Deep-Sea Research II ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

# Biological and physical controls on $O_2$/Ar, Ar and $pCO_2$ variability at the Western Antarctic Peninsula and in the Drake Passage

R. Eveleth [a,*], N. Cassar [a], S.C. Doney [b], D.R. Munro [c], C. Sweeney [d,e]

[a] Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, NC, USA
[b] Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA
[c] Department of Atmospheric and Oceanic Sciences and Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO, USA
[d] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
[e] NOAA Earth System Research Laboratory, Boulder, CO, USA

ARTICLE INFO

*Keywords:*
Oxygen
Carbon
Gas exchange
Variability
Southern Ocean

ABSTRACT

Using simultaneous sub-kilometer resolution underway measurements of surface $O_2$/Ar, total $O_2$ and $pCO_2$ from annual austral summer surveys in 2012, 2013 and 2014, we explore the impacts of biological and physical processes on the $O_2$ and $pCO_2$ system spatial and interannual variability at the Western Antarctic Peninsula (WAP). In the WAP, mean $O_2$/Ar supersaturation was $(7.6 \pm 9.1)$% and mean $pCO_2$ supersaturation was $(-28 \pm 22)$%. We see substantial spatial variability in $O_2$ and $pCO_2$ including sub-mesoscale/mesoscale variability with decorrelation length scales of ~4.5 km, consistent with the regional Rossby radius. This variability is embedded within onshore–offshore gradients. $O_2$ in the LTER grid region is driven primarily by biological processes as seen by the median ratio of the magnitude of biological oxygen ($O_2$/Ar) to physical oxygen (Ar) supersaturation anomalies (%) relative to atmospheric equilibrium (2.6), however physical processes have a more pronounced influence in the southern onshore region of the grid where we see active sea-ice melting. Total $O_2$ measurements should be interpreted with caution in regions of significant sea-ice formation and melt and glacial meltwater input. $pCO_2$ undersaturation predominantly reflects biological processes in the LTER grid. In contrast we compare these results to the Drake Passage where gas supersaturations vary by smaller magnitudes and decorrelate at length scales of ~12 km, in line with latitudinal changes in the regional Rossby radius. Here biological processes induce smaller $O_2$/Ar supersaturations (mean $(0.14 \pm 1.3)$%) and $pCO_2$ undersaturations (mean $(-2.8 \pm 3.9)$%) than in the WAP, and pressure changes, bubble and gas exchange fluxes drive stable Ar supersaturations.



## 1. Introduction

Rapid climate change, large uncertainty and communication with deep waters make the Southern Ocean, including productive coastal marginal ice zones such as the Western Antarctic Peninsula (WAP) and open ocean regions like the Drake Passage, a key region for the study of carbon cycling and sequestration via the biological and solubility pumps (e.g. Arrigo et al., 2008; Caldeira and Duffy, 2000). As atmospheric $CO_2$ levels rise and ice melts we have insufficient knowledge of how the flux of carbon between atmosphere and ocean might change. A critical component of this is our understanding of biological–physical coupling and the scales at which those processes are occurring. Dissolved gases including oxygen ($O_2$), argon (Ar) and carbon dioxide ($CO_2$) serve as valuable tools for investigating this relationship because together they record biological and physical processes at high spatial resolutions (Carrillo et al., 2004; Eveleth et al., 2014; Shadwick et al., 2015; Stanley et al., 2010; Tortell et al., 2014, 2015).

Exploiting the similar solubility properties of $O_2$ and argon (Ar), we isolate the biological oxygen supersaturation ($\sim\Delta(O_2/Ar)$), a record of net community production (NCP) in the mixed layer, and physical oxygen supersaturation ($\Delta Ar$), a signal of abiotic processes including those that alter solubility (e.g. temperature, salinity and atmospheric pressure changes) and change Ar concentration (e.g. bubbles, ice melt/freeze). Using Equilibrator Inlet Mass Spectrometry (EIMS) (Cassar et al., 2009) we are able to continuously measure the $O_2$/Ar ratio underway in the surface mixed layer at sub-kilometer resolution. As first presented in Eveleth et al. (2014), concurrent total oxygen measurements allow us to isolate Ar.

* Correspondence to: Duke University, EOS, Old Chemistry Bldg., Box 90227, Durham, NC 27708, USA.
*E-mail address:* rachel.eveleth@duke.edu (R. Eveleth).

http://dx.doi.org/10.1016/j.dsr2.2016.05.002
0967-0645/

This decomposed oxygen signal can also help elucidate biotic and abiotic drivers of the $CO_2$ system after accounting for the differing re-equilibration time scales of $O_2$ (weeks) and $pCO_2$ (seasons–year) (Broecker and Peng, 1974). The surface water partial pressure of $CO_2$ ($pCO_2$) is controlled by sea surface temperature (SST), sea surface salinity (SSS), dissolved inorganic carbon (DIC) and alkalinity (Alk), with DIC and Alk in turn determined by air–sea gas exchange, horizontal and vertical transport, mixing and biological processes.

In this paper, we document the relative contribution of biological and physical processes to the total $O_2$ and $pCO_2$ signals recorded at the WAP and assess the magnitude and spatial scales of variability to inform our understanding of these processes and how best to sample them. Additionally, we compare dynamics in the WAP with open ocean conditions in the Drake Passage. While others have addressed the relative roles of biological and physical processes on the $O_2$, $pCO_2$ and dissolved inorganic carbon systems of the Southern Ocean (Carrillo et al., 2004; Hauri et al., 2015; Shadwick et al., 2015; Tortell et al., 2015), here we additionally investigate the interannual variability in these signals and quantify physical contributions. In a companion paper (Eveleth et al., in review b, this issue), we use these underway $O_2$/Ar and $pCO_2$ measurements to estimate NCP in the WAP and subsequently detail the mechanisms and limiting factors controlling the biological variability that we expose in this first paper. The companion paper focuses on the role of glacial and sea-ice meltwater as they relate to iron and light availability.

## 2. Methods

Underway measurements were collected onboard the ARSV *Laurence M. Gould* (LMG) during the austral summer (January–early February) 2012, 2013 and 2014 in conjunction with the Palmer Long-Term Ecological Research Project (LTER) annual cruise which occupies a ~700 km × 250 km sampling grid along the WAP typically with discrete sampling every 20–100 km along gridlines that run perpendicular to the coast (Fig. 1). Conductivity–temperature–depth (CTD) casts were taken at each discrete station with a SeaBird 911plus instrument (temperature sensor model 3plus with accuracy ±0.001 °C, conductivity sensor model 4C with accuracy ±0.002 S/m). Mixed layer depth was defined as the depth at which the density increased 0.125 kg m$^{-3}$ relative to the surface. Meteoric water and sea-ice meltwater estimates were completed at each station using the $\delta^{18}O$ approach as detailed in Meredith et al. (2013). Briefly, discrete water samples were analyzed at the the Natural Environment Research Council Isotope Geochemistry Laboratory (NIGL) for $\delta^{18}O$ on a VG Isoprep 18 and SIRA 10 mass spectrometer, and these data were used with salinity to determine a three end-member mass balance that quantifies fractions of circumpolar deep water, sea-ice melt and meteoric water. Temperature and salinity were measured continuously underway from a thermosalinograph (SBE 45 MicroTSG accuracy ±0.0003 S/m, ±0.002 °C) at 5 m depth. These values are reported as 2-min averages and referred to as sea surface properties (SST and SSS respectively).

$O_2$/Ar measurements were taken using equilibrator inlet mass spectrometry (EIMS) in which seawater from the ship's underway flow-through system is pumped through a gas–permeable membrane contactor cartridge (MicroModule® 0.75 × 1) allowing gases in the headspace of the cartridge to equilibrate with gases in seawater, and the air is sent via a fused silica capillary to a quadrupole mass spectrometer (Pfeiffer Prisma model QMG 220 M1) to measure the ratio of $O_2$ to Ar and other dissolved gases. The system calibrates by sampling the atmosphere for 20 min every 4 h. Atmospheric $O_2$/Ar is very stable and there is no observable instrument drift; the average difference between consecutive air calibrations was 0.2%. The instrument precision is ±0.3% or better and the EIMS e-folding response time is 7.75 ± 0.25 min (Cassar et al., 2009). We present 2-min averages of continuous underway data collected every 8 s in the surface mixed layer.

Concurrent optode measurements of total $O_2$ concentration were collected using an Aanderaa Optode Model 4835 (precision ±0.2 μM). In 2012, Winkler titrations were completed at 19 discrete stations allowing calibration of the surface dissolved $O_2$ at 59 surface CTD stations (mean value from two optodes mounted on the CTD rosette) via a model II least-squares regression. Underway optode measurements (every 30 s) were then fit to these corrected discrete measurements (Fig. S1). While the root mean squared error of this fit is 10.1 μM, we observe no significant drift in the fit over time, and the scatter can likely be attributed to some temporal and spatial incoherence of the optode, Winkler titrations and CTD measurement matches, which is difficult to avoid. Oxygen depletion in the underway lines of the ship is likely negligible here as Winkler titration comparisons of bottle and underway samples on the LMG show a mean difference of 0.06% ($n=9$). Additionally, Juranek et al. (2010) show that the respiration effect is low (0.5% or less) at low temperatures and the distance from the seawater intake to the sampling sink is quite short so water residence time in the lines of the LMG is approximately one minute. Total $O_2$ and $O_2$/Ar measurements were averaged in 8-min bins to account for differing response times of the optode (sensor response time < 25 s) and EIMS, and ΔAr was then derived as in Eveleth et al. (2014) using

$$\Delta Ar = \frac{\Delta(O_2)_{total} + 1}{(1 + \Delta(O_2/Ar))} - 1 \quad (1)$$

where ΔAr is equal to the physical oxygen supersaturation (alternatively $[Ar]/[Ar]_{sat} - 1$), $\Delta(O_2)_{total}$ is the total $O_2$ supersaturation ($[O_2]/[O_2]_{sat} - 1$) and

$$\Delta(O_2/Ar) = \left[\frac{([O_2]/[Ar])}{([O_2]/[Ar])_{sat}} - 1\right]. \quad (2)$$

$\Delta(O_2/Ar)$ is generally accepted to approximate the biological oxygen supersaturation especially as $[Ar]/[Ar]_{sat}$ approaches 1 (Cassar et al., 2011). We measure $\Delta(O_2/Ar)$ using EIMS, total $O_2$ concentration ($[O_2]$) with an Optode, and calculate equilibrium saturation concentrations of $O_2$ ($[O_2]_{sat}$, < ±0.3%) and Ar ($[Ar]_{sat}$, ±0.13%) using underway temperature and salinity and the equations of Garcia and Gordon (1992) and Hamme and Emerson (2004), respectively. Saturation concentrations were corrected for atmospheric pressure history as in Shadwick et al. (2015) by multiplying saturations by the ratio of the weighted sea level pressure history (NCEP/NCAR Reanalysis daily average surface level pressure, http://www.esrl.noaa.gov/psd/) to standard pressure. This allows us to solve for physical oxygen supersaturation, ΔAr. Ar supersaturations are pressure history corrected unless otherwise noted; in discussion of variability and relative contributions of biological and physical processes to total oxygen supersaturation, we use pre-pressure corrected ΔAr so as to include all physical influences. ΔAr is only available for 2012 at this time due to the lack of Winkler titrations in 2013 and 2014 and resultant inability to calibrate the Optode.

$pCO_{2meas}$ was measured every 2.5 min (the approximate integration time of the equilibration system) using a 30 l shower-type air–water equilibrator and an IR $CO_2$ analyzer; analytical precision for $pCO_{2meas}$ was estimated to be approximately ±1.5 μatm due mostly to uncertainty in equilibration temperature, and $pCO_{2atm}$ is estimated to be ±0.2 μatm (Munro et al., 2015). $pCO_2$

Please cite this article as: Eveleth, R., et al., Biological and physical controls on $O_2$/Ar, Ar and $pCO_2$ variability at the Western Antarctic Peninsula and in the Drake Passage. Deep-Sea Res. II (2016), http://dx.doi.org/10.1016/j.dsr2.2016.05.002