

High-sensitivity sulfur isotopic measurements for Antarctic ice core analyses[†]

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Sulfur isotopic measurements have been widely applied in earth sciences to investigate the origin and behavior of sulfur compounds in the lithosphere, hydrosphere, and atmosphere. Recently, sulfur isotopic analyses have also been utilized to elucidate the origin and circulation of various materials in nature in order to develop various scientific research fields, such as environmental, biological, archaeological, and so on.^{1,2)} Sulfur isotopic compositions are reported as per mil (‰) variations relative to a standard material (typically Vienna Canyon Diablo Troilite, VCDT) as follows:

$$\delta^{34}\text{S} = \left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{sample}} / \left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{standard}} - 1$$

In Antarctic ice and snow samples, it is considered that the sulfur isotopic ratios reflect the origin and pathway of sulfur compounds from their precursor materials, thus indicating the Antarctic environmental (hydrospheric and atmospheric) conditions. Sulfate and methane-sulfonic acids are the main sulfur components in ice and snow samples, and the sulfate ion is particularly dominant among those species. Several studies have examined the origins and geochemical implications of sulfates based on the sulfur isotopic composition of Antarctic ice and snow samples. Several studies^{3,4)} have analyzed the sulfur isotopic compositions of surface snow to investigate the origin of sulfate aerosols and their alteration during transport from coastal areas to the Antarctic interior. Sulfur isotopic compositions in ice cores elucidate the paleo-climatic changes: Cole-Dai *et al.*⁵⁾ and Baroni *et al.*⁶⁾ measured the sulfur isotopic compositions of ice core samples influenced by large volcanic eruptions (*e.g.* Pinatubo, Tambora) to investigate the origin and isotopic fractionation of sulfates during their transport through the stratosphere. In those studies, more than 200 g (containing more than 150 nmol sulfate) samples were required to obtain sulfur isotopic ($\delta^{34}\text{S}$) data.

We developed a high-sensitivity sulfur isotopic ($\delta^{34}\text{S}$) analytical system equipped with an elemental analyzer, a cryo-flow device, and an isotope ratio mass spectrometer, and established a measurement and calibration procedure. Using this system, we precisely measured the sulfur isotopic ratio ($\delta^{34}\text{S}$) of samples containing 5–40 nmol sulfate. Test runs were performed on samples from the Antarctic shallow ice core DF01. Figure 1 shows the depth profiles of the sulfate concentration and the sulfur isotopic ratio ($\delta^{34}\text{S}$) for the samples taken from DF01 at a depth of 8.49 to 9.39 m. The sample taken from a depth of 8.79 m depth is regarded as

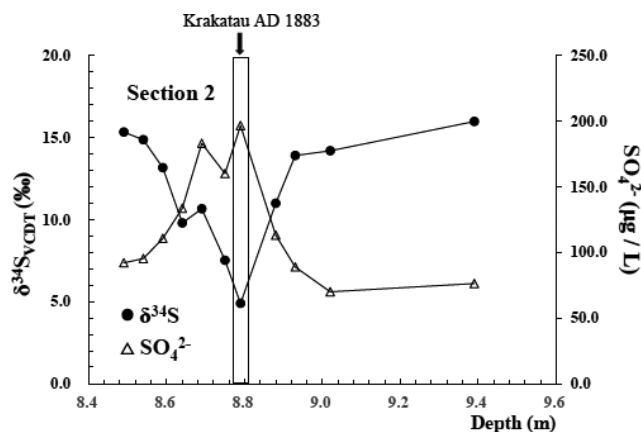


Fig. 1. $\delta^{34}\text{S}$ (solid circles) and sulfate concentration (open triangles) depth profiles for the two analyzed sections from ice core DF01. The minimum $\delta^{34}\text{S}$ value and the peak sulfate concentration at 8.79 m depth in section 2 are considered to be due to the AD 1883 eruption of the Krakatau volcano.

corresponding in time to the AD 1883 eruption of the Krakatau volcano. As shown in Fig. 1, it showed a peak sulfate concentration in its depth profile, which is considered to have resulted from a large volcanic eruption. The $\delta^{34}\text{S}$ value obtained at that depth in the sample was distinct from the values at other depths and consistent with the reported values for volcanic sulfates. The analytical system developed herein is a powerful tool for trace sulfur isotopic analyses. The results obtained from the DF01 ice core samples are the first step towards elucidating high-time-resolution (less than one year) paleo-environmental changes through sulfur isotopic analyses. Furthermore, the other analyses method shown in this study can be applied not only to the analyses of ice core samples, but also to other analyses, such as the analysis of tree rings,²⁾ which require small-scale analyses. Therefore, this measurement system is expected to be widely applicable to sulfur isotopic analyses in environmental and geochemical sciences.

References

- 1) F. Fourrel *et al.*, Proc. Earth Planetary Science **13**, 232 (2015).
- 2) P. M. Wynn *et al.*, Biochemistry **114**, 255 (2013).
- 3) R. Uemura *et al.*, Geophys. Res. Lett. **43**, (11), 5878 (2016).
- 4) N. Akata *et al.*, Seppyo **73**, (5), 339 (2011).
- 5) J. Cole-Dai *et al.*, Geophys. Res. Lett. **36**, (22), L22703 (2009).
- 6) M. Baroni *et al.*, Science **315**, 84 (2007).

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