Defining the Carbonate System from Oceanographic Moorings: A Robotic Analyzer for the TCO_2 System (RATS)

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Support from: NSF: OCE-Ocean Technology & WHOI

OUTLINE:

- What is it and what does it do?
- How does it do it?
- How well does it perform?
  - Lab results
  - In Situ results
- And now what?

The Objective of RATS: Permit Automated Analysis of the CO_2 System from Oceanographic Moorings

- Measure TCO_2
- Measure pH
- Precision:
  - pH: ~.003
  - TCO_2: ~$\pm$5 umol/kg
- Endurance:
  - $\geq$ 6 months/ ~700 Analyses
  - (with no external batteries)
- In Situ Standardization

Analytical: Not much is new

- TCO_2- membrane exchange of CO_2
  e.g. medical industry, Hall and Aller(1992)
- pH- Spectrophotometric
  after Byrne and co-workers

What is new: Implementation

- Robotics
- In Situ operation
- Endurance

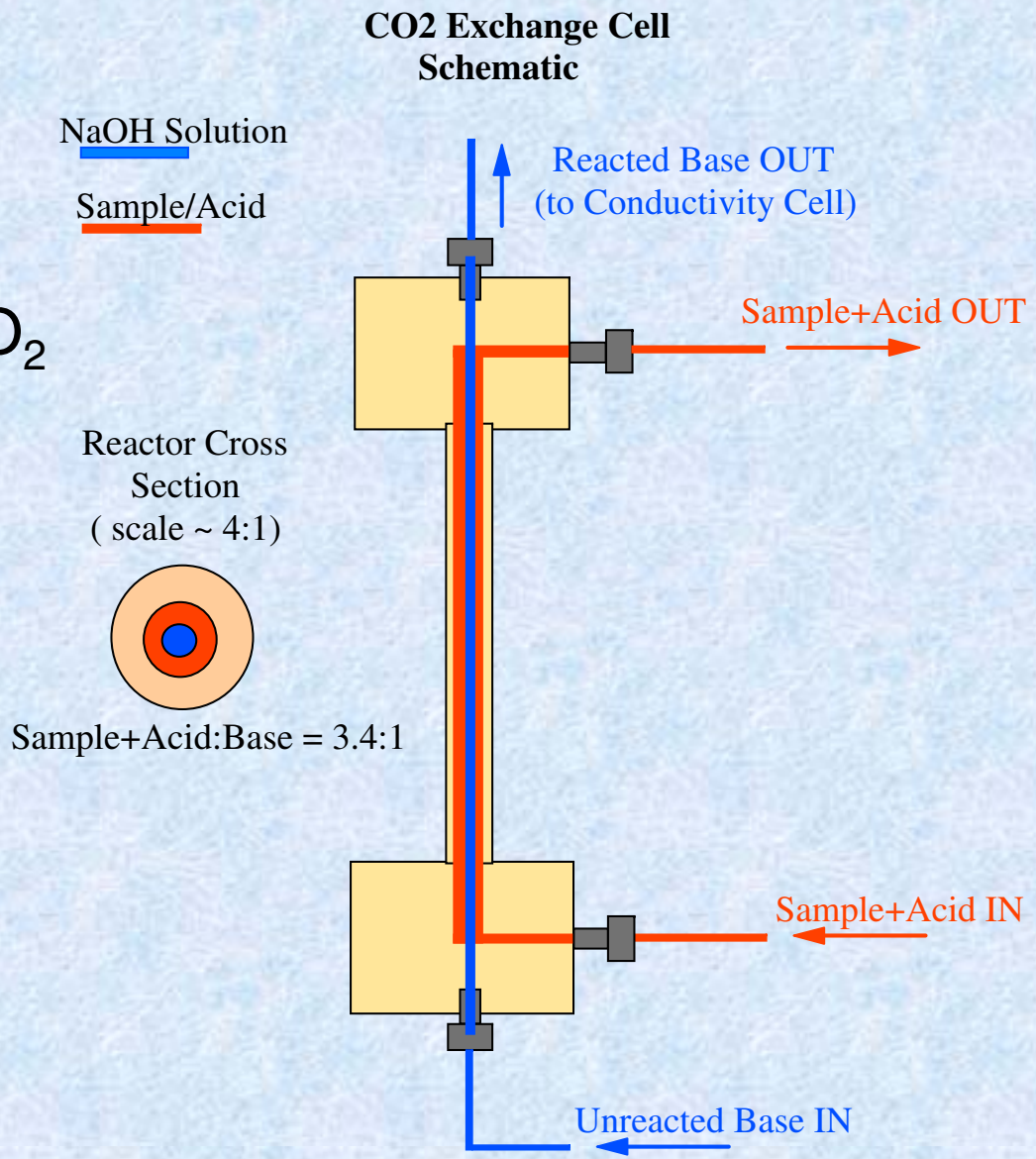
= Time series measurements over prolonged periods

Hurdles:

- Achieving required precision,
  typical of most methods development
- Establish long term stability of standards, reagents
- Maintain precision submerged for many months.

CO2 Analysis: Specifics

- Conductivity based:
  reaction of NaOH with CO_2
  L-OH= 198 vs
  L-CO_3= 69.3,
  L-HCO_3=44.4



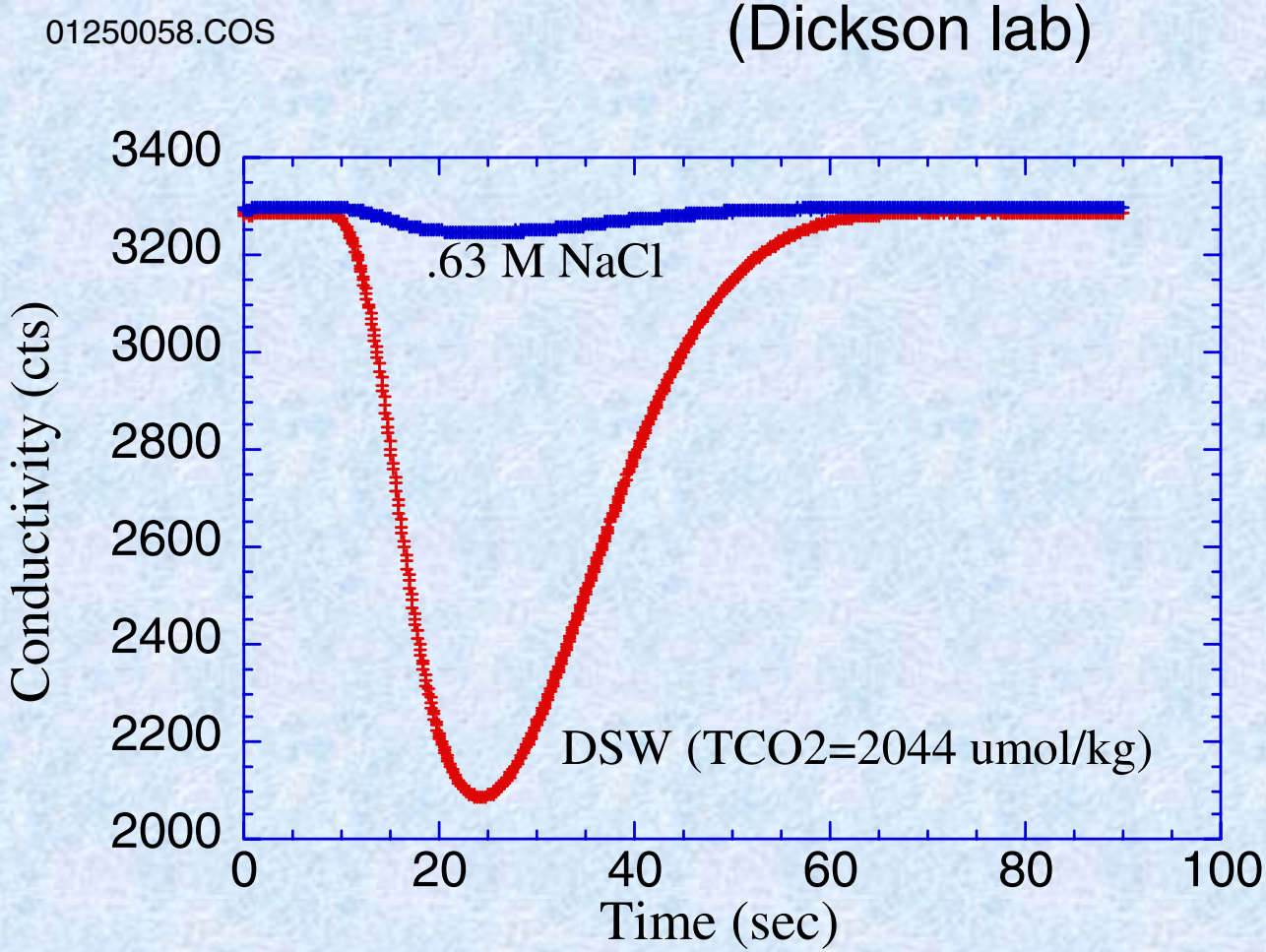
Signal Characteristics (Good News, Bad news)

- Negative Peak
- Precise Measurement

Signal Treatment

- Peak Area or Area/Bsl
- Temperature Correction

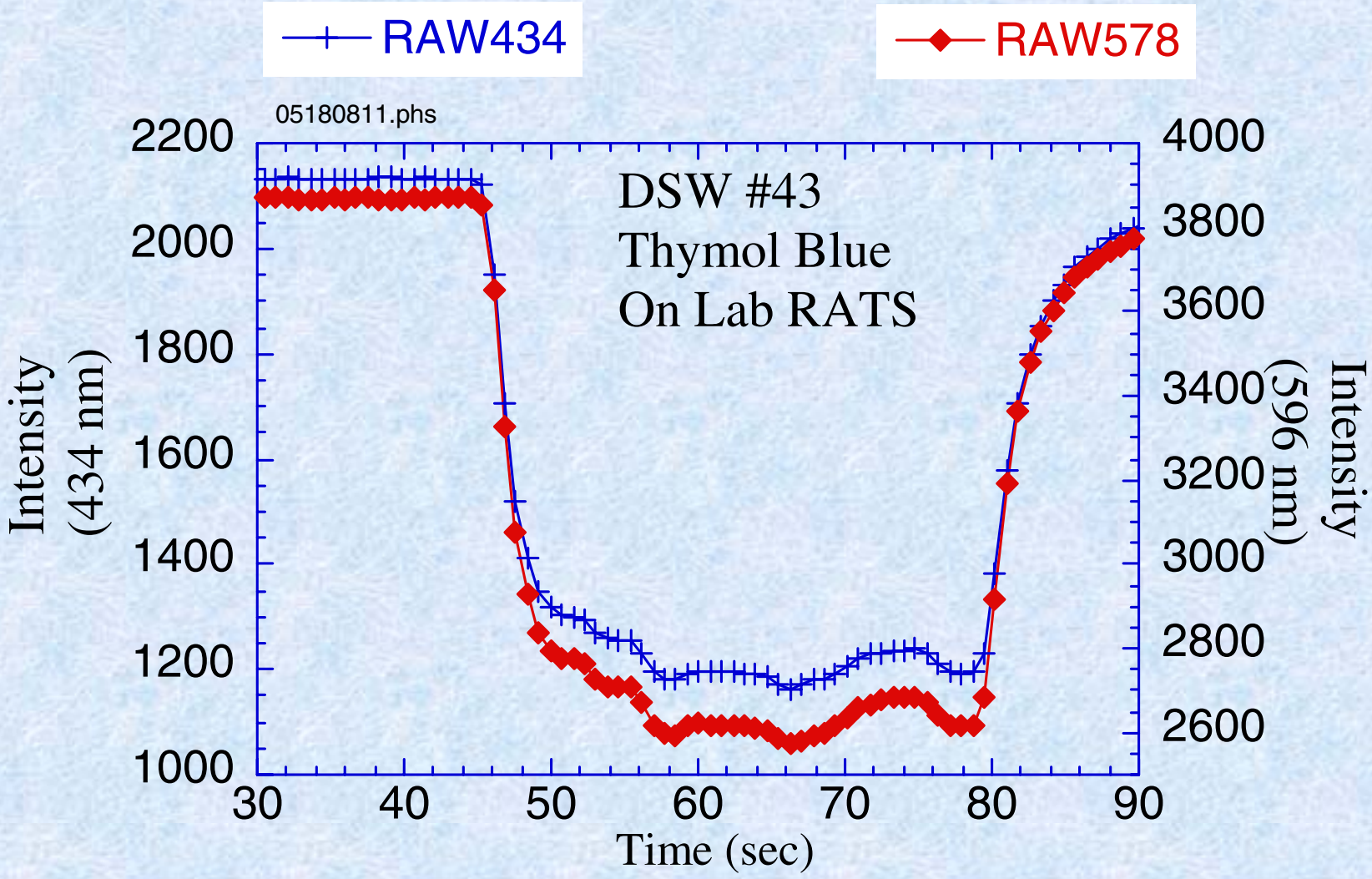
DSW= reference SW;
(Dickson lab)



pH Signals:

- Run time: 90 sec
- Intensity / mixing
- Absorbance ratios

•Optical Cell: 20 cm lcw



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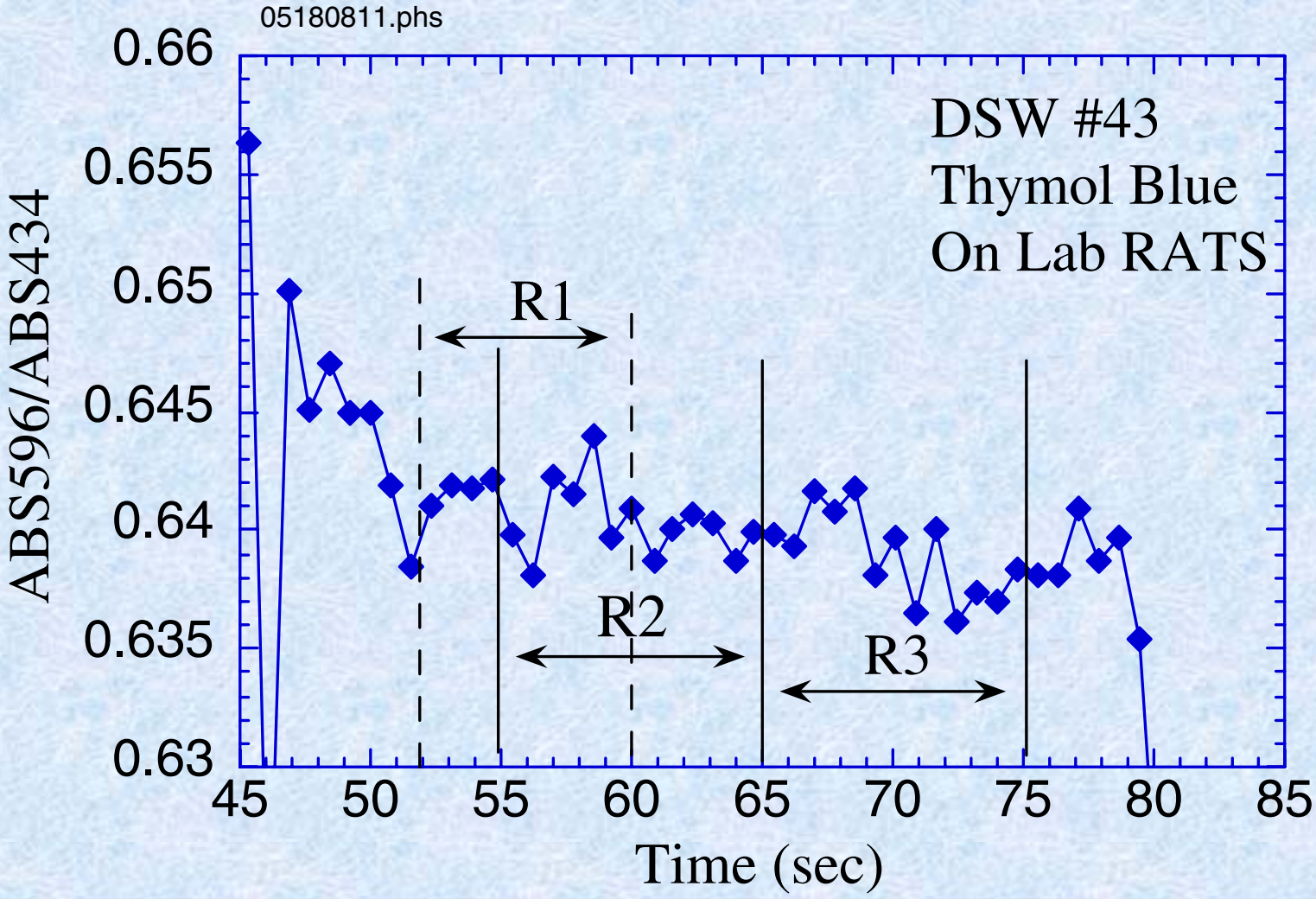


How well does RATS Perform?

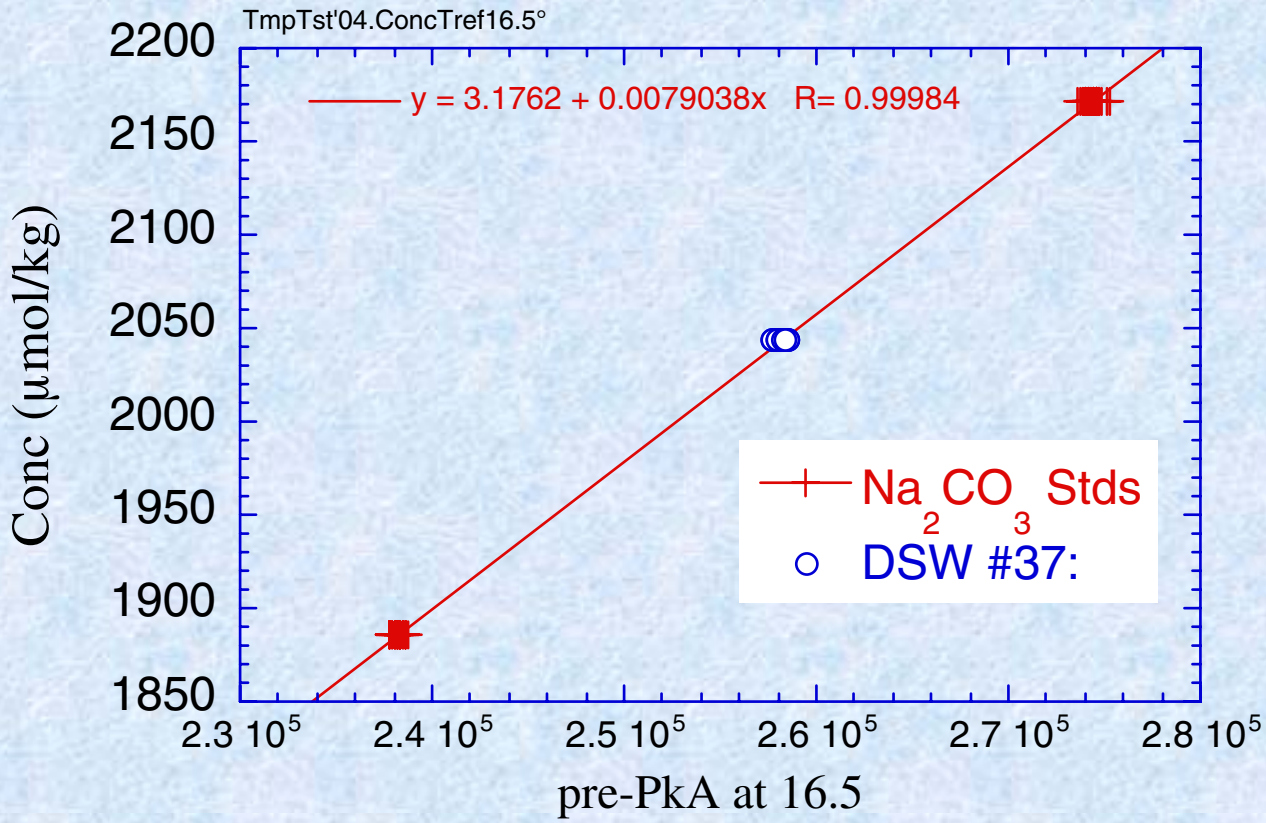
- Lab version
- Illustrate with-
  - 40 day experiment
  - Temperatures: 8° - 25°
- Assess TCO2
  - Calibration
  - Precision:
    - short term: 25 hrs
    - “long”: 40 days

TCO2 Calibration:

(40 days, 8-25°)

- Standards: Na_2CO_3
- "Sample": DSW 37

- Temperature correction: large based on Na_2CO_3 Stds
- DSW plotted: Given Conc = 2044 umol/kg

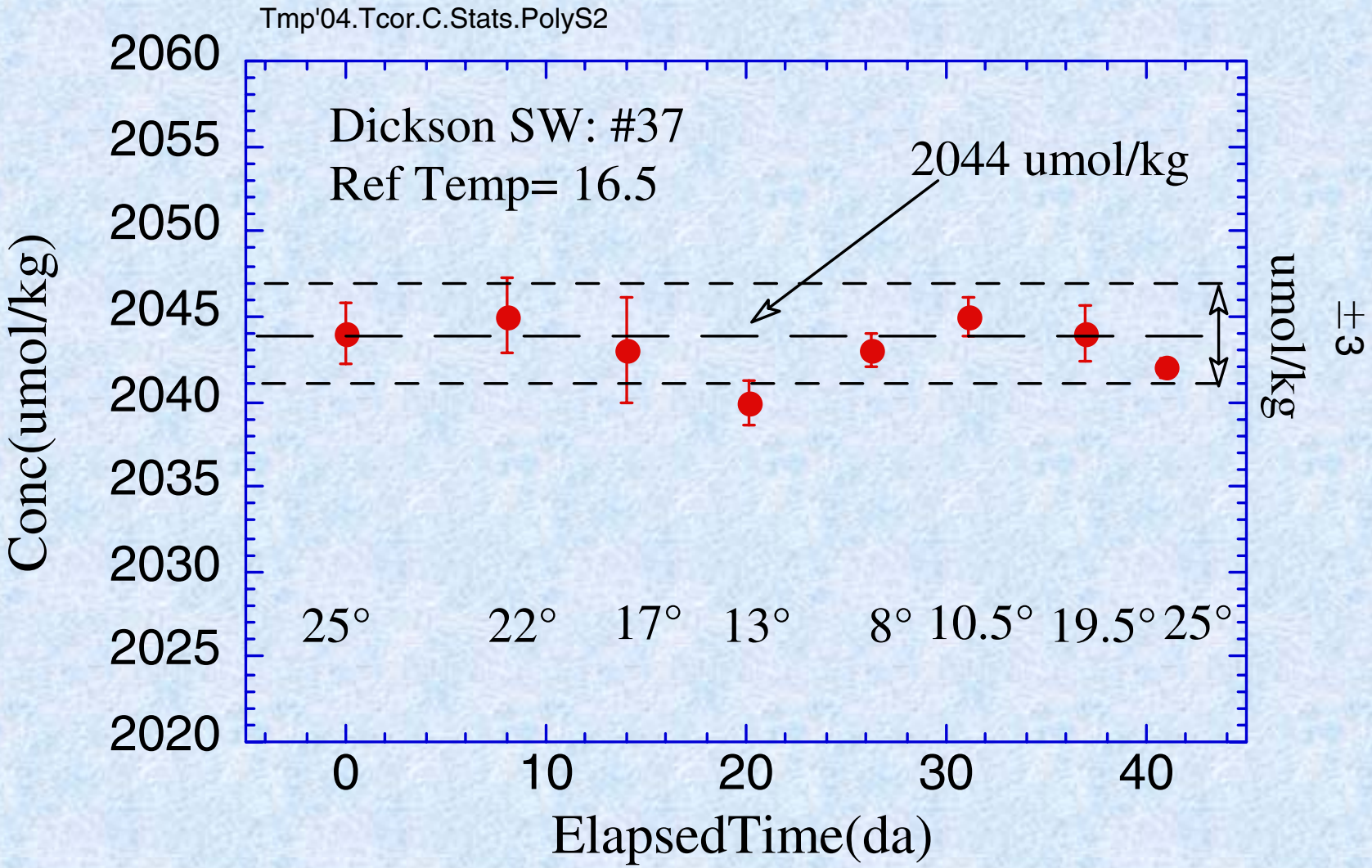


TCO_2 Calibration Statistics

- DSW Given Conc: 2044 umol/kg
- Licor conc: 2044 $\pm$ 4 umol/kg
- RATS conc: 2043 $\pm$ 2.3 umol/kg

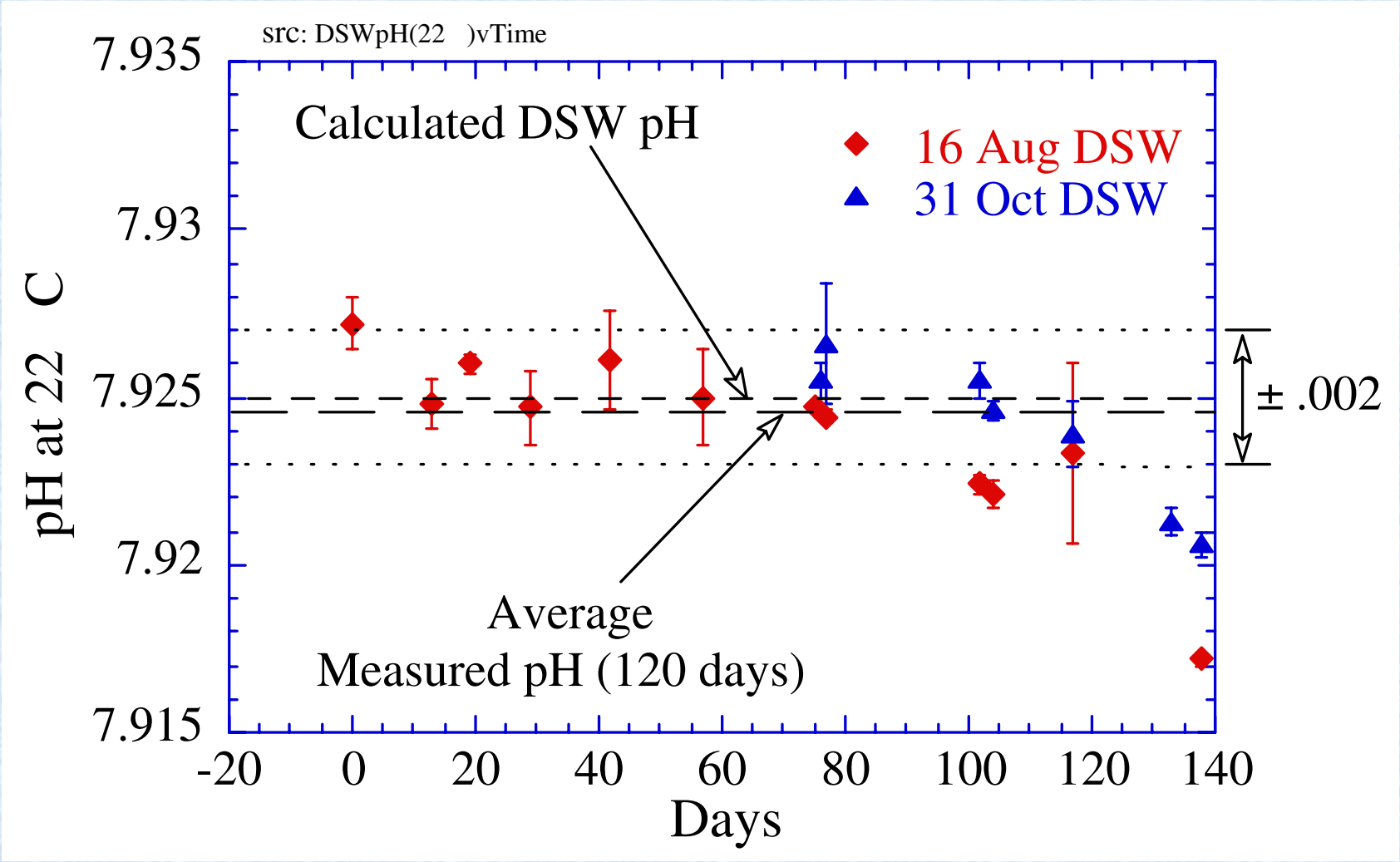
Precision over Time (umol/kg):

- Short term(~25 hours, n=5)
  8 temps: range= 2040-2045,avg±=2.0
- Long term (40 da, 8-25°)
  2043 ±2.3



pH Measurement Over Time

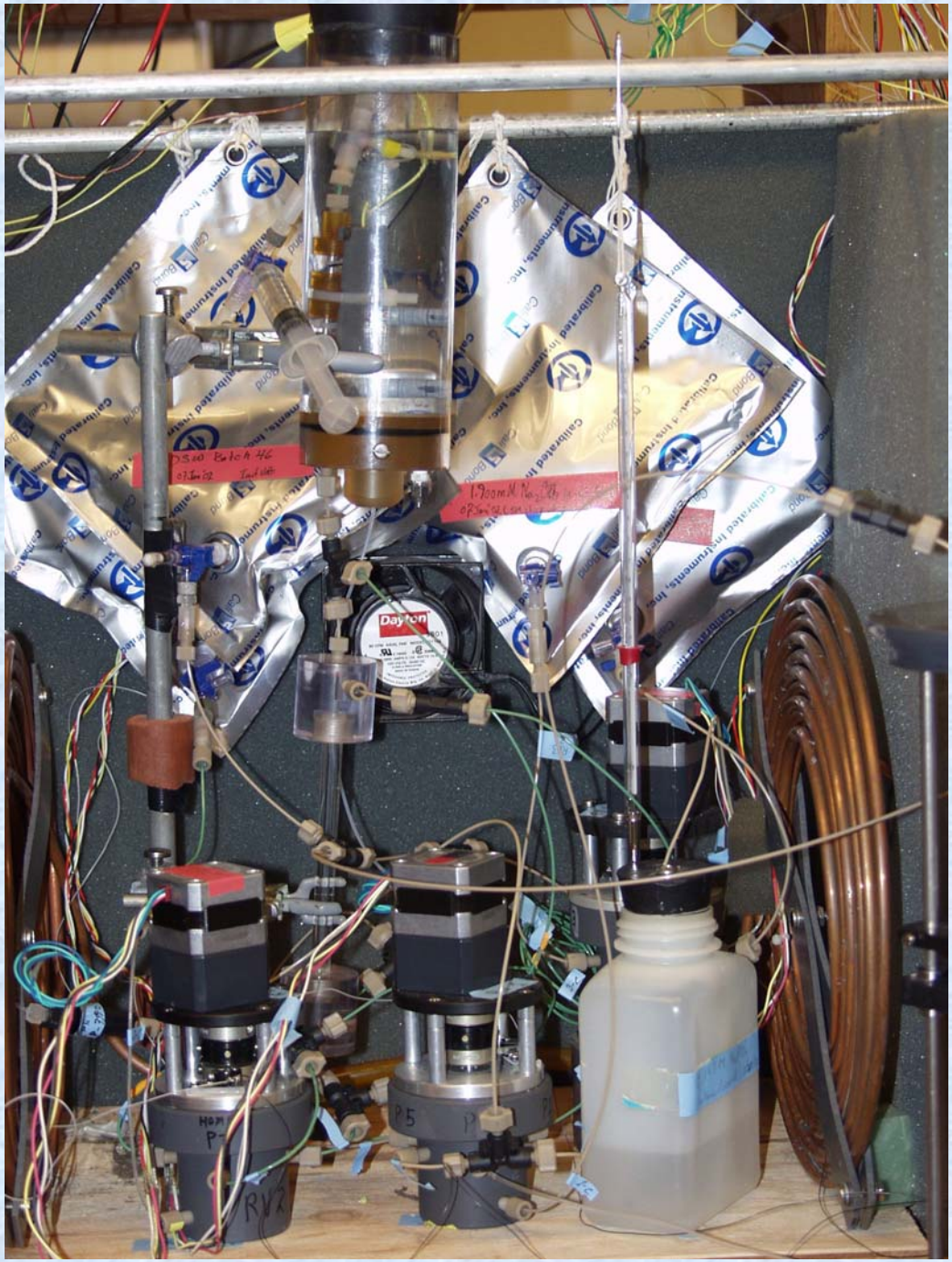
- 140 Days, T= 22° , m cresol purple
- Periodic measurement: 5/24 hrs
- Calculated: DSW alk & TCO_2



Summary
Lab RATS Measurements

- TCO2-
  - accuracy: ~within stdev
  - precision: ± 2-2.5 umol/kg
- pH-
  - accuracy: ~within stdev
  - precision: ± .002

- Reagent Stability
  - On- going assesment


Dayton
P5

RATS In Situ Deployments

- Location: WHOI Dock

Dec ‘03- 14 days

Jun ‘04- 21 days

Sep ‘04- 28 days

Nov ‘04- 41 days

104

Discuss Nov-Dec results

Depth= 10m Temp= 10° to 3°

Programmed- weekly

Communication cable

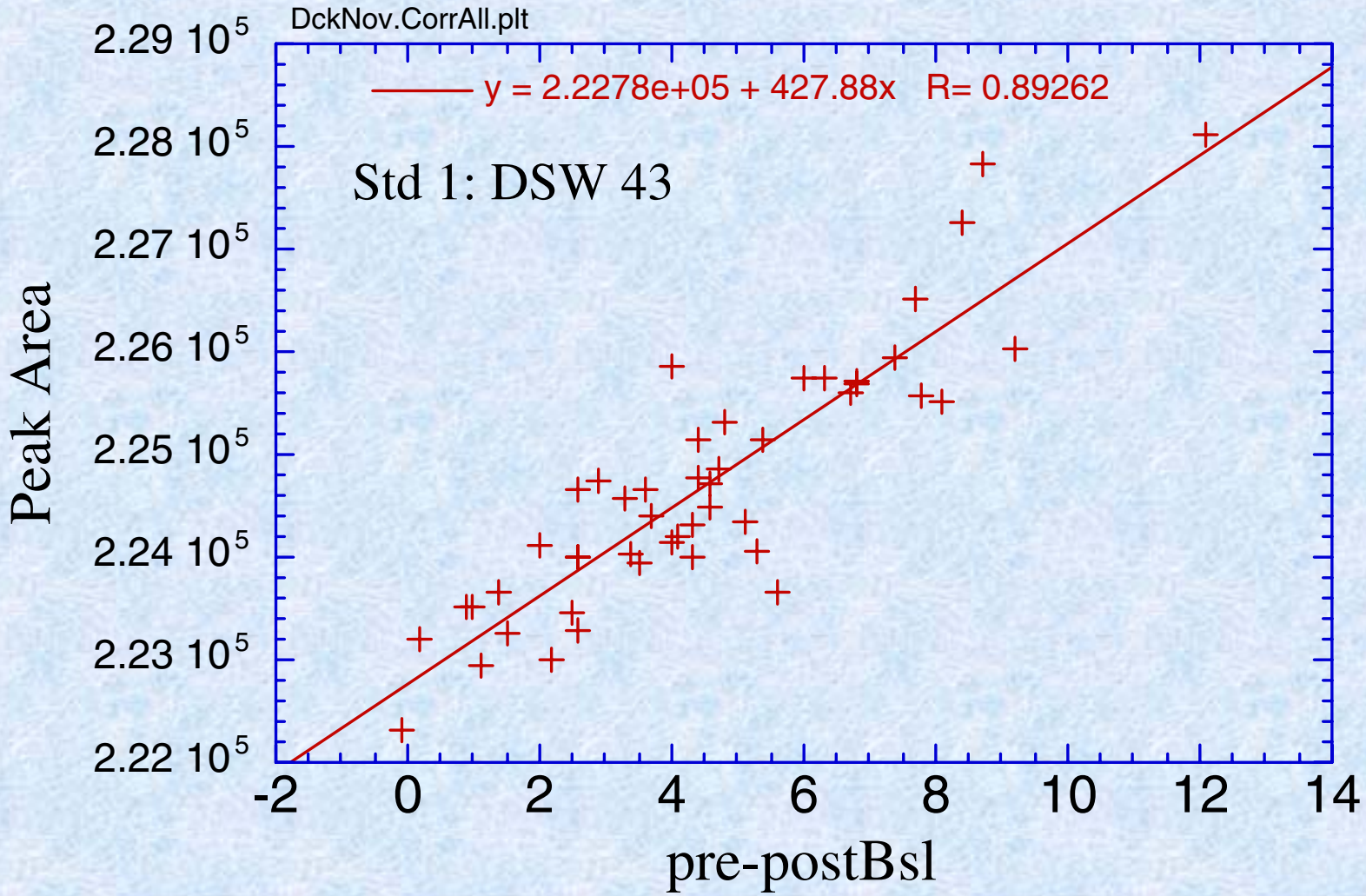
Analyses: ~200 dock water, ~100 Stds

Performance: DSW based

TCO_2 Analysis:

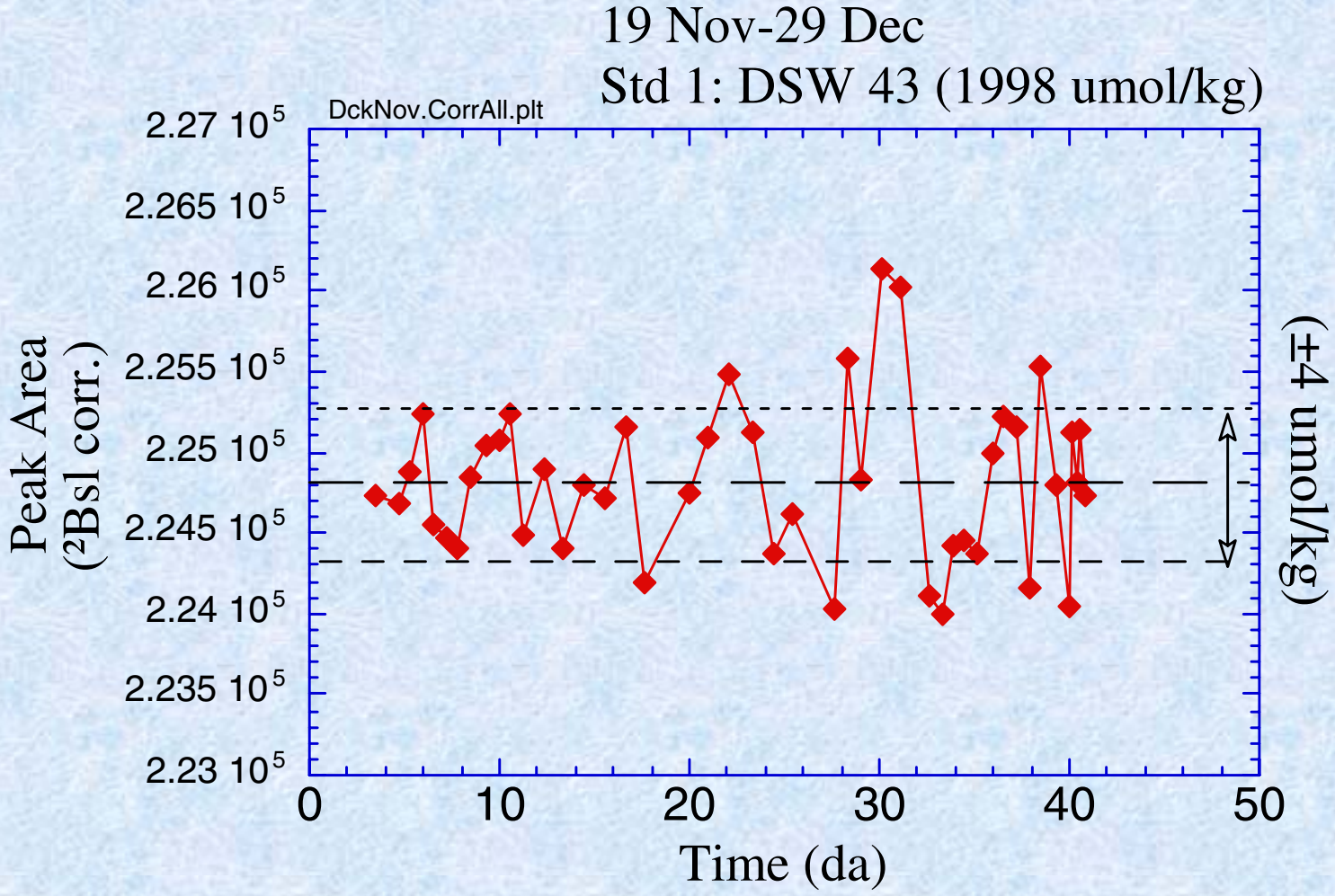
2 “new” features

- Baseline offset: variable, significant
- Baseline noise: electrical; cable?



In Situ TCO2 Record

- Baseline offset corrected
- Precision: ± .25%; ± 5 umol/kg
  electrical noise accts for ≥1/2

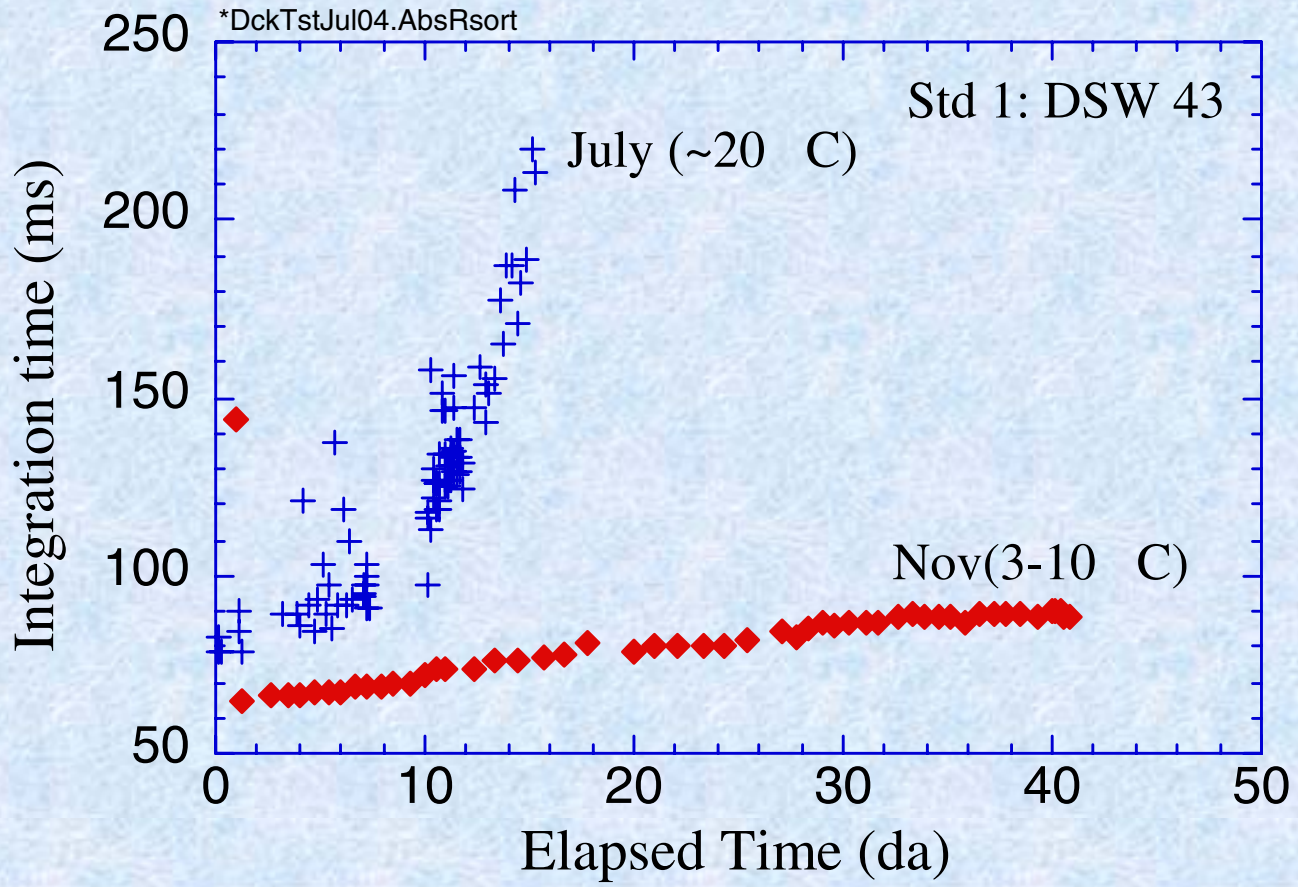


In Situ pH Analysis

Also 2 new challenges-

- Challenge 1: refraction
- Solvable

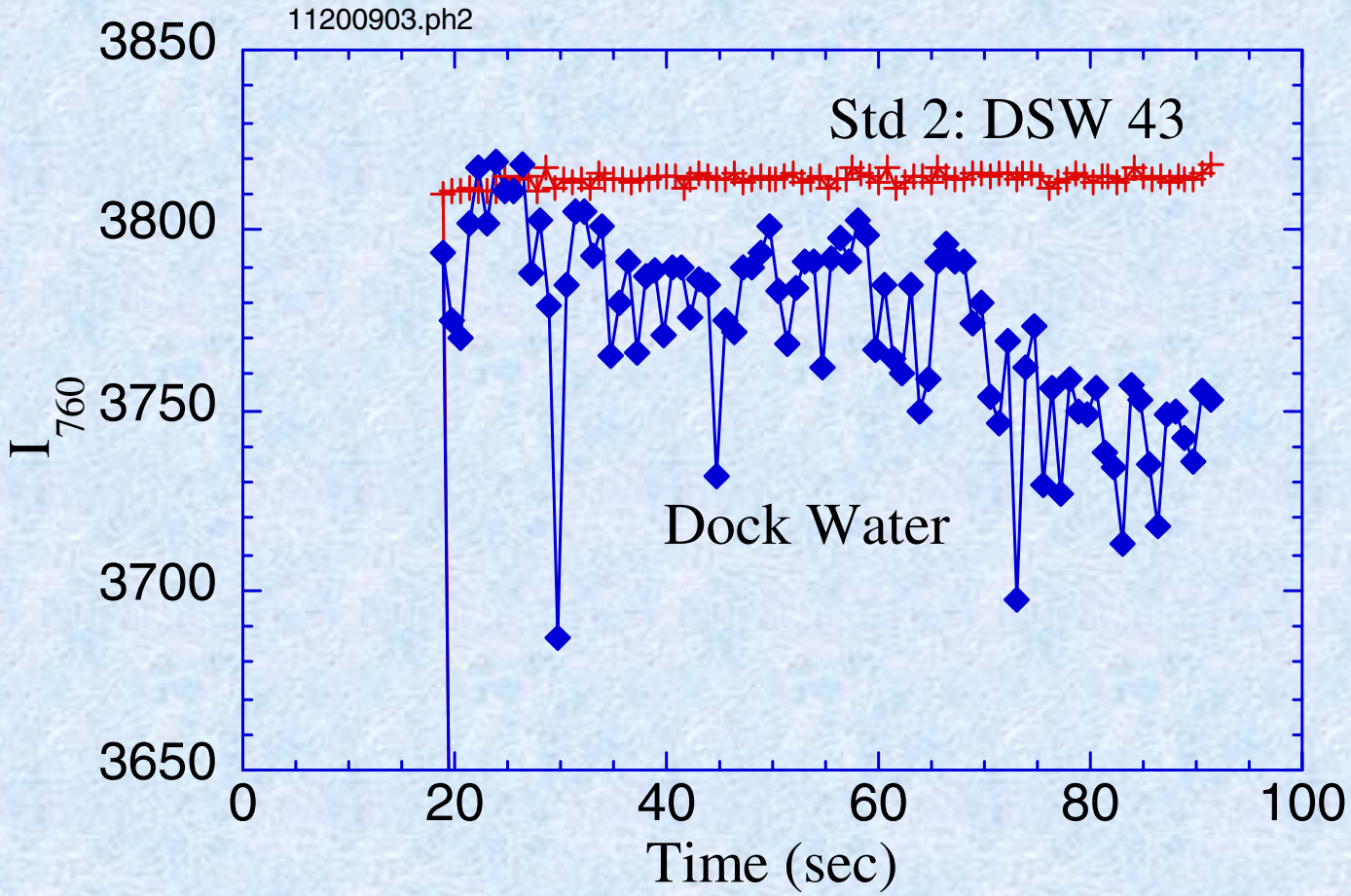
- non abs line
- reversible
- P^2 related?



In Situ pH

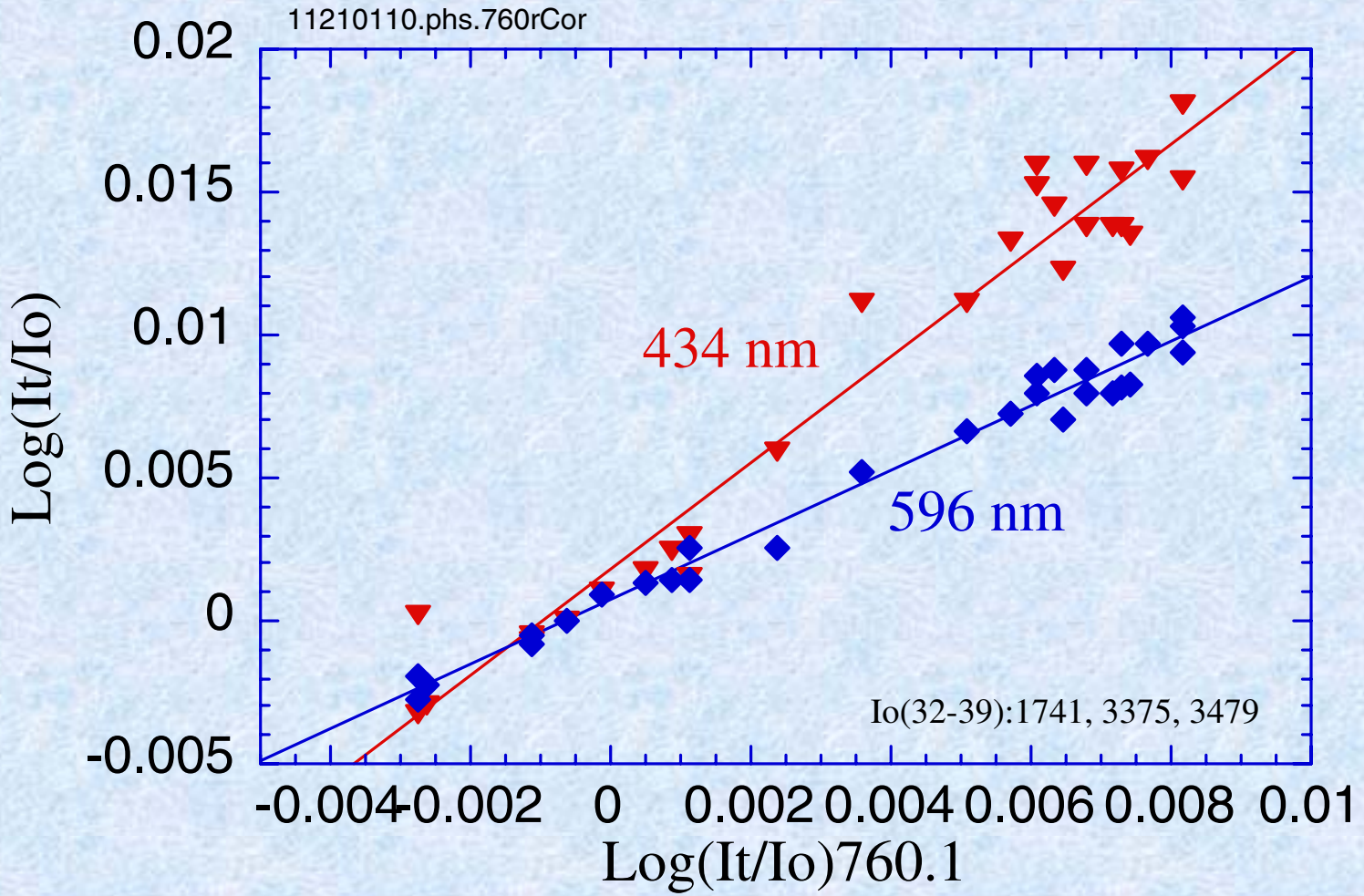
Challenge 2: Particle “shadowing”

- Dock water only
- All lines
- Abs lines similar to but ≠ non-abs



In Situ pH:Correcting for Particles?

- Specific abs: ΔAbs_{760} insufficient
- Correct for specific Abs?
- The right Experiment not done



Summary
In Situ RATS

- Lab procedures and components
  readily adaptable to submerged operation
- TCO_2
  accuracy: yet to be determined (~ std dev?)
  precision: ±5 umol/kg, improvable to lab?
- pH
  accuracy: yet to be determined
  precision: Stds= ±.002
  Dock water=yet to be determined
  (abnormal environment??)
- Challenges to be met
  TCO2- electrical noise,baseline offset
  pH- particle effect, correction assessment
  Reagent stability- Track long term
  Na_2CO_3 a known issue

Recap
Lab RATS

- TCO2
  - accuracy: ~ standard deviation
  - precision: ±2-2.5 umol/kg
- pH
  - accuracy: ~ standard deviation
  - precision: ~± .002
- Reagent Stability
  - Dickson SW, NaOH-acceptable
  - Dye- some work
  - TCO2 Stds- unacceptable