

Comment on Enghoff et al., "An isotope view on ionising radiation as a source of sulphuric acid"

This paper reports on potential existence of a new SO<sub>2</sub> oxidation pathway to form sulphuric acid. It has been recognized recently that photochemical or dark OH production is not necessarily enough to explain the measured sulphuric acid concentrations in different environments. Therefore the studies focusing on "missing" atmospheric oxidation capacity, including the present work, are of importance and potentially deserve publication in ACP.

Authors have investigated the isotopic enrichment of sulphur in conversion of sulphur dioxide to sulphuric acid. Based on the experimental results from different oxidation mechanisms, authors propose that ionization of air can result in formation of hydrated clusters. These clusters, based on the experimental results and theoretical considerations cited might be responsible on the enormous enhancement of sulphate production compared to that expected from gamma ray produced OH in the presented experiment. If true, this would be interesting new information. Though the atmospheric relevance of the proposed mechanism in much lower SO<sub>2</sub> concentrations of ambient air seem unlikely, it cannot be excluded. Therefore, I would have no objections for publication this paper in ACP. However, as I am not familiar with the experimental methods I cannot judge whether the obtained experimental results justify the presented conclusions. My concern arises mainly from the limited statistics, only 1 experiment from each system is presented (understandably, since one experiment runs for a week). On the otherhand, the experiments with and without gamma-radiation differ significantly in amount of recovered mass – probably that is really indicating the significant contribution from ionizing radiation.

Still, I would recommend authors slightly amend the presentation of the used method, and explanations concerning e.g. expected and observed  $\Delta^{33}\text{S}$ . As a non-expert reader I had significant problems in understanding the data.

I understood that  $\Delta^{33}\text{S}=0$  is assumed except of the reaction proceeding via SO<sub>2</sub> excitation. What is causing then negative NMD? Because O3-gamma-1 is closer to MDF line than O3-1 wouldn't it mean that the gamma-radiation related process have positive NMD to balance the negative from O3-1. Furthermore I did not understand the "Isotopic mixing line", is that just a line to guide an eye?

I did not understand why recovered mass in O3-3 sample is 100-fold to O3-1? How much mass was in O3-gamma-3 and O3-UV-gamma-3 ?

Fig. 2. Legend. Please write out MDF (mass dependent fractionation?)

Authors state that in atmospheric [SO<sub>2</sub>] the efficiency of gamma-radiation related mechanism drops drastically. The atmospheric significance should be possible to assess based on the data because the ionization rate and [SO<sub>2</sub>] are known. Is it negligible? Can it explain any of the observed "missing" sulphuric acid in atmosphere. In current form the connection of paper's conclusions to "atmospheric chemistry and physics" is still weak.