Chromium concentration and isotopic composition of Cr(III) and Cr(VI) in the Eastern Tropical North Pacific from samples collected on R/V Roger Revelle and R/V Kilo Moana in April-May 2018 and Sept-Oct 2019

Website: https://www.bco-dmo.org/dataset/925782
Data Type: Cruise Results
Version: 1
Version Date: 2024-04-23

Project
» Cr Isotope Oceanography of the Eastern Tropical North Pacific Ocean (ETNP Cr Isotopes)

Contributors	Affiliation	Role
Boyle, Edward A.	Massachusetts Institute of Technology (MIT)	Principal Investigator
Huang, Tianyi	Massachusetts Institute of Technology (MIT)	Student
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
Understanding the cycling of chromium (Cr) and how chromium stable isotopes (δ53Cr) are altered in response to different processes in the modern ocean is important in our interpretation of marine sedimentary δ53Cr records, a promising redox proxy. Therefore, it is crucial to investigate the geochemical processes of Cr in reducing environments such as oxygen deficient zones (ODZs). In this study, we investigated the cycling of Cr in the Eastern Tropical North Pacific (ETNP) ODZ by analyzing the [Cr] and δ53Cr of total dissolved Cr and Cr(III). Our Cr(III) data at two inshore stations shows profile features and Cr reduction isotopic fractionation factor (-1.5‰) similar to an offshore station in a previous study. We also observed significant Cr scavenging signals in the upper 1000 meters (m) throughout the ODZ with an inshore-offshore variability in its magnitude. Specifically, anoxic bottom waters on the continental slope see the greatest Cr scavenging with heaviest δ53Cr (+1.85‰). Our estimates of the scavenged Cr isotopic composition are within error of the anoxic and euxinic marine sedimentary δ53Cr. This implies that the vertical transport of Cr to the seafloor and subsequent diagenesis may not generate significant isotopic fractionation for Cr. This is the first thorough investigation into the Cr cycling in the ETNP ODZ and demonstrated promising usage of marine sedimentary δ53Cr as a redox proxy for ancient oceans. In the ODZ, oxygen is consumed by degrading sinking particles and reaches extremely low levels (too low to support aerobic life) from 100m to 800m depth. However, microbes that can use other oxidants such as nitrate to metabolize organic carbon live there, and we showed that they also convert soluble anionic chromate Cr(VI) to cationic Cr(III), about half of which is scavenged onto sinking particles and removed to the seafloor. This reduction is accompanied by preferential reduction of light Cr isotopes, so the Cr(III) is 1.3‰ lighter than the source Cr(VI). The removal of part of this light Cr(III) by scavenging leaves the residual total Cr heavier than the source Cr. The analyzed samples listed here were chosen to be from the center and margins of the ETNP ODZ and over extremely reducing continental margin sediments.

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Coverage

Location: Eastern Tropical North Pacific
Spatial Extent: **N**:21.8 **E**:-106 **S**:17 **W**:-110
Temporal Extent: 2018-03 - 2019-10

Methods & Sampling

Sample sites and collection methods:
Seawater samples were collected from cruises R/V Roger Revelle RR1804 and RR1805 from April to May 2018 and R/V Kilo Moana 1919 and 1920 in September 2019. Samples above 750 meters from both cruises were collected in 5-liter (L) acid-cleaned Teflon-coated external-spring "Niskin-type" bottles (Ocean Test Equipment) on a powder-coated trace metal clean rosette (Sea-Bird Electronics). After the recovery of the rosette, the Niskin-like bottles were carried into a laminar-flow clean van, pressurized with nitrogen, and filtered through either 0.2 µm AcroPak® capsule filters or 0.4µm Nuclepore® membrane filters. Samples deeper than 1000 m were collected by regular internal spring closure Niskin bottles, and filtered through 0.2 µm AcroPak® capsule filters. Samples between 300 m to 500 m were collected in both sampling systems and demonstrated no contamination from regular Niskin bottles on both cruises.

The locations of the stations are summarized in Table S1 and Fig. 1 of Huang et al, 2021. Station 23 is off the west coast of Baja California Mexico at the northern fringe of the ODZ, where its oxygen level is never below 2 µM. Station P3 is located at the mouth of the Gulf of California which is controlled by complex and dynamic currents and mesoscale eddies (i.e. Lavin et al., 2003). Station P1 is an onshore station near the west coast of Mexico. The "coring station" is on the continental margin slope, with fully anoxic bottom waters down to the bottom at 460 m. Station 15 is an offshore station near the center of the ETNP ODZ.

Cr Purification and Analysis:
The total dissolved chromium (Cr) and Cr(III) isotope analysis procedures were described in detail in Moos and Boyle (2019) and Huang, et al. (2021), respectively. Briefly, seawater samples were acidified with concentrated HCl to pH ~1.9 after being shipped back to MIT. Lowering the pH reduces Cr(VI) to Cr(III). To accelerate this process, samples were put in a 60°C oven for 7 to 14 days. After that, a 50Cr-54Cr double spike (DS) was added to samples (0.5~1L) in 1 L separatory funnels with a roughly 1:1 double spike/sample Cr ratio. This mixture was put on a shaker table overnight for sample Cr(III) and double spike Cr(III) to reach equilibrium. Cr was then pre-concentrated using a Mg(OH)2 co-precipitation method by adding concentrated NH3·H2O. Mg(OH)2 pellets were dissolved in HCl, and the pH of the solution was adjusted to reach a [H+] of 0.02M for column chromatography.

Cr(III) isotope analysis was conducted on frozen samples. The frozen samples were stored in either -80°C or -20°C freezers on the ship and in the lab to preserve Cr redox species. They were taken out of the freezers to thaw at room temperature on a shaker table, minimizing the time for thawing. Immediately after complete thawing, 2 nanomoles (nmol) of the double spike were added into the sample bottles and allowed for sample-double spike equilibrium before transferring the samples to separatory funnels and Mg(OH)2 co-precipitation. Spiked samples were equilibrated for 0.5 - 12 hours. We have shown that this range of equilibration time gives identical [Cr(III)] and δ53Cr(III) (Huang et al., 2021). The procedure afterwards was the same as the total dissolved Cr analysis method above.

Cr(VI) isotope ratios were measured from seawater samples where their Cr(III) had been extracted by Mg(OH)2 co-precipitation. The Cr(III)-extracted seawater samples were filtered through clean 0.4µm Nuclepore® filter membranes to remove any Mg(OH)2 precipitate. They were then acidified to pH 1.9 and put in a 60°C oven for 14 days to accelerate the reduction of Cr(VI) to Cr(III). They can then be treated as acidified seawater following the same procedure for the total dissolved Cr analysis.

Three-step ion chromatography was conducted to remove all matrix and isobaric ions (Moos and Boyle, 2019). All three chromatography columns use AG1X8 anion exchange resin. The first column is designed to remove major seawater matrix cations. This is done by oxidizing sample Cr(III) to Cr(VI) with ammonium persulfate (APS, (NH4)2S2O8) (1 hour, 110°C) before loading it onto the first column, and following elutation of matrix cations, reducing it back to Cr(III) while retained on the resin by eluting with 2M HNO3 + 2% (v/v) H2O2. This process releases the Cr(III) from the anion resin. The second column is aimed at removing polyatomic sulfur interferences, which come from both the seawater itself and the degradation from the APS in the previous step. The third mini-column was to remove traces of Fe. This is achieved by dissolving the dried-down samples in 6M HCl. In the strong acidic medium, Fe would complex with Cl- to form FeCl4-, which has a high affinity to

the anion exchange resin, whereas Cr(III) would pass through. The second and the third columns were each followed by digestion with 100µL aqua regia to decompose resin residues. The final samples were dissolved in 2% (v/v) HNO3 to be analyzed on a multi-collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS).

Blanks and reproducibility:
One quality control seawater sample from the surface Atlantic Ocean has been measured repeatedly with each batch of samples since November 2017. The external reproducibility of δ53Cr and [Cr] are 1.02 ± 0.10‰ (2SD, n=29) and 3.19 ± 0.12 (SD, n=29), respectively. The external reproducibility of low-Cr (i.e. Cr(III) or Cr(VI)) analysis was also determined using the same quality control seawater with a sample Cr to double spike ratio of 0.3. The resulting reproducibility of the δ53Cr and [Cr] of low-Cr samples are 1.02 ± 0.15‰ (2SD, n=9) and 3.24 ± 0.06 nmol/kg (SD, n=9), respectively.

Procedural Cr blanks were on the order of 0.02 nmol, which is comparable to that in Moos and Boyle (2019). Considering a typical Cr amount for total dissolved Cr analysis (2 nmol), the blank is negligible. Therefore, total dissolved Cr data was not corrected for the blank. As for Cr(III) and Cr(VI) analyses, sample Cr varies from 0.44 to 1.66 nmol. The blank accounts for less than 5% of the sample Cr. No correction was made on Cr(III) or Cr(VI) isotope data, either.

Instruments:
All Cr isotope measurements were made on an IsoProbe MC-ICP-MS. A ‘peak-jump’ mode was applied in the Cr isotope analysis on IsoProbe MC-ICP-MS. The plasma mass spectrometer was tuned on an 100 mM NH4S2O8solution with 1 µM Cr to minimize polyatomic sulfur interferences (i.e. 32S16O1H+ on mass 49, 34S16O+ on mass 50 and 34S16O1H+ on mass 51) by lowering the signal of mass 49 (polyatomic) relative to mass 52 (Cr). Each sample was bracketed by two SRM-DS mixtures with the same sample Cr to DS ratio and similar signal level (within 10%). The δ53Cr data was calculated by iteration on each isotope correction and instrumental mass fractionation (β) in an Excel spreadsheet (Moos and Boyle, 2019). The [Cr] concentration was calculated by averaging the results from the single isotope dilution formula using corrected 50Cr and 54Cr.

Data Processing Description

Isotope data was processed using the double spike method as described in Moos and Boyle (2019).

BCO-DMO Curation Notes

- Imported original file "SI Table S3r.xlsx" into the BCO-DMO system.
- Made the longitude values negative to indicate West direction.
- Renamed fields to comply with BCO-DMO naming conventions.
-Saved the final file as "925782_v1_sitables3r_cr_conc_isotopes_rr1804-05_km1919-20.csv".

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Data Files

File
925782_v1_sitables3r_cr_conc_isotopes_rr1804-05_km1919-20.csv (Comma Separated Values (.csv), 1.60 KB) MD5:4a8bf5dba93d9d0a830a6982f271c8af Primary data file for dataset ID 925782, version 1

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Related Publications

Huang, T. and Boyle, E.A. (submitted) Redox processing and Scavenging determine the Distribution of Chromium Isotopes in the Eastern Tropical North Pacific Oxygen Deficient Zone, submitted to Geochimica et Cosmochimica Acta.
Results

Huang, T., Moos, S. B., Boyle, E. A. (2021). Trivalent chromium isotopes in the eastern tropical North Pacific oxygen-deficient zone. Proceedings of the National Academy of Sciences, 118(8). https://doi.org/10.1073/pnas.1918605118
Results

Moos, S. B., and Boyle, E. A. (2019). Determination of accurate and precise chromium isotope ratios in seawater samples by MC-ICP-MS illustrated by analysis of SAFe Station in the North Pacific Ocean. Chemical Geology, 511, 481–493. https://doi.org/10.1016/j.chemgeo.2018.07.027
Methods

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Related Datasets

IsRelatedTo

Boyle, E. A. (2024) **Total dissolved chromium (Cr) concentration and isotopic composition in the Eastern Tropical North Pacific from samples collected on R/V Roger Revelle and R/V Kilo Moana in April-May 2018 and Sept-Oct 2019.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-06-05 doi:10.26008/1912/bco-dmo.925726.1 [view at BCO-DMO]

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Parameters

Parameter	Description	Units
Cruise	Cruise identifier	unitless
Station	Station number	unitless
Latitude	Latitude of sample station, positive values = North	decimal degrees
Longitude	Longitude of sampling station, negative values = West	decimal degrees
Depth	Depth from which the water sample was collected	meters (m)
CTD_Oxygen	In-situ oxygen electrode concentration from CTD	micromoles per kilogram (umol/kg)
dissolved_CrIII	Dissolved chromium (III) concentration of the sample	nanomoles per kilogram (nmol/kg)
dissolved_d53CrIII	Chromium isotope ratio of dissolved Cr(III) in the sample, permil relative to SRM979	permil (‰)
measured_CrVI	Directly measured dissolved chromium (VI) concentration of the sample	nanomoles per kilogram (nmol/kg)
measured_d53CrVI	Directly measured chromium isotope ratio of dissolved Cr(VI) in the sample, permil relative to SRM979	permil (‰)
calculated_CrVI	Total dissolved Cr(VI) concentration of the sample calculated from [Cr(III)] and total dissolved [Cr]	nanomoles per kilogram (nmol/kg)
calculated_d53CrVI	Cr isotope ratio of Cr(VI) in the sample, calculated from [Cr(III)] and total dissolved [Cr]], nmol/kg and d53Cr(III) and total dissolved d53Cr	permil (‰)

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Instruments

Dataset-specific Instrument Name	IsoProbe MC-ICP-MS
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

Dataset-specific Instrument Name	5 L acid-cleaned Teflon-coated external-spring "Niskin-type" bottles (Ocean Test Equipment)
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

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Deployments

RR1804

Website	https://www.bco-dmo.org/deployment/776766
Platform	R/V Roger Revelle
Start Date	2018-03-27
End Date	2018-04-13
Description	More information is available from R2R: https://www.rvdata.us/search/cruise/RR1804

RR1805

Website	https://www.bco-dmo.org/deployment/779193
Platform	R/V Roger Revelle
Start Date	2018-04-14
End Date	2018-05-02
Description	More information is available at R2R: https://www.rvdata.us/search/cruise/RR1805

KM1919

Website	https://www.bco-dmo.org/deployment/849503
Platform	R/V Kilo Moana
Start Date	2019-09-21
End Date	2019-10-01
Description	More information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/km1919 Cruise DOI: 10.7284/908382

KM1920

Website	https://www.bco-dmo.org/deployment/849547
Platform	R/V Kilo Moana
Start Date	2019-10-02
End Date	2019-10-22
Description	More information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/km1920 Cruise DOI: 10.7284/908379

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Project Information

Cr Isotope Oceanography of the Eastern Tropical North Pacific Ocean (ETNP Cr Isotopes)

Coverage: Eastern Tropical North Pacific

NSF Award Abstract:
Surface seawater equilibrates with the atmosphere and has high oxygen levels, supporting the sea life within it. When this water is cooled in the winter, it becomes denser and sinks into the depths of the ocean, and begins to lose its oxygen as microbes respire while feeding on sinking organic matter falling from the upper ocean. In some regions, such as the eastern tropical North Pacific Ocean, this process leads to such low oxygen concentrations that oxygen-respiring organisms such as fish cannot survive. There is evidence that these regions are growing larger in recent decades raising concerns over the consequences should these trends continue. Geologists looking at ancient sediments have surmised that some periods in the past have had much larger oxygen-depleted portions of the ocean, so we know the possibility exists. We are working on a new tracer of these oxygen deficient zones, the chromium isotope ratio of seawater. Chromium (Cr) is a trace element found throughout the ocean; in oxygen depleted zones it is reduced from the highly soluble 6+ oxidation state (hexavalent Cr, a toxic pollutant at high concentrations) to the relatively insoluble 3+ state (trivalent Cr) which is removed from the ocean attached to sinking particles. This process favors lighter Cr isotopes hence Cr with 24 protons and 28 neutrons is preferentially transformed compared to Cr with 24 protons and 29 neutrons. This transformation can be used to study the extent and activity of oxygen deficient zones in the modern ocean and in geological ancient oceans. There is very little data for Cr isotopes in these environments, and this project will obtain some of the first data with fieldwork sample collection in the eastern tropical North Pacific Ocean and laboratory measurements using plasma mass spectrometry. This research can contribute to sedimentary geological and geochemical understanding. A female Ph.D. student at Massachusetts Institute of Oceanography will participate in the project that will comprise most of her thesis research.

Chromium (Cr) in the aquatic environment exists in two redox states, Cr(III) and Cr(VI). Cr(VI) is thermodynamically stable and the dominant form observed in the oxic ocean, although a few percent of unstable Cr(III) is also observed. Cr(III) is particle-reactive and is scavenged onto sinking particulate matter, whereas Cr(VI) is relatively unreactive. Both species can be taken up by marine biota, although diatoms take up Cr(III) ~20 times faster. Cr(III) has biochemical functionality (e.g. lipid and protein metabolism), whereas Cr(VI) is a toxin that damages cellular biochemistry. When oxygen is less than about 2 uM, Cr(III) becomes the thermodynamically stable species, but slow reaction kinetics lets microbial activity or environmental reductants

such as Fe(II) dominate the conversion. Theory and lab experiments indicate that this redox transformation should be accompanied by a stable isotope ratio shift when partial conversion occurs, with Cr(III) enriched in the lighter isotopes. Of the four Cr stable isotopes, this process is observed using the ratio of the most abundant natural isotopes 53Cr and 52Cr while using an enriched double spike of the scarce 50Cr and 54Cr isotopes to correct for laboratory and instrument mass fractionation. This sensitivity to environmental oxygen has inspired geologists to use Cr isotope ratios as an indicator of past oxygenation conditions on earth. But there is little data on the Cr isotope composition in marine aquatic systems with which to ground-truth the geological inferences. We will illuminate the Cr isotope geochemistry of the marine environment with measurements on the horizontal and vertical distribution of Cr concentrations and Cr isotope ratios for the Cr redox species and particulate matter for samples from the eastern tropical North Pacific oxygen deficient zone. Cr isotope ratios are sensitive to biological uptake and regeneration in the oxic ocean and redox processes in oxygen deficient zones (and the latter's consequent outmixing into adjacent oxic zones). This data will be examined in relationship to standard hydrographic properties and nutrients and to the oceanic redox systems of nitrogen, iron, and manganese.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1924050

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