Contribution ID: **19** Type: **Poster**

Post-depositional fractionation of nitrate stable isotopes in Antarctic snow: towards an ice core proxy of surface UV

Monday 6 June 2011 12:05 (1h 10m)

Recent studies on atmospheric particulate nitrate (NO3-) have shown that the nitrogen and triple oxygen stable isotopic composition of NO3- allows constraining atmospheric sources and sinks, in particular oxidation pathways of reactive nitrogen. However, extending this tool to past atmospheres using ice cores can be complicated by post-depositional mass loss and fractionation via UV-photolysis and evaporation. In regions, where these alterations are strong, we propose that the post-depositional process itself leaves a specific isotopic fingerprint in the snow, which can be related to past environmental surface conditions.

From this point of view we discuss a new 60-yr firn record of 15N/14N ratios in NO3- from Dome C, Antarctica (75° S, 123° E), which shows strong fractionation compared to the atmospheric signal. Recent estimates of the photolytic fractionation constant for the nitrogen isotope 15ε in snow based on a simple Zero-Point-Energy (ZPE) shift model are consistent with field and laboratory observations. This suggests that the isotopic enrichment observed is largely caused by post-depositional UV photolysis of nitrate. Therefore, the extent of isotopic enrichment is expected to depend on two factors: a) the residence time of a given snow layer within the photolytic zone of the upper snow pack, which in turn is controlled by accumulation rate variability and b) the spectrum of incident UV radiation. The latter depends mostly on the ozone over-head column, which has undergone significant changes over the past decades. Indeed, we find a strong correlation between nitrogen isotopic ratios and modeled annual UV radiation ($r = 0.7$, $p<0.001$). We then discuss sensitivities of isotopic fractionation to the variability in accumulation rate and timing. Past accumulation rate variability will introduce uncertainty in the use of the nitrogen stable isotope as a proxy of past UV radiation, but is among the parameters typically derived from ice core measurements.

Please list some keywords

nitrate photolysis, nitrate stable isotopes, Antarctica, ice core proxy, UV radiation

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Session Classification: Lunch and Poster