

Investigation of unique oxidizing capacity of the Antarctic atmosphere based on O-MIF signatures in atmospheric sulfate and nitrate

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O-MIF signatures ($\Delta^{17}\text{O}$) in sulfate and nitrate in the Antarctic ice cores are used as proxy for the reconstruction of oxidizing capacity in the past Earth's atmosphere because they reflect the relative importance of O_3 ($\Delta^{17}\text{O} = 25\text{-}35\text{‰}$) and other oxidants (e.g. OH radical; $\Delta^{17}\text{O} = 0\text{‰}$) during their formation [1]. While it is necessary to understand the oxidizing capacity of the present Antarctic atmosphere for the interpretation of the proxy, it still remains to be constrained because of the complicated chemistry induced by high NO_x emissions from snowpack [2]. For this issue, we investigated the seasonal variations of $\Delta^{17}\text{O}$ values of both sulfate and nitrate in the aerosols collected at Dumont d'Urville, coastal Antarctica, throughout the year 2011.

The $\Delta^{17}\text{O}$ values of sulfate and nitrate showed the clear seasonal variations with summer minima and winter maxima. These trends are resulted from the seasonal changes in the O_3 / OH ratios decreased in summer by ozone destruction and OH production via UV irradiance. Indeed, both $\Delta^{17}\text{O}$ values of sulfate and nitrate were correlated with ozone mixing ratios. Despite the almost same ranges of ozone mixing ratios for spring and autumn, the sensitivity of $\Delta^{17}\text{O}$ values of sulfate to ozone mixing ratios in spring was lower than that in autumn. In contrast, this phenomenon was not observed for nitrate. The relatively low $\Delta^{17}\text{O}$ values of sulfate in spring may be due to the lower O_3 / OH ratios caused by the NO_x emission from snowpack triggered by the UV irradiance, which enhances OH production exceeding O_3 production [3]. It is not easy to identify the precise processes, but this study shows first observational evidence of the contribution of snow-sourced NO_x emission on sulfate production through the changes in the oxidizing capacity.

[1] Alexander and Mickley (2015) *Curr. Pollution Rep.* **1**, 57–69. [2] Chen *et al.* (2001) *Geophys. Res. Lett.* **28**, 19, 3633–3636. [3] Zatko *et al.* (2015) *Atmos. Chem. Phys. Discuss* **15**, 18963–19015.