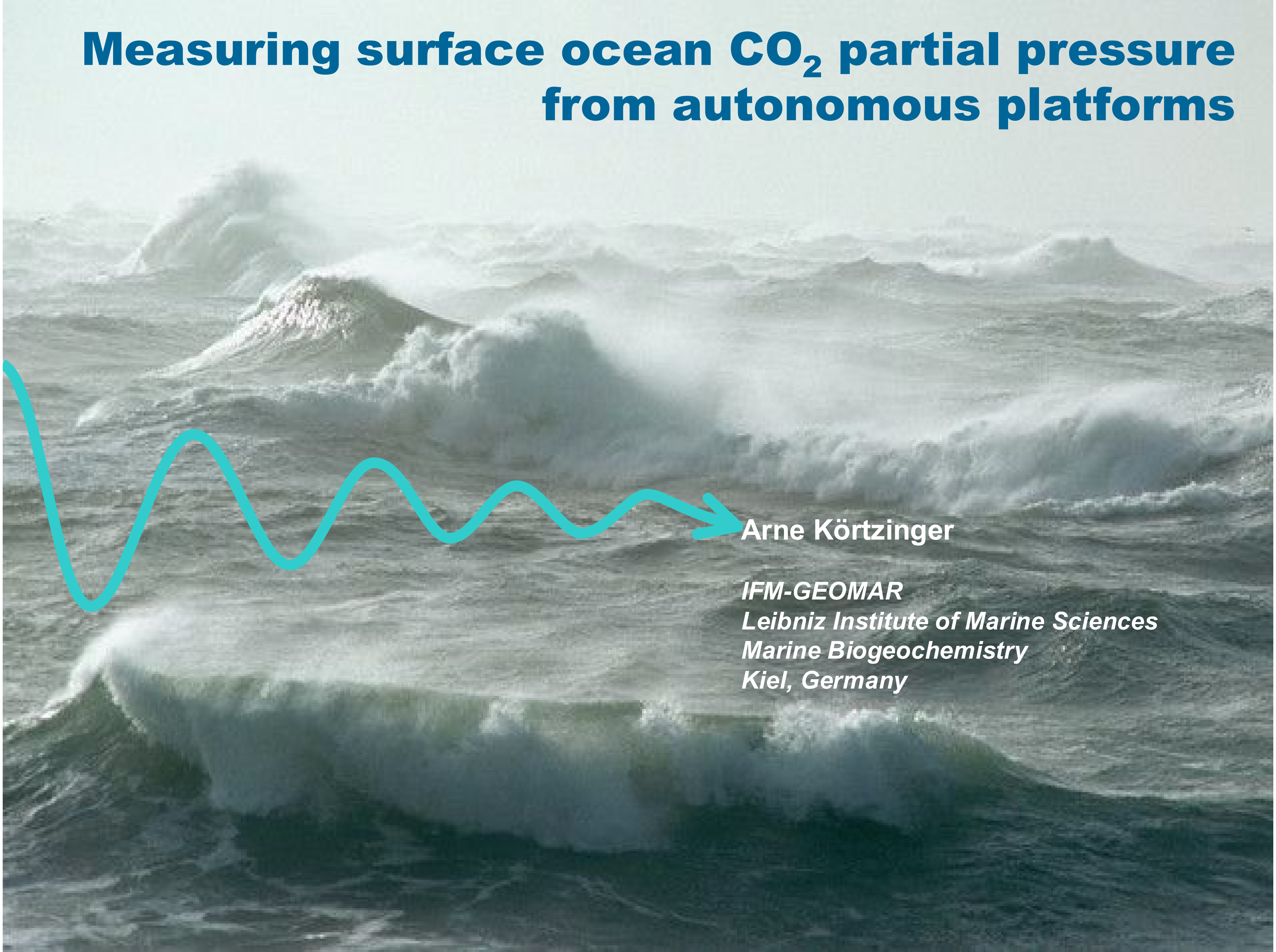
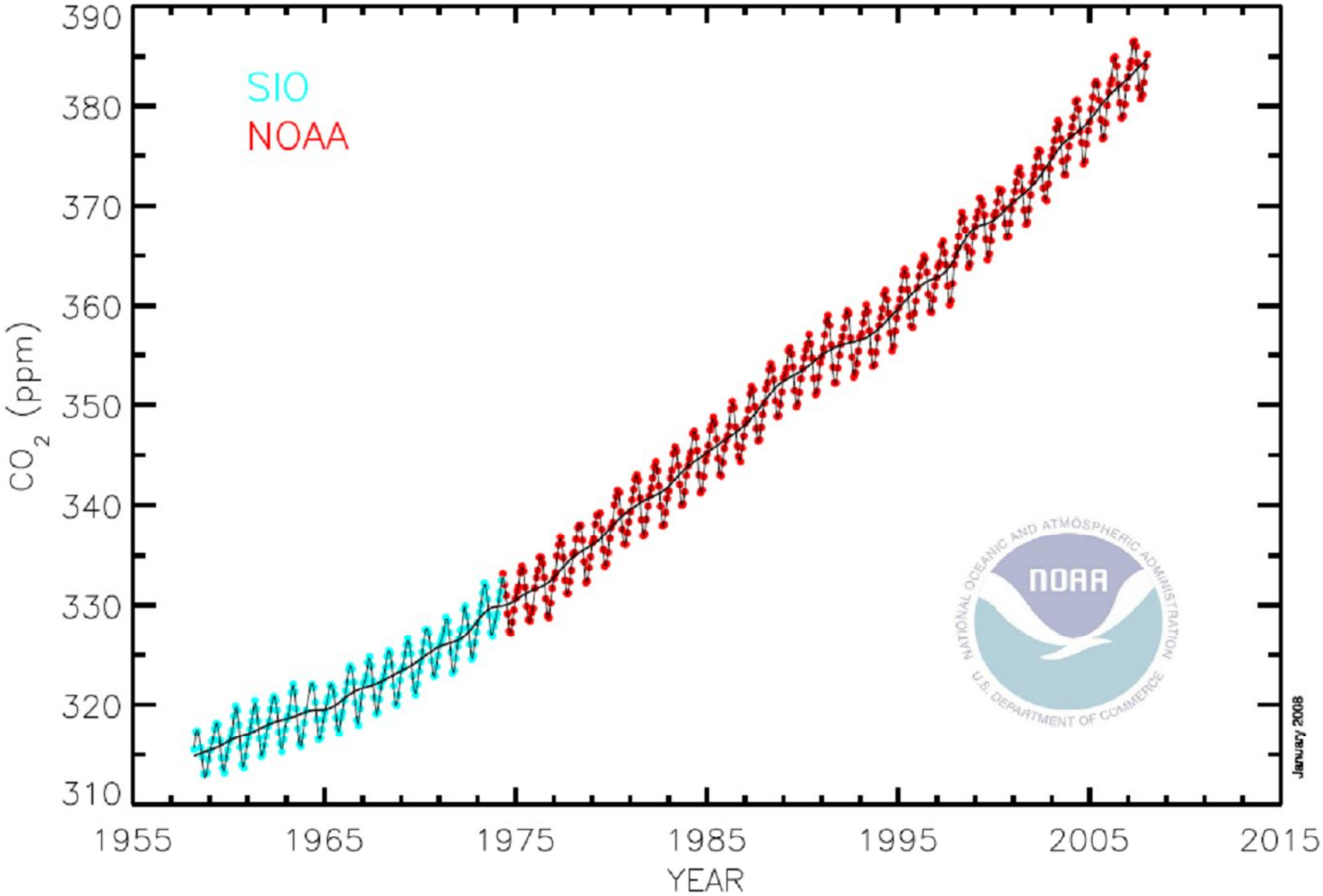
Measuring surface ocean CO_2 partial pressure from autonomous platforms



Arne Körtzinger

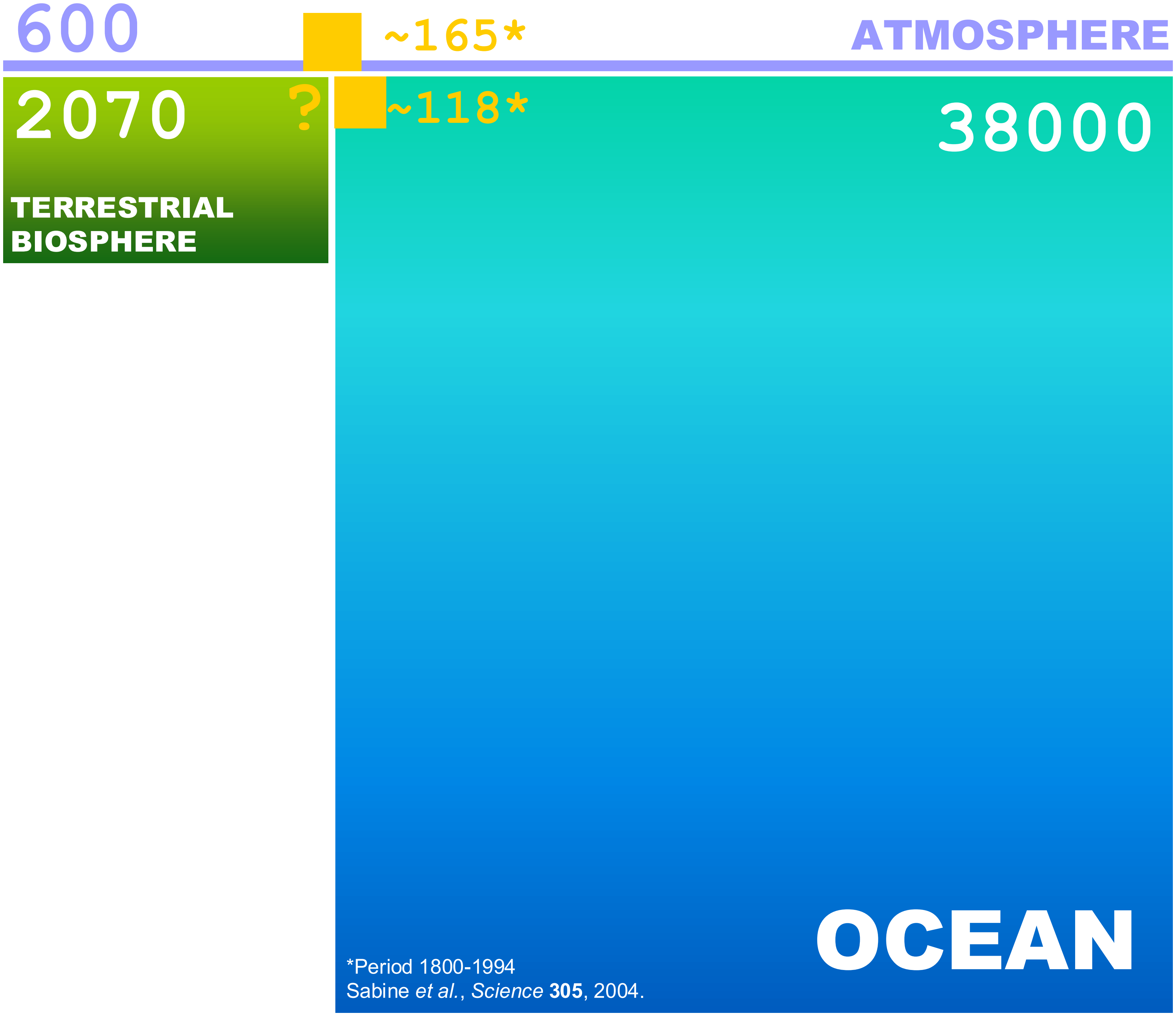
IFM-GEOMAR
Leibniz Institute of Marine Sciences
Marine Biogeochemistry
Kiel, Germany

Mauna Loa monthly mean CO_2 – the "Keeling Curve"

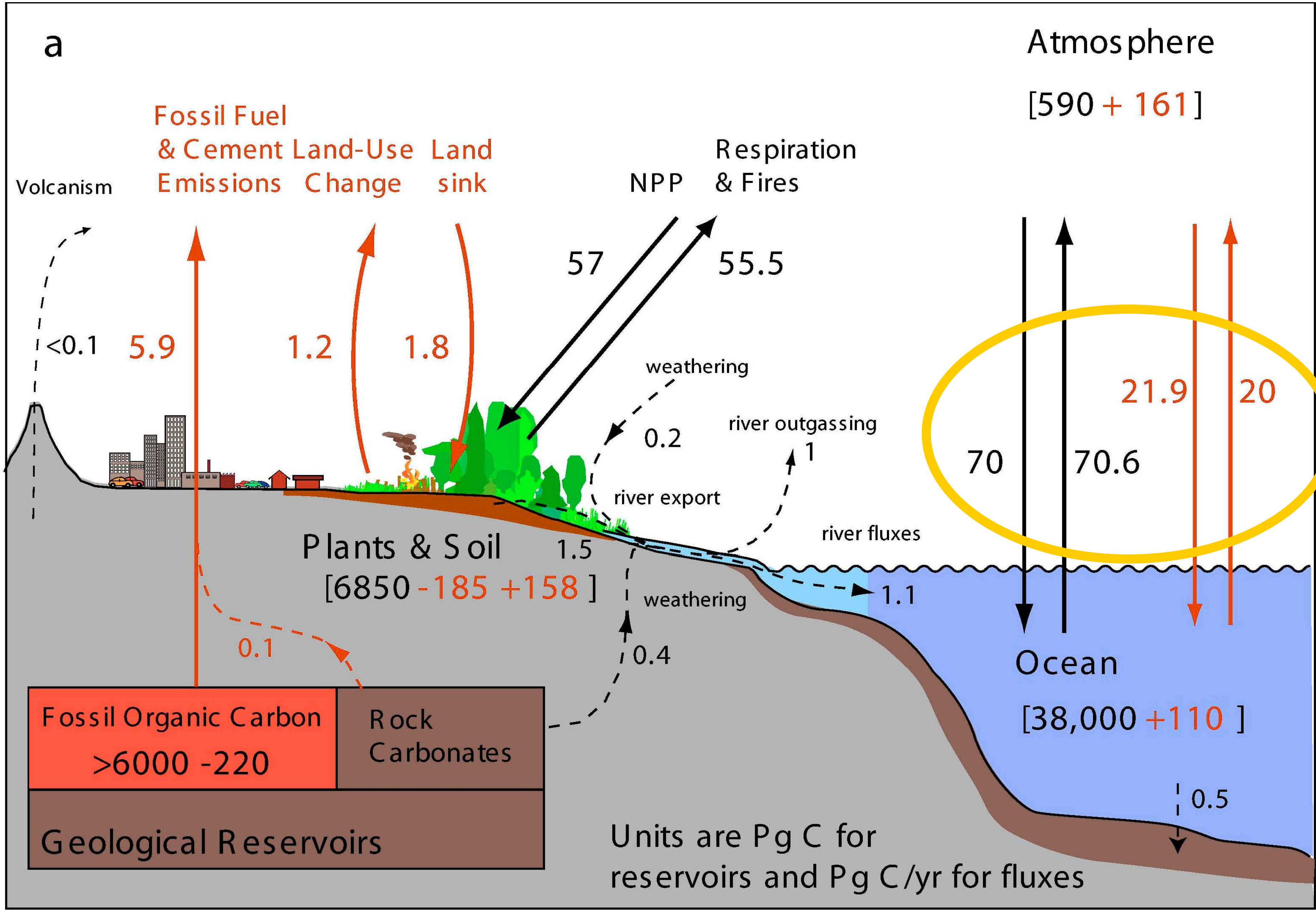


Atmospheric carbon dioxide monthly mean mixing ratios. Data prior to May 1974 are from the Scripps Institution of Oceanography (SIO, blue), data since May 1974 are from the National Oceanic and Atmospheric Administration (NOAA, red). A long-term trend curve is fitted to the monthly mean values. Contact: Dr. Pieter Tans, NOAA ESRL Carbon Cycle, Boulder, Colorado, (303) 497-6678, pieter.tans@noaa.gov, and Dr. Ralph Keeling, SIO GRD, La Jolla, California, (858) 534-7582, rkeeling@ucsd.edu.

Global Carbon Cycle – the most simple depiction...

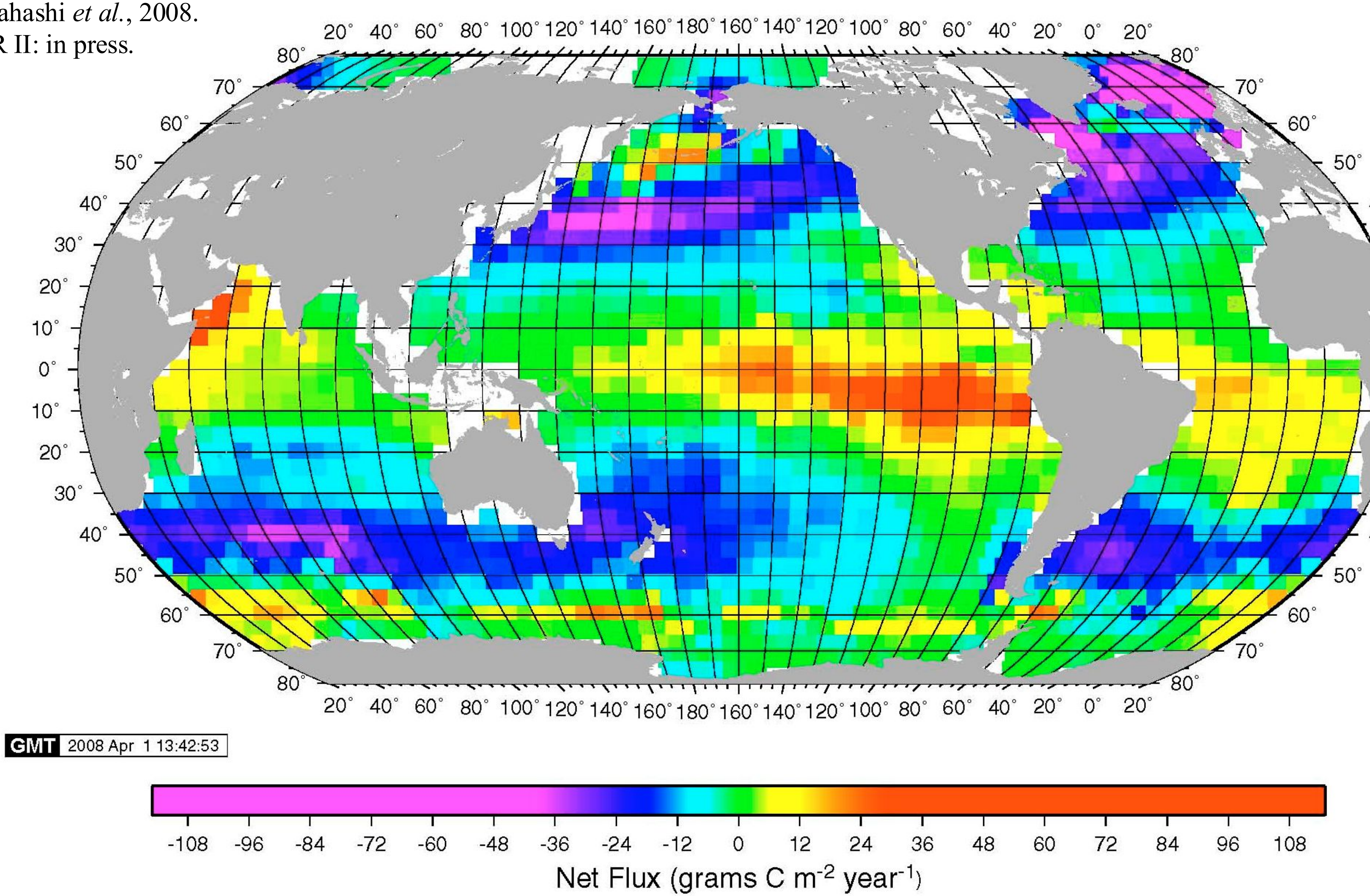


Global Carbon Cycle – the slightly more complicated version...



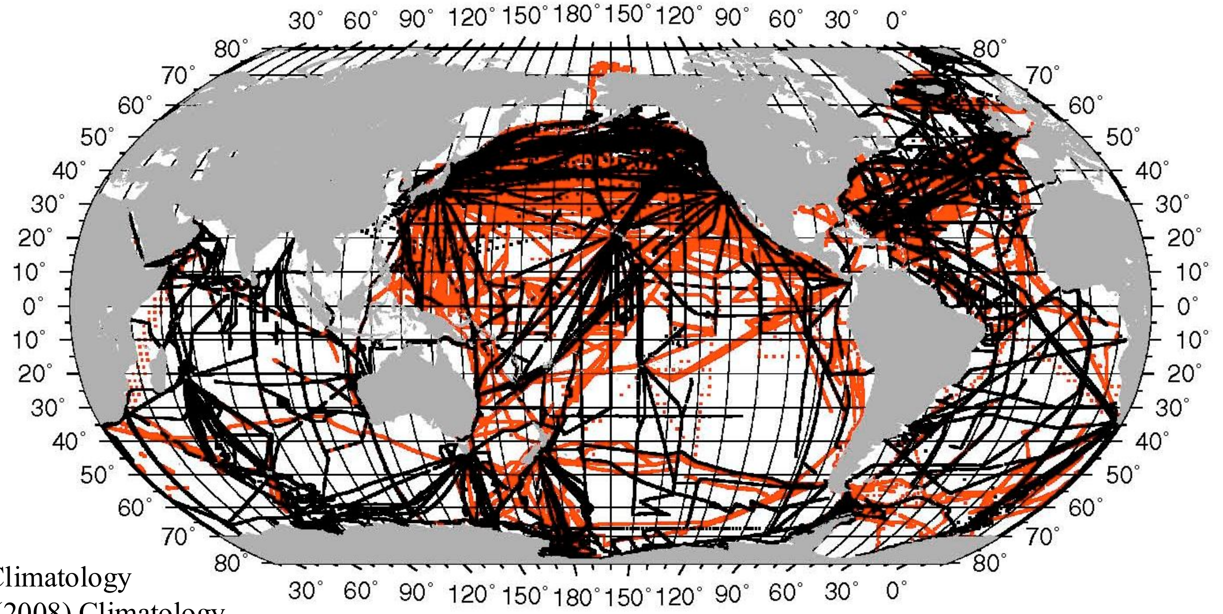
WANTED: pCO$_2$ climatology

Takahashi *et al.*, 2008.
DSR II: in press.

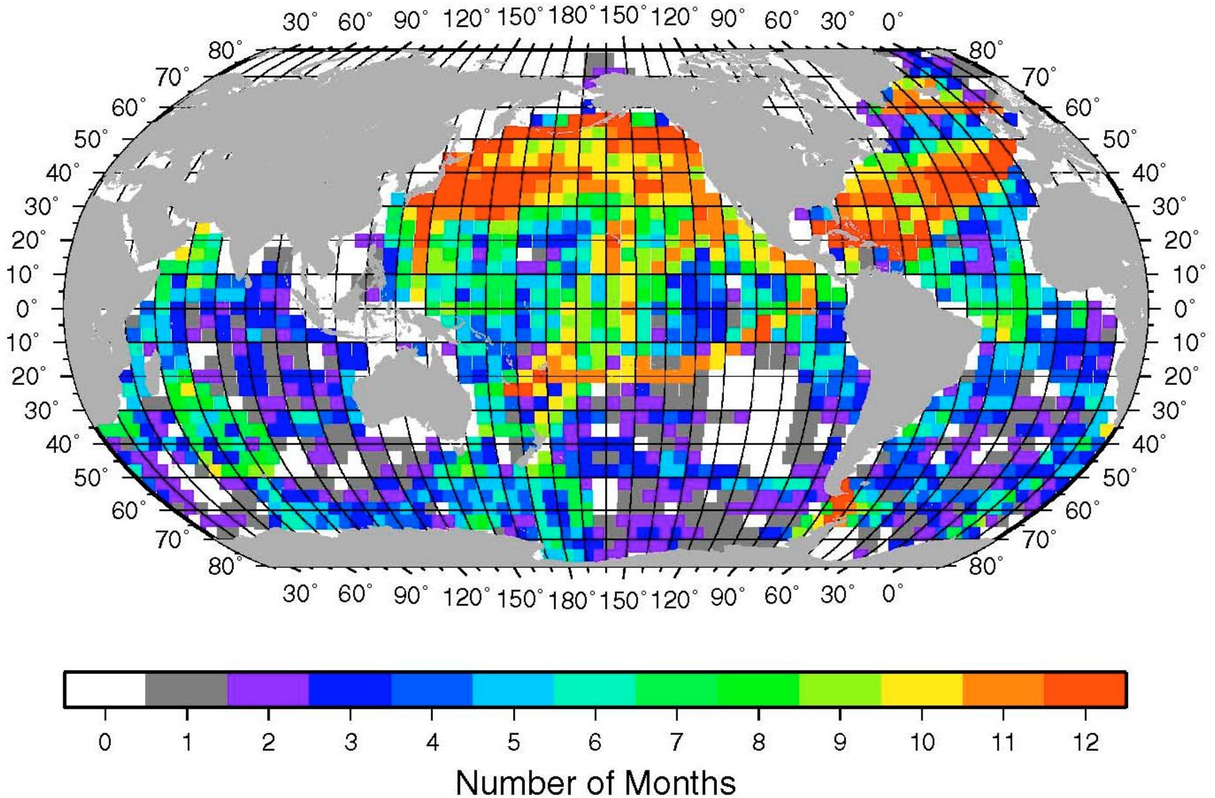


Giant task behind a simple figure

Takahashi *et al.*, 2008.
DSR II: in press.



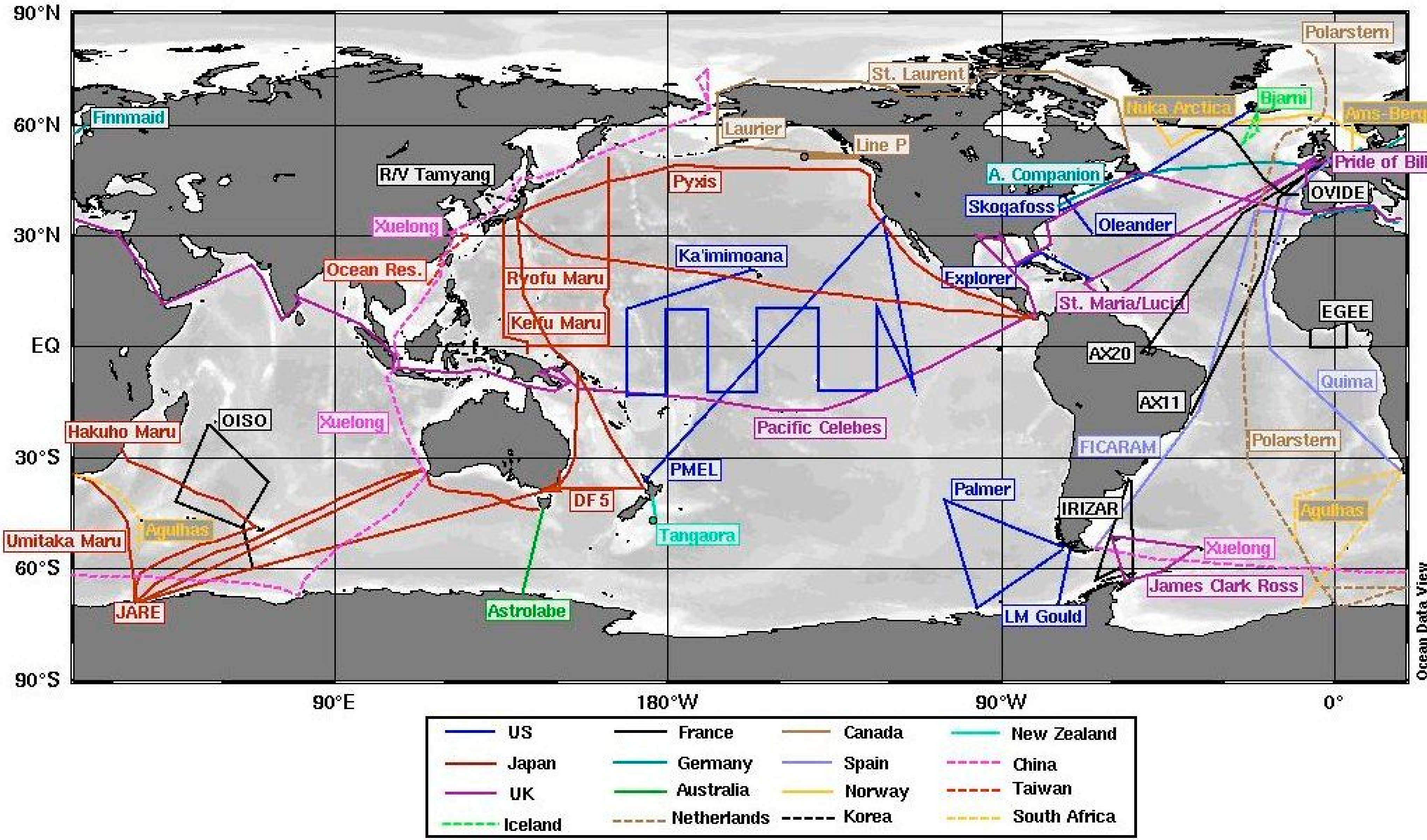
Black: Takahashi *et al.* (2002) Climatology
Red: Added in Takahashi et al. (2008) Climatology



“Voluntary Observing Ships“

European projects: CAVASSOO (2001-2003), CarboOcean (2005-2009)

Global VOS network for pCO_2 measurements



1^{st} Kiel VOS line: M/V *Falstaff*

- M/V *Falstaff*: Wallenius Lines, Stockholm/Sweden
- Established and operated under CAVASSOO in 2002-2003
- Re-activated under CarboOcean in April 2005
- Operation discontinued in summer 2006

- Continuous meas. with telemetry: pCO_2^{sea}, pCO_2^{atm}, T, S, O_2, chlorophyll (worldwide)
- Discrete meas.: DIC, TA, DOC/DON, POC/PON, nutrients, δ^{13}C-DIC (only Atlantic)

2nd Kiel VOS line: M/V *Atlantic Companion*

- M/V *Atlantic Companion*: Atlantic Container Lines, NJ/USA
- Agreement with ACL settled in June 2005
- Ship-side installations: Oct.-Dec. 2005
- GO/Neill pCO_2 system installed in Jan. 2006
- In operation since Feb 2006 with trans-Atlantic crossings every 2.5 weeks

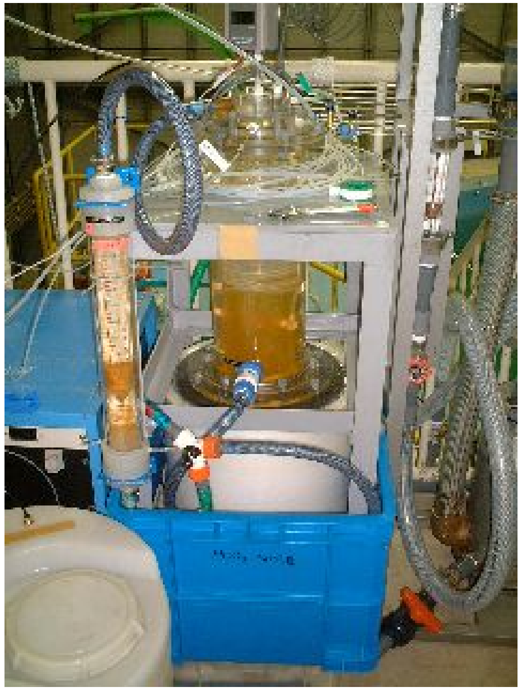
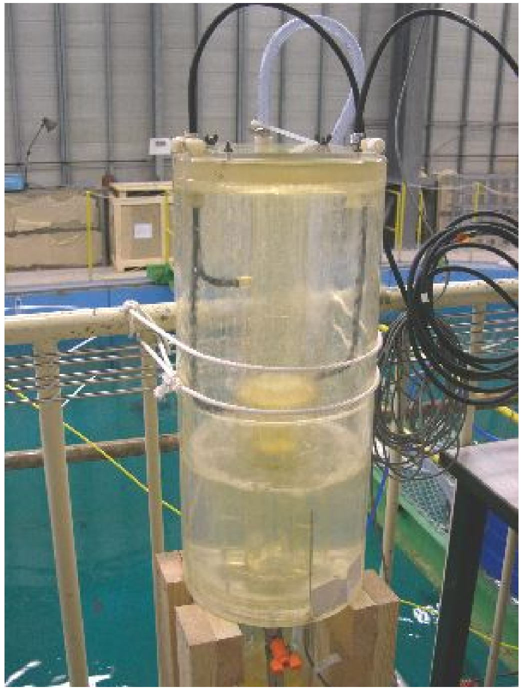
- Continuous meas. with telemetry: pCO_2^{sea}, pCO_2^{atm}, T, S, O_2, chlorophyll
- Discrete meas.: DIC, TA, DOC/DON, POC/PON, nutrients, δ^{13}C-DIC

Kiel VOS lines

CARBOOCEAN, WP4, IFM-GEOMAR contribution

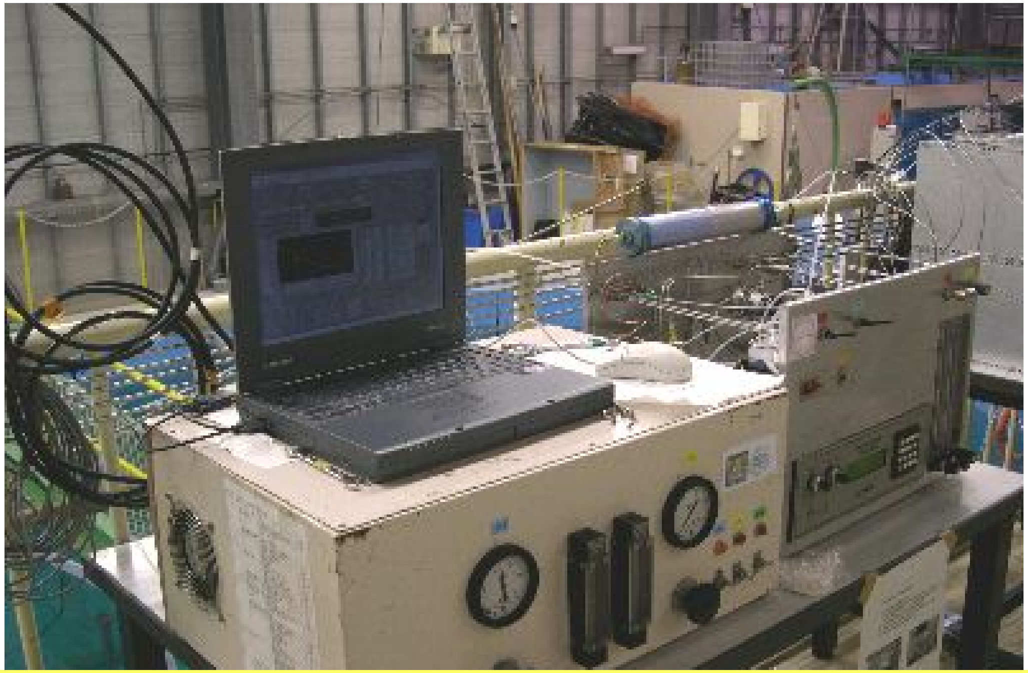
IFM-GEOMAR

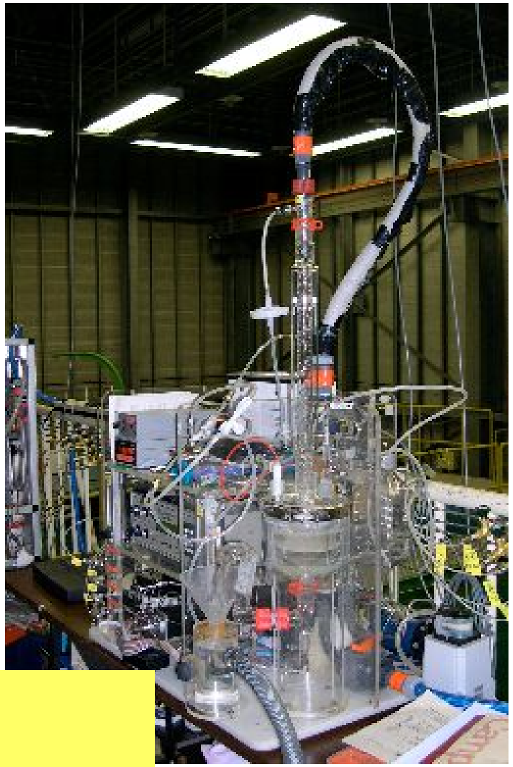
A seemingly simple measurement: take an equilibrator...




... and a CO_2 detector – and you are done!?

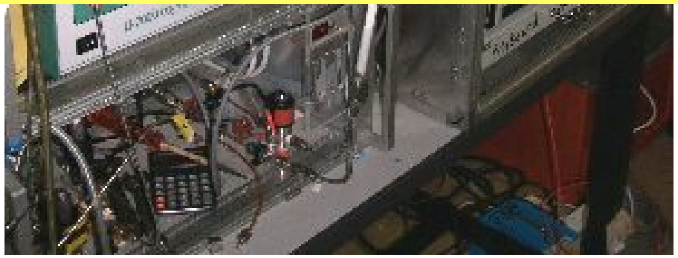


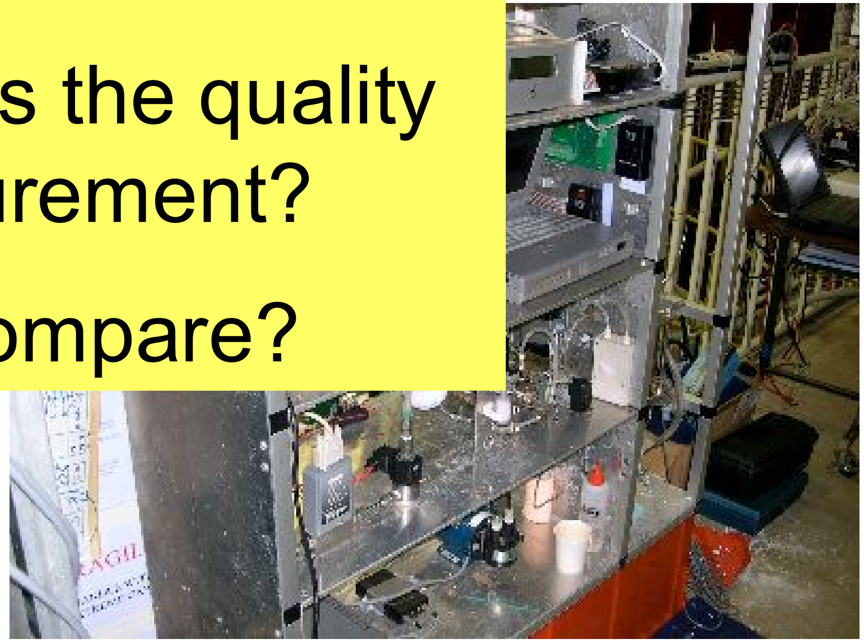


But how good are the data?

How can we assess the quality of the $p\text{CO}_2$ measurement?

How do the data compare?



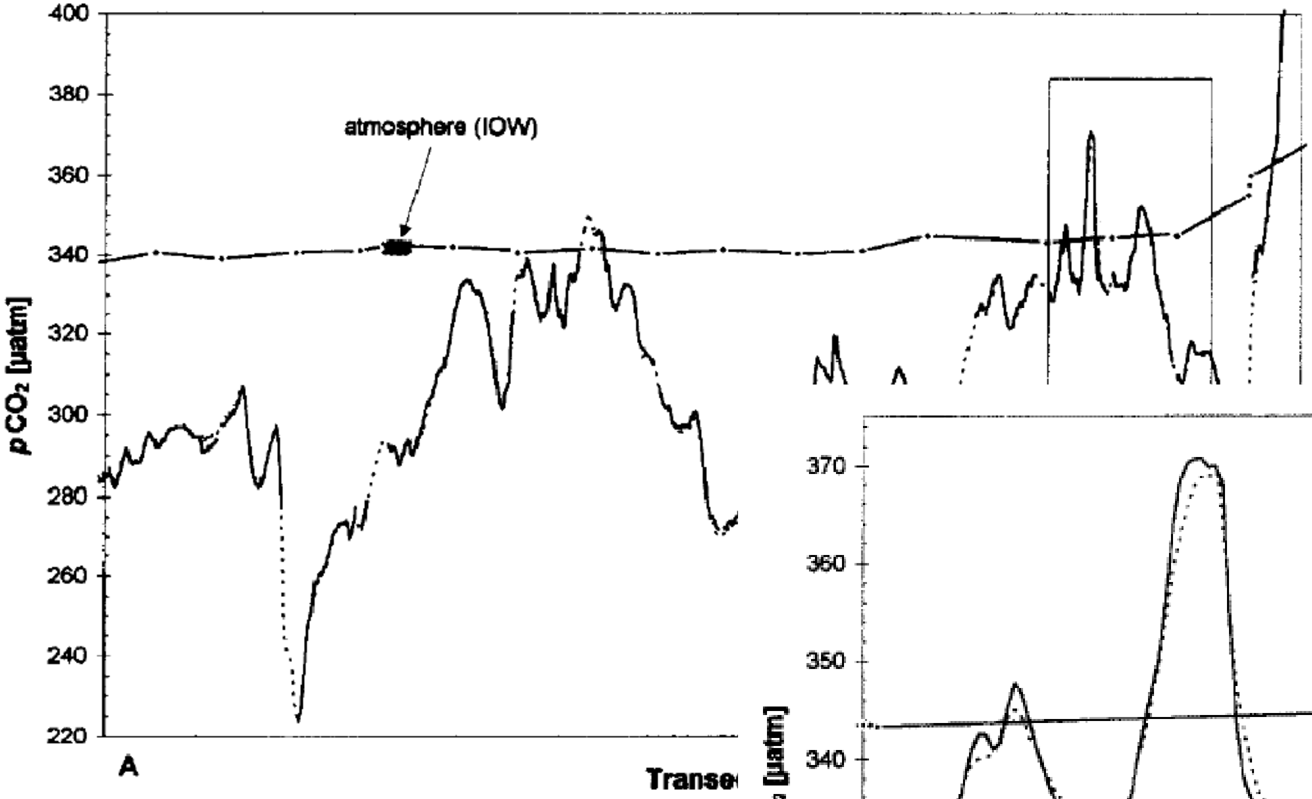


At-sea intercomparison of two pCO_2 systems in the North Sea (Sept. 1994)

Marine Chemistry 52 (1996) 133–145

At-sea intercomparison of two newly designed underway pCO_2 systems — encouraging results

Arne Körtzinger [a,*], Helmuth Thomas [b], Bernd Schneider [b], Nicole Gronau [b], Ludger Mintrop [a], Jan C. Duinker [a]



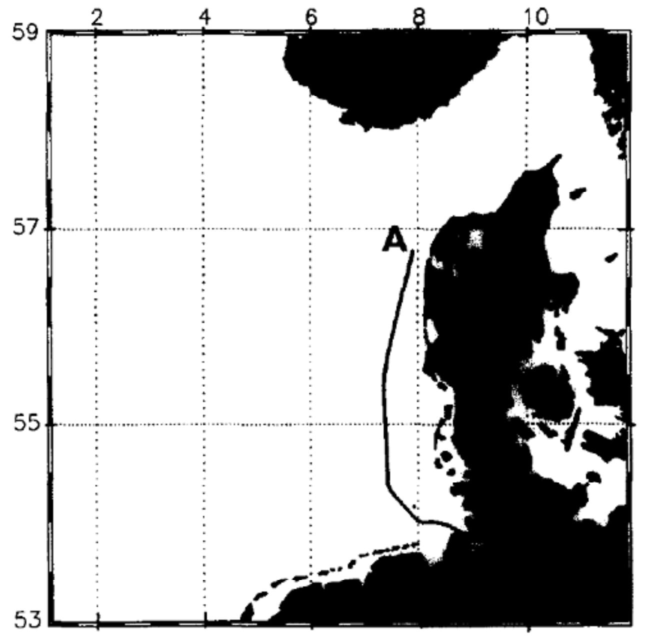
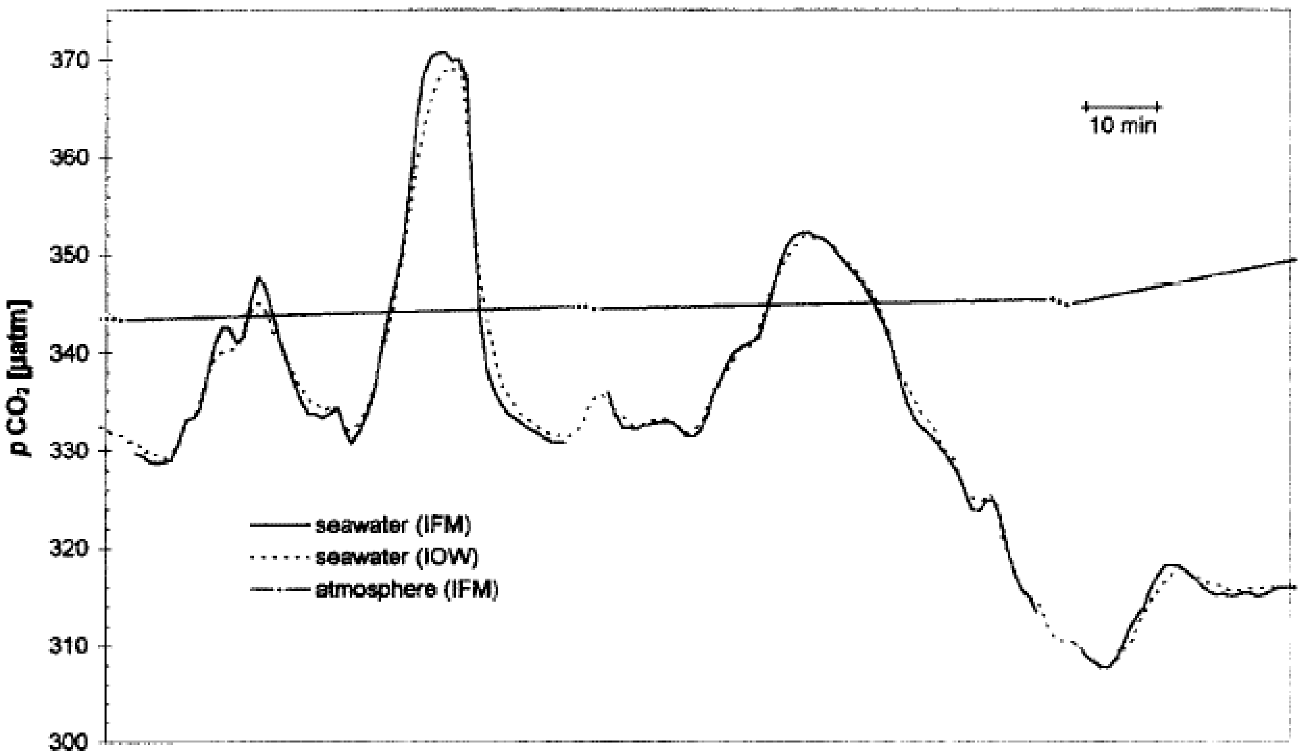


Fig. 4. Location of transect A–B during R/V *Valdivia* cruise no. 148-2 in September 11–14, 1994.

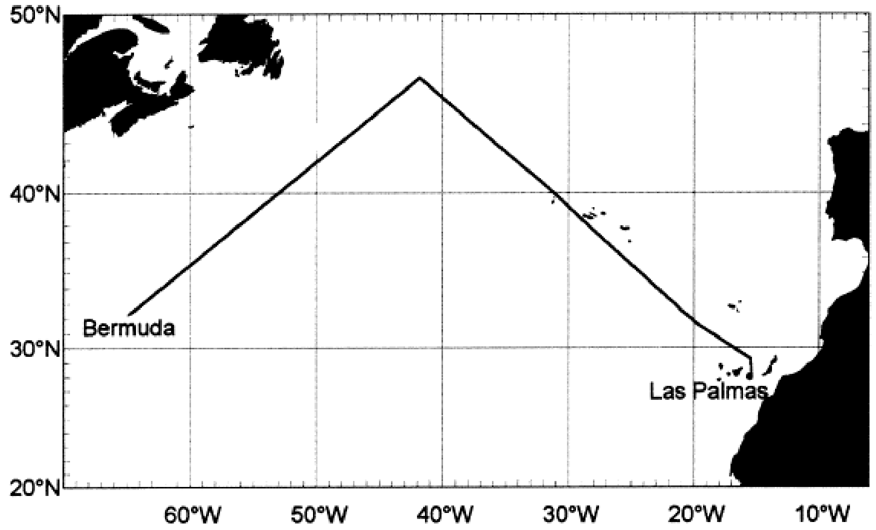


Mean offset:
0.2 ± 1.5 µatm

Marine Chemistry 72 (2000) 171–192

The international at-sea intercomparison of fCO_2 systems during the R/V Meteor Cruise 36/1 in the North Atlantic Ocean

Arne Körtzinger [a,*], Ludger Mintrop [a,b], Douglas W.R. Wallace [a], Kenneth M. Johnson [a,c], Craig Neill [c], Bronte Tilbrook [d], Philip Towler [d], Hisayuki Y. Inoue [e], Masao Ishii [e], Gary Shaffer [f], Rodrigo F. Torres Saavedra [g], Eiji Ohtaki [h], Eiji Yamashita [i], Alain Poisson [j], Christian Brunet [j], Bernard Schauer [j], Catherine Goyet [k], Greg Eischeid [k]



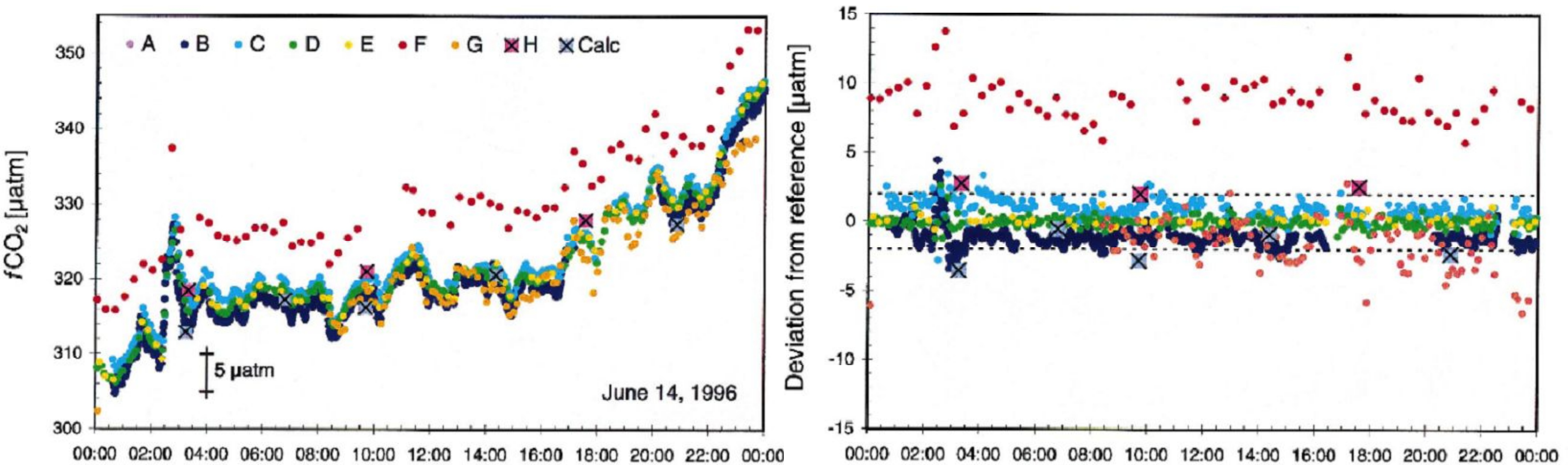


Fig. 8. Results for June 14: seawater fCO_2 as measured by system "A"–"G" (underway) and "H" (discrete) or calculated from A_T and C_T measured on discrete samples (top panel), deviations of seawater fCO_2 from reference (11-min running mean of "D" and "E", middle panel), and in situ surface temperature and salinity (bottom panel).

International at-sea pCO_2 intercomparison during R/V Meteor Cruise 36/1 (June 1996)

Körtzinger *et al.*, Mar. Chem. 72 (2000), 171-192.

xCO_2 calibrations are typically not better than 1 ppmv

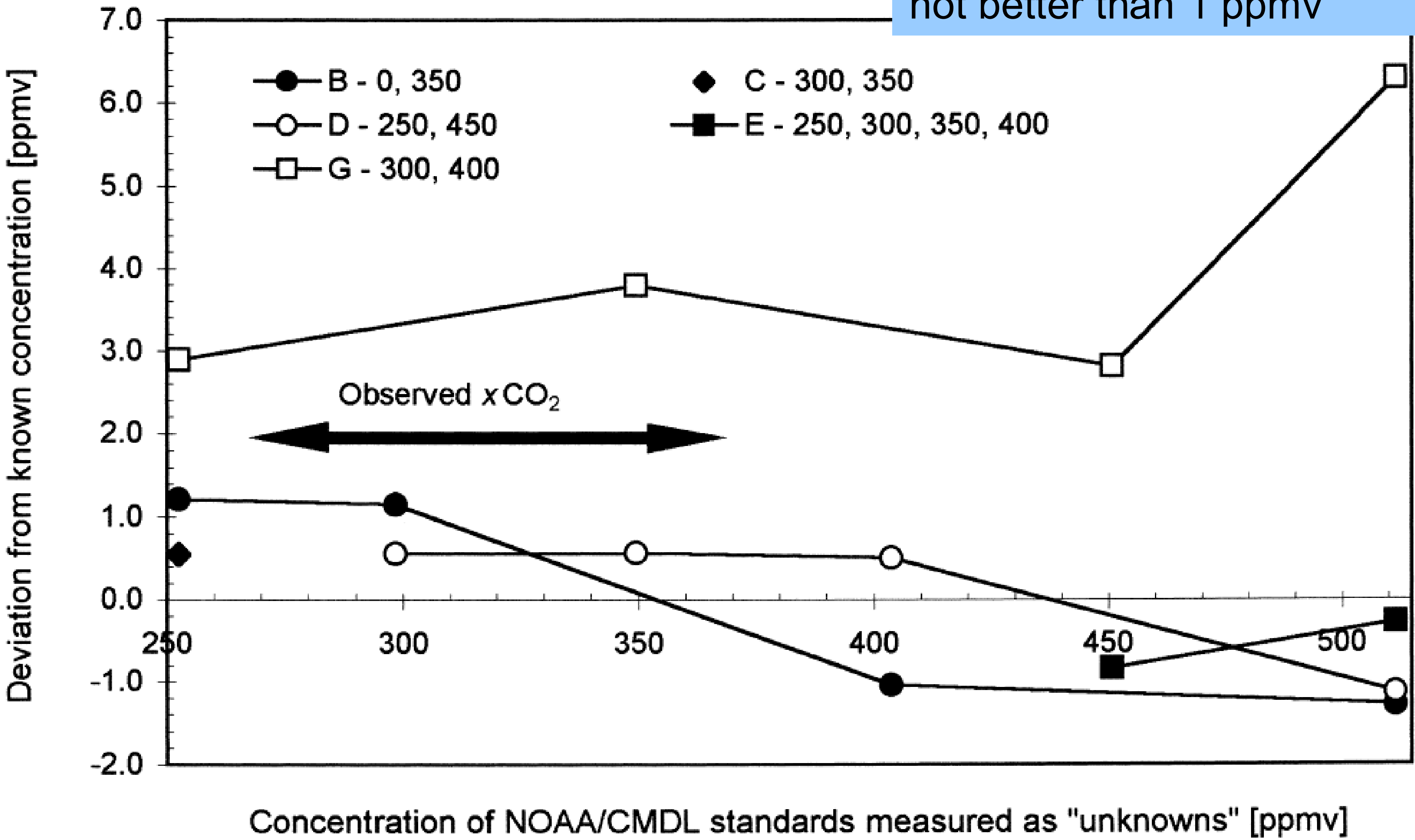


Fig. 3. Results from the check of the CO_2 calibration performance: shown are observed deviations from the concentrations of all NOAA-CMDL CO_2 standards measured as “unknowns”. See legend for details of the nominal concentrations used by each system for calibration. Also shown is the range of measured xCO_2 during the whole intercomparison.

Körtzinger *et al.*, Mar. Chem. 72 (2000), 171-192.

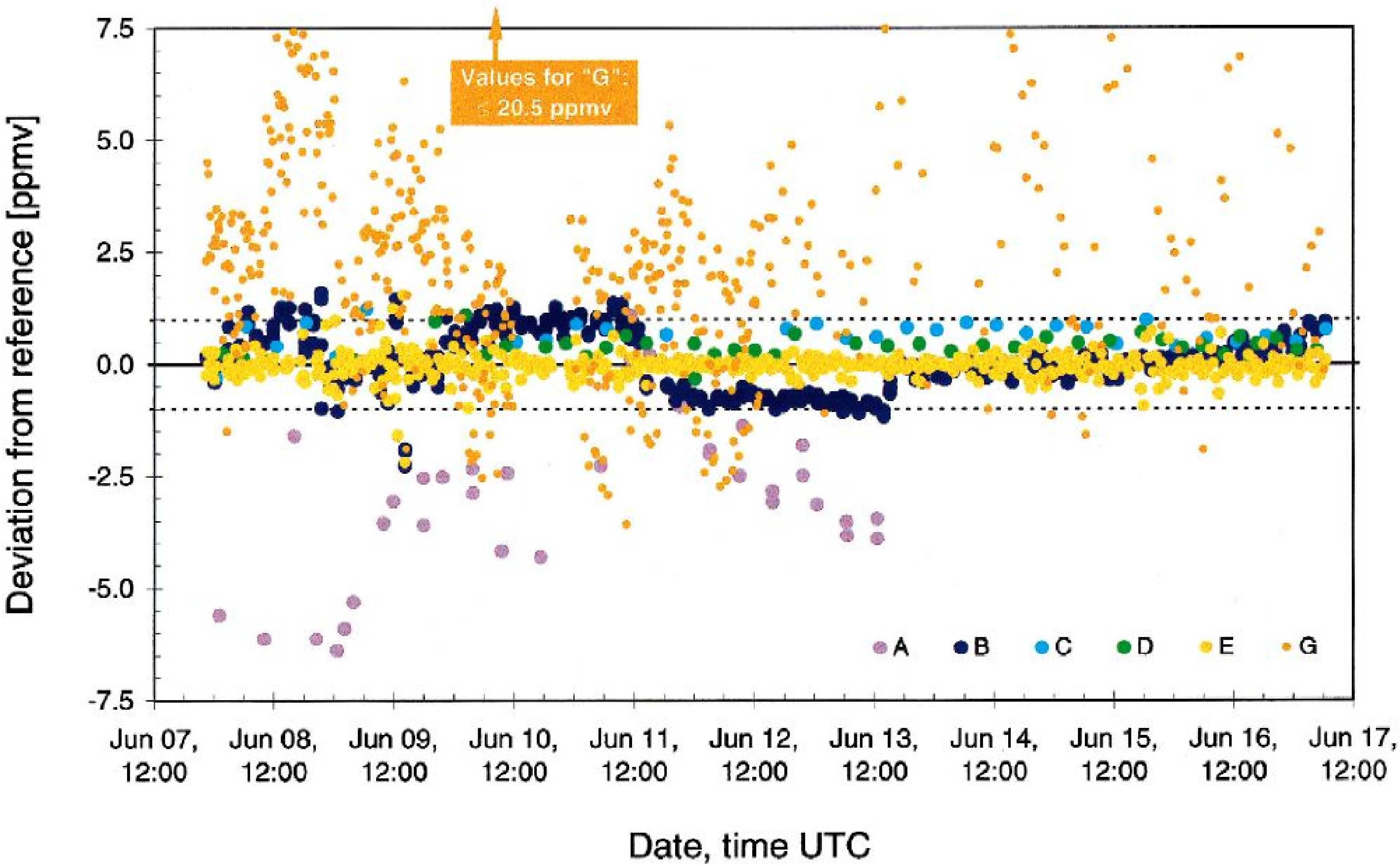
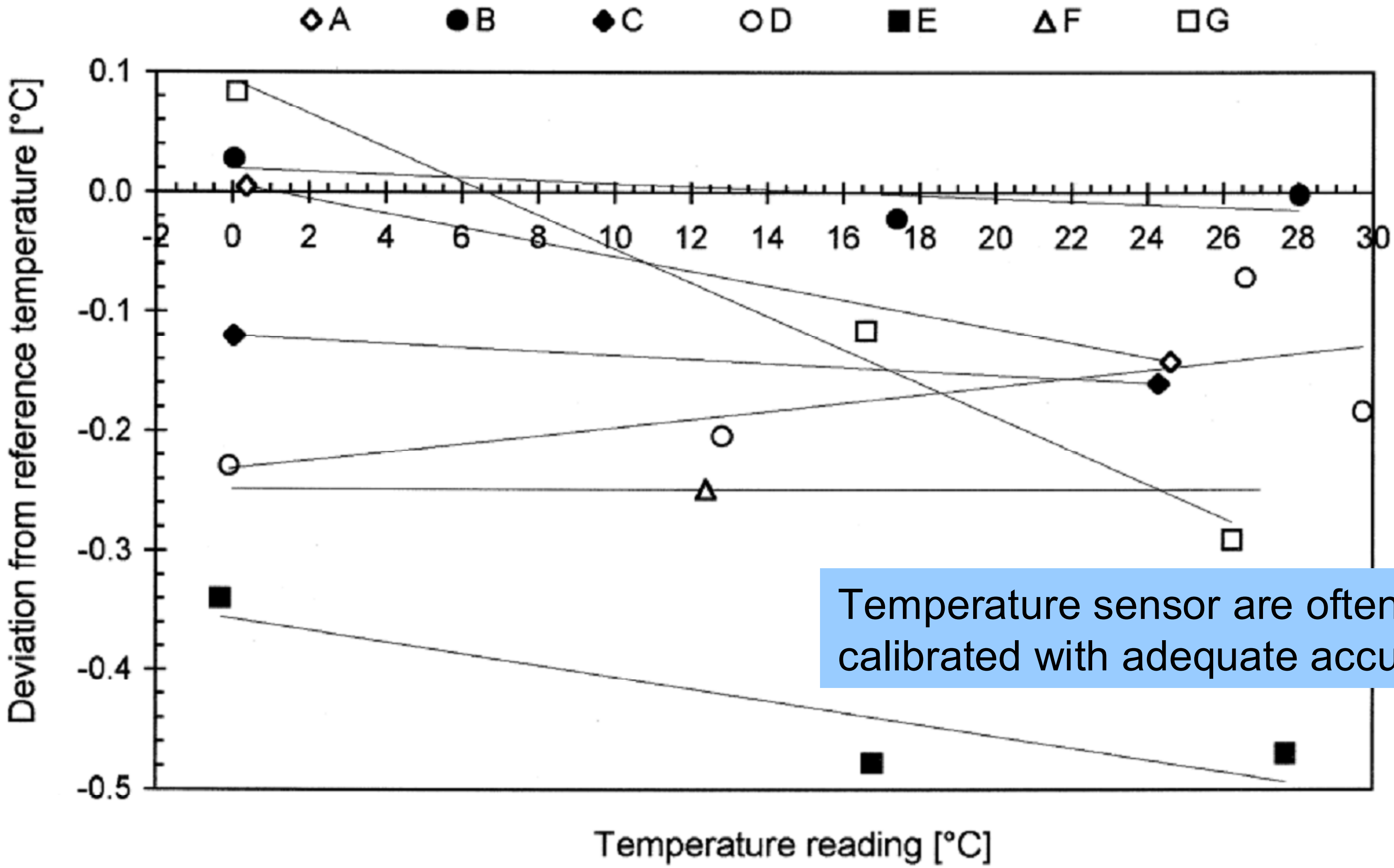


Fig. 6. Results of atmospheric CO_2 measurements: deviation of the CO_2 mole fraction in dry air [xCO_2 (air)] as measured by laboratories "A"–"E" and "G" from a running mean of "D" and "E" for the period from June 7, 2230 UTC to June 17, 0630 UTC.

International at-sea pCO_2 intercomparison during R/V Meteor Cruise 36/1 (June 1996)

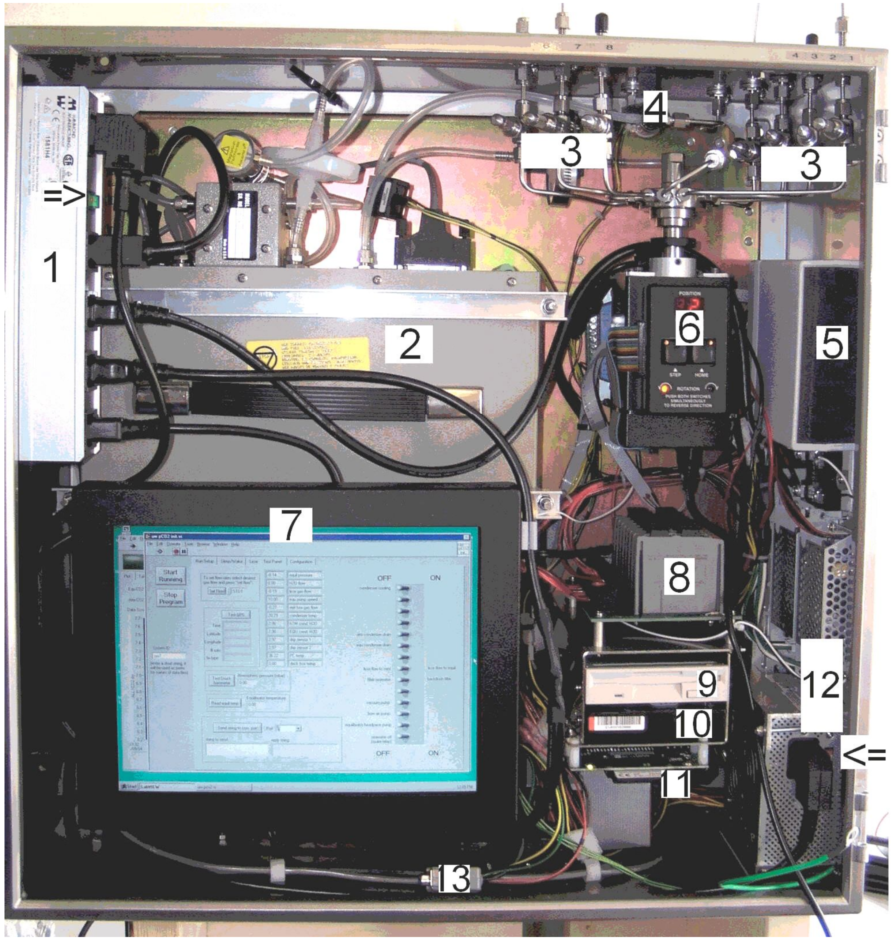
Körtzinger *et al.*, Mar. Chem. 72 (2000), 171-192.



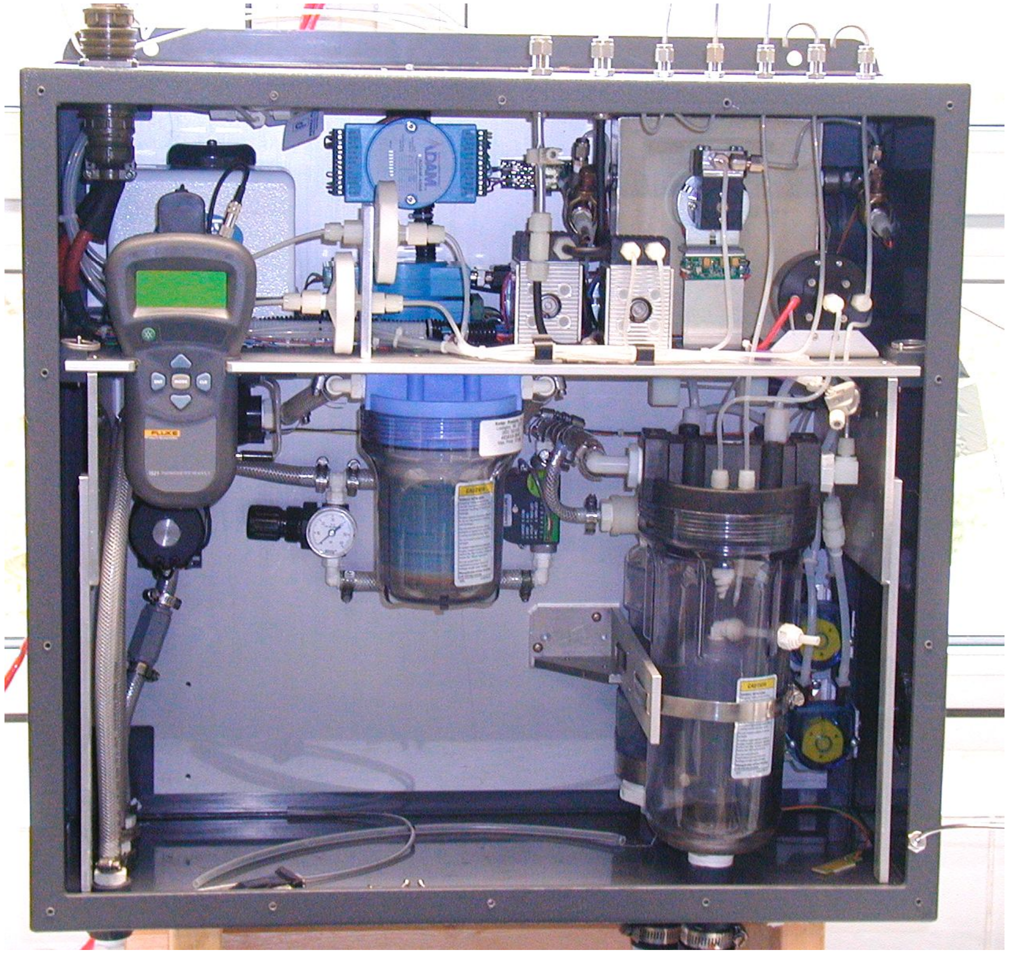
Temperature sensor are often not calibrated with adequate accuracy!

Fig. 4. Results of the check of the equilibrator temperature probes of systems "A"–"G": shown are deviations of measured temperatures from the reference temperature, when equilibrator probe and reference probe were kept together in the same water bath until readings had become stable. Also shown are the linear correction lines that were applied to temperature readings of a given system.

A new commercial system that has learned from all these exercises ...



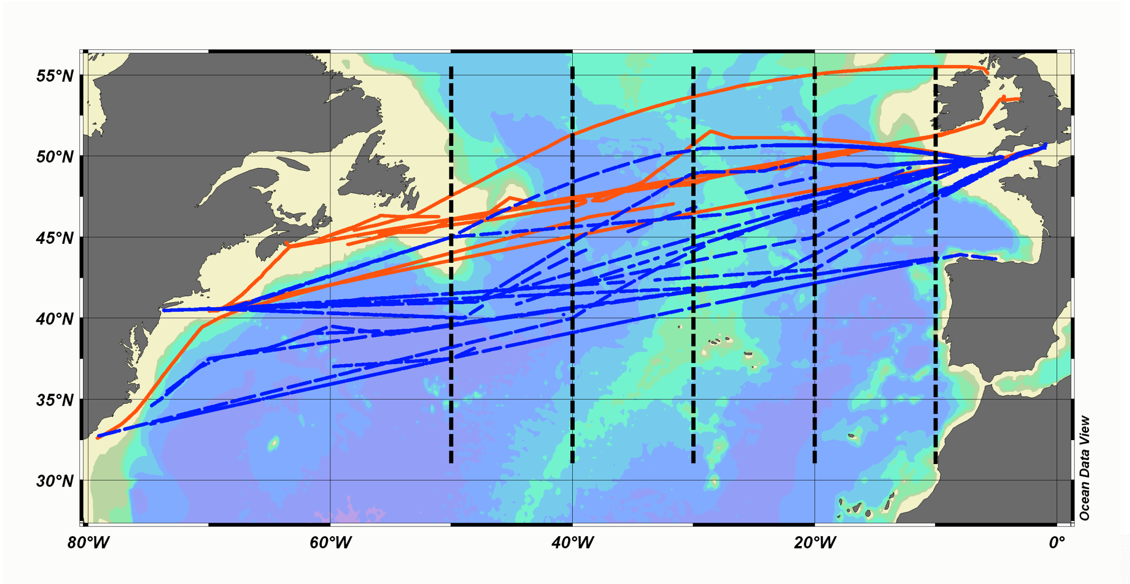
Dry Box

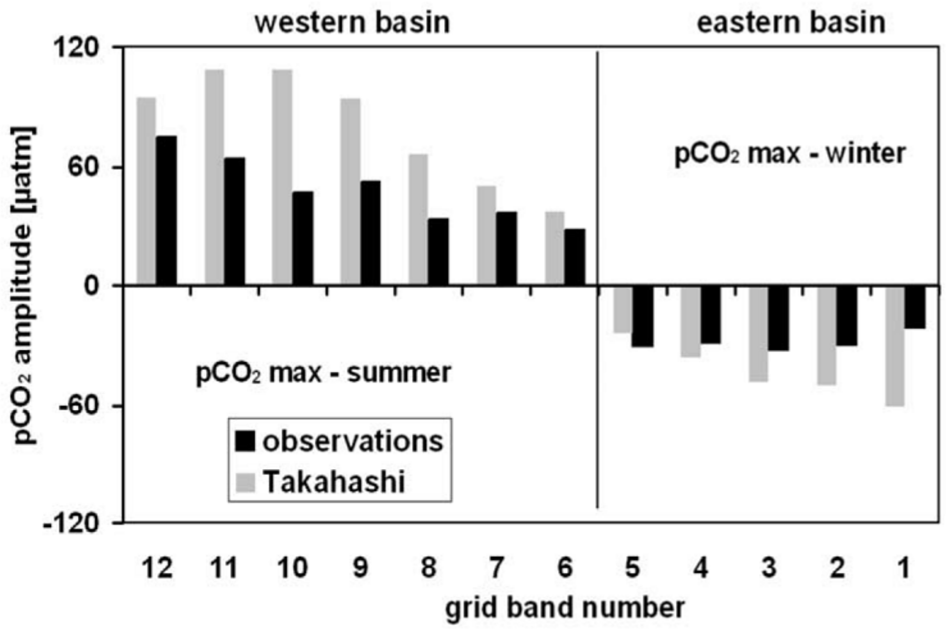


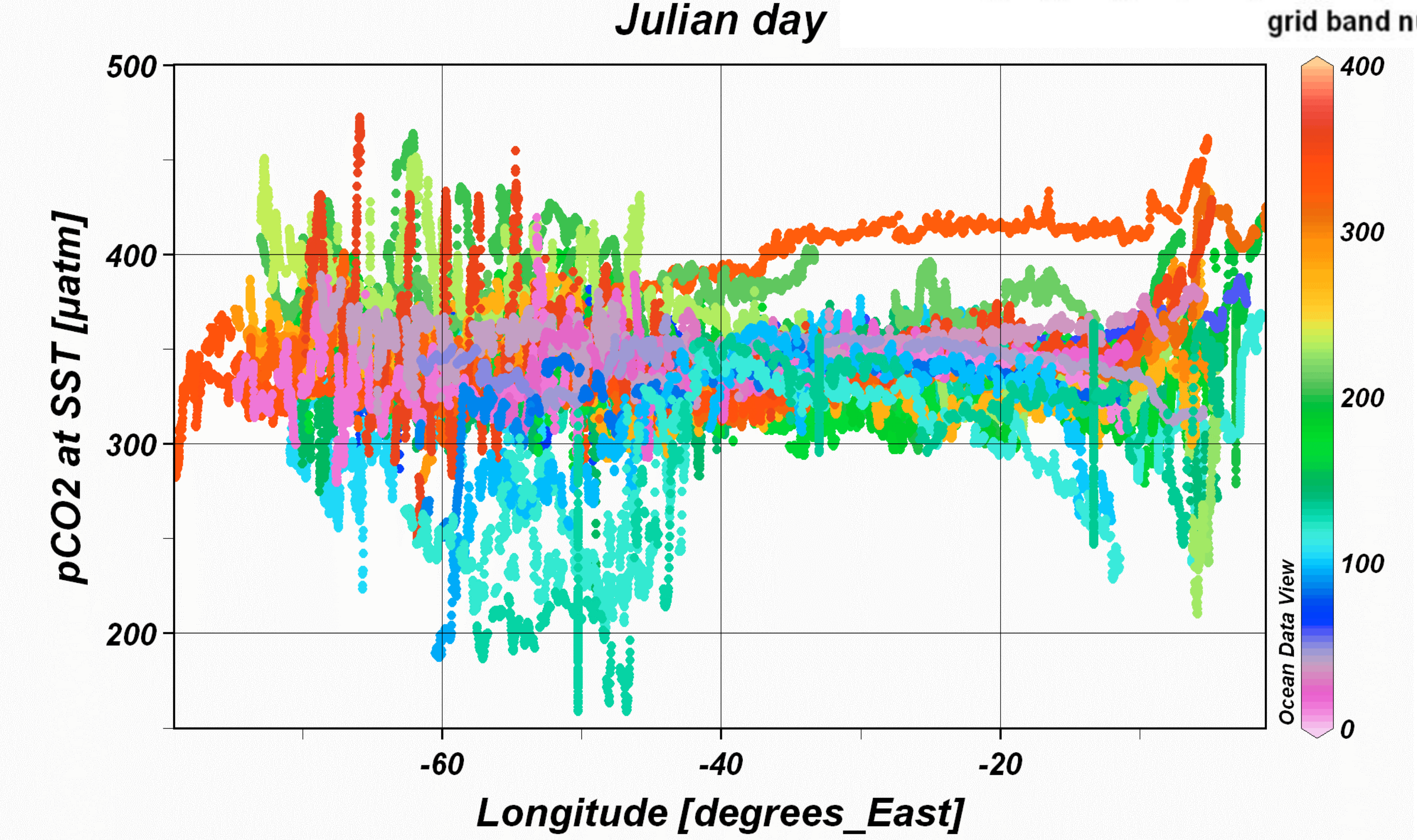
Wet Box

- Developed by Craig Neill at the University of Bergen/Norway
- First series of instruments produced at University of Bergen
- Production handed over to General Oceanics Inc., Miami/FL, U.S.A.
- First GO/Neill Model 8050 series delivered after further modification
- Instrument is being used on many VOS lines worldwide

... and allows us to do very nice measurements

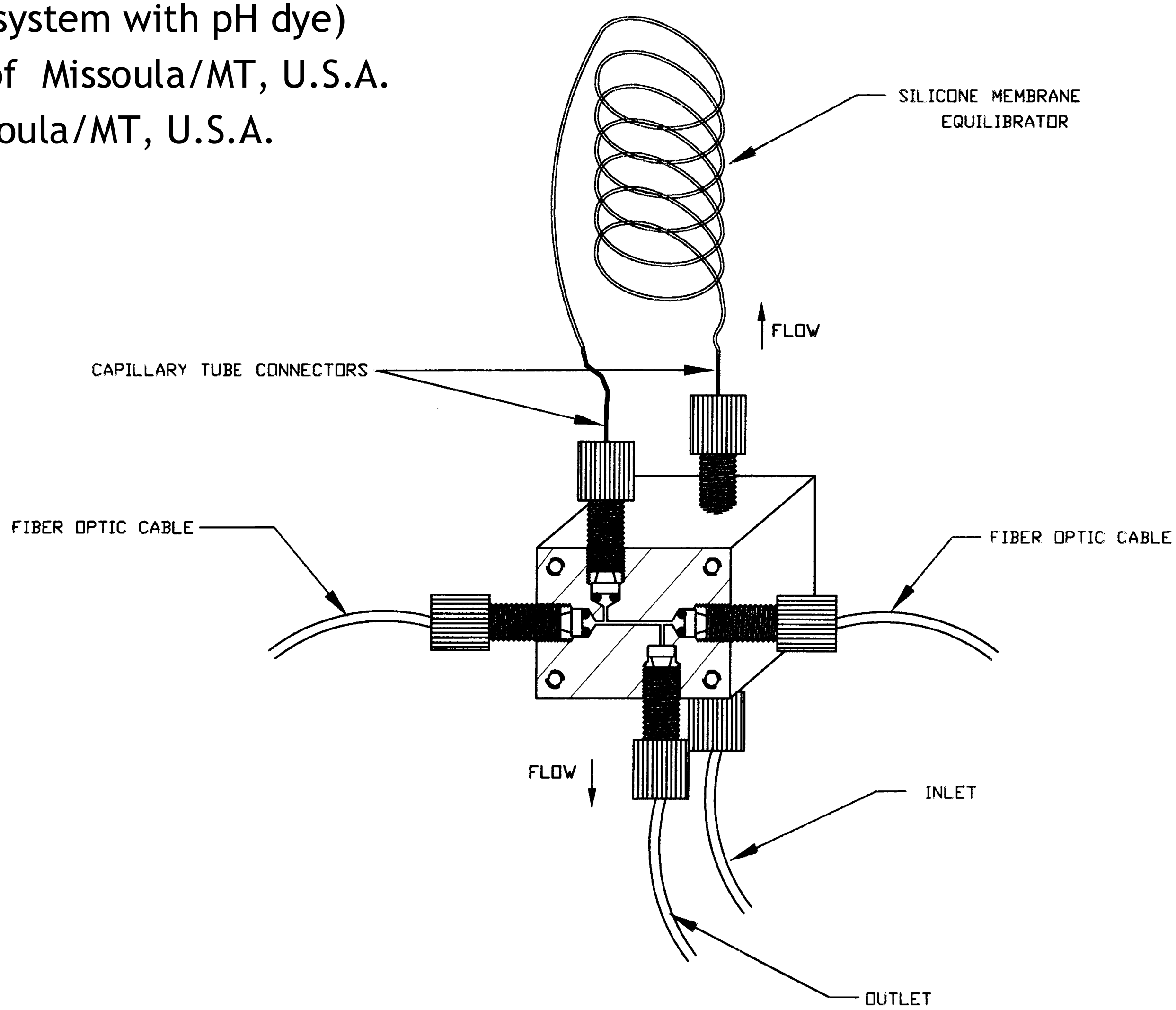






How to do autonomous sub-surface pCO_2 measurements?

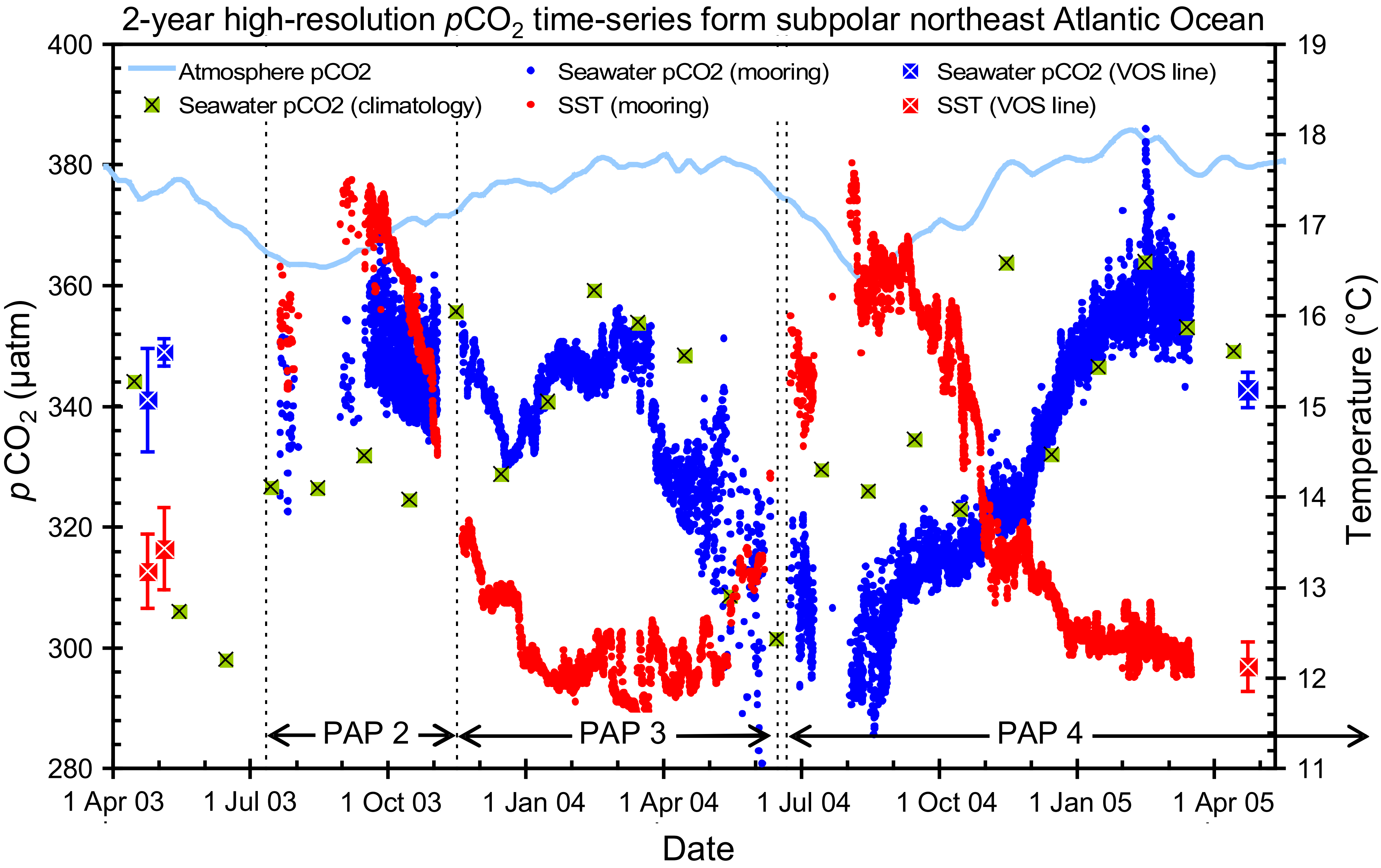
- SAMI-pCO_2 Sensor (spectrophotometric system with pH dye)
- Developed by Mike DeGrandpre, Univ. of Missoula/MT, U.S.A.
- Produced by Sunburst Sensors LLC, Missoula/MT, U.S.A.



$$pH = pK_S + \log \frac{\left[\mathrm{Ind}^{2-}\right]}{\left[\mathrm{HInd}^{-}\right]}$$

$$\frac{\left[\mathrm{Ind}^{2-}\right]}{\left[\mathrm{HInd}^{-}\right]} = \frac{E^{620}/E^{434} - \varepsilon_{\mathrm{HInd}^-}^{620}/\varepsilon_{\mathrm{HInd}^-}^{434}}{\varepsilon_{\mathrm{Ind}^{2-}}^{620}/\varepsilon_{\mathrm{HInd}^-}^{434} - E^{620}/E^{434}\cdot\varepsilon_{\mathrm{Ind}^{2-}}^{434}/\varepsilon_{\mathrm{HInd}^-}^{434}}$$

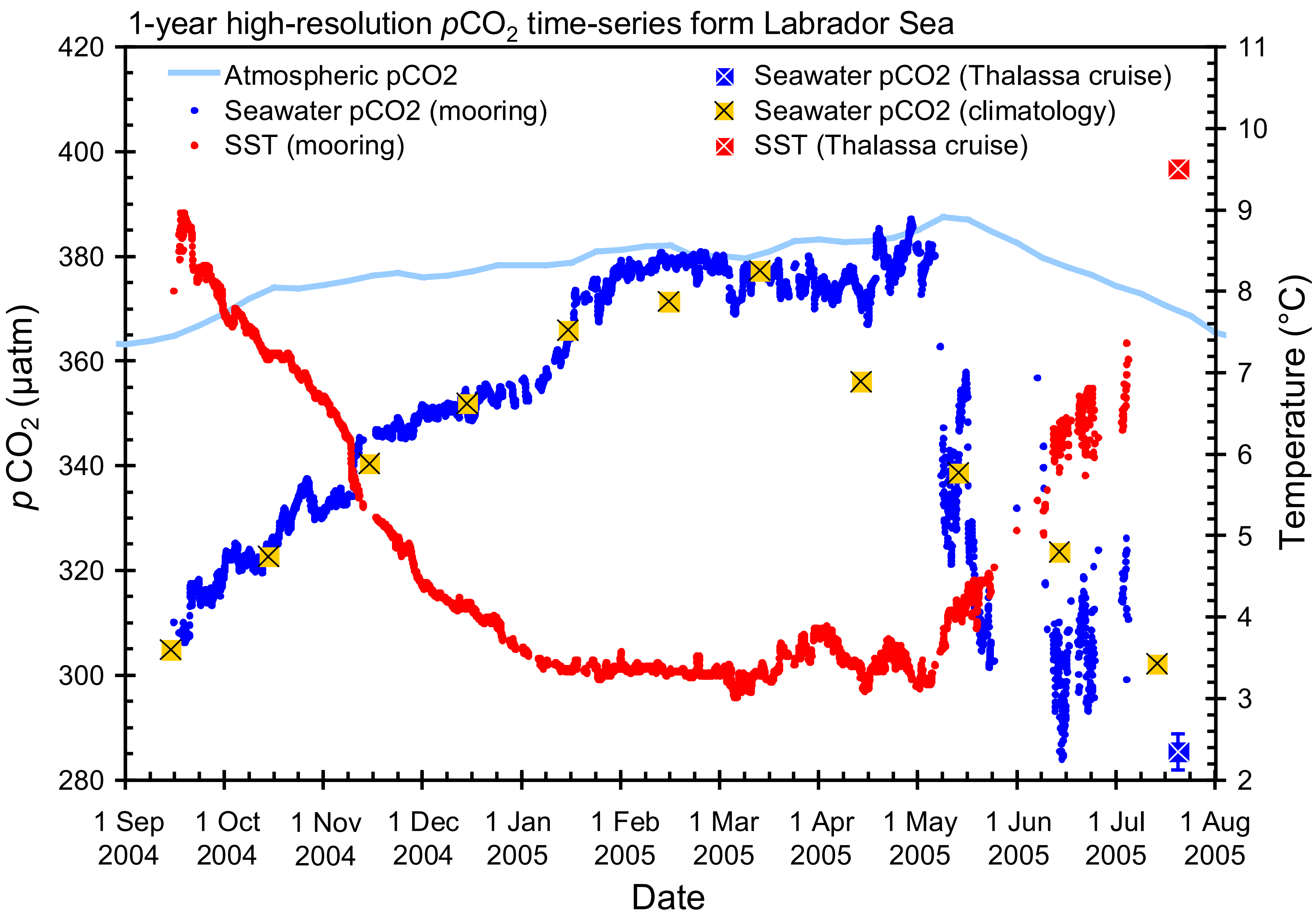
Another instrument for doing great measurements*



Körtzinger *et al.*, 2008. *J. Geophys. Res.* **113**, C04020, doi:10.1029/2007JC004347.

**if it works...*

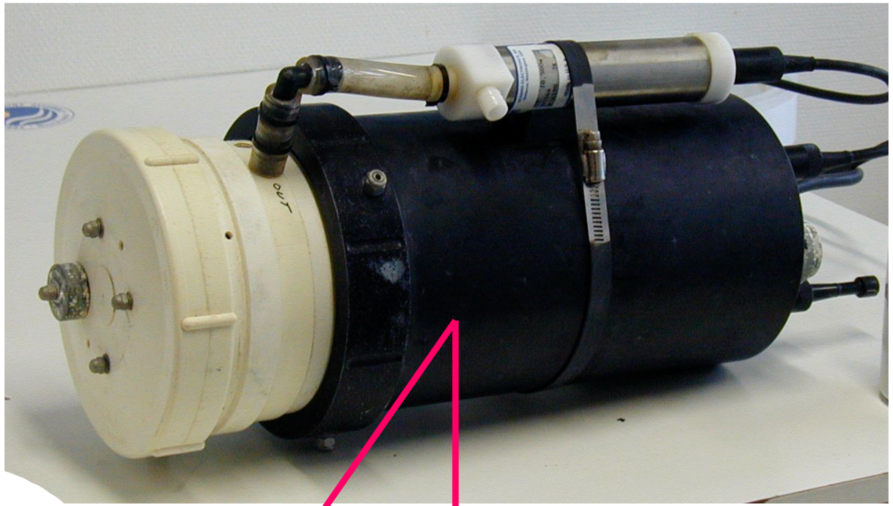
Another instrument for doing great measurements*



Körtzinger *et al.*, 2008. *Global Biogeochem. Cycles* **22**, GB1014, doi:10.1029/2007GB003029.

Can we go even smaller and more robust with sub-surface pCO_2 measurements?

- NDIR-based pCO_2 sensors
- Membrane-separated headspace
- Commercially available (e.g. Pro Oceanus, Halifax/Canada; Contros GmbH, Kiel/Germany)
- First tests on autonomous profiling floats



How can we fight the old biofouling problem?

What is the long-term goal for CO_2 sensors – the oxygen example

Aanderaa Instruments
Bergen, Norway

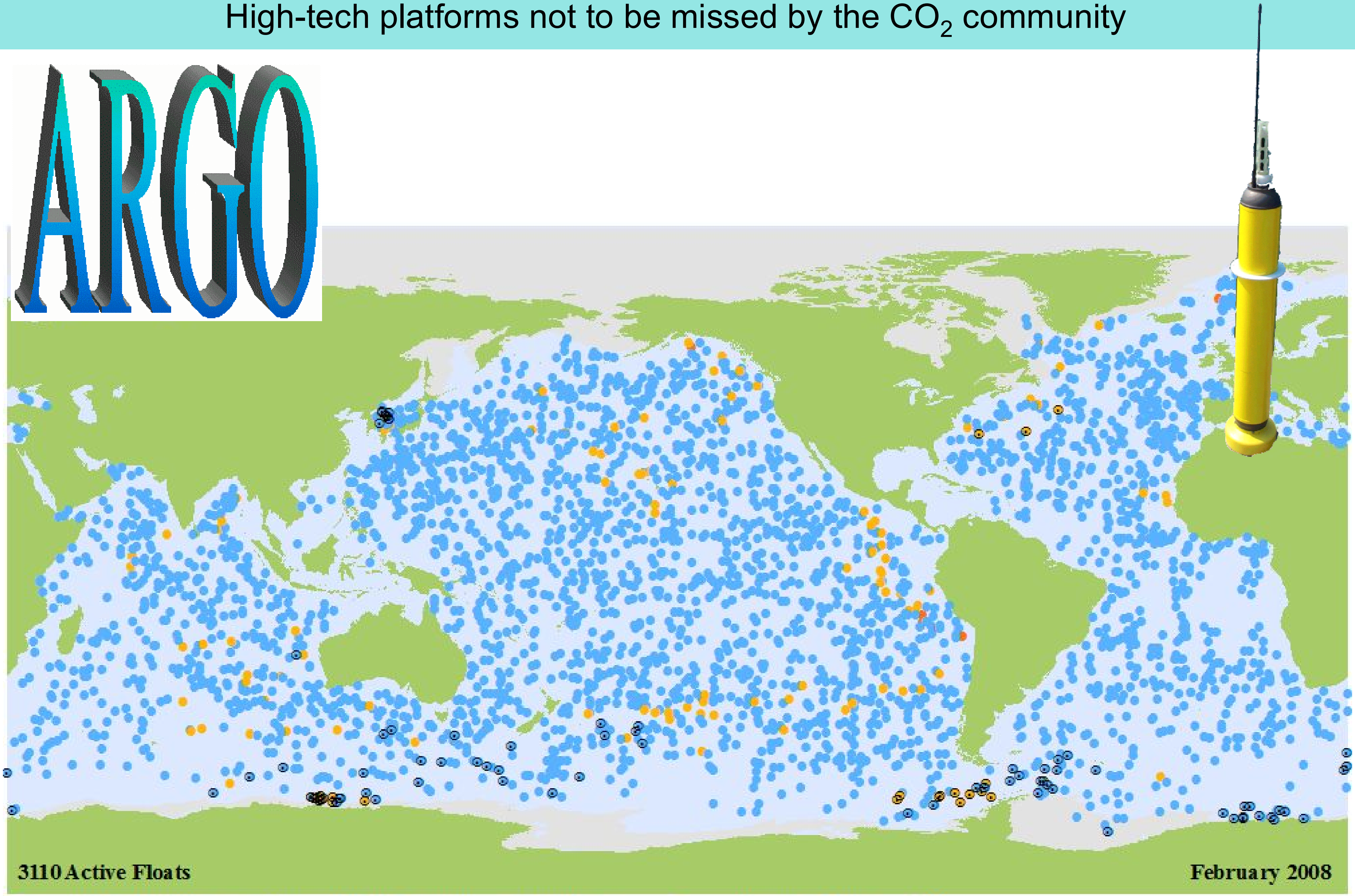
WEBB RESEARCH CORPORATION
E. Falmouth, Massachusetts, U.S.A.

Martec Serpe-Iesm France

Ifremer

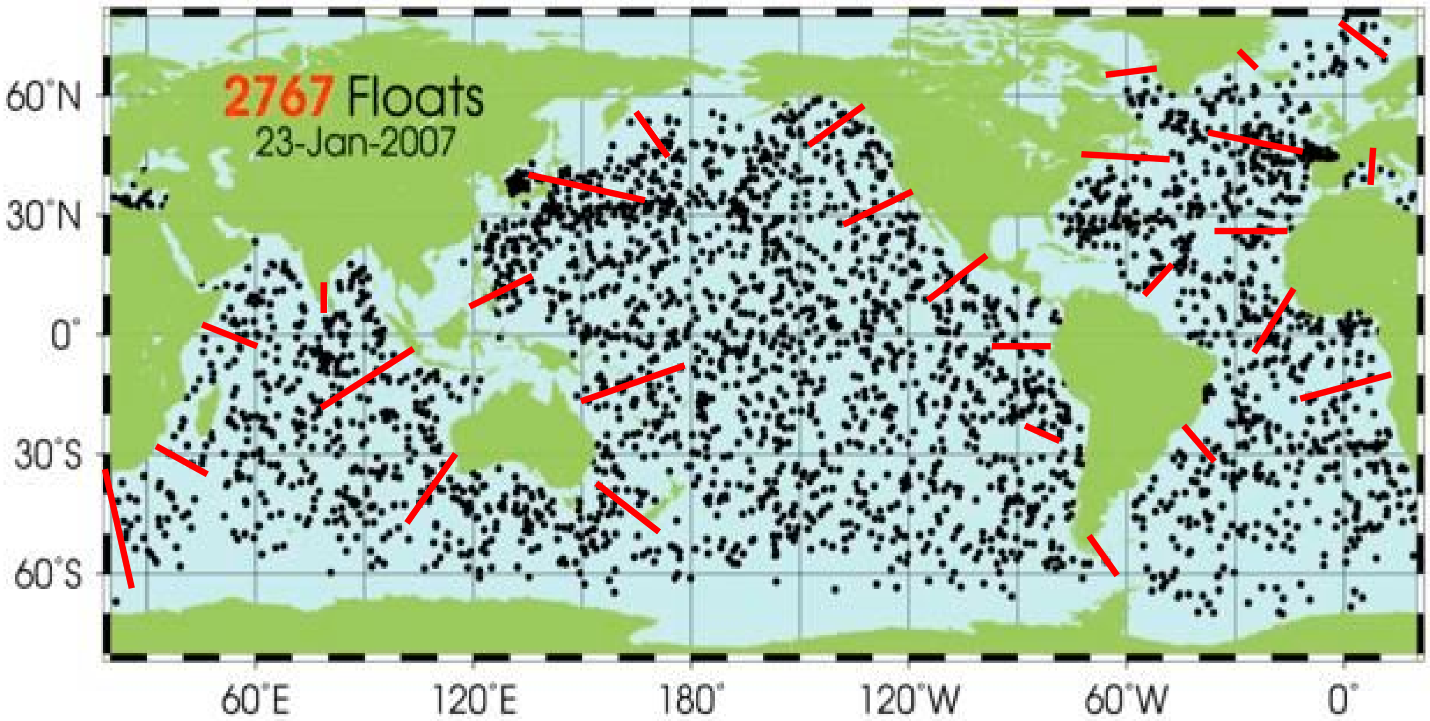
High-tech platforms not to be missed by the CO_2 community

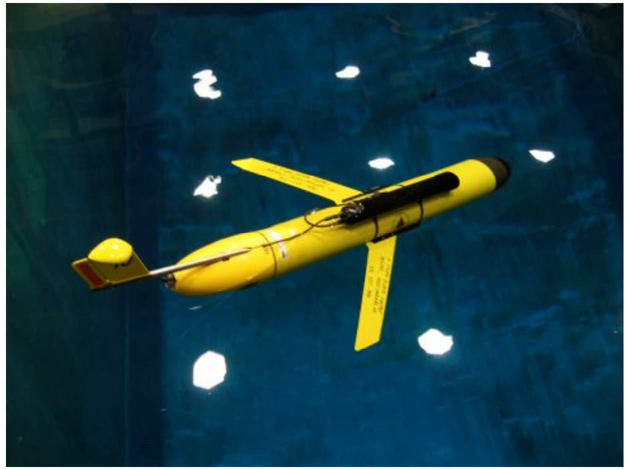
ARGO

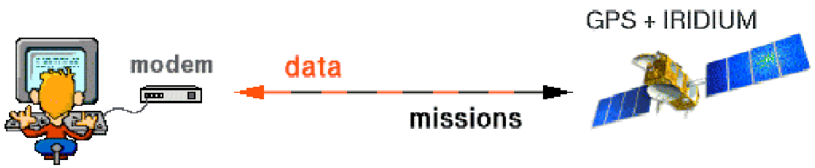


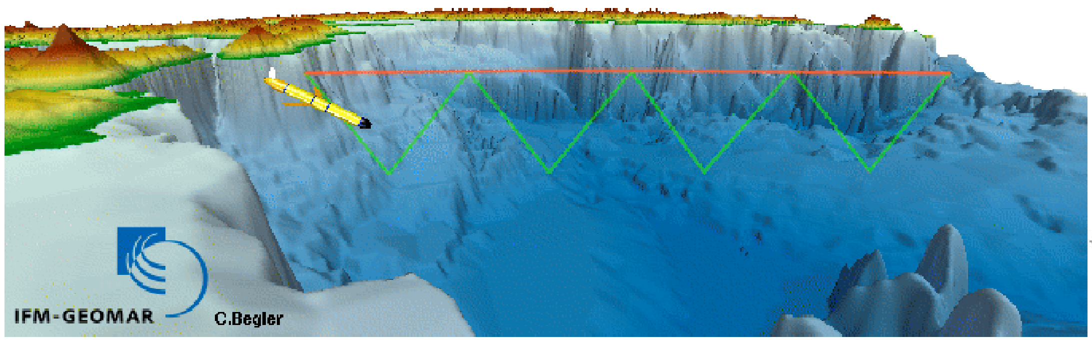
- Dissolved Oxygen, Chlorophyll Fluorescence, Turbidity (7)
- Dissolved Oxygen (126)
- Standard Argo: Pressure, Temperature, Salinity (3110)
- Ice Detection (98)

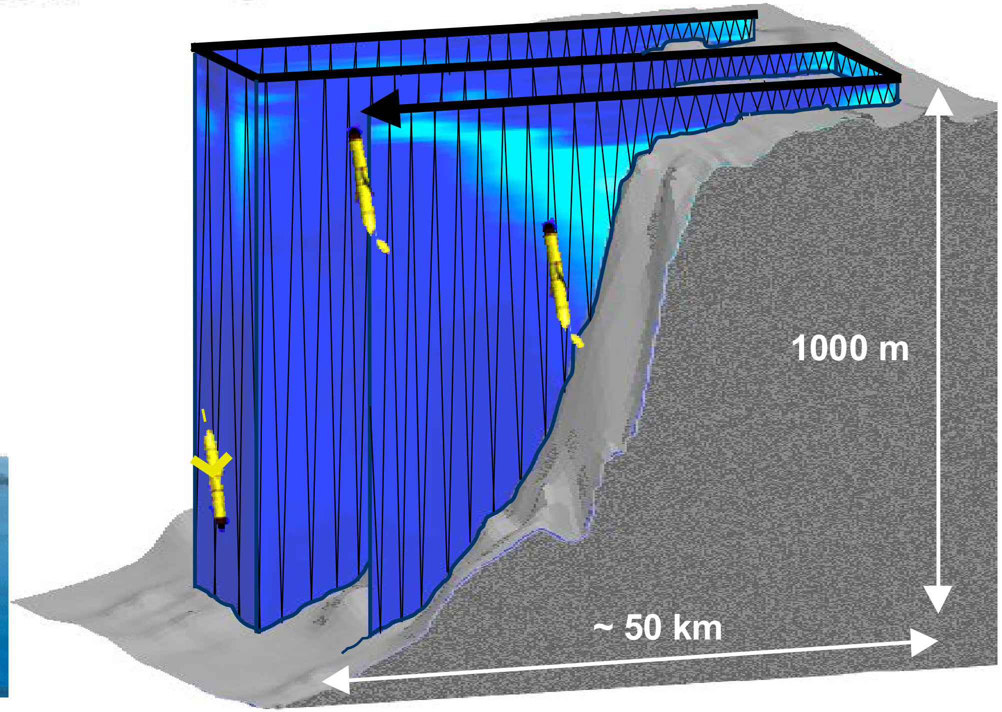
High-tech platforms not to be missed by the CO_2 community

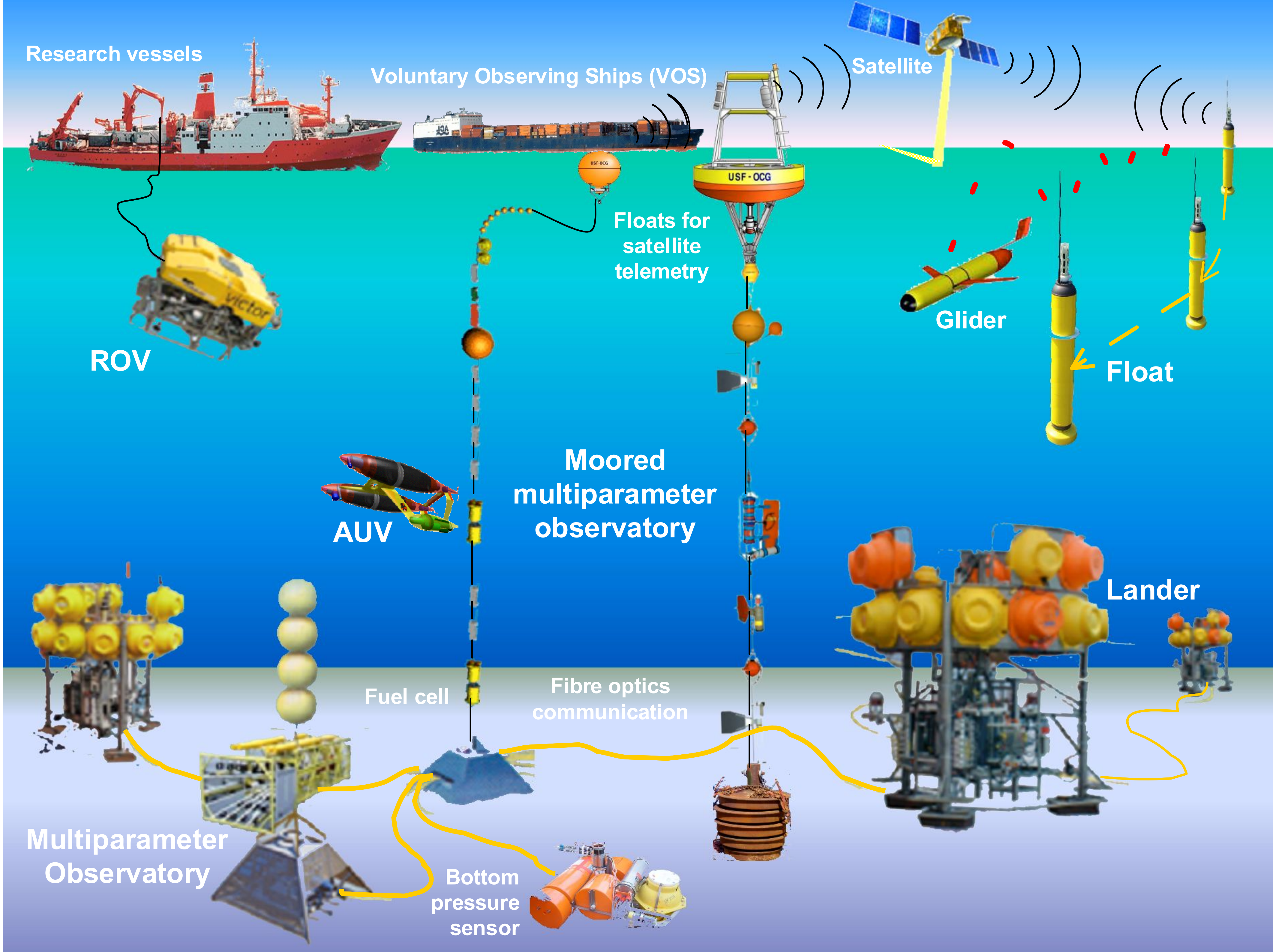











Research vessels
Voluntary Observing Ships (VOS)
Satellite
USF-OCG
Floats for
satellite
telemetry
ROV
Glider
Float
Moored
multiparameter
observatory
AUV
Lander
Fuel cell
Fibre optics
communication
Multiparameter
Observatory
Bottom
pressure
sensor