New data from the 40 year old Dye 3 core

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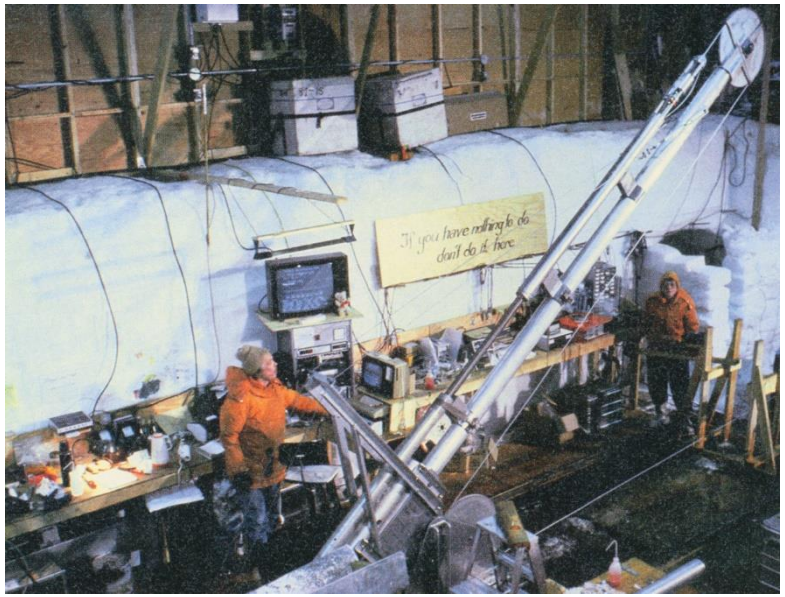
The Dye3 core was drilled at Dye3 (65°11'N, 43°50'W) in 1979 – 1981. The core has been analyzed for numerous components over the last decades. We measured remaining sections, the Younger Dryas and a larger portion of the last glacial, in a continuous flow setup in fall 2019. Here we focus on gas measurements. We measured methane, $\delta^{15}N$, $\delta^{40}Ar$, and the elemental ratio of Ar and N_2. We present the continuous flow setup for measuring those components in parallel and first results with a focus on the exact timing of changes in methane and $\delta^{15}N$ and $\delta^{40}Ar$ at the Younger Dryas and Dansgaard-Oeschger transitions.

Dye 3 1979-1981

Dye3 station

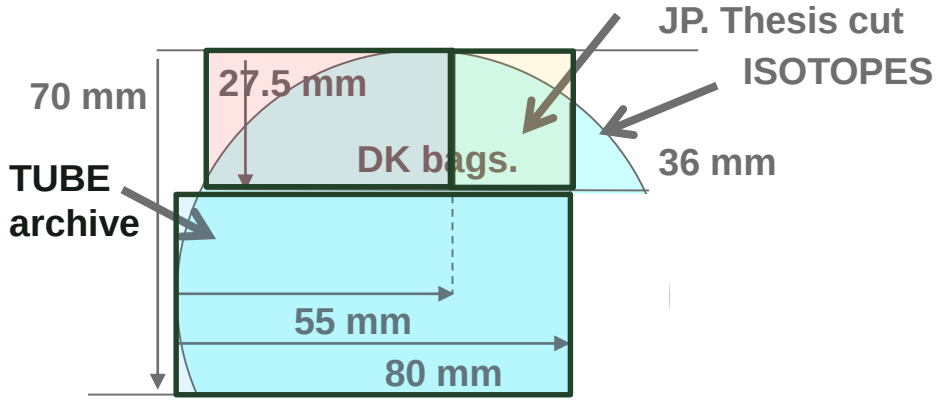


GISP drill trench at Dye3 station

The US radar station Dye 3 was the location where the Greenland Ice Sheet Project (GISP) deep drilling took place between 1979 and 1981. It was a collaboration between three nations, Denmark, Switzerland and the United States. The core was divided between laboratories. Numerous key publications on the past northern hemispheric climate are based on the Dye 3 core.

In the course of this project most of the remaining core in Denmark has been used up.

From the TUBE archive a continuous flow stick was cut. In places samples were also taken for discreet measurements.



Reconstructed cutting scheme (Ø = 98 mm)

Copenhagen continuous flow system

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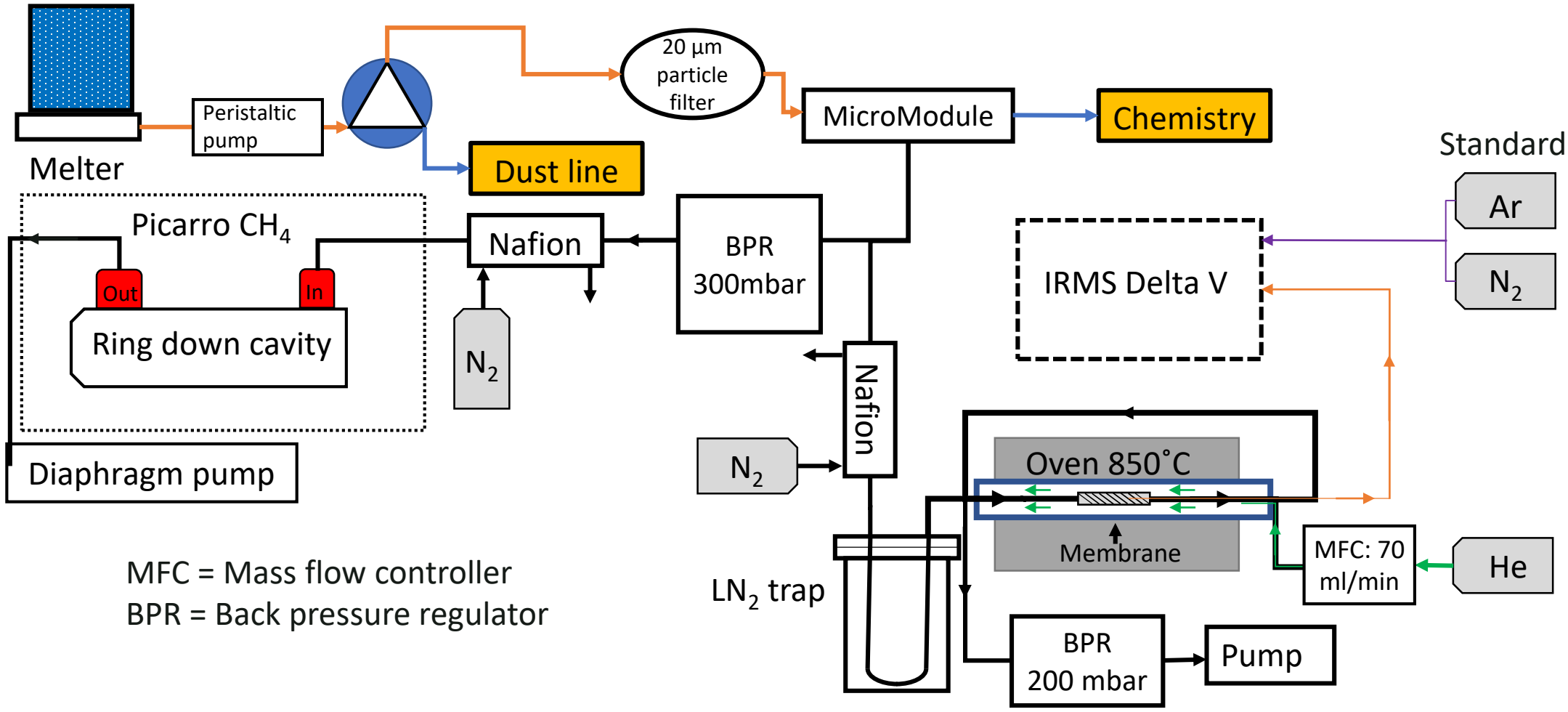
Picture of the Copenhagen melter



MFC = Mass flow controller
BPR = Back pressure regulator

The continuous flow setup used in the Dye 3 campaign focuses on gas analyses. Only a fraction of the water is separated before the MicroModule (0.75" X 1", 3M Liqui-Cel) for dust analysis while the bulk water flow goes directly to the MicroModule. Pressure at the module is held constant by a backpressure regulator (BPR). A constant small fraction of the sample is directed to the mass spectrometer for $\delta^{15}N$, $\delta^{40}Ar$ measurements passing a Nafion dryer, LN_2-trap to remove CO_2, and a membrane for Oxygen removal. The bulk air is directed to the Picarro analyzer for CH_4 concentration measurements passing a Nafion dryer.

O_2 removal oven setup

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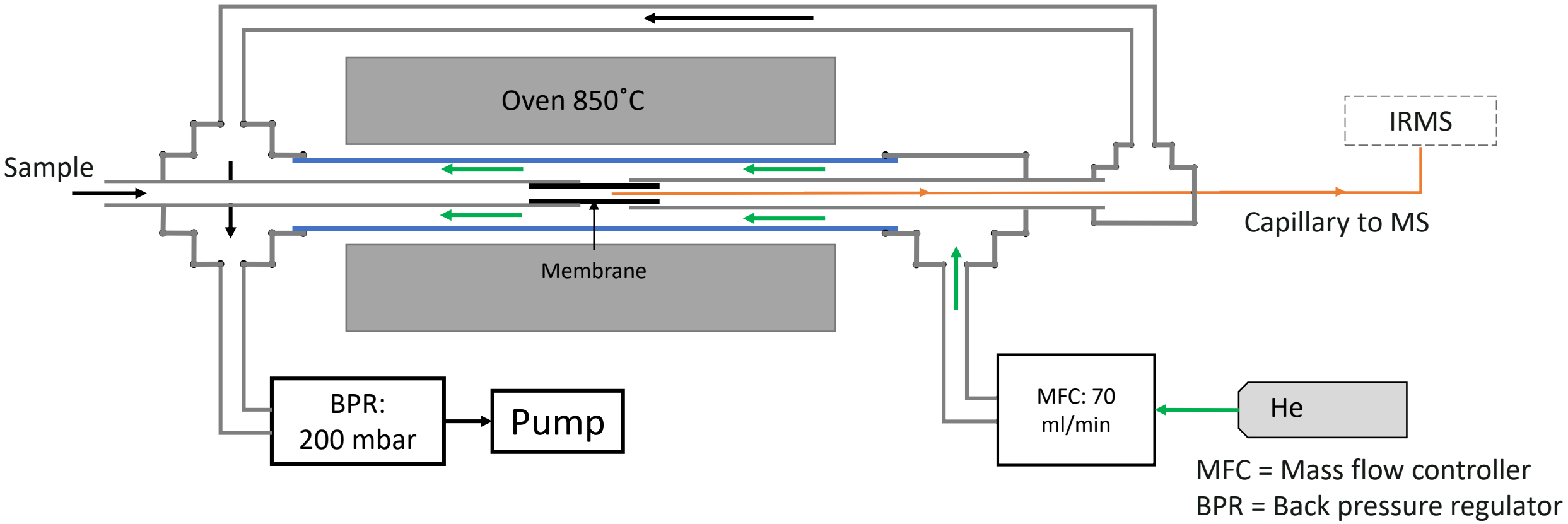

The core of the oxygen removal is a mixed ionic/electronic conducting tubular perovskite membrane we obtained from the Frauenhofer-Institute for Interfacial Engineering and Biotechnology Inorganic Surfaces and Membranes (Germany). The sealing of the membrane at 850°C is problematic and the system we used is not leak tight. We probably loose part of our sample before entering the membrane section and we cannot exclude that some of the He purge gas is entering the inner membrane section. The total amount of O_2 removed is in the high 90% range.

Results overview

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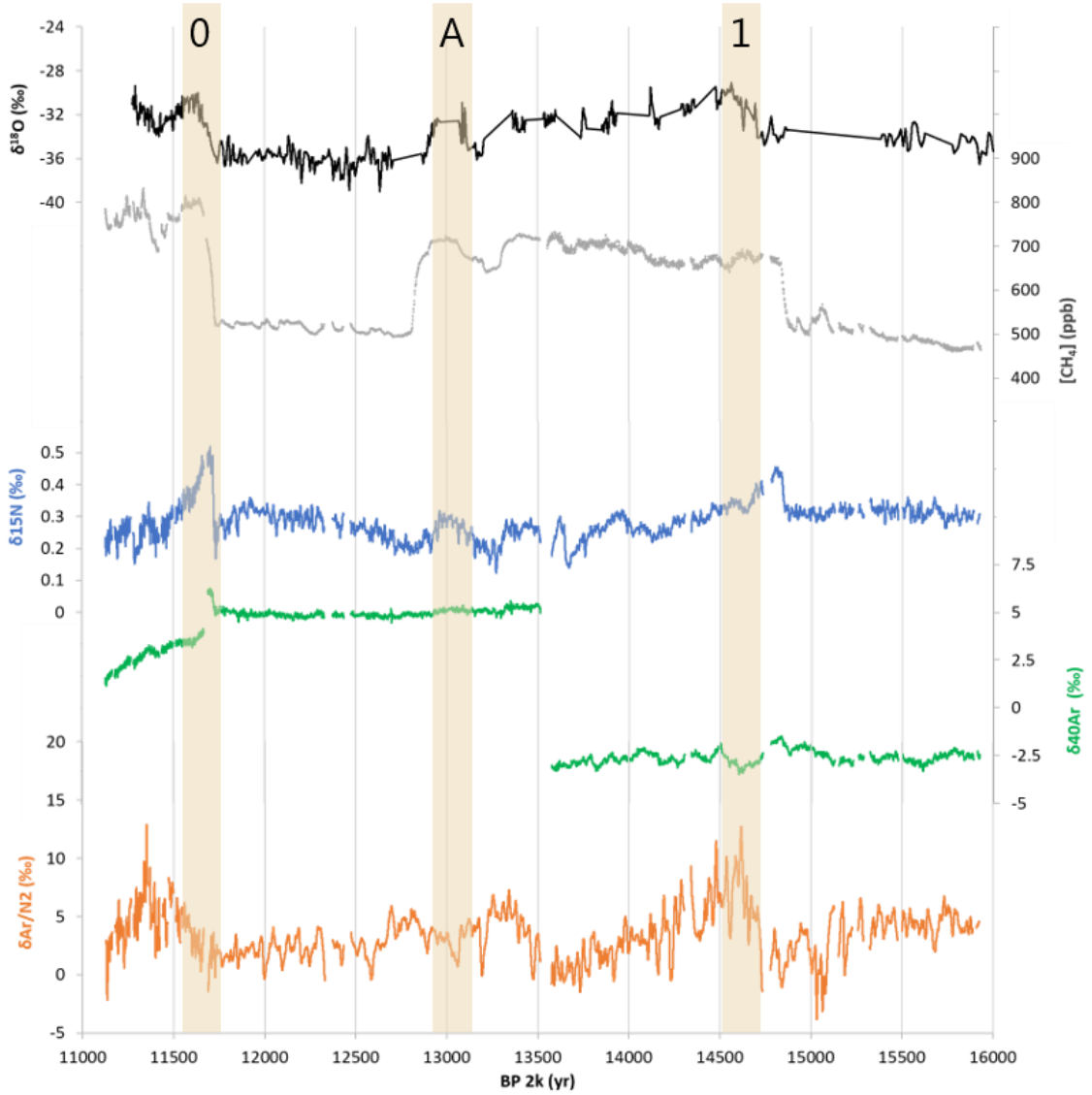

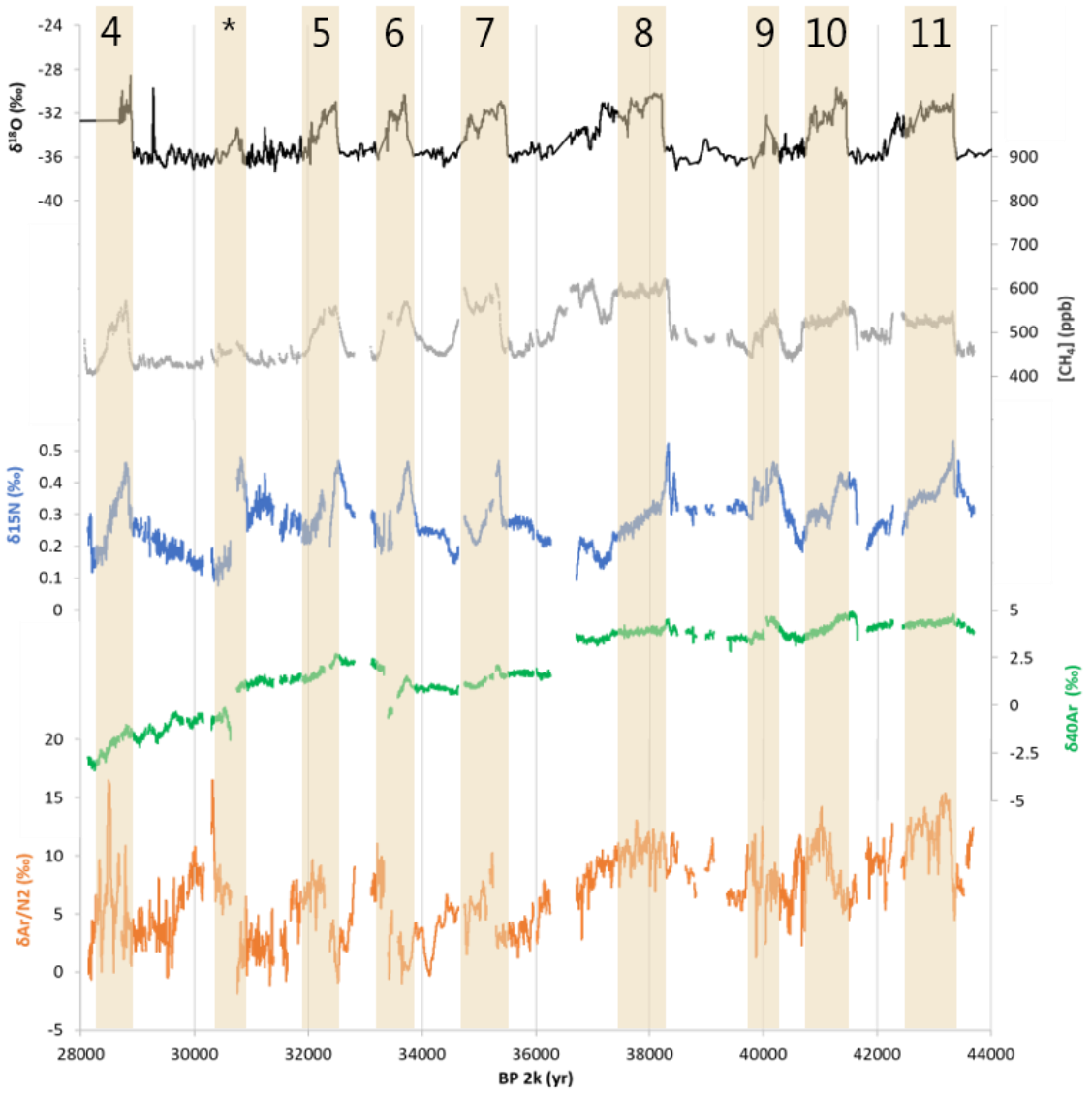

Overview of the results: Top to bottom Original $\delta^{18}O$ measurements from Dye3 [1], On-line CH_4 (gray), $\delta^{15}N$ (blue), $\delta^{40}Ar$ (green) and $\delta Ar/N_2$ (orange) data. There are clear problems in the calibrations of the isotope data especially in $\delta^{40}Ar$.

[1] Langway, C. C., H. Oeschger, and W. Dansgaard (**1985**), *Greenland ice core: geophysics, geochemistry, and the environment*, 118 pp., American Geophysical Union, Washington, DC.

Comparison with NGRIP $\delta^{15}N$ data

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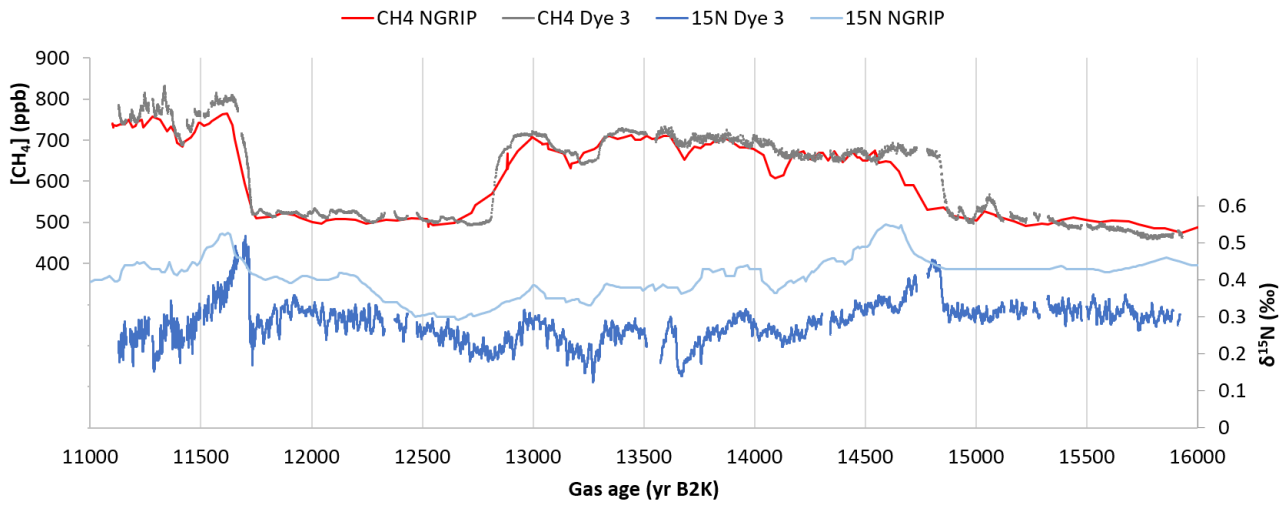

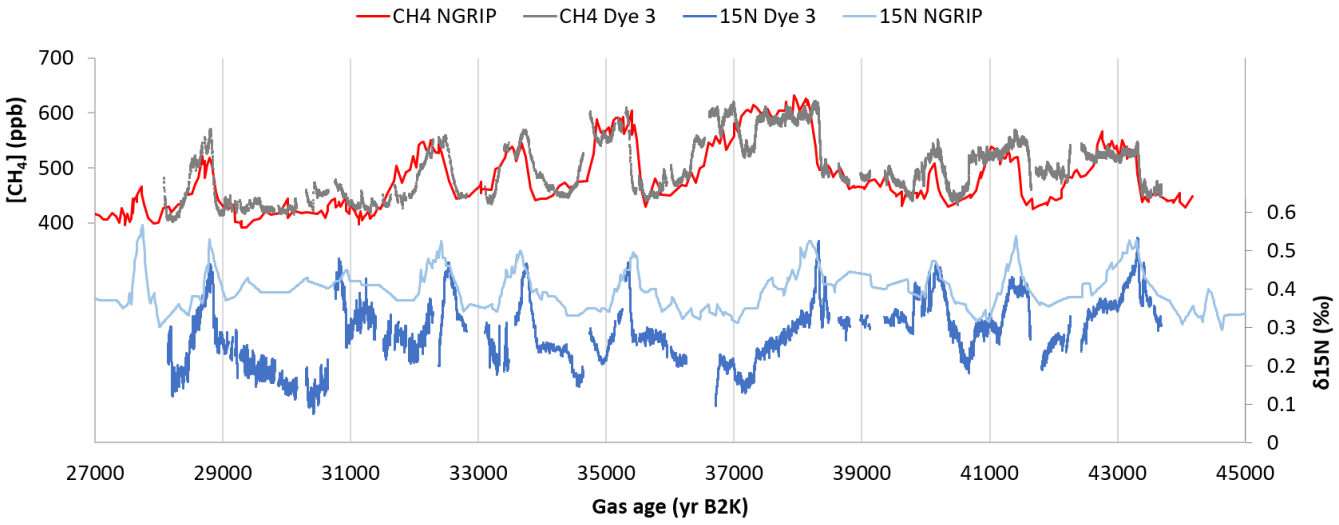

$\delta^{15}N$ excursions at the start of Dansgaard-Oeschger events				
	NGRIP		Dye3	
Age (kyr)	Duration of increase (yr)	$\delta^{15}N$ increase (‰)	Duration of increase (yr)	$\delta^{15}N$ increase (‰)
11.7	170	0.124	43	0.242
14.7	83	0.074	61	0.121
29.0	261	0.160	59	0.192
32.4	333	0.176	175	0.142
33.9	249	0.111	287	0.214
35.6	152	0.090	202	0.210

The gas time scales of NGRIP and Dye3 have been synchronized. This relative time scale may need further adjustment given the different resolution and smoothing in the core and the analytical system. The $\delta^{15}N$ response at rapid temperature events is generally larger and faster at Dye3 than at NGRIP which probably originates from a larger temperature jump at Dye3 compared to central Greenland. Such a finding is consistent with a 1.5 times larger LGM-Holocene temperature increase at Dye3 comparted to central Greenland from borehole temperature reconstruction (Dahl-Jensen et al., 1998).

We find no significant time offset in the increase of CH_4 and $\delta^{15}N$ in the Dye 3 core. Further analysis will allow to substantiate that conclusion.

Discussion

As already demonstrated by Huber and Leuenberger (2004) it is possible to measure major isotope ratios from on line system. The calibration of the system and drifts are a challenge. We are confident, that the system can be improved by minimizing volumes, a better introduction of standards into the mass spectrometer and a better measurement protocol. The advantage of an online system is unprecedented time resolution but it comes at the cost of accuracy. We, however, expect that relative changes over a limited measurement time span are reliable. Individual samples for isotope measurements have been taken and will allow judging that expectation.

The gas time scales of NGRIP and Dye3 have been synchronized. This relative time scale may need further adjustment given the different resolution and smoothing in the core and the analytical system. The $\delta^{15}N$ response at rapid temperature events is generally larger and faster at Dye3 than at NGRIP which probably originates from a larger temperature jump at Dye3 compared to central Greenland. Such a finding is consistent with a 1.5 times larger LGM-Holocene temperature increase at Dye3 comparted to central Greenland from borehole temperature reconstruction (Dahl-Jensen et al., 1998). In combination with individual samples it will be possible to absolutely calibrate the on-line measurements of $\delta^{15}N$, $\delta^{40}Ar$. We hope that the combination of on-line and individual samples will allow us to reliably reconstruct the temperature amplitudes and timing over rapid climate change at Dye3. We find no significant time offset in the increase of CH_4 and $\delta^{15}N$ in the Dye 3 core. Further analysis will allow to substantiate that conclusion.

Dahl-Jensen, D., K. Mosegaard, N. S. Gundestrup, G. D. Clow, S. J. Johnsen, A. W. Hansen, and N. Balling (1998), Past temperatures directly from the Greenland ice sheet, Science, 282, 268-271

Huber, C., and M. Leuenberger (**2004**), Measurements of isotope and elemental ratios of air from polar ice with a new on-line extraction method, *Geochem Geophys Geosyst*, *5*(Q10002), doi: 10.1029/2004GC000766