3rd Belbar Project Annual Workshop

Influence of the Physico-chemical and Crystallographic properties of Clay Minerals on Erosion Processes

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CIEMAT (Madrid, Spain)

WP2: MECHANISMS OF BENTONITE EROSION AND COLLOID GENERATION FROM COMPACTED BENTONITE

BACKGROUND

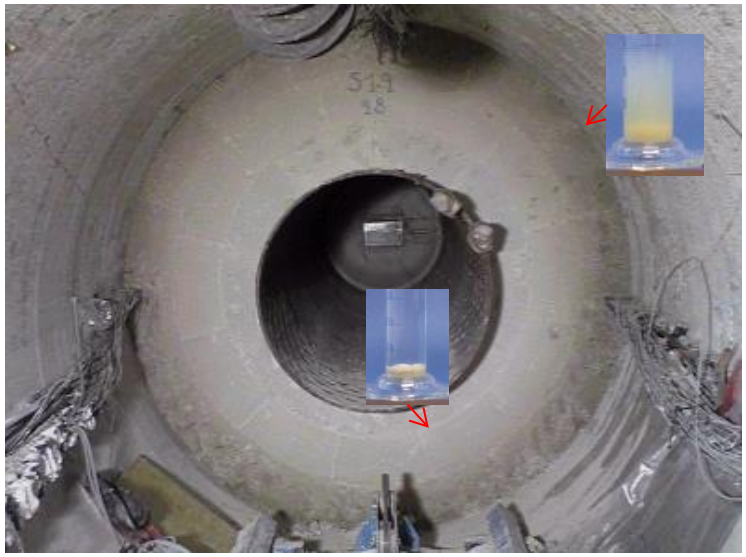
Smectite particles in gels and suspensions are strongly influenced by:

- Decreases in dry densities of the compacted bentonite due to swelling or changes in the chemical stability of smectite (montmorillonite/bentonite volume fraction or concentration).
- Pore water/groundwater chemistry: I, pH, ionic composition, which governs the edge charge.
- Changes in cation composition in CEC (in particular the Ca/Na content).
- Crystallochemistry of the clay minerals.

WP2: MECHANISMS OF BENTONITE EROSION AND COLLOID GENERATION FROM COMPACTED BENTONITE

BACKGROUND

After installation



Final Status

SECTION 19

FEBEX

BENTONITES AND CLAY MINERALS ANALYSED

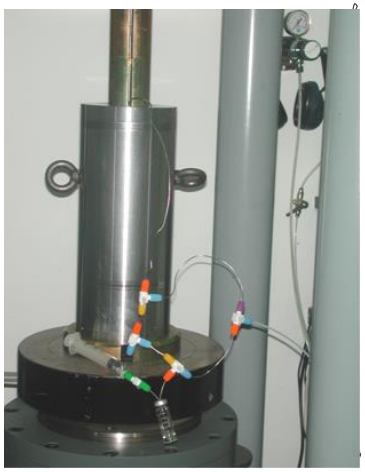
Smectitic Clay Minerals

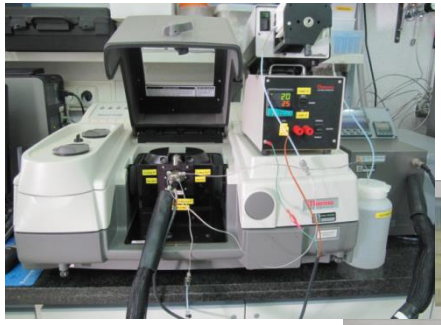
- Bentonite MX-80, a mainly Na-bentonite from Wyoming (USA)
- Bentonite FEBEX, a Ca-Mg-Na bentonite from Almería (Spain)
- Bentonite Ibeco, a Ca-bentonite from Milos (Greece)
- Czech bentonites from Rockle deposit:
  - RO2K6-F02 (Ca-Mg bentonite)
  - Bentonit E75 (Na-Ca bentonite)
  - Sabenil S65 (Na-bentonite)
- A Russian Bentonite from Khakassiya deposit (Russia)
- Nanocor

Other types of Clay Minerals

- Illite du Puy (France)
- Kaolinite KGa-1b
- Saponite MCA-C (Cerro del Aguila, Spain)

PORE WATER CHEMISTRY LABORATORY AT CIEMAT





PORE WATER CHEMISTRY LABORATORY

PHYSICAL CHARACTERIZATION

- Grain Density
- Dry Bulk Density
- Gravimetric Water Content
- Physical Porosity

MINERALOGICAL CHARACTERIZATION

- X-Ray Diffraction
- Thermal Analysis, DSC
- SEM, TEM
- FTIR

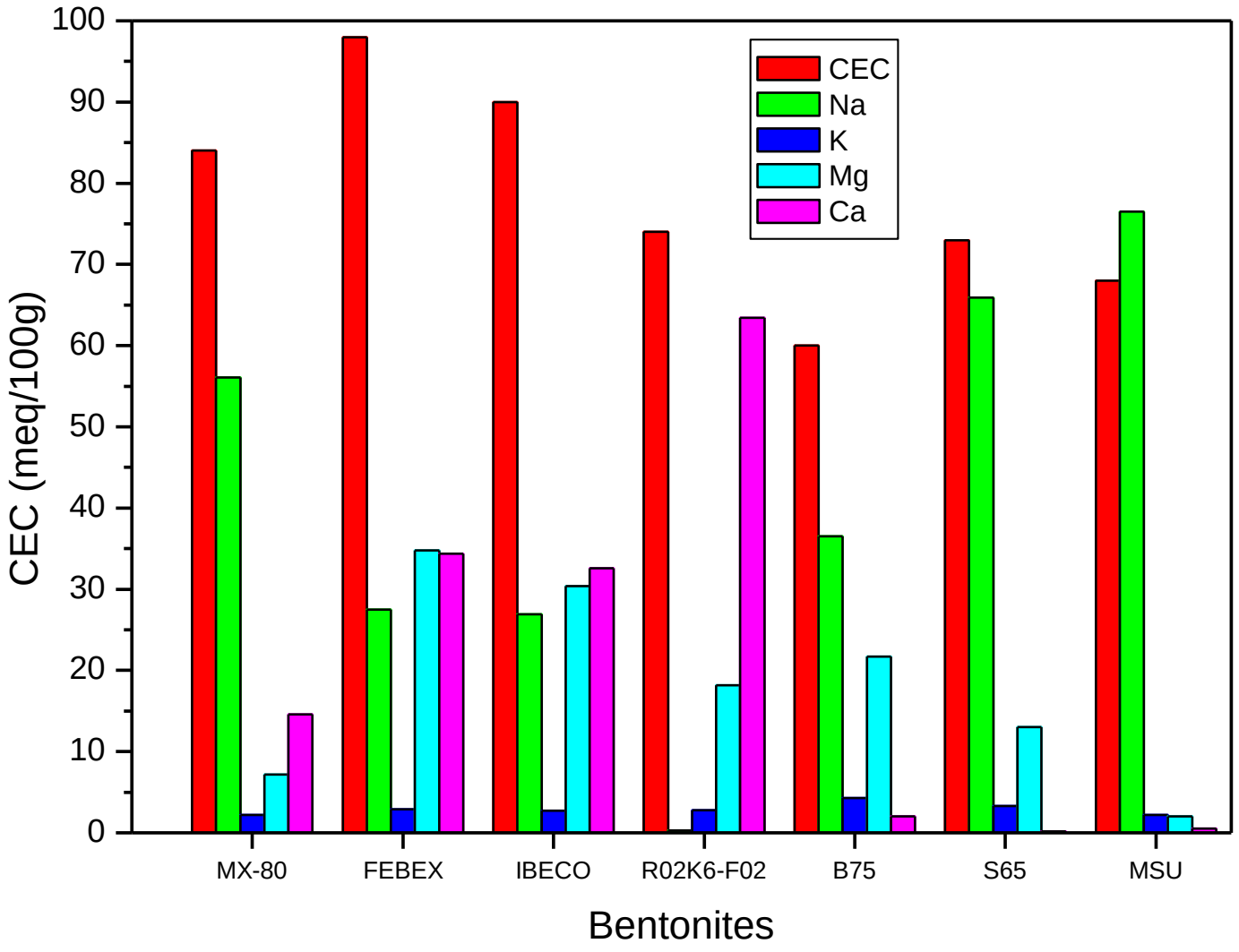
SURFACE PROPERTIES CHARACTERIZATION

- Total surface area
- Characterization of the dry state:
  - N_2 adsorption isotherm
  - Porosimetry
- Charaterization of the saturated state:
  - H_2O adsorption isotherm
  - d(001) basal spacings

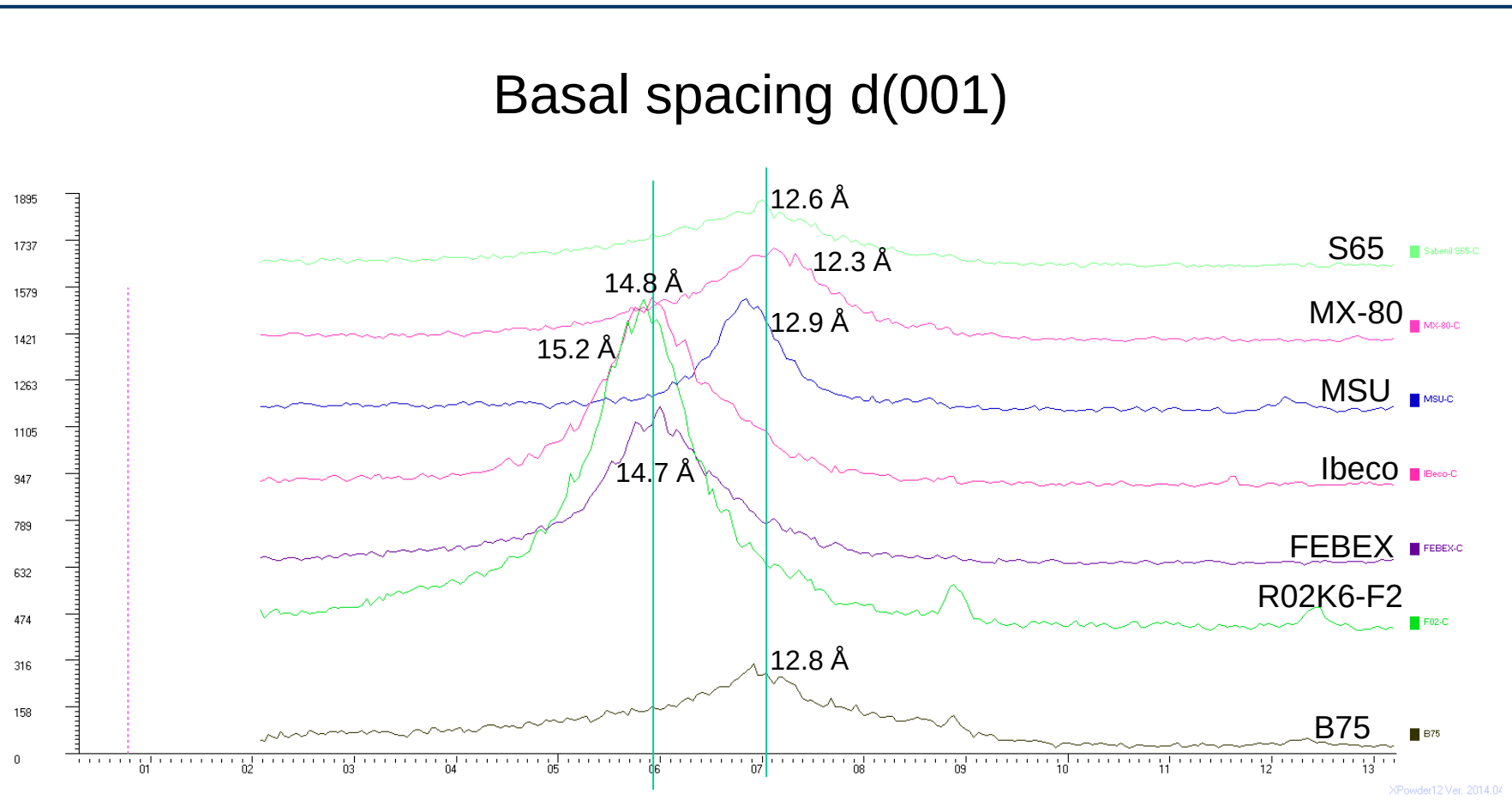
PHYSICO-CHEMICAL PROPERTIES

- Cation exchange population
- Total CEC
- Variable Charges
- Potentiometric titrations
- Soluble salts content
- Pore water extracted by *Squeezing*

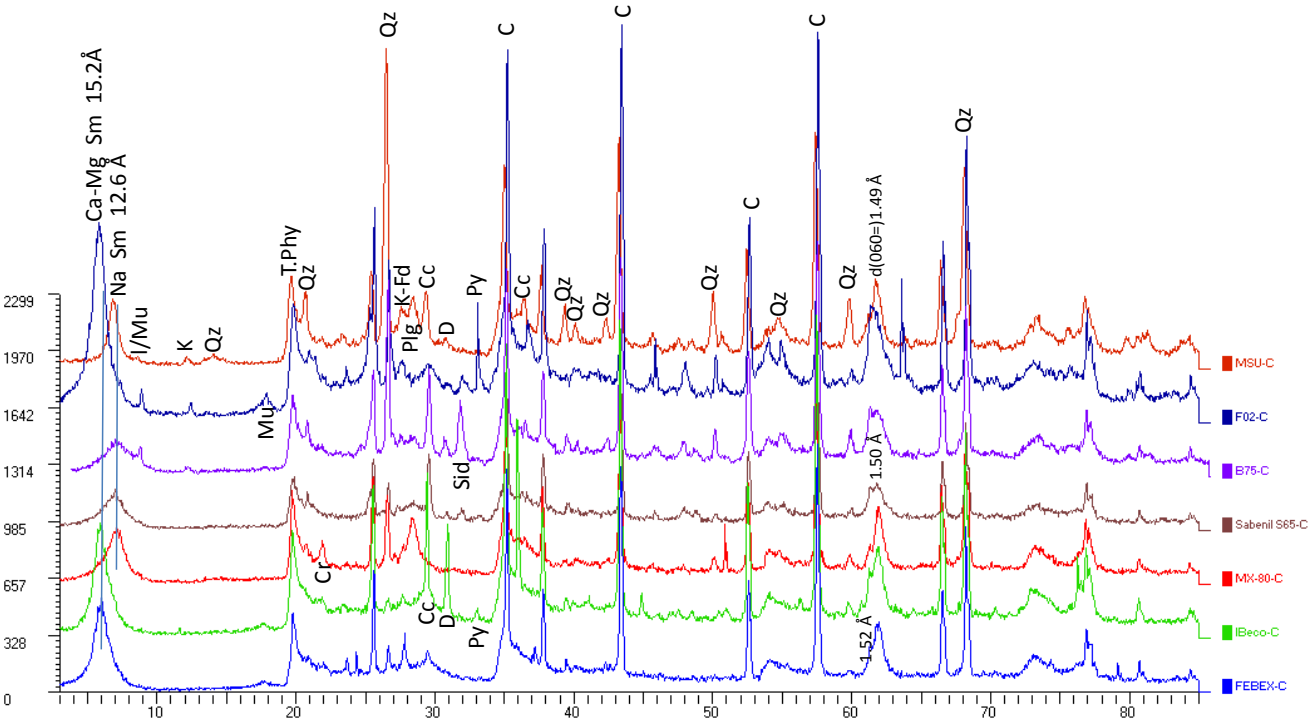
CEC AND CATION EXCHANGE POPULATION



001 Reflection in DRX patterns (TF/< 2 μm Oriented aggregate non- homoionized)

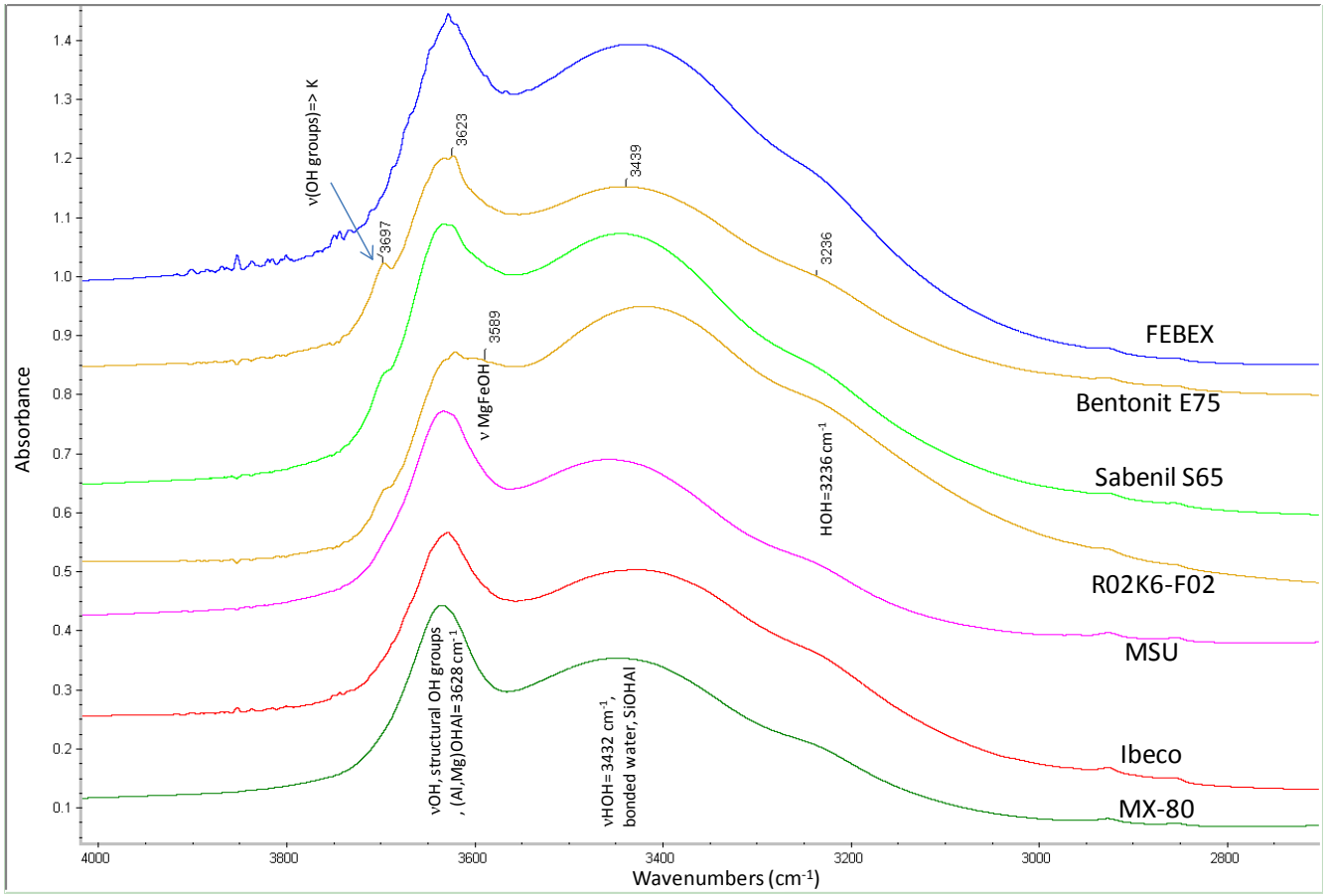


MINERALOGICAL COMPOSITION BY XRD

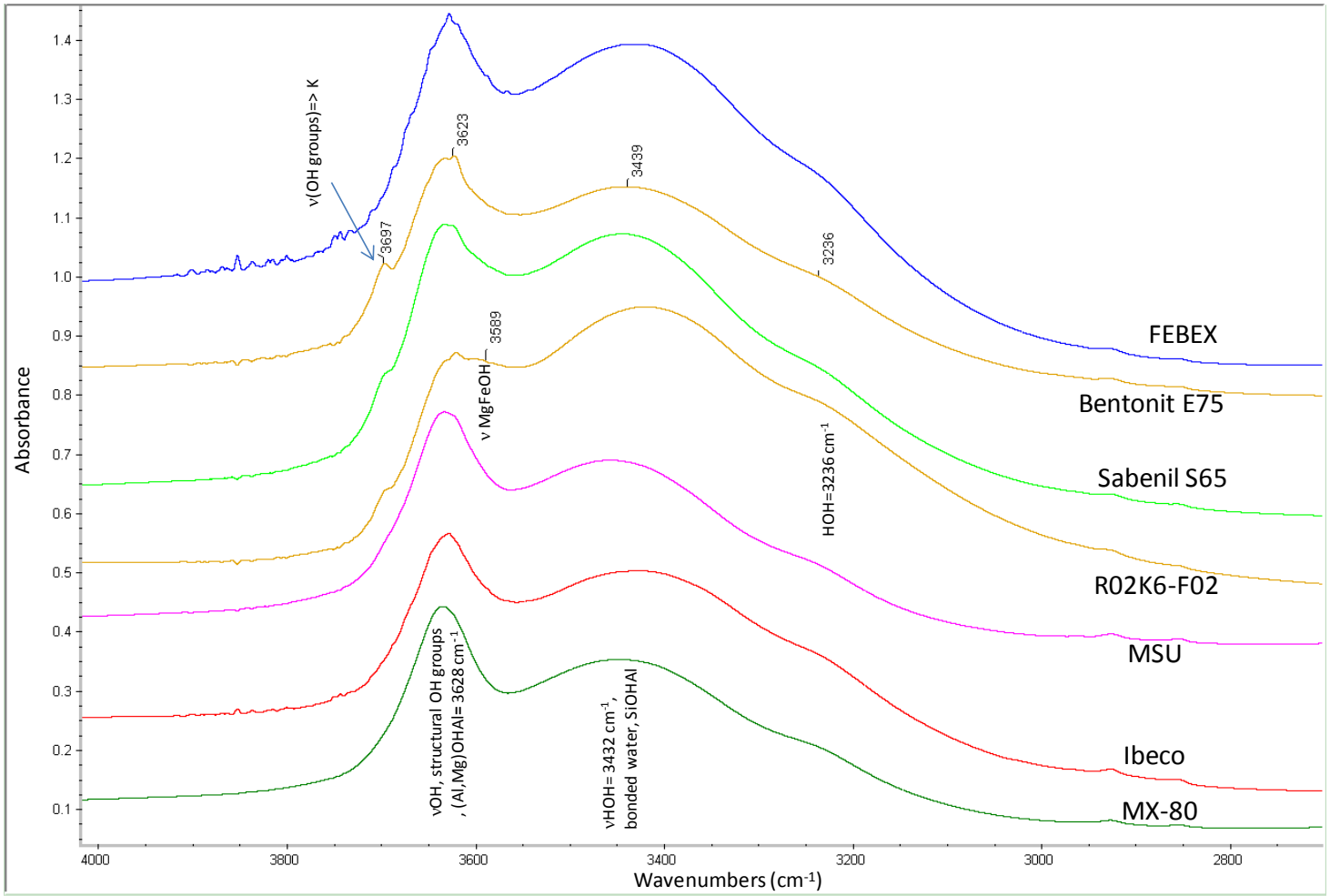


Bentonite	FEBEX	IBECO	MX-80	R02K6-F02	B75	S65	MSU
Phyllosilicates (w.t.%)	94	90	89	87	81	97	80
Smectite (w.t.%)	94	88	89	n.d.	78	94	79
Illite (w.t.%)	--	2	Tz	n.d.	1	2	Tz
Kaolinite (w.t.%)	--	--	--	n.d.	2	1	1
Chlorite (w.t.%)	--	--	--	n.d.	--	--	Tz

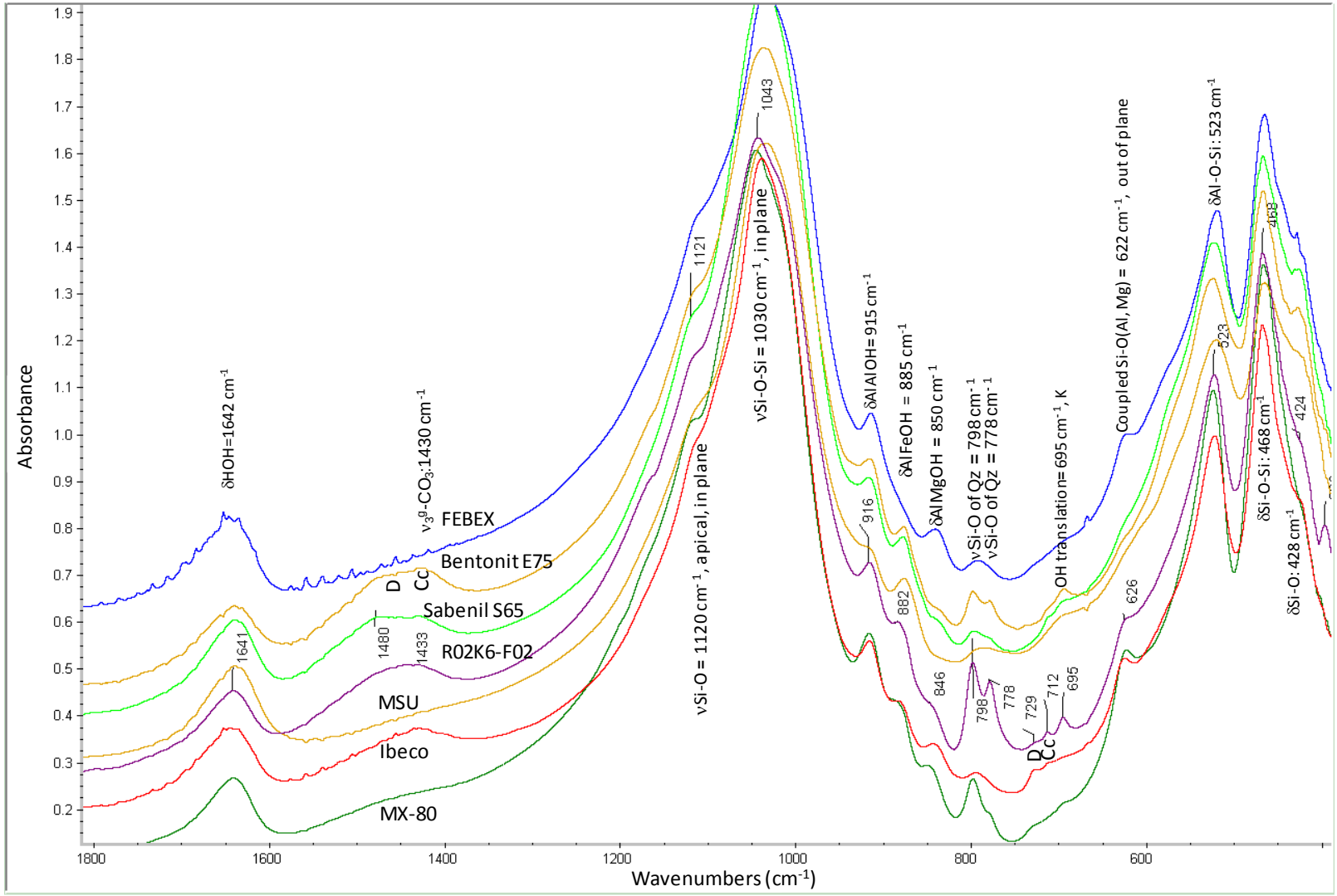
MINERALOGICAL COMPOSITION BY FT-IR



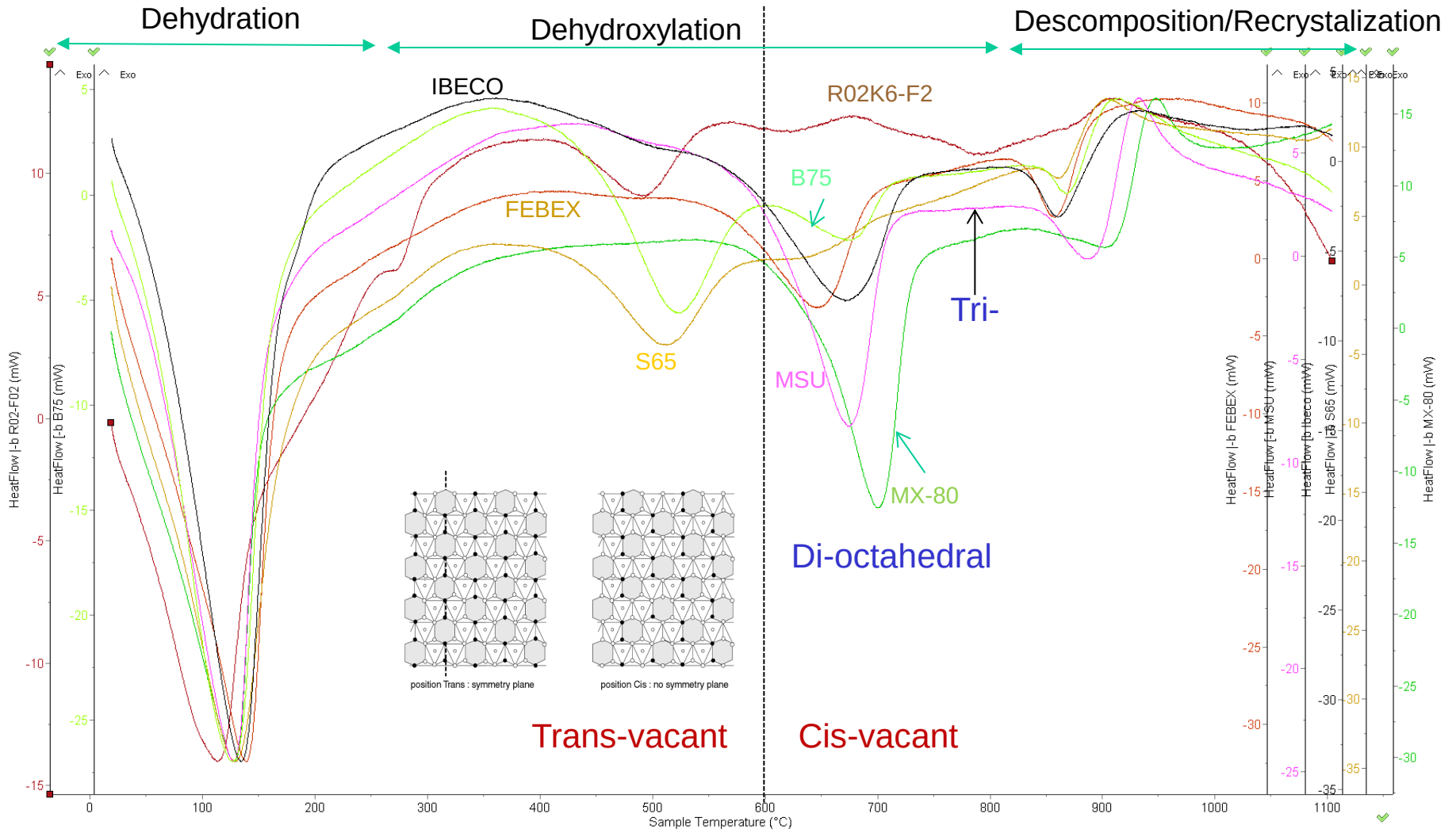
MINERALOGICAL COMPOSITION BY FT-IR



MINERALOGICAL COMPOSITION BY FT-IR



MINERALOGICAL COMPOSITION BY TG-DSC



Chemical Composition of the Total Fraction by XRF

Bentonite	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	LOI	Sum
	%	%	%	%	%	%	%	%	%	%	%	%	%
MX-80	62.89	19.87	3.53	0.01	2.40	1.24	2.09	0.52	0.07	0.03	0.19	8.46	101.29
Ibeco	50.32	15.70	4.76	0.12	4.76	5.29	0.89	0.55	0.63	0.11	0.19	18.65	101.95
Febex	55.46	17.28	3.09	0.03	4.37	1.75	1.16	0.99	0.15	0.03	0.04	16.82	101.17
R02K6-F02	48.06	14.52	15.94	0.19	2.12	2.85	0.26	1.00	4.51	0.84	0.05	9.37	99.73
B-75	51.08	14.94	8.93	0.13	3.71	4.29	1.17	1.23	1.94	0.36	0.05	12.21	100.05
S-65	47.96	14.22	12.30	0.09	3.57	3.88	1.97	0.58	2.62	0.31	0.04	11.55	99.09
MSU	61.73	15.98	3.41	0.10	2.60	3.10	2.70	1.05	0.59	0.11	0.12	8.01	99.49

Bentonite	Cl	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ag
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MX-80	31.7	5.7	8.4	0.6	2.7	1.8	4.5	62.6	27.2	N.D.	8.7	0.2	0.1	12.0	256.8	41.6	203.2	29.4	3.7	N.D.
Ibeco	92.4	14.2	141.9	14.8	11.8	7.5	12.4	56.6	17.6	N.D.	12.8	0.4	0.3	36.9	130.7	15.8	161.4	7.6	1.6	N.D.
Febex	236.0	9.6	15.9	5.2	5.7	12.0	10.0	59.5	20.6	N.D.	6.8	0.1	1.5	40.4	197.0	25.7	183.9	11.3	N.D.	N.D.
R02K6-F02	22.0	33.0	409.9	89.6	40.8	47.0	163.5	147.7	21.2	N.D.	7.9	0.5	1.0	45.6	321.8	29.2	408.3	126.5	3.4	N.D.
B-75	17.6	15.9	190.4	335.0	27.6	131.3	40.7	85.3	18.7	N.D.	2.7	0.3	0.1	71.0	119.9	19.6	244.8	57.9	0.7	N.D.
S-65	19.0	20.9	219.4	409.7	45.0	198.1	49.6	99.2	19.7	N.D.	0.7	0.0	1.1	45.5	108.0	23.3	302.9	75.0	1.2	N.D.
MSU	166.8	7.5	35.5	11.4	2.7	6.0	11.4	81.4	17.5	N.D.	3.6	0.1	0.5	37.4	331.7	33.5	298.6	13.4	1.5	N.D.

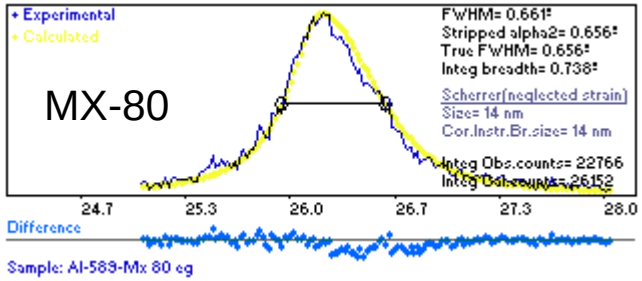
Bentonite	Cd	Sn	Sb	Te	I	Cs	Ba	La	Ce	Nd	Sm	Yb	Hf	Ta	W	Tl	Pb	Bi	Th	U
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MX-80	N.D.	10.2	3.2	0.2	1.0	6.3	185.8	49.8	105.3	43.8	12.6	2.3	10.2	2.8	0.8	N.D.	38.6	0.3	37.0	12.8
Ibeco	N.D.	2.2	3.6	N.D.	N.D.	11.9	146.6	27.5	47.8	20.3	5.9	1.0	5.6	0.3	2.0	N.D.	9.8	N.D.	7.7	7.9
Febex	N.D.	9.4	3.2	1.1	1.3	5.1	61.6	35.3	63.5	25.6	7.2	1.6	7.1	1.3	1.4	N.D.	33.7	N.D.	14.3	0.4
R02K6-F02	1.1	4.7	N.D.	N.D.	1.2	N.D.	650.7	99.5	189.2	83.6	11.1	1.8	7.9	7.3	1.3	N.D.	12.0	0.1	12.6	0.4
B-75	N.D.	4.9	2.3	1.6	2.5	N.D.	187.7	55.1	85.7	39.9	8.1	0.7	5.3	5.3	4.9	1.9	N.D.	12.7	0.1	11.9
S-65	N.D.	4.0	N.D.	N.D.	N.D.	N.D.	162.6	60.1	102.2	48.8	5.0	1.7	6.8	6.8	4.9	0.5	0.5	5.4	N.D.	6.0
MSU	N.D.	5.9	2.1	0.5	0.5	1.6	253.6	47.0	95.8	43.3	11.6	2.0	6.8	0.0	1.1	N.D.	22.5	N.D.	9.5	2.7

Structural Formulae and Crystallographic characteristics

Smectite		FEBEX	Ibeco	MX-80	B-75	S-65
Tetrahedral layer	Si	7.90	7.80	8.00	7.48	7.00
	Al	0.10	0.20	0.00	0.52	1.00
	Total	8.00	8.00	8.00	8.00	8.00
Octahedral layer	Al	2.73	2.68	3.02	2.30	1.56
	Ti	0.01	0.09	0.01	0.37	0.74
	Fe^{3+}	0.41	0.52	0.44	0.84	1.26
	Mg	0.98	0.82	0.48	0.45	0.47
	Total	4.14	4.11	3.96	3.96	4.02
Interlamellar layer:	Ca	0.17	0.20	0.13	0.08	0.13
	K	0.13	0.09	0.02	0.23	0.13
	Na	0.20	0.11	0.30	0.34	0.28
	Total	0.49	0.40	0.45	0.64	0.54
Tetrahedral charge:		-0.10	-0.20	0.00	-0.52	-1.00
Octahedral Charge:		-0.56	-0.40	-0.58	-0.20	0.00
Total:		-0.66	-0.60	-0.58	-0.72	-1.00
Interlamellar Charge (+):		0.66	0.60	0.58	0.72	0.67
% tetrahedral charge		15	33	0	73	100
% octahedral Charge		85	67	100	27	0
F.W. (half-unit cell)		749.76	752.10	744.26	769.35	787.28
a (Å)		1.2889	1.2896	1.2902	1.2898	1.2871
b (Å)		1.5002	1.4994	1.5001	1.5010	1.5045
c (Å)		14.74	14.86	12.33	12.76	12.60
Surface charge density (C/m^2)		0.126	0.116	0.108	0.077	0.126
Charge per unit cell		0.73	0.67	0.63	0.45	0.55
S (m^2/g)		747	744	752	730	713

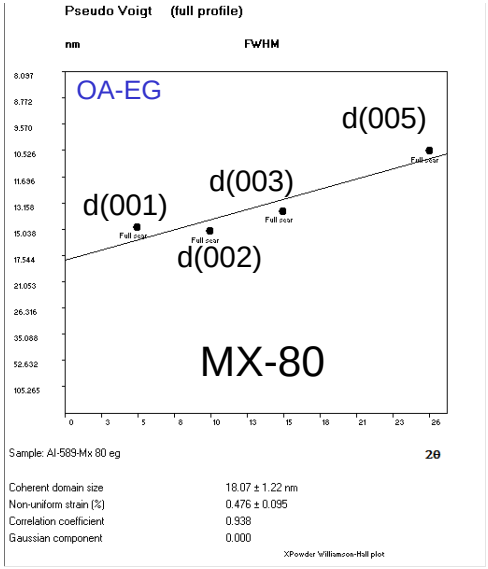
XRD PROFILE ANALYSES FOR CRYSTALLINE SIZE: SCHERRER AND WILLIAMSON-HALL METHODS

Scherrer equation

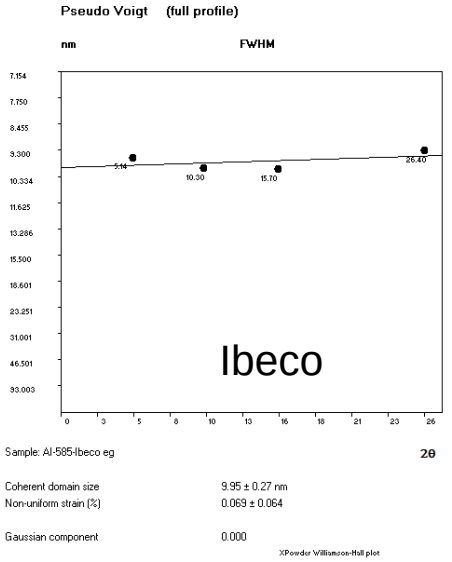


Size = 14 nm

Williamson-Hall plots



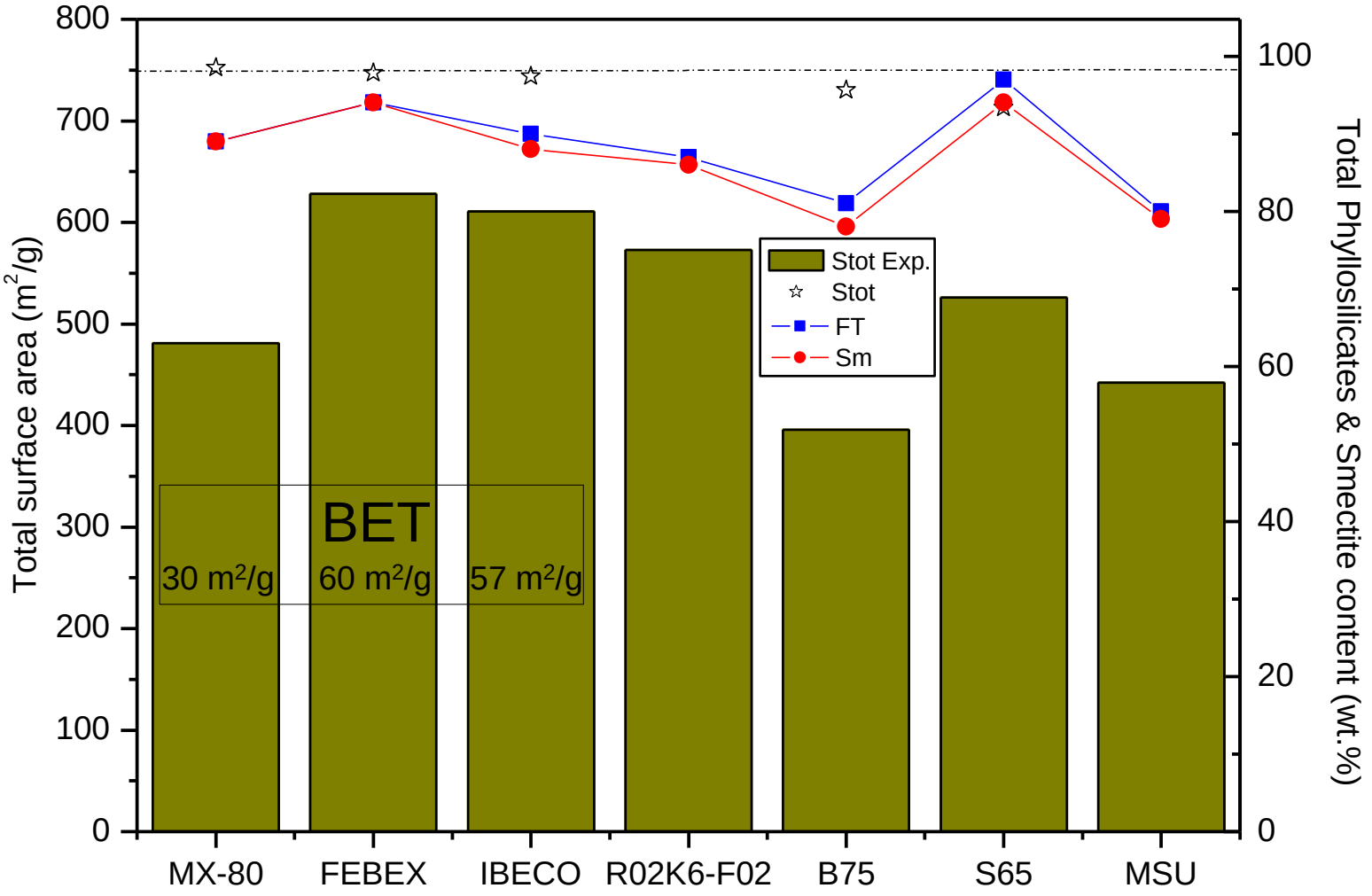
Size = 18.07 nm



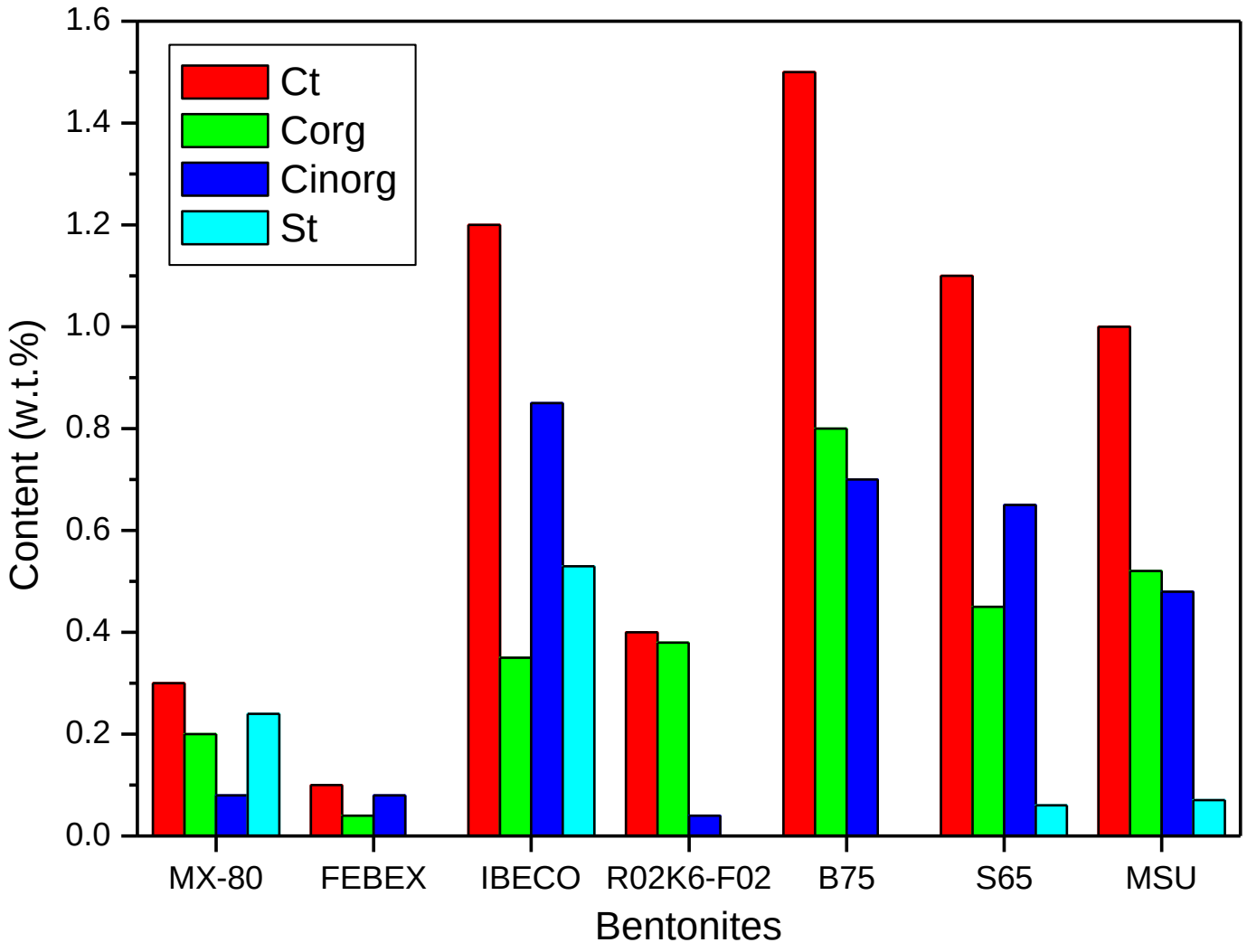
Scherrer Eq. Size = 11.5 nm
WH Size = 9.95 nm

	FEBEX	Ibeco	MX-80	B-75	S-65	F02	MSU
d(001) EG (Å)	16.9	17	17	17	17	17	17
Cristallite Size (Å)	102	115	140	80	70	80	105
Nº Lamellae/cristallite	6	7	8	5	4	5	6

SPECIFIC SURFACE AREA AND BET EXTERNAL SURFACE



TOTAL CARBON, C_{ORG}, C_{INOG} AND TOTAL SULPHUR

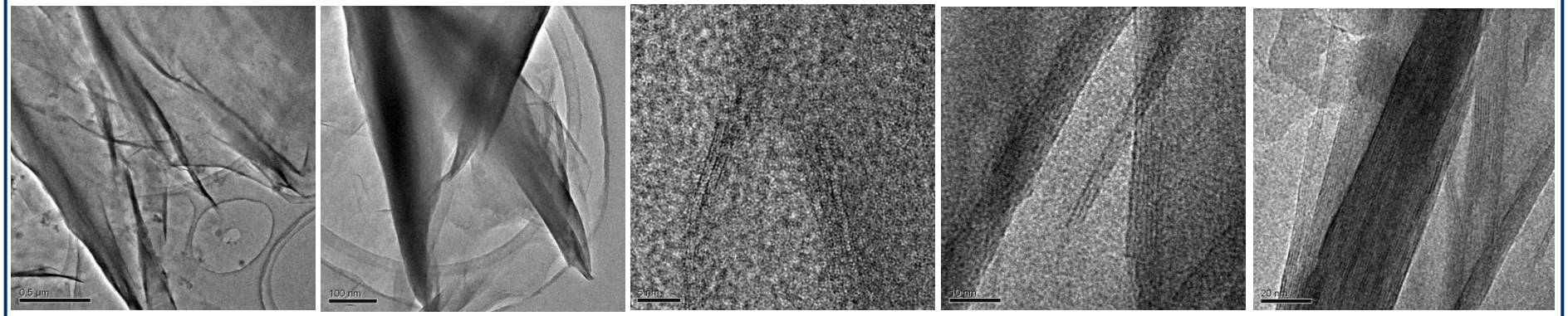


PORE WATER CHEMISTRY OBTAINED BY SQUEEZING

Bentonites	Febex 28.2% w.c.	Milos 28.9% w.c.	MX80 25.6% w.c.
pH	7.3	7.8	8.0
I (M)	0.27	0.19	0.33
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
HCO_3^- (mg/L)	125.66	175.68	--
Alk. (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
Cu (mg/L)	0.24	<0.38	<0.8
Mn (mg/L)	0.22	0.96	<0.8
Ba (mg/L)	<0.15	<0.38	<0.8
Zn (mg/L)	0.63	1.1	1.9
pCO_2 (bar)	-2.37	-2.7	--

TEM Analyses: Texture, microstructure, crystallochemistry

MX-80

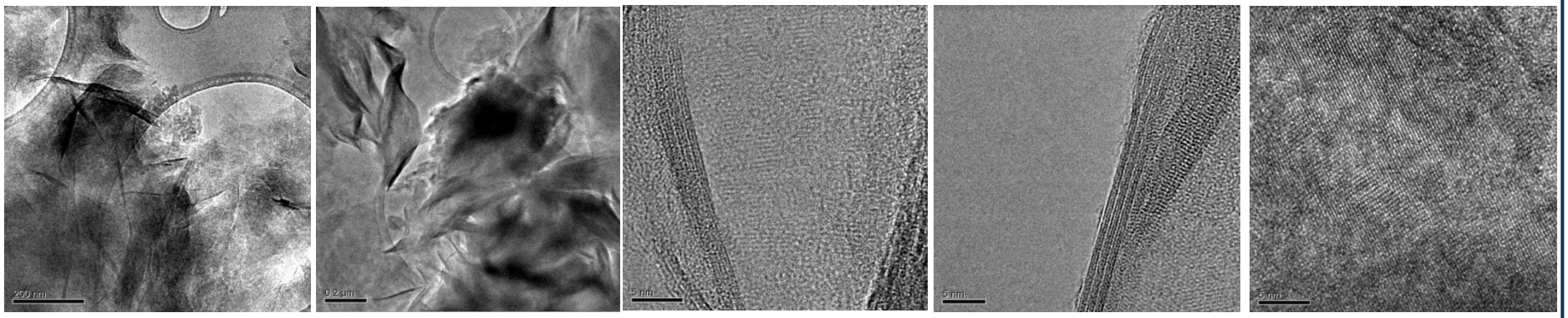


$(Mg_{0.49}Al_{3.33}Fe^{3+}_{0.28})(Si_{7.83}Al_{0.17})Na_{0.27}Ca_{0.03}K_{0.01}O_{20}(OH)_4$

τ charge = -0.17; O. charge = -0.17

Total charge = -0.34 (τ% = 50; o% = 50)

FEBEX



$(Mg_{0.73}Al_{3.00}Fe^{3+}_{0.35})(Si_{7.40}Al_{0.60})Na_{0.46}Ca_{0.01}K_{0.63}O_{20}(OH)_4$

τ charge = -0.60; O. charge = -0.50

Total charge = -1.11 (τ% = 54; o% = 46)