Long-term autonomous chemical measurements on ocean platforms

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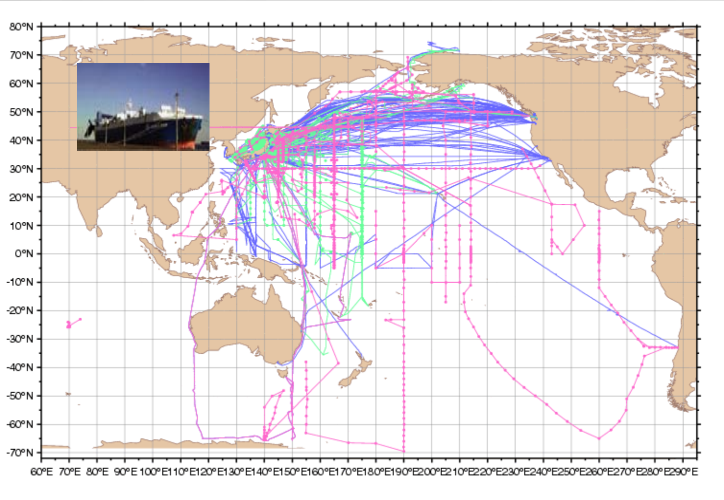
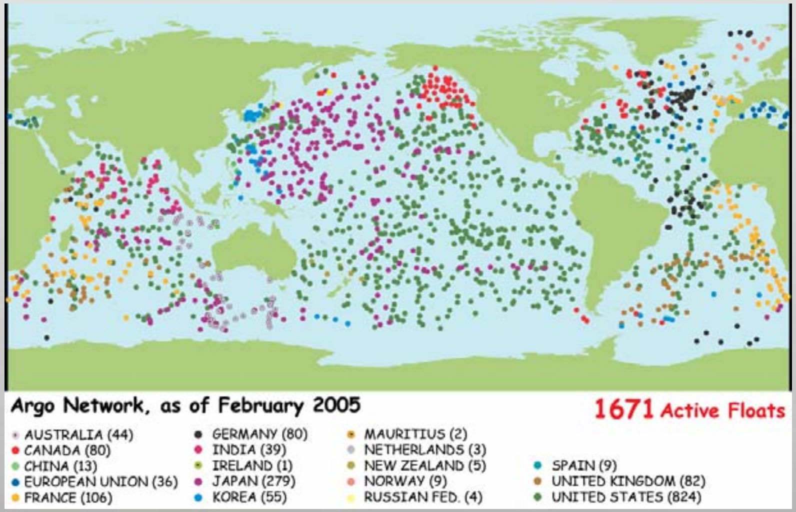
Our experience in developing and using autonomous chemical sensors

I. Need for new technologies in ocean science
II. Chemical sensor/analyzer requirements
III. Analytical methodologies to enhance performance
IV. Field data and experience

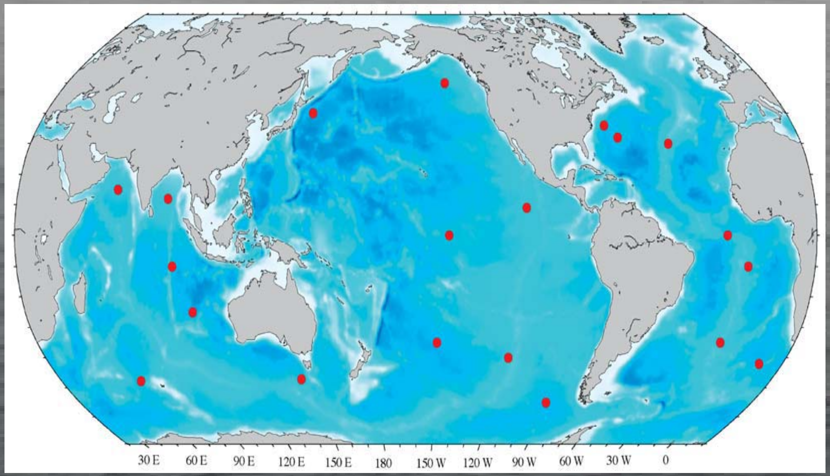
High demand for autonomous chemical measurements



VOS CO_2 cruises



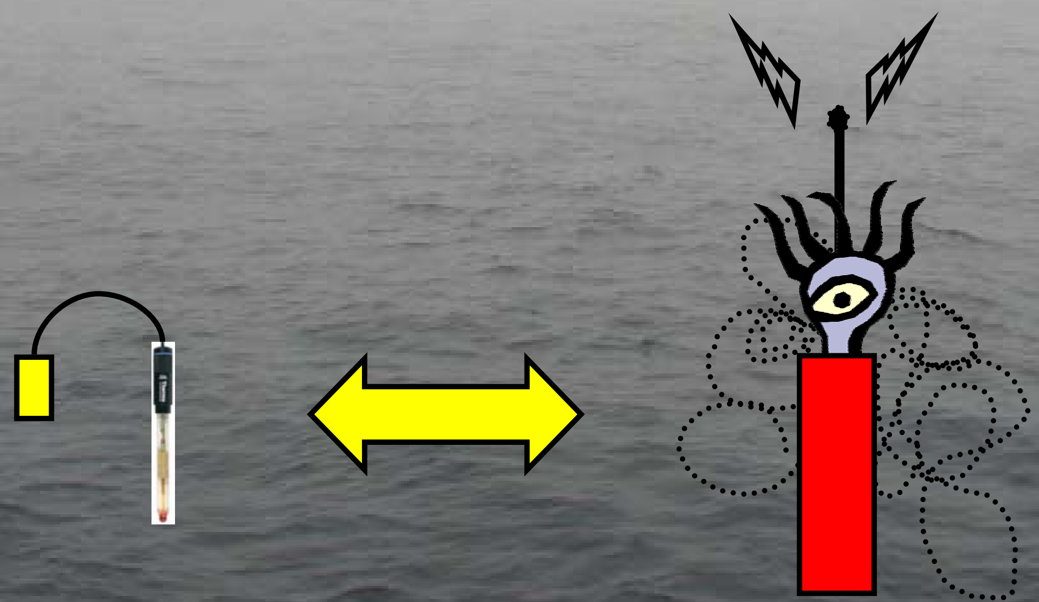
Argo Network

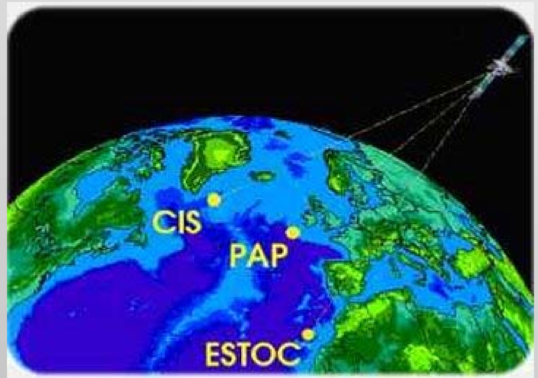


ORION Moorings

Desired features of autonomous chemical sensors

Accurate – no drift
Sensitive and precise – resolution of < +/- 0.05% to 1%
Reliable – low failure rates
Low power – 6 months to 1 year





EU ANIMATE Project (2001-2004)

MicroCat

Sensor – Microcat measuring temperature and salinity			
Deployment	CIS	ESTOC	PAP
1	Good data set	Good data set	Good data set
2	Good data set	Good data set	Good data set
3	Good data set	Good data set	Good data set
4	Deployed	Recovered	Deployed

ADCP

Sensor – ADCP measuring current speed and direction			
Deployment	CIS	ESTOC	PAP
1	Good data set	Good data set	Good data set
2	Good data set	Good data set	Good data set
3	Good data set	Good data set	Good data set
4	Deployed	Recovered	Deployed

Fluorometer

Sensor – HS2 measuring fluorescence/chlorophyll			
Deployment	CIS	ESTOC	PAP
1	Sensor lost	Good data set	Data not usable
2	Good data set	Good data set	Good data set
3	Not Deployed	Good data set	Good data set
4	Deployed	Recovered	Deployed

SAMI CO_2 sensor

Sensor – SAMI measuring Carbon Dioxide			
Deployment	CIS	ESTOC	PAP
1	Sensor Lost	Not Deployed	No data recovered
2	Good data set	Failed	Good data set
3	3 weeks good data	Good data set	Good data set
4	Deployed	Failed	Deployed

Sediment trap

Sensor – McLane Sediment trap			
Deployment	CIS	ESTOC	PAP
1	Unreliable data	Not Deployed	Good data set
2	Unreliable data	Good data set	Good data set
3		Unreliable data	
4	Deployed	Not Deployed	Deployed

Nitrate sensor

Sensor – NAS2 measuring Nitrate level			
Deployment	CIS	ESTOC	PAP
1	Sensor lost	Sensor lost	4 months good data *
2	Good data set	0 months good data *	0 months good data *
3	Not Deployed	Not Deployed	0 months good data *
4	Deployed	Recovered	Deployed
* more data may be usable after further processing			

Submersible Autonomous Moored Instrument for CO_2 (SAMI-CO_2)

pCO_2 specific pros and cons

- ***pros***
  - precision & accuracy >0.3%
  - membrane based analysis
- ***cons***
  - gas phase calibrations

SAMI-CO_2 Operating Principle

CO_2 equilibrium between an indicator solution and seawater separated by a gas permeable membrane

Indicator equilibrium:

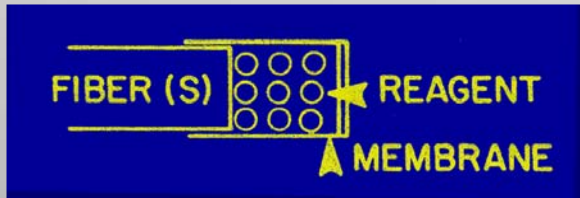
CO_2

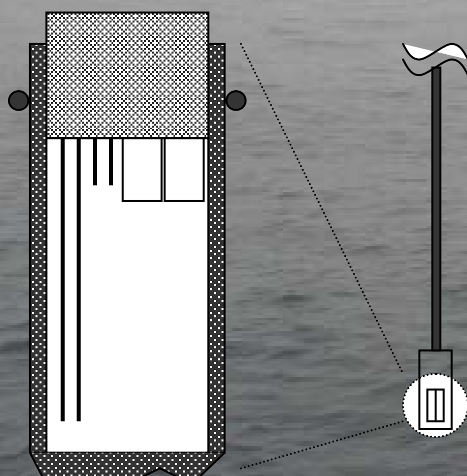
$$HI^{-} \leftrightarrow H^{+} + I^{2-}$$

(bromothymol blue)

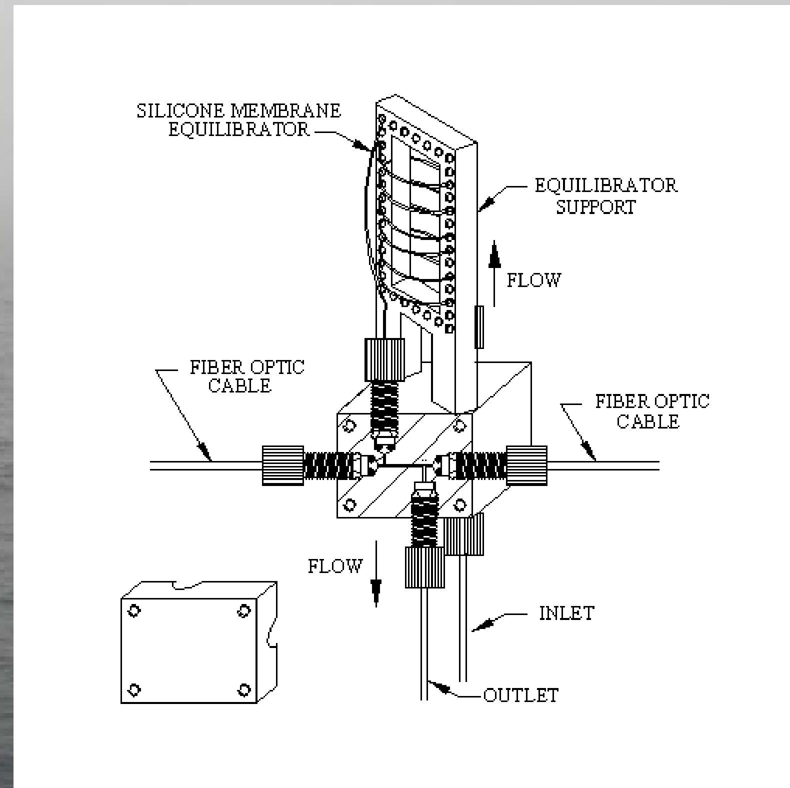
Optical Sensor Designs

fixed reagent sensor (optrode)





flow optrode



SAMI-CO_2 sensor cell

SAMI-CO_2 Operating Principle (cont.)

$$HI^{-} \leftrightarrow H^{+} + I^{2-}$$

Absorbance ratio response:

$$R = \frac{A_{620}}{A_{440}}$$

$$A_{\lambda} = -\log \frac{I_{\lambda}}{I_{0\lambda}}$$

$$I_{0\lambda} = k_{\lambda} I_{740}$$

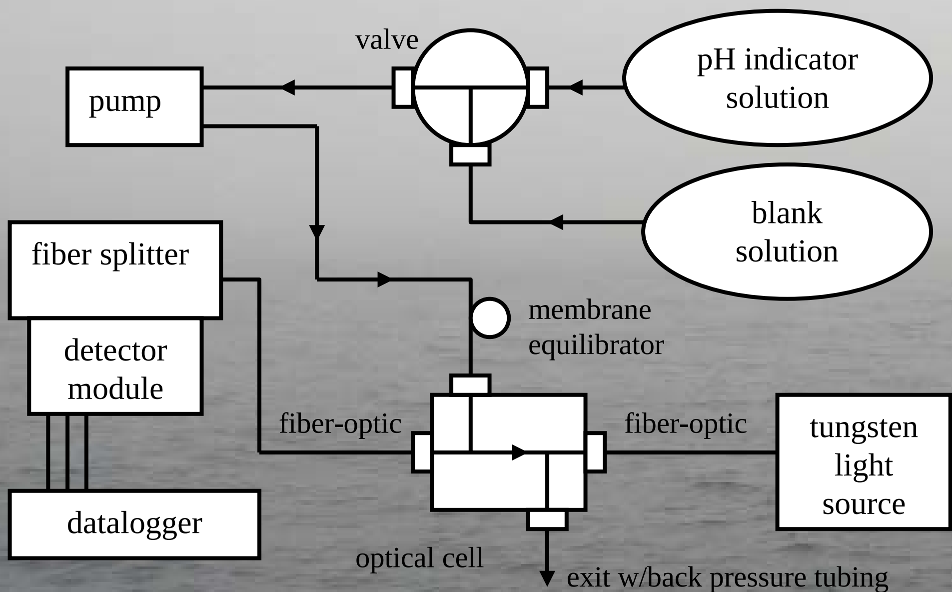
Advantages

Spectrophotometric stability

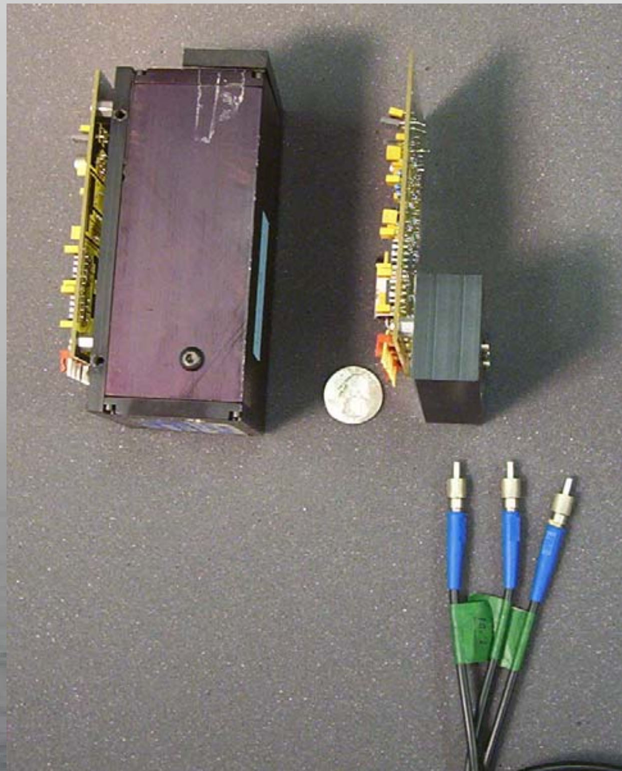
Simple optical design

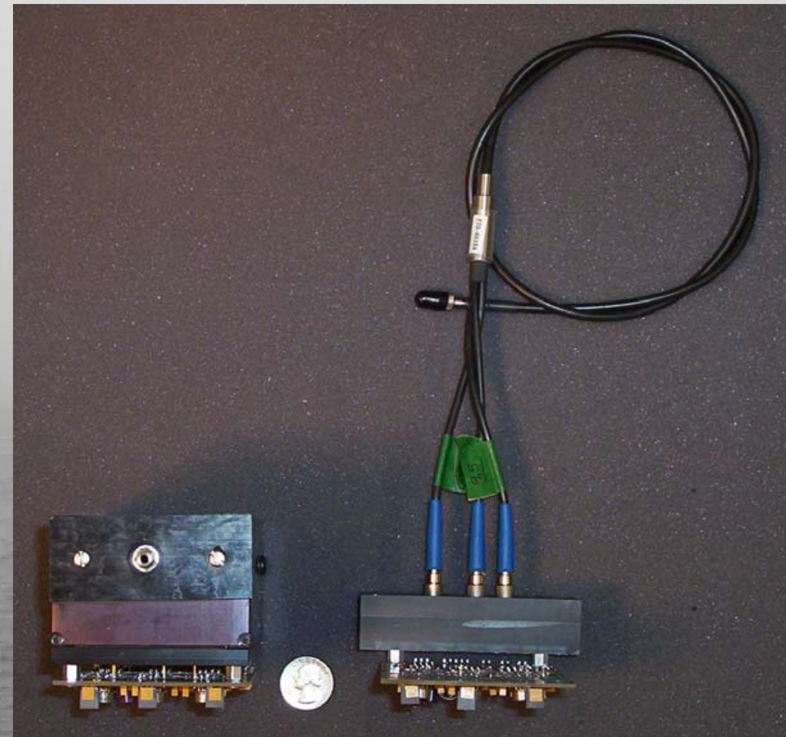
R = f(*p*CO_2,alkalinity, T, P, λ)

SAMI-CO_2 flow diagram



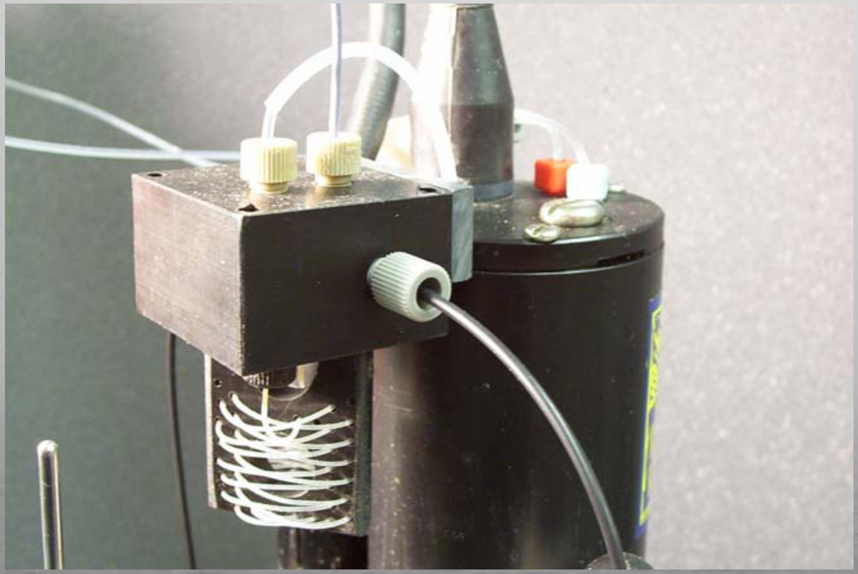
SAMI-CO_2 fiber based detection system





- improve throughput and wavelength stability
- minimize size and cost

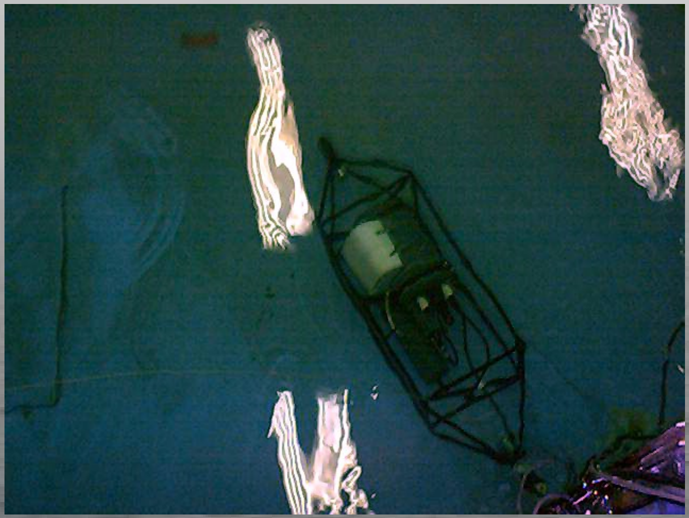
SAMI-CO_2 plumbing

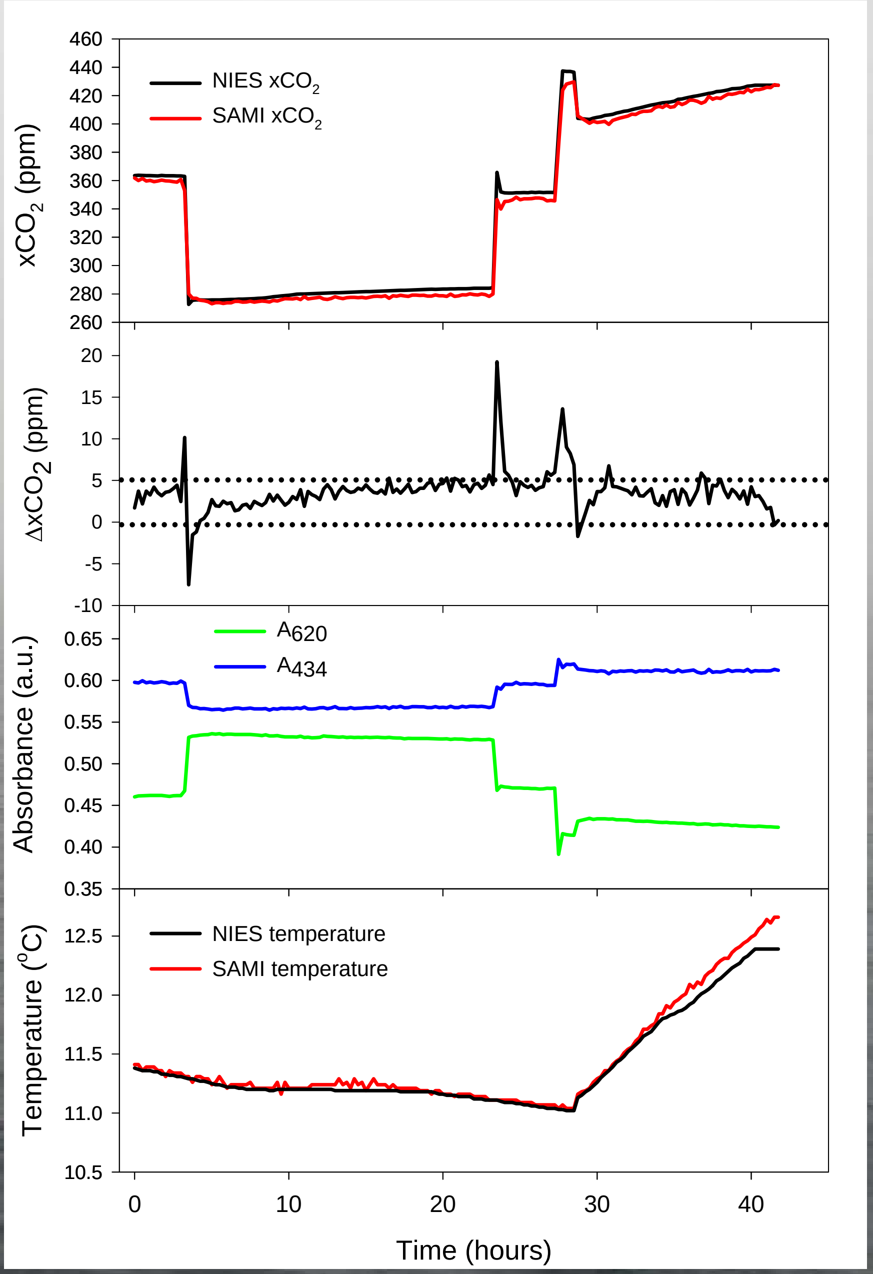


minimize volume to reduce power and reagent consumption

Performance

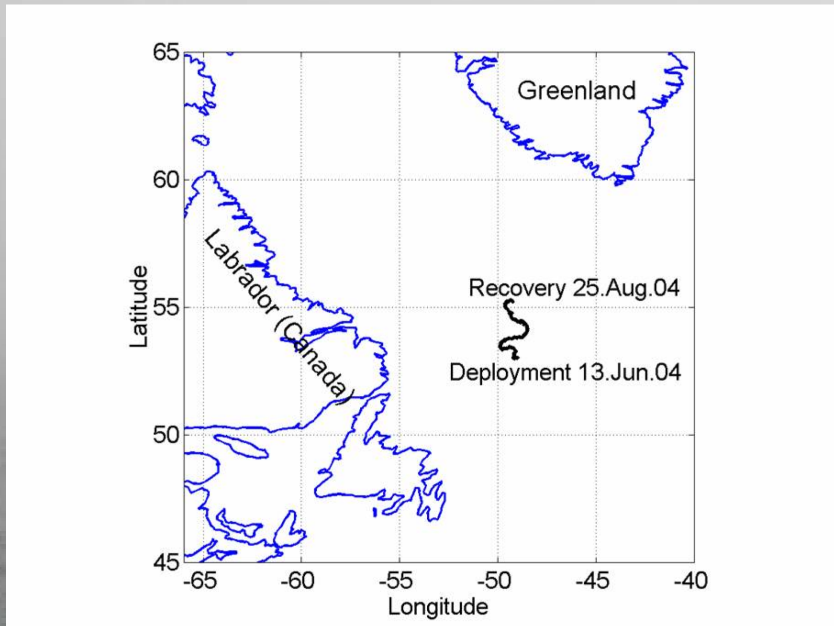
March 2003 *p*CO_2 intercomparison (NIES Japan)



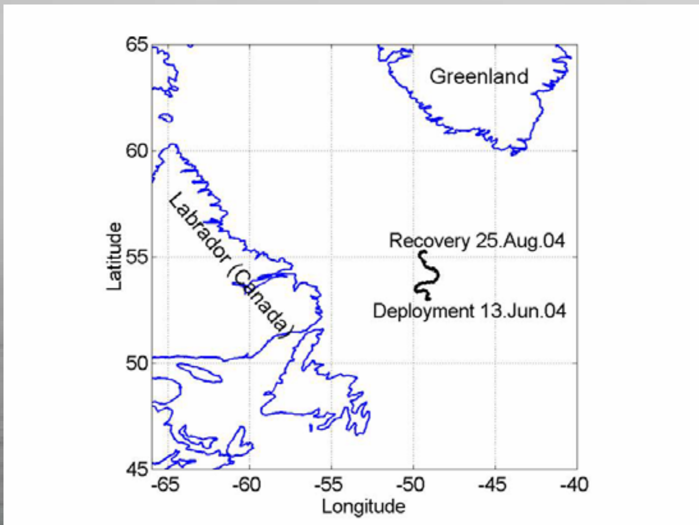


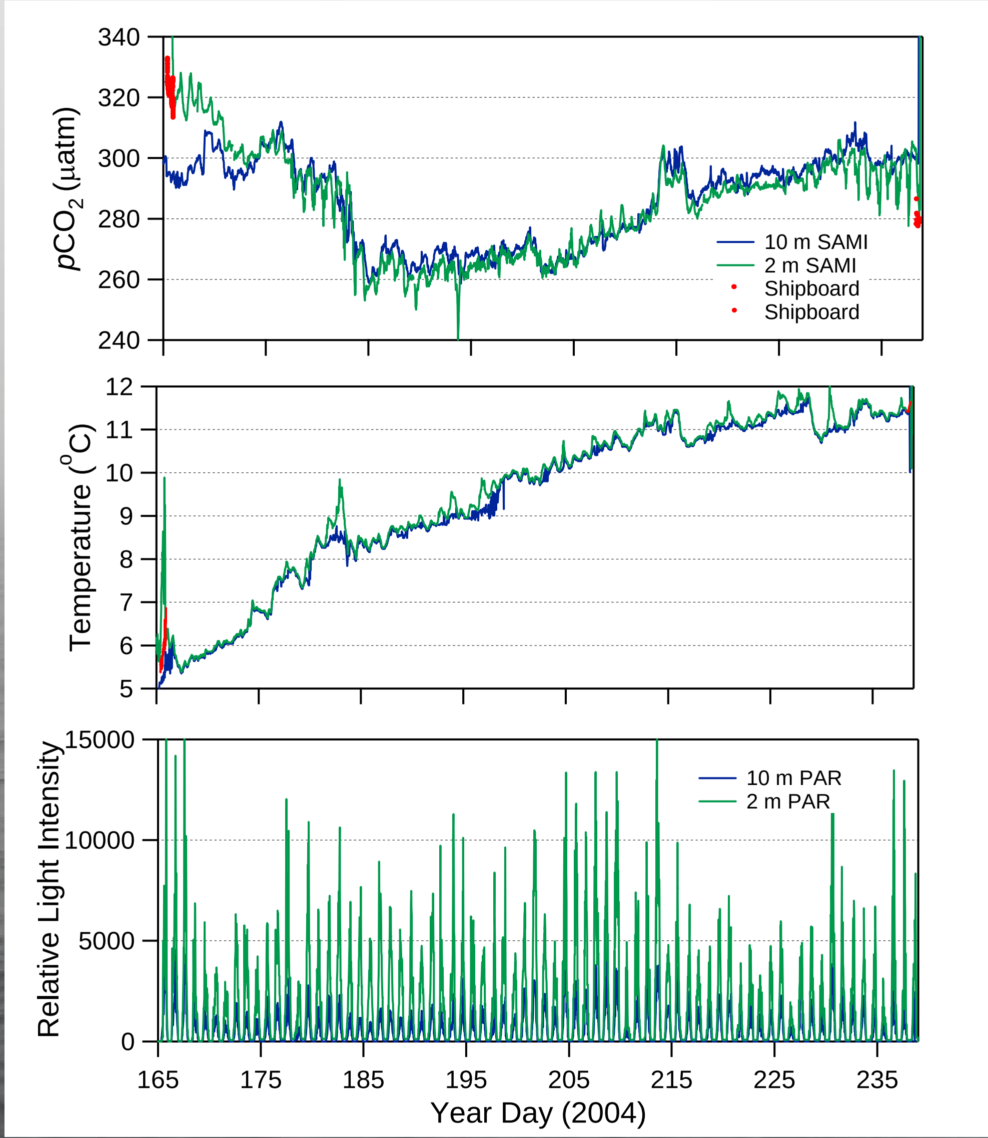
Labrador Sea air-sea exchange experiment (June – August 2004)

(M.DeGrandpre in collaboration with W. Drennan, W. McGillis, P. Strutton)



Labrador Sea air-sea exchange experiment June 2004

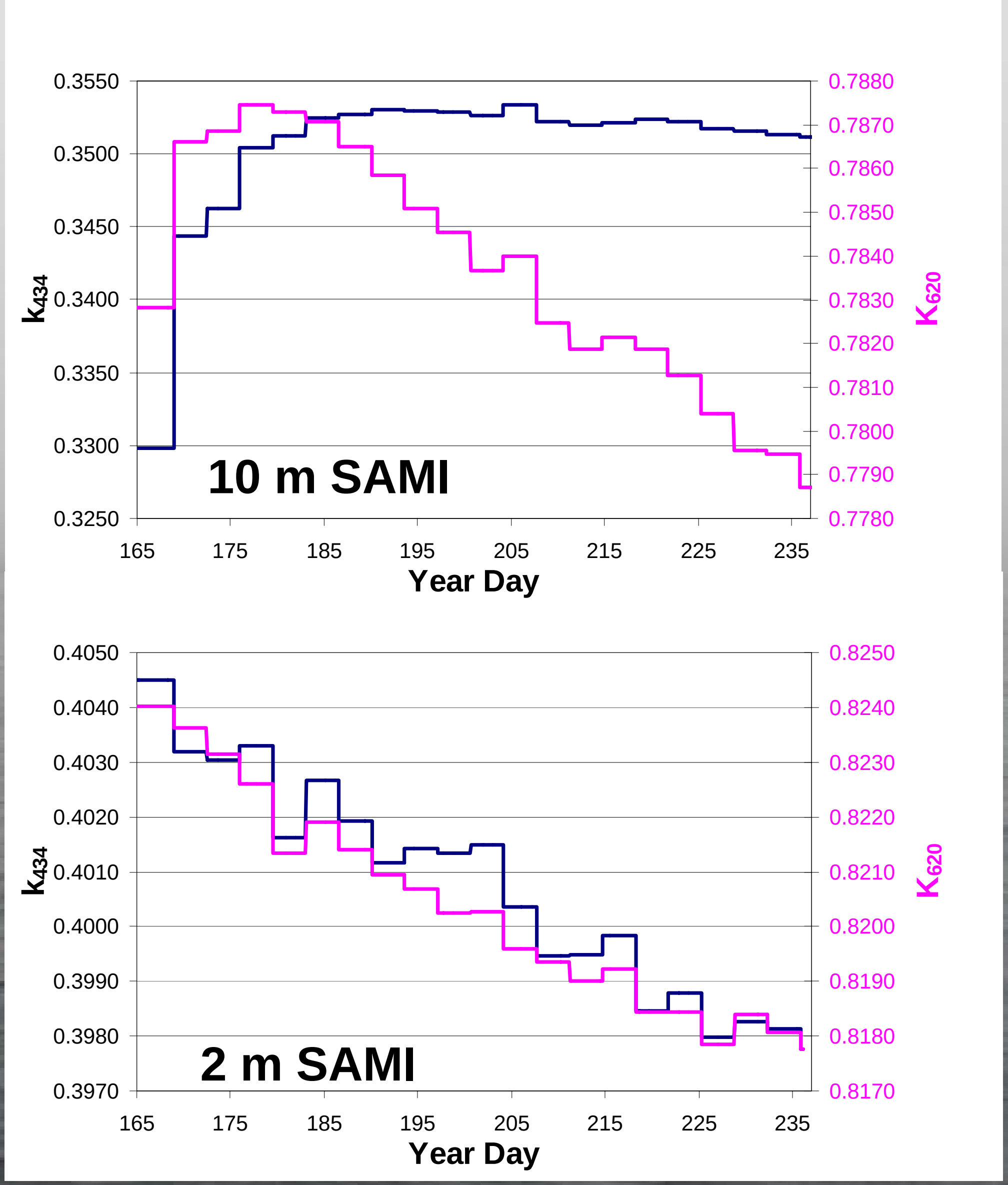




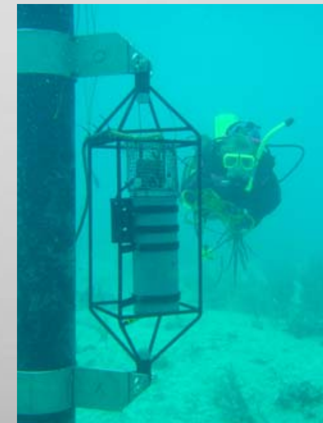
Labrador Sea air-sea exchange experiment June 2004

$$A_\lambda = -\log \frac{I_\lambda}{I_{0\lambda}}$$

$$I_{0\lambda} = k_\lambda I_{740}$$



Autonomous sensor platforms used for SAMI deployments



Primary Failure Mechanisms

Table 1: Most common sources of SAMI failures within 2 weeks of deployment

failure mechanism	percent of total failures
pump or valve	20%
clogged or damaged tubing	20%
data logger or software	10%
434 nm drift	10%
miscellaneous (flooding, electronics, rapid fouling, optical fiber breakage, reagent bag leak and others)	40%

ESTOC SAMI extreme biofouling

Reasons for optimism

- new commercial autonomous chemical sensors in the last 10 years (O_2, *p*CO_2, nitrate)
- pH, alkalinity, TCO_2 and other systems being developed
- need to understand human impacts

SAMI deployment locations

☆ past sites
★ current sites