OXYGEN MEASUREMENTS FROM AUTONOMOUS VEHICLES: APPLICATIONS AND CHALLENGES

Seth M. Bushinsky[(1)], Roberta C. Hamme[(2)], David P. Nicholson[(3)], Kenneth S. Johnson[(4)]

[(1)] Princeton University, Atmospheric and Oceanic Sciences, 300 Forrestal Road, Sayre Hall, Princeton, NJ 08544, United States, sb17@princeton.edu
[(2)] University of Victoria, School of Earth and Ocean Sciences, P.O. Box 1700 STN CSC, Victoria, BC V8W 2Y2, Canada, rhamme@uvic.ca
[(3)] Woods Hole Oceanographic Institution, Marine Chemistry and Geochemistry, 226 Woods Hole Rd., MS#25, Woods Hole, MA 02543, United States, dnicholson@whoi.edu
[(4)] Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95309, johnson@mbari.org

ABSTRACT

Since the initial Autonomous and Lagrangian Platforms and Sensors meeting in 2003, oxygen sensors have become the most commonly deployed biogeochemical sensor on autonomous vehicles. Pre-deployment drift and poor stability plagued early efforts, but have largely been solved with newer sensors and in situ atmospheric calibration. While some outstanding questions remain about long-term stability of deployed sensors, oxygen sensors are currently being used in a wide range of research involving floats and gliders. Measurements in the mixed layer are being used to constrain air-sea fluxes and estimate net community production, requiring high accuracy to minimize uncertainty. Studies in the thermocline have determined seasonal production and respiration while long term measurements in the deepest mixed layers can be used to assess changes in water mass ventilation. Ocean oxygen content is projected to decrease in the thermocline and deeper waters, with rates slow enough to require high accuracy measurements over multiple platform deployments in order to capture the signal. Projected changes in the extent of oxygen deficient zones will also require precise measurements at low oxygen levels. Improvements in sensor stability and response are active areas of research and development, especially for sensors designed for operation in near anoxic waters. In this paper, our goal is to summarize the current state of oxygen sensors deployed on autonomous vehicles and highlight many of the current and future uses of oxygen measurements from floats and gliders in understanding ocean processes.

1. INTRODUCTION

Oxygen sensors have been deployed on autonomous vehicles since at least 2002 (jcommops.org). Having been used on shipboard conductivity, temperature, and depth (CTD) packages for decades, oxygen sensors were mature relative to other biogeochemical sensors and could be readily adapted for low power, long-term deployments. Inconsistent initial accuracy and drift were problems for early sensors of multiple types. While largely addressed by multiple calibration efforts, work is on-going to address long-term stability and best practices for future deployments.

Over 200 oxygen sensors are currently deployed on Argo floats and scores more on short-term glider deployments, yielding an expanding dataset that vastly exceeds water samples from

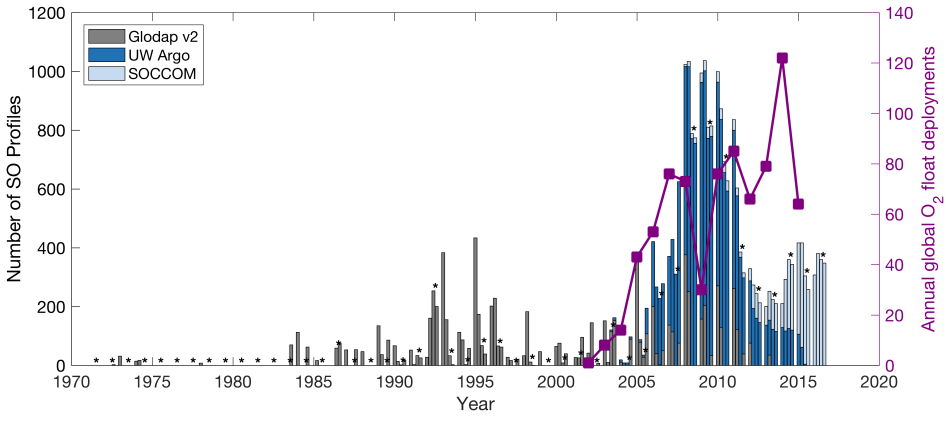

Figure 1. Southern Ocean oxygen profiles and global Argo oxygen float deployments. Number of oxygen profiles collected in the Southern Ocean grouped by season, with asterisks marking winter (left y-axis). GLODAPv2 is a quality controlled dataset of ship-board profiles (gray bars; Olsen et al., 2016; Key et al., 2015), UW Argo data are corrected to co-located historical cruise data and seasonal climatology, and SOCCOM data are air-calibrated optode measurements. Global deployment of Argo O_2 floats are close to 100/year, with almost 800 floats deployed as of 2016 (purple, right axis, jcommops.org).

research vessels (Figure 1). In this white paper for the second Autonomous and Lagrangian Platforms and Sensors meeting, we seek to outline the advances made in oxygen sensors on autonomous vehicles and their current and potential use in different areas of the water column.

2. SENSOR CALIBRATION

2.1 Accuracy and drift

Problems with oxygen sensors have largely centered around initial absolute accuracy and post-deployment drift. These issues present distinct problems requiring their own solutions. Precision has not been a significant concern. Before considering the magnitude of expected oxygen changes in the ocean, it is useful to consider our ability to actually measure these changes. Chemical titrations of water samples using the modified Carpenter-Winkler method remain the most accurate measurement of oxygen concentration (Carpenter, 1965). Expected accuracies of 0.1-0.2% of saturation concentration are possible with a trained analyst (Dickson, 1994). Accuracy decreases with oxygen concentration, to roughly ±1% at concentrations ~60 μmol kg^{-1} (compared with surface oxygen concentrations of ~220-350 μmol kg^{-1}).

In-situ oxygen measurements on floats and gliders are typically made with either a Clark cell electrochemical sensor (Clark, 1965) or an optode (commonly Aanderaa optodes or a Seabird 63). While Clark electrodes have very fast response times, they are more prone to drift in situ than optodes, so optodes have been almost exclusively deployed on new floats and gliders. This white paper will focus on Aanderaa optodes, while noting where Seabird 63 sensors significantly differ in functionality.

Aanderaa optodes (e.g., current models 4330 or 4831) are manufacturer rated to an accuracy of <8 μmol/kg or 5%. Improved laboratory calibration equations (Uchida et al., 2008) and multipoint calibrations have improved initial accuracy, with demonstrated accuracies of better than 1% in empirical field tests. However, they have a known loss of sensitivity of 3-8% yr^{-1} prior to deployment (Bittig et al., 2012; Bittig and Körtzinger, 2015; Bushinsky et al., 2016; D'Asaro and McNeil, 2013) that leads to typical deployment inaccuracies of 10% or more.

2.2 In situ and post-deployment calibration

Calibration of Argo float and glider oxygen sensors has traditionally been performed using Winkler titrations on water samples collected directly after deployment. The profiling

behavior of Argo floats presents a problem, as the first measurements collected are on ascent after the float completes a dive down to 2000 m, resulting in a typical delay of at least 18 hours. For gliders, coordinating ship operations and glider piloting allows for contemporaneous Winkler casts to be conducted within about 100 m of a glider dive location. Re-visitation of floats can decrease the temporal and spatial separation between float profile and Winkler comparison measurements, but small scale variability prevents accuracies better than ±0.5% (Bushinsky et al., 2016). Post-deployment calibration of sensors offers a significant improvement over un-calibrated measurements, with expected accuracies of better than 3% using monthly climatological averages (Takeshita et al., 2013) and better than 1% matching float measurements to cruise data co-located in time and space (UW Argo oxygen dataset, Drucker and Riser, 2016).

Calibration of optodes against atmospheric oxygen was proposed over a decade ago (Körtzinger et al., 2005) and in recent years has become the most widely used approach for in-situ optode calibration on Argo floats. The approach has also recently been adapted for Slocum gliders (Nicholson and Feen., in press). This technique involves exposing optodes to air after each profile and making measurements of atmospheric oxygen. With a known mole fraction of oxygen and measured or reanalysis atmospheric pressure and relative humidity, a true oxygen partial pressure can be calculated and used to correct optode measurements. Initial implementation of this method involved optodes on short stalks making single measurements after each profile (Johnson et al., 2015) and since evolved to making measurements before and after inflating an external bladder to further raise floats out of the water (Bittig and Körtzinger, 2015) or multiple measurements on extended stalks (Bushinsky et al., 2016). In-situ air calibrations additionally revealed drift of several tenths of a percent per year (Bushinsky et al., 2016), subsequently confirmed (Bittig and Körtzinger, 2017; Drucker and Riser, 2016). While an order of magnitude smaller than pre-deployment drift, in-situ drift displays either an increase or decrease in sensitivity of the optodes, indicating either different or multiple mechanisms of drift. Seabird 63 optodes are placed in the pumped flow stream of the CTD and are not currently configurable for air calibration.

Atmospheric calibration provides calibration points at saturation. While saturation concentration will change throughout the year, no calibration data is provided for the low concentrations and temperatures found in deep waters. Initial reports suggested little to no drift at zero oxygen (Bittig et al., 2012; Bittig and Körtzinger, 2015; D'Asaro and McNeil, 2013), which could imply that a gain correction across the entire oxygen-temperature surface is appropriate, and is currently the simplest and most used approach. The Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM, www3.mbari.org/soccom/SOCCOM_Data_Archive/; NSF Polar Programs (NSF PLR -1425989), supplemented by NOAA and NASA) project

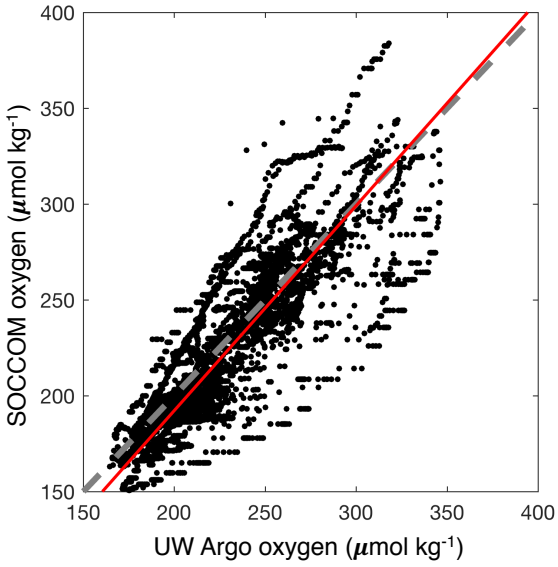

Figure 2. SOCCOM and UW Argo oxygen data comparison. Matched points (n=21466) are collocated in space, time, and density. The red line is a model II regression (slope, 1.07; intercept, -21.6). SOCCOM data are calibrated against atmospheric oxygen and UW Argo are corrected to cruise data and seasonally varying climatology.

represents the largest deployment of air calibrated oxygen sensors on floats to date. To check for large-scale biases between the SOCCOM air calibration and the UW Argo oxygen dataset (Drucker and Riser, 2016), measurement crossovers within 0.25° and ±5 days in any year, and ±0.01 σ_θ are plotted in Figure 2 (Bushinsky et al. in prep.). A model II regression indicates a mean concentration difference between the two datasets of 0.8 μmol/kg at 300 μmol/kg and 7.8 μmol/kg at 200 μmol/kg. Significant spread is present in the data, due in part to spatial and temporal variability on smaller scales than the search criteria and interannual variability, but overall agreement indicates no significant bias for near surface measurements.

Where high quality deep oxygen measurements exist, oxygen sensors can be calibrated against stable deep values. We present an example for the Labrador Sea where the layer at 1800-2000 m, mainly remnant Labrador Sea Water from very deep convection in the mid-1990s (Yashayaev 2007), has had constant oxygen values of 277 ± 2 μmol kg^{-1} since at least 2004 based on annual May surveys of the AR7W hydrographic line by Fisheries and Oceans Canada (data courtesy of Igor Yashayaev). An optode equipped float launched in August 2011 in the Irminger Sea (PI Virginie Thierry of IFREMER) measured an oxygen saturation anomaly in the 1800-2000 m layer that declined from -19% to -22%, an average drift rate of -2.9 μmol kg^{-1} yr^{-1}. Following D'Asaro and McNeil (2013), we fit an exponentially decaying function to the oxygen saturation and calculated a time-dependent gain relative to the deep layer observations (Figure 3, Wolf et al. in prep). The North Atlantic is particularly suited for this calibration technique because deep oxygen values are high (-14% or 277 μmol kg^{-1} in the targeted layer), so a similar degree of correction is applied to both deep and surface values. In areas where deep stable values are significantly undersaturated, extrapolation of correction values to the surface will

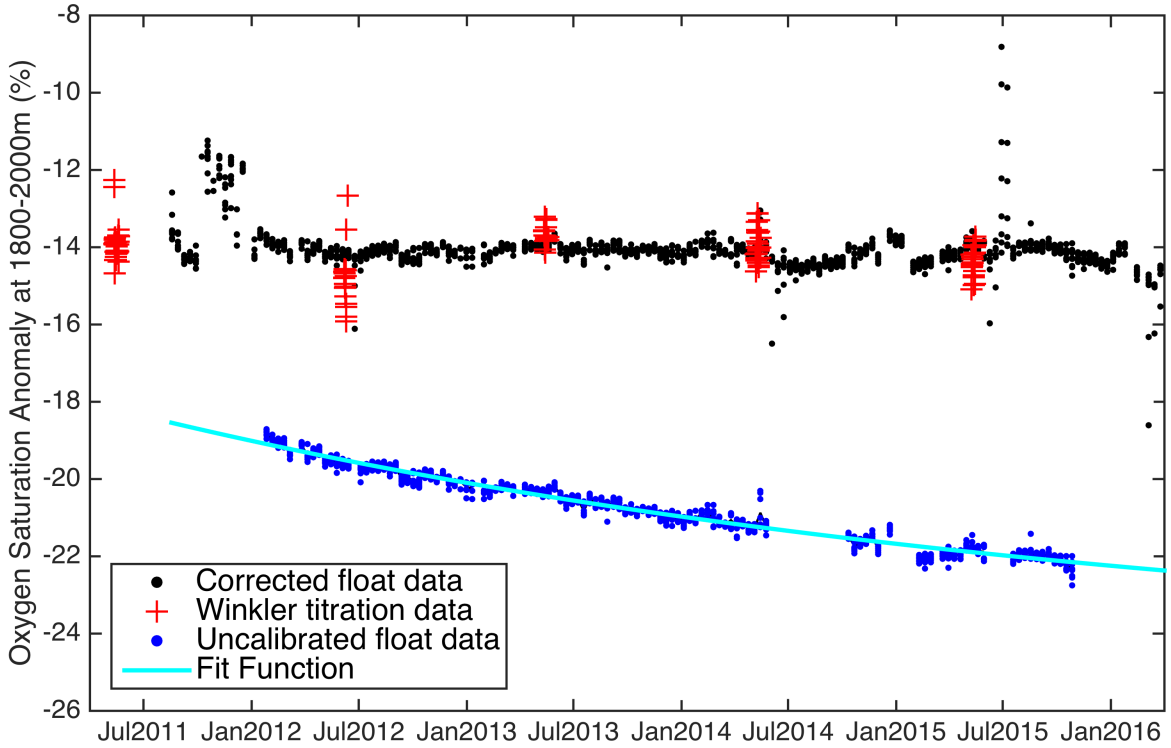

Figure 3. Blue points show un-corrected oxygen saturation anomalies at 1800-2000m from Argo float 1901210 when located in a defined deep convection region in the Labrador Sea, with the cyan line a fit to those data. Red data are Winkler titration data in the same water mass and in the same region (AR7W). Black points show the corrected float data in the same layer for all locations after the time-dependent gain is applied.

introduce uncertainty.

Sensor response time is also a critical consideration when evaluating O_2 optode data. Optode response is governed by the flux of oxygen through a diffusive boundary layer, across an optical isolation layer and into the sensing foil, which yields nominal ~45 second, 90% response times (Tengberg et al., 2006). However, because boundary layer diffusion is a function of both water flow and temperature, sensor response time can depend on temperature and on the physical orientation of an optode relative to the platform (Bittig et al., 2014). Optodes measuring in significant gradients will smooth the signal and smear oxygen gradients, impacting mixed layer calculations. This sensor lag is clearly evident in glider profiles through strong oxygen gradients, as gliders typically sample both during ascent and descent (Figure 4). For floats the lag can be partially corrected if the ascent speed and exact sample times are known and sampling frequency is sufficiently fast (Bittig and Körtzinger, 2017). Ascent speed and sample time can be approximated from the high-resolution Argo data files if exact times are not recorded, allowing a partial improvement in accuracy.

3. MIXED LAYER MEASUREMENTS

Oxygen concentrations in the mixed layer vary seasonally due to physical and biological processes. During the summer, decreases in solubility due to warming waters and the addition of oxygen from photosynthesis result in a higher oxygen concentration than saturation, driving a net outgassing of oxygen to the atmosphere. In the winter, low net production (or net respiration) and increased solubility due to cooling create an influx of oxygen to the ocean. Physical transport throughout the year is a function of the oxygen gradient and physical transport terms. The magnitude of the air-sea flux is primarily a function of the air-sea partial pressure gradient and the wind speed dependent transfer velocity. At certain times of the year, bubble injection from high winds can decouple the air-sea flux from oxygen supersaturation (Emerson and Bushinsky, 2016; Liang et al., 2013). Mixed-layer oxygen concentrations drive the air-sea flux, which are important to mass balance calculations of net community production.

Oxygen mass balances exploit the stoichiometric relationship (the photosynthetic quotient) between oxygen and organic carbon production and degradation during photosynthesis and respiration. Mixed layer oxygen mass balances rely on accurate estimates of the air-sea flux, which is the dominant flux of oxygen in the upper ocean (Emerson and Stump, 2010; Juranek et al., 2012) and air calibrated optodes on floats provide the wintertime measurements needed to constrain the full seasonal cycle (Bushinsky and Emerson, 2015). The accuracy needed for mixed layer measurements is largely a function of the mean saturation state for a given area of the ocean. For much of the ocean, with supersaturations of 1-3%, knowing surface

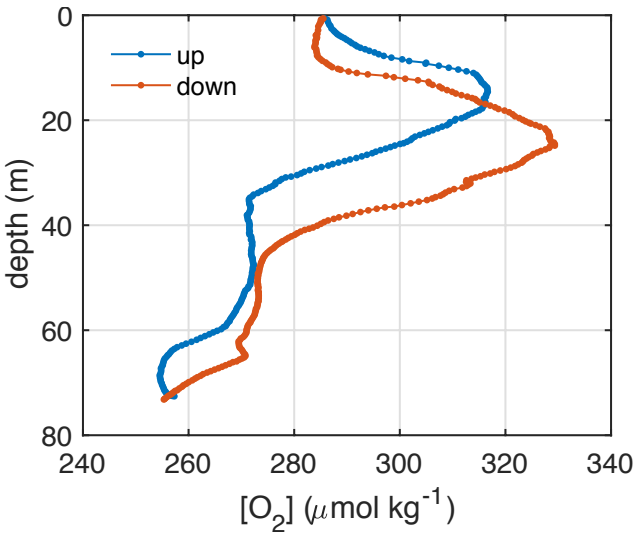

Figure 4. Effect of sensor response time on profiles in steep oxygen gradients. Measurements from the New England Shelf Break from a Teledyne Webb Research Slocum Glider equipped with an Aanderaa 4831 optode.

oxygen to better than 0.5% is necessary for estimating the air-sea gas flux.

Autonomous oxygen sensors also have great utility to investigate oxygen cycling, because they can provide full-depth data over a complete annual cycle in hard-to-access locations. Oxygen sensors on Argo floats in the Labrador Sea are being used to diagnose interannual variability in the oxygen saturation of newly convected waters (Wolf et al. in prep). With full depth profiles over the convective zone, changes in oxygen inventory can be related to the depth and length of convection. The final oxygen saturation of newly formed Labrador Sea water varies by only about one percent when convection is deep and the float is in the deepest convective region.

4. THERMOCLINE

Many of the long-term oxygen changes have been observed in the ocean's thermocline. Oxygen is depleted in these waters through respiration as organic matter sinks from above and is replenished through air-sea exchange at seasonal outcrops. Seasonal changes in the oxygen content are primarily due to the seasonal cycle in production. Long-term changes in the production or respiration of organic matter or in the ventilation of water to the atmosphere will manifest as long-term increases or decreases in the oxygen content of these waters.

In areas with shallow mixed layer depths, a significant amount of production can occur in the seasonal thermocline, and the increase of oxygen at this depth can be used to determine seasonal production from floats using relative changes in oxygen concentration (Riser and Johnson, 2008). Conversely, drawdown of oxygen in the permanent thermocline or below the compensation depth in the seasonal thermocline is directly related to degradation of new production from the surface waters above (Martz et al., 2008; Hennon et al., 2016). By utilizing the change in measured oxygen, these methods are not reliant on high absolute accuracy. Given the switch from autotrophic production above, and heterotrophic respiration below, the thermocline also is a region of strong vertical gradients, with entrainment and mixing being significant contributors to oxygen mass balance in the thermocline, as determined from glider O_2 measurements (Nicholson et al., 2008; Pelland, 2015). Seasonal cycles of oxygen concentration range in the tens of μmol O_2 kg^{-1} over several months, making this one of the largest observable biological signals in the oxygen cycle.

Long-term decreases in ocean oxygen content are expected due to increases in ocean temperature, reducing solubility and increasing respiration by phytoplankton and zooplankton (Keeling et al., 2010). In addition to changes in intermediate waters due to changes in the export flux, solubility, and respiration, models have shown changes in ocean oxygen content due to changing ventilation. Matear et al. (2000) predicted decreases in Southern Ocean subsurface oxygen due to decreased ventilation. The largest decreases predicted were ~70 μmol kg^{-1} by 2100, or roughly 0.7 μmol kg^{-1} yr^{-1}, largely due to changes in ventilation. Repeat WOCE sections in the Pacific found decreases in intermediate waters of 0.7-6 μmol kg yr^{-1} (Emerson et al., 2004; Watanabe et al., 2001) and time-series observations at Ocean Station Papa in the Northeast Pacific show similar declines of 0.4-0.7 μmol kg^{-1} yr^{-1} (Whitney et al., 2007). Modeled attribution of this oxygen decrease indicates decreased ventilation and changes in circulation rather than biological processes (Deutsch et al., 2006). Decreases of this magnitude will be at the detection threshold for a 5-year float deployment, but should be observable with a well inter-calibrated oxygen observing system over a decade.

5. DEEP WATER

In deeper waters, changes in the oxygen content similar to those in intermediate waters are expected. However, the rates of these changes are likely to be smaller in magnitude (tenths of $\mu mol\ kg^{-1}\ yr^{-1}$ or less were observed in the North Atlantic (Stendardo and Gruber, 2012)) and more difficult to observe. In some areas of the ocean, respiration of large amounts of sinking organic matter deplete oxygen beyond its resupply from advection and diffusion, creating oxygen deficient zones (ODZs). These have been shown to be spreading (Diaz and Rosenberg, 2008), and therefore should be targeted by future deployments.

6. FUTURE SENSOR IMPROVEMENTS AND NEW SCIENCE

The oxygen sensor has been a clear example of the success of improving technology. The first oxygen sensors deployed on autonomous platforms were relatively simple electrodes with significant calibration and stability problems. The technology has progressed to much more sophisticated fluorescence lifetime optical sensors. Despite the advances, significant problems remain due to response time, capability to detect near zero oxygen concentrations, and sensor stability. New generations of sensors, such as the JFE Rinko and the CONTROS Hydroflash oxygen sensors, are being introduced with greatly reduced sensor response times. Improved performance is made possible by basic research programs that identify new materials, such as brighter oxygen-sensitive fluorophores (Hutter et al., 2014) that allow thinner optical films and faster response times, as well as lower detection limits (Larsen et al., 2016).

We can expect that future research programs will have access to sensors with improved performance characteristics, enabling entirely new areas of research into biogeochemical processes using autonomous platforms. For example, recent research suggests that the critical oxygen concentrations for the onset of anammox and classical denitrification are in the nanomolar range (Dalsgaard et al., 2014), which is at the practical limit of concentrations routinely detectable with the current generation oxygen sensors on autonomous vehicles. Brighter fluorophores have enabled a new generation of oxygen sensor (Lehner et al., 2014) that would allow these processes at very low oxygen concentrations to be studied with autonomous platforms. The influence of climate driven processes on oxygen minimum zones and denitrification would then be feasible (Deutsch 2014).

7. CONCLUSIONS

The oxygen optode is arguably the most robust and ready biogeochemical sensor currently available to the oceanographic community. Optodes have been adopted on a wide range of platforms and are proven to be reliable and resistant to fouling over multi-year deployments. A number of recent advances in calibration makes it possible to achieve significantly improved accuracy and current sensors and techniques allow in situ measurements of oxygen from autonomous vehicles to rival the accuracy of Winkler titrations. As the network of oxygen equipped floats and gliders expands and improves, new oceanographic questions can be added to the long list of areas in which data from autonomous vehicles has greatly improved our understanding of biogeochemical cycles and processes.

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