Isotopic makeup of atmospheric sulfate and nitrate

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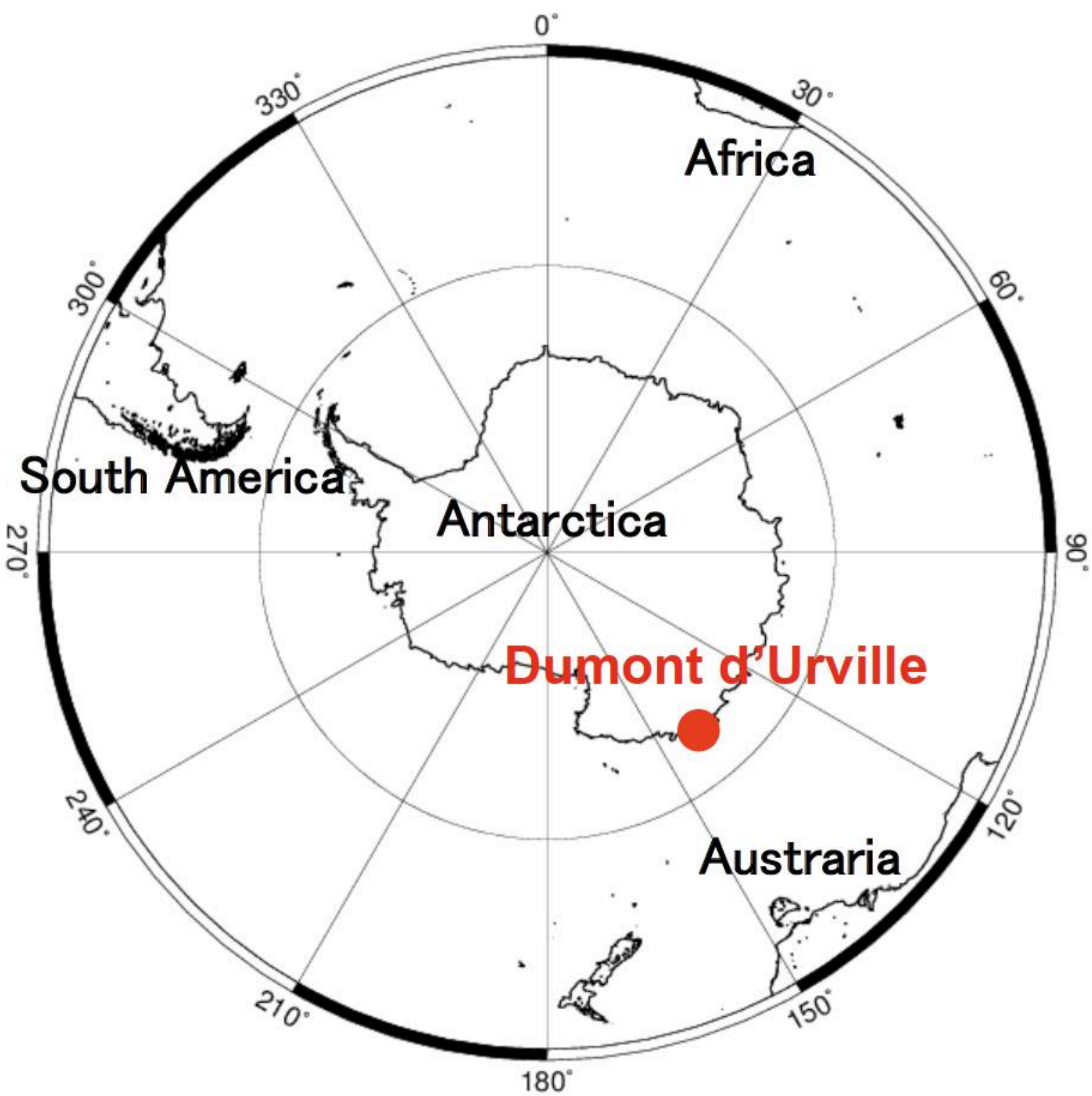
This photograph is by Sakiko Ishino in 2017 (supported by the French Polar Institute (Institut Polaire Français Paul Emile Victor).IPEV)) Credit: Sakiko Ishino, Tokyo Institute of Technology

Oxygen has three stable isotopes (^{16}O, ^{17}O and ^{18}O). Enrichment of ^{17}O relative to the dominant ^{16}O is normally about half of that of ^{18}O for various physicochemical processes, except for ozone (O_3) production, which uniquely enriches ^{17}O. This anomalous enrichment of ^{17}O ($\Delta^{17}O$) is inherited by other photochemical oxidants and oxidation products derived from the precursor ozone through various atmospheric oxidative pathways. Thus, the oxygen isotopic compositions of sulfate (SO_4^{2-}) and nitrate (NO_3^-) fluctuate seasonally, but the extent to which these seasonal changes are related to changes in isotopic compositions of ozone or to contribution of other photochemical oxidants is unknown. This can only be established by simultaneous measurement of oxygen isotopes in nitrate, sulfate, and ozone from the present-day Antarctic atmosphere. However, there is a paucity of such data, and the complex chemistry is only partly understood.

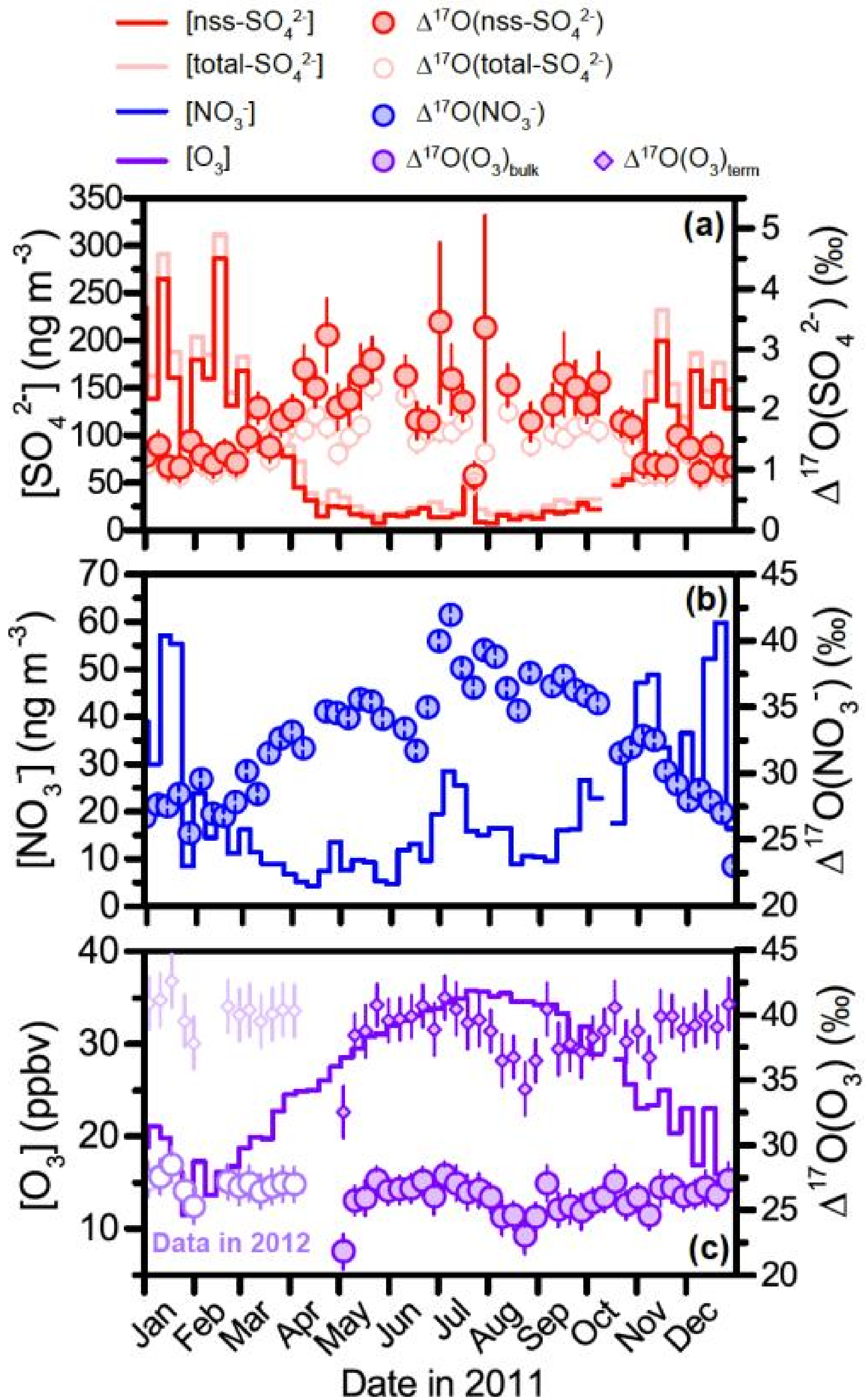
Because of its role in the life cycle of trace gases, reconstructing the oxidative capacity of the atmosphere is very important in understanding climate change. Triple oxygen isotopic compositions ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) of atmospheric sulfate and nitrate in Antarctic ice cores may have potential as atmospheric proxies of atmospheric oxidants because they reflect the oxidative chemical processes of their formation. This new approach may well allow scientists to peer back into the history of chemical reactions in the Antarctic atmosphere.

To address this challenge, Sakiko Ishino, Shohei hattori and colleagues from at Tokyo Institute of Technology and Université Grenoble Alpes, France conducted simultaneous measurement of $\Delta^{17}O$ values of atmospheric sulfate, nitrate and ozone collected at Dumont d'Urville, the coastal site in Antarctica. The French team collected aerosol samples weekly over a one-year period, Japan-French collaborative team conducted various analyses of the ionic species and isotopic compositions, and monitoring the movement of air masses over Antarctica. Both sulfate and nitrate oxygen isotopic compositions varied significantly over the course of a year, with minimum values in summer and maximum values in winter. Ozone, however, showed comparatively limited variability. The scientists were able to demonstrate that ozone variations have no significant influence on the seasonal fluctuations of sulfate and nitrate ^{17}O enrichment. Instead, these fluctuations are likely to reflect sunlight-driven changes in the relative importance of different oxidation pathways.



The location of Dumont d'Urville Station in Antarctica Credit: Tokyo Institute of Technology

Analysis of aerosols collected from Antarctic inland sites in the future should help identify the processes contributing to the formation of sulfate and nitrate during spring and fall. Extending the analysis to ice cores might aid in the quantitative estimation of changes to the atmospheric oxidation environment on Earth, for example, glacial cycles of the Pleistocene (Ice Age).



[nss-SO4 2-]
Δ17O(nss-SO4 2-)
[total-SO4 2-]
Δ17O(total-SO4 2-)
[NO3-]
Δ17O(NO3-)
[O3]
Δ17O(O3)bulk
Δ17O(O3)term
[SO4 2-] (ng m-3)
Δ17O(SO4 2-) (‰)
(a)
[NO3-] (ng m-3)
Δ17O(NO3-) (‰)
(b)
[O3] (ppbv)
Δ17O(O3) (‰)
Data in 2012
(c)
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
Date in 2011

Seasonal changes in the concentration (solid line) and ^{17}O enrichments of sulfate (top) and nitrate (center) are not due to changes in the ^{17}O values of ozone (bottom). Credit: Atmospheric Chemistry and Physics

More information: Sakiko Ishino et al, Seasonal variations of triple oxygen isotopic compositions ofatmospheric sulfate, nitrate and ozone at Dumont d'Urville, coastalAntarctica, *Atmospheric Chemistry and Physics Discussions* (2016). DOI: 10.5194/acp-2016-930

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