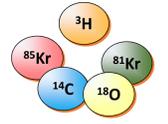


Groundwater age determination (^{81}Kr , ^{14}C etc.)

from an interval in the Beggingen Member of the calcareous Staffelegg Formation of Mont Terri Rock Laboratory

ID #574



Hydroisotop

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Introduction

Water sampling and isotope analysis from groundwater in the Beggingen Member of the Staffelegg Formation from the borehole BHS-1 in the Mont Terri Rock Laboratory (CH) as part of the HS and HS-A experiment focused on the 'Hydrogeological survey of aquifers around the Opalinus Clay'. Water collecting and rinsing in an IBC tank over a period of about 4 weeks allowed the successful sampling of enough Kr gas for the measurement of ^{81}Kr , though the water flow of about 0.25 L/min is very low.

Sampling and on-site measurement



BHS-1 borehole with sensor lines and the green outflow pipe (top), IBC tank with bottom outflow pipe, gas extraction device and the transporter (bottom) during the groundwater sampling and gas extraction.

Rinsing of IBC tank and water collection from 1st April to 29th April 2022 (1 month), filling of the tank lasts about 3 days (0.25 L/min), then overflowing on the top.

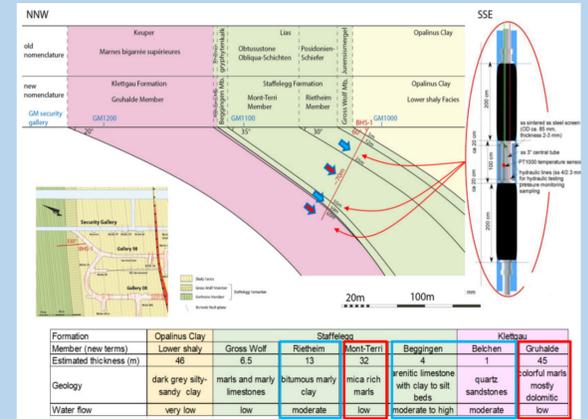
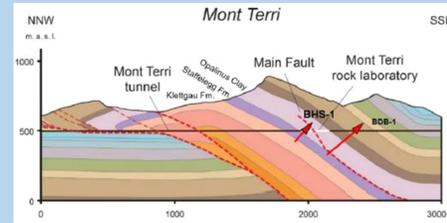
Water pressure was too low for reliable sampling for noble gas analysis (He, Ne, Ar, Kr, Xe) in copper tubes.

On-site measured O_2 is far too high for the analysed gas contents.

On-site measurement at the top of IBC		28.04.2022,		Gas composition	
Parameter	Unit	Value	Unit	Extracted	Dissolved
Temperature	[°C]	17.15			
Oxygen	[mg/L]	4.3			
Redox potential (calculated as Eh [SHE])	[mV]	247		H_2	< 0.05
Spec. electr. Conductivity (25 °C)	[µS/cm]	7'260		He	0.15
pH value		7.73		Ar	1.76
Total Alkalinity (pH 4.3)	[meq/L]	6.2		O_2	1.7
Base capacity (pH 8.2)	[meq/L]	0.44		N_2	88.1
				CO_2	7.9
				CH_4	0.074
					0.0072



Geological and hydrological situation

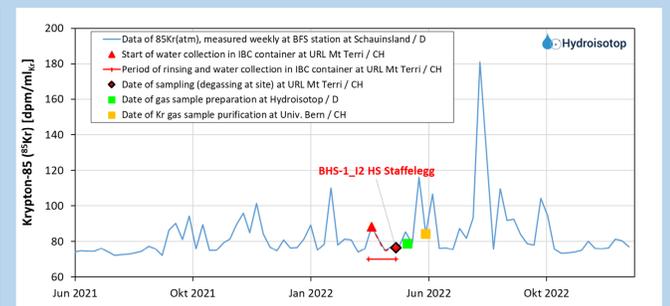


Formation	Estimated thickness (m)	Geology	Water flow
Opalinus Clay	46	dark grey silty-sandy clay	very low
Gross Wolf	6.5	marls and marly limestones	low
Rietheim	13	bituminous marly clay	moderate
Mont Terri	32	micaceous marls	low
Beggingen	4	arenitic limestone with clay to silt beds	moderate to high
Belchen	1	quartz sandstones	moderate
Grubühle	45	colorful marls mostly dolomitic	low

Inflow of water was detected at a depth of 44.63 to 48.17 m in a porous section of arenitic limestone with clay to silt beds of the Beggingen Member (former called Gryphitenkalk). The inflow at 45.84 to 47.84 m depth was separated from the rest of the borehole by a multi packer system (MPS) for long-term pressure / temperature monitoring, resulting in a flow rate of approximately 0.25 L/min.

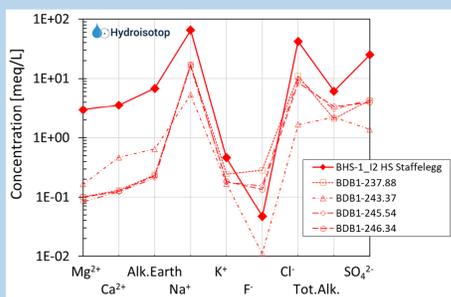
Correction of air contamination by ^{85}Kr (artificial isotope)

BHS-1_I2 Staffelegg	
$^{85}\text{Kr}_m$ [dpm/cc _{Kr}]	4.9 ± 0.3
$^{85}\text{Kr}_{corr}$ [dpm/cc _{Kr}]	5.0 ± 0.3
$^{81}\text{Kr}_m$ [pm ⁸¹ Kr]	88.0 ± 1.6
Maximum $^{85}\text{Kr}_{atm}$ [dpm/cc _{Kr}]	84.2
Maximum air contamination [%]	6.6
$^{81}\text{Kr}_{corr}$ [pm ⁸¹ Kr]	87.2 ± 2.5



Krypton-85 in air (weekly samples) measured at BFS station Schauinsland (D) and marked dates for IBC filling, gas extraction, preparation and purification for the sample BHS-1_I2.

Hydrochemical composition



Na-Cl-SO₄
TDS 4.8 g/L, Br/Cl ratio: 0.0031

Main anions and cations	[mg/L]	[meq/L]	[meq%]
Na^{2+}	1'500	66.1	90.0
K^+	18	0.5	0.6
Ca^{2+}	71	3.6	4.8
Mg^{2+}	36	3.0	4.1
Sr^{2+}	14	0.3	0.4
Total Alkalinity		6.2	8.3
Cl^-	1'500	42.3	57.0
SO_4^{2-}	1'230	25.6	34.5
Br^-	4.7	0.06	0.08
F^-	0.9	0.05	0.06

^{14}C -DIC model age: 12 to 15 thousand years

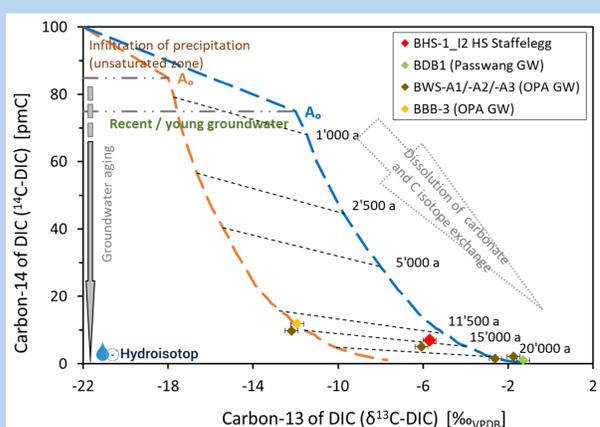
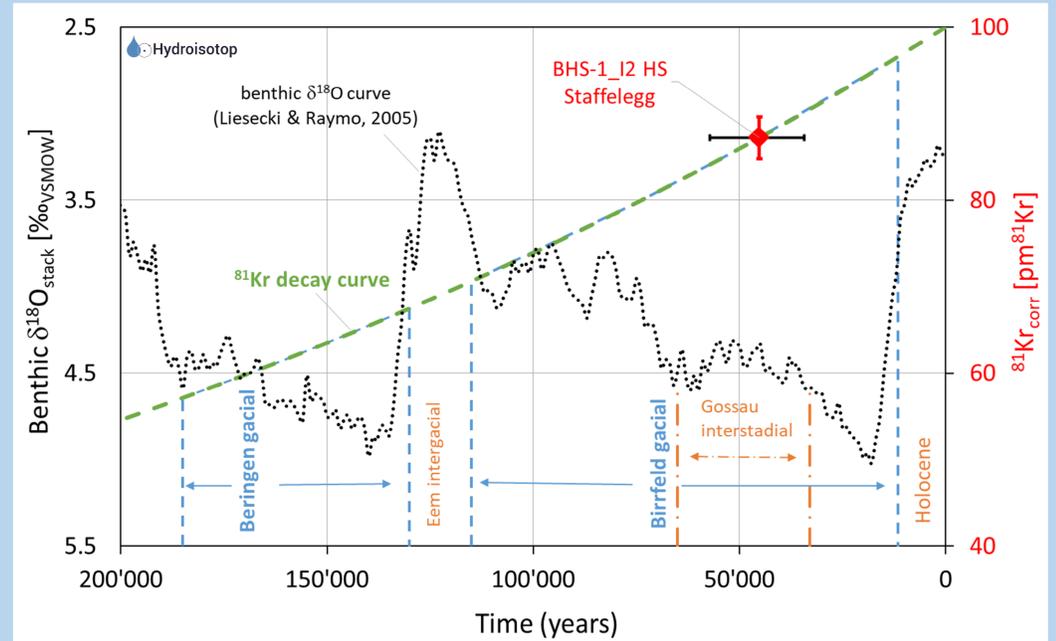


Diagram presenting the analysed $^{13}\text{C}/^{14}\text{C}$ -DIC values together with modelled development of carbon isotopes with dissolution, isotope exchange and radiocarbon decay for different rock conditions (more siliciclastic in orange, carboniferous in blue).

A contamination of the C isotopes by secondary C sources (e.g. drilling fluid) is not excluded, But a contamination of 7 pmC seems unlikely.

^{81}Kr model age: 34 to 57 thousand years



Joint representation of the derived value for $^{81}\text{Kr}_{corr}$ (with error bars) of the examined groundwater sample BHS-1_I2, the ^{81}Kr decay curve presenting a ^{81}Kr piston flow model age and the periods of the glacial and interglacial periods.

Parameter (methods)

Parameter	Method	Lab preparation	Lab measurement
Hydrochemical composition	Na-Cl-SO ₄ TDS 4.8 g/L	IC	Hydroisotop
^3H -H ₂ O	< 0.3 TU	LSC	Hydroisotop
$\delta^{18}\text{O}$ -/ $\delta^2\text{H}$ -H ₂ O	-9.86/-63.9 ‰ _{SMOW}	CRDS	Hydroisotop
$\delta^{13}\text{C}$ -DIC	-5.7 ‰ _{VPDB}	IRMS	Hydroisotop
^{14}C -DIC	7.0 ± 0.1 pmC	AMS	ETH Zurich
^{81}Kr	88.0 ± 1.6 pm ⁸¹ Kr	ATTA	Hydroisotop / Argonne Nat. Lab.
$\delta^{34}\text{S}$ -/ $\delta^{18}\text{O}$ -SO ₄	18.0/12.1 ‰ _{VCDT/NAIR}	IRMS	Hydroisotop
$^{87}\text{Sr}/^{86}\text{Sr}$	0.707765 ± 0.000050	TIMS	Hydroisotop

Results and Conclusions

Using ^{85}Kr for calculating possible air contamination, the measured result is interpreted for a ^{81}Kr model age of approximately 34 to 57 thousand years. This implies a recharge during the Birrfeld glacial, possibly within the period of Gossau interstadial.

Interpreting the ^{14}C -DIC result of 7.0 ± 0.1 pmC gives a ^{14}C model age of approximately 12 to 15 thousand years. The differences are maybe caused by a DIC contamination during the borehole exploration. The ^{14}C content in the in-situ groundwater could consequently be lower resulting in a potential higher groundwater age.

The overall hydrochemical and isotope composition of the groundwater sample including ^{81}Kr , ^{14}C , ^3H , $\delta^{18}\text{O}$ -/ $\delta^2\text{H}$ -H₂O, $\delta^{34}\text{S}$ -/ $\delta^{18}\text{O}$ -SO₄ and $^{87}\text{Sr}/^{86}\text{Sr}$ and the interpreted model ages support a groundwater system dominated by meteoric water derived during the Birrfeld glacial - maybe Gossau interstadial - and a small portion of a marine end member.

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