NHRF · TPCI Applied Spectroscopy Laboratory

Direct compositional evaluation of palygorskite by Near Infrared Spectroscopy

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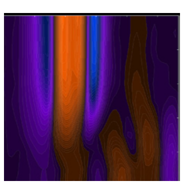
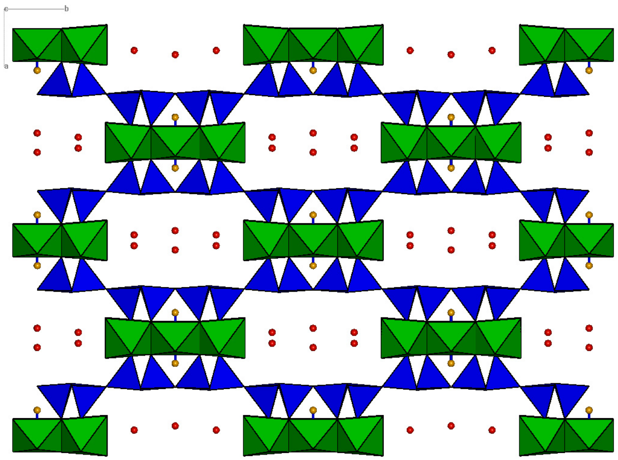
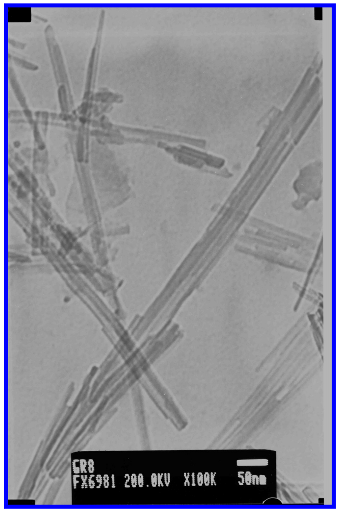


September 2008

Structure of palygorskite

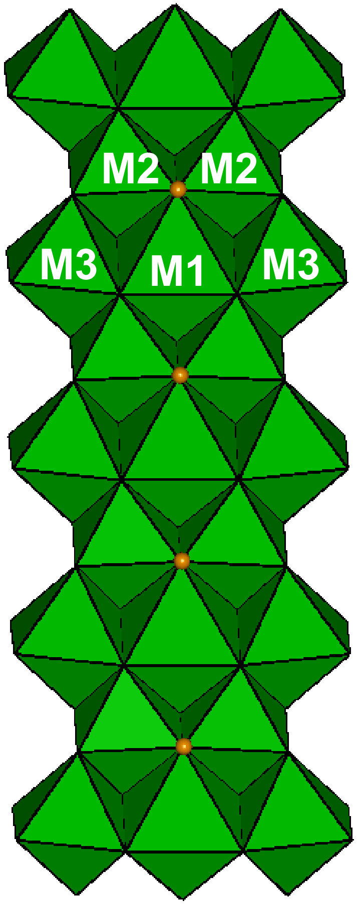


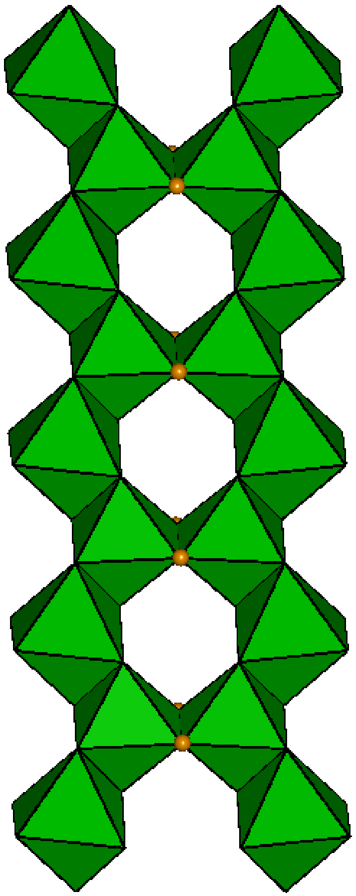
$M^{II}_5Si_8O_{20}(OH)_2$



XRD identification by d 110 at ca. 10.5 Å

Structure of the octahedral sheet





3 types of O-sites

M1M2M2OH

All refined Pal structures concern dioctahedral specimens:
$M^{II}_2M^{III}_2Si_8O_{20}(OH)_2$

Chemical composition of palygorskite

$$[\ M^{II}_{3x+2}M^{III}_{2(1-x)}\ \square_{1-x}\ ]Si_8O_{20}(OH)_2$$

no or very low CEC
very low ^{IV}Al, less than 0.15
variable type and number of octahedral cations

$x \rightarrow 0$: $\Sigma Oc \rightarrow 4$, $[\ Mg_2(Al, Fe)_2\ \square\ ]Si_8O_{20}(OH)_2$

but often, $4 < \Sigma Oc < 5$, Mg>(Al+Fe)

Paquet et al. 1985
Galán & Carretero 1999
Suárez et al. 2007

OH species by mid-infrared spectroscopy

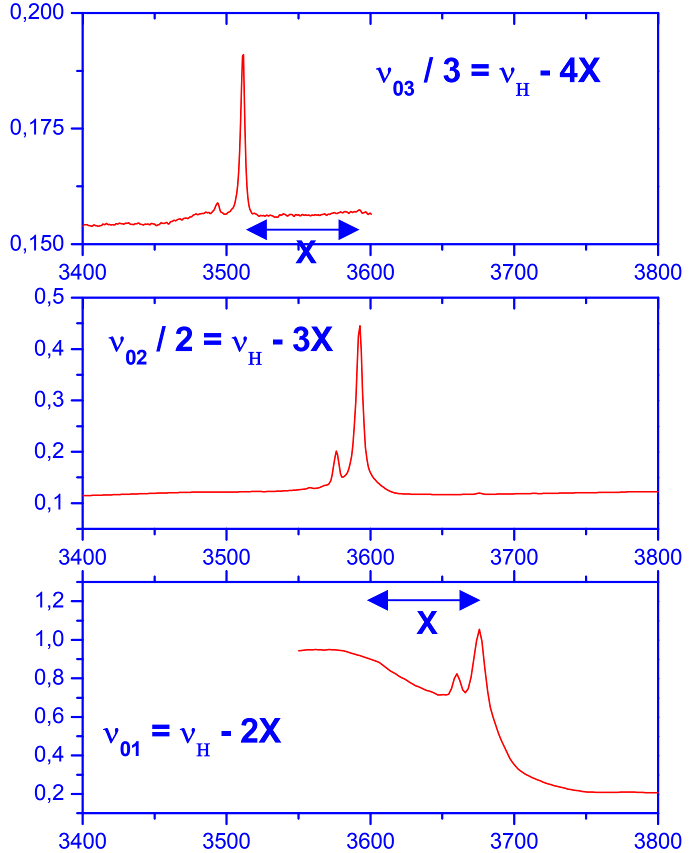
identified from the position of δ(OH), ν(OH)

Dioctahedral M2M2OH: AlAlOH, AlFeOH, AlMgOH...
Triotahedral M1M2M2OH: Mg_3OH, $Mg(Al,Fe)_2OH$...

M1: Mg
M2: Al, Fe, Mg
M3: Mg

Mid-infrared: high ε, effect of accessory minerals, overlap of OH and H_2O stretching modes

NIR spectroscopy



$X_{Mg3OH(talc)}$=84 cm^{-1}

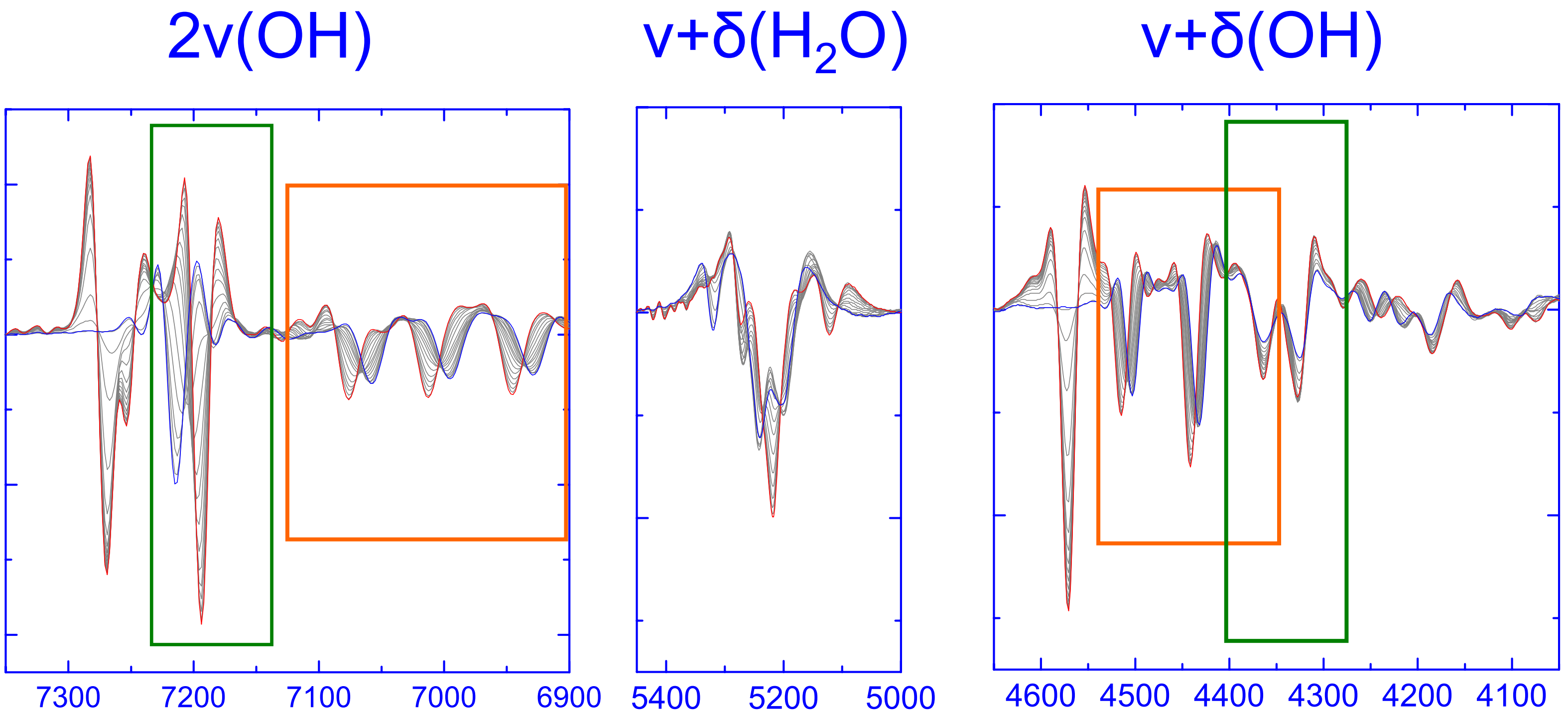
Overtone & combination modes

Specific to O-H: non hydrous phases are silent

Low ε: no dilution

X_{H2O} >>X_{OH}: Separation of OH from H2O modes

Zeolitic dehydration of Pal
NIR, 2nd derivative



Dioctahedral M2M2OH: **AlAlOH, AlFeOH, FeFeOH**

Triotahedral M1M2M2OH: **Mg_3OH**

Gionis et al., Am. Min. 2006

Several hundred samples later,

no NIR evidence for Mg in M2 sites
no NIR evidence for Al, Fe in M1 sites

Simplified bulk Pal formula

$$yMg_5\ T_8O_{20}(OH)_2 \cdot (1-y)[xMg_2Fe_2 \cdot (1-x)Mg_2Al_2]\ T_8O_{20}(OH)_2$$

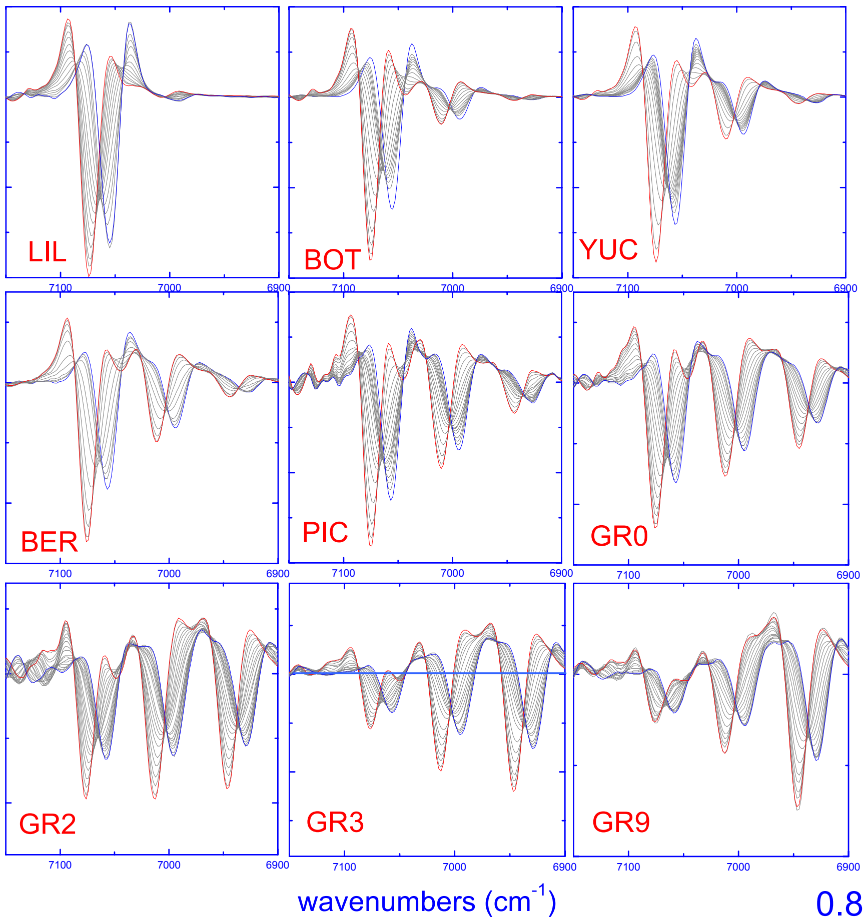
trioctahedral	dioctahedral

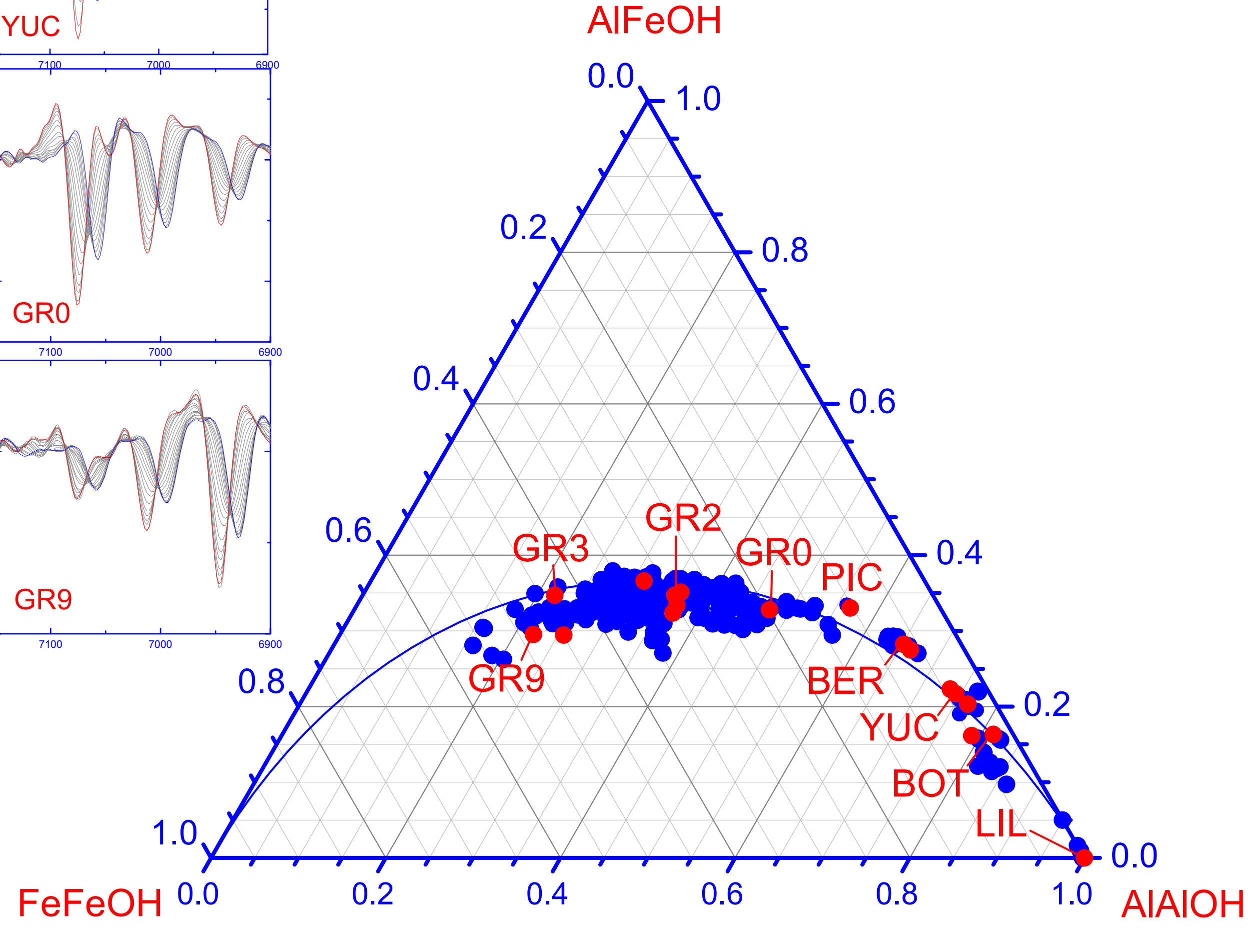
y independent of x | **x = Fe/(Fe+Al)**

Determination of x, y?
Mixture of dioctahedral & trioctahedral particles?
Limits of Pal octahedral composition?

Gionis et al., C&CM. 2007

Determination of x from NIR



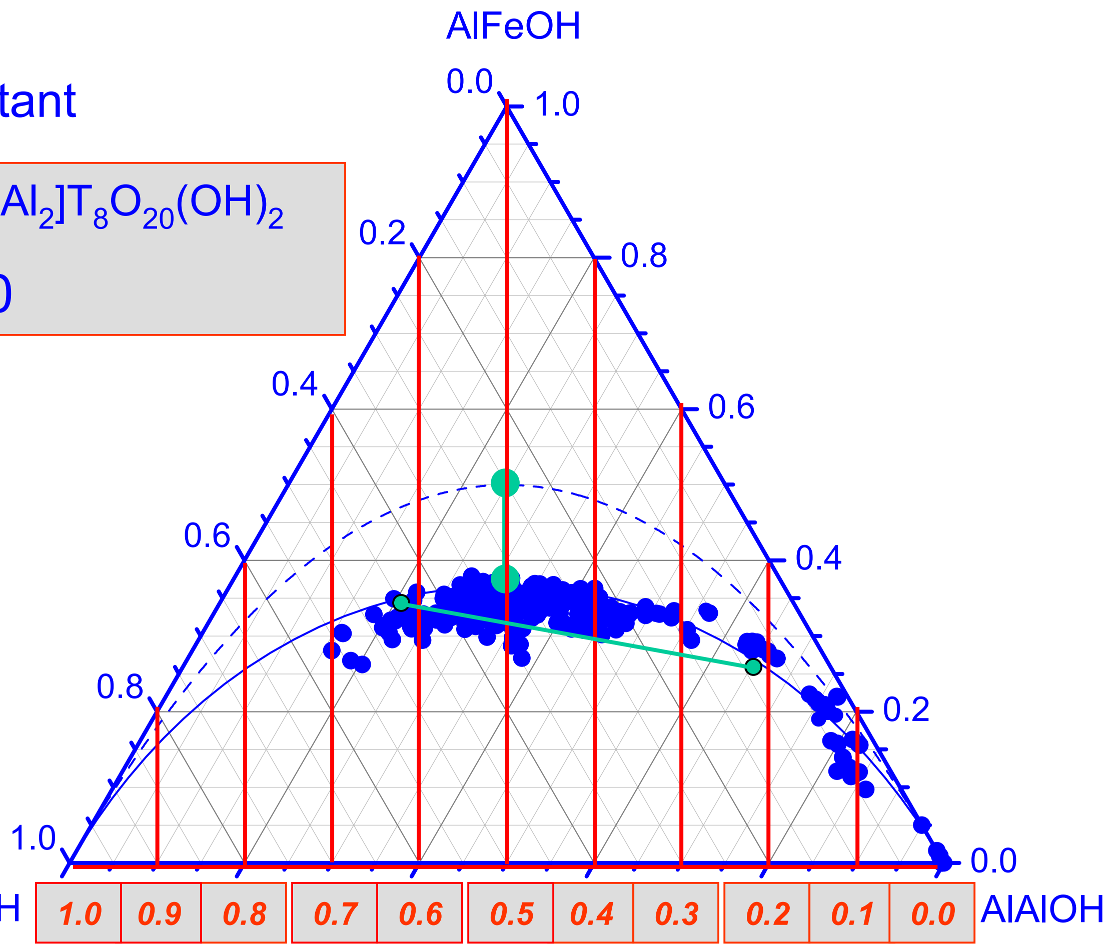


Gionis et al., C&CM. 2007 +

Properties of the M2M2OH ternary plot

Assumption:
$\varepsilon(2\nu_{M2M2OH})$ constant

$x\mathrm{Mg_2Fe_2}\cdot(1-x)\mathrm{Mg_2Al_2]T_8O_{20}(OH)_2}$
$0 < x_{(NIR)} < 0.70$

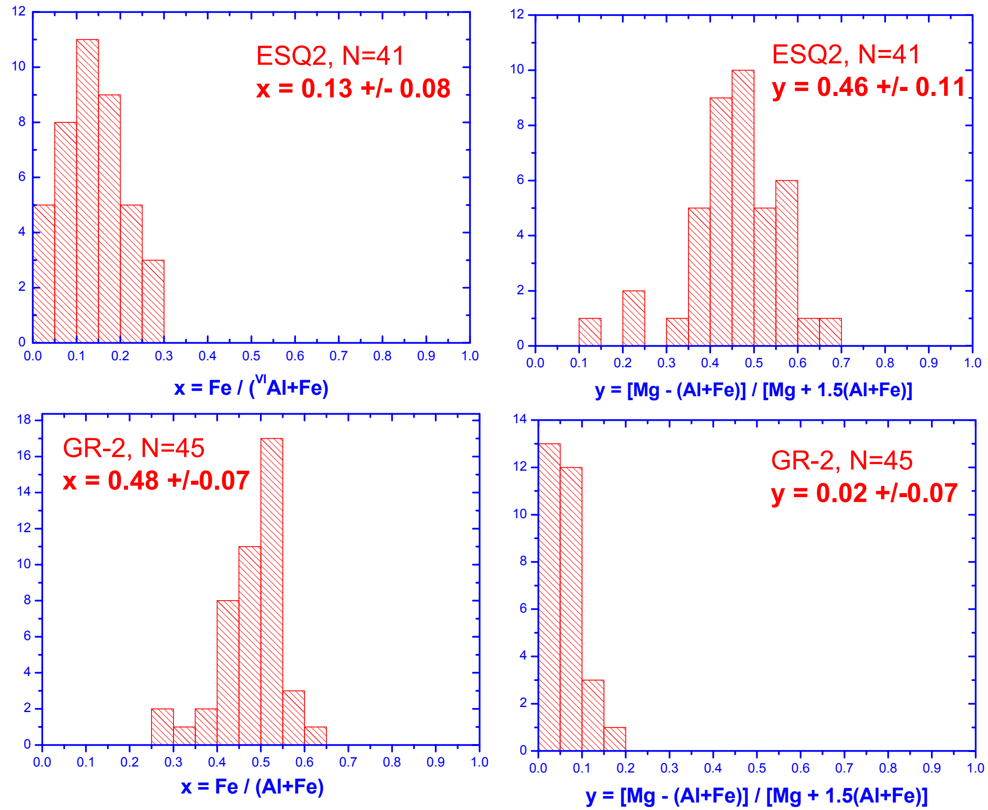


x, fraction of M2 sites occupied by Fe^{III}

single particle AEM data

ESQ2, N=41: $[Mg_{3.34}Al_{0.92}Fe_{0.14}](Si_{7.95}Al_{0.08})O_{20}(OH)_2$, 4.4 OC / 8T

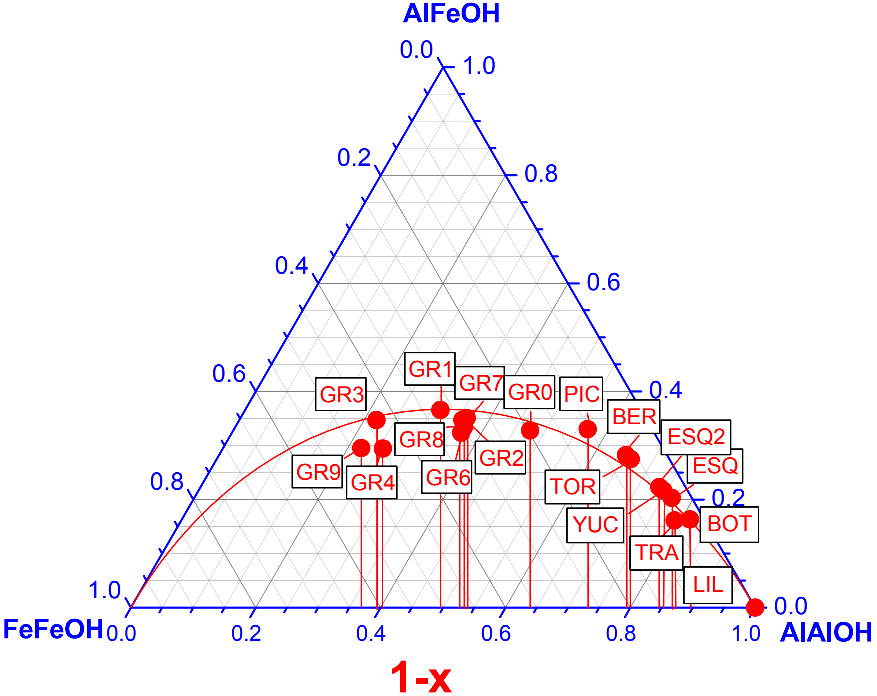
GR-1, N=45: $[Mg_{1.99}Al_{1.00}Fe_{0.90}](Si_{7.96}Al_{0.06})O_{20}(OH)_2$, 3.9 OC / 8T

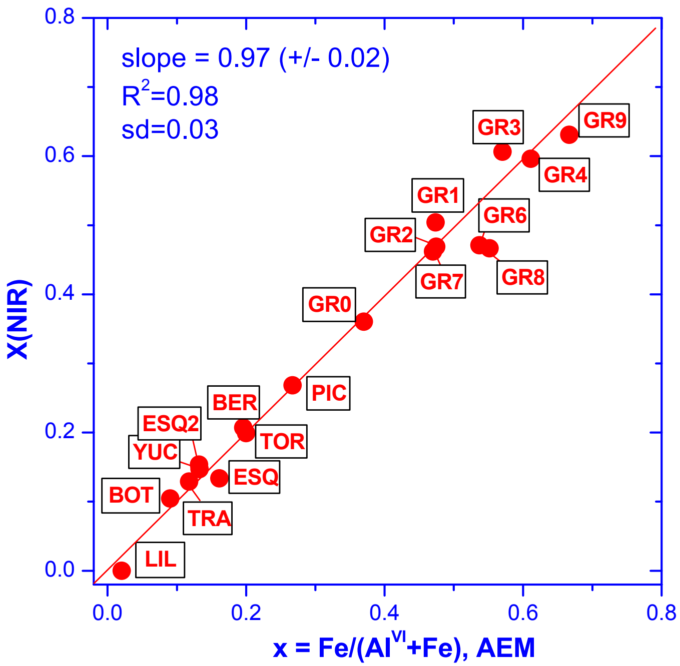


Suárez et al., 2007 +

NIR- AEM correlation

18 pal samples, Greek & Spanish collections





average data from single particles

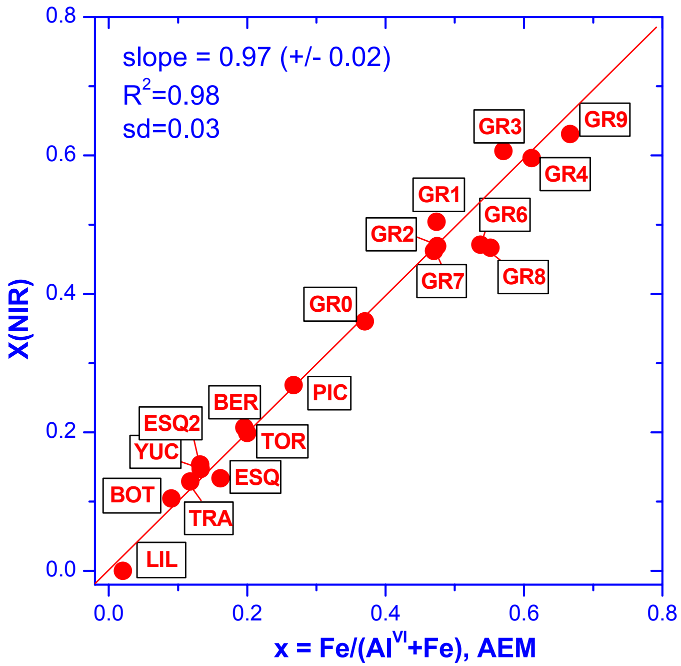
Chryssikos, Am. Min., submitted 2008

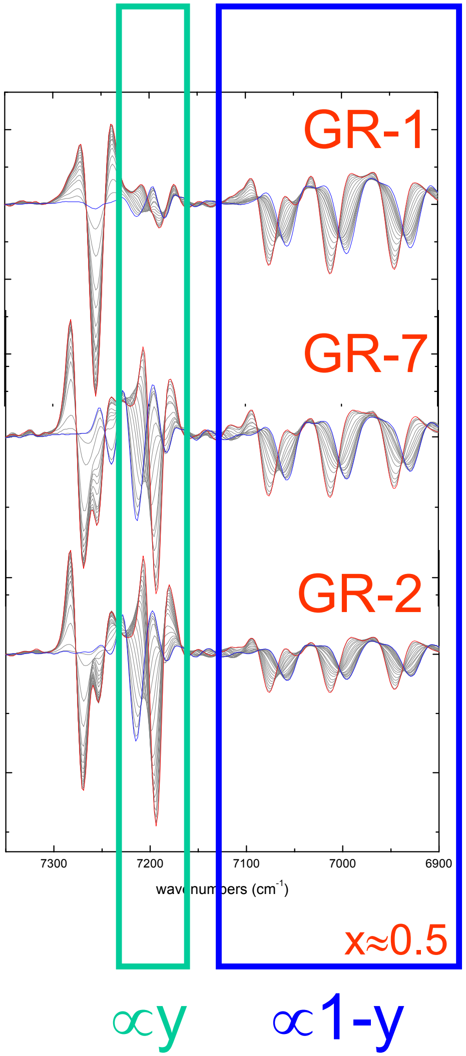
Implications:

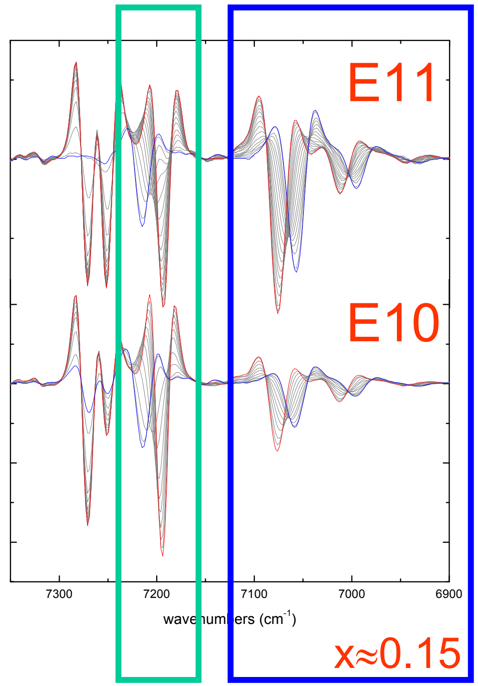
^{VI}Al(AEM) in M2M2OH sites only. x(NIR) is not biased by the need to balance 8T with ^{IV}Al

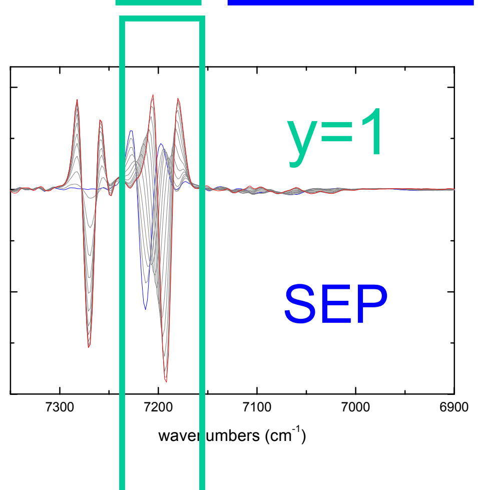
Fe(AEM) is Fe^{III} in M2M2OH sites only. $0 < x < 0.7$ (avg), $x \rightarrow 1.0$ (particle)

Extinction coeff $\varepsilon(2v_{M2M2OH})$ indeed constant. Sum of triplet intensity proportional to (1-y).









Mg_3OH by NIR

Intensity independent of **x**

Quantifying y from NIR

$K_{NIR}=I_{Mg3OH} / \Sigma I_{M2M2OH}$

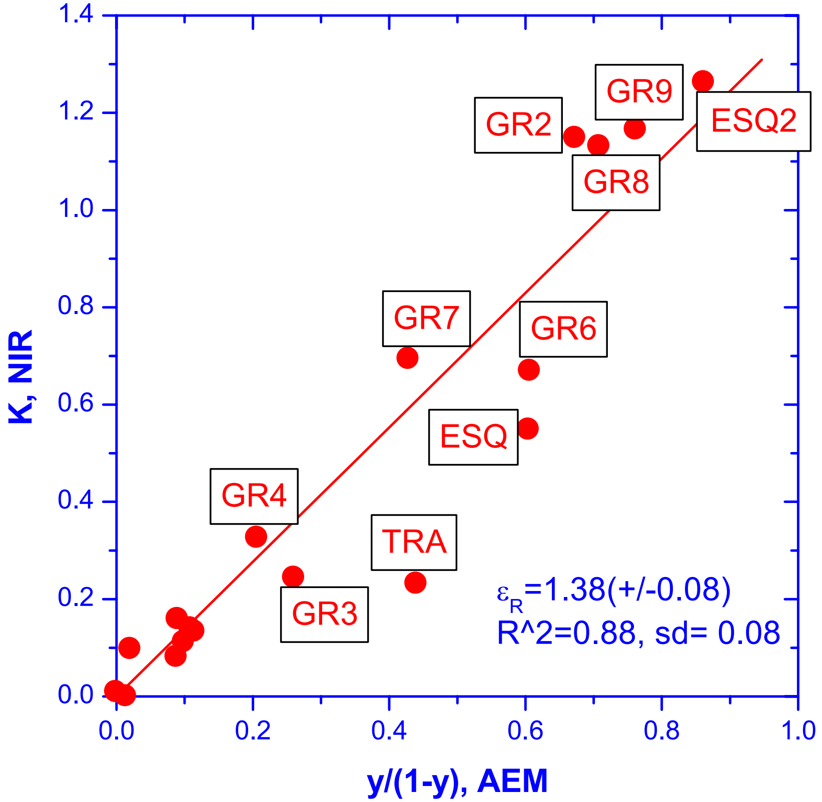
$y/(1-y) = \varepsilon_R K_{NIR}$

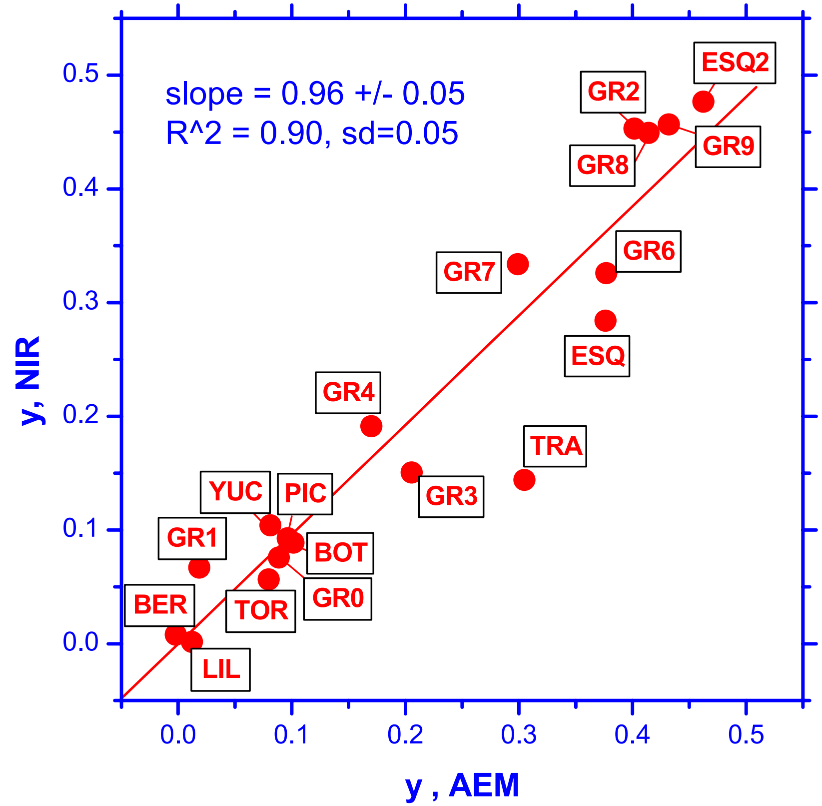
hence $y=K_{NIR} / (\varepsilon_R + K_{NIR})$

$\varepsilon_R \neq 1$,

requires calibration from AEM

Quantifying y from NIR





Octahedral cation composition of Palygorskite

$$yMg_5\,T_8O_{20}(OH)_2 \cdot (1-y)[xMg_2Fe_2 \cdot (1-x)Mg_2Al_2]T_8O_{20}(OH)_2$$

x, y conveniently determined by NIR

$0 < x \rightarrow 1$

Fe for Al substitution, no compositional gaps

$0 < y \rightarrow 0.5$

y not related to x

Pal → Sep?