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Outstanding Student & PhD candidate Presentation contest

Sources of cave CO_2 at Milandre cave, Switzerland constrained through multipool analysis of ^{14}C and $\delta^{13}C$

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1) Background

- The contributing **sources** and **mechanisms of delivery** of **subsurface CO_2** in karst systems are not well understood. The traditional model suggests that the **dominant source** originates from the **respiration of catchment vegetation and soils**[1].
- **Additional sources** of vadose CO_2 found in recent studies [2]:
  - Exchange of air flow with the **outside atmosphere**.
  - Degassing of ancient CO_2 from the **carbonate host rock**.
  - A reservoir of **respired organic carbon** within the epikarst [3].
- A long-term **process** study of **Milandre cave** (Fig.1) is taking place aiming to trace the **fluxes of carbon** in the cave system and determine **potential sources** and **spatial-temporal variations**. The **$\delta^{13}C$ and $F^{14}C$** of catchment CO_2 from the atmosphere, wells in the catchment area, and cave atmosphere was analysed. Samples were taken once every two months for over a year.
- In paleoclimate studies this analysis could assist in tracing **past ecosystem state and response to climate change.**

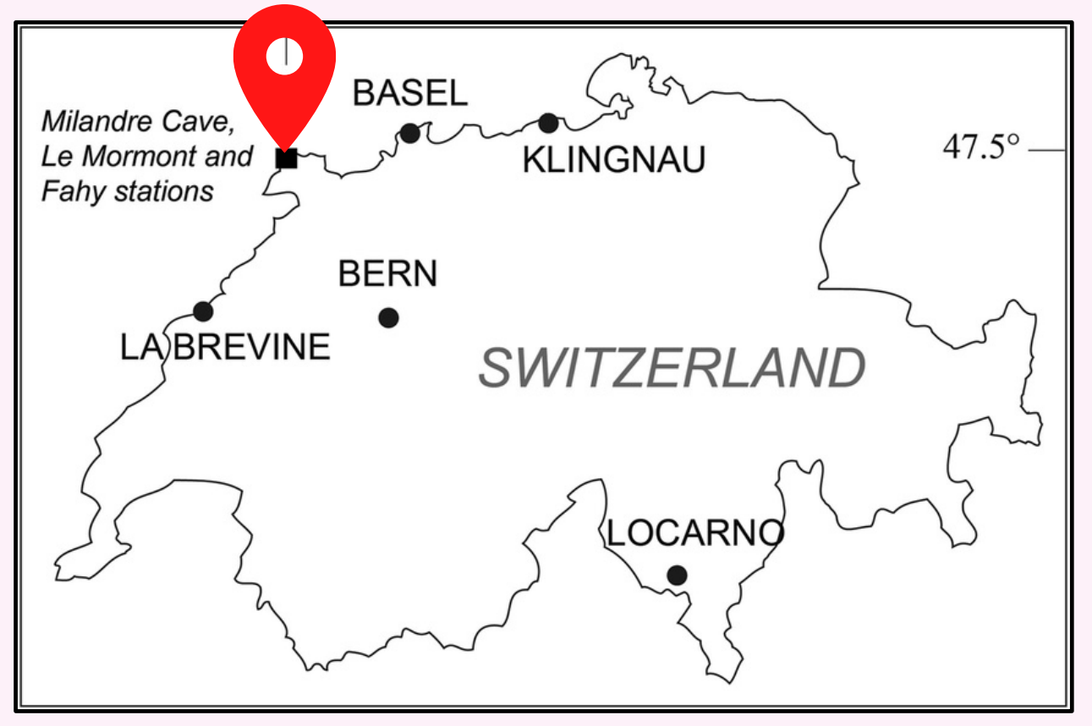

Fig..1: Location of Milandre cave- (Source 4).

2) Temperature driven cave ventilation dynamics

- **Cave gas** samples of 5 L were taken in Cali-5-bond bags from **two sites**, GF (downstream) & GR (upstream), nearby both cave entrances (Fig.2). The upstream entrance lies at 509m.asl, and the downstream entrance lies at 402m.asl [5,6]. Samples were also taken from borehole **wells** of 0.5-5m depth throughout the catchment (Fig.3) which can give insight to the possible production locations of CO_2.
- **CO_2 concentration** and **$\delta^{13}C$** were analysed with a **PICARRO isotopic analyser**. The **$F^{14}C$** was determined by **AMS analysis** with a **MICADAS** (Mini Carbon Dating System).

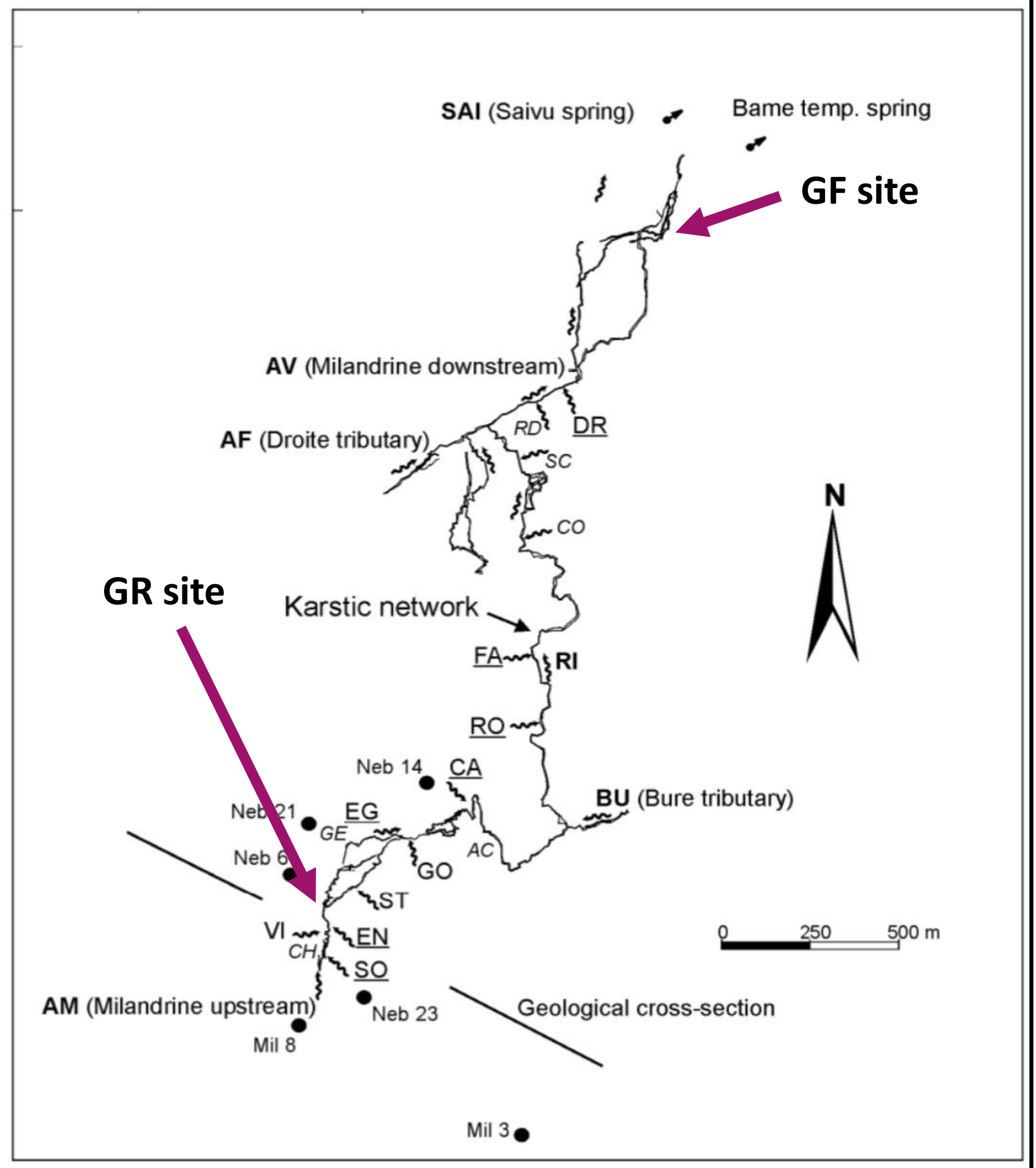

Fig.2: Map of Milandre cave with GF and GR sampling sites annotated. After source 6.

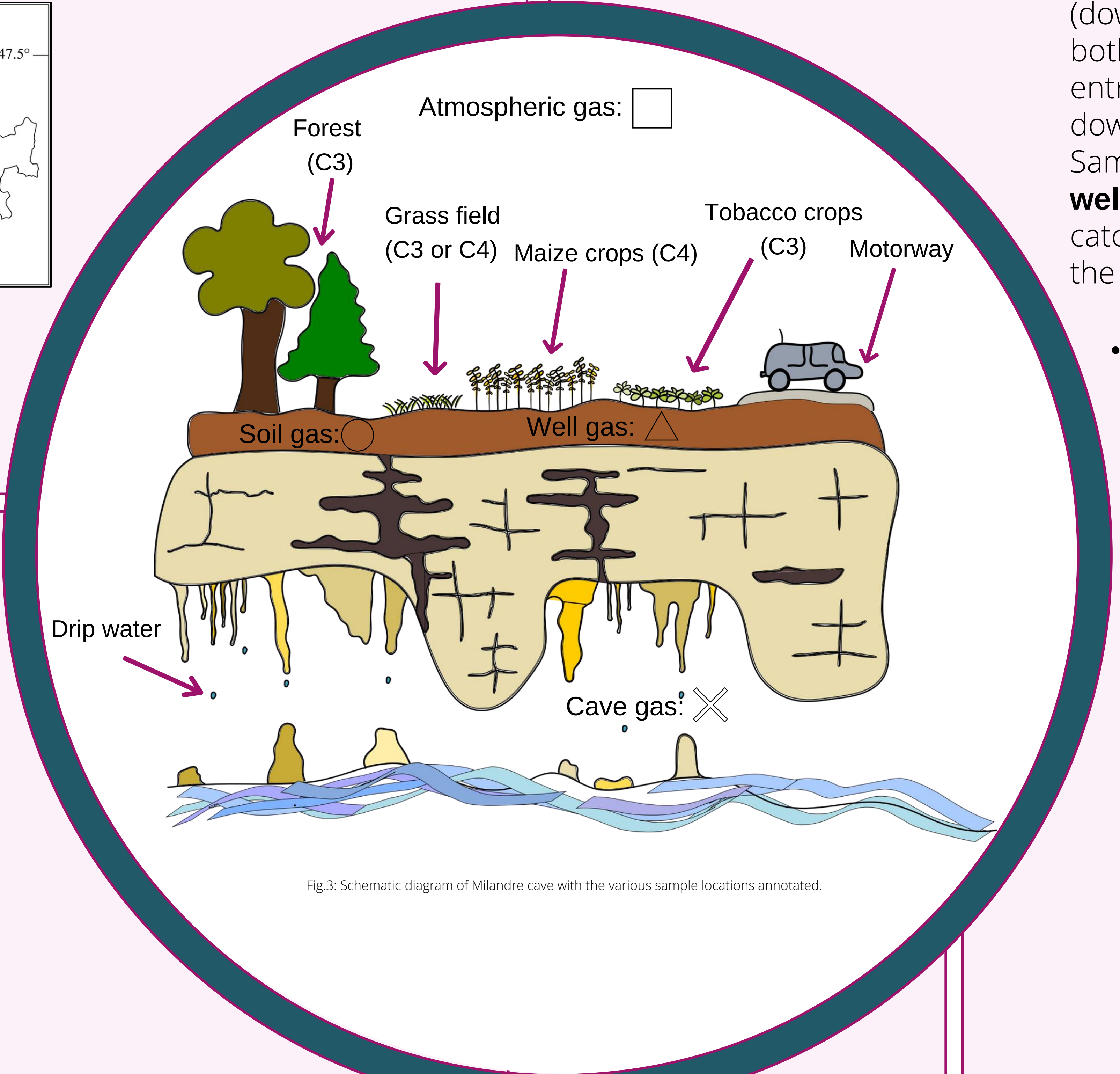

Fig.3: Schematic diagram of Milandre cave with the various sample locations annotated.

Table 1: Summary of seasonal cave air dynamics

Parameter	Season	GF	GR
Airflow	Winter	→	
	Summer	←	
pCO_2 (Fig.4)	Winter	Lower	Higher
	Summer	Higher	Lower
$\delta^{13}C$ (Fig.5)	Winter	Enriched	Depleted
	Summer	Depleted	Depleted
$F^{14}C$ (Fig.5)	Winter	Enriched	Depleted
	Summer	Depleted	Enriched

- Air flow direction changes when the outside temperature is 8 °C [5].

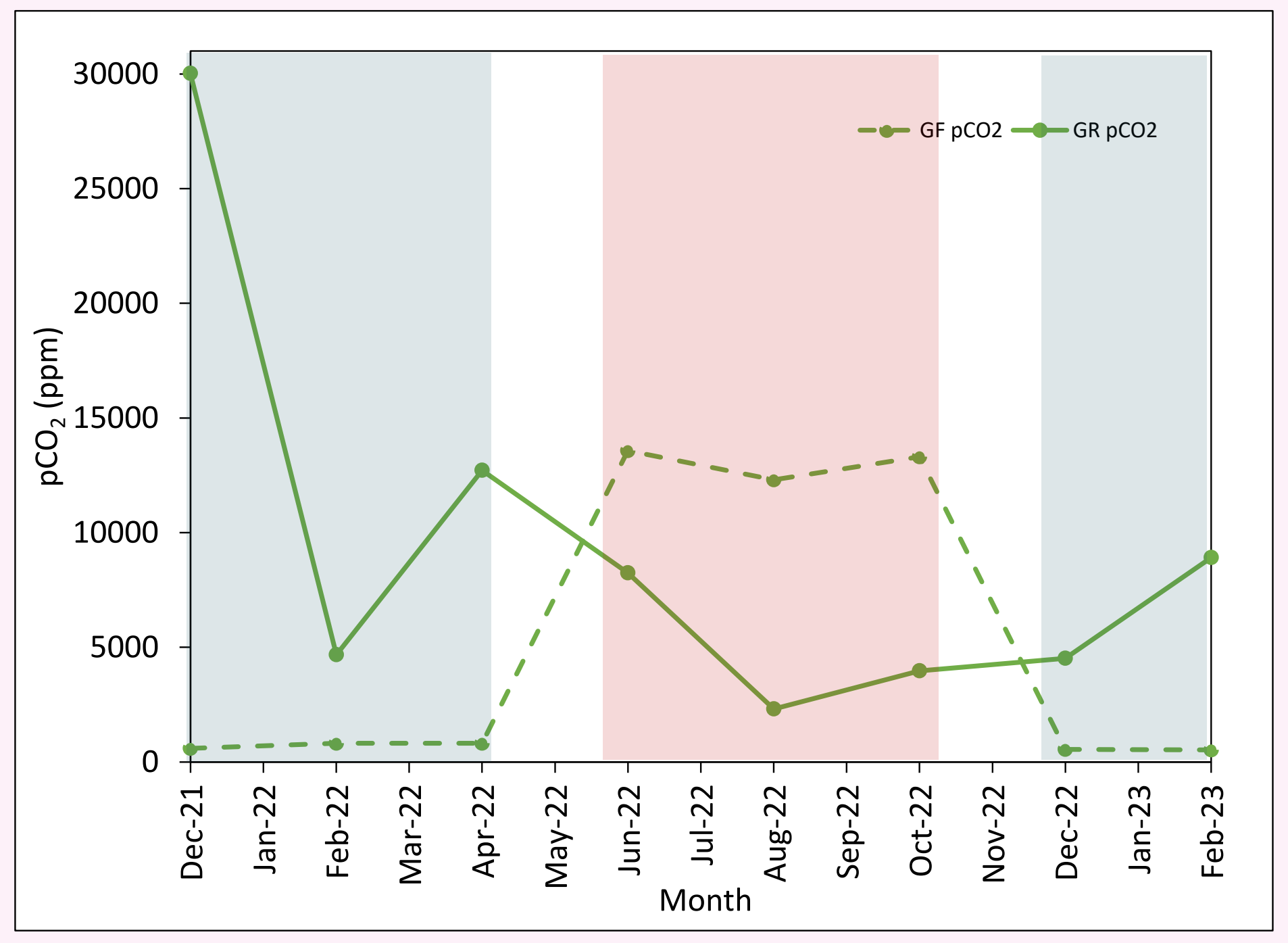

Fig.4: CO_2 concentration of cave gas of both sampling sites GF (dashed line) and GR (solid line) over one year. Blue bars notate winter ventilation regime, red bar notates summer ventilation regime.

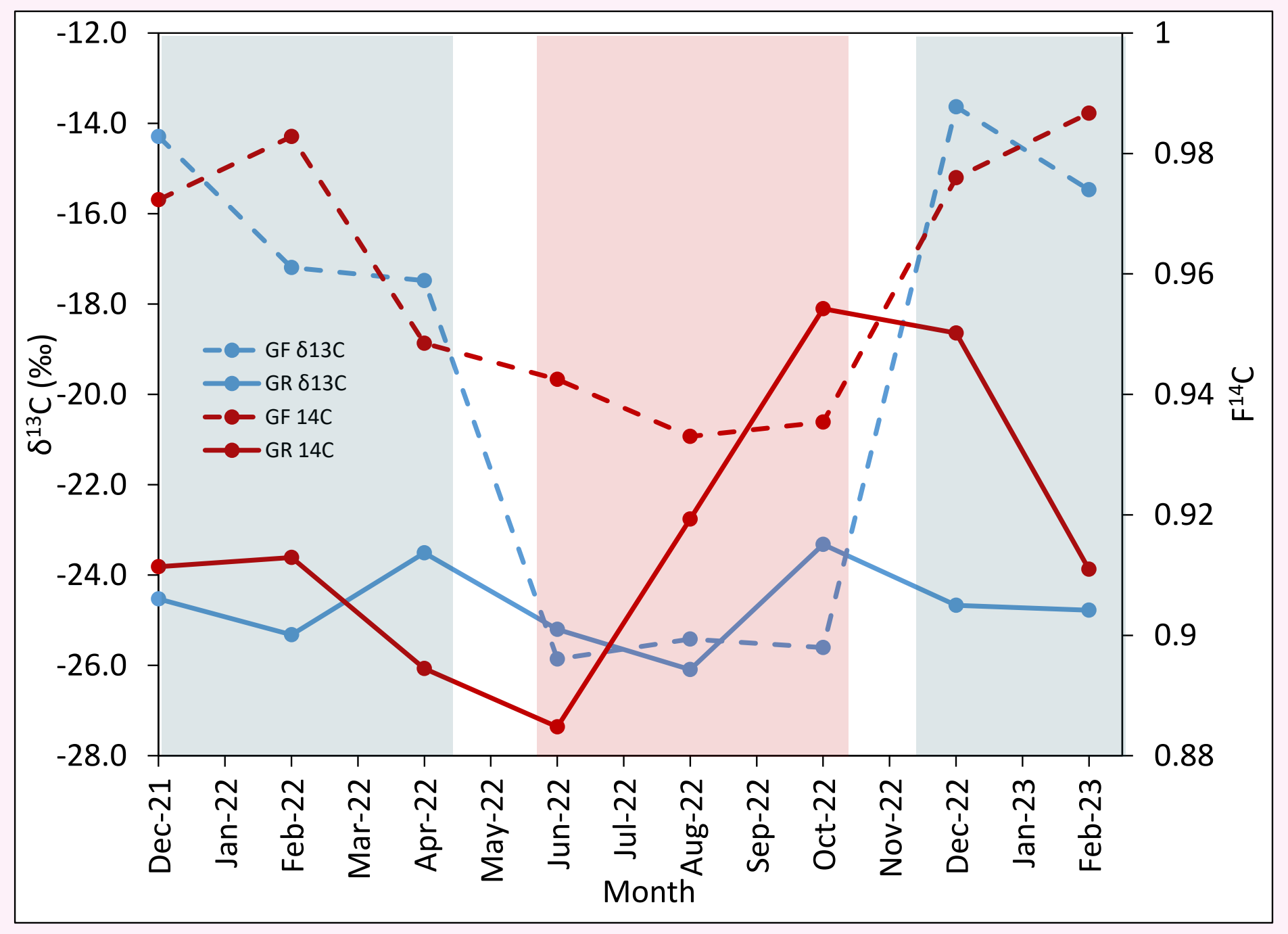

Fig.5: $\delta^{13}C$ and $F^{14}C$ of cave CO_2 of both sampling sites GF (dashed lines) and GR (solid lines) over one year. Blue bars notate winter ventilation regime, red bar notates summer ventilation regime.

3) Cave Gas

1. Modern to above modern $F^{14}C$ and depleted $\delta^{13}C$ signature in **soil and well gas** showing influence of **biological respiration and average decadal scale turnover times** (Fig.6).
2. Depleted $F^{14}C$ and depleted $\delta^{13}C$ of cave gas samples suggesting an **additional "aged" source of CO_2**. Potential influence of **old reservoir of biological carbon or from carbonate host rock dissolution.**

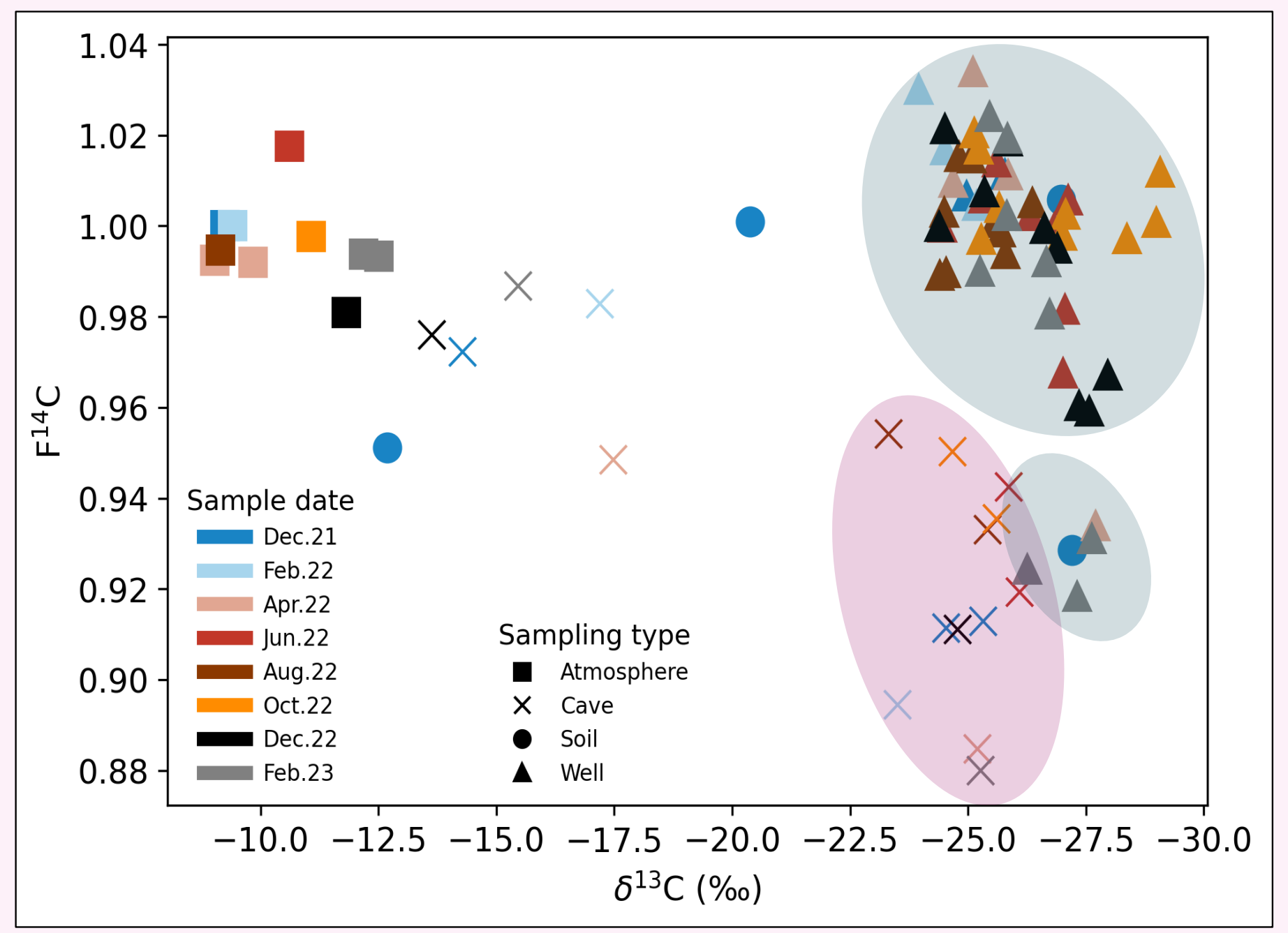

Fig.6: $\delta^{13}C$ and $F^{14}C$ of atmospheric, soil, well, and cave gas samples taken over one year.

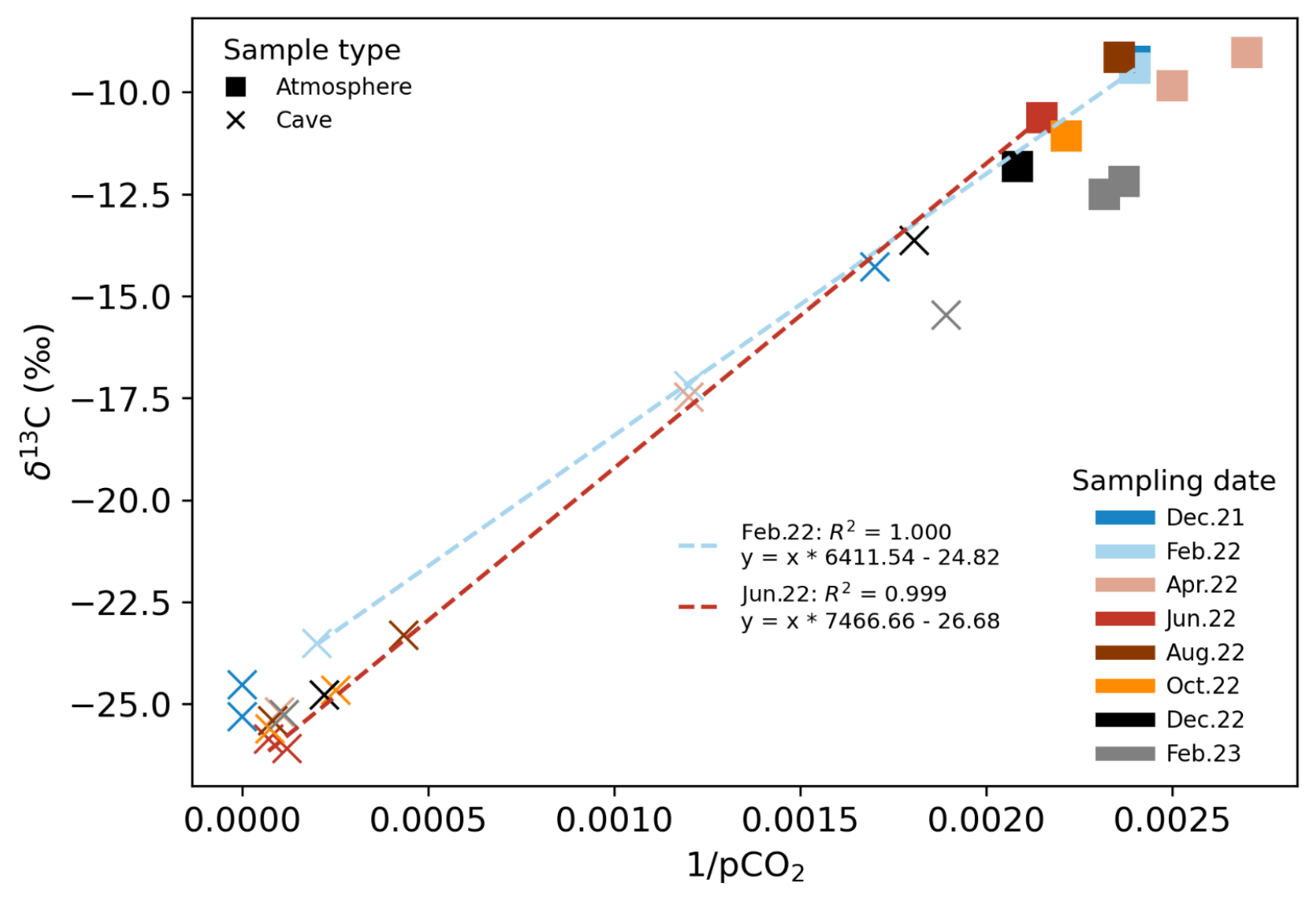

Fig.7: Keeling plot of cave gas and well gas samples $\delta^{13}C$ and $1/pCO_2$. Linear regressions of the months with the maximum (Feb'22) and minimum (Jun'22) y-intercepts.

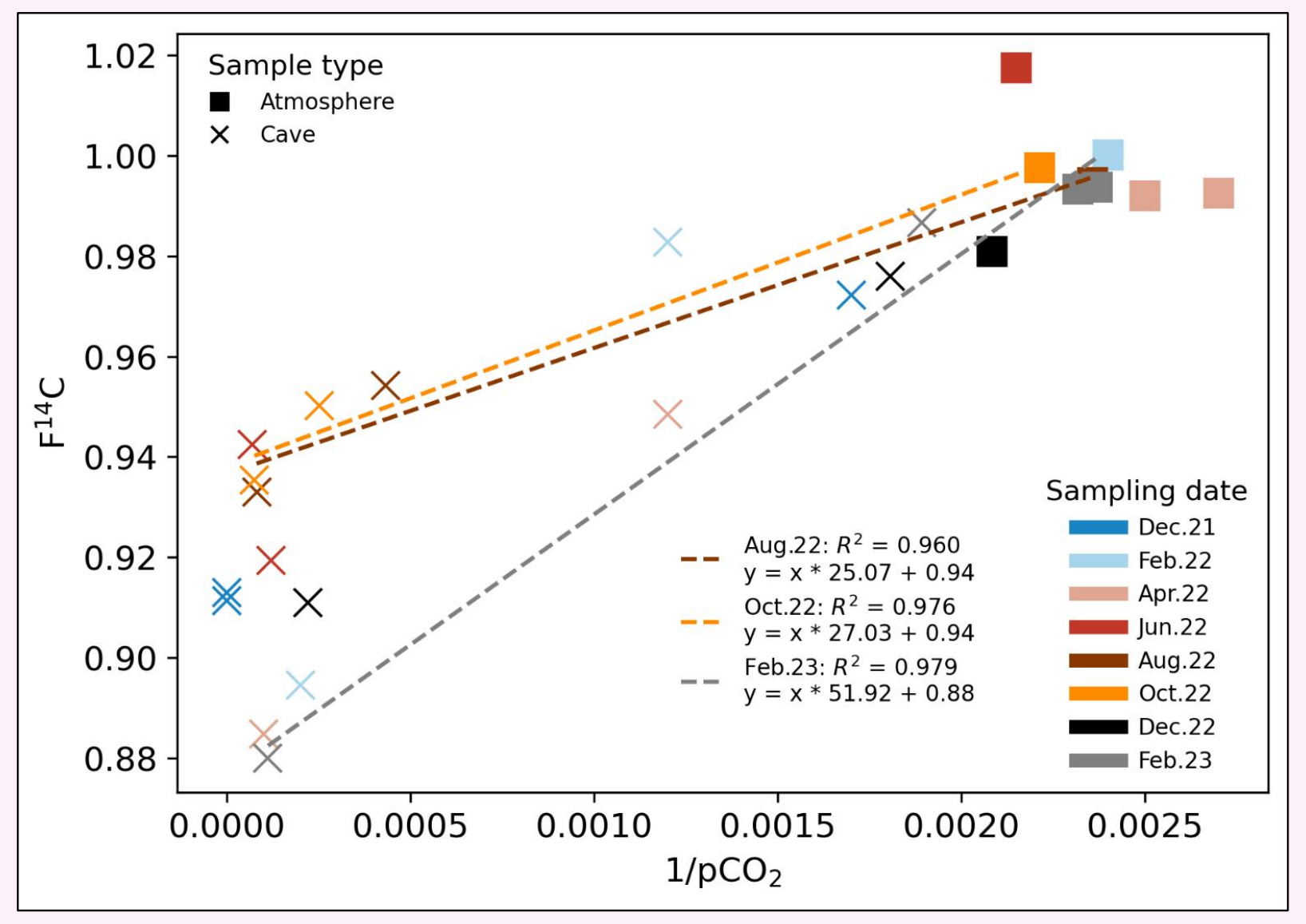

Fig.8: Keeling plot of cave gas and well gas samples $F^{14}C$ and $1/pCO_2$. Linear regressions of the months with the maximum (Aug & Oct'22) and minimum (Feb'23) y-intercepts.

- **Keeling plots** show the two end members **(atmosphere and respired) contributing CO_2**. Deviations and variability in one end member could point towards either **variability in the end member composition** or **additional processes** e.g., contribution of carbon from **degassing of cave river and drip water** (Fig.7 & 8).

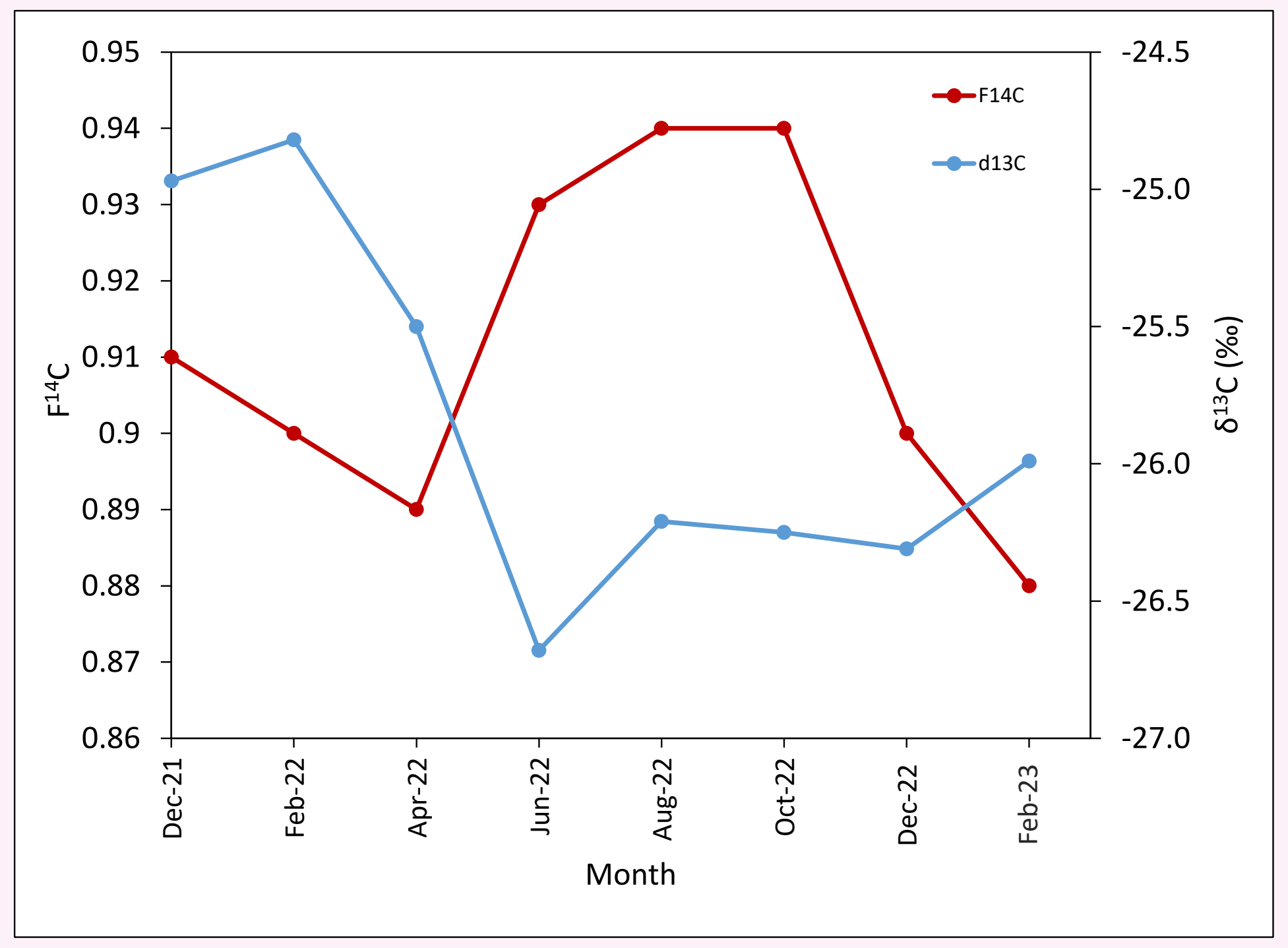

Fig.9: Y-intercepts of $\delta^{13}C$ and $F^{14}C$ over one year.

- **The isotopic signature** of the **endmember** becomes **more depleted in $\delta^{13}C$ and more enriched in $F^{14}C$ over summer** (Fig.9).
- Increased influence of **vegetation respiration** during the **growing season**, and **drip & river degassing** over **winter**.

4) Conclusions

- There is a contribution of CO_2 from a **more $F^{14}C$ modern** and **$\delta^{13}C$ depleted endmember** to the cave atmosphere during the **summer** months. This could be an input from the **respiration of catchment vegetation** into the cave carbon cycle.
- In **winter**, the cave CO_2 composition is dominated by a more **$F^{14}C$ depleted** and **$\delta^{13}C$ enriched endmember**, suggesting an input of **degassing** from the cave river and drip water.
- These results have implications for the understanding of the **subterranean carbon cycle** and the interpretation of speleothem carbon isotope records for paleoclimate studies.

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