Substitutional Iron (Fe) in 2:1 clays

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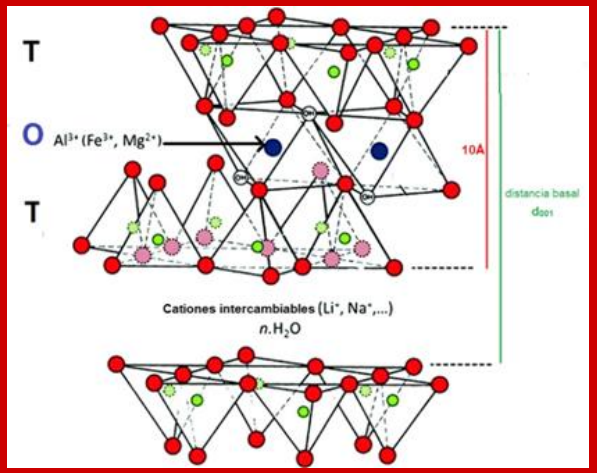
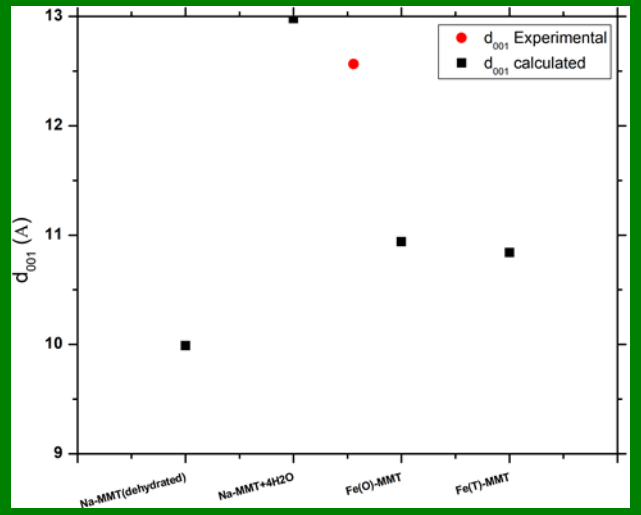
System

Montmorillonite (MMT)



$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot 4H_2O$

Results



d_{001} ➔ structure parameter ➔ results experimental

Conclusions and future work

¿Effect of Fe on MMT?

- d_{001}
- Band structure: Band gap

¿ Effect in other dilutions?

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Motivation

Water pollution ➔ one of the most important issues due to its direct impact on life
Widely extended remediation technologies ➔ based on the process of sorption of the contaminants.
Among sorbent materials ➔ montmorillonite (MMT) (1) ➔ well ranked.

Objective

Search for materials with good adsorption properties and magnetic response to allow their manipulation, through external magnetic fields, thus reducing the potential health risks associated with direct manipulation methods (2).

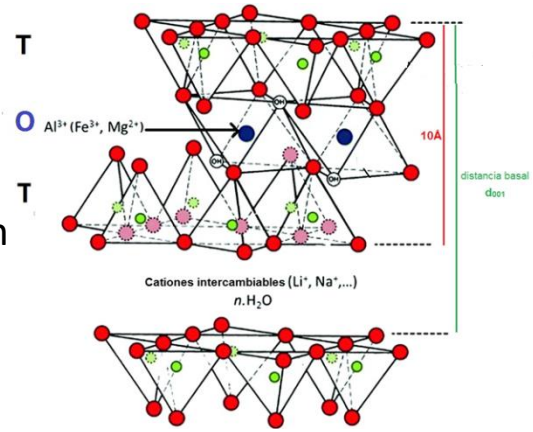
Preliminary results of the influence of substitutional Fe on Na-MMT

System

MMT: 2:1 clay, smectite group
$Na_{0.41}[(MgAl_3O_8(OH)_4(Si_8O_{12})]_2, 4(H_2O)$.
composed of two structural units:
2 T (tetrahedra) layers: 4 oxygen atoms surrounding a central atom, usually Si^{4+}
1 O (octahedra) layer: 6 oxygen or OH atoms surrounding a lower valence atom usually Al^{3+} (o Fe^{2+} - Mg^{2+})

Structural Model proposed by Eva Scholtzova et al.(5)
Oxygen are labeled as Basals, apicals and belonging to OH.

Montmorillonite (MMT)



Methodology

The modelling was performed within the Density Functional Theory (DFT)
Pseudopotential and plane-wave method (Quantum Espresso Code (3)) was used for the *ab-initio* calculations, with the GGA-PBE approximation for the exchange correlation term (4).
Structure for explore ➔ Na-MMT(dehydrated), Na-MMT+4H_2O, replacement Fe by Mg in octahedral site Fe,Mg(O)-MMT, substitution Fe by Si in tetrahedral site Fe, Si (T)-MMT.

Analized parameters

- DOS
- Band structure ➔ Band gap
- d_{001}
- Isomer shift (IS), quadrupole splitting(ΔEQ): Fe case comparison with experimental data ➔ Mössbauer spectroscopy

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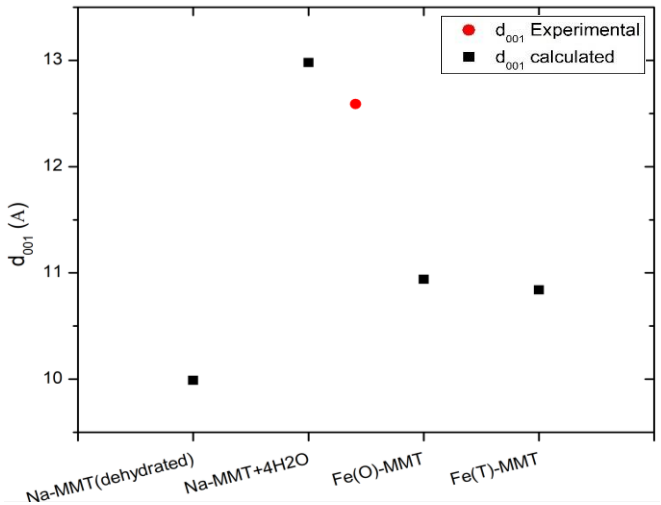
Results

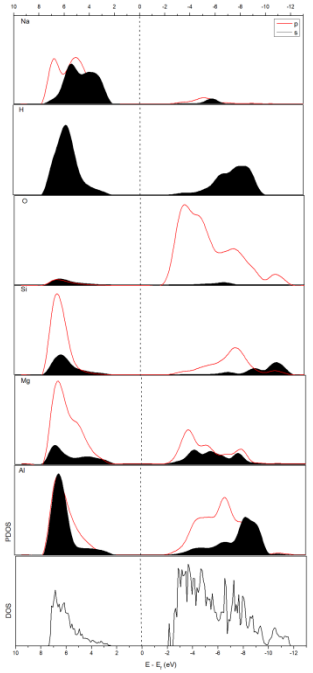
Basal spacing

Calculated d_{001} all propose structures and experimental results

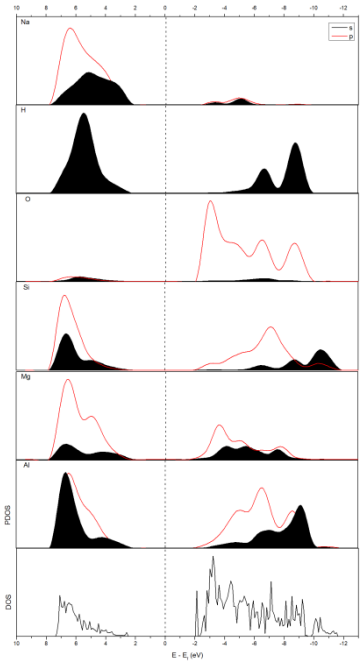


DOS

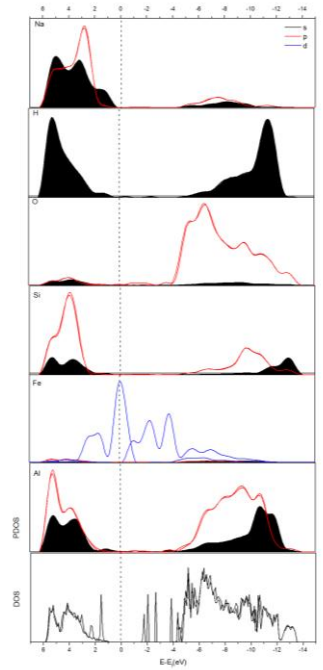
Na-MMT-dehydrated



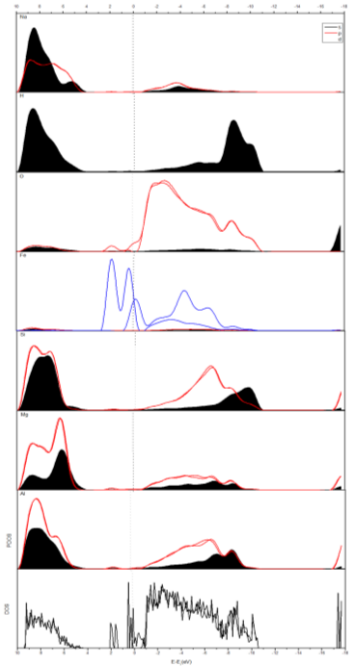
Na-MMT-4H2O



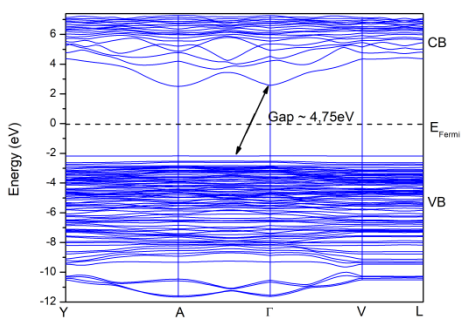
Fe(O)-MMT

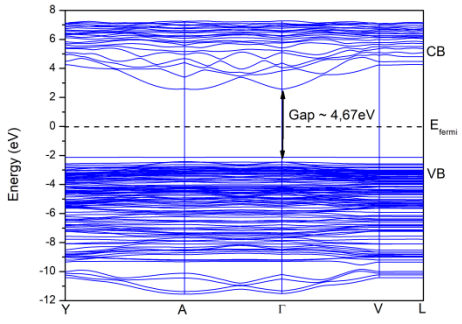


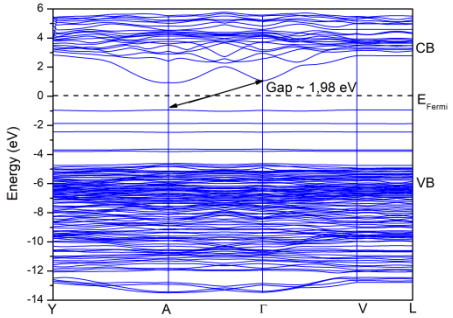
Fe(T)-MMT

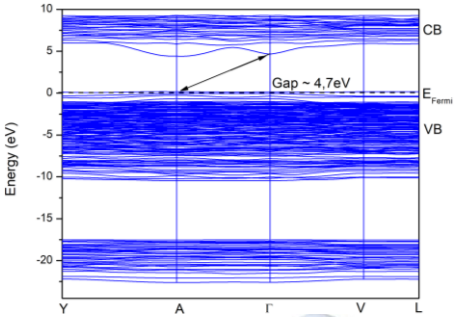


Band estructure









Na-MMT (dehydrated) d_{001} close to reported by Fonseca et. al. (6) d_{001} for Na- MMT close to that determined by XRD. Iron substituted MMT: d_{001} lower than the determined experimentally Causes?

The incorporation of Fe in octahedral site decreases the band gap, so in the calculations the parameter U will be incorporated

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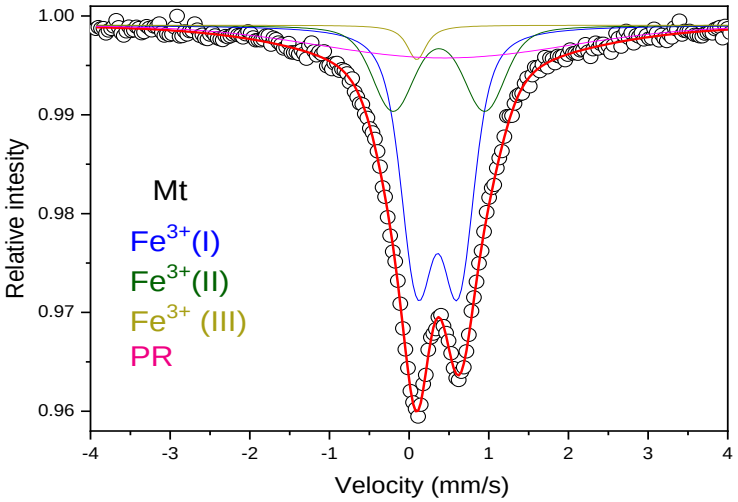
Espectroscopy Mössbauer

Na-MMT natural



$$\Delta E_Q = \frac{1}{2} eQV_{33}\sqrt{1+\frac{\eta^2}{3}} \qquad \delta = \alpha(\rho_0^{Sample} - \rho_0^{Reference})$$

unidad (mm/s)	MMT natural		Fe (O)-MMT	Fe(T)-MMT
ΔEQ1	0,51	ΔEQ	1,8536	0,2589
ΔEQ2	1,15	η	0.34311	0.5350
ΔEQ3	0,018			
IS(δ_1)	0,36		0,53 (7)	0,34 (7)
IS(δ_1)	0,37			
IS(δ_3)	0,45			

Conclusions

- Na-MMT proposed structure reproduces clay
- Substitution of Fe at T or O sites decreases d_{001}
- Incorporation of Fe in the octahedral site reduce gap
- Calculated quadrupole splitting greater is than experimentally determined.
- Isomeric shift of corresponding site 1 was well

Future work

- Incorporation of parameter U for calculations band gap
- Other dilutions of Fe in MMT will be explored

Reference

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