Hydrogeochemical impact on the karst watershed of the Krka River in Slovenia interpreted by U and Th isotopic composition

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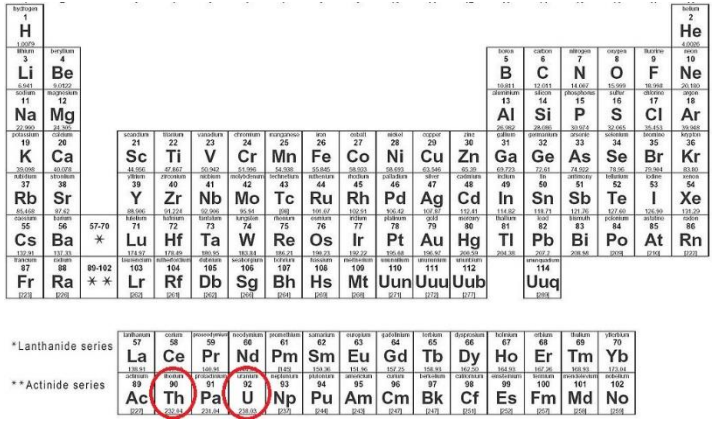
Main objective:

Use of U & Th isotopes as a complimentary tool to traditional geochemical parameters and stable isotopes.

Check possible U & Th fractionations in environment with predominantly carbonate lithology,

→ with the help of MC-ICP-MS.

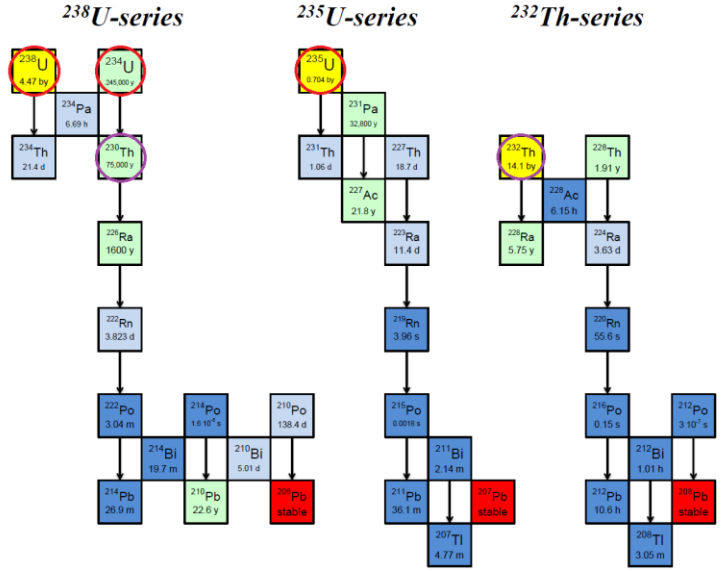
Uranium (U) & Thorium (Th)



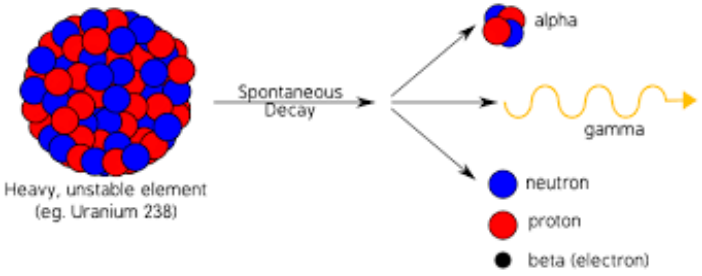
- Natural occurring radionuclides
- Oxidation states: U(VI) (soluble)
  U(IV) (insoluble)
  Th(IV) (insoluble)
- U & Th isotopes:

Characteristic	^{238}U	^{235}U	^{234}U	^{232}Th	^{230}Th
Half-life (years)	4.47×10^9	7.04×10^8	2.45×10^5	1.41×10^{10}	7.54×10^4
Natural abundance (%)	99.27	0.72	0.0054	99.82	0.02
Oxidation state	+4, +6	+4, +6	+4, +6	+4	+4

Radioactive decay chain series:



- Radioactive → unstable and decaying…



Reference: Internet

U & Th isotope fractionations in nature

- **$^{234}U/^{238}U$:**

→ Short-term chronometer & tracer of U mobility.

>10% from secular equilibrium

* Alpha recoil process

- **$^{238}U/^{235}U$:**

→ Studying redox variation in the past.

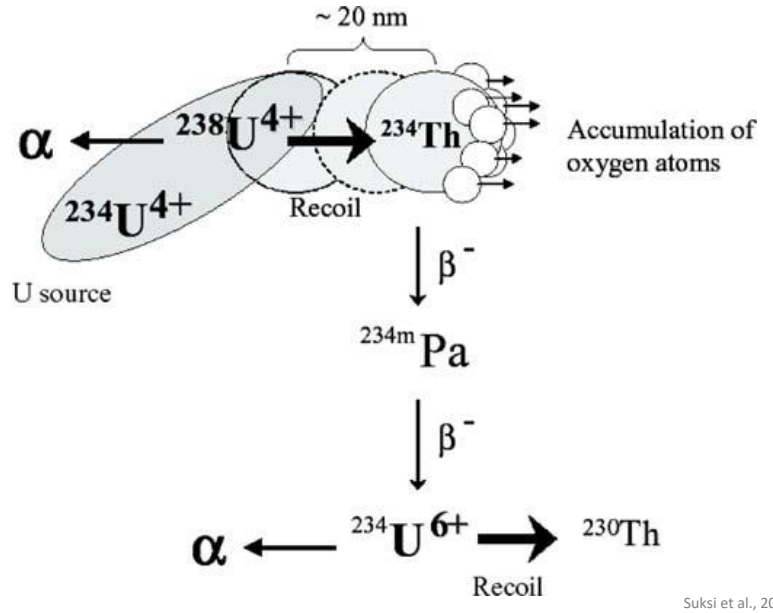
~0.03% from secular equilibrium

* Solubility in different redox state

* Nuclear field shift effect

- **$^{230}Th/^{232}Th$**

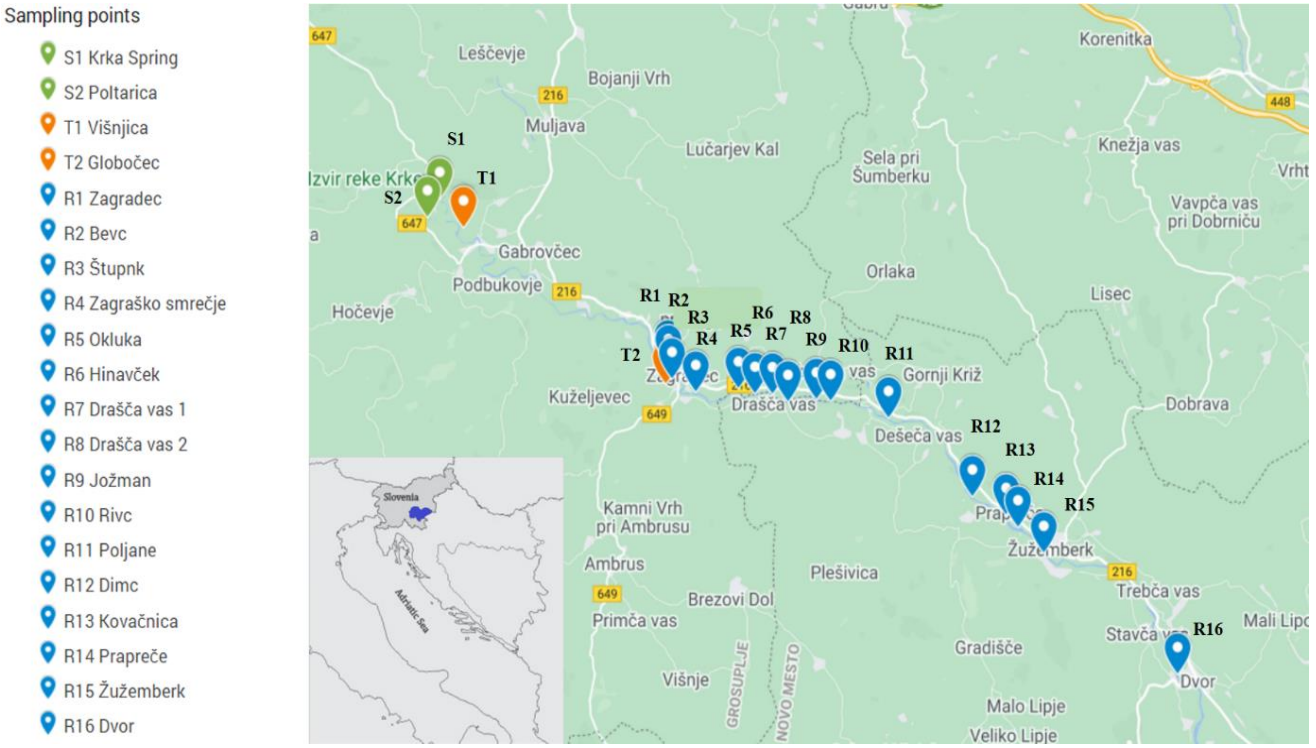
→ Geochemical tracer & indicator of carbonate detrital contaminations.



A conceptual model of oxidation-based ^{234}U fractionation.

Study area: Krka River in Slovenia

Map of the examined area and locations of the sampling sites:



- Mesozoic Dinaric Carbonate Platform
- River charged by:
  - Groundwater in the headwater catchment area
  - Tributaries
  - Diffused groundwater input throughout the course of the river

- Spring
- Tributary
- Mainstream

W: Water
B: Bedrock
T: Tufa

Site	Dominant Bedrock lithology	Distance from the spring [km]
S1 Krka spring; **W, B**	Dolomite	0
S2 Poltarica (second, minor spring); W, B	Dolomite	0.50
T1 Višnjica (tributary); W, B	Alluvial sediment	0.90
T2 Globočec (tributary); W, B	Limestone	8.50
R1 Zagradec; W, T	Limestone	7.40
R2 Bevc; W, T	Limestone	7.77
R3 Štupnk; W, T	Limestone	8.40
R4 Zagraško smrečje; W, T	Limestone	9.04
R5 Okluka; W, T	Limestone	9.92
R6 Hinavček; W, T	Limestone	10.27
R7 Drašča vas 1; W, T	Limestone	10.53
R8 Drašča vas 2; W, T	Limestone	10.79
R9 Jožman; W, T	Limestone	11.18
R10 Rivc; W, T	Limestone	11.42
R11 Poljane; W, T	Dolomite & Limestone	12.86
R12 Dimc; W, T	Dolomite & Limestone	15.24
R13 Kovačnica; W, T	Dolomite & Limestone	16.22
R14 Prapreče; W, T	Dolomite & Limestone	16.52
R15 Žužemberk; W, T	Dolomite & Limestone	17.14
R16 Dvor; W, T	Dolomite & Limestone	21.20

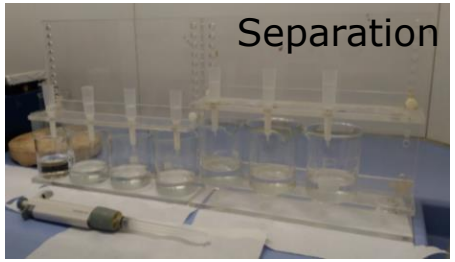
Methodology: Analytical procedure

Sampling → Sample preparation → Measurement → Calculation

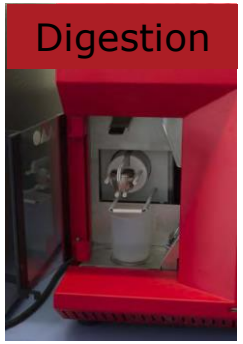
River water,
tufa,
Bedrock.

Pre-concentration

Separation



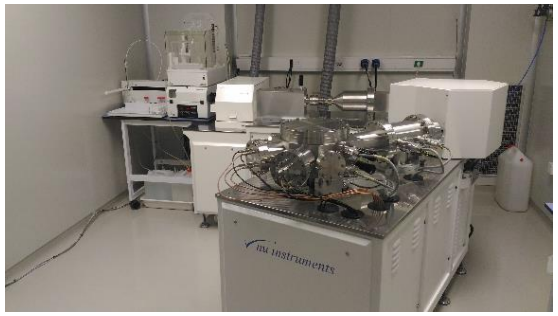
Digestion



Leaching
(1M NaAc+HAc)

ICP-QQQ-MS

MC-ICP-MS



U and Th concentrations

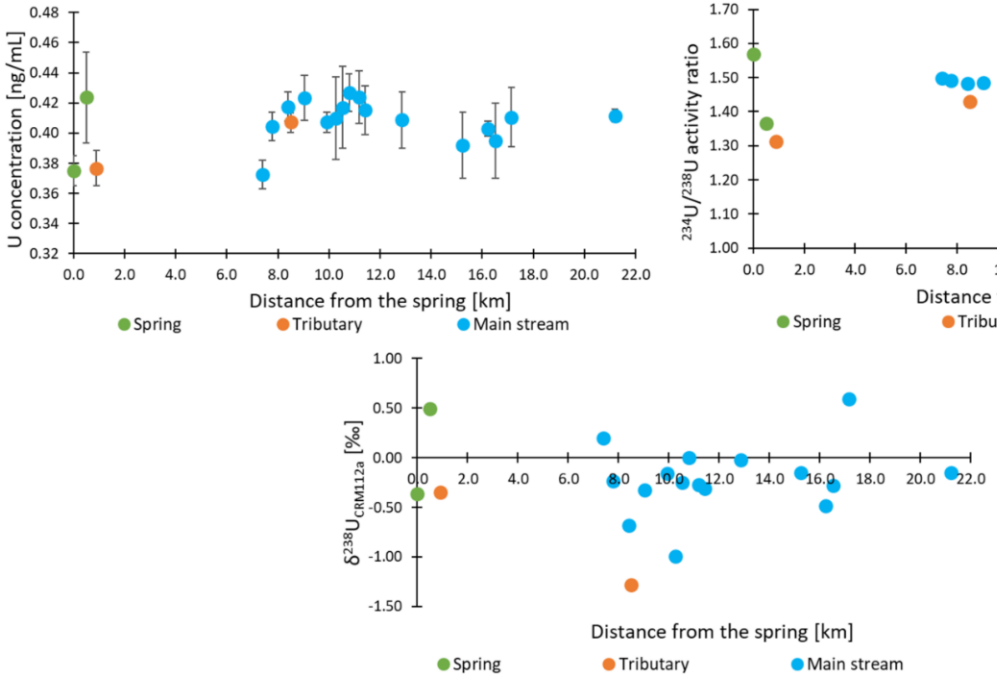
$\delta^{238}U$ value

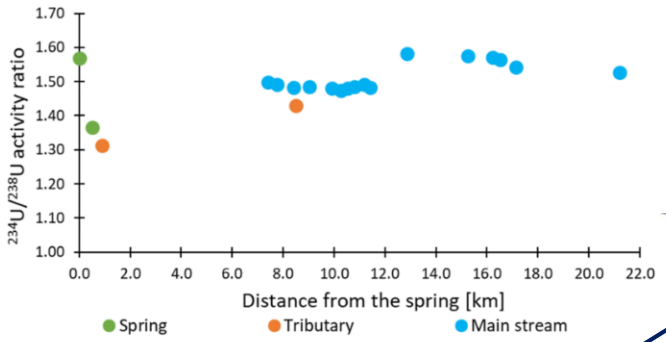
$^{234}U/^{238}U$ activity ratio

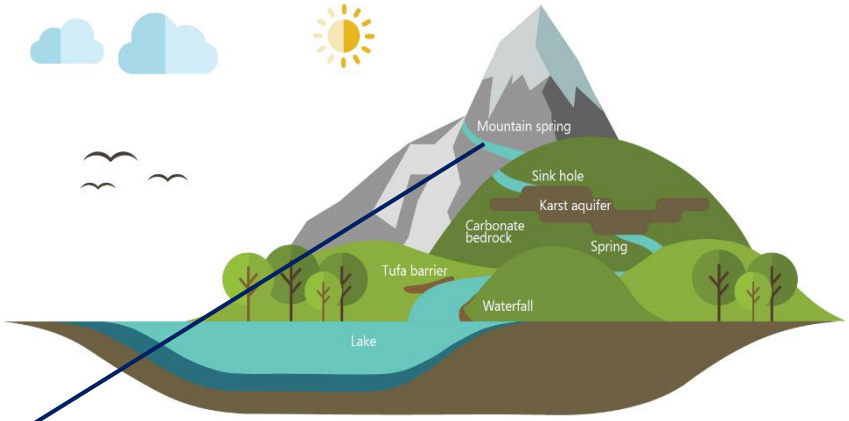
$^{230}Th/^{232}Th$ activity ratio

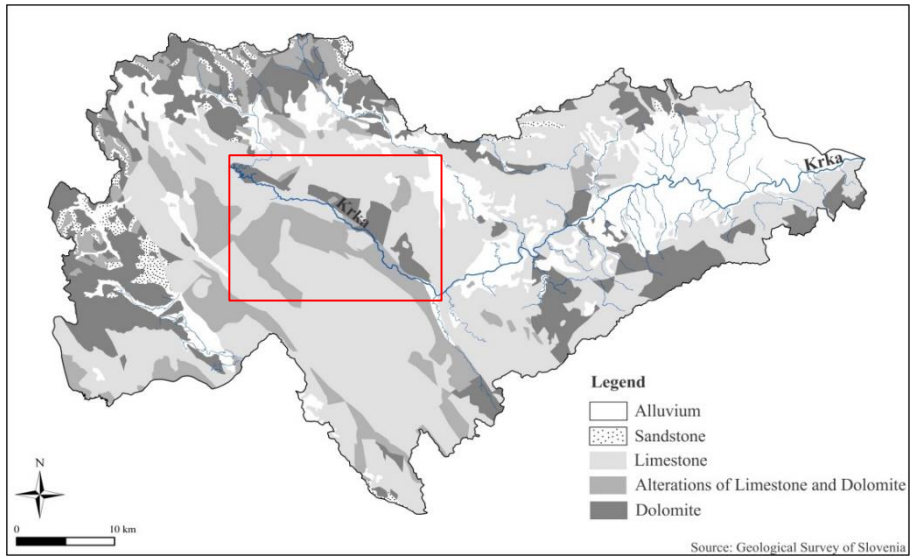
Results: U isotopic composition in water samples

U concentration, $^{234}U/^{238}U$ activity ratio, and $\delta^{238}U_{CRM112a}$ value in analyzed water samples with the distance from the spring:





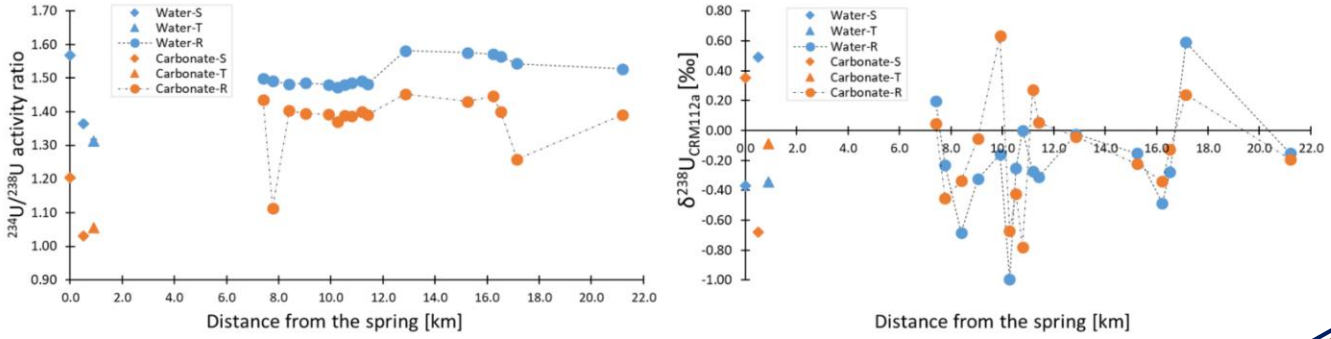


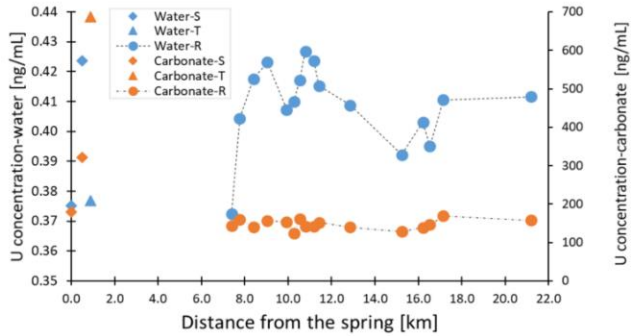


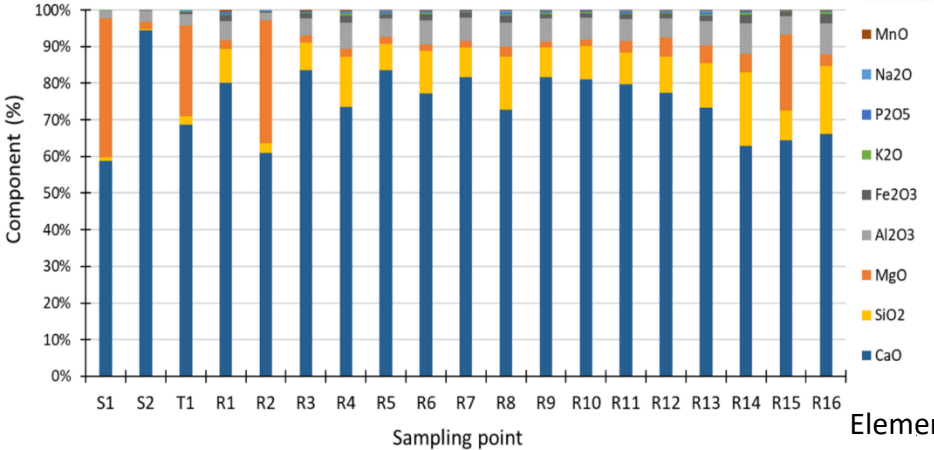
Geological map with lithological units.

Results: U isotopic composition in carbonate and water samples

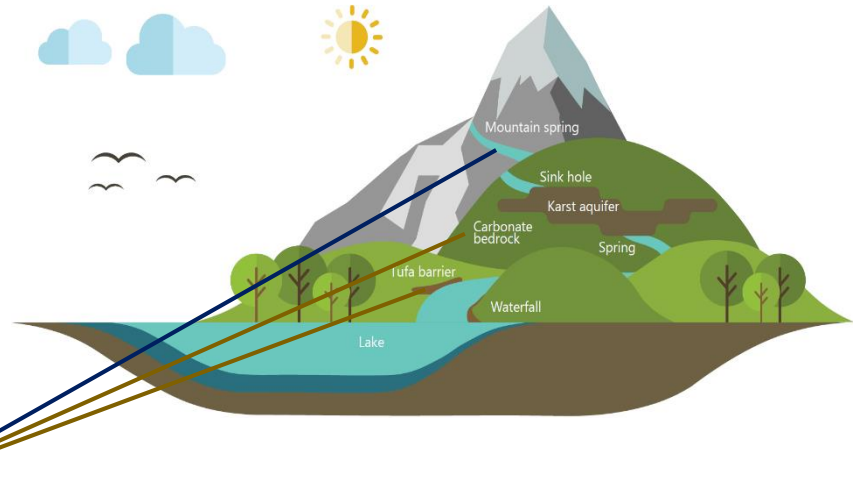
Comparison of $^{234}U/^{238}U$ activity ratio, $\delta^{238}U_{CRM112a}$ value and U concentration in water, tufa and carbonate bedrock samples; S: spring, T: tributary, and R: mainstream:

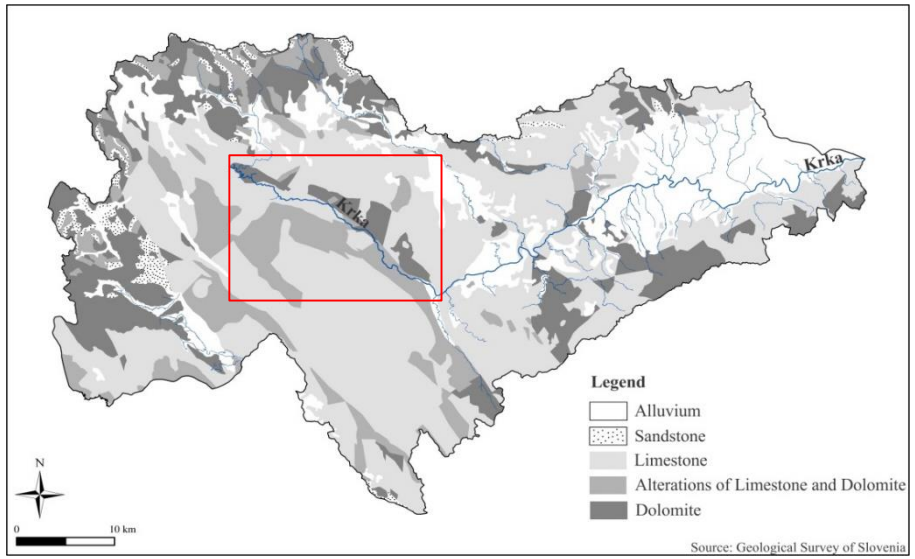






Elemental mineral composition of tufa and carbonate bedrock samples from the XRF.

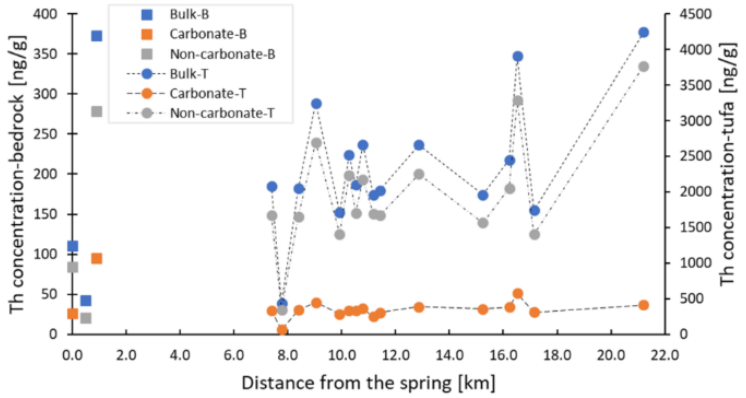


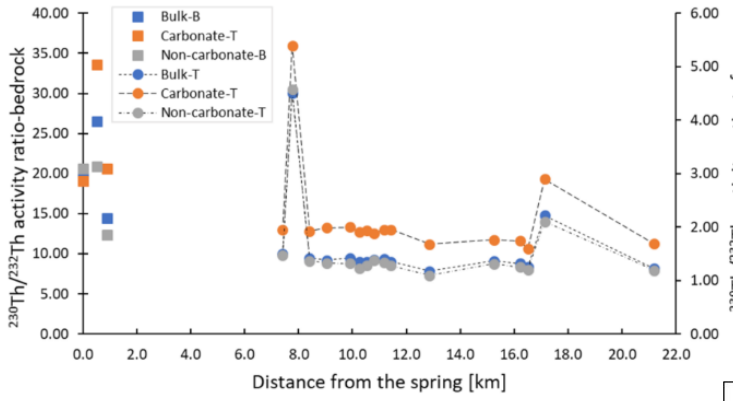


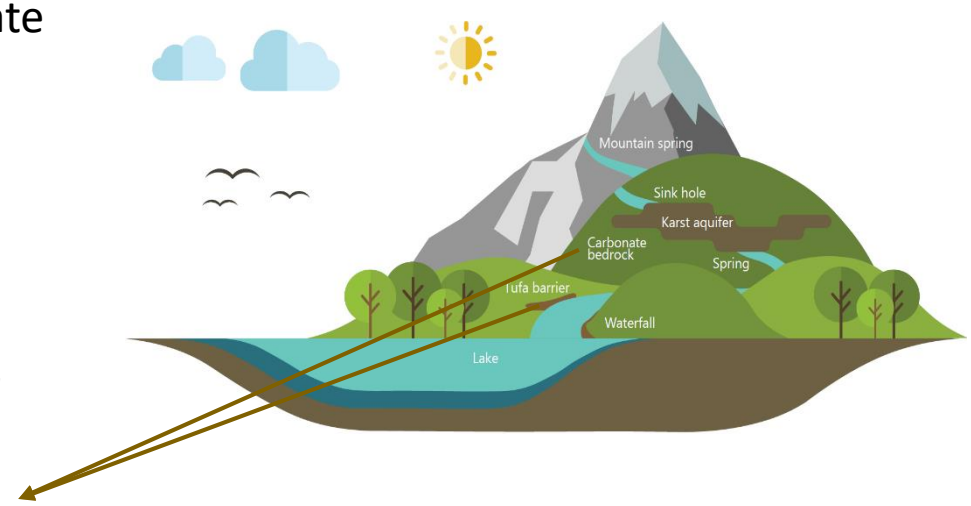
Geological map with lithological units.

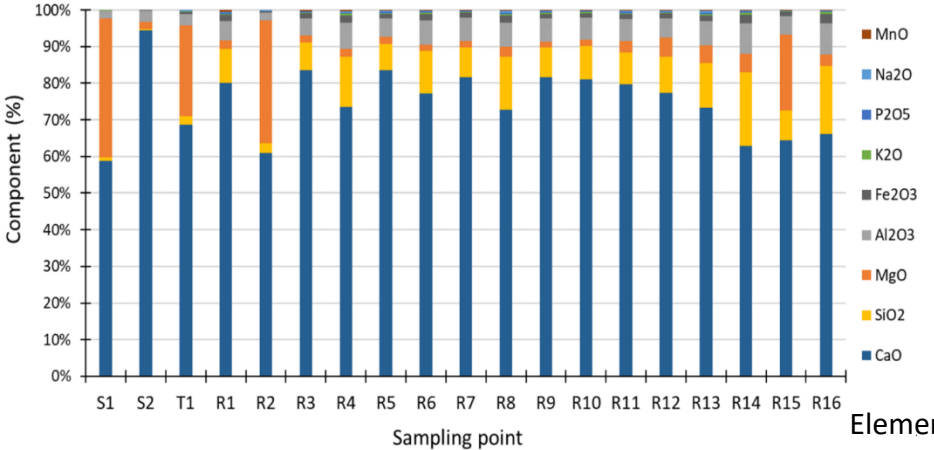
Results: Th isotopic composition in carbonate samples

Th concentration and $^{230}Th/^{232}Th$ activity ratio in analyzed tufa (T) and carbonate bedrock samples (B) with the distance from the spring:









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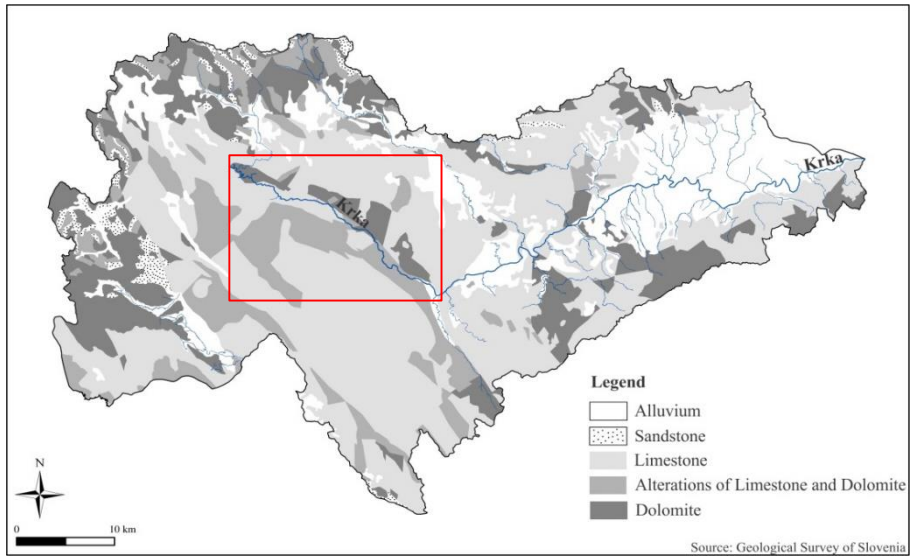
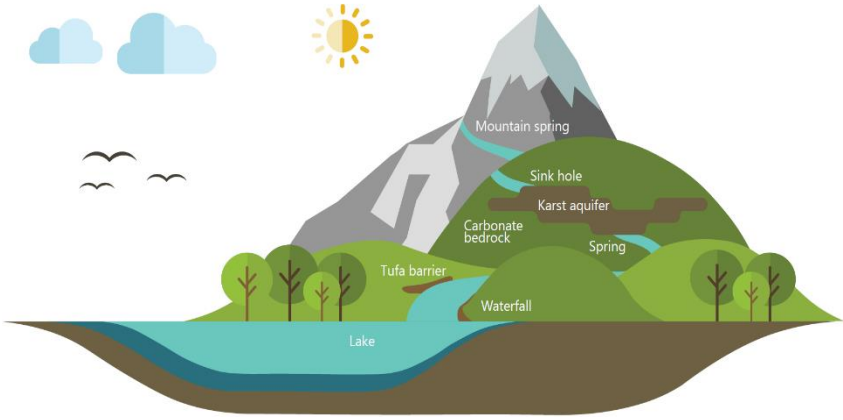


Geological map with lithological units.

Conclusions



- U isotopic composition shows potential as a tracer:
  - lithological characteristics of the bedrock;
  - mixing waters from different origins;
  - to track seasonal variations along the flow of karstic waters;
  - indicator for the storage of CO_2 as authigenic carbonate in tufa and carbonate detrital contamination.
- Th isotopic ratio demonstrates as an indicator to:
  - differentiate between authigenic and detrital carbonate in tufa.

Data presented new evidence on the U and Th isotope disequilibrium in river water and its tufa appearance and brings broader knowledge on fluxes and their governing mechanisms within the local and global biogeochemical C cycle.

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