2010.10.27, PICES2010,
Portland, Oregon

Good on board practice for ocean carbon measurement and effort toward international collaboration

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National Institute for Environmental Studies (NIES)

Grandchildren or nephew of Prof. T.Parsons

- Prof. Akira Otsuki was my first boss in NIES (1981-1988).

  Profs. Humitake Seki and Masayuki Takahashi spent in IOS with Prof. Parsons, but Prof. Otsuki spent in Prof. R.G.Wetzel's lab (Michigan State Univ.). Prof. Otsuki were a good friend of them and they often visited our lab, because all of them were in Tsukuba in 1980's.

  <Example of Takahashi, Seki & Parsons joint papers>

  Observation on the decomposition of a marine sediment, H.Seki, J.Skelding & T.R.Parsons, L&O, 13, 440-447, 1968.

  Environmental control of phytoplankton cell size, T.R.Parsons & M.Takahashi, L&O, 18, 511-515, 1973.

  A comparison of four methods for integrating ^{14}C-primary productivity measurements per unit area, S.Ichimura, T.R.Parsons, M.Takahashi & H.Seki, JO, 36, 259-262, 1980.

- Dr. C.S.Wong opened my gateway of ocean CO_2 from the joint VOS work with IOS, Canada, and Dr. Jiye Zeng, who got PhD at Parson's lab, were my colleague in M/S Skaugran observation. He is working in NIES as an atmospheric data manager, developing very useful air trajectory program.

Ocean carbon measurement

- Total inorg. carbon (DIC) & alkalinity (At) from hydrocast

  ⇩

  Vertical distribution of carbonate species in the water column

  ⇩

  Historical accumulation of inorganic carbon in the ocean

- pCO_2 measurement from underway water

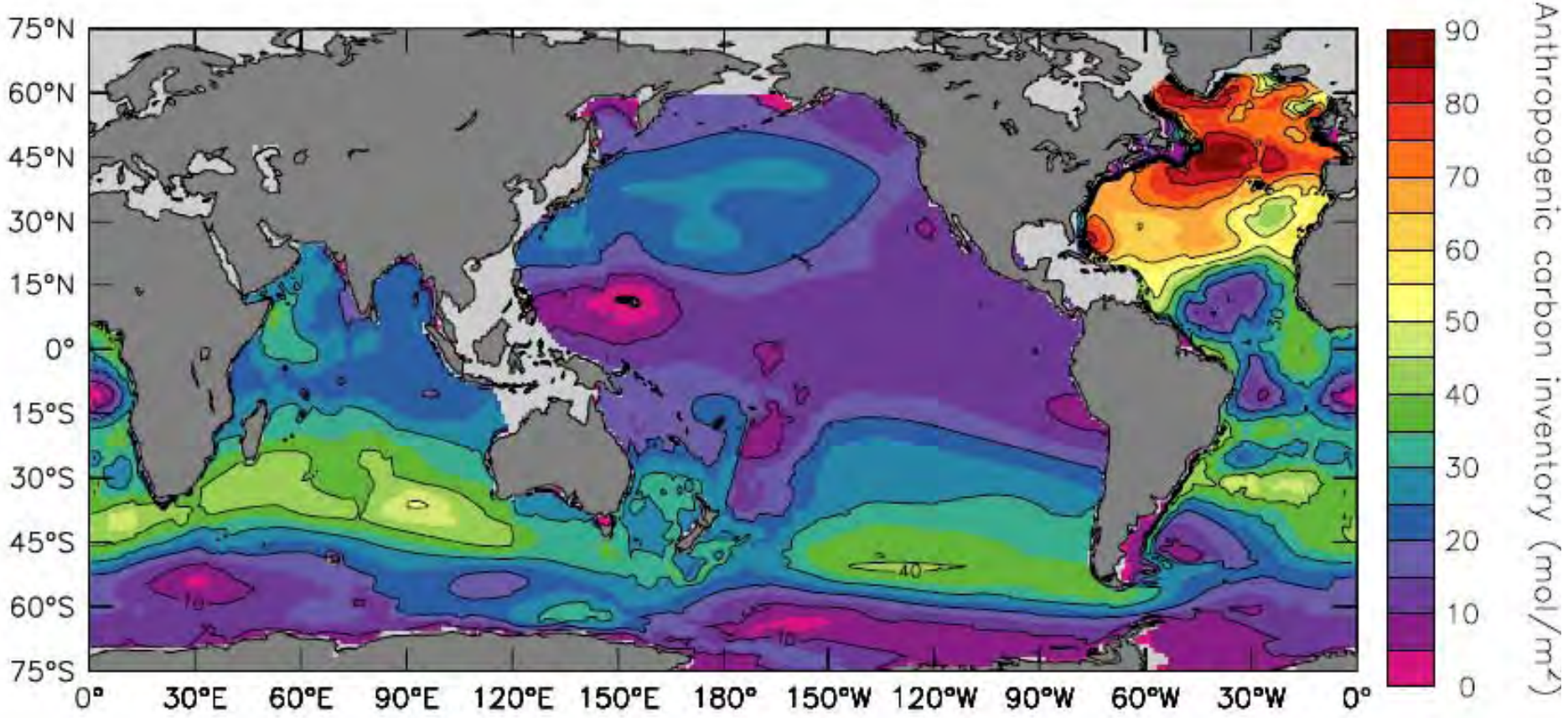
  ⇩

  Spatial distribution and temporal change of ocean surface CO_2

  ⇩

  Present CO_2 gas exchange flux of the ocean

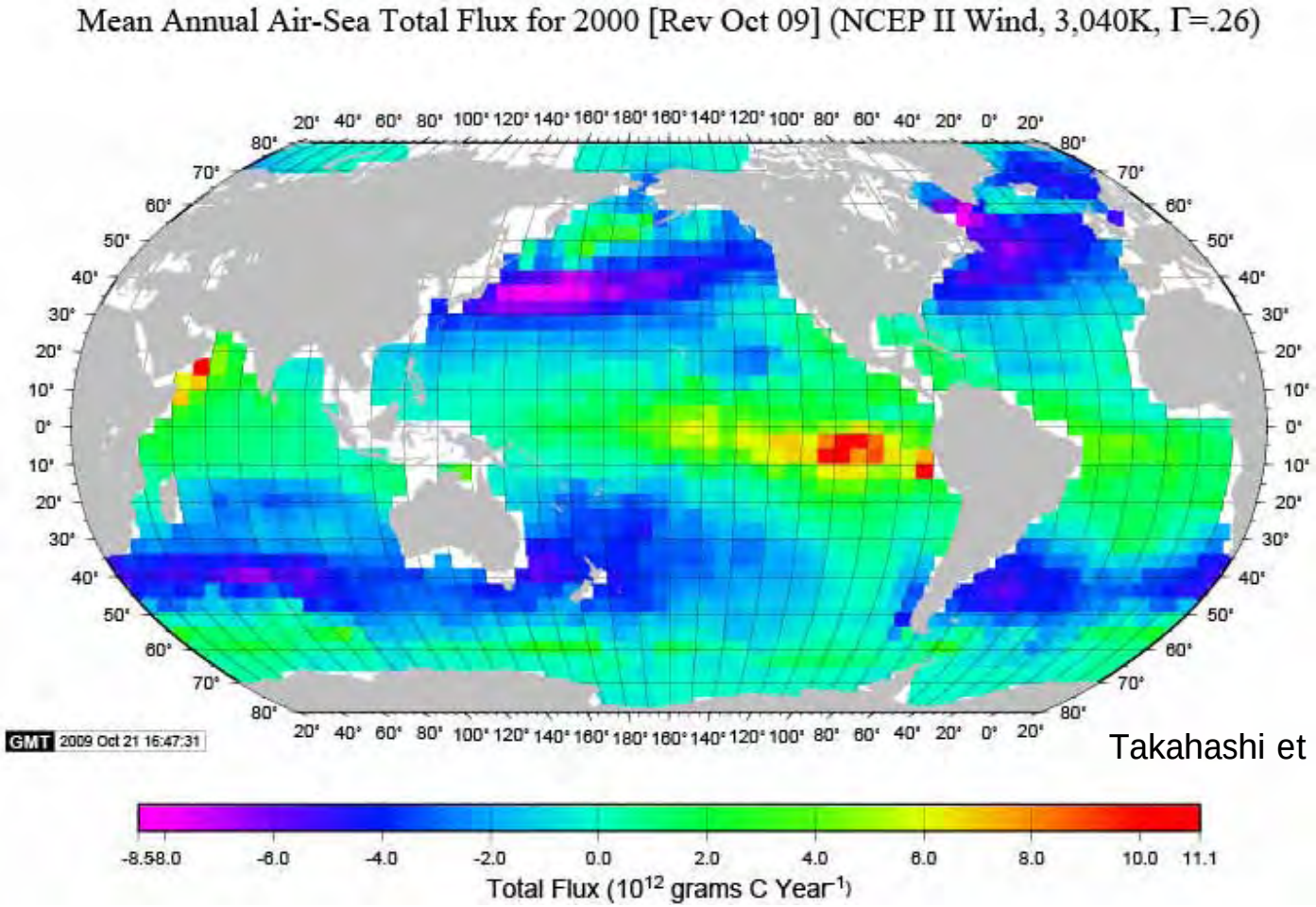
Global data integration of ocean interior carbon accumulation



Sabine et al. (2004)

Oceanic sink of anthropogenic carbon was estimated as 118±19GtC (1750-1994) and recently as 53±9GtC (1980-2005). These estimated was done from the global data integration of ocean interior carbon measurement, as DIC and At after precise calibration using seawater carbon CRM prepared by SIO.

Global data integration of ocean surface pCO_2 observation



Takahashi et al. (2009)

A climatological mean distribution for the surface water pCO_2 in non-El Niño conditions has been constructed for a reference year 2000 based upon about 3 million measurements of surface water pCO_2 obtained from 1970 to 2007. The total ocean uptake flux (anthropogenic CO_2) is estimated to be -2.0 ± 1.0 Pg-C/y in 2000.

Methods of ocean carbon measurements

- Dissolved inorg. carbon (DIC) & alkalinity (At)

  Chemical analysis of discrete water sample

  Acid-base or coulometric titration

- Underway/buoy pCO_2

  Gas analysis of equil. air

  NDIR (non-dispersive infrared) spectrometer with air-liquid equilibrator

  Application of colorimetric analysis using liquid-liquid equilibration for autonomous buoy

Global data integration needs data QC

- Primary data quality control should be accuracy, not be precision.

  However, precision is necessary to achieve higher accuracy.
- DIC/At quality control has been remarkably advanced by CRM distribution.

- For pCO_2, problems were accuracy of equilibrator and gas analysis scheme (dryer, pressure control) than standard gases.
- We need total system inter-comparison with equilibrator and gas analyzer, gathering at a single location with large amount of seawater supply.

Talk today

- PICES inter-comparison for DIC & At (1999, 2000)
- pCO_2 inter-comparison (1998 within Japanese institutes)
- pCO_2 international inter-comparison (2003, 2009)

- Acknowledgement

inter-comparison participants

National Research Institute of Fishery Engineering/FRA

Designing of PICES 1999/2000 inter-comparison

- Method study
  - Total dissolved inorganic carbon (C_T)
  - Total alkalinity (A_T)
- Four samples (including CRM) to be distributed to participating laboratories
- Follow up with detailed technical workshop involving participants

- Four samples distributed
  - Certified reference material
  - A. Unknown surface sea water sample
  - B. Unknown surface sea water sample
  - C. Unknown deep sea water sample

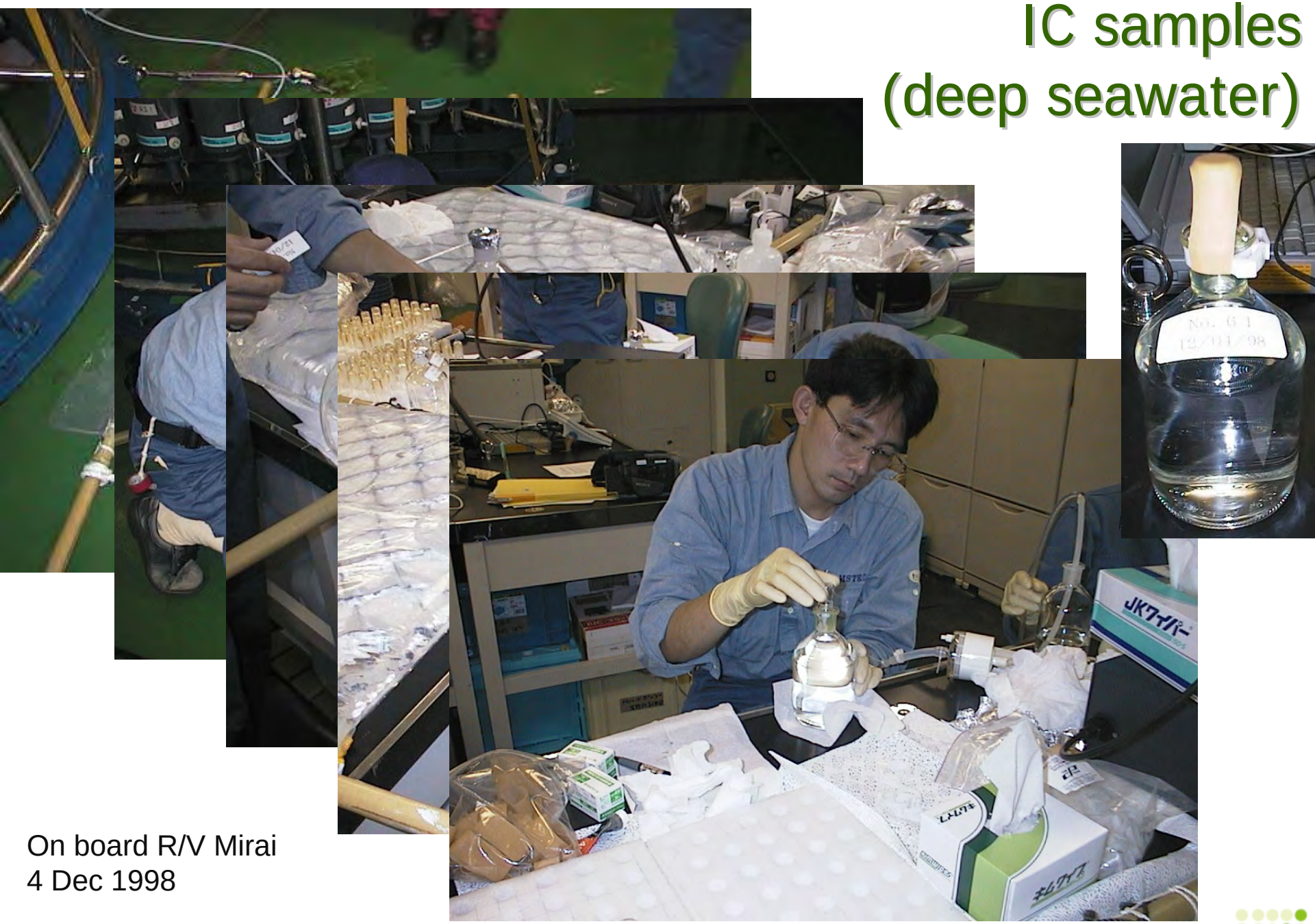
Inter-comparison samples

PICES inter-comparison batch
SIO CRM batch 45
North Pacific deep water by MIRAI

Prof. A. Dickson (SIO) collaborated for preparation of CRM and common surface seawater samples.

Dr. Murata (JAMSTEC) and members took care to prepare the common deep water sample.

IC samples (deep seawater)



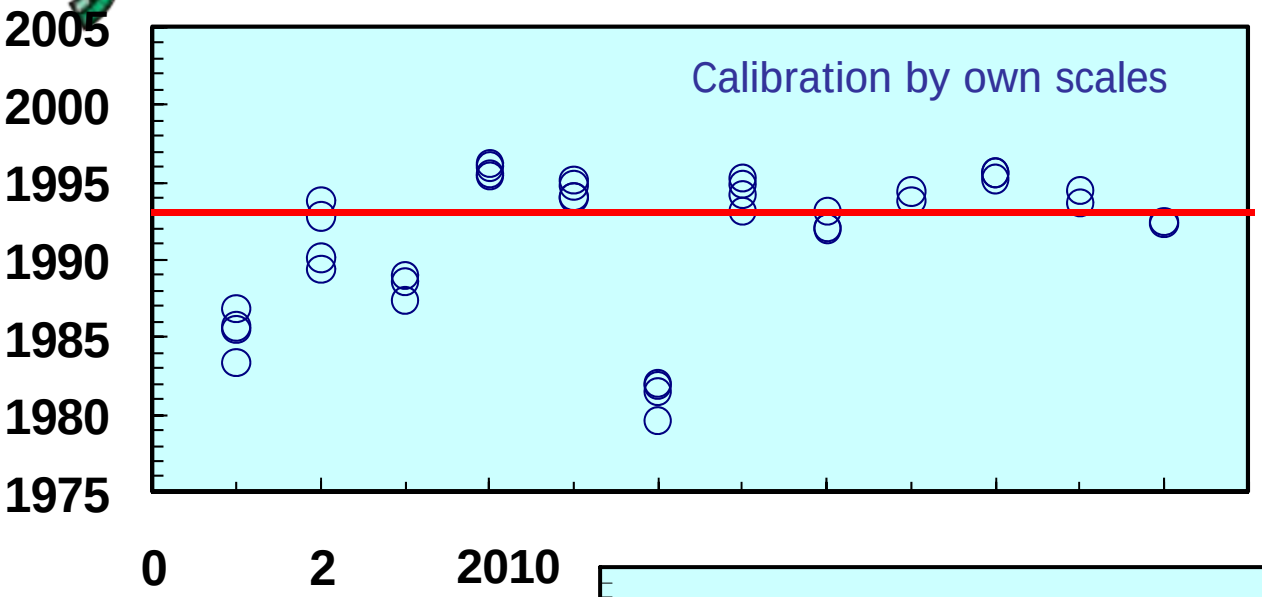
On board R/V Mirai
4 Dec 1998

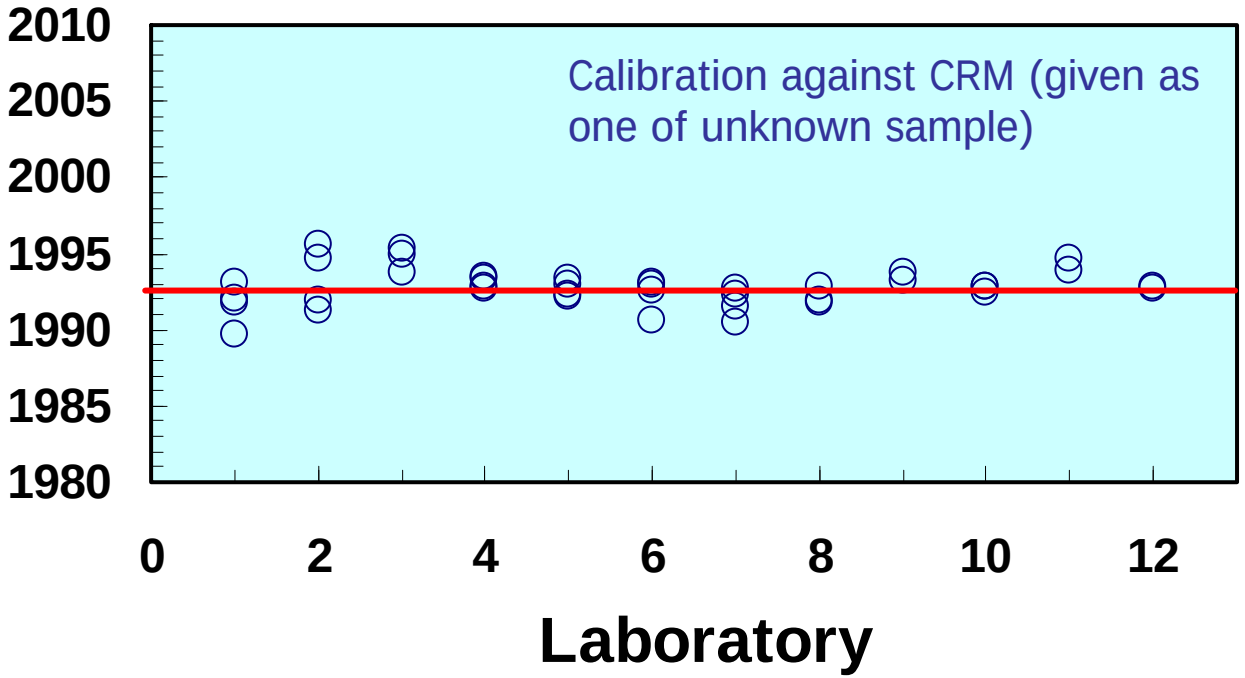
PICES inter-calibration exercise of DIC/At (Tsukuba meeting on 21-22 Apr. 1999)

Workshop participants including institutes analyzed the comparison samples

- Canada
  - Inst. Ocean Sciences
- Korea
  - Seoul National Univ.
- Russia
  - Pacific Ocean. Inst.
- United States
  - NOAA/PMEL
  - Univ. California / SIO
  - Univ. Hawaii
- Taiwan
  - National Sun Yat Sen U.
- Japan
  - CREST (JSTC/NIES)
  - CRIEPI
  - JAMSTEC
  - KEEC
  - Marine Works Japan Ltd
  - NIRE
  - NRIFS (SAGE)
  - MRI
  - RIOC, Osaka
  - Tokyo Univ. Fisheries
  - Univ. Hokkaido

DIC results in 1999 inter-comparison

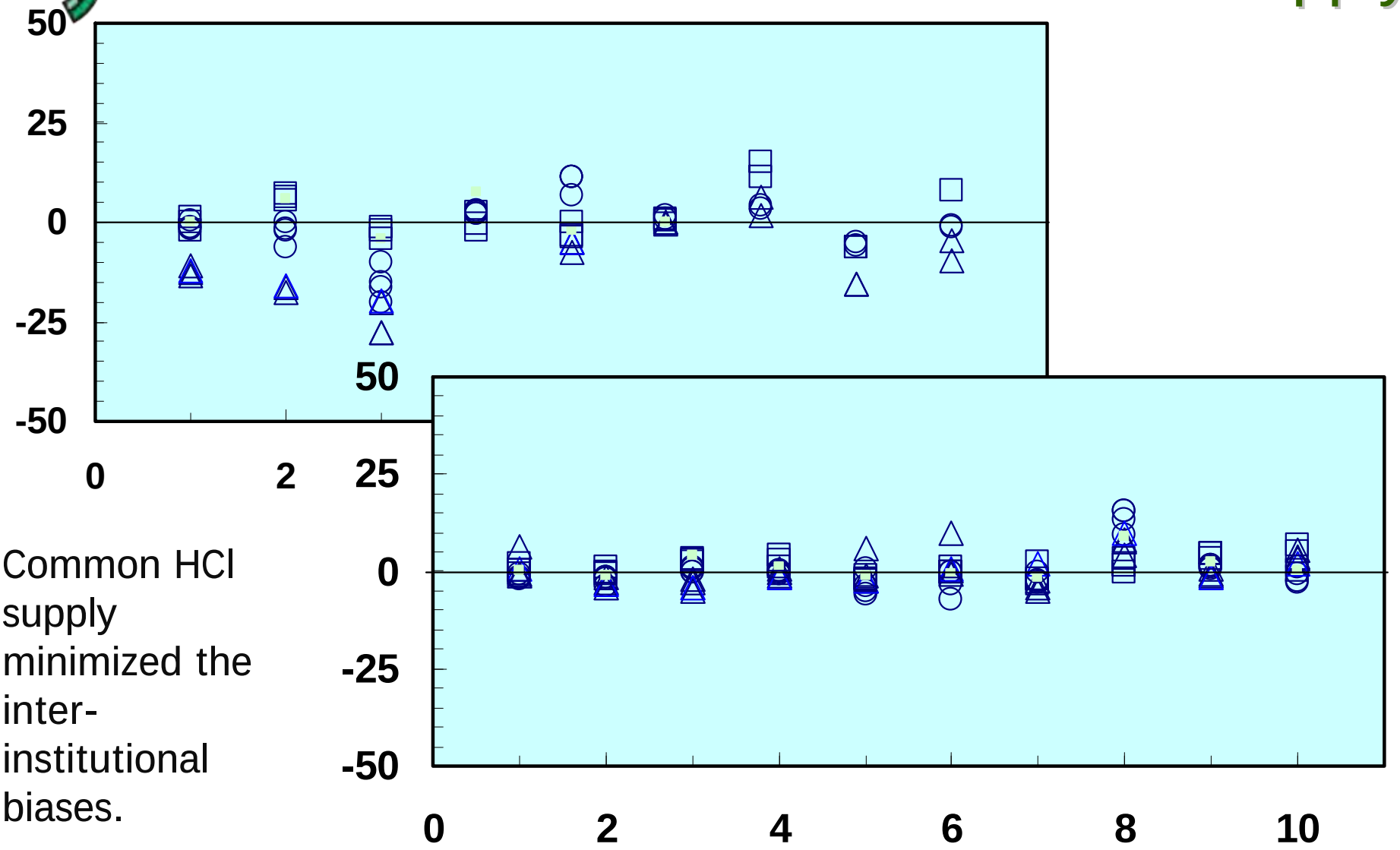




CRM calibration minimized the inter-institutional biases.

At met much serious disagreement.

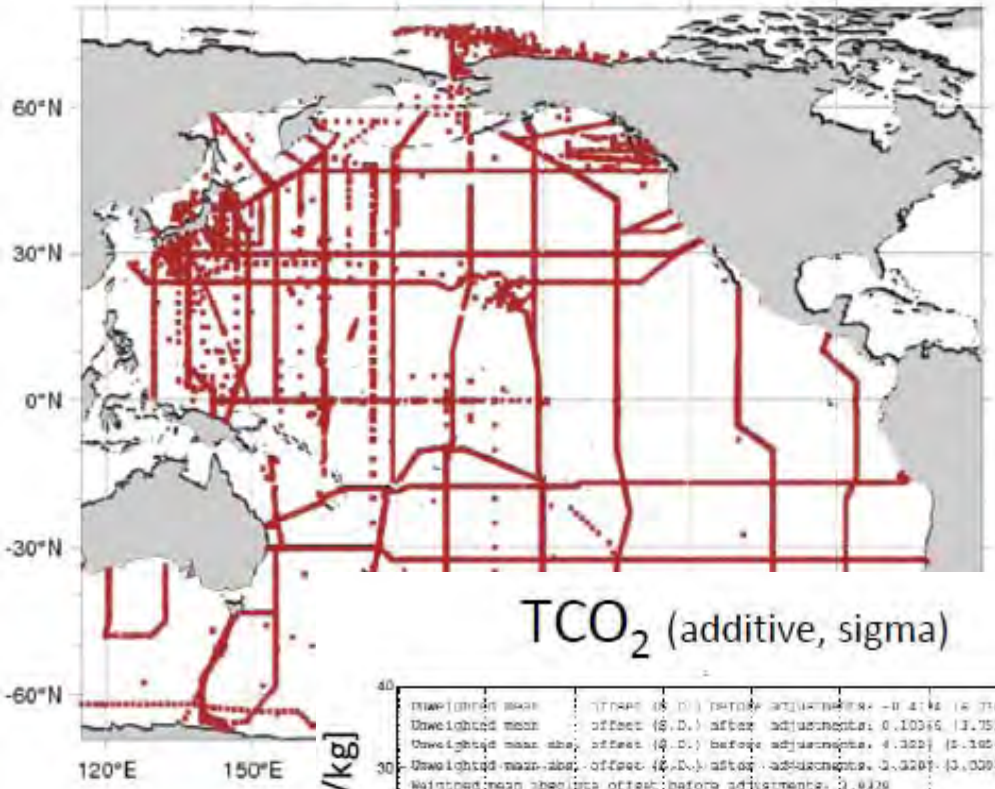
A_T deviations – 1999/2000 with common acid supply



Common HCl supply minimized the inter-institutional biases.

1999/2000 exercise conclusions

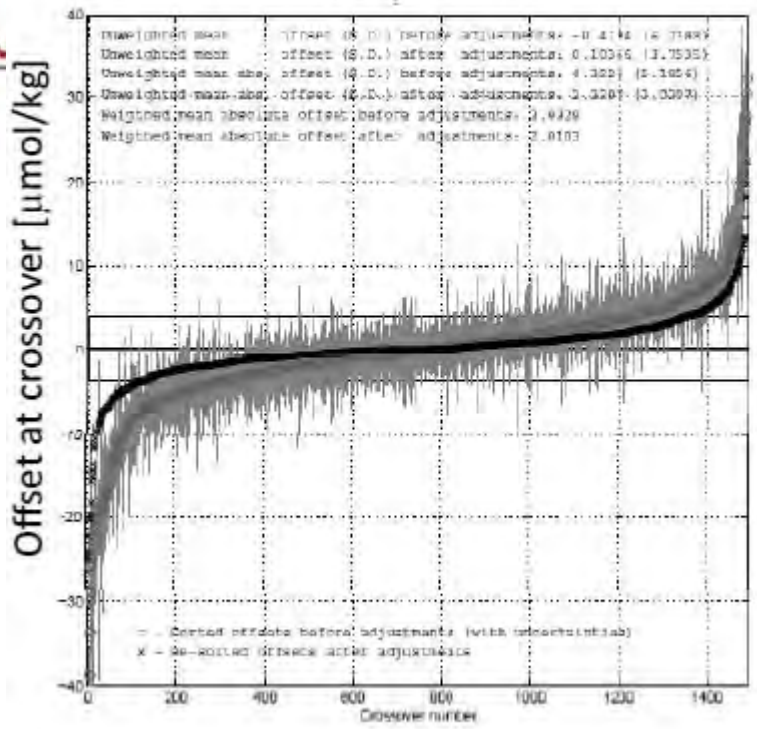
- 1999 exercise-DIC conclusions
  - Results are very encouraging
  - Analytical precision is acceptable (though better for more experienced labs)
  - Calibration problems exist (correctable with CRM)
- 2000 exercise-At conclusions
  - Significant improvement over 1999
  - Although acid was supplied, some calibration problems still exist (removable by CRM adjustment)
- Apparent analytical skill up has been achieved within PICES countries – toward the PACIFICA synthesis project



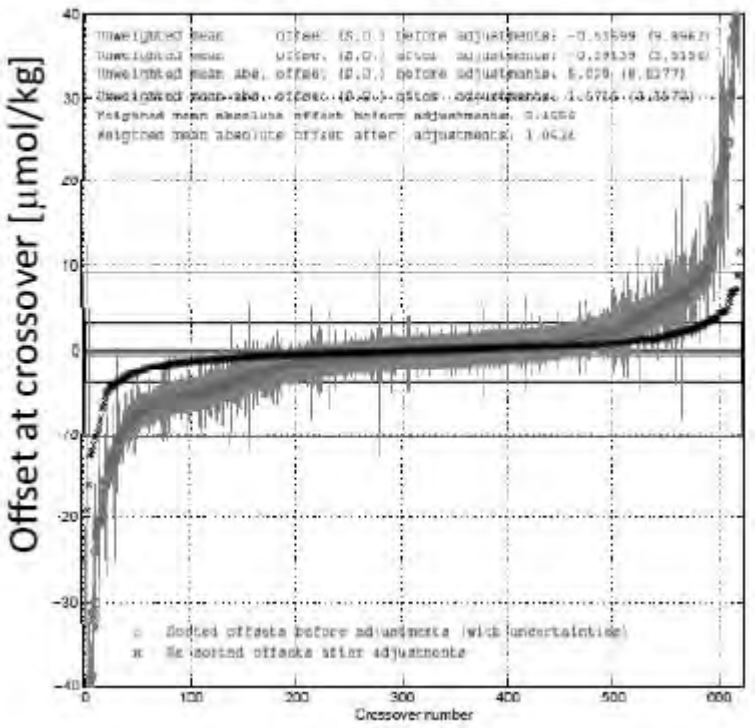
From presentation document by M. Ishi, T. Suzuki, PICES CC-S & WG members,

Cross over analysis (cruise by cruise comparison of stable >1500 m depth water) of all available Pacific DIC-At data sets.

TCO_2 (additive, sigma)



TA (additive, sigma)



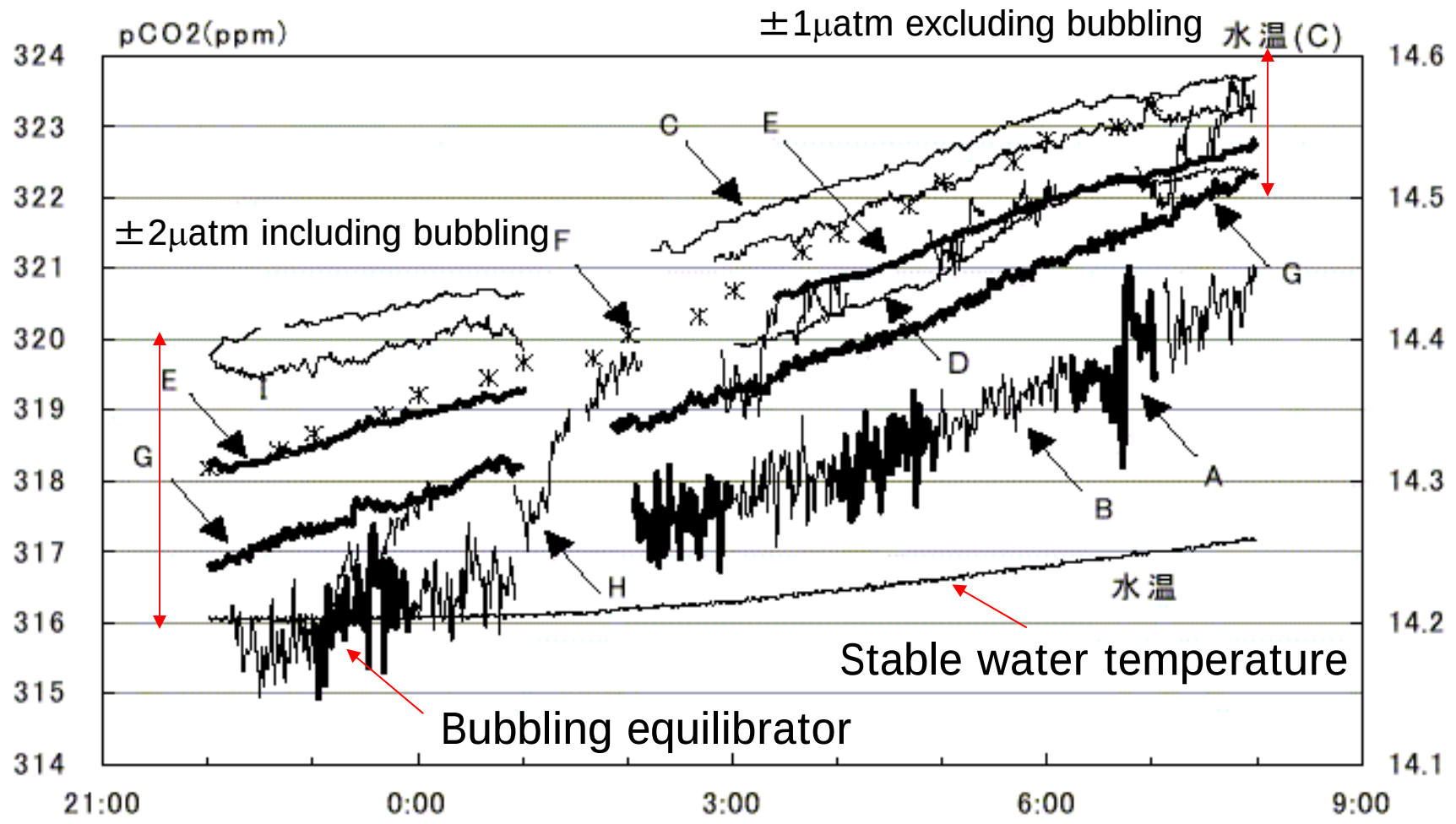
pCO_2 inter-comparison using an indoor seawater Pool in NRIFE/FRA

Seawater pool of 170t
stable temperature and pCO_2
manageable pCO_2 by HCl/NaOH

Pool building with wet and dry laboratories

- dimension = 15 x 8 m, 2 m in depth
- uniform temperature by circulation

Japanese inter-comparison in 1998



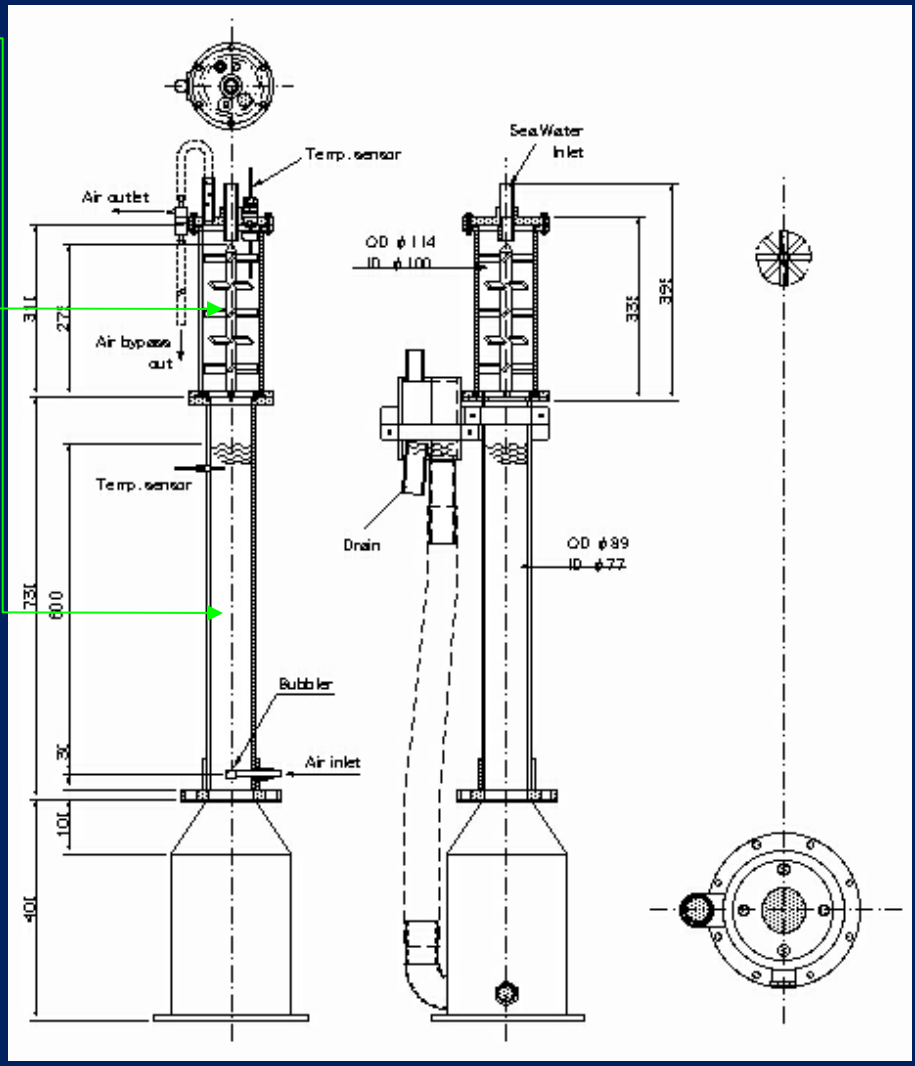
After Scripps (1994) and R/V Meteor (1996) pCO_2 inter-comparison, we started Japanese inter-comparison because of the easier logistics. NIES, NIRE, NRLM, Hokkaido Univ., Kyushu Univ., and IOS (equilibrator) participated.

Development of New pCO_2 system (Tandem)

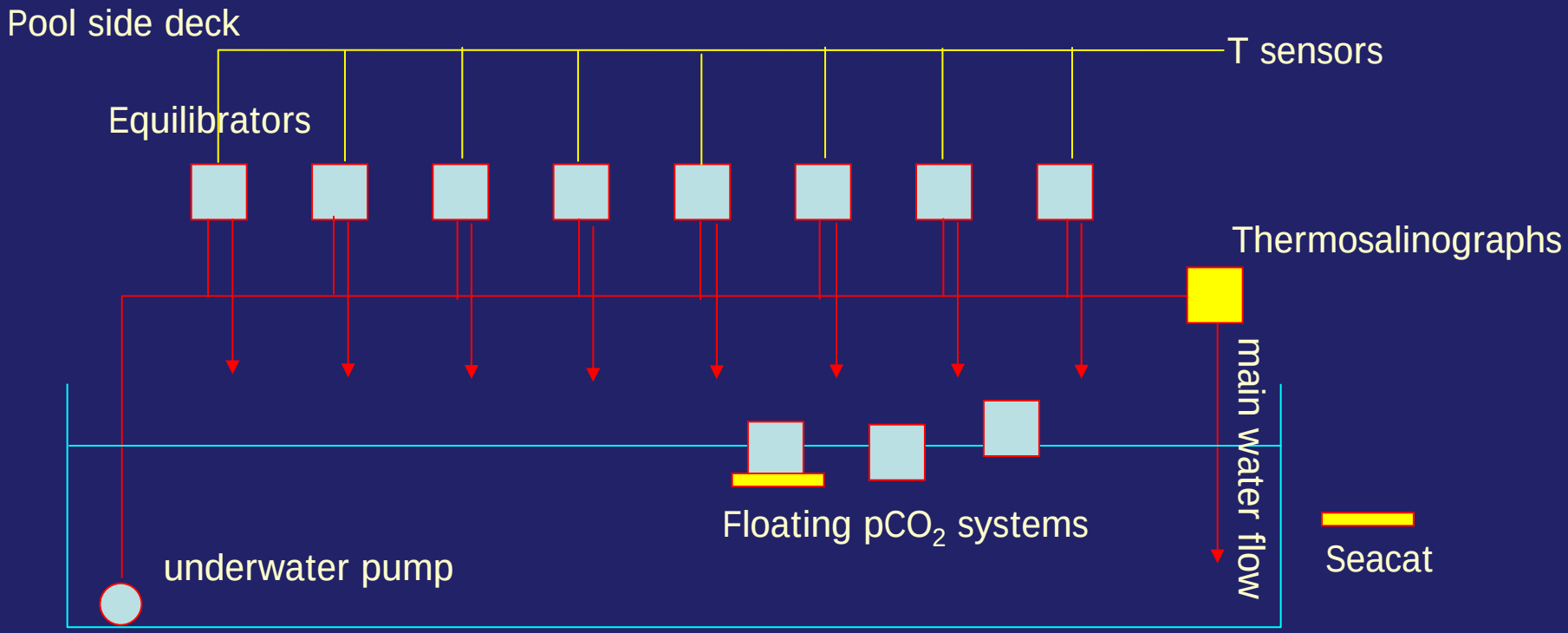
Tandem equilibrator (two stage equilibrator)
1st stage: bubbling
2nd stage: static mixer

Surface tension effect gives systematic (0.8 %) low bias to bubbling equilibrator, which is compensated by the second stage mixer equilibrator, which has large diameter vent to the ambient.

Patent:
2 stage equilibrator design
flow through pCO_2 measurement
feed back air supply to equilibrator



Much serious cares were taken for 2003/2009 inter-comparison setup from the experience in the Japanese inter-comparison 1998

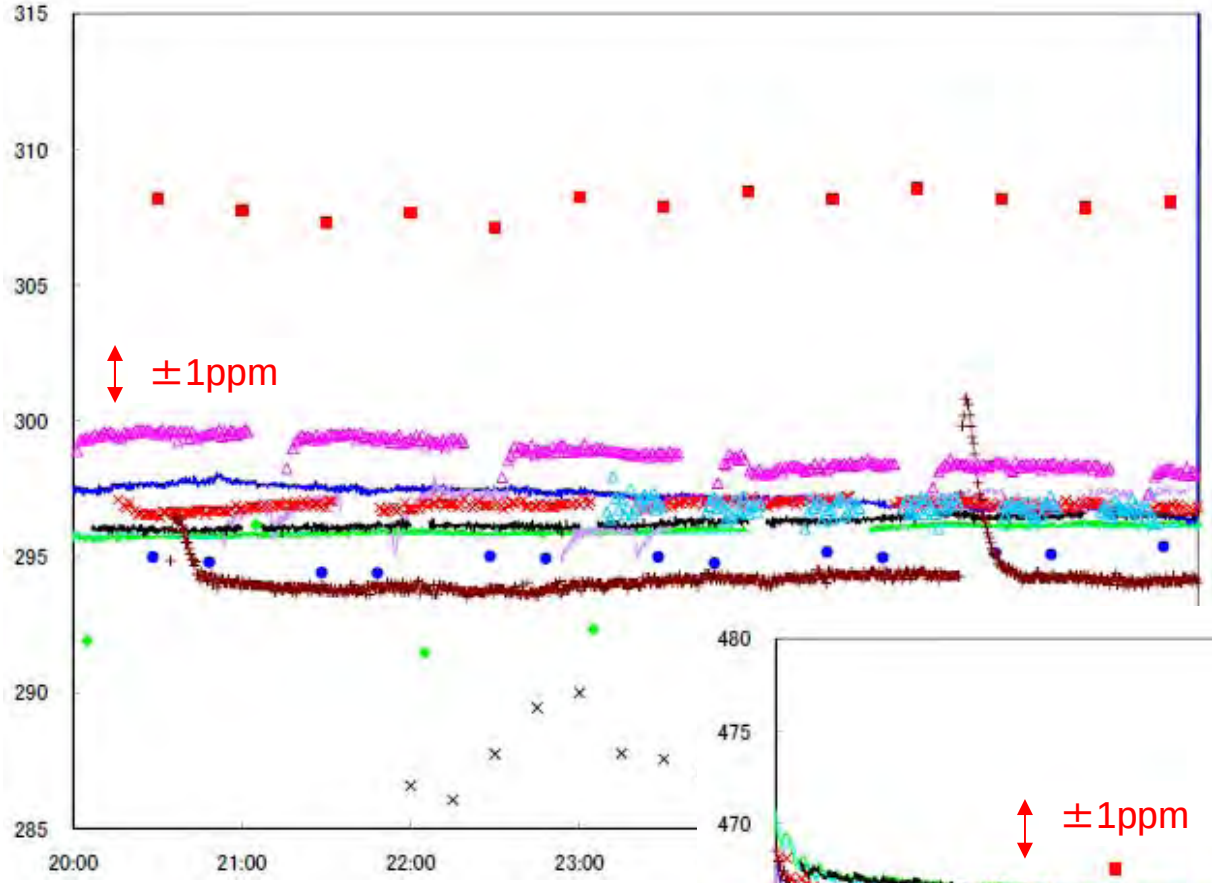


- Common standard gas supply (0, 270, 330, 390, 450 ppm CO_2 in air).
- Large seawater flow rate at 300 L/min.
- Critical pool and water line temperature comparison by the two SEABIRDs, which revealed warming up by heat from underwater pump (0.04-0.06C).
- Temperature check for each equilibrator by calibrated Pt sensors (0.02 C accuracy), which showed no T change from the water line. It corresponded to ensure 0.3 ppm (xCO_2 in dry eq. air) resolution for comparison.

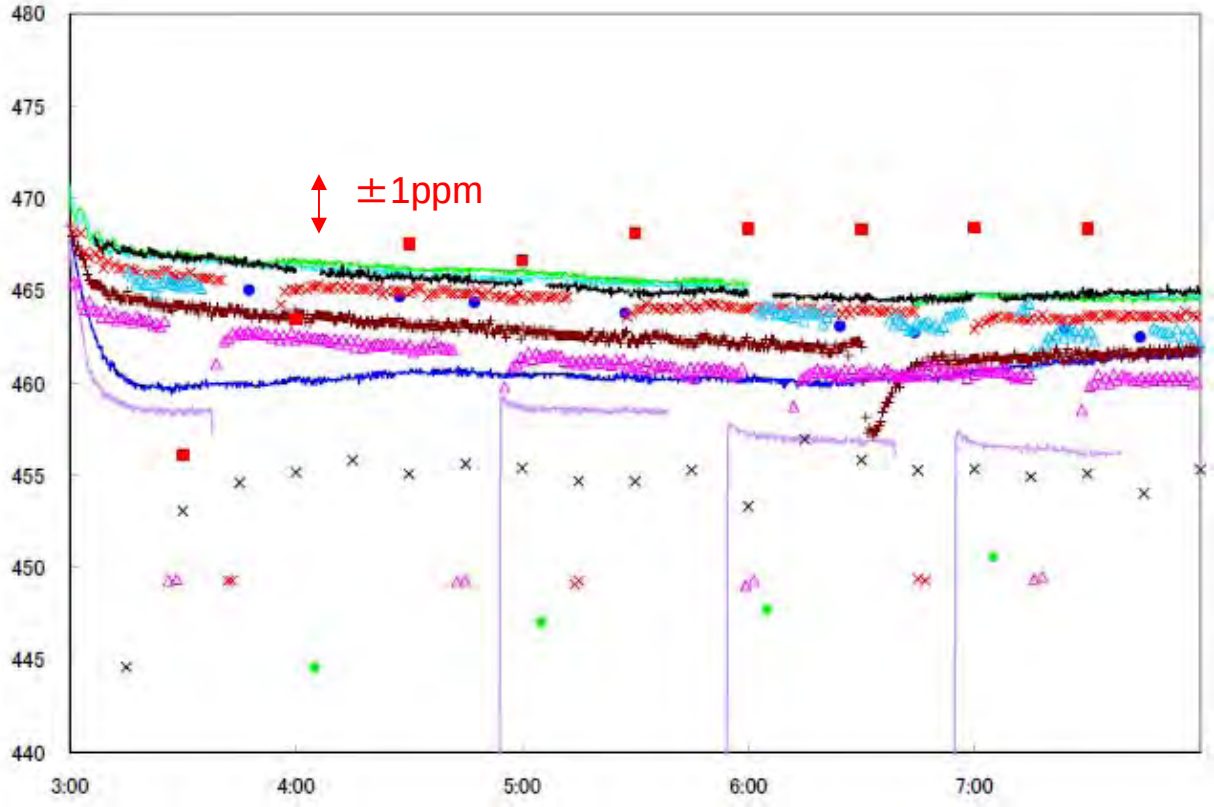
2003 International Inter-comparison of pCO_2 systems

NIES
KEEC
NRIFS
MBARI
NOAA
UEA
Kiel
NIWA
KNU
Montana
Paris

2009 IC data example (Day1)



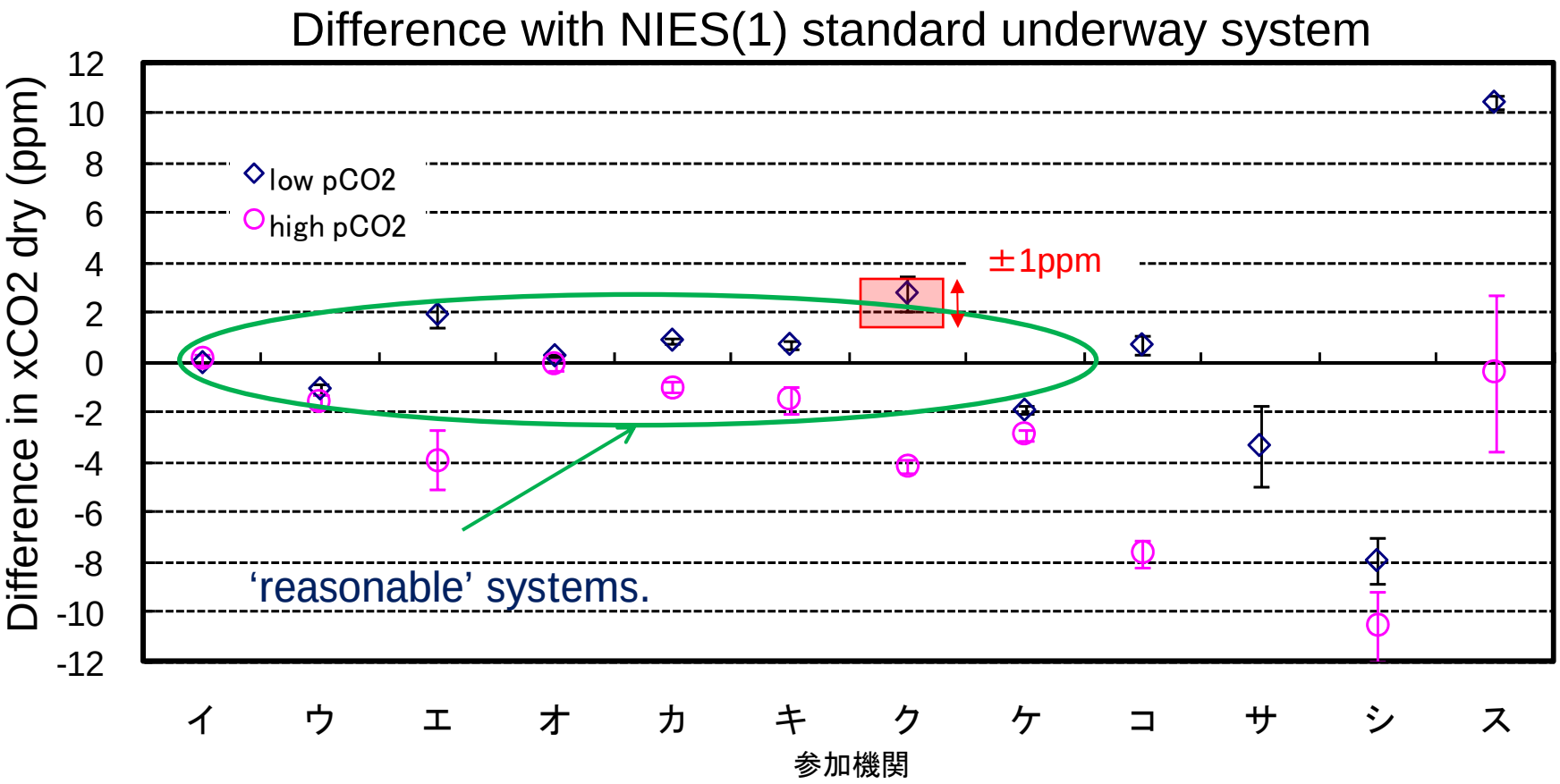
xCO_2 adjusted from low (296) to high (465) ppm

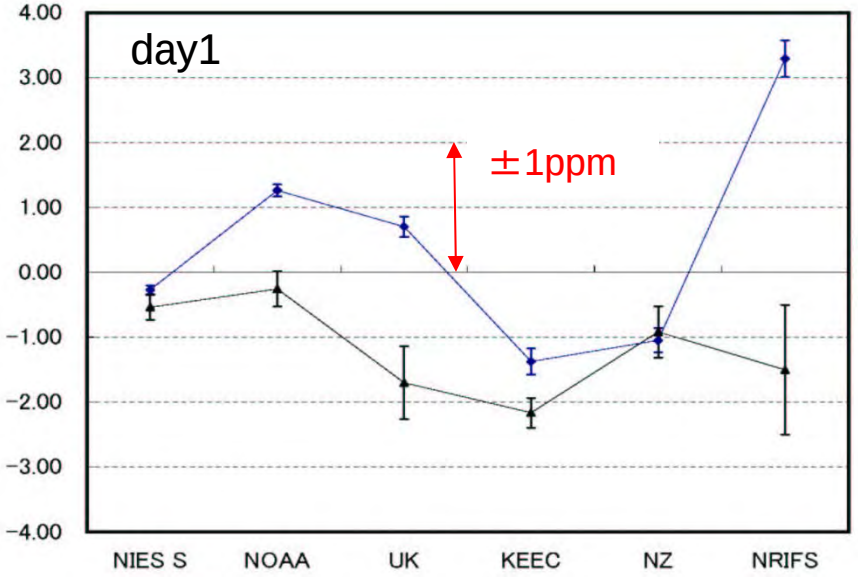


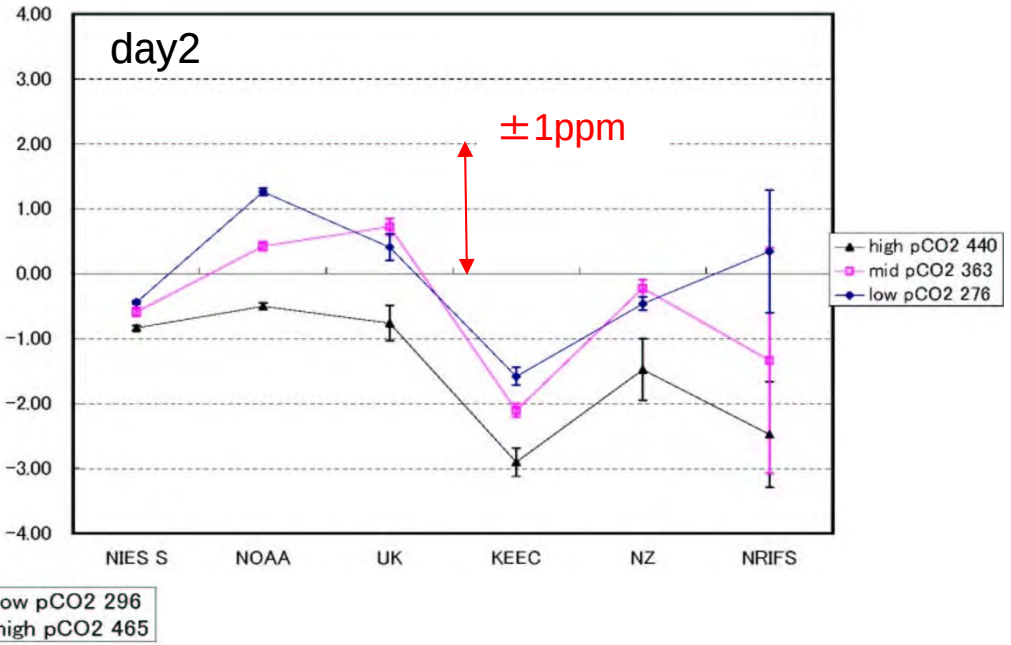
±2~3 μatm deviation was observed within 'reasonable' systems.

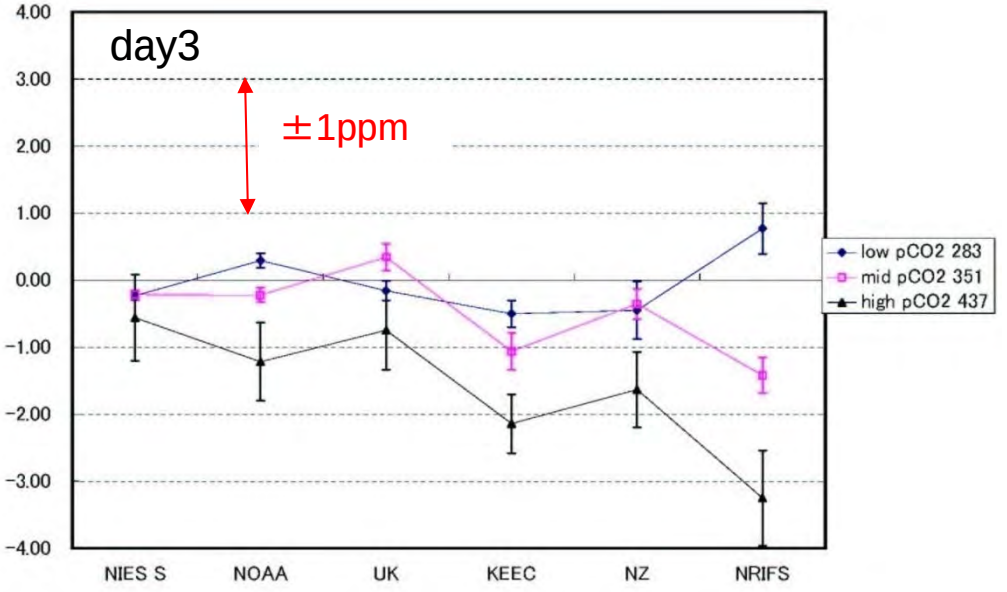
2003 inter-comparison results summary

Colorimetric buoy systems met several ppm of deviation from reference system but major underways showed within 1.5 ppm difference. Resupply gas contamination was thought a possible reason of difference. Organic decomposition was suspected for buoy systems without sterilization.





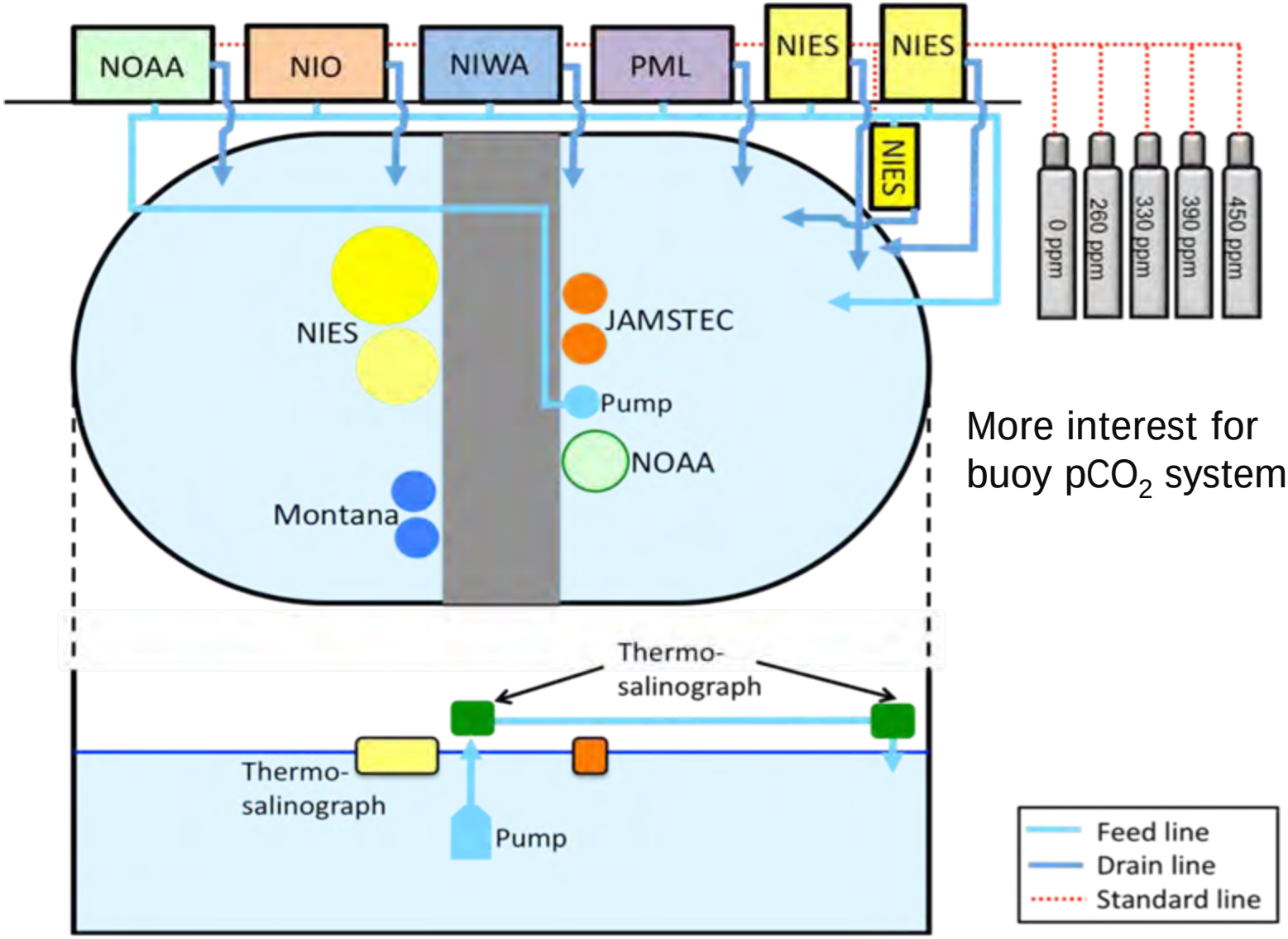




Many underway systems showed concentration dependence, which gives negative bias in high pCO_2 and positive bias in low pCO_2, suggesting resupply air contamination. NOAA system was modified after the IC, adding a pre-equilibrator to reduce the effect.

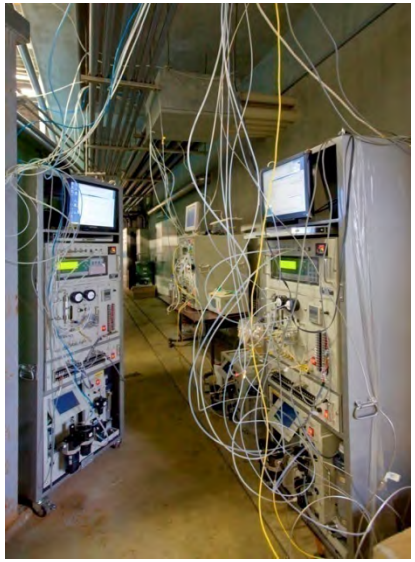
2009 international inter-comparison of pCO_2 systems

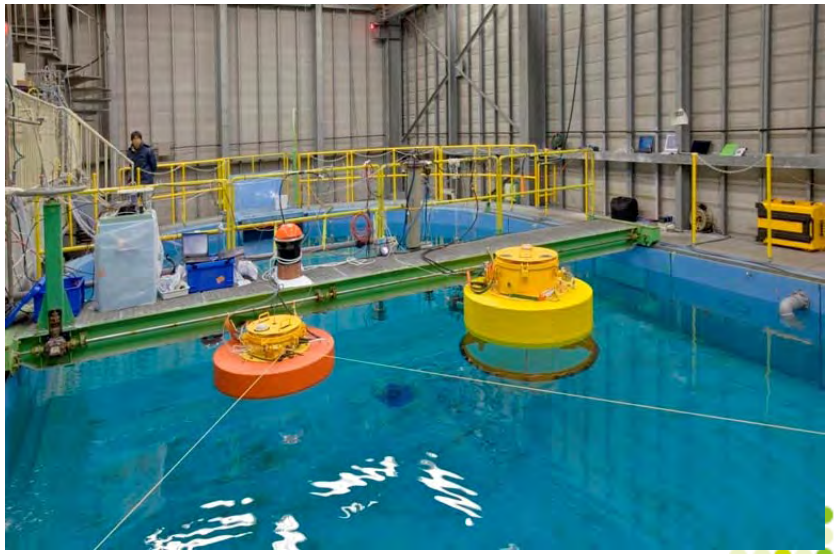
NOAA and NIO were identical instruments



More interest for buoy pCO_2 systems

2009 IC





Improved comparison results for underway systems

- At 2003 inter-comparison, a few underway systems showed ±1.5 μatm accuracy, although it was an apparent improvement from 1994 and 1996 inter-comparisons.
- At 2009 inter-comparison, well operated NDIR-underway systems showed ±0.5 μatm agreement, close to the resolution of the comparison.
- The cause of discrepancy smaller than ±0.5 μatm could not be identified, even under very stable operational condition in a indoor pool.
- From 2003/2009 inter-comparisons, we had an understanding of good on-board (at sea) practices for pCO_2.

Comparison results for buoy systems

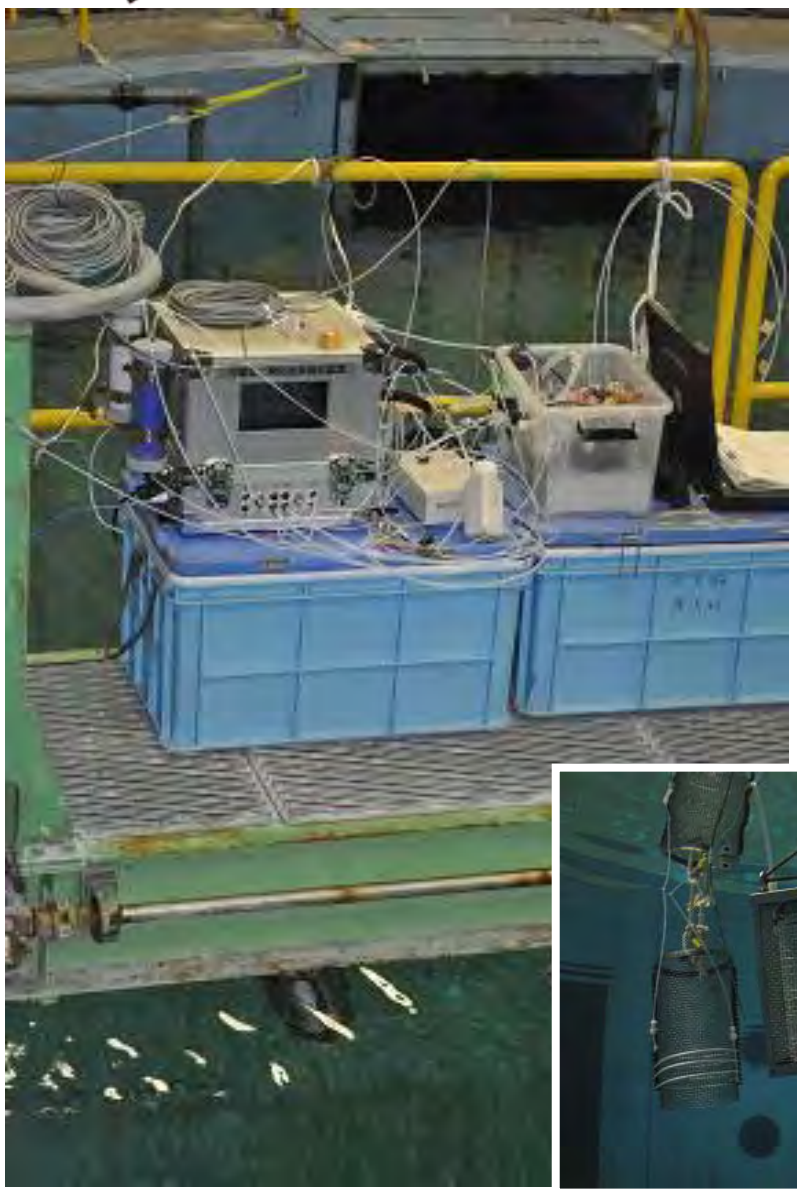
- Well designed NDIR buoy system can be operated with a similar accuracy as underway pCO_2 system like ± 0.5 μatm.
- At sea condition test is very difficult, but the pool test is a benchmark test for the performance of the system.
- Colorimetric buoy accuracy and reproducibility should be much improvement, and it may have at least a possible error of ± 3 μatm.

Good on board practice

- pCO_2 inter-comparison result feedback to improvement of system (e.g. NOAA, NIWA).
- Possible error causes were revealed, pump heating up, organic matter decomposition, equilibrator pressure and etc.

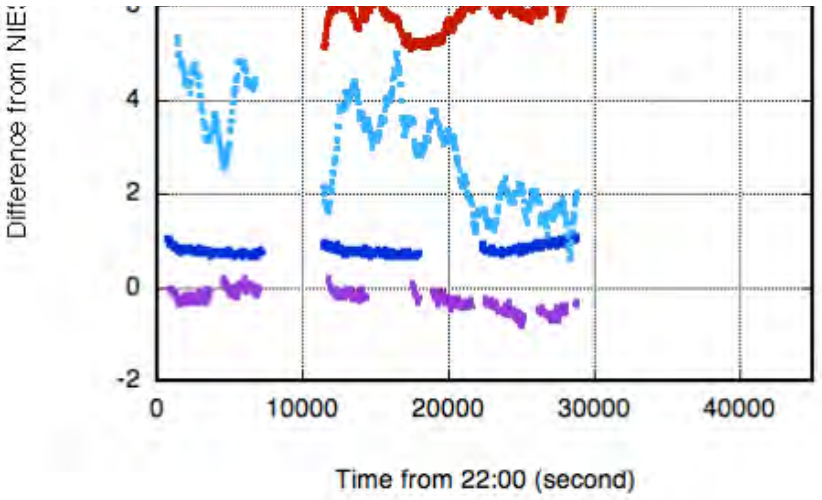
- Periodical equilibrator cleaning
- NIES checked for pipe line on board VOS about organic matter deposit, and then, practicing periodical cleaning.
- Ship bottom temperature sensor must be located prior to the in-line pump, which gives heating up.

New tip for OA manipulation QC

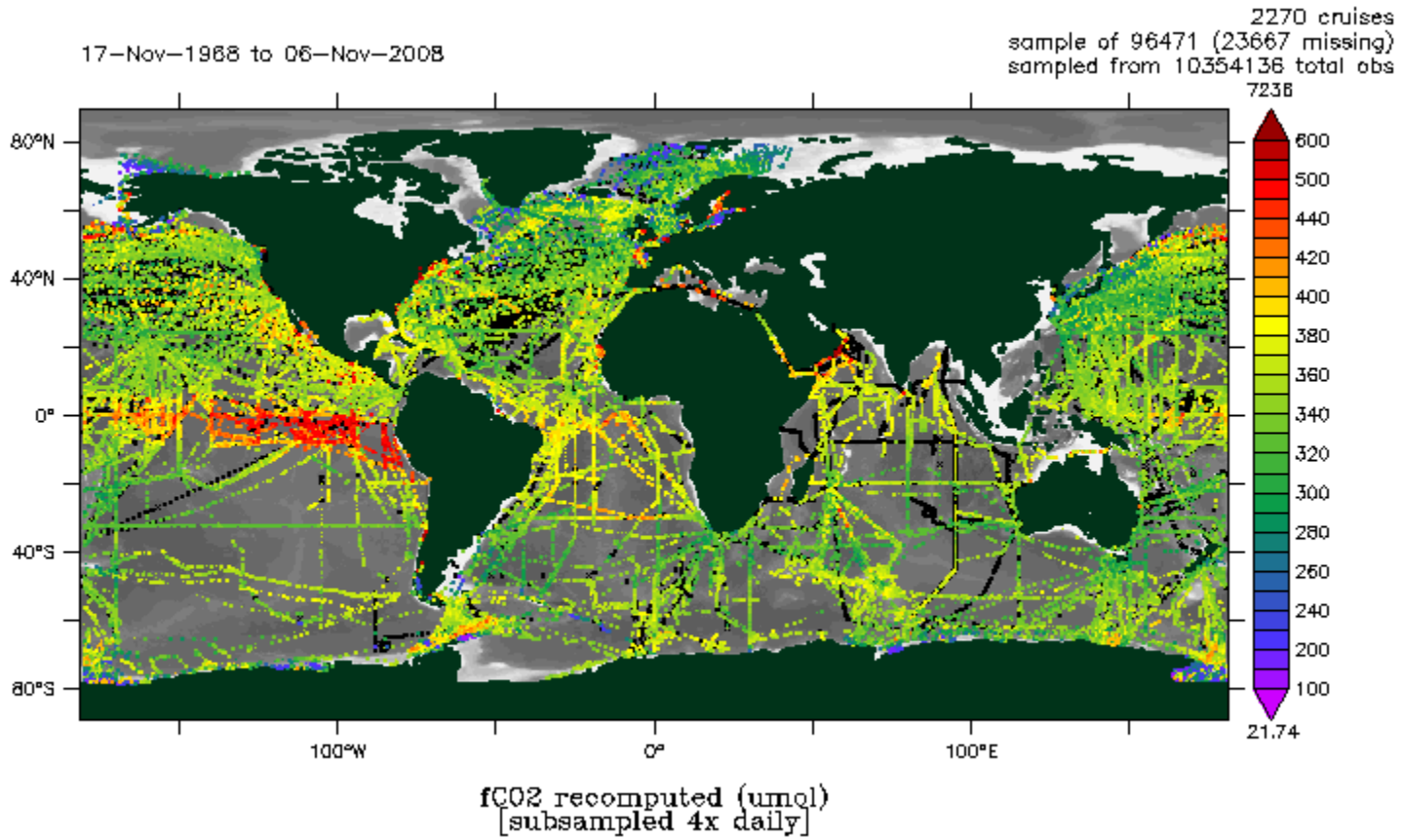


New portable pCO_2 systems were tested at NRIFE indoor pool. Manufactured system (left, 30cm cubic) is using LICOR840 NDIR and the barrack (right in a plastic case) is using NDIR CO_2 sensor chip for air conditioning. 10 & 2m length Goatex equilibrators were tested (below) and results were fine (within 1 or 4 ppm) enough.

System with (2m tube)+(NDIR chip) can construct throw in pCO_2 sensor at a budget price for CO_2 manipulation experiments and pCO_2 is straight forward parameter than others.



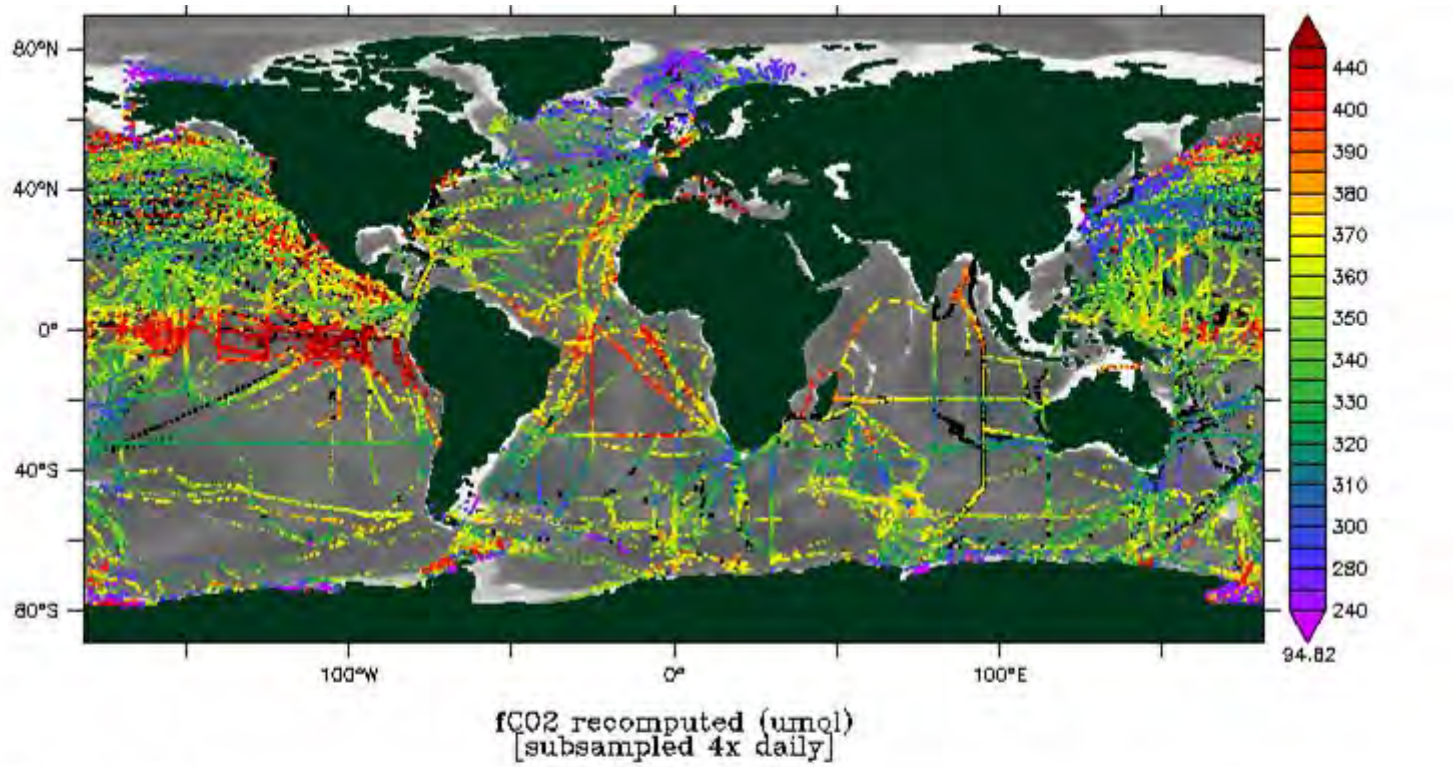
SOCAT by IOCCP, submitted cruises



SOCAT (Surface Ocean CO_2 Atlas): New international integration of surface pCO_2 data by IOCCP (International Ocean Carbon Coordination Project)

- 2nd level quality controlled (QC) global surface ocean fCO_2 data set
- Gridded global SOCAT product of monthly surface water fCO_2 means, with no temporal or spatial interpolation (i.e. bin averages).
- These data products will be made publicly available soon.

SOCAT QCed by 02/10/2010



Where flag = A,B,C,D

17 Nov 1968 — 06 Nov 2008

-89.0 ≤ Latitude ≤ 89.33 -181.3 ≤ Longitude ≤ -178.8

Longitude <

Longitude <

Subsampling: Auto, None, hourly, 4x daily

Region: North Pacific, Tropical Pacific, Southern Ocean, Indian, North Atlantic

QC Flag: No flag, A, B, C, D

cruise_ID: 0001SFC_PRT, 0002SFC_PRT, 0003SFC_PRT, 0004SFC_PRT, 0005SFC_PRT

Ship: A.V. Humboldt, Akademik Korolev, Albert Rickmers, Alligator Hope, Astrolabe