Application of isotope analysis of nitrate and sulfate for ice cores and polar environments

Shohei Hattori[1], Naohiro Yoshida[1,2]

[1]*Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Japan*

[2]*Earth-Life Science Institute, Tokyo Institute of Technology, Japan*

Isotope analysis is generally known useful tool to identify sources and formation pathways for atmospheric trace species. So far, isotope analysis of SO_4^{2-} and NO_3^- preserved in ice core at Summit, Greenland, anthropogenic impact for atmospheric sulfur dioxide (SO_2) and nitrogen oxides (NO_x = NO + NO_2) have been reported (e.g. Patris et al., 2000; Hasting et al., 2009). In addition to conventional isotopes of $\delta^{15}N$ and $\delta^{34}S$, triple oxygen isotope compositions ($\Delta^{17}O$) and quadruple sulfur isotope compositions ($\Delta^{33}S$ and $\Delta^{36}S$) are new atmospheric finger prints which enable us to reconstruct how atmospheric reactions work/worked in the past and present atmosphere. In this presentation, we introduce general concepts, methods, and recent our studies applying isotope analysis of SO_4^{2-} and NO_3^- to polar environments.

1. Theory and concepts

With two, three and four isotopes for N, O, S respectively, a total six isotope ratios can be considered ($\delta^{15}N$, $\delta^{17}O$, $\delta^{18}O$, $\delta^{33}S$, $\delta^{34}S$, $\delta^{36}S$). Thus, SO_4^{2-} and NO_3^- are isotopically defined by three and four δ values, respectively. However, most of chemical and physical processes follow mass-dependent fractionation (MDF), following relationship hold for the oxygen and sulfur isotope systems.

$\delta^{17}O = 0.52 \times \delta^{18}O$

$\delta^{33}S = 0.515 \times \delta^{34}S$

$\delta^{36}S = 1.91 \times \delta^{34}S$

Thus, it had been unnecessary to measure all six δ values, as they were thought not to be providing useful information for long time. However, since Mark Thiemens and his colleagues at University of California in San Diego have found mass-independent fractionation (MIF) for oxygen in O_3 formation (Thiemens and Heidenreich, 1983) and sulfur in Archean Rock (Farquhar et al., 2000), and these new definitions of deviation from MDF are defined as following formulas and started to apply to various geochemical studies.

$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$

$\Delta^{33}S = \delta^{33}S - 0.515 \times \delta^{34}S$

$\Delta^{36}S = \delta^{36}S - 1.91 \times \delta^{34}S$

Atmospheric ozone (O_3) possesses high $\Delta^{17}O$ values of approximately 26‰ in contrast to most of the oxygen bearing compounds such as O_2 and H_2O which have $\Delta^{17}O$ values of approximately 0‰. The oxygen atoms of O_3 are directly or indirectly transferred to SO_4^{2-} and NO_3^- through the various oxidation pathways of their precursors, SO_2 and NO_x. For sulfur isotopes, a series of groundbreaking studies has shown that sulfur isotopes in sulfate from Plinian eruptions show MIF (e.g. Baroni et al., 2007), but background stratospheric sulfate aerosols from atmospheric carbonyl sulfide (OCS) and its breaking down OCS mainly photolysis, show no evidence of sulfur MIF (Hattori et al., 2011; Schmidt et al., 2013). Consequently, $\Delta^{17}O$, $\Delta^{33}S$ and $\Delta^{36}S$ are new proxy for the ice core and polar environmental studies.

2. Measurement methods

2.1 Nitrate

Previously, the measurements of nitrogen isotope and oxygen isotopes are needed separately, new approach that uses the generation of N_2O from NO_3^- reduction enable us to measure $\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$ simultaneously. Recently we developed automated method measuring $\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$ simultaneously by using the bacterial method (Sigman et al., 2001) coupled with N_2O decomposition via microwave-induced plasma (MIP) (Hattori et al., 2016).

2.2 Sulfate

In contrast to NO_3^-, isotope analysis of oxygen and sulfur for SO_4^{2-} need to be performed separately. For $\Delta^{17}O$ measurement of SO_4^{2-}, first SO_4^{2-} is separated from other ions by ion chromatographic method (Geng et al., 2013) or anion-exchange resin method (Le Gendre et al. 2017). Separated SO_4^{2-} chemically converted to silver sulfate, and this Ag_2SO_4 powder is converted to O_2 with high temperature (1000°C) for isotope measurements (see Geng et al., 2013; Ishino et al., 2017 for more detailed protocols). For $\Delta^{33}S$ and $\Delta^{36}S$, SO_4^{2-} is converted to SF_6 by fluorination for measuring SF_5^+ ions of m/z 127, 128, 129, 131.

3. Application for Antarctic study

Some studies have applied above methods for Antarctic ice cores (e.g. Sofen et al., 2014), but information of temporal and spatial variations of atmospheric SO_4^{2-} and NO_3^- are limited. In particular, there remain many theoretical assumptions for the controlling factors of $\Delta^{17}O$ of SO_4^{2-} and NO_3^- in those model estimations. To test one of those assumption that $\Delta^{17}O$ of O_3 have a flat value and do not influence the seasonality of $\Delta^{17}O$ values of SO_4^{2-} and NO_3^-, we performed the first simultaneous measurement of $\Delta^{17}O$ values of O_3, SO_4^{2-} and NO_3^- collected at Dumont d'Urville (DDU) Station, Antarctica. As a result, $\Delta^{17}O$ values of SO_4^{2-} and NO_3^- exhibited seasonal variation characterized by minima in the austral summer and maxima in winter, while $\Delta^{17}O$ values of O_3 showed no significant seasonal variation. These contrasting seasonal trends suggest that seasonality in $\Delta^{17}O$ values of atmospheric SO_4^{2-} and NO_3^- is not the result of changes in $\Delta^{17}O$ values of O_3, but of the changes in oxidation chemistry (Ishino et al., 2017). We have also measured $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ for the same samples, and found seasonal pattern of $\delta^{34}S$, showing not only biogenic sulfur source but also volcano and stratospheric sulfur sources might contribute in winter. In

addition, no significant deviation of sulfur MIF is found, suggesting different mechanisms worked for atmospheric SO_4^{2-} production of polluted air in which small sulfur MIF was typically observed.

Conversely, we also found the annual mean $\Delta^{17}O$ values for atmospheric SO_4^{2-} at coastal Antarctica (Ishino et al., 2017) is not matched with the $\Delta^{17}O$ values preserved in the inland Antarctic ice core records (e.g. Alexander et al., 2002; Sofen et al., 2014). In order to test this, spatial variation of isotopic compositions between coastal site and inland in eastern Dronning Maud Land, East Antarctica collected during the 54th and 57th Japanese Antarctic Research were performed. $\Delta^{17}O$ values of nss-SO_4^{2-} at the East Antarctica ranges from 2.2 to 3.3‰, and the $\Delta^{17}O$ value of nss-SO_4^{2-} for coastal site was lower than those for inland site. Thus, this result suggested that oxidizing chemistry for biogenic sulfur is different among coastal and inland sites, although small sulfur isotopic variations are observed and source of sulfur is biogenic and homogeneous (Uemura et al., 2016). For the isotopic compositions of NO_3^-, considerably increasing values of $\delta^{15}N$ of NO_3^- are observed from coastal to inland sites. The $\delta^{18}O$ and $\Delta^{17}O$ of NO_3^- values, on the other hand, decreases with increasing of $\delta^{15}N$ values, indicating the secondary formation of NO_3^-. Thus, spatial variations of isotopic compositions of NO_3^- reflect the post-depositional processes on the East Antarctic snow, as reported widely in Antarctica (Erbrand et al., 2013; Shi et al., 2016).

4. Application for Arctic study

In previous study, the decrease in $\delta^{15}N$ of NO_3^- is strongly correlated with fossil fuel emissions estimates since 1750 (Hasting et al., 2009), showing $\delta^{15}N$ as potential tool for reconstruction of past natural and anthropogenic NO_x emission. For $\Delta^{17}O$ in ice-core NO_3^- is also reported to provide information on past ratio of O_3 / (HO_2 + RO_2) (Geng et al., 2017). Certainly, nitrogen and oxygen isotopic compositions of NO_3^- provide information on changes in the nitrogen source and its formation pathways, but ice core records for NO_3^- concentrations and its isotopic compositions are problematic because of post depositional loss of NO_3^- via photolysis. Although Greenland generally have higher accumulation of snow than that in Antarctica, but post-depositional loss of NO_3^- in ice cores in Greenland is still controversial. We analyzed isotopic compositions of NO_3^- preserved in the high-accumulation dome ice core, South East Greenland (SE-Dome), which has a dome with high accumulation rate (about 1 m yr^{-1}) drilled by Iizuka and his colleagues (Iizuka et al., 2016). The nitrogen isotopic compositions for NO_3^- were generally lower than those reported in Summit, Greenland, suggesting that some extent of NO_3^- deposited in Summit was removed via photolysis. We found decreases of $\delta^{15}N$ of NO_3^- in SE-Dome, but no significant changes for $\Delta^{17}O$ during past 60 years.

References

Patris, N., R. J. Delmas, M. Legrand, M. De Angelis, F. A. Ferron, M. Stiévenard, and J. Jouzel, First sulfur isotope measurements in central Greenland ice cores along the preindustrial and industrial periods, J. Geophys. Res., 107(D11), 2002.

M. G. Hastings, J. C. Jarvis and E. J. Steig Anthropogenic Impacts on Nitrogen Isotopes of Ice-Core Nitrate, Science 324 (5932), 1288.

Thiemens, M.H. and J. E. Heidenreich III. The Mass-Independent Fractionation of Oxygen: A Novel Isotope Effect and Its Possible CosmoChemical Implications. Science 219:1073-1075, March 4, 1983.

Farquhar, J., Bao, H., & Thiemens, M. (2000). Atmospheric influence of Earth's earliest sulfur cycle. Science, *289*(5480), 756-758.

Baroni, M., Thiemens, M.H., Delmas, R.J., Savarino, J. Mass-independent sulfur isotopic compositions in stratospheric volcanic eruptions. Science 315, 84-8, 2007.

Hattori, S., Danielache, S. O., Johnson, M. S., Schmidt, J. A., Kjaergaard, H. G., Toyoda, S., Ueno, Y., and Yoshida, N.: Ultraviolet absorption cross sections of carbonyl sulfide isotopologues OC32S, OC33S, OC34S and O13CS: isotopic fractionation in photolysis and atmospheric implications, Atmos. Chem. Phys., 11, 10293-10303, 2011.

Schmidt, J. A., Johnson, M. S., Hattori, S., Yoshida, N., Nanbu, S., and Schinke, R.: OCS photolytic isotope effects from first principles: sulfur and carbon isotopes, temperature dependence and implications for the stratosphere, Atmos. Chem. Phys., 13, 1511-1520, 2013.

D. M. Sigman, K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, J. K. Böhlke A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater, Analytical Chemistry, 73 (17), 4145-4153, 2001.

Hattori, S., Savarino, J., Kamezaki, K., Ishino, S., Dyckmans, J., Fujinawa, T., Caillon, N., Barbero, A., Mukotaka, A., Toyoda, S., Well, R., Yoshida, N.: Automated system measuring triple oxygen and nitrogen isotope ratios in nitrate using the bacterial method and N2O decomposition by microwave discharge, Rapid Commun. Mass Spectrom., 30(24), 2635-2644, 2016.

Le Gendre, E., Martin, E., Villemant, B., Cartigny, P., and Assayag, N. A simple and reliable anion-exchange resin method for sulfate extraction and purification suitable for multiple O- and S-isotope measurements. Rapid Commun. Mass Spectrom., 31: 137–144, 2017.

Geng, L., Schauer, A. J., Kunasek, S. A., Sofen, E. D., Erbland, J., Savarino, J., Allman, D. J., Sletten, R. S., and Alexander, B.: Analysis of oxygen-17 excess of nitrate and sulfate at submicromole levels using the pyrolysis method, Rapid Commun. Mass Sp., 27, 2411–2419, 2013.

Ishino, S., Hattori, S., Savarino, J., Jourdain, B., Preunkert, S., Legrand, M., Caillon, N., Barbero, A., Kuribayashi, K., Yoshida, N.: Seasonal variations of triple oxygen isotopic compositions of atmospheric sulfate, nitrate and ozone at Dumont d'Urville, coastal Antarctica, Atmos. Chem. Phys., 17, 3713-3727, 2017.

Sofen, E. D., Alexander, B., Steig, E. J., Thiemens, M. H., Kunasek, S. A., Amos, H. M., Schauer, A. J., Hastings, M. G., Bautista, J., Jackson, T. L., Vogel, L. E., McConnell, J. R., Pasteris, D. R., and Saltzman, E. S.: WAIS Divide ice core suggests sustained changes in the atmospheric formation pathways of sulfate and nitrate since the 19th century in the extratropical Southern Hemisphere, Atmos. Chem. Phys., 14, 5749-5769, 2014.

R. Uemura, K. Masaka, K. Fukui, Y. Iizuka, M. Hirabayashi, H. Motoyama, Sulfur isotopic composition of surface snow along a latitudinal transect in East Antarctica, Geophysical Research Letters, **43**, 11, 5878, 2016.

Alexander, B., Savarino, J., Barkov, N. I., Delmas, R. J., & Thiemens, M. H. Climate driven changes in the oxidation pathways of atmospheric sulfur. Geophysical research letters, 29(14), 2002.

Erbland, J., Vicars, W. C., Savarino, J., Morin, S., Frey, M. M., Frosini, D., Vince, E., and Martins, J. M. F.: Air-snow transfer of nitrate on the East Antarctic Plateau – Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium in summer, Atmos. Chem. Phys., 13, 6403–6419, 2013.

Shi, G., Buffen, A. M., Hastings, M. G., Li, C., Ma, H., Li, Y., Sun, B., An, C., and Jiang, S.: Investigation of post-depositional processing of nitrate in East Antarctic snow: isotopic constraints on photolytic loss, re-oxidation, and source inputs, Atmos. Chem. Phys., 15, 9435-9453, 2015.

Geng, L., Murray, L. T., Mickley, L. J., Lin, P., Fu, Q., Schauer, A. J., & Alexander, B. "Isotopic evidence of multiple controls on atmospheric oxidants over climate transitions." Nature, 546.7656, 133-136, 2017

Iizuka, Y., Matoba, S., Yamasaki, T., Oyabu, I., Kadota, M., & Aoki, T. Glaciological and meteorological observations at the SE-Dome site, southeastern Greenland Ice Sheet. Bulletin of Glaciological Research, 34, 1-10, 2016.