

Air-snow exchange of nitrate

A modelling approach to investigate physicochemical processes in surface snow at Dome C, Antarctica

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- Nitrate is ubiquitous in snow
- Nitrate concentration in snow is related to:
 - Photolysis efficiency
 - NO_x concentration

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- O_3 , OH and oxidative capacity
- Long range transport



Adapted from Erbland et al, ACPD 2015

• The interpretation of the ice core records is hampered by a poor understanding of the post-deposition processes

 \rightarrow need a better understanding of all processes



Nitrate in snow, and its modelling



Where is located nitrate inside snow grains?

- On the one hand, lab experiments:
 - Adsorption studies
 - Solid solution

Nitrate is adsorbed on ice surfaces, and forms solid solution in bulk ice

• On the other hand, oversimplified QLL approach in current snow chemistry models

→ gap between the lab evidences and current modelling approach

Sources and sinks

Sinks:



- Uptake onto/into the snow:
 - Adsorption
 - Solid state diffusion
 - Co-condensation
 - Other?

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- Physical exchange
- Chemical source

Initial loading

- Nitrate photolysis
- Physical exchange ("evaporation")



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- At Dome C: nitrate concentration in the skin layer (top ~4 mm) is much higher in summer
 - → The sink (photolysis) is lower than the source (physical uptake processes)

Model framework

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Adsorption



• Surface coverage parameterisation based on lab measurements, IUPAC review and recommendations (Crowley et al, ACP 2010)



- Large overestimation (paper under review in ACP for discussion)
- Adsorbed nitrate is likely to be a minor fraction of total snow nitrate, except maybe during spring



Diffusion thermodynamic equilibrium

Thermodynamic equilibrium concentration

$$X_{eq}^{0} = 2.37 \times 10^{-12} \exp\left(\frac{3532.2}{T}\right) \left(P_{HNO_3}\right)^{1/2.3}$$

Thibert & Dominé, JPC B 1998

Boundary condition



Diffusion thermodynamic equilibrium



Modelled concentration in winter is roughly consistent with the measurements

- The slight underestimation could be due to the remaining adsorbed fraction
- Thermodynamic equilibrium is unable to explain summer concentrations \rightarrow out of equilibrium, a kinetic process occurs





Co-condensation



 Definition: condensation of trace gases present in the interstitial air along with water vapour fluxes





Co-condensation



- Definition: condensation of trace gases present in the interstitial air along with water vapour fluxes
- The flux of water vapour depends on the thermal gradient, which is highest close to the snow surface











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~real









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$$X_{average} = X_{kin} + \frac{X_{eq} - X_{kin}}{h} \int_{0}^{h} erfc \left(\frac{X}{2\sqrt{(D \cdot \tau)}}\right) dx$$

Dominé & Thibert, GRL 1996

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- Step 2: thickness of the condensed layer
 - Growth law as a function of water vapour gradient: $\frac{dm}{dt} = 4\pi R^2 D_v \left(\frac{d\rho_v}{dx}\right)_{x=R}$

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- The water vapour is a function of temperature (Goff-Gratch equation for ice)
- The mass increase is converted into a radius increase: h $X_{average} = X_{kin} + \frac{X_{eq} - X_{kin}}{h} \int_{0}^{h} erfc \left(\frac{x}{2\sqrt{D \cdot \tau}}\right) dx$

Boundary condition

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Co-condensation: results

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 Timing and shape of the modelled concentration are in good agreement with the observations

- Only co-condensation is able to explain high summer concentration in the skin layer
- The developed approach allows to predict a distribution inside the snow grain → apply different photolysis rates
- Implement this parameterisation into a 1D model
- Improvement of the physical and geometrical descriptions: take advantage of microphysical models and 2D/3D micro-tomography studies
- Need for new studies to correct adsorption parameterisation