DY125-31 cruise. Samples were from Caiwei Guyot (155°E, 15°N) and Caiqi Guyot (154°E, 15°N) from the Magellan Seamount cluster, and Weiyuan Seamount (154°W, 9°N) from Clarion-Clipperton Fe-Mn Nodule Zone (C-C zone) at water depths of 1720–4420 m, 2000–2400 m, and 5200 m, respectively. The samples studied here were obtained from the surface of the seafloor to avoid the potential diagenetic process that have occurred post burial. Some samples are from the surface. The Fe-Mn crusts and nodules studied here were collected at 2013 from three seamounts or guyots at the West Pacific Ocean using the Chinese manned submersible Jiaolong during DY125-31 cruise. Samples were

from Caiwei Guyot (155°E, 15°N) and Caiqi Guyot (154°E, 15°N) from the Magellan Seamount cluster, and Weiyuan Seamount (154°W, 9°N) from Clarion-Clipperton Fe-Mn Nodule Zone (C-C zone) at water depths of 1720–4420 m, 2000–2400 m and 5200 m, respectively. The samples studied here were obtained from the surface of the seafloor to avoid the potential diagenetic process that have occurred post burial. All samples from Caiwei Guyot and Caiqi Guyot are Fe-Mn crusts, while samples from Weiyuan Seamount include both Fe-Mn crusts and nodules. Some samples are from the surface layer of the ferromanganese crust to study the spatial variations of V isotope of 'recently' or near modern precipitated ferromanganese crust. Furthermore, some Fe-Mn crust samples were removed perpendicular to growth layers, which best represents a stratigraphic record of ocean chemistry.

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

**Elemental Quantification:** The collected Fe-Mn crust and nodule samples were first cleaned by ultrasonication with deionized water and then dried in an oven at 105°C for six hours. Then samples were powdered using an agate mortar and pestle until the sample passed through a 200 mesh sieve. Prior to powdering, crust samples were cut into layers using a hacksaw with a vertical thickness of 1–3 cm. Nodule samples with diameters of 2–5 cm were cut in half from center prior to powdering. Whole-rock major and trace element measurements of Fe-Mn crusts and nodules were conducted in Guangzhou, China (<http://www.alsglobal.net.cn/>). The sample powders were combined with lithium borate flux and fused in a furnace at 1000°C. The resulting melt was then cooled and dissolved in nitric acid and hydrochloric acid. This solution was then analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for major elements measurements. For trace element measurements, the powders were digested with a mixture of perchloric, nitric, and hydrofluoric acids, and then dissolved with dilute hydrochloric acid. The prepared solutions were then analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

**Vanadium Purification:** Approximately 10–20 mg of sample powders containing 5–10 mg of V were digested for V isotope analysis. Samples were first treated with aqua regia. After evaporation to dryness, samples were dissolved with a 3:1 (v/v) mixture of concentrated HF and HNO<sub>3</sub> to digest the remaining oxide and silicate phases. Then, samples were dried and further treated with aqua regia and concentrated HNO<sub>3</sub> and dried down in between each step. All the samples were finally dissolved in 1 mL of 1 M HNO<sub>3</sub> for ion-exchange chromatography. Briefly, V was purified with a multistep ion-exchange procedure by coupling cation- and anion-exchange columns. The cation resin AG50W-X12 (200–400 mesh) was applied to remove Fe, Ti, and other main matrix elements (e.g., Al, Ca, Mn, and Cr). Then AG1-X8 (200–400 mesh) chloride-form anion resin was used to further remove residual matrix and isobaric elements (e.g., K, Na, Mg, and trace amount of Cr). The total procedural blank was less than 2 ng, thus is negligible compared with the loaded amount of V (5–10 mg). The V yields of the total chemical procedures are >99%.

**Isotope Instrumental Configuration:** Vanadium isotopic ratios were measured using a sample-standard bracketing method on a Thermo Scientific Neptune plus 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+). Jet sample and Ni X-skimmer cones were used to obtain the highest possible V transmission efficiency. In addition, the amplifiers with 10<sup>10</sup>Ω and 10<sup>11</sup>Ω resistor were applied to monitor <sup>51</sup>V and <sup>50</sup>V signal, respectively. We applied dry plasma inlet system with Aridus II desolvator (CETAC Technologies).

## **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 <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. 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 <sup>49</sup>Ti, <sup>50</sup>Ti, <sup>50</sup>Cr and <sup>53</sup>Cr in the standard solutions (de Laeter et al., 2003). The ion beam intensities of <sup>50</sup>Ti and <sup>50</sup>Cr were then subtracted from the signal mass 50 from the measured <sup>49</sup>Ti and <sup>53</sup>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( $\delta^{51}\text{V} = ((^{51}\text{V}/^{50}\text{V})_{\text{sample}} / ^{51}\text{V}/^{50}\text{V})_{\text{AA}} - 1) \times 1,000$ ).

The AA V standard solution is defined as  $\delta^{51}\text{V} = 0\text{‰}$  (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  $\delta^{51}\text{V}$  values of the nodule standards are  $-1.57 \pm 0.09\text{‰}$  (2 SD, n = 4, NOD-P) and  $-0.98 \pm 0.01\text{‰}$  (2 SD, n = 3, NOD-A), within analytical error of previously reported values (NOD-P:  $-1.65 \pm 0.06\text{‰}$ , n = 10 and NOD-A:  $-0.99 \pm 0.10\text{‰}$ , n = 19). The reproducibility of in-house standards and duplicated samples for V isotope analyses are always better than  $0.10\text{‰}$  (2 SD).

#### BCO-DMO Processing:

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

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### Data Files

File
<b>V_isotopes_oxic_sediment.csv</b> (Comma Separated Values (.csv), 4.97 KB) MD5:4d12abf953e3a3ed8bf9ad502c4bd249
Primary data file for dataset ID 819983

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### Related Publications

Wu, F., Owens, J. D., Tang, L., Dong, Y., & Huang, F. (2019). Vanadium isotopic fractionation during the formation of marine ferromanganese crusts and nodules. *Geochimica et Cosmochimica Acta*, 265, 371–385. doi:[10.1016/j.gca.2019.09.007](https://doi.org/10.1016/j.gca.2019.09.007)  
*Methods*

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### Parameters

Parameter	Description	Units
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)
Type	Material type	unitless

Depth	Bulk is a homogenized sample and numbers are the depth from top	centimeters (cm)
d51V	Measured V isotope value	per mil (‰)
two_sd	2 standard deviation error from all analyses	per mil (‰)
n	Number of isotope analyses	unitless
Si_pcmt	Quantified silicon concentration in weight percent	weight percent
Al_pcmt	Quantified aluminum concentration in weight percent	weight percent
Mn_pcmt	Quantified manganese concentration in weight percent	weight percent
Fe_pcmt	Quantified iron concentration in weight percent	weight percent
P_pcmt	Quantified phosphorus concentration in weight percent	weight percent
Li_ppm	Quantified lithium concentration in weight percent	parts per million (ppm)
V_ppm	Quantified vanadium concentration in weight percent	parts per million (ppm)
Co_ppm	Quantified cobalt concentration in weight percent	parts per million (ppm)
Ni_ppm	Quantified nickel concentration in weight percent	parts per million (ppm)
Cu_ppm	Quantified copper concentration in weight percent	parts per million (ppm)
Zn_ppm	Quantified zinc concentration in weight percent	parts per million (ppm)
Mn_Fe_ratio	Elemental ratio of manganese and iron; both in weight percent	unitless (ratio)

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## Instruments

<b>Dataset-specific Instrument Name</b>	Thermo Element II Inductively Coupled Plasma Mass Spectrometry 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.

<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.

<b>Dataset-specific Instrument Name</b>	Inductively Coupled Plasma Atomic Emission Spectroscopy
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Optical Emission Spectrometer
<b>Generic Instrument Description</b>	Also referred to as an Inductively coupled plasma atomic emission spectroscope (ICP-AES). These instruments pass nebulised samples into an inductively-coupled gas plasma (8-10000 K) where they are atomised and excited. The de-excitation optical emissions at characteristic wavelengths are spectroscopically analysed. It is often used in the detection of trace metals.

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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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