



## **CAPRAM modelling of the speciation and redox-cycling of iron in deliquescent particles and cloud droplets**

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The most abundant TMI in tropospheric particles is iron which plays a crucial role in aqueous phase chemistry of fog and cloud droplets. The redox-cycling of iron is responsible for many chemical interactions such as the  $\text{HO}_x/\text{HO}_y$  processing. However, still large uncertainties of TMI chemistry exist and less is known about the TMI speciation in the particulate phase. To this end, the iron speciation and redox cycling in deliquescent particles and cloud droplets were investigated in more detail by means of model studies using the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM). The parcel model SPACCIM includes a complex microphysical and multiphase chemistry model. In chemistry model, the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i with about 1100 processes was applied incorporating a detailed description of the tropospheric multiphase processes. Simulations were carried out for different environmental conditions using a non-permanent meteorological scenario. The model results have been analysed including time-resolved source and sinks studies. The model studies were particularly focused on temporal variations in the of iron speciation and redox-cycling in the condensed phase including its importance for other important chemical subsystems such as the multiphase  $\text{HO}_{x,y}$  and organic chemistry. For this purpose, sensitivity studies have been performed on the importance of the water soluble iron content for the aqueous phase oxidation capacity and chemical organic processing.

The model results have shown characteristic diurnal profiles of the iron speciation in both deliquescent particles and clouds. Moreover, up to about 20 to 50% of the soluble iron is shown to be still present as  $\text{Fe}^{2+}$  during the night which reflects an efficient nighttime iron-redox-cycling under polluted environmental conditions. Performed comparisons with available cloud water measurements and former model calculations revealed reasonable agreements as well as some differences.

The model results have additionally pointed out considerable differences between the iron cycling in deliquescent particles and cloud droplets. The model results revealed chemical differences in the sink and source reactions caused by different pH conditions as well as the different  $\text{HO}_2/\text{O}_2^-$  budget in the two aqueous environments. Moreover, the model results implicated the role of deliquescent particles to be a reactive medium for the TMI redox-cycling which is potentially important for other chemical subsystems. Under urban conditions, the modelled total daytime fluxes in the deliquescent particles are partly about 2 times larger than in daytime clouds.

Finally, the performed studies regarding the relevance of the water soluble iron content for tropospheric multiphase processes have pointed out that the oxidation budget is quite sensitive to changes of this crucial parameter. Accordingly, the sensitivity studies corroborate the need for an iron-redox-chemistry treatment in higher scale chemistry transport models. However, the studies have also confirmed the necessity for further experimental work concerning the iron-organic aqueous photochemical interactions to clarify open scientific issues and mechanism limitations.