BIOTOXMET – MUL first results

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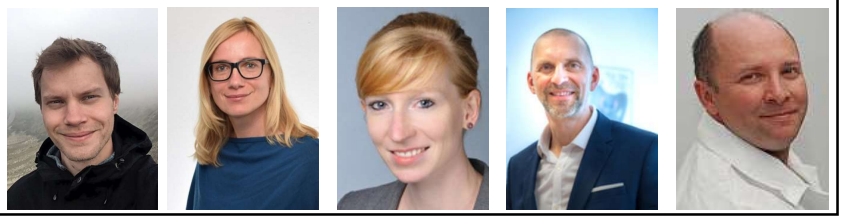

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Contribution to BIOTOXMET (from poposal)

1.1.3. MEASUREMENT OF $^{87}Sr/^{86}Sr$ ISOTOPE RATIOS IN WATER

$^{87}Sr/^{86}Sr$ isotope ratios in the river water samples will be measured by double-focusing sector field MC ICP-MS (Nu Plasma HR, Nu Instruments, Ltd). External calibration will be performed by application of the reference material SRM986 SrCO3 (NIST). For isotope analysis, samples will be subjected to Rb/Sr separation procedure (Retzmann et al., 2017) using prepFAST–MC system (Elemental Scientific).

2.4. MEASUREMENT OF METAL CONCENTRATIONS IN FISH CALCIFIED STRUCTURES

Calcified structures will be cleaned by Milli-Q water and dried. Otoliths will be ground and polished. For each sample 4-6 scales will be prepared and mounted on small glass slides using adhesive tape and the scale with the most visible growth zones per sample will be analyzed. Measurement of metals will be conducted by connecting a laser ablation system (NWR193, Electro Scientific Industries) to an ICP-QMS (NexION 350D, PerkinElmer) and the laser lines will be taken through the middle of the hard tissues. Calcium, as a main element in the aragonite of otoliths and hydroxyapatite of scales, will be used as internal standard.

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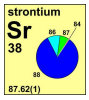
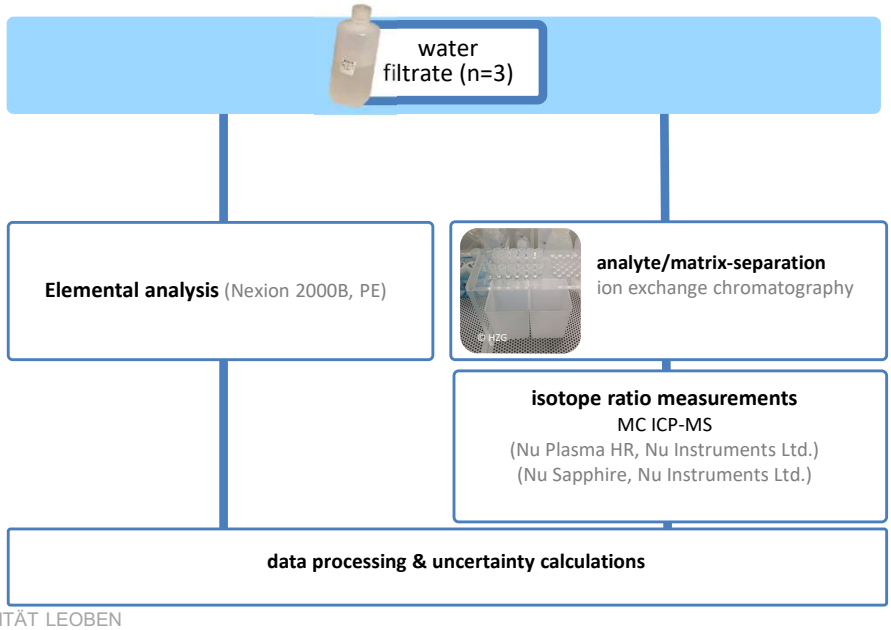
Background information

Why is $^{87}Sr/^{86}Sr$ ratio a good indicator … ?

- mainly varies according to the radioactive ß$^-$ decay of ^{87}Rb to ^{87}Sr ($t_{1/2}$ nearly 50 billion years)
- function of the geochemical origin, Rb concentration, and age of the source rock
- fingerprint of its geological source
- extensively used in geochemical fingerprinting, source tracking, contamination prediction, and migration/mobility studies.



Experimental procedure



Sr isotopic analysis via MC ICP-MS

Sample preparation

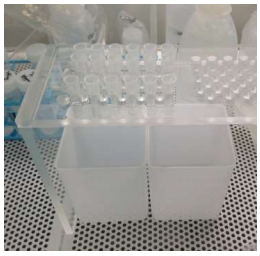
- Requires a measurement solution containing only the analyte
- Sr isotopic composition suffers from isobaric and polyatomic spectral interferences

Sr
$^{84}Kr^{+}$, $^{86}Kr^{+}$, $^{87}Rb^{+}$, REE^{2+}, Ca-dimers, Ca-argides

- Substantial amounts of matrix elements (Ca, Mg, Na etc) can lead to signal suppression and changes in the instrumental isotopic fractionation

ANALYTE / MATRIX SEPARATION

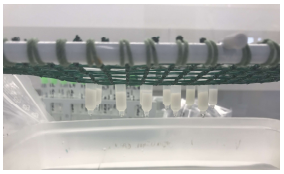
- Chromatography (LP, HP)
  - **Off line separation**
  - On line separation
  - Automated separation



Analyte/matrix separation

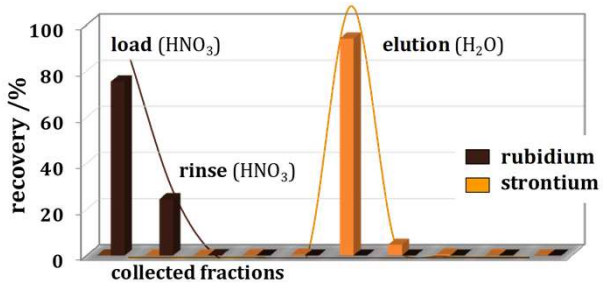
Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Off line separation



step	reagent	volume / mL
column packing	Sr Resin in 0.3 mol L^{-1} HNO_3	0.5
cleaning	6 mol L^{-1} HNO_3	3
	subb. H_2O	3
	6 mol L^{-1} HCl	3
	subb. H_2O	3
conditioning	8 mol L^{-1} HNO_3	3
sample loading	sample in 8 mol L^{-1} HNO_3	0.5
rinsing	8 mol L^{-1} HNO_3	10
elution	subb. H_2O	2

Horsky M, Irrgeher J, Prohska T, ANAL BIOANAL CHEM, 2016



Irrgeher J., Prohaska T., Sturgeon R.E., Mester Z., Yang L.. Anal Methods, 5 (7), 1687 – 1694, (2013).

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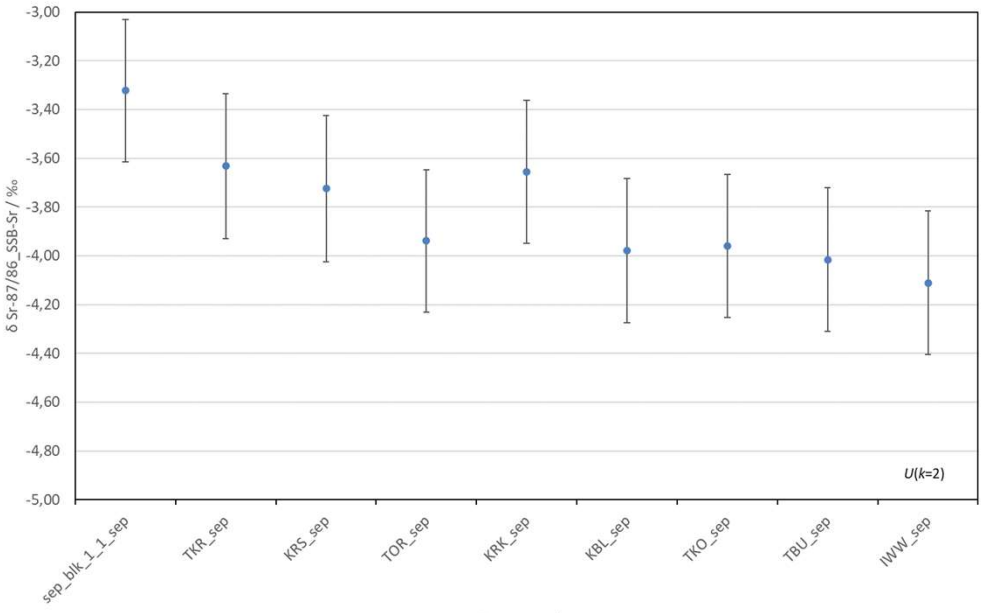
$^{87}Sr/^{86}Sr$ in water samples



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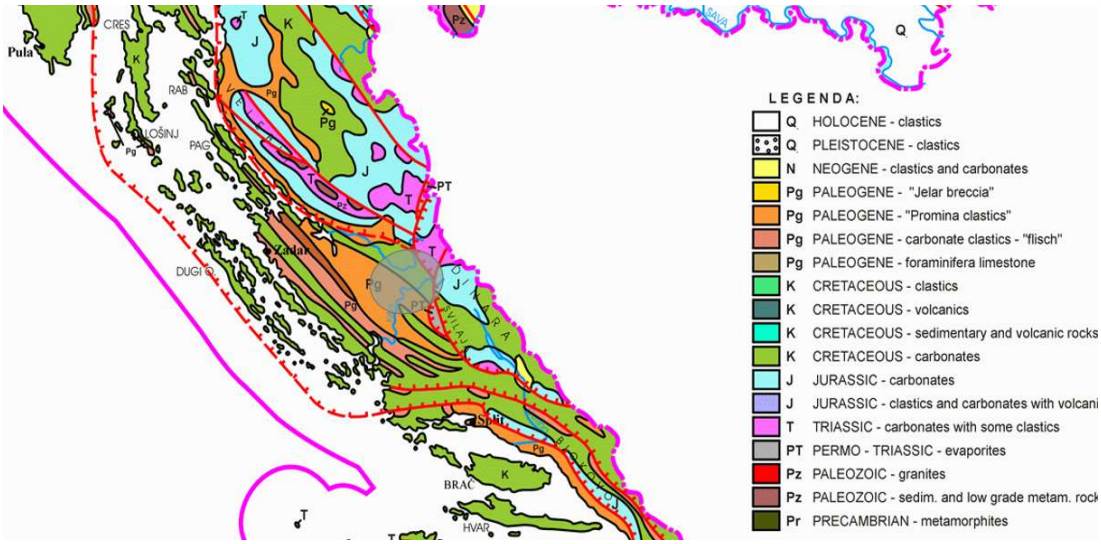
Geological map of Croatia



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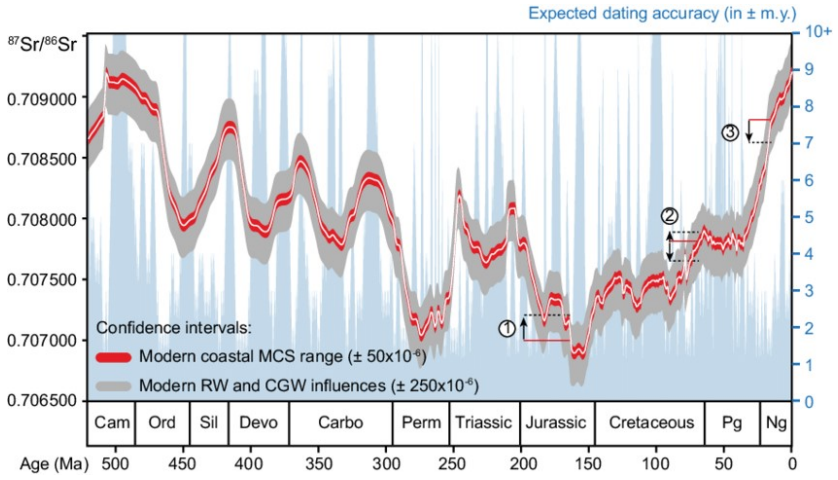
Geological map of Croatia

Absolute ratios

Sample	Sr-87/86_internal
KRK	0,70762
TOR	0,70741
TKR	0,70776
IWW	0,70748
KBL	0,70743
TKO	0,70742
TBU	0,70745
KRS	0,70771



Phanerozoic seawater 87 Sr/ 86 Sr variations (white line) and corresponding time

Sofia El Meknassi et al. GEOLOGY, 2018

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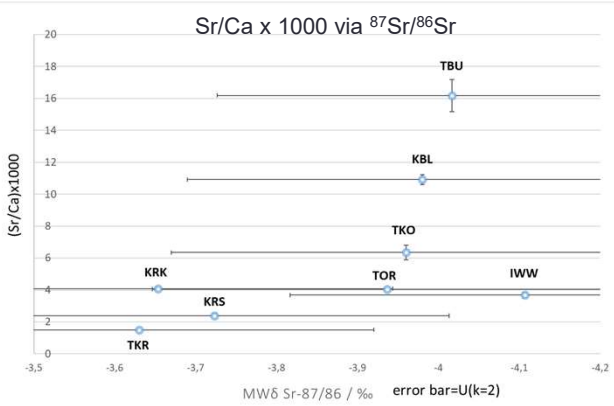
$^{87}Sr/^{86}Sr$ in water samples



Sample	Ca µg/g	Sr ng/g	(SR/Ca)*1000	δ Sr-87/86 / ‰	Sr-87/86_internal
KRK	12,1	49,4	4,08	-3,65	0,70762
TOR	9,11	36,9	4,05	-3,94	0,70741
TKR	5,75	8,67	1,51	-3,63	0,70776
IWW	90,5	333	3,68	-4,11	0,70748
KBL	10,6	115	10,9	-3,98	0,70743
TKO	29,7	188	6,35	-3,96	0,70742
TBU	17,6	285	16,2	-4,02	0,70745
KRS	6,26	14,9	2,38	-3,72	0,70771

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Thank you for your attention!

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