

# Depth profiles of dissolved O<sub>2</sub> saturation and isotopologues from the R/V Yellowfin and R/V Kilo Moana from 2016-09-14 to 2017-08-28

**Website:** <https://www.bco-dmo.org/dataset/753594>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2018-11-30

## Project

- » [Collaborative Research: New Constraints on Marine Oxygen Cycling](#) (O<sub>2</sub> isotopologues in the N. Pacific)
- » [Collaborative Research: CaCO<sub>3</sub> Dissolution in the North Pacific Ocean: Comparison of Lab and Field Rates with Biogenic and Abiogenic Carbonates](#) (CDISK\_4)

| Contributors                         | Affiliation   | Role                      |
|--------------------------------------|---|---------------------------|
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## Abstract

Seawater was sampled from Niskin bottles associated with CTD casts on each cruise. Water for these dissolved gas isotope samples was the first to be sampled from a given Niskin bottle. When possible, bottles from the same cast were sampled, but depth profiles often came from separate casts at the same site.

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## Coverage

**Spatial Extent:** N:60 E:-118.4 S:22.75 W:-158

**Temporal Extent:** 2016-09-14 - 2017-08-28

## Dataset Description

Seawater was sampled from Niskin bottles associated with CTD casts on each cruise. Water for these dissolved gas isotope samples was the first to be sampled from a given Niskin bottle. When possible, bottles from the same cast were sampled, but depth profiles often came from separate casts at the same site.

## Methods & Sampling

In general, procedures followed those of Reuer et al. 2007. Briefly, 1 and 2-L bottles were pre-poisoned with

200  $\mu\text{L}$  and 400  $\mu\text{L}$  saturated  $\text{HgCl}_2$  solution, dried, and then evacuated to a pressure of  $< 10^{-3}$  mbar before the gas-tight valve was closed. The Louwer-Hapert 9mm valve sidearm was then filled with distilled water and capped, making sure to remove all visible bubbles, to retard any atmospheric leaks. During sampling, water from the bottom of the Niskin flask was allowed to flow into the sidearm for several seconds (to flush out the distilled water) before the vacuum valve was opened to allow water to be siphoned into the sampling bottle. After sampling—each bottle typically being half full—the sidearm was filled again with seawater and capped until analysis. All gas samples were analyzed within 4 months of sampling.

Before gas analysis, bottles were gently agitated on a shaker table for 48h to equilibrate dissolved gases with the headspace at room temperature (25C). Next, bottles were inverted and the seawater pumped out. Finally, the headspace gases were extracted and purified according to Li et al. (2019), Yeung et al. (2016), and Yeung et al. (2018), in which  $\text{O}_2$  is separated from Ar and  $\text{N}_2$  by gas chromatography.  $\text{O}_2/\text{Ar}$  ratios are standardized relative to atmospheric  $\text{O}_2$  and air dissolved in distilled water. Bulk  $\delta^{18}\text{O}$  and  $17\Delta$  values are standardized against atmospheric  $\text{O}_2$  and  $\text{O}_2$  derived from laser-fluorination of San Carlos Olivine (Yeung et al. 2018). Clumped-isotope  $\Delta^{35}$  and  $\Delta^{36}$  values are standardized against laboratory-generated photolytic and heated-gas standards (Yeung et al. 2014).

$\text{O}_2/\text{Ar}$  ratios were determined by integrating the peak areas for each species on an Aglient 7890B gas chromatograph utilizing thermal conductivity detection. Dissolved  $\text{O}_2$  saturation was determined from these  $\text{O}_2/\text{Ar}$  measurements and checked independently through manometric determination of  $\text{O}_2$  yield and weighing the seawater from which it was extracted. Isotopologue analyses were performed on a custom Nu Instruments Perspective IS high-resolution isotope ratio mass spectrometer at Rice University.

Data was processed as was done in Yeung et al. (2018) for  $\delta^{18}\text{O}$  and  $17\Delta$  values and Yeung et al. (2016) for clumped-isotope values. Dissolved oxygen saturation is calculated using potential temperature and salinity and the  $\text{O}_2$  and Ar saturation calculated using MATLAB programs by Roberta Hamme ( $\text{O}_2\text{sol}$  and  $\text{Arsol}$  from <https://web.uvic.ca/~rhamme/download.html>). These calculated values were compared to measured values to determine  $\text{O}_2/\text{O}_2\text{sat}$ .

## Data Processing Description

BCO-DMO Processing Notes:

- added date and description column
- added conventional header with dataset name, PI name, version date
- modified parameter names to conform with BCO-DMO naming conventions

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## Data Files

| File   |
|--|
| <b>SPOT_CDISK.csv</b> (Comma Separated Values (.csv), 8.88 KB)<br>MD5:27ce15dd8d0ea77901a512bb0f7377a4 |
| Primary data file for dataset ID 753594  |

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## Related Publications

Li, B., Yeung, L. Y., Hu, H., & Ash, J. L. (2019). Kinetic and equilibrium fractionation of  $\text{O}_2$  isotopologues during air-water gas transfer and implications for tracing oxygen cycling in the ocean. *Marine Chemistry*, 210, 61–71. doi:[10.1016/j.marchem.2019.02.006](https://doi.org/10.1016/j.marchem.2019.02.006)

*Results*

Reuer, M. K., Barnett, B. A., Bender, M. L., Falkowski, P. G., & Hendricks, M. B. (2007). New estimates of Southern Ocean biological production rates from O<sub>2</sub>/Ar ratios and the triple isotope composition of O<sub>2</sub>. Deep Sea Research Part I: Oceanographic Research Papers, 54(6), 951–974. doi:[10.1016/j.dsr.2007.02.007](https://doi.org/10.1016/j.dsr.2007.02.007)  
*Methods*

Yeung, L. Y., Ash, J. L., & Young, E. D. (2014). Rapid photochemical equilibration of isotope bond ordering in O<sub>2</sub>. Journal of Geophysical Research: Atmospheres, 119(17), 10552–10566. doi:10.1002/2014jd021909  
<https://doi.org/10.1002/2014jd021909>  
*Methods*

Yeung, L. Y., Hayles, J. A., Hu, H., Ash, J. L., & Sun, T. (2018). Scale distortion from pressure baselines as a source of inaccuracy in triple-isotope measurements. Rapid Communications in Mass Spectrometry, 32(20), 1811–1821. doi:[10.1002/rcm.8247](https://doi.org/10.1002/rcm.8247)  
*Methods*

Yeung, L. Y., Murray, L. T., Ash, J. L., Young, E. D., Boering, K. A., Atlas, E. L., ... Eastham, S. D. (2016). Isotopic ordering in atmospheric O<sub>2</sub> as a tracer of ozone photochemistry and the tropical atmosphere. Journal of Geophysical Research: Atmospheres, 121(20), 12,541–12,559. doi:10.1002/2016jd025455  
<https://doi.org/10.1002/2016jd025455>  
*Methods*

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## Parameters

| Parameter                          | Description  | Units              |
|------------------------------------|--|--------------------|
| description                        | description of the site  | unitless           |
| date                               | date of observation in YYYYMMDD format                                 | unitless           |
| Latitude                           | latitude north   | decimal degrees    |
| Longitude                          | longitude east   | decimal degrees    |
| Depth                              | niskin bottle closing depth  | meters (m)         |
| O <sub>2</sub> _O <sub>2</sub> sat | Dissolved O <sub>2</sub> saturation                                    | unitless           |
| d18O                               | 18O value of O <sub>2</sub> relative to air-O <sub>2</sub>             | parts per thousand |
| D17O                               | 17Δ value of O <sub>2</sub> relative to air-O <sub>2</sub> ; λ = 0.518 | parts per million  |
| D35                                | 35 value of O <sub>2</sub>   | parts per thousand |
| D36                                | 36 value of O <sub>2</sub>   | parts per thousand |

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## Instruments

|   |   |
|---|---|
| <b>Dataset-specific Instrument Name</b> | mass spectrometer   |
| <b>Generic Instrument Name</b>          | Mass Spectrometer   |
| <b>Dataset-specific Description</b>     | Isotopologue analyses were performed on a custom Nu Instruments Perspective IS high-resolution isotope ratio mass spectrometer at Rice University.  |
| <b>Generic Instrument Description</b>   | General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components. |

|   |   |
|---|---|
| <b>Dataset-specific Instrument Name</b> | Niskin bottles  |
| <b>Generic Instrument Name</b>          | Niskin bottle   |
| <b>Dataset-specific Description</b>     | Seawater was sampled from Niskin bottles associated with CTD casts on each cruise.  |
| <b>Generic Instrument Description</b>   | 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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## Project Information

### Collaborative Research: New Constraints on Marine Oxygen Cycling (O<sub>2</sub> isotopologues in the N. Pacific)

**Coverage:** San Pedro Ocean Time Series (33.5 N 118.4 W)

NSF Abstack:

Marine oxygen is strongly linked to the cycling of organic matter in the marine environment, and as such, its budget is central to addressing many of the outstanding questions in oceanography. In this study, researchers will measure the amounts of three isotopes of oxygen that can combine to make up the molecular oxygen gas dissolved in oceanic waters. When oxygen reacts with other substances, the three isotopes can behave in slightly different ways depending on the type of reactions; this makes it possible to identify the kinds of processes that have led to the existence of the oxygen found at different places in the ocean. These results are expected to yield new insights into how oxygen interacts with organisms, organic matter, minerals, and other substances under a variety marine environmental conditions, with important implications for future studies of ocean productivity and hypoxic (low oxygen) zones in the ocean. A female graduate student will gain hands-on experience with these new methods, and results from the research will be disseminated to the general public through social media and a video.

In this project, researchers will make simultaneous measurements of five stable isotopic variants of O<sub>2</sub>, known

as quintuple-isotopologue analysis, to provide new constraints on marine oxygen cycling. Using a combined field and experimental study they will evaluate the potential for the quintuple-isotopologue method to trace marine O<sub>2</sub> cycling. Utilizing these novel analytical methods, they will analyze depth profiles and dark bottle incubations of O<sub>2</sub> isotopologues in the water column at San Pedro Ocean Time Series (SPOT). These measurements, combined with nutrient profiles and complementary laboratory experiments, will yield a first-order understanding of how photosynthesis, respiration, and mixing affect the isotopologue composition of dissolved marine O<sub>2</sub>.

## **Collaborative Research: CaCO<sub>3</sub> Dissolution in the North Pacific Ocean: Comparison of Lab and Field Rates with Biogenic and Abiogenic Carbonates (CDISK\_4)**

**Coverage:** NE Pacific transect (22.75 N to 60 N, 150-160 W)

### *NSF Award Abstract:*

Ocean acidification (OA) is the decrease in seawater pH due to increased oceanic uptake of anthropogenic carbon dioxide (CO<sub>2</sub>) from the atmosphere. The impact of this uptake in the marine environment is lessened by the dissolution of calcium carbonate (CaCO<sub>3</sub>) to calcium and carbonate ions, allowing carbonate ions to bind free hydrogen ions that cause the decrease in pH. Researchers from the University of Southern California and California Institute of Technology have developed a new method for determining carbonate dissolution rates that work in both laboratory and field settings. Preliminary data using this technique has revealed a distinct difference in measured rates between those obtained in the laboratory and those in the field. It is crucial that laboratory and field measurements be standardized to be able to accurately study and compare dissolution rate studies. As such, the researchers will perform extensive fieldwork and laboratory to bridge the gap between these dissolution rate measurements. Results will be widely useful to the ocean chemistry community, especially modelers, wishing to study any aspect of ocean carbonate chemistry, as well as paleoceanographers using carbonate material to study past ocean conditions. Graduate students will be co-mentored by the researchers, and the University of Southern California's (USC) Young Researcher Program will allow the researchers to involve local high school students. USC International Relations students will be involved in the project, not only gaining scientific experience, but also will learn the policy aspect of the science.

Calcium carbonate (CaCO<sub>3</sub>) dissolution helps to mitigate the effects of ocean acidification (OA) and is a key factor in the ocean's alkalinity balance. The researchers have recently developed a novel tracer methodology which can monitor carbonate dissolution rates in both the lab and field. This method traces the transfer of <sup>13</sup>C from labeled solids to seawater. Using this method has led to breakthroughs in understanding the controls of CaCO<sub>3</sub> dissolution kinetics, but it has also revealed that the measurements made in a lab and in the field are not entirely in line. It is crucial to be able to correlate these two measurements to be able to fully study and understand the dynamics of CaCO<sub>3</sub> dissolution. Therefore, the researchers will extend their previous work to standardize the results of measurements in the lab with those in the ocean. The North Pacific Ocean with a gradient in carbonate saturation states will be used for the field study, and lab-based experiments will allow the researchers to constrain variables such as pressure, the dissolved inorganic carbon/alkalinity ratio, and concentrations of phosphate. This research will further understanding of OA, the mechanisms controlling carbonate dissolution, and how the ocean modulates its alkalinity budget.

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## **Funding**

| <b>Funding Source</b>                                    | <b>Award</b>                |
|--|-----------------------------|
| <a href="#">NSF Division of Ocean Sciences (NSF OCE)</a> | <a href="#">OCE-1436590</a> |
| <a href="#">NSF Division of Ocean Sciences (NSF OCE)</a> | <a href="#">OCE-1533501</a> |
| <a href="#">NSF Division of Ocean Sciences (NSF OCE)</a> | <a href="#">OCE-1436326</a> |
| <a href="#">NSF Division of Ocean Sciences (NSF OCE)</a> | <a href="#">OCE-1559004</a> |
| <a href="#">NSF Division of Ocean Sciences (NSF OCE)</a> | <a href="#">OCE-1559215</a> |

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