Groundwater age determination with $^{81}Kr/^{85}Kr$ in the framework of Nagra's exploratory boreholes for a deep geological repository

ID #580

- highlights and lessons learned

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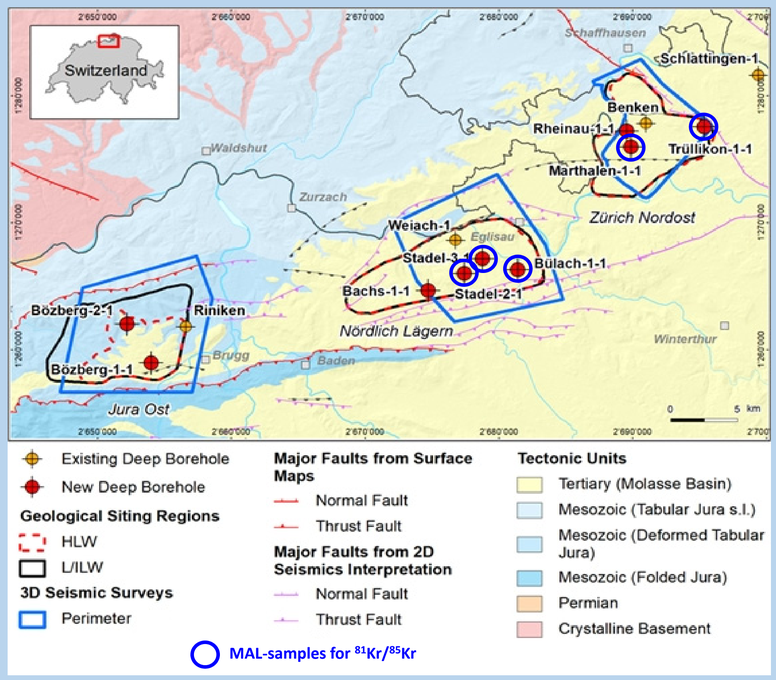
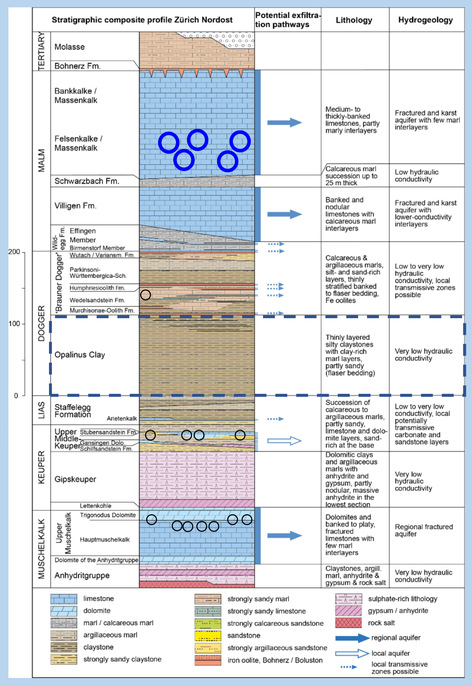
Introduction and sampling

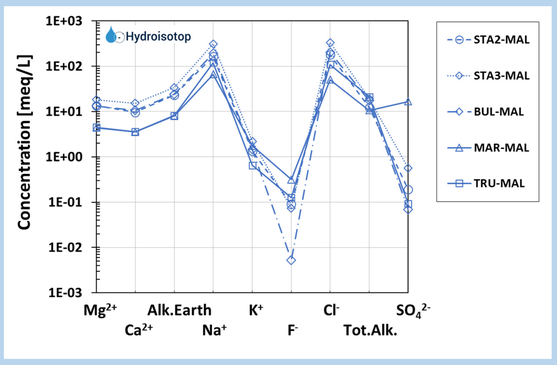
Nagra carried out multi-purpose exploratory boreholes (TBO) for a comparative evaluation of possible sites in northern Switzerland for a deep geological repository for radioactive waste. In the frame of these interdisciplinary works, precise pumping test (100 h) with groundwater sampling and analytical data interpretation focused to obtain reliable information on groundwater composition, evolution and residence times e.g. in the Malm aquifer (**MAL,** pumped flow rate < 5 L/min) above the low permeability sequence of the host rock (Opalinus Clay). Water sampling at the well head and for **$^{81}Kr/ ^{85}Kr$** with continuous flushing in IBC tanks (1-2) allowed the successful extraction of Kr gas (2 samples had to be spiked with well known Kr due to degassing effects).

Regional geological situation

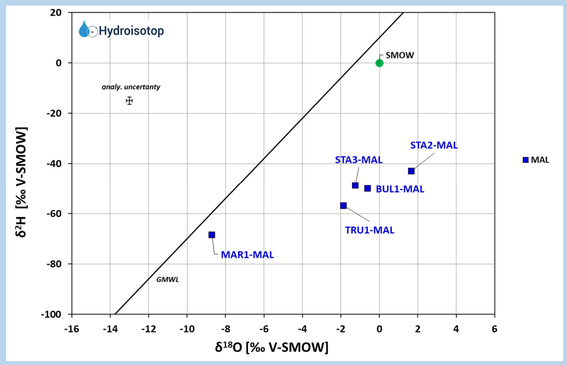




Hydrochemical and stable water isotope composition

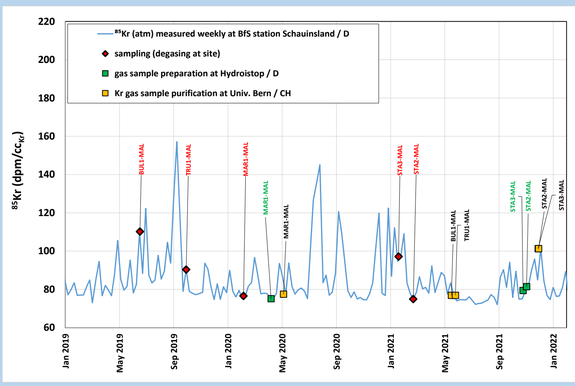


Na-Cl-type
Br/Cl ratios close to seawater +
Cl almost equal to extracted MAL pore waters



enriched isotope signatures
almost equal to extracted MAL pore waters
(complex evolution and mixing with meteoric end member)

Correction of air contamination using max. $^{85}Kr_{atm}$ (for upper ^{81}Kr limit)



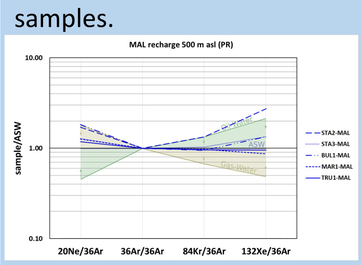
		STA2-MAL	STA3-MAL	BUL1-MAL (spiked)	MAR1-MAL	TRU1-MAL (spiked)
samling date		22.02.2021	20.01.2021	18.06.2019	03.03.2020	30.09.2019
$^{81}Kr_m$	pm ^{81}Kr	**56**	**41**	**71**	**66**	**88**
±	pm ^{81}Kr	**6**	**5**	**6**	**2**	**9**
$^{85}Kr_{m\ (decay\text{-}corr)}$	dpm/ccKr	**45.7**	**30.2**	**14.7**	**4.7**	**19.2**
±	dpm/ccKr	**3.1**	**2.1**	**1.3**	**0.2**	**1.9**
max. $^{85}Kr_{atm}$	dpm/ccKr	**101.3**	**101.3**	**110.2**	**77.5**	**90.4**
±	dpm/ccKr	**3.0**	**3.0**	**3.0**	**3.0**	**3.0**
max. contamination	%	49.6	32.9	**spiked**	6.5	**spiked**
$^{81}Kr_{corr}$	pm ^{81}Kr	**18.3**	**15.4**	**0.0**	**63.8**	**64.8**
±	pm ^{81}Kr	**24.8**	**15.2**	**22.1**	**3.3**	**26.9**

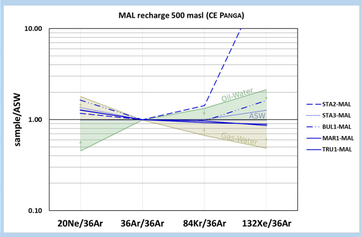
$^{85}Kr_{atm}$ measured at BfS station Schauinsland (D) and dates for sampling, preparation and purification (Hydroisotop and Univ. Bern). The ATTA-analysis for $^{81}Kr_m/^{85}Kr_m$ was performed at Argonne National Laboratory, USA.

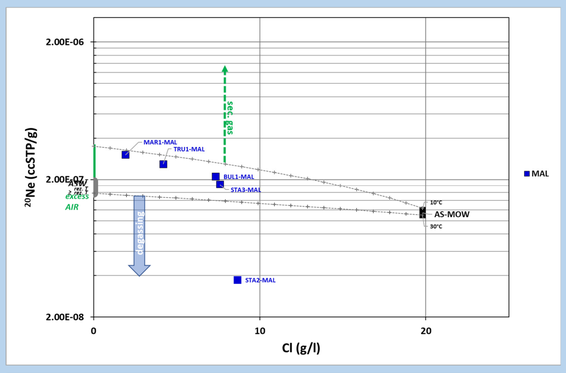
Noble gas test for sample qualification

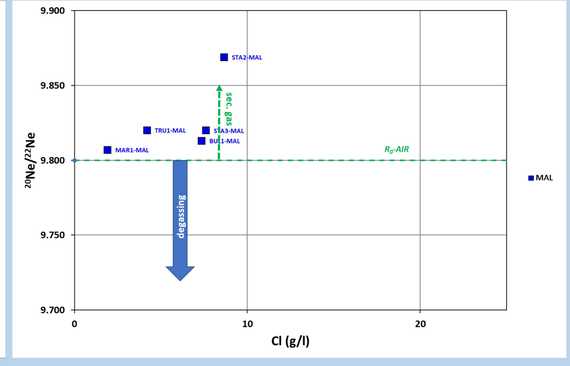
	sample		STA2-MAL	STA3-MAL	BUL1-MAL	MAR1-MAL	TRU1-MAL
	recharge altitude	m asl	500	500	500	500	500
	Salinity (s)	mol/L	0.01	0.01	0.01	0.01	0.01
PR-Stute et al. (1995)	Ne	°C	100.0	22.1	69.2	8.7	4.6
	Ar	°C	100.0	17.3	83.3	5.7	4.4
	Kr	°C	90.5	29.8	72.9	8.5	4.5
	Xe	°C	73.5	19.0	51.6	11.5	4.8
	Δ Ne	%	0.0	8.9	41.1	54.1	72.2
	T av	°C	**91.0**	22.1	**69.3**	8.6	4.6
	±	°C	**12.5**	5.5	**13.2**	2.4	0.2
	T (Kr+Xe)	°C	**82.0**	24.4	**62.3**	10.0	4.7
	±	°C	**12.0**	7.6	**15.1**	2.1	0.2
CE-Panga-1Fit	T av	°C	97.6	19.7	69.4	15.1	4.7
	±	°C	0.0	4.9	1.4	1.1	5.1
	T (Ne+Ar+Xe)	°C	**97.6**	**19.3**	**69.4**	**15.6**	**4.4**
	±	°C	**0.0**	>>	**1.4**	**1.2**	>>
	Eq-Ne	ccSTP/g	2.81E-08	1.78E-07	1.27E-07	1.84E-07	2.05E-07
	Δ Ne	%	**46**	**14**	**83**	**81**	**40**
qualification	*Ne-Xe-pattern*		**degassed**	**OK**	**degassed + bubbles**	**1st bubble**	**OK**
	Kr-loss (diffusion)	PR: T comparison (Kr > Xe)	possible	possible	possible	**no**	**no**
		PR: T comparison (Kr > Ne)	**no**	possible	possible	**no**	**no**
		CE: T comparison (av > Ne+Ar+Xe)	**no**	-	possible	possible	-
	Kr-gain (flux)	PR: T comparison (Kr < Xe)	**no**	**no**	**no**	**no**	**no**
		PR: T comparison (Kr < Ne)	-	**no**	**no**	**no**	**no**
		CE T comparison (av < Ne+Ar+Xe)	**no**	-	**no**	**no**	-

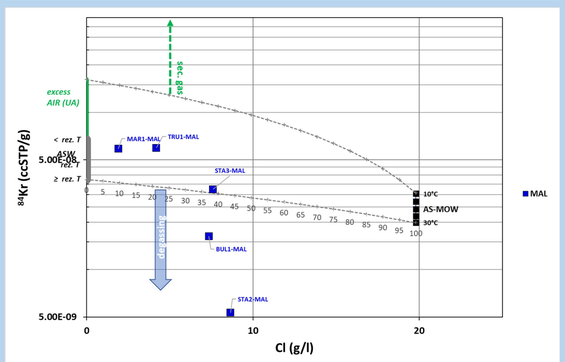
Results of noble gas recharge temperatures using PR[a] and CE[b] (1 Fit) software models and normalised isotope plots[c] for comparison of the noble gas pattern to assess possible external influences (Kr loss or gain) in the MAL samples.









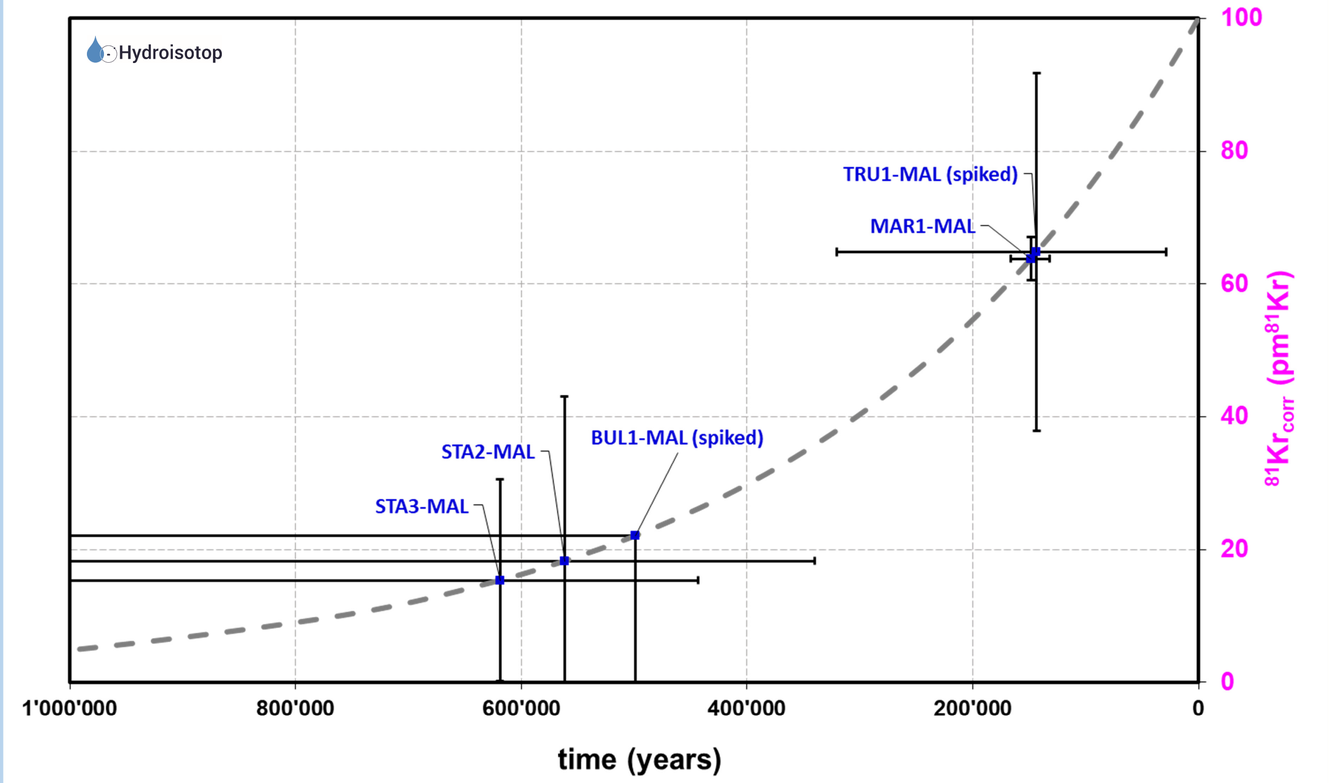


Noble gas isotope values versus Cl contents of MAL samples in a postulated mixing system of meteoric with marine end members (close to modern seawater) using a simplified approach[d].

Noble gas isotope values uncorrected due to elevated $^{20}Ne/^{22}Ne$ ratios.

Arrows indicate degassing effects or possible external gas flux.

„^{81}Kr model age"



Joint presentation of the derived results for $^{81}Kr_{corr}$ of the MAL groundwater samples along with the ^{81}Kr decay curve representing a ^{81}Kr piston flow model age

Results and Conclusions

We present a workflow for the evaluation of sample quality based on the suite of noble gas isotopes analysed. To account for sample contamination, we use max. $^{85}Kr_{atm}$ from the time series data of the BfS Schauinsland station to conservatively calculate the air contamination.

The sampled Na-Cl-waters represent various degrees of mixtures between fossil marine components (devoid of ^{81}Kr) and Pleistocene meteoric water. Owing to different solubility constraints, the resulting $^{81}Kr/Kr$ ratios in these mixtures are considered to be predominantly indicative for the residence time of the younger component.

The derived $^{81}Kr_{corr}$ results show up different sets of ^{81}Kr model age ranges for the investigated sites in northern Switzerland.

A further assessment may require additional investigations to characterise the complex evolution of the marine components and sophisticated approaches for the noble gas correction of degassing during pumping and sampling.

Due to elevated gas contents, the need to spike two samples led to significantly higher uncertainties in the correction of contamination and spike.

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References:

[a] Stute M., Forster M., Frischkorn H., Serejo A., Clarke J.F., Schlosser P., Broecker W.S. and Bonani G. (1995) Cooling of tropical Brazil (5°C) during the last glacial maximum. Science 269: 379-383

[b] Aeschbach-Hertig W., El-Gamal H., Wieser M. and Palscu L. (2008) Modeling excess air and degassing in groundwater by equilibrium partitioning with a gas phase: modeling gas partitioning. Water Resources Research, 44, W08449, https://doi.org/10.1029/2007WR006454

[c] Bryne D., Barry P., Lawson M. and Ballentine C. (2017) Noble gases in conventional and unconventional petroleum systems. Geological Society, London, Special Publications. 468. SP468.5. 10.1144/SP468.5., https://doi.org/10.1144/SP468.5

[d] Gerber C., Vaikmäe R., Aeschbach W., Babre A., Jiang W., Leuenberger M., Lu Z.-T., Mokrik R., Müller P., Raidla V., Saks T., Waber H.N., Weissbach T., Zappala J.C. and Purtschert R. (2017) Using 81Kr and noble gases to characterize and date groundwater and brines in the Baltic Artesian Basin on the one-million-year timescale, Geochim Cosmochim Acta. 205:187-210

For detailed information on the Nagra investigation program and results see **http://nagra.ch**