Pore water geochemistry from sediment cores collected on the R/V Nathaniel B. Palmer cruise NBP1601 to the West Antarctic continental shelf in January of 2016

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Project
» Organic Carbon Oxidation and Iron Remobilization by West Antarctic Shelf Sediments (Antarctic Shelf Sediments)

Contributors	Affiliation	Role
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Abstract
Pore water geochemistry from sediment cores collected on the R/V Nathaniel B. Palmer cruise NBP1601 to the West Antarctic continental shelf in January of 2016.

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Coverage

Spatial Extent: **N**:-64.1583 **E**:-62.7317 **S**:-67.7717 **W**:-71.2217
Temporal Extent: 2016-01-14 - 2019-01-28

Methods & Sampling

Sediment and pore water collection:

Short sediment cores were collected using a Bowers & Connelly megacorer, a multiple coring device that can collect ~20-40 cm long sediment cores with undisturbed sediment surfaces. At two sites (stations 41 and 64) longer cores (up to ~2 m) were also collected with a Kasten corer.

Megacorer cores were either sectioned for solid phase analysis, profiled with polarographic microelectrodes to determine dissolved O2 concentrations, or sectioned in a cold van under N2 for pore water sample extraction (for details see, Komada et al., 2016). Kasten cores were brought into a large cold room on-board ship, laid on their side and one side of the core box removed to expose the sediment in the core. A plastic block was placed against the top of the core to prevent slumping of the sediment during processing, and pore waters were collected from these cores using Rhizon samplers (Seeberg-Elverfeldt et al., 2005) inserted directly into the

cores at measured intervals.

Pore water samples collected from both types of cores were filtered through 0.45 µm polycarbonate filters and processed as follows. Samples for alkalinity determinations were stored without a headspace in 3-ml plastic syringes sealed with 3-way stopcocks. Titrated alkalinity samples (acidified to pH ~4 after titration) were stored in plastic snap cap vials, refrigerated and returned to ODU for the analysis of dissolved sulfate. Pore water samples collected for the analysis of total dissolved Fe and Mn were acidified to pH <2 on-board ship with trace metal grade HCl, and store refrigerated until analyzed back at ODU. Samples for pore water silicate analyses were analyzed on board the research vessel. Additional samples for the analysis of other dissolved nutrients (nitrate, nitrite, ammonium, phosphate) were filtered into tightly capped sample vials and frozen for return to NEOL for analysis. Selected pore water samples (collected as described above) were also used for the determination of dissolved organic carbon (DOC). These samples were filtered directly into acid-cleaned and muffled (550 °C for at least 4 h) glass ampules and were then acidified to pH < 2 with 6 N trace metal grade HCl and flame-sealed under a stream of UHP N2 gas. The sealed ampules were stored refrigerated and returned to ODU for analysis.

While it is possible to recover cores with intact sediment-water interfaces using a megacorer, loss of surface sediments is typical during Kasten coring, making it not possible to directly determine absolute depths below the sediment-water interface in a Kasten core. We therefore determined the absolute depths of pore water and solid phase sample intervals from Kasten cores by aligning Kasten core profiles of pore water alkalinity to megacore alkalinity profiles from the same site (Berelson et al., 2005; Komada et al., 2016).

Bottom water collection:

Bottom waters were collected by GO-Flo Bottles ~5-10 m off the seafloor. They were filtered through 0.45 µm polycarbonate filters and processed as described above for pore water samples.

Pore water analyses: Sampled collected for alkalinity determination were titrated aboard ship within 12 hours of collection by automated Gran titration (Hu and Burdige, 2008). Dissolved sulfate was determined on titrated alkalinity samples returned to ODU by ion chromatography and conductivity detection (Thermo-Scientific Dionex ICS-5000; Burdige and Komada, 2011; Komada et al., 2016). Concentrations of DOC were determined at ODU by high temperature combustion using a Shimadzu TOC-V total carbon analyzer (Komada et al., 2013; Komada et al., 2016). Frozen samples for the determination of dissolved nutrients were returned to NEOL and analyzed by autoanalyzer for nitrate and nitrite (Armstrong et al., 1967; Pavlou, 1972), ammonium (Koroleff, 1970; Slawyk and MacIsaac, 1972) and dissolved inorganic phosphate (Drummond and Maher, 1995). Pore water silicate was determined on board the research vessel used fresh pore water samples and a manual colorimetric method following Armstrong et al. (1967).

Pore water dissolved iron was determined colorimetrically at ODU using the ferrozine technique (Stookey, 1970; Viollier et al., 2000). Hydroxylamine-HCl (0.2% final concentration) was added to the samples before analysis, to reduce any dissolved Fe3+ in the samples to Fe2+. The pore water iron results reported here therefore represent total dissolved iron (i.e., Fe2+ plus any Fe3+ in the samples). This was done largely as a precaution against any iron oxidation that may have occurred during sample storage, since it is assumed that virtually all of the dissolved iron in these pore waters exists in situ as Fe2+ (e.g., Viollier et al., 2000).

Samples for the analysis of dissolved manganese were determined with a modification of the colorimetric formaldoxime method (Armstrong et al., 1979; Goto et al., 1962). These modifications were made based on the observation that the amount of EDTA typically added to destroy the Fe-formaldoxime complexes that interfere with the colorimetric determination of the Mn-formaldoxime complexes was insufficient because of the complexation (and presumed competition) of this EDTA by the much higher levels of dissolved Ca2+ and Mg2+ in our pore water samples (60 mM assuming a pore water salinity of ~35). Thus it was necessary to increase the amount of EDTA added to the samples so that it exceeded these Ca2+ plus Mg2+ levels.

In our method we made the formaldoxime mixed reagent by dissolving 8 g of hydroxylamine hydrochloride and 4ml formaldehyde (37%) in 200 ml of distilled deionized water. Next we combined 0.5 ml of either a pore water sample or Mn2+ standard with 0.5 ml of distilled deionized water and: 50 µl of the formaldoxime mixed reagent, 50 µl of concentrated (50%) NH4OH, 50 µl of a 20% hydroxylamine hydrochloride solution, and 0.2 ml of a 250 mM EDTA solution. The color of the solution was allowed to develop for 20 min. and then analyzed at 450 nm.

Data Processing Description

BCO-DMO Data Manager Processing Notes:
* Data from file "pore water data.txt" imported into the BCO-DMO data system.
* added a conventional header with dataset name, PI name, version date
* modified parameter names to conform with BCO-DMO naming conventions (spaces, +, and - changed to underscores).
* blank values and values "-" in this dataset are displayed as "nd" for "no data." nd is the default missing data identifier in the BCO-DMO system. Conrimed that "-" is a missing data identifier with the data submitter.
* Joined with supplemental station information file to add station lat, lon, and ISO 8601 timestamp (UTC) into the dataset.

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Data Files

File
porewater.csv (Comma Separated Values (.csv), 42.67 KB) MD5:b2cbfa4d5edc5a0744618f2589005419 Primary data file for dataset ID 813166

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Supplemental Files

File
NBP 1601 Station Information filename: stations.csv (Comma Separated Values (.csv), 1.63 KB) MD5:2d8b6e6a1341ed3f9d2e6e61d7368c6c Station locations and sampling information on cruise NBP 1601 (R/V Nathaniel B. Palmer, January 2016). Comma delimited file with column names: St_ID,Mo,Da,Yr,Time,Lat,Lon,Activity,ISO_DateTime_UTC Parameter information: St_ID,Station identifier,unitless Mo,"Month (local time, Punta Arenas, UTC-3)",unitless Da,"Day (local time, Punta Arenas, UTC-3)",unitless Yr,"Year in format yyyy (local time, Punta Arenas, UTC-3)",unitless Time,"Time in format HH:MM (local time, Punta Arenas, UTC-3)",unitless Lat,Station latitude,decimal degrees Lon,Station longitude,decimal degrees Activity,"C = CTD cast; M = Mega-core collected; K = Kasten core collected",unitless ISO_DateTime_UTC,Station date and time (UTC) in ISO 8601 format yyyy-mm-ddTHH:MMZ,unitless

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Related Publications

Armstrong, F. A. J., Stearns, C. R., & Strickland, J. D. H. (1967). The measurement of upwelling and subsequent biological process by means of the Technicon Autoanalyzer® and associated equipment. Deep Sea Research and Oceanographic Abstracts, 14(3), 381–389. doi:10.1016/0011-7471(67)90082-4

Methods

Armstrong, P. B., Lyons, W. B., & Gaudette, H. E. (1979). Application of Formaldoxime Colorimetric Method for the Determination of Manganese in the Pore Water of Anoxic Estuarine Sediments. Estuaries, 2(3), 198. doi:10.2307/1351736
Methods

Burdige, D. J., & Komada, T. (2011). Anaerobic oxidation of methane and the stoichiometry of remineralization processes in continental margin sediments. Limnology and Oceanography, 56(5), 1781–1796. doi:10.4319/lo.2011.56.5.1781
Methods

Drummond, L., & Maher, W. (1995). Determination of phosphorus in aqueous solution via formation of the phosphoantimonylmolybdenum blue complex. Re-examination of optimum conditions for the analysis of phosphate. Analytica Chimica Acta, 302(1), 69–74. doi:10.1016/0003-2670(94)00429-p https://doi.org/10.1016/0003-2670(94)00429-P
Methods

Goto, K., Komatsu, T., & Furukawa, T. (1962). Rapid colorimetric determination of manganese in waters containing iron. Analytica Chimica Acta, 27, 331–334. doi:10.1016/s0003-2670(00)88510-4 https://doi.org/10.1016/S0003-2670(00)88510-4
Methods

Hu, X., & Burdige, D. J. (2008). Shallow marine carbonate dissolution and early diagenesis—Implications from an incubation study. Journal of Marine Research, 66(4), 489–527. doi:10.1357/002224008787157449
Methods

Komada, T., Burdige, D. J., Crispo, S. M., Druffel, E. R. M., Griffin, S., Johnson, L., & Le, D. (2013). Dissolved organic carbon dynamics in anaerobic sediments of the Santa Monica Basin. Geochimica et Cosmochimica Acta, 110, 253–273. doi:10.1016/j.gca.2013.02.017
Methods

Komada, T., Burdige, D. J., Li, H.-L., Magen, C., Chanton, J. P., & Cada, A. K. (2016). Organic matter cycling across the sulfate-methane transition zone of the Santa Barbara Basin, California Borderland. Geochimica et Cosmochimica Acta, 176, 259–278. doi:10.1016/j.gca.2015.12.022
Methods

Koroleff, F. (1970) Revised version of "Direct determination of ammonia in natural waters as indophenol blue, Int. Con. Explor. Sea, C. M. 1969/C:9". ICES Information on Techniques and Methods for Sea Water Analysis Interlab. Rep. No. 3, pp 19-22.
Methods

Pavlou, S. P. (1972) Phytoplankton growth dynamics. Technical series 1, chemostat methodology and chemical analyses. Special Report No 52, Dept. of Oceanography, University of Washington, Seattle, WA 98195, p. 130.
Methods

Seeberg-Elverfeldt, J., Schlüter, M., Feseker, T., & Kölling, M. (2005). Rhizon sampling of porewaters near the sediment-water interface of aquatic systems. Limnology and Oceanography: Methods, 3(8), 361–371. doi:10.4319/lom.2005.3.361
Methods

Slawyk, G., & MacIsaac, J. J. (1972). Comparison of two automated ammonium methods in a region of coastal upwelling. Deep Sea Research and Oceanographic Abstracts, 19(7), 521–524. doi:10.1016/0011-7471(72)90019-8
Methods

Stookey, L. L. (1970). Ferrozine---a new spectrophotometric reagent for iron. Analytical Chemistry, 42(7), 779–781. doi:10.1021/ac60289a016
Methods

Viollier, E., Inglett, P. ., Hunter, K., Roychoudhury, A. ., & Van Cappellen, P. (2000). The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. Applied Geochemistry, 15(6), 785–790. doi:10.1016/s0883-2927(99)00097-9 https://doi.org/10.1016/S0883-2927(99)00097-9
Methods

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Parameters

Parameter	Description	Units
St_ID	station ID number	unitless
Sa_ID	sample ID (station ID #- core ID #-sample # (BW = bottom water sample; note BW samples have no sample #)	unitless
Core	core type (H = samples collected by hydrocast; M = mega-corer; K = Kasten corer)	unitless
Samp	how pore waters/bottom waters were collected (C = centrifugation; R = rhizon sampler; G = hydrocast/GO-Flo bottle; see Methodology for details)	unitless
Depth	sediment depth (relative to the sediment-water interface; 0 = bottom water sample)	centimeters (cm)
Error	half the thickness of the sediment sample (note: Rhizon samples are collected at discrete depths and there is no error associated with their depths)	centimeters (cm)
pH	initial pH of sample titrated for alkalinity	NBS scale
Alk	pore water alkalinity	millimolar (mM)
Fe	pore water total dissolved iron	micromolar (uM)
Mn	pore water dissolved Mn	micromolar (uM)
SO4	pore water dissolved sulfate	millimolar (mM)
DOC	pore water dissolved organic carbon	micromolar (uM)
NO3	pore water dissolved nitrate	micromolar (uM)
NO2	pore water dissolved nitrite	micromolar (uM)
NH4	pore water dissolved ammonium	micromolar (uM)
PO4	pore water dissolved orthophosphate	micromolar (uM)
Si	pore water dissolved silicate	micromolar (uM)

ISO_DateTime_UTC	station timestamp (UTC) in ISO 8601 format yyyy-mm-ddTHH:MMZ	unitless
Lat	station latitude, south is negative	decimal degrees
Lon	station longitude, west is negative	decimal degrees

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	GO-FLO Bottle
Generic Instrument Description	A GO-FLO (also written as "Go-Flo") bottle is used to collect discrete water samples at depth, often for analyses of pigments, nutrients, plankton, etc. The GO-FLO sampling bottle, made by General Oceanics, 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	Kasten corer
Generic Instrument Name	Gravity Corer
Generic Instrument Description	The gravity corer allows researchers to sample sediment layers at the bottom of lakes or oceans. The coring device is deployed from the ship and gravity carries it to the seafloor. From: http://www.whoi.edu/instruments/viewInstrument.do?id=1079

Dataset-specific Instrument Name	Bowers & Connelly megacorer
Generic Instrument Name	Multi Corer
Generic Instrument Description	The Multi Corer is a benthic coring device used to collect multiple, simultaneous, undisturbed sediment/water samples from the seafloor. Multiple coring tubes with varying sampling capacity depending on tube dimensions are mounted in a frame designed to sample the deep ocean seafloor. For more information, see Barnett et al. (1984) in Oceanologica Acta, 7, pp. 399-408.

Dataset-specific Instrument Name	
Generic Instrument Name	Nutrient Autoanalyzer
Dataset-specific Description	Frozen samples for the determination of dissolved nutrients were returned to NEOL and analyzed by autoanalyzer for nitrate and nitrite (Armstrong et al., 1967; Pavlou, 1972), ammonium (Koroleff, 1970; Slawyk and MacIsaac, 1972) and dissolved inorganic phosphate (Drummond and Maher, 1995).
Generic Instrument Description	Nutrient Autoanalyzer is a generic term used when specific type, make and model were not specified. In general, a Nutrient Autoanalyzer is an automated flow-thru system for doing nutrient analysis (nitrate, ammonium, orthophosphate, and silicate) on seawater samples.

Dataset-specific Instrument Name	Shimadzu TOC-V total carbon analyzer (Komada et al., 2013; Komada et al., 2016).
Generic Instrument Name	Shimadzu TOC-V Analyzer
Generic Instrument Description	A Shimadzu TOC-V Analyzer measures DOC by high temperature combustion method.

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Deployments

NBP1601

Website	https://www.bco-dmo.org/deployment/813143
Platform	RVIB Nathaniel B. Palmer
Start Date	2016-01-08
End Date	2016-02-03

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Project Information

Organic Carbon Oxidation and Iron Remobilization by West Antarctic Shelf Sediments (Antarctic Shelf Sediments)

Coverage: West Antarctic Continental Shelf

NSF Award Abstract:

General Statement:

The continental shelf region west of the Antarctic Peninsula has recently undergone dramatic changes and ecosystem shifts, and the community of organisms that live in, or feed off, the sea floor sediments is being impacted by species invasions from the north. Previous studies of these sediments indicate that this community may consume much more of the regional productivity than previously estimated, suggesting that sediments are a rich and important component of this ecosystem and one that may be ripe for dramatic change. Furthermore, under richer sediment conditions, iron is mobilized and released back to the water column. Since productivity in this ecosystem is thought to be limited by the availability of iron, increased rates of iron release from these sediments could stimulate productivity and promote greater overall ecosystem

change. In this research, a variety of sites across the shelf region will be sampled to accurately evaluate the role of sediments in consuming ecosystem productivity and to estimate the current level of iron release from the sediments. This project will provide a baseline set of sediment results that will present a more complete picture of the west Antarctic shelf ecosystem, will allow for comparison with water column measurements and for evaluation of the fundamental workings of this important ecosystem. This is particularly important since high latitude systems may be vulnerable to the effects of climate fluctuations. Both graduate and undergraduate students will be trained. Presentations will be made at scientific meetings, at other universities, and at outreach events. A project web site will present key results to the public and explain how this new information improves understanding of Antarctic ecosystems.

Technical Description of Project:
In order to determine the role of sediments within the west Antarctic shelf ecosystem, this project will determine the rates of sediment organic matter oxidation at a variety of sites across the Palmer Long Term Ecosystem Research (LTER) study region. To estimate the rates of release of iron and manganese from the sediments, these same sites will be sampled for detailed vertical distributions of the concentrations of these metals both in the porewaters and in important mineral phases. Since sediment sampling will be done at LTER sites, the sediment data can be correlated with the rich productivity data set from the LTER. In detail, the project: a) will determine the rates of oxygen consumption, organic carbon oxidation, nutrient release, and iron mobilization by shelf sediments west of the Antarctic Peninsula; b) will investigate the vertical distribution of diagenetic reactions within the sediments; and c) will assess the regional importance of these sediment rates. Sediment cores will be used to determine sediment-water fluxes of dissolved oxygen, total carbon dioxide, nutrients, and the vertical distributions of these dissolved compounds, as well as iron and manganese in the pore waters. Bulk sediment properties of porosity, organic carbon and nitrogen content, carbonate content, biogenic silica content, and multiple species of solid-phase iron, manganese, and sulfur species will also be determined. These measurements will allow determination of total organic carbon oxidation and denitrification rates, and the proportion of aerobic versus anaerobic respiration at each site. Sediment diagenetic modeling will link the processes of organic matter oxidation to metal mobilization. Pore water and solid phase iron and manganese distributions will be used to model iron diagenesis in these sediments and to estimate the iron flux from the sediments to the overlying waters. Finally, the overall regional average and distribution of the sediment processes will be compared with the distributions of seasonally averaged chlorophyll biomass and productivity.

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Funding

Funding Source	Award
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1551195

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