Assessing sources of cave air CO_2

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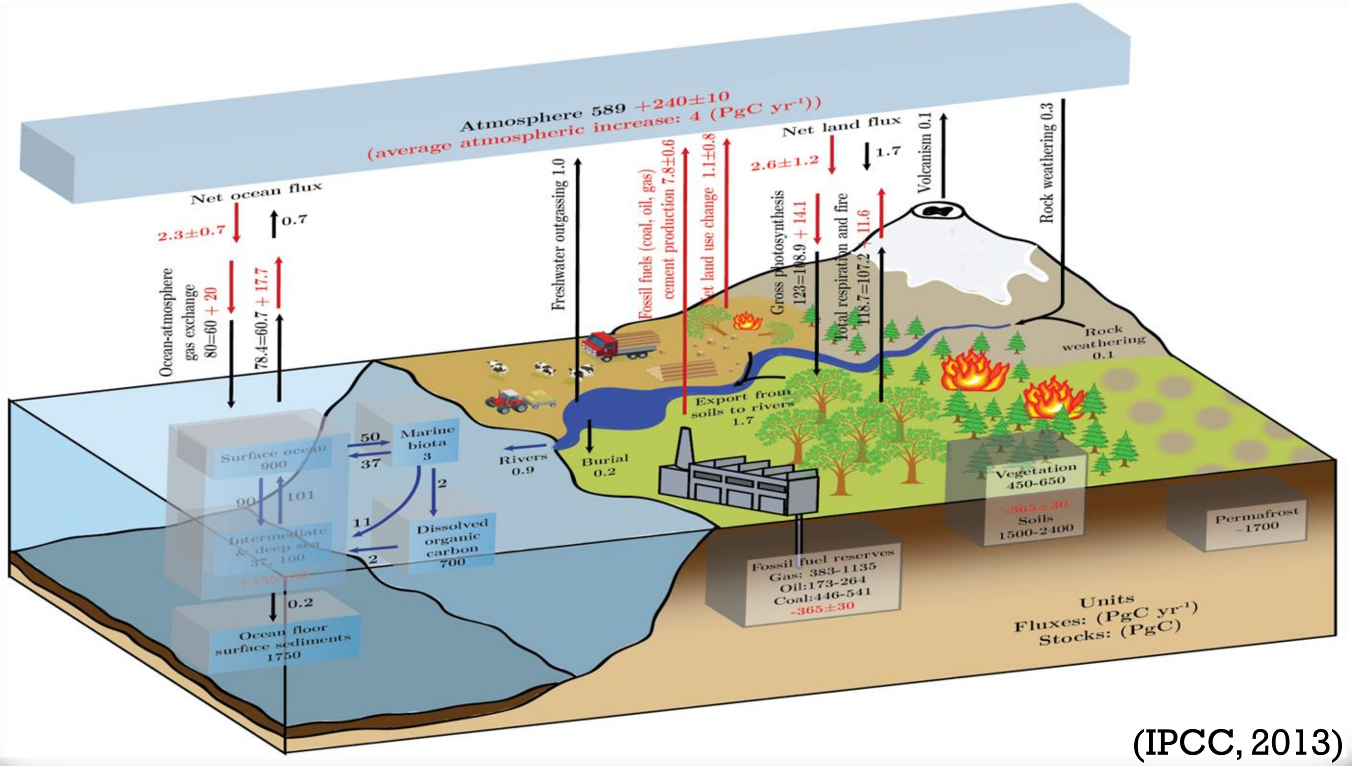
Carbon cycle



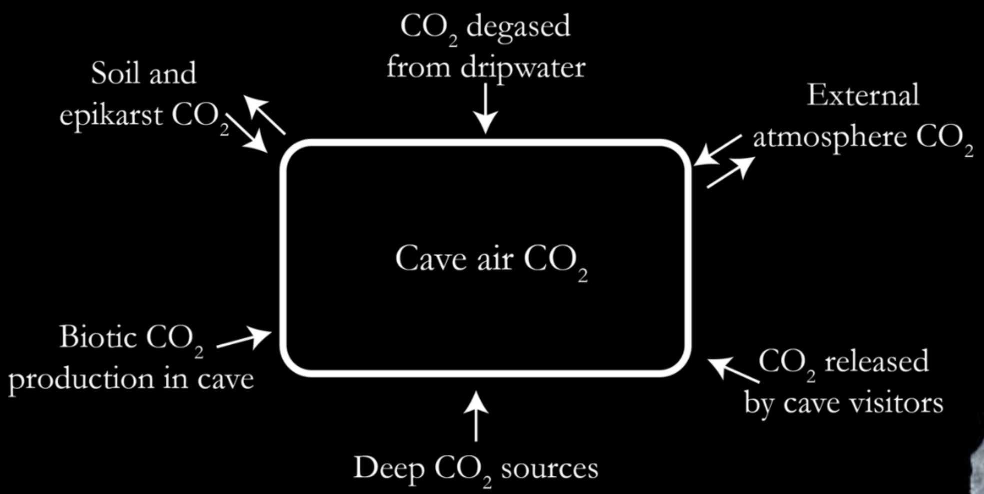
(IPCC, 2013)

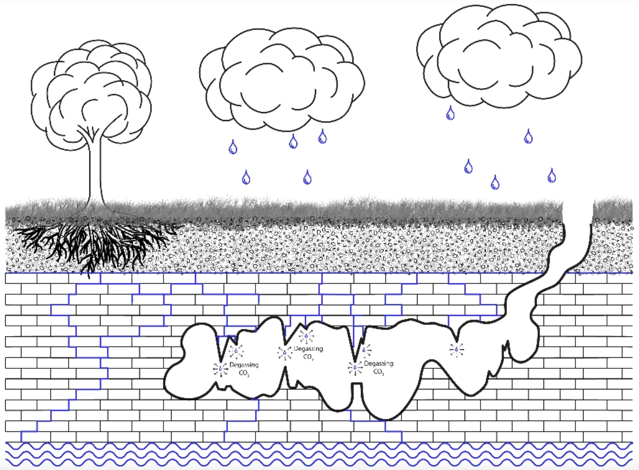
The carbon cycle is the set of biogeochemical processes by which carbon undergoes chemical reactions, changes form, and moves through different reservoirs on earth, including living organisms.

CO_2 in caves

CO_2 accumulating in caves can come from different sources trough different pathways:

- External atmosphere
- Directly from overlaying soil and epikarst
- Degassing from dripwaters
- Cave visitors,
- in-cave biotic production,
- deep sources



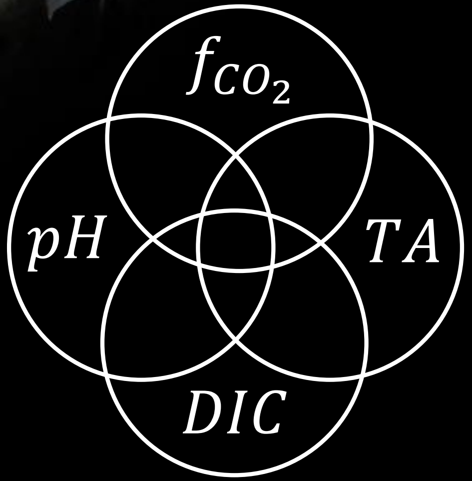


$$CO_{2(g)} + H_2O_{(aq)} \Leftrightarrow H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} + CaCO_{3(s)} \Leftrightarrow 2HCO_{3(aq)}^- + Ca_{(aq)}^{2+}$$

$$2HCO_{3(aq)}^- + Ca_{(aq)}^{2+} \Leftrightarrow CO_{2(g)} + CaCO_{3(s)} + H_2O_{(aq)}$$

Carbonate equilibrium



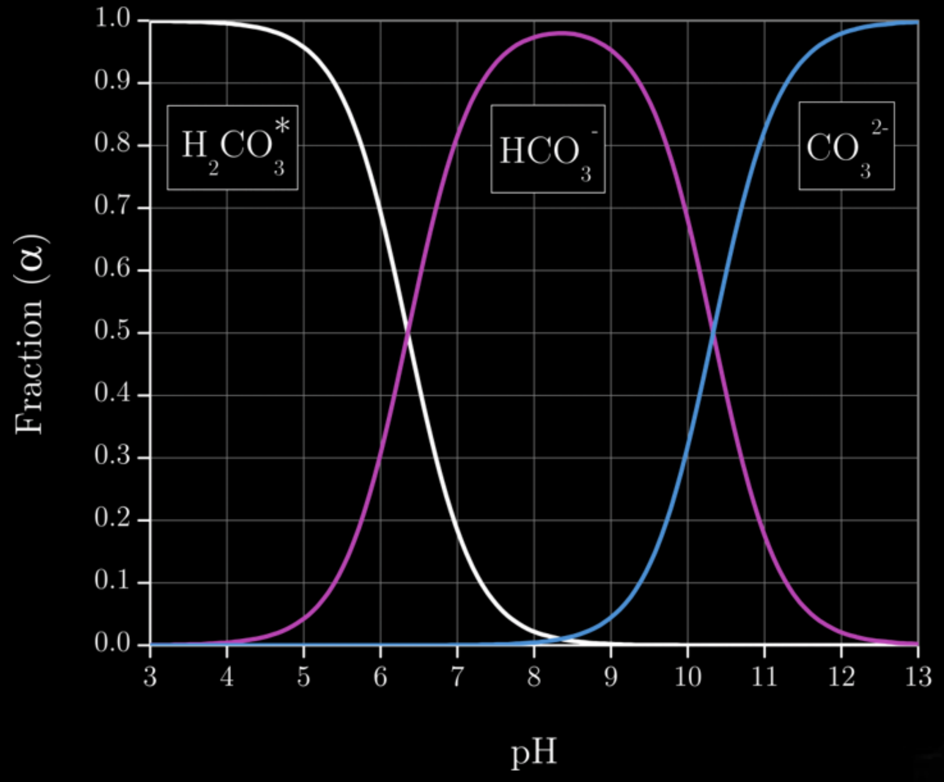
$$CO_{2(aq)} + H_2O \overset{K_H}{\Leftrightarrow} H_2CO_3$$

$$H_2CO_3^* \overset{K_1}{\Leftrightarrow} H^+ + HCO_3^-$$

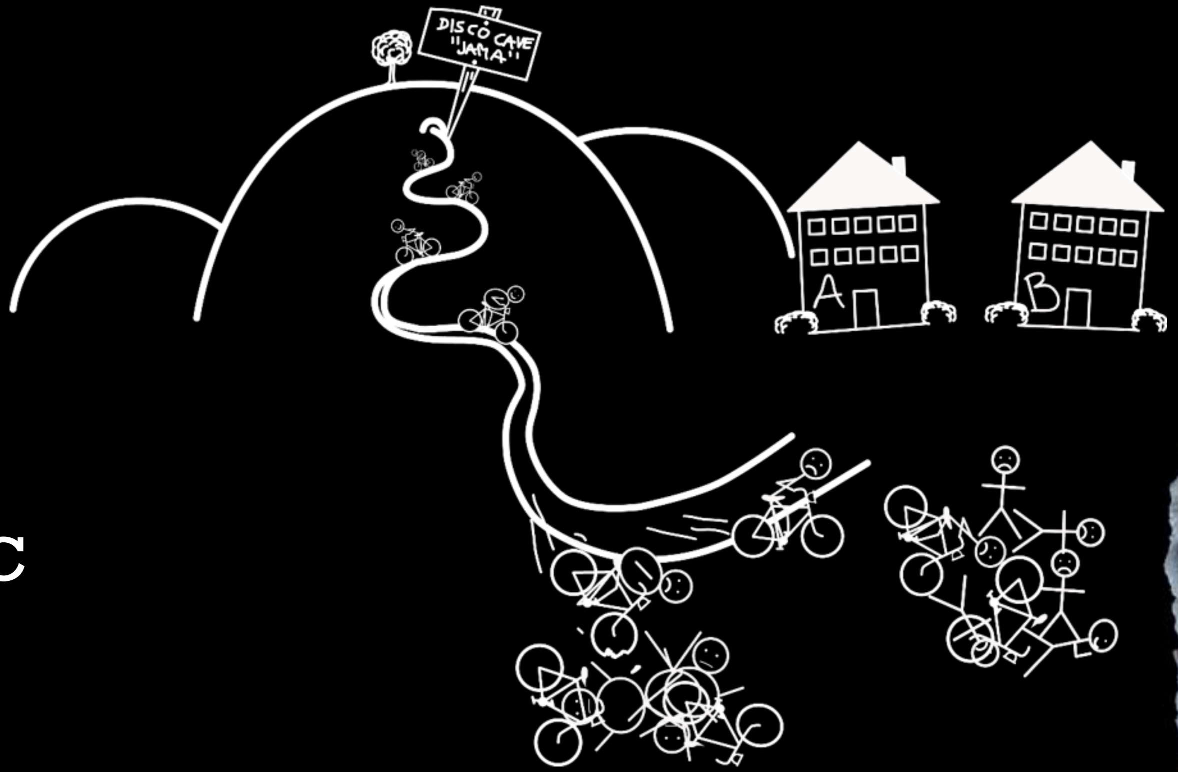
$$HCO_3^- \overset{K_2}{\Leftrightarrow} H^+ + CO_3^{2-}$$

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$\mathrm{TA} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^-] + \cdots$$



Source assessment

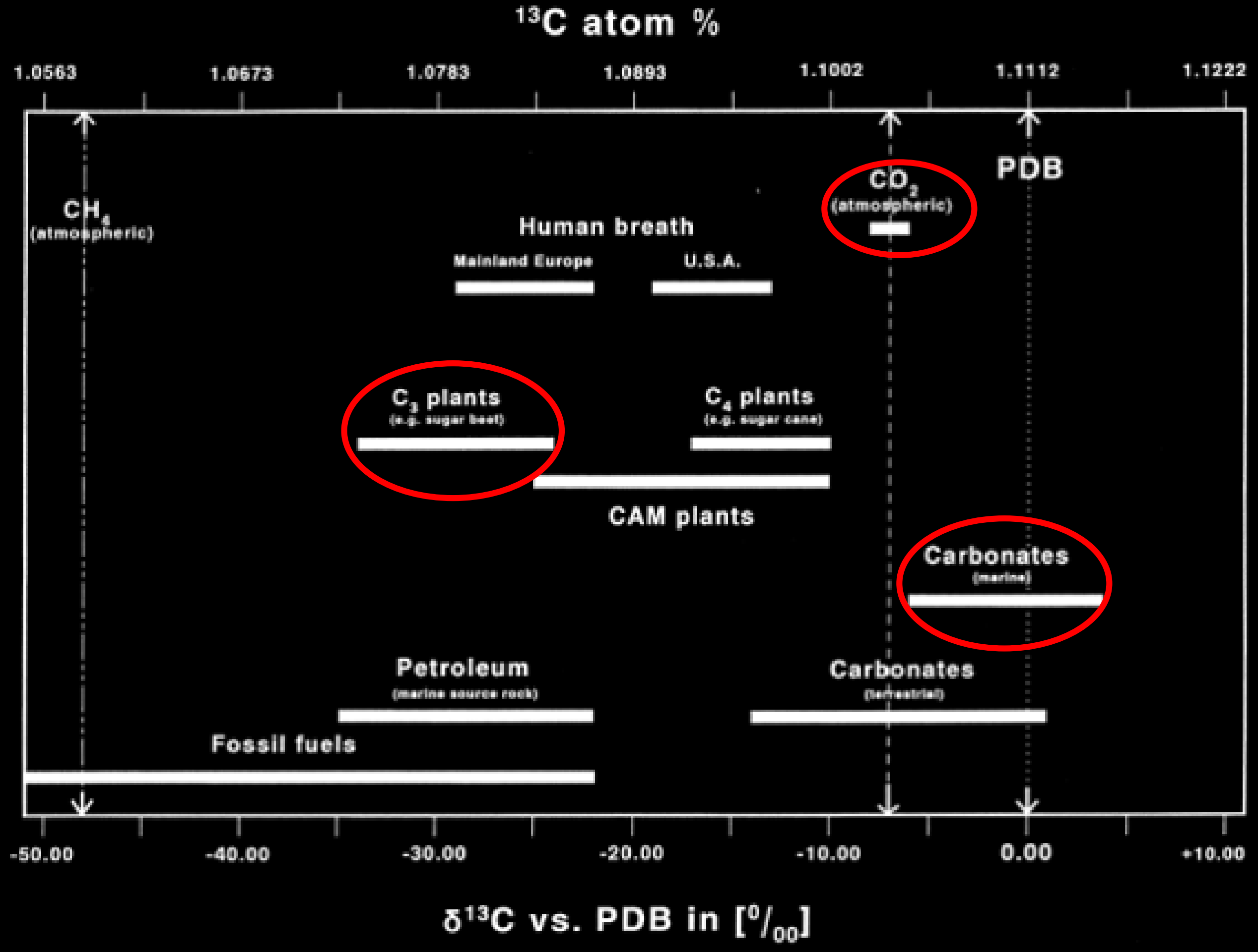


Use of tracers:

- Stable carbon isotopes, $\delta^{13}C$
- Radiocarbon, $\Delta^{14}C$
- Radon, ^{222}Rn

Stable carbon isotopes ($^{13}C/^{12}C$)

δ^{13}**C** - a useful tool to study the carbon cycle

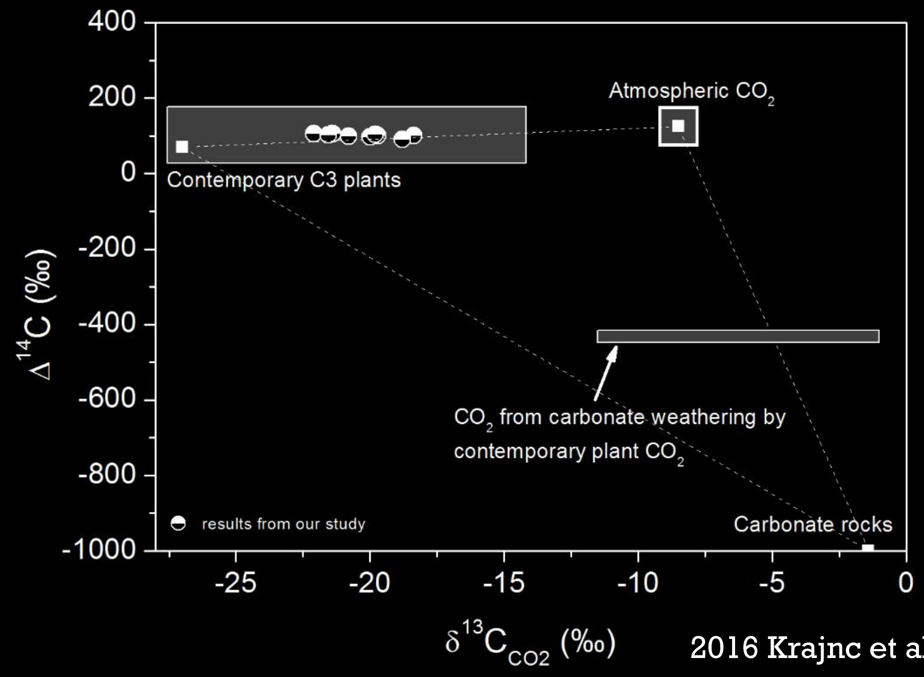


Some typical examples of natural $\delta^{13}C$ values grouped according to origin along the scale of ^{13}C natural abundance (Meier-Augenstein, 1999)

Radiocarbon (^{14}C)

- Unstable with half-life of 5730 ± 40 years
- Enters plant and animal life trough photosynthesis and food chain
- After the death of the organism only ^{14}C decay (basis for ^{14}C dating)
- Useful to distinguish between „young“ and „old“ sources (e.g. atmospheric CO_2 and C from carbonate bedrock)

We used it as the second tracer which enabled us to partition between up to 3 carbon sources:

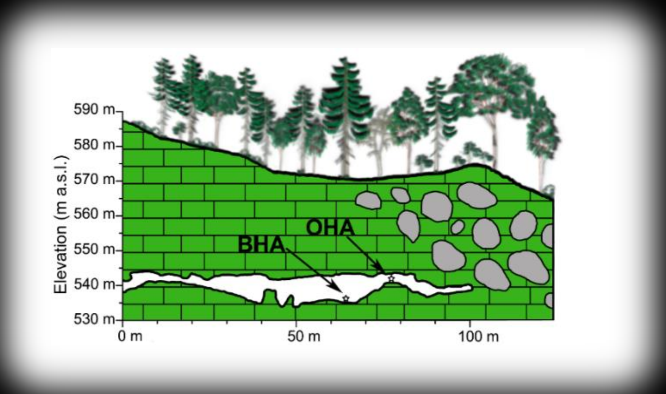


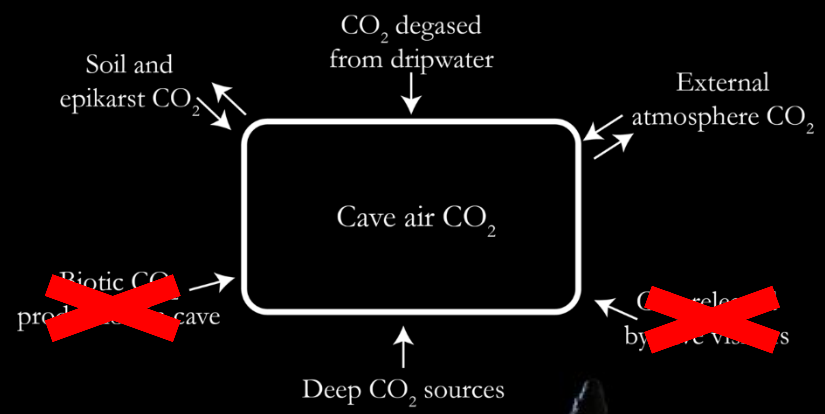
2016 Krajnc et al., Environ. Earth Sci.

Radon (^{222}Rn)

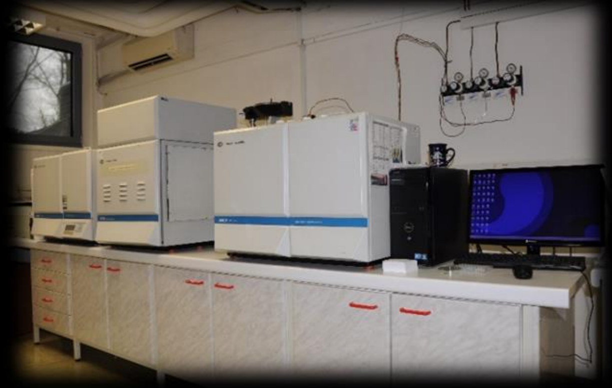
- Nobel gas (chemically inert)
- Radioactive with half-life of 3.82 days (easy to detect)
- Caves can have high radon concentrations (low ventilation with constant emissions from walls, water etc.)
- If CO_2 is the carrier gas a significant correlation exists between both gasses
- Investigation of cave ventilation and movement of cave air CO_2 (carrier gas)

Sources of cave CO_2





Methods



Sampling and measurements:

<u>AIR (soil and cave):</u>

- CO_2 concentration: NDIR probe (TESTO-453)
- Carbon stable isotopes: IRMS (Europa scientific 20-20)
- $\Delta^{14}C$ (sampled with NaOH solution, measured at AMS in JAEA, Mutsu, Japan)
- ^{222}Rn: scintillation cells + alpha counter (PRM-145; AMES)

<u>SOC and parent rock material:</u>

- IRMS (Europa scientific 20-20)

<u>METEOROLOGICAL DATA:</u>

- Meteorological data form *in-situ* and/or
- Nearby meteorological station (ARSO)

Methods

Sampling and measurements:

WATER (soil and dripwater):

- DIC (calculated from T, pH and Alkalinity)
- $\delta^{13}C_{DIC}$ (IsoPrime IRMS + MultiFlow Bio module)
- Cation concentrations (ICP-OES)
- Anion concentration (ion chromatography)
- pH (Corning 315 pH Meter + Orion Ross pH electrode)
- Conductivity (Myron Ultrameter IITM)
- Alkalinity (Gran titration)

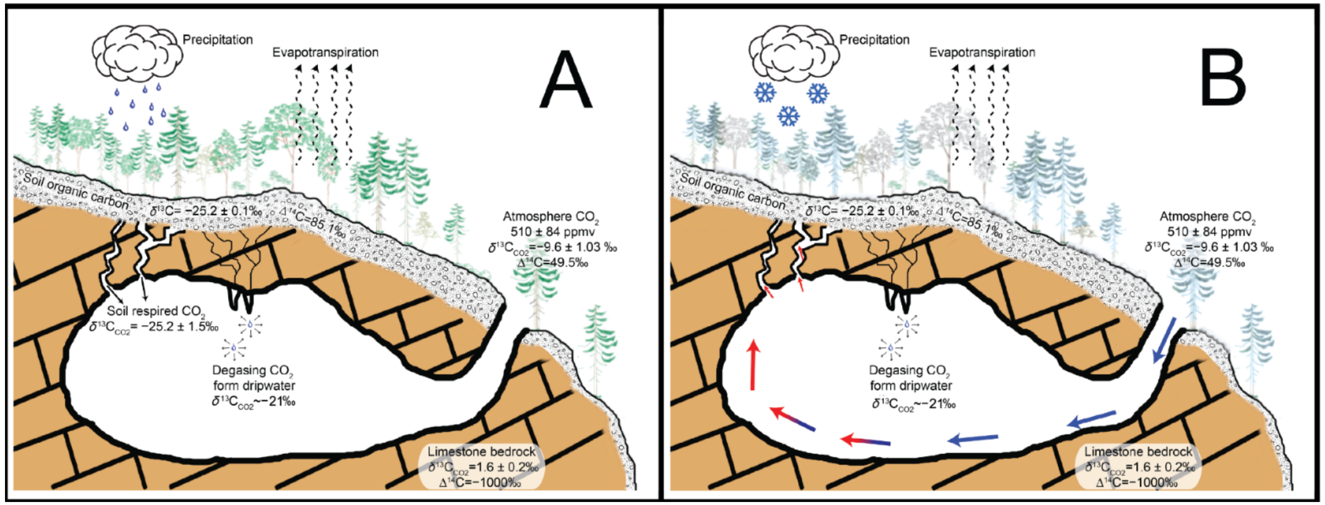
DATA MANIPULATION AND MODELING:

- Raw data manipulation and statistical analysis (R statistical environment)
- Modeling of the carbonate equilibrium and isotopic fractionation (PHREEQC and MIX4)

Sources of cave CO_2

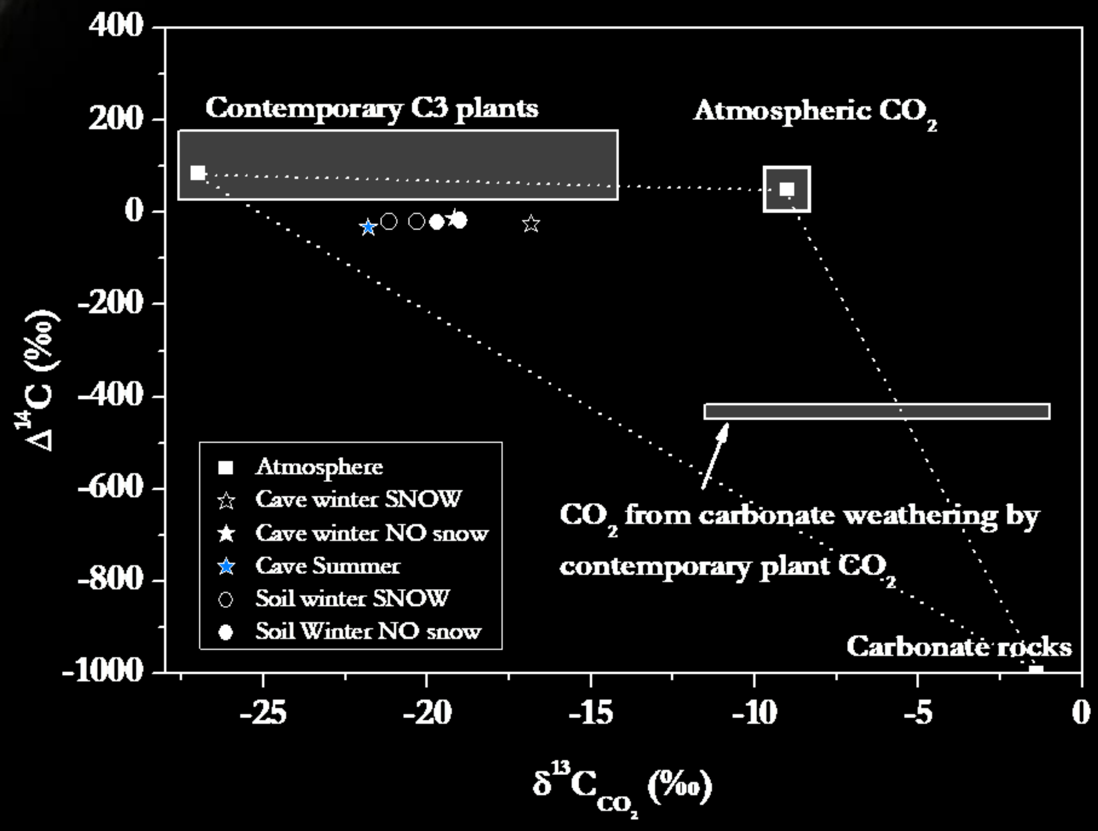
Results:

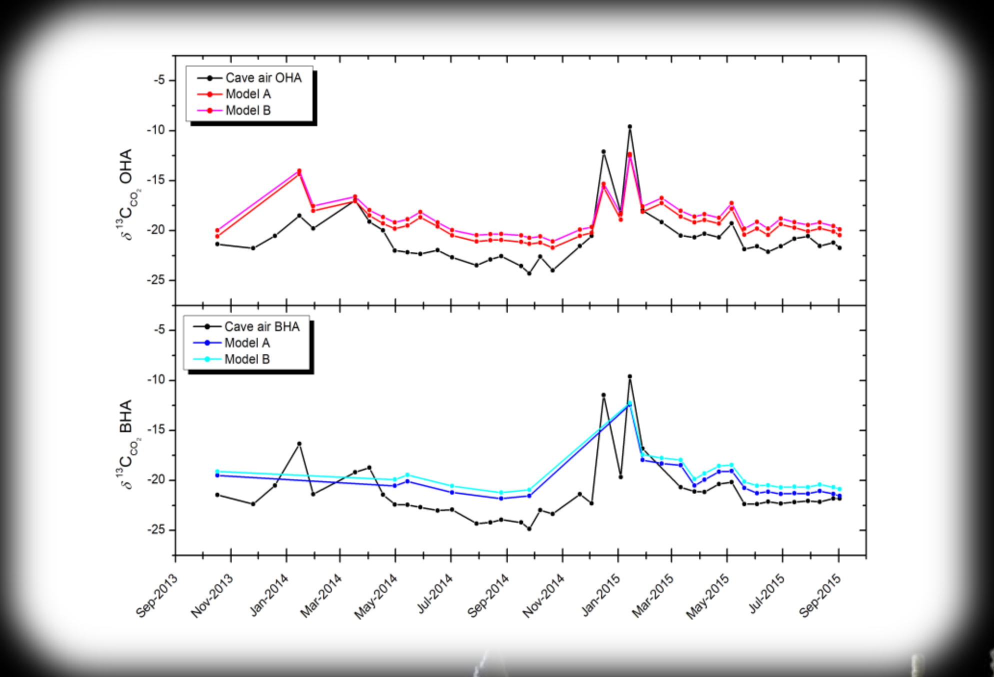
- Outside temperature is the main factor affecting cave ventilation
- During snow cover and freezing temperatures, the ventilation is inhibited
- Good correlation between CO_2 and ^{222}Rn (common driving force)



Results: Sources of cave CO_2

- Majority of cave CO_2 indeed comes from soil respiration
- Comparison of modelled values with measured values suggests that CO_2 degassing from dripwaters can not be a major CO_2 source

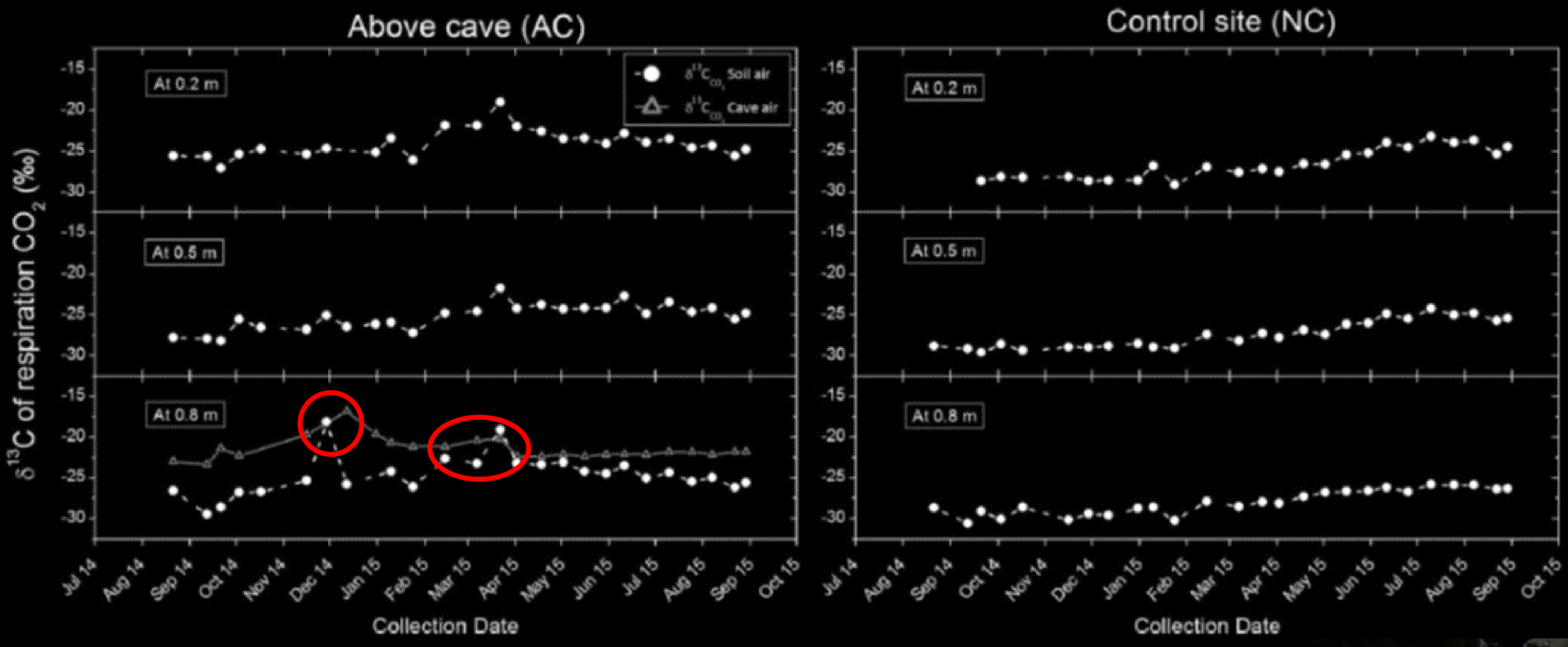




Krajnc et al., (in press) Geochim. Cosmochim Acta

Soil CO_2 sources above the subterranean cave

There was an additional source of CO_2 present in the soil above the cave during the cold periods which coincided with the period of cave ventilation.



(2016, Krajnc et al., J Soils Sediments)

Conclusions

The levels of CO_2 concentrations, $\delta^{13}C_{CO2}$ and ^{222}Rn in the cave air have typical seasonal pattern

These values are not primarily controlled by soil CO_2 productivity, but are mainly caused by the ventilation

Major source of cave CO_2 in the studied chamber is the CO_2 originating from soil respiration, transported directly to the cave,

The findings of this study demonstrate that isotope geochemistry is a very useful tool to address the sources of CO_2.

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