15th
International Symposium on the Interactions Between Sediments and Water

Are isotopes of Mg, Sr and U in fluvial sediments identifiers of authigenic carbonate?

S. Lojen, T. Zuliani, L. Rovan, M. Štrok, T. Kanduč, P. Vreča

Jožef Stefan Institute, Ljubljana, Slovenia

University of Ljubljana

Q. Jamil

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

Funded by Slovenian Research Agency (J1-9179, P1-0143, P2-0075)

Authigenic carbonate: „third major CO_2 sink“

Schrag et al. 2013, doi.org/10.1126/science.1229578

It comes in different forms…

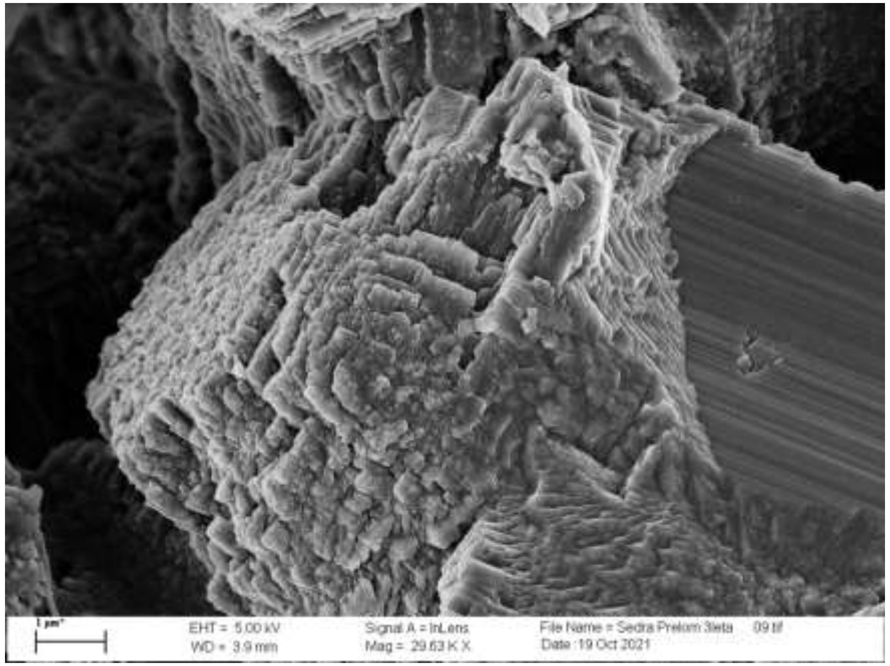
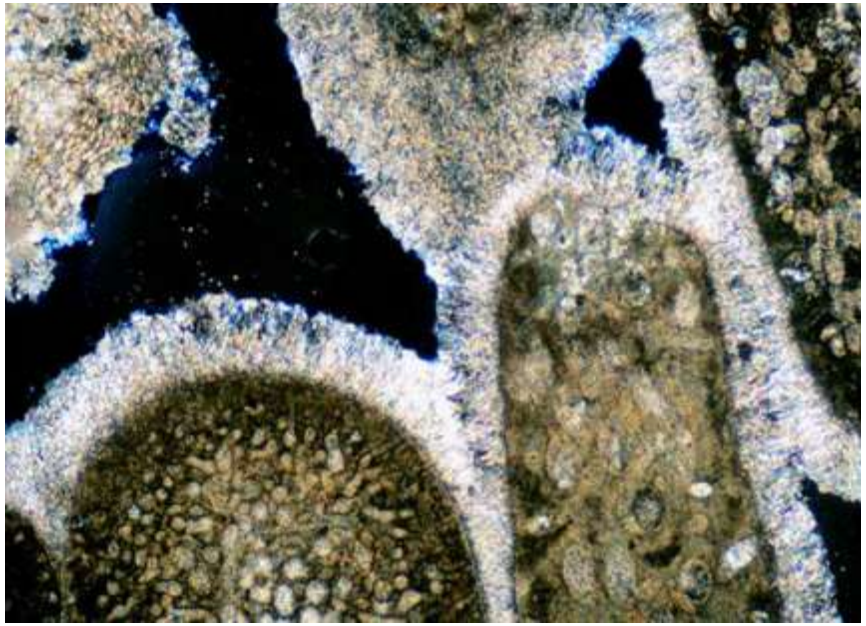
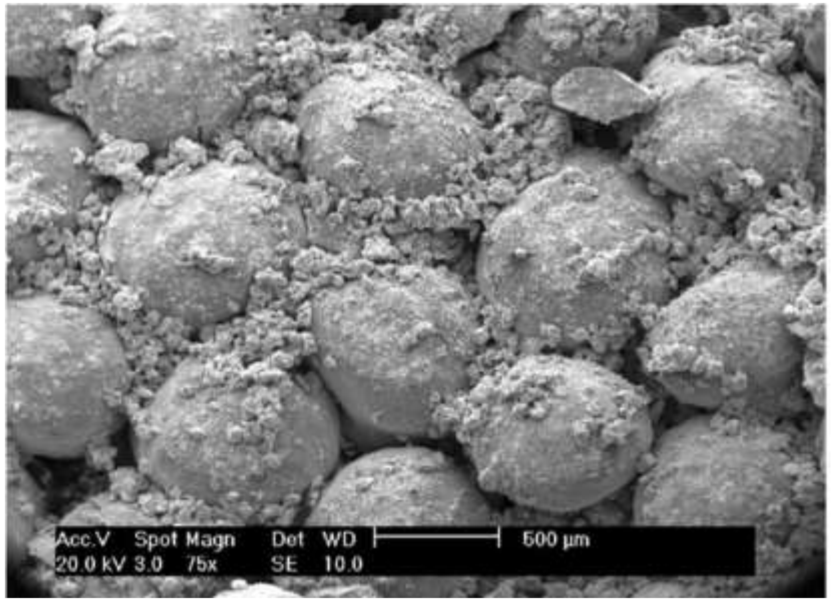


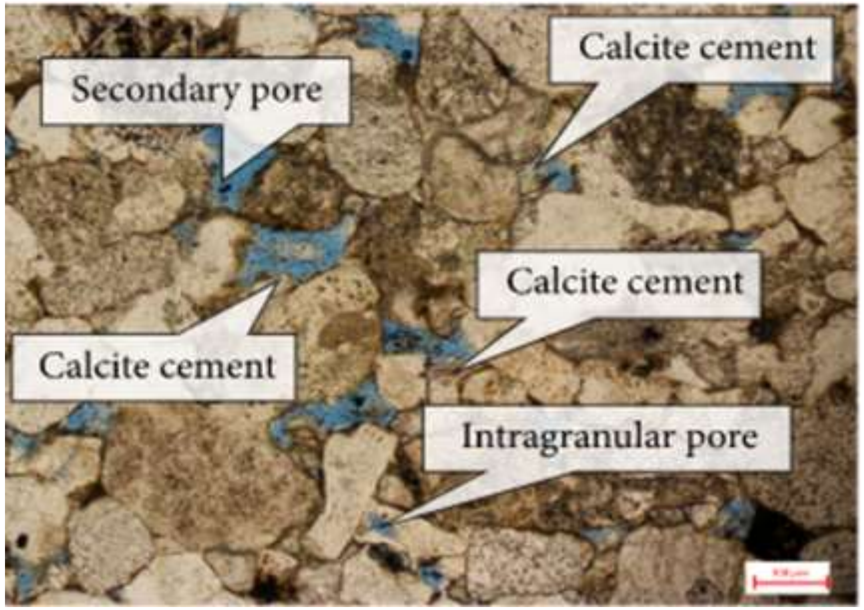
Photo: S.D. Škapin, JSI

Zrmanja, Croatia

…but most of them you can‘t see







Furong et al. 2017, https://doi.org/10.1155/2017/1020648

What is the problem?

Identification of authigenic carbonate is…

→ Relatively easy in siliciclastic sediments

→ Not so easy in limestone (Zhao et al. 2016, Nat Commun 7, 2016, 10885)

→ Complicated in terrigenous sediments at areas with dominant carbonate lithology

Why traditional isotopes ($\delta^{13}C$, $\delta^{18}O$) often fail?

→ Mixing of different sources of C and O

→ Different formation pathways of CaCO3

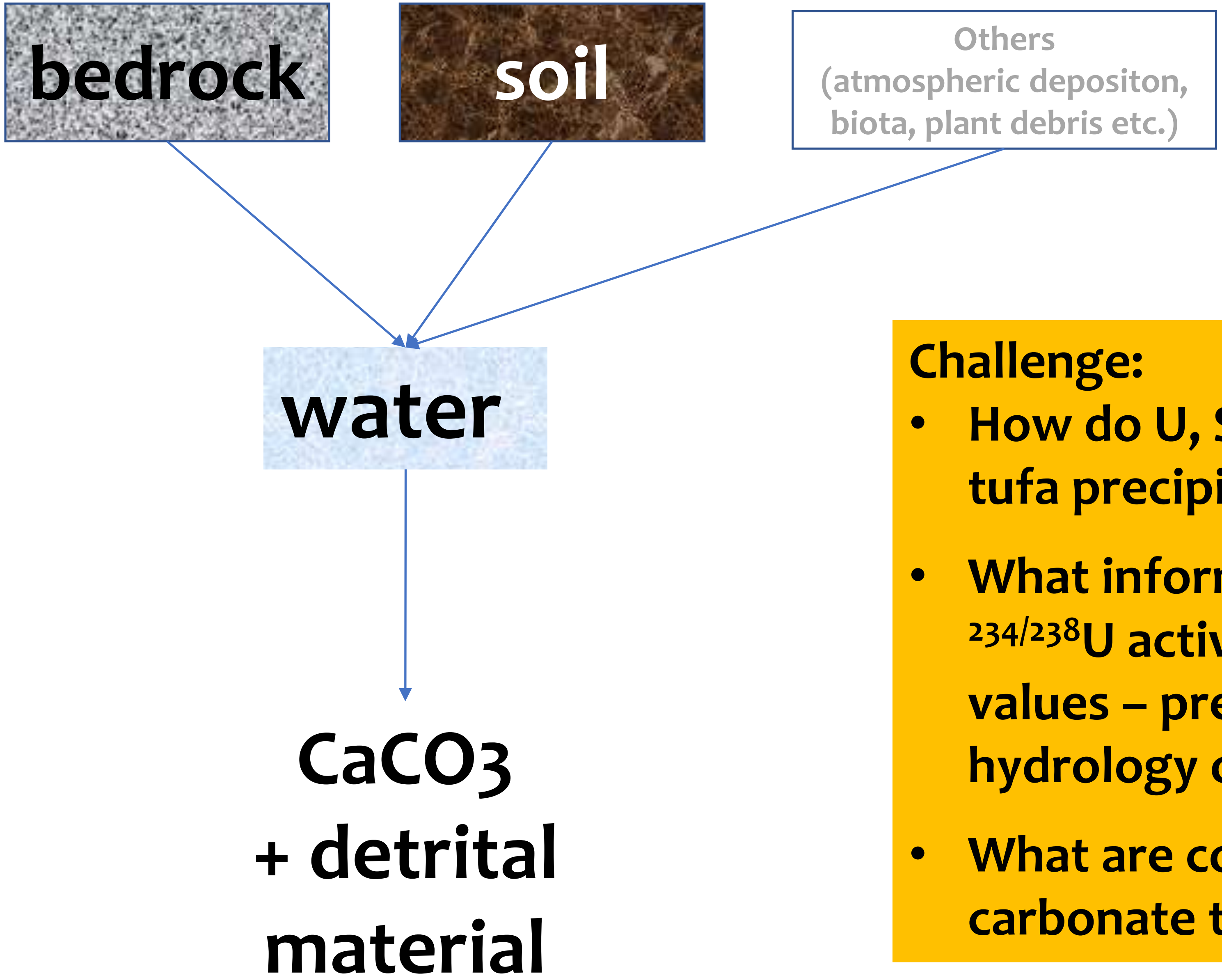
→ „Vital“ effects

→ Simultaneous, consexutive or cyclic early diagenetic processes that fractionate isotopes in different directions (e.g. CaCO3 precipitation and methanogenesis)

How non-traditional isotopes could help?

→ **$^{234}U/^{238}U$** activity ratio identifies „young" precipitating (ground)water of meteoric origin that was in contact with the aquifer as opposed to the seawater, where primary carbonate was formed

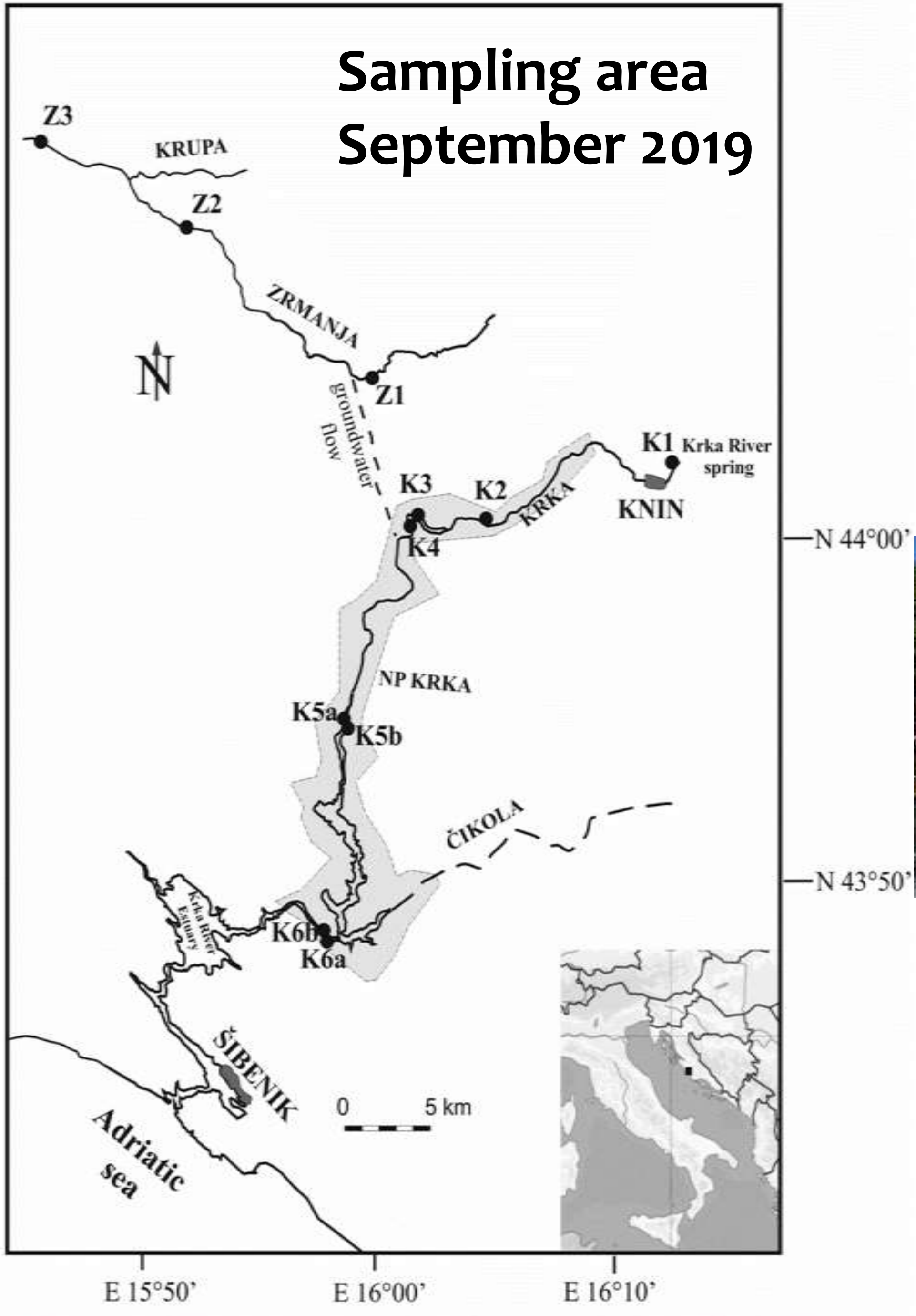
→ δ **^{88}Sr** and δ **^{26}Mg** identify the source and recycling of Sr and Mg – typical isotopic fractionation between carbonate and the dissolved Sr^{2+} and Mg^{2+} in precipitating water

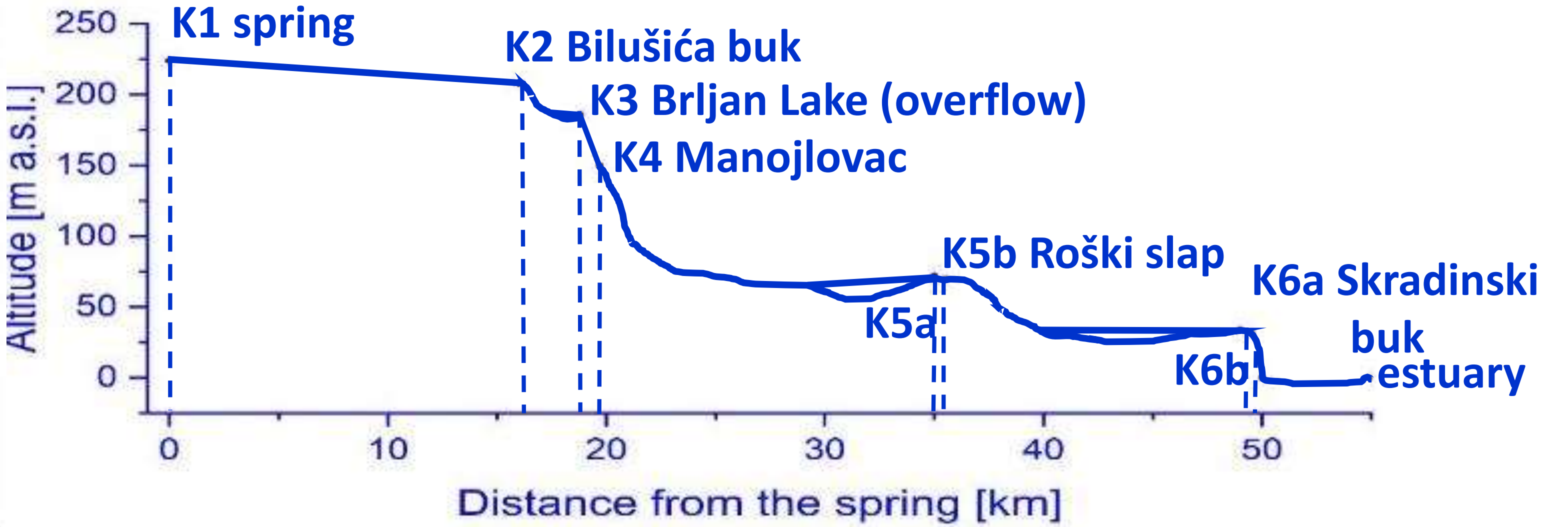


Challenge:

- How do U, Sr and Mg isotopes behave in a tufa precipitating stream
- What information can be obtained from $^{234/238}U$ activity ratios, $\delta^{26}Mg$ and $\delta^{88}Sr$ values – precipitation of carbonate or hydrology or both?
- What are contributions of detrital carbonate to the stream sediment (tufa)

Sampling area September 2019





Analyses

- **Water: T, pH, Eh, T, Ca^{2+}, Mg^{2+}, Sr^{2+}, U, $^{234/238}U$, $\delta^{88}Sr$, $\delta^{26}Mg$, $\delta^{18}O$, $\delta^{13}C$-DIC**

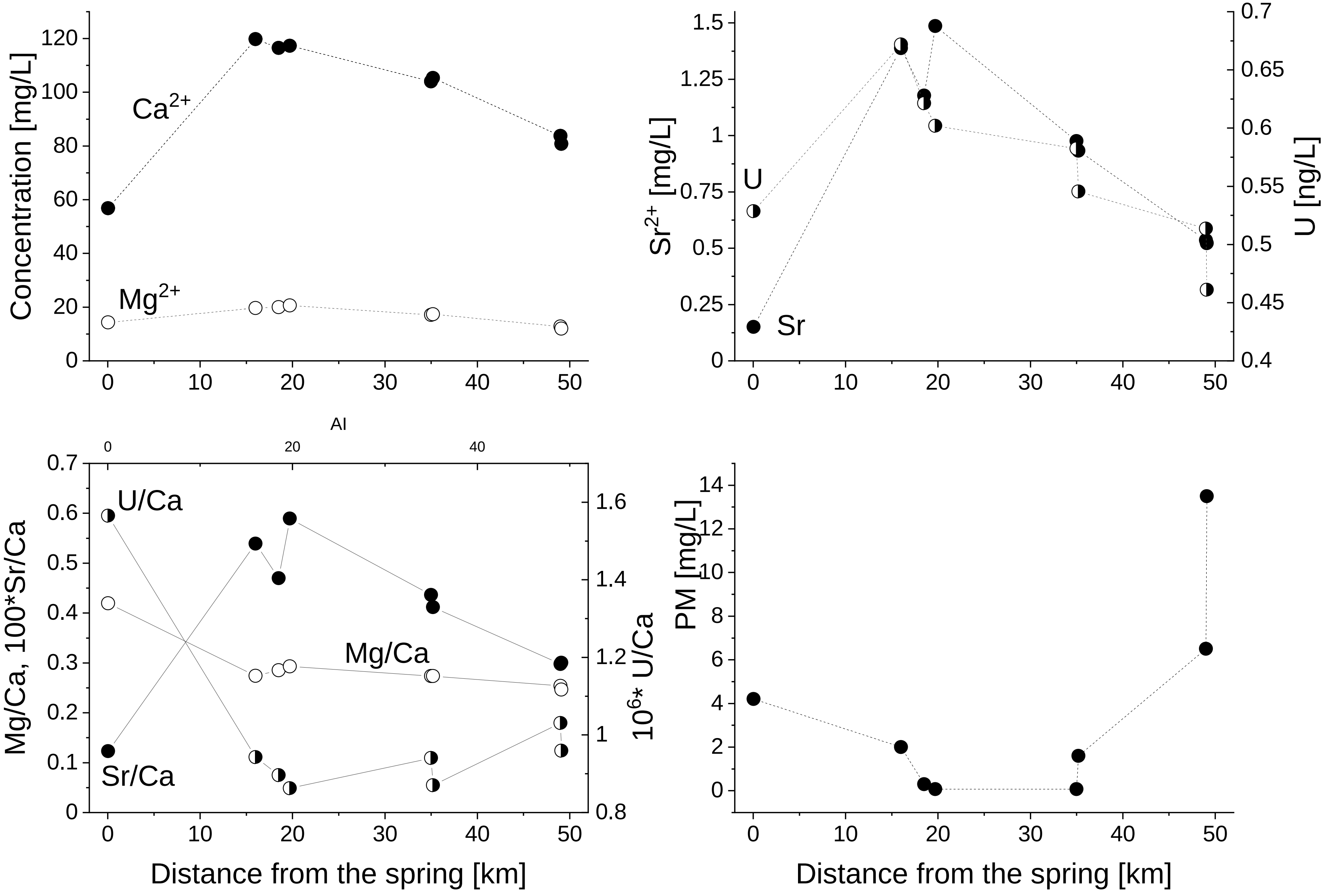
- **Bedrock, soil, tufa**

  - **Bulk CaO, MgO, SrO, SiO_2, Fe_2O_3, Al_2O_3, U, $^{234/238}U$, $\delta^{88}Sr$, $\delta^{26}Mg$ $\delta^{18}O$, $\delta^{13}C$**

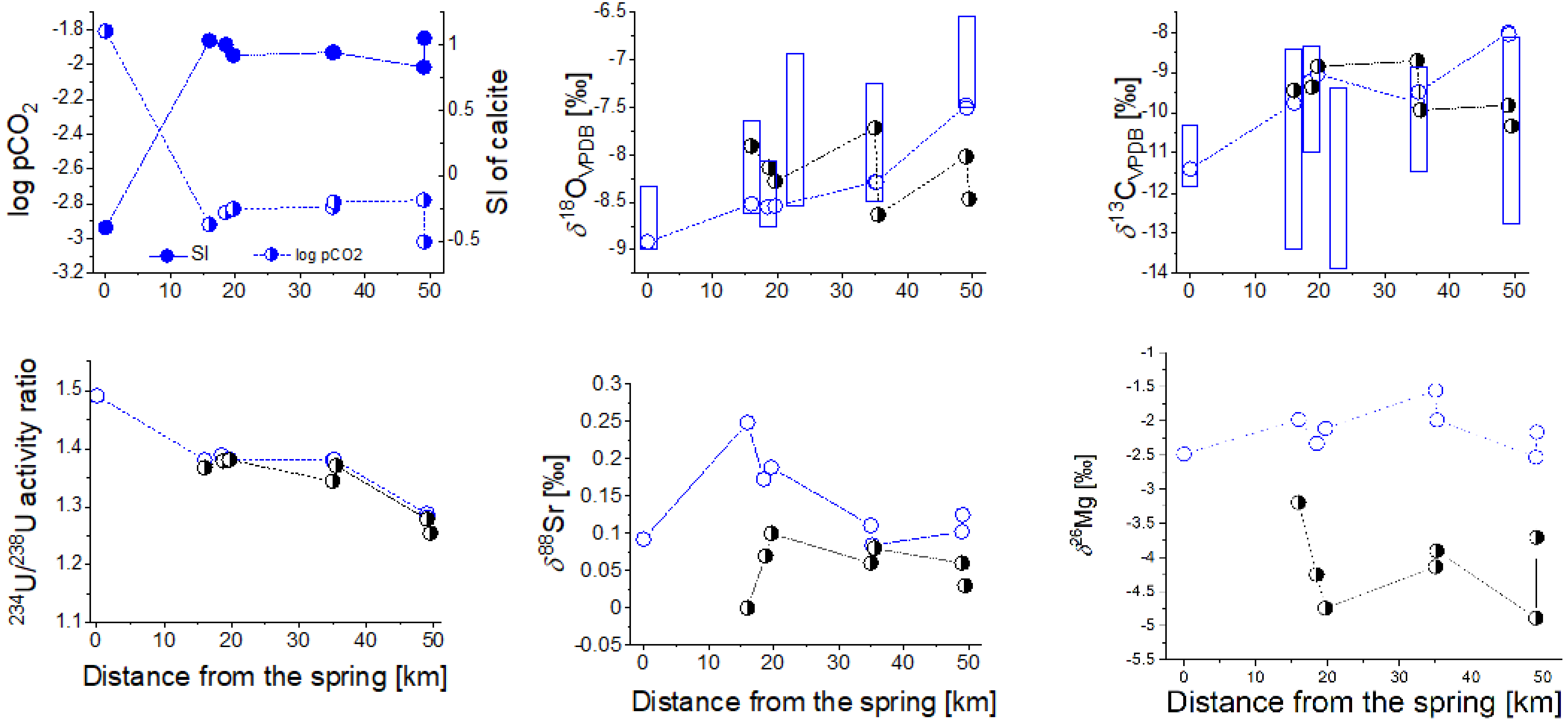
  - **Leaching (NaAc + Hac at pH = 5): Ca, Mg, Sr, U, $^{234/238}U$, $\delta^{88}Sr$, $\delta^{26}Mg$**

  - **XRF, XRD**

Water



Concentration [mg/L]
Ca2+
Mg2+
Sr2+ [mg/L]
U [ng/L]
U
Sr
Al
Mg/Ca, 100*Sr/Ca
10^6* U/Ca
U/Ca
Mg/Ca
Sr/Ca
PM [mg/L]
Distance from the spring [km]
Distance from the spring [km]

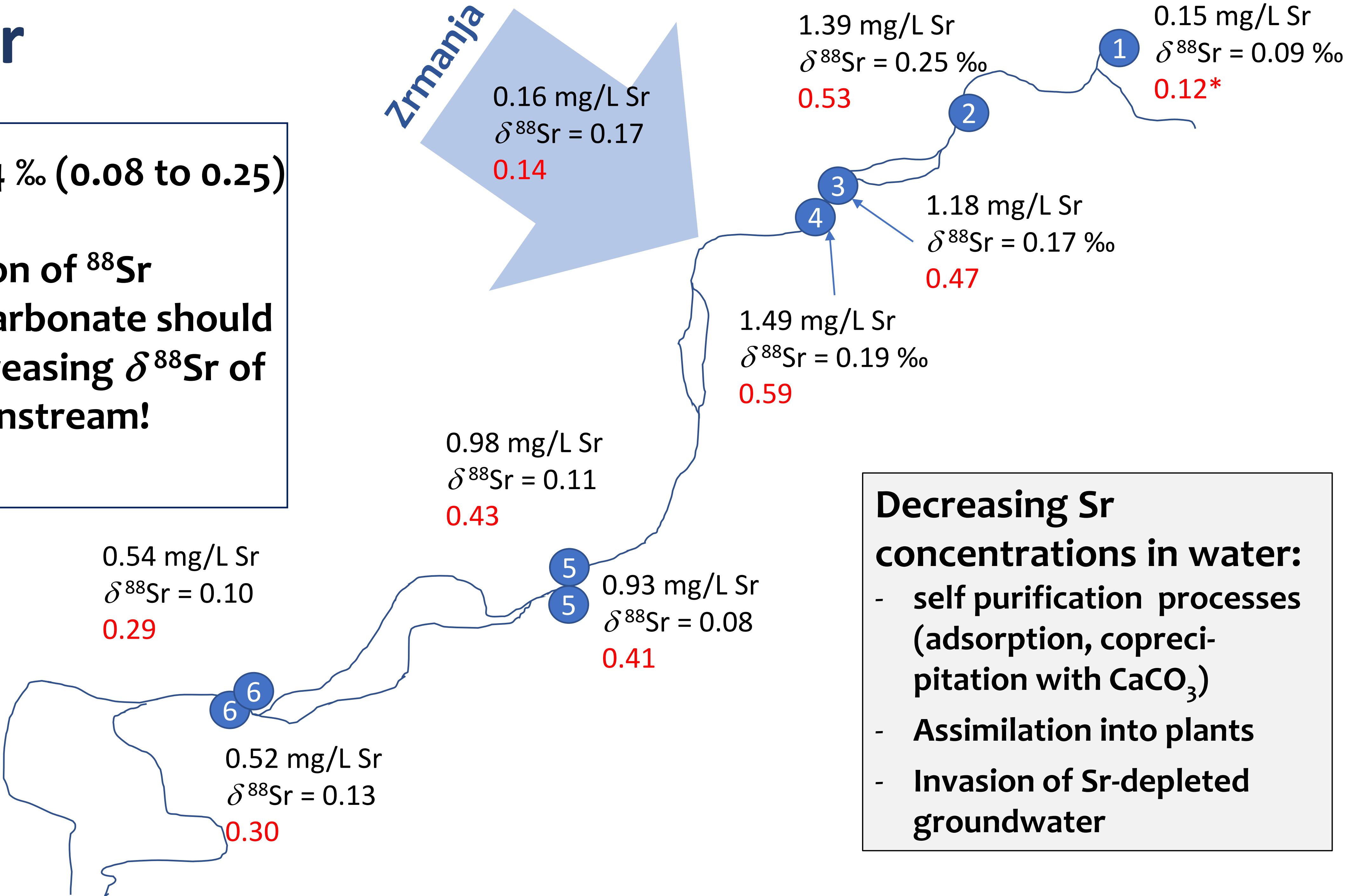


Blue symbols: water; black symbols: tufa, leachable fraction

Water

$\delta^{88}Sr$ = 0.14 ‰ (0.08 to 0.25)

Precipitation of ^{88}Sr depleted carbonate should lead to increasing $\delta^{88}Sr$ of water downstream!

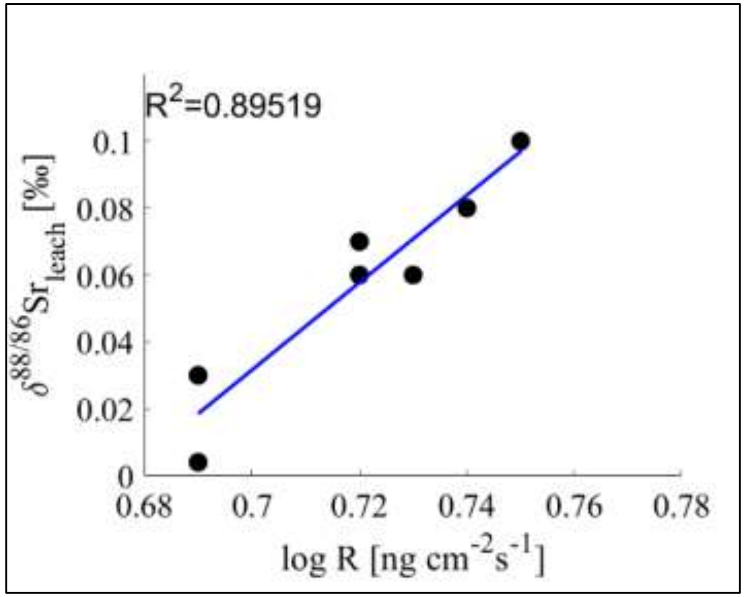


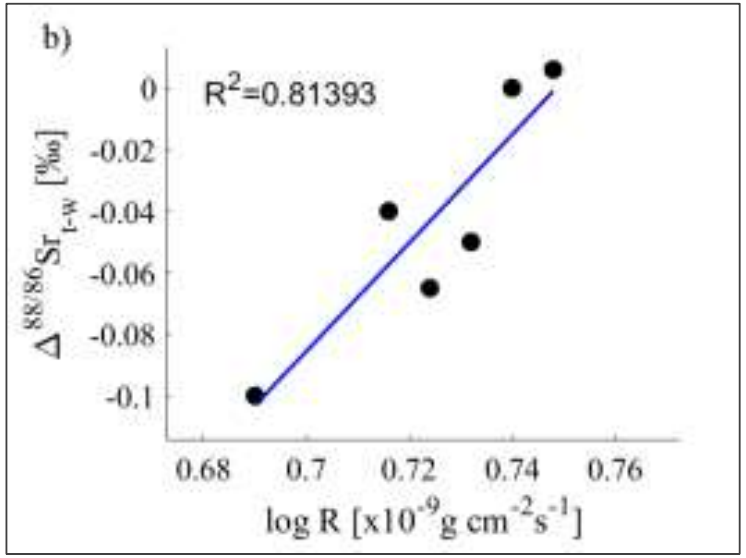
Decreasing Sr concentrations in water:

- **self purification processes (adsorption, copreci-pitation with $CaCO_3$)**
- **Assimilation into plants**
- **Invasion of Sr-depleted groundwater**

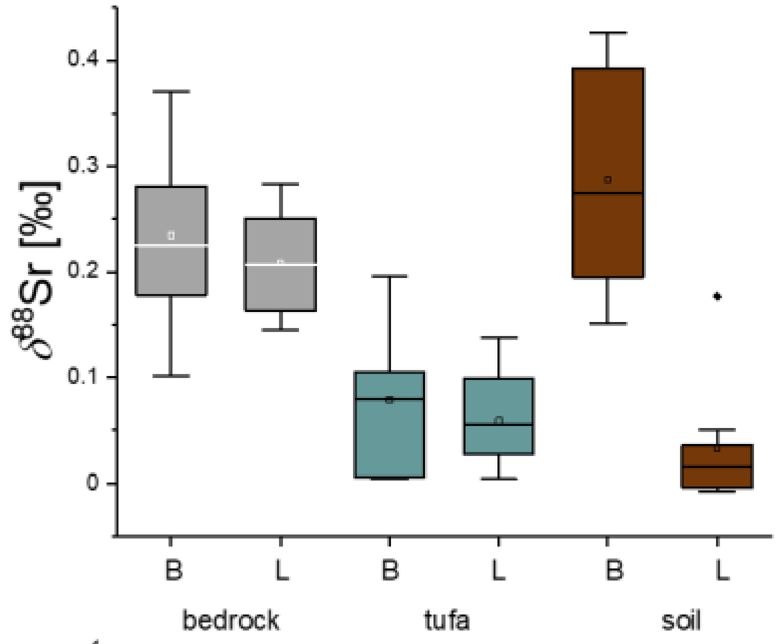
(*100 x Sr/Ca)

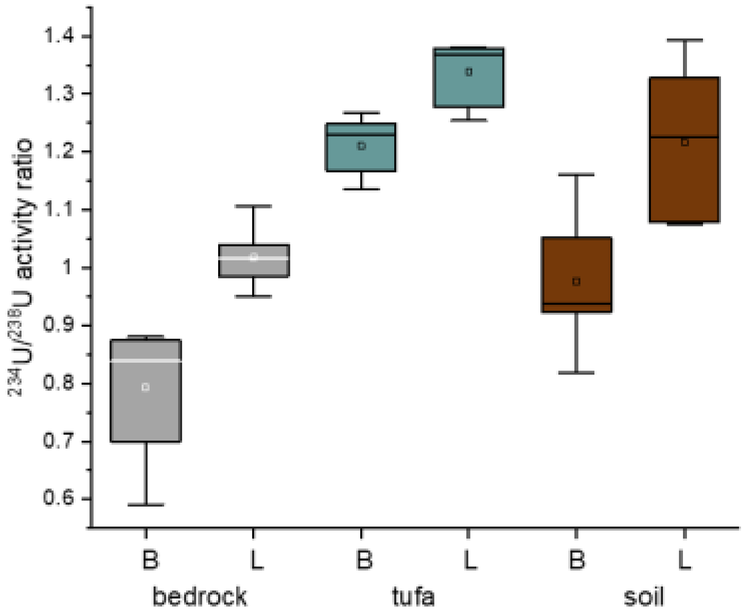
- Downstream increasing U/Ca trend is consistent with tufa precipitation, while the Mg/Ca and Sr/Ca ratios are insonsistent with tufa precipitation – most probably related to the hydrological situation
- 234/238U activity ratio of water and of authienic carbonate match along the entire stream flow
- δ^{88}Sr values of leachable fraction of tufa are lower than those of dissolved Sr by 0.00 to 0.25 ‰, while the δ^{26}Mg values leachable tufa fraction are lower by 1.22 to 2.63 ‰ comapred to dissolved Mg
- Sr partitioning and isotope fractionation depend upon carbonate precipitation rate and to a lesser extrent to the temperture, while the Mg partitioning depends on temperature, but seems to be unaffected by precipitation rate

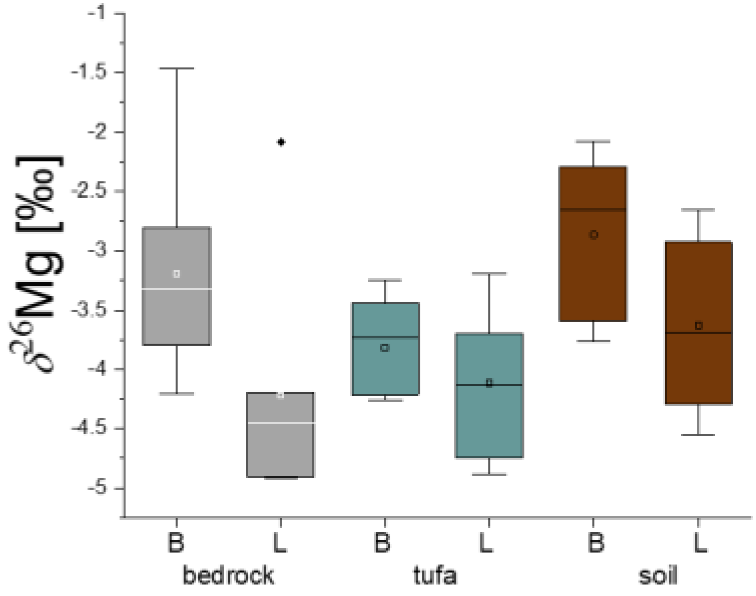




	$^{234/238}U$ [activity ratio]	$\delta^{88}Sr$ [‰]	$\delta^{26}Mg$ [‰]
water	1.28 - 1.39	0.09 - 0.25	-2.53 to -1.55
bedrock-bulk	0.60 - 0.87	0.10 - 0.37	-4.20 to -1.50
bedrock - leach	0.95 - 1.11	0.14 - 0.20	-4.91 to -2.09
soil - bulk	0.82 - 1.12	0.15 - 0.43	-3.8 to -2.1
soil-leach	1.08 - 1.39	-0.01 - 0.18	-4.55 to -2.66
tufa-bulk	1.14 - 1.22	0.00 - 0.19	-4.26 to -3.25
tufa - leach	1.28 - 1.39	0.00 - 0.14	-4.88 to -3.196







The most feasible combinations of sources of carbonate in tufa barriers estimated using the IsoSource mixing model for partitioning an excess number of sources (EPA)

	Authigenic		Soil-derived		Bedrock-deived	
	$^{234/238}U$	$\delta^{88}Sr$	$^{234/238}U$	$\delta^{88}Sr$	$^{234/238}U$	$\delta^{88}Sr$
K2	80	80	13	12	7	8
K3	82	82	11	11	7	7
K4	83	81	12	14	5	5
K5A	81	77	13	18	6	6
K5B	69	73	18	19	13	8
K6A	66	72	22	18	12	10
K6B	61	69	28	20	11	11

CO_2 accumulation rate in tufa based on calcite precipitation rate and Sr isotope data

Precipitation rate estimated using the diffusion boundary layer (DBL) model (Liu & Dreybrodt 1997) considering the DBL thickness of 50 µm for turbulent conditions and a thickness of water layer at the cascade of 10 cm

$$R_{calc} = \alpha \cdot ([Ca^{2+}] - [Ca^{2+}]_{eq})$$

Site	**Precipitation rate [g m^{-2} yr^{-1}]**	**Waterfall area [m^2]**	**Annual CO_2 storage [tonnes]**
K2	1540	530	0.36
K3	1670	4800	3.54
K4	1760	6300	4.86
K5	1720	105000	79.4
K6	1580	123000	85.5

7.2 t/ha

Instead of conclusions:

Are isotopes of Mg, Sr and U in fluvial sediments identifiers of authigenic carbonate?

Yes (U) / at least to a certain extent (Sr) /not really in this case (Mg)

Several environmental factors affect the metal distribution, partition and isotope fractionation, in particular hydrogeological situation, precipitation rate, biological („vital“) effects, seasonality (temperarutre, turbulence and related effects)