SAMPLING AND PRESERVATION OF SEAWATER FOR CO_2 ANALYSES

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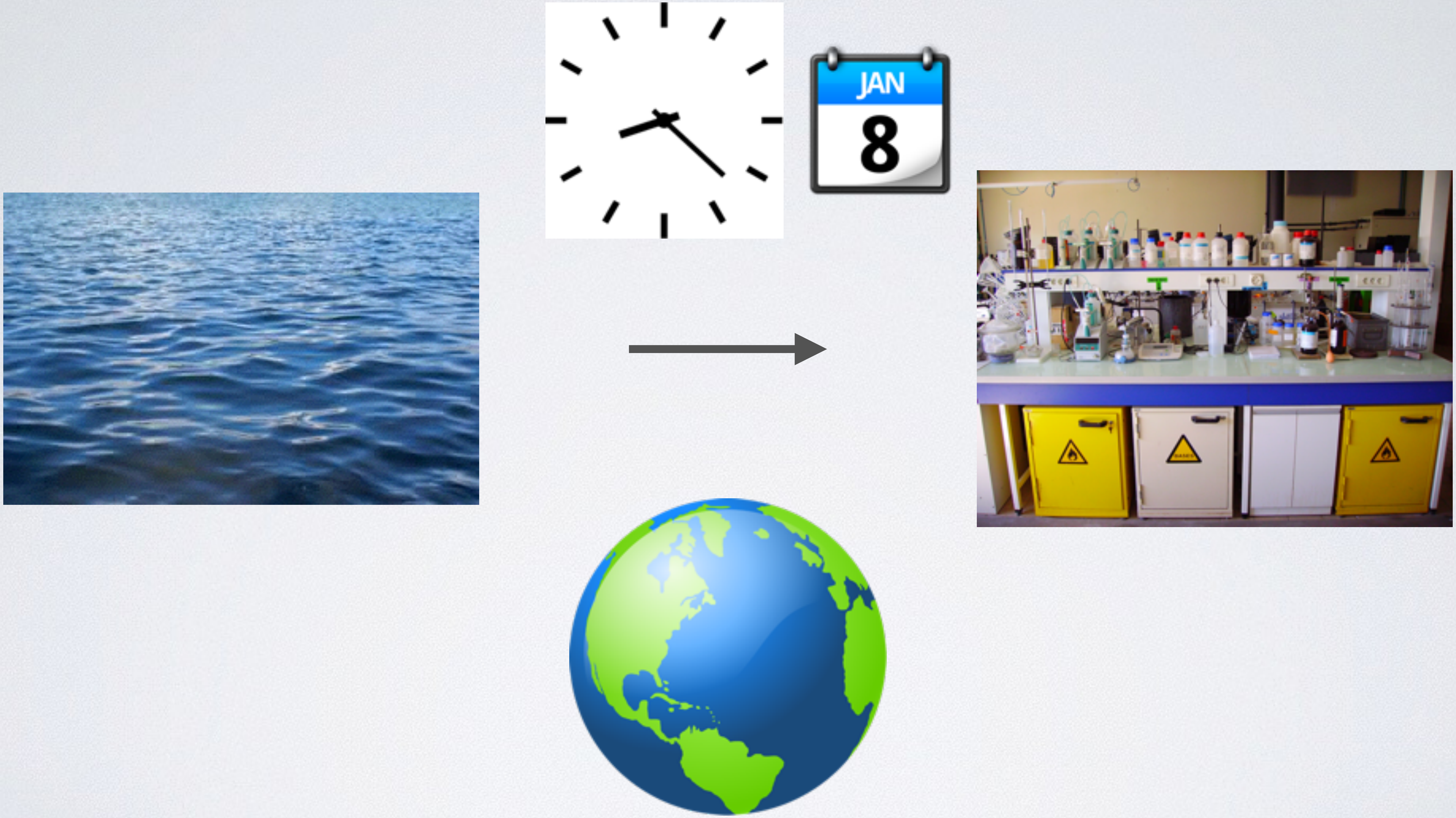
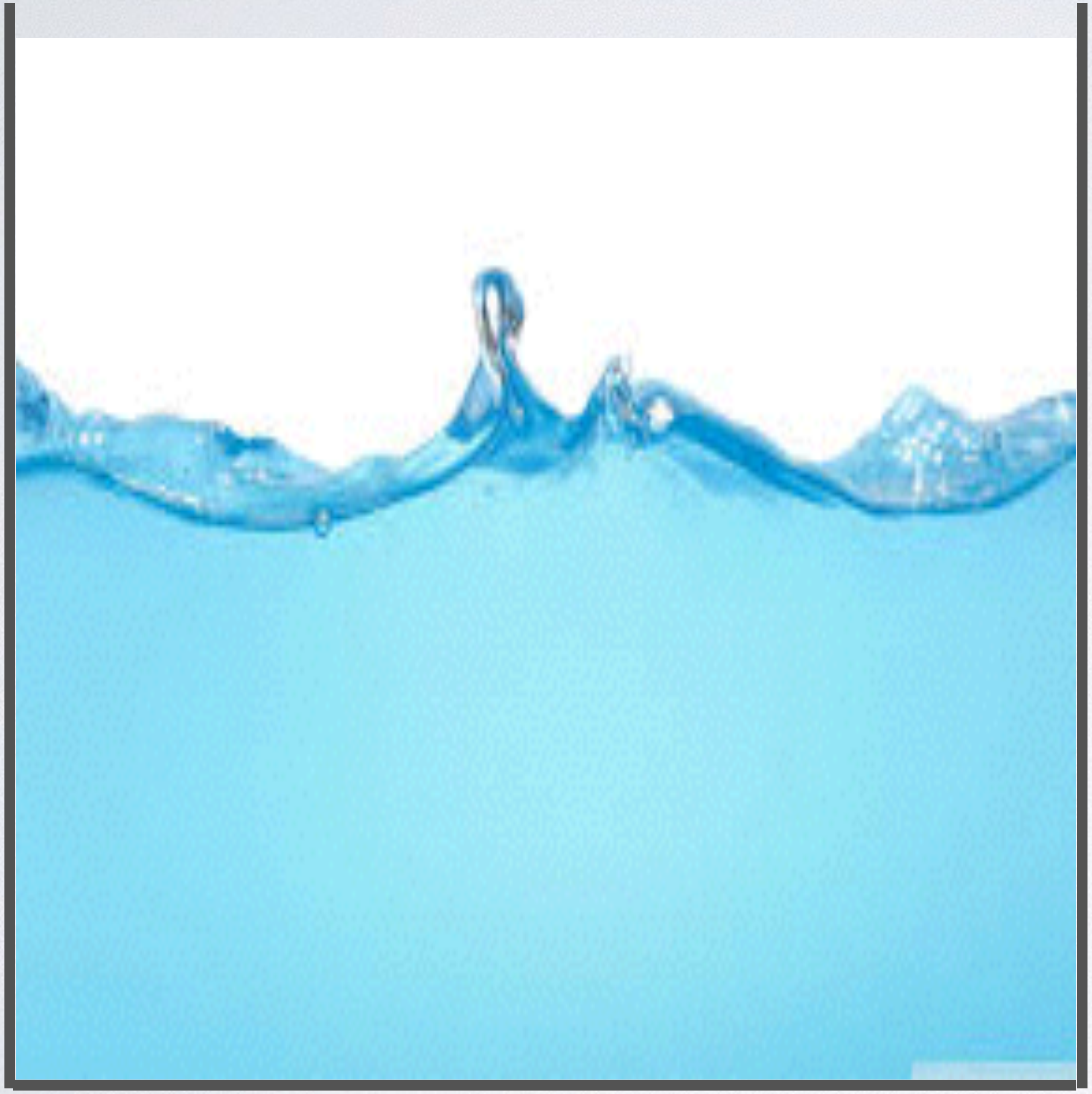
GOAL



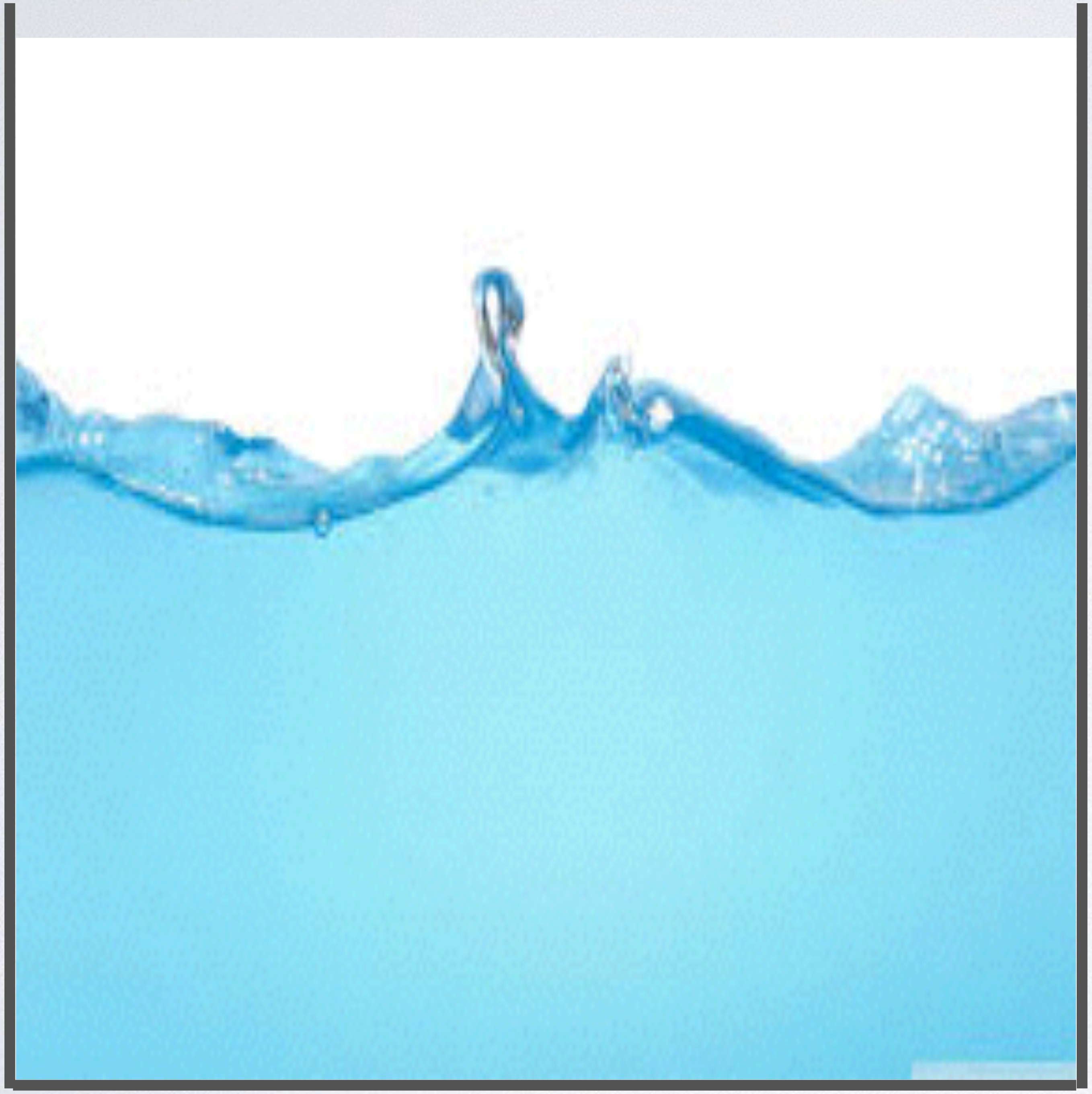
Without a change in CO_2 system

How can we achieve this reliably?

IMAGINE A SAMPLE OF SEAWATER IN A CONTAINER

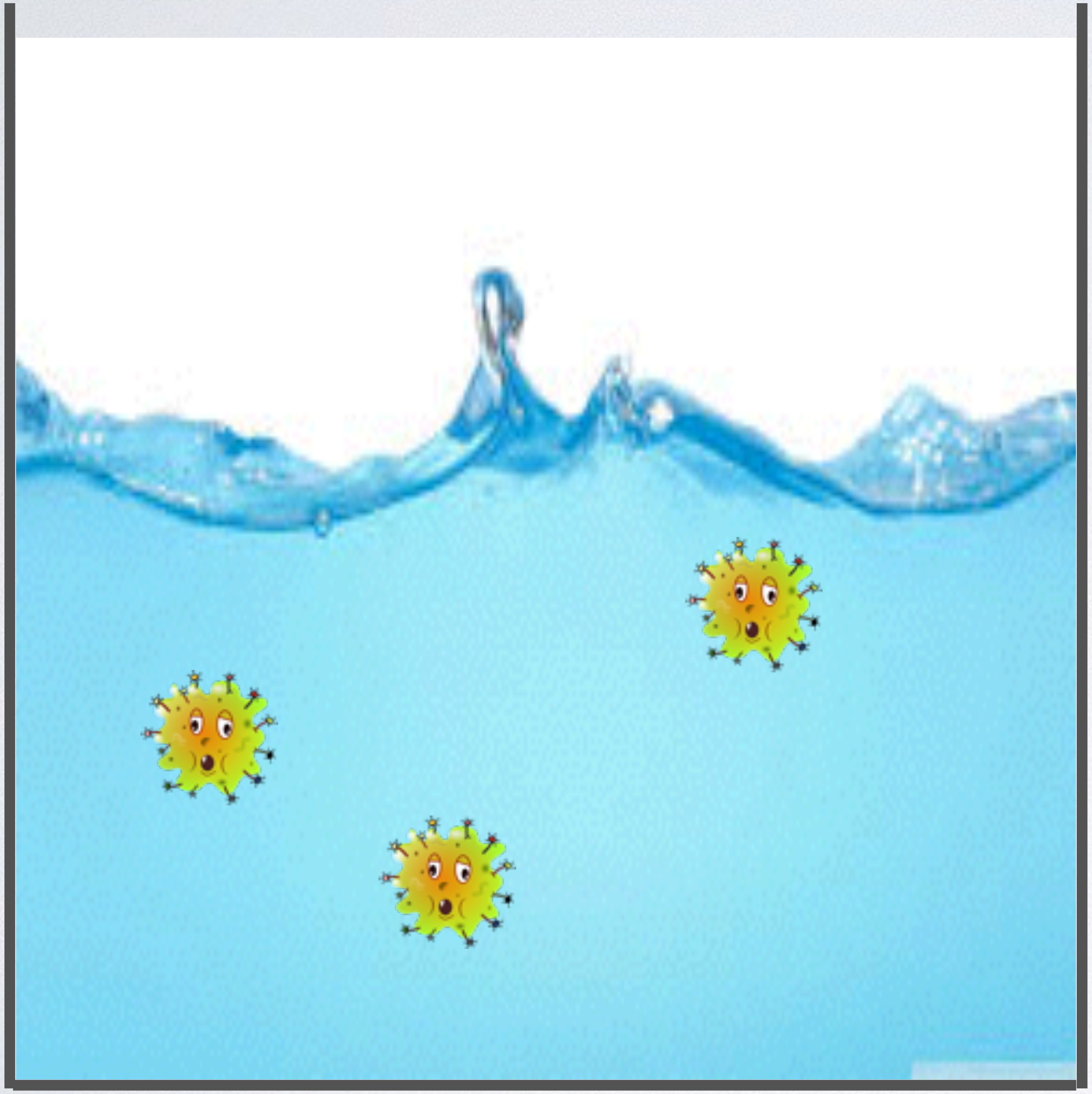


HOW CAN ITS CO_2 COMPOSITION CHANGE?



By changing the total dissolved inorganic carbon, the total alkalinity, or both.

NEED TO AVOID:



Biological activity in the water after sampling.

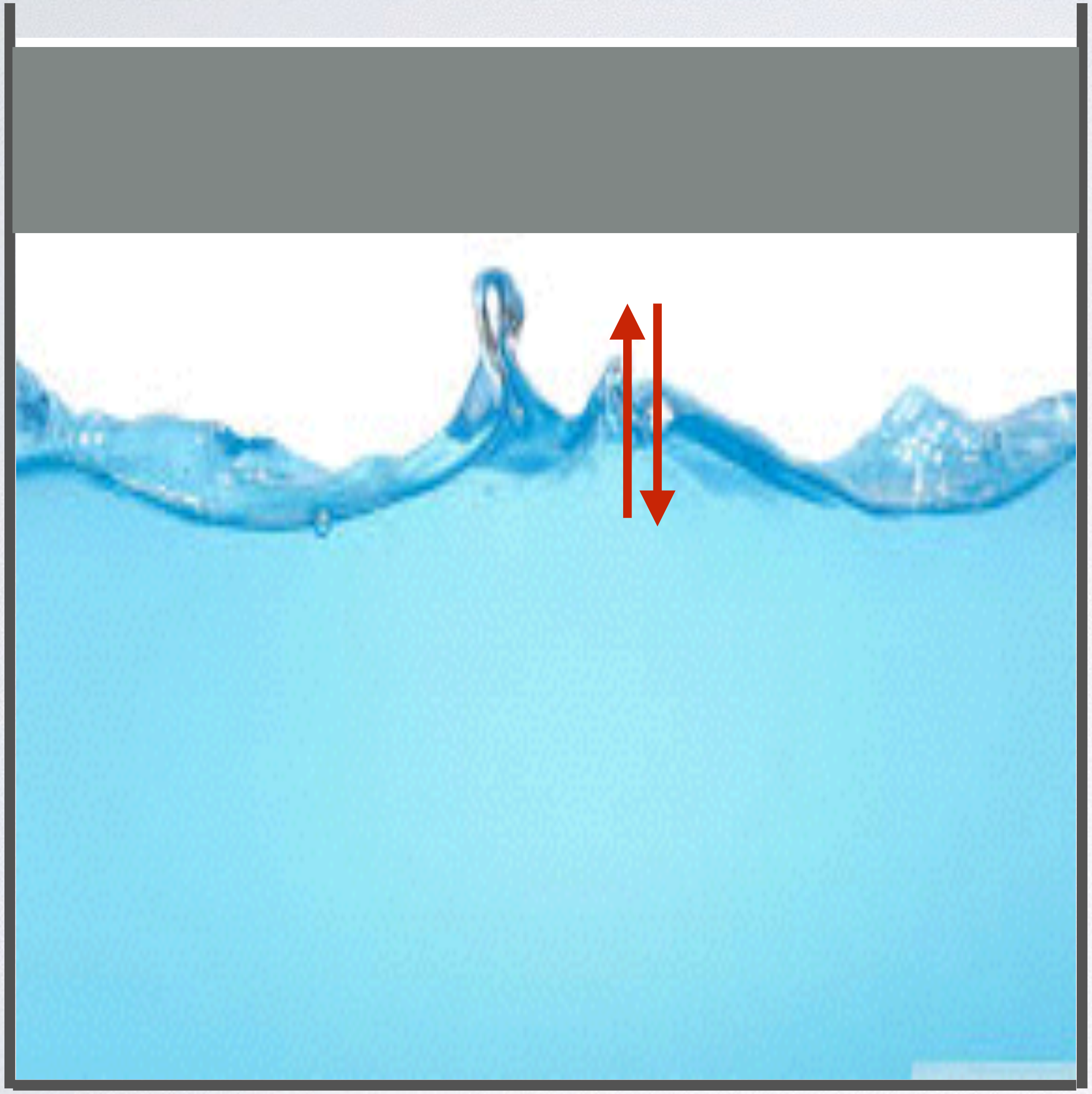
WHY?

$$6CO_2 + 6H_2O \underset{\textit{respiration}}{\overset{\textit{photosynthesis}}{\rightleftarrows}} C_6H_{12}O_6 + 6O_2$$

HOW?

Add small amount of mercury(II) chloride

ALSO NEED TO AVOID:



Exchange between the water and the air above.

A. Loss of water by evaporation
B. Gain / loss of CO_2 as gas
C. Further contamination by microorganisms

HOW?

Seal the container

Closed pyrex bottle with air-tight seal

We use a greased, ground-glass joint

Note: the bottle is not completely full

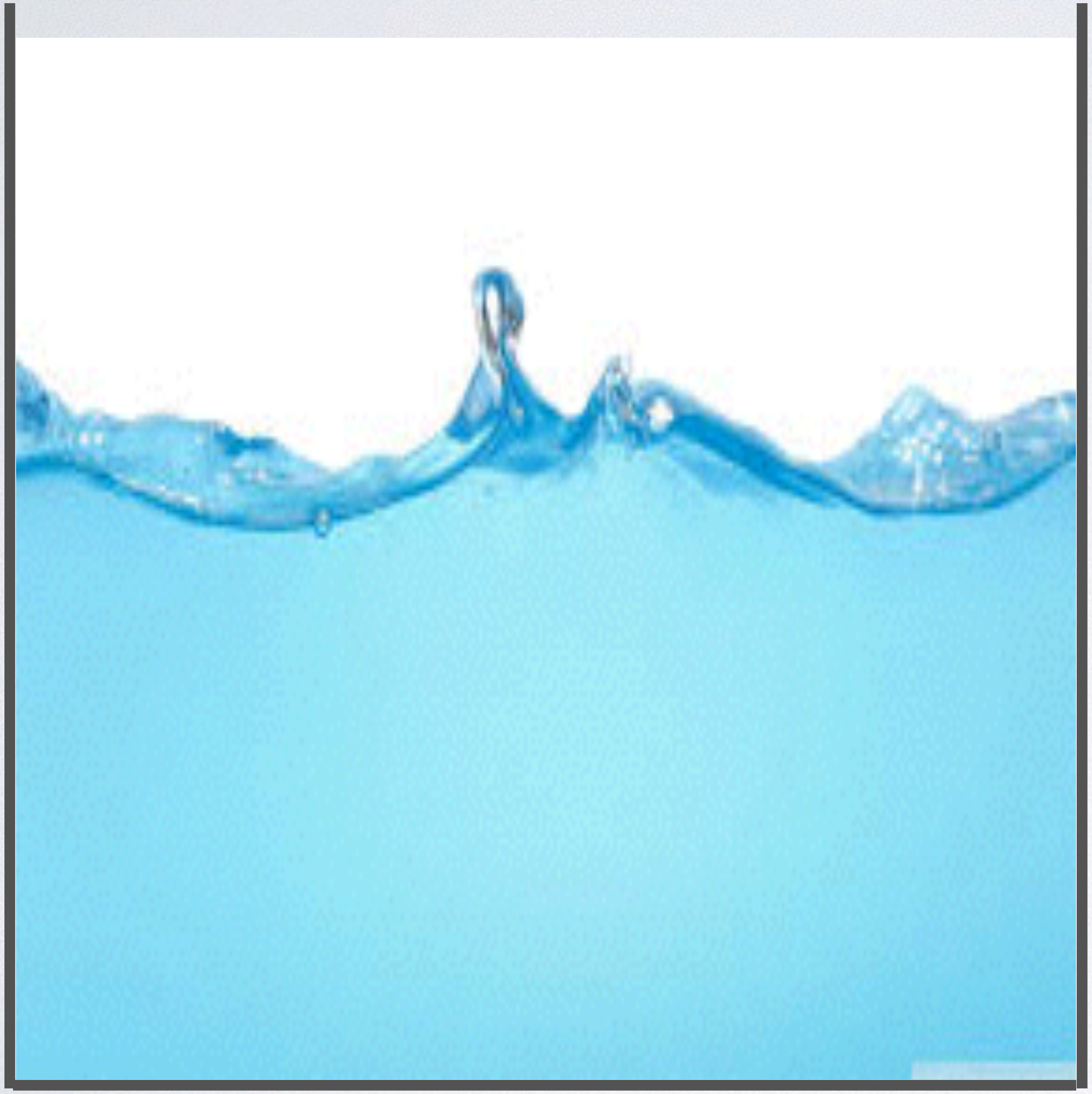
WHY?

An ideal head-space is about 1% of the total volume.

Too small, and the pressure increase as water expands may push out the stopper

Too large, and the gas exchange with the head-space may be significant.

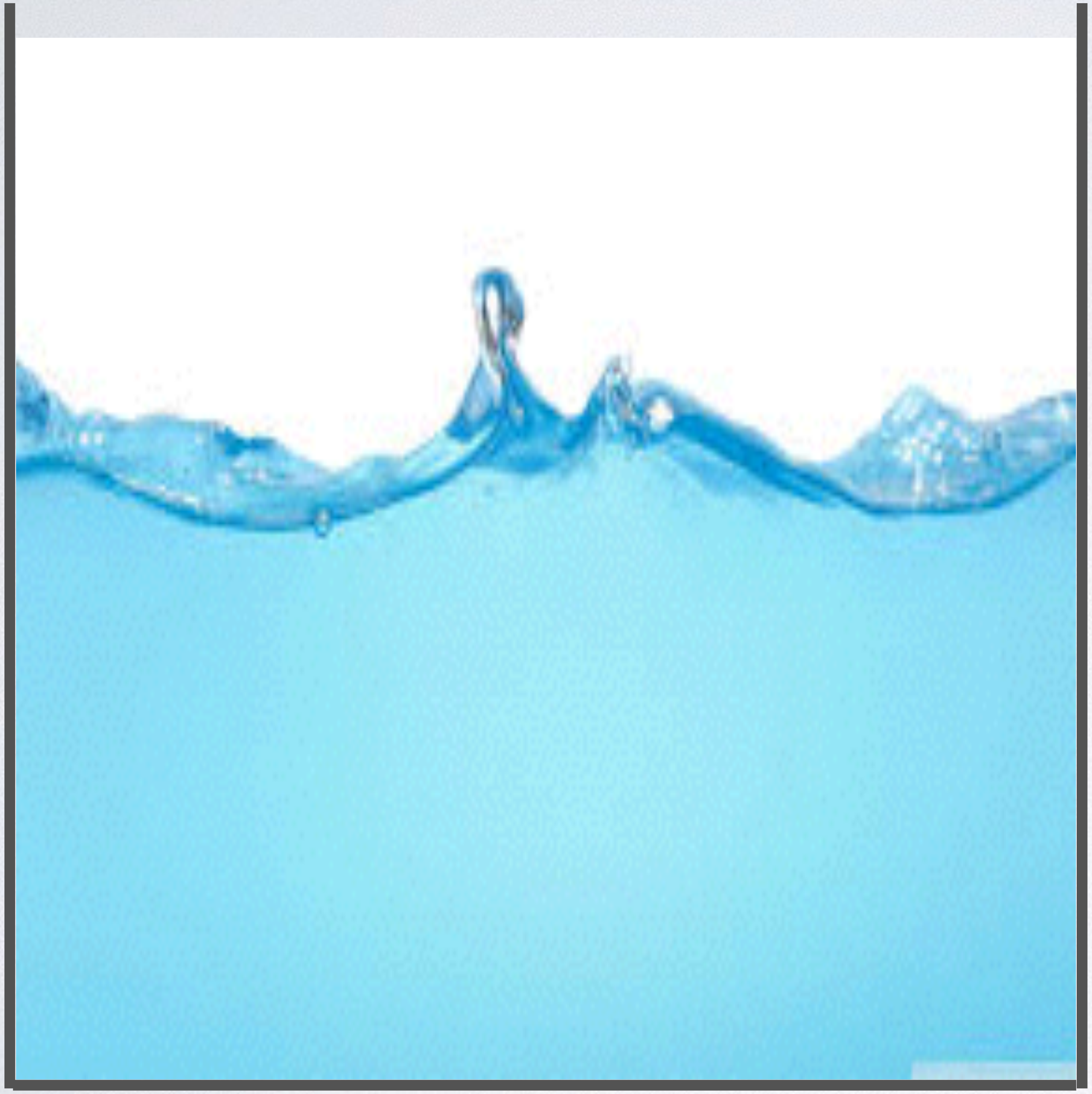
IS THERE ANYTHING ELSE?



Important to fill gently so that opportunities for exchange with the atmosphere are limited.

Can overflow the bottle to reduce effect of such exchange.

IS THERE ANYTHING ELSE?



The container must be clean before being filled

The seawater must not react with the material the container is made of.

The container must be impervious to CO_2 and H_2O.

Guide to Best Practices for Ocean CO_2 Measurements

PICES SPECIAL PUBLICATION 3
IOCCP REPORT No. 8

PICES

International Council for Science
Scientific Committee on Oceanic Research

CDIAC

http://cdiac.ornl.gov/oceans/Handbook_2007.html

SOP 1

Water sampling for the parameters of the oceanic carbon dioxide system

1. Scope and field of application

This SOP describes how to collect discrete samples, from a Niskin or other water sampler, that are suitable for the analysis of the four measurable inorganic carbon parameters: total dissolved inorganic carbon, total alkalinity, pH and CO_2 fugacity.

2. Principle

A sample of sea water is collected in a clean glass container in a manner designed to minimize gas exchange with the atmosphere (note: CO_2 exchange affects the various carbon parameters to differing degrees ranging from the very sensitive CO_2 fugacity, $f(CO_2)$, to alkalinity which is not affected by gas exchange). The sample may be treated with a mercuric chloride solution to prevent biological activity, and then the container is closed to prevent exchange of carbon dioxide or water vapor with the atmosphere.

LIMNOLOGY
and
OCEANOGRAPHY: METHODS

Limnol. Oceanogr.: Methods 12, 2014, 191–195

A seawater filtration method suitable for total dissolved inorganic carbon and pH analyses

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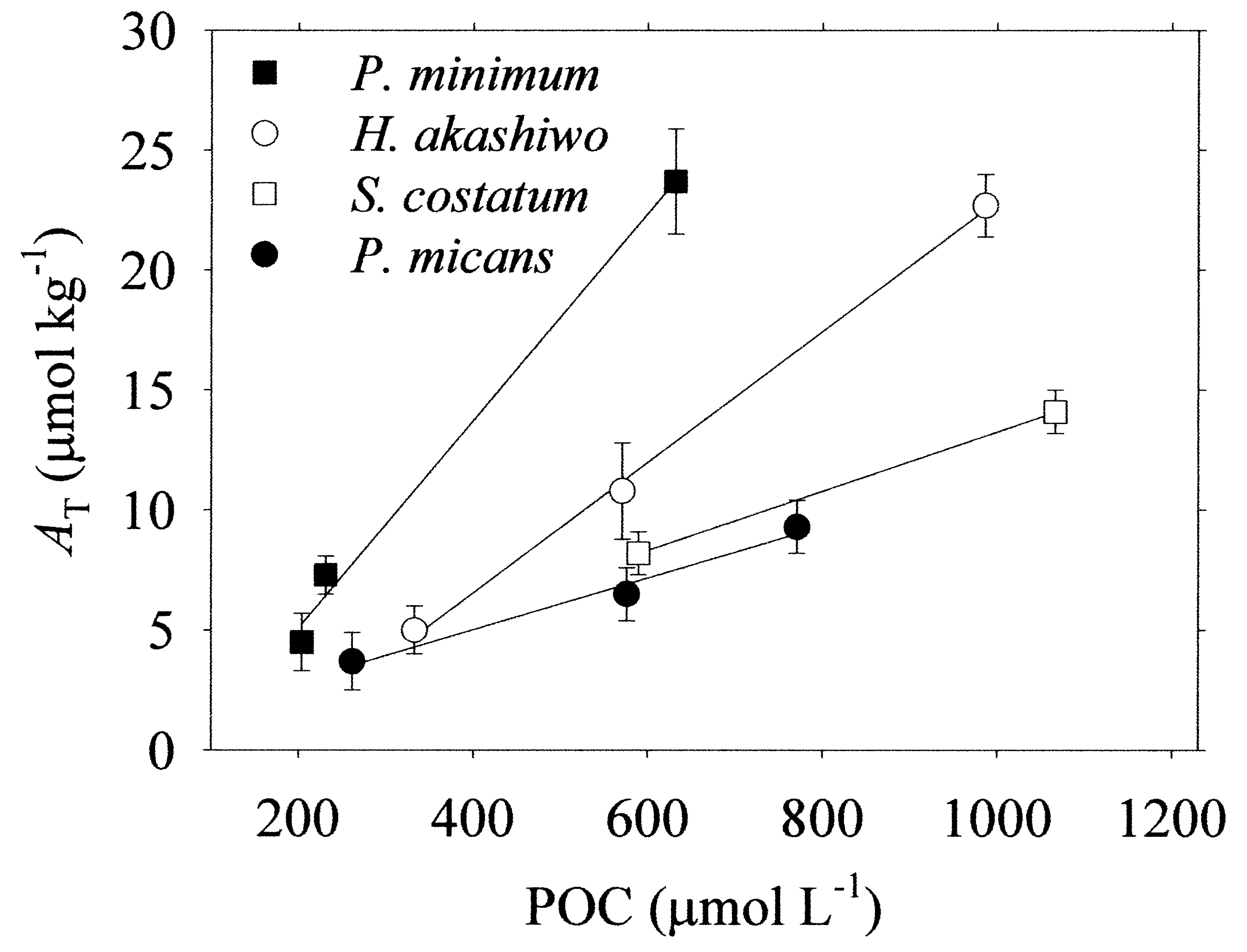
Abstract

High biomass and heavy particle loads may interfere with carbonate chemistry analyses of samples from experimental aquaria and cultures used to investigate the impact of ocean acidification on organisms, as well as from biologically productive coastal regions. For such samples, a filtration method is needed that does not change the dissolved CO_2 content, and consequently does not alter the total dissolved inorganic carbon and pH of the sample. Here, a filtration method is presented in which the sample seawater is pumped by a peristaltic pump through a replaceable 0.45 μm filter in a 50 mm polycarbonate filter holder and then into the sample bottle. Seawater samples of known carbonate composition were filtered to confirm that the filtration method did not alter the CO_2 content, and compromise the subsequent sample analysis and data usefulness. Seawater samples with added phytoplankton concentrations in the range of $1–5 \times 10^5$ cells mL^{-1} were also filtered successfully. Finally, seawater with added biogenic $CaCO_3$ was tested to prove that the method could successfully filter out such particles and produce dependable results. This approach will help to ensure more consistent and reliable carbonate chemistry measurements in coastal environments and from ocean acidification aquaria and cultures, by providing a well-tested method for sample filtration.

Photo Credit: Eddie Kisfaludy SciFly LLC Sept 5, 2013

PHYTOPLANKTON CAN CONTRIBUTE ALKALINITY



Kim, H. C., K. Lee, and W. Y. Choi. 2006. Contribution of phytoplankton and bacterial cells to the measured alkalinity of seawater. *Limnol. Oceanogr*. 51: 331-338.

Whitings in the Bahamas

CACO$_3$ PARTICLES CAN BE A BIG PROBLEM!

Dissolution or precipitation of $CaCO_3$ will change both total alkalinity and total dissolved inorganic carbon

Worse yet, methods for the determination of both total alkalinity and total dissolved inorganic carbon usually involve adding acid to the sample, guaranteeing dissolution of $CaCO_3$. This either increases the acid needed to measure alkalinity (biasing the result high), or releases extra CO_2, increasing the apparent total dissolved inorganic carbon.

BUT SIMPLE FILTRATION CAN BE A PROBLEM

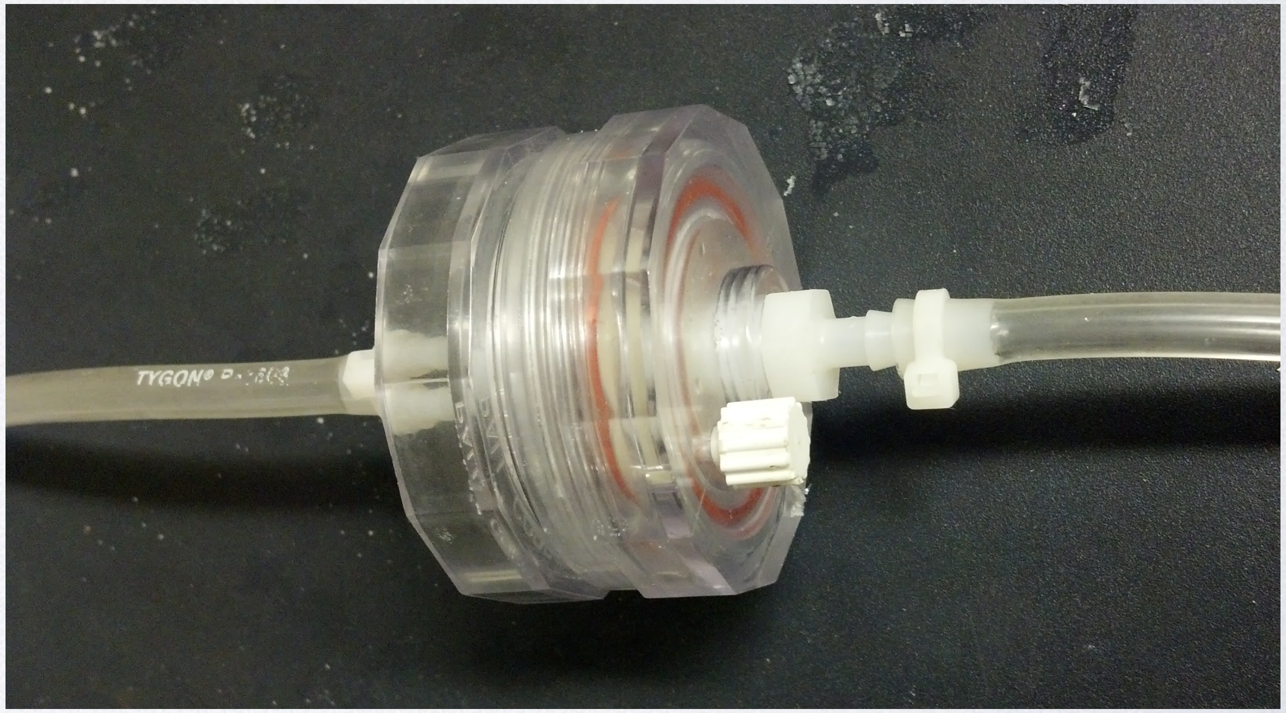
WHY?

It increases the opportunity for gas exchange between the seawater sample and the atmosphere — thus changing the total dissolved inorganic carbon, and thus the pH and $p(CO_2)$.

FILTRATION METHOD FOR CO_2 ANALYSES

Use a peristaltic pump thus minimizing gas exchange.

Use an enclosed, flow-through filter, again to minimize gas exchange. (0.45 µm; 47 mm)



FILTRATION METHOD FOR CO_2 ANALYSES

Table 1. Measured results for C_T, pH, and A_T for the various experiments reported here. The certified values for CRM Batches 124 and 125 are included for comparison. In each case, values are expressed as mean ± one standard deviation (number of analyses).

	C_T (μmol kg^{-1})	pH (Total scale)	A_T (μmol kg^{-1})
Measurements of CRM Batch 124			
Batch 124 certified values	2015.72 ± 0.74 (9)*	7.8796 ± 0.0019 (18)†	2215.08 ± 0.49 (24)
Filtered samples	2016.18 ± 0.93 (12)	7.8799 ± 0.0006 (12)	2215.40 ± 0.76 (24)
Measurements of CRM Batch 125			
Batch 125 certified values	2141.94 ± 0.37 (6)*	7.5541 ± 0.0020 (18)†	2216.26 ± 0.52 (18)
Filtered samples	2141.19 ± 1.07 (12)	7.5569 ± 0.0020 (12)	2216.30 ± 0.78 (24)
Measurements of CRM Batch 124 with *P. tricornutum*			
Batch 124 certified values	2015.72 ± 0.74 (9)*	7.8796 ± 0.0019 (18)†	2215.08 ± 0.49 (24)
Filtered samples	2015.79 ± 0.61 (7)	7.8807 ± 0.0007 (7)	2215.53 ± 0.89 (14)
Unfiltered samples	2016.25 ± 0.98 (7)	7.8799 ± 0.0012 (7)	2218.45 ± 0.68 (14)
Measurements of seawater with $CaCO_3$ particles			
Filtered samples	2000.17 ± 0.49 (7)	7.8860 ± 0.0006 (7)	2201.74 ± 1.07 (13)
Unfiltered samples	2071 ± 11 (7)	7.8855 ± 0.0007 (7)	2457 ± 145 (14)

*The certified C_T values for reference materials were not measured using the SOMMA-Coulometric system used for the other measurements reported here. They were measured using a more involved vacuum extraction/manometric method.

†The assigned pH values for reference materials were measured by the same technique used here over a period of 4 months.

EVIDENCE FOR SAMPLE STABILITY

1. Duplicate samples collected at the Bermuda and Hawaii time-series stations for later analysis at Scripps agree closely even if not analyzed for ~2 years.
2. Reference materials which are treated the same way (filtered, and poisoned with mercury(II) chloride) have been shown to be stable for >3 years (C_T) and for 10 years (A_T).

KNOWN PROBLEMS

1. Samples are less stable when stored in bottles that are not scrupulously clean. (We clean by heating to 550 °C in oven.)
2. Glasses other than Pyrex (or with a similar low coefficient of expansion) react with seawater over time, increasing alkalinity.
3. Microorganisms exist that can tolerate mercury(II) chloride
4. Plastic bottles are permeable to water and to CO_2.
5. It is difficult to make a perfect gas-tight seal with a screw-capped bottle.
6. To use serum bottles, use a solid aluminum crimp seal

Has been demonstrated to be impermeable to water vapor.

OK with CO_2

CONCLUSIONS

It is possible to take seawater samples, and to preserve them for later analysis on shore without compromising the overall measurement quality.

Nevertheless this requires the use of Pyrex bottles (which are quite expensive) and mercury(II) chloride (a known hazard) to ensure success.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