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Saharan dust composition on the way to the Americas and potential impacts on atmosphere and biosphere

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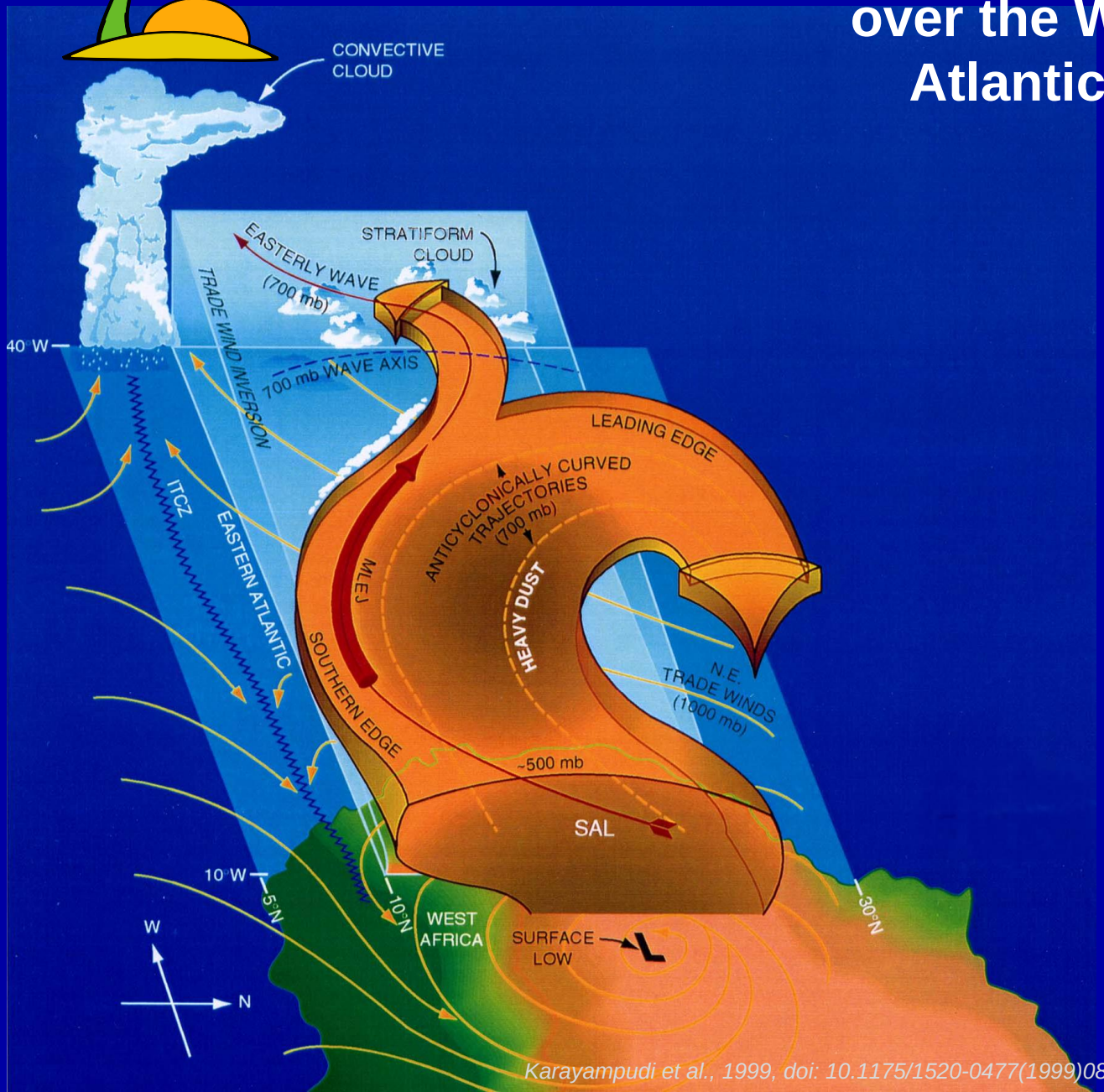
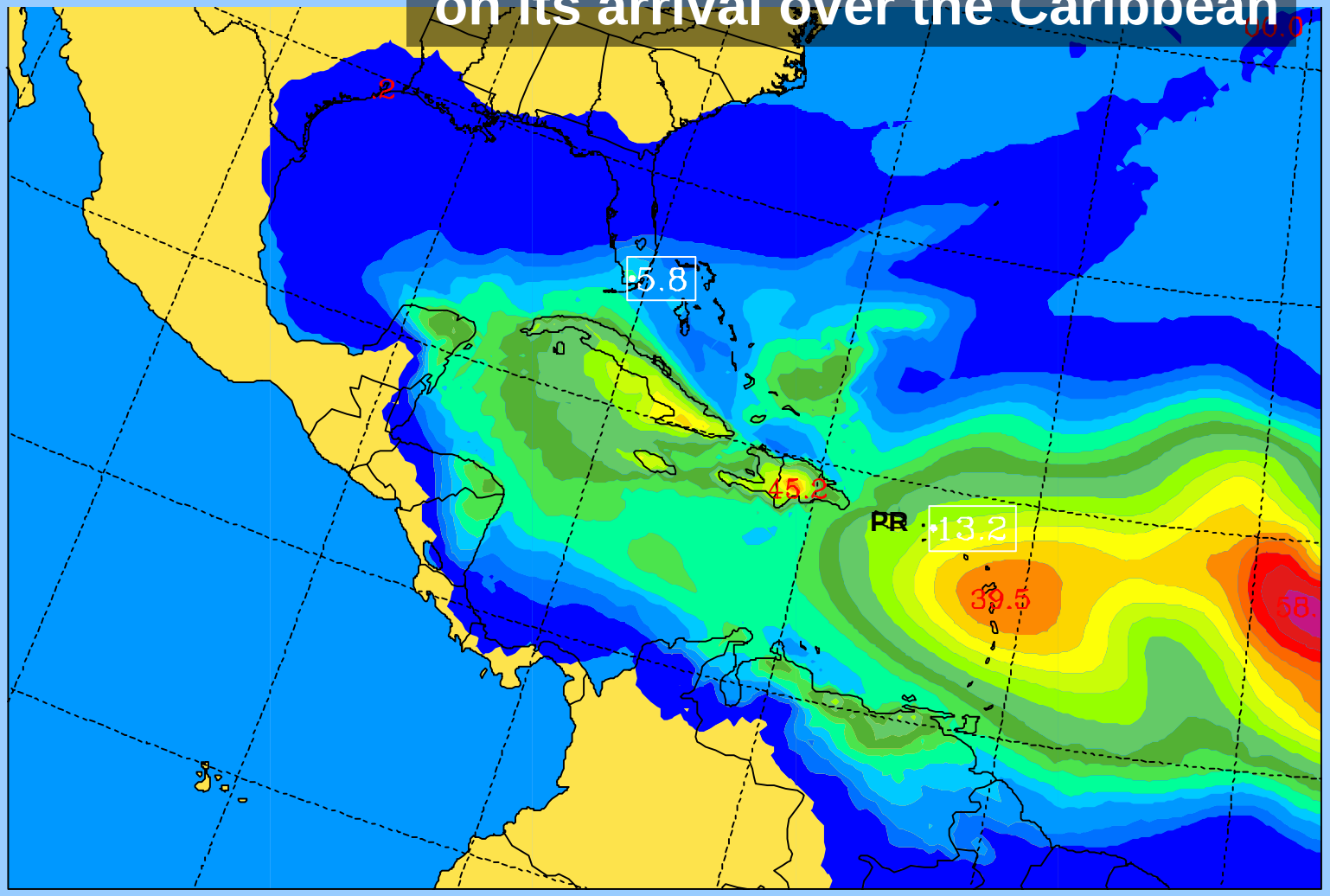
The Saharan dust plume over the Western Atlantic Ocean



Karayampudi et al., 1999, doi: 10.1175/1520-0477(1999)080

The Saharan dust plume on its arrival over the Caribbean



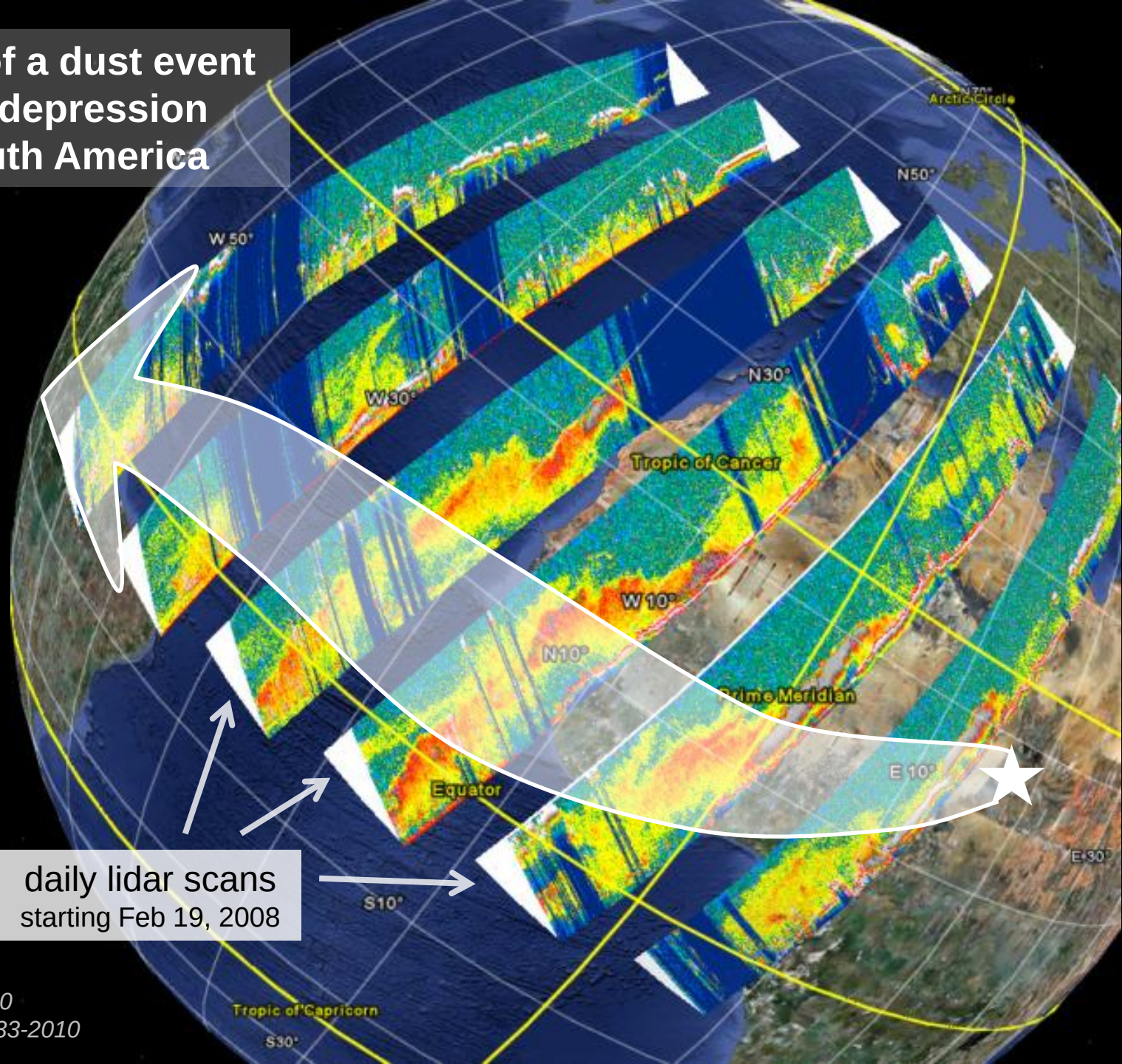
daily averaged surface dust concentration (in μg^{-3}), modelled for 23 June 1993

0.0 0.5 1.0 2.0 3.0 5.0 7.0 10.0 15.0 20.0 25.0 30.0 35.0 40.0 45.0 50.0 55.0 60.0 65.0

Kallos et al. 2006, doi: 10.1029/2005JD006207

Karayampudi et al., 1999, doi: 10.1175/1520-0477(1999)080

Case study of a dust event from Bodélé depression reaching South America



daily lidar scans
starting Feb 19, 2008

from Ben-Ami et al. 2010
doi: 10.5194/acp-10-7533-2010

Dust composition and its dependencies, interaction and potential impacts

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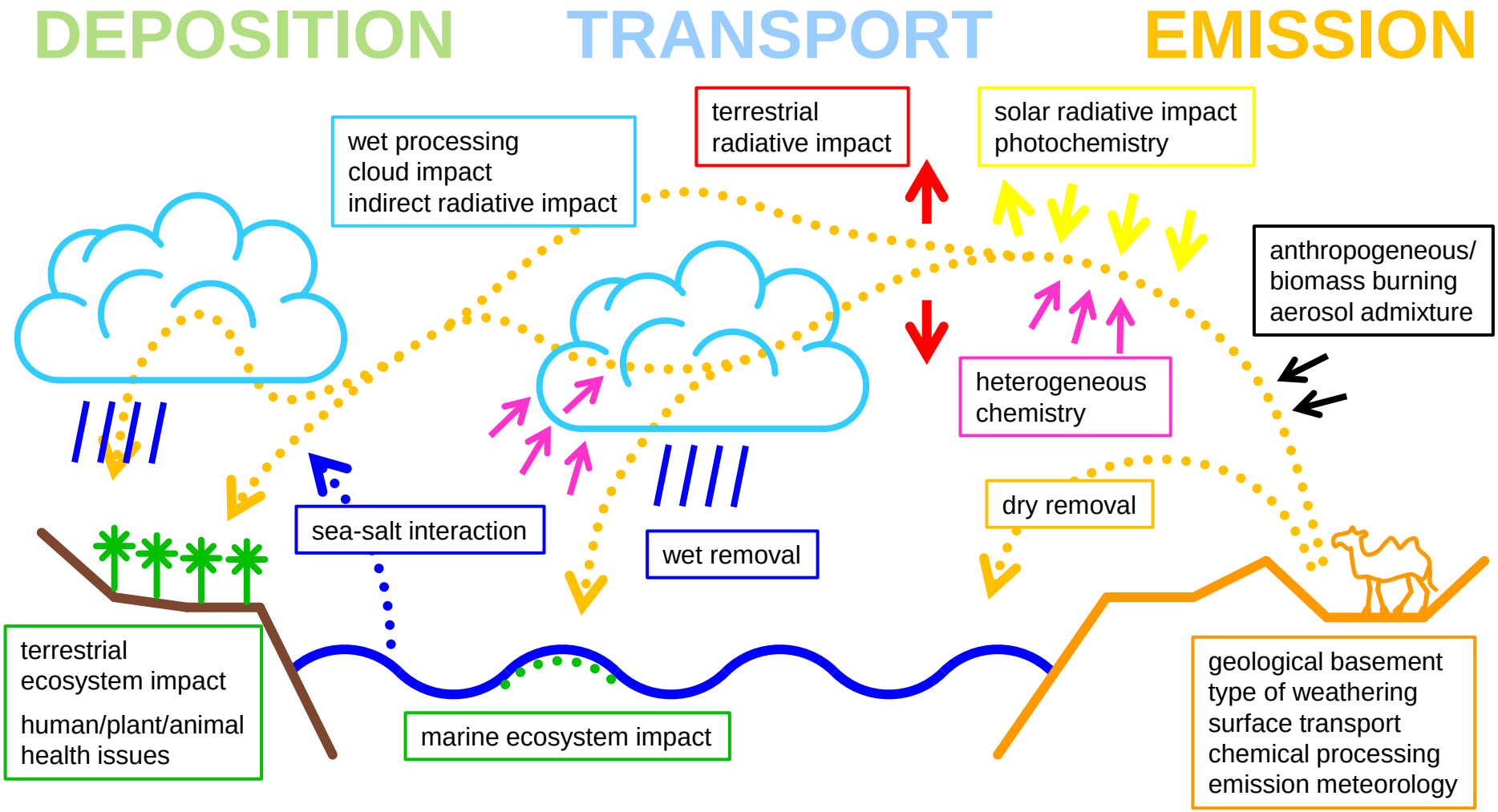

Implications for radiation transfer – dust radiative forcing

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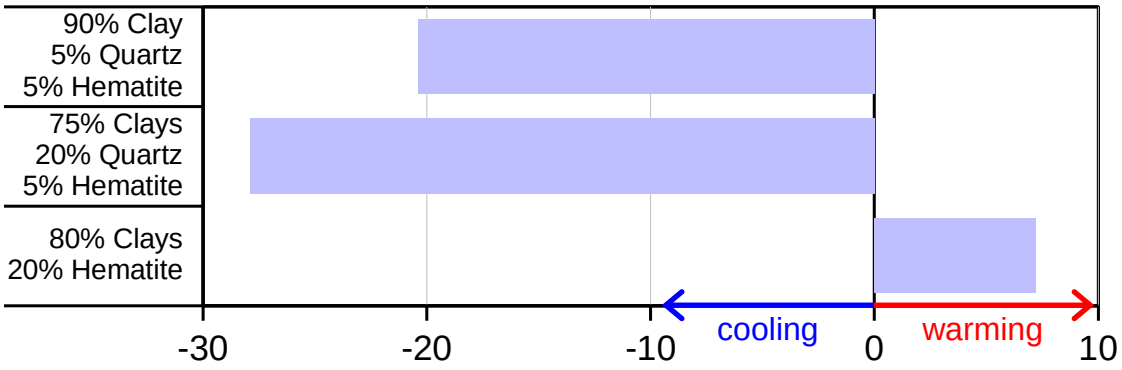
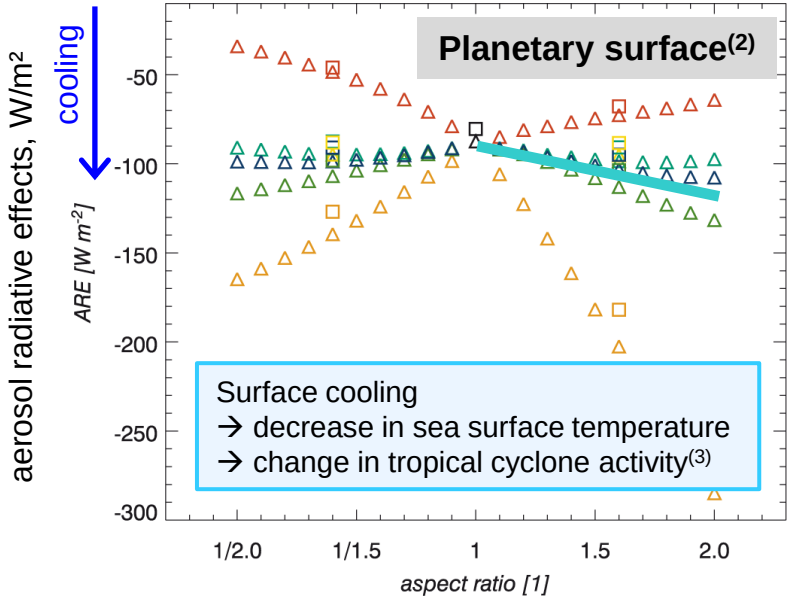
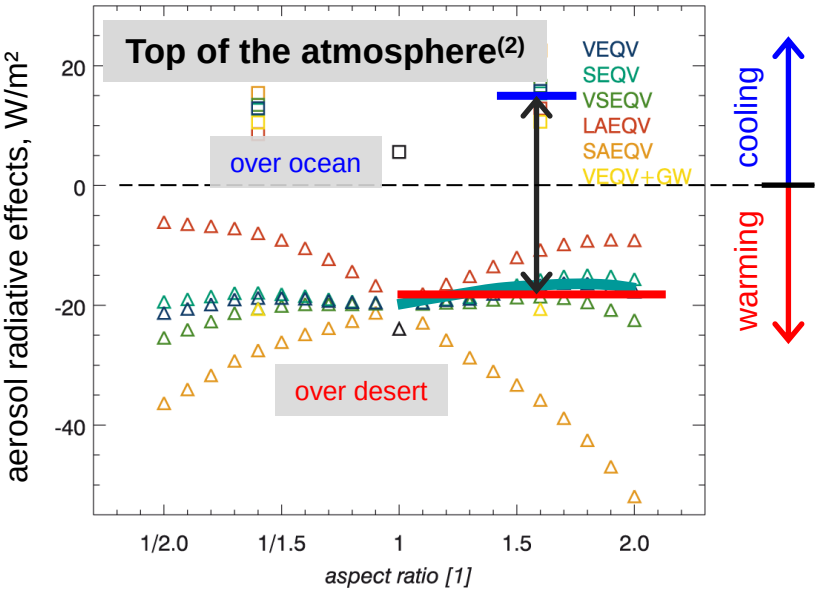
Top-of the atmosphere (TOA) net radiative forcing for different dust mineralogical compositions[1]



Shortwave forcing case study, including

- measured aerosol size distribution
- measured vertical aerosol distribution
- measured planetary surface albedo
- measured particle shape
- derived particle refractive index
- derived particle single scattering albedo





[1]data from Sokolik et al. 1999, doi: 10.1029/1998JD200048 [2]Otto et al. 2009, doi: 10.1111/j.1600-0889.2008.00389.x
[3]Evan et al. 2008, doi: 10.1029/2007GC001774

Implications for radiation transfer – dust composition and terrestrial radiation

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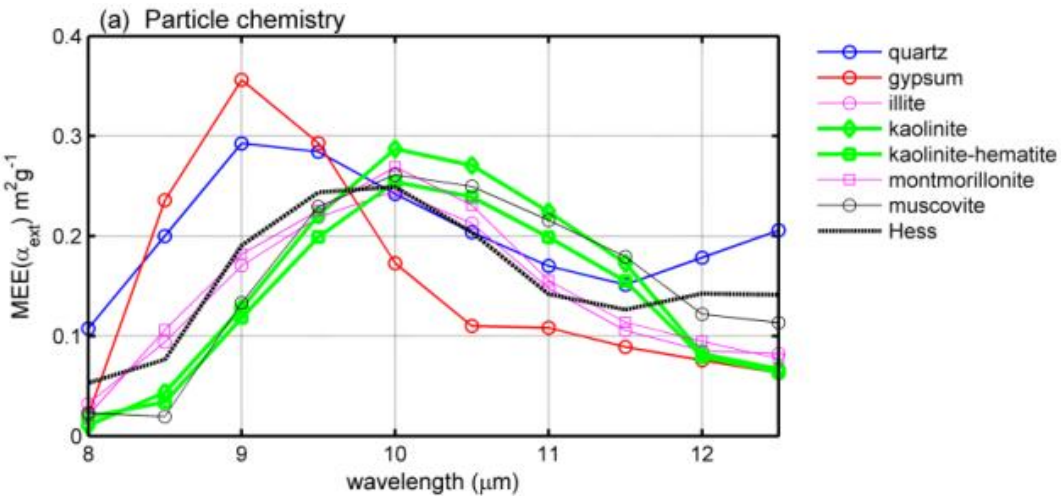
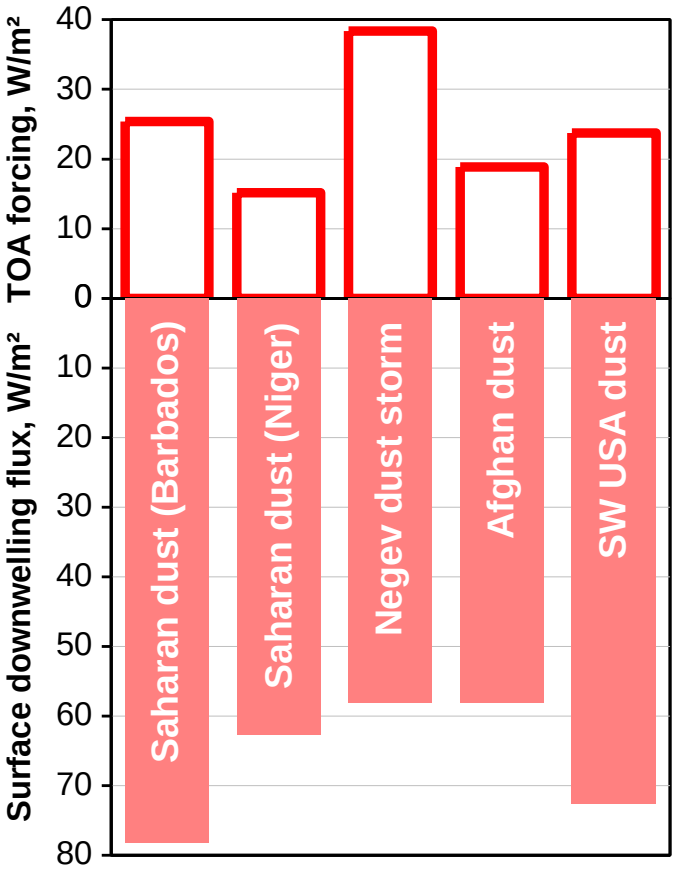
Mass extinction efficiency for different minerals in the atmospheric window wavelength region[1]



Thermal infrared radiative forcing for different dust compositions[2]



[1]Hansell et al. 2011, doi:10.5194/acp-11-1527-2011 [2]data from Sokolik et al. 1998, doi: 10.1029/98JD00049

Dust composition and clouds

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Modification by clouds

- Uptake of gaseous precursor species via aqueous chemistry
- Aqueous reaction with (acidic) species
- Composition-selective removal by wet deposition
- Internal mixing by droplet/particle scavenging or coalescence

Impact on clouds

- Fresh dust particles can act as cloud condensation nuclei (dependency on mineralogy)(1)
- Dust particles as giant cloud condensation nuclei (GCCN) may alter precipitation(2)
- Increase of ice nucleus (IN) concentrations, IN at higher temperatures(3)
- Mineral dust contributes by 21 to 84% to the IN concentration(4) over the Amazon basin
- In a case study, more than 79 % of cloud droplets at Cape Verde contained dust particles(5)
- Water vapor competition of GCCN versus smaller dust particles makes precipitation impact depending on cloud conditions (i. e. liquid water content, but also gaseous chemistry)(6)
  → impact is ambiguous, depending on cloud microstructure(7)
- Short-lived convective clouds are most sensitive(6)
- Indirect impact through change of atmospheric dynamics by radiative impact (surface cooling, increase in atmospheric stability)(6)

[1]Kumar et al. 2011, 10.5194/acp-11-3527-2011 [2]Yin et al. 2000, 10.1016/S0169-8095(99)00046-0 [3]Sassen et al. 2003, doi: 10.1029/2003GL017371
[4]Prenni et al. 2009, doi: 10.1038/NGEO517 [5]Twohy et al. 2009, doi: 10.1029/2008GL035846 [6]Rosenfeld et al. 2001, doi: 10.1073/pnas.101122798
[7]Seifert et al. 2011, doi: 10.5194/acpd-11-20203-2011

Dust and ecosystems

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Marine ecosystems

- Fe (and possibly, P) can limit bio-productivity on Oceans directly or by co-limiting N fixation[1,2]
- Saharan dust is made responsible for the degradation of coral reefs[3], but possible pathways are still explored[4]
- Toxic red tides in the Gulf of Mexico need dust Fe (and maybe P) input to start[5]
- On the nature (and impact) of P on marine ecosystems "remarkably little is known"[2]
- P input by dust can increase bacterial activity in Mediterranean freshwater ecosystems[6]

Terrestrial ecosystems

- Forest ecosystems on extremely leached soils (like Amazonia) are short in nutrients (**P**, K) which can be provided by dust fall[7,8]
- For example, half of the total inputs to soil-and-biomass P can be derived from dust in Puerto Rico's Luquillo Mountains[9]
- Forests on less leached soils can have deficit of Ca and K[10]
- A tropical Andean forest in Ecuador receives considerable amounts of Ca and Mg from Saharan dust[11]

[1]Jickells et al. 2005, doi: 10.1126/science.1105959 [2]Okin et al. 2011, doi: 10.1029/2010GB003858 [3]Shinn et al. 2000, doi: 10.1029/2000GL011599
[4]Rypien 2008, doi: 10.3354/meps07600 [5]Walsh et al. 2006, doi: 10.1029/2004JC002813 [6]Reche et al. 2009, doi: 10.4319/lo.2009.54.3.0869
[7]Swap et al. 1992, doi: 10.1034/j.1600-0889.1992.t01-1-00005.x [8]Okin et al. 2004, doi: 10.1029/2003GB002145
[9]Pett-Ridge 2009, doi: 10.1007/s10533-009-9308-x [10]Bond 2010, doi: 10.1007/s11104-010-0440-0 [11]Boy et al. 2008, doi: 10.1029/2007GB002960

Emission stage – sources, composition, variation

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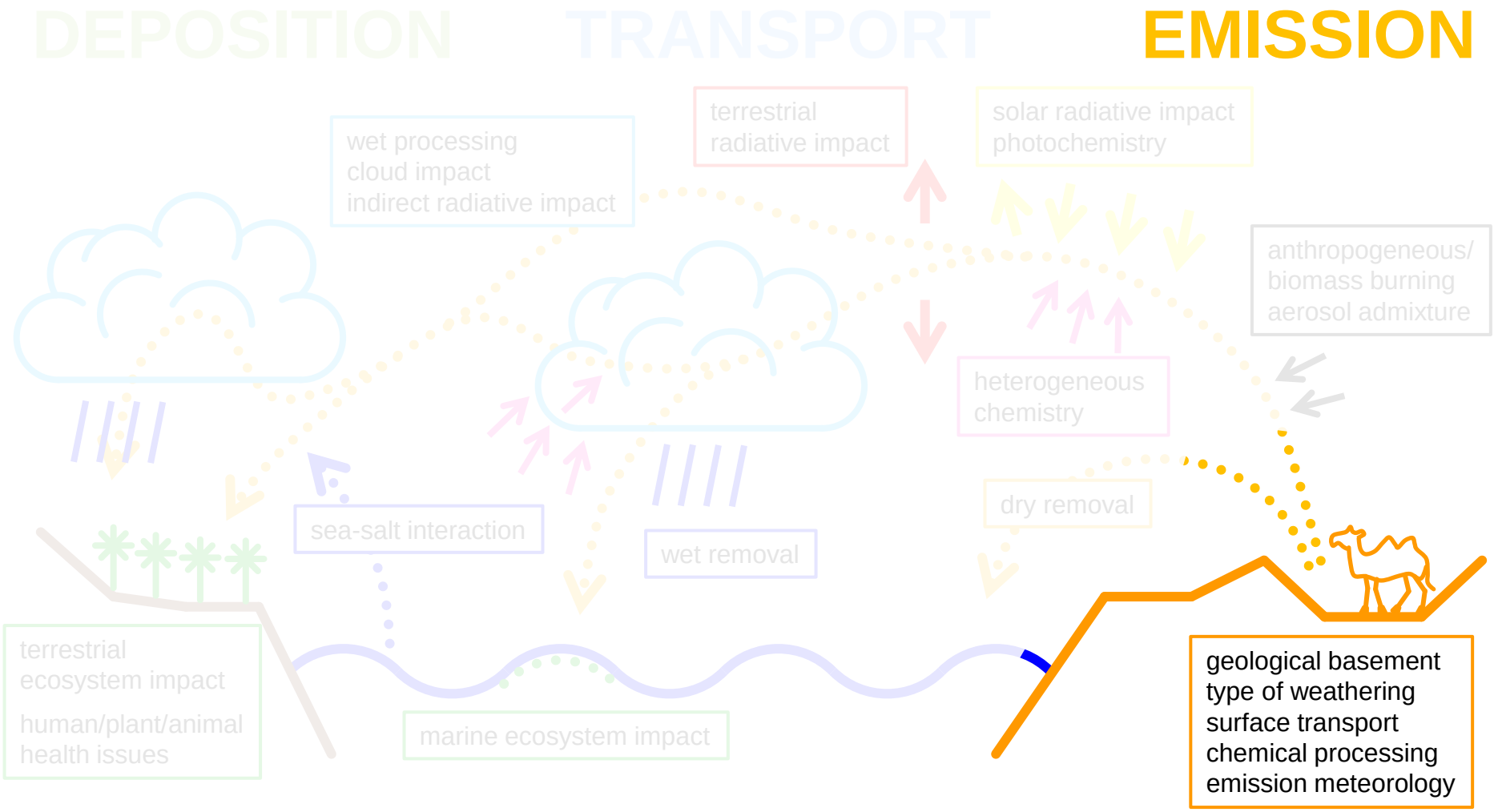

Emission stage – general mineralogy

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- Dust composition is highly variably
- Quartz and phyllosilicates are omnipresent
- Phyllosilicates might be
  - (frequently reported) kaolinite, illite
  - (less frequently) chlorite, muscovite, montmorillionite, biotite, palygorskite, smectites and inter-stratified clay minerals
- Mostly, additional silicates are reported
  - (frequently) albite, anorthite, K-feldspars
  - (less frequently) chrysotile, orthoclase
- Calcite, dolomite and sometimes apatite are found in varying abundance
- Hematite, goethite and sometimes ilmenite are the main iron compounds
- Sulfates, nitrates and chlorides are usually not reported with their mineralogical denomination (some of them might [fractionally] recrystallize depending on environmental conditions)
- In addition, a plethora of other mineral species are reported, including biological debris (diatomite), metal oxides (rutile, periclase, baddeleyite, spinel), iron-rich minerals (lepidocrocite, limonite), carbonates (aragonite, magnesite), sulfates (anhydrite, gypsum, thenardite, mirabilite, mascagnite, glauberite), silicates (chloritoid, leucite, forsterite, zircon, enstatite) and graphite

Emission stage – sources and composition

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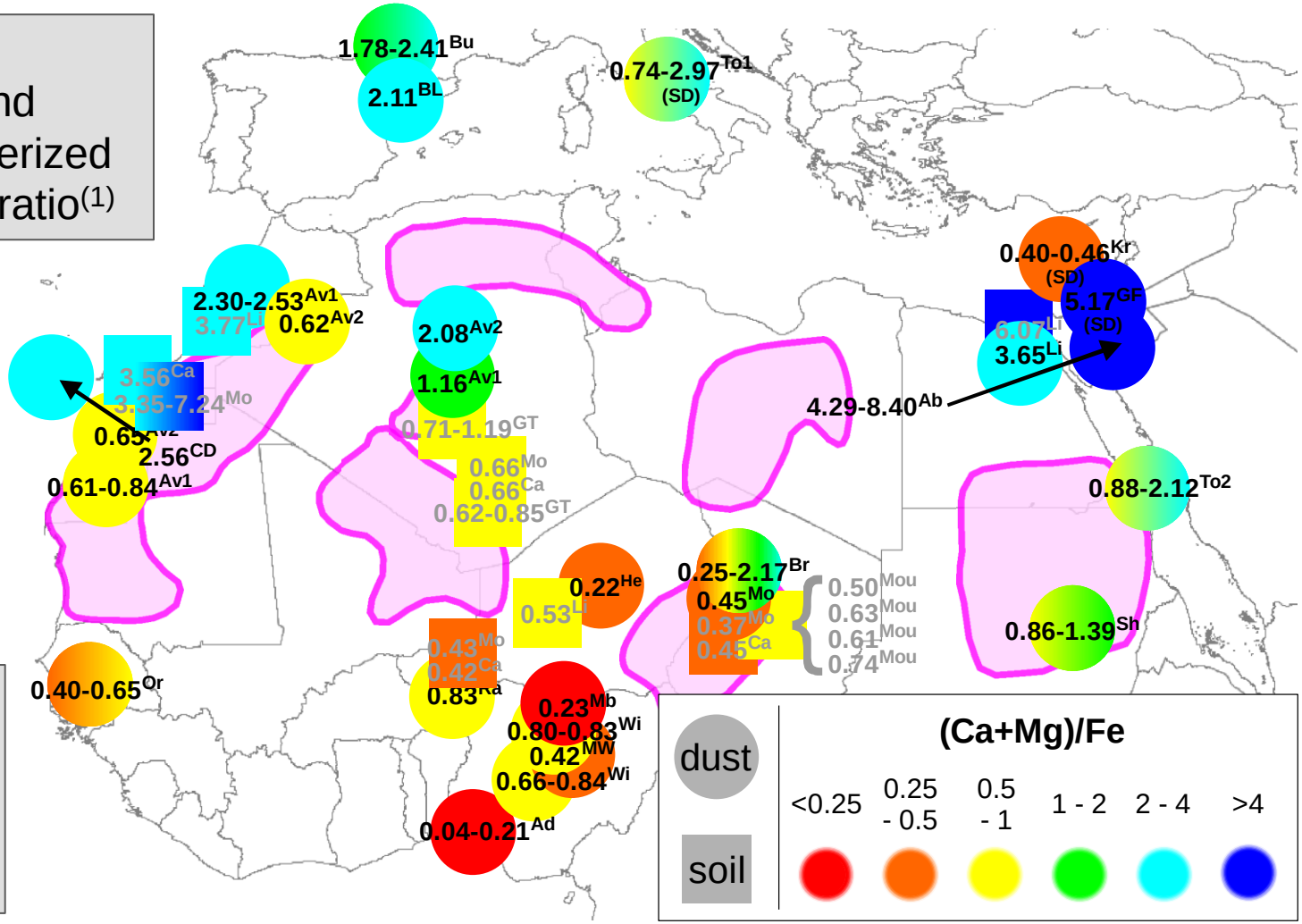
Composition of Saharan dust and topsoils characterized by (Ca+Mg)/Fe ratio[1]



Major source regions compiled from different techniques are identified[2]

[1] Scheuvens et al., in preparation for Earth. Sci. Reviews – details on original literature are given there

[2] Formenti et al. 2011, doi: 10.5194/acp-11-8231-2011

Mineralogical composition as function of source regions – an example

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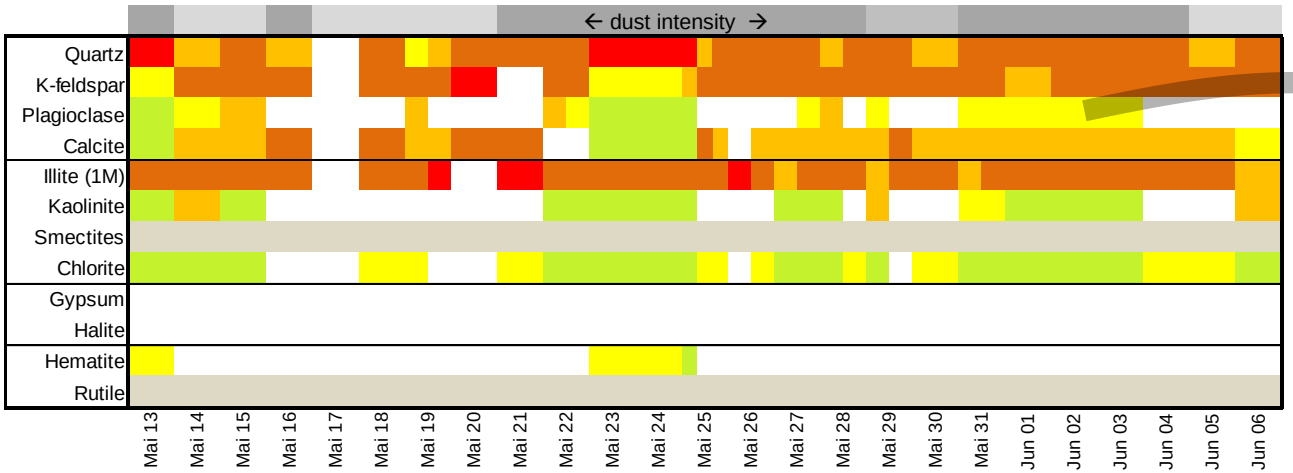

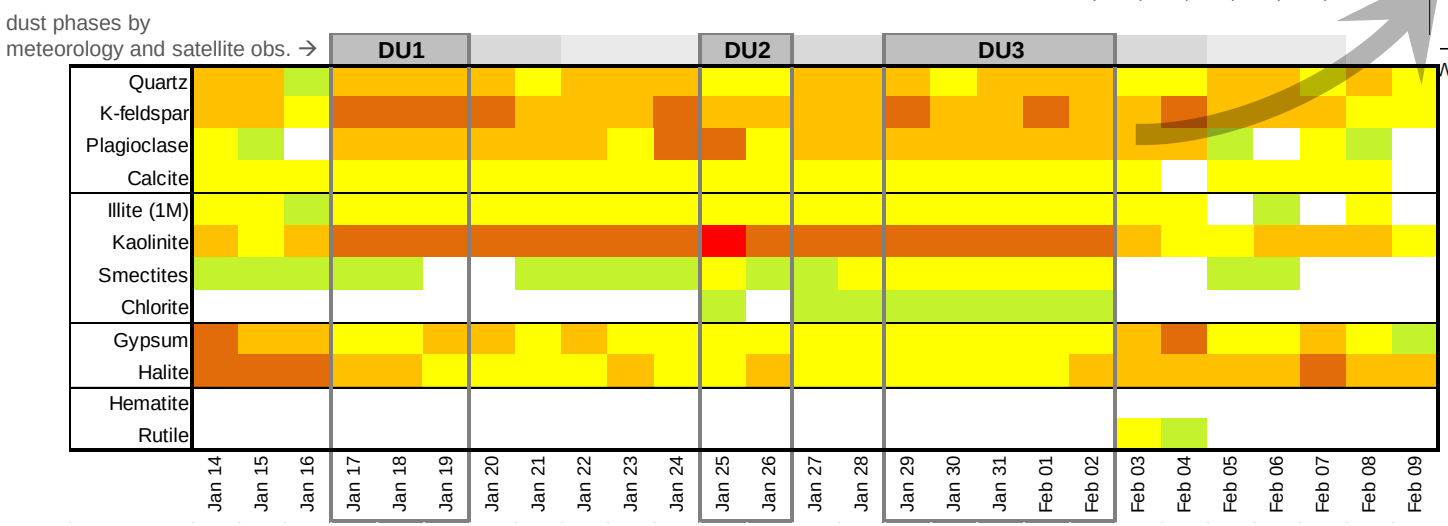

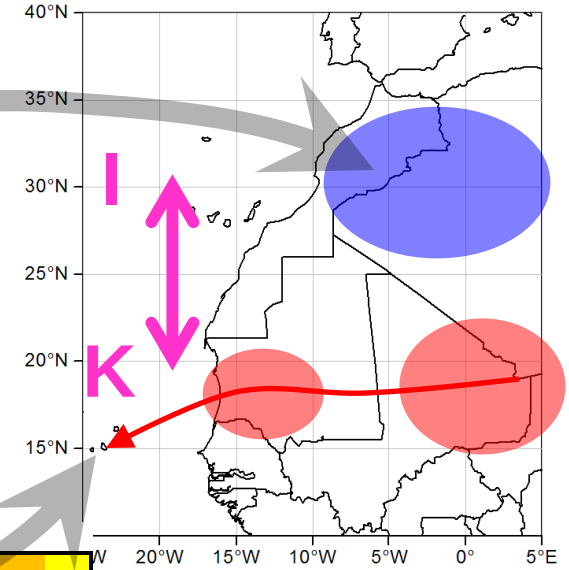

dominant
major
minor
traces
detected
not det.
not invest.

data from Kandler et al. 2009, doi: 10.1111/j.1600-0889.2008.00385.x and Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x

Change in mineralogical composition with particle size seen by chemical fingerprints

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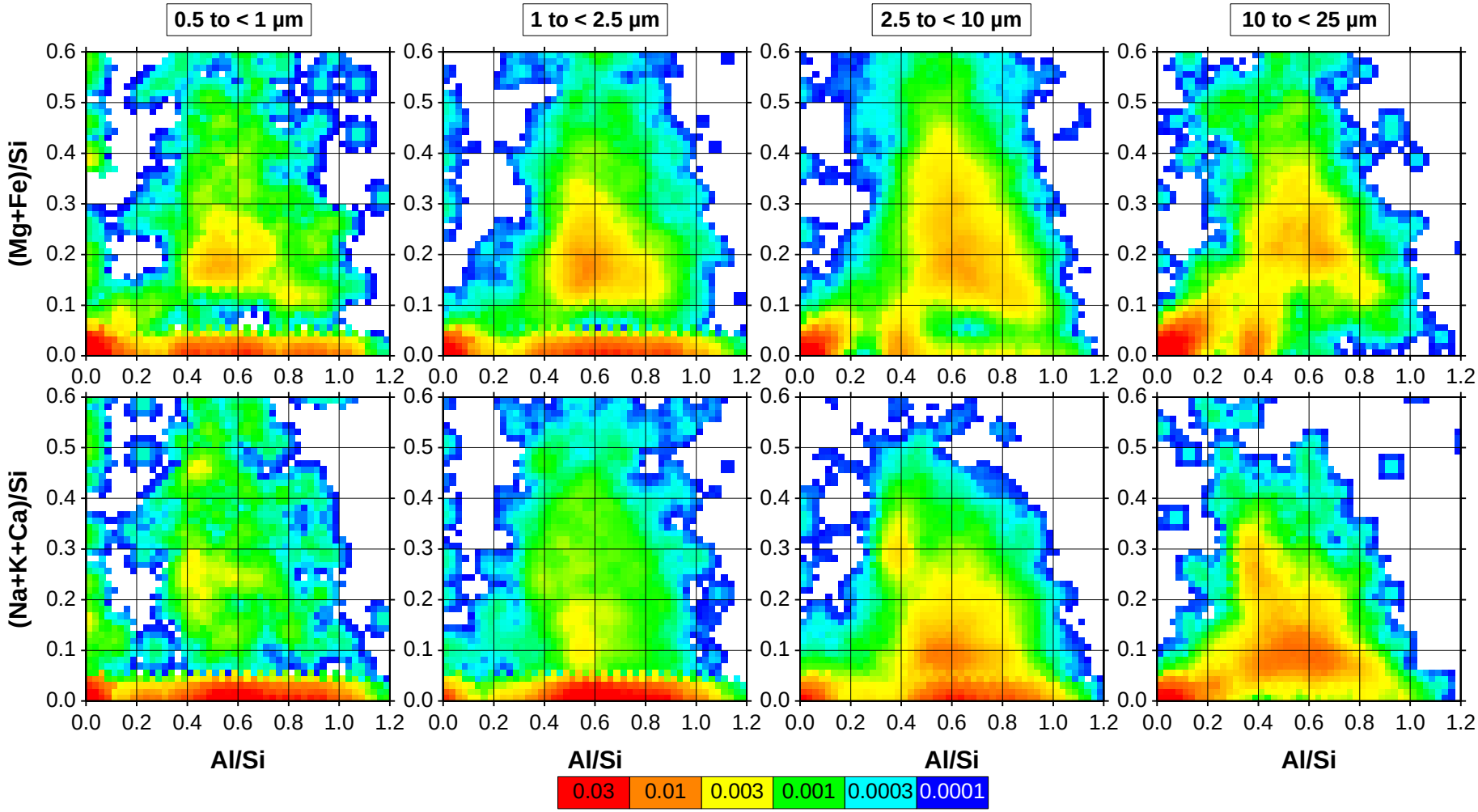

data from Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x

Change in mineralogical composition with particle size seen by chemical fingerprints

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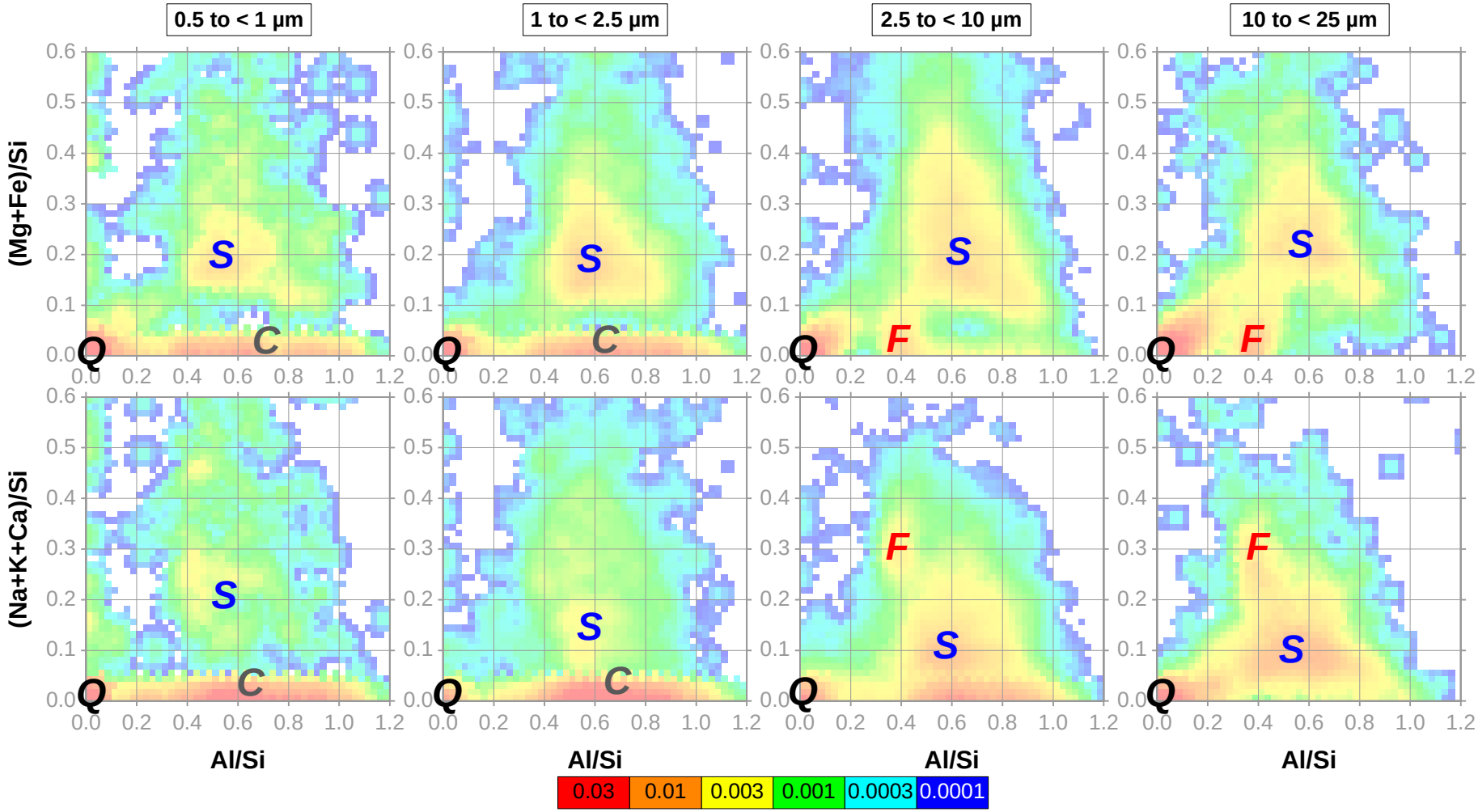

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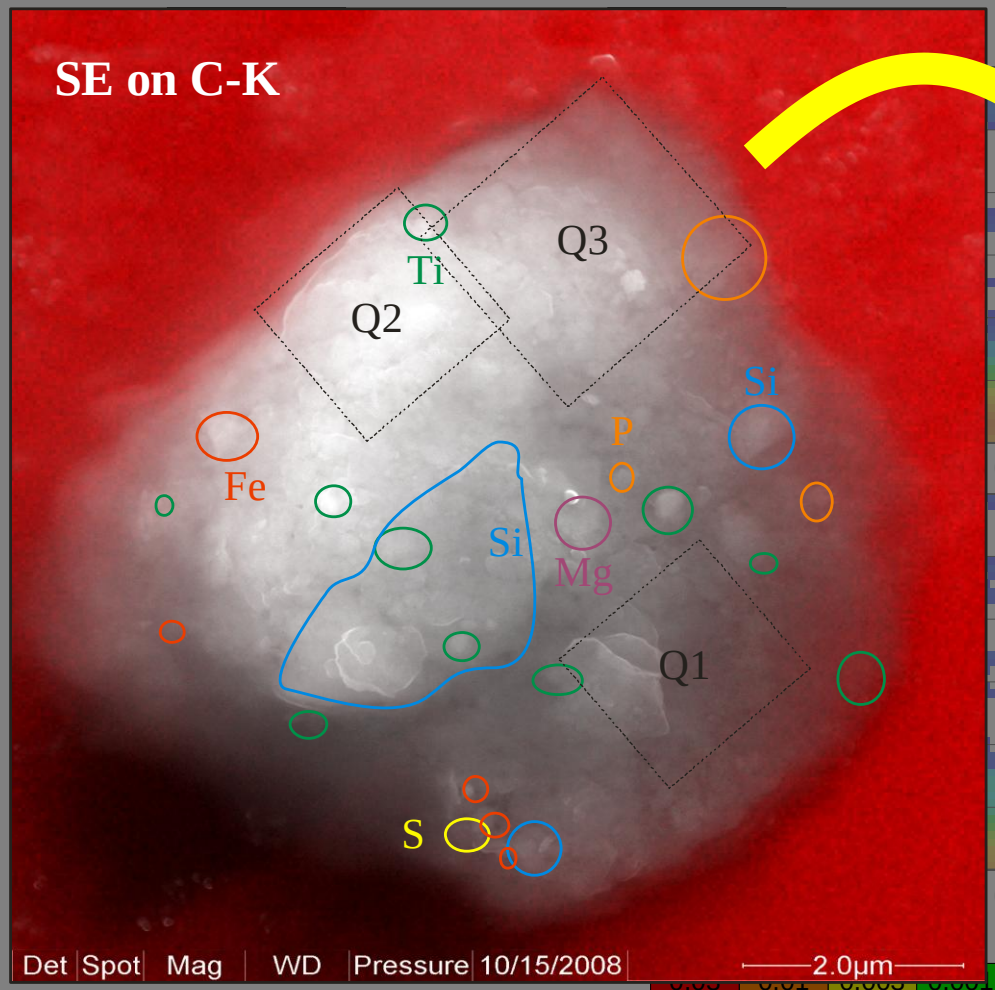
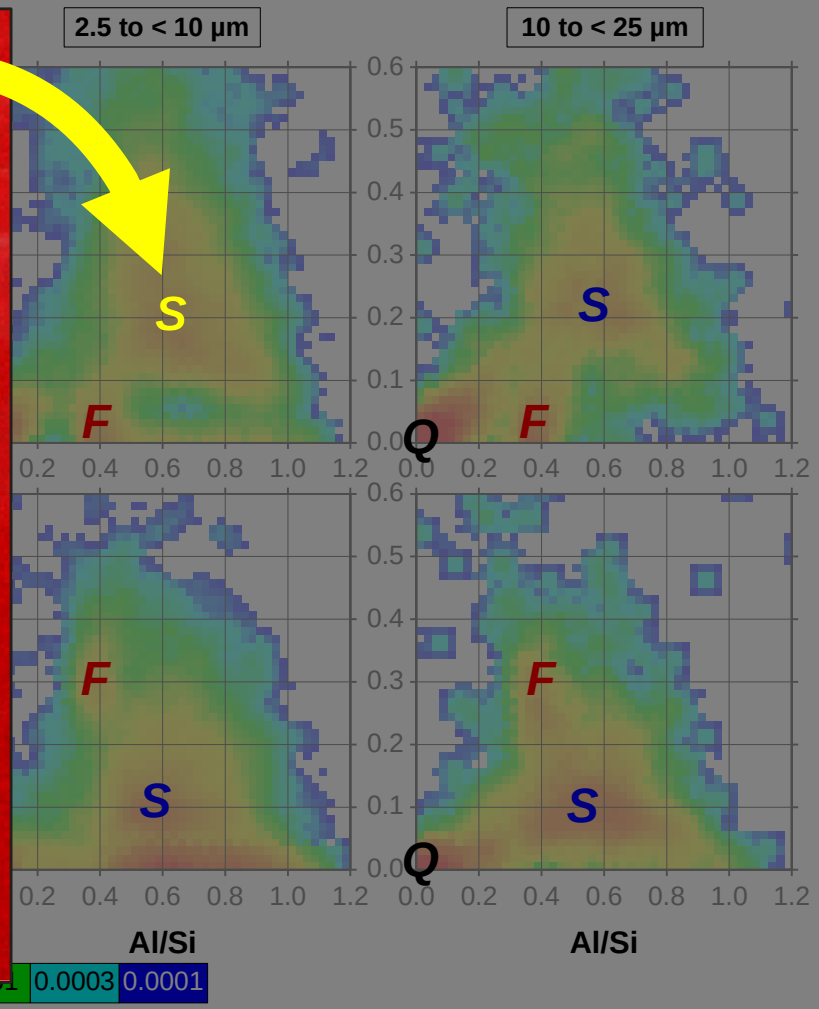
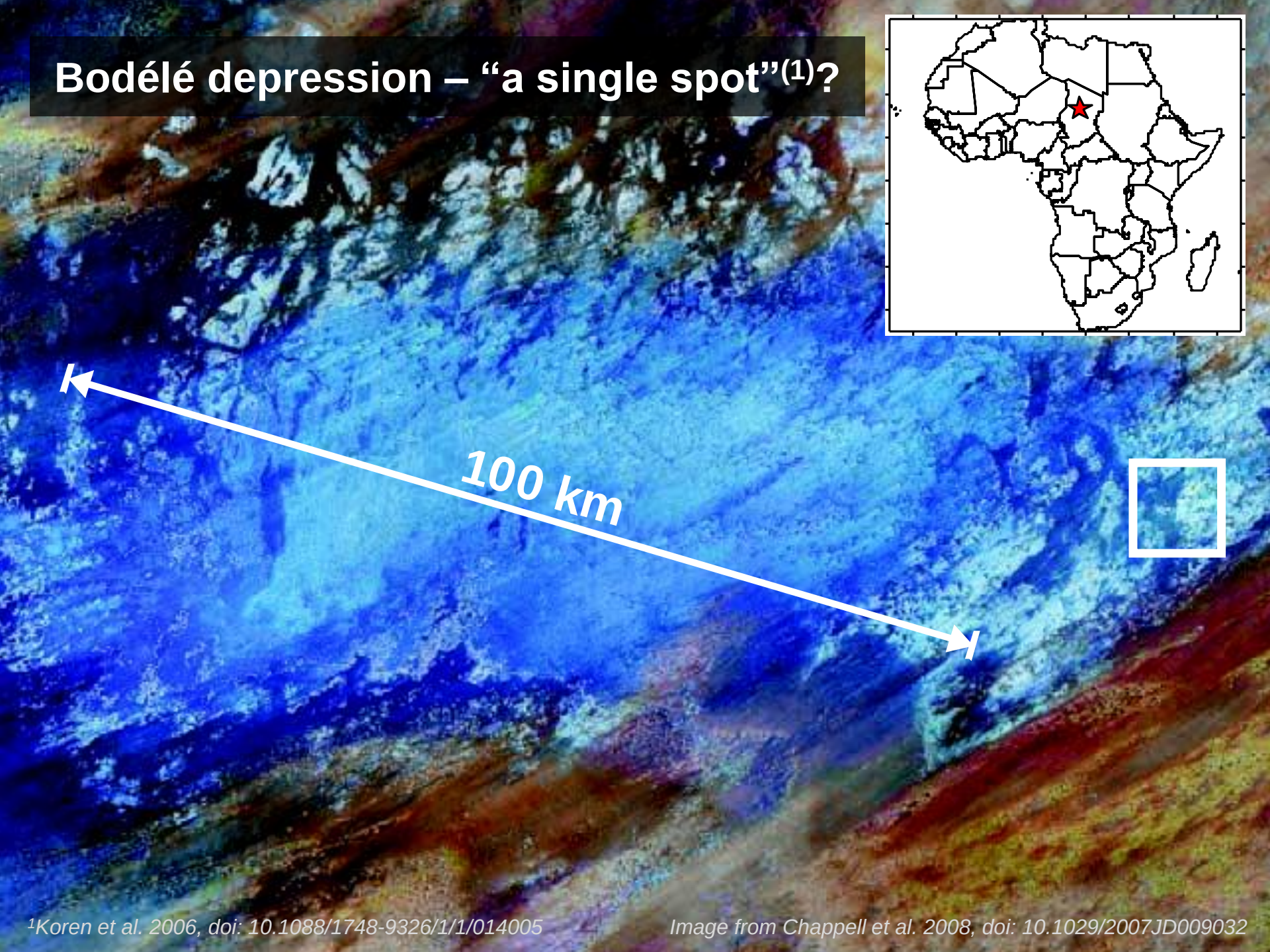




data from Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x

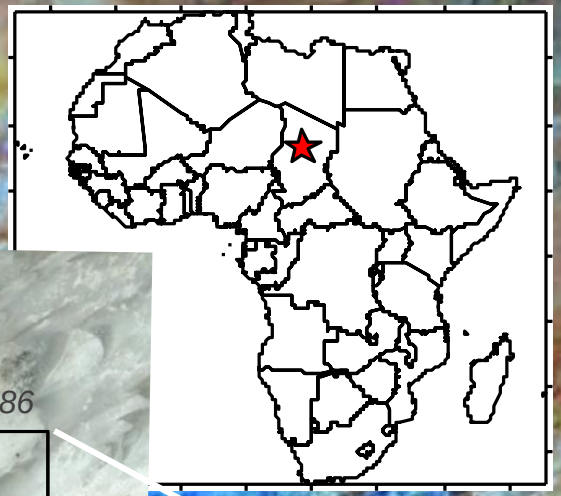
Bodélé depression – “a single spot”[1]?

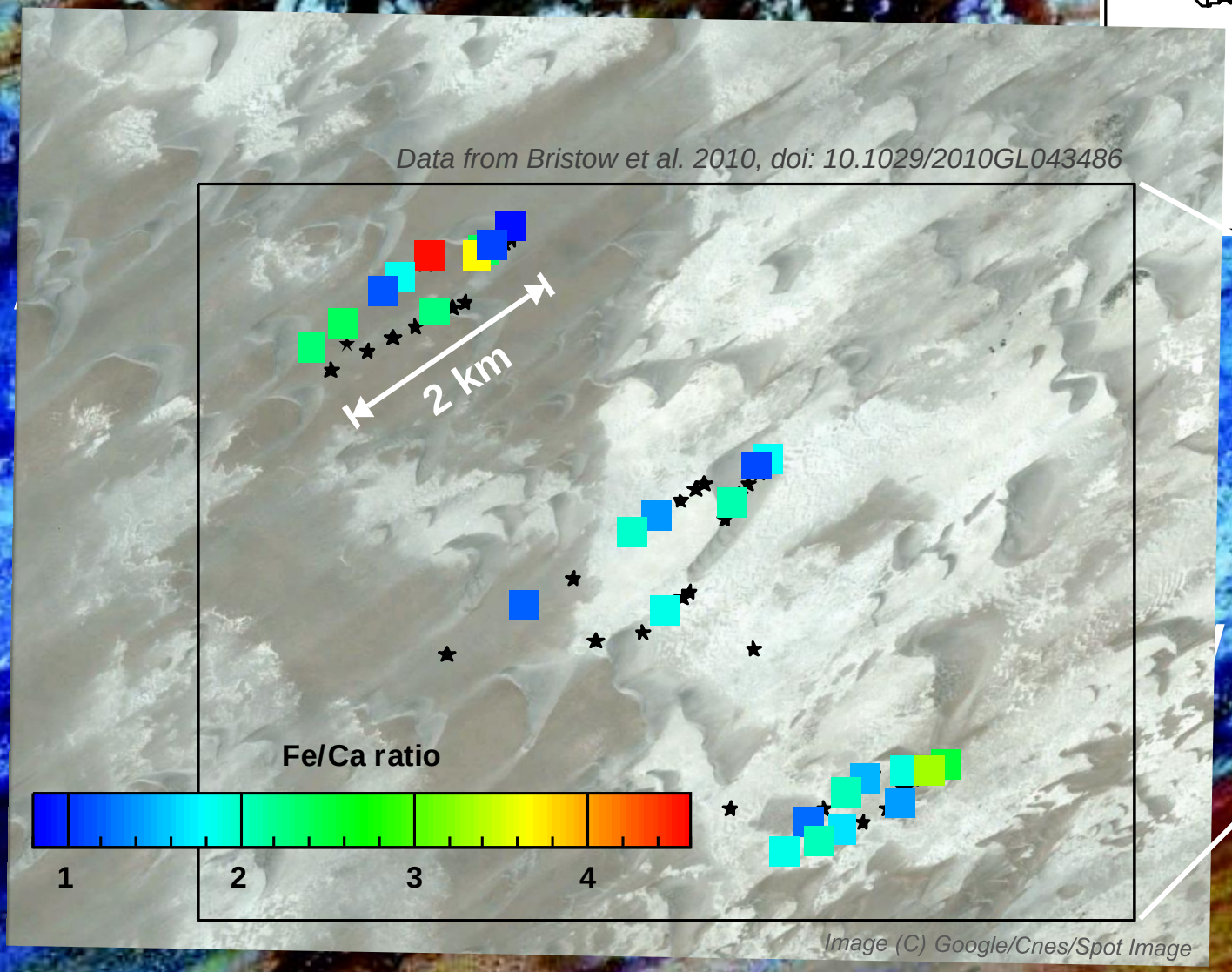


[1]Koren et al. 2006, doi: 10.1088/1748-9326/1/1/014005

Image from Chappell et al. 2008, doi: 10.1029/2007JD009032

Bodélé depression – “a single spot”[1]?





Data from Bristow et al. 2010, doi: 10.1029/2010GL043486

Image (C) Google/Cnes/Spot Image

[1]Koren et al. 2006, doi: 10.1088/1748-9326/1/1/014005

Image from Chappell et al. 2008, doi: 10.1029/2007JD009032

Variability across the Ocean – Fe/Ca as a tracer

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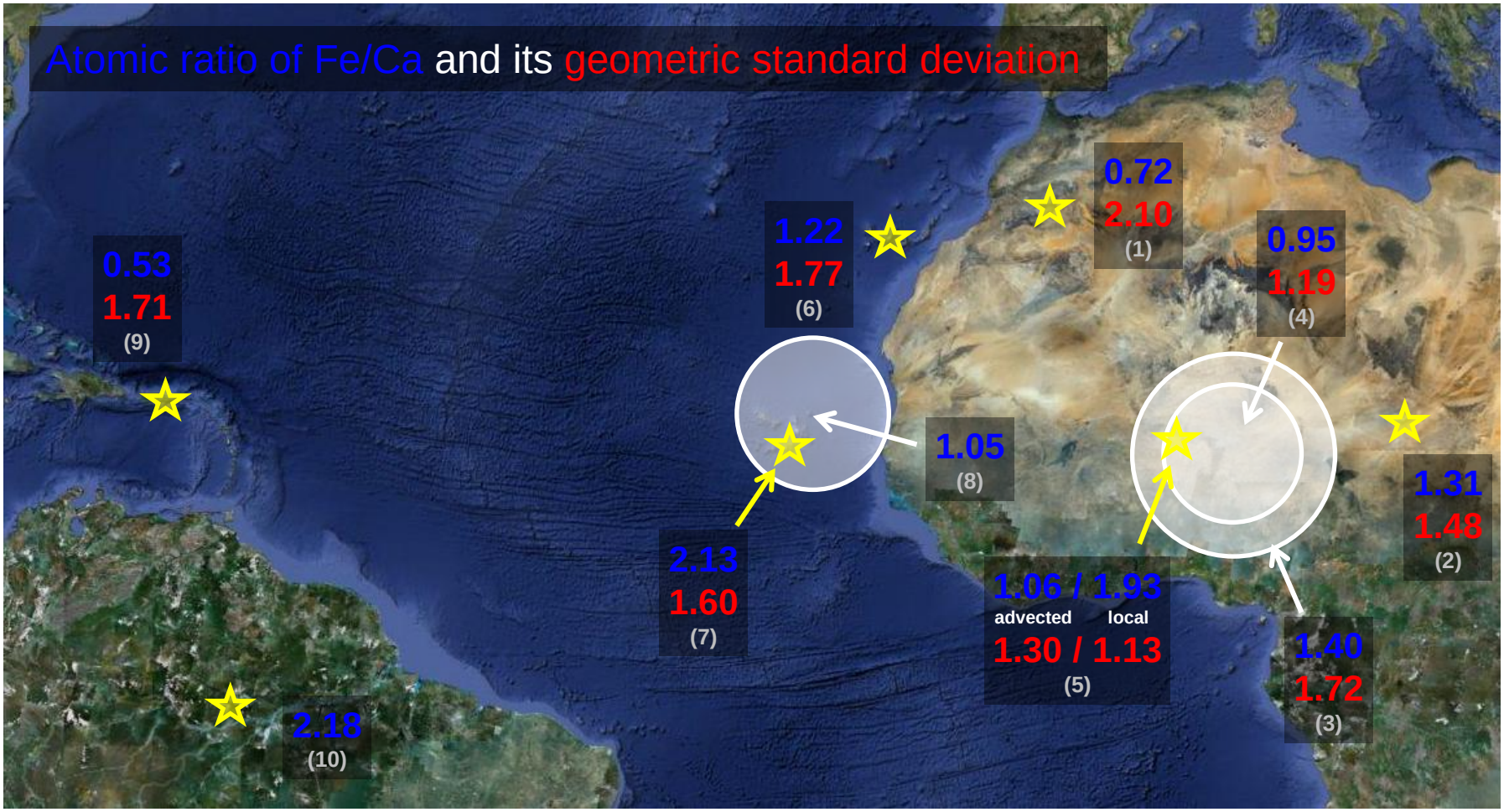

[1]Kandler et al. 2009, doi: 10.1111/j.1600-0889.2008.00385.x [2]Bristow et al. 2010, doi: 10.1029/2010GL043486 [3]Klaver et al. 2011, doi: 10.1002/qj.889
[4]DUST, Paris et al. 2010, 10.5194/acp-10-4273-2010 [5]Formenti et al. 2008, doi: 10.1029/2008JD009903
[6]Kandler et al. 2007, doi: 10.1016/j.atmosenv.2007.06.047 [7]Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x
[8]Formenti et al. 2003, doi: 10.1029/2002JD002648 [9]Reid et al. 2003, doi: 10.1029/2002JD002935 [10]Formenti et al. 2001, doi: 10.1029/2000JD900827

Variability across the Ocean – Fe/Ca as a tracer

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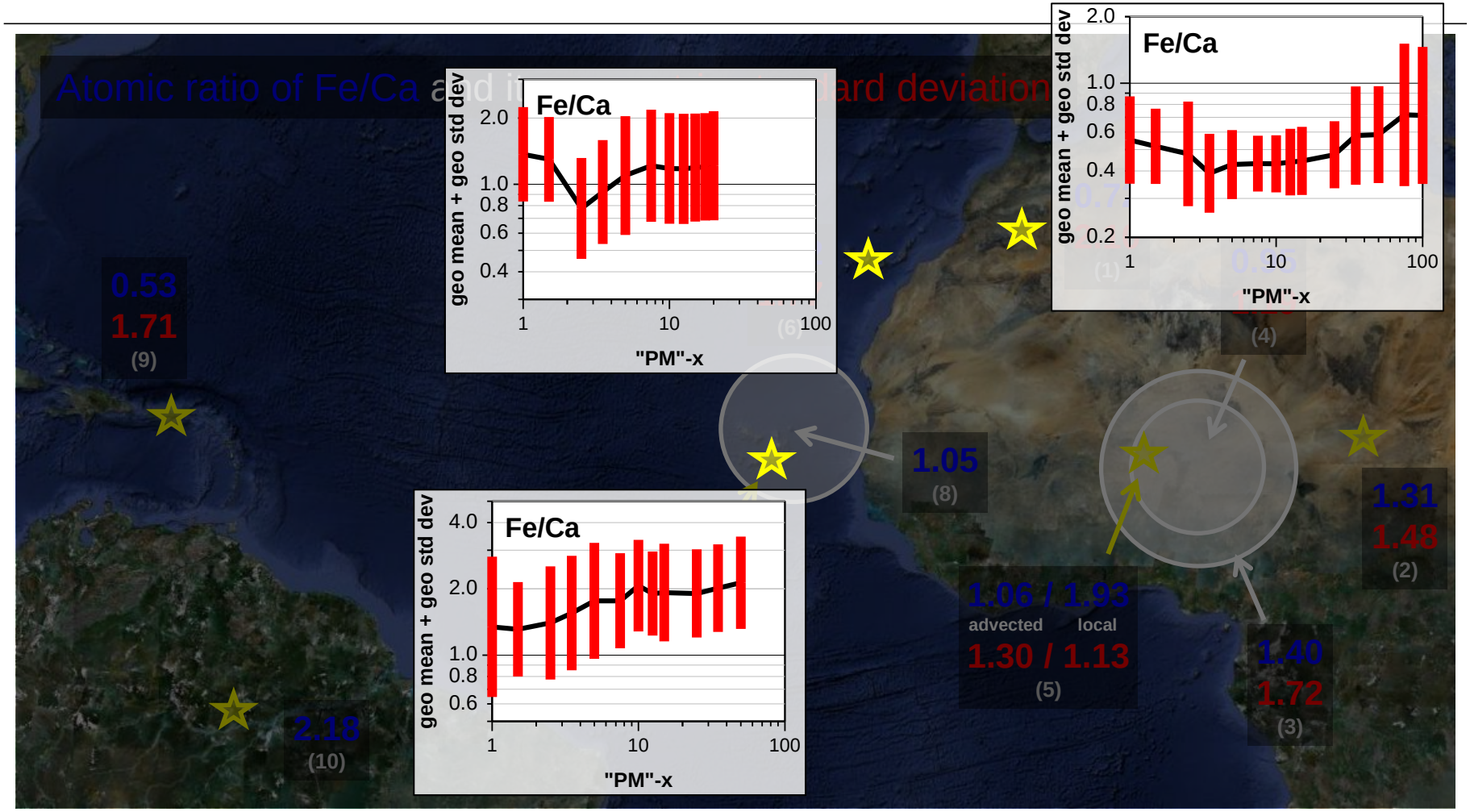

[1]Kandler et al. 2009, doi: 10.1111/j.1600-0889.2008.00385.x [2]Bristow et al. 2010, doi: 10.1029/2010GL043486 [3]Klaver et al. 2011, doi: 10.1002/qj.889
[4]DUST, Paris et al. 2010, 10.5194/acp-10-4273-2010 [5]Formenti et al. 2008, doi: 10.1029/2008JD009903
[6]Kandler et al. 2007, doi: 10.1016/j.atmosenv.2007.06.047 [7]Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x
[8]Formenti et al. 2003, doi: 10.1029/2002JD002648 [9]Reid et al. 2003, doi: 10.1029/2002JD002935 [10]Formenti et al. 2001, doi: 10.1029/2000JD900827

Transport stage – selective removal and admixture

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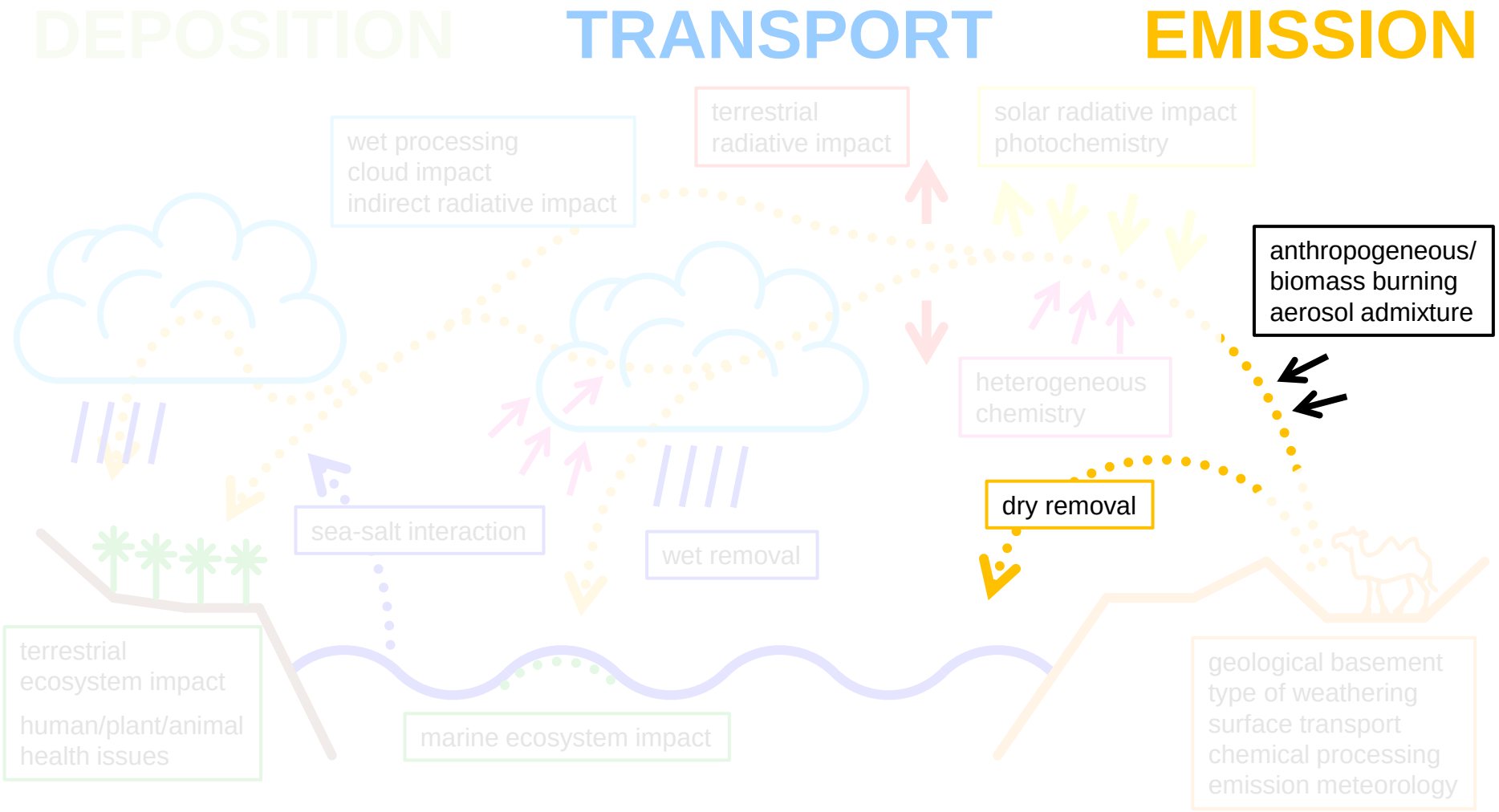

Transport stage – selective removal and admixture

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By sedimentation

- The largest particles > 50 µm are quickly removed
  → relative abundance of quartz and feldspars decreases, that of clay minerals increases (carbonate contents are usually not strongly impacted)
- Direct result: soil composition does not necessarily reflect generated dust composition, even close to source

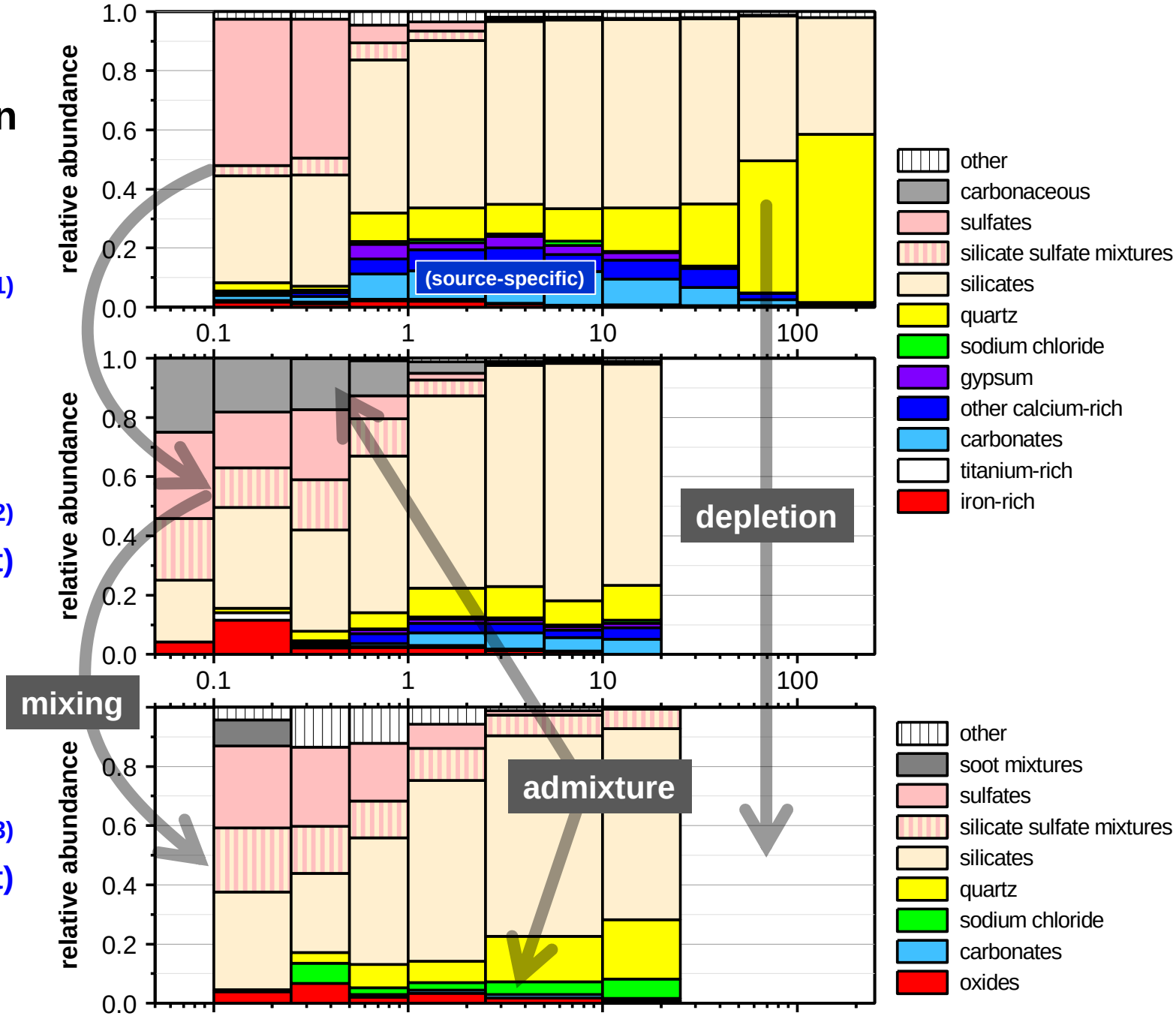
By admixing

- For example, sulfate and soot particles may be added do dust aerosol (or vice versa) and form an external mixture, which than can affect its radiative properties

By selective wet deposition

- Dust particles containing larger amounts of soluble material may be preferentially removed by rain-out / washout
- Dust particles more sensitive to chemical processing (i. e. carbonates to nitric acid) may quickly grow into large droplets under humid conditions and can be removed

Average Chemical composition at different locations



[1]Kandler et al. 2009, doi: 10.1111/j.1600-0889.2008.00385.x [2]Kandler et al. 2007, doi: 10.1016/j.atmosenv.2007.06.047 [3]Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x

Transport stage – processing and mixing

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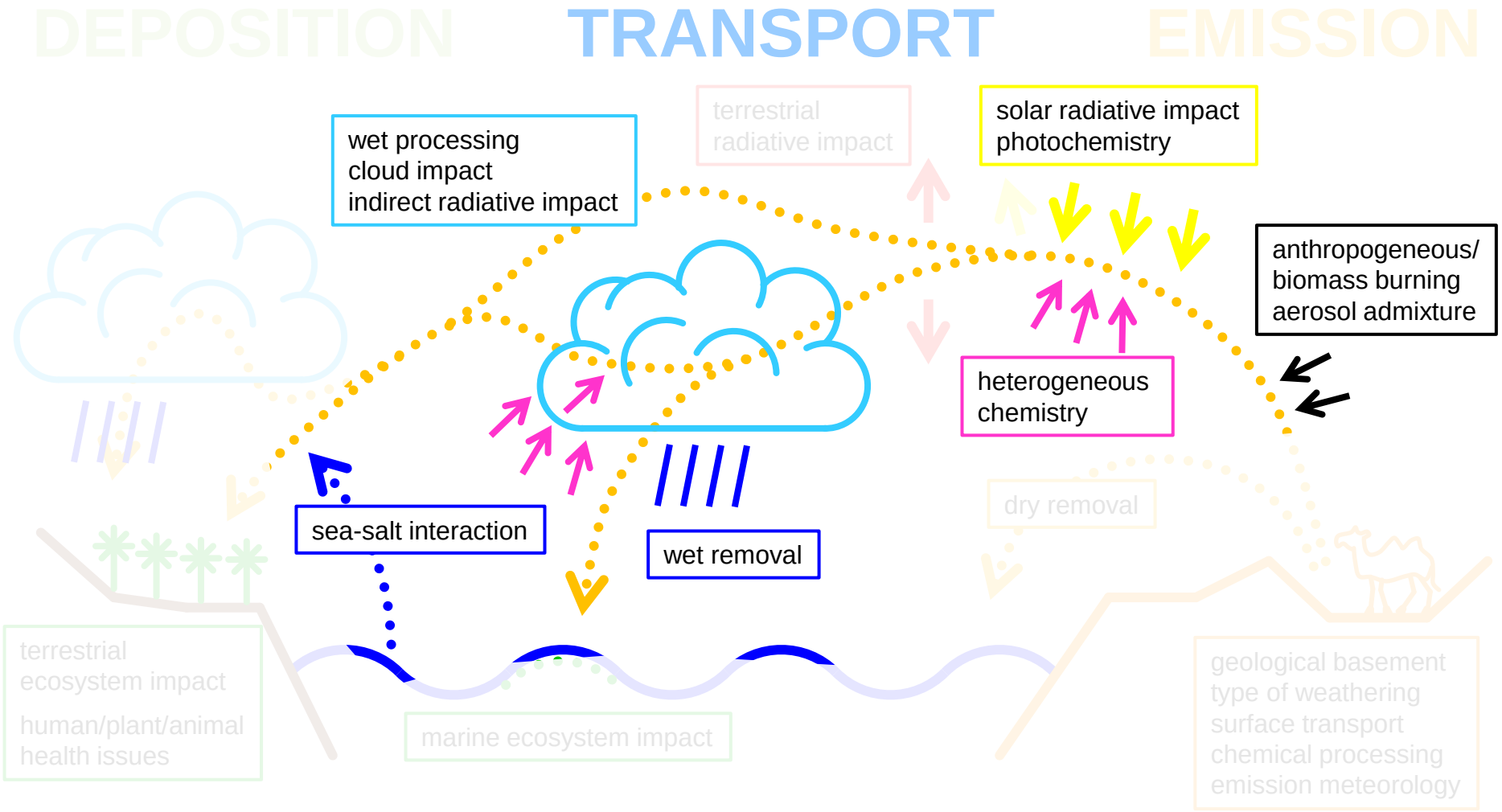

Transport stage – processing

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Processes affecting dust composition

- Uptake of non-dust species by mechanical mixing (sea-salt mixture not found at Cape Verde[1,2], but reported in America[3]; mixing seems most efficient for the transition size range 0.5 to 2 µm particle diameter)
- Condensation of secondary species (e. g., organics) on the dust surface[4]
- Reaction of dust with (acidic) species, depending on dust composition (e. g., calcic vs. silicic)[5]
- SO_2 can be oxidized in dry state on dust surface in presence of ozone[6,7], but effect saturates[8,9]
- Many pathways in aqueous state from SO_2 to sulfate, efficiency depending on conditions (like gaseous concentrations, cloud water pH, photochemistry...)[5,10]

Resulting changes in dust properties

- Increase in sedimentation removal by increase in particle size[11]
- Deposition of hygroscopic matter on dust particles increases CCN ability[12]
- Sulfuric acid/sulfate and some organic matter decrease IN ability, but strength of effect depends on mineralogy[13,14]
- Changes in solubility of nutrients

[1]Dall'Osto et al. 2010, doi: 10.1016/j.atmosenv.2010.05.030 [2]Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x [3]Worobiec et al. 2007, doi: 10.1016/j.atmosenv.2007.07.056
[4]Deboudt et al. 2010, doi: 10.1029/2010JD013921 [5]Cwiertny et al. 2008, doi: 10.1146/annurev.physchem.59.032607.093630 [6]Usher et al. 2002, doi: 10.1029/2002JD002051
[7]Ullerstam et al. 2002, 10.1039/b203529b [8]Goodman et al 2001, doi: 10.1021/jp004423z [9]Manktelow et al. 2010, doi: 10.5194/acp-10-365-2010 [10]Seinfeld & Pandis, Wiley 2006
[11]Zhang 2008, doi: 10.1111/j.1600-0889.2008.00358.x [12]Gibson et al. 2007, doi: 10.1080/02786820701557222 [13]Cziczo et al. 2009, doi: 10.1088/1748-9326/4/4/044013
[14]Eastwood et al. 2009, doi: 10.1029/2008GL035997

Dependence of the chemical reactivity on particle material over Niger

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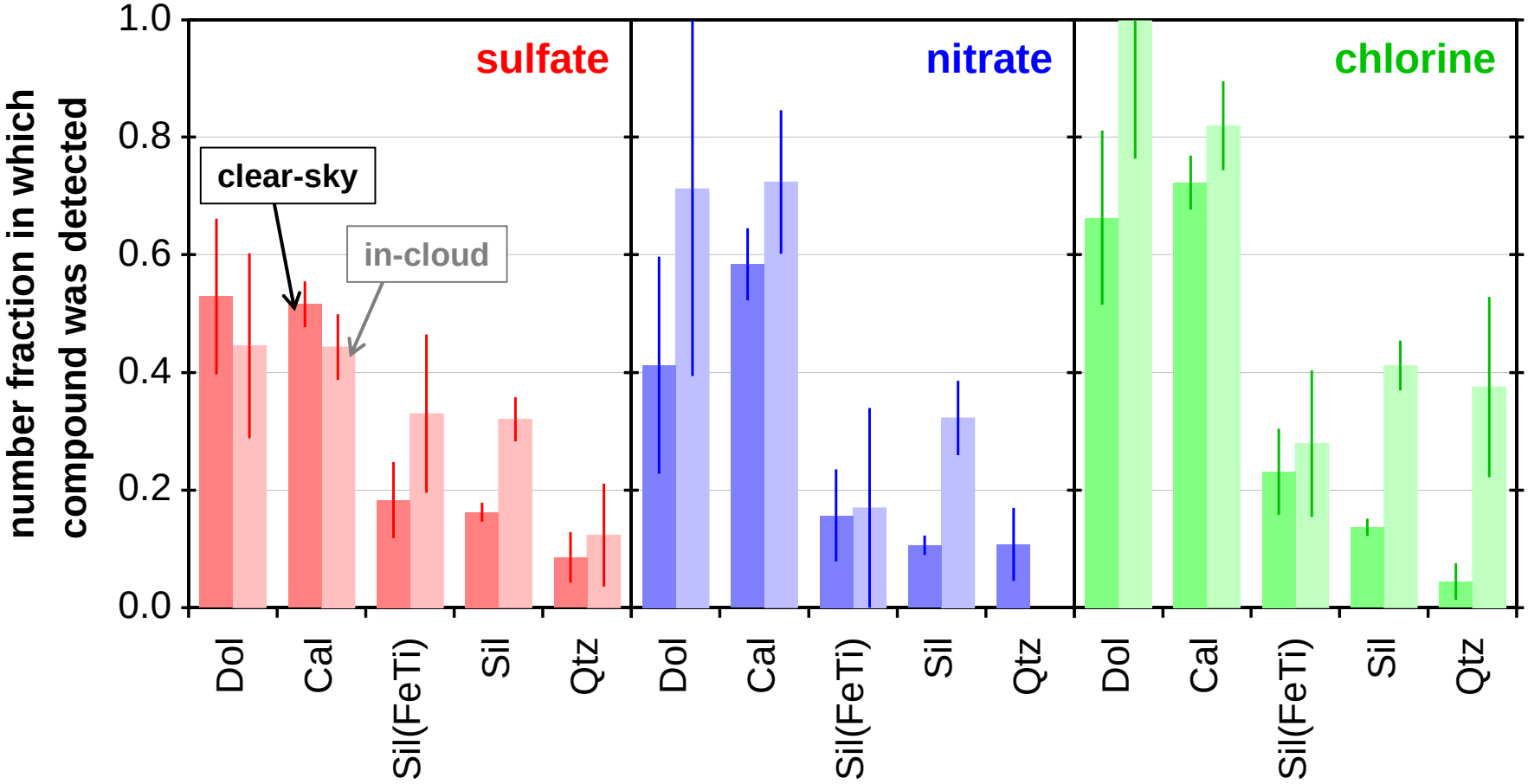

data from Matsuki et al. (2010), 10.5194/acp-10-1057-2010

Dependence of the chemical reactivity on particle material over Niger

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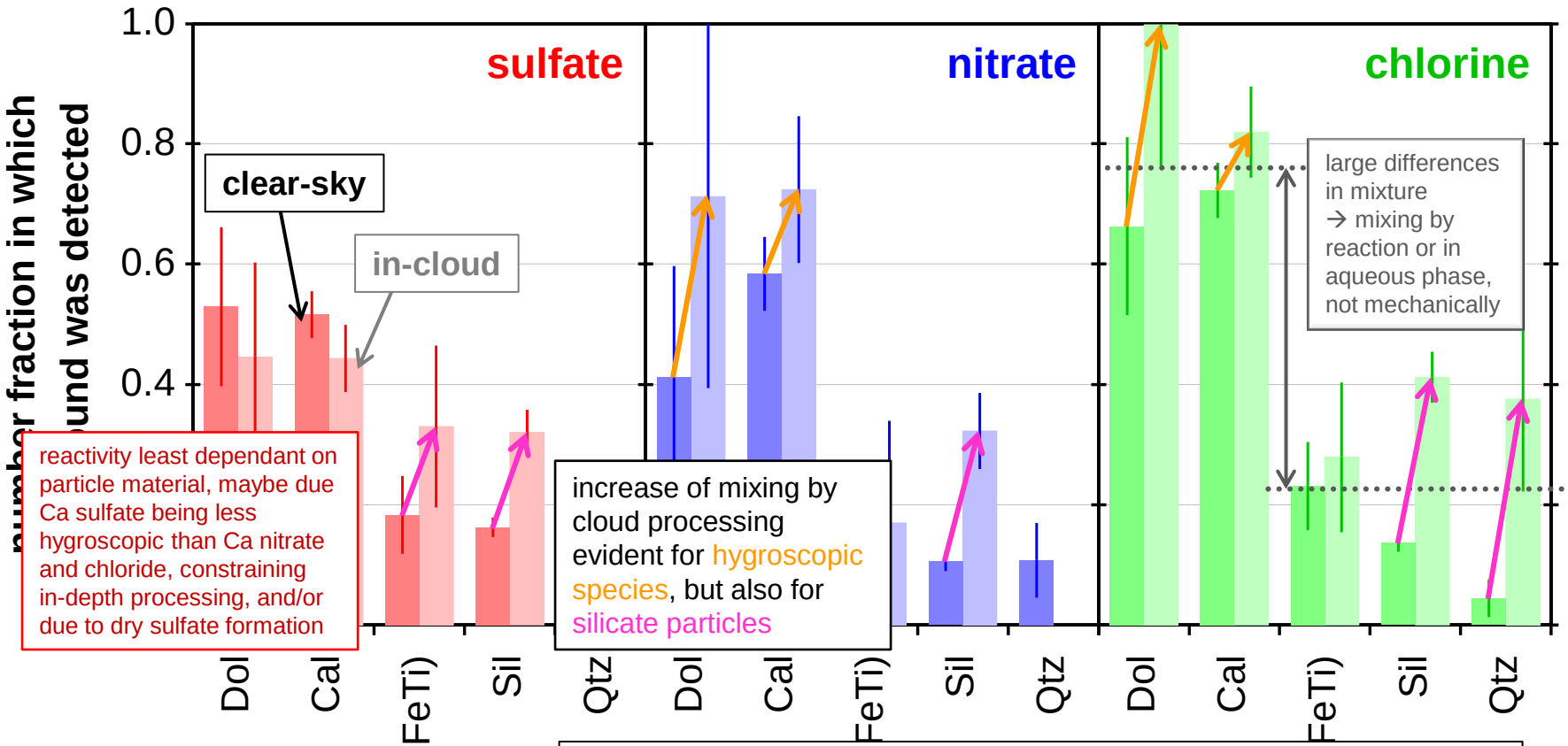

reactivity least dependant on particle material, maybe due Ca sulfate being less hygroscopic than Ca nitrate and chloride, constraining in-depth processing, and/or due to dry sulfate formation

increase of mixing by cloud processing evident for hygroscopic species, but also for silicate particles

in general, also for clear-sky conditions reactivity increases with relative humidity (not shown)

data from Matsuki et al. (2010), 10.5194/acp-10-1057-2010

Mixing of dust with sulfate at Praia, Cape Verde

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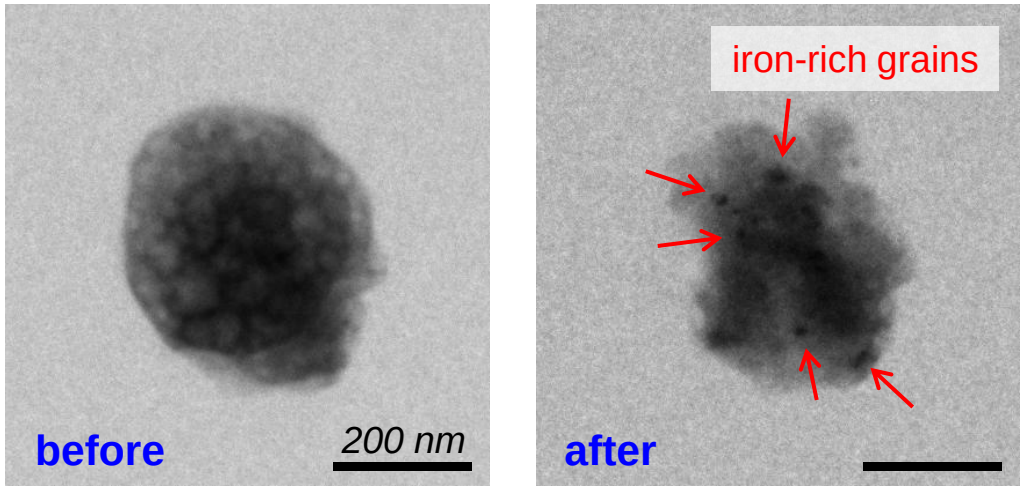
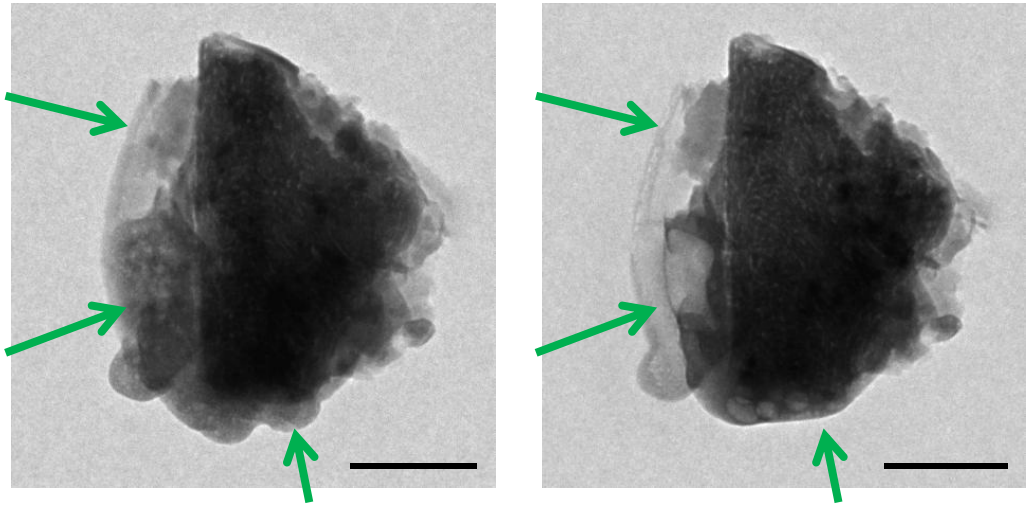
silicate + sulfate



Particles are shown before and after extensive electron bombardment

silicate + sulfate + ?



loss of volatile material

Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x

Mixing of dust and organics observed in Senegal

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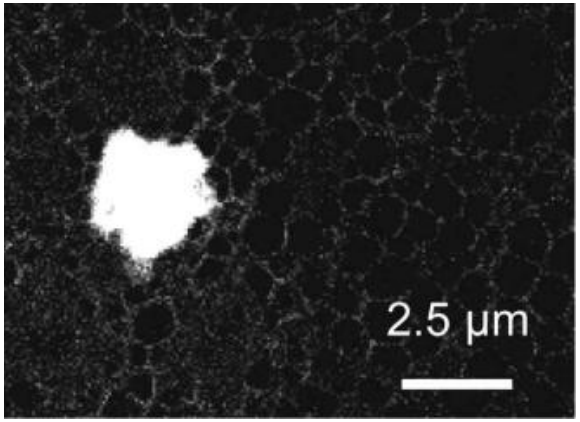
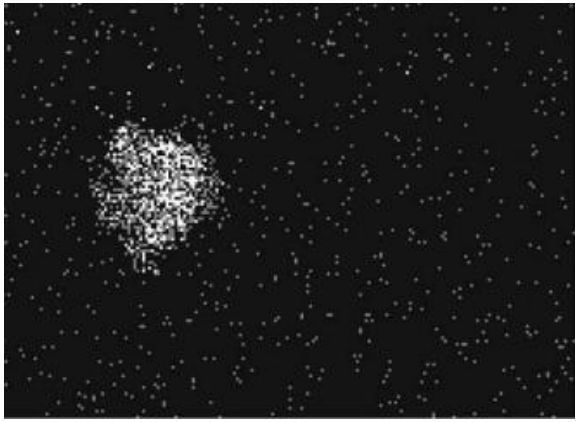
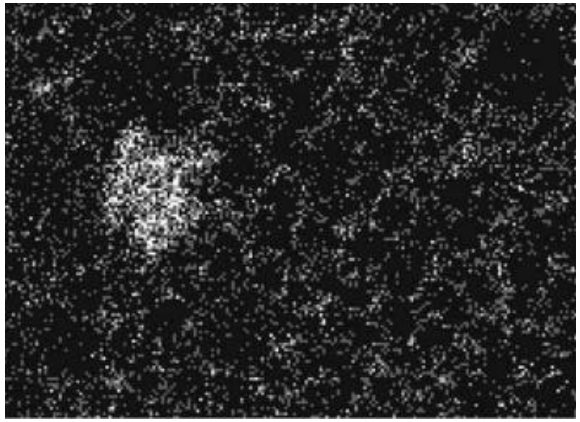
SE image
particle and mesh support



Si map
particle only



C map
particle (and support) visible



- Internal mixing of dust and carbonaceous matter is observed in a region with coexisting dust and biomass burning aerosol
- Relative abundance of internally mixed particles versus pure ones is highly variable (5 to 50 % in this case study)
- Carbonaceous matter is distributed homogeneously around the particle
  → most probably organic coating
- Is coating reversible or not (high adsorption efficiency of clays for organics)?

Deboudt et al. 2010, doi: 10.1029/2010JD013921

Transport/Deposition stage – particular importance of iron and phosphorus

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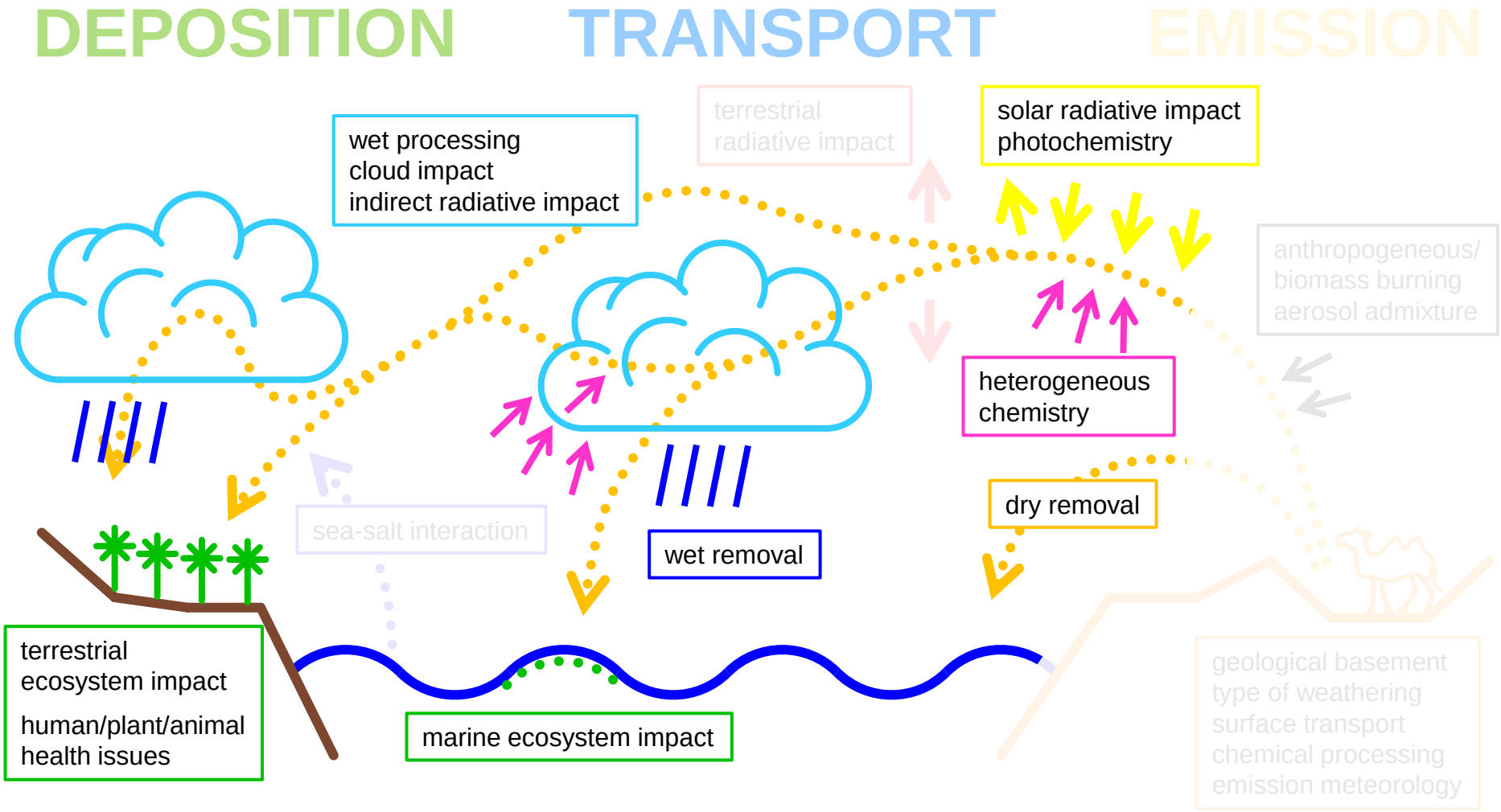

Iron and phosphorus as nutrients

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- As of today, **Fe** and **P** seem to be the most **important nutrients**, but knowledge about dust **Ca, Mg, K** supply is sparse
- For soluble Fe fraction (i. e. bio-availability), a range between 0.01 and 80 % is reported[1,2]
- Fe solubility depends on source composition, atmospheric processing, already existing Fe concentrations, dust concentration, biological influences[2,3]
- Fe solubility increases with decreasing pH especially for low pH values[4]
- Fe solubility was found to increase with atmospheric processing intensity[5]
- Most soluble Fe comes from clay minerals, not from Fe oxides[6]
- Fe-rich nanoparticles can form after acidic solution of soil[7], which may be directly or at least at higher rates bio-available[2]
- High aerosol Fe content in general does not mean similarly high bio-available Fe[5,6]
- Total P content in Saharan dust between 0.04 and 1.7% (mostly below 1%)[8,9,10]
- Acidification of aerosol (e. g. anthropogenic gas emissions) makes P more bio-available[11]
- High relative humidity may be counterproductive in increasing P-availability due to more neutral pH[11]
- P is assumed to be present as apatite, but also other phases are very probable

[1]Mahowald et al. 2005, doi: 10.1029/2004GB002402 [2]Baker et al. 2010, doi: 10.1016/j.marchem.2008.09.003 [3]Shi et al. 2011, doi: 10.1029/2010GB003837
[4]Cwiertny et al 2008, doi: 10.1029/2007JD009332 [5]Chen et al. 2004, doi: 10.1029/2003JD003958 [6]Journet et al. 2008, doi: 10.1029/2007GL031589
[7]Shi et al. 2009, doi: 10.1021/es901294g [8]Guerzoni et al. 2005, doi: 10.1007/b107149 [9]Guieu et al. 2002, doi: 10.1029/2001JD000582
[10]Singer et al. 2003, doi: 10.1006/jare.2002.1023 [11]Nenes et al 2011, doi: 10.5194/acp-11-6265-2011

Phosphorus in Saharan dust

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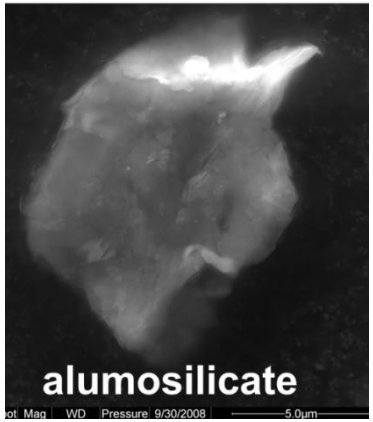
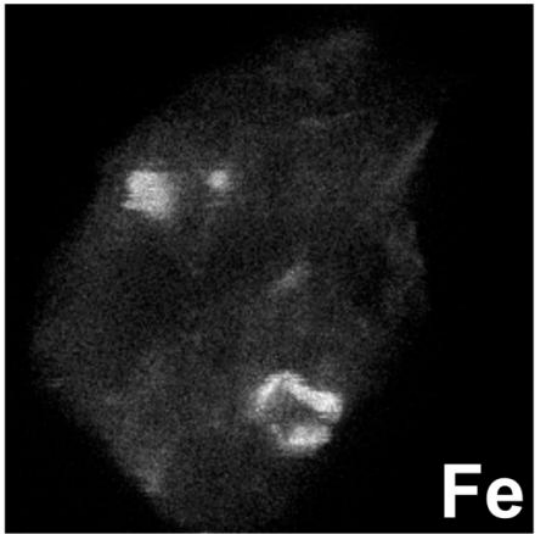
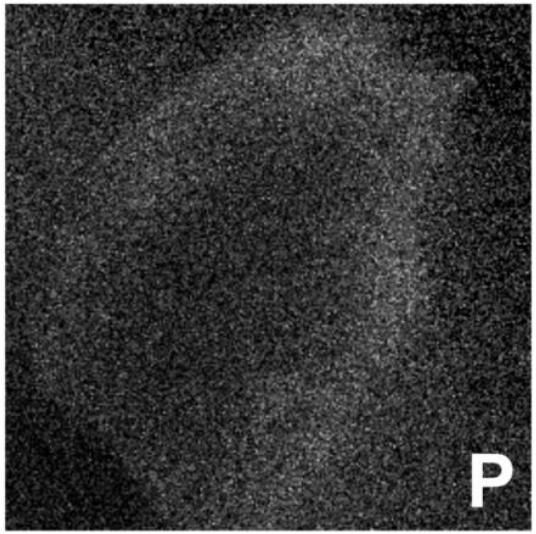
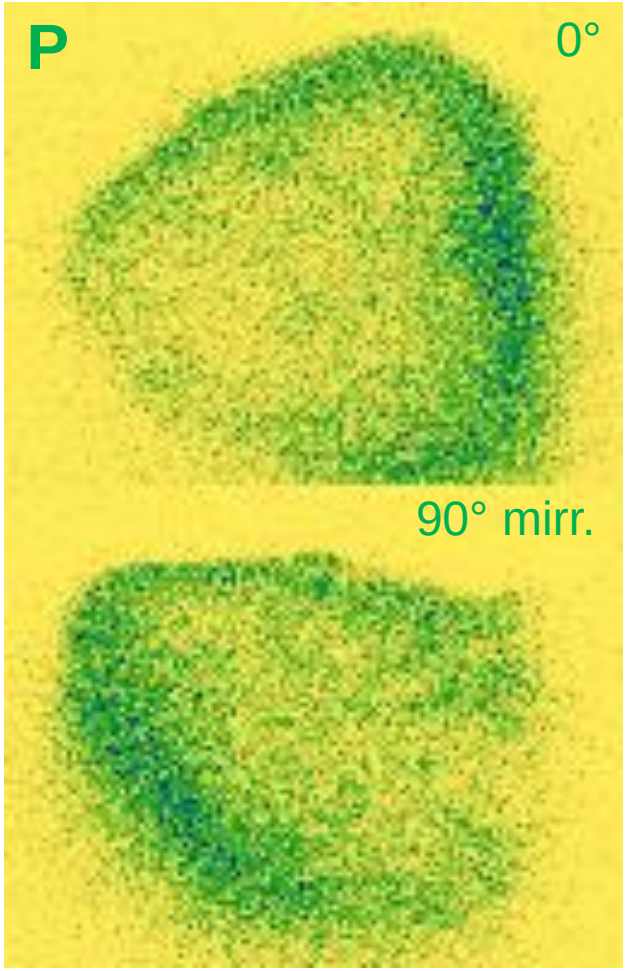
Position of P on single dust particles









in part from Scheuvens et al. 2011, doi: 10.1111/j.1600-0889.2011.00554.x

Deposition stage – variability and future needs

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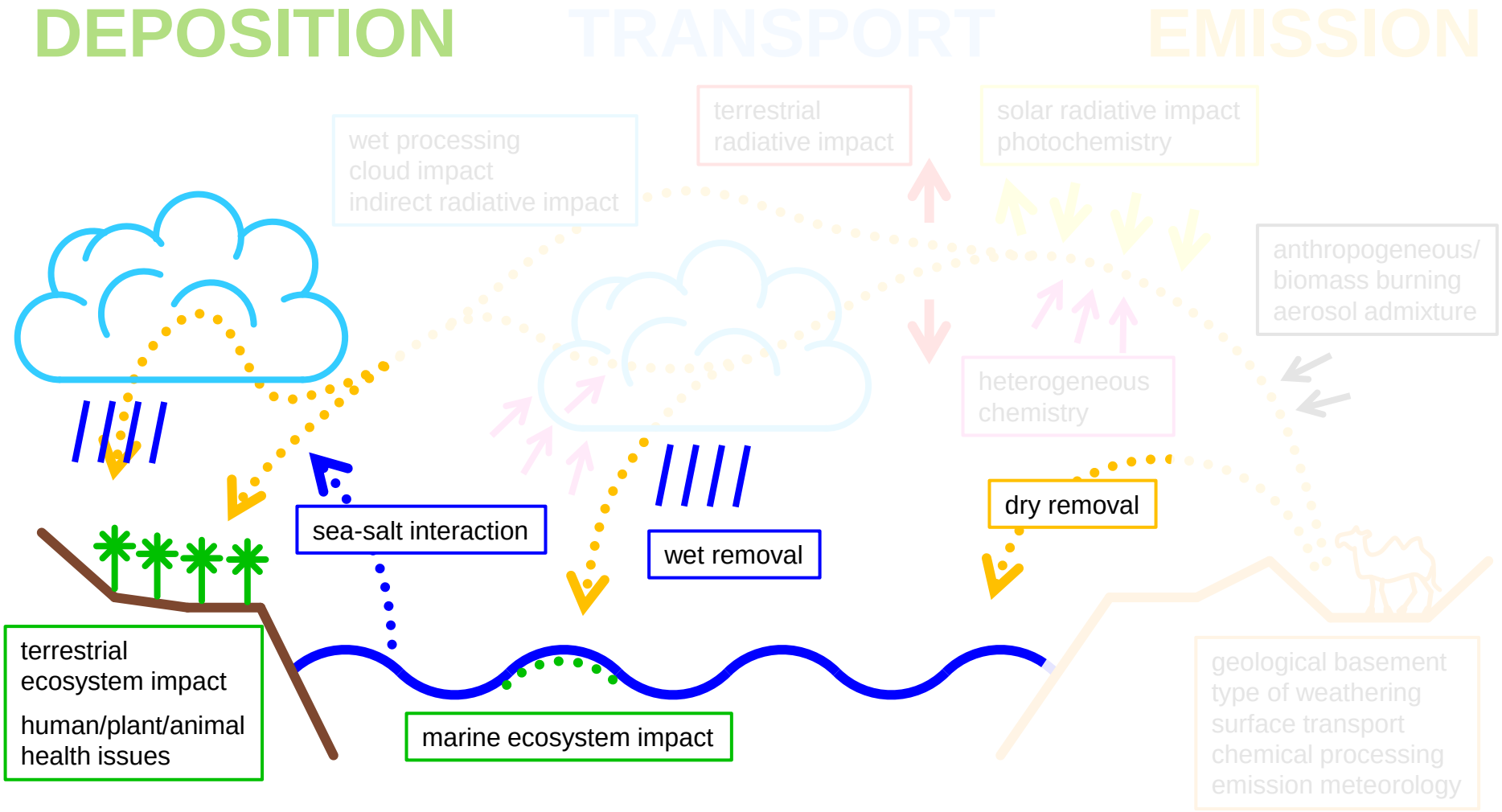

Deposition stage – phenomenology and dust composition

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Type of deposition

- In Florida, most dust is deposited by wet deposition[1]
- At Bermuda, most dust is deposited by dry deposition[2]
- Mixing with sea-salt could increase particle size and promote (dry) deposition[2,3,4,5]

Variability

- High temporal variation in mass: 30 to 90% of annual dust deposition occurs on 5% of the days, particularly at the edge of the Saharan dust plume[6,7]
- Low temporal variation in composition: two years of measurement at Florida and Barbados[8] and low spatial variation in composition over Florida[1]
- Temporal variability (Fe/Ca) at Puerto Rico still in the same range as over the Ocean[9,10]

General

- Dust arrives internally mixed with different species in America[5,11]
- Information on speciation of major nutrients and their availability is sparse[12]

[1]Prospero et al 2010, doi: 10.1029/2009JD012773 [2]Tian et al. 2008, doi: 10.1029/2007GC001868 [3]Zhang et al. 2006, doi: 10.1016/j.atmosenv.2005.10.037
[4]Deboudt et al. 2010, doi: 10.1029/2010JD013921 [5]Worobiec et al. 2007, doi: 10.1016/j.atmosenv.2007.07.056
[6]Mahowald et al. 2009, doi: 10.1146/annurev.marine.010908.163727 [7]Bonnet et al. 2006, doi: 10.1029/2005JC003213
[8]Trapp et al. 2008, doi: 10.1016/j.marchem.2008.10.004 [9]Reid et al. 2003, doi: 10.1029/2002JD002935
[10]Kandler et al. 2011, doi: 10.1111/j.1600-0889.2011.00550.x [11]Krejci et al. 2005, doi: 10.5194/acp-5-3331-2005 [12]Okin et al. 2011, doi: 10.1029/2010GB003858

Composition of aerosol deposited in the northern Amazonian basin

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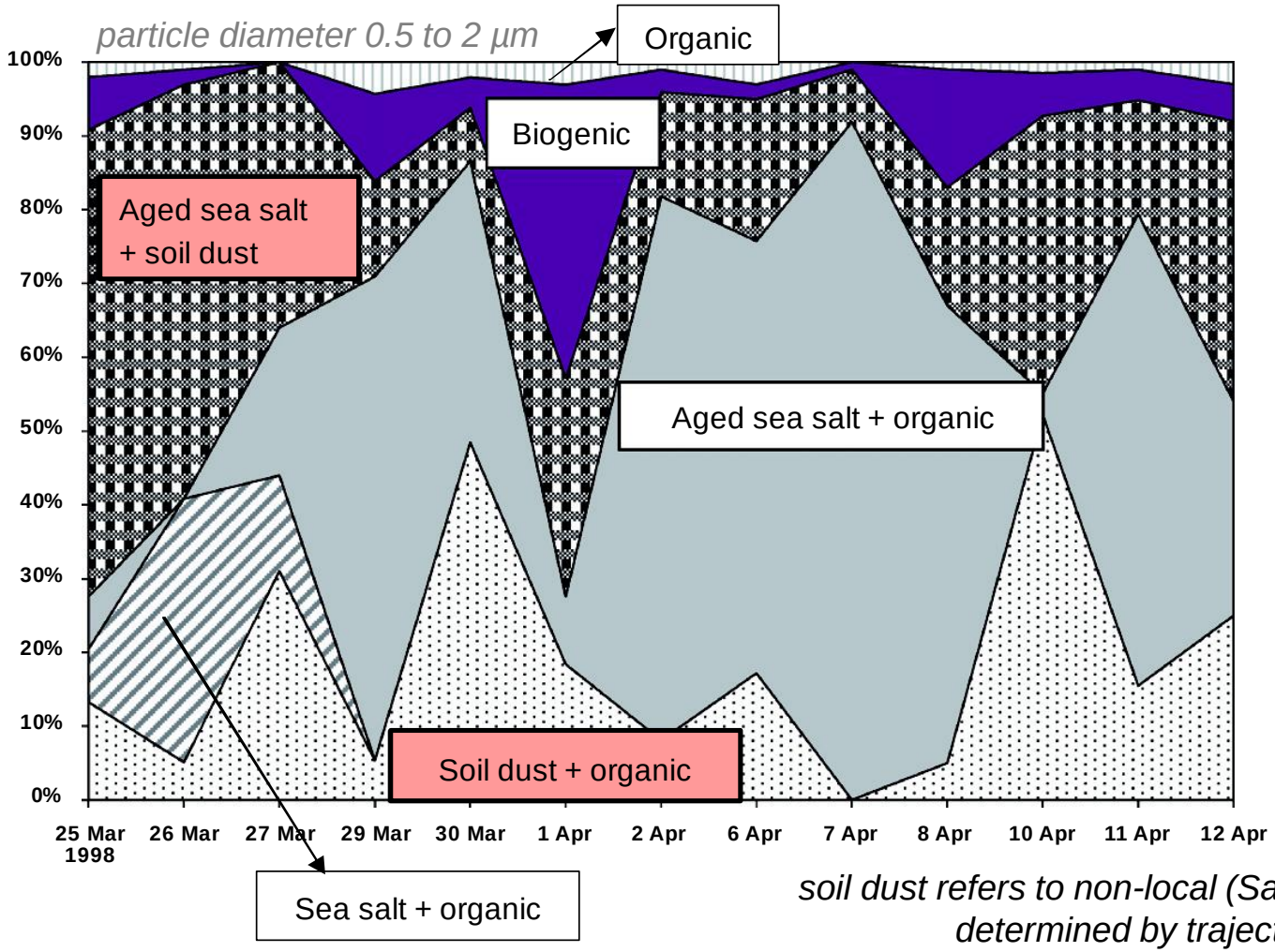

soil dust refers to non-local (Saharan) dust, determined by trajectory analysis

Worobiec et al. 2007, doi: 10.1016/j.atmosenv.2007.07.056

What is missing?

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General effects

- *Emission:* We have seen considerable amounts of sulfate already on dust in Africa – what is the degree of processing at the soil surface, and how much is it processed during transport?
- *Emission/Transport:* Regarding the Fe solubility and bio-availability, we need to know more on their dependence on source mineralogy, on in-soil and in-air processing (which gaseous or particular species yield what effect?), and how these impact on ecosystems with shorter or longer retention time
- *Emission/Transport:* Similar questions arise for phosphorus availability, but the level of knowledge is even lower than for iron
- *Transport:* For cloud impact and also the dust processing, we need to know more about the particle mixing state – preferrably spatially (3D) and particle-size-resolved
- *Transport/Deposition:* We know that dust has an non-linear impact on cloud droplet and ice nucleation and, thus, precipitation, but which are the dominating effects? – Possibly by a combination of an intensive field campaign and subsequent quantification (monitoring)
- *Transport/Deposition:* Besides Fe and P, also Ca, Mg and K from African dust are termed as potential nutrient for terrestrial ecosystems – what is their impact in relation to other sources? How changes their bioavailability by processing dependent of different atmospheric acids?
- *Transport/Deposition:* We know that organic coatings exist on dust – do they derive from biomass burning (only), from marine processes, can they be acquired just before deposition? What do they do to cloud impact (CCN, IN properties), and can organic acids promote bioavailability in time?
- *Deposition:* Does internal mixing increase deposition flux? Does particle shape have an impact?

What is missing? (continued)

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Spatial and temporal variation

- Dust sources have small-scale compositional variation and are not time-invariant
  - → Is it feasible to create a adequately-resolved "cadaster"? What can we generalize?
  - → What is the influence of this variation on the receptors (clouds, ecosystems)?
- Several intensive field experiments with different foci yielded information on dust composition, but the longest ones lasted one season
  - → How should they be rated, given a considerable variability on inter-seasonal scale (NAO) and the strong event-like occurrence of large dust loads?
- Many measurements show high daily variation, measures for variability change as single days are excluded → measurements on too short time scales to capture variability
  - → Need of long-term monitoring (in terms of composition, single particle measurements would be useful)

  With respect to complexity of dust interactions
  - → "Supersite" monitoring – which locations can be set-up upgraded?
- We know that dust plumes can be sharp-edged on inhomogeneous (particularly on vertical axis, but also on horizontal one), but we can only monitor at single spots continuously
  - → Need of network-like observations (aircraft- and ship-based monitoring, e. g. CARIBIC package)