Rapid changes of soil clay mineralogy: from qualitative to quantitative description

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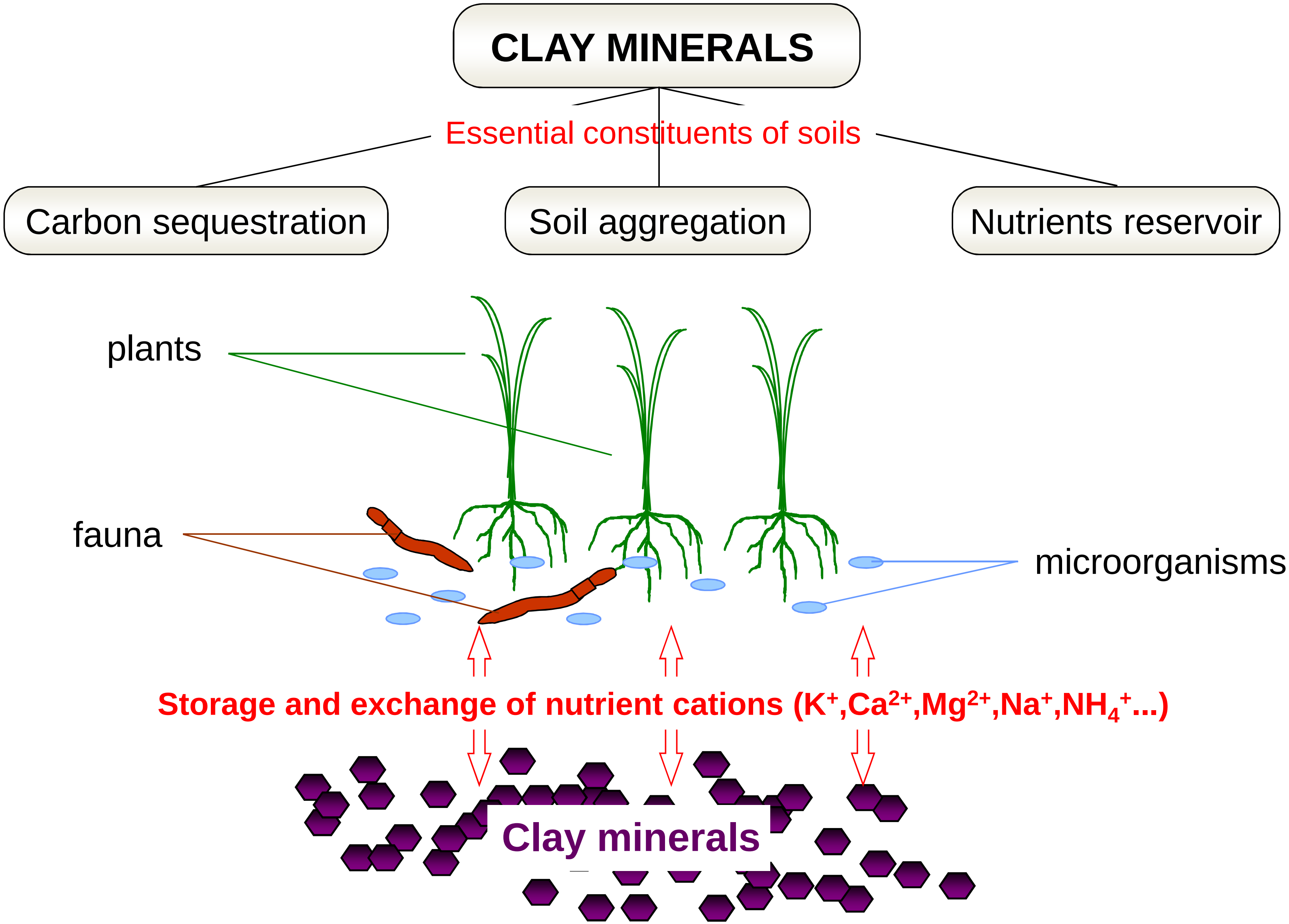
- INTRODUCTION
- QUALITATIVE CLAY MINERALOGY DESCRIPTION
- DECOMPOSITION OF XRD PATTERNS AND LIMITS
- TOWARDS QUANTIFICATION: XRD PATTERN MODELING
- INFRA-MICROMETRIC FRACTIONATIONS
- INSIGHTS OF MODELING AND LIMITS
- CONCLUSIONS

Soils evolves but rates are poorly known

Known rates

- Wilkinson et al. (2005): average age of soils = 10^4 to 10^5 years
- Burt & Alexander (1996) : O-horizon formed in 38 y and a E/Bs layering within 70 y
- Cornu et al. (1995): kaolinite dissolution within 6 months
Calvaruso et al. (2009): clay transformation in the rhizosphere in few months

- Soil formation
- Processes
- Mecanisms

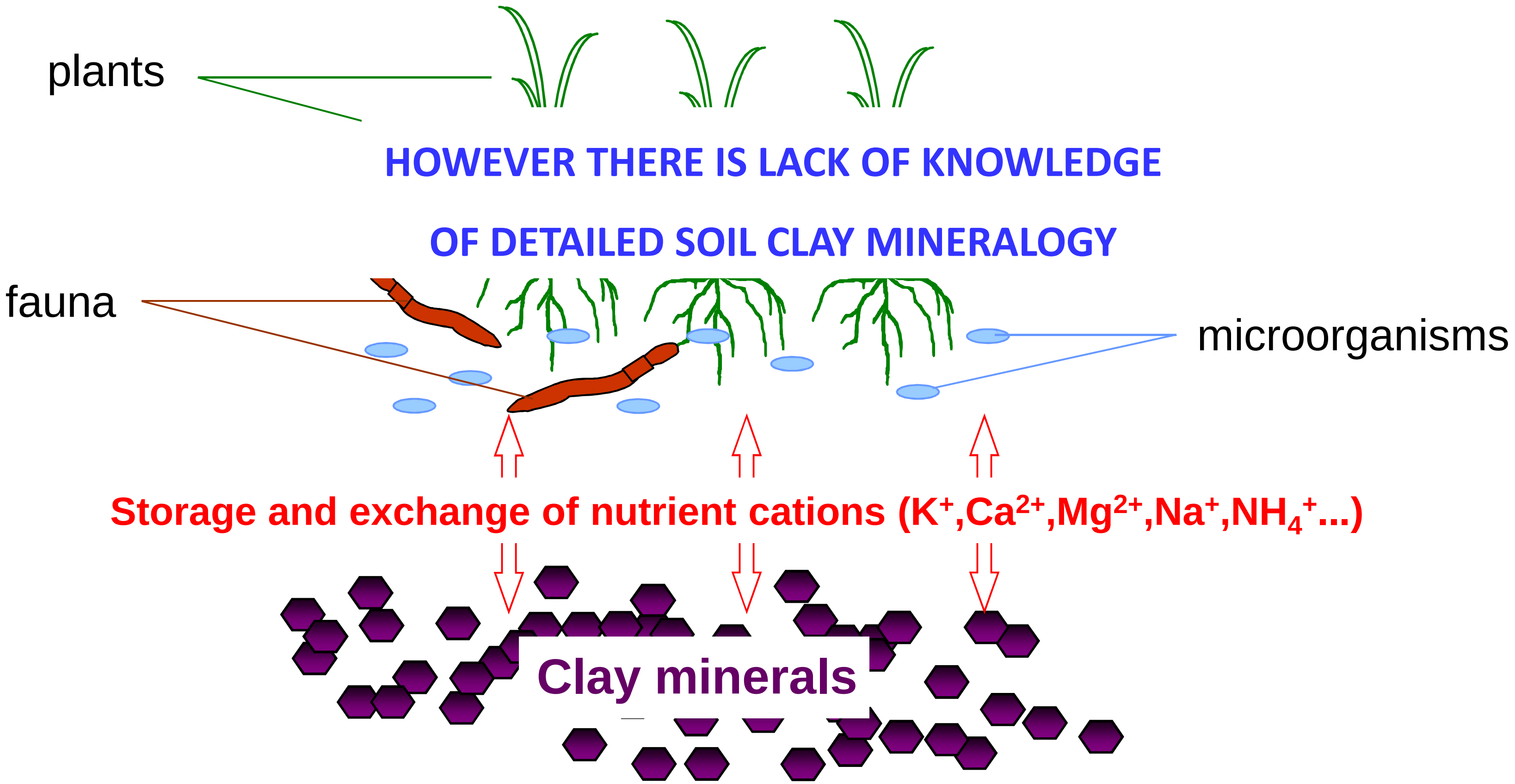

CLAY MINERALS
Essential constituents of soils
Carbon sequestration
Soil aggregation
Nutrients reservoir
plants
fauna
microorganisms
Storage and exchange of nutrient cations (K^+,Ca^{2+},Mg^{2+},Na^+,NH_4^+...)
Clay minerals

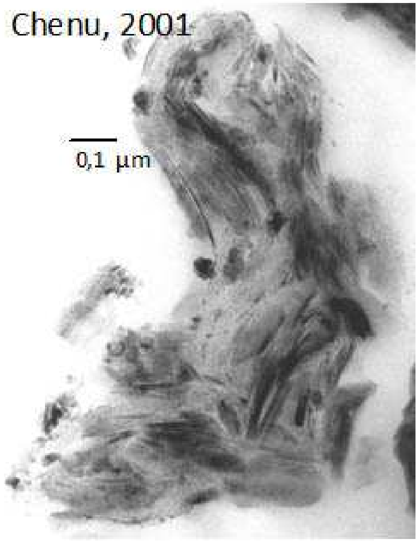
CLAY MINERALS

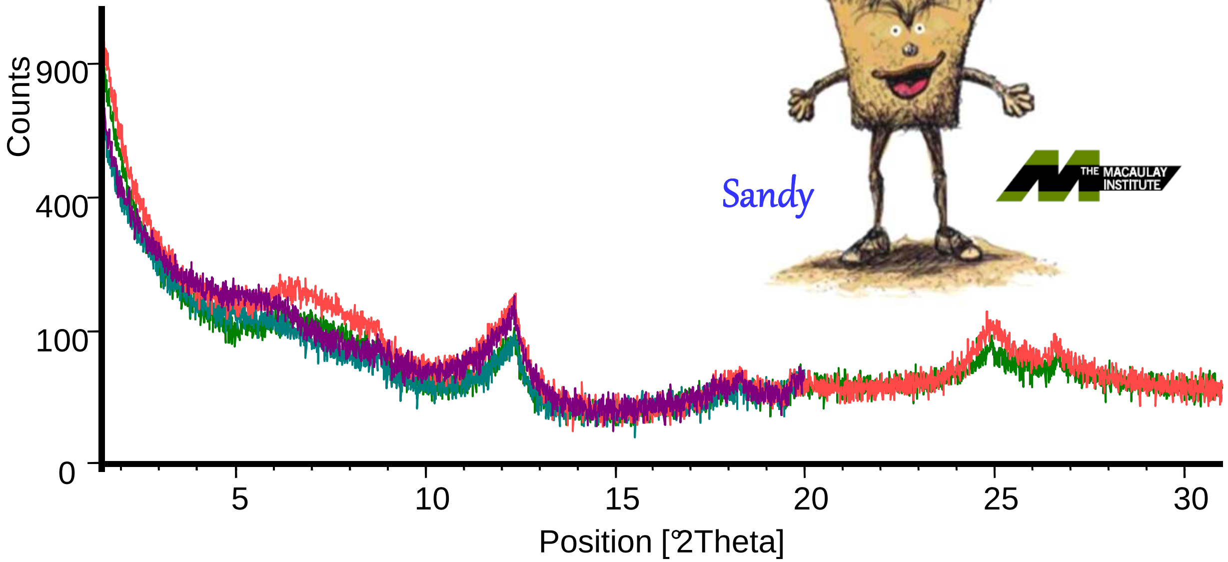
Essential constituents of soils

- Carbon sequestration
- Soil aggregation
- Nutrients reservoir

HOWEVER THERE IS LACK OF KNOWLEDGE OF DETAILED SOIL CLAY MINERALOGY




Chenu, 2001
0,1 µm


Counts
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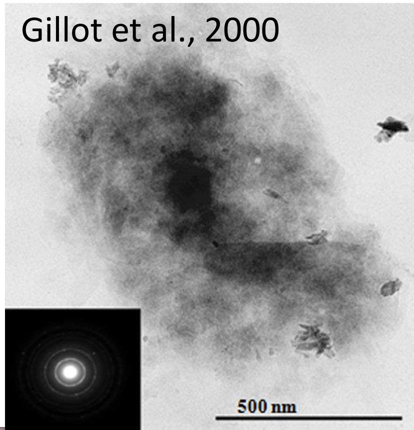
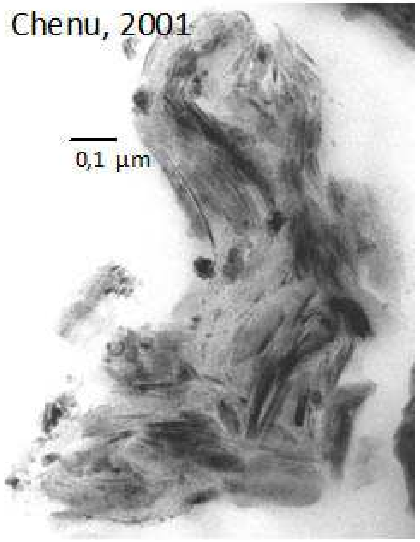
25
30
Position [°2Theta]

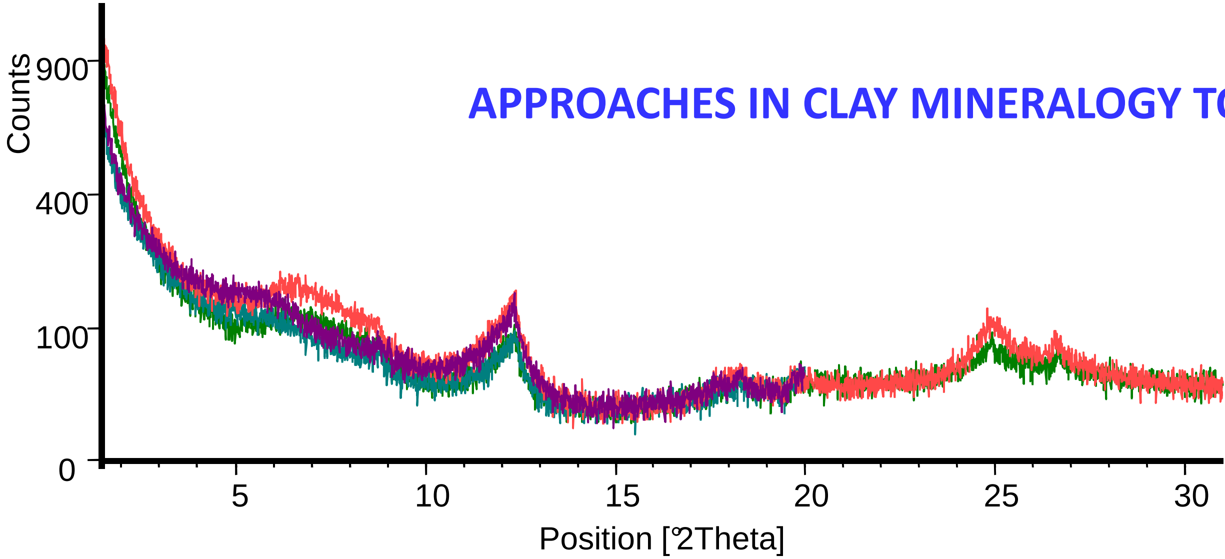

Soil or Dirt ?
Sandy
THE MACAULAY INSTITUTE

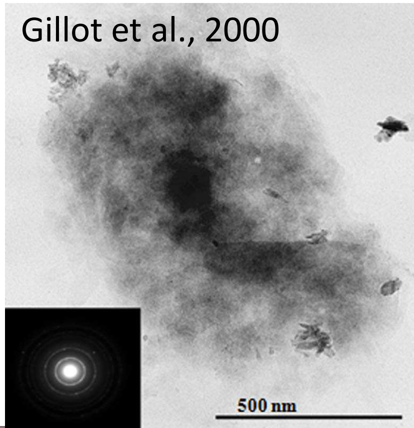

Gillot et al., 2000
500 nm



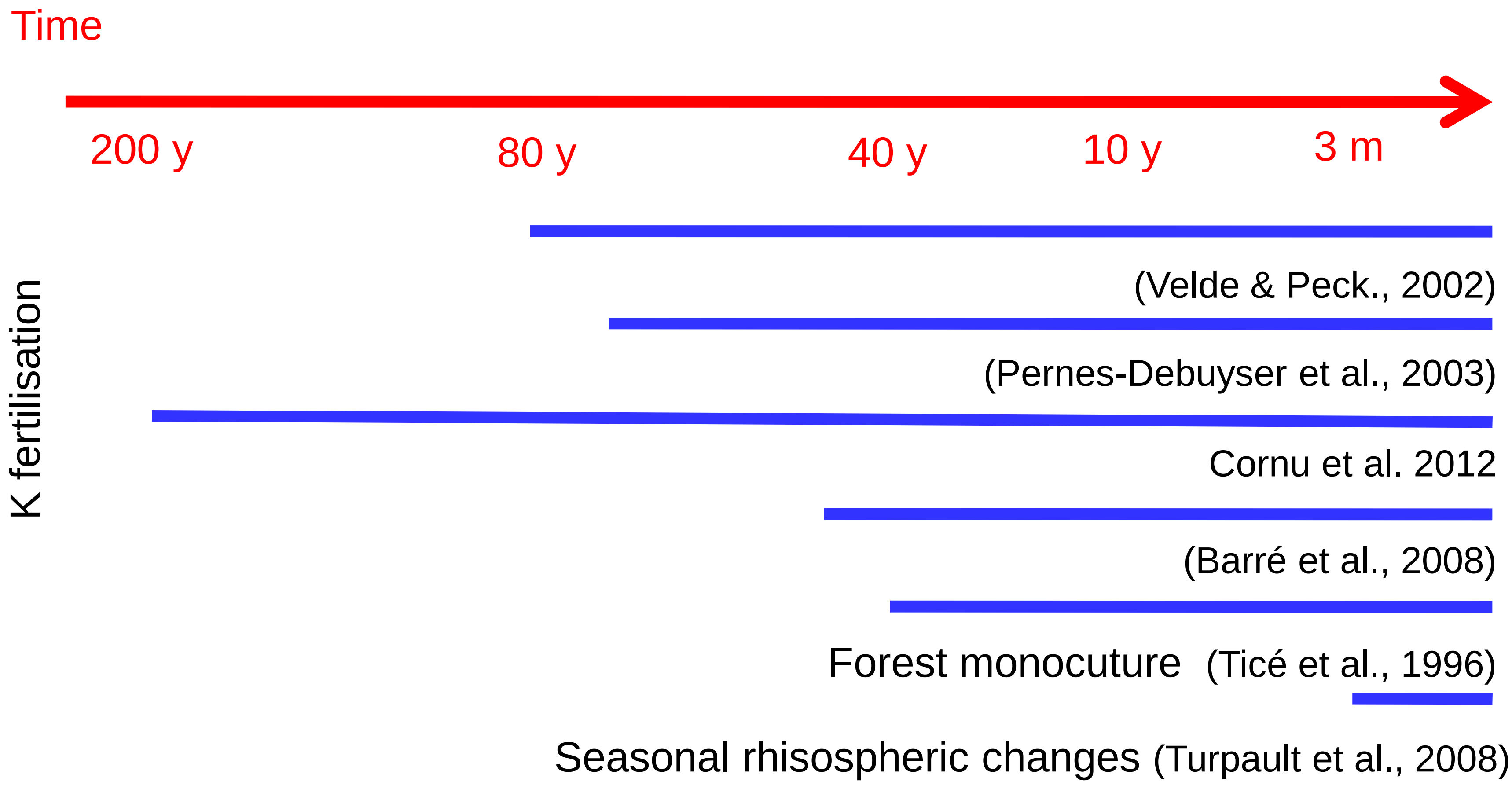
CLAY EVOLUTION STUDIED ON LONG TERM SCALE

APPROACHES IN CLAY MINERALOGY TOO QUALITATIVE

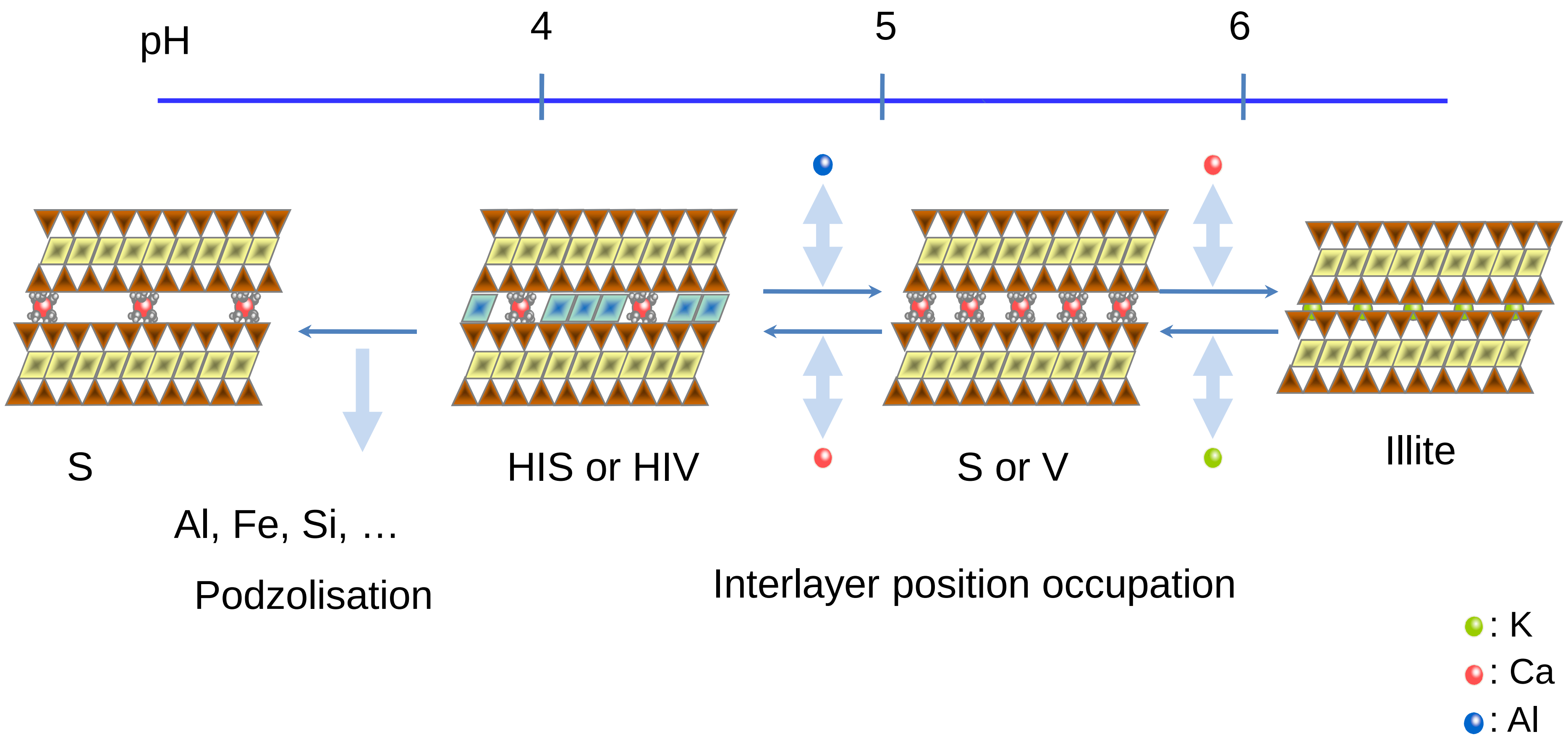




Rapidity and reversibility of clay mineral evolution



Short time clay mineral evolutions mainly concern interlayer cations exchanges



Key role of 2:1 clay minerals even in small amounts

- Progress in XRD treatment allows better identification of clay minerals and semi-quantification

- Studies on soil sequences impacted by human activities provide an oportunity to study short time scale evolution

METHOD CURRENTLY EMPLOYED

CLAY FRACTION EXTRACTION (with or without OM destruction and dispersion)

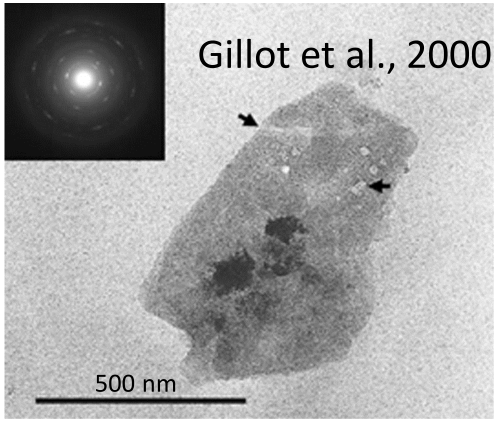
CHEMICAL CHARACTERISATION OF THIS FRACTION (elemental composition, CEC, SSA)

X-Ray DIFFRACTION OF ORIENTED SLIDES AND POWDERS

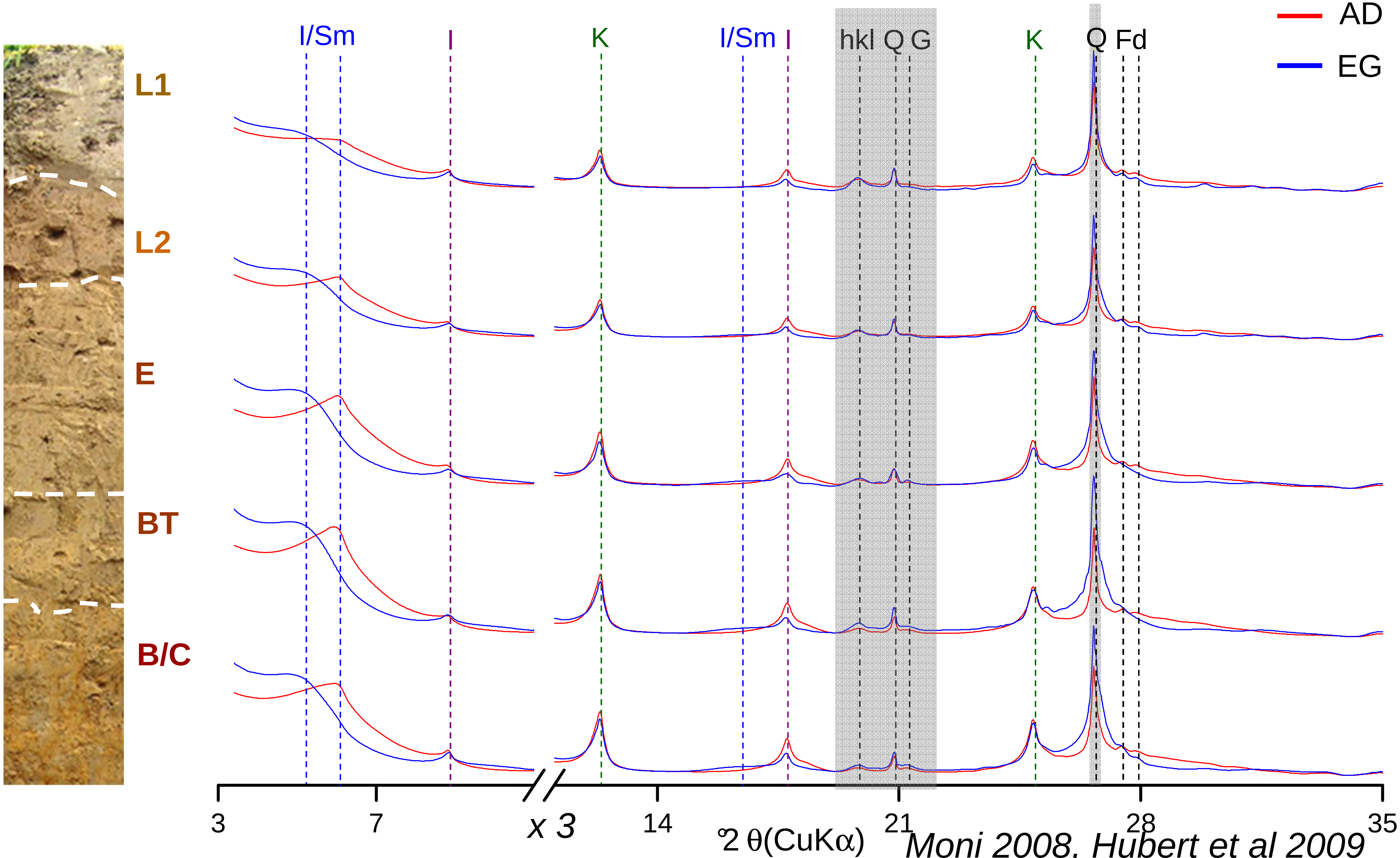
< 0.1 OR 0.2 µm FRACTIONATION

XRD PATTERNS DECOMPOSTION (00ℓ OU 060)

CALCULATION WITH NEWMOD © Reynolds



< 2 µm size fraction - *Luvisol Versailles France* - Ca saturation



Moni 2008, Hubert et al 2009

Experimental XRD patterns
< 2µm , oriented slides

Qualitative description

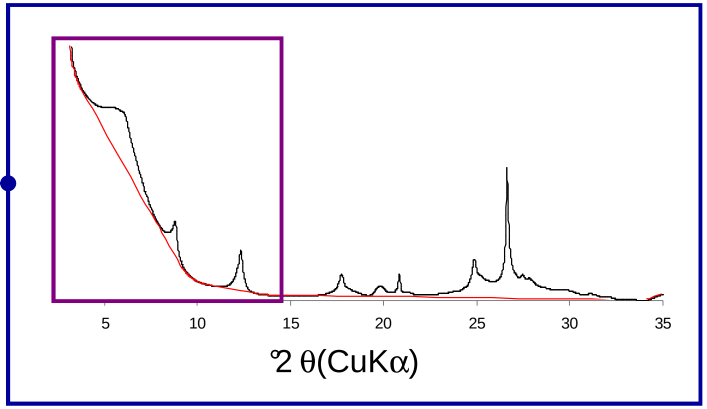
Usual treatments
Ca^{2+} & Ca^{2+}/EG saturations

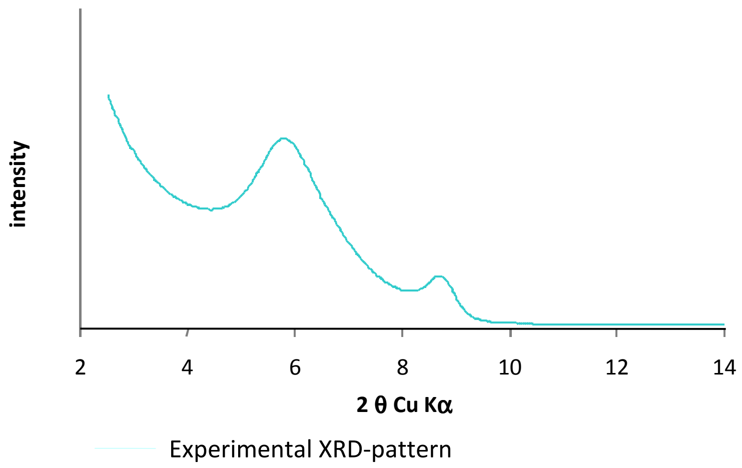
Additional treatments
Other saturations (K^{+},Mg^{2+}), Heating

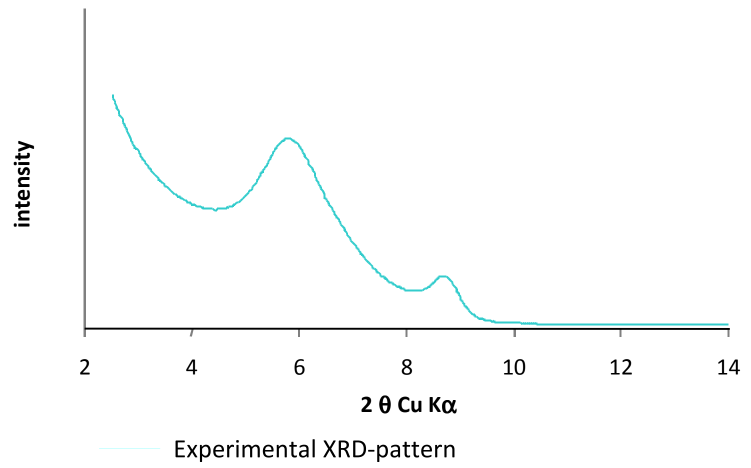
→ **Kaolinite, illite, MLM illite/smectite**

Diffractogram treatment

Decomposition
Curve fitting of XRD patterns
FWHM, maximum intensity,
location of Gaussian curves




intensity
2
4
6
8
10
12
14
2 θ Cu Kα
Experimental XRD-pattern


intensity
2
4
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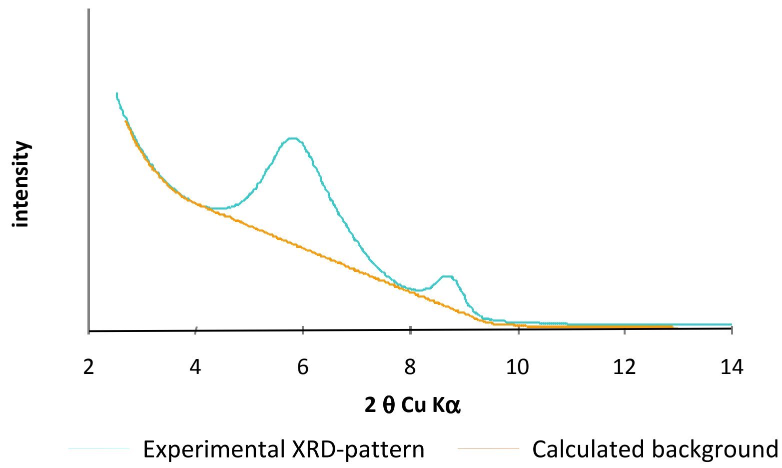
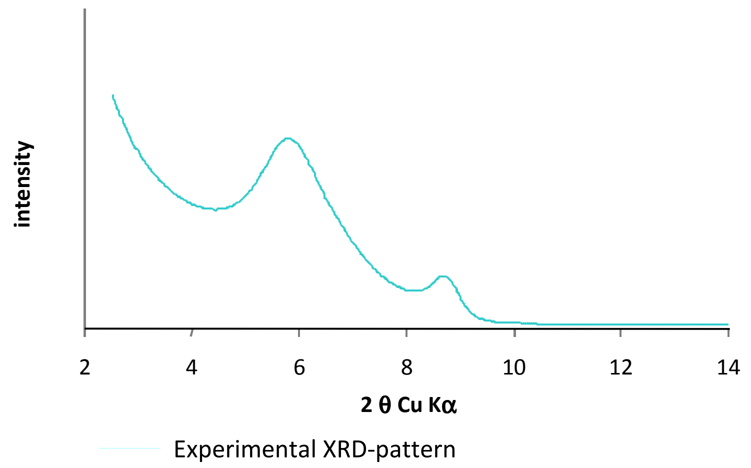
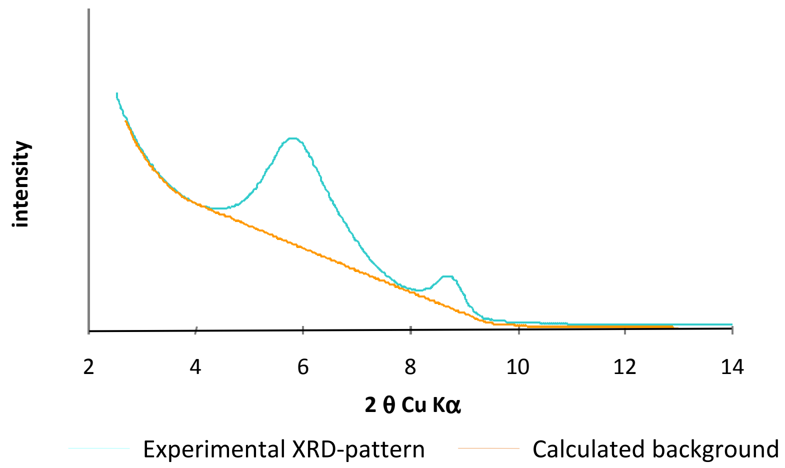
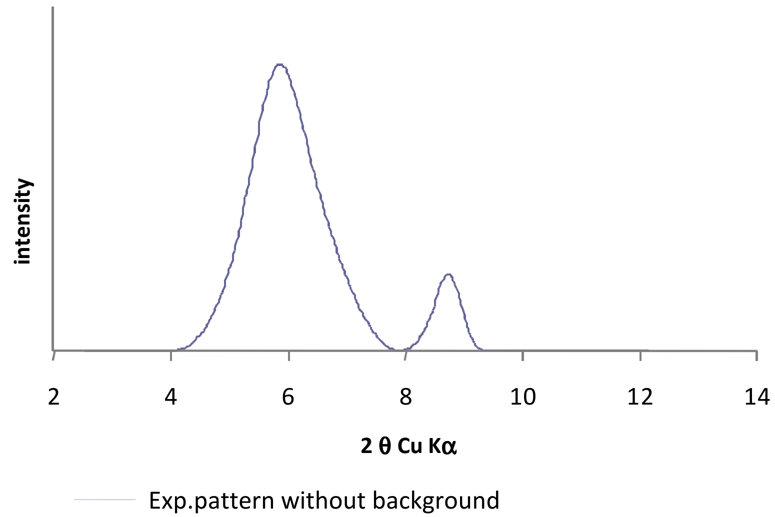
8
10
12
14
2 θ Cu Kα
Experimental XRD-pattern

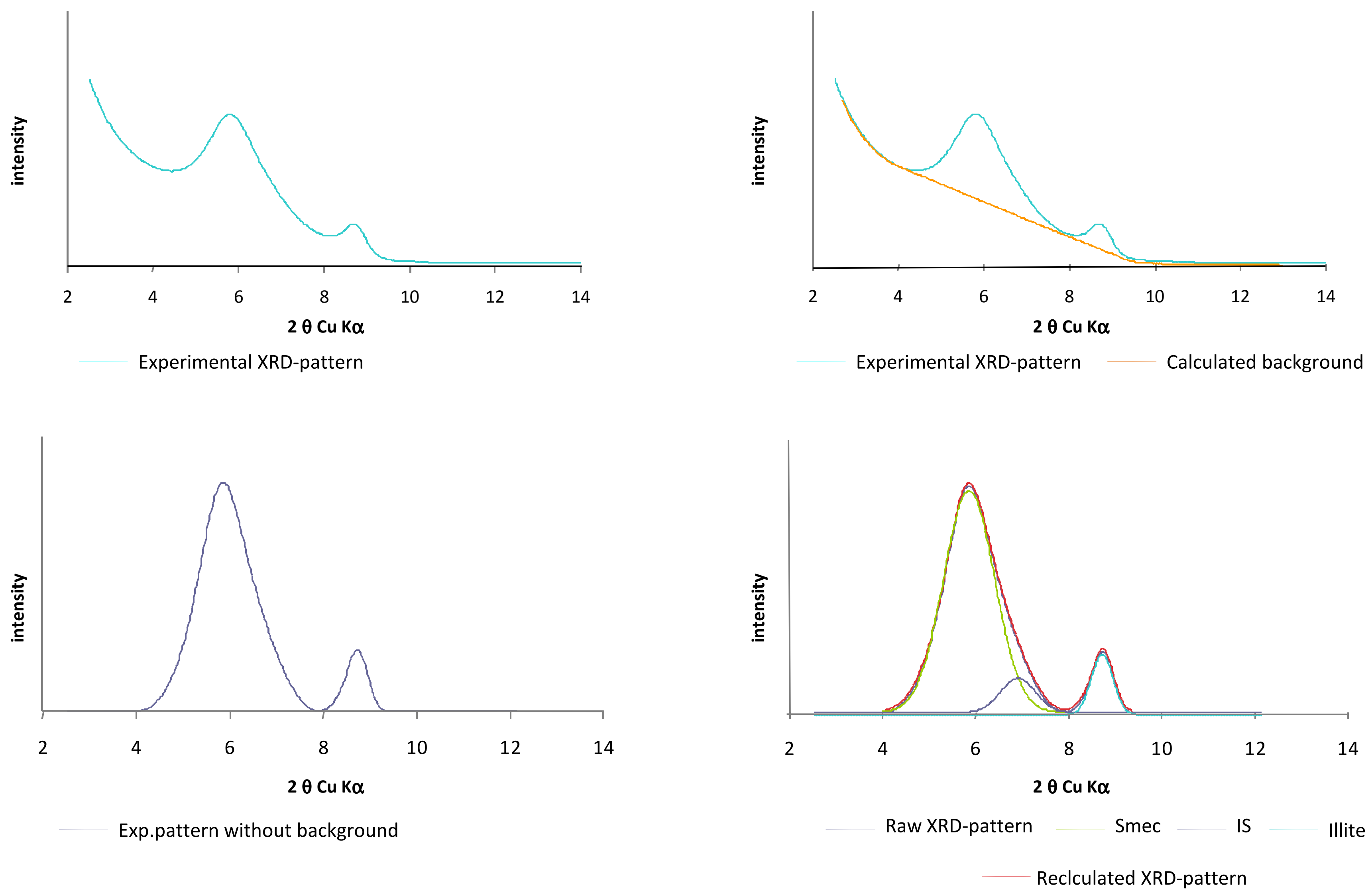

intensity
2
4
6
8
10
12
14
2 θ Cu Kα
Experimental XRD-pattern
Calculated background


intensity
2
4
6
8
10
12
14
2 θ Cu Kα
Experimental XRD-pattern

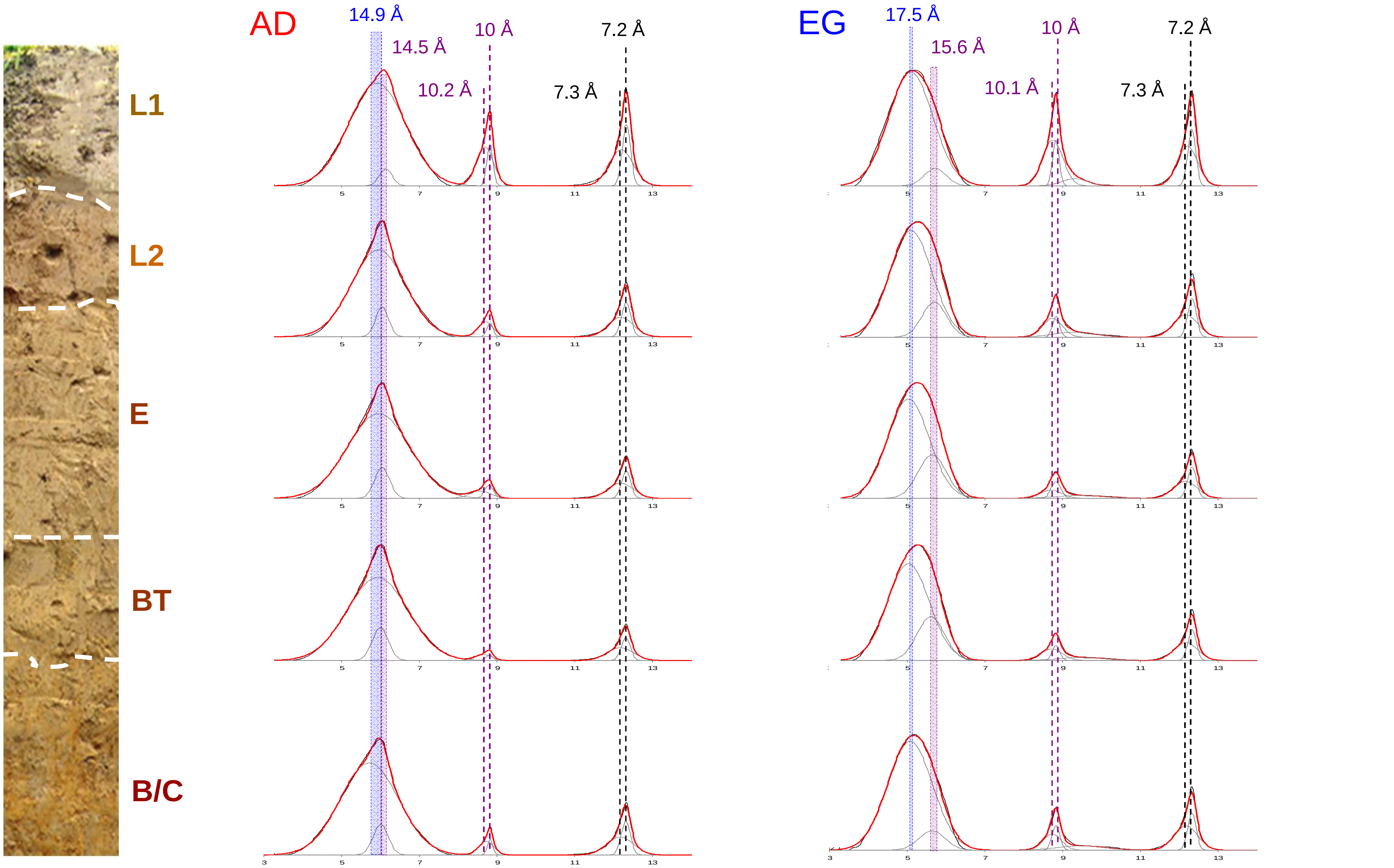

intensity
2
4
6
8
10
12
14
2 θ Cu Kα
Experimental XRD-pattern
Calculated background


intensity
2
4
6
8
10
12
14
2 θ Cu Kα
Exp.pattern without background

PATTERN DECOMPOSITION



PATTERN DECOMPOSITION



Experimental XRD patterns
< 2µm , oriented slide

Qualitative description

- **Usual treatments** — *Ca^{2+} & Ca^{2+}/EG saturations*
- **Additional treatments** — *Other saturations (K^{+},Mg^{2+}), Heating*

→ **Kaolinite, illite,**
MLM illite/smectite, (chlorite)

Diffractogram treatment

Decomposition
Curve fitting of XRD patterns
FWHM, maximum intensity,
position of Gaussian curves

→ **2 kaolinites (well & poor crystallised)**
2 illites (WCI & PCI)
2 MLMs (illite/smectite?)

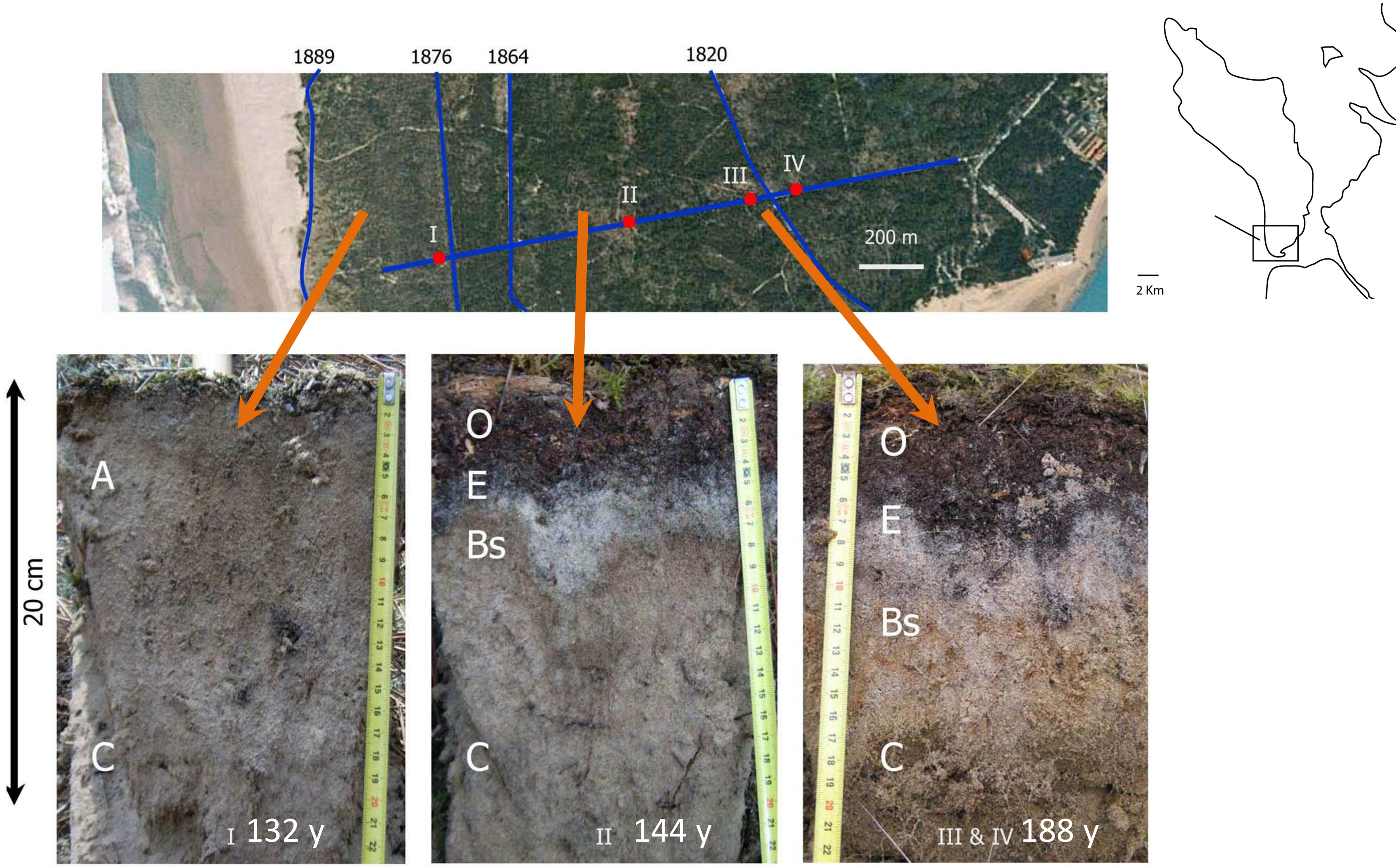
MLMs identification

One-Dimensional XRD pattern calculation
Newmod (2 layer types)
visual comparison

M. Pernes et al. 2003

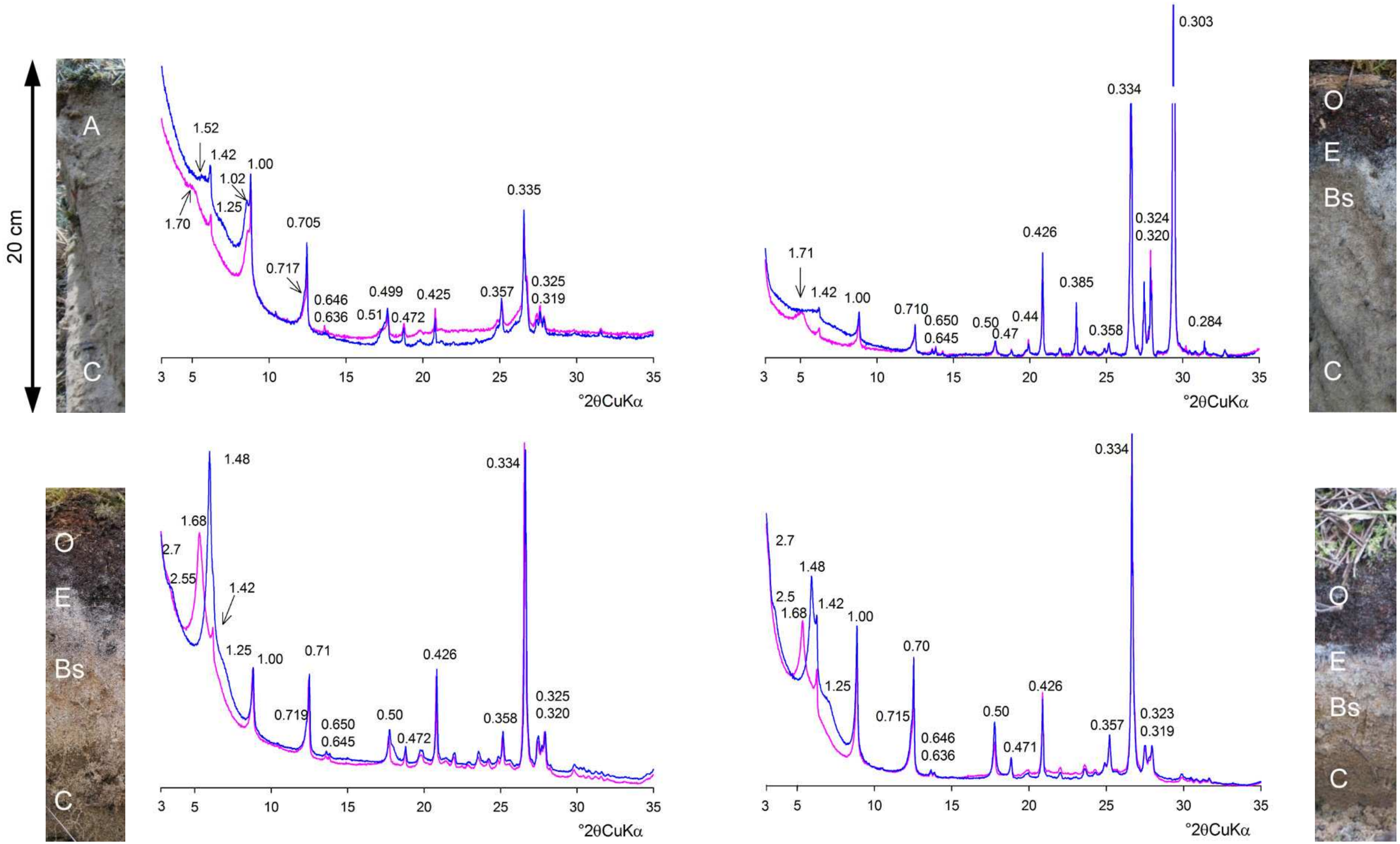
→ **Illite/smectite R0 50/50 1 < CSDS < 4**
Illite/smectite R0 50/50 3 < CSDS < 6

CHRONOSEQUENCE SPODOSOLS IN OLERON ISLAND FRANCE



(Caner et al. 2010 JPNSS)

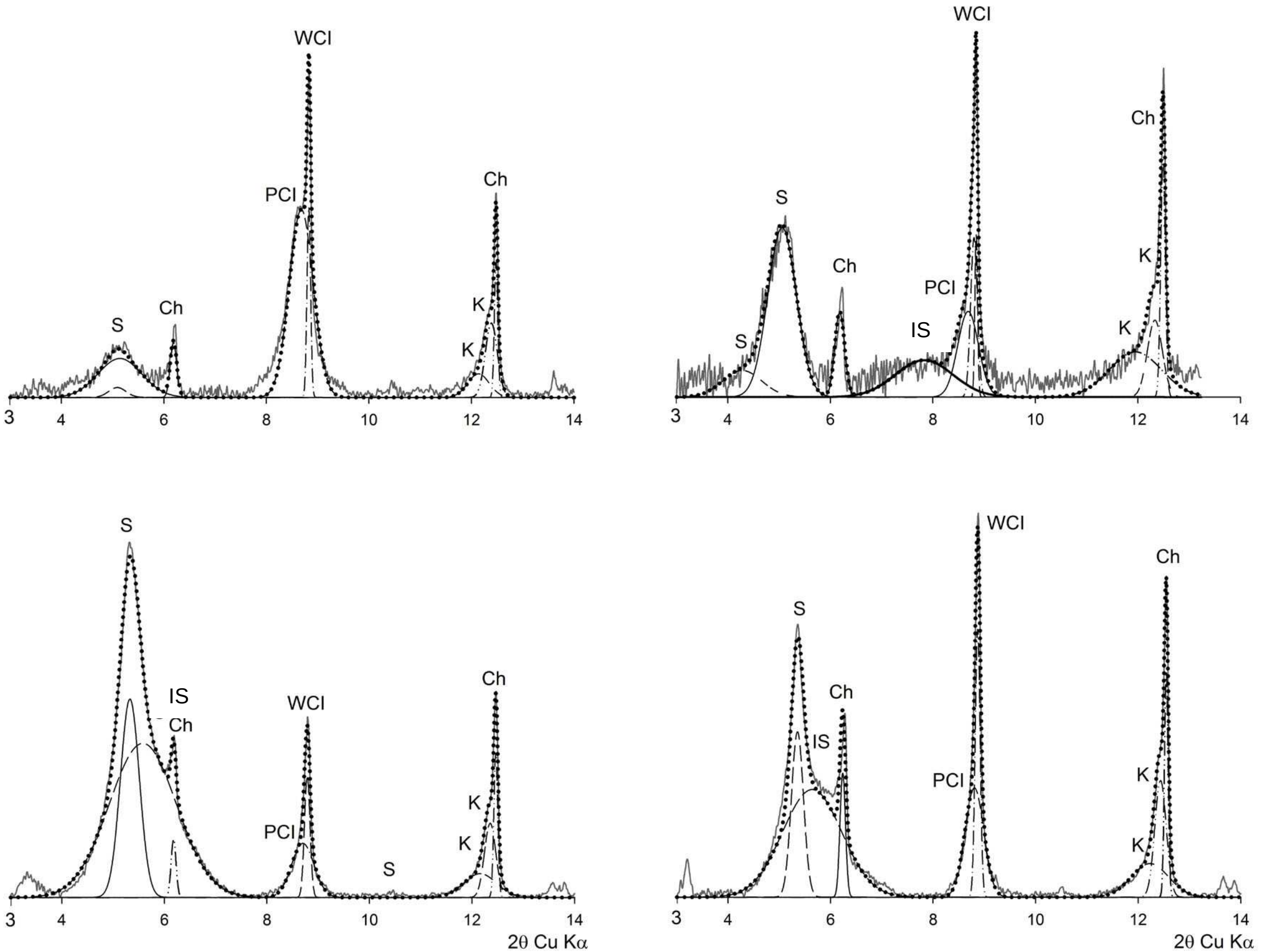
CHRONOSEQUENCE SPODOSOLS IN OLERON ISLAND FRANCE



(Caner et al. 2010 JPNSS)

CHRONOSEQUENCE SPODOSOLS IN OLERON ISLAND FRANCE

XRD patterns decomposition - EG



(Caner et al. 2010 JPNSS)

CONTRIBUTION OF DIFFERENTS SPECIES IN DIFFRACTED INTENSITY

Profil	Age parent material	pH eau	Chlorite	Illite (WCI)	Illite (PCI)	Illite/ Smectite	Smectite
I	132 y	6,2	0,39	0,40	0,11	0	0,10
II	144 y	5,1	0,46	0,12	0,12	0,06	0,24
II	144 y	5,2	0,21	0,09	0,10	0,26	0,34
IV	188 y	4,3	0,35	0,14	0,16	0,14	0,21

Chlorite : ± stable

Illite PCI → Illite/smectite → smectite

Illite WCI → Illite/smectite R1 → smectite

Formation of smectite in few tenth of years

Favorable case favorable to apply decomposition

BUT : IT IS NOT QUANTIFICATION BUT COMPARISON

(Caner et al. 2010 JPNSS)

LIMITS OF XRD PATTERNS DECOMPOSITION FOR SOIL SAMPLES

IDENTFICATION OF SPECIES WITH LOW CSDS

- REMOVAL OF BACKGROUND
- DISCRETE SPECIES
- MOSTLY MIXED LAYERS (MLMs)

DOMINANT AND CHARACTERISTIC SPECIES IN SOILS

→ RESTRICTED TO HOMOGENOUS PARENT MATERIAL

→ SMALL TRANSFORMATION HARDLY EVIDENCED

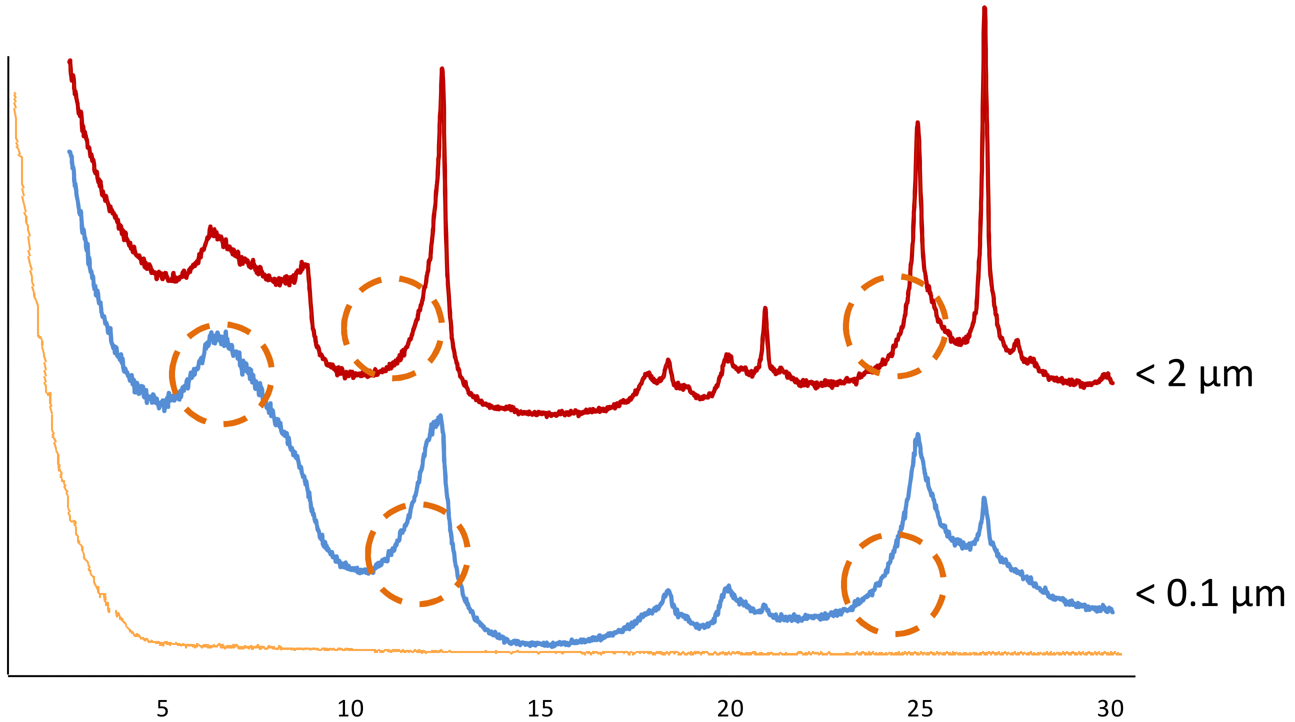
→ IMPOSSIBLE TO « QUANTIFY » THOSE TRANSFORMATIONS

HOW TO IMPROVE SOIL CLAY MINERALS IDENTIFICATION AND QUATIFICATION?

METHODS RECENTLY DEVELOPED

Position and intensity of the peaks **: not sufficient**

Important information : **diffraction profile**



XRD patterns of particles collected at the outlet of a drain

METHODS RECENTLY DEVELOPED

Position and intensity of the peaks : not sufficient

Important information : diffraction profile

To get the information contained in the full diffraction profile:

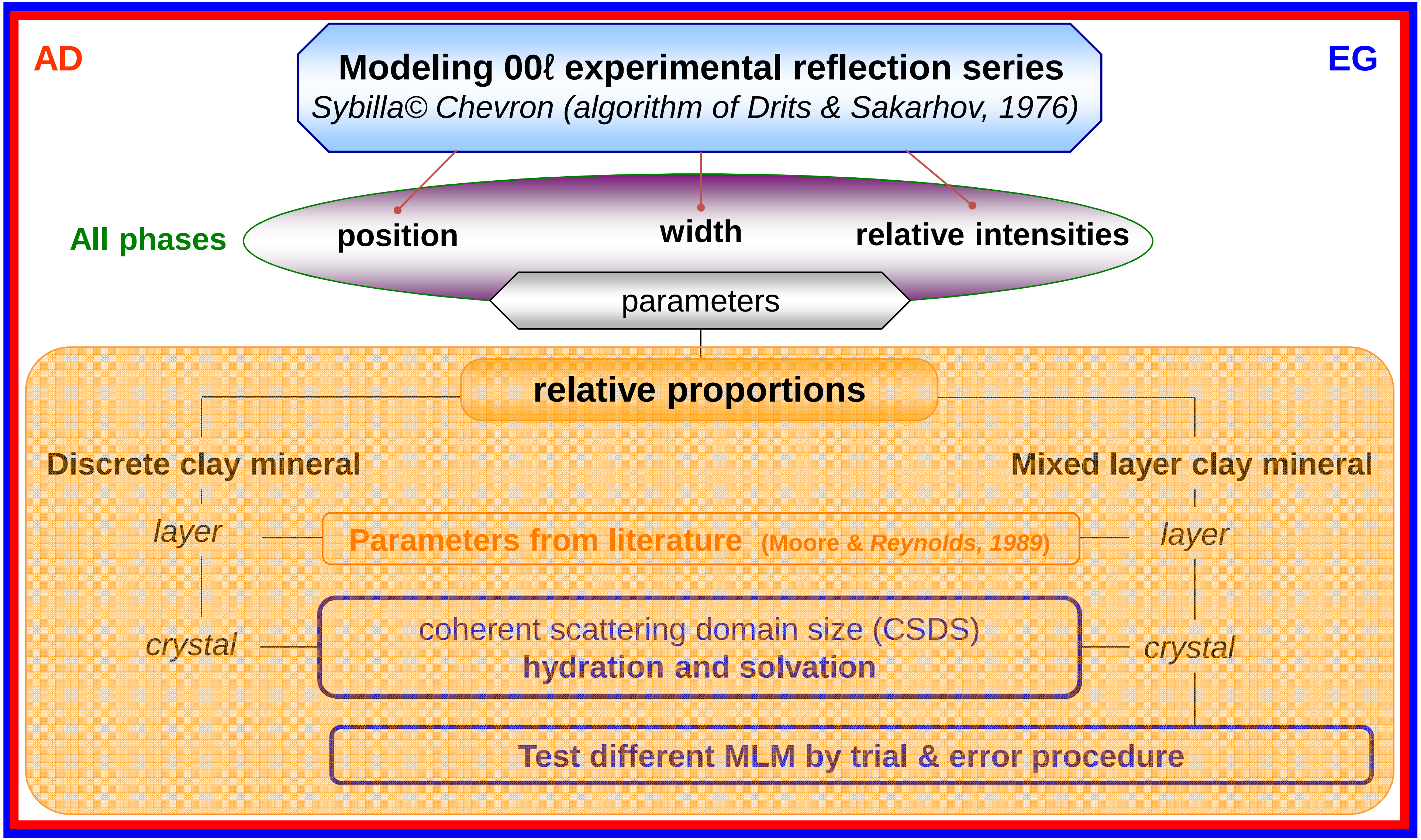
Fitting of the experimental pattern with a 'modeled' pattern obtained with programs calculating 00ℓ peak diffraction profiles

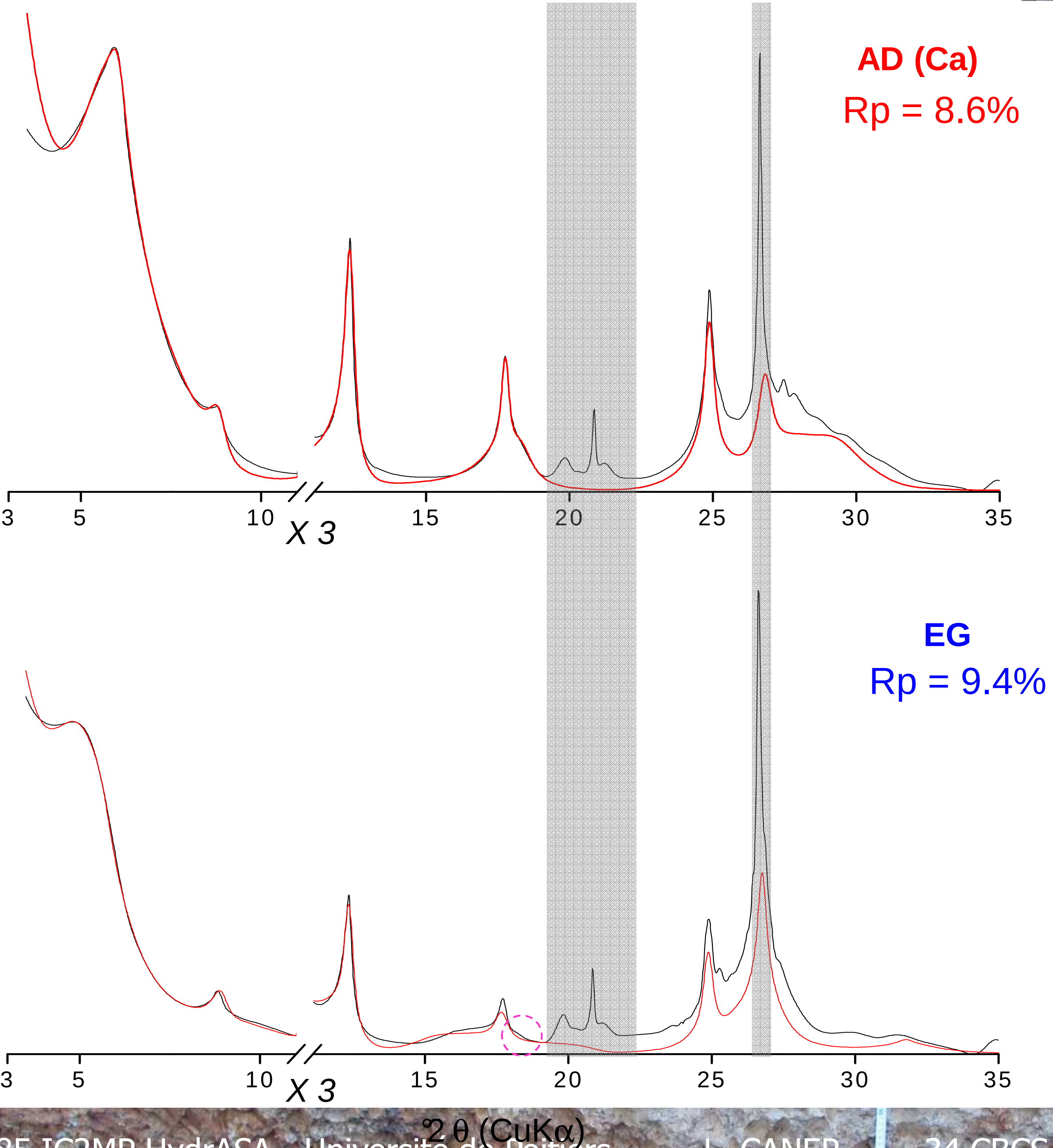
Record high quality diffractograms

Use of Sybilla © CHEVRON Petrol Corporation

Adaptating this method developped for diagenesis burial to soils - Hubert (2008) Hubert et al. (2009)

Direct comparison of experimental and calculated XRD patterns





Kaolinite (**K^W**)
(CSDS = 19)

Kaolinite (**K^B**)
(CSDS = 5)

Illite (**I**)
(CSDS = 17)

Smectite (**Sm**)
(CSDS = 3)

Illite/smectite (**MLM I/S**)
(R0, 63/37, CSDS = 6)

Chlorite/smectite (**MLM C/S**)
(R0, 52/48, CSDS = 8)

Proposed new clay species

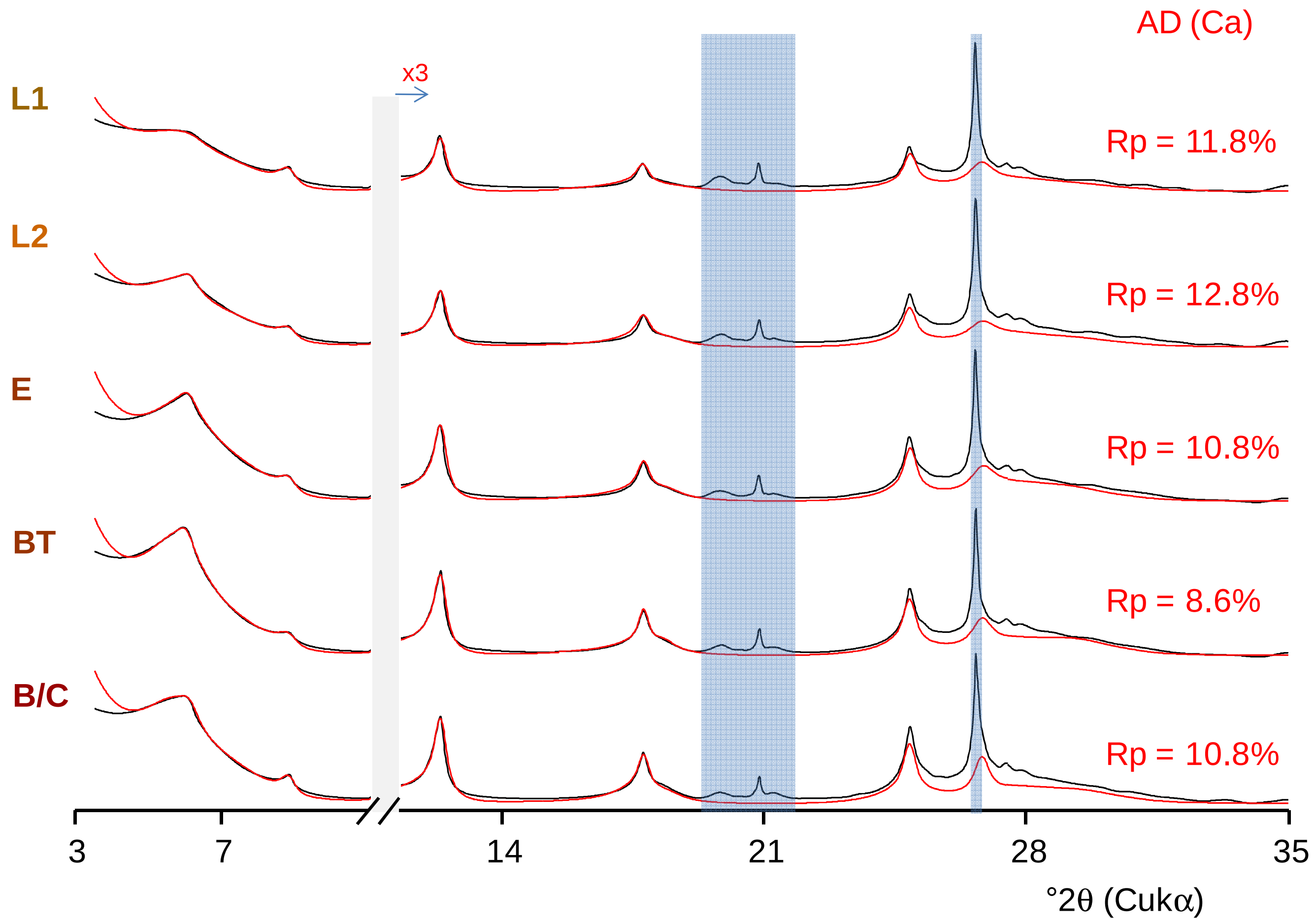
6 species with 3 MLMs

(Hubert et al. 2009 EJSS)

METHODS RECENTLY DEVELOPED

Fitting of the < 2 µm fraction of the B horizon of a Luvisol – INRA Versailles France

Use of a same model for all horizons



(Hubert et al. 2009 EJSS)

METHODS RECENTLY DEVELOPED

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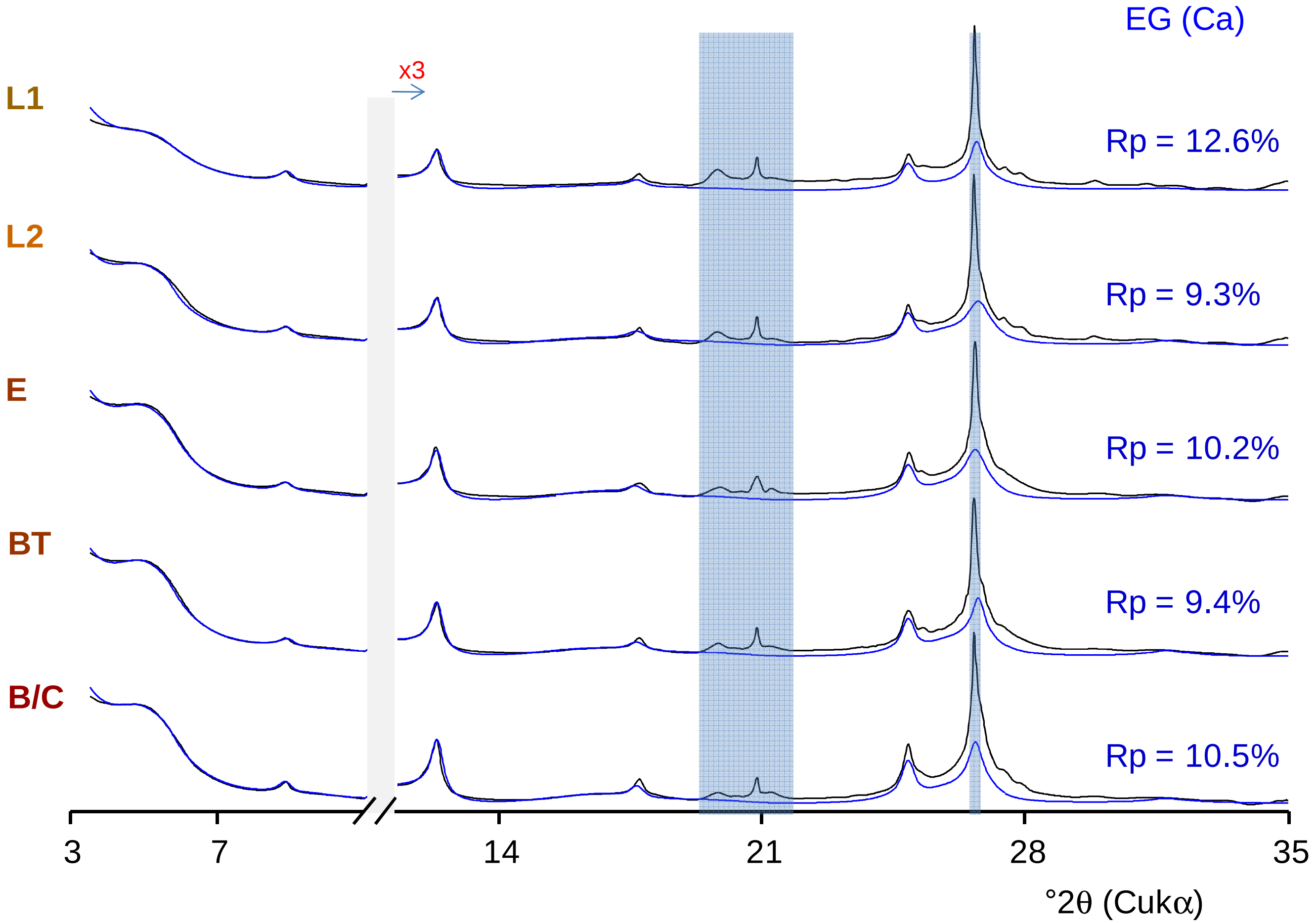


(Hubert et al. 2009 EJSS)

METHODS RECENTLY DEVELOPED

What are the data obtained?

Structural parameters of the minerals used in the fitting

Species	Horizon	L1	E	BT
Illite	CSDS	18	18	18
	I/S2w	98/2	97/3	97/3
	I/S2g	98/2	97/3	97/3
kaolinite	CSDS	20	20	20
kaolinite	CSDS	6	6	6
smectite	CSDS	3	3	3
	S1w/S2w	33/67	47/53	36/64
	S1g/S2g	21/79	17/83	24/76
Illite/smectite (R0)	CSDS	9	6	6
	I/S1w/S2w	63/6/31	63/11/26	63/13/24
	I/S1g/S2g	57/13/30	63/3/34	63/8/29
chlorite/smectite (R0)	CSDS	9	6	6
	Ch/S1w/S2w	62/13/25	52/6/42	52/2/46
	Ch/S1g/S2g	62/0/38	52/6/42	52/0/48

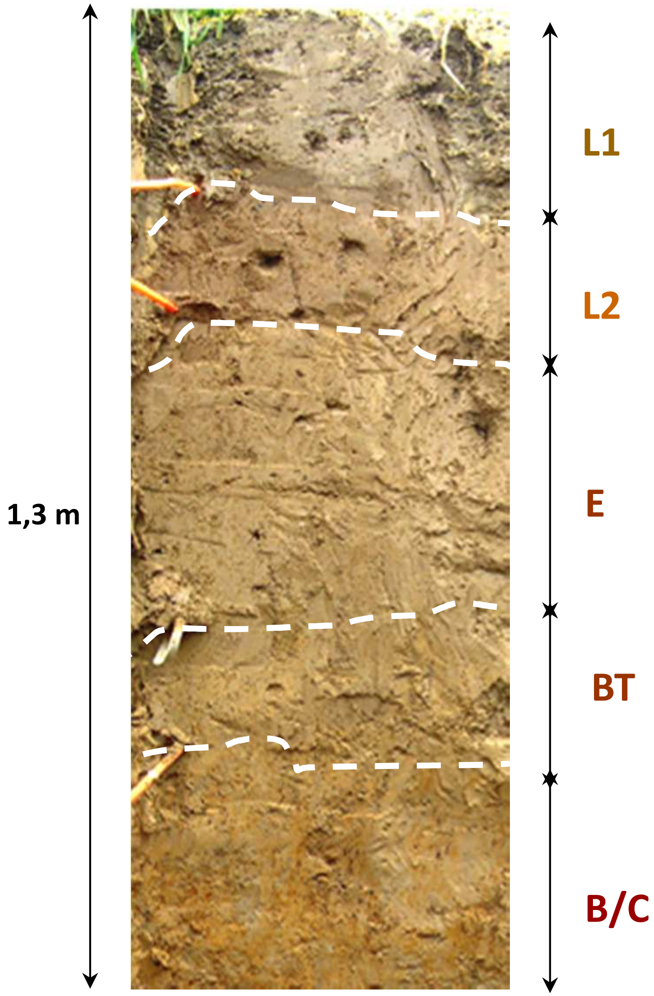
Homogenous clay mineral assemblage for the profile

(Hubert et al. 2009 EJSS)

METHODS RECENTLY DEVELOPED

What are the data obtained?

Relative proportions of the different clay minerals in the complex assemblage



	K^W	K^B	I	Sm	MLM C/S	MLM I/S
L1	9	10	18	**18**	7	38
L2	9	9	21	**27**	5	29
E	11	8	17	**26**	5	33
BT	10	7	17	**32**	8	26
B/C	11	9	18	**23**	7	32

(Hubert et al. 2009 EJSS)

IMPROVEMENTS OF THE FITTING PROCEDURE

DECREASE HETEROGENEITY OF < 2 µm FRACTION

QUANTITATIVE INFRA-MICROMETRIC FRACTIONATION

(after Laird et al., 1991)

Extraction < 2 µm fraction

Quantitative infra-micrometric extraction with or without pretraitments (e.g. CBD, H_2O_2)

(< 0.05 µm – 0.05-0.1 µm – 0.1-0.2 µm – 0.2-2 µm)

X-ray diffraction of the sub-fractions

Complementary analyses (e.g. Chemical composition, TEM, FTIR, …)

Fitting of the XRD patterns of the sub-fractions

Fitting the < 2 µm fraction

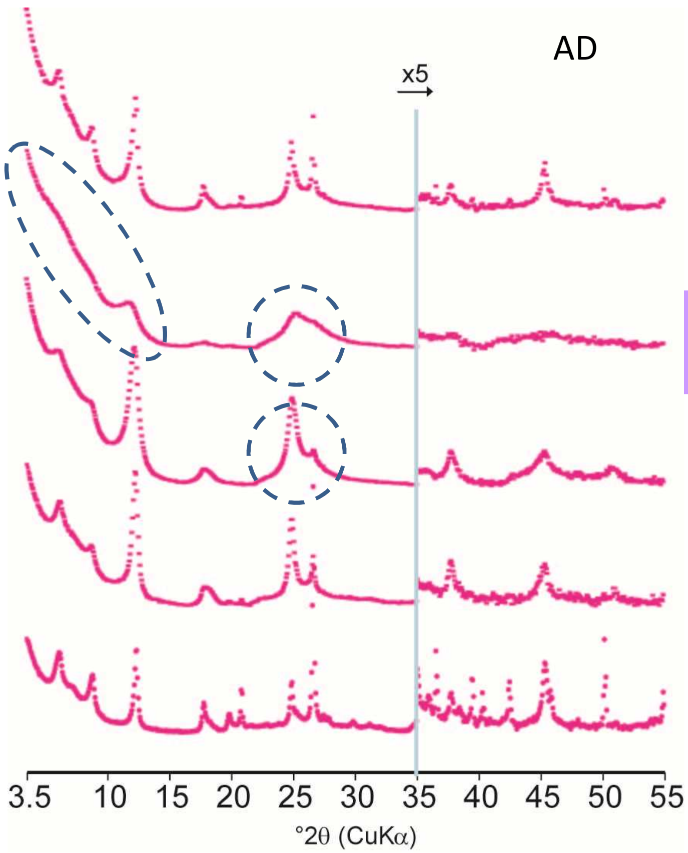
Calculate the pattern of < 2µm fraction

INFRA-MICROMETRIC FRACTIONNATION OF THE SAMPLES

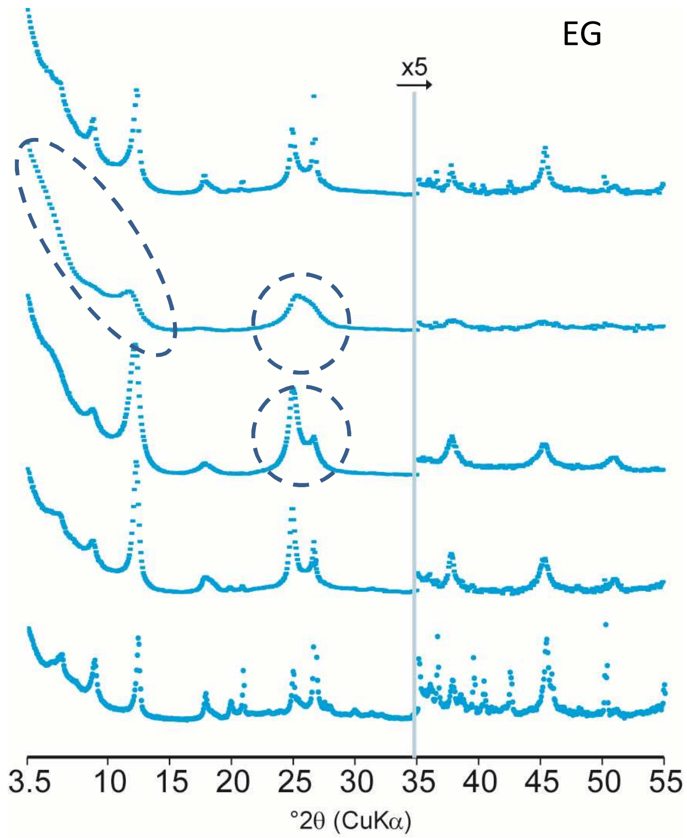
Specify soil formation of a Cambisol developed on an ancient ferralitic paleosol

INFRA-MICROMETRIC FRACTIONNATION OF THE SAMPLES

Specify soil formation of a Cambisol developed on an ancient ferralitic paleosol



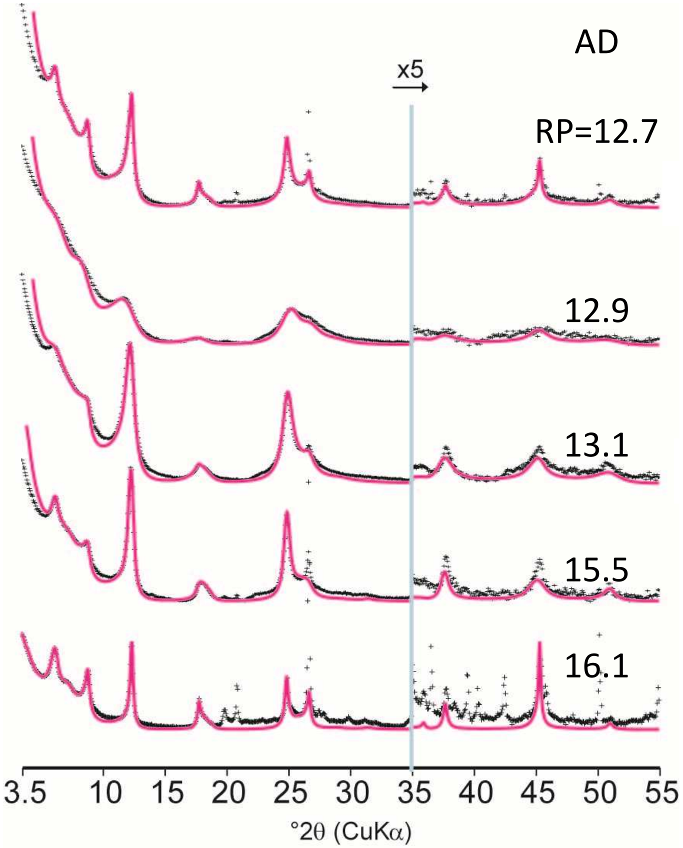
Fraction	% mass
<2 µm	
<0.05 µm	32
0.05-0.1 µm	32
0.1-0.2 µm	15
0.2-2 µm	21



(Hubert *et al*. 2012 American Mineralogist)

INFRA-MICROMETRIC FRACTIONNATION OF THE SAMPLES

Specify soil formation of a Cambisol developed on an ancient ferralitic paleosol



Fraction	% mass
<2 µm	
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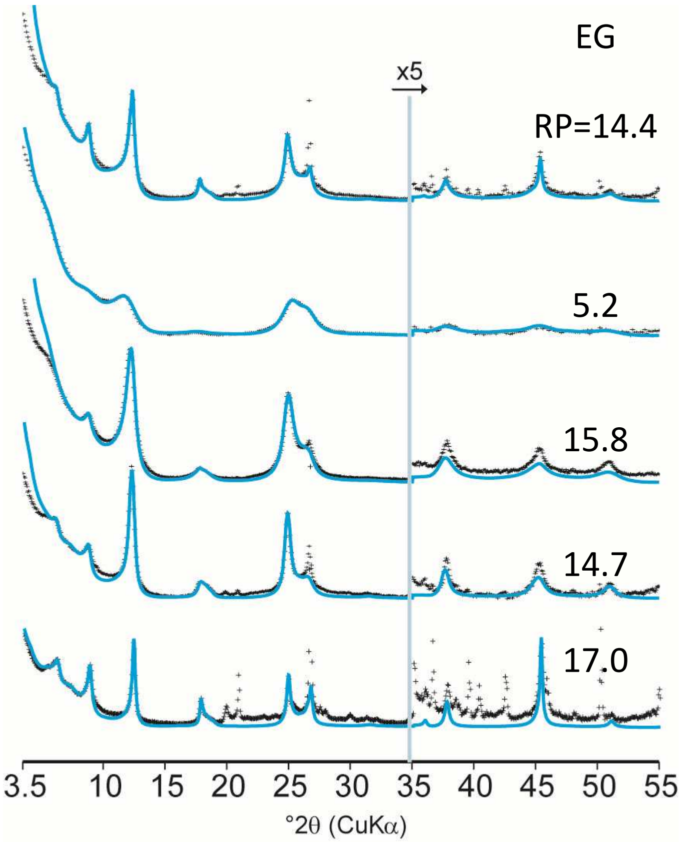

(Hubert *et al*. 2012 American Mineralogist)

INFRA-MICROMETRIC FRACTIONNATION OF THE SAMPLES

What are the clay minerals employed

Fraction	<0.05 µm		0.05-0.1 µm		0.1-0.2 µm		0.2-2 µm		Bulk <2 µm	
% mass	32		32		15		21			
	AD	EG	AD	EG	AD	EG	AD	EG	AD	EG
Chlorite	-	-	-	-	<5	<5	6	5	<5	<5
Kaolinite	-	-	-	-	-	-	16	16	<5	<5
Illite/chlorite R0	-	-	<5	<5	5	7	18	20	8	9
Kaolinite/illite R0	-	-	35	37	33	37	7	9	23	24
Illite/smectite/chlorite R0	-	-	18	14	21	18	19	16	16	16
Illite/smectite/chlorite R0	18	18	14	15	15	12	20	19	14	11
Illite/smectite R0	11	12	6	5	<5	<5	<5	<5	<5	<5
Kaolinite/illite R1s	71	70	23	26	19	19	11	11	28	32
Rp (%)	**12.9**	**5.2**	**13.1**	**15.8**	**15.5**	**14.7**	**16.1**	**17.0**	**12.7**	**14.4**

6 out the 8 clay minerals are mixed layers

(Hubert *et al*. 2012 American Mineralogist)

INFRA-MICROMETRIC FRACTIONNATION OF THE SAMPLES

A way to validate the fitting procedure?

Calculate the pattern of < 2 µm with the mass % of each fraction

Fraction < 2 µm = 0.32 x f. <0.05 + 0.32 x f. 0.05-0.1 + 0.16 x f. 0.01-0.2 + 0.21 x f 0.2-2

Fraction	AD < 2µm modeled	AD < 2 µm calculated	AD difference	EG < 2µm modeled	EG < 2 µm calculated	EG difference
Kaolinite/illite R1s	28	35	**+7**	32	36	**+4**
Illite/smectite R0	<5	7	**<5**	<5	7	**<5**
Illite/smectite/chlorite R0	14	17	**+3**	11	16	**+5**
Illite/smectite/chlorite R0	16	13	**-3**	16	11	**-5**
Illite/chlorite R0	8	6	**+2**	9	6	**-3**
Kaolinite/Illite R0	23	18	**-5**	24	19	**-5**
Kaolinite	<5	<5	**<5**	<5	<5	**<5**
Chlorite	<5	<5	**<5**	<5	<5	**<5**
Rp (%)			**25**			**22**

For each clay mineral the error is < 7 %

Higher errors for the species of the finest fractions

WHAT ARE THE INSIGHTS OF XRD PATTERNS FITTING?

Detailed description of the clay minerals in the < 2 µm fraction : discrete and MLM

Semi-quantification of the clay mineralogy : Proportions of the different clay minerals

Structural model relevant for clay reactivity

Insights in understanding pedogenesis and clay transformations

WHAT ARE THE LIMITS?

Time needed to fit the experimental data / Accessibility of the programs

Not a routine method : valauable for selected samples

Comparison with data obtained with other techniques

However it is a real improvment in the in the description of soil clay mineralogy

TOOLS ALLOWING TO REVISIT AND SPECIFY SOIL CLAY MINERALOGY

ARE NOWADAYS AVAILABLE

THERE IS MUCH TO CLARIFY FOR SOIL CLAY MINERALS

Species with low number of layers, low CSDS and

complex mixed-layers

Reactivity of these different clay minerals: exchange properties

Velocity of weathering and transformations

CONCLUSIONS

TOOLS ALLOWING TO REVISIT AND SPECIFY SOIL CLAY MINERALOGY

ARE NOWADAYS AVAILABLE

There is much to clarify for soil clay minerals

Species with low number of layers and low CSDS CSDS and complex mixed-layers

Reactivity of these different clay minerals

Velocity of weathering and transformations

What has to be done?

Dynamise works on soil clay minerals

Find new field sites and experiments

Apply it to the context of Brazil

THIS PRESENTATION WAS MADE POSSIBLE BY FOLLOWING SUPPORTS

PROJECT CAPES-COFECUB TE 761/12

Evolução mineralógica dos solos do sul do Brasil : caracterização dos processos de alteração e de impacto antrópico

Evolution minéralogique des sols du sud du Brésil: caractérisation des processus d'altération et de l'impact anthropique

and invitation by Sociedade Brasileira de Ciência do Solos – SBCS

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Erasmus Mundus Master Course : Master IMACS

International Master in Advanced Clay Science

IMACS

IMACS is an integrated Master of Science by 5 institutions in clay science :

- the University of Poitiers (UP) in France
- the University of Aveiro (UA) in Portugal,
- the Technical University of Crete (Chania) in Greece,
- the University of Ottawa (UO) in Canada,
- the Federal University of Rio Grande do Sul (UFRGS) (Porto Alegre).

Clay mineral structure and chemistry, Identification

Industrial clay deposits, clay in geological systems

Soil clay minerals and interaction with OM and organisms

Environment, soil and Geological systems

Geomaterials and civil engineering / assessment and processing

Advanced clay / nanomaterials

Healing minerals

Education and Culture DG

ERASMUS MUNDUS

http://sfa.univ-poitiers.fr/geosciences/spip.php

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