

Supplementary Materials

Table S1. Recipes for the synthetic Opalinus clay pore water [23] and diluted cap rock solution [24] used for the batch experiments and the substrates added to selected samples for stimulating microbial processes. AQDS = Anthraquinone-2,6-disulfonate

Additives	Chemical formula	Opalinus clay pore water (OPA)	Diluted cap rock solution (CAP)
		mol·L ⁻¹	mol·L ⁻¹
pH		7.8	7.3
Sodium chloride	NaCl	0.212	2.496
Calcium chloride	CaCl ₂	0.026	0.032
Sodium sulfate	Na ₂ SO ₄	0.014	0.038
Potassium chloride	KCl	0.002	0.005
Magnesium chloride	MgCl ₂	0.017	-
Strontium chloride	SrCl ₂	0.0005	-
Sodium hydrogen carbonate	NaHCO ₃	0.0005	-
Total		0.27	2.57
Sodium lactate ¹	C ₃ H ₅ NaO ₃	0.05	0.05
Sodium acetate ¹	C ₂ H ₃ NaO ₂	0.05	0.05
Methanol ¹	CH ₃ OH	0.003	0.003
AQDS ¹	C ₁₄ H ₆ O ₈ S ₂	0.0001	0.0001

¹ substrate added to selected samples

Table S2. XRF results of main elements of bentonite SD80. DUR: duration; T: temperature; SOL: solution; S: substrate; LOI: loss-on-ignition, OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	TiO ₂	Na ₂ O	MnO	P ₂ O ₅	SO ₃	Cl	F	sum
		[a]	[°C]			wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
SD80	raw	0	20	-	-	16.5	51.7	17.9	4.8	2.9	2.5	0.9	0.7	0.7	0.1	0.2	<0.05	<0.05	<0.05	99.4
SD80	35974	1	25	OPA	-	13.6	52.5	18.2	4.8	2.8	2.8	1.0	0.8	0.3	0.1	0.1	<0.05	<0.05	<0.05	97.2
SD80	35962	1	25	OPA	+	13.4	52.8	18.3	4.8	2.9	2.4	0.9	0.8	0.1	0.1	0.2	0.16	<0.05	<0.05	97.2
SD80	35976	1	90	OPA	-	12.8	55.7	19.3	5.0	3.3	2.4	0.9	0.8	0.2	0.1	0.2	0.09	<0.05	0.09	101.2
SD80	35964	1	90	OPA	+	12.9	52.9	18.2	4.9	2.9	2.5	0.9	0.8	0.1	0.1	0.2	0.22	<0.05	0.07	97.1
SD80	35977	2	25	OPA	-	14.3	53.2	18.5	4.8	2.9	2.1	0.9	0.8	0.1	0.1	0.2	<0.05	<0.05	<0.05	98.1
SD80	35965	2	25	OPA	+	13.8	52.3	18.2	4.9	2.9	2.6	0.9	0.8	0.1	0.1	0.2	0.39	<0.05	<0.05	97.5
SD80	35967	2	90	OPA	+	21.1	47.1	16.2	4.4	2.6	2.4	0.8	0.7	0.3	0.1	0.2	0.09	<0.05	<0.05	96.5
SD80	35950	1	25	CAP	-	18.0	53.2	18.3	4.8	2.7	1.9	1.0	0.8	0.2	0.1	0.1	0.07	<0.05	<0.05	101.4
SD80	35938	1	25	CAP	+	11.5	54.8	18.9	5.0	2.7	2.1	1.0	0.8	0.7	0.1	0.2	<0.05	<0.05	0.13	98.2
SD80	35952	1	90	CAP	-	18.2	52.2	18.0	4.8	2.7	2.1	1.0	0.8	0.4	0.1	0.2	<0.05	<0.05	<0.05	100.8
SD80	35940	1	90	CAP	+	11.1	52.2	18.1	4.8	2.6	1.9	0.9	0.8	0.7	0.1	0.2	0.06	<0.05	0.06	94.0
SD80	35953	2	25	CAP	-	11.9	54.7	18.8	5.0	2.7	1.9	1.0	0.8	0.8	0.1	0.2	0.05	<0.05	<0.05	98.3
SD80	35941	2	25	CAP	+	11.5	49.6	17.4	4.6	2.5	1.8	0.8	0.7	0.7	0.1	0.2	<0.05	<0.05	<0.05	90.3
SD80	35955	2	90	CAP	-	11.6	54.1	18.7	5.0	2.7	2.2	1.0	0.8	0.9	0.1	0.2	0.06	<0.05	0.05	98.1
SD80	35943	2	90	CAP	+	12.1	54.7	18.9	4.9	2.8	2.1	1.0	0.8	0.7	0.1	0.2	0.07	<0.05	<0.05	98.7

Table S3. XRF results of main elements of bentonite B36. DUR: duration; T: temperature; SOL: solution; S: substrate; LOI: loss-on-ignition, OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	TiO ₂	Na ₂ O	MnO	P ₂ O ₅	SO ₃	Cl	F	sum
		[a]	[°C]			wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
B36	raw	0	20	-	-	13.9	58.6	16.3	7.4	1.5	1.2	1.5	0.8	0.4	0.1	0.1	<0.05	<0.05	0.06	101.8
B36	35968	1	25	OPA	-	15.8	56.9	15.8	6.9	1.3	1.1	1.5	0.8	0.5	0.1	0.1	<0.05	<0.05	0.08	100.8
B36	35956	1	25	OPA	+	9.9	57.7	16.4	7.4	1.4	1.1	1.4	0.7	0.4	0.1	0.1	<0.05	<0.05	<0.05	96.6
B36	35970	1	90	OPA	-	10.0	61.0	17.4	7.7	1.6	1.2	1.5	0.8	0.5	0.1	0.1	<0.05	<0.05	0.09	101.9
B36	35958	1	90	OPA	+	10.0	57.5	16.8	7.6	1.5	1.1	1.4	0.7	0.4	0.1	0.1	<0.05	<0.05	<0.05	97.3
B36	35971	2	25	OPA	-	11.6	56.8	16.3	7.3	1.4	1.0	1.4	0.7	0.4	0.1	0.1	<0.05	<0.05	<0.05	97.2
B36	35959	2	25	OPA	+	16.9	52.5	15.7	7.0	1.5	1.1	1.2	0.6	0.3	0.1	0.1	<0.05	<0.05	<0.05	97.1
B36	35961	2	90	OPA	+	14.4	55.1	15.2	6.7	1.4	1.0	1.4	0.8	0.5	0.1	0.1	<0.05	<0.05	0.05	96.7
B36	35944	1	25	CAP	-	15.3	57.6	16.3	7.2	1.4	1.1	1.4	0.8	0.5	0.1	0.1	<0.05	<0.05	<0.05	101.9
B36	35932	1	25	CAP	+	9.3	56.8	17.2	7.9	1.4	0.8	1.3	0.6	0.9	0.1	0.1	<0.05	<0.05	<0.05	96.4
B36	35946	1	90	CAP	-	12.0	58.9	16.7	7.4	1.3	0.8	1.5	0.8	0.9	0.1	0.1	<0.05	<0.05	<0.05	100.6
B36	35934	1	90	CAP	+	8.6	58.6	17.3	7.8	1.4	0.9	1.4	0.7	1.0	0.1	0.1	<0.05	<0.05	0.08	98.0
B36	35947	2	25	CAP	-	8.1	59.6	17.0	7.5	1.3	0.7	1.5	0.8	1.2	0.1	0.1	<0.05	<0.05	<0.05	97.9
B36	35935	2	25	CAP	+	8.8	59.1	17.4	7.8	1.4	0.8	1.4	0.7	1.1	0.1	0.1	<0.05	<0.05	0.12	98.9
B36	35949	2	90	CAP	-	9.1	59.4	17.0	7.5	1.3	0.7	1.5	0.7	1.2	0.1	0.1	<0.05	<0.05	0.05	98.8
B36	35937	2	90	CAP	+	9.4	57.9	17.3	7.8	1.4	0.8	1.4	0.6	1.1	0.1	0.1	<0.05	<0.05	<0.05	97.9

Table S4. EDX measurement statistics of smectite SD80 by collecting three spatially independent maps to determine sample homogeneity (values are rounded). DUR: duration, SOL: solution, S: substrate (Na-lactate, Na-acetate, methanol, AQDS), OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	SiO ₂		Al ₂ O ₃		Fe ₂ O ₃		MgO		CaO		K ₂ O		Na ₂ O	
		[a]	[°C]			mean	STD	mean	STD	mean	STD	mean	STD	mean	STD	mean	STD	mean	STD
						[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
SD80	raw	0	20	-	-	66.57	0.04	21.43	0.04	5.87	0.06	4.13	0.01	1.48	0.01	0.42	0.01	0.09	0.01
SD80	35974	1	25	OPA	-	66.35	0.28	21.41	0.10	5.53	0.27	3.86	0.04	2.24	0.04	0.42	0.02	0.19	0.02
SD80	35962	1	25	OPA	+	66.70	0.05	21.58	0.03	5.31	0.07	4.02	0.00	1.92	0.00	0.39	0.00	0.08	0.00
SD80	35976	1	90	OPA	-	66.64	0.06	21.33	0.06	5.46	0.09	4.08	0.00	1.93	0.02	0.44	0.01	0.11	0.00
SD80	35964	1	90	OPA	+	66.19	0.03	21.70	0.06	5.24	0.10	4.24	0.03	2.16	0.03	0.37	0.00	0.11	0.01
SD80	35977	2	25	OPA	-	66.18	0.05	21.73	0.01	5.14	0.04	4.16	0.01	2.21	0.02	0.44	0.00	0.13	0.00
SD80	35965	2	25	OPA	+	66.08	0.13	22.15	0.04	5.12	0.07	4.15	0.02	2.03	0.03	0.38	0.01	0.10	0.00
SD80	35979	2	90	OPA	-	66.44	0.06	21.98	0.05	4.96	0.08	4.14	0.01	1.80	0.02	0.45	0.01	0.23	0.01
SD80	35967	2	90	OPA	+	66.44	0.02	22.00	0.03	4.96	0.02	4.14	0.01	1.87	0.02	0.40	0.00	0.19	0.01
SD80	35950	1	25	CAP	-	66.76	0.01	22.55	0.04	4.67	0.06	3.75	0.01	1.79	0.00	0.36	0.01	0.11	0.00
SD80	35938	1	25	CAP	+	65.91	0.10	21.98	0.10	5.08	0.11	3.75	0.03	1.77	0.02	0.43	0.00	1.07	0.06
SD80	35952	1	90	CAP	-	66.26	0.01	22.35	0.01	4.99	0.02	3.92	0.00	1.94	0.01	0.47	0.01	0.06	0.01
SD80	35940	1	90	CAP	+	66.02	0.02	22.26	0.01	5.07	0.02	3.92	0.02	1.82	0.00	0.61	0.01	0.30	0.01
SD80	35953	2	25	CAP	-	66.10	0.14	21.63	0.07	5.36	0.04	3.61	0.04	1.74	0.04	0.43	0.01	1.13	0.05
SD80	35941	2	25	CAP	+	66.00	0.01	21.90	0.01	5.11	0.02	3.75	0.01	1.78	0.02	0.43	0.00	1.03	0.01
SD80	35955	2	90	CAP	-	65.45	0.08	21.95	0.08	5.76	0.09	4.05	0.04	1.91	0.01	0.61	0.01	0.28	0.01
SD80	35943	2	90	CAP	+	65.77	0.10	21.99	0.02	5.45	0.08	4.01	0.02	1.92	0.01	0.63	0.00	0.23	0.01

Table S5. EDX measurement statistics for smectite B36 by collecting three spatially independent maps to determine sample homogeneity (values are rounded). DUR: duration, SOL: solution, S: substrate (Na-lactate, Na-acetate, methanol, AQDS), OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	SiO ₂		Al ₂ O ₃		Fe ₂ O ₃		MgO		CaO		K ₂ O		Na ₂ O	
		[a]	[°C]			mean	STD	mean	STD	mean	STD	mean	STD	mean	STD	mean	STD	mean	STD
						[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
B36	raw	0	20	-	-	62.62	0.30	22.31	0.25	10.20	0.52	2.44	0.09	1.68	0.09	0.44	0.03	0.12	0.01
B36	35968	1	25	OPA	-	63.04	0.19	22.38	0.14	10.26	0.19	2.38	0.03	1.38	0.08	0.43	0.03	0.13	0.01
B36	35956	1	25	OPA	+	63.22	0.06	21.77	0.01	10.50	0.04	2.49	0.02	1.44	0.01	0.42	0.02	0.16	0.00
B36	35970	1	90	OPA	-	62.97	0.14	22.42	0.13	10.19	0.16	2.37	0.03	1.36	0.06	0.45	0.01	0.23	0.01
B36	35958	1	90	OPA	+	63.13	0.08	21.96	0.07	10.74	0.16	2.27	0.02	1.35	0.01	0.43	0.02	0.13	0.00
B36	35971	2	25	OPA	-	61.38	0.29	22.57	0.27	11.25	0.07	2.51	0.02	1.57	0.04	0.51	0.00	0.22	0.01
B36	35959	2	25	OPA	+	61.77	0.31	22.20	0.03	11.09	0.25	2.63	0.04	1.73	0.02	0.43	0.01	0.14	0.01
B36	35973	2	90	OPA	-	62.71	0.05	22.88	0.03	9.78	0.07	2.39	0.01	1.22	0.02	0.57	0.02	0.45	0.00
B36	35961	2	90	OPA	+	62.57	0.19	22.49	0.15	10.18	0.26	2.37	0.01	1.57	0.03	0.48	0.00	0.35	0.01
B36	35944	1	25	CAP	-	62.91	0.06	22.11	0.06	10.43	0.07	2.42	0.03	1.61	0.02	0.41	0.00	0.12	0.00
B36	35932	1	25	CAP	+	63.14	0.05	21.54	0.07	10.35	0.08	2.23	0.01	1.03	0.00	0.39	0.00	1.32	0.02
B36	35946	1	90	CAP	-	60.73	0.08	26.55	0.22	8.49	0.10	2.13	0.02	0.93	0.01	0.84	0.02	0.33	0.00
B36	35934	1	90	CAP	+	60.45	0.12	24.12	0.22	10.10	0.09	2.62	0.01	1.23	0.01	0.90	0.01	0.59	0.02
B36	35947	2	25	CAP	-	61.37	0.05	24.64	0.30	9.47	0.28	2.17	0.02	0.77	0.01	0.73	0.00	0.84	0.03
B36	35935	2	25	CAP	+	62.82	0.02	21.29	0.04	10.70	0.07	2.22	0.01	0.90	0.01	0.41	0.01	1.65	0.01
B36	35949	2	90	CAP	-	60.82	0.14	26.12	0.17	8.52	0.04	2.19	0.01	1.06	0.01	1.01	0.01	0.29	0.01
B36	35937	2	90	CAP	+	59.82	0.17	23.27	0.15	11.04	0.22	3.05	0.05	0.80	0.02	1.06	0.01	0.95	0.03

Table S6. Overview of extracted DNA and successful sequencing for the incubated batch-experiments after one and two years. Shown are the concentrations of isolated DNA and the result of the successful amplification of the V4-region from 16S rRNA gene, where “-” means no amplification and “+” means successful amplification and sequencing, S: substrate, OPA: Opalinus clay pore water, CAP: diluted cap rock solution (listed are selected samples from Matschiavelli et al. [43]).

sample	T [°C]	Porewater	S	1 year		2 years	
				DNA [ng/μl]	16S rRNA gene sequencing	DNA [ng/μl]	16S rRNA gene sequencing
SD80	25	OPA	-	3.1	-	3.5	-
SD80	25	OPA	+	89.9	+	297.2	+
SD80	90	OPA	-	2.0	-	3.1	-
SD80	90	OPA	+	3.1	-	4.6	-
SD80	25	CAP	-	1.1	-	5.3	-
SD80	25	CAP	+	38.4	-	4.7	-
SD80	90	CAP	-	1.8	-	1.7	-
SD80	90	CAP	+	3.4	-	3.7	-
B36	25	OPA	-	5.6	-	3.3	-
B36	25	OPA	+	7.9	+	9.9	-
B36	90	OPA	-	3.4	-	8.2	-
B36	90	OPA	+	5.7	-	6.1	-
B36	25	CAP	-	1.7	+	3.8	-
B36	25	CAP	+	4.7	+	3.0	-
B36	90	CAP	-	0.4	-	3.0	-
B36	90	CAP	+	2.3	-	6.5	-

Table S7. XRD quantification results of bentonite SD80 using Rietveld-Refinement and XRD parameters of purified smectite SD80 oriented slides (peak position, peak broadening, peak intensity). DUR: duration, SOL: solution, S: substrate, Ant = anatase, Brt = barite, Cal = calcite, Fsp = feldspar, Sme = smectite, Py = pyrite, Qz = quartz, R_{wp} = weighted residual square sum, R_{exp} = possible minimum value for R_{wp} , AD: air dried, EG: ethylene glycol-saturated, FWHM: full-width at half maximum, OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	Sme	Fsp	Qz	Cal	Brt	Ant	Py	R_{wp}	R_{exp}	d(001)		FWHM(001)		max. intensity	
		[a]	[°C]			wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	%	%	[nm]		[°]		[cps]	
															AD	EG	AD	EG	AD	EG
SD80	raw	0	20	-	-	89.1	7.2	<1	<1	1.1	<1	<1	3.4	2.1	1.45	1.68	1.8	0.6	980	2420
SD80	35974	1	25	OPA	-	87.4	9.3	<1	<1	<1	1.0	<1	3.7	2.1	1.49	1.69	1.0	0.6	460	920
SD80	35962	1	25	OPA	+	88.6	7.3	<1	<1	1.1	1.0	<1	2.8	1.4	1.48	1.69	1.0	0.6	520	920
SD80	35976	1	90	OPA	-	88.0	8.5	1.0	<1	1.0	1.1	<1	3.5	2.0	1.49	1.69	1.1	0.5	410	770
SD80	35964	1	90	OPA	+	87.3	8.3	<1	2.2	<1	1.0	<1	4.1	1.5	1.49	1.69	1.1	0.6	800	1550
SD80	35977	2	25	OPA	-	88.3	7.8	1.1	<1	1.1	1.2	<1	3.2	1.5	1.51	1.69	0.9	0.5	600	980
SD80	35965	2	25	OPA	+	87.1	8.0	<1	<1	1.6	1.3	<1	3.1	1.5	1.51	1.69	0.8	0.5	690	1040
SD80	35979	2	90	OPA	-	84.6	8.3	<1	3.3	1.3	1.1	<1	3.7	1.5	1.48	1.69	1.2	0.5	550	1350
SD80	35967	2	90	OPA	+	85.6	8.3	<1	3.4	<1	1.2	<1	3.7	1.5	1.47	1.69	1.1	0.5	870	1710
SD80	35950	1	25	CAP	-	84.3	10.8	<1	1.7	<1	1.0	<1	3.6	1.9	1.49	1.69	1.0	0.6	480	810
SD80	35938	1	25	CAP	+	88.2	7.9	1.0	<1	<1	<1	<1	2.8	1.4	1.46	1.69	2.0	0.6	340	960
SD80	35952	1	90	CAP	-	90.9	6.6	<1	<1	<1	<1	<1	3.0	2.1	1.45	1.65	1.2	0.5	220	460
SD80	35940	1	90	CAP	+	86.4	9.0	<1	<1	1.1	1.2	<1	2.8	1.4	1.49	1.67	1.0	0.6	420	650
SD80	35953	2	25	CAP	-	88.5	7.8	<1	<1	<1	<1	<1	2.8	1.4	1.42	1.69	2.2	0.6	480	1630
SD80	35941	2	25	CAP	+	87.3	8.7	<1	<1	1.1	1.0	<1	2.7	1.5	1.48	1.69	2.1	0.6	490	1380
SD80	35955	2	90	CAP	-	85.3	8.7	1.0	<1	2.0	1.2	<1	2.5	1.4	1.48	1.67	1.0	0.6	410	640
SD80	35943	2	90	CAP	+	88.6	8.1	<1	<1	<1	<1	<1	2.5	1.4	1.49	1.67	0.9	0.6	530	870

Table S8. XRD quantification results of bentonite B36 using Rietveld-Refinement and XRD parameters of purified smectite SD80 oriented slides (peak position, peak broadening, peak intensity). DUR: duration, SOL: solution, S: substrate, Ant = anatase, Brt = barite, Cal = calcite, Fsp = feldspar, Sme = smectite, Py = pyrite, Qz = quartz, R_{wp} = weighted residual square sum, R_{exp} = possible minimum value for R_{wp} , AD: air dried, EG: ethylene glycol-saturated, FWHM: full-width at half maximum, OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	Sme	Fsp	Qz	Kln	CrS	Ant	Cal	R_{wp}	R_{exp}	d(001)		FWHM(001)		max. intensity	
		[a]	[°C]			wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	%	%	[nm]		[°]		[cps]	
															AD	EG	AD	EG	AD	EG
B36	raw	0	20	-	-	64.6	15.1	11.5	4.3	3.9	<1	n/a	3.2	2.0	1.48	1.68	1.4	0.8	320	510
B36	35968	1	25	OPA	-	63.7	16.0	12.3	4.6	2.7	<1	n/a	3.0	2.0	1.46	1.71	1.7	0.9	180	360
B36	35956	1	25	OPA	+	65.6	14.7	10.3	4.8	3.7	<1	n/a	2.7	1.4	1.48	1.71	1.6	0.8	320	570
B36	35970	1	90	OPA	-	68.0	13.4	10.3	4.8	3.0	<1	n/a	2.8	1.9	1.43	1.69	1.9	0.8	160	350
B36	35958	1	90	OPA	+	66.1	15.5	10.7	3.4	3.8	<1	n/a	2.7	1.4	1.42	1.71	1.8	0.8	240	570
B36	35971	2	25	OPA	-	64.0	14.6	11.8	5.3	3.7	<1	n/a	2.6	1.4	1.49	1.69	1.6	0.8	190	350
B36	35959	2	25	OPA	+	68.5	14.6	9.1	3.8	3.3	<1	n/a	2.3	1.4	1.49	1.71	1.5	0.8	360	620
B36	35973	2	90	OPA	-	62.1	15.6	13.5	4.5	3.7	<1	n/a	2.6	1.4	1.38	1.70	2.1	0.8	150	340
B36	35961	2	90	OPA	+	61.2	15.5	14.4	4.6	3.7	<1	n/a	2.8	1.5	1.40	1.71	2.0	0.8	200	510
B36	35944	1	25	CAP	-	59.0	16.1	15.8	4.7	3.6	<1	n/a	3.2	2.1	1.48	1.69	1.6	0.9	220	360
B36	35932	1	25	CAP	+	69.2	14.3	8.7	3.9	3.2	<1	n/a	2.6	1.4	1.33	1.72	2.3	1.0	170	400
B36	35946	1	90	CAP	-	64.6	14.4	12.4	4.5	3.6	<1	n/a	3.1	2.0	1.39	1.69	2.2	0.9	90	180
B36	35934	1	90	CAP	+	62.2	16.0	13.5	3.4	4.1	<1	n/a	2.7	1.4	1.46	1.67	1.9	1.0	110	170
B36	35947	2	25	CAP	-	62.9	15.8	12.6	4.3	3.7	<1	n/a	2.5	1.4	1.28	1.66	1.9	0.9	80	200
B36	35935	2	25	CAP	+	62.3	16.1	12.7	4.5	3.6	<1	n/a	2.5	1.4	1.30	1.70	2.3	1.0	330	800
B36	35949	2	90	CAP	-	58.8	16.9	14.9	4.6	4.3	<1	n/a	2.8	1.4	1.34	1.66	2.1	1.1	80	120
B36	35937	2	90	CAP	+	66.9	15.5	8.9	4.2	3.8	<1	n/a	2.5	1.4	1.42	1.64	2.1	1.1	100	150

Table S9. Layer charge distribution of smectite SD80 (rounded mean values after mineral formula calculation). DUR: duration, SOL: solution, S: substrate, TET: tetrahedral, OCT: octahedral, OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	tetrahedral		octahedral			interlayer				TET	OCT	total	%TET
		[a]	[°C]			Si ⁴⁺	Al ³⁺	Al ³⁺	Fe ³⁺	Mg ²⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	charge	charge	LC	charge
SD80	raw	0	20	-	-	3.94	0.06	1.44	0.26	0.30	0.09	0.06	0.01	0.03	-0.06	-0.30	-0.36	17
SD80	35974	1	25	OPA	-	3.94	0.06	1.43	0.25	0.32	0.14	0.02	0.02	0.03	-0.06	-0.32	0.38	16
SD80	35962	1	25	OPA	+	3.95	0.05	1.45	0.24	0.31	0.12	0.04	0.01	0.03	-0.05	-0.31	-0.37	14
SD80	35976	1	90	OPA	-	3.95	0.05	1.44	0.24	0.32	0.12	0.04	0.01	0.03	-0.05	-0.32	-0.37	14
SD80	35964	1	90	OPA	+	3.92	0.08	1.44	0.23	0.33	0.14	0.05	0.01	0.03	-0.08	-0.33	-0.41	20
SD80	35977	2	25	OPA	-	3.92	0.08	1.44	0.23	0.33	0.14	0.04	0.02	0.03	-0.08	-0.33	-0.41	20
SD80	35965	2	25	OPA	+	3.91	0.09	1.46	0.23	0.31	0.13	0.05	0.01	0.03	-0.09	-0.31	-0.40	23
SD80	35979	2	90	OPA	-	3.93	0.07	1.46	0.22	0.32	0.11	0.05	0.03	0.03	-0.07	-0.32	-0.39	18
SD80	35967	2	90	OPA	+	3.93	0.07	1.46	0.22	0.32	0.12	0.05	0.02	0.03	-0.07	-0.32	-0.39	18
SD80	35950	1	25	CAP	-	3.94	0.06	1.50	0.21	0.29	0.11	0.04	0.01	0.03	-0.06	-0.29	-0.35	17
SD80	35938	1	25	CAP	+	3.91	0.09	1.45	0.23	0.32	0.11	0.01	0.12	0.03	-0.09	-0.32	-0.41	22
SD80	35952	1	90	CAP	-	3.92	0.08	1.48	0.22	0.30	0.12	0.05	0.01	0.04	-0.08	-0.30	-0.38	21
SD80	35940	1	90	CAP	+	3.91	0.09	1.47	0.23	0.31	0.12	0.04	0.03	0.05	-0.09	-0.31	-0.39	23
SD80	35953	2	25	CAP	-	3.93	0.07	1.44	0.24	0.32	0.11	0.00	0.13	0.03	-0.07	-0.32	-0.39	18
SD80	35941	2	25	CAP	+	3.92	0.08	1.45	0.23	0.32	0.11	0.01	0.12	0.03	-0.08	-0.32	-0.40	20
SD80	35955	2	90	CAP	-	3.89	0.11	1.43	0.26	0.31	0.12	0.05	0.03	0.05	-0.11	-0.31	-0.42	26
SD80	35943	2	90	CAP	+	3.91	0.09	1.44	0.24	0.31	0.12	0.04	0.03	0.05	-0.09	-0.31	-0.41	22

Table S10. Layer charge distribution of smectite B36 (rounded mean values after mineral formula calculation). DUR: duration, SOL: solution, S: substrate, TET: tetrahedral, OCT: octahedral, OPA: Opalinus clay pore water, CAP: diluted cap rock solution.

Sample ID		DUR	T	SOL	S	tetrahedral		octahedral			interlayer				TET	OCT	total	%TET
		[a]	[°C]			Si ⁴⁺	Al ³⁺	Al ³⁺	Fe ³⁺	Mg ²⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	charge	charge	LC	charge
B36	raw	0	20	-	-	3.79	0.21	1.37	0.46	0.16	0.11	0.06	0.01	0.03	-0.21	-0.16	-0.38	56
B36	35968	1	25	OPA	-	3.80	0.20	1.39	0.47	0.15	0.09	0.06	0.02	0.03	-0.20	-0.15	-0.35	57
B36	35956	1	25	OPA	+	3.81	0.19	1.36	0.48	0.17	0.09	0.06	0.02	0.03	-0.19	-0.17	-0.35	54
B36	35970	1	90	OPA	-	3.79	0.21	1.39	0.46	0.15	0.09	0.06	0.03	0.03	-0.21	-0.15	-0.36	58
B36	35958	1	90	OPA	+	3.81	0.19	1.37	0.49	0.15	0.09	0.06	0.01	0.03	-0.19	-0.15	-0.34	56
B36	35971	2	25	OPA	-	3.72	0.28	1.34	0.51	0.15	0.10	0.08	0.03	0.04	-0.28	-0.15	-0.42	67
B36	35959	2	25	OPA	+	3.74	0.26	1.33	0.51	0.16	0.11	0.07	0.02	0.03	-0.26	-0.16	-0.42	62
B36	35973	2	90	OPA	-	3.78	0.22	1.40	0.44	0.15	0.08	0.06	0.05	0.04	-0.22	-0.15	-0.38	58
B36	35961	2	90	OPA	+	3.78	0.22	1.38	0.46	0.16	0.10	0.05	0.04	0.04	-0.22	-0.16	-0.38	58
B36	35944	1	25	CAP	-	3.79	0.21	1.37	0.47	0.16	0.10	0.06	0.01	0.03	-0.21	-0.16	-0.37	57
B36	35932	1	25	CAP	+	3.82	0.18	1.35	0.47	0.18	0.07	0.02	0.15	0.03	-0.18	-0.18	-0.36	50
B36	35946	1	90	CAP	-	3.65	0.35	1.53	0.38	0.08	0.06	0.11	0.04	0.06	-0.35	-0.08	-0.43	81
B36	35934	1	90	CAP	+	3.67	0.33	1.31	0.54	0.15	0.05	0.09	0.09	0.08	-0.33	-0.15	-0.48	69
B36	35947	2	25	CAP	-	3.70	0.30	1.45	0.43	0.12	0.05	0.08	0.10	0.06	-0.30	-0.12	-0.41	73
B36	35935	2	25	CAP	+	3.81	0.19	1.33	0.49	0.18	0.06	0.02	0.19	0.03	-0.19	-0.18	-0.38	50
B36	35949	2	90	CAP	-	3.66	0.34	1.51	0.39	0.10	0.07	0.10	0.03	0.08	-0.34	-0.10	-0.44	77
B36	35937	2	90	CAP	+	3.65	0.35	1.32	0.51	0.17	0.05	0.11	0.11	0.08	-0.35	-0.17	-0.52	67