UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA

Iron solubility in mineral dust and aerosol generated from soil samples

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Máster en Oceanografía

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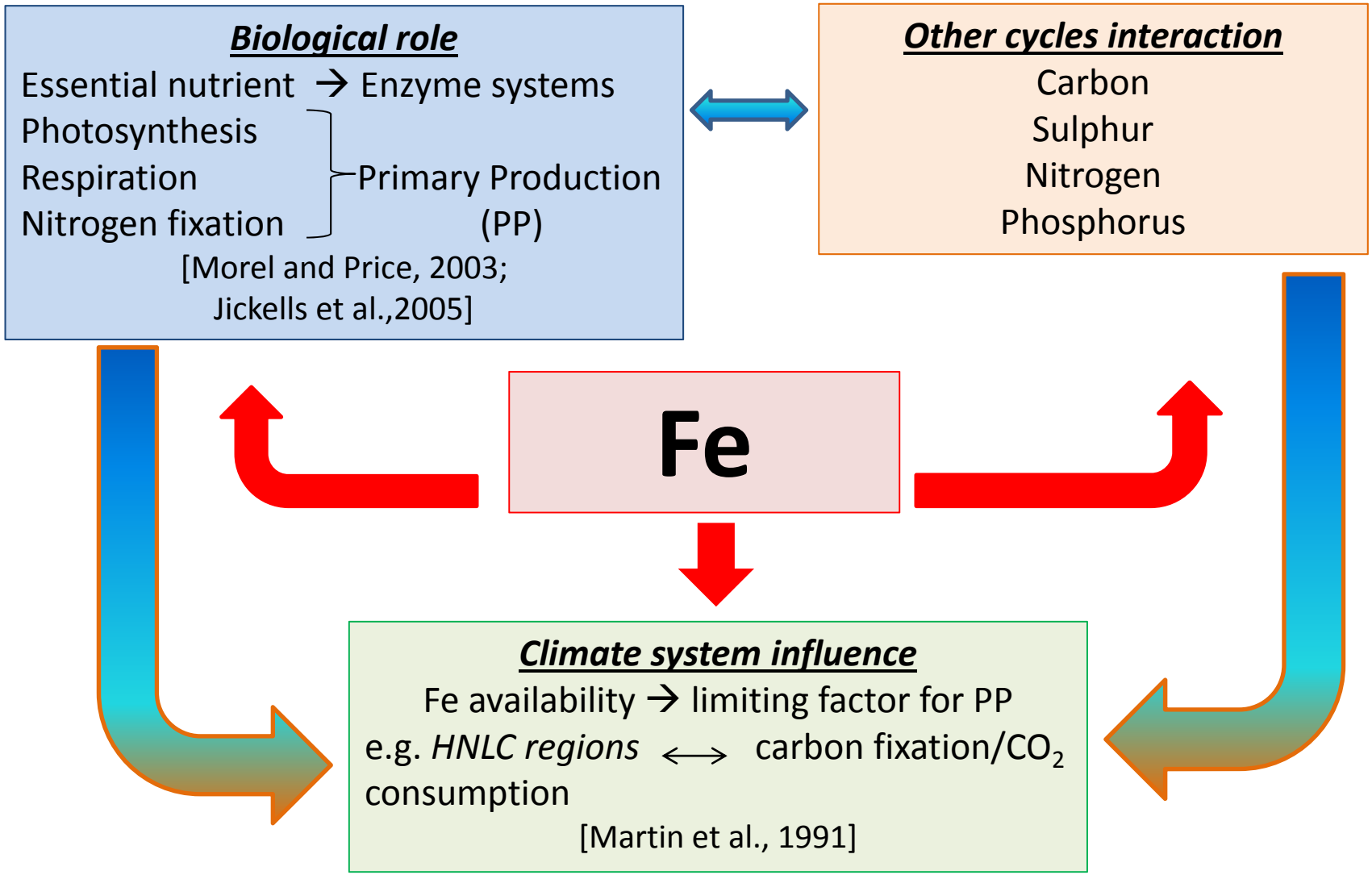
1.Introduction

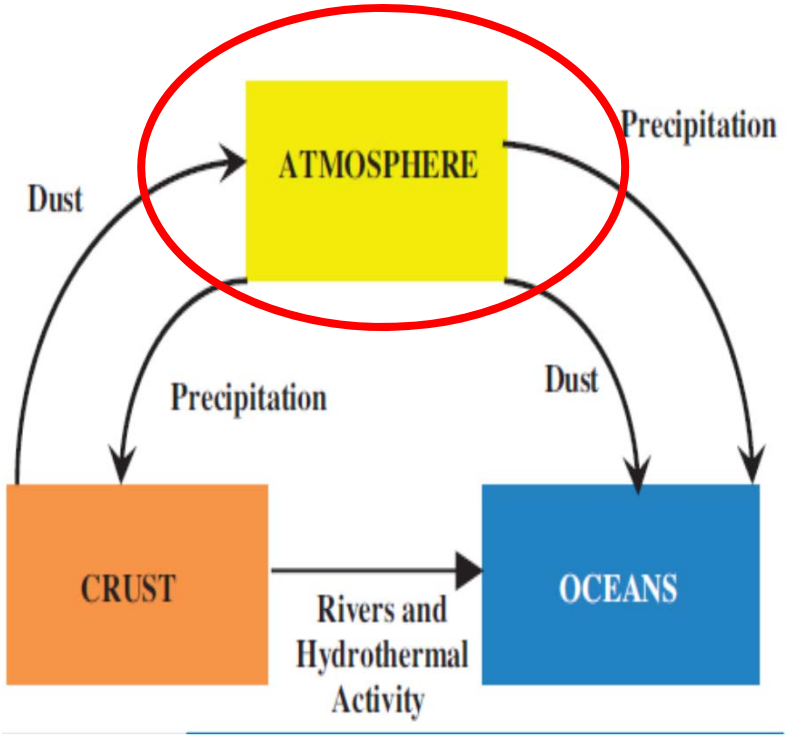


1.Introduction

Atmospheric dust input → Global Impact

Global iron fluxes to the ocean [Jickells et al., 2005]

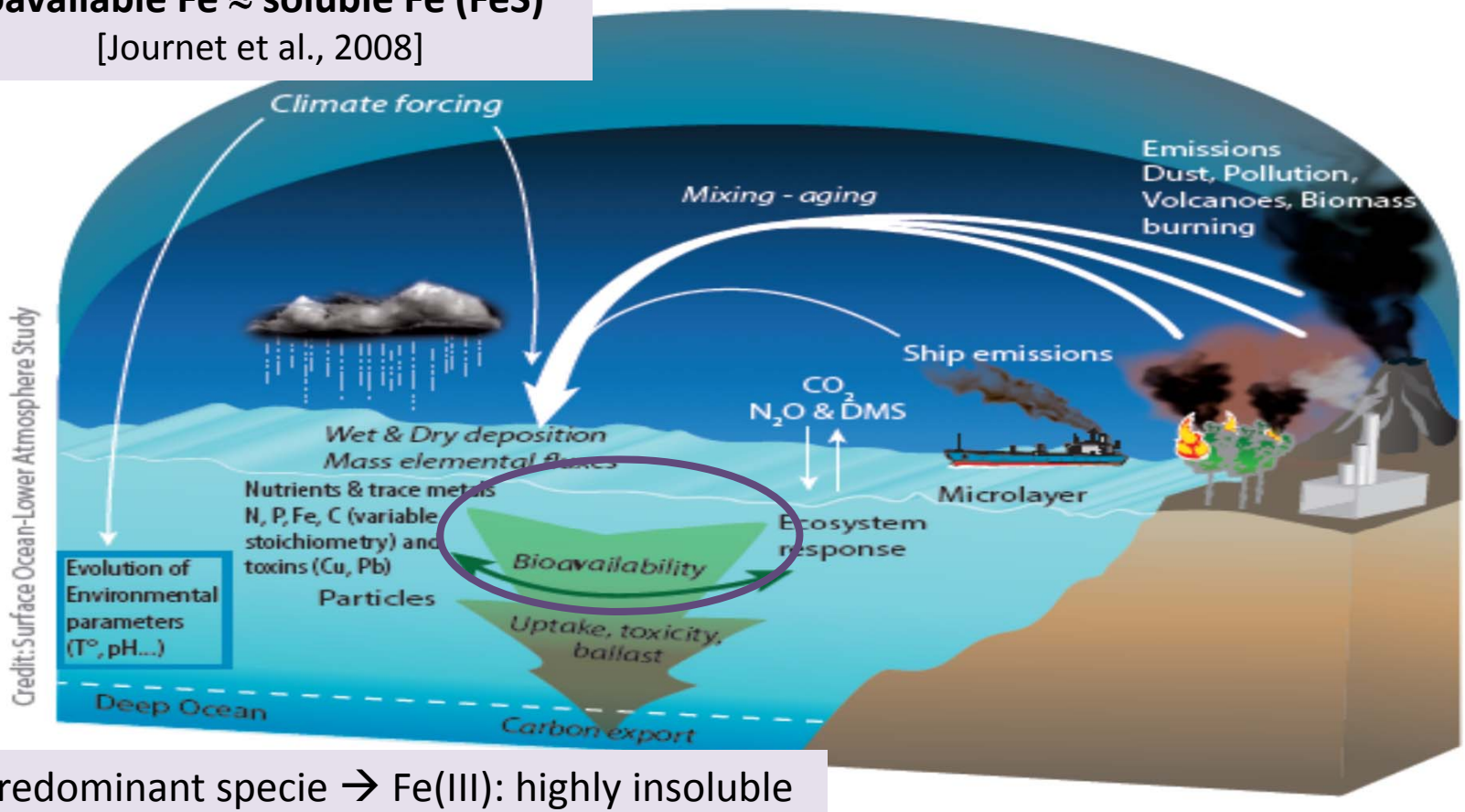
Source	Flux (Tg Fe year^{-1})
Fluvial particulate total iron	625 to 962
Fluvial disolved iron	1.5
Glacial sediments	34 to 211
Atmospheric	16
Coastal erosion	8
Hydrotermal	14
Authigenic	5



The Iron cycle [Raiswell et al., 2012]

1.Introduction

Bioavailable Fe ≈ soluble Fe (FeS)
[Journet et al., 2008]



Predominant specie → Fe(III): highly insoluble
Soluble specie → Fe(II): un-stable

Conceptual diagram illustrating the main issues, processes and species relating to the SOLAS EBUSs and OMZs research programmes. Processes are indicated in italic. [Evolving Research Directions in Surface Ocean-Lower Atmosphere (SOLAS) Science by Cliff Law et al. in Environmental Chemistry 2013, 10, 1-16]

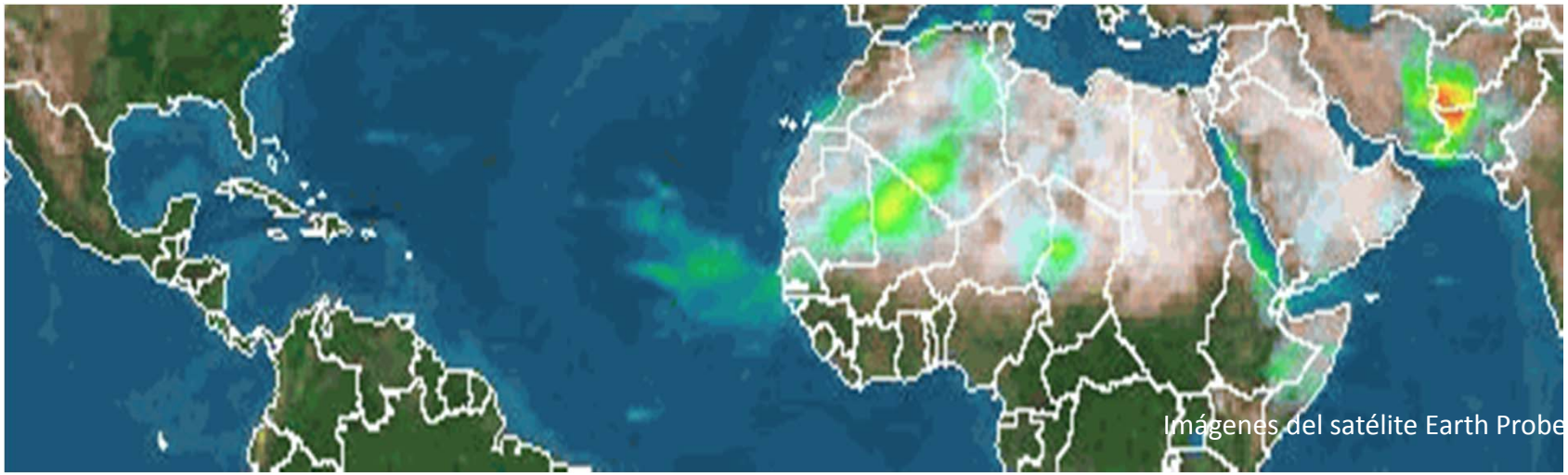
1.Introduction

Mineral aerosol

- generated from soils
- Chemical and mineralogical composition conditioned for place origin

  Main mineral: quartz, clay, calcilte, gibbsite and Fe oxides

- Size particle conditioned distance transport (mean size 0.1-10μm)



1.Introduction

Fe solubility (FeS)

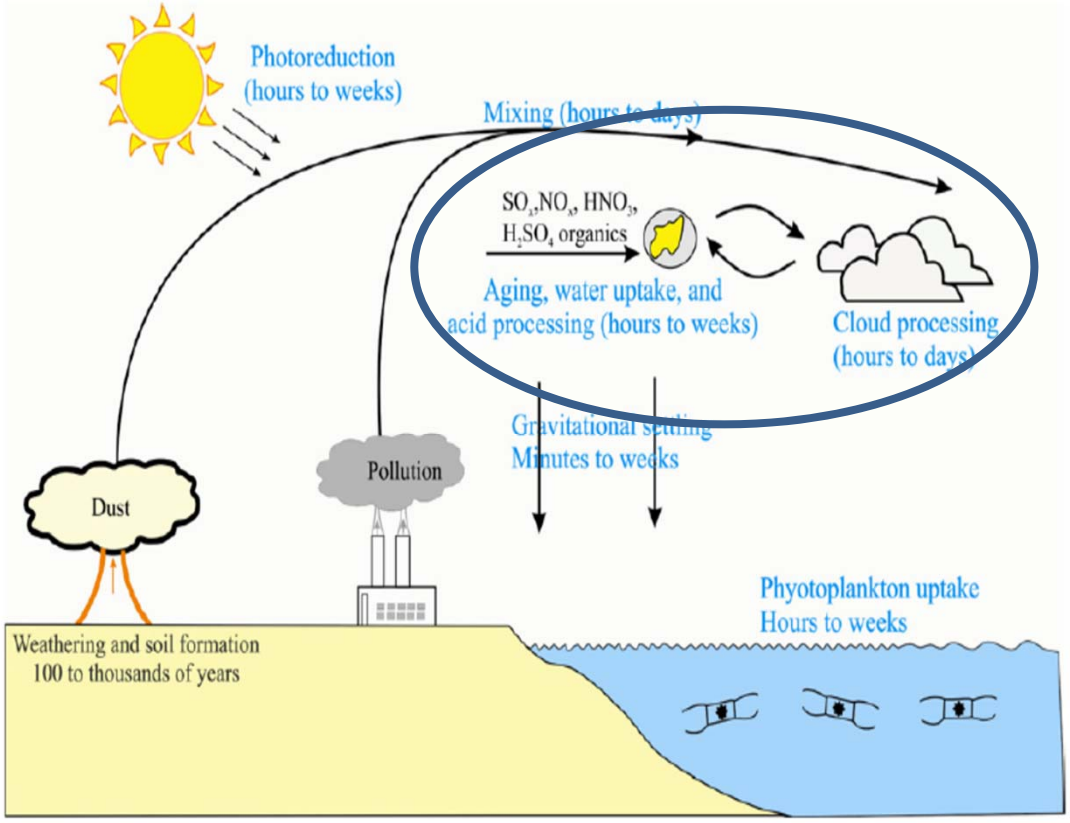
FeS in soils <0.1% vs 80% FeS in aerosols over remote ocean

[Baker and Jickells, 2006: Maholwald et al., 2009; Shi et al.,2012]

Atmospheric processes
→change Fe solubility

- Gravitational settling
- Mixing with anthropogenic and biomass burning aerosols
- Uptake of acidic gases
- Photoreduction

ΔpH → Cloud processes



(*Shi et al.*, 2012)

1.Introduction

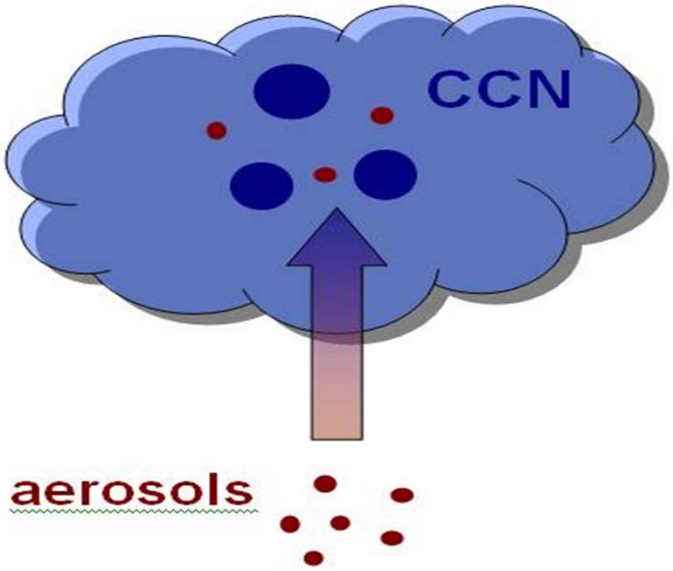
Dust particles as cloud condensation nuclei (CNN)

- Several condensation and evaporation cyles → **ΔpH**
- Main mechanism for uptake:

  CO_2, SO_x, NO_x,…

  [Seinfeld and Pandis, 2006]

  ↓pH
- Evaporation step pH<3 → the highest ↑ Fe solubility
  ↑ dust/liquid ratio
  ↑Ionic strength



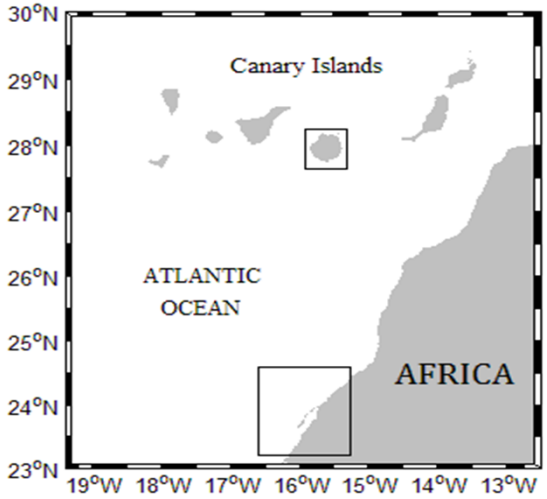
http://fiji.ucsd.edu/~greg/streamwiseCCN.htm

Objectives

1. Fe speciation in aerosols collected in the Canary Islands
2. Fe speciation in African soils
3. Reproduce aerosols “precursors” through a chemical process in soils
4. Validate whether these aerosol precursors have the same speciation that aerosols collected in Canary Islands

2. Methodology

2.1. Sampling sites



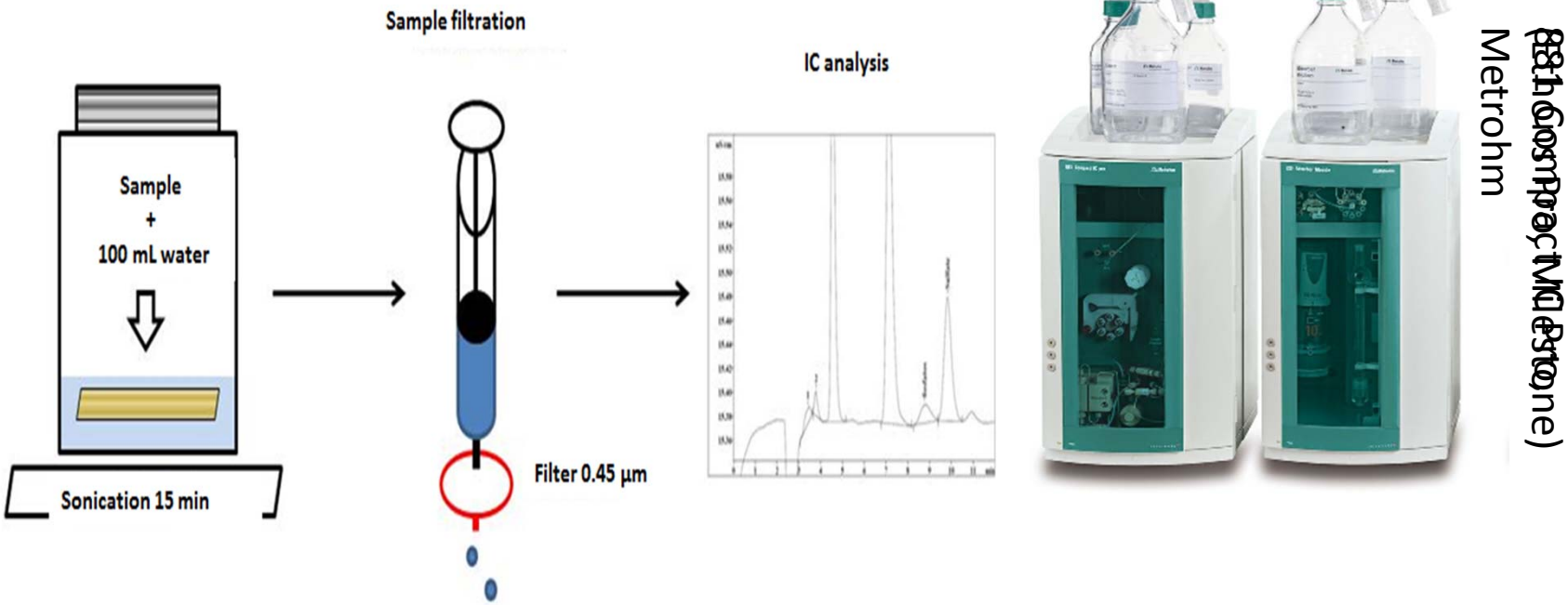
Type	Collection site	Sampling Method	Sample identification	Weight (g)	<20 µm (%)	Collection date
AEROSOL Dry Deposition	Gran Canaria, Tafira 15^0 27'17.28"W 28^0 04' 52.8"N	Plastic trays & buckets (ARS 1000, MTX Italy)	DD1	0.19	100	2013/02/4-6
			DD2	0.12	100	2012/08/28
			DD3	0.09	100	2012/03/8-9
			DD4	0.08	100	2013/09/18
			DD5	0.08	100	2010/08/13
			DD6	0.09	100	2013/09/18
			DD7	0.05	100	2013/04/19-21
SOIL	Western Sahara 15^0 44'05.27"W 23^0 47'34.58"N	Manual /Dry sieving	L23	510.55	0.11	08/2013

2. Methodology

2.2. Method

Soluble ions in DD → Ion chromatographer

[López-García, 2012]



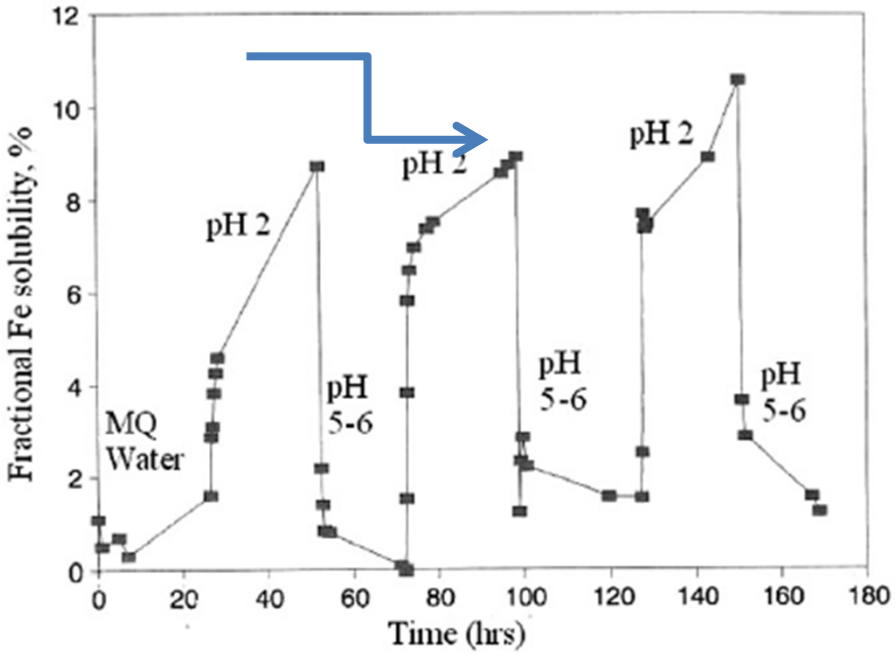
2. Methodology

2.2. Method

AFRICAN SOIL → AEROSOL PRECURSOR

Cloud processing simulation

[Spokes et al., 1994]



[Spokes et al., 1994]

3 cycles :

pH 2

(24h, H_2SO_4 (3 M))

pH 5-6

(24h, NH_4OH (3 M))

2. Methodology

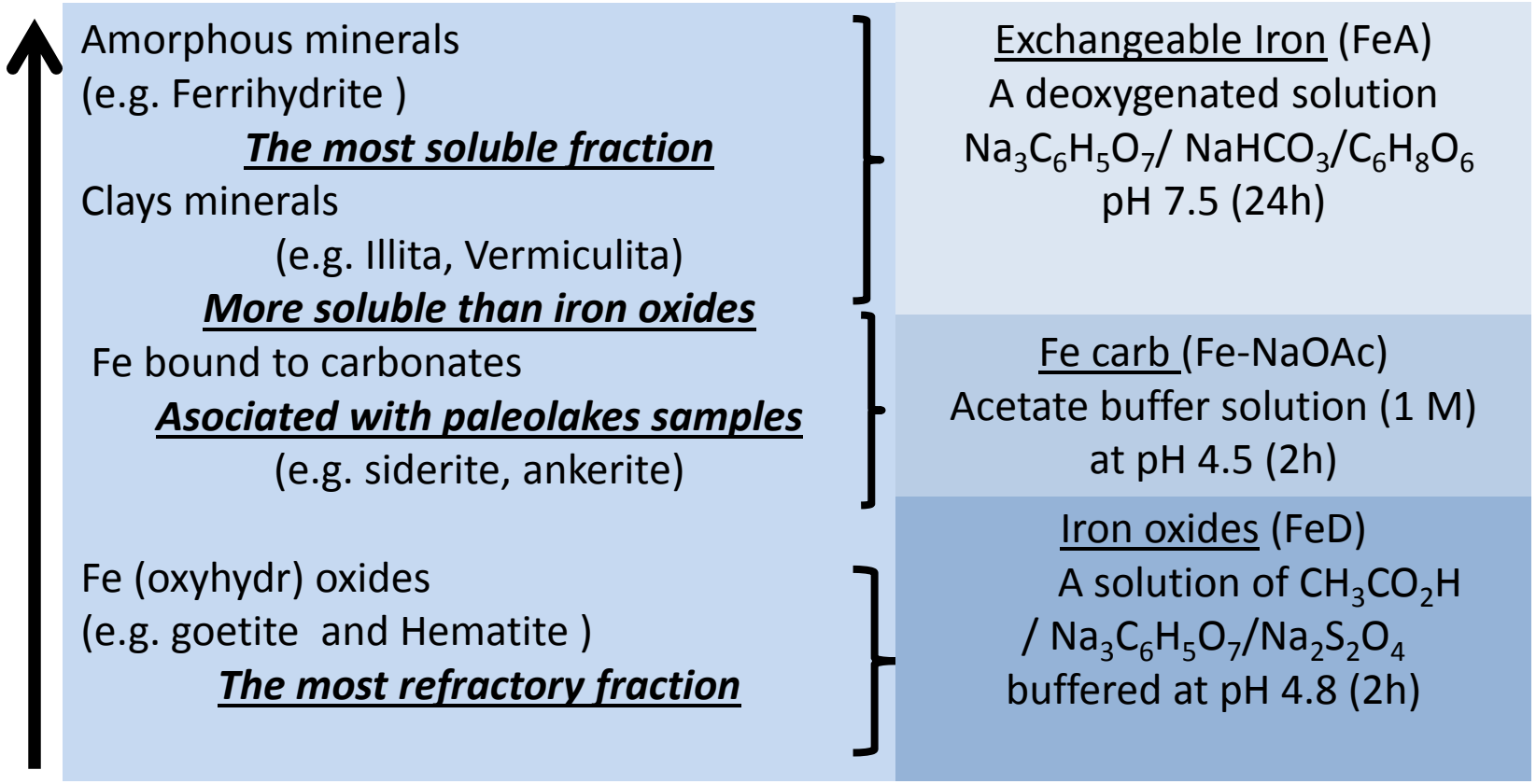
2.2. Method

SEQUENTIAL EXTRACTION PROCEDURE

Fe speciation study

[Tessier et al., 1970]

+ FeS

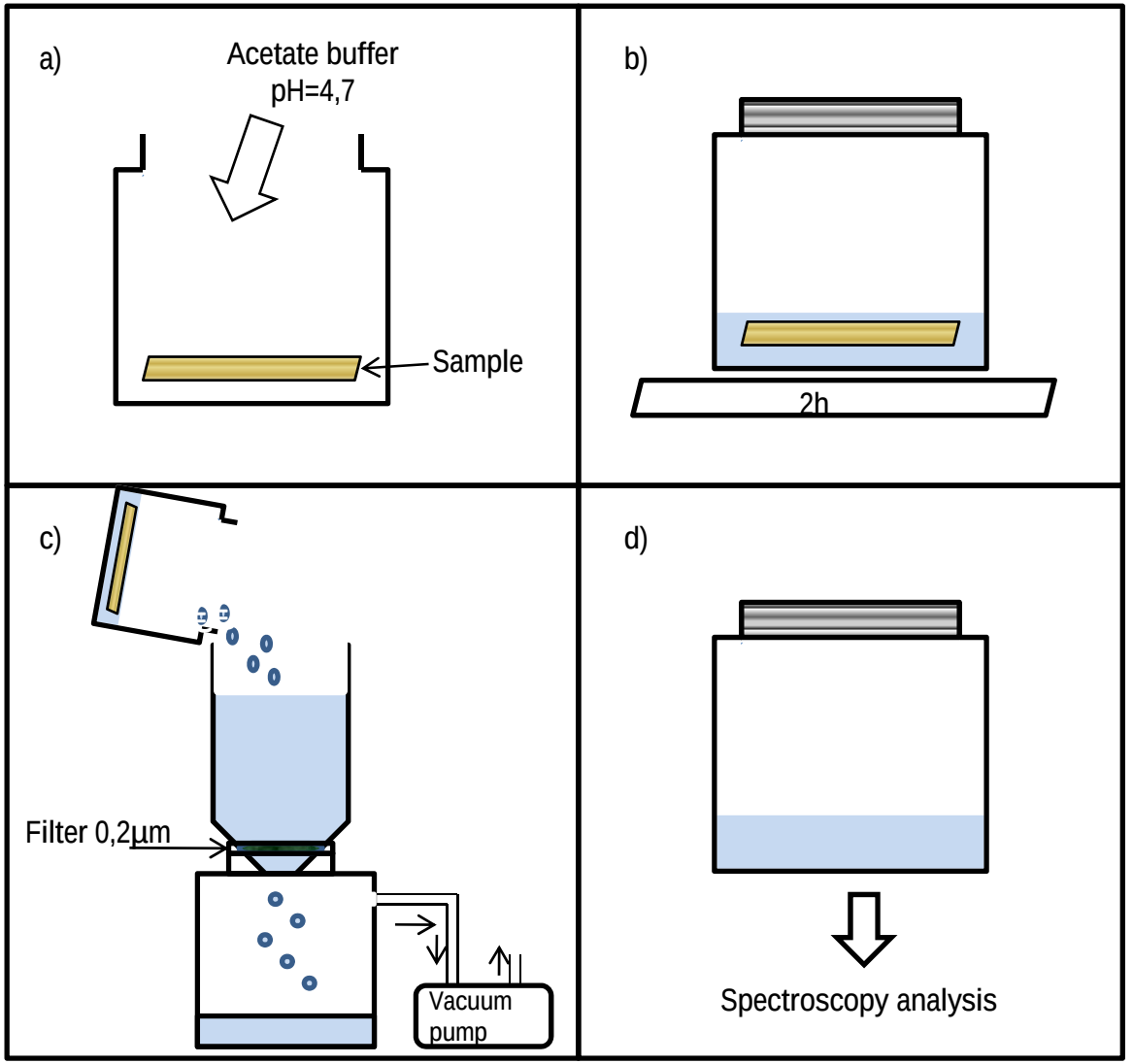


2. Methodology

2.2. Method

FeS in acetate buffer
(1.1 M, 10mL, pH 4.7, 2h)

(FeS%=(FeS/FeT)x100)
[Sarthou et al., 2003]



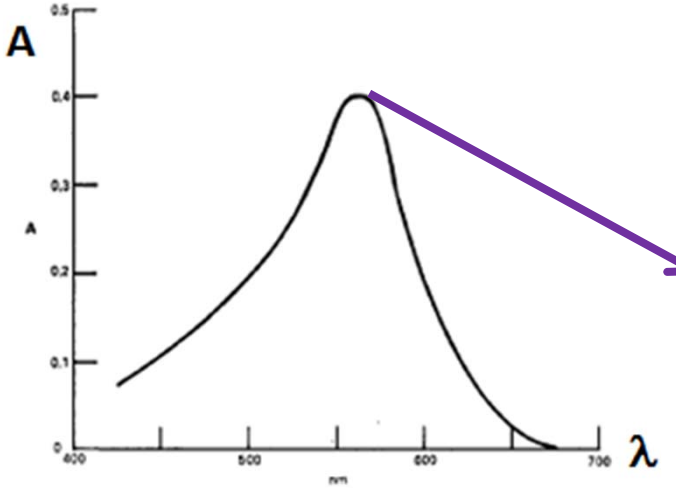
2. Methodology

2.2. Method

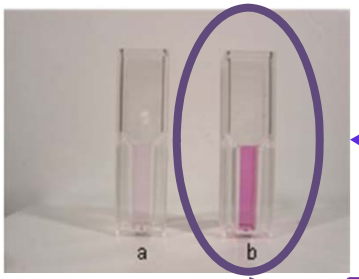
FERROZINE METHOD [Stookey et al., 1970; Violler et al., 2000]

Soluble and total Fe

UV-Vis spectroscopy



λ=562nm
pH 5.5



Reductant: Hydroxylamine (1.4M)

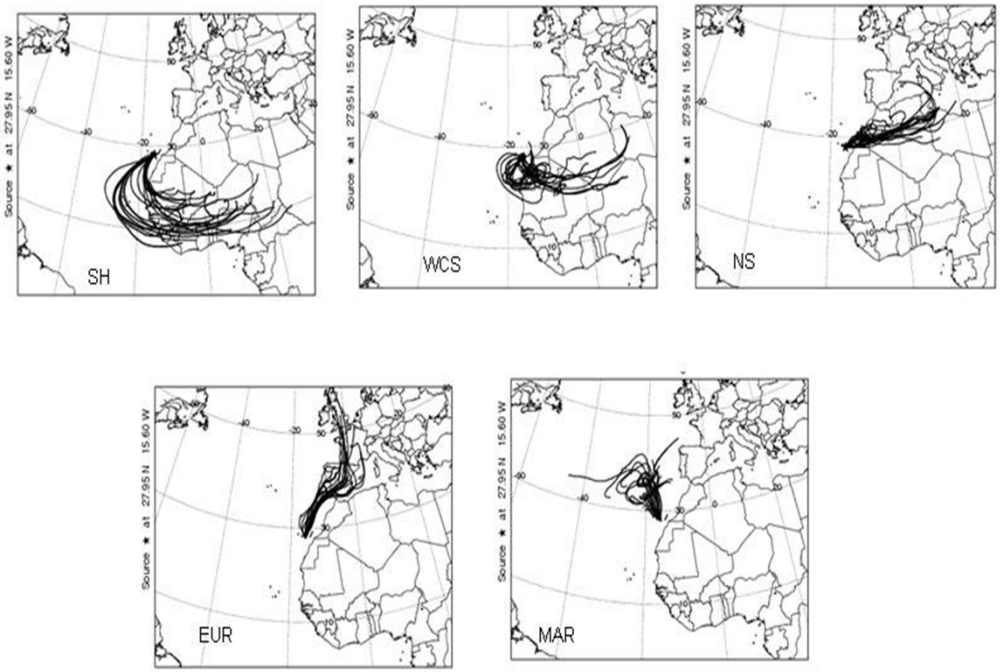
Ferrozine-Fe(II) complex

2. Methodology

2.3. Air mass classification

5 geographic sectors:

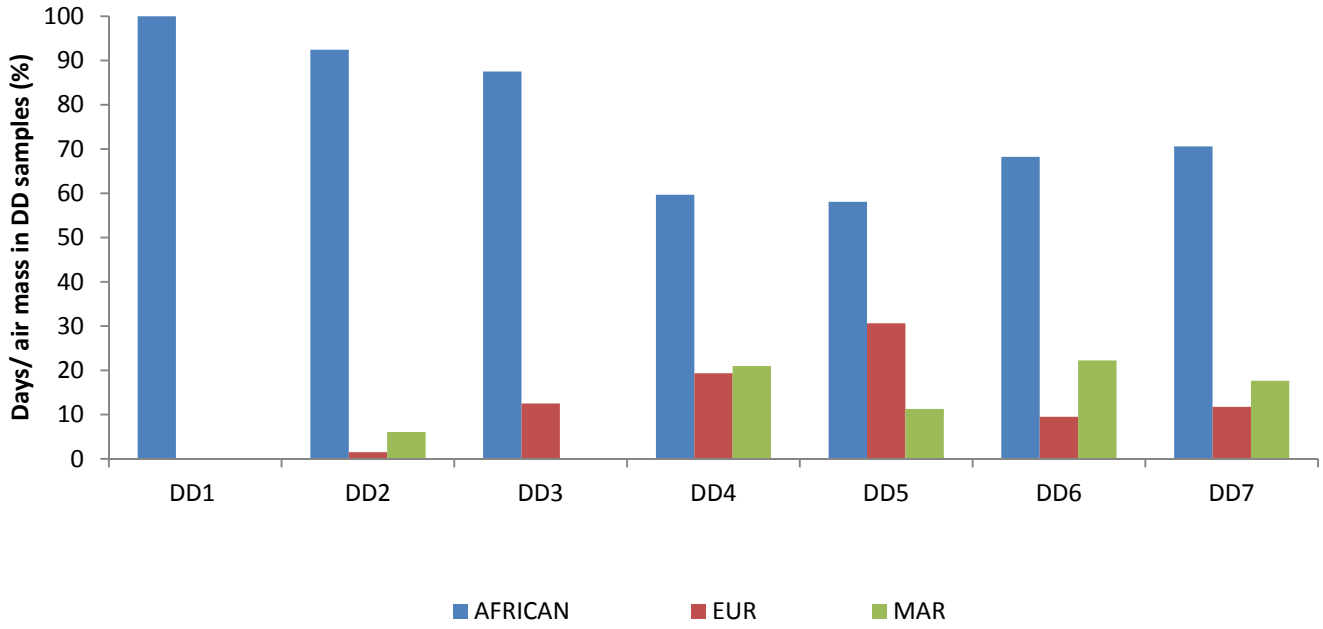
- SH sector (Sahel: 0^0-20^0N, 18^0W-20^0E)
- WCS (West and Central Sahara: 20-30^0N, 18^0W-20^0E)
- NS (Northern Sahara: 38^0-30^0N, 18^0W-15^0E, North Morocco, North Algeria and Tunisia)
- EUR (European and maritime aerosol, trajectories that cross the European continent and Atlantic ocean)
- MAR (maritime aerosol, trajectories over the Atlantic ocean)



Air mass identification classification of different back trajectories of the air masses with end point at Gran Canaria. Geographic sectors: (a) SH (Sahel: 0°–20°N, 18°W–20°E), (b) WCS (West and Central Sahara: 20°N– 30°N, 18°W–20°E), (c) NS (North of Sahara: 38°N–30°N, 18°W–15°E), (d) EUR (air masses over continental Europe and the Atlantic Ocean) and (e) MAR (trajectories over the Atlantic ocean) [Gelado – Caballero et al., 2012].

2. Methodology

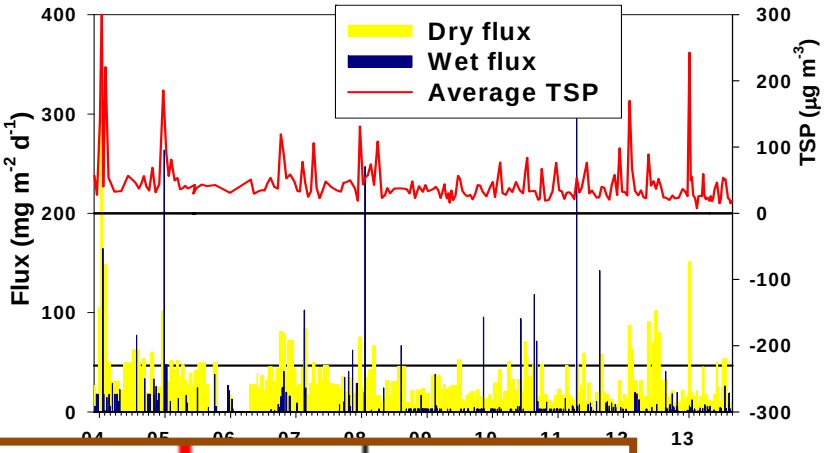
2.4. Dry Deposition samples characteristics

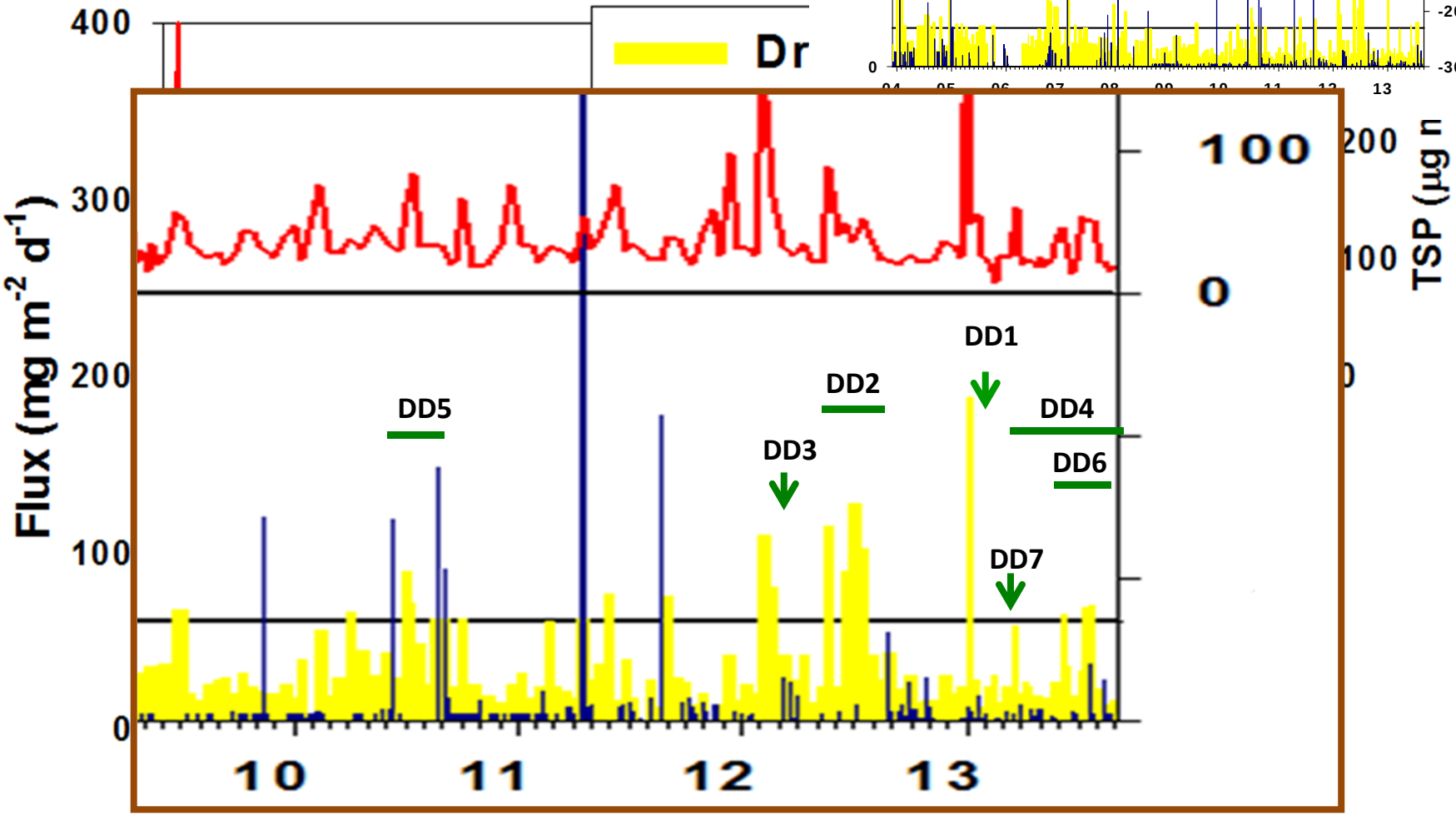


Percentage of days for each origin of the air masses in the dry deposition samples (African, European and marine)

2. Methodology

2.4. Dry Deposition sample





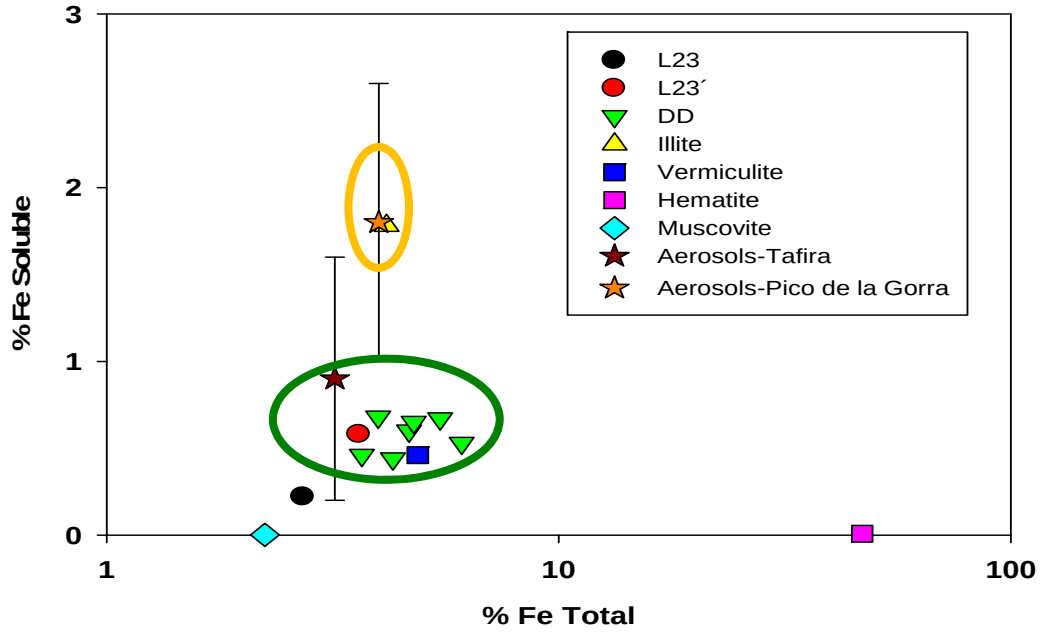
3. Results and discussion

FeS

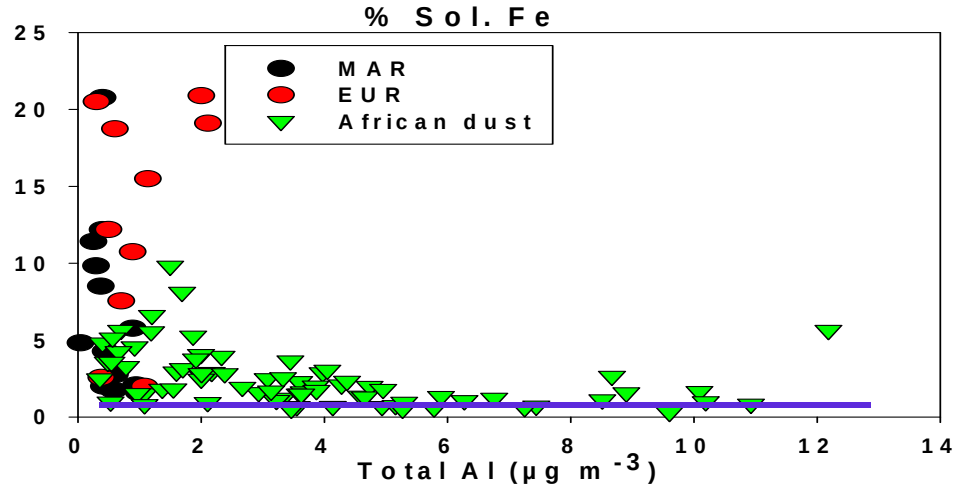
	FeT (mg g^{-1})	FeS (mg g^{-1})	%FeS
DD1	43.59	0.19	0.44
DD2	46.74	0.28	0.60
DD3	36.77	0.08	0.23
DD4	61.01	0.28	0.46
DD5	47.81	0.25	0.53
DD6	54.80	0.36	0.65
DD7	39.90	0.27	0.68
L23'	31.57	0.21	0.67
L23	31.75	0.06	0.19
Hematite	469.14	0.03	0.01
Illite	41.67	0.75	1.79
Vermiculite	48.87	0.23	0.46(n=1)
Muscovite	22.42	0.003	0.001(n=1)

3. Results and discussion

FeS



DD → FeS
0.49%(±0.18)



3. Results and discussion

Fe speciation

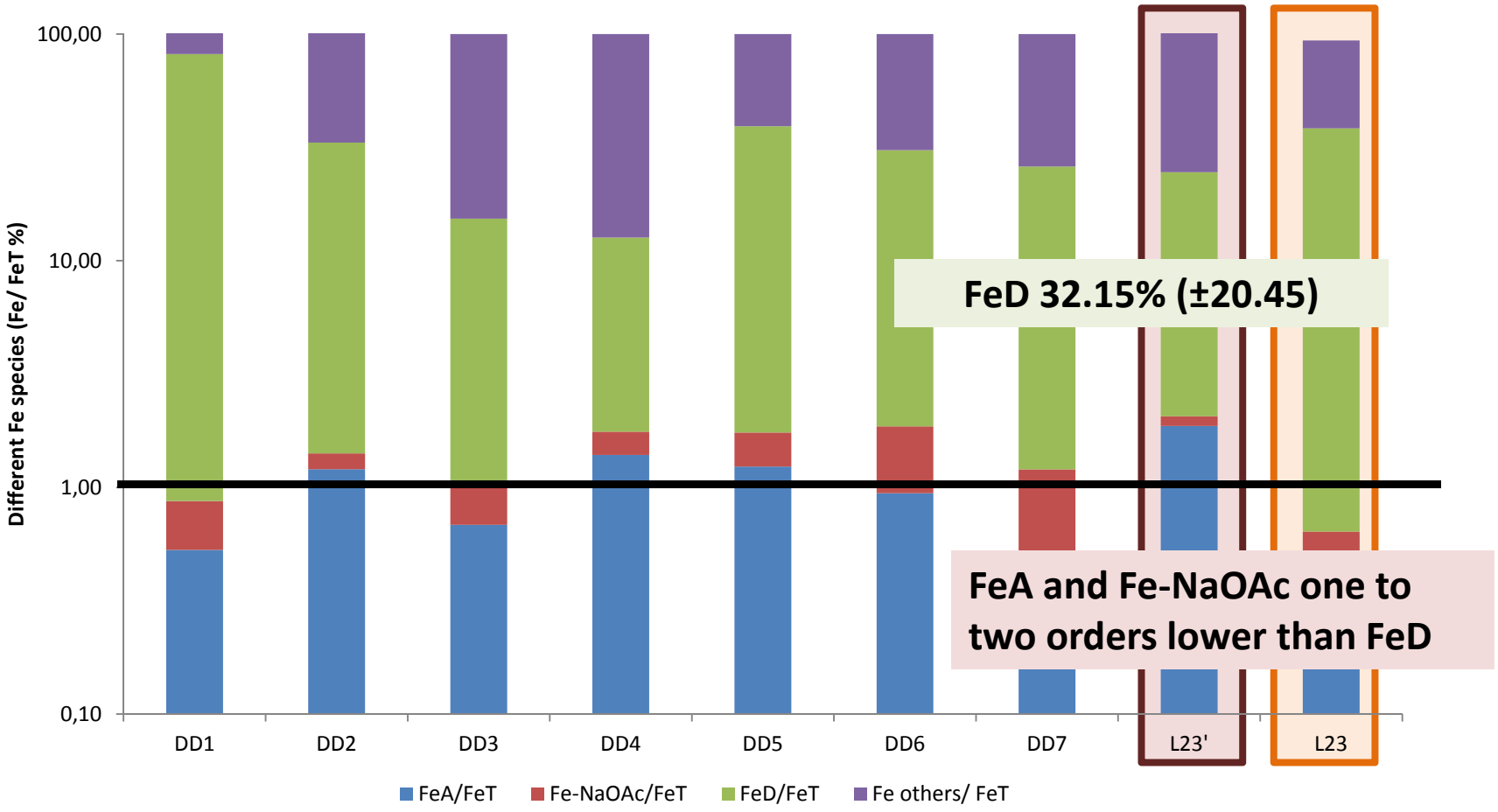
Sample	FeT (mg Fe/g sample)	FeA (mg Fe/g sample)	Fe – NaOAc (mg Fe/g sample)	FeD (mg Fe/g sample)	FeA/FeT (%)	Fe-NaOAc/FeT (%)	FeD/FeT (%)	(FeA+FeD)/FeT (Free Fe Ratio)	FeA/(FeA + FeD) (%)
DD1	43.59 (±0.25, n= 3)	0.23 (±0.03, n= 3)	0.15 (±0.01, n= 3)	35.20 (±7.97, n= 3)	0.53 (±0.06, n=3)	0.34 (±0.03, n=3)	80.75 (±18.30,n=3)	0.81 (±0.18, n=3)	0.65 (±0.05, n=3)
D				= 3)	1.20 (±0.02, n=3)	0.21 (±0.04, n=3)	31.78 (±1.99, n=3)	0.33 (±0.02, n=3)	3.65 (±0.29, n=3)
D	(n=1)	(±0.03, n= 3)	(±0.02, n= 3)	(±0.81, n= 3)	0.68 (±0.08, n=3)	0.35 (±0.04, n=3)	14.30 (±2.20, n=3)	0.15 (±0.02, n=3)	4.61 (±0.63, n=3)
DD4	61.01 (n=1)	0.85 (±0.04, n= 3)	0.23 (±0.02, n= 3)	6.64 (±0.51, n= 3)	1.39 (±0.06, n=3)	0.37 (±0.03, n=3)	10.89 (±0.83, n=3)	0.12 (±0.01, n=3)	11.36 (±1.09, n=3)
DD5	47.81 (n=1)	0.59 (±0.03, n= 3)	0.24 (±0.04, n= 3)	17.90 (±2.54, n= 3)	1.24 (±0.06, n=3)	0.51 (±0.08, n=3)	37.45 (±5.32, n=3)	0.39 (±0.05, n=3)	3.24 (±0.54, n=3)
DD6	54.80 (n=1)	(±0.							3.26 (±1.40, n=3)
DD7	39.90 (n=1)	(n=1)	(n=1)	(n=1)	(n=1)	(n=1)	(n=1)	(n=1)	2.05 (n=1)
L23'	31.57 (±5.63, n=3)	0.59 (±0.37, n= 3)	0.06 (±0.02, n= 3)	7.16 (±0.31, n= 3)	1.88 (±1.16, n=3)	0.19 (±0.05, n=3)	22.67 (±0.98, n=3)	0.25 (±0.003,n=3)	7.62 (±4.64, n=3)
L23	31.75 (±6.36, n=3)	0.12 (±0.02, n= 3)	0.08 (±0.02, n= 3)	11.99 (±0.62, n= 3)	0.37 (±0.05, n=3)	0.27 (±0.07, n=3)	37.77 (±1.94,n=3)	0.38 (±0.02,n=3)	0.97 (±0.08,n=3)

FeS 0.49%(±0.18)
FeA/FeT 0.97% (±0.50)

4.72%(±0.84) in DD → similar results in aerosols collected in Gran Canaria [Gelado-Caballero et al., 2012]

3. Results and discussion

Fe speciation



Log scale graphical representation of the various Fe species in the samples

3. Results and discussion

Table . Summary of results of the speciation of Fe in this study and compared with others compiled in the review of Shi et al., 2012 (NM is not measured)

Collected in Shi et al., 2012	Number of samples	Sources	FeA/FeT (%)	FeD/FeT (%)	(FeA+FeD)/FeT	FeT (%)	FeA/(FeA+FeD) (%)	References
Sahara: dust precursors	2	Tibest Mountains, South Libya: Western Sahara	0.5 (± 0.2)	35.3(±3.4)	0.36(±0.04)	4.7(±0.1)	1.4	Shi et al., 2011b
Paleolakes: dust precursors or potential dust precursors	4	Bodele Depression, Chad; Chott el Djerid, Tunisia; Wadi al Hyatt, Libya; Wadi Ash Satti, Libya	1.5(± 1.1)	18.8(± 10.1)	0.2(±0.11)	1.6(± 1.3)	7.4	
Bejjing: dry deposition dust	1	Not Known	1.7	22.3	0.24	3.5	7.1	Shi et al., 2011a
E. Mediterranean: dry deposition dust	1	Not Known	0.9	35.1	0.36	2.81	2.5	Shi et al., 2009
W. Mediterranean: wet deposition dust	1	Not Known	2.4	35.6	0.38	3.58	6.3	
Canary Island: aerosol	12	Saharan origin by back trajectory	NM	NM	0.35 (±0.07)	NM	NM	Lazaro et al., 2008
	2	Sahel origin by back trajectory	NM	NM	0.58 (±0.03)	NM	NM	
This study								
L23 (african soil, potential dust precursors)	3	Western Sahara	0.37 (±0.05)	37.77 (±1.94)	0.38 (±0.02)	3.17 (±0.01)	0.97(±0.08)	
L23' (dust precursors)	3	Western Sahara	1.88 (±1.16)	22.67 (±0.98)	0.25 (±0.03)	3.17 (±0.01)	7.62(±4.64)	
DD, Gran Canaria	7	Sahara NS/WSC	0.93 (±0.36)	32.70 (±23.18)	0.34 (±0.23)	4.72 (±0.84)	4.08(±3.42)	

3. Results and discussion

Dry Deposition Fluxes for major elements from IC

Table. Dry deposition Fluxes for major elements in this study and compare with estimated fluxes from Johansen et al., 2000 dates.

	Fluxes for elements (μg m^{-2} d^{-1})							
	This study							
Samples	**DD1**	**DD2**	**DD3**	**DD5**	**DD6**	**Coarse**	**Fine**	**Averange**
F^-	0.13	0.04	0.04	0.03	0.02	0.27	0.01	0.22
Cl^-	29.33	2.73	4.13	5.98	3.92	90.43	2.39	62.21
Br^-	<0.01	<0.01	<0.01	0.01	<0.01	0.14	0.004	0.10
NO_3^-	1.27	0.15	0.44	0.24	0.45	9.22	0.52	8.16
SO_4^{2-}	38.07	11.51	9.73	19.32	11.83	18.72	1.73	23.59
$C_2O_4^{2-}$	2.58	0.84	0.86	0.31	0.59	0.54	0.05	0.68
Na^+	17.46	1.85	2.92	3.84	2.21	57.60	1.79	41.99
NH_4^+	2.73	0.05	0.50	0.06	0.06	0.99	0.20	2.27
K^+	<0.01	<0.01	1.62	0.76	0.53	2.61	0.13	2.36
Mg^{2+}	4.47	0.59	1.11	1.08	1.05	7.11	0.23	5.21
Ca^{2+}	77.29	9.92	24.48	9.32	6.27	10.97	0.32	7.84

Ca^{2+} are in agreement with the African origin of samples

4. Preliminary Conclusions

1. The amounts of aerosol collected by deposition systems are very low. For this reason, “ prepared aerosols ” from soils, to mimics the chemical properties of mineral aerosol, is so important.
2. Sequential extraction process results have demonstrated that the Fe speciation in dry deposition samples is similar to aerosol precursors from African soils collected in the source regions.
3. The solubility of the more labile Fe fractions is on average 0.97% (±0.49) of the total Fe content in the samples. The highly reactive Fe (FeA+FeD) corresponds to a significant fraction of the FeT in the samples, an average of 33.10% (±20.27). This Fe can be readily dissolved at low pH.
4. The high variability in the speciation of Fe in dry deposition samples suggest that atmospheric transport may be an important factor controlling aerosol solubility.