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Daylight Promotes a Transient Uptake of SO_2 by Icelandic Volcanic Dust

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European Geosciences Union

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Volcanic Dust in the Atmosphere

- Volcanic ash is emitted with gases during explosive eruptions

- Ash emissions = 176-256 Tg/yr, *i.e.*, 5%-7.5% of total primary aerosol emission. They can increase to 90% of aerosol emissions when a large eruption occurs[1,2]

- Ash settles on the ground, and may be later remobilized by winds; it is then called "dust"

Eruption of Eyjafjallajökull Volcano, Iceland, 7th of May 2010
© NASA GSFC, MODIS Rapid Response Team

[1] Andreae, in *World Survey in Climatology* **16**, 341 (1995)
[2] Durant *et al.*, *Elements* **6**, 235 (2010)

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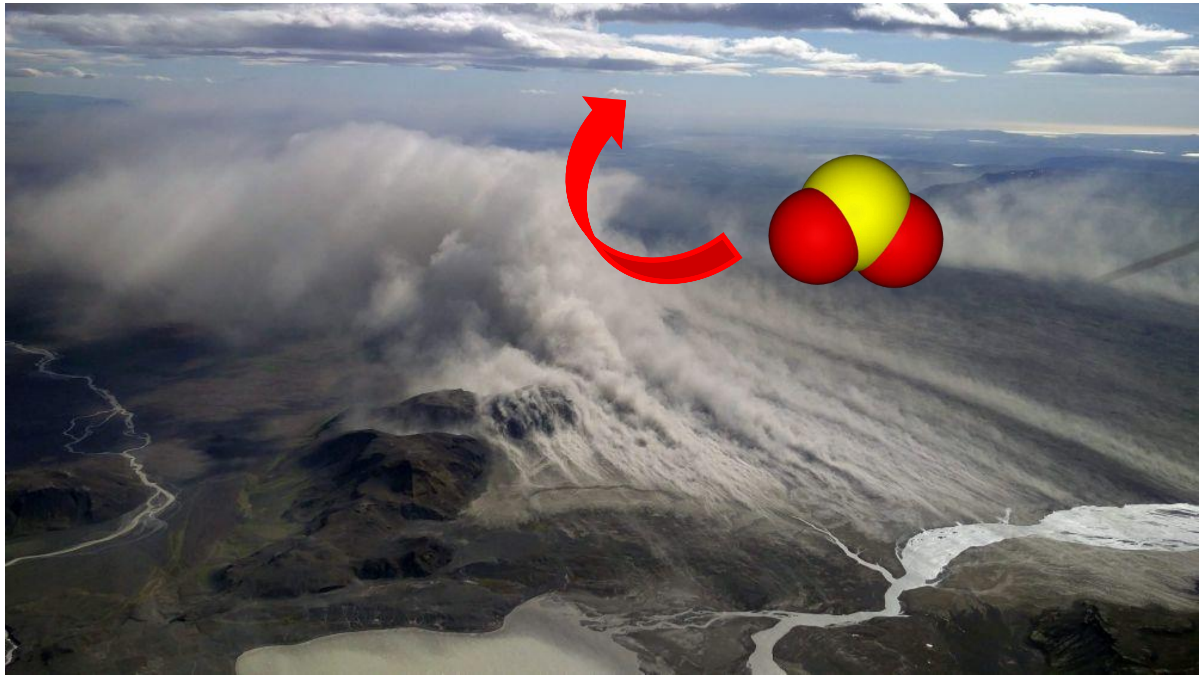
Interaction of SO_2 with Volcanic Dust

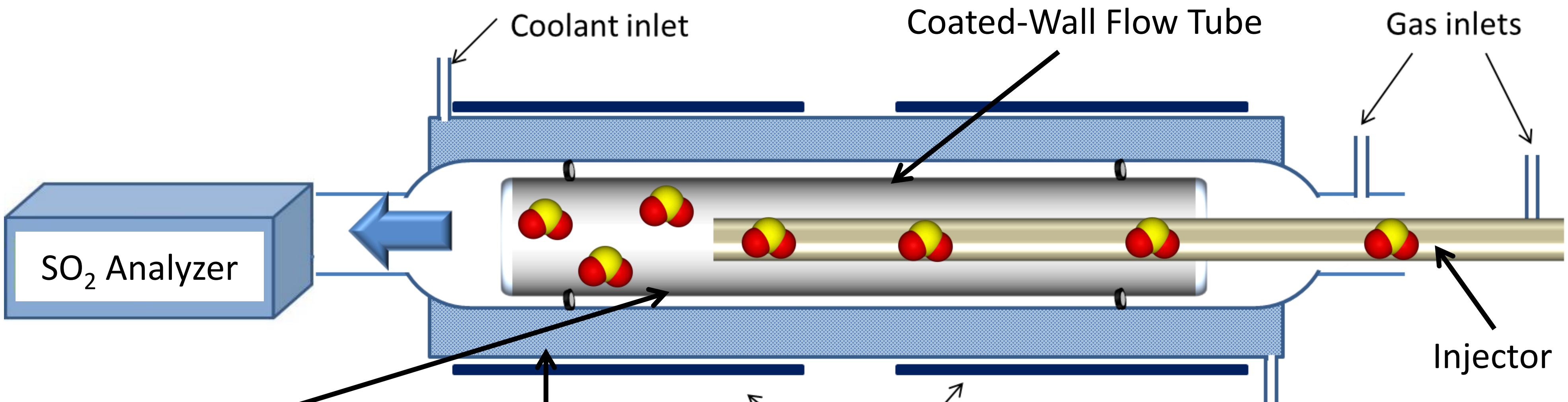


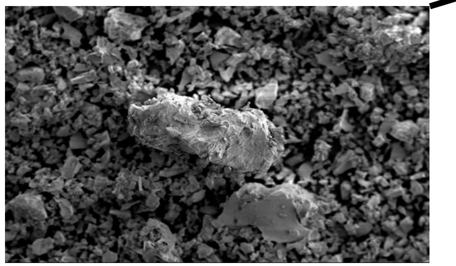
Remobilized volcanic dust during a storm in Iceland
Source: https://icelandmag.is/article/huge-dust-storm-swept-across-area-around-langjokull-glacier-west-iceland

- Icelandic volcanic dust (v-dust) remobilized by winds: 30-40 Tg/yr [3]
- Average [SO_2] in the plume of Eyjafjallajökull (Iceland) during the 2010 eruption = 40 ppb [4]
- Models show that SO_2 heterogeneous uptake by v-dust dominates reaction with OH to dictate SO_2 atmospheric lifetime[4]; 43% more SO_2 is removed when heterogeneous chemistry is included[5]
- V-dust contains Fe- and Ti-oxides that may be photoactivated. **How does solar UV light impact the heterogeneous uptake of SO_2?**

[3] Arnalds *et al.*, *Aeolian Res.* **20**, 176 (2016)
[4] Heue *et al.*, *Atmos. Chem. Phys.* **11**, 2973 (2011)
[5] Zhu *et al.*, *Nat. Commun.* **11**, 4526 (2020)

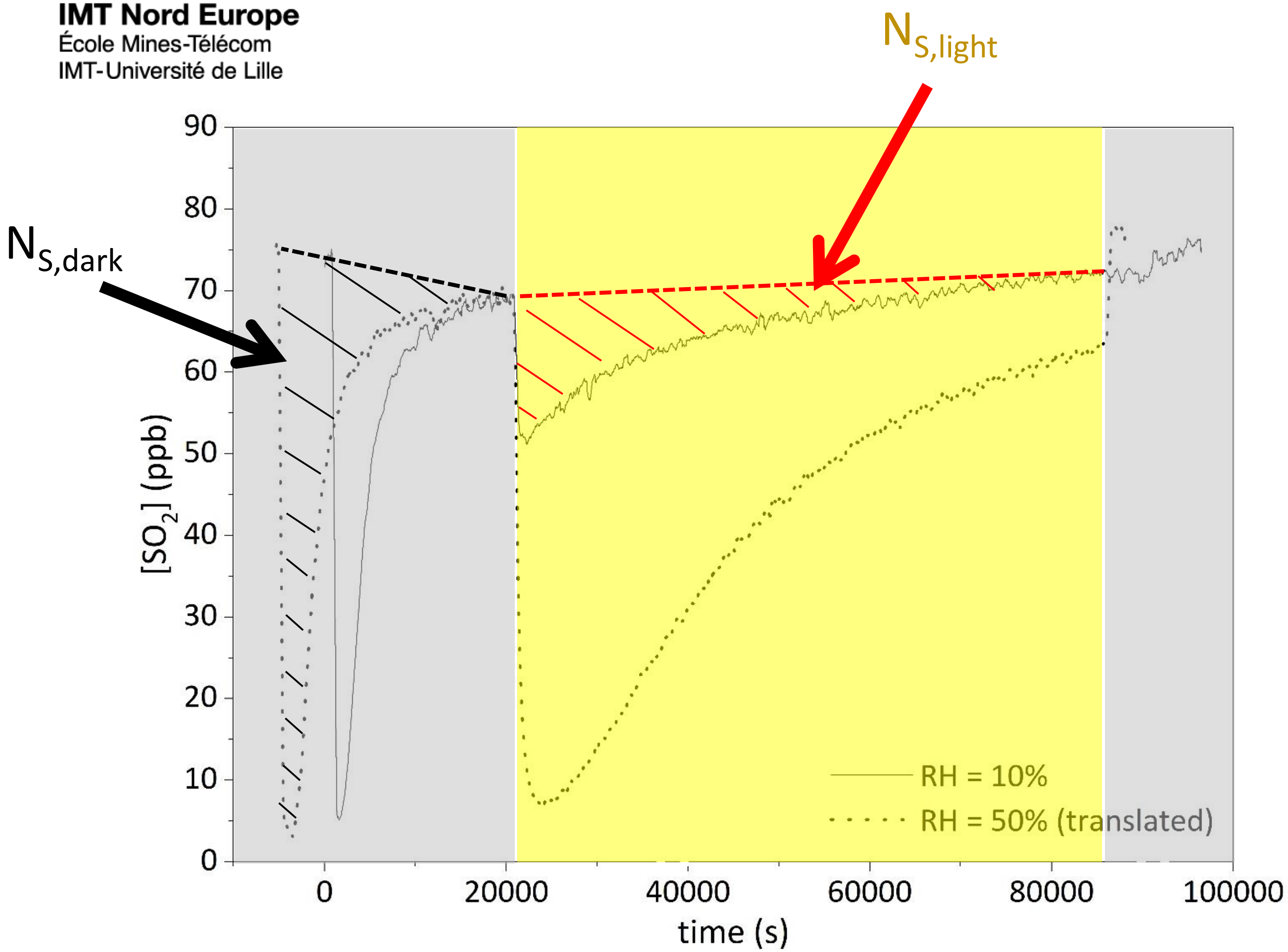
Coated-Wall Flow Tube Reactor





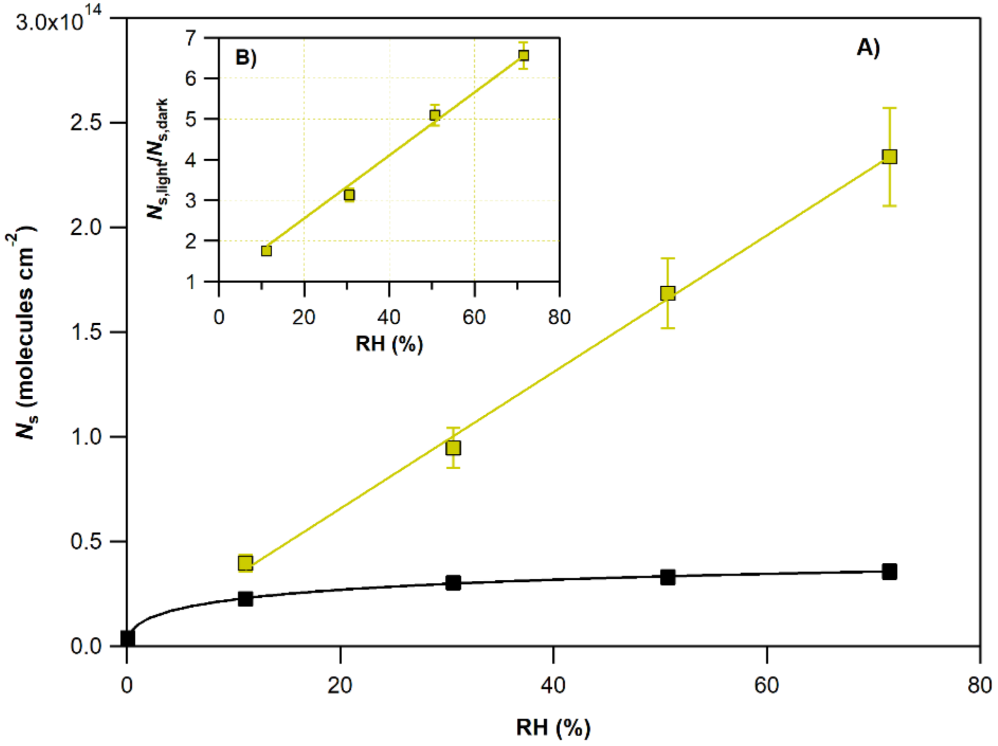
Icelandic v-dust coating

SO_2 Uptake by V-dust



- Mýrdalssandur v-dust
  $[SO_2]$ = 75 ppb, T = 296 K
- Addition of UV light ($J_{NO2} = 4.5\times10^{-3}\ s^{-1}$) triggers a new transient uptake of SO_2
- Relative humidity (RH) has an impact on N_S, especially under UV

SO_2 Uptake by V-dust: Effect of Relative Humidity (RH)



- $N_{S,dark}$ increases with RH in a Langmuir-like fashion. Saturation about RH = 30%, corresponding to the formation of the H_2O monolayer on volcanic ash[6]

[6] Joshi *et al.*, *Aeolian Research* **27**, 35 (2017)

- $N_{S,light}$ (J_{NO2} = 4.5×10^{-3} s^{-1}) increases linearly with RH, and so does the amplification of N_S by solar UV light, $N_{S,light}/N_{S,dark}$

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Photo-enhanced uptake of SO_2 on Icelandic volcanic dusts†

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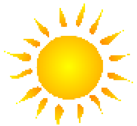
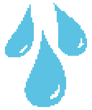
Global Parametrization of N_S Enhancement by Solar UV Light

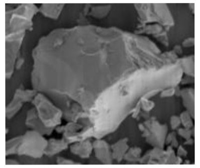
- We have established the dependence of $N_{S,light}/N_{S,dark}$ on: RH, J_{NO2}, [Ti]/[Si]. An empirical relationship has been determined[7]:

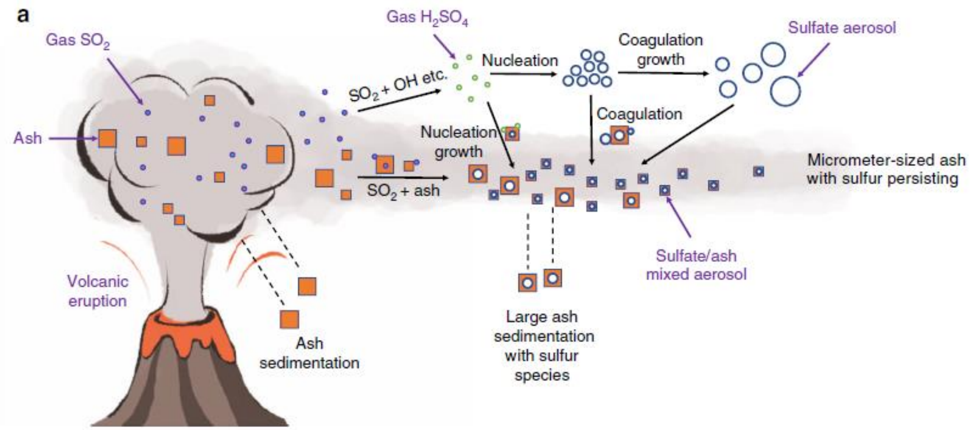
$$N_{s,light}/N_{s,dark} = 6.1 \times [(1 + 7.76 \times 10^{-2} \times (\%RH)] \times (1 + 480.5 \times J_{NO2}) \times ([Ti]/[Si])$$

- This equation can be implemented in chemical models[8] of the atmosphere









[7] Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

[8] and Illustration: Zhu *et al.*, *Nat. Commun.* **11**, 4526 (2020)

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Conclusions

- We have quantified the uptake of SO_2 by natural Icelandic v-dust under realistic atmospheric conditions

- SO_2 uptake is efficiently promoted by solar UV light and relative humidity; the UV-promoted process is transient

- Models show the efficiency of heterogeneous processes on the removal of SO_2 from the atmosphere. This new data, and the empirical parametrization, show that these processes are much stronger under solar UV irradiation, and could decrease even more SO_2 lifetime, and the sulfur burden in the atmosphere

Acknowledgements

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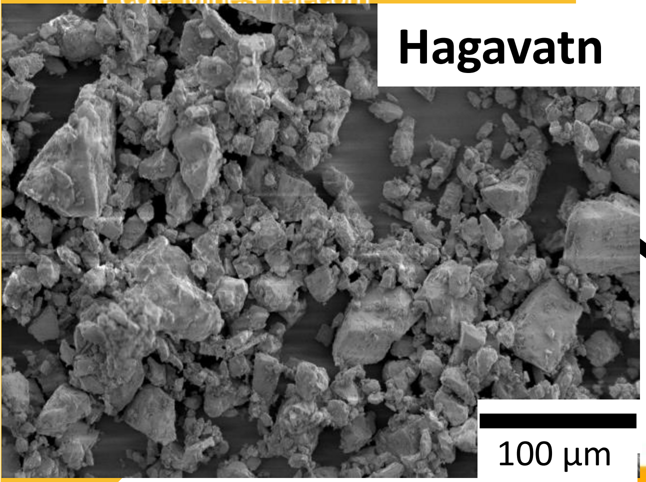
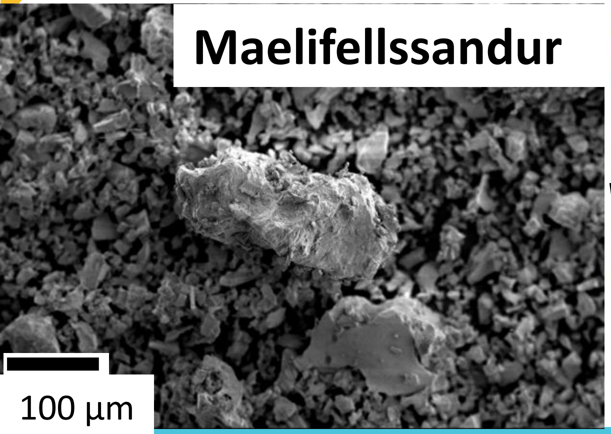
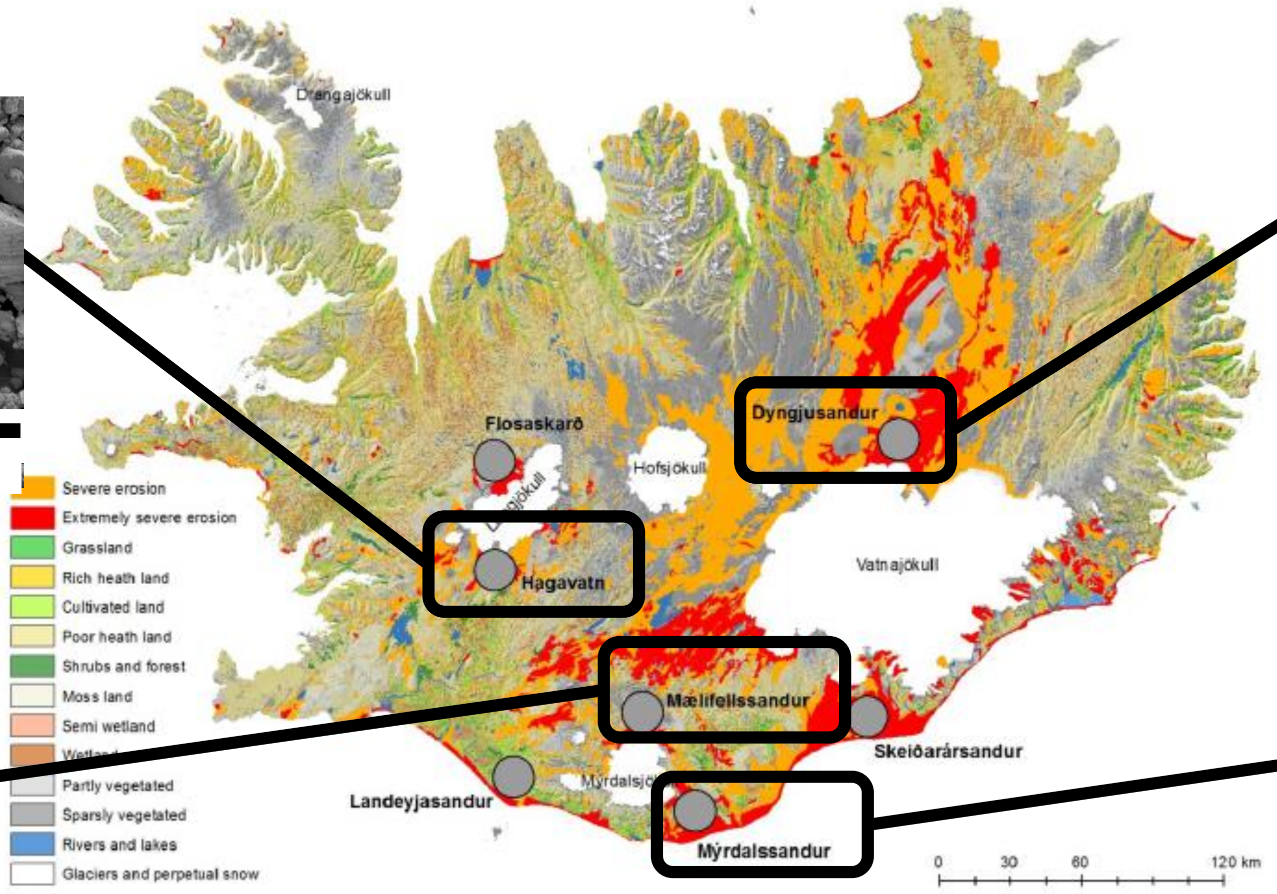
Backup

V-dust Samples: Origin

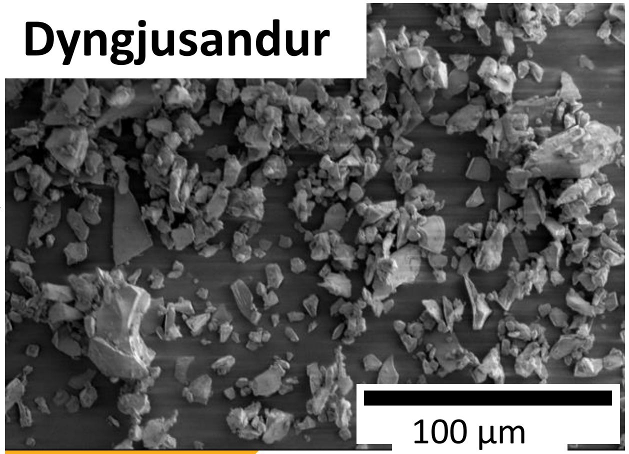
SEM images thanks to V. Thiéry
(CERI MP, IMT Nord Europe)

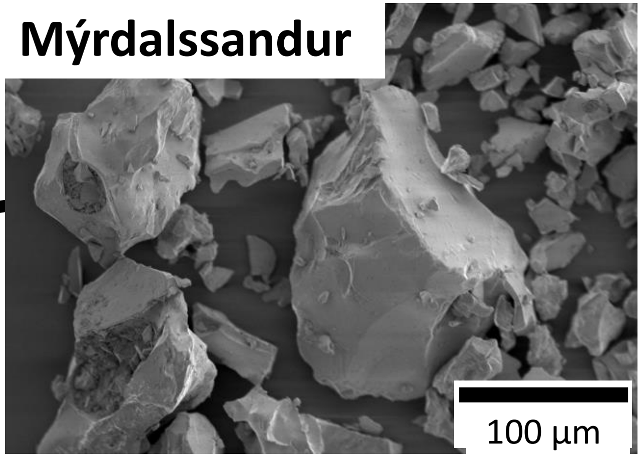






Arnalds *et al.*, *Biogeosciences* **11**, 6623 (2014)





Volcanic Dust Samples: Origin

- **<u>Hagavatn</u>**:
- Severe erosion region
- Small area (10 km^2)
- Receding glacier and glacial lake with fluctuating water levels
- More crystalline materials
- **<u>Maelifellssandur</u>**:

Extremely severe erosion region
Medium size area (40 km^2)
Glacio-fluvial highland plain with fluctuating glacial waters
Frequent dust storms

- **<u>Dyngjusandur</u>**:

Extremely severe erosion region
Large area (140 km^2)
Glacio-fluvial plain flooded in summer
Presence of sediments
Frequent dust storms

- **<u>Mýrdalssandur</u>**:

Extremely severe erosion region
Medium size area (60 km^2)
Glacio-fluvial lowland with fluctuating water levels
Presence of sediments
Frequent dust storms

Arnalds *et al.*, *Aeolian Research* **20**, 176 (2016)

Volcanic Dust Samples: Surface Composition

XPS Analysis of Icelandic Volcanic Dusts

Surface Composition (at.%)	**Hagavatn**	**Maelifellssandur**	**Dyngjusandur**	**Mýrdalssandur**
Si	45.0	49.8	53.9	53.1
Al	35.8	22.3	19.9	17.6
Fe	5.7	13.0	9.1	11.7
Ca	6.9	5.2	7.7	6.6
Na	1.9	1.9	1.4	3.3
Mg	3.1	4.1	6.4	4.4
Ti	1.1	3.0	1.4	2.6
K	< 0.1	0.4	< 0.1	0.7
Mn	0.1	0.4	0.3	< 0.1

Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

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Volcanic Dust Samples: Specific Surface Area

BET Specific Surface Area of Icelandic Volcanic Dusts

	Hagavatn	Maelifellssandur	Dyngjusandur	Mýrdalssandur
S_{BET} (m^2 g^{-1})	4.5 ± 1.1	8.2 ± 2.0	7.0 ± 1.8	1.5 ± 0.38

Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

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Experimental Method

1) A stable $[SO_2]_0$ is set in the reactor; dust is not exposed yet

2) Dust is exposed to SO_2 until a steady-state ($[SO_2]_{SS,dark}$) is reached

3) UV lamps are turned on; a new steady-state $[SO_2]_{SS,UV}$ is reached

4) The UV lamps are turned off, and the injector is pushed back in to go back to the initial level, $[SO_2]_0$

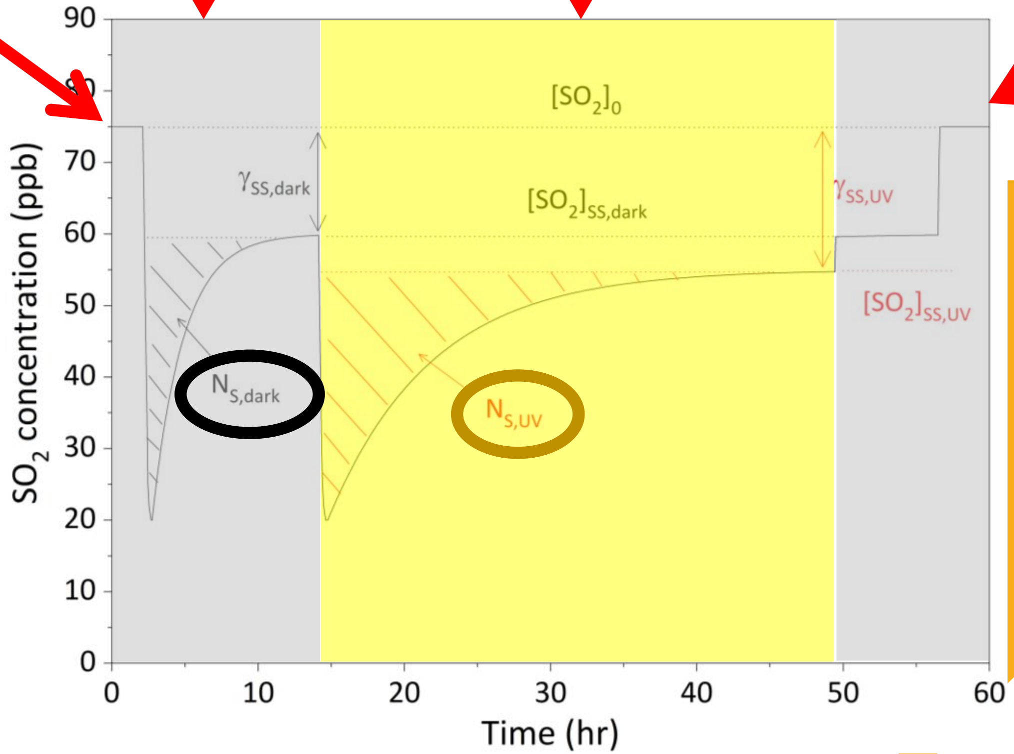
$$k_{obs} = \frac{v \times \ln\left({[SO_2]_0}/{[SO_2]_{SS,dark}}\right)}{L_{coating}}$$

Correction for SO_2 diffusion

$$k_{kin} = \frac{k_{obs}}{1 - \alpha P k_{obs}}$$

Steady-state uptake coefficient

$$\boxed{\gamma_{ss} = \frac{4 k_{kin} V}{cS}}$$



We have access to the number of SO_2 molecules taken up by dust, $N_{S,dark}$ and $N_{S,light}$

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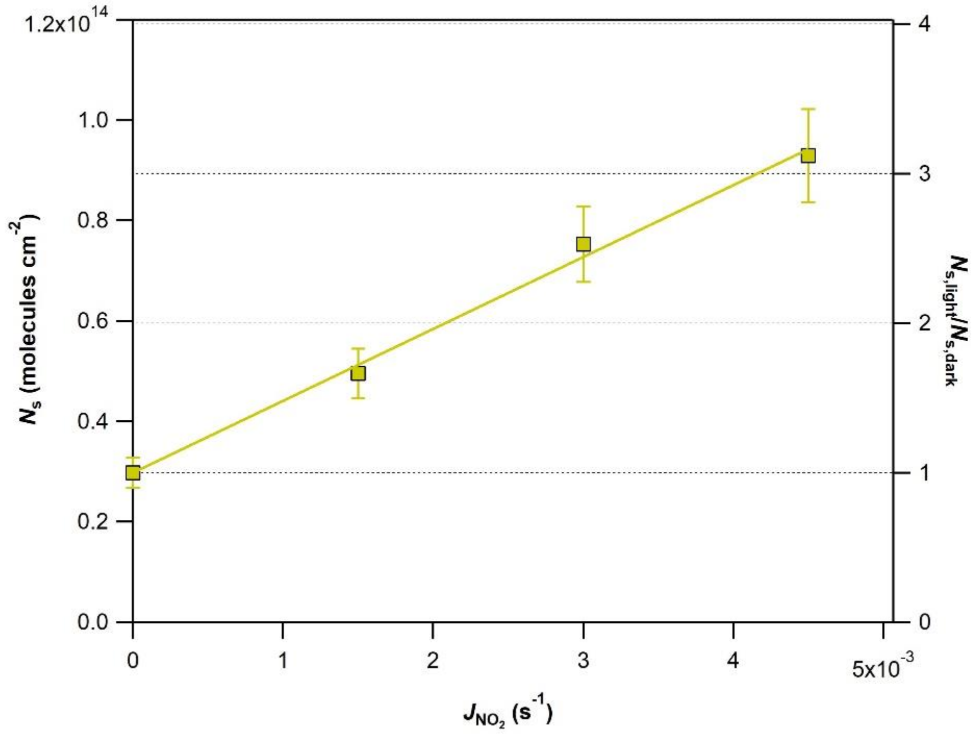
Volcanic Dust Samples: Specific Surface Area

Number of SO_2 Molecules Taken Up by Icelandic Volcanic Dusts
$[SO_2]$ = 75 ppb, T = 296 K, RH = 30%

	Hagavatn	Maelifellssandur	Dyngjusandur	Mýrdalssandur
$N_{S,dark}$ (10^{13} molecules cm^{-2})	1.2 ± 0.4	0.96 ± 0.29	2.1 ± 0.6	2.5 ± 0.8
$N_{S,light}$ (10^{13} molecules cm^{-2})	2.0 ± 0.6	3.7 ± 1.1	3.6 ± 1.0	7.8 ± 2.5
$N_{S,light}$ / $N_{S,dark}$	1.7	3.8	1.7	3.1

Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

SO_2 Uptake by V-dust: Effect of Light Flux



Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

- UV light irradiating dust is characterized by J_{NO2}, the photolysis rate of NO_2 (in s^{-1}) in the setup (typical atmospheric values = 10^{-3} – 10^{-2} s^{-1})

- N_S and $N_{S,light}/N_{S,dark}$ increase linearly with J_{NO2} at RH = 30%

- Photocatalysis (activation of the surface by UV photons), or photochemistry (alteration of SO_2 by UV photons)?

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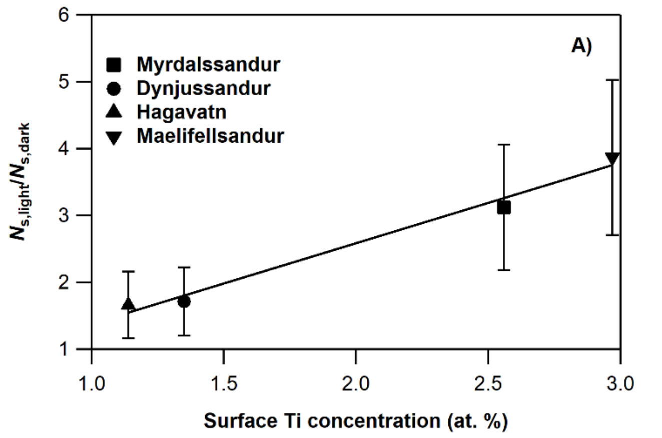
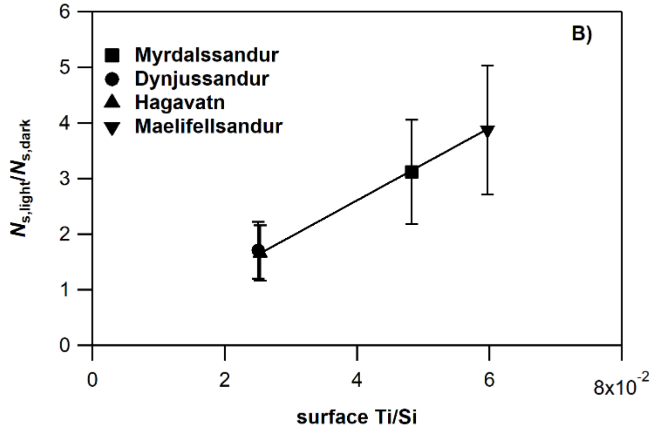
SO_2 Uptake by V-dust: Correlation with Surface Composition





- Surface elemental composition (in at.%) measured by XPS
- $N_{S,light}/N_{S,dark}$ for $J_{NO2} = 4.5\times10^{-3}$ s^{-1}, RH = 30% increases linearly with surface [Ti], and with surface [Ti]/[Si]
- Proportionality of $N_{S,light}/N_{S,dark}$ with surface Ti content suggests photocatalysis, but photochemistry cannot be ruled out!

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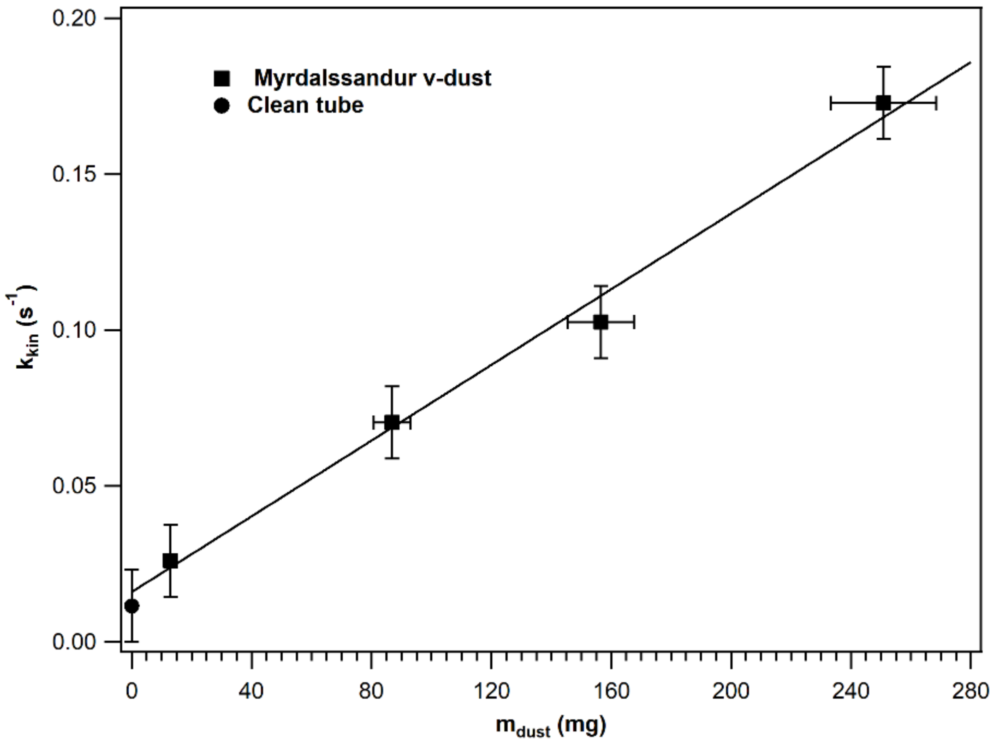
Volcanic Dust Samples: Specific Surface Area

BET Steady-State Uptake Coefficients of SO_2 by Icelandic Volcanic Dusts
$[SO_2]$ = 75 ppb, T = 296 K, RH = 30%

	Hagavatn	Maelifellssandur	Dyngjusandur	Mýrdalssandur
$\gamma_{SS,BET,dark}$ (10^{-8})	0.66 ± 0.26	3.2 ± 1.3	1.6 ± 0.6	6.2 ± 2.5
$\gamma_{SS,BET,light}$ (10^{-8})	2.6 ± 1.0	6.6 ± 2.7	7.3 ± 2.9	7.1 ± 2.9
$\gamma_{SS,BET,light}$ / $\gamma_{SS,BET,dark}$	3.9	2.0	4.6	1.1

Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

SO_2 Uptake by V-dust: Steady-State Uptakes



- Linear increase of SO_2 uptake with v-dust mass
- No saturation → all the dust is exposed to SO_2 in the mass range < 250 mg

Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

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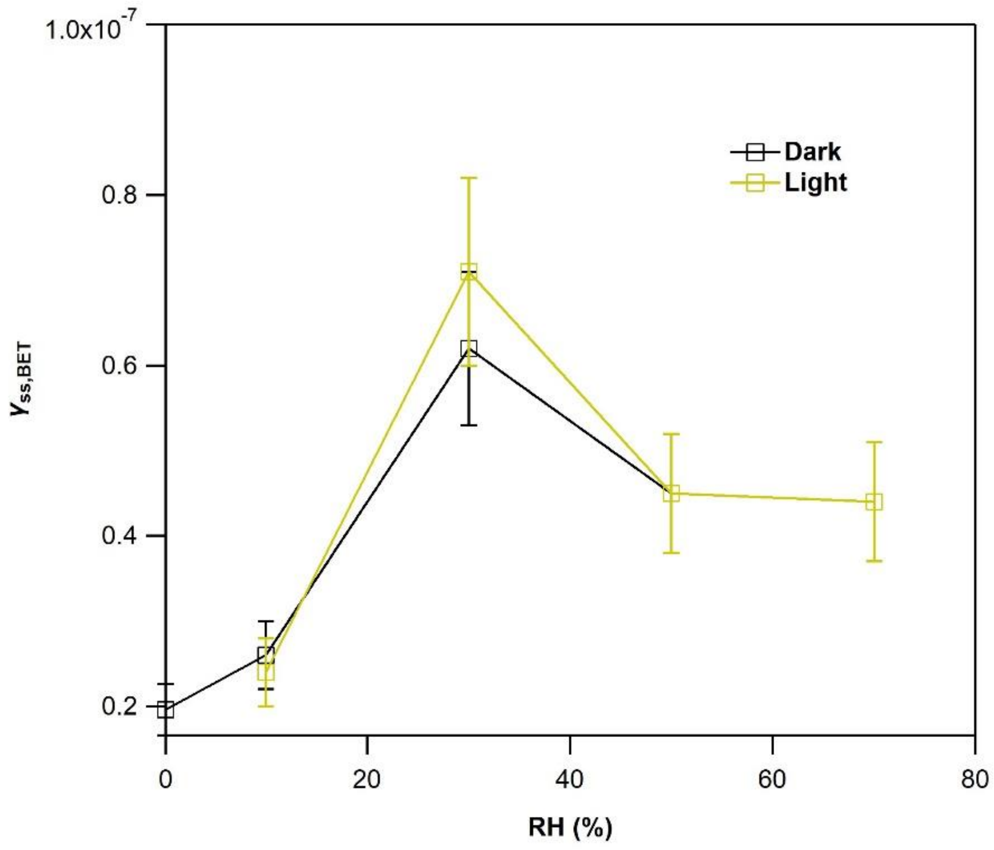
SO_2 Uptake by V-dust: Steady-State Uptakes



Lasne *et al.*, *Environ. Sci.: Atmos.*, Advance article (2022)

$$\gamma_{ss,BET} = \gamma_{ss,geom} \times \frac{S_{geom}}{S_{BET}}$$

- SO_2 uptake increases up to RH = 30%, then decreases and plateaus at 50%; this behaviour could be linked to the formation of the H_2O ML [6]

- Steady-state uptakes of SO_2 by Mýrdalssandur v-dust are, within error, similar in the dark and under UV-irradiation; UV-irradiation does not produce any detectable quantitative modification of the steady-state

[6] Joshi *et al.*, *Aeolian Research* **27**, 35 (2017)