

Characterization of Bentonites from the *in situ* ABM5 Heater Experiment at Äspö Hard Rock Laboratory, Sweden

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Table S1. Mineral phases observed in the bentonite samples by means of XRD, FTIR and SEM techniques.

Type of mineral phases	Mineral phases	Original Samples	Granite contact	Medium part	Heater contact
Fe-oxyhydroxides	Goethite (weak FM) (Gth)	Asha 505 Rokle	Asha B28 Rokle B14	Asha B28 Febex B25 Rokle B14 MX-80 B1	Asha B28 Febex B25 Rokle B14 MX-80 B1
	Hematite (AFM) (Hem)	Asha 505 MX-80	Asha B28 MX-80 B1	Asha B28 MX-80 B1	Asha B28 Rokle B14 MX-80 B1
	Magnetite (FM) (Mag)	NO	NO	NO	NO
	Titanomagnetite (Tmag)	NO	NO	NO	NO
	Maghemite (FM) (Mgh)	NO	NO	NO	NO
	Ferrihydrite (Fhy)	NO	NO	NO	NO
Carbonates	Calcite (Cal)	All	All	All	All
	Monohydrocalcite (MhCal)	NO	NO	NO	MX-80 B1
	Dolomite (Dol)	Rokle	Rokle B14	Rokle B14	Rokle B14
	Magnesite (Mgs)	NO	NO	NO	NO
	Siderite (Sd)	Rokle MX-80	Rokle B14 MX-80 B1	Febex B25 Rokle B14 MX-80 B1	Febex B25 Rokle B14 MX-80 B1
Sulfides	Pyrrhotite (Pyh)	NO	NO	NO	NO
	Mackinawite (Mkw)	NO	NO	NO	NO
	Pyrite (Py)	MX-80	MX-80 B1	Asha B28 Rokle B14 MX-80 B1	Asha B28 Rokle B14 MX-80 B1
	Sphalerite (Sp)	NO	NO	NO	MX-80 B1
Sulfates	Gypsum (Gp)	MX-80	MX-80 B1	Asha B28 MX-80 B1	Asha B28 MX-80 B1
	Barite (Ba)	?	?	?	Febex B25 Rokle B14
Silica oxides	Quartz (Qz)	All	All	All	All
	Cristobalite (Crs)	All	All	All	All
	Tridymite (Trd)	?	?	?	Rokle B14
Feldspars	K-feldspars (KFs)	All	All	All	All
	Plagioclases (Pl)	All	All	All	All
Titanium oxides	Anatase (Ant)	Rokle	Rokle B14	Asha B28 Rokle B14	Rokle B14
Mg-hydroxides	Brucite (Brc)	No	No	No	No
Zeolites	Clinoptilolite (Cpt)	No	No	Asha B28	Asha B28
Smectites	Montmorillonite (Mnt)	All	All	All	All
	Saponite (Sap)	No	No	No	No
Illite/Muscovite	Illite (Ilt)/Muscovite (Ms)	Febex B25 Rokle MX-80	Febex B25 Rokle B14 MX-80 B1	Febex B25 Rokle B14 MX-80 B1	Febex B25 Rokle B14 MX-80 B1
Kaolinites	Kaolinite (Kln)	Asha 505 Rokle	Asha B28 Rokle B14	Asha B28 Rokle B14	Asha B28 Rokle B14
Chlorites	Clinochlore(Clc)/ Chamosite (Chm)	No	No	No	No

Table S2. Positions and assignments of vibrational bands of dioctahedral smectites, kaolinite and illite

Wavenumber (cm ⁻¹)	Assignment ^[1,2,3,4]
3800-3500	OH stretching of inner structural hydroxyl groups (influenced by nature of the coordinated octahedral cations): <ul style="list-style-type: none"> - AlAlOH (dioctahedral): 3623 cm⁻¹ - Mg₃OH (trioctahedral): 3680 cm⁻¹ - FeFeOH: 3567 cm⁻¹
3426	OH stretching of adsorbed water
3240	OH stretching of adsorbed water
3150-3170	Fe-oxyhydroxide
1634	OH bending of adsorbed water
1430 (872, 712)	ν_3 -CO ₃ asymmetric stretching of calcite (ν_2 : out of plane bending, ν_4 : planar bending): calcite
1115	Si-O stretching vibration (out-of-plane)
1030-1020	Si-O stretching vibration (in-plane): <ul style="list-style-type: none"> - Dioctahedral: 1030 cm⁻¹ - Trioctahedral: 1020 cm⁻¹
917	Kaolinite inner OH deformation
915	AlAlOH bending
885	AlFeOH bending
850	AlMgOH bending
820	FeFeOH bending (nontronite: 817, 676 cm ⁻¹)
795	MgMgOH bending
765	FeMgOH bending
792	Kaolinite Si-O-Al vibrations
792 790/800 798 & 780 doublet 794	Si-O stretching of silica Amorphous silica (opal, volcanic glass, etc.) Quartz Cristobalite
754	Kaolinite Si-O-Al vibrations
750	Illite Al-O-Si vibration
700	Illite OH bending
698	Kaolinite OH translation
655-660	Mg ₃ OH bending (saponite)
644	Kaolinite inner surface OH vibration
626 792, 624 790	Coupled Al-O and Si-O (out-of-plane), Si-O of cristobalite Si-O of tridymite
624	R-O-Si with R=Al, Mg, Fe
539	Kaolinite Si-O-Al (out of plane) bending (Al in tetrahedral sheet)
520	Si-O-Al bending (Al tetrahedral cation)
465	Si-O-Si bending vibration
426	Si-O bending vibration
825, 750	Illite
740, 790, 890, 1150	Fe oxyhydroxide
Complex bands 400-900	Feldspars

Table S3. Chemical composition of the solid phase (total fraction) for different samples obtained after dismantling of ABM5 experiment: Asha Block 28, Febex Block 25 and Rokle Block 11.

Samples / wt.%	Asha Block 28				FEBEX Block 25				Rokle Block 11			
	Ref. ^[5]	G	H	M	Ref.	G	M	H	Ref.	G	M	H
Distance to Heater (cm)	10	8.3	5.0	1.7	10	8.3	5.0	1.7	10	8.3	5.0	1.7
SiO ₂	46.48	45.53	44.56	45.51	55.46	61.48	61.04	60.57	48.06	43.62	44.02	42.98
Al ₂ O ₃	20.64	19.44	18.94	19.34	17.28	18.02	17.98	18.09	14.52	14.15	14.16	14.14
Fe ₂ O ₃	12.16	23.34	24.05	21.87	3.09	6.64	6.60	8.16	15.94	24.04	23.75	24.62
MgO	2.01	2.60	2.60	2.60	4.37	4.10	4.20	4.10	2.12	2.50	2.40	2.50
CaO	0.84	3.23	3.55	3.87	1.75	4.02	3.89	3.32	2.85	3.45	3.45	3.31
Na ₂ O	1.97	1.60	1.60	1.60	1.16	1.40	1.90	1.30	0.26	1.30	1.50	1.60
K ₂ O	0.14	0.39	0.38	0.43	0.99	1.77	1.79	1.76	1.00	1.50	1.47	1.48
SrO	0.02	0.04	0.04	0.03	0.02	0.05	0.06	0.07	0.04	0.08	0.08	0.08
TiO ₂	1.01	1.74	1.51	1.68	0.15	0.23	0.30	0.31	4.51	6.61	6.50	6.58
P ₂ O ₅	0.09	< d.l.	0.16	0.16	0.03	< d.l.	0.10	0.11	0.84	0.71	0.67	0.65
MnO	0.05	0.08	0.06	0.07	0.03	0.04	0.04	0.03	0.19	0.09	0.09	0.08
ZnO	0.02	0.05	0.04	0.05	0.01	0.02	0.02	0.02	0.02	0.03	0.03	0.03
Cr ₂ O ₃	0.04	0.13	0.11	0.13	< d.l.	0.02	0.02	< d.l.	0.03	0.00	0.08	0.09
CuO	0.02	0.04	0.03	0.03	< d.l.	< d.l.	< d.l.	< d.l.	0.03	0.04	0.04	0.04
NiO	0.01	0.02	0.02	0.03	< d.l.	0.01	< d.l.	< d.l.	0.01	0.01	< d.l.	< d.l.
ZrO ₂	0.01	0.02	0.02	0.01	0.02	0.03	0.04	0.05	0.06	0.10	0.10	0.11
SnO ₂	< d.l.	0.01	0.01	0.01	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.01
CdO	< d.l.	< d.l.	0.01	0.01	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
V ₂ O ₅	0.07	0.04	< d.l.	< d.l.	0.01	< d.l.	< d.l.	0.01	< d.l.	< d.l.	< d.l.	< d.l.
PbO	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.02	0.02	0.02	< d.l.	< d.l.	< d.l.	< d.l.
SO ₃	0.15	0.58	1.12	1.42	< d.l.	0.59	0.59	0.64	0.05	0.57	0.55	0.61
Cl	0.30	1.16	1.19	1.10	0.024	1.58	1.45	1.40	0.002	1.19	1.08	1.02

Table S4. Chemical composition of the solid phase (total fraction) for different samples obtained after dismantling of ABM5 experiment: IBECO Block 11, MX-80 Block 1.

Samples / wt.%	IBECO Block 11				MX-80 Block 1		
	Ref.	G	3	2	Ref.	G	M
Distance to Heater (cm)	10	8.75	6.25	3.75	10	8.3	5.0
SiO ₂	50.32	60.34	60.36	60.90	62.89	60.64	60.15
Al ₂ O ₃	15.7	17.71	18.63	18.41	19.87	20.03	20.01
Fe ₂ O ₃	4.76	6.52	6.71	6.94	3.53	7.60	7.50
MgO	4.76	5.30	4.60	4.40	2.40	2.70	2.70
CaO	5.29	3.47	3.52	3.69	1.24	4.22	4.23
Na ₂ O	0.89	2.40	2.10	1.60	2.09	1.60	1.70
K ₂ O	0.55	1.23	1.29	1.24	0.52	0.91	0.87
SrO	0.02	0.05	0.06	0.06	0.03	0.08	0.08
TiO ₂	0.63	0.60	0.61	0.55	0.07	< d.l.	0.21
P ₂ O ₅	0.11	0.07	< d.l.	0.14	0.03	< d.l.	0.15
MnO	0.12	0.08	0.06	0.06	0.01	0.05	0.03
ZnO	0.01	0.03	0.03	0.02	0.01	0.02	0.02
ZrO ₂	0.02	0.03	0.04	0.04	0.03	0.04	0.04
PbO	0.00	0.01	< d.l.	< d.l.	0.00	0.02	0.02
SO ₃	0.19	0.63	0.59	0.66	0.19	1.18	1.40
Cl	0.009	1.41	1.34	1.29	0.003	0.85	0.81

Table S5. Fe(II), Fe(III) and total Fe contents obtained after dismantling of ABM5 experiment.

Samples	Distance to heater (cm)	Fe(II) wt. %	Total Fe wt. %	Fe(III) wt. %	Fe(II)/Fe(III)	Fe(II) in Total Fe wt. %
MX-80 Ref.	--	0.27	2.40	2.13	0.13	11.25
MX-80 B1 G	8.3	0.62	2.88	2.26	0.27	21.54
MX-80 B1 M	5.0	0.63	2.85	2.22	0.28	22.14
MX-80 B1 H	1.7	0.66	5.11	4.44	0.15	12.99
IBECO Ref.	--	0.19	3.10	2.91	0.07	6.13
IBECO B11 G	8.75	0.29	2.15	1.86	0.16	13.65
IBECO B11 3	6.25	0.30	2.19	1.89	0.16	13.57
IBECO B11 2	3.75	0.35	2.22	1.87	0.19	15.86
IBECO B11 H	1.25	0.60	3.36	2.76	0.22	17.81
Rokle Ref.1	--	0.37	6.97	6.60	0.06	5.28
Rokle B14 G	8.3	0.26	8.98	8.72	0.03	2.94
Rokle B14 M	5.0	0.30	8.96	8.66	0.03	3.31
Rokle B14 H	1.7	0.36	9.59	9.22	0.04	3.81
Febex Ref.	--	0.15	2.30	2.15	0.07	6.52
FEBEX 25 G	8.3	0.14	1.86	1.72	0.08	7.54
FEBEX B25 M	5.0	0.16	1.90	1.74	0.09	8.37
FEBEX B25 H	1.7	0.30	2.21	1.91	0.16	13.51
Asha B28 G	8.3	0.19	5.74	5.55	0.03	3.32
Asha B28 M	5.0	0.21	6.66	6.45	0.03	3.18
Asha B28 H	1.7	0.27	5.60	5.34	0.05	4.74

Table S6. Parameters deduced from the BET and *t*-plot treatment on the adsorption of N₂ at 77 K from samples obtained after dismantling of ABM5 experiment.

Sample	Distance to heater (cm)	C _{BET}	V _m ¹ (cm ³ /g)	S _{BET} (m ² /g)	S _{tot} ² (m ² /g)	V _{tot} ³ (cm ³ /g)	S _{micro} ⁴ (m ² /g)	V _{micr} ⁵ (cm ³ /g)	S _{ext micro} ⁶ (m ² /g)	S _{ext meso} ⁷ (m ² /g)	V _{meso} ⁸ (cm ³ /g)
Asha B28 G	8.30	209.4	2.31·10 ⁻² (l)	65.41	66.19	1.06·10 ⁻¹	13.54	5.28·10 ⁻³	52.66	41.31	1.15·10 ⁻² (l)
Asha B28 M	5.00	176.0	1.98·10 ⁻² (l)	55.99	56.18	1.02·10 ⁻¹	8.29	3.29·10 ⁻³	47.88	39.10	7.99·10 ⁻³ (l)
Asha B28 H	1.70	243.8	2.18·10 ⁻² (l)	61.49	61.58	1.08·10 ⁻¹	13.09	5.50·10 ⁻³	48.49	41.53	9.39·10 ⁻³ (l)
Febex B25 G	8.30	258.3	1.35·10 ⁻² (l)	38.01	37.53	7.80·10 ⁻²	8.47	3.78·10 ⁻³	29.06	22.98	7.03·10 ⁻³ (l)
Febex B25 M	5.00	471.3	1.62·10 ⁻² (l)	45.76	46.62	8.90·10 ⁻²	13.69	5.59·10 ⁻³	32.93	26.02	9.28·10 ⁻³ (l)
Febex B25 H	1.70	239.4	1.28·10 ⁻² (l)	36.20	36.21	8.41·10 ⁻²	7.76	3.27·10 ⁻³	28.44	25.36	4.99·10 ⁻³ (l)
Rokle B14 G	8.30	341.8	2.37·10 ⁻² (l)	66.90	67.32	1.19·10 ⁻¹	17.53	7.38·10 ⁻³	49.78	38.76	1.33·10 ⁻² (l)
Rokle B14 M	5.00	349.8	2.27·10 ⁻² (l)	64.09	64.77	1.15·10 ⁻¹	17.57	7.27·10 ⁻³	47.20	38.80	1.18·10 ⁻² (l)
Rokle B14 H	1.70	287.8	2.08·10 ⁻² (l)	58.70	59.39	1.16·10 ⁻¹	14.42	5.88·10 ⁻³	44.94	41.01	7.94·10 ⁻³ (l)
IBECO B11 G	8.75	319.8	1.76·10 ⁻² (l)	49.75	51.19	9.77·10 ⁻²	13.90	5.35·10 ⁻³	37.29	26.29	1.14·10 ⁻² (l)
IBECO B11 3	6.25	403.4	1.73·10 ⁻² (l)	48.98	50.76	9.58·10 ⁻²	16.28	6.25·10 ⁻³	34.49	25.75	1.11·10 ⁻² (l)
IBECO B11 2	3.75	284.7	1.59·10 ⁻² (l)	45.04	46.21	9.06·10 ⁻²	11.80	4.54·10 ⁻³	34.42	25.68	9.42·10 ⁻³ (l)
IBECO B11 H	1.25	400.8	1.83·10 ⁻² (l)	51.71	53.88	1.00·10 ⁻¹	16.52	6.23·10 ⁻³	37.36	27.55	1.15·10 ⁻² (l)
MX 80 B1 G	8.30	436.5	7.96·10 ⁻³ (l)	22.48	23.45	6.32·10 ⁻²	6.94	2.60·10 ⁻³	16.52	14.45	3.73·10 ⁻³
MX 80 B1 M	5.00	188.7	6.69·10 ⁻³ (l)	18.91	19.19	6.04·10 ⁻³	3.17	1.19·10 ⁻³	16.02	14.91	1.78·10 ⁻³
MX 80 B1 H	1.70	256.9	7.69·10 ⁻³ (l)	21.72	22.33	6.82·10 ⁻²	4.74	1.77·10 ⁻³	17.60	16.05	2.61·10 ⁻³

¹V_m: monolayer capacity derived from the BET treatment; expressed as (l): liquid; S_{BET}: BET Surface area²S_{tot}: Total surface area derived from the slope of the straight line passing through the origin of the *t*-plot³V_{tot}: Total pore volume, derived from the amount of nitrogen adsorbed at p/p₀ of 0.98⁴S_{micro}: S_{BET} - S_{ext micro}: Surface area of the micropores⁵V_{micr}: Liquid microporous volume derived from the ordinate at the origin in the second straight line of the *t*-plot⁶S_{ext micro}: Surface area derived from the slope of the second straight line of the *t*-plot⁷S_{ext meso}: Surface area derived from the slope of the third straight line of the *t*-plot⁸V_{meso}: Liquid microporous volume derived from the ordinate at the origin in the third straight line of the *t*-plot

Table S7. Total cation exchange capacity (CEC) and cation exchange population prior and after dismantling of the ABM5 experiment (in meq/100g).

Sample	Distance to heater (cm)	Na	K	Mg	Ca	Sr	Ba	Σ CEC	CEC
Asha 505 Ref.	--	62.0	0.4	12.3	19.0	--	--	93.7	88.6
Asha B28 G	8.3	15.28	1.76	7.69	33.07	0.18	0.002	58.0	85.8
Asha B28 M	5.0	17.19	1.53	6.19	42.68	0.23	0.002	67.8	83.9
Asha B28 H	1.7	26.40	2.18	7.09	48.21	0.26	0.012	84.1	81.3
FEBEX Ref.	--	27.97	5.46	34.17	32.72	0.37	0.008	100.7	98.1
Febex B25 G	8.3	18.12	2.65	11.80	41.81	0.31	0.013	74.7	97.6
Febex B25 M	5.0	22.28	2.86	14.51	45.81	0.46	0.010	85.9	96.5
Febex B25 H	1.7	22.73	2.62	15.55	41.83	0.41	0.009	83.2	93.1
Rokle Ref.	--	0.61	4.72	19.08	52.48	0.14	0.010	77.1	73.8
Rokle B14 G	8.3	21.82	3.01	13.15	32.89	0.15	0.012	71.0	73.1
Rokle B14 M	5.0	23.06	3.02	11.42	30.94	0.14	0.012	68.6	73.0
Rokle B14 H	1.7	22.01	3.01	12.10	29.78	0.15	0.014	67.1	70.3
IBECO Ref.	--	25.19	4.31	31.37	34.67	0.20	0.019	95.8	90.2
IBECO B11 G	8.75	36.63	3.44	9.68	46.40	0.24	0.022	96.4	97.1
IBECO B11 3	6.25	37.64	3.15	9.31	46.32	0.24	0.019	96.7	97.9
IBECO B11 2	3.75	37.43	3.97	9.97	44.17	0.26	0.073	95.9	88.6
IBECO B11 H	1.25	34.38	3.16	8.95	43.94	0.23	0.017	90.7	95.0
MX-80 Ref.	--	58.49	4.18	6.86	15.63	0.44	0.009	85.6	83.6
MX-80 B1 G	8.3	23.95	1.31	8.78	48.42	0.53	0.008	83.0	84.1
MX-80 B1 M	5.0	23.45	1.32	8.80	47.15	0.53	0.006	81.2	87.6
MX-80 B1 H	1.7	24.52	1.40	12.65	46.31	0.55	0.007	85.4	87.8

Table S8. Soluble salts from aqueous leaching tests a 1:4 solid to liquid ration, in mg/L.

	Asha B28 G	Asha B28 M	Asha B28 H	Febex B25 G	Febex B25 M	Febex B25 H	Rokle B14 G	Rokle B14 M	Rokle B14 H	Ibeco B11 G	Ibeco B11 3	Ibeco B11 2	Ibeco B11 H	MX 80 B1 G	MX 80 B1 M	MX 80 B1 H
Distance to heater (cm)	8.30	5.00	1.70	8.30	5.00	1.70	8.30	5.00	1.70	8.75	6.25	3.75	1.25	8.30	5.00	1.70
w.c. (%)	16.8	17.6	13.4	13.8	13.3	13.2	8.6	8.9	8.1	13.6	13.1	13.6	13.6	11.6	11.6	11.4
Tot. mass (g)	5.02	5.00	5.01	5.00	5.00	5.01	5.00	5.00	5.01	5.04	5.00	2.50	5.01	5.00	5.01	5.00
Tot. water (g)	20.72	20.75	20.59	20.61	20.59	20.58	20.40	20.41	20.38	20.60	20.58	10.30	20.60	20.52	20.52	20.51
pH	7.8	7.6	7.8	7.7	7.8	7.7	7.8	8	7.9	7.8	7.8	7.7	7.9	7.7	7.5	7.6
Alk (meq/L)	1.23	0.77	1.5	0.86	1.18	0.87	1.38	1.74	1.76	1.10	1.22	1.40	1.25	1.17	1.06	1.03
F ⁻	1.1	0.52	0.15	1.1	1.2	1.3	1.6	1.7	1.7	1.1	0.94	1.1	0.8	1.2	0.86	0.98
Br ⁻	3.1	2.9	3	4.6	3.9	3.7	4.2	3.3	3	4.2	3.8	4.1	3.4	1.1	0.91	0.83
Cl ⁻	517	490	521	800	680	645	675	543	495	761	668	670	602	206	176	168
NO ₃ ⁻	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SO ₄ ²⁻	155	937	742	147	182	114	151	144	128	103	95	99	100	635	930	939
Si	10	13	12	19	17	19	10	13	19	9.8	9.8	4.4	13	1.2	14	9.3
Na	420	650	630	570	510	470	520	450	420	550	500	500	470	440	500	500
K	5.1	9.3	9.3	11	11	11	18	17	16	14	13	14	13	12	14	15
Ca	13	78	61	23	18	13	15	11	8.8	13	10	11	9	29	54	53
Mg	1.4	6.5	8	4.5	4	3.5	4.2	3.2	2.6	1.8	1.4	1.5	1.2	3.3	5.9	5.9
Sr	0.13	0.67	0.56	0.32	0.34	0.25	0.17	0.14	0.11	0.16	0.13	0.14	0.11	0.71	1.4	1.5
Ba	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.07	0.06	0.05	0.05	0.04	0.04	0.03	0.04	0.05	0.06
B	0.66	1.1	1.4	0.53	0.8	0.31	0.09	0.05	<0.03	0.19	<0.22	<0.3	<0.16	<0.3	<0.3	<0.3
Fe	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.3	<0.03	<0.3	<0.3	<0.3
Mn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.04	0.04	<0.03	<0.03	<0.3	<0.03	<0.3	<0.3	<0.3
Al	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.03	<0.03	0.05	<0.03	<0.03	<0.3	<0.03	<0.3	<0.3	<0.3
Ti	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.3	<0.03	<0.3	<0.3	<0.3
Zn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.07	<0.03	0.22	<0.3	<0.3
Acetate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	3.0
Formate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Table S9. Ion inventory obtained from aqueous leaching tests, in mol/100g.

Sample	Distance to heater (cm)	pH	Cl ⁻	F ⁻	Br ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Asha B28 G	8.30	7.8	7.0309	0.0279	0.0187	0.7780	0.5928
Asha B28 M	5.00	7.6	6.7447	0.0134	0.0177	4.7601	0.3756
Asha B28 H	1.70	7.8	6.8495	0.0037	0.0175	3.6003	0.6989
Febex B25 G	8.30	7.7	10.5830	0.0272	0.0270	0.7177	0.4032
Febex B25 M	5.00	7.8	8.9476	0.0295	0.0228	0.8839	0.5503
Febex B25 H	1.70	7.7	8.4615	0.0318	0.0215	0.5520	0.4045
Rokle B14 G	8.30	7.8	8.4344	0.0373	0.0233	0.6964	0.6111
Rokle B14 M	5.00	8.0	6.8080	0.0398	0.0184	0.6663	0.7732
Rokle B14 H	1.70	7.9	6.1383	0.0393	0.0165	0.5858	0.7735
IBECO B11 G	8.75	7.8	9.9682	0.0269	0.0244	0.4979	0.5112
IBECO B11 3	6.25	7.8	8.7709	0.0230	0.0221	0.4604	0.5660
IBECO B11 2	3.75	7.9	7.9313	0.0197	0.0199	0.4863	0.6532
IBECO B11 H	1.25	7.7	8.8444	0.0271	0.0240	0.4823	0.5851
MX 80 B1 G	8.30	7.7	2.6612	0.0289	0.0063	3.0276	0.5372
MX 80 B1 M	5.00	7.5	2.2692	0.0207	0.0052	4.4255	0.4824
MX 80 B1 H	1.70	7.6	2.1656	0.0236	0.0047	4.4672	0.4706

Table S10. Calculated parameters and saturation indexes of the pore waters.

Sample	Asha Block 28 S	FEBEX Block 25 W	Rokle Block 14 NW	IBECO Block 11 S	MX-80 Block 1 IN
Sq. Pressure (MPa)	20	30	20	20	30
a _w	0.997	0.979	0.978	0.982	0.994
Specific Conductance (μS/cm, 25°C)	63461	59715	60189	50531	18908
I (M)	0.91	0.85	0.82	0.69	0.26
Water type	Na-Ca-Cl	Na-Ca-Cl	Na-Ca-Cl	Na-Ca-Cl	Na-Cl
SI Anhydrite	0.24	0.14	0.15	0.24	-0.15
SI Gypsum	0.39	0.29	0.30	0.40	
SI Celestine	-0.08	0.04	-0.04	0.01	-0.02
SI Barite	1.16	1.26	1.31	--	1.84
SI Calcite	0.98	0.41	0.79	0.01	-0.02
SI Dolomite	1.16	0.67	1.01	-0.20	-0.15
SI Magnesite	0.45	0.53	0.50	0.06	0.14
SI Strontianite	-0.73	-1.08	-0.79	-1.62	-1.28
SI CO ₂ (g)	-3.63	-2.87	-3.28	-2.71	-2.79
SI Chalcedony	1.35	-0.12	-0.41	1.33	-0.06
SI Quartz	1.64	0.17	-0.13	1.62	0.22
Greenrust (OH)	--	6.79	--	--	3.23
Lepidrocrocite	--	5.57	--	--	4.45
Jarosite (K)	--	3.26	--	--	0.31
Goethite	--	7.06	--	--	5.94
Maghemite (dis)	--	12.01	--	--	9.76
Magnetite	--	13.69	--	--	10.05
Hematite	--	14.89	--	--	12.65
Ferrihydrite	--	4.01	--	--	2.89
SI Halite	-2.49	-2.59	-2.51	-2.69	-3.54

Table S11. Chemical composition of the pore waters obtained by squeezing at 25 MPa for water vapour saturated FEBEX, IBECO RW C16, and MX-80 bentonites at initial conditions.

Bentonites	Febex 28.2% w.c. ^(*)	IBECO RW C16 28.9% w.c. ^(*)	MX80 25.6% w.c. ^(*)
Volume (mL)	5	1.75	2
pH	7.3	7.8	8.0
E. C. ($\mu\text{S}/\text{cm}$)	21695	13785	22596
I (M)	0.27	0.19	0.33
Water type	Na-Mg-Cl	Na-SO ₄ -Cl	Na-SO ₄
Cl (mg/L)	6600	2800	1100
SO ₄ ²⁻ (mg/L)	2600	4300	9300
Br (mg/L)	12	5	<5
NO ₃ (mg/L)	143	58	1200
Alkalinity (meq/L)	2.06	2.88	n.d.
Si (mg/L)	14	8.5	<0.8
Na (mg/L)	3200	2400	4900
K (mg/L)	34	43	59
Ca (mg/L)	649	380	278
Mg (mg/L)	591	312	146
Sr (mg/L)	11	4	6.8
Fe (mg/L)	≤ 0.15	< 0.38	< 0.8
Al (mg/L)	0.27	<0.38	< 0.8
B (mg/L)	1.2	1.2	< 0.8
Mn (mg/L)	0.22	0.96	< 0.8
Ba (mg/L)	< 0.15	< 0.38	< 0.8
pCO ₂ (bar)	-2.37	-2.70	--

^(*)Raw bentonites samples were submitted to a relative humidity of 100% inside a dessicator containing water during at least 3 months prior to squeezing test.

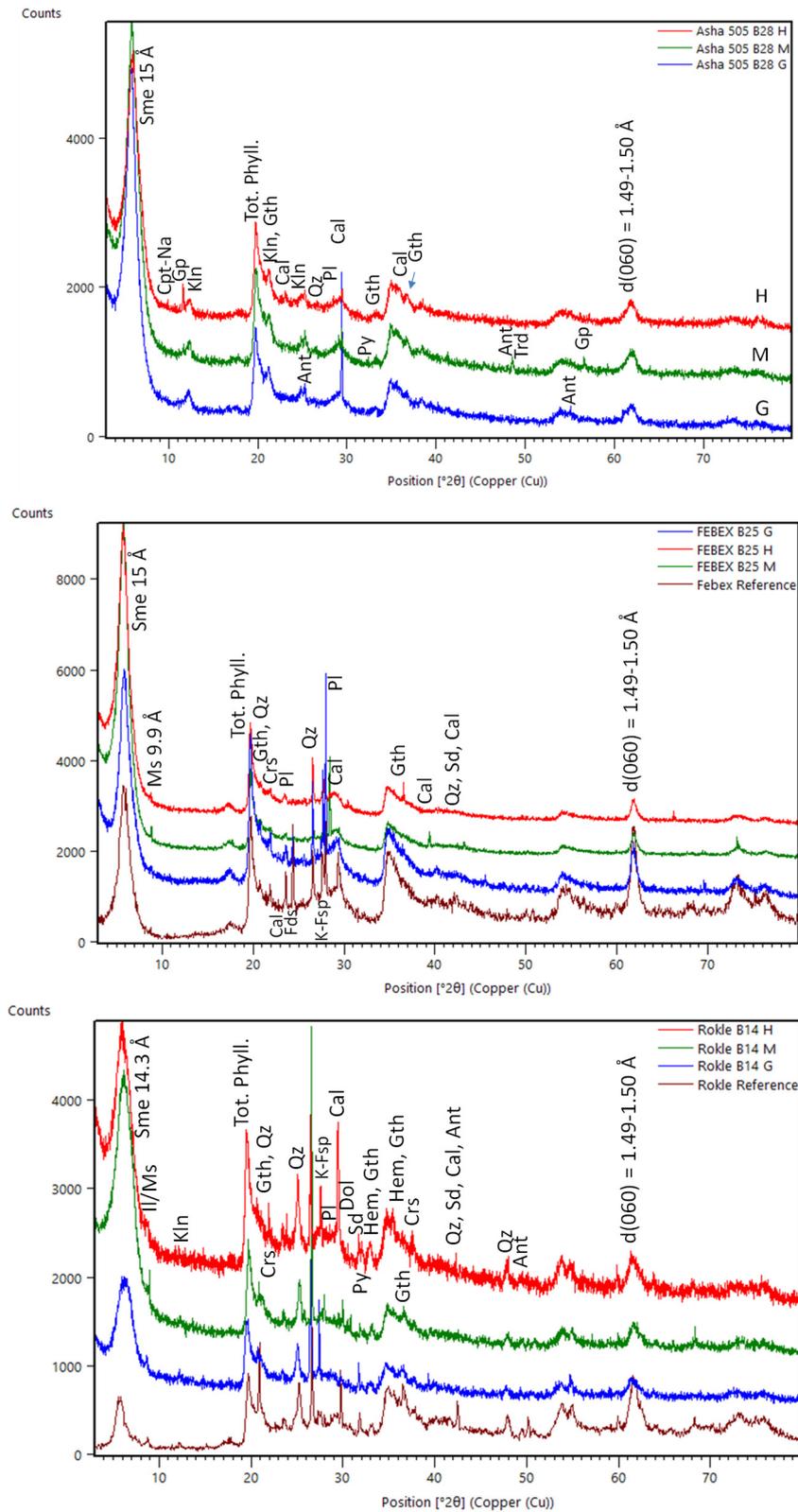


Figure S1. XRD patterns of total fraction samples from ABM5 experiment. Symbols according to [6]. Sme: smectite, Ill/Ms: illite/muscovite, Cpt-Na: Clinoptilolite, Gp: Gypsum, Tot. Phyll: total phyllosilicates, Crs: cristobalite, Cal: calcite, MhCl: monhydrocalcite, Qz: quartz, K-Fsp: potassium feldspar, Pl: Plagioclase, Dol: dolomite, Mgs: magnesite, Gth: goethite, Hem: hematite.

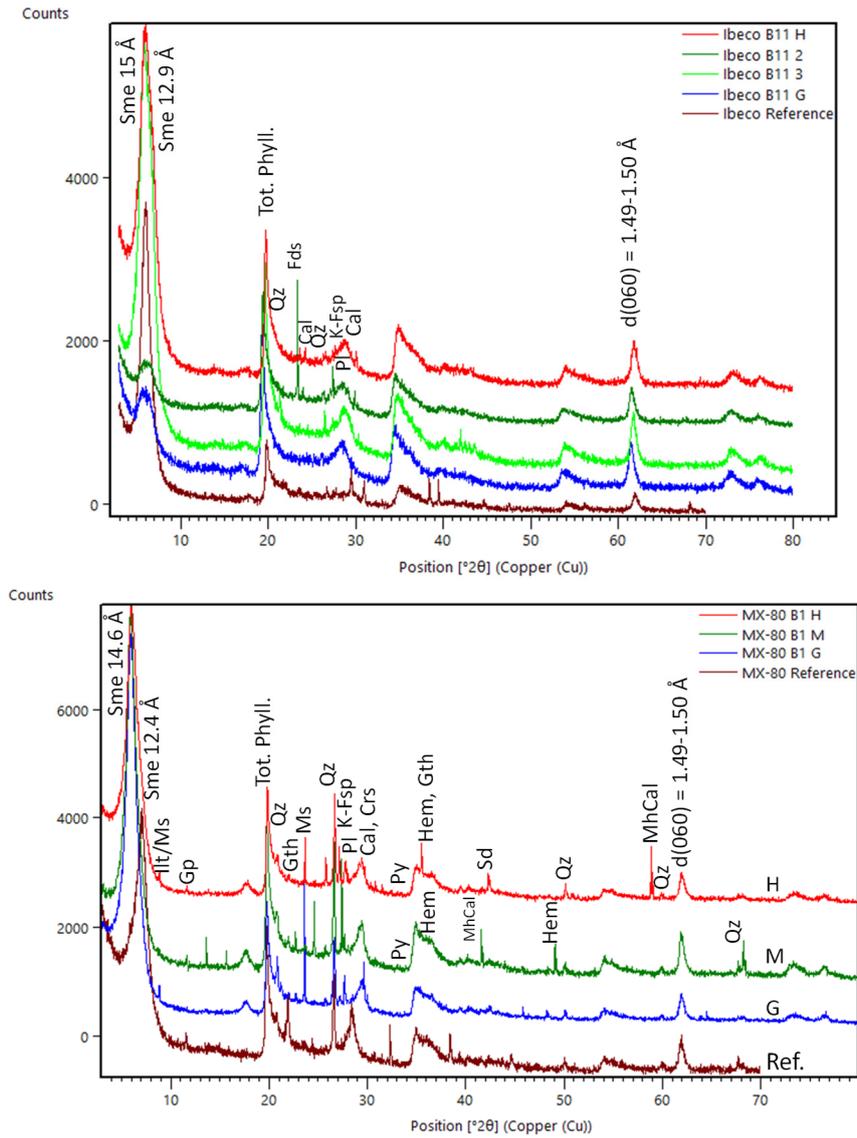


Figure S1. XRD patterns of total fraction samples from ABM5 experiment. Continuation. Symbols according to [6]. Sme: smectite, Ilt/Ms: illite/muscovite, Cpt-Na: Clinoptilolite, Gp: Gypsum, Tot. Phyll: total phyllosilicates, Crs: cristobalite, Cal: calcite, MhCla: monohydrocalcite, Qz: quartz, K-Fsp: potassium feldspar, Pl: Plagioclase, Dol: dolomite, Mgs: magnesite, Gth: goethite, Hem: hematite.

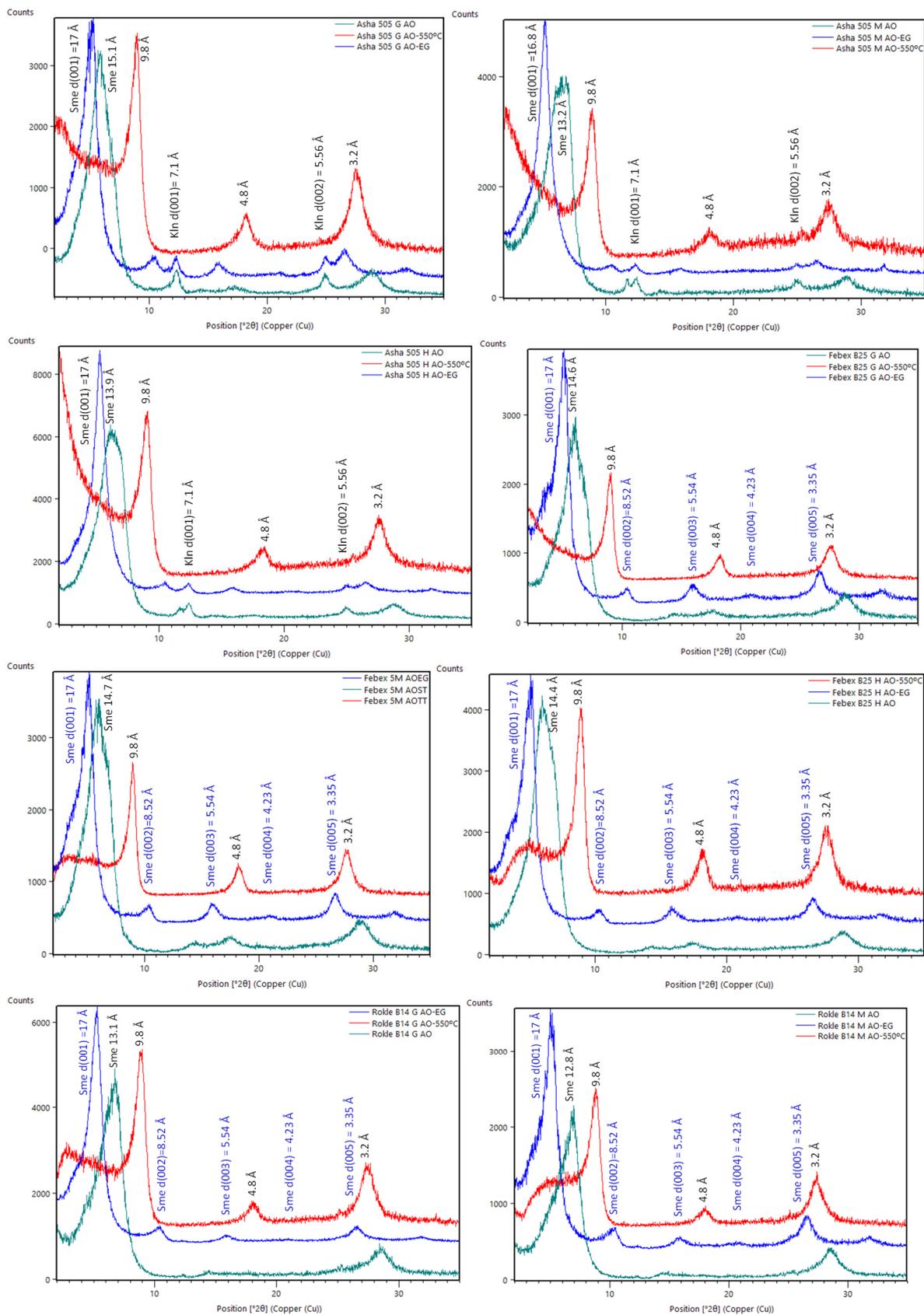


Figure S2. XRD patterns of oriented aggregate samples from ABM5 experiment (normal and after ethylene glycol and heating at 550 °C treatments).

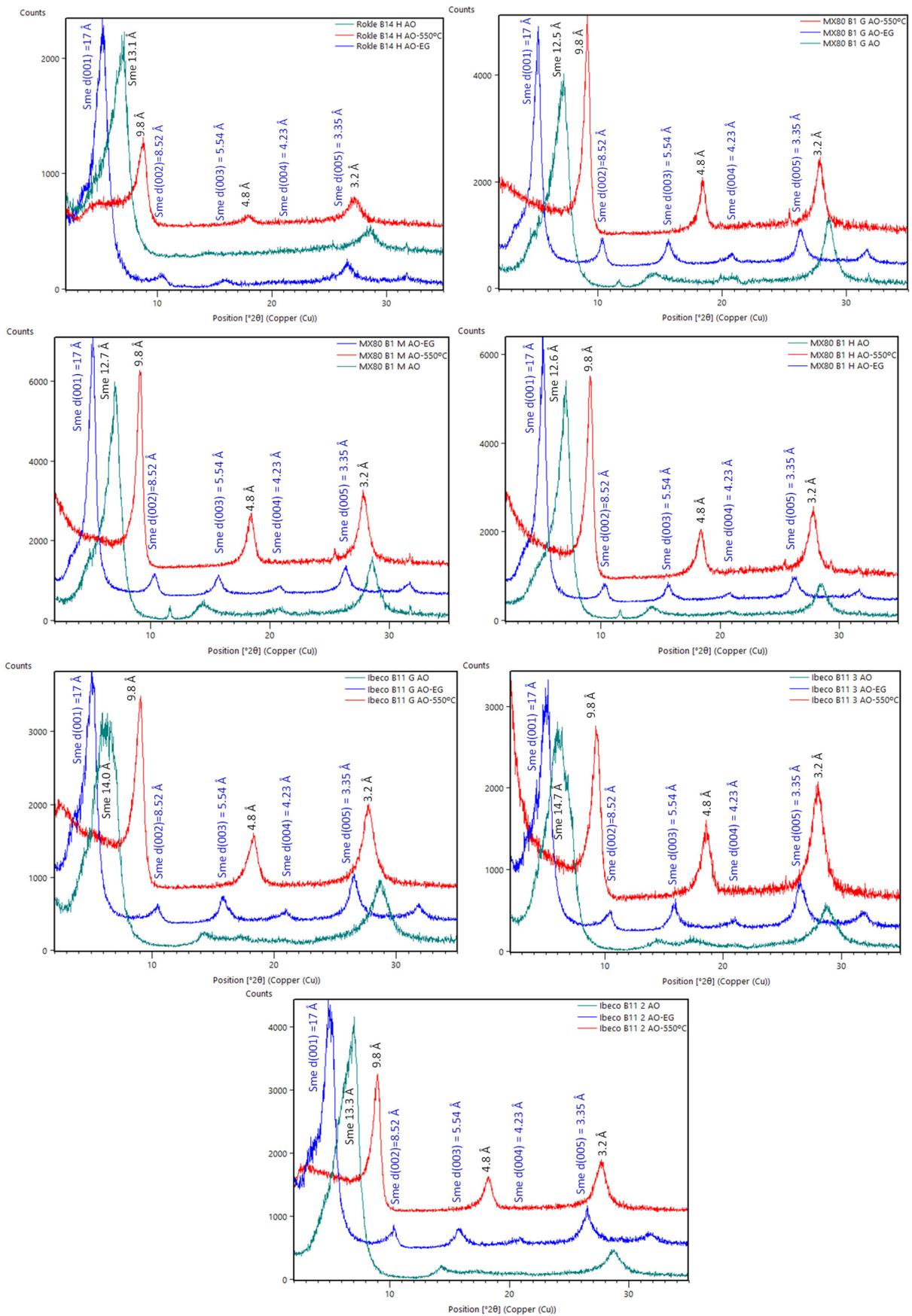


Figure S2. XRD patterns of oriented aggregate samples from ABM5 experiment (normal and after ethylene glycol and heating at 550 °C treatments). Continuation.

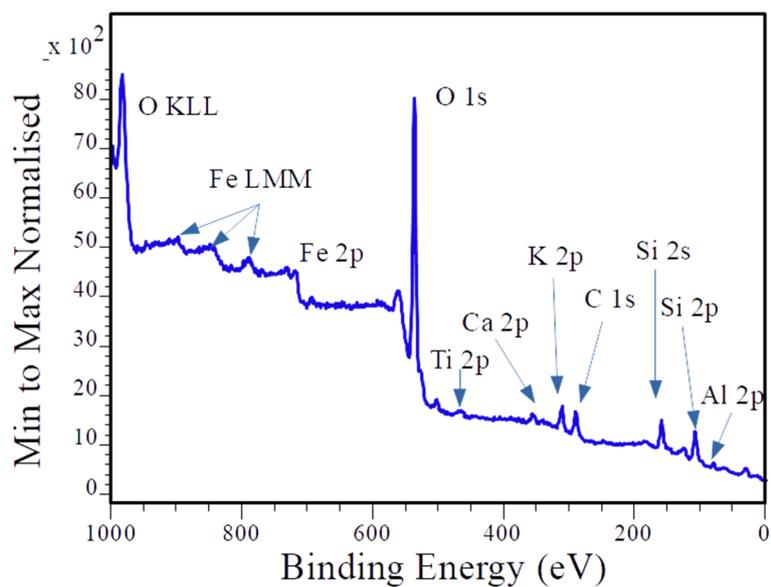


Figure S3. Wide scan XPS spectrum recorded from sample Rokle 4H at heater contact.

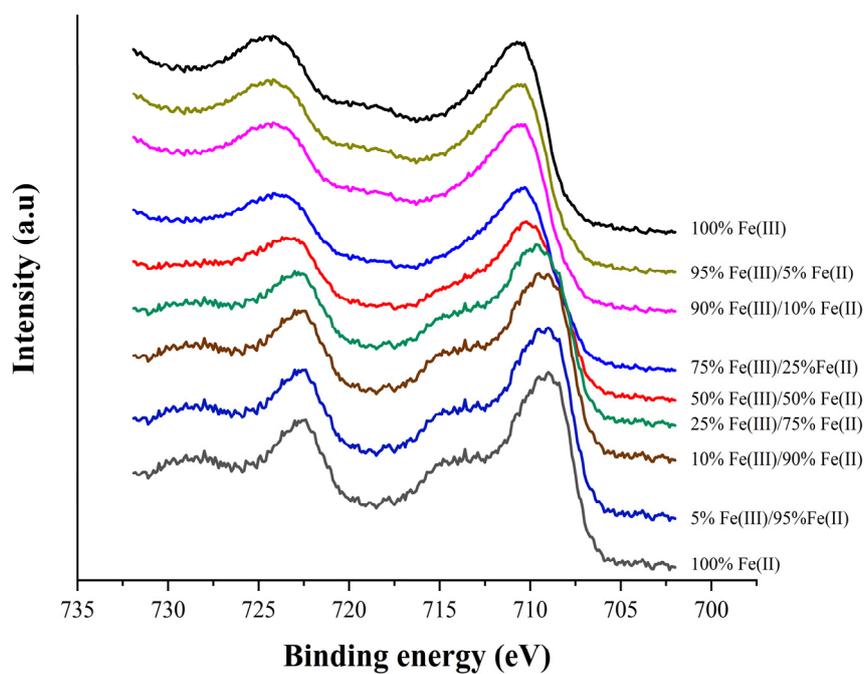


Figure S4. Fe 2p XPS spectra recorded from samples containing different concentrations of Fe(III) and Fe(II) standard compounds.

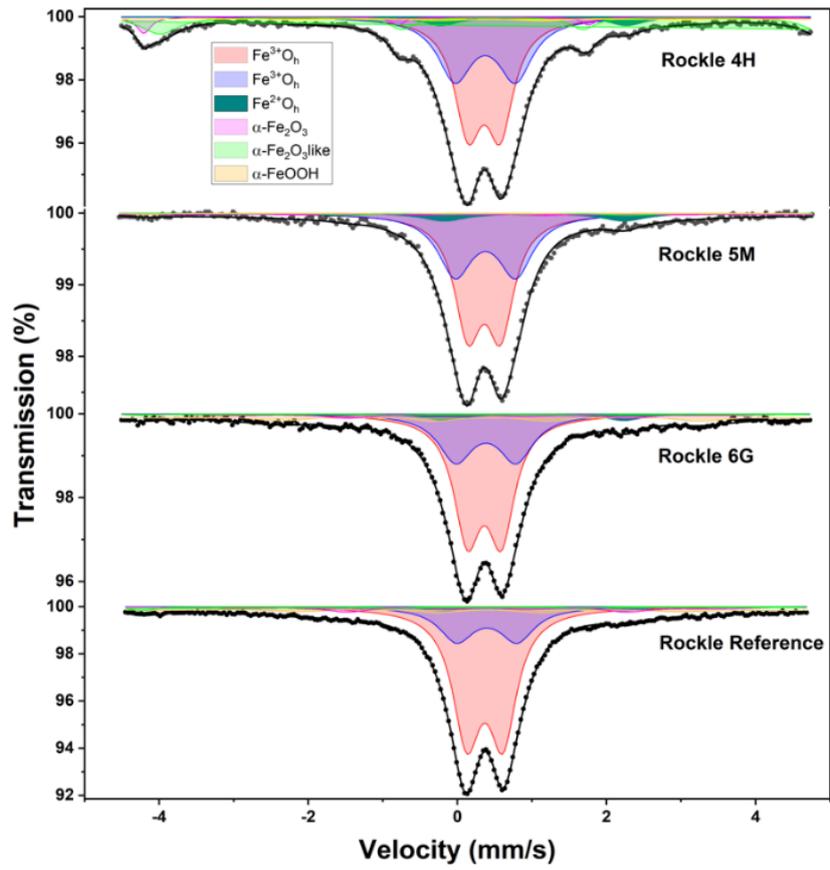


Figure S5. Room temperature Mössbauer spectra recorded in a narrow range of velocities for Rokle samples: reference, 4H: close to heater interface, 5M: middle, and 6G: close to granite interface, i.e., at 1.67 cm, 5.00 cm and 8.33 cm from heater contact, respectively.

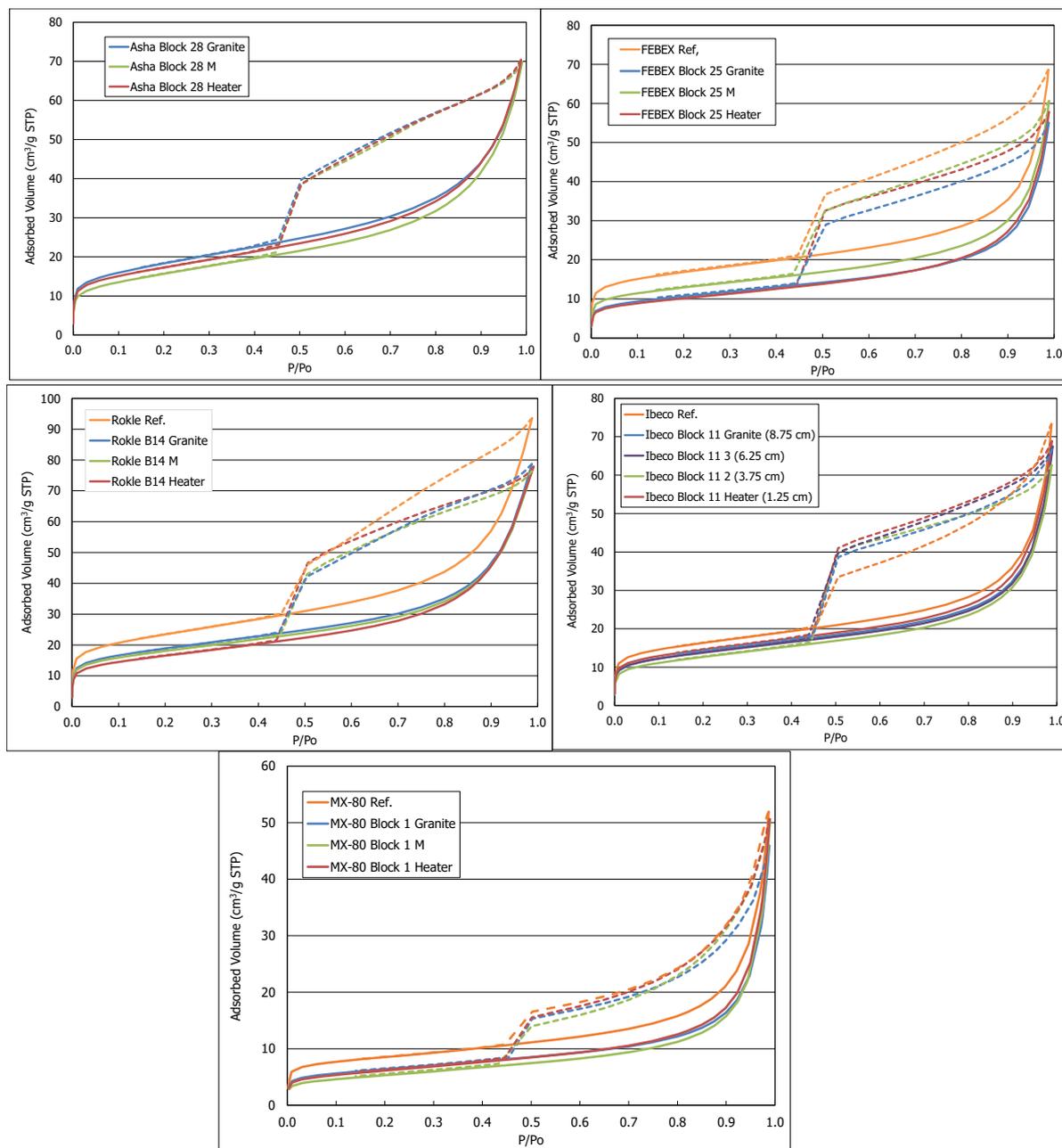


Figure S6. N₂ adsorption/desorption isotherms from reference and retrieved ABM5 samples.

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