Measurements of δ^{18}O of atmospheric O_2 (δ$^{18}O_{atm}$) by optical spectroscopy

Application to biological chambers experiments

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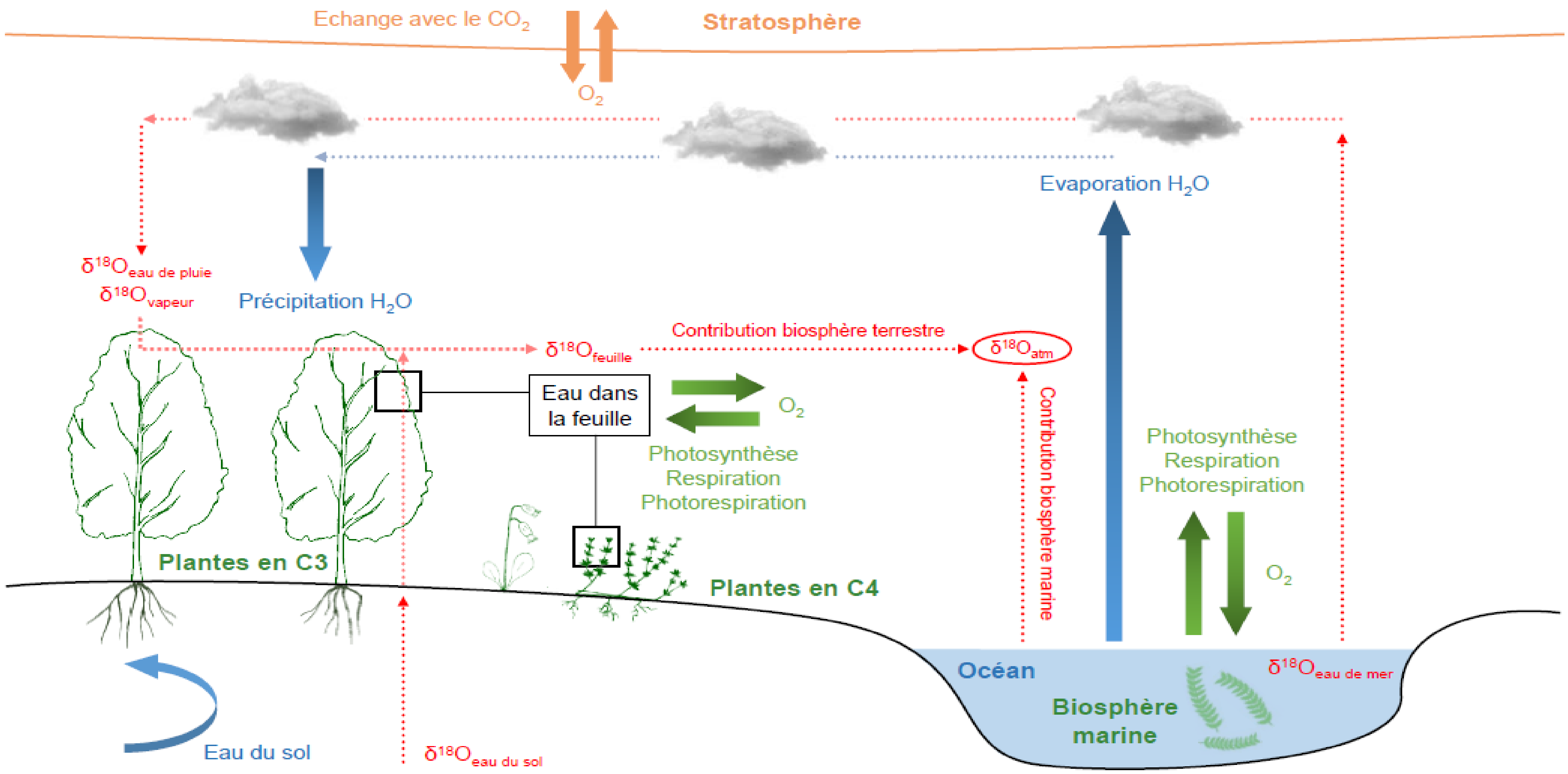
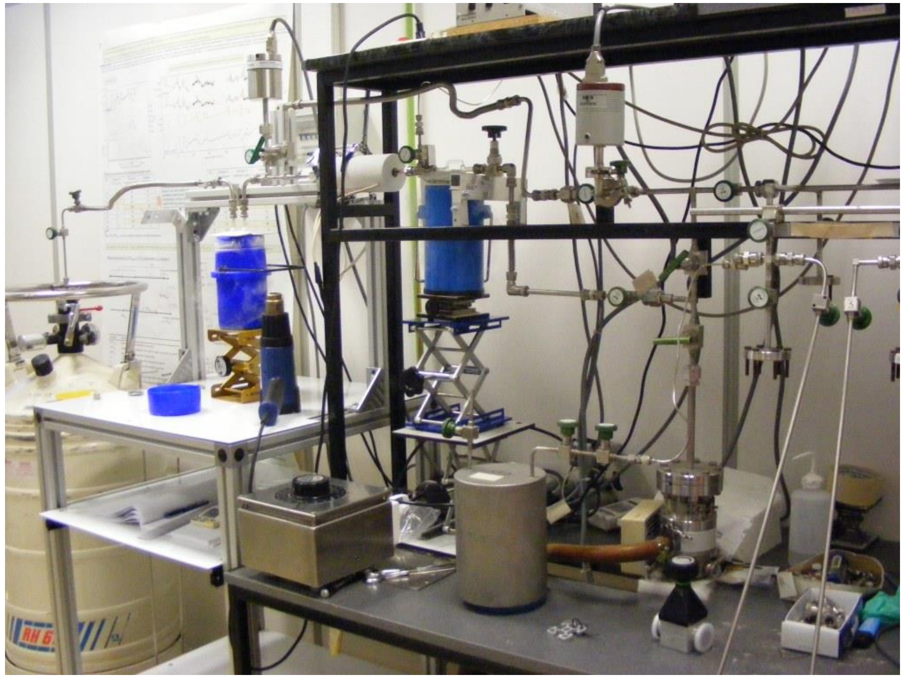
Oxygen cycle and influences on the isotopic composition of oxygen



Classical measurements of $\delta^{18}O$ of O_2 and $\delta O_2/N_2$



1- Extraction of air from ice bubbles

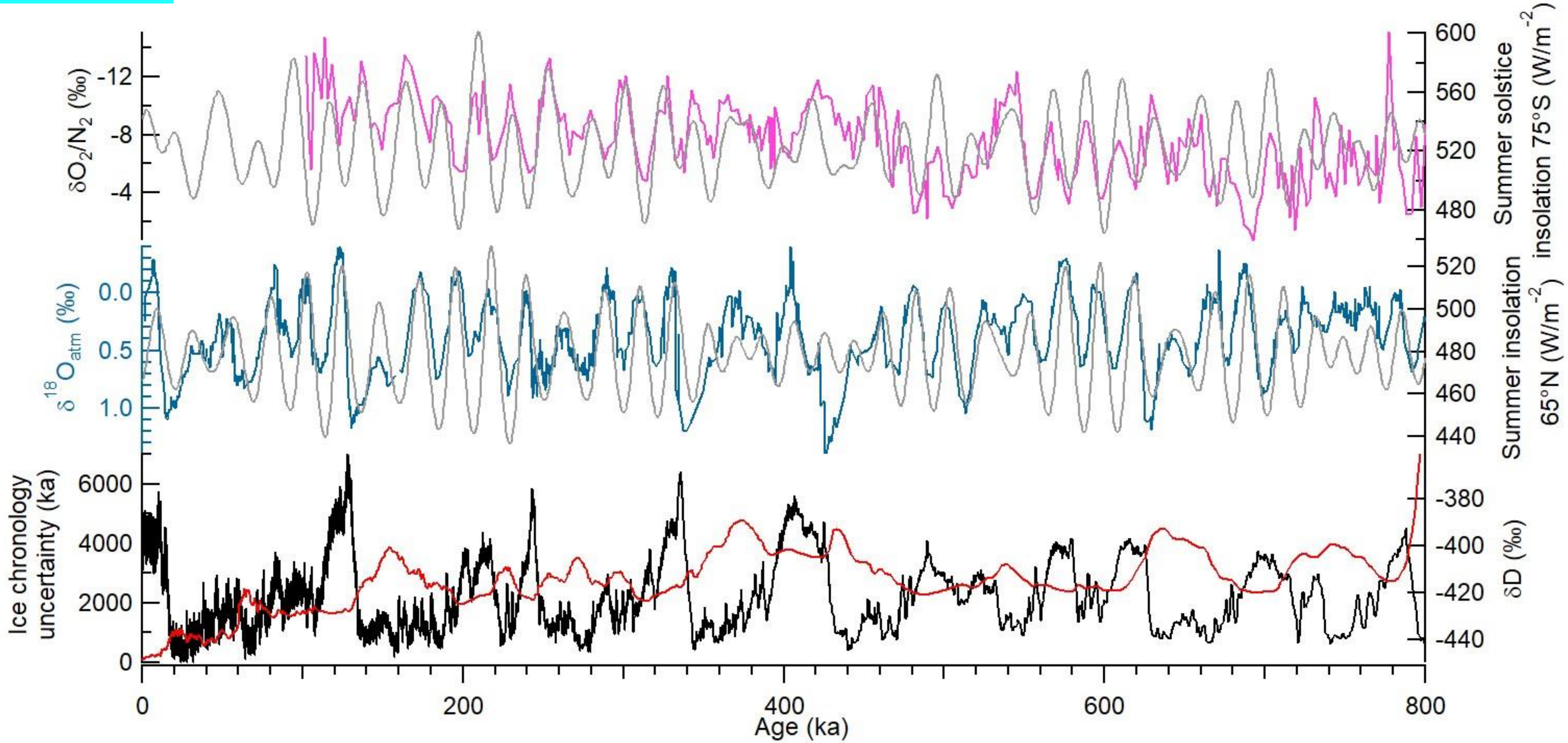
2- Drying and CO_2 removal

3- Measurements by IRMS with dual inlet (1 h for each sample)

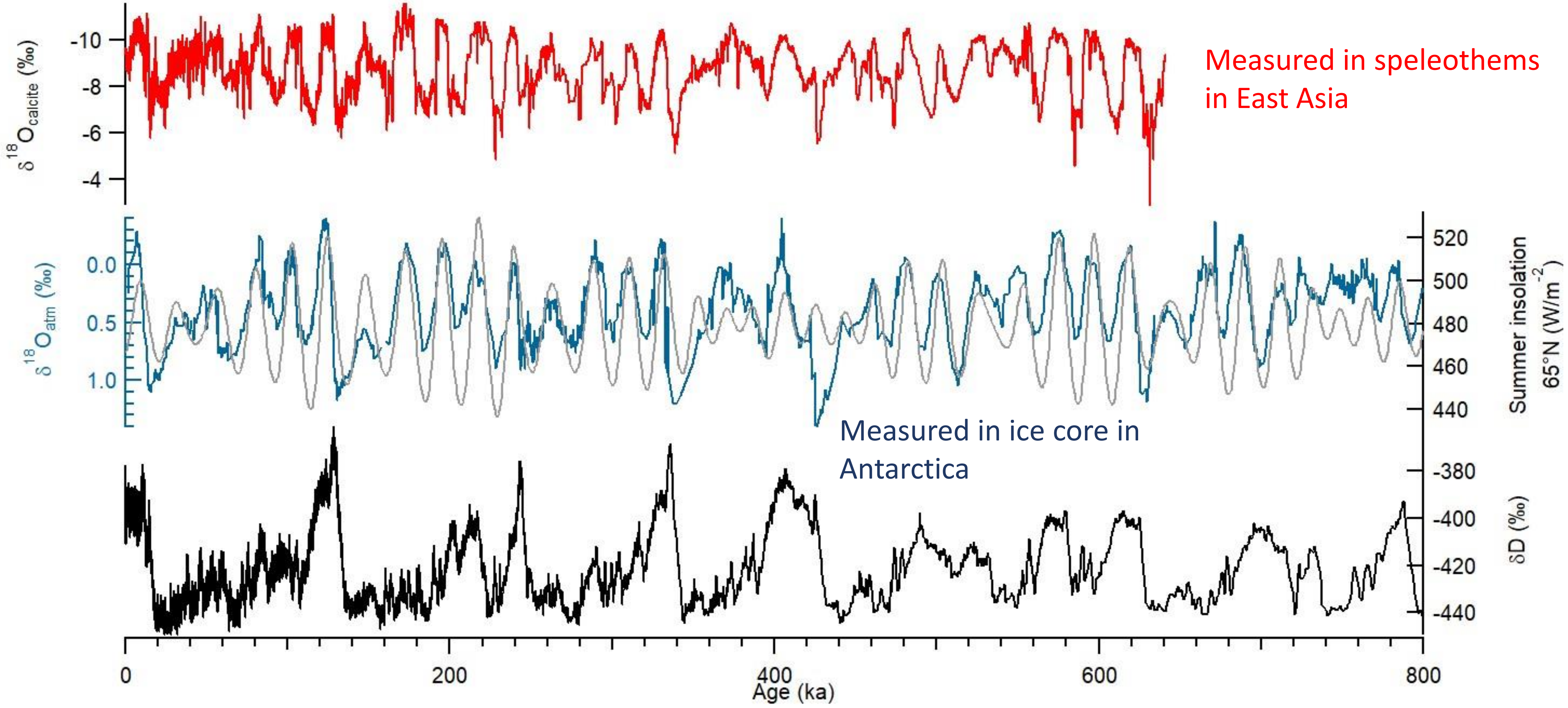
4- $\sigma <\delta^{18}O \text{ of } O_2> = 0.02$ ‰ ; $\sigma <\delta O_2/N_2> = 1$ ‰

5- Need 1 cc of air (10 g of ice)

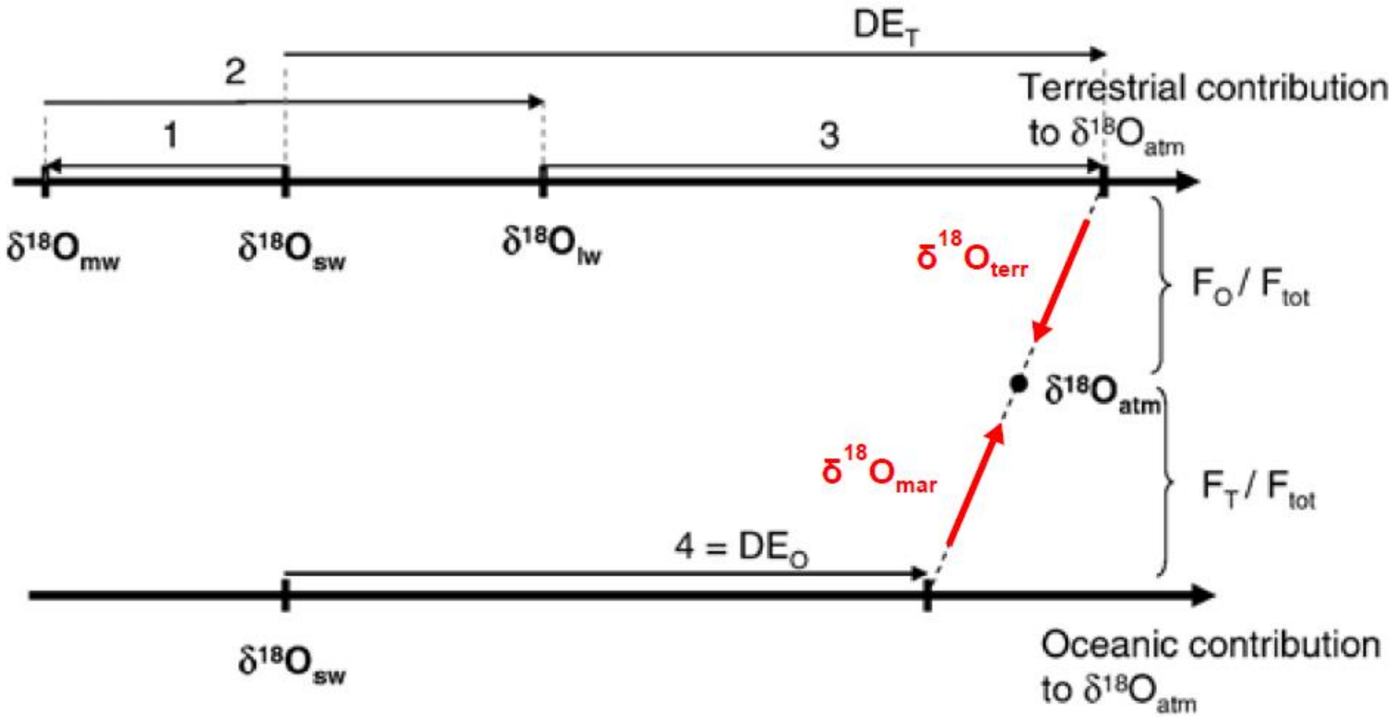
$\delta O_2/N_2$ and $\delta^{18}O_{atm}$: essential tools for the ice core chronology

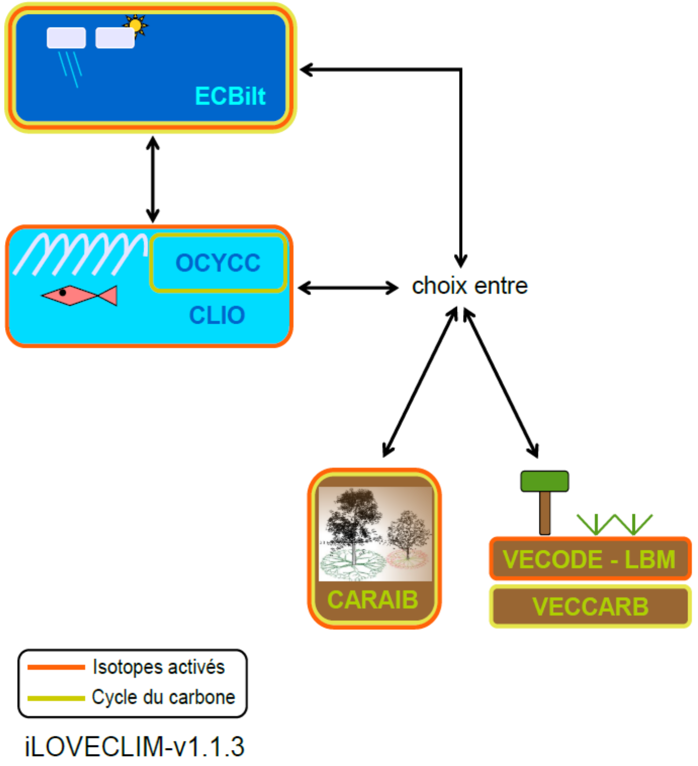


$\delta^{18}O_{atm}$ in ice core : tracer of low latitude water cycle



Toward a quantitative interpretation of $\delta^{18}O_{atm}$

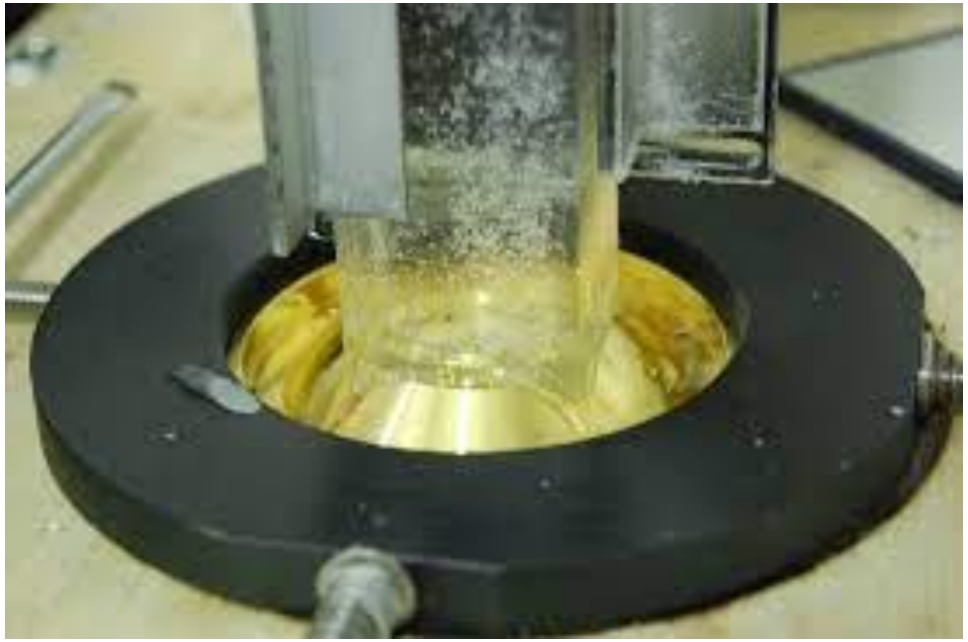




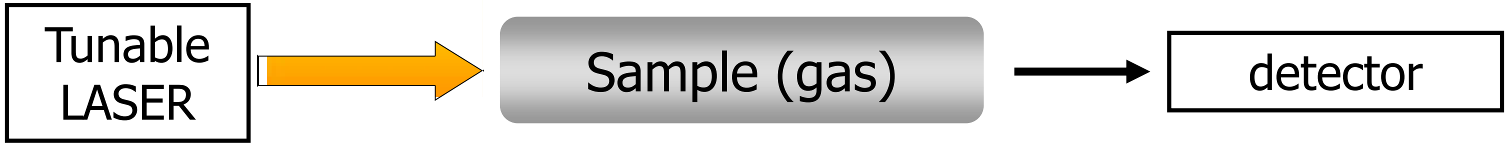
Thomas Extier, Ji-Woong Yang, Didier Roche, Nathaëlle Bouttes

Need continuous measurements of $\delta^{18}O_{atm}$

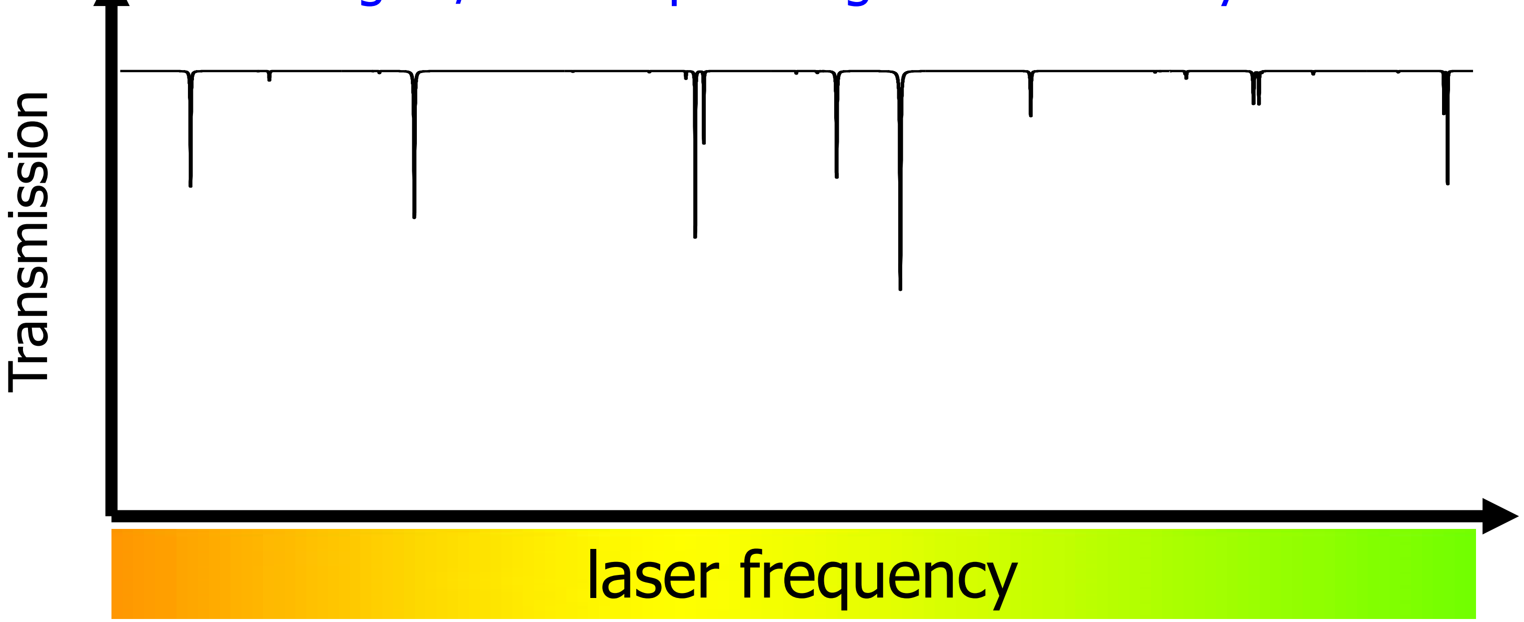
- In controlled biology experiments: quantification of fractionnation coefficients during biological O_2 uptake and production processes
- In ice cores: continuous measurements of $\delta^{18}O_{atm}$ on ice core for providing a chronology (new ice core Beyond EPICA – 1.5 Myrs ?)



Absorption spectroscopy & trace analysis…



spectral resolution -> selectivity
signal/noise & pathlength -> sensitivity



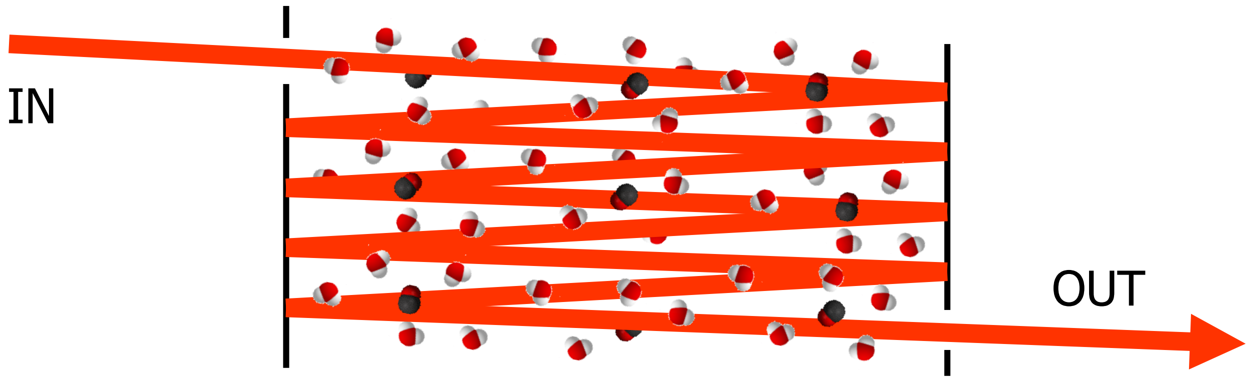
Lambert-Beer law
$I_{out} / I_{in} = \exp(-\alpha(\nu) L)$

$\alpha(\nu) \sim n\, k(\nu)$

Detect small α and choose strong transitions (large k) -> trace analysis !

Increase path -> sensitivity?

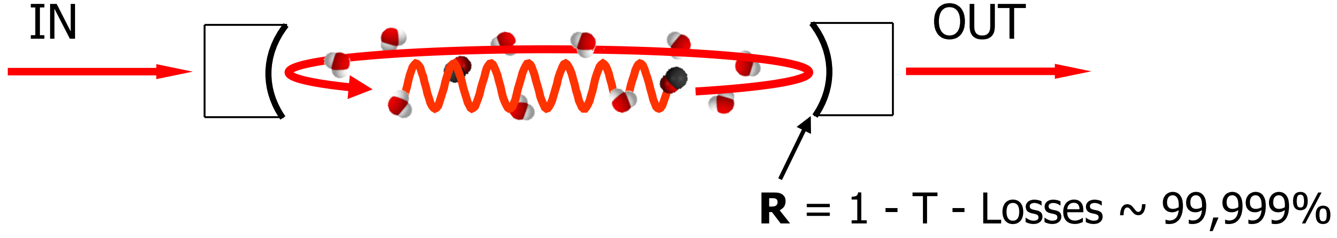
Multipass cell



100 x path (>10km)

volume / 100…!

Optical cavity



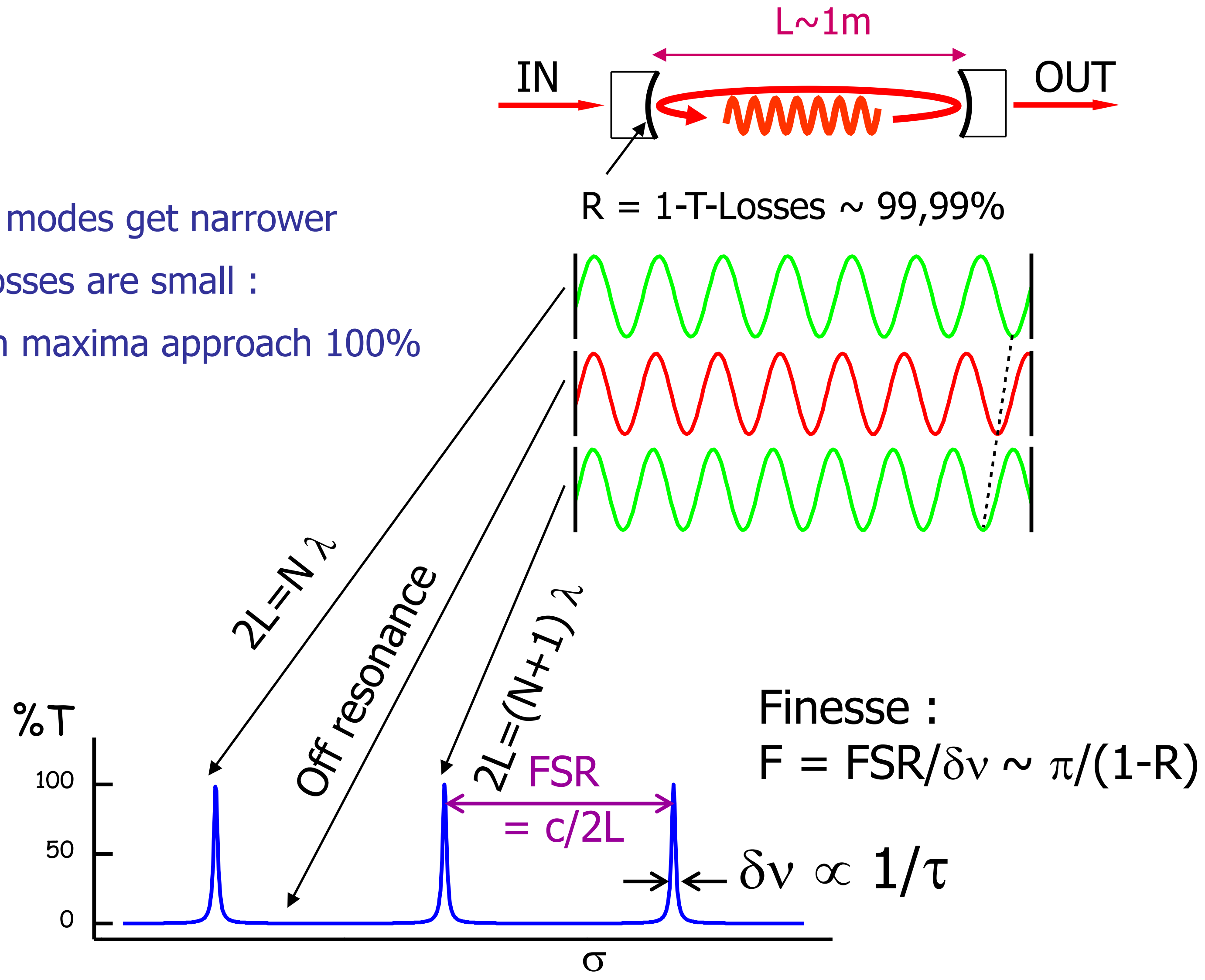
The optical resonator (optical cavity)

Notes:

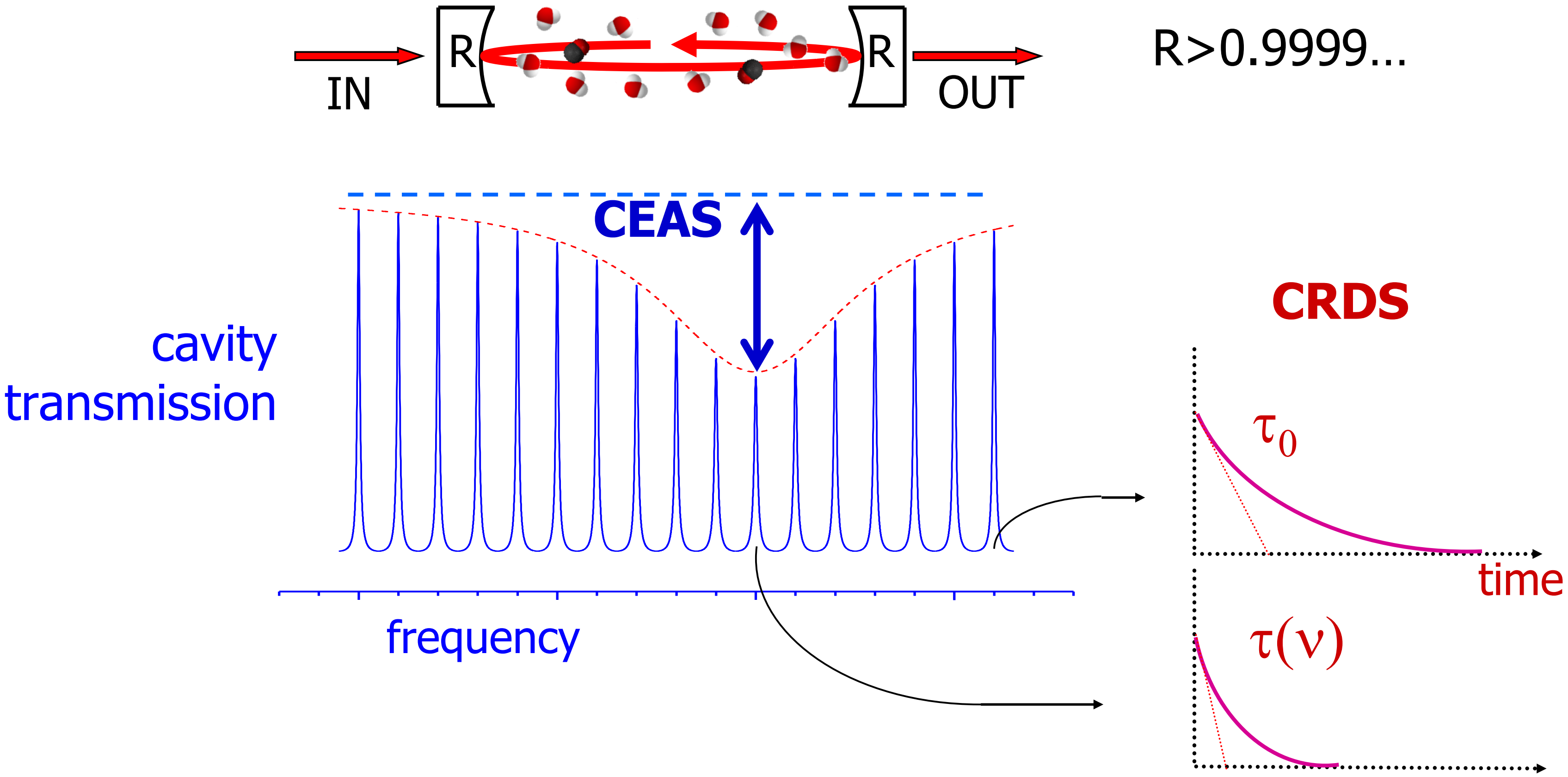
1) If R approaches 1 : modes get narrower

2) When intra-cavity losses are small :

Transmission maxima approach 100%



Cavités optiques -> spectre d'absorption?



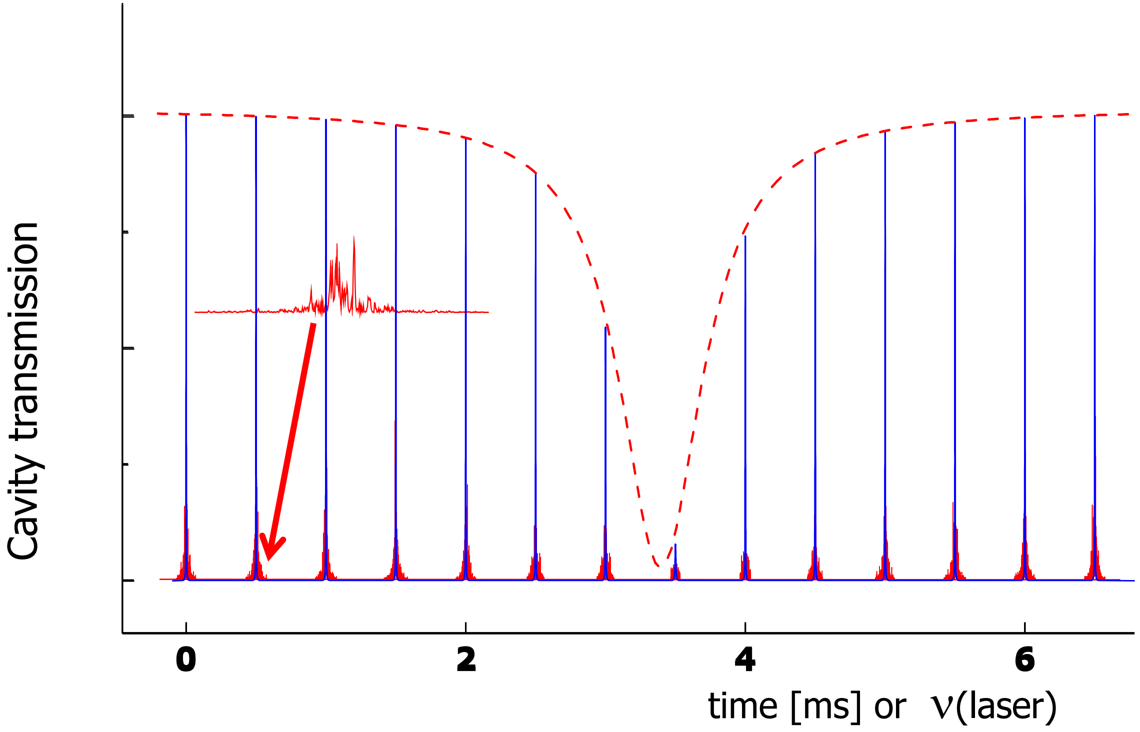
Cavity **E**nhanced **A**bsorption **S**pectroscopy

Cavity **R**ing-**D**own **S**pectroscopy

CEAS in real life…

Laser frequency noise : A problem for cavity injection!

A solution : CEAS with Optical Feedback (OF-CEAS)



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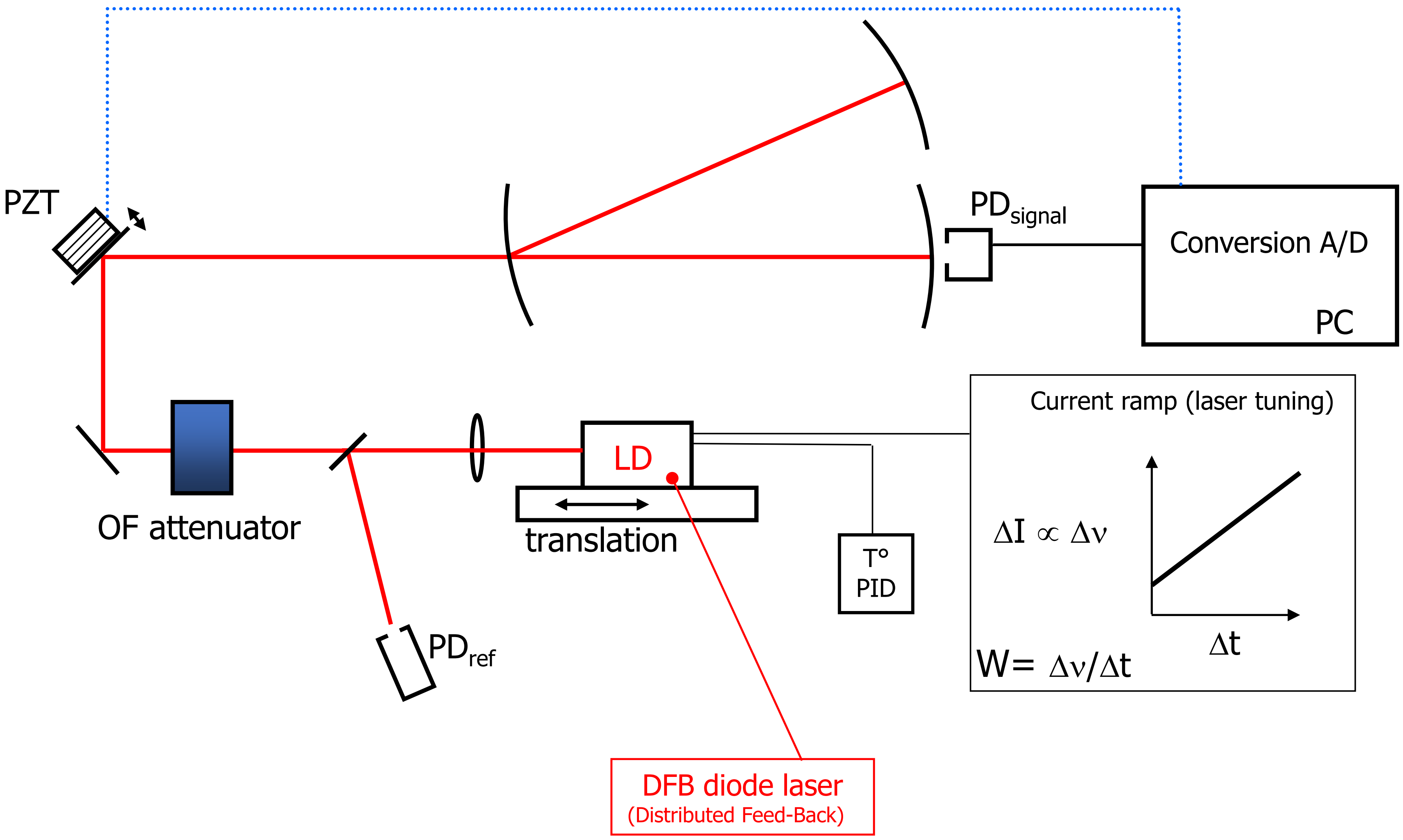
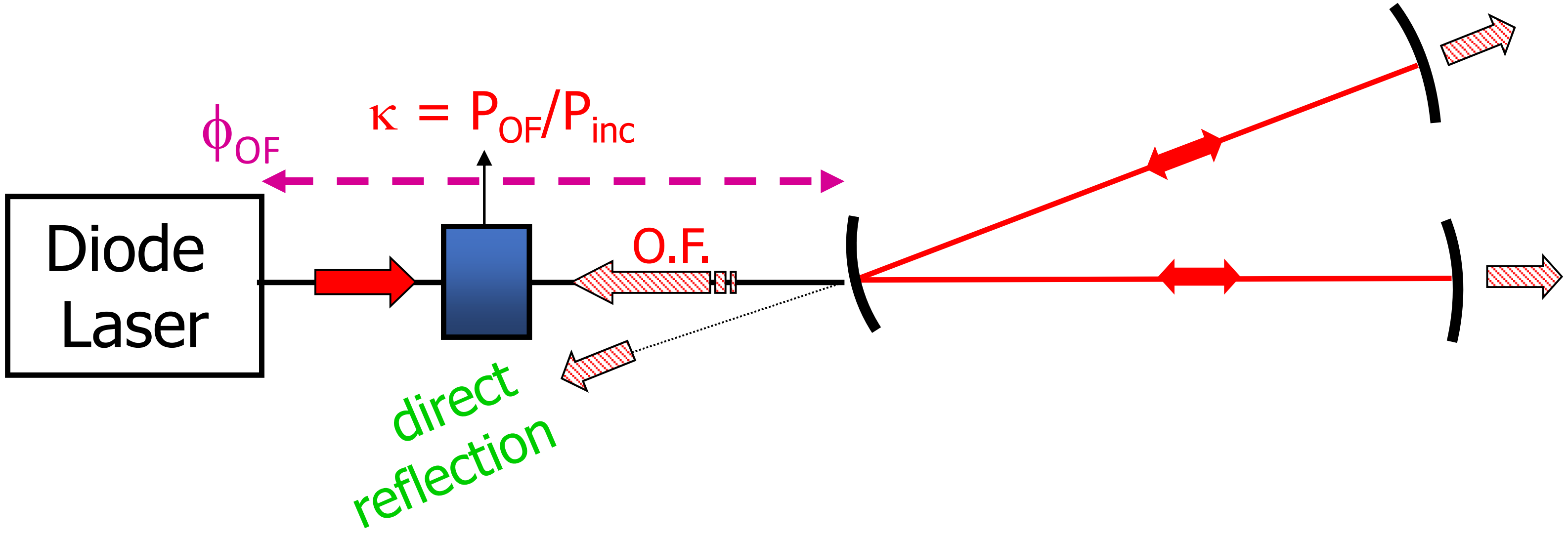
OF-CEAS : experimental scheme

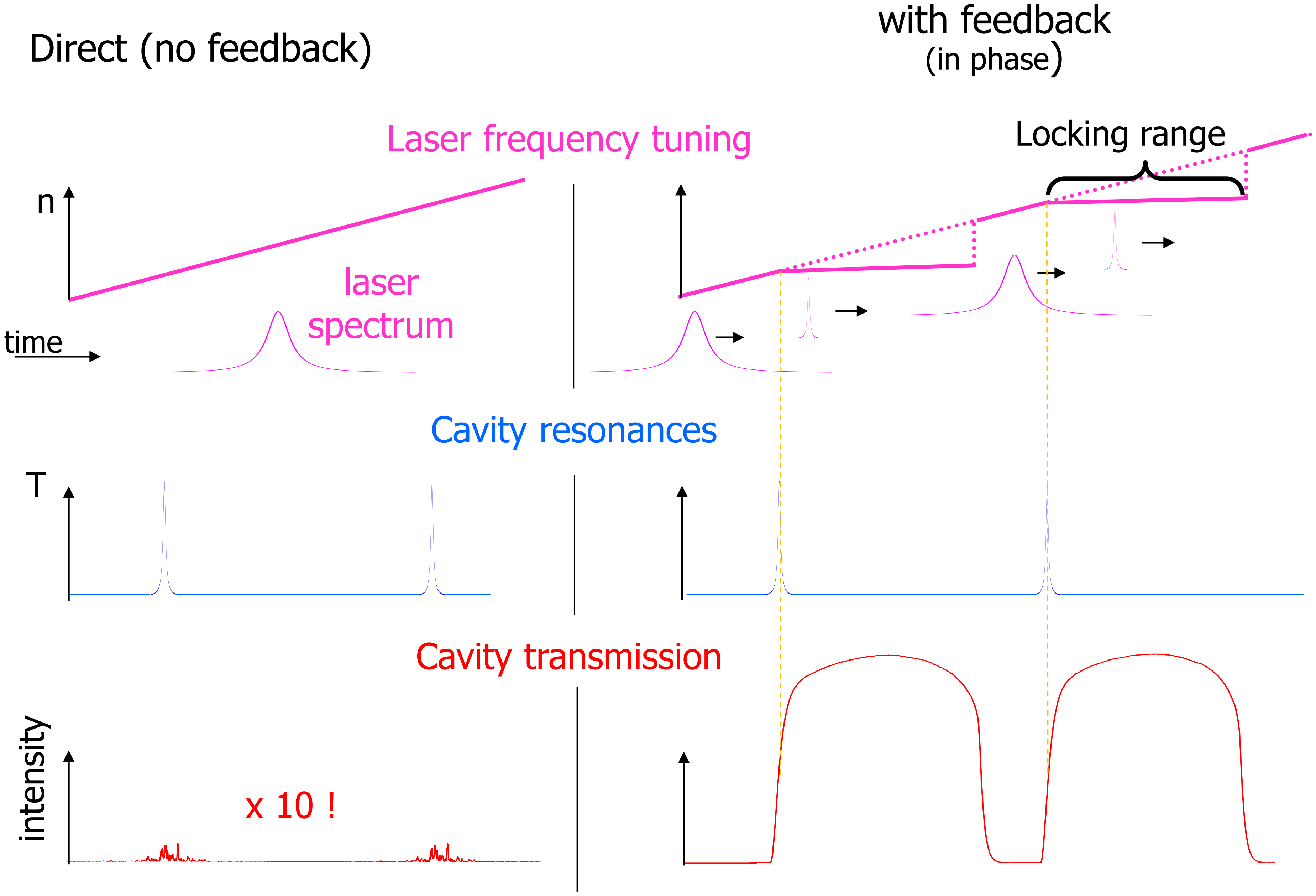


Injection by Optical Feedback

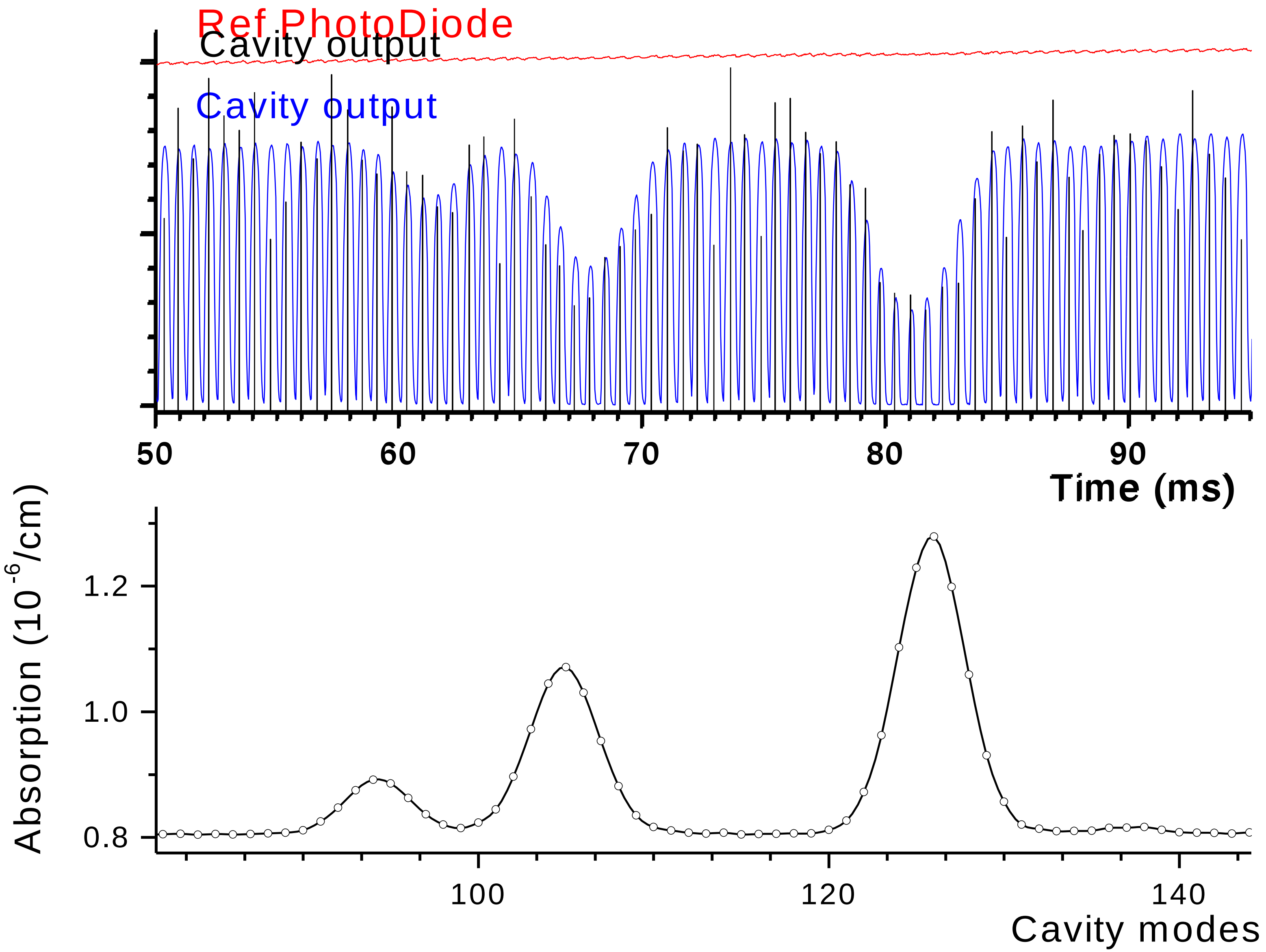
V cavity : OF only at resonance



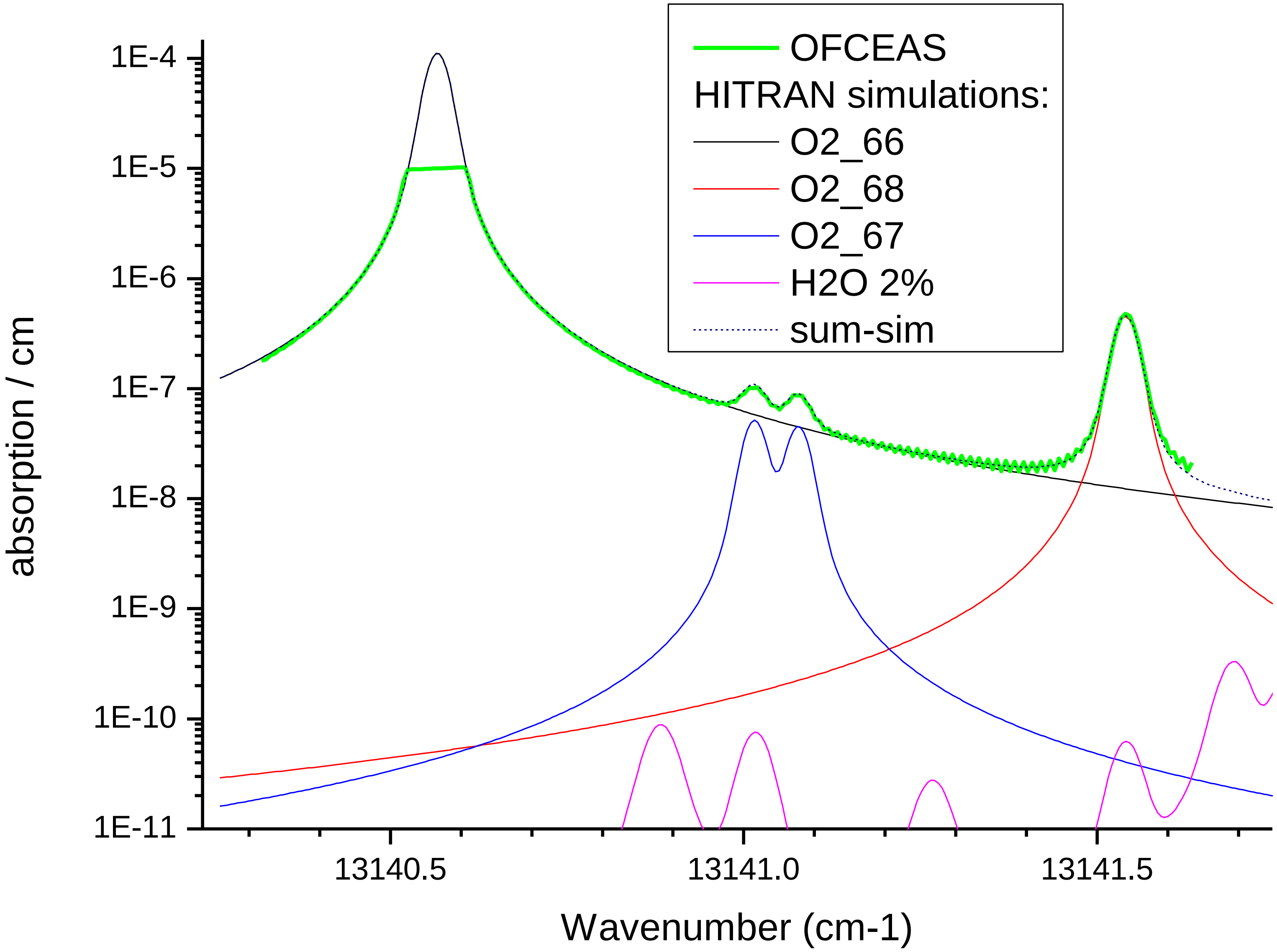
Cavity injection…



OF- CEAS (control OF phase and intensity…)



Comparison with HITRAN spectral database



AP2E - SARA O_2 :
Performance assessment and tests

- Instrument overview
- Precision for $\delta^{18}O$ and O_2 mixing ratio
- Calibration strategy for increased precision
- Water vapor and O_2 mixing ratios dependancies
- Experimental system design and comparisons with IRMS

Instrument overview

High precision measurements : **$\delta^{18}O$, O_2 mixing ratio**

Designed for **open** and **closed-system** applications

Flow rate 8ml/min

Active **temperature** and **pressure control**

Integrated computer with **control/visualization software**

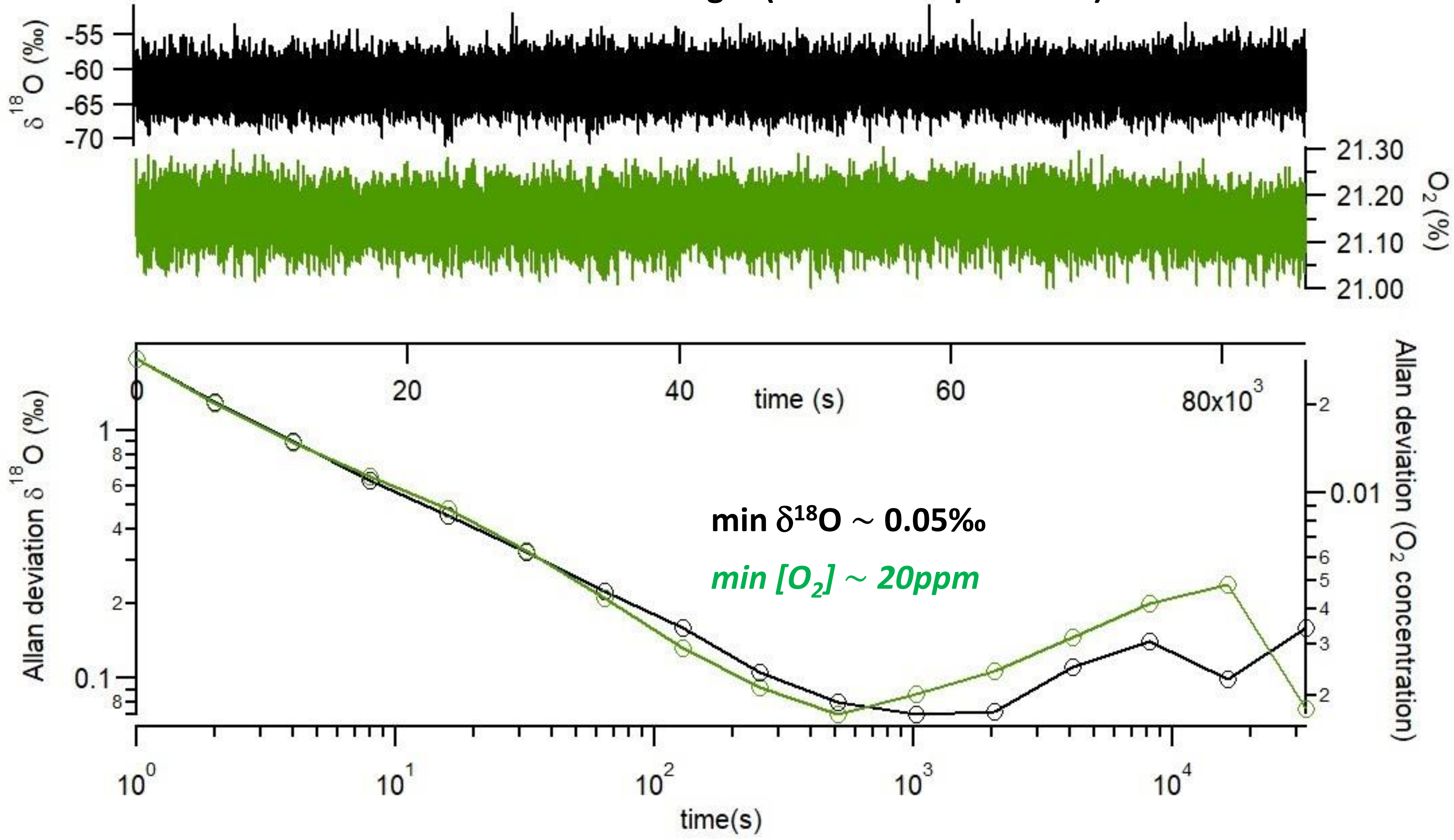
Integrated screen for real time raw **data visualization**

TCP/IP communication

Precision for $\delta^{18}O$ and O_2 mixing ratio

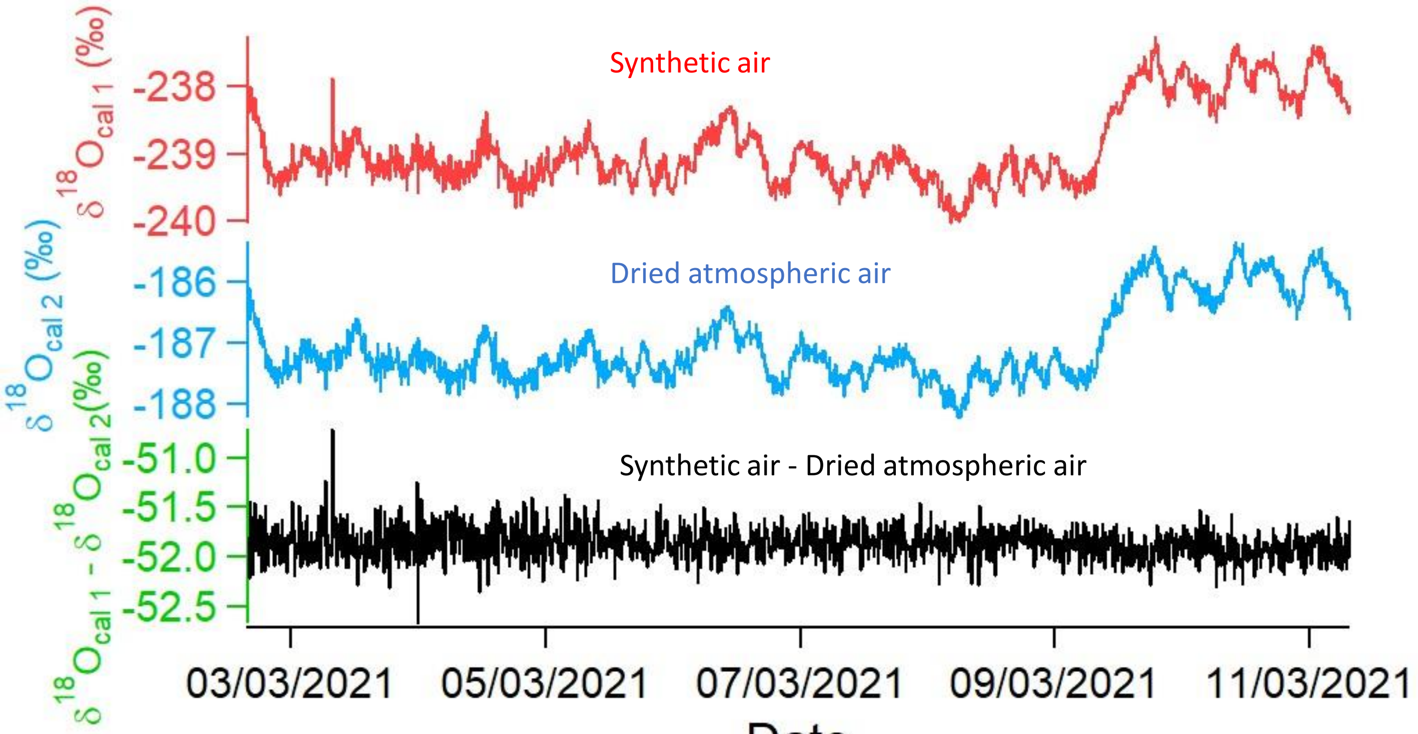
Allan deviation

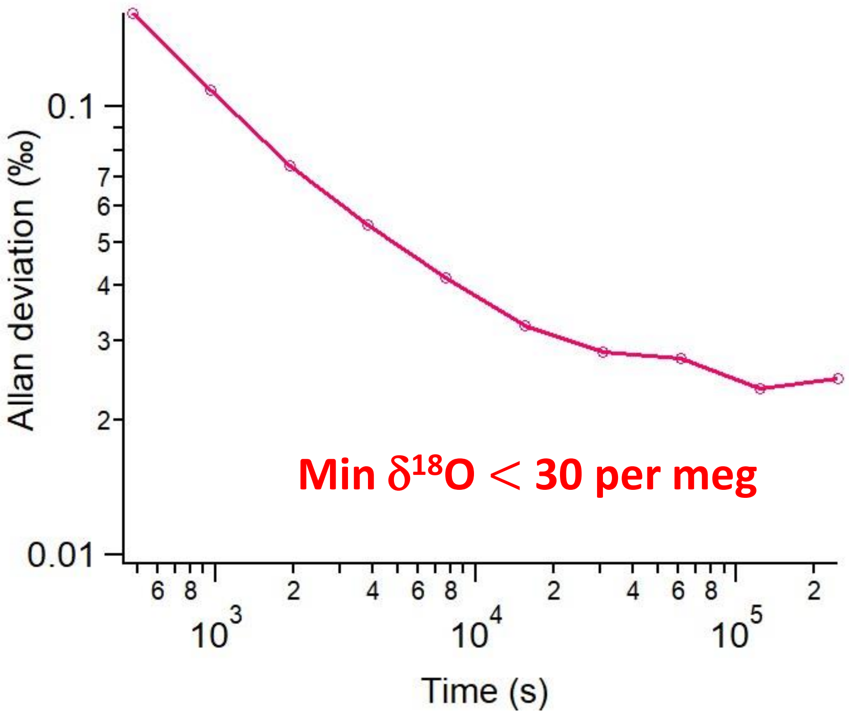
1Hz raw data with reference gas (dried atmospheric air)



Calibration strategy for increased precision

Fast valve switching (4min) between synthetic air and atmospheric air



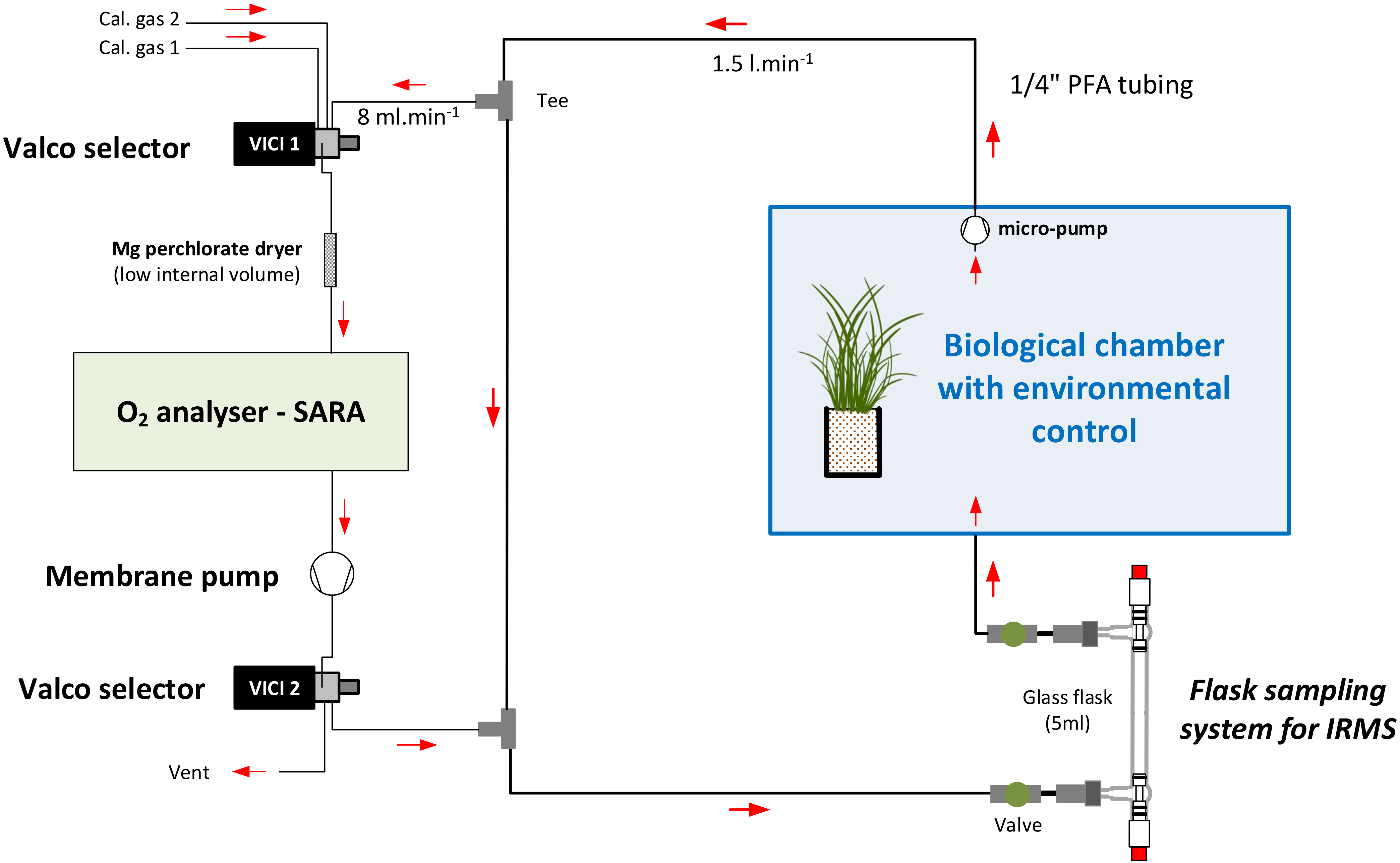


Water vapor and O_2 mixing ratios dependancies

Water vapor dependancy ~0.06‰ per $mmol.mol^{-1}$ H_2O ⇨ *Air will be dried before analysis*

O_2 mixing ratio dependancy Not significant if close to ambient (work in progress)

Experimental system design and comparison with IRMS

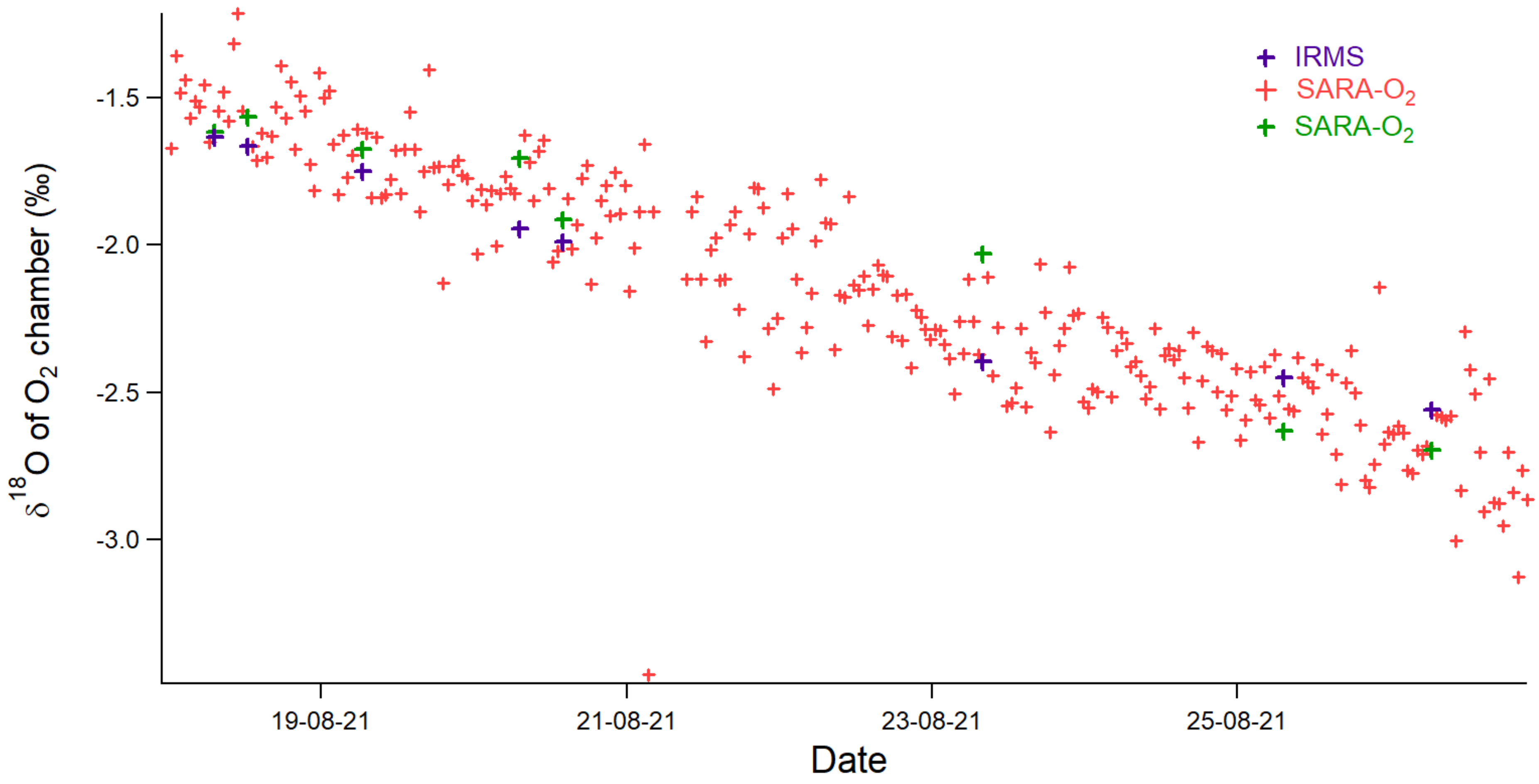


Experimental system design and comparison with IRMS

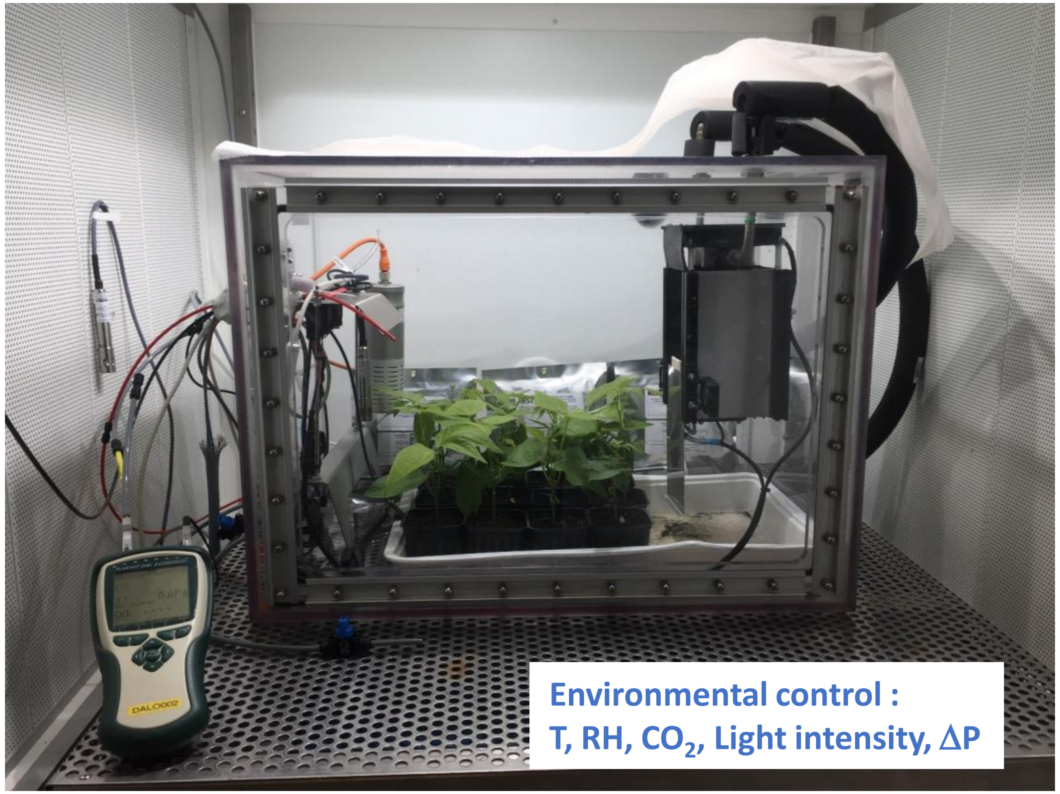
Closed system with plants and soil (up to 1 month confinement)

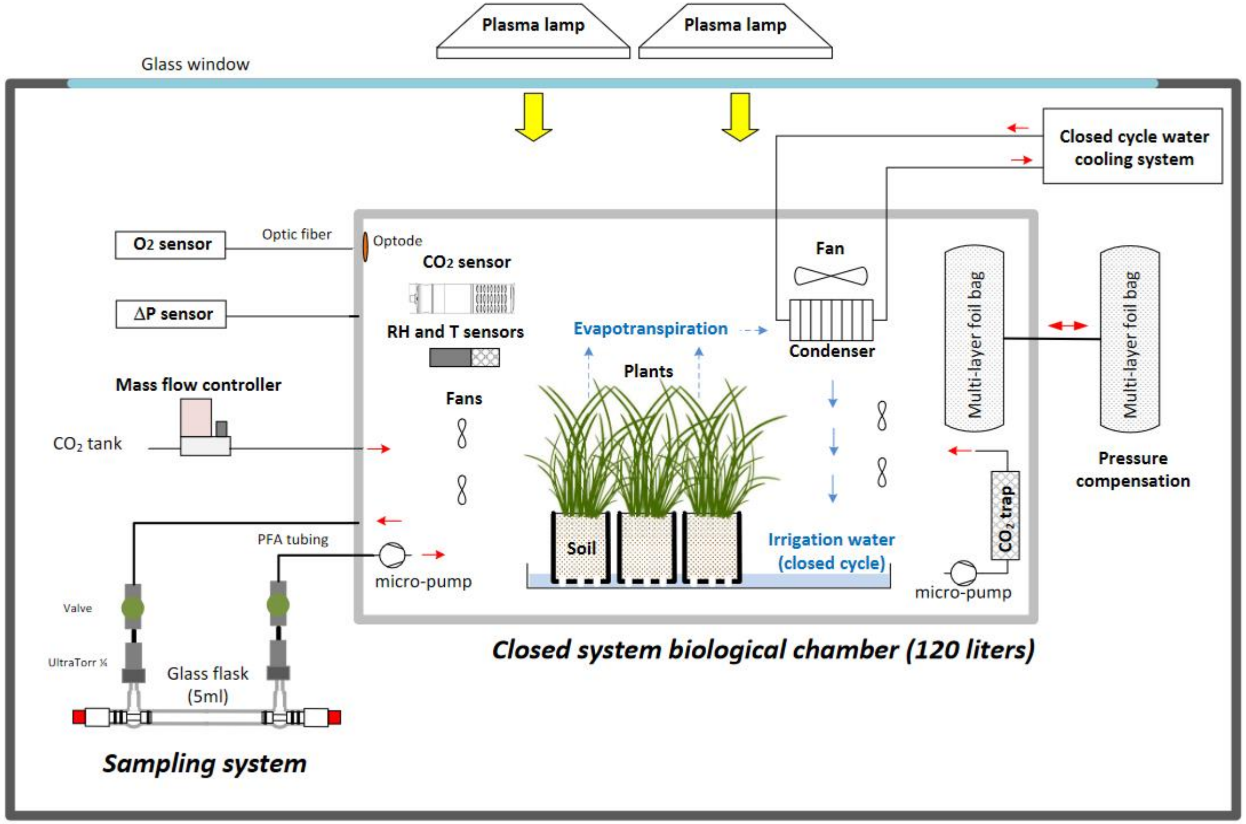
Valve switching : 15 min (2 min purge time)

Two standard gases : dried ambient air, synthetic air



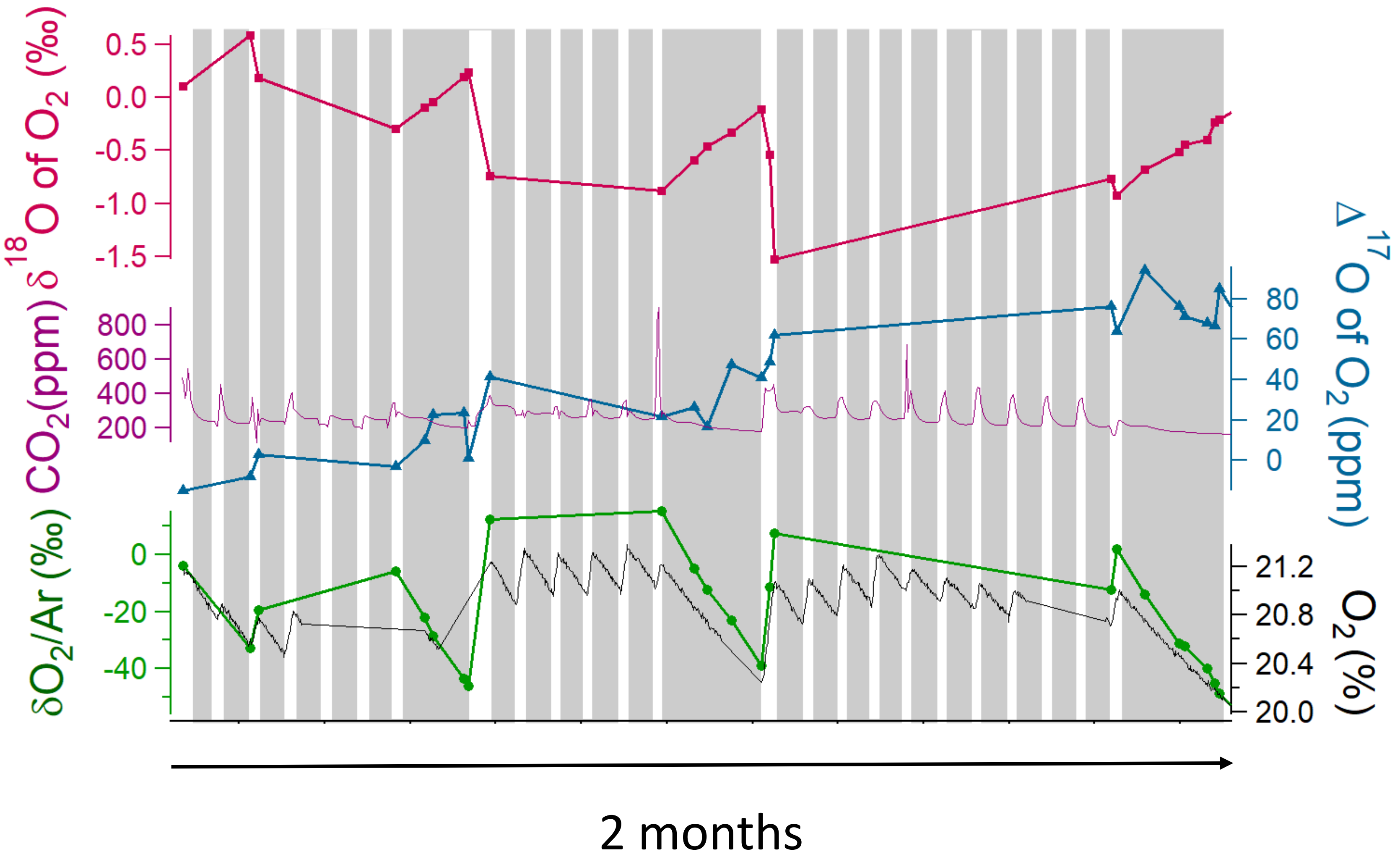
Biological chamber application



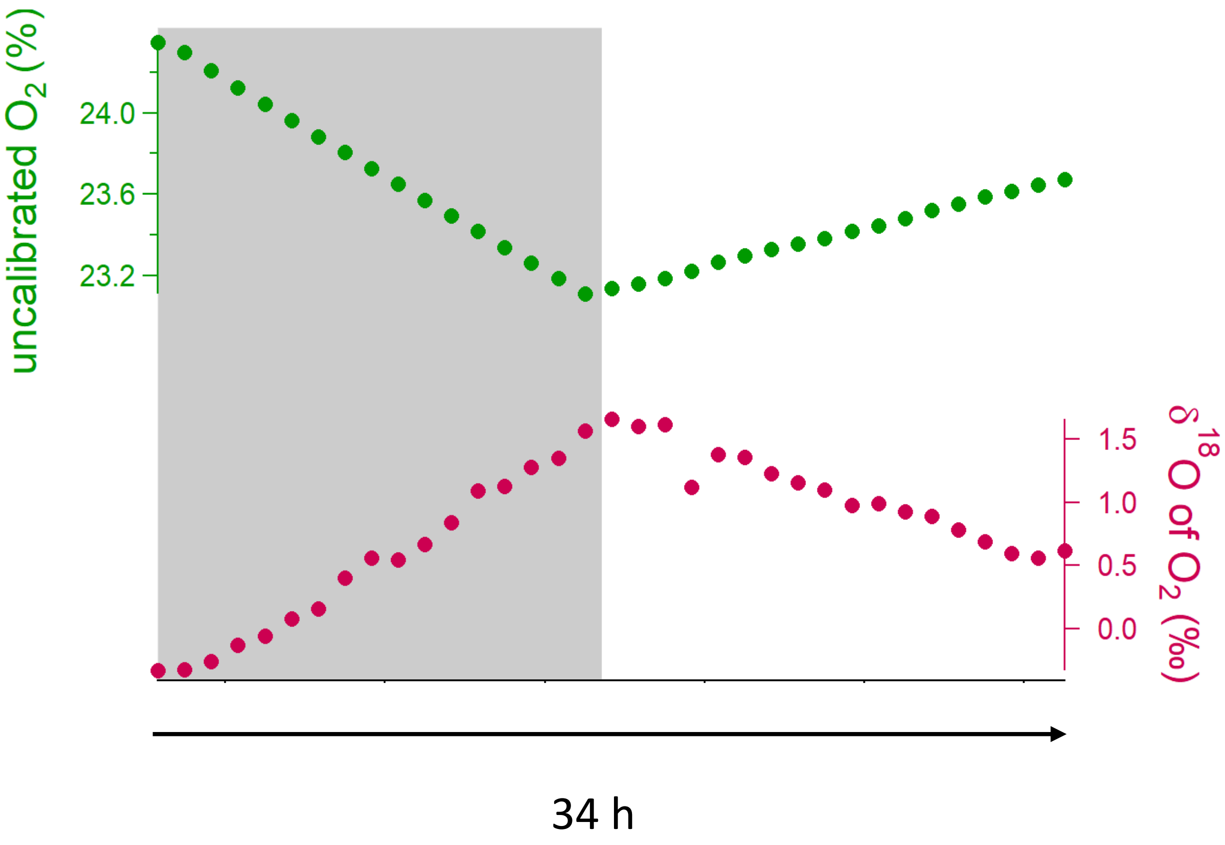


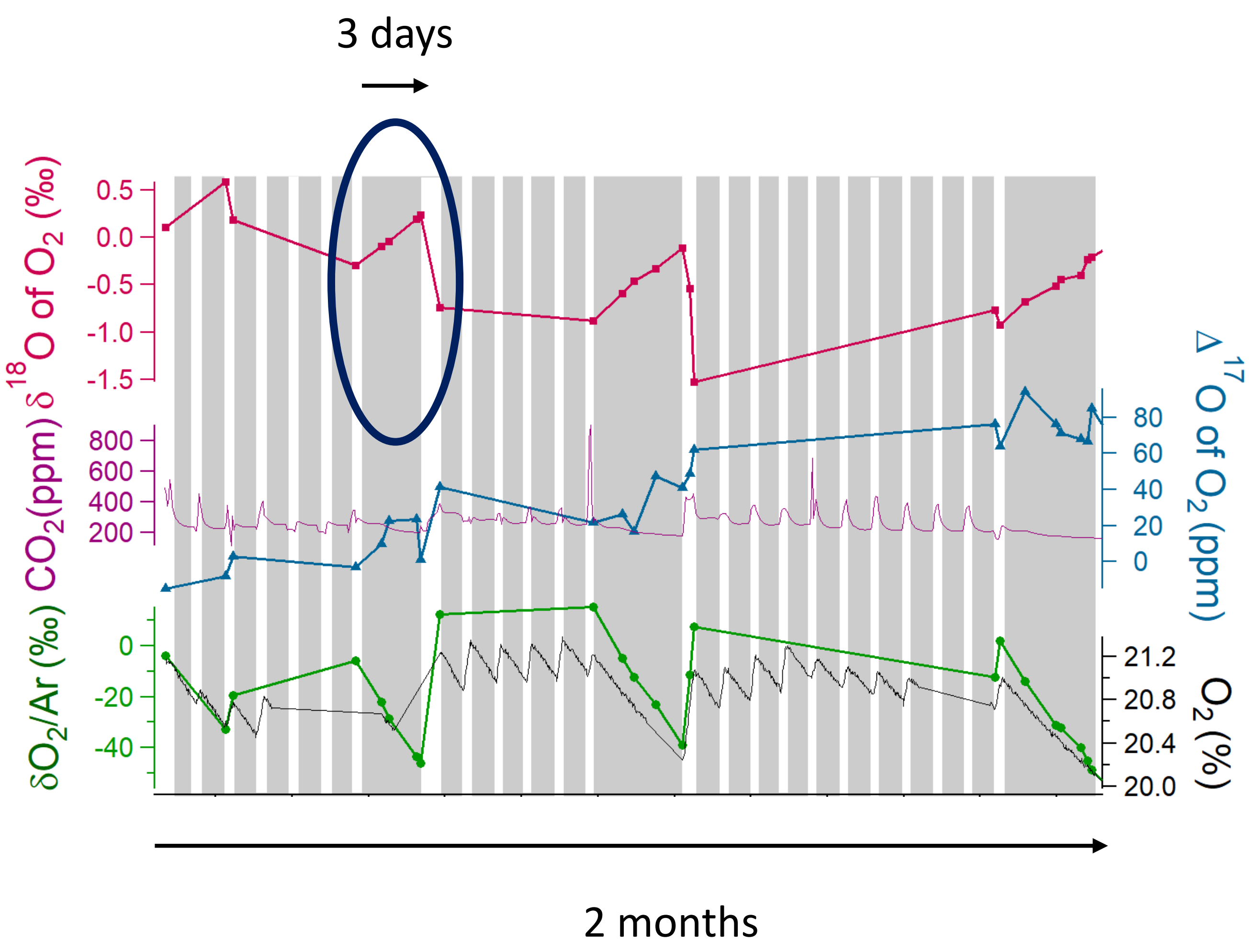
Photosynthesis and respiration experiment :

IRMS analysis



SARA-O_2 test



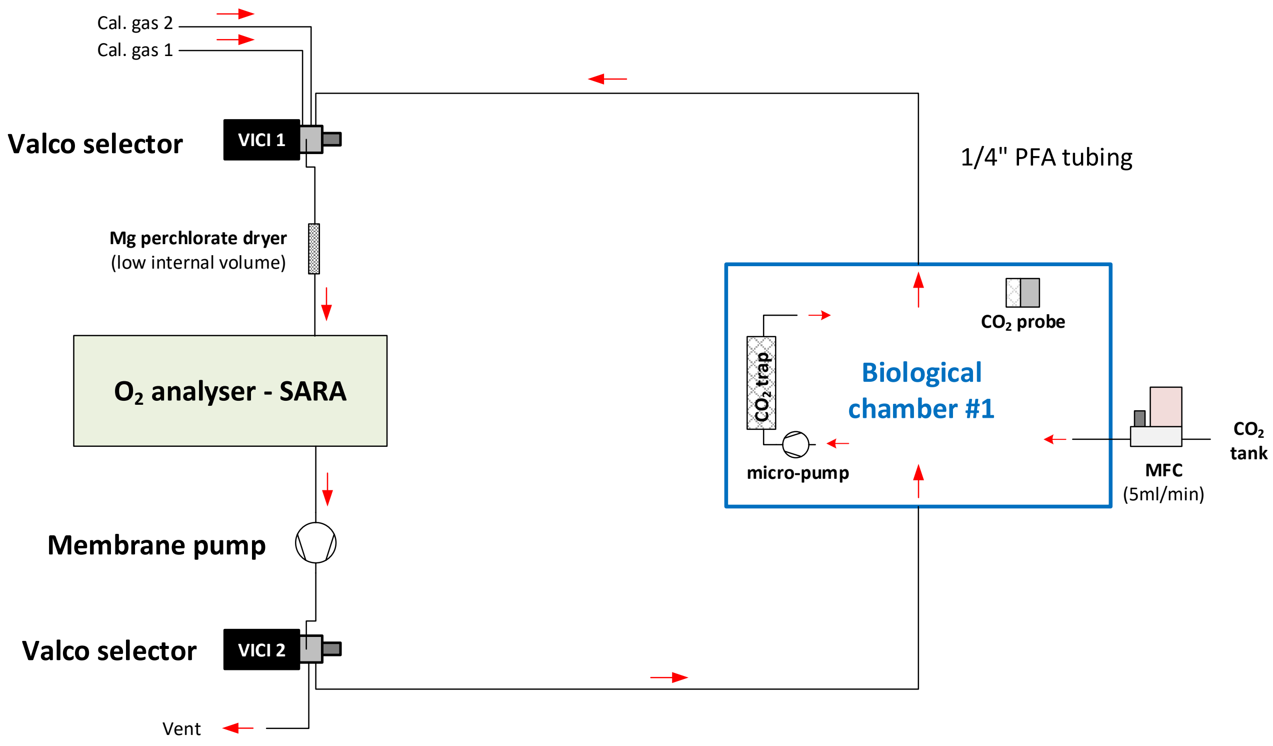


SARA-O_2 : continous data

IRMS : discontinuous data

Perspectives

- Quantification of fractionation coefficients for different plants (6 chambers working in parallel)
- Application to aquatic systems



6 biological chambers with environmental control