Continuous carbon isotope data of CO<sub>2</sub> and CH<sub>4</sub> measured along the coast of NW Africa and SW Europe reveal changes in greenhouse gas sources.



# High-precision cavity ringdown measurements of $\delta^{13}CO_2$ and $\delta^{13}CH_4$ along the Eastern North Atlantic onboard the sailing research vessel *Fleur de Passion*

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### INTRODUCTION

- Differentiating microbial, anthropogenic, and thermogenic sources of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) in background air is an important element of understanding upper ocean ecosystem processes.
- Here we present isotopic data of carbon dioxide and methane from the *Fleur de Passion* sailing research vessel which traveled from Dakar (Senegal) to Carbo Verde, the Azores, and to France between April and October 2019 as part of the larger Ocean Mapping Expedition by the Geneva based NPO *Fondation Pacifique*.

#### **INSTRUMENTATION**

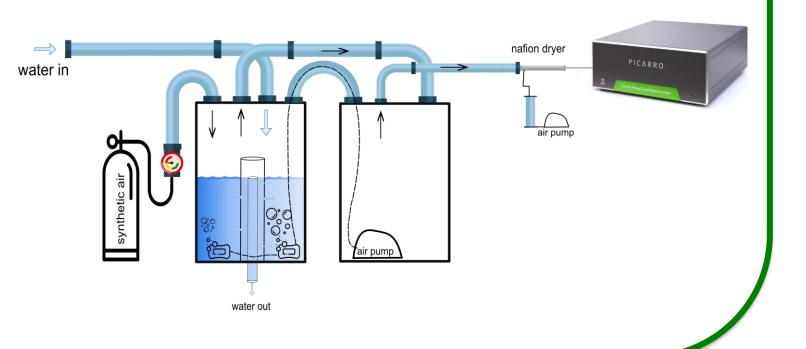
# Picarro G2201-*i* analyzer (near infrared)

- Field-deployable analyzer for simultaneous high-precision δ¹³C analysis of CH<sub>4</sub> and CO<sub>2</sub>.
- Precision (1- $\sigma$ , 1-hour window, 5-minute averages):  $\delta^{13}\text{C-CO}_2 < 0.16\%, \, \delta^{13}\text{C-CH}_4 < 1.15\%$



## Dissolved gas analysis with the dual carbon isotope analyzer G2201-i

- In this study, the isotopic composition of carbon dioxide and methane was measured on the mast of the sailing boat. However, source apportionment of aquatic systems can also require to measure the isotopic composition of dissolved gases. Currently, Picarro does not provide a complete solution for dissolved gas analysis but the Picarro analyzers can be coupled with gas extraction or equilibrator devices (see Becker et al., 2012; Maher et al., 2013; Webb et al., 2016; Pohlman et al., 2017; Becker et al., 2018).
- As an example of a setup for dissolved gas analysis, this schematic shows a bubble type equilibrator that is currently being tested by César Ordóñez, Daphne Donis and coworkers (University of Geneva).



# REFERENCES

[1] Becker M., Andersen N., Fiedler B., Fietzek P., Körtzinger A., Steinhoff T. and Friedrichs G. (2012) Using cavity ringdown spectroscopy for continuous monitoring of δ¹³C(CO₂) and fCO₂ in the surface ocean. Limnol. Oceanogr. Methods 10, 752–766.
 [2] Becker M., Steinhoff T. and Körtzinger A. (2018) A Detailed View on the Seasonality of Stable Carbon Isotopes Across the North Atlantic. Global Biogeochem. Cycles 32, 1406–1419.

[3] Maher D. T., Santos I. R., Leuven J. R. F. W., Oakes J. M., Erler D. V., Carvalho M. C. and Eyre B. D. (2013) Novel use of cavity ring-down spectroscopy to investigate aquatic carbon cycling from microbial to ecosystem scales. *Environ. Sci. Technol.* **47**, 12938–12945.
[4] Pohlman J. W., Greinert J., Ruppel C., Silyakova A., Vielstädte L., Casso M., Mienert J. and Bünz S. (2017) Enhanced CO<sub>2</sub> uptake at a shallow Arctic Ocean seep field overwhelms the positive warming potential of emitted methane. *Proc. Natl. Acad. Sci.* **114**, 5355–5360.
[5] Webb J. R., Maher D. T. and Santos I. R. (2016) Automated, in situ measurements of dissolved CO<sub>2</sub>, CH<sub>4</sub>, and δ<sup>13</sup>C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators. *Limnol. Oceanogr. Methods* **14**, 323–337.

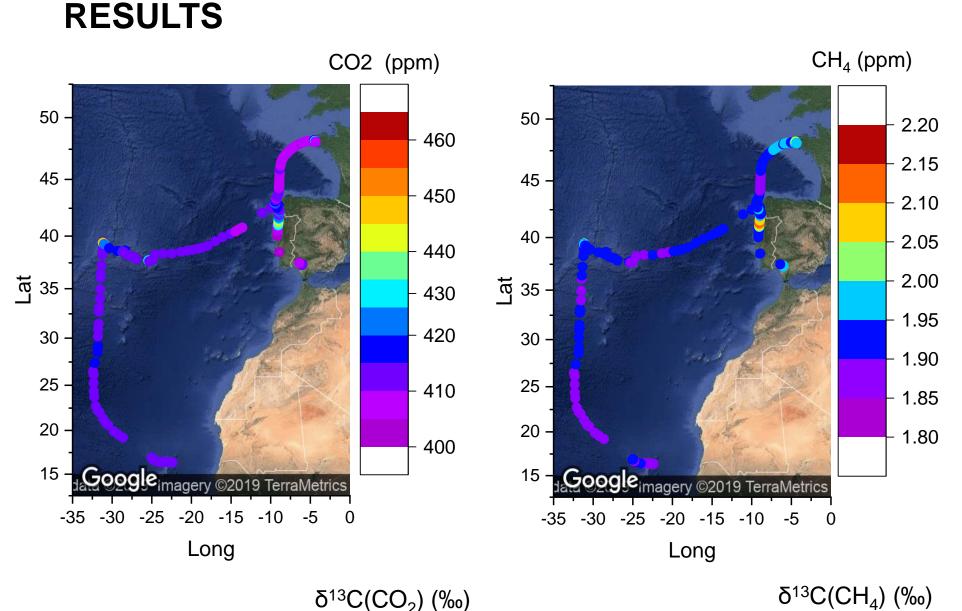


Fig. 1: Carbon dioxide and methane concentration measured onboard the sailing boat *Fleur de Passion*. The cruise started in April in Dakar and ended in October in France. On the open sea, the concentrations were close to background concentrations. Close to the coastland and the Azores concentrations were enriched.

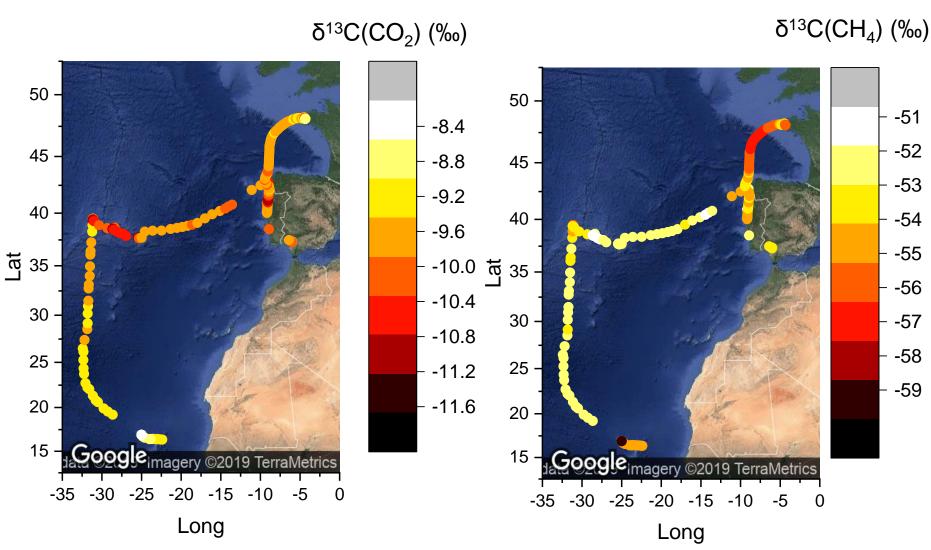
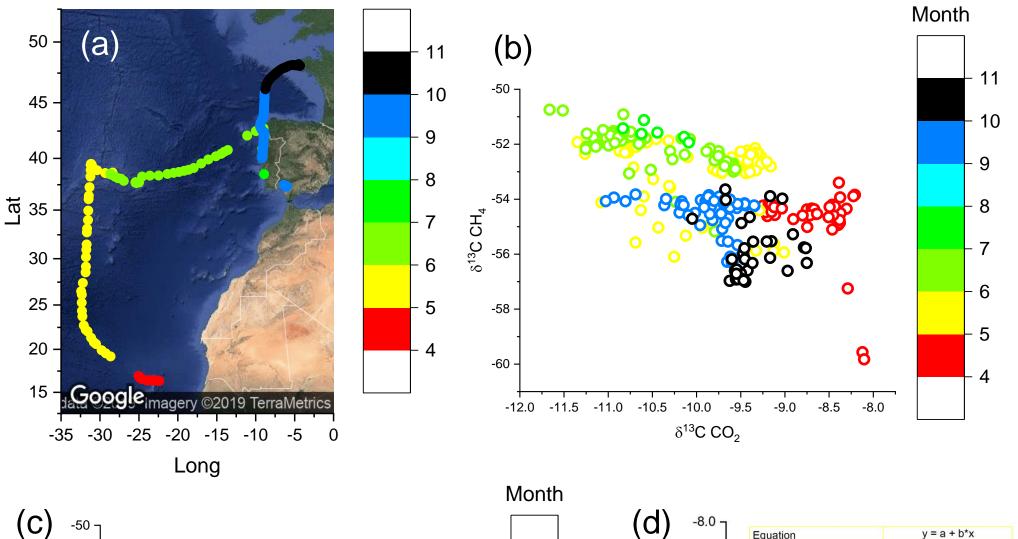
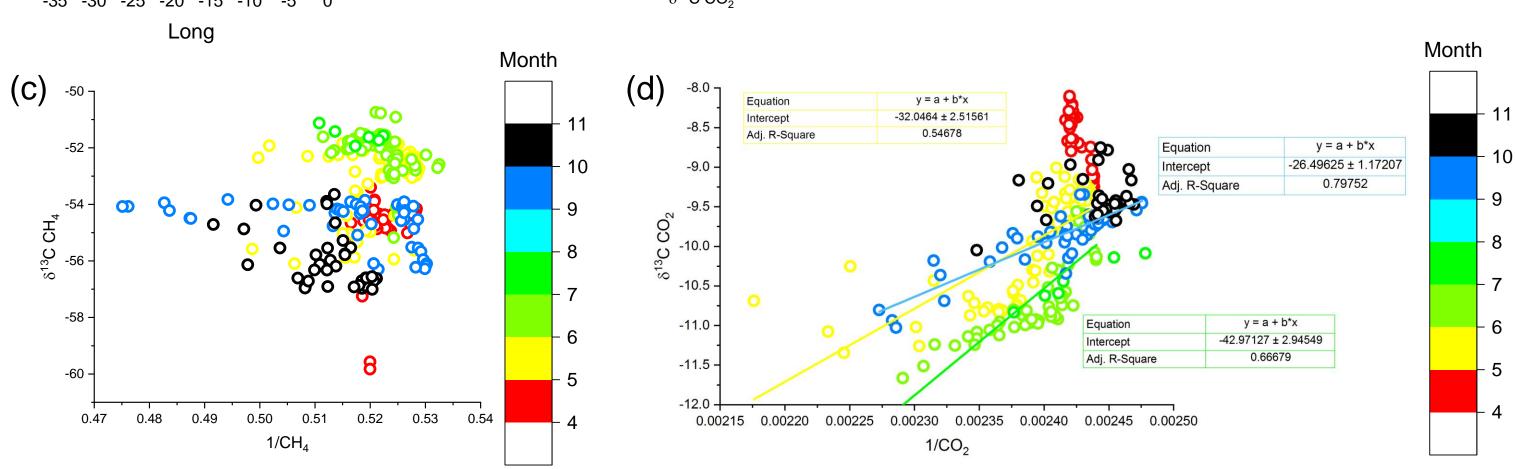


Fig. 2: Carbon isotope composition of carbon dioxide and methane measured along the track of the sailing research vessel. For easier readability, the data points are displayed as 4h-averages. The carbon isotope signature shows distinct changes.



**Fig. 3**: (a) Map illustrating the sailing boat track as a function of time. (b) Overall,  $\delta^{13}C(CO_2)$  and  $\delta^{13}C(CH_4)$  show an anticorrelation. (c) The  $CH_4$  Keeling plot does not exhibit distinct isotopic end-members. (d) However, the  $CO_2$  Keeling plot shows distinct source signatures for May, June and September.



## CONCLUSIONS

- The Picarro G2201-*i* analyzer on board the research sailing vessel *Fleur de Passion* allowed to measure among the longest carbon dioxide and methane isotope records along the coast of Africa.
- The continuous data show distinct variations in the isotopic composition that are controlled by season and measurement location.







