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Regional differences in the photochemical reaction paths of NO_X estimated from the $D^{17}O$ tracer of nitrate

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Anthropogenic activities emitted large quantities of NO_X to the atmosphere. NO_X are oxidized to nitrate via photochemical reactions with O_3 and OH radical. The photochemically produced nitrate finally depositied on to surface environments as dry and wet depositions during polluted air-mass transport. Increasing anthropogenic activities could increase the deposition flux. Besides, they could also change the photochemical reaction paths. However, it is difficult to determine the major photochemical path through the observation only on the concentration of either NO_X in atmosphere or nitrate in wet depostion.

The triple oxygen isotopic composition ($D^{17}O = d^{17}O - 0.52 * d^{18}O$) of nitrate can be a useful tracer to quantify the contribution of O_3 within the photochemical paths. The photochemically produced nitrate via O_3 having large ^{17}O anomaly shows large $D^{17}O$ value, whereas that via OH radical, by contrast, shows small $D^{17}O$ value. Thus, we could clarify the major photochemical oxidation path of NO_X using $D^{17}O$ values of depositional nitrate.

We have collected wet deposition (precipitation) samples extensively in Japan (Figure 1). Except for the site in sub-tropical region (Minamitorishima), the $D^{17}O$ values of nitrate showed distinct seasonal variations. In summer, the reaction between NO_X and OH is the dominant photochemical oxidation path for the production of nitrate. In contrast, the reaction of NO_X with O_3 becomes relatively important in winter. In addition, we found that the annual average $D^{17}O$ values at Sado-Seki and Kosugi were larger than that at Rishiri located at high latitude (Figure 1). Generally, as the contributions of O_3 increase with latitude, the annual average $D^{17}O$ values become larger in higher latitude. The inverse latitudinal distributions of $D^{17}O$ value can be explained by regional differences in the photochemical reaction paths of NO_X.

Keywords: triple oxygen isotope, photochemical reaction paths, nitrate

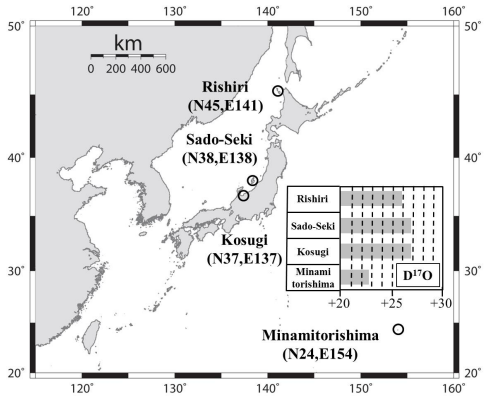

Figure 1 Sampling locations and annual average $D^{17}O$ values