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Sustained surface nitrate recycling on the Antarctic plateau throughout the last climatic cycle : a stable isotopic view

Joseph Erbland (1), Joël Savarino (1), Samuel Morin (2), and Markus M. Frey (3)

(1) Université Joseph Fourier - Grenoble 1 / CNRS, LGGE, St Martin d'Heres Cedex, France, (2) Météo-France/CNRS, CNRM-GAME, Centre d'Etude de la Neige, St. Martin d'Hères, France, (3) British Antarctic Survey, Natural Environment Research Council, Cambridge, UK

Nitrate (NO_3^-) originates from the oxidation of nitrogen oxides (NO_x = NO + NO_2) in the atmosphere. Nitrate deposition to the surface of the snow is not irreversible especially at sites with low snow accumulation rates such as Vostok or Dome C (East Antarctica plateau). Indeed, nitrate undergoes strong post-depositional processing which hampers the interpretation of nitrate concentration records in ice cores in terms of past levels of atmospheric nitrogen. Nitrate loss from the snowpack followed by atmospheric gas-phase chemistry, deposition and/or transport is referred to as "recycling". This complex cycle is not well constrained, although the situation should improve thanks to measurements of the nitrogen stable isotopic ratios in nitrate, δ^{15}N. Indeed, high $\delta^{15}N(NO_3^-)$ values (up to $+339$ ‰) have been observed in the upper firn at Dome C and are attributed to nitrate recycling at the snow surface. The oxygen isotopic anomaly denoted Δ^{17}O reflects the influence of ozone (O_3) in NO_x oxidation chains and is generally used to trace the oxidation pathways leading to nitrate formation.

We measured the comprehensive isotopic composition (δ^{15}N, δ^{18}O, Δ^{17}O) of selected samples of nitrate from the Vostok ice core and found that throughout the last 150 000 years, δ^{15}N spans a range of [89; 316] ‰, δ^{18}O of [28; 71] ‰, and Δ^{17}O of [23; 36] ‰. High positive $\delta^{15}N(NO_3^-)$ values reveal that nitrate recycling has always occurred at the surface of the Antarctic plateau over this period. We suggest that this sustained recycling has some relevance to the nitrogen cycle in coastal Antarctica possibly explaining the extraordinarily low δ^{15}N values measured in nitrate from soils (e.g. in the dry valleys). More importantly, nitrogen export from the Antarctic plateau may fuel coastal ecosystems (marine and terrestrial) with an hitherto ignored additional reactive nitrogen source. The highest $\Delta^{17}O(NO_3^-)$ (36 ‰) are observed during glacial maxima suggesting 100% nitrate formation by ozone oxidation or a direct stratospheric oxidation.