

Arbeitsbericht NAB 20-08

**TBO Bülach-1-1:
Data Report**

**Dossier VIII
Rock Properties, Porewater Characterisation and Natural Tracer Profiles**

March 2021

**National Cooperative
for the Disposal of
Radioactive Waste**

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Rock Properties, Porewater Characterisation and Natural Tracer Profiles

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This NAB aims at reporting drilling results at an early stage. Additional borehole-specific data will be published elsewhere.

In the event of inconsistencies between dossiers of this NAB, the dossier addressing the specific topic takes priority. In the event of discrepancies between Nagra reports, the chronologically later report is generally considered to be correct. Data sets and interpretations laid out in this NAB may be revised in subsequent reports. The reasoning leading to these revisions will be detailed there.

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Table of Contents

Table of Contents	I
List of Tables.....	IV
List of Figures	VI
Electronic Appendices.....	XI
1 Introduction	1
1.1 Context.....	1
1.2 Location and specifications of the borehole	2
1.3 Documentation structure for the BUL1-1 borehole	5
1.4 Scope and objectives of this dossier	6
2 Ancilliary geoscientific data of interest for this report.....	7
2.1 Geological information.....	7
2.2 Hydrogeological conditions.....	7
2.3 Groundwater samples	7
2.4 Structural logging	8
3 Sampling and applied methods.....	11
3.1 Sampling strategy	11
3.2 Laboratory programme	11
3.3 Analytical methods	13
3.4 Methods of raw-data processing.....	13
3.4.1 Calculations for high-salinity porewaters: Porewater content, porosities, solute concentrations	13
3.4.2 Formalisms pertinent to the evaluation of diffusive-exchange experiments	18
4 Results.....	21
4.1 Documentation of measured and calculated data	21
4.2 Mineralogical composition	23
4.2.1 Whole rock	23
4.2.2 Clay minerals.....	30
4.2.3 Sulphate minerals in the Opalinus Clay and in the confining units.....	34
4.3 Petrophysical parameters.....	38
4.3.1 Water content.....	43
4.3.2 Grain density.....	45
4.3.3 Bulk wet density	47
4.3.4 Porosity.....	47
4.3.5 N ₂ surface area (BET) and N ₂ ad-/desorption isotherms	53
4.4 Data from aqueous extraction tests.....	63
4.4.1 Sample material and overview of analytical work.....	64

4.4.2	Aqueous extraction tests at different S*/L* ratios	65
4.4.2.1	Anion concentrations (Cl, Br, SO ₄ , F, alkalinity)	66
4.4.2.2	Cation concentrations (Na, K, Ca, Mg, Sr)	69
4.4.2.3	Mineral saturation states and partial pressure of CO ₂ (P _{CO2})	70
4.4.3	AqEx tests at S*/L* ratio of 1	71
4.4.3.1	Comparison of different data sets	72
4.4.3.2	Anion concentrations (Cl, Br, SO ₄ , F, alkalinity)	73
4.4.3.3	Cation concentrations (Na, K, Mg, Ca, Sr)	80
4.4.3.4	Mineral saturation states	84
4.4.3.5	Cl-isotopes in AqEx solutions	87
4.4.4	Chloride and bromide concentrations at water-loss porosity	88
4.5	Cation-exchange extraction data	92
4.6	Data from squeezing experiments	98
4.6.1	Mass recovery	99
4.6.2	Chemical composition of squeezed waters	102
4.6.3	Depth trends	106
4.6.4	Geochemical modelling and mineral saturation states	108
4.6.5	Water content and aqueous extraction of squeezed core material	110
4.6.6	Chloride-accessible porosity	110
4.6.7	Stable isotopic composition of squeezed water	113
4.7	Data from advective displacement experiments	116
4.7.1	Sample material and overview of analytical work	116
4.7.2	Conditions of advective displacement experiments	118
4.7.3	Mineralogy and petrophysical properties	119
4.7.4	Aqueous extracts, CEC and cation selectivity of AD samples	124
4.7.5	Chemical and isotopic evolution of displaced porewater aliquots	131
4.7.5.1	Artificial porewater used for advective displacement	131
4.7.5.2	Physical conditions, hydraulic conductivity, sampling, and pore volume equivalents	133
4.7.5.3	Inline measurement of electric conductivity and pH	134
4.7.5.4	Evolution of major and minor components	136
4.7.5.5	Early displaced aliquots representing the porewater composition	146
4.7.5.6	Initial values and evolution of stable water isotope composition	148
4.7.6	Derivation of anion-accessible porosity	150
4.7.7	Transport properties marked by breakthrough of $\delta^2\text{H}$, $\delta^{18}\text{O}$, Cl and Br	151
4.7.8	Concluding remarks and open issues	154
4.8	Data from out-diffusion experiments	154
4.8.1	Sample material and overview of analytical work	155
4.8.2	Mineralogy and petrophysical properties	156
4.8.3	Final OD experiment solutions	159

4.8.3.1	Chemical composition of final solutions	162
4.8.3.2	Mineral saturation states	166
4.8.4	Solute elution curves (time-series)	168
4.8.5	Concentrations of Cl and Br at water-loss porosity	172
4.9	Water-isotope data from diffusive-exchange experiments	173
5	Discussion of porewater data	179
5.1	Chloride data and estimation of Cl ⁻ and Br ⁻ -accessible porosity	179
5.2	Chloride, bromide and Br/Cl profiles	182
5.3	Sulphate and SO ₄ /Cl profiles	187
5.4	Some details related to the Muschelkalk aquifer and adjacent units	191
5.4.1	Localisation of the aquifer	191
5.4.2	Depth profiles of Cl ⁻ and water isotopes in the vicinity of the Muschelkalk aquifer	192
5.5	Cation concentrations in porewaters.....	194
5.5.1	General considerations.....	194
5.5.2	Constraints from aqueous extract data.....	195
5.5.3	Constraints from porewater squeezing and advective displacement data.....	195
5.5.3.1	Differences and commonalities between porewaters obtained from squeezing and advective displacement	197
5.5.3.2	Significance of porewater aliquots from advective displacement	198
5.5.3.3	The sulphate issue and its link to porewater cation concentrations	199
5.5.4	Implications for defining formation and location-specific porewaters.....	199
5.6	Dissolved carbon species (inorganic, organic), alkalinity, pH, and P _{CO2}	200
5.6.1	General considerations.....	200
5.6.2	Organic carbon	200
5.6.3	Dissolved inorganic carbon, alkalinity	204
5.6.4	pH and partial pressure of CO ₂	204
5.7	Cation exchange capacity and exchangeable cation population.....	205
5.7.1	Corrected exchangeable cation data	205
5.7.2	Comparison with data from PSI	209
5.7.3	Summary and conclusions	215
5.8	Stable water isotopes	216
5.8.1	Comparison between different methods for the determination of stable porewater isotope compositions	216
5.8.2	Comparison with groundwater data and depth profiles	216
5.8.3	δ ¹⁸ O versus δ ² H and comparison with Global Meteoric Water Line (GMWL)....	217
6	Final remarks and main conclusions	219
7	References.....	223

List of Tables

Tab. 1-1:	General information about the BUL1-1 borehole.....	2
Tab. 1-2:	List of dossiers included in NAB 20-08	5
Tab. 2-1:	Results of hydraulic packer tests	7
Tab. 2-2:	Conservative parameters for waters from the Malm and Muschelkalk aquifers corrected for drilling fluid contamination.....	8
Tab. 2-3:	Fault zones in the cored section of the BUL1-1 borehole	8
Tab. 3-1:	Sample types and sampling strategy.....	11
Tab. 3-2:	Numbers of samples analysed for the different geological units.....	12
Tab. 3-3:	Analytical programme performed for the different sample types.....	12
Tab. 4.2-1:	Bulk-rock mineralogy: formation-specific means, medians, standard deviations and ranges.....	23
Tab. 4.2-2:	Mineralogical composition of the clay fraction: formation-specific means, medians, standard deviations and ranges.....	31
Tab. 4.2-3:	Samples selected for SEM studies	34
Tab. 4.3-1:	Summary of measured and calculated petrophysical data	39
Tab. 4.4-1:	Summary of analytical work performed on samples for aqueous extraction tests..	65
Tab. 4.4-2:	Stratigraphy and lithology of samples used for AqEx tests at different S*/L* ratios	66
Tab. 4.4-3:	Summary of mineralogical and petrophysical data of individual samples used for AqEx tests at different S*/L* ratios	66
Tab. 4.5-1:	Cation data from Ni-en extracts at a S/L ratio around 1 (University of Bern data).....	93
Tab. 4.5-2:	Anion data from Ni-en extracts (University of Bern data)	94
Tab. 4.5-3:	Cation data from Ni-en extracts carried out at variable S/L ratios (University of Bern data).....	95
Tab. 4.6-1:	Mineralogical composition of samples subjected to squeezing experiments	99
Tab. 4.6-2:	Water mass squeezed at different pressure steps	100
Tab. 4.6-3:	Chemical composition of squeezed waters: full data set	103
Tab. 4.6-4:	Chemical composition of squeezed waters: summary of selected analyses to be used for interpretation.....	104
Tab. 4.6-5:	Mineral saturation indices for squeezed waters.....	109
Tab. 4.6-6:	Water contents and results of aqueous-extraction tests on previously squeezed samples.....	110
Tab. 4.6-7:	Anion-accessible porosity fractions derived from squeezing and aqueous-extraction experiments	112
Tab. 4.6-8:	Stable isotopic composition of squeezed waters.....	114

Tab. 4.7-1: Summary of analytical work performed on samples for advective displacement experiments.....	118
Tab. 4.7-2: Conditions of advective displacement experiments.....	119
Tab. 4.7-3: Mineralogy of advective displacement samples, including C and S analyses.....	120
Tab. 4.7-4: Core dimensions and derived petrophysical parameters.....	121
Tab. 4.7-5: Composition of aqueous extract solutions from pre-characterisation.....	124
Tab. 4.7-6: Cation ratios and details of carbon system in aqueous extract solutions from pre-characterisation.....	125
Tab. 4.7-7: Saturation indices calculated for aqueous extract solutions from pre-characterisation.....	126
Tab. 4.7-8: Composition of aqueous extract solutions from post-mortem characterisation....	127
Tab. 4.7-9: Saturation indices calculated for aqueous extract solutions obtained post-mortem.....	128
Tab. 4.7-10: Composition of Ni-en extract solutions and related parameters from pre-characterisation.....	129
Tab. 4.7-11: Composition of Ni-en extract solutions and related parameters obtained post-mortem.....	130
Tab. 4.7-12: Composition and recipe for the artificial porewater	132
Tab. 4.7-13: Recipe for the artificial porewater for a 2-litre batch	132
Tab. 4.7-14: Hydraulic conductivity of AD samples	134
Tab. 4.7-15: Composition of earliest aliquots from advective displacement experiments.....	147
Tab. 4.7-16: Saturation state of earliest aliquots from advective displacement experiments....	148
Tab. 4.7-17: Chloride and bromide-accessible porosity fractions.....	151
Tab. 4.8-1: Summary of analytical work performed on samples for out-diffusion experiments.....	157
Tab. 4.8-2: Mineralogy and CNS-data and isotope composition of matrix calcite of OD samples.....	158
Tab. 4.8-3: Core dimensions and petrophysical parameters derived of OD samples.....	160
Tab. 5.7-1: Sum of cations and cation occupancies obtained from Ni-en extraction after correction (University of Bern data).....	206
Tab. 5.7-2: Extraction conditions applied by the University of Bern and PSI	209

List of Figures

Fig. 1-1:	Tectonic overview map with the three siting regions under investigation	1
Fig. 1-2:	Overview map of the investigation area in the Nördlich Lägern siting region with the location of the BUL1-1 borehole and the existing Weiach-1 borehole	3
Fig. 1-3:	Lithostratigraphic profile and casing scheme for the BUL1-1 borehole	4
Fig. 4.2-1:	Mineral contents in the bulk rock as a function of depth.....	26
Fig. 4.2-2:	Mineralogical composition of studied samples in the Füchtbauer triangle	27
Fig. 4.2-3:	Depth trends of mineral contents in the bulk rock in the interval Staffelegg Formation – Wedelsandstein Formation.....	29
Fig. 4.2-4:	Mineralogical composition of the clay fraction as a function of depth	33
Fig. 4.2-5:	Depth trends of clay minerals in the bulk rock in the interval Staffelegg Formation – Wedelsandstein Formation.....	34
Fig. 4.2-6:	BE image of sample 881.54 (Wedelsandstein Formation) with locations high in Ca, S and low in Fe shown in red.....	36
Fig. 4.2-7:	BE image of sample 897.27 (Opalinus Clay) with possible Ca sulphate locations overlaid in red.....	36
Fig. 4.2-8:	BE image of sample 889.36 ('Murchisonae-Oolith Formation') with possible Ca sulphate locations overlaid in red.....	37
Fig. 4.3-1:	Water content as a function of depth	43
Fig. 4.3-2:	Correlation of water contents based on gravimetry and on isotope diffusive exchange	44
Fig. 4.3-3:	Water content (wet) as a function of depth in the interval Staffelegg Formation – Wedelsandstein Formation.....	45
Fig. 4.3-4:	Depth profile of bulk wet and grain densities.....	46
Fig. 4.3-5:	Grain density as a function of the contents of anhydrite and dolomite/ankerite.....	47
Fig. 4.3-6:	Water-loss porosity calculated from gravimetric water content using either bulk wet or grain density	48
Fig. 4.3-7:	Correlation of water-loss porosity and porosity from isotope diffusive exchange	49
Fig. 4.3-8:	Correlation of pycnometer porosity and porosity from isotope diffusive exchange	49
Fig. 4.3-9:	Correlation of water-loss and pycnometer porosity.....	50
Fig. 4.3-10:	Depth trends of porosities obtained by different methods	51
Fig. 4.3-11:	Porosity as a function of clay-mineral content	52
Fig. 4.3-12:	Best fits to the correlation between clay-mineral content and porosity.....	52
Fig. 4.3-13:	Porosity of anhydrite-bearing samples	53
Fig. 4.3-14:	Depth profile of specific surface areas (S_{BET}) derived from N_2 adsorption	54
Fig. 4.3-15:	Specific surface areas (S_{BET}) derived from N_2 adsorption plotted against the bulk dry density of the samples	55

Fig. 4.3-16: Specific surface areas (S_{BET}) derived from N_2 adsorption plotted against the gravimetric water content per dry mass of the samples	56
Fig. 4.3-17: Relation between external specific surface area (S_{BET}) derived from N_2 adsorption and content of clay minerals	57
Fig. 4.3-18: Relation between external specific surface area (S_{BET}) derived from N_2 adsorption and contents of specific clay end-members	58
Fig. 4.3-19: Average external pore radius calculated from S_{BET} and the gravimetric water content (assuming insignificant interlayer pore volume) plotted against the gravimetric dry water content of the samples (a) and against the total clay mineral content (b).....	59
Fig. 4.3-20: Distribution of (external) pore sizes derived from N_2 desorption for (a) limestone and (sample BUL1-1 1'002.19) calcareous marl samples, (b) (argillaceous) sandstone/ siltstone samples, (c) (sandy/silty) claystone and argillaceous marl samples, and (d) dolostone samples	61
Fig. 4.3-21: Comparison of maximum amount of adsorbed N_2 (recalculated to H_2O wt.-%) with water content per dry sample mass.....	62
Fig. 4.3-22: Average external pore radius (assuming insignificant interlayer pore volume) based on the BJH pore size distribution from the N_2 isotherms (closed symbols: adsorption; open symbols: desorption) plotted against the gravimetric dry water content of the samples (a) and against the total clay mineral content (b).....	63
Fig. 4.4-1: Chloride concentrations vs. the S^*/L^* ratio in AqEx solutions from rocks of variable mineralogy of formations from the Malm, Dogger and Lias.....	67
Fig. 4.4-2: Chloride vs. Br concentrations in AqEx solutions at different S^*/L^* ratios from rocks of variable mineralogy of formations from the Malm, Dogger and Lias.....	68
Fig. 4.4-3: Sulphate concentrations vs. the S^*/L^* ratio in AqEx solutions from rocks of variable mineralogy of formations from the Malm, Dogger and Lias.....	69
Fig. 4.4-4: Values of pH (solid symbols) and partial pressure of CO_2 (P_{CO_2} ; open symbols) of AqEx solutions from rocks of variable mineralogy of formations from the Malm ('Felsenkalke' / 'Massenkalk', Wildegg Formation), Dogger ('Herrenwis Unit', Wedelsandstein Formation, Opalinus Clay) and Lias (Staffelegg Formation).....	71
Fig. 4.4-5: Cl concentrations in AqEx solutions vs. depth of rocks from the Malm to the Muschelkalk in borehole BUL1-1	74
Fig. 4.4-6: Photograph of sample BUL1-1 1'192.08 (Leutschenberg & Kienberg Members of the Schinznach Formation, former Hauptmuschelkalk) with stylolites (black) and a chaotic set of microfractures with darker halos.....	75
Fig. 4.4-7: Cl vs. Br in AqEx solutions of rocks from the Malm to the Muschelkalk in borehole BUL1-1	76
Fig. 4.4-8: $\text{Br}^*1'000/\text{Cl}$ ratio in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	77
Fig. 4.4-9: SO_4 in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1 in comparison with sulphide and sulphate mineral contents of the different lithologies	78

Fig. 4.4-10: SO ₄ /Cl ratio in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	79
Fig. 4.4-11: Na/Cl in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	80
Fig. 4.4-12: Na/K in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	81
Fig. 4.4-13: (Ca+Mg)/(Na+K) in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	82
Fig. 4.4-14: Sr in AqEx of rocks from the Malm to the Muschelkalk in borehole BUL1-1 in comparison with sulphide and sulphate mineral contents of the different lithologies	84
Fig. 4.4-15: Sr in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1 in comparison with the clay content of the different lithologies	85
Fig. 4.4-16: Saturation index of celestite in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	87
Fig. 4.4-17: Cl isotopes, expressed as $\delta^{37}\text{Cl}$, in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	88
Fig. 4.4-18: Cl concentration at WL-Porosity as derived from AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	91
Fig. 4.4-19: Br concentration at WL-Porosity as derived from AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1	92
Fig. 4.5-1: Depth profile of Ni consumption and sum of cations (uncorrected)	96
Fig. 4.5-2: Ni consumption vs. clay-mineral content and content of the smectite end-member	96
Fig. 4.5-3: Depth profiles of Ca/Na and (Ca+Mg)/Na ratios in Ni-en extracts	97
Fig. 4.6-1: Cumulative water mass obtained by squeezing as a function of the squeezing pressure	101
Fig. 4.6-2: Correlation of the original water content and total water mass obtained by squeezing	102
Fig. 4.6-3: Ion concentrations in squeezed waters as a function of squeezing pressure.....	105
Fig. 4.6-4: Depth trends of ion concentrations and ion ratios in squeezed waters	107
Fig. 4.6-5: Cl ⁻ -accessible porosity fractions derived from squeezing experiments as a function of the clay-mineral content	112
Fig. 4.6-6: Depth trends of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in squeezed waters	113
Fig. 4.6-7: Plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for squeezed waters.....	115
Fig. 4.6-8: Depth trend of deuterium excess	115
Fig. 4.7-1: Location of samples used for advective displacement experiments (red dots).....	116
Fig. 4.7-2: X-ray CT images of AD samples.....	117
Fig. 4.7-3: Details of water content measurements before and after AD experiments.....	123

Fig. 4.7-4: Evolution of hydraulic conductivity during advective displacement experiments.....	133
Fig. 4.7-5: Sampling schedule and sample volumes taken.....	134
Fig. 4.7-6: Evolution of electric conductivity (22 °C) during advective displacement experiments.....	135
Fig. 4.7-7: Evolution of inline pH during advective displacement experiments	136
Fig. 4.7-8: Evolution of major components during advective displacement experiments	138
Fig. 4.7-9: Evolution of select major components during advective displacement experiments.....	139
Fig. 4.7-10: Evolution of minor components during advective displacement experiments	141
Fig. 4.7-11: Evolution of select minor components during advective displacement experiments.....	142
Fig. 4.7-12: Evolution of carbon system during advective displacement experiments	143
Fig. 4.7-13: Evolution of select carbon components during advective displacement experiments.....	144
Fig. 4.7-14: Evolution of pH during advective displacement experiments	145
Fig. 4.7-15: Evolution of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ during advective displacement experiments.....	149
Fig. 4.7-16: Stable isotope composition of aliquots from advective displacement experiments.....	150
Fig. 4.7-17: Breakthrough of Cl, Br, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ during advective displacement experiments.....	153
Fig. 4.8-1: Sub-cored limestone cylinders subjected to OD experiments from the 'Felsenkalk' / 'Massenkalk' (top) and the Villigen Formation (bottom left) of the Malm, and the 'Herrenwis Unit' (bottom right) of the Dogger	156
Fig. 4.8-2: Bulk wet density derived from volume and mass of OD and AD core samples compared to values obtained by paraffin-displacement of PW samples	161
Fig. 4.8-3: Grain density derived by He-pycnometry on OD and PW samples compared to values obtained from volume and mass of AD samples.....	161
Fig. 4.8-4: Water-loss porosity of OD core samples compared to values of PW and AD samples.....	162
Fig. 4.8-5: Cl concentrations in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth.....	164
Fig. 4.8-6: Br concentrations in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth.....	164
Fig. 4.8-7: Br/Cl ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth	165
Fig. 4.8-8: Na/Cl ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth	165
Fig. 4.8-9: SO_4/Cl ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth	167

Fig. 4.8-10: Sr/SO ₄ ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth	167
Fig. 4.8-11: Ca/Mg ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth	168
Fig. 4.8-12: Elution curves of Cl (left) and Br (right) during out-diffusion over 198 days at 45 °C in OD experiments.....	170
Fig. 4.8-13: Evolution of Br/Cl (left) and Na/Cl (right) ratios during out-diffusion over 198 days at 45 °C in OD experiments	170
Fig. 4.8-14: Elution curves of SO ₄ (left) and F (right) during out-diffusion over 198 days at 45 °C in OD experiments.....	171
Fig. 4.8-15: Elution curves of Sr (left) and Mg (right) during out-diffusion over 198 days at 45 °C in OD experiments.....	171
Fig. 4.8-16: Cl concentration at water-loss porosity (WL-P) derived from OD experiments and compared to those derived from AqEx solutions of PW and AD samples as a function of depth.....	172
Fig. 4.8-17: Br concentration at water-loss porosity (WL-P) derived from OD experiments and compared to those derived from AqEx solutions of PW and AD samples as a function of depth.....	173
Fig. 4.9-1: Relative deviation of water contents obtained from $\delta^{18}\text{O}$ and $\delta^2\text{H}$ mass balance.....	174
Fig. 4.9-2: Depth trends of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in porewater based on the isotope diffusive exchange technique.....	175
Fig. 4.9-3: Depth trend of Deuterium excess in porewater based on the isotope diffusive exchange technique.....	176
Fig. 4.9-4: $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for porewaters based on the isotope diffusive exchange technique.....	177
Fig. 5.1-1: Anion-accessible porosity fraction as a function of clay mineral content (left: Cl, right: Br).....	180
Fig. 5.1-2: Cl-accessible porosity fraction as a function of depth.....	181
Fig. 5.2-1: Cl profile with data from squeezing, advective displacement, aqueous extraction, and groundwater samples.....	184
Fig. 5.2-2: Cl in anion-accessible porewater in the Opalinus Clay and in the Staffelegg Formation using an alternative approach to constrain anion accessibility	185
Fig. 5.2-3: Br and Br/Cl profiles with data from squeezing, advective displacement, aqueous extraction and groundwater samples	186
Fig. 5.2-4: $\delta^{37}\text{Cl}$ profile for aqueous extracts, rock-forming halite and groundwaters.....	187
Fig. 5.3-1: SO ₄ profile with data from squeezing, advective displacement, aqueous extraction, and groundwater samples.....	189
Fig. 5.3-2: SO ₄ profile with data from aqueous and Ni extraction, compared with squeezing, advective displacement and groundwater data	190
Fig. 5.3-3: Profiles showing molar SO ₄ /Cl ratios obtained from different methods in logarithmic and linear scales	191

Fig. 5.4-1:	Vertical joint in the dolomites of the Stamberg Member (Schinznach Formation)	193
Fig. 5.4-2:	Depth profile of Cl ⁻ concentrations in pore- and groundwater in the Muschelkalk.....	194
Fig. 5.5-1:	Concentrations of Na and Ca in aliquots from squeezing experiments and advective displacement experiments.....	196
Fig. 5.5-2:	Concentrations of K, Mg and Sr in aliquots from squeezing experiments and advective displacement experiments.....	197
Fig. 5.6-1:	TOC (total organic carbon) in rock samples.....	201
Fig. 5.6-2:	TOC in aliquots from AD and SQ, and upscaled from aqueous extracts	202
Fig. 5.6-3:	LWMOA (acetate and formate) for AD aliquots and recalculated aqueous extract data.....	203
Fig. 5.7-1:	Ni consumption vs. sum of cations (data of the University of Bern)	207
Fig. 5.7-2:	CEC parameters as a function of clay-mineral content (data of the University of Bern).....	208
Fig. 5.7-3:	CEC parameters as a function of BET surface area (data of the University of Bern).....	208
Fig. 5.7-4:	Comparison of CEC data from the University of Bern and from PSI	211
Fig. 5.7-5:	Differences pertaining to Ni consumption and corrected sums of cations for the six samples studied by both University of Bern and PSI	211
Fig. 5.7-6:	Na (left) and Ca (right) occupancies according to University of Bern and PSI data.....	213
Fig. 5.7-7:	K ⁺ and NH ₄ occupancies according to University of Bern and PSI data.....	213
Fig. 5.7-8:	Content of the illite end-member vs. extracted K.....	214
Fig. 5.7-9:	Mg (left) and Sr (right) occupancies according to University of Bern and PSI data.....	214
Fig. 5.8-1:	Depth trends of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in porewater based on all available technique, together with groundwater data	217
Fig. 5.8-2:	$\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for porewaters based on the isotope diffusive exchange technique.....	218

Electronic Appendices

- Appendix 1 Comprehensive data base with results of laboratory analyses (xls format)
- Appendix 2 Results of aqueous-extraction tests at different solid/liquid ratios, mineral saturation indices (xls format)
- Appendix 3 Detailed documentation of advective displacement experiments (xls format)
- Appendix 4 Detailed documentation of out-diffusion experiments (xls format)
- (Available upon request)*

1 Introduction

1.1 Context

To provide input for site selection and the safety case for deep geological repositories for radioactive waste, Nagra has drilled a series of deep boreholes in Northern Switzerland. The aim of the drilling campaign is to characterise the deep underground of the three remaining siting regions located at the edge of the Northern Alpine Molasse Basin (Fig. 1-1).

In this report, we present the results from the Bülach-1-1 borehole.

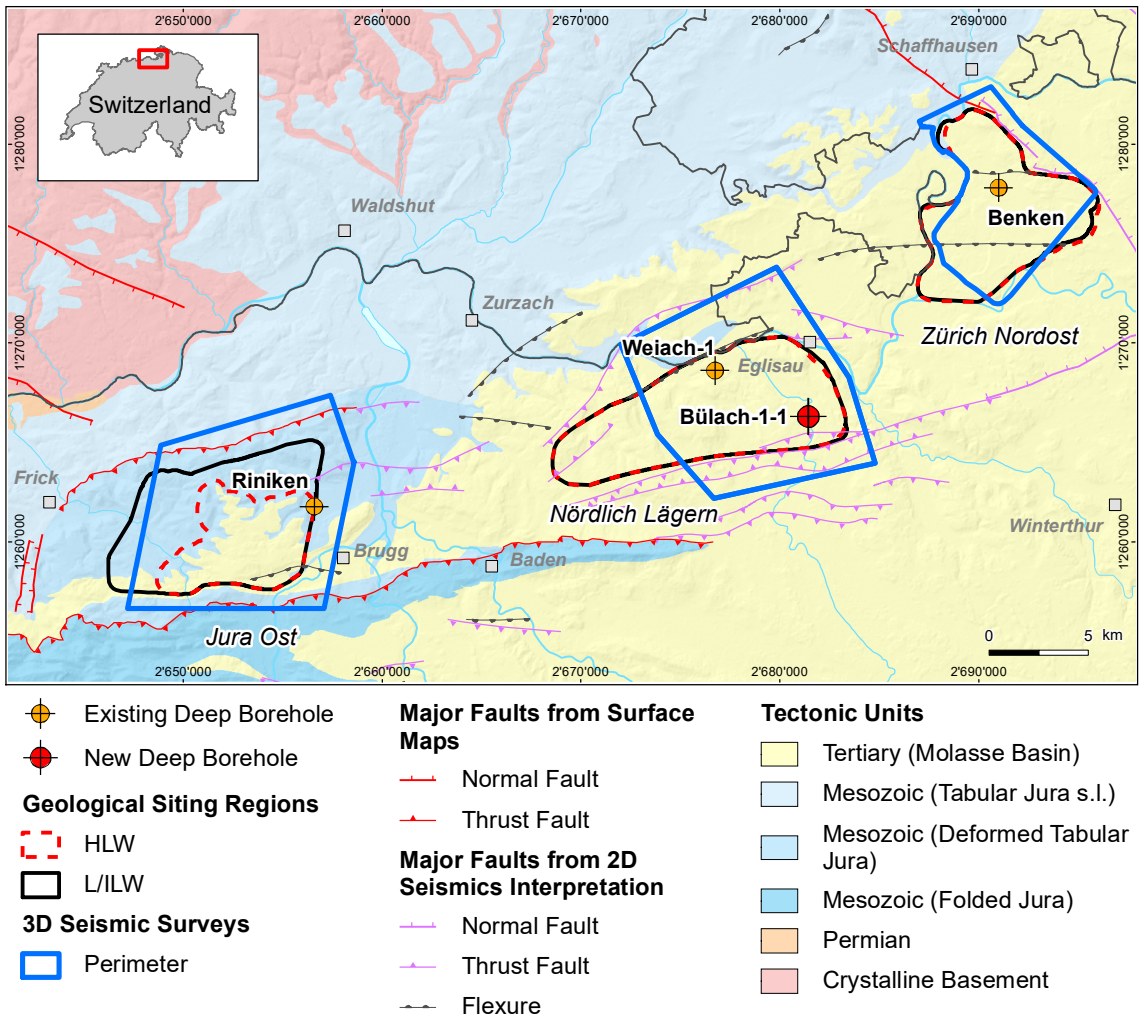


Fig. 1-1: Tectonic overview map with the three siting regions under investigation

1.2 Location and specifications of the borehole

The Bülach-1-1 (BUL1-1) exploratory borehole is the first deep borehole drilled within the framework of the TBO project. BUL1-1 is a vertical borehole. The drill site is located in the south-eastern part of the Nördlich Lägern siting region (Fig. 1-2). The borehole specifications are provided in Tab. 1-1. The lithostratigraphic profile and the casing scheme are shown in Fig. 1-3. Due to instabilities, the borehole was plugged back from 1'043.00 m to 918.70 m (*cf.* Dossier I). Resuming coring operations, a sidetrack was initiated with a kickoff point at 995.85 m. This sidetrack was labelled Bülach-1-1B (BUL1-1B). BUL1-1B reached the final depth of 1'370.19 m (measured depth MD core depth)¹. For easier communication and labelling, the name BUL1-1 is generally used for the complete vertical borehole unless stated otherwise. Fig. 1-3 shows the combined lithostratigraphic profile of BUL1-1.

Tab. 1-1: General information about the BUL1-1 borehole

Location	Bülach (Canton Zurich / ZH), Switzerland
Siting region	Nördlich Lägern
Coordinates	2'681'446.028 / 1'266'298.472
Elevation	389.62 m asl (top of rig cellar)
Borehole depth	1'370.19 m MD core depth
Drilling period	15 April 2019 – 27 November 2019 (spud – rig release)
Drilling company	Daldrup & Söhne AG
Drilling rig	Wirth B 152t
Drilling fluid	Water-based mud with varying amounts of Pure-Bore®, Pure-Bore® ULV, soda ash, sodium bicarbonate, xanthan gum

¹ *Measured depth (MD)* below top rig cellar along borehole trajectory. In all dossiers, depth refers to MD unless stated otherwise.

MD core depth refers to the depth marked on the cores. Note that petrophysical logs have not been shifted to core depth, hence MD log depth differs from MD core depth. The depth shift between core depth and log depth is documented in Dossier V, Appendix E-1.

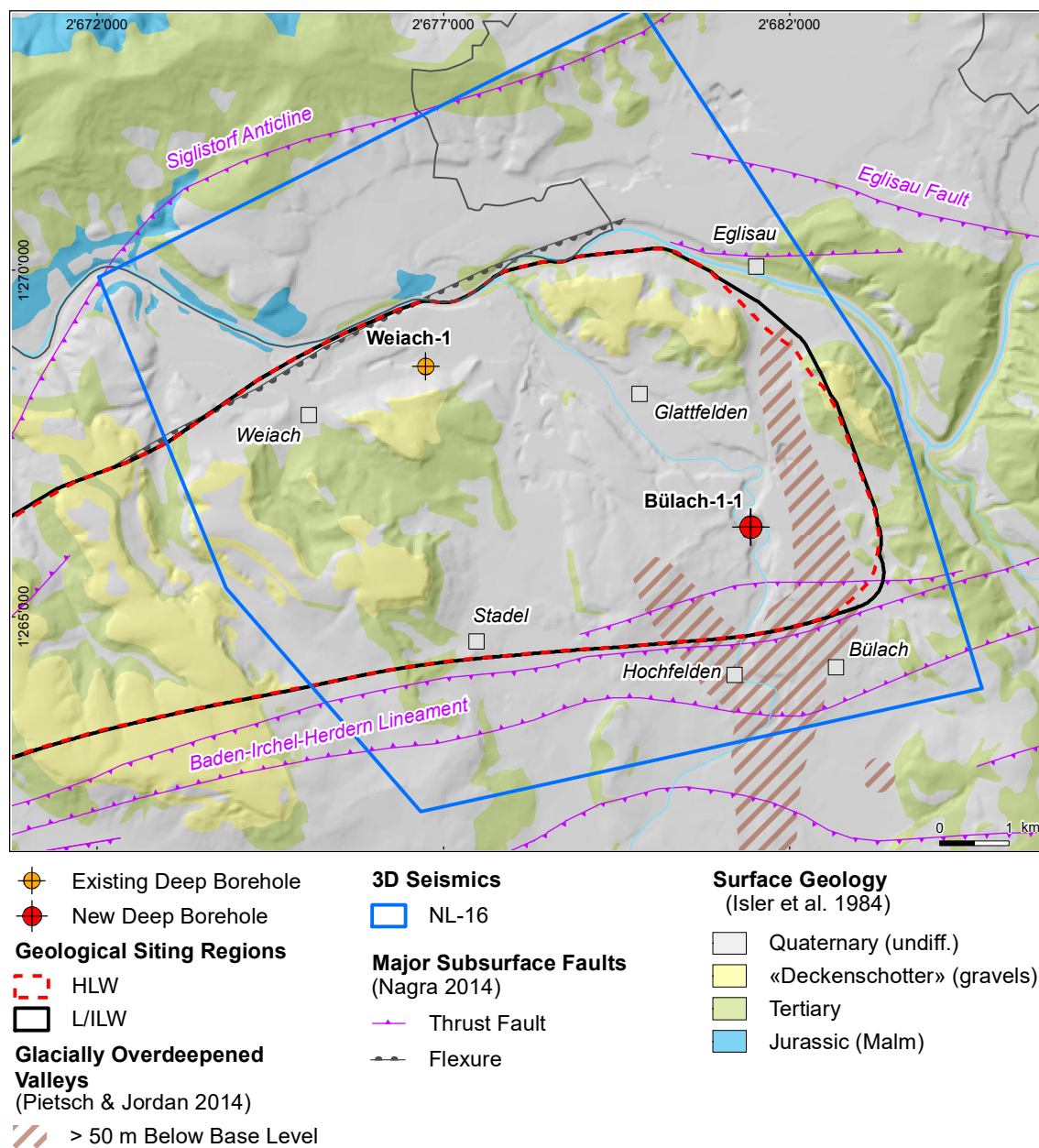


Fig. 1-2: Overview map of the investigation area in the Nördlich Lägern siting region with the location of the BUL1-1 borehole and the existing Weiach-1 borehole

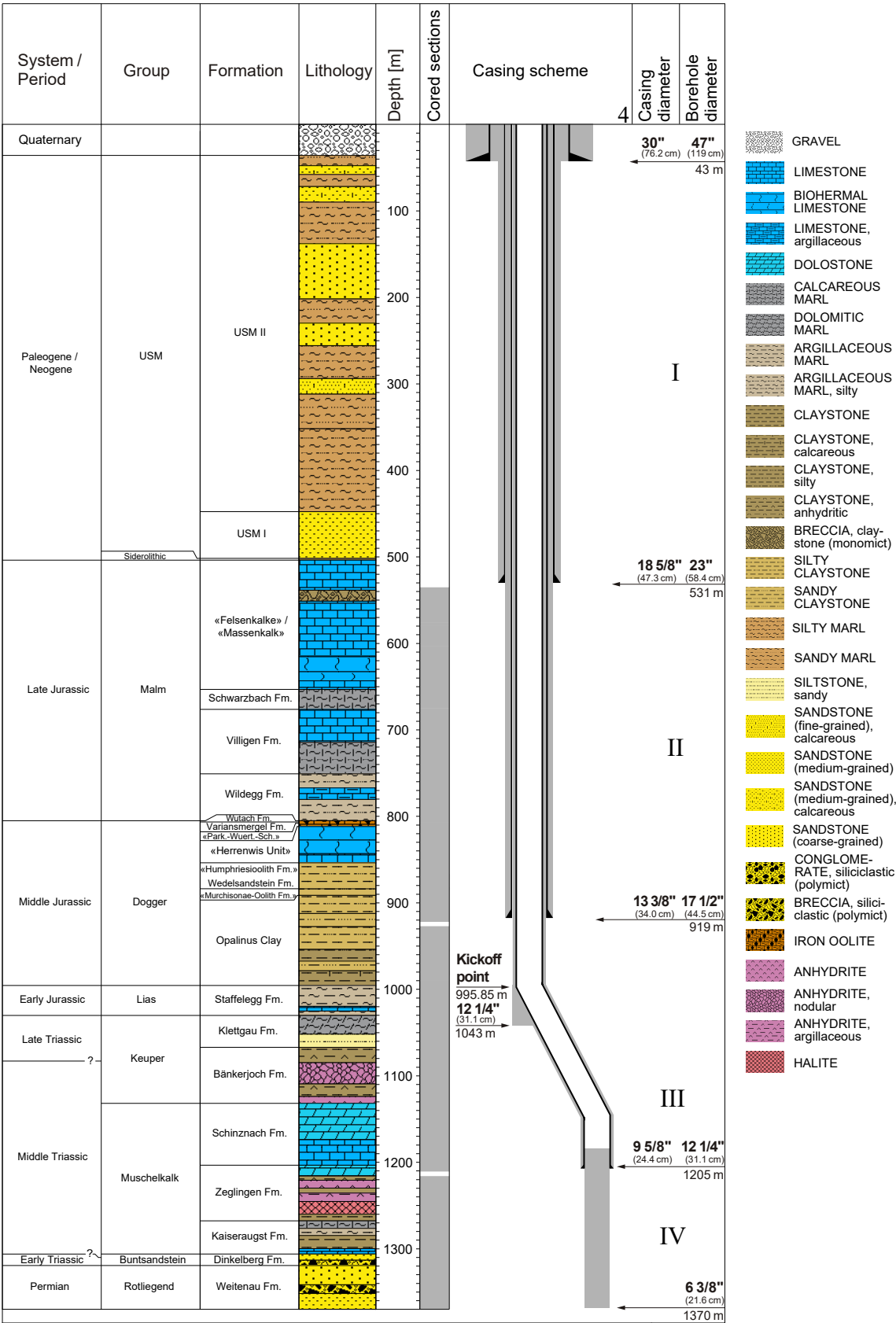


Fig. 1-3: Lithostratigraphic profile and casing scheme for the BUL1-1 borehole

1.3 Documentation structure for the BUL1-1 borehole

NAB 20-08 documents the majority of the investigations carried out in the BUL1-1 borehole, including laboratory investigations on core material. The NAB comprises a series of stand-alone dossiers addressing individual topics and a final dossier with a summary composite plot (Tab. 1-2).

This borehole documentation aims at early publication of the data collected in the BUL1-1 borehole. It includes the majority of the data available approximately one year after completion of the borehole. Some analyses are still ongoing (e.g. diffusion experiments, analysis of veins, hydrochemical interpretation of water samples) and will be published in separate reports.

The current borehole report will provide an important basis for the integration of datasets from different boreholes. The integration and interpretation of the results in the wider geological context will be documented later in separate geoscientific reports.

Tab. 1-2: List of dossiers included in NAB 20-08

Black marks the dossier at hand.

Dossier	Title	Authors
I	TBO Bülach-1-1: Drilling	M. Ammen & P.-J. Palten
II	TBO Bülach-1-1: Core Photography	D. Kaehr & M. Gysi
III	TBO Bülach-1-1: Lithostratigraphy	P. Jordan, H. Naef, P. Schürch, M. Schwarz, T. Ibele, R. Felber & M. Gysi
IV	TBO Bülach-1-1: Microfacies, Bio- and Chemostratigraphic Analysis	S. Wohlwend, H.R. Bläsi, S. Feist-Burkhardt, B. Hostettler, U. Menkveld-Gfeller, V. Dietze & G. Deplazes
V	TBO Bülach-1-1: Structural Geology	A. Ebert, L. Gregorczyk, E. Hägerstedt & M. Gysi
VI	TBO Bülach-1-1: Wireline Logging and Microhydraulic Fracturing	R. Garrard, J. Gonus, J. Desroches & E. Bailey
VII	TBO Bülach-1-1: Hydraulic Packer Testing	R. Schwarz, L. Schlickenrieder & T. Vogt
VIII	TBO Bülach-1-1: Rock Properties, Porewater Characterisation and Natural Tracer Profiles	M. Mazurek, L. Aschwanden, L. Camesi, T. Gimmi, A. Jenni, M. Kiczka, U. Mäder, D. Rufer, H. N. Waber, P. Wanner, P. Wersin & D. Traber
IX	TBO Bülach-1-1: Rock-mechanical and Geomechanical Laboratory Testing	E. Crisci, L. Laloui & S. Giger
X	TBO Bülach-1-1: Petrophysical Log Analysis	S. Marnat & J.K. Becker
	TBO Bülach-1-1: Summary Plot	Nagra

1.4 Scope and objectives of this dossier

The dossier at hand summarises the laboratory work of the Rock-Water Interaction Group (RWI) of the University of Bern dedicated to rock and porewater characterisation of core materials obtained from the BUL1-1 borehole. The level of ambition is to document observations and measurements and to provide a quality-assured data set. The obtained data are evaluated and discussed to some degree, including consistency and plausibility checks. On the other hand, an in-depth discussion, sophisticated modelling efforts and regional comparisons with data from other sites are beyond the scope of the report. Data obtained by other groups (e.g. hydraulic tests, ground-water sampling, geophysical borehole and core logging, structural logging) are considered in several cases but not in a comprehensive way. Given the fact that those data were not available in complete and final form at the time when this report was written, an integrated interpretation of all available data needs to be deferred to later stages of the TBO programme.

Throughout this report, rock samples used for analysis are identified by their mid-sample depth in m.

Note that in this report 'Brauner Dogger' is used for the Dogger units overlying the Opalinus Clay. In the Sectoral Plan Stage 1 and 2, 'Brauner Dogger' is referred to clay-rich rocks only (Nagra 2008).

2 Ancillary geoscientific data of interest for this report

Martin Mazurek

2.1 Geological information

As illustrated in Chapter 1, the BUL1-1 borehole is located in the Deformed Tabular Jura (Vorfallenzzone), about 1 – 2 km north of the Stadel – Irchel Anticline / Baden – Irchel – Herdern Lineament running parallel to the Main Jura Thrust, which is located about 4 – 5 km south of the borehole. Compressive structures that delineate the northern end of the Deformed Tabular Jura are located north of the Rhine, 4 km or more away from the borehole. More detail is provided in Dossier V.

A lithostratigraphic profile of the borehole is shown in Fig. 1-3. The Molasse section was percussion drilled, and core drilling started in the limestones of the Malm. A continuous core profile is available to the final depth in the Permian.

2.2 Hydrogeological conditions

A set of hydraulic packer tests were conducted, and the results are summarised in Tab. 2-1. Enhanced hydraulic conductivities were identified in the Malm and Muschelkalk aquifers, whereas the upper Triassic Klettgau Formation has a conductivity that is substantially below that identified in the Benken borehole.

Tab. 2-1: Results of hydraulic packer tests

The best estimates for transmissivity T, hydraulic conductivity K and (apparent) hydraulic head are indicated. Data are from Dossier VII.

Top [m b.g.]	Bottom [m b.g.]	Length [m]	Geological unit	T [m ² /s]	K [m/s]	Head [m asl]
537.2	545	7.8	'Felsenkalk' / 'Massenkalk'	1.5×10^{-11}	1.9×10^{-12}	349
608.8	641.5	32.7	'Felsenkalk' / 'Massenkalk' (Malm aquifer)	8.5×10^{-7}	2.6×10^{-8}	378
814	846.7	32.7	'Herrenwis Unit'	6.5×10^{-11}	2.0×10^{-12}	302
848.2	869	20.8	'Herrenwis Unit' – Wedelsandstein Fm.	4.6×10^{-11}	2.2×10^{-12}	505
1'052.2	1'074	21.8	Klettgau Fm. – Bänkerjoch Fm.	2.0×10^{-08}	9.3×10^{-10}	331
1'137.7	1'173.73	36.03	Schinznach Fm. (Muschelkalk aquifer)	1.7×10^{-6}	4.8×10^{-8}	358

2.3 Groundwater samples

Groundwater samples with variable degrees of drilling-fluid contamination were obtained from the Malm and Muschelkalk aquifers. While both waters are of the chemical Na-Cl type, the high salinity of the Muschelkalk water is a feature not previously observed in northern Switzerland. For the present report, values for the chemically conservative parameters Cl and Br and the water-

isotope ratios $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are of interest, as these serve as boundary conditions for the porewater data. These values were corrected by Lorenz (2020) for drilling fluid contamination and are reproduced in Tab. 2-2.

Tab. 2-2: Conservative parameters for waters from the Malm and Muschelkalk aquifers corrected for drilling fluid contamination

From Lorenz (2020)

Parameter	Unit	Malm aquifer	Muschelkalk aquifer
Chloride (Cl ⁻)	[mg/L]	7'350	86'000
Bromide (Br ⁻)	[mg/L]	27.5	2.5
$\delta^{18}\text{O}$ of water	[‰ VSMOW]	-0.61	-12.24
$\delta^2\text{H}$ of water	[‰ VSMOW]	-50.0	-88.3

2.4 Structural logging

The results of structural core logging are documented in Dossier V, where the following types are distinguished:

- fault planes (shear structures, mostly compressional)
- fractures, veins and joints
- stylolites

The large majority of all structures is found in the Malm and in the Triassic (Dossier V). A number of fault zones was defined and is listed in Tab. 2-3.

Tab. 2-3: Fault zones in the cored section of the BUL1-1 borehole

From Dossier V.

Top [m a.h.]	Bottom [m a.h.]	Thickness [m a.h.]	Unit
535.18	535.27	0.09	'Felsenkalke' / 'Massenkalk'
537.66	537.83	0.17	'Felsenkalke' / 'Massenkalk'
539.56	541.21	1.65	'Felsenkalke' / 'Massenkalk'
543.55	543.58	0.03	'Felsenkalke' / 'Massenkalk'
546.28	546.31	0.03	'Felsenkalke' / 'Massenkalk'
546.74	548.13	1.39	'Felsenkalke' / 'Massenkalk'
621.93	622.75	0.82	'Felsenkalke' / 'Massenkalk'
626.64	628.71	2.07	'Felsenkalke' / 'Massenkalk'
747.15	747.70	0.55	Villigen Fm.
890.02	890.37	0.35	'Murchisonae-Oolith Fm.'
890.71	890.83	0.12	'Murchisonae-Oolith Fm.'

Tab. 2-3: (continued)

Top [m a.h.]	Bottom [m a.h.]	Thickness [m a.h.]	Unit
1'021.77	1'021.91	0.14	Staffelegg Fm.
1'036.74	1'036.93	0.19	Klettgau Fm.
1'037.50	1'038.55	1.05	Klettgau Fm.
1'039.34	1'039.50	0.16	Klettgau Fm.
1'040.68	1'041.71	1.03	Klettgau Fm.
1'047.28	1'048.03	0.75	Klettgau Fm.
1'048.14	1'049.05	0.91	Klettgau Fm.
1'049.75	1'050.88	1.13	Klettgau Fm.
1'052.36	1'054.09	1.73	Klettgau Fm.
1'055.89	1'056.73	0.84	Klettgau Fm.
1'068.74	1'068.93	0.19	Bänkerjoch Fm.
1'069.18	1'070.38	1.20	Bänkerjoch Fm.
1'070.93	1'070.99	0.06	Bänkerjoch Fm.
1'071.15	1'071.30	0.15	Bänkerjoch Fm.
1'072.06	1'072.27	0.21	Bänkerjoch Fm.
1'072.62	1'072.65	0.03	Bänkerjoch Fm.
1'073.46	1'073.74	0.28	Bänkerjoch Fm.
1'075.34	1'075.59	0.25	Bänkerjoch Fm.
1'075.97	1'076.07	0.10	Bänkerjoch Fm.
1'077.04	1'077.90	0.86	Bänkerjoch Fm.
1'078.61	1'078.70	0.09	Bänkerjoch Fm.
1'078.80	1'078.97	0.17	Bänkerjoch Fm.
1'079.10	1'079.20	0.10	Bänkerjoch Fm.
1'079.45	1'080.70	1.25	Bänkerjoch Fm.
1'083.06	1'086.40	3.34	Bänkerjoch Fm.
1'086.63	1'086.68	0.05	Bänkerjoch Fm.
1'086.99	1'087.18	0.19	Bänkerjoch Fm.
1'088.00	1'089.50	1.50	Bänkerjoch Fm.
1'092.09	1'092.50	0.41	Bänkerjoch Fm.
1'092.66	1'093.20	0.54	Bänkerjoch Fm.
1'093.71	1'096.02	2.31	Bänkerjoch Fm.
1'096.53	1'100.57	4.04	Bänkerjoch Fm.
1'102.12	1'104.78	2.66	Bänkerjoch Fm.
1'106.21	1'106.49	0.28	Bänkerjoch Fm.
1'108.15	1'108.94	0.79	Bänkerjoch Fm.
1'362.15	1'362.25	0.10	Weitenau Fm.
1'362.60	1'362.65	0.05	Weitenau Fm.
1'362.76	1'362.80	0.04	Weitenau Fm.
1'363.08	1'363.14	0.06	Weitenau Fm.

3 Sampling and applied methods

3.1 Sampling strategy

Martin Mazurek

A suite of different sample types as defined by Rufer (2019) were investigated, and Tab. 3-1 provides a summary. All samples arrived at RWI in a state according to the instructions, i.e. no single sample was inflated or showed other evidence of loss of tightness of the wrapping. Some samples had bedding-parallel fractures that were created after on-site conditioning.

Tab. 3-1: Sample types and sampling strategy

Sample type	Main study targets	Sampling (by on-site team)
PW (pore-water chemistry), RP (various rock properties)	Characterisation of rock and porewater	Sample lithology representative of the current lithofacies and the sampled core section (usually 3 m). Sampling with a regular spacing, in order to obtain a representative data set
SQ (squeezing)	Characterisation of pore-water chemistry	Focussed on clay-rich lithologies due to methodological constraints
AD (advective displacement)	Characterisation of pore-water chemistry	Focussed on clay-rich lithologies due to methodological constraints
DI (diffusion experiments)	Diffusion coefficients (at PSI)	Coverage of a wide range of lithologies (in particular clay mineral contents)
OD (out-diffusion)	Out-diffusion experiments (diffusion coefficient for Cl ⁻ , Cl ⁻ concentration in bulk porewater)	Focussed on clay-poor lithologies due to methodological constraints
NG (noble gas analysis)	Concentrations and isotopic compositions of dissolved noble and reactive gases	Sampling with a regular spacing, with situational tightening of the sampling interval close to potentially water-conducting features
GM (geomechanics)	Mineralogy and grain density of samples studied for their geomechanical properties by other laboratories	Representative sampling of the most relevant lithologies within the Opalinus Clay and the overlying Wedelsandstein Fm.
V (vein studies)	Petrography, structure and geochemistry of veins	Opportunistic sampling at later stages

3.2 Laboratory programme

Martin Mazurek

In total, 258 samples were investigated in the RWI laboratories, and Tab. 3-2 provides an overview. In Tab. 3-3, the analytical programme for the various sample types is shown in more detail.

Tab. 3-2: Numbers of samples analysed for the different geological units

In the case of the NG samples, the number refers to the total number of samples taken.

Unit	PW, RP	SQ	AD	DI	OD	NG	GM	V	Total
Malm	19	4		4	3	19			49
'Brauner Dogger'	28	2	3	9	1	9	6		58
Opalinus Clay	31	5	2	11		11	12		72
Staffelegg Fm.	9	2	1	5		4	1		22
Klettgau Fm.	13					5			18
Bänkerjoch Fm.	15					3			18
Schinznach Fm.	13					3			16
Zeglingen Fm.								5	5
All	128	13	6	29	4	54	19	5	258

Tab. 3-3: Analytical programme performed for the different sample types

×× = standard programme, × = selected samples only, calc. = calculated.

Method	PW, RP	SQ	AD	DI	OD	NG	GM	V
Bulk mineralogical composition including CNS analysis	××	××	××	××	××		××	
Clay mineralogy	×		××	××	××			
Bulk wet density	××		calc.		××	××		
Grain density	××		calc.	××	××		××	
Water content	××	××	××	××	××	××		
BET surface area	×			××	××			
Cation-exchange properties (Ni-en method)	×		××					
Aqueous extraction	××	××	××		××			
Pore-water squeezing		××						
Advective displacement of porewater			××					
Out-diffusion					××			
Water isotopes	××	××	××					
$\delta^{37}\text{Cl}$	×							×
Dissolved noble gases						×		
Dissolved reactive gases						×		

3.3 Analytical methods

Martin Mazurek

Experimental procedures, analytical methods and data processing, including error calculations, are documented in Waber (ed.) (2020) and are not repeated here.

3.4 Methods of raw-data processing

Thomas Gimmi & Martin Mazurek

Approaches and formalisms to evaluate and process measured data are also documented in Waber (ed.) (2020), including formalisms for the quantification of propagated errors. This information is not repeated here, but additional information is provided for situations where the current practice is not documented or deviates from that described in Waber (ed.) (2020).

3.4.1 Calculations for high-salinity porewaters: Porewater content, porosities, solute concentrations

In the lowermost part of the BUL1-1 profile, porewater salinity increases drastically and therefore cannot be neglected for the calculation of various parameters. In particular, the following calculated parameters are affected by high salinity:

- Porewater content PWC_{wet} and PWC_{dry} (Eqs. 12, 13)
- Solute concentrations $C_{pw}^{m_{pw}}$ in porewater calculated from aqueous-extraction data (Eq. 14)
- Bulk dry density ρ_{bd} and ρ_{bd}^* (Eqs. 23, 24)
- Pycnometer porosity ϕ_{pyc} (Eq. 25)
- Water-loss porosity ϕ_{WL} (Eqs. 26, 27).

List of symbols

Note: *Water* refers to H₂O only

Porewater and *solution* refer to H₂O + dissolved salts

$C_{aqex}^{m_{solution}}$ = concentration in aqueous extract [g/mass of solution]

$C_{aqex}^{m_w}$ = concentration in aqueous extract [g/mass of water]

$C_{pw}^{m_{pw}}$ = concentration in porewater [g/mass of porewater]

$C_{pw}^{m_w}$ = concentration in porewater [g/mass of water]

$C_{pw}^{V_{pw}}$ = concentration in porewater [g/volume of porewater]

$C_{pw}^{V_w}$ = concentration in porewater [g/volume of water]

m_{dry} = dry rock mass, including mass of salts from porewater [g]

m_{wet} = wet rock mass [g]

m_r = mass of rock [g]

m_s	= mass of salts in porewater [g]
m_w	= mass of water [g]
m_{pw}	= mass of porewater [g]
$m_{w \text{ added}}$	= mass of water added for aqueous extraction [g]
s	= salinity fraction [–]
WC_{dry}	= water content relative to dry mass [–]
WC_{wet}	= water content relative to wet mass [–]
PWC_{dry}	= porewater content relative to dry mass [–]
PWC_{wet}	= porewater content relative to wet mass [–]
S/L	= ratio of mass of dried rock (including porewater salts) to total water mass [–]
S/L_{pw}	= ratio of mass of dried rock (including porewater salts) to total mass of solution (including salts) [–]
TDS	= total dissolved solids [mg/kg _{solution} or mg/kg _{porewater}]
V_{pw}	= volume of porewater [cm ³]
V_r	= volume of rock [cm ³]
V_s	= volume of salts precipitated from porewater [cm ³]
ρ_{bw}	= bulk wet density [g/cm ³]
ρ_{bd}	= bulk dry density [g/cm ³]
ρ_g	= grain density [g/cm ³]
ρ_{pw}	= density of porewater [g/cm ³]
ρ_w	= density of water [g/cm ³]
ϕ_{pyc}	= pycnometer porosity [–]
ϕ_{WL}	= water-loss porosity [–]

Measured or inferred parameters: m_{wet} , m_{dry} , $m_{w \text{ added}}$, s , ρ_{pw}

Masses m_{wet} , m_{dry} and $m_{w \text{ added}}$ are measured directly during drying and aqueous-extraction tests. The salinity fraction s can be derived from direct sampling methods, such as advective displacement or squeezing, or estimated based on other information (see below). Porewater density can be estimated from salinity or obtained from geochemical models, such as PHREEQC, when the chemical composition of the water is known.

Calculated parameters (first set): m_w , m_{pw} , m_r , m_s

$$m_{wet} = m_w + m_r + m_s \quad (1)$$

$$m_{dry} = m_r + m_s \quad (2)$$

$$m_w = m_{wet} - m_{dry} \quad (3)$$

$$m_{pw} = \frac{m_{wet} - m_{dry}}{1 - s} \quad (4)$$

$$s = \frac{m_s}{m_s + m_w} \text{ (definition) and } m_w + m_s = \frac{m_w}{1-s}; \text{ therefore:} \quad (5)$$

$$m_s = \frac{s m_w}{1-s} = \frac{s(m_{wet} - m_{dry})}{1-s} \quad (6)$$

Combine Eqs. (1), (2), (3), (6):

$$m_r = m_{wet} - m_w - m_s = m_{dry} - \frac{s(m_{wet} - m_{dry})}{1-s} \quad (7)$$

Calculated parameters (second set): S/L , S/L_{pw} , WC_{wet} , WC_{dry} , PWC_{wet} , PWC_{dry}

Combine definition of S/L with Eq. (3):

$$S/L = \frac{m_r + m_s}{m_w + m_{w \text{ added}}} = \frac{m_{dry}}{m_{wet} - m_{dry} + m_{w \text{ added}}} \quad (8)$$

Combine definition of S/L_{pw} with Eqs. (3), (6):

$$S/L_{pw} = \frac{m_r + m_s}{m_w + m_s + m_{w \text{ added}}} = \frac{m_{dry}}{\frac{m_{wet} - m_{dry}}{1-s} + m_{w \text{ added}}} = \frac{(1-s) m_{dry}}{m_{wet} - m_{dry} + (1-s) m_{w \text{ added}}} \quad (9)$$

$$WC_{wet} = \frac{m_w}{m_w + m_r + m_s} = \frac{m_{wet} - m_{dry}}{m_{wet}} = \frac{WC_{dry}}{1 + WC_{dry}} \quad (10)$$

$$WC_{dry} = \frac{m_w}{m_r + m_s} = \frac{m_{wet} - m_{dry}}{m_{dry}} = \frac{WC_{wet}}{1 - WC_{wet}} \quad (11)$$

Combine definition of PWC_{wet} with Eqs. (3), (6), (7):

$$\begin{aligned} PWC_{wet} &= \frac{m_w + m_s}{m_w + m_r + m_s} = \frac{m_{wet} - m_{dry}}{m_{wet} (1-s)} = \frac{WC_{wet}}{1-s} = \frac{PWC_{dry}}{1 + (1-s)PWC_{dry}} \\ &= \frac{WC_{dry}}{(1-s)(1 + WC_{dry})} \end{aligned} \quad (12)$$

Combine definition of PWC_{dry} with Eqs. (3), (6), (7):

$$\begin{aligned} PWC_{dry} &= \frac{m_w + m_s}{m_r + m_s} = \frac{m_{wet} - m_{dry}}{(1-s) m_{dry}} = \frac{WC_{dry}}{(1-s)} = \frac{PWC_{wet}}{1 - (1-s)PWC_{wet}} \\ &= \frac{WC_{wet}}{(1-s)(1 - WC_{wet})} \end{aligned} \quad (13)$$

Calculated parameters (third set): $C_{pw}^{m_{pw}}$, $C_{pw}^{m_w}$, $C_{pw}^{V_{pw}}$, $C_{pw}^{V_w}$

If the extract is prepared from a wet sample, we have:

$$C_{pw}^{m_{pw}} = \frac{C_{aqex}^{m_{solution}}}{PWC_{dry} S/L_{pw}} = C_{aqex}^{m_{solution}} \left(\frac{1}{PWC_{dry} S/L} + s \right) \quad (14)$$

This equation is valid for conservative (non-reactive) species only and furthermore assumes that the pore space is fully accessible (no ion exclusion). Partial ion exclusion could be corrected by dividing the middle and right terms in Eq. (14) by the ion-accessible porosity fraction.

If the extract is prepared from a dry sample, we have:

$$C_{pw}^{m_{pw}} = C_{aqex}^{m_{solution}} \left(\frac{s WC_{dry} S/L_{add} + (1-s)}{WC_{dry} S/L_{add} + (1-s)} \right) \left(\frac{1-s}{WC_{dry} S/L} + s \right) \quad (14a)$$

with

$$S/L_{add} = \frac{m_r + m_s}{m_w added} = \frac{m_{dry}}{m_w added} \quad (14b)$$

S/L_{add} is a measured parameter in the case of dry extraction, and S/L (as defined in Eq. 8) can be calculated from:

$$S/L = \frac{m_r + m_s}{m_w + m_w added} = \frac{1}{WC_{dry} + \frac{1}{S/L_{add}}} \quad (14c)$$

$$C_{pw}^{m_w} \approx C_{aqex}^{m_{solution}} \text{ (at sufficient dilution)} \quad (15)$$

$$C_{pw}^{m_w} = \frac{C_{pw}^{m_{pw}}}{1-s} \quad (16)$$

$$\rho_{pw} = \frac{m_w + m_s}{V_{pw}} \text{ (definition)} \quad (17)$$

$$\rho_{pw} \approx \frac{\rho_w}{1-s} \quad (18)$$

(rough approximation assuming constant volume, overestimates density of solution especially at high salinity). More appropriately, ρ_{pw} can be calculated using geochemical models, such as PHREEQC, if the chemical composition is known.

$$C_{pw}^{V_{pw}} = C_{pw}^{m_{pw}} \rho_{pw} \quad (19)$$

$$C_{pw}^{V_w} = C_{pw}^{m_w} \rho_w \quad (20)$$

Densities: ρ_{bw} , ρ_{bd} , ρ_g

ρ_g : The effect of salts (density of halite = 2.16 g/cm³) has only marginal effects in rocks of porosities that we encounter in the deep boreholes. Thus, we have:

$$\rho_g = \frac{m_s + m_r}{V_s + V_r} \approx \rho_g^* = \frac{m_r}{V_r} \quad (21)$$

with ρ_g the grain density measured on a dried sample and ρ_g^* the true grain density of the rock not including precipitated salts.

$$\rho_{bw} = \frac{m_w + m_s + m_r}{V_{pw} + V_r} \quad (22)$$

This is what is measured according to a general definition of bulk wet density. Note that the bulk wet density defined in this way tends to increase with increasing salinity of the pore solution (the numerator tends to increase, while the denominator remains constant).

$$\rho_{bd} = \frac{m_s + m_r}{V_{pw} + V_r} = \frac{\rho_{bw}}{1 + WC_{dry}} = \frac{\rho_{bw}}{1 + (1-s) PWC_{dry}} \quad (23)$$

The dry bulk density ρ_{bd} defined in this way also tends to increase with increasing salinity. One can also define a bulk density ρ_{bd}^* that is independent of the salinity as:

$$\rho_{bd}^* = \frac{m_r}{V_{pw} + V_r} = \rho_{bd} \frac{m_r}{m_s + m_r} = \rho_{bd} (1 - s \text{PWC}_{dry}) = \rho_{bd} \left(1 - \frac{s \text{WC}_{dry}}{1-s}\right) \quad (24)$$

Porosities: ϕ_{pyc} , ϕ_{WL}

$$\phi_{pyc} = 1 - \frac{\rho_{bd}^*}{\rho_g} \approx 1 - \frac{\rho_{bd}}{\rho_g} = 1 - \frac{\rho_{bd}(1-s \text{PWC}_{dry})}{\rho_g} \quad (25)$$

That is, in order to obtain correct porosities for high-salinity samples, the bulk density ρ_{bd}^* , which is independent of the salinity and has to be used (whereas, as explained above, ρ_g^* can be well approximated by ρ_g):

$$\phi_{WL} = \frac{\text{PWC}_{wet} \rho_{bw}}{\rho_{pw}} = \frac{\text{PWC}_{dry} \rho_{bd}}{\rho_{pw}} \quad (26)$$

$$\phi_{WL} = \frac{\text{PWC}_{wet} \rho_g}{\text{PWC}_{wet} \rho_g + (1-\text{PWC}_{wet}) \rho_{pw}} \quad (27)$$

with Eq. (27) being appropriate for fully water saturated samples only.

Estimation of the salinity fraction s and of porewater density ρ_{pw}

The equations above show that the calculation of porewater content, pycnometer and water-loss porosities and porewater concentrations of solutes analysed in aqueous extracts require knowledge of the salinity fraction s of the porewater. Further, solute concentrations calculated using Eq. (14) yield results in units per mass of porewater. In order to convert these data to units per volume, the porewater density ρ_{pw} is needed.

Porewater density can in principle be obtained from model calculations (e.g. using PHREEQC), provided the major-ion composition is known. However, no pertinent data from advective displacement or squeezing are available for the deep section of the Bülach-1-1 borehole. An attempt was made to roughly constrain the porewater composition by simple recalculation of aqueous-extraction data to porewater concentrations using Equation 6-1 in Waber (ed.) (2020). Because this approach is only adequate for conservative species, the calculated water is strongly over-saturated with respect to carbonate and sulphate minerals. In PHREEQC, calcite and anhydrite were therefore allowed to precipitate until equilibrium, and porewater density was then calculated for the modelled water composition. Both the PHREEQC and the Pitzer thermodynamic data bases were used and yielded comparable results except for the highest salinities. However, given the fact that the way the water composition was derived is dubious and the related error cannot be properly quantified, this route to constrain porewater density is not recommended.

An alternative way to estimate water density has therefore been attempted. In the groundwater sample taken in the Muschelkalk aquifer ($TDS = 145 \text{ g/L}$, $Cl = 86 \text{ g/L}$, see Tab. 2-2), density was measured directly and yielded a value of 1.10096 g/cm^3 . Assuming that the ion ratios in the porewaters are identical to that in the groundwater sample, an estimate of the density can be obtained from the Cl concentration in the porewater, which in turn can be derived from that in the aqueous extracts. While the assumption of constant ion ratios cannot be rigorously defended (it is not correct for reactive species and possibly neither for conservative species), this route is nevertheless considered more robust.

The error on ρ_{pw} propagates into the error on Cl^- and Br^- concentrations in porewater when expressed in units per volume. However, this error cannot be well constrained and thus its contribution is not considered in the total errors listed in this report.

In order to constrain the salinity fraction s , it follows from Eqs. (5) and (14):

$$s = \frac{m_s}{m_s + m_w} = \frac{m_s}{m_{pw}} = TDS_{pw}^{m_{pw}} = \frac{TDS_{aq\ ex}^{m_{solution}}}{PWC_{dry} S/L_{pw}} \quad (28)$$

s is needed as an input parameter to calculate PWC_{dry} as well as S/L_{pw} , so it appears on both sides of the equation. Expressing PWC_{dry} (Eq. 13) as well as S/L_{pw} (Eq. 9) in terms of m_{wet} , m_{dry} , $m_{w\ added}$ and s and inserting them into Eq. (28), we can derive s as:

$$s = \frac{TDS_{aq\ ex}^{m_{solution}}(m_{wet}-m_{dry}+m_{w\ added})}{(m_{wet}-m_{dry}+TDS_{aq\ ex}^{m_{solution}} m_{w\ added})} = \frac{(m_{wet}-m_{dry}+m_{w\ added})}{(\frac{m_{wet}-m_{dry}}{TDS_{aq\ ex}^{m_{solution}}}+m_{w\ added})} \quad (29)$$

However, Eq. (14) and therefore also Eq. (29) assume conservative behaviour for $TDS_{aq\ ex}^{m_{solution}}$, which is not the case due to mineral dissolution and cation exchange induced by the addition of water during aqueous extraction (same problem as discussed above for porewater density).

A probably more adequate constraint of s can be obtained based on the groundwater sample from the Muschelkalk aquifer where TDS (145 g/L = 131.8 g/kg), s (0.1318) and Cl^- (86 g/L; Tab. 2-2) are known. Assuming identical ion ratios in the groundwater and in the adjacent highly saline porewaters (and therefore a constant ratio TDS/Cl^-) allows the derivation of TDS and therefore s from Cl^- concentrations in the porewaters using $TDS = 145/86 \cdot Cl^-$. Cl^- in the porewaters can be properly calculated using Eq. (14). Given the fact that the lithologies in this zone are calcareous and clay-poor, anion-accessibility is likely high and neglecting it as done in Eq. (14) probably incurs only a minor error. In any case, partial exclusion of ions could be corrected if the ion-accessible porosity fraction was known.

In principle, the error on s propagates into the errors on porewater content, pycnometer and water-loss porosities and porewater concentrations of solutes analysed in aqueous extracts. However, this error cannot be well constrained and thus its contribution to the error on s is not considered in the total errors listed in the report.

3.4.2 Formalisms pertinent to the evaluation of diffusive-exchange experiments

List of symbols

C_{pw}	Isotope concentration in porewater
C_{twi}	Isotope concentration in initial test water
C_{twf}	Isotope concentration in final test water
m_{rw}	Mass of wet rock sample
m_{tw}	Mass of test water

Calculation of isotope concentrations in porewater

The formalism to evaluate diffusive-exchange experiments is summarised in Waber (ed.) (2020). In general, two isotope exchange experiments with different initial concentrations of the test water are performed on two subsamples. To date, it was generally assumed that these subsamples have identical water content, w_w , which leads to the following equation for the isotopic composition of the porewater (using subscripts 1 and 2 for the two experiments):

$$C_{pw} = \frac{m_{tw2}m_{rw1}C_{twf1}(C_{twf2} - C_{twi2}) - m_{tw1}m_{rw2}C_{twf2}(C_{twf1} - C_{twi1})}{m_{tw2}m_{rw1}(C_{twf2} - C_{twi2}) - m_{tw1}m_{rw2}(C_{twf1} - C_{twi1})} \quad (30)$$

If the water contents of the two subsamples differ significantly, the application of Eq. (30) may lead to biased concentrations, with the bias not appearing in the propagated uncertainties. Therefore, an alternative approach is chosen here that considers the ratio $q = w_{w1}/w_{w2}$ explicitly. The water contents w_{w1} and w_{w2} were measured gravimetrically from the wet mass and the dry mass (mass loss at 105 °C) after the termination of the experiment, the wet mass being corrected for a possible water transfer between test water and the rock material during the experiment. The isotope porewater concentration is then calculated as:

$$C_{pw} = \frac{a q C_{twf1} - b C_{twf2}}{a q - b} \quad (31)$$

The propagated error is calculated from:

$$\begin{aligned} \sigma_{C_{pw}}^2 = & (g_1 \sigma_{m_{tw1}})^2 + (g_2 \sigma_{m_{tw2}})^2 + (g_3 \sigma_{m_{rw1}})^2 + (g_4 \sigma_{m_{rw2}})^2 \\ & + (g_5 \sigma_{C_{twi1}})^2 + (g_6 \sigma_{C_{twi2}})^2 + (g_7 \sigma_{C_{twf1}})^2 \\ & + (g_8 \sigma_{C_{twf2}})^2 + (g_9 \sigma_q)^2 \end{aligned} \quad (32)$$

with:

$a = m_{tw2}m_{rw1}(C_{twf2} - C_{twi2})$	$b = m_{tw1}m_{rw2}(C_{twf1} - C_{twi1})$
$d = a q b (C_{twf1} - C_{twf2})/(a q - b)^2$	$g_1 = \frac{d}{m_{tw1}}$
$g_2 = \frac{-d}{m_{tw2}}$	$g_3 = \frac{-d}{m_{rw1}}$
$g_4 = \frac{d}{m_{rw2}}$	$g_5 = \frac{-d}{(C_{twf1} - C_{twi1})}$
$g_6 = \frac{d}{(C_{twf2} - C_{twi2})}$	$g_7 = \frac{a q}{a q - b} + \frac{d}{(C_{twf1} - C_{twi1})}$
$g_8 = -\frac{b}{a q - b} - \frac{d}{(C_{twf2} - C_{twi2})}$	$g_9 = -\frac{d}{q}$

A propagated error for q has to be used in this case, e.g., $\sigma_q = q \sqrt{\left(\frac{\sigma_{w_{w1}}}{w_{w1}}\right)^2 + \left(\frac{\sigma_{w_{w2}}}{w_{w2}}\right)^2}$.

This formalism explicitly considers unequal w_{w1} and w_{w2} (i.e., does not assume $q = 1$). It is thus valid even for cases in which q deviates substantially from 1. If $q > 1$, experiment 1 (typically performed with tap water) obtains a higher weight in the calculation of the isotope concentrations in porewater, and the opposite is the case for $q < 1$, in which case experiment 2 (typically performed with depleted water) obtains more weight. As the error on the calculated isotope concentration of the porewater is typically smaller for the experiment with tap water, the error bars tend to become smaller in cases where $q > 1$.

Back-calculation of water contents from isotope concentrations in porewater

After having obtained isotope porewater concentrations according to Eq. (31), it is possible to calculate the corresponding water content from the mass balance of the $\delta^{18}\text{O}$ or the $\delta^2\text{H}$ data of either of the two experiments as:

$$w_w = \frac{m_{tw} (C_{twf} - C_{twi})}{m_{rw} (C_{pw} - C_{twf})} \quad (33)$$

The propagated error is calculated from:

$$\begin{aligned} \sigma_{w_w}^2 = & \left(\frac{w_w}{m_{tw}} \sigma_{m_{tw}} \right)^2 + \left(\frac{w_w}{m_{rw}} \sigma_{m_{rw}} \right)^2 \\ & + \left(\left[\frac{w_w}{C_{twf} - C_{twi}} + \frac{w_w}{C_{pw} - C_{twf}} \right] \sigma_{C_{twf}} \right)^2 \\ & + \left(\frac{w_w}{C_{twf} - C_{twi}} \sigma_{C_{twi}} \right)^2 + \left(\frac{w_w}{C_{pw} - C_{twf}} \sigma_{C_{pw}} \right)^2 \end{aligned} \quad (34)$$

From the two isotopes and the two subsamples (i.e. the two experiments), four values for w_w are obtained. However, only the water contents obtained for a single subsample with the two tracers are independent; the water contents of the two subsamples are related by the imposed condition $q = w_{w1}/w_{w2}$. The most accurate water contents are those obtained from the experiment with a test water that is isotopically substantially different from the porewater (e.g. strongly depleted glacial water), while the uncertainty is larger for water contents obtained from the experiment with water isotopically similar to the porewater (e.g. tap water). Accordingly, only the back-calculated water contents obtained from the strongly depleted glacial test water will be presented.

4 Results

4.1 Documentation of measured and calculated data

Martin Mazurek

Raw data collected in the frame of the analytical programme are organised in a FileMaker data base, including raw-data files, graphics and photographs. The main purpose of this data base is to ensure the full documentation and traceability of original and derived data presented in this report. From this data base, the relevant data were exported into a comprehensive Excel sheet, which is attached in Appendix 1. The objective of this sheet is not to fully document all analyses made but, per parameter and sample, to indicate the "best" or most representative value in case multiple measurements were made, and to list parameters calculated from the original measurements. For example, only one composition is given for squeezed and advectively displaced porewaters in a sample, even though multiple aliquots were collected and analysed. Explanatory notes to this sheet follow here.

Bulk mineralogy (X-ray diffraction and CNS analysis)

- Contents of minerals not detected by X-ray diffraction are set to 0, as the actual detection limits are difficult to quantify. "tr" = present in trace amounts.
- Clay-mineral content is not measured directly but is calculated by difference to 100 %.
- Pyrite content is calculated from the measured S content, assuming that pyrite is the main S reservoir in the rock. This is not the case in anhydrite-bearing rocks, which are typically free of pyrite. Here, the S is used to calculate the content of anhydrite.
- Column "Füchtbauer name" refers to the nomenclature of clastic rocks as defined in Naef et al. (2019). Names are listed only for rock compositions that have < 10 wt.-% minerals not represented in the Füchtbauer triangle (i.e. minerals other than clays, calcite, dolomite/ankerite, siderite, quartz, K-feldspar, plagioclase). In particular, this means that evaporitic rocks are not given a Füchtbauer name. If a rock contains ≥ 90 wt.-% minerals represented in the Füchtbauer triangle but also contains anhydrite, this is stated in brackets.

The Füchtbauer triangle does not distinguish between limestones and dolostones. In cases when the contents of calcite exceed those of dolomite/ankerite, the terms "limestone" or "calcareous" are used in this report, and "dolostone" or "dolomitic" are used if the opposite applies.

Clay groups

- All data refer to wt.-% of the total rock.
- Illite/smectite ML (85 – 90) refers to a mixed-layer phase with 85 – 90 % illite layers, Chl/Sm ML (85 – 95) designates a chlorite – smectite mixed-layer phase with 85 – 95 % chlorite (analogous for the other listed mixed-layer phases).

End-member clays

- All data refer to wt.-% of the total rock.

- Illite, smectite and chlorite partially occur in mixed-layer phases. Here, the respective total contents of the end-members are calculated. For example, if a sample contains 10 wt.-% illite and 8 wt.-% illite/smectite mixed layers containing 75 % illite, the end-member illite content would be 16 wt.-%.

Petrophysical parameters

- Bulk wet density was measured, and bulk dry density was calculated using Equation 5-14 in Waber (ed.) (2020).
- Pycnometer porosity was calculated from densities using Equation 5-16 in Waber (ed.) (2020).
- Water content (dry) was calculated from water content (wet) using $w_d = w_w / (1 - w_w)$.
- Water-loss porosity was calculated using bulk wet density (Equation 5-9 in Waber (ed.) 2020) or grain density (Equation 5-7 in Waber (ed.) 2020).
- The formalisms to calculate water content from isotope diffusive exchange experiments are detailed in Section 3.4.2.

Aqueous extraction @ S/L $\approx$ 1 repeat

- In the standard procedure, gravimetric water content is obtained by drying about 200 – 300 g rock chips. Aqueous extraction is performed on 30 g adjacent material. The recalculation of Cl^- contents in aqueous extracts to porewater concentrations thus uses a water content that was not measured on the identical piece of rock, which is not an issue in most cases. However, for rocks that are highly heterogeneous on the cm scale, the materials used for the two different analyses may differ. In such cases, in particular for some low-porosity Triassic samples, aqueous extraction was repeated using a representative split of the material that was previously used for water-content determination. Porewater concentrations of Cl^- were then calculated using the Cl^- contents from the repeat extractions.

Cl^- and Br^- from aqueous extracts recalculated to porewater concentrations using water content

- Concentrations are given relative to bulk and anion-accessible porewater. The calculation is made using Equation 6-1 in Waber (ed.) (2020) or using the formalism for high-salinity samples as described in Section 3.4.1. The dependence of anion accessibility on clay-mineral content and other rock characteristics is discussed in Chapter 5.

Errors

- The error columns refer to analytical uncertainty for measured parameters and to propagated errors for calculated parameters, following the formalisms documented in Waber (ed.) (2020).

Calculations for high salinities

- In the Triassic section of the BUL1-1B borehole, porewater salinities are far above that of seawater, which complicates a number of calculations, such as porewater contents, densities, porosities and solute concentrations based on aqueous-extraction data. The respective formalisms are documented and discussed in detail in Section 3.4.1.

4.2 Mineralogical composition

Martin Mazurek & Andreas Jenni

4.2.1 Whole rock

A total of 195 mineralogical analyses were performed in the section Malm – Muschelkalk. The full data set is documented in Appendix 1, and Tab. 4.2-1 provides formation-specific summaries. The depth trends for the most relevant minerals are shown graphically in Fig. 4.2-1, and a representation in the Füchtbauer triangle is given in Fig. 4.2-2. Clay-mineral contents increase with depth at the expense of calcite between the Villigen Formation and the Opalinus Clay, where the highest values are reached. This trend is interrupted by the reef facies ('Herrenwis Unit'), which is dominated by limestone. Below the Opalinus Clay, clay-mineral contents tend to decrease and reach low values in the Schinznach Formation. The highest contents of silt-size clastic minerals (quartz, feldspars) are identified in the interval Wedelsandstein – Klettgau Formations. Dolomite may reach high contents in the Triassic, and a smaller peak is seen in the 'Herrenwis Unit'.

Tab. 4.2-1: Bulk-rock mineralogy: formation-specific means, medians, standard deviations and ranges

For the calculation of statistical parameters, values below detection were set to 0. In several cases, systematic depth trends of mineral contents are observed (see below). This means that in these cases the data do not follow a Gaussian distribution, which is a pre-requisite for the calculation of meaningful standard deviations. In such cases, the ranges (also listed) are more meaningful.

Formation (no. of analyses)	Member / Sub-unit		S	C(inorg)	C(org)	Quartz	K-feldspar	Plagioclase	Calcite	Dolomite / Ank.	Siderite	Anhydrite	Celestite	Pyrite	Clay minerals
			[wt.-%]												
'Felsenkalk' / 'Massenkalk' (10)		Mean	0.00	11.74	0.07	0.3	0.0	0.0	97.8	0.0	0.0	0.0	0.0	0.0	1.9
		Median	0.00	11.77	0.05	0.0	0.0	0.0	98.1	0.0	0.0	0.0	0.0	0.0	1.5
		Stdev	0.00	0.20	0.07	0.5	0.0	0.0	1.8	0.0	0.0	0.0	0.0	0.0	1.4
		Min	0.00	11.37	0.01	0.0	0.0	0.0	94.2	0.0	0.0	0.0	0.0	0.0	0.5
		Max	0.00	11.94	0.22	1.1	0.0	0.0	99.5	0.0	0.0	0.0	0.0	0.0	4.7
Schwarzbach Fm. (2)		Mean	0.03	10.97	0.17	1.8	0.0	0.0	90.7	0.6	0.0	0.0	0.0	0.0	6.6
		Median	0.03	10.97	0.17	1.8	0.0	0.0	90.7	0.6	0.0	0.0	0.0	0.0	6.6
		Stdev	0.04	0.62	0.04	0.9	0.0	0.0	6.1	0.9	0.0	0.0	0.0	0.1	4.2
		Min	0.00	10.53	0.14	1.2	0.0	0.0	86.3	0.0	0.0	0.0	0.0	0.0	3.7
		Max	0.05	11.40	0.19	2.5	0.0	0.0	95.0	1.3	0.0	0.0	0.0	0.1	9.6
Villigen Fm. (6)		Mean	0.02	11.15	0.19	0.7	0.0	0.0	91.9	0.8	0.0	0.0	0.0	0.0	6.3
		Median	0.02	11.29	0.17	0.5	0.0	0.0	91.7	0.0	0.0	0.0	0.0	0.0	5.8
		Stdev	0.02	0.50	0.08	0.8	0.0	0.0	3.8	1.4	0.0	0.0	0.0	0.0	3.5
		Min	0.00	10.49	0.12	0.0	0.0	0.0	87.4	0.0	0.0	0.0	0.0	0.0	1.9
		Max	0.05	11.66	0.32	1.6	0.0	0.0	96.8	3.2	0.0	0.0	0.0	0.1	10.6
Wildeggen Fm. (10)	Effingen Mb.	Mean	0.04	8.35	0.30	5.9	2.9	0.2	68.1	1.3	0.0	0.0	0.0	0.1	21.2
		Median	0.03	8.63	0.29	5.0	2.9	0.0	69.1	0.0	0.0	0.0	0.0	0.1	19.4
		Stdev	0.05	1.03	0.07	2.2	0.9	0.5	8.9	2.3	0.0	0.0	0.0	0.1	5.7
		Min	0.00	6.62	0.21	4.1	1.4	0.0	53.1	0.0	0.0	0.0	0.0	0.0	13.5
		Max	0.16	9.69	0.45	10.1	4.4	1.2	80.7	7.1	0.0	0.0	0.0	0.3	30.5
Variansmergel Fm. (1)		Mean	0.35	2.95	0.50	15.0	6.3	1.5	17.8	6.2	0.0	0.0	0.0	0.6	52.1
		Median	0.35	2.95	0.50	15.0	6.3	1.5	17.8	6.2	0.0	0.0	0.0	0.6	52.1

Tab. 4.2-1: (continued)

Formation (no. of analyses)	Member / Sub-unit		S	C(inorg)	C(org)	Quartz	K-feldspar	Plagioclase	Calcite	Dolomite / Ank.	Siderite	Anhydrite	Celestite	Pyrite	Clay minerals
			[wt.-%]												
'Parkinsoni-Württ.-Sch.' (3)		Mean	0.58	3.97	0.54	14.6	5.0	0.8	31.3	1.6	0.0	0.0	0.0	1.1	45.0
		Median	0.65	3.09	0.50	14.6	4.9	1.0	25.8	1.9	0.0	0.0	0.0	1.2	50.6
		Stdev	0.21	1.92	0.19	4.5	0.3	0.7	15.0	1.5	0.0	0.0	0.0	0.4	10.5
		Min	0.35	2.64	0.37	10.0	4.8	0.0	19.9	0.0	0.0	0.0	0.0	0.7	33.0
		Max	0.75	6.17	0.74	19.1	5.4	1.5	48.2	3.0	0.0	0.0	0.0	1.4	51.5
'Herrenwis Unit' (18)		Mean	0.04	10.71	0.16	4.5	0.8	0.1	85.0	3.9	0.0	0.0	0.0	0.1	5.5
		Median	0.00	10.86	0.12	3.1	1.1	0.0	84.3	2.1	0.0	0.0	0.0	0.0	5.4
		Stdev	0.06	0.89	0.10	4.8	0.8	0.4	8.1	5.0	0.0	0.0	0.0	0.1	3.0
		Min	0.00	8.15	0.06	0.0	0.0	0.0	66.7	0.0	0.0	0.0	0.0	0.0	1.0
		Max	0.17	11.73	0.43	19.9	2.5	1.7	97.7	19.9	0.0	0.0	0.0	0.3	10.3
'Humphriesi-ool. Fm.' (1)		Mean	0.00	11.11	0.13	2.4	0.0	0.0	92.5	0.0	0.0	0.0	0.0	0.0	5.0
		Median	0.00	11.11	0.13	2.4	0.0	0.0	92.5	0.0	0.0	0.0	0.0	0.0	5.0
Wedelsandstein Fm. (21)		Mean	0.58	2.47	0.52	32.8	5.8	3.3	20.0	0.1	0.5	0.0	0.0	1.1	35.8
		Median	0.54	2.28	0.50	34.6	6.0	3.3	18.3	0.0	0.0	0.0	0.0	1.0	34.6
		Stdev	0.47	1.48	0.15	7.0	1.0	0.6	12.7	0.3	1.3	0.0	0.0	0.9	14.1
		Min	0.00	0.89	0.19	20.7	3.6	1.6	6.0	0.0	0.0	0.0	0.0	0.0	6.6
		Max	2.36	7.86	0.79	47.7	7.4	4.2	65.5	1.3	5.9	0.0	0.0	4.4	60.1
'Murchisonae-Oolith Fm.' (4)		Mean	0.64	0.34	0.77	33.0	5.0	3.4	2.4	0.0	0.5	0.0	0.0	1.2	53.7
		Median	0.58	0.28	0.84	25.6	5.4	3.4	1.6	0.0	0.5	0.0	0.0	1.1	61.8
		Stdev	0.19	0.22	0.22	19.0	1.5	1.1	2.0	0.0	0.5	0.0	0.0	0.4	20.1
		Min	0.49	0.16	0.46	19.8	2.9	2.0	0.9	0.0	0.0	0.0	0.0	0.9	23.9
		Max	0.91	0.63	0.95	61.1	6.4	4.6	5.3	0.0	1.2	0.0	0.0	1.7	67.5
Opalinus Clay (61)	All	Mean	0.34	1.31	0.93	24.5	5.3	3.3	8.0	0.1	3.3	0.0	0.0	0.6	54.1
		Median	0.30	1.22	0.94	22.9	5.2	3.3	6.9	0.0	3.2	0.0	0.0	0.6	56.5
		Stdev	0.23	0.41	0.14	7.8	0.6	0.3	3.6	0.4	1.4	0.0	0.0	0.4	9.9
		Min	0.00	0.74	0.63	14.9	3.8	2.5	3.8	0.0	0.0	0.0	0.0	0.0	31.8
		Max	1.27	3.21	1.32	42.3	7.1	3.9	24.4	3.2	7.7	0.0	0.0	2.4	69.2
Opalinus Clay (14)	Sub-unit with silty calcareous beds	Mean	0.47	1.42	0.91	32.8	5.7	3.2	9.6	0.3	2.2	0.0	0.0	0.9	44.4
		Median	0.44	1.42	0.94	38.8	5.7	3.2	9.0	0.0	2.1	0.0	0.0	0.8	40.8
		Stdev	0.29	0.50	0.13	9.6	0.9	0.4	4.3	0.9	1.7	0.0	0.0	0.5	11.4
		Min	0.00	0.78	0.66	19.2	3.8	2.6	4.3	0.0	0.0	0.0	0.0	0.0	31.8
		Max	1.27	2.20	1.08	42.3	7.1	3.9	17.5	3.2	6.4	0.0	0.0	2.4	60.8
Opalinus Clay (12)	Upper silty sub-unit	Mean	0.35	1.53	0.89	28.3	5.3	3.3	10.4	0.0	2.8	0.0	0.0	0.7	48.4
		Median	0.32	1.52	0.83	28.6	5.4	3.3	9.7	0.0	2.8	0.0	0.0	0.6	48.3
		Stdev	0.20	0.59	0.21	2.9	0.4	0.3	4.9	0.0	0.7	0.0	0.0	0.4	6.4
		Min	0.07	0.86	0.63	24.4	4.4	3.0	5.7	0.0	1.7	0.0	0.0	0.1	33.8
		Max	0.68	3.21	1.32	32.8	5.9	3.9	24.4	0.0	4.1	0.0	0.0	1.3	57.3
Opalinus Clay (27)	Mixed clay-silt-carbonate sub-unit	Mean	0.24	1.17	0.96	21.0	5.1	3.3	6.3	0.0	3.9	0.0	0.0	0.5	58.9
		Median	0.19	1.17	0.95	21.2	5.1	3.3	6.0	0.0	3.7	0.0	0.0	0.4	59.1
		Stdev	0.19	0.24	0.12	3.5	0.4	0.3	1.9	0.0	1.2	0.0	0.0	0.4	4.9
		Min	0.06	0.74	0.72	15.2	4.4	2.6	3.8	0.0	2.2	0.0	0.0	0.1	48.4
		Max	0.92	2.01	1.31	26.4	5.9	3.9	13.0	0.0	7.7	0.0	0.0	1.7	69.2
Opalinus Clay (8)	Clay-rich sub-unit	Mean	0.39	1.24	0.94	16.1	4.9	3.1	7.2	0.0	3.6	0.0	0.0	0.7	63.4
		Median	0.39	1.21	0.95	16.1	5.0	3.1	6.8	0.0	3.6	0.0	0.0	0.7	63.3
		Stdev	0.12	0.14	0.04	1.0	0.2	0.4	1.1	0.0	0.9	0.0	0.0	0.2	1.4
		Min	0.24	1.10	0.88	14.9	4.6	2.5	6.4	0.0	2.4	0.0	0.0	0.4	61.5
		Max	0.58	1.51	0.98	17.6	5.1	3.7	9.5	0.0	5.2	0.0	0.0	1.1	65.7
Staffellegg Fm. (18)		Mean	0.41	3.82	1.00	26.1	4.1	2.1	30.1	1.4	0.3	0.0	0.0	0.8	34.1
		Median	0.26	1.49	0.67	34.0	4.7	3.0	9.8	1.7	0.0	0.0	0.0	0.5	39.7
		Stdev	0.43	3.46	1.27	15.1	1.7	1.4	29.7	0.9	0.6	0.0	0.0	0.8	12.4
		Min	0.00	0.94	0.13	1.7	0.0	0.0	5.0	0.0	0.0	0.0	0.0	0.0	5.2
		Max	1.82	11.12	4.81	42.1	6.9	3.8	92.7	2.7	1.7	0.0	0.0	3.4	47.7

Tab. 4.2-1: (continued)

Formation (no. of analyses)	Member / Sub-unit		S	C(inorg)	C(org)	Quartz	K-feldspar	Plagioclase	Calcite	Dolomite / Ank.	Siderite	Anhydrite	Celestite	Pyrite	Clay minerals
			[wt.-%]												
Klettgau Fm. (12)		Mean	0.18	5.20	0.22	13.5	7.2	5.2	6.3	34.1	0.0	0.6	0.0	0.1	32.9
		Median	0.00	6.55	0.18	8.8	5.9	3.3	1.0	40.6	0.0	0.0	0.0	0.0	31.3
		Stdev	0.33	4.14	0.15	10.5	3.8	4.1	8.6	29.0	0.0	1.4	0.0	0.1	14.0
		Min	0.00	0.00	0.04	1.8	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.3
		Max	1.04	12.09	0.52	30.0	13.7	11.6	22.4	91.9	0.0	4.4	0.0	0.4	55.5
Bänkerjoch Fm. (15)		Mean	7.58	2.51	0.21	10.8	4.2	1.4	2.0	17.4	0.0	32.0	0.8	0.0	31.2
		Median	3.37	2.52	0.19	7.9	4.8	1.3	0.0	19.0	0.0	14.3	0.0	0.0	28.0
		Stdev	7.46	1.76	0.09	11.8	3.4	1.8	4.0	14.8	0.0	31.9	1.3	0.0	15.6
		Min	0.04	0.00	0.06	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.8
		Max	20.00	5.89	0.34	41.3	9.8	6.7	15.0	45.2	0.0	84.9	4.0	0.1	54.7
Schinznach Fm. (13)	All	Mean	0.04	11.36	0.73	1.4	0.0	0.0	32.8	57.0	0.0	0.1	0.0	0.0	8.0
		Median	0.00	11.35	0.36	1.2	0.0	0.0	19.0	67.2	0.0	0.0	0.0	0.0	7.5
		Stdev	0.08	0.48	0.63	1.7	0.0	0.0	36.4	32.7	0.0	0.3	0.0	0.1	3.9
		Min	0.00	10.41	0.14	0.0	0.0	0.0	0.0	5.3	0.0	0.0	0.0	0.0	2.5
		Max	0.25	12.06	1.87	6.3	0.0	0.0	87.6	92.3	0.0	1.0	0.0	0.3	14.8
Schinznach Fm. (5)	Stamberg Mb.	Mean	0.03	11.22	1.20	1.6	0.0	0.0	0.0	86.1	0.0	0.0	0.0	0.1	11.0
		Median	0.00	11.04	1.25	0.0	0.0	0.0	0.0	84.8	0.0	0.0	0.0	0.0	12.6
		Stdev	0.07	0.66	0.69	2.7	0.0	0.0	0.0	5.1	0.0	0.0	0.0	0.1	3.5
		Min	0.00	10.41	0.23	0.0	0.0	0.0	0.0	79.9	0.0	0.0	0.0	0.0	6.9
		Max	0.15	12.02	1.87	6.3	0.0	0.0	0.0	92.3	0.0	0.0	0.0	0.3	14.8
Schinznach Fm. (7)	Leutschenberg + Kienberg Mb.	Mean	0.02	11.47	0.45	1.0	0.0	0.0	60.9	32.0	0.0	0.0	0.0	0.0	5.7
		Median	0.00	11.40	0.33	1.2	0.0	0.0	66.4	26.3	0.0	0.0	0.0	0.0	5.0
		Stdev	0.03	0.36	0.40	0.7	0.0	0.0	25.5	23.1	0.0	0.0	0.0	0.1	2.9
		Min	0.00	11.04	0.14	0.0	0.0	0.0	19.0	5.3	0.0	0.0	0.0	0.0	2.5
		Max	0.09	12.06	1.27	1.9	0.0	0.0	87.6	67.2	0.0	0.0	0.0	0.2	11.1

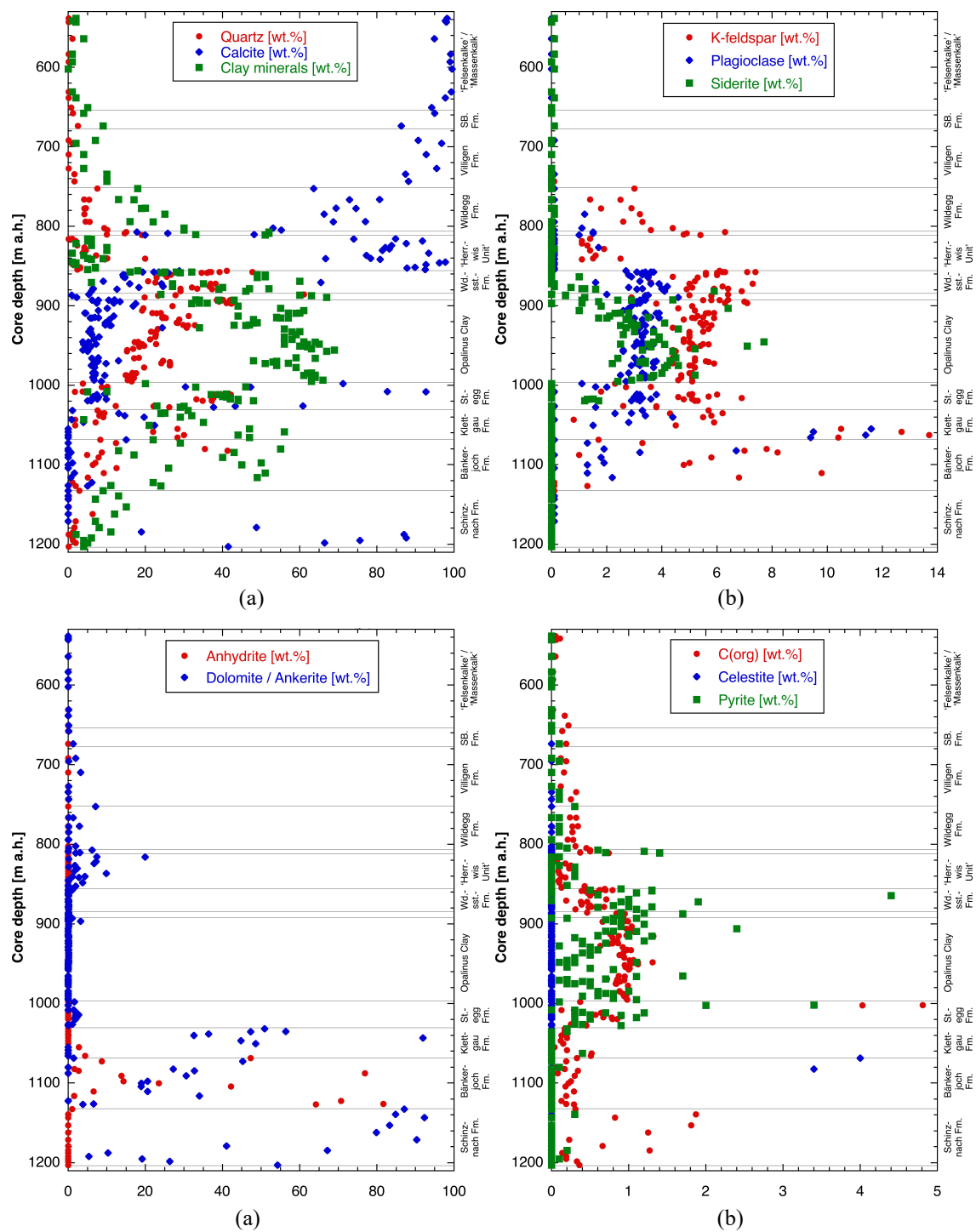


Fig. 4.2-1: Mineral contents in the bulk rock as a function of depth
Detailed lithostratigraphic subdivision according to Dossier III.

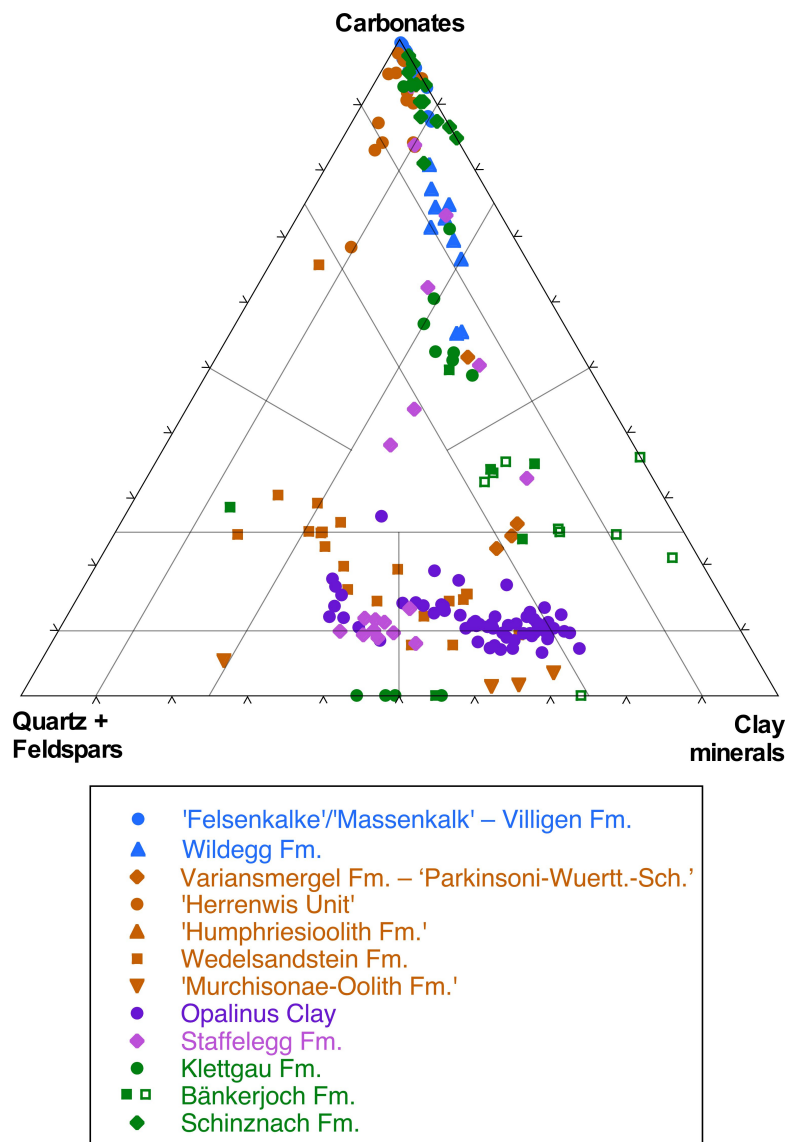


Fig. 4.2-2: Mineralogical composition of studied samples in the Füchtbauer triangle

Open symbols in the Bänkerjoch Formation indicate samples containing > 10 wt.-% minerals other than those represented by the Füchtbauer triangle (i.e. clays, calcite, dolomite/ankerite, siderite, quartz, K-feldspar, plagioclase). In most cases, anhydrite is the main additional phase.

A closer look at the clay-rich section Staffelegg Formation – Opalinus Clay – Wedelsandstein Formation

The graphics shown in Fig. 4.2-3 indicates systematic depth trends in particular of quartz and clay-mineral contents, whereas calcite and other minerals show less systematic variability.

Staffelegg Formation

- Quartz contents increase from the base until the top of the Frick Member before dropping to low values in the upper part.
- Clay-mineral contents drop upwards within the Frick Member.

Opalinus Clay

Informal sub-units within the Opalinus Clay were defined by Mazurek & Aschwanden (2020) on a regional basis. In Dossier III this scheme was successfully applied to the BUL1-1 core, and their sub-unit boundaries are included in Fig. 4.2-3.

- The base of the Opalinus Clay correlates with the onset of more homogeneous mineral contents, in contrast to a substantial scatter in the underlying Staffelegg Formation. In the clay-rich sub-unit at the base of the Opalinus Clay, quartz contents increase and clay-mineral contents decrease upwards.
- In the overlying mixed clay – silt – carbonate sub-unit, quartz contents first decrease and then increase upwards. An inverse trend is seen for clay minerals. This means that, from a mineralogical point of view, a boundary exists at about 956 m where the trends reverse, likely in response to a change of sedimentary facies. Thus, the mixed clay – silt – carbonate sub-unit can probably be further subdivided into two cycles.
- The boundary between the clay-rich and the mixed clay – silt – carbonate sub-units corresponds to a discontinuity of quartz contents and a reversal of the trend. On the other hand, clay-mineral contents keep decreasing across the boundary and reverse at a higher level, around 970 m.
- The boundary between the mixed clay – silt – carbonate and the overlying upper silty sub-unit corresponds to a major discontinuity and a trend reversal of both quartz and clay-mineral contents.
- The boundary between the upper silty sub-unit and the overlying sub-unit with silty calcareous beds is clearly mappable based on macroscopic core logging. Interestingly, the obvious lithological boundary is not reflected by the contents of quartz and clay minerals, whose trends continue up to a boundary at about 904 m within the sub-unit with silty calcareous beds. At this depth, a lithological boundary within this sub-unit was defined (*cf.* Dossier III). The base of the sub-unit with silty calcareous beds can at best be correlated with the onset of increasing calcite contents.
- The top of the Opalinus Clay correlates with a major discontinuity of quartz and clay-mineral contents and a reversal of calcite contents.

'Murchisonae-Oolith Formation' and Wedelsandstein Formation

- From a mineralogical viewpoint, the 'Murchisonae-Oolith Formation' and the lower part of the Wedelsandstein Formation are part of a single trend with increasing quartz and calcite contents, and decreasing clay-mineral contents. On the other hand, the hardground that separates the lower and upper Wedelsandstein Formation according to Dossier III represents a major discontinuity of mineral contents.

Conclusion

A number of mineralogical discontinuities and changes in depth trends were identified. In most cases, these correlate well with the lithostratigraphic subdivision of Dossier III. In some cases, this is not the case, e.g. a boundary at 960 m that was identified from the mineralogical data but not by lithostratigraphic core logging. Quartz and clay-mineral contents show the most pronounced trends and discontinuities in their depth profiles, whereas for calcite this is the case only in the uppermost part of the Opalinus Clay and in the overlying units.

As the depth trends of quartz and clay minerals always show inverse depth trends, the ratio quartz : clay minerals most clearly highlights the depositional cycles that govern the mineralogical composition and is shown in Fig. 4.2-3d. Last, note that the sub-units of the Opalinus Clay as

defined by Mazurek & Aschwanden (2020) are not zones with constant properties but rather zones with constant trends, i.e. sedimentological cycles. Given the much higher sample density in comparison to all previous campaigns, this can now be shown for the BUL1-1 profile for the first time.

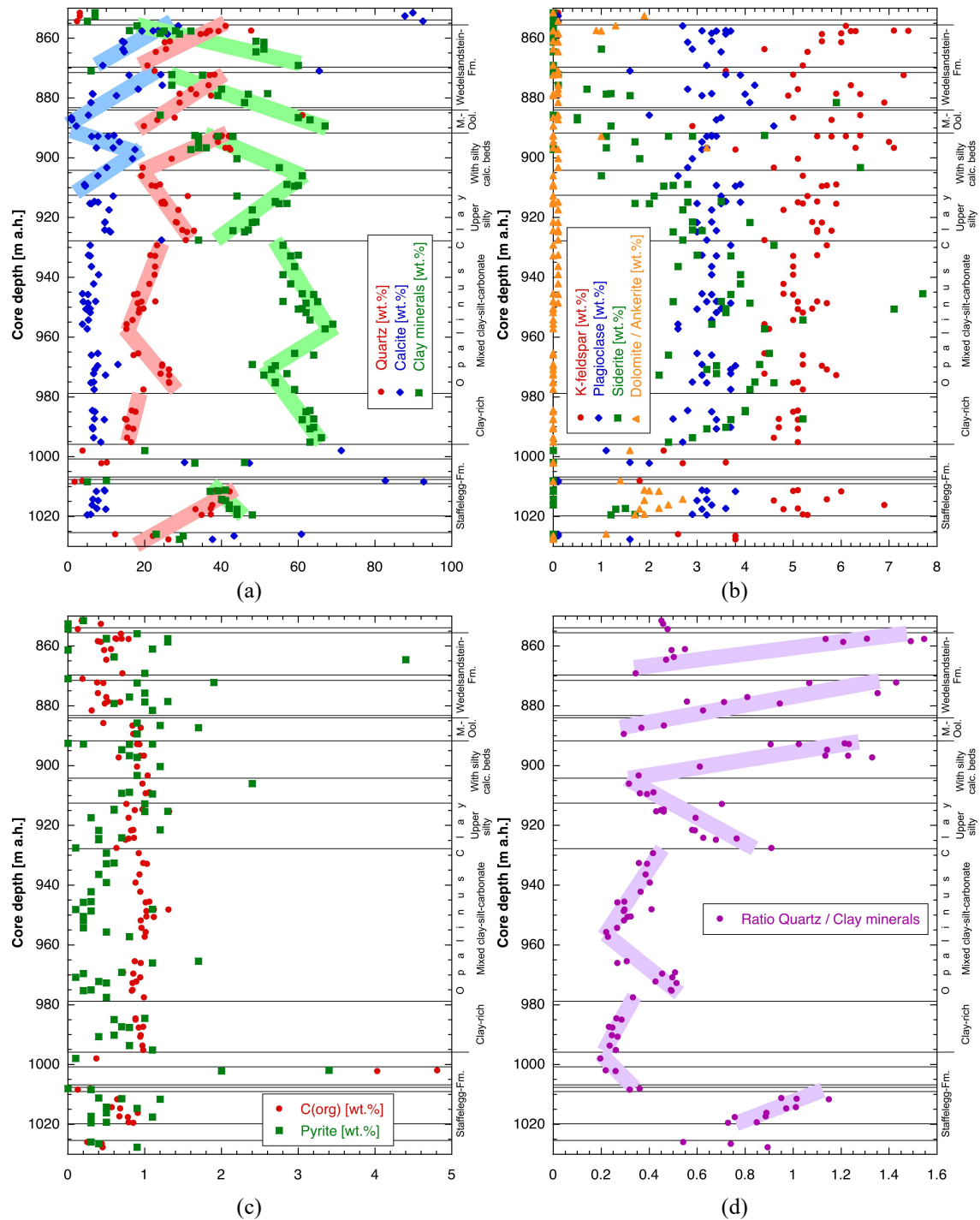


Fig. 4.2-3: Depth trends of mineral contents in the bulk rock in the interval Staffelegg Formation – Wedelsandstein Formation

Coloured bars highlight systematic trends. Detailed lithostratigraphic subdivision according to Dossier III.

4.2.2 Clay minerals

A total of 61 mineralogical analyses of the clay fraction were performed in the section Malm – Lias. The full data set is documented in Appendix 1, and Tab. 4.2-2 provides formation-specific summaries, normalising the contents of individual clay phases to the sum of all clay minerals.

The identified clay-mineral species include illite, smectite, illite/smectite mixed layers, kaolinite, chlorite and chlorite/smectite mixed layers. The identification of chlorite/smectite mixed layers in all samples is in contrast with previous data from northern Switzerland where this mineral was rarely identified (Mazurek 2017). However, this is not a real difference but due to the improved methodology of the evaluation of X-ray patterns that was applied for the BUL1-1 campaign (details in Waber ed. 2020). Because the chlorite/smectite mixed-layer phase contains 85 – 95 % chlorite layers, its XRD reflections are close to those of pure chlorite. Another difference to previous data is the occasional identification of traces of pure smectite, again a consequence of the new evaluation method. Overall, both the identification of limited amounts of smectite layers in chlorite and traces of smectite does not change the overall picture, and the current data are still consistent and well comparable with older data sets. The new methodology also allows to better resolve the fraction of smectite layers in the illite/smectite mixed-layer phase. As seen in Tab. 4.2-2, illite-rich mixed layers dominate, but minor amounts of illite-poorer mixed layers also occur.

Given the fact that the contents of mixed-layer phases and the smectite fractions in these are known, the end-member compositions of illite, smectite, chlorite and kaolinite (whether in mixed layers or as a discrete phase) can be calculated and are also listed in Tab. 4.2-2.

Depth trends are shown graphically in Fig. 4.2-4 for individual clay phases (a) and end-member clays (b). The depth plot of the latter is less noisy than that of the individual clay minerals. The Staffelegg Formation is dominated by the illite and kaolinite end-members, but the contents are variable and do not show evident systematic depth trends. In the overlying Opalinus Clay, the contents of end-member clays are more homogeneous. Illite contents are the lowest and kaolinite are the highest in the whole drilled profile. Above the Opalinus Clay, illite contents increase sharply, and kaolinite contents decrease. The 'Herrenwis Unit' has the most extreme composition, with 81 % illite end-member and only 2 % kaolinite end-member on average (however, note that the absolute clay-mineral contents in the rock are quite low).

Tab. 4.2-2: Mineralogical composition of the clay fraction: formation-specific means, medians, standard deviations and ranges

In some cases, systematic depth trends of clay-mineral contents are observed. This means that in these cases the data do not follow a Gaussian distribution, which is a pre-requisite for the calculation of meaningful standard deviations. In such cases, the ranges (also listed) are more meaningful. MIL: Mixed layer.

Formation (number of analyses)	Member / Sub-unit		Individual clay phases [wt.-% of clay fraction]										End-member clays [wt.-% of clay fraction]			
			Illite	Ill/Sm ML (85 – 90)	Ill/Sm ML (75 – 80)	Ill/Sm ML (50 – 70)	Ill/Sm ML (20 – 40)	Total Ill/Sm	Smectite	Kaolinite	Chlorite	Chl/Sm ML (85 – 95)	Illite	Smectite	Kaolinite	Chlorite
'Felsen- kalke' / 'Massen- kalk' (2)		Mean	45.6	16.9	8.8	3.2	6.4	35.3	0.3	11.9	4.3	2.6	71.5	10.1	11.9	6.5
		Median	45.6	16.9	8.8	3.2	6.4	35.3	0.3	11.9	4.3	2.6	71.5	10.1	11.9	6.5
		Stdev	11.6	4.0	5.4	4.6	9.0	2.9	0.5	8.7	3.6	3.2	11.7	2.2	8.7	0.8
		Min	37.4	14.1	5.0	0.0	0.0	33.2	0.0	5.8	1.7	0.4	63.2	8.5	5.8	6.0
		Max	53.8	19.7	12.7	6.5	12.7	37.4	0.7	18.0	6.8	4.8	79.8	11.6	18.0	7.1
Villigen Fm. (2)		Mean	39.5	7.2	21.4	6.3	0.7	35.6	0.4	16.0	2.4	6.1	66.8	9.4	16.0	7.8
		Median	39.5	7.2	21.4	6.3	0.7	35.6	0.4	16.0	2.4	6.1	66.8	9.4	16.0	7.8
		Stdev	5.2	1.0	14.1	0.9	1.0	11.3	0.4	4.0	0.8	1.7	4.4	1.9	4.0	2.3
		Min	35.8	6.5	11.4	5.6	0.0	27.6	0.1	13.2	1.8	4.8	63.7	8.1	13.2	6.1
		Max	43.2	7.9	31.4	7.0	1.4	43.6	0.7	18.9	2.9	7.3	69.9	10.8	18.9	9.4
Wildeggen Fm. (5)	Effingen Mb.	Mean	43.6	6.1	25.3	4.6	1.2	37.1	0.0	12.5	2.2	4.7	71.9	9.3	12.5	6.3
		Median	42.9	0.0	28.8	5.3	0.9	37.6	0.0	12.4	2.0	4.4	70.7	8.8	12.4	5.7
		Stdev	3.2	9.6	9.8	1.3	1.3	3.3	0.0	3.7	1.0	1.0	4.6	1.2	3.7	1.7
		Min	40.8	0.0	10.8	2.8	0.0	33.3	0.0	7.0	1.0	3.6	66.7	8.0	7.0	4.7
		Max	48.6	22.0	36.4	5.9	2.9	41.7	0.0	17.1	3.4	6.1	79.2	10.7	17.1	8.3
Variansm. Fm. (1)		Mean	38.5	1.8	24.0	1.1	0.6	27.4	0.0	25.2	3.4	5.5	60.0	6.6	25.2	8.2
		Median	38.5	1.8	24.0	1.1	0.6	27.4	0.0	25.2	3.4	5.5	60.0	6.6	25.2	8.2
'Parkin- soni- Württ.- Sch.' (3)		Mean	38.9	6.1	22.6	4.0	0.6	33.3	0.0	19.0	2.1	6.7	64.7	8.3	19.0	8.0
		Median	38.9	2.3	23.4	2.5	0.5	33.2	0.0	20.0	2.0	6.1	64.3	8.5	20.0	7.7
		Stdev	2.7	7.3	5.6	3.3	0.7	5.6	0.1	9.1	0.2	1.0	7.0	1.5	9.1	0.9
		Min	36.1	1.5	16.6	1.7	0.0	27.8	0.0	9.4	1.9	6.0	57.9	6.8	9.4	7.2
		Max	41.6	14.5	27.8	7.8	1.3	38.9	0.1	27.6	2.3	7.9	71.9	9.7	27.6	9.0
'Herrenwis Unit' (9)		Mean	47.2	17.2	12.8	11.7	0.6	42.2	0.4	1.9	2.3	6.0	79.0	11.5	1.9	7.6
		Median	48.6	15.9	14.3	11.3	0.0	42.2	0.3	0.2	2.5	5.8	79.3	11.3	0.2	6.5
		Stdev	5.2	12.2	8.4	4.5	1.8	4.6	0.6	2.4	1.3	2.7	2.9	2.5	2.4	2.0
		Min	38.1	0.0	0.0	5.0	0.0	34.0	0.0	0.0	0.7	1.3	74.0	8.8	0.0	5.7
		Max	53.7	39.2	22.2	19.9	5.4	50.6	1.9	5.5	4.5	9.3	83.2	16.7	5.5	10.5
Wedelsand- stein Fm. (7)		Mean	37.8	4.5	23.4	8.3	0.2	36.3	0.1	16.2	3.9	5.6	64.8	10.0	16.2	9.0
		Median	38.0	4.7	25.2	5.3	0.0	33.6	0.0	16.3	4.0	6.7	63.8	8.6	16.3	10.9
		Stdev	4.2	2.5	5.9	6.4	0.3	9.3	0.2	8.5	0.6	3.2	7.8	3.5	8.5	3.3
		Min	31.0	0.0	13.2	3.3	0.0	24.6	0.0	5.6	3.2	1.2	50.6	5.9	5.6	4.3
		Max	43.8	8.0	30.3	18.6	0.9	51.6	0.4	32.0	4.9	9.0	76.1	15.8	32.0	11.8
'Mur.-Ool. Fm.' (1)		Mean	28.6	6.5	14.8	2.0	1.0	24.3	0.0	34.9	3.8	8.4	47.5	6.4	34.9	11.2
		Median	28.6	6.5	14.8	2.0	1.0	24.3	0.0	34.9	3.8	8.4	47.5	6.4	34.9	11.2

Tab. 4.2-2: continued

Formation (number of analyses)	Member / Sub-unit		Individual clay phases [wt.-% of clay fraction]										End-member clays [wt.-% of clay fraction]			
			Illite	Ill/Sm ML (85 – 90)	Ill/Sm ML (75 – 80)	Ill/Sm ML (50 – 70)	Ill/Sm ML (20 – 40)	Total Ill/Sm	Smectite	Kaolinite	Chlorite	Chl/Sm ML (85 – 95)	Illite	Smectite	Kaolinite	Chlorite
Opalinus Clay (21)		Mean	28.5	11.4	10.6	2.4	0.2	24.6	0.0	35.4	4.1	7.3	48.2	5.8	35.4	10.6
		Median	29.4	11.2	11.3	2.4	0.0	24.5	0.0	35.6	3.9	7.2	48.6	5.9	35.6	10.6
		Stdev	2.8	5.4	4.5	1.1	0.3	2.3	0.1	2.9	1.6	1.5	2.6	0.6	2.9	1.3
		Min	24.1	2.1	0.4	0.9	0.0	20.3	0.0	28.2	1.2	4.6	44.1	4.9	28.2	7.7
		Max	33.4	24.3	18.3	5.1	1.1	30.9	0.5	39.9	7.2	10.7	54.0	6.9	39.9	12.5
Opalinus Clay (2)	With silty calc. beds	Mean	31.2	11.2	10.9	2.9	0.1	25.1	0.0	33.2	3.1	7.4	51.3	6.0	33.2	9.6
		Median	31.2	11.2	10.9	2.9	0.1	25.1	0.0	33.2	3.1	7.4	51.3	6.0	33.2	9.6
		Stdev	0.4	2.6	0.5	0.6	0.2	2.7	0.0	3.5	1.9	1.6	2.8	0.1	3.5	0.6
		Min	30.9	9.3	10.6	2.4	0.0	23.2	0.0	30.7	1.7	6.3	49.3	5.9	30.7	9.2
		Max	31.5	13.0	11.3	3.3	0.3	27.0	0.0	35.6	4.4	8.5	53.2	6.1	35.6	10.0
Opalinus Clay (5)	Upper silty	Mean	28.9	13.9	9.5	2.8	0.2	26.5	0.1	33.4	3.8	7.3	50.1	6.1	33.4	10.3
		Median	29.4	13.0	8.1	2.3	0.0	25.4	0.0	34.2	3.5	7.7	49.7	6.2	34.2	10.8
		Stdev	3.3	7.5	5.9	1.3	0.5	2.6	0.1	3.6	1.1	1.7	2.4	0.6	3.6	1.6
		Min	24.5	5.3	3.7	1.8	0.0	24.7	0.0	28.2	2.5	4.9	47.3	5.4	28.2	7.7
		Max	33.4	24.3	17.8	5.1	1.1	30.9	0.2	36.8	5.2	9.4	54.0	6.9	36.8	12.1
Opalinus Clay (10)	Mixed clay-silt- carb.	Mean	28.2	10.6	10.6	2.1	0.2	23.6	0.0	36.5	4.6	7.1	47.1	5.6	36.5	10.8
		Median	29.0	9.9	10.7	2.0	0.0	23.7	0.0	35.9	4.1	6.9	47.9	5.5	35.9	10.6
		Stdev	3.0	5.6	5.4	1.2	0.3	1.4	0.1	1.7	1.6	1.6	2.1	0.6	1.7	1.1
		Min	24.1	2.1	0.4	0.9	0.0	22.0	0.0	34.7	2.7	4.6	44.1	4.9	34.7	9.5
		Max	31.4	21.5	18.3	4.4	0.9	26.2	0.5	39.9	7.2	10.7	49.6	6.7	39.9	12.5
Opalinus Clay (4)	Clay-rich	Mean	27.5	10.3	11.9	2.1	0.2	24.5	0.0	36.2	4.0	7.7	47.1	5.9	36.2	10.8
		Median	26.7	10.3	11.8	2.0	0.0	24.8	0.0	36.8	4.5	7.7	46.5	5.9	36.8	11.5
		Stdev	2.1	2.9	0.7	0.8	0.3	3.2	0.1	3.3	2.1	1.2	1.8	0.9	3.3	1.6
		Min	26.0	6.9	11.2	1.5	0.0	20.3	0.0	31.8	1.2	6.4	45.7	4.9	31.8	8.4
		Max	30.6	13.8	12.8	3.1	0.6	28.1	0.1	39.6	5.7	9.3	49.8	6.8	39.6	11.8
Staffelegg Fm. (10)		Mean	31.1	16.2	12.6	2.1	0.3	31.2	0.1	24.3	5.9	7.5	56.4	6.7	24.3	12.7
		Median	29.9	17.7	11.2	1.7	0.0	30.6	0.0	23.7	5.2	7.2	57.2	6.5	23.7	11.7
		Stdev	5.7	10.9	12.4	1.8	0.4	4.7	0.1	6.1	2.9	2.6	7.0	1.2	6.1	4.3
		Min	25.5	0.0	0.0	0.0	0.0	25.3	0.0	13.2	2.3	3.3	46.6	5.3	13.2	8.3
		Max	43.6	30.0	37.6	4.7	1.0	41.4	0.3	32.5	12.1	12.6	70.3	9.2	32.5	23.8

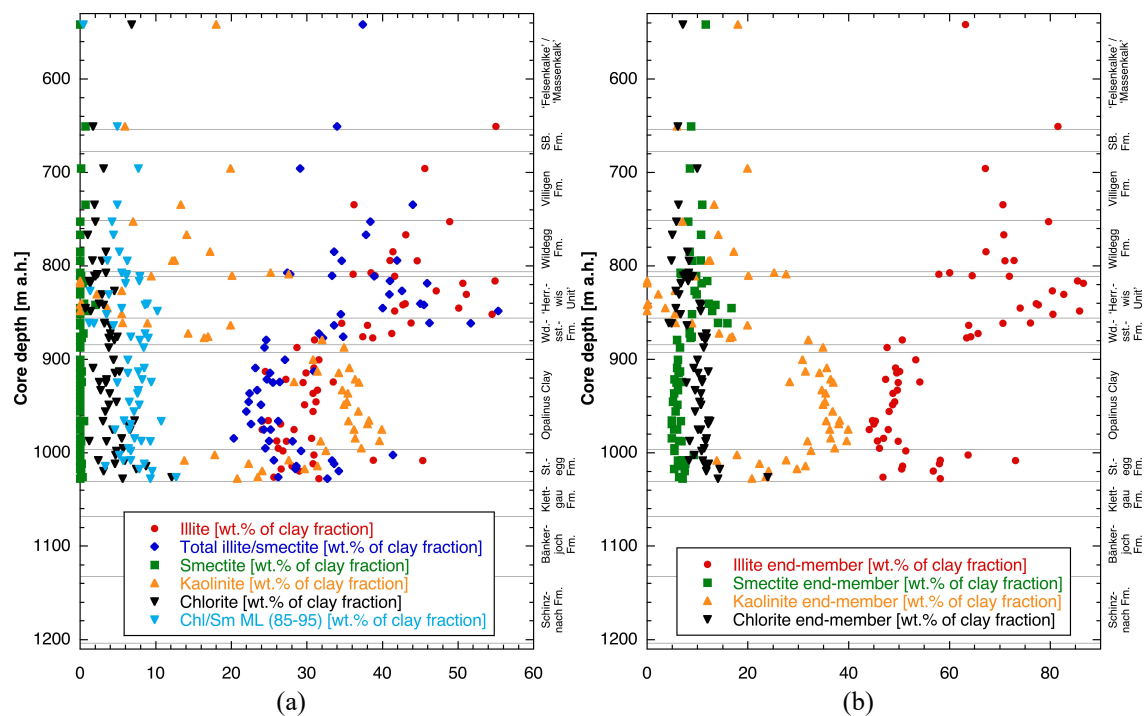


Fig. 4.2-4: Mineralogical composition of the clay fraction as a function of depth
Individual clay minerals (a), End-member clays (b). Detailed lithostratigraphic subdivision according to Dossier III.

A closer look at the clay-rich section Staffelegg Formation – Opalinus Clay – Wedelsandstein Formation

The composition of the clay fraction shows less variability with depth than that of the total clay content (Section 4.2.1), and only few sections with depth trends can be identified (Fig. 4.2-5). In the Staffelegg Formation, chlorite and chlorite/illite mixed layers decrease upwards and then remain at constant level higher up. The other clay minerals show a wide scatter, and no trends can be identified. In the Opalinus Clay, the illite end-member slightly decreases upwards, and the trend is broken at about 970 m, in the lowermost part of the mixed clay – silt – carbonate sub-unit. Kaolinite shows the opposite trend. The kink at 970 m coincides with the minimum total clay-mineral content (Fig. 4.2-3). Above 970 m, the illite end-member slightly increases at the expense of kaolinite. Overall, the variability of the relative proportions of clay minerals is low in the Opalinus Clay. The top of the 'Murchisonae-Oolith Formation' represents a discontinuity in that the content of the illite end-member increases sharply within the overlying Wedelsandstein Formation, and an inverse trend is identified for kaolinite.

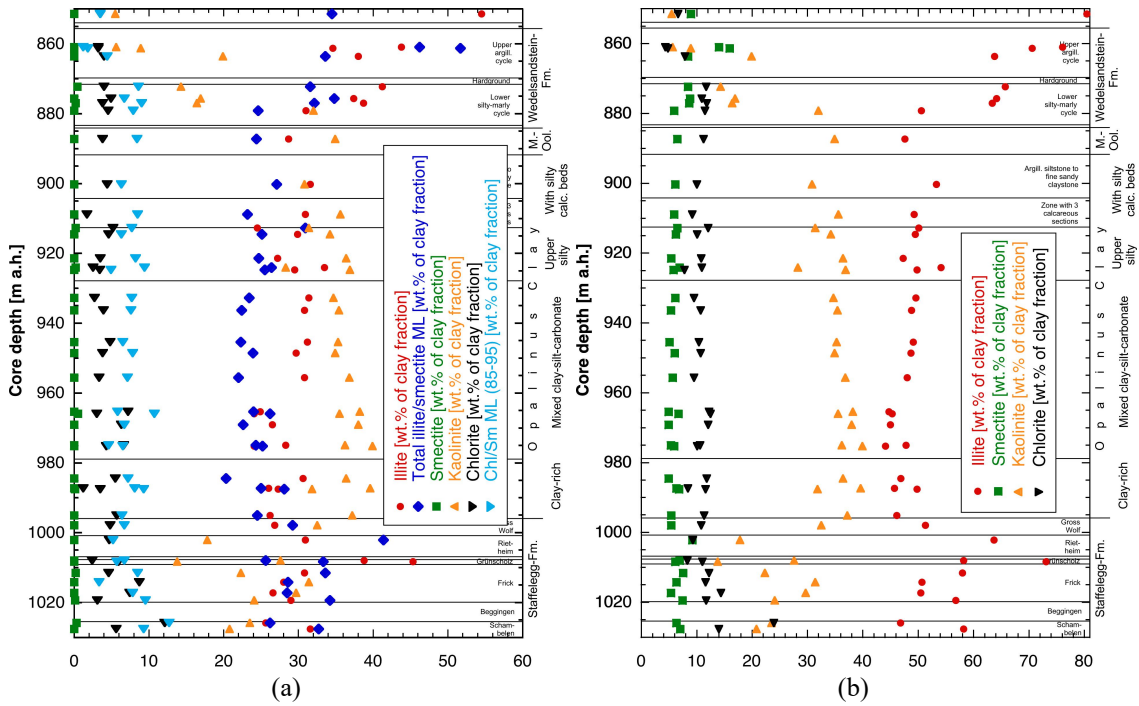


Fig. 4.2-5: Depth trends of clay minerals in the bulk rock in the interval Staffelegg Formation – Wedelsandstein Formation
Individual clay minerals (a), End-member clays (b). Detailed lithostratigraphic subdivision according to Dossier III.

4.2.3 Sulphate minerals in the Opalinus Clay and in the confining units

Sulphate minerals, such as anhydrite, celestite or barite, act as important controls of porewater chemistry, in particular of SO_4^{2-} concentrations, even if present in trace amounts only. By X-ray diffraction, sulphate phases were not identified with certainty in the Dogger and Lias units, even though small amounts could not be excluded. Moreover, calculations of saturation indices suggest calcium sulphate saturation in the BUL1-1 core, unlike at other sites. Therefore, four samples from the Opalinus Clay and the 'Brauner Dogger' were analysed by scanning electron microscopy combined with energy-dispersive spectroscopy (SEM-EDX) to investigate the possible presence of sulphur-containing mineral grains larger than 3 μm . A sample list is provided in Tab. 4.2-3.

Tab. 4.2-3: Samples selected for SEM studies

Sample depth [m]	Geological unit	Clay-mineral content [wt.-%]	Comments
881.54	Wedelsandstein Fm.	47	Relatively clay-poor; possible traces of gypsum and barite according to XRD
889.36	'Murchisonae-Oolith Fm.'	65	Clay-rich, possible traces of gypsum and barite according to XRD
897.27	Opalinus Clay	32	Clay-poor
927.52	Opalinus Clay	34	Clay-poor

Methodology

SEM-EDX detects elements but cannot reveal their valence state. The interaction between the incident electron beam and the sample occurs in a pear-shaped volume with a diameter of 1 – 2 μm , depending on the sample material and the properties of the electron beam. This constraint of the interaction volume places the physical limit to spatial resolution. In the fine-grained sedimentary rocks at hand, where single particles may be smaller than the interaction volume, a single measurement (resulting in one pixel on an element map) often represents a mixture of several phases. This has to be considered when processing such maps.

Samples were cut perpendicular to bedding, and the resulting surface was ground and polished without using water. Four sets of elemental maps and a backscattered electron (BE) image were acquired on the four different samples in low-vacuum mode (no carbon coating of the sample required). Two different sets of parameters were used:

1. Total area 2.1 mm $\times$ 1.6 mm, resolution 2.7 $\mu\text{m}/\text{pixel}$, dwell time 200 $\mu\text{s}/\text{pixel}$, 32 frames, acceleration voltage 20 keV, beam current 986 pA, yielding a dead time of approx. 10 %.
2. Total area 2.6 mm $\times$ 0.9 mm, resolution 1.35 $\mu\text{m}/\text{pixel}$, dwell time 320 $\mu\text{s}/\text{pixel}$, 32 frames, acceleration voltage 20 keV, beam current 1.2 nA, yielding a dead time of approx. 10 %.

The resulting maps were processed by image analysis. The S map was segmented to reveal locations with S above background concentration. Locations high in Fe (pyrite) were subtracted. The resulting binary map was inspected and further processed by subtracting bright areas of the BE image (other heavy elements like Zn, Sr, Ba). The resulting binary map was combined with locations high in Ca, resulting in possible locations of calcium sulphate. Sr and Ba were not mapped because these elements require a higher acceleration voltage, which would increase the interaction volume and impair the detection of sub-micron grains. The approach taken to detect celestite or barite was to subtract areas high in Fe (mostly pyrite) from bright BE areas (i.e. minerals containing elements with high atomic numbers) and to combine these with high S areas.

Results and conclusions

The maps for all samples do not contain any grains $> 3 \mu\text{m}$ with S above background and no Fe or other heavy elements. However, some pixels (grains $< 3 \mu\text{m}$) reveal locations with high S and Ca, and no Fe. Fig. 4.2-6 shows such locations overlaid on the BE image. Such measurements are located:

- at pyrite-calcite interfaces, where S from pyrite is still above background, but Fe from pyrite is still within background or so not detected. EDX detection of Fe is less sensitive compared to S;
- within calcite grains. The spotty occurrence suggests the presence of very small pyrite grains, or grains below the surface but still within the measurement volume. The BE signal is generated closer to the surface and does not show compositions as deep as EDX does. Pyrite inclusions in calcite are commonly observed at various grain sizes, but also elevated S contents in calcite have been measured (Jenni et al. 2019);
- within apatite grains (Fig. 4.2-7, also observed in Jenni et al. 2019).

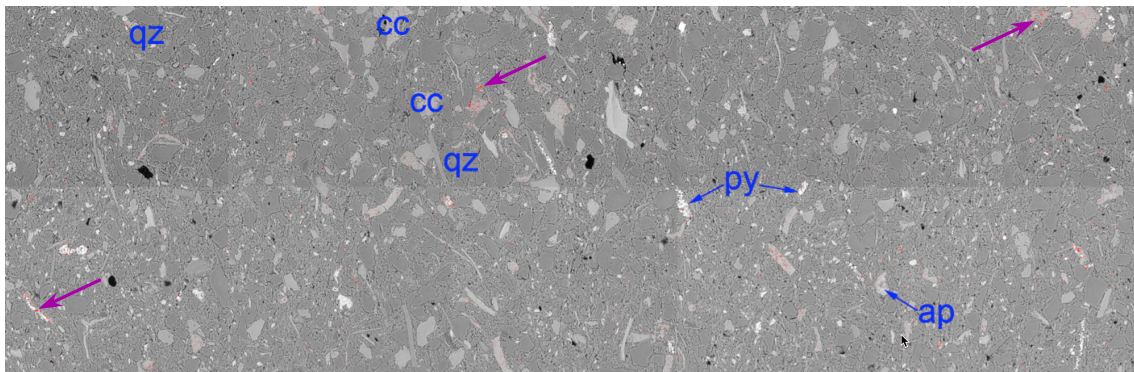


Fig. 4.2-6: BE image of sample 881.54 (Wedelsandstein Formation) with locations high in Ca, S and low in Fe shown in red

Purple arrows point to some of the locations. 2.6 mm image width, brighter areas represent higher average atomic number. Acquisition parameters 2. Black areas represent resin-filled holes (artefacts from preparation). qz = quartz, cc = calcite, py = pyrite, ap = apatite.

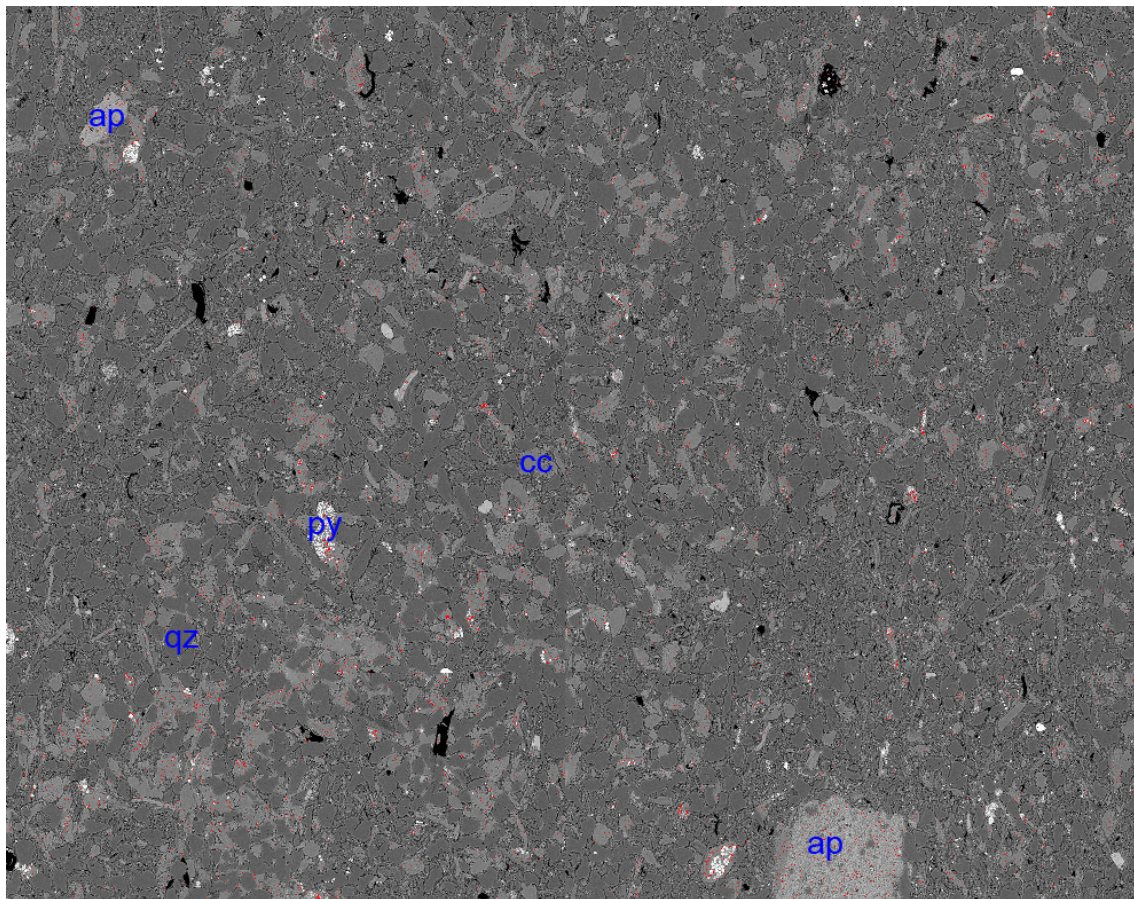


Fig. 4.2-7: BE image of sample 897.27 (Opalinus Clay) with possible Ca sulphate locations overlaid in red

1.4 mm image width, brighter areas represent higher average atomic number. Acquisition parameters 1. Black areas represent resin-filled holes (artefacts from preparation). qz = quartz, cc = calcite, py = pyrite, ap = apatite.

In conclusion, the candidate locations segmented by the conditions of S above background, low Fe (within background), and Ca above background do not represent occurrences of very fine-grained Ca sulphate minerals. Because the majority of the locations with high S and Ca are associated with calcite, samples with low calcite content (Fig. 4.2-8, clay-rich) show less candidate locations for Ca sulphate. In addition, S was detected in one sphalerite grain. Celestite has not been detected by the approach described above, but occurrences of sub-micron grains cannot be ruled out based on the current methodology.

The SEM-EDX study confirms the absence of Ca sulphate grains $> 3 \mu\text{m}$ in the examined areas of four samples (clay-rich and clay-poor). Despite the limited area analysed, the maps are large compared to the grain sizes and contain layers or domains of different characteristics (clay-rich, clay-poor, calcite-cemented, pyrite enrichments). Apart from S within detected pyrite and sphalerite grains, small amounts of S are present in apatite and calcite (very likely as sub-micron pyrite grains in the latter).

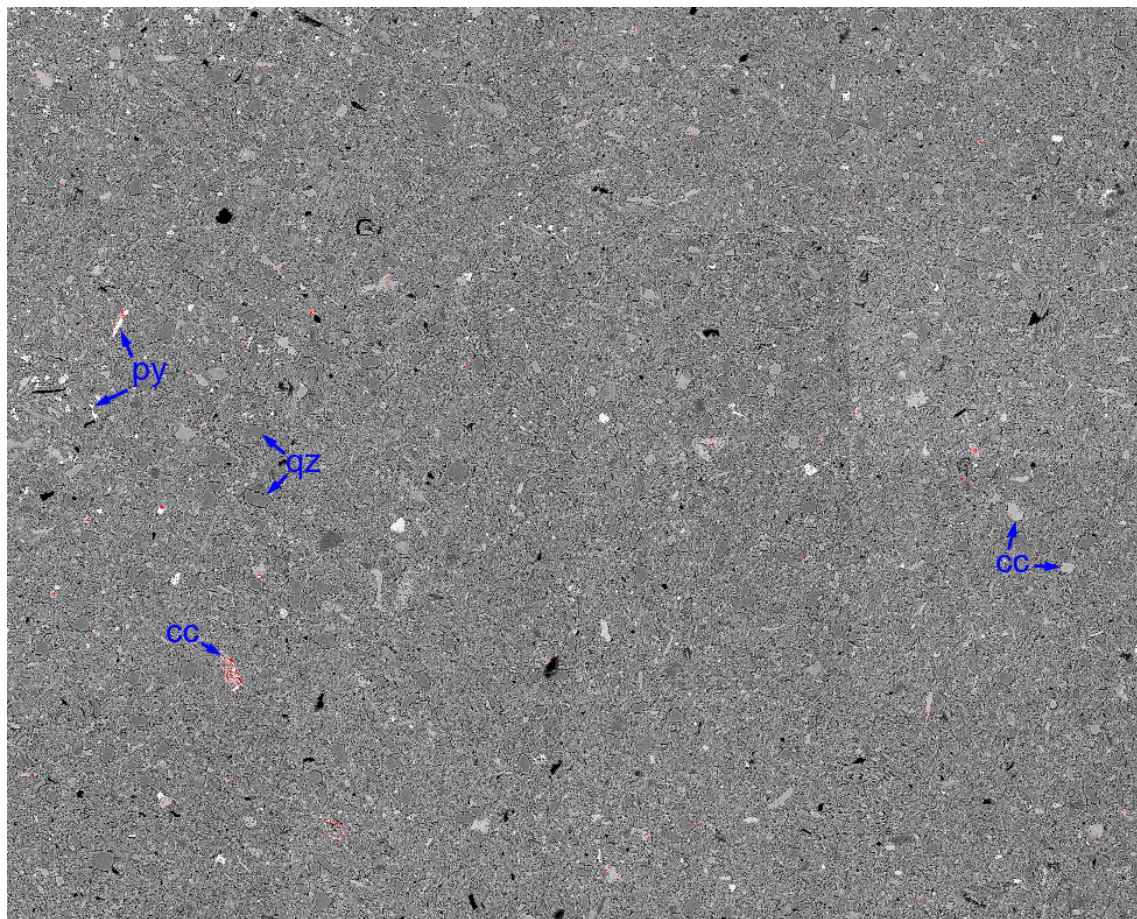


Fig. 4.2-8: BE image of sample 889.36 ('Murchisonae-Oolith Formation') with possible Ca sulphate locations overlaid in red

1.4 mm image width, brighter areas represent higher average atomic number. Acquisition parameters 1. Black areas represent resin-filled holes (artefacts from preparation). qz = quartz, cc = calcite, py = pyrite.

4.3 Petrophysical parameters

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The formalisms to calculate porosity from gravimetric water content are detailed in Waber (ed.) (2020). They all valid for systems with low porewater salinity, where porewater density is close to 1 g/cm^3 and the mass of dissolved constituents can be neglected. In the BUL1-1 core, porewater salinity is high in the Schinznach Formation, where the concentration of Cl^- in bulk porewater calculated from aqueous-extraction tests mostly exceeds 20 g/L . Therefore, the more complex formalisms as detailed in Section 3.4.1 are used to derive porewater content (wet and dry), bulk dry density, pycnometer and water-loss porosity in the Schinznach Formation. This is also the case for the calculation of the Cl^- concentration in porewater from aqueous-extraction data (Section 4.4). For the rest of the profile, the salinity effect is negligible, and the standard formalisms presented in Waber (ed.) (2020) are used.

Formation-specific statistical data for petrophysical parameters are summarised in Tab. 4.3-1, and the full data set is documented in Appendix 1.

Tab. 4.3-1: Summary of measured and calculated petrophysical data

Listed wet water contents are averages of measurements performed on typically 3 sub-samples. Formalisms for high pore-water salinities were used to calculate parameters for the Schinznach Formation. Thus, pore-water contents instead of water contents are listed as well as bulk dry density* (as defined in Section 3.4.1) instead of bulk dry density. These data result in slightly different calculated porosities. Data derived from isotope diffusive exchange are unchanged. n = number of analyses.

Formation	Member / Sub-unit		Bulk wet density [g/cm ³]	Bulk dry density, calc. [g/cm ³]	Grain density [g/cm ³]	Pycnometer porosity [-]	Gravimetry				Isotope mass bal.			External surface area (BET) [m ² /g dry rock]
							Water cont. (wet) (105 °C) [wt.-%]	Water cont. (dry) (105 °C) [wt.-%]	Water-loss porosity using bulk wet density [-]	Water-loss porosity using grain density [-]	Water cont. (wet) based on isotope diff. exchange [wt.-%]	Porosity based on isot. diff. exch. using bulk wet dens. [-]	Porosity based on isotope diff. exch. using grain dens. [-]	
'Felsenkalke' / 'Massenkalk'		Mean	2.670	2.657	2.721	0.024	0.514	0.518	0.014	0.015	0.488	0.013	0.013	2.11
		Median	2.672	2.659	2.722	0.019	0.437	0.438	0.012	0.012	0.449	0.012	0.012	2.11
		Stdev	0.022	0.027	0.008	0.012	0.276	0.281	0.007	0.010	0.108	0.003	0.003	1.46
		Min	2.630	2.590	2.706	0.013	0.276	0.277	0.007	0.009	0.348	0.009	0.009	1.08
		Max	2.708	2.701	2.732	0.052	1.506	1.529	0.040	0.040	0.655	0.018	0.018	3.14
		n	20	20	10	10	20	20	20	10	7	7	7	2
Schwarzbach Fm.		Mean	2.676	2.653	2.727	0.023	0.836	0.845	0.022	0.020	0.920	0.025	0.025	
		Median	2.670	2.649	2.727	0.023	0.802	0.809	0.021	0.020	0.920	0.025	0.025	
		Stdev	0.014	0.024	0.002	0.010	0.447	0.455	0.012	0.013	0.589	0.016	0.016	
		Min	2.666	2.630	2.725	0.016	0.401	0.403	0.011	0.011	0.503	0.014	0.014	
		Max	2.696	2.685	2.729	0.031	1.340	1.358	0.036	0.029	1.337	0.036	0.036	
		n	4	4	2	2	4	4	4	2	2	2	2	0
Villigen Fm.		Mean	2.661	2.644	2.713	0.023	0.839	0.848	0.017	0.020	0.874	0.023	0.023	7.71
		Median	2.658	2.645	2.716	0.026	0.807	0.813	0.013	0.018	0.756	0.020	0.020	7.71
		Stdev	0.029	0.034	0.010	0.010	0.466	0.475	0.009	0.011	0.496	0.013	0.013	0.56
		Min	2.624	2.603	2.697	0.010	0.303	0.304	0.008	0.008	0.454	0.012	0.012	7.31
		Max	2.698	2.690	2.725	0.034	1.560	1.585	0.034	0.034	1.528	0.040	0.040	8.10
		n	9	9	6	5	12	12	9	6	4	4	4	2
Wildeggen Fm.	Effingen Mb.	Mean	2.612	2.551	2.710	0.056	2.278	2.333	0.060	0.056	2.583	0.068	0.067	15.64
		Median	2.617	2.558	2.714	0.053	2.142	2.189	0.059	0.054	2.340	0.061	0.061	15.63
		Stdev	0.030	0.039	0.008	0.013	0.442	0.464	0.012	0.013	0.662	0.017	0.016	2.11
		Min	2.557	2.490	2.698	0.041	1.618	1.645	0.045	0.043	1.873	0.049	0.049	13.08
		Max	2.651	2.606	2.719	0.076	3.086	3.184	0.080	0.080	3.473	0.090	0.089	18.23
		n	8	8	8	5	13	13	8	8	5	5	5	4

Tab. 4.3-1: (continued)

Formation	Member / Sub-unit		Bulk wet density [g/cm ³]	Bulk dry density, calc. [g/cm ³]	Grain density [g/cm ³]	Pycnometer porosity [–]	Gravimetry				Isotope mass bal.			External surface area (BET) [m ² /g dry rock]
							Water cont. (wet) (105 °C) [wt.-%]	Water cont. (dry) (105 °C) [wt.-%]	Water-loss porosity using bulk wet density [–]	Water-loss porosity using grain density [–]	Water cont. (wet) based on isotope diff. exchange [wt.-%]	Porosity based on isot. diff. exch. using bulk wet dens. [–]	Porosity based on isotope diff. exch. using grain dens. [–]	
Varians-mergel Fm.		Mean	2.486	2.360	2.736	0.120	5.088	5.363	0.126	0.117	4.943	0.125	0.125	
		Median	2.486	2.360	2.736	0.120	5.088	5.363	0.126	0.117	4.943	0.125	0.125	
		Stdev	0.056	0.069			0.641	0.712	0.013					
		Min	2.447	2.311			4.634	4.859	0.117					
		Max	2.526	2.409			5.541	5.866	0.136					
		n	2	2	1	1	2	2	2	1	1	1	1	0
'Parkinsoni-Württ.-Sch.'		Mean	2.503	2.367	2.732	0.135	5.387	5.695	0.135	0.135	5.720	0.144	0.142	37.62
		Median	2.503	2.367	2.730	0.135	5.360	5.664	0.135	0.133	5.720	0.144	0.142	37.62
		Stdev	0.015	0.029	0.013	0.014	0.422	0.472	0.014	0.010				
		Min	2.492	2.347	2.720	0.125	4.979	5.240	0.125	0.125				
		Max	2.513	2.388	2.746	0.145	5.823	6.183	0.145	0.145				
		n	2	2	3	2	3	3	2	3	1	1	1	1
'Herrenwis Unit'		Mean	2.671	2.651	2.733	0.030	0.767	0.774	0.021	0.020	0.868	0.026	0.024	3.48
		Median	2.669	2.651	2.727	0.029	0.706	0.711	0.021	0.019	0.852	0.027	0.026	3.05
		Stdev	0.030	0.031	0.015	0.009	0.316	0.322	0.005	0.009	0.285	0.006	0.008	2.23
		Min	2.618	2.596	2.717	0.019	0.313	0.314	0.015	0.008	0.457	0.015	0.012	1.14
		Max	2.729	2.710	2.766	0.045	1.476	1.498	0.034	0.039	1.342	0.033	0.032	7.20
		n	12	12	12	7	23	23	12	18	12	6	7	6
'Humphriesool. Fm.'		Mean	2.712	2.699	2.758	0.022	0.499	0.502	0.014	0.014	0.642	0.017	0.018	
		n	1	1	1	1	1	1	1	1	1	1	1	0
Wedel-sandstein Fm.		Mean	2.533	2.429	2.703	0.100	4.110	4.296	0.104	0.103	4.610	0.118	0.116	25.10
		Median	2.520	2.409	2.699	0.108	4.147	4.327	0.106	0.103	4.665	0.127	0.125	23.80
		Stdev	0.046	0.070	0.014	0.026	0.958	1.039	0.026	0.023	1.218	0.031	0.031	5.94
		Min	2.482	2.351	2.688	0.050	2.252	2.304	0.059	0.059	2.598	0.069	0.068	19.57
		Max	2.638	2.579	2.743	0.127	5.530	5.854	0.138	0.137	6.341	0.158	0.155	33.22
		n	12	12	18	9	18	18	12	14	8	7	7	4
'Murch.-Oolith Fm.'		Mean	2.499	2.376	2.683	0.114	4.838	5.085	0.122	0.121	5.995	0.150	0.146	
		Median	2.502	2.376	2.689	0.117	4.859	5.107	0.126	0.125	6.122	0.153	0.150	
		Stdev	0.036	0.025	0.017	0.007	0.308	0.340	0.011	0.009	0.433	0.013	0.010	
		Min	2.461	2.351	2.664	0.107	4.477	4.687	0.110	0.111	5.512	0.136	0.135	
		Max	2.532	2.402	2.697	0.119	5.158	5.439	0.131	0.128	6.349	0.161	0.154	
		n	3	3	3	3	4	4	3	3	3	3	3	0

Tab. 4.3-1: (continued)

Formation	Member / Sub-unit		Bulk wet density [g/cm ³]	Bulk dry density, calc. [g/cm ³]	Grain density [g/cm ³]	Pycnometer porosity [–]	Gravimetry				Isotope mass bal.			External surface area (BET) [m ² /g dry rock]
							Water cont. (wet) (105 °C) [wt.-%]	Water cont. (dry) (105 °C) [wt.-%]	Water-loss porosity using bulk wet density [–]	Water-loss porosity using grain density [–]	Water cont. (wet) based on isotope diff. exchange [wt.-%]	Porosity based on isot. diff. exch. using bulk wet dens. [–]	Porosity based on isotope diff. exch. using grain dens. [–]	
Opalinus Clay	All	Mean	2.535	2.429	2.696	0.099	4.208	4.396	0.105	0.106	4.623	0.117	0.115	29.23
		Median	2.536	2.428	2.694	0.100	4.342	4.539	0.108	0.108	4.786	0.120	0.120	30.22
		Stdev	0.029	0.037	0.011	0.011	0.511	0.555	0.012	0.013	0.601	0.015	0.014	4.37
		Min	2.433	2.323	2.671	0.071	2.691	2.765	0.069	0.069	2.844	0.073	0.073	19.15
		Max	2.620	2.535	2.719	0.118	5.208	5.494	0.122	0.130	5.359	0.136	0.133	35.54
		n	43	43	56	33	60	60	43	44	31	31	31	16
Opalinus Clay	With silty calc. beds	Mean	2.546	2.445	2.698	0.098	4.100	4.281	0.101	0.101	4.386	0.111	0.110	25.33
		Median	2.536	2.437	2.697	0.104	4.461	4.669	0.106	0.106	4.571	0.115	0.115	25.33
		Stdev	0.037	0.051	0.010	0.018	0.733	0.792	0.018	0.019	0.995	0.024	0.024	8.74
		Min	2.507	2.386	2.686	0.071	2.691	2.765	0.069	0.069	2.844	0.073	0.073	19.15
		Max	2.620	2.535	2.715	0.116	4.806	5.049	0.120	0.120	5.359	0.136	0.133	31.51
		n	9	9	13	6	11	11	9	7	6	6	6	2
Opalinus Clay	Upper silty	Mean	2.542	2.449	2.695	0.093	3.708	3.852	0.093	0.094	4.024	0.102	0.101	26.64
		Median	2.545	2.452	2.694	0.096	3.637	3.774	0.092	0.093	4.075	0.103	0.103	26.64
		Stdev	0.011	0.015	0.011	0.006	0.281	0.303	0.007	0.007	0.298	0.007	0.007	2.74
		Min	2.520	2.422	2.677	0.085	3.216	3.323	0.082	0.082	3.651	0.093	0.093	24.70
		Max	2.551	2.469	2.715	0.099	4.104	4.279	0.103	0.104	4.486	0.114	0.112	28.58
		n	8	8	11	7	11	11	8	9	6	6	6	2
Opalinus Clay	Mixed clay-silt-carb.	Mean	2.530	2.420	2.693	0.100	4.343	4.542	0.110	0.110	4.844	0.123	0.120	29.93
		Median	2.535	2.425	2.694	0.101	4.364	4.563	0.110	0.109	4.817	0.123	0.120	30.22
		Stdev	0.033	0.037	0.010	0.009	0.427	0.466	0.008	0.010	0.320	0.008	0.007	3.89
		Min	2.433	2.323	2.671	0.083	3.401	3.521	0.096	0.087	4.347	0.111	0.109	23.96
		Max	2.586	2.490	2.717	0.118	5.208	5.494	0.122	0.130	5.324	0.136	0.132	35.54
		n	19	19	25	15	28	28	19	21	15	15	15	10
Opalinus Clay	Clay-rich	Mean	2.523	2.410	2.702	0.107	4.501	4.713	0.113	0.113	5.051	0.128	0.126	32.21
		Median	2.530	2.412	2.702	0.108	4.516	4.730	0.113	0.114	5.034	0.128	0.125	32.21
		Stdev	0.019	0.017	0.011	0.007	0.103	0.113	0.003	0.002	0.109	0.002	0.002	0.16
		Min	2.494	2.385	2.690	0.099	4.319	4.514	0.108	0.111	4.956	0.126	0.123	32.10
		Max	2.540	2.428	2.719	0.117	4.671	4.900	0.118	0.115	5.178	0.129	0.129	32.32
		n	7	7	7	5	10	10	7	7	4	4	4	2
Staffelegg Fm.		Mean	2.574	2.505	2.686	0.074	2.754	2.848	0.069	0.073	3.076	0.078	0.078	16.18
		Median	2.560	2.479	2.692	0.080	3.219	3.326	0.082	0.082	3.272	0.084	0.083	19.18
		Stdev	0.090	0.119	0.050	0.025	1.225	1.281	0.031	0.027	1.218	0.029	0.029	10.40
		Min	2.386	2.282	2.562	0.020	0.360	0.361	0.010	0.013	0.794	0.021	0.021	1.25
		Max	2.709	2.699	2.740	0.109	4.383	4.584	0.105	0.105	5.170	0.123	0.123	27.26
		n	14	14	16	10	21	21	14	15	9	9	9	7

Tab. 4.3-1: (continued)

4.3.1 Water content

Martin Mazurek & Lukas Aschwanden

The distribution of the gravimetric water content in the studied section Malm – Muschelkalk is shown in Fig. 4.3-1. Water contents are low in the 'Felsenkalke' / 'Massenkalk' and in the upper part of the Villigen Formation. Then, the values start increasing with depth and reach high values in the uppermost Dogger. In the underlying reef facies of the 'Herrenwis Unit', water contents are again low. An abrupt change to higher values is observed in the Wedelsandstein Formation, and these persist to the base of the Staffelegg Formation. Values in the Triassic are heterogeneous, reflecting the lithological diversity in this section. The highest water contents are observed in the dolomites in uppermost part of the Schinznach Formation (Asp and Stamberg Members).

Water contents from gravimetry and from isotope diffusive exchange correlate well (Fig. 4.3-2), but the latter shows values that are consistently higher, about 12 ‰_{rel} on the average.

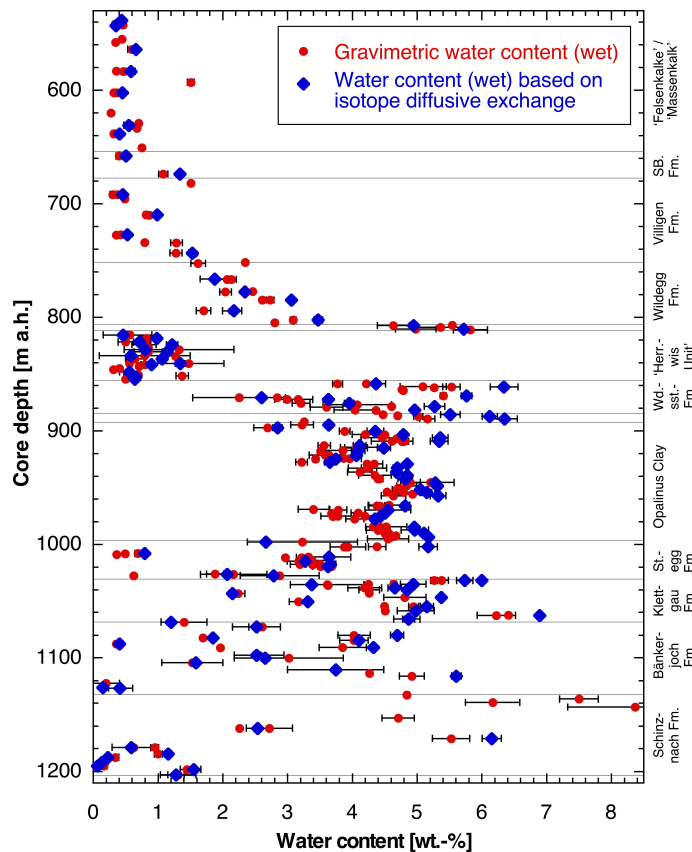


Fig. 4.3-1: Water content as a function of depth

Black bars for gravimetric water content indicate 1 σ variability among several aliquots of the same sample. Black bars for water content from isotope diffusive exchange represent the propagated analytical error.

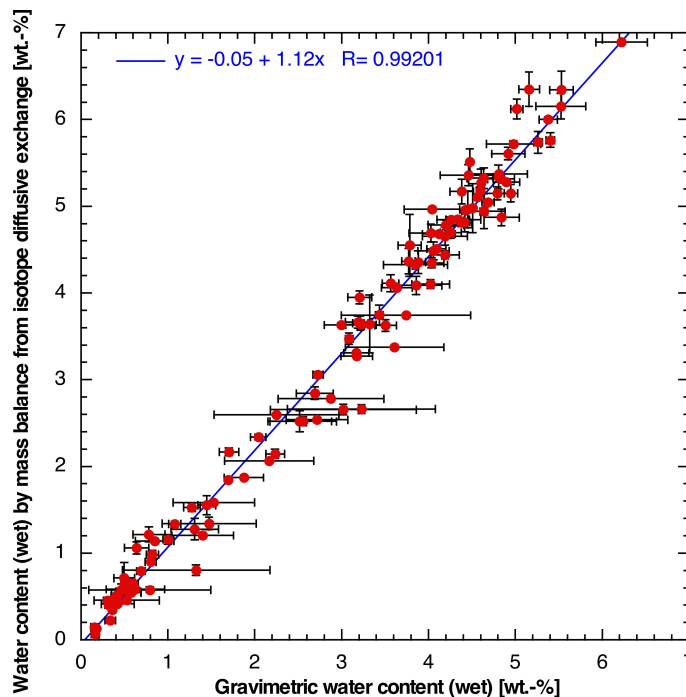


Fig. 4.3-2: Correlation of water contents based on gravimetry and on isotope diffusive exchange

Black bars for gravimetric water content indicate 1σ variability among several aliquots of the same sample. Black bars for water content from isotope diffusive exchange represent the propagated analytical error.

A closer look at the clay-rich section Staffelegg Formation – Opalinus Clay – Wedelsandstein Formation

As shown in Fig. 4.3-3, water contents in the clay-rich section of the Lias – Dogger show systematic depth trends. These correlate with those identified for clay-mineral contents (Section 4.2.1, Fig. 4.2-3) and show a negative correlation with the ratio quartz/clay minerals. It is evident that a substantial part of the porewater is related to the presence of clay minerals.

The depth trends are identical for gravimetric water content and that obtained from isotope diffusive exchange, with the exception of the kink at 970 – 980 m. Here, gravimetric water content (as well as clay-mineral content) suggest a reversal of the trend at about 970 m, i.e. within the mixed clay – silt – carbonate sub-unit of the Opalinus Clay. In contrast, the reversal fits with the boundary to the underlying clay-rich sub-unit at about 980 m in the case of water contents obtained from isotope diffusive exchange.

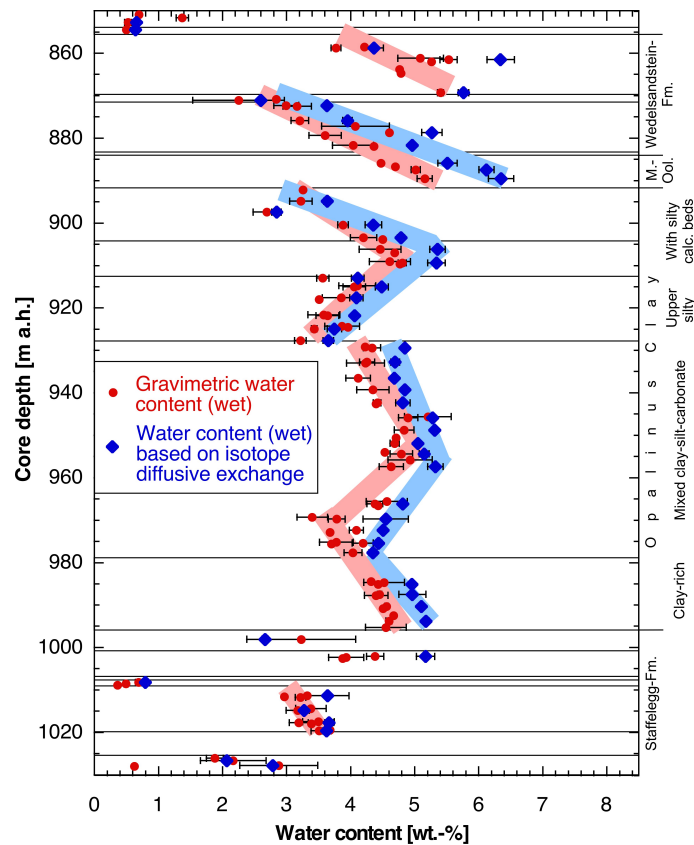


Fig. 4.3-3: Water content (wet) as a function of depth in the interval Staffelegg Formation – Wedelsandstein Formation

Black bars for gravimetric water content indicate 1σ variability among several aliquots of the same sample. Black bars for water content from isotope diffusive exchange represent the propagated analytical error.

4.3.2 Grain density

Martin Mazurek & Lukas Aschwanden

The grain-density profile is shown in Fig. 4.3-4.

- In the limestone-dominated Malm section ('Felsenkalke' / 'Massenkalk' – Wildegg Formation), grain density shows little variation ($2.716 \pm 0.010 \text{ g/cm}^3$, range $2.697 - 2.732 \text{ g/cm}^3$, $n = 26$).
- In the 'Herrenwis Unit', grain density is slightly higher and shows more variability ($2.733 \pm 0.015 \text{ g/cm}^3$, range $2.717 - 2.766 \text{ g/cm}^3$, $n = 12$). This is likely due to the somewhat higher dolomite contents.
- In the section Wedelsandstein-Formation – Opalinus Clay – Staffelegg Formation, grain density is lower than in the overlying units and shows little variability ($2.698 \pm 0.013 \text{ g/cm}^3$, range $2.664 - 2.743 \text{ g/cm}^3$, $n = 91$, excluding the two very low values in the Staffelegg Formation).

- Two outliers in the Rietheim Member of the Staffelegg Formation (this unit is better known as Posidonien-schiefer) have low grain densities ($2.562 - 2.569 \text{ g/cm}^3$) because of their high content of organic matter ($3.8 - 4.8 \text{ wt.-%}$).
- In the Triassic, grain densities scatter widely, reflecting the lithological variability. Fig. 4.3-5 shows linear correlations between grain density and the contents of anhydrite and dolomite/ankerite. These minerals are the main causes for the heterogeneous distribution of grain densities in this part of the profile.

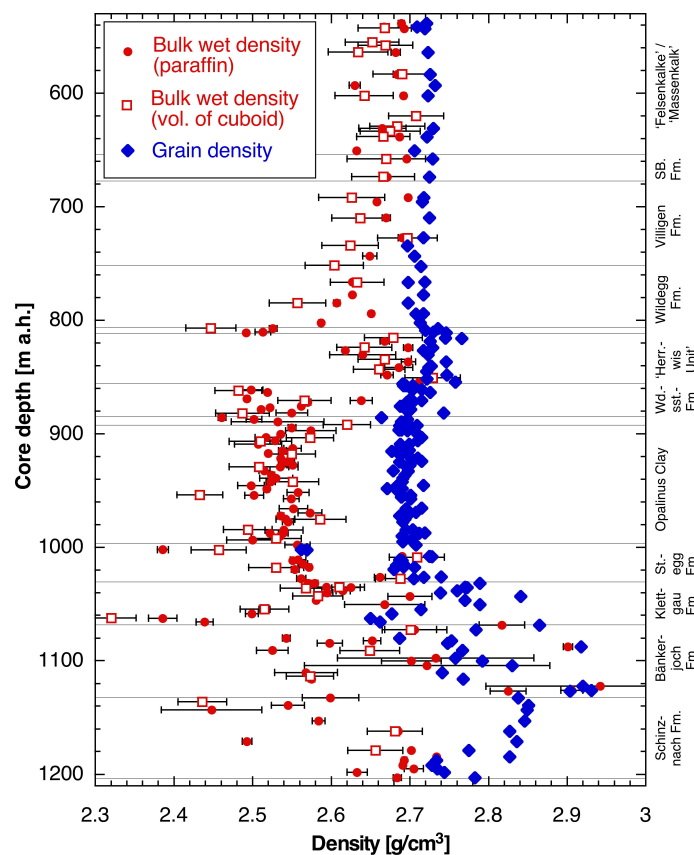


Fig. 4.3-4: Depth profile of bulk wet and grain densities

Black bars for bulk wet density indicate 1σ variability among several (mostly 3) pieces of the same sample. Analytical error bars for grain density are smaller than the symbol size.

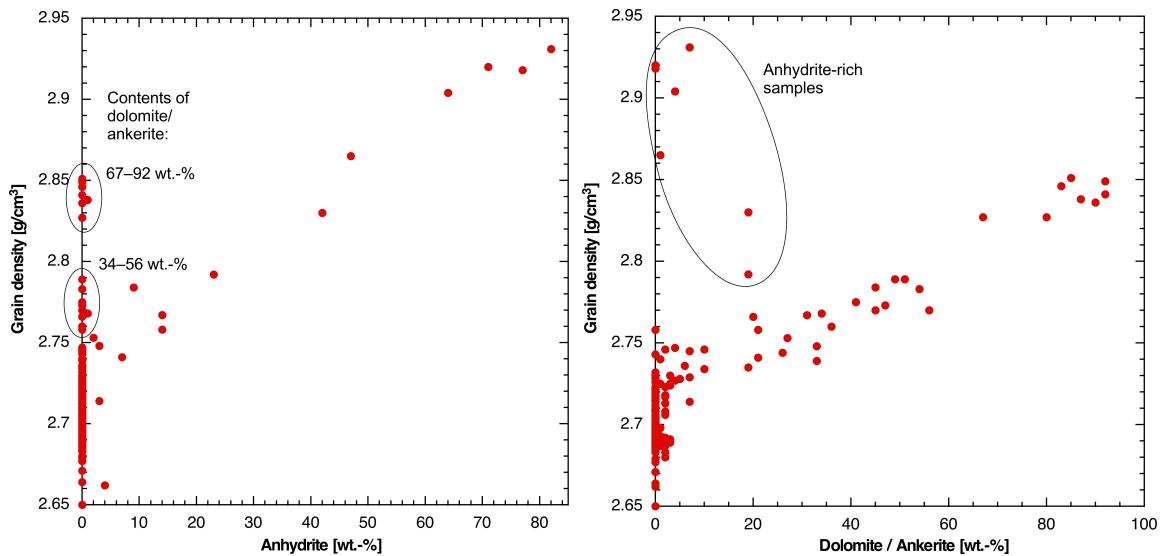


Fig. 4.3-5: Grain density as a function of the contents of anhydrite and dolomite/ankerite

4.3.3 Bulk wet density

Martin Mazurek & Lukas Aschwanden

In addition to the data obtained by the paraffin displacement method based on Archimedes' principle (Waber ed. 2020), bulk density data were also obtained on the samples used for noble-gas analysis. In this case, sample volume was obtained by the measurement of the edge lengths of the cuboids. Given the presence of geometric irregularities, the propagated error of bulk wet density is larger. Data obtained from both methods are shown as a function of depth in Fig. 4.3-4. The method based on the measured cuboid volume yields comparable, sometimes slightly lower values compared to the paraffin method.

4.3.4 Porosity

Martin Mazurek & Lukas Aschwanden

Three different approaches were used to constrain rock porosity (for details see Waber ed. 2020):

- *Water-loss porosity*: calculation from the gravimetric water content using either bulk wet or grain density
- *Porosity from isotope diffusive exchange*: calculation from the water content obtained by mass balance using either bulk wet or grain density
- *Pycnometer porosity*: calculation from bulk dry and grain densities; bulk dry density is calculated from bulk wet density and water content.

Water-loss porosity and porosity from isotope diffusive exchange were calculated using bulk wet density by default. If the latter was not available, grain density was used (assuming fully saturated pores). The graphic in Fig. 4.3-6 shows that the two densities yield near-identical porosities, so the choice of the density for the calculation incurs no additional uncertainty. This is also evidence for full water saturation of the samples.

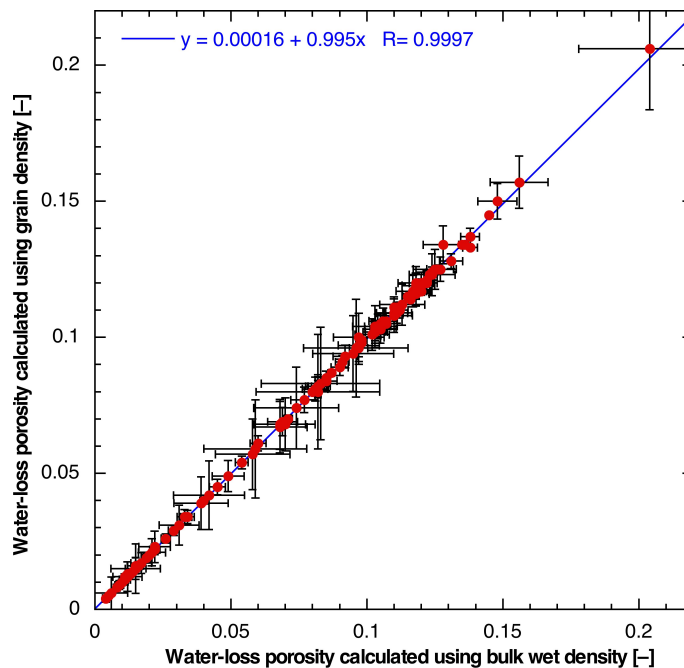


Fig. 4.3-6: Water-loss porosity calculated from gravimetric water content using either bulk wet or grain density

Bars indicate propagated errors.

Comparison of porosities obtained by different methods

- An excellent linear correlation is observed between water-loss porosity and porosity from isotope diffusive exchange (Fig. 4.3-7). The latter yields about 11 % higher values.
- A slightly less good linear correlation is found between pycnometer porosity and porosity from isotope diffusive exchange (Fig. 4.3-8). The latter yields about 19 % higher values. Samples from the Schinznach Formation lie to the right of the regression line. The relative difference between the two methods is most substantial for low-porosity samples, where porosity from isotope diffusive exchange comes close to zero.
- The correlation between water-loss and pycnometer porosity is shown in Fig. 4.3-9, where the data are colour-coded for clay-mineral content. For several clay-poor samples with typical porosities < 0.05 (and also some samples with higher porosities), pycnometer porosity exceeds water-loss porosity. Whether the volume occupied by fluid inclusions contributes to this effect is yet to be explored. The opposite is observed for clay-rich samples with porosities in the range 0.08 – 0.13. These two effects result in a linear regression line with a slope well below 1.

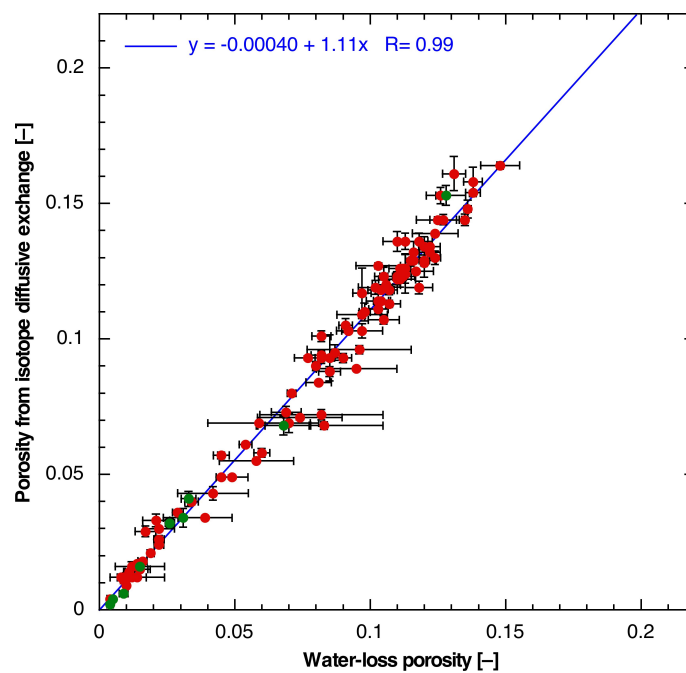


Fig. 4.3-7: Correlation of water-loss porosity and porosity from isotope diffusive exchange
Green symbols highlight samples from the Schinznach Formation. Bars indicate propagated errors.

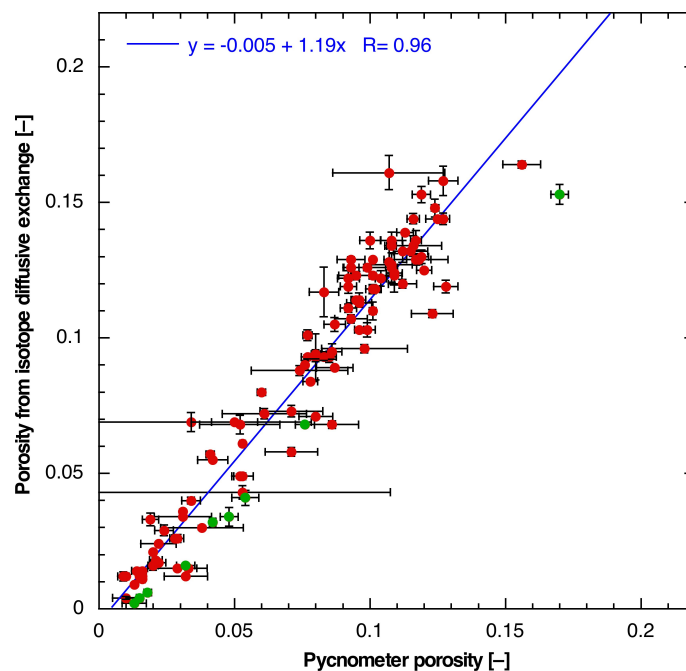


Fig. 4.3-8: Correlation of pycnometer porosity and porosity from isotope diffusive exchange
Green symbols highlight samples from the Schinznach Formation. Bars indicate propagated errors.

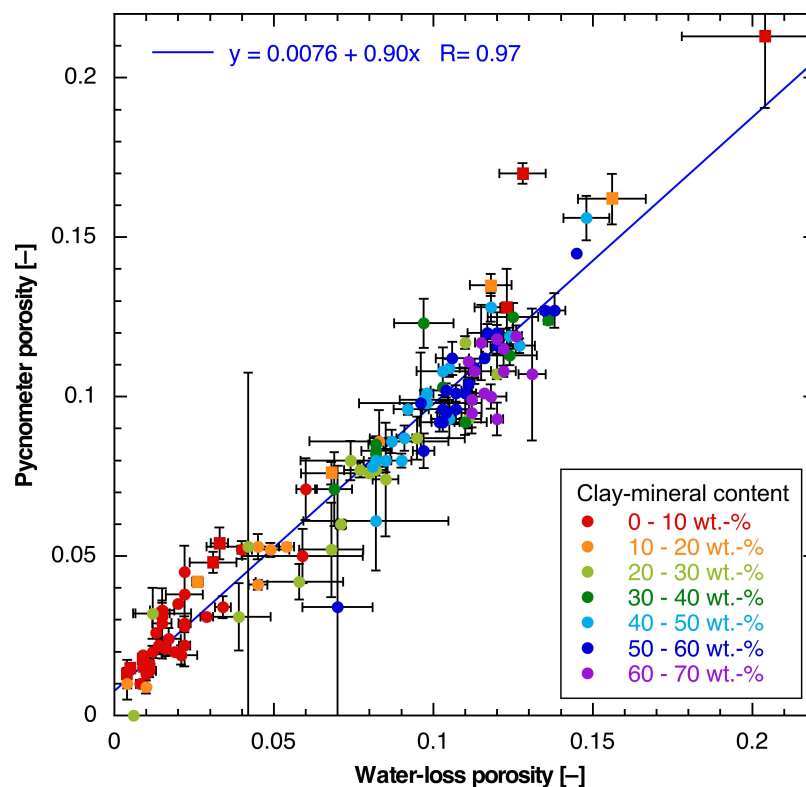


Fig. 4.3-9: Correlation of water-loss and pycnometer porosity

Squares highlight samples from the Schinznach Formation. Bars indicate propagated errors.

Depth trends

In Fig. 4.3-10, porosity is shown as a function of depth. Low porosities are found in the limestone-dominated section 'Felsenkalke' / 'Massenkalk' to the upper half of the Villigen Formation. In the lower part of the Villigen Formation, porosity starts increasing and reaches the highest values in the uppermost metres of the Dogger. This trend correlates well with increasing clay-mineral contents (Fig. 4.2-1). An abrupt drop of porosity is observed in the limestones of the 'Herrenwis Unit'. High porosities are then found in the clay-rich section 'Brauner Dogger' – Staffelegg Formation. Porosities in the Triassic units are heterogeneous, reflecting the lithological heterogeneity. Particularly high values are observed in the dolomites in the upper part of the Schinznach Formation.

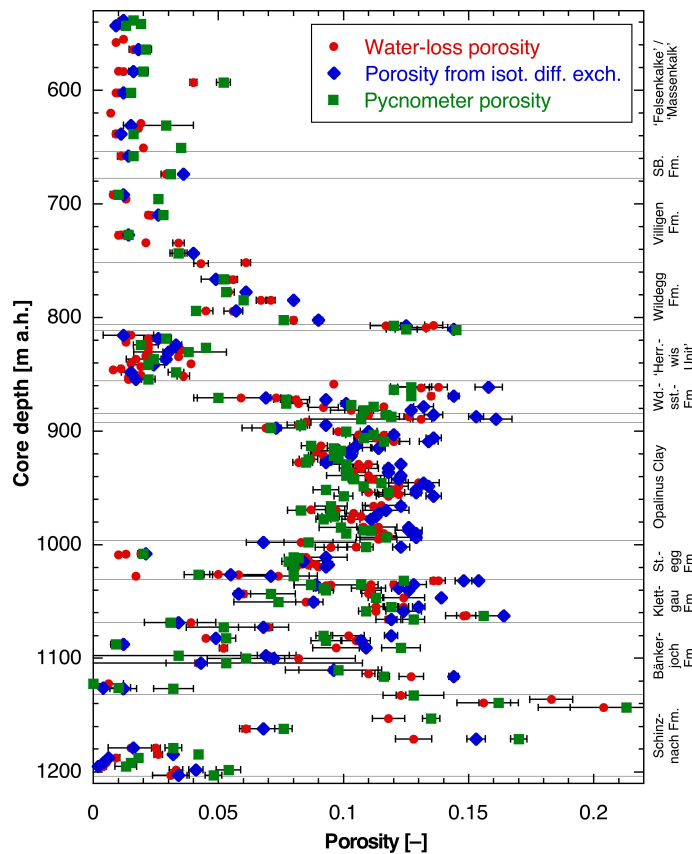


Fig. 4.3-10: Depth trends of porosities obtained by different methods

Bars indicate propagated errors.

Porosity as a function of mineralogical composition

As expected, porosity correlates with clay-mineral content (Fig. 4.3-11). However, given the fact that the correlation is far from perfect, clay-mineral content is not the only parameter that determines porosity. For example, dissolution features in the dolomites in the upper part of the Schinz-nach Formation (Asp and Stamberg Members) can lead to high porosities even in clay-poor rocks. Further, there appears to be a break in the slope in Fig. 4.3-11 at a clay-mineral content of about 30 – 35 wt.-%, with a more limited dependence of porosity on clay-mineral content above this threshold. The reason for this is not entirely clear but could be related to the switch from particle-supported to matrix-supported fabrics. Bourg (2015) came to the same conclusion in a study of sealing properties, considering data from a wide range of argillaceous rocks. Fig. 4.3-12 shows linear and square fits to the data in Fig. 4.3-11.

Another conspicuous mineralogical effect on porosity is the presence of anhydrite. Anhydrite content shows a negative correlation with porosity, which comes close to zero for anhydrite contents > 70 wt.-% (Fig. 4.3-13).

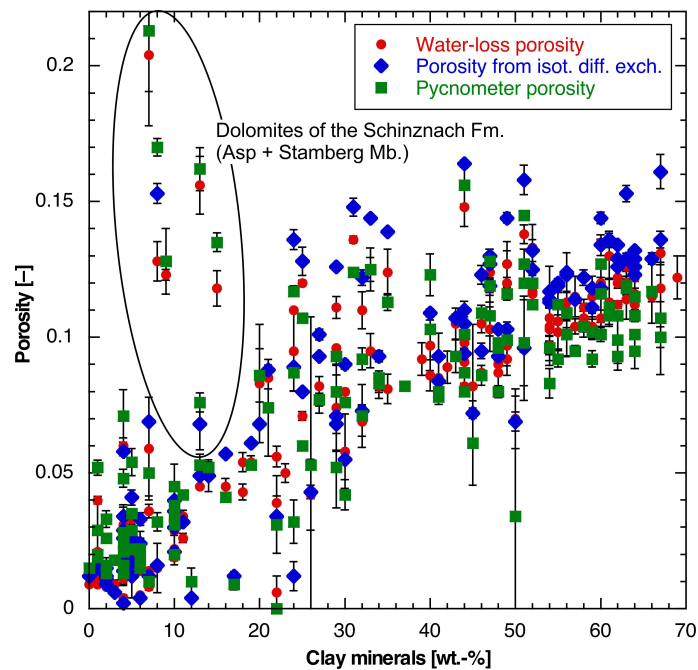


Fig. 4.3-11: Porosity as a function of clay-mineral content

Bars indicate propagated errors.

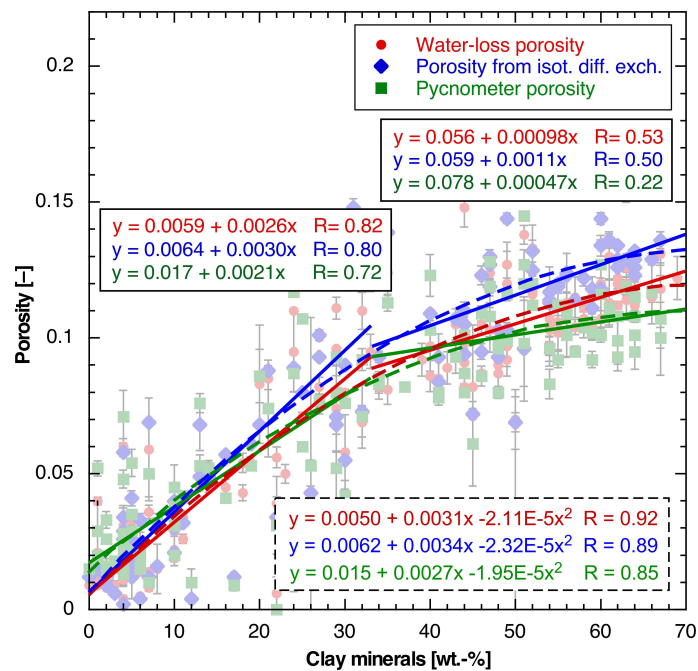


Fig. 4.3-12: Best fits to the correlation between clay-mineral content and porosity

Solid lines: separate linear fits for the regions 0 – 33 and > 33 wt.-% clay minerals. Dashed lines: square fits to the entire range of clay-mineral contents. Dolomites of the Schinznach Formation (Asp and Stenberg Members) were not considered for fitting.

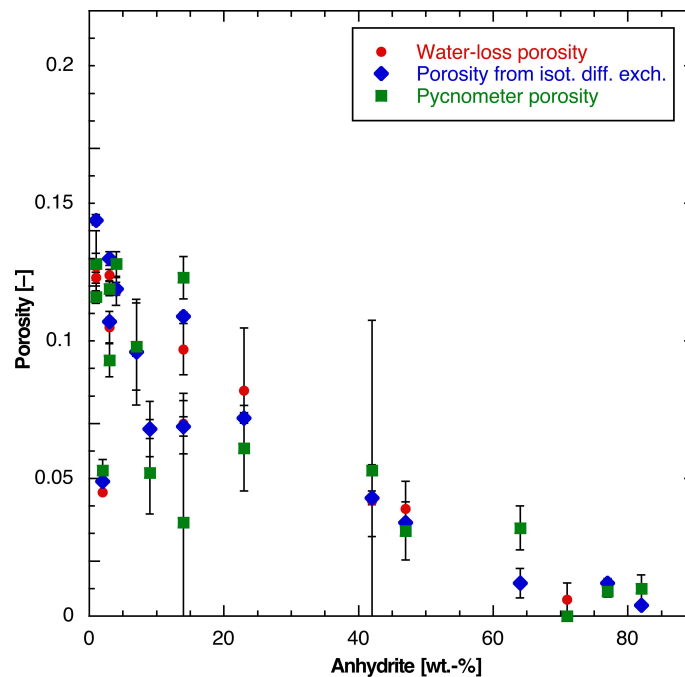


Fig. 4.3-13: Porosity of anhydrite-bearing samples

Bars indicate propagated errors.

4.3.5 N₂ surface area (BET) and N₂ ad-/desorption isotherms

Thomas Gimmi

Depth trends

Specific surface areas S_{BET} clearly vary with the rock formation (Tab. 4.3-1 and Fig. 4.3-14). They are denoted as external surface areas in the plots because only external pores, excluding any inter-layer pores of smectites, are reached by N₂. Largest values in the range of about 20 to 35 m²/g were found for clay-rich units, such as the Opalinus Clay, the Wedelsandstein Formation, the 'Parkinsoni-Württembergica-Schichten' and (in large parts) the Staffelegg Formation. Lowest values occur in predominantly calcareous lithologies, such as the Malm at the top of the sequence ('Felsenkalk' / 'Massenkalk'), the 'Herrenwis Unit', the Schinznach Formation, and in two samples from the Grünschholz Member. in the Staffelegg Formation which have a low clay mineral content. The large range of values found in the Staffelegg Formation points to a pronounced heterogeneity in this formation, as also evidenced by the clay mineral contents.

The variation of the specific surface areas S_{BET} follows trends observed in other physical properties of samples from the Bülach borehole, notably the bulk dry density, the gravimetric water content, the water-loss porosity or the clay mineral content. Accordingly, clear correlations of specific surface areas with these properties are found, as displayed in the following plots.

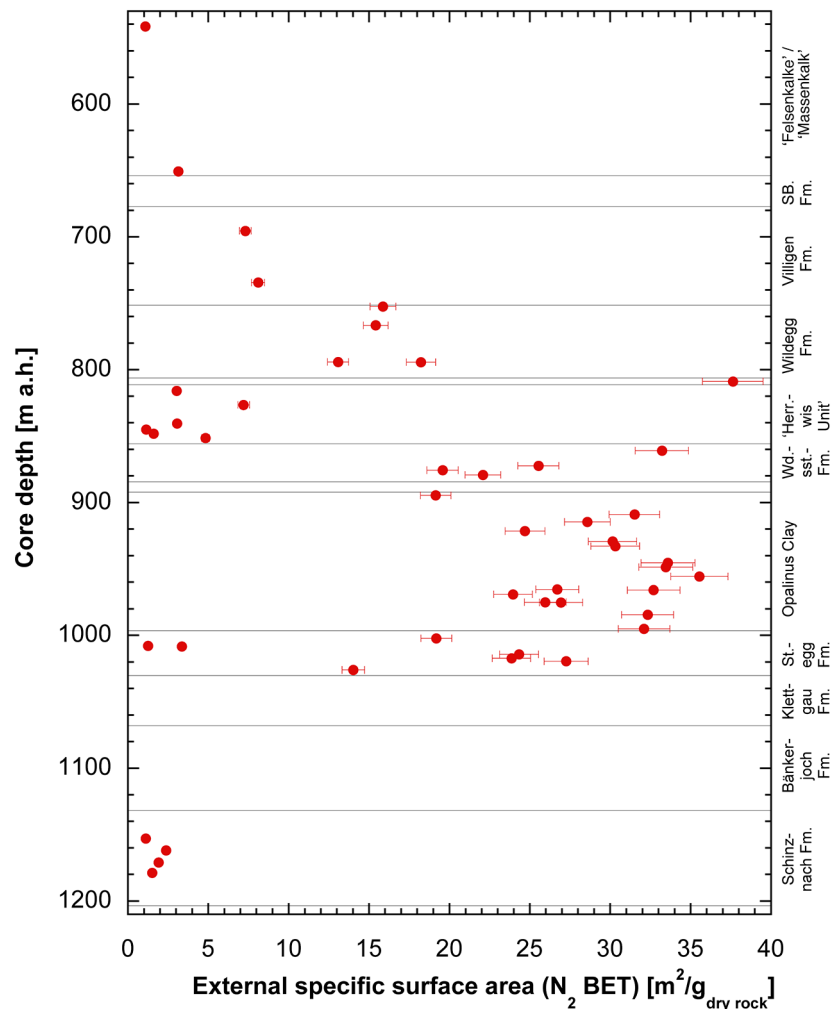


Fig. 4.3-14: Depth profile of specific surface areas (S_{BET}) derived from N_2 adsorption

S_{BET} represents external surfaces only. The total specific surface area, including interlayer surfaces, would be larger depending on the smectite content of the sample. Errors resulting from sample preparation and handling are estimated to be $\pm 5\%$ in general and $\pm 10\%$ for $S_{\text{BET}} < 2 \text{ m}^2 \text{ g}^{-1}$, as given by the error bars.

Correlation of S_{BET} with other physical parameters

The larger the bulk dry density of the sample, the smaller the measured specific surface area S_{BET} in general (Fig. 4.3-15). As bulk dry densities were not obtained for all samples for which specific surface areas are available, the number of data points in this plot is smaller than that in the previous profile plot. Most data points follow approximately a common linear trend given by the linear regression line. Two of the three samples from the Stamborg Member in the Schinznach Formation, however, are clearly offset. They have a small bulk dry density, which often points to a large porosity, but have at the same time a small specific surface area S_{BET} . These samples are clay-poor dolomites showing dissolution features and have a rather different pore architecture, probably with much larger pores, compared to the other measured samples. These three samples were excluded when calculating the regression line.

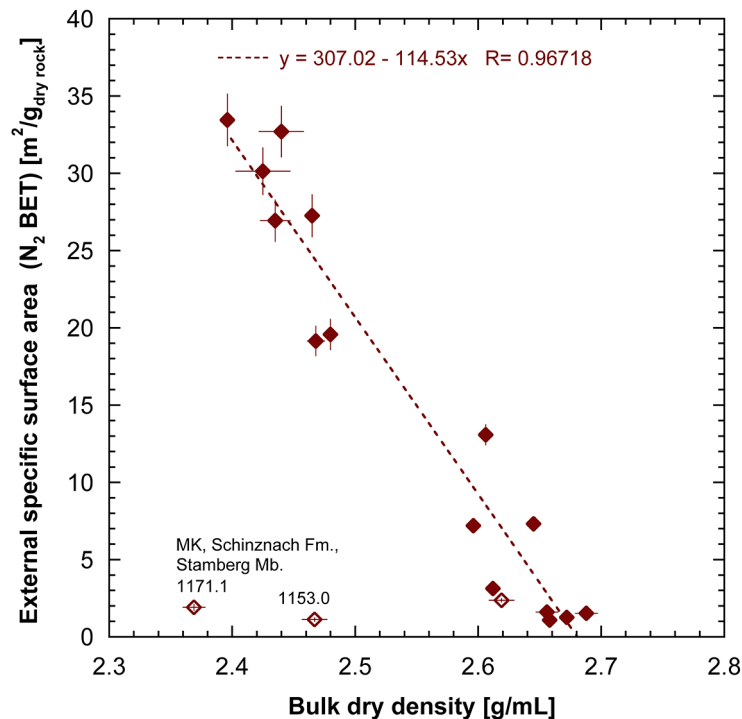


Fig. 4.3-15: Specific surface areas (S_{BET}) derived from N_2 adsorption plotted against the bulk dry density of the samples

The three values of the Stamberg Member in the Schinznach Formation are shown as open symbols; they were not considered for the linear regression. Error bars show propagated errors of the bulk dry density and estimated errors for S_{BET} .

The relation between S_{BET} and the gravimetric water content relative to the dry sample mass follows a linear trend in general as well (Fig. 4.3-16). Water contents per dry mass were obtained for all samples for which specific surface areas were measured, leading to a larger number of samples compared to that in the previous figure. We see that the largest S_{BET} in the 'Parkinsoni-Württembergica-Schichten', in the Wedelsandstein Formation, the Opalinus Clay and in the Staffelegg Formation are all related to comparably large water contents. In this plot, all three data points from the Stamberg Member in the Schinznach Formation appear as outliers with regard to the general linear relation: they have comparably small S_{BET} but comparably large water contents.

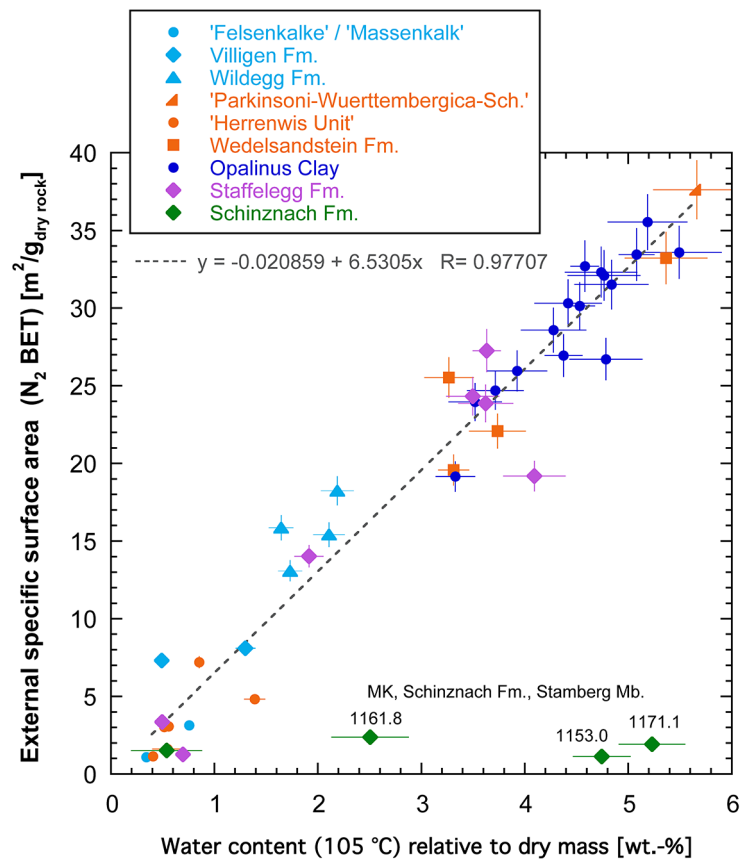


Fig. 4.3-16: Specific surface areas (S_{BET}) derived from N_2 adsorption plotted against the gravimetric water content per dry mass of the samples

The three data points from the Stenberg Member in the Schinznach Formation (with depths given) were not considered for the linear regression. Error bars show propagated errors for the dry water content (based on standard deviations of the wet water content) and estimated errors for S_{BET} .

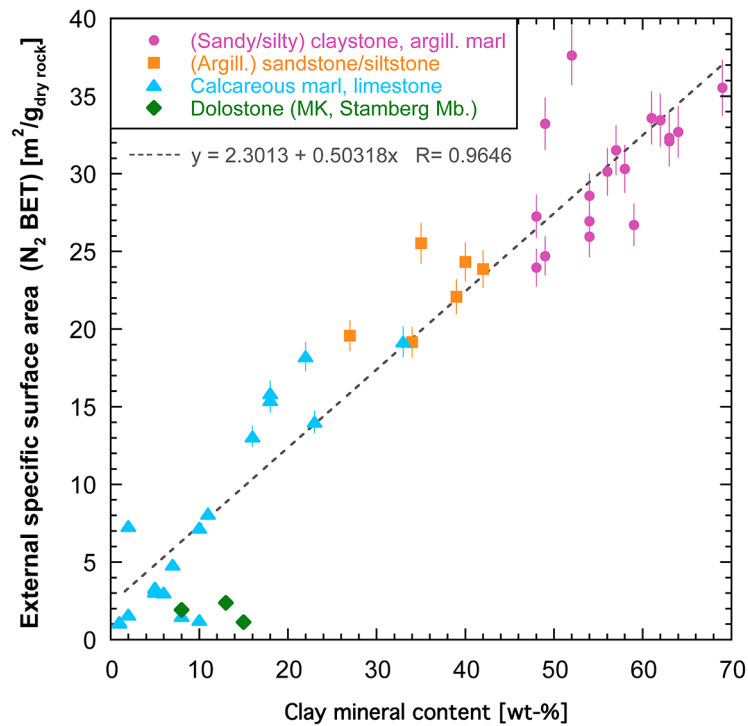


Fig. 4.3-17: Relation between external specific surface area (S_{BET}) derived from N_2 adsorption and content of clay minerals

The samples are assigned to four classes according to their positions in the Füchtbauer diagram (i.e. according to lithological rock types). The linear regression is obtained for all samples.

The water content and the bulk density are related to the mineral composition of the samples, notably the clay mineral content, as shown in previous subsections. Thus, it can be expected that the specific surface area S_{BET} is also positively correlated with the total content of clay minerals. Indeed, such a positive correlation exists (Fig. 4.3-17). Positive correlations exist also with contents of illite, smectite, kaolinite and chlorite end-members (Fig. 4.3-18), with the strongest one with the illite end-member content. The correlations with the kaolinite and chlorite end-member contents are weaker and tend to have non-zero intercepts, that is, non-zero S_{BET} for zero end-member contents, illustrating the mutual interrelations. Overall, the correlations demonstrate the influence of the clay minerals on the pore architecture and relevant pore sizes of the multi-mineral samples. Clay minerals form typically particles of small size, leading to small pores that have a large surface to volume ratio.

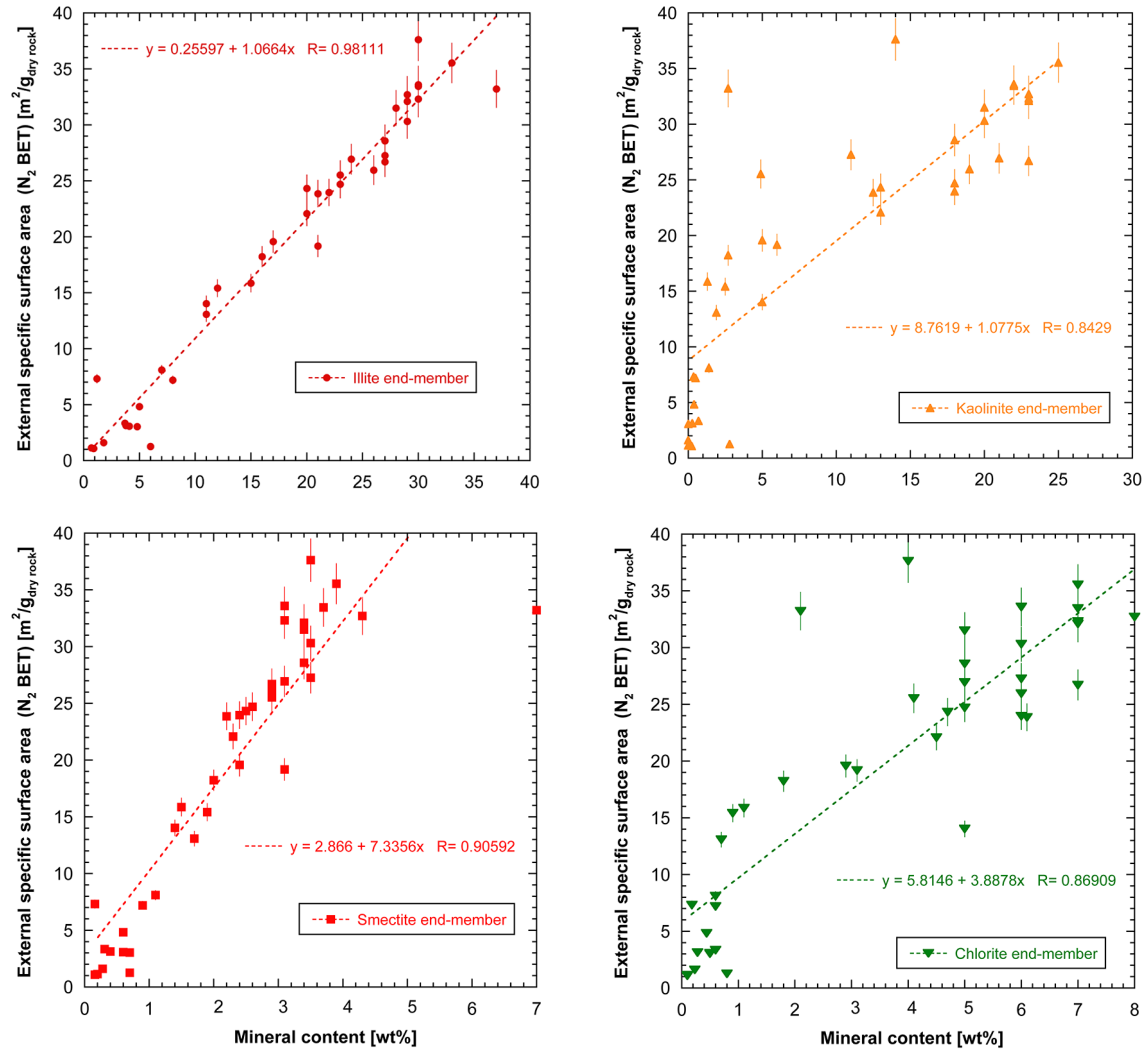


Fig. 4.3-18: Relation between external specific surface area (S_{BET}) derived from N_2 adsorption and contents of specific clay end-members

Average sizes of external pores derived from S_{BET}

Assuming negligible pore volumes in interlayer pores, i.e. attributing the measured water content to external pores only (which is, however, not correct for samples with large smectite end-member contents), we can calculate average sizes of external pores from the specific surface area S_{BET} and the water content per dry mass WC_d as

$$\overline{r_{ext}} = WC_d / (\rho_w S_{BET}),$$

with ρ_w the water density taken to be 1 g/mL.

From the inverse of the slope of the linear relation in Fig. 4.3-16 (the slope represents S_{BET}/WC_d), we obtain an overall average layer thickness (or radius) of external pores for all samples of 1.5 nm, which corresponds to about 5 or 6 water layers.

Instead of calculating an overall average from the linear regression, it is more interesting to derive an average layer thickness for each sample. Fig. 4.3-19 plots average external pore sizes (attributing all water to external surfaces) for each sample as a function of the gravimetric dry water content (a) and as a function of the total clay mineral content (b). As hypothesised, the three dolomite samples of the Stamberg Member have a clearly larger average external pore size (~ 10 to ~ 43 nm based on S_{BET}) than the other samples. Obviously, the pores in these samples are characterised by a very different architecture compared to all other samples.

Zooming into the lower average external pore sizes, we see that the values of the upper Malm formations, the 'Herrenwis Unit' and partly the Staffelegg Formation (Fig. 4.3-19a) scatter considerably, while the Wildegg Formation, the Wedelsandstein Formation, the Opalinus Clay and the rest of the Staffelegg Formation have values in a similar range of about 1.5 nm. When plotting the average external radius against the clay mineral content (Fig. 4.3-19b) we see a large variability at low clay mineral contents and a narrower range at intermediate to high clay mineral contents. The samples with the largest clay mineral fractions are very likely those with some interlayer water in smectites. Accordingly, these average external pore sizes may represent maximum values. A correction of average external pore sizes that accounts for the volume of interlayer water based on the smectite end-member content could be made assuming typical smectite particle geometries. However, in view of the involved uncertainties this is not done at present.

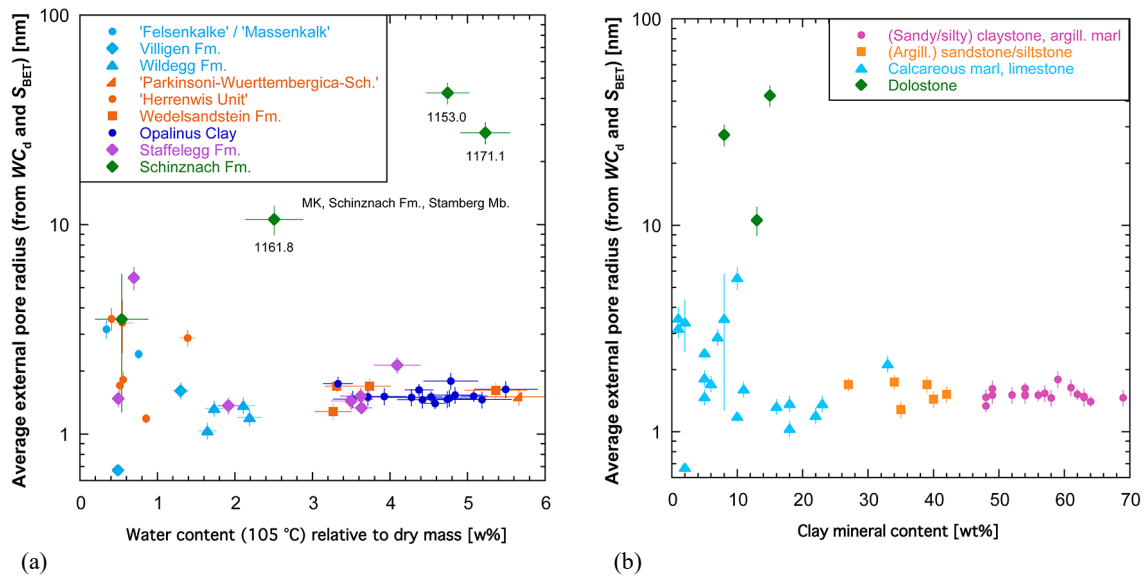


Fig. 4.3-19: Average external pore radius calculated from S_{BET} and the gravimetric water content (assuming insignificant interlayer pore volume) plotted against the gravimetric dry water content of the samples (a) and against the total clay mineral content (b)

Samples are grouped according to geological units (a) or according to rock lithology (b). Error bars show propagated errors for the dry water content (based on standard deviations of the wet water content) and propagated errors for the average external pore radius.

Distribution of external pore sizes derived from N₂ isotherms

Pore size distributions of external pores were derived by the standard BJH algorithm from N₂ ad- and desorption isotherms. The figures in the following present results from N₂ desorption for the samples of the different formations, grouped according to rock lithology.

Calcite-rich and clay-poor samples, classified as limestones or calcareous marl according to the Füchtbauer nomenclature, show bi- or multimodal size distributions (Fig. 4.3-20a). These samples originate from the Malm (BUL1-1 541.60 to 794.35), the 'Herrenwis Unit' in the Upper Dogger (BUL1-1 815.90 to 851.50), the Staffelegg Formation in the Lias (BUL1-1 1'002.19 to 1'025.96), and the Schinznach Formation in the Muschelkalk (BUL1-1 1178.88). A majority of the pore volume corresponds to comparably large pores (diameter > 100 nm), but some pores in the intermediate range (20 – 100 nm) and in the low range (< 10 nm) are also present. Several samples exhibit comparably large peaks at the maximum derived pore sizes of > ~ 300 nm. These large peaks should be interpreted with care. They are very likely artefacts, caused by N₂ adsorption on external surfaces of these often low porosity samples, as evidenced by the maximum amount of N₂ being adsorbed at highest N₂ pressures clearly exceeding the (in situ) water content (Fig. 4.3-21). When checking the corresponding isotherms, it becomes clear that the adsorbed amount increases very steeply at the highest relative pressures in these cases. Peaks at about 4 nm are often related to the closure of the hysteresis of the isotherm and could thus be attributed to liquid instabilities rather than to a distinct pore volume in this size range. The sample BUL1-1 1'002.19 from the Rietheim Member of the Staffelegg Formation, a calcareous marl, shows clearly larger amounts of pores < 10 nm compared to the limestone samples. This may be due to the high content of organic matter (C_{org} = 4 wt.-%) in this sample.

Pore size distribution of samples classified as (argillaceous) sandstone/siltstone according to the Füchtbauer nomenclature (Fig. 4.3-20b) mostly show only a small amount of pores in the 100 nm range and hardly pores > 100 nm, with the exception of sample BUL1-1 1'017.33 from the Staffelegg Formation. The other samples originate from the Wedelsandstein Formation (BUL1-1 872.35 to 879.20), from a sub-unit with silty-calcareous beds of Opalinus Clay (BUL1-1 894.68), and from the Staffelegg Formation (BUL1-1 1'014.23).

Compared to the (argillaceous) sandstones/siltstones, all samples classified as (sandy/silty) claystone or argillaceous marl exhibit a larger volume of pores in the < 10 nm range (Fig. 4.3-20c). The distributions of external pore sizes of the samples from the 'Parkinsoni-Württembergica-Schichten' (BUL1-1 808.92), the Wedelsandstein Formation (BUL1-1 861.00), the Opalinus Clay (BUL1-1 908.93 to 995.09) and the Staffelegg Formation (BUL1-1 1'019.49) are remarkably similar, with some pores in the 100 nm range but a majority of pores around and below the 10 nm range. The sample BUL1-1 965.98 has no pores in the 100 nm range.

Finally, the three samples from the Stamberg Member in the Schinznach Formation classified as dolostones exhibit a clearly distinct pore size distribution (Fig. 4.3-20d): Mainly pores in the 100 nm range, nearly no small pores. Interestingly, the maximum amount of adsorbed N₂ for sample BUL1-1 1'161.83 is, when recalculated, similar to its water content of 2.5 wt.-%, whereas the maximum adsorbed amounts for samples BUL1-1 1'153.02 and 1'171.10 are much smaller than their water contents of 4.8 and 5.2 wt.-%, respectively, in contrast to the observation for limestones with low water contents (Fig. 4.3-21). Accordingly, it is very likely that some of the largest pores that are present in situ could not be probed by N₂ adsorption for the latter two samples.

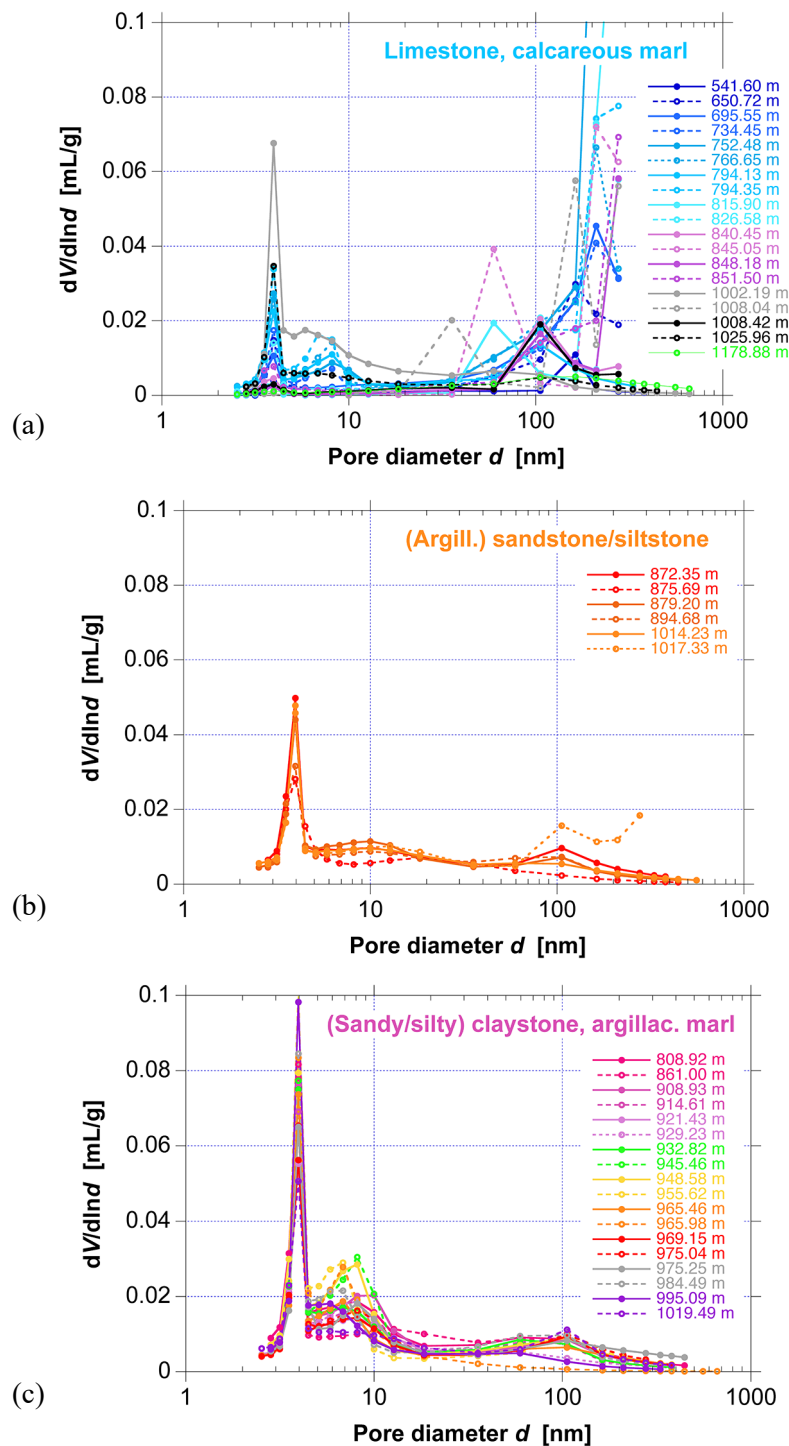


Fig. 4.3-20: Distribution of (external) pore sizes derived from N_2 desorption for (a) limestone and (sample BUL1-1 1'002.19) calcareous marl samples, (b) (argillaceous) sandstone/siltstone samples, (c) (sandy/silty) claystone and argillaceous marl samples, and (d) dolostone samples

The partly very high values at large pore sizes of limestone samples in (a) are likely artefacts caused by adsorption on external surfaces. The y-axis scale of (d) is four times reduced compared to that of (a) – (c).

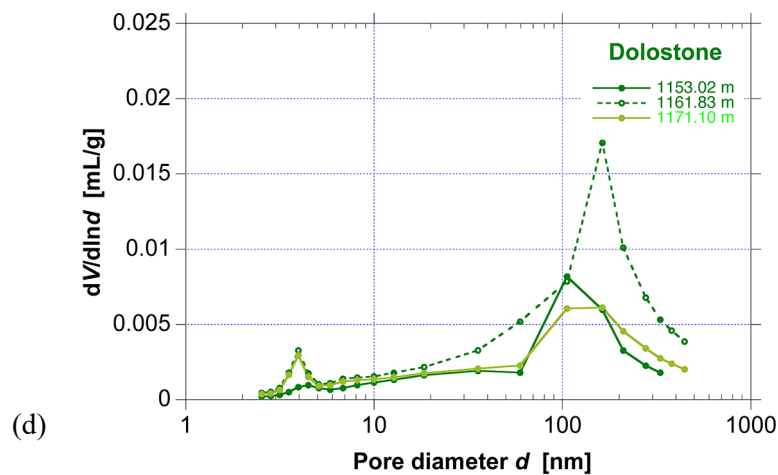


Fig. 4.3-20: (continued)

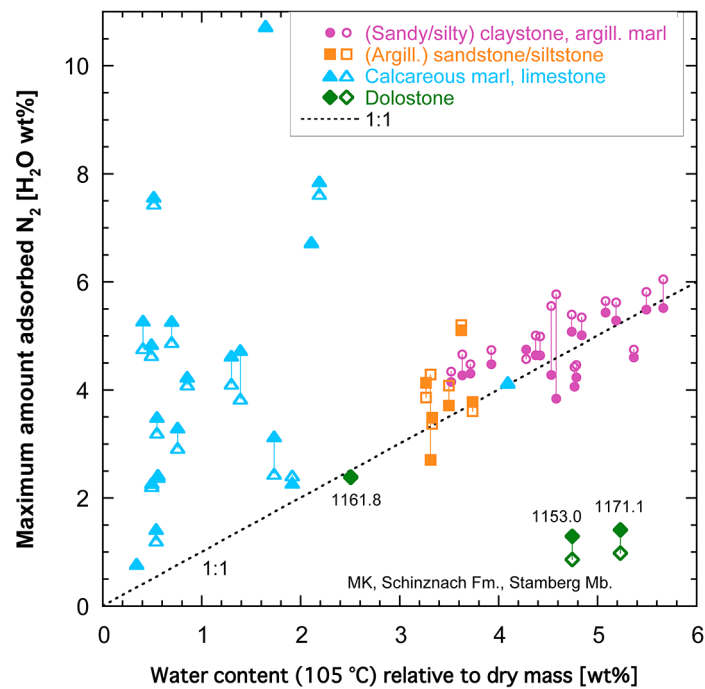


Fig. 4.3-21: Comparison of maximum amount of adsorbed N_2 (recalculated to H_2O wt.-%) with water content per dry sample mass

Open symbols: adsorption, closed symbols: desorption.

Average sizes of external pores based on pore size distributions calculated from the N_2 isotherms

Average sizes of external pores cannot only be derived from S_{BET} and the water content as shown above, but also directly from the N_2 isotherms. In both cases, it is assumed that interlayer pore volumes (which are not probed by N_2 adsorption) are insignificant. Values directly derived by averaging the BJH pore size distributions (Fig. 4.3-22) are somewhat larger when compared with the average sizes determined from S_{BET} and the gravimetric water content (Fig. 4.3-19), but show

the same tendencies: smallest values (around 3 nm here) for the claystones and argillaceous marls and clearly larger values for the limestones. When comparing these numbers, one has to keep in mind that the maximum adsorbed N_2 volume is not always similar to the water content of the samples (Fig. 4.3-21), as discussed above. Accordingly, for limestone samples with strongly exceeding maximum adsorbed N_2 amounts, average pore sizes estimated from the size distribution tend to be too large, whereas for the dolostones, with their comparably small maximum adsorbed amounts, they tend to be too low.

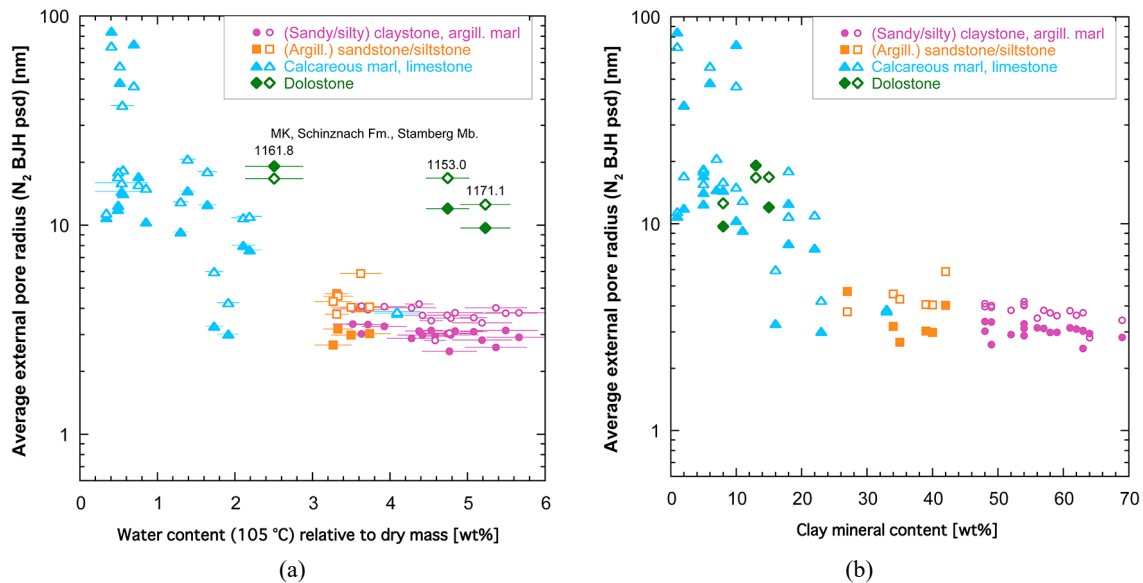


Fig. 4.3-22: Average external pore radius (assuming insignificant interlayer pore volume) based on the BJH pore size distribution from the N_2 isotherms (closed symbols: adsorption; open symbols: desorption) plotted against the gravimetric dry water content of the samples (a) and against the total clay mineral content (b)

Samples are grouped according to rock lithology. Error bars show propagated errors for the dry water content (based on standard deviations of the wet water content).

4.4 Data from aqueous extraction tests

H. Niklaus Waber

This section provides the data of aqueous extraction (AqEx) tests conducted at different solid:liquid (S/L or S^*/L^* , see below) ratios and of the numerous AqEx tests conducted at a S^*/L^* of 1 on rocks from the Malm to the Muschelkalk. The full data sets are provided in Appendix 1 and 2. Integration of the data into context and – for chemically conservative compounds – conversion to porewater concentrations are given in Chapter 5. Details about the methodology are given in the method report by Waber (ed.) (2020).

Note that the parameter S^*/L^* relates to the mass ratio of the wet rock sample to the mass of the added water, i.e. to values measured at the onset of the experiment. The parameter S/L, defined as the mass ratio of dry rock to the sum of pore and added water (eq. 8 in Section 3.4.1), can be

calculated from S^*/L^* using the water content. For the 128 PW/RP²-samples subjected to AqEx tests the average difference between S^*/L^* and S/L is 5.6 ± 3.4 %. The effect on calculated solute concentration values is therefore within the propagated uncertainty for most solutes.

The chemical composition of aqueous-extract solutions at $S^*/L^* = 1$ is documented in Appendix 1. Further data are included in Appendix 2, which contains 2 sheets:

- Sheet "*AqEx Data 4SL*": Chemical composition and mineral saturation indices of aqueous-extract solutions at $S^*/L^* = 0.1, 0.25, 0.5, 1$ (NB: only a subset of all samples was investigated at different S^*/L^*);
- Sheet "*SI-Values AqEx SLI*": Mineral saturation indices of aqueous-extract solutions at $S^*/L^* = 1$.

4.4.1 Sample material and overview of analytical work

A total of 128 rock samples ("PW/RP samples") collected at variable intervals from drill cores of borehole BUL1-1 were subjected to AqEx tests at a S^*/L^* ratio of 1. Of these 105 AqEx solutions at $S^*/L^* = 1$ have been analysed for their chemical composition. The AqEx tests were conducted by using approximately 30 g of originally saturated rock material of the central part of the cores. From the Malm to the Staffelegg Formation one sample per formation was extracted at 4 different S^*/L^* ratios by reducing the mass of rock and keeping the volume of extract solution constant at about 30 mL. These tests were performed to obtain information about the leaching behaviour of the different solutes as a function of the mineralogical composition of the different lithologies.

From the Bänkerjoch Formation and the Schinznach Formation a total of 12 core samples have been extracted twice, once using the conventional AqEx sample aliquot and once using the rock material previously used for the determination of the water content. The latter tests were conducted to investigate the effect of heterogeneously distributed porosity and extracted mass of porewater, respectively, in the rock material used for the AqEx tests and the water-content measurements. Note that these samples were exposed to air in the drying oven and so affected by oxidation. Therefore, they provide relevant information for Cl and Br only.

In addition, AqEx data of the 6 samples subjected to advective displacement experiments ("AD-samples") are also included for comparison. On these samples 2 to 4 duplicate extraction tests were performed under the same conditions as for the "PW/RP samples" before the AD experiment with the details given in Section 4.7.

Tab. 4.4-1 lists all samples used for AqEx tests and the analytical work performed on these samples. Details about the experimental and analytical procedures can be found in Waber (ed.) (2020). Corresponding data of the mineralogy, water-content and water-loss porosity are given in Sections 4.2 and 4.3, respectively.

² See Tab. 3-1 and method report by Waber (ed.) (2020) for abbreviations of different core sample types.

Tab. 4.4-1: Summary of analytical work performed on samples for aqueous extraction tests

Sample type: PW/RP: porewater sample, AD: Advective displacement sample, PW Dupl.: duplicate extraction of PW/RP sample material, AqEx: aqueous extraction tests.

Group	Formation	Sample Type	No of Samples	AqEx at $S^*/L^* = 1$	AqEx at $S^*/L^* = 0.1, 0.25, 0.5, 1$	pH & Alk.	Chemistry	$\delta^{37}\text{Cl}$
Malm	"Felsenkalke" / "Massenkalk" / "Massenkalk"	PW/RP	8	8	1	11	11	1
Malm	Schwarzbach Fm.	PW/RP	2	2	-	2	2	1
Malm	Villigen Fm.	PW/RP	4	4	-	4	4	1
Malm	Wildeggen Fm.	PW/RP	5	5	1	8	8	2
Dogger	Varansmergel Fm.	PW/RP	1	1	-	1	1	-
Dogger	'Parkinsoni-Württ.-Sch.'	PW/RP&AD	2	2	-	2	2	-
Dogger	'Herrenwis Unit'	PW/RP	13	7	1	10	10	2
Dogger	'Humphriesoolith Fm.'	PW/RP	1	1	-	1	1	-
Dogger	Wedelsandstein Fm.	PW/RP&AD	11	11	1	13	13	3
Dogger	'Murchisonae-Oolith Fm.'	PW/RP	3	1	-	1	1	1
Dogger	Opalinus Clay	PW/RP&AD	33	29	1	32	32	2
Lias	Staffellegg Fm.	PW/RP&AD	10	11	1	14	14	3
Keuper	Klettgau Fm.	PW/RP	13	13	-	13	13	2
Keuper	Bänkerjoch Fm.	PW/RP	15	15	-	15	15	2
Muschelkalk	Schinzach Fm.	PW/RP	13	13	-	13	13	3
Keuper	Bänkerjoch Fm.	PW Dupl.	4	4	-	-	4	
Muschelkalk	Schinzach Fm.	PW Dupl.	8	8	-	-	8	
Total		PW/RP&AD	146	146	6	152	164	23

4.4.2 Aqueous extraction tests at different S^*/L^* ratios

Aqueous extraction tests at S^*/L^* ratios of 0.1, 0.25, 0.5 and 1.0 were conducted on porewater samples from different lithologies of the Malm, Dogger and Lias (Tab. 4.4-2). The S^*/L^* ratio was adjusted by using different rock masses of 3.0 g, 7.5 g, 15 g and 30 g while keeping the volume of extract solution constant at 30 mL. The complete data are given in Appendix 2.

The mass of porewater extracted in AqEx tests at different S^*/L^* ratios ranges from 0.013 – 0.161 g/kg_{rock} at the lowest S^*/L^* ratio and from 0.126 – 1.456 g/kg_{rock} at the highest S^*/L^* ratio for the different rock types including limestone to silty claystone (Tab. 4.4-3). In addition, the rocks extracted at different S^*/L^* ratios cover a large range of clay mineral content and with that a large range in the cation exchange inventory contributing to the extract solutions (Tab. 4.4-3, see also Section 4.5). Furthermore, the different rocks also have greatly variable contents of total sulphur and pyrite, respectively (Tab. 4.4-3). This large variability in mineralogical compositions and thus the different inventories contributing to the extract solutions allows deciphering the behaviour of not only of chemically conservative, but also of reactive compounds when extracted at different S^*/L^* ratios.

Tab. 4.4-2: Stratigraphy and lithology of samples used for AqEx tests at different S^*/L^* ratios

See also Tab. 4.4-3 for more details.

Mean depth [m]	Group	Formation	Lithology
538.45	Malm	'Felsenkalke' / 'Massenkalk'	limestone
794.13	Malm	Wildegge Fm.	argillaceous limestone
848.18	Dogger	'Herrenwis Unit'	limestone
875.69	Dogger	Wedelsandstein Fm.	very argillaceous sand-/siltstone
948.58	Dogger	Opalinus Clay	very sandy/silty claystone
1'008.04	Lias	Staffelegg Fm.	limestone *

* Note that the sample from the Staffelegg Formation is atypical for this otherwise more argillaceous formation and represents a pyrite-free limestone from the Grünschholz Member (former Numismalis-Amaltheen-Schichten).

Tab. 4.4-3: Summary of mineralogical and petrophysical data of individual samples used for AqEx tests at different S^*/L^* ratios

See Section 4.2 for complete mineralogical data and Section 4.3 for complete petrophysical data of all samples (mean, min. max. values); WC wet = water content relative to wet rock.

Mean depth [m]	Group	Formation	WC wet [wt.-%]	Mass Porewater [g]	Tot. Carbonate [wt.-%]	Tot. Clay [wt.-%]	Tot. Sulphur [wt.-%]	Pyrite [wt.-%]
538.45	Malm	'Felsenkalke' / 'Massenkalk'	0.426	0.013 – 0.126	98	2	< 0.05	< 0.1
794.13	Malm	Wildegge Fm.	1.703	0.057 – 0.509	77	16	< 0.05	< 0.1
848.18	Dogger	'Herrenwis Unit'	0.545	0.017 – 0.162	96	2	< 0.05	< 0.1
875.69	Dogger	Wedelsandstein Fm.	3.207	0.098 – 0.962	25	28	0.53	1.0
948.58	Dogger	Opalinus Clay	4.835	0.161 – 1.456	9	63	0.15	0.3
1'008.04	Lias	Staffelegg Fm.	0.690	0.022 – 0.205	84	10	< 0.05	< 0.1

4.4.2.1 Anion concentrations (Cl, Br, SO₄, F, alkalinity)

Concentrations of Cl in extract solutions of rocks from the various stratigraphic units from Malm to Lias display a high linear correlation with the S^*/L^* ratio during aqueous extraction (Fig. 4.4-1). The same accounts for the concentrations of Br. The resulting high correlation between Cl and Br in the extract solutions of these rocks (Fig. 4.4-2) indicates the same unique origin for these two anions, which is the porewater. This behaviour of Cl and Br during extraction is consistent with the mineralogy of these marine sedimentary rocks, which are not known to contain any Cl- and/or Br-bearing minerals. It further supports the applied preparation technique (gently disintegrated rock vs. milling) and indicates that porewater is the only source of these two anions.

Concentrations of dissolved SO₄ concentrations in extract solutions of the 6 rocks from the Malm to the Lias also display a high linear correlation with the S^*/L^* ratio during aqueous extraction (Fig. 4.4-3). For SO₄, however, the linear behaviour as function of the S^*/L^* ratio does not necessarily indicate a chemically conservative behaviour and thus the porewater as the only origin. Such linear behaviour could similarly be the combined effect of elution of the porewater and the

dissolution of i) a mineral phase that is not completely dissolved and has fast reaction kinetics during the extractions or ii) the complete dissolution of a mineral present in small enough amounts. The latter can be assessed by data comparison of numerous samples extracted at $S^*/L^* = 1$ and at different S^*/L^* ratios across rock formations of variable mineralogy (see below). Sulphate concentrations in the AqEx solutions of all rock types are also highly correlated with Cl and Br with correlation coefficients between SO_4 and Cl of > 0.999 for the samples of the Wedelsandstein, Opalinus Clay and Staffelegg Formation and > 0.99 for the samples from the 'Felsenkalke' / 'Massenkalk', Wildegg Formation and 'Herrenwis Unit'. The fact that SO_4 and Cl are similarly highly correlated with Cl and Br in pyrite-bearing rocks and pyrite-free rocks indicates that a) pyrite oxidation has been successfully suppressed during extraction and b) that the porewater is the dominant inventory for the SO_4 contents analysed in the AqEx solutions.

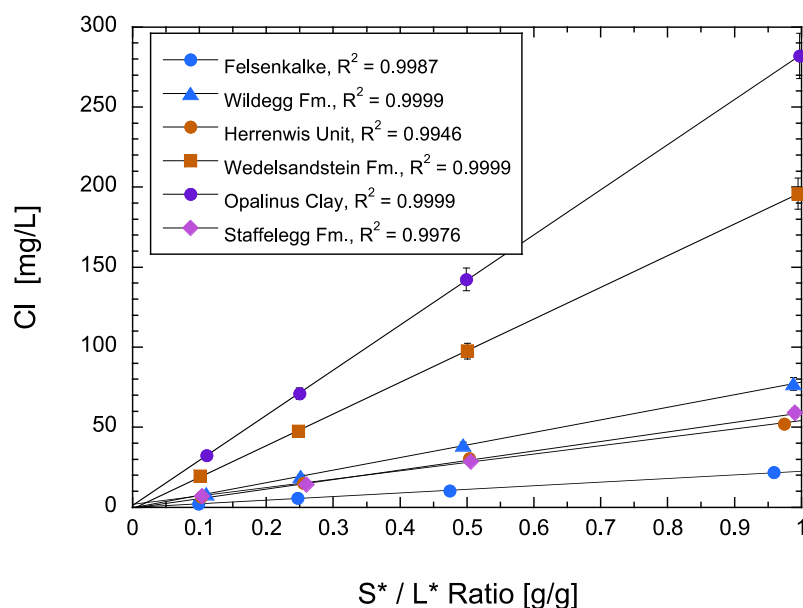


Fig. 4.4-1: Chloride concentrations vs. the S^*/L^* ratio in AqEx solutions from rocks of variable mineralogy of formations from the Malm, Dogger and Lias

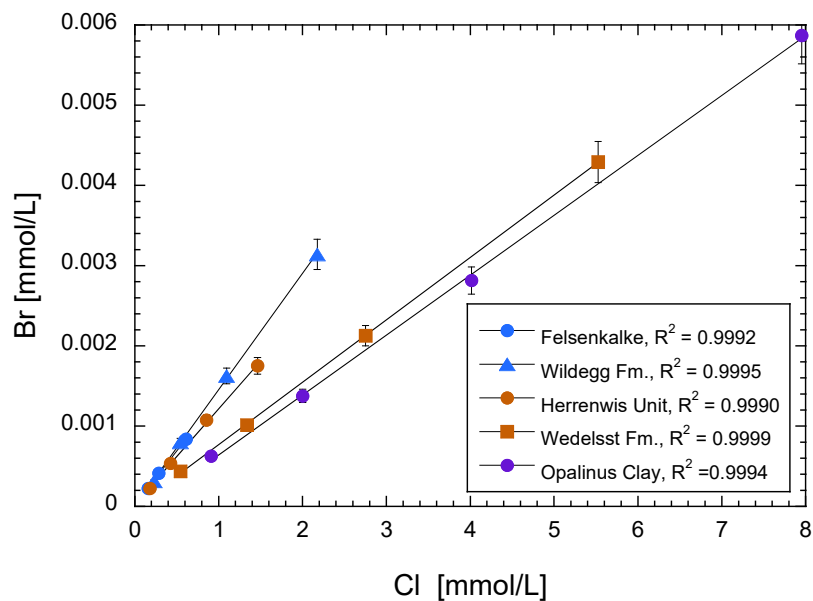


Fig. 4.4-2: Chloride vs. Br concentrations in AqEx solutions at different S^*/L^* ratios from rocks of variable mineralogy of formations from the Malm, Dogger and Lias

Br in AqEx solutions at $S^*/L^* < 1$ of the sample from Staffelegg Formation below detection limit of 0.016 mg/L.

Concentrations of F and the titrated total alkalinity show a non-linear behaviour with increasing S^*/L^* ratio indicating a strong influence by mineral dissolution reaction. The mineral source of F is yet unknown. It could either be trace amounts of fluorite (CaF_2) or F incorporated as solid solution in other mineral phases (e.g. apatite). The major source for the carbonate alkalinity (i.e. HCO_3^- and CO_3^{2-}) is calcite dissolution as indicated by the generally achieved calcite equilibrium during extraction (*cf.* Section 4.4.2.3). As shown by the AD samples, the AqEx solutions may contain considerable amounts of TOC depending on lithology (*cf.* Section 4.7). Such TOC contributes to the titrated alkalinity and combined with the mildly alkaline pH-values (8.68 – 9.45 for the present samples at $S^*/L^* = 1$) disables a direct conversion of the titrated alkalinity to concentrations of HCO_3^- without speciation calculations.

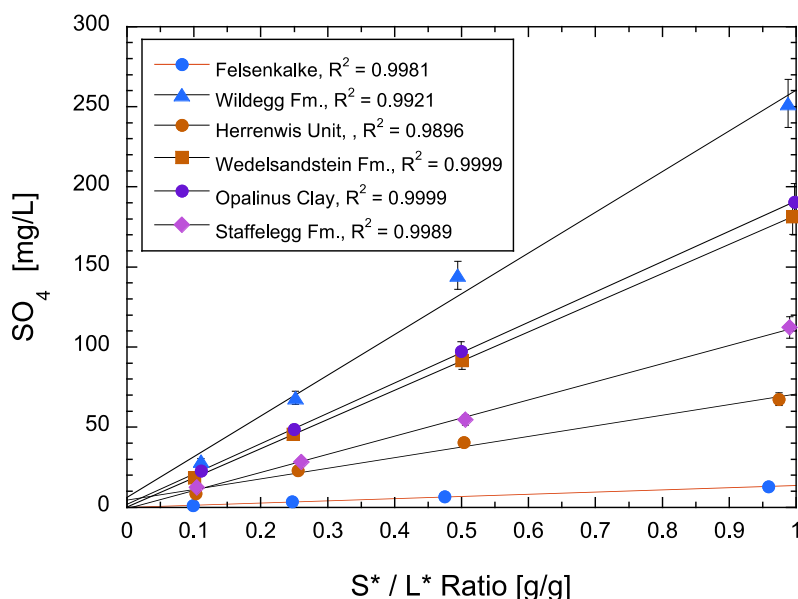


Fig. 4.4-3: Sulphate concentrations vs. the S^*/L^* ratio in AqEx solutions from rocks of variable mineralogy of formations from the Malm, Dogger and Lias

4.4.2.2 Cation concentrations (Na, K, Ca, Mg, Sr)

In all AqEx solutions of rocks from the Malm to the Lias Na is the dominant cation at all S^*/L^* ratios except for the limestone from 'Felsenkalke' / 'Massenkalk' where Ca becomes more abundant at the lowest S^*/L^* ratio of 0.1. Potassium is the second most abundant cation at all S^*/L^* ratios in the clay-bearing rocks of the Wildegge Formation, Wedelsandstein Formation, Opalinus Clay and Staffelegg Formation, but becomes surpassed by Ca in the pure limestones of the 'Felsenkalke' / 'Massenkalk' and 'Herrenwis Unit'. In none of these rocks readily dissolvable Na- and/or K-bearing mineral phases occur, however both cations are subjected to exchange reactions in the presence of clay minerals.

Concentrations of Na and K in the AqEx solutions display a more or less well-established linear behaviour as function of the S^*/L^* ratio. For Na correlation coefficients R^2 of 0.9815 – 0.9977 are established and for K those of 0.9128 – 0.9923. Both cations are also correlated with Cl with correlation coefficients R^2 of > 0.966 for Na and > 0.900 for K. The best correlation is observed for the clay-richest sample of the Opalinus Clay. Although these correlations suggest the porewater as the dominant origin for Na and K, the poorer correlation with Cl compared to those with the S^*/L^* ratio indicates the non-negligible impact of cation exchange reactions on the eluted Na and K concentrations, especially in the clay-bearing rocks.

Calcium is the most abundant earth alkaline element in the AqEx solutions with molal concentrations that are generally about a factor of 2 – 5 higher than those of Mg, but always considerably lower than those of Na and mostly also K. Concentrations of Ca and Mg in the AqEx solutions display a non-linear behaviour as function of the S^*/L^* ratio that depends on the rock type. In the AqEx solutions of all rock types Ca and Mg concentrations are well correlated except for the limestones of the 'Felsenkalke' / 'Massenkalk' and the Staffelegg-Formation. These correlations suggest that the concentrations of Ca and Mg in AqEx solutions are controlled by mineral dissolution combined with exchange reactions in clay-rich rocks and strongly depend on the carbonate mineralogy of the rock. In all rock types a general increase of Ca and Mg is observed with decreasing S^*/L^* ratio indicating the stronger impact of carbonate dissolution at lower S^*/L^* ratios.

The only exception from this general rule is the limestone of the 'Herrenwis Unit', which displays a decrease of Ca concentrations with decreasing S^*/L^* ratio. The reason for this behaviour is yet unknown.

Concentrations of Sr in the AqEx solutions are very low and commonly below 0.1 mg/L (1.1×10^{-3} mmol/L) at all S^*/L^* ratios, except for the AqEx solutions of the limestone from the 'Herrenwis Unit' where concentrations reach values up to 0.41 mg/L (4.7×10^{-3} mmol/L). The good correlation between Sr and Ca and the relationships established between Sr and the Sr/Cl and Sr/SO₄ ratios indicate that in the AqEx solutions Sr is mainly associated with carbonate mineral dissolution (in clay-rich rocks combined with exchange reactions) and not with the dissolution of a sulphate mineral phase such as celestite (SrSO₄) in accordance with mineralogy of the rock samples (*cf.* Section 4.4.2). As observed for Ca and Mg, the limestone of the 'Herrenwis Unit' constitutes the exception of this general behaviour and this is most likely related to the carbonate mineral composition of this limestone.

4.4.2.3 Mineral saturation states and partial pressure of CO₂ (P_{CO2})

Based on the experimental set-up utilising degassed ultrapure water and closed system conditions for the aqueous extraction tests, the extract solutions become alkaline during the interaction with carbonate-bearing rocks.

AqEx solutions at $S^*/L^* = 1$ have pH values around 8.7 after interaction with the limestones of the Wildegg Formation and 'Herrenwis Unit' and the very sandy/silty claystone of the Opalinus Clay. Higher pH values between 9.10 and 9.45 are obtained for the limestones of the 'Felsenkalke' / 'Massenkalk' and Staffelegg Formation and the argillaceous sand/siltstone of the Wedelsandstein Formation. In general pH-values increase with decreasing S^*/L^* ratio indicating the increased carbonate mineral dissolution under closed system conditions at low S^*/L^* ratios (Fig. 4.4-4). This increase is accompanied by a decrease in P_{CO2}, which is already below that of the atmosphere (log P_{CO2} ~ -3.5) and constantly decreases towards the lowest S^*/L^* ratio of 0.1 (Fig. 4.4-4). Exceptions to these general trends seem to be the two low-mineralised AqEx solutions of the limestone from the 'Felsenkalke' / 'Massenkalk' and Staffelegg Formation in which the pH slightly decreases. The corresponding slight increase in P_{CO2}, however, suggests that these effects are more likely due to slight ingassing of atmospheric CO₂ during the time of the pH measurement and thus an experimental artefact.

At these pH-P_{CO2} conditions the AqEx solutions at S^*/L^* ratios of 1 are at equilibrium with calcite at S^*/L^* ratios of 1 in all different rock types from the Malm to the Lias. AqEx solutions of clay-bearing limestone of the Wildegg Formation, the argillaceous sand/siltstone of the Wedelsandstein Formation and the sandy/silty claystone of the Opalinus Clay are also at calcite equilibrium at all lower S^*/L^* ratios. In turn, the limestones of the 'Felsenkalke' / 'Massenkalk', 'Herrenwis Unit' and Staffelegg Formation show some more variability that is most probably associated with a different mineral chemistry (solid solutions), larger grain size and thus different solubility and reactivity in these rocks, besides the above mentioned experimental artefacts.

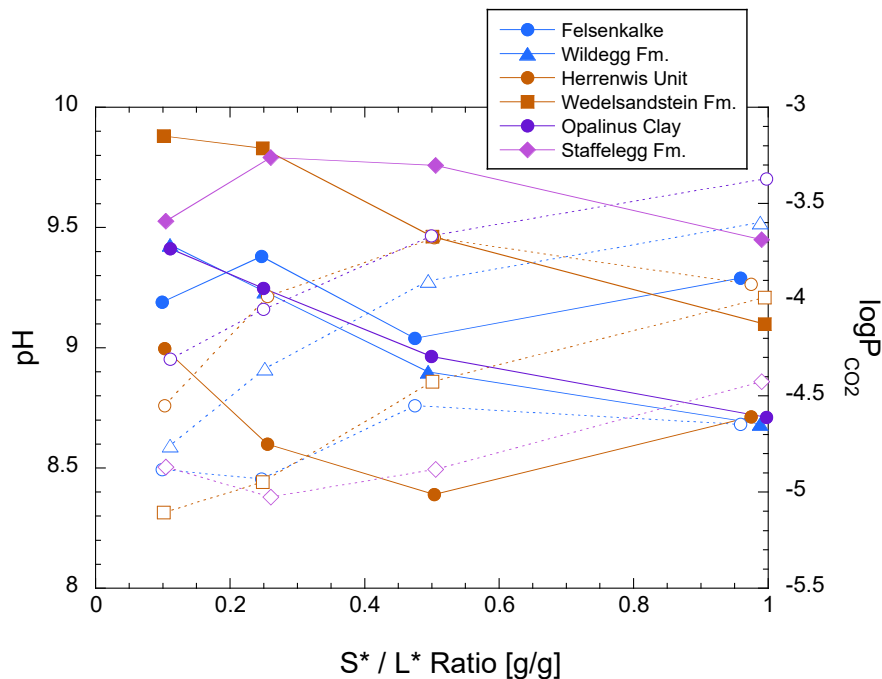


Fig. 4.4-4: Values of pH (solid symbols) and partial pressure of CO₂ (P_{CO2}; open symbols) of AqEx solutions from rocks of variable mineralogy of formations from the Malm ('Felsenkalke' / 'Massenkalk', Wildegge Formation), Dogger ('Herrenwis Unit', Wedelsandstein Formation, Opalinus Clay) and Lias (Staffelegg Formation)

During the 24 hours of interaction equilibrium with dolomite is not reached and all AqEx solutions are undersaturated with respect to (disordered) dolomite at all S*/L* ratios. This is due to the more sluggish dissolution kinetic of dolomite/ankerite compared to that of calcite.

The sulphate mineral phases gypsum and celestite are strongly undersaturated in all rock types and at all S*/L* ratios (SI_{celestite} = -4.55 to -2.33, SI_{gypsum} = -4.39 to -22.25). For both mineral phases the undersaturation increases with decreasing S*/L* ratio. Combined with the relationships established between Sr/Cl, Ca/Cl, Sr/SO₄ and Ca/SO₄ ratios with decreasing S*/L* ratios (*cf.* Appendix 2), the behaviour of SO₄ during extraction and in agreement with the mineralogy (*cf.* Section 4.2) it seems rather unlikely that celestite is – if at all – present in amounts sufficient to have an impact on aqueous extractions in the rock matrix from the Malm to the Lias.

4.4.3 AqEx tests at S*/L* ratio of 1

In the light of information about the long-term porewater evolution across the entire Mesozoic sedimentary sequence and because of the large variability in mineralogical composition of the lithologies in borehole BUL1-1, the large chemical data set of AqEx solutions at an S*/L* of 1 is most conveniently presented as a function of depth.

Aqueous extraction tests base on the assumption that the porewater-containing pore space is distributed rather homogeneously so that the subsample subjected to extraction delivers information about the porewater composition at least on the dm³ scale and also corresponds to the water-loss porosity determined on an adjacent subsample of the same rock. This assumption becomes especially crucial during a) the comparison of AqEx solution data of lithologies with highly variable porosity and b) the conversion of concentrations of chemically conservative solutes in

the AqEx solution to concentrations of these solutes at water-loss porosity (i.e. the apparent pore-water concentration). Such effects are expected to be larger in clay-poor, coarse-grained rocks of low porosity compared to high-porosity, clay-rich and fine-grained rocks.

4.4.3.1 Comparison of different data sets

Possible effects induced by the distribution of the porewater-containing pore space were assessed by maximising the mass of rock subjected to aqueous extraction and water-loss measurements depending on rock type and within the limits given by practicability and the sample size obtained from the drillcore (see Waber (ed.) 2020 for details). In addition, such effects on the cm- to dm-scale were assessed by comparing the Cl concentrations in AqEx solutions from adjacent PW and AD samples and by comparing Cl concentrations extracted from the average PW sample material (default procedure) with those extracted from the material used for water-loss measurement from the same sample, the latter being called "PW-Duplicate".

Comparison of AqEx data of adjacent PW and AD samples cover the lithologies from the 'Parkinsoni-Württembergica-Schichten' to the Staffelegg Formation (calcareous marl, argillaceous sand/siltstone, sandy/silty claystone, claystone). Comparison of AqEx data produced from the default PW sample material and that extracted from the material used for water-loss measurement (PW-Duplicate) was performed for lithologies from the Bänkerjoch Formation (interbedded anhydrite – marl) and the Schinznach Formation (dolostone and limestone).

Chloride concentrations in AqEx solutions from PW and adjacent AD samples from the 'Parkinsoni-Württembergica-Schichten' to the Staffelegg Formation are identical within the analytical uncertainty indicating little variation in the dm-scale (Appendix 1). As shown in Section 4.7, however, larger variations of up to 35 % are sometimes observed within the same AD sample on the cm-scale (e.g. Wedelsandstein Formation). Differences up to about 16 % are observed in the water content of the same PW and AD samples from the 'Parkinsoni-Württembergica-Schichten' to the Staffelegg Formation and by about 17 % for the Wedelsandstein Formation samples. This indicates that differences in the Cl-concentrations at water-loss porosity are mainly related to the variation in water content and not to the analyses of Cl (*cf.* Chapter 5).

A similar picture arises for the Cl concentration extracted from the PW sample and the PW-Duplicate samples, i.e. the Cl from the material used for water-loss measurement of the PW sample of samples from the Bänkerjoch and Schinznach Formations. Chloride concentrations in AqEx solutions of dolostone and limestone samples from the Schinznach Formation correlate well with only 2 samples at intermediate concentration showing differences outside the analytical error (Appendix 1).

Chloride concentrations in AqEx solutions of interbedded anhydrite-marl sample from the Bänkerjoch still show an acceptable correlation, but 2 of the 4 samples deviate by more than the analytical error. The larger differences in Cl concentrations correlate with a high variability and thus large differences in the water content of the same samples in the lithologies of the Bänkerjoch and the Schinznach Formations (Appendix 1).

These differences in water contents and related Cl concentrations in the AqEx solutions reflect the heterogeneous distribution of the porewater-containing pore space in the sample splits used for AqEx and water content measurements. Such uncertainty propagates into Cl concentrations calculated at water-loss porosity and results in a significant scatter in these lithologies (*cf.* Section 4.4.3.5).

4.4.3.2 Anion concentrations (Cl, Br, SO₄, F, alkalinity)

Chloride and bromide

From the Malm to the Muschelkalk Cl concentrations in AqEx solution cover a large range with the minimum and maximum value occurring in the Schinznach Formation (Fig. 4.4-5). Large scatter with variation in Cl concentration by a factor of 10 or more is observed in massive deposits and layers of limestone from the 'Felsenkalke' / 'Massenkalk' (Malm) to the Wedelsandstein (Dogger), in the interlayered marl-anhydrite lithologies of the Bänkerjoch Formation (Keuper) and in dolostone and limestone sequences in the Schinznach Formation (Muschelkalk). In the clay-rich rocks of the lower Wedelsandstein Formation, 'Murchisonae-Oolith Formation', Opalinus Clay and Staffelegg Formation very similar Cl concentrations are eluted from the rock during aqueous extraction, except for a few carbonate- and/or sand-rich layers (Fig. 4.4-5). As outlined above, in these latter formations, Cl concentrations extracted from adjacent PW and AD samples agree well. In contrast, duplicate extractions of limestone and dolostone of the Schinznach Formation and especially of interlayered marl-anhydrite lithologies of the Bänkerjoch Formation display larger differences (Fig. 4.4-5).

Three samples collected within the water-conducting zone of the Stamberg Member (former *Trigonodus Dolomite*) of the Schinznach Formation and with water contents of 4.5 – 8.3 wt.-% give indication of contamination by the drilling fluid (samples at 1'139.28, 1'143.33 and 1'153.02 m of depth). For all three drillcore samples a wet appearance and an intense rotten smell was noticed during preparation. Contamination of the porewater samples is mainly indicated by the aberrant alkalinity obtained for the moderately mineralised AqEx solutions (TDS ~ 1.6 – 2.8 g/L) of these core samples (see below), but also by their irregular anion and cation concentrations compared to neighbouring samples. The drilling fluid used in this interval was highly mineralised (EC = 107 mS/cm) and exhibited high concentrations of Na (8.7 g/L), SO₄ (6.9 g/L), TOC (7.6 g/L), alkalinity (130.8 meq/L), Si (72.7 mg/L), K (137 mg/L) and elevated contents of Cl (1.9 g/L), but low contents of Br (1.2 mg/L; Lorenz 2020). It thus differs notably in many ion/ion ratios from those in uncontaminated AqEx solutions, especially also in its Br/Cl ratio (see below). Similar indications of drilling fluid contamination of drillcore samples also exist for three samples between 1'187 m and 1'195 m (samples at 1'187.57, 1'192.08, 1'195.09 m of depth). However, these samples In contrast to the dolomites above, these limestone samples from the Leutschenberg and Kienberg Members of the Schinznach Formation have very low water contents (0.16 – 0.33 wt.-%), no pores are visible by eye and the modification is less obvious. However, they come from a zone penetrated by a dense network of microfractures with dark halos in the adjacent matrix (Fig. 4.4-6). These alteration rims are again crumbly and friable, with an enhanced porosity. It is possible that this network is responsible for an enhanced connectivity within the rock and thus explains the suspected penetration of drilling fluid into the samples. Detailed petrographic work on the distribution of porosity around the microfractures is pending at this stage.

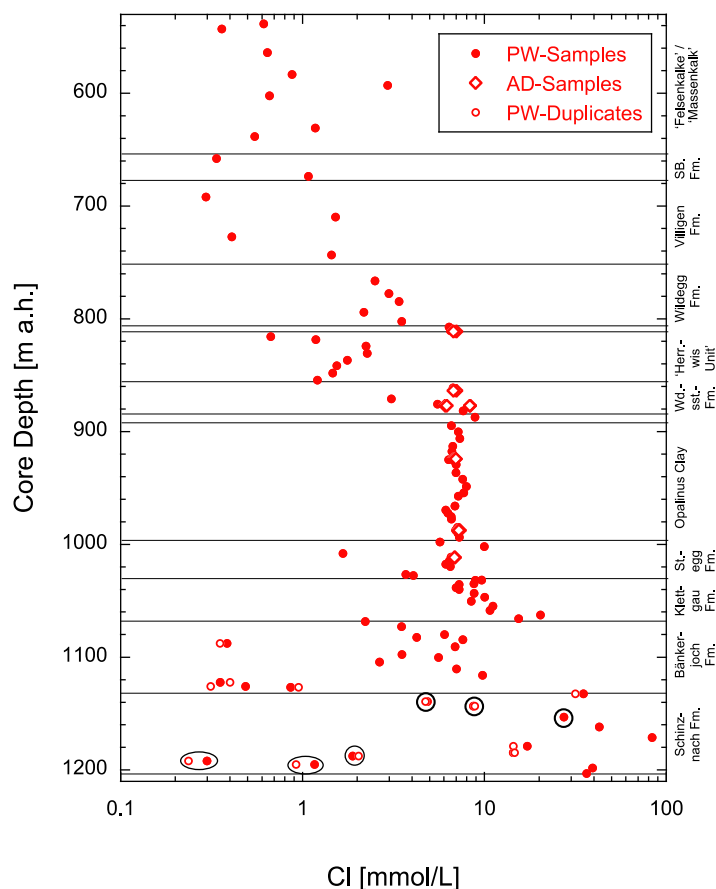


Fig. 4.4-5: Cl concentrations in AqEx solutions vs. depth of rocks from the Malm to the Muschelkalk in borehole BUL1-1

Samples with black circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. PW-Samples = porewater samples, AD-Samples = advective displacement samples, PW-Duplicates = duplicate AqEx test on PW-Sample material used for water-loss measurement

AqEx solutions of all these samples require more detailed clarification of the degree of contamination. Until available, the anion and cation concentrations of these samples should therefore be treated with great care, also regarding the conservative natural tracers Cl and Br.

Concentrations of Br mimic to some degree the distribution of Cl from the Malm to the Lias. In the interlayered marl – anhydrite lithologies of the Bänkerjoch Formation and the limestones and dolostones of the Schinznach Formation Br concentrations contrast those of Cl and show rather small variation at generally lower concentrations compared to the overlying formations (Appendix 1). Chloride and Bromide concentrations in AqEx solutions of all lithologies from the Malm to the Bänkerjoch Formation in the Keuper correlate well with $R^2 > 0.99$ in the solutions of the individual formations, except for the Opalinus Clay and one sample from the Bänkerjoch Formation (Fig. 4.4-7). The rather poorly defined correlation coefficient between Cl and Br in AqEx solutions of the Opalinus Clay is associated to the rather constant Cl and Br concentrations with only small variations (average Cl = 6.987 ± 0.415 mmol/L, average Br = 0.0059 ± 0.0005 mmol/L, $n = 29$).

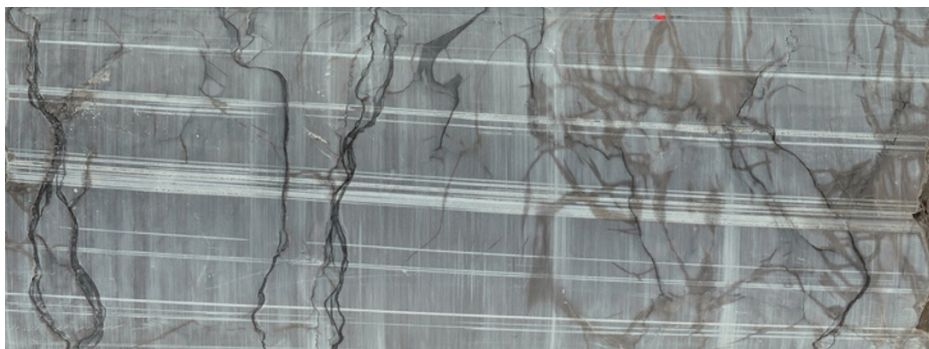


Fig. 4.4-6: Photograph of sample BUL1-1 1'192.08 (Leutschenberg & Kienberg Members of the Schinznach Formation, former Hauptmuschelkalk) with stylolites (black) and a chaotic set of microfractures with darker halos

Sample length is 25 cm, top to the left.

Chloride and Br concentrations in AqEx solutions of the Malm plot on the seawater dilution line and those of the 'Upper Dogger' lithologies plot parallel to, but below this line (Fig. 4.4-7). From the Opalinus Clay down to the water-conducting zone in the Schinznach Formation the Cl and Br concentrations of AqEx solutions also plot parallel to, but even further below the seawater dilution line.

In the Schinznach Formation Cl and Br concentrations of AqEx solutions are grouped according to the sample's occurrence with respect to the water-conducting zone in the Stamberg Member (former *Trigonodus* Dolomite). Samples above the water inflow have Cl-Br relationship similar to those in samples from the overlying Bänkerjoch Formation, except for one sample at the interface Bänkerjoch Formation – Schinznach Formation (Fig. 4.4-7). In contrast, samples below the water inflow have lower Br concentrations, but significantly higher Cl concentrations. It should be noted that the Cl-Br relationship in the drilling fluid differs from that in AqEx solutions. The molar Br/Cl ratio (expressed as $\text{Br} \cdot 1'000/\text{Cl}$) of the drilling fluid averages at 0.243. Therefore, contamination of the 3 samples of the Stamberg Member above the water-conducting could have shifted the Br/Cl ratio in AqEx solutions only to lower values so that the in situ porewater values have to be expected even somewhat higher (Fig. 4.4-8).

Observed differences in Cl and Br concentrations result in a very specific depth profile of the Br/Cl ratio (expressed as $\text{Br} \cdot 1'000/\text{Cl}$; Fig. 4.4-8). From the 'Felsenkalke' / 'Massenkalk' to the base of the Villigen Formation Br/Cl ratio of AqEx solutions fall within the range of modern seawater and overlap with the ratio obtained for the groundwater sampled from the 'Felsenkalke' / 'Massenkalk'. Porewater in these lithologies is likely to have conserved a marine signature with respect to its Br-Cl systematics although at much lower absolute concentrations.

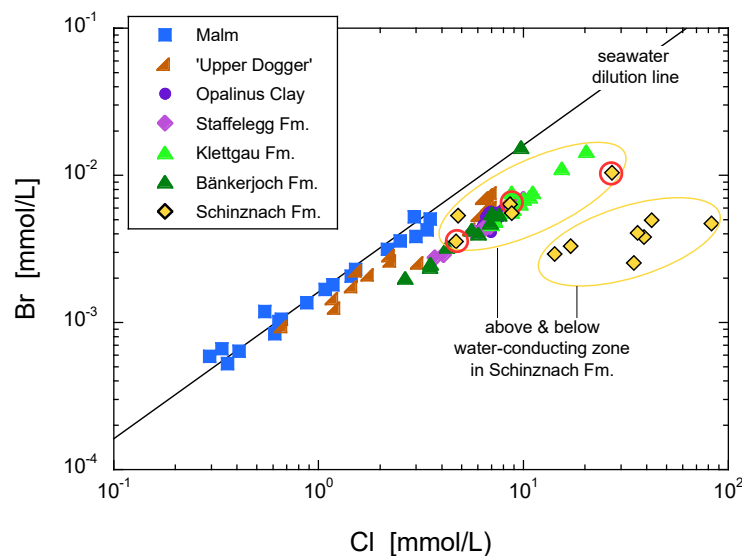


Fig. 4.4-7: Cl vs. Br in AqEx solutions of rocks from the Malm to the Muschelkalk in borehole BUL1-1

Here the group 'Upper Dogger' comprises the lithologies from the Variansmergel Formation to the 'Murchisonae-Oolith Formation'. Note the two groups with different Cl – Br relations in the Schinznach Formation above and below the water-conducting zone. Samples with red circles are contaminated by drilling fluid to the centre of the drillcore.

From the base of the Villigen Formation Br/Cl ratios become lower compared to that of modern seawater and decrease rather smoothly to the top of the Opalinus Clay. The decrease continues across the Opalinus Clay to its base, but at a much lower slope. From the base of the Opalinus Clay to the base of the Bänkerjoch Formation Br/Cl ratios remain then almost constant (Fig. 4.4-8). The increasing deviation of the Br/Cl ratio from that of modern seawater indicates in this depth section a different evolution for Cl and Br, which is due to a different behaviour of Cl in the exchange with the over- und underlying aquifers, the latter having of non-marine characteristics. Except for the drilling fluid contaminated samples, the Br/Cl ratios in the Schinznach Formation are similar to that of the Muschelkalk groundwater and indicative for an origin of Cl by halite dissolution in the underlying Salzlager. Such origin is further confirmed by the Cl-isotope signatures (*cf.* Section 4.4.3.5).

Sulphate

Concentrations of SO₄ in AqEx solutions are shown in Fig. 4.4-9 in relation to S-bearing mineral phases. Rather constant and similar SO₄ concentrations are obtained for all AqEx solutions of PW and AD samples within the Wedelsandstein Formation and the Opalinus Clay. In all these marine sedimentary rocks the variation and constancy, respectively, is independent of the pyrite content, the latter being the only important S-bearing mineral phase in these rocks.

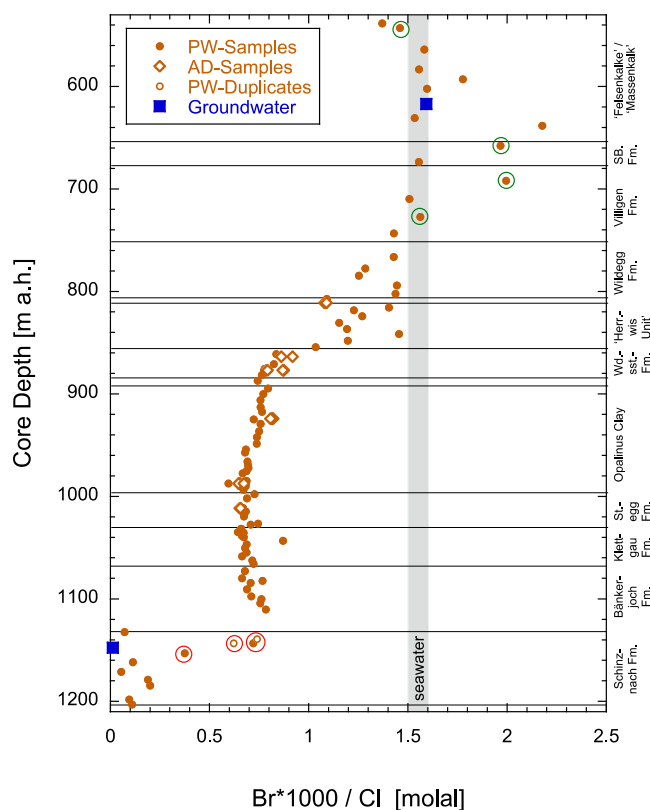


Fig. 4.4-8: Br*1'000/Cl ratio in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

The quantification limit for Br is 2×10^{-4} mmol/L (0.016 mg/L); samples with green circles have Br concentrations close to this value. Samples with red circles are contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

In certain layers of the Klettgau Formation and then below in lithologies of the Bänkerjoch Formation the SO_4 concentrations in AqEx solutions increase strongly by a factor of about 10 – 20. The increase is highly correlated with the occurrence of anhydrite and partly also celestite in the rocks subjected to extraction (Fig. 4.4-9). In these solutions equilibrium with gypsum is attained (*cf.* Section 4.4.3.4). In the pyrite-bearing rocks of the Schinznach Formation the SO_4 concentrations in AqEx solutions decrease rather smoothly to a minimum at 1'187.6 m of depth.

As for Cl and Br, good agreement is obtained for SO_4 concentrations in AqEx solutions obtained from PW samples and adjacent AD samples and PW samples and duplicate extractions of the material used for water-loss measurement of the same sample. The agreement is obtained across the entire profile and independent of the presence of sulphide or sulphate mineral phases (Fig. 4.4-9).

Molar ratios of SO_4/Cl in the 'Felsenkalk' / 'Massenkalk' display a considerable scatter, which is mainly attributed to the very low eluted concentrations of SO_4 and Cl in these rocks of very low porosity (Fig. 4.4-10). More robust SO_4/Cl ratios are obtained for the AqEx solutions from the Schwarzbach Formation to the base of the Staffelegg Formation. There, the SO_4/Cl ratios are all significantly above that of modern seawater. As for the Br/Cl ratios rather constant SO_4/Cl ratios are observed across the Opalinus Clay (0.312 ± 0.023) although a gap is indicated at about 955 m

of depth followed by a slight increase towards the top (Fig. 4.4-10). Influenced by anhydrite (and locally also celestite) dissolution highest SO_4/Cl ratios are observed in AqEx solutions of the anhydrite-bearing, marly rocks in the Bänkerjoch Formation.

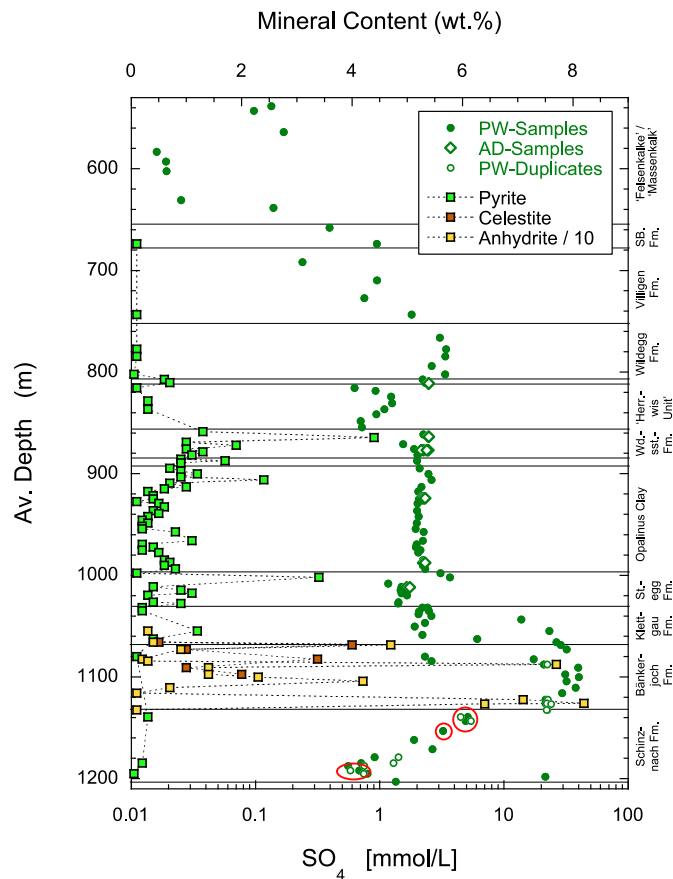


Fig. 4.4-9: SO_4 in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in bore-hole BUL1-1 in comparison with sulphide and sulphate mineral contents of the different lithologies

Samples with red circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

Fluoride

Fluoride concentrations in AqEx solutions vary over a large range from 0.02 – 0.49 mmol/L (0.4 – 9.4 mg/L). Lowest concentrations are observed for the limestones of the 'Felsenkalke' / 'Massenkalk', Schwarzbach and Villigen Formations, anhydrite-rich layers of the Bänkerjoch Formation and the limestones and dolostones of the Schinznach Formation. In contrast, elevated F concentrations are eluted from clay-rich lithologies in which F concentrations are related to some degree to the clay content. A peculiar behaviour is observed in the Opalinus Clay where F concentrations in AqEx solutions describe a smoothly curved profile as a function of depth (Appendix 1).

Total Alkalinity

Total alkalinity values in AqEx solutions cover a large range from 0.3 – 7.54 meq/L. Corresponding pH values are mildly alkaline between 8.1 and 9.9 in extract solutions of all lithologies except for those where anhydrite occurs (Appendix 1). In anhydrite-bearing, marly rock sequences total alkalinity is lowest (0.3 – 1.42 meq/L) and so are the corresponding pH values (7.4 – 8.6). This reflects the induced anhydrite dissolution, which – in presence of dolomite – appears to also result in calcite precipitation during extraction according to the typical de-dolomitisation reaction as indicated by the attainment of gypsum equilibrium in the solutions (*cf.* Section 4.4.3.3). Conversion of total alkalinity to concentrations of HCO_3^- on a mass basis and the hypothesis of de-dolomitisation, however, requires confirmation by further geochemical modelling.

High total alkalinity values between 3.41 and 4.62 meq/L at corresponding pH values of 8.6 – 8.9 are obtained for AqEx solutions of the Opalinus Clay (*cf.* Appendix 1) and reflects the strong impact of cation exchange on carbonate dissolution upon extraction.

The overall highest total alkalinity values of 5.5 – 7.4 meq/L are recorded for three dolostone samples from Stamberg Member of the Schinznach Formation that are contaminated with drilling fluid.

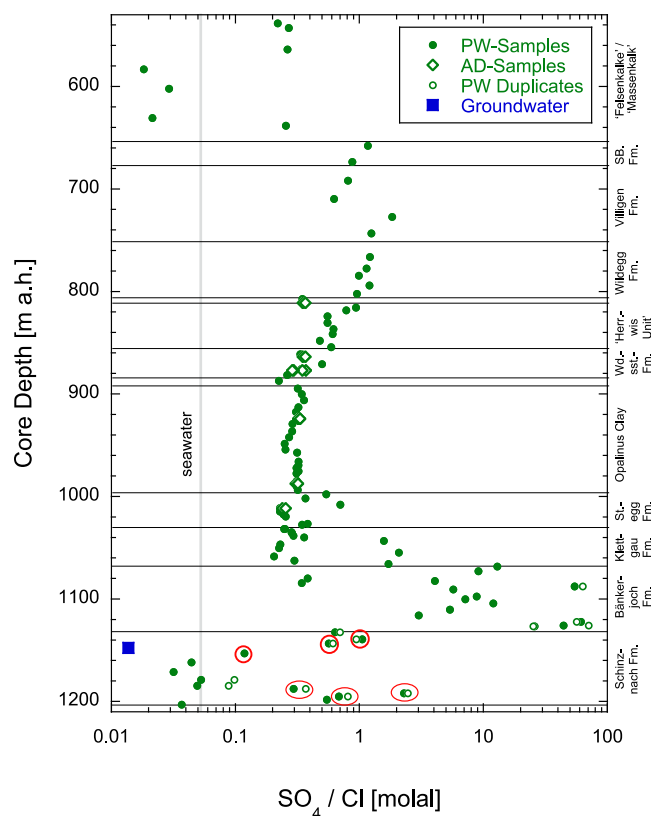


Fig. 4.4-10: SO_4/Cl ratio in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

Samples with red circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

4.4.3.3 Cation concentrations (Na, K, Mg, Ca, Sr)

Sodium and potassium

Sodium is in all AqEx solution the dominant cation so that all solutions across the entire profile are of a general $\text{Na}[\text{Cl}/\text{HCO}_3/\text{SO}_4]$ chemical type with variably changing major anion. In AqEx test over 24 hours at ambient temperature Na is unlikely to be derived from mineral dissolution unless halite would be present in the rocks. The main inventories for Na are thus the porewater and cation exchange. Consequently, Na concentrations in the AqEx solutions also depend on the clay content of the extracted rock sample.

Sodium concentrations in AqEx solutions are higher at most depths and in most lithologies except for samples in clay-free limestones of the 'Felsenkalke' / 'Massenkalk' and in and around the water-conducting zone in the Stamberg Member of the Schinznach Formation.

The excess of Na over Cl in the AqEx solutions and its variation with lithologies and depth is reflected in the Na/Cl ratios (Fig. 4.4-11). The ratios show a large scatter in the clay-poor limestones of the Malm and 'Upper Dogger' down to the Wedelsandstein where Cl concentrations in the AqEx solutions are low (*cf.* Fig. 4.4-5). Rather constant Na/Cl ratios then occur from the Wedelsandstein Formation across the Opalinus Clay into the Staffelegg Formation followed by again variable ratios in the Klettgau Formation and extremely high Na/Cl ratios in the Bänkerjoch Formation. In the Schinznach Formation the Na/Cl ratios are close to one, except for the samples that are contaminated with the high-Na, but low-Cl drilling fluid (*cf.* Section 4.4.3.2).

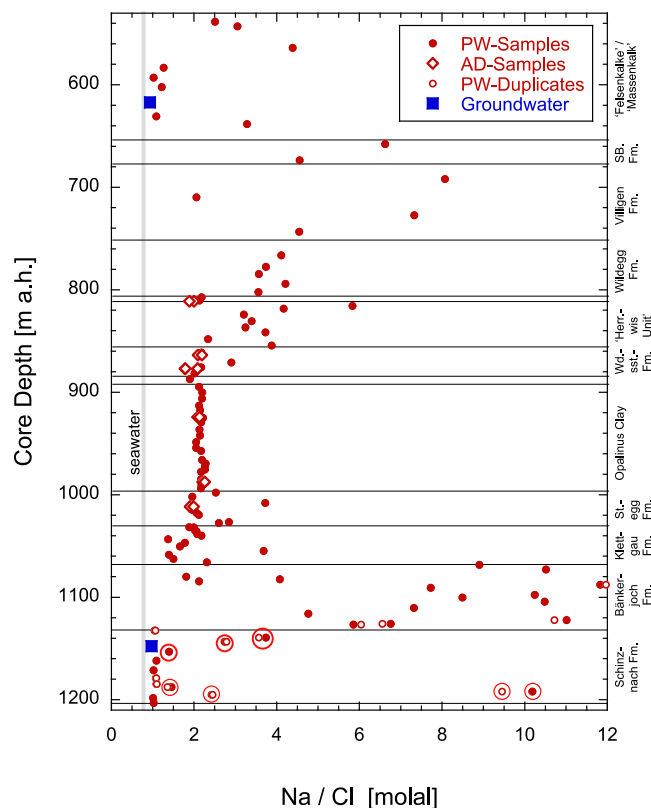


Fig. 4.4-11: Na/Cl in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

Samples with red circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

In the marine sedimentary rocks of the Malm and Dogger formations Na/Cl ratios are all above that of modern seawater indicating that the modification/dilution of the original seawater occurred differently for Na and Cl. Exceptions are a few samples in the near-vicinity of the present Malm groundwater, which yield Na/Cl ratios similar to that of the groundwater and to that of present-day seawater in accordance with the Br/Cl ratios (*cf.* Fig. 4.4-7).

In the Schinznach Formation the few samples with reliable Na and Cl concentrations also yield Na/Cl ratios similar to that of the Muschelkalk groundwater, which is one (Fig. 4.4-11). In combination with the very low Br/Cl ratios (*cf.* Fig. 4.4-7), however, the origin of Na in the pore-water of these rocks stems from halite dissolution as also deduced from the Cl-Br systematics.

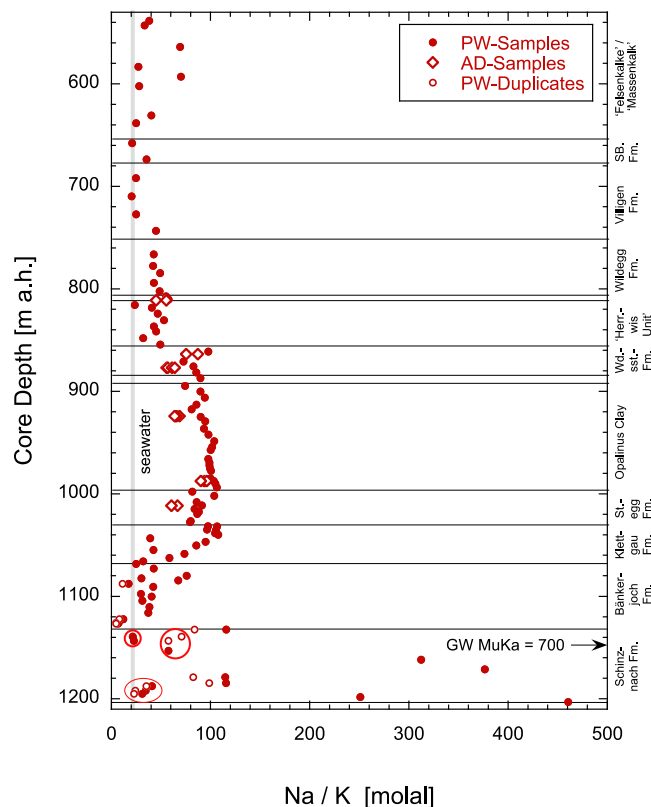


Fig. 4.4-12: Na/K in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

Samples with red circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

The Na/K ratios of AqEx solution are rather homogenous from the 'Felsenkalk' / 'Massenkalk' to the 'Herrenwis Unit', and higher but still rather homogenous from the Wedelsandstein to the Staffelegg Formation. Associated with a large scatter, lower Na/K ratios occur in the Klettgau Formation followed by very high Na/K ratios in the Schinznach Formation (Fig. 4.4-12). The latter is related to the high Na concentrations compared to the low K concentrations (*cf.* Appendix 1) in agreement with the postulated impact of Na and Cl being derived in these pore-waters from halite dissolution.

An unusual spread in Na/K ratios of AqEx solution is observed for the different sample types (PW samples, AD samples, PW-Duplicates; Fig. 4.4-12 and Appendix 1) that is not observed for any other cation or anion. The spread is due to differences in K concentrations of up to 30 % between solutions of different samples. This appears to be an analytical problem as the peaks of Na may overlap with that of K during in IC measurements, especially at high Na/K ratios.

Calcium and magnesium

Concentrations of Ca and Mg in AqEx tests of carbonate-bearing rocks will inevitably be influenced by carbonate mineral dissolution. If the rocks also contain clay minerals, then both solutes will also be affected by cation exchange reactions.

As shown below in Section 4.4.3.4, Ca concentrations are controlled by calcite equilibrium that is attained in the solutions during the 24 hours extraction time. In contrast, Mg concentrations describe a transient state of mineral dissolution due to the more sluggish reaction kinetic of dolomite/ankerite mineral phases and the control is dominated by cation exchange. Exceptions to this general rule are Ca-sulphate bearing rocks and pure dolostone where the Mg concentration in AqEx solutions is controlled by dolomite equilibrium (*cf.* Section 4.4.3.4).

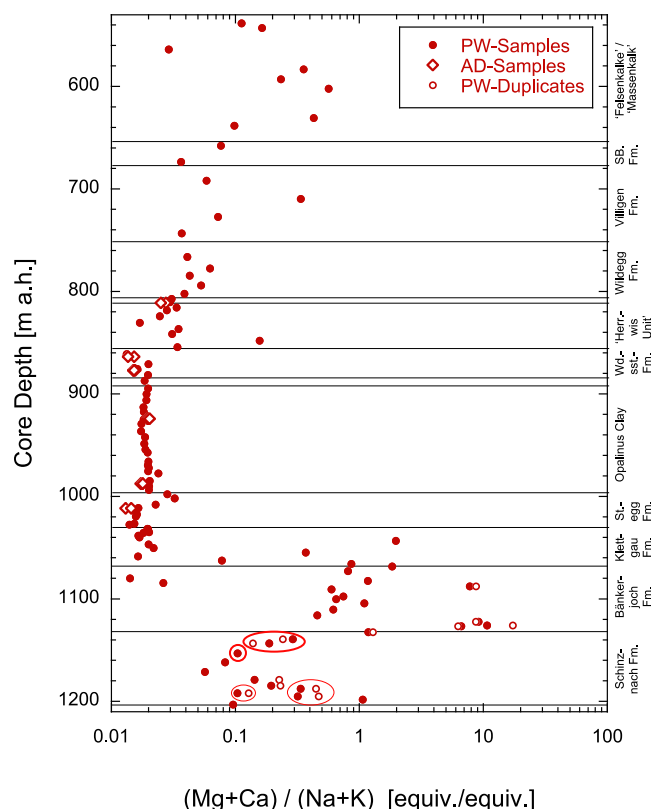


Fig. 4.4-13: $(Ca+Mg)/(Na+K)$ in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

Samples with red circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

The effect of cation exchange reaction on the concentrations of Ca and Mg in AqEx solutions is shown in Fig. 4.4-13. Equivalent ratios of $(\text{Mg}+\text{Ca})/(\text{Na}+\text{K})$ are very constant at low levels in the clay-rich rocks of the Wedelsandstein Formation, Opalinus Clay and Staffelegg Formation. These ratios highlight the large buffer capacity by cation exchange of these lithologies.

Higher ratios are observed in the limestones low clay content of the Malm, in the anhydrite-bearing, marly lithologies of the Bänkerjoch Formation and the clay-poor dolostones and limestones in the Schinznach Formation. Elevated concentrations of Ca and Mg are due to the calcite and dolomite in the rocks of the Malm and Schinznach Formation (here mainly dolomite) and due to the dissolution of anhydrite, calcite and dolomite in the rocks of the Bänkerjoch Formation.

Strontium

Concentrations of Sr in AqEx tests of carbonate-bearing rocks will similarly be affected by carbonate mineral dissolution, in which it commonly occurs a trace component, and in clay-rich rocks by cation exchange. In addition, Sr might also be affected by the dissolution of Sr-bearing sulphate minerals (celestite, anhydrite). As no mineral chemistry data are available, Sr concentration cannot be associated unambiguously to a certain Sr-bearing carbonate or sulphate mineral phase except for celestite that is identified in rocks of the Keuper lithologies.

Concentrations of Sr in AqEx solutions are very low in the marine sedimentary rocks from the 'Felsenkalke' / 'Massenkalk' to the Staffelegg Formation and again in the Schinznach Formation. Very high concentrations are obtained for AqEx solutions of the evaporitic rocks of the Klettgau and Bänkerjoch Formations (Fig. 4.4-14). In all different rock types, there is excellent agreement within the analytical error ($\pm 4\%$) of Sr concentrations in AqEx solutions of PW samples, AD samples and PW-Duplicate samples.

In the Opalinus Clay Sr concentrations show little variation at very low concentrations compared to the about 100 times higher average Sr concentrations in the anhydrite-bearing, marly lithologies of the Bänkerjoch Formation (*cf.* Appendix 1). This large difference is in contrast to the SO_4 concentrations in AqEx solutions of rocks from these two formations, which differ in average only by a factor of 10.

There exists in general a one to one correlation between high Sr concentrations and the occurrence of anhydrite and celestite in the rock (Fig. 4.4-14). Larger variation at very low Sr concentrations are also observed in the Limestones from the 'Felsenkalke' / 'Massenkalk' to the 'Herrenwis Unit' where elevated Sr concentrations are correlated with the occurrence of dolomite/ankerite besides calcite. In both cases, refined mineralogical analyses and mineral chemical analyses need to be conducted to identify the mineral inventory of Sr.

Concentrations of Sr in AqEx solutions are not correlated with the total clay content or the clay composition of the rock (Fig. 4.4-15). This is illustrated by the rocks from the Wedelsandstein Formation, 'Murchisonae-Oolith Formation', Opalinus Clay compared to the rocks of the anhydrite-bearing, marly lithologies of the Bänkerjoch Formation, which have highly variable clay contents. It thus appears that the uptake of Sr onto the exchange during aqueous extraction at a S^*/L^* ratio of 1 is small compared to the contribution of Sr from mineral dissolution, especially if there is an independent Sr mineral phase such as celestite present. This is in agreement with the observations made in AqEx solutions produced at different S^*/L^* ratio where an increase of Sr concentrations is observed at the lowest S^*/L^* ratio where the preference for Sr on the exchanger is expected to be highest (*cf.* Section 4.4.2).

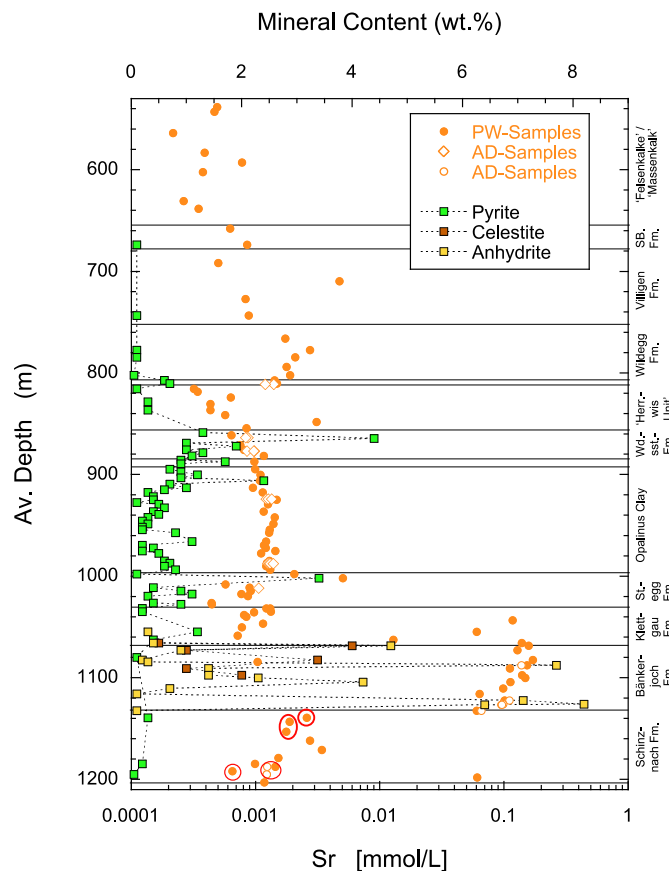


Fig. 4.4-14: Sr in AqEx of rocks from the Malm to the Muschelkalk in borehole BUL1-1 in comparison with sulphide and sulphate mineral contents of the different lithologies

Samples with red circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

4.4.3.4 Mineral saturation states

Calcite

In the dolostones of the Klettgau and Schinznach Formations (Stamberg Member) calcite is oversaturated in the AqEx solutions (Appendix 2). This reflects the transient state of the solutions with respect to the sluggish dissolution of dolomite/ankerite and impediment of calcite precipitation by increasing Mg concentrations in the solutions. An even higher oversaturation with respect to calcite is modelled for the AqEx solutions of the anhydrite-bearing marly layers of the Bänkerjoch Formation (Appendix 2).

Dolomite

In the marine sediments from the 'Felsenkalk' / 'Massenkalk' to the Staffelegg Formation AqEx solutions at a S^*/L^* of 1 are undersaturated with respect to disordered dolomite (Appendix 2). Variations in the degree of undersaturation correlate with the presence/absence of dolomite/ankerite in the rock and its grain size.

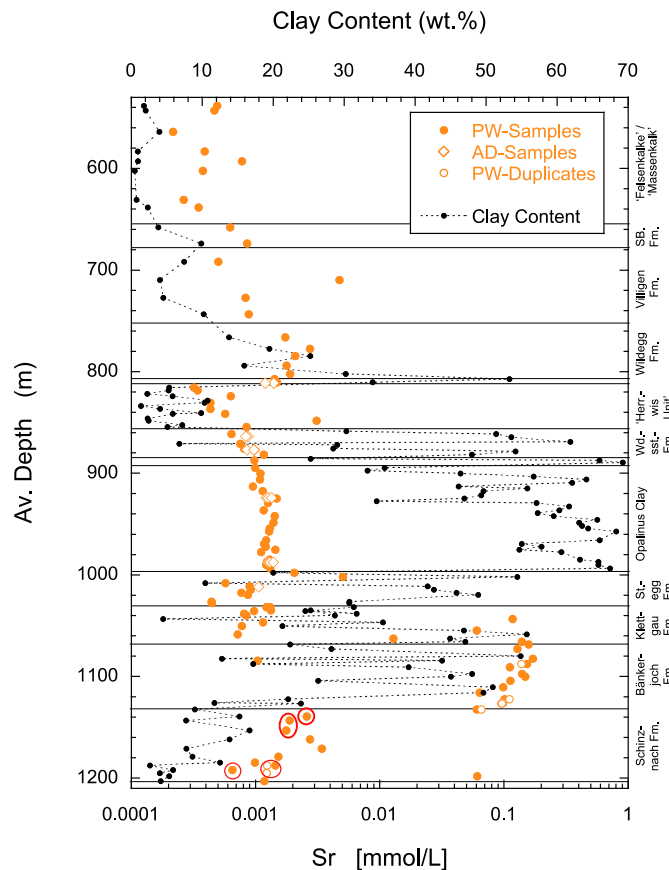


Fig. 4.4-15: Sr in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1 in comparison with the clay content of the different lithologies

Samples with red circles are (thick lines) or appear to be (thin lines) contaminated by drilling fluid to the centre of the drillcore. Sample designation as in Fig. 4.4-5.

In the dolostones of the Klettgau Formation equilibrium with disordered dolomite is attained or slightly surpassed in the AqEx solutions (Appendix 2). An even stronger supersaturation is modelled for the dolostones and dolomite/ankerite-bearing limestones of the Schinznach Formation whereas pure limestones are undersaturated with respect to dolomite. In the Schinznach Formation, however, the modelled strong oversaturation in the samples from 1'139 – 1'153 m and 1'187 – 1'195 m of depth is also due to contamination of the AqEx solution's alkalinity by drilling fluid (see above).

Dolomite supersaturation is also modelled for the AqEx solutions of the dolomite/ankerite- and anhydrite-bearing marly layers of the Bänkerjoch Formation (Appendix 2) in agreement with the there occurring de-dolomitisation during extraction.

Gypsum

Aqueous extract solutions of all marine sedimentary rocks from the 'Felsenkalk' / 'Massenkalk' to the Staffelegg Formation and again in the Schinznach Formation are undersaturated with respect to gypsum (Appendix 2). Similarly, AqEx solutions of the anhydrite-free horizons of the Klettgau and Bänkerjoch Formations are also strongly undersaturated with respect to gypsum.

Gypsum equilibrium is, however, attained in the AqEx solutions of the anhydrite-bearing, marly layers of the Klettgau Formation and the Bänkerjoch Formation (Appendix 2). It should be noted that at ambient temperature and a water activity of almost 1 equilibrium with gypsum is reached earlier than that with anhydrite (difference in SI value about 0.2 log units). The rock contains, however, anhydrite as identified by XRD (*cf.* Chapter 4.2). Thus, during aqueous extraction anhydrite will dissolve and not gypsum, but the thermodynamic equilibrium with gypsum is reached before that of anhydrite.

The saturation with respect to gypsum can also indicate the presence of a CaSO_4 phase that was not detected in the mineralogical investigations. This is e.g. indicated by the attained equilibrium with gypsum in the AqEx solution in the limestone sample from 1'198.18 m of depth in the Schinznach Formation (Appendix 2).

Celestite

Aqueous extract solutions of all marine sediments from the 'Felsenkalke' / 'Massenkalk' to the Staffelegg Formation and again in the Schinznach Formation are all undersaturated by two or more orders of magnitude with respect to celestite. (Fig. 4.4-16). Celestite-undersaturation is variable in the limestones of the 'Felsenkalke' / 'Massenkalk' to the 'Herrenwis Unit' where the concentrations of Sr and SO_4 in AqEx solutions show considerable variation (*cf.* Figs. 4.4-9 and 4.4-14). Aqueous extract solutions are, however, also strongly undersaturated with respect to celestite in the Wedelsandstein ($\text{SI}_{\text{celestite}} = -3.01 \pm 0.33$) and Opalinus Clay ($\text{SI}_{\text{celestite}} = -2.62 \pm 0.08$) where the concentrations of Sr and SO_4 in the extract solutions are rather constant (*cf.* Figs. 4.4-9 and 4.4-14).

In turn, AqEx solutions are in equilibrium with celestite saturation in all anhydrite-bearing marly layers of the Klettgau Formation and the Bänkerjoch Formation (Fig. 4.4-16). In most of these samples celestite is also observed in the mineralogical analyses (*cf.* Fig. 4.4-14).

Celestite saturation indices support the statements made based on the concentrations of Sr and SO_4 in the AqEx solution in that this mineral phase does not act as a control for Sr or SO_4 in the marine sediments from the 'Felsenkalke' / 'Massenkalk' to the Staffelegg Formation.

In contrast, in the evaporitic rocks of the Klettgau Formation and the Bänkerjoch Formation, celestite might indeed act a solubility control on the Sr concentrations whereas that of SO_4 seems more likely to be controlled by the there present anhydrite.

Fluorite

The AqEx solutions of all lithologies are variably undersaturated with respect to fluorite, except for the anhydrite-bearing marly layers of the Bänkerjoch Formation where fluorite is close or at equilibrium (Appendix 2). Across the Opalinus Clay the saturation indices of fluorite mimic the peculiar curved distribution pattern of the F concentrations in the AqEx solutions. If of interest this behaviour would have to be investigated with specific mineralogical and mineral chemical investigations.

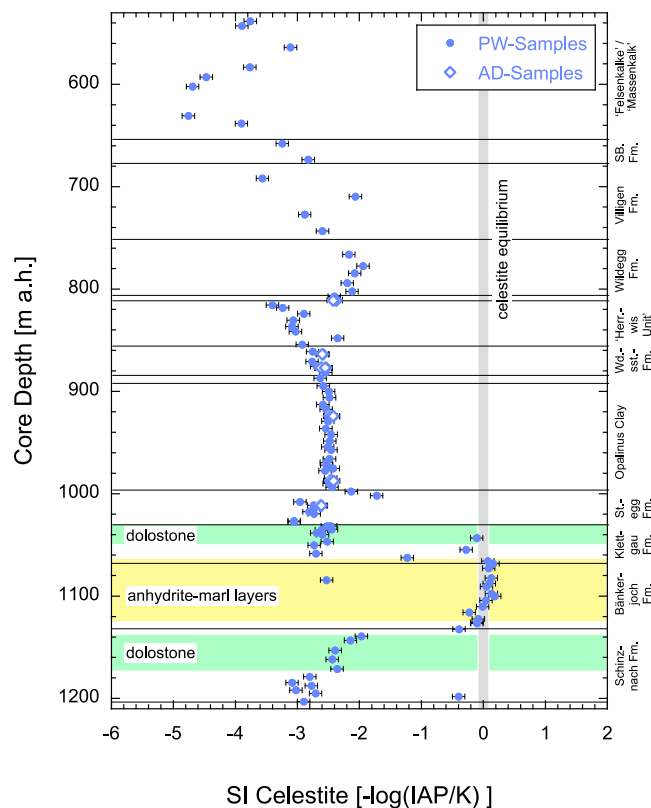


Fig. 4.4-16: Saturation index of celestite in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

PW-Samples = porewater samples, AD-Samples = advective displacement samples, no data on carbonate system of PW-Duplicates available.

4.4.3.5 Cl-isotopes in AqEx solutions

The stable isotopes signature of Cl in solutions, expressed as $\delta^{37}\text{Cl}$ versus the SMOC standard, carries in first line information about the origin of Cl. Thus, Cl isotope ratios may be used to discern an origin of Cl from seawater and of rock salt dissolution. Over long periods of time, however, Cl-isotopes get also fractionated during Cl diffusion across low-permeability rocks (e.g. Gimmi & Waber 2004).

Compared to the $\delta^{37}\text{Cl}$ signatures observed across the Opalinus Clay at Benken (Gimmi & Waber 2004), the $\delta^{37}\text{Cl}$ signatures of AqEx solutions across the entire profile from the 'Felsenkalk' / 'Massenkalk' to the Schinznach Formation display a different distribution pattern that seems to indicate several overlapping and long-lasting processes. The resolution of the profile is, however, not high enough to unravel these processes.

In the 'Felsenkalk' / 'Massenkalk' $\delta^{37}\text{Cl}$ values in AqEx solutions are around that of modern seawater and essentially overlap with the value of the Malm groundwater (Fig. 4.4-17). From there the $\delta^{37}\text{Cl}$ values constantly increase to maximum values in the Wedelsandstein Formation where they show some variation outside the analytical uncertainty. In the Opalinus Clay $\delta^{37}\text{Cl}$ values appear to decrease from top to bottom although there is large gap in data between the only two samples (Fig. 4.4-17).

Across the Staffelegg Formation and the Klettgau Formation, $\delta^{37}\text{Cl}$ values in AqEx solutions are similar before they constantly increase from the Bänkerjoch Formation down into the Schinznach Formation to rather constant values (Fig. 4.4-17). An exception to this general trend is the sample contaminated by drilling fluid at 1'153.02 m of depth (*cf.* Section 4.4.3).

These values overlap with those of halite collected from the Zeglingen Formation some 60 – 100 m below the lowest AqEx solution sample with Cl-isotope data (Fig. 4.4-17). This supports the hypothesis stated above that the origin of Cl (and Na) in the porewater of the Schinznach Formation is rock salt dissolution. At this time, no $\delta^{37}\text{Cl}$ values are yet available for the groundwater in the Stamberg Member (former Trigonodus Dolomite). It further appears that some of the halite derived Cl migrated upwards at least to the base of the Klettgau Formation or some halite might also have been present in the evaporite layers of the Bänkerjoch Formation. At this stage and with the present data a more detailed interpretation cannot be made.

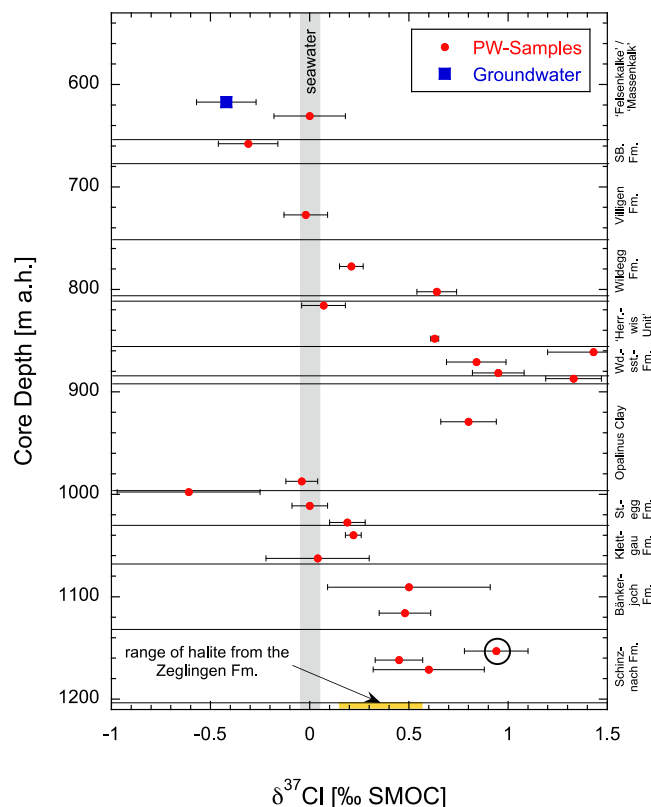


Fig. 4.4-17: Cl isotopes, expressed as $\delta^{37}\text{Cl}$, in AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

PW-Samples = porewater samples. The sample with a black circle is contaminated by drilling fluid to the centre of the drillcore.

4.4.4 Chloride and bromide concentrations at water-loss porosity

The first step in deriving porewater concentration from aqueous extraction data is the back-calculation of such data to water-loss porosity. For Cl and Br it is commonly assumed that these ions occur as free, negatively charged ions that are not subjected to complexation in the solution. As such the concentrations of these anions can be scaled to the wet rock water content (or water-

loss porosity, WL-P) using the formulation given in Waber (ed.) (2020). Whereas such scaling directly delivers the porewater concentrations of Cl and Br in clay-free rocks, it is well known for clay-bearing rocks that this scaling has also to account for anion-exclusion to obtain the porewater concentration. The derivation of the Cl- and Br- accessible porosity and calculation of porewater concentrations is further established in Chapter 5.

A different case arises for SO₄ in AqEx solutions although it is shown that SO₄ behaves conservatively during extraction and the porewater appears to be the only inventory for SO₄ in the AqEx solutions (*cf.* Sections 4.4.2 and 4.4.3). However, scaling SO₄ in AqEx solutions to the water content (or water-loss porosity) of the rock samples delivers unusually high SO₄ concentrations in the various lithologies. Interestingly, such – still hypothetical – concentrations would be reasonable in the clay-free limestones of the 'Felsenkalke' / 'Massenkalk' and even similar to that of the Malm groundwater. In contrast, very high SO₄ concentrations of > 12 g/L would be obtained for the also clay-poor limestones in the 'Herrenwis Unit' and SO₄ concentrations in the clay-rich Opalinus Clay and Staffelegg Formation would be about 4 – 6 g/L. Although scaling to the SO₄-accessible porosity in clay-rich rocks will have to take the complexation of dissolved SO₄⁻² and dynamically changing anion exclusion into account, these hypothetical concentrations at water-loss porosity appear rather high and in the same range as the Cl concentrations (see below). This issue is further elaborated in Chapter 5.

Scaling of Cl- and Br- concentrations obtained from AqEx tests to water-loss porosity require knowledge of the water content of the rocks. As shown in Section 4.3, water content of various subsamples may show considerable scatter especially in rocks of low porosity due to the heterogeneously distributed porosity in these rocks. To illustrate the effect of this scatter, Fig. 4.4-18 shows the Cl concentrations scaled with the water content of the PW sample aliquot and scaled with the average of PW sample aliquot and the two aliquots used for isotope diffusive exchange experiments.

Chloride concentrations at water-loss porosity (WL-P) cover a range of about 3.7 – 7.4 g/kg_{H2O} in the limestone-dominated lithologies from the 'Felsenkalke' / 'Massenkalk' to the Variansmergel Formation (Fig. 4.4-18). The concentrations obtained by scaling with the individual and average water-content values agree within the propagated error, except for two samples. Chloride concentrations of porewater samples in the near vicinity of the Malm groundwater in the 'Felsenkalke' / 'Massenkalk' overlap with that of the groundwater. This suggests that the Cl-accessible porosity is similar if not identical to the water-loss porosity in these clay-poor rocks and the Cl concentrations at WL-P represent the porewater Cl concentrations.

In the limestones of the 'Herrenwis Unit' Cl concentrations at WL-P are higher (about 5.5 – 13.6 g/kg_{H2O}) and differ outside the propagated error between the scaling using the individual and average water-content values. Nevertheless, porewater Cl concentrations appear to be higher compared to those in the overlying rocks of the Wildeggen Formation as the limestones of the 'Herrenwis Unit' have only very low clay content (< 10 wt.-%, *cf.* Appendix 1) and the fraction of Cl-accessible porosity appears to be close to one.

In the Wedelsandstein Formation Cl concentrations at WL-P agree fairly well for the porewater (PW)-samples scaled using the individual and average water-content values (Fig. 4.4-18). However, larger scatter is observed between PW samples and adjacent AD samples indicating heterogeneous porosity distribution and Cl-accessible porosity on the dm-scale in this formation.

From the base of the Wedelsandstein Formation to the base of the Opalinus Clay good agreement Cl concentrations at WL-P is observed between different scaling and different sample types (Fig. 4.4-18). At the elevated water content in these rock types this suggests a rather homogenous

distribution of the pore space also some heterogeneity on the cm- to dm-scale is indicated at the top of the Opalinus Clay. In general Cl concentrations at WL-P decrease from about 7.9 g/kg_{H2O} to 5.9 g/kg_{H2O} towards the base of the Opalinus Clay. This may, however, be counteracted by the generally higher clay content towards the base of the Opalinus Clay and thus a change in Cl-accessible porosity (*cf.* Chapter 5).

In the Staffelegg Formation Cl concentrations at WL-P are again somewhat higher (5.1 – 8.7 g/kg_{H2O}) and differently derived concentrations agree well. The agreement occurs in spite of strong variation in lithologies (limestone to argillaceous marl) over short distances, which is also responsible for the suggested gap in Cl concentrations towards the overlying Opalinus Clay. This gap is related to limestone layers with low clay contents at the top of the Staffelegg Formation (*cf.* Appendix 1) and thus different Cl-accessible porosity (*cf.* Chapter 5).

Larger variation in Cl concentrations at WL-P is again observed in the lithologically heterogeneously composed Klettgau Formation and Bänkerjoch Formation (Fig. 4.4-18). Especially in the Bänkerjoch Formation where marly layers alternate with anhydrite or dolomitic layers on the cm-scale a large scatter outside the propagated error is observed between the scaling using the individual and average water-content values. The highly variable clay content over short distance (*cf.* Appendix 1) will further pose a challenge to combine Cl from AqEx solutions, water content and Cl-accessible porosity in order to derive the in situ porewater Cl concentrations (*cf.* Chapter 5).

Even more pronounced is the scatter of Cl concentrations at WL-P in the low-porosity dolostones and limestone of the Schinznach Formation (Fig. 4.4-18). As noted in Section 4.4.3.1, Cl (and Br) concentrations in the AqEx solutions of duplicate extractions agree well and the scatter obtained when scaling these concentrations to WL-P is mainly related to the mismatch of eluted Cl concentration and water content. For such rocks, determination of extractable Cl and water content should preferably occur on the very same rock material.

Nevertheless, it becomes obvious that Cl concentrations at WL-P increase strongly from values of about 7.1 – 11.5 g/kg_{H2O} at the base of the Bänkerjoch Formation to values of about 60 g/kg_{H2O} to more than 100 g/kg_{H2O} around and below the water-conducting zone in the Stamberg Member (former *Trigonodus Dolomite*) of the Schinznach Formation (Fig. 4.4-18). In the dolostones and limestone of the Schinznach Formation these concentrations essentially correspond to porewater concentrations as these have very low clay content (mainly < 10 wt.-%, *cf.* Appendix 1). Contamination with drilling fluid of porewater drillcore samples between 1'139 – 1'153 m and 1'187 – 1'195 m of depth disables the derivation of the concentration gradients developed between the base of the Bänkerjoch Formation and the water-conducting zone in the Stamberg Member.

As Br concentrations in AqEx solutions are highly correlated with Cl concentrations (*cf.* Section 4.4.3.2), the same depth distribution and discrepancies between scaling with different water contents are obtained as described above for Cl (Fig. 4.4-19).

Most importantly Br concentrations at WL-P coincide with those of the groundwater in the 'Felsenkalk' / 'Massenkalk' of the Malm and possibly also with those of the groundwater in the Stamberg Member (former *Trigonodus Dolomite*) of the Muschelkalk. With respect to the latter it has to be noted that the contamination of the porewater samples with drilling fluid is less pronounced compared to Cl due to the much lower Br concentration in the drilling fluid.

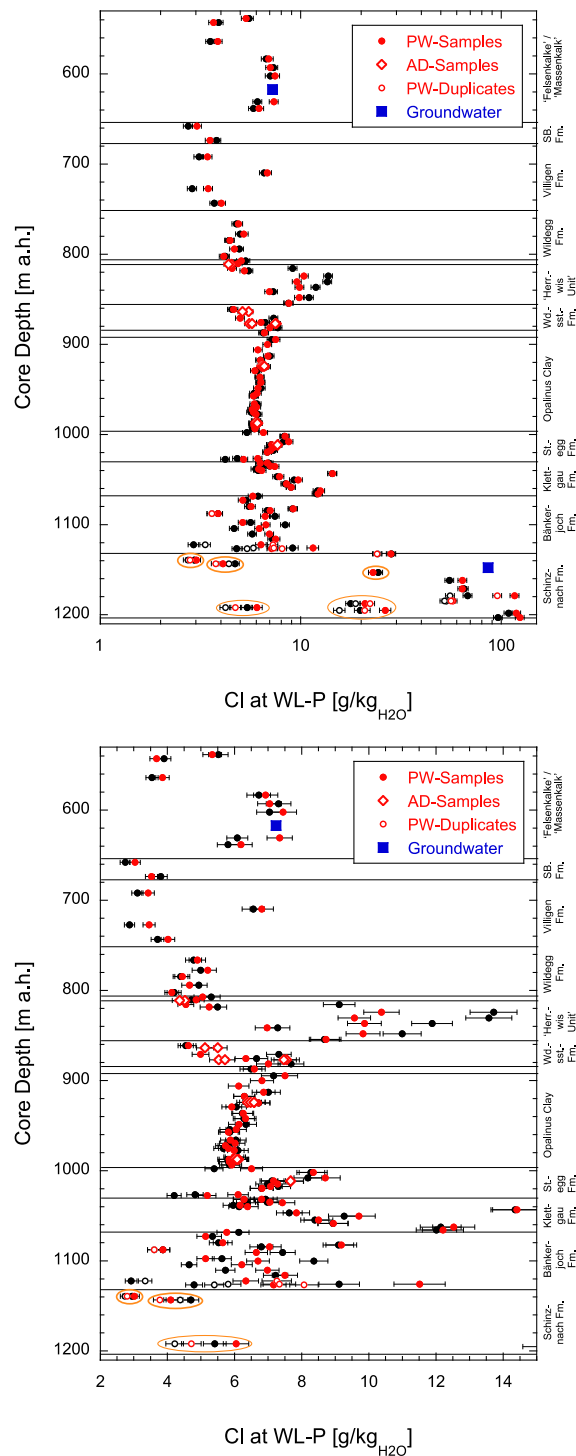


Fig. 4.4-18: Cl concentration at WL-Porosity as derived from AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

Top: complete x-axis in log-scale, bottom: enlargement of x-axis in linear scale.

Black symbols: Cl scaled with WC of PW-Sample; red dots: Cl scaled with average WC ($n = 3$, aliquots from PW-sample and isotope diffusive exchange experiments); PW-Duplicates are Cl concentrations extracted of the PW-sample aliquot after drying. Framed samples in the Schinz- nach Formation are contaminated by drilling fluid (see text).

Also for Br exceptionally high concentrations at WL-P are obtained for the limestones in the 'Herrenwis Unit' as for Cl. Whereas the difference to the underlying Wedelsandstein Formation might disappear due to differences in clay content and thus Br-accessible porosity (Fig. 4.4-19), the difference towards the overlying Wildegg Formation might remain (*cf.* Chapter 5).

One sample each in the Klettgau Formation and the Bänkerjoch Formation display high Br concentrations at WL-P that fall off the general trend (Fig. 4.4-19). From the analytical point of view there are no anomalies and the high concentrations appear to be related to issues of mineralogy, mineral chemistry, and Br-accessible porosity.

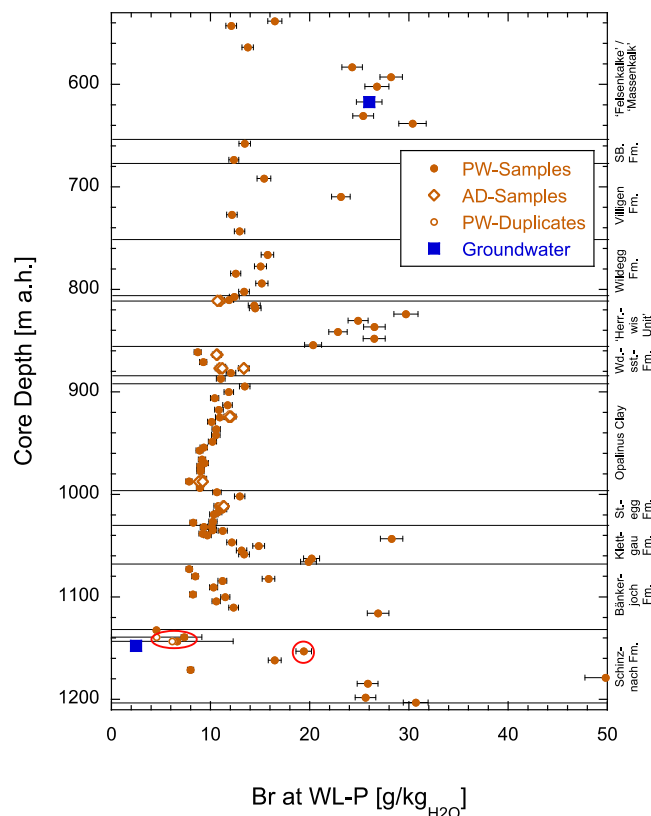


Fig. 4.4-19: Br concentration at WL-Porosity as derived from AqEx solutions of rocks vs. depth from the Malm to the Muschelkalk in borehole BUL1-1

Br scaled with average WC ($n = 3$, aliquots from PW-Sample and isotope diffusive exchange experiments); PW-Duplicates are Cl concentrations extracted of the PW-Sample aliquot after drying. Framed samples in the Schinznach Formation are contaminated by drilling fluid (see text).

4.5 Cation-exchange extraction data

Paul Wersin & Martin Mazurek

A total amount of 18 samples were analysed at the University of Bern with the nickel ethylenediamine (Ni-en) extraction method to determine the cation exchange capacity (CEC) and the composition of the clay exchanger (for methodology see Waber *ed.* 2020). A larger number of samples were studied by the team of Bart Baeyens at PSI using the CsNO_3 extraction method

(Marques Fernandes & Baeyens *in prep.*). The objective of the Ni-en extraction study was (i) to compare and verify the PSI study with an alternative method and (ii) to complement the PSI cation exchange dataset.

The CEC can be derived in two ways: (1) the consumption of the index cation (Ni in this case) during extraction and (2) the sum of extracted cations (Σ CAT). Note that the latter includes (i) the exchangeable cations, (ii) cations dissolved in the porewater and (iii) cations released from potentially dissolving minerals (e.g. carbonates, sulphates) during extraction. Thus, in principle, the CEC derived from the sum of cations requires correction from contributions of (ii) and (iii). Corrected CEC and exchangeable cation data are discussed in Section 5.7, where the data from the University of Bern is also compared with that of PSI.

Tab. 4.5-1 shows the Ni consumption and extracted cation data (Na, K, Ca, Mg, Sr, Ba, Fe) for solid/liquid ratios (S/L) around 1³. Anion data (Cl, Br, SO₄, NO₃) is depicted in Tab. 4.5-2. Note that Ni nitrate was added to the samples, which explains the high NO₃ contents.

Tab. 4.5-1: Cation data from Ni-en extracts at a S/L ratio around 1 (University of Bern data)

Type	Depth [m]	Formation	S/L [g/g]	Na	K	Ca	Mg	Sr	Ba	Fe	Σ CAT	Ni cons.
				[meq/kg _{dry rock}]								
PW	794.13	Wildegge Fm.	0.920	16.2	2.2	12.1	5.7	0.13	0.001	0.004	36.4	35.9
AD	811.12	'Park.-Württ.-Sch.'	0.896	59.6	8.8	45.1	22.7	0.67	0.003	0.005	136.8	151.1
PW	848.18	'Herrenwis Unit'	0.961	3.7	0.3	5.3	1.6	0.09	0.003	< 0.002	11.0	7.8
AD	863.66	Wedelsandstein Fm.	0.903	71.7	6.8	40.9	15.0	0.60	0.006	0.020	134.9	156.1
PW	875.69	Wedelsandstein Fm.	0.909	40.1	3.7	26.2	9.0	0.35	0.005	0.005	79.4	84.7
AD	877.03	Wedelsandstein Fm.	0.906	53.7	5.8	32.9	11.0	0.45	0.005	0.017	103.8	111.3
PW	894.68	Opalinus Clay	0.913	40.7	3.9	25.3	9.0	0.30	0.005	0.031	79.3	83.7
AD	924.18	Opalinus Clay	0.901	51.3	5.2	30.9	10.5	0.50	0.012	0.003	98.3	110.1
PW	929.23	Opalinus Clay	0.900	57.5	5.2	37.6	12.3	0.57	0.013	0.083	113.3	119.4
PW	948.58	Opalinus Clay	0.886	64.8	5.3	42.2	13.3	0.62	0.011	0.098	126.3	135.6
PW	965.98	Opalinus Clay	0.905	61.2	5.1	39.3	11.3	0.57	0.008	< 0.002	117.5	122.0
PW	975.25	Opalinus Clay	0.897	57.5	4.9	35.7	11.4	0.59	0.020	0.016	110.1	118.5
AD	987.55	Opalinus Clay	0.895	63.5	5.3	44.3	13.9	0.63	0.013	0.011	127.6	120.7
PW	1'008.04	Staffelegg Fm.	0.925	10.0	1.1	9.3	2.3	0.08	0.004	< 0.002	22.8	23.2
AD	1'011.62	Staffelegg Fm.	0.915	43.8	4.9	26.4	7.9	0.46	0.021	< 0.004	83.5	75.8
PW	1'019.49	Staffelegg Fm.	0.898	56.5	4.5	34.2	9.8	0.49	0.007	< 0.002	105.5	112.2
PW	1'161.83	Schinznach Fm.	0.903	48.8	0.4	6.5	11.0	0.01	0.004	< 0.002	66.6	22.0
PW	1'178.88	Schinznach Fm.	0.942	17.9	0.4	4.3	7.5	0.01	0.007	< 0.002	30.0	22.0

³ A water mass equal to the mass of the wet rock was added, leading to S/L (mass of dry rock / [mass of added water + porewater]) slightly below 1.

Tab. 4.5-2: Anion data from Ni-en extracts (University of Bern data)

F contents are < 0.16 mg/L or < 0.01 meq/kg_{dry rock} for all samples.

Type	Depth [m]	Formation	Cl	Br	NO ₃ ^a	SO ₄
			[meq/kg _{dry rock}]			
PW	794.13	Wildegge Fm.	2.5	0.003	346	3.1
AD	811.12	'Park.-Württ.-Sch.'	7.6	0.007	346	4.0
PW	848.18	'Herrenwis Unit'	2.0	< 0.002		1.6
AD	863.66	Wedelsandstein Fm.	7.8	0.006	347	3.2
PW	875.69	Wedelsandstein Fm.	6.1	0.004	347	3.0
AD	877.03	Wedelsandstein Fm.	7.6	0.006	355	3.7
PW	894.68	Opalinus Clay	7.1	0.005	346	3.3
AD	924.18	Opalinus Clay	7.0	0.005	357	3.2
PW	929.23	Opalinus Clay	7.2	0.005		3.0
PW	948.58	Opalinus Clay	8.6	0.006		3.1
PW	965.98	Opalinus Clay	7.7	0.005	358	3.1
PW	975.25	Opalinus Clay	7.0	0.005	363	2.9
AD	987.55	Opalinus Clay	7.6	0.005	365	3.3
PW	1'008.04	Staffelelegg Fm.	1.8	< 0.002	370	2.1
AD	1'011.62	Staffelelegg Fm.	8.3	0.005	362	2.5
PW	1'019.49	Staffelelegg Fm.	6.9	0.004	369	2.6
PW	1'161.83	Schinznach Fm.	46.3	0.005	378	4.5
PW	1'178.88	Schinznach Fm.	20.2	0.004	365	2.1

^a Nitrate is part of the added Ni-en stock solution

Some tests were carried out with variable S/L ratios. Ratios of wet rock to added water of 0.1, 0.25, 0.5 and 1.0 were used, resulting in S/L ratios (i.e. ratio of dry rock to the sum of added and porewater) as listed in Tab. 4.5-3. The data obtained at different S/L ratios are broadly consistent but variations beyond the analytical error are noted. There is a tendency of increasing Ca at lower S/L ratio in some of the samples, which is presumably due to enhanced calcite dissolution. Marked increases of Mg with decreasing S/L in samples 848.18 and 1008.04 correlate with dolomite contents of 1 – 4 wt.-% in these samples, while the other samples have only traces of dolomite according to X-ray diffraction data. According to previous experiences (Wersin et al. 2013, Hadi et al. 2019), the tests carried out at the highest S/L ratio of 1 are deemed to be most reliable.

Tab. 4.5-3: Cation data from Ni-en extracts carried out at variable S/L ratios (University of Bern data)

Type	Depth [m]	Formation	S/L [g/g]	pH	Na	K	Ca	Mg	Sr	ΣCAT	Ni cons.
					[meq/kg _{dry rock}]						
PW	794.13	Wildegge Fm.	0.92	8.34	16.2	2.2	12.1	5.7	0.13	36.4	35.9
			0.48	8.57	17.0	2.5	14.0	6.4	0.15	40.1	50.1
			0.26	8.81	16.8	2.4	14.0	6.3	0.14	39.7	41.4
			0.11	9.1	16.6	2.2	15.3	6.1	0.15	40.4	40.1
PW	848.18	'Herrenwis Unit'	0.96	8.42	3.7	0.3	5.3	1.6	0.09	11.0	7.8
			0.48	8.61	3.7	0.3	6.1	1.9	0.24	12.3	15.0
			0.26	8.87	3.4	0.3	6.9	2.2	0.36	13.1	5.5
			0.10	9.22	3.9	0.3	9.6	2.7	0.14	16.6	11.2
PW	875.69	Wedelsandstein Fm.	0.91	8.36	40.1	3.7	26.2	9.0	0.35	79.4	84.7
			0.47	8.55	40.7	4.1	26.7	9.6	0.36	81.4	97.5
			0.24	8.8	39.4	4.2	25.5	8.7	0.34	78.2	77.0
			0.10	9.04	40.3	4.1	28.7	9.0	0.36	82.5	86.4
PW	948.58	Opalinus Clay	0.89	8.33	64.8	5.3	42.2	13.3	0.62	126.3	135.6
			0.46	8.45	62.8	6.2	40.8	14	0.64	124.6	140.5
			0.24	8.62	60.2	6.7	39.5	13.5	0.60	120.5	129.1
			0.10	8.86	59.6	7.4	42.9	13.9	0.62	124.4	137.9
PW	1'008.04	Staffelegg Fm.	0.93	8.36	10.0	1.1	9.3	2.3	0.08	22.8	23.2
			0.49	8.58	10.8	1.2	9.4	2.4	0.09	23.9	39.1
			0.25	8.8	10.6	1.4	11.4	2.7	0.48	26.7	33.1
			0.12	9.04	10.6	1.5	13.6	3.1	0.15	29.0	30.5

The depth profiles of Ni consumption and ΣCAT data both show consistent trends (Fig. 4.5-1). The values for ΣCAT in the Opalinus Clay are within a range of 79 – 128 meq/kg_{rock}. The samples in the underlying Staffelegg Formation and the overlying 'Brauner Dogger' exhibit a wider range. The sample from the Wildegge Formation and the two samples from the Schinznach Formation, reflecting the top and bottom of the profile, display low values. The CEC data shows a clear positive correlation with the clay-mineral content ($R^2 = 0.8782$; Fig. 4.5-2), and an even slightly better correlation with the content of the smectite end-member ($R^2 = 0.8926$; see Section 4.1 for definition), even though the smectite content is much lower. This is explained by the very high CEC of smectite compared to illite and the other clay minerals.

Na is the main extracted cation in all samples, except in the sample in the 'Herrenwis Unit' (reef facies) where Ca is slightly higher than Na, and in one sample in the Staffelegg Formation in which the concentrations of Na and Ca are similar. Thus, the Ca/Na ratio (eq/eq) is generally below 1 and shows little variation (0.6 – 0.7) with depth over most of the profile (Fig. 4.5-3). The two samples mentioned above stand out and display higher ratios. Both these samples are clay-poor and have a low CEC, so the dissolution of calcite may play a larger relative role in these samples and lead to the higher Ca/Na ratios. Over the whole profile, the Mg/Na ratio displays a similar behaviour and consequently the (Ca+Mg)/Na ratio as well (Fig. 4.5-3) follows the same trend as the Ca/Na ratio. The K/Na and Sr/Na ratios vary in the range of 0.08-0.1 and 0.008-0.011, respectively, for most of the samples.

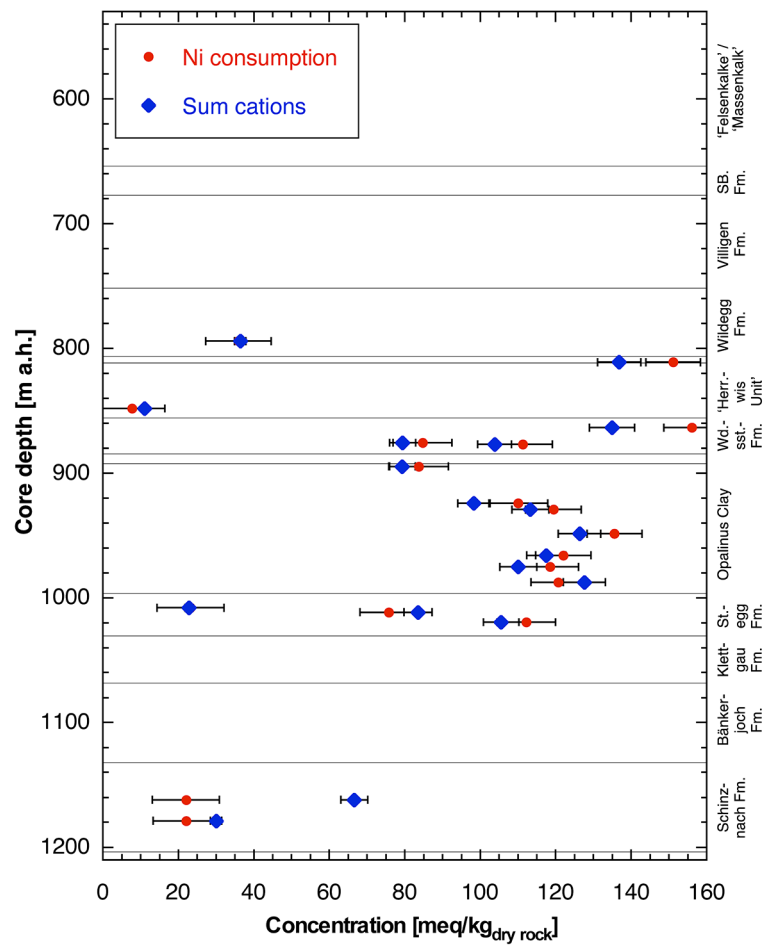


Fig. 4.5-1: Depth profile of Ni consumption and sum of cations (uncorrected)

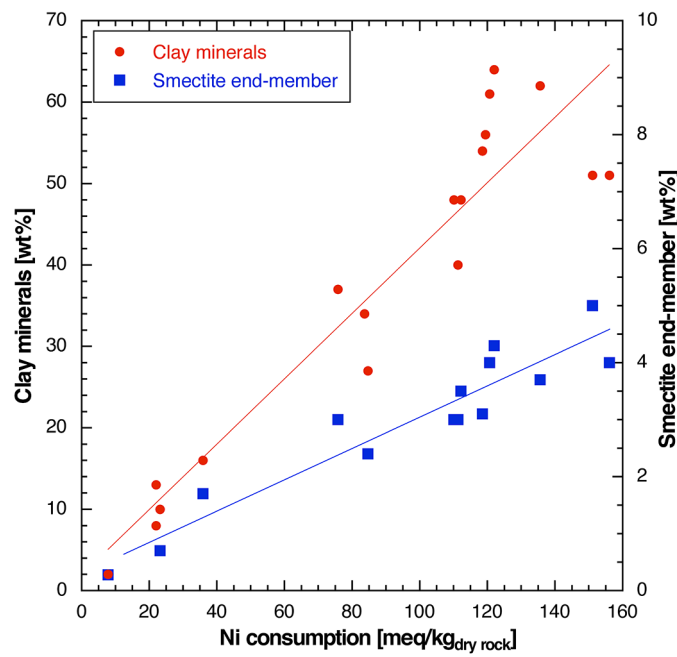


Fig. 4.5-2: Ni consumption vs. clay-mineral content and content of the smectite end-member

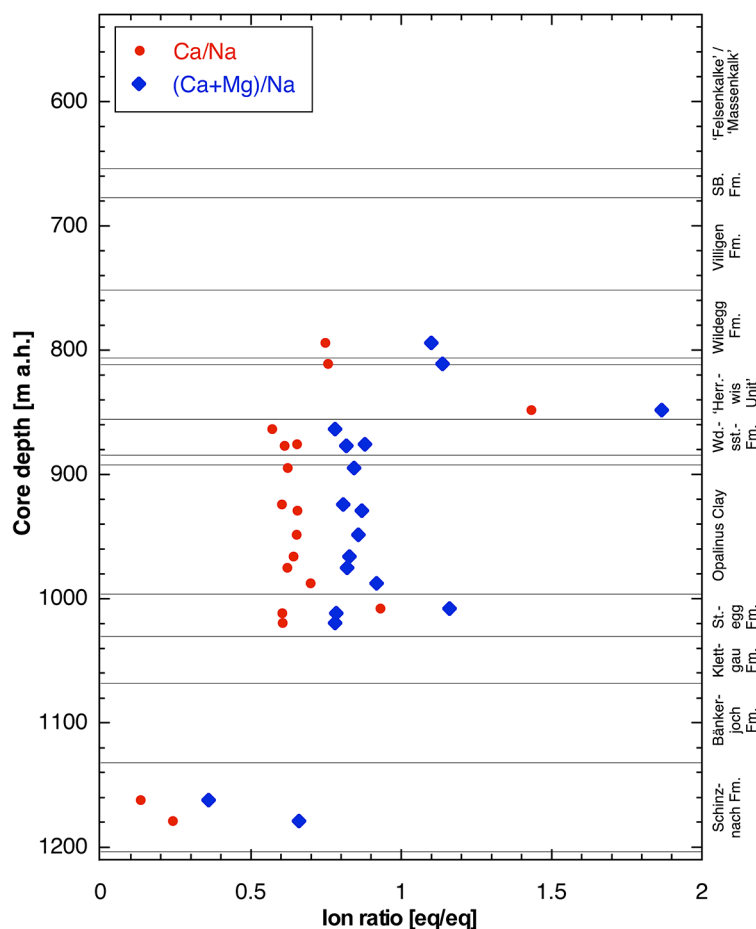


Fig. 4.5-3: Depth profiles of Ca/Na and (Ca+Mg)/Na ratios in Ni-en extracts

Speciation calculations on the Ni-en extracts were carried out with the PHREEQC Version 3 code (Parkhurst & Appelo 2013) and the PSI/Nagra thermodynamic database (Thoenen et al. 2014) assuming a temperature of 25 °C. The ethylene diamine complexes were taken from the MINTEC database (Allison et al. 1991) and included in the calculations. The concentration of ethylene diamine in the extracts, which was not analysed, was constrained by charge balance. The dissolved carbonate concentration (not measured) was constrained by assuming calcite equilibrium. The calculated partial pressures of CO₂ (pCO₂) and saturation indices for selected minerals are depicted in Tab. 4.5-4. The Ni-en extracts are clearly undersaturated with regard the carbonate minerals dolomite, strontianite and siderite. They are also undersaturated with regard to the sulphate minerals gypsum and celestite, but close to saturation or oversaturated with regard to barite.

Tab. 4.5-4: Saturation indices of selected minerals and log (pCO₂) for Ni-en extract solutions
Calcite saturation was assumed.

Type	Depth [m]	Formation	pH ^a	log pCO ₂ [log bar]	Gypsum	Celestite	Barite	Calcite	Dolomite (ord)	Dolomite (dis)	Strontianite	Siderite
PW	794.13	Wildeggen Fm.	8.34	-4.22	-1.65	-1.54	-0.37	0	-0.20	-0.75	-1.16	-2.26
AD	811.12	'Park.-Württ.-Sch.'	8.42	-4.04	-2.21	-1.94	-0.02	0	-0.38	-0.93	-1.00	
PW	848.18	'Herrenwis Unit'	8.36	-4.59	-1.40	-1.21	0.31	0	-0.33	-0.88	-1.08	-2.89
AD	863.66	Wedelsandstein Fm.	8.30	-4.46	-1.37	-1.24	0.32	0	-0.32	-0.87	-1.14	-2.01
PW	875.69	Wedelsandstein Fm.	8.31	-4.64	-1.30	-1.06	0.61	0	-0.36	-0.91	-1.03	-1.70
AD	877.03	Wedelsandstein Fm.	8.33	-4.73	-1.26	-1.03	0.53	0	-0.37	-0.92	-1.04	-1.80
PW	894.68	Opalinus Clay	8.32	-4.69	-1.26	-1.05	0.45	0	-0.41	-0.96	-1.05	
AD	924.18	Opalinus Clay	8.28	-4.56	-1.33	-1.05	0.82	0	-0.36	-0.91	-0.99	-2.61
PW	929.23	Opalinus Clay	8.36	-4.16	-1.88	-1.90	0.11	0	-0.49	-1.04	-1.28	
PW	948.58	Opalinus Clay	8.28	-4.55	-1.39	-1.17	0.30	0	-0.41	-0.96	-1.05	
PW	965.98	Opalinus Clay	8.51	-4.29	-1.78	-2.65	0.45	0	0.36	-0.19	-2.14	
PW	975.25	Opalinus Clay	8.43	-3.96	-2.23	-2.81	0.35	0	0.38	-0.17	-1.85	
AD	987.55	Opalinus Clay	8.34	-4.78	-1.14	-0.91	0.11	0	-0.17	-0.72	-1.04	-3.18
PW	1'008.04	Staffelegg Fm.	8.33	-4.72	-1.25	-1.02	0.29	0	-0.31	-0.86	-1.05	-2.76
AD	1'011.62	Staffelegg Fm.	8.41	-4.79	-1.25	-1.05	0.35	0	-0.35	-0.90	-1.07	-2.63
PW	1'019.49	Staffelegg Fm.	8.34	-4.62	-1.33	-1.06	0.66	0	-0.34	-0.89	-1.00	-3.36
PW	1'161.83	Schinzach Fm.	8.29	-4.67	-1.21	-1.00	0.64	0	-0.38	-0.93	-1.06	-2.78
PW	1'178.88	Schinzach Fm.	8.35	-4.58	-1.46	-1.16	0.83	0	-0.39	-0.94	-0.97	

^a input data based on measurements

4.6 Data from squeezing experiments

Martin Mazurek

A set of 13 samples were subjected to porewater squeezing. The mineralogical composition of the samples is listed in Tab. 4.6-1. In the Malm, lithologies are predominantly clay-poor, and the same is the case for the sample from the Wedelsandstein Formation. Clay-mineral contents are substantially higher in the Opalinus Clay and decrease somewhat in the Staffelegg Formation.

Tab. 4.6-1: Mineralogical composition of samples subjected to squeezing experiments

tr = trace, empty field = mineral not identified.

Depth [m]	Formation	Member / Sub-unit	S [wt.-%]	C(inorg) [wt.-%]	C(org) [wt.-%]	Quartz [wt.-%]	K-feldspar [wt.-%]	Plagioclase [wt.-%]	Calcite [wt.-%]	Dolomite / Ank. [wt.-%]	Siderite [wt.-%]	Pyrite [wt.-%]	Clay minerals [wt.-%]
681.94	Villigen Fm.		No mineralogical analysis										6*
743.65	Villigen Fm.		No mineralogical analysis										9*
777.30	Wildegge Fm.	Effingen Mb.	0.04	8.72	0.34	5	3		69	3		0.1	20
804.57	Wildegge Fm.	Effingen Mb.	0.10	6.62	0.45	10	4	tr	55	tr		0.2	31
858.34	Wedelsandstein Fm.		0.69	3.46	0.39	36	6	3	29	tr		1.3	24
886.60	'Murchisonae-Oolith Fm.'		0.65	0.16	0.84	28	5	3	1		1	1.2	60
909.46	Opalinus Clay	With silty calcareous beds	0.59	0.78	1.08	23	6	4	5		2	1.1	59
924.36	Opalinus Clay	Upper silty	0.22	1.61	0.79	33	6	3	11		3	0.4	43
950.43	Opalinus Clay	Mixed clay-silt-carbonate	0.08	1.07	1.02	20	5	3	6		4	0.2	61
972.72	Opalinus Clay	Mixed clay-silt-carbonate	0.28	1.41	0.84	26	6	3	10		2	0.5	51
990.66	Opalinus Clay	Clay-rich	0.24	1.11	0.94	17	5	3	7		3	0.4	63
1'011.44	Staffelegg Fm.	Frick Mb.	0.37	1.41	0.67	40	5	3	10	2		0.7	39
1'019.27	Staffelegg Fm.	Frick Mb.	0.29	1.13	0.79	37	5	3	6	2	2	0.5	44

* Based on the evaluation of geophysical borehole and core logs (c.f. Dossier VI).

4.6.1 Mass recovery

The water masses obtained by squeezing are listed in Tab. 4.6-2 and shown graphically in Fig. 4.6-1 as a function of the squeezing pressure. The total mass recovery correlates with the initial water content of the sample (Fig. 4.6-2). The latter was measured at CRIEPI on the cut-off materials adjacent to the squeezed rock pieces. Given the low clay and therefore water contents, no water was recovered from the uppermost two samples (Villigen Formation), and high pressures were needed to obtain limited amounts of water from samples of the Wildegge Formation and the Wedelsandstein Formation. Samples from the Opalinus Clay yielded sufficient water for analysis at minimum pressures of 200 – 400 MPa, whereas recoveries were low in the Staffelegg Formation.

Tab. 4.6-2: Water mass squeezed at different pressure steps

Pressure step 500(2) refers to an extended period (2 – 6 d) of squeezing at 500 MPa for samples that yielded no or only small amounts of water in the preceding steps. CR: CRIEPI; pw: porewater.

Depth [m]	Formation	Initial sample mass (CR) [g]	Initial wet water content (CR) [wt.-%]	Mass of pw prior to squeezing [g]	Mass squeezed at P =							Total mass squeezed [g]
					100 MPa [g]	150 MPa [g]	200 MPa [g]	300 MPa [g]	400 MPa [g]	500 MPa [g]	500(2) MPa [g]	
681.94	Villigen Fm.	426.70	1.51	6.44			0	0	0	0	0	0
743.65	Villigen Fm.	433.54	1.56	6.76			0	0	0	0	0	0
777.30	Wildeggen Fm.	434.50	2.46	10.69			0	0	0	0	0.07	0.07
804.57	Wildeggen Fm.	474.85	2.80	13.30	0	0	0	0	0.36	0.95	0.20	1.51
858.34	Wedelsandstein Fm.	468.50	4.22	19.77	0	0	0	0.03	0.20	0.48	0.25	0.96
886.60	'Murchisonae-Oolith Fm.'	460.43	4.70	21.64			2.57	1.76	1.21	1.07		7.96
909.46	Opalinus Clay	427.23	4.77	20.38			0.33	1.70	0.85	1.05		3.93
924.36	Opalinus Clay	402.51	3.96	15.94			0	0.22	0.45	0.97		1.64
950.43	Opalinus Clay	417.51	4.71	19.66			0.72	1.60	1.21	1.27		4.80
972.72	Opalinus Clay	460.25	3.68	16.94	0	0	0	0.74	0.75	0.95		2.44
990.66	Opalinus Clay	415.17	4.51	18.72	0	0.17	0.65	1.52	0.97	1.09		4.40
1'011.44	Staffelegg Fm.	398.59	2.97	11.84	0	0	0	0	0.04	0	0.29	0.33
1'019.27	Staffelegg Fm.	386.22	3.68	14.21	0	0	0	0	0.28	0	0.81	1.09

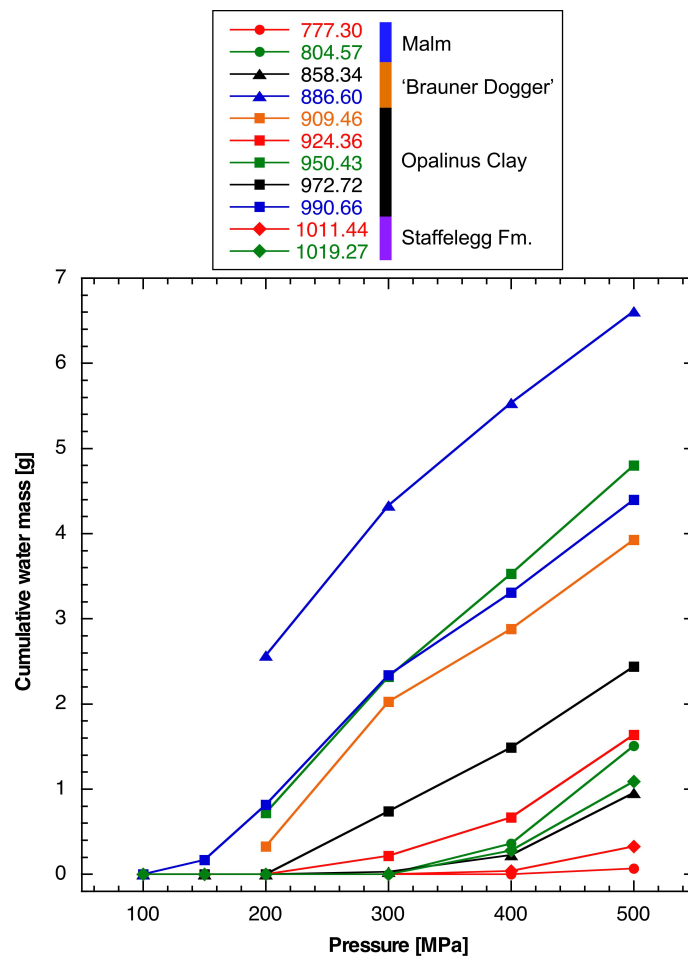


Fig. 4.6-1: Cumulative water mass obtained by squeezing as a function of the squeezing pressure

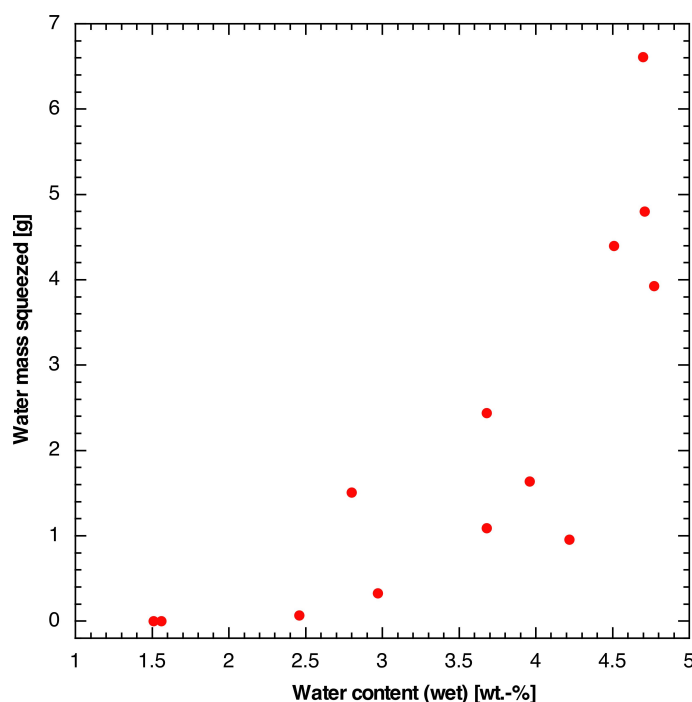


Fig. 4.6-2: Correlation of the original water content and total water mass obtained by squeezing

4.6.2 Chemical composition of squeezed waters

Major-ion compositions of squeezed waters are listed in Tab. 4.6-3 and shown graphically as a function of squeezing pressure in Fig. 4.6-3. All waters are dominated by Na^+ and Cl^- . The concentrations of monovalent ions (Na^+ , K^+ , Cl^- , Br^- , NO_3^-) generally decrease with squeezing pressure, likely due to ion-filtration effects that become important at higher pressures (Mazurek et al. 2015). Ca^{2+} , Mg^{2+} and Sr^{2+} remain constant with pressure or increase slightly, which is considered to be due to the dissolution of carbonate minerals that becomes important at higher pressures. In general, SO_4^{2-} concentrations do not vary substantially with pressure. As discussed in Mazurek et al. (2015) and Rufer & Mazurek (2018), the composition of the first water aliquot recovered from a sample is considered to be closest to that of the porewater, and these analyses are highlighted by bold print in Tab. 4.6-3. For clarity, the subset of the data that is considered to be useful for further interpretation is summarised in Tab. 4.6-4. For sample 1'019.27, the aliquot obtained at 500 MPa is preferred over that at 400 MPa because the squeezed mass is larger, and the analysis is therefore more complete. Note that the higher the pressure, the more strongly expressed artefacts, such as ion filtration or mineral dissolution, may become (Mazurek et al. 2015).

In the clay-rich samples 886.60 and 950.43, the concentrations of some ions in the first aliquot (obtained at 200 MPa), in particular of Na^+ and Cl^- , are below those in the aliquot squeezed at 300 MPa, which is unusual and not straightforward to explain. Beyond the maximum values reached at 300 MPa, Na^+ and Cl^- concentrations follow the usual decreasing trend with pressure (Fig. 4.6-3). It is unclear at this stage what causes the unexpected behaviour at the lowest pressure step, and the results obtained from these samples are considered uncertain.

Tab. 4.6-3: Chemical composition of squeezed waters: full data set

Bold print indicates the selected ("best") aliquots. Italics refer to semi-quantitative analyses. F⁻ concentrations, in particular in the first squeezed aliquots, are contaminated by F⁻ leached from the fiberglass filters and so are not representative of the porewater. Pressure step 500(2) refers to an extended period of squeezing at 500 MPa for samples that yielded no or only small amounts of water in the preceding steps.

Depth [m]	Formation	Pressure [MPa]	Squeezing time [d]	Mass squeezed [g]	Na ⁺ [mg/L]	NH ₄ ⁺ [mg/L]	K ⁺ [mg/L]	Ca ²⁺ [mg/L]	Mg ²⁺ [mg/L]	Sr ²⁺ [mg/L]	Ba ²⁺ [mg/L]	F ⁻ [mg/L]	Cl ⁻ [mg/L]	Br ⁻ [mg/L]	NO ₃ ⁻ [mg/L]	SO ₄ ²⁻ [mg/L]	pH	TIC [mg/L]	TOC [mg/L]	TDS [mg/L]	Charge balance [%]	
777.30	Wildegge Fm.	500 (2)	2	0.07	5'294	<10	123.9	969	251			14.0	8'158	22.4	27.52	2'224				17'083	4.3	
804.57	Wildegge Fm.	400	2	0.36	4'958	<10	106.3	1'082	292			13.3	7'957	21.1	5.72	2'682				17'117	2.7	
		500	2	0.95	4'594	<10	83.5	1'157	312	17.3	<0.5	7.0	7'760	20.6	3.33	2'709	8.24	11.3	251.2	16'926	1.6	
		500 (2)	3	0.20	4'506	<10	77.5	1'258	317			5.8	7'258	19.2	2.46	2'604	8.01			16'048	5.1	
858.34	Wedelsand- stein Fm.	400	2	0.20	6'389	<10	87.1	1'471	261	19.6	<0.5	10.4	11'063	19.9	5.65	2'970	7.34			22'297	0.1	
		500	2	0.48	6'544	<10	87.3	1'443	288	23.7	<0.5	7.4	10'933	20.2	3.88	2'844	7.94			22'196	2.0	
		500 (2)	3	0.25	7'584	<10	102.8	1'413	246	19.6	<0.5	6.1	11'936	21.8	3.41	3'117	7.88			24450	2.6	
886.60	'Murchisonae- oolith Fm.'	200	3	3.92	5'486	<10	60.2	1'157	312	18.1	<0.5	8.1	9'078	15.1	7.97	2'685	8.37	14.6	234.7	19'076	1.6	
		300	3	1.76	5'754	<10	43.7	1'182	307	18.9	<0.5	4.0	9'359	15.8	3.82	2'640	8.34	10.4	181.6	19'520	2.4	
		400	2	1.21	4'980	<10	29.7	1'240	313	18.1	<0.5	3.9	8'522	14.1	2.80	2'559	8.39	9.3	159.2	17'852	1.8	
		500	2	1.07	4'578	<10	23.1	1'245	314	17.9	<0.5	3.4	7'974	13.2	2.00	2'465	8.32	11.6	145.3	16'793	1.9	
		200	3	0.33														8.07				
909.46	Opalinus Clay	300	3	1.70	6'815	<10	64.0	1'246	312	23.2	<0.5	5.2	11'464	18.8	4.81	2'429	8.48	11.8	201.8	22'597	1.4	
		400	2	0.85	5'342	<10	35.2	1'287	330	21.8	<0.5	3.8	9'379	15.3	<1.6	2'276	8.56	<10	144.4	18'841	1.9	
		500	2	1.05	4'415	<10	24.5	1'337	334	21.4	<0.5	3.6	8'183	13.3	1.71	2'139	8.77	<10	123.3	16'605	2.0	
924.36	Opalinus Clay	300	2	0.22	7'095	<10	109.6	996	184	18.1	<0.5	10.8	11'413	18.7	7.76	1'736	8.26			21'589	2.4	
		400	2	0.45	6'465	<10	83.6	1'333	278			7.1	10'498	17.1	6.07	2'146	8.33			20'835	4.5	
950.43	Opalinus Clay	500	3	0.97	6'257	<10	69.6	1'259	284	22.8	<0.5	6.5	10'479	17.2	5.78	2'298	8.32			20'700	2.4	
		200	3	0.72	5'589	<10	74.1	1'157	276	21.3	<0.5	10.8	9'408	15.0	4.93	1'668	8.25			18'224	4.0	
		300	2	1.60	5'796	<10	50.8	1'239	302	25.1	<0.5	5.2	9'959	16.1	2.82	1'932	8.34	11.8	185.6	19'526	2.7	
		400	2	1.21	4'628	<10	30.3	1'268	312	26.3	<0.5	4.0	8'988	13.7	2.11	2'126	8.39	<10	157.8	17'564	-1.3	
		500	3	1.27	3'900	<10	21.5	1'388	339	26.4	<0.5	3.5	7'657	12.1	<1.6	1'809	8.46	<10	143.3	15'309	2.4	
972.72	Opalinus Clay	300	4	0.74	6'830	<10	78.1	1'371	248	25.8	<2.5	7.1	11'181	17.4	8.25	2'207		28.5	269.1	22'272	3.2	
		400	2	0.75	6'330	<10	57.7	1'355	254	27.0	<2.5	5.0	10'755	16.6	5.85	2'213		19.3	291.0	21'329	2.0	
990.66	Opalinus Clay	200	2	0.65	6'709	<10	71.6	1'444	290	29.8	<2.5	5.9	11'315	17.7	5.29	2'225	8.10	36.1	278.7	22'429	2.8	
		300	4	1.52	5'634	<10	49.2	1'379	283	27.6	<2.5	5.0	9'851	15.2	3.70	2'132	8.35	26.6	234.2	19'640	2.1	
		400	2	0.97	4'556	<10	28.4	1'424	292	25.9	<2.5	4.3	8'423	12.6	2.90	2'036	7.97	30.7	179.3	17'016	2.0	
1'011.44	Staffellegg Fm.	500 (2)	3	0.29	6'569	<10	70.1	1'444	271	21.2		11.2	11'000	16.5	5.67	2'440				21'848	2.7	
1'019.27	Staffellegg Fm.	400	4	0.28	6'593	<10	76.8	1'276	198	23.6		11.1	11'029	15.9	7.34	2'119				21'350	1.8	
		500 (2)	3	0.81	6'970	<10	83.0	1'237	205	23.5	<2.5	9.2	11'571	17.4	5.64	2'142		8.24	44.3	206.2	22'515	1.2

Tab. 4.6-4: Chemical composition of squeezed waters: summary of selected analyses to be used for interpretation

Data for samples 886.60 and 950.43 m are less certain and therefore listed in *italics*. Values in brackets refer to semi-quantitative analyses.

Depth [m]	Formation	Pressure [MPa]	Na ⁺ [mg/L]	NH ₄ ⁺ [mg/L]	K ⁺ [mg/L]	Ca ²⁺ [mg/L]	Mg ²⁺ [mg/L]	Str ²⁺ [mg/L]	Ba ²⁺ [mg/L]	Cl ⁻ [mg/L]	Br ⁻ [mg/L]	NO ₃ ⁻ [mg/L]	SO ₄ ²⁻ [mg/L]	pH	TIC [mg/L]	TOC [mg/L]
777.30	Wildegge Fm.	500 (2)	5'294	< 10	123.9	969	251			8'158	22.4	27.52	2'224			
804.57	Wildegge Fm.	400	4'958	< 10	106.3	1'082	292			7'957	21.1	5.72	2'682			
858.34	Wedelsandstein Fm.	400	6'389	< 10	87.1	1'471	261	19.6	< 0.5	11'063	19.9	5.65	2'970	7.34		
886.60	'Murchisonae-Oolith Fm.'	200	<i>5'486</i>	<i>< 10</i>	<i>60.2</i>	<i>1'157</i>	<i>312</i>	<i>18.1</i>	<i>< 0.5</i>	<i>9'078</i>	<i>15.1</i>	<i>7.97</i>	<i>2'685</i>	<i>8.37</i>	<i>14.6</i>	<i>234.7</i>
909.46	Opalinus Clay	300	6'815	< 10	64.0	1'246	312	23.2	< 0.5	11'464	18.8	4.81	2'429	8.48	11.8	201.8
924.36	Opalinus Clay	300	7'095	< 10	109.6	996	184	18.1	< 0.5	11'413	18.7	7.76	1'736	8.26		
950.43	Opalinus Clay	200	<i>5'589</i>	<i>< 10</i>	<i>74.1</i>	<i>1'157</i>	<i>276</i>	<i>21.3</i>	<i>< 0.5</i>	<i>9'408</i>	<i>15.0</i>	<i>4.93</i>	<i>1'668</i>	<i>8.25</i>		
972.72	Opalinus Clay	300	6'830	< 10	78.1	1'371	248	25.8	< 2.5	11'181	17.4	8.25	2'207		28.5	269.1
990.66	Opalinus Clay	200	6'709	< 10	71.6	1'444	290	29.8	< 2.5	11'315	17.7	5.29	2'225	8.10	(36.1)	278.7
1'011.44	Staffelegg Fm.	500 (2)	6'569	< 10	70.1	1'444	271	21.2		11'000	16.5	5.67	2'440			
1'019.27	Staffelegg Fm.	500 (2)	6'970	< 10	83.0	1'237	205	23.5	< 2.5	11'571	17.4	5.64	2'142	8.24	(44.3)	206.2

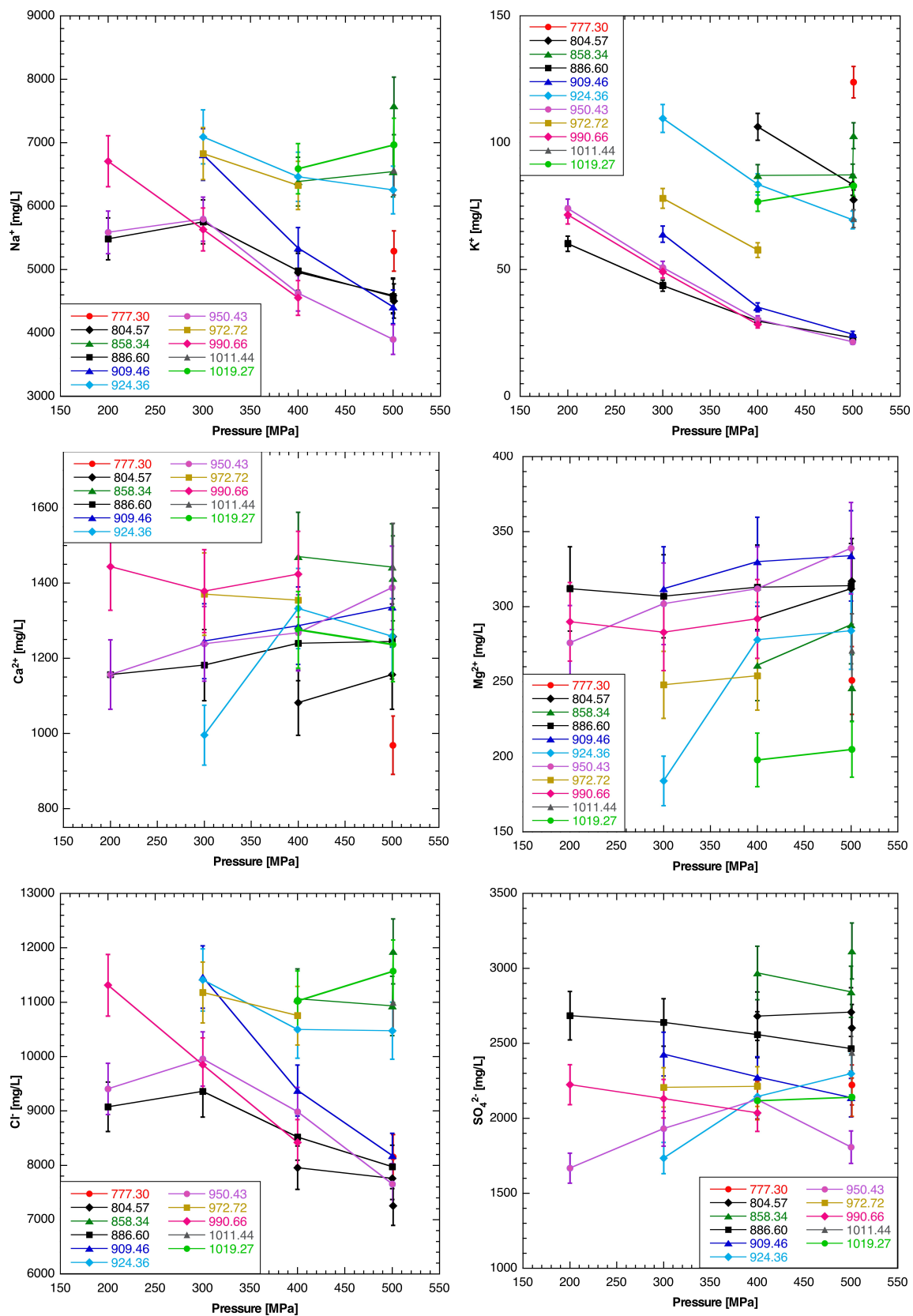


Fig. 4.6-3: Ion concentrations in squeezed waters as a function of squeezing pressure

Bars indicate analytical errors of ion-chromatography analysis.

4.6.3 Depth trends

Considering only the selected aliquots of each sample (Tab. 4.6-4), depth trends are illustrated in Fig. 4.6-4.

- Na^+ and Cl^- show a marked increase from the Wildegg Formation to the base of the 'Brauner Dogger' and then remain constant in the Opalinus Clay and the Staffelegg Formation.
- K^+ decreases from the Wildegg Formation to the base of the 'Brauner Dogger' and then remains constant in the Opalinus Clay and the Staffelegg Formation.
- Ca^{2+} , Mg^{2+} , Sr^{2+} and SO_4^{2-} show some variability but no systematic depth trends.
- Br^- shows a limited decrease with depth in the Malm and in the 'Brauner Dogger'.
- The molar ratio Br^-/Cl^- shows a substantial decrease with depth in the Malm and in the 'Brauner Dogger' and a weaker but systematic decrease in the Opalinus Clay and in the Staffelegg Formation. Nevertheless, even the highest ratios in the Malm are well below the modern seawater range of $1.52 \times 10^{-3} - 1.60 \times 10^{-3}$.
- The molar ratio $\text{SO}_4^{2-}/\text{Cl}^-$ shows a decrease with depth over the entire studied profile. All values are higher than that of modern seawater (about 0.0515).
- Overall, both ion concentrations and ion ratios show some systematic variations in the section Malm – 'Brauner Dogger' but less variability in the underlying Opalinus Clay and Staffelegg Formation.

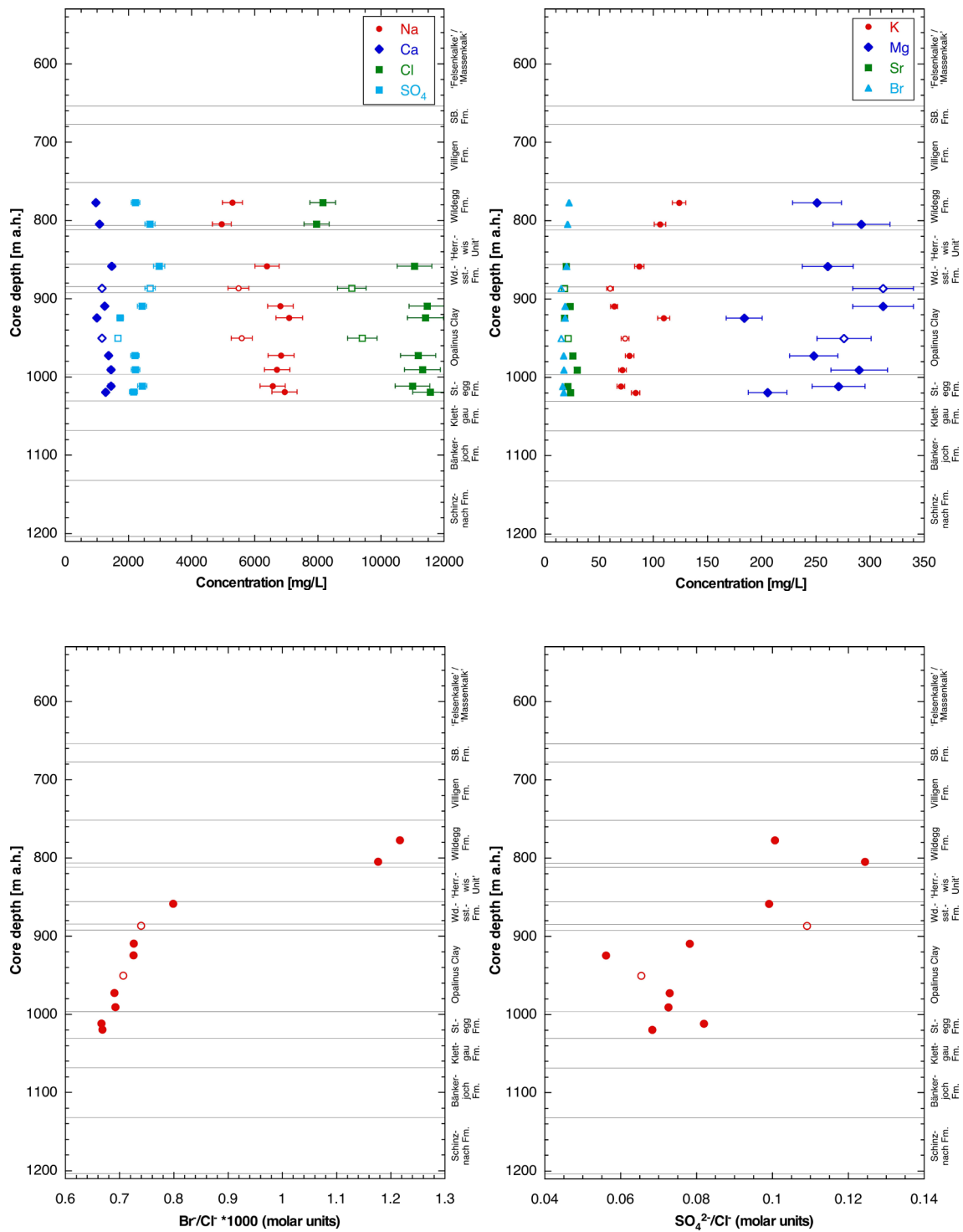


Fig. 4.6-4: Depth trends of ion concentrations and ion ratios in squeezed waters

Only the selected aliquots are shown for each sample. Open symbols indicate samples with uncertain data. Bars indicate analytical errors of ion-chromatography analysis.

4.6.4 Geochemical modelling and mineral saturation states

Mineral saturation indices for squeezed waters were calculated using PHREEQC Version 3 and the PSI/Nagra thermodynamic data base (Thoenen et al. 2014) and are shown in Tab. 4.6-5.

- Calcite and dolomite are strongly oversaturated, a feature already known from previous studies (e.g. Mazurek et al. 2015). The oversaturation is possibly due to the fact that mineral solubility at high pressures during squeezing is higher than at atmospheric pressure. Further, outgassing of CO₂ during the squeezing process increases the pH and the saturation indices of calcite and dolomite (Tournassat et al. 2015). The comparatively low calculated P(CO₂) suggest that some outgassing may have taken place, which also affects pH. However, this nevertheless does not markedly affect the obtained major-ion composition due to the large buffering capacity of the rock-water system in clay-rich lithologies. Last, lattice defects in carbonate minerals induced by deformation during squeezing might increase the solubility of these minerals. On the other hand, outgassing during sample storage in glass vessels is not considered to contribute to outgassing. Such a process should also be seen by higher δ values of water isotopes, which is not the case (see Section 5.8).
- Strontianite is undersaturated, except for the deep samples 990.66 and 1'019.27 where it is slightly oversaturated.
- Gypsum is close to saturation for all waters. This is a new finding, given the fact that gypsum was undersaturated in squeezed waters from the Schlattingen-1 borehole (Mazurek et al. 2015) as well as in seepage waters in the Opalinus Clay from the Mont Terri Rock Laboratory (Pearson et al. 2003). In some of the waters, suspended solid material was identified. An attempt was made to identify the nature of this material under the SEM. Apart from quartz and some clay minerals that passed through the filters, calcite, halite and rarely a Ca sulphate were identified. It is evident that halite precipitated from solution upon drying (for the SEM study, drops of the squeezed waters were evaporated on glass mounts, and then the solid residues were studied). For calcite and for the Ca sulphate, the results are ambiguous. A more elaborated and demanding technique would be required to separate suspended material from the liquid prior to SEM analysis.
- Celestite is at saturation, consistent with previous experience.
- Using the data from Tab. 4.6-3, fluorite is strongly oversaturated, which is a consequence of the contamination of F⁻ concentrations by the filter material. Therefore, no F⁻ data are listed in Tab. 4.6-4.

Tab. 4.6-5: Mineral saturation indices for squeezed waters

Bold print indicates the selected ("best") aliquots.

Depth [m]	Formation	Pressure [MPa]	pH	TIC [M]	Log(P _{CO2})	SI Calcite	SI Dolomite (ordered)	SI Dolomite (disordered)	SI Strontianite	SI Gypsum	SI Anhydrite	SI Celestite	SI Fluorite
777.30	Wildegge Fm.	500 (2)								-0.09	-0.31		1.63
804.57	Wildegge Fm.	400 500 500 (2)	8.24 8.01	9.57×10^{-4}	-3.69	0.94	1.65	1.10	-0.43	0.02 0.05 0.06	-0.20 -0.17 -0.15	-0.06	1.61 1.07 0.94
858.34	Wedelsandstein Fm.	400 500 500 (2)	7.34 7.94 7.88							0.15 0.12 0.14	-0.07 -0.10 -0.07	-0.01 0.06 0.01	1.51 1.20 1.03
886.60	'Murchisonae-Oolith Fm.'	200 300 400 500	8.37 8.34 8.39 8.32	1.24×10^{-3} 8.83×10^{-4} 7.88×10^{-4} 9.82×10^{-4}	-3.73 -3.84 -3.95 -3.77	1.17 1.00 1.02 1.06	2.10 1.75 1.78 1.86	1.55 1.20 1.23 1.31	-0.18 -0.34 -0.36 -0.33	0.03 0.03 0.04 0.04	-0.19 -0.19 -0.17 -0.18	-0.06 -0.05 -0.07 -0.09	1.19 0.59 0.59 0.48
909.46	Opalinus Clay	300 400 500	8.48 8.56 8.77	1.00×10^{-3}	-3.96	1.20	2.13	1.58	-0.08	0.00 0.00 0.01	-0.21 -0.21 -0.21	-0.01 -0.05 -0.07	0.83 0.58 0.55
924.36	Opalinus Clay	300 400 500	8.26 8.33 8.32							-0.20 -0.02 -0.01	-0.41 -0.23 -0.22	-0.22 -0.03	1.44 1.15 1.05
950.43	Opalinus Clay	200 300 400 500	8.25 8.34 8.39 8.46	1.00×10^{-3}	-3.80	1.10	1.91	1.36	-0.15	-0.15 -0.08 -0.02 -0.04	-0.37 -0.29 -0.23 -0.26	-0.17 -0.05 0.02 -0.04	1.47 0.85 0.63 0.55
972.72	Opalinus Clay	300 400		2.43×10^{-3} 1.64×10^{-3}	-3.05 -3.22					0.00 0.00	-0.21 -0.21	0.00 0.03	1.17 0.86
990.66	Opalinus Clay	200 300 400	8.10 8.35 7.97	3.07×10^{-3} 2.26×10^{-3} 2.60×10^{-3}	-3.06 -3.46 -2.98	1.41 1.49 1.23	2.46 2.63 2.10	1.91 2.08 1.55	0.18 0.25 -0.06	0.02 0.00 0.01	-0.19 -0.21 -0.21	0.06 0.02 -0.01	1.01 0.86 0.75
1'011.44	Staffelegg Fm.	500 (2)								0.06	-0.15	-0.05	1.58
1'019.27	Staffelegg Fm.	400 500 (2)	8.24	3.77×10^{-3}	-3.11	1.57	2.70	2.15	0.30	-0.03 -0.04	-0.24 -0.26	-0.04 -0.04	1.55 1.37

4.6.5 Water content and aqueous extraction of squeezed core material

After the squeezing experiment, each core was dried at 105 °C, from which the mass of water remaining in the sample was obtained. The dry core was then subjected to aqueous extraction, from which the mass of Cl⁻ remaining in the sample could be calculated. The results are summarised in Tab. 4.6-6. Given the fact that oven-drying was performed with air, some degree of rock oxidation occurred. Therefore, results are only given for the conservative constituents Cl⁻ and Br⁻.

Tab. 4.6-6: Water contents and results of aqueous-extraction tests on previously squeezed samples

Depth [m]	Formation	Water content (wet) of squeezed sample [wt.-%]	Aqueous extraction of squeezed sample				
			Mass of dry rock [g]	Mass of added water [g]	S/L [g/g]	Cl ⁻ [mg/L _{extract solution}]	Br ⁻ [mg/L _{extract solution}]
777.30	Wildegge Fm.	2.24	30.20	29.98	1.007	110	0.24
804.57	Wildegge Fm.	2.73	30.12	29.96	1.005	109	0.21
858.34	Wedelsandstein Fm.	2.61	30.10	29.96	1.005	146	< 0.16
886.60	'Murchisonae-Oolith Fm.'	3.81	30.16	29.95	1.007	181	< 0.16
909.46	Opalinus Clay	3.65	30.01	29.97	1.002	189	0.20
924.36	Opalinus Clay	2.91	30.10	29.97	1.005	159	< 0.16
950.43	Opalinus Clay	3.58	30.04	29.97	1.002	163	< 0.16
972.72	Opalinus Clay	2.88	30.08	29.96	1.004	131	< 0.16
990.66	Opalinus Clay	3.45	30.07	29.95	1.004	159	0.16
1'011.44	Staffelegg Fm.	3.11	30.02	29.94	1.003	216	0.24
1'019.27	Staffelegg Fm.	3.26	30.06	29.95	1.004	192	0.19

4.6.6 Chloride-accessible porosity

Combining the data for squeezed waters (Tab. 4.6-3) and for the samples after squeezing (Tab. 4.6-6) permits the reconstruction of the total Cl⁻ and water inventories, therefore also the Cl⁻ concentrations in the bulk porewater. Assuming that the squeezed water represents the composition of the anion-accessible water, the Cl⁻-accessible porosity fraction f_{Cl} can be calculated. The formalism is as follows (m = mass, C = concentration, V = volume, S/L = solid/liquid ratio used for extraction):

Mass of Cl⁻ squeezed:

$$m_{Cl \text{ squeezed}} = V_{\text{pore water squeezed}} C_{Cl \text{ in squeezed pore water}}$$

Mass of Cl^- remaining in core after squeezing (obtained by aqueous extraction):

$$C_{\text{Cl extracted}} = \frac{m_{\text{Cl extracted}}}{V_{\text{water added}}}$$

$$S/L = \frac{m_{\text{dry rock}}}{V_{\text{water added}}}$$

Therefore:

$$m_{\text{Cl extracted}} = C_{\text{Cl extracted}} \frac{m_{\text{dry rock}}}{S/L}$$

Using the calculated Cl^- masses yields

$$C_{\text{Cl in bulk pore water}} = \frac{m_{\text{Cl squeezed}} + m_{\text{Cl extracted}}}{V_{\text{pore water squeezed}} + V_{\text{water remaining}}}$$

The volume of the water remaining in the sample after squeezing is obtained from the water content of the squeezed core, assuming a porewater density of 1 g/cm^3 . Note that this equation also assumes that the dead volume of the squeezing system is negligible. While the dead volume is indeed likely small, a sensitivity calculation was performed on its impact. Assuming a dead volume of 1 mL results in an anion-accessible porosity fraction that is 0.01 – 0.04 higher than the value without consideration of a dead volume. The most strongly expressed shift is found in samples where only a small water volume was squeezed, while it becomes insignificant for samples with a good water yield.

The Cl^- -accessible porosity fraction is finally obtained from:

$$f_{\text{Cl}} = \frac{C_{\text{Cl in bulk pore water}}}{C_{\text{Cl in squeezed water}}}$$

The resulting Cl^- -accessible porosity fractions are listed in Tab. 4.6-7 and shown as a function of the clay-mineral content in Fig. 4.6-5. Excluding samples 886.60 and 950.43, for which the composition of the squeezed water is considered uncertain, the mean value for f_{Cl} is 0.52. It is in line with previous data from Mont Terri (Pearson et al. 2003) and Schlattingen-1 (Mazurek et al. 2015).

Tab. 4.6-7: Anion-accessible porosity fractions derived from squeezing and aqueous-extraction experiments

Data for samples 886.60 and 950.43 m are uncertain and therefore listed in *italics*.

Depth [m]	Formation	Cl ⁻ -accessible porosity fraction f_{cl} [-]
777.30	Wildegge Fm.	0.59
804.57	Wildegge Fm.	0.54
858.34	Wedelsandstein Fm.	0.53
886.60	'Murchisonae-Oolith Fm.'	<i>0.63</i>
909.46	Opalinus Clay	0.51
924.36	Opalinus Clay	0.52
950.43	Opalinus Clay	<i>0.59</i>
972.72	Opalinus Clay	0.43
990.66	Opalinus Clay	0.44
1'011.44	Staffelegg Fm.	0.62
1'019.27	Staffelegg Fm.	0.53

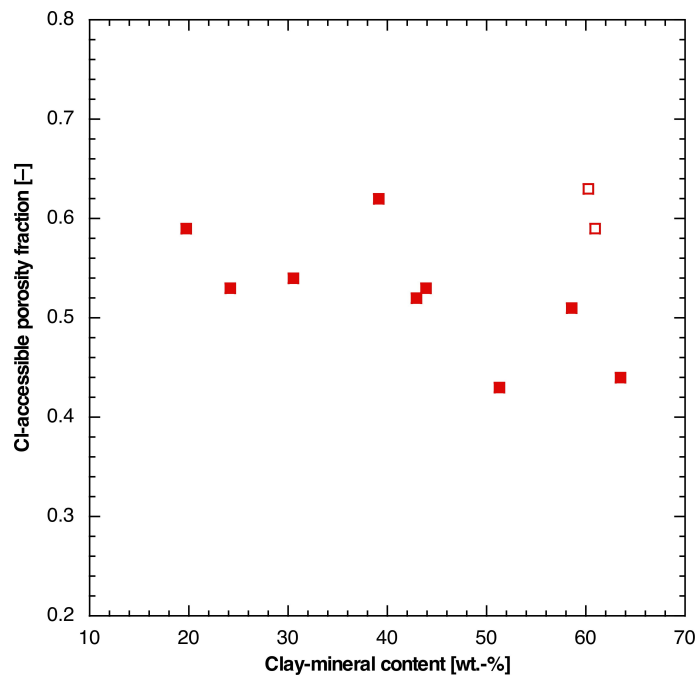


Fig. 4.6-5: Cl⁻-accessible porosity fractions derived from squeezing experiments as a function of the clay-mineral content

Open symbols indicate samples with uncertain data.

4.6.7 Stable isotopic composition of squeezed water

Results of stable water-isotope analyses are listed in Tab. 4.6-8 and shown as a function of depth in Fig. 4.6-6. In general, the same aliquots were selected for further interpretation as those for the chemical composition. However, in some cases, this was not possible because the mass of squeezed water was insufficient for isotope analysis. In such cases, an aliquot obtained at a higher pressure was selected. The selected "best" analyses for each sample are shown by bold print in Tab. 4.6-8. The following observations can be made:

- Within any sample, the variation of the δ values with squeezing pressure is small (typically within analytical error) and not systematic.
- $\delta^{18}\text{O}$ decreases systematically with depth, more strongly so in the 'Brauner Dogger' and Wild-egg Formation than in the underlying units.
- $\delta^2\text{H}$ increases slightly with depth in the section Wildegge Formation to 'Brauner Dogger' but does not show a systematic depth trend in the Opalinus Clay and the Staffelegg Formation.
- In a plot $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$, all squeezed waters are on the right side of the global ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$) and the local ($\delta^2\text{H} = 7.55 \delta^{18}\text{O} + 4.8$) meteoric water lines (Fig. 4.6-7).
- Given the different depth trends shown by the two isotopes, deuterium excess ($\delta^{18}\text{O} - 8 \delta^2\text{H}$) increases systematically with depth (Fig. 4.6-8). This means that the deviation from the meteoric water line increases upwards, towards the Malm aquifer.

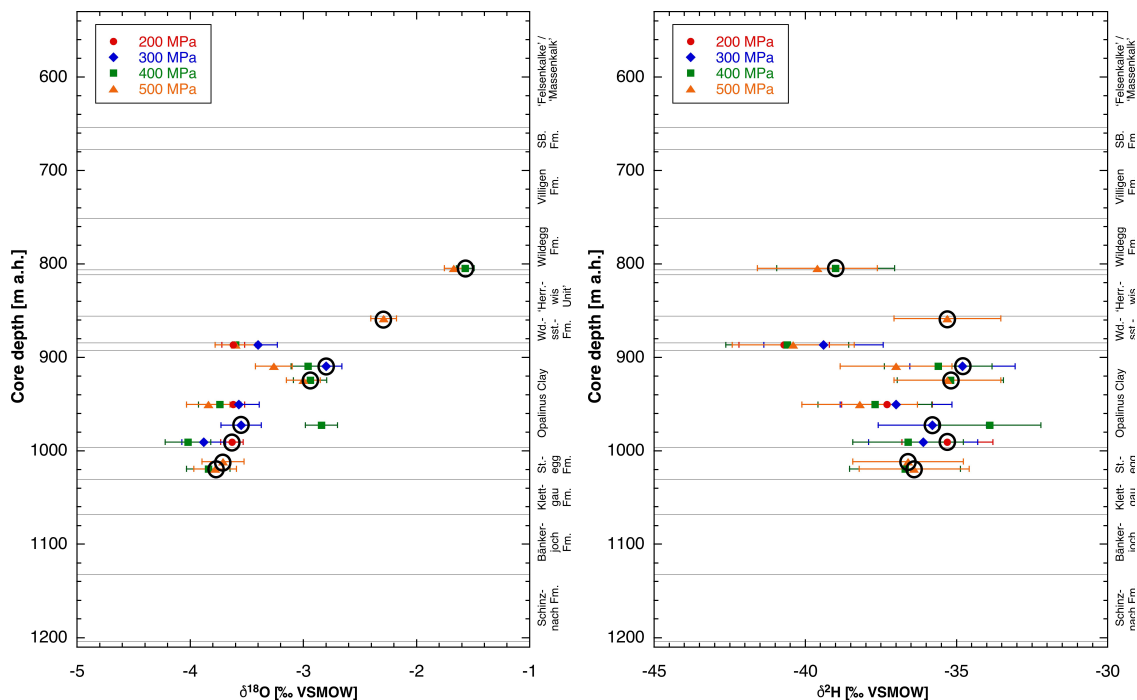


Fig. 4.6-6: Depth trends of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in squeezed waters

Selected values are highlighted by circles.

Tab. 4.6-8: Stable isotopic composition of squeezed waters

The aliquots selected for interpretation are shown in bold. Given the fact that the chemical compositions of waters from samples 886.60 and 950.43 m are considered uncertain (*cf.* Section 4.6.2), no isotope values are selected here for further interpretation.

Depth [m]	Formation	Pressure [MPa]	$\delta^{18}\text{O}$ [‰ VSMOW]	$\delta^2\text{H}$ [‰ VSMOW]	D excess [‰]
804.57	Wildegge Fm.	400	-1.57	-39.0	-26.4
		500	-1.67	-39.6	-26.3
858.34	Wedelsandstein Fm.	500	-2.29	-35.3	-17.0
886.60	'Murchisonae-Oolith Fm.'	200	-3.62	-40.7	-11.8
		300	-3.40	-39.4	-12.2
		400	-3.60	-40.6	-11.8
		500	-3.60	-40.4	-11.6
909.46	Opalinus Clay	300	-2.80	-34.8	-12.4
		400	-2.96	-35.6	-11.9
		500	-3.26	-37.0	-10.9
924.36	Opalinus Clay	400	-2.94	-35.2	-11.6
		500	-3.00	-35.3	-11.3
950.43	Opalinus Clay	200	-3.62	-37.3	-8.4
		300	-3.57	-37.0	-8.4
		400	-3.74	-37.7	-7.8
		500	-3.84	-38.2	-7.5
972.72	Opalinus Clay	300	-3.55	-35.8	-7.4
		400	-2.84	-33.9	-11.2
990.66	Opalinus Clay	200	-3.63	-35.3	-6.3
		300	-3.88	-36.1	-5.1
		400	-4.02	-36.6	-4.4
1'011.44	Staffelegg Fm.	500 (2)	-3.71	-36.6	-6.9
1'019.27	Staffelegg Fm.	400	-3.84	-36.7	-6.0
		500 (2)	-3.78	-36.4	-6.1

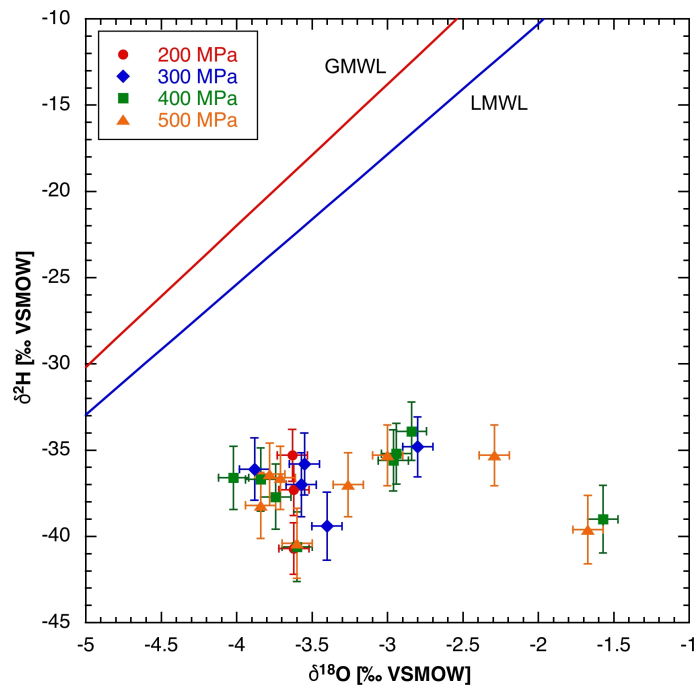


Fig. 4.6-7: Plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for squeezed waters

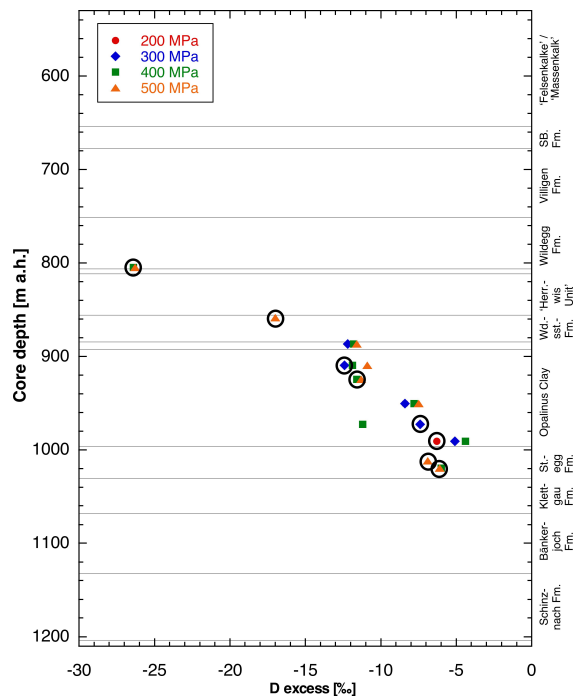


Fig. 4.6-8: Depth trend of deuterium excess
Selected values are highlighted by circles.

4.7 Data from advective displacement experiments

Urs Mäder, Mirjam Kiczka, Andreas Jenni & H. Niklaus Waber

Advective displacement (AD) experiments are a methodology for a comprehensive physico-chemical characterisation, including porewater chemistry and certain transport properties (details in method report, Waber ed. 2020). This section presents summary data, and details where important, with short comments. The full data sets are provided in Appendix 3. Integration of the data into context and depth profiles is included in Chapter 5.

Six samples from the clay-rich confining units were processed. One experiment failed (accidentally kinked outflow capillary) and yielded only data from pre-characterisation. The other five experiments were successful and were subjected to a similar analytical program, with differences mainly related to the duration of an experiment (numbers of sampled fluid aliquots) and to the extent of post-mortem characterisation. The program fulfilled the planned work but provided much longer periods of advective displacement than requested. The duration of the percolation period was 174 – 344 days, transporting 1.2 – 2.9 pore volumes of fluid. This was possible only for the first borehole study and had to be economised for later programs due to limitations in laboratory capacity and analytical costs.

4.7.1 Sample material and overview of analytical work

The six sample cores (Fig. 4.7-1) span 200 m of clay-rich confining units (811 – 1'012 m depth), from the 'Parkinsoni-Württembergica-Schichten' ('Brauner Dogger') to the Staffelegg Formation and include two samples of Opalinus Clay.

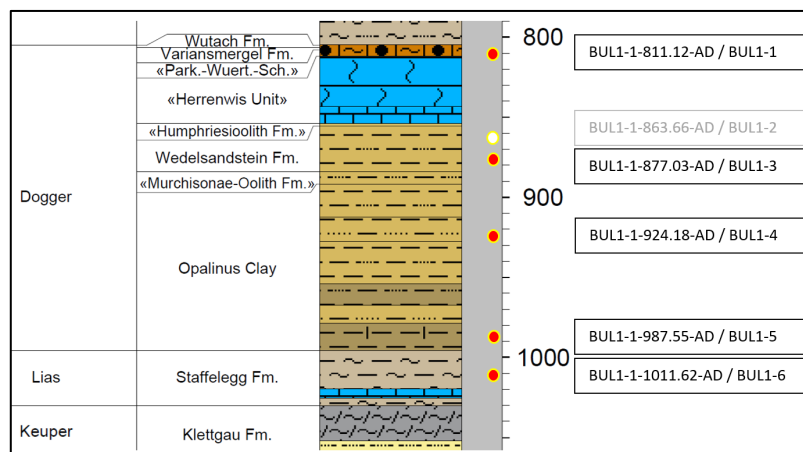


Fig. 4.7-1: Location of samples used for advective displacement experiments (red dots)

Short labels are consecutively numbered laboratory abbreviations. Sample BUL1-1-863.66-AD (yellow dot) was not successful and was aborted.

X-ray computed tomography (CT) was performed on a medical scanner (Waber ed. 2020) for sample selection (Fig. 4.7-2), detection of disturbing features (fractures, pyrite accumulations, macro-fossils etc.). Dry cutting was used for obtaining a central core segment for AD experiments, and adjacent 1 or 2 discs for accompanying characterisation (green in Fig. 4.7-2). The central core segment (yellow in Fig. 4.7-2) was turned on a lathe to 80 mm diameter.

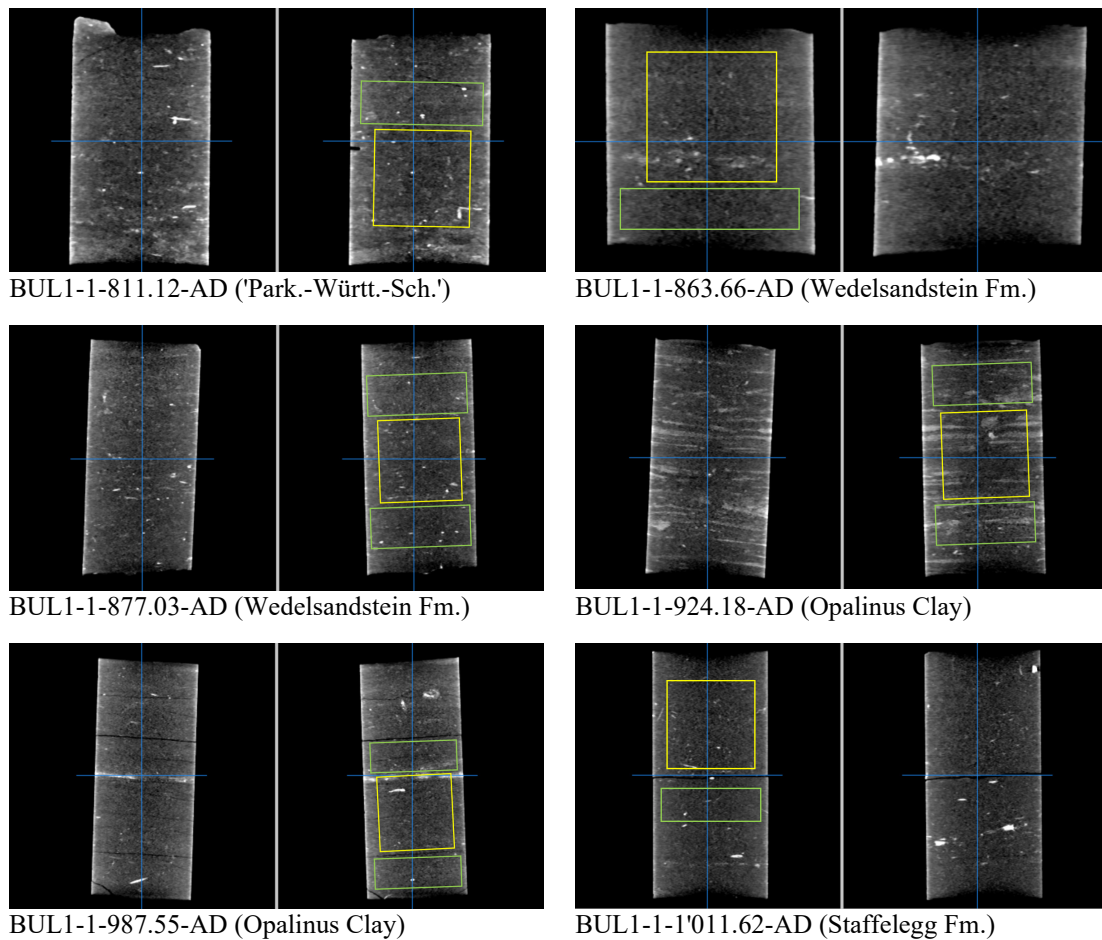


Fig. 4.7-2: X-ray CT images of AD samples

Central sections parallel to core axis at right angle. Grey scale range setting is 1'700 – 2'500 HU. Yellow segments are used for advective displacement, green segments for pre-characterisation. Low X-ray absorbance represents clay/quartz-rich sections (darker grey), slightly lighter grey indicates carbonate-rich parts, siderite is brighter, and pyrite is white (strongest absorbance). Black lines/gaps represent fractures.

Tab. 4.7-1 lists all analytical work performed on the six samples. Samples taken during abrasion of outermost 7.5 mm on a lathe during trimming of cores for the AD experiments are related to a study of drilling fluid contamination (reported separately).

Tab. 4.7-1: Summary of analytical work performed on samples for advective displacement experiments

Parameter / exp	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Lab sample ID	BUL1-1xx-AD	BUL1-2xx-AD	BUL1-3xx-AD	BUL1-4xx-AD	BUL1-5xx-AD	BUL1-6xx-AD
Depth [m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geological unit	'Park.-Württ.-Sch.'	Wedelsandstein Fm.	Wedelsandstein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
Member						Frick Mb.
AD_exp	y	n	y	y	y	y
Pre_WC	2 (top)	2 (base)	2+2	2+2	2+2	4 (base)
Pre_M	y	y	y	y	y	y
Pre_V,A,L	y	y	y	y	y	y
Pre_Min	1	1	1+1	1+1	2+2	4 (base)
Pre_Clay	1	1	1+1	1+1	2+2	4 (base)
Pre_AqEx	2 (top)	2 (base)	2+2	2+2	2+2	2 (base)
Pre_Ni-en	2 (top)	1	1+1	1+1	1+1	1 (base)
Post_WC	5		5	5	5	5
Post_M	y		y	y	y	y
Post_V,A,L	y		y	y	y	y
Post_AqEx	1+1		1+1	1+1	1+1	1+1
Post_Ni-en	1+1		1+1	n	n	1+1
Abras_Drilling_Fl	7	5	5	5	5	5

y = yes = done; n = no = not done; integer numbers refer to the number of samples processed; +: samples from above (left number) and below (right number) a core were processed; 2: duplicate samples; Pre: sample pre-characterisation; Post: post-mortem characterisation; WC: water content; M: mass; V,A,L: core volume, sectional area and length; Min: mineralogy; Clay: clay mineralogy; AqEx: aqueous extracts; Ni-en: cation selectivity with Ni-en method; Post_WC: post-mortem water content determined along a profile with 5 segments; AD_exp: complete analysis of fluid sample aliquots collected during advective displacement; Abras_Drilling_Fl: samples taken during abrasion of outermost 7.5 mm on a lathe during trimming of cores.

4.7.2 Conditions of advective displacement experiments

Sample preparation was performed according to Waber (ed.) (2020). The overview table (Tab. 4.7-2) presents some experiment specific parameters such as sample processing dates, storage time and other characteristic times like arrival of first fluid drop and its electric conductivity. Several variants for filters (between sample core and titanium adapter) were tested, including PEEK fabric and some different titanium foil spacers, as detailed in Waber (ed.) (2020). Numbers of samples taken and analysed are listed as well as average pressures for confining and injection. The number of pore volumes percolated are based on the water content determined from pre-characterisation. Confining pressure was set to 63 – 65 bar, pressurised by Ar on water, and 48.7 bar (initial, and average) for infiltration of the artificial porewater (APW) by He pressure. The hydraulic gradients are large, 5'000 – 7'000 m_{H₂O}/m (sample dimensions are in Tab. 4.7-4). Experiments were started within 3 – 14 days of sample delivery, and the time until arrival of a first fluid drop at the electric conductivity cell (outflow, before sampling syringe) was 4 – 11 days after start of infiltration.

Tab. 4.7-2: Conditions of advective displacement experiments

Parameter / exp	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth [m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geological unit	'Park.- Württ.-Sch.'	Wedelsand- stein Fm.	Wedelsand- stein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
Drilled	07.06.2019	09.06.2019	27.06.2019	02.07.2019	07.09.2019	09.09.2019
Delivered	11.06.2019	17.06.2019	01.07.2019	08.07.2019	16.09.2019	16.09.2019
Prep_AD	24.06.2019	27.06.2019	03.07.2019	11.07.2019	18.09.2019	18.09.2019
Injection	26.06.2019 12:30	28.06.2019	04.07.2019 11:06	12.07.2019 11:50	20.09.2019 09:20	19.09.2019 07:49
First drop	07.07.2019 12:54	aborted	15.07.2019 15:48	20.07.2019 22:02	29.09.2019 11:48	23.09.2019 13:44
Days to first drop	11.0		11.0	8.4	9.1	4.3
Initial gas [ml]	0.06		0.06	0.07	0.03	0.01
End_AD	04.06.2020 07:00	aborted	03.06.2020 08:40	11.03.2020 12:00	12.03.2020 12:00	04.06.2020 07:00
Duration [d]	343.8		334.9	243.0	174.1	259.0
Pore-volumes	1.38		1.34	1.21	1.7	2.85
EC_initial (25 °C) (max. in 1 st 24 h)	29.5		33.3	37.0	39.1	41.4
Filter	2×PEEK mesh	2×PEEK mesh	2×PEEK mesh	2×PEEK mesh + Ti spacers	PEEK mesh + Ti mask	PEEK mesh
AD-aliquots	23		20	19	16	20
AD-samp_chem	18		15	13	10	14
AD-samp_isotopes	17		15	13	11	14
in-line pH	9		8	7	6	7
P_Conf [bar]	64	64	64	65	65	63
P_Inf [bar]	48.7	48.7	48.7	48.7	48.7	48.7

4.7.3 Mineralogy and petrophysical properties

Mineralogy was determined on subsamples cut adjacent to the core segment used for the AD experiments (Tab. 4.7-1). Averaged values for subsamples (Tab. 4.7-3) are plotted in Section 4.2 and cover a range of clay contents from 37 – 62 wt.-%, calcite contents of 7 – 20 wt.-%, and quartz contents of 15 – 42 wt.-%. All samples contain pyrite, between 0.6 – 1.4 wt.-%. Of the clays, the dominant minerals are illite (11 – 21 wt.-%), illite/smectite mixed layers (12 – 20 wt.-%), and kaolinite (5 – 20 wt.-%). The ratio of (illite/smectite+smectite)/(total_clay) is rather uniform in the range of 0.27 – 0.39.

Included are also carbon and sulphur analysis. Pyrite contents are moderately low because pyrite-rich lithologies were avoided based on X-ray CT characterisation (Fig. 4.7-2). More details, including end-member clays, are included in Appendix 3.

A plethora of petrophysical parameters may be derived from sample dimensions, mass, water content, and changes in these parameters determined before and after an AD experiment (Tab. 4.7-4). Derived quantities include porosity, bulk density, grain density, water uptake during the experiments, and unsaturated porosity (saturation ratio). The relationships are given in Waber

(ed.) (2020). Note that the water content determined for pre-characterisation is based on 2 – 4 subsamples adjacent to the AD core segment, but it is determined for post-mortem characterisation along a 5-sample profile of the entire AD core segment itself. Accounting for the usually observed slight core volume expansion during an AD experiment, one can derive a corrected initial water content, as well as any unsaturated (gas-filled) porosity fraction.

Tab. 4.7-3: Mineralogy of advective displacement samples, including C and S analyses

Average values of subsamples (see text); b.d.: below detection limit.

Parameter / exp	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth [m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geol. unit	'Park.-Württ.-Sch.'	Wedelsandstein Fm.	Wedelsandstein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
S [wt.-%]	0.8	0.3	0.4	0.4	0.4	0.6
C(inorg) [wt.-%]	2.6	1.8	2.3	1.5	1.5	1.2
C(org) [wt.-%]	0.7	0.6	0.5	0.9	0.9	0.6
Quartz [wt.-%]	19	25	32	30	15	42
K-feldspar [wt.-%]	5	4	5	6	5	6
Plagioclase [wt.-%]	1	3	3	3	3	3
Calcite [wt.-%]	20	14	18	10	9	7
Dolomite / Ankerite [wt.-%]	2	b.d.	tr	tr	b.d.	2
Siderite [wt.-%]	b.d.	1	1	3	4	b.d.
Anhydrite [wt.-%]	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Celestite [wt.-%]	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Pyrite [wt.-%]	1	1	1	1	1	1
Clay minerals [wt.-%]	51	51	40	48	62	37
Illite [wt.-%]	21	19	15	16	17	11
Illite/smectite ML (85 – 90) [wt.-%]	7	1	3	6	9	6
Illite/smectite ML (75 – 80) [wt.-%]	8	13	8	4	7	5
Illite/smectite ML (50 – 70) [wt.-%]	4	2	3	2	2	1
Illite/smectite ML (20 – 40) [wt.-%]	b.d.	b.d.	0.1	0.1	0.01	0.04
Smectite [wt.-%]	0.07	b.d.	0.07	0.10	0.07	0.06
Kaolinite [wt.-%]	4.8	10.1	6.5	13.4	19.5	8.2
Chlorite [wt.-%]	1.0	2.0	1.5	1.2	2.1	1.7
Chl/Sm ML (85 – 95) [wt.-%]	4.0	2.2	3.6	4.5	5.7	3.1
Total illite/smectite [wt.-%]	20	17	13	13	17	12
(tot_ill/sm+sm)/(total_clay)	0.39	0.34	0.32	0.27	0.28	0.34
(tot_ill+ill/sm+sm)/(total_clay)	0.81	0.72	0.71	0.60	0.55	0.65

Core volume is seen to increase by 0.8 – 1.3 % (Tab. 4.7-4) during AD experiments, accompanied by a water uptake of 2.7 – 5.5 g. Accounting for volume expansion, there remains a small water uptake that must reflect an initially small volume of unsaturated porosity, ranging from 0 to 1.6 ml, or a saturation ratio in the range of 1 – 0.97. The initial state is essentially saturated for all samples within measurement uncertainty, and in agreement with the observed negligible amounts of gas expelled at the beginning of the experiments (Tab. 4.7-2).

Tab. 4.7-4: Core dimensions and derived petrophysical parameters

Parameter / exp	Unit	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geol. unit		'Park.-Württ.-Sch.'	Wedelsandstein Fm.	Wedelsandstein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
Pre_Core_M	[g]	1'033.57	860.80	1'246.72	1'135.71	903.01	915.70
Pre_Core_DM	[cm]	7.993	8.001	8.004	7.988	8.021	8.025
Pre_Core_L	[cm]	8.266	6.797	9.826	8.900	7.086	7.096
Pre_Core_A	[cm ²]	50.17	50.28	50.32	50.11	50.53	50.58
Pre_Core_V	[cm ³]	414.72	341.74	494.39	445.98	358.09	358.93
Post_Core_M	[g]	1'039.59		1'252.28	1'139.99	908.07	918.43
Post_Core_DM	[cm]	8.016		8.018	8.009	8.029	8.028
Post_Core_L	[cm]	8.328		9.870	8.932	7.146	7.147
Post_Core_A	[cm ²]	50.46		50.49	50.38	50.63	50.61
Post_Core_V	[cm ³]	420.23		498.31	449.95	361.79	361.76
Delta_M	[g]	6.02		5.56	4.29	5.06	2.73
Delta_Core_DM	[cm]	0.023		0.014	0.021	0.008	0.003
Delta_Core_L	[cm]	0.062		0.044	0.032	0.059	0.051
Delta_Core_A	[cm ²]	0.29		0.17	0.26	0.10	0.03
Delta_Core_V	[cm ³]	5.52		3.92	3.97	3.70	2.83
Delta_Core_V-%	[%]	1.33		0.79	0.89	1.03	0.79
Pre_Bulk_WD	[g/cm ³]	2.492	2.519	2.522	2.547	2.522	2.551
Post_Bulk_WD	[g/cm ³]	2.474		2.513	2.534	2.510	2.539
Delta_Bulk_WD	[g/cm ³]	-0.018		-0.009	-0.013	-0.012	-0.012
Delta_Bulk_WD-%	[%]	-0.74		-0.34	-0.51	-0.47	-0.49
Pre_GD	[g/cm ³]	2.746	2.726	2.696	2.715	2.712	2.690
Post_GD	[g/cm ³]	2.736		2.714	2.689	2.716	2.695
Delta_GD	[g/cm ³]	-0.009		0.018	-0.027	0.004	0.005
Corr_Pre_GD	[g/cm ³]	2.732		2.704	2.686	2.704	2.696
Pre_WCw		0.05823	0.04766	0.04075	0.03867	0.04398	0.03219
Post_WCw		0.0611		0.0467	0.0362	0.0478	0.0363
Delta_WCw		0.00287		0.00592	-0.00245	0.00382	0.00408
Corr_Pre_WCw		0.05563		0.04241	0.03259	0.04247	0.03339
Pre_H2O_Core	[g]	60.18	41.02	50.80	43.92	39.71	29.48
Post_H2O_Core	[g]	63.52		58.44	41.29	43.40	33.31
Delta_H2O_Core	[g]	3.34		7.64	-2.62	3.69	3.84
Corr_Pre_H2O_Core	[g] or [ml]	57.50		52.88	37.01	38.35	30.58
Unsat_Vol	[g] or [ml]	0.50		1.64	0.31	1.35	-0.09
Pore_Vol_tot	[ml]	58.00		54.52	37.32	39.70	30.48
Sat_ratio		0.991		0.970	0.992	0.966	1.003
Pre_Poro_WL		0.1451	0.1200	0.1028	0.0985	0.1109	0.0821
Post_Poro_WL		0.1511		0.1173	0.0918	0.1200	0.0921
Delta_Poro_WL		0.0060		0.0145	-0.0067	0.0091	0.0100
Delta_Poro_WL-%	[%]	4.16		14.13	-6.80	8.18	12.13
Corr_Pre_Poro_WL		0.1386		0.1070	0.0830	0.1071	0.0852
Corr_Pre_Poro_tot		0.1399		0.1103	0.0837	0.1109	0.0849

_L = length; _A = area; _V = volume; _M = mass; WD = wet density; GD = grain density; WCw = water content relative to wet mass; _WL = water loss

There are significant differences in water content measured in adjacent samples (pre-characterisation) and in the core itself (post-mortem) of 5 – 10 %, and 15 % in one case (Wedelsandstein Formation) even when accounting for core expansion (Fig. 4.7-3). This leads to different values of bulk wet density, water-loss porosity and grain density (assuming saturated conditions) derived from pre-characterisation and post-mortem data. This spread is significantly larger than measurement uncertainties, and illustrates that the largest contribution to uncertainty is sample heterogeneity for parameters that depend on water content. In contrast, measurements on replicate samples agree well within measurement uncertainty. Differences in water content commonly correlate with differences in clay content, such that this heterogeneity is mainly an issue of lamination in fine-grained sediments.

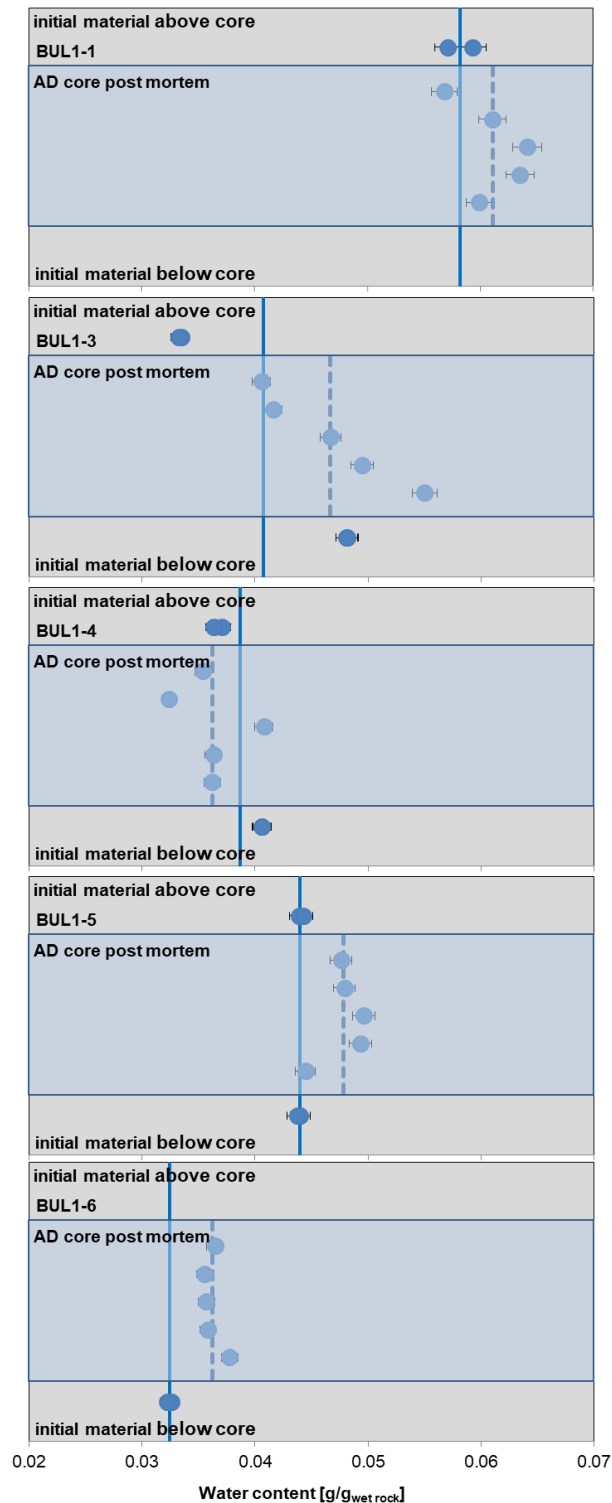


Fig. 4.7-3: Details of water content measurements before and after AD experiments

BUL1-1 = BUL1-1-811.12 ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = BUL1-1-877.03 (Wedelsandstein Formation); BUL1-4 = BUL1-1-924.18 (Opalinus Clay); BUL1-5 = BUL1-1-987.55 (Opalinus Clay); BUL1-6 = BUL1-1-1'011.62 (Staffellegg Formation). Average values are indicated for pre-characterisation (solid line) and post-mortem characterisation (dashed line). Error bars refer to a measurement uncertainty of 2 %. See dimensions in Tab. 4.7-4, the bluish zone refers to the core section used in the experiment.

4.7.4 Aqueous extracts, CEC and cation selectivity of AD samples

Aqueous extracts, CEC and cation selectivity determinations were carried out on all AD samples during pre-characterisation, and during post-mortem analysis for select samples only. Detailed analyses are provided in Appendix 3. Methods are the same as used for other core samples (Waber ed. 2020), with the exception of sample masses that may have been smaller than used for regular core sample analysis. Averaged data – also used for integrative data plots – are presented in this section. Averaging refers to duplicates and to measurements performed on pieces above and below the segment used for the AD experiments (indicated in Fig. 4.7-2 and Tab. 4.7-5).

Tab. 4.7-5: Composition of aqueous extract solutions from pre-characterisation

Parameter	Unit	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geol. unit		'Park.- Württ.-Sch.'	Wedelsand- stein Fm.	Wedelsand- stein Fm.	Opalinus Clay	Opalinus Clay	Staffellegg Fm.
Averaging		top (ave 2)	base (ave 2)	top+base (ave 2+2)	top+base (ave 2+2)	top+base (ave 2+2)	base (ave 2)
I/WCw*L/Sw		17.16	20.72	24.60	25.66	22.71	30.44
Rock wet	[g]	15.25	15.30	30.09	30.44	30.15	30.77
Water	[g]	15.24	15.11	30.17	30.20	30.11	30.16
S/L	[g/g]	0.891	0.920	0.919	0.933	0.917	0.956
pH at Titration		8.85	8.85	9.20	8.81	8.67	8.97
Na	[mg/L]	309	341	319	336	373	308
NH ₄	[mg/L]	2.3	2.4	3.5	2.3	2.0	2.1
K	[mg/L]	10.5	7.1	9.1	8.7	6.8	8.3
Ca	[mg/L]	5.0	3.2	3.2	4.3	4.5	3.1
Mg	[mg/L]	1.35	0.72	0.68	0.98	0.76	0.43
Sr (OES)	[mg/L]	0.114	0.075	0.080	0.112	0.115	0.093
Ba (OES)	[mg/L]	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
F	[mg/L]	6.4	6.3	4.2	2.1	2.9	5.0
Cl	[mg/L]	245	245	257	244	257	244
Br	[mg/L]	0.60	0.49	0.48	0.45	0.38	0.36
NO ₃	[mg/L]	0.24	0.35	0.26	0.29	0.47	1.26
SO ₄	[mg/L]	238	238	223	217	219	163.5
I	[mg/L]					< 0.08	0.129
Alk (Titration)	[meq/L]	2.30	3.27	2.26	3.55	4.08	2.91
Alk as HCO ₃	[mg/L]	141	199	138	217	249	178
TOC	[mg/L]	18.4	20.4	40.7	60.1	22.3	17.2
TIC	[mg/L]	24.4	32.9	23.4	41.0	45.1	32.7
lactate	[mg/L]	< 0.2	< 0.2	< 0.2	< 0.2	< 2	< 2
acetate	[mg/L]	3.45	9.01	9.28	10.94	9.17	5.29
propionate	[mg/L]	< 0.2	< 0.2	< 0.2	< 0.2	< 2	< 2
formate	[mg/L]	0.32	0.42	< 0.2	< 0.2	< 2	< 2

All averaged aqueous extract solutions (Tab. 4.7-5) from pre-characterisation processed at $S/L \approx 1$ contain low concentrations of NH_4 (2 – 3.5 mg/L), NO_3 (0.24 – 1.3 mg/L), and iodide was measured in two samples, but detected only in one at 0.13 mg/L. The factor $(1/WCw \cdot L/Sw)$ refers to the scaling factor required to scale aqueous concentrations for conservative components to porewater concentrations.

Some characteristic molar cation ratios (Tab. 4.7-6) indicate a systematic decrease with depth for Br/Cl and a slight decrease in SO_4/Cl . Most of the titrated alkalinity is accounted for by TIC and the titratable acetate concentrations. Conspicuous are elevated concentrations of TOC (17 – 60 mg/L) of which only a small portion is identified as low-molecular-weight organic acids (acetate, formate, lactate, propionate). The maximum value is located in a sample of Opalinus Clay (BUL1-4), but the other Opalinus Clay sample (22 mg/L) is close to a median value.

Tab. 4.7-6: Cation ratios and details of carbon system in aqueous extract solutions from pre-characterisation

Parameter	Unit	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geol. unit		'Park.- Württ.-Sch.'	Wedelsand- stein Fm.	Wedelsand- stein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
$Br/Cl \cdot 1'000$	[molar]	1.08	0.89	0.82	0.81	0.66	0.65
SO_4/Cl	[molar]	0.36	0.36	0.32	0.33	0.31	0.25
Ca/Mg	[molar]	2.25	2.66	2.83	2.64	3.63	4.37
Ca/Sr	[molar]	96	93	87	84	86	72
$(Ca+Mg)/(Na+K)$	[eq/eq]	0.026	0.014	0.015	0.020	0.018	0.014
Alk (Titration)	[meq/L]	2.30	3.27	2.26	3.55	4.08	2.91
TIC	[meq/L]	2.03	2.74	1.95	3.41	3.75	2.72
acetate	[meq/L]	0.06	0.15	0.16	0.19	0.16	0.09
TOC	[mg/L]	18.4	20.4	40.7	60.1	22.3	17.2
acetate (as C)	[mg/L]	1.40	3.67	3.78	4.45	3.73	2.15

Calculations of speciation and saturation indices (Tab. 4.7-7) of the aqueous extract solutions from Tab. 4.7-5 reveal a systematic surplus cationic charge (except BUL1-1) as positive imbalance that is largely explained by acetate that was not included in the speciation (included in the table as equivalent for illustration). Solutions are at or very close to calcite saturation, and not far from dolomite saturation. Extracts are distinctly undersaturated with respect to sulphates and also fluorite. TIC was used as input for the carbon system, because the titrated alkalinity would also include acetate.

Tab. 4.7-7: Saturation indices calculated for aqueous extract solutions from pre-characterisation

Parameter	Unit	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geological unit		'Park.- Württ.-Sch.'	Wedelsand- stein Fm.	Wedelsand- stein Fm.	Opalinus Clay	Opalinus Clay	Staffellegg Fm.
Charge	[eq/kg]	-1.9×10^{-4}	2.2×10^{-4}	1.2×10^{-4}	1.1×10^{-4}	9.2×10^{-4}	3.9×10^{-4}
% Error		-0.69	0.73	0.43	0.37	2.85	1.44
Acetate	[eq/kg]	5.8×10^{-5}	1.5×10^{-4}	1.6×10^{-4}	1.9×10^{-4}	1.6×10^{-4}	9.0×10^{-5}
Ionic strength	[mol/kg w]	0.017	0.018	0.017	0.017	0.019	0.015
tot_Alk	[eq/kg]	2.18×10^{-3}	2.93×10^{-3}	2.27×10^{-3}	3.62×10^{-3}	3.91×10^{-3}	2.95×10^{-3}
pH		8.85	8.85	9.20	8.81	8.67	8.97
log P(CO ₂)	[bar]	-3.81	-3.68	-4.20	-3.54	-3.35	-3.80
SI (calcite)		0.013	-0.069	0.105	0.119	0.050	0.046
SI (dolomite)		-0.20	-0.43	-0.10	-0.05	-0.33	-0.41
SI (gypsum)		-2.48	-2.69	-2.72	-2.60	-2.58	-2.84
SI (celestite)		-2.40	-2.59	-2.58	-2.45	-2.45	-2.62
SI (anhydrite)		-2.70	-2.91	-2.94	-2.82	-2.80	-3.06
SI (fluorite)		-0.68	-0.90	-1.25	-1.75	-1.41	-1.09

WATEQ4F thermodynamic data base and ordered dolomite; kg w = kg water; charge = Σ (cation charge) – $|\Sigma$ (anion charge)|; % Error = charge / (Σ (cation charge) + $|\Sigma$ (anion charge)|).

Aqueous extracts of all cores were produced after termination of the experiments. A thin disc (10 – 17 mm) from the top and base of each core were processed according to the same protocols. The base of the core represents the inlet of the artificial porewater, whereas the top represents the outflow to sampling. The two may yield different results depending on the overall progress of fluid percolation, and averaging is therefore meaningless. Results (Tab. 4.7-8) show that Br (not present in the APW) was effectively flushed out of each core, whereas other minor anionic components were buffered (e.g. F, NO₃). More than half of the initially observed elevated TOC was also flushed out, and essentially no acetate or propionate was detected > 2 mg/L. Cation concentrations did not change markedly, but need to be interpreted in more detail considering ion-exchange processes. Sr concentrations did decrease slightly from 0.08 – 0.11 mg/L to 0.04 – 0.11 mg/L at the end of the experiments. A more in-depth analysis will be required to reconcile differences between extracts from pre-characterisation and post mortem.

Calculation of speciation and saturation indices (Tab. 4.7-9) of the aqueous extract solutions from Tab. 4.7-8 are at calcite saturation, and at or not far from dolomite saturation. Extracts are distinctly undersaturated with respect to sulphates and also fluorite. TIC was used as input for the carbon system.

Tab. 4.7-8: Composition of aqueous extract solutions from post-mortem characterisation

Parameter	Unit	BUL1-1		BUL1-3		BUL1-4		BUL1-5		BUL1-6	
Depth	[m]	811.12		877.03		924.18		987.55		1'011.62	
Geological unit		'Park.-Württ.-Sch.'		Wedelsandstein Fm.		Opalinus Clay		Opalinus Clay		Staffelegg Fm.	
Position		Top	Base	Top	Base	top	base	top	base	top	base
1/WCw*L/Sw		17.65	16.65	24.77	18.25	28.19	28.00	21.44	22.84	27.53	26.11
Rock wet	[g]	30.14	30.20	30.03	30.10	15.27	15.01	14.82	15.02	30.11	30.66
Water	[g]	30.23	30.14	30.18	30.22	15.23	15.22	15.13	15.26	30.23	30.23
Sw/L	[g/g]	0.997	1.002	0.995	0.996	1.002	0.986	0.979	0.984	0.996	1.014
pH at Titrat.		8.71	8.77	8.99	9.03	8.93	8.96	8.79	8.5	8.94	8.86
Na	[mg/L]	269	262	271	244	305	265	337	358	220	216
NH ₄	[mg/L]	2.6	2.3	2.7	2.6	2.3	2.2	2.2	2.0	1.9	1.5
K	[mg/L]	10.6	9.7	7.6	6.4	9.7	9.1	10.0	11.8	5.5	5.4
Ca	[mg/L]	5.2	4.5	4.1	3.0	3.9	3.8	4.3	5.9	2.6	2.8
Mg	[mg/L]	1.00	0.88	0.52	0.39	0.60	0.60	0.67	1.47	0.24	0.38
Sr (OES)	[mg/L]	0.090	0.064	0.080	0.035	0.101	0.083	0.094	0.113	0.042	0.044
Ba (OES)	[mg/L]	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
F	[mg/L]	6.6	6.8	4.6	5.1	2.3	2.3	3.4	2.6	5.5	5.0
Cl	[mg/L]	181	172	141	155	115	99	119	117	110	115
Br	[mg/L]	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16
NO ₃	[mg/L]	0.53	0.42	0.49	0.59	0.27	0.31	0.25	0.32	0.46	0.78
SO ₄	[mg/L]	244	230	269	190	269	246	305	263	145	144
Alk (tit)	[meq/L]					4.42	4.28	4.57	6.50		
Alk as HCO ₃	[mg/L]	101	114	131	154	270	261	279	397	189	196
TOC	[mg/L]	8.3	8.9	13.1	10.1	5.5	< 5	11.9	5.1	13.6	10.4
TIC	[mg/L]	19.9	22.4	25.8	30.2	49.7	48.9	47.7	71.1	37.3	38.5
lactate	[mg/L]	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
acetate	[mg/L]	< 2	< 2	3.91	< 2	< 2	< 2	< 2	< 2	< 2	< 2
propionate	[mg/L]	< 2	< 2	< 2	< 2	2.5	2.1	2.8	2.3	< 2	< 2
formate	[mg/L]	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2

Cation exchange capacities and cation selectivities determined by the Ni-en method (Waber ed. 2020) were performed on the same subset of sample material as used for aqueous extracts. Averaged values (Tab. 4.7-10) indicate uncorrected (for porewater contribution and mineral dissolution/precipitation) capacities of 84 – 137 meq/kg (dry rock) with errors of $\sim \pm 5\%$, compared to Ni consumptions that are systematically ca. 10 % higher. Ammonium was not measured, but is expected to be present on the exchanger judged by the presence of 2 – 3 mg/L of NH_4^+ in the aqueous extracts performed at the same S/L ratio (Tab. 4.7-5).

Tab. 4.7-9: Saturation indices calculated for aqueous extract solutions obtained post-mortem

Parameter	Unit	BUL1-1		BUL1-3		BUL1-4		BUL1-5		BUL1-6	
Depth	[m]	811.12		877.03		924.18		987.55		1'011.62	
Geological unit		'Park.-Württ.-Sch.'		Wedelsandstein Fm.		Opalinus Clay		Opalinus Clay		Staffelelegg Fm.	
Position		Top	Base	Top	Base	Top	Base	Top	Base	Top	Base
Charge	[eq/kg]	1.6×10^{-4}	8.5×10^{-5}	1.9×10^{-4}	-2.6×10^{-4}	4.8×10^{-4}	-3.0×10^{-4}	1.2×10^{-3}	1.4×10^{-3}	2.2×10^{-4}	-1.2×10^{-4}
% Error		0.67	0.36	0.80	-1.19	1.79	-1.26	4.27	4.64	1.12	-0.60
Ionic strength	[mol/kg w]	0.015	0.014	0.015	0.013	0.016	0.015	0.018	0.018	0.011	0.011
tot_Alk	[eq/kg]	1.75×10^{-3}	1.98×10^{-3}	2.36×10^{-3}	2.76×10^{-3}	4.45×10^{-3}	4.39×10^{-3}	4.19×10^{-3}	6.06×10^{-3}	3.33×10^{-3}	3.39×10^{-3}
pH		8.71	8.77	8.99	9.03	8.93	8.96	8.79	8.5	8.94	8.86
log P(CO ₂)	[bar]	-3.74	-3.75	-3.92	-3.90	-3.58	-3.61	-3.45	-2.98	-3.70	-3.61
SI (calcite)		-0.18	-0.13	0.07	0.07	0.26	0.27	0.14	0.18	0.04	0.01
SI (dolomite)		-0.73	-0.63	-0.40	-0.39	0.05	0.10	-0.17	0.11	-0.61	-0.50
SI (gypsum)		-2.43	-2.51	-2.51	-2.76	-2.56	-2.60	-2.48	-2.40	-2.91	-2.88
SI (celestite)		-2.47	-2.63	-2.49	-2.96	-2.42	-2.52	-2.41	-2.39	-2.97	-2.95
SI (anhydrite)		-2.65	-2.73	-2.73	-2.98	-2.78	-2.82	-2.70	-2.62	-3.13	-3.10
SI (fluorite)		-0.62	-0.65	-1.05	-1.08	-1.70	-1.72	-1.33	-1.42	-1.05	-1.10

WATEQ4F thermodynamic data base and ordered dolomite; kg w = kg water; charge = Σ (cation charge) – $|\Sigma$ (anion charge)|; % Error = charge / (Σ (cation charge) + $|\Sigma$ (anion charge)|).

The cation occupancies (selectivities) derived from Ni-en extracts and applying a correction for the porewater contribution are presented in Section 4.5.

Br/Cl ratios in the Ni-en solutions are quite similar to those in the aqueous extracts, the former being slightly but systematically larger. Interesting is that the SO₄/Cl ratios are significantly and systematically smaller in the Ni-en solutions compared to the aqueous extracts, suggesting that there is either a sulphate source in the aqueous extracts or a sink in the Ni-en solutions.

Ni-en extracts were also determined post mortem for three experiments from discs at the top and base of a sample core (Tab. 4.7-11). An adjustment was made to the method (Waber ed. 2020) such that significantly less excess Ni was provided in the initial solution (ca. 6 g/L vs. 9 g/L). It appears that this adjustment led to perfect agreement between nickel consumption and the sum of displaced cations. The post-mortem sum of displaced (uncorrected) values closely agree with the sum of cations determined for pre-characterisation. One would have to compare corrected values for a more in-depth analysis because the ionic strength of the porewater at post-mortem time is significantly less than that of the initial porewater. The sulphate concentrations in the Ni-en extracts post mortem are similar to those from pre-characterisation. The chloride concentrations are much less post-mortem (resembling the injected fluid) such that the SO₄/Cl ratios are much larger post-mortem, and also well above that of the injected fluid.

Tab. 4.7-10: Composition of Ni-en extract solutions and related parameters from pre-characterisation

Parameter	Unit	BUL1-1	BUL1-2	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	863.66	877.03	924.18	987.55	1'011.62
Geological unit		'Park.- Württ.-Sch.'	Wedelsand- stein Fm.	Wedelsand- stein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
S/L (wet)		0.952	0.948	0.944	0.938	0.936	0.945
S/L (dry)		0.896	0.9025	0.9055	0.901	0.895	0.915
pH (initial)		8.26	8.26	8.29	8.29	8.29	8.29
Ni (initial)	[mg/L]	8'854	9'114	8'922	8'922	8'544	8'544
pH (final)		8.34	8.33	8.41	8.34	8.29	8.35
Na	[mg/L]	1'229	1'487	1'113	1'062	1'305	922
K	[mg/L]	308	239	205	183	185	176
Mg	[mg/L]	247	164	121	115	151	88
Ca	[mg/L]	810	738	594	558	794	483
Sr	[mg/L]	26.0	23.5	17.8	19.6	24.5	18.3
Ba	[mg/L]	0.20	0.36	0.33	0.76	0.78	1.31
Fe	[mg/L]	0.13	0.27	0.42	0.06	0.28	<0.1
Ni	[mg/L]	4'391	4'569	5'637	5'686	5'024	6'249
F	[mg/L]	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16
Cl	[mg/L]	243	251	245	225	240	269
Br	[mg/L]	0.53	0.42	0.42	0.36	0.36	0.33
NO ₃	[mg/L]	19'220	19'405	19'912	19'958	20'239	20'529
SO ₄	[mg/L]	174	140	159	138	141	111
TDS	[mg/L]	26'647	27'018	28'003	27'943.5	28'104.5	28'848
Balance	[eq]	-0.081	-0.076	-0.074	-0.080	-0.082	-0.082
Na	[meq/kg d]	59.6	71.7	53.7	51.3	63.5	43.8
K	[meq/kg d]	8.8	6.8	5.8	5.2	5.3	4.9
Mg	[meq/kg d]	22.7	15.0	11.0	10.5	13.9	7.9
Ca	[meq/kg d]	45.1	40.9	32.9	30.9	44.3	26.4
Sr	[meq/kg d]	0.67	0.60	0.45	0.50	0.63	0.46
Ba	[meq/kg d]	0.003	0.006	0.005	0.012	0.013	0.021
Fe	[meq/kg d]	0.005	0.020	0.017	0.003	0.011	< 0.004
SumCat	[meq/kg d]	137	135	104	98	128	84
SumCat_err	[meq/kg d]	5.7	6.0	4.5	4.3	5.6	3.7
Ni_cons	[meq/kg d]	151	156	111	110	121	76
Ni_cons_err	[meq/kg d]	7.2	7.5	7.8	7.8	7.3	7.7
Br/Cl*1000	[molar]	0.97	0.73	0.75	0.71	0.66	0.54
SO ₄ /Cl	[molar]	0.26	0.21	0.24	0.23	0.22	0.15

Balance = Σ (cation charge) – $|\Sigma$ (anion charge)|; kg d = kg dry rock.

Tab. 4.7-11: Composition of Ni-en extract solutions and related parameters obtained post-mortem

Parameter	Unit	BUL1-1		BUL1-3		BUL1-6	
Depth	[m]	811.12		877.03		1'011.62	
Geological unit		'Park.-Württ.-Sch.'		Wedelsandstein Fm.		Staffelegg Fm.	
Position		Top	Base	Top	Base	Top	Base
S/L (wet)		0.953	0.961	0.971	0.931	0.957	0.948
S/L (dry)		0.899	0.903	0.932	0.88	0.922	0.912
pH (initial)		8.3	8.3	8.3	8.3	8.3	8.3
Ni (initial)	[mg/L]	5'879	5'879	5'879	5'879	5'879	5'879
pH (final)		8.44	8.41	8.44	8.46	8.41	8.41
Na	[mg/L]	1'122	1'202	1'081	1'323	946	856
K	[mg/L]	281	272	193	227	143	174
Mg	[mg/L]	219	227	115	154	79	115
Ca	[mg/L]	889	900	543	736	462	482
Sr	[mg/L]	23.4	21.0	17.5	18.3	15.9	13.7
Ba	[mg/L]	0.14	0.13	0.69	0.23	0.76	1.26
Fe	[mg/L]	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Ni	[mg/L]	1'925	1'897	3'026	2'299	3'456	3'447
F	[mg/L]	1.5	1.47	0.87	1.01	1.1	1.04
Cl	[mg/L]	167	151	131	134	100	103
Br	[mg/L]	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16
NO ₃	[mg/L]	12'752	12'548	12'886	12'599	13'191	12'994
SO ₄	[mg/L]	189	164	190	139	99	110
TDS	[mg/L]	17'568	17'383	18'184	17'632	18'492	18'296
Balance	[eq]	-0.074	-0.056	-0.058	-0.046	-0.062	-0.054
Na	[meq/kg d]	54.3	57.9	50.4	65.4	44.6	40.8
K	[meq/kg d]	8.0	7.7	5.3	6.6	4.0	4.9
Mg	[meq/kg d]	20.1	20.7	10.1	14.4	7.0	10.3
Ca	[meq/kg d]	49.4	49.7	29.1	41.7	25.0	26.4
Sr	[meq/kg d]	0.60	0.53	0.43	0.47	0.39	0.34
Ba	[meq/kg d]	0.002	0.002	0.011	0.004	0.012	0.02
Fe	[meq/kg d]	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
SumCat	[meq/kg d]	132	137	95	129	81	83
SumCat_err	[meq/kg d]	5.5	5.7	4.2	5.6	3.6	3.5
Ni_cons	[meq/kg d]	138	137	96	127	82	83
Ni_cons_err	[meq/kg d]	4.5	4.4	4.7	4.7	4.9	5.0
Br/Cl*1'000	[molar]	-	-	-	-	-	-
SO ₄ /Cl	[molar]	0.42	0.40	0.54	0.38	0.37	0.39

No measurements for BUL1-4 and BUL1-5 experiments; balance = Σ (cation charge) – $|\Sigma$ (anion charge)|; kg d = kg dry rock.

4.7.5 Chemical and isotopic evolution of displaced porewater aliquots

An artificial porewater (APW) composition was injected to force advective displacement. The outflow of each experiment was continuously sampled in small syringes (Waber ed. 2020). These syringe aliquots were analysed for chemical and water isotopic composition. Hydraulic conductivity was evaluated for each sampled aliquot (Darcy's law), and any expelled gas was also recorded, although gas-tightness is commonly good, but cannot be ensured for a syringe sampling system. Most data for each experiment are included in some tables and graphs in this section, and more details are provided in Appendix 3.

According to the method of advective displacement (Mäder 2018), it is expected that the first few sampled aliquots are of similar composition and represent the displaced porewater from the sample core. After this, a gradual breakthrough of the injected APW should be observed, until full breakthrough of conservative components (e.g. Cl, Br), given enough time.

4.7.5.1 Artificial porewater used for advective displacement

In the absence of constraining data, an artificial porewater composition (Tab. 4.7-12) was chosen that was based on work performed for the deep geothermal well in Schlattingen (advective displacement experiments detailed in Mäder & Waber 2017). The composition was calculated with PHREEQC for 25 °C, to be saturated with respect to calcite and dolomite, and a partial pressure of CO₂ of 10^{-2.2} bar. This partial pressure was imposed by bubbling with an Ar/CO₂ gas mixture during mixing and again when the fluid reservoir was filled before experiments. A recipe with the appropriate amounts of PA-grade chemicals is given in Tab. 4.7-13.

Deuterium was added as a water tracer for advective-diffusive transport, aiming for a $\delta^2\text{H}$ of approximately +100 ‰(VSMOW). There is no Br contained in the APW and therefore bromide-breakout can be used as an anionic tracer. In case the Cl concentration in the APW is significantly different from the displaced early aliquots, Cl breakthrough forms an additional anionic tracer for transport.

All five experiments were fed from the same PFA-coated fluid tank containing the APW and a pressurised head space filled with He after bubbling with the Ar/CO₂ gas mixture mentioned above. The composition of the APW and the pressure evolution of infiltration is therefore identical for all experiments.

Tab. 4.7-12: Composition and recipe for the artificial porewater

Parameter	Unit	Recipe	Calculated*	Measured	Compounds
pH	[-]	7.19	7.28	7.44	
Na	[mg/L]	3'989	3'988	4'036	NaCl; NaHCO ₃ ; Na ₂ SO ₄
NH ₄	[mg/L]			< 1	
K	[mg/L]	79.4	79.5	71.1	KCl
Ca	[mg/L]	503	503	507	CaCl ₂ ·2H ₂ O
Mg	[mg/L]	226	226	225	MgCl ₂ ·6H ₂ O
Sr (OES)	[mg/L]			< 0.25	
Ba	[mg/L]			< 0.25	
Si	[mg/L]			< 0.5	
Al	[mg/L]			< 2.5	
F	[mg/L]			< 0.16	
Cl	[mg/L]	5'992	5'984	5'919	CaCl ₂ ·2H ₂ O; KCl; MgCl ₂ ·6H ₂ O
Br	[mg/L]			< 0.16	
NO ₃	[mg/L]			6.8	
SO ₄	[mg/L]	2'305	2'305	2'157	Na ₂ SO ₄
I	[mg/L]			n.a.	
TOC	[mg/L]			13.8	
TIC	[mg/L]	29.3	29.32	31.0	NaHCO ₃
lactate	[mg/L]			< 20	
acetate	[mg/L]			< 20	
propionate	[mg/L]			< 20	
formate	[mg/L]			< 20	
δ ¹⁸ O	[‰VSMOW]		-10.90	-11.47	
δ ² H	[‰VSMOW]	100	110.0	108.2	D ₂ O

* calculated from the weighed-in chemical compounds; pH measured; CO₂-Ar bubbling not taken into account.

Tab. 4.7-13: Recipe for the artificial porewater for a 2-litre batch

Chemical	Manufacturer	Grade	Recipe		weighed in
			[g/kg w]	[g/2kg w]	[g/2 L]
NaHCO ₃	Merck	p.a.	0.2051	0.4101	0.4102
CaCl ₂ ·2H ₂ O	Merck	p.a.	1.8465	3.6930	3.6923
KCl	Merck	p.a.	0.1514	0.3029	0.3031
MgCl ₂ ·6H ₂ O	Merck	p.a.	1.8907	3.7814	3.7824
NaCl	Merck	p.a.	7.1916	14.3831	14.3800
Na ₂ SO ₄	AnalaR NORAMAPUR	Ph.Eur.	3.4089	6.8177	6.8171
D ₂ O (100 %)	Roth	> 99.8 % D	0.0310	0.0620	0.0659

4.7.5.2 Physical conditions, hydraulic conductivity, sampling, and pore volume equivalents

All core samples were subjected to 63 – 65 bar hydraulic confining pressure, and an infiltration pressure of initially 48.7 bar set by a He headspace. The infiltration pressure was gradually decreasing with time (displaced APW, and any small He leak), and was replenished about 5 times until the end of the last experiment. The pressure range covered 47.5 – 49.5 bar. The only exception, experiment BUL-1 (811.12 m, 'Parkinsoni-Württembergica-Schichten') was initiated at 40 bar infiltration pressure for the first 6 days, followed by 48.5 bar average pressure.

Temperature conditions were stable without diurnal fluctuations, ranging seasonally from 21.5 to 25.5 °C. Critical temperature-sensitive measurements, such as electric conductivity, pH and hydraulic conductivity, were temperature-compensated, either intrinsically or explicitly (details in Waber ed. 2020).

Hydraulic conductivity referenced to 25 °C was evaluated for all sampled aliquots based on sample mass and Darcy's law (detailed data in Appendix 3, method in Waber ed. 2020). Earliest aliquots commonly show low apparent hydraulic conductivities due to the expulsion of gas from the dead volume in the outflow, and any small unsaturated volume in the sample core itself. All cores (Fig. 4.7-4) except one share an initial maximum hydraulic conductivity that is gradually decreasing with time, approaching a steady-state value. The values for the early conductivity and that measured towards the end of the experiments (Tab. 4.7-14) span a relatively narrow range from $0.8 - 1.4 \times 10^{-13}$ m/s. This conductivity refers to a direction perpendicular to bedding and a sample length of 8 – 9 cm, measured at very large hydraulic gradients (Tab. 4.7-2). A gradual but rather minor decrease after an early maximum value may be due to slow sample consolidation, and this was also observed in earlier work (Mäder 2018). These latter values are most representative for in situ conditions, although the confining stress of 60 bar (6 MPa) in the experiments is still considerably less than the lithostatic stress at 800 – 1'000 m depth.

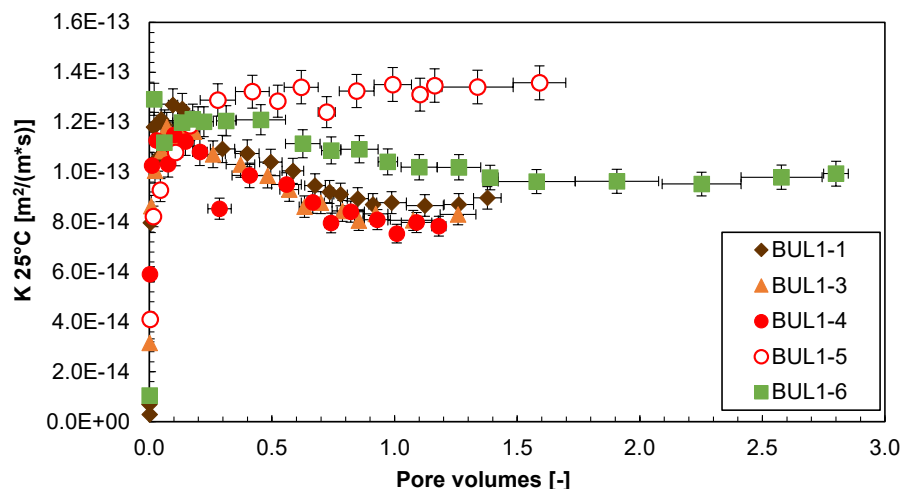


Fig. 4.7-4: Evolution of hydraulic conductivity during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties.

Tab. 4.7-14: Hydraulic conductivity of AD samples

Parameter	Unit	BUL1-1	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	877.03	924.18	987.55	1'011.62
Geological unit		'Park.-Württ.-Sch.'	Wedelsandstein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
Early_K (25 °C)	[m/s]	1.27×10^{-13}	1.18×10^{-13}	1.15×10^{-13}		1.11×10^{-13}
Late_K (25 °C)	[m/s]	8.97×10^{-14}	8.31×10^{-14}	7.83×10^{-14}	1.36×10^{-13}	9.94×10^{-14}

The time axis for all data representations of sequential fluid aliquots is converted to pore volume fractions by dividing the cumulative sample mass (volume) by the water content of the core. In this way, experiments with very different hydraulic conductivities or different water contents can be represented in a meaningful way for transport. There may be some minor ambiguities in case where water contents from pre-characterisation deviate from the true water content of a sample core, or if a significant initial unsaturated porosity fraction would be present. The chosen approximation is sufficient for a visual presentation of data.

Sampled aliquots (mass) plotted versus pore volume fraction (time) provides an overview of all syringe samples taken for all five successful AD experiments (Fig. 4.7-5). Up to 20 samples were collected.

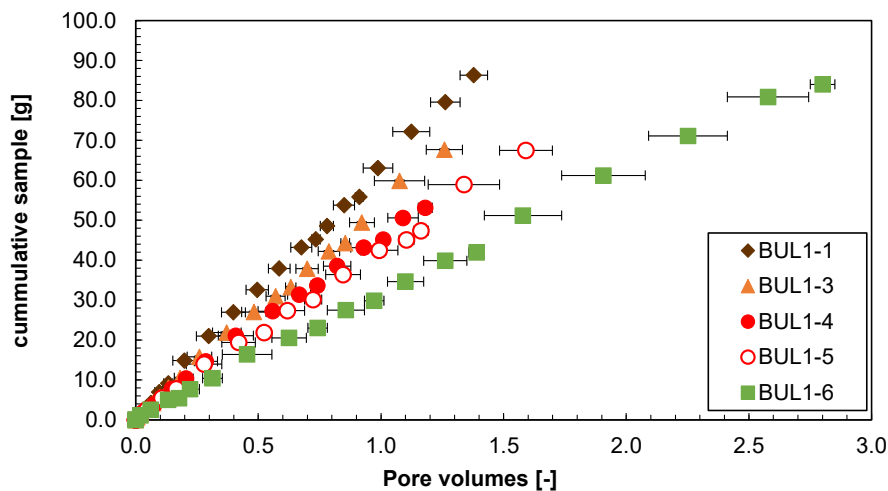


Fig. 4.7-5: Sampling schedule and sample volumes taken

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelegg Formation). Each data point represents a syringe aliquot taken, with the horizontal bar indicating the duration for sampling, here converted to pore volume fraction percolated. Different slopes reflect different volumetric flow rates scaled by porosity.

4.7.5.3 Inline measurement of electric conductivity and pH

Electric conductivity (EC) was continuously monitored in all experiments (Fig. 4.7-6, Waber ed. 2020, for method). Conductivity cells were initially calibrated, but may show a drift to varying extent over time due to electrode corrosion, commonly resulting in low apparent readings. The

artificial porewater injected has a lower conductivity compared to the displaced porewater for all experiments, and this value of the APW is gradually reached with progress of advective displacement. Some – or all – of the steps seen in several experiments may be due to corrosion effects, or to stagnant gas bubbles residing in the cell that would also decrease the EC readings.

The electric conductivities at early times (at/near maximum) are all similar, 35 – 39 mS/cm (22 °C laboratory reference), except for the shallowest core (BUL1-1, 'Parkinsoni-Württembergica-Schichten') with only 27 mS/cm initially. These values are only meant to provide an indication of salinity but are not used quantitatively due to corrosion issues mentioned above that may affect EC readings with increasing duration. This is indicated by the value obtained for the APW during initial calibration (ca. 18.3 mS/cm) that is above a value of 16 – 18 mS/cm that is approached towards the end of the percolation experiments. Specifically, a calibration offset of 1 mS/cm was established for BUL1-5 by post-mortem re-calibration for the APW. This sample also shows a jump in EC to lower values after percolation of 0.6 pore volumes, and this is interpreted as a sudden apparent decrease in conductivity due to corrosion. Corrosion may not only affect the inner surface of the flow-through electrodes, but may also lead to diffusion-dominated short-circuits between the two electrodes. Alternatively, data may indicate that a full breakthrough of the APW is not achieved and some ionic strength is precipitated in the samples (e.g. sulphates).

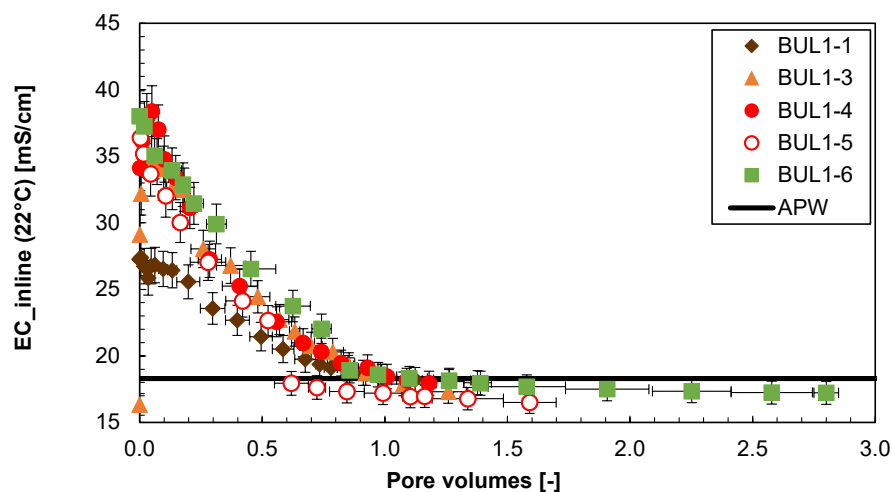


Fig. 4.7-6: Evolution of electric conductivity (22 °C) during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffellegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties.

The aim was to measure pH inline three times before/after sampling of the first four aliquots, and less frequently at later times (method in Waber ed. 2020). Measurements took 12 – 24 hrs in most cases, to ensure that the dead volume of the very small flow-through pH cell was sufficiently flushed given the very slow flow rates of the experiments. The micro-electrode was left installed in the flow-through cell and was checked before and after each pH measurement period with a standard solution. The initial calibration was made at pH 7 and 9, and simple drift checks and corrections were made with a standard solution at pH 7. The electrode slope was checked from

time to time and was found to remain remarkably stable. In most cases, drift corrections over 12 – 24 hrs were ≤ 0.1 pH units. The overall uncertainty is difficult to assess because these small electrodes may respond to manipulations at the flow-through cell (response to small strains) and also small gas bubbles may temporarily affect readings. It is estimated that an error of ± 0.2 pH units is appropriate for most measurements. pH values of early aliquots are also tabulated below.

These in-line pH measurements (Fig. 4.7-7) are rather tricky and require careful handling of equipment. Criteria to accept a value include a small drift and a reasonably well-defined pH-plateau. It cannot be excluded that for long measurement durations some effect from outgassing or in-gassing may influence the readings. The measurement series define rather smooth trends, and this indicates that random errors or disturbed signals are not a dominant feature. More details are discussed further below.

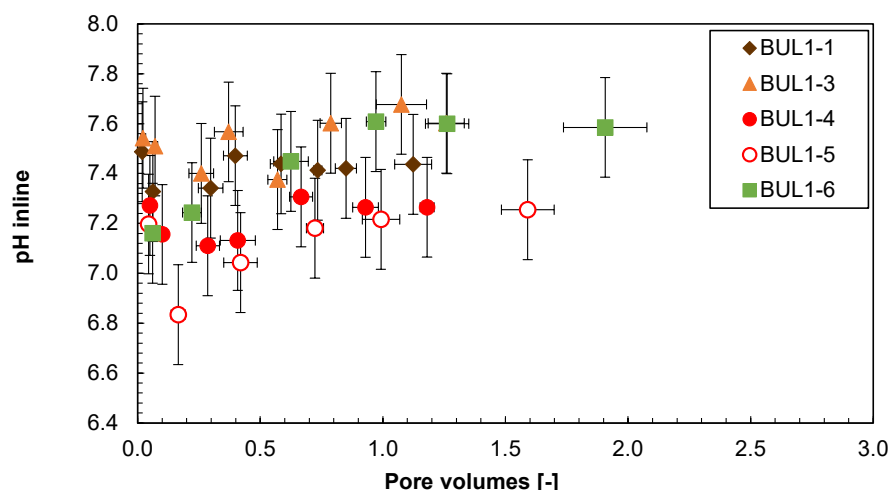


Fig. 4.7-7: Evolution of inline pH during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffellegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties.

4.7.5.4 Evolution of major and minor components

Evolution of concentrations with progress of percolation are shown in Figs. 4.7-8 to 4.7-13. Select analytical data for the first two aliquots sampled are summarised in Tab. 4.7-15 further below, with full details in Appendix 3. The composition of the earliest aliquots displaced from the core samples are the most representative for the pore fluid extracted, and this is highlighted and interpreted in a separate Section 4.7.5.5.

Major components (Cl, SO₄, Na, Ca, Mg) displaced initially are all more concentrated than in the APW (Fig. 4.7-8) except for sulphate that elutes initially only at slightly elevated concentrations. Also, cation concentrations tend to converge to APW concentrations with progress of percolation attesting to an ion-exchanger population in situ that is compatible with ion ratios in the APW (but different in ionic strength). An exception is Mg that tends to decrease with time (pore volume) to concentrations below the APW, largely compensated by Na concentrations (detailed

in Fig. 4.7-9). Ion-exchange equilibrium with the APW across the entire sample core is not yet reached in the experiments and this would require several more pore volumes of percolation. Sr concentrations are shown further below at an expanded scale.

For several components an early period of small gradient is seen for the first 2 – 3 aliquots, such as for Cl in most cases, and this is interpreted to represent the porewater composition displaced from the core sample at the imposed physical conditions. This early phase spans the percolation period required for 0.05 – 0.1 pore volume fractions. A choice was made to use average compositions of the first two analysed aliquots to represent this pore fluid composition, and these values are summarised in Tab. 4.7-15 (Section 4.7.5.5), and are also used in the integrative plots in Chapter 5.

The same information as depicted in Fig. 4.7-8 is summarised for select components for all experiments (Fig. 4.7-9). Chloride concentrations perfectly merge with the APW as percolation progresses. This is not the case for all experiments for sulphate. Mg concentrations tend to evolve to concentrations distinctly below the APW (except for BUL1-1, 'Parkinsoni-Württembergica-Schichten'), attesting to an imbalance with the exchanger.

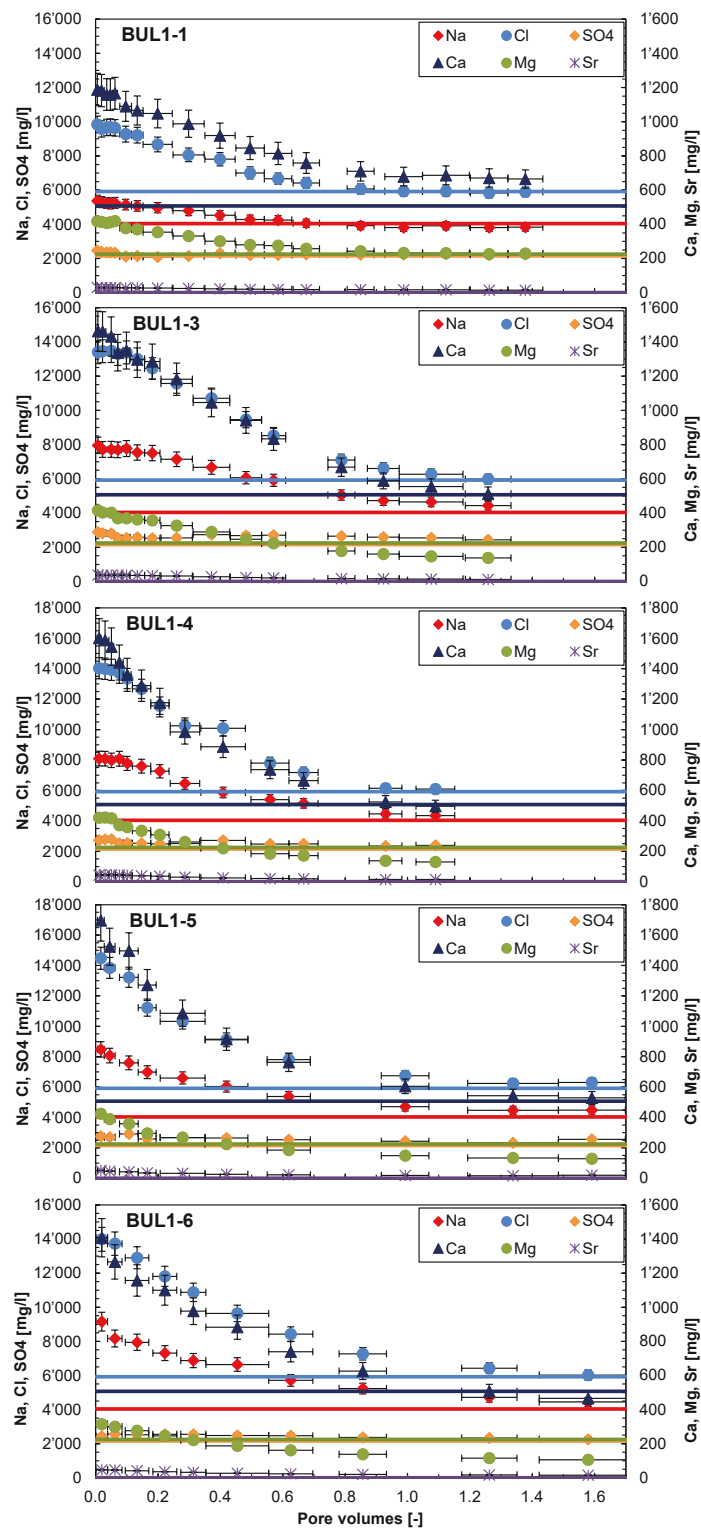


Fig. 4.7-8: Evolution of major components during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties. Horizontal lines represent the composition of the injected APW. Data for BUL1-6 is truncated and would extend to 2.8 pore volume fractions.

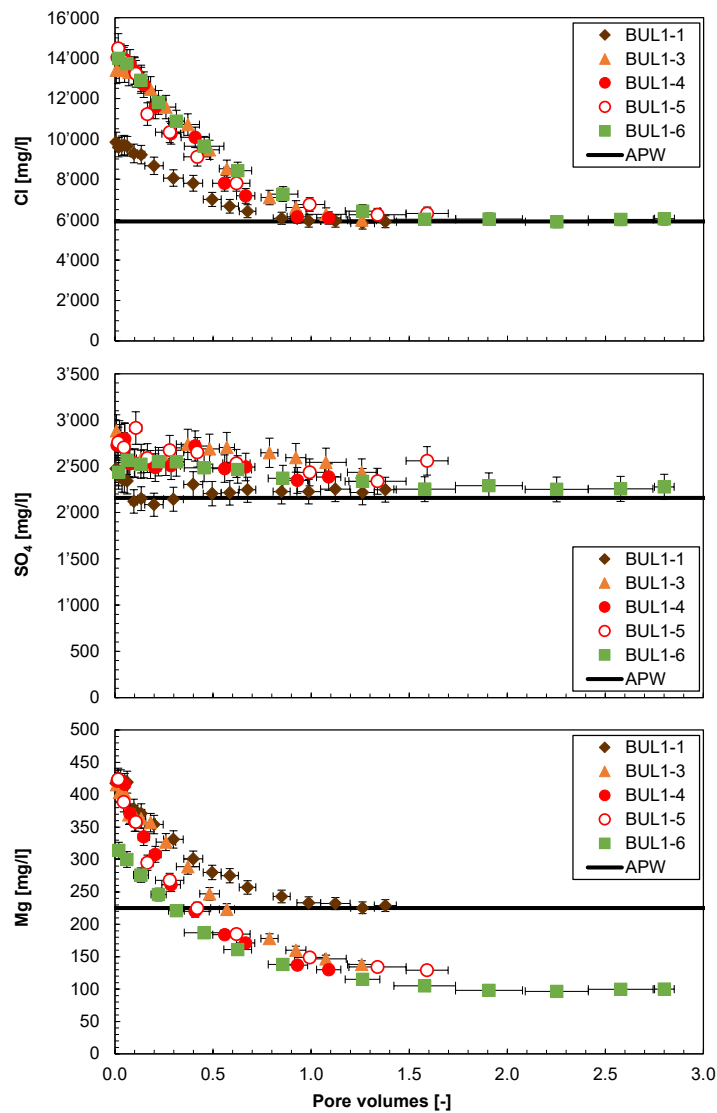


Fig. 4.7-9: Evolution of select major components during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffellegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties. Horizontal lines represent the composition of the injected APW.

Of the **minor components (Br, NO₃, K, Sr, Si)**, only potassium is present in the injected APW, and the evolution is decreasing from concentrations near the APW to lower concentrations, clearly a transient effect of ion-exchange (Fig. 4.7-10). Strontium is gradually decreasing in all experiments (details in Fig. 4.7-11). Bromide elutes from initial values representative of the pore fluid (20 – 24 mg/L) to very low values, just by being flushed out (details in Fig. 4.7-11). This can be used as a reversed break-through of an anionic tracer (see below). Dissolved silica elutes from initial 5 – 6.5 mg/L to slightly lower values with time/pore volume.

The elution behaviour of NO₃ is somewhat variable (Fig. 4.7-9, Tab. 4.7-15, Appendix 3): early values exclusive of BUL1-5 are from 10 – 20 mg/L, and decreasing to below a detection limit of 1.6 mg/L within 0.03 – 0.3 pore volumes of percolation. The sample from the Staffelegg Formation (BUL1-5) contains 45 mg/L nitrate in the first aliquot, decreasing to below detection after 0.6 pore volumes. Ammonium (NH₄) is below a detection limit of 10 mg/L, except for a substantial concentration of 144 mg/L measured in the first aliquot of BUL1-3 (Wedelsandstein Formation).

Iodide concentrations were 4.4 – 7.6 mg/L (Tab. 4.7-15) in early aliquots, not detected in earliest aliquots from BUL1-6 (Staffelegg Formation), and 29 mg/L in BUL1-1 ('Parkinsoni-Württembergica-Schichten'). Iodide was not detected in the aqueous extracts (< 0.1 mg/L).

Ba and Al were measured by ICP-OES but always below detection limits. The detection limits depend on dilution factors and were 0.25 – 1 mg/L for Ba, and 1 – 2 mg/L for Al (10 mg/L in some cases with large dilutions).

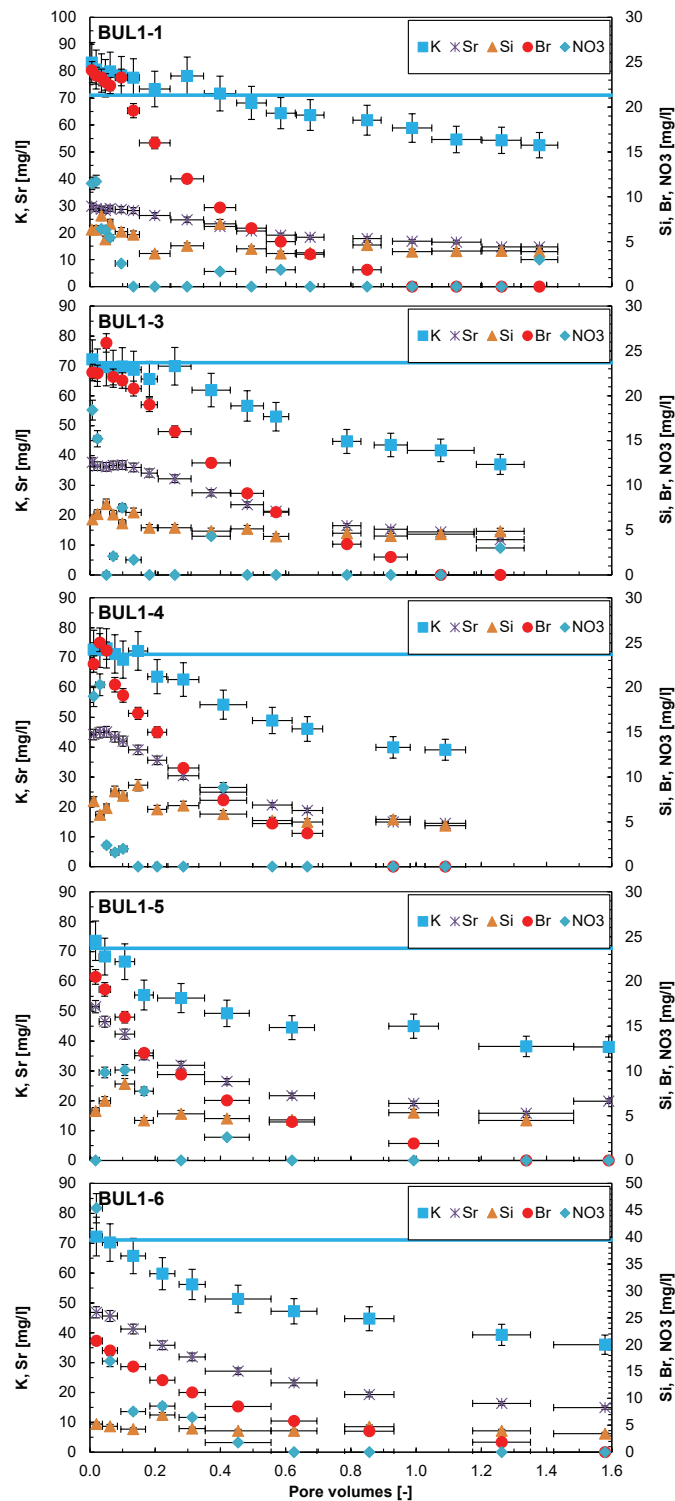


Fig. 4.7-10: Evolution of minor components during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffellegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties. Horizontal line represent the composition of the injected APW for K (0 for others). Data for BUL1-6 is truncated and would extend to 2.8 pore volume fractions.

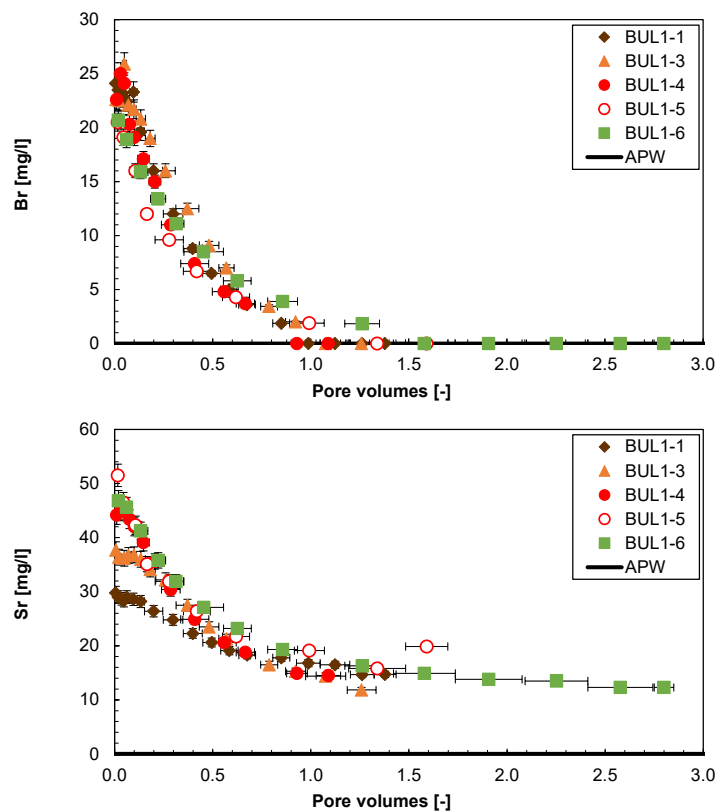


Fig. 4.7-11: Evolution of select minor components during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174-345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties. Br and Sr in the APW are 0. Br concentrations below detection are plotted at 0.

The **carbon system (TIC, TOC, TC, lmwoa)** shares as a common feature, namely that relatively large TOC concentrations are eluted initially (350 – 1'100 mg/L) that gradually decrease to 30 – 100 mg/L with progressive percolation (Fig. 4.7-12, Tab. 4.7-15 shows averages of first 2 aliquots). TOC clearly dominates the dissolved carbon inventory (TC) at early times. Some 10 – 25 % of TOC is explained by low-molecular-weight organic acids (LMWOA), namely acetate and very minor formate. Acetate concentrations of up to 860 mg/L (Fig. 4.7-12 shows acetate and formate as carbon equivalents, Fig. 4.7-13 in mg/L) were measured in one of the Opalinus Clay samples (BUL1-4). Aqueous extracts (Tab. 4.7-6) imply TOC values 300 – 1'500 mg/L when scaled to porewater content and this covers well the range seen in the early aliquots. Aqueous extracts carried out post-mortem (Tab. 4.7-8) show a clear depletion of TOC compared to the initial state by a factor of 2 – 4. The strongest depletion by a factor of 12 is seen in the Opalinus Clay sample that elutes initially the most TOC (BUL1-4). These observations are similar to previous work, with samples from the Schlattingen-1 geothermal well (Mäder & Waber 2017).

TIC elutes initially at much lower concentrations than TOC, but covers a wide range of concentrations, and trends for each experiment are dissimilar to some extent (Figs. 4.7-12, 4.7-13). There is an unusually large TIC value of 235 mg/L obtained for the 1st analysed syringe of BUL1-5 (Opalinus Clay), but only 47 mg/L in a subsequent sample. Tab. 4.7-15 contains average concentrations and the corresponding value is still considered anomalously high.

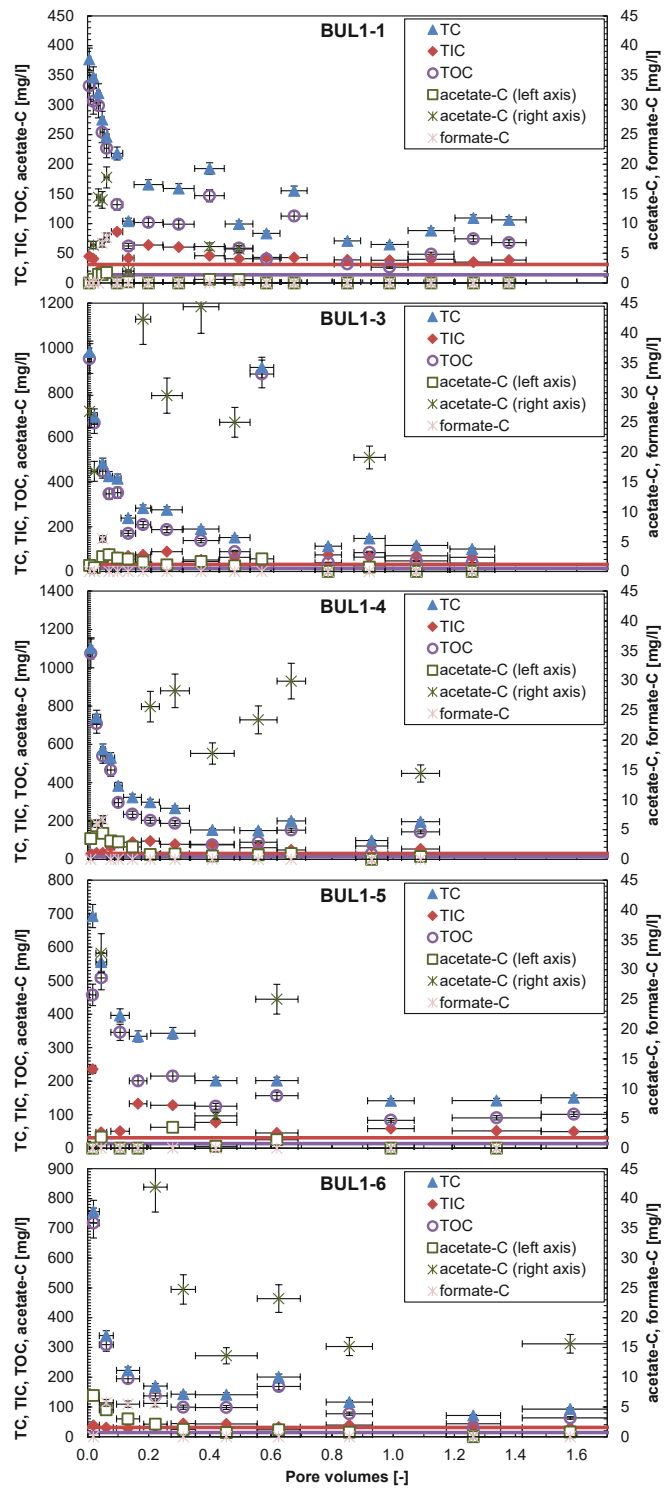


Fig. 4.7-12: Evolution of carbon system during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties. Horizontal lines represent the composition of the injected APW. Data for BUL1-6 is truncated and would extend to 2.8 pore volume fractions.

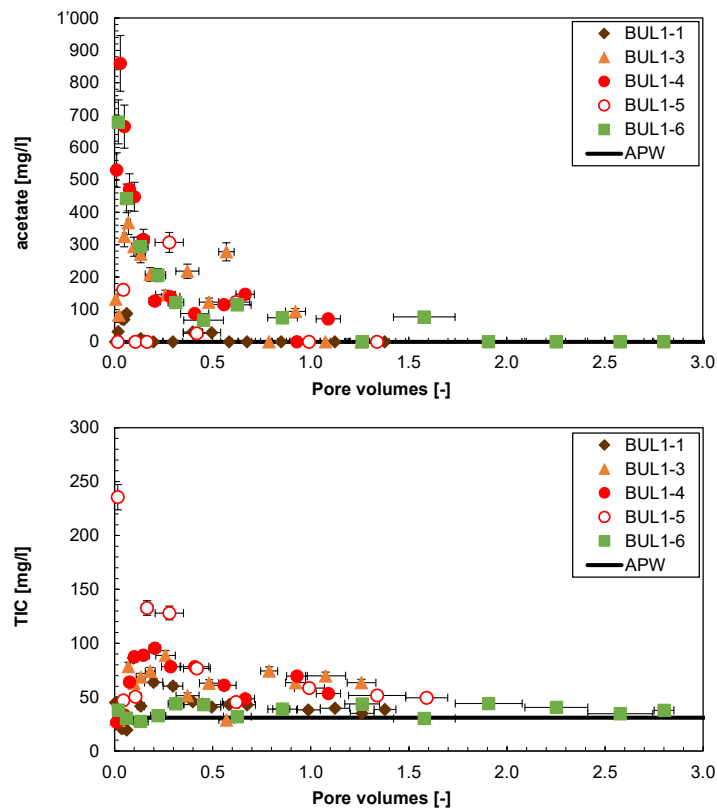


Fig. 4.7-13: Evolution of select carbon components during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties. Horizontal lines represent the composition of the injected APW. Concentrations below detection (acetate) are plotted at 0.

Because microbial activity may be an issue during extended sampling durations (e.g. organic carbon oxidation, sulphate reduction), a test was made to pre-load some syringes with a known amount of Na-chromate solution as an inhibitor. This was done for all BUL1 experiments for 2 – 3 syringes during later stages of advective displacement. Samples included are 1715, 1717, 1718, 3713, 3715, 3716, 4715, 4716, 5711, 5712, 6713, 6714 (keyed to analysis numbers, e.g. BUL1-1715-AD, Appendix 3). Of these twelve samples, seven were analysed, and no systematic deviations in TOC and TIC were detected compared to trends defined by samples not treated. This procedure was dismissed for subsequent samples. Stable isotope compositions cannot be measured on these samples due to the chromate admixture, and the chromate has to be removed by cartridge filters prior to analysis and this is inconvenient for small samples. The **measurement of pH** was performed in-line between some of the sampling intervals (setup in Waber ed. 2020) and in the laboratory when syringe aliquots were prepared/preserved for analysis. The latter was done in most cases very shortly after sampling (one to a few hours), or after a few days of cold storage. The total range covered for all samples, in-line and laboratory, is 6.8 – 7.8 (Fig. 4.7-14), with laboratory values showing more spread than the in-line measurements.

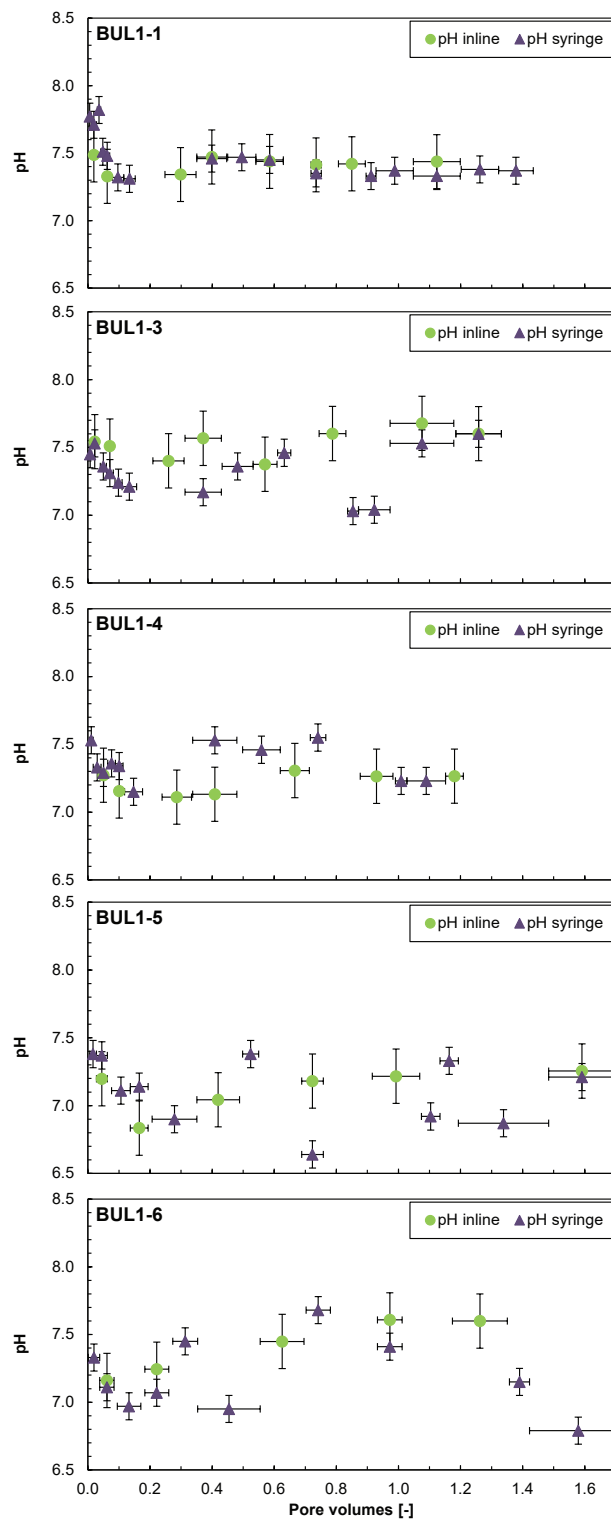


Fig. 4.7-14: Evolution of pH during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedel-sandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval, vertical bars are an estimate of combined uncertainties. Data for BUL1-6 is truncated and would extend to 2.8 pore volume fractions.

All experiments show an early decreasing trend for pH measured in the laboratory, but this is less clearly seen in the early in-line values. The in-line pH series define relatively smooth trends with percolation progress, but not a very systematic behaviour. The spread is relatively small, ranging from 0.2 – 0.5 pH units. Some of the low apparent pH values measured in syringe samples may relate to sample storage issues, including microbial activity. The partial pressure of CO₂ is larger than atmospheric in the aliquots, and this bears the potential for outgassing and resultant supersaturation with respect to calcite, and a possibility for some loss of Ca and TIC by precipitation.

4.7.5.5 Early displaced aliquots representing the porewater composition

Interpretation of early displaced aliquots (Tab. 4.7-15) – tabulated as averages of the first two samples – as being representative of the in situ porewater contained in the core at the time of the experiment requires integration and interpretation of the entire data set supported with geochemical calculations. Only speciation calculations are included in this data report for the early compositions. A reduced TIC value of 47 mg/L was used for BUL1-5 (Opalinus Clay), corresponding to the value of the 2nd aliquot instead of the average value that is biased by a very large TIC value obtained from the 1st aliquot (see comment above, section on the carbon system). In-line pH values were used for the speciation calculations.

The speciation calculations (Tab. 4.7-16) reveal a cation charge surplus (positive 'Charge') that is not large and partially explained by significant acetate concentrations that were not included in the speciation, but listed in the table. TIC was used as constraint for inorganic carbon. The aliquots are all significantly oversaturated with respect to calcite and also dolomite. Such oversaturation may result from shifts in pH linked to potential in-gassing or outgassing of CO₂ during sampling and storage. Alternatively, the large TOC (and TC) contents pose analytical difficulties to obtain TIC and associated errors may be larger than commonly assigned to TIC measurements.

Saturation is also reached or slightly exceeded for celestite and gypsum. The implication is that the ion-activity products ($[Sr] \cdot [SO_4]$) and ($[Ca] \cdot [SO_4]$) are controlling factors, but this does not necessarily mean that these minerals are also present in the core before the experiments. There is only a small difference between sulphate concentrations in the APW and the early aliquots (Fig. 4.7-8) for all experiments, but both Ca and Sr are eluted initially at much higher concentrations compared to the APW, and are decreasing quite rapidly. To maintain above mentioned ion-activity products at the value of the equilibrium constant, the decreasing cation concentrations are compensated by increasing activity coefficients as a function of decreasing ionic strength. These cation trends are therefore coupled to the relatively rapid breakthrough of the anions that dictate the evolution of the ionic strength. A more in-depth analysis and interpretation will have to be carried out, including reconstructions by geochemical modelling.

Tab. 4.7-15: Composition of earliest aliquots from advective displacement experiments

Parameter / exp		BUL1-1	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth [m]		811.12	877.03	924.18	987.55	1'011.62
Geological unit		'Park.-Württ.-Sch.'	Wedelsandstein Fm.	Opalinus Clay	Opalinus Clay	Staffelelegg Fm.
pH inline	[-]	7.49	7.54	7.27	7.20	7.16
pH lab	[-]	7.74	7.49	7.43	7.38	7.22
Na	[mg/L]	5'334	7'833.5	8'089.5	8'276	8'661.5
NH ₄	[mg/L]	< 10	144	< 10	10	10
K	[mg/L]	81.9	70.8	72.95	70.95	71.2
Ca	[mg/L]	1'185	1'461.5	1'594	1'610	1'337
Mg	[mg/L]	416.25	409.55	421.2	406.5	307
Sr	[mg/L]	29.4	37.05	44.55	49	46.22
Ba	[mg/L]	< 1	< 1	< 1	< 0.5	< 0.5
Si	[mg/L]	6.34	6.49	6.53	6.085	5.01
Al	[mg/L]	< 2	< 2	< 2	< 1	< 1
F	[mg/L]	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6
Cl	[mg/L]	9'711.5	13'426.5	14'013	14'162.5	13'854
Br	[mg/L]	23.8	22.55	23.8	19.8	19.8
NO ₃	[mg/L]	11.6	16.8	19.65	9.83	31.175
SO ₄	[mg/L]	2'435	2'852.5	2'754.5	2'730	2'500
I	[mg/L]	29.1	7.59	5.735	4.44	N/A
TOC	[mg/L]	319	808	891.5	483.05	513.5
TIC	[mg/L]	42.9	29.25	30	141.3	34.2
lactate	[mg/L]	< 20	< 20	< 20	< 20	< 20
acetate	[mg/L]	31.4	107.25	695.5	161	561
propionate	[mg/L]	< 20	< 20	< 20	< 20	< 20
formate	[mg/L]	< 20	< 20	22.4	< 20	21.36
δ ¹⁸ O	[‰VSMOW]	-2.11	-2.85	-3.30	-3.73	-3.55
δ ² H	[‰VSMOW]	-44.9	-42.7	-43.7	-40.4	-38.3

Tab. 4.7-16: Saturation state of earliest aliquots from advective displacement experiments

Parameter	Unit	BUL1-1	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	877.03	924.18	987.55	1'011.62
Geological unit		'Park.-Württ.-Sch.'	Wedelsandstein Fm.	Opalinus Clay	Opalinus Clay	Staffellegg Fm.
Charge	[eq]	-4.7×10^{-4}	1.4×10^{-2}	1.4×10^{-2}	1.7×10^{-2}	2.6×10^{-2}
% Error		-0.07	1.55	1.51	1.83	2.88
Acetate	[eq]	4.4×10^{-4}	1.8×10^{-3}	1.2×10^{-2}	1.5×10^{-3}	9.5×10^{-3}
Ionic strength	[mol/kg w]	0.37	0.50	0.52	0.53	0.51
tot_alk	[eq/kg]	3.57×10^{-3}	2.54×10^{-3}	2.46×10^{-3}	3.81×10^{-3}	2.74×10^{-3}
pH		7.49	7.54	7.27	7.20	7.16
log P(CO ₂)	[bar]	-2.36	-2.59	-2.32	-2.06	-2.15
SI (calcite)		0.80	0.74	0.50	0.63	0.38
SI (dolomite-o)		1.51	1.30	0.81	1.05	0.51
SI (dolomite-d)		0.96	0.75	0.26	0.50	-0.04
SI (gypsum)		-0.05	0.02	0.04	0.03	-0.06
SI (celestite)		0.06	0.15	0.20	0.24	0.20
SI (anhydrite)		-0.27	-0.19	-0.17	-0.17	-0.27

WATEQ4F thermodynamic data base; dolomite-o: ordered dolomite; dolomite-d: disordered dolomite.

4.7.5.6 Initial values and evolution of stable water isotope composition

Common to all five experiments (Fig. 4.7-15) is a relatively smooth evolution of $\delta^{18}\text{O}$ towards the APW value with progress of percolation. Unlike some major chemical components (e.g., chloride), the breakthrough trend starts immediately already with the first sample aliquot. There is the occasional apparent outlier that plots off the rather well-defined trends and these may relate to issues of sampling, storage and sample preparation (very small samples had to be processed in some cases).

The behaviour for $\delta^2\text{H}$ is distinctly different and shows initially a reverse trend that goes through a minimum after percolation of 0.15 – 0.25 pore volumes. The extent of breakthrough is much less compared to $\delta^{18}\text{O}$ for reasons that may not be intuitively obvious.

One hypothesis is that there is an effect from dry cutting the core surfaces during sample preparation that might lead to heavier isotopic residues due to a small amount of evaporation. Percolation would then first yield water isotopes that are too heavy, and that are gradually mixed with the in situ signature, and increasingly also affected by the breakthrough of the heavy traced APW (ca. +100 ‰ for $\delta^2\text{H}$, -11.5 ‰ for $\delta^{18}\text{O}$). For $\delta^{18}\text{O}$ a reverse situation is the case, namely that the APW is significantly lighter than the in situ porewater, such that any evaporation effect would initially tend to deliver slightly too heavy aliquots, a possible explanation for the immediate apparent breakthrough behaviour. The suspected evaporation effect on $\delta^{18}\text{O}$ is much less than on $\delta^2\text{H}$. A more in-depth analysis is attempting to quantify this process. In past studies, wet cutting was used rather than dry cutting, and this led to a small component of contamination by tap water seen on the early extracted water isotopes (details in Mäder & Waber 2017). The high contents of DOC may also influence the water isotopic system, or any microbial activity, as well as any precipitation of hydrous minerals that may be induced by advective displacement.

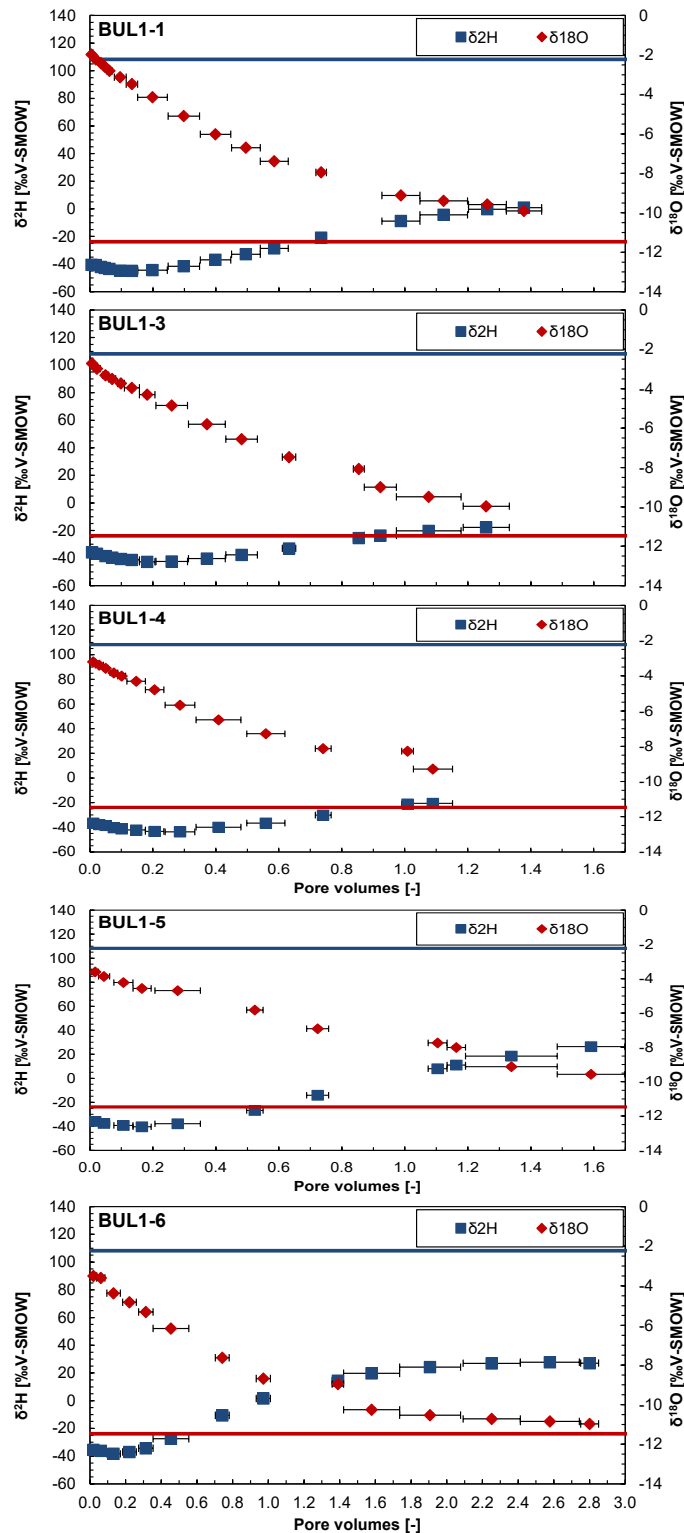


Fig. 4.7-15: Evolution of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Stäffelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers the sampling interval. Measurement errors are 1.5 ‰ for $\delta^2\text{H}$ and 0.1 ‰ for $\delta^{18}\text{O}$. Horizontal lines represent the composition of the injected APW.

The observed differences between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ concerning the extents of breakthrough are discussed below.

The stable isotope composition in $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ coordinates (Fig. 4.7-16) displays a slightly curved data array for each experiment extending from the earliest and isotopically light ($\delta^2\text{H}$) / heaviest ($\delta^{18}\text{O}$) extracts towards the APW isotopic composition. Earliest aliquots of each experiment (on right side of arrays) define a trend distinctly below the global meteoric water line, and also slightly inclined towards the GMWL with increasing sample depth. This is compared to other data sources in more details in Chapter 5.

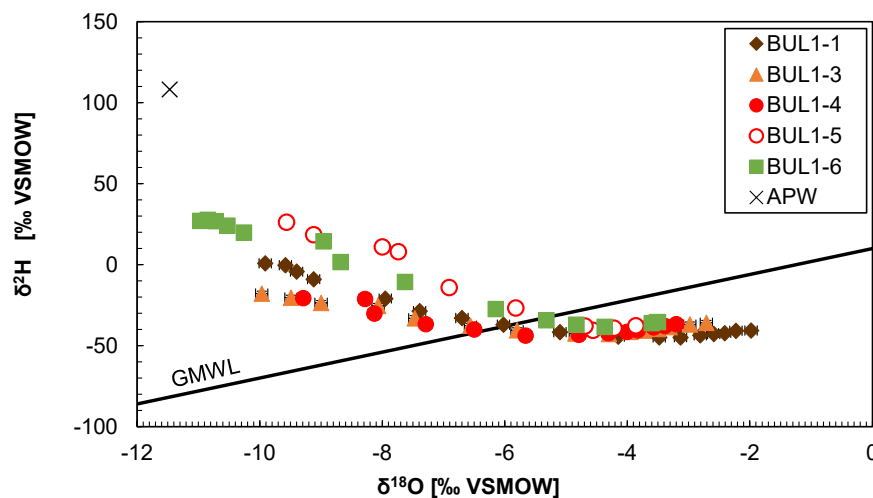


Fig. 4.7-16: Stable isotope composition of aliquots from advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelegg Formation). Measurement errors are 1.5 ‰ for $\delta^2\text{H}$ and 0.1 ‰ for $\delta^{18}\text{O}$. GMWL is the global meteoric water line. 1st aliquots are located the furthest to the right, and evolve towards the left.

4.7.6 Derivation of anion-accessible porosity

There are several ways by which chloride and bromide accessible porosity fractions may be obtained. The principle is the same: namely the ratio between the anion concentration obtained from aqueous extracts up-scaled to porewater content divided by that obtained from earliest extracts from the percolation experiments (discussion in Waber ed. 2020 and Mäder 2018). In case a full breakthrough is captured for chloride and bromide, such a ratio may also be obtained by post-mortem aqueous extracts and the latest aliquots sampled before the end of the experiments. In most cases bromide drops below detection and only the chloride data can be evaluated. There are some variants depending on how water contents were measured and averaged.

The top three data lines (Tab. 4.7-17) list the average concentrations (Cl, Br) for the first two aliquots, and that of the last aliquot for Cl. The subsequent six lines list the up-scaled concentrations to water content, in three different ways for both chloride and bromide. The suffix "_top" indicates that a subsample was used adjacent to the top of the core for water content and aqueous extract, and "_base" in analogy to a subsample adjacent to the base. The observed range in up-scaled concentrations is an indication of heterogeneity, mainly in water content. The suffix

"_ave_corr" indicates averaging of data from top and base, and also applies a correction for the initial water content by measurement of the post-mortem water content obtained from the core itself (Section 4.7.3 and Tab. 4.7-3). The following two lines list the chloride concentrations obtained from post-mortem analysis (a disc from the top, one from the base) up-scaled to water content. The last data block lists the accessible porosity fraction obtained by various combinations. The first four lines list values that would be derived without knowledge from post-mortem analysis (water content from pre-characterisation), with the most meaningful combinations shaded in grey. Shaded in blue are the "best" values after applying a correction for water contents as mentioned above. Finally, the last line highlighted in blue are ratios obtained from post-mortem analysis for chloride using aqueous extracts from the base of a core (APW inlet). It appears that in three experiments the chloride breakthrough was not complete enough to reach the top of the sample (outflow) as seen in still slightly elevated chloride concentrations in the extracts (shaded in brown) that would lead to apparent larger accessible porosity fractions (2nd last line, shaded in brown).

Tab. 4.7-17: Chloride and bromide-accessible porosity fractions

Preferred values are shaded in blue.

Parameter	Unit	BUL1-1	BUL1-3	BUL1-4	BUL1-5	BUL1-6
Depth	[m]	811.12	877.03	924.18	987.55	1'011.62
Geological unit		'Park.- Württ.-Sch.'	Wedelsand- stein Fm.	Opalinus Clay	Opalinus Clay	Staffelegg Fm.
Cl-AD_ave (1-2)	[mg/L]	9'712	13'427	14'013	14'163	13'854
Br-AD_ave (1-2)	[mg/L]	23.80	22.55	23.80	19.80	19.80
Cl_AD_last	[mg/L]	5'897	5'981	6'084	6'308	6'043
Cl-AqEx-upscaled_top	[mg/L]	4'196	6'602	6'521	5'842	
Cl-AqEx-upscaled_base	[mg/L]		6'108	6'037	5'829	7'418
Cl-AqEx-upscaled_ave_corr	[mg/L]	4'392	6'069	7'437	6'043	7'160
Br-AqEx-upscaled_top	[mg/L]	10.25	12.98	12.04	8.59	
Br-AqEx-upscaled_base	[mg/L]		10.86	11.03	8.67	10.94
Br-AqEx-upscaled_ave_corr	[mg/L]	10.73	11.28	13.66	8.94	10.56
Cl-AqEx-upscaled_top_p-m	[mg/L]	3'195	3'492	3'242	2'551	3'028
Cl-AqEx-upscaled_base_p-m	[mg/L]	2'864	2'829	2'772	2'672	3'002
Cl-AqEx_top / Cl-AD_ave		0.43	0.49	0.47	0.41	0.54
Br-AqEx_top / Br-AD_ave		0.43	0.58	0.51	0.43	0.55
Cl-AqEx_ave / Cl-AD_ave			0.47	0.45	0.41	
Br-AqEx_ave / Br-AD_ave			0.53	0.48	0.44	
Cl-AqEx_ave_corr / Cl-AD_ave		0.45	0.45	0.53	0.43	0.52
Br-AqEx_ave_corr / Br-AD_ave		0.45	0.50	0.57	0.45	0.53
Cl_AqEx_p-m_top / Cl_last_AD		0.54	0.58	0.53	0.40	0.50
Cl_AqEx_p-m_base / Cl_last_AD		0.49	0.47	0.46	0.42	0.50

There is in general excellent agreement and consistency among the different ways of evaluation and pre-characterisation and post-mortem characterisation. This renders this data set quite robust. Sample BUL1-924.18 (Opalinus Clay) shows some modest discrepancy between non-corrected and corrected evaluations, and this is due to the fact that this core showed a small water loss rather than an uptake as seen in all other tests. It is unclear if this water loss is indeed reliable. The post-

mortem evaluation suggests otherwise, and agrees perfectly well with the uncorrected data and other measurements. There is also very good agreement between the chloride and bromide accessible porosity fraction, attesting among other factors to the excellent analytical work for bromide analysis at low concentrations in the aqueous extracts.

The five experiments span a range of accessible porosity fraction for chloride from 0.42 to 0.52, and 0.45 to 0.53 for bromide. This is quite consistent with earlier work from Opalinus Clay and 'Brauner Dogger'. The accuracy is limited by the basic assumptions underlying the approach and by sample heterogeneity to some degree, mainly in water content. The combined measurement uncertainties are dominated by the analytical error associated with Cl and Br concentrations, and are probably not more than $\pm 10\%$.

4.7.7 Transport properties marked by breakthrough of $\delta^2\text{H}$, $\delta^{18}\text{O}$, Cl and Br

There are four components that can be used to elucidate on transport properties by their breakthrough behaviour, namely Cl, Br, and the water isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$. Chloride is a good tracer in these experiments because the APW is distinctly less saline than the in situ porewater. The resolution towards a full breakthrough is diminished because small differences between large concentrations can no longer be resolved. Bromide is a breakout tracer that is gradually flushed out of the core (no Br in the APW). Again, as a full breakout is approached, bromide concentrations tend to fall below the detection limit. Water tracers also feature a contrast between the in situ porewater and the APW. Particularly, $\delta^2\text{H}$ was traced to ca. $+100\%$ in the APW, but also $\delta^{18}\text{O}$ has a contrast of nearly 10% .

For comparison (Fig. 4.7-17) all breakthrough data are normalised to 1 and the breakout of bromide is inverted to mimic a breakthrough behaviour. The normalised breakthrough of chloride, for example, is given by $1 - (\text{Cl} - \text{Cl}_{\text{APW}}) / (\text{Cl}_{\text{PW}} - \text{Cl}_{\text{APW}})$, where Cl_{PW} refers to the value of the first aliquot that most closely represents the in situ porewater composition. Chloride and bromide breakthrough are nearly identical, with bromide showing a small but consistent tendency to break through slightly faster than chloride. This same behaviour was illustrated in earlier work by Mäder (2018). Cl and Br achieve a full breakthrough before or at the end of the experiments. Bromide breakthrough cannot be tracked beyond the percolation progress where it drops below detection (seemingly missing points in Fig. 4.7-17). There are some few data points for Br at early times that seem to be outliers compared to an otherwise smoothly defined trend. It is not clear what the reason for this may be, but such behaviour was also observed in earlier work. There is some ambiguity in dealing with data scatter that may be present in the first few syringe compositions (e.g. Br), and the choice made to define the initial value that is used for normalisation of breakthrough curves. Different choices may shift curves somewhat but this is a minor effect for these relatively smooth data trends.

$\delta^{18}\text{O}$ breaks through more slowly compared to the anions Br and Cl, and does not reach a full breakthrough during the duration of the experiments. $\delta^2\text{H}$ displays an anomalous behaviour during the early breakthrough, possibly for reasons discussed in Section 4.7.5. Deuterium lags considerably behind oxygen suggesting some sort of retardation mechanism that is presently not well understood. The two water tracers may interact differently with the accessible porewater volumes and mineral surfaces. This behaviour was also observed with samples from the Schlattingen-1 geothermal well (Mäder & Waber 2017).

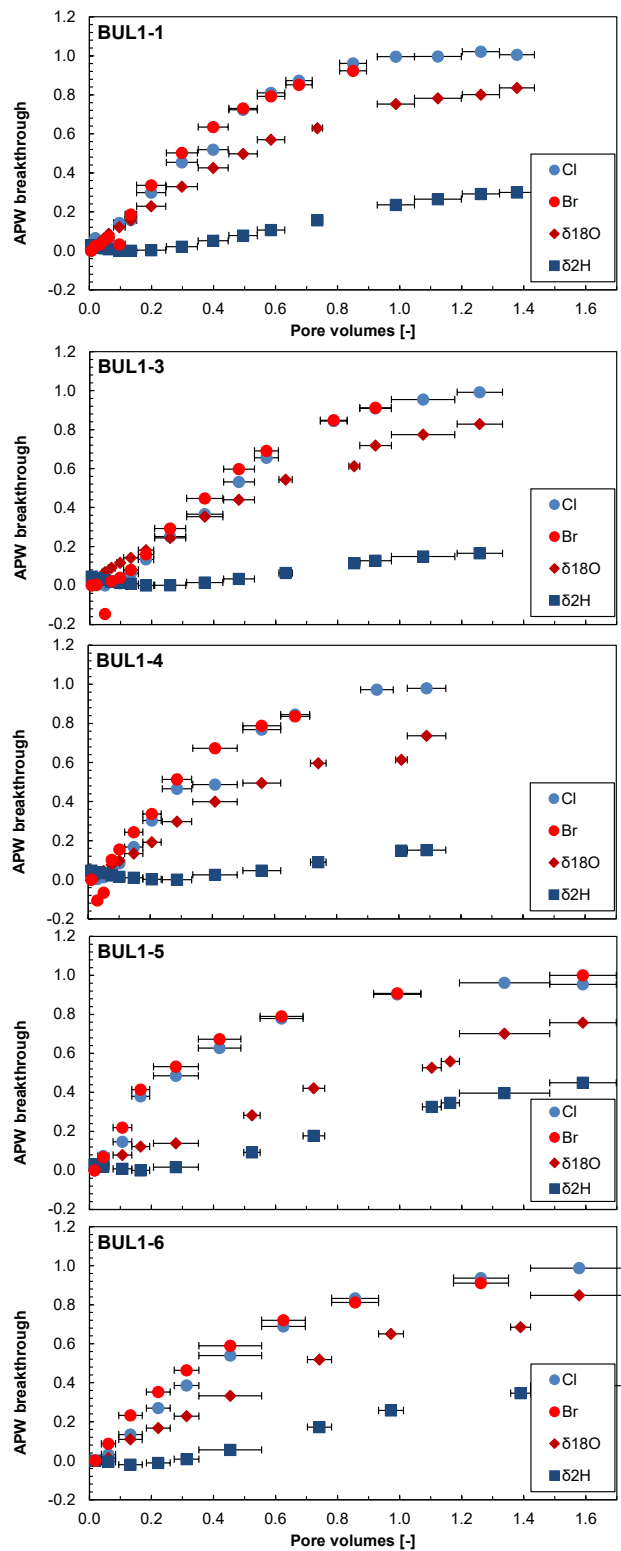


Fig. 4.7-17: Breakthrough of Cl, Br, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ during advective displacement experiments

BUL1-1 = 811.12 m ('Parkinsoni-Württembergica-Schichten'); BUL1-3 = 877.03 m (Wedelsandstein Formation); BUL1-4 = 924.18 m (Opalinus Clay); BUL1-5 = 987.55 m (Opalinus Clay); BUL1-6 = 1'011.62 m (Staffelegg Formation). Pore volume fractions relate to transport time based on water content. Experiment duration is 174 – 345 days. Horizontal length of symbol bar covers sampling interval. Data for BUL1-6 is truncated and would extend to 2.8 pore volume fractions.

4.7.8 Concluding remarks and open issues

Advective displacement experiments on samples from the clay-rich confining units supplied a large amount of systematic, consistent and plausible data on petrophysical and geochemical properties of high quality. Samples covered a clay content of 37 – 51 wt.-%, with similar proportions of (illite/smectite + smectite) compared to total clay, and a derived anion-accessible porosity proportion of 0.42 – 0.53 for chloride and bromide. The hydraulic conductivities are very similar for all core samples tested, but porosities differ and thus also volumetric fluxes induced by identical head gradients.

Earliest displaced aliquots are representative of the porewater contained in the sample cores, possibly subject to some artefacts, but these aliquots are not equally representative for the in situ porewater due to issues of drilling, unloading, handling and storage. While derived Cl and Br concentrations are robust with respect to such artefacts, the sulphate system in all aliquots appears to be controlled by celestite and gypsum equilibrium. This either implies that such a control is imposed by these minerals being initially present, or that a disturbance causes to reach such a solubility-product control. In the latter case, the reconstruction of the porewater sulphate concentration is more challenging, and also influences the carbonate system and clay-exchanger complex by ways of interdependent thermodynamic mass-action equilibria.

Like in all earlier work, there are unusually high concentrations of DOC mobilised in the earliest aliquots, decreasing gradually to values more in line with aqueous extracts, but still at significant concentrations. An interesting feature – not yet well understood – is the observed delayed breakthrough of deuterium ($\delta^2\text{H}$ traced in the APW) compared to $\delta^{18}\text{O}$ that elutes more regularly as expected for a water tracer.

There are no fundamental adaptations to the methods prompted by this study. The mechanical, hydraulic and electronic or sensor aspects of the experimental setup reliably performed for experimental durations up to almost a year. Likewise, the analytical procedures were already optimised and adequate, naturally limited by very small sample volumes for some cases.

4.8 Data from out-diffusion experiments

H. Niklaus Waber

Out-diffusion (OD) experiments are another methodology to get insight into the porewater – rock system. Originally designed for crystalline rocks (e.g. Waber et al. 2012), OD experiments for sedimentary rocks are still in a developing stage. OD experiments are non-destructive with respect to the rock and run at higher S:L ratios compared to aqueous extraction tests (*cf.* Section 4.4). A disadvantage of OD experiments is the long duration over several months. Details about the methodology are given in the method report by Waber (ed.) (2020).

Out-diffusion experiments conducted on originally saturated rock material from borehole BUL1-1 deliver information about:

- Concentrations of chemically conservative elements (Cl, Br) at water-loss porosity.
- Effects of possible contribution to solute concentrations from mineral fluid inclusions to AqEx solutions due to the destructive nature of such experiments.
- Effects of large S:L ratios on the dissolution behaviour of readily dissolvable mineral phases also allowing identification of trace amounts of minerals possibly present in the rock.

- Identification of dominant mineral reactions over extended periods of time and at elevated temperature.
- Water saturation state of rock material.
- Elution behaviour of conservative and reactive solutes as a function of time.
- Pore diffusion coefficients of the chemically conservative solutes Cl and Br (and possibly others).

A full documentation of the acquired data is provided in Appendix 4, which contains 2 sheets:

- Sheet "*OD time series*": Chemical composition of all aliquots extracted and analysed over the runtime of the experiments;
- Sheet "*OD Final Solutions*": Chemical composition and mineral saturation indices of the final solutions.

4.8.1 Sample material and overview of analytical work

The nature of OD experiments restricts such experiments to non-swelling rocks that do not disintegrate during immersion into water over several months. To test the applicability of such experiments to sedimentary rocks 4 limestone samples with low clay mineral content were chosen from the 'Felsenkalk' / 'Massenkalk', Villigen Formation and the 'Herrenwis Unit'. From the vacuum-packed entire core samples a sub-core was drilled, which was then subjected to the experiment (Fig. 4.8-1). Preparation of the sub-core lasted about 4 – 10 minutes during which a minimum amount of water was for used for drilling. The remainder of the core was used for the analyses of mineralogy, water content and C-isotopes of the bulk matrix carbonate.

The 4 cylindrical limestone core samples had a mass of about 560 – 580 g and the S^*/L^* ratio in the OD experiments was around 7 compared to the AqEx tests with a ratio of about 1. The mass of porewater in the core samples ranged from about 2 to 5 g. As for the AqEx tests (*cf.* Section 4.4) the parameter S^*/L^* relates to the mass ratio of the wet rock sample to the mass of the added water, i.e. to values measured at the onset of the experiment. The parameter S/L , defined as the mass ratio of dry rock to the sum of pore and added water (Eq. 8 in Section 3.4-1), can be calculated from S^*/L^* using the water content.

Tab. 4.8-1 lists all samples used for OD experiments and the analytical work performed. Details about the experimental and analytical procedures can be found in Waber (ed.) (2020).

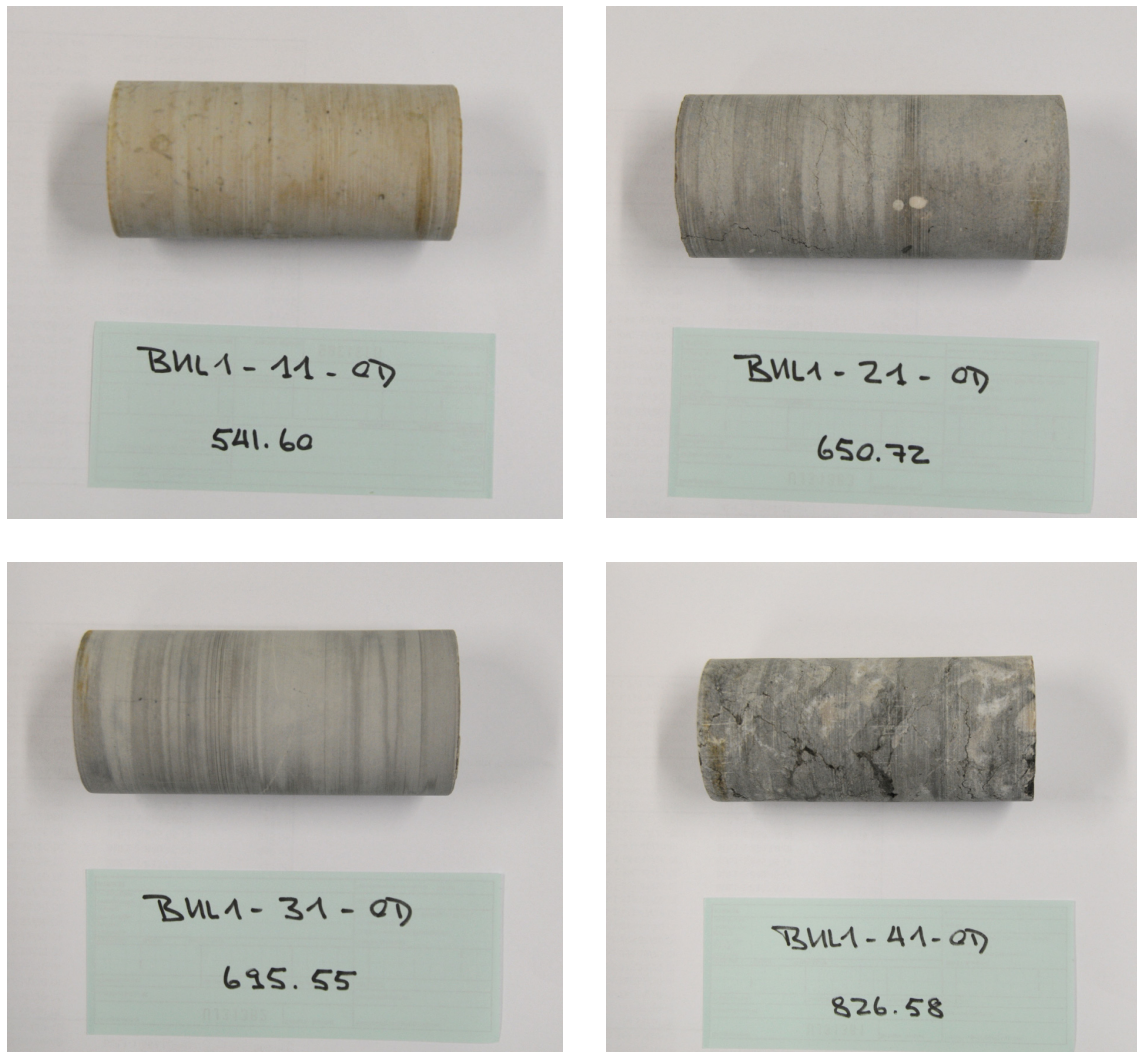


Fig. 4.8-1: Sub-cored limestone cylinders subjected to OD experiments from the 'Felsenkalke' / 'Massenkalk' (top) and the Villigen Formation (bottom left) of the Malm, and the 'Herrenwis Unit' (bottom right) of the Dogger

See Tab. 4.8-2 and 4.8-3 for details about mineralogy and water content.

4.8.2 Mineralogy and petrophysical properties

Mineralogy was determined on subsamples cut adjacent to the core segment used for the OD experiments. The 4 OD samples all classify as limestone and have low clay contents of 1 – 10 wt.-% (Tab. 4.8-2). Calcite is by far the most abundant mineral and carbonate phase in the rocks and dolomite/ankerite is only present in the core section from the 'Herrenwis Unit' in quantifiable amounts. Contents of quartz are very low, and feldspars are absent in the limestone from the 'Felsenkalke' / 'Massenkalk' to the Villigen Formation and slightly higher and present, respectively, in the limestone of the 'Herrenwis Unit'.

Tab. 4.8-1: Summary of analytical work performed on samples for out-diffusion experiments

V,A,L = core dimensions volume, sectional area, lengths.

Parameter	BUL1-11-OD	BUL1-21-OD	BUL1-31-OD	BUL1-41-OD
Sample ID RWI	BUL1-1-541.60-OD	BUL1-1-650.72-OD	BUL1-1-695.55-OD	BUL1-1-826.58-OD
Lab sample ID	BUL1-1x-OD	BUL1-2x-OD	BUL1-3x-OD	BUL1-4x-OD
Depth along BH [m]	541.60	650.72	695.55	826.58
Stratigraphy	'Felsenkalke' / 'Massenkalk'	'Felsenkalke' / 'Massenkalk'	Villigen Fm.	'Herrenwis Unit'
OD experiment	yes	yes	yes	yes
Chemistry final sol.	yes	yes	yes	yes
Chemistry time-series	yes	yes	yes	yes
Pre_Mass	yes	yes	yes	yes
Pre_Water content	yes	yes	yes	yes
Pre_V,A,L	yes	yes	yes	yes
Post_Mass	yes	yes	yes	yes
Post_Water content	yes	yes	yes	yes
Post_V,A,L	yes	yes	yes	yes
Mineralogy	yes	yes	yes	no
$\delta^{13}\text{C}$ Rock matrix	yes	yes	yes	yes

The CNS analyses of total sulphur are below the detection limit of 0.05 wt.-% in the limestone cores of the 'Felsenkalke' / 'Massenkalk' samples, just at detection limit in that of the Villigen Formation and with 0.07 wt.-% slightly above the detection limit in that of the 'Herrenwis Unit'. The latter value converts to a pyrite content of about 0.1 wt.-%. Contents of organic carbon in the rocks are low and between 0.11 wt.-% and 0.25 wt.-% (Tab. 4.8-2).

Core volume and wet mass of limestone samples subjected to out-diffusion experiments were similar with about 210 – 212 cm³ and 559 – 581 g, respectively (Tab. 4.8-3). Core dimensions of the limestones from the 'Felsenkalke' / 'Massenkalk' and Villigen Formation did not measurably change during the experiment. In contrast, core dimensions of the clay-richest limestone sample from the 'Herrenwis Unit' showed breakouts along the thin clay layers (*cf.* Fig. 4.8-1) inhibiting an exact derivation of the post-experiment core dimensions. As a consequence, no post-experiment bulk wet density can be derived from volume and mass for this sample. The uptake of water during the 198 days of full immersion into the out-diffusion test water at 45 °C is essentially within the measurement uncertainty and was 0.018 – 0.143 g. Taking the small amount of mineral dissolution during the experiments into account the mass of the rock cylinders remained constant indicating these limestone samples were at full water saturation from the time of sample reception in the lab to the end of the experiment.

Tab. 4.8-2: Mineralogy and CNS-data and isotope composition of matrix calcite of OD samples

Values of "0" in mineralogy indicate minerals with no identifiable peak in the XRD pattern.

Parameter	BUL1-11-OD	BUL1-21-OD	BUL1-31-OD	BUL1-41-OD
Depth along BH [m]	541.60	650.72	695.55	826.58
Stratigraphy	'Felsenkalke' / 'Massenkalk'	'Felsenkalke' / 'Massenkalk'	Villigen Fm.	'Herrenwis Unit'
Lithology	limestone	limestone	limestone	limestone
Units	[wt.-%]	[wt.-%]	[wt.-%]	[wt.-%]
Mineralogy (XRD)				
Quartz	1	1	1	4
K-feldspar	0	0	0	0.5
Plagioclase	0	0	0	2
Calcite	98	94	97	82
Dolomite/Ankerite	0	0.5	0.5	2
Siderite	0	0	0	0
Anhydrite	0	0	0	0
Celestite	0	0	0	0
Pyrite	< 0.1	< 0.1	0.1	0.1
Clay content	1	5	2	10
CNS-Analyses				
C inorg.	11.7	11.4	11.7	10.1
C org.	0.11	0.22	0.19	0.25
S	< 0.05	< 0.05	0.05	0.07
Clay Minerals (XRD)				
Illite	0.5	2.5	0.8	4.6
Total Ill/Sm	0.5	1.6	0.5	4.1
Smectite	0	0.03	0	0
Kaolinite	0.24	0.27	0.37	0.5
Chlorite	0.09	0.08	0.06	0.44
Chl/Sm ML (85 – 95)	0	0.23	0.14	0.13
Matrix Calcite Isotopes				
$\delta^{13}\text{C}$ [‰ V-PDB]	1.08 ± 0.05	2.4 ± 0.01	3.49 ± 0.10	1.84 ± 0.07
$\delta^{18}\text{O}$ [‰ V-PDB]	-7.31 ± 1.15	-5.92 ± 0.40	-5.85 ± 1.46	-2.42 ± 0.99

Bulk wet density derived from core volume and core wet mass range from 2.618 g/cm³ of the clay-richest limestone from the 'Herrenwis Unit' to 2.667 g/cm³ of the pure limestone of sample BUL1-11-OD of the 'Felsenkalke' / 'Massenkalk'. Because the wet mass of rock and the core dimensions remained constant from before to after the experiment, the pre bulk wet density is also identical with the post wet density, except for the clay-richest limestone from the 'Herrenwis Unit' where this parameter could no longer be derived (see above). Compared to wet density measurements by the paraffin displacement technique of small sample aliquots of PW samples (for simplification, in fact PW and RP samples) it appears that the wet density derived from volume and mass of the OD core samples is somewhat lower by about 0.02 – 0.04 g/cm³ (Fig. 4.8-2). The

reason for this difference outside the analytical uncertainty is currently not understood. However, the distance between PW and OD samples in the drillcore is 1 – 7 m and so mineralogical and textural heterogeneities have to be taken into account as well.

The almost identical grain density of $2.712 \pm 0.005 \text{ g/cm}^3$ (Tab. 4.8-3) of all OD samples reflects the similar mineralogy (Tab. 4.8-2) of the cores subjected to out-diffusion experiments. Compared to surrounding neighbouring PW samples the OD cores from the 'Felsenkalk' / 'Massenkalk' are slightly lower what is most likely associated to mineralogical heterogeneities (Fig. 4.8-3). In turn, the limestone OD core samples have identical grain density values as surrounding PW samples in the Villigen Formation and the 'Herrenwis Unit'.

The water content of the OD core samples varies between 0.349 and 0.845 wt.-% with a relative difference between water content before and after the experiment of 0.91 – 3.25 %, what reflects essentially the analytical uncertainty (Tab. 4.8-3). These water contents correspond to about 1.9 – 4.9 g of porewater that exchanged with the surrounding test water of about 80 – 84 g resulting in S^*/L^* ratios of 6.6 – 6.9 (Tab. 4.8-3).

Larger differences are observed between the water content of the OD core and the aliquot sub-samples separated from the central part of the received drillcore. The latter have water contents 0.348 – 0.628 wt.-%. Whereas the two water contents are identical for sample BUL1-11-OD of the 'Felsenkalk' / 'Massenkalk', they differ by almost a factor of 2 for the limestone of the 'Herrenwis Unit' (Tab. 4.8-3). This highlights the strong heterogeneity in certain rock types in the cm-range what often disables the combination of petrophysical parameters obtained for different sample aliquots of the same drillcore sample (e.g. wet density, grain density, water content). In combining such values such heterogeneity in mineralogy and pore space distribution has to be accounted for and optimal results can be obtained if all parameters are analysed on the very same sample.

The water-loss porosity, WL-P, of the OD core samples varies between 0.94 vol.-% in the limestone sample BUL1-11-OD of the 'Felsenkalk' / 'Massenkalk' to 2.24 vol.-% in that of the 'Herrenwis Unit'. The water-loss porosity obtained for the OD core samples compares well with that derived for neighbouring PW samples and overlaps within the propagated uncertainty (Fig. 4.8-4).

4.8.3 Final OD experiment solutions

After an out-diffusion time of 198 days at 45 °C the closed cylinders were cooled to room temperature (20 °C) followed by removal of the test water and immediate analyses of pH, alkalinity and TIC. During the entire experiment time, small volumes (0.5 mL) were collected from the initial test water for the so-called time-series samples. This removal results in continuously lowering the mass and solute concentrations of the test water what need to be corrected for. Such correction can strictly be only applied to chemically conservative dissolved components whereas the contribution of mineral dissolution has to be taken into account in addition for all reactive compounds. By applying complex geochemical modelling strategies such correction can be done. This is, however, outside the scope of this report.

Nevertheless, the chemical composition of the uncorrected final solution also delivers (qualitative) information about the processes taking place during the out-diffusion experiment.

Tab. 4.8-3: Core dimensions and petrophysical parameters derived of OD samples

* post-experiment core dimensions of the core sample from the 'Herrenwis Unit' can no longer be derived due to breakout along clay layers; the mass of rock material could, however, be completely recovered.

Parameter	Units	BUL1-11-OD	BUL1-21-OD	BUL1-31-OD	BUL1-41-OD
Depth along BH [m]		541.60	650.72	695.55	826.58
Stratigraphy		'Felsenkalke' / 'Massenkalk'	'Felsenkalke' / 'Massenkalk'	Villigen Fm.	'Herrenwis Unit'
Lithology		limestone	limestone	limestone	limestone
Core length	[cm]	10.712	11.192	11.052	11.192
Core diameter	[cm]	4.992	5.012	4.993	5.017
Core volume	[cm ³]	209.66	220.81	216.40	221.25
Pre_Core wet mass	[g]	559.107	580.936	575.176	579.141
Post_Core wet mass	[g]	559.125	581.079	575.196	579.209
Delta Core wet mass	[g]	0.018	0.143	0.020	0.068
Mass of test water	[g]	80.366	80.488	80.275	84.138
S*/L* ratio	[-]	6.957	7.218	7.165	6.883
Pre_Core bulk wet density	[g/cm ³]	2.667	2.631	2.658	2.618
Post_Core bulk wet density	[g/cm ³]	2.667	2.632	2.658	n.a. *
Delta WCwet	[%]	0.00	0.02	0.00	—
Pre_Core WCwet	[wt.-%]	0.349	0.727	0.485	0.845
Post_Core WCwet	[wt.-%]	0.352	0.751	0.489	0.857
Delta WCwet	[%]	0.91	3.25	0.71	1.36
Pre_Core H ₂ O core	[g]	1.949	4.222	2.791	4.893
Post_Core H ₂ O core	[g]	1.967	4.365	2.811	4.961
DeltaCore H ₂ O core	[g]	0.018	0.143	0.020	0.068
Saturation ratio	[-]	0.991	0.967	0.993	0.986
Pre_Core WL-P	[vol.-%]	0.93	1.91	1.29	2.21
Post_Core WL-P	[vol.-%]	0.94	1.98	1.30	2.24
Delta WL-P	[%]	0.923	3.253	0.708	1.369
Subsample					
Grain density	[g/cm ³]	2.709	2.706	2.716	2.717
Wet mass rock	[g]	382.766	332.631	251.989	363.533
Mass H ₂ O	[g]	1.332	2.090	1.103	1.750
WC wet	[wt.-%]	0.348	0.628	0.438	0.481
WL-P	[vol.-%]	0.94	1.69	1.18	1.30

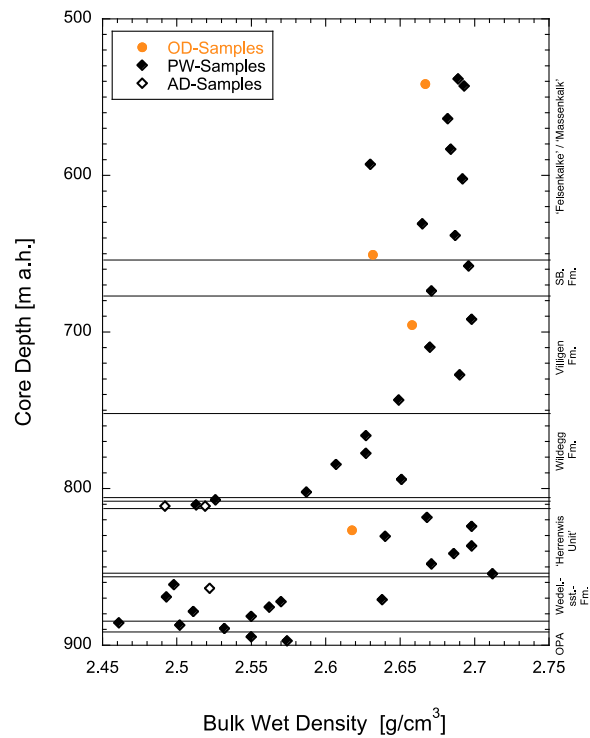


Fig. 4.8-2: Bulk wet density derived from volume and mass of OD and AD core samples compared to values obtained by paraffin-displacement of PW samples

Error bars are within the symbol size.

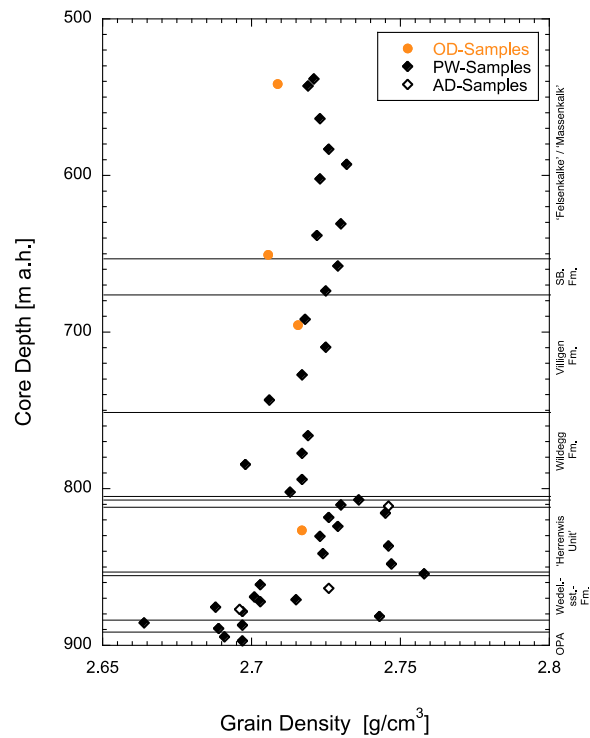


Fig. 4.8-3: Grain density derived by He-pycnometry on OD and PW samples compared to values obtained from volume and mass of AD samples

Error bars are within the symbol size.

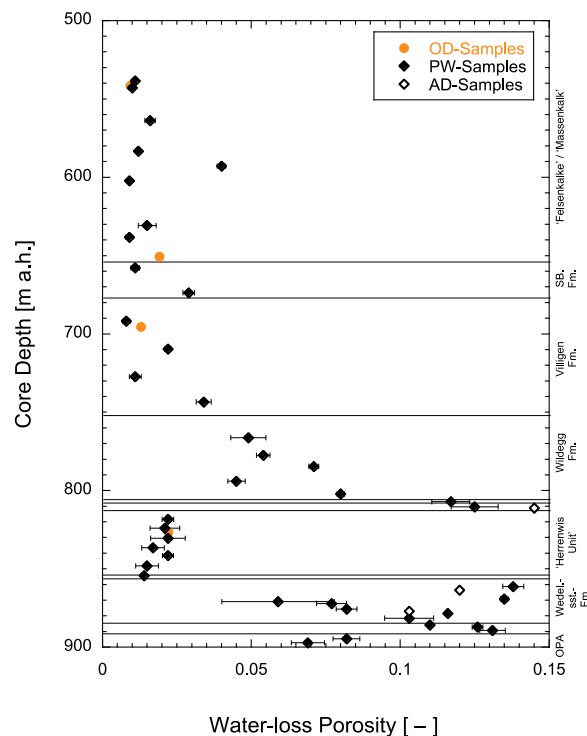


Fig. 4.8-4: Water-loss porosity of OD core samples compared to values of PW and AD samples
Error bars of AD and OD samples are within the symbol size.

Thus, mineral saturation states (*cf.* Section 4.8.3.2) indicate possible solubility controls of mineral phases present in the rock. Because of the much larger S/L ratio compared to aqueous extraction tests (*cf.* Section 4.4), information is also obtained about minerals in much lower contents in the rock.

The elution curves described by the time-series subsamples (*cf.* Section 4.8.4) give indications if the exchange between porewater and test water has reached an equilibrium state, i.e. equal concentrations in the test water and the pore space of the rock. In turn, the behaviour of reactive solutes yields information about the mineral reaction vs. out-diffusion of the concentration present in the porewater, the attainment of a solubility control during the experiment and/or a reaction that has not yet come to completeness.

4.8.3.1 Chemical composition of final solutions

The final solutions of the 4 OD cores display different chemical compositions. This might be surprising on first sight as the mineralogy of the rock samples is very similar, may be except for the limestone of the 'Herrenwis Unit' with its elevated clay content and its also notable pyrite content. The differences in chemical composition thus also reflect the different impact of the porewater onto the test water. Obviously, such impact depends on the mass of porewater present in the core samples and is expected to be largest in sample BUL1-21-OD the limestone of the 'Felsenkalk' / 'Massenkalk' and 'Herrenwis Unit' and lowest in the limestone sample BUL1-11-OD of the 'Felsenkalk' / 'Massenkalk' (*cf.* Tab. 4.8-3). Difference can, however, also be induced by different compositions of the porewater in the rock samples.

The final solutions have total dissolved solids (TDS) from 723 mg/L in sample BUL1-11-OD of the 'Felsenkalke' / 'Massenkalk' to 2648 mg/L in the sample from the 'Herrenwis Unit'. The solutions are of the general chemical type of Na-HCO₃-Cl-type for sample BUL1-11-OD of the 'Felsenkalke' / 'Massenkalk', Na-SO₄-HCO₃-Cl-type for sample BUL1-21-OD of the 'Felsenkalke' / 'Massenkalk' and the sample of the Villigen Formation and Na-SO₄-type for the sample of the 'Herrenwis Unit'. As the limestone of the 'Felsenkalke' / 'Massenkalk' have pyrite contents below the detection limit (*cf.* Tab. 4.8-2), it is interesting to note that dissolved SO₄ becomes the major anion in one of the final solution but not in the other. Similarly interesting is the fact that the solution of the 'Herrenwis Unit' with a pyrite content only slightly above the detection limit, the Cl concentration makes only 15 meq-% of all anions whereas that of SO₄ makes 70 meq-%.

Chloride concentrations in the final out-diffusion solution vary between 113 and 214 mg/L (*cf.* Appendix 4) what reduces to 109 to 207 mg/L when corrected for the mass of test water and Cl removed by the time-series subsamples. Because of its chemical inertness Cl concentrations can be converted to the S^*/L^* ratio of 1 and thus compared to the Cl concentrations of aqueous extraction test (AqEx) solutions at the same S^*/L^* ratio. As shown in Fig. 4.8-5 Cl concentrations obtained from non-destructive out-diffusion experiments agree well with those of the destructive aqueous extraction tests. This indicates that no other inventory than the porewater contributes to the Cl concentrations in both types of experiments and the impact of potential mineral fluid inclusion leakage is successfully suppressed by the gentle disintegration (and not milling) of the material used in aqueous extraction tests.

Bromide concentrations in the final out-diffusion solution vary between 0.31 and 0.65 mg/L (*cf.* Appendix 4) what reduces to 0.30 to 0.34 mg/L when corrected for the mass of test water and Br removed by the time-series subsamples. Bromide concentrations in OD final solutions and AqEx solutions at S^*/L^* ratio of 1 agree similarly well as for Cl (Fig. 4.8-6).

Overall Cl and Br concentrations in OD final solutions support the trends with sample depth given by the concentrations in AqEx solutions (Figs. 4.8-5 and 4.8-6). Similarly, the Br/Cl ratios agree with those of the AqEx solutions although they are slightly lower in the limestone sequences of the Malm and also slightly below that of modern seawater (Fig. 4.8-7). In the limestone of the 'Herrenwis Unit' the Br/Cl ratios of the OD final solution is identical to that of neighbouring AqEx solutions and below that of modern seawater.

Reactive solutes cannot be linearly scaled from the S^*/L^* ratio in the OD experiments to that of the aqueous extraction tests and direct comparison of absolute concentrations is inhibited. However, ion-ion ratios can be used for comparison.

The molal Na/Cl ratios in OD final solutions are identical to those in AqEx solutions of the clay-poor limestones of the Malm (Fig. 4.8-8). In the OD solution of the 'Herrenwis Unit' some scatter is observed in Na/Cl ratios with that of the OD final solution falling in the range of ratios Na/Cl ratios given by the AqEx solutions. The Na/Cl ratios of all OD final solutions are significantly above that of modern seawater indicating the modification of the initial porewater in these marine sediments over geologic time scales (Fig. 4.8-8).

Molal SO₄/Cl ratios in OD final solutions are identical to those in AqEx solutions in the pyrite-free limestone of the 'Felsenkalke' and the limestone of the Villigen Formation, which has 0.1 wt.-% of pyrite (Fig. 4.8-9). In the also pyrite-free limestone of the 'Felsenkalke' / 'Massenkalk' the SO₄/Cl ratio in the OD final solution supports the trend given by neighbouring AqEx solutions. In all these marine limestone units the SO₄/Cl ratios are above that of modern seawater. The OD final solution of the limestone of the 'Herrenwis Unit' has a significantly higher SO₄/Cl ratio (Fig. 4.8-9). This limestone also has the highest pyrite content (*cf.* Tab. 4.8-2).

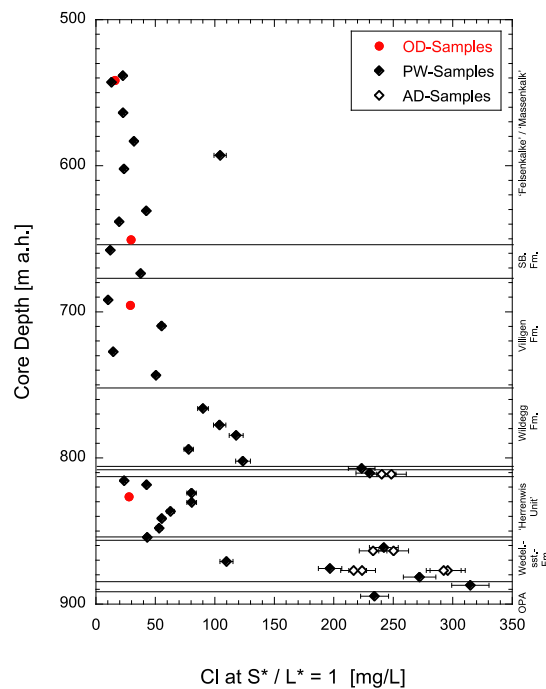


Fig. 4.8-5: Cl concentrations in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth

Cl concentrations of OD final solutions are corrected for time-series samples.

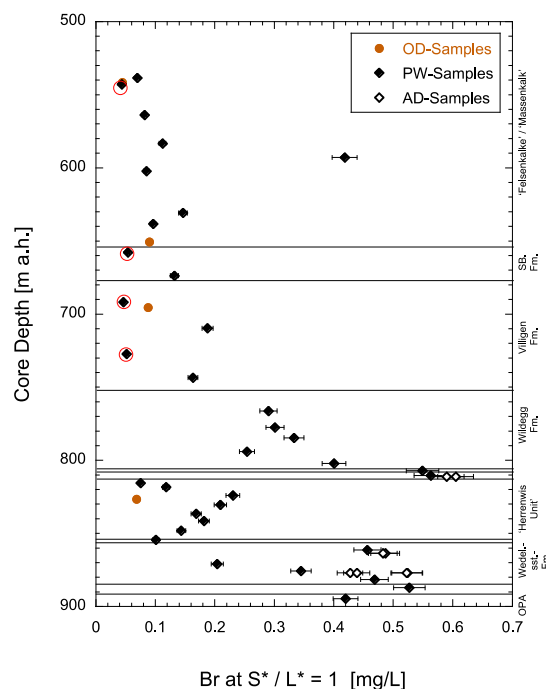


Fig. 4.8-6: Br concentrations in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth

Br concentrations of OD final solutions are corrected for time-series samples. Framed samples of low-mineralised AqEx solutions have Br values at quantification limit.

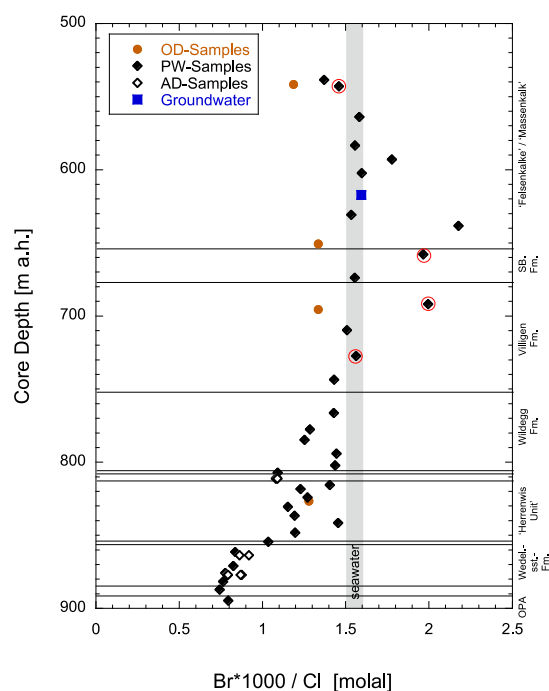


Fig. 4.8-7: Br/Cl ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth

Cl and Br concentrations of OD final solutions are corrected for time-series samples. Framed samples of low-mineralised AqEx solutions have Br values at quantification limit.

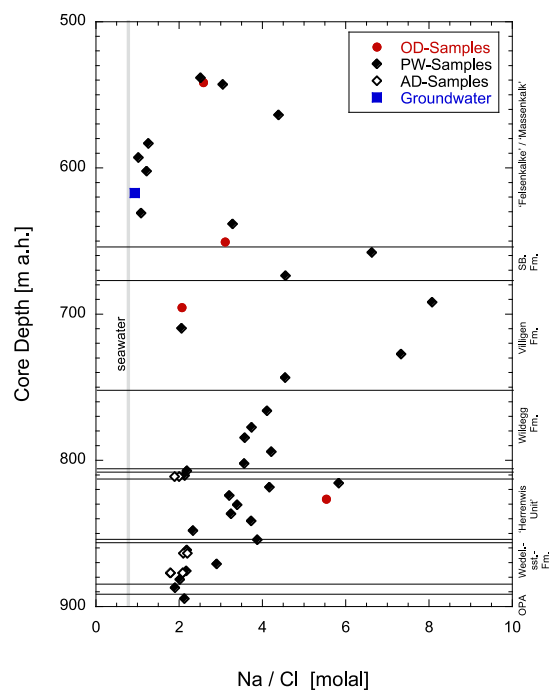


Fig. 4.8-8: Na/Cl ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth

The groundwater ratio is not corrected for contamination.

As described above, the headspace air in the out-diffusion cylinders could not be completely removed and collection of time-series samples could not be performed under completely controlled conditions. Therefore, the experiments are semi-confined, and some gas exchange will take place, especially at the beginning of the experiments. Based on that pyrite oxidation is expected to occur at least to some degree. As will be shown below in Section 4.8.4. the elution behaviour of SO_4 and the SO_4/Cl ratio indicates that such oxidation mainly takes place during the initial phase of the experiment before it ceases and the ratio of SO_4 from pyrite oxidation to SO_4 from the porewater decreases. The SO_4 concentration measured in the final OD solution therefore is the sum of these two inventories. The SO_4/Cl ratio in the OD final solution of the limestone of the 'Herrenwis Unit' thus reflects a combination of SO_4 from pyrite oxidation and SO_4 from the porewater.

Molal Sr/SO_4 ratios in OD final solutions are almost identical compared to those in AqEx solutions in the limestones of the Malm where pyrite is absent or only present in trace amounts (Fig. 4.8-10). A somewhat larger difference is observed for the limestone of the 'Herrenwis Unit' where substantial pyrite oxidation occurs. A similar relationship is observed for the Sr/Cl ratio. In the AqEx tests the dissolution of calcite with incorporated Sr was identified as the most important source of Sr (*cf.* Section 4.4). The behaviour of Sr and SO_4 during out-diffusion from the limestones of the Malm is consistent with this interpretation. The slightly larger amount of Sr compared to SO_4 in these solutions originates in the larger amount of calcite dissolution in the OD experiments compared to the AqEx tests. In the limestone of the 'Herrenwis Unit' the observed pyrite oxidation will be buffered by additional calcite dissolution releasing additional Sr from calcite.

The dominance of the fast carbonate mineral dissolution and the solubility control by calcite (*cf.* Section 4.8.3.2) during OD experiments and AqEx test is illustrated the Ca/Mg ratios in the solutions of these different experiments (Fig. 4.8-11). Independent of pyrite and clay content the Ca/Mg ratios of OD final solutions are identical to those of AqEx solutions.

4.8.3.2 Mineral saturation states

Mineral saturation states in the OD final solution were calculated at 20 °C using the value of total dissolved carbon (TIC) that was immediately analysed after termination of the experiments (Appendix 4). Extrapolation to experiment temperature of 45 °C will require assumptions on the carbonate system as all analyses were performed on the solution at 20 °C. Note that the test water was still in contact with the rock during cooling from 45 °C to 20 °C.

All solutions contain quite significant amounts of dissolved organic carbon (DOC) of 47 – 62 mg/L (*cf.* Appendix 4). By far most of this organic carbon is, however, not derived from the rock or the porewater, but from the experimental set-up (cylinders made of PP) as shown by the high DOC content of 42 mg/L in the blank experiment that was run over the same time and at the same temperature as the OD experiments. While this DOC contributes to the titrated alkalinity the effect on carbonate saturation indices is on the second digits when calculated using TIC or total alkalinity.

The OD final solutions have pH values of 7.28 – 7.96 with the lower values reached in the pyrite-bearing limestones of the Villigen Formation and the 'Herrenwis Unit' and the higher values reached in the pyrite-free limestones of the 'Felsenkalk' / 'Massenkalk'. All OD final solution are exactly at calcite equilibrium and corresponding $\log P_{\text{CO}_2}$ values are between -2.11 and -2.61 (Appendix 4). The $\log P_{\text{CO}_2}$ values of the solutions are significantly higher than that in air-saturated water indicating that the experiments did not continuously and completely exchange with the atmosphere.

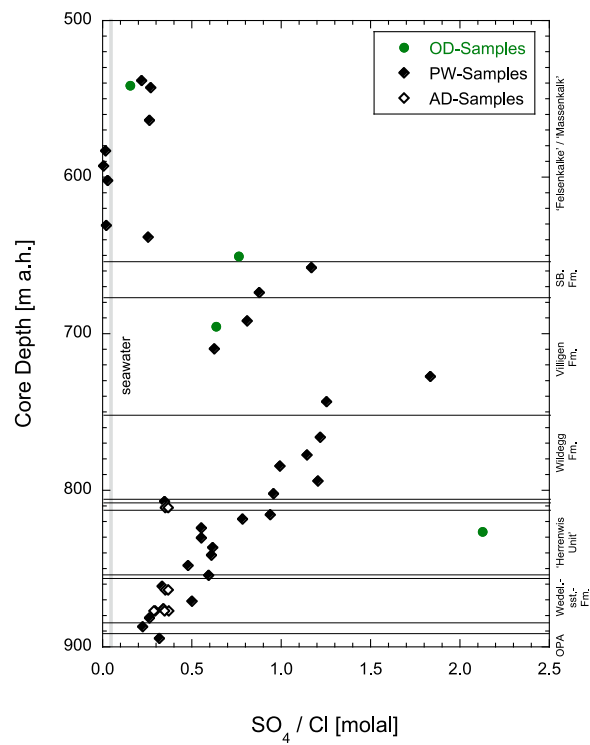


Fig. 4.8-9: SO_4/Cl ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth

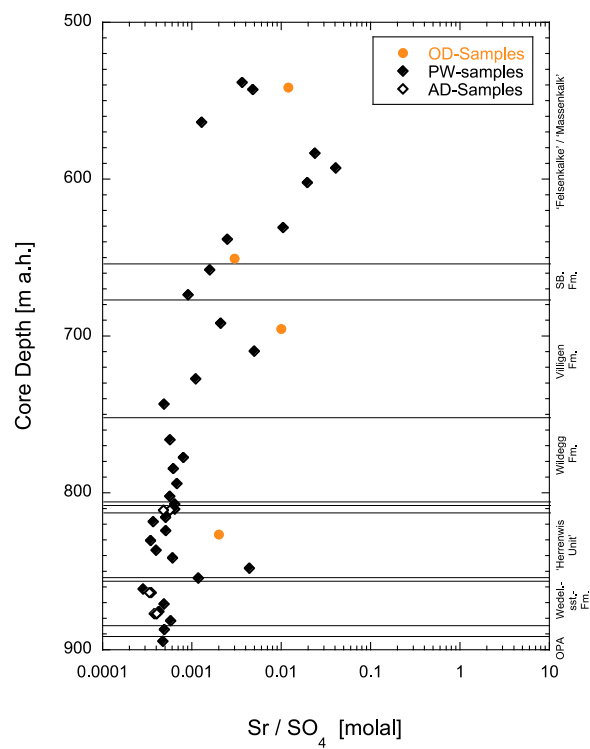


Fig. 4.8-10: Sr/SO_4 ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth

The groundwater ratio is not corrected for contamination.

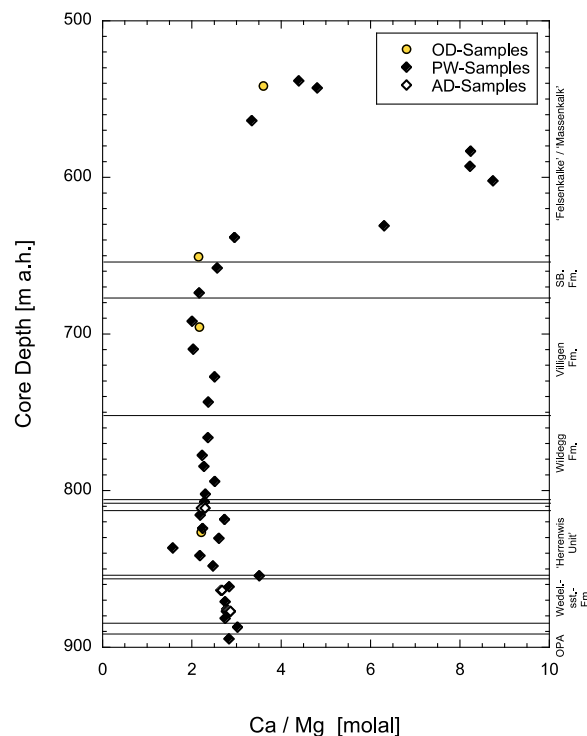


Fig. 4.8-11: Ca/Mg ratio in OD experiment final solutions compared to AqEx solutions all scaled to $S^*/L^* = 1$ as a function of sample depth

The groundwater ratio is not corrected for contamination.

At these conditions the OD final solutions are undersaturated with respect to disordered dolomite in agreement with the absence or only trace amounts present of dolomite/ankerite in the limestone samples.

The sulphate minerals anhydrite, gypsum and celestite are all strongly undersaturated as already observed in the AqEx solutions (*cf.* Section 4.4). The strong undersaturation with sulphate minerals remains in spite of the significantly larger S^*/L^* ratio of about 7 compared to that of 1 (or lower) in the AqEx tests and a reaction time over 198 days at 45 °C. This argues against the presence of such mineral phases in the marine limestones of the 'Felsenkalk' / 'Massenkalk' to the 'Herrenwis Unit' as already concluded from AqEx tests.

Fluorite is at equilibrium in the limestone of the Villigen Formation and the 'Herrenwis Unit', but undersaturated in those of the 'Felsenkalk' / 'Massenkalk'. So far fluorite was not identified in mineralogical investigations and the proof of its occurrence is pending.

The OD final solutions are still slightly undersaturated with respect to quartz, which occurs in very small amounts in these rocks (*cf.* Tab. 4.8-2).

4.8.4 Solute elution curves (time-series)

Small volume (0.5 mL) time-series subsamples were collected in intervals of hours to days in the initial phase of the OD experiments and intervals of weeks to months towards the end of the experiment.

Immediately after the collection of the subsamples, pH was analysed using a Metrohm micro-electrode. The first subsamples had pH values of 8.89 – 9.72 reflecting calcite dissolution in CO₂-free water and under (semi-)closed system conditions. As a function of time pH values decreased in a very regular way to the values recorded for the final solutions between 7.28 and 7.96. Information about dissolved carbon is not available for the small volume time-series samples but can be well approximated by charge balance for future modelling purposes.

The elution of Cl and Br during the 198 days of experiment time is shown in Fig. 4.8-12. In the limestone sample BUL1-21-OD of the 'Felsenkalke' / 'Massenkalk' and the limestones of the Villigen Formation and the 'Herrenwis Unit' Cl and Br concentrations reach a plateau after about 33 days suggesting diffusion in the rock matrix as the dominant transport process. The initial phase is characterised by a steep slope and the maximum concentrations in this phase even exceed those of the plateau. Such effects are well known from crystalline rocks and can be associated to the drilling disturbed zone induced by the sub-coring process of the OD core sample. The effects are commonly more pronounced in coarser-grained lithologies compared to fine-grained, well-cemented lithologies. This is exemplified by the elution behaviour of Cl and Br in the limestone sample BUL1-11-OD of the 'Felsenkalke' / 'Massenkalk' (Fig. 4.8-12). Here the change in slope from the initial out-diffusion phase to the later phase is much less pronounced and the plateau is not reached before about 140 days. This indicates a much less strong disturbance of the rim of the core by the drilling process and a significantly lower pore diffusion coefficient for Cl and Br in this rock type.

In spite of this obvious disturbance of the original pore space in some samples, pore diffusion coefficients can nevertheless be derived from these OD experiments by applying 2D-transport models using heterogeneous transport properties across the core samples (Waber et al. 2011, Meier et al. 2015). Such modelling is, however, outside the scope of this report.

The ratio of Br/Cl becomes constant after about 33 days in the limestone sample BUL1-21-OD of the 'Felsenkalke' / 'Massenkalk', Villigen Formation and the 'Herrenwis Unit' and already after about 3 days in the limestone sample BUL1-11-OD of the 'Felsenkalke' / 'Massenkalk' (Fig. 4.8-13). Again, this illustrates the much lower disturbance of the rim of the massive limestone of sample BUL1-11-OD. It further suggests that in these limestones Cl and Br diffuse at the same velocity across the rock matrix.

The ratio of Na/Cl shows a different behaviour during out-diffusion (Fig. 4.8-13). Here the limestones of the 'Felsenkalke' / 'Massenkalk' and Villigen Formation display a similar behaviour and the Na/Cl ratios become constant after about 67 – 96 days. As there are no significant amounts of dissolvable Na-bearing minerals present in these limestones, Na might also behave conservatively, and the eluting Na is essentially from the porewater. The attainment of constant Na/Cl ratios after that of constant Cl concentrations suggest a slower diffusion of Na compared to Cl.

A completely different behaviour of the Na/Cl ratio is observed for the limestone of the 'Herrenwis Unit'. After a first rapid decline indicating the drilling disturbed zone the ratio continuously increases to the end of the experiment after 198 days. As this limestone has about 10 % of clay content, this behaviour is attributed to Na exchange in clay minerals in addition to the Na inventory in the porewater.

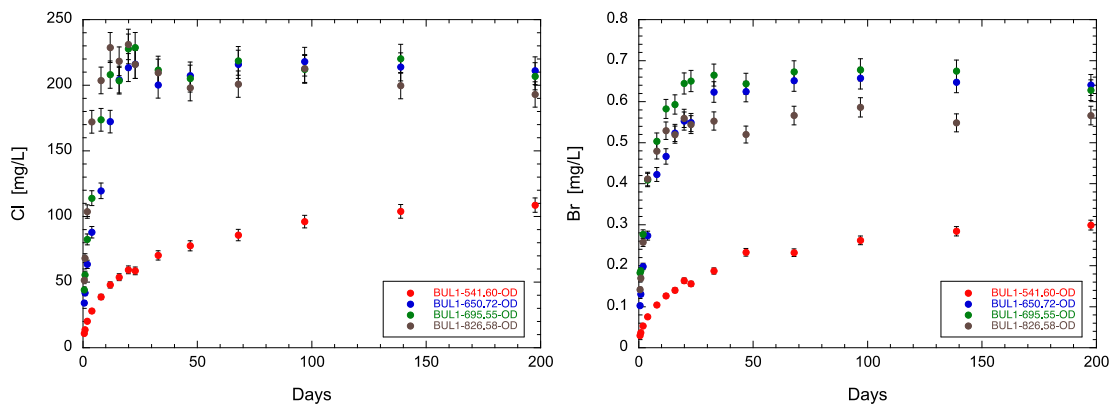


Fig. 4.8-12: Elution curves of Cl (left) and Br (right) during out-diffusion over 198 days at 45 °C in OD experiments

BUL1-541.60-OD and BUL1-650.72-OD: 'Felsenkalke' / 'Massenkalk', BUL1-695.55-OD: Villigen Formation, BUL1-826.58-OD: 'Herrenwis Unit'.

Concentrations of OD time-series solutions are corrected removal of time-series samples.

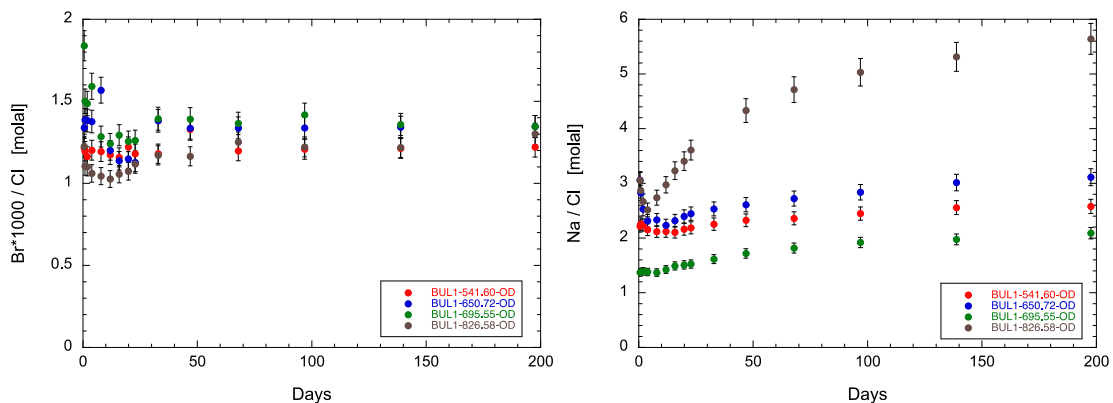


Fig. 4.8-13: Evolution of Br/Cl (left) and Na/Cl (right) ratios during out-diffusion over 198 days at 45 °C in OD experiments

BUL1-541.60-OD and BUL1-650.72-OD: 'Felsenkalke' / 'Massenkalk', 'Massenkalk', BUL1-695.55-OD: Villigen Formation, BUL1-826.58-OD: 'Herrenwis Unit'.

Concentrations of OD time-series solutions are corrected removal of time-series samples.

The elution of SO_4 displays a rather complex behaviour especially in the pyrite-bearing limestones of the Villigen Formation and the 'Herrenwis Unit' (Fig. 4.8-14). In both rock types the almost linear increase in SO_4 at the beginning illustrates the addition of SO_4 by pyrite oxidation. Towards the end of the experiment concentrations become constant indicating that pyrite oxidation ceased or came to completion. The final concentrations of SO_4 differ greatly and vary between about 370 and 1'150 mg/L. In the pyrite-free limestone sample BUL1-11-OD of the 'Felsenkalke' / 'Massenkalk' concentrations of eluted SO_4 are much lower and increase in a diffusion type manner to about 46 mg/L until the end of the experiment without reaching a plateau (Fig. 4.8-14).

Fluoride displays more similar elution behaviour in all different limestone samples and appear to still slightly increase in sample BUL1-11-OD of the 'Felsenkalke' / 'Massenkalk' whereas it reaches a plateau in sample BUL1-21-OD of the 'Felsenkalke' / 'Massenkalk' and those of the

Villigen Formation and the 'Herrnwis Unit' (Fig. 4.8-14). In sample BUL1-21-OD and the 'Herrnwis Unit' samples F concentrations in fact appear to slightly decrease towards the final solution in which fluorite equilibrium is reached (*cf.* Appendix 4).

Concentrations of Sr and Mg display a rather similar behaviour during out-diffusion from the limestones of sample BUL1-21-OD of the 'Felsenkalk' / 'Massenkalk', the Villigen Formation and the 'Herrnwis Unit' with increasing concentrations over the entire experiment time (Fig. 4.8-15). The similar behaviour supports the dissolution of calcite and possible dolomite/ankerite as a source for both these solutes. In contrast Sr and Mg concentration appear to reach a plateau of constant concentrations in sample BUL1-11-OD from the dolomite-free 'Felsenkalk' / 'Massenkalk'.

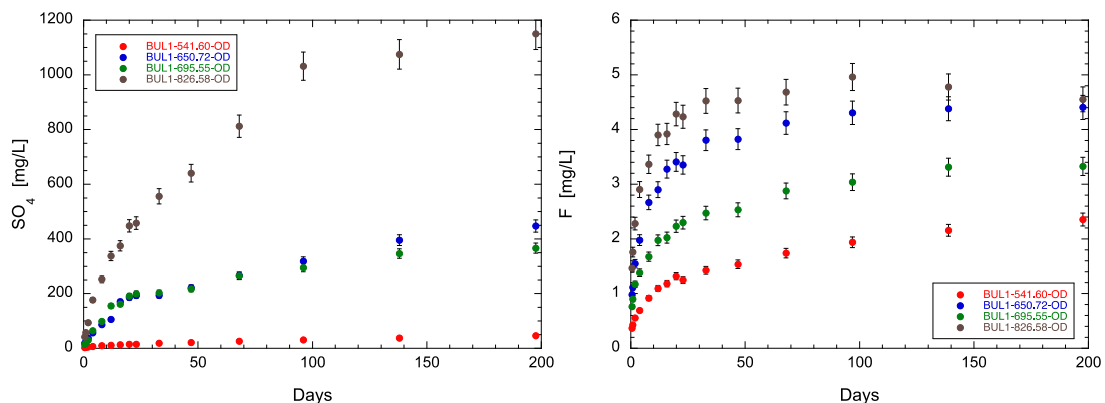


Fig. 4.8-14: Elution curves of SO_4 (left) and F (right) during out-diffusion over 198 days at 45 °C in OD experiments

BUL1-541.60-OD and BUL1-650.72-OD: 'Felsenkalk' / 'Massenkalk', BUL1-695.55-OD: Villigen Formation, BUL1-826.58-OD: 'Herrnwis Unit'. Concentrations of OD time-series solutions are corrected removal of time-series samples.

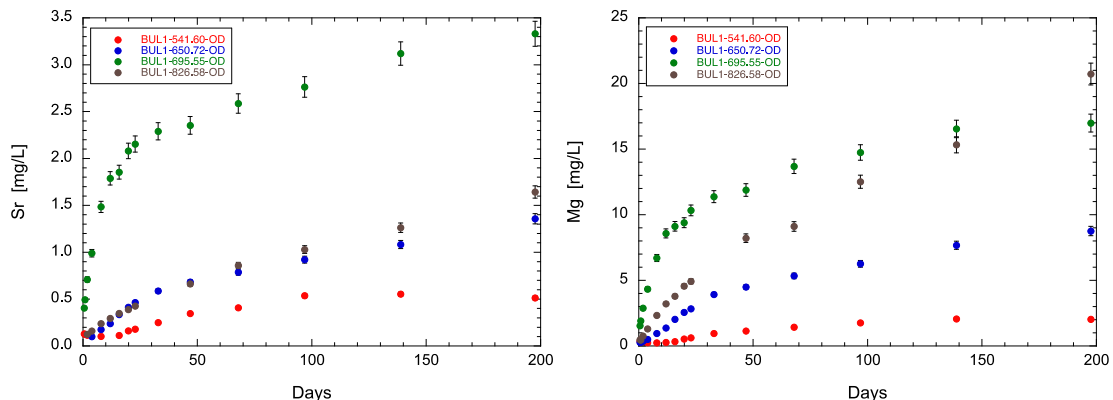


Fig. 4.8-15: Elution curves of Sr (left) and Mg (right) during out-diffusion over 198 days at 45 °C in OD experiments

BUL1-541.60-OD and BUL1-650.72-OD: 'Felsenkalk' / 'Massenkalk', BUL1-695.55-OD: Villigen Formation, BUL1-826.58-OD: 'Herrnwis Unit'. Concentrations of OD time-series solutions are corrected removal of time-series samples.

4.8.5 Concentrations of Cl and Br at water-loss porosity

Concentrations of Cl and Br of the final OD solutions, corrected for the mass of water and Cl concentrations removed by time-series samples and then scaled to water-loss porosity are in agreement with the similar values obtained from AqEx tests (Figs. 4.8-16 and 4.8-17). Across the limestone sequence from the 'Felsenkalke' / 'Massenkalk' to the 'Herrenwis Unit' the Cl and Br values from the OD experiments complete the depth profile and support also apparent excursions of individual AqEx samples as for example in the limestones of the Villigen Formation and 'Herrenwis Unit'.

The limestones of the 'Felsenkalke' / 'Massenkalk' and the Villigen Formation have clay contents of 1, 5 and 2 wt.-%, respectively. In these clay-poor limestones the water-loss porosity is or comes very close to the Cl- and Br-accessible porosity and the concentrations at water-loss porosity represent within their error the porewater concentration. Similar might account for the limestone of the 'Herrenwis Unit' also its porewater concentration might even be somewhat higher due to the clay content of 10 wt.-% in this rock. It thus appears that the excursion towards higher porewater Cl and Br contents in the 'Herrenwis Unit' is real.

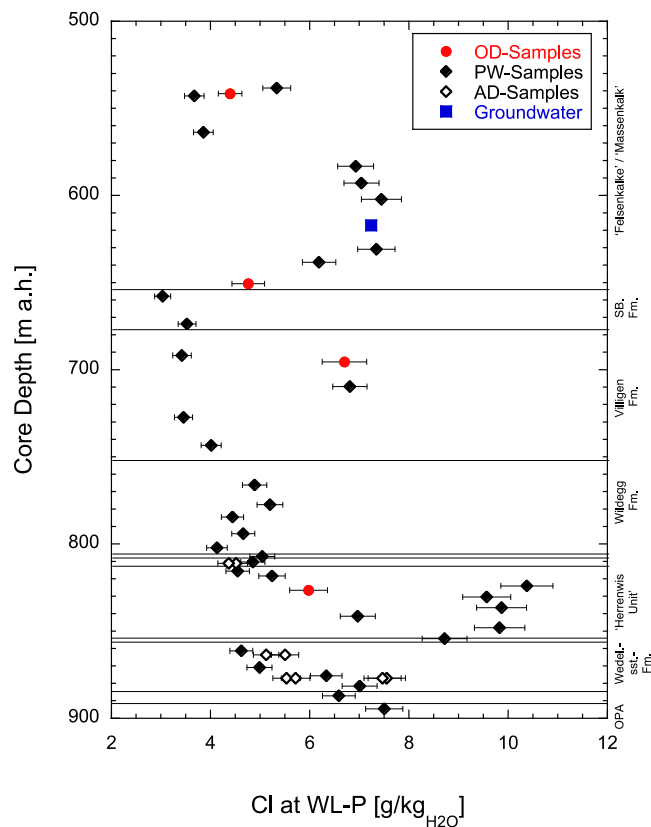


Fig. 4.8-16: Cl concentration at water-loss porosity (WL-P) derived from OD experiments and compared to those derived from AqEx solutions of PW and AD samples as a function of depth

Error bars indicate propagated error.

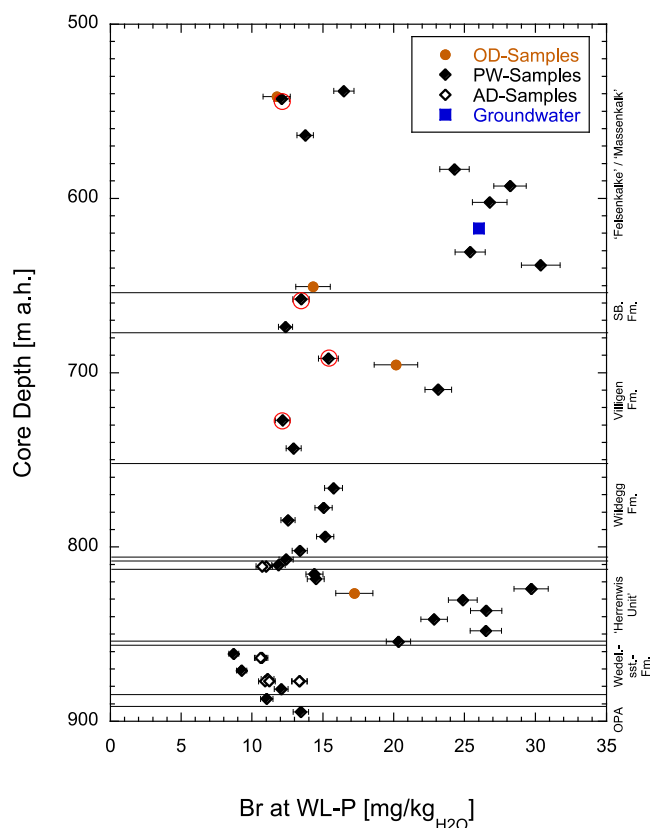


Fig. 4.8-17: Br concentration at water-loss porosity (WL-P) derived from OD experiments and compared to those derived from AqEx solutions of PW and AD samples as a function of depth

Error bars indicate propagated error. Framed samples of low-mineralised AqEx solutions have Br values at quantification limit.

4.9 Water-isotope data from diffusive-exchange experiments

Philipp Wanner, Martin Mazurek & Thomas Gimmi

Highly resolved stable porewater isotope ratio profiles were determined over a vertical depth interval of 664.5 m ranging from the 'Felsenkalke' / 'Massenkalk' to the Schinznach Formation. In total, 127 diffusive-exchange experiments were conducted and are fully documented in Appendix 1. Out of these, only 6 failed. The main reasons for failure were either a substantial mass transfer between test and porewater (mainly in the Schinznach Formation where the porewater has a much higher salinity than the test water) or water loss from the system during the experiment (leakage). For the remaining 121 experiments, an additional quality criterion was applied. As explained in Section 3.4.2, water contents can be obtained by mass balance based on either the $\delta^{18}\text{O}$ or the $\delta^2\text{H}$ data (Eq. 33). The relative deviation of the water contents obtained from the two isotope ratios is shown in Fig. 4.9-1. While the consistency is mostly good, some outliers are identified where the water contents differ substantially. In particular, the deviation exceeds 20 % in some cases, and so the isotope data obtained from such experiments are considered to be uncertain. In all these cases, the gravimetric water content is < 0.5 wt.-%, i.e. the mass of porewater in the test sample is small. Lithologically, these samples are either almost pure limestones or anhydrite-rich rocks. Last, on the basis of aqueous extracts, contamination of some samples by drilling

fluid even in the central parts of the core was identified for some samples from the Schinznach Formation (details in Section 4.4). Accordingly, the isotope data for these samples are also considered uncertain.

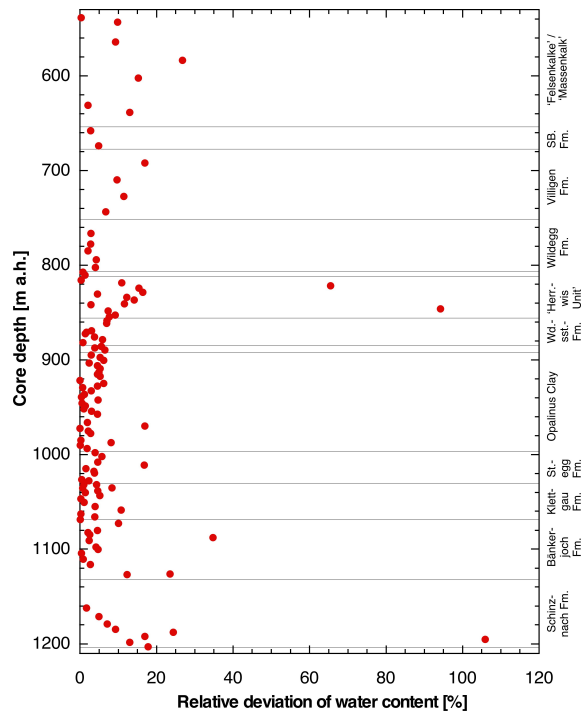


Fig. 4.9-1: Relative deviation of water contents obtained from $\delta^{18}\text{O}$ and $\delta^2\text{H}$ mass balance

The relative deviation is defined as the difference between the water contents obtained from $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data divided by the water content based on $\delta^2\text{H}$.

The depth profiles of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are shown in Fig. 4.9-2. In the Malm, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ increase slightly with depth. In the section 'Brauner Dogger' to Bänkerjoch Formation, $\delta^{18}\text{O}$ shows a consistent decrease, while $\delta^2\text{H}$ remains essentially constant. The excursions of $\delta^{18}\text{O}$ to more negative values in the 'Herrenwis Unit' are considered to be related to analytical difficulties in a heterogeneous, low-porosity lithology. A minor excursion towards lower δ values with a peak at the base of the Wedelsandstein Formation can be observed. The amplitude is only slightly higher than the experimental error.

Starting in the lowermost part of the Bänkerjoch Formation (at about 1'126 m), $\delta^{18}\text{O}$ and $\delta^2\text{H}$ decrease sharply with depth and reach a minimum in the Schinznach Formation in the interval 1'160 – 1'170 m. This section is located in the lower part of the Stamberg Member (formerly named Trigonodus Dolomite), which is known for its high permeability on a regional scale. From there, $\delta^{18}\text{O}$ increases again with depth, while $\delta^2\text{H}$ shows no clear trend.

It is remarkable that the shapes of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ profiles differ. This is also illustrated in Fig. 4.9-3, which shows the depth profile of deuterium excess (defined as $\delta^2\text{H} - 8 \delta^{18}\text{O}$). A consistent trend of increasing deuterium excess is seen in the section Villigen Formation – centre of the Schinznach Formation. Fig. 4.9-4 shows that porewaters at 1'160 – 1'170 m depth (Stamberg Member of the Schinznach Formation) lie close to the meteoric water line, whereas a shift to the

right is observed with increasing depth. All waters from the interval Klettgau Formation – Malm also lie to the right of the meteoric water line, and the shift increases progressively towards shallow levels. Porewaters in the Malm are massively shifted and even reach positive $\delta^{18}\text{O}$ values.

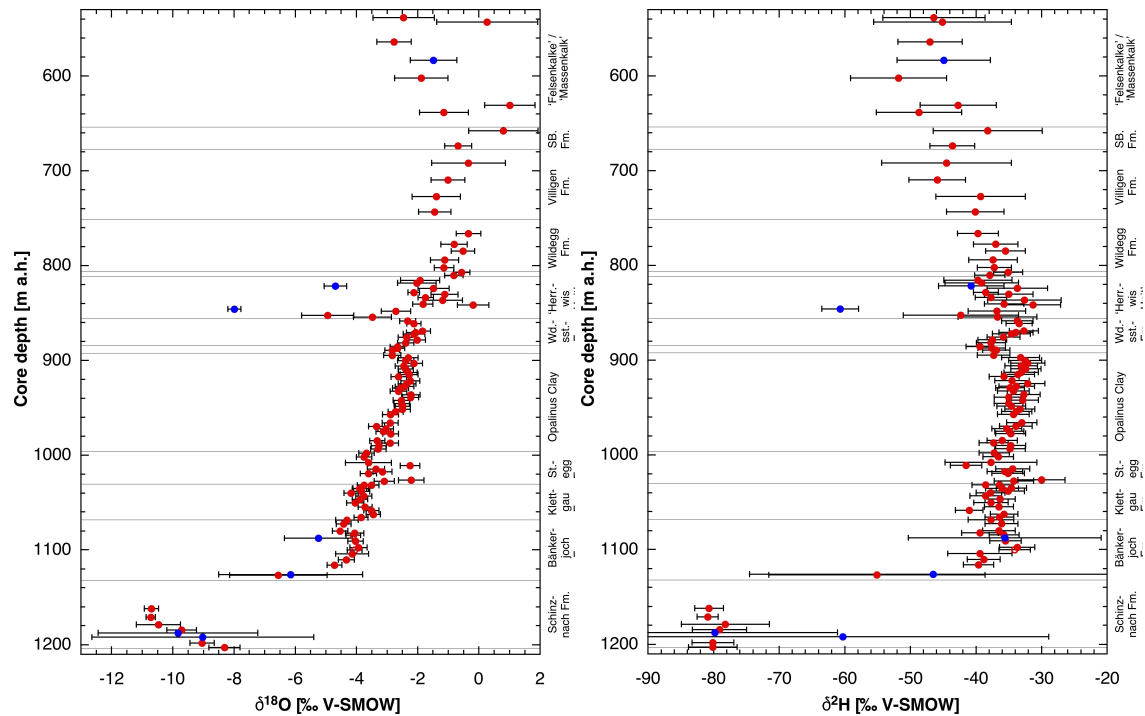


Fig. 4.9-2: Depth trends of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in porewater based on the isotope diffusive exchange technique

Uncertain values are shown by blue symbols. Uncertainties arise from the experiment itself or from contamination of the sample by drilling fluid (the latter in the Schinz-nach Formation, see Section 4.4). Bars indicate propagated analytical errors.

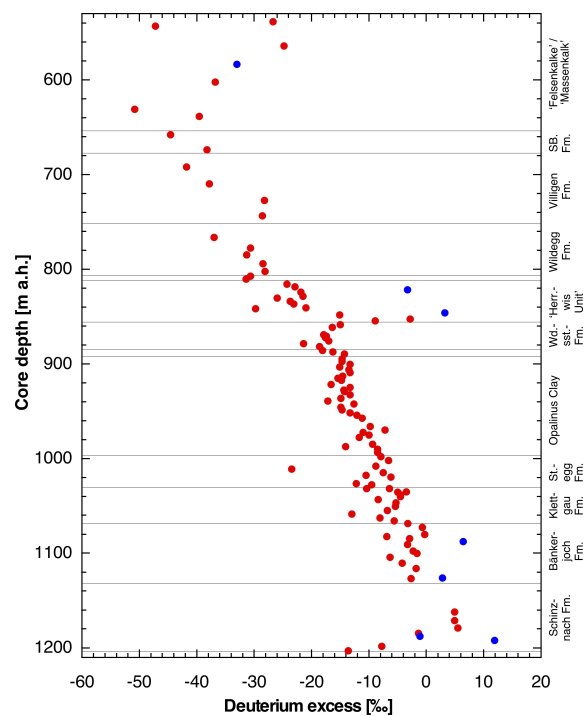


Fig. 4.9-3: Depth trend of Deuterium excess in porewater based on the isotope diffusive exchange technique

Deuterium excess is +10 for a sample that lies on the GMWL. Lower values of deuterium excess reflect sample positions to the right of the GMWL in a plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$. Uncertain values are shown by blue symbols. Uncertainties arise from the experiment itself or from contamination of the sample by drilling fluid (the latter in the Schinz nach Formation, see Section 4.4). Note that the deuterium excess as used at this stage carries no genetic implications about the origin of H_2O , e.g. on palaeo-climate at the time of infiltration.

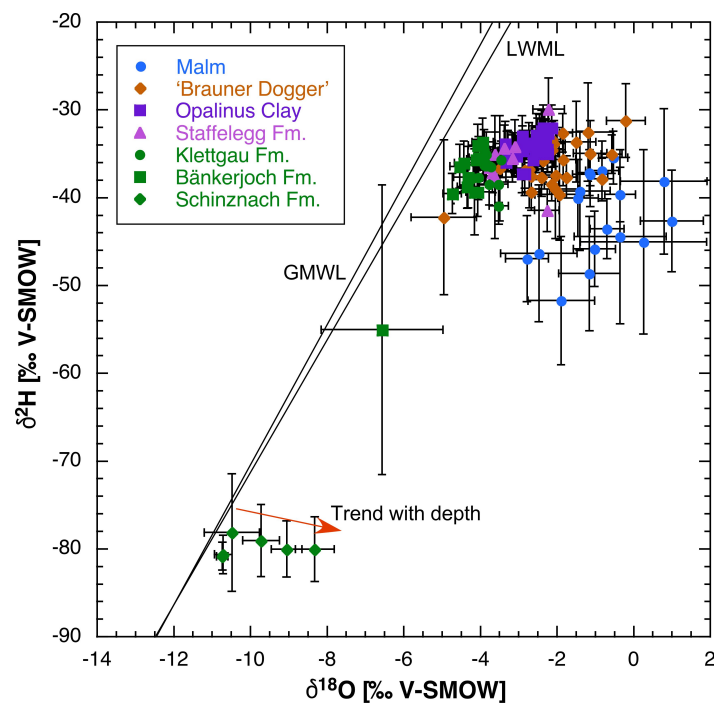


Fig. 4.9-4: $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for porewaters based on the isotope diffusive exchange technique

Uncertain data are not shown. GMWL = Global Meteoric Water Line ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$),
 LMWL = Local Meteoric Water Line ($\delta^2\text{H} = 7.55 \delta^{18}\text{O} + 4.8$, Kullin & Schmassmann 1991).

5 Discussion of porewater data

5.1 Chloride data and estimation of Cl⁻ and Br⁻-accessible porosity

Paul Wersin & Martin Mazurek

Chloride, a major compound in the porewater, has been determined by squeezing (Section 4.6), advective displacement (Section 4.7) and aqueous extraction (Section 4.4). This anion is considered to behave as a conservative species with no or very limited interaction with the minerals. The same can be said for bromide, which occurs at much lower concentrations in the porewater. In argillaceous rocks, anions are repelled from the negative structural charge of the clay surfaces and are thus affected by ion exclusion. In other words, they only "see" part of the total water-filled porosity, the fraction of which is often termed anion-accessible porosity (Pearson et al. 2003).

Knowing the concentration of Cl and/or Br in a sample from aqueous extraction ($C_{Cl \text{ in bulk porewater}}$), the anion accessible porosity fraction f can be estimated from Cl and/or Br measurements in squeezing ($C_{Cl \text{ in squeezed water}}$) or advective displacement ($C_{Cl \text{ in adv. displaced water}}$) experiments:

$$f_{Cl} = \frac{n_{anion-accessible}}{n_{total}} = \frac{C_{Cl \text{ in bulk pore water}}}{C_{Cl \text{ in squeezed or adv. displaced water}}}$$

$C_{Cl \text{ in bulk porewater}}$ is calculated from:

$$C_{Cl \text{ in bulk pore water}} = \frac{C_{Cl \text{ in aq. extract}}}{WC_{dry} S/L}$$

with C = concentration [mg/L], n = porosity [–], WC_{dry} = water content relative to dry rock mass [–], S/L = solid/liquid ratio of aqueous extraction experiment [g/g]. The Br-accessible porosities are derived in an analogous fashion.

The anion-accessible porosities have been derived according to above equation for squeezed and advectively displaced porewaters (Tabs. 4.6-7 and 4.7-17). In the case of the squeezed waters it is assumed that the waters squeezed at the lowest pressure reflect the in situ porewater (Mazurek et al. 2015, Wersin et al. 2016). For the advectively displaced waters, the first two samples are assumed to be the most representative of the in situ porewater (Section 4.7).

A further possibility to estimate anion-accessible porosities in argillaceous rocks is via through-diffusion tests with anionic tracers (Cl, Br) in combination with a water tracer (e.g. HTO). Such a dataset was acquired for 29 samples from the BUL1-1 borehole by Van Loon & Glaus (*in prep.*). The samples span across a 300 m thick rock sequence (from Villigen Formation to Staffelegg Formation) and include a wide range of clay-mineral contents. From the initial transient phase of the through-diffusion tests, the diffusion-accessible porosity of HTO and Cl was calculated (approach described in Van Loon 2014).

The derived values of the Cl-accessible porosity fraction (f_{Cl}) for the three datasets are shown as a function of clay-mineral content in Fig. 5.1-1 (left). For clay-mineral contents > 20 wt.-%, the f_{Cl} values from the diffusion experiments do not show any clear trend and yield a mean value around 0.5. The average value obtained from squeezing is 0.52 ± 0.06 . For the advective displacement the average value is slightly lower (0.47 ± 0.03). For clay-mineral contents ≥ 20 wt.-%, the range $f_{Cl} = 0.42 - 0.62$ includes most of the data from all 3 methods and apparently does not show a systematic trend with clay-mineral content (grey area in Fig. 5.1-1, left). This range is rather

wide and can also be expressed as $f_{Cl} = 0.52 \pm 20 \%$. For clay-poor lithologies, only a limited number of data points are available from through-diffusion experiments, and several of the samples are from the heterogeneous 'Herrenwis Unit'. The few data points exhibit a wide scatter and do not permit a proper definition of a range for f_{Cl} . The only fixed point is $f_{Cl} = 1$ at zero clay content. Nevertheless, in the sense of a working hypothesis, a range for f is defined in Fig. 5.1-1 (shaded area), but clearly more data would be needed to substantiate this choice. The fact that f_{Cl} shows such a wide range when plotted against clay-mineral content suggests that the latter is not the only parameter that determines anion accessibility. Correlations with individual clay minerals (e.g. illite or smectite end-members) are not better than those with total clay-mineral content. Mean grain size, grain-size distribution, fabric and other phases are expected to affect anion accessibility as well. Furthermore, according to theory, anion accessibility varies also with the composition of the pore water, i.e., is not just a material property. All these partly interdependent effects cannot be properly quantified at this stage, which severely limits the application of theoretical models. Accessibilities for Br are only available from advective-displacement experiments (Fig. 5.1-1, right). These are similar to those obtained for Cl by the same method. Therefore, the same relationship with clay content is assumed as for Cl.

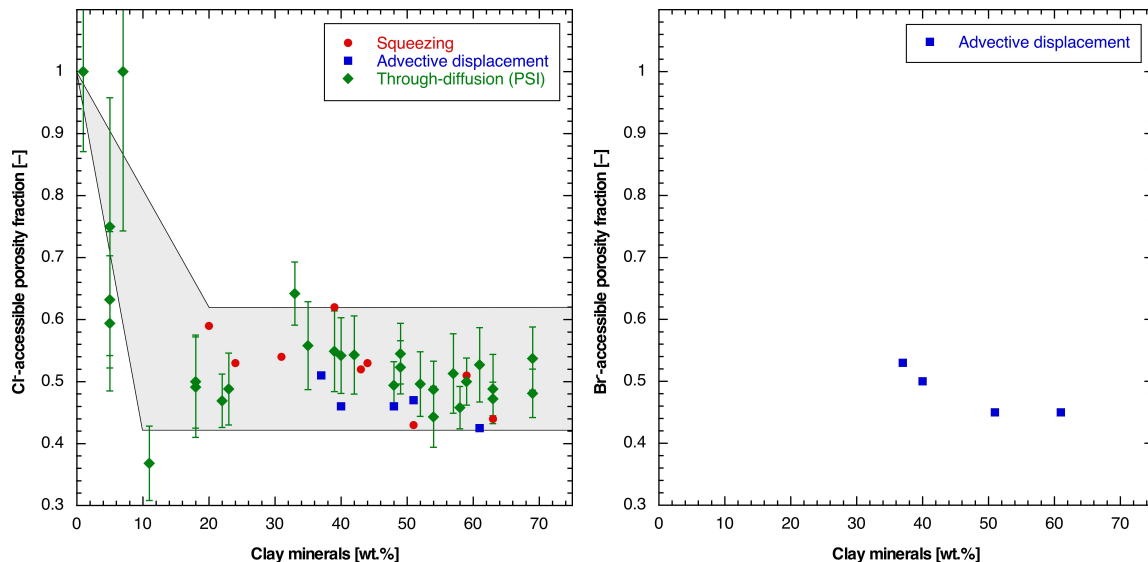


Fig. 5.1-1: Anion-accessible porosity fraction as a function of clay mineral content (left: Cl, right: Br)

Grey range in the left graphic is the envelope that contains most data points (except for clay-poor lithologies where scatter is even larger). Diffusion data based on Van Loon & Glaus (*in prep.*), with error bars indicating propagated analytical errors.

Within the interval between the Malm and Muschelkalk aquifers, the lithologies in the BUL1-1 profile vary substantially. In order to derive a porewater profile for Cl, anion accessibility in these lithologies must be known or assumed. In the present situation, a value for f_{Cl} of 0.52 is used for clay-mineral contents ≥ 20 wt.-%, and a linear increase towards 1 is considered for the range from 20 to 0 wt.-% clay-mineral content. An uncertainty range of $\pm 20 \%$ is considered for f_{Cl} , which is probably sufficient for clay-rich lithologies but may still be an underestimation for clay-poor rocks. This uncertainty propagates into the calculated Cl concentrations per anion-accessible porewater, i.e. an error of $\pm 20 \%$ must be considered in addition to the propagated analytical error.

Fig. 5.1-2 illustrates the Cl-accessible porosity fraction as a function of depth. Anion accessibility within the Opalinus Clay is slightly lower in the lowermost part of the formation, probably due to the high clay-mineral content of the lowermost sub-unit. A major step towards higher accessibility is identified in the uppermost part of the underlying Staffelegg Formation, from where accessibility becomes lower with depth. Note that the two uppermost data points from the Staffelegg Formation (based on diffusion experiments) come from the organic-rich Rietheim Member (former Posidonienschiefer), but the next underlying sample (obtained from squeezing), with a similarly high Cl accessibility, is from the Frick Member with a low content of organic C. A more detailed evaluation of the variability of f_{Cl} follows below.

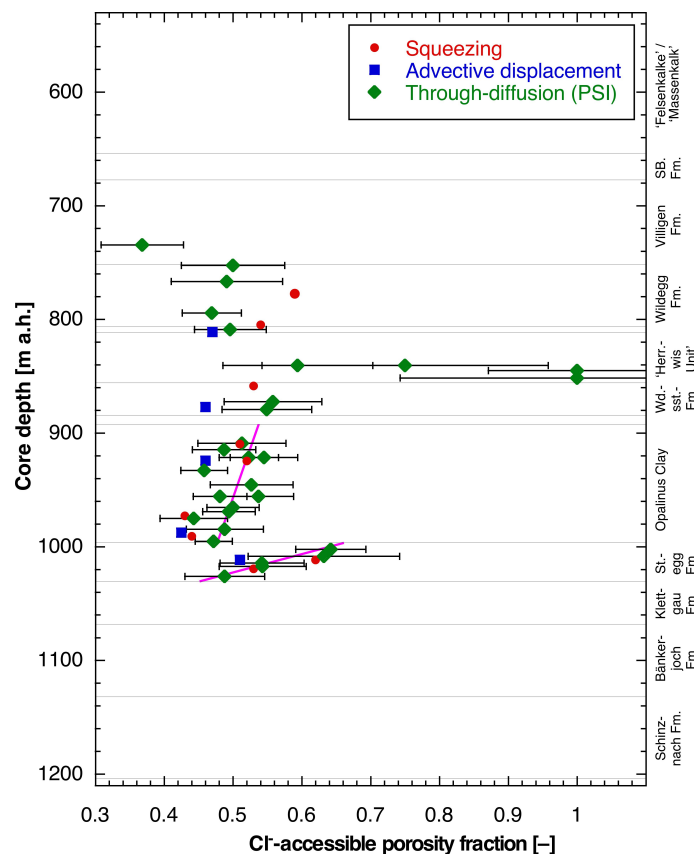


Fig. 5.1-2: Cl-accessible porosity fraction as a function of depth

Purple trend lines are discussed in Section 5.2. Error bars on the through-diffusion data indicate propagated analytical errors.

5.2 Chloride, bromide and Br/Cl profiles

Paul Wersin & Martin Mazurek

The chloride profile depicted in Fig. 5.2-1 includes aqueous extraction data extrapolated to in situ conditions assuming the relationship between clay-mineral content and f_{Cl} as discussed in Section 5.1. The Cl data based on squeezing and advective displacement, as well as those for the groundwaters in the Malm and in the Muschelkalk, are also shown. The error bars include the propagated analytical uncertainty and an additional 20 % that reflect the uncertainty related to f_{Cl} (see Section 5.1, Fig. 5.1-1). Data from aqueous extraction and squeezing are consistent, while data from advective displacement tend to be slightly higher (representing their lower f_{Cl} , see Section 5.1), even though still within the extended error bars. Note that contamination by drilling fluid was identified in 6 samples from the Schinznach Formation (Section 4.4). These samples are not included in Fig. 5.2-1 and the following graphics.

The lower part of the rock sequence (Keuper and Muschelkalk units) exhibits a large scatter in the aqueous extraction data, which is the only dataset for these units. Note that for older deep boreholes in the region no corresponding dataset is available in the Keuper and Muschelkalk. Concentrations are high in the Schinznach Formation and may reach values of up to more than 100 g/L. Heterogeneity persists throughout the Bänkerjoch, Klettgau and Staffelegg Formations, even though maximum concentrations are much lower than in the Schinznach Formation. The large concentration contrast may be due to the presence of anhydrite-rich beds in the Bänkerjoch Formation, which have very small water contents and presumably also diffusion coefficients (even though measurements are not available). At least part of the heterogeneity is likely due to the sometimes very small water contents (enhancing analytical errors and potential artefacts) and to the small-scale lithological heterogeneity (relevant if different analyses needed to obtain porewater concentrations cannot be measured on the same material). Nevertheless, the apparent scatter is somewhat de-emphasised when considering the extended error bars in Fig. 5.2-1 (which are dominated by the uncertainty of the anion-accessible pore fraction), bearing in mind that in clay-poor lithologies the uncertainty may be even larger. The scatter in the Cl profile contrasts with the much more regular profiles of Br/Cl and of water isotopes (see below), which do not depend on any assumptions pertinent to anion accessibility. Therefore, much of the scatter in the Cl profile down to the Bänkerjoch Formation is considered to be related to the limits to predict anion accessibilities (i.e. large uncertainties of the anion-accessible porosity fraction), in particular in clay-poor and heterogeneous lithologies. What remains undisputed is the massive increase of Cl concentrations in the Schinznach Formation.

In the Opalinus Clay and most of the overlying units, the profile is better defined. In the Opalinus Clay, a weak upward increase of Cl concentration is seen in the aqueous-extraction data, but this is not confirmed by data obtained by squeezing and advective displacement. The overlying section is characterised by a near-linear decrease of Cl concentration to about 5 g/L in the top of the drilled Malm section. The sampled groundwater from the Malm exhibits a similar concentration as the nearby aqueous extracts. In the section Opalinus Clay to Malm, the Cl profile displays a similar shape as those from the Benken and Schlattingen-1 boreholes in northeastern Switzerland (Gimmi & Waber 2004, Wersin et al. 2013). These have been interpreted to be the result of the diffusive exchange with the bounding aquifers. Note that in the latter boreholes a marked decrease in Cl levels (also manifested in the δ^2H and $\delta^{18}O$ signals) in the Liassic towards the Keuper aquifer was observed, which is not the case for BUL1-1, in part due to the substantial scatter of the data in this unit.

In contrast to the regular Cl profile in the Opalinus Clay, scatter is substantial in the underlying units. For the Opalinus Clay and the Staffelegg Formation (but not for any of the other units), a decent number of determinations of f_{Cl} are available, suggesting trends as indicated by the lines

in Fig. 5.1-2. A mild decrease of f_{Cl} with depth can be identified in the Opalinus Clay. This trend is broken at the top of the Staffelegg Formation, where f_{Cl} is larger and then decreases sharply with depth. Recalculation of aqueous-extraction data using f_{Cl} derived from these trend lines yields an alternative Cl profile that is shown in Fig. 5.2-2. This profile shows less scatter in the Staffelegg Formation than that shown in Fig. 5.2-1. More importantly, the discontinuity at the base of the Opalinus Clay disappears. Within the Opalinus Clay, the mentioned slight upward increase of Cl concentrations also disappears, consistent with the findings based on advective displacement and squeezing. In summary, the following conclusions can be drawn:

- The discussed Cl data based on aqueous extraction are correct and adequate from the analytical perspective, as are the concentrations recalculated to bulk porewater (illustrated in Section 4.4).
- Major uncertainties are incurred when recalculating Cl data to concentrations per anion-accessible porewater because the anion-accessible porosity fraction f_{Cl} is sample-specific and not well known. Expressing f_{Cl} as a function of the clay-mineral content alone appears to be the best what can be done at this stage but results in an additional uncertainty estimated at $\pm 20\%$, possibly more for clay-poor samples. Note that a similar assumption was made when deriving Cl profiles in the Opalinus Clay and its bounding units at other locations, such as at Mont Terri and Benken (Pearson et al. 2003, Gimmi & Waber 2004, Mazurek et al. 2011) and in the Schlattingen-1 borehole (Wersin et al. 2016). In the latter case, the observed close-to-constant anion-accessible porosity fraction over a range of clay-mineral contents was tentatively explained by the association of the major part of the porosity to the clay particles distributed in a (nearly) nonporous carbonate-tectosilicate material.
- It is clear that sample- or formation-specific factors other than clay-mineral content also affect f_{Cl} but cannot be quantified at this stage. Thus, it cannot be excluded that future attempts to quantify the Cl profile based on more substantial knowledge on anion accessibility will yield somewhat different results.
- The factors that determine anion accessibility over a range of lithologies deserve further studies. Formation-specific trends were empirically identified in those units for which sufficient data are available, but a mechanistic understanding of these trends is not currently available or is limited by the availability of the required sample-specific parameters.

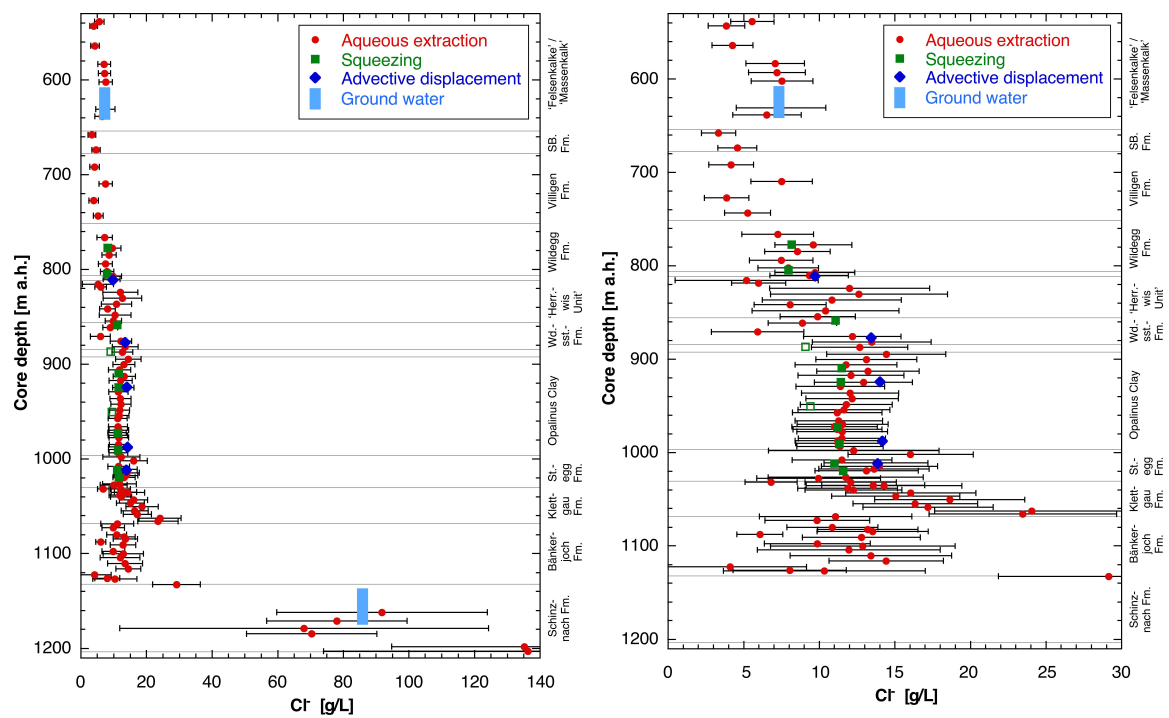


Fig. 5.2-1: Cl profile with data from squeezing, advective displacement, aqueous extraction, and groundwater samples

Left: full range of data; right: data with Cl concentrations < 30 g/L. Aqueous extraction data back-calculated to Cl-accessible porosity assuming the relationship between accessibility and clay-mineral content as discussed in Section 5.1. Error bars on the data from aqueous extraction include propagated analytical uncertainty plus another 20 % that reflect the uncertainty related to f_{Cl} . Open symbols indicate uncertain data from squeezing. Samples affected by drilling-fluid contamination (Section 4.4) are omitted.

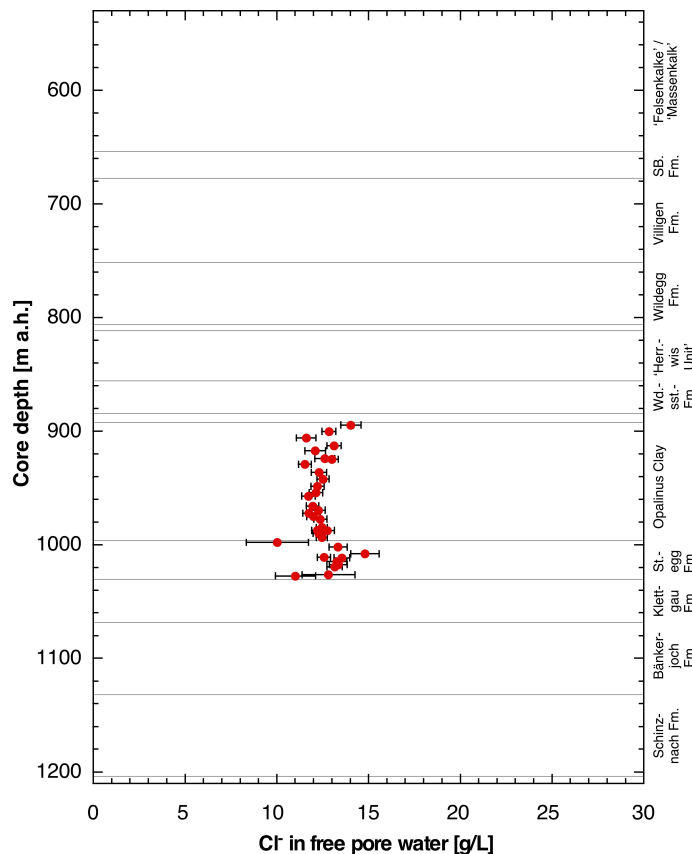


Fig. 5.2-2: Cl in anion-accessible porewater in the Opalinus Clay and in the Staffelegg Formation using an alternative approach to constrain anion accessibility

The Cl-accessible porosity fraction f_{Cl} was derived from the trend lines illustrated in Fig. 5.1-2. Bars indicate propagated analytical errors (but not the uncertainty related to f_{Cl}).

The Br profile is depicted in Fig. 5.2-3 (left) and shows much less variability than Cl. Scatter is most substantial in the Muschelkalk and Keuper formations, and concentrations remain near-constant throughout the overlying units up to the Malm, with some higher values in the reef facies of the 'Herrenwis Unit'. However, these values are somewhat uncertain due to the low water contents, high degree of small-scale rock heterogeneity and uncertainties related to anion accessibility in this unit. While the Br concentration of the Malm groundwater fits well with the adjacent porewaters, the Br content in the Muschelkalk groundwater is below that of the adjacent porewaters.

Br/Cl ratios (Fig. 5.2-3, right) can be obtained from aqueous-extraction data without any recalculation (no need to consider water content or assumptions on anion accessibility). Similarly, low water contents or rock heterogeneity affect the Br/Cl ratio to a much lesser degree than the individual concentrations. The fact that the depth trend of the Br/Cl ratio is so much smoother than that of the individual ions confirms the suspicion that methodological artefacts may affect the latter in heterogeneous, low-porosity rocks. Data obtained by squeezing and advective displacement are consistent with those from aqueous extraction.

In the section between the Bänkerjoch Formation and the top of the Opalinus Clay, the Br/Cl ratios are remarkably constant ($\sim 0.7 - 0.8$) and substantially below the value for modern seawater. Above, a steady increase up to a depth of about 600 m to values of ~ 1.5 is observed. The

latter value is close to that of modern seawater. Note also that the Br/Cl ratios of the Opalinus Clay porewaters and bounding formations are in the same range as those from the deep boreholes of Benken and Schlattingen-1.

In the Schinznach Formation, the Br/Cl ratio is substantially lower than in the overlying units. This could be taken as an argument for halite dissolution as the source of salinity in this section.

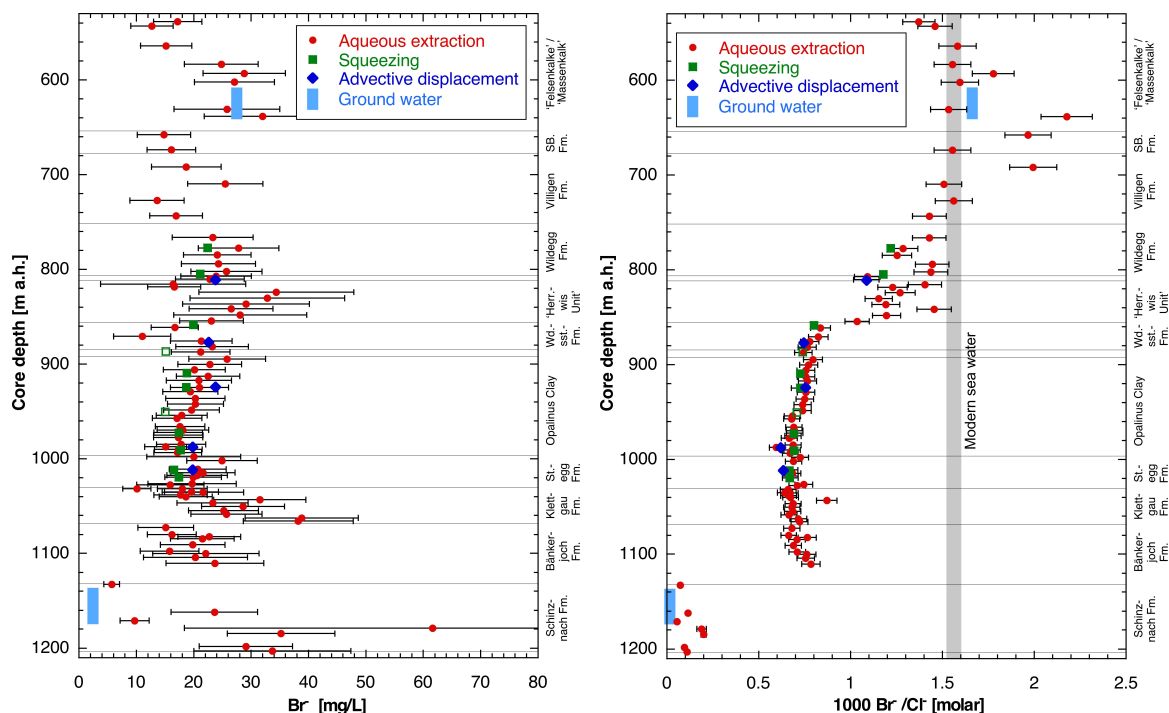


Fig. 5.2-3: Br and Br/Cl profiles with data from squeezing, advective displacement, aqueous extraction and groundwater samples

Aqueous extraction data in the Br profile back-calculated to Br-accessible porosity assuming the relationship between accessibility and clay-mineral content as discussed in Section 5.1. In the Br graphic (left), error bars on the data from aqueous extraction include propagated analytical uncertainty plus another 20 % that reflect the uncertainty related to f_{Br} . Error bars for Br/Cl (right graphic) represent propagated analytical uncertainties, given the fact that anion accessibility is not needed to calculate the ion ratio. Open symbols indicate uncertain data from squeezing. Samples affected by drilling-fluid contamination (Section 4.4) are omitted.

The profile for $\delta^{37}\text{Cl}$ is shown in Fig. 5.2-4. Pore- and groundwater values in the Schinznach Formation are close to those obtained for halite in the underlying Zeglingen Formation, supporting the hypothesis that the latter may be the main source of salinity. A decreasing trend is observed up to about the Staffelegg Formation/Opalinus Clay boundary. From there, the $\delta^{37}\text{Cl}$ values exhibit an increasing trend and reach a maximum in the Wedelsandstein Formation. Further upwards, a decreasing trend is noted, reaching similar values as the sampled groundwater in the 'Felsenkalk' / 'Massenkalk'. Overall, the $\delta^{37}\text{Cl}$ profile shows some similar trends as the Cl profile but less scatter, in particular in the Triassic.

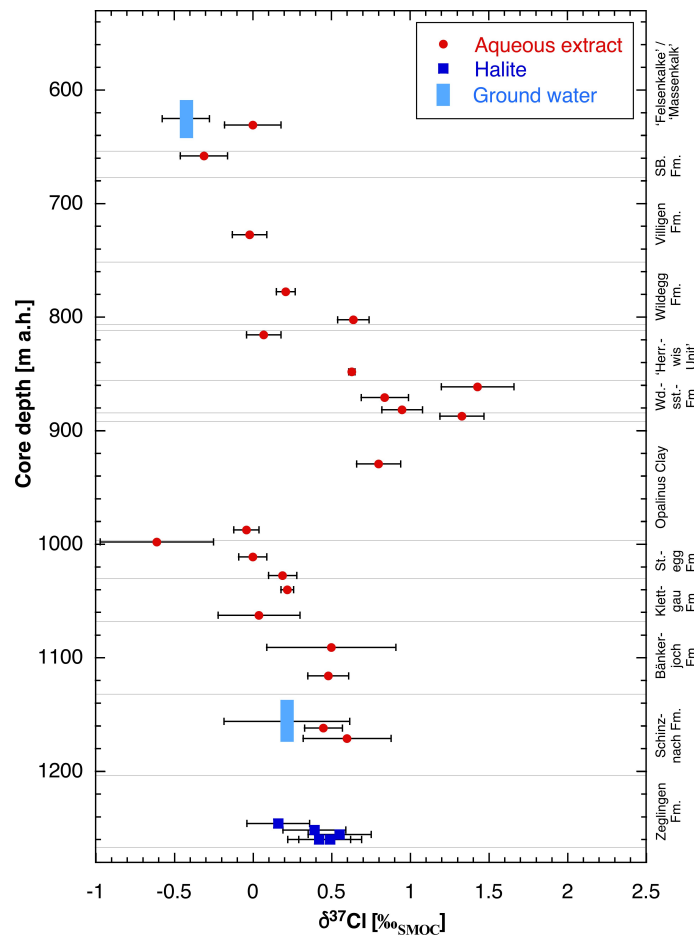


Fig. 5.2-4: $\delta^{37}\text{Cl}$ profile for aqueous extracts, rock-forming halite and groundwaters

Samples affected by drilling-fluid contamination (Section 4.4) are omitted.

5.3 Sulphate and SO_4/Cl profiles

Paul Wersin & Martin Mazurek

Sulphate data from squeezing, advective displacement, aqueous extraction and groundwaters are illustrated in logarithmic and linear scales in Fig. 5.3-1. Data from aqueous extraction were recalculated to concentrations in bulk porewater assuming conservative behaviour of sulphate. This assumption is not true at least in anhydrite-bearing lithologies where mineral dissolution contributed to SO_4 concentrations in the extracts. Anion exclusion has not been considered at this stage. Note that the groundwater data are not corrected for drilling fluid contamination, which however is considered to be minor (Lorenz 2020).

From a qualitative perspective, the highest sulphate levels are observed in the Triassic, whereas approximately constant levels are displayed from the Staffelegg Formation to the Wedelsandstein Formation. Further up, a general decreasing trend towards the sampled Malm aquifer is noted, starting from relatively high values in the 'Herrenwis Unit'.

The very high SO_4 concentrations obtained for many of the back-calculated aqueous extracts in the Keuper are physically not meaningful because of anhydrite/gypsum dissolution during extraction. The corresponding porewaters are likely controlled by gypsum equilibrium, which is

also manifested in most of the $S/L \approx 1$ extracts in anhydrite-bearing samples from the Klettgau and Bänkerjoch Formations (Section 4.4). In this context, it should be noted that the Muschelkalk groundwater (although slightly contaminated by the drilling fluid) is also slightly below gypsum saturation as suggested from speciation calculation with PHREEQC (Parkhurst & Appelo 2013) and the Pitzer database (*pitzer.dat*).

A closer look at the Opalinus Clay and the under- and overlying confining units (Staffellegg Formation and 'Brauner Dogger') reveals approximately constant and consistent concentrations between squeezing and advective displacement data (Fig. 5.3-1, right). Conversely, the back-calculated aqueous extraction data exhibits systematically higher and more variable concentrations. The mismatch with squeezing/advective displacement data increases in the overlying Wildeggen Formation. Note that the squeezing/advective displacement samples from these units display similar levels as the corresponding samples from the lower units. The discrepancy between aqueous extraction and squeezing/advective displacement data becomes even larger when anion exclusion is considered, e.g. by assuming the same relationship between anion-accessible porosity and clay-mineral content as that applied for Cl (Fig. 5.3-2). However, it should be noted that the anion exclusion effect of SO_4 in the considered rocks is not well known. From double layer theory, the exclusion of SO_4 in clayrocks is predicted to be higher because of its higher charge (Gimmi & Alt-Epping 2018). On the other hand, SO_4 has a larger tendency to form weak complexes, such as with alkaline earths, thus partly compensating the charge effect.

A similar discrepancy between squeezing/advective displacement data on the one hand and aqueous extraction data on the other has been observed for the Schlattigen-1 borehole and in the Mont Terri Rock Laboratory (Wersin et al. 2020). In the latter case, waters sampled from packed-off boreholes exhibit similar sulphate concentrations and SO_4/Cl ratios as waters squeezed from near-by drillcores. One difference between these former porewater data and that of BUL1-1 is the higher salinity, thus higher Cl levels in the latter. Comparing squeezing/advective displacement data, one can note higher SO_4 and Ca concentrations and close-to gypsum equilibrium conditions in BUL1-1, but clear undersaturation of the Mont Terri and Schlattigen-1 porewaters with respect to this mineral. On the other hand, all porewaters are close to equilibrium with regard to celestite. The latter phase could be identified in the matrix of Opalinus Clay and 'Brauner Dogger' samples at Mont Terri and Schlattigen-1 by a combined SEM/microprobe analysis (Jenni et al. 2019). In the case of BUL1-1, where in view of the higher sulphate levels, higher amounts of sulphate phases such as anhydrite and celestite could be expected, no such phase (with grain sizes of $> 3 \mu m$) could be identified by SEM analysis so far (Section 4.2.3). The reason for the higher sulphate levels derived from aqueous extraction is not understood at this stage, in spite of a recent systematic aqueous extraction study on Opalinus Clay including Mont Terri and BUL1-1 samples (Debure & Gailhanou 2019, Aschwanden & Wersin 2020). Interestingly, the SO_4 concentrations obtained from back-calculated Ni-en extracts used for obtaining cation exchange parameters are systematically lower than those obtained from aqueous extraction, but still higher than those displayed by squeezing/advective displacement data (Fig. 5.3-2). The reason for this difference is not known at this point.

The profile of SO_4/Cl ratios (Fig. 5.3-3) shows similar trends as the SO_4 profile. The high molar SO_4/Cl ratios up to almost 100 in the lower sequence point to the dissolution of sulphate-bearing phases in the aqueous extracts. In the central part, SO_4/Cl ratios remain below 1, whereby the values obtained from squeezing and advective displacement are clearly lower than those of the aqueous and Ni extracts. The ratios in the aqueous extracts increase strongly upwards in the interval 'Herrenwis Unit' to Villigen Formation, from where they decrease again, reaching low values towards the groundwater sample in the Malm. Both groundwater samples display ratios markedly below that of modern seawater (0.052). The ratios of squeezing/advective displacement samples are slightly above this value (0.06 – 0.12) and show an increasing trend towards shallower levels.

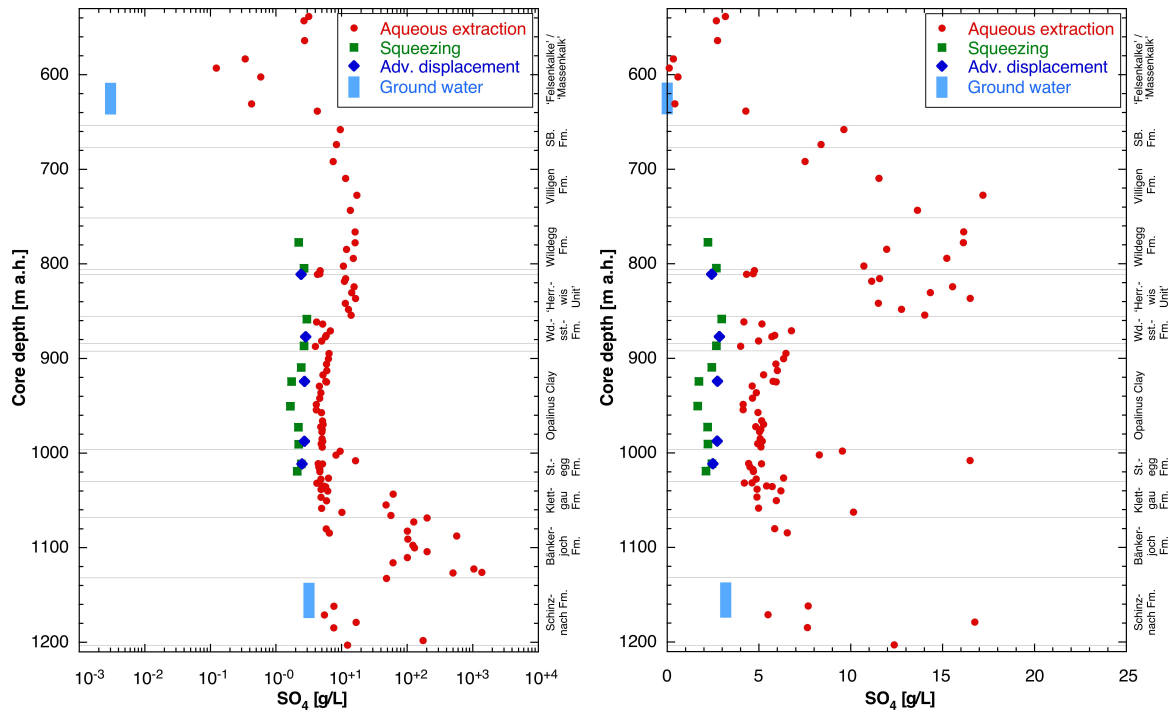


Fig. 5.3-1: SO_4 profile with data from squeezing, advective displacement, aqueous extraction, and groundwater samples

Left: entire data (logarithmic scale); right: data with SO_4 concentrations < 25 g/L (linear scale).

Aqueous extraction data back-calculated to contents in bulk porewater using water-loss porosity. Samples affected by drilling-fluid contamination (Section 4.4) are omitted.

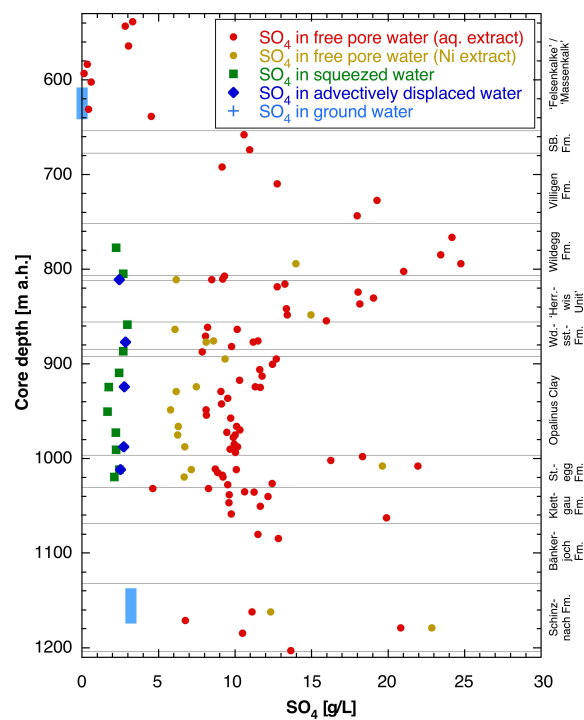


Fig. 5.3-2: SO_4 profile with data from aqueous and Ni extraction, compared with squeezing, advective displacement and groundwater data

Aqueous and Ni extraction data back-calculated to SO_4 -accessible porosity assuming the same relationship between accessibility and clay-mineral content as applied above for Cl. Samples affected by drilling-fluid contamination (Section 4.4) are omitted.

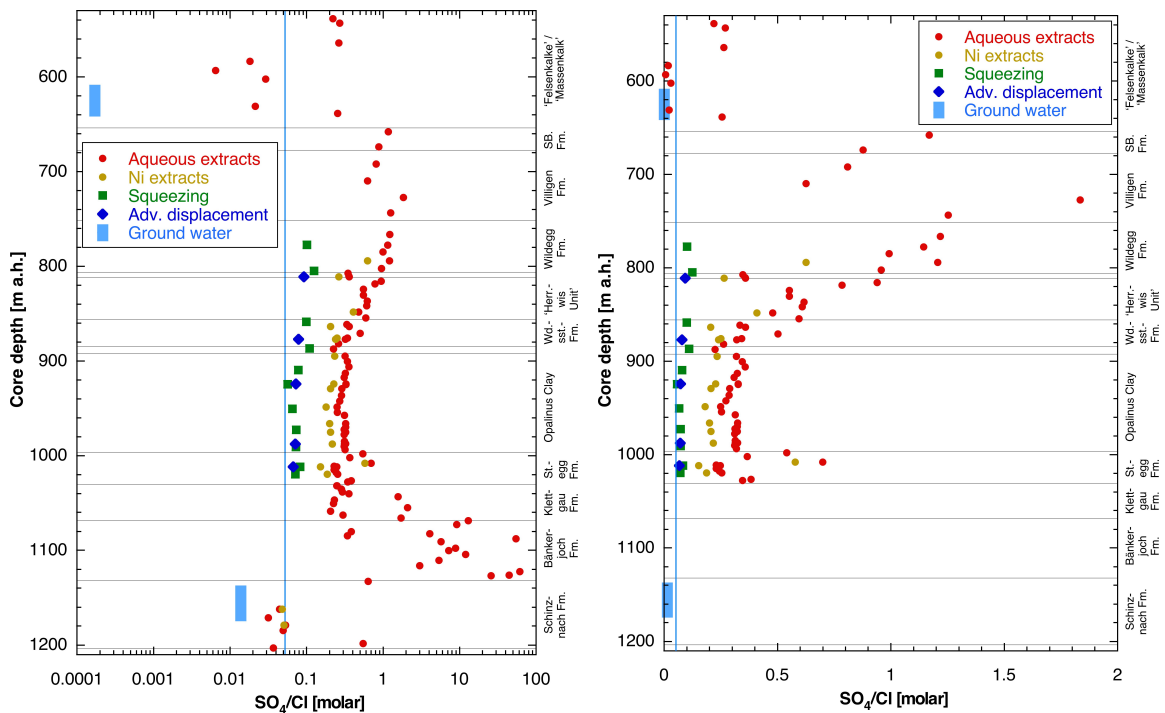


Fig. 5.3-3: Profiles showing molar SO_4/Cl ratios obtained from different methods in logarithmic and linear scales

Blue line represents modern seawater. Data from aqueous and Ni extracts not shown for the Triassic in the right graphic (most points would fall out of the plotted range). Samples affected by drilling-fluid contamination (Section 4.4) are omitted.

5.4 Some details related to the Muschelkalk aquifer and adjacent units

Martin Mazurek

5.4.1 Localisation of the aquifer

In the absence of fluid-logging data, the localisation of the Muschelkalk aquifer within the packer interval (1'137.7 – 1'173.73 m) is not trivial. A mud loss of 5 m³ was observed during drilling in the interval 1'153 – 1'162 m. From a structural perspective, the most conspicuous structure within the whole packer interval is a vertical joint that cross cuts the core in the section 1'156.32 – 1'160.63 m (Fig. 5.4-1). This joint with an orientation of 74/90 belongs to a set of steeply dipping N-S striking joints observed mainly in the interval 1'152.88 – 1'165.21 m within the Stamberg Member. Given the steep angles of dip, it is further possible that a joint runs closely parallel to the borehole without being identified in the core or in borehole logs. A hydraulic connection could nevertheless exist via the numerous dissolution features (open vugs) of the dolomite.

Assuming that the chemical and isotopic composition of the groundwater is identical to that of the adjacent porewaters also provides constraints on the localisation. For Cl⁻, the interval where this condition is potentially fulfilled is 1'153.02 – 1'161.83 m (Fig. 5.4-2). Based on the water-isotope data, a potential consistency may be present at depths < 1'161.83 m (Fig. 5.8-1; a more detailed constraint cannot be provided due to the presence of a data gap for water isotopes). Thus,

the observed mud loss during drilling, structures observed in the core and hydrochemical arguments all point to a localisation of the most permeable zone within the Muschelkalk aquifer in the interval 1'153 – 1'162 m.

5.4.2 Depth profiles of Cl^- and water isotopes in the vicinity of the Muschelkalk aquifer

The Cl^- profile shows a substantial increase of concentration with depth within the Schinznach Formation (Fig. 5.4-2). Sample 1'161.83, originating from the zone considered to represent the Muschelkalk aquifer (see above), yields a concentration in anion-accessible porewater quite close to that in the groundwater. Somewhat lower values are identified around 1'180 m, with the highest values at the base of the Schinznach Formation. Let us note that anion accessibility in clay-poor rocks is not well known (Section 5.1), so the details of the profile should not be over-interpreted at this stage.

The water isotopes in sample 1'161.83 show higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values than the groundwater. While $\delta^{18}\text{O}$ increases with depth below the Muschelkalk aquifer, $\delta^2\text{H}$ remains constant, and this leads to a progressive shift below the GMWL with depth (Figs. 5.8-1, 5.8-2).



Fig. 5.4-1: Vertical joint in the dolomites of the Stamberg Member (Schinznach Formation)
Core diameter is 10 cm.

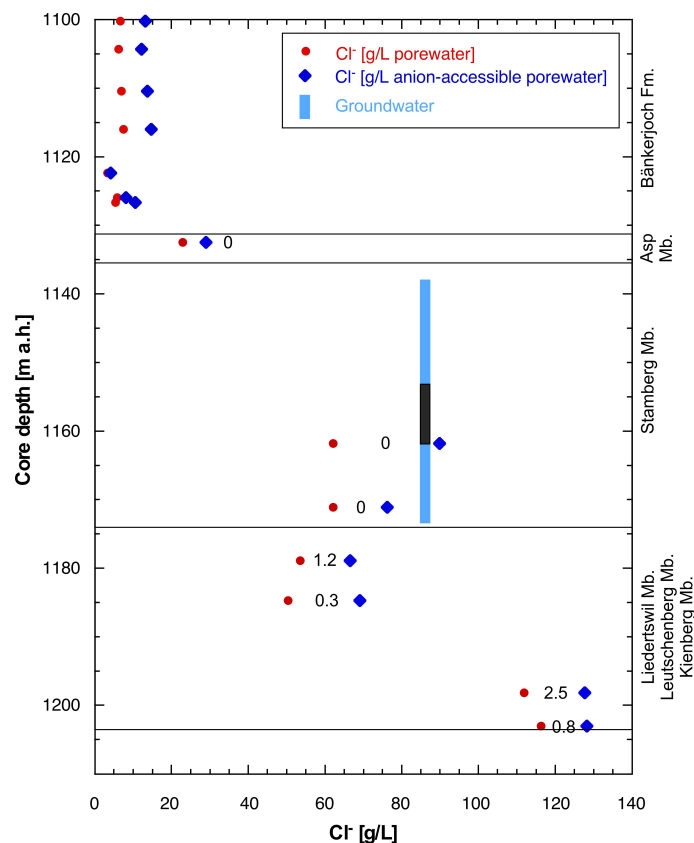


Fig. 5.4-2: Depth profile of Cl^- concentrations in pore- and groundwater in the Muschelkalk

Blue bar indicates the packer interval from which groundwater was pumped, and the most likely position of the Muschelkalk aquifer within this interval is shown in black. Red symbols indicate porewater concentrations in bulk porewater, not considering anion exclusion. Blue symbols consider anion exclusion according to the relationship between clay-mineral content and anion-accessible porosity as discussed in Section 5.1. This relationship is particularly uncertain for clay-poor lithologies, and this uncertainty propagates into the calculated Cl^- concentrations in anion-accessible porewater. Due to the difficulty to quantify this uncertainty, no error bars are indicated. Numbers indicate the ratio calcite/dolomite (mass units).

5.5 Cation concentrations in porewaters

Urs Mäder

5.5.1 General considerations

Deriving cation concentrations involves a discussion about controlling processes and disturbing effects (mineral dissolution/precipitation, cation exchange, oxidation, others) that operate invariably when handling drill core samples, in our case for performing aqueous extractions, Ni-en extractions, porewater squeezing and advective displacement experiments.

The seemingly least-affected cation is Na (no mineral source except for halite if present), not because it does not interact, but because it is in most units the major positive charge-carrying cation and thus is not sensitive to small relative changes, and a priori correlates well with chloride concentrations where chloride is the major anion charge-carrier. With increasing sulphate concen-

trations (and ionic strength), however, charge compensation may increasingly also relate to Ca concentrations, and Na forms an important ligand for sulphate complexation (NaSO_4^-) and is no longer a quasi-conservative component. In some porewater models, Na is used to top up cation charge, with other major cation concentrations constrained by mineral equilibria and measured exchanger composition.

All cations interact to variable degrees with the clay exchanger, an inventory that far exceeds the dissolved load (except in very clay-poor limestones), and disturbances are thus interlinked. Some cations are directly involved in mineral saturation equilibria (calcite, dolomite, sulphates where present), and all are directly or indirectly linked to the carbonate system (detailed in Section 5.7).

Some data were obtained for minor or trace cations such as Ba. These are not drivers for interactions but may be controlled by mineral saturation equilibria. A minor cation of some significance is ammonium (NH_4^+) that is known to be present in porewater and on the clay exchanger, but relatively few data exist. The Fe-system is analytically not well-constrained for the solutes and exchanger concentrations due to the inherent sensitivity of Fe to redox processes: it is normally constrained by modelling and linked to the more reactive Fe-bearing minerals pyrite and Fe-carbonates. Little comprehensive data exists on trace cations (e.g., transition metals) and none were measured in this study.

5.5.2 Constraints from aqueous extract data

Aqueous extracts are affected by mineral dissolution of calcite to saturation, by dolomite to a variable degree, and by anhydrite where present (Bänkerjoch Formation), as detailed in Section 4.4.3.3. This adds Ca and some Mg to the extract solutions, charge-compensated by alkalinity and sulphate in case of anhydrite. Ionic strength is low in extracts compared to porewater, and this is causing a much stronger preference for the divalent cations relative to Na and K to populate the exchanger population. This combined disturbance renders all cation concentrations to be non-conservative and therefore cannot be scaled to porewater concentrations (by water content). This is occasionally done for Na, but as discussed above, it is an approximation, and likely fails for porewaters that are not of Na-Cl type.

It may be possible to perform modelling calculations to back-track mineral dissolution contributions during aqueous extraction and the dilution induced by the added water, and so arrive at a model porewater composition. This has not yet been rigorously attempted and it remains to be demonstrated that it is possible to constrain a unique reaction pathway for back-calculation.

5.5.3 Constraints from porewater squeezing and advective displacement data

The two so-called direct sampling methods, porewater squeezing and advective displacement, aim at obtaining sample aliquots that are porewater like. Both approaches mobilise porewater and it is thought that the mobile part is more kin to the anion-accessible porewater (not affected by electrostatic effects / charged clay surfaces and interlayers). Past experience and comparison to through-diffusion experiments attest some degree of consistency to this end. One method implies high-pressure deformation and destruction of the rock fabric to squeeze porewater, the other applies large hydraulic gradients and an artificial porewater to displace the in situ porewater. The two methods are therefore quite contrasting regarding the mechanism of extraction, and some method-specific artefacts may be expected. Both methods are also expected to show agreement in a subset of characteristic porewater parameters. Also important are additional constraints for certain parameters by independent methods to identify any systemic shortcomings.

Most significant for porewater composition are the squeezed aliquots at lowest pressures (Tab. 4.6-3) and the first 1 – 3 small sample aliquots from advective displacement (Tab. 4.7-15, average of first 2 aliquots). The small sample volumes available typically allow not for analysing all parameters, may lead to high detection limits for some parameters due to required dilution, and analytical uncertainties may be larger than commonly adopted for standard analytical procedures.

The measured concentrations of major and some minor cations in squeezing aliquots from lowest pressure and the average concentration from the first two aliquots from advective displacement (Figs. 5.5-1, 5.5-2) are discussed below. Data interpretation is on-going, and data below thus represent squeezed or displaced aliquot concentrations, potentially subject to experimental artefacts as indicated below.

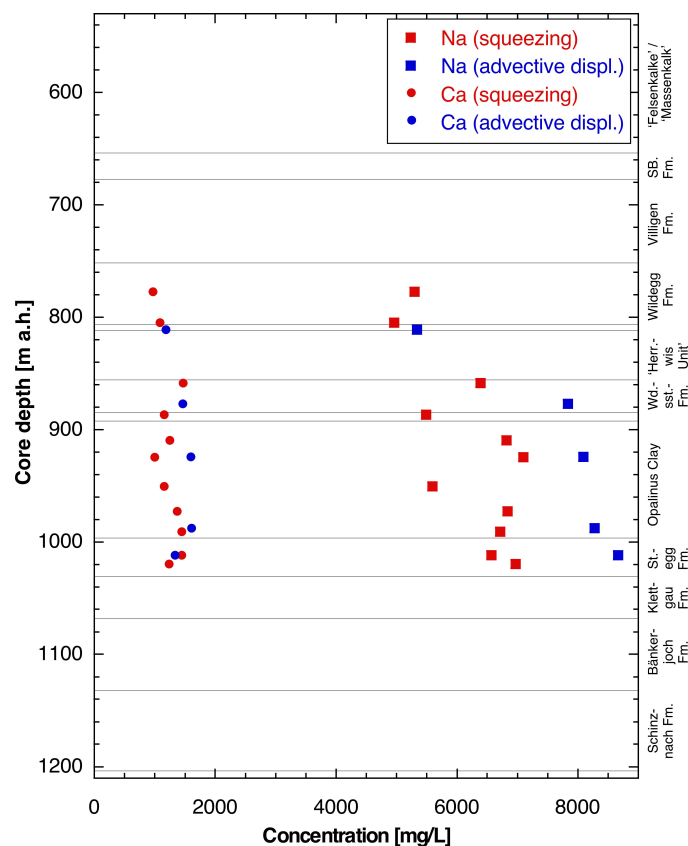


Fig. 5.5-1: Concentrations of Na and Ca in aliquots from squeezing experiments and advective displacement experiments

Only aliquots squeezed at lowest pressures are shown, and average values for the first two aliquots obtained from advective displacement.

- Because the sum of anion charge in SQ samples is ca. 20 % smaller than that in AD samples, also the sum of cations is 20 % smaller. A comparison value-by-value is therefore not meaningful, and approximately all cation concentrations in SQ samples are smaller than those in AD samples (except for K, Fig. 5.5-2).
- The carbonate system (details in Sections 5.7, 4.6, 4.7) in SQ samples is characterised by an alkaline pH (8.1 – 8.4), strong supersaturation with respect to calcite (SI 1.2 – 1.6), and a low calculated partial pressure of CO₂ (-3 to -4 in log bar units). pH from first AD aliquots cluster at 7.2 – 7.5, SI-values of calcite are 0.5 – 0.8 and log P_{CO2} ranges from -2.1 to -2.6.
- Dissolved organic carbon content are distinctly lower in SQ samples (200 – 300 mg/L, where measured) than in AD samples (300 – 900 mg/L).
- Saturation indices for celestite and gypsum are at, or slightly below or above saturation in both data sets.
- Compared to earlier SQ data sets from other boreholes, minimum pressures required to obtain first squeezing samples are distinctly higher in this study (200 MPa for 2 samples, 300 – 500 MPa for all others).
- Calculated chloride-accessible porosity fractions obtained from AD samples average 0.47 (range: 0.42 – 0.52) for the clayey sequence, and that from SQ samples 0.54 (range: 0.43 – 0.66), with overlap in the low range, but unusually large values for some SQ samples despite clay-rich compositions. It is interesting to note that the difference of 20 % in chloride concentration of the aliquots (AD vs. SQ) diminished to a difference of 15 % in the accessible porosity fraction, despite that both methods relate the extracted aliquots to the same basis, namely the initial bulk concentration. Evaluation for SQ data is more complex and relies on chloride balances to restore bulk concentration and this may be subject to larger uncertainty' and may need some more in-depth evaluation. It is also possible that the two methods do not probe the same chloride-accessible sub-volume, although in previous studies agreement in chloride concentrations was quite acceptable, but only based on few samples.

5.5.3.2 Significance of porewater aliquots from advective displacement

The aqueous extract data for chloride concentrations and for Br/Cl ratios are rather smooth across the Opalinus Clay and define a plateau. (Sections 4.4, 5.2). This is more in line with the rather homogenous data set from advective displacement. The first three aliquots for each experiment form a chloride plateau in elution trend for the top-three (811.12 m, 877.03 m, 924.18 m) AD samples (within 70 – 100 mg/L, only resolvable by high-precision analyses), and display a modest gradient in the bottom-two samples (987.55 m, 1'011.62 m; with a difference of 1'100 – 1'250 mg/L, relative to 14'000 mg/L). The squeezing data are more heterogeneous, with some outliers and a rather large range for the chloride-accessible porosity fraction. Preference is therefore given to earliest aliquots from advective displacement samples to constrain porewater composition in the confining units, along with other data (e.g., aqueous extracts, Ni-en extracts). This is not to say that advective displacement is not associated with some artefacts, one being the substantial concentrations of DOC being initially mobilised.

Chloride-accessible porosity proportion is on average smaller in AD samples, also compared to those derived from a substantial number of through-diffusion tests (where the average for samples with clay contents > 20 wt.-% is 0.51 ± 0.04). One possibility to explain the difference is that the two quite contrasting methods (advection plus diffusion vs. diffusion-only) do not exactly probe the same sub-volume of total porosity. At present, when recalculating aqueous-extraction data to porewater concentrations, adopting chloride-accessible porosity fractions from AD experiments

leads to somewhat larger salinities compared to adopting the average of all data of 0.51 (clay-rich samples) used in scaling aqueous extracts in Section 5.2. The differences are rather small, and likely within the accuracy of the methodologies.

5.5.3.3 The sulphate issue and its link to porewater cation concentrations

Substantial efforts over the past few years in form of dedicated laboratory studies and some modelling work had been directed to better constrain the sulphate concentration in porewaters. While a detailed analysis is not within the scope of this data report, some points that are directly evident from measurements and speciation calculations presented in this report are briefly addressed.

The sulphate issue relates to the observation that sulphate concentrations in aqueous extracts for the marine strata appear to be largely derived from porewater without an obvious or significant contribution from mineral dissolution (details in Section 4.4 and also 5.3). Such concentrations up-scaled to porewater content – even without considering an anion-exclusion effect – are larger than those observed in advective displacement aliquots or squeezing samples. If there is not a source – or only a limited contribution – for sulphate in aqueous extracts, there may possibly be a sink in the AD and SQ approaches. This is a possibility because the AD or SQ aliquots are at saturation with respect to celestite and gypsum, and investigations to date did not reveal the presence of these sulphates (detection limits are an issue as well). For such a sink to operate, some initial disturbance is needed that drives the porewater composition towards sulphate saturation, and from then on the squeezing or advective-displacement process might remain solubility controlled (ion-activity products of $[\text{Ca}][\text{SO}_4]$ and/or $[\text{Sr}][\text{SO}_4]$), as indicated by the data series. The amount of sulphate is not large in terms of the amounts of solids to be precipitated. Such a hypothesis obviously will need further evaluation. If such a sink exists, the original porewater will contain more sulphate, and accordingly also more cations.

5.5.4 Implications for defining formation and location-specific porewaters

The corollary of the sulphate issue is that at present the sulphate concentration in the porewater of the drill core samples cannot reliably be deduced, but may be gauged by two end-members: one with concentrations from advective displacement samples, and one from restoration of sulphate from aqueous extract data. The latter requires modelling to speciate and re-distribute sulphate and sulphate complexes across the two porosity domains. A higher-sulphate variant will accordingly contain a larger cation inventory, and this will also require a modelling interpretation based on possible processes that are supported by our data.

For a low-sulphate end-member, values may be derived from advective displacement data (Tab. 4.7-15) by restoring calcite-dolomite equilibrium, and observing that the model porewater does not become super-saturated with respect to gypsum and celestite. Such a preliminary composition had been defined in 2019 for the purpose of laboratory experiments (through-diffusion tests performed at PSI, among others).

5.6 Dissolved carbon species (inorganic, organic), alkalinity, pH, and P_{CO_2}

Urs Mäder

5.6.1 General considerations

The carbonate system (dissolved inorganic species/alkalinity, carbonate minerals, P_{CO_2}) plays a pivotal role for porewater composition as it links measurable parameters like pH, alkalinity/TIC (total inorganic carbon) to difficult-to-measure quantities like partial pressure of CO_2 . Inorganic carbon species in combination with the solid carbonate system (calcite, dolomite, etc.) intimately link dissolved Ca and Mg to the exchange complex that contains an inventory of cations that far exceeds the dissolved load (except for pure limestones). Via this link to the exchanger, also Sr, K and to a lesser extent Na are interlinked. Due to potentially solubility-limiting sulphates (anhydrite, gypsum, celestite), there is also a link to the sulphate system. With other words: the controlling carbonate equilibria, or any disturbing effects to the carbonate system, affect the entire porewater composition. By the same token, the exchanger capacity has a buffering effect on external disturbances.

Constraining the in situ porewater composition – or even that of the porewater chemical state of a sample core after drilling – involves different levels of data interpretation based on geochemical equilibrium models (like PHREEQC) and cannot be simply derived from aqueous extracts by scaling (like for conservative anions) or from one-to-one adoption from advective-displacement or squeezing aliquots. This data report does not include such modelling interpretation and therefore can only elucidate on some aspects of porewater composition.

The dissolved organic carbon species pose analytical challenges, cannot be characterised to any degree of completeness, and the measured TOC (total dissolved organic carbon) contents seem to be dependent on sample handling and sampling techniques. There is evidence that some TOC components may readily get involved in microbial processes. The link of TOC to the solid organic matter – and thus the potential TOC reservoir – is not well understood.

We use solely TOC in referring to dissolved organic carbon, and not TOC and DOC, with the latter being designated to filtrated solutions. In most cases, our TOC concentrations represent DOC values. Filtration was commonly applied to aqueous extract samples (0.2 μm), but not to small aliquots from squeezing or advective displacement, except for few cases where suspended particles were visible after dilution. In-line filtration was involved in IC analysis for low-molecular-weight organic acids.

5.6.2 Organic carbon

Available data includes (LMWOA: low-molecular-weight organic acids):

1. TOC in aqueous extracts associated with AD experiments (6 samples, clayey sequence)
2. TOC in aliquots from AD (5) and SQ (7) (clayey sequence)
3. TOC in rock samples (PW/RP samples, AD, SQ, DI, OD, GM)
4. LMWOA in PW/RP and AD aqueous extract samples
5. LMWOA in direct samples of AD and SQ
6. TOC and LMWOA in groundwaters (Malm, Muschelkalk), but all contaminated by high-TOC containing drilling fluid

TOC in rock samples (Fig. 5.6-1) show consistent and typical values near 1 wt.-% organic carbon for Opalinus Clay (average of 0.94 wt.-%, $n = 61$, and range of 0.63 – 1.32), and lower values on average, but more variable, in the 'Brauner Dogger' and Staffelegg Formation. Highest values of up to 4.8 wt.-% are associated with the Rietheim Member (Posidonienschiefer) in the Staffelegg Formation, and also select strata in the Schinznach Formation, although the latter samples show evidence for contamination by drilling fluid. There were no specific analyses performed for further characterisation of the solid organic matter.

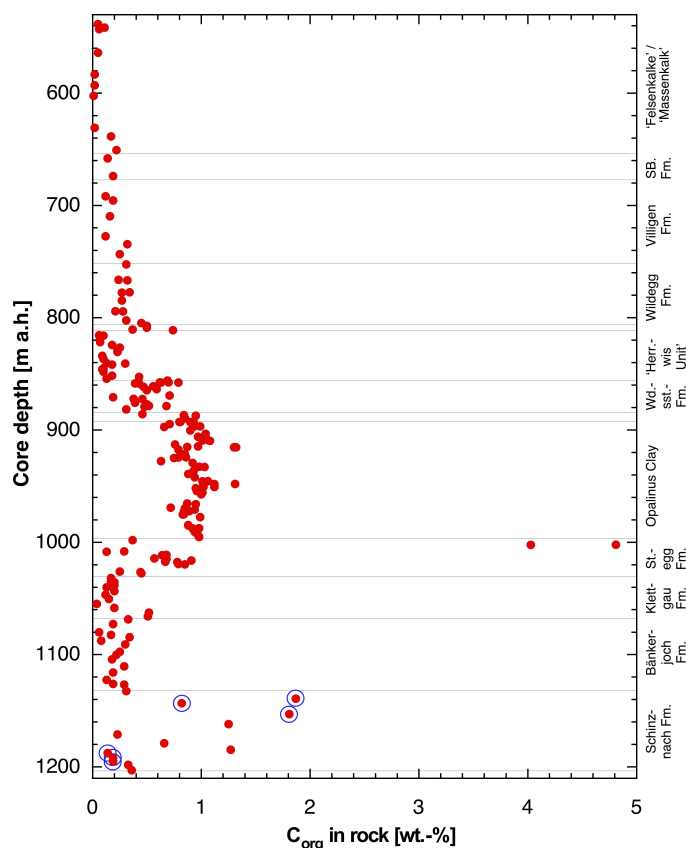


Fig. 5.6-1: TOC (total organic carbon) in rock samples

Samples from 1'139.28 to 1'153.02 m and 1'187.57 to 1'195.09 m show evidence for contamination by high-TOC bearing drilling fluid (marked by blue rings). The contamination is more evident in the upper set due to the much higher water contents. CNS-analyses were performed on chips from off-cuts adjacent to the outer margin of drill cores.

Organic carbon in liquid samples (TOC) is either determined by direct measurement (NPOC, non-purgeable organic carbon), or by difference (total carbon – TIC). Almost all TOC determinations for this study were performed by difference.

TOC (DOC) measurements for earliest sample aliquots from advective displacement (AD) contain elevated TOC of 300 – 900 mg/L for the clayey sequence (Fig. 5.6-2), but less for porewater squeezing (SQ) sample aliquots (only data shown for aliquots obtained at lowest squeezing pressures). TOC values from aqueous extracts from AD samples (pre-characterisation) are in a similar range as the AD aliquots, when up-scaled to porewater content. Such an upscaling may be subject to debate, because the nature of the organic species is mostly not known, except that a

portion is present as acetate (see below). Acetate is expected to show some kind of anion-exclusion effect, resulting in higher calculated concentrations in the anion-accessible part of the pore-water.

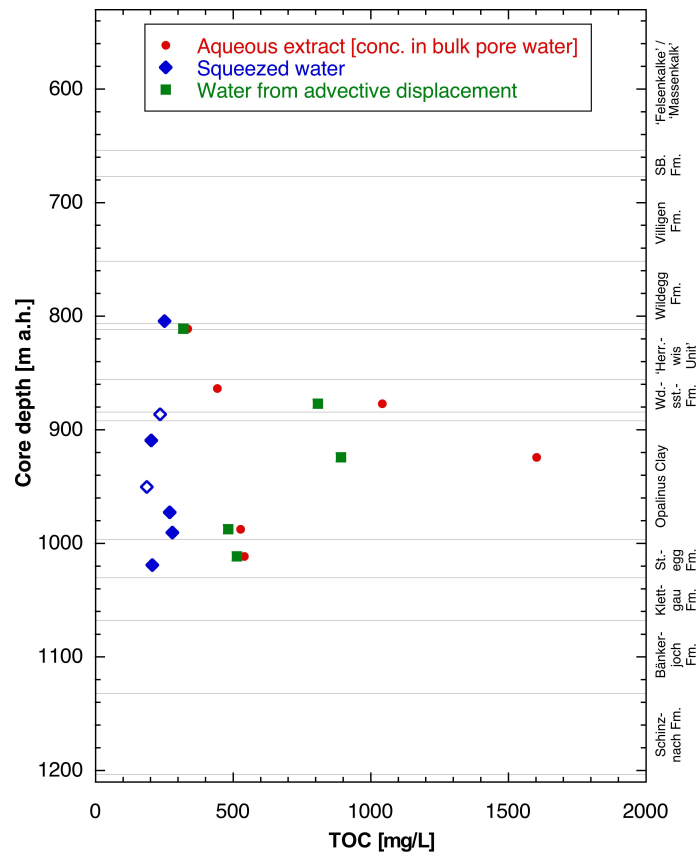


Fig. 5.6-2: TOC in aliquots from AD and SQ, and upscaled from aqueous extracts

Aqueous extract samples from advective displacement samples are scaled to porewater content. Data from squeezing refer to the lowest pressure at which a TOC analysis could be performed. Uncertain data from squeezing shown by open symbols.

Low-molecular-weight organic acids (LMWOA) that are detectable by our IC separation column include acetate, formate, lactate and propionate. These were analysed in aqueous extracts from some PW/RP samples and all AD samples, and in aliquots from AD and groundwater samples (Fig. 5.6-3). Organic acids were not quantified in aqueous extracts from PW/RP samples, except below 1'105 m (Bänkerjoch and Schinznach Formations) where acetate could be commonly quantified.

Note that an upscaling to the chloride-accessible porosity proportion – as done in Fig. 5.6-3 – is not necessarily correct because these organic acids are not only subject to purely electrostatic effects, but also to interactions specific to functional groups or surfaces. It should be viewed as an illustration.

Up-scaled acetate concentrations (aqueous extracts of AD samples) are significant in the clayey sequence ('Brauner Dogger' – Opalinus Clay – Staffelegg Formation) and overlap with the concentrations seen in earliest AD aliquots, ranging from 25 to 700 mg/L. Formate was detected only in few AD samples (clayey sequence) and lactate and propionate were below detection for all

samples. Some samples from the Schinznach Formation where acetate was measured show evidence for contamination by drilling fluid, and these data should not be used. Concentrations of acetate, formate and in part propionate were measured in Malm groundwater and in the Muschelkalk aquifer, but these samples are all contaminated by TOC-bearing drilling fluid and should not be used.

Note, that detection limits for LMWOA may vary widely, due to sample dilution implied for aqueous extracts and required for AD samples but are much lower for low-salinity groundwater samples.

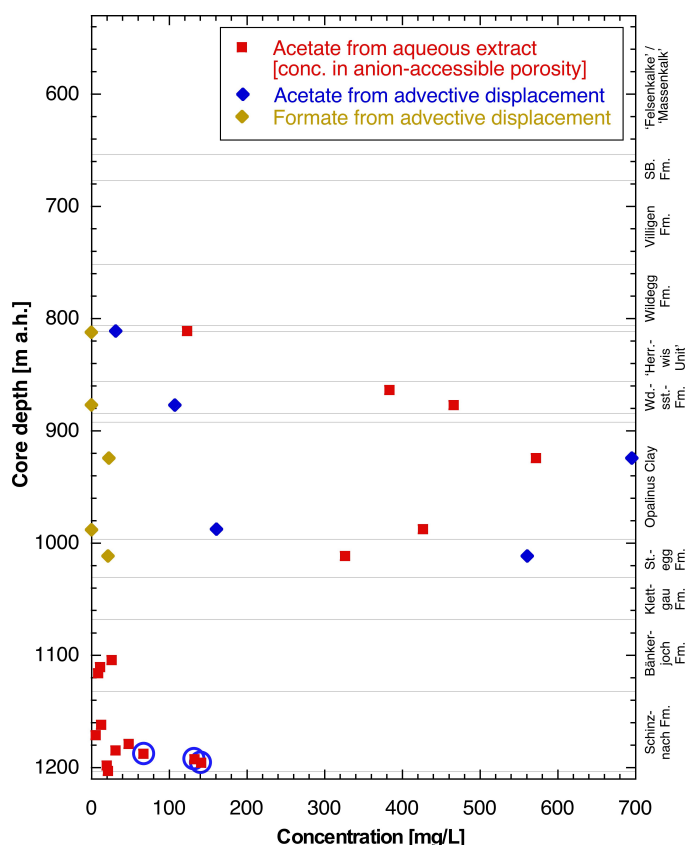


Fig. 5.6-3: LWMOA (acetate and formate) for AD aliquots and recalculated aqueous extract data

Low-molecular-weight organic acids (measured were acetate, formate, lactate, propionate) scaled to the chloride-accessible porosity proportion (0.51 for clayey samples, more for clay-poor samples; see Fig. 5.1-1). Formate data below detection (20 mg/L) in AD samples are plotted at 0. Samples from the Malm aquifer show strong evidence for contamination by the high-TOC bearing drilling fluid and so are not shown. Samples from 1'187.57 to 1'195.09 m show evidence for contamination by high-TOC bearing drilling fluid (marked by blue rings).

It is not straightforward to interpret or transfer this data directly to in situ porewater conditions. The process of aqueous extraction, porewater squeezing (limited data in this study) and advective displacement seem to mobilise TOC and LMWOA above values that have been determined from long-term in situ sampling (e.g. at Mont Terri Rock Laboratory). Furthermore, TOC concentrations strongly decrease with progress of advective displacement (Section 4.7) and the advection process seems to wash out this labile initial TOC pool. Likewise, TOC concentrations also decrease with increasing squeezing pressure (Section 4.6), and seem to be preferentially mobilised

during early squeezing stages where anion-exclusion processes are thought to be dominant. It seems certain, however, that TOC and LMWOA are part of the porewater system, presumably in some kind of long-term disequilibrium situation with the solid organic matter (some kind of sorbed form?) and the inorganic carbon system. Apparently, any disturbance (drilling, sampling, EDZ, experiments, etc.) is able to mobilise TOC significantly.

5.6.3 Dissolved inorganic carbon, alkalinity

Inorganic carbon species are either analysed directly as TIC or titrated as alkalinity. The latter is a summation parameter for all acids that can be protonated to a pH of ~ 4.3 , such that it would also include acetate, for example.

The inorganic carbon system in aqueous extracts is affected by calcite/dolomite dissolution induced by dilution and does not reflect porewater composition (see Section 4.4 for data graphs). Alkalinity in these samples largely reflects the carbonate alkalinity. Because calcite/dolomite dissolution evolves in a closed and initially CO_2 -free system during extraction, the pH rises strongly (pH 8.2 – 9.9 for Malm to Staffelegg Formation, for example) and bears no similarity to porewater pH.

The sample aliquots from advective displacement and porewater squeezing potentially may yield information on porewater TIC. TIC analyses were conducted within hours after sample collection for AD sample aliquots and after some weeks including an air-freight transport for the SQ aliquots. Alkalinity titration is not advisable for early aliquots because it may be dominated by organic acids (acetate) and thus overestimate carbonate alkalinity, and alkalinity titration also requires more sample volume than is commonly available. TIC concentration in earliest AD aliquots ranges from 29 to 43 mg/L (2.4 – 3.6 mmol/l) for the clayey sequence except for one value of 141 mg/L (987.55 m, Opalinus Clay) that is likely an outlier (Tab. 4.7-15). Straight speciation of these AD aliquots results in significant supersaturation with respect to calcite with SI values of 0.4 to 0.8, such that a geochemical modelling interpretation to restore calcite saturation may adjust some of these values. TIC measured in earliest porewater squeezing aliquots are available from 7 samples and range from 12 to 15 mg/L (1 – 1.3 mmol/l) (quantitative analyses) and 28 – 44 mg/L (2.3 – 3.7 mmol/l) (semi-quantitative analyses) (Tab. 4.6-4). Some of these values are lower than those from AD, but calculated saturation indices for calcite are strongly supersaturated, 1.2 to 1.6. These SQ samples will also require a more in-depth geochemical modelling interpretation.

In summary, a tentative range of 1.0 – 3.7 mmol/l of inorganic carbon (61 – 226 mg/L HCO_3^-) is covered by AD and SQ sample aliquots, but this somewhat large range may also be due to method-specific artefacts, and this will have to be further constrained by geochemical modelling analysis.

5.6.4 pH and partial pressure of CO_2

Like for carbonate alkalinity, it is not possible to adopt pH and calculated partial pressures of CO_2 from aqueous extract solution for reasons explained above.

pH measurements were done for advective displacement experiments, both in-line during sampling and shortly after sampling (one to few hours) on aliquots collected in syringes. Earliest in-line measurements cluster at pH 7.2 – 7.5 (Fig. 4.7-7, Tab. 4.7-15) and laboratory measurements range from pH 7.2 – 7.7 (Fig. 4.7-14, Tab. 4.7-15), covering the clayey units ('Brauner Dogger' – Opalinus Clay – Staffelegg Formation). pH measurements on SQ aliquots were performed after storage and transportation from Japan and are distinctly larger than those from AD aliquots, namely pH 8.1 – 8.4 except for one value at 7.3 (Tab. 4.6-4). Most of the aliquots contained visible precipitates of carbonates.

Partial pressures of CO₂ in log-bar units from first AD aliquots range from -2.1 to -2.6 based on straight speciation calculations, without restoration of calcite equilibrium at this stage. Depending on how calcite saturation is restored (CO₂ in/outgassing or adjustments to carbonate alkalinity) this will somewhat adjust both pH and P_{CO2} values. Partial pressures calculated for first SQ aliquots are distinctly lower than those from AD aliquots, namely -3 to -4 in log-bar units. This is a range from above atmospheric (-3.4 log bar) to distinctly below atmospheric. Again, these values will require further interpretation.

If one attests advective displacement a more gentle treatment compared to squeezing (stress concentrations, strain, destruction of fabric, transportation of sample aliquots) it would appear that the perturbations with respect to the carbonate system (pH, alkalinity, P_{CO2}) are less severe in AD aliquots compared to SQ aliquots (distinctly alkaline pH, low P_{CO2}, very strong calcite supersaturation). The expected in situ porewater pH values and partial pressures of CO₂ may therefore be closer to values obtained from early AD aliquots. These ranges observed in this study are quite comparable to those obtained from other sites (Mont Terri Rock Laboratory, Schlattingen-1 geothermal well), although only a more limited data set was available at that time. So far, the large acetate concentrations have not been rigorously addressed in the modelling interpretations, but may have some impact on the carbonate system and pH control (buffering processes). The exact process of liberation of acetate is at present poorly constrained, and so are potential interactions. Apart from effects discussed above, there are also potentially disturbing processes involved that are common to all methods, namely related to drilling, unloading, sample handling and cooling from in situ temperature. Also, these processes will have to be included in restoring in situ porewater compositions.

5.7 Cation exchange capacity and exchangeable cation population

Paul Wersin & Martin Mazurek

5.7.1 Corrected exchangeable cation data

As mentioned in Section 4.5, in order to obtain the exchangeable cation concentrations, the extracted cation data needs to be corrected for cations dissolved in the porewater and the cations released from (potential) mineral dissolution. As shown from previous work (e.g. Hadi et al. 2019), carbonate mineral dissolution can be largely suppressed with the appropriate S/L ratio, extraction time and pH conditions. Such conditions were applied for the University of Bern dataset.

Two correction methods were applied based on the concentrations of the main anions chloride and sulphate (Bradbury & Baeyens, 1998, Hadi et al. 2019). The first correction method (NaCl/Na₂SO₄) attributes dissolved Cl and SO₄ from the Ni-extracts to Na and leaves the other cations unchanged. The second method (NaCl/CaSO₄) attributes Cl to Na and SO₄ to Ca, leaving the other cations unchanged. In both methods, the CEC is calculated from the sum of cations (Σ CAT) minus the concentrations (normalised to meq/kg_{dry rock}) of Cl and SO₄. The corresponding data is shown in Tab. 5.7-1.

The relative difference between the uncorrected and corrected sums of extracted cations (Σ CAT) for the clay-rich samples is within 9 – 15 %. For the clay-poor (< 20 wt.-%) and carbonate-rich samples the difference can be substantially larger. This is particularly evident for the two samples from the Schinznach Formation where the difference is about 300 %. This clearly shows the limitation of the correction procedure for these carbonate-rich rocks and probably highlights the larger relative contribution of mineral dissolution to the cation load in solution.

Tab. 5.7-1: Sum of cations and cation occupancies obtained from Ni-en extraction after correction (University of Bern data)

First line for each sample indicates cation occupancies obtained by the NaCl/Na₂SO₄ correction method, the second line those obtained by the NaCl/CaSO₄ method.

Type	Depth [m]	Formation	Clay-mineral content	Σ CAT raw	Σ CAT corr.	Na	K	Ca	Mg	Sr
			[wt.-%]	[meq/kg _{dry} rock]		Fractional occupancy [equivalent units]				
PW	794.13	Wildegge Fm.	16	36.4	30.8	0.34 0.45	0.07	0.39 0.29	0.18	0.004
AD	811.12	'Park.-Württ.-Sch.'	51	136.8	125.1	0.38 0.42	0.07	0.36 0.33	0.18	0.005
PW	848.18	'Herrenwis Unit'	2	11.0	(7.4) ^a	(0.01) ^a (0.23) ^a	(0.04) ^a	(0.72) ^a (0.50) ^a	(0.22) ^a	(0.012) ^a
AD	863.66	Wedelsandstein Fm.	51	134.9	123.8	0.49 0.52	0.05	0.33 0.30	0.12	0.005
PW	875.69	Wedelsandstein Fm.	27	79.4	70.3	0.44 0.48	0.05	0.37 0.33	0.13	0.005
AD	877.03	Wedelsandstein Fm.	40	103.8	92.5	0.46 0.50	0.06	0.36 0.32	0.12	0.005
PW	894.68	Opalinus Clay	34	79.3	68.9	0.38 0.49	0.06	0.41 0.32	0.14	0.005
AD	924.18	Opalinus Clay	48	98.3	88.0	0.47 0.50	0.06	0.35 0.31	0.12	0.006
PW	929.23	Opalinus Clay	56	113.3	103.2	0.46 0.49	0.05	0.36 0.34	0.12	0.006
PW	948.58	Opalinus Clay	62	126.3	114.6	0.42 0.53	0.05	0.40 0.37	0.13	0.006
PW	965.98	Opalinus Clay	64	117.5	106.8	0.47 0.50	0.05	0.37 0.34	0.11	0.005
PW	975.25	Opalinus Clay	54	110.1	100.2	0.47 0.50	0.05	0.36 0.33	0.11	0.006
AD	987.55	Opalinus Clay	61	127.6	116.7	0.45 0.48	0.05	0.38 0.35	0.12	0.005
PW	1'008.04	Staffelegg Fm.	10	22.8	18.8	0.32 0.43	0.06	0.49 0.38	0.12	0.004
AD	1'011.62	Staffelegg Fm.	37	83.5	72.7	0.45 0.49	0.07	0.36 0.33	0.11	0.006
PW	1'019.49	Staffelegg Fm.	48	105.5	96.1	0.49 0.52	0.05	0.36 0.33	0.10	0.005
PW	1'161.83	Schinzach Fm.	13	66.6	(15.8) ^a	(0.73) ^b	(0.01) ^b	(0.10) ^b	(0.17) ^b	(1.5E-4) ^b
PW	1'178.88	Schinzach Fm.	8	30.0	(7.70) ^a	(0.60) ^b	(0.01) ^b	(0.14) ^b	(0.25) ^b	(1.5E-4) ^b

^a data deemed unreliable (see text); ^b uncorrected data, also deemed unreliable.

The correlation between Ni consumption and ΣCAT is illustrated in Fig. 5.7-1. The slope is below 1 (0.89 and 0.83 for the uncorrected and corrected data, respectively), indicating the generally slightly larger CEC values derived from Ni consumption. Further, Figs. 5.7-2 and 5.7-3 indicate good correlations between clay-mineral content and BET surface area with CEC parameters.

The exchangeable cations are expressed as cation occupancies (in equivalent fractions) in Tab. 5.7-1. Na and Ca are the main exchangeable cations, followed by Mg and K. The Sr occupancies are considerably lower (generally below 1 %). In the case of the carbonate-rich sample from the 'Herrenwis Unit', the Na occupancy is significantly below the general trend and arises from the large amount of Cl in the Ni-extracts, which reduces Na in the correction procedure. The two samples from the Schinznach Formation even yield negative Na values (not shown) with the applied correction methods, underscoring the limitation of the approach for these samples. The other samples indicate broadly consistent trends.

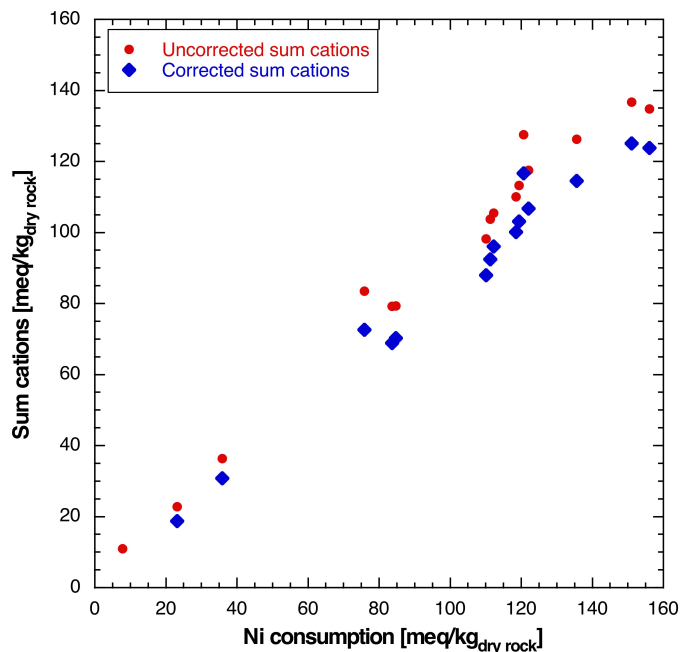


Fig. 5.7-1: Ni consumption vs. sum of cations (data of the University of Bern)

Data considered to be unreliable (Tab. 5.7-1) are not shown.

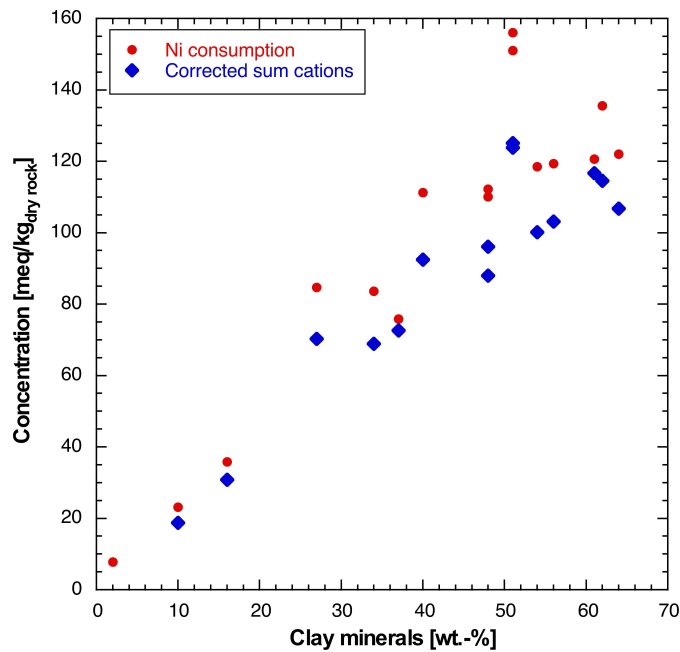


Fig. 5.7-2: CEC parameters as a function of clay-mineral content (data of the University of Bern)

Data considered to be unreliable (Tab. 5.7-1) are not shown.

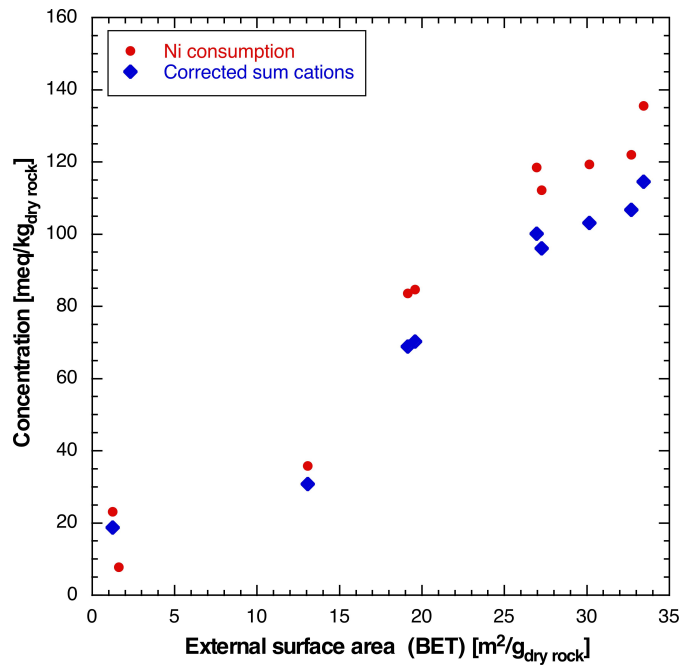


Fig. 5.7-3: CEC parameters as a function of BET surface area (data of the University of Bern)

Data considered to be unreliable (Tab. 5.7-1) are not shown.

5.7.2 Comparison with data from PSI

An extensive cation exchange dataset for the BUL1-1 borehole was elaborated by PSI (Marques Fernandes & Baeyens *in prep.*). Of the 34 samples, six samples were taken from the same drill-cores as the samples of the University of Bern.

In a first step, the CEC at PSI was determined from Ni consumption with the Ni-en extraction method. Subsequently, the main dataset was generated via CsNO₃ extraction, from which the CEC and the exchanger population were obtained. The CEC was derived by subtracting the anions (Cl, SO₄, HCO₃/CO₃) from the cations (Na, Ca, Mg, K, NH₄, Sr). The exchanger population was derived by two correction methods: (1) attributing Cl and SO₄ to Na and TIC to Ca, and (2) attributing Cl to Na and SO₄ and TIC to Ca. Note that these two methods are analogous to the ones used for the University of Bern samples presented above, except for the additional consideration of TIC.

The conditions applied in the different extraction methods of PSI and Uni Bern are compared in Tab. 5.7-2. Important differences of the PSI methods relative to that of the University of Bern are (i) the lower solid/liquid ratios, (ii) the smaller amount of solid mass and (iii) the variable concentration of the index cation depending on the expected CEC. Note that extractions at the University of Bern were conducted at the same initial Ni concentrations irrespective of the CEC of the sample.

Tab. 5.7-2: Extraction conditions applied by the University of Bern and PSI

	University of Bern	PSI	PSI
Extraction method	Ni-ethylenediamine	Ni-ethylenediamine	CsNO ₃
Extract solution concentration	~ 135 mmol/L	2.5 mmol/L	43 mmol/L
Solid/Liquid ratio	~ 0.9 kg/L	~ 0.034 kg/L	0.055 – 0.28 kg/L
Amount of solid used	~ 30 g	~ 1 – 3 g ^{a)}	~ 2 – 10 g ^{a)}
Extraction time	24 h	24 h	24 h
Final pH	8.3 – 8.5	7.8 – 8.4	8.6 – 9.3
Sample disaggregation	Disintegration by hand to a few mm ³ pieces	Milled and passed through 1 mm sieve	Milled and passed through 1 mm sieve
Sample storage time prior to preparation	1 – 14 days	Several months	Several months
Extraction in glovebox	Yes	No	Yes

^{a)} S/L ratio adjusted to obtain the expected index cation consumption-to-CEC ratio.

Cation exchange capacity and corrected sum of extracted cations

The Ni-en consumption and the corrected Σ CAT data (the latter from Ni-en extraction in the case of the University of Bern and CsNO_3 in the case of PSI) are shown in Fig. 5.7-4. From the comparison of these two datasets, in particular considering the six samples from the same drillcores, the following findings can be derived (see also Fig. 5.7-5):

- The CEC values obtained from Ni consumption exhibit the same trends in both datasets. Comparison of the samples from the same drillcores indicates higher Ni consumption for the University of Bern samples (increase of about 20 – 30 %). An exception is one sample (BUL1-1 1'008.04) from the Staffelegg Formation, for which lower Ni consumption (-35 %) was obtained by the University of Bern.
- The corrected sum of cations also shows broad consistency for both datasets. Data of the samples from the same drillcores from the University of Bern is somewhat lower (-3 to -25 %) compared to that of PSI. Only for sample BUL1-1 1'008.04 (limestone with 10 wt.-% clay minerals), the discrepancy is larger (-56 %).
- Comparing the Ni consumption data from PSI with the corrected Σ CAT from the University of Bern, a remarkable agreement (within 6 – 14 %) is manifested, again except for sample BUL1-1 1'008.04 (-35 %).

These findings are interpreted as follows:

- The corrected Σ CAT data from the University of Bern and Ni-consumption data from PSI are considered to be the most representative measures of the CEC.
- The Ni consumption data from the University of Bern is likely somewhat too high with regard to CEC because of the rather high initial Ni-en concentration applied irrespective of the clay-mineral content of the sample. This may have resulted in polymerisation of Ni-en complexes at the clay surface (surface precipitation).
- The corrected Σ CAT of PSI is likely somewhat too high with regard to CEC because of selective leaching of K and probably also of NH_4 (see discussion below).
- The discrepancy found for sample BUL1-1 1'008.04, which constitutes a clay-poor and carbonate-rich rock from the Staffelegg Formation, is interpreted as being affected by mineral dissolution, but to a different extent in the different extraction procedures. Perhaps sample heterogeneity may also explain part of the difference although the drillcore visually appeared rather homogeneous.

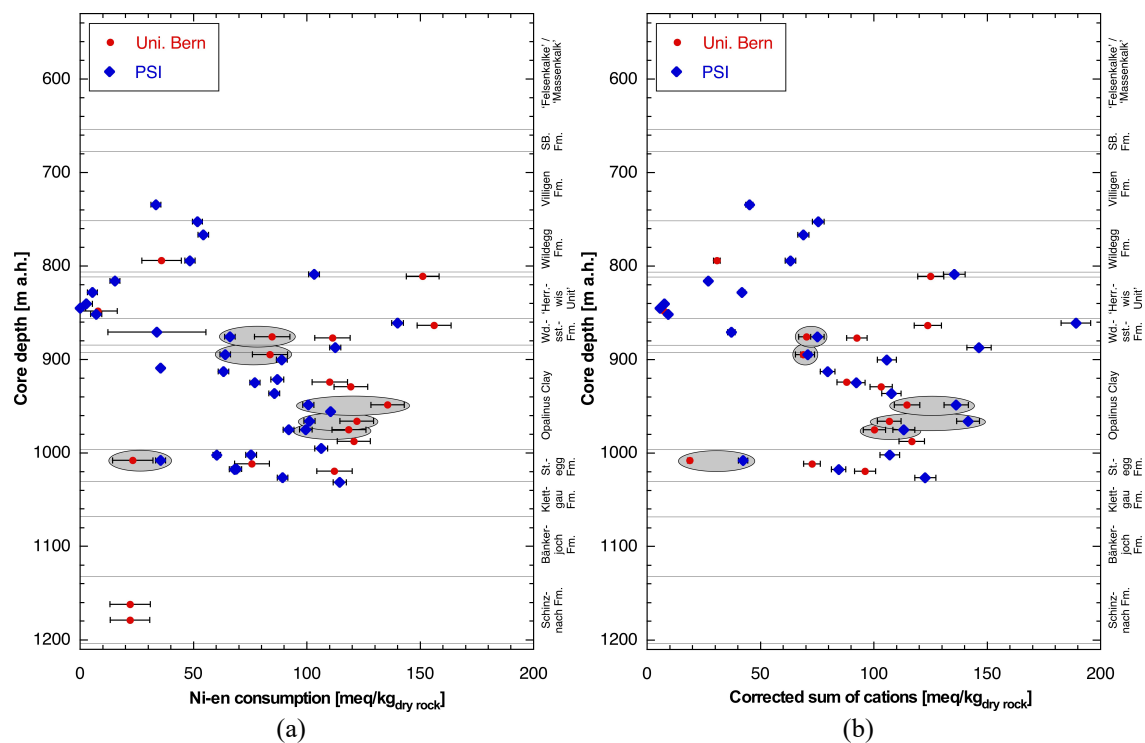


Fig. 5.7-4: Comparison of CEC data from the University of Bern and from PSI

(a) Ni consumption data; (b) Corrected sum of cations. Grey ellipses highlight materials from the same core.

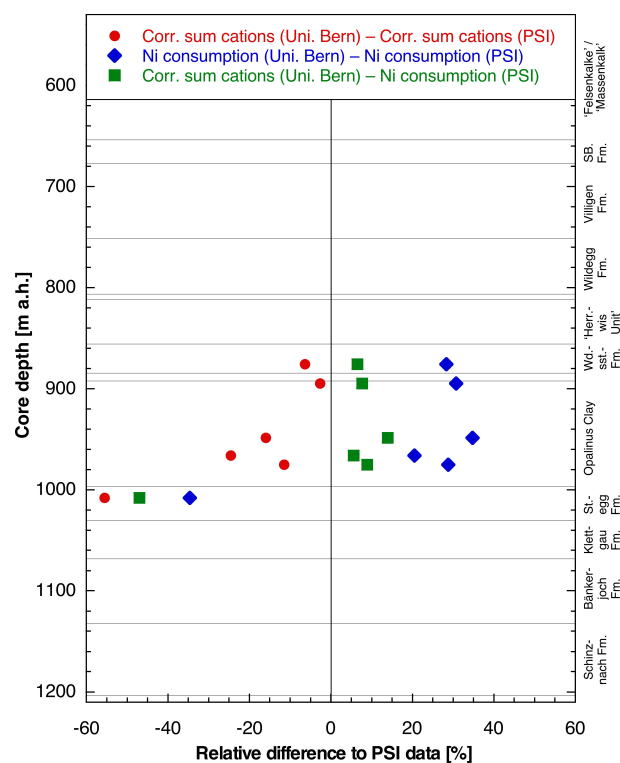


Fig. 5.7-5: Differences pertaining to Ni consumption and corrected sums of cations for the six samples studied by both University of Bern and PSI

Exchangeable cation occupancies

The advantage of comparing fractional cation occupancies rather than the extracted cation concentrations is that they are normalised to the sum of cations (as proxy for the CEC) and do not directly depend on the clay-mineral content of the sample.

Fig. 5.7-6 shows the Na and Ca occupancies derived from the two correction methods. Note that in method 1 Cl and SO₄ are attributed to Na, whereas in method 2, SO₄ and, in the case of PSI data, also TIC is attributed to Ca. Thus, the Na fraction is minimised in method 1 and maximised in method 2, while the opposite is true for Ca. Comparison of University of Bern and PSI data illustrates very similar trends for Na and Ca as main exchangeable cations. Both Na and Ca occupancies derived from University of Bern data are slightly higher than those of PSI. This is particularly evident in the clay-rich units of the Opalinus Clay, the Staffelegg Formation and the Klettgau Formation. The reason for this is not the higher extracted amount of these two cations. In fact, in the case of Na, the samples from the same drillcores show very similar extracted amounts (not shown). For Ca, there is more variation, but no systematic trend can be deduced. The reason lies more likely in the higher amount of K extracted by the PSI method and, to a lesser extent, in the contribution of NH₄, which lowers the fraction of the other cations (Fig. 5.7-7). In fact, the sum of K and NH₄ occupancy determined from the PSI data makes up more than 20 % of the CEC for most samples. The K occupancies from University of Bern are a factor of 2 – 3 lower than the corresponding ones of PSI. While both datasets show a strong correlation between illite content and concentration of extracted K, the dependence is much stronger for the PSI data (Fig. 5.7-8). This suggests that an additional pool of K present in illite (possibly from the inter-layer) is mobilised by Cs in the case of PSI, which is less the case for the Ni method used by the University of Bern.

The comparison of the Mg and Sr occupancies reveals agreement in terms of trends between the two datasets (Fig. 5.7-9). For Mg, the fractional occupancies are similar, but the absolute values for the same core samples tend to be higher in the case of PSI data. Thus, the similar occupancies appear to be result of the compensation by the lower fraction of Mg due to the higher K occupancy in the PSI extracts. The reason for the somewhat higher Mg concentrations is possibly due to dolomite dissolution in the Cs extracts which were conducted at lower solid/liquid ratio than the Ni-en extracts of the University of Bern. This effect is particularly strong in the 'Herrenwis Unit', which contains up to 10 wt.-% dolomite. In the case of Sr, the occupancies are generally somewhat higher for the University of Bern data. This is partly due to the slightly larger amount of Sr extracted when comparing the samples from the same drillcores (not shown) and partly because of the lower fraction of K.

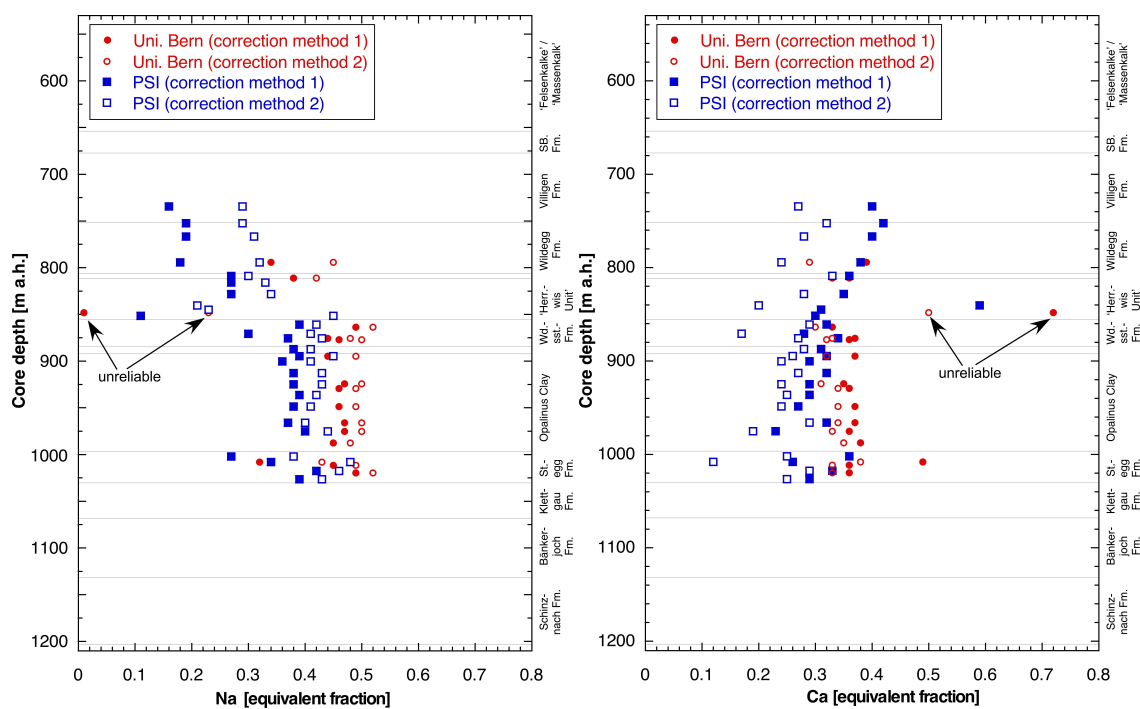


Fig. 5.7-6: Na (left) and Ca (right) occupancies according to University of Bern and PSI data

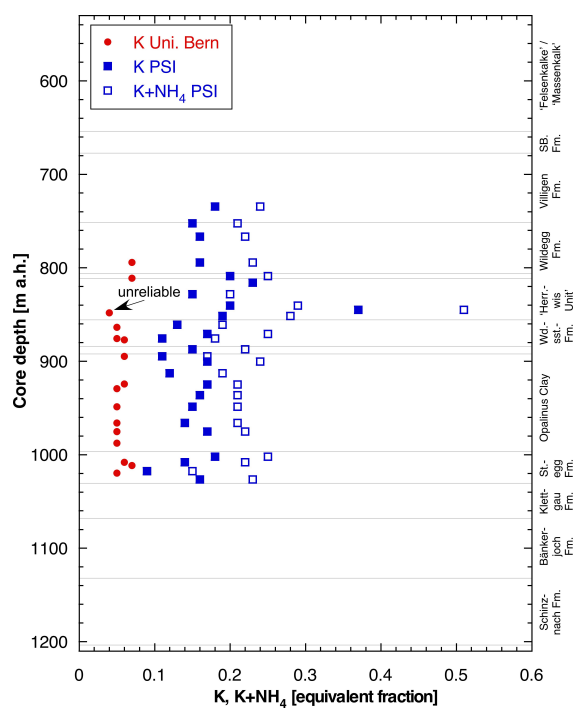


Fig. 5.7-7: K⁺ and NH₄⁺ occupancies according to University of Bern and PSI data

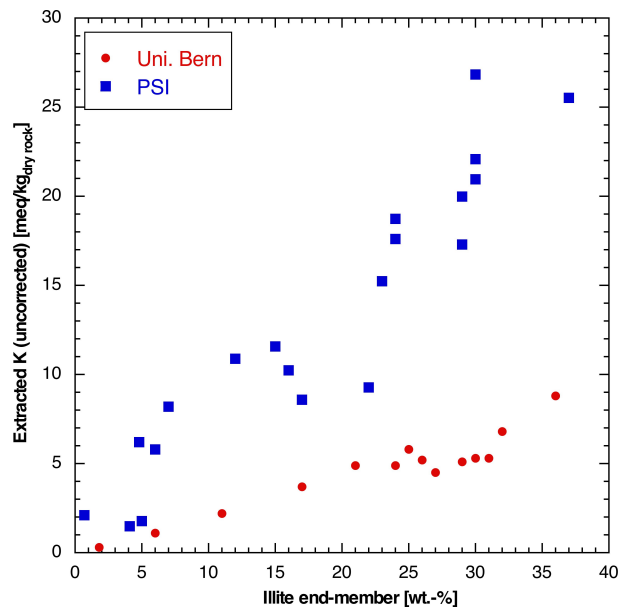


Fig. 5.7-8: Content of the illite end-member vs. extracted K

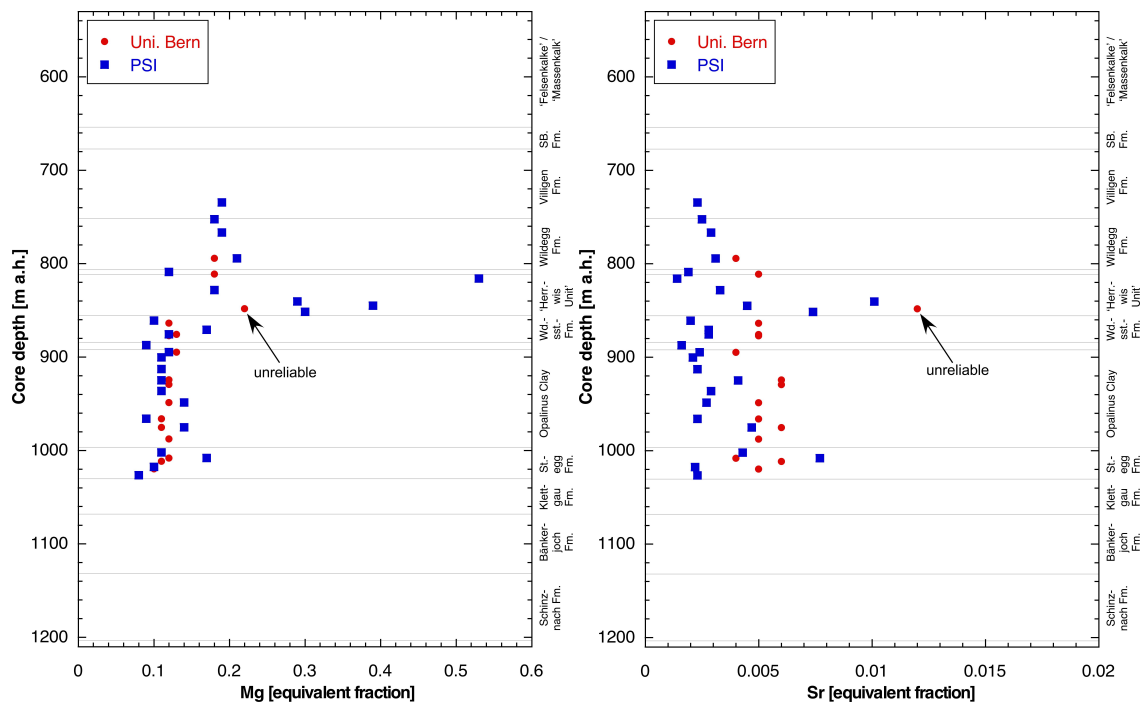


Fig. 5.7-9: Mg (left) and Sr (right) occupancies according to University of Bern and PSI data

Extracted anions

The amounts of Cl extracted are consistent between the two datasets (Fig. 5.7-10). Regarding SO_4 , the trends are similar but the PSI data is somewhat higher than that of University of Bern. Note that the extracted sulphate amounts in the PSI extracts are similar to those obtained by aqueous extraction at University of Bern. Thus, pyrite oxidation is likely not the reason for the higher sulphate in the PSI extracts.

Total inorganic carbon (TIC) measured in the PSI extracts is several mmol/kg_{dry rock} (not shown). This is higher than expected for University of Bern extracts. The latter were not measured but calculated to be in the range of 0.1 – 0.6 mmol/kg_{dry rock} based on the assumption of calcite equilibrium (data not shown). The higher TIC in the PSI extracts is explained by the lower S/L ratio which induces a higher proportion of dissolved carbonate from carbonate minerals.

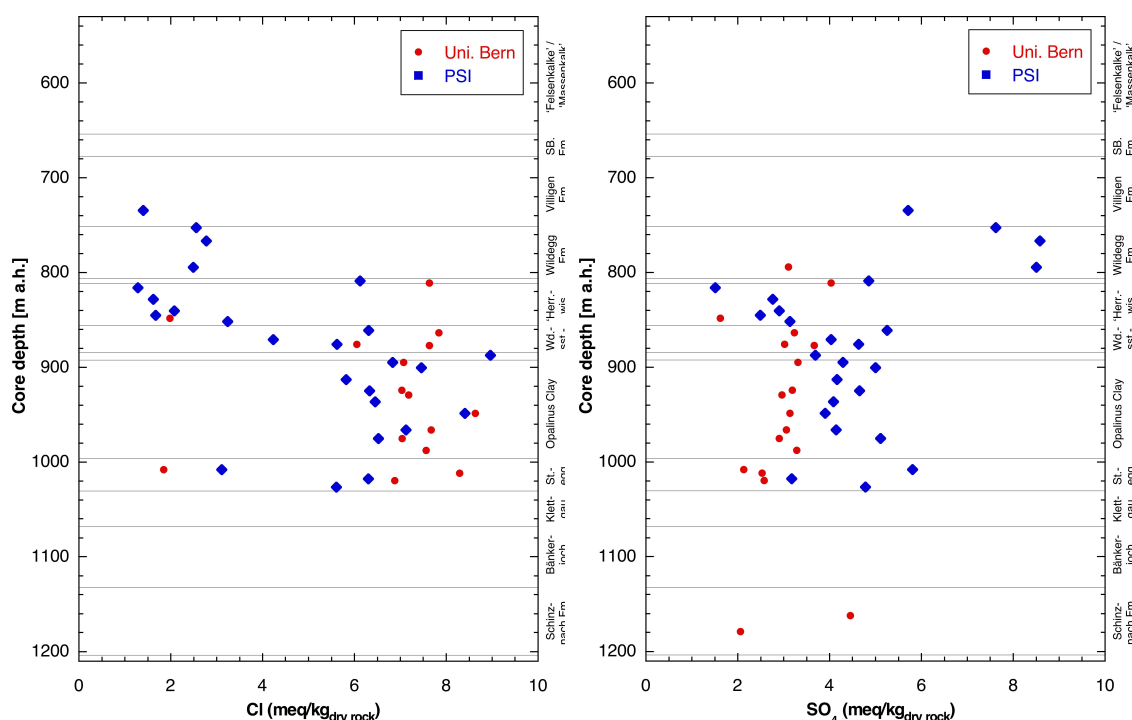


Fig. 5.7-10: Extracted Cl (left) and SO_4 (right) according to University of Bern and PSI data

5.7.3 Summary and conclusions

The datasets of University of Bern and PSI obtained with different methods yield broadly consistent data in terms of CEC and exchangeable cation population. Specifically, the following findings are worth mentioning:

- The CEC data obtained from the consumption of the index cation (Ni) and the corrected sum of cations display consistent trends. The values correlate with the clay-mineral content. The data thought to be the most representative for the "true" CEC are the Ni consumption data from PSI and the ΣCAT data from the University of Bern, which show a close match.
- The cation occupancies obtained from the two datasets reveal broad consistency in terms of trends. Some heterogeneity is observed in the Staffelegg Formation, whereas the interval Opalinus Clay – Wedelsandstein-Formation is characterised by rather constant occupancies. Towards the Malm, a gradual decrease in Na and concomitant gradual increase of Ca is noted.

- The differences noted between the two datasets can largely be explained by the higher amounts of K extracted by Cs the extraction method used by PSI. In that dataset, the strong dependence of the extracted K on the illite content suggests that an additional K pool from illite is mobilised with this extraction method.
- With regard to Ni consumption, the higher values obtained by the University of Bern are suspected to be influenced by artefacts such as polymerisation on the clay surface, so the PSI data for which a lower Ni concentration was used is preferred.

5.8 Stable water isotopes

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5.8.1 Comparison between different methods for the determination of stable porewater isotope compositions

The stable-isotope composition of the porewater was determined using three different methods including the diffusive exchange (Section 4.9), squeezing (Section 4.6) and advective displacement (Section 4.7) methods. All data, together with those for the two groundwater samples, are shown in Fig. 5.8-1. $\delta^2\text{H}$ data from advective-displacement experiments are excluded at this stage due to the anomalous and currently not fully understood breakthrough behaviour (see Section 4.7). Apart from this, the consistency between the methods is good.

5.8.2 Comparison with groundwater data and depth profiles

The groundwater in the Malm aquifer fits well into the trend of the adjacent porewater data. It is remarkable that it approximately coincides with the depth of the highest $\delta^{18}\text{O}$ values in the profile, with trend towards lower values up- and downwards. It also coincides with the most negative deuterium excess values (Fig. 4.9-3). The gradients of $\delta^{18}\text{O}$ in both vertical directions are minor, those of $\delta^2\text{H}$ even more so, indicating that the isotopic composition of the groundwater remained constant over geological periods of time.

The groundwater in the Muschelkalk aquifer has distinctly lower δ values than the adjacent porewaters. This does not necessarily have to be an inconsistency, given the substantial gradients in this section and the fact that the diffusive-exchange experiments in the interval 1'127 – 1'161 m failed, resulting in an information gap. Indications exist from drilling operations and hydraulic testing that the main water inflow within the packed-off interval occurred within the information gap (Section 5.4), so a direct comparison is not feasible. In any case, the groundwater appears to represent minima of $\delta^{18}\text{O}$ and $\delta^2\text{H}$, with remarkably steep gradients towards higher values up- and downwards. Such steep gradients indicate either that the isotope signal in the groundwater is geologically young, and/or the diffusion coefficients in the lower Bänkerjoch Formation are very low.

Besides the large-scale trends, the profiles show some minor undulations, only slightly larger than the experimental error. These undulations are not explained at this stage. Should they have a hydrogeological meaning, they should also be seen in the profiles of other tracers, such as Cl and possibly Br/Cl, which, however, is not the case. When judging the hydrogeological significance of these undulations, one should keep in mind that the reported propagated errors consider only the known analytical errors. In principle, the error of the data points may be larger due to other potential sources of error (e.g. slight contamination with drilling fluid or on-site rinsing fluid, variable on-site handling times, slight desaturation, effects of pressure release when brought to the surface ...). It is impossible to quantify these potential errors, but careful quality checks were run to exclude clearly affected data.

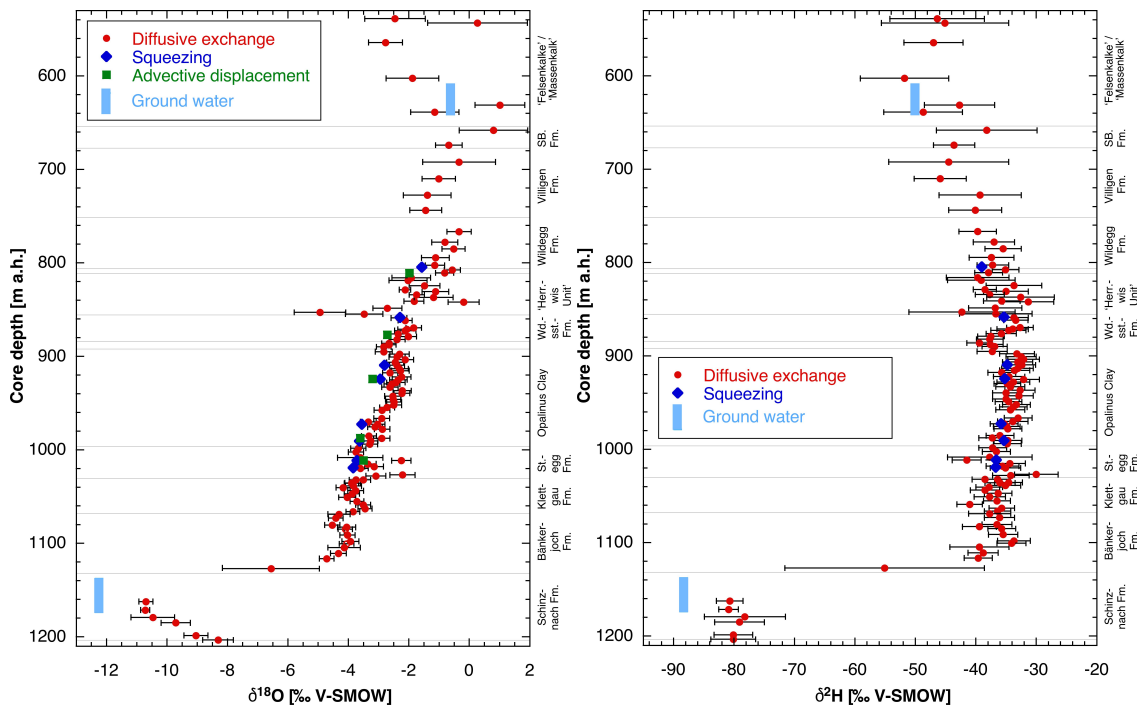


Fig. 5.8-1: Depth trends of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in porewater based on all available technique, together with groundwater data

Uncertain values are not shown: 1) Results from the diffusive-exchange technique that did not pass the quality criteria discussed in Section 4.9; 2) data for 2 squeezed samples that indicated anomalous behaviour of solute concentrations with squeezing pressure (Section 4.6); 3) $\delta^2\text{H}$ data from advective-displacement experiments (anomalous behaviour of the $\delta^2\text{H}$ breakthroughs; Section 4.7). Bars indicate propagated analytical errors (diffusive exchange). Groundwater data are from Lorenz (2020).

5.8.3 $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ and comparison with Global Meteoric Water Line (GMWL)

Fig. 5.8-2 illustrates all data in a graphic of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$. All porewater data lie below the GMWL, which can be taken as evidence of long underground residence times. As shown by the green arrow, $\delta^{18}\text{O}$ increases from the Bänkerjoch Formation towards the Malm aquifer, while $\delta^2\text{H}$ first increases slightly and then decreases. All isotope data in this section have δ values substantially higher than current precipitation, which indicates that the component of meteoric water in these porewaters is limited at best.

The situation is completely different in the Schinznach Formation, where the Muschelkalk groundwater composition lies on the GMWL and has $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values below those of current precipitation, indicative of cold-climate infiltration. Below the aquifer, porewater data start deviating from the GMWL with depth, mainly due to increasing $\delta^{18}\text{O}$ values.

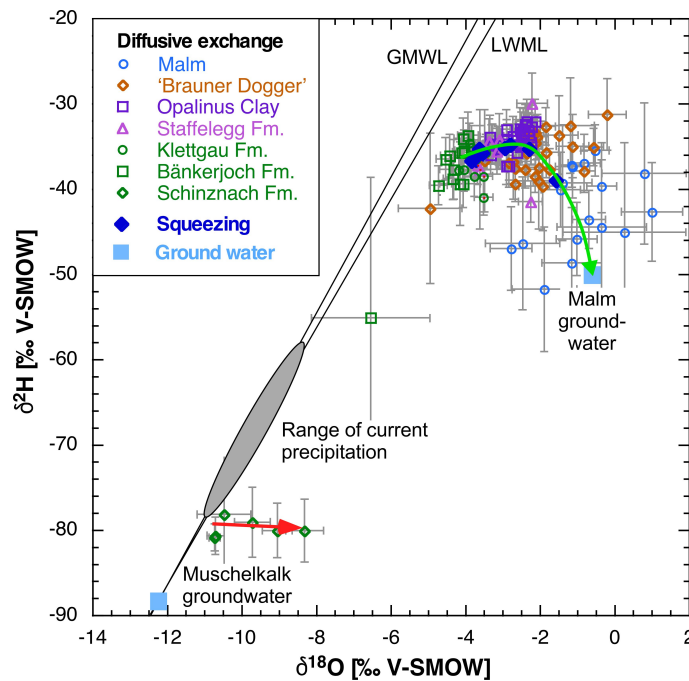


Fig. 5.8-2: $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for porewaters based on the isotope diffusive exchange technique

Green arrow indicates the trend from the Bänkerjoch Formation towards the Malm aquifer. Red arrow indicates the trend with depth below the Muschelkalk aquifer. Uncertain data are not shown. Bars indicate propagated analytical errors (diffusive exchange) or simple analytical errors (squeezing, advective displacement). Groundwater data are from Lorenz (2020). GMWL = Global Meteoric Water Line ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$), LMWL = Local Meteoric Water Line ($\delta^2\text{H} = 7.55 \delta^{18}\text{O} + 4.8$; Kullin & Schmassmann 1991).

6 Final remarks and main conclusions

RWI team

The average clay-mineral content of the Opalinus Clay is 54 ± 10 wt.-%, a typical value when compared with other locations. Given the unprecedented dense sample spacing (typically 3 m), specific depth trends of various parameters within the formation were identified, presumably correlating with depositional cycles. Boundaries of sub-units within the Opalinus Clay as defined by lithostratigraphic core logging generally correlate with discontinuities or trend reversals, best seen for water content and the ratio quartz/clay minerals. Systematic depth trends can also be seen in the Staffelegg Formation and in the 'Brauner Dogger'. The composition of the clay-mineral fraction within the Opalinus Clay is relatively constant, with a limited upward increase of the ratio illite/kaolinite. In the overlying 'Brauner Dogger', this ratio increases substantially upwards.

Porosity of all rock units increases with clay-mineral content, but a break in slope is identified at about 30 – 35 wt.-% clay minerals, where the increase becomes weaker. This break could be related to the transition from a grain-supported to a matrix-supported fabric. However, the correlation is far from perfect, meaning that parameters other than clay-mineral content also affect the porosity of a rock sample. In the evaporitic section of the profile, porosity decreases with anhydrite content and tends towards very small values in lithologies with > 80 wt.-% anhydrite.

The external surface area (BET, N₂ adsorption) correlates well with water and clay-mineral content except in dolomites of the Schinznach Formation, which are affected by mineral dissolution and so have a distinct pore-space architecture. In clay-rich lithologies, the average diameter of external pores derived from N₂ adsorption (ignoring interlayer water) is around 6 – 8 nm but varies more strongly (towards higher values) in limestones and dolomites. The latter rocks show bimodal pore-size distributions, with peaks at diameters < 10 nm and 100 – 300 nm. The more clay-rich the lithology, the more dominant the < 10 nm peaks become, while they are nearly missing in limestones and dolostones.

A detailed inspection of aqueous-extract data indicated that some high-porosity dolomites as well as low-porosity limestones in the Schinznach Formation were strongly contaminated by drilling fluid, in spite of the fact that only the central parts of the cores were used for extraction. All these samples have in common that they are affected by diagenetic mineral dissolution, leading to friable fabrics dominated by large pores. The extract compositions for these samples do not represent in situ signatures and had to be discarded.

More generally, the rocks from the Triassic section, in particular from the Bänkerjoch and Schinznach Formations, were challenging for several investigation methods. The main reasons include the partially high salinity (rendering water-isotope analyses by the diffusive-exchange method difficult), sometimes low water content, lithological heterogeneity on the cm scale and, as stated above, diagenetic dissolution effects leading to a penetrative contamination by drilling fluid.

The depth profiles of water isotopes in the section Malm – Bänkerjoch Formation show smooth trends with only minor depth gradients (more so for $\delta^{18}\text{O}$ than for $\delta^2\text{H}$). Deuterium excess decreases in a linear way upwards, which means that the porewaters lie progressively farther below the meteoric water line. These observations are consistent with long underground residence times of the porewaters. Some outliers of $\delta^{18}\text{O}$ in the 'Herrenwis Unit' are attributed to the low water contents and heterogeneous nature of this unit, potentially leading to analytical issues.

The Cl^- depth profile shows a gradual increase of concentration with depth between the Malm aquifer and the top of the Opalinus Clay. Within the Opalinus Clay, Cl^- concentrations and Br/Cl ratios lie within a remarkably narrow range and show a slight decrease with depth. In the underlying units, concentrations obtained by the approach discussed in Section 5.1 vary substantially. The interpretation of the Cl^- profile is less straightforward than that of water isotopes because assumptions need to be made about anion accessibility in the pore space of rocks with widely variable mineralogical compositions and microfabrics. The error associated with these assumptions is substantial (see error bars in Fig. 5.2-1), and much of the observed variability is within error. It needs to be emphasised that from an analytical perspective, the Cl^- data are final and will not change, whereas future improvements in the understanding of anion accessibility in different lithologies and geological formations may lead to updates in the recalculation procedure to concentrations per anion-accessible porosity. This means that the Cl^- and Br depth profiles, which are the basis for modelling diffusive solute transport in the low-permeability sequence, may be subject to revisions in the future. On the other hand, the rather smooth Br/Cl profile does not depend on assumptions pertinent to anion accessibility and is not expected to change.

The depth profile of the Br/Cl ratio is better constrained than that of Cl or Br , likely due to the fact that no assumptions on anion accessibility need to be made. Data from aqueous extraction, advective displacement and squeezing are consistent and show a decrease from values similar to that in recent seawater in the Malm to the top of the Opalinus Clay. In the section Opalinus Clay–Bänkerjoch Formation, Br/Cl is essentially constant, but even much smaller values are identified in the underlying Schinznach Formation.

The $\delta^{37}\text{Cl}$ depth profile shows some similar trends as the Cl^- profile but less scatter, in particular in the Triassic. In the Schinznach Formation, pore- and groundwater values are close to those obtained for halite in the underlying Zeglingen Formation, supporting the hypothesis that the latter may be the main source of salinity.

The sulphate profile displays the highest levels in the lowest part including the Muschelkalk and Keuper units, whereas approximately constant levels occur in the Staffelegg Formation to the Wedelsandstein Formation. In the Malm, a decreasing trend towards the sampled aquifer is noted. Data obtained from squeezing and advective displacement, which cover the 'Brauner Dogger', Opalinus Clay and Staffelegg Formation, are consistent. On the other hand, aqueous extraction data systematically exhibit higher and more variable values when recalculated to total or anion-accessible porosity. The same discrepancy has been found in the Schlattingen-1 borehole and at the Mont Terri Rock Laboratory. In the lower part of the profile, i.e. in the Keuper and Muschelkalk, aqueous extraction data are clearly affected by anhydrite dissolution. The SO_4/Cl ratios from the squeezing/advective displacement are slightly above those of modern seawater and show a weakly increasing trend towards shallower levels.

The cation exchange capacity is correlated with the clay-mineral content and, more specifically, with the content of the smectite end-member. The main exchangeable cations are Na and Ca, followed by Mg and K. In the argillaceous Staffelegg Formation, Opalinus Clay and Wedelsandstein Formation, the exchanger composition (cation occupancies) is relatively constant. In the Malm, a trend with higher Ca/Na ratios towards shallower levels is noted. Comparing cation exchange data with those obtained at PSI reveals broadly consistent datasets in spite of the different methodologies employed. The differences in cation occupancies are largely explained by the higher amounts of K extracted by the Cs extraction method used by PSI. It appears that with that method more strongly bound K is mobilised during the extraction process.

Even though an in-depth comparison of the findings obtained from core and borehole studies at BUL1-1 with pre-existing data is beyond the scope of this report, a few points can nevertheless be made:

- The limestone reef facies ('Herrenwis Unit') at the top of the Dogger is a feature not known from other sites to date. While the clay-mineral content is low and macropores are seen by naked eye, neither hydraulic tests nor porewater characteristics point towards a higher permeability and an enhanced mobility of the formation water. The somewhat increased variability of some parameters (Cl^- , $\delta^{18}\text{O}$) is attributed to cm-scale heterogeneity and low water contents, making the analyses more demanding and potentially incurring additional errors not considered by the calculated propagated errors.
- Porewater samples obtained by advective displacement and squeezing in the section 'Brauner Dogger' – Opalinus Clay – Staffelegg Formation are near saturation with respect to gypsum, whereas waters from other sites (Schlattingen-1 geothermal borehole, Mont Terri) are under-saturated. In spite of some efforts to identify gypsum or anhydrite by SEM, sulphate minerals were not found in the clay-rich section of the core profile.
- The porewaters in the clay-rich section are of the Na-Cl type, which is in line with findings at other sites. However, the salinity is markedly higher.

7 References

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