# Trace element concentrations in dissolved and particulate fractions from samples collected by GO-Flo bottles on R/V Thomas G. Thompson cruise TN280 along Line P in the NE Pacific in May 2012 (GeoMICS project)

Website: https://www.bco-dmo.org/dataset/664975 Data Type: Cruise Results Version: 16 Nov 2016 Version Date: 2016-11-16

#### Project

 <u>The relationship between microbial biogeography and ocean chemistry across a persistent oceanographic</u> <u>&quot;hot spot&quot; in the NE Pacific Ocean</u> (GeoMICS Chem)
 <u>Characterizing biological function across a persistent oceanographic &quot;hotspot&quot; in the NE Pacific</u> <u>Ocean</u> (GeoMICS Bio)

#### Programs

- » GeoMICS (GeoMICS)
- » GeoMICS (GeoMICS)

Contributors	Affiliation	Role
<u>Twining, Benjamin</u>	Bigelow Laboratory for Ocean Sciences	Principal Investigator
Moffett, James W.	University of Southern California (USC-WIES)	Co-Principal Investigator
<u>Saito, Mak A.</u>	Woods Hole Oceanographic Institution (WHOI)	Co-Principal Investigator
Rauschenberg, Sara	Bigelow Laboratory for Ocean Sciences	Contact
<u>Rauch, Shannon</u>	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

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#### Coverage

Spatial Extent: N:48.817 E:-125.500957 S:48.575 W:-128.665833

#### **Dataset Description**

Trace element concentrations in dissolved and particulate fractions collected with GO-Flo bottles and analyzed with inductively-coupled plasma mass spectrometry (ICP-MS). Concentrations of labile, refractory, and total particulate metal fractions are reported. Total dissolved cobalt, iron, copper, zinc and manganese are also reported. Samples were collected on R/V Thomas G. Thompson cruise TN280 in 2012.

#### Methods & Sampling

#### Particulate Elements (Twining)

Samples were collected from sub-surface waters using the GEOTRACES GO-Flo rosette. The filtration was performed directly from pressured GO-Flo bottles onto membranes (25-mm diameter Supor 0.45-um polyethersulfone) mounted in Swinnex polypropylene filter holders. Filters were cleaned following the protocol outlined in the GEOTRACES Sampling Document (Cutter et al. 2010). Pressurization to <8 psi was achieved with 0.2-um filtered air. Prior to filtration each GO-Flo bottle was gently mixed by manually inverting the bottle several times (after removal of unfiltered salt samples to provide some headspace). Filtration was continued until the entire bottle was empty or 2 hours had elapsed. An average of 4.6-L of water was filtered through each membrane. Filter holders were removed from the GO-Flo bottles and a vacuum applied to remove any residual water. Filters were then folded, stored in acid-washed centrifuge tubes, and frozen at -20 degrees C until digestion and analysis.

Filters were digested in rigorously cleaned 22-mL PFA digestions vials (Savillex). All digestion steps were performed in a Class-100 clean room using standard clean techniques. Filters were first digested in a solution of 25% Optima-grade acetic acid and 0.02 M hydroxylamine hydrochloride following the protocol of Berger et al. (2008). One milliliter of this solution was added to the filter stored in a 1.7-mL polypropylene vial. Following the recommendation of Berger et al. (2008), the solution was heated to 95 degrees C in a water bath for 10 minutes and then allowed to cool to room temperature. The filter was in contact with the acetic acid leach for a total of two hours. The filter was removed to an acid-cleaned PFA bomb and was later digested using the mixture of concentrated acids described below to recover the refractory elements. The acetic acid/hydroxylamine leachate was centrifuged at 14,000 rpm for 10 minutes to sediment all particles. Without disturbing particles on the bottom of the tube, approximately 0.8-mL of leachate was transferred into a 7-mL PFA digestion vial. Optima-grade HNO3 was added (100 uL) to the 7-mL digestion vial, which was subsequently heated uncapped at 110 degrees C to near dryness. Vial contents were redissolved with 2% HNO3 (Optima grade).

The refractory fraction of particulate metals was then measured on the sample filters. The filter was transferred to a 22-mL PFA vial, 2-mL of a mixture of 4M HCl, 4M HNO3, and 4M HF (all Optima grade) was added, and the vial was tightly capped and heated to 110 degrees C for 4 hours. This procedure has been determined to be adequate for digestion of all particulate material, while allowing the Supor filter to remain intact (Ohnemus et al. 2014). Following heating, the acid solution in the bomb was poured into a second PFA vial. To ensure complete transfer of acid, the bombs were thoroughly rinsed with  $3 \times 0.5$ -mL aliquots of ultrapure water. This water was also poured into the secondary vial. The secondary vial was then heated to dryness and the contents redissolved with 2-mL of a 50% Optima-grade HNO3 + 15% Optima-grade H2O2 solution. This solution was again dried down and the contents redissolved with 2% HNO3.

All digests were analyzed using a Finnegan-MAT Element2 HR-ICP-MS at the University of Maine following the protocols outlined in Twining et al. (2011). The instrument is equipped with an ESI Apex desolvation nebulizer, an autosampler contained under a HEPA filter, and nickel cones. Cd-111 was analyzed in low-resolution mode, and the remaining isotopes were analyzed in medium-resolution mode. Multiple isotopes were analyzed for some elements, and the isotopes used to derive the reported concentration are as follows for each element: Fe (56 and 57), Cu (63 and 65), Zn (66, 64 and 68). Mean agreement was 2% for the two Cu isotopes, 5% for the two Fe isotopes, and within 3% for the Zn isotopes. Quantification was performed by external calibration, and In-115 was used as an internal standard to correct for variations in instrumental sensitivity during analyses.

Digestions of the certified reference materials BCR-414 (plankton, Community Bureau of Reference, Commission of the European Communities) and PACS-2 (marine sediment, National Research Council of Canada) were done alongside sample digestions in order to assess accuracy. Recoveries were typically within 10% of the certified values (and within the error of the data, taken from replicate measurements). Total elemental recoveries for the Certified Reference Materials (CRMs) are available in the '<u>Total Elemental Recoveries</u> <u>CRMs</u>' PDF (converted from an original Excel file named 'GEOMics metadata').

#### Dissolved Fe, Zn, Cu, Mn (Moffett)

500 mL samples were filtered through 0.2 um acropak filters acidified to pH 2 and stored for analysis ashore. Fe, Zn and Cu were analyzed by ICPMS with isotope dilution using the NTA Superflow method developed by Lee et al (2010) and Chappell et al., (2016). Mn was determined using the approach of Field et al., (1999).

#### Dissolved Cobalt (Saito)

Sample storage and reagent bottles were soaked for >1 week in the acidic detergent Citranox, rinsed thoroughly with 18.2 M-Ohm Milli-Q water (Millipore), filled with 10% HCl to soak for 10 days, and rinsed thoroughly with Milli-Q water adjusted to pH 2 with TM-grade HCl. Reagent purification protocols were identical to those previously published (Saito and Moffett 2001).

Concentrations of total dissolved cobalt were determined using a previously described cathodic stripping voltammetry (CSV) method (Saito and Moffett 2001, Saito et al. 2004). Measurements were made using the Eco-Chemie uAutolabIII systems connected to Metrohm 663 VA Stands equipped with hanging mercury drop electrodes and Teflon sampling cups. Sample preparation was modified slightly to accommodate use of a Metrohm 837 Sample processor, operated with NOVA 1.8 software (Metrohm Autolab B.V.).

For dissolved cobalt analyses, samples were UV-irradiated for 1 h prior to analysis in a Metrohm 705 UV digester to degrade the organic ligands that bind cobalt, enabling full chelation by the added electroactive ligand, dimethylglyoxime (DMG). 11 ml of sample was pipetted into 15ml polypropylene tubes. Recrystallized DMG (0.1M in methanol) was added to a final concertation of 400 uM and purified N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid) (EPPS) buffer (0.5 M in Milli-Q water) was added to a final concentration of 3.8 mM. Tubes were inverted several times before being placed in the autosampler queue, where 8.5 ml of the mixture was dosed into the teflon analysis cup using a 800 Dosino automated burrette (Metrohm). 1.5 ml of purified sodium nitrite (1.5M in Milli-Q water) was added directly to the Teflon cup using a dedicated 800 Dosino burrette. Once loaded, samples were purged with high purity (>99.99%) N2 for 3 min and cobalt concentrations were determined by standard addition, with triplicate measurement of the sample followed by four 25 pM cobalt additions. 5 nM Co stock was diluted from a certified 1ppm reference (SPEX) and added to the analysis cup via a third Dosino burrette.

The analytical blank was determined by analyzing seawater that had been UV-irradiated for 1 h, equilibrated overnight with prepared Chelex 100 resin beads (Bio-Rad), and UV-irradiated a second time to degrade any leached synthetic ligands. Mean blank was 4.6 +/- 0.7 pM, and the detection limit was calculated as triple the standard deviation of the blank, 2.1 pM. A portion of this dataset was published previously in Saito et al. 2014; the blank for those samples was 3.5 pM.

The Saito laboratory has participated in the GEOTRACES intercalibration effort using this electrochemical Co method. Acidified standards were neutralized with concentrated ammonium hydroxide (Seastar), mixing the entire sample between drops, prior to UV digestion. We report our laboratory values for the GEOTRACES and SAFe standard analyses using this electrochemical method, including those conducted during analysis of the EPZT samples to be:

SAFe D1 = 48.5 +/- 2.4 (n=3, at sea), SAFe D2 = 45.0 +/- 2.7 (n=7), GEOTRACES GSP = 2.5 +/- 2.0 (n=10), GEOTRACES GSC = 77.7 +/- 2.4 (n=4).

These results are in good agreement with those from the GEOTRACES intercalibration effort for Co and demonstrate that the methodologies employed to produce this dataset detect concentrations within the standard deviation of current consensus values for UV irradiated samples, which can be found on the International GEOTRACES Program website.

#### **References cited:**

Berger, C. J. M., S. M. Lippiatt, M. G. Lawrence, and K. W. Bruland. 2008. Application of a chemical leach technique for estimating labile particulate aluminum, iron, and manganese in the Columbia River plume and coastal waters off Oregon and Washington. Journal of Geophysical Research-Oceans, 113. doi: 10.1029/2007JC004703

Chappell, P. Dreux; Vedmati, Jagruti; Selph, Karen E.; et al (2016) Preferential depletion of zinc within Costa Rica upwelling dome creates conditions for zinc co-limitation of primary production. J. Plankton Res. Volume:38. Issue:2; Pages:244-255. doi: <u>10.1093/plankt/fbw018</u>

Cutter, G. and others 2010. Sampling and sample-handling protocols for GEOTRACES cruises.

Field, M.P., Cullen, J.T., Sherrell, R.M., (1999). Direct determination of 10 trace metals in 50 mu L samples of coastal seawater using desolvating micronebulization sector field ICP-MS. J. Anal. At. Spectrom. 14, 1425-1431. doi: <u>10.1039/A901693G</u>

Lee, J.-M., E. A. Boyle, Y. Echegoyen-Sanz, J. N, Fitzsimmons et al. (2011). Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. Anal. Chim. Acta 686: 93–101, doi: <u>10.1016/j.aca.2010.11.052</u>

Ohnemus, D.C., M.E. Auro, R.M. Sherrell, M. Langerstrom, P.L. Morton, B.S. Twining, S. Rauschenberg, P.J. Lam. 2014. Laboratory intercomparison of marine particulate digestions including Piranha: a novel chemical method for dissolution of polyethersulfone filters. Limnology and Oceanography, 12:530-547. doi: 10.4319/lom.2014.12.530

Saito, M. A., and J. W. Moffett. 2001. Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. Marine Chemistry. 75 (49-68). doi: <u>10.1016/S0304-4203(01)00025-1</u>

Saito, M. A., J. W. Moffett, and G. DiTullio. 2004. Cobalt and Nickel in the Peru Upwelling Region: a Major Flux of Cobalt Utilized as a Micronutrient. Global Biogeochemical Cycles. 18 GB4030. doi: <u>10.1029/2003GB002216</u>

Twining, B. S., S. B. Baines, J. B. Bozard, S. Vogt, E. A. Walker, and D. M. Nelson. 2011. Metal quotas of plankton in the equatorial Pacific Ocean. Deep-Sea Research II, 58:325-341. doi: <u>10.1016/j.dsr2.2010.08.018</u>

#### **Data Processing Description**

#### Particulate Elements (Twining)

All data were normalized to an In-115 internal standard and quantified using an external calibration curve. After accounting for sample dilutions due to acid digestion steps, quantities of each element per filter (pmol/filter) were calculated. The contribution of the 'process blank' (measured as the elements contained in an acid-washed filter through which 0.2-um filtered water was passed during the cruise) were then subtracted. Separate process blanks were calculated for the labile (acetic acid/hydroxylamine) and refractory (HCl/HNO3/HF following acetic acid/hydroxylamine) digestions. The average process blanks for each digestion scheme and each element is given in the 'Blanks and Detection Limits' PDF (converted from an original Excel file named 'GEOMics metadata').

Following blank corrections, element concentrations (per volume of water filtered) were calculated by dividing the pmol/filter measurements by the volume of water passed through each filter (measured volumetrically on the ship following each filtration).

Nearly all of the samples were well above the instrumental detection limits for all elements. The factor limiting our ability to detect particulate elements in the water is the signal associated with the process blank (ie, the filter substrate). We therefore calculated the detection limits for the whole method as 3x the standard deviation of the process blanks for the relevant digestion procedure (labile or refractory). Detection limits for total particulate concentrations were calculated by propagating the uncertainty of labile and refractory process blank standard deviations. Detection limits are given inthe 'Blanks and Detection Limits' PDF (converted from an original Excel file named 'GEOMics metadata').

The standard Ocean Data View flags were used (reference all flags at <u>https://www.bodc.ac.uk/data/codes\_and\_formats/odv\_format/</u>):

- 1: Good Value: Used when the reported value reflects analysis of multiple replicates.
- 2: Probably Good Value: Used when the reported value reflects analysis of a single replicate.
- 3: Probably Bad Value: Used when a value appears abnormally high or low (oceanographically inconsistent).
- 6: Value Below Detection Limit: We report an empty value rather than zero or a detection limit value.

#### **Dissolved Cobalt (Saito)**

Peak height (in nA) was measured relative to a linear baseline for the Co reduction peak ca. -1.15V. All seven scans (3 baseline and 4 standard additions) were used to determine a sample specific sensitivity (nA/pM Co added, mean r2 = 0.998). Cobalt concentrations were calculated from the baseline peak height, divided by the sensitivity and corrected from volume changes from sodium nitrite addition, followed by subtraction of the mean blank for at sea, or in lab analyses.

Analyses were characterized with mild electrical inference that required additional processing before peak height could be reliably measured. We adopted a simplified least squared fitting routine included in the NOVA software package that conducted a 15-point weighted moving average according to a 2nd order polynomial. This method did not distort cobalt concentrations when noise was low.

On occasion, analyses were repeated due to obvious electrode malfunction or to confirm oceanographic consistency of measured values. If the repeated measurement was similar to the initial, the initial value is reported. If the repeated analysis was more oceanographically consistent with adjacent values in the water column, that analysis was used instead.

#### Data Files

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File

diss_partic_elements.csv(Comma Separated Values (.csv), 24.02 KB)

MD5:7ba98db73f3032c248ebac7237e29fb5

Primary data file for dataset ID 664975

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#### **Related Publications**

Twining, B. S., Antipova, O., Chappell, P. D., Cohen, N. R., Jacquot, J. E., Mann, E. L., ... Tagliabue, A. (2020). Taxonomic and nutrient controls on phytoplankton iron quotas in the ocean. Limnology and Oceanography Letters. doi:<u>10.1002/lol2.10179</u> *Results* 

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#### Parameters

Parameter	Description	Units
cruise_id	Cruise identifer	unitless
station	Station number	unitless
lat	Latitude; positive values = North	decimal degrees
lon	Longitude; Negative values = West	decimal degrees
depth	Sample depth	meters (m)
bottom_depth	Bottom depth	meters (m)
dCo	Dissolved (	picomolar (pM)
dCo_stdev	Standard deviation of dissolved Cobalt concentration	picomolar (pM)
dFe	Dissolved (	nanomolar (nM)
dFe_stdev	Standard deviation of dissolved Iron concentration	nanomolar (nM)
dCu	Dissolved (	nanomolar (nM)
dCu_stdev	Standard deviation of dissolved Copper concentration	nanomolar (nM)
dMn	Dissolved (	nanomolar (nM)
dMn_stdev	Standard deviation of dissolved Manganese concentration	nanomolar (nM)
dZn	Dissolved (	nanomolar (nM)
dZn_stdev	Standard deviation of dissolved Zinc concentration	nanomolar (nM)
pCd_L	Concentration of labile particulate (>0.45 um) fraction of Cadmium (Cd)	picomoles per liter (pmol/L)
pAl_L	Concentration of labile particulate (>0.45 um) fraction of Aluminium (Al)	picomoles per liter (pmol/L)
pMn_L	Concentration of labile particulate (>0.45 um) fraction of Manganese (Mn)	picomoles per liter (pmol/L)
pFe_L	Concentration of labile particulate (>0.45 um) fraction of Iron (Fe)	picomoles per liter (pmol/L)
pCo_L	Concentration of labile particulate (>0.45 um) fraction of Cobalt (Co)	picomoles per liter (pmol/L)

pCu_L	Concentration of labile particulate (>0.45 um) fraction of Copper (Cu)	picomoles per liter (pmol/L)
pP_L	Concentration of labile particulate (>0.45 um) fraction of Phosphorus (P)	picomoles per liter (pmol/L)
pTi_L	Concentration of labile particulate (>0.45 um) fraction of Titanium (Ti)	picomoles per liter (pmol/L)
pV_L	Concentration of labile particulate (>0.45 um) fraction of Vanadium (V)	picomoles per liter (pmol/L)
pNi_L	Concentration of labile particulate (>0.45 um) fraction of Nickel (Ni)	picomoles per liter (pmol/L)
pZn_L	Concentration of labile particulate (>0.45 um) fraction of Zinc (Zn)	picomoles per liter (pmol/L)
pCd_R	Concentration of refractory particulate (>0.45 um) fraction of Cadmium (Cd)	picomoles per liter (pmol/L)
pAl_R	Concentration of refractory particulate (>0.45 um) fraction of Aluminium (Al)	picomoles per liter (pmol/L)
pMn_R	Concentration of refractory particulate (>0.45 um) fraction of Manganese (Mn)	picomoles per liter (pmol/L)
pFe_R	Concentration of refractory particulate (>0.45 um) fraction of Iron (Fe)	picomoles per liter (pmol/L)
pCo_R	Concentration of refractory particulate (>0.45 um) fraction of Cobalt (Co)	picomoles per liter (pmol/L)
pCu_R	Concentration of refractory particulate (>0.45 um) fraction of Copper (Cu)	picomoles per liter (pmol/L)
pP_R	Concentration of refractory particulate (>0.45 um) fraction of Phosphorus (P)	picomoles per liter (pmol/L)
pTi_R	Concentration of refractory particulate (>0.45 um) fraction of Titanium (Ti)	picomoles per liter (pmol/L)
pV_R	Concentration of refractory particulate (>0.45 um) fraction of Vanadium (V)	picomoles per liter (pmol/L)
pNi_R	Concentration of refractory particulate (>0.45 um) fraction of Nickel (Ni)	picomoles per liter (pmol/L)
pZn_R	Concentration of refractory particulate (>0.45 um) fraction of Zinc (Zn)	picomoles per liter (pmol/L)
pCd_T	Concentration of total particulate (>0.45 um) Cadmium (Cd). Total = labile + refractory.	picomoles per liter (pmol/L)
pAI_T	Concentration of total particulate (>0.45 um) Aluminium (Al). Total = labile + refractory.	picomoles per liter (pmol/L)
pMn_T	Concentration of total particulate (>0.45 um) Manganese (Mn). Total = labile + refractory.	picomoles per liter (pmol/L)
pFe_T	Concentration of total particulate (>0.45 um) Iron (Fe). Total = labile + refractory.	picomoles per liter (pmol/L)
pCo_T	Concentration of total particulate (>0.45 um) Cobalt (Co). Total = labile + refractory.	picomoles per liter (pmol/L)
pCu_T	Concentration of total particulate (>0.45 um) Copper (Cu). Total = labile + refractory.	picomoles per liter (pmol/L)
pP_T	Concentration of total particulate (>0.45 um) Phosphorus (P). Total = labile + refractory.	picomoles per liter (pmol/L)
pTi_T	Concentration of total particulate (>0.45 um) Titanium (Ti). Total = labile + refractory.	picomoles per liter (pmol/L)

pV_T	Concentration of total particulate (>0.45 um) Vanadium (V). Total = labile + refractory.	picomoles per liter (pmol/L)
pNi_T	Concentration of total particulate (>0.45 um) Nickel (Ni). Total = labile + refractory.	picomoles per liter (pmol/L)
pZn_T	Concentration of total particulate (>0.45 um) Zinc (Zn). Total = labile + refractory.	picomoles per liter (pmol/L)
pCd_L_flag	Quality flag for pCd_L (particulate labile Cadmium); follows ODV flag format.	unitless
pAl_L_flag	Quality flag for pAI_L (particulate labile Aluminium); follows ODV flag format.	unitless
pMn_L_flag	Quality flag for pMn_L (particulate labile Manganese); follows ODV flag format.	unitless
pFe_L_flag	Quality flag for pFe_L (particulate labile Iron); follows ODV flag format.	unitless
pCo_L_flag	Quality flag for pCo_L (particulate labile Cobalt); follows ODV flag format.	unitless
pCu_L_flag	Quality flag for pCu_L (particulate labile Copper); follows ODV flag format.	unitless
pP_L_flag	Quality flag for pP_L (particulate labile Phosphorus); follows ODV flag format.	unitless
pTi_L_flag	Quality flag for pTi_L (particulate labile Titanium); follows ODV flag format.	unitless
pV_L_flag	Quality flag for pV_L (particulate labile Vanadium); follows ODV flag format.	unitless
pNi_L_flag	Quality flag for pNi_L (particulate labile Nickel); follows ODV flag format.	unitless
pZn_L_flag	Quality flag for pZn_L (particulate labile Zinc); follows ODV flag format.	unitless
pCd_R_flag	Quality flag for pCd_R (particulate refractory Cadmium); follows ODV flag format.	unitless
pAl_R_flag	Quality flag for pAI_R (particulate refractory Aluminium); follows ODV flag format.	unitless
pMn_R_flag	Quality flag for pMn_R (particulate refractory Manganese); follows ODV flag format.	unitless
pFe_R_flag	Quality flag for pFe_R (particulate refractory Iron); follows ODV flag format.	unitless
pCo_R_flag	Quality flag for pCo_R (particulate refractory Cobalt); follows ODV flag format.	unitless
pCu_R_flag	Quality flag for pCu_R (particulate refractory Copper); follows ODV flag format.	unitless
pP_R_flag	Quality flag for pP_R (particulate refractory Phosphorus); follows ODV flag format.	unitless
pTi_R_flag	Quality flag for pTi_R (particulate refractory Titanium); follows ODV flag format.	unitless
pV_R_flag	Quality flag for pV_R (particulate refractory Vanadium); follows ODV flag format.	unitless
pNi_R_flag	Quality flag for pNi_R (particulate refractory Nickel); follows ODV flag format.	unitless
pZn_R_flag	Quality flag for pZn_R (particulate refractory Zinc); follows ODV flag format.	unitless

pCd_T_flag	Quality flag for pCd_T (total particulate Cadmium); follows ODV flag format.	unitless
pAI_T_flag	Quality flag for pAI_T (total particulate Aluminium); follows ODV flag format.	unitless
pMn_T_flag	Quality flag for pMn_T (total particulate Manganese); follows ODV flag format.	unitless
pFe_T_flag	Quality flag for pFe_T (total particulate Iron); follows ODV flag format.	unitless
pCo_T_flag	Quality flag for pCo_T (total particulate Cobalt); follows ODV flag format.	unitless
pCu_T_flag	Quality flag for pCu_T (total particulate Copper); follows ODV flag format.	unitless
pP_T_flag	Quality flag for pP_T (total particulate Phosphorus); follows ODV flag format.	unitless
pTi_T_flag	Quality flag for pTi_T (total particulate Titanium); follows ODV flag format.	unitless
pV_T_flag	Quality flag for pV_T (total particulate Vanadium); follows ODV flag format.	unitless
pNi_T_flag	Quality flag for pNi_T (total particulate Nickel); follows ODV flag format.	unitless
pZn_T_flag	Quality flag for pZn_T (total particulate Zinc); follows ODV flag format.	unitless

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#### Instruments

Dataset- specific Instrument Name	GEOTRACES GO-FLO Rosette
Generic Instrument Name	GO-FLO Bottle
Generic Instrument Description	GO-FLO bottle cast used to collect water samples for pigment, nutrient, plankton, etc. The GO- FLO sampling bottle is specially designed to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

Dataset- specific Instrument Name	Finnegan-MAT Element2 HR-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	Metrohm 663 VA Stands
Generic Instrument Name	Metrohm 663 VA Stand mercury electrode
Generic Instrument Description	The Metrohm 663 VA stand forms the wet chemical part of a polarographic and voltammetric analytical system. It features a mercury electrode, an Ag/AgCl reference electrode and a glassy carbon counter electrode. The size of the mercury drop and the stirrer speed are set manually on the VA Stand. The VA Stand can be operated in Dropping Mercury Electrode (DME), Hanging Mercury Drop Electrode (HMDE) and Static Mercury Drop Electrode (SMDE) modes. The VA Stand can be controlled by a potentiostat in conjunction with the Metrohm IME663 interface.

Dataset-specific Instrument Name	Eco-Chemie uAutolabIII
Generic Instrument Name	Voltammetry Analyzers
Generic Instrument Description	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

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#### Deployments

#### TN280

Website	https://www.bco-dmo.org/deployment/664928	
Platform	R/V Thomas G. Thompson	
Start Date	2012-05-16	
End Date	2012-05-22	

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#### **Project Information**

The relationship between microbial biogeography and ocean chemistry across a persistent oceanographic "hot spot" in the NE Pacific Ocean (GeoMICS Chem)

Coverage: Northeast Pacific Ocean: 48.5N 126W

#### NSF Award Abstract:

The oceans are undergoing dramatic changes. Currently, two largely independently operating research communities -- geochemists and molecular ecologists -- examine potential biological repercussions of changes in ocean chemistry and physics. Geochemists focus primarily on large-scale resultant chemical features, with limited knowledge of underlying biological drivers. Molecular ecologists focus primarily on biodiversity of microbial ecosystems, with few direct linkages to process rates.

With funding from this Early-Concept Grant for Exploratory Research (EAGER), a marine molecular biologist from the University of Washington, a marine inorganic biochemist from the University of Southern California, and a marine trace metal geochemist from Old Dominion University will conduct a multi-parameter exploratory survey cruise to collect and analyze shared geochemical and molecular data to identify chemical and physical drivers of distinct biogeochemical provinces in the sea. They have targeted a well-defined gradient in biogeochemical properties in the northeast Pacific where high nutrient, low chlorophyll waters limited by iron meet low nutrient, iron-replete waters with the long-term goal of understanding the sensitivity of province boundaries to climate change. The transition zone is a surrogate for a geochemical province boundary and is characterized by high biological activity and strong gradients in chemical parameters.

The team hypothesizes that the physical/chemical front creates a distinctive biome with a disproportionate impact on the biogeochemistry of the region, an attribute that may be a fundamental feature of province boundaries. Accordingly, they will characterize multiple biological and chemical parameters on a detailed surface to seafloor zonal survey across this zone. Biological parameters include metagenomes and metatranscriptomes of the microbial community from surface to seafloor at carefully selected stations and gene-focused surveys at more broadly distributed stations. Chemical parameters at all stations include nutrients and dissolved concentrations of Fe, Cu, Zn, Cd, Mn, Co and Ni, key parameters in the GEOTRACES program. Shipboard work will include short-term (12-24 hr) on-deck incubations to examine relationships between rate processes and changes in community composition.

This project is well suited to EAGER funding. The high risk associated with bringing these two research communities together to synthesize resulting data in meaningful ways is mitigated by the high reward associated with learning how to conduct oceanographic work in entirely new ways, moving beyond correlations to causations between biology and chemistry.

This study is motivated by the results from an NSF-sponsored community workshop that highlighted the transformative potential of bringing these two communities together to address underlying drivers of geochemical provinces. The team will invite cruise participation by a broad representation of the two communities, with a central requisite that all participants are broad thinkers that will readily share data in a timely fashion. Member of the U.S. Ocean Carbon and Biogeochemistry (OCB) Scientific Steering Committee have encouraged submission of a proposal for a post-cruise meeting to share successes and "lessons learned". The results of this EAGER project will allow evaluation of the feasibility of joint molecular/geochemical sectional surveys on the scale of programs such as CLIVAR and GEOTRACES

## Characterizing biological function across a persistent oceanographic "hotspot" in the NE Pacific Ocean (GeoMICS Bio)

Coverage: Northeast Pacific Ocean: 48.5N 126W

#### NSF Award Abstract:

Every cubic centimeter of oceanic water is home to millions of single celled organisms that are the engines of the majority of biological activity in the ocean. These organisms form functional communities that are key to our understanding of how the ocean benefits us through providing ecosystem services and hinders us through disease and harmful algal blooms. The underlying causes that shape the distribution and activity of organisms remain elusive, resulting in impaired predictive ability. This project will bring oceanographic research into the post-genomic era by joining genomics and transciptomics with state of the art tools in proteomics, metabolomics and trace metal analyses to understand the causes for observed biogeography and biological activity. The project is a multi-faceted study of the structure and function of microbial communities along a transect in the Northeast Pacific that crosses an oceanographic "hotspot" that results from the mixing of high nutrient low chlorophyll waters with coastal iron rich waters.

This project is appropriate as an EAGER award due to the high risk associated with combining numerous cutting edge techniques carried out by a highly multidisciplinary team for the first time. The team includes individuals in the geochemistry community that are accustomed to viewing the end result of biological activity on a large spatial and time integrated scale, and molecular ecologists who interrogate organisms and communities for their evolutionary roots, metabolic capabilities and physiological status. The project is a test bed for an integrated study that includes a complete set of "omics" data along with cell quotas for trace metals. The project will generate a large data set that will be shared with the broader community as well as analyzed by the PIs. Cells in the environment carry out their metabolic processes in the context of a chemical environment. By interrogating cellular functions in the form of the proteome, metabolome and metallome, the investigators are asking the cells to tell us what they sense in the environment and how they respond to what they are sensing. These findings will represent a major step toward redefining how we do oceanography such that a complete understanding of microbial communities can lead us to predictions of how the ocean will respond to ongoing change.

This project follows on an ocean carbon and biogeochemistry workshop that discussed how molecular ecologists might collaborate with geochemists to better understand biogeochemical processes in the world oceans. It is expected that successful completion of this proof of concept cruise will lead to larger interdisciplinary program with the ongoing U.S. Geotraces program. This particular project will demonstrate how using -omics approaches, in conjunction with metagenomic and geochemical sampling, can provide the key to linking structure with function across ocean biomes. As part of this project there will be training for the next generation of oceanographers to work in a multidisciplinary community. Undergraduate students will participate on the cruise and will be entrained in research projects using the data generated. A large data set will be made available to the entire oceanographic community, so that participation will be considerably larger than the small group of investigators participating in the cruise.

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#### **Program Information**

#### GeoMICS (GeoMICS)

Coverage: Northeast Pacific Ocean: 48.5N 126W

The GeoMICS (Global scale Microbial Interactions across Chemical Surveys) research effort grew out of an Ocean Carbon and Biogeochemistry (OCB) workshop that discussed how molecular ecologists might collaborate with geochemists to better understand biogeochemical processes in the world oceans. The workshop highlighted the potential of bringing these two communities together. The first GeoMICS cruise was carried out in May 2012 on the R/V Thompson along a subset of Line P. Goals included:

- Identify interactions between changes in microbial diversity, community functions, and chemical features across a gradient.
- Coordinate sampling protocols: inorganic geochemistry, organic geochemistry, and molecular biology.

In February 2013, an OCB-sponsored workshop was held to coordinate data analysis among the groups of participants (inorganic geochemists, organic geochemists, molecular ecologists, modelers, and computer scientists).

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### Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1205232
NSF Division of Ocean Sciences (NSF OCE)	OCE-1205233
NSF Division of Ocean Sciences (NSF OCE)	OCE-1233261

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