



Significance and role of clay minerals in soils : Use of recent experimental data

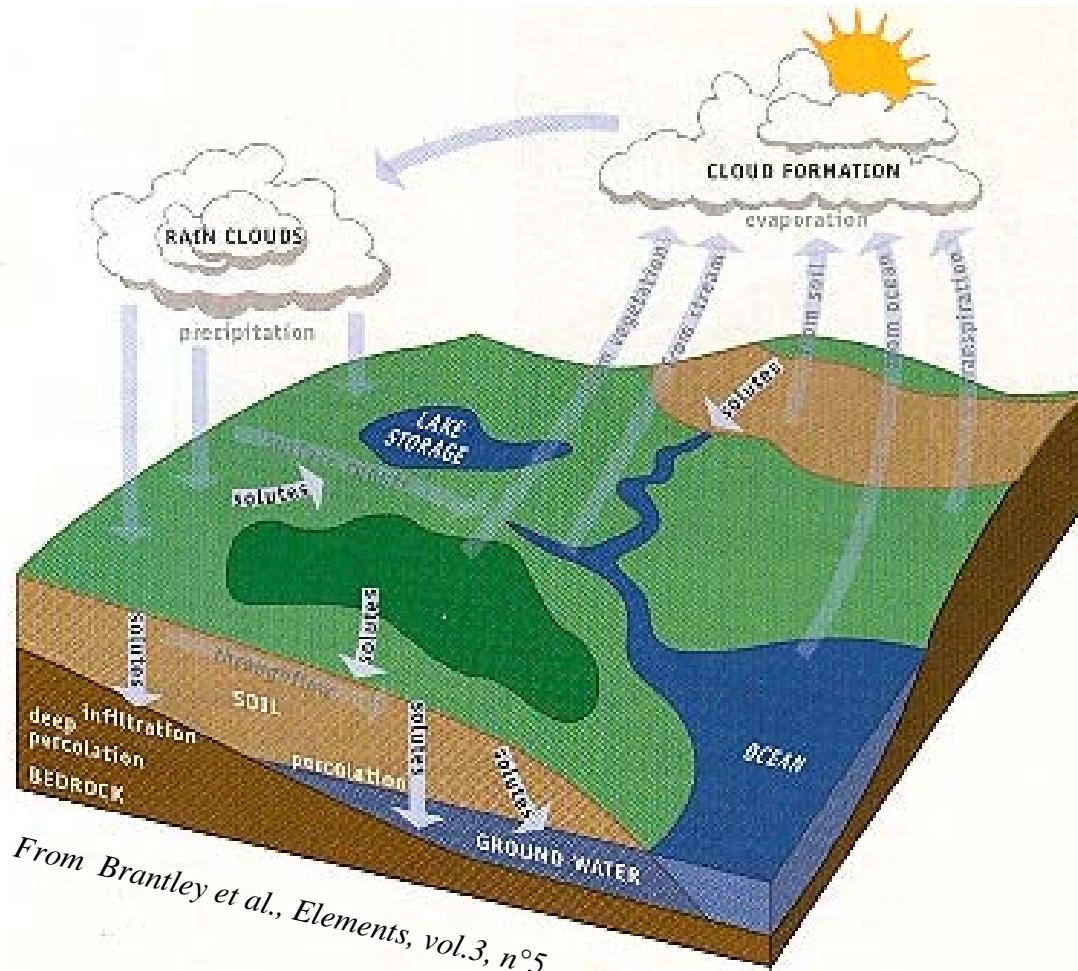
Sabine PETIT

Dominique RIGHI

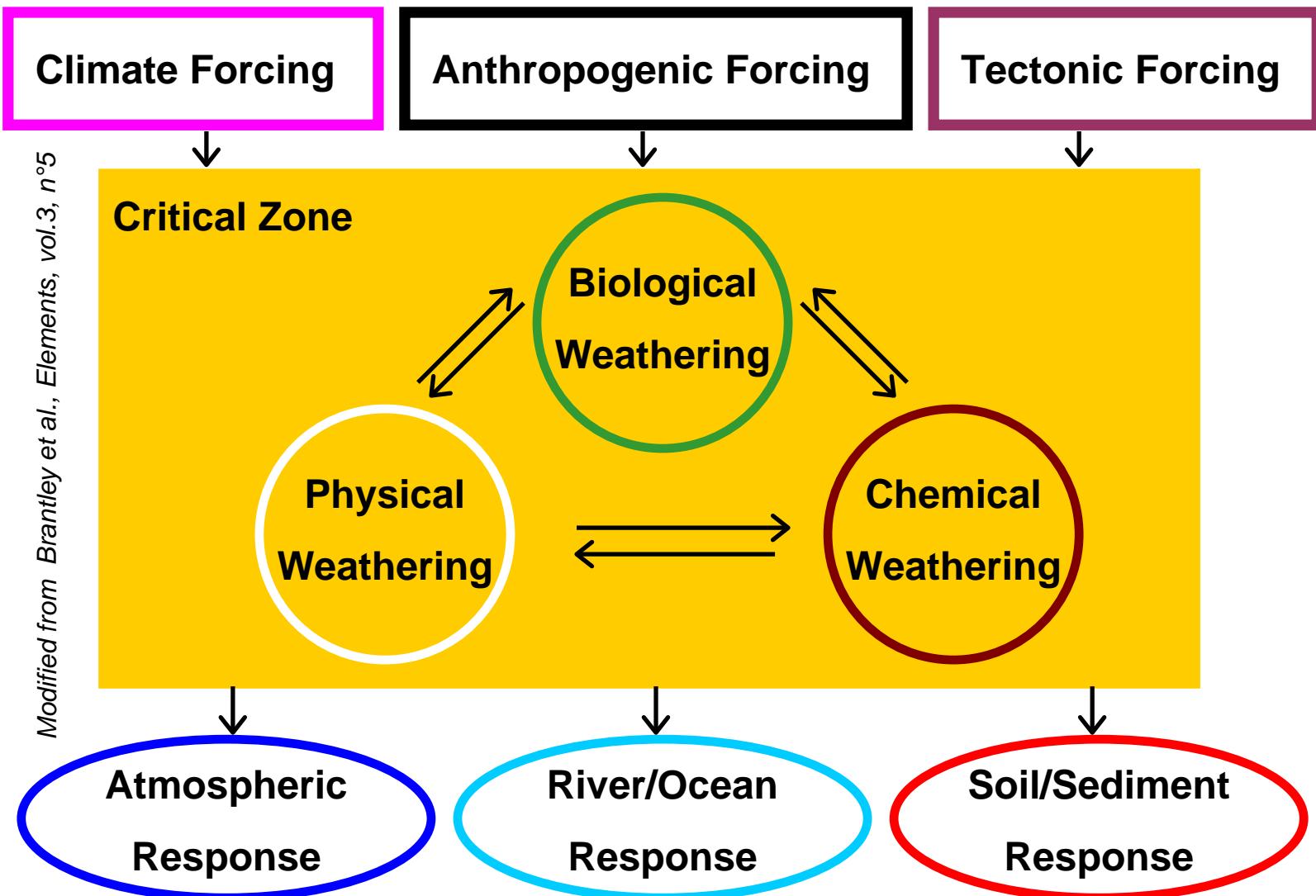
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Université de Poitiers
40, ave. du Recteur Pineau
86022 POITIERS Cedex
France

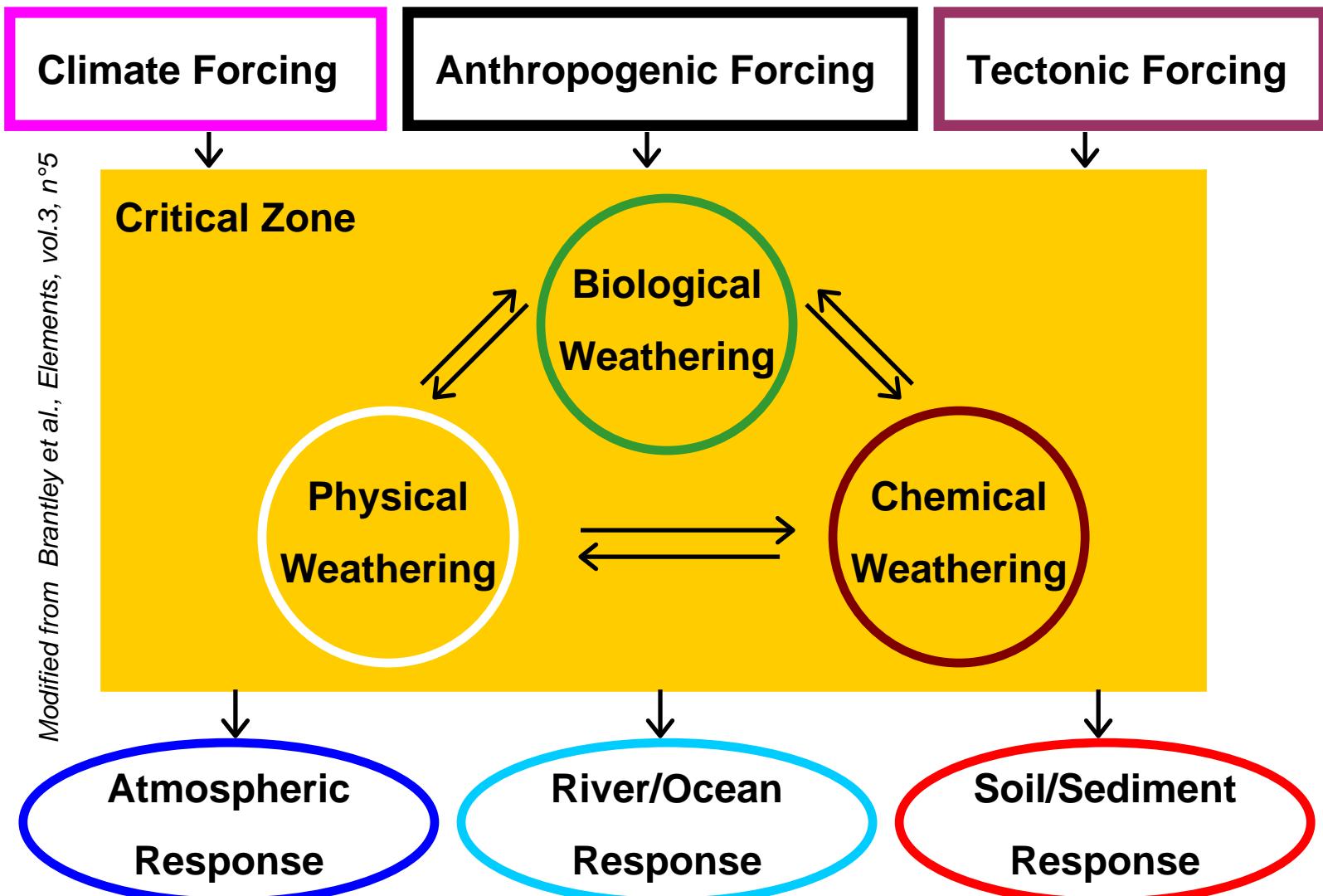
e-mail: sabine.petit@univ-poitiers.fr

All life on Earth is supported by the fragile skin of the planet defined from the outer extent of vegetation down to the lower limits of groundwater.



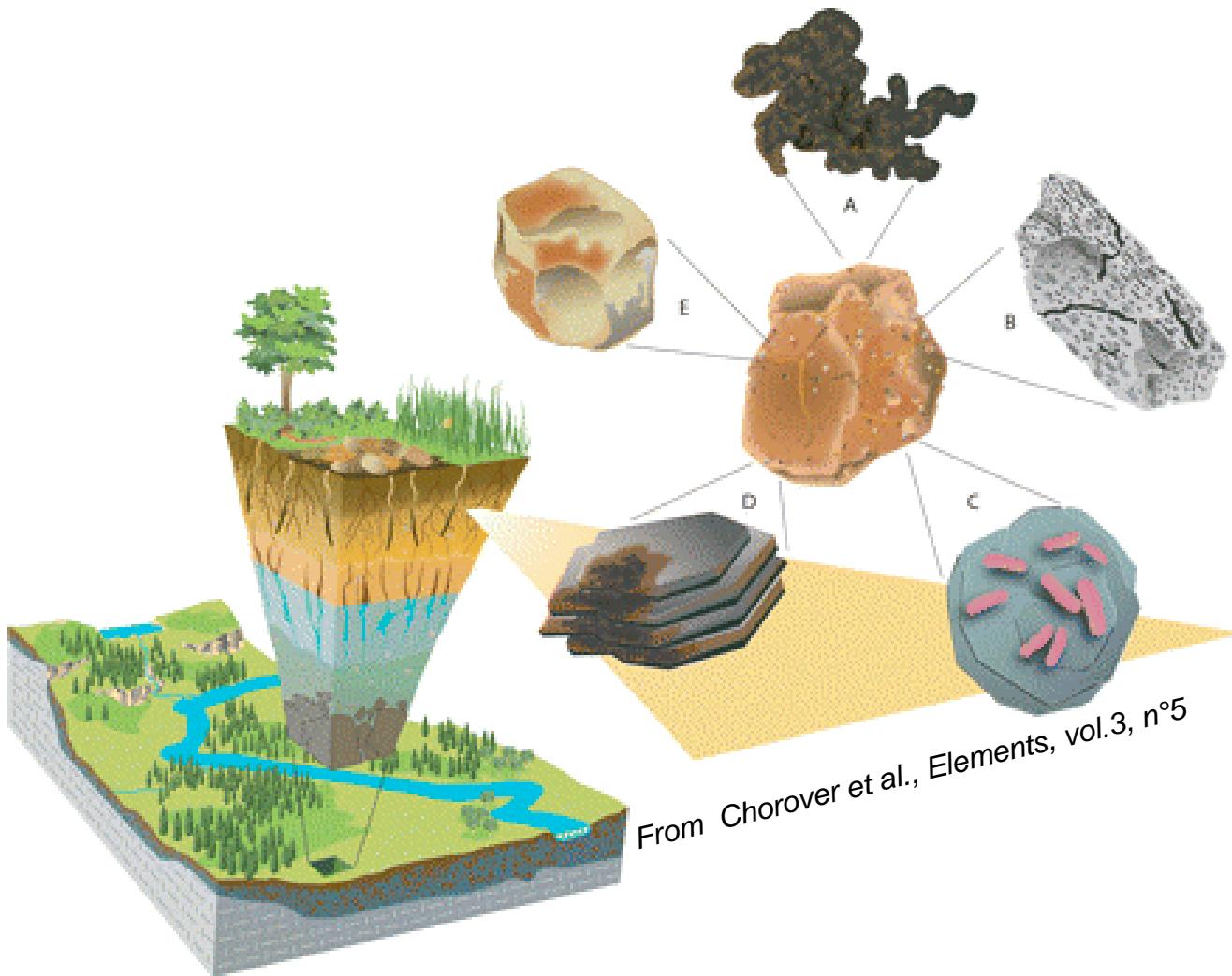
This volume has been recently labelled the *Critical Zone* because of its essential role in natural and managed ecosystems.



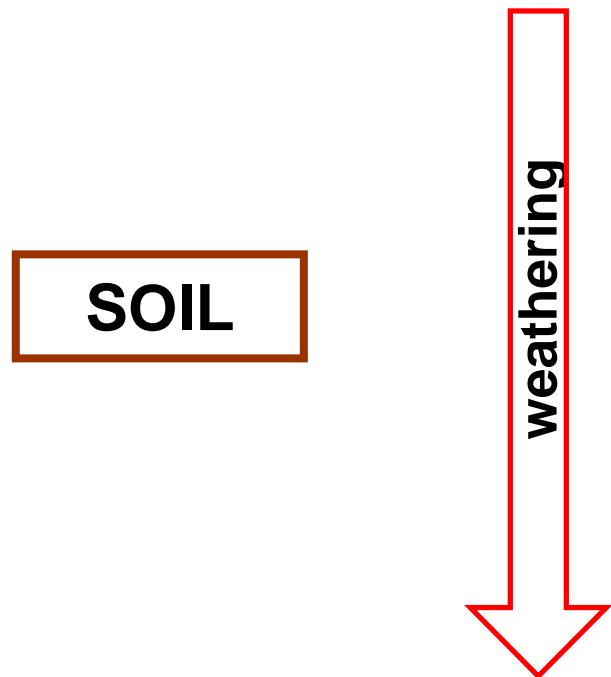


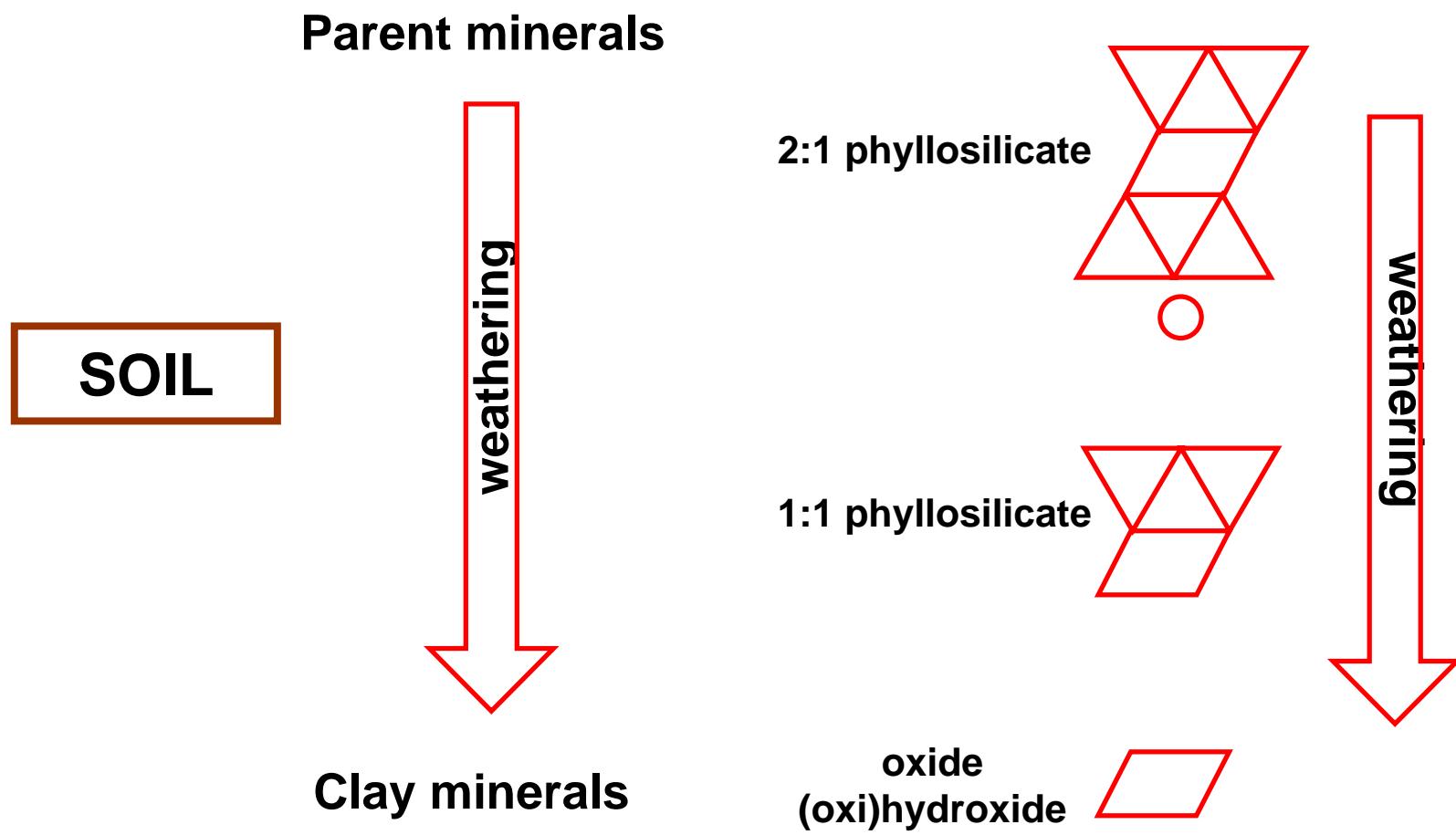
Interpreting the Record

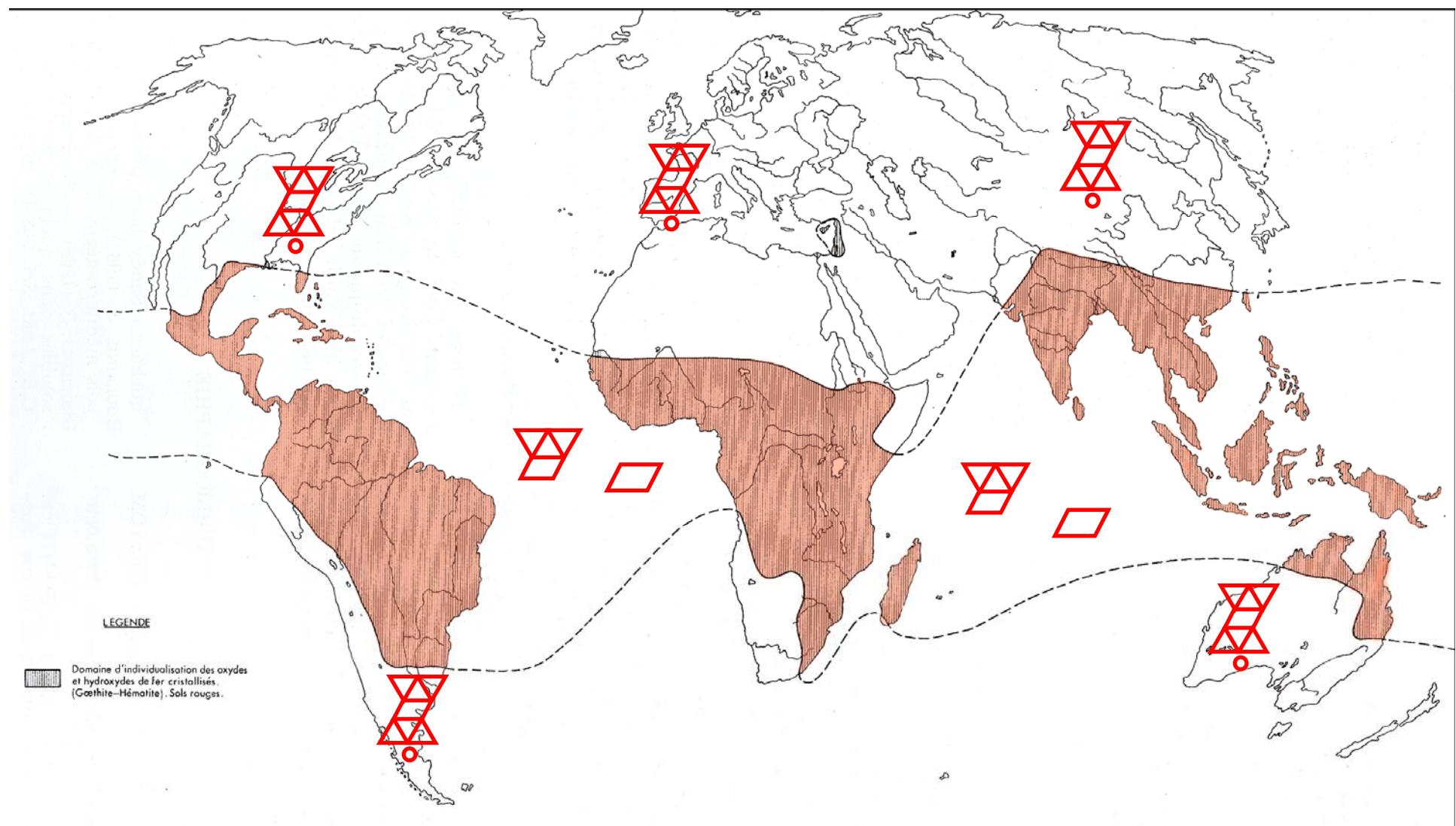
The soil system



Parent minerals

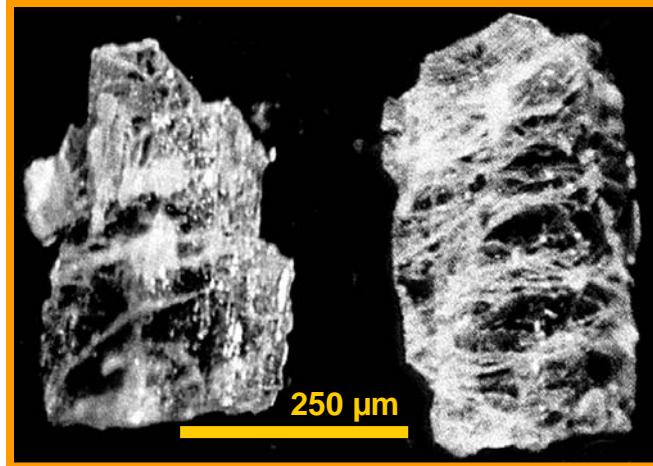




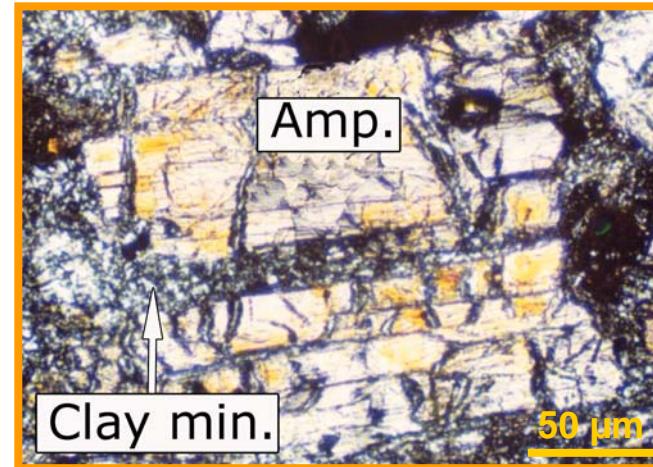


Modified from Pedro (1968)

Weathering patterns in amphibole crystals



Optical microscopy
Cross-polarized light

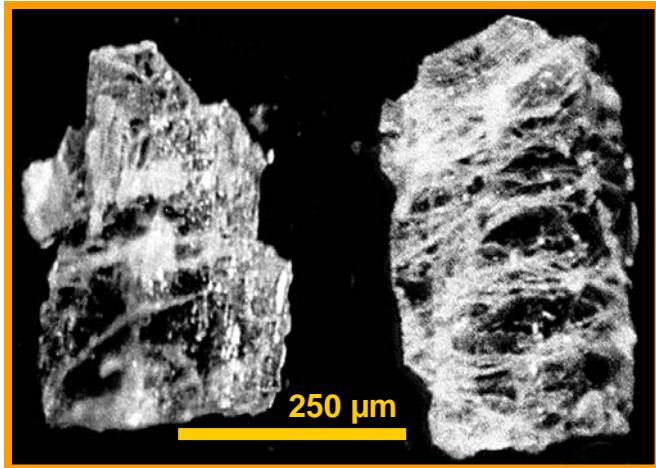


courtesy of Dominique Proust (HydrASA)

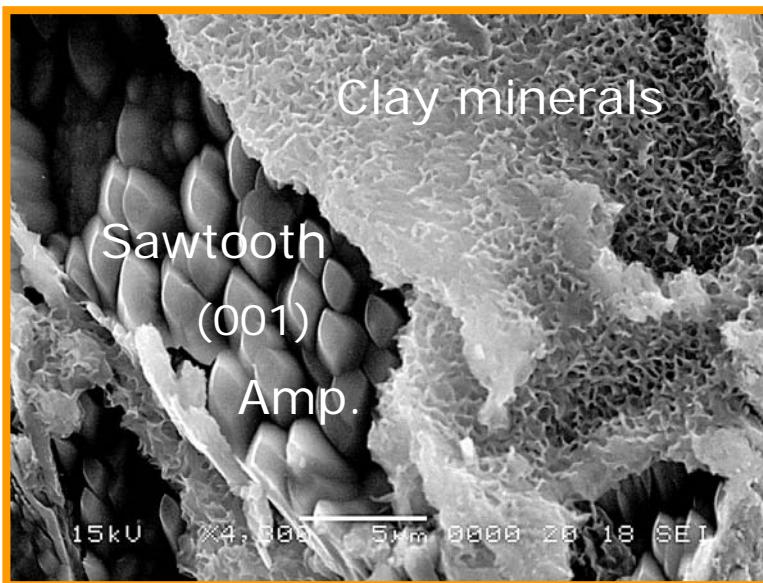
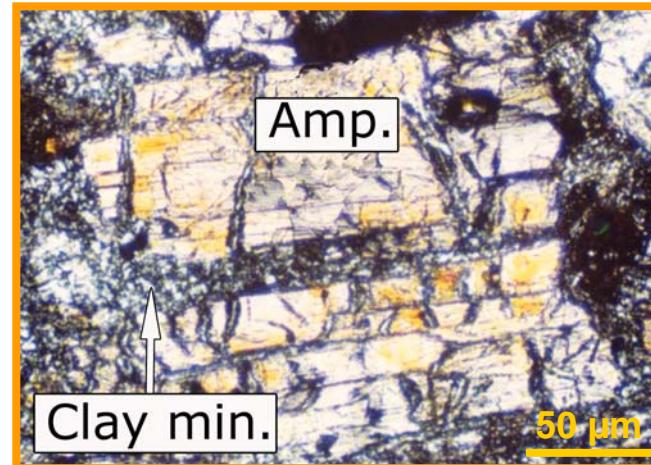
Clays and Clay Minerals, 54, 351-363, 2006

« Colloque Minéralogie environnementale - Académie des sciences - 14-15 septembre 2009 »

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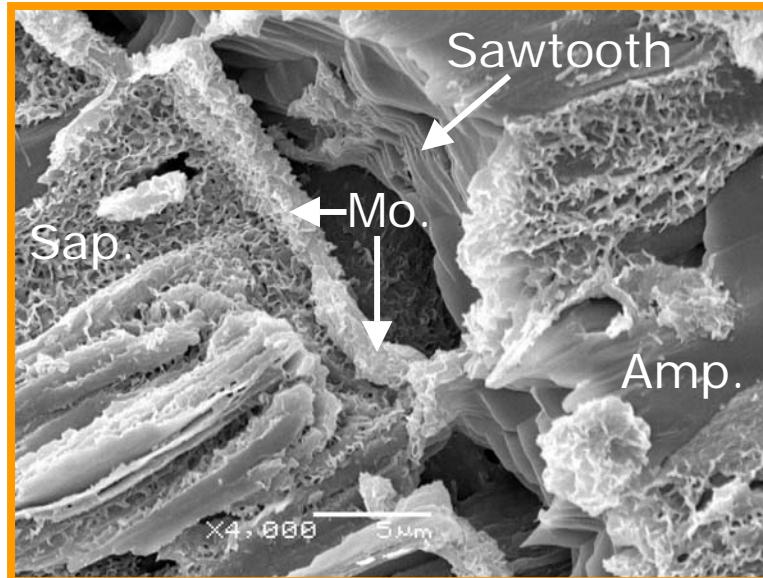
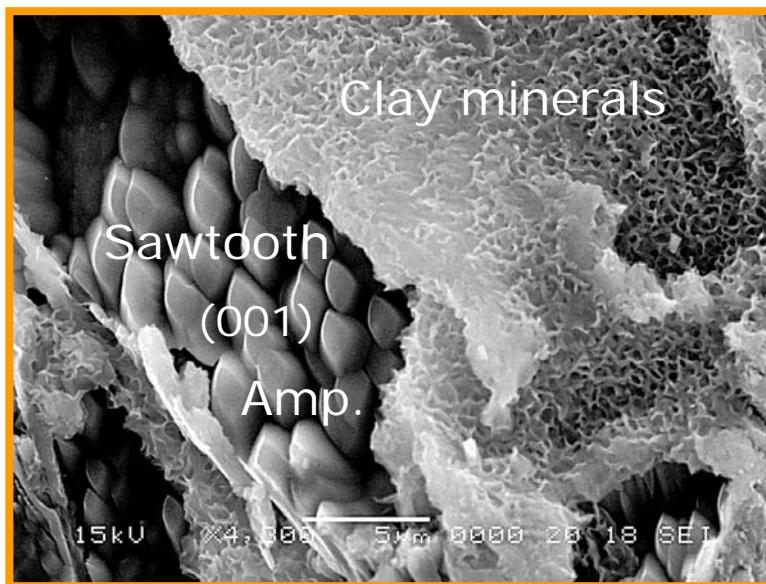
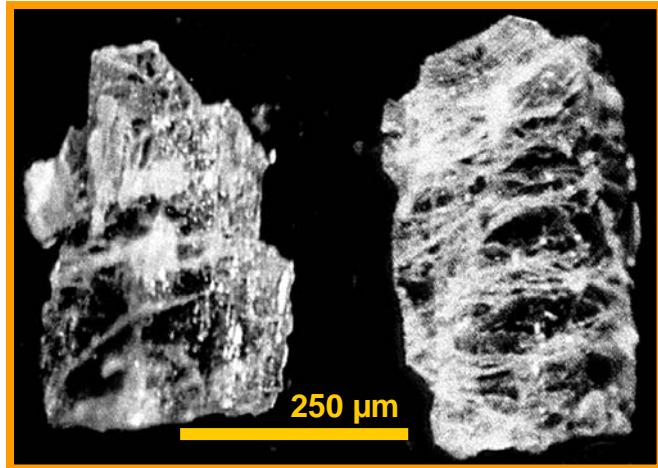
SEM microscopy

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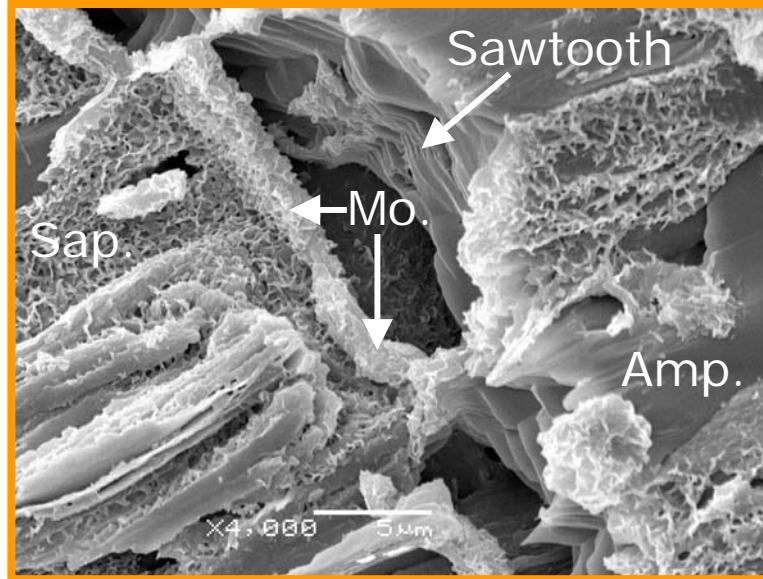
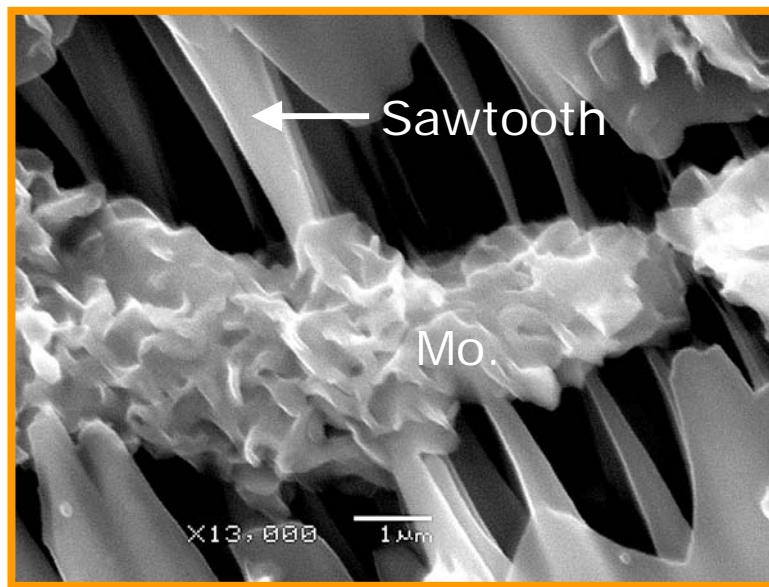
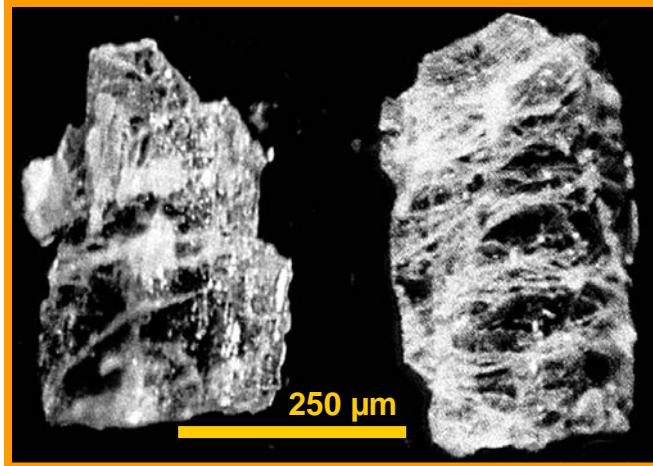
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Crystallization sites

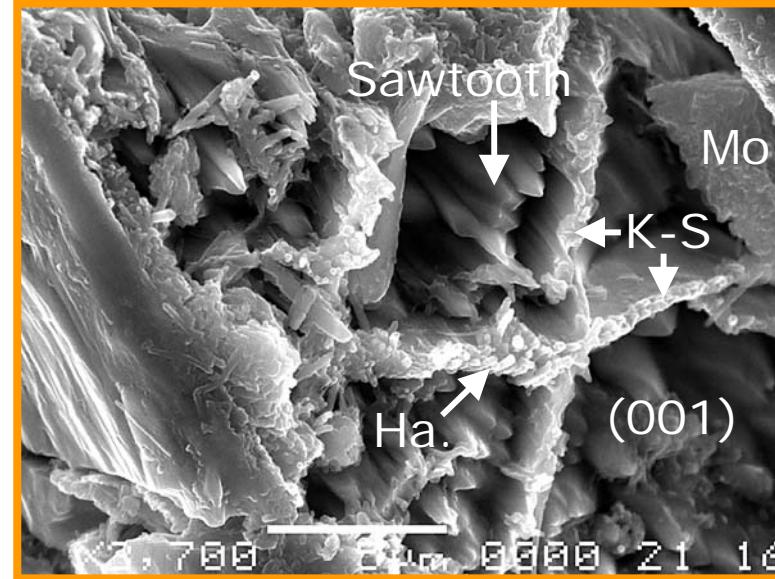
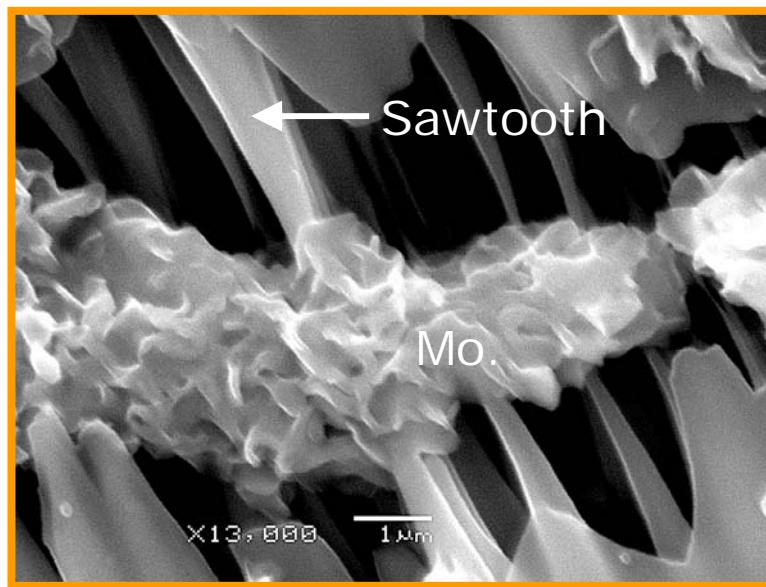
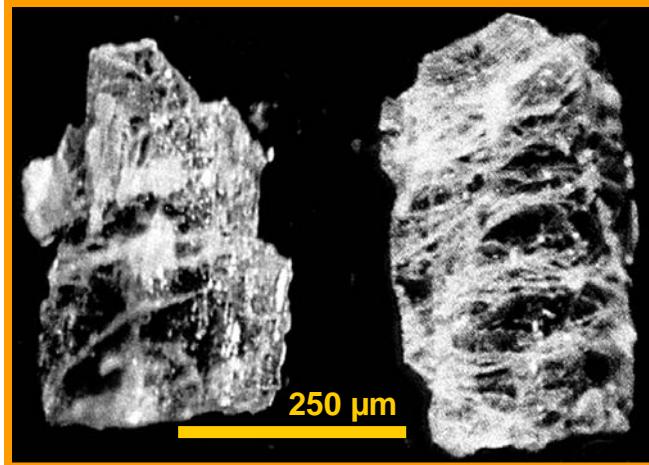
- Saponite on (110) planes
- Montmorillonite on (001) planes
- K-S on amphibole sawtooth (001)
- Halloysite on K-S or amphibole

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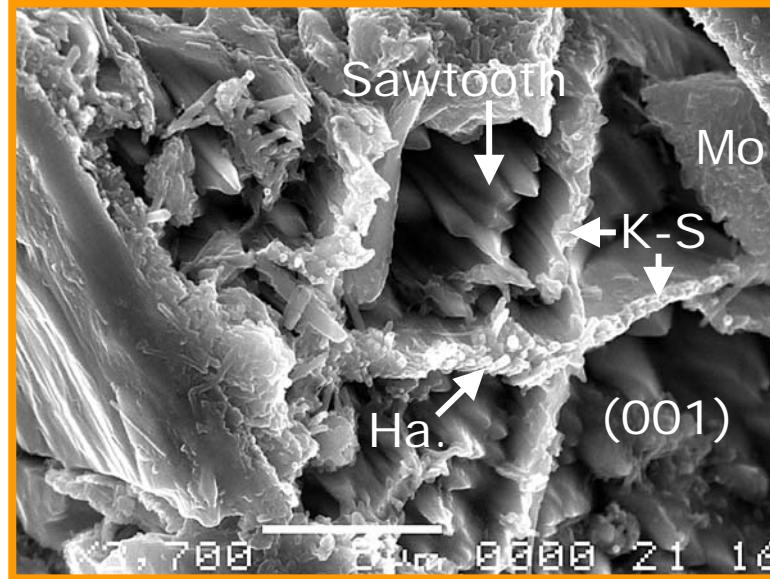
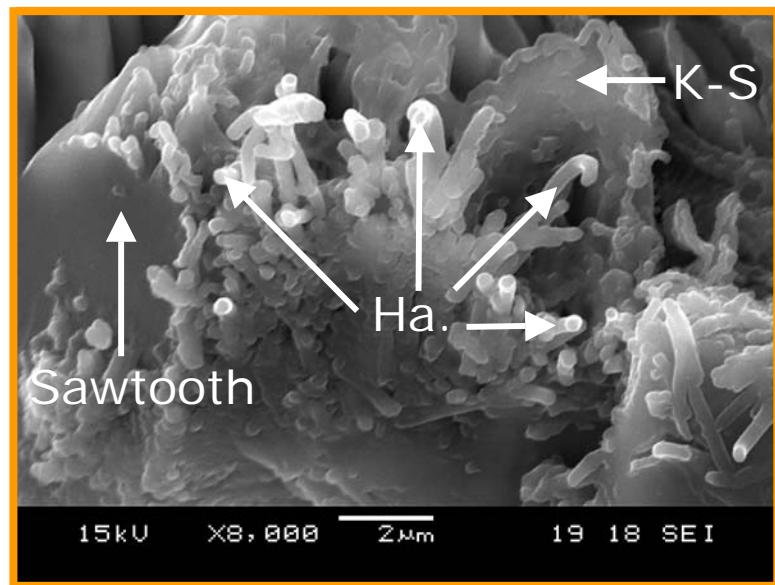
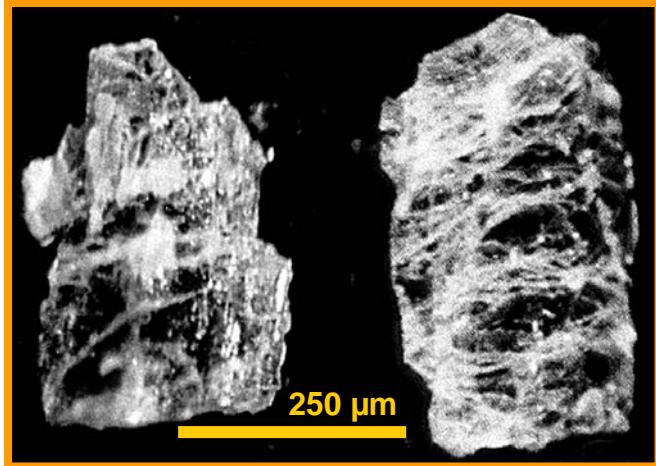
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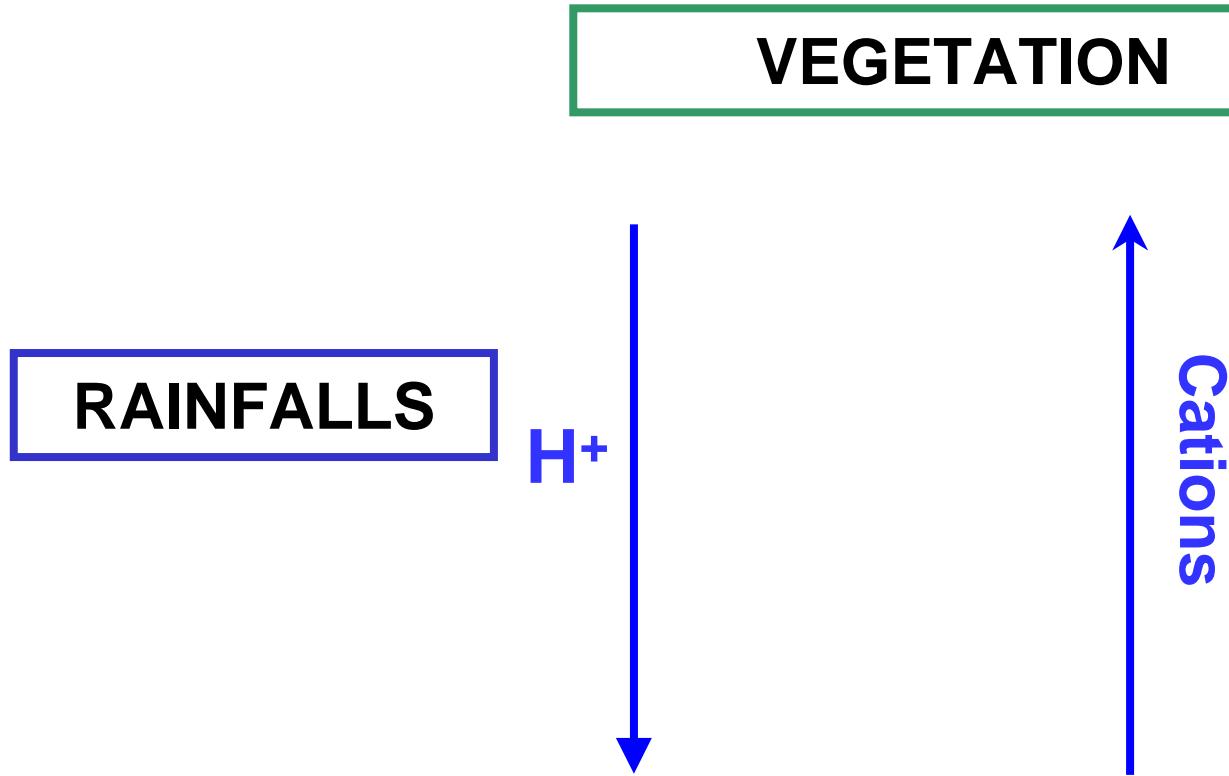
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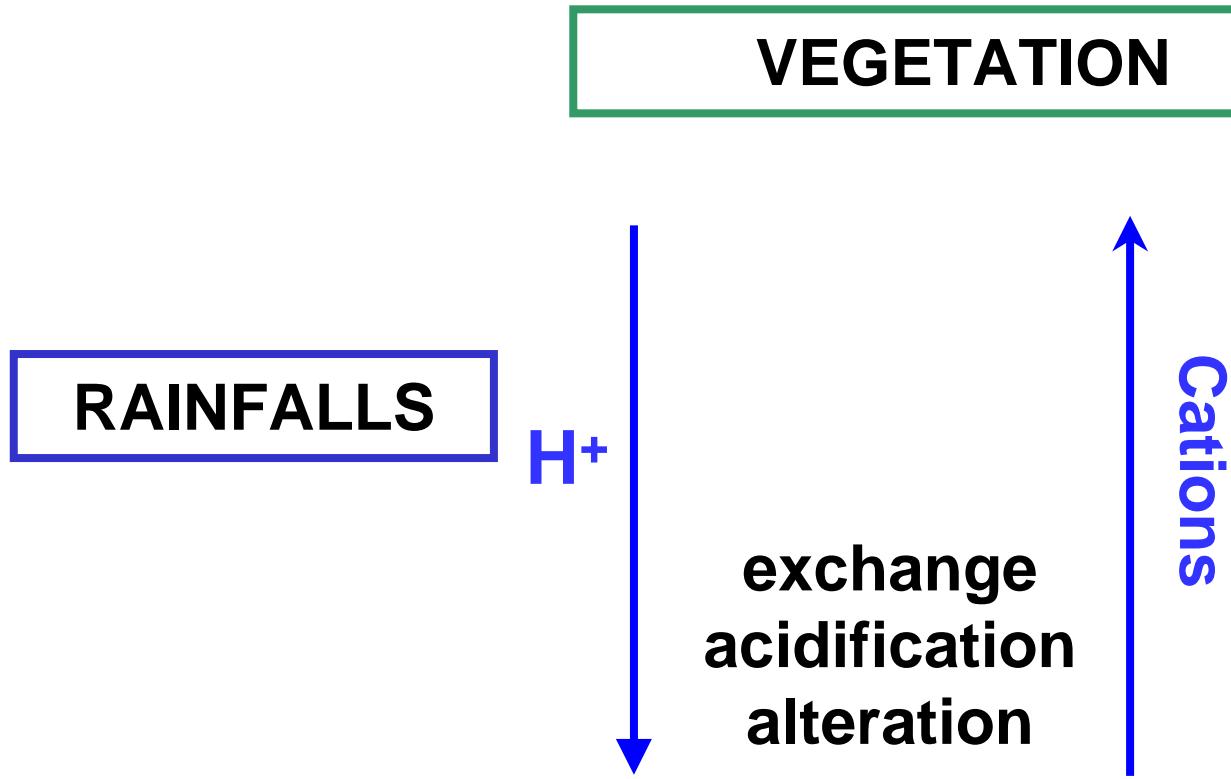
VEGETATION



Clay minerals

SOIL

VEGETATION



Clay minerals

SOIL

Cation exchange capacity of clay minerals

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- corresponds to the property to exchange cations from the surface of mineral by cations in solution

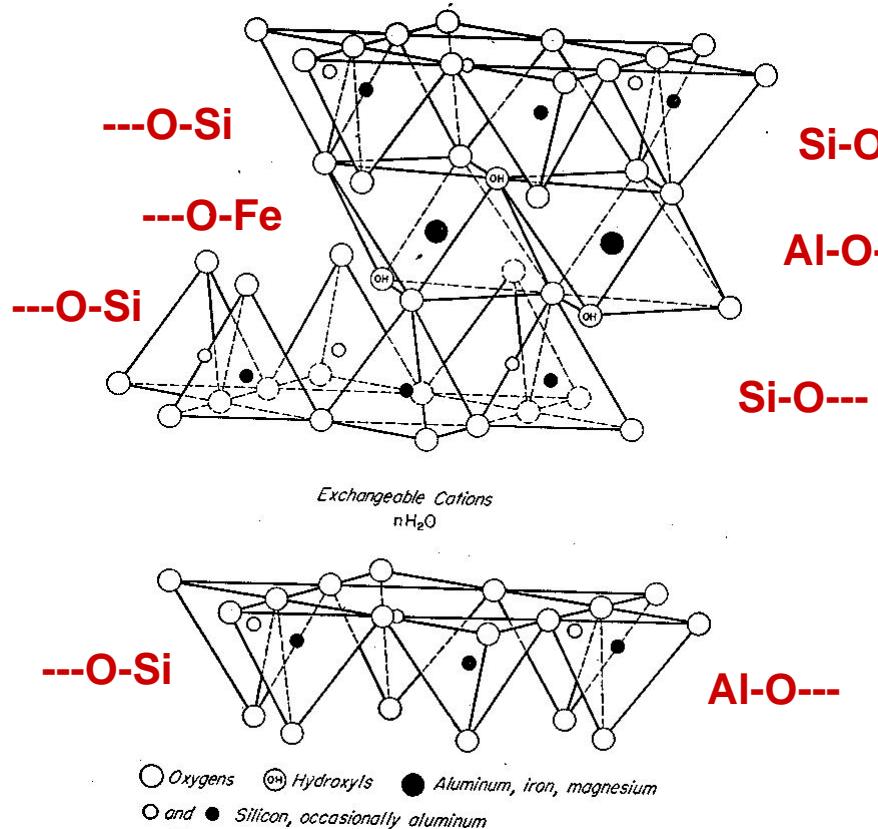
Cation exchange capacity of clay minerals

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- corresponds to the property to exchange cations from the surface of mineral by cations in solution
- is issued from the structural charge of mineral which is the sum of 2 types of charges:

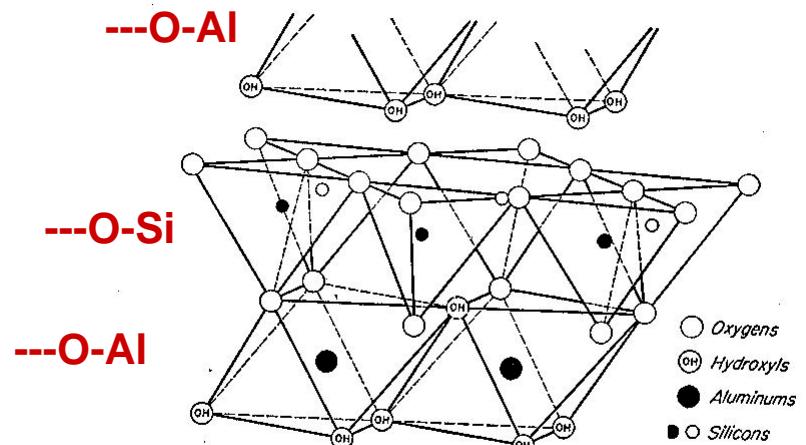
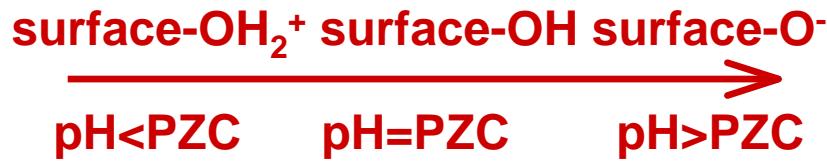
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 - pH-dependent charge by (de)protonation of species at edges

1:1 and 2:1 phyllosilicates – edge surface charge



2:1 structure
ex: smectite



1:1 structure
ex: kaolinite

edge charge:
pH- dependent « variable charge »

Cation exchange capacity of clay minerals

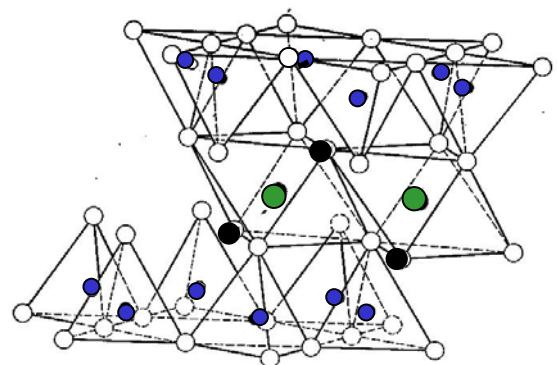
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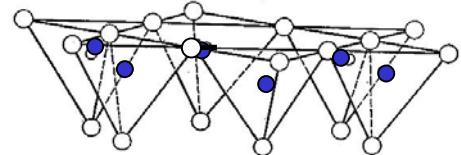
for smectites: CECperm>>CECvar

Smectite – permanent charge

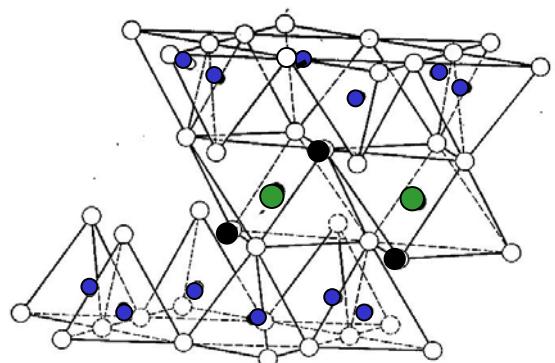


- (IV) : Si^{4+} , Al^{3+} , Fe^{3+} ,
- (VI) : Al^{3+} , Fe^{3+} , Mg^{2+} , Fe^{2+} , Li^+ , , ...
- OH
- O

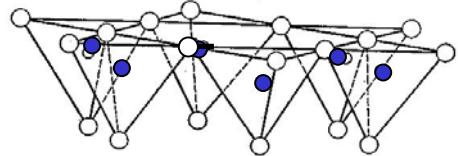
interlayer space



Smectite – permanent charge



interlayer space

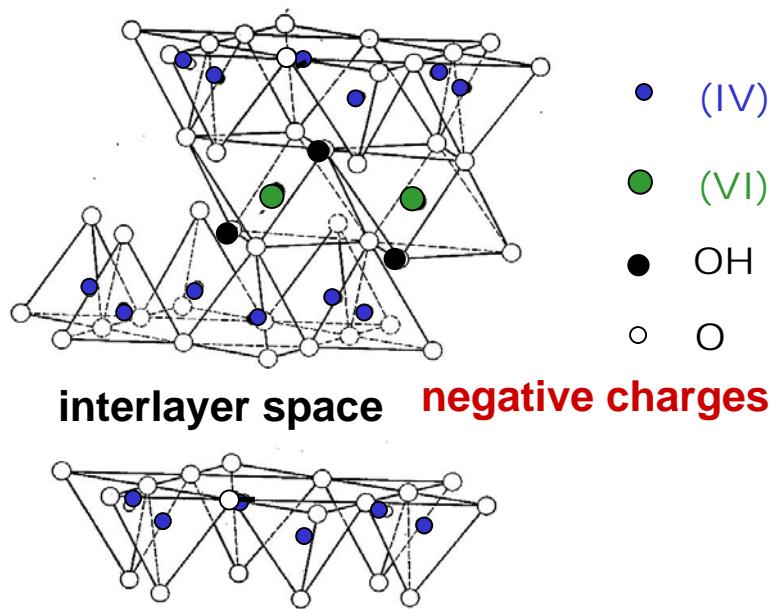


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Heterovalent substitution

- $\text{Si}^{4+} / \text{R}^{3+}$ $\text{R}^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}, \dots$
- $\text{R}^{3+} / \text{R}^{2+}$ $\text{R}^{2+} = \text{Mg}^{2+}, \text{Fe}^{2+}, \dots$
- $\text{R}^{2+} / \text{R}^+$ $\text{R}^+ = \text{Li}^+$
- $\text{R}^{2+} /$

Smectite – permanent charge

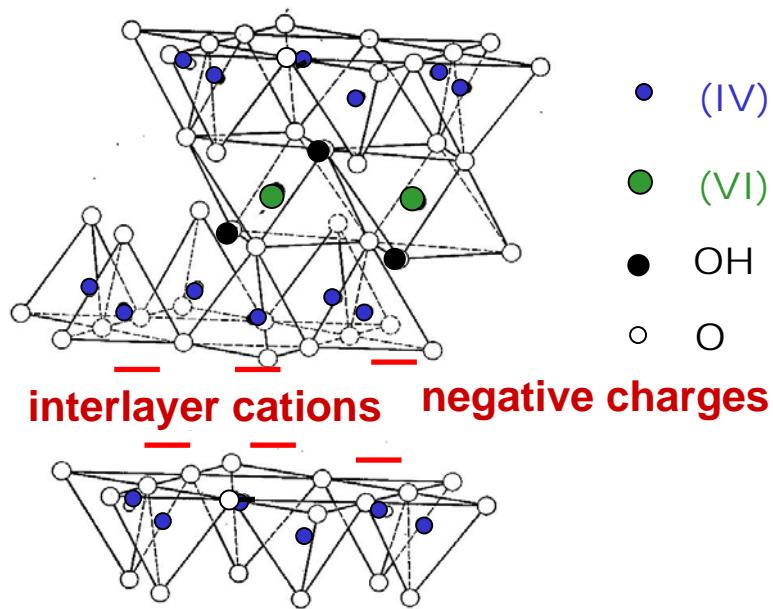


- (IV) : Si⁴⁺, Al³⁺, Fe³⁺,
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Heterovalent substitution

- Si⁴⁺ / R³⁺ R³⁺ = Al³⁺, Fe³⁺, ...
- R³⁺ / R²⁺ R²⁺ = Mg²⁺, Fe²⁺, ...
- R²⁺ / R⁺ R⁺ = Li⁺
- R²⁺ /

Smectite – permanent charge

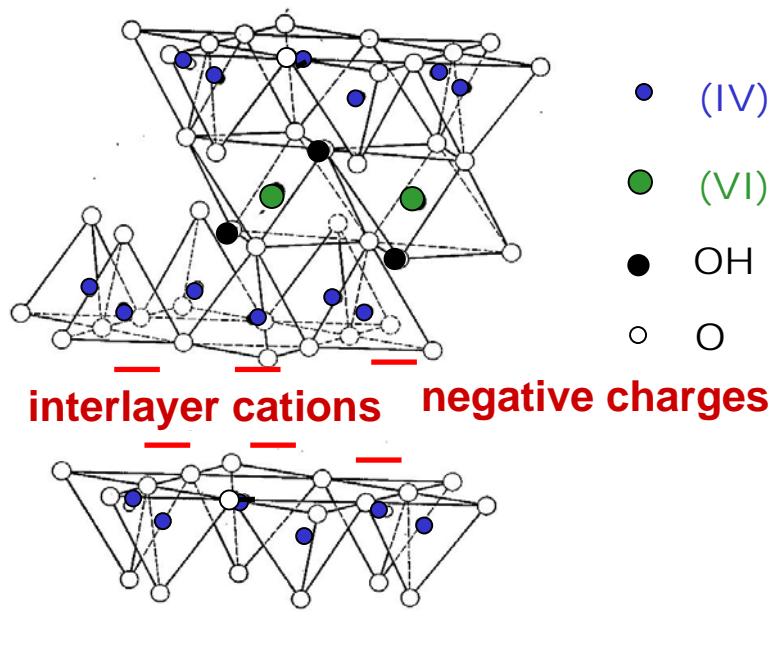


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- R²⁺ /**

Smectite – permanent charge



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|------------------------------------|---|
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| R ²⁺ / | |

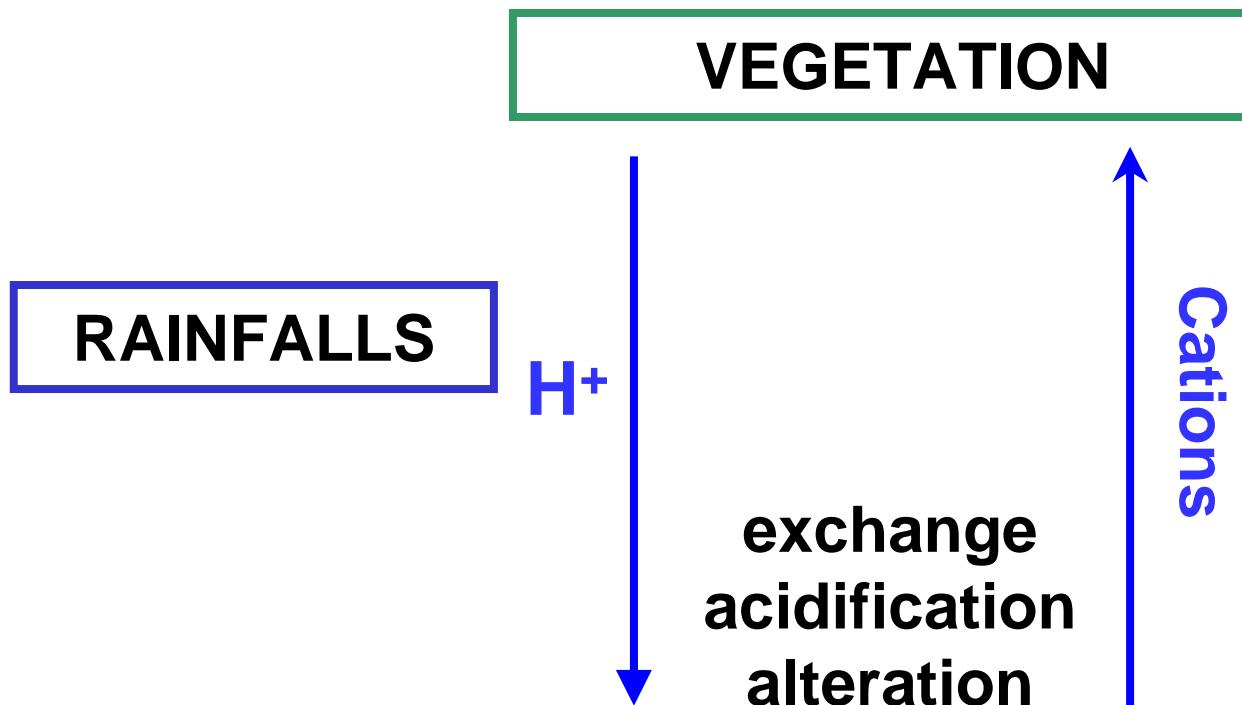


Tetrahedral charge per half unit cell = - x

Octahedral charge per half unit cell = (3a + 2b + c) - 6 = - y

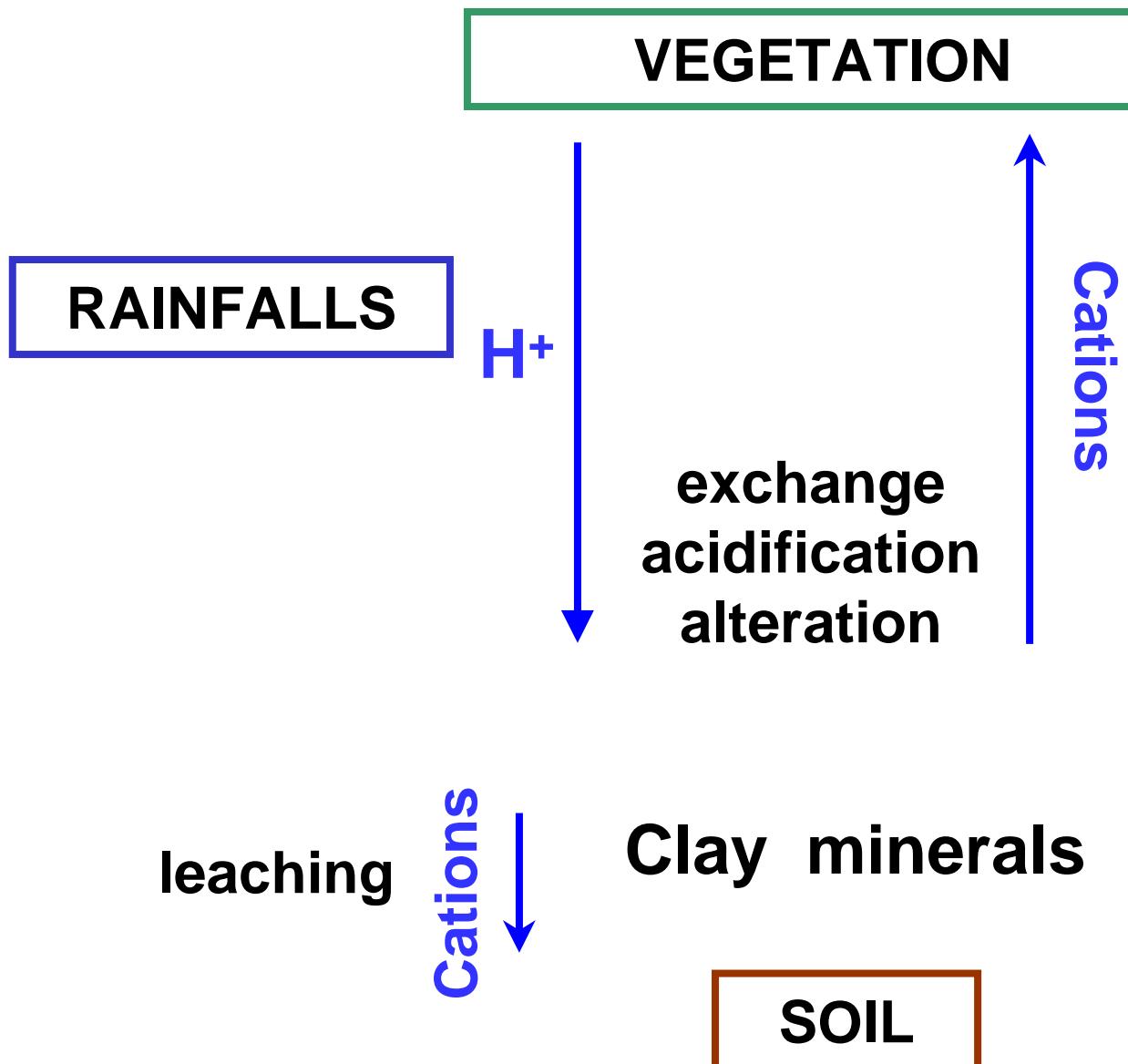
Permanent charge per half unit cell = z = x + y

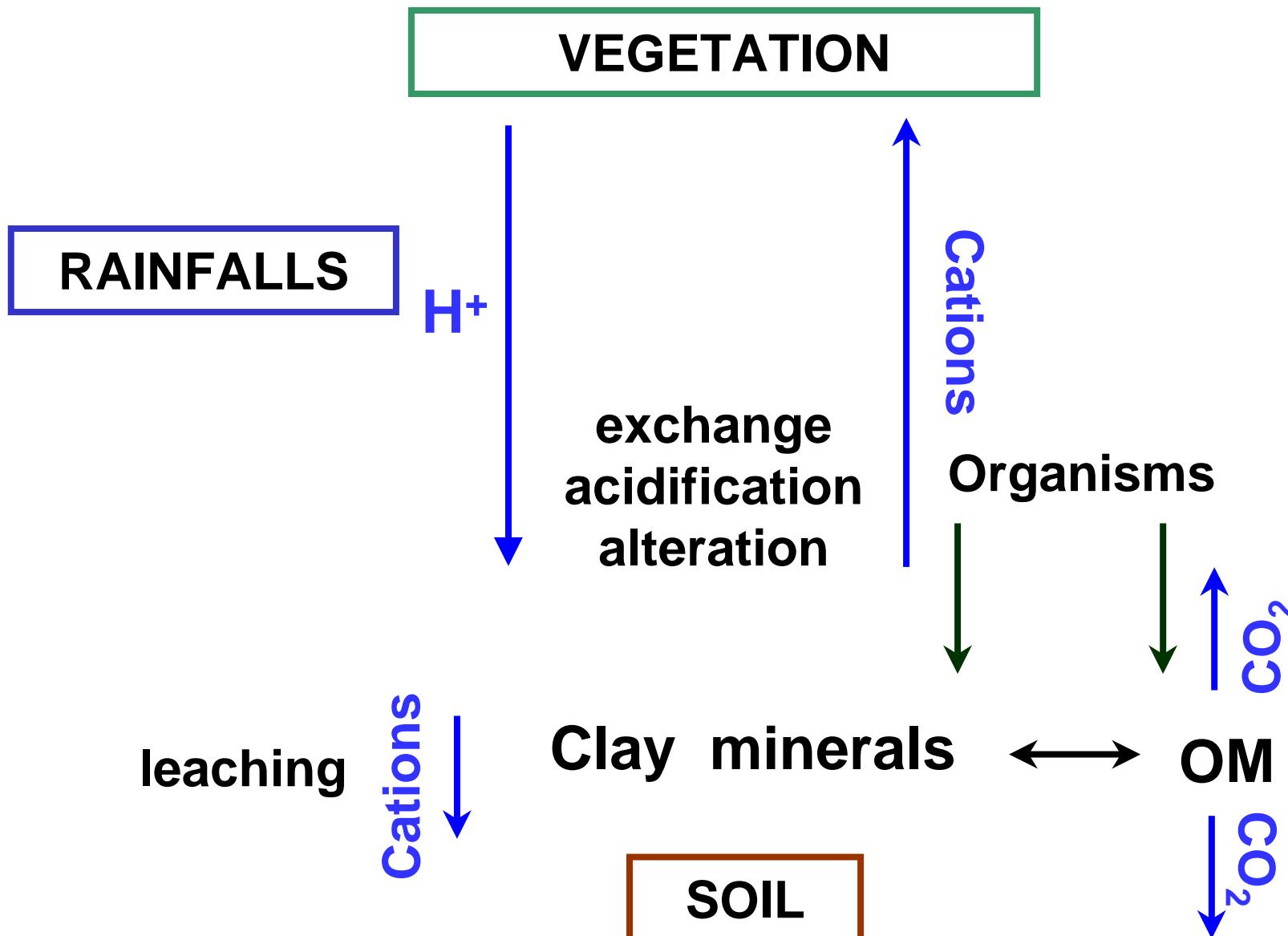
$$(a + b + c + d = 3)$$



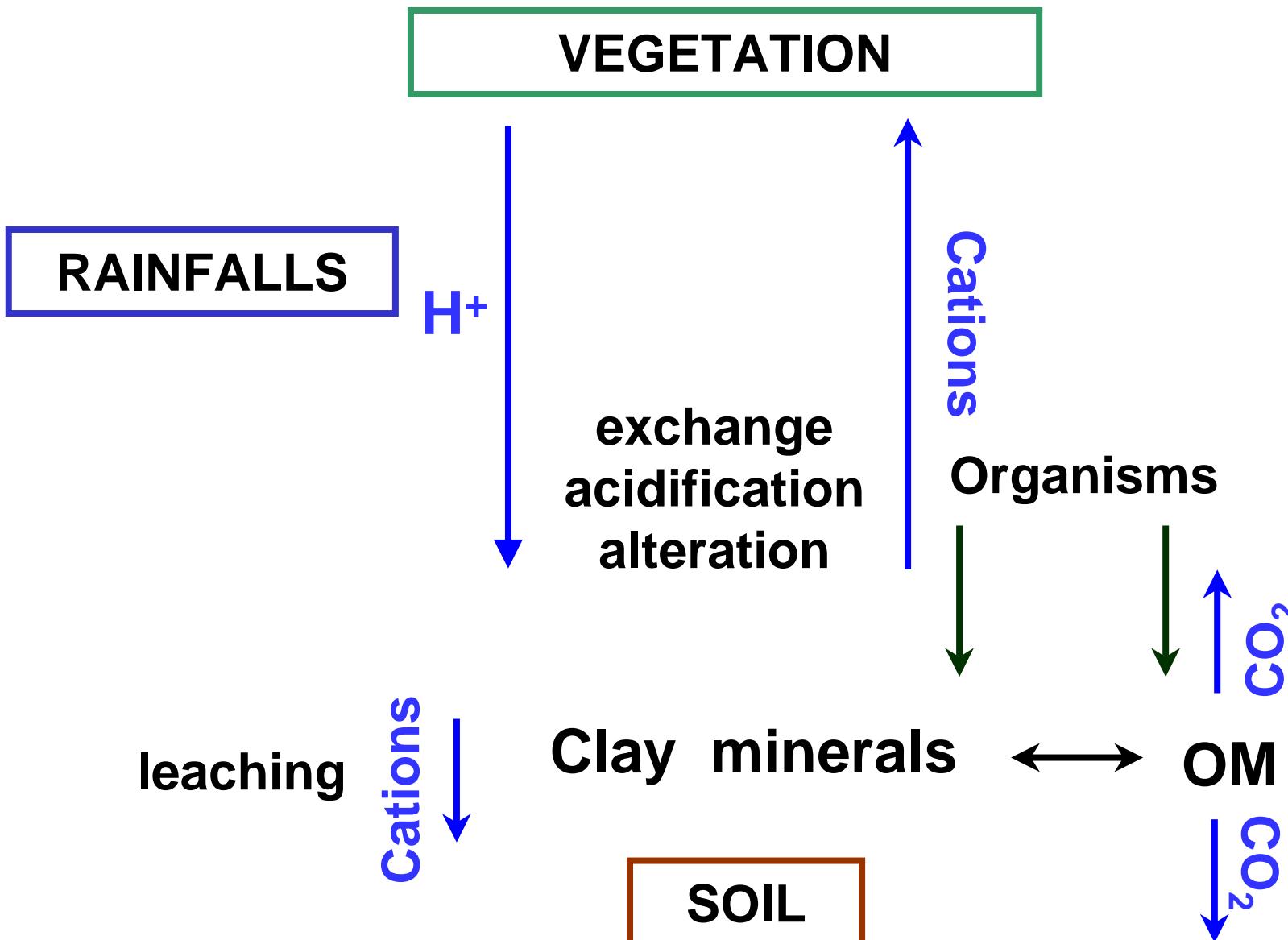
Clay minerals

SOIL

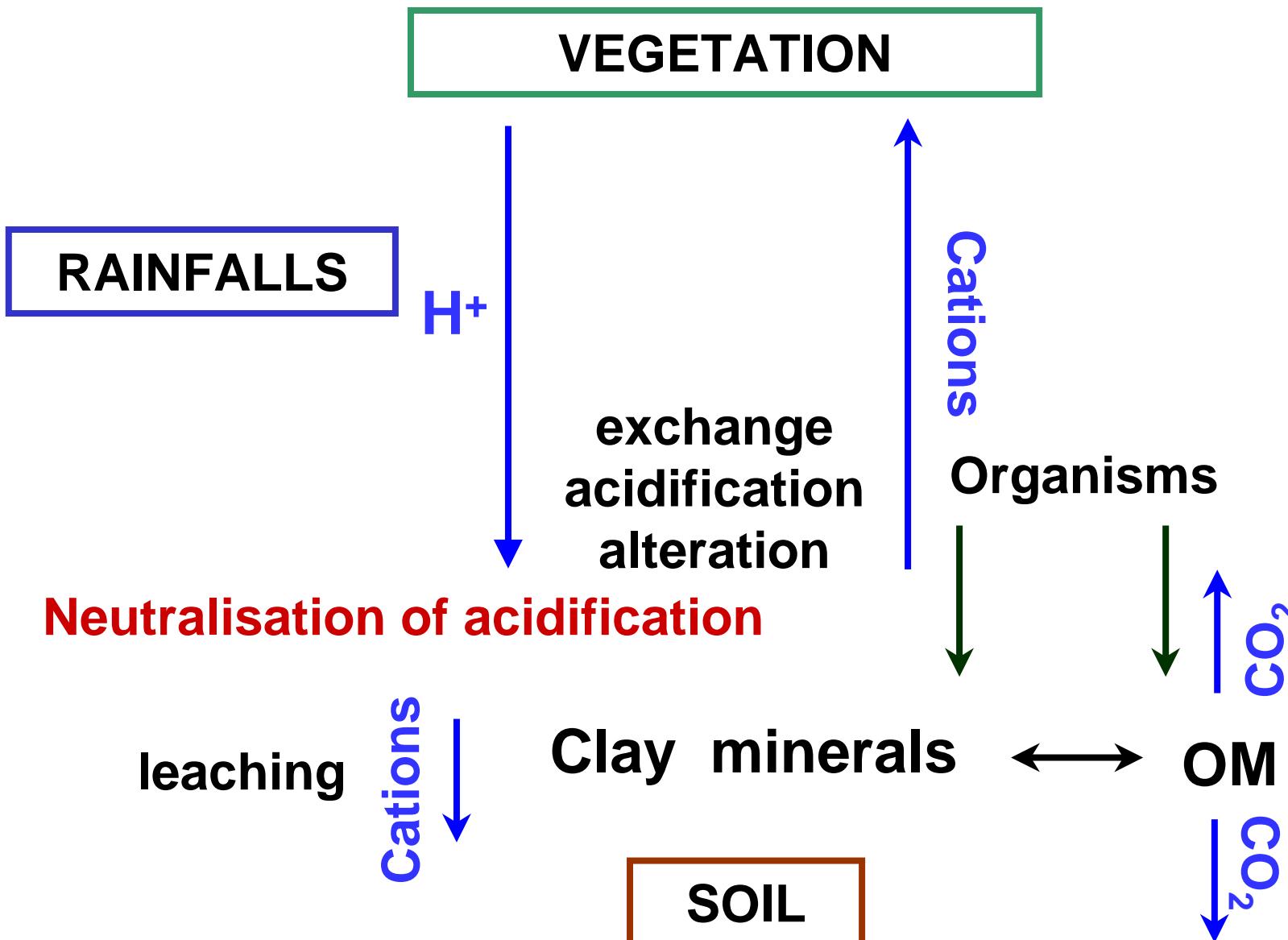




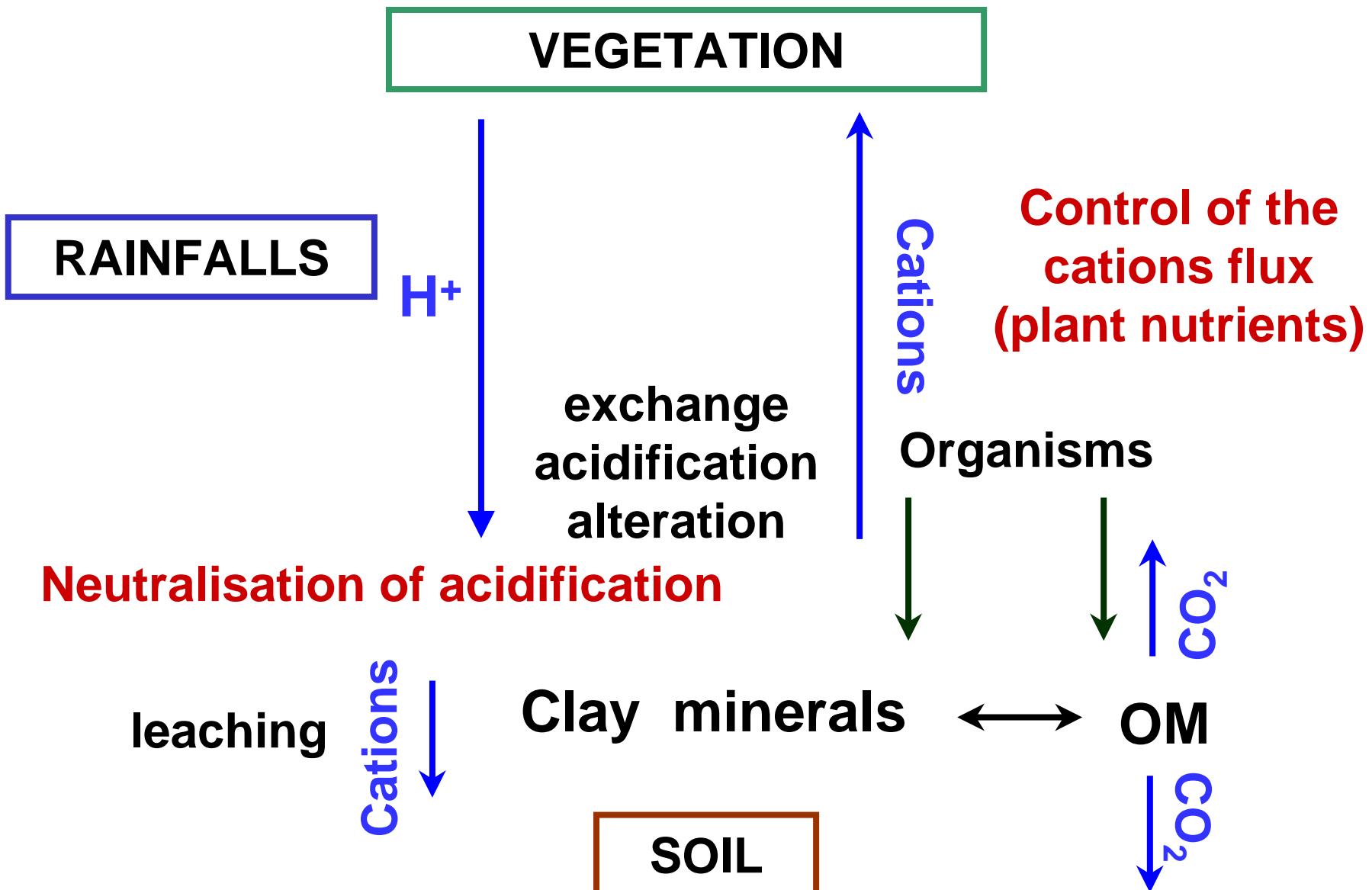
Role of clay minerals in soil



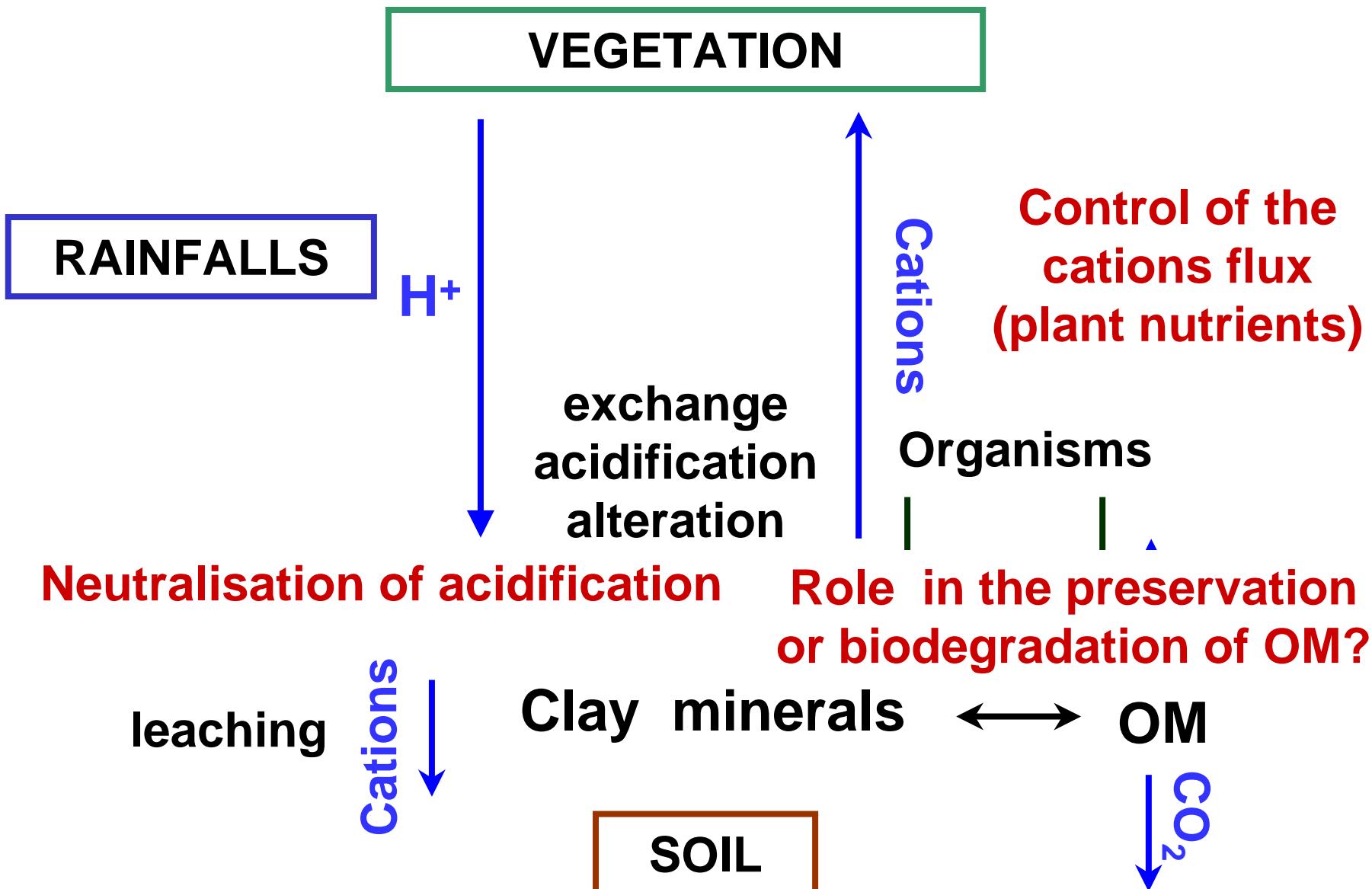
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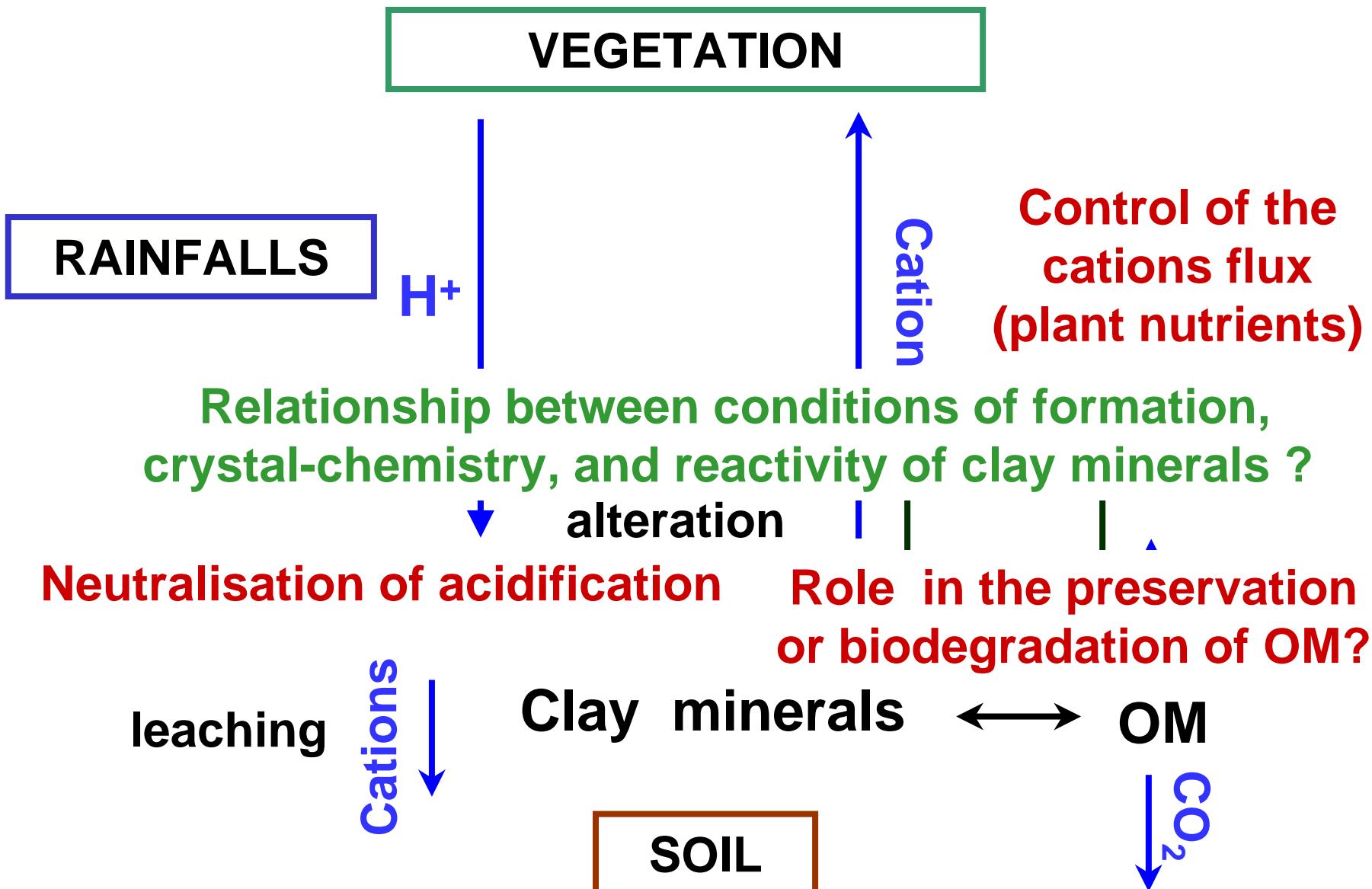
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Role of clay minerals in soil



Role of clay minerals in soil



Relationship between conditions of formation, crystal-chemistry, and reactivity of clay minerals

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- Study the natural soil system:
 - complex and the process is not necessarily understood

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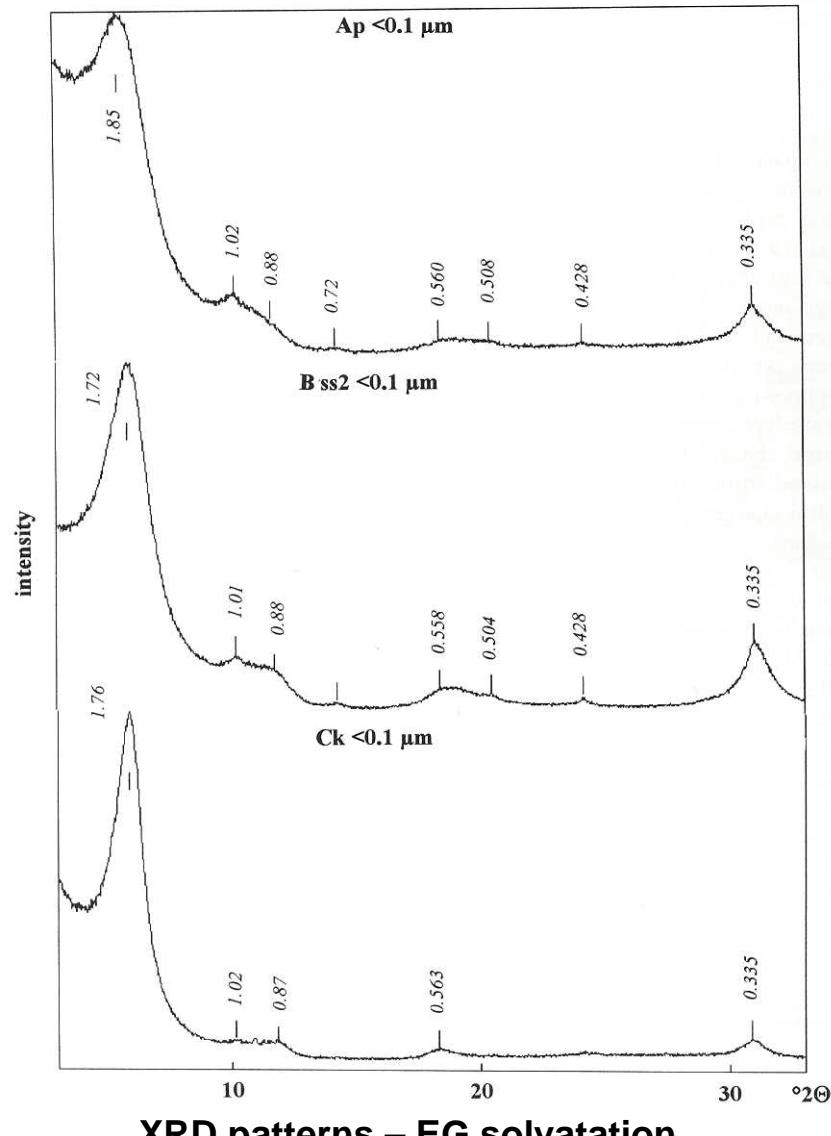
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 - minerals alteration mimicking natural weathering
 - clay syntheses to better determine the link between conditions of formation of clay minerals and their crystal – chemistry and physico-chemical properties

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Example : Vertisol of Suelli, Sardinia (Italy)

Righi et al. Clays & Clay Minerals, 167-177, 1998



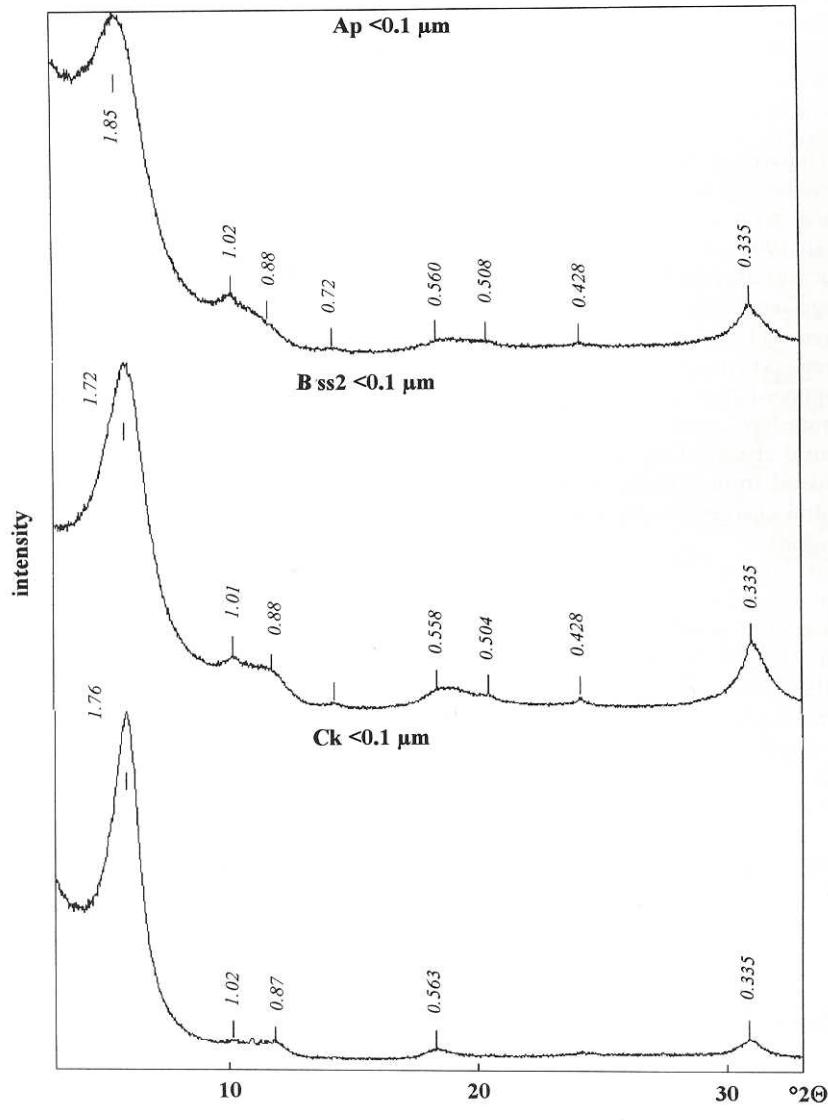
<0.1 μm fraction

Sample	CEC	var.	perm.	IV acces.	VI acces.
Ap	71	18	53	33	20
Bss2	70	18	52	34	18
Ck	68	16	52	24	29

(cmol /kg)

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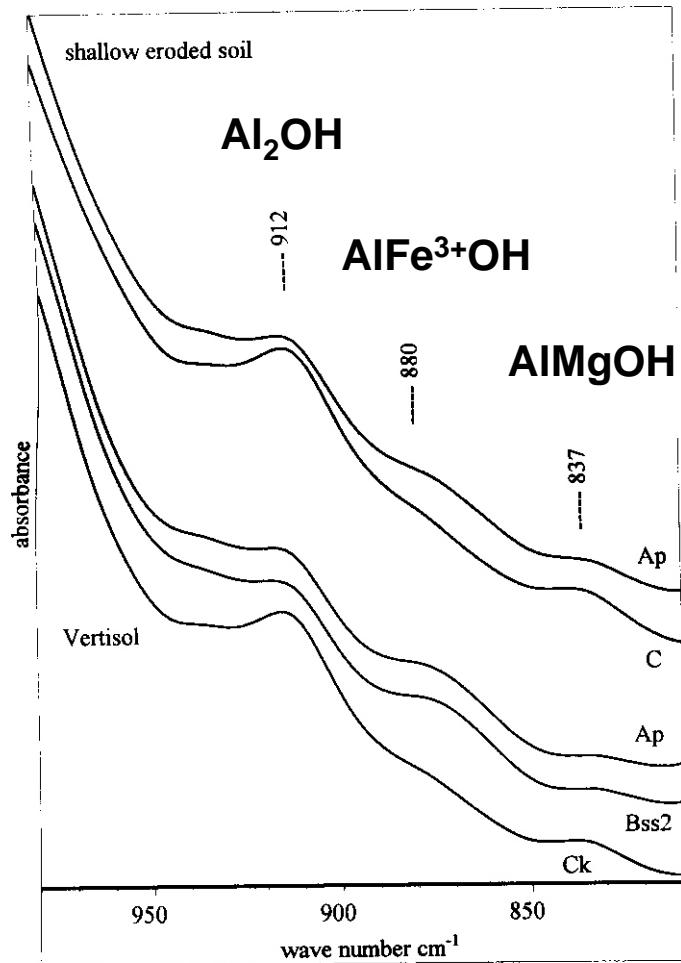
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XRD patterns – EG solvation

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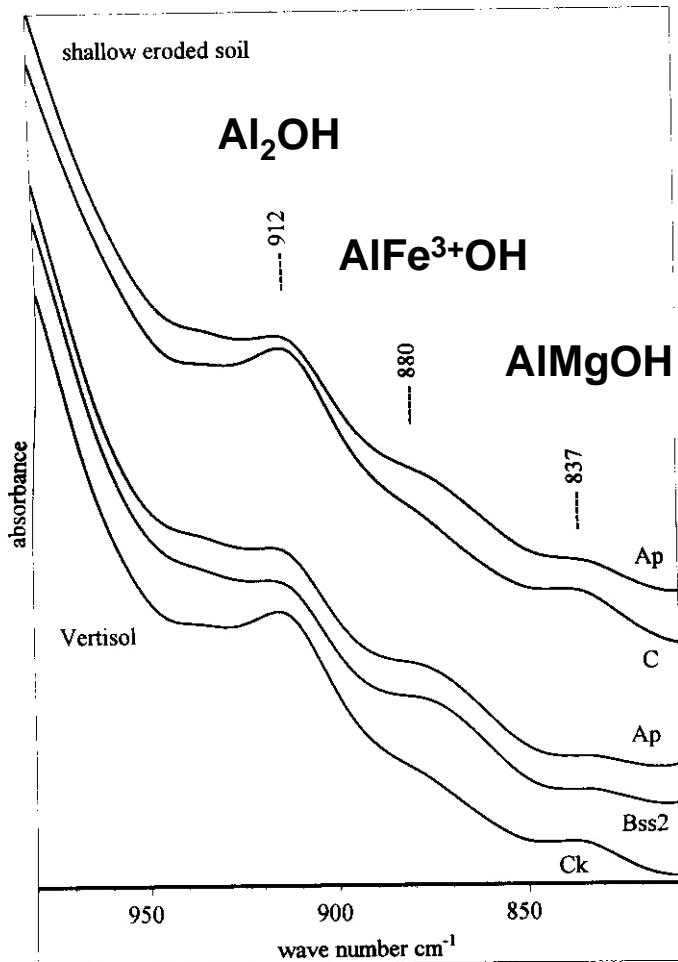
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FTIR spectra for the Vertisol and shallow eroded soil fine clay ($<0.1 \mu\text{m}$) fractions.

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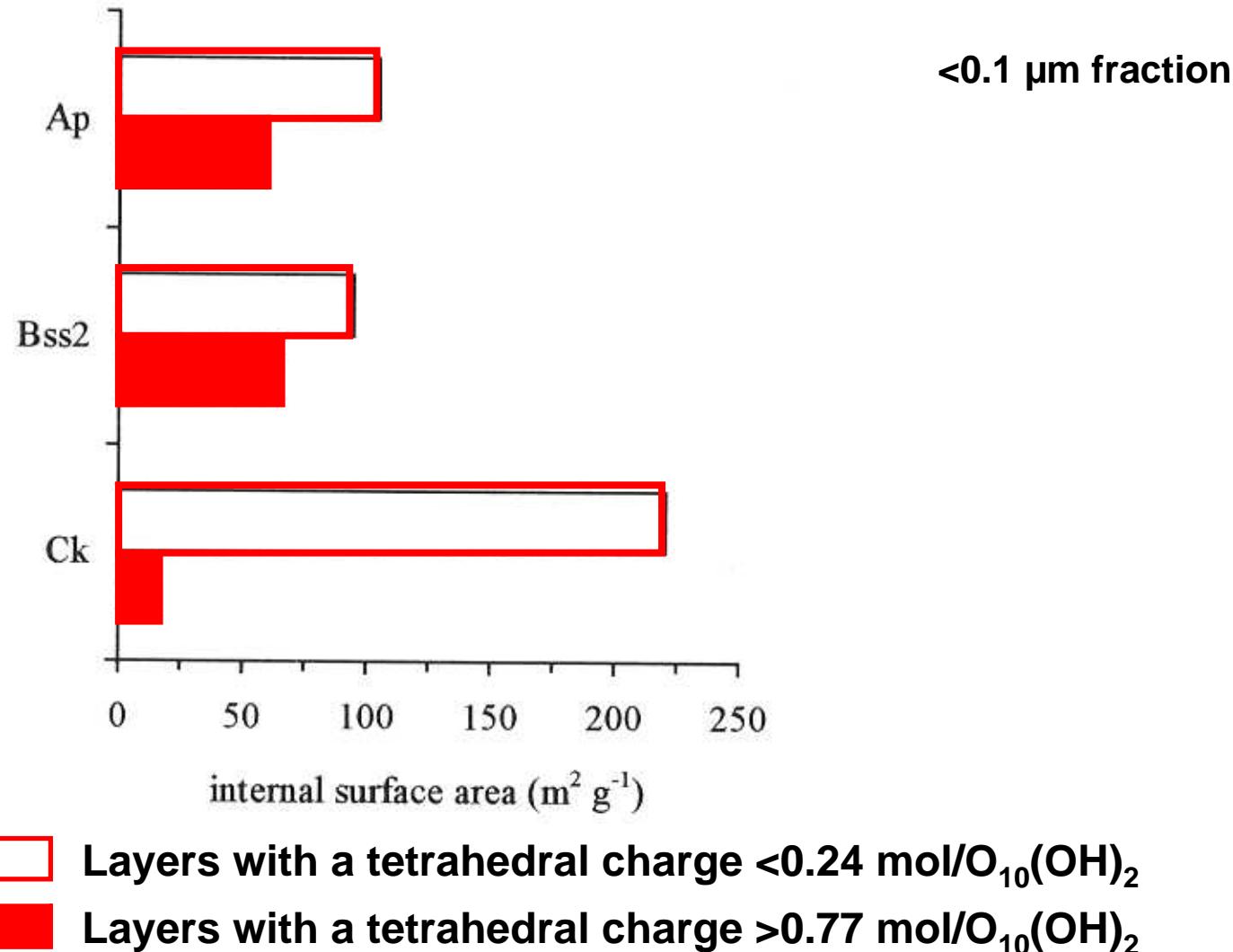
Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	... LOI
Ap	51.2	18.4	9.8	2.5	2.9	... 13.4
Bss2	51.4	18.0	9.6	2.6	2.8	... 13.6
Ck	50.9	18.8	8.8	3.2	2.4	... 14.3

(cmol /kg)

FTIR spectra for the Vertisol and shallow eroded soil fine clay (<0.1 μm) fractions.

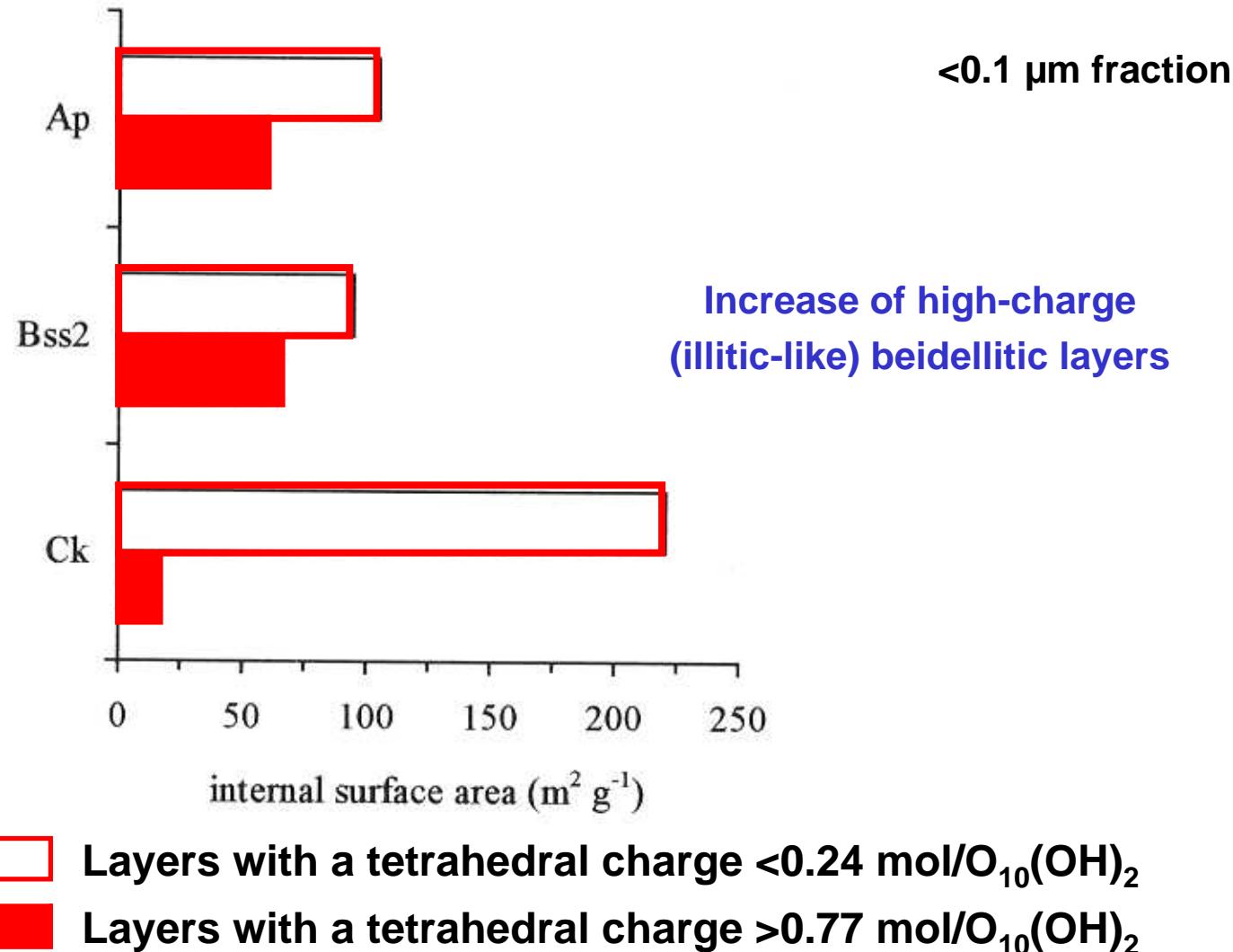
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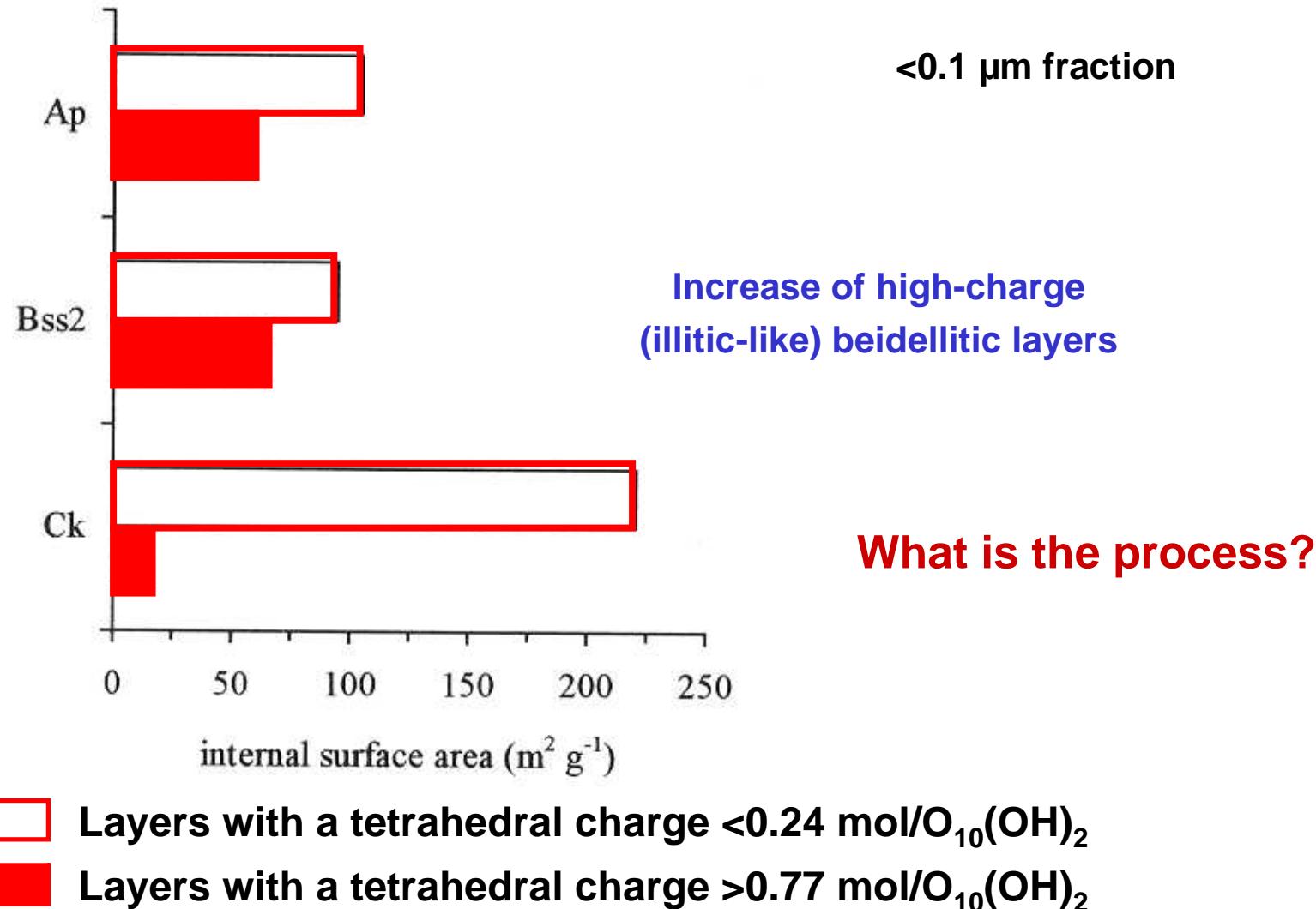
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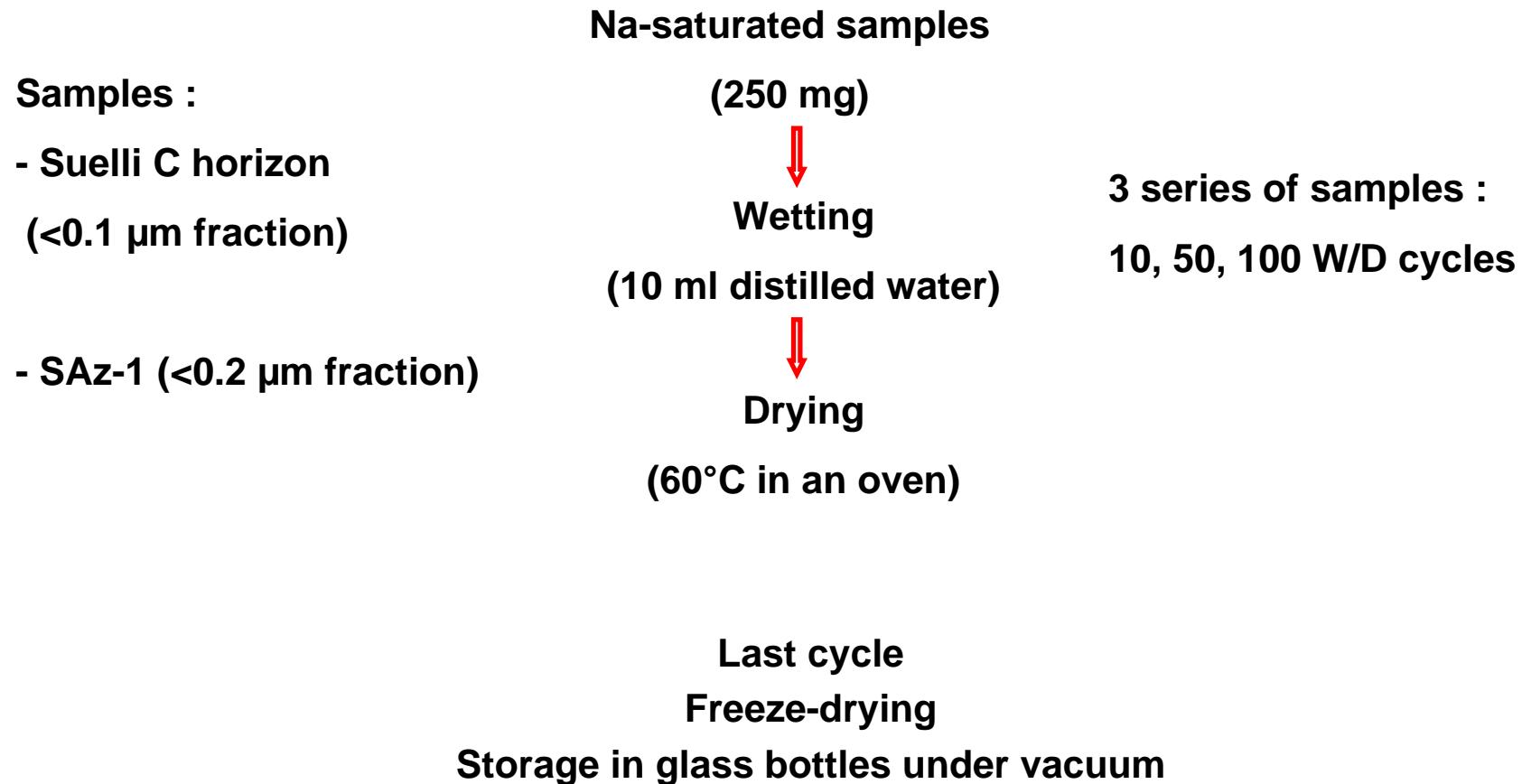
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Experimental alteration of smectites

Ramirez et al. *Clays Minerals*, 15-24, 2005



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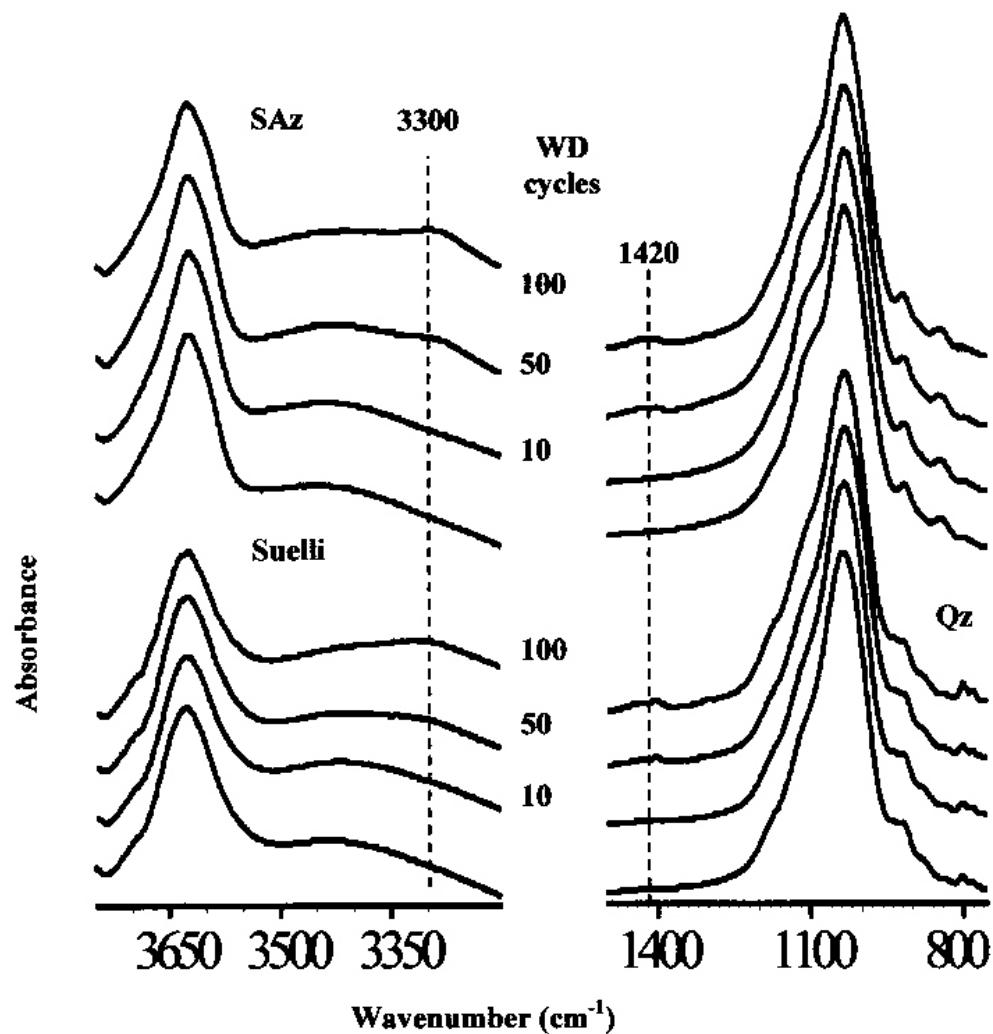


FIG. 6. IR spectra of the samples SAz and Suelli, initial stage and after 10, 50 and 100 WD cycles. Qz: quartz.
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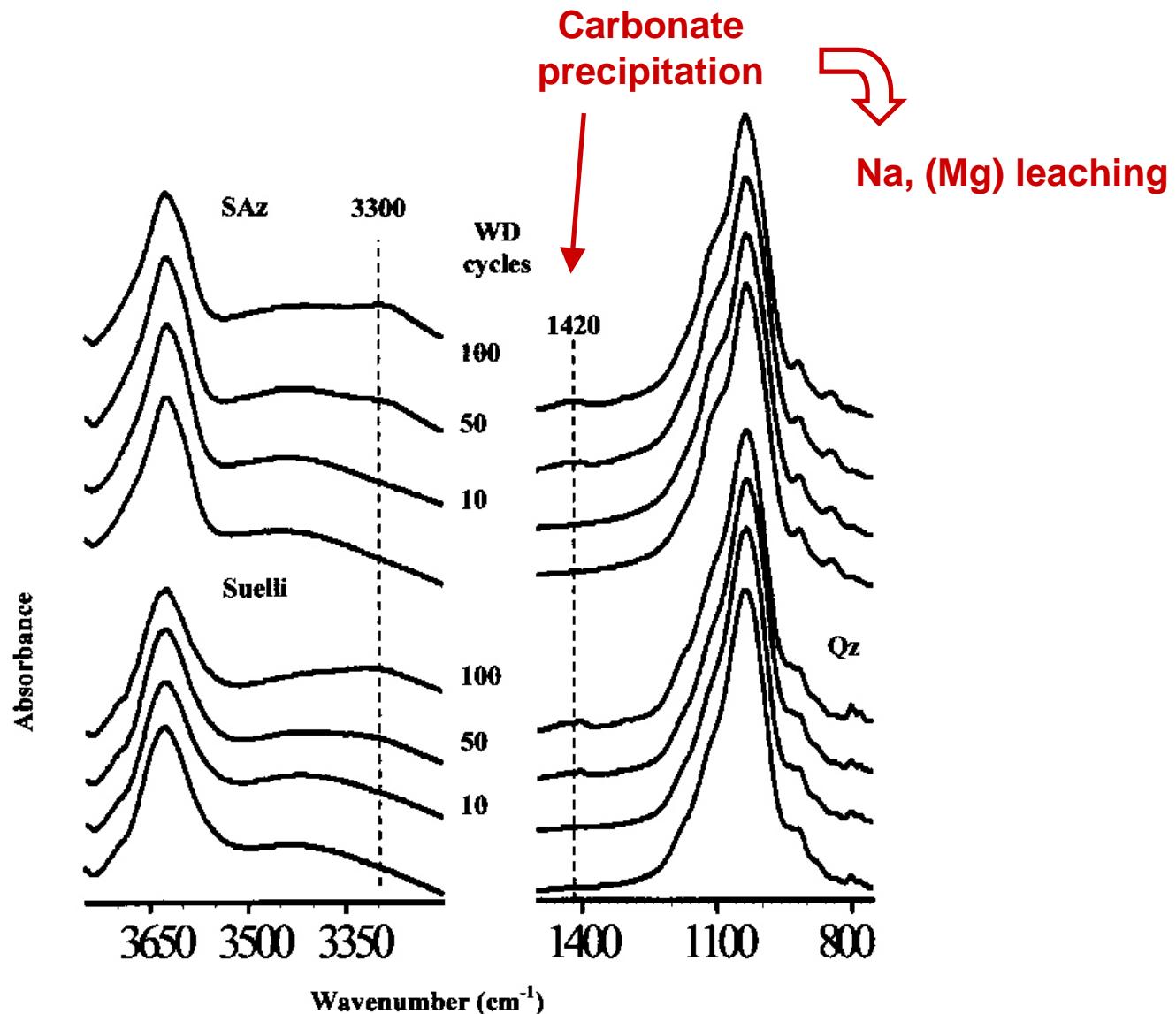


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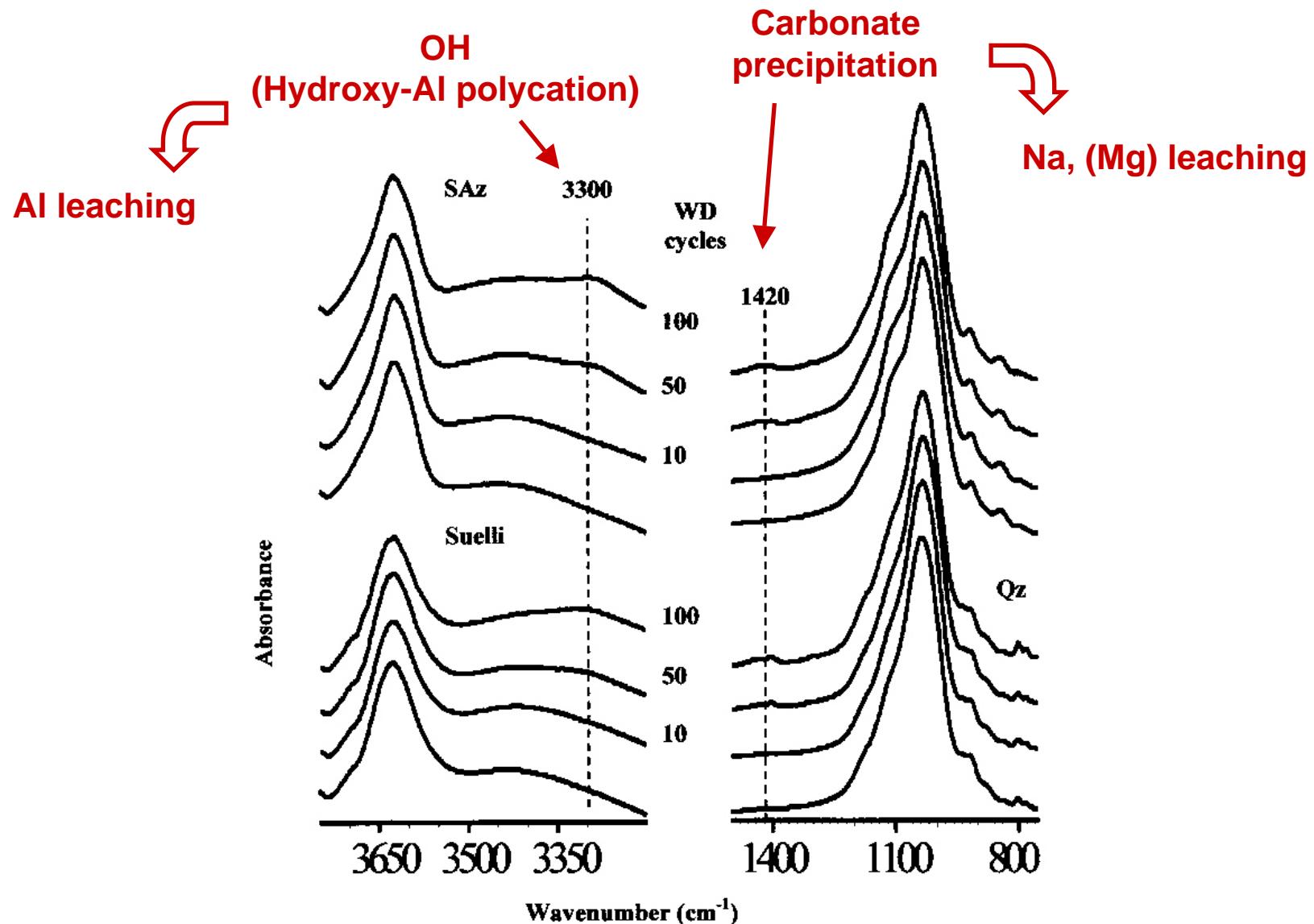


FIG. 6. IR spectra of the samples SAz and Suelli, initial stage and after 10, 50 and 100 WD cycles. Qz: quartz.
« Colloque Mineralogie environnementale - Académie des sciences - 14-15 septembre 2009 »

Experimental alteration of smectites

Ramirez et al. *Clays Minerals*, 15-24, 2005

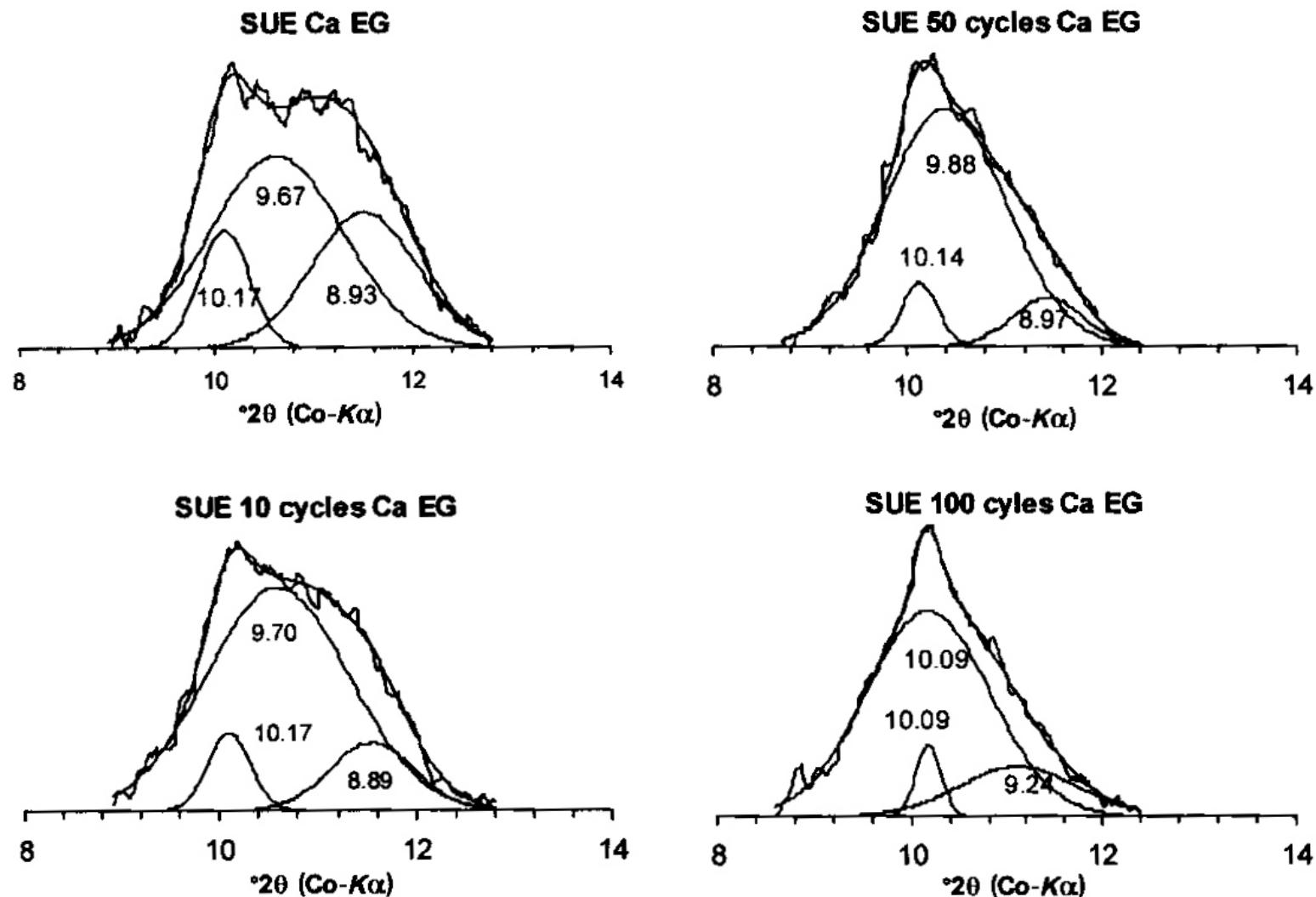


FIG. 2. Decomposition of the XRD pattern of Suelli (SUE) samples (Ca-saturated and ethylene glycol solvated) in « Colloque Minéralogie environnementale - Académie des sciences - 14-15 septembre 2009 »

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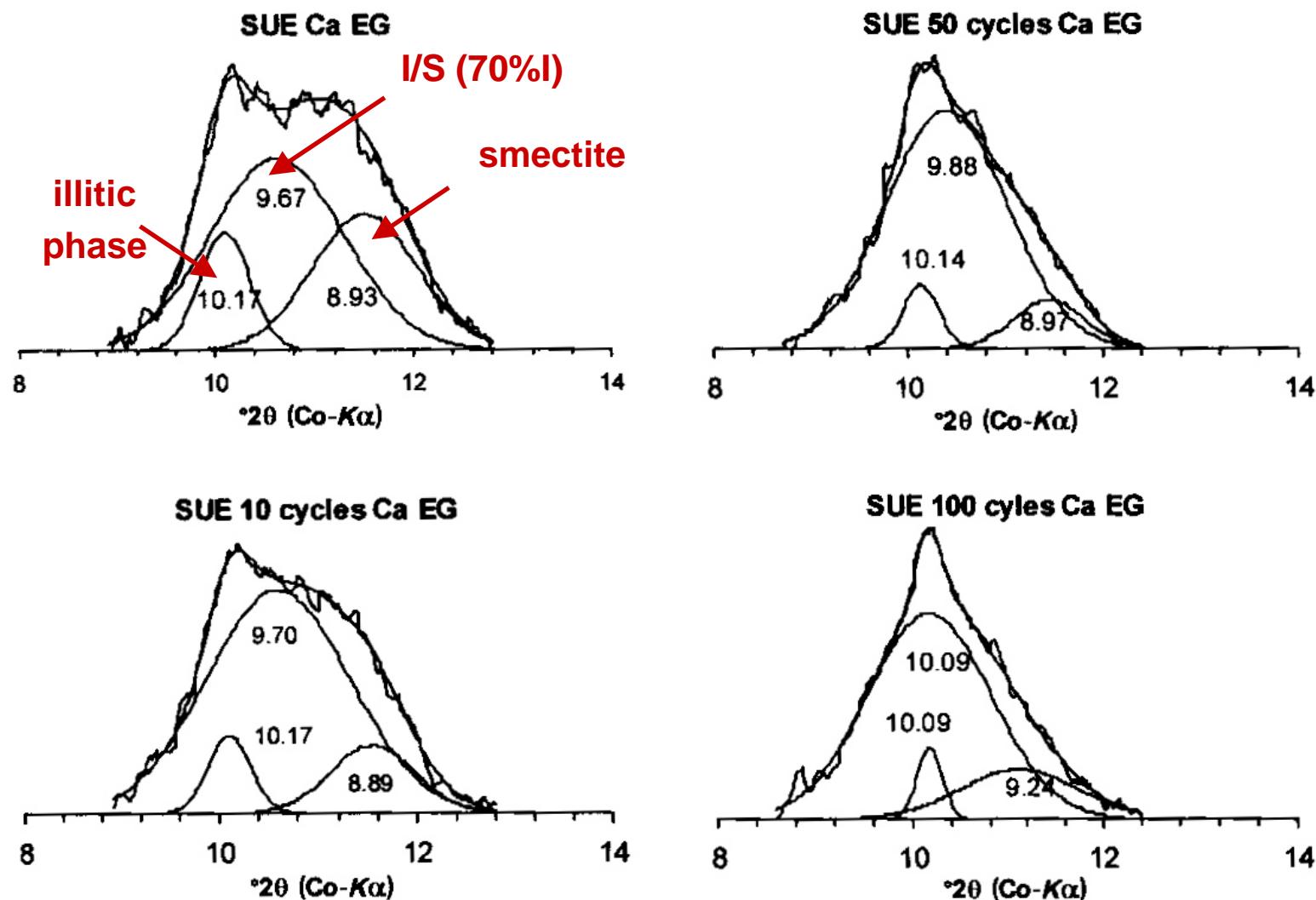


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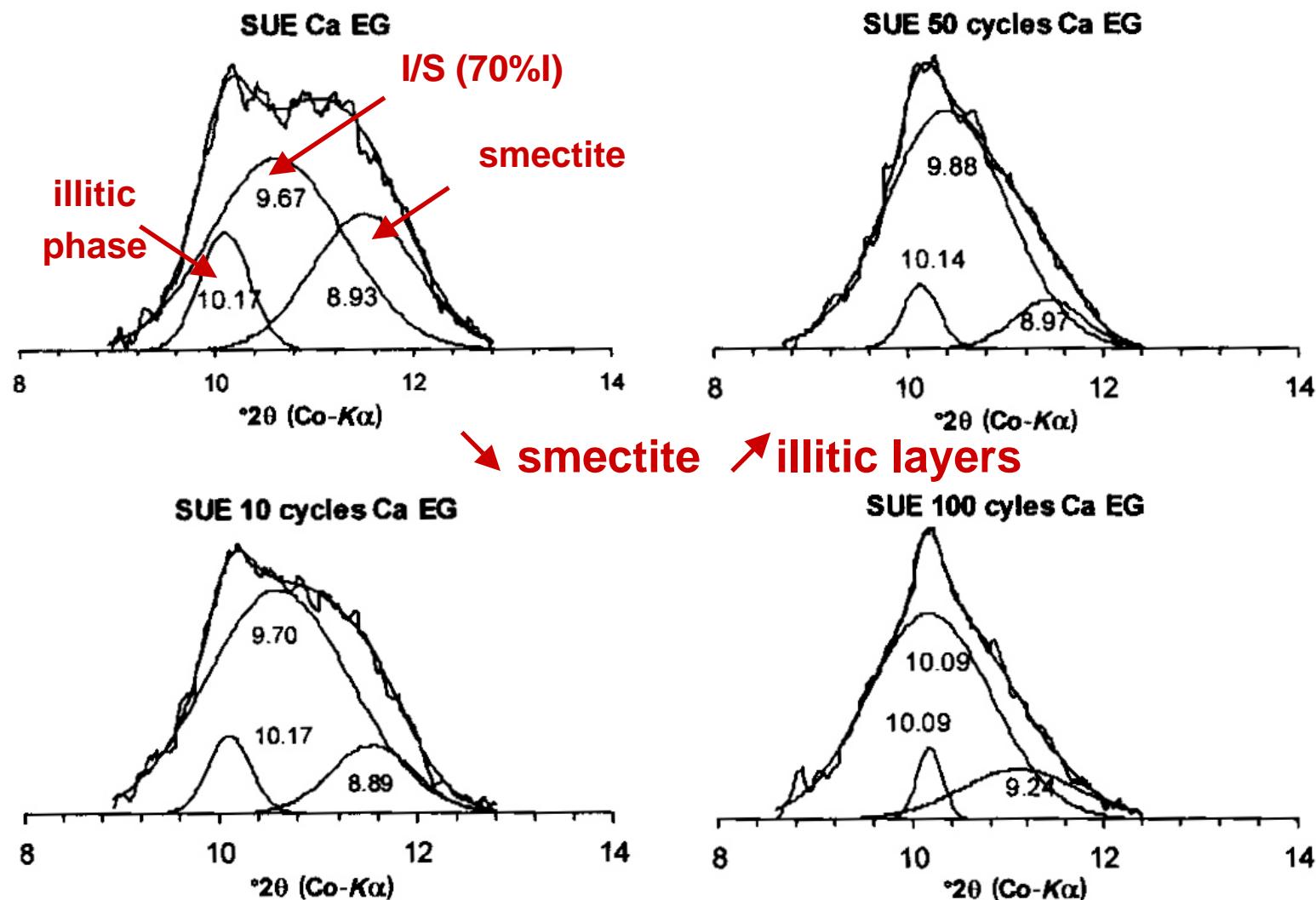


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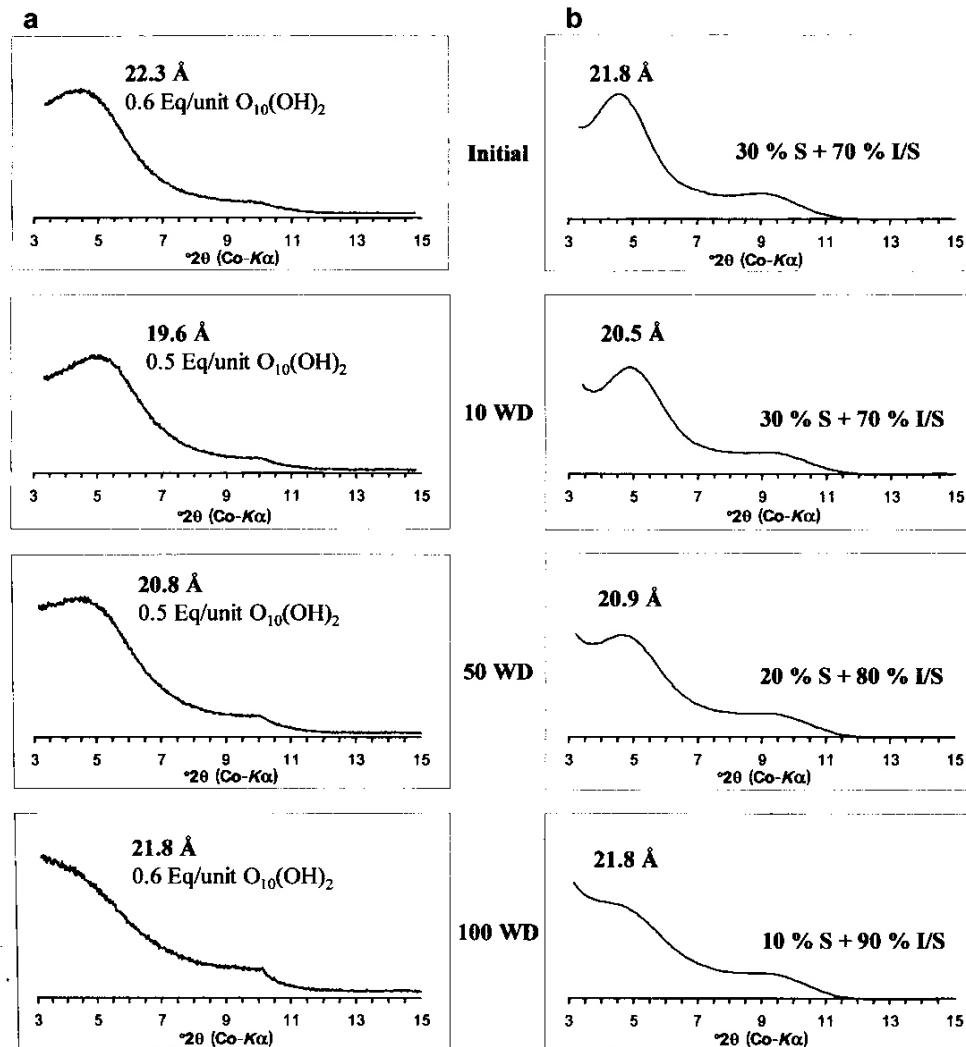


FIG. 4. Experimental (a) and simulated (b) XRD pattern of Suelli samples after intercalation with the alkylammonium cation ($nC = 12$). S: smectite pure phase. I-S: mixed-layer smectite-illite.

Experimental alteration of smectites

Ramirez et al. Clays Minerals, 15-24, 2005

W/D cycles	Accessible permanent charge (cmol/kg)	BET surface area (m ² /g)
0	48	178
10	43	194
50	41	181
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Apparent mineralogical change : Acidic decomposition of the structure in part (preferentially « low charge » montmorillonitic layers) and relative increase of illitic (beidellite) layers

Relationship between conditions of formation, crystal-chemistry, and reactivity of clay minerals

- Study the natural soil system:
 - complex and the process is not necessarily understood
- Experimental studies - laboratory experiments
 - minerals alteration mimicking natural weathering
 - clay syntheses to better determine the link between conditions of formation of clay minerals and their crystal – chemistry and physico-chemical properties

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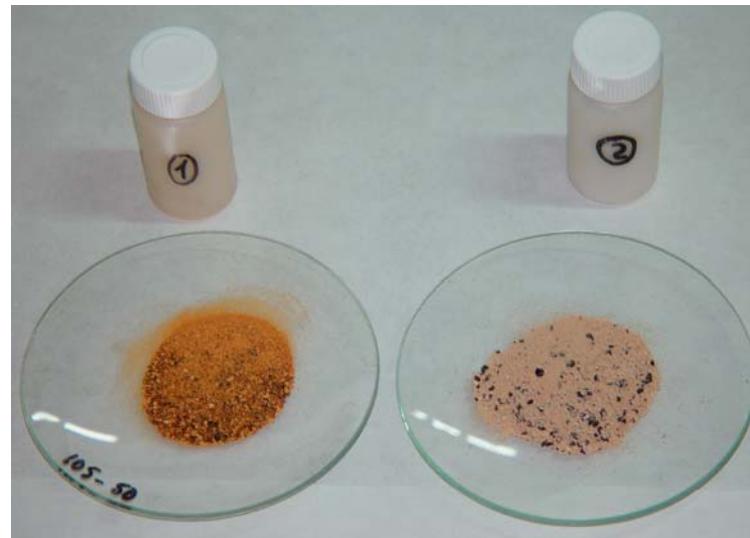
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Clay synthesis

The starting material

Requirements:

- minimize the variables of the system**
- reproducibility**
- homogeneous and definite chemical composition**

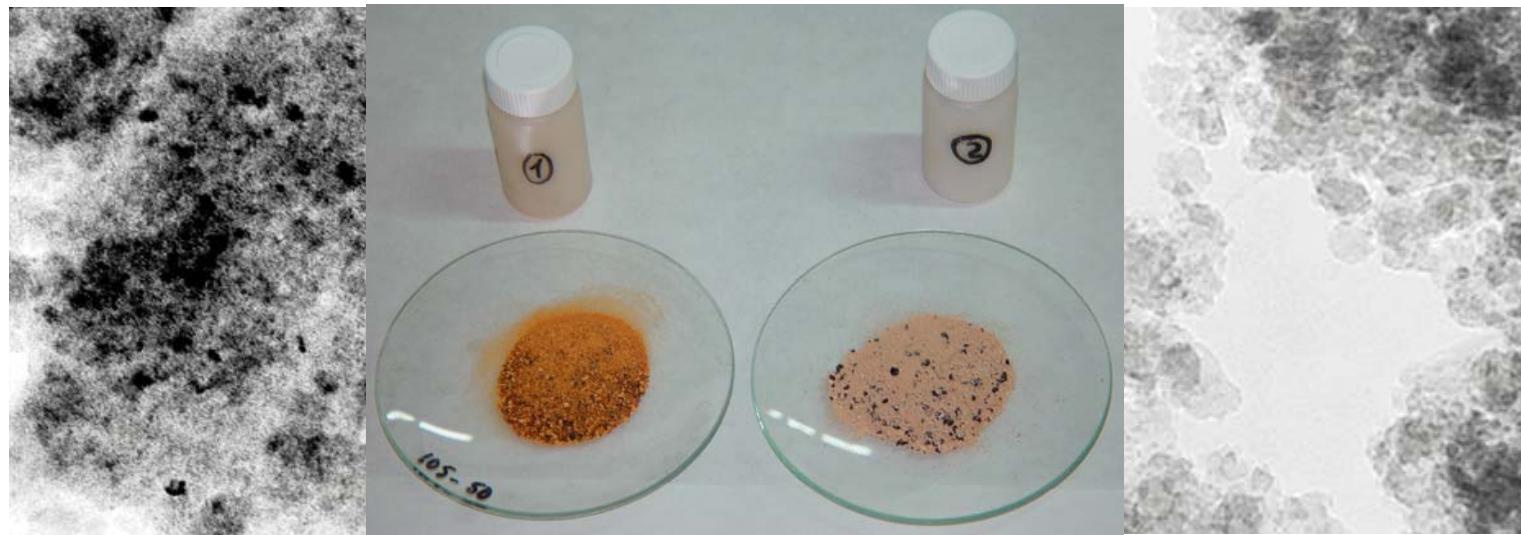


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- reproducibility
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**Use an amorphous gel with the clay stoichiometry :
Decarreau (1983) 's protocol**



Clay synthesis Protocol



Basis reaction :

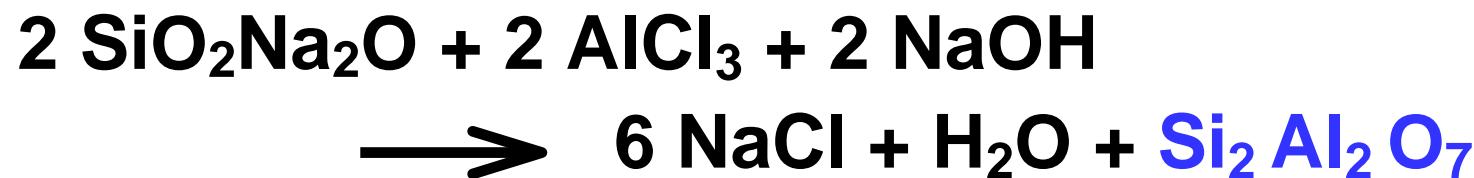
Gel coprecipitation

silica source: $\text{SiO}_2\text{Na}_2\text{O}$

metal source: salt (chlorides, nitrates, sulfates)

equilibrated agent: HCl, NaOH,

Ex: kaolinite $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$



Clay synthesis Protocol

The coprecipitate is:

- centrifuged and washed**
- dried and crushed**
- (or freeze dried)**



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The starting material is ready to use.



Clay synthesis Temperature and ageing time

Aim : Reproduce in laboratory clay formation

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Problem: we cannot use geological times !

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Rayner [1962] calculated a half-reaction time of $16 \cdot 10^4$ years at 20°C from kaolinite syntheses performed at several temperatures (180 - 300°C).

Clay synthesis Temperature and ageing time

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Problem: we cannot use geological times !

Rayner [1962] calculated a half-reaction time of $16 \cdot 10^4$ years at 20°C from kaolinite syntheses performed at several temperatures ($180 - 300^\circ\text{C}$).

The rate constant of an heterogeneous chemical reaction in aqueous phase is given by :



$$k = A \cdot \exp - (\Delta E / RT)$$

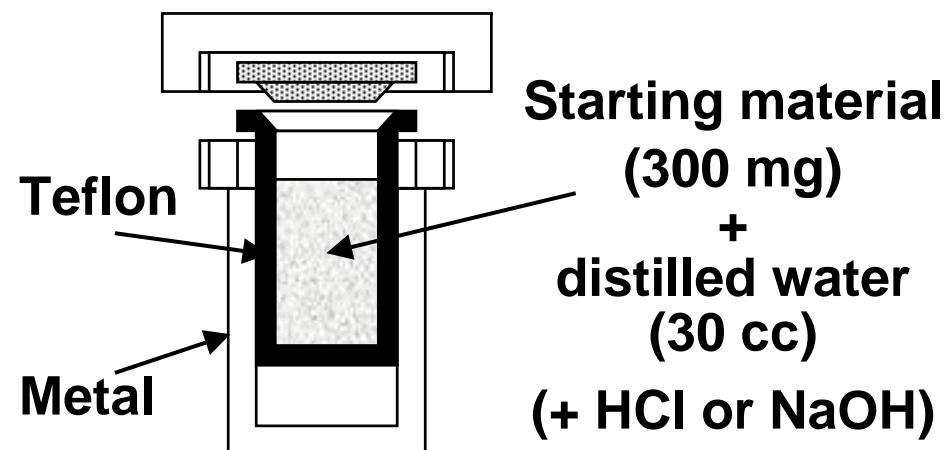
Ageing time of clay synthesis can be minimized by an increase of T.

Clay synthesis Experimental conditions

From ambient to 100°C : PFA reactors
(copolymer of ethylene tetrafluor)

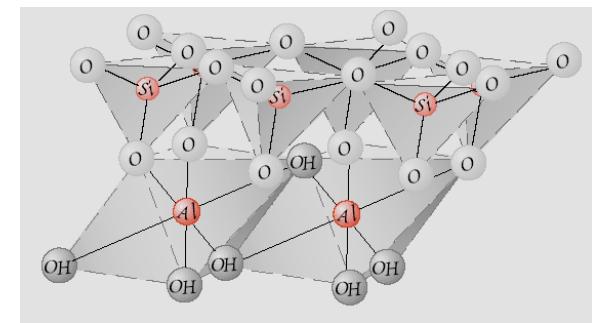
From 100 to 240°C : bombs with metal bodies
and removable Teflon liners

From 240 to 300°C : bombs in titanium

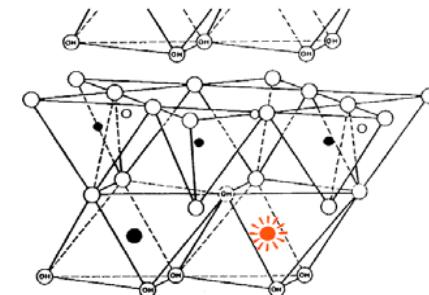


Clay synthesis Kaolinite

Influence of conditions of formation



Al-Fe³⁺ substitutions



Kaolinite Syntheses

Influence of experimental conditions

Kaolinite were synthesized under these conditions :

- Temperatures and Pressures :

150 - 300 °C (equilibrium water pressure)

200 - 400 °C P = 1.5 to 3 kbar

- ageing time : 2 days to 6 months

- pH_{ini} 1 to 13 (pH_{fin} 1 to 8)

- from gel*, glass, poorly crystallized kaolinite, metakaolin*****

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** Fialips et al. (2000) *Clays & Clay Min.*, 48, 173-184.

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Fialips (1999) PhD Thesis.

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Crucial role of pH in kaolinite characteristics

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Kaolinite Syntheses

Influence of experimental conditions

Coprecipitated gel



220°C (23 bar) - 14 days

spontaneous pH: 5

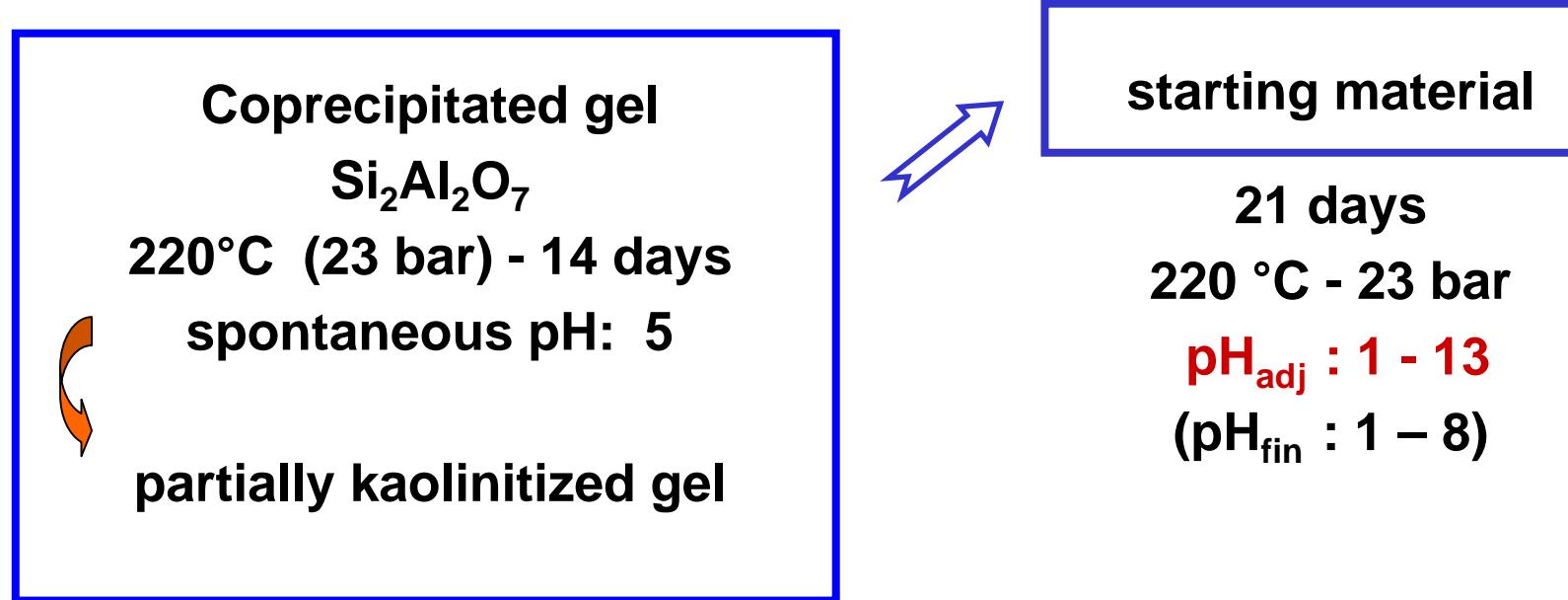


partially kaolinitized gel

Fialips et al. (2000) *Clays & Clay Min.*, 48, 173-184.

Kaolinite Syntheses

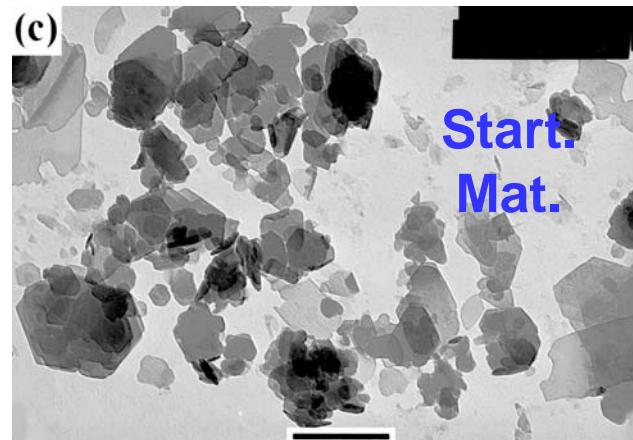
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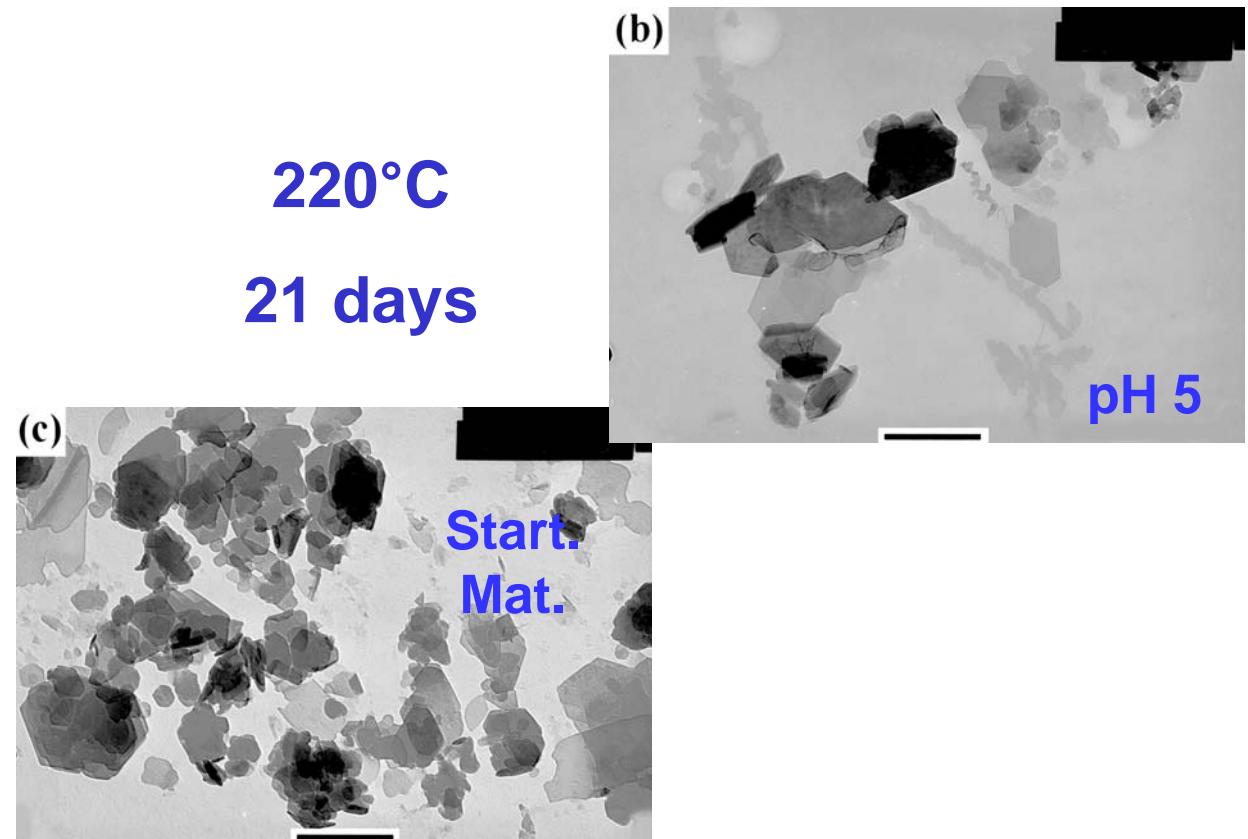
Influence of experimental conditions



Scale bar : 0.4 μm

Kaolinite Syntheses

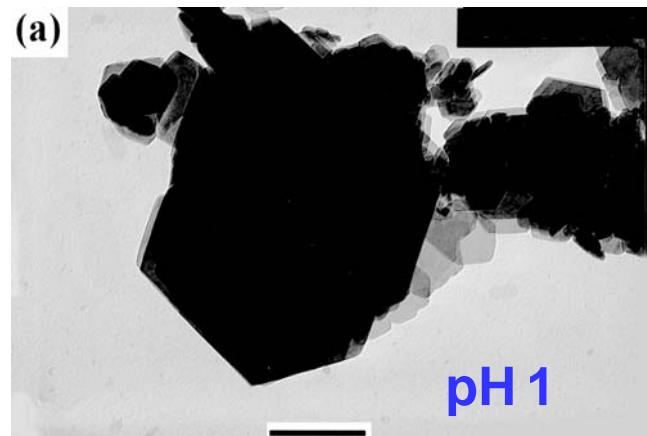
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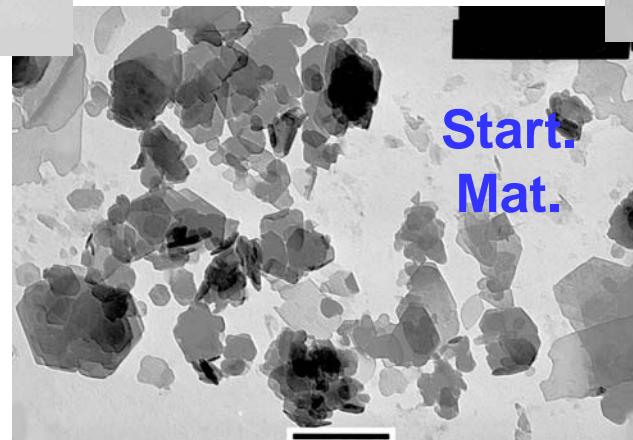
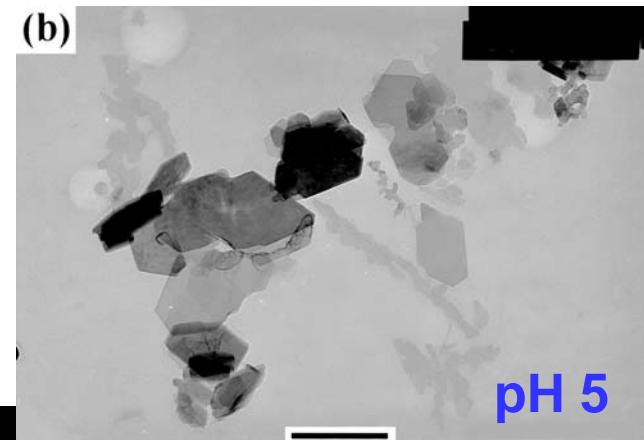
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Kaolinite Syntheses

Influence of experimental conditions



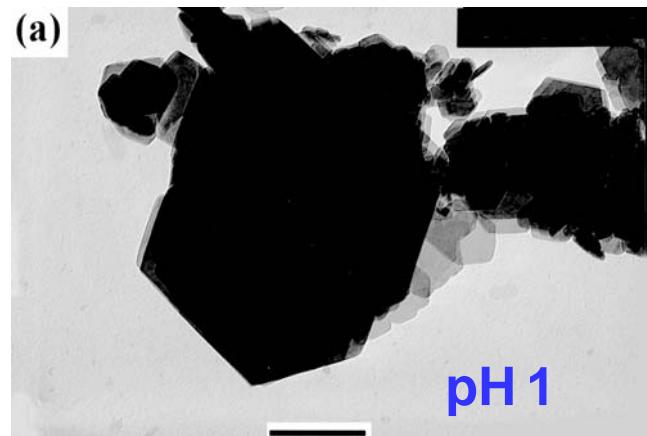
220°C
21 days



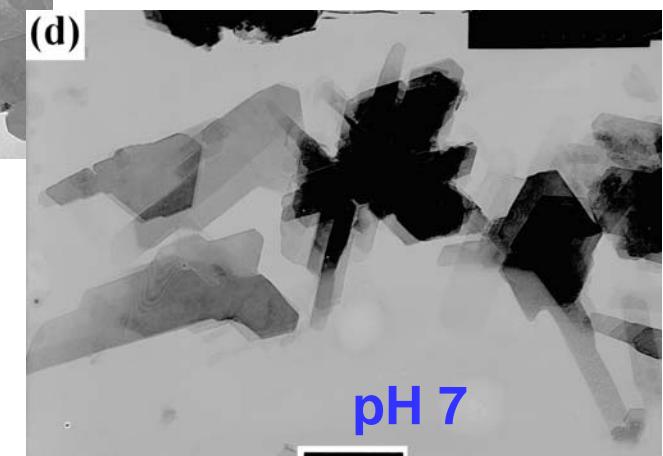
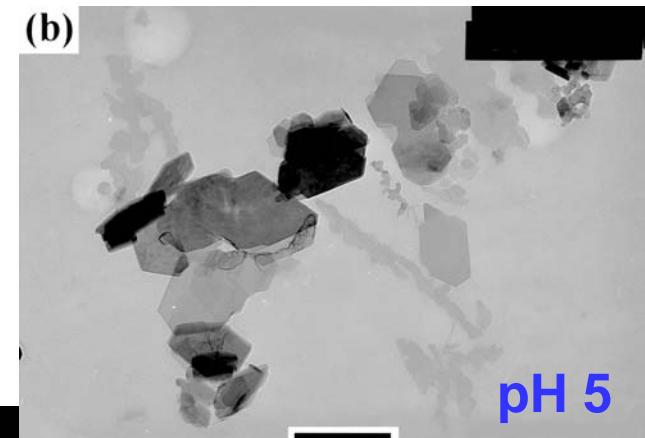
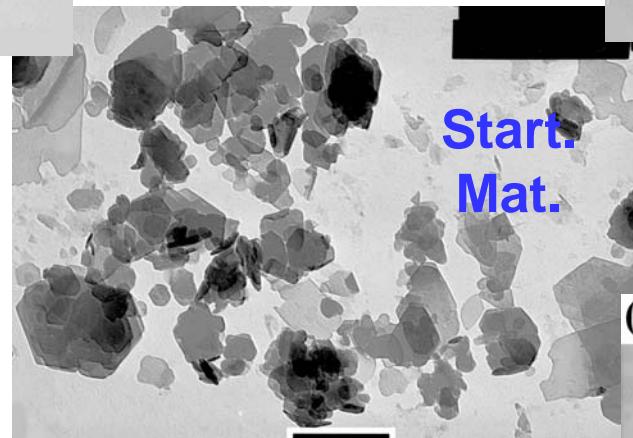
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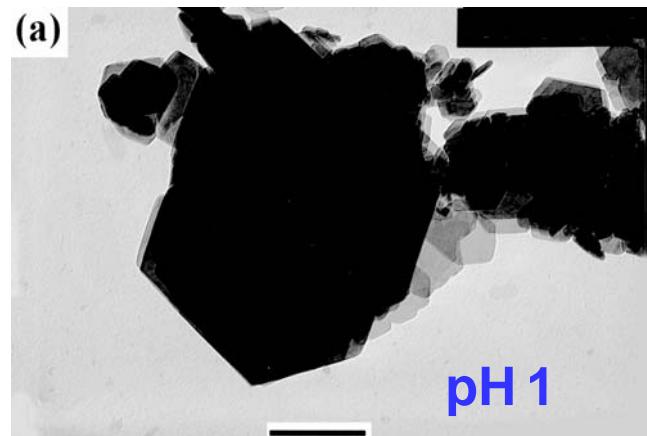
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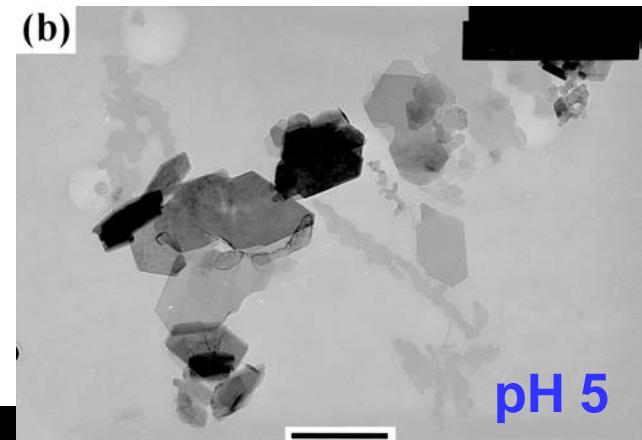
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Kaolinite Syntheses

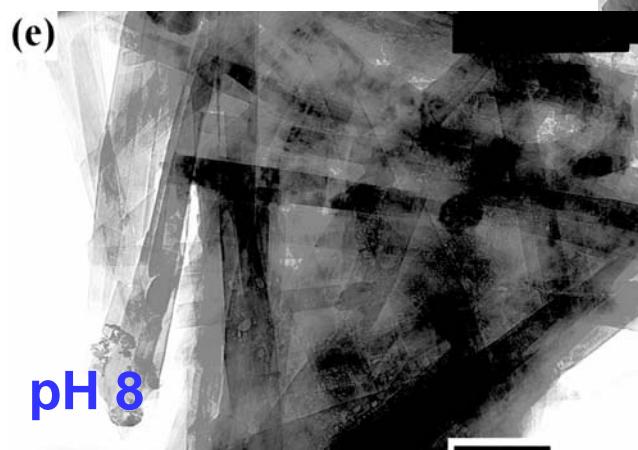
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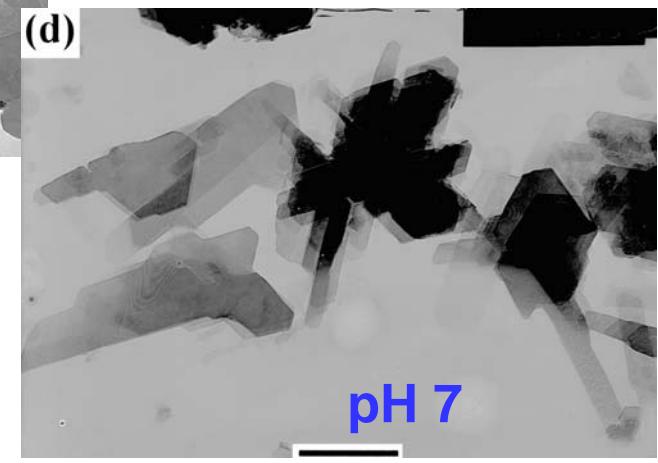
220°C
21 days



Start.
Mat.



Scale bar : 0.4 μm

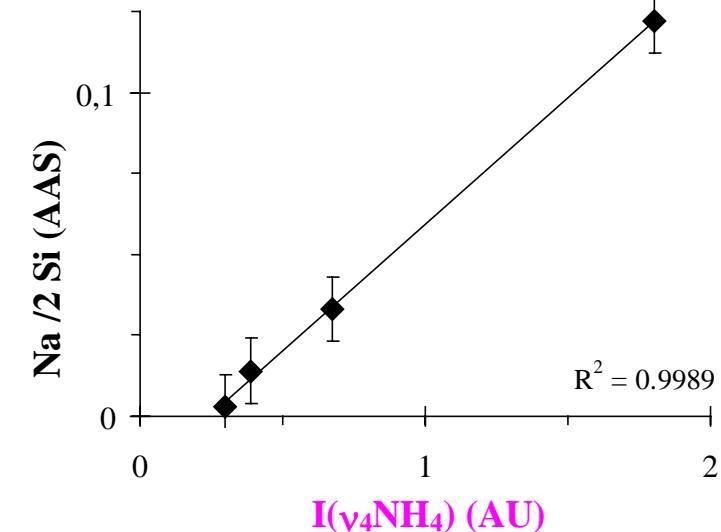
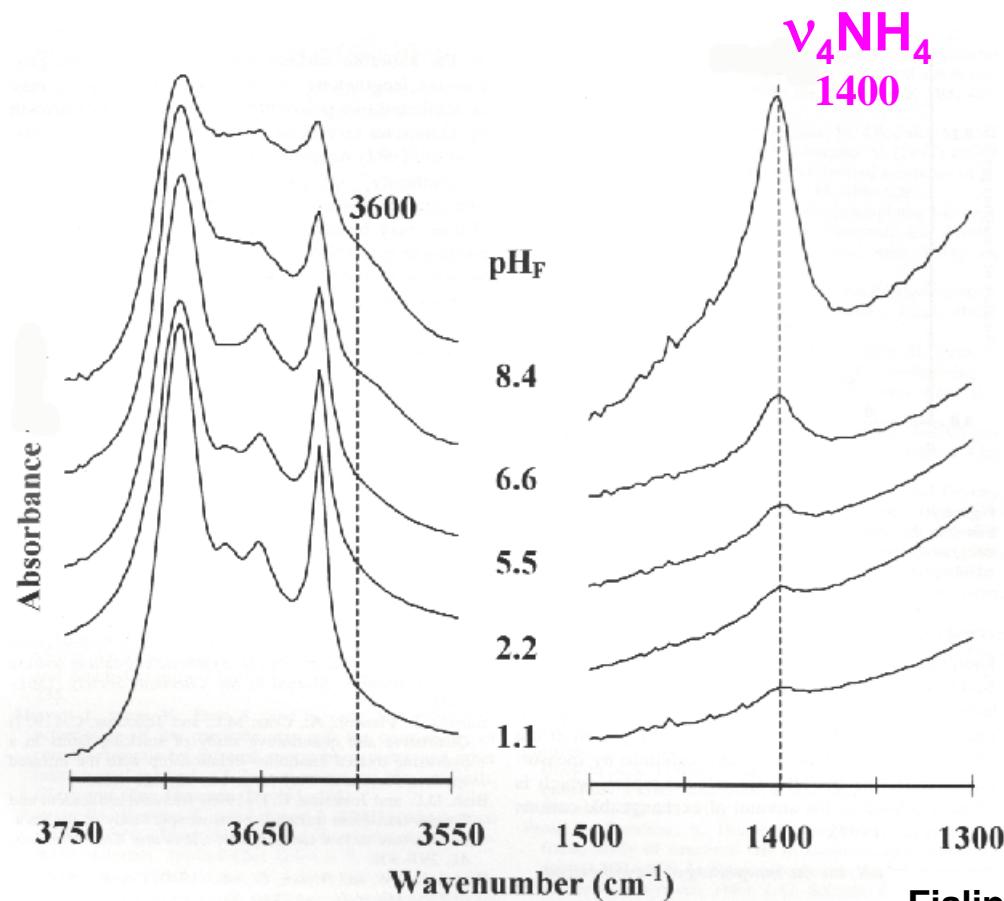


Kaolinite Syntheses

Influence of experimental conditions

FTIR (NH_4 - samples)

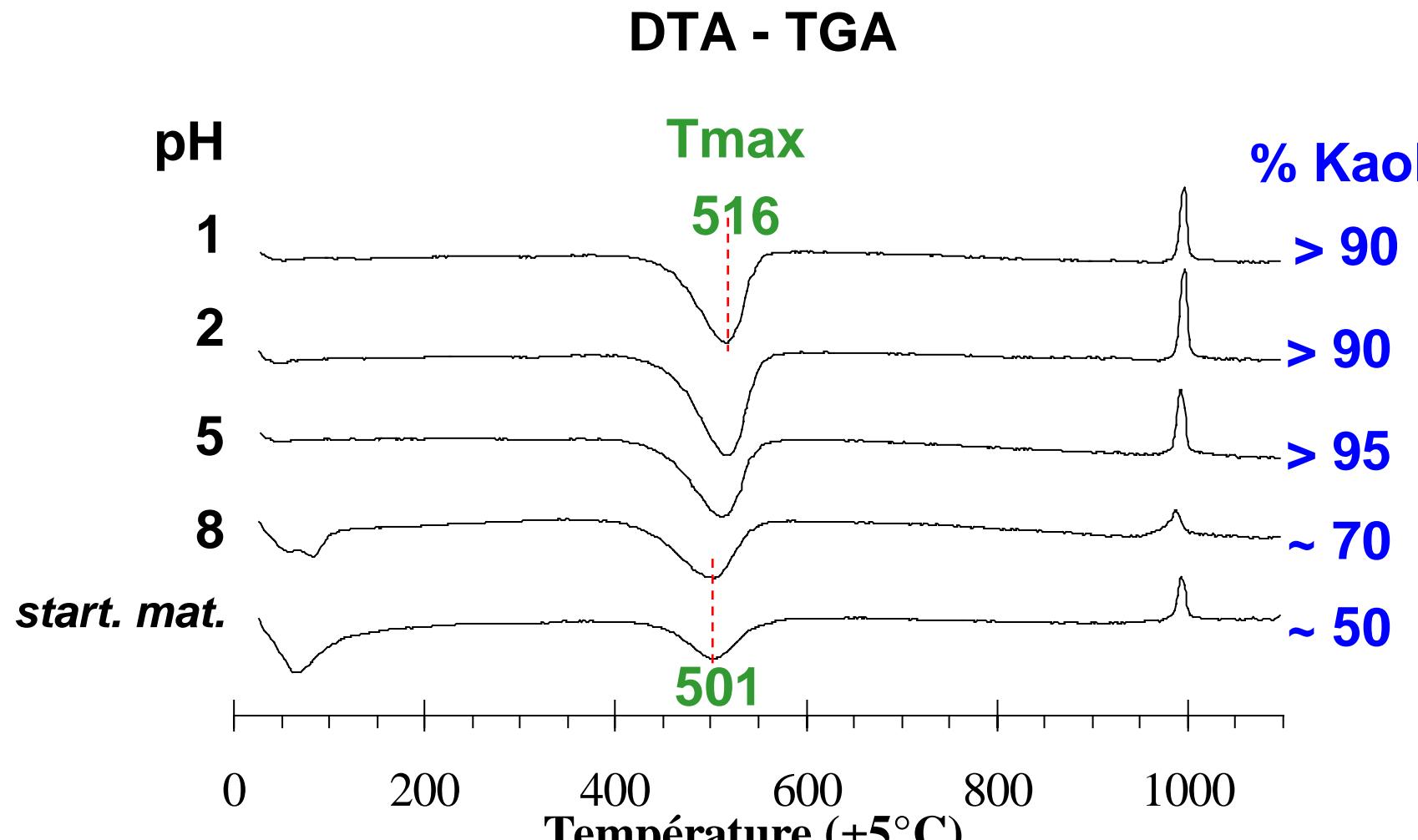
(Spectra normalized with SiO band)



Fialips et al. (2000) *Clays & Clay Min.*, 48, 173-184.

Kaolinite Syntheses

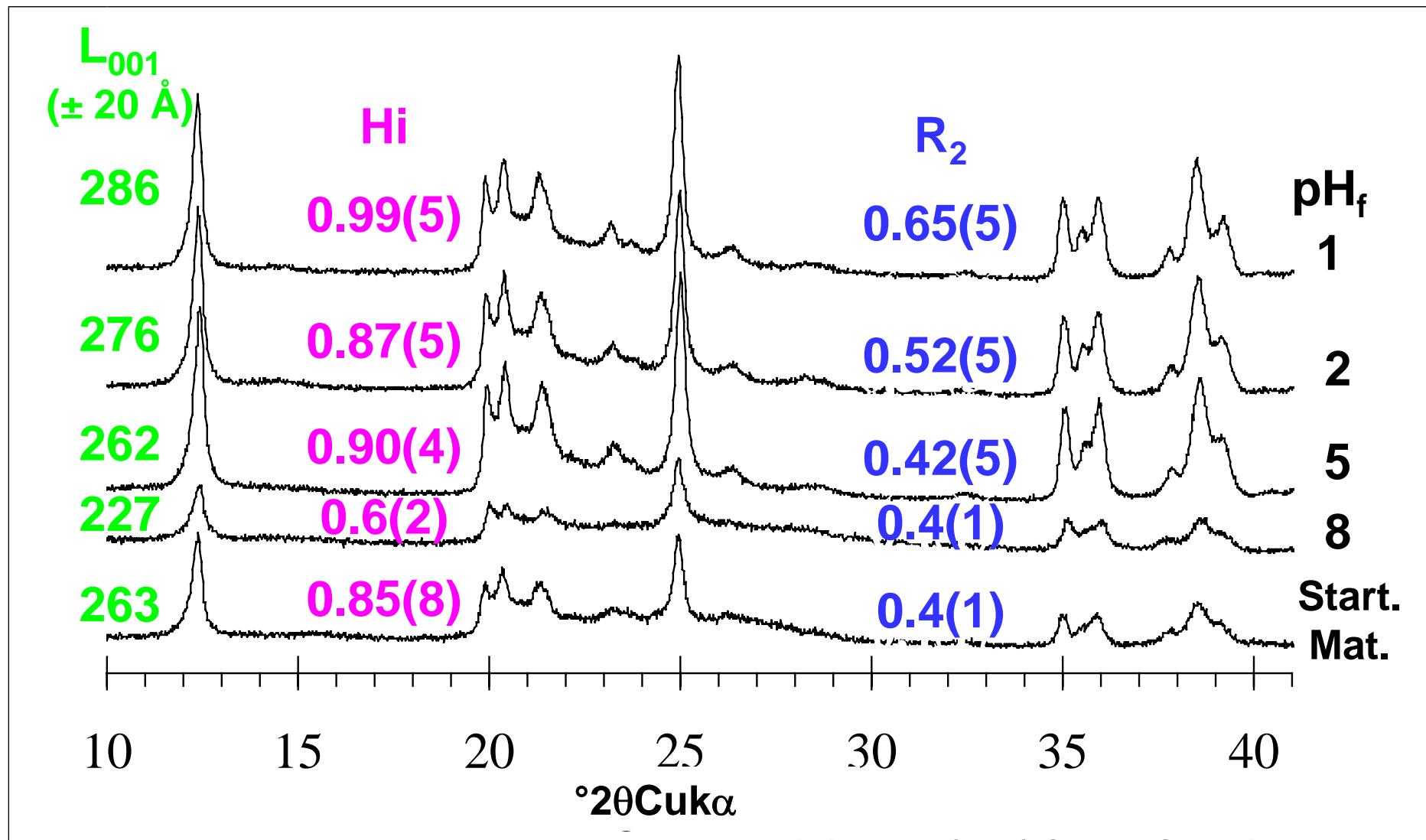
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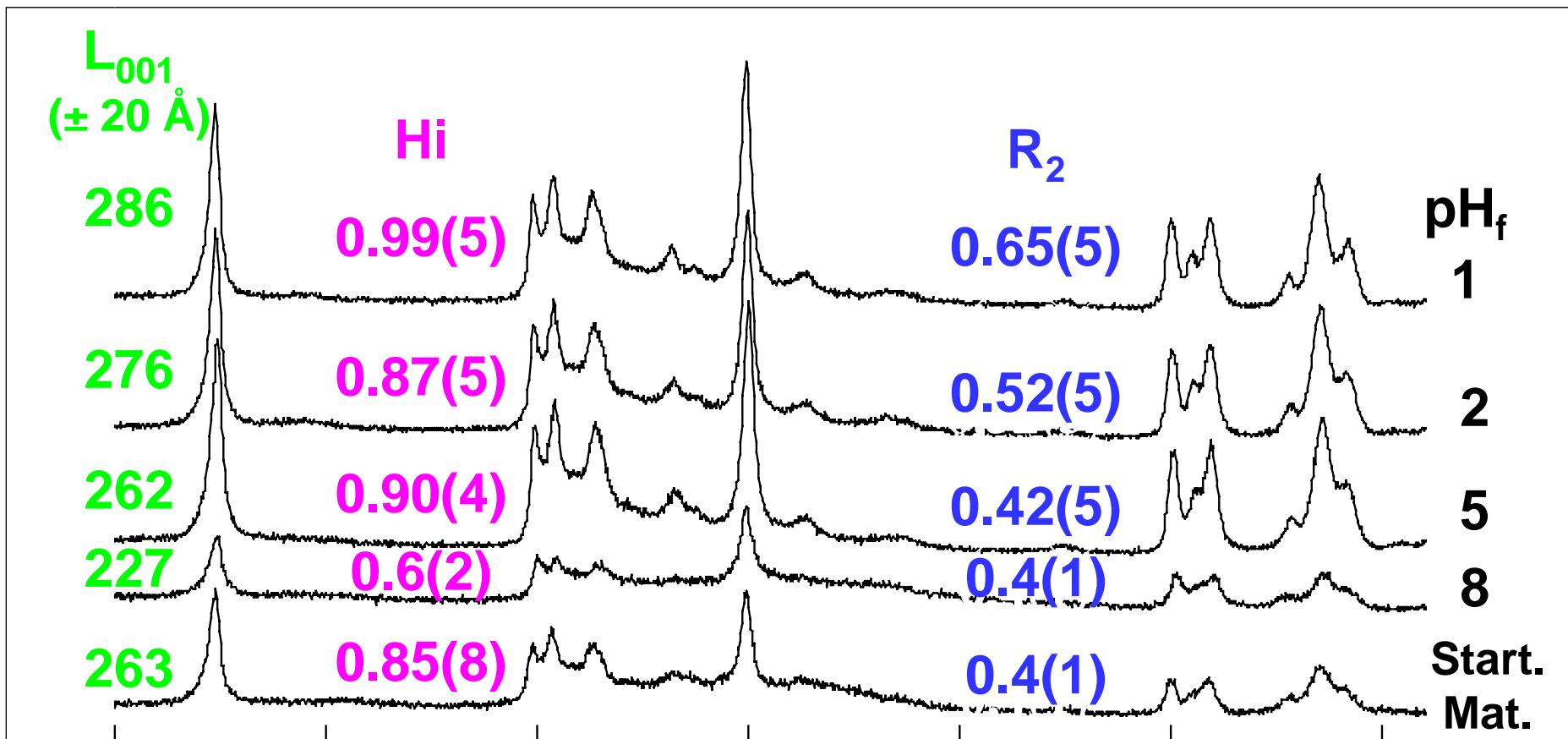
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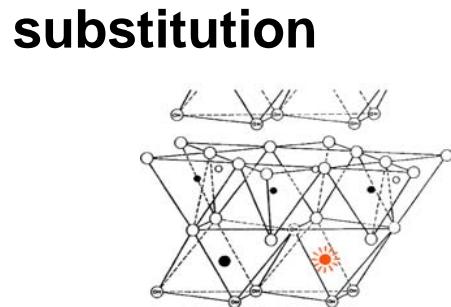
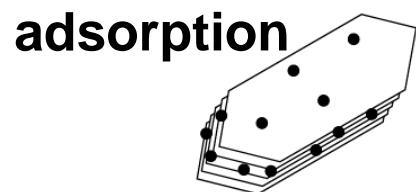
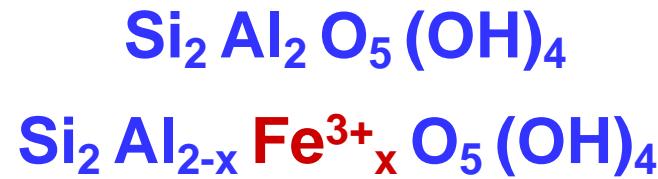
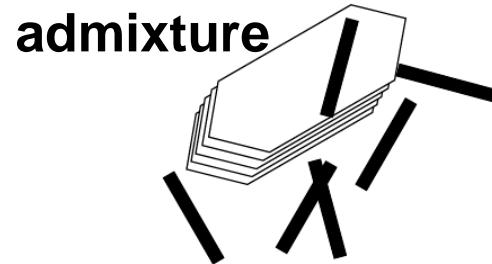
Influence of experimental conditions



All these kaolinites have thermodynamical functions similar to natural kaolinites Fialips et al. Amer. Miner., 86, 304-311, 2001

Fialips et al. (2000) Clays & Clay Min., 48, 173-184.

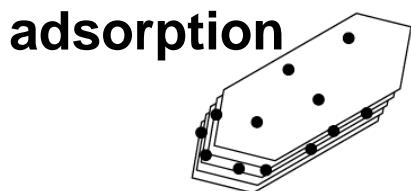
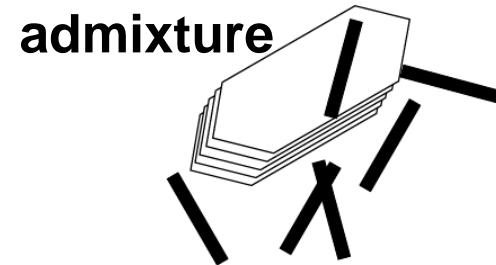
Kaolinite syntheses Fe³⁺-Al substitutions



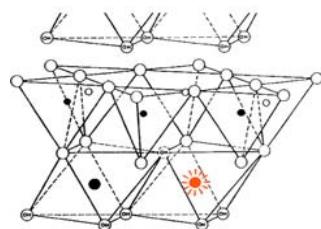
Fe³⁺ status

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Kaolinite syntheses Fe³⁺-Al substitutions



substitution



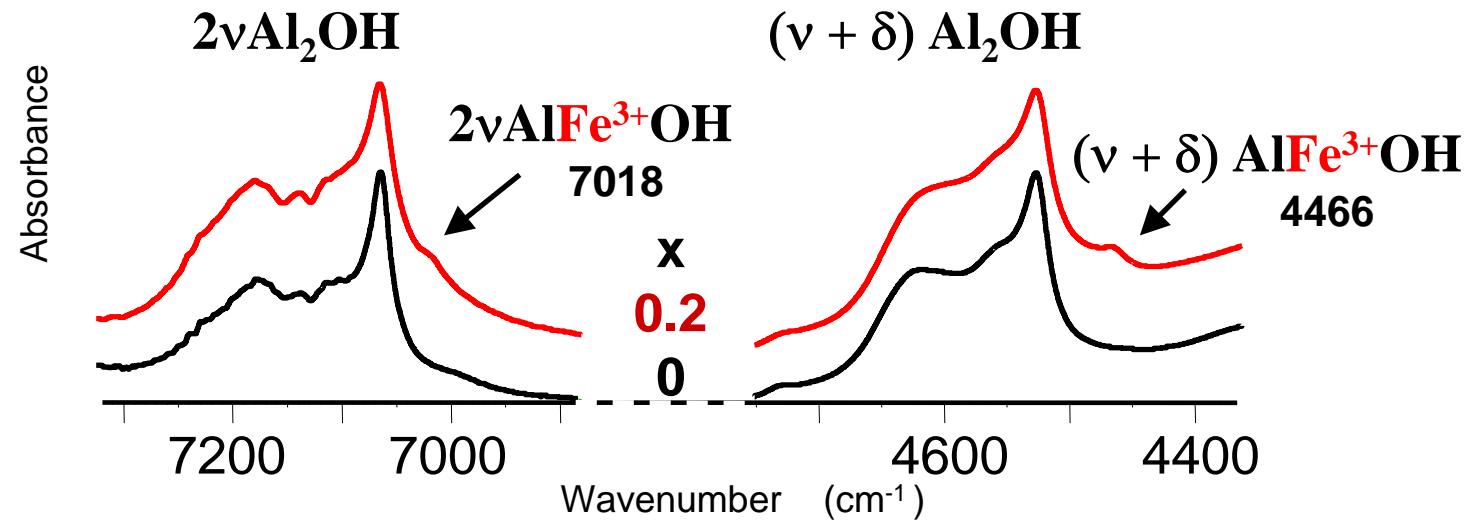
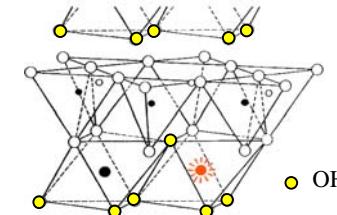
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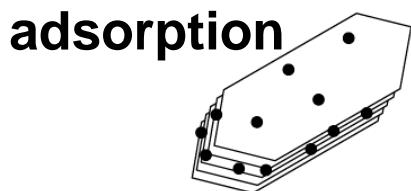
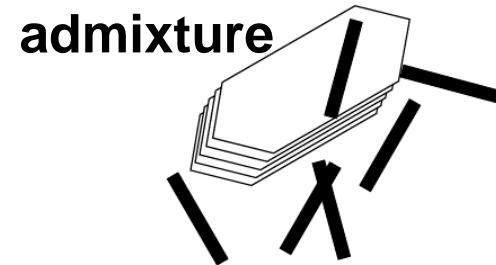
Kaolinite syntheses Fe³⁺-Al substitutions

FTIR spectra (NIR region)

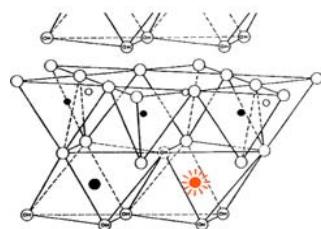


Petit et al. (1999) *Clays & Clay Min.*, 47, 103-108.

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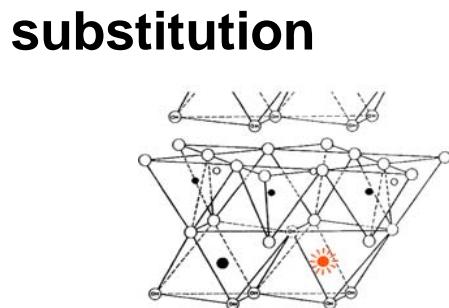
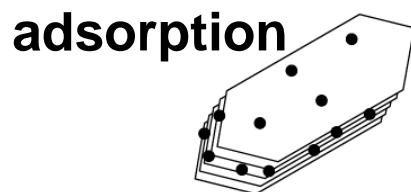
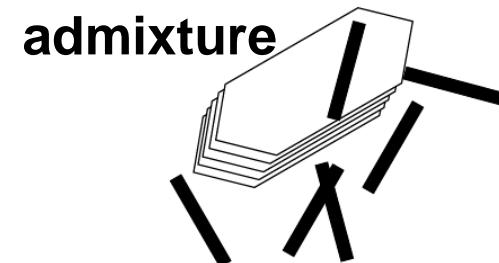


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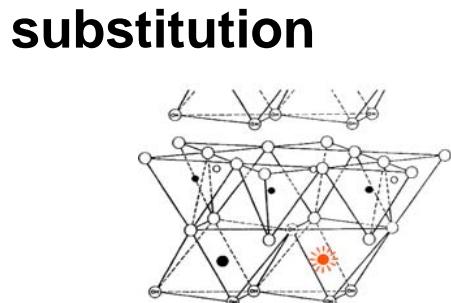
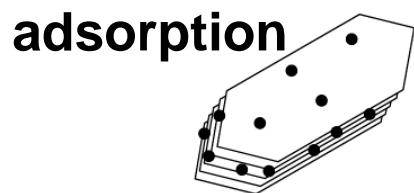
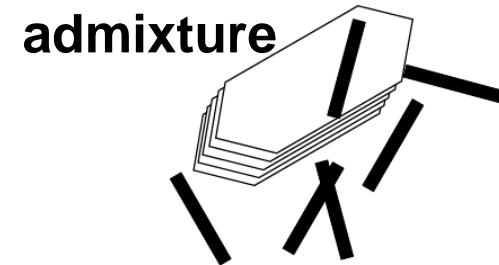


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Fe³⁺ status

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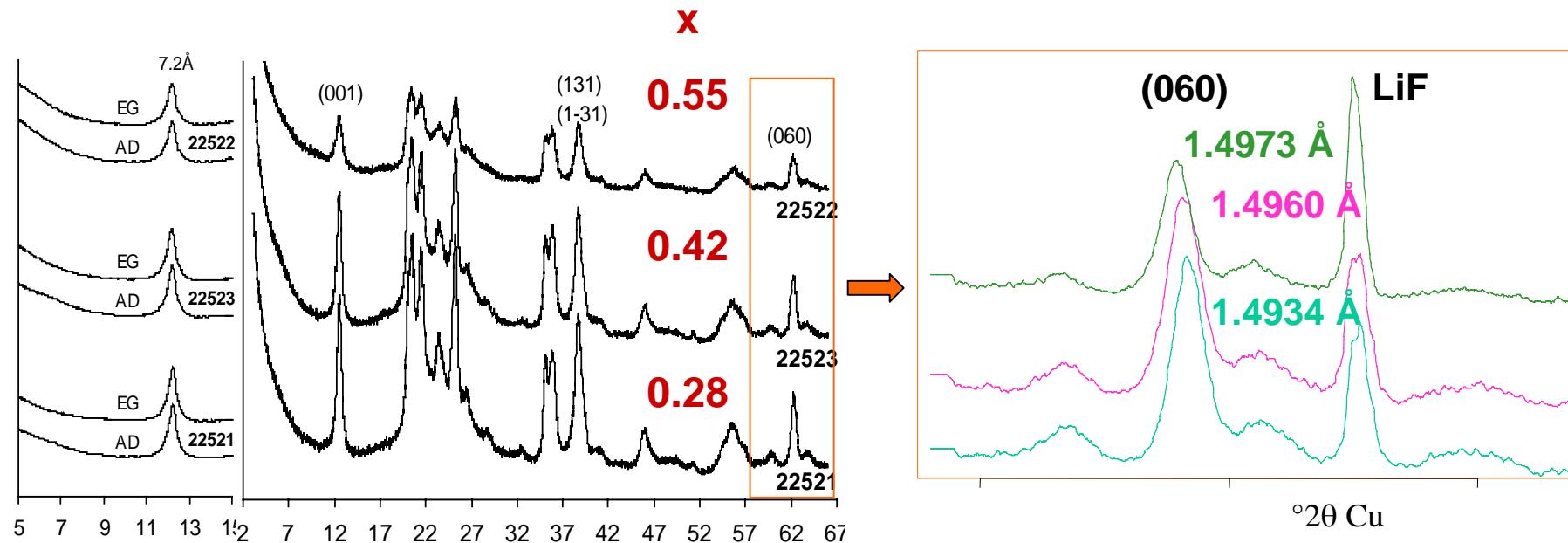
Iriarte et al. (2005) *Clays & Clay Min.*, 53, 1-10 :

- It is possible to synthesize kaolinite with a higher level of Fe³⁺-Al substitutions ($x = 0.28, 0.42, 0.55$)

Kaolinite syntheses Fe³⁺-Al substitutions

$\text{Si}_2 \text{Al}_{2-x} \text{Fe}^{3+}_x \text{O}_5 (\text{OH})_4$
 $x = 0.28, 0.42, 0.55$

pH_f = 5, 60 days, 225 °C

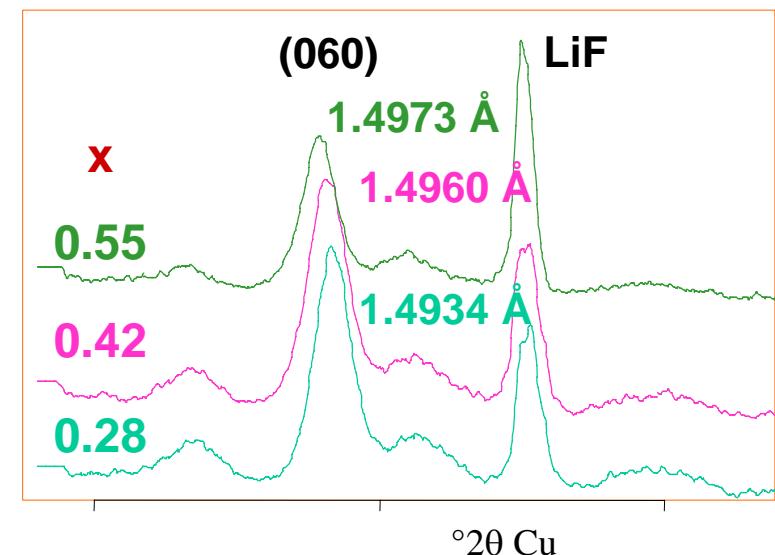
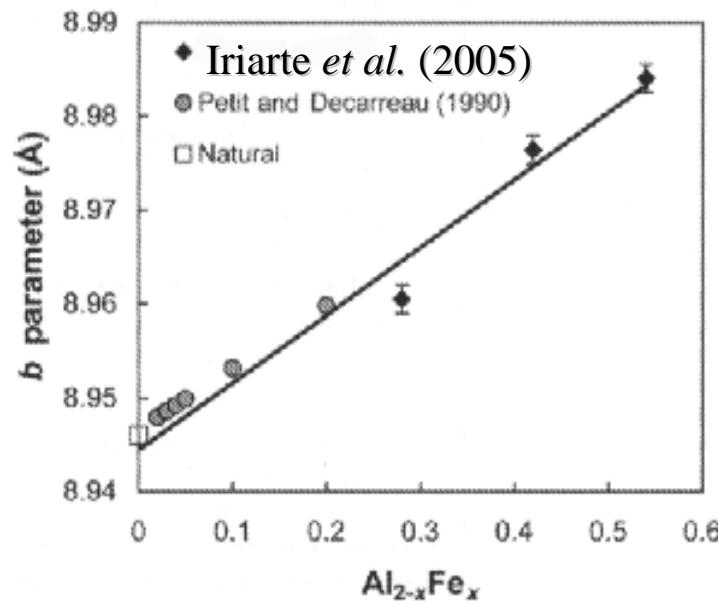


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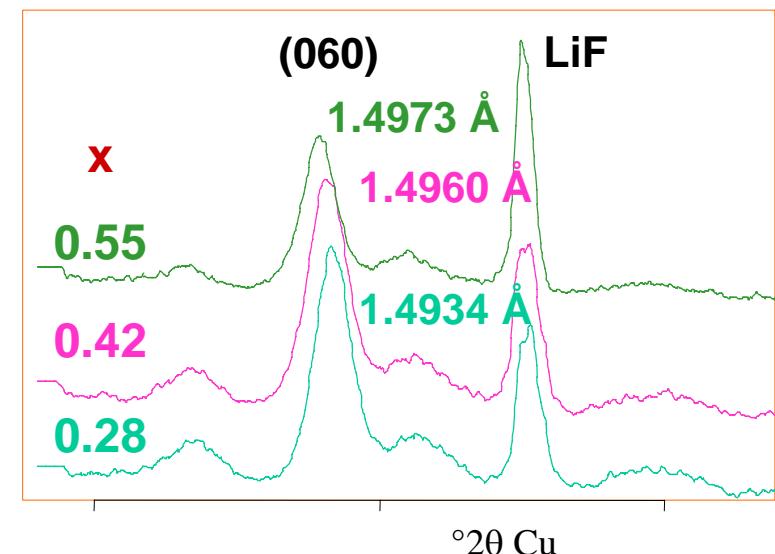
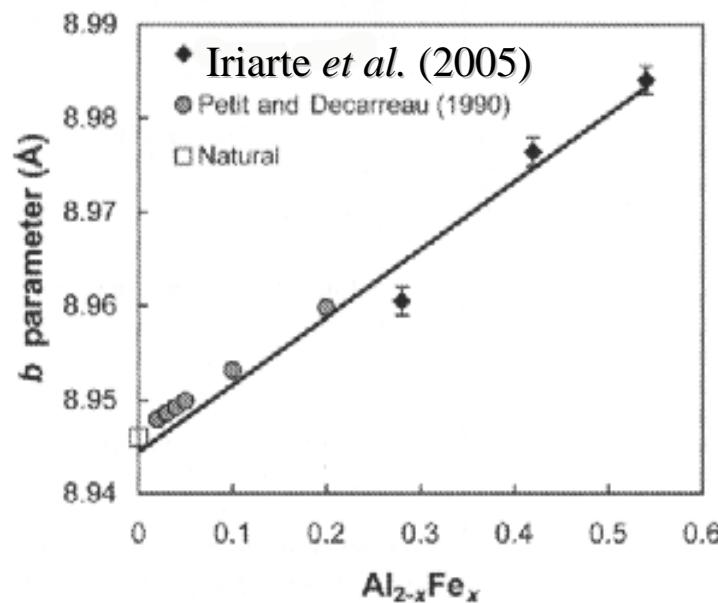
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Why Fe contents are so low in natural kaolinites ?

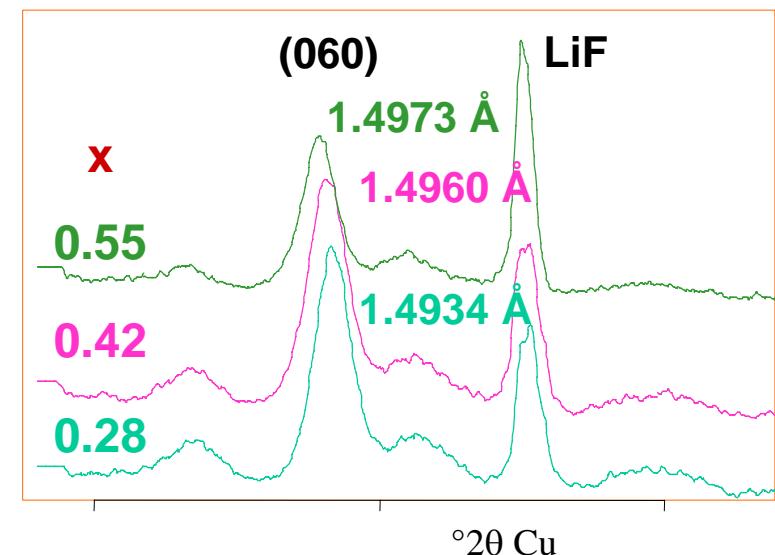
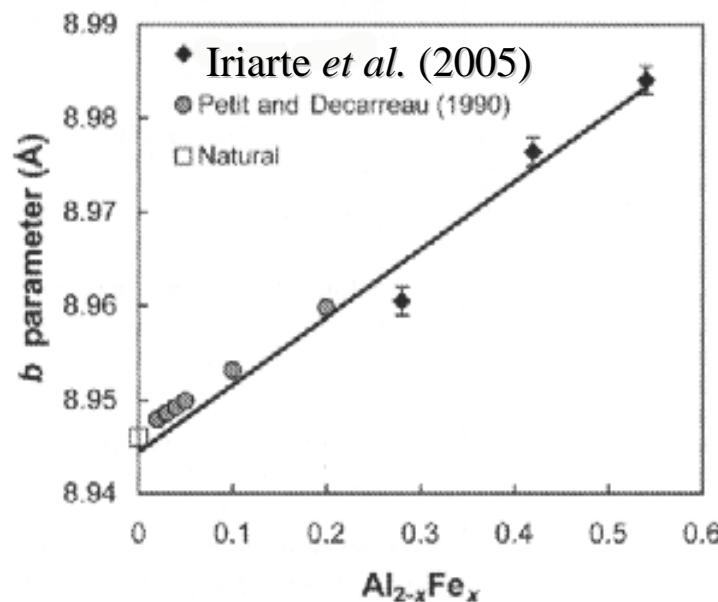
Iriarte et al. (2005) *Clays & Clay Min.*, 53, 1-10.

« Colloque Minéralogie environnementale - Académie des sciences - 14-15 septembre 2009 »

Kaolinite syntheses Fe³⁺-Al substitutions

$\text{Si}_2 \text{Al}_{2-x} \text{Fe}^{3+}_x \text{O}_5 (\text{OH})_4$
 $x = 0.28, 0.42, 0.55$

pH_f = 5, 60 days, 225 °C



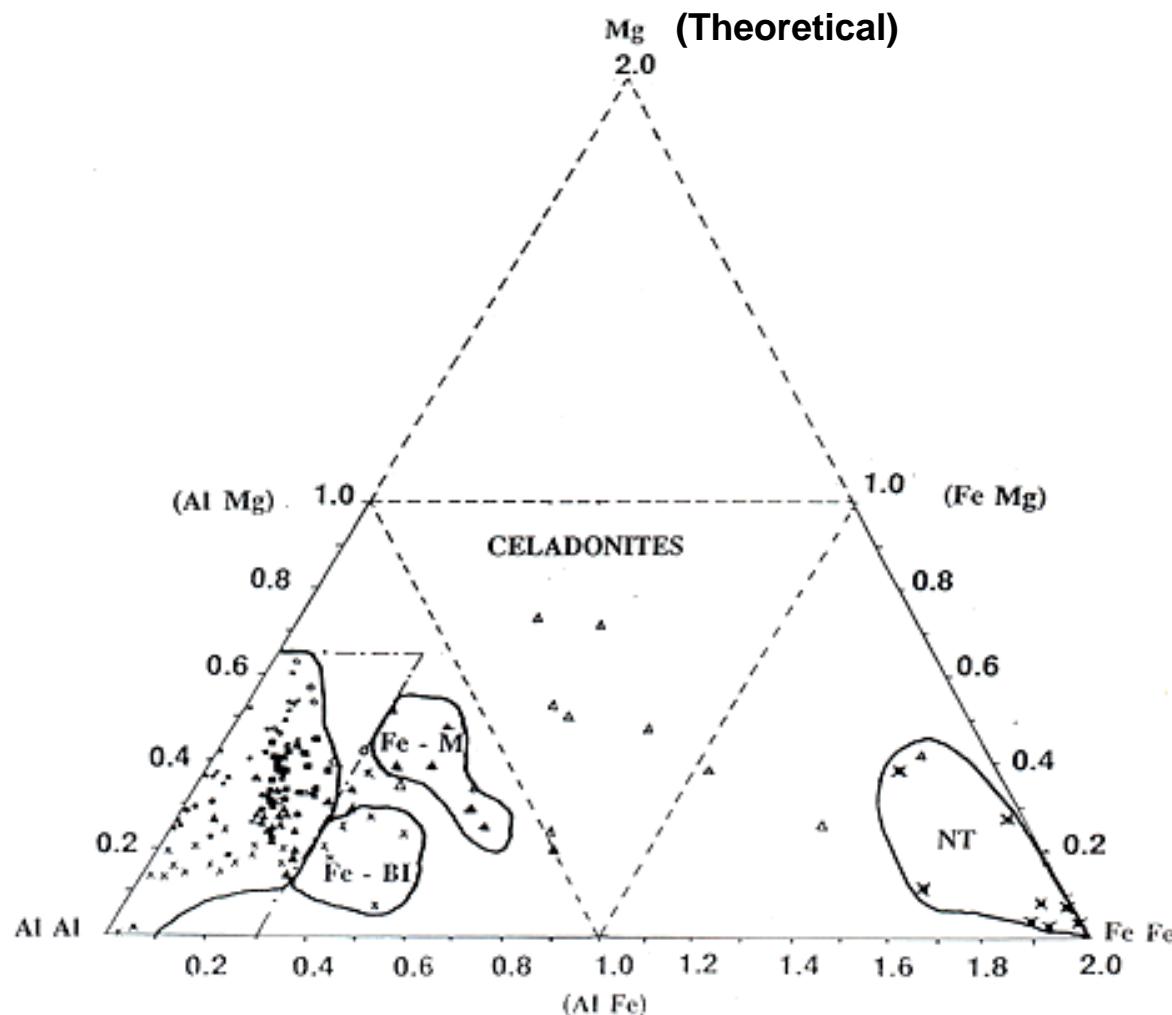
Why Fe contents are so low in natural kaolinites ?

Study the kaolinite-iron experimental system versus pH

Iriarte et al. (2005) *Clays & Clay Min.*, 53, 1-10.

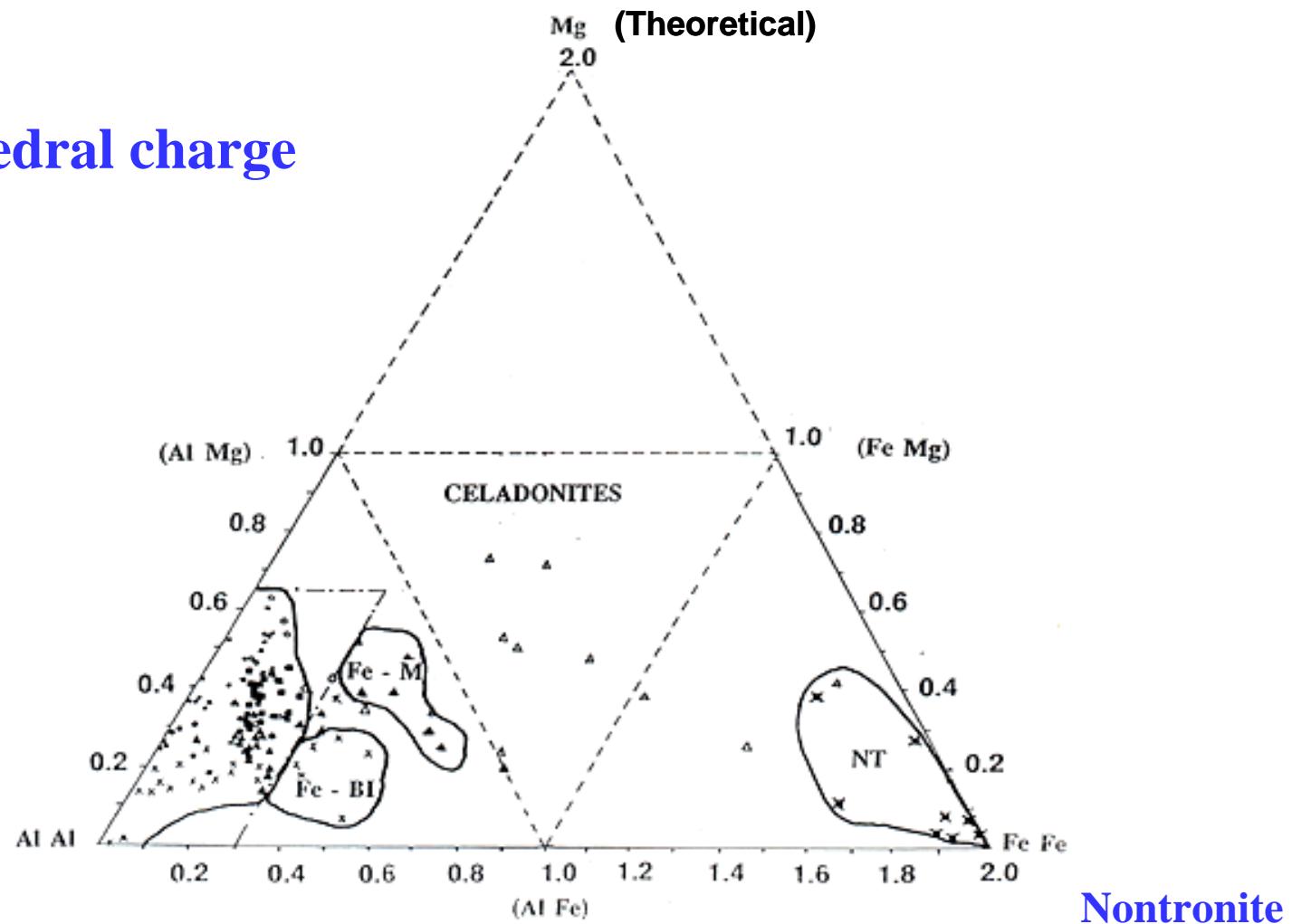
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Ternary diagram of octahedral compositions for natural dioctahedral smectites (after Güven, 1988)

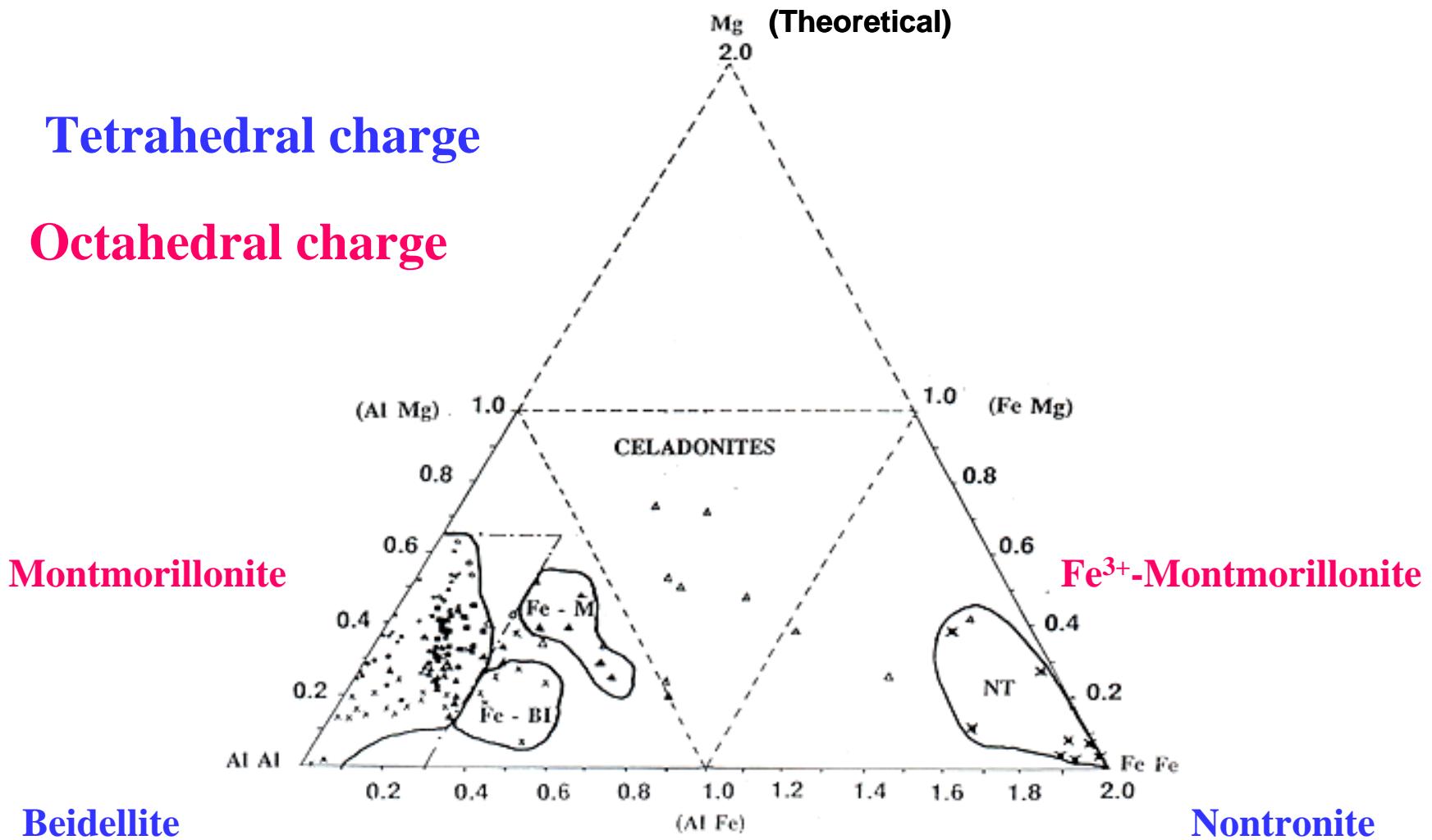


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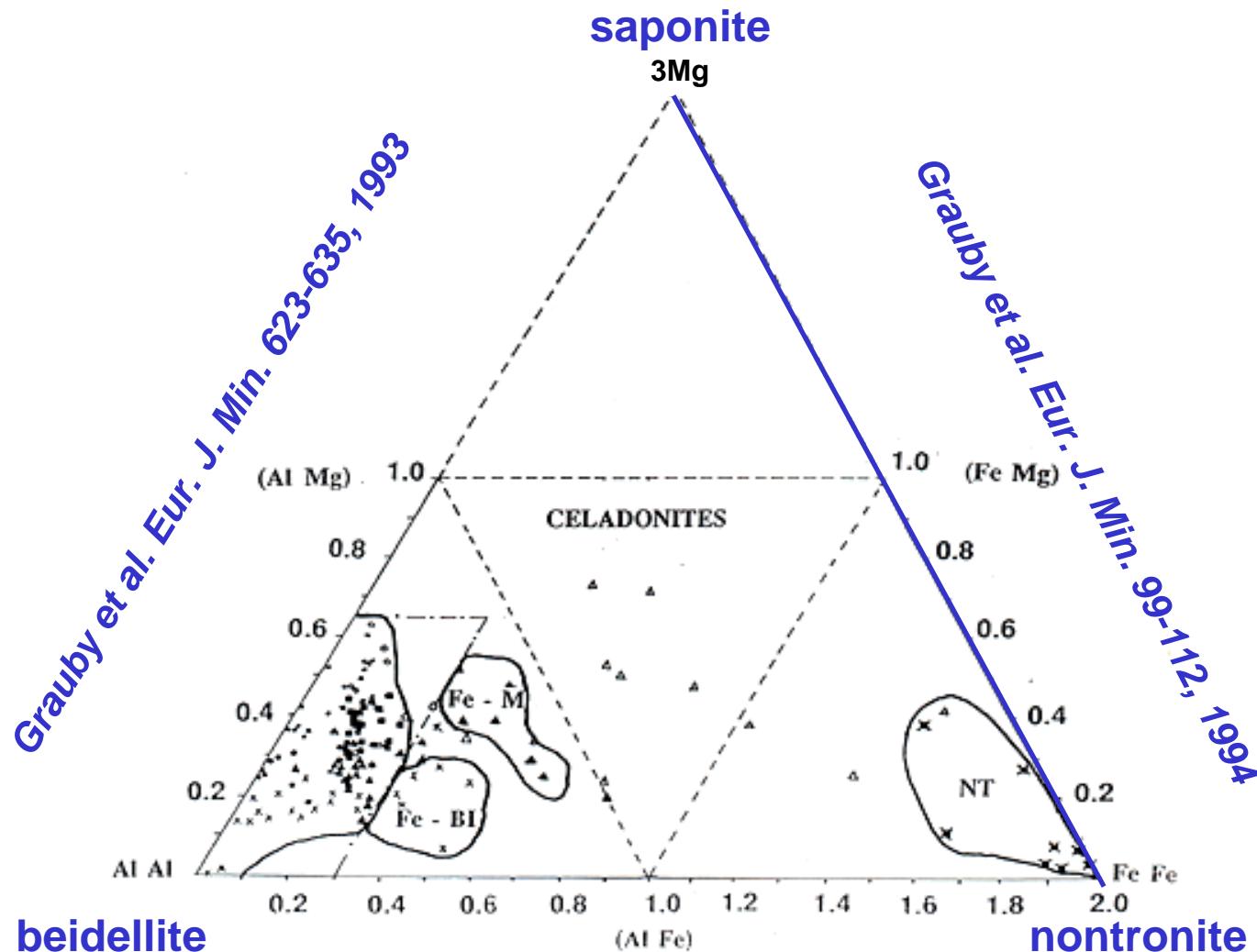
Tetrahedral charge



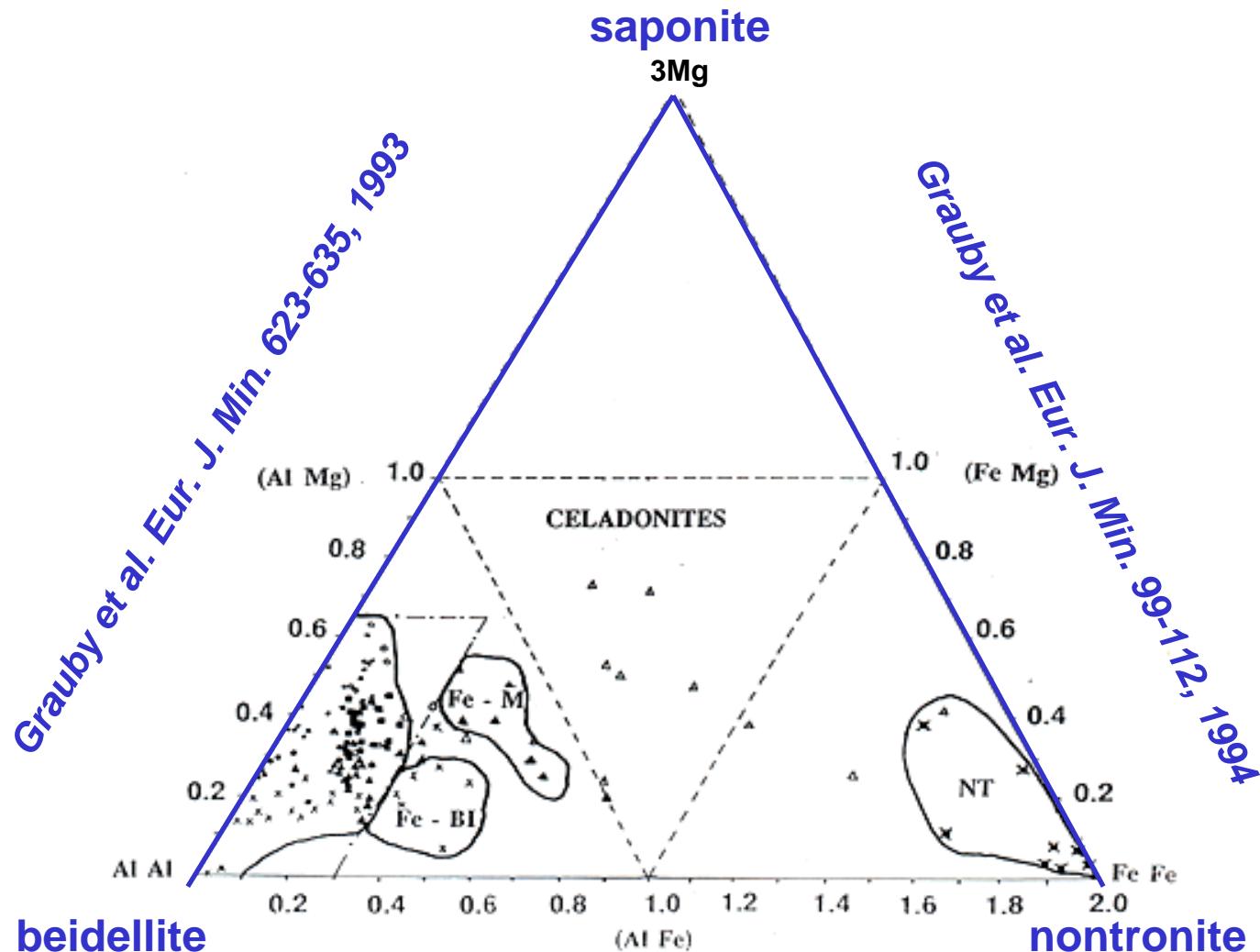
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(after Güven, 1988)



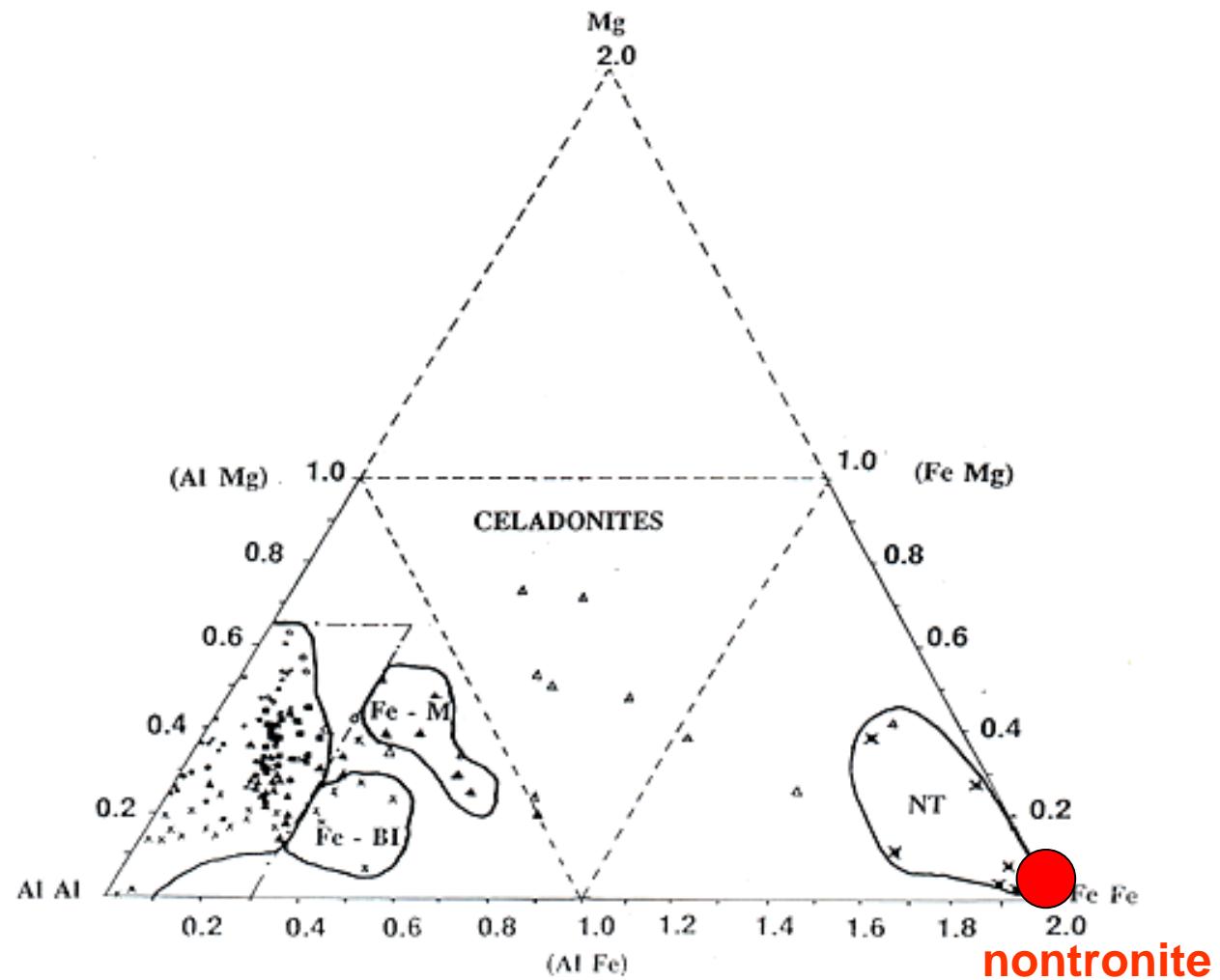
Smectite synthesis Chemical series studied



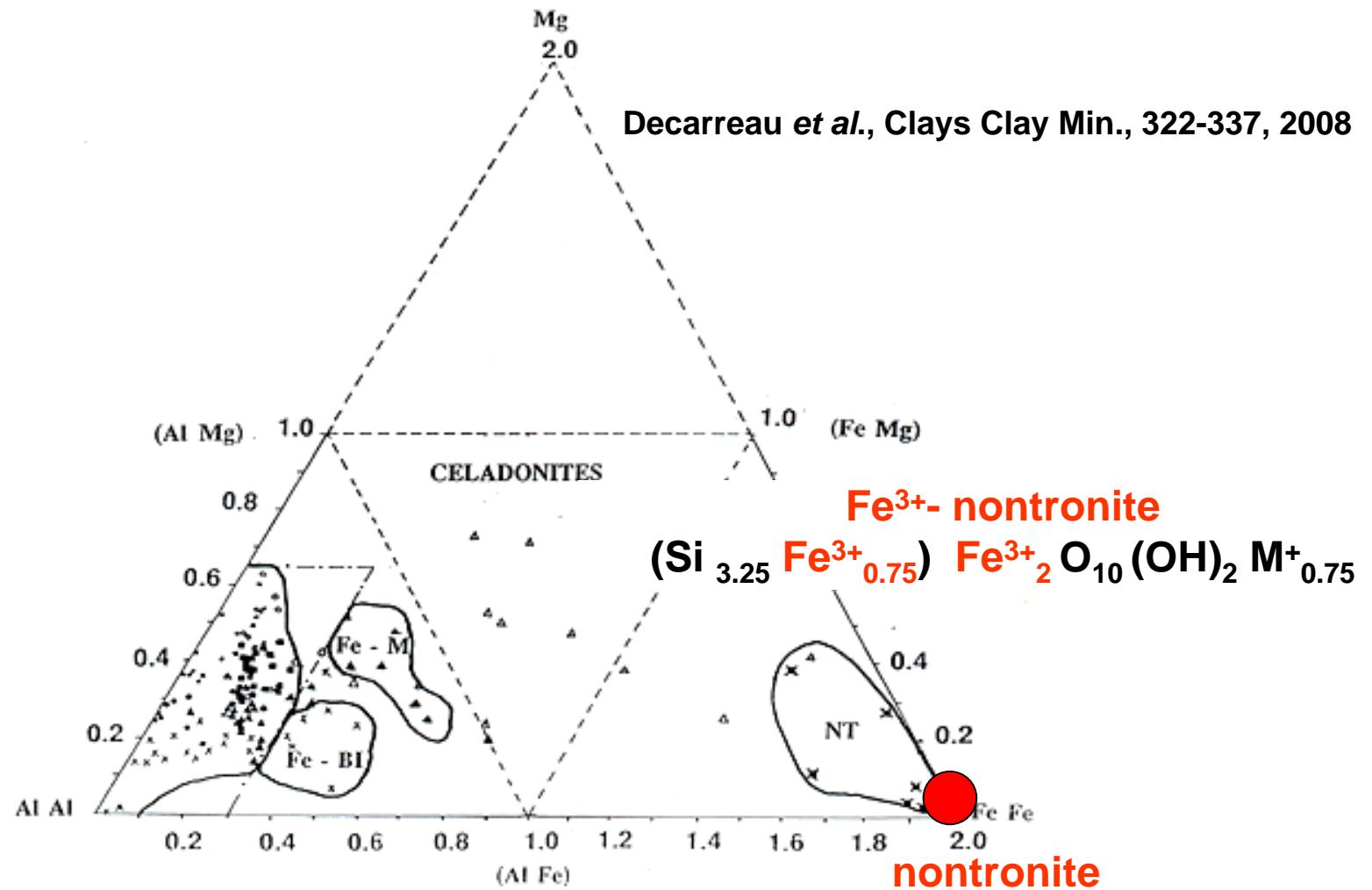
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Smectite synthesis Chemical series studied



Synthesis of Fe³⁺-nontronite

Decarreau et al., Clays Clay Min., 322-337, 2008

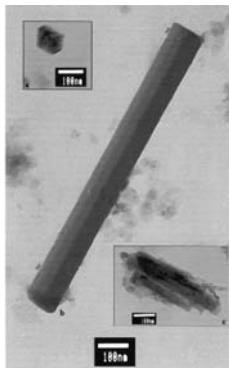
- High-charge Fe³⁺- nontronites were synthesized from 75 to 150°C.



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Decarreau et al., Clays Clay Min., 322-337, 2008

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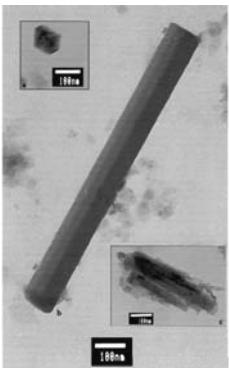
- The range of synthesis pH is narrow (12 to 12.5)
 - at lower pH hematite or hisingerite are formed
 - at higher pH and for temperatures >180°C aegirine is formed

Decarreau et al., Eur. J. Min., 85-90, 2004

Synthesis of Fe³⁺-nontronite

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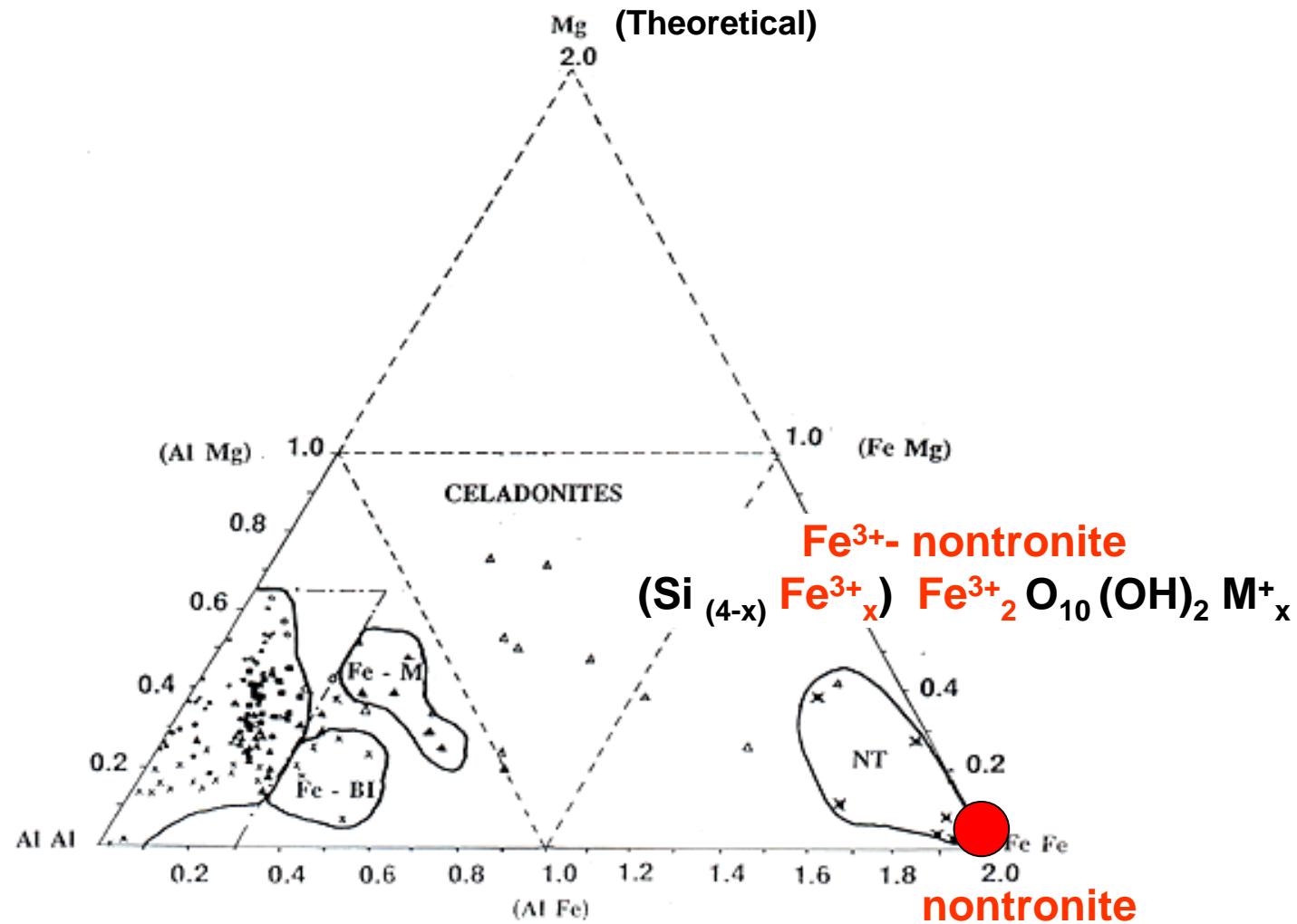


- The range of synthesis pH is narrow (12 to 12.5)
 - at lower pH hematite or hisingerite are formed
 - at higher pH and for temperatures >180°C aegirine is formed
- The expandability of the nontronites is linked to their « crystallinity » (Tsynth) and ranges from smectite to vermiculite-like behavior

Decarreau et al., Eur. J. Min., 85-90, 2004

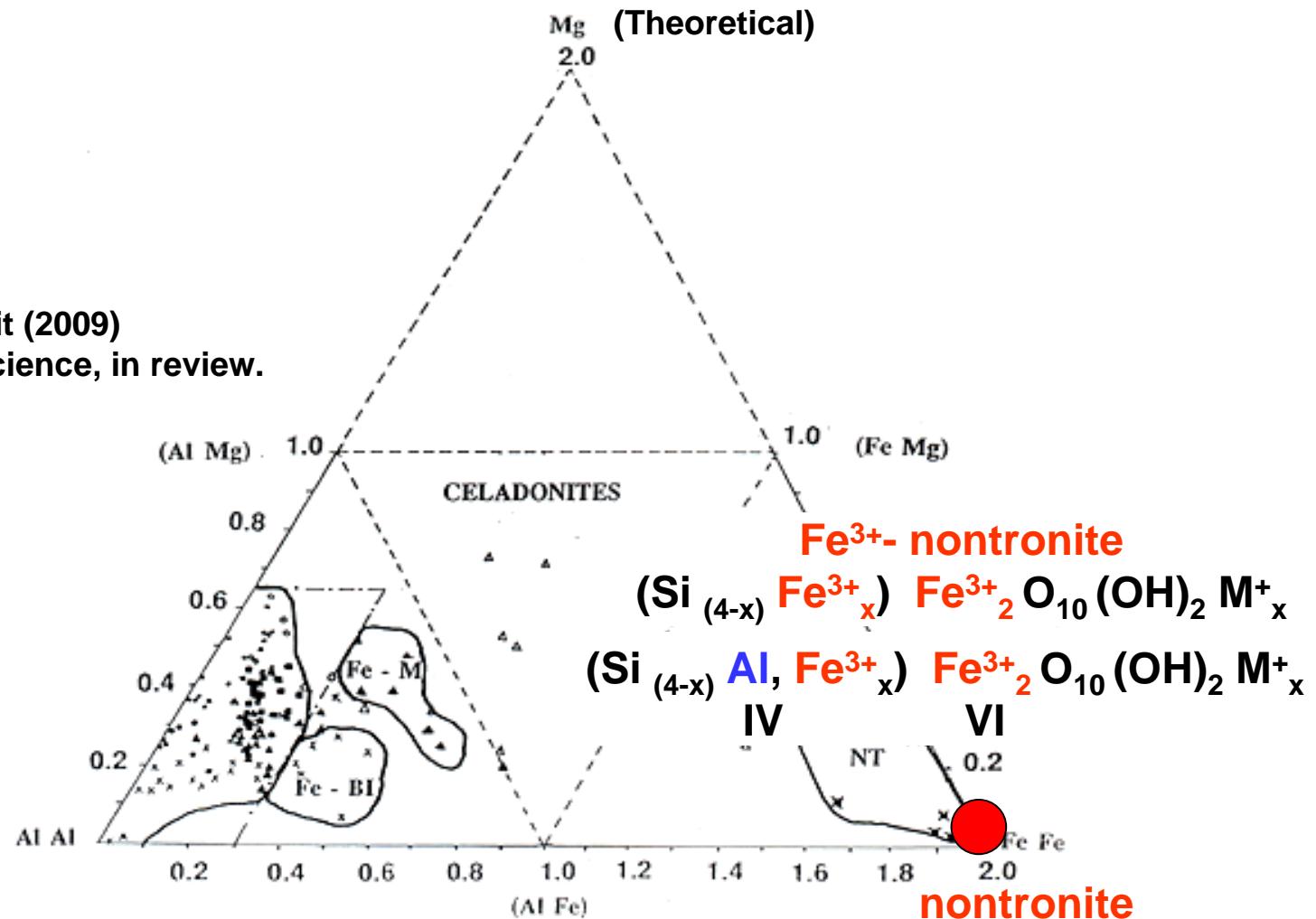
T (°C)	EG - Na (Å)	EG - Ca (Å)	Alkylammonium (12C) (Å)	Perm. charge (half unit cell)
75	15.3	(17)	23.8	0.75
90	15.8	16.53	23.8	0.75
100	16.54	16.17	23.8	0.75
110	14.86	16.04	23.8	0.75
125	12.54	15.83	23.8	0.75
150	12.54	15.48	23.8	0.75

Smectite synthesis Chemical series studied



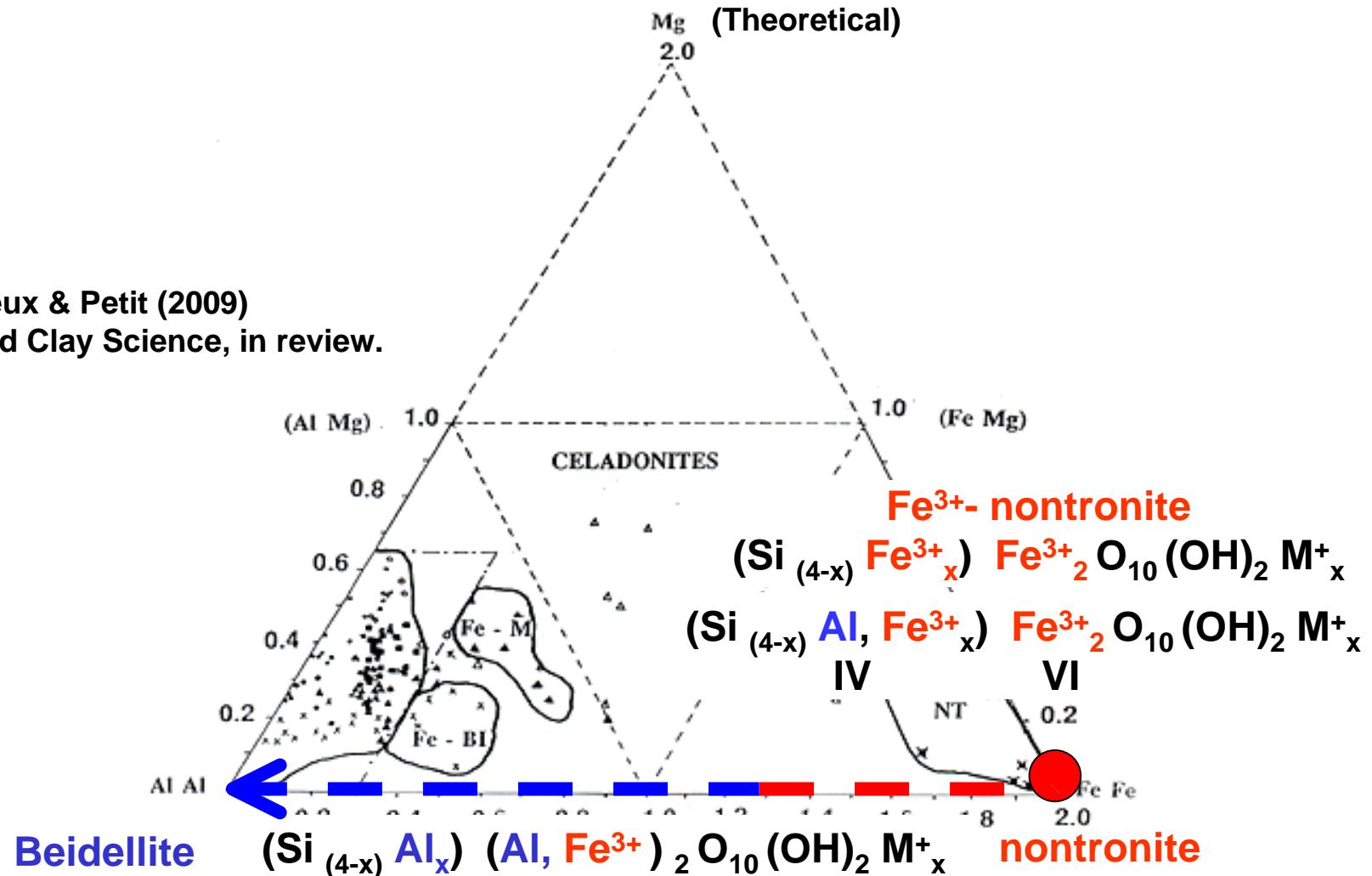
Smectite synthesis Chemical series studied

Andrieux & Petit (2009)
Applied Clay Science, in review.



Smectite synthesis Chemical series studied

Andrieux & Petit (2009)
Applied Clay Science, in review.



Many trials and errors !

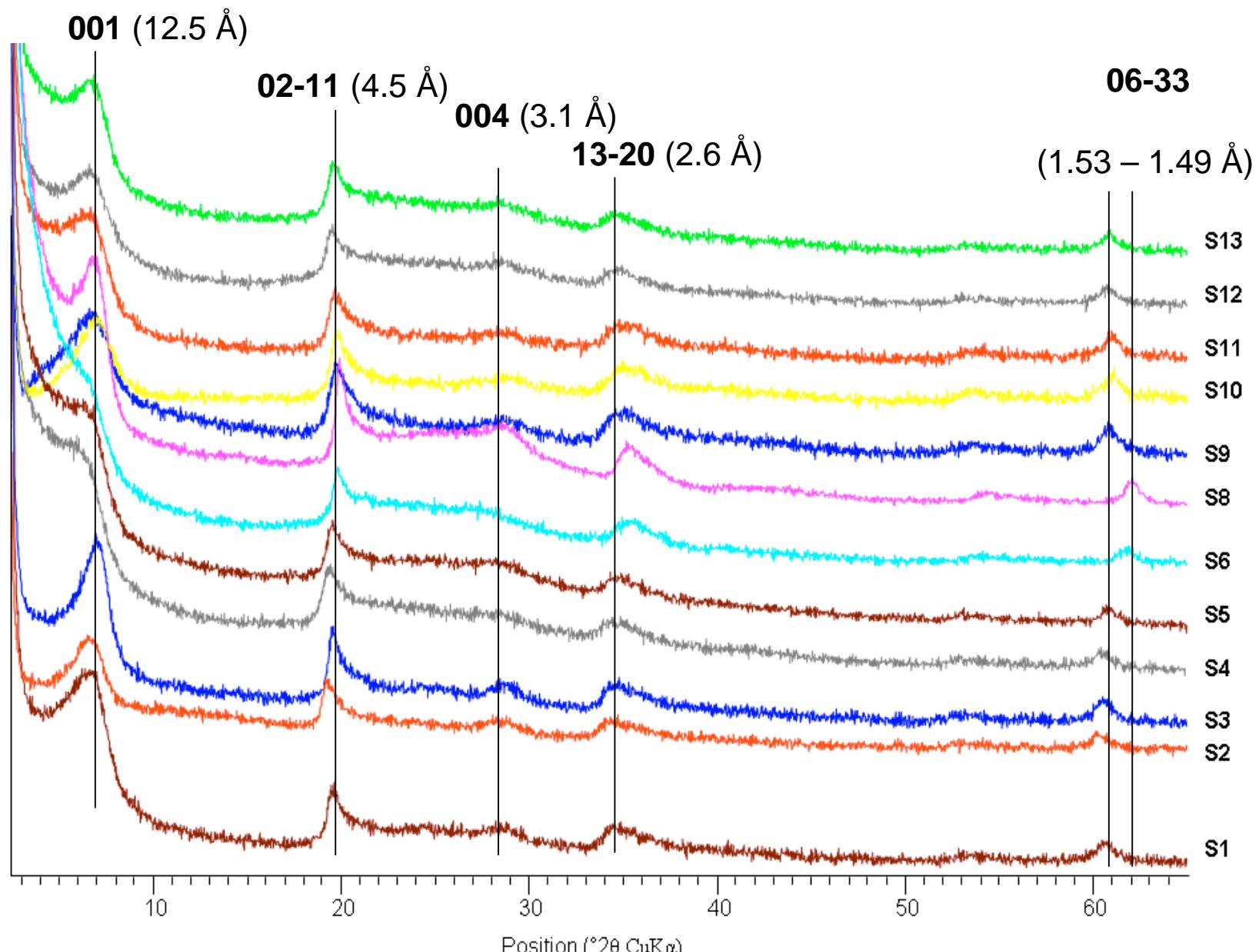
N°	FeCl ₃ /FeCl ₂	pH _i	pH _f	T (°C)	Time (days)	Crystallized product
Gel Si ₄ Al _{0,2} Fe _{1,8} O ₁₁						
1	Fe ³⁺	10.5	10.82	150	30	Smectite
2	Fe ³⁺	10.5	10.81	170	30	Smectite
3	Fe ³⁺	10.6	10.68	200	13	Smectite
4	Fe ³⁺	10.4	10.28	220	13	Smectite + aegirine
5	Fe ²⁺	10.7	11	150	75	Smectite + analcime
6	Fe ²⁺	10.9	10.78	170	75	Smectite + analcime + aegirine
7	Fe ²⁺	10.7	10.66	200	75	Smectite + analcime + aegirine
Gel Si ₄ Al _{0,4} Fe _{1,6} O ₁₁						
8	Fe ³⁺	10.4	10.12	170	13	Hisingerite
9	Fe ³⁺	10.5	10.23	200	13	Hisingerite
10	Fe ³⁺	10.5	10.23	220	13	Hisingerite
11	Fe ²⁺	10.9	11.59	170	13	Smectite + zeolite
12	Fe ²⁺	10.7	11.27	200	13	Smectite + analcime
13	Fe ²⁺	11.1	10.81	220	13	Smectite+analcime+ aegirine
14	Fe ²⁺	10.3	10.71	200	75	Smectite
15	Fe ²⁺	6.0	5.26	200	75	Akaganeite
16	Fe ²⁺	11.7*	8.30	200	75	Akaganeite
Gel Si ₄ AlFeO ₁₁						
17	Fe ³⁺	10.6	10.74	200	30	Zeolite
18	Fe ²⁺	10.9	11.51	200	13	Smectite + analcime
19	Fe ²⁺	8.4	10.39	200	75	Smectite
20	Fe ²⁺	6.1*	10.42	200	14	Smectite
21	Fe ²⁺	6.9*	10.88	200	14	Smectite
22	Fe ²⁺	9.2	8.65	200	14	Smectite
23	Fe ²⁺	6.3	6.73	200	75	Smectite

N°	FeCl ₃ /FeCl ₂	pH _i	pH _f	T (°C)	Time (days)	Crystallized product
Gel Si ₄ AlFeO ₁₁						
24	Fe ²⁺	12.8*		10.17	200	75
25	Fe ²⁺	8.4*	7.72	200	14	Smectite
26	Fe ²⁺	7.5*	7.79	200	14	Smectite
Gel Si ₄ Al _{1,8} Fe _{0,2} O ₁₁						
29	Fe ³⁺	9.5	10.38	220	30	Zeolite
30	Fe ²⁺	9.7	11.0	220	13	Smectite + zeolite
31	Fe ²⁺	7.4	9.3	220	75	Smectite
32	Fe ²⁺	11.9*	7.3	220	75	Smectite + analcime
33	Fe ²⁺	7.4	9.5	240	14	Smectite
34	Fe ²⁺	6.6	5.0	220	75	Kaolinite
35	Fe ²⁺	12.4*	7.7	220	75	Smectite + kaolinite
Gel Si _{3,6} Al _{0,4} Fe ₂ O ₁₁						
36	Fe ³⁺	4.7	3.0	150	13	Akaganeite
37	Fe ³⁺	4.8	2.5	200	13	Akaganeite + kaolinite
38	Fe ³⁺	12.3*	10.2	200	13	Akaganeite
39	Fe ²⁺	10.2	10.5	150	13	Smectite
40	Fe ²⁺	10.2	10.2	200	13	Smectite + analcime
Gel Si _{3,4} Al _{0,6} Fe ₂ O ₁₁						
41	Fe ²⁺	8.7	9.7	200	13	Smectite
42	Fe ²⁺	8.7	9.3	220	13	Smectite
Gel Si _{3,4} Al _{0,8} Fe _{1,6} O ₁₁						
43	Fe ²⁺	9.8	10.8	200	13	Smectite
44	Fe ²⁺	9.8	9.9	220	13	Smectite

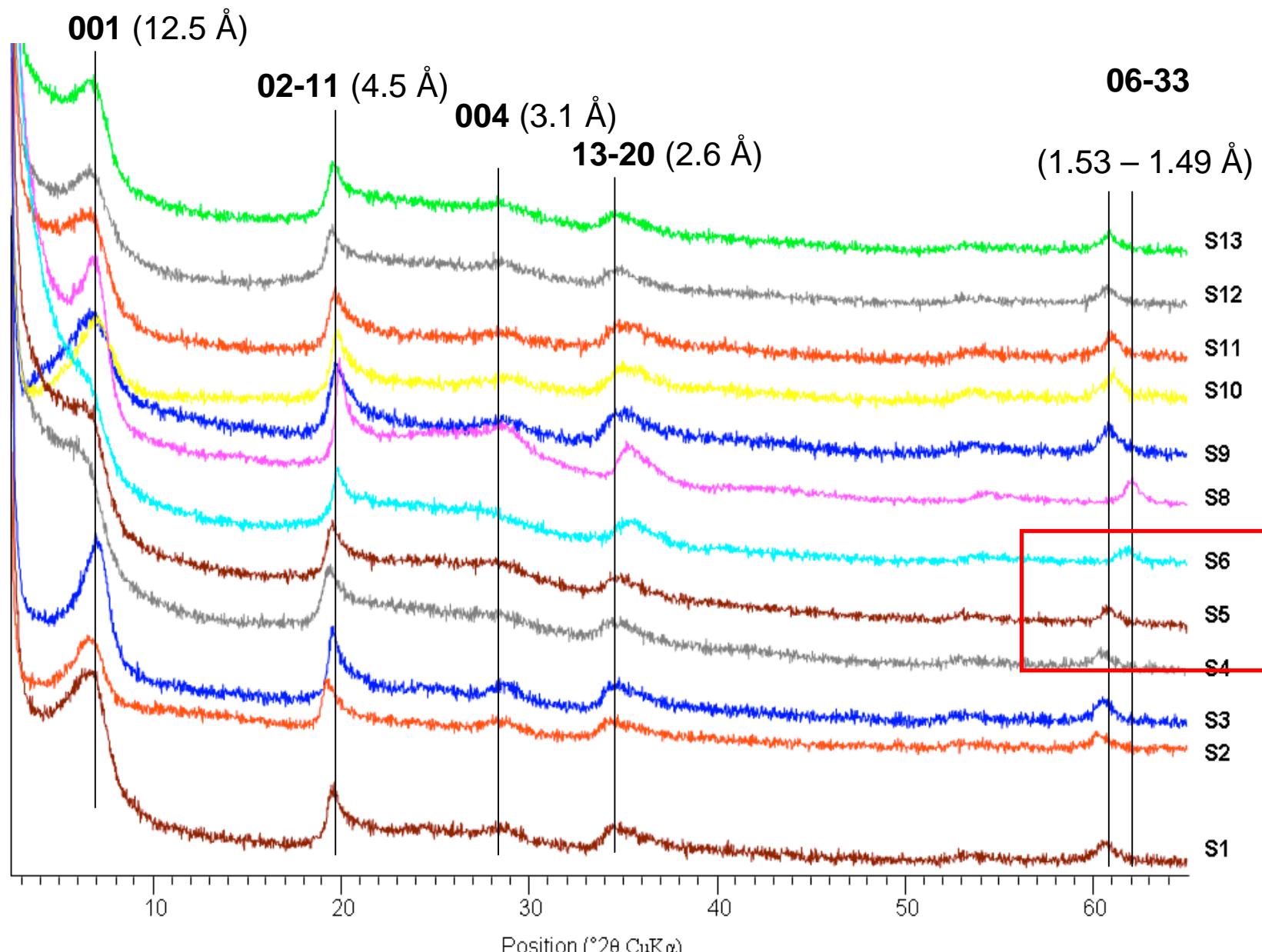
Successfull smectite syntheses

Sample	gel (Si/Al/Fe)	Temp. (°C)	Time (days)	FeCl ₃ /FeCl ₂	pH _i	pH _f
S1	4/0.2/1.8	150	30	Fe ³⁺	10.5	10.8
S2	4/0.2/1.8	170	30	Fe ³⁺	10.5	10.8
S3	4/0.2/1.8	200	13	Fe ³⁺	10.5	10.7
S9	3.6/0.4/2	150	13	Fe ²⁺	10.2	10.5
S4	4/0.4/1.6	200	75	Fe ²⁺	10.3	10.7
S10	3.4/0.6/2	200	13	Fe ²⁺	8.7	9.7
S11	3.4/0.6/2	220	13	Fe ²⁺	8.7	9.3
S12	3.6/0.8/1.6	200	13	Fe ²⁺	9.8	10.8
S13	3.6/0.8/1.6	220	13	Fe ²⁺	9.8	9.9
S5	4/1/1	200	75	Fe ²⁺	8.4	10.4
S6	4/1/1	200	75	Fe ²⁺	6.3	6.7
S8	4/1.8/0.2	220	75	Fe ²⁺	7.4	9.3

XRD powder patterns



XRD powder patterns



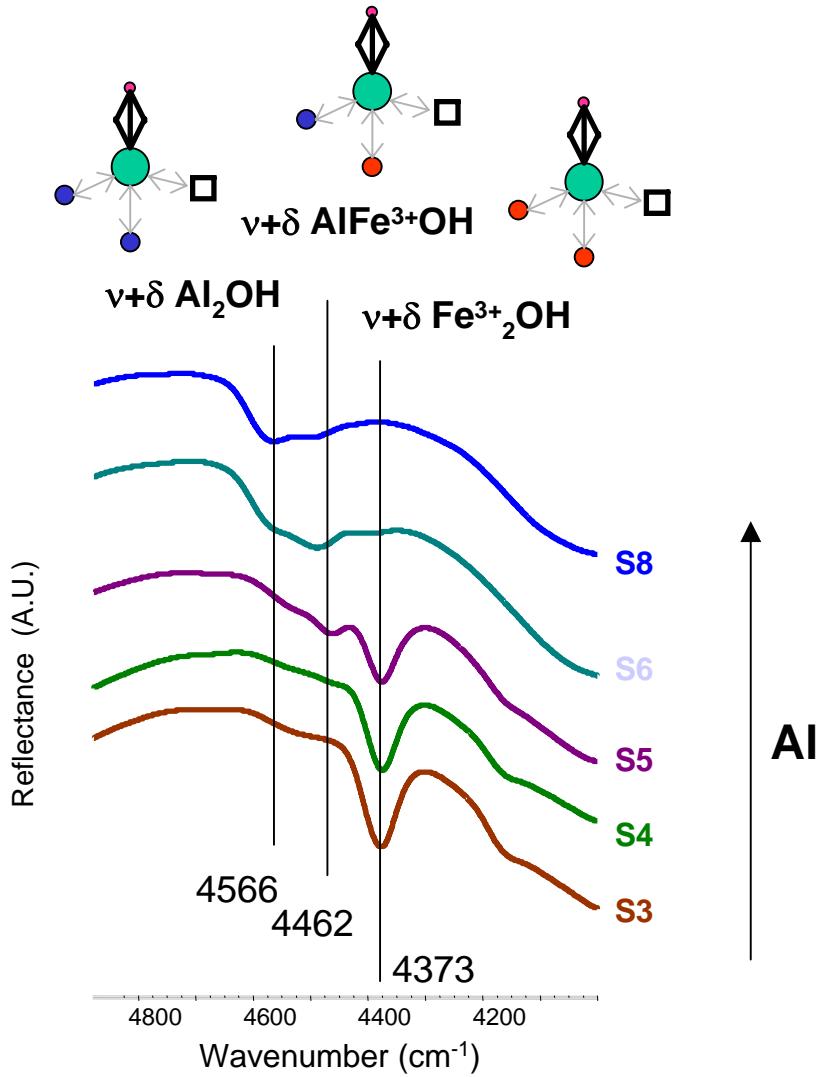
Successfull smectite syntheses

Sample	gel (Si/Al/Fe)	Temp. (°C)	Time (days)	FeCl_3 $/\text{FeCl}_2$	pH _i	pH _f
S1	4/0.2/1.8	150	30	Fe^{3+}	10.5	10.8
S2	4/0.2/1.8	170	30	Fe^{3+}	10.5	10.8
S3	4/0.2/1.8	200	13	Fe^{3+}	10.5	10.7
S9	3.6/0.4/2	150	13	Fe^{2+}	10.2	10.5
S4	4/0.4/1.6	200	75	Fe^{2+}	10.3	10.7
S10	3.4/0.6/2	200	13	Fe^{2+}	8.7	9.7
S11	3.4/0.6/2	220	13	Fe^{2+}	8.7	9.3
S12	3.6/0.8/1.6	200	13	Fe^{2+}	9.8	10.8
S13	3.6/0.8/1.6	220	13	Fe^{2+}	9.8	9.9
S5	4/1/1	200	75	Fe^{2+}	8.4	10.4
S6	4/1/1	200	75	Fe^{2+}	6.3	6.7
S8	4/1.8/0.2	220	75	Fe^{2+}	7.4	9.3

1.53 Å

1.49 Å

FTIR data (NIR)



Relevance of clay synthesis in environmental studies

Conclusion

- To determine the experimental conditions which led to mineral crystallization (in very simplified systems)
 - ↳ to constrain possible conditions of formation for those minerals

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to use them for in situ experiments