Interactive comment on “Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica” by J. Savarino et al.

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We thank Adrian Tuck for his comments. We acknowledge his work done on the meteorology and dynamic of the stratosphere. We agree that the denitrification and dehydration of the stratosphere is a complex phenomenon that is far from being spatially uniform over the entire vortex and at its edges. However, as a first study ever made on the complete nitrate isotopic composition in Antarctica, we consciously choose a simplification of the denitrification process, assuming a spatially uniform and isotropic denitrification process. Our aim here is to give the general directions on which further studies can sit on. In a second step, only when inter-annual variability being documented, we will be able to move forward and compare the stratospheric dynamic with the nitrate isotopic signal. We have archived more than 5 years of continuous aerosol collection, and such work is planned in the future. Regarding the possible isotopic
exchange, either in an aqueous phase/high concentrated electrolyte or stimulated by photo-absorption, the best proof of the absence of such isotopic exchanges is the presence of an oxygen isotopic anomaly that is preserved in nitrate, both in aerosols and in hundreds of years old ice (Alexander et al. 2004). Indeed, water doesn’t possess any oxygen isotopic anomaly and therefore if such exchange should have been efficient we would have observed an absence of such isotopic anomaly in the nitrate. Furthermore, water-nitrate oxygen isotopic exchange is only possible in aqueous phase at very low pH and high concentration (molar range) which permit the presence of nitrite, acting as a catalyst (Böhlke et al., 2003). If such conditions exist in the atmosphere, they play obviously a minor role. We further thank Adrian to bring to our attention the Miller’s paper (J. Chem. Phys, 110, 5342, 2006). It is a very interesting paper, and will be certainly referenced in one of our future lab experimental work. Currently, there is only one study dealing with the oxygen isotopic exchange between nitrate and ice under light influence (McCabe et al., 2005). According to this paper, the O exchange tends to be minimal toward lower temperatures and is small at -30°C, (exchange < 5%). However, we are conscious that this study has a major flaw by using nitrate salts as the doping agent instead of nitric acid. Mobility of O atom may be significantly impaired by the presence of the huge cation in the ice cage. So far the presence of an oxygen isotopic anomaly in atmospheric nitrate, in different phases and materials, at different locations and with similar value ranges is the best argument against oxygen isotopic exchanges.

References


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