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## Theoretical estimation of iron isotope fractionation during cloud processing of aerosols

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## Introduction

Iron (Fe) is an essential micronutrient for the development of oceanic biomass, which is one of the main carbon sinks on a global scale. In about 30% of the oceans, the development of this biomass is constrained by an iron deficiency that limits primary production. This deficiency is related to the very low concentrations of bioaccessible Fe in the surface waters. In order to understand the origin and consequences of these low Fe levels (some ng Fe/L), various models have sought to determine the variability of Fe inputs to the ocean, particularly via aerosols. Recent progress in the measurement of Fe isotopic composition has made it possible to test the sensitivity of these models to spatiotemporal variations in inputs<sup>[1]</sup>. However, this approach is made difficult by the existence of isotopic fractionation phenomena that would be linked to the dissolution of particles within clouds. Our previous works<sup>[2],[3]</sup> seem to show that this isotopic effect is linked to the existence of a competition between Fe-ligand complexes in solution and the presence of some similar complexes on the surface of particles. The FAAR project aims to explain these processes through a double approach. First, it will simulate the dissolution of Fe aerosol-like particles in solutions mimicking cloud water. Changes over time in both Fe solubility and isotopic composition will be measured. Second, Fe isotopic fractionation solid-solution will be estimated via quantum chemical methods and compared, in the same way, to the respective stabilities of the surface and solution complexes, in order to conclude on the possibility of extending our simulations to more realistic atmospheric conditions.

## Nanocrystals Synthesis

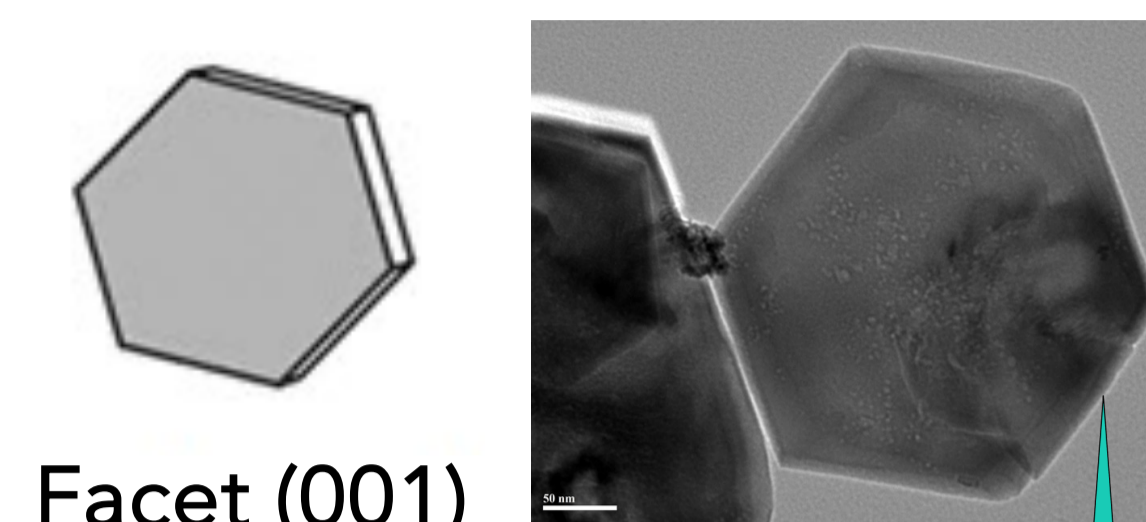
### Synthesis of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates (001)

The nanocrystals are prepared by hydrothermal synthesis. Such preparation is taking place Teflon lined in stainless steel autoclave, by using Fe precursors and a directing agent like aluminum acetate.

#### Precursors:

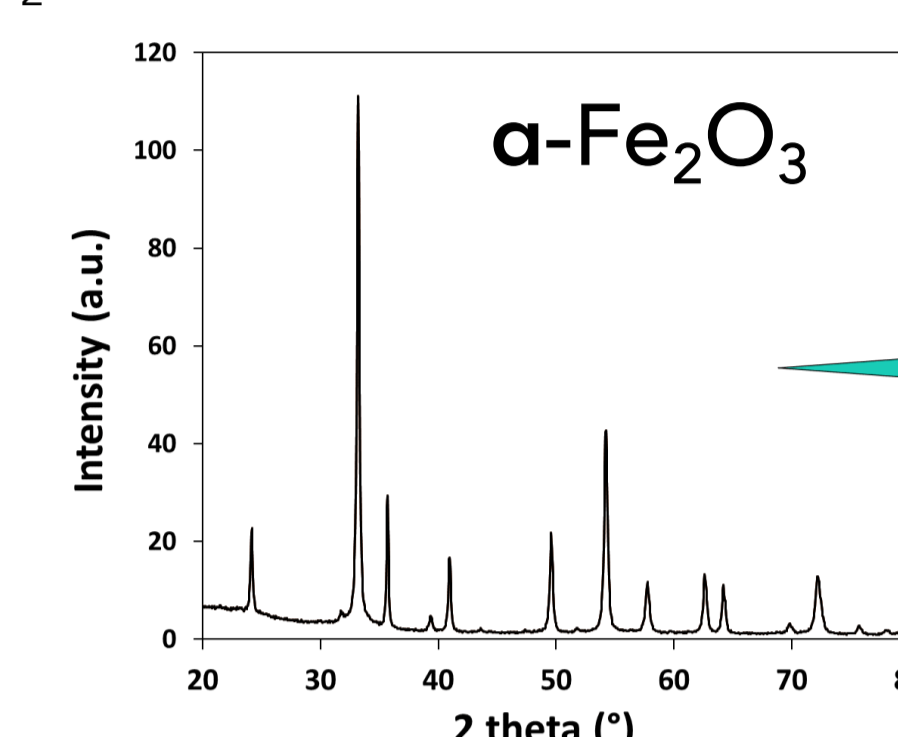
- Iron nitrate nonahydrate : Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O
- Aluminum Acetate : C<sub>4</sub>H<sub>7</sub>AlO<sub>5</sub>
- Solvent: NH<sub>4</sub>OH

**Procedure:** 12 h at 160 °C in autoclave



Facet (001)

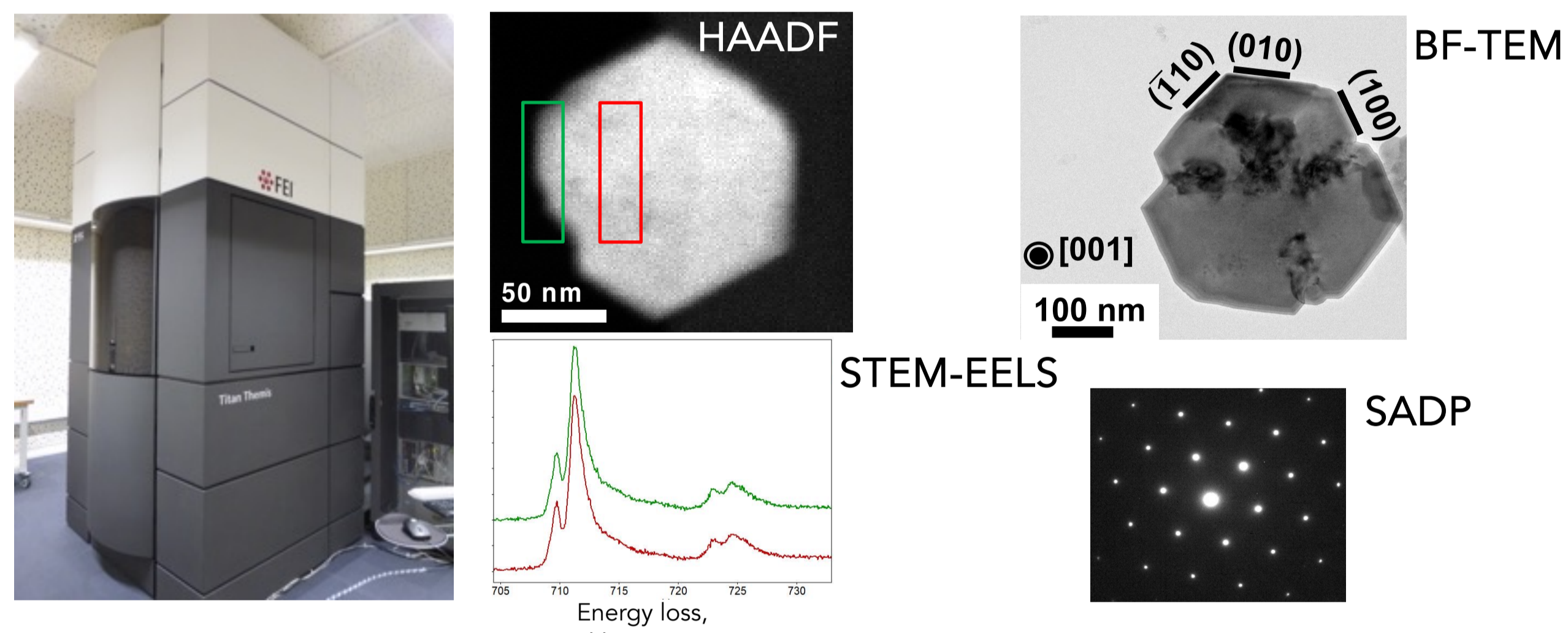
SEM image of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates



Wide angle XRD spectrum indicates the formation of an Fe<sub>2</sub>O<sub>3</sub> hematite phase

## Characterization Methods

The morphology and crystalline defects of (001) nano-crystals are studied by TEM using a Tecnai™ G2 Microscope. Elemental mapping, high resolution imaging and iron speciation are performed using a S/TEM TITAN Themis microscope.



**TITAN Themis characteristics:** High brightness Schottky FEG with Wien type monochromator (energy resolution <0.2 eV); Probe Cs corrector (spatial resolution < 70 nm); Four quadrant Super-X detector chemical mapping. GATAN post-column high-resolution energy filter (Quantum ERS/966) with a direct electron detector.

## Dissolution Experiments

### Simulated cloud water composition:

- [α-Fe<sub>2</sub>O<sub>3</sub>] = 250 mg/L
- [oxalic acid] = 1 mM (pH = 2, fixed with perchloric acid)

### Analyses (soluble phase):

- [Fe]<sub>soluble</sub> by atomic absorption spectrometry (GFAAS)
- [Fe<sup>2+</sup>] and [Fe<sup>3+</sup>] by the ferrozine method
- Fe isotopic composition ( $\delta^{56}\text{Fe}$  and  $\delta^{57}\text{Fe}$  scales) by MC-ICP-MS (G-Time Laboratory, Free Univ. Brussels)

### Analyses (solid phase):

- Infrared Spectra of Fe-oxalate surface complexes (SOLEIL Synchrotron AILES-C beamline – Preliminary results)



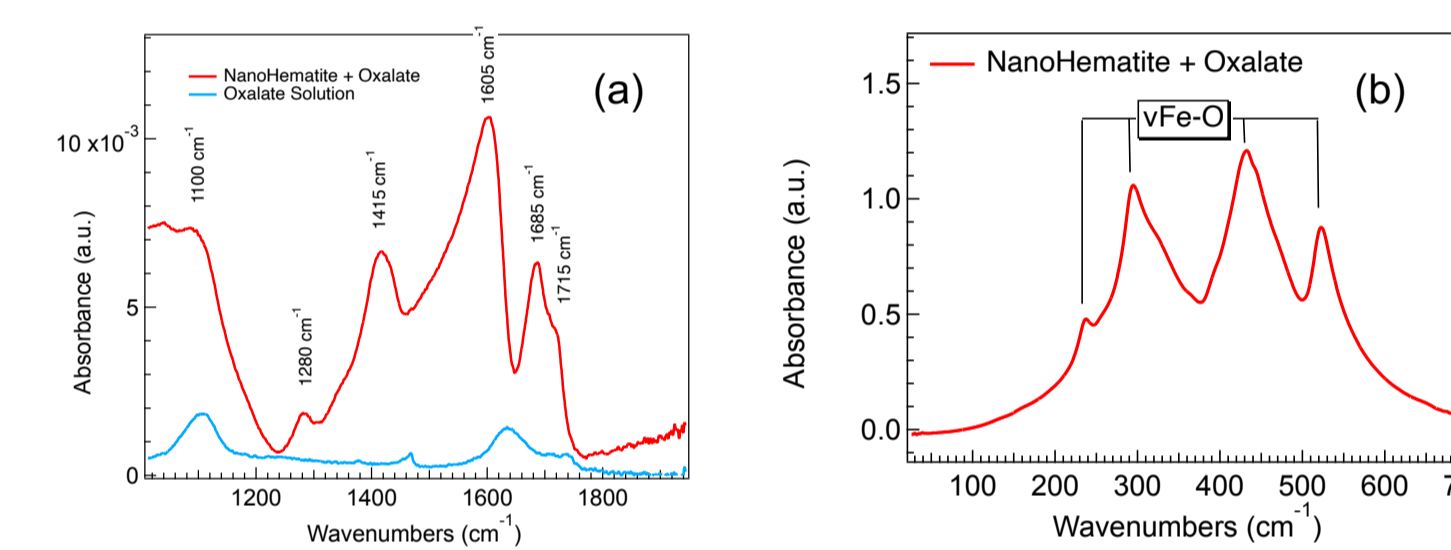
Experimental Setup in ISO 6 Cleanroom:

- Dissolution Temperature: 20° C
- Sun Simulation: 1000 W/m<sup>2</sup> (λ = 400-1100 nm)
- 25 mL PFA reactor in water bath, under magnetic stirring
- Dissolution test duration: 1-10 days

Courtesy of Jean-Blaise Brubach

AILES Beamline

Synchrotron SOLEIL Facility



(a) Mid-Infrared spectra of a mixture of Hematite Nanoplates and Oxalic solution (red) and solution of acid oxalic in water at pH=2 (Blue). (b) Far-Infrared spectra of a mixture of Hematite Nanoplates and Oxalic solution

## Estimation of Fe isotope fractionation factors by Density Functional Theory

Iron isotope exchange equation: A<sup>54</sup>Fe + B<sup>56</sup>Fe ⇌ A<sup>56</sup>Fe + B<sup>54</sup>Fe where A and B are two phases.

At thermodynamic equilibrium, the isotope fractionation factor is:

$$\alpha_{A,B} = \frac{Z(A^{56}\text{Fe}) \times Z(B^{54}\text{Fe})}{Z(A^{54}\text{Fe}) \times Z(B^{56}\text{Fe})} = \frac{\beta_A}{\beta_B}$$

where Z represents the partition function of Fe, and β is the reduced partition function ratio (RPF), defined in the harmonic approximation as:

$$\beta = \prod_i \frac{u_{h_i}}{u_{l_i}} \cdot \frac{\exp(-u_{h_i}/2)(1 - \exp(-u_{l_i}))}{\exp(-u_{l_i}/2)(1 - \exp(-u_{h_i}))}$$

h: heavy isotope (i.e., <sup>56</sup>Fe)

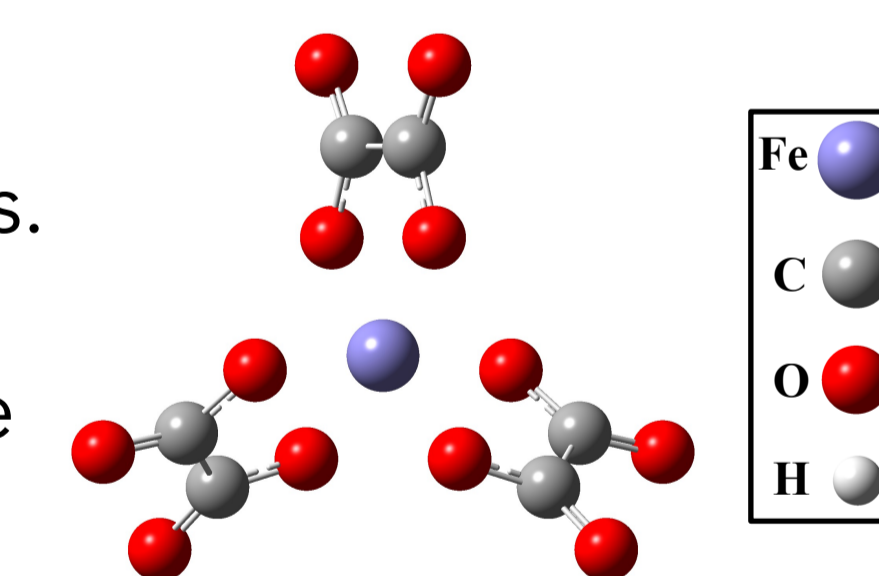
l: light isotope (i.e., <sup>54</sup>Fe)

u<sub>i</sub> = hc2πω<sub>i</sub>/(kT), and ω<sub>i</sub> is the vibrational frequency of mode i.

➤ The vibrational frequencies of A<sup>54</sup>Fe, A<sup>56</sup>Fe, B<sup>54</sup>Fe, B<sup>56</sup>Fe are required.

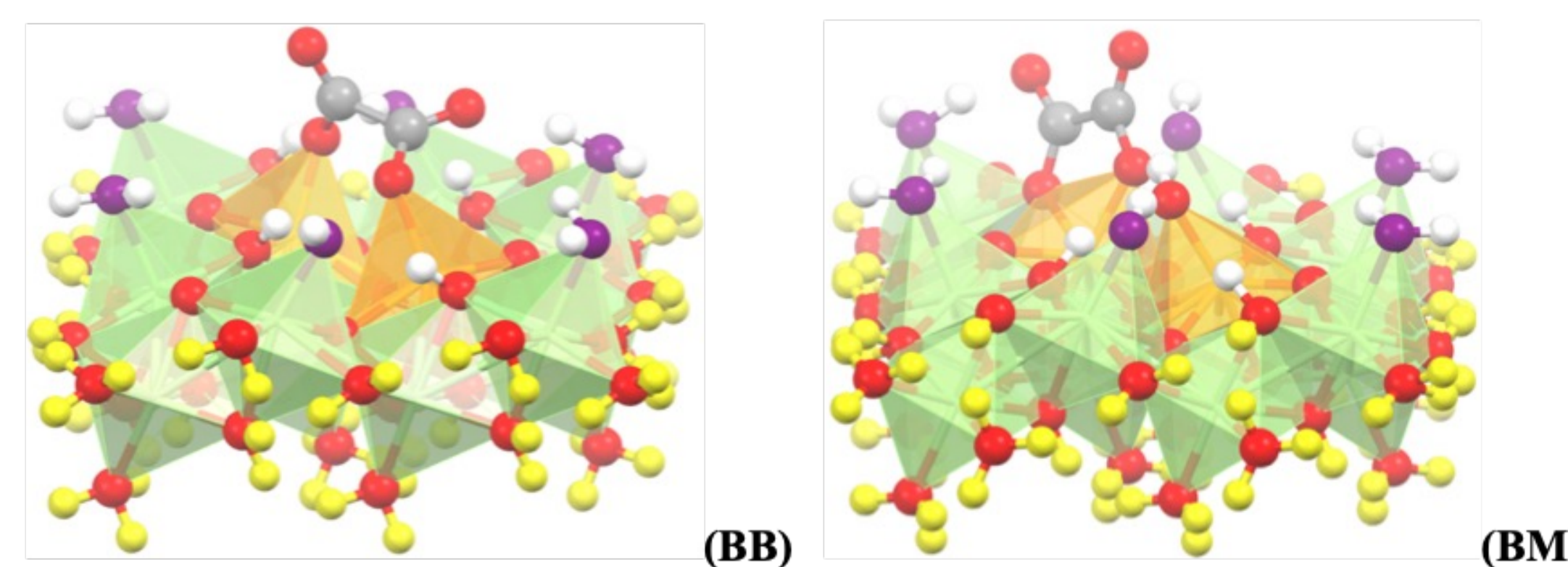
### Oxalate complexes in aqueous phase

- Method: B3LYP
- 6-31G\* basis set was used for the C, O and H atoms.
- Ahlrichs' valence triple ζ basis for the Fe atom.
- Effects of the water solvent were modeled using the Polarizable Continuum Model (PCM).



### Oxalate on hematite (012) surface<sup>[4]</sup> (using embedding cluster model)

- Method: B3LYP
- Polarized double ζ basis set for all Fe atoms (m6-31G\*).
- 6-31G\* basis set for O and H atoms in the core region.
- 3-21G basis set for all atoms in the embedding region, including hydrogen basis functions on the quasi-atoms.



BB = Bidentate Binuclear

BM = Bidentate Mononuclear

Adapted from [5]

### Take home messages and perspectives

- Preliminary results<sup>[5]</sup> show a negative fractionation during Fe aerosol-like particles dissolution in simulated cloud water: soluble Fe exhibits an enrichment in "light" Fe (<sup>54</sup>Fe) compared to remaining particulate Fe
- Comparison of experimental results with the estimation of Fe isotope fractionation factors calculated by DFT methods seems to show that this fractionation is due to kinetic effects
- To go further new dissolution experiments will be performed with single crystalline hematite ([001] nanoplates)
- The use of nanoplates facilitates the comparison of experimental results with their theoretical counterparts arising from DFT calculations.
- For that, the theoretical work on hematite (012) surface will be adapted to the hematite (001) surface.

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