Measuring the carbon dioxide system in seawater: status and needs

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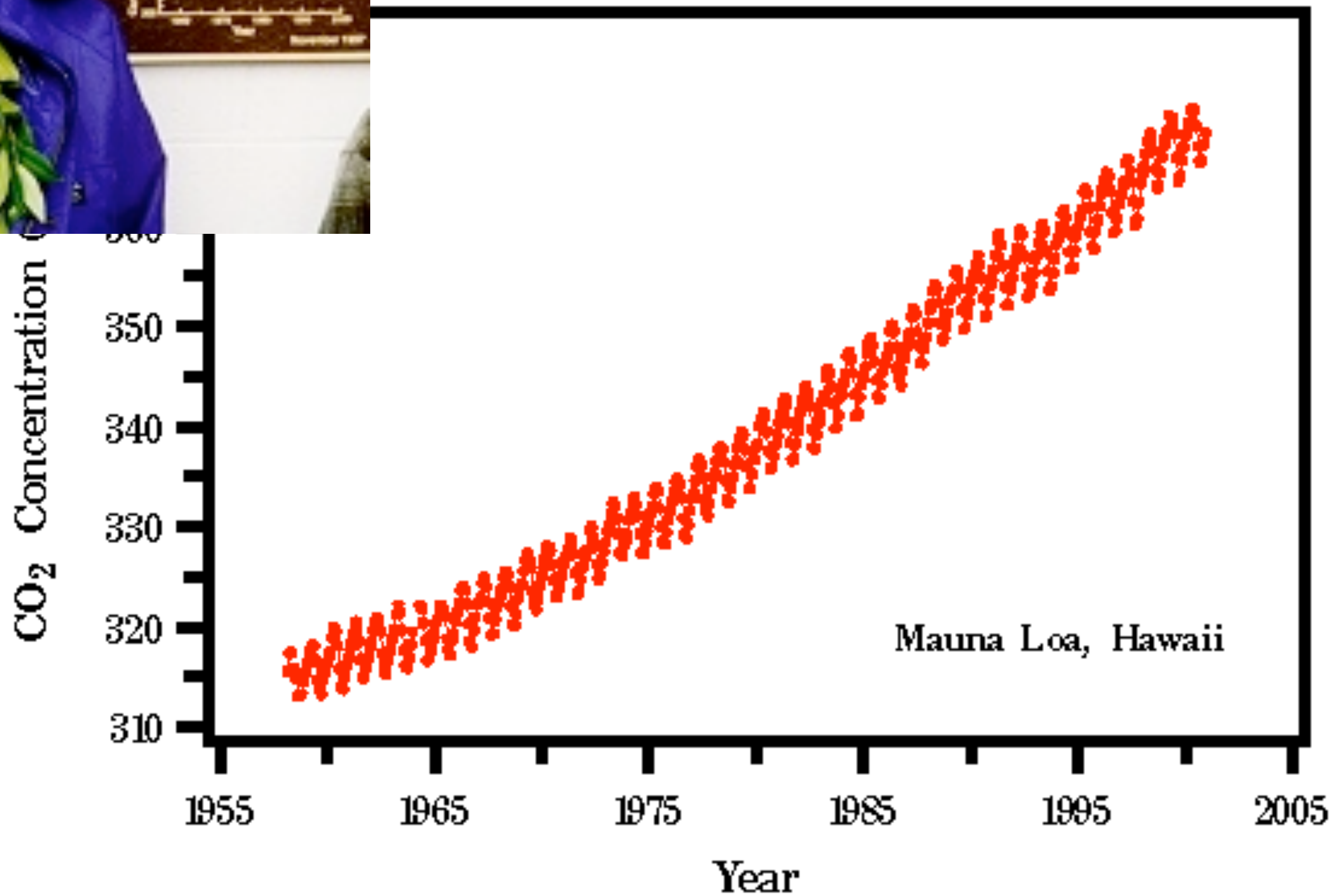


The CO_2-in-air program

- Developed international calibration scales linked to a central laboratory
- Emphasized attention to the details of measurement technique
- Depended on experienced and capable research staff
- Showed the benefits of both global and time-series data sets

Measured parameters

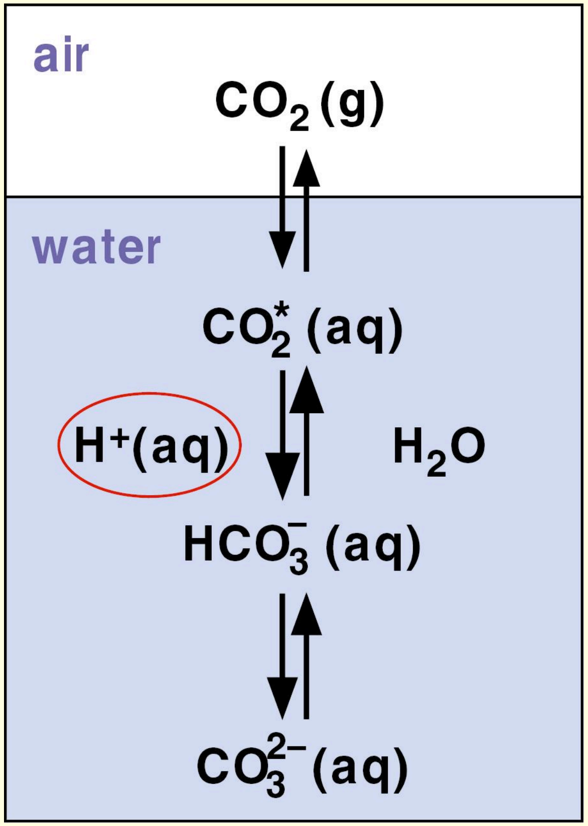
- Total dissolved inorganic carbon – C_T
- Total alkalinity – A_T
- Hydrogen ion concentration – pH
- Partial pressure of CO_2 in equilibrium with a sample of seawater – $p(CO_2)$

CO_2 in seawater

$$K_0 = [CO_2^*] / p(CO_2)$$

$$K_1 = [H^+][HCO_3^-] / [CO_2]$$

$$K_2 = [H^+][CO_3^{2-}] / [HCO_3^-]$$



$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$$

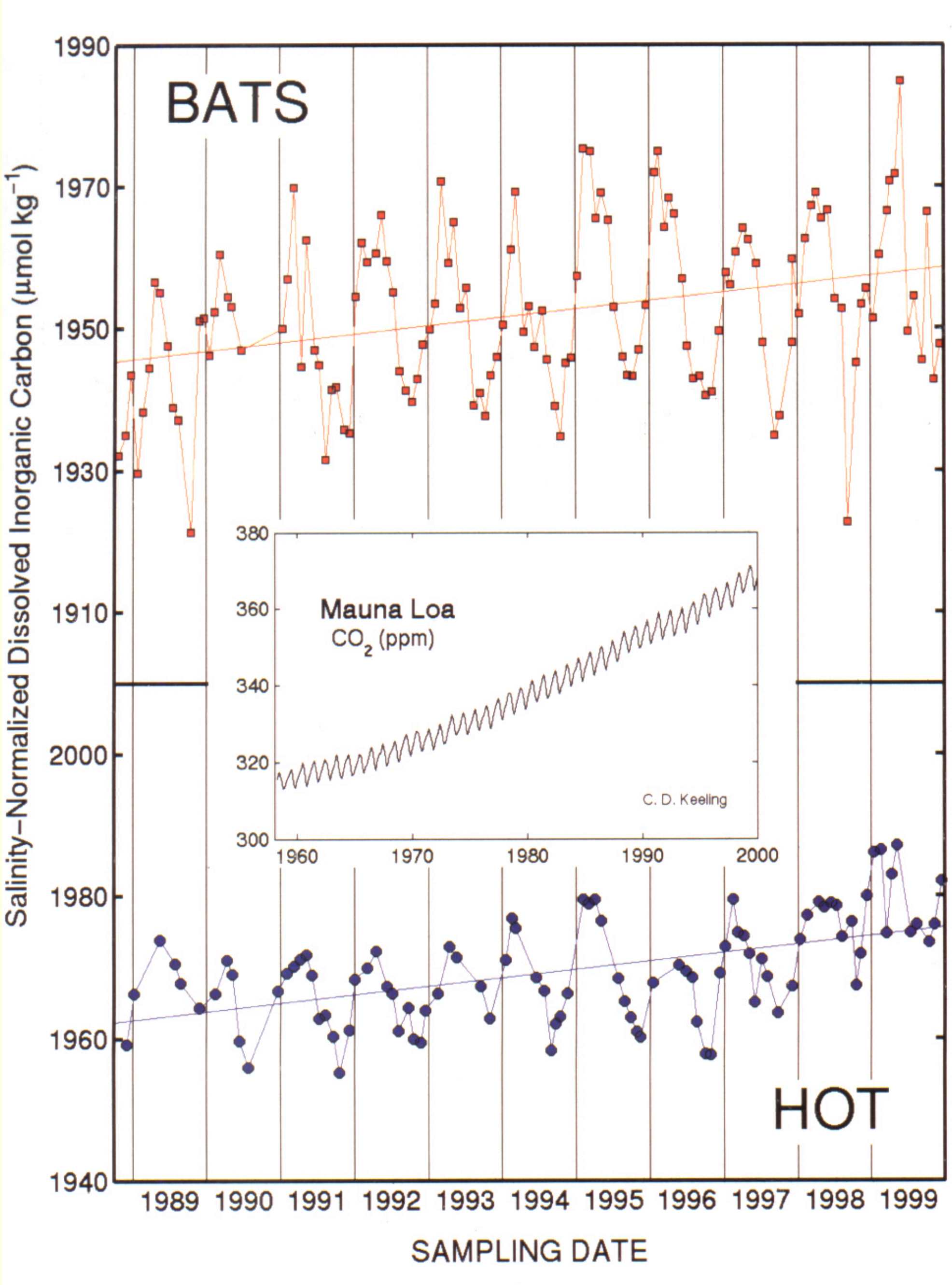
$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + \ldots$$

Current measurement techniques

	Analytical approach	Calibration approach	Quality control materials
C_T	Acidification / extraction / coulometry	Pure CO_2 gas (p, V, T)	CRMs
A_T	Acidimetric titration	HCl analysis by coulometry	CRMs
pH	pH indicator dye / spectrophotometry	Indicator dye properties	Buffers
$p(CO_2)$	Equilibration / infra-red analysis	CO_2 in air mixtures	–

State-of-the-art measurement capabilities

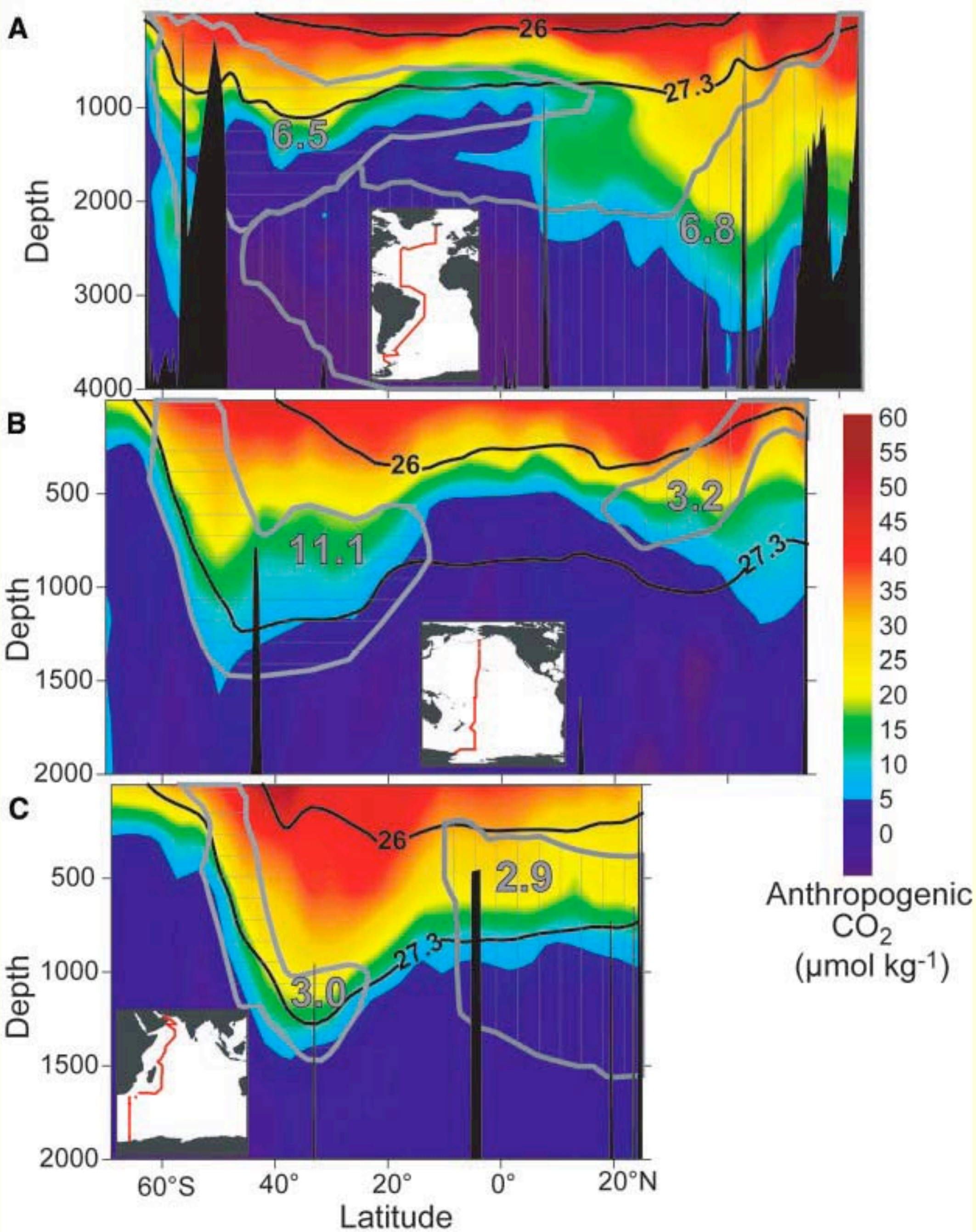
	Oceanic range	Best precision	Estimated uncertainty
C_T / µmol kg^{-1}	1,900 – 2,350	0.5	1.5
A_T / µmol kg^{-1}	1,900 – 2,300	0.7	2.0
pH / 1	7.45 – 8.25	0.0005	0.003
$p(CO_2)$ / µatm	200 – 2,000	<1%	1.5%



Bermuda
Atlantic
Time-Series

Hawaii
Ocean
Time-series

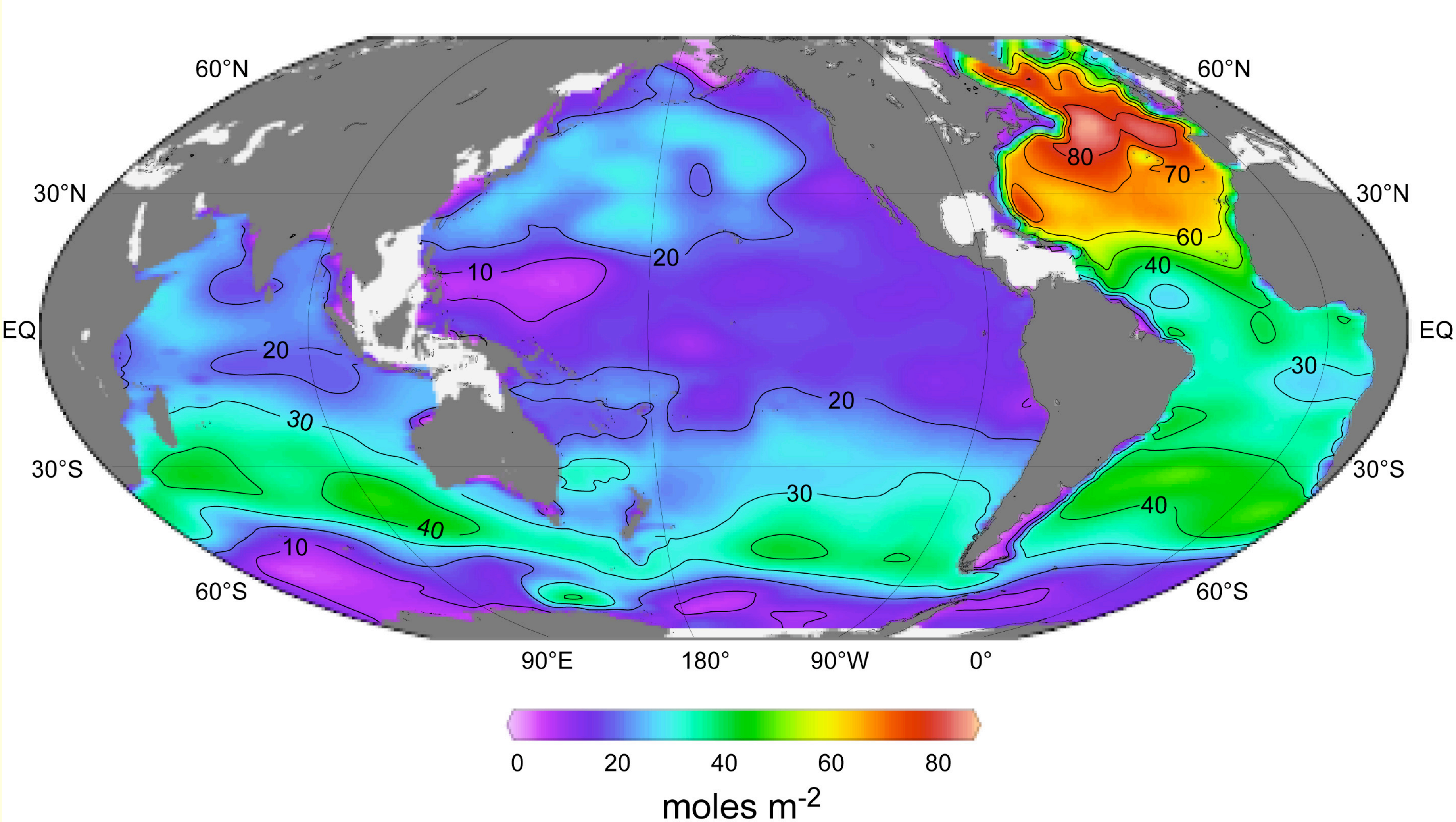
Karl *et al.* (2001)



Anthropogenic CO_2 distributions along ocean sections

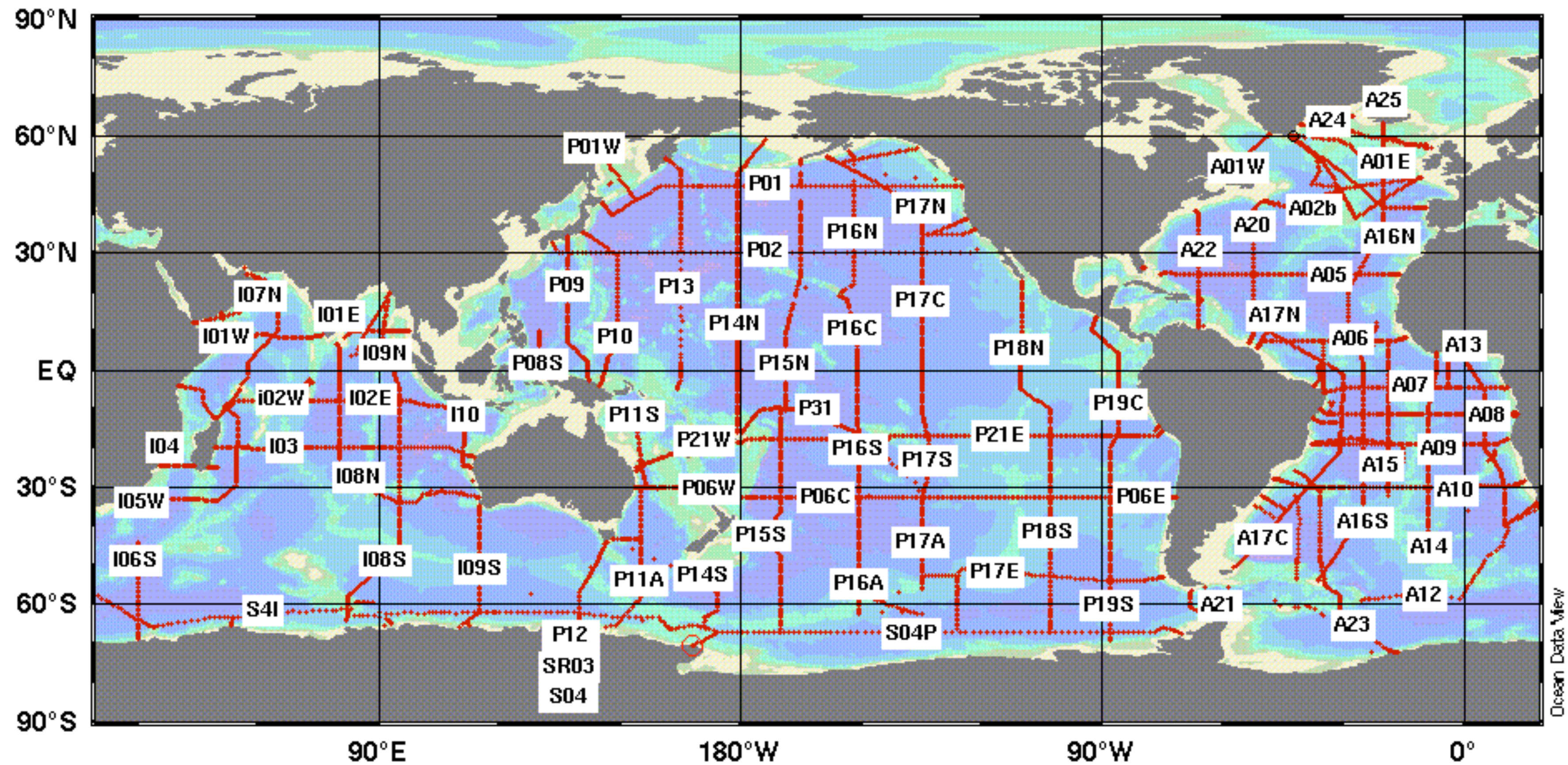
Sabine *et al.* (2004)

Anthropogenic CO_2 inventory



Sabine *et al.* (2004)

1990s Global Survey
(WOCE Hydrographic Program)



Final CO_2 data set comprises:

- 95 cruises (> 15 laboratories)
- 9,618 hydrographic stations
- ~30,000 samples with results reported for C_T and A_T

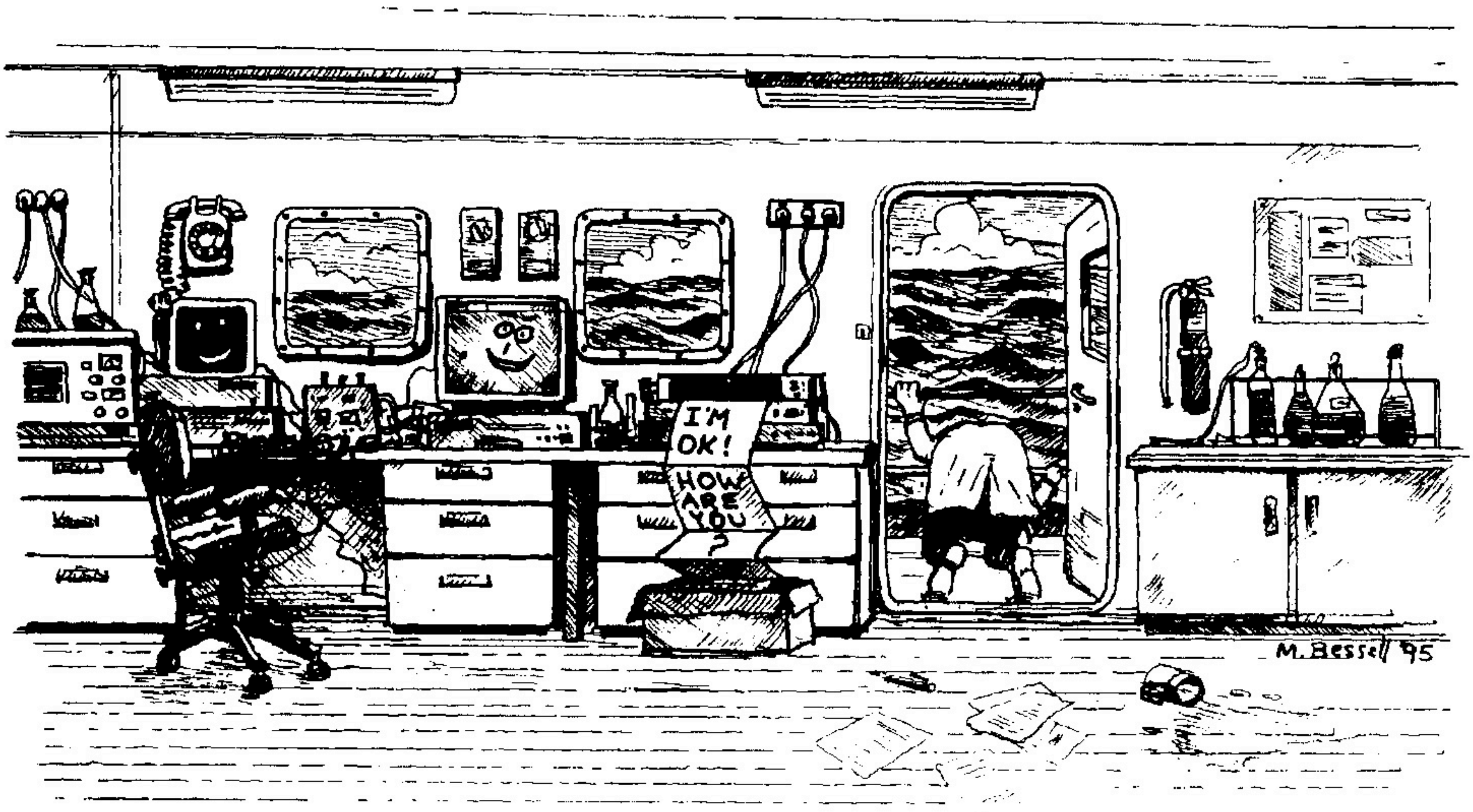
Note: these are not all of the measurements that were made, just those considered of sufficient quality.

Analytical costs for discrete samples

	Equipment costs ($1,000)	No. of anal. per hour	Water needs (L)	Reagent use / disposal needs*
C_T	60 – 70	3	~1.0	Acidified sample Hazardous reagents
A_T	15 – 35	5	~0.4	Acidified sample
pH	15 – 20	5	~0.5	Indicator dye
$p(CO_2)$	20 – 40	4 (20)	~1.2 (0.2)	Calibration gases

* All samples are poisoned with $HgCl_2$ upon collection.

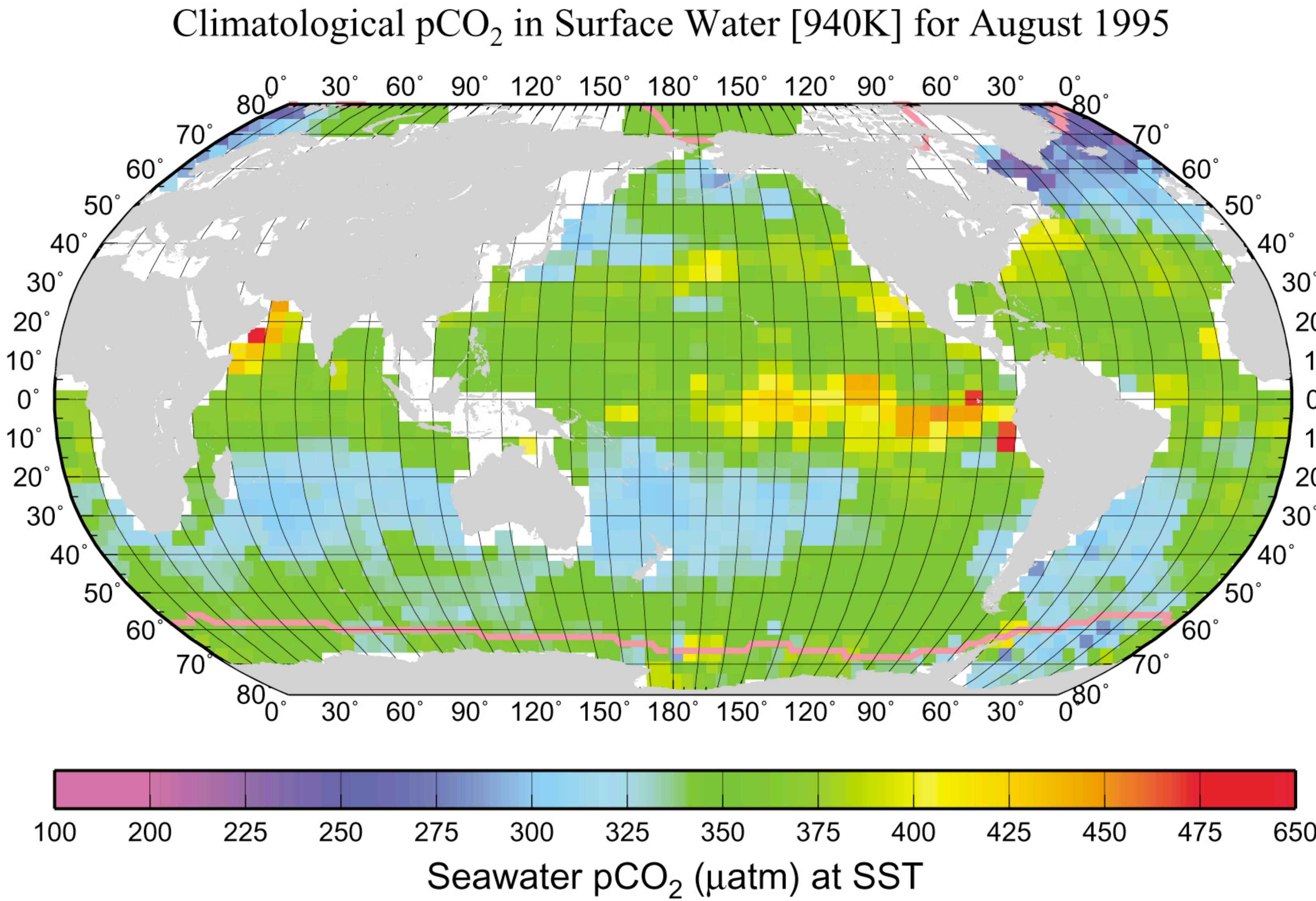
Personnel costs



Significant other costs

- Cruise logistics including shipping of bulky equipment and hazardous chemicals
- Post-cruise data evaluations and data adjustments
- Data archival

There are, of course, benefits too!



Takahashi *et al.* (2002)

Economist, July 24, 2003

Faster, better, cheaper?

Faster, better, cheaper?

Choose any two!

Sampling & analysis strategies

- Discrete samples (collected from different depths in a rosette sampler, poisoned with $HgCl_2$, then analyzed on board ship)
- Underway analysis (a stream of sea water pumped into the ship's laboratory and analyzed there)
- Instruments operated in a *profiling* mode, *e.g.* as part of a CTD package
- Remote instruments able to carry out their analyses autonomously in the ocean

Development state of CO_2 measurement systems

Level 0 – No working system available

Level 1 – Prototype system available in single lab

Level 2 – 2nd generation prototype in use

Level 3 – Home-built systems in a number of labs

Level 4 – Can be purchased commercially

Level 5 – Commercially available and supported

Development state of CO_2 measurement systems

	Discrete samples	Underway analysis	Profiling instrument	Remote instruments in ocean
C_T	3 / 4	1 / 2	0	0
A_T	3 / 4	1	0	0
pH	3	2	1 / 2	1 / 2
$p(CO_2)$	3 / 4	3 / 4	1	3 / 4

Needs

Faster

1. Instrument development time-line
2. Analysis rate

Better

1. Instrument reliability
2. Quality control
3. Smaller sized instrument
4. Less chemical usage

Cheaper

1. Operating costs
2. Purchase costs

A challenge!

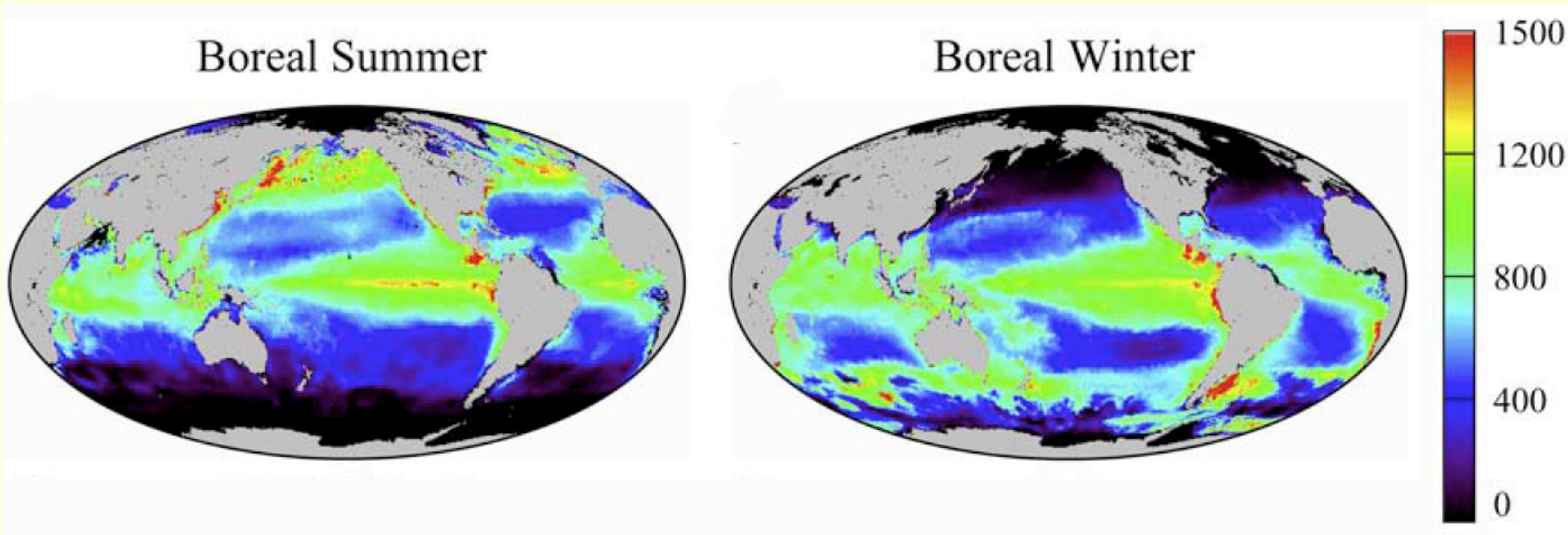
Can we measured integrated, net primary production directly?

And hence track future changes?

Net Primary Production

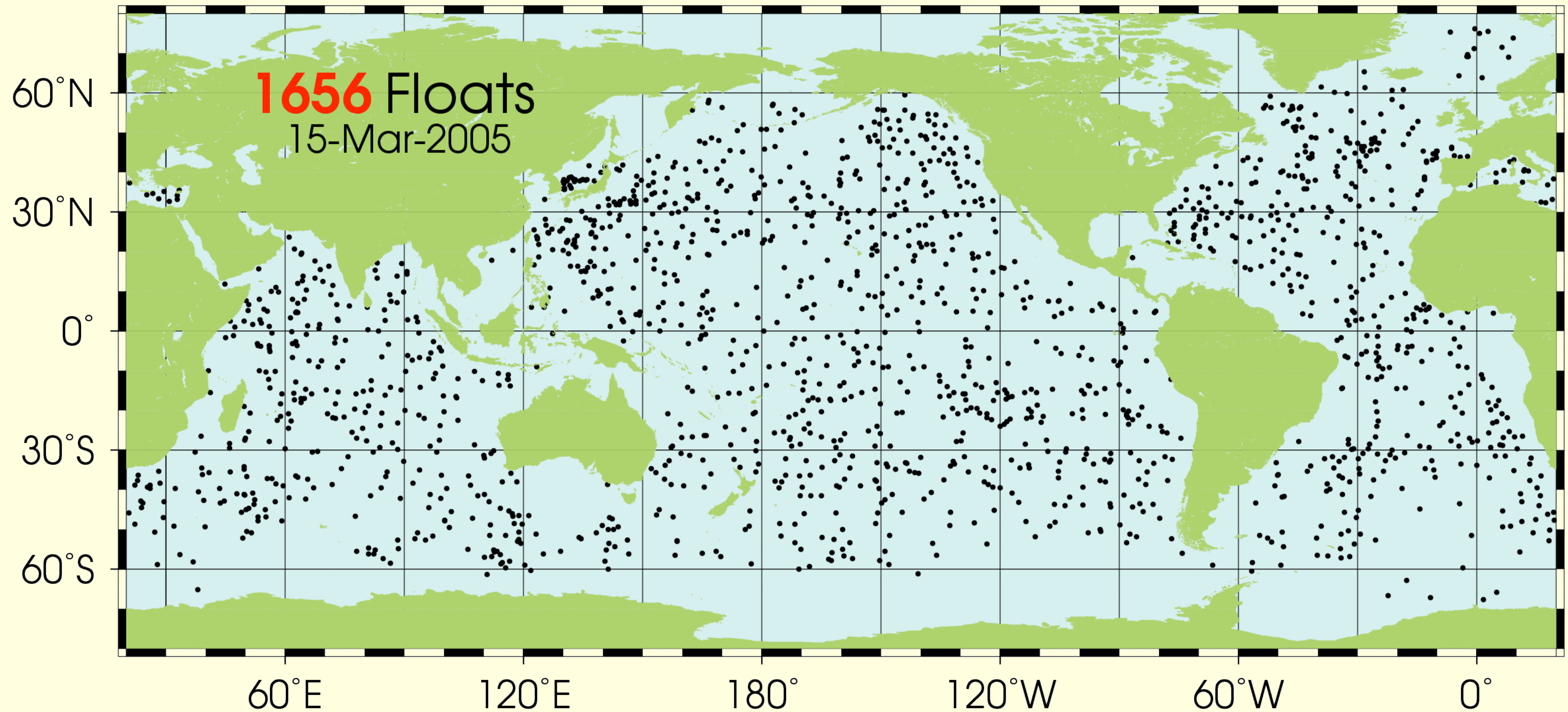
estimated from satellite here

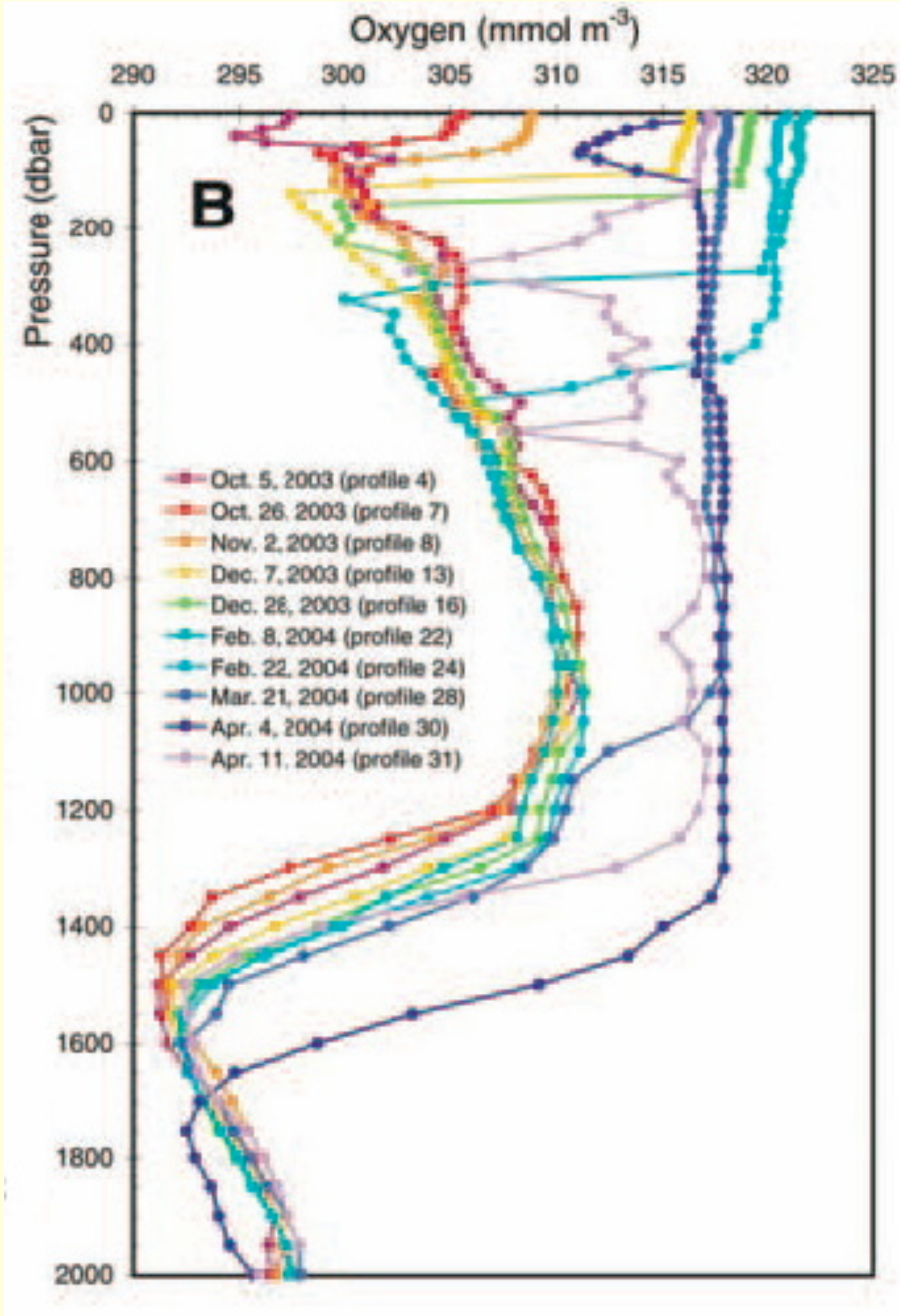
(mg C m^{-2} d^{-1})



Behrenfeld *et al.* (2005)

Argo profiling float program





Oxygen profiles in the Labrador Sea

Measured with an Aanderaa oxygen sensor on a profiling float

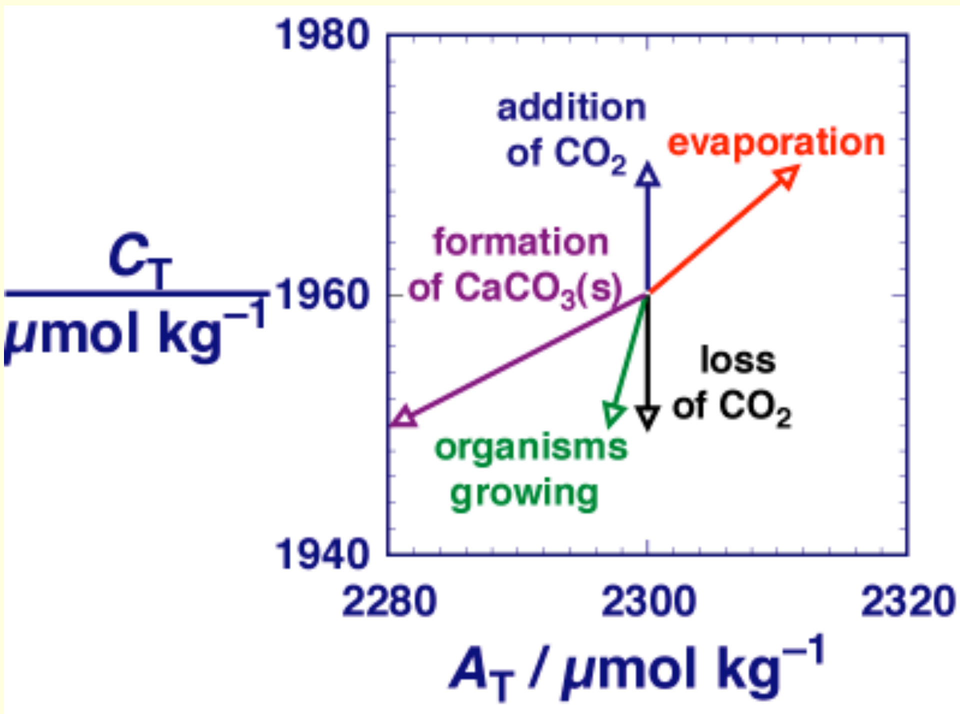
Körtzinger *et al.* (2004)

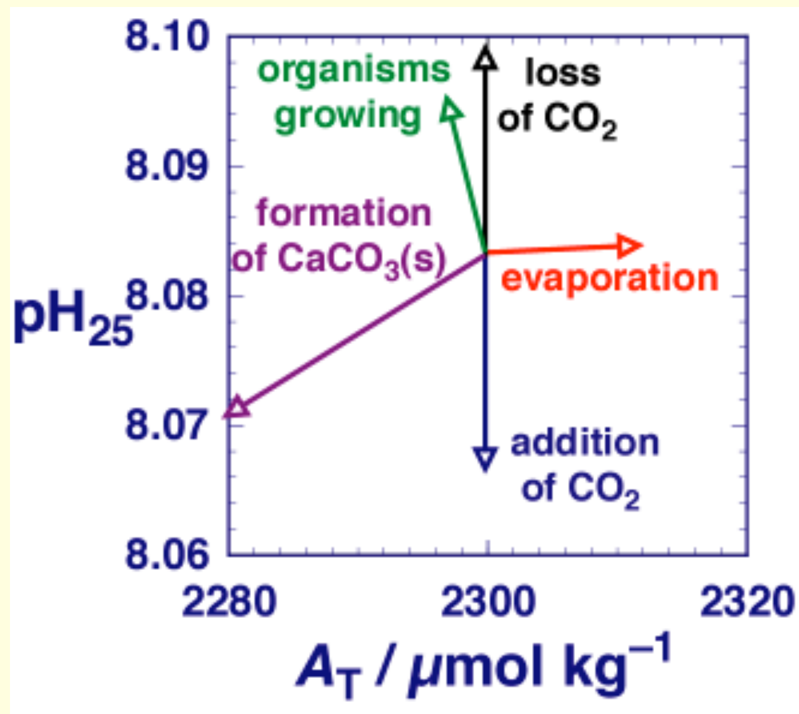
But need a CO_2 measurement

The current most likely candidate is pH

- A prototype system exists (SEAS-II)
- High sensitivity to changes in A_T/C_T
  - still needs significant calibration work
- Need development/testing to ensure:
  - Sufficient lifetime (power, reagent usage)
  - Fouling resistance

Information from pH / A_T
(after removing mixing effects)






THINK!
THERE MIGHT BE
A BETTER WAY