In-situ calibration of Oxygen Optodes in the Southeast Pacific Oxygen Minimum Zone

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5th EGO Meeting
16. March 2011, Gran Canary, Spain

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<u>In-situ calibration:</u>

Using the field measurements in combination with "known" environmental conditions to improve the calibration

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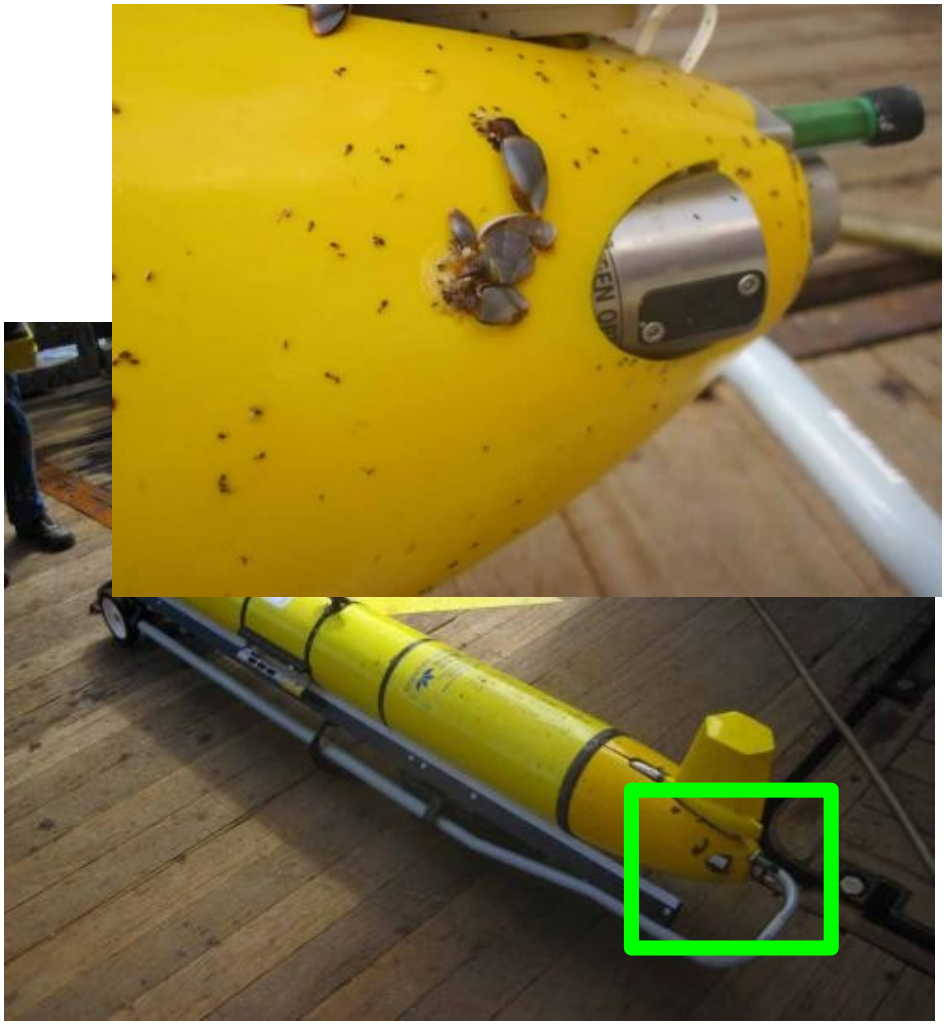
Introduction Oxygen Optode



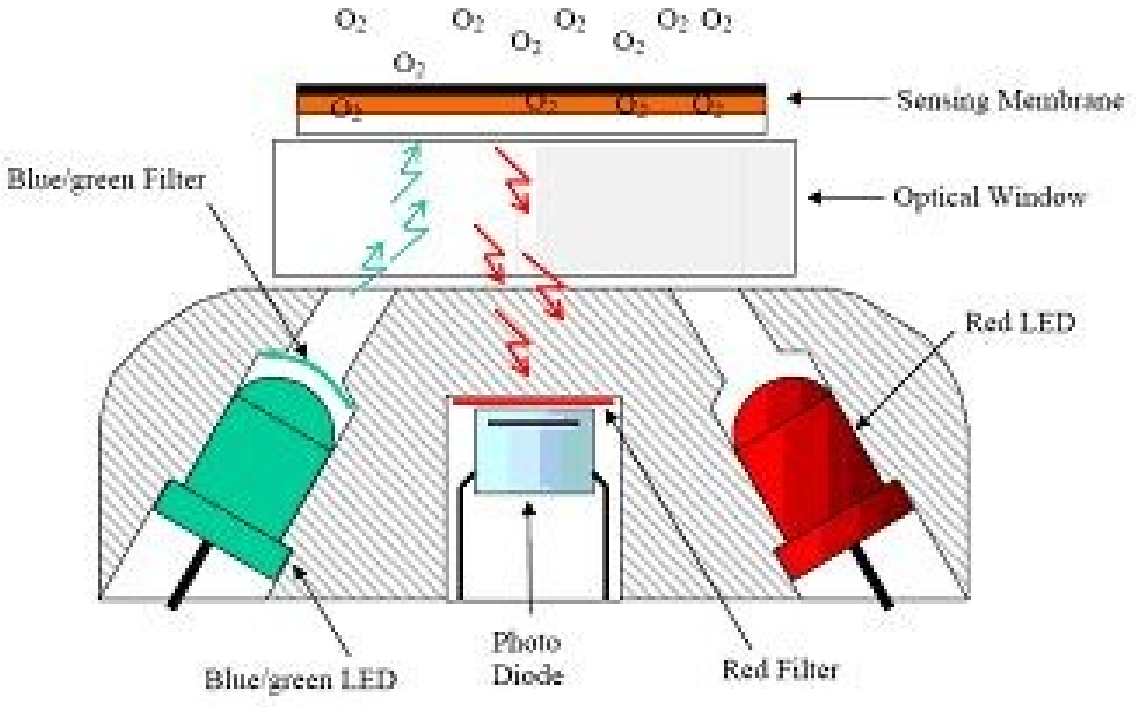
Characteristic:

- Long term stability
- Non-invasive
  (no oxygen consumption)
- NOT made for
  oceanographers seeking for
  decadal change of
  ~ 1 µmol/kg...

Introduction Oxygen Optode

Principle of operation:

- Oxygen luminescence quenching
- Foil is excited with a blue-green light → The phase shift of returning red luminescence is proportional to oxygen



Introduction Oxygen Optode

Principle of operation:

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- Foil is excited with a blue-green light → The phase shift of returning red luminescence is proportional to oxygen
- Observed quantity:
  - Dphase = difference (Bphase / Rphase)
- where
  - Bphase – phase obtained with blue-green light
  - Rphase – phase obtained with red light (often set 0)

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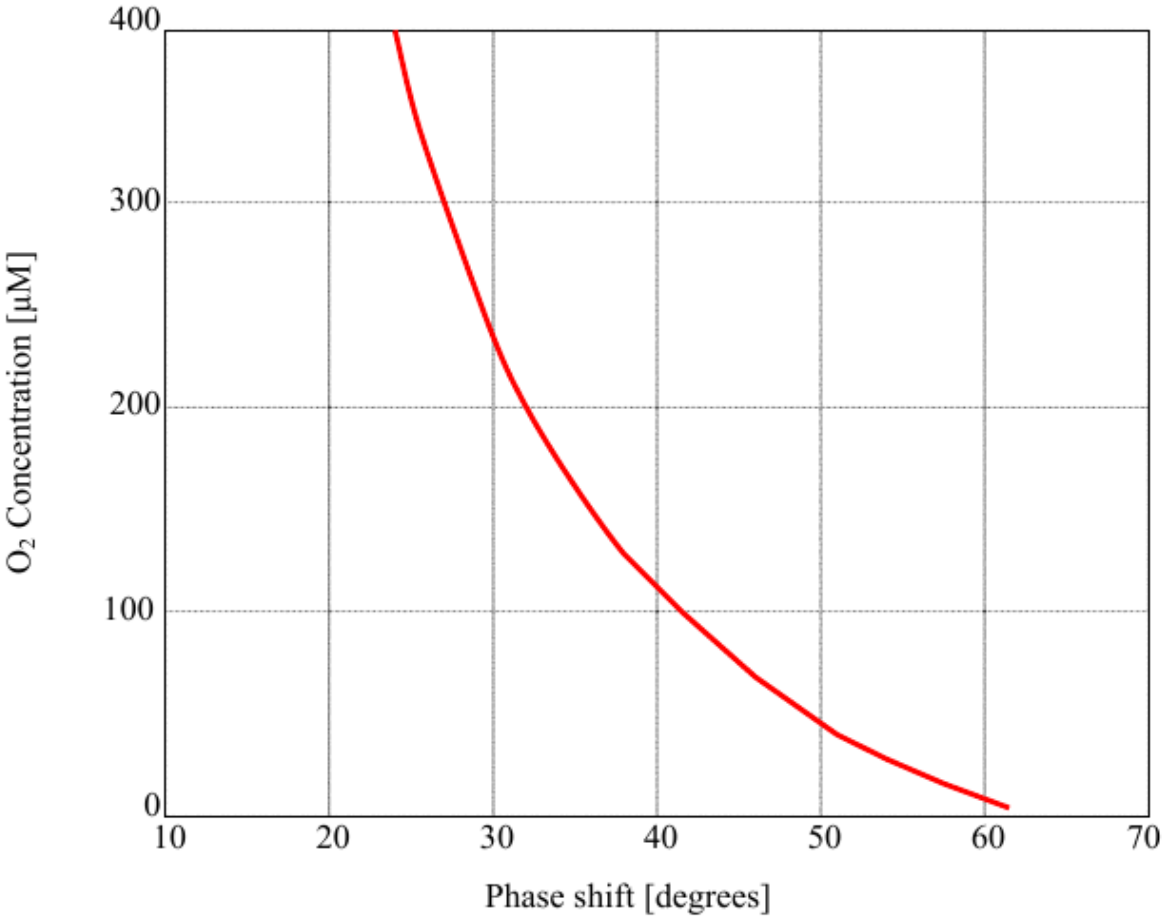

Introduction Oxygen Optode

From the Phase shift to oxygen:

- AADI purchases sensing foil from PreSense Incorporation (good for 100 optodes)

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- AADI purchases sensing foil from PreSense Incorporation (good for 100 optodes)
- The sensing foil batch (good for 100 optodes) is “bulk” calibrated by finding an Dphase/oxygen relation which depends on temperature:
  - typically **5 temperatures** (between 3° and 40°C) and **7 oxygen concentrations** (0 to 400µmol/l)

Introduction Oxygen Optode

$$[\ O_2\ ] = C_0 + C_1 P + C_2 P^2 + C_3 P^3 + C_4 P^4$$

where P = Dphase and each C is a 3rd order polynom on temperature T:

$$C_X = C_{X,0} + C_{X,1} T + C_{X,2} T^2 + C_{X,3} T^3$$

Results are reported in a data sheet that comes with each optode...

Introduction Oxygen Optode

Calibration points and phase readings (degrees)

Temperature (°C)		3.04	10.78	20.35	30.00	39.56
Pressure (hPa)		972.00	972.00	972.00	972.00	972.00
O2 in % of O2+N2	0.00	72.89	72.27	71.36	70.47	69.51
	1.00	68.28	67.21	65.74	64.29	62.76
	2.00	64.58	63.19	61.34	59.57	57.76
	5.00	55.90	54.05	51.72	49.51	47.43
	10.00	46.52	44.50	42.07	39.84	37.85
	20.90	35.52	33.65	31.50	29.61	28.00
	30.00	30.42	28.73	26.82	25.16	23.79

Laboratory calibration

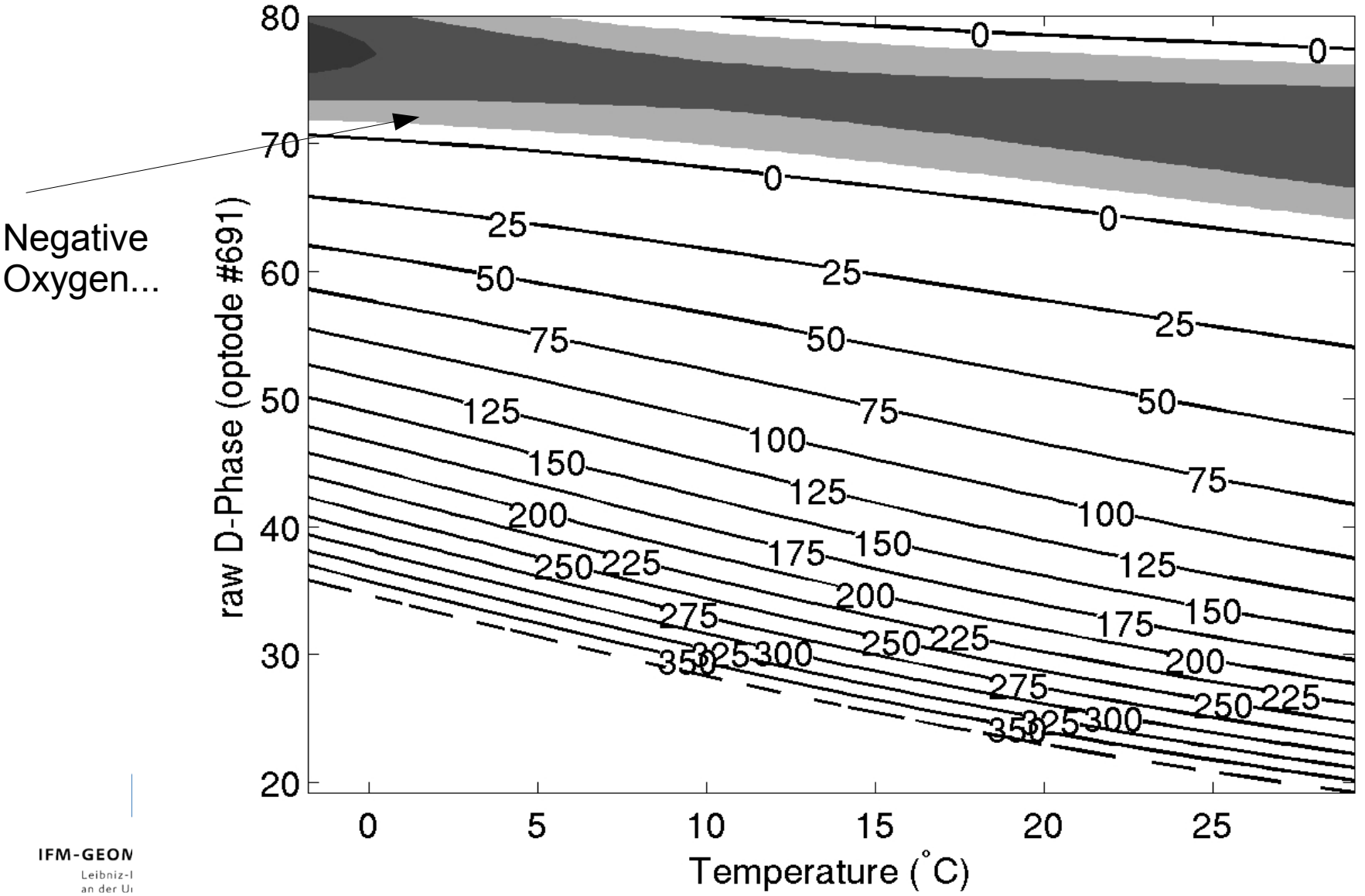
Giving these coefficients [1)]

Index	0	1	2	3
C0 Coefficient	4.60262E+03	-1.56352E+02	3.11002E+00	-2.63289E-02
C1 Coefficient	-2.56549E+02	7.84126E+00	-1.55660E-01	1.32344E-03
C2 Coefficient	5.79714E+00	-1.58265E-01	3.17570E-03	-2.71486E-05
C3 Coefficient	-6.10916E-02	1.48660E-03	-3.05830E-05	2.62173E-07
C4 Coefficient	2.46453E-04	-5.32422E-06	1.13945E-07	-9.73074E-10

$C_{X,0,\ldots}$

Batch Calibration

- Example: Foil-batch no. 4804



Fine-tuning: Individual foil Calibration

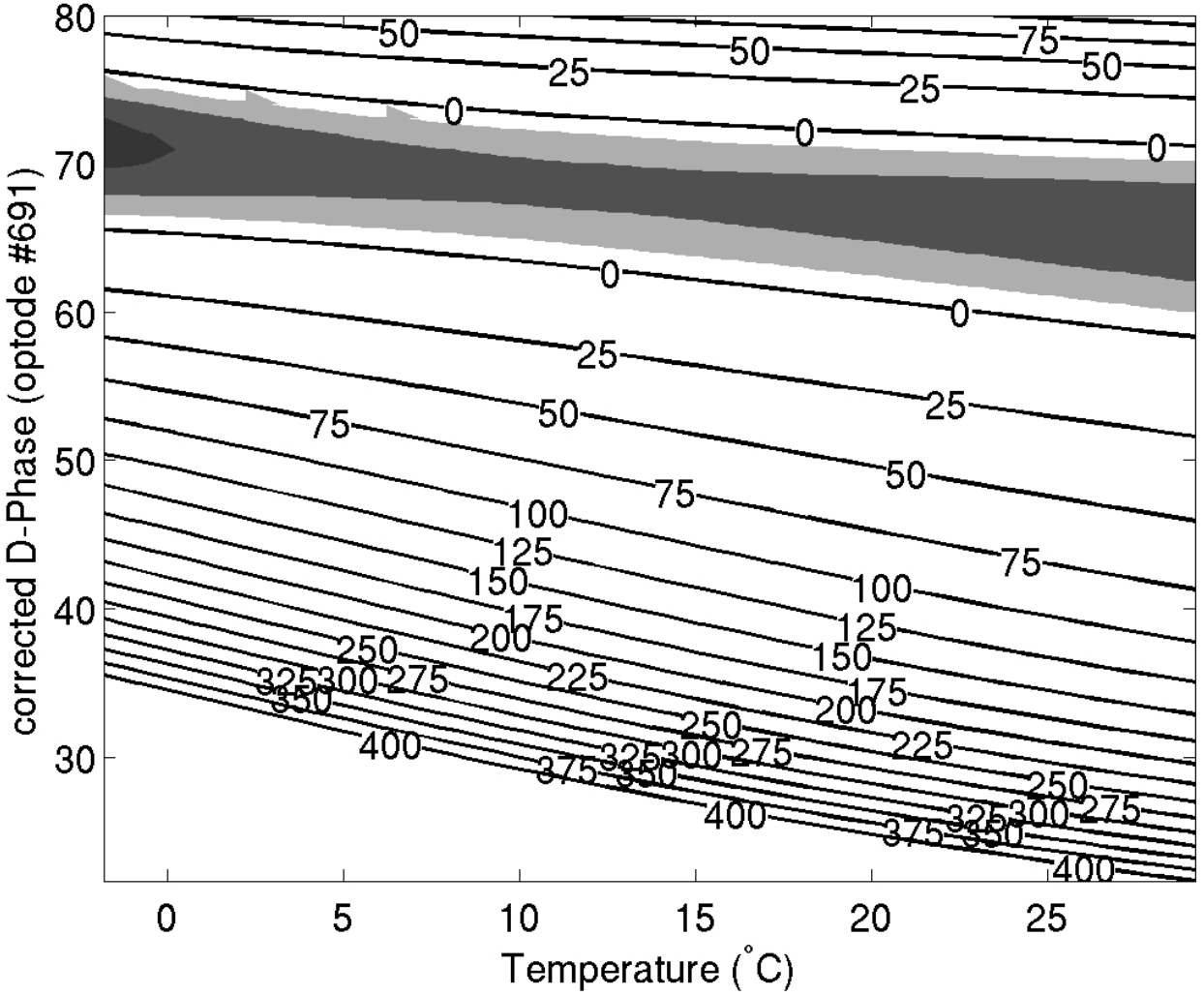
- Two – point calibration for raw Dphase
  (1^{st} order polynom is derived)
- Two – point calibration (see also Aanderaa manual)
  - O_2 = 0% (Temp. T1, pressure p1)
  - O_2 = 100% (Temp. T2, pressure p2)

for 0%: use sodium sulfite (Na_2SO_3) to remove oxygen

for 100%: inject bubbles

Batch foil calibration + 2-point calibration

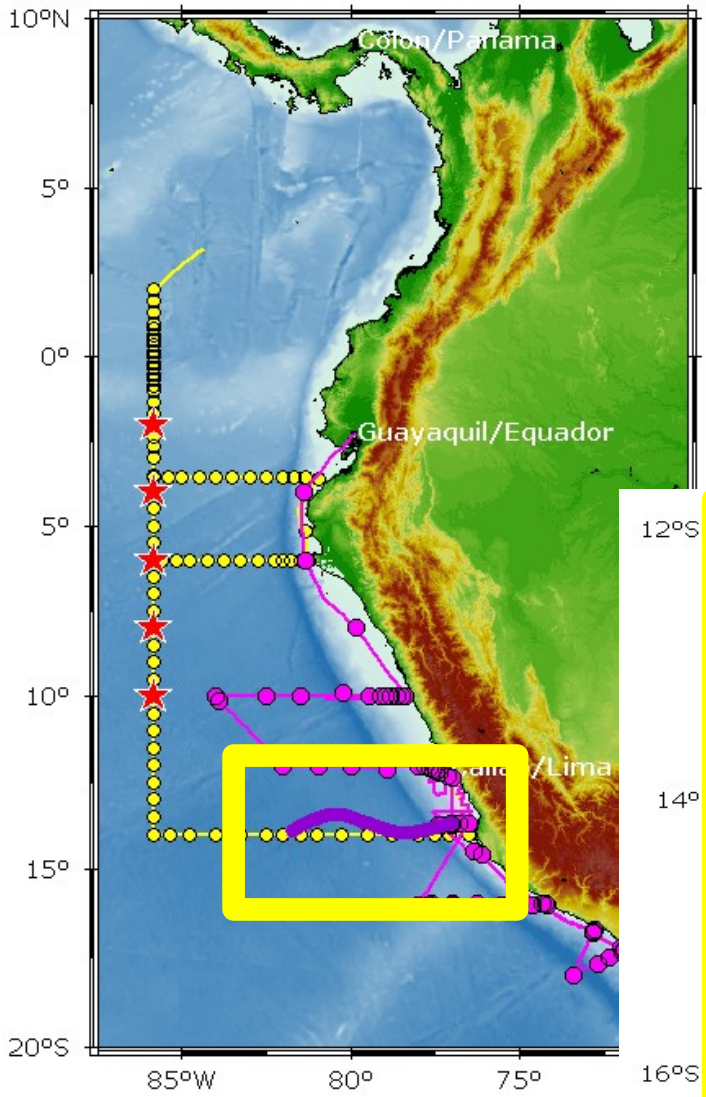
- Dphase (corr) = - 7.4948 + 1.713 * Dphase (raw)



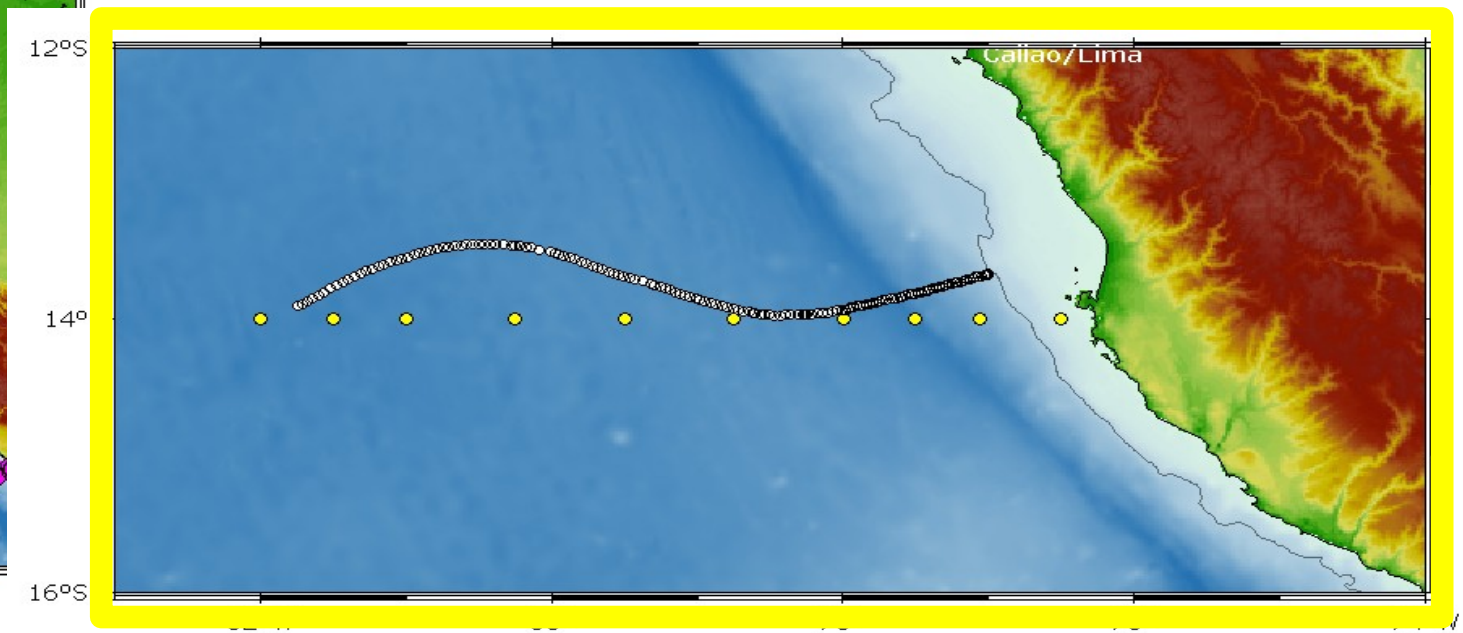
Calibration problem

- Two – point calibration (0/100%) with only one temperature does not constrain well the correction
- Some laboratories calibrate the optode based on a range of temperature/oxygen/pressure situations
- Not always possible!! → in-situ calibration

Mission in the Southeast Pacific



- 20 days: Jan. 2009
- 185 profiles
- 560km section



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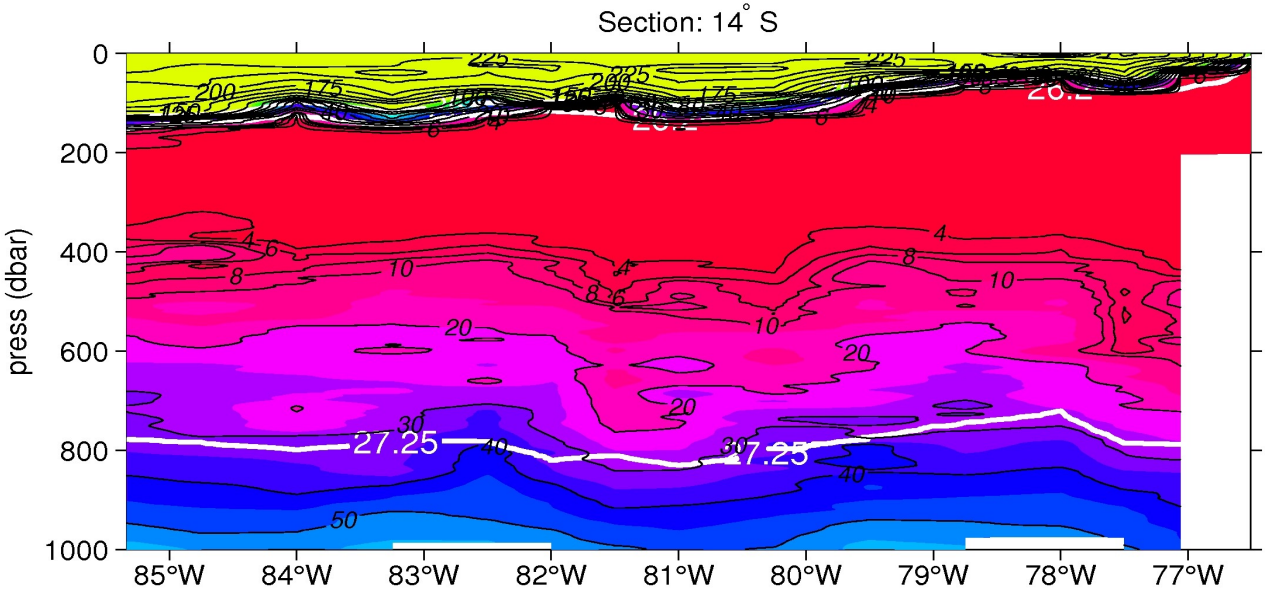
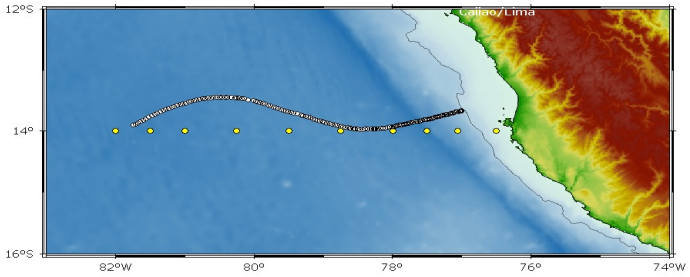
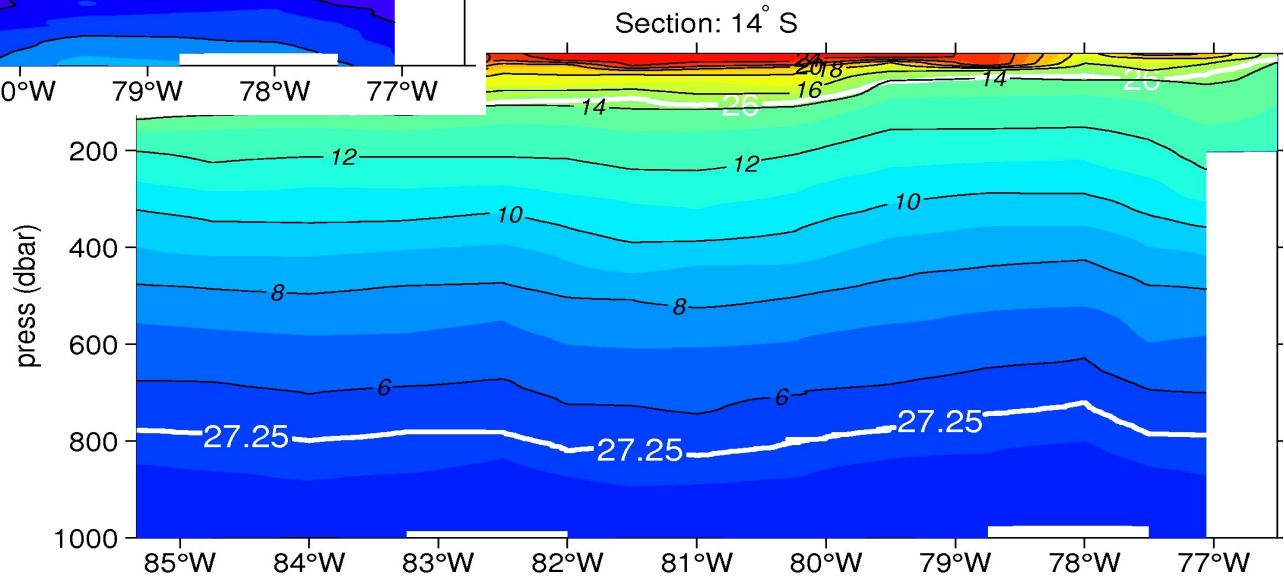
Mission in the Southeast Pacific

- Observations in core of the oxygen minimum zone (150 to 500m depth range)







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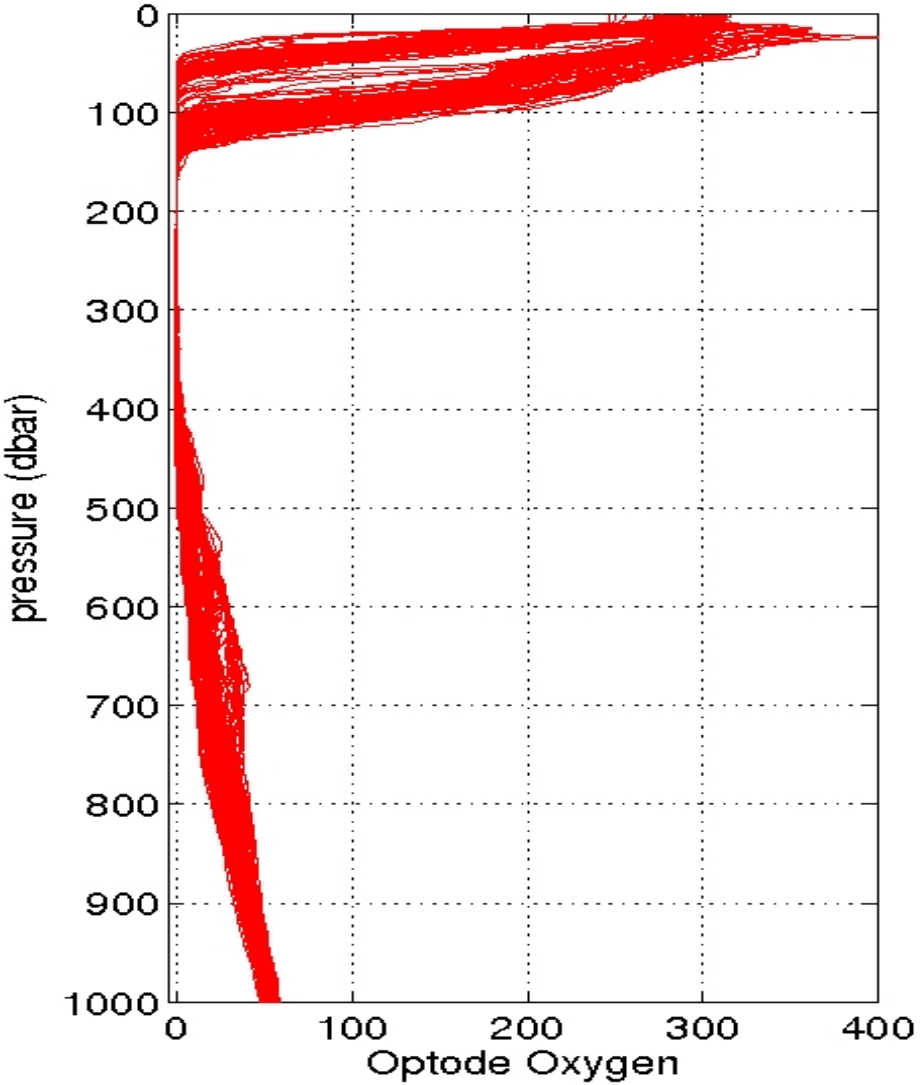
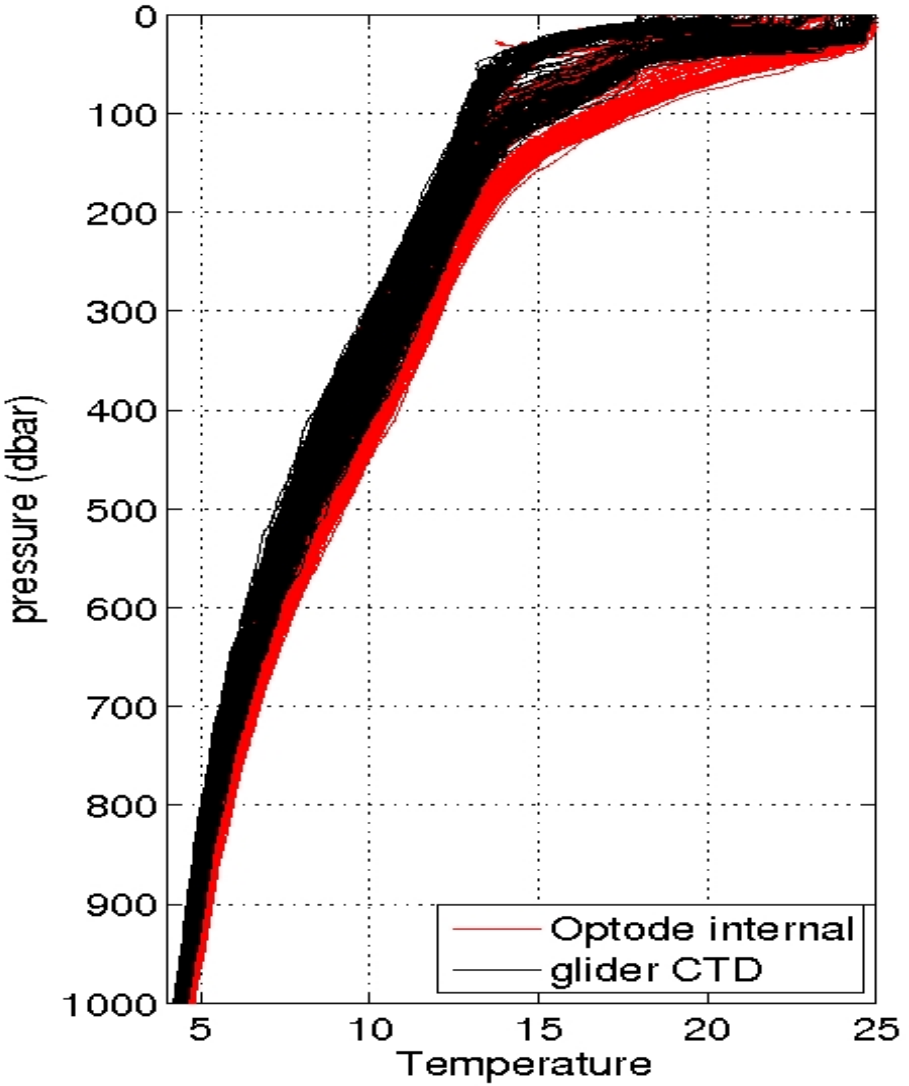
Mission in the Southeast Pacific

- Profiles:
  - Oxygen in Minimum <0
  - Hysteresis in gradient zone (oxycline)



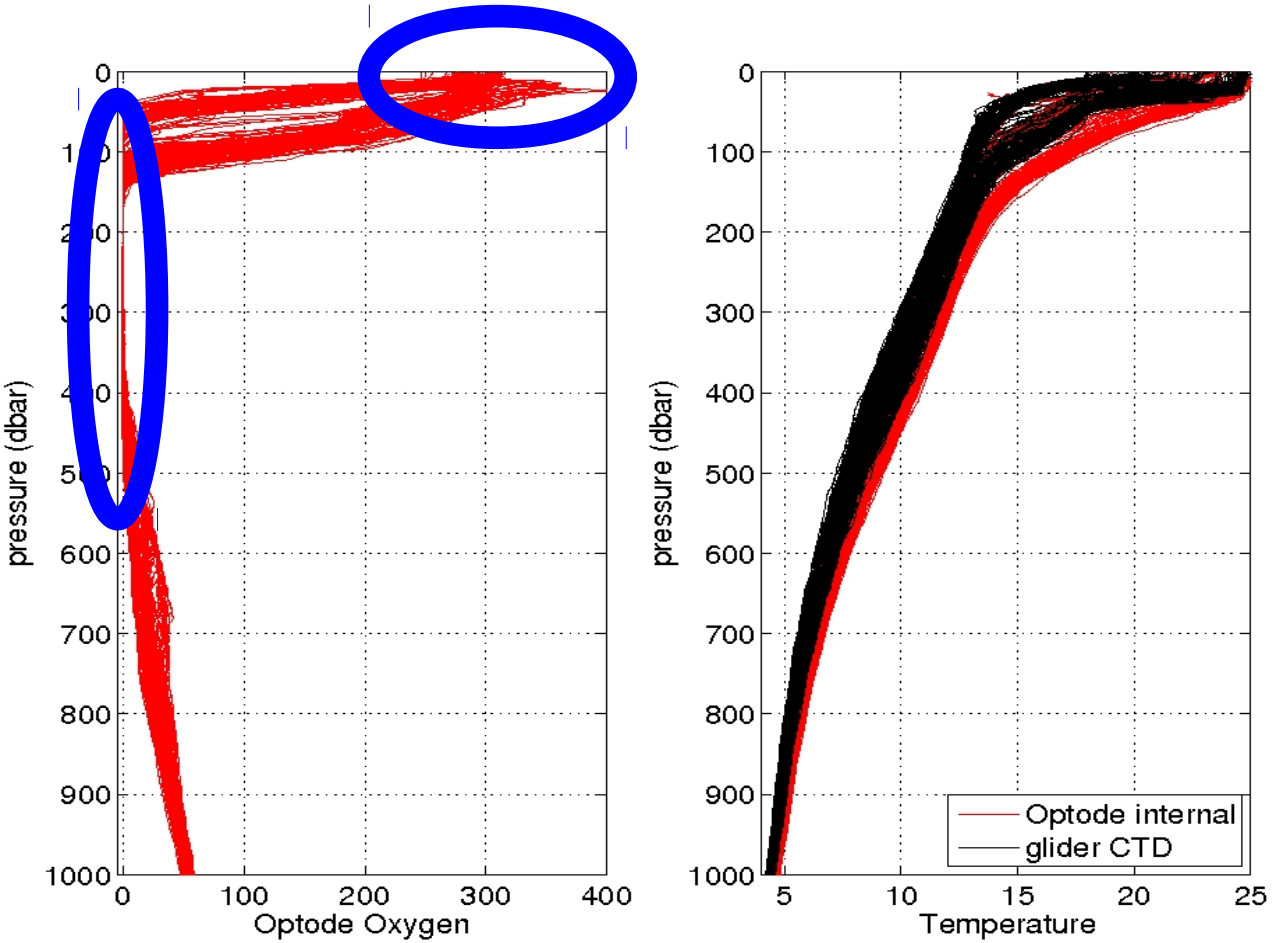
Mission in the Southeast Pacific

- Profiles:
  - Oxygen in Minimum <0
  - Hysteresis in gradient zone (oxycline)
  - Optode temperature too slow → correct by using glider CTD temperature (& salinity)



Mission in the Southeast Pacific

- Good:
  two T/oxygen range with “known” concentration
  → OMZ~3µmol/l; surface=100% saturated



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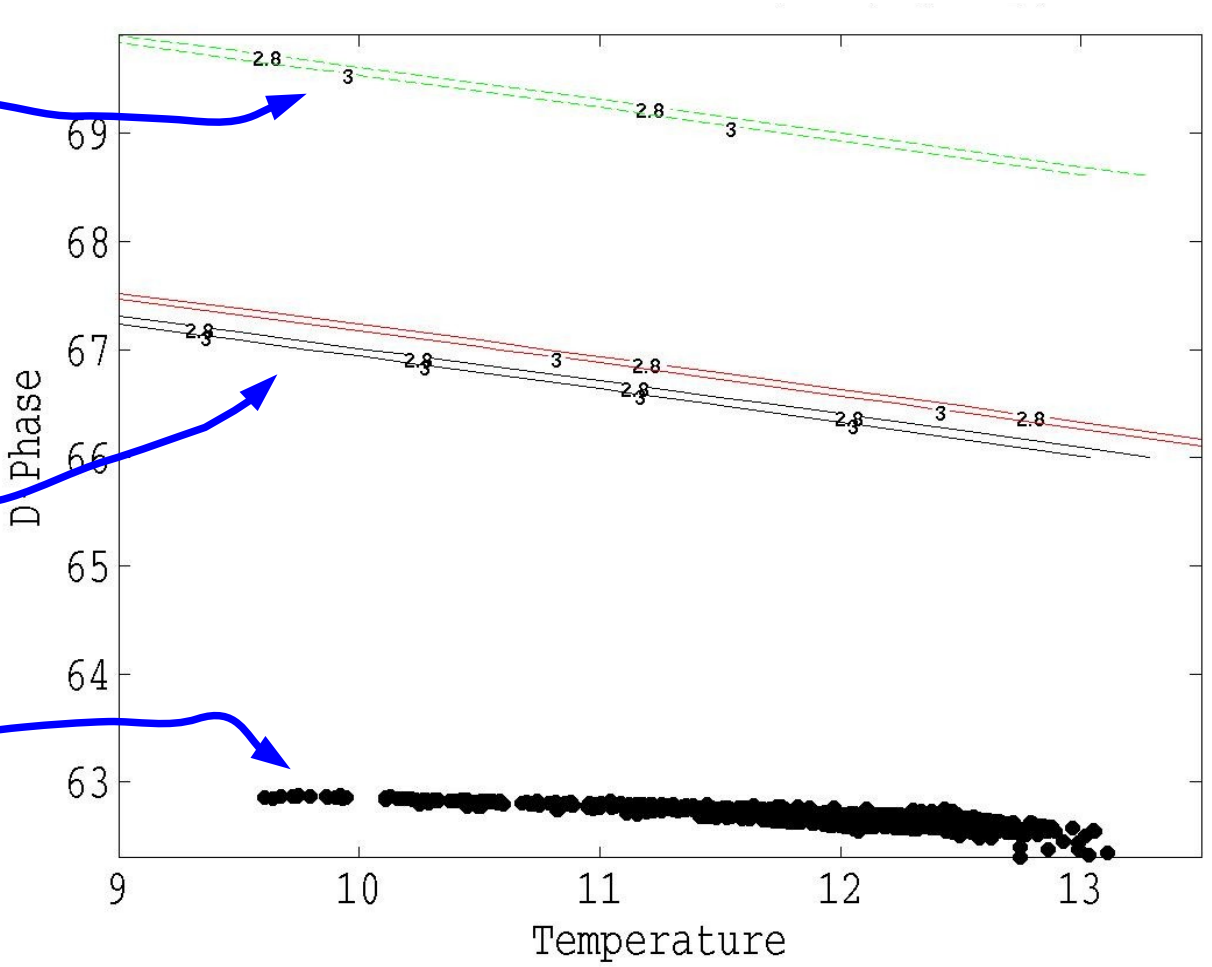
Optode data in “known” concentrations: OMZ (~ 3 mmol/l)

Batch foil calibration (2.8 - 3 µmol/l)

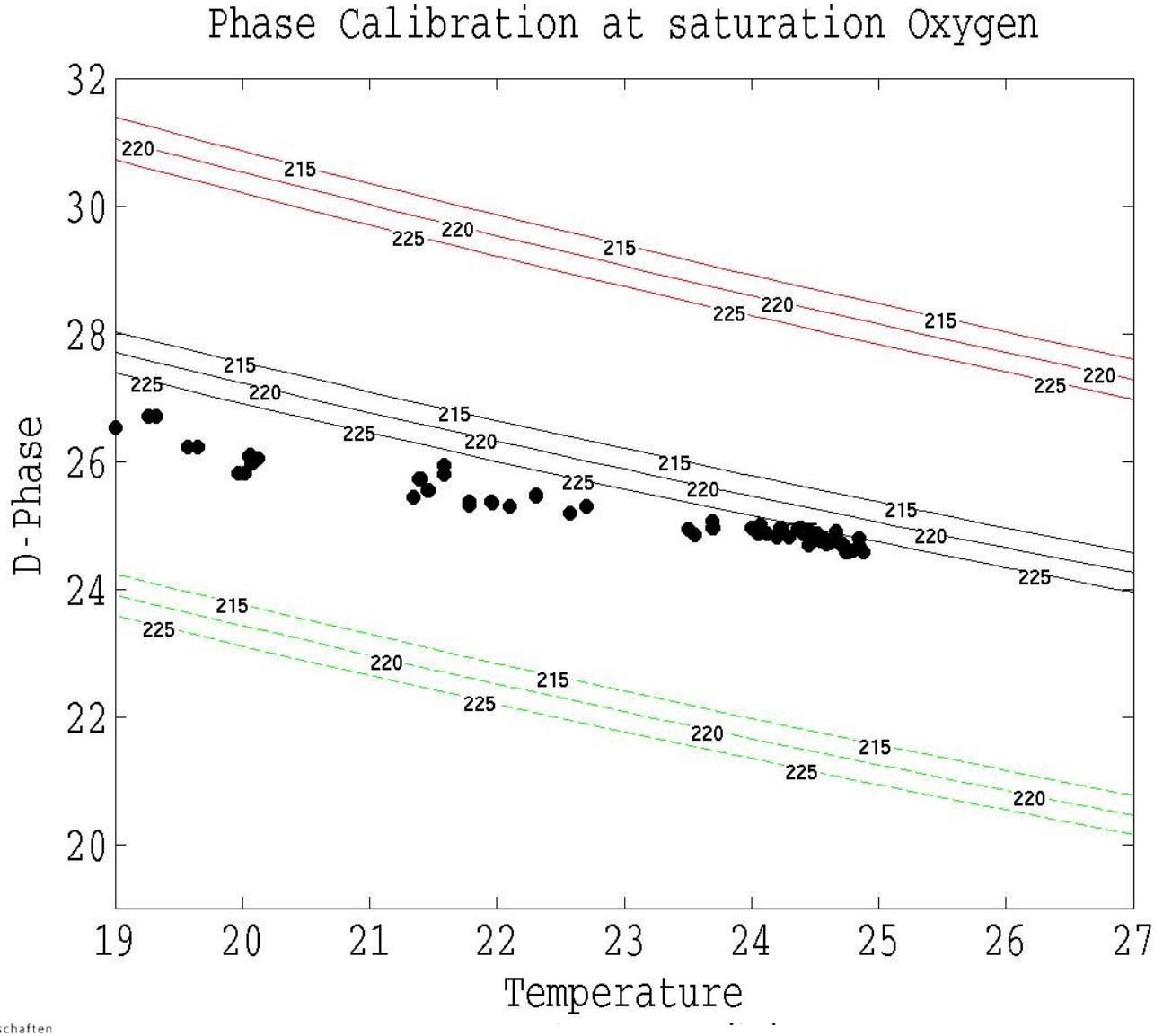
2-point lab & Batch foil calibration (2.8 to 3 µmol/l)

Observed (2.8 to 3 µmol/l)



Optode data in “known” concentrations

- Similar for 100% saturation



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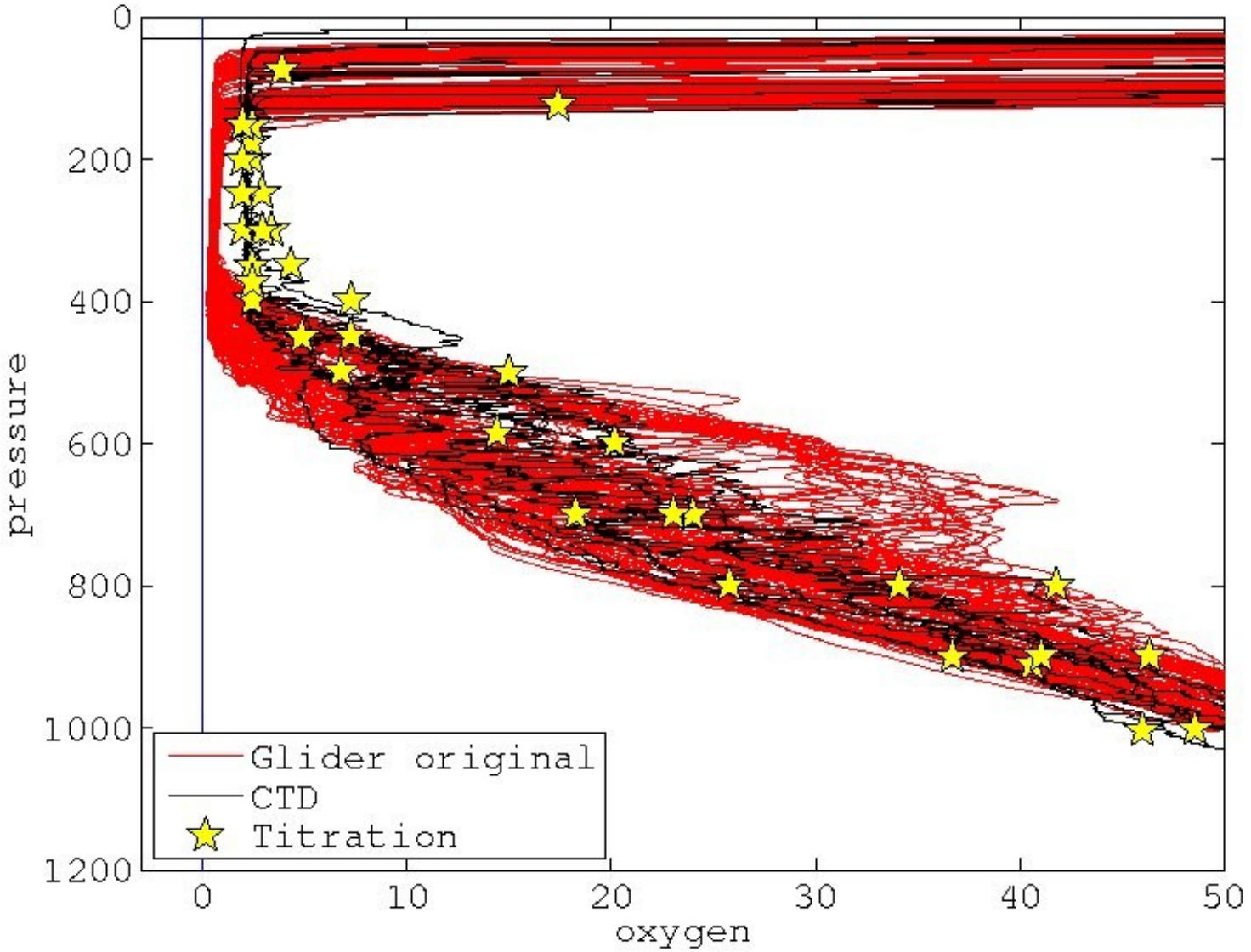
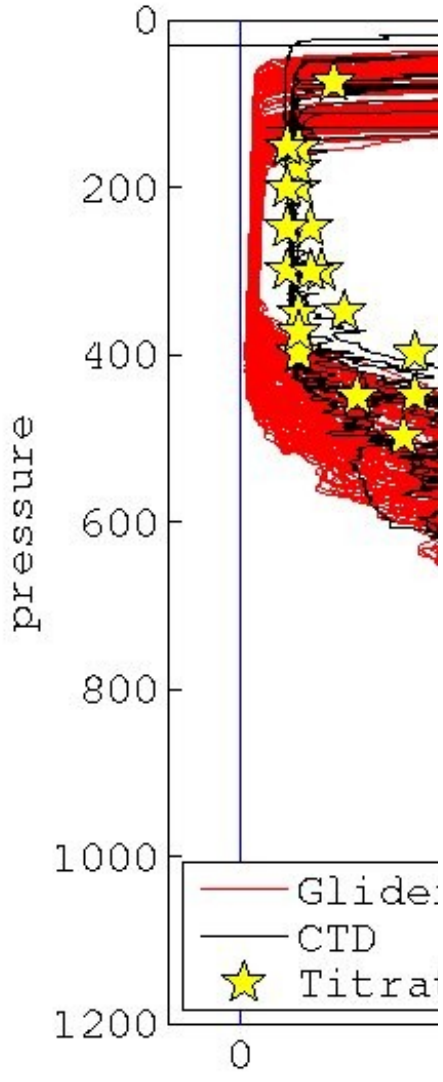
Do a calibration

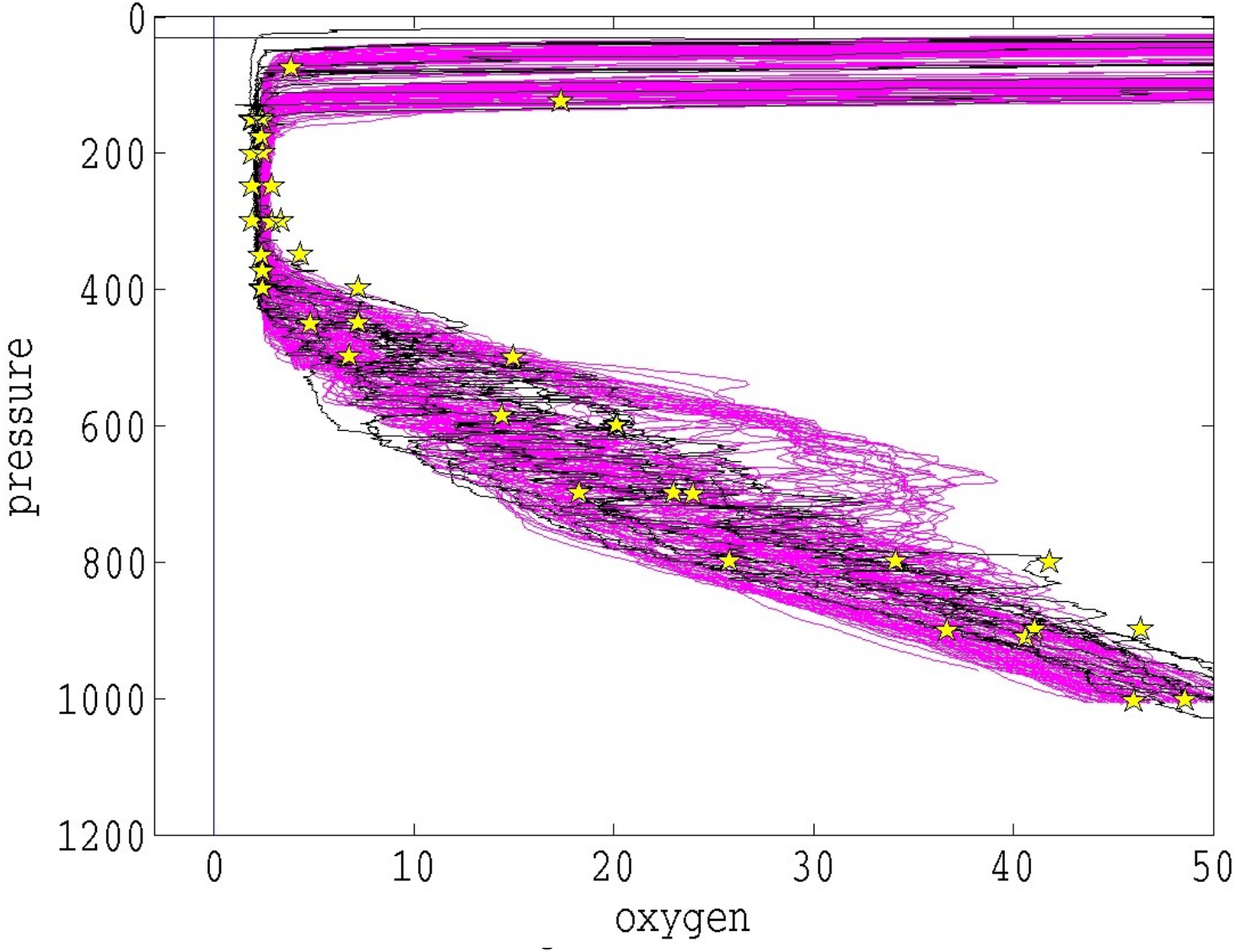
- Advantage of Pacific OMZ data:
  constant & known oxygen content over a wide temperature range
  → A robust least square fit is possible
- Different combinations of variables (T, S, p, O_2) in the constrained Dphase ranges (3µmol/l & 100%) are possible.
- We found a good overall agreement (Winkler & Optode) for a (p, T, T^2) fit.

Before & After



Before & After (with p, T, T^2 fit)





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Recommendations

Before Deployment:

- Always record Dphase
- Do at least a 0% & 100% saturation calibration before deployment
- After 0% & 100% calibration:
  Read out ALL calibration from optode before glider deployment

Deployment:

- Sample 1 sec (SLOCUM glider software > V7.0)
- Record data (at least at some) up AND downcasts

After Deployment:

- Always use calibrated glider CTD temperature and salinity for conversion Dphase → Oxygen (µmol/l)

Thanks

In certain cases calibration is hopeless...

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Manufacturer specification

Table A 2 Specifications for the Oxygen Optode 3830

	Channel1 Oxygen	
	O_2-Concentration	Air saturation
Measuring Range	0-500 µM[3]	0 – 120%
Resolution	< 1 µM	0.4%
Accuracy	< 8 µM or 5%[4] whichever is greater	< 5%[4]
Settling time (63%)	< 25 sec	