Drying induced acidity at the mineral-water interface: ATR-FTIR Spectroscopy

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Introduction

Why mineral-water interface is important?

- Interfacial phenomena govern some of the most fundamental processes, including adsorption/desorption equilibria, speciation, redox reactions, reaction kinetics...

- Wetting - drying cycles are frequent events in terrestrial geochemical systems, most of our understanding of chemical conditions on mineral surfaces is confined to fully hydrated systems

- The chemical conditions on dry or drying mineral surfaces are different to those on a fully hydrated surface

Introduction

Why surface drying is important?

- Drying a clay surface is an acidifying process due to the dissociation of the last few monolayers of water surrounding adjacent polarising cations → arid areas

- Very little is known about how acidic the surface gets, at what critical moisture content acidification begins to occur or how reversible drying- induced acidification is

Why infrared spectroscopy is indispensable?

- Limitation → Difficulty in measuring changes in an ever diminishing film of water

- Vibration spectroscopy in the IR region is particularly sensitive to the presence of water

- ATR-FTIR spectroscopy allows real time changes in probe molecules to be measured during moisture loss

Objectives

The present study aims to delineate the pH range of various drying environments with respect to:

i) The effect of mineral type and surface charge

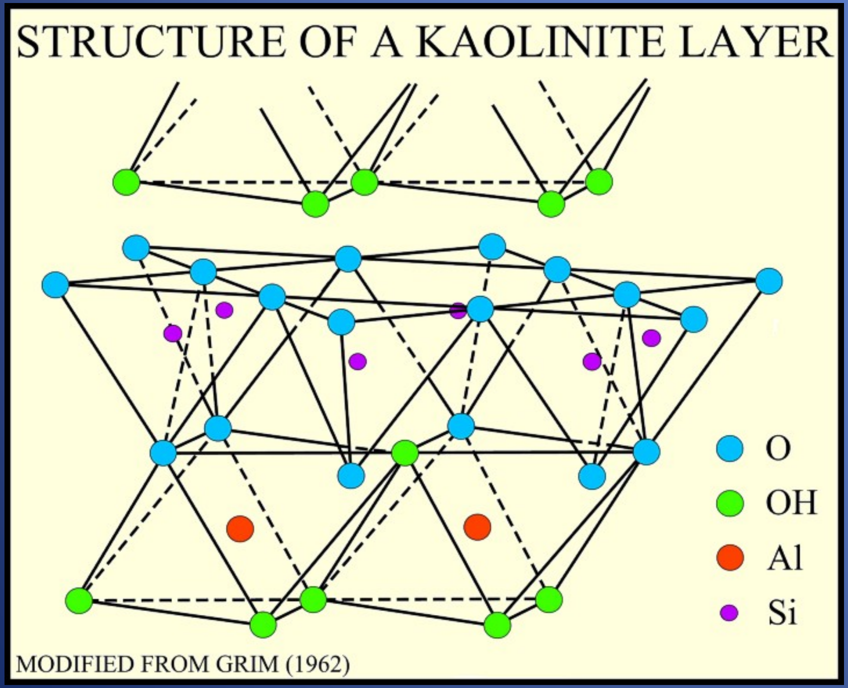
ii) The critical moisture content at which pH changes are observed

iii) The reversibility of acidification after rehydration

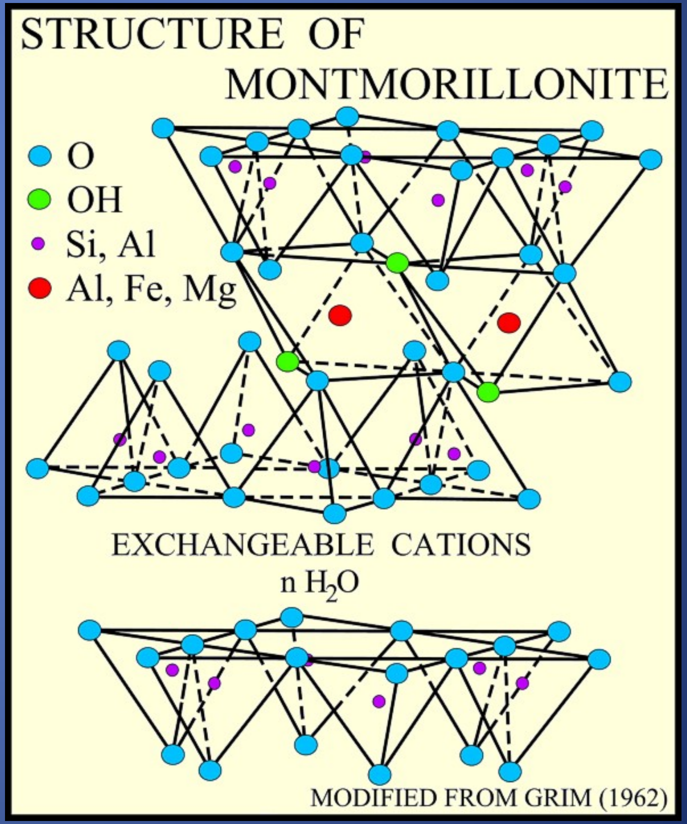
Materials and Methods

Minerals

- Clay minerals (Clay Mineral Society Source Clays Repository)
- Fraction <2 µm
- Homoionic clays (Na^+, Ca^{2+}, Mg^{2+}, Al^{3+})



Kaolinite (KGa-1b)



Smectite (STx-1)

Materials and Methods

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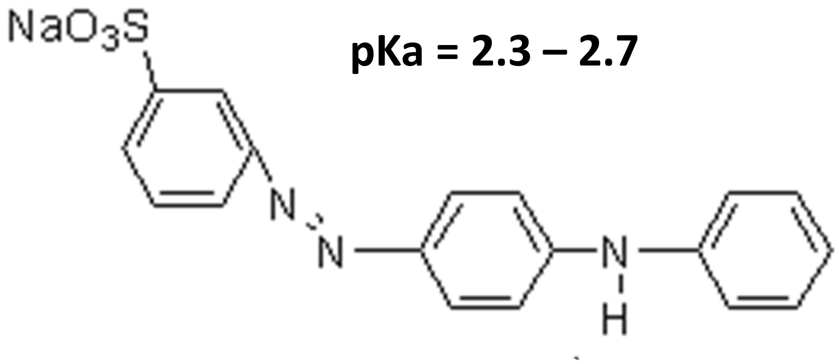
Smectite (STx-1)	pH	Kaolinite (Kga-1b)	pH
Na-Sm	7.0	Na-Kaol	6.4
Ca-Sm	6.5	Ca-Kaol	6.2
Mg-Sm	6.6	Mg-Kaol	5.7
Al-Sm	4.8	Al-Kaol	5.6

Materials and Methods

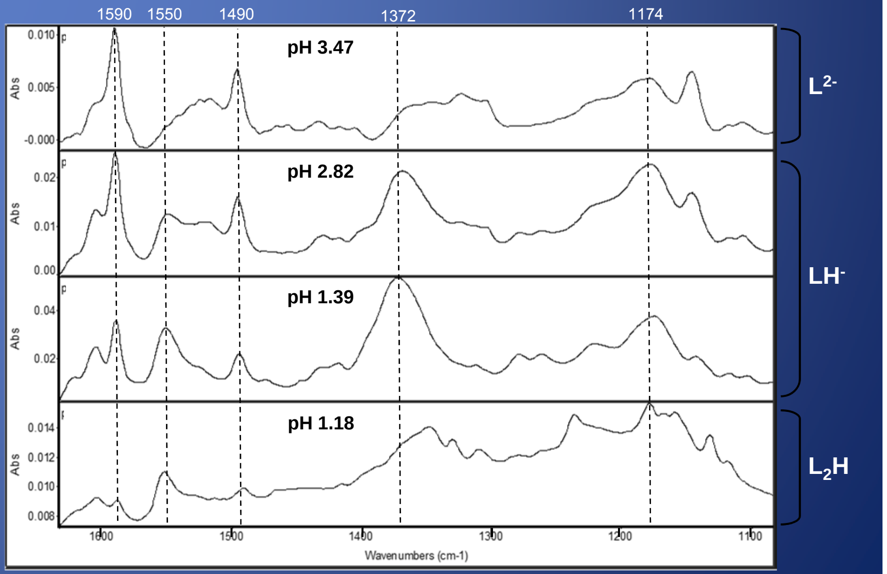
Indicator

pKa = 2.3 – 2.7



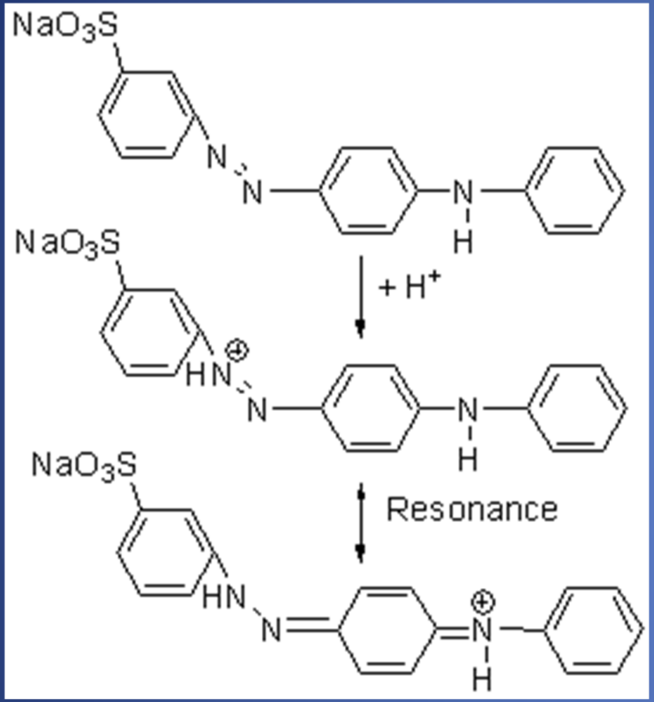
Metanil Yellow (AY 36)

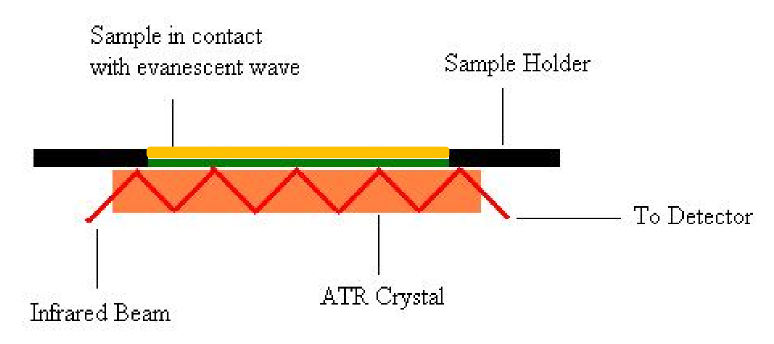
Fingerprint region of AY 36 falls outside:
H_2O (3400 and 1640 cm^{-1})
CO_2 (2350 cm^{-1})



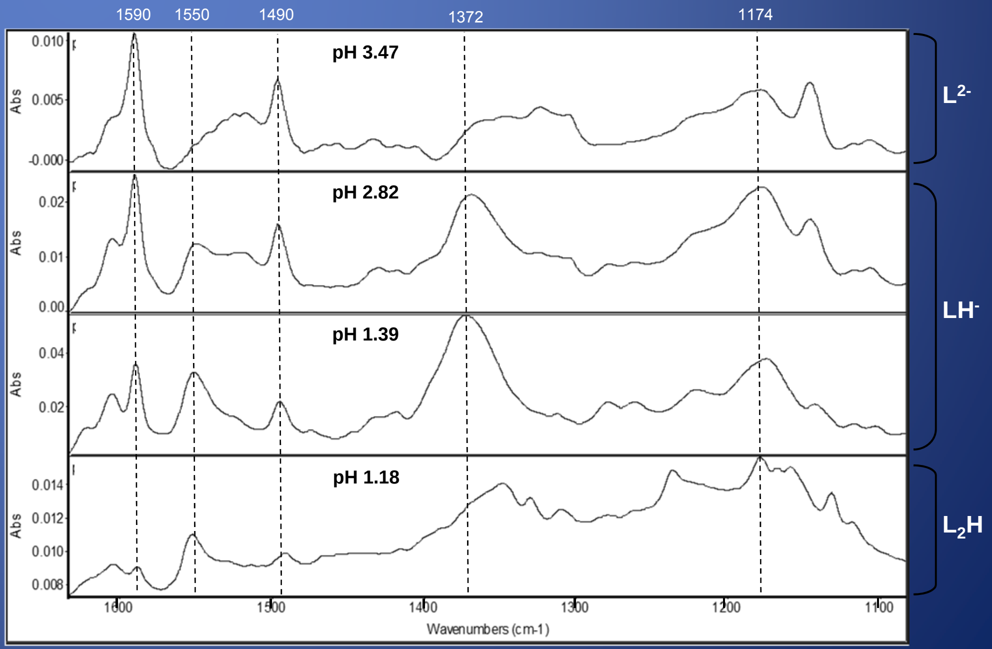
Materials and Methods

Indicator





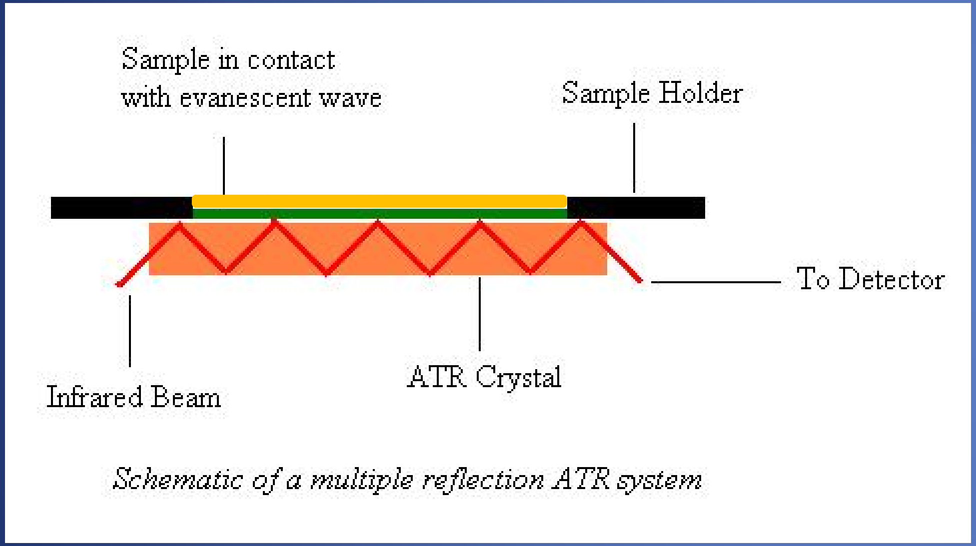
Schematic of a multiple reflection ATR system



Indicator standards

Homoionic clay–H_2O complexes

Experimental procedure: Step 1 – Cation effect



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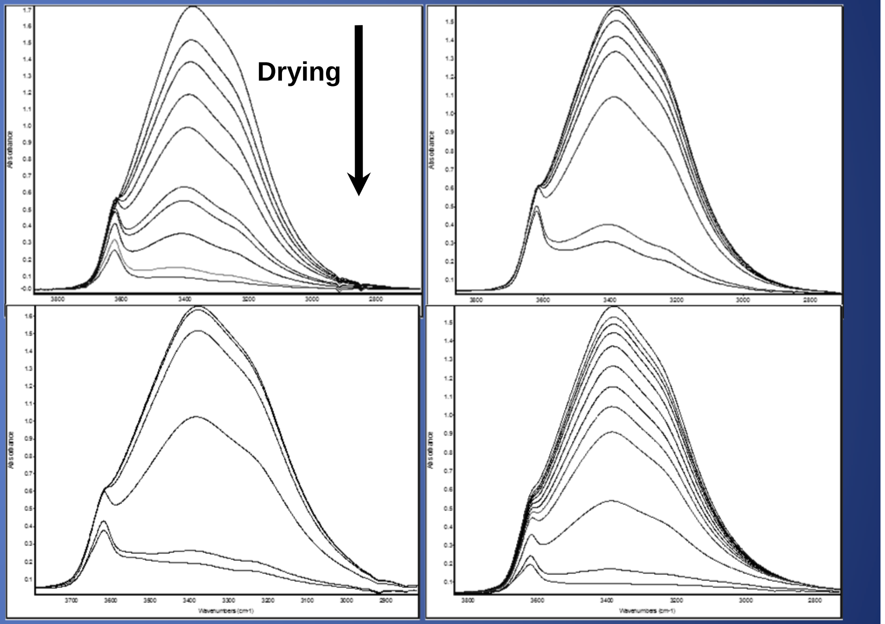
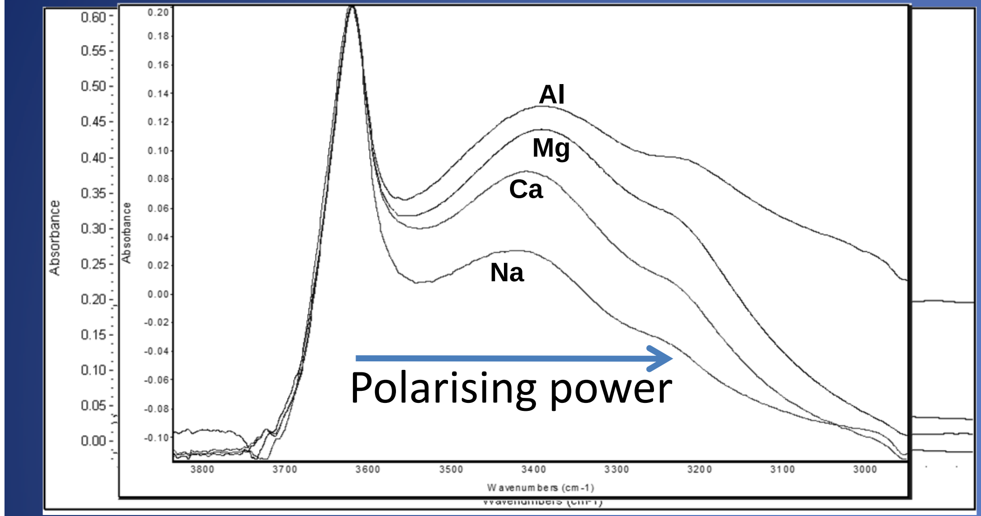
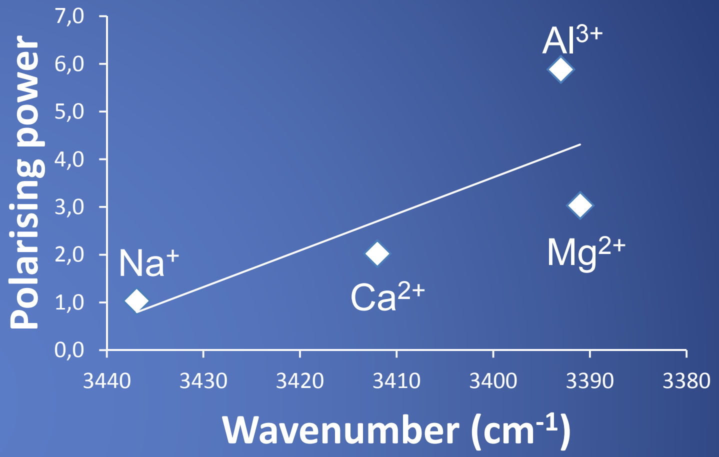


- Addition of homoionic clay (3g/L) (H$_2$0:Ethanol 40:60)
- Air-dried → spectra collection

Homoionic clay–H_2O complexes

Experimental procedure: Step 1 – Cation effect





- Position of the OH-stretching band decreases following the order Na^+, Ca^{2+}, $Mg^{2+} \approx Al^{3+}$

cation polarising power (charge/ Å radius)

- Strongly polarising cations result in stronger hydrogen bonding of adsorbed water on dried smectite clays

- Similar band position (Mg – Al) but different shape

- No cation influence on water band shifts with kaolinites → $CEC_{Sm} = 84.4\ m_{eq}/100g$

$CEC_K = 2\ m_{eq}/100g$

Materials and Methods

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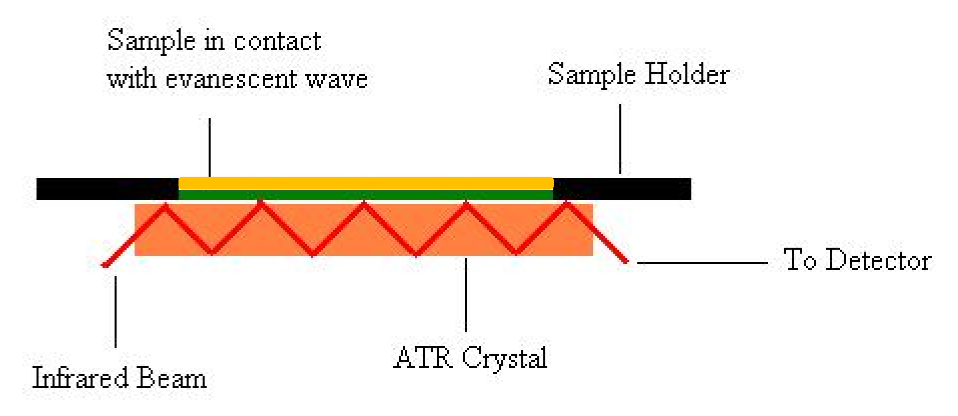
Homoionic clay–indicator complexes

Experimental procedure: Step 2 – Indicator addition



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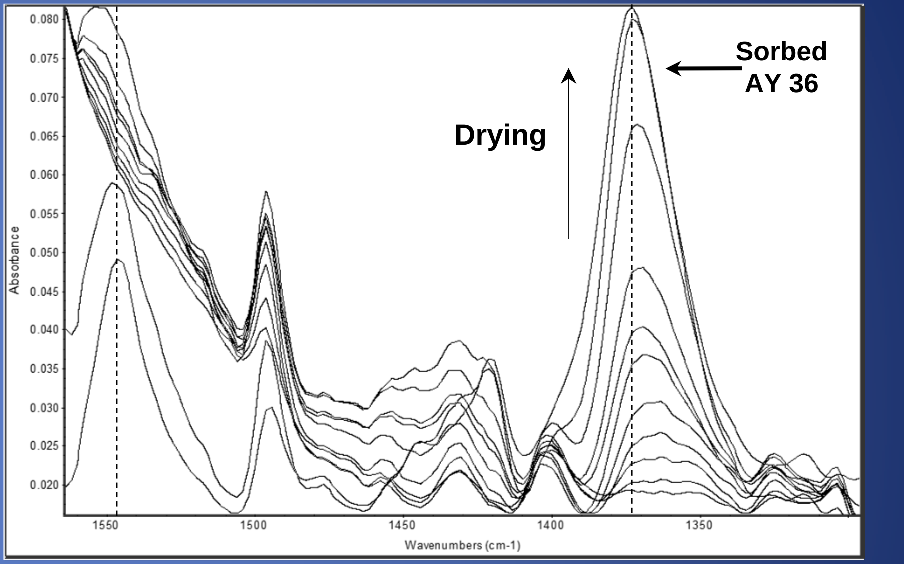
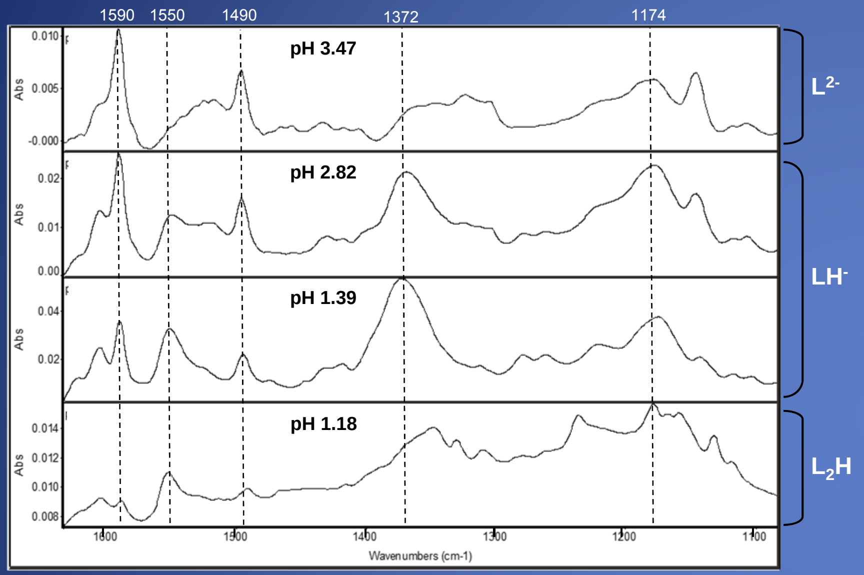
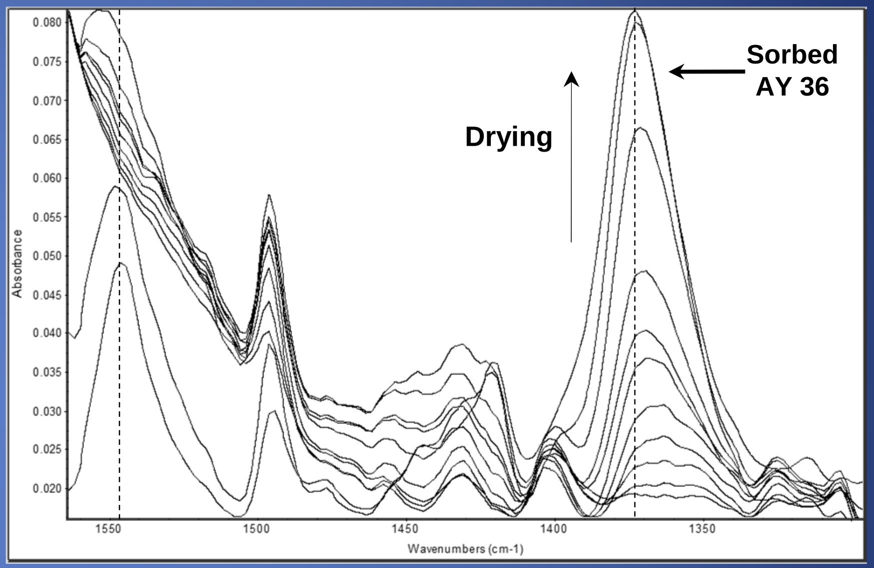


- Crystal + dried clay → dried background
- Al-Sm – AY 36 spectra recorded during drying period (ratioed against dried background)
- Band position → identification of protonated/deprotonated forms

Homoionic clay–indicator complexes

Experimental procedure: Step 2 – Indicator addition



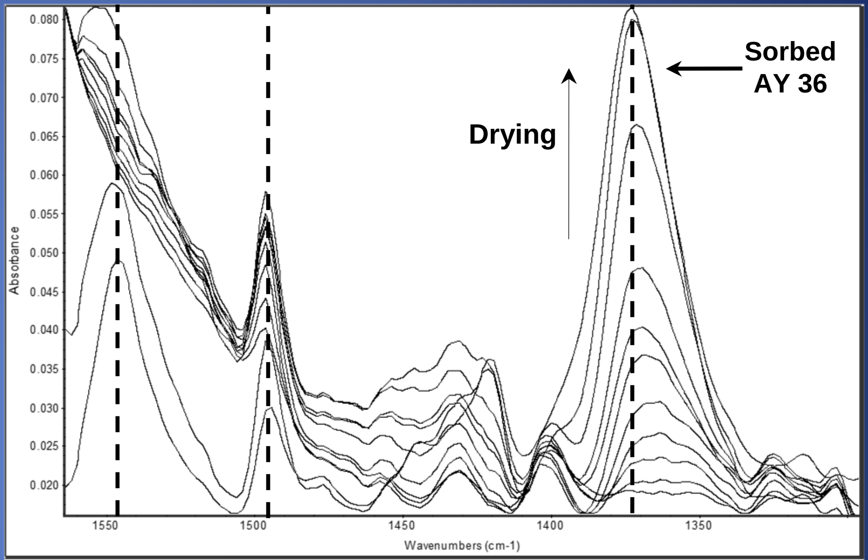


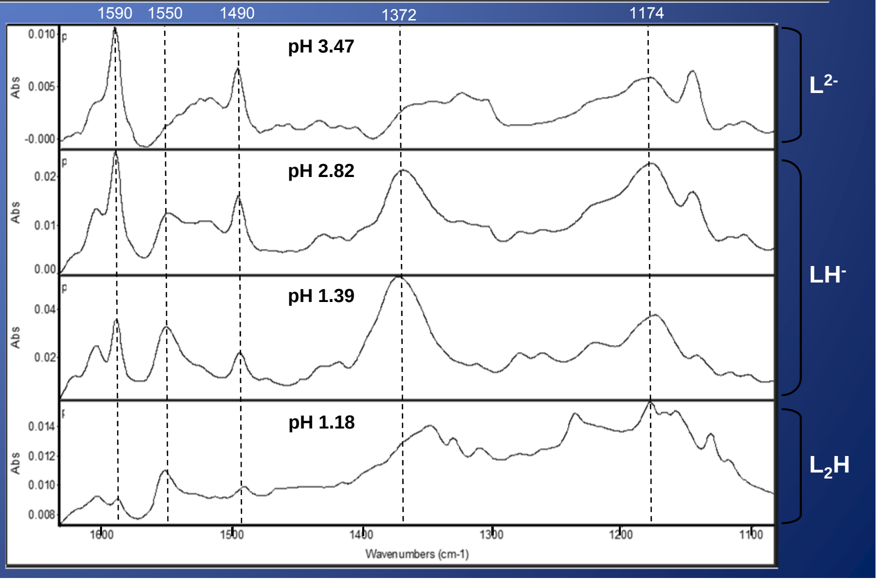
- Crystal + dried clay → dried background
- Al-Sm – AY 36 spectra recorded during drying period (ratioed against dried background)
- Band position → identification of protonated/deprotonated forms
- Hydrated state, the spectra correspond to that of the deprotonated (L^{2-}) indicator
- ↓ water content, ↑ intensity 1372 and 1550 cm^{-1} peaks → pH decreases

Homoionic clay–indicator complexes

How low the pH falls on dehydration?

pH	Peak height ratio			
	1496/1550	1496/1373	1590/1550	1590/1373
3.18	8.00	1.36	13.75	2.34
2.82	1.65	0.72	2.91	1.26
2.54	1.09	0.55	1.90	0.97
2.24	0.74	0.43	1.33	0.78
1.88	0.71	0.35	1.29	0.64
1.68	0.54	0.32	0.99	0.59
1.39	0.50	0.29	0.90	0.53
R^2	*0.84*	*0.92*	*0.84*	*0.92*
Al-Sm-AY 36	0.37	0.20	0.51	0.27



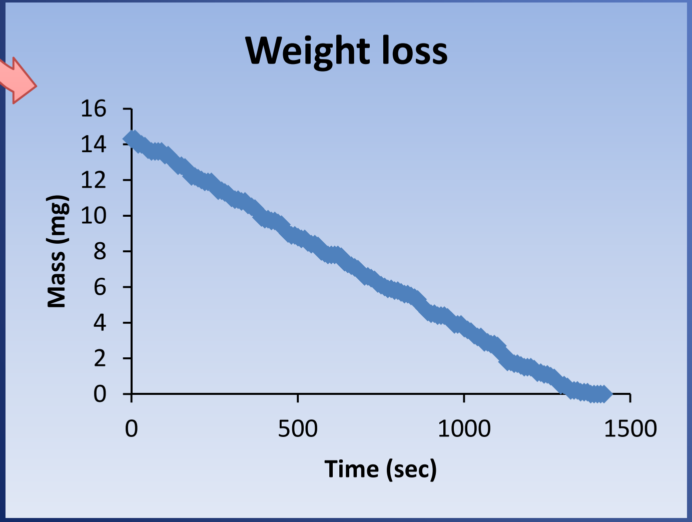


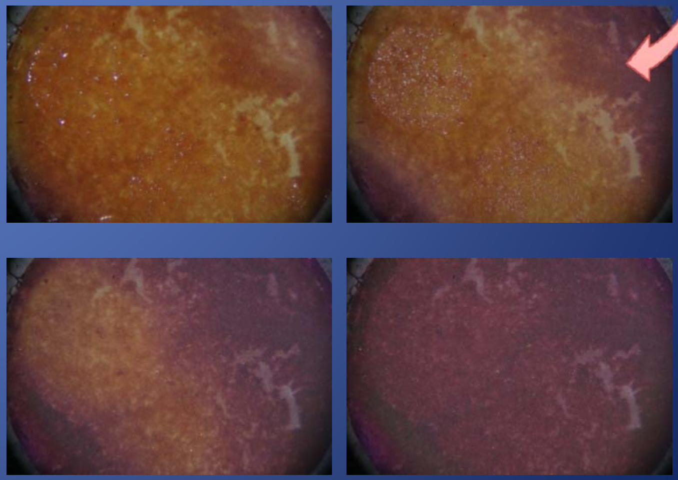
- Peak height ratio of the aqueous standards and sorbed indicator spectra
- Reasonable correlation between peak height ratio and pH
- pH of the clay surface drops 1.4 > pH > 1.2
- Air-drying an Al-Sm creates a **highly** acidic environment

Homoionic clay–indicator complexes

Experimental procedure: Step 3 – Critical moisture content

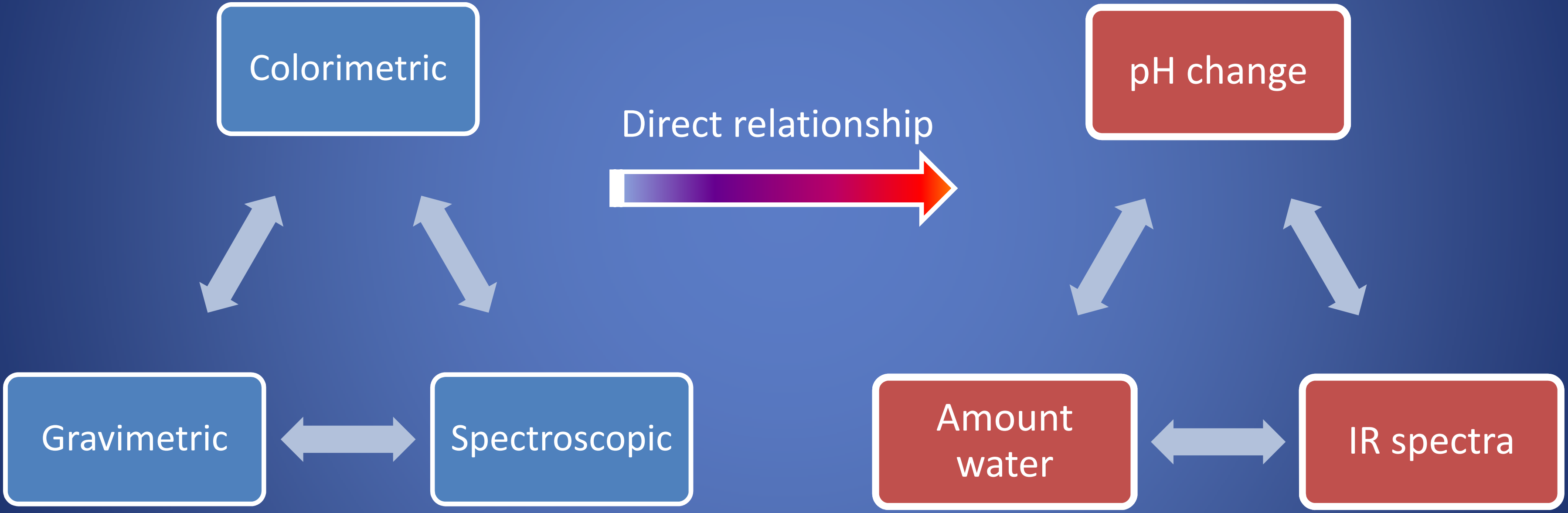
- In situ colorimetric and gravimetric analysis: dye-clay complex ↔ degree of surface hydration





Homoionic clay–indicator complexes

Critical moisture content



Colorimetric

Gravimetric

Spectroscopic

Direct relationship

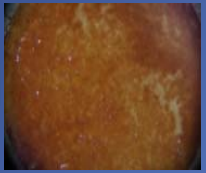
pH change

Amount water

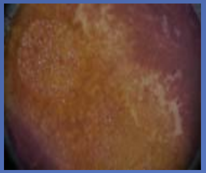
IR spectra

Homoionic clay–indicator complexes

Critical moisture content



100%

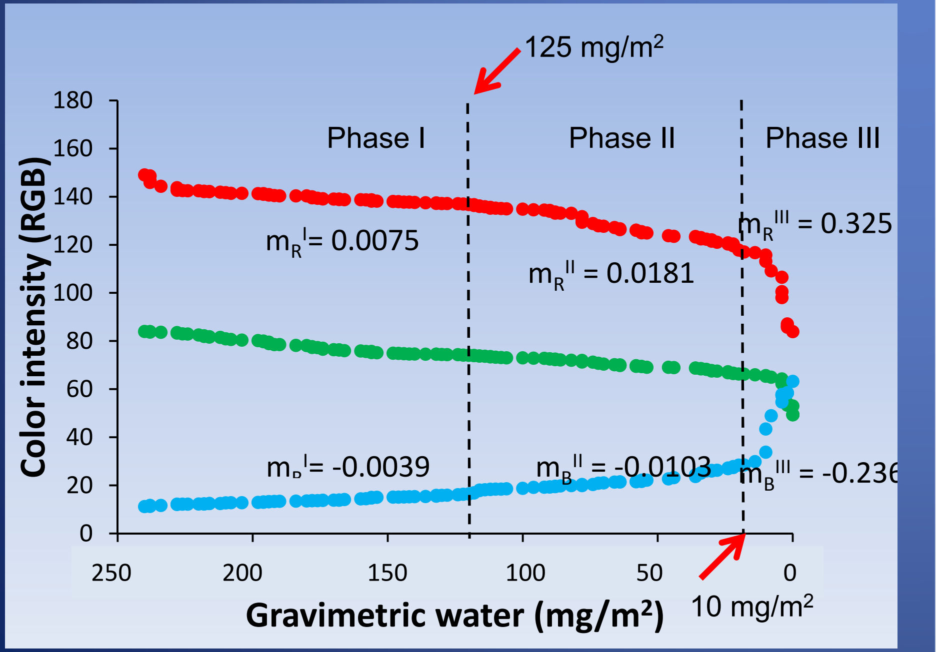


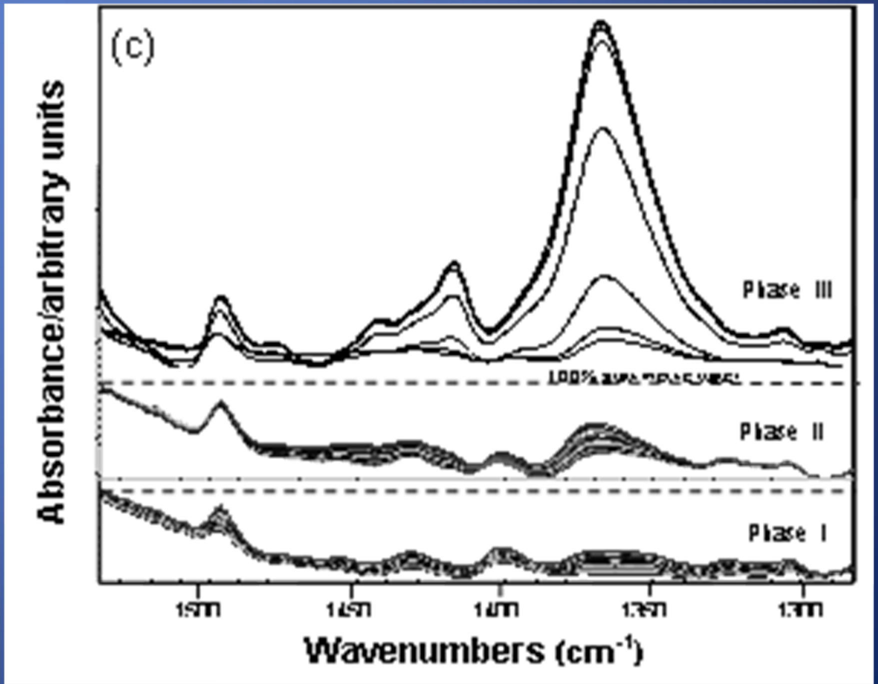
80%

40%

20%

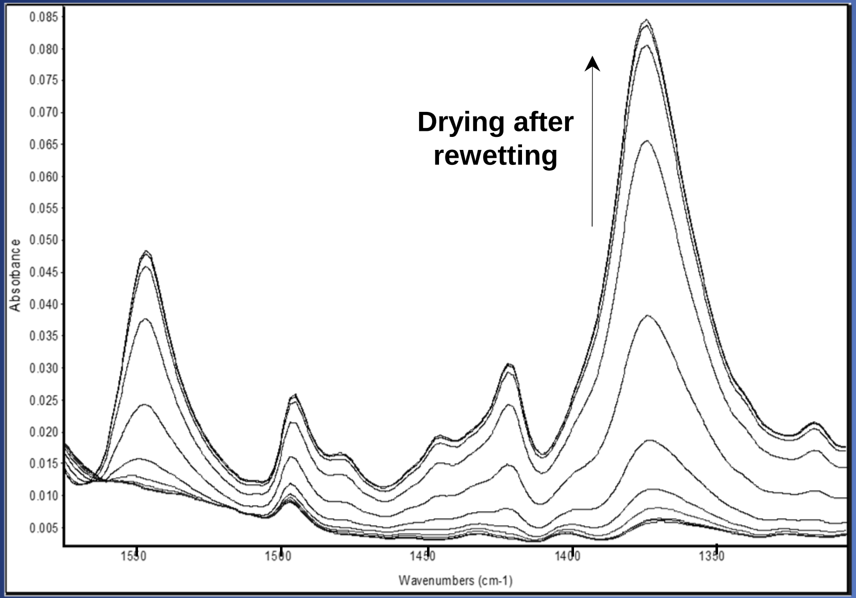
0%

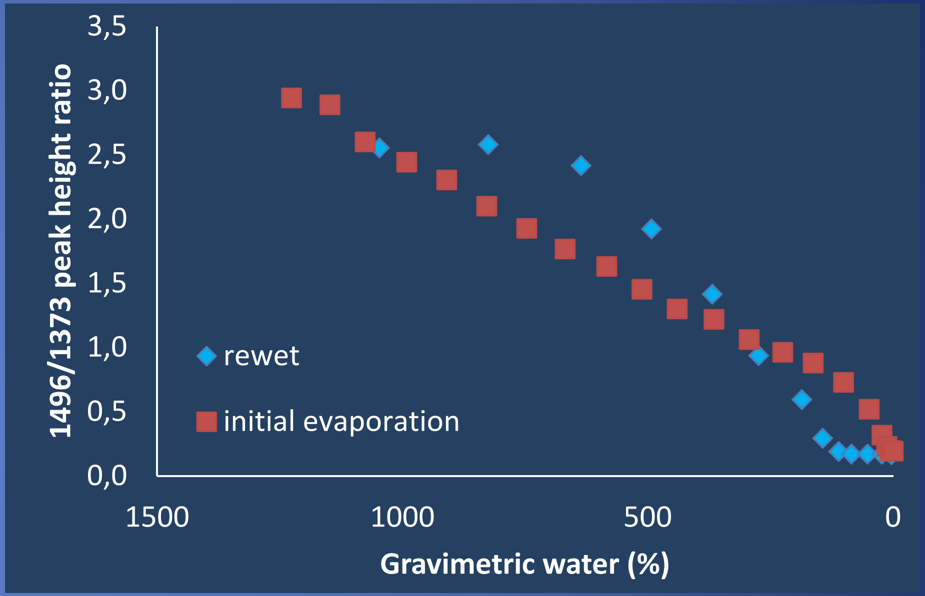




Homoionic clay–indicator complexes

Experimental procedure: Step 4 – Rehydration…a reversible process?





- After rewet ting, rapid colour change from deep purple to orange

- IR spectra similar to non-protonated form (L^{2-}), then changed to partially protonated (HL^{-}) as water evaporates

- Peak height ratio values similar to those obtained BEFORE rehydration → Reversibility

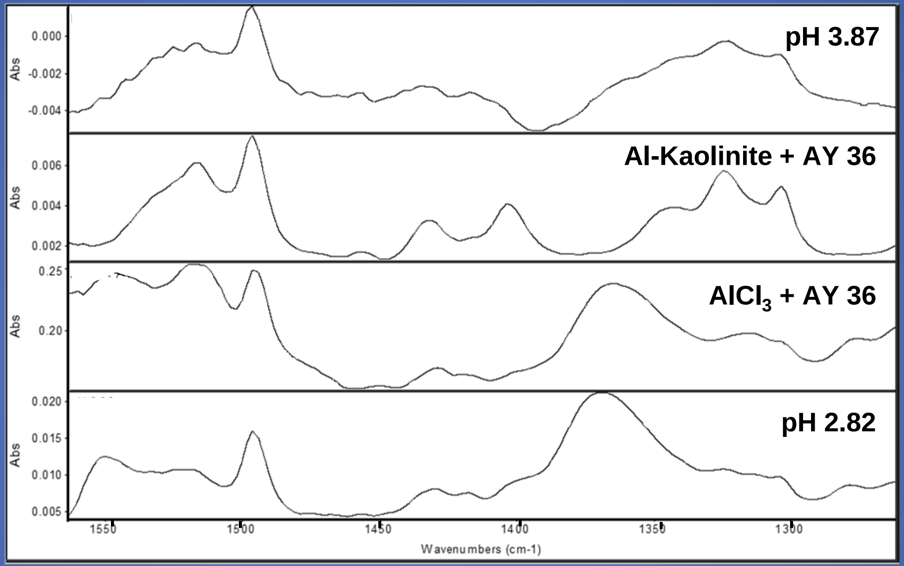
- Faster desorption pathway → impartial rewetting of the dried Al-Sm clay → hydration of the exchangeable Al

Homoionic clay–indicator complexes

Experimental procedure: Step 5 – Other systems

- Na^+, Ca^{2+}, and Mg^{2+} saturated smectites → No protonation (even with Bromocresol Green pKa 4.8)

- Al^{3+} effect on Kaolinite



- No protonation on the kaolinite surface – low surface charge

- Limited degree of protonation (pH 2.82) of the indicator evaporated in the $AlCl_3$ solution

- Charged clay surfaces play a role in the polarisation of water molecules

- Increased polarization → reduce the energy required to break OH bonds → pH decrease in the drying Al-Sm even when the sample was significantly hydrated (125 mg/m^2)

Geochemical implications

- pH can decrease below pH 4 even on moderately hydrated smectite surfaces, when strongly polarising cations are present on clay exchange sites

- Montmorillonite-rich soils which have greater amounts of exchangeable acidity than kaolinite-rich soils due to the higher CEC of montmorillonitic soils

- Surface and subsoil horizons, partially dry out during the dry season, may experience acidity beyond what is usually measured in conventional methods

- The reversibility with rewetting → large pH oscillations during wetting /drying cycles on smectite surfaces with appreciable Al content and could play a significant role in weathering process in arid climates

- Kaolinitic soils are also not likely to be influenced by wetting /drying cycles, regardless of the exchangeable cation

- Pivotal role of highly charged surfaces in the hydrolysis reactions3

More details?

Clarke C., Aguilar-Carrillo J. and Roychoudhury AN, 2011. *Geochimica et Cosmochimica Acta 75*

Questions?