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New analytical approach in monitoring of CO_2 cycle in aquatic ecosystems

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Keywords

isotope ratio infrared analysis, carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$), marine environment, CO_2 fluxes

Goal

To understand pathways, processes and the fate of CO_2 molecules in particular in the marine environment.

Introduction

The isotopic signatures of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) can be used as a tool to understand pathways, processes and the fate of CO_2 molecules, particularly in the marine environment (Figure 1). The reason for this can be found in the fact that $\delta^{13}C$-values are controlled by species specific metabolic processes of respiration and photosynthesis, while the $\delta^{18}O$-values are affected by the oxygen exchange between the molecules of CO_2 and the ambient water. Here we present a new analytical approach to determine $\delta^{13}C$ and $\delta^{18}O$ changes using a mid-infrared laser (IRIS) absorption spectrometer, Thermo Scientific™ Delta Ray™ IRIS with (Universal Reference Interface) URI™ Connect.

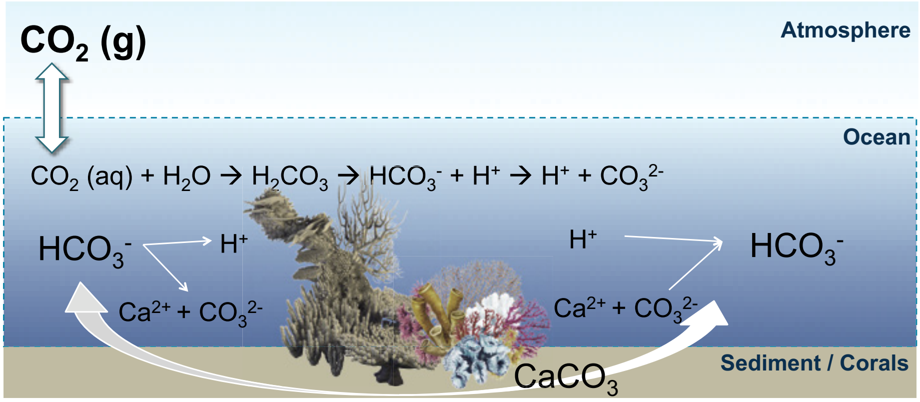

Figure 1. Simplified view of CO_2 air-ocean flux.

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With IRIS technology, it is possible to record online changes of carbon and oxygen isotopes with time resolutions of seconds, and with this to have a better insight in CO_2 fluxes.

Delta Ray IRIS with URI Connect

The instrument is based on direct absorption spectroscopy and it uses mid-infrared laser that operates at 4.3 µm. Measurement of different carbon dioxide isotopologues and determination of stable isotope ratios from spectrum is possible due to absorption lines which are shifted relative to each other (Figures 2 and 3).

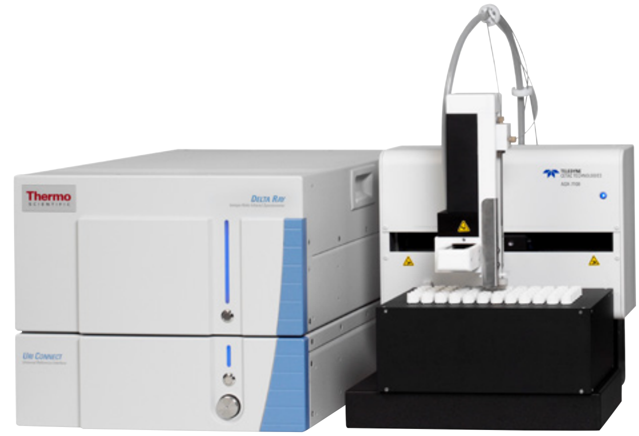

Figure 3. Thermo Scientific™ Delta Ray™ IRIS with URI™ Connect and Teledyne CETAC™ ASX-7100 Autosampler.

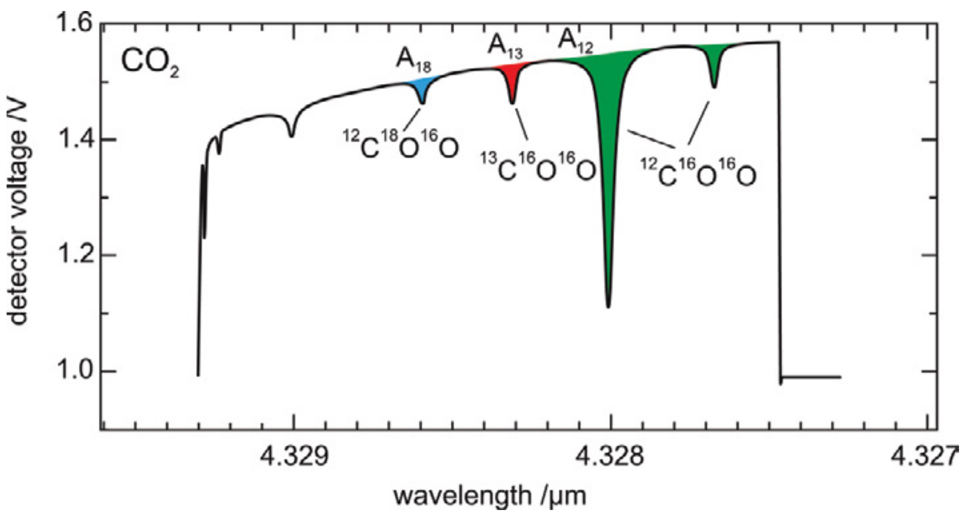

Figure 2. Mid-infrared spectral region at a wavelength of 4.3 µm. The laser scans over the absorption lines at 500 Hz. The stable isotope ratios of carbon dioxide can be calculated from the respective peak areas of the different isotopologues.

Coral culturing facilities

This new approach was tested in a 600 l reef coral culturing tank at GEOMAR, Kiel.

The setup comprised three tanks with a closed recirculation system and with controlled day-night cycle (Figures 4 and 5). All water parameters are monitored to keep the system in a stable state. Decrease of calcium concentration and carbonate alkalinity was compensated by calcium reactor, addition of bicarbonate and $CaCl_2$ solutions. Due to photosynthesis and respiration, the seawater pH ranges from 8.0 during the day and to 7.7 in the night, while temperature is kept constant at 26 ± 1°C.

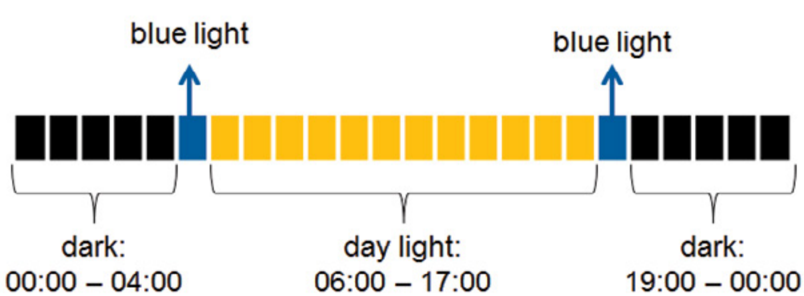

Figure 4. The scheme shows day-night cycle control.

Figure 5. Coral culturing setup: 1) Main reef tank, 2) Culture tank, 3) Cleaning unit with three compartments; the first contains live rock, the second holds a protein skimmer, the third contains return pumps and sensors.

Measurements in controlled environment

IRIS technology enables us to conduct continuous measurements, with time resolution of seconds, and it also gives us opportunity to measure discrete samples.

Experimental setup: Air measurements

Equilibrator like setup was used for air measurements (Figure 6). Air was continuously pumped through the Delta Ray Analyzer with a flow of 80 mL/min. Measurement per sample was 3 minutes and with integration time of 60 seconds we achieved internal precision better than 0.05‰ for both $\delta^{13}C$ and $\delta^{18}O$, per sample run.

Experimental setup: DIC measurements of discrete seawater samples

Along with continuous measurement of air, we collected water samples from the main reef tank every 1 to 3 hours during a period of 24 hours. The $\delta^{13}C$-values of dissolved inorganic carbon (DIC) were analyzed with Delta Ray with URI Connect, using Teledyne CETAC™ ASX-7100 Autosampler, following the gas evolution method with orthophosphoric acid (McCrea, 1950).

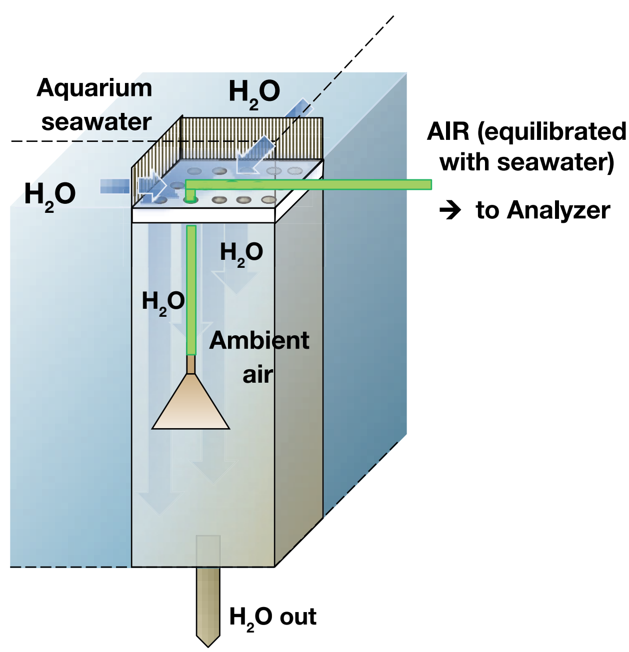

Figure 6. Equilibrator like column used for mixing air and water from the main reef.

Air measurements: CO_2 (ppm), $\delta^{13}C$ and $\delta^{18}O$

- Results present the daily average of approximately 100 days of continuous measurement.
- Due to biological production, isotopic change occur rapidly when light intensity is changed. Photosynthesis preferentially removes the light isotope ^{12}C from seawater.
- Amplitude of change in CO_2 concentration during day-night cycle was approximately 740 ppm, while the average day-night amplitudes for $\delta^{13}C$ and $\delta^{18}O$ were about 2.7‰ and 0.6‰ (Figure 7, 8).

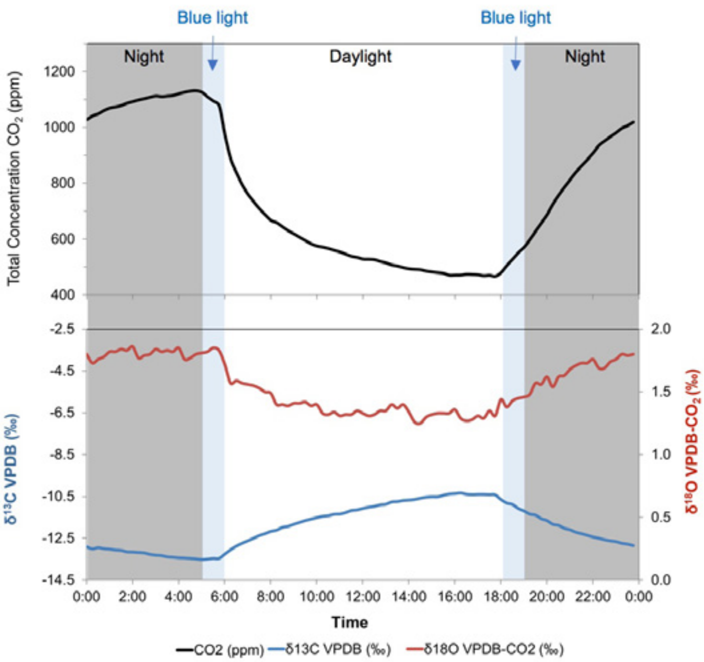

Figure 7. Daily average for approximately 100 days of continuous measurements. Black line shows the change in CO_2 concentration, while red and blue lines indicate changes in $\delta^{13}C$ and $\delta^{18}O$.

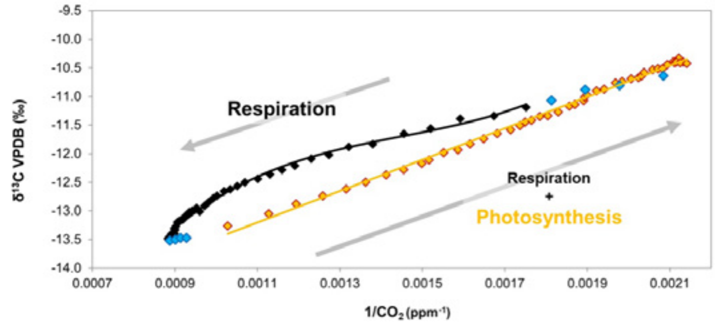

Figure 8. CO_2 sources can be distinguished due to the $\delta^{13}C$ changes within a diurnal cycle.

$\delta^{13}C$ and $\delta^{18}O$ – Air and DIC measurements

- The $\delta^{13}C$-values of dissolved inorganic carbon (DIC) follow the same trend as it was observed during continuous air measurements, with an average amplitudinal change in $\delta^{13}C$ of about 2.4‰. DIC in water becomes enriched in $\delta^{13}C$ due to preferential uptake of ^{12}C during photosynthesis.
- Measured data also showed that fractionation of CO_2 (g), relative to DIC (dissolved HCO_3^-) is -7.5 ± 0.2‰, which is in a close agreement with isotope fractionation of -7.92‰ in the equilibrium system CO_2-HCO_3- at 26 °C (Mook et al. 1974) (Figure 9).

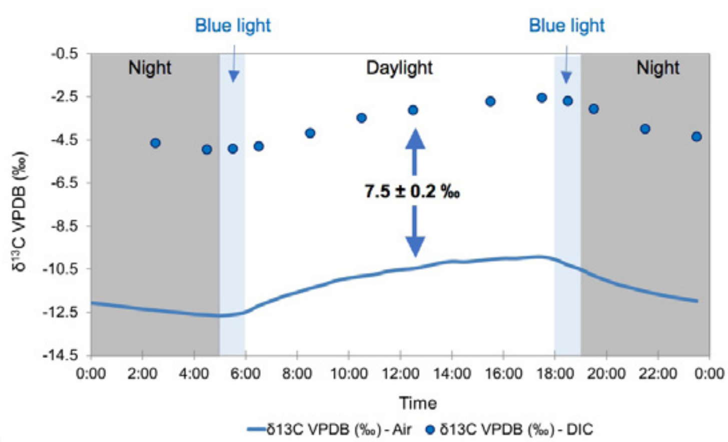

Figure 9. Comparison of continuous air measurements and measurements of DIC samples.

Conclusion and future work

- Delta Ray IRIS with URI Connect offers a possibility for in-situ monitoring of $\delta^{13}C$ and $\delta^{18}O$ changes in aquatic environments

- When combined with Equilibrator, Delta Ray IRIS with URI Connect offers possibility for measurements of CO_2 fluxes across air-seawater interface, and direct insight in $\delta^{13}C_{DIC}$ changes in the aquatic system

- Field experiments of this technique will show if a large-scale measurement of CO_2 fluxes is possible, and whether this system may be used to monitor status of coral reef metabolism to estimate the influence of human activity in coastal areas

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References

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