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Quantitative conversion of sulfate oxygen for high-precision triple oxygen isotope analysis

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Triple oxygen isotope composition ($\Delta'^{17}O$) of sulfate carries information on sulfur cycle as well as signatures of atmospheric O_2, O_3, and surface water of the geological past. However, existing analytical techniques can only achieve partial oxygen yield during the conversion from sulfate to the analyte O_2, which results in isotope fractionation and impedes the $\Delta'^{17}O$ comparison with other oxygen-bearing compounds (e.g., H_2O) on the VSMOW-SLAP scale. Here, we present an analytical method involving high-temperature graphite reduction, CO discharge, and Pt-catalyzed CO_2-O_2 isotope exchange, the R-D-E method, that achieves ~100% conversion of sulfate oxygen to CO_2. Compared with the widely-used CO_2-laser-fluorination technique, our R-D-E method has a better $\Delta'^{17}O$ precision (9 per meg) and requires a smaller sample amount, as low as 4 μmol of sulfate (equivalent to 1 mg $BaSO_4$), with both $\Delta'^{17}O$ and $\delta^{18}O$ being determined simultaneously. Using this method, we report the triple oxygen isotope compositions of three international reference materials (NBS127, IAEA-SO-5, and IAEA-SO-6) and three in-house references on the VSMOW-SLAP scale. We found that the sulfate $\Delta'^{17}O$ values measured on the partially-yielded O_2 from the fluorination technique are 10−200 per meg higher than those obtained by our R-D-E method, depending on the oxidant used (e.g., F_2 or BrF_5). Incomplete conversion of sulfate oxygen during the high-temperature graphite reduction would result in lower $\delta^{18}O$ and higher $\Delta'^{17}O$ values. This work highlights the needs for recalibration and re-interpretation of the published sulfate $\Delta'^{17}O$ data when sulfate $\Delta'^{17}O$ values of interest are small.