Measuring Oxygen from Argo ----- 1st Euro-Argo Users Meeting

Oceanic dissolved **oxygen concentration is a key quantity for ocean ecology and biogeochemistry. It permits study and quantification of a diverse and crucial set of processes. These processes include the detection of the oceanic impact of global warming on ocean biogeochemistry and circulation, the addition of unprecedented constraints on the export of biologically formed organic matter, and improved estimates of the oceanic uptake of anthropogenic CO2. (*From the White Paper of N. Gruber et al.*)**

Outline:

Motivation: Why Oxygen on Argo? Makes Argo attractive to new user Communities

Status: 12000 O2 Profiles generated by Argo floats

Process studies: O2 measured in convective areas -- Labrador Sea
OMZ's in Pacific and Atlantic
Biogeochemical studies

Technical issues: Sensors
Sensor location
O2 on other platforms --- Glider, MMP
calibration

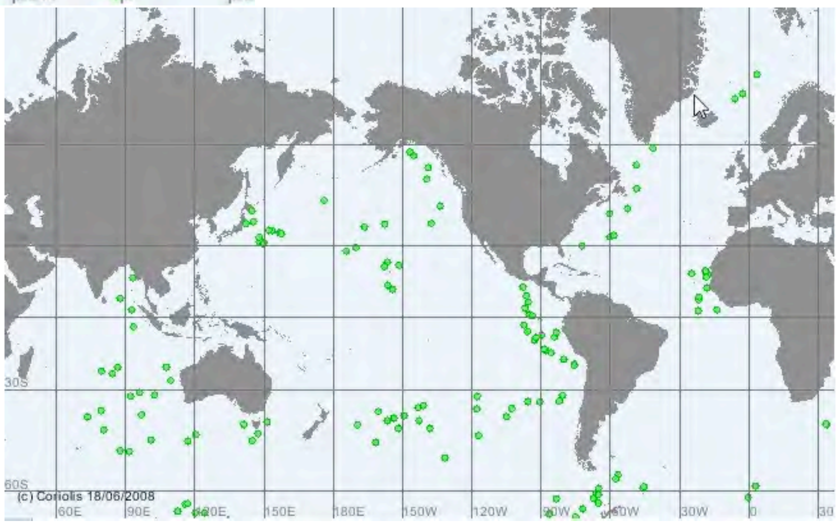
Future: Friends of Oxygen
National science programs
Oxywatch (EU-proposal)

Oxygen Floats in the global Ocean

Distribution of Oxygen Profiles measured by profiling Floats since year 2000

Total No. of Profiles is : 12000 and is presently increasing by 5400 per year

Average NOP per 10day interval ~ 150
but
very scattered due to focus on regional process studies



Why oxygen on Argo? OMZ's

…improve understanding of the coupling of climate variability and circulation with the ocean's oxygen and nutrient balance, to quantitatively evaluate the nature of oxygen-sensitive tipping points, as well as to assess consequences for the ocean's future.

Oxygen at isopycnal 26.9 kg/m^3, ~300-600 m depth

Hypoxic < ~80 µmol/kg
Suboxic < ~10 µmol/kg (~0

Oxygen changes (decrease) may have dramatic consequences for ecosystems and coastal economics!

Oxygen time series for selected areas:

Tropical North Atlantic Ocean

Stramma et al. 2008

300-700 m layer
Temp. trend: +0.009+/- 0.008°C/year
Oxygen trend: -0.34+/-0.13μmol/kg/year

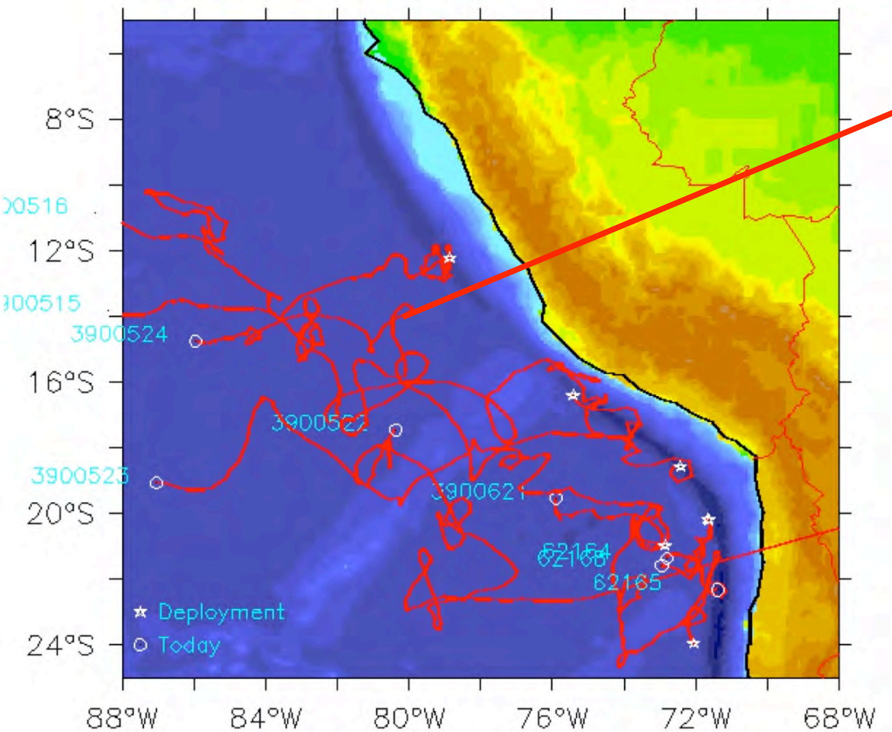
90 μmol/kg, 85%
1960: 370 m
2006: 690 m

Measuring Oxygen from Argo

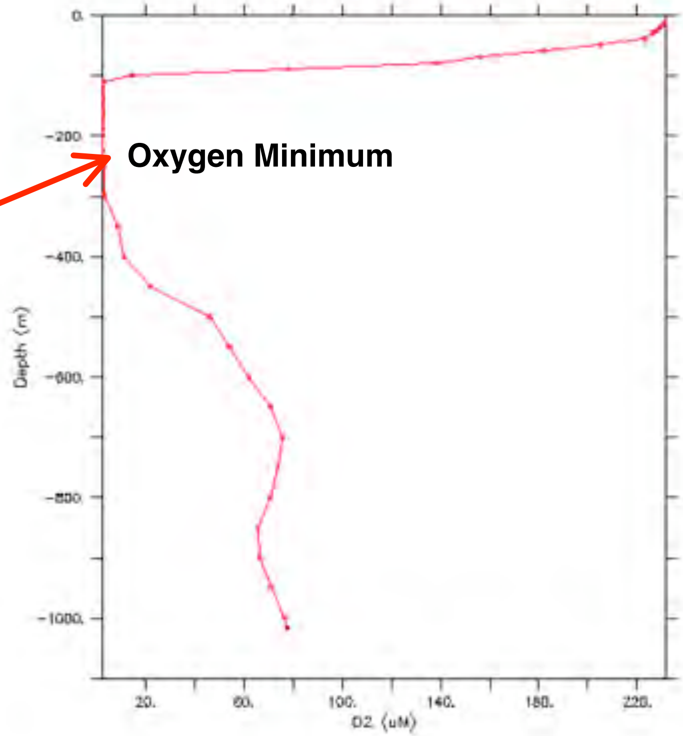
Goal: To characterize the spatial and temporal variability of the OMZ in the ESP and to understand the physical mechanisms behind it, we will monitor the dissolved oxygen concentration together with physical and bio-optical properties of the water column with autonomous profiling ARGO floats and moored instruments.

The Eastern South Pacific Oxygen Minimum Zone

Chile: 10 Argo Floats in Action With O2 Optodes for OMZ investigation



Profiler Trajectories



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EOS, TRANSACTIONS, AMERICAN GEOPHYSICAL UNION

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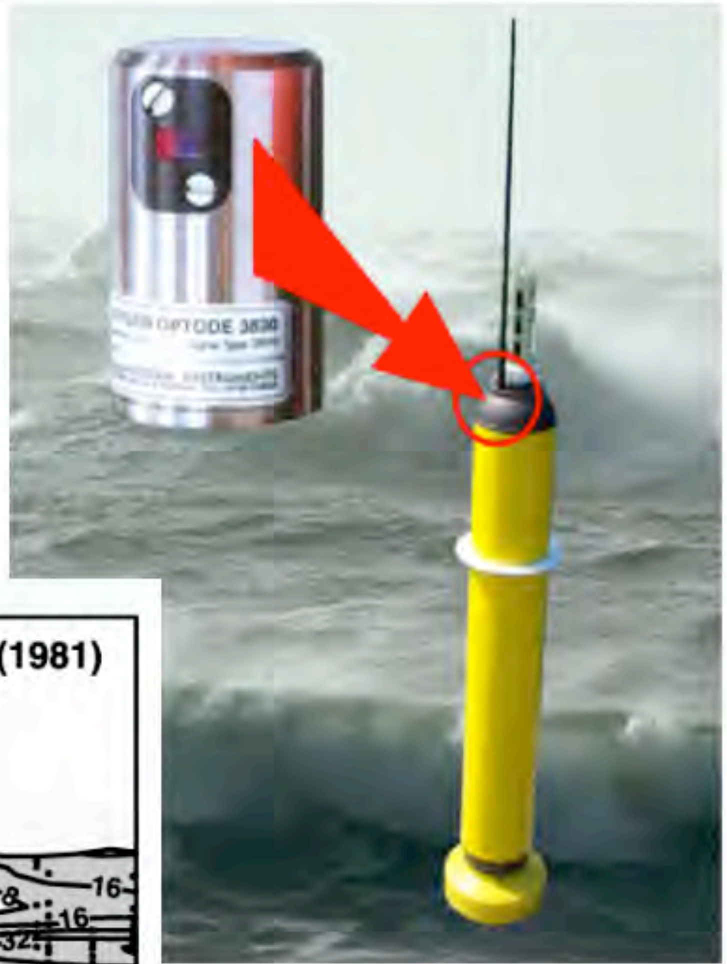
Trends in Marine Dissolved Oxygen: Implications for Ocean Circulation Changes and the Carbon Budget



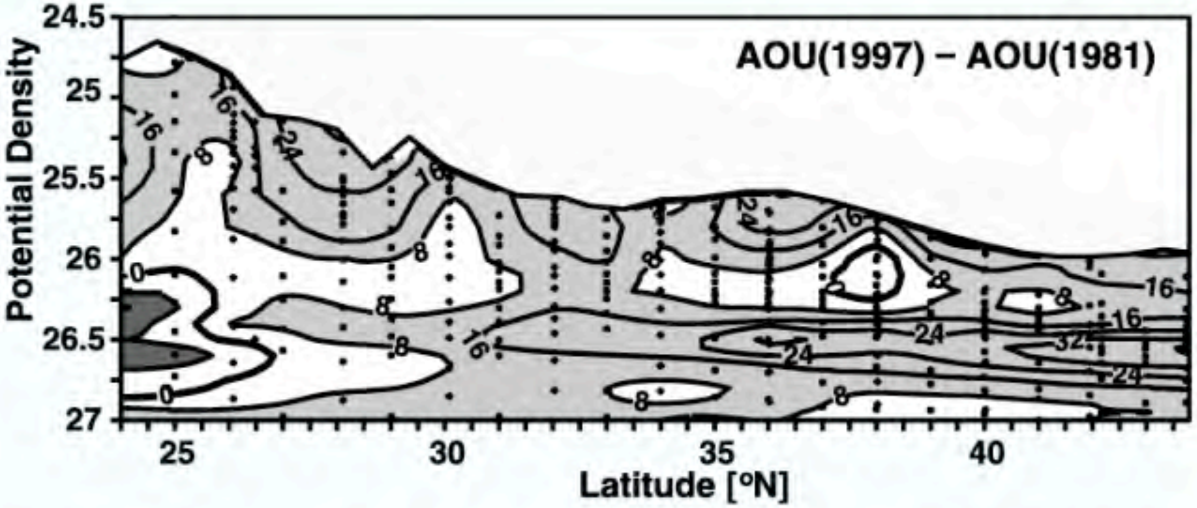
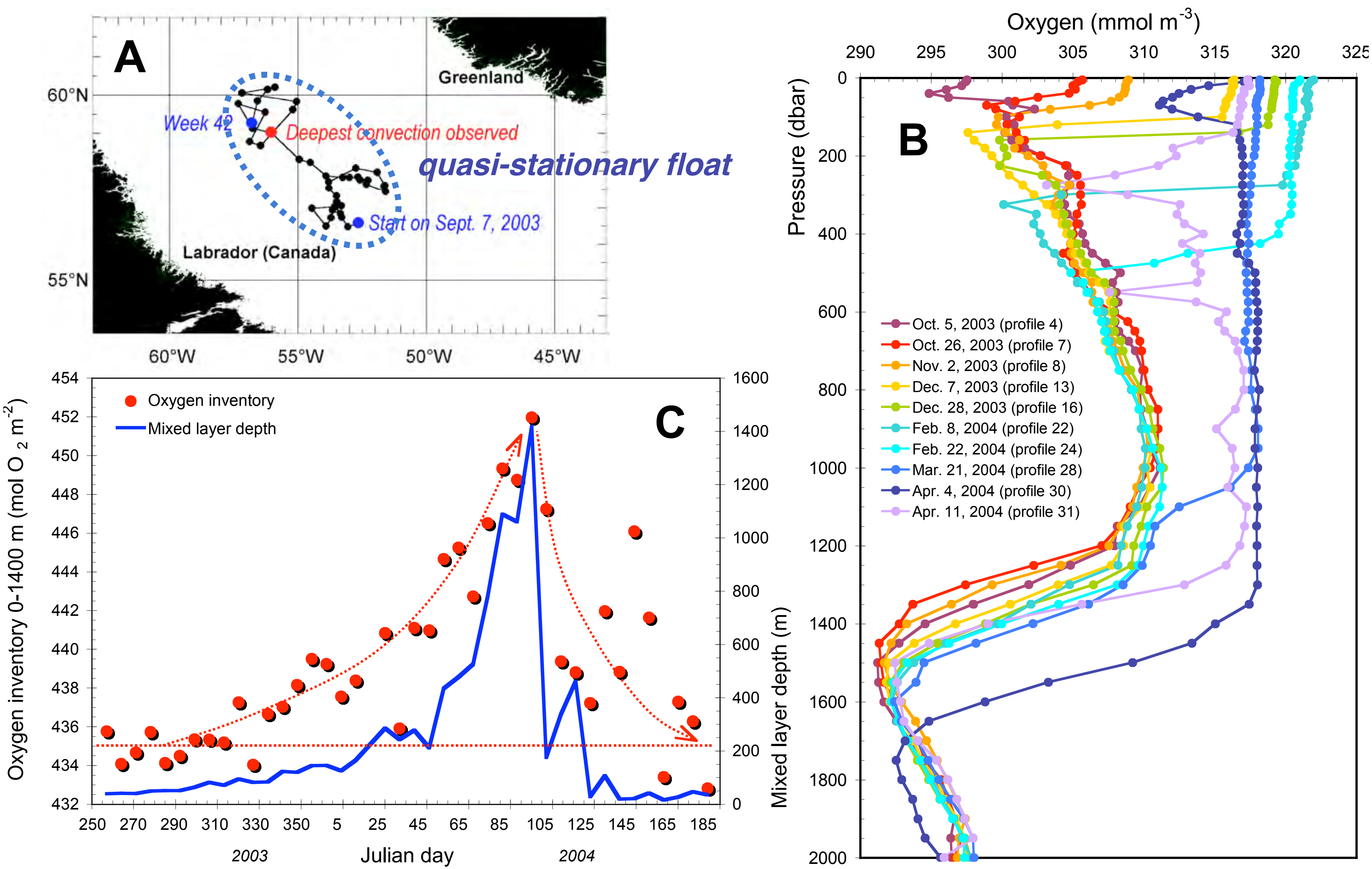


Fig. 1. Observed decrease in dissolved oxygen concentration in the thermocline of the North Pacific [Emerson et al., *2001*]. *Plotted are differences in apparent oxygen utilization (AOU) as measured on two cruises on the same transect between 24°N and 44°N in 1981 and 1997. The contour interval is 4 µmol kg^{-1}. AOU is the difference between the O_2 equilibrium concentration, calculated from the observed in-situ temperature and salinity and atmospheric O_2 pressure at sea level, and the measured in-situ concentration of O_2. An increase in AOU corresponds to a decrease in dissolved oxygen. (Figure courtesy of Steve Emerson).*

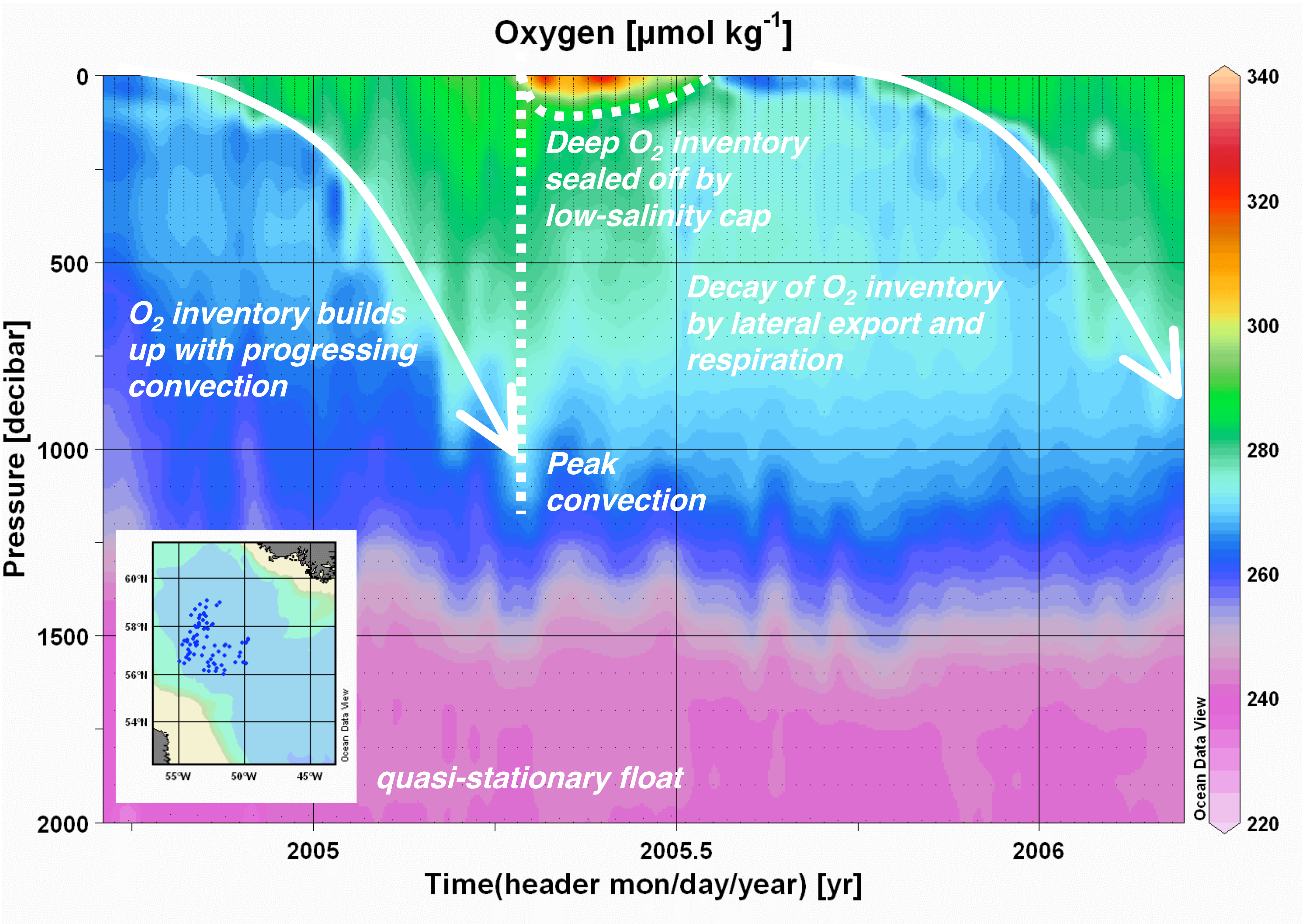
Joos, F., G.-K. Plattner, T.F. Stocker, A. Körtzinger, and D.W.R. Wallace (2003). *EOS* 84(21), 197-204.

The Labrador Sea pilot study: The ocean's breathing



Körtzinger *et al.* (2004). The ocean takes a deep breath. *Science* 306, 1337.

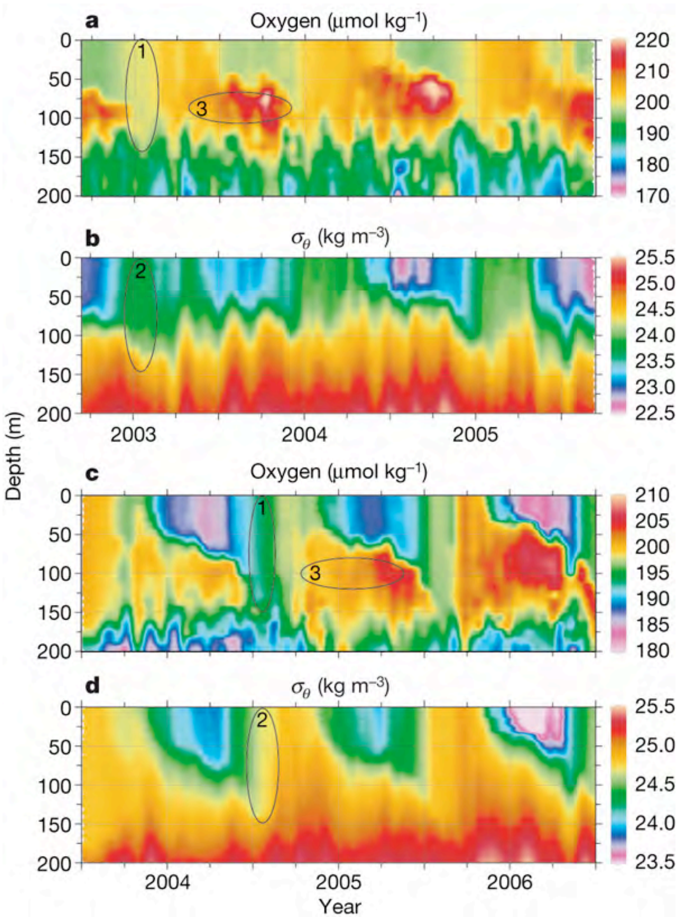
The Labrador Sea pilot study: The ocean's breathing



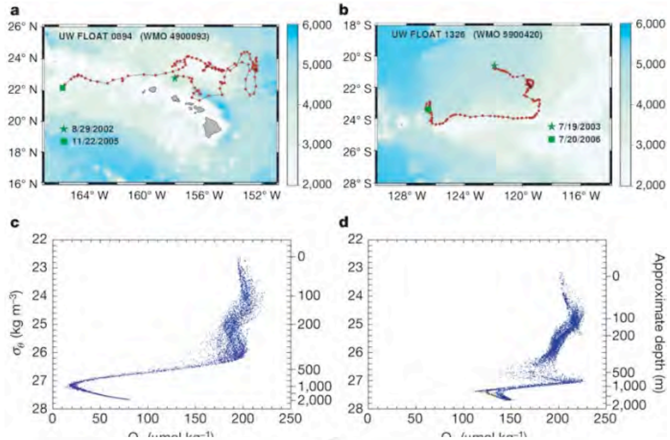
Nature 451, 323-325 (17 January 2008)

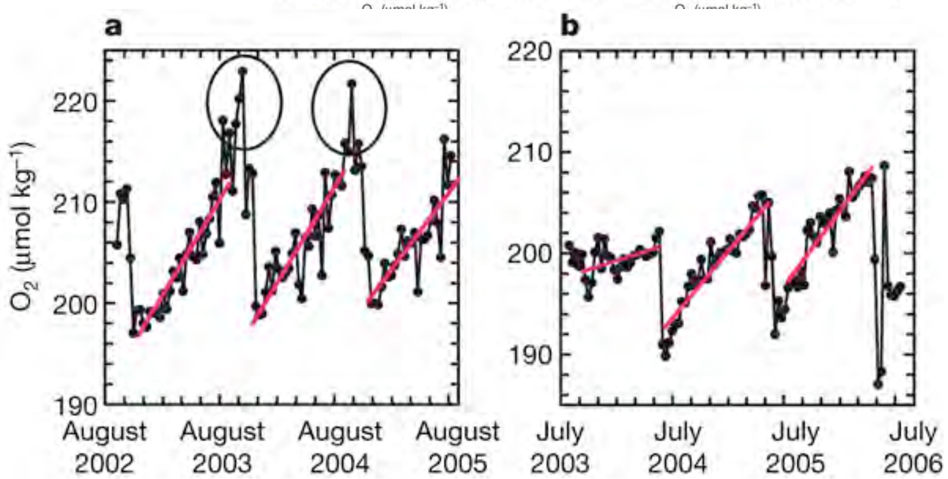
Net production of oxygen in the subtropical ocean

Stephen C. Riser[1] & Kenneth S. Johnson[2]



Oxygen (a, c) and potential density (*b, d) are shown during the three years that floats 0894 (a, b) and 1326 (c, d) operated.*





Oxygen concentrations at 78 m for float 0894 (a) and 87 m for float 1326 (b) are shown. Black lines and solid circles are oxygen concentrations measured by the float at each depth. Pink lines are fitted to the oxygen data each year by least squares to estimate the rate of oxygen production.

Sensors

Requirements

In order to meet the scientific goals of the Argo - Oxygen program, a target accuracy of 1 µmol/kg and a threshold accuracy of 5 µmol/kg in Dissolved Oxygen (DO) measurements are required. The target response time of the sensor is 10 seconds, with a maximum threshold of 30 seconds (Gruber et al., 2007).

To date, two types of dissolved O2 sensors have been employed on profiling floats ---- about parity
Initially more electrochemical cells, later more optical sensors

The SBE-IDO (formerly known as the SBE-43) implementation, from SeaBird Electronics, is an electrochemical sensor (Clark cell) (Clark *et al., 1953) whose design is similar to the O2* -sensors on SeaBird shipboard CTD units.

Advantage at high O2 concentrations and high gradients

The Anderaa Optode is an optical sensor making use of Dynamic Quenching of Luminescence; Sensor is coated with a thin layer of oxygen-sensitive fluorescent dye.

LED shines light on the dye layer, causing the dye to emit red fluorescent light .

Oxygen concentration in the sample is related to luminescence intensity .

Low Oxygen – high luminescence – measures well at low O2 concentrations

How to get oxygen on ARGO floats: Promising oxygen sensors

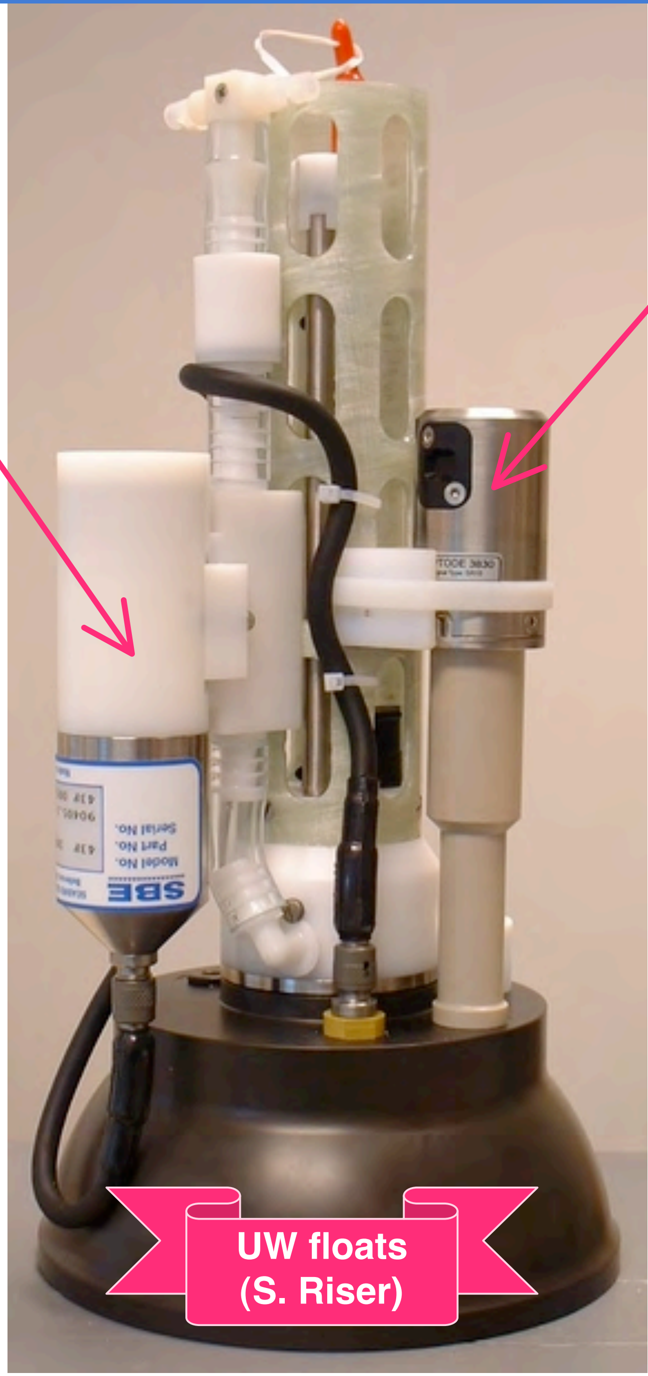
Electrochemical sensor (Seabird SBE 43/IDO)

***Principle*:**
Clark-type polarographic membrane sensor

Measurement range:
120% of surface saturation

Initial accuracy:
2% of saturation

Response time:
6 s (e-folding time)



Optode sensor (Aanderaa 3830)

***Principle*:**
Life time based dynamic fluorescence quenching

Measurement range:
0-120% of surface saturation (0-500 μM)

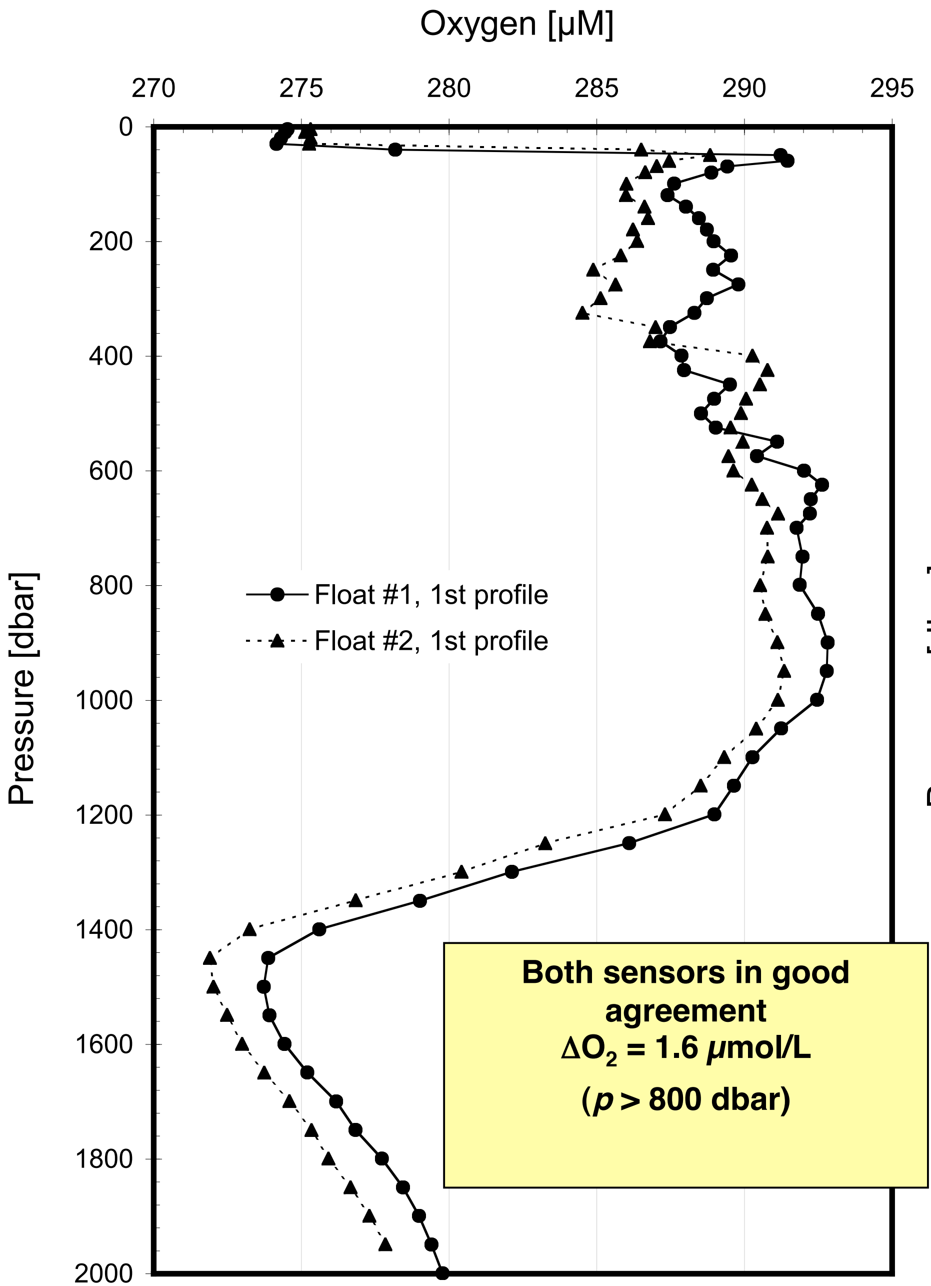
Precision:
<1 μM (0.4%)

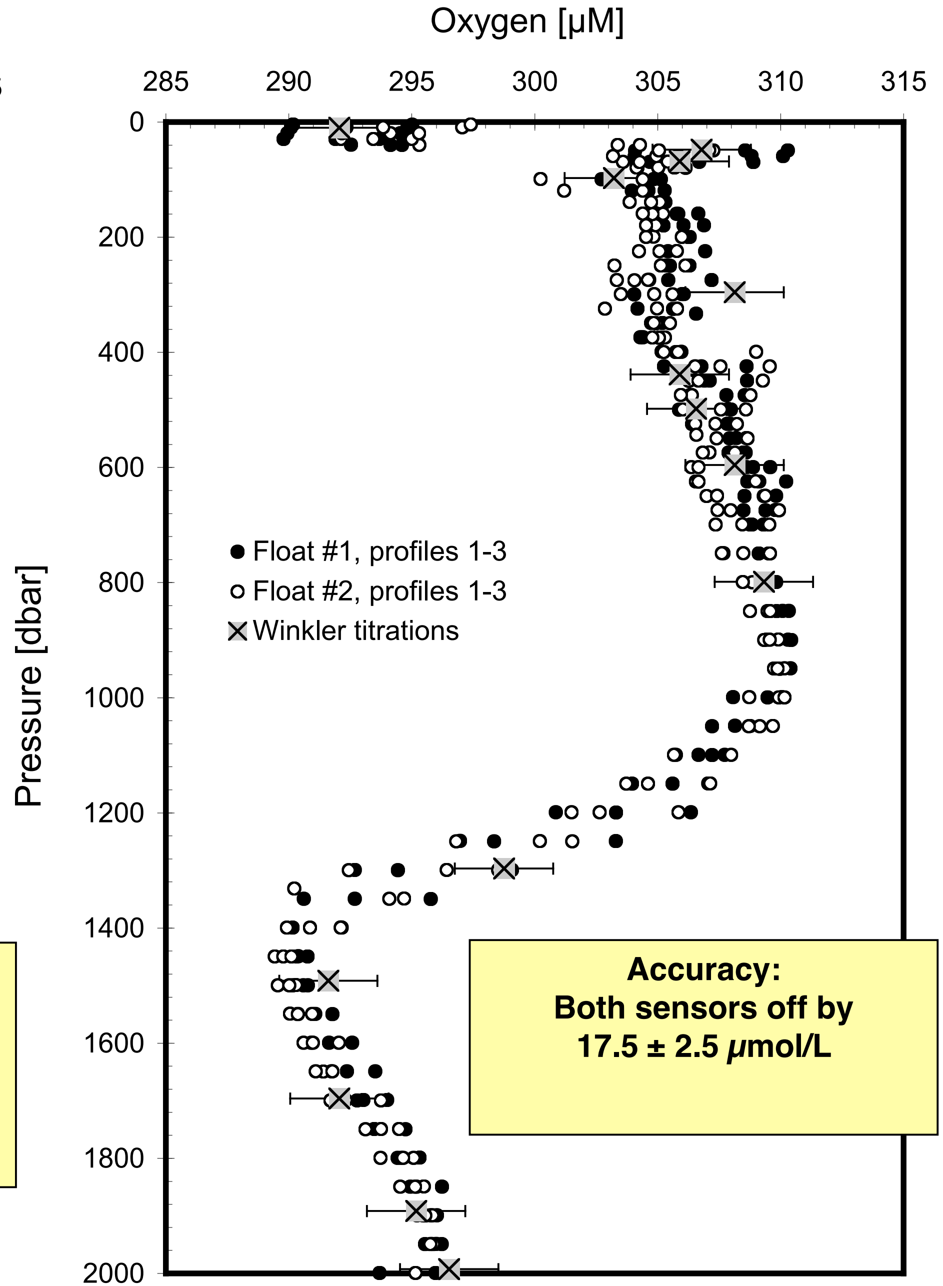
Initial accuracy:
8 μM or 5% (whichever is greater)

Response time:
25 s (63% e-folding time)

The Kiel oxygen float project (since 2002)

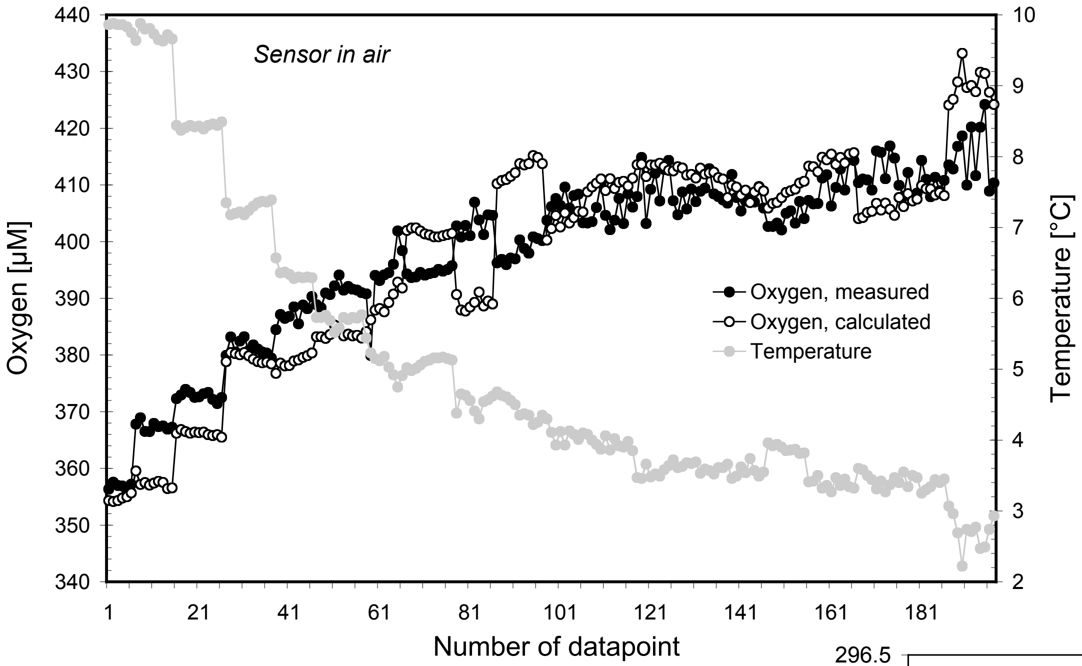
Sensor-to-sensor agreement / Accuracy of sensor batch (optode)





Körtzinger *et al.* (2005). *J. Atm. Ocean. Techn.* 22, 302-308.

Drift check / Long-term stability



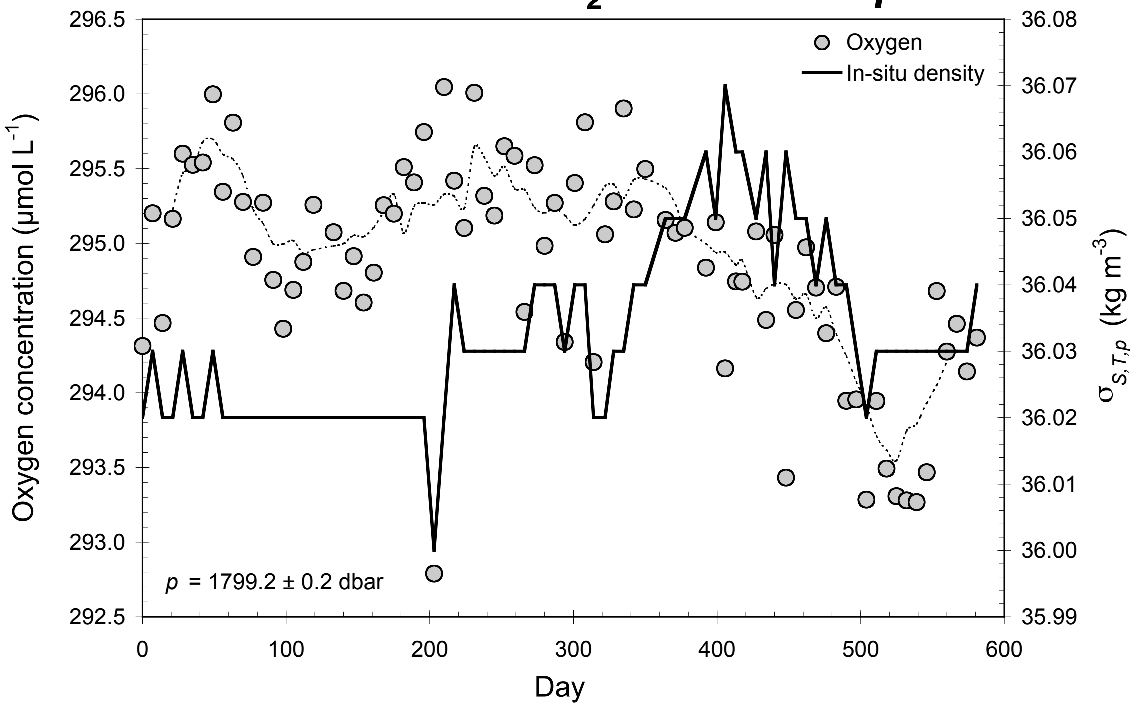
Körtzinger et al. (2005). High-quality oxygen measurements from profiling floats: A promising new technique. ***J. Atm. Ocean. Techn.*** **22, 302-308.**

Drift check possible through air measurements

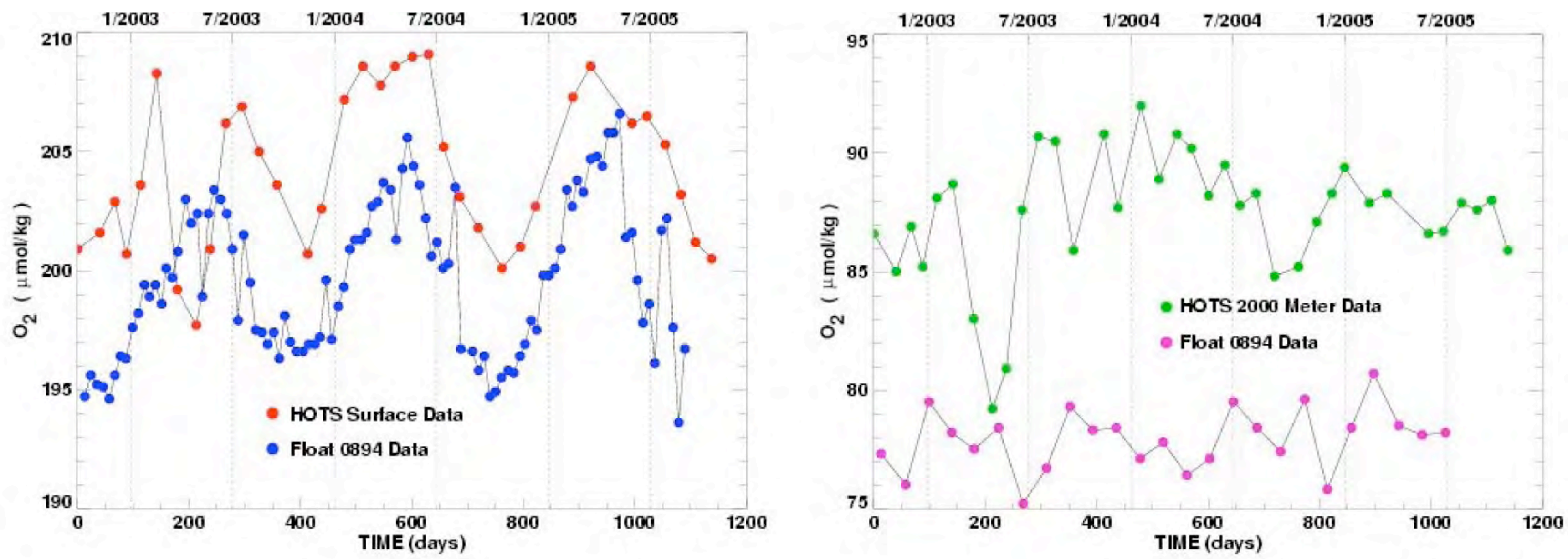
High long-term stability

Tengberg et al. (2006). Evaluation of a life time based optode to measure oxygen in aquatic systems. ***Limnol. Oceanogr. Methods*** **4, 7-17.**

O_2 = 295.0 ± 0.7 µmol/L



Experience with the IDO sensor has also been generally positive. For example, an IDO-equipped APEX float near Hawaii showed very little sensor drift over 3 years both near the sea surface and at 2000 m, albeit with a significant offset relative to independent in-situ determinations of the dissolved oxygen content by Winkler titrations of bottle samples (Gruber et al.).

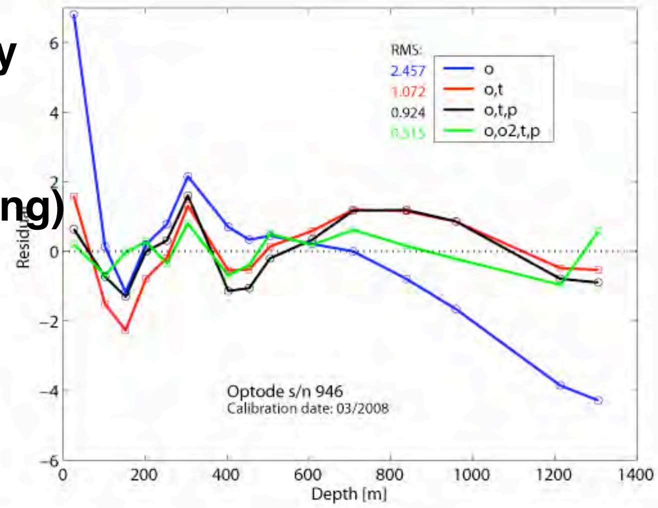


O2 from seabird sensor on float (near surface and at 2000m) vs. Winkler derived oxygen. (UW –float S. Riser)

Measuring Oxygen from Argo – in-situ calibration

Major issue for both sensors is sensor cal. and stability

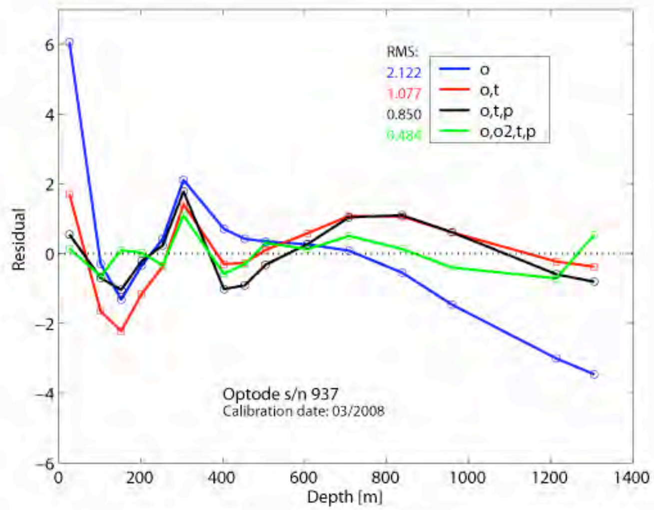
1) Factory calibration
2) Compare float data with nearby CTDO2-station (timing)
3) Develop calibration routine for sensors only



- Optodes attached to data loggers were mounted on the CTD rosette
- During the up-cast, 12 bottle stops are taken of at least 2 minutes each with water samples for Winkler titration

- Optode oxygen values are corrected for salinity and pressure effects
 using manufacturers formula

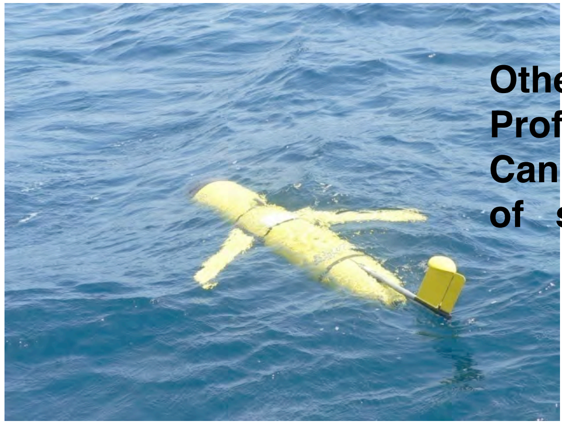
Multifit regressions are performed for a correlation between CTD oxygens and (corrected) optode oxygens, in the following configurations (see graph of residuals for the fits)



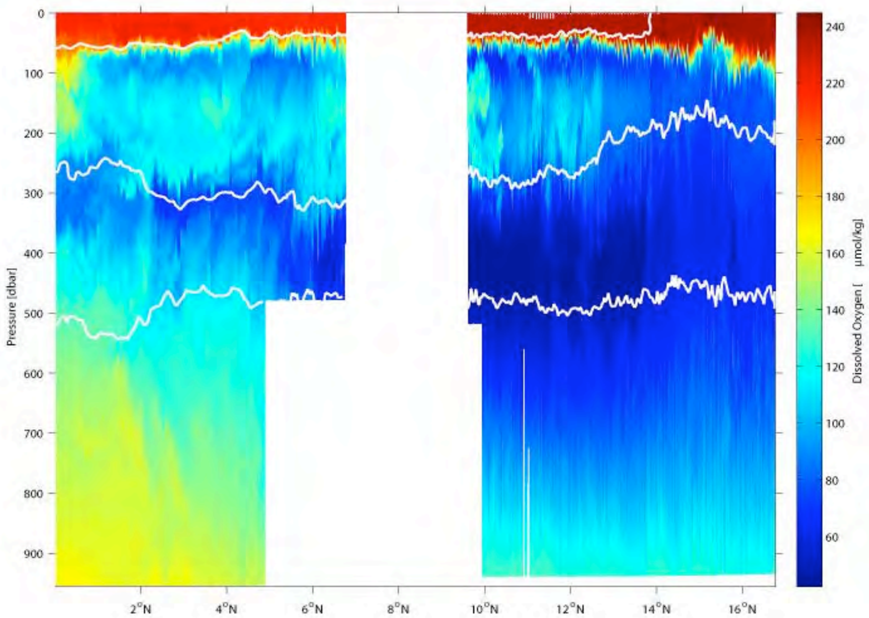
Result: Predetermined calibration is not sufficient when high accuracy is required. Pressure dependence is not adequately handled by general algorithm

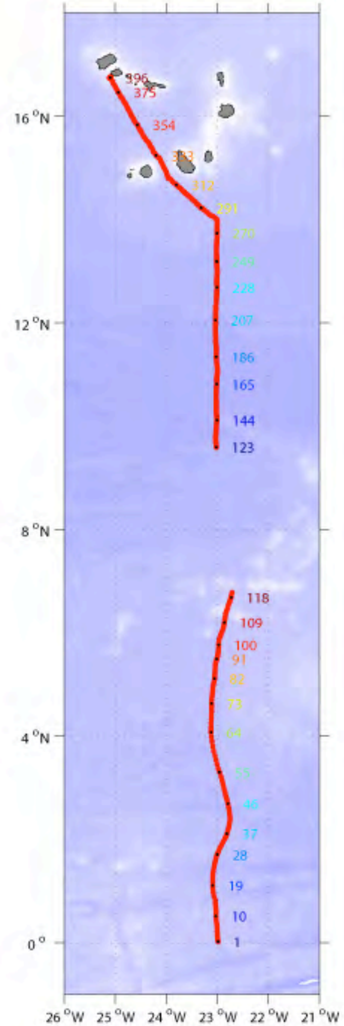
Next step for Optodes on Argo floats will be: purchase the sensors and perform in-situ calibration – then send sensors to float manufacturer for mounting

Measuring Oxygen from Argo



Other platforms (gliders, moored CTDO2 Profilers also carry these sensors.
Can be used to evaluate long term stability of sensors (post deployment calibrations)





Measuring Oxygen from Argo ---- next steps

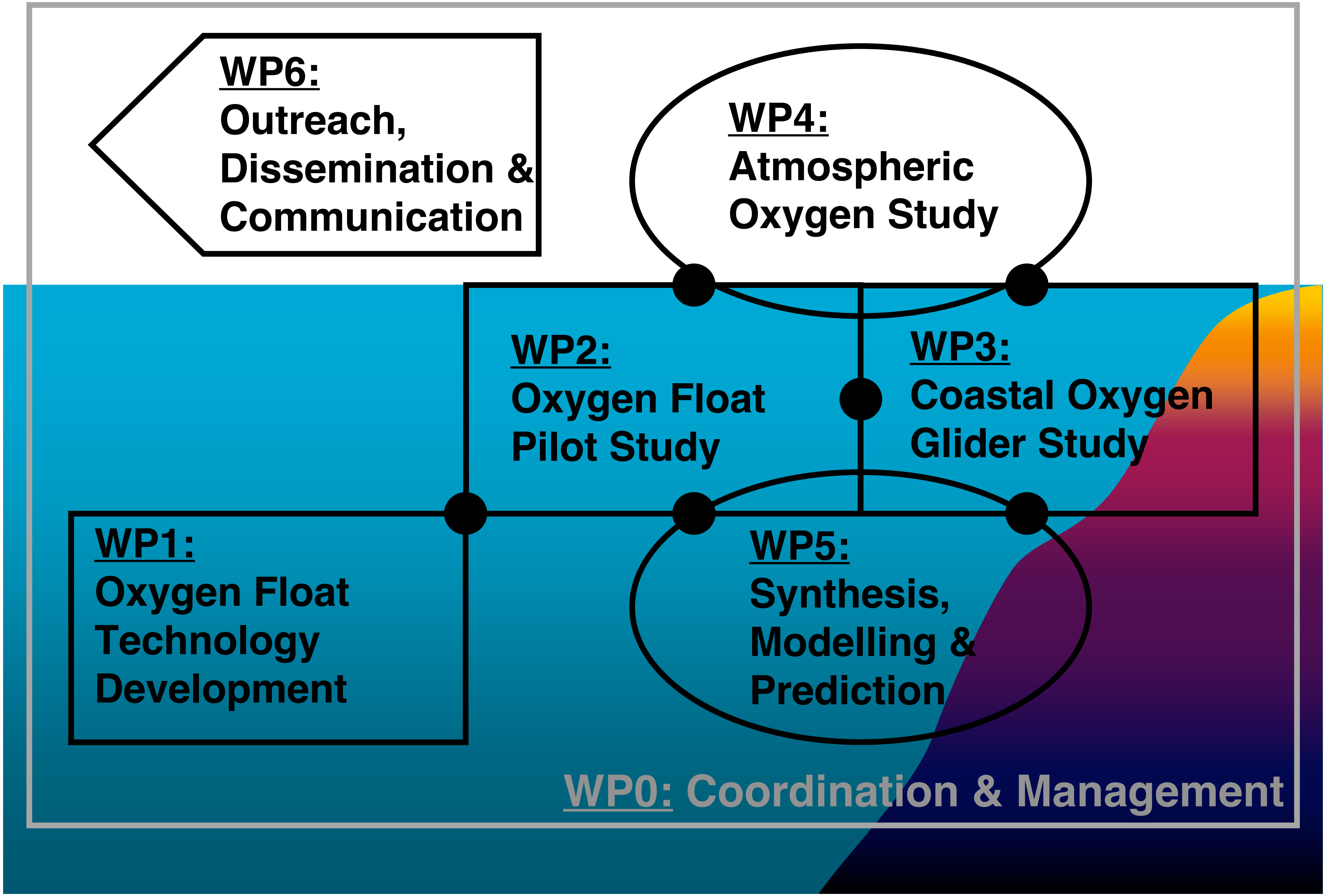
National longterm funding for OMZ studies (Atlantic, Pacific and may be Indic) with substantial float numbers (10 this year + 10 in 2011) is underway (German Science Foundation).

Other science communities (SOLAS) also use O2- floats – North Atlantic

EU- Proposal : OXYWATCH

Within this proposal the relevant questions for O2 on Argo are addressed

OXYWATCH ----- Project Components --- will not be funded this time



<u>Oxywatch ----- Oxygen Float Technology Development</u>

Address known deficiancies of the current version of the oxygen optode sensor and develop and test the Mk II optode, improve integration to PROVOR float, develop quality control methods for real-time and delayed-mode oxygen data

Develop Mk II optode sensor:
(aspects: time constant, temperature measurement, optics, electronics, etc.).

Improve and assess calibration accuracy and strengthen calibration competence at AADI.

Carry out laboratory and field tests of Mk II optode

Evaluate optimal integration into profiling floats.

Evaluate potential for barometric pressure measurement from floats for oxygen sensor calibration purposes.

Develop metadata format for float/glider oxygen data.

Develop quality control measures for real-time and delayed mode float/glider oxygen data.