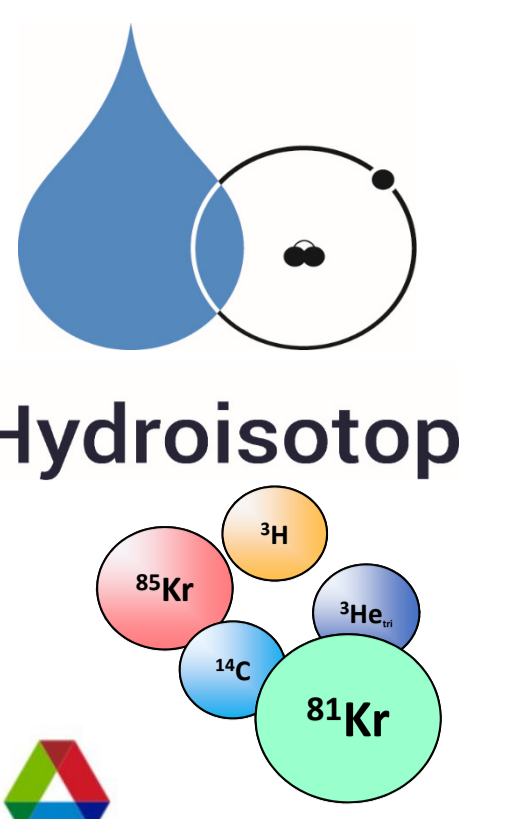


# Dating (<sup>81</sup>Kr) deep thermal groundwater in the Austrian Alpine Foreland Basin

Martin Kralik<sup>1</sup>, Michael Heidinger<sup>2</sup>

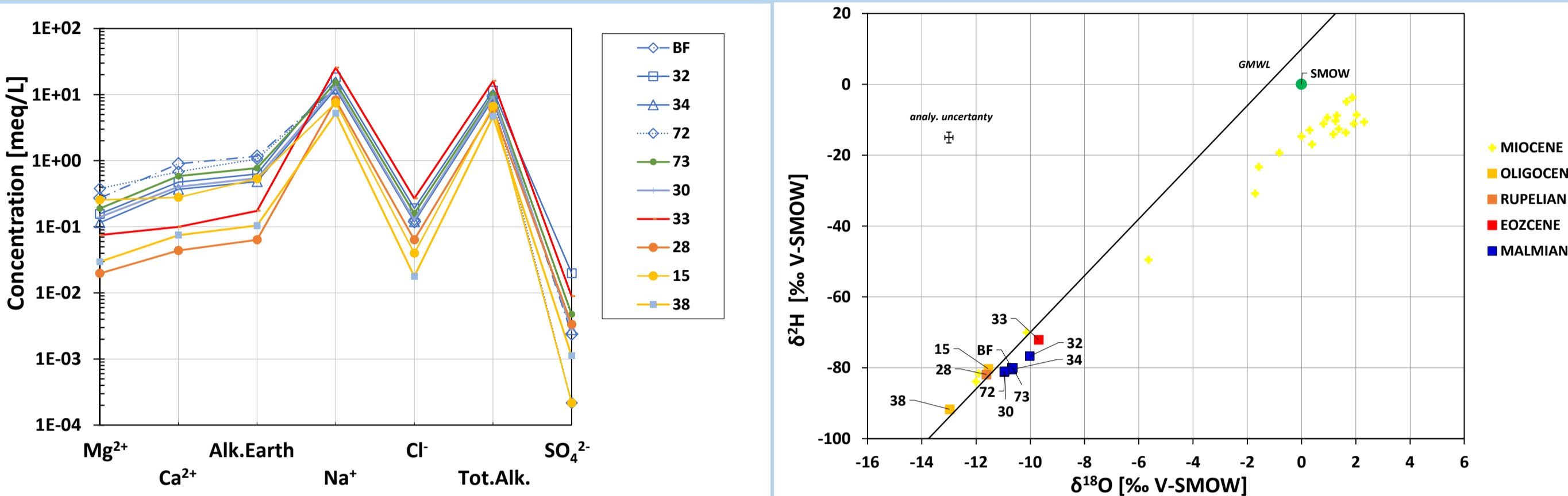


## Introduction and sampling

The Austrian Alpine Foreland Basin (Aafb) is home to a large population and an important industry location. The subsurface of the Aafb is intensively used since decades for drinking, energetic (hydrocarbons and geothermal energy) and balneologic purposes. Deeper groundwater systems in the Malmian and in the Oligocene Formation are utilised for geothermal energy and balneology, shallow sedimentary strata are used for water supply. In addition, hydrocarbon production is conducted since several decades. To appose these individual interests and to secure a sustainable usage of the resources, the understanding of the basin history, their hydrostratigraphic ages and their interactions is crucial.

Within a ÖAW-project <sup>81</sup>Kr/<sup>85</sup>Kr gas samples of nine water wells from different hydrostratigraphic formations were analysed for their groundwater residence time.

## Hydrochemical and stable water isotope composition

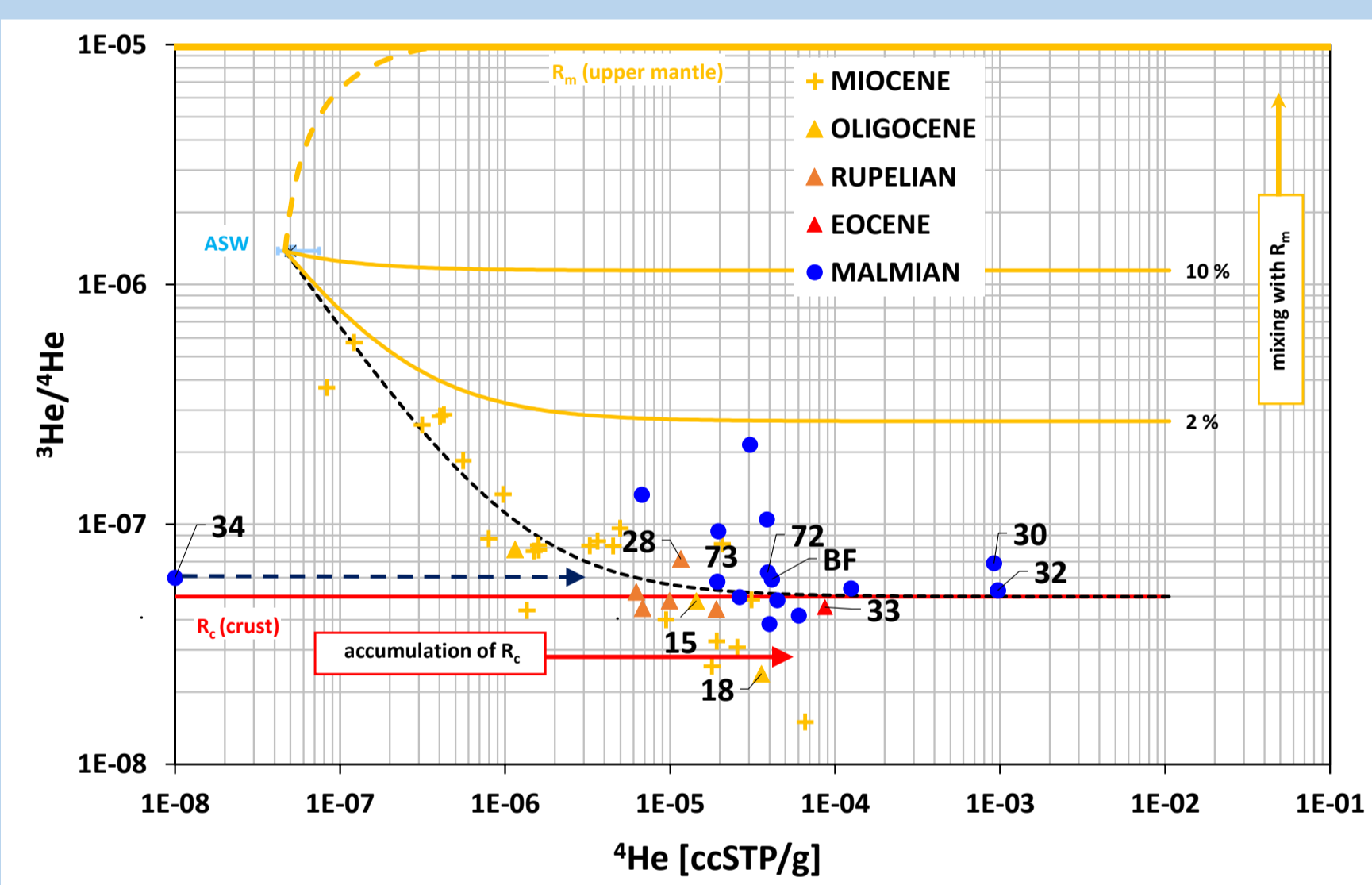


low mineralised Na-HCO<sub>3</sub>-Type (OLIGOCENE) to medium mineralised Na-HCO<sub>3</sub>-Cl type

deep thermal groundwater slightly enriched isotope signatures (minor mixing with MIOCENE marin end member)

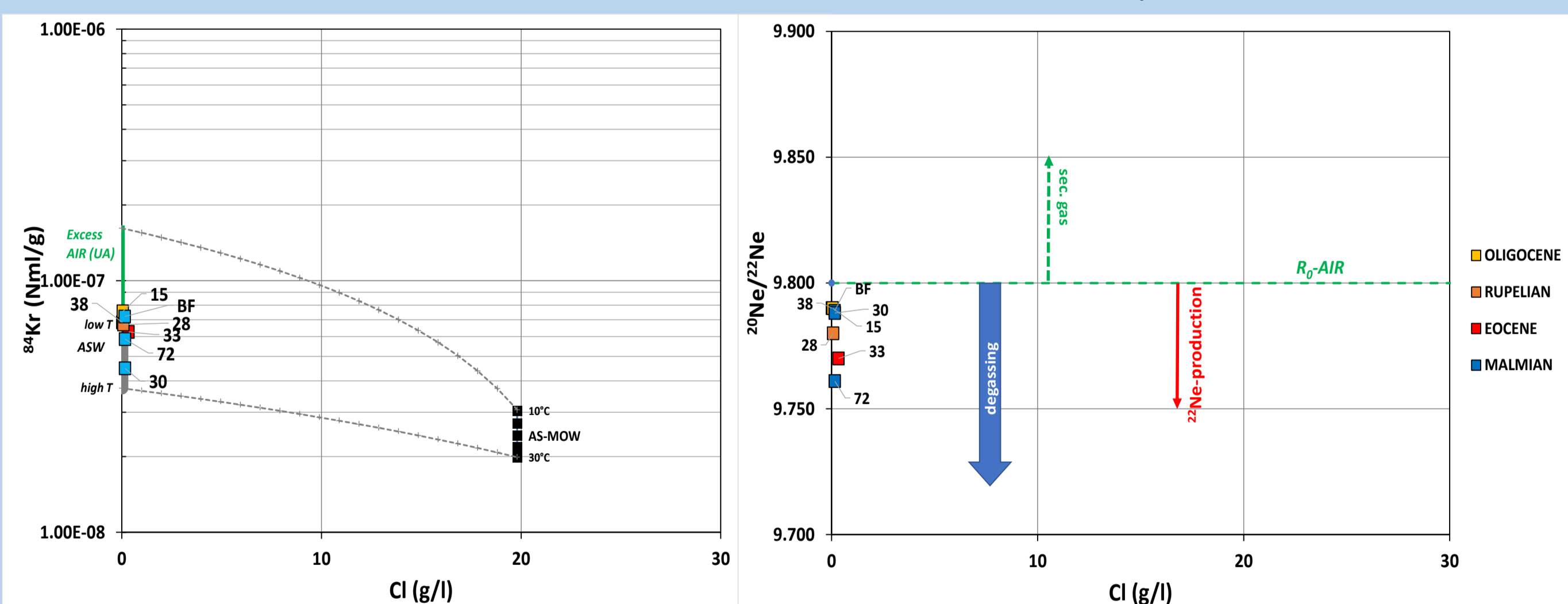
## Gas and Noble gas results for sample qualification

Nr.	BF	32	34	72	73	30	33	28	15	38	
CH <sub>4</sub>	vol. %	49.0	58.2	56.9	59.8	49.7	50.7	79.0	45.0	48.2	19.8
N <sub>2</sub> /Ar		32.7	51.6	60.9	47.7	39.6	35.5	45.3	41.5	46.3	43.5
<sup>3</sup> He/ <sup>4</sup> He		6.78E-08	5.31E-08	6.00E-08	6.32E-08	5.78E-08	6.88E-08	4.52E-08	7.18E-08	4.79E-08	2.38E-08
<sup>4</sup> He	ccSTP/g	5.59E-05	9.67E-04		3.91E-05	1.93E-05	9.16E-04	8.69E-05	1.16E-05	1.44E-05	3.57E-05
<sup>20</sup> Ne	ccSTP/g	2.72E-07	1.86E-05		2.08E-07	1.67E-07	1.46E-07	2.50E-07	2.33E-07	3.49E-07	2.45E-07
<sup>36</sup> Ar	ccSTP/g	1.94E-06			1.48E-06		9.99E-07	1.64E-06	1.99E-06	1.64E-06	
<sup>84</sup> Kr	ccSTP/g	7.20E-08			5.86E-08		4.48E-08	6.26E-08	6.70E-08	7.55E-08	6.83E-08
<sup>132</sup> Xe	ccSTP/g	4.75E-09			4.14E-09		3.32E-09	4.12E-09	4.67E-09	4.76E-09	4.80E-09
<sup>40</sup> Ar/ <sup>36</sup> Ar		302			300		302	304	299	301	303

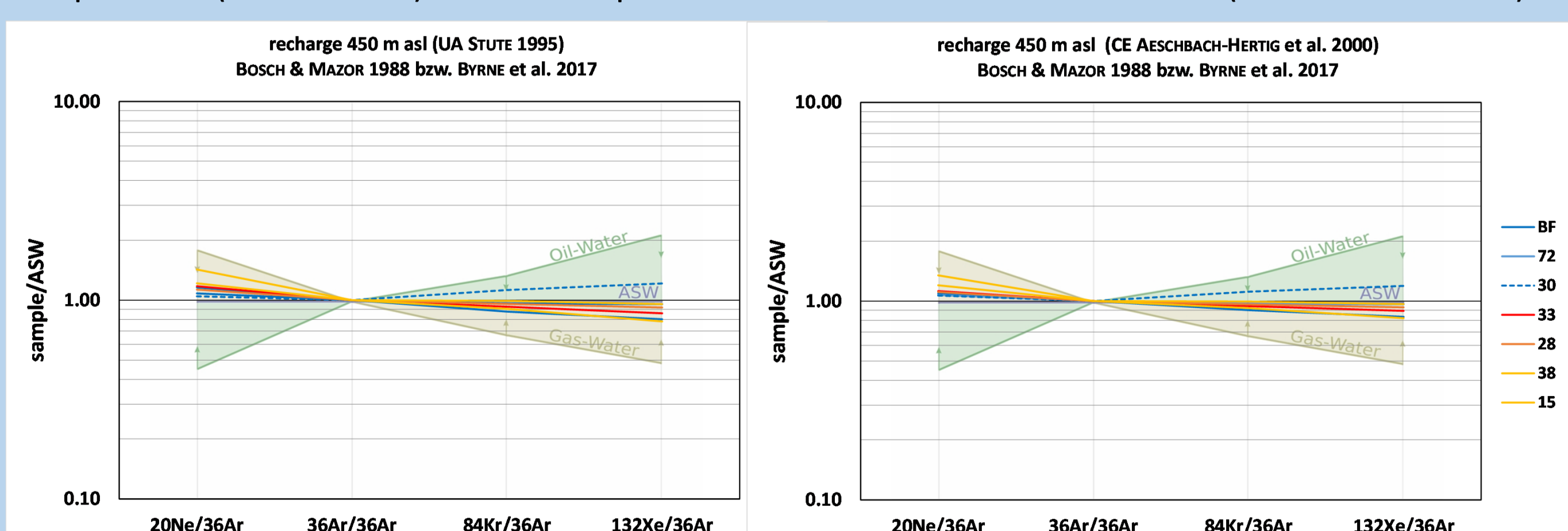


All samples show influences of regional gas reservoirs whereas the He-results indicate different accumulation effects for deeper hydrostratigraphic formations.

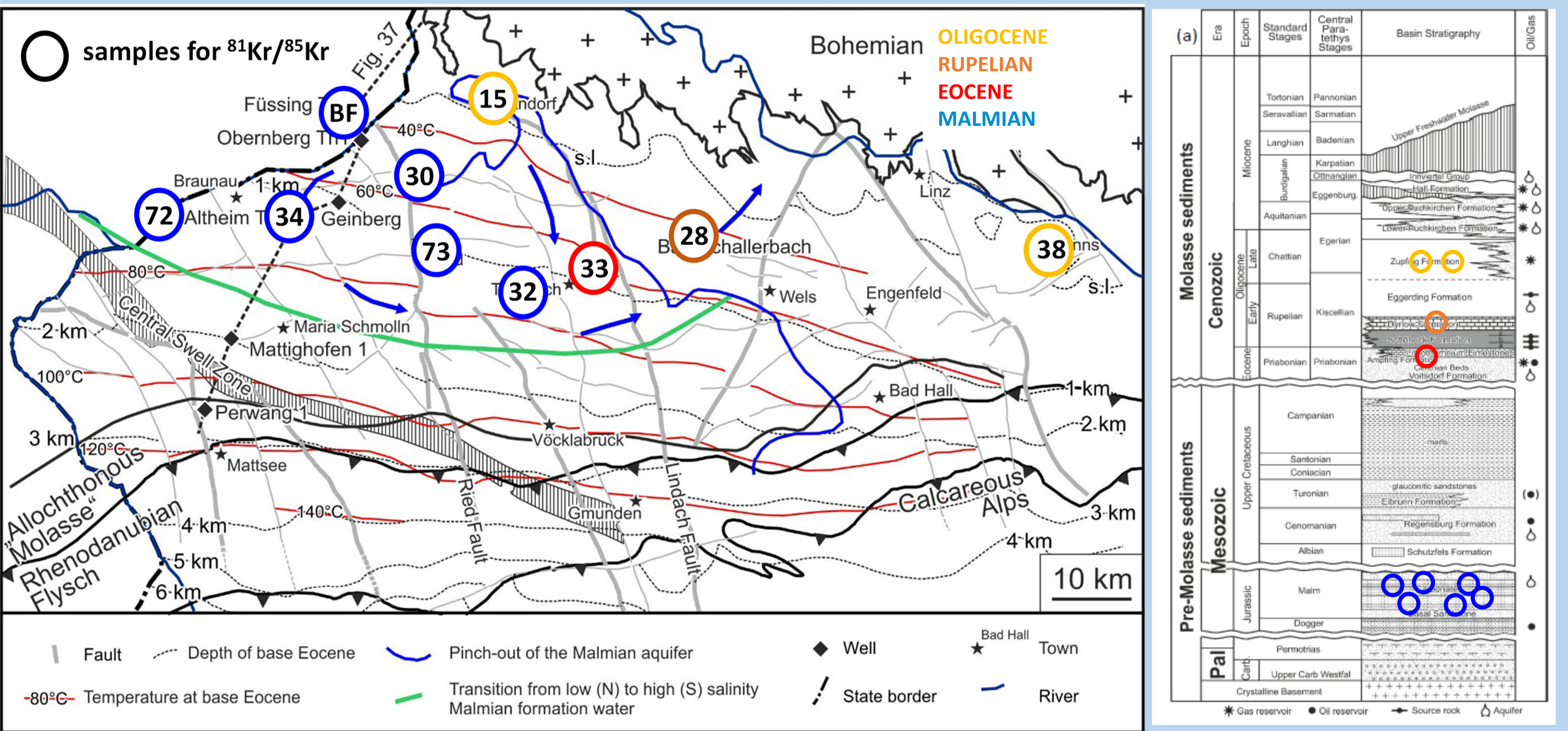
The simplified approach<sup>a</sup> to test possible effects for the noble gas isotope values versus Cl in a postulated mixing system of meteoric with marine end members (close to modern seawater) indicated only minor degassing and predominant atmospheric characteristics.



Results of noble gas recharge temperatures using PR<sup>b</sup> and CE<sup>c</sup> (1 Fit) software models and normalised isotope plots<sup>d</sup> for comparison of the noble gas pattern to assess possible external influences (Kr loss or gain) in the ÖAW-samples. The test indicates minor alterations, characterised by a tendency toward minor losses of the 'heavy' atmospheric noble gas components (Ar < Kr < Xe). For atmospheric Kr these losses are low in total (maximum ≈ 10 %).



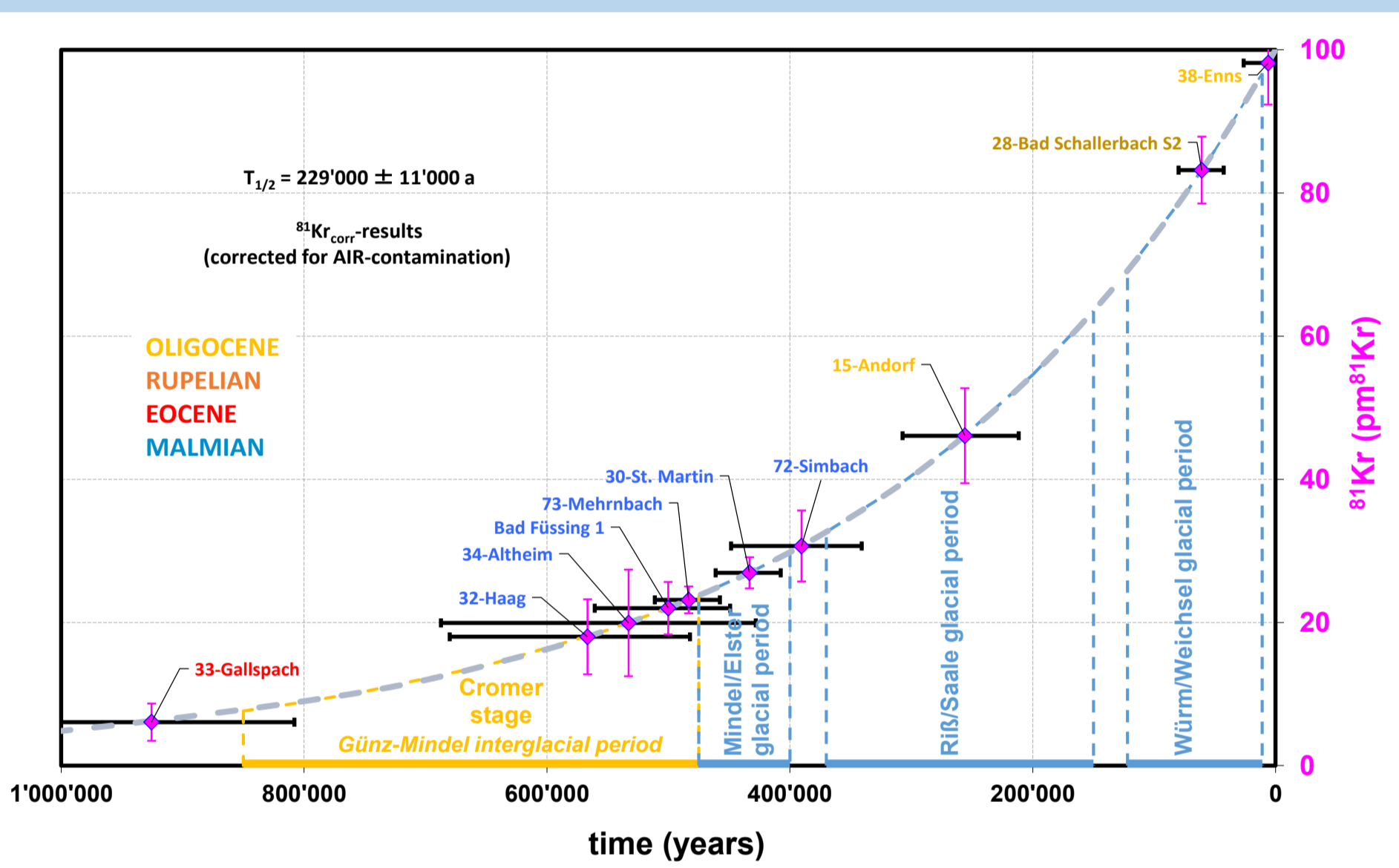
## Regional geological situation



## <sup>81</sup>Kr/<sup>85</sup>Kr results (ATA Argonne National Laboratory USA) and air contamination using <sup>85</sup>Kr<sub>atm</sub> (mean 2018/2019: ≈ 80 dpm/cc Kr measured at BFS station Schauinsland; Germany)

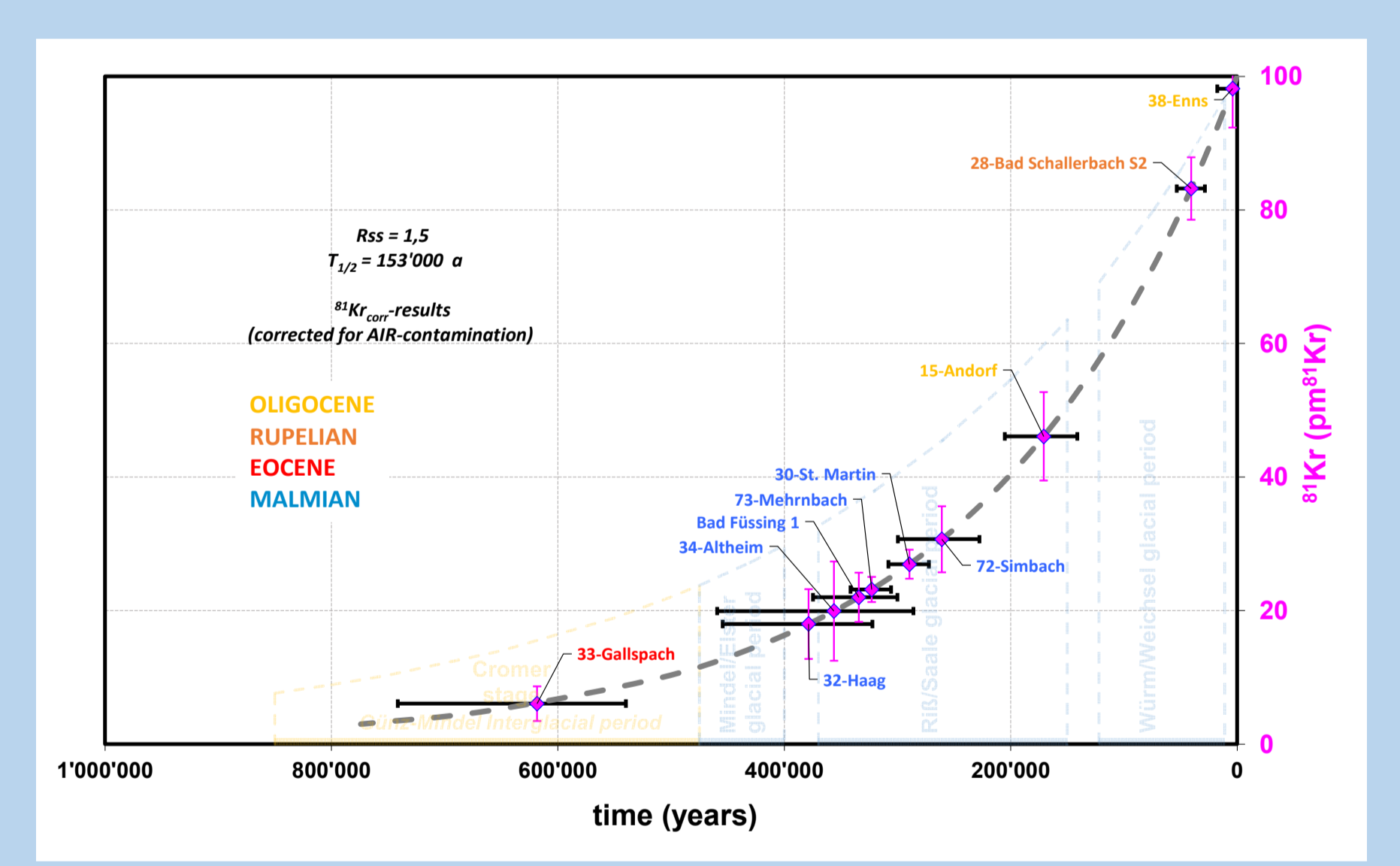
Nr.	BF	32	34	72	73	30	33	28	15	38	
date	22.09.2017	20.06.2018	20.06.2018	10.10.2018	10.10.2018	26.06.2019	26.06.2019	30.07.2019	27.06.2019	25.06.2019	
<sup>85</sup> Kr	dpm/cc Kr	0.0	0.0	9.24	1.04	0.75	1.15	9.84	3.66	22.4	0.67
±		0.48	0.56	0.79	0.39	0.1	0.11	0.39	0.22	0.7	0.09
<sup>81</sup> Kr	pm <sup>81</sup> Kr	22	18	33	32	24.1	28.4	20.1	88	85	99
±		2	3	4	3	1.2	1.4	1.2	3	3	4
AIR-contamination	%	0.6	0.7	12.54	1.79	1.06	1.58	12.79	4.85	28.88	0.95
<sup>81</sup> Kr-corr. (α)	pm <sup>81</sup> Kr	22	18	19.9	30.7	23.2	26.9	6.1	83.5	45.8	98.2
±		2	3	7.4	5.0	1.9	2.2	2.6	5.0	7.0	5.8

## „<sup>81</sup>Kr model age“



Joint presentation of the derived results for <sup>81</sup>Kr<sub>corr</sub> of the deep thermal groundwater samples along with the <sup>81</sup>Kr decay curve representing a <sup>81</sup>Kr piston flow model age. For the hydrochemically very similar, low mineralised Malm deep waters of the geothermal developments, the derived <sup>81</sup>Kr model ages fall into the phases of the Riss/Mindel glacial periods or the Cromer stage complex (alternation of cold and warm periods). A significantly higher <sup>81</sup>Kr model age of approx. 925,000 years can be derived for the more highly mineralised sample from 33-Gallsbach, which originates from the EOCENE hydrostratigraphic cover.

A further consideration of retardation processes (R<sub>ss</sub><sup>e</sup>) or 'steady state' conditions not reached leads to R<sub>ss</sub> in the range of 1.3 to max. 1.5 and a corresponding correction of the half-life (T<sub>1/2,corr</sub> 218'000 or max. 153'000 years) if the geological and hydrogeological framework conditions in the subsurface of the Aafb are treated conservatively. In conjunction with the climatic information on the formation conditions that can be derived from noble gas pattern or δ<sup>18</sup>O/δ<sup>2</sup>H signatures, however, contradictions arise when using the max. R<sub>ss</sub> factors or max. T<sub>1/2,corr</sub> of 153,000 years, which indicate an overestimation of the retardation effects.



## Results and Conclusions

<sup>81</sup>Kr investigations on nine water samples from different hydrostratigraphic units of the Austrian Alpine Foreland Basin (Aafb) imply a differentiated picture of the groundwater residence times.

Exceptional high <sup>81</sup>Kr model ages of deep MALMIAN thermal groundwater samples (around 500'000 years) would suggest low velocities (incl. the cross formation flow) which contradict the existing hydrogeological model concepts of a dynamic thermal water flow in the MALMIAN reservoir.

Very old deep groundwater portions (> 900'000 years) are visible in an EOCENE sample (33-Gallsbach) whereas samples from younger strata (RUPELIAN and OLIGOCENE) exhibit the youngest <sup>81</sup>Kr model ages (< 25'000-240'000 years).

The discrepancy between the high derived <sup>81</sup>Kr model ages of the deep MALMIAN thermal groundwaters and the current hydrogeological models could not yet be resolved. Possible explanations include diffusion processes in contact areas between the aquifers with the aquicludes and the presence of hydrocarbons within the aquifer that could influence the <sup>81</sup>Kr model ages.

The analytical methods available for this purpose (complete spectrum of the noble gas isotopes) should be carried out on samples of the migrating hydrocarbon gases in addition to the analysed deep thermal groundwaters in order to verify or approximate the subsurface processes in deep basins like the Austrian Alpine Foreland Basin.

## References:

- <sup>a</sup> 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 <sup>81</sup>Kr 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
- <sup>b</sup> 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
- <sup>c</sup> Aeschbach-Hertig W., El-Gamal H., Wieser M. and Palcu 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>
- <sup>d</sup> 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>
- <sup>e</sup> Purtschert R., Yokochi, R. & Sturchio, N. 2013. Krypton-81 dating of old groundwater, In: Isotope methods for dating old groundwater, International Atomic Energy Agency (IAEA), S. 91-124, Vienna

