Temperature vs ozone concentration:
new insights to the CCN-activity and LDSA of soot particles after long term exposure to ambient Ozone concentrations.

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Franz Friebel and Amewu. A. Mensah.

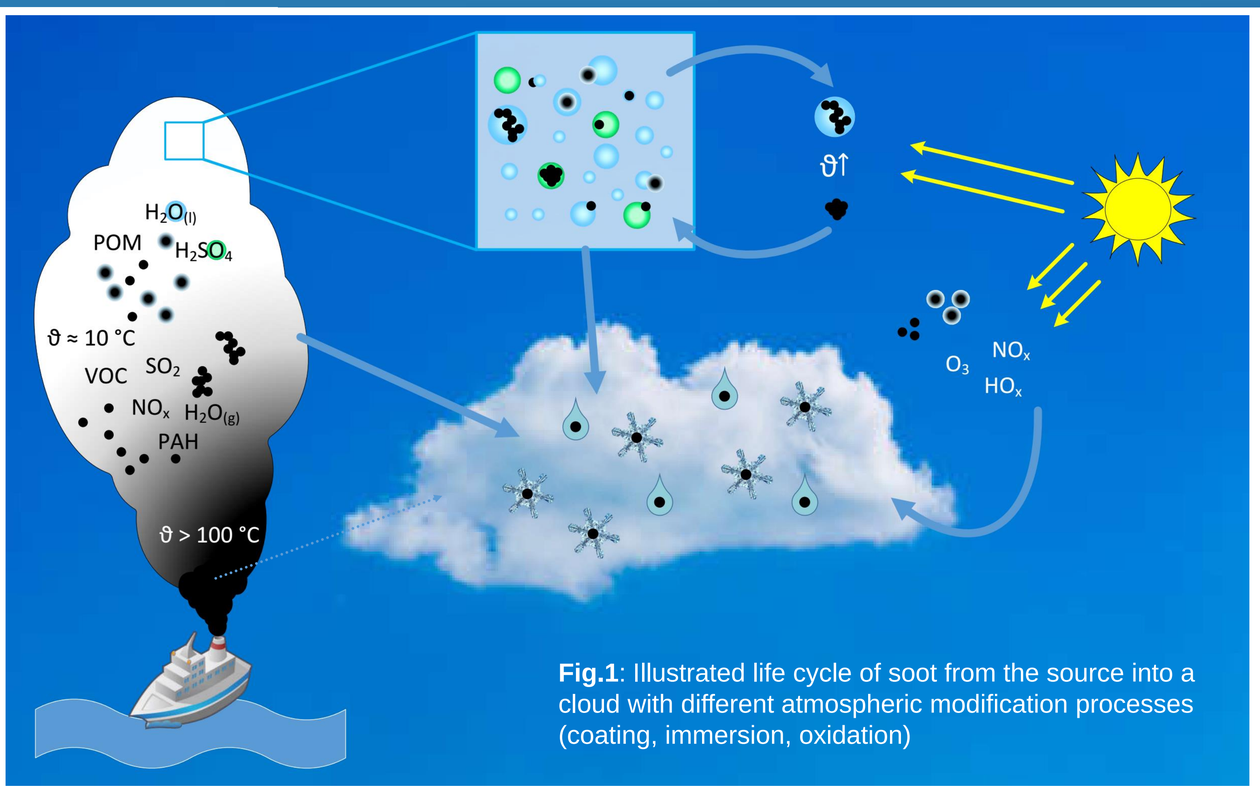

Fig.1: Illustrated life cycle of soot from the source into a cloud with different atmospheric modification processes (coating, immersion, oxidation)

Can soot particles form clouds?

Soot particles that are freshly emitted into the atmosphere are typically hydrophobic and are therefore not able to act as cloud condensation nuclei (CCN). However, soot particles can be CCN-active in the atmosphere [1]. During the **atmospheric lifetime of approx. one week** different **aging processes** can change the properties of soot significantly. One of these aging processes is nicely illustrated in the video (QR-code).

Here we present results from a lab campaign conducted in Winter 17/18 at ETH Zürich where we investigated the **heterogeneous oxidation of soot particles with ozone** under **atmospheric conditions** for up to 16 h. We propose that the oxidation follows a Langmuir-type kinetic and therefore shows an non-linear dependency on the ozone gas phase concentration. Additionally we suggest that under atmospheric conditions the impact of the temperature be considered equally important as the ozone concentration.

[1] IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp, doi:10.1017/CBO9781107415324

1. **Scan me**
2. **Watch me**

Langmuir-type reaction mechanism

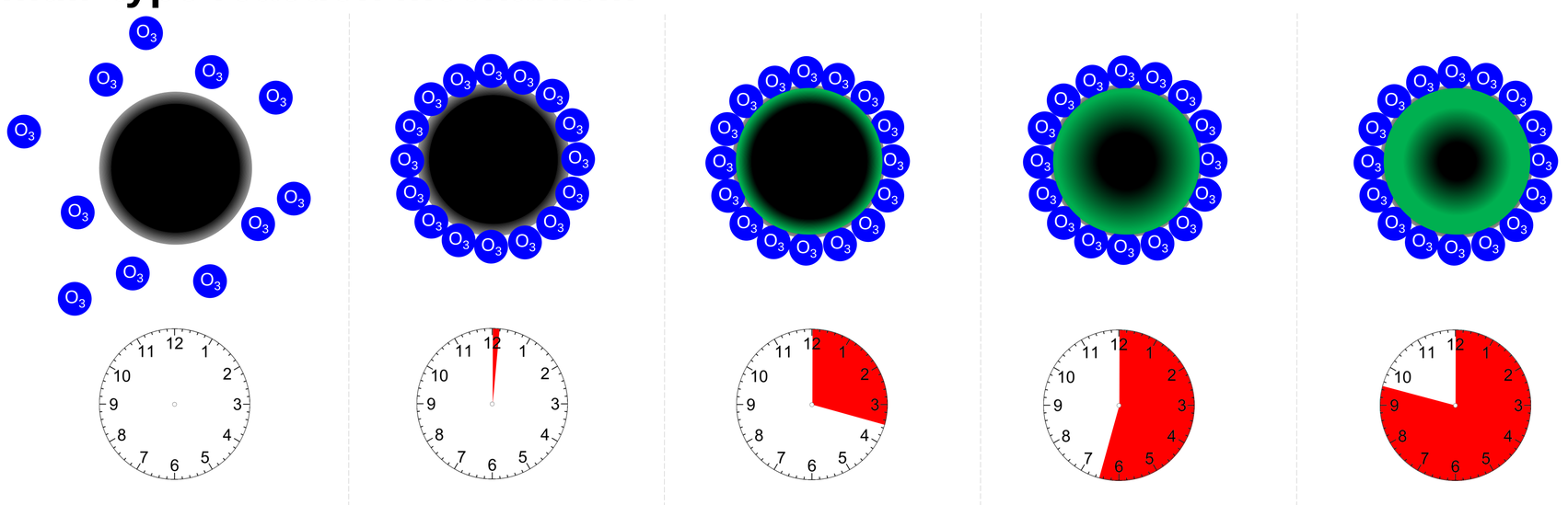

Fig.2: A fast adsorption of an ozone monolayer (several minutes) is followed by a slow reaction (several hours) of adsorbed ozone with the soot particle surface and/or bulk material. The increasing degree of oxidation increases the hydrophilicity and/or the hygroscopicity and therefore reduces the critical super saturation.

	Fresh particle	10 min exposure to 200ppb O_3	After 3.5 h	After 6.5h	After 9.5h
Particle Diameter	102 nm	106 nm	106 nm	106 nm	106 nm
Particle mass	0.26 fg	0.31 fg	0.31 fg	0.31 fg	0.31 fg
Lung-deposited Surface area	0.0057 µm²/particle	0.0057 µm²/particle	0.0057 µm²/particle	0.0057 µm²/particle	0.0057 µm²/particle
CCN-activity					

Setup

- 3 m^3 aerosol chamber (steel)
  → continuously stirred tank reactor
- 100 nm size-selected soot particles
- miniCAST set point 6 → organic-rich

- ozone: 0 – 200 ppb
- Temperature 5 °C – 35 °C
- aging time: max. 16 h
- concentration: ~1500 particles/cm^3
- *RH*: 4 %

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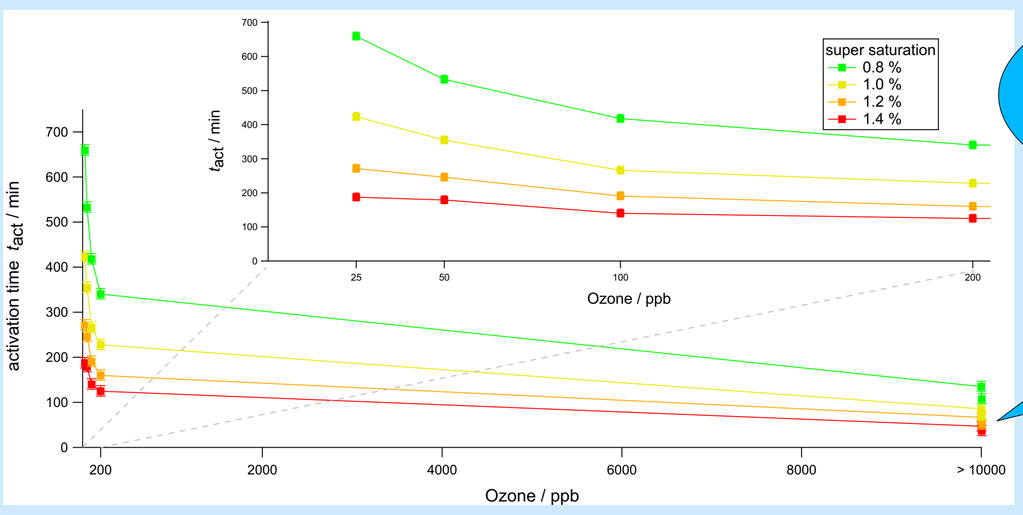
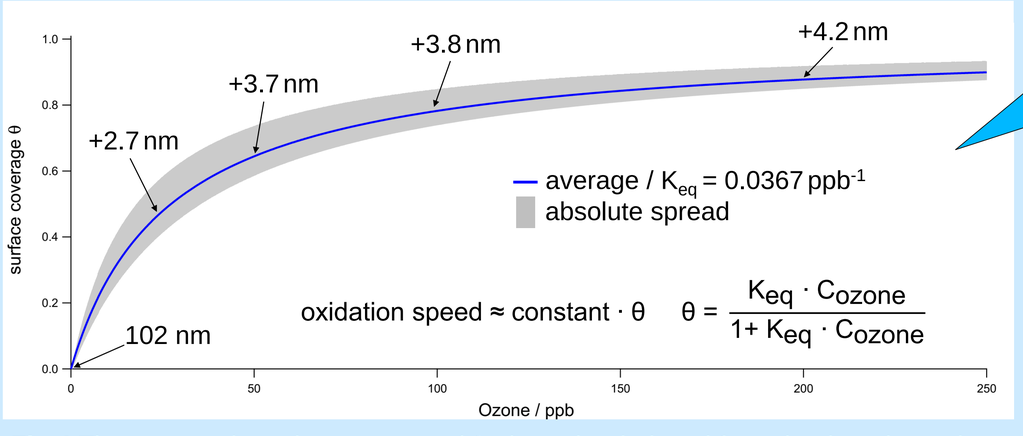
Ozone concentration



5 °C → 35 °C
≈ 5-times faster oxidation

Increasing the ozone concentration does **not** lead to a linear increase of the oxidation speed.

Fig.3: Impact of different Ozone concentrations on the necessary aging time (t_{act}) to CCN-activate soot particle at different SupSats at a constant temperature of 25 °C



The Increase in the particle diameter correlates with the **adsorption** of an **ozone-monolayer**

Fig.4:The ozone adsorption constants (K_{eq}) can be deduced from the time dependent CCN-activation data under the assumption of an Langmuir-type reaction mechanism

Temperature

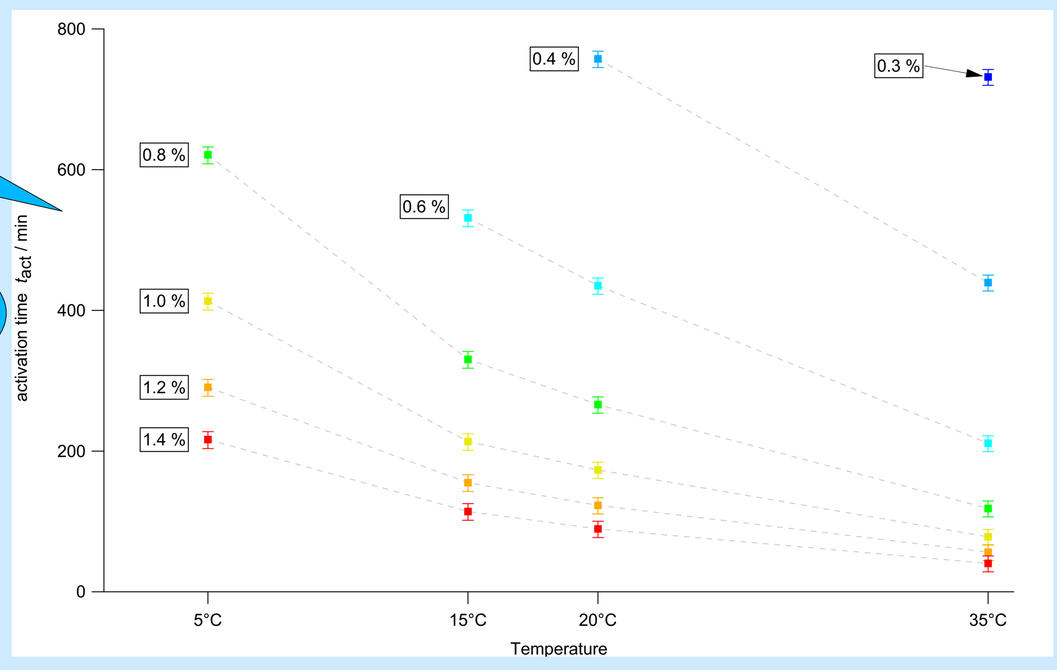


Fig.5.: Impact of the temperatue on the t_{act} / oxidation speed at a constant ozone background concentration of 200 ppb

Summary

The heterogeneous oxidation of soot particles with Ozone can effectively increase the **CCN-activity** even at **atmospheric Ozone concentrations**.

The **activation energy** for the oxidation reaction is **40 kJ/mol** and therefore shows a strong **temperature dependency.**

no collapse of the soot aggregate ← **constant LDSA**