ATARRI:
Dust heterogeneous chemistry and iron cycle

Funded by the European Union

GA No 101160258

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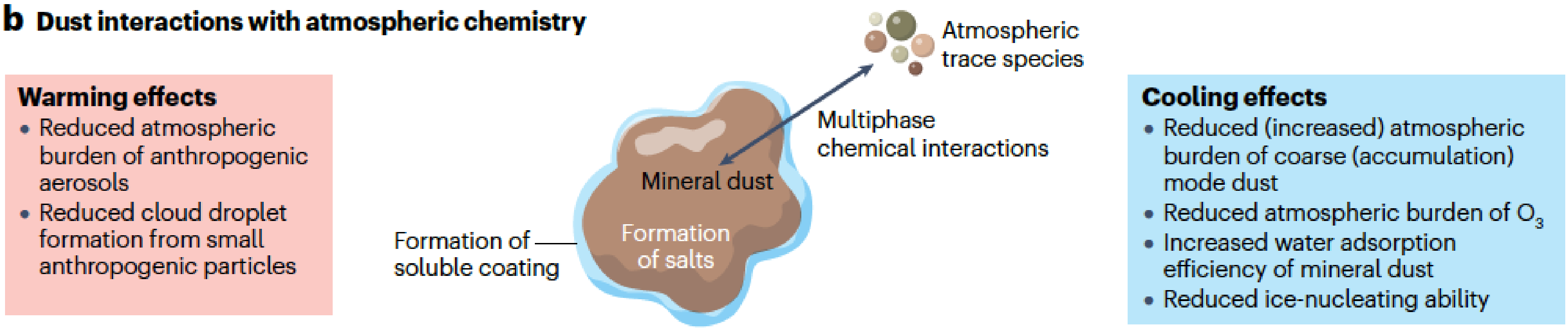
BSC and ICREA

Dust interactions with atmospheric chemistry



b **Dust interactions with atmospheric chemistry**

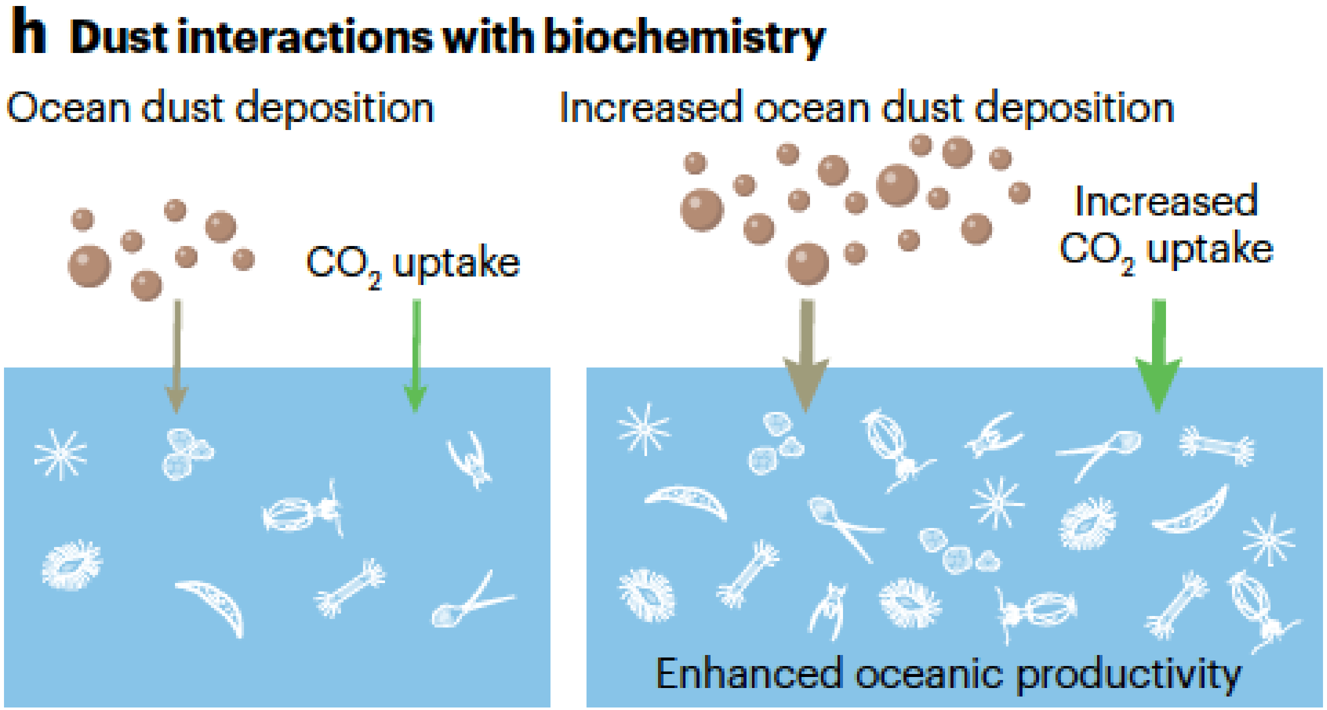
Warming effects

- Reduced atmospheric burden of anthropogenic aerosols
- Reduced cloud droplet formation from small anthropogenic particles

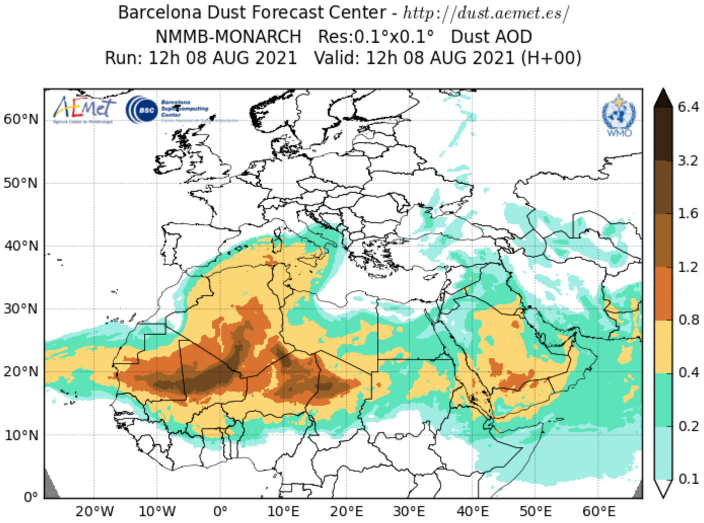
Cooling effects

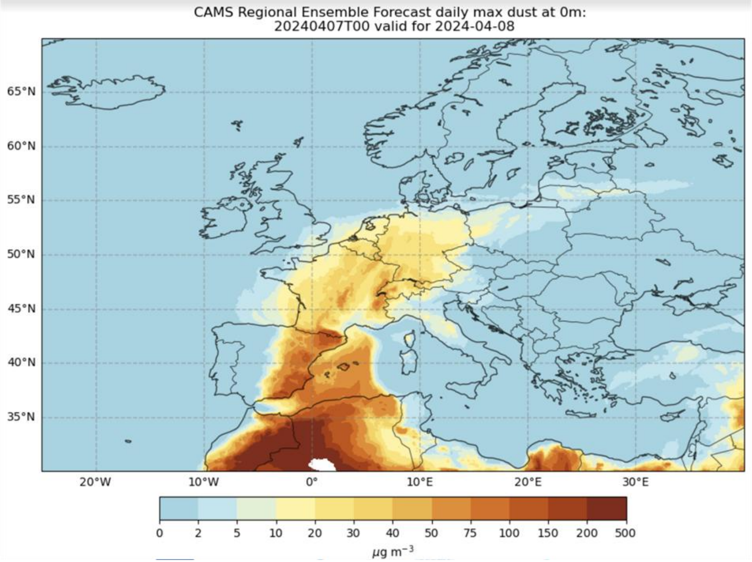
- Reduced (increased) atmospheric burden of coarse (accumulation) mode dust
- Reduced atmospheric burden of O_3
- Increased water adsorption efficiency of mineral dust
- Reduced ice-nucleating ability

Dust interactions with biogeochemistry



Dust intrusions are common in populated areas (e.g. East Asia, Australia, Europe…)


Barcelona Dust Forecast Center - *http://dust.aemet.es/*
NMMB-MONARCH Res:0.1°x0.1° Dust AOD
Run: 12h 08 AUG 2021 Valid: 12h 08 AUG 2021 (H+00)


CAMS Regional Ensemble Forecast daily max dust at 0m:
20240407T00 valid for 2024-04-08

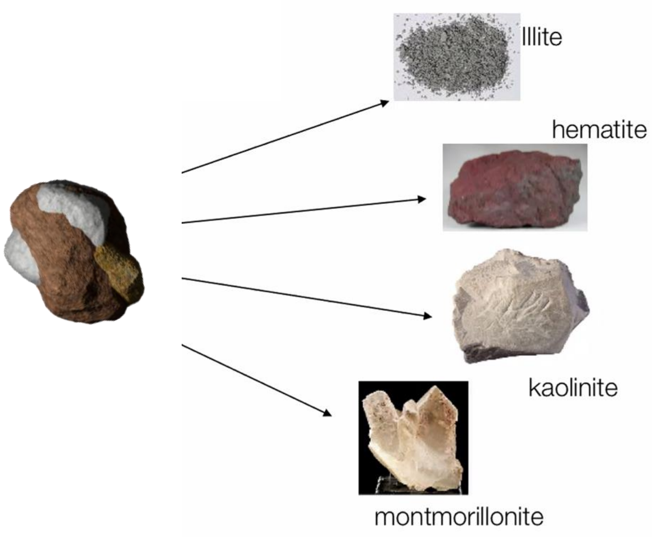
Dust intrusions are common in populated areas (e.g. East Asia, Australia, Europe…)

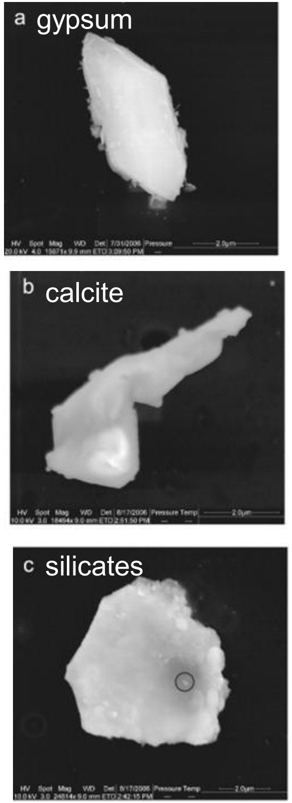
Erenhot (Mongolia)

Madrid (Spain)

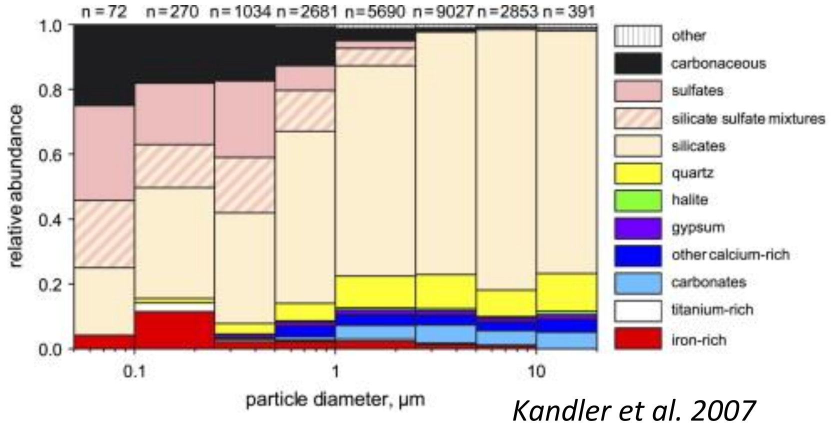
Sydney (Australia)

Introduction:
What is dust heterogeneous chemistry?





Kandler et al. 2007



Kandler et al. 2007

Introduction:
What is dust heterogeneous chemistry?

$CaMg(CO_3)_2$
reaction
with HNO_3

Krueger et al., 2004

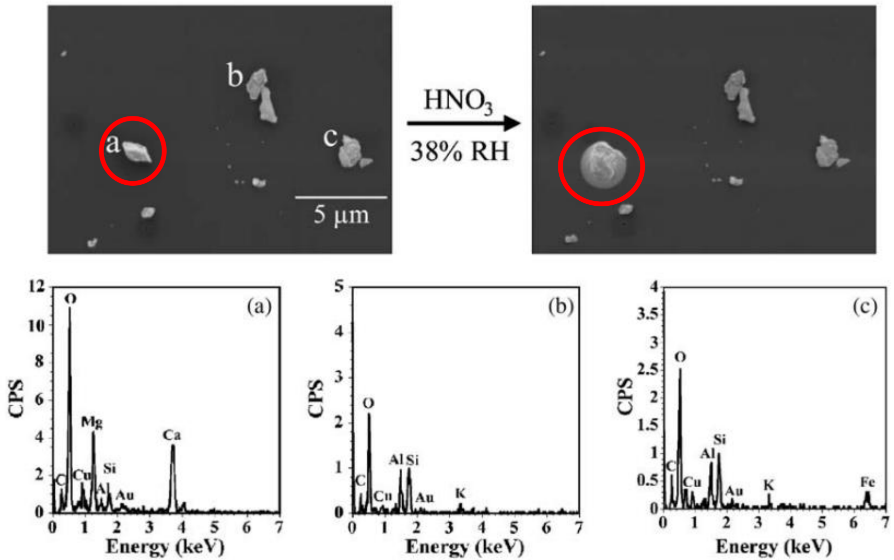


Fig. 3. (a–c) SEM images of individual particles of China Loess are shown before and after exposure to nitric acid vapor at 38% RH. The EDX spectra for several individual particles (labeled a, b and c) prior to nitric acid exposure are also shown. The particle labeled a with high levels of Ca and Mg is identified as dolomite, $CaMg(CO_3)_2$. This particle shows unique morphological changes after reaction with nitric acid consistent with the formation of a hygroscopic nitrate salt. The other particles identified as aluminum silicates (b and c) show no change in morphology upon exposure to nitric acid. (*Note*: Trace amounts of Cu and Au in the EDX spectra are due to background signals from the sample holder and grid.)

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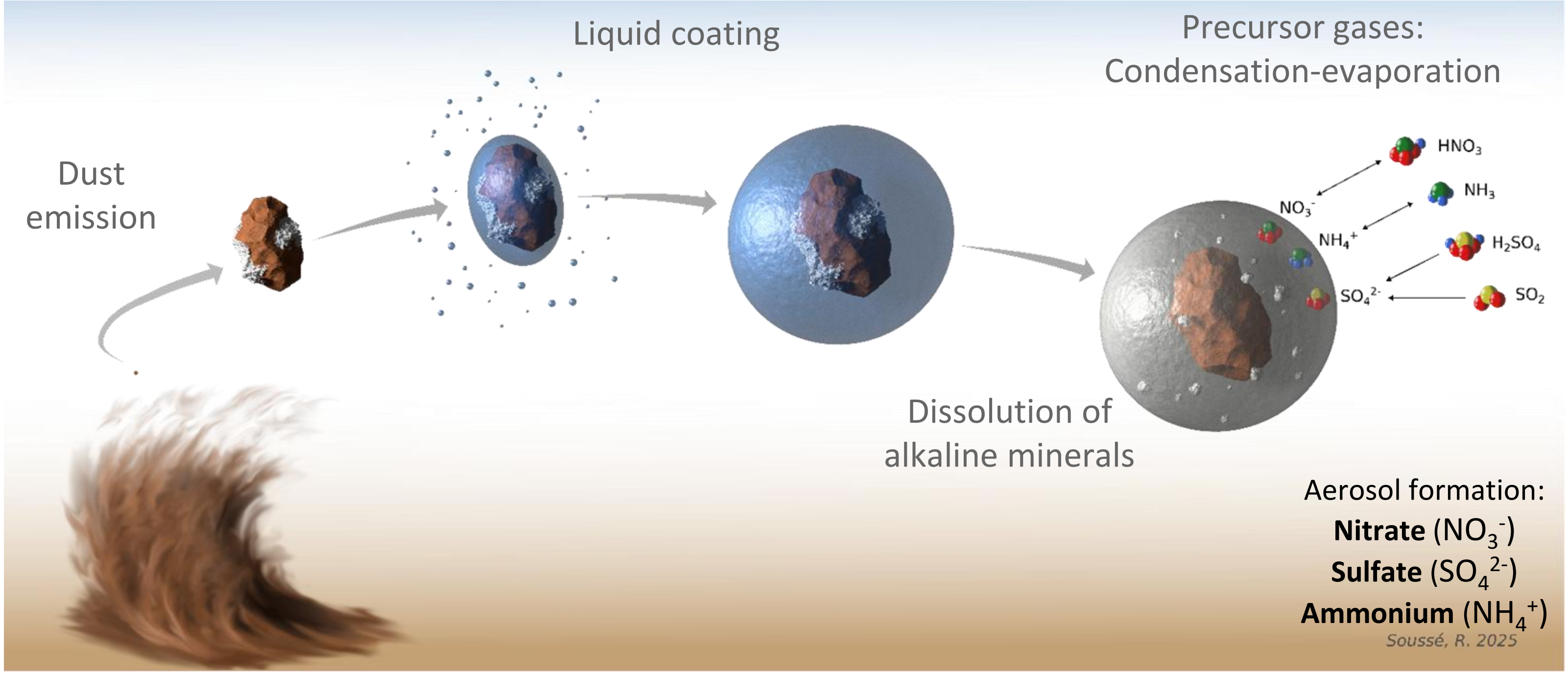
What is dust heterogeneous chemistry?



Dust emission

Liquid coating

Precursor gases: Condensation-evaporation

Dissolution of alkaline minerals

Aerosol formation:
Nitrate (NO_3^-)
Sulfate (SO_4^{2-})
Ammonium (NH_4^+)

Soussé, R. 2025

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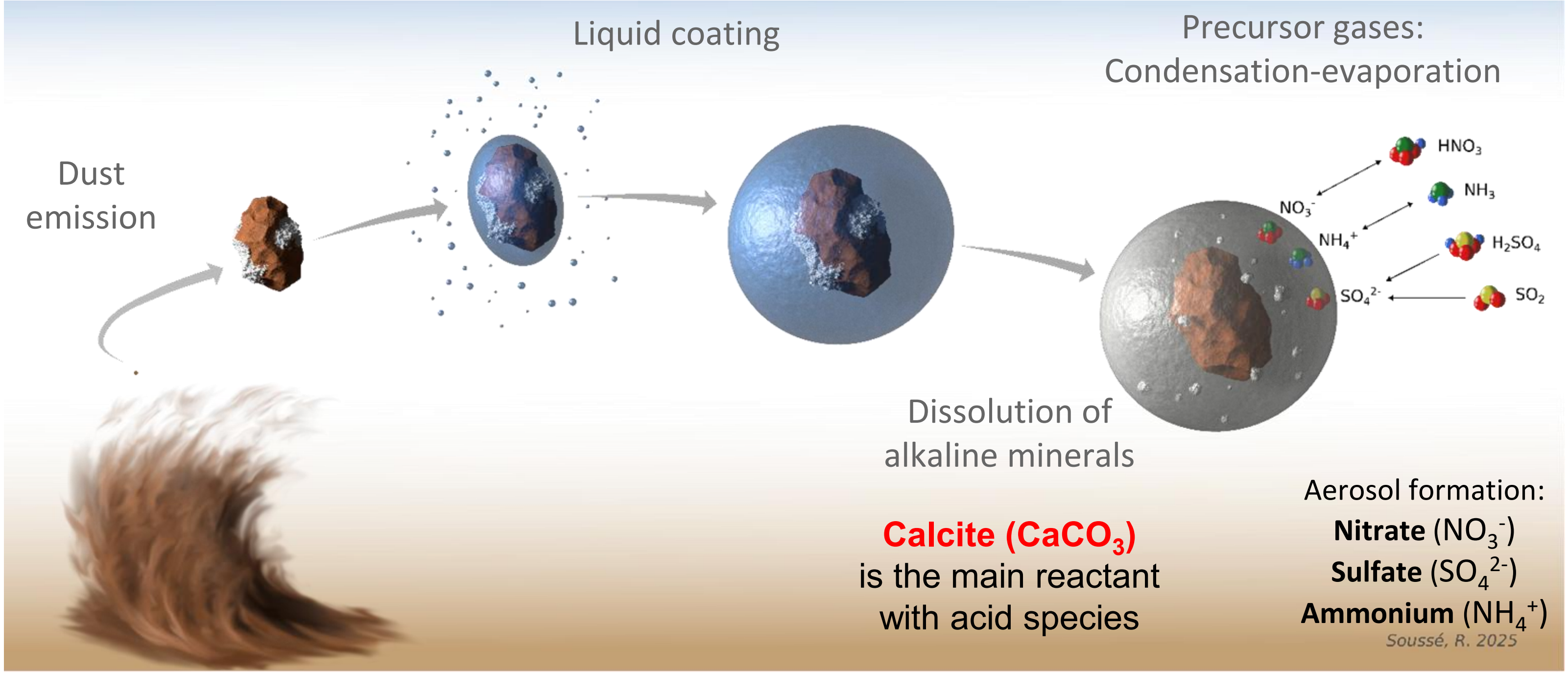

Dust emission

Liquid coating

Precursor gases:
Condensation-evaporation

Dissolution of alkaline minerals

Calcite ($CaCO_3$)
is the main reactant
with acid species

Aerosol formation:
Nitrate (NO_3^-)
Sulfate (SO_4^{2-})
Ammonium (NH_4^+)

Soussé, R. 2025

Implementation in atmospheric models

- Previous studies
- Implementation in MONARCH at BSC

Implementation in atmospheric models:
Previous studies

How do atmospheric models simulate dust heterogeneous reactions?

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Atmospheric models have struggled with some problems:

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Fine particles can reach thermodynamic equilibrium with gases within a model timestep (seconds to minutes) but coarse particles cannot

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Dynamic mass transfer (DMT)

Direct calculation of condensation/evaporation of species.

+ Rigorous

- Complex and computationally expensive

Meng et al. 1998, Capaldo et al. 2000, Feng et al. 2007, Zaveri et al 2008, Trump et al. 2015

Irreversible uptake reaction (UPTK)

Simplifying DMT to a first-order uptake reaction

+ Simple and efficient

- Irreversible, does not account for evaporation

Feng et al. 2007, Bauer et al. 2004, Li et al. 2012, Uno et al 2017

Thermodynamic equilibrium (TEQ)

Calculation of TEQ that all particles reach TEQ

Can be **fixed with weighting factors**

+ Simple and efficient

- Overestimation/underestimation of particle formation

Wu et al. 2025, Watanabe et al. 2011, Schmidt et al. 2014, Bian et al.2017, Binkowski et al. 1995, Lurmann et al. 1997

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Hybrid method (HYB)

- TEQ for fine
- UPTK for coarse

Simple and irreversible only for the coarse mode

Double call of TEQ (DBCLL)

- TEQ for fine
- TEQ for coarse

Uses kinetic limitations to distribute gas species between fine/coarse

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Dust mineralogy poorly represented in atmospheric

Implementation in atmospheric models:
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Dust mineralogy poorly represented in atmospheric

X **Do not incorporate dust mineral fractions**
Usher et al. 2003, Sokolik et al. 2001, Nickovic et al. 2012, Bian et al 2017

? **Assume dust mineralogy as regionally/globally homogeneous**
No geographical heterogeneity of dust surface mineralogy
Feng et al. 2007, Fairle et al. 2010, Hauglustaine et al. 2014, Trump et al. 2015, Paulot et al. 2016, Bian et al. 2017, Kakavas et al. 2020, Jones et al. 2021

~ **Incorporate inaccurate mineral distributions**
Like **Claquin et al. 1999** and **Journet et al. 2014** mineral atlases, or others
→ EMAC (Karydis et al. 2016)
→ IFS-COMPO (Rémy et al. 2024)

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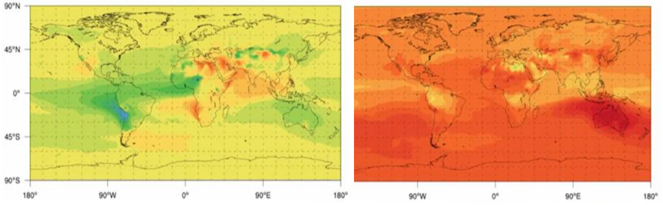
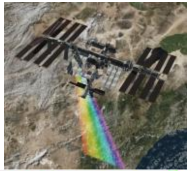
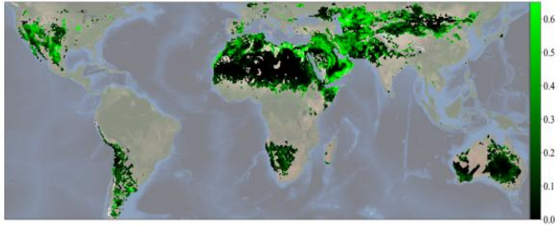
Calcite from
Claquin et al. 1999 & Journet et al. 2014



Calcite from spaceborne
EMIT 2023





Implementation in atmospheric models:
Investigation at BSC

Using the MONARCH atmospheric model, we have investigated…

Implementation in atmospheric models:
Investigation at BSC

Using the MONARCH atmospheric model, we have investigated…

1 Sensibility to the **heterogeneous chemistry mechanism**
- Fine TEQ
- Fine TEQ + coarse UPTK
- Fine TEQ + coarse TEQ with kinetic limitations

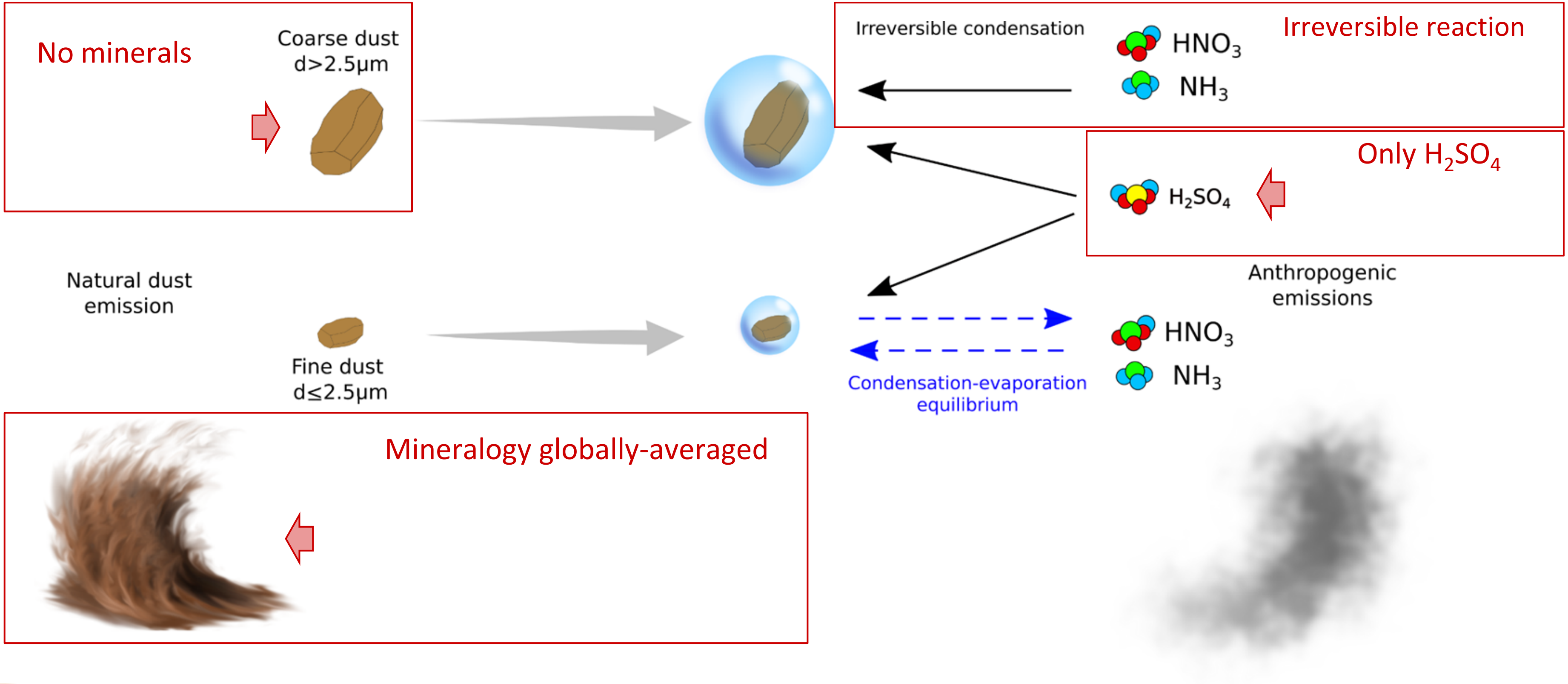
2 Sensibility to **dust mineralogy**
- No mineralogy
- Claquin et al. 1999
- Journet et al. 2014
- **EMIT 2023 (first time in an atmospheric model)**

3 Sensibility to **calcite distribution**
- Simplified global averaged
- Realistic source-based

4 Impacts on **aerosol optical properties**
- Aerosol optical depth
- Single Scattering albedo

Implementation in atmospheric models:

Developments



No minerals

Coarse dust
d>2.5μm

Irreversible condensation

HNO_3

NH_3

Irreversible reaction

Only H_2SO_4

H_2SO_4

Anthropogenic
emissions

Natural dust
emission

Fine dust
d≤2.5μm

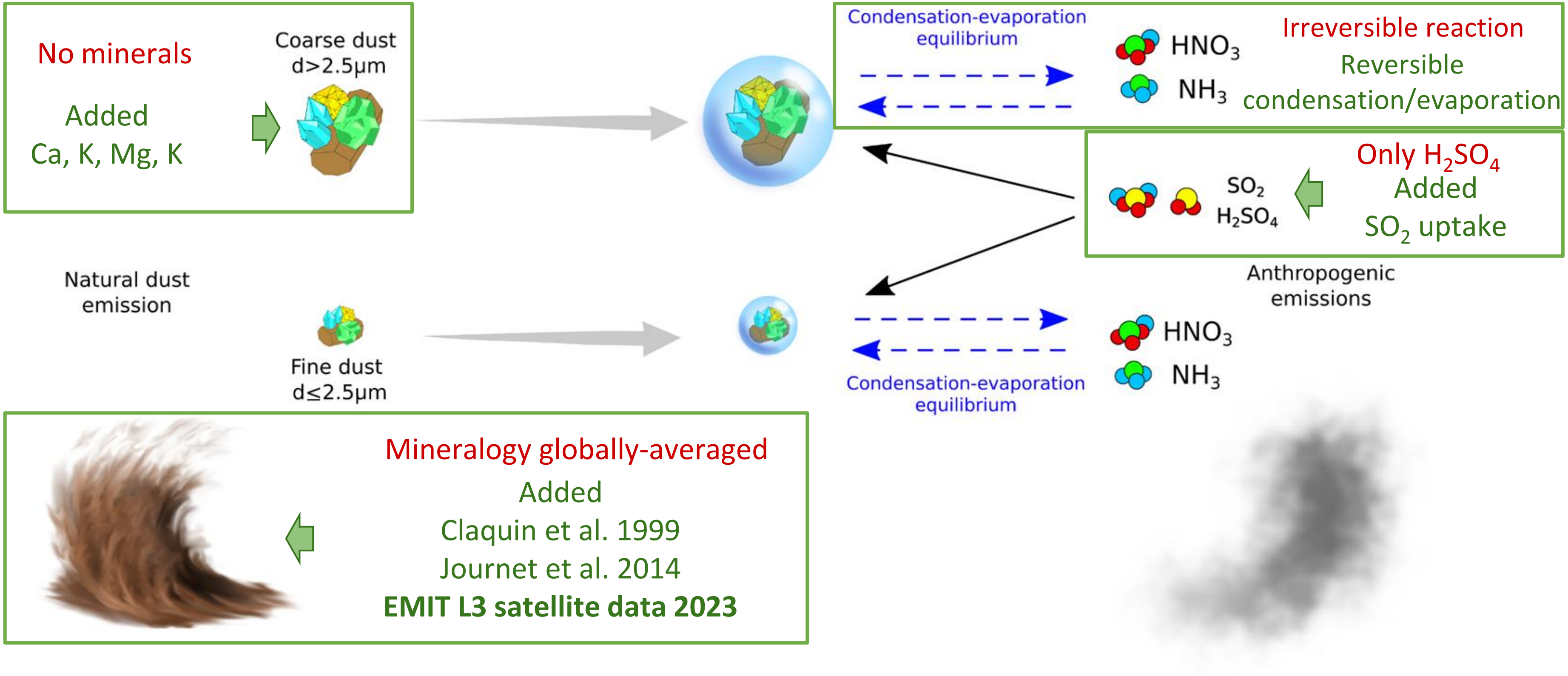
HNO_3

NH_3

Condensation-evaporation
equilibrium

Mineralogy globally-averaged

Implementation in atmospheric models:
Developments



No minerals

Added
Ca, K, Mg, K

Coarse dust
d>2.5μm

Natural dust
emission

Fine dust
d≤2.5μm

Condensation-evaporation
equilibrium

HNO_3

NH_3

Irreversible reaction
Reversible
condensation/evaporation

Only H_2SO_4
Added
SO_2 uptake

SO_2
H_2SO_4

Anthropogenic
emissions

HNO_3

NH_3

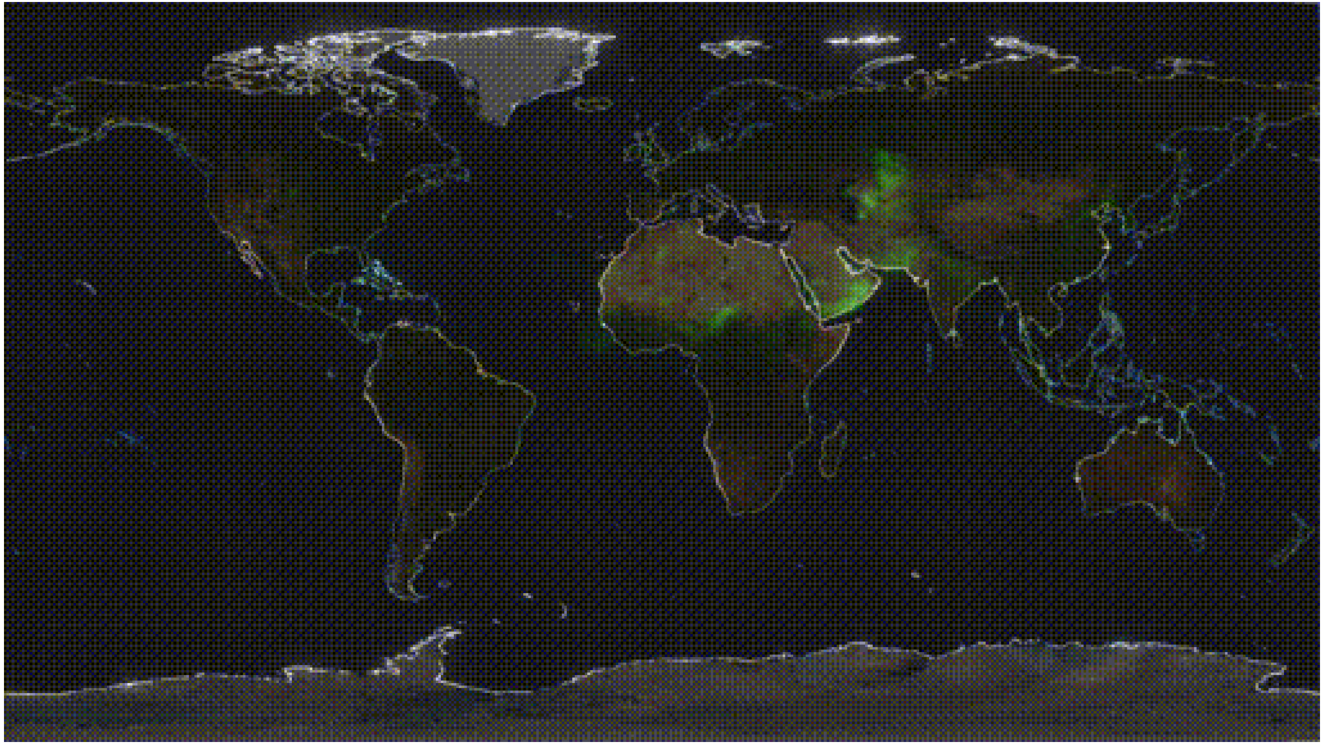
Condensation-evaporation
equilibrium

Mineralogy globally-averaged
Added
Claquin et al. 1999
Journet et al. 2014
EMIT L3 satellite data 2023

Results

Results:

Global simulations of nitrate formation



Calcite (Ca^{2+}) from dust

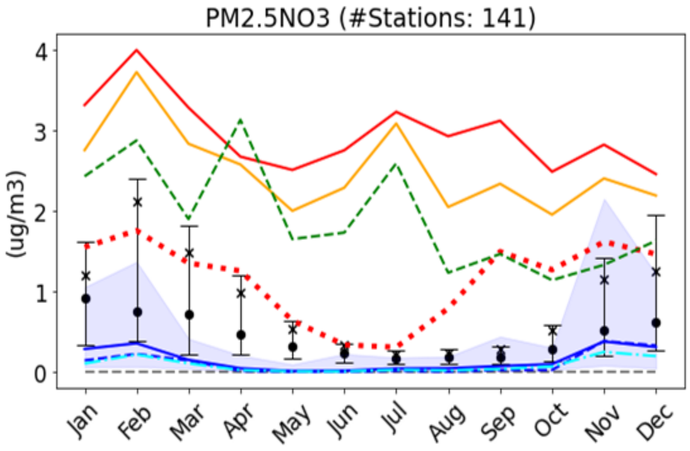
Nitric acid (HNO_3)

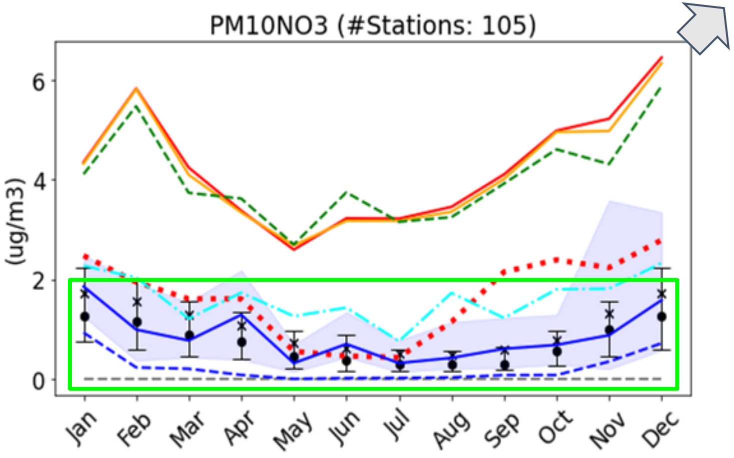
Particulate nitrate (NO_3^-)

Results:

Test of heterogeneous chemistry mechanism

1	fTEQ_noAlk fTEQ_Alk	**Thermodynamic equilibrium** is computed with only on fine mode of dust and sea salt, with/without alkalinity (Alk & noAlk).
2	HYB	**Hybrid**: fTEQ + uptake reaction of HNO_3 on coarse mode.
3.1	HYB_DL	Same as HYB (case 2), using diffusion kinetic limitation from [7].
3.2	DBCLL_noAlk DBCLL_JourAlk	**Double Call:** TEQ on fine and coarse, using diffusion kinetic limitation from [7], without/with alkalinity (noAlk & JourAlk).
3.3	DBCLL+UPTK	Same as DBCLL (case 3.2) with uptake of the leftover HNO_3 gas on coarse mode of dust.


PM2.5NO3 (#Stations: 141)


PM10NO3 (#Stations: 105)

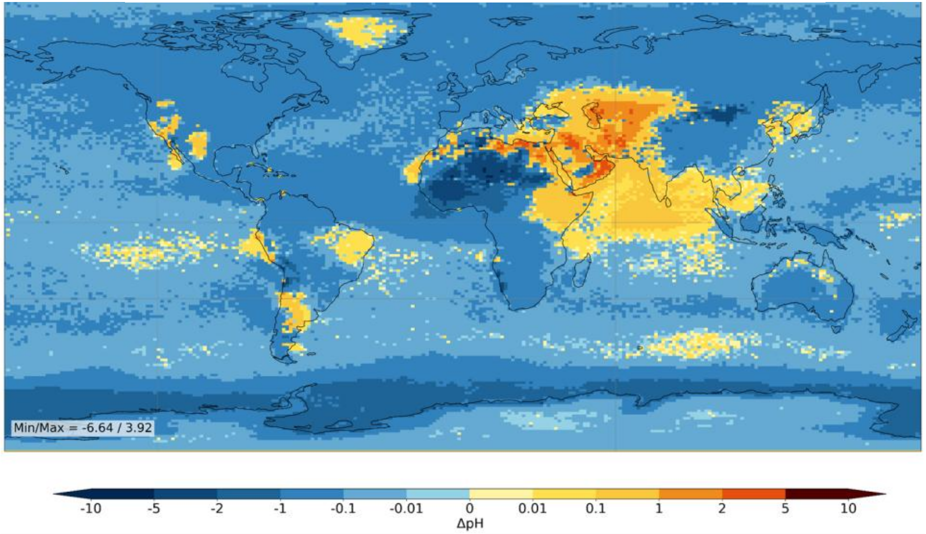
Double call of thermodynamic equilibrium mechanism provides the best performance

Results:

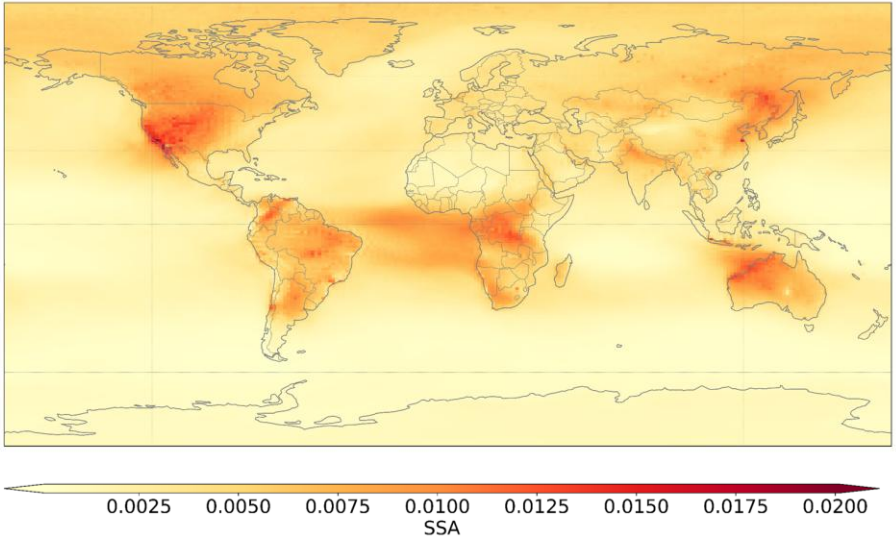
Changes in Aerosol pH and SSA

Source-based vs. **globally-averaged**
Calcite distribution

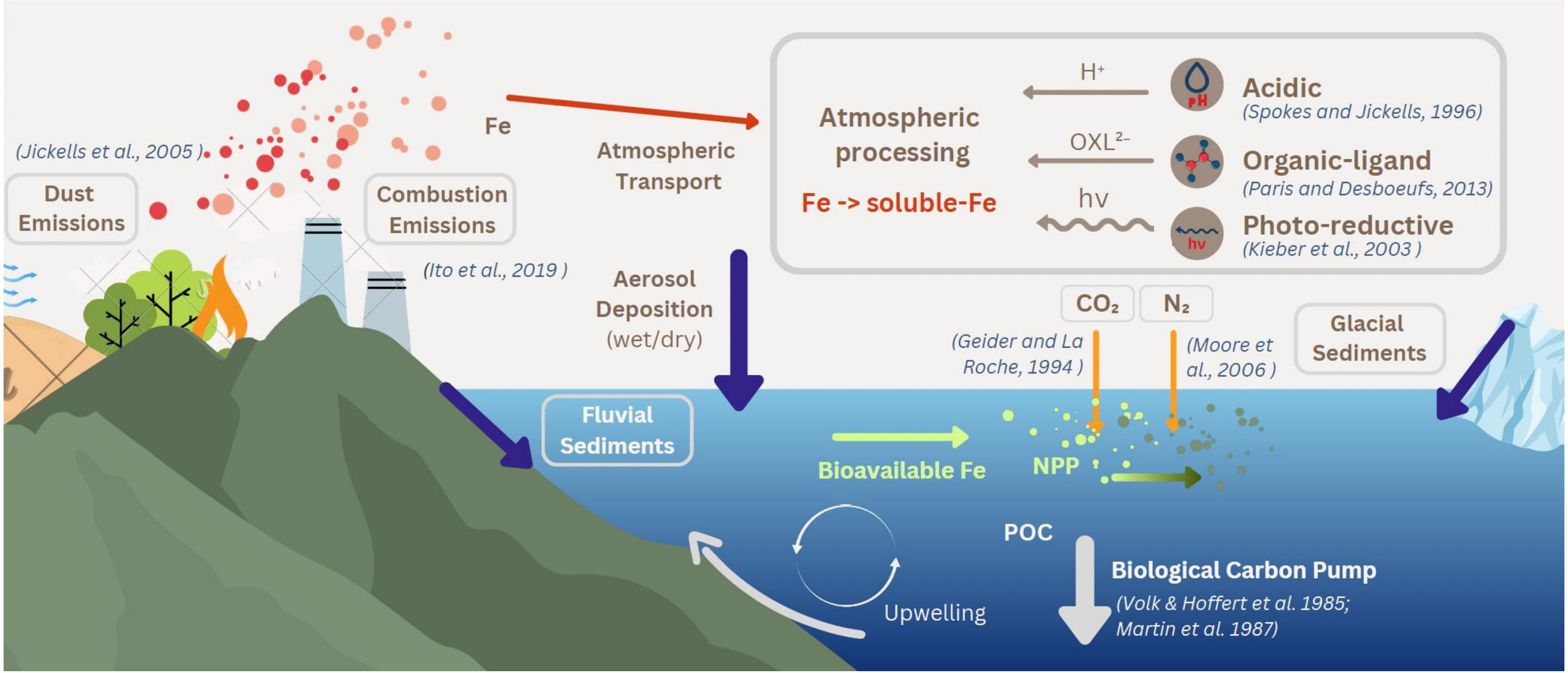
ΔpH



ΔSSA



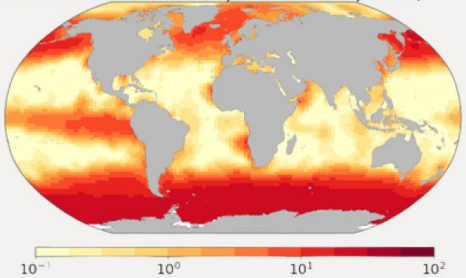
The atmospheric iron cycle



Fe-limited regions

Nitrate ocean surface concentrations

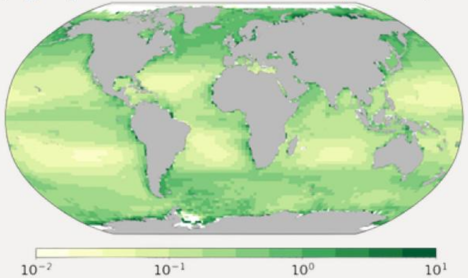
(moles of nitrate per unit mass in sea water, based on the world ocean atlas 2023; *Garcia et al., 2024*)



High Nutrient

Surface chlorophyll (SChl) concentrations

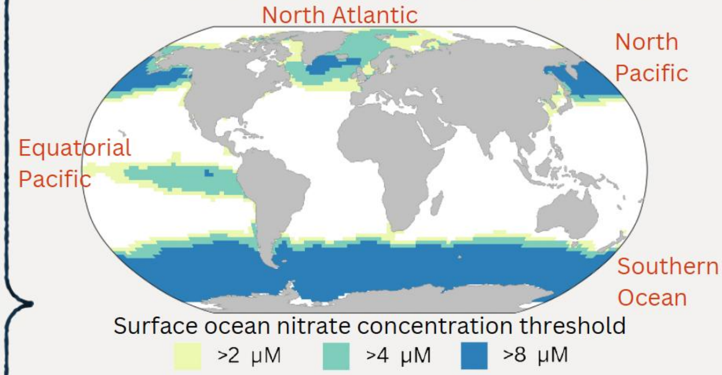
(mg/m^3, based on ESA OCI satellite product)



Low Chlorophyll

High-Nutrient Low-Chlorophyll (HNLC) regions

(based on the world ocean atlas 2023; *Garcia et al., 2024*)



Nitrogen fixers (diazotrophs) **extend this sensitivity to other ocean regions** *(Moore et al., 2006)*

$\frac{1}{3}$ of the global ocean marine productivity is affected by aerosol Fe deposition

(Mahowald et al., 2018)

(Moore et al., 2013)

Some ocean regions need Fe more than others

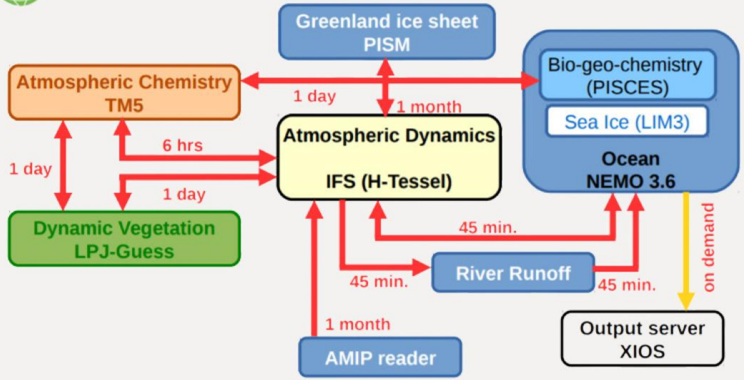
The EC-Earth3 Earth System Model

The EC-Earth3 Earth System Model

- **Earth System Model (ESM):** Simulates interactions between the atmosphere, oceans, land, and biosphere
- EC-Earth3 has participated in the **CMIP6** (Coupled Model Intercomparison Project Phase 6)

Schematics of the EC-Earth version 3

(model components and the coupling frequency between them)



(Döscher et al., 2022)

Earth System Models are a valuable tool for studying the Fe cycle.

EC-Earth3-Iron

The EC-EARTH3-Iron Earth System Model

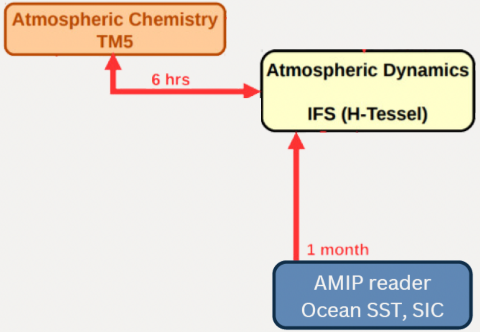
(Myriokefalitakis et al. 2022)

1. **New Fe tracers for the different sources** (accumulation/coarse soluble/insoluble):
   - **Fe-dust** (soil mineralogical composition) *(Claquin et al., 1999, Kok, 2011)*
   - **Fe-biomass burning**
   - **Fe-anthropogenic combustion** *(Ito et al., 2018)*
2. **Acidity calculations** for fine and coarse aerosols & for cloud droplets *(ISORROPIA II, Fountoukis and Nenes, 2007)*
3. Formation of **OXL is online computed** considering a **comprehensive aqueous phase chemistry scheme**
4. An **explicit description of the Fe-containing aerosol dissolution processes** for both dust and combustion Fe *(Ito and Shi, 2016; Ito, 2015)*

Schematics of the EC-Earth3-Iron atmosphere-only configuration

(model components and the coupling frequency between them)

resolution: 3ºx2º, 34 vertical levels



A version of the model that includes the atmospheric Fe cycle has been developed

Iron dissolution

The dissolved Fe in the model is produced via dissolution processes in aerosol water and cloud droplets depending on the acidity levels of the solution (i.e., proton-promoted dissolution scheme), the OXL concentration (i.e., ligand-promoted dissolution scheme), and irradiation (photo-reductive dissolution scheme), following Ito (2015) and Ito and Shi (2016). The Fe release from different types of minerals thus depends on the solution acidity (pH) and the temperature (*T*), as well as on the degree of solution saturation. In more detail, the dissolution rates for each of the three dissolution processes considered can be empirically described (e.g., Ito, 2015; Ito and Shi, 2016; Lasaga et al., 1994) as follows:

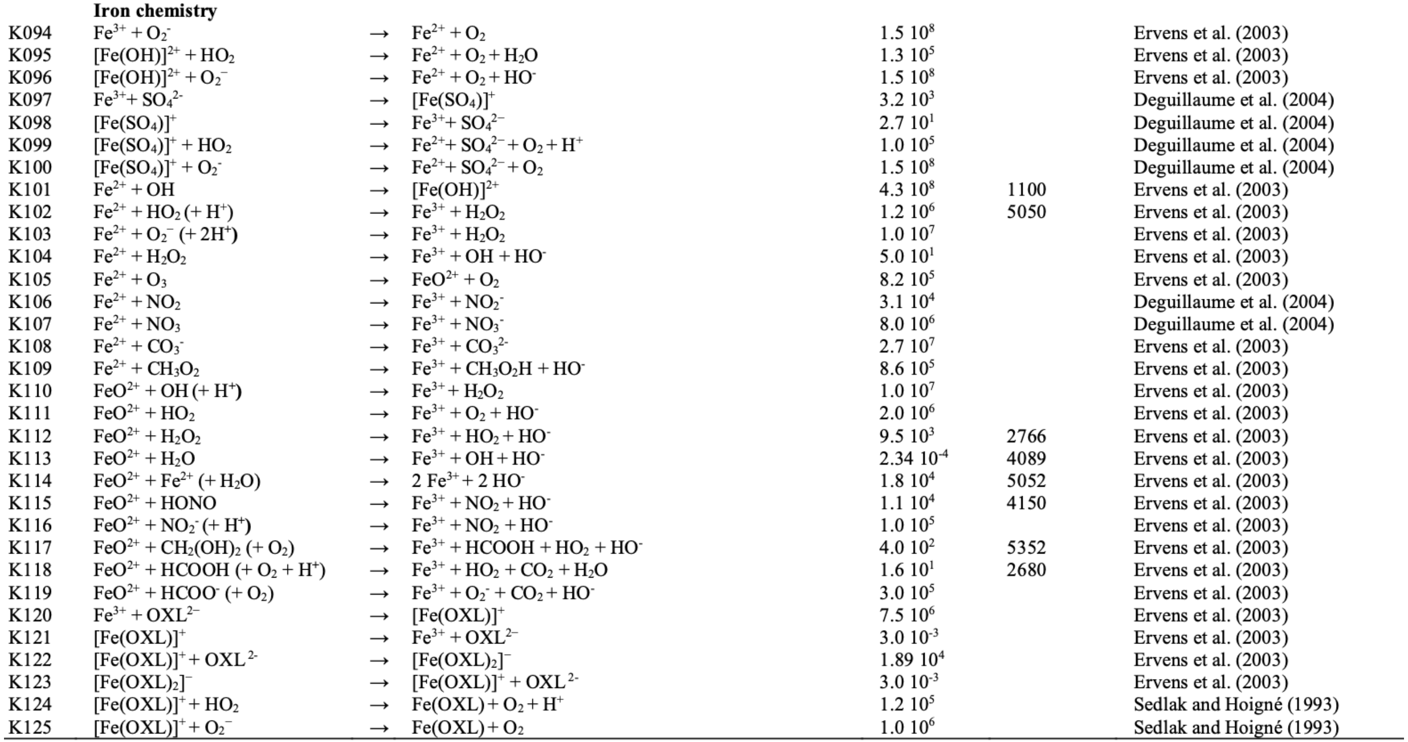
$$\mathrm{RFe}_i = K_i\,(\mathrm{pH},T)\cdot \alpha(\mathrm{H}^+)^{m_i}\cdot f_i \cdot g_i \qquad (2)$$

where K_i ($\mathrm{mol\,Fe}\,g_i^{-1}\,\mathrm{s}^{-1}$) is the Fe release rate due to the dissolution process *i*, $\alpha(\mathrm{H}^+)$ is the H^+ activity of the solution, and m_i is the empirical reaction order for protons derived from experimental data. The functions f_i and g_i represent the suppression of the different dissolution rates due to the solution saturation state as follows:

$$f_i = 1 - \left(a_{\mathrm{Fe}^{3+}} \cdot a_{\mathrm{H}^+}^{-n_i}\right)/K_{\mathrm{eq}_i}, \qquad (3)$$

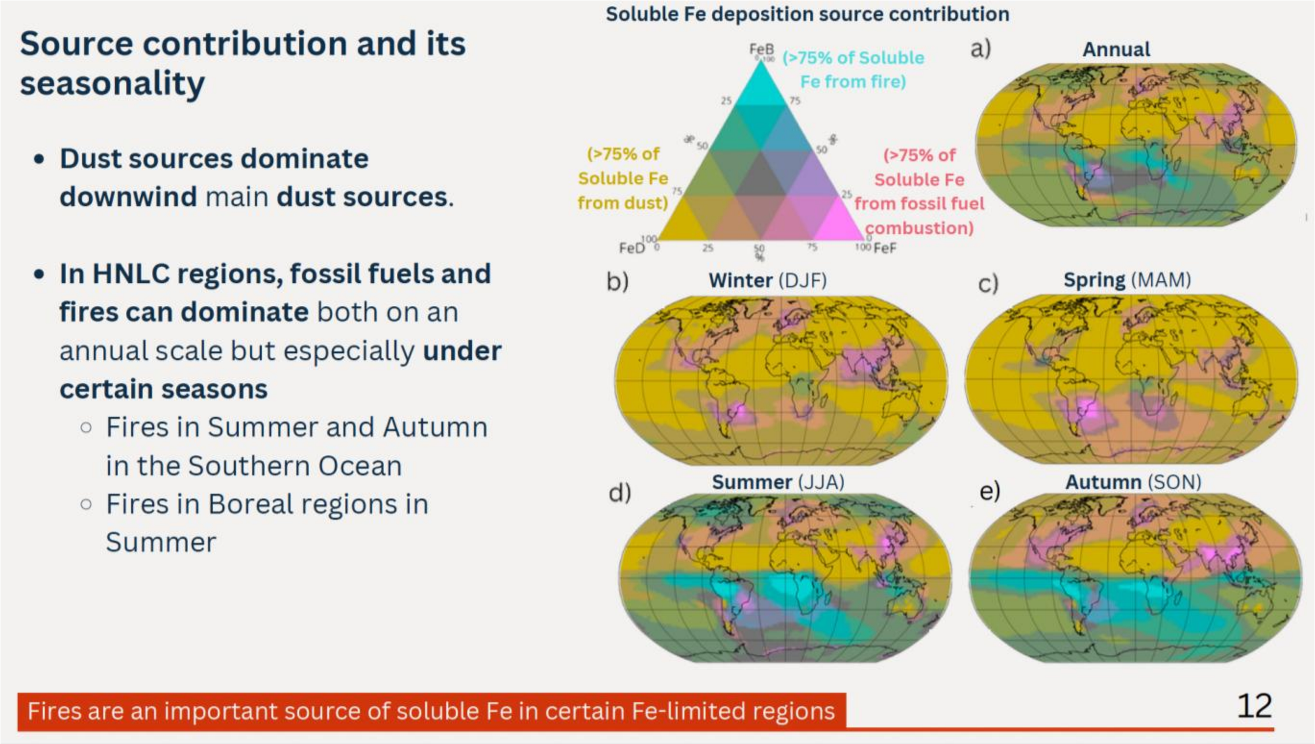
$$g_i = 0.17 \cdot \ln\left(\frac{a_{\mathrm{OXL}}}{a_{\mathrm{Fe}^{3+}}}\right) + 0.63, \qquad (4)$$

Iron chemistry



	Iron chemistry					
K094	$Fe^{3+} + O_2^-$	→	$Fe^{2+} + O_2$	$1.5\ 10^8$		Ervens et al. (2003)
K095	$[Fe(OH)]^{2+} + HO_2$	→	$Fe^{2+} + O_2 + H_2O$	$1.3\ 10^5$		Ervens et al. (2003)
K096	$[Fe(OH)]^{2+} + O_2^-$	→	$Fe^{2+} + O_2 + HO^-$	$1.5\ 10^8$		Ervens et al. (2003)
K097	$Fe^{3+} + SO_4^{2-}$	→	$[Fe(SO_4)]^+$	$3.2\ 10^3$		Deguillaume et al. (2004)
K098	$[Fe(SO_4)]^+$	→	$Fe^{3+} + SO_4^{2-}$	$2.7\ 10^1$		Deguillaume et al. (2004)
K099	$[Fe(SO_4)]^+ + HO_2$	→	$Fe^{2+} + SO_4^{2-} + O_2 + H^+$	$1.0\ 10^5$		Deguillaume et al. (2004)
K100	$[Fe(SO_4)]^+ + O_2^-$	→	$Fe^{2+} + SO_4^{2-} + O_2$	$1.5\ 10^8$		Deguillaume et al. (2004)
K101	$Fe^{2+} + OH$	→	$[Fe(OH)]^{2+}$	$4.3\ 10^8$	1100	Ervens et al. (2003)
K102	$Fe^{2+} + HO_2\ (+ H^+)$	→	$Fe^{3+} + H_2O_2$	$1.2\ 10^6$	5050	Ervens et al. (2003)
K103	$Fe^{2+} + O_2^-\ (+ 2H^+)$	→	$Fe^{3+} + H_2O_2$	$1.0\ 10^7$		Ervens et al. (2003)
K104	$Fe^{2+} + H_2O_2$	→	$Fe^{3+} + OH + HO^-$	$5.0\ 10^1$		Ervens et al. (2003)
K105	$Fe^{2+} + O_3$	→	$FeO^{2+} + O_2$	$8.2\ 10^5$		Ervens et al. (2003)
K106	$Fe^{2+} + NO_2$	→	$Fe^{3+} + NO_2^-$	$3.1\ 10^4$		Deguillaume et al. (2004)
K107	$Fe^{2+} + NO_3$	→	$Fe^{3+} + NO_3^-$	$8.0\ 10^6$		Deguillaume et al. (2004)
K108	$Fe^{2+} + CO_3^-$	→	$Fe^{3+} + CO_3^{2-}$	$2.7\ 10^7$		Ervens et al. (2003)
K109	$Fe^{2+} + CH_3O_2$	→	$Fe^{3+} + CH_3O_2H + HO^-$	$8.6\ 10^5$		Ervens et al. (2003)
K110	$FeO^{2+} + OH\ (+ H^+)$	→	$Fe^{3+} + H_2O_2$	$1.0\ 10^7$		Ervens et al. (2003)
K111	$FeO^{2+} + HO_2$	→	$Fe^{3+} + O_2 + HO^-$	$2.0\ 10^6$		Ervens et al. (2003)
K112	$FeO^{2+} + H_2O_2$	→	$Fe^{3+} + HO_2 + HO^-$	$9.5\ 10^3$	2766	Ervens et al. (2003)
K113	$FeO^{2+} + H_2O$	→	$Fe^{3+} + OH + HO^-$	$2.34\ 10^{-4}$	4089	Ervens et al. (2003)
K114	$FeO^{2+} + Fe^{2+}\ (+ H_2O)$	→	$2\ Fe^{3+} + 2\ HO^-$	$1.8\ 10^4$	5052	Ervens et al. (2003)
K115	$FeO^{2+} + HONO$	→	$Fe^{3+} + NO_2 + HO^-$	$1.1\ 10^4$	4150	Ervens et al. (2003)
K116	$FeO^{2+} + NO_2^-\ (+ H^+)$	→	$Fe^{3+} + NO_2 + HO^-$	$1.0\ 10^5$		Ervens et al. (2003)
K117	$FeO^{2+} + CH_2(OH)_2\ (+ O_2)$	→	$Fe^{3+} + HCOOH + HO_2 + HO^-$	$4.0\ 10^2$	5352	Ervens et al. (2003)
K118	$FeO^{2+} + HCOOH\ (+ O_2 + H^+)$	→	$Fe^{3+} + HO_2 + CO_2 + H_2O$	$1.6\ 10^1$	2680	Ervens et al. (2003)
K119	$FeO^{2+} + HCOO^-\ (+ O_2)$	→	$Fe^{3+} + O_2^- + CO_2 + HO^-$	$3.0\ 10^5$		Ervens et al. (2003)
K120	$Fe^{3+} + OXL^{2-}$	→	$[Fe(OXL)]^+$	$7.5\ 10^6$		Ervens et al. (2003)
K121	$[Fe(OXL)]^+$	→	$Fe^{3+} + OXL^{2-}$	$3.0\ 10^{-3}$		Ervens et al. (2003)
K122	$[Fe(OXL)]^+ + OXL^{2-}$	→	$[Fe(OXL)_2]^-$	$1.89\ 10^4$		Ervens et al. (2003)
K123	$[Fe(OXL)_2]^-$	→	$[Fe(OXL)]^+ + OXL^{2-}$	$3.0\ 10^{-3}$		Ervens et al. (2003)
K124	$[Fe(OXL)]^+ + HO_2$	→	$Fe(OXL) + O_2 + H^+$	$1.2\ 10^5$		Sedlak and Hoigné (1993)
K125	$[Fe(OXL)]^+ + O_2^-$	→	$Fe(OXL) + O_2$	$1.0\ 10^6$		Sedlak and Hoigné (1993)

A reconstruction of soluble Fe deposition



Source contribution and its seasonality

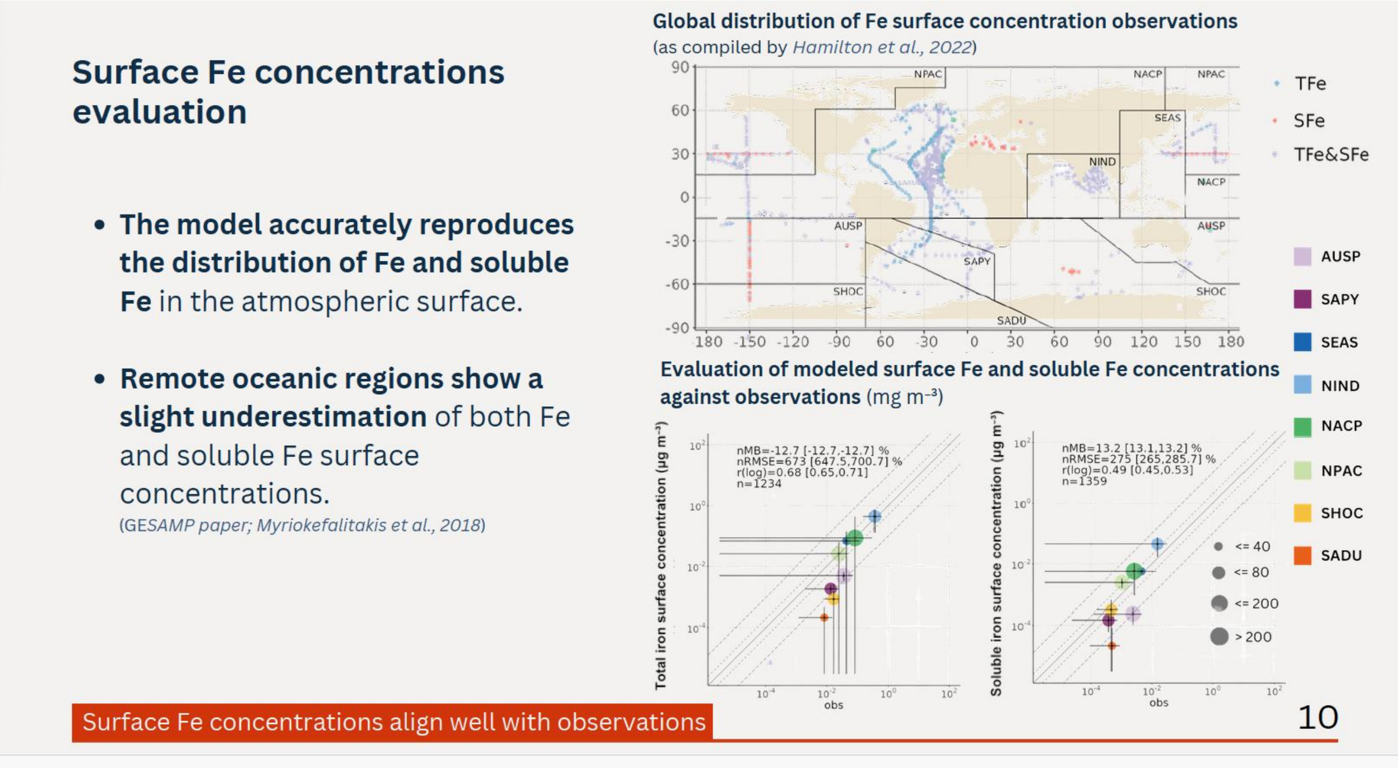
- **Dust sources dominate downwind** main **dust sources**.
- **In HNLC regions, fossil fuels and fires can dominate** both on an annual scale but especially **under certain seasons**
  - Fires in Summer and Autumn in the Southern Ocean
  - Fires in Boreal regions in Summer

Soluble Fe deposition source contribution

Fires are an important source of soluble Fe in certain Fe-limited regions

Bergas et al. 2024

Evaluation



Surface Fe concentrations evaluation

- **The model accurately reproduces the distribution of Fe and soluble Fe** in the atmospheric surface.
- **Remote oceanic regions show a slight underestimation** of both Fe and soluble Fe surface concentrations.

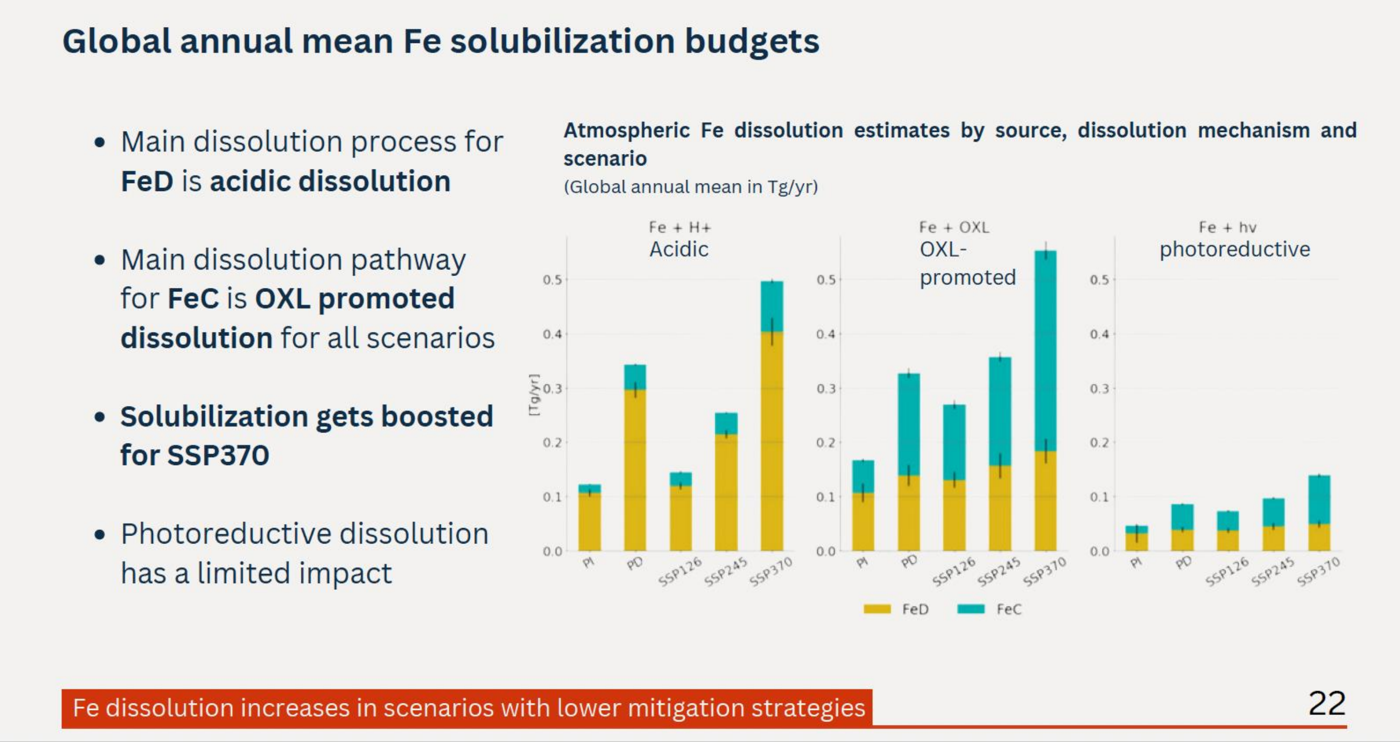
(GESAMP paper; *Myriokefalitakis et al., 2018*)

Global distribution of Fe surface concentration observations
(as compiled by *Hamilton et al., 2022*)

Evaluation of modeled surface Fe and soluble Fe concentrations against observations (mg m⁻³)

Surface Fe concentrations align well with observations

Projections for the end of the 21st century



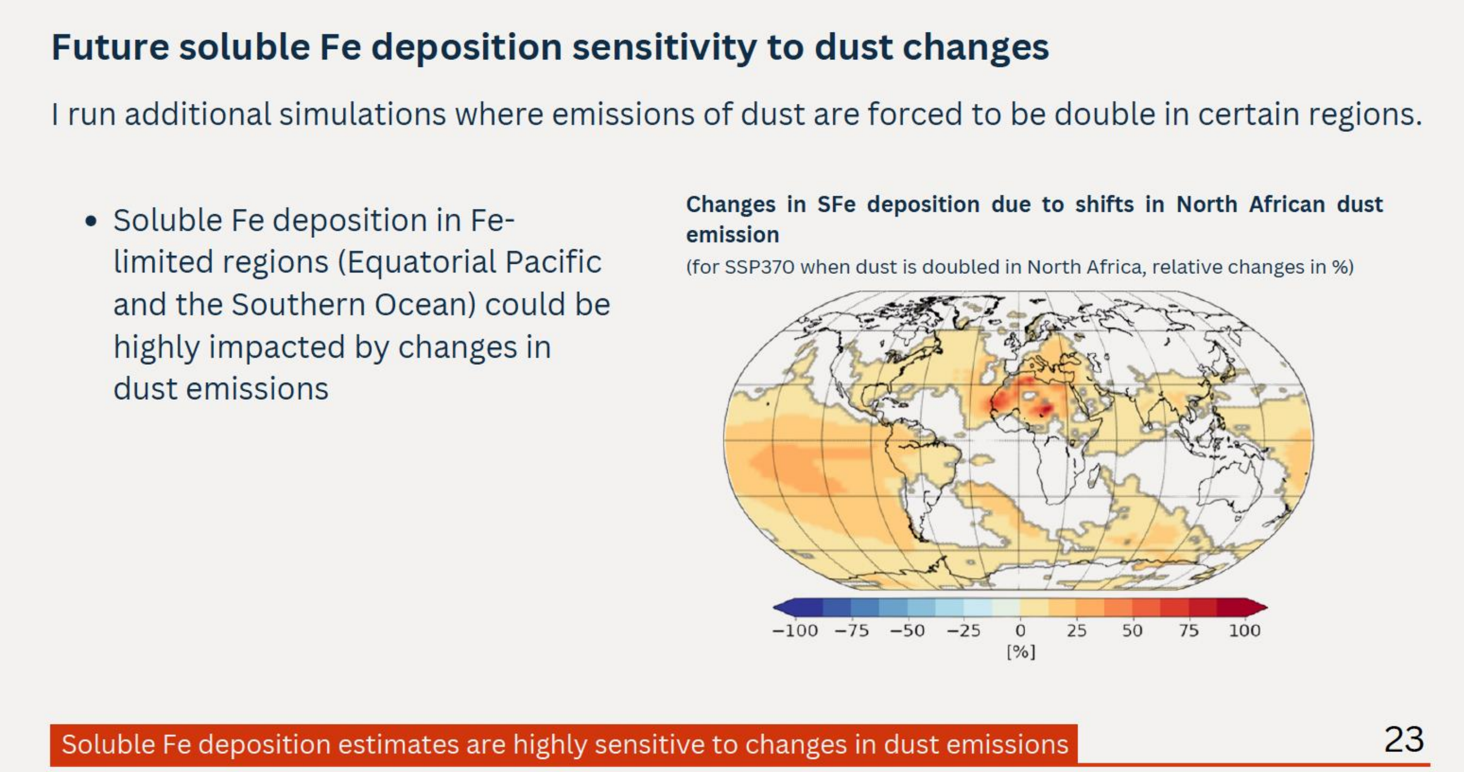
Global annual mean Fe solubilization budgets

- Main dissolution process for **FeD** is **acidic dissolution**
- Main dissolution pathway for **FeC** is **OXL promoted dissolution** for all scenarios
- **Solubilization gets boosted for SSP370**
- Photoreductive dissolution has a limited impact

Atmospheric Fe dissolution estimates by source, dissolution mechanism and scenario
(Global annual mean in Tg/yr)

Fe dissolution increases in scenarios with lower mitigation strategies

Future soleble deposition sensitivity to dust changes



Future soluble Fe deposition sensitivity to dust changes

I run additional simulations where emissions of dust are forced to be double in certain regions.

- Soluble Fe deposition in Fe-limited regions (Equatorial Pacific and the Southern Ocean) could be highly impacted by changes in dust emissions

Changes in SFe deposition due to shifts in North African dust emission

(for SSP370 when dust is doubled in North Africa, relative changes in %)

Soluble Fe deposition estimates are highly sensitive to changes in dust emissions

ATARRI

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