

## Application of fluorination method to isotopologue biogeochemistry

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Clumped isotope geochemistry has been developed from the study on <sup>13</sup>C-<sup>18</sup>O clumping in carbonate/CO<sub>2</sub> system, which is now widely used as a geothermometer. The temperature dependence of the <sup>13</sup>C-<sup>18</sup>O clumping largely relies on rapid oxygen exchange between H<sub>2</sub>O and dissolved carbonate and subsequent precipitation quenching the <sup>13</sup>C-<sup>18</sup>O bonding in carbonate. In general, such a prerequisite for geothermometer is not met for the other molecules. For example, oxygen exchange between sulfate and water is known to be very slow. Hence, <sup>34</sup>S-<sup>18</sup>O-clumping in sulfate does not reflect precipitation temperature, but may be resulted from its source with distinct <sup>34</sup>S-<sup>18</sup>O-clumping [1]. Therefore, clumped isotopologues in other molecules could have potential to be utilized as a tracer for understanding biogeochemical cycling.

To extend the clumped isotopologue biogeochemistry, we have developed fluorination methods for measuring <sup>34</sup>S-<sup>18</sup>O-clumping in sulfate and for <sup>13</sup>C-<sup>13</sup>C clumping in ethane, ethene and ethanol [2]. In these fluorination methods, the samples are first converted into SO<sub>2</sub>F<sub>2</sub> or C<sub>2</sub>F<sub>6</sub>, which can simplify the analytical issue of isobaric interferences. Especially, <sup>13</sup>C<sub>2</sub>F<sub>6</sub> can be measured by conventional IRMS, not required high-mass resolution. Therefore, in principle, the fluorination method can be applicable to measure many other isotopologues in molecules including various organics.

In both systems, observed natural variations in  $\Delta^{34}\text{S}^{18}\text{O}$  and  $\Delta^{13}\text{C}^{13}\text{C}$  values are much wider than the expected temperature range assuming equilibrium [1,2]. Hence, in nature, isotopic ordering in <sup>34</sup>S-<sup>18</sup>O and <sup>13</sup>C-<sup>13</sup>C is not largely controlled by temperature, but reflect the processes accompanied by kinetic effect. In accord with the bulk isotope analysis, the S-O and C-C clumping could provide additional and independent insights into biogeochemical S, C and O cycling.

[1] Katsuta et al., in this volume; [2] Taguchi et al. (2020) *Rapid Commun Mass Spectrom.* 34, e8761. Taguchi et al. in this volume