U and Sr in recent and interglacial tufa in Krka National park (Croatia)

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Questions and Challenges

- Terrestrial authigenic carbonate can be a potent, but highly dispersed CO_2 sink – how to quantify it?

- Moreover - how to identify authigenic carbonate in terrestrial settings, where multiple carbon sources with overlapping isotope compositions and multiple processes that fractionate C isotopes in opposite ways can operate simultaneously? Or in sediments, where both detrital and authigenic carbonate occur?

- New identifiers of authigenic carbonate have to be established - non-traditional isotopes seem to be and obvious choice; but can we rely on them?

Challeges:
- How do $\delta^{88}Sr$, $\delta^{238}U$ values and $^{234/238}U$ activity ratios in water and tufa behave downstream the river and during precipitation of tufa?
- What information can be obtained from isotope compositions of Sr and U – conditions of precipitation of carbonate or hydrology or both?
- Can we quantify the amount of authigenic carbonate in tufa based on Sr and U isotope composition of carbonate?

Some background on Sr and U isotopes in rivers

- Concentration and isotope composition of Sr and U in river water and river carbonate (tufa) depend upon the lithology of the catchment, hydrological situation and climate

- Sr and U in tufa occur in detrital mineral phases, in organic matter and in authigenic carbonate – precipitation of authigenic carbonate fractionates $^{88/86}$Sr, while U isotope ratios in carbonate ressemble those of the dissolved U in the precipitating water

- The δ^{88}Sr value behaves conervatively during water mass mixing and stream transport, but changes by about 0.2 ‰ during carbonate precipitation

- The δ^{238}U value of dissolved U depends upon redox conditions in the solution; U isotope ratios can change during adsorption and co-precipitation
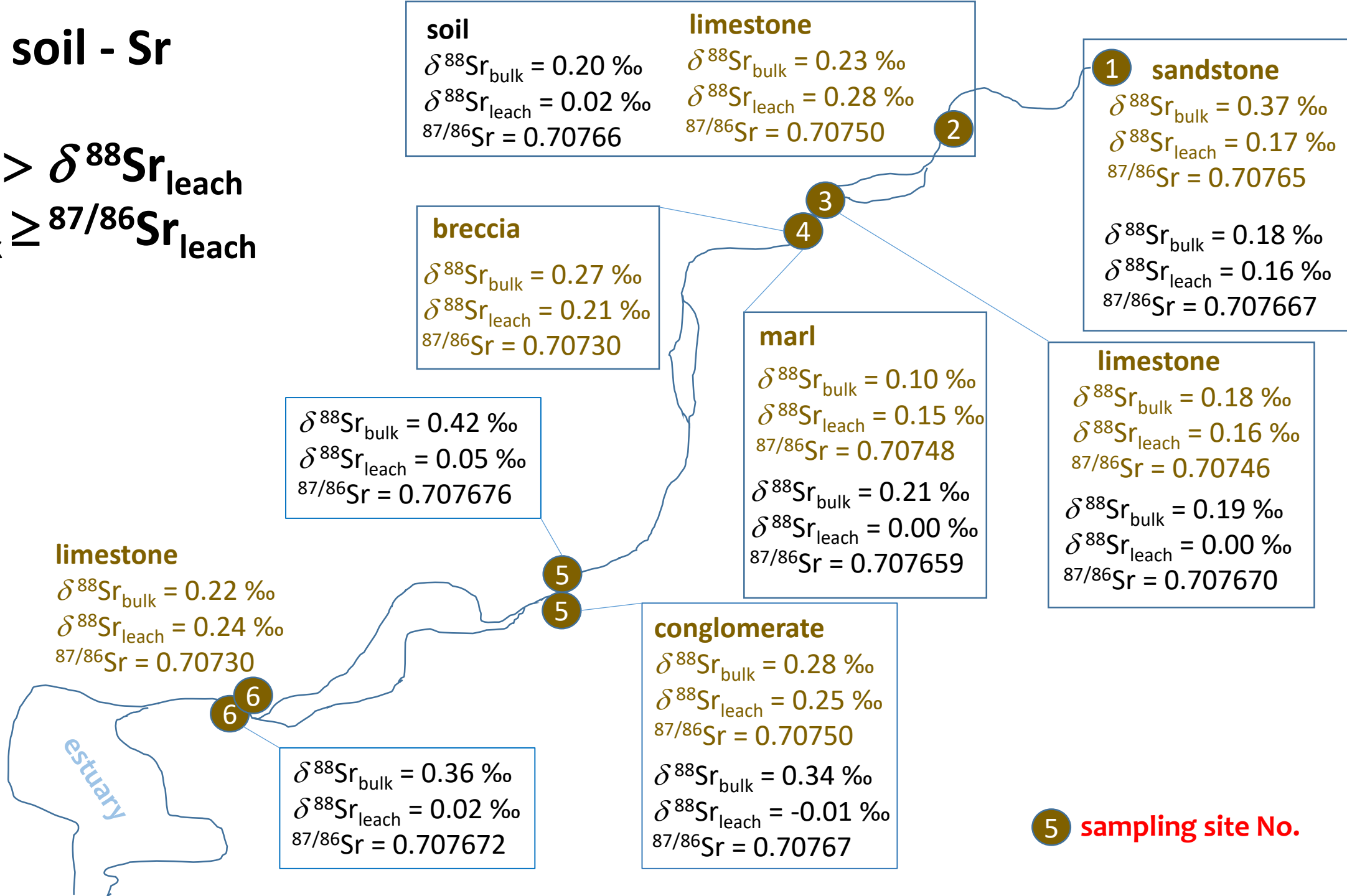
Sampling area
(September 2019)
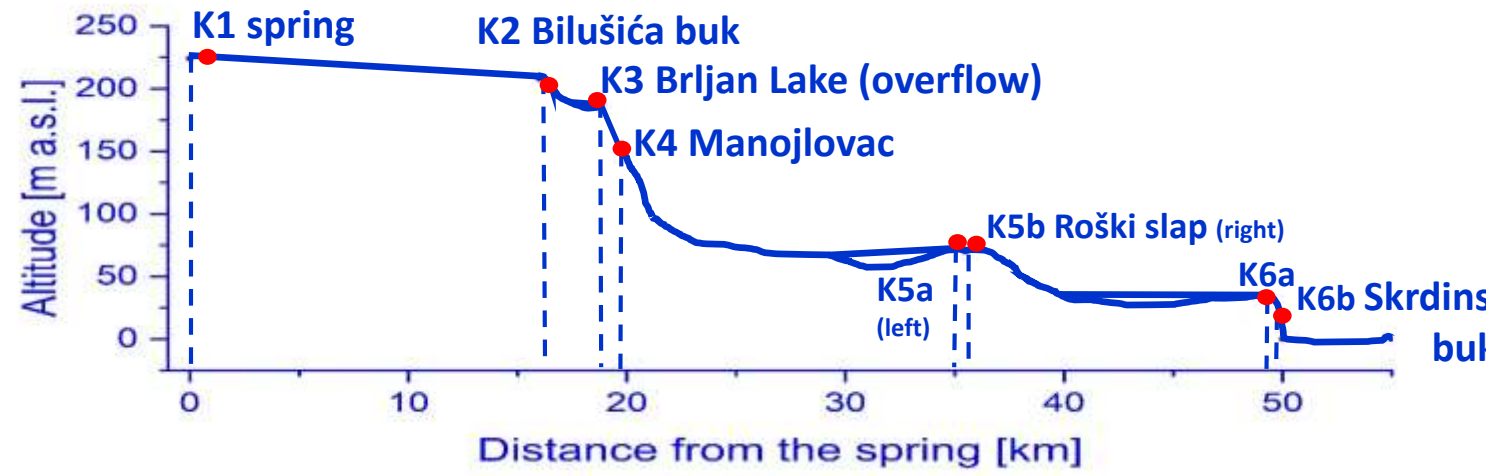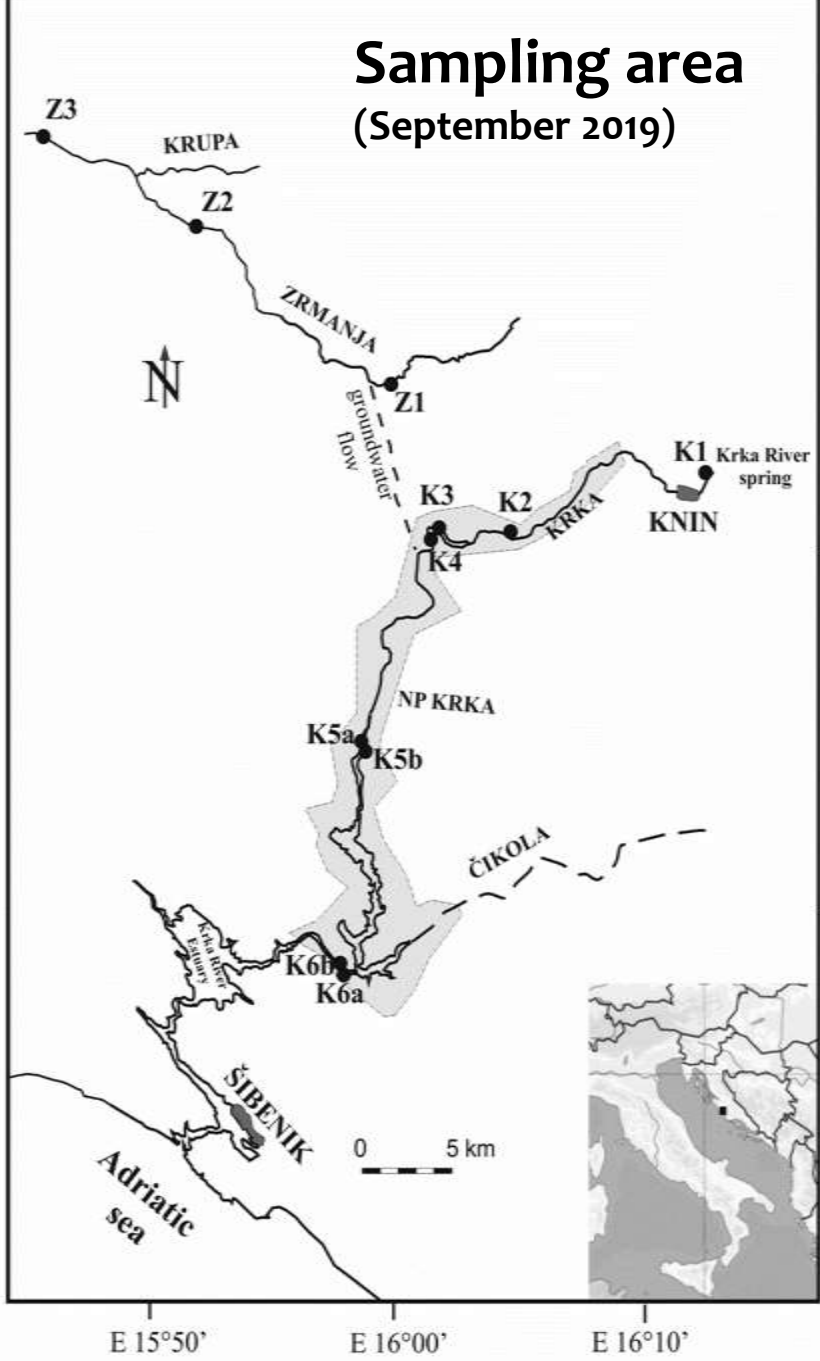
Analyses

- Water: T, pH, Eh, T, Ca^{2+}, Mg^{2+}, Sr^{2+}, U, $\delta^{238}U$, $^{234/234}U$ activity ratio, $\delta^{88}Sr$, $^{87}Sr/^{86}Sr$, $\delta^{18}O$, $\delta^{13}C$-DIC

- Bedrock, soil, tufa

  - Bulk CaO, MgO, SrO, SiO_2, Fe_2O_3, Al_2O_3, U, $\delta^{238}U$, $^{234/234}U$ activity ratio , $\delta^{88}Sr$, $^{87}Sr/^{86}Sr$, $\delta^{18}O$, $\delta^{13}C$

  - Leachate (NaAc + Hac at pH = 5): Ca, Mg, Sr, U, $\delta^{88}Sr$, $^{87}Sr/^{86}Sr$, $\delta^{238}U$, $^{234/234}U$ activity ratio

  - XRD

Soft leaching eluted calcite-bound Sr and U, hydroxide-bound Sr and U and some dolomite (found only in tufa at K2 (1.5 %) and K5a (0.1 %))

Bedrock, soil - Sr

$$\delta^{88}Sr_{bulk} > \delta^{88}Sr_{leach}$$
$$^{87/86}Sr_{bulk} \geq\, ^{87/86}Sr_{leach}$$

soil
$\delta^{88}Sr_{bulk}$ = 0.20 ‰
$\delta^{88}Sr_{leach}$ = 0.02 ‰
$^{87/86}Sr$ = 0.70766

limestone
$\delta^{88}Sr_{bulk}$ = 0.23 ‰
$\delta^{88}Sr_{leach}$ = 0.28 ‰
$^{87/86}Sr$ = 0.70750

① sandstone
$\delta^{88}Sr_{bulk}$ = 0.37 ‰
$\delta^{88}Sr_{leach}$ = 0.17 ‰
$^{87/86}Sr$ = 0.70765

$\delta^{88}Sr_{bulk}$ = 0.18 ‰
$\delta^{88}Sr_{leach}$ = 0.16 ‰
$^{87/86}Sr$ = 0.707667

breccia
$\delta^{88}Sr_{bulk}$ = 0.27 ‰
$\delta^{88}Sr_{leach}$ = 0.21 ‰
$^{87/86}Sr$ = 0.70730

marl
$\delta^{88}Sr_{bulk}$ = 0.10 ‰
$\delta^{88}Sr_{leach}$ = 0.15 ‰
$^{87/86}Sr$ = 0.70748

$\delta^{88}Sr_{bulk}$ = 0.21 ‰
$\delta^{88}Sr_{leach}$ = 0.00 ‰
$^{87/86}Sr$ = 0.707659

limestone
$\delta^{88}Sr_{bulk}$ = 0.18 ‰
$\delta^{88}Sr_{leach}$ = 0.16 ‰
$^{87/86}Sr$ = 0.70746

$\delta^{88}Sr_{bulk}$ = 0.19 ‰
$\delta^{88}Sr_{leach}$ = 0.00 ‰
$^{87/86}Sr$ = 0.707670

$\delta^{88}Sr_{bulk}$ = 0.42 ‰
$\delta^{88}Sr_{leach}$ = 0.05 ‰
$^{87/86}Sr$ = 0.707676

limestone
$\delta^{88}Sr_{bulk}$ = 0.22 ‰
$\delta^{88}Sr_{leach}$ = 0.24 ‰
$^{87/86}Sr$ = 0.70730

conglomerate
$\delta^{88}Sr_{bulk}$ = 0.28 ‰
$\delta^{88}Sr_{leach}$ = 0.25 ‰
$^{87/86}Sr$ = 0.70750

$\delta^{88}Sr_{bulk}$ = 0.34 ‰
$\delta^{88}Sr_{leach}$ = -0.01 ‰
$^{87/86}Sr$ = 0.70767

$\delta^{88}Sr_{bulk}$ = 0.36 ‰
$\delta^{88}Sr_{leach}$ = 0.02 ‰
$^{87/86}Sr$ = 0.707672

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⑤ sampling site No.

Bedrock, soil - U

- Soil is enriched in total U and ^{234}U compared to the bedrock
- Leachable fractions of soil and bedrock are enriched in ^{234}U compared to bulk samples
- $^{234/238}$U is similar in bulk soil and bedrock, while leachable fraction of soil is considerably enriched in ^{234}U comapred to leachable bedrock fraction
- δ^{238}U values between -0.78 and -0.06 ‰

soil

$\delta^{238}U_{bulk}$ = -0.15 ‰
$\delta^{238}U_{leach}$ = -0.06 ‰
$^{234/238}U_{bulk}$ = 0.12
$^{234/238}U_{leach}$ = 1.39

② limestone

$\delta^{238}U_{bulk}$ = -0.23 ‰
$\delta^{238}U_{leach}$ = -0.13 ‰
$^{234/238}U_{bulk}$ = 1.11
$^{234/238}U_{leach}$ = 1.12

① sandstone

$\delta^{238}U_{bulk}$ = -0.14 ‰
$\delta^{238}U_{leach}$ = -0.21 ‰
$^{234/238}U_{bulk}$ = 0.98
$^{234/238}U_{leach}$ = 1.02

$\delta^{238}U_{bulk}$ = -0.27 ‰
$\delta^{238}U_{leach}$ = -0.19 ‰
$^{234/238}U_{bulk}$ = 0.95
$^{234/238}U_{leach}$ = 1.08

④ breccia

$\delta^{238}U_{bulk}$ = -0.35 ‰
$\delta^{238}U_{leach}$ = -0.48 ‰
$^{234/238}U_{bulk}$ = 1.04
$^{234/238}U_{leach}$ = 1.05

④ marl

$\delta^{238}U_{bulk}$ = -0.17 ‰
$\delta^{88}Sr_{leach}$ -0.78 ‰
$^{234/238}U_{bulk}$ = 0.95
$^{234/238}U_{leach}$ = 1.06

$\delta^{238}U_{bulk}$ = -0.39 ‰
$\delta^{238}U_{leach}$ = -0.51 ‰
$^{234/238}U_{bulk}$ = 1.16
$^{234/238}U_{leach}$ = 1.38

$\delta^{238}U_{bulk}$ = -0.45 ‰
$\delta^{238}U_{leach}$ = -0.15 ‰
$^{234/238}U_{bulk}$ = -0.56
$^{234/238}U_{leach}$ = 1.08

③ limestone

$\delta^{238}U_{bulk}$ = -0.13 ‰
$\delta^{238}U_{leach}$ = -0.15 ‰
$^{234/238}U_{bulk}$ = 1.03
$^{234/238}U_{leach}$ = 1.04

$\delta^{238}U_{bulk}$ = -0.26 ‰
$\delta^{238}U_{leach}$ = -0.06 ‰
$^{234/238}U_{bulk}$ = 0.92
$^{234/238}U_{leach}$ = 1.28

⑥ limestone

$\delta^{238}U_{bulk}$ = -0.29 ‰
$\delta^{238}U_{leach}$ = -0.41 ‰
$^{234/238}U_{bulk}$ = 1.00
$^{234/238}U_{leach}$ = 1.01

$\delta^{238}U_{bulk}$ = -0.43 ‰
$\delta^{238}U_{leach}$ = -0.03 ‰
$^{234/238}U_{bulk}$ = 0.99
$^{234/238}U_{leach}$ = 1.23

conglomerate

$\delta^{238}U_{bulk}$ = -0.40 ‰
$\delta^{238}U_{leach}$ = -0.11 ‰
$^{234/238}U_{bulk}$ = 1.02
$^{234/238}U_{leach}$ = 1.02

$\delta^{238}U_{bulk}$ = -0.39 ‰
$\delta^{238}U_{leach}$ = -0.56 ‰
$^{234/238}U_{bulk}$ = 0.93
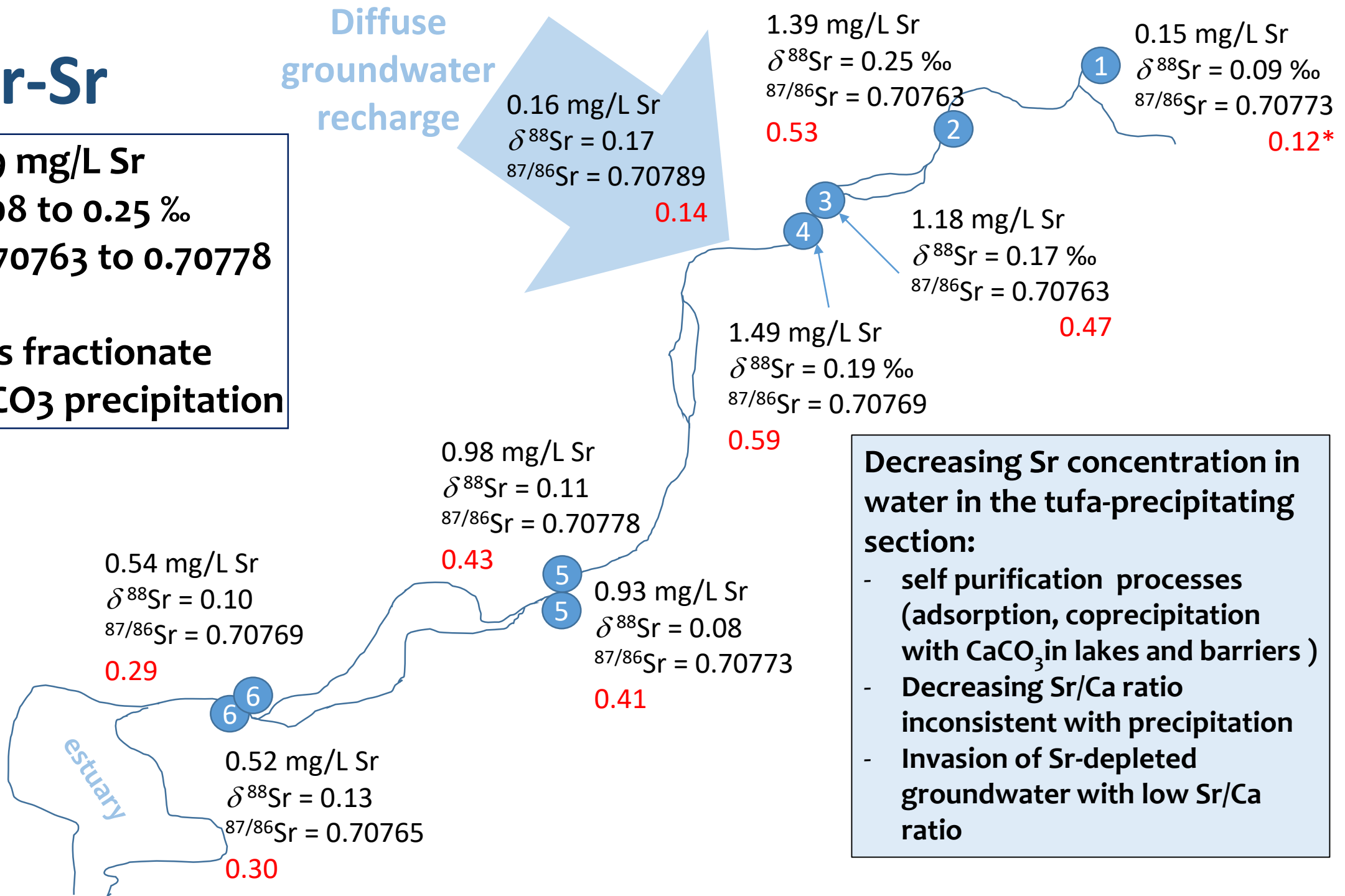$^{234/238}U_{leach}$ = 1.22

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$^{234/238}$U = activity ratio

Water-Sr

0.15 to 1.49 mg/L Sr
$\delta^{88}Sr$ = 0.08 to 0.25 ‰
$^{87/86}Sr$ = 0.70763 to 0.70778

Sr isotopes fractionate during CaCO3 precipitation

Diffuse groundwater recharge

0.15 mg/L Sr
$\delta^{88}Sr$ = 0.09 ‰
$^{87/86}Sr$ = 0.70773
0.12*

1.39 mg/L Sr
$\delta^{88}Sr$ = 0.25 ‰
$^{87/86}Sr$ = 0.70763
0.53

0.16 mg/L Sr
$\delta^{88}Sr$ = 0.17
$^{87/86}Sr$ = 0.70789
0.14

1.18 mg/L Sr
$\delta^{88}Sr$ = 0.17 ‰
$^{87/86}Sr$ = 0.70763
0.47

1.49 mg/L Sr
$\delta^{88}Sr$ = 0.19 ‰
$^{87/86}Sr$ = 0.70769
0.59

0.98 mg/L Sr
$\delta^{88}Sr$ = 0.11
$^{87/86}Sr$ = 0.70778
0.43

0.93 mg/L Sr
$\delta^{88}Sr$ = 0.08
$^{87/86}Sr$ = 0.70773
0.41

0.54 mg/L Sr
$\delta^{88}Sr$ = 0.10
$^{87/86}Sr$ = 0.70769
0.29

0.52 mg/L Sr
$\delta^{88}Sr$ = 0.13
$^{87/86}Sr$ = 0.70765
0.30

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Decreasing Sr concentration in water in the tufa-precipitating section:
- **self purification processes (adsorption, coprecipitation with $CaCO_3$ in lakes and barriers)**
- **Decreasing Sr/Ca ratio inconsistent with precipitation**
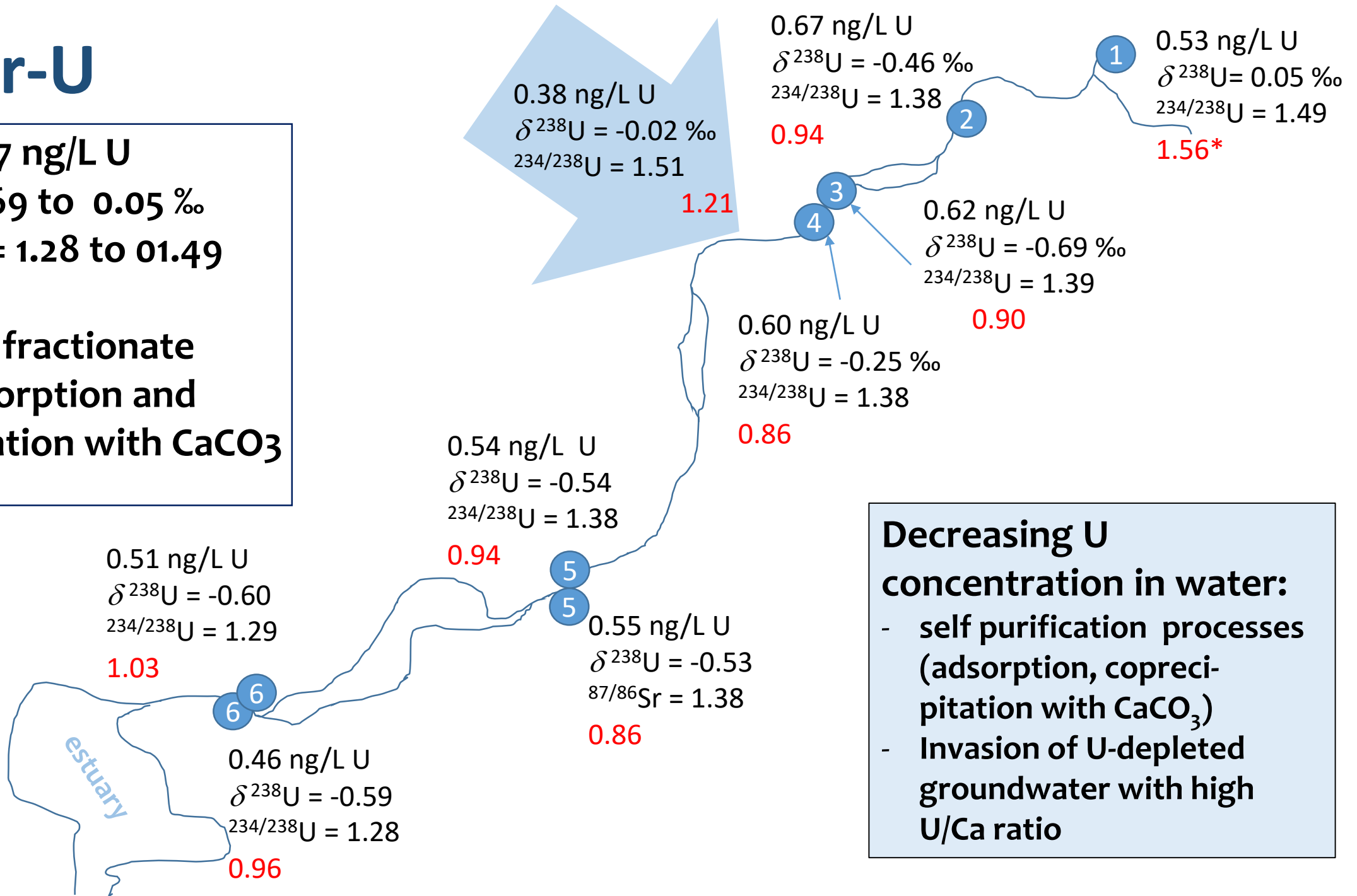- **Invasion of Sr-depleted groundwater with low Sr/Ca ratio**

(*100 x Sr/Ca)

Water-U

0.46 to 0.67 ng/L U
δ^{238}U = -0.69 to 0.05 ‰
$^{234/238}$Ua.r. = 1.28 to 01.49

U isotopes fractionate during adsorption and coprecipitation with CaCO3

0.53 ng/L U
δ^{238}U= 0.05 ‰
$^{234/238}$U = 1.49
1.56*

0.67 ng/L U
δ^{238}U = -0.46 ‰
$^{234/238}$U = 1.38
0.94

0.38 ng/L U
δ^{238}U = -0.02 ‰
$^{234/238}$U = 1.51
1.21

0.62 ng/L U
δ^{238}U = -0.69 ‰
$^{234/238}$U = 1.39
0.90

0.60 ng/L U
δ^{238}U = -0.25 ‰
$^{234/238}$U = 1.38
0.86

0.54 ng/L U
δ^{238}U = -0.54
$^{234/238}$U = 1.38
0.94

0.55 ng/L U
δ^{238}U = -0.53
$^{87/86}$Sr = 1.38
0.86

0.51 ng/L U
δ^{238}U = -0.60
$^{234/238}$U = 1.29
1.03

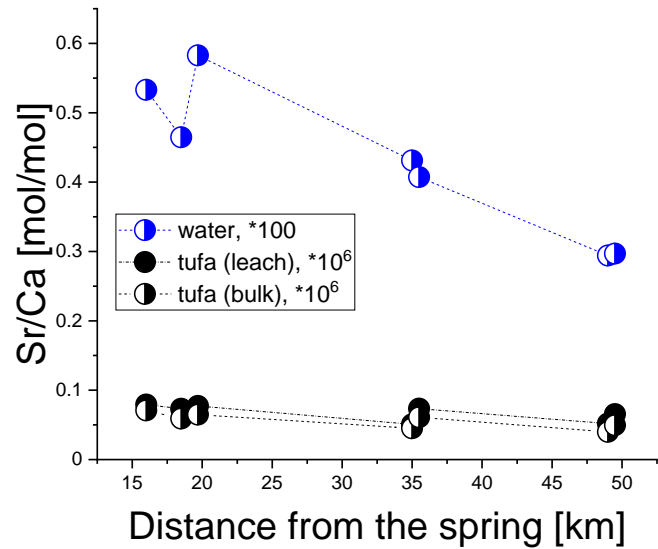0.46 ng/L U
δ^{238}U = -0.59
$^{234/238}$U = 1.28
0.96

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Decreasing U concentration in water:
- self purification processes (adsorption, copreci-pitation with $CaCO_3$)
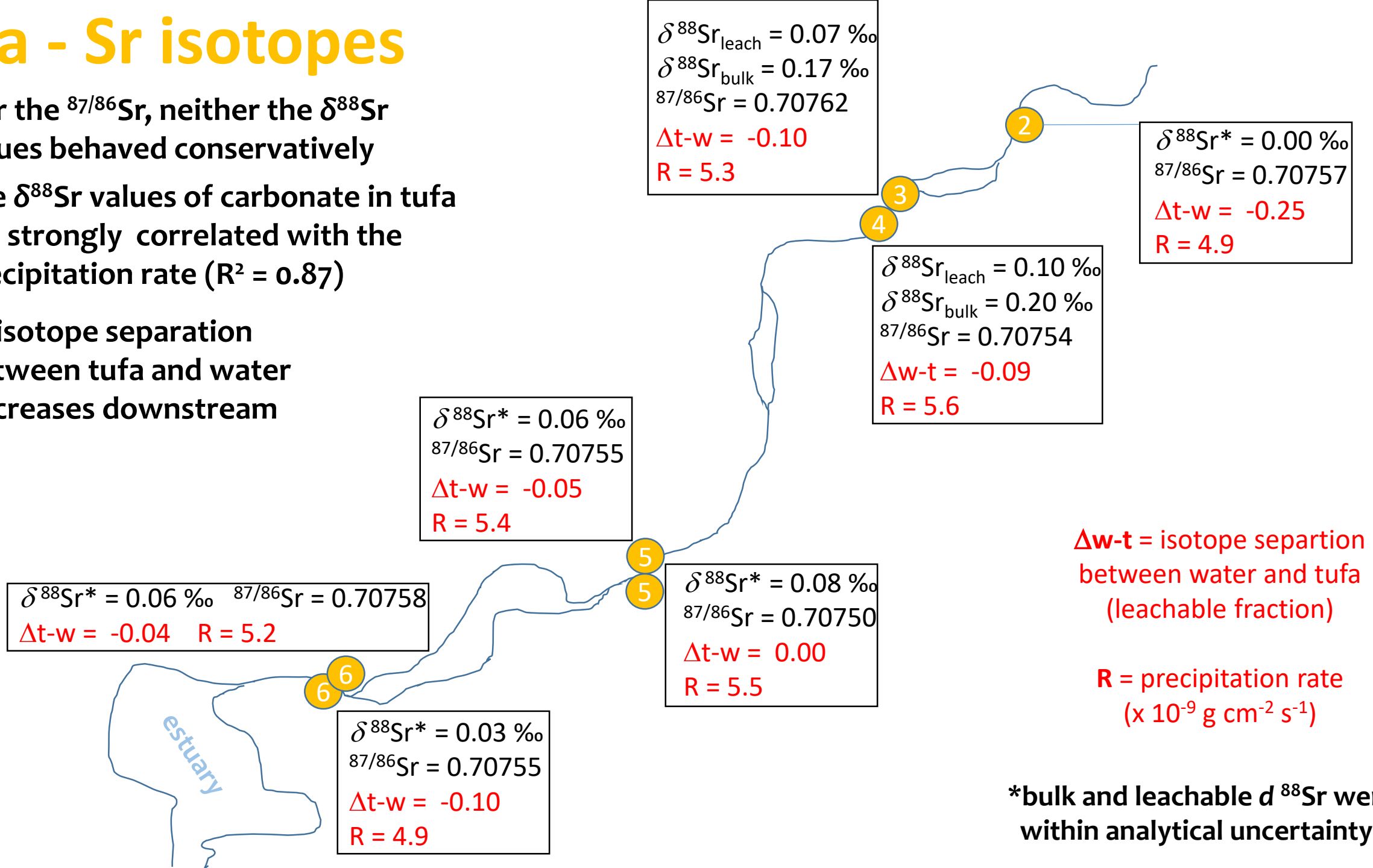- Invasion of U-depleted groundwater with high U/Ca ratio

(*10^6 U/Ca)

Water and leachable fraction of tufa
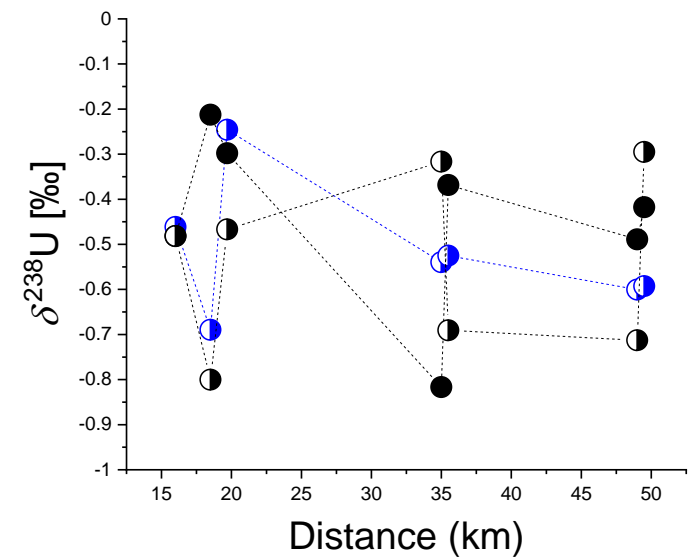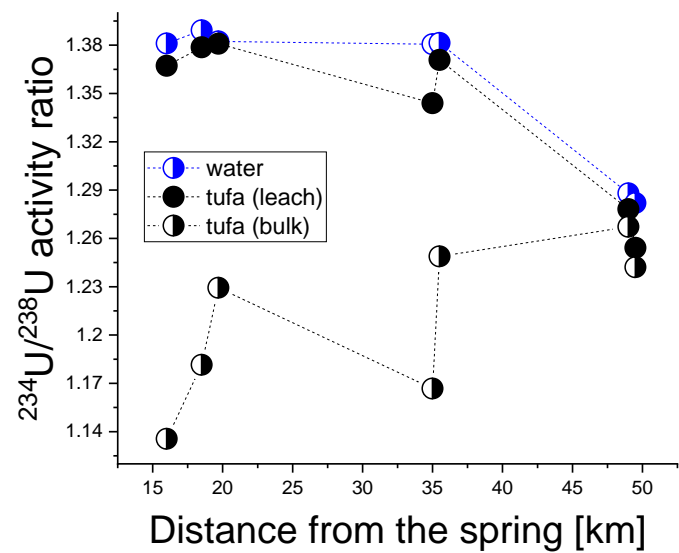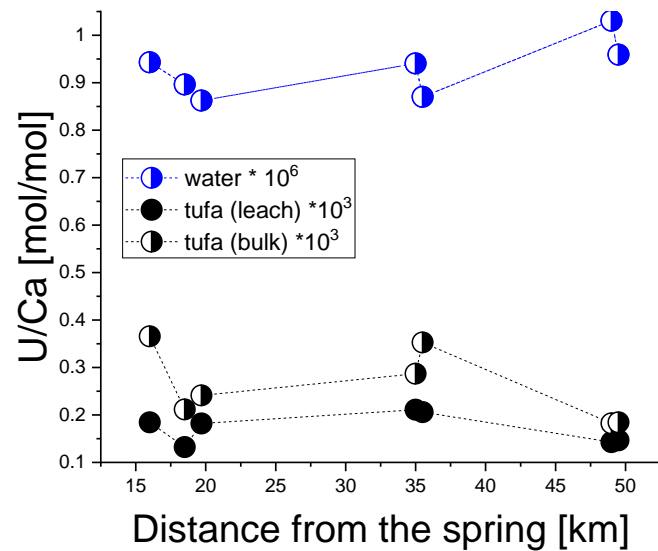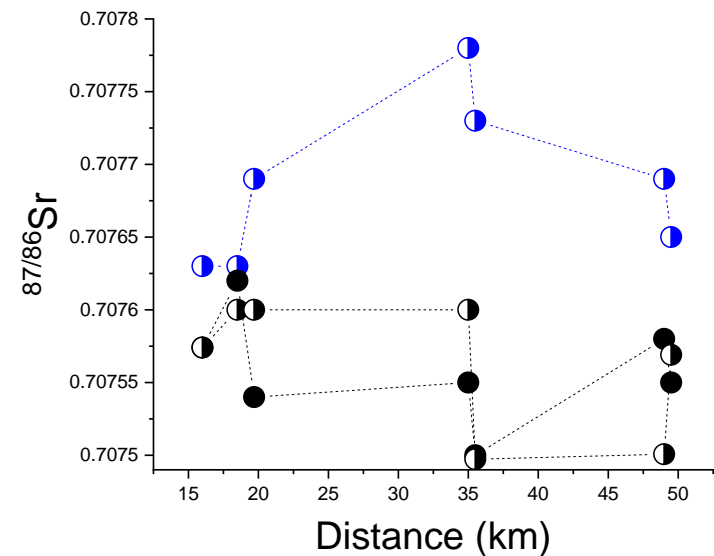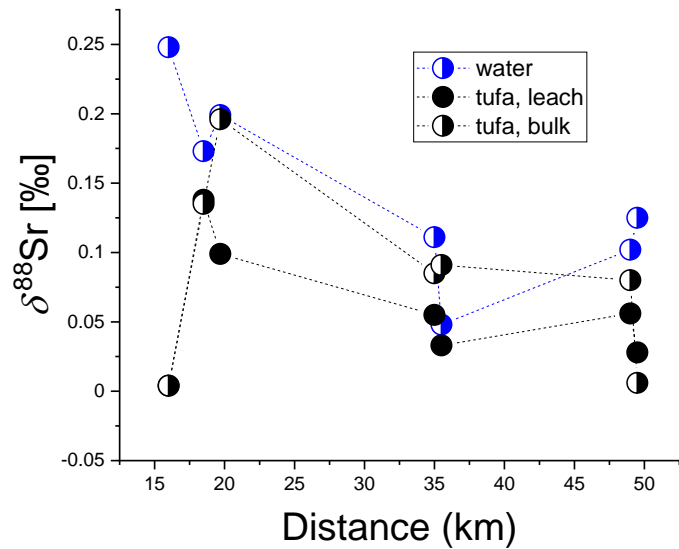
Tufa - Sr isotopes

- **Nor the $^{87/86}Sr$, neither the $\delta^{88}Sr$ values behaved conservatively**

- **The $\delta^{88}Sr$ values of carbonate in tufa are strongly correlated with the precipitation rate ($R^2 = 0.87$)**

- **Sr isotope separation between tufa and water decreases downstream**

$\delta^{88}Sr_{leach} = 0.07$ ‰
$\delta^{88}Sr_{bulk} = 0.17$ ‰
$^{87/86}Sr = 0.70762$
Δt-w = -0.10
R = 5.3

$\delta^{88}Sr* = 0.00$ ‰
$^{87/86}Sr = 0.70757$
Δt-w = -0.25
R = 4.9

$\delta^{88}Sr_{leach} = 0.10$ ‰
$\delta^{88}Sr_{bulk} = 0.20$ ‰
$^{87/86}Sr = 0.70754$
Δw-t = -0.09
R = 5.6

$\delta^{88}Sr* = 0.06$ ‰
$^{87/86}Sr = 0.70755$
Δt-w = -0.05
R = 5.4

$\delta^{88}Sr* = 0.08$ ‰
$^{87/86}Sr = 0.70750$
Δt-w = 0.00
R = 5.5

$\delta^{88}Sr* = 0.06$ ‰ $^{87/86}Sr = 0.70758$
Δt-w = -0.04   R = 5.2

$\delta^{88}Sr* = 0.03$ ‰
$^{87/86}Sr = 0.70755$
Δt-w = -0.10
R = 4.9

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Δ**w-t** = isotope separtion between water and tufa (leachable fraction)

R = precipitation rate (x 10^{-9} g cm^{-2} s^{-1})

*bulk and leachable *d* ^{88}Sr were within analytical uncertainty

Tufa - U isotopes

- $^{234/238}$U a.r. of tufa mostly ressemble that of water

- detrital carbonate can partly be discriminated from authigenic based upon the $^{234/238}$U activity ratio

- large scattering of δ^{238}U values

$\delta^{238}U_{bulk}$ = -0.80 ‰
$\delta^{238}U_{leach}$ = -0.21 ‰
Δt-w = 0.48
$^{234/238}U_{bulk}$ = 1.18
$^{234/238}U_{leach}$ = 1.38
Δw-t = -0.01

$\delta^{238}U_{bulk}$ = -0.48‰
$\delta^{238}U_{leach}$ = -0.48 ‰
Δt-w = -0.02
$^{234/238}U_{bulk}$ = 1.14
$^{234/238}U_{leach}$ = 1.37
Δw-t = -0.01

$\delta^{238}U_{bulk}$ = -0.32 ‰
$\delta^{238}U_{leach}$ = -0.82 ‰
Δt-w = -0.28
$^{234/238}U_{bulk}$ = 1.17
$^{234/238}U_{leach}$ = 1.34
Δw-t = -0.04

$\delta^{238}U_{bulk}$ = -0.47 ‰
$\delta^{238}U_{leach}$ = -0.30 ‰
Δw-t = -0.05
$^{234/238}U_{bulk}$ = 1.23
$^{234/238}U_{leach}$ = 1.38
Δw-t = 0.00

$\delta^{238}U_{bulk}$ = -0.71 ‰
$\delta^{238}U_{leach}$ = -0.49 ‰
Δt-w = 0.11
$^{234/238}U_{bulk}$ = 1.27
$^{234/238}U_{leach}$ = 1.28
Δw-t = -0.01

$\delta^{238}U_{bulk}$ = -0.69 ‰
$\delta^{238}U_{leach}$ = -0.67 ‰
Δt-w = 0.16
$^{234/238}U_{bulk}$ = 1.25
$^{234/238}U_{leach}$ = 1.37
Δw-t = -0.01

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$\delta^{238}U_{bulk}$ = -0.30 ‰
$\delta^{238}U_{leach}$ = -0.42 ‰
Δt-w = 0.18

$^{234/238}U_{bulk}$ = 1.24
$^{234/238}U_{leach}$ = 1.25
Δt-w = -0.03

Δ**w-t** = isotope separtion between tufa and water (leachable fraction)

Findings – recent tufa

- The Sr and U concentrations, as well as Sr/Ca and U/Ca ratios decrease downstream and are influenced by the diffuse recharge of the river from the Zrmanja river; decreasing Sr/Ca ratios indicate that the inflow of the Sr-poor water affect the Sr concentratins more than the co-precipitation with carbonate and sorption on mineral particles

- The diffuse discharge is not localized to the short section between 19 and 22 km downstream the spring as previously reported, but continues downstream to the head of the estuary

- The δ^{88}Sr values in river water were on the lower side, but within the reported range of the δ^{88}Sr values of world rivers (0.09 to 0.25 ‰); <u>seasonal variability was not determined</u>, but in a comparable karst river in Slovenia the seasonal range of δ^{88}Sr values of river water was within 0.11 to 0.23 ‰

- $^{234/238}$U activity ratios of water indicate relatively short mean water transit times in the aqiufer; $^{234/238}$U of tufa indicate the dominance of authigenic carbonate fraction, while detrital carbonate leached from soil and bedrock is present, too; source appointment using $^{234/238}$U activity ratios of water and leachable fractions of soil and bedrock gave results with large uncertainties . In upper reaches, 80-84 % of carbonate in tufa was authigenic, while in lower reches of the stream, only 41 – 61 % of carbonate were authigenic. Contributions of soil carbonate varied between 13 and 38 % and of the bedrock between 6 and 13 %

What about old tufa?

- Old Holocene tufa was collected a few m above the recent river bed at sites 2 and 4, while at site 5a a profile of Pleistocene tufa was sampled; reported ages were between 140.000 and 96.000 years B.P

- Holocene tufa was clearly district from interglacial samples regarding the C_{org}/N ratio, which was between 10 and 22 in recent tufa and 12 to 16 in old Holocene tufa just above the river, indicating the strong contribution of soil-derived organic matter and vascular plants; old tufa samples had C/N ratios between 3 and 10, which is attributed to diagenetical changes and changing origin of organic matter

- Pleistocene tufa had significantly higher $\delta^{18}O$ values than recent or Holocene samples, on average by about 0.5 ‰. $\delta^{13}C$ values of carbonate and organic matter in tufa were higher in Pleistocene samples, too; the diagenesis of organic matter most probalby affected the $\delta^{13}C_{org}$ values, while higher $\delta^{13}C_{carb}$ values reflect less biogenic dissolved inorganic carbon
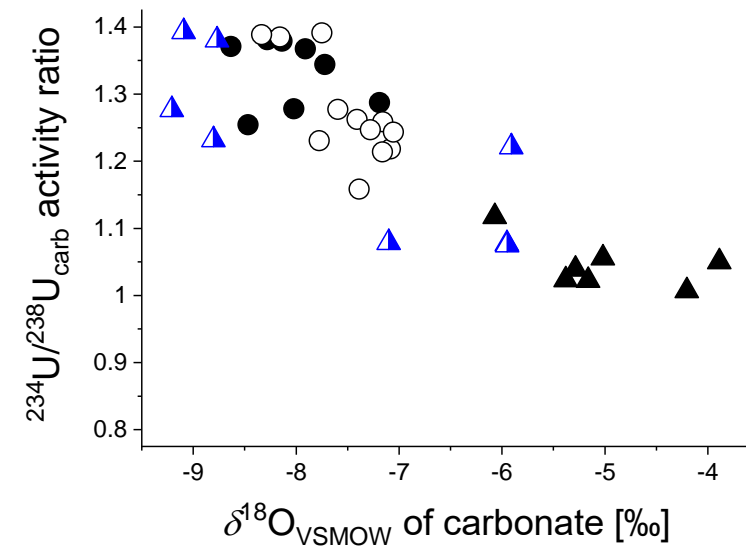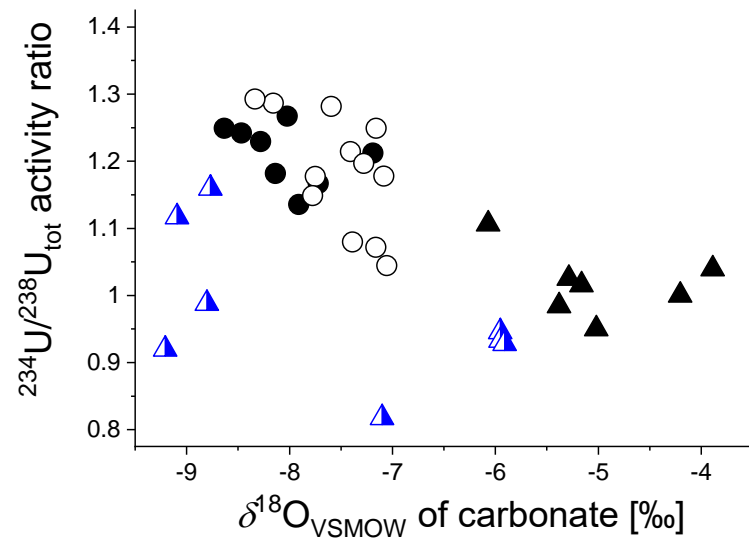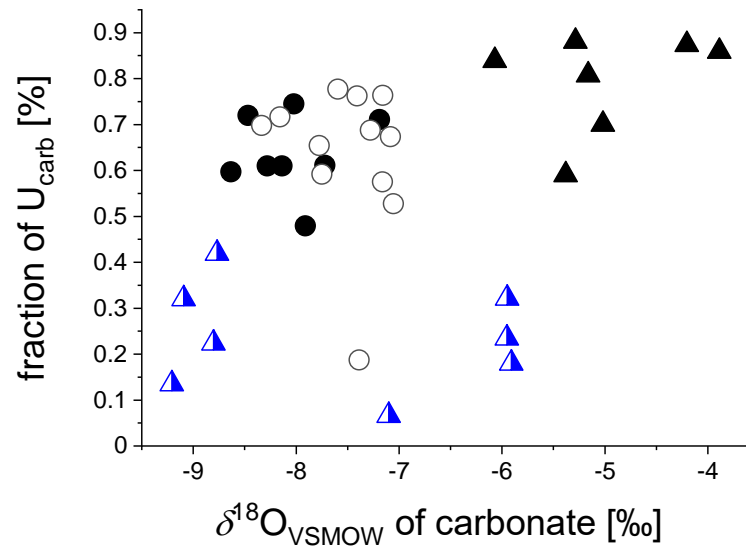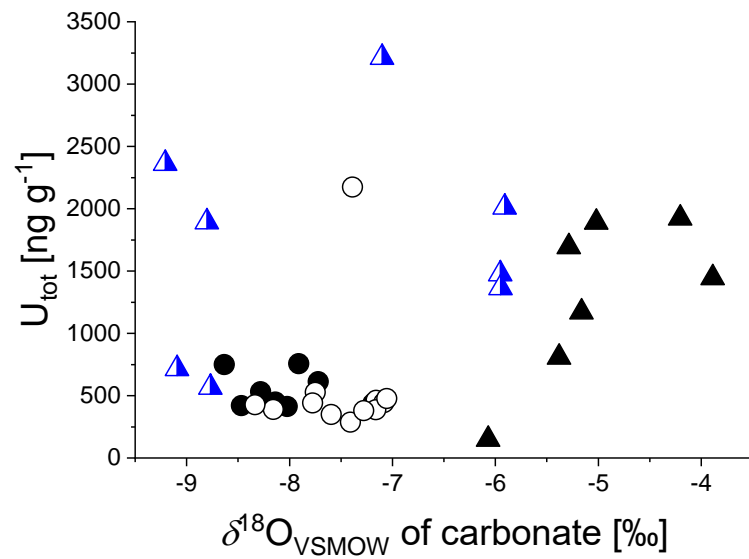
- Slightly higher $^{234/238}$U activity ratios were determined in bulk Pleistocene tufa than in recent samples , probably related to the differences in supply of detrital material

- In the Pleistocene tufa profile, slightly lower U/Ca and Sr/Ca ratios were recorded than in recnt tufa at the same site, HOWEVER, the depositional setting is completely different (cascade in Pleistocene, paludal recently)

- No significant differences were observed in the amount of non-carbonate phases in Pleistocene tufa compared to Holocene and recent samples, however, the higher Al/Si ratio in Pleistocene samples indicates some difference in the origin of detrital minerals, i.e. more alumosilicates in Pleistocene period

- U/Th ages of Pleistocene samples were determined between 20.000 and 90.000 years, but the results are obscured by diagenetical changes and the fact that some of the analysed samples were of secondary carbonate formation because of the long-term exposition of the tufa surface to the atmosphere

Acknowledgement

Sincere thanks to all of them!