

Methane (CH₄) isotopes from vertical profiles from multi- and gravity cores from cruises R/V Robert Gordon Sproul SP1215 and R/V New Horizon NH1319 in the Santa Barbara and Santa Monica Basins in 2012 and 2013

Website: <https://www.bco-dmo.org/dataset/662754>

Data Type: Cruise Results

Version: 15 June 2016

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Project

» [Dissolved organic carbon \(DOC\) transformations in deep sub-surface sediments and its role as a source of "old" DOC to the water column](#) (DOC cycling in sediments)

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Dataset Description

Methane isotopes from vertical profiles from multi- and gravity cores from two research cruises, SP1215 and NH1319, in the Santa Monica and Santa Barbara Basins.

Related datasets:

[POC and Isotopes](#)

[DOC and Isotopes](#)

[Other Solutes](#)

[Porosity](#)

[DIC and Isotopes](#)

Methods & Sampling

Sediment cores were recovered using the following coring equipment:
Ocean Instruments multicorer MC-800 (SP1215) and MC-400 (NH1319)
OSU Gravity Core (6 meters long, 4 inch diameter)
OSU "Big Bertha" Core (12 meters long, 4 inch diameter)

Multi cores were immediately transferred into a refrigerated van. They were then extruded in an N₂ atmosphere within 2-12 hours of recovery.

Gravity cores were sectioned on deck immediately upon recovery. All but one of the gravity cores were secured horizontally on the ship's deck and sampled from the bottom of the core upwards by sequentially removing 10 cm sediment intervals by cutting the core liner using a pipe cutter. One core was secured vertically and sampled similarly, but from the top down. Freshly exposed sediment was immediately subsampled using 3- to 60-mL push corers made of plastic syringes with the tips removed. All subcores, except those for methane (see next paragraph), were immediately transferred to a N₂ filled glove bag in the refrigerated van for further processing.

All sediment aliquots were centrifuged in polycarbonate tubes at 4 degrees C. The supernatant was collected into all-polypropylene syringes with stainless steel needles, and filtered through disposable 0.2 μ m nylon filters with 0.7 μ m GF/F pre-filter (Whatman 6870-2502). The first 3 mL were discarded. To minimize the DOC blank, 100 mL of UV-irradiated deionized water were pushed through each disposable filter prior to use. DIC samples for $\delta^{13}\text{C}$ and $\delta^{14}\text{C}$ abundances were immediately flame-sealed under a stream of ultra-high-purity (UHP) N₂ into 10-15 mL borosilicate tubes spiked with HgCl₂ following (McCorkle et al., 1985). DOC samples for concentration determination only were acidified and ampouled under a stream of UHP N₂ gas and refrigerated. DOC samples for isotopic analyses were frozen without acidification in 20 mL scintillation vials with Teflon-lined caps. Samples for methane concentration and $\delta^{13}\text{C}$ values were immediately placed into 20-mL serum glass vials (Wheaton) containing a 5-mm glass bead, basified, sealed with a blue butyl rubber septum (Chemglass), homogenized, crimp sealed, and stored upside down at room temperature until analysis. For analysis of $\delta^{14}\text{C}$ values of methane, 150- and 250-mL sediment aliquots were immediately placed into 250- and 500-mL glass media bottles (VWR) containing 80 and 100 mL of 1 M KOH solution, respectively. The bottles were immediately capped with #7 rubber stoppers, sealed thoroughly with electric tape, screw capped, and stored upside down at room temperature until analysis. Centrifuge tubes containing sediment were frozen.

All tools and parts were first cleaned with household dish soap, then acid rinsed (exclusive of metal parts). Plasticware was air dried; glassware and metal tools were baked at 550 degrees C for 4 hours. Bottom-water DIC and DOC samples were collected with a Go Flo bottle following DOE (1994) and Beupré et al. (2007), respectively.

For further details including quality assurance measures for DOC, see Komada et al. (2013) and Komada et al. (2016). Also refer to [the table of information on the methods, relative uncertainty, and references for each analyte](#) (PDF).

References:

- Beupré S. R., Druffel E. R. M. and Griffin S. (2007) A low-blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic carbon. *Limnol. Oceanogr. Methods* 5, 174-184.
- Burdige D. J. and Gardner K. G. (1998) Molecular weight distribution of dissolved organic carbon in marine sediment pore waters. *Mar. Chem.* 62, 45-64.
- Burdige D. J. and Zheng S. L. (1998) The biogeochemical cycling of dissolved organic nitrogen in estuarine sediments. *Limnol. Oceanogr.* 43, 1796-1813.
- Cline J. D. (1969) Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454-458.
- DOE (1994) Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water; version 2. eds. A. G. Dickson and C. Goyet, ORNL/CDIAC-74.
- Druffel E. R. M., Williams P. M., Bauer J. E. and Ertel J. R. (1992) Cycling of dissolved and particulate organic matter in the open ocean. *J. Geophys. Res. Ocean.* 97, 15639-15659.
- Gieskes J. M., Gamo T. and Brumsack H. (1991) Chemical methods for interstitial water analysis aboard JOIDES RESOLUTION: Ocean Drilling Program, Technical Note 15.
- Hall P. O. J. and Aller R. C. (1992) Rapid, small-volume, flow injection analysis for SCO₂, and NH₄⁺ in marine and freshwaters. *Limnol. Oceanogr.* 37, 1113-1119.
- Hu X. and Burdige D. J. (2008) Shallow marine carbonate dissolution and early diagenesis - Implications from an incubation study. *J. Mar. Res.* 66, 489-527.
- Hwang J. and Druffel E. R. M. (2005) Blank Correction for $\delta^{14}\text{C}$ measurements in organic compound classes of oceanic particulate matter. *Radiocarbon* 47, 75-87.

Johnson L. and Komada T. (2011) Determination of radiocarbon in marine sediment porewater dissolved organic carbon by thermal sulfate reduction. *Limnol. Oceanogr. Methods* 9, 485–498.

Kanamori S. and Ikegami H. (1980) Computer-processed potentiometric titration for the determination of calcium and magnesium in sea water. *J. Oceanogr. Soc. Japan* 36, 177–184.

Kessler J. D. and Reeburgh W. S. (2005) Preparation of natural methane samples for stable isotope and radiocarbon analysis. *Limnol. Oceanogr. Methods* 3, 408–418.

Komada T., Anderson M. R. and Dorfmeier C. L. (2008) Carbonate removal from coastal sediments for the determination of organic carbon and its isotopic signatures, $\delta^{13}\text{C}$ and $\delta^{14}\text{C}$: comparison of fumigation and direct acidification by hydrochloric acid. *Limnol. Oceanogr. Methods* 6, 254–262.

Komada T., Burdige D. J., Crispo S. M., Druffel E. R. M., Griffin S., Johnson L. and Le D. (2013) Dissolved organic carbon dynamics in anaerobic sediments of the Santa Monica Basin. *Geochim. Cosmochim. Acta* 110, 253–273.

Komada T., Burdige D. J., Li H. L., Magen C., Chanton J. P. and Cada A. K. (2016) Organic matter cycling across the sulfate-methane transition zone of the Santa Barbara Basin, California Borderland. *Geochim. Cosmochim. Acta* 176, 259–278.

Lang S. Q., Butterfield D. A., Schulte M., Kelley D. S. and Lilley M. D. (2010) Elevated concentrations of formate, acetate and dissolved organic carbon found at the Lost City hydrothermal field. *Geochim. Cosmochim. Acta* 74, 941–952.

Lustwerk R. L. and Burdige D. J. (1995) Elimination of dissolved sulfide interference in the flow injection determination of SCO_2 , by addition of molybdate. *Limnol. Oceanogr.* 40, 1011–1012.

Magen C., Lapham L. L., Pohlman J. W., Marshall K., Bosman S., Casso M. and Chanton J. P. (2014) A simple headspace equilibration method for measuring dissolved methane. *Limnol. Oceanogr. Methods* 12, 637–650.

McCorkle D. C., Emerson S. R. and Quay P. D. (1985) Stable carbon isotopes in marine porewaters. *Earth Planet. Sci. Lett.* 74, 13–26.

McNichol A. P., Jones G. A., Hutton D. L., Gagnon A. R. and Key R. M. (1994) The rapid preparation of seawater Sigma CO (sub 2) for radiocarbon analysis at the National Ocean Sciences AMS facility. *Radiocarbon* 36, 237–246.

Data Processing Description

$\delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values were blank-corrected following Hwang and Druffel (2005) and Kessler and Reeburgh (2005).

BCO-DMO Processing:

- replaced blank cells with nd (no data);
- modified parameter names to conform with BCO-DMO naming conventions.

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Data Files

File
CH4.csv (Comma Separated Values (.csv), 4.88 KB) MD5:26ac2e2dd742b9ee12b80b26f2979354 Primary data file for dataset ID 662754

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Parameters

Parameter	Description	Units
cruise_id	Cruise identifier	unitless
core_id	Core identifier	unitless
station	Station number	unitless
nom_depth	Nominal depth in the sediment column	centimeters (cm)
layer_num	Sediment layer ID (for internal record keeping)	unitless
del14C	delta 14C value of methane (Stuiver M. and Polach H.A. 1977, Radiocarbon 19 (3), 355-363.)	per mil
del14C_unc	delta 14C of methane uncertainty	per mil
del13C	delta 13C value (against VPDB standard)	per mil

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	Accelerator Mass Spectrometer
Generic Instrument Description	<p>An AMS measures "long-lived radionuclides that occur naturally in our environment. AMS uses a particle accelerator in conjunction with ion sources, large magnets, and detectors to separate out interferences and count single atoms in the presence of 1×10^{15} (a thousand million million) stable atoms, measuring the mass-to-charge ratio of the products of sample molecule disassociation, atom ionization and ion acceleration." AMS permits ultra low-level measurement of compound concentrations and isotope ratios that traditional alpha-spectrometry cannot provide. More from Purdue University:</p> <p>http://www.physics.purdue.edu/primelab/introduction/ams.html</p>

Dataset-specific Instrument Name	Gravity Core
Generic Instrument Name	Gravity Corer
Dataset-specific Description	Sediment cores were recovered using the following coring equipment: Ocean Instruments multicorer MC-800 (SP1215) and MC-400 (NH1319) OSU Gravity Core (6 meters long, 4 inch diameter) OSU "Big Bertha" Core (12 meters long, 4 inch diameter)
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. (http://www.whoi.edu/instruments/viewInstrument.do?id=1079).

Dataset-specific Instrument Name	
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	multicorer
Generic Instrument Name	Multi Corer
Dataset-specific Description	Sediment cores were recovered using the following coring equipment: Ocean Instruments multicorer MC-800 (SP1215) and MC-400 (NH1319) OSU Gravity Core (6 meters long, 4 inch diameter) OSU "Big Bertha" Core (12 meters long, 4 inch diameter)
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.

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Deployments

SP1215

Website	https://www.bco-dmo.org/deployment/662522
Platform	R/V Robert Gordon Sproul
Start Date	2012-08-19
End Date	2012-08-28

NH1319

Website	https://www.bco-dmo.org/deployment/662448
Platform	R/V New Horizon
Start Date	2013-08-01
End Date	2013-08-09

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Project Information

Dissolved organic carbon (DOC) transformations in deep sub-surface sediments and its role as a source of "old" DOC to the water column (DOC cycling in sediments)

Coverage: Santa Monica Basin

Description from NSF award abstract:

Organic carbon (Corg) remineralization rates are typically highest near the sediment-water interface, and decrease with depth as labile substrates and strong oxidants are consumed. However, in many ocean margin sediments, at the depth interval where sulfate (SO₄=) is exhausted and CH₄ concentrations begin to increase (the sulfate-methane transition; SMT), SO₄= reduction rates typically show strong sub-surface maxima, indicating locally-enhanced microbial activity and carbon turnover. These hot spots for SO₄= reduction are generally attributed to anaerobic oxidation of CH₄ by SO₄=, but a number of studies have found an excess of SO₄= reduction over CH₄ oxidation, indicating the presence of a major additional SO₄= sink in the SMT.

In this project a research team from San Francisco State University, Florida State University, and Old Dominion University will investigate the nature of this SO₄= sink by combining cutting-edge porewater compositional analyses -- δ¹⁴C and δ¹³C of CH₄, dissolved organic and inorganic carbon (DOC and DIC), and 1H-NMR on DOC -- with numerical reactive transport modeling. They will test the hypothesis that the SMT is an oxidation front for not just CH₄, but also for DOC that is produced deeper in the sediment column, and transported upward into the SMT. They will also test the idea that not all of this DOC is oxidized in the SMT, and that some reaches the surface sediments, and represents a source of ¹⁴C-depleted (pre-aged) DOC to the oceans. The premise is that DOC production from Corg is enhanced in methanogenic sediments due to an uncoupling in the anaerobic food chain between terminal metabolism and fermentation reactions involved in the overall Corg remineralization process. The work will focus on two ocean margin sites, Santa Monica Basin and Santa Barbara Basin, which despite their geographic proximity, appear to have different CH₄ dynamics in the deep sediments.

This study should result in a greater understanding of the role of sub-surface sediments in the overall benthic Corg remineralization process, and in the exchange of major elements between the sea floor and the water column. It will also allow testing of the hypothesis that marine sediments are sources of ¹⁴C-depleted, recalcitrant DOC to the overlying water column, thereby addressing a problem that has perplexed chemical oceanography for several decades: what factors control the ¹⁴C signature of DOC in the deep oceans?

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1155764
NSF Division of Ocean Sciences (NSF OCE)	OCE-1155562
NSF Division of Ocean Sciences (NSF OCE)	OCE-1155320

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