Chromium (Cr) concentration and isotope data of chelex-100 extraction method from samples collected on R/V New Horizon cruise NH1410 in May-June 2014

Website: https://www.bco-dmo.org/dataset/925670
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
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Abstract
Changes in chromium (Cr) isotope ratios due to fractionation between trivalent (Cr(III)) and hexavalent (Cr(VI)) are being utilized by geologists to infer oxygen conditions in past environments. But there is little information available on Cr in the modern ocean to ground-truth these inferences. Transformations between the two chromium redox species are important processes in oceanic Cr cycling. Here we present profiles of hexavalent and trivalent Cr concentrations and stable isotope ratios from the Eastern Tropical North Pacific (ETNP) oxygen deficient zone (ODZ) which support theoretical and experimental studies that predict that lighter Cr is preferentially reduced in low oxygen environments, and that residual dissolved Cr becomes heavier due to removal of particle-reactive Cr(III) on sinking particles. The Cr(III) maximum dominantly occurs in the upper portion of the ODZ, implying that microbial activity (dependent on the sinking flux of organic matter) may be the dominant mechanism for this transformation, rather than a simple inorganic chemical conversion between the species depending on the redox potential.

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Coverage

Location: Eastern Tropical North Pacific
Spatial Extent: **Lat**:20.88272 **Lon**:-107.97113
Temporal Extent: 2014-05 - 2014-06

Methods & Sampling

In this study, we report chromium (Cr) isotopes for Cr(III), Cr(VI), and total Cr from three stations within the eastern tropical North Pacific (ETNP) oxygen deficient zone (ODZ) (see Figs. 1 and 2 of Huang, et al. 2021). Two of these stations (P1 and P2) were collected on cruises Roger Revelle 1804-5 (April to May 2018) and KM1920 (September 2019). The third (2T) was collected on cruise New Horizon 1410 (May 2014) whose primary data are reported in Moos, et al. (2020). Water samples were collected using Niskin Bottles on a CTD rosette or Niskin-X bottles on a TE clean rosette.

To separate Cr species and analyze their isotopic compositions, we used a Mg(OH)2 coprecipitation method similar to that reported in Janssen, et al. (2020) and Davidson, et al. (2019) with some differences in the details:

(1) A 50Cr–54Cr double spike was added to each sample before collecting Mg(OH)2. The double-spike was allowed to equilibrate with samples for ~6 hours. Tests of equilibration time between 0.5 and 12 hours show no difference in isotopic values.

(2) No iron coprecipitation was done to separate Cr(III) from the Mg matrix. The Mg(OH)2 pellets were dissolved in HCl, pH-adjusted, and ready for column chromatography as described in Moos and Boyle (2019).

(3) To determine Cr(VI) isotopic composition, we filtered the supernatant after the Mg(OH)2 coprecipitation and acidified it to pH 1.9 with HCl for an extended time afterward.

The Cr(VI) that was left in solution converts to Cr(III) which we then analyze by a second double-spike Mg(OH)2 coprecipitation and column purification. Some Cr(VI) isotopic compositions were calculated using the concentration and isotopic composition of total Cr and Cr(III) by mass balance.

Additionally, we analyzed Cr(III) concentrations and isotope ratios by Cr(III) double-spike isotope dilution either at sea or immediately following thawing of frozen samples. Three samples were processed in both ways and all give the same results. The method for total Cr concentration and isotopic composition is described in detail in Moos and Boyle (2019). All of our samples have a within-run error of 0.02 to 0.19‰ (2 SE) on δ53Cr. The average [Cr] and δ53Cr values of a long-term in-house seawater standard are 3.20 ± 0.12 nmol/kg (SD, n = 20) and 1.02 ± 0.13‰ (2 SD, n = 20), respectively.

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 NH4S2O8 solution 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 Processing Description

- Imported original file "Table S2r.xlsx" into the BCO-DMO system.
- Made the longitude values negative to indicate West direction.
- Renamed fields to comply with BCO-DMO naming conventions.
- Rounded Latitude and Longitude columns to 5 decimal places.
- Saved the final file as "925670_v1_tables2_cr_conc_and_isotopes_nh1410.csv".

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Data Files

File
925670_v1_tables2_cr_conc_and_isotopes_nh1410.csv (Comma Separated Values (.csv), 687 bytes) MD5:28a525b9eea184e51a67cd21767f62d1 Primary data file for dataset ID 925670, version 1

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Related Publications

Davidson, A. B., Semeniuk, D. M., Koh, J., Holmden, C., Jaccard, S. L., Francois, R., & Crowe, S. A. (2019). A Mg(OH)2 coprecipitation method for determining chromium speciation and isotopic composition in seawater. Limnology and Oceanography: Methods, 18(1), 8–19. Portico. https://doi.org/10.1002/lom3.10342
Methods

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

Janssen, D. J., Rickli, J., Quay, P. D., White, A. E., Nasemann, P., & Jaccard, S. L. (2020). Biological Control of Chromium Redox and Stable Isotope Composition in the Surface Ocean. Global Biogeochemical Cycles, 34(1). Portico. https://doi.org/10.1029/2019gb006397
Methods

Moos, S. B., Boyle, E. A., Altabet, M. A., & Bourbonnais, A. (2020). Investigating the cycling of chromium in the oxygen deficient waters of the Eastern Tropical North Pacific Ocean and the Santa Barbara Basin using stable isotopes. Marine Chemistry, 221, 103756. https://doi.org/10.1016/j.marchem.2020.103756
Related Research

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) **Chromium (Cr) concentration and isotope data determined using dissolved Cr and different Cr species from samples collected on R/V Roger Revelle cruise RR1805 in April-May 2018.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-04-23 doi:10.26008/1912/bco-dmo.925569.1 [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)
Corrected_CrIII	Measured Cr concentration from Chelex resin, corrected for the resin blank	nanomoles per kilogram (nmnol/kg)
Corrected_d53Cr	Corrected Cr isotope ratio	permil (‰)
Measured_CrVI	Directly measured dissolved chromium (VI) concentration of the sample	nanomoles per kilogram (nmnol/kg)
Measured_d53CrVI	Directly measured chromium isotope ratio of dissolved Cr(VI) in the sample, permil relative to SRM979	permil (‰)
Calculated_total_Cr	Total dissolved Cr concentration of the sample calculated from [Cr(III)] and [Cr(VI)]	nanomoles per kilogram (nmnol/kg)
Calculated_total_d53Cr	Cr isotope ratio of total Cr in the sample, calculated from [Cr(III)] and [Cr(VI)], nmol/kg and d53Cr(III) and d53Cr(VI)	permil (‰)

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Instruments

Dataset-specific Instrument Name	IsoProbe MC-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.

Dataset-specific Instrument Name	Niskin bottles and Niskin-X bottles
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

NH1410

Website	https://www.bco-dmo.org/deployment/628491
Platform	R/V New Horizon
Report	http://dmoserv3.whoi.edu/data_docs/OMZ_SulfurCycling/Cruise_Report_NH1410.pdf
Start Date	2014-05-10
End Date	2014-06-08
Description	Oxygen Minimum Zone Microbial Biogeochemistry Expedition 2 (OMZoMBiE 2) Cruise Track (PDF) Cruise information and original data are available from R2R: https://www.rvdata.us/search/cruise/NH1410

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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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