The fundamentals: OA theory and ocean carbon chemistry measurements

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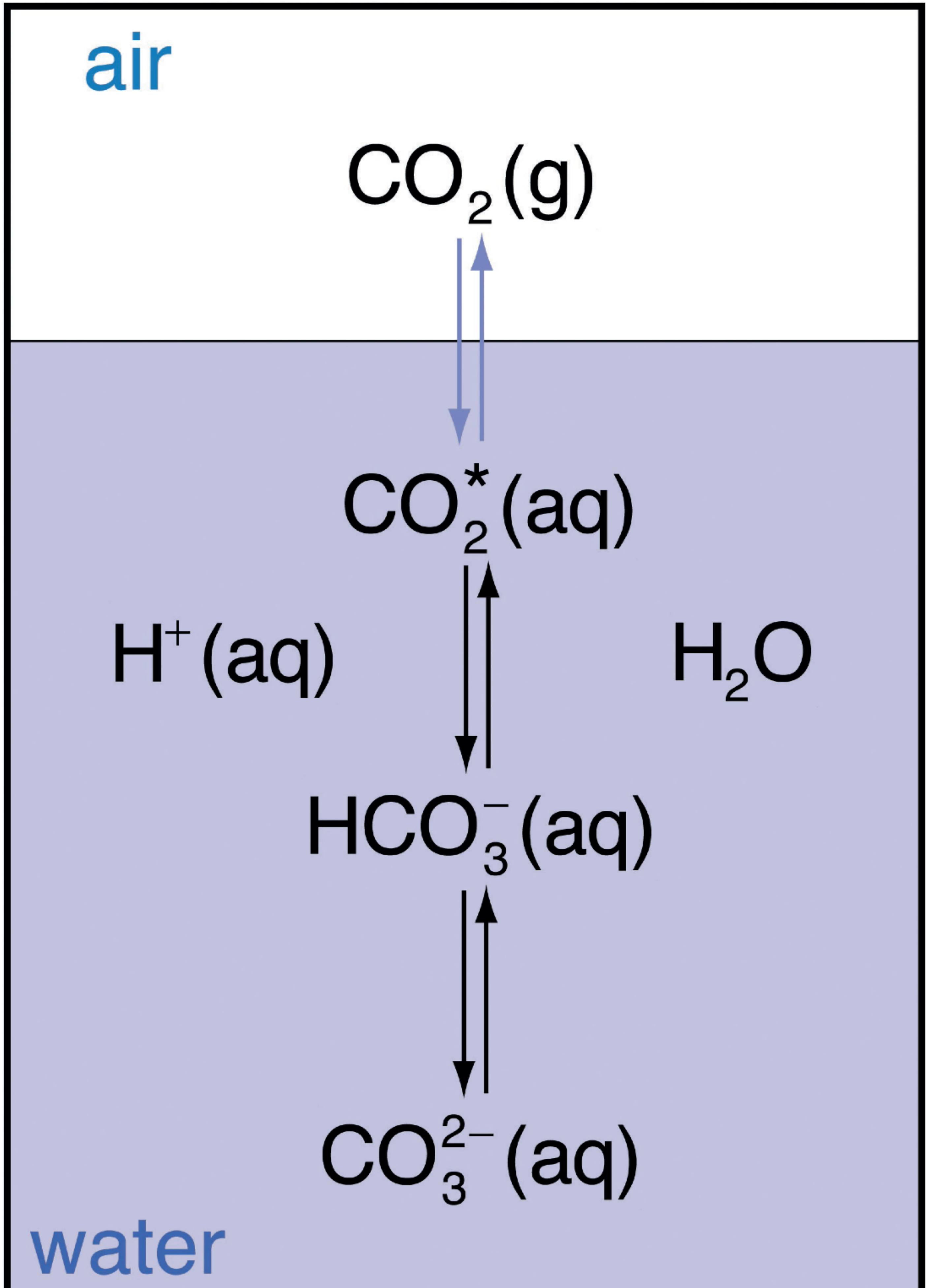


GOA-ON (2014)

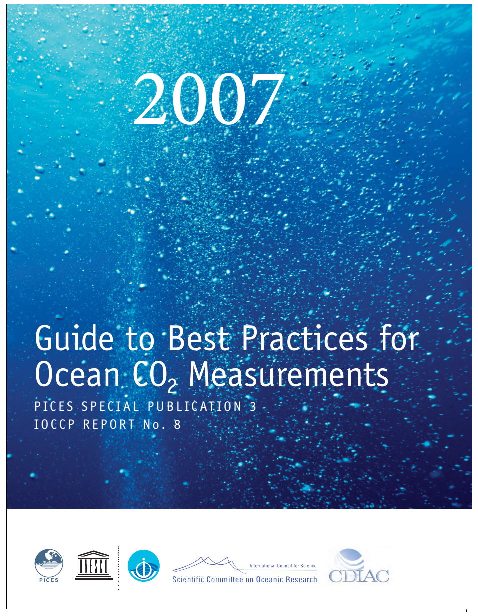
At each GOA-ON measuring site, a complete description of the seawater carbonate system will be needed.

C-CAN (2015)

Measurements should facilitate determination of aragonite saturation state (Ω_{arag}) and a complete description of the carbonate system, including pH and pCO_2.

This is also extremely desirable for laboratory OA experiments

TIMELINE FOR CO_2 MEASUREMENT METHODOLGY



2011

Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements

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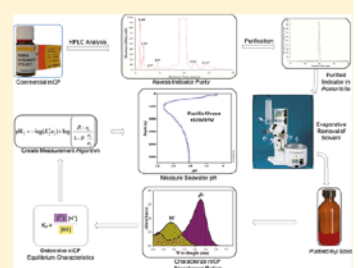
Supporting Information

ABSTRACT: Spectrophotometric procedures allow rapid and precise measurements of the pH of natural waters. However, impurities in the acid−base indicators used in these analyses can significantly affect measurement accuracy. This work describes HPLC procedures for purifying one such indicator, meta-cresol purple (mCP), and reports mCP physical−chemical characteristics (thermodynamic equilibrium constants and visible-light absorbances) over a range of temperature (T) and salinity (S). Using pure mCP, seawater pH on the total hydrogen ion concentration scale (pH_T) can be expressed in terms of measured mCP absorbance ratios ($R = {}_{\lambda_2}A/{}_{\lambda_1}A$) as follows:

$$pH_T = -\log\left(K_2^T e_2\right) + \log\left(\frac{R - e_1}{1 - R\frac{e_3}{e_2}}\right)$$

where $-\log(K_2^T e_2) = a + (b/T) + c \ln T - dT$; $a = -246.64209 + 0.315971S + 2.8855 \times 10^{-4}S^2$; $b = 7229.23864 - 7.098137S - 0.057034S^2$; $c = 44.493382 - 0.052711S$; $d = 0.0781344$; and mCP molar absorbance ratios (e_i) are expressed as $e_1 = -0.007762 + 4.5174 \times 10^{-5}T$ and $e_3/e_2 = -0.020813 + 2.60262 \times 10^{-4}T + 1.0436 \times 10^{-4}(S - 35)$. The mCP absorbances, ${}_{\lambda_1}A$ and ${}_{\lambda_2}A$, used to calculate R are measured at wavelengths (λ) of 434 and 578 nm. This characterization is appropriate for $278.15 \le T \le 308.15$ and $20 \le S \le 40$.



2013

Contents lists available at SciVerse ScienceDirect
Marine Chemistry
journal homepage: www.elsevier.com/locate/marchem

Purification of meta-cresol purple and cresol red by flash chromatography: Procedures for ensuring accurate spectrophotometric seawater pH measurements

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Environmental Science & Technology
Article
pubs.acs.org/est

Spectrophotometric Measurement of Calcium Carbonate Saturation States in Seawater

Regina A. Easley,[†] Mark C. Patsavas,[†] Robert H. Byrne,[†,*] Xuewu Liu,[†] Richard A. Feely,[+] and Jeremy T. Mathis[§]

2015

Contents lists available at ScienceDirect
Marine Chemistry
journal homepage: www.elsevier.com/locate/marchem

Procedures for direct spectrophotometric determination of carbonate ion concentrations: Measurements in US Gulf of Mexico and East Coast waters

CrossMark

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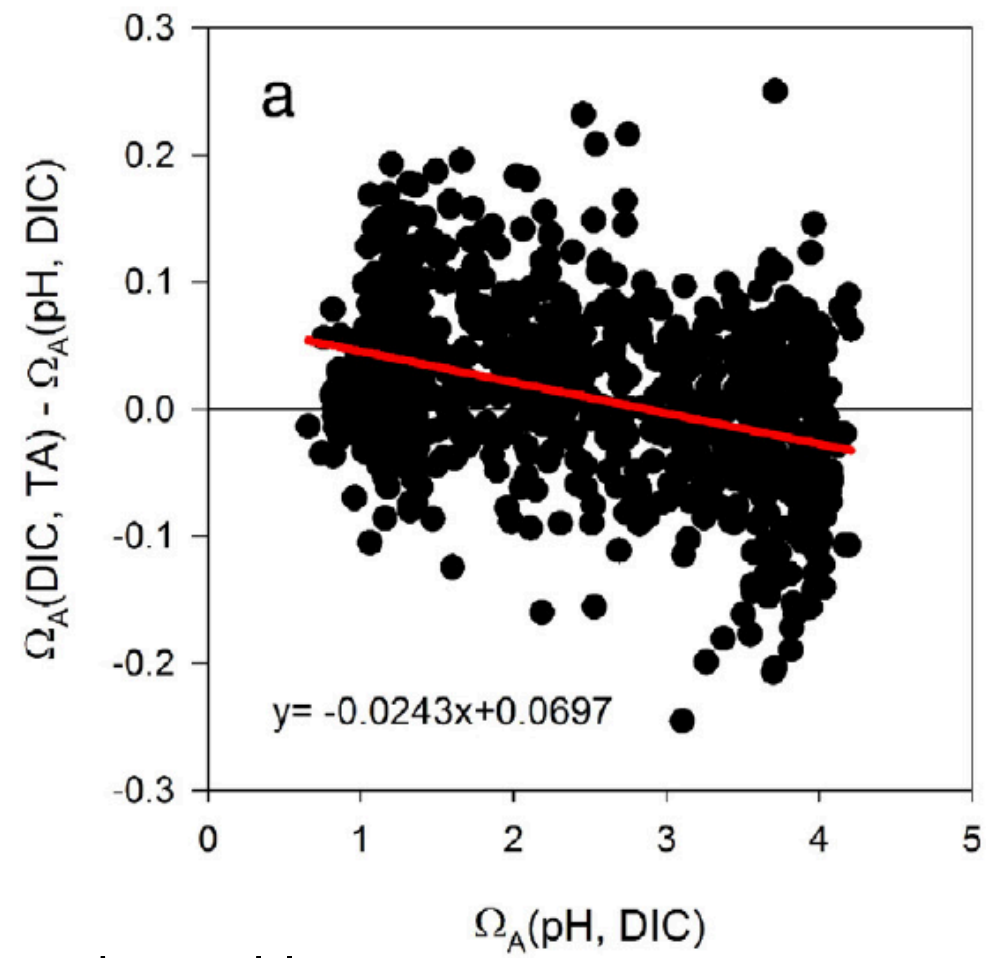
INTERNAL CONSISTENCY STILL IMPERFECT

Patsavas et al. (2015) *Mar.Chem.* ***176***, *9*



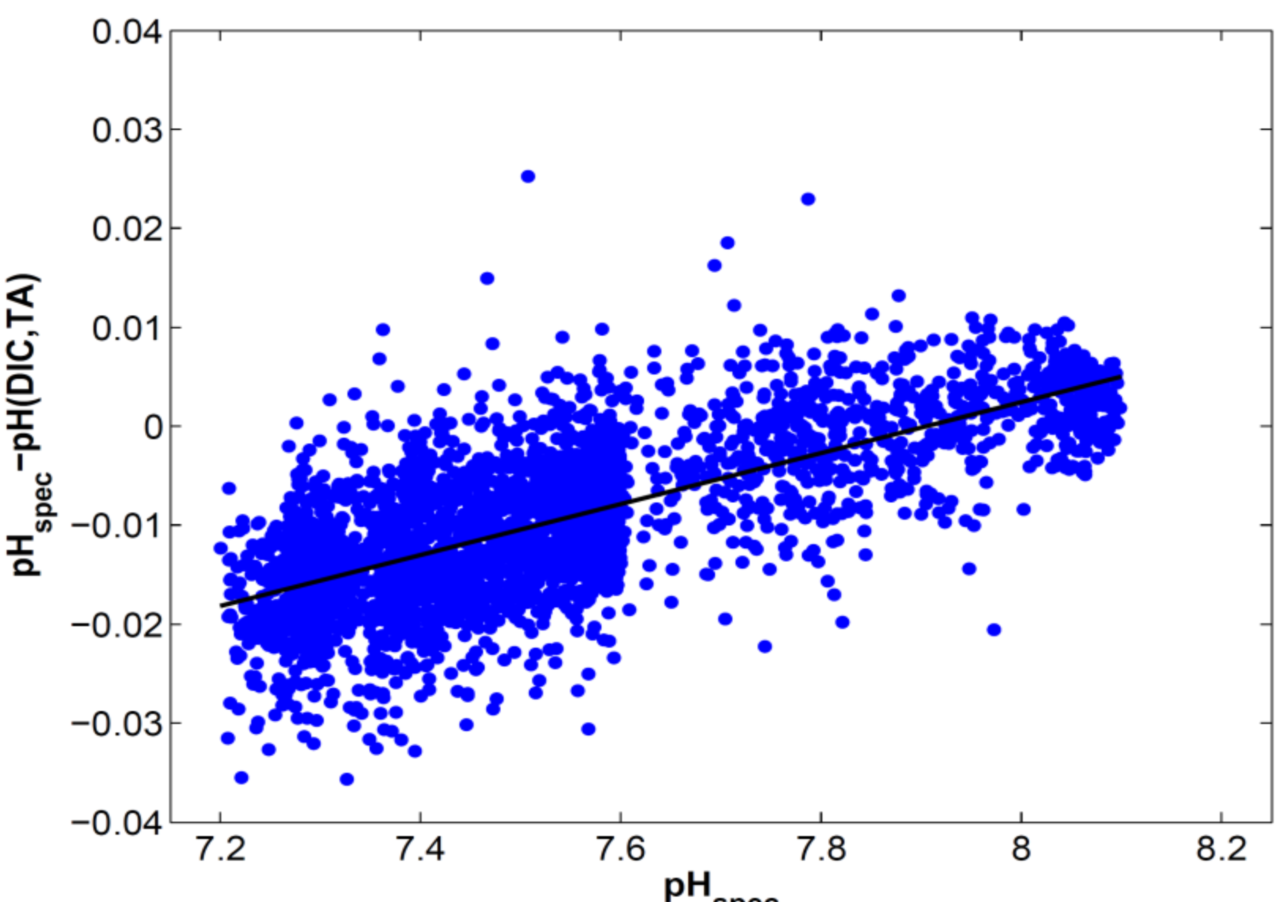


Fig. 1. The problem.
Example of the pH-dependent pH discrepancy on 2015 P16N. A least squares line fit to the data has a significant non-zero slope and non-zero mean ΔpH.

FongDickson - poster at OSM18

Defining ocean acidification requirements

GOA-ON (Global Ocean Acidification Observing Network):

Newton J.A., Feely, R.A., Jewett, E.B., Williamson, P., Mathis, J., 2014. Global Ocean Acidification Observing Network: Requirements and Governance Plan. http://goa-on.org/docs/GOA-ON_plan_print.pdf

The ***weather*** objective requires the carbonate ion concentration (used to calculate saturation state) to have a relative standard uncertainty of 10%.

> "***Weather***" Defined as data of sufficient and defined quality used to identify relative spatial patterns and short-term variation. With respect to ocean acidification, this is to support mechanistic interpretation of the ecosystem response to and impact on local, immediate ocean acidification dynamics

GOA-ON Weather Quality Objective

The "weather" goals are achievable provided that the standard uncertainties of measurement for the various carbon system parameters are:

$u(A_{\mathrm{T}}) \sim 10\ \mu\mathrm{mol\ kg^{-1}}$

$u(C_{\mathrm{T}}) \sim 10\ \mu\mathrm{mol\ kg^{-1}}$

$u(\mathrm{pH}) = 0.02$

$u_r(p\mathrm{CO_2}) = 2.5\%$

Note, these are uncertainties not precisions

Achievable by "good" labs

Note too that these assume that AT is well understood. Still needs to be addressed.

DEFINING OCEAN ACIDIFICATION REQUIREMENTS

GOA-ON (Global Ocean Acidification Observing Network):

The ***climate*** objective requires the observed change in carbonate ion concentration (used to calculate saturation state) to have a relative standard uncertainty of ~1%.

> "***Climate***" Defined as measurements of quality sufficient to assess long-term trends with a defined level of confidence. With respect to ocean acidification, this is to support detection of the long-term anthropogenically-driven changes in hydrographic conditions and carbon chemistry over multi-decadal timescales

GOA-ON Climate Quality Objective

The "climate" goals require that the standard uncertainties of measurement for the various carbon system parameters are:

$u(A_\mathrm{T}) \sim 2\ \mu\mathrm{mol\ kg^{-1}}$

$u(C_\mathrm{T}) \sim 2\ \mu\mathrm{mol\ kg^{-1}}$

$u(\mathrm{pH}) = 0.003$

$u_r(p\mathrm{CO_2}) = 0.5\%$

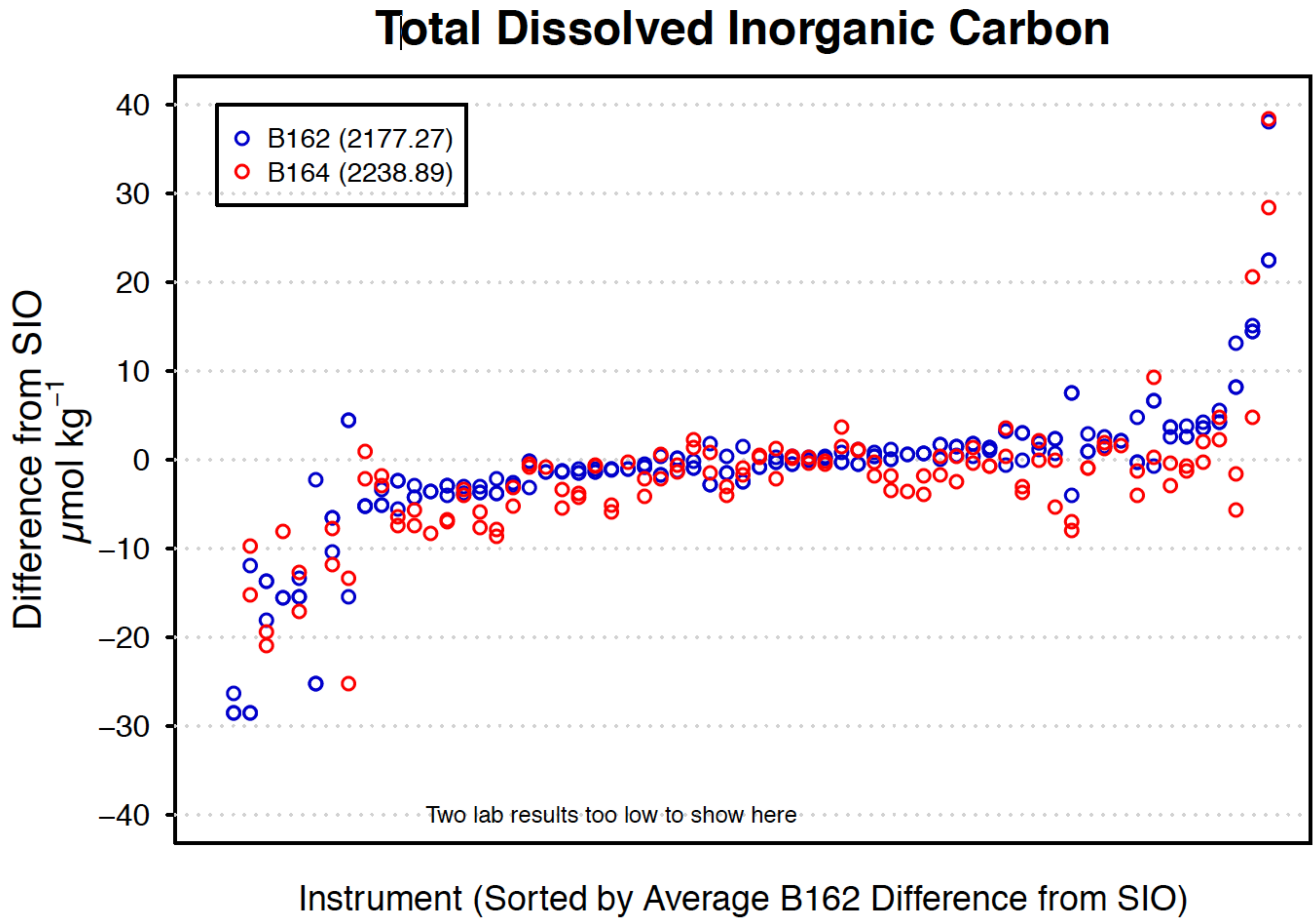
Note, these are uncertainties not precisions

May be achievable by "the best" labs, but see earlier caveat about A_T

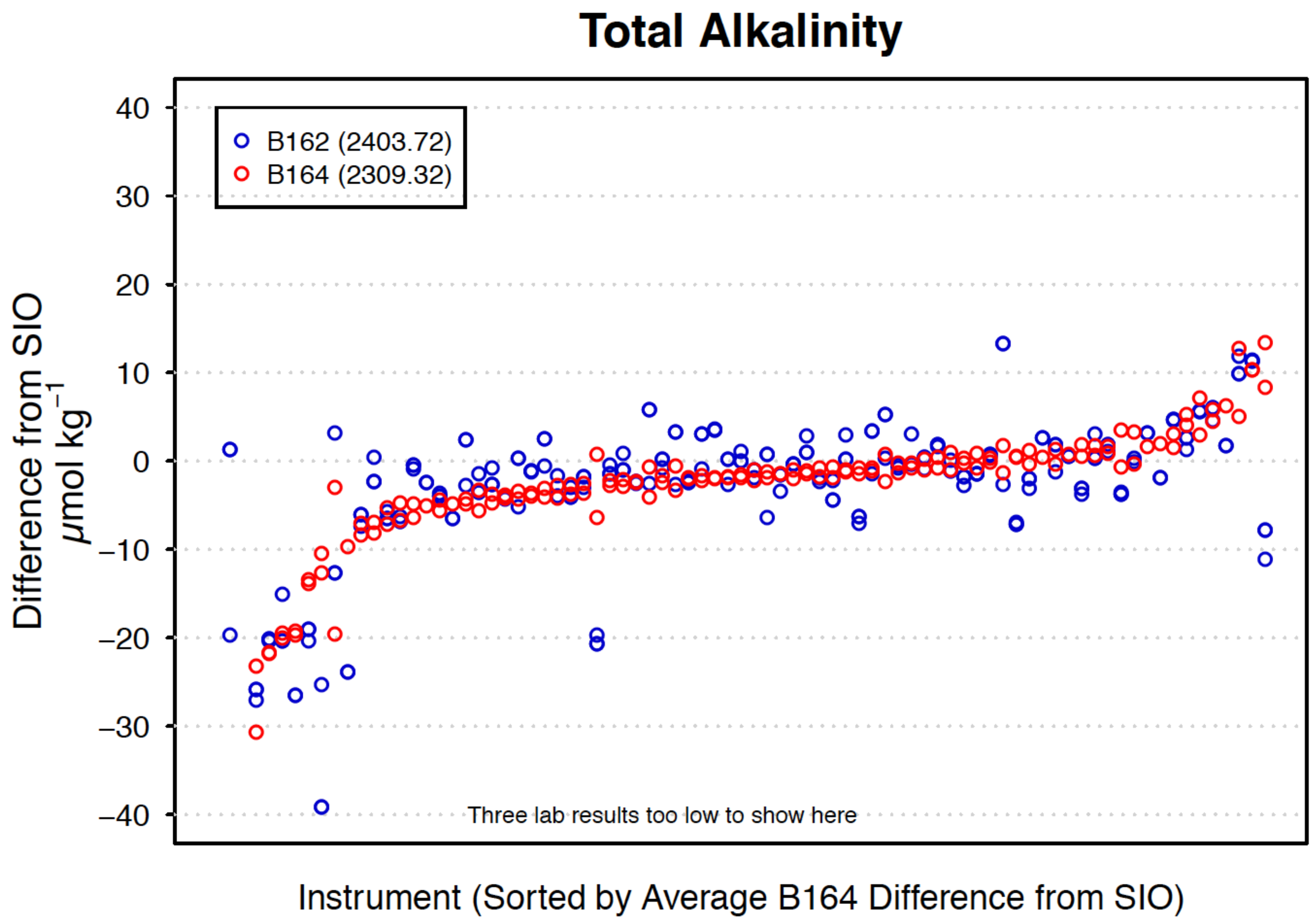
Can these uncertainty requirements be achieved reliably by a wide range of laboratories?

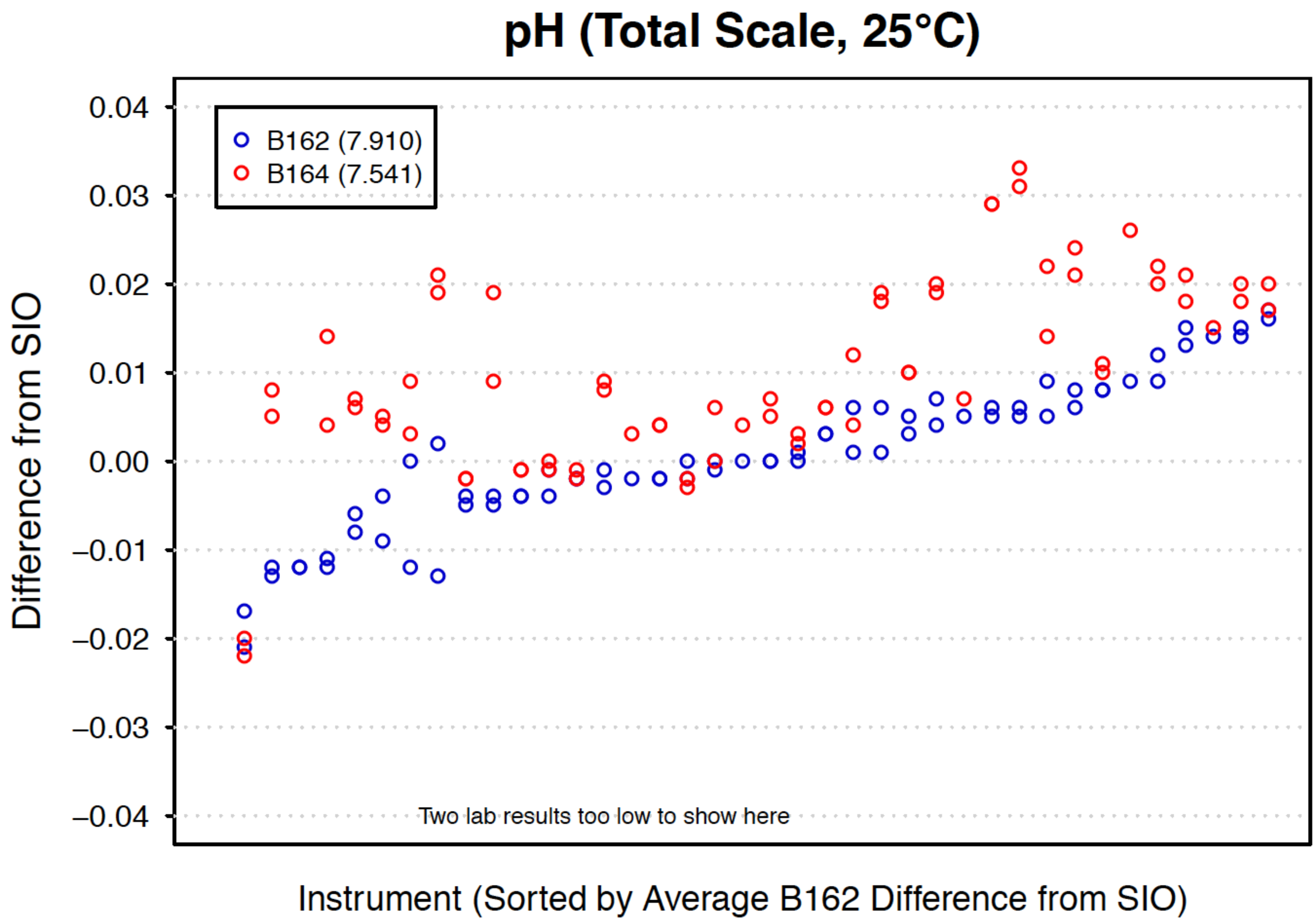
Approach

Two *unknowns* with substantially different CO_2 levels were prepared from natural seawater (*S* ~ 33.2*)* at the Scripps Institution of Oceanography at UC San Diego. These were bottled; analyzed at Scripps for salinity, total dissolved inorganic carbon, total alkalinity, and pH(25 °C); and then distributed to the various participating labs for analysis using their standard techniques.



Total Dissolved Inorganic Carbon
B162 (2177.27)
B164 (2238.89)
40
30
20
10
0
−10
−20
−30
−40
Difference from SIO
μmol kg−1
Two lab results too low to show here
Instrument (Sorted by Average B162 Difference from SIO)


Total Alkalinity
B162 (2403.72)
B164 (2309.32)
40
30
20
10
0
−10
−20
−30
−40
Difference from SIO
μmol kg−1
Three lab results too low to show here
Instrument (Sorted by Average B164 Difference from SIO)


pH (Total Scale, 25°C)
B162 (7.910)
B164 (7.541)
0.04
0.03
0.02
0.01
0.00
−0.01
−0.02
−0.03
−0.04
Difference from SIO
Two lab results too low to show here
Instrument (Sorted by Average B162 Difference from SIO)

What is still needed to make OA-related measurements more straightforward?

Needs for the future

Awareness of desirability of defining required uncertainty for OS studies, as well as the need to ensure that it is achieved.

Evaluation of simpler (& cheaper), commercially available systems for CO_2 measurements, including documentation of methods, of necessary training, and of appropriate QC procedures.

Recognition of the need to consider propagation of uncertainty when calculating CO_2 parameters rather than measuring them directly. (Including uncertainties in all the various *constants* considered. (Software exists for this*)

*Availability:
via CRAN for seacarb (J.-P. Gattuso)
via Github for CO2SYS-Excel, CO2SYS-Matlab, & mocsy (search for jamesorr)
→ These archives include docs, examples, & interactive Jupyter notebooks