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The triple oxygen isotope composition of sulfate on the VSMOW-SLAP scale using a novel fully automated high-temperature reduction, CO to CO_2 conversion and high precision laser spectroscopy method

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The investigation of all three stable oxygen isotopes (^{16}O, ^{17}O, ^{18}O) is a constantly advancing approach in the field of geochemistry. Laser fluorination methods to analyze triple oxygen isotope variations ($\Delta'^{17}O$) of silicate or oxide samples to the lower per meg scale are now well established. For other solid samples, such as sulfate, the same analytical approach lacks such very high precision, mainly due to low yields. Furthermore, the high reactivity of water prevents respective triple oxygen isotope analyses using the same approach. Therefore, accurately referencing samples to the VSMOW-SLAP standard reference scale is not straight forward.

We present an analytical approach that is well suited for sulfate and water, but also for other Earth materials, such as organics. The material in question is introduced into a Thermo Finnigan High Temperature Conversion Elemental Analyzer (TC/EA) at temperatures ≥1350°C to convert all sample oxygen into CO. The CO is then collected and transferred to a discharge reactor where it is converted to CO_2 with the help of high voltage electric discharge [1]. The CO_2 is analyzed for triple oxygen isotopes using a Aerodyne Research tunable infrared laser direct absorption spectrometer (TILDAS). All three individual steps are already used for high precision $\Delta'^{17}O$ analyses [2,3,4], but not in this combination. The custom-built reduction and conversion line is fully automated, ensuring high reproducibility and sample throughput.

The TC/EA approach allows for the direct calibration of international sulfate standards and other material to the VSMOW-SLAP reference scale by analyzing VSMOW and SLAP waters within the same analytical session and protocol. The method thus provides high accuracy and reproducibility in $\Delta'^{17}O$ (<10 per meg 1σ) while requiring small sample amounts (21 µmol $O_2 \triangleq 2.5$ mg $BaSO_4$). For sulfate, water and benzoic acid a quantitative yield is achieved, effectively avoiding isotope fractionation and $\Delta'^{17}O$ variations linked to partial oxygen release.

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