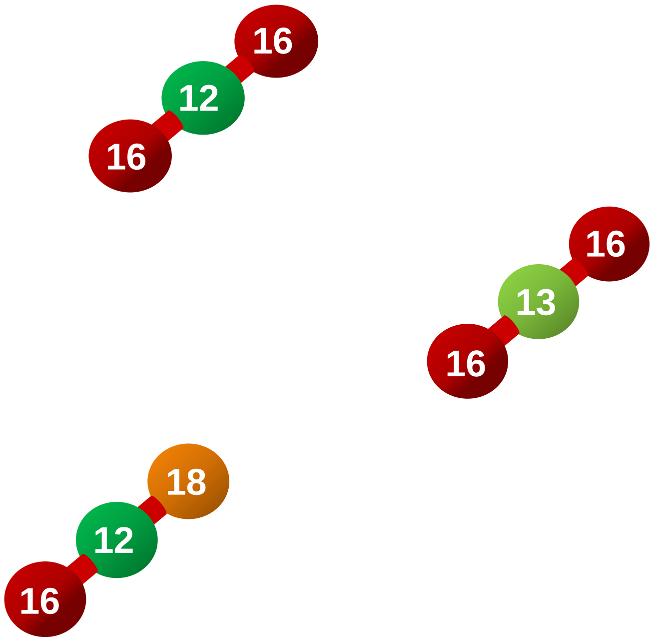
Optical spectrometer for real-time and on-site measurements of stable isotopes of combustion originated carbon dioxide

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

VTT Technical Research Centre of Finland

Stable Isotopologues of CO_2

Molecule	Abundance
$^{16}O^{12}C^{16}O$	0.9842
$^{16}O^{13}C^{16}O$	0.0111
$^{16}O^{12}C^{18}O$	0.0039



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The delta notation (symbol: δ) expresses the variation of an isotopic ratio of an element C or O (per mil, ‰)

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} - 1 \right) \times 1000$$

Typical standard for CO_2: VPDB (Vienna Pee Dee Belemnite)

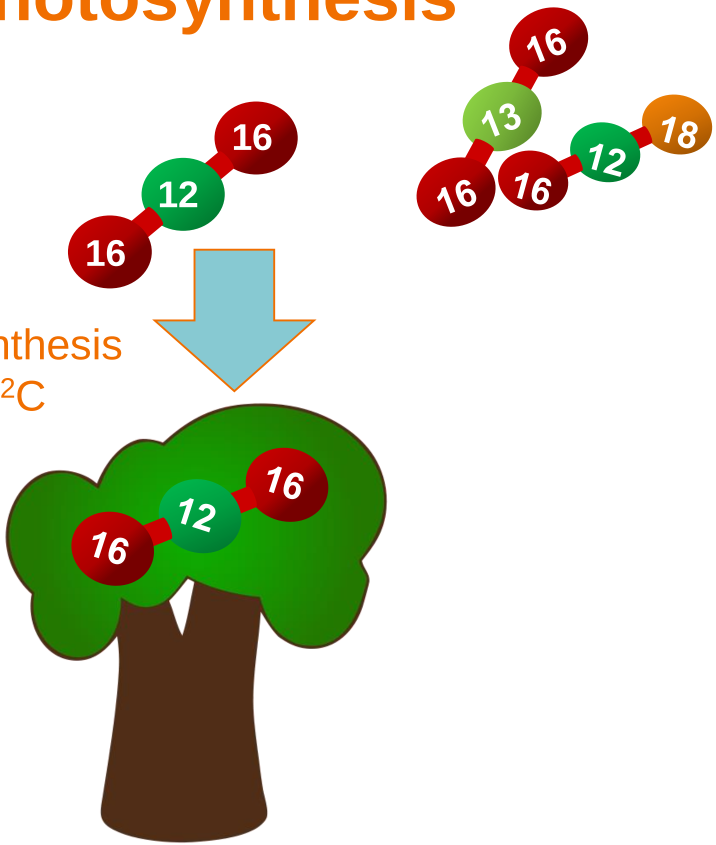
Typical $\delta^{13}C$ and $\delta^{18}O$ values are negative.

Stable Isotopologues of CO_2

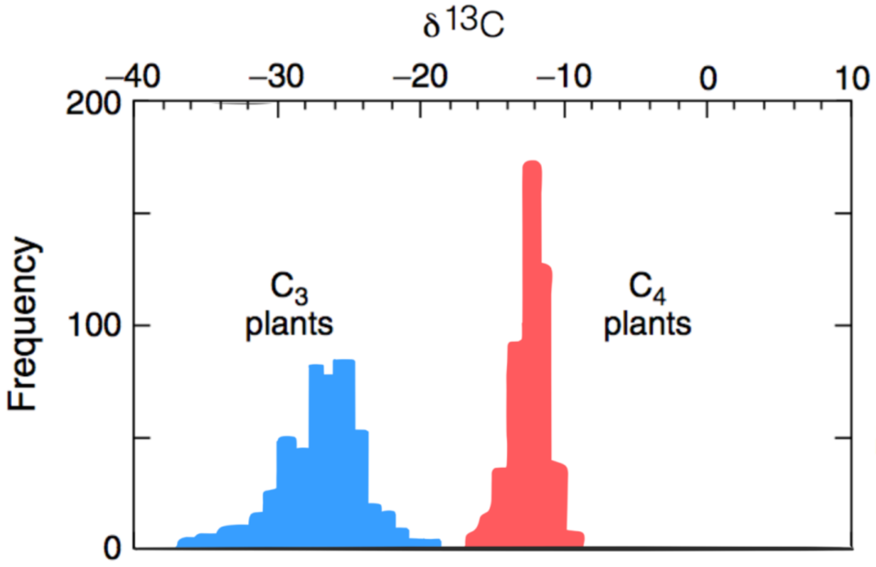
CO_2 pool	$\delta^{13}C$ value (per mil, ‰)
Fossil Fuels	-28
Terrestrial Biosphere	-26
Ocean	-10
Atmosphere	-8

NOAA https://www.esrl.noaa.gov/gmd/ccgg/isotopes/mixing.html

Fractionation of carbon isotopes in oxygenic photosynthesis



Photosynthesis favours ^{12}C



Different plants have different isotopic fingerprint:
- C3 plants in moderate temperatures
- C4 plants in dry and hot environment

https://en.wikipedia.org/wiki/Fractionation_of_carbon_isotopes_in_oxygenic_photosynthesis

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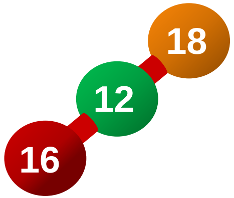
Measurement	Trend	Why?
CO_2 Levels	↑	CO_2 is currently being released from burning fossil fuels faster than it is taken up either on land or in the ocean.
$\delta^{13}C$	↓	Fossil fuels add CO_2 to the atmosphere that have less ^{13}C. This addition of CO_2 is more than the amount of CO_2 removed by the terrestrial biosphere.

NOAA https://www.esrl.noaa.gov/gmd/ccgg/isotopes/mixing.html

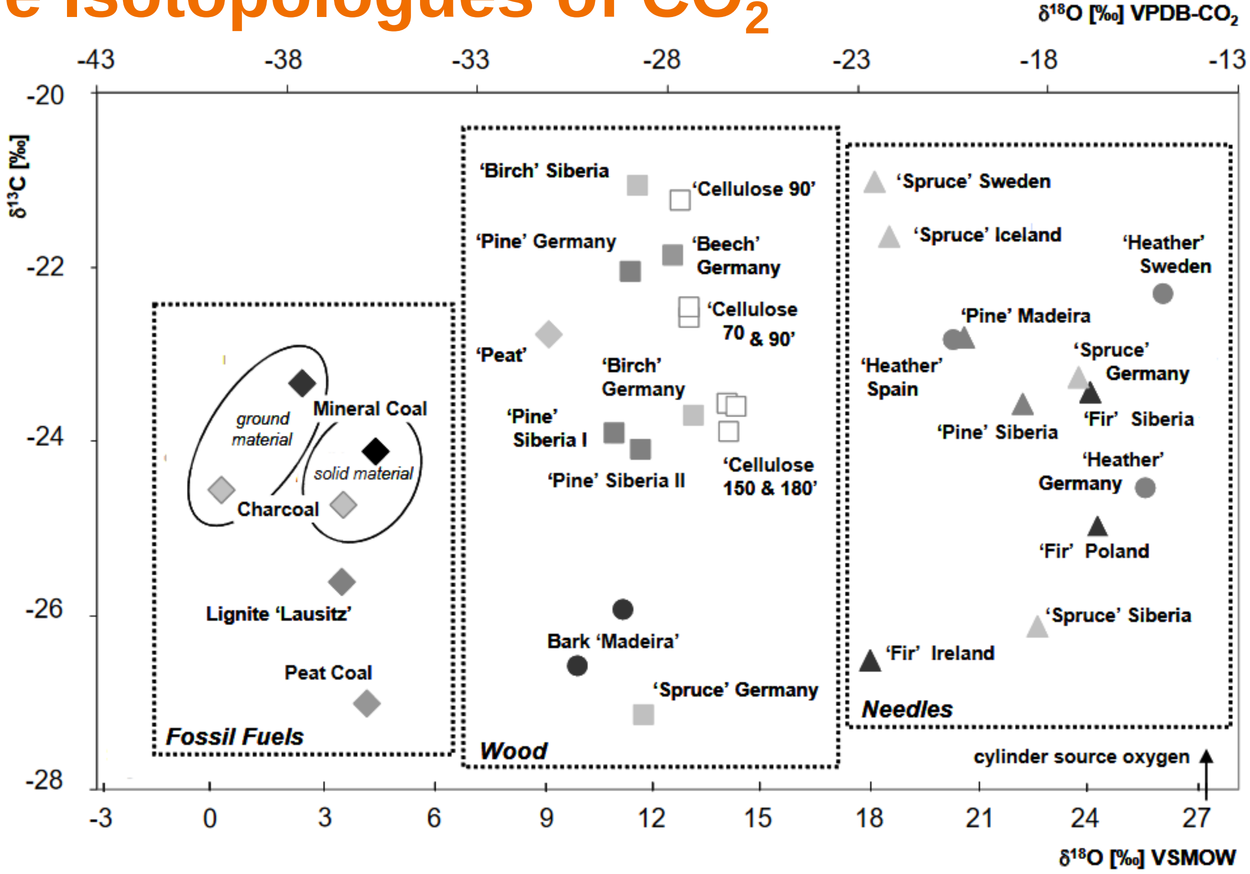
Stable Isotopologues of CO_2 - δ^{18}O values



- Shows large scale cycling (between sinks and sources)
- Highly variable and fluctuates a lot
- Harder to interpret the reasons behind these fluctuations
- Isotopic exchange with water

NOAA https://www.esrl.noaa.gov/gmd/ccgg/isotopes/otherisotopes.html

Stable Isotopologues of CO_2



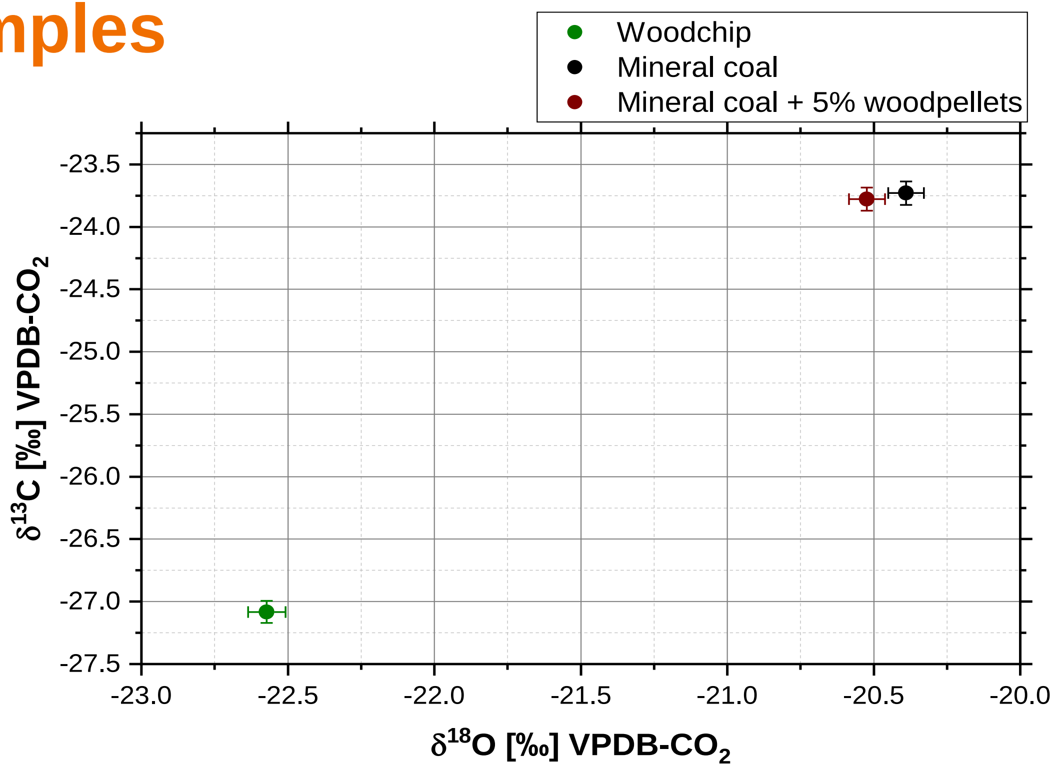
Schumacher M. *et al*, "Oxygen isotopic signature of CO2 from combustion processes," Atmos. Chem. Phys., 11, 1473–1490. **2011**.

Optical Isotope Ratio Spectroscopy (OIRS) instrument

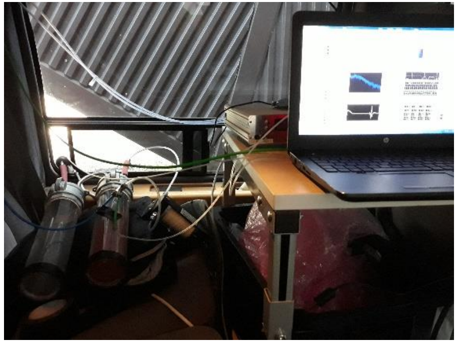
- Tunable diode laser absorption spectroscopy (TDLAS)
  - Nanoplus Interband Cascade laser (ICL), centre wavelength of ~4329 nm (~2310 cm^{-1}, with 1 cm^{-1} tuning range).
- Thermally stabilized single pass absorption cell, optical path length 10 cm.
  - 10-20% absorption of the light when CO_2 concentration in the sample is ~5% (pressure ~75 mbar).
- Probes three absorption profiles of the CO_2 isotopologues
  - $\delta^{13}C$ and $\delta^{18}O$ values simultaneously

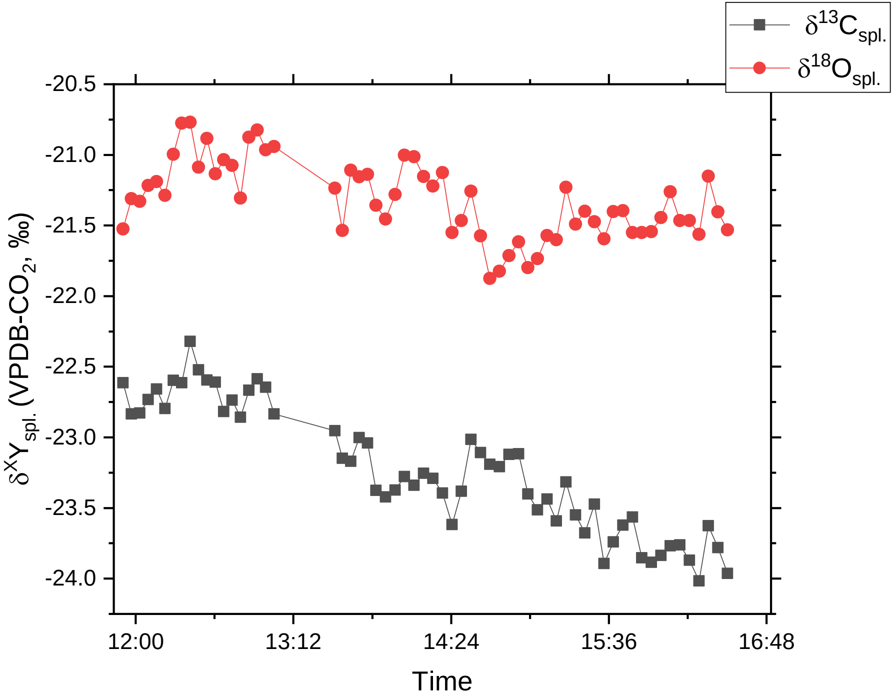
Stack emission samples

- Bag CO_2 emission samples collected from three different power station
- Samples have distinguishable isotopic fingerprints
- How the signal will change in time?

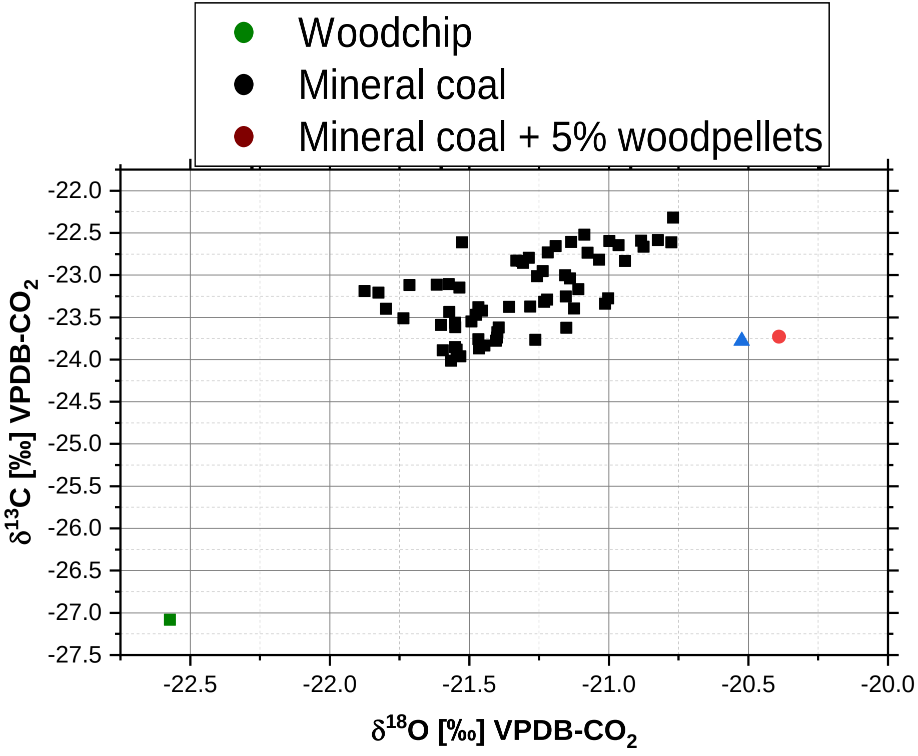


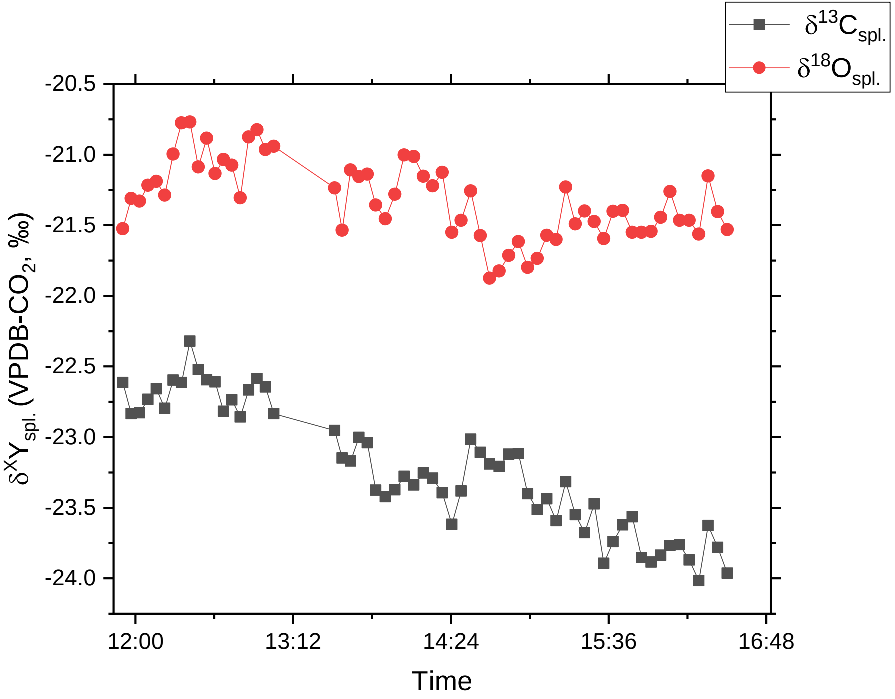
Stack emission – on-line measurements





Stack emission – on-line measurements

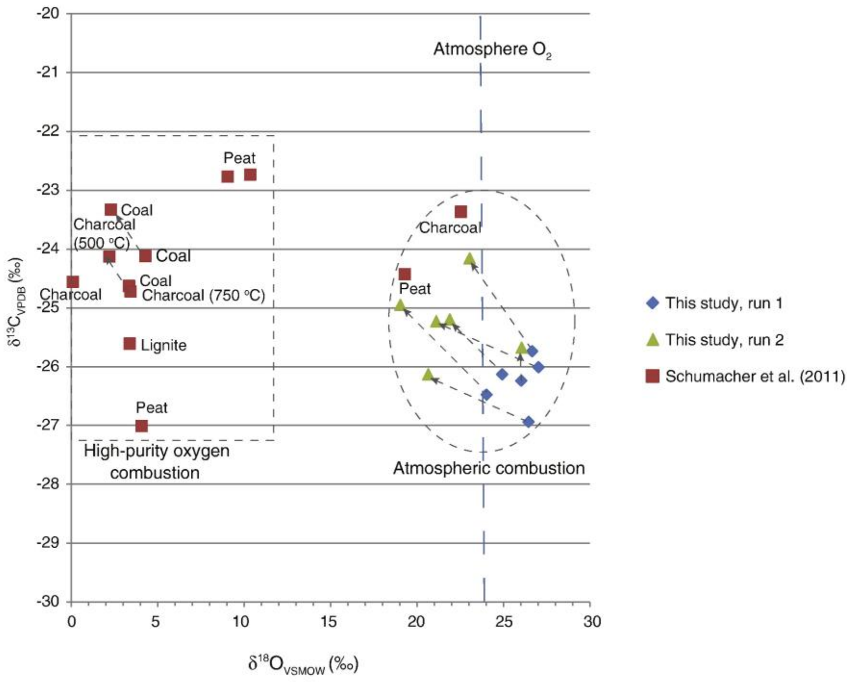




Conclusions

- Optical isotope ratio spectroscopy instrument developed, validated and tested in industrial conditions
  - $\delta^{13}C$ and $\delta^{18}O$ values simultaneously
  - On-line CO_2 emission monitoring possible

- Possible issues
  - Is $\delta^{18}O$ reliable parameter?
    - Moisture of the fuel and ambient conditions?
    - Most of the used fuel contain only little oxygen?
  - What affects fractionation of the isotopes?
    - Grain size of fuel?
    - How emission filtering and cleaning affect isotopic signature?
    - Burning process?



Warwick, Ruppert, Int. J. of Coal Geology, 166, 2016, https://doi.org/10.1016/j.coal.2016.06.009.

VTT – Optical Spectroscopy

Monitoring stable CO_2 isotopes at vertical farm

Radiocarbon monitoring ($^{14}CO_2$) at nuclear power plant

Remote material identification with active hyperspectral sensing

Optical Isotope Ratio Spectroscopy (CO_2 N_2O, CH_4 etc.), radiocarbon spectroscopy, trace gas spectroscopy, active hyperspectral sensing, near&mid-infrared laser development (supercontinuums, frequency combs).

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