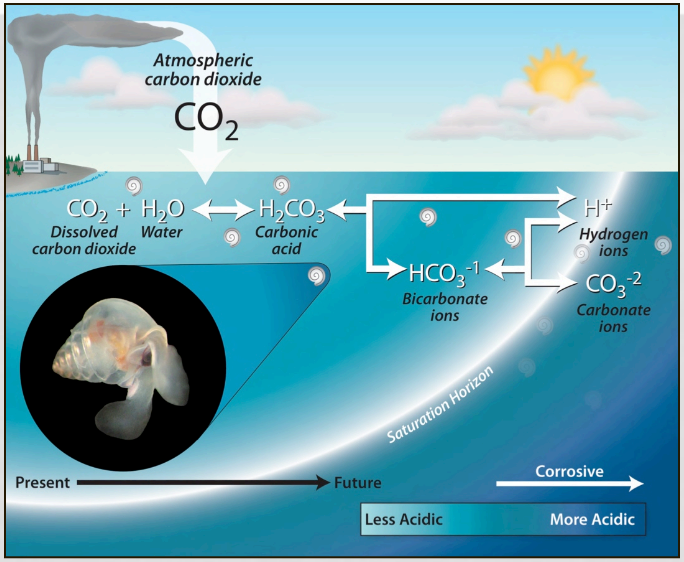
Advancing sensors and technologies for ocean acidification research

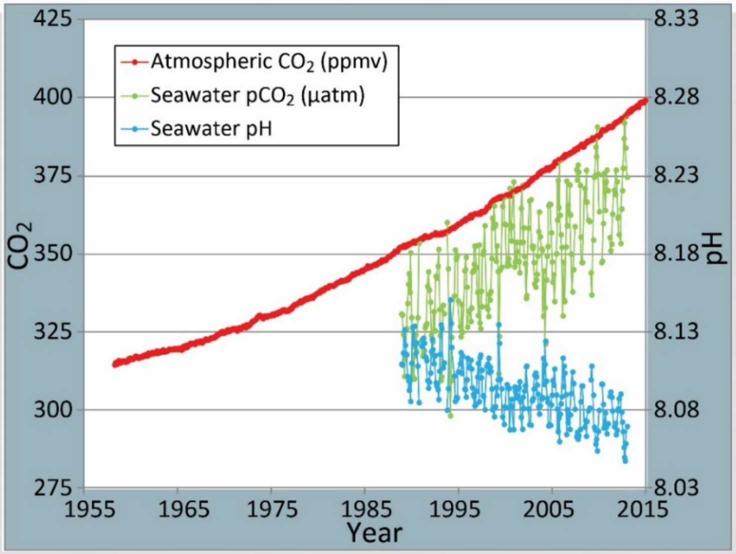
Z. Aleck Wang
Woods Hole Oceanographic Institution

4th U.S Ocean Acidification PI Meeting
Portland, OR
February 2018

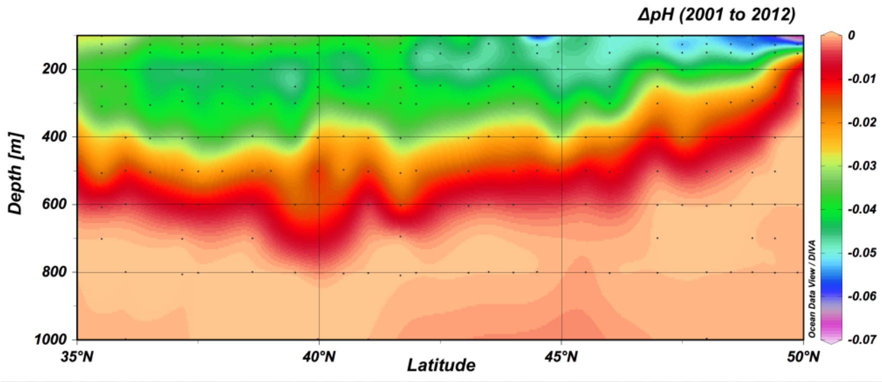
OCEAN ACIDIFICATION

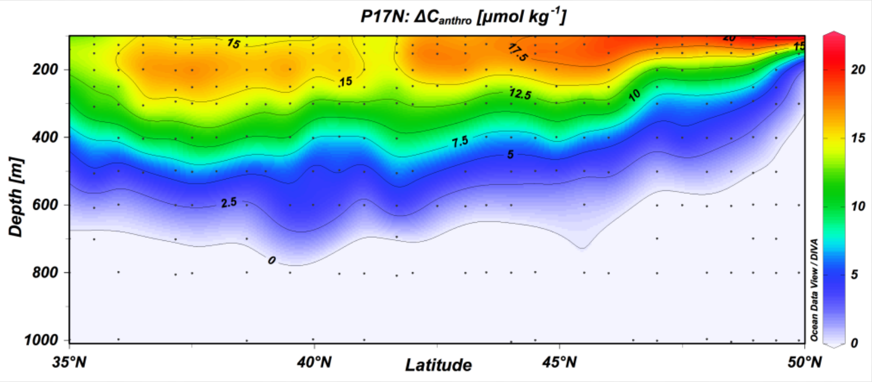


Hawaii Time-series



Northeast Pacific P17 (Chu et al. 2016)





Challenges for OA Sensor Development

- OA signals are analytically small
  ΔpH ~ -0.001 – 0.003/yr; ΔDIC ~+1 – 3 µmol kg^{-1}/yr ;
  ΔpCO_2 ~ +1 – 3 µatm/yr
  but depends on what signals you want to detect:
  -- Long-term small signal (climatology)
  -- Short-term large variability

- Simultaneous measurements of two CO_2 parameters
  Which pair matters

- ✓ pCO_2 and pH sensors are robust and commercially available
- ✓ DIC and TA sensors are less mature

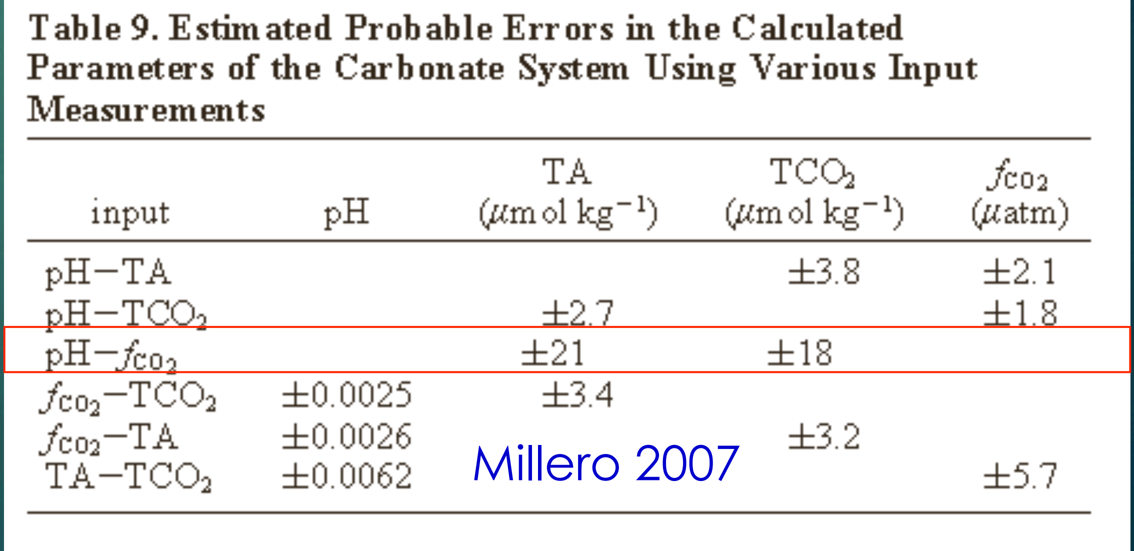
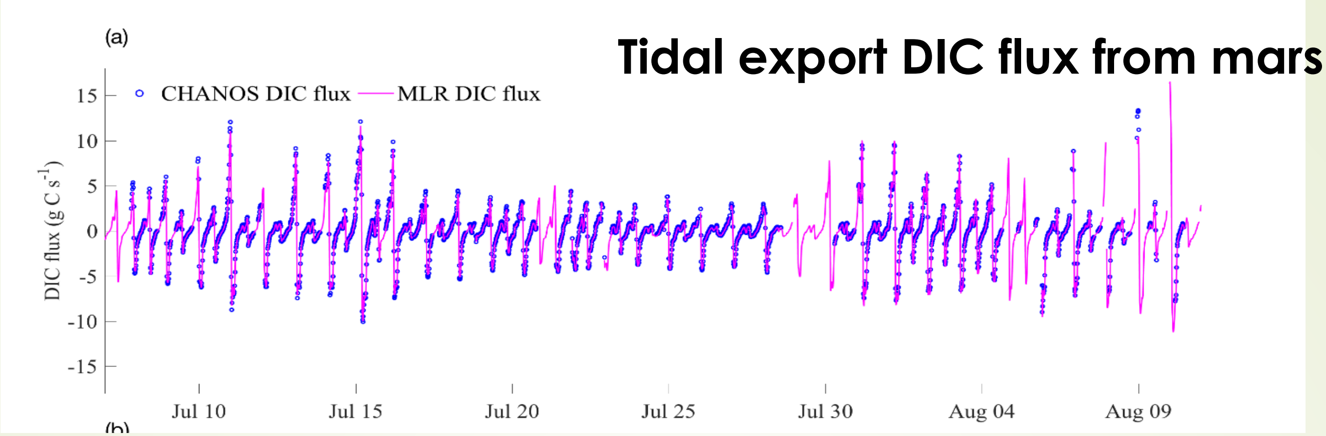


Table 9. Estimated Probable Errors in the Calculated Parameters of the Carbonate System Using Various Input Measurements

input	pH	TA (µmol kg^{-1})	TCO_2 (µmol kg^{-1})	f_{CO_2} (µatm)
pH−TA			±3.8	±2.1
pH−TCO_2		±2.7		±1.8
pH−f_{CO_2}		±21	±18	
f_{CO_2}−TCO_2	±0.0025	±3.4		
f_{CO_2}−TA	±0.0026		±3.2	
TA−TCO_2	±0.0062			±5.7

Millero 2007

Tidal export DIC flux from marshes



Probability of obtaining a good DIC flux estimate (within 25% of the true mean) for a given tide using different sampling protocols

	12 hrs sampling with a 15 min interval	8 hrs sampling with a 15 min interval	12 hrs sampling with a 60 min interval	12 hrs sampling with a 120 min interval
July 7 to August 11	88%	22%	36%	17%
November 30 to December 18	92%	35%	27%	15%

Need to sample complete tide

Sampling interval matters

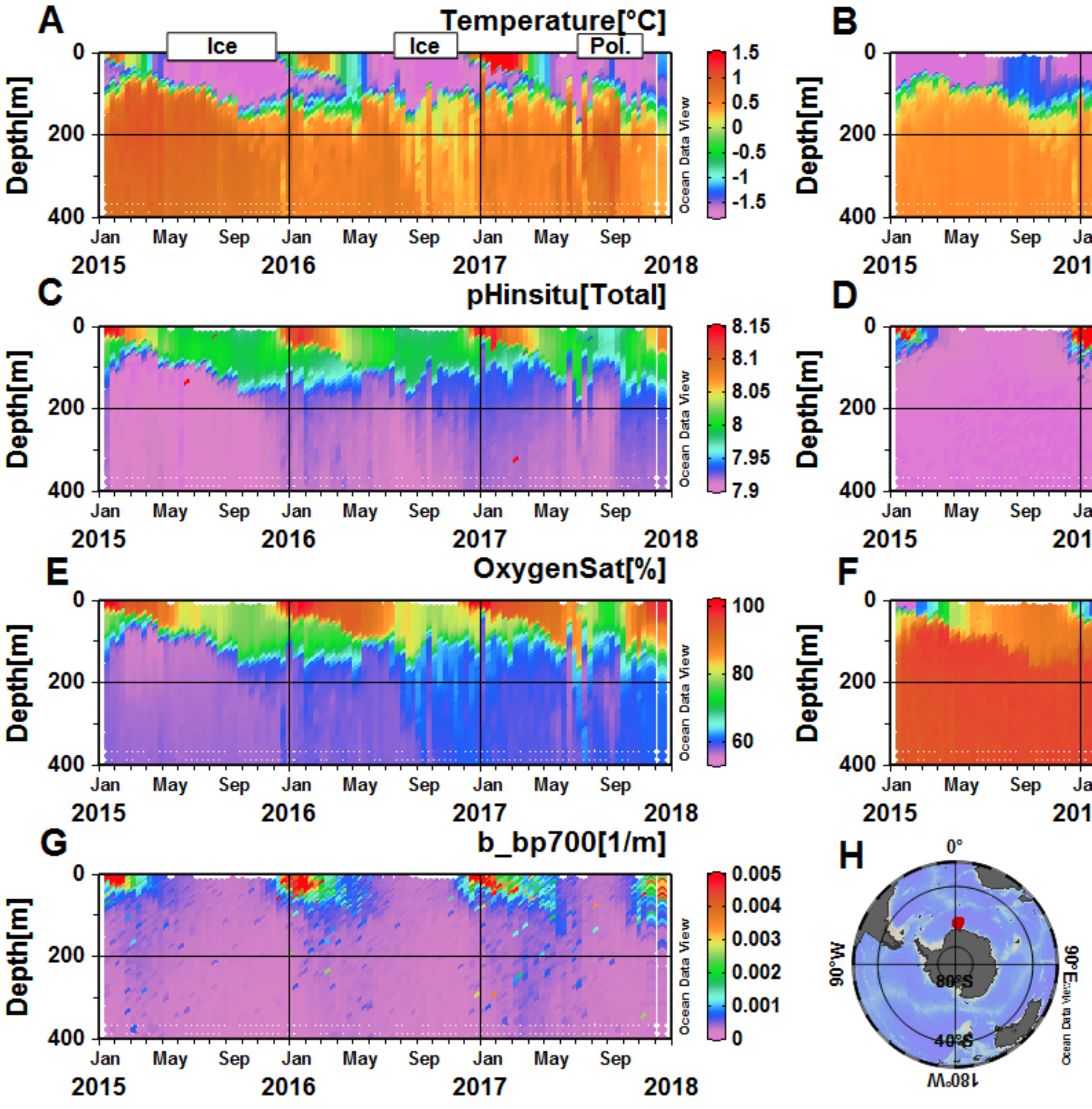
✓ **Measurement frequency and duration matters**

Recent Development

- New-generation $p\mathrm{CO}_2$ and pH sensors

Deep SeaFET

Sensors operational in difficult environments. WMO #5904468 3 years under ice in Weddell Sea, first biogeochemical record from the Weddell Polyna.



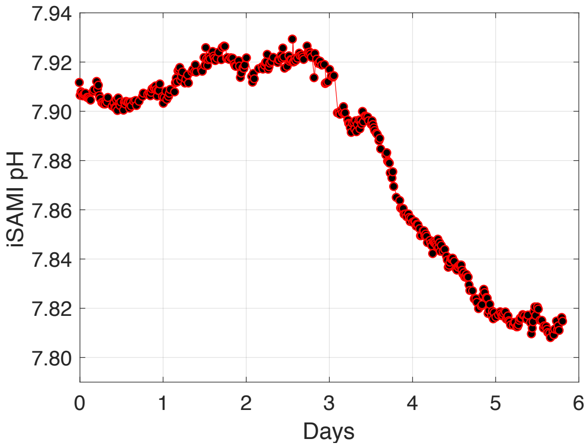
SOCCOM

Courtesy of K. Johnson

New spectrophotometric pH instrumentation

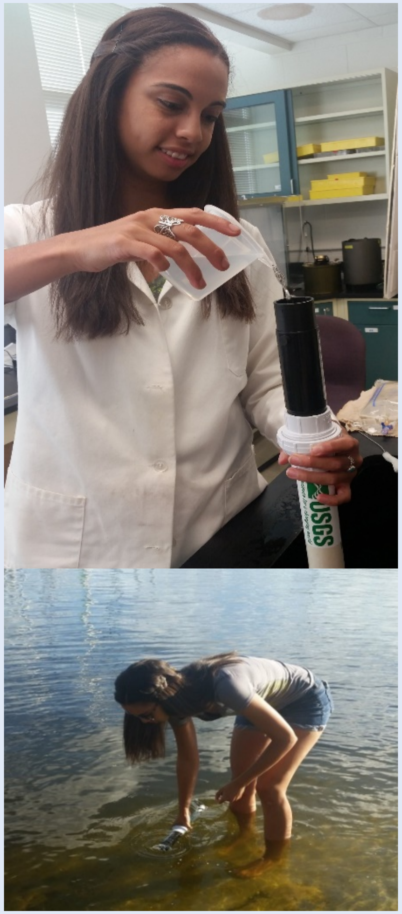
Handheld “pHyter”

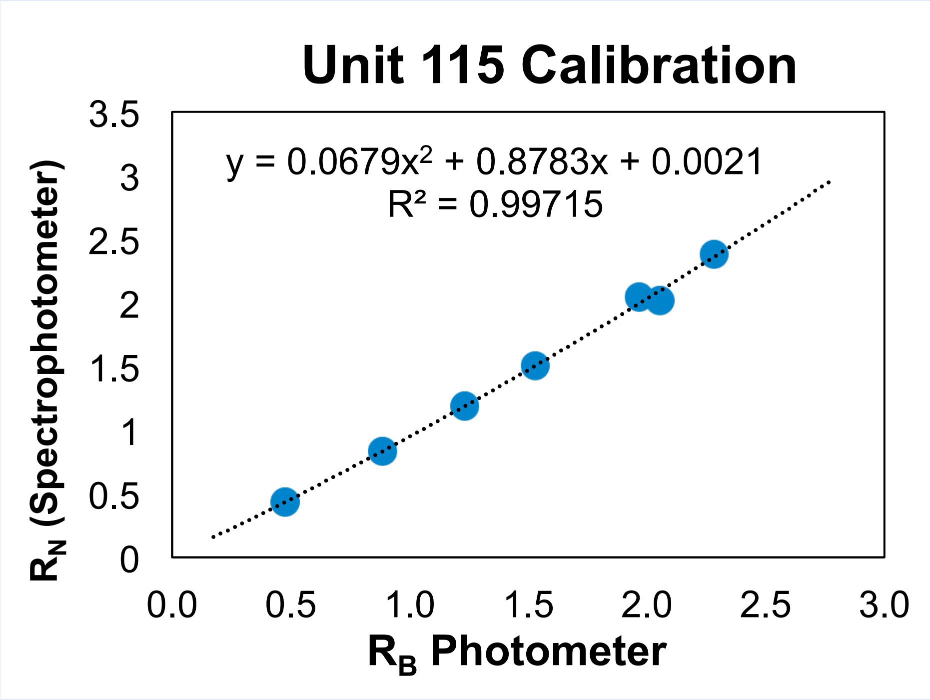
XPRIZE supported
***i*SAMI pH**
technology



Courtesy of M. DeGrandpre

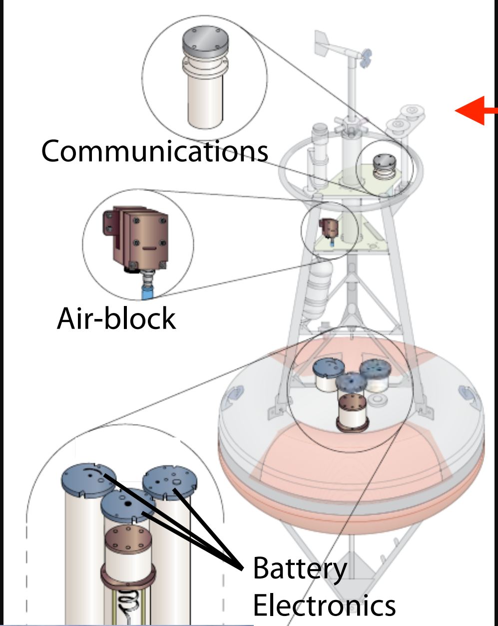
Next Generation pH Photometers
(Low cost)



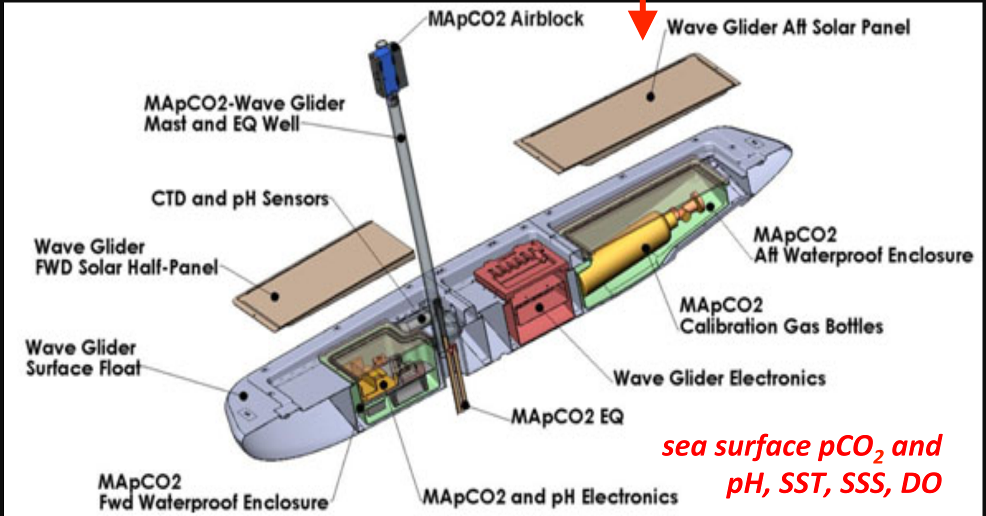


Courtesy of R. Byrne

New technologies: Autonomous Surface Vehicle (ASVs)
Wave glider and Saildrone



PMEL Carbon and Engineering groups adapted Moored Autonomous *p*CO_2 (MAPCO$_2$) system, currently deployed at >50 sites globally, into an Autonomous Surface Vehicle CO_2 (ASVCO$_2$) system for a wave glider



sea surface pCO_2 and pH, SST, SSS, DO

Work of PMEL Engineering and Carbon groups. Contact: adrienne.sutton@noaa.gov

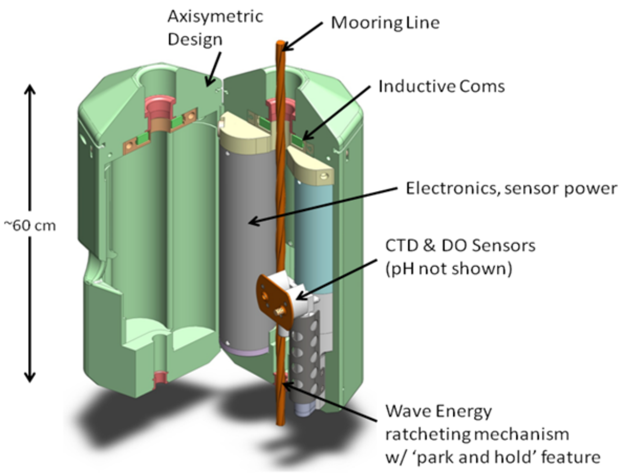
Courtesy of A. Sutton

Low power, compact pCO$_2$ optode

- Same footprint as Aanderaa O$_2$ optode
- Fluorescence lifetime based
- 80 mW at 5 second sampling
- Calibration pre and post deployment

Courtesy of S. Chu and A. Sutton, PMEL

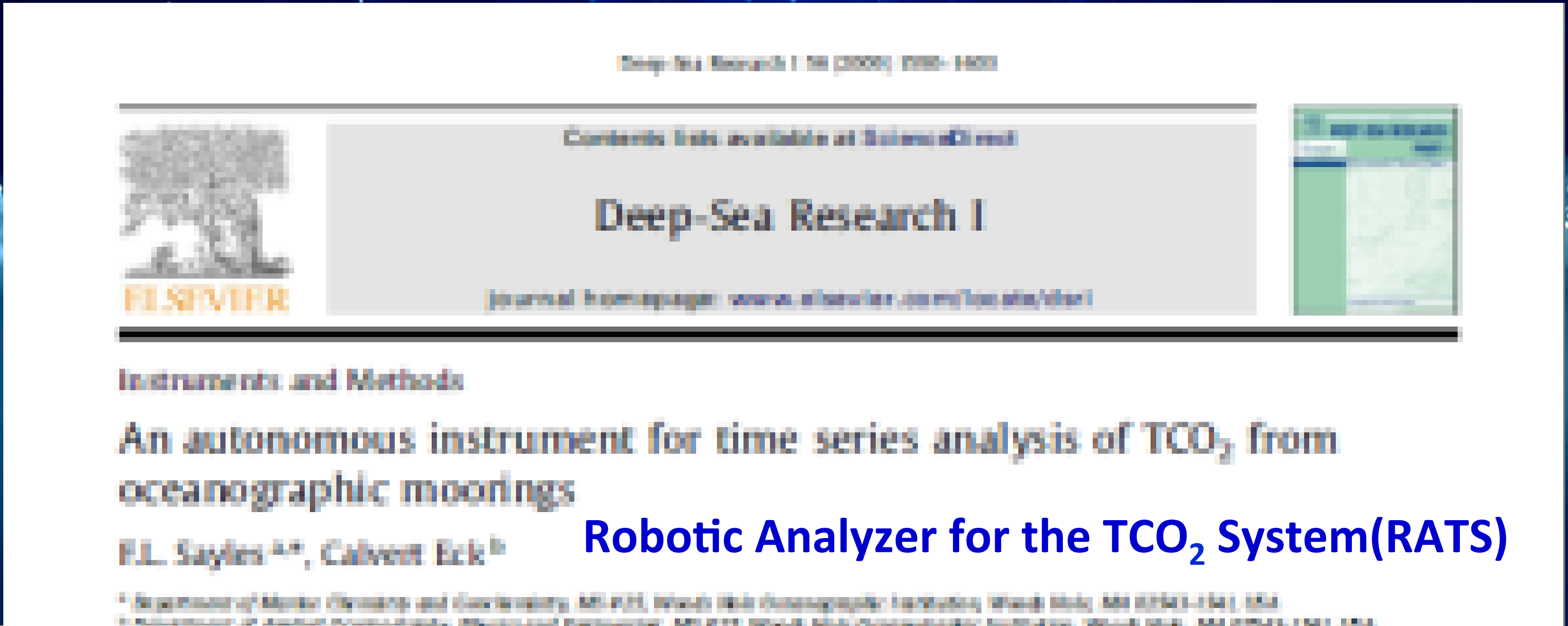
"Prawler"
(Profiler+Crawler)



Atamunchuk et al. 2014

Emerging DIC and Alk sensors

Robotic Analyzer for the TCO_2 System(RATS)



Deep-Sea Research I 56 (2009) 1590–1600

Contents lists available at ScienceDirect

Deep-Sea Research I

journal homepage: www.elsevier.com/locate/dsri

Instruments and Methods

An autonomous instrument for time series analysis of TCO_2 from oceanographic moorings

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[a] Department of Marine Chemistry and Geochemistry, MS #25, Woods Hole Oceanographic Institution, Woods Hole, MA 02543-1541, USA

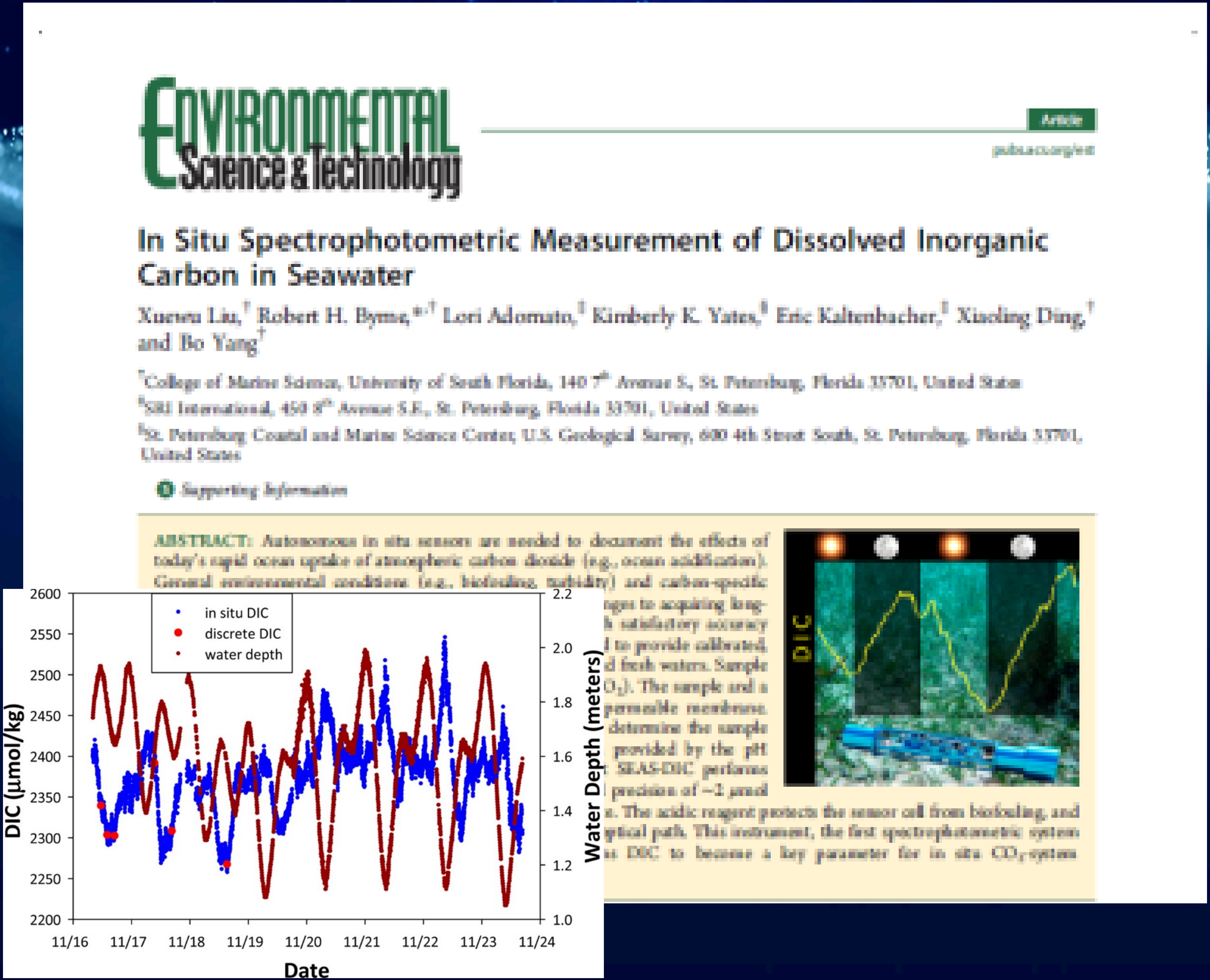
aphy, Physics and Engineering, MS #25, Woods Hole Oceanographic Institution, Woods Hole, MA 02543-1541, USA

ABSTRACT

The design and testing of a robotic analyzer for autonomous TCO_2 measurement from oceanographic moorings is described. The analyzer employs a conductimetric method of TCO_2 measurement wherein CO_2 from an acidified sample diffuses across a semi-permeable membrane into a NaOH solution decreasing the conductivity of the base. The instrument is capable of ~850 analyses over a period of at least six months. It is designed to operate to depths of at least 1000m. TCO_2 calibration is based on in situ standardization throughout a deployment.

We report both laboratory and in situ tests of the analyzer. In the laboratory automated analyses over a period of 30 days at temperatures ranging from 8° to 25 °C yielded a TCO_2 accuracy and precision of ±2.7 µmol/kg. In situ tests were conducted at the WHOI dock with a deployment of 8 weeks at in situ temperatures of 9°–13 °C. The accuracy and precision of TCO_2 analyses over the deployment period, based on in situ calibration, was ±3.6 µmol/kg.

Laboratory tests of reagent and standard solution stability are also reported.



Environmental Science & Technology

Article

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In Situ Spectrophotometric Measurement of Dissolved Inorganic Carbon in Seawater

Xuewu Liu,[†] Robert H. Byrne,*[,†] Lori Adornato,[‡] Kimberly K. Yates,[§] Eric Kaltenbacher,[‡] Xiaoling Ding,[†] and Bo Yang[†]

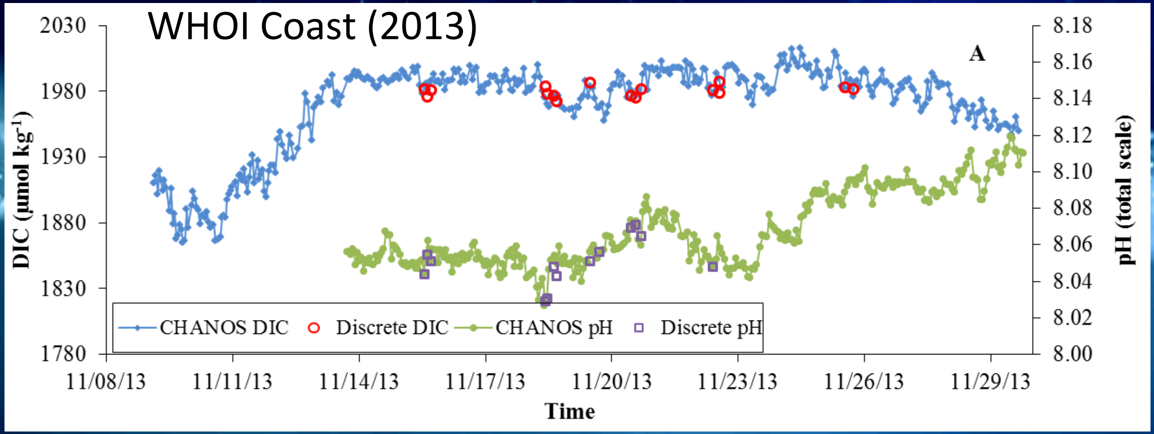
[†]College of Marine Science, University of South Florida, 140 7th Avenue S., St. Petersburg, Florida 33701, United States
[‡]SRI International, 450 8th Avenue S.E., St. Petersburg, Florida 33701, United States
[§]St. Petersburg Coastal and Marine Science Center, U.S. Geological Survey, 600 4th Street South, St. Petersburg, Florida 33701, United States

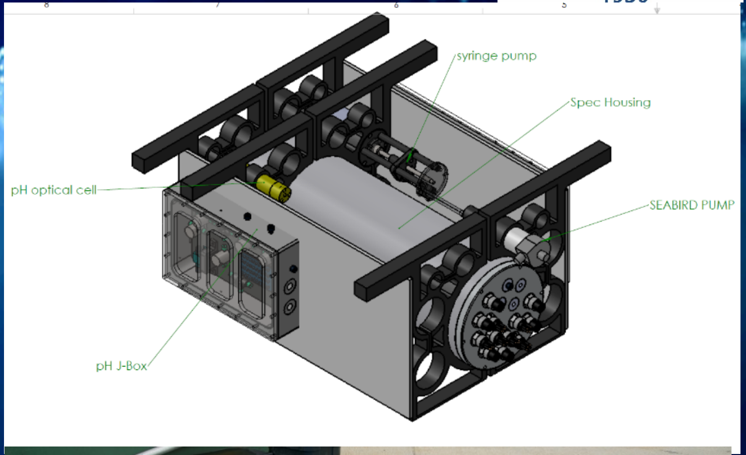
Supporting Information

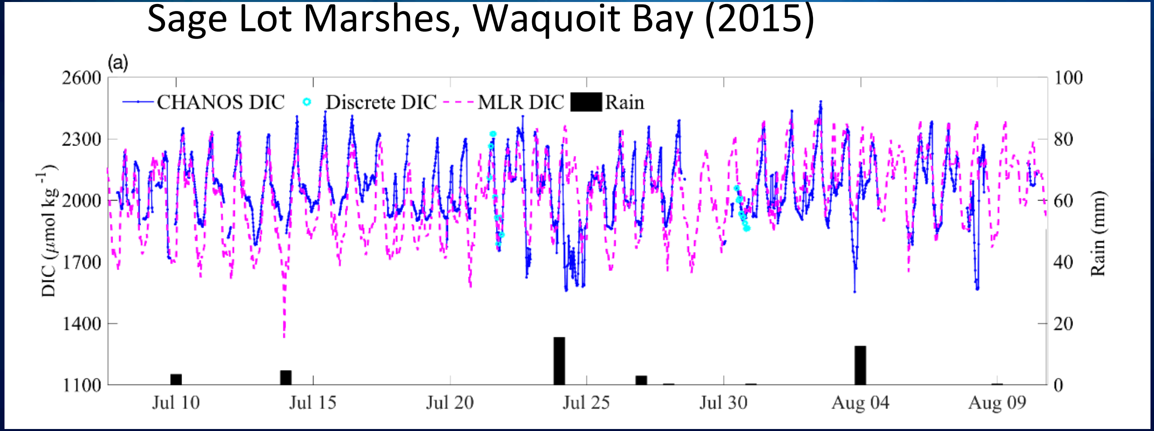
ABSTRACT: Autonomous in situ sensors are needed to document the effects of today's rapid ocean uptake of atmospheric carbon dioxide (e.g., ocean acidification). General environmental conditions (e.g., biofouling, turbidity) and carbon-specific
…nges to acquiring long-
…h satisfactory accuracy
…d to provide calibrated,
…d fresh waters. Sample
…O_2). The sample and a
…permeable membrane.
…determine the sample
…provided by the pH
…SEAS-DIC performs
…precision of ~2 μmol
…s. The acidic reagent protects the sensor cell from biofouling, and
…ptical path. This instrument, the first spectrophotometric system
…s DIC to become a key parameter for in situ CO_2-system

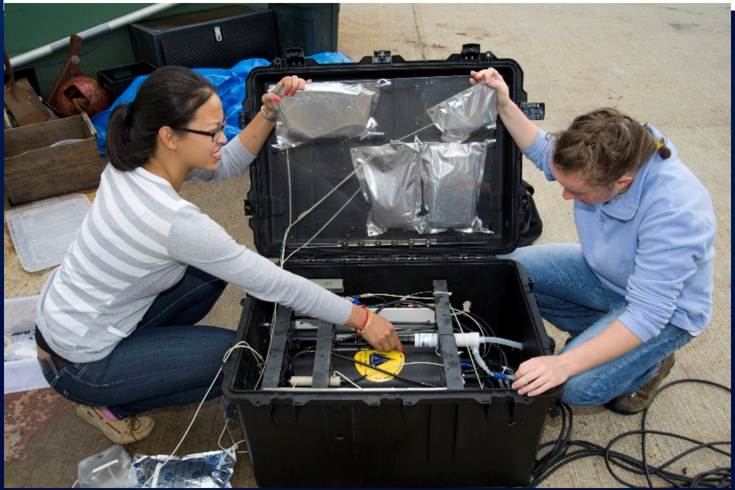
Channelized Optical System (CHANOS) – DIC + pH

WOODS HOLE OCEANOGRAPHIC INSTITUTION
1930


WHOI Coast (2013)




Sage Lot Marshes, Waquoit Bay (2015)



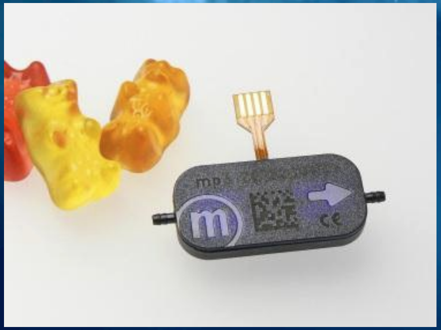
- ✓ Two independent channels: spectrophotometric pH and DIC
- ✓ Designed for fixed platforms, e.g. buoys

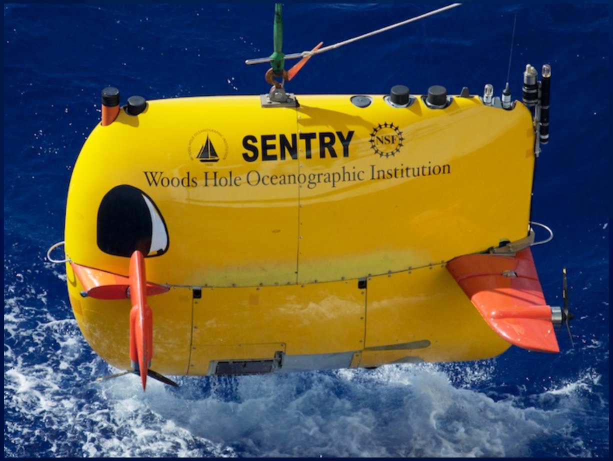
Uncertainties: DIC: 0.8±5.2 µmol/kg
pH: -0.001±0.003

(Wang et al. 2015)

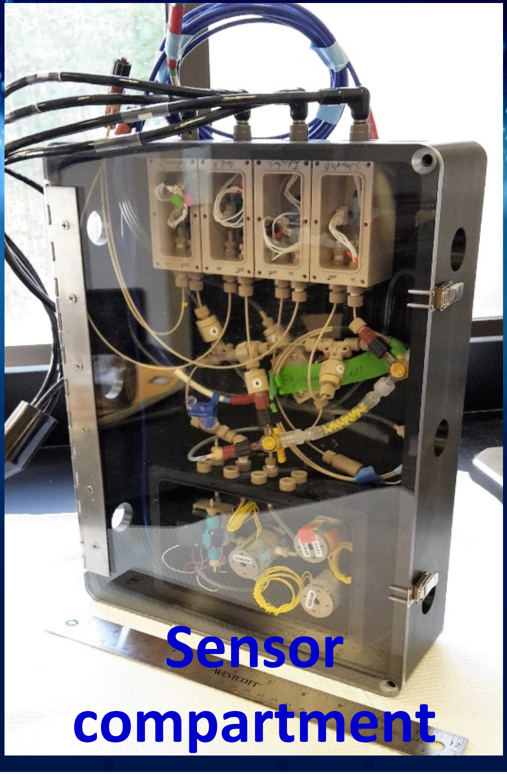
NIST
National Institute of Standards and Technology
U.S. Department of Commerce

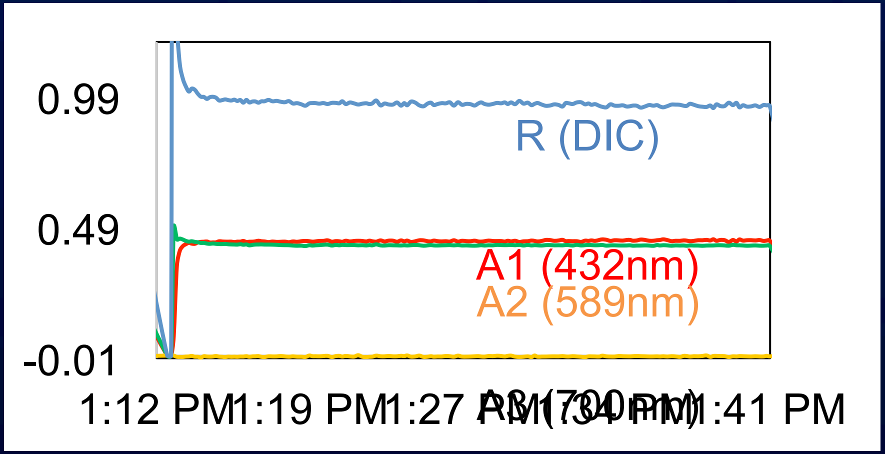
CHANOS II DIC+pCO$_2$: AUVs and CTD Rosette





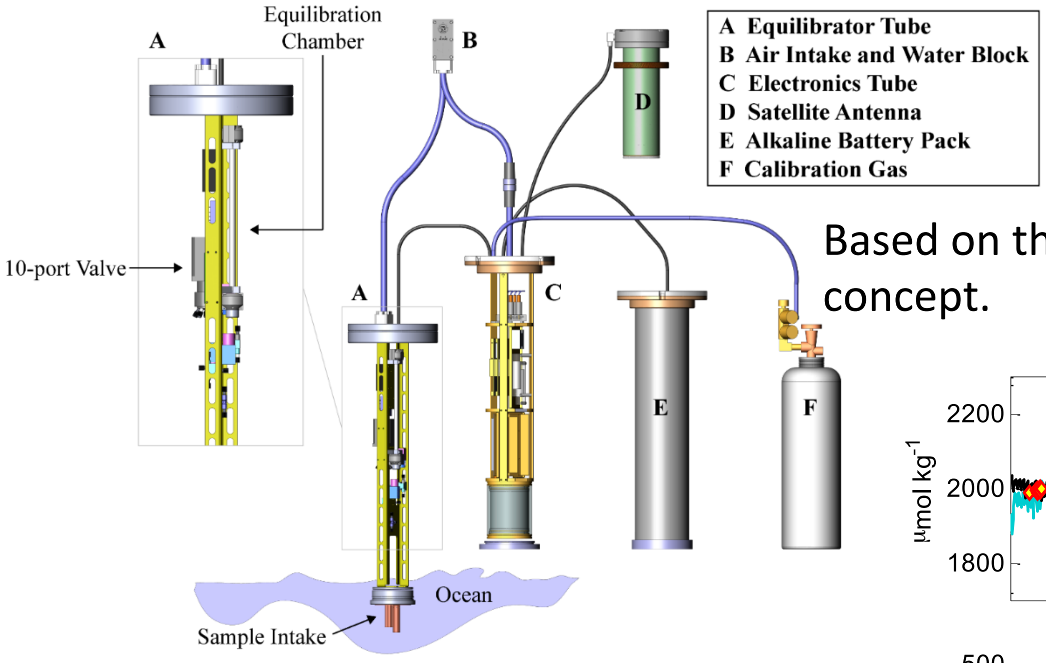
12”





moored autonomous DIC (MADIC)

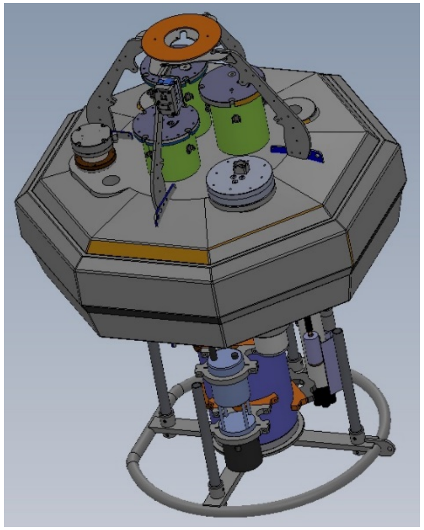
Fassbender et al. *ES&T*, 2015

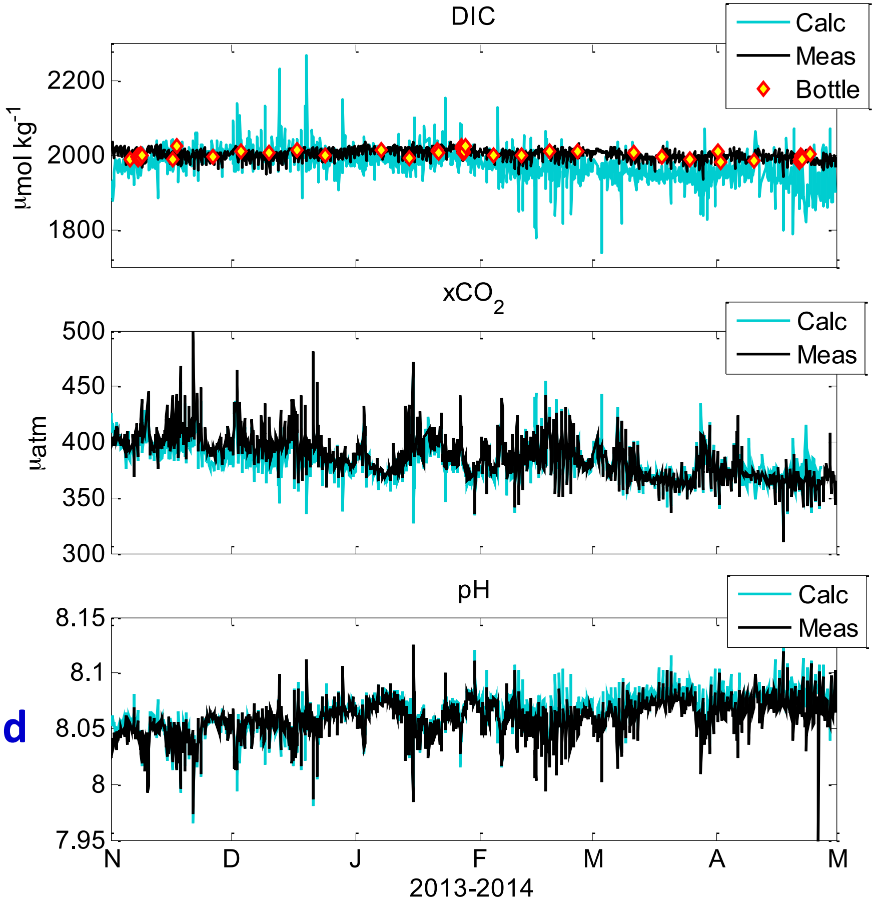


A **Equilibrator Tube**
B **Air Intake and Water Block**
C **Electronics Tube**
D **Satellite Antenna**
E **Alkaline Battery Pack**
F **Calibration Gas**

Friederich et al. *DSR Pt. I*, 1995
Sutton et al. *ESSD*, 2014

Based on the MAPCO$_2$ system design, for proof of concept.





Courtesy of A. Fassbender and C. Sabine

TECHNOLOGY REPORT

Looking Ahead: A Profiling Float Micro-Rosette

By Philip Bresnahan, Todd Martz, Joao de Almeida, Brian Ward, and Paul Maguire

NSF #1538580: Integrating and ground truthing the profiling float microrosette

Under controlled lab conditions, DIC precision of <0.2%RSD or ±4 µmol/kg on sub-milliliter volumes (<250µL). Working now to test in situ.

32 *Oceanography* | Vol.30, No.2

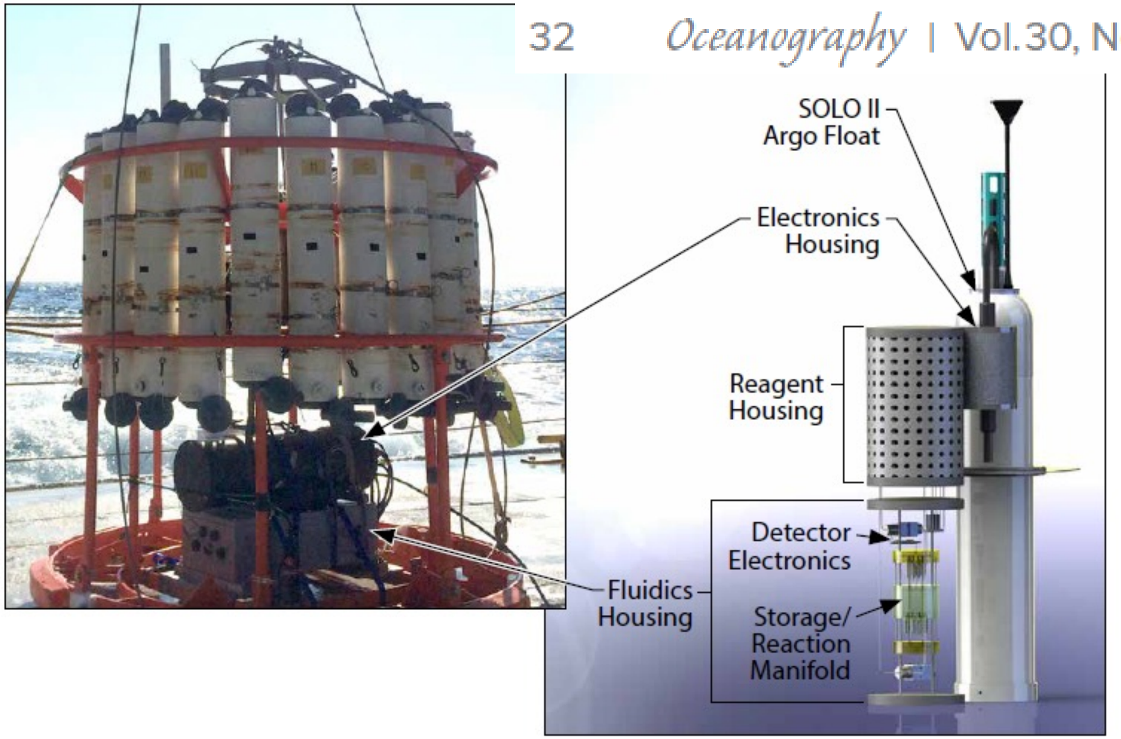


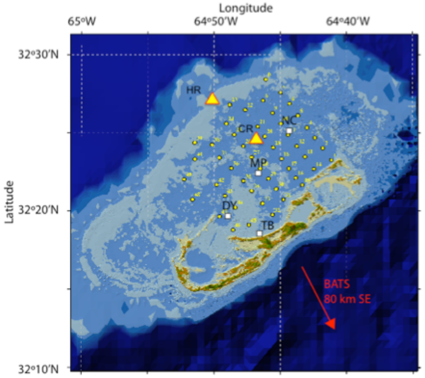
FIGURE 1. (left) Prototype Micro-Rosette fastened to bottom of R/V *Sproul's* rosette frame. (right) Conceptual schematic of the Micro-Rosette integrated into a profiling float. For scale, the SOLO-II float has an overall length of 1.3 m (4'4").

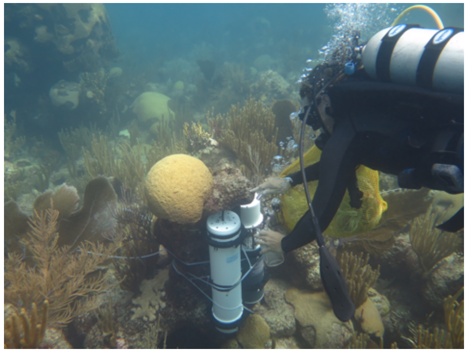
Gas Diffusion Cell Geometry for a Microfluidic Dissolved Inorganic Carbon Analyzer

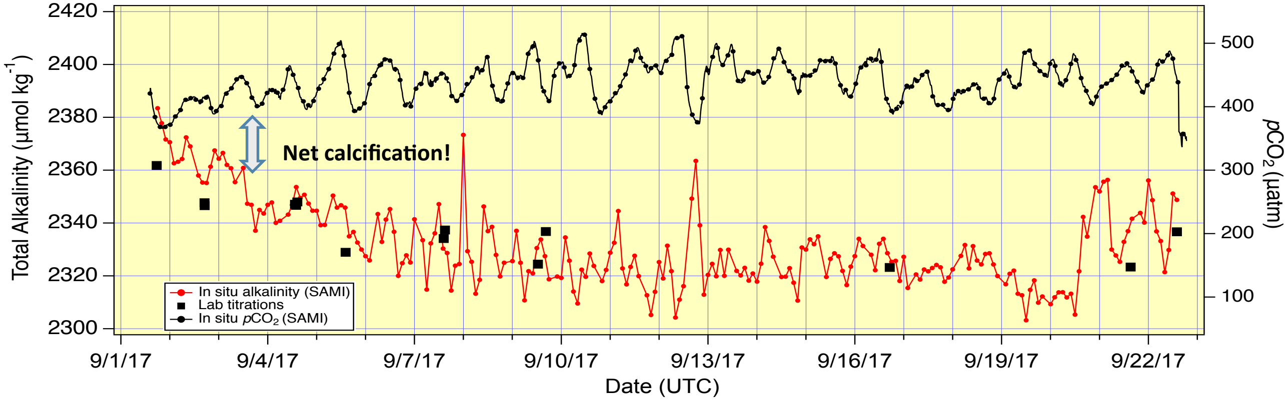
Philip J. Bresnahan, *Member, IEEE*, and Todd R. Martz

IEEE Sensors Journal, 2018. doi: 10.1109/JSEN.2018.2794882

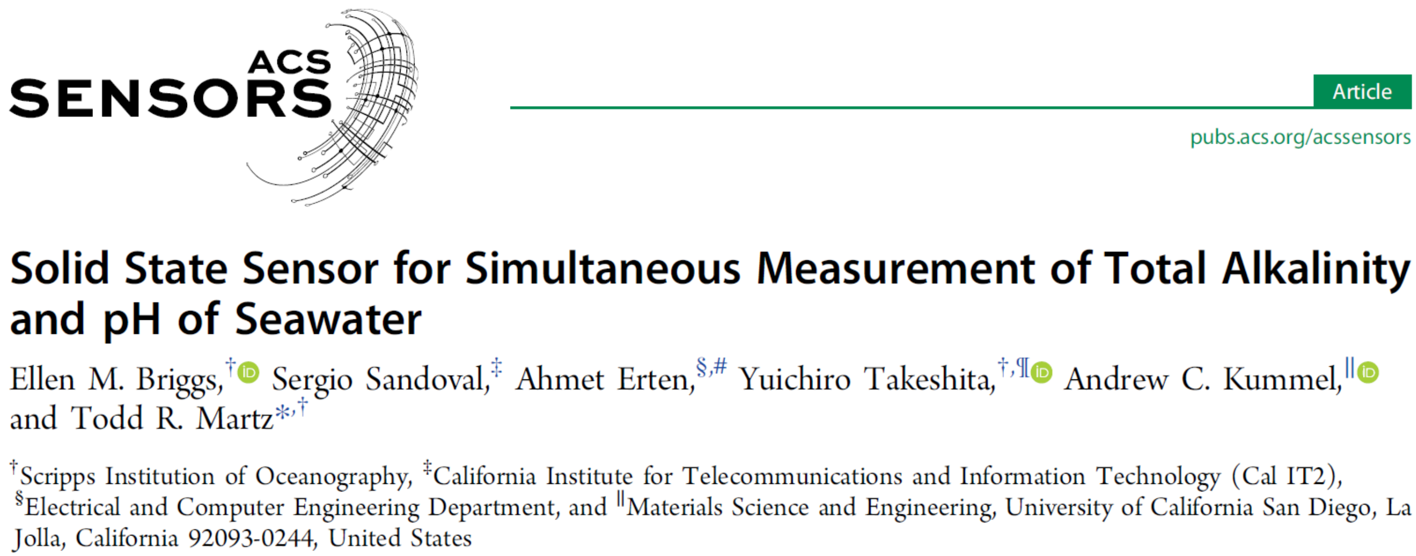
In situ measurements of total alkalinity and $p\mathrm{CO_2}$ on Hogs Reef, Bermuda Sept. 2017 (DeGrandpre et al.)







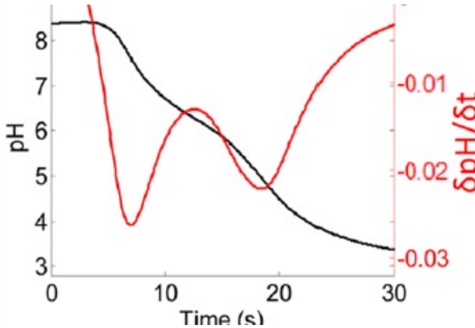
(DeGrandpre and Andersson, unpubl.)

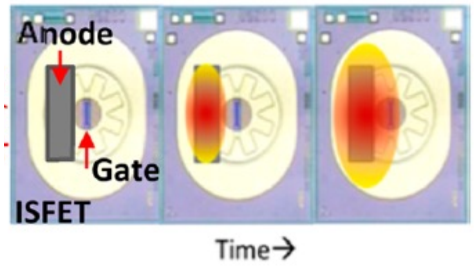

ACS SENSORS
Article
pubs.acs.org/acssensors

Solid State Sensor for Simultaneous Measurement of Total Alkalinity and pH of Seawater

Ellen M. Briggs,[†] Sergio Sandoval,[‡] Ahmet Erten,[§,#] Yuichiro Takeshita,[†,¶] Andrew C. Kummel,[∥] and Todd R. Martz[*,†]

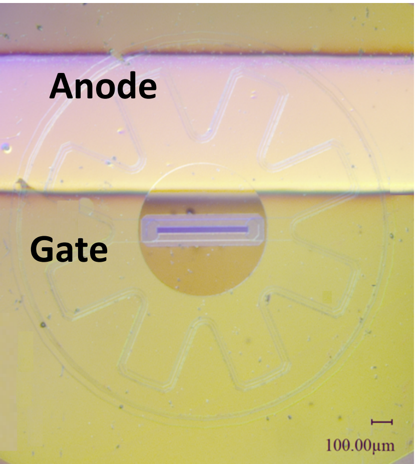
[†]Scripps Institution of Oceanography, [‡]California Institute for Telecommunications and Information Technology (Cal IT2), [§]Electrical and Computer Engineering Department, and [∥]Materials Science and Engineering, University of California San Diego, La Jolla, California 92093-0244, United States

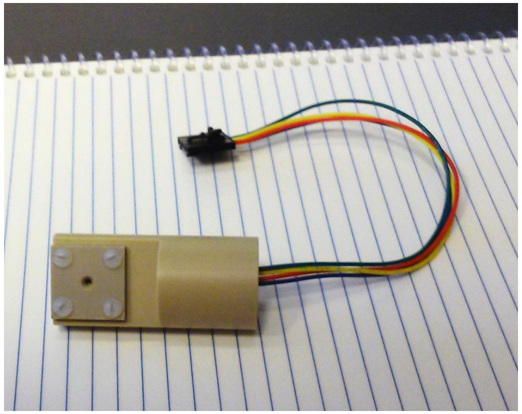


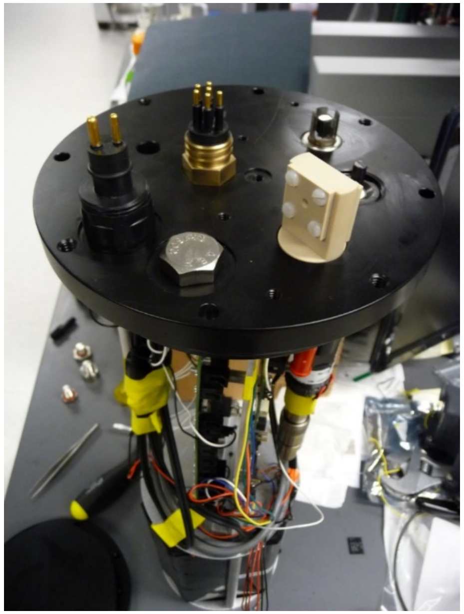


Reagentless, low-power, rapid coulometric titrations are now feasible using a modified version of the Honeywell Durafet pH sensor. This results in a combined pH-TA measurement.

NSF #1155122 Development of an ISFET sensor for seawater Total Alkalinity and pH

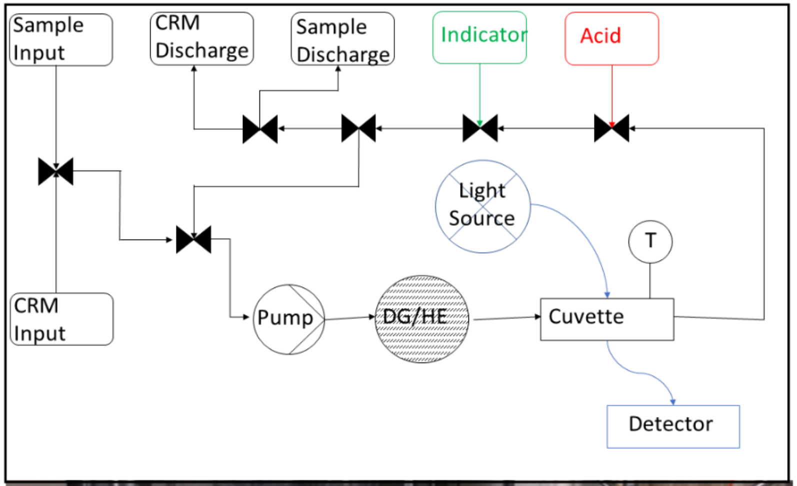


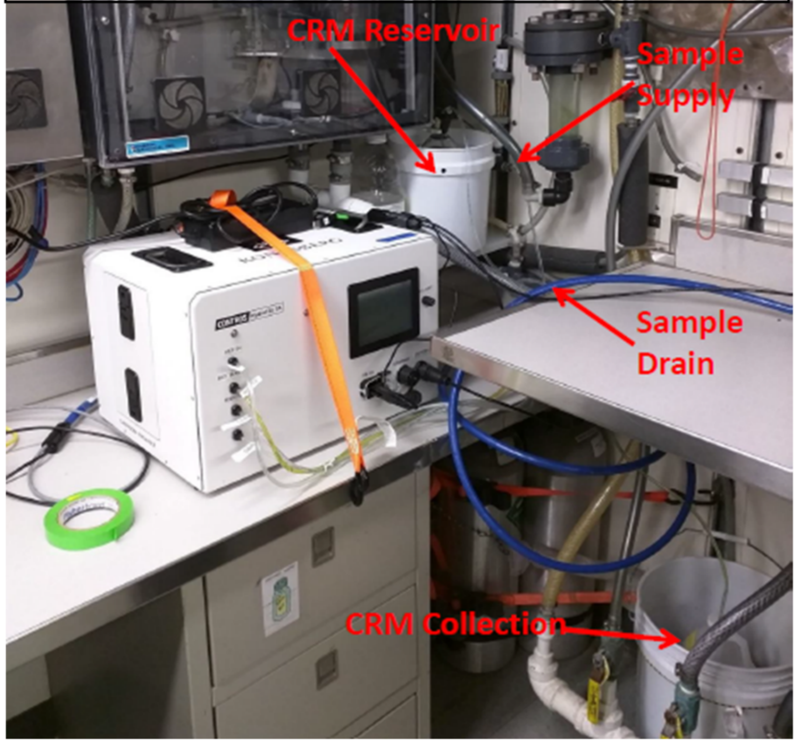




UNH TA Analyzer Project (TAACT)

- Partnership with CONTROS GmbH
- Ability to assess (and maintain) accuracy over long, unsupervised deployments with automated CRM checks
- Integrated host platform data feed
- Simplified operation for shipboard personnel (one-button operation)
- Installations on NOAA RV Bigelow (below), NOAA RV Hi'ialakai, Mook Sea Farms and UNH Coastal Marine Lab





Joe Salisbury and Chris Hunt (UNH)
Funding from NOAA IOOS and OAP

DIC SENSOR TECHNOLOGIES

	SEAS-DIC	MADIC	RATS	CHANOS /CHANOS II	Micro-Rosette
Parameters measured	DIC	DIC	• DIC • pH	• DIC • pH	DIC
DIC Uncertainty (±μmol kg^{-1})	2	5.0	2-3	3.0	4
Sampling Frequency (mins)	~1	~12	6	0.1	10?
Platforms	Mooring, Buoy	Mooring, Buoy	Mooring, Buoy	Mooring, Buoy CTDs, AUV/ROV	Float
Max Depth	~1000m?	Surface	3000m	3000m	~2000m?
Principles	Spectrophotometric	Infra-red	Conductimetric	Spectrophotometric	Conductimetric

ALKALINITY SENSOR TECHNOLOGIES

	SAMI-Alk	**TAACT**	**Durafet-coulometry**	**CHANOS-Alk**
Parameters measured	Alk	Alk	Alk pH	Alk
Alk Uncertainty (±μmol kg^{-1})	8.4	2.0	?	1.0-2.0
Sampling Frequency (mins)	~12	~10?	~10?	~10
Platforms	Mooring, Buoy	Underway	Mooring, Buoy	Underway and lab
Principles	Spectrophotometric	Spectrophotometric	Coulometric	Spectrophotometric

Summery

- ✓ pH and pCO_2 sensors are more robust and versatile; operational
- ✓ DIC and Alk sensors are improving
- ✓ DIC sensors seems to be the next for operation; the methods are relatively robust (acid, less prone to fouling)
- ✓ Simultaneous in-situ measurements are emerging
- ✓ Smaller and cheaper; Microfluidic

Areas that need improvements…

- ✓ In-situ calibration or quality control
- ✓ High-frequency sensors are limited, and limited deployments on mobile platforms (e.g., AUVs, profilers, gliders)
- ✓ Expert use vs. scientist use
- ✓ Reliability: Fouling, pumps, valves, consumables…
- ✓ Theoretical issues: e.g., low salinity pH; Org Alk
- ✓ Funding the development, but not improvement…

Thank you!