Dust mineralogy and iron solubility: integrative study to model the iron dissolution

FERATMO+ Project

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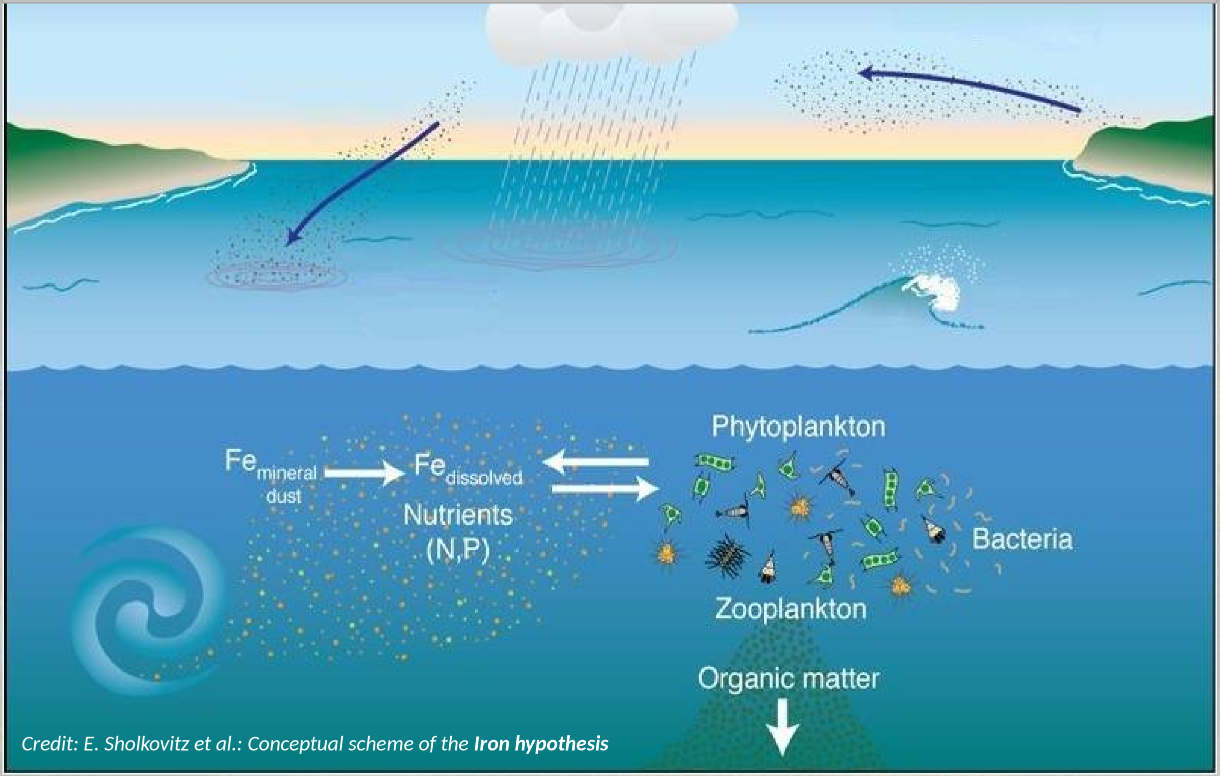
Stagiaires: M. Bandak; S. Mohamed; C. Fabarez; S. Katrou; N. Katrou

Dust/iron fertilization

Fe-dust act as a micronutrient for oceanic phytoplankton



Credit: E. Sholkovitz et al.: Conceptual scheme of the ***Iron hypothesis***

State of play:

- **Biogeochemical impact** of dust depends notably on the **bioavailability of iron**
- The **solubility** of dust-Fe is used as a **proxy for bioavailability**
- **Dust-Fe solubility**, that **varies largely**, is affected by many factors (origin, transport, way of deposition, pH, ligands,..)

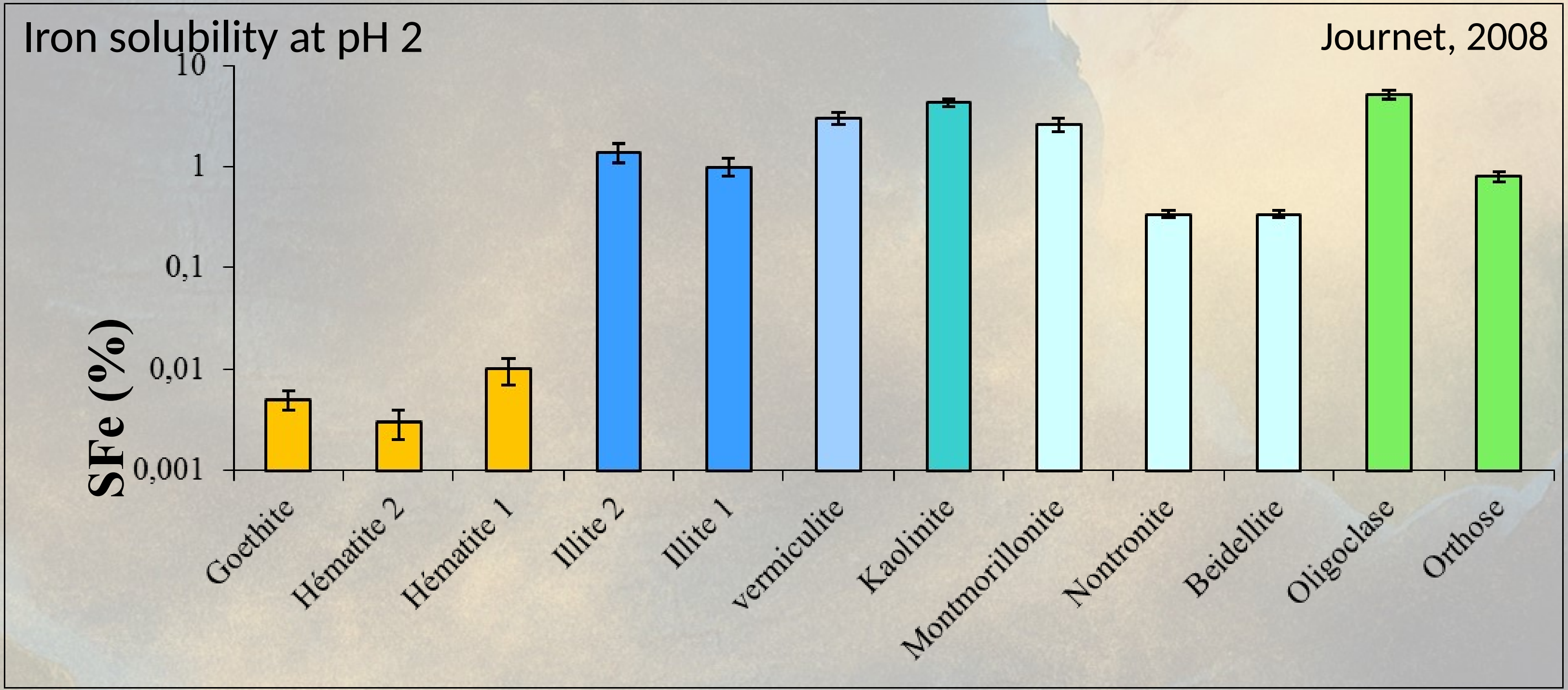
A current challenge: **Improve the modeling** of the bioavailable fraction of iron deposit to the oceans

=> Need to describe the **mineralogical properties** of dust

Iron solubility and dust mineralogy

<u>A finding</u>: The solubility of iron varies greatly from one mineral to another

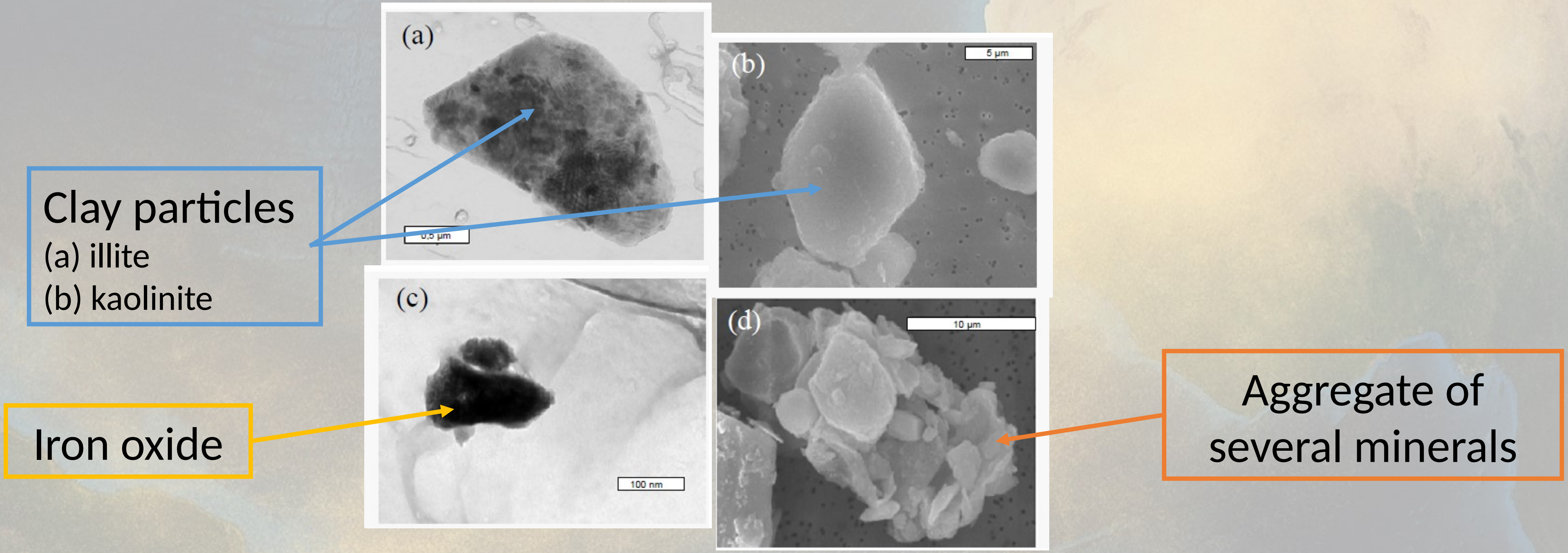
(Journet et al., 2008; Schroth et al., 2009; Trapp et al., 2010)



What is the mineralogical composition of dust? How does it vary?

Mineralogy of dust

Dust is a complex mixture of different minerals whose proportions, at emission, depend on the mineralogy of the source region

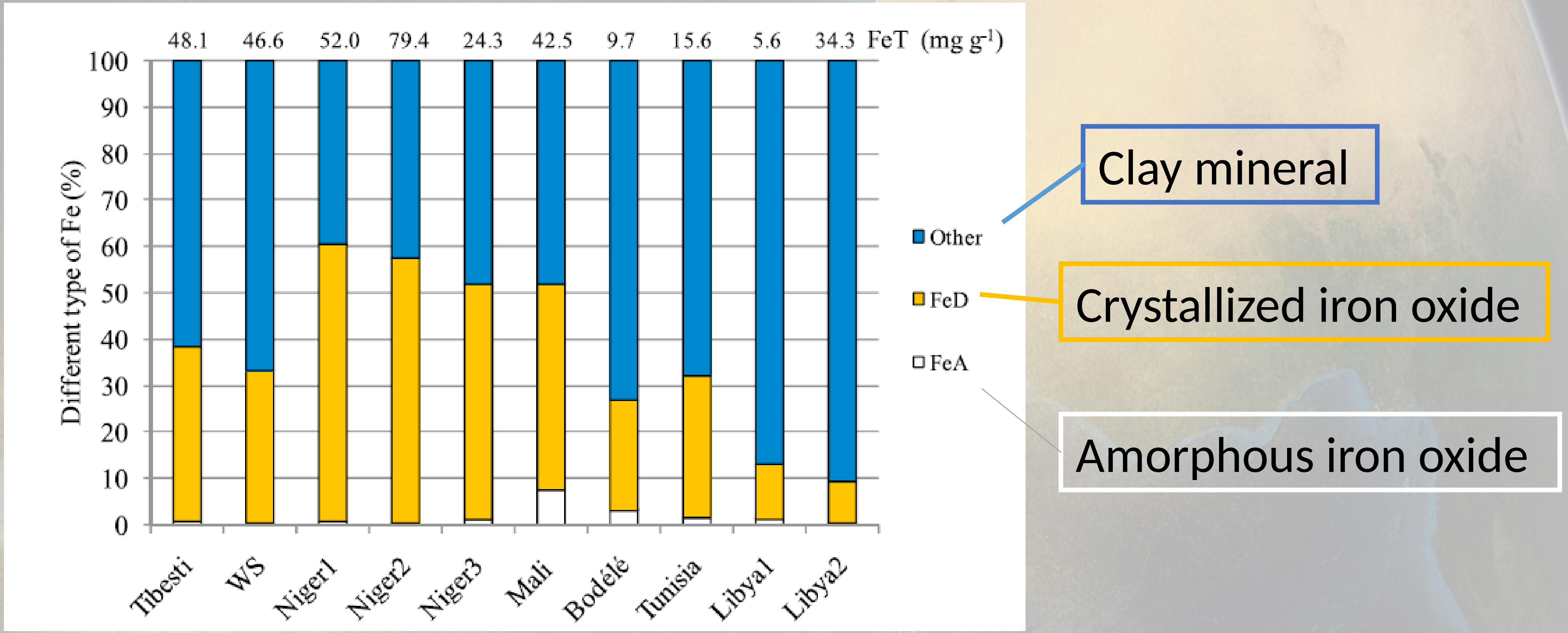


Lafon, 2004

Where is the iron? How is it distributed among the different minerals?

Mineralogical iron status

Dust iron can be classified into three mineralogical phases.
There is significant regional variability in the Fe mineralogical status.



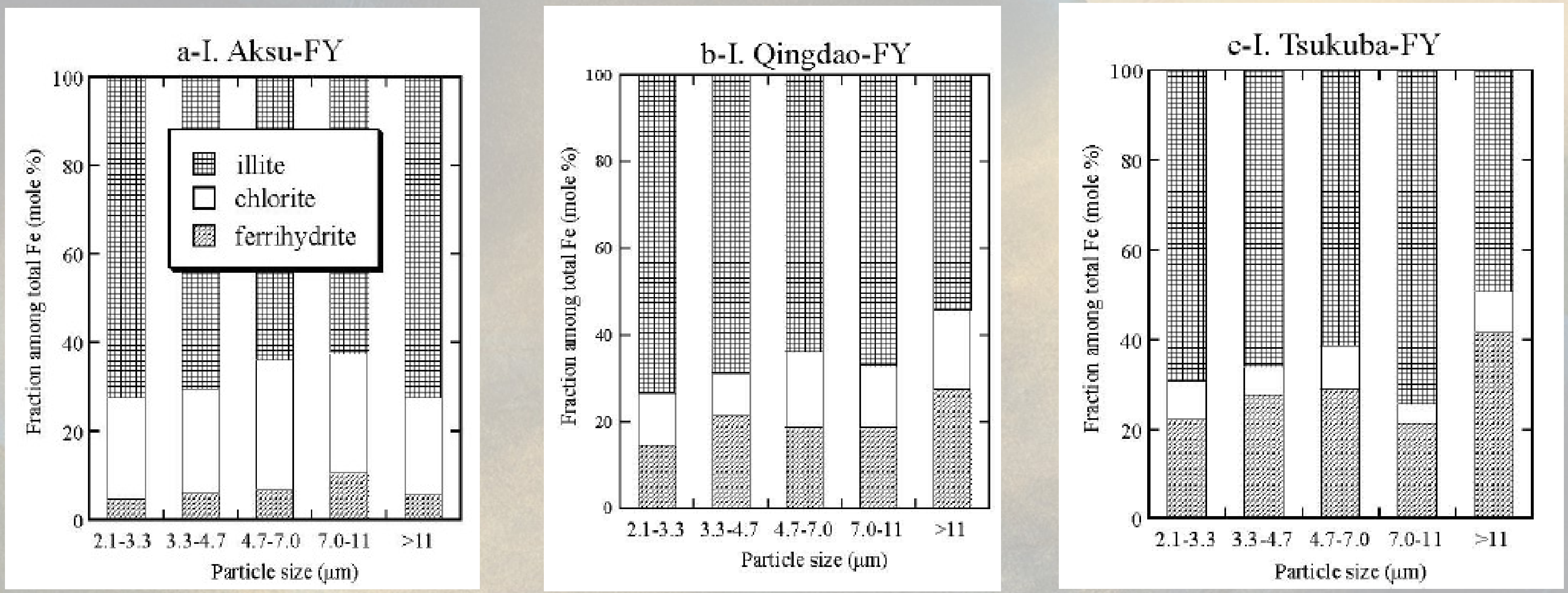
Shi et al., 2011

Does the mineralogy status of iron evolve after emission?

Evolution during atmospheric transport

The secondary formation of ferrihydrite during the transport is observed

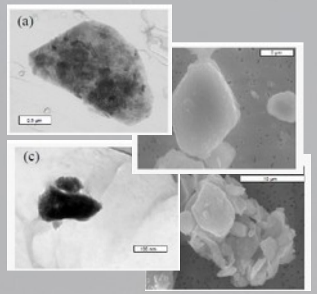
Distance from the source



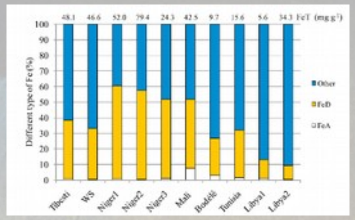
Takahashi et al., 2011

Finally, how iron solubility is linked with dust mineralogy?

Links between solubility and mineralogy



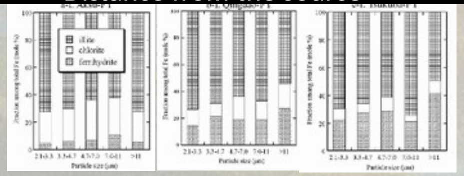
- Mineralogy can influence indirectly the solubility of iron by modifying the pH of the aqueous phase



- Mineralogy influence directly the solubility of iron:

  Crystallized iron oxide << Clay << Amorphous iron oxide

Distance from the source



- iron solubility increases after the transport possibly due to the formation of amorphous iron oxide

An increased focus on dust mineralogy would be an important step toward an improved understanding of dust iron dissolution

Objective of FERATMO+

The global objective is to describe iron dissolution processes from a mineralogical point of view in order to improve modeling of dissolved iron inputs to surface ocean.

- How iron status and content in dust varies according to the dust mineralogy/source and particle size?

- What is the solubility of the different iron-bearing mineral found in dust? How solubility is sensible to the size particle? to the dissolution condition (pH, organic complexation, light…)?

- Are there iron status differences of freshly emitted dust play significantly on iron solubility?

- How solubility of iron dust can be parametrized by knowing mineralogical composition of dust?

Strategy of FERATMO+

Pure minerals aerosols generated in lab

Dust aerosols generated in lab from arid soils

Atmospheric dust aerosols collected close to the sources

WP1 (S. Lafon)

Fine characterization of mineralogical status of iron in dust

WP2 (E. Journet)

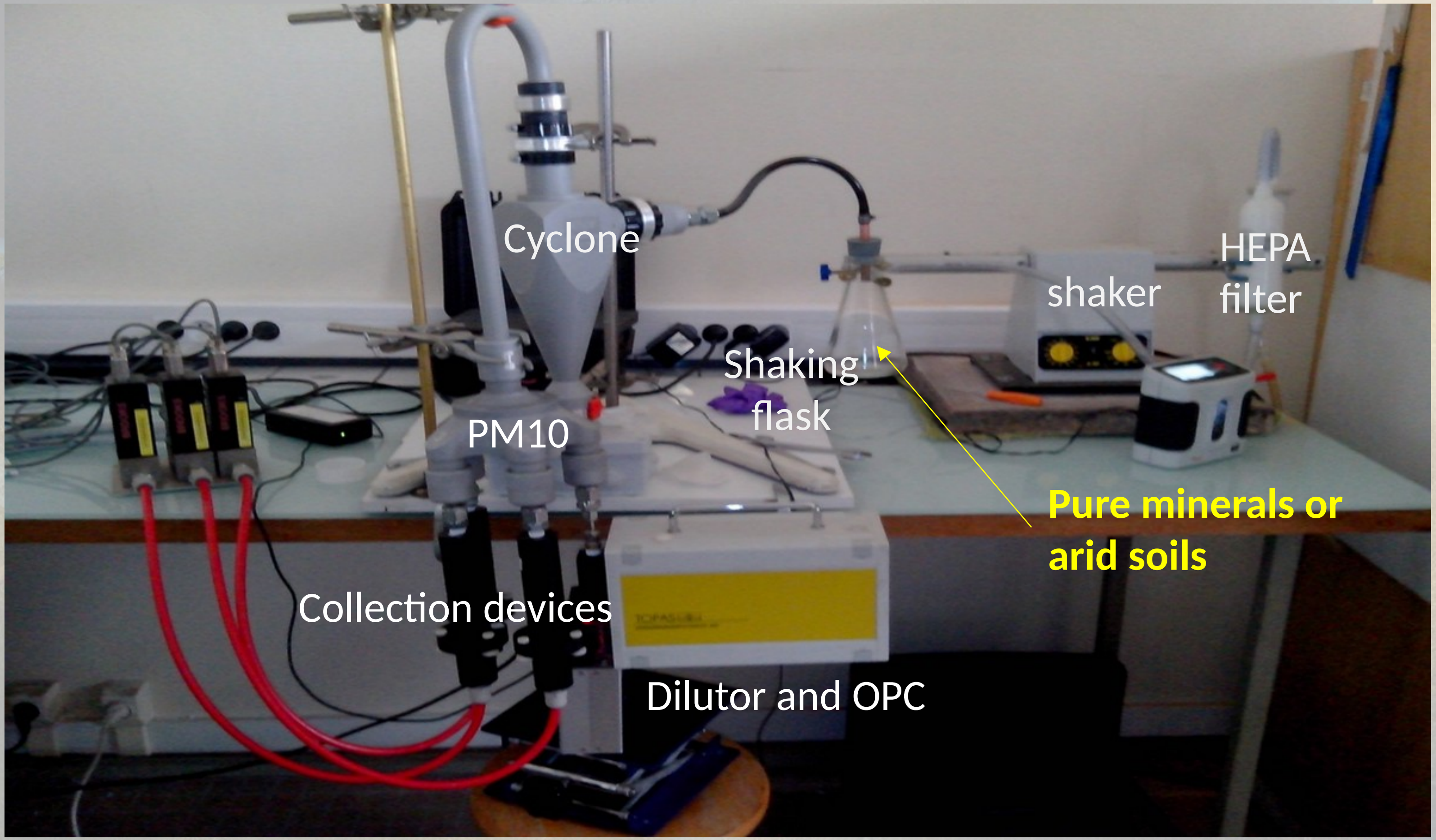
Dissolution experiments under different conditions

WP3 (B. Laurent)

Parametrization of iron solubility from mineralogical composition of dust

Lab generation of aerosols

A new generator for aerosol production in the laboratory: GAMEL (Lafon et al., 2014)



<u>GAMEL allows to:</u>

-Generate aerosol from pure mineral and arid soil samples

-Generate as many replicates as necessary to perform all required analyzes

-to overcome of mixing effects

-to compare different materials by putting them in a similar form (aerosols)

Studied samples

- **18 Reference mineral samples from 8 different species**

Iron oxides, illite, smectite, kaolinite, palygorskite, chlorite, feldspars, interstratified

- **6 desert soil samples from three continents**

North Africa, South America and East Asia

- **5 atmospheric dust samples collected close to emission areas**

(North Africa and South America)

GAMEL

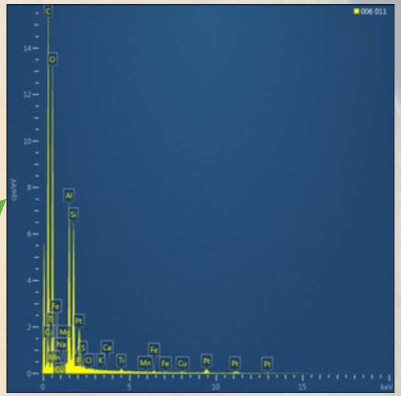
Characterization of the samples

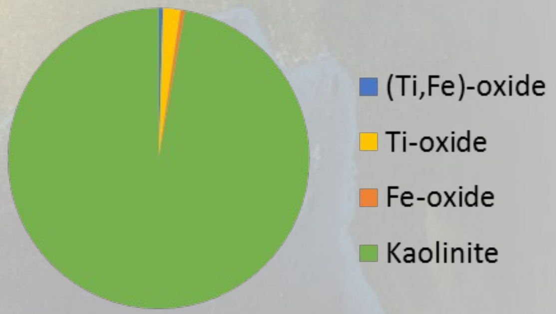
Individual particles analyses :

➢ **Routine methods**: SEM-EDS

Example of kaolinite (KGa2)

particle size distribution





mineralogical composition of KGA2 in number

➢ **Developing method** : RAMAN spectroscopy

Try to identify amorphous iron particles…

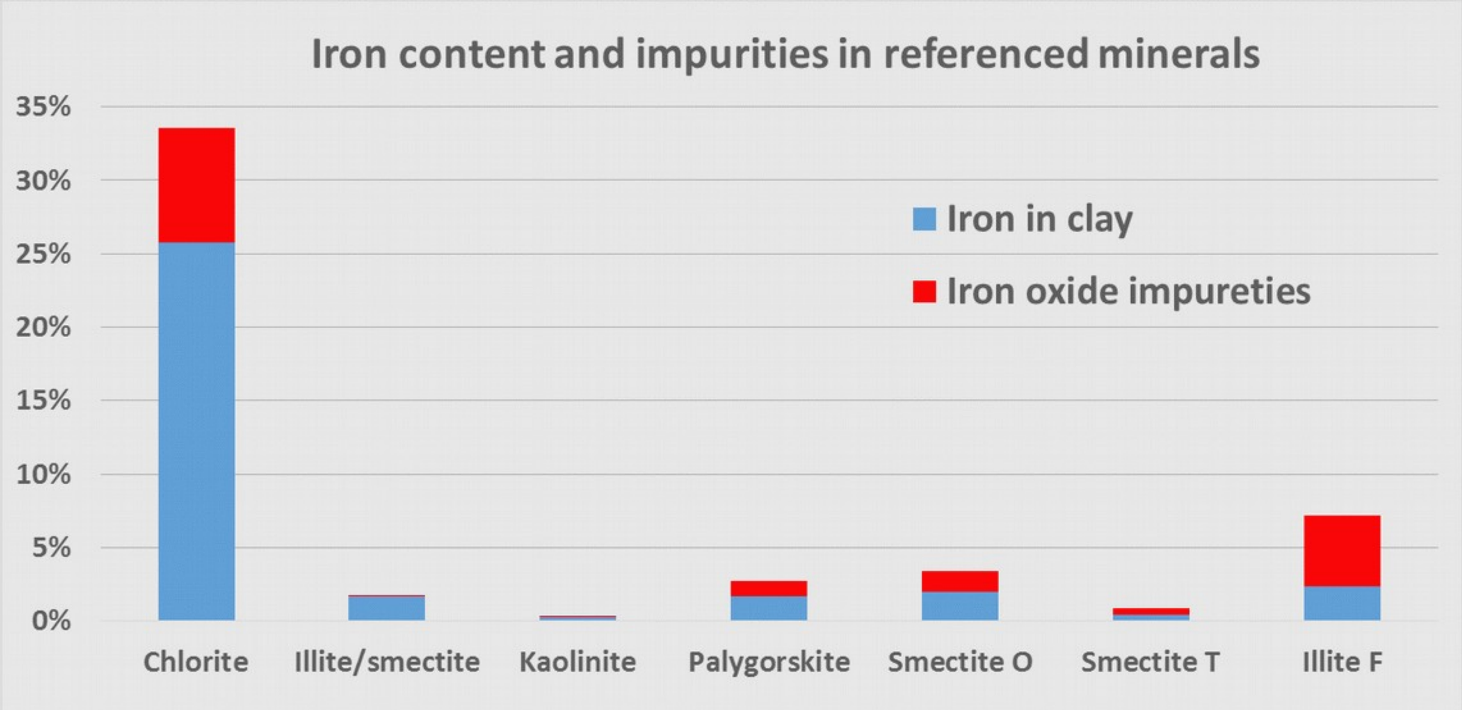
C. Fabarez (IUT training period)

Characterization of the samples

Bulk analyses :

➢ **routine methods**

- SFX => Elemental composition (Al, Si, Fe, Ca, Na, P, Mg, Mn, Ti)
- CBD extraction (Lafon et al., 2004) => structural iron to oxide iron ratio



M. Bandak (M2 trainee)

Characterization of the samples

Bulk analyses :

➢ **Developing method**

- a new XRD analytical method to quantify the mineralogical composition of dust (Nowak et al., in prep)

Ratio of peak height in DRX spectra for Illite F obtained for different sample preparation mode

	ratio of peak height I(002)/I(11-1)
Theory	**0.56**
Deposited (Caquineau et al., 2002)	3.02
Capillary	0.36

- CBA extraction: Amorphous iron oxide content (CBA adapted to low mass)

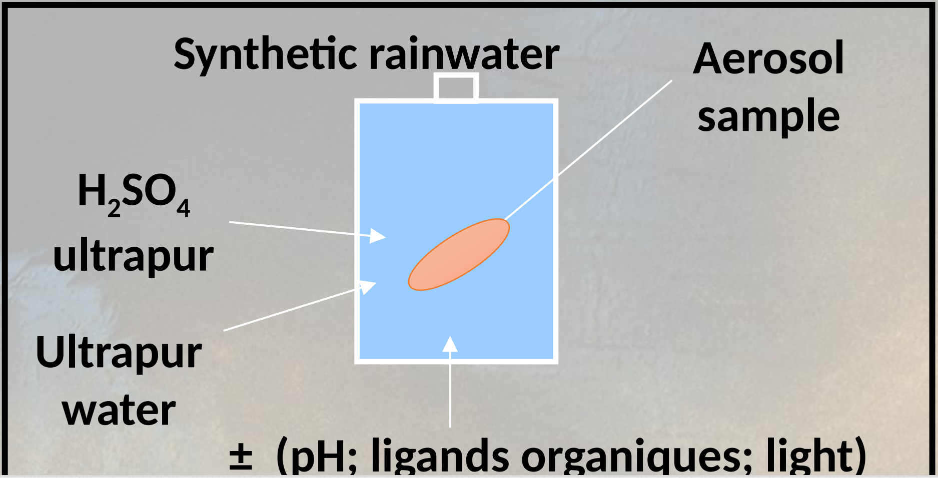
First tests realized by S. and N. Katrou (L3 training period)

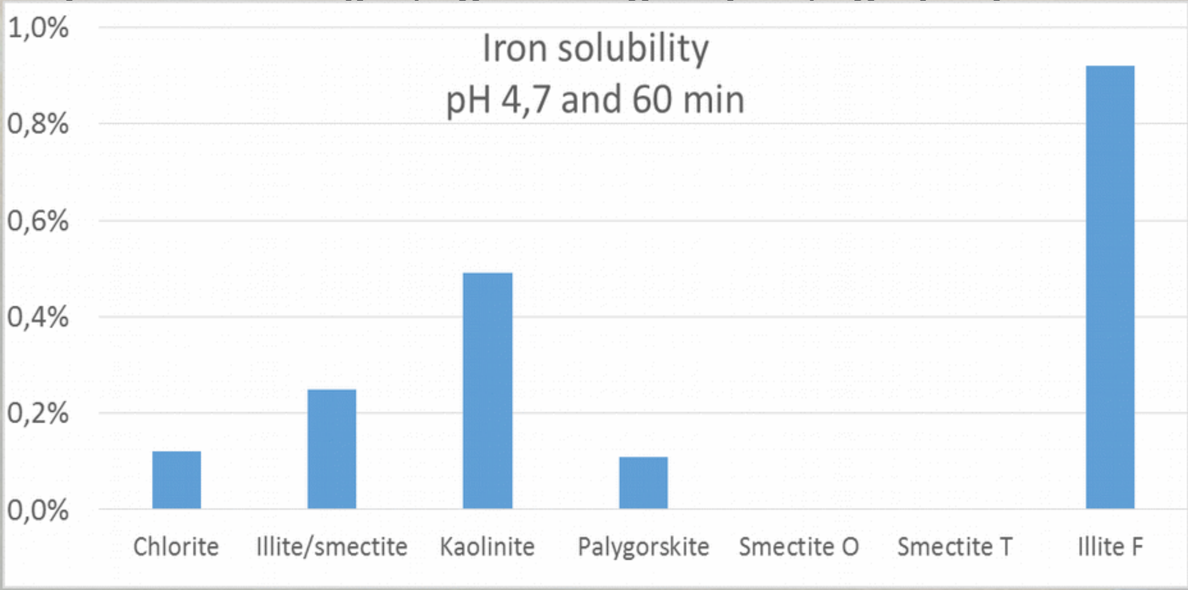
- BET: Specific surface measurement (BET adapted to low mass)

First tests realized by S. Mohamed (M1 training period)

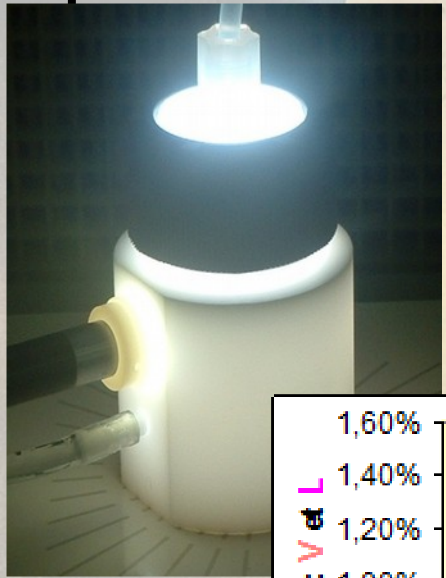
Dissolution experiments

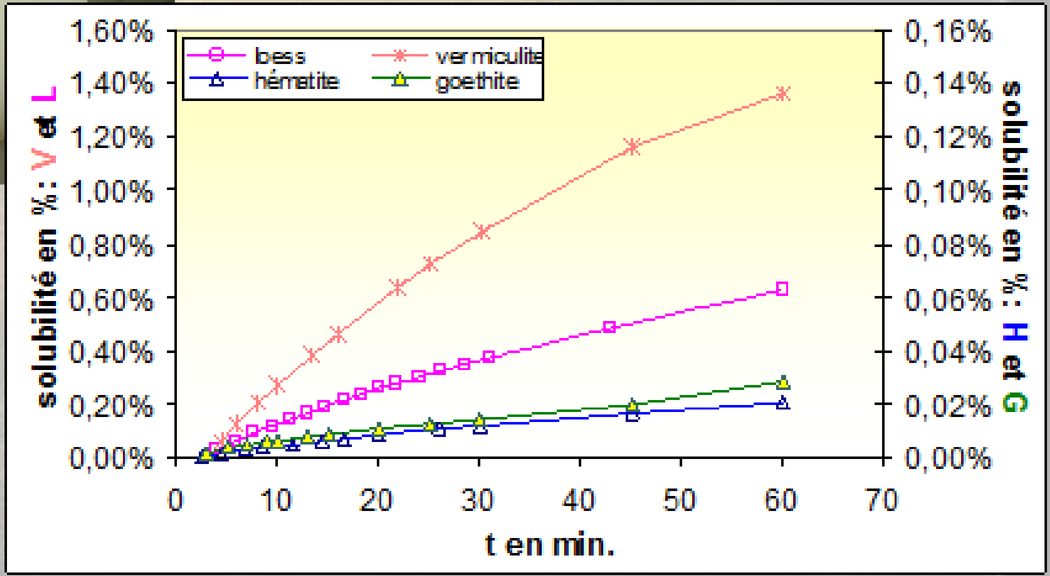
- **Iron solubility for each under different conditions :**





- **Establishment of the kinetics of dissolution of pure minerals:**





Sokikitis, 2004

Numerical developments

What is planned

Based on the FEARTMO+ experimental analyses, new parameterizations of the solubility of atmospheric Dust-Fe will be established

➢ To formalize the relationship between mineralogy, particles size distribution and iron content/mineralogical status.

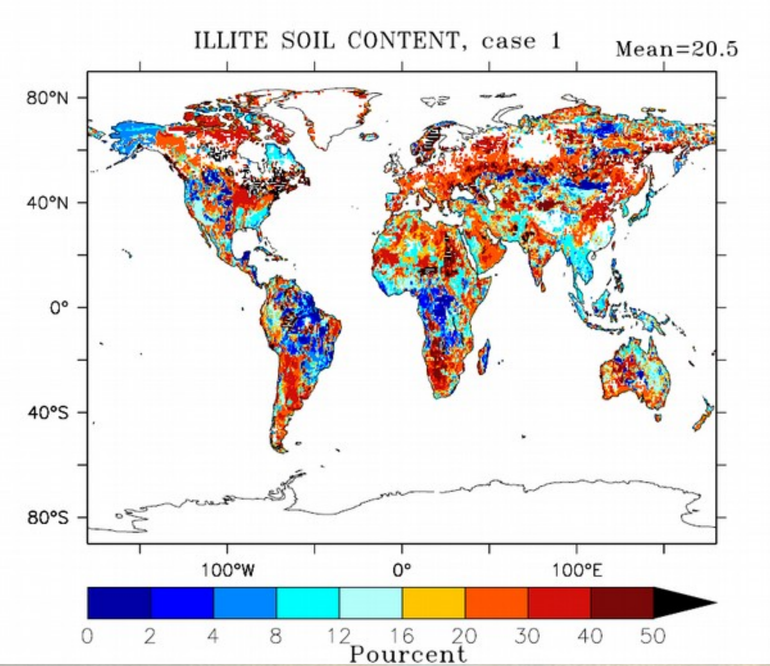
➢ To parametrize the dissolution of iron as a function of intrinsic properties of dust and the dissolution condition.

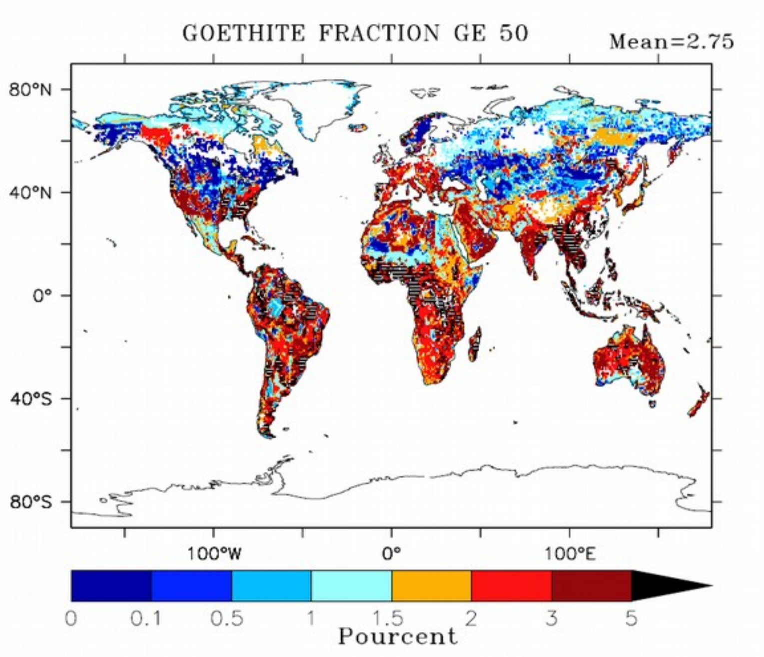
DFe = f (mineralogy, size, Surface Specific, pH; complexation, light)

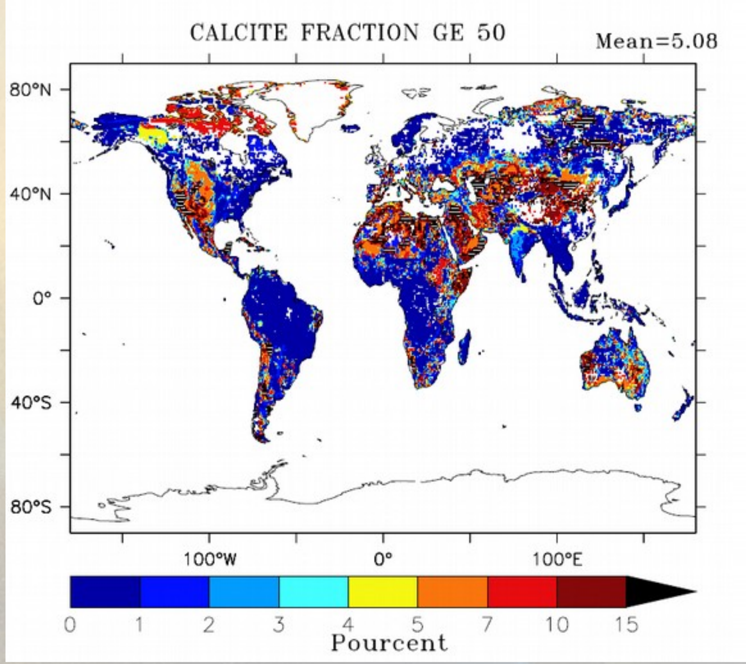
Perspectives

Final objective:

Modeling the flux of dissolved iron from the mineral soil maps







Journet et al., 2014

A major obstacle:

How the composition of the mobilized soil dust is related to that of the parent soil?