

# Clumped isotope analyses of sulfate using HR-IRMS help decipher the global sulfur cycle

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Traditional oxygen and sulfur stable isotopes of sulfate are well established tools to investigate the biogeochemical sulfur cycle and atmospheric conditions in the modern environment and throughout Earth's history. In addition to conventional stable isotope systems, multiple substitutions of rare (heavy) isotopes in molecules ('clumping') in various analytes (e.g., CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O) have proven to be a valuable extension to the isotope geochemist's toolbox, with an increasing number of applications in Earth and atmospheric sciences.

We describe an all-new approach to analyze clumped isotopes of sulfate in geologic BaSO<sub>4</sub> samples by means of low-temperature fluorination and high-resolution gas source isotope ratio mass spectrometry (HR-IRMS). The analysis of the <sup>34</sup>S-<sup>18</sup>O isotopologue in the fluorination product SO<sub>2</sub>F<sub>2</sub> by conventional low-resolution IRMS is complicated by the interferences of interfering isotopologues which share the same cardinal mass as <sup>34</sup>S<sup>18</sup>O<sup>16</sup>OF<sub>2</sub> (e.g., <sup>36</sup>S<sup>16</sup>O<sub>2</sub>F<sub>2</sub>, <sup>34</sup>S<sup>18</sup>O<sup>16</sup>OF<sub>2</sub>, and <sup>32</sup>S<sup>18</sup>O<sub>2</sub>F<sub>2</sub>). HR-IRMS overcomes this limitation and enables the direct measurement of sulfate  $\Delta^{34}\text{S}^{18}\text{O}$  (Eq. 1) along with the conventional isotopic signatures  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{33}\text{S}$ .

$\Delta^{34}\text{S}^{18}\text{O} = \ln(\alpha^{34-18}) \cdot 1000$  (‰) with  $\alpha^{34-18} = \frac{{}^{34-18}\text{R}_{\text{sample}}}{{}^{34-18}\text{R}_{\text{random}}}$  (Eq. 1)

We show that the relative abundance of co-substituted <sup>34</sup>S and <sup>18</sup>O in sulfate can be analyzed at high precision by means of HR-IRMS, providing a new and unique tool to identify original sulfate sources and to reconstruct the global sulfur cycle.