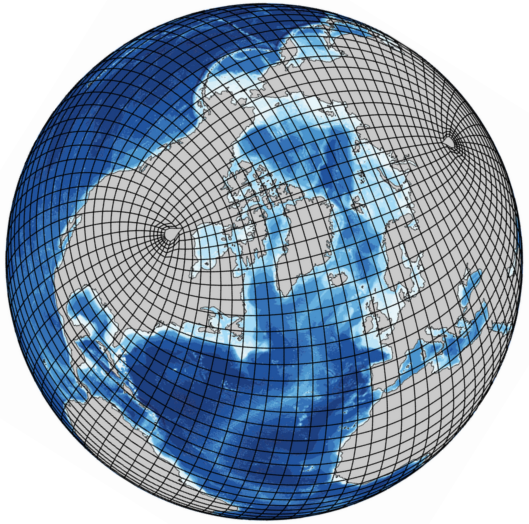
Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

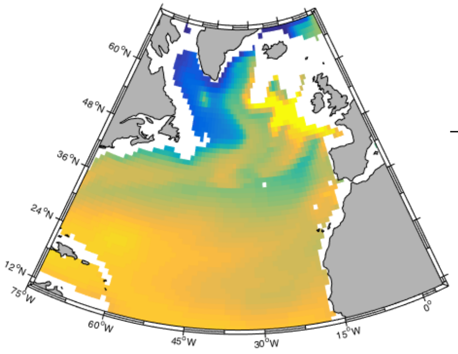
Does SOCAT capture the annual variability in surface fCO_2?

Introduction to **Observation System Experiments (OSEs):**

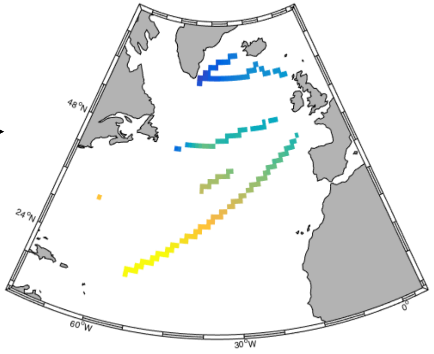
Models are numerical tools that are perfectly defined at each time steps and grid grid cells of the model's resolution. They therefore act as a tools to explore sampling uncertainties.



Model data



Subsample the model data like pCO2 observation coverage



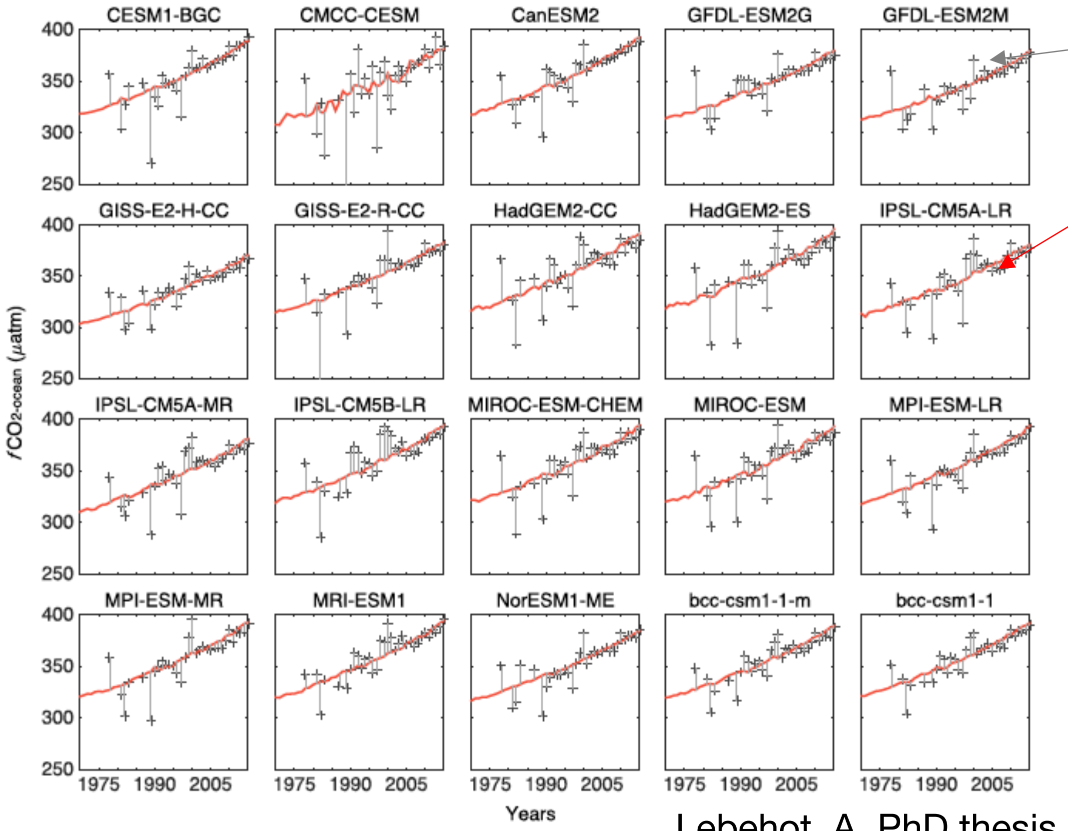
Virtual research voyages can also be added to the model subsampling stage, to see the impact and importance of improving observational coverage to capture the mean and variability of the studied field.

Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

Does SOCAT capture the annual variability in surface fCO_2?

Case-study in the North Atlantic, **using OSEs**.

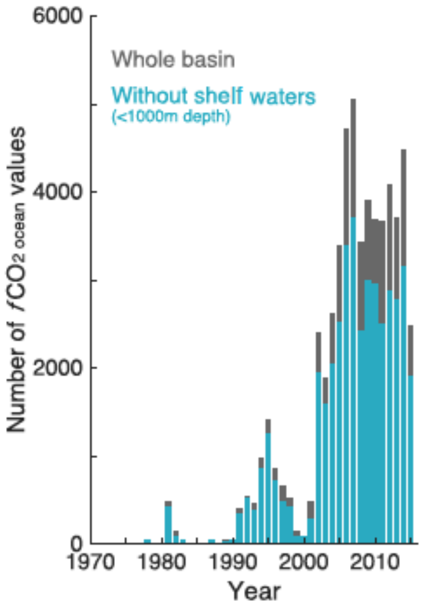


Lebehot, A. PhD thesis

Annual means from sampled model-field. A sampling that follows the observational coverage in SOCAT version 4.

Annual means from complete model-field (no-subsampling).

As more data is collected in the North Atlantic (and spread across the basin), the more we capture the interannual-decadal variability.
Note that the North Atlantic is one of the most sampled basins.



Ocean CO_2: Theory and Observations

The Oceanography of CO_2

Part 1: Observing ocean biogeochemistry

1. Introduction
2. Observing surface pCO_2
3. Observing column DIC and TA
4. Observing pH

Part 2: Conceptual patterns and mechanisms of ocean biogeochemistry

1. Air-Sea CO_2 exchange
2. Biological processes

UCT, SOCCO-CSIR

pmonteir@csir.co.za; alice.Lebehot@uct.ac.za

22.05.2019

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

QUIZ #1

When collecting seawater for DIC and TA measurements, it is important to:

A. Collect the sample shortly after the Niskin bottle is open
B. Make sure that there is no bubbles in the sampling bottle
C. Fill up the sampling bottle completely (no air space)
D. Add mercuric chloride right after sampling

Explain your choice.

GO TO WWW.MENTI.COM & USE CODE 69 991

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

QUIZ #1

When collecting seawater for DIC and TA measurements, it is important to:

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D. Add mercuric chloride right after sampling

Explain your choice.

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

QUIZ #2

To remove DIC in seawater and turning it to CO_2 in the gas phase, one needs to:

A. Warm up the sampling bottle to 100 degree Celsius
B. Shake the sampling bottle
C. Add acid
D. Progressively lower the temperature of the sample to its original water mass temperature

Explain your choice.

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

QUIZ #2

To remove DIC in seawater and turning it to CO_2 in the gas phase, one needs to:

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Explain your choice.

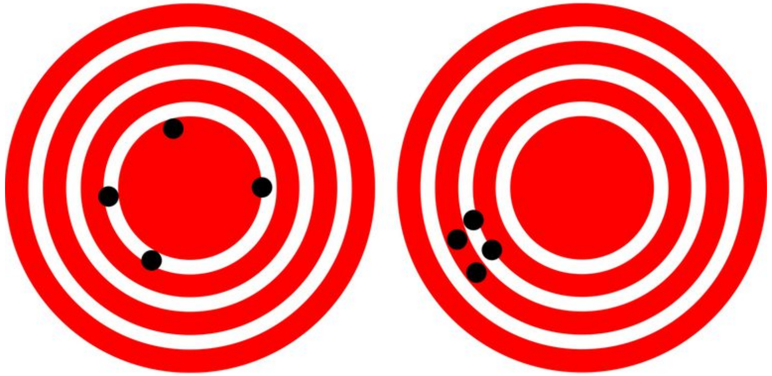
Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

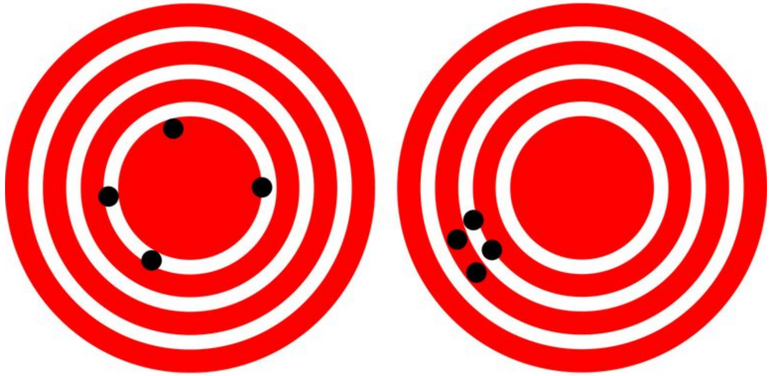
QUIZ #3

What’s the difference between precision and accuracy?

A. Accuracy Precision



B. Precision Accuracy



Part 1: Observing ocean biogeochemistry

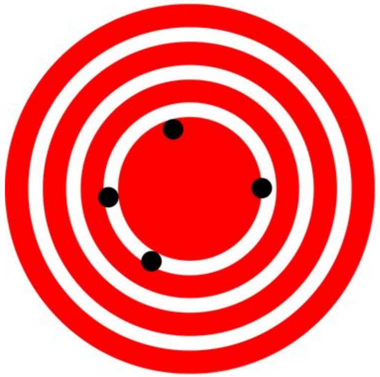
3. Observing column DIC and TA

QUIZ #3

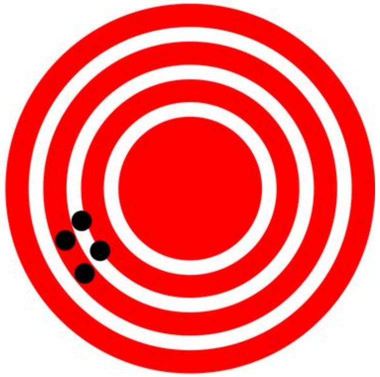
What’s the difference between precision and accuracy?

A.

Accuracy



Precision

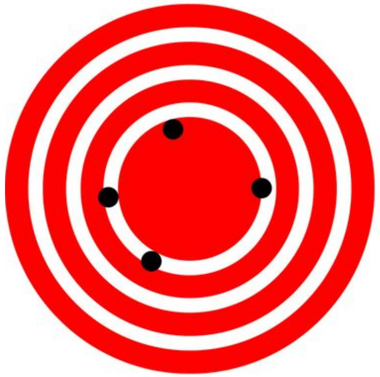


How close is the measurement to the (unknown) true value?

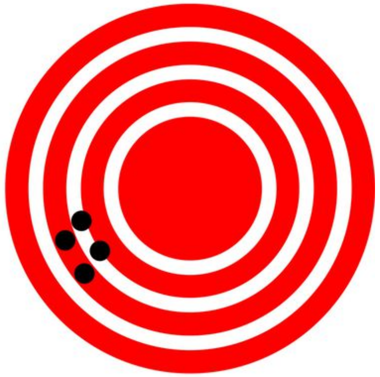
How reproducible is a measure within the same experimental design?

B.

Precision



Accuracy



Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

QUIZ #4

What happens when we sample replicate bottles?

A. We allow to test the precision of our measurements.
B. We allow to test the accuracy of our measurements.
C. We are able to get a measurement if a technical issue occurs with the first replicate.
D. If replicates are both analysed, we increase the cost and the analysis time, which ultimately impacts the amount of analysed new samples.

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

QUIZ #4

What happens when we sample replicate bottles?

A. We allow to test the precision of our measurements.
B. We allow to test the accuracy of our measurements.
C. We are able to get a measurement if a technical issue occurs with the first replicate.
D. If replicates are both analysed, we increase the cost and the analysis time, which ultimately impacts the amount of analysed new samples.

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How is DIC and TA measured in the ocean?

All Sampling and Measurements guidelines are described as **Standard Operation Procedures** (SOP), by Dickson et al., 2007.

Guide to Best Practices for Ocean CO_2 Measurements

PICES SPECIAL PUBLICATION 3

IOCCP REPORT No. 8

October 2007

Edited by
Andrew G. Dickson, Christopher L. Sabine, James R. Christian

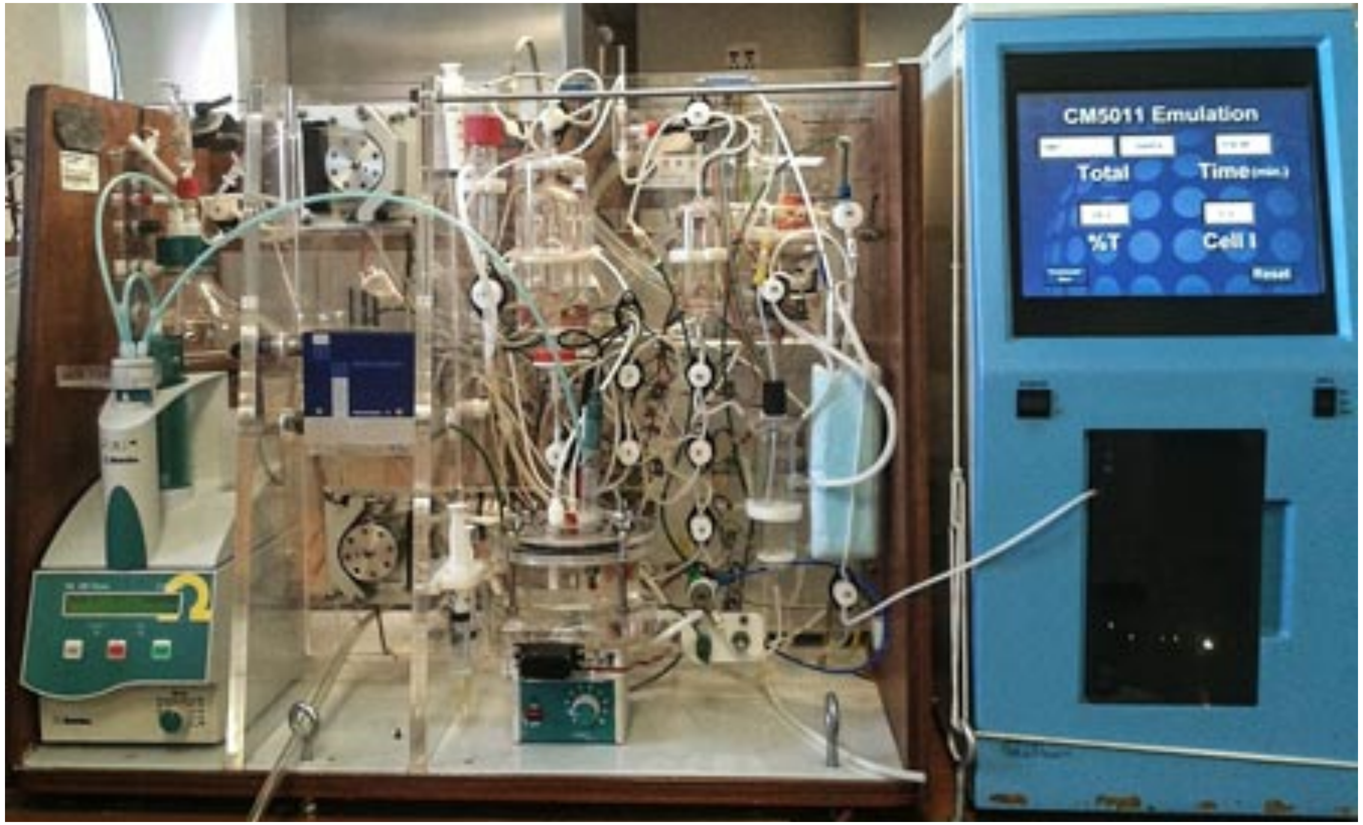
Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How is DIC and TA measured in the ocean?

DIC and TA are measured with Versatile INstruments for the Determination of Titration Alkalinity (VINDTA; Marianda, Kiel, Germany), discrete sampling.

DIC is measured via **coulometric titration**, after the sub-sample is acidified and the CO2 gas is transported with (usually) nitrogen and dried (with a Peltier) with via coulometry (here). Note that DIC can also can also be measured with a **infrared gas analyser** (as opposed to a coulometer).



Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

How is DIC and TA measured in the ocean?

TA is usually determined from the titration of sea water (in a closed cell) with a solution of hydrochloric acid. Note that the acid solution is made with NaCl to approximate the ionic strength of seawater to maintain the activity coefficients to approximate constant values during the measurement. The closed cell allows to assume that DIC is constant (neglecting the effect of the titration that dilutes DIC in the sample), although the coulometric method (SOP 2) is more accurate to determine DIC.

TA is derived from the titrant volume and e.m.f.(electromotive force) data (Dickson et al., 2007).

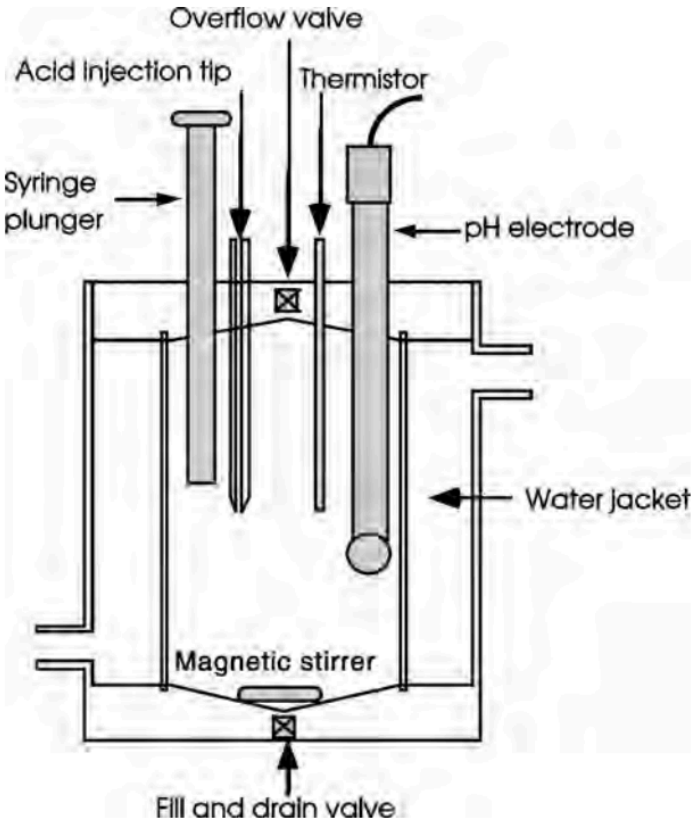


Fig. 1 Closed titration cell for the determination of alkalinity.

(Dickson et al., 2007)

Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

What are the challenges to provide high-quality DIC & TA data?

(1) Sampling Strategy

- vertical sampling limited at each station to the number of Niskins available
- faulty Niskins impact vertical resolution

Challenge when dealing with discrete data is to provide a representative “snapshot” of the carbonate system by finding an appropriate horizontal/vertical sampling resolution, which is constrained by number of available Niskins, the duration of the voyage and often limited time allocated for sample analysis.

Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

What are the challenges to provide high-quality DIC & TA data?

(1) Sampling Strategy
(2) First Quality Control

First QC aims at identifying outliers due to technical or instrumental issues and at discerning the “Acceptable” to the “Questionable” data.

- Allow any technical or instrumental issues to be addressed immediately
- Exhaustive laboratory investigations are often constrained by limited on-board time
- Ultimately rely on the experience/intuition of the on-board carbon team in identifying questionable or suspicious instrumental behaviour.

Part 1: Observing ocean biogeochemistry

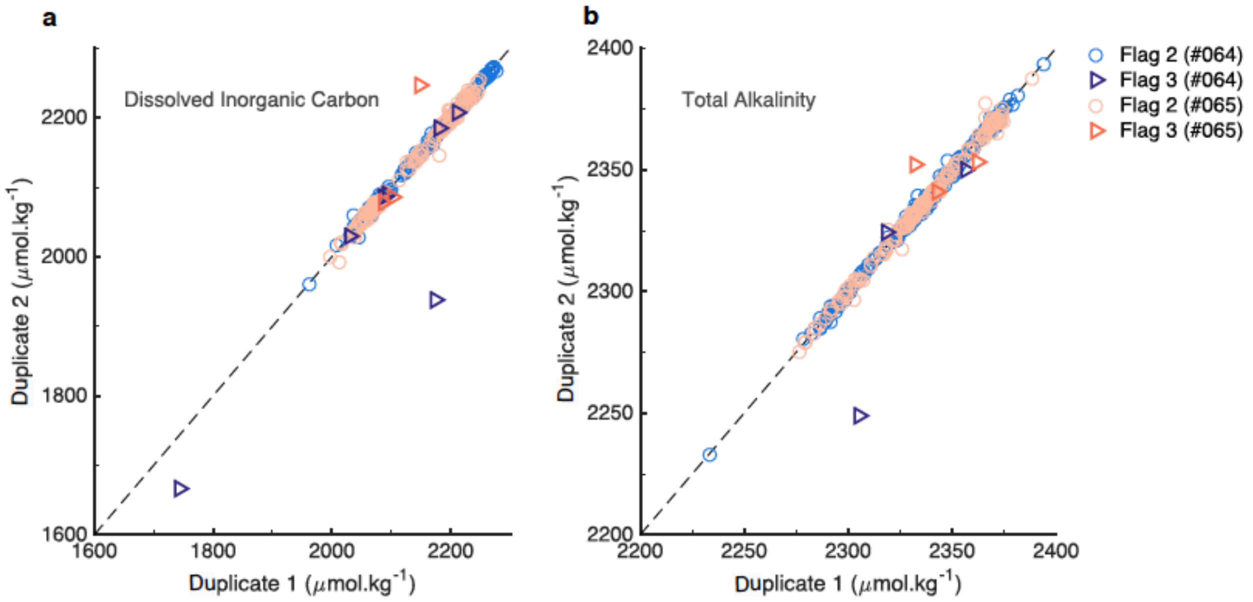
3. Observing column DIC and TA

What are the challenges to provide high-quality DIC & TA data?

(1) Sampling Strategy
(2) First Quality Control
(3) Precision Analysis

The precision of DIC and TA measurements is determined through the comparison of duplicate results (SOP 2, 3; Dickson et al., 2007).

- Due to time restrictions, duplicate analysis achieved on few samples per station.
- If two different results between duplicates: is this difference due to poor precision or to a specific experimental issue? Which one is likely to be closest to the unknown truth?
- Precision can vary across machines (unlike what is stated by manufacturer)



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Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

What are the challenges to provide high-quality DIC & TA data?

(1) Sampling Strategy
(2) First Quality Control
(3) Precision Analysis
(4) Calibration

Certified Reference Materials (CRMs) were created in 1995, providing to this day the highest degree of precision and accuracy standards (Key et al., 2004) and have been used ever since (A. Dickson, Scripps Institution of Oceanography, USA). The DIC and TA values provided by the CRM batch reference (treated as the truth) are compared to the values returned by the devices. This comparison allows the quantification of the instrumental offset (hence calibration).

- Due to time and cost constrains, CRMs cannot be analysed between each samples.
- Calibration is done to the nearest-in-time analysed CRMS, which might not be appropriate when there is a significant drift in the instrumental offset.

Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

What are the challenges to provide high-quality DIC & TA data?

(1) Sampling Strategy
(2) First Quality Control
(3) Precision Analysis
(4) Calibration
(5) Second Quality Control

The 2nd level QC identified, through cross-over analyses, potential systematic biases in the collected data with reference to historical measurements (Lauvset and Tanhua, 2015).

- Comparison assumes that (1) within the observational-record timescales, the deep water properties remain invariant, and (2) the previous voyages are bias-corrected (questionable, especially for pre-CRM era data).

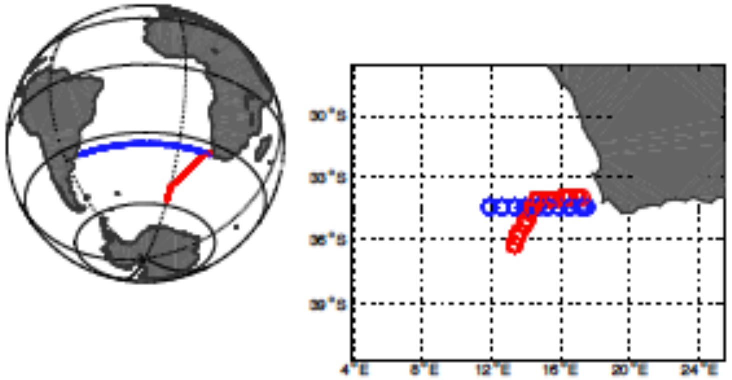
Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

What are the challenges to provide high-quality DIC & TA data?

(1) Sampling Strategy
(2) First Quality Control
(3) Precision Analysis
(4) Calibration
(5) Second Quality Control

Example of a cross-over analysis (cruise MSM060):



Additative offset

max distance [km] 222

weighted offset -2.13663

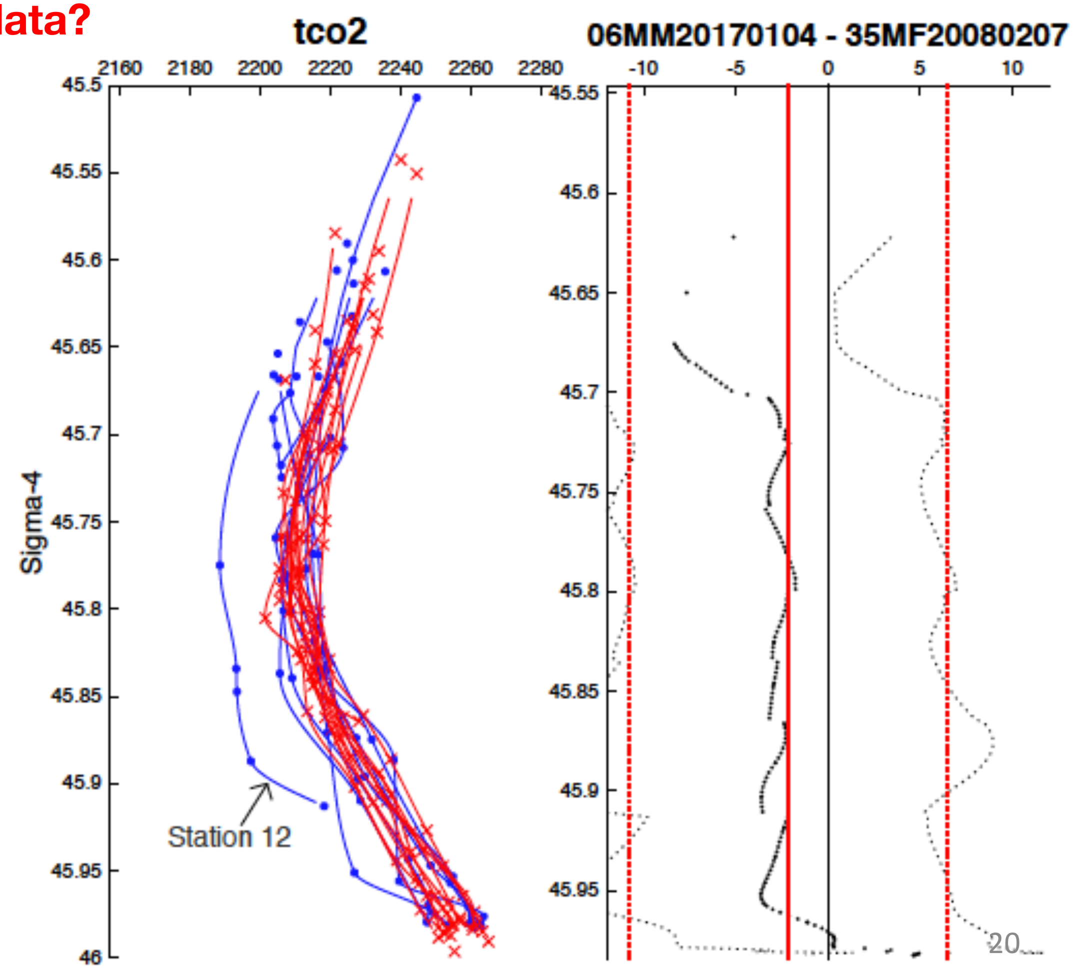
weighted stddev 8.62079

samples C1 (blue) 68

samples C2 (red) 119

stations C1 (blue) 13

stations C2 (red) 14



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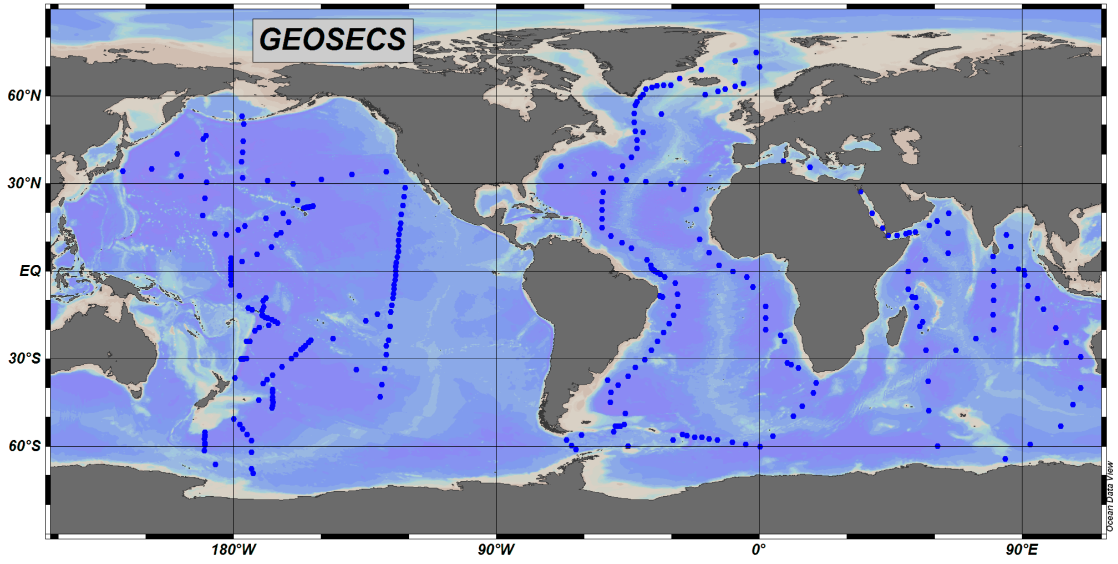
Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

What are the platforms that measure DIC and TA?

Repeated hydrographic sections allows to capture the change in global DIC and TA.

Over the past decades, joint international efforts have led to increased in-situ oceanographic measurements throughout the basins and depths, providing an extremely valuable resource for documenting the changing state of the oceans (Talley et al., 2016).

(1) The Geochemical Ocean Sections (**GEOSECS**) programme (Craig and Gordon, 1972) achieved in the 1970s. While this collaborative initiative has set the baseline of our current knowledge of marine biogeochemistry (e.g. Stuiver et al., 1983), the **lack of robust accuracy standards** at the time led to occasionally inaccurate DIC and TA measurements (Key et al., 2004; Olsen et al., 2016).

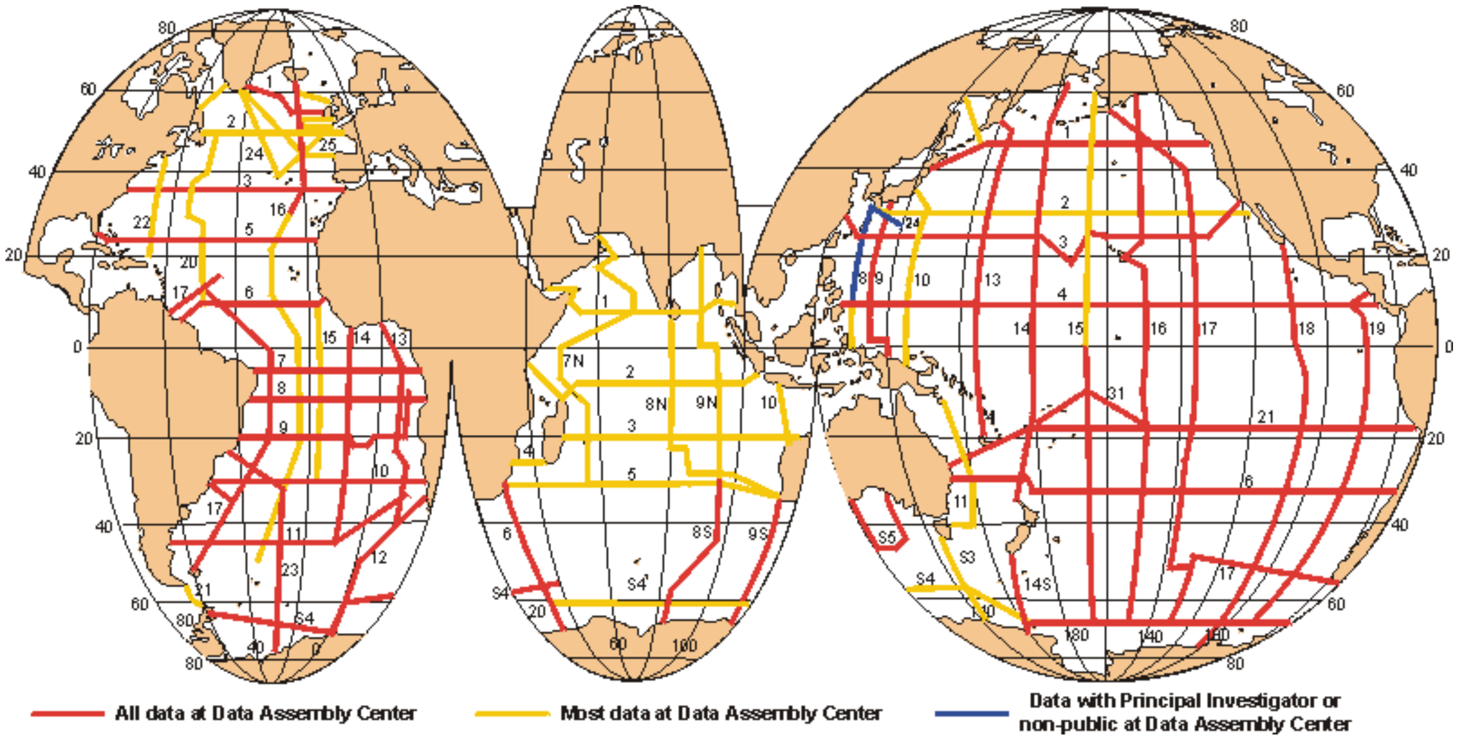


Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

What are the platforms that measure DIC and TA?

(2) The World Ocean Circulation Experiment (**WOCE**) in the 1990s, a global survey that significantly contributed to the extension of repeated hydrographic sections and to the use of a variety of devices (e.g. floats, moorings) (WOCE, 2002).

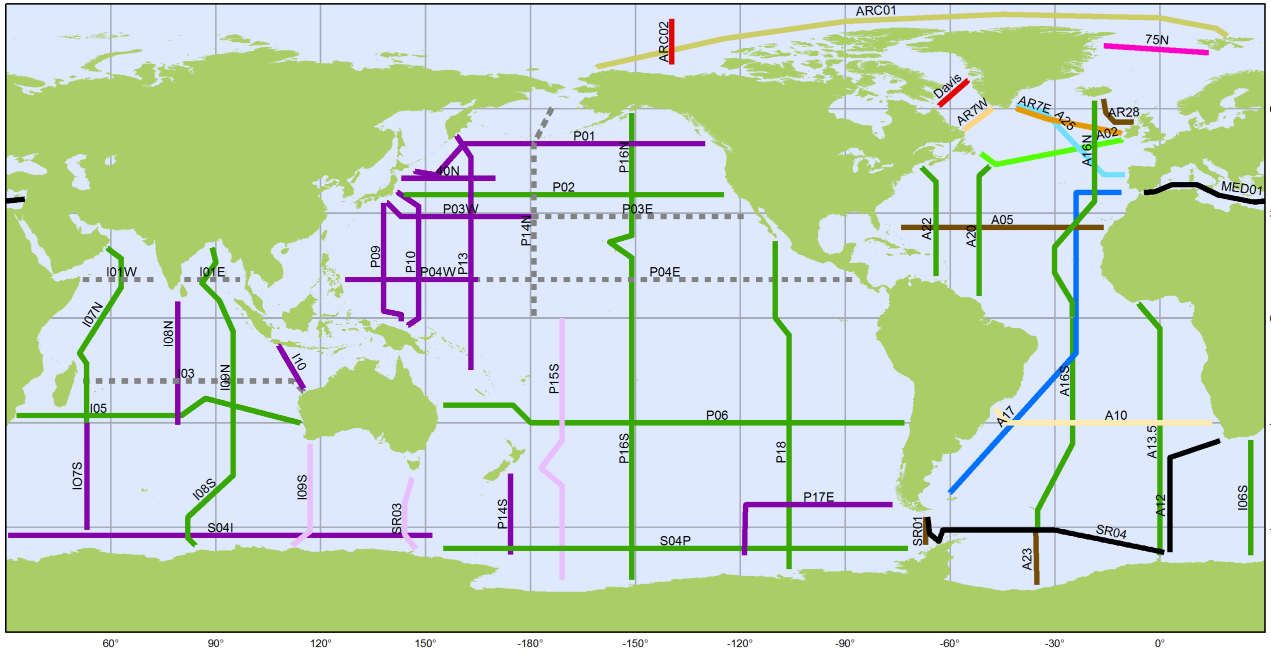


Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

What are the platforms that measure DIC and TA?

(3) More recently, the Climate and Ocean: Variability, Predictability and Change (**CLIVAR**) / Global Ocean Ship-based Hydrographic Investigations Program (**GO-SHIP**) survey has also defined hydrographic sections to be repeated on a decadal frequency, to quantify the interior decadal variability of the seawater CO_2 system, among other oceanographic variables (Talley et al., 2016).



GO-SHIP — 2012-2023 Survey (55 Core Lines): Lines by Nation — October 2018

AUS, ESP, IRE, NOR-UK, USA-GER, CAN-USA, FRA-ESP, JAP, UK, USA-UK-GER, CAN-UK, GER, NOR, USA, nil

Generated by www.jcommops.org, 16-Oct-18

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How are the observations gathered for easy public use?

The Global Ocean Data Analysis Project (**GLODAP**) grids global DIC and TA data into climatologies.

https://www.glodap.info/

Earth Syst. Sci. Data, 8, 325–340, 2016
www.earth-syst-sci-data.net/8/325/2016/
doi:10.5194/essd-8-325-2016

Open Access Earth System Science Data

A new global interior ocean mapped climatology: the 1° x 1° GLODAP version 2

Siv K. Lauvset[1,2], Robert M. Key[3], Are Olsen[1,2], Steven van Heuven[4], Anton Velo[5], Xiaohua Lin[3], Carsten Schirnick[6], Alex Kozyr[7], Toste Tanhua[6], Mario Hoppema[8], Sara Jutterström[9], Reiner Steinfeldt[10], Emil Jeansson[2], Masao Ishii[11], Fiz F. Perez[5], Toru Suzuki[12], and Sylvain Watelet[13]

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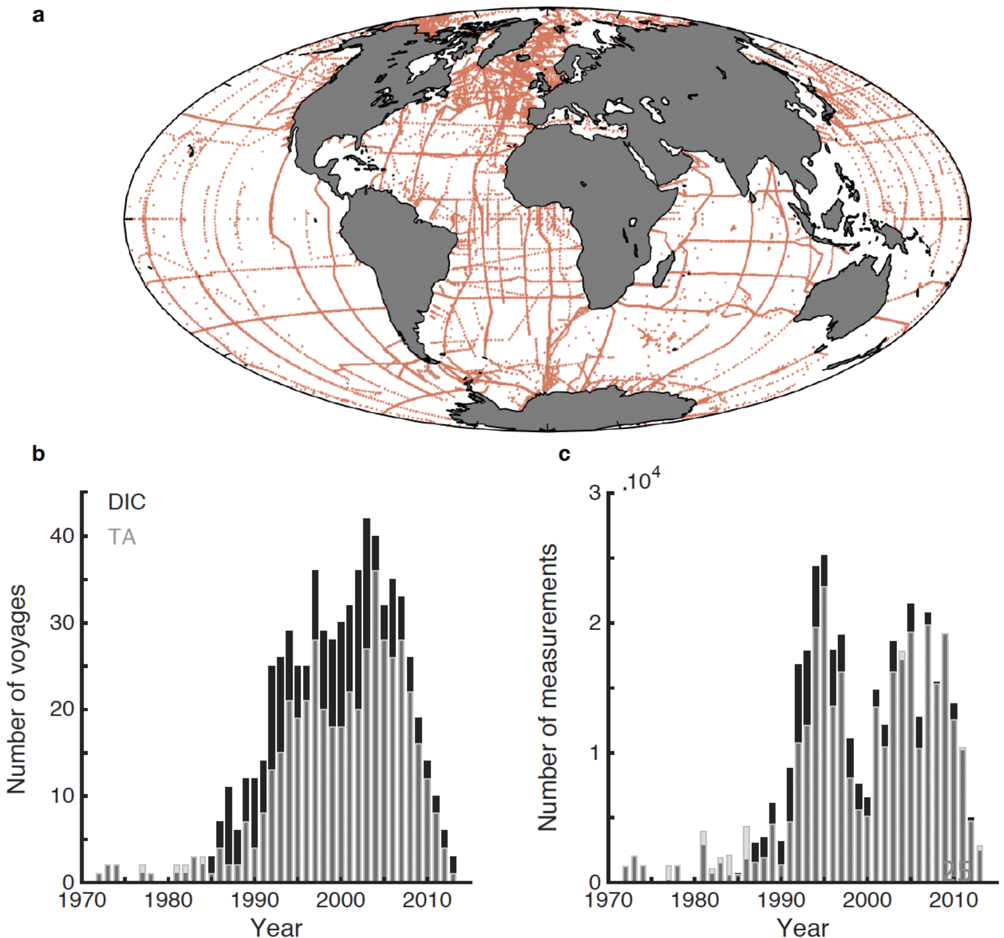
[2]Uni Research Climate, Bjerknes Centre for Climate Research, Allegt. 55, 5007 Bergen, Norway
[3]Atmospheric and Oceanic Sciences, Princeton University, 300 Forrestal Road, Sayre Hall, Princeton,

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How are the observations gathered for easy public use?

The limited temporal and spatial coverages of the various research programmes, as well as their different measurement standards between the periods prior and after the SOP and CRM era, has led to relatively **heterogenous biogeochemical *in-situ* data**. To provide a useful DIC and TA dataset for model evaluation studies, as well as for understanding the current state of the global ocean carbon cycle, **the main challenge for the GLODAP community was therefore to uniformly merge these measurements.**



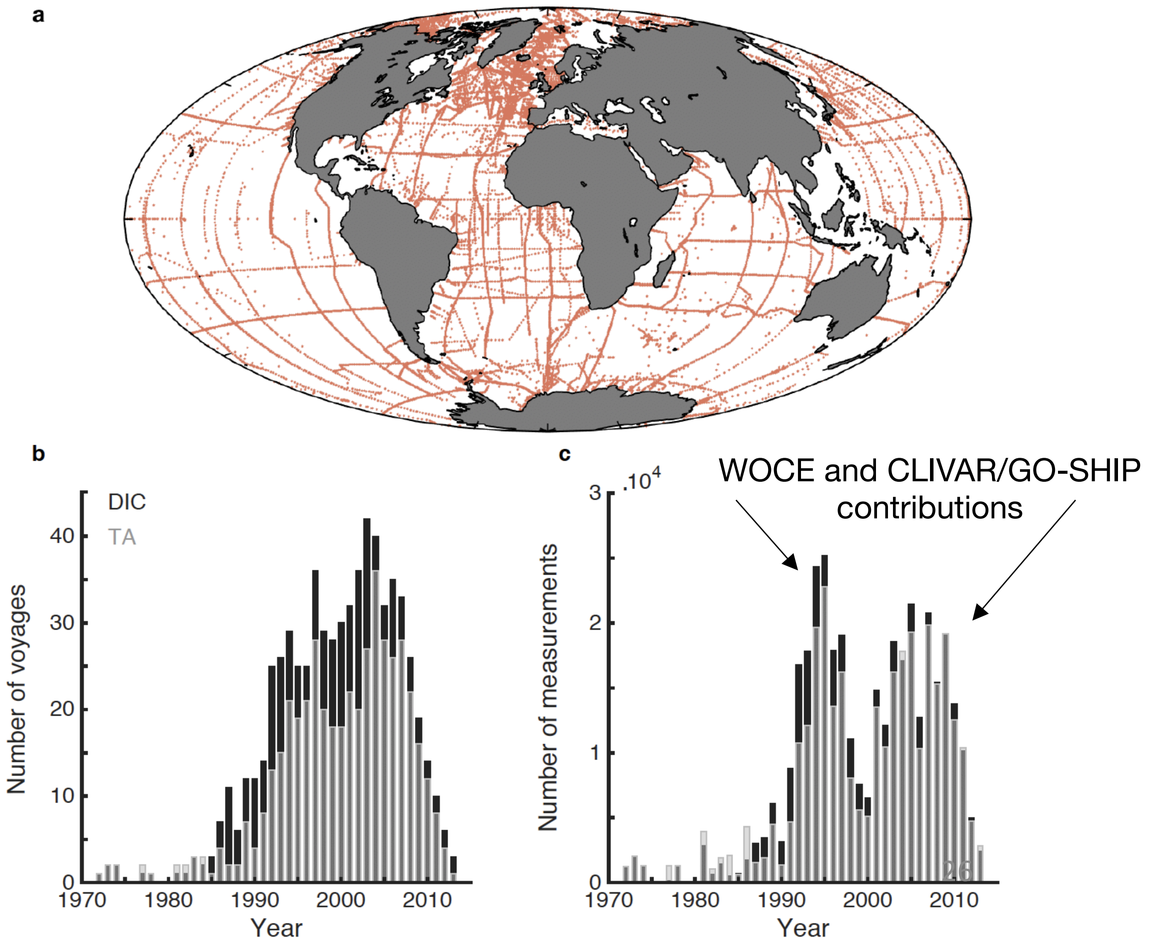
Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How are the observations gathered for easy public use?

From 1972 to 2013, a total of 689,279 DIC and TA measurements were globally integrated in GLODAPv2, of which ~22% were taken from the top 100 m of the water column and ~56% measured in the Northern Hemisphere.

Over the 42 years of data collection, more DIC than TA measurements were made on average.



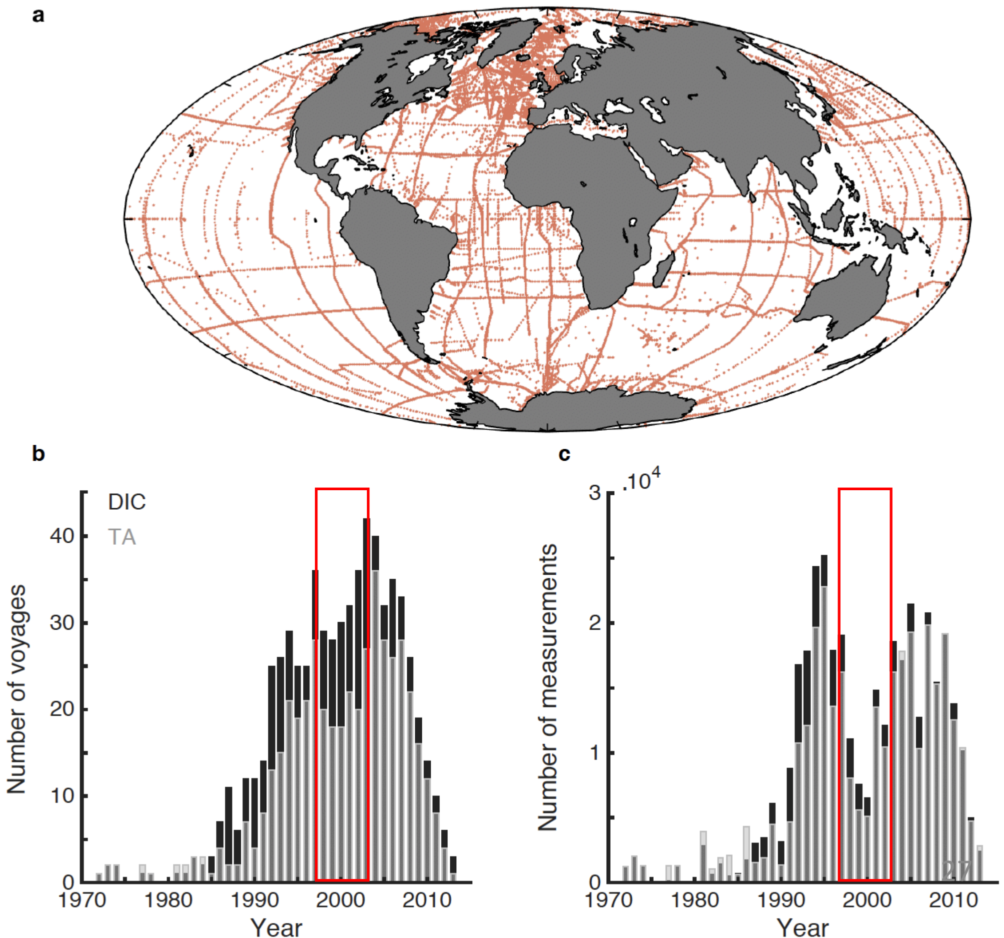
Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How are the observations gathered for easy public use?

Interestingly, the number of measurements dropped slightly prior to 2000 while there is no corresponding drop in the number of voyages.

The lack of consistent correlation between the numbers of voyages and measurements also highlights the “trade off” between improving the spatial gaps across the basins and improving the horizontal and vertical resolution in a transect. However, the mismatch observed prior 2000 could have also been due to more specific reasons, such as poor weather conditions leading to fewer stations or poor quality data which were then flagged out.



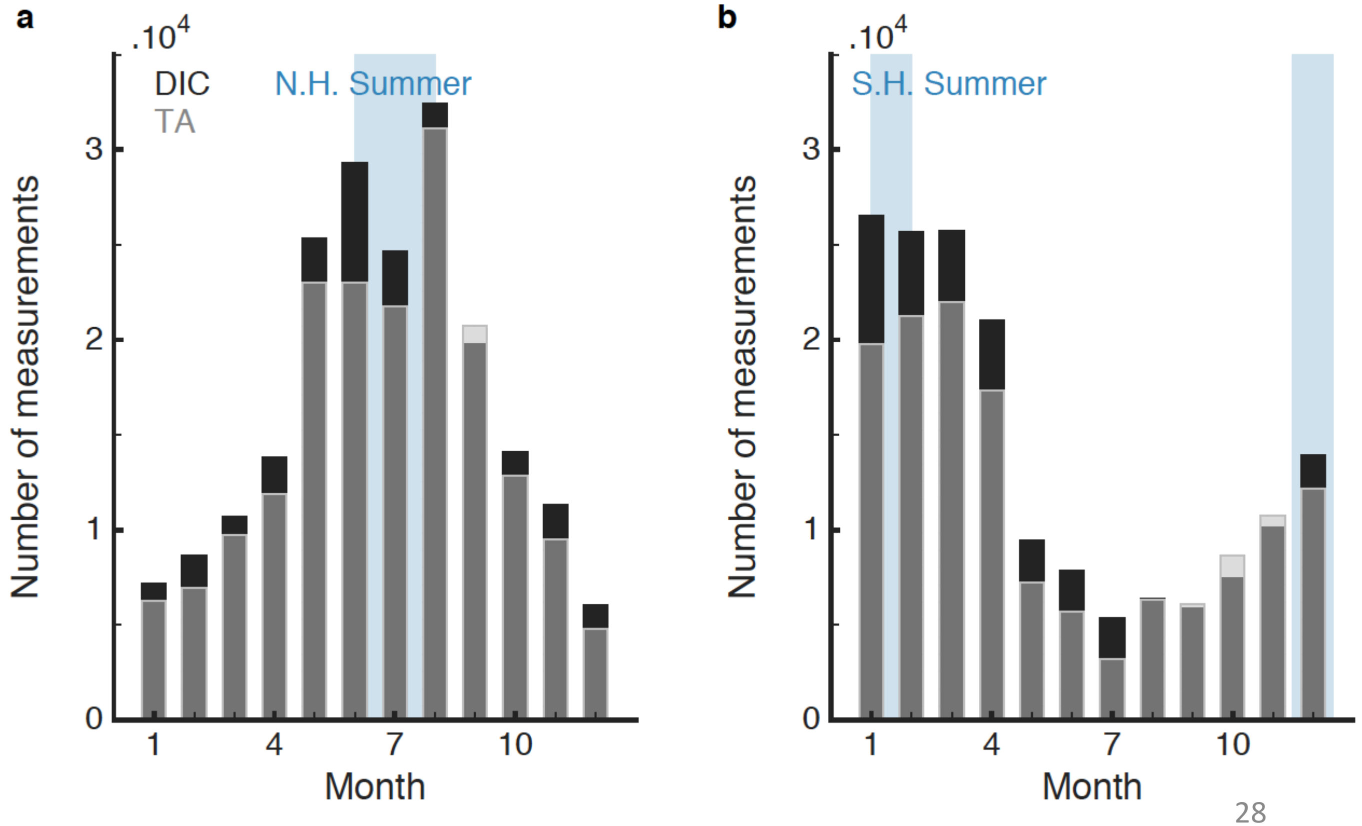
Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How are the observations gathered for easy public use?

The total number of winter DIC & TA measurements is about 4 times lower than in the summer (due to challenging winter sea weather conditions, particularly at the high latitudes) (Lauvset et al., 2016).

Unless the next decades of global observations become evenly spread across seasons with potential development of biogeochemical floats (e.g. Monteiro et al., 2015), tackling the seasonal bias within the next generation of GLODAP will surely be a challenging task.



Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How are the observations gathered for easy public use?

GLODAP summarises discrete oceanic in-situ measurements of a selection of physical and biogeochemical variables into **interpolated climatologies** (Key et al., 2015; Lauvset et al., 2016; Olsen et al., 2016), which has been particularly appreciated by the modelling community for **model evaluation** purposes (e.g Ilyina et al., 2013).

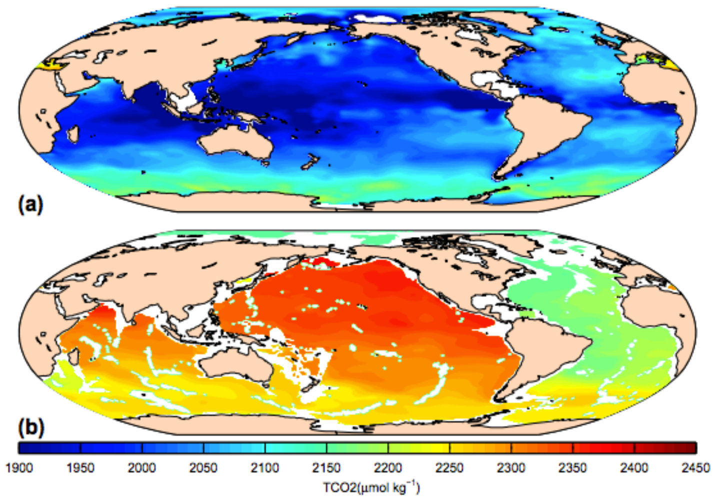


Figure 3. Mapped climatology of TCO_2 at 10 m **(a)** and 3000 m **(b)**.

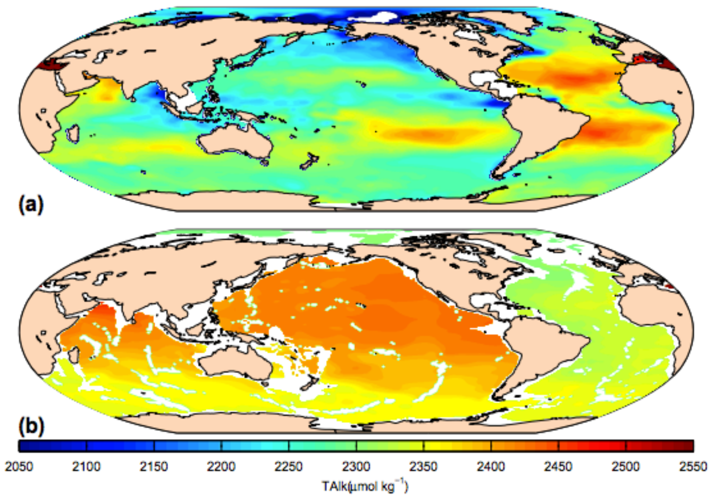


Figure 4. Mapped climatology of TAlk at 10 m **(a)** and 3000 m **(b)**.

Lauvset et al., 2016

Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

How are the observations gathered for easy public use?

GLODAP also provides errors estimates on their interpolated product.

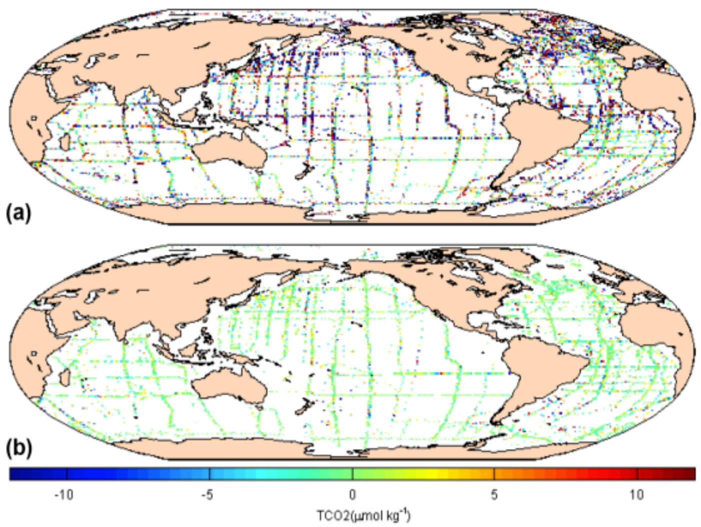


Figure 6. Difference between the gridded TCO_2 input data and the mapped climatologies at 10 m **(a)** and 3000 m **(b)**.

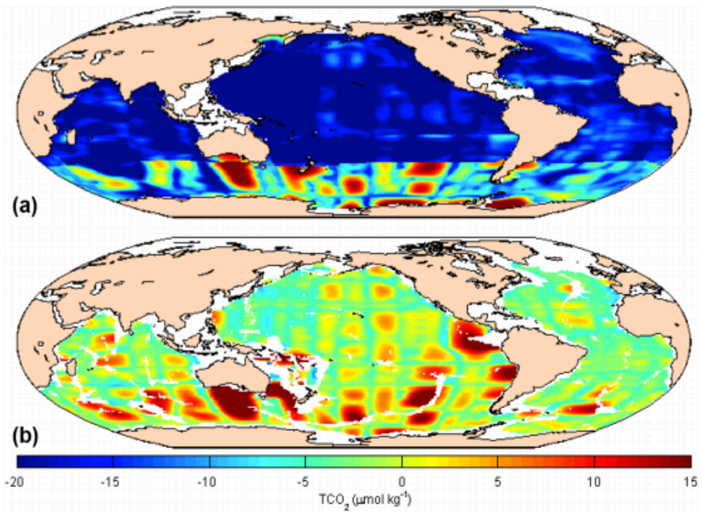


Figure 12. Mapping error for TCO_2 in GLODAPv2.2016b minus mapping error for TCO_2 in GLODAPv1.1 at 10 m **(a)** and 3000 m **(b)**. Note that the differences are mainly attributable to differences in method and not real reductions/increases in mapping error.

Lauvset et al., 2016

Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

How are the observations gathered for easy public use?

Main characteristics of GLODAP v1 (Key et al., 2014) and v2 (Lauvset et al., 2016):

GLODAP version	Voyages	Horizontal resolution	Depth levels	Climatology period	Variables	Mapping Method	References
1	116	$1^{\circ} \cdot 1^{\circ}$	33	1972-1999 except DIC, CFC $<$ 1.2 km : WOCE only	TA, DIC potential alkalinity anthropogenic CO_2 $\Delta^{14}C$ (bombed & natural) CFC-11, CFC-12 pCFC-11, pCFC-12	Optimal Interpolation	Key et al., 2004
2	724	$1^{\circ} \cdot 1^{\circ}$	33	1972-2013, for all variables except: pH, Ω_C, Ω_A, $< \sim 1$ km: 1986-1999 & 2000-2013 DIC normalised in 2002	DIC, TA, pH Ω_C, Ω_A, $CO_{2\text{-anthro}}$ nitrate, phosphate, silicate salinity, theta	DIVA	Key et al., 2015 Olsen et al., 2016 Lauvset et al., 2016

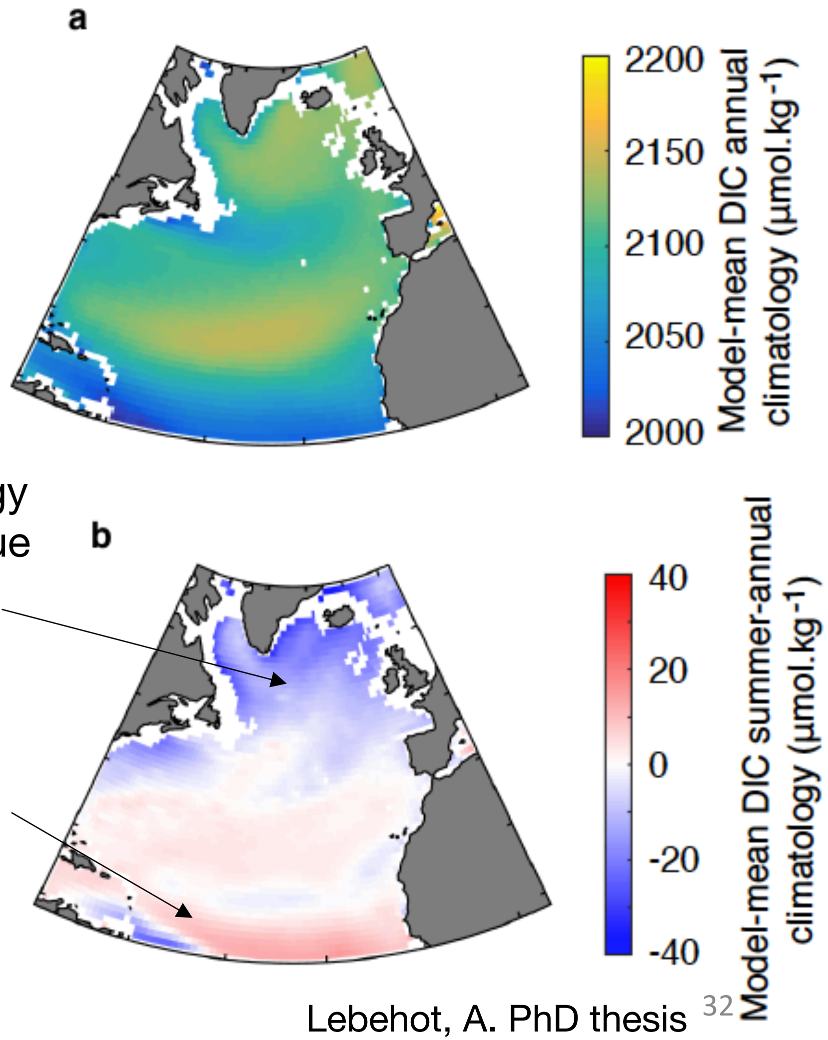
Note that a recent version of GLODAP v2 was recently released, integrating about 840 additional research campaigns within the climatologies (https://www.glodap.info/index.php/2016/05/19/update-2-2/)

Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

What's the impact of seasonal sampling bias on climatologies?

An hypothetical model case study:

	DIC
Summer climatology	averaging only summer months of modelled DIC from 1996-2008
Annual climatology	averaging all months of modelled DIC from 1996-2008



DIC summer climatology **underestimates** the true climatological state

DIC summer climatology **overestimates** the true climatological state

Lebehot, A. PhD thesis

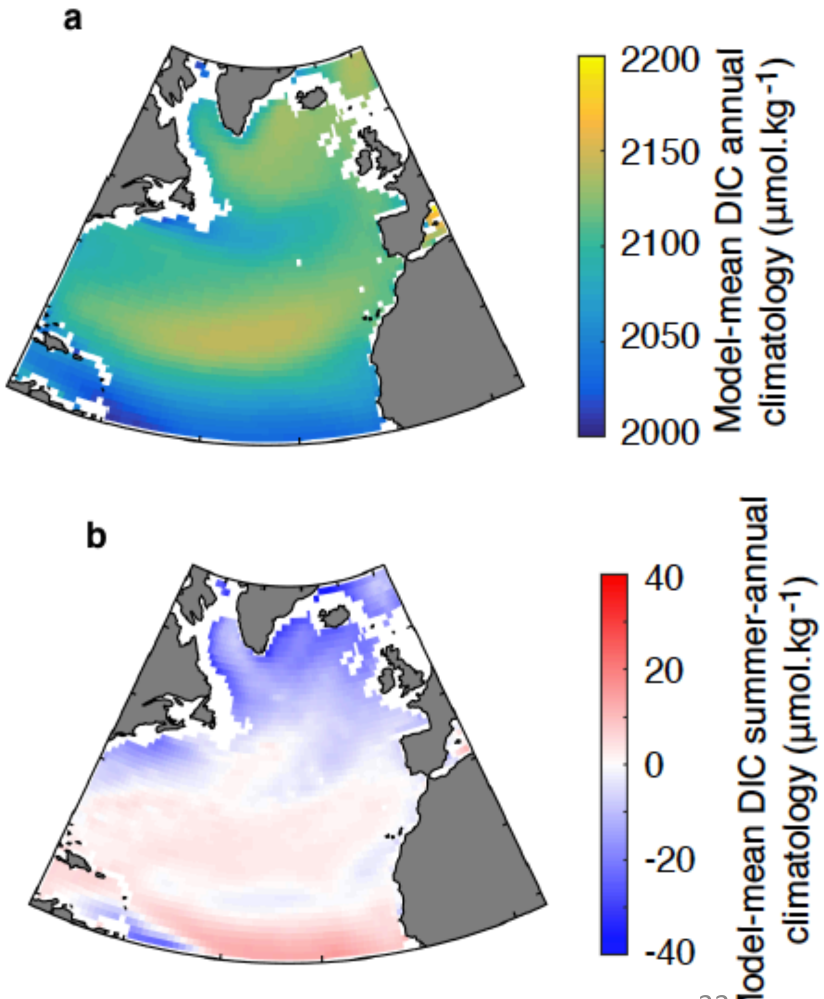
Part 1: Observing ocean biogeochemistry

3. Observing column DIC and TA

What's the impact of seasonal sampling bias on climatologies?

An hypothetical model case study:

The larger amplitude difference in the subpolar than in the subtropical gyre suggests that important physical and biogeochemical **mechanisms in the subpolar region are not captured by the summer months** (e.g. the entrainment of carbon enriched water to the surface occurring during the winter deepening of the mixed layer), while the mechanisms in the subtropical region are overall similar throughout the year.



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Part 1: Observing ocean biogeochemistry
3. Observing column DIC and TA

Synthesising observations into a high-quality product with minimal sources of uncertainties is challenging because:

1. measurements present some potential instrumental uncertainties and accuracy errors,
2. mapped products use interpolation techniques whose basin-wide uncertainties are unknown,
3. the data incorporated in those mapped products are irregularly distributed in both space and time, adding some potential biases toward regions and times which are more sampled than others,
4. derived observational products from interpolated products potentially lead to unrealistic results (through the accumulation of errors due to non-ideal ordering calculation steps).

As such, **observational products should not be treated as the true state of the system**, especially climatologies as they only represent a specific mean state.

Ocean CO_2: Theory and Observations

The Oceanography of CO_2

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Part 2: Conceptual patterns and mechanisms of ocean biogeochemistry

1. Air-Sea CO_2 exchange
2. Biological processes

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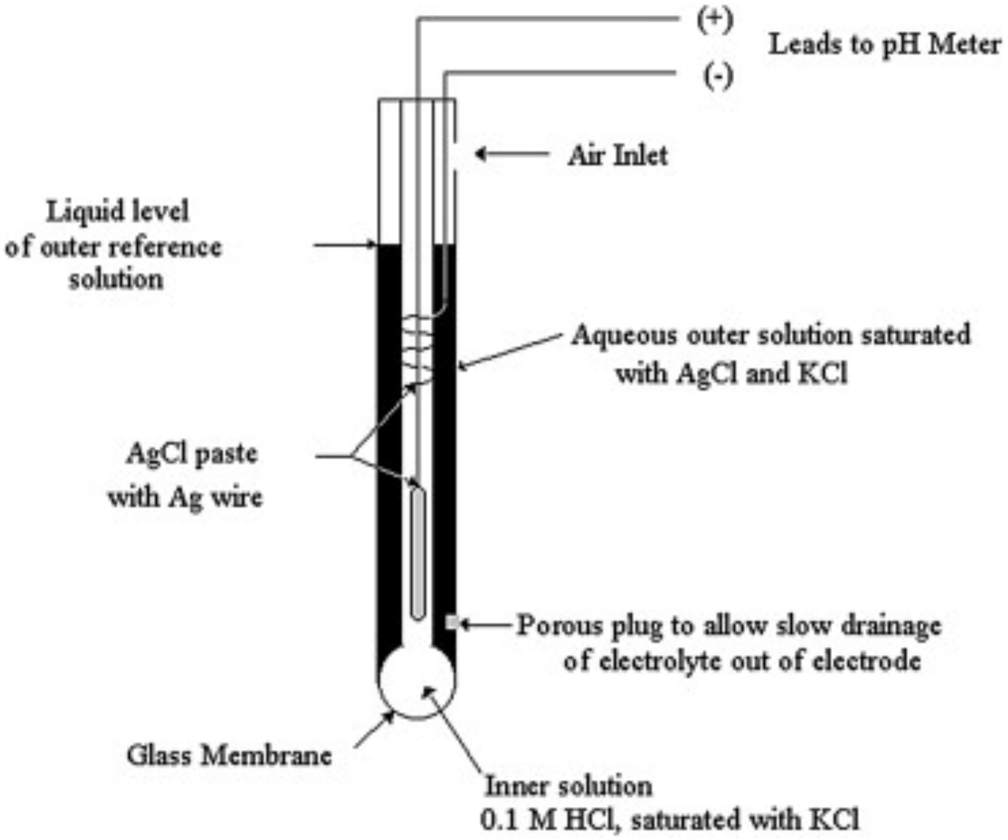
pmonteir@csir.co.za; alice.Lebehot@uct.ac.za

Part 1: Observing ocean biogeochemistry

4. Observing pH

A range of sensing techniques exist for pH sensors. See the International Ocean Carbon Coordination Project (www.ioccp.org), which maintains an online database with the current status of technology for carbonate chemistry instrumentation.

During TA titration, a glass pH probe is used = electric chemical cell with two electrodes (a reference electrode with a fixed potential in the outer tube and a glass electrode in the inner tube which as a potential that varies according to the solution). The electrical potential difference between the two electrodes sets the concentration of H+ in the seawater.
Ion selective probe, which respond to specific ions in the solution (here H+).



https://www.sciencedirect.com/topics/earth-and-planetary-sciences/glass-electrodes

Part 1: Observing ocean biogeochemistry

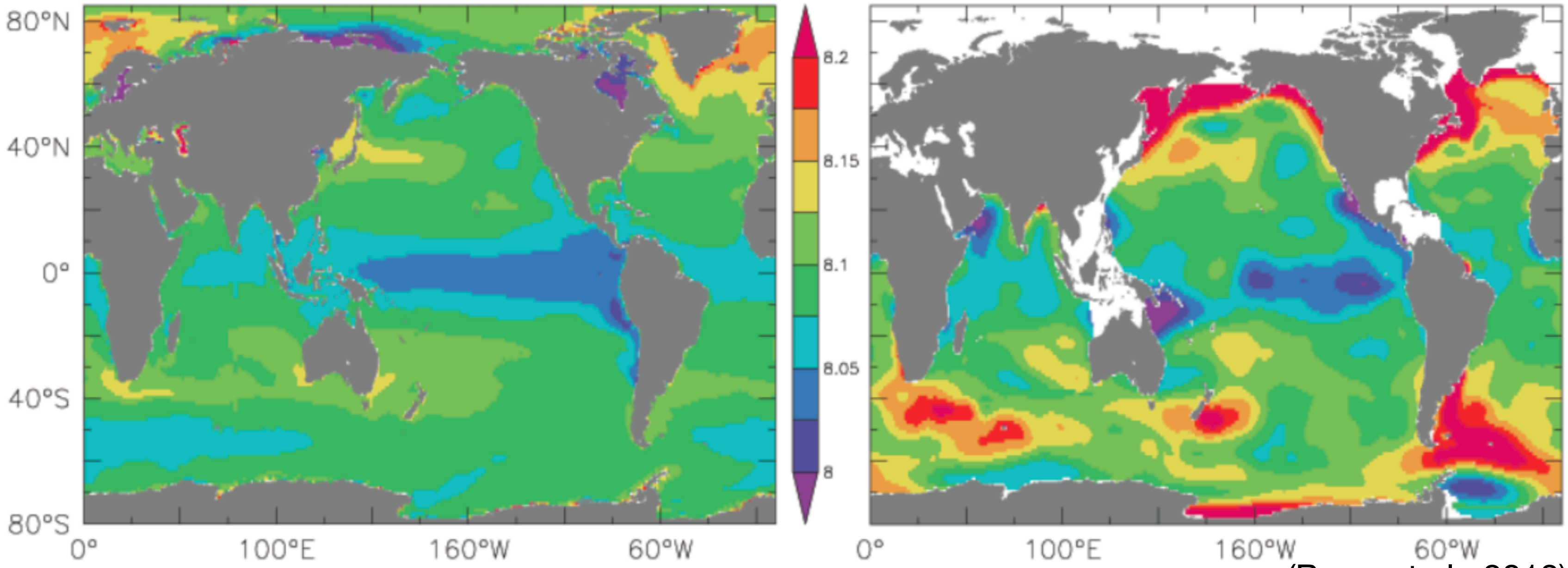
4. Observing pH

What's the impact of calculating pH climatology from DIC and TA climatologies?

pH climatology was not integrated in the version 1 of GLODAP (only bottle pH data was made available), which lead the community to various assumptions, e.g. in this model evaluation study:

Model-mean surface pH climatology (1990-1999)

Observation-based surface pH climatology using GLODAPv1



(Bopp et al., 2013)

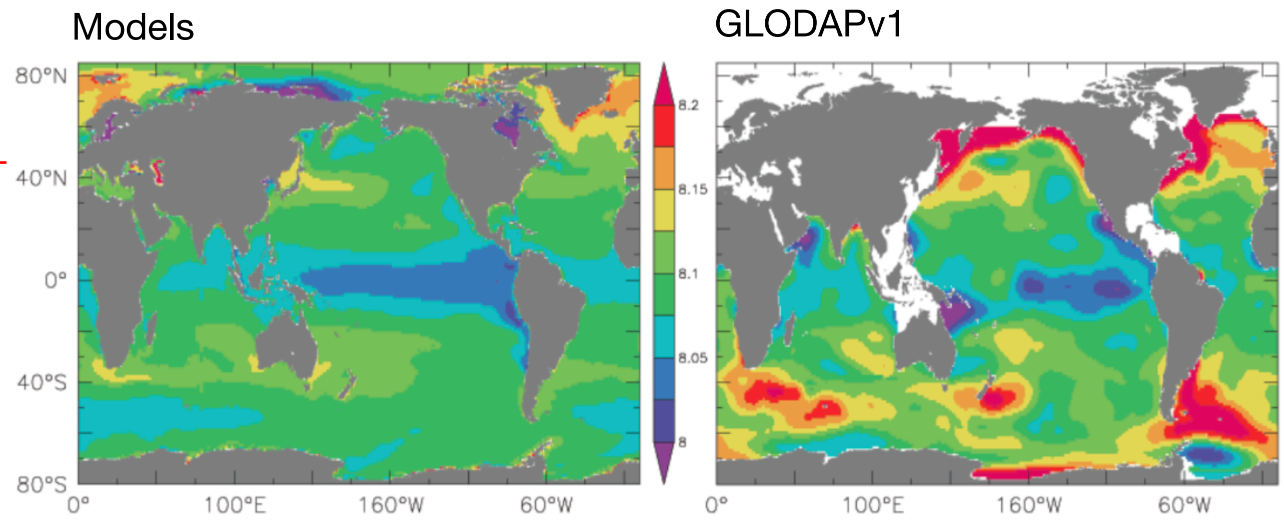
Part 1: Observing ocean biogeochemistry

4. Observing pH

QUIZ #5

From this figure, would you say that:

A. The models significantly underestimate the observed surface pH variability.
B. High latitude ocean is significantly more acidic than equatorial ocean.
C. Models certainly need to improve their simulation of surface pH.
D. None of the above.



Part 1: Observing ocean biogeochemistry

4. Observing pH

QUIZ #5

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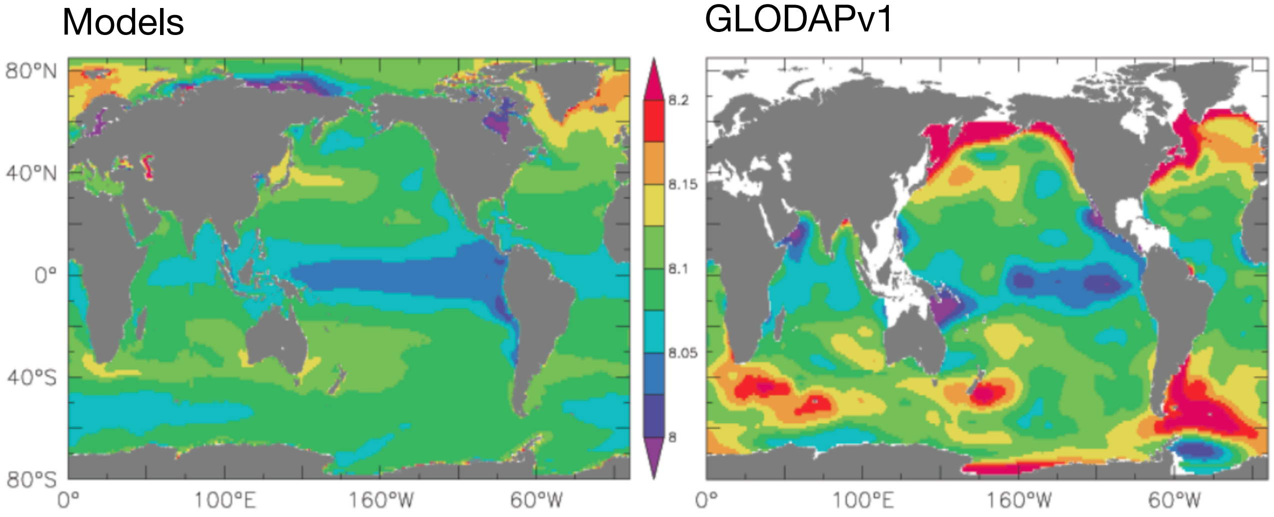
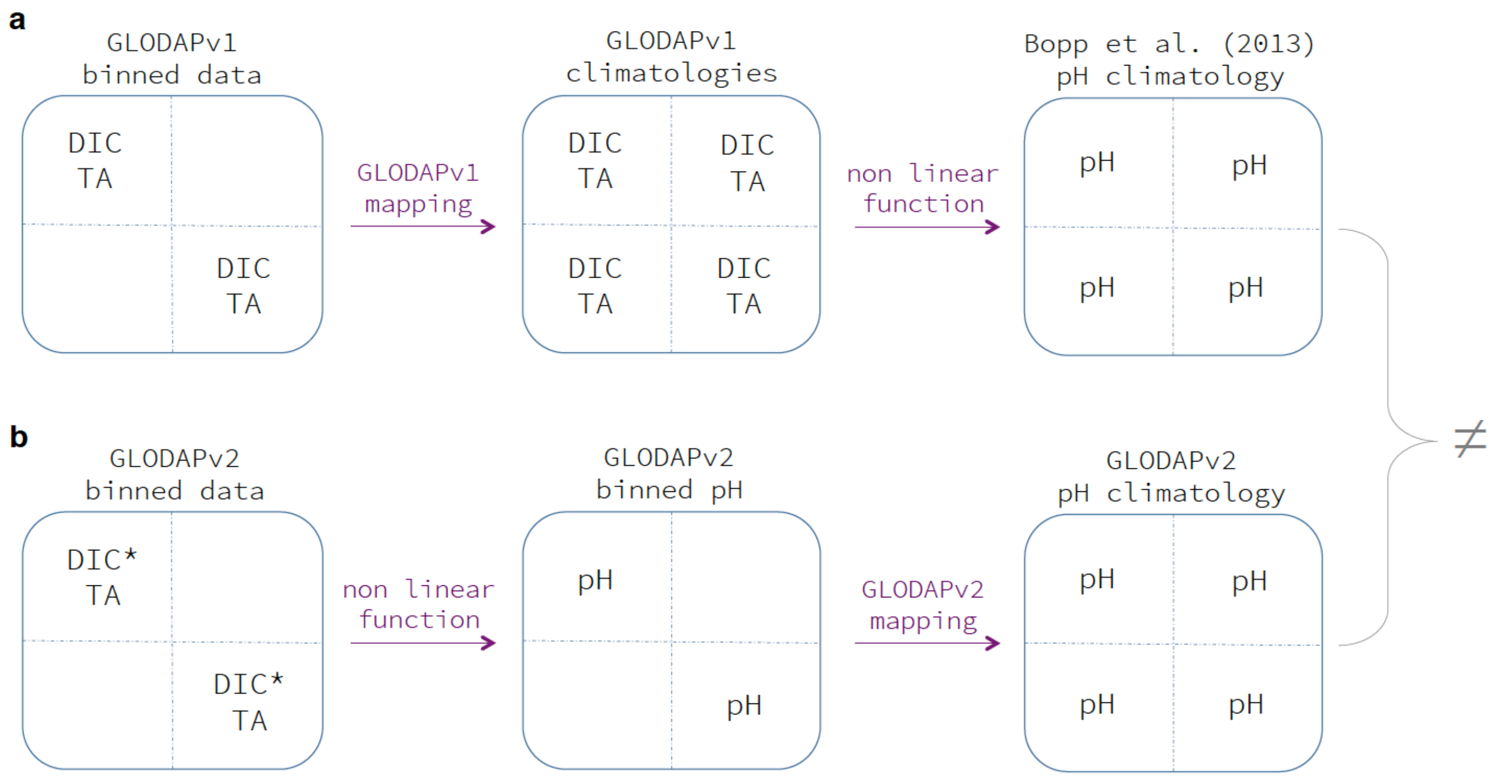


Part 1: Observing ocean biogeochemistry

4. Observing pH

What's the impact of calculating pH climatology from DIC and TA climatologies?



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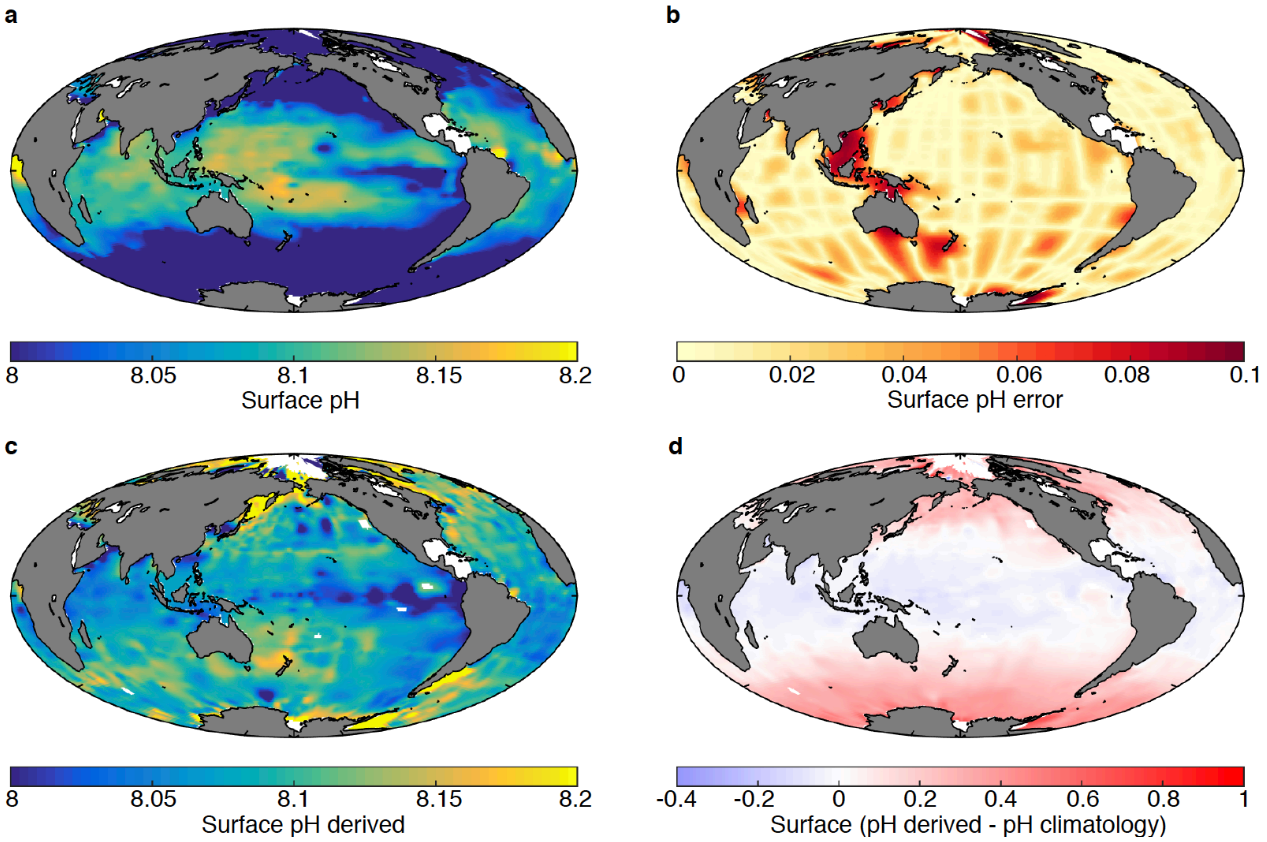
Part 1: Observing ocean biogeochemistry
4. Observing pH

What's the impact of calculating pH climatology from DIC and TA climatologies?



GLODAP v2 results

pH derived as in Bopp et al., 2013, using GLODAP v2 DIC and TA

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The Oceanography of CO_2

Part 1: Observing ocean biogeochemistry

RECAP'

	Advantages	Drawbacks
SOCAT	Measurements can be made on VOS Quality Controlled Time-varying (monthly gridded)	Summer biased Spatial gaps
GLODAP	Quality Controlled	Measurements are limited to hydrographic sections Gap-filled Summer biased Climatology

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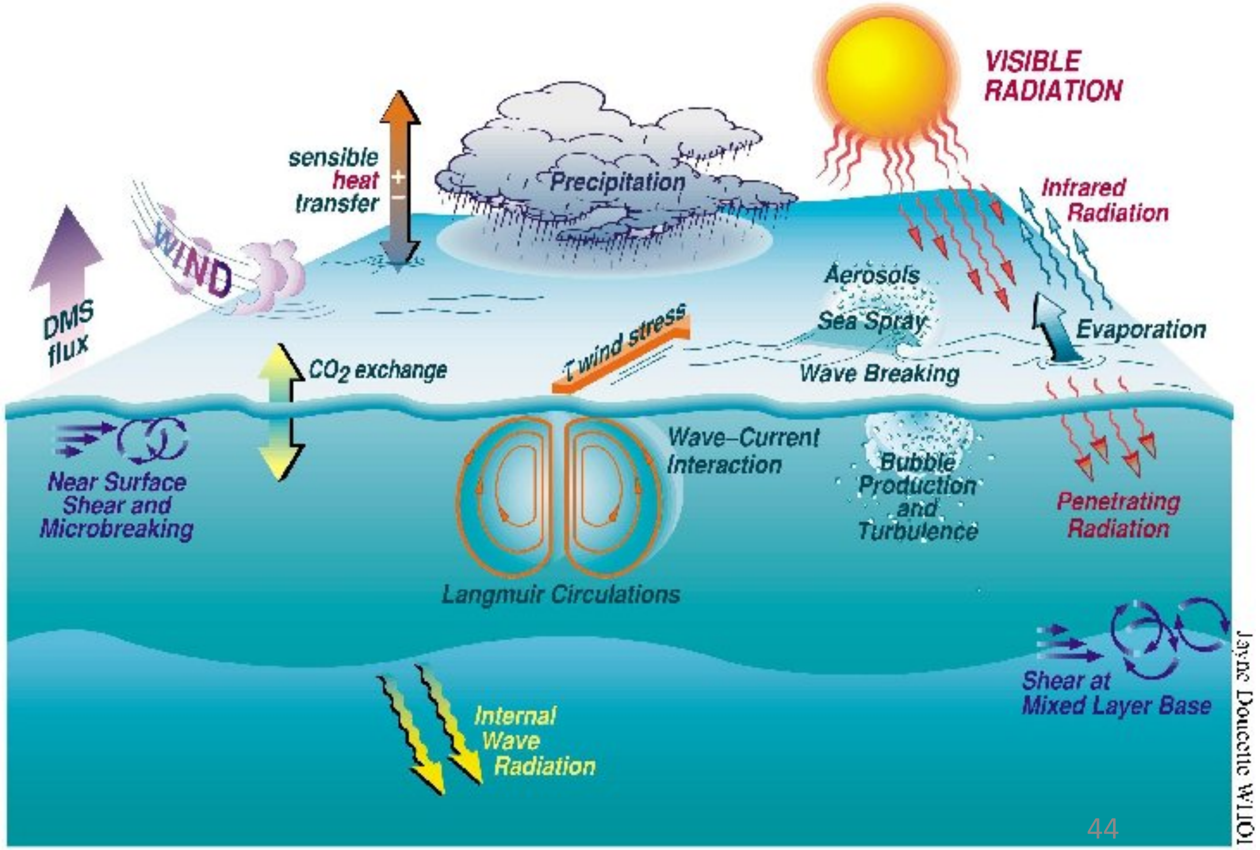
22.05.2019

Part 2: Concepts and mechanisms

1. Air-Sea CO_2 exchange

What are the physical processes that could impact the air-sea CO_2 exchange?

- Surface winds / Ekman transport
- State of surface waters (ice, bubbles, spray..)
- SST (solubility and K dissociation coefficients)
- Precipitation/Evaporation (diluting/concentrating surface DIC concentration)
- Stratification / Mixing / Buoyancy changes



Part 2: Concepts and mechanisms

1. Air-Sea CO_2 exchange

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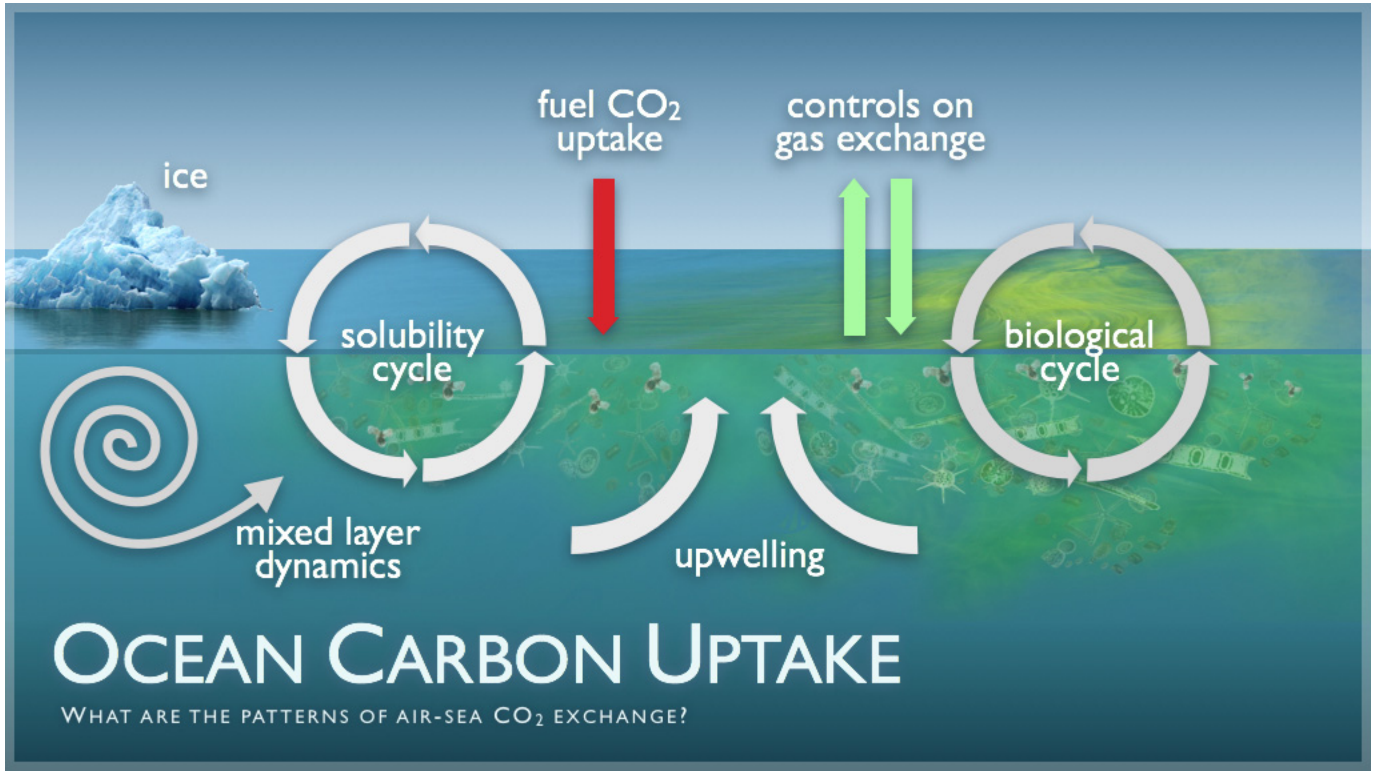


https://www.pmel.noaa.gov/co2/story/Ocean+Carbon+Uptake

Atmospheric CO_2 is relatively homogeneous relative to the ocean, so changes in Delta-pCO_2 is driven by changes in surface ocean pCO_2. Note that it takes about one year to equilibrate CO_2 in the surface ocean with atmospheric CO_2 so it is common to depict large air-sea differences in CO_2 concentrations.

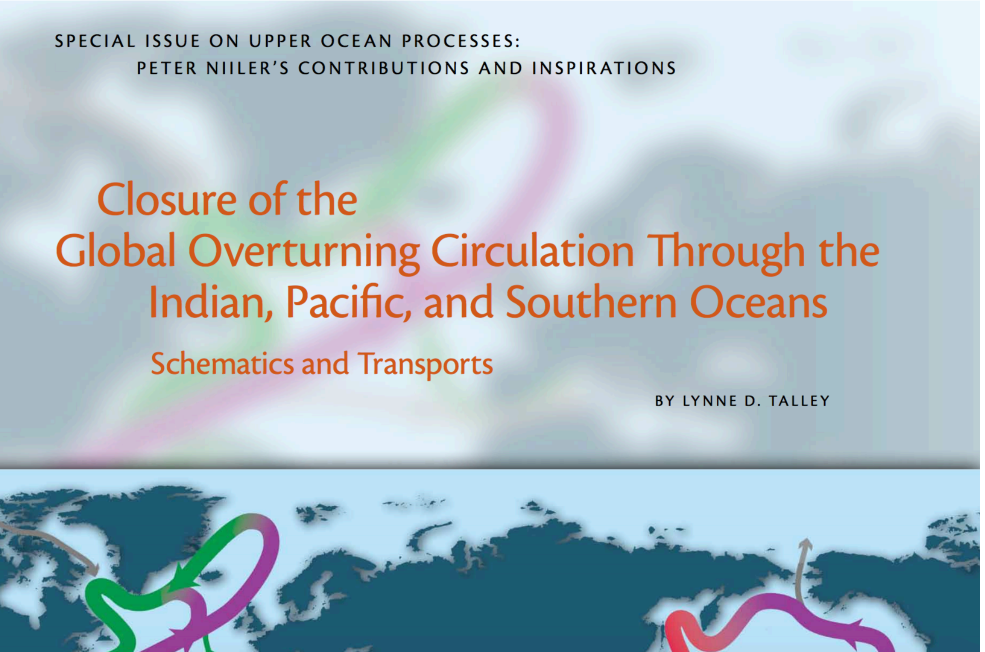
Most of the air-sea differences are caused by variability in the oceans due to biology and ocean circulation (buoyancy forcing).

Part 2: Concepts and mechanisms

1. Air-Sea CO_2 exchange

What are the physical processes that could impact the air-sea CO_2 exchange?

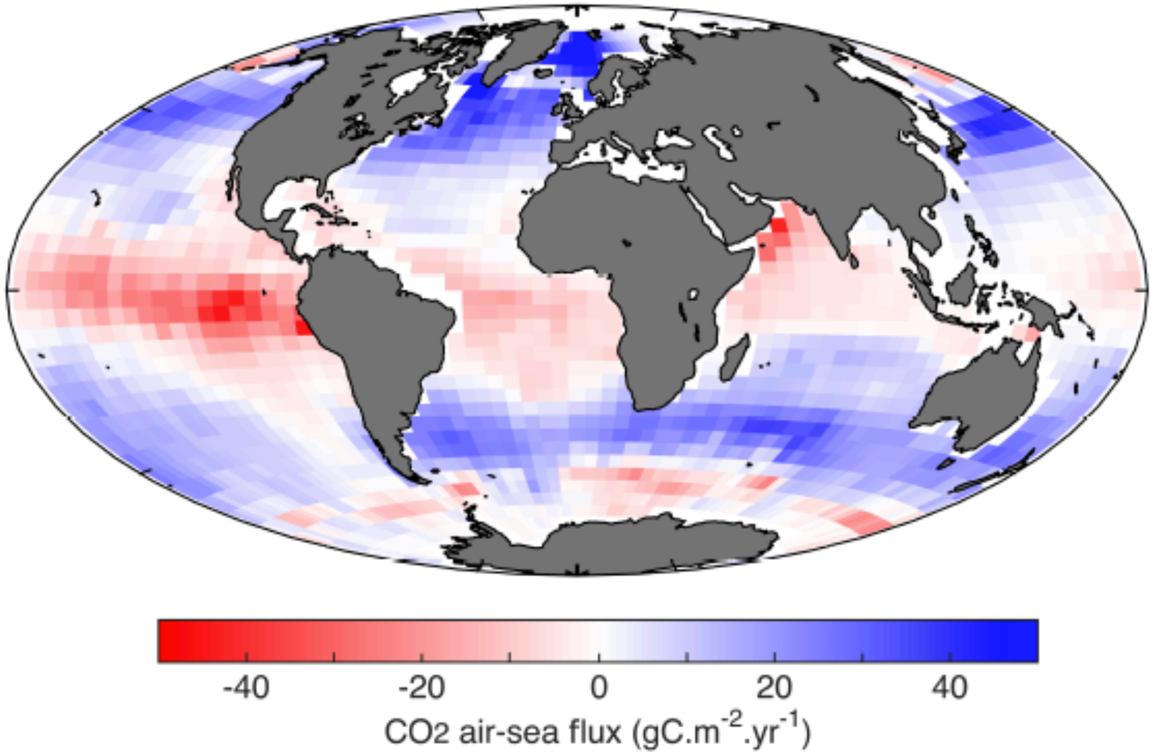
Large scale processes:


SPECIAL ISSUE ON UPPER OCEAN PROCESSES:
PETER NIILER'S CONTRIBUTIONS AND INSPIRATIONS

Closure of the Global Overturning Circulation Through the Indian, Pacific, and Southern Oceans

Schematics and Transports

BY LYNNE D. TALLEY



Air-sea CO_2 flux climatology. Red indicates CO_2 outgassing region (negative air-to-sea flux) and blue of uptake (positive air-to-sea flux) (Takahashi et al., 2009).

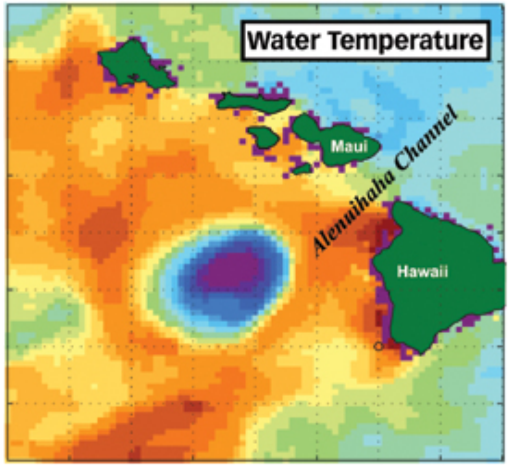
Part 2: Concepts and mechanisms

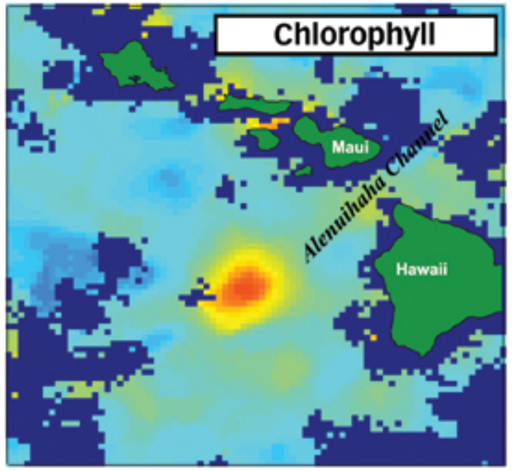
1. Air-Sea CO_2 exchange

What are the physical processes that could impact the air-sea CO_2 exchange?

Mesoscale processes:

cool-water eddy bringing up nutrients-enriched waters to the surface, and fertilizing phytoplankton growth





Part 2: Concepts and mechanisms

1. Air-Sea CO_2 exchange

What are the physical processes that could impact the air-sea CO_2 exchange?

Mesoscale processes:

Geophysical Research Letters

Research Letter | Free Access

Investigation into the impact of storms on sustaining summer primary productivity in the Sub-Antarctic Ocean

Sarah-Anne Nicholson, Marina Lévy, Joan Llort, Sebastiaan Swart, Pedro M. S. Monteiro

First published: 28 August 2016 | https://doi.org/10.1002/2016GL069973 | Cited by: 6

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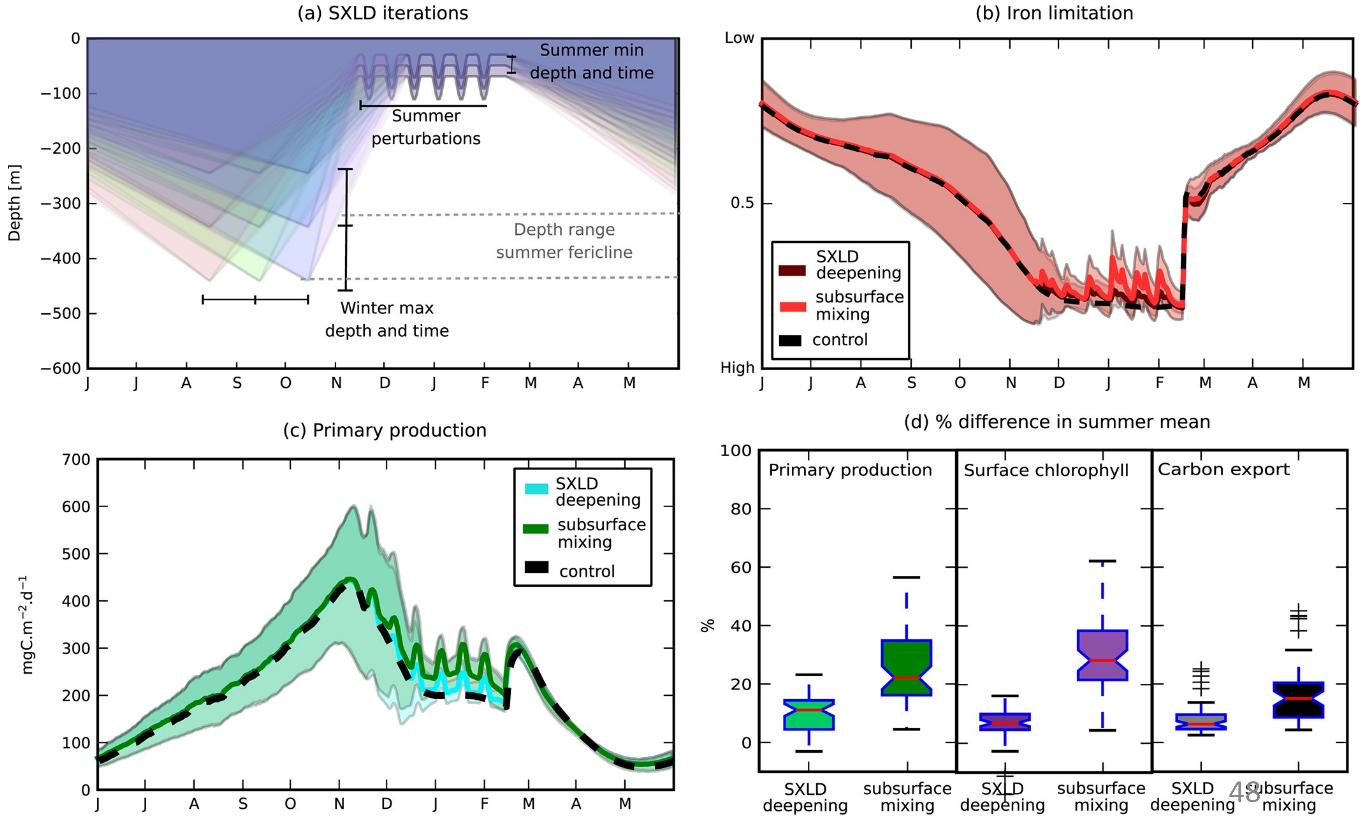

Ocean CO_2: Theory and Observations

The Oceanography of CO_2

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2. **Biological processes**

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Part 2: Concepts and mechanisms
2. Biological processes

What is the soft-tissue pump?

The soft-tissue pump broadly corresponds to the cycling of organic matter that is formed in the surface waters (via photosynthesis) into inorganic compounds at depth.

$6CO_2 + 6H_2O$ + nutrients (e.g. NO_3^-)+ photons ––> $C_6H_{12}O_6 + 6O_2$

By consuming CO_2 and nutrients such as nitrate (NO_3^-), photosynthesis leads to a decrease in DIC and an increase in TA.

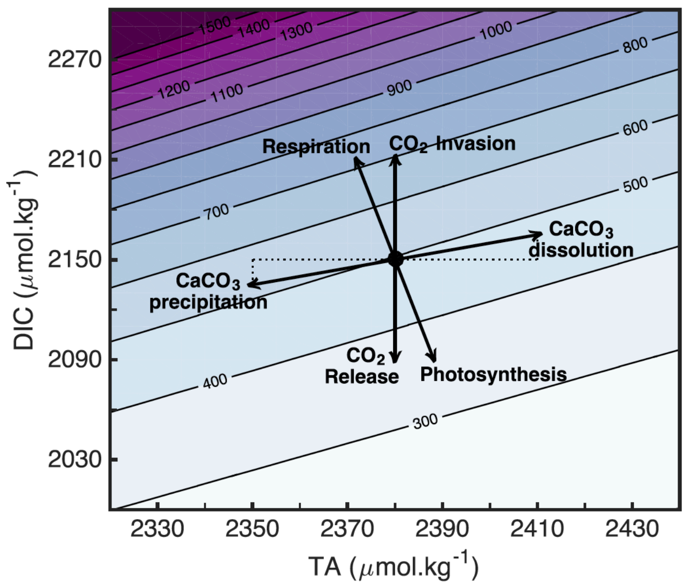

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Figure 1.7: Impact of biological processes and CO_2 invasion on marine chemistry. DIC, TA and $fCO_{2\text{-ocean}}$, which is given in µatm by the isolines, were calculated using the CO2SYS Matlab toolbox, for a salinity of 35 and a temperature of 20°C (Van Heuven et al., 2011; Sarmiento and Gruber, 2006). The ratio 1:2 in DIC:TA involved with $CaCO_3$ formation/dissolution is highlighted by the dotted lines.

Part 2: Concepts and mechanisms
2. Biological processes

What is the soft-tissue pump?

The carbon that is fixed into organic matter follows two possible routes:
1**. It remains in the surface layers** and returns to its inorganic form through bacteria activities or respiration of zooplankton (De La Rocha, 2007). Respiration is the opposite reaction of photosynthesis, which therefore corresponds to the oxidation of organic matter and leads to an increase in DIC and a decrease in TA (Williams and Follows, 2011).

2**. It is exported to the deep ocean** through advection or sinking of particles (Sarmiento and Gruber, 2006). Nevertheless, **only a small fraction** (about 5-10%) of the sinking particles (the relatively large particles, that mostly result from optimal coagulation conditions or the packaging of material into faecal pellets) eventually **reach the seafloor** and therefore contribute to the burial of carbon into sedimentation (Buesseler, 1998; De La Rocha, 2007). The rest of the sinking particles are decomposed by microbial activities and/or zooplankton grazing throughout the water column (De La Rocha, 2007). **The remineralisation of organic carbon into inorganic carbon therefore contributes to the increase of DIC with depth**. Those enriched DIC intermediate/deep waters eventually return to the surface through specific oceanic circulation patterns (e.g. upwelling).

Part 2: Concepts and mechanisms

2. Biological processes

What is the soft-tissue pump?

The efficiency of the soft-tissue pump depends on the efficiency of primary production (hence availability of nutrients in the euphotic layer, brought up through intense vertical motion e.g. strengthening of thermocline in spring).

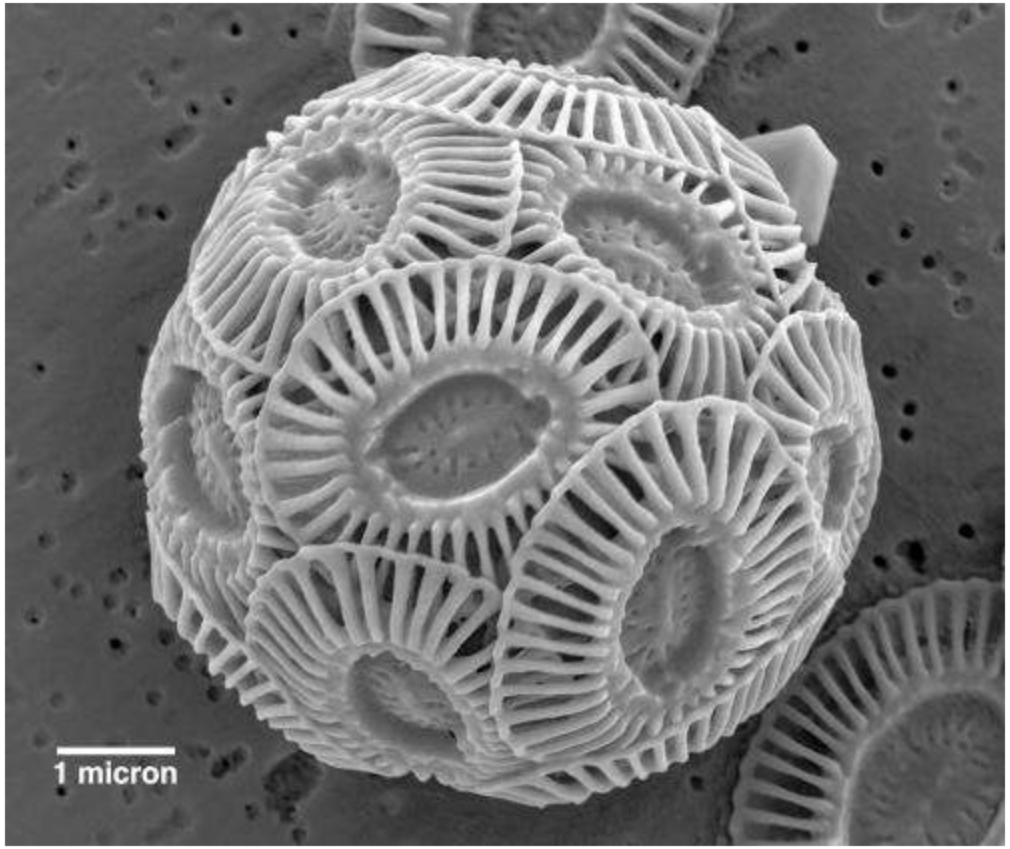
Under global warming conditions, while the increase of SST would generally be expected to increase phytoplankton growth and therefore stimulate primary production, the induced increase in stratification would reduce vertical mixing and hence decrease the supply of nutrients in the euphotic layer (Denman et al., 2007). In nutrient limiting regions (i.e. low latitudes), such impacts could potentially lead toward a decrease in the soft-tissue pump's efficiency (Kwiatkowski et al., 2017).
However in light limiting regions (i.e. high latitudes), a narrowing of the initially nutrient-enriched mixed layer could concentrate phytoplankton into the euphotic layer, which would enhance primary production and thus increase the soft tissue pump's efficiency.

Part 2: Concepts and mechanisms

2. Biological processes

What is the carbonate pump?

The carbonate pump corresponds to the cycling of calcium carbonate ($CaCO_3$) from the surface to the deep ocean. Calcium carbonate is a mineral formed through calcification generated by coccolithophores or other calcareous organisms.



Part 2: Concepts and mechanisms

2. Biological processes

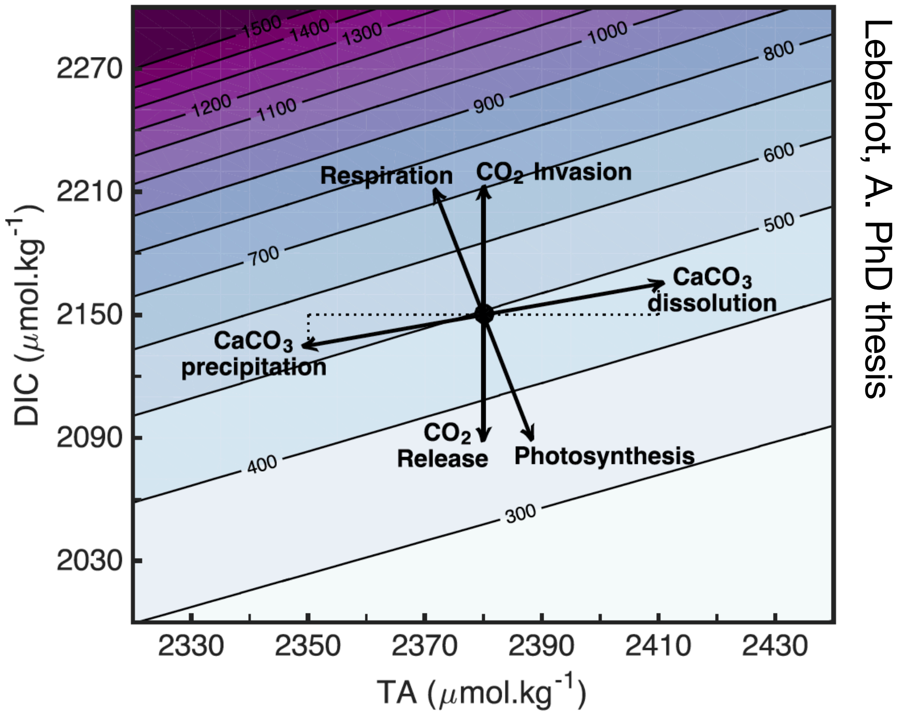
What is the carbonate pump?

Each mole of $CaCO_3$ precipitated leads to the decrease of one mole of DIC and two moles of TA (due to the stoichiometric number 2 in front of the carbonate ion concentration in TA definition) (Zeebe and Wolf-Gladrow, 2001).

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

What does this mean in terms of the direction of the flux?

As such, calcification increases $fCO_{2\text{-ocean}}$, which can either reduce the air-sea CO_2 flux or lead to a localised CO_2 outgassing to the atmosphere.



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Part 2: Concepts and mechanisms

2. Biological processes

What is the carbonate pump?

Once precipitated in the surface layers, calcareous shells sink into intermediate/deep waters. As in the soft-tissue pump, **only a small fraction of calcareous shells reach the seafloor and is buried into sedimentation**. Most of the sinking shells are progressively dissolved due to the increase of their solubility with depth (i.e. solubility increases with lower temperature and higher pressure), contributing to a vertical increase in DIC and TA (Williams and Follows, 2011).

The depth at which calcium carbonate changes from supersaturation (i.e. favourable to precipitation) to undersaturation (i.e. favourable to dissolution) state is referred as the **saturation horizon** (Williams and Follows, 2011).

Under rising atmospheric CO_2 concentrations, the saturation horizon is expected to become shallower, due to a decrease in pH that reduces CO_3^{2-} concentrations and therefore promotes the dissolution of calcium carbonate.

https://www.youtube.com/watch?v=kmpzDfrqliU

Part 2: Concepts and mechanisms

2. Biological processes

RECAP'

Highlight the challenges for the modelling community when representing this cycle in biogeochemical models (e.g. sinking rate, horizon saturation, nutrient availability).

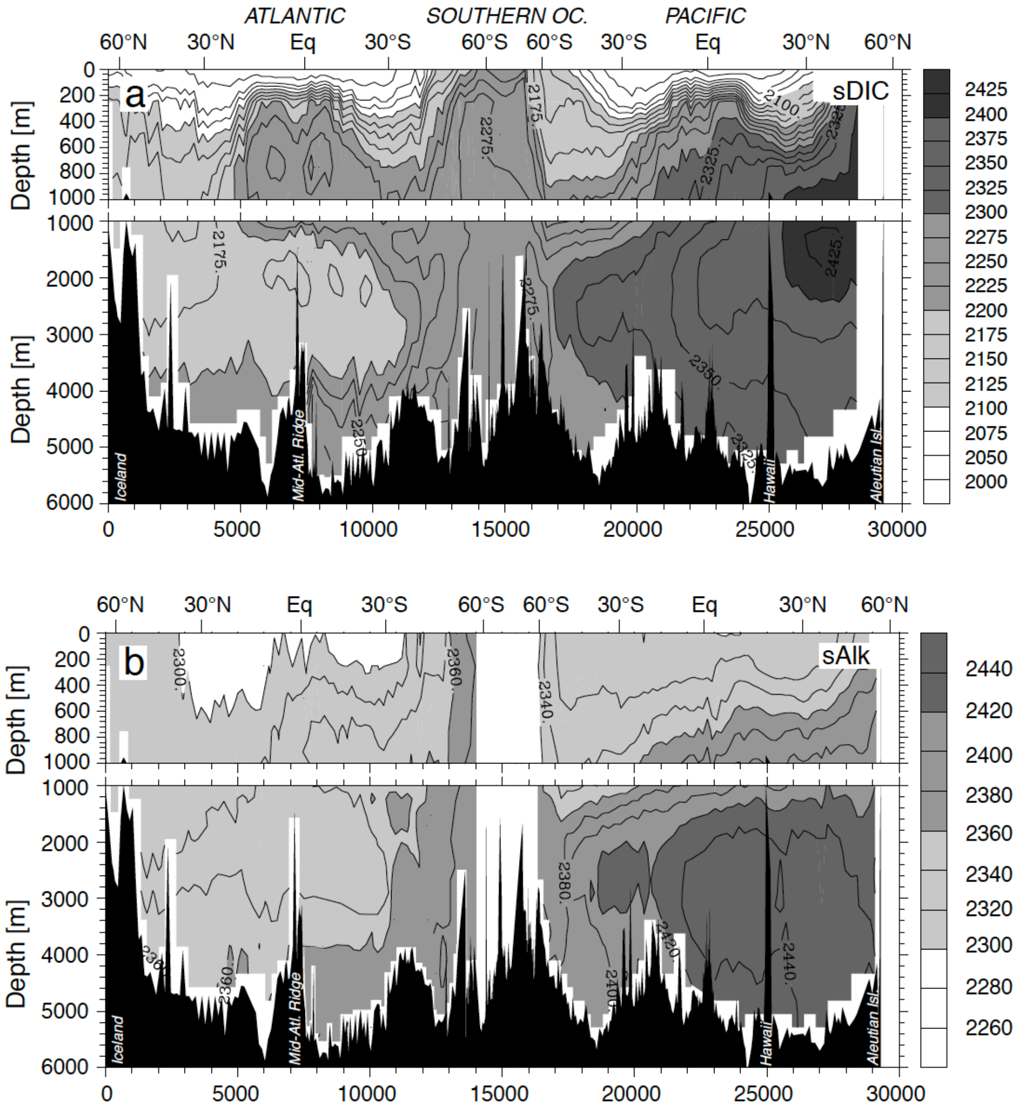
Soft Tissue Pump	Carbonate Pump
Increase of DIC with depth (remineralisation)	Increase of DIC with depth (dissolution)
Decrease of TA with depth (remineralisation)	Increase of TA with depth (remineralisation)

Part 2: Concepts and mechanisms

2. Biological processes

RECAP'

Why is DIC and TA higher in the deep North Pacific than in the deep North Atlantic?



The Oceanography of CO_2

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