Thallium isotope data from a Cretaceous Oceanic Anoxic Event

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

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Abstract
This thallium isotope dataset from a Cretaceous Oceanic Anoxic Event constrains the magnitude and timing of oceanic deoxygenation.

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Dataset Description

This thallium isotope dataset from a Cretaceous Oceanic Anoxic Event constrains the magnitude and timing of oceanic deoxygenation.

Methods & Sampling

Methodology:
Approximately 50 to 100 mg of sediment were initially treated with 3 ml of 2 M HNO_3 and heated at 130°C for ~12 h to chemically separate the authigenic and detrital fraction of Tl. This treatment dissolves pyrite, which is thought to contain the authigenic Tl fraction, while the undissolved portion is dominated by silicate minerals. The two sample fractions were then separated via three cycles of centrifugation, pipetting off the supernatant (henceforth termed 'the authigenic fraction') and rinsing in MQ water. After separation of the authigenic and silicate fractions, both fractions were digested separately in the HPA using ~3 ml of concentrated nitric and ~3 ml of concentrated hydrochloric acid in order to break down organic molecules. After the HPA digestion, authigenic fractions were prepared for anion exchange separation of Tl from the sample matrix; no hydrofluoric acid treatment was used on the authigenic fraction, thereby reducing possible Tl contributions from silicates. Residual silicates were dissolved using a hydrofluoric/nitric acid mixture and then prepared for anion exchange separation (henceforth termed 'the silicate fraction') for thallium purification.

Sampling and analytical procedures:
Thallium Purification: Thallium was isolated from a sample matrix using previously described anion exchange chromatography techniques. Briefly, thallium purification was accomplished using two separate columns, one large and one micro-column, using AG1X8 anion exchange resin from Biorad. The two columns quantitatively remove lead (Pb) from the sample, which is required to monitor mass-bias during mass spectrometric analysis.

NIST SRM 981 Pb is added to every sample to monitor for instrumental mass bias. In addition, this allows for determination of Tl concentrations during isotopic analysis because the yield of the Tl column chemistry is within error of 100%. However, only one column was used during Tl purification. Testing of standards and samples showed that there was no difference in concentration or isotope composition between samples that had been processed through one or two columns.

Isotope Instrumental Configuration: Samples were analyzed for Tl isotopic compositions using a Thermo Scientific Neptune multi-collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS) located in the WHOI Plasma Facility. Measurement were performed using low resolution with jet sample and Ni X-skimmer cones coupled with a dry plasma inlet system with Aridus II desolvator (CETAC Technologies).

Data Processing Description

Data processing:
Thallium isotope analyses utilize standard sample bracketing as well as external normalization to the added SRM NIST 981 Pb. Thallium isotope compositions are reported relative to NIST SRM 997. Thallium isotopic data are reported in ε notation relative to NIST 997 as $\varepsilon^{205}Tl = [(205/203Tl_{sample}) / (205/203Tl_{NIST997}) - 1] \times 10{,}000$. The authigenic fraction of SCo-1 yielded a mean Tl-isotope composition of $\varepsilon^{205}Tl = 3.0 \pm 0.2$ and Tl concentration of 214 ± 74 pg/g (n = 18) with sample dissolutions and measurements. Previously described techniques that used both external normalization to NIST SRM (Standard Reference Materials) 981 Pb and standard-sample bracketing were applied for mass bias correction. Because of the quantitative yields of Tl from the column chemistry procedure, Tl concentrations were determined by monitoring the ^{205}Tl signal intensities of the samples during the isotopic measurements. A known quantity of NIST SRM 981 Pb was added to the sample Tl, and the measured $^{205}Tl/^{208}Pb$ ratios were then converted directly into Tl abundances. The U.S. Geological Survey (USGS) shale standard SCO-1 was processed and analyzed, with each sample set to monitor long-term precision and accuracy of our Tl isotope data (average calculated $\varepsilon^{205}Tl = -2.64 \pm 0.24$), and was found to be better than most recent Tl isotope studies, which have 2-SD uncertainties of ~0.3 to 0.5 $\varepsilon^{205}Tl$ units.

BCO-DMO Processing:
- modified parameter names;
- replaced dashes with "nd" (no data).

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Data Files

File
Tl_isotopes.csv (Comma Separated Values (.csv), 2.55 KB) MD5:702245f4013b0589ce7138e0ccc64840 Primary data file for dataset ID 819793

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Related Publications

Ostrander, C. M., Owens, J. D., & Nielsen, S. G. (2017). Constraining the rate of oceanic deoxygenation leading up to a Cretaceous Oceanic Anoxic Event (OAE-2: ~94 Ma). Science Advances, 3(8), e1701020. doi:10.1126/sciadv.1701020
Results

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Parameters

Parameter	Description	Units
Sample	Ocean drilling program naming scheme: leg-site(hole), core(half)-section depth	unitless
Depth	Meters composite depth (mcd – spliced sections) below seafloor	meters (m)
Tl	Bulk thallium concentration	parts per million (ppm)
f_authigenic	Authigenic fraction of bulk value	unitless
E205Tl_authigenic	Measured Tl isotope value from authigenic fraction	epsilon units
two_sd_E205Tl_authigenic	2 standard deviation error from all authigenic analysis	epsilon units
n_E205Tl_authigenic	Number of authigenic isotope analysis. * signifies multiple powder digestions for the same sample.	unitless
E205Tl_detrital	Measured Tl isotope value from detrital fraction	epsilon units
two_sd_E205Tl_detrital	2 standard deviation error from all detrital analysis	epsilon units
n_E205Tl_detrital	Number of detrital isotope analysis. * signifies multiple powder digestions for the same sample.	unitless

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Instruments

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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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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