

Dripwater monitoring in a shallow karst cave (Jama v Dovčku, SE Slovenia): O, H and C stable isotopes as input parameters for climate reconstruction

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Why is the monitoring of drip water necessary for reconstruction of cave climate from carbonate speleothems?

- 1 – Water (O, H) isotopes in precipitation and dripwater → mean groundwater travel time (MTT), temperature
- 2 – Dissolved inorganic C, CO₂ (concentration, stable isotope composition) → carbon sources, cave ventilation, land use, precipitation
- 3 – Trace elements (Mg/Ca, Sr/Ca), Sr isotopes → water-rock interactions, lithology, prior calcite precipitation (PCP), groundwater routing

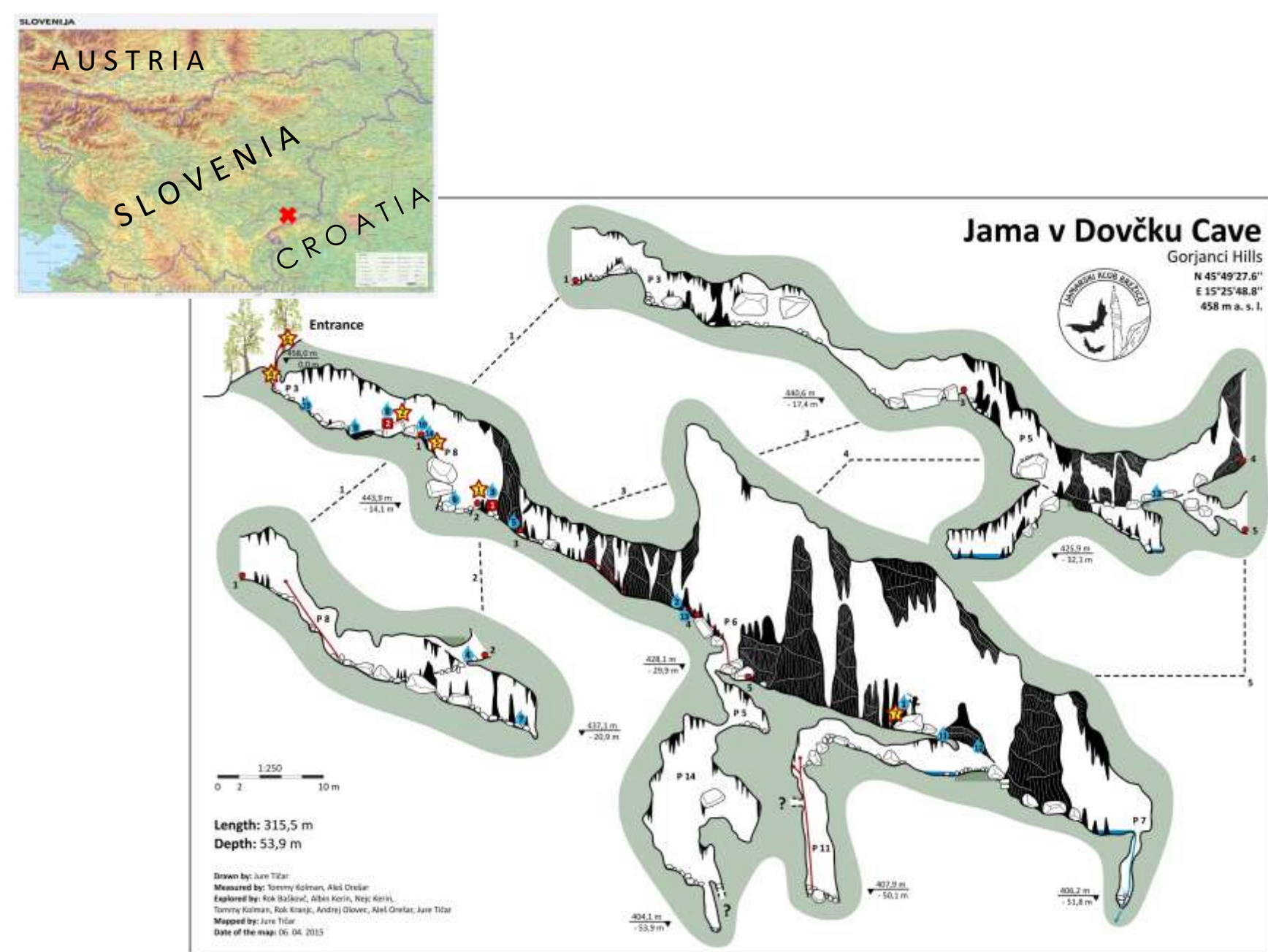


Fig. 1: Location map (●: monthly dripwater; ☆: temperature sensors)

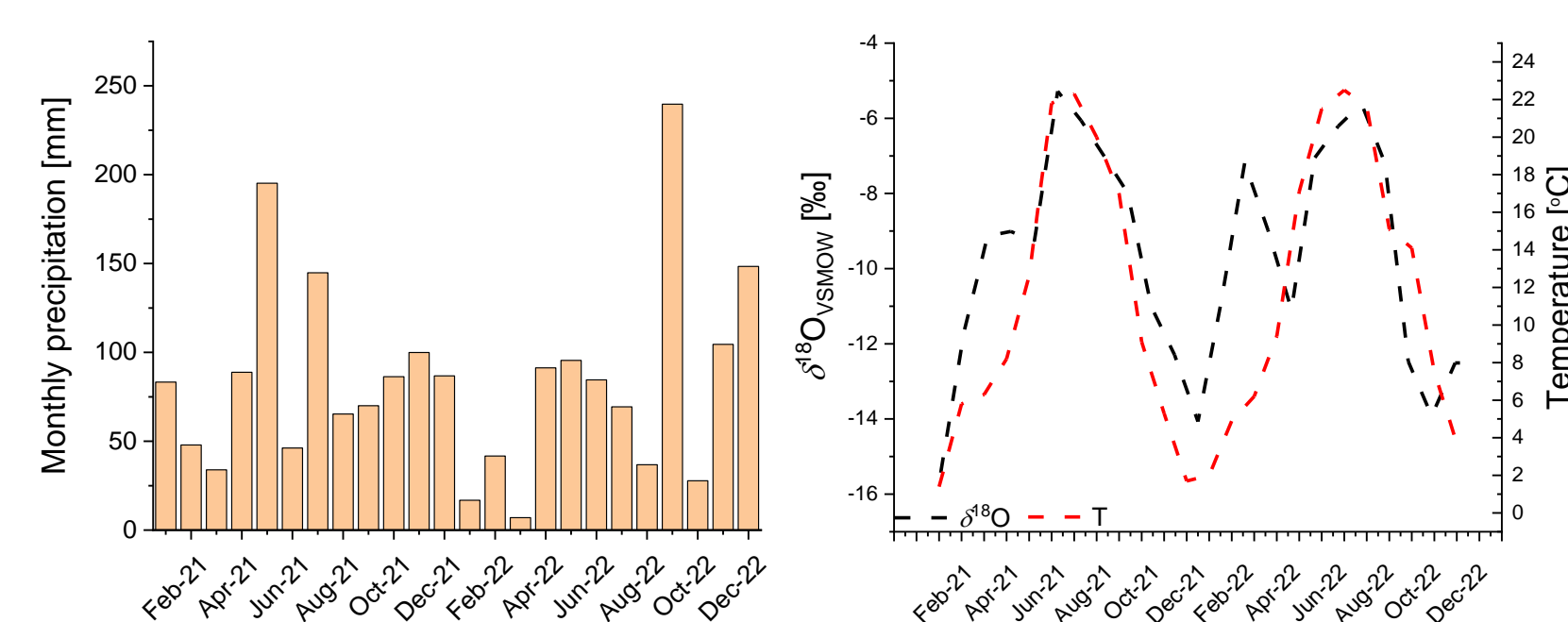


Figure 2: Monthly amount of precipitation (left); the temperature correlates well with the isotopic composition of oxygen in precipitation at the investigated area (right)

Mean groundwater travel time (MTT)

Sine wave model¹:

$$\delta^{18}\text{O} = \delta^{18}\text{O}_{\text{mean}} + A \cdot [\cos(c \cdot t - \theta)]$$

$$\text{MTT} = c^{-1} \cdot [(A_d/A_p) - 1]^{1/2}$$

A = amplitude (of drip water, precipitation); c = radial frequency of annual fluctuation; t = time (days); θ = phase lag

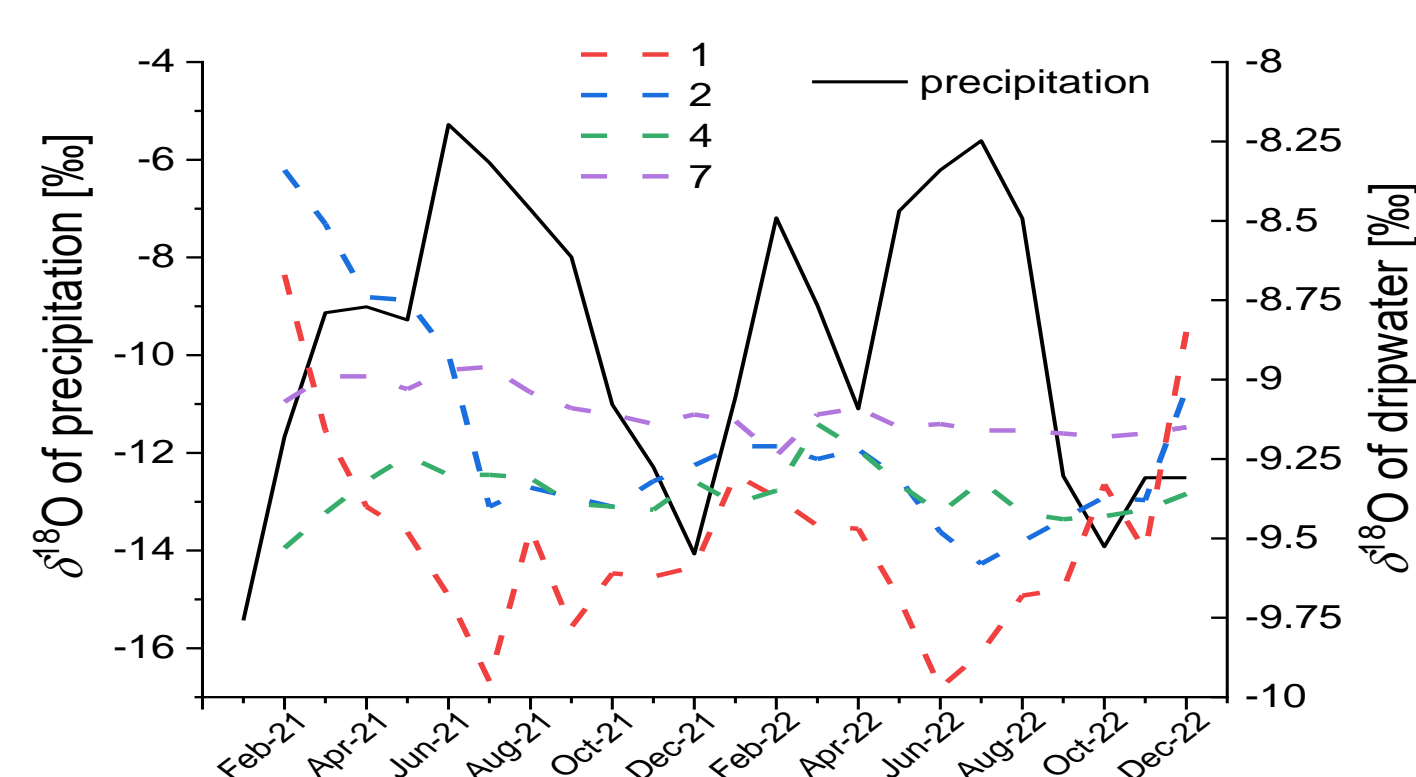


Fig. 3: O isotope composition of precipitation and dripwater; the calculated MTTs are listed in the table below.:

Site	Depth [m]	MTT δ ¹⁸ O [yr]	MTT δ ² H [yr]
1	37.3	1.65	1.88
2	28.0	3.47	3.06
3	16.6	1.81	2.42
4	16.9	1.95	2.64
5	13.8	2.24	2.04
6	16.2	4.24	3.71
7	21.3	2.72	2.31
8	4.8	2.46	2.24
9	1.6	1.81	1.87
10	3.5	3.05	2.55
11	37.0	3.18	3.16
12	49.1	3.32	2.69
13	28.9	3.05	2.27
14	3.1	2.31	2.16
15	0.9	1.43	1.58

Considering the mean travel times of dripwater, an annual to decadal time resolution of isotope and elemental signals in speleothem carbonate can be expected.

The cave: Jama v Dovčku is located in SE Slovenia close to the Croatian border (Fig. 1). It is about 315 m long with a max. depth of 53.5 m. The cave developed along a fault zone in a patchy dolomite – limestone carbonate formation. The surface is hilly and covered with a mixed forest. The temperature at the bottom of the cave was 9.73 ± 0.01°C and 9.90 ± 0.13°C at a depth of 16m, with the highest values in the winter and the lowest in the summer. The temperature at the entrance to the cave varied between -9 and 32.4°C.

Monitoring programme: December 2020 – December 2022

- Hydrometeorological data obtained by the Environment Agency of Slovenia (ARSO, www.meteo.si)
- Cumulative monthly samples of precipitation at the closest meteorological station
- Dripwater at 15 sites at depths from 1 to 50 m
- Cave air composition and isotope composition of CO₂ in discrete samples
- Analyses: δ¹⁸O and δ²H values of precipitation and dripwater, δ¹³C values of dissolved inorganic C and CO₂, pH, T, total alkalinity, elemental composition of water, stable Sr isotopes

Carbon geochemistry

The concentrations and δ¹³C values of dissolved inorganic carbon (DIC) in dripwater showed consistent seasonal variations, except at sites with constantly high drip rates (2, 7) or those which seep only occasionally (3, 8, 15; Fig. 4). Most drips showed a dominantly biogenic origin of DIC, with δ¹³C values of the added CO₂ of about -23 ‰; this is consistent with the dominant vegetation in the area (mixed forest and meadows). The measured CO₂ concentrations in the cave were ~850 - 950 ppm during the winter and ~5000-7000 ppm during the rest of the year; a correlation of pCO₂ with depth was observed only in the short periods of ventilation. The δ¹³C values of CO₂ were in or close to the equilibrium with the δ¹³C_{DIC}. The measured and calculated (Phreeqc) pCO₂ mostly matched within a few 100 ppm, except in the periods of ventilation and strong degassing, when calculated pCO₂ in dripwater at some sites reached the order of magnitude of 10^{1.4} (Fig. 5).

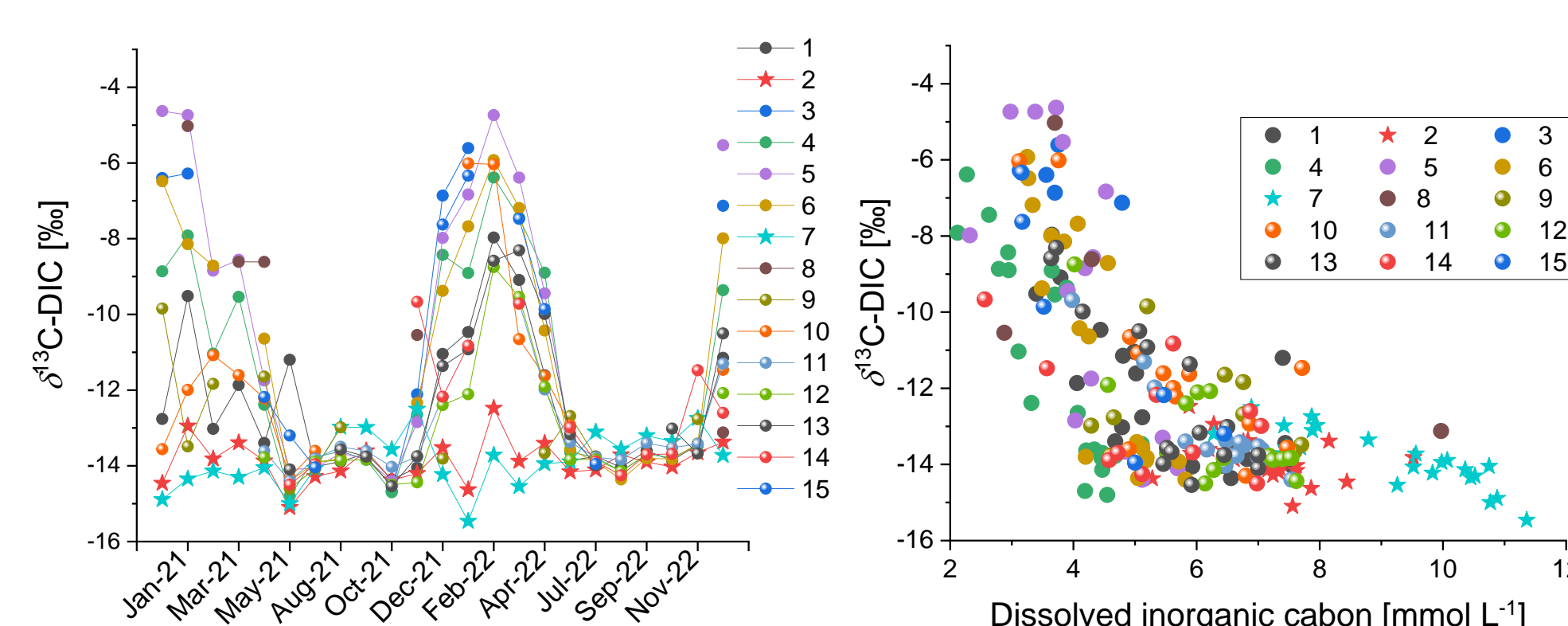


Fig. 4: Temporal fluctuation of the C isotope composition of DIC in dripwater and relation between concentration and δ¹³C value of DIC; the calculated δ¹³C value of added DIC was -23 ‰

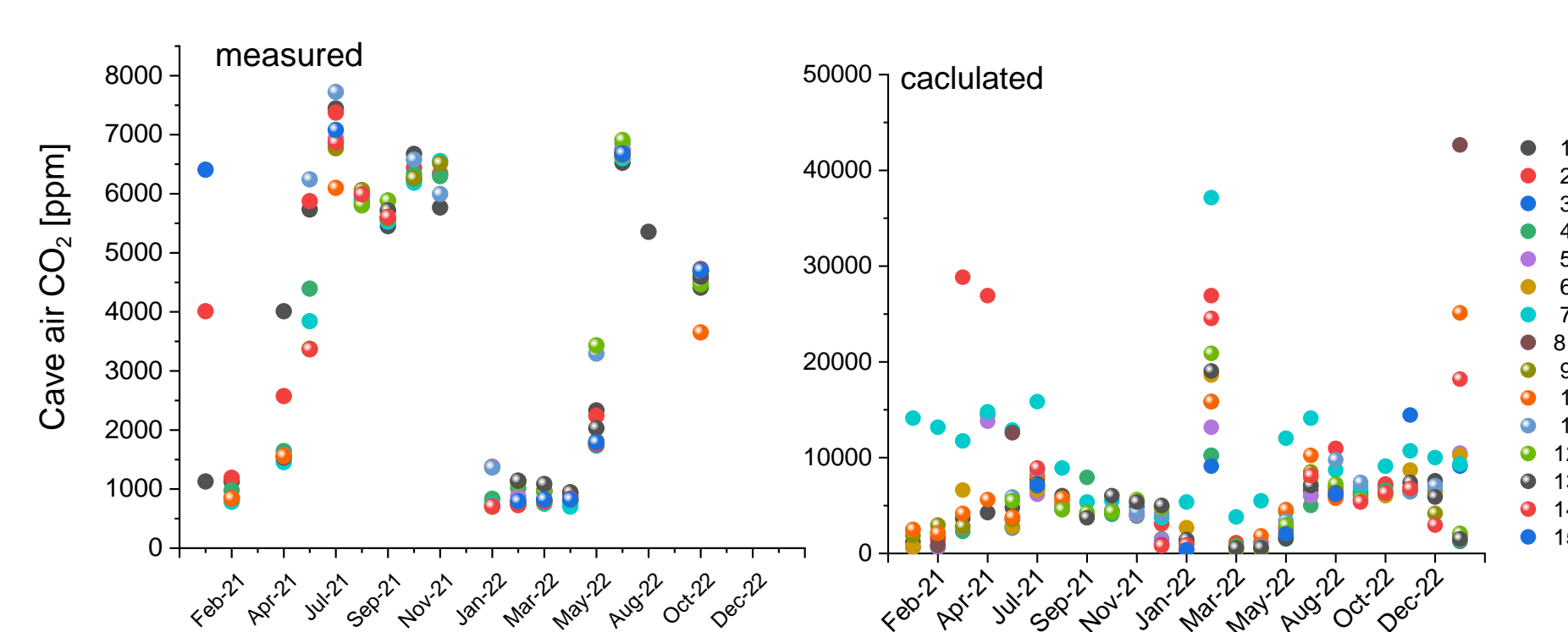


Fig. 5: Measured concentration of CO₂ in the cave air (left) and calculated pCO₂ from the chemical composition of water; extremely high values are recorded in the periods of ventilation in the winter.

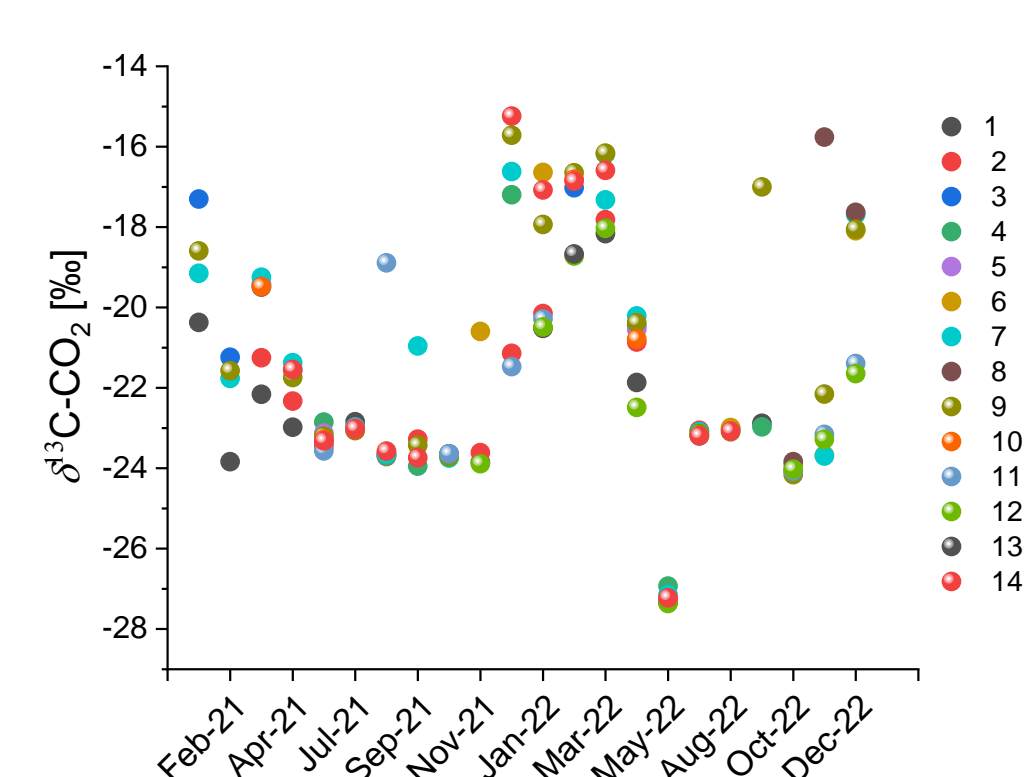


Fig. 6: The isotopic composition of the cave air CO₂ is in or close to the equilibrium with the δ¹³C value of DIC (cf. Fig. 4).

Trace elements

The Mg/Ca ratios of dripwater (0.13 – 2.07) were consistently exceeding those of the bedrock (0.01-0.10 for limestone, 0.13 – 0.27 for dolomite); the high values are attributed to the incongruent dissolution of dolomite and silicate weathering, but the prior calcite precipitation (PCP) can also affect the solutes ratios, increasing the Mg/Ca^{3,4}.

The Sinclair test^{5,6} (correlated ln(Mg/Ca) and ln(Sr/Ca), slope between 0.71 and 1.45) confirmed that the PCP influences the Mg-Sr-Ca chemistry at 8 out of 15 sites (1, 4, 5, 9-13). At these sites, the Me/Ca ratios in speleothems depend on the amount of precipitation and infiltration, where dryer conditions favour the PCP and elevated Mg/Ca ratios.

Preliminary results of δ^{88/86}Sr analyses of dripwater (0.18-0.30 ‰) were not consistently higher at sites with PCP, but rather point toward the dissolution of secondary carbonate in the aquifer and differences in groundwater routing.

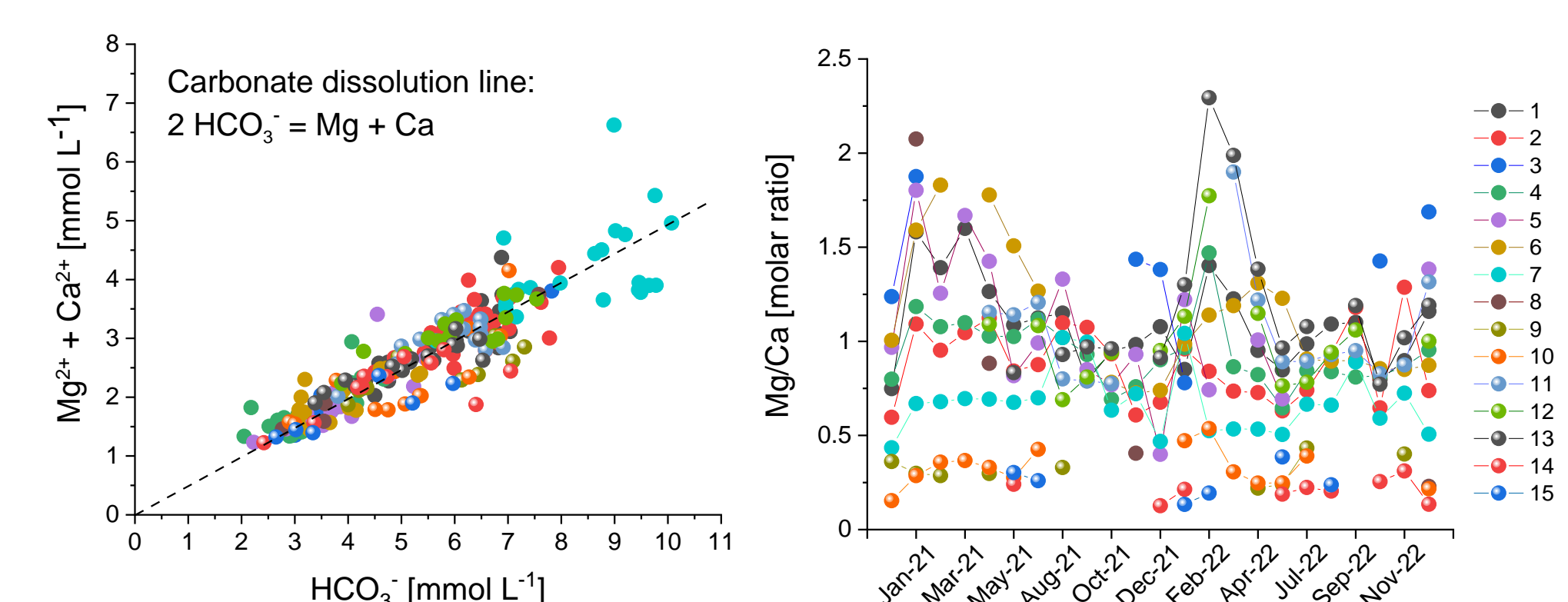


Fig. 7: Most of the dripwater samples match with the carbonate dissolution line (left) and only a few show significant contribution of the dissolved load from silicate weathering. Note the large seasonal variability (>100%) of Mg/Ca ratios at all sites irrespective of the MTT.

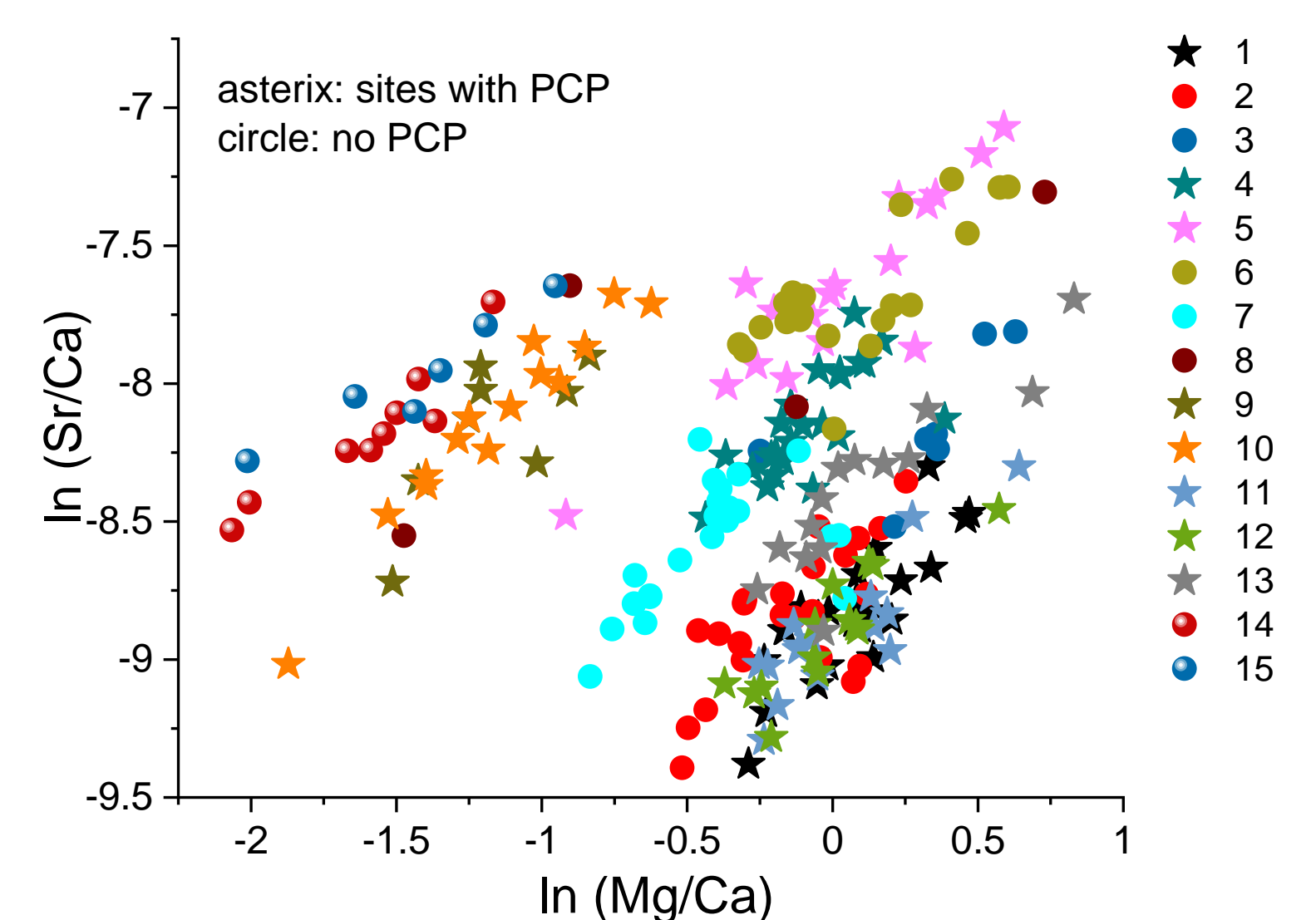


Fig. 8: The PCP in the aquifer occurs at groundwater routes feeding drips with ln(Sr/Ca) vs. ln(Mg/Ca) between 0.733 (site 4) and 1.03 (site 10). The average slope of drips with PCP is 0.845, which indicates that the mineralisation of dripwater originates from the dissolution of dolomite⁶.

References: ¹Rodgers et al., Hydrol. Earth. Sys. Sci. 2005, 9, 139-155. ²Sayles & Curry, Geochim. Cosmochim. Acta 1988, 52, 2963– 2978; ³Fairchild et al., Chem. Geol. 2000, 166, 255-269; ⁴Reichelmann et al., Chem. Geol. 2022, 590, 120704; ⁵Sinclair et al., Chem. Geol. 2012, 294-295, 1-17; ⁶Wassenburg et al. Geochim. Cosmochim. Acta 2020, 269, 581-596.

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