# A new method for measuring $^{34}S$-$^{18}O$ clumping of sulfate

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We have developed a new $SO_2F_2$ method to analyze both sulfur and oxygen isotopes of sulfate simultaneously as well as measuring a S-O clumped isotopologue ($^{34-18}\Delta$). First, we have succeeded to transform sulfate into $SO_2F_2$ quantitatively by fluorination reaction of barium sulfate ($BaSO_4$) and elemental fluorine ($F_2$) at 280°C. By using this method, over 90% yield can be attained for international standard $BaSO_4$ sample, NBS127. The produced $SO_2F_2$ can be purified by gas chromatography, and then measured by a high-mass-resolution mass spectrometer (MAT253-Ultra). The developed analytical protocol allows us to measure $\delta^{34}S$, $\Delta^{33}S$, $\delta^{18}O$ and $^{34-18}\Delta$ values simultaneously with a precision of ±0.1 ‰, ±0.03 ‰, ±0.3 ‰ and ±0.2 ‰, respectively. Preliminary analysis of two Archean barite samples show negative $^{34-18}\Delta$ values by about 0.5 ‰ with respect to the standard NBS127, which represents sulfate deposited from modern seawater. The observed high $^{34}S$-$^{18}O$ clumping in modern seawater sulfate is qualitatively consistent with the oxidative weathering as a main sulfate source into ocean. This may suggest a possibility that the $^{34}S$-$^{18}O$-bonding in seawater sulfate increased in response to the enhanced oxidative weathering.