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The oxygen isotope anomaly (Δ^{17}O) of nitrate in the Vostok ice core : insights in possible changes in NO_x oxidation pathways over the last 150 000 years

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The oxygen isotope anomaly of nitrate (Δ^{17}O) is increasingly used as an indicator of NO_x ($NO+NO_2$) oxidation pathways in the atmosphere. Nitrate deposited at the surface of ice sheets and ultimately recovered in ice cores is thus believed to harbour information about the oxidative capacity of ancient atmospheres. Unfortunately, post-depositional processes at the surface of low accumulation sites (e.g. Central Antarctica) drastically modify the concentration of nitrate and thus also affect its isotopic composition. New analytical methods of the comprehensive isotopic composition of nitrate in small nitrate samples allow to study ice-core nitrate samples from low accumulation sites. We measured the comprehensive isotopic composition of selected samples of nitrate from the Vostok ice core (Δ^{17}O, δ^{15}N, δ^{18}O) and found that throughout the last 150 000 years, Δ^{17}O spans a range of [23; 36]‰, δ^{18}O of [34; 66]‰, and δ^{15}N of [89; 306]‰. Recent studies carried out at Dome C (Antarctica) have showed strong post-depositional processes leading to δ^{15}N values higher than 300‰, i.e. as high as our observations at Vostok over the last 150 000 years, but having much lower impact on Δ^{17}O (changes on the order of 4‰ maximum). Our measured range of Δ^{17}O values over the last glacial cycle, larger than the predicted impact of post-depositional processing of nitrate, could thus be a direct signature of changes in the NO_x oxidation pathways. Combined isotopic measurements in nitrate are used to disentangle the signature of post-depositional processes and that of reactive atmospheric chemistry, thereby providing new constraints on the oxidative capacity of the Antarctic atmosphere at climatic timescales.