Supplementary information

Preparation and characterization of new sulfate reference materials for $\Delta^{17}O$ analysis

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Supplementary Information Text

Text 1 The details of $\Delta^{17}O$ (SO_4^{2-}) measurement using pyrolysis system

For sample analysis, sliver sulfate samples in home-made quartz or platinum capsules are loaded in the zero-blank autosampler sitting on top of TC/EA. The sample is then delivered to the pyrolysis tube inside TC/EA, where Ag_2SO_4 is heated at 1000 °C to produce O_2 and byproducts (e.g., SO_2). The gas products are carried by He to a LN_2 trap where condensable gases are scrubbed while O_2 passes through. For samples with micromole levels of SO_4^{2-}, O_2 from the LN_2 trap is introduced directly to the high-flow peripheral of ConFlo IV after further purified by a 60 cm gas chromatography (GC) column (1/4") packed with 5 Å molecular sieve held at 30 °C, and then to the IRMS for *m/z* 32, 33, and 34 measurements. This is the TC/EA-IRMS mode as indicated in Figure 2.

For samples with sub-micromole levels of SO_4^{2-}, the produced O_2 has to be first concentrated by the home-made pre-concentration system prior to entering IRMS, otherwise the sample peak would be too small to be precisely quantified.[1] This is the TC/EA-Precon-IRMS mode as shown in Figure 2, where O_2 after the LN_2 trap is first trapped in a 60 cm stainless steel 1/16" tubing packed with silica gel (Trap A) at LN_2 temperature through an eight-way valco valve at the load position. After 5 minutes of trapping, the valco valve is switched to inject position. Then 'Trap A' is thawed and O_2 is transferred to a second cold trap (Trap B) which is a 60 cm capillary tubing packed with silica gel. After O_2 is transferred to 'Trap B', it is then thawed and O_2 is carried to a capillary GC (5 Å molecular sieve, 30 m × 0.32 mm i.d., Agilent Technologies Inc., USA) at 30 °C where O_2 is further purified before entering IRMS through the low-flow peripheral of ConFlo IV.

Table S1. The raw $\Delta^{17}O$ values of sulfate measured in quartz capsules from all experiments. The Na_2SO_3 mass indicates the starting amount of sulfide in solution; amount of O_3 trapped was indicated by total trapping time (total trapping time = trapping times × 20 minutes each time); Total reaction time indicates the total duration of O_3 thawing in an experiment; Yield is referred to the fraction of sulfate in solution after an experiment.

Number	Mass of Na_2SO_3(g)	Total trapping time (minute)	Total reaction time (minute)	Yield (%)	Raw $\Delta^{17}O$ (‰)
Sulf-A					
S1-H_2O_2	1.8	NA	NA	100	0.0
S21-O_3	0.63	100 (5 × 20)	220	70	1.2
S39-O_3	1.26	160 (8 × 20)	440	100	1.1
Sulf-B					
S2-H_2O_2	0.7	NA	NA	100	0.0
S13-O_3	0.0252	20 (1 × 20)	40	100	3.0
S14-O_3	0.063	40 (2 × 20)	90	100	2.8
S15-O_3	0.063	40 (2 × 20)	60	50	2.0
S17-O_3	0.189	60 (3 × 20)	110	100	1.8
S22-O_3	0.063	60 (3 × 20)	80	100	1.8
S24-O_3	1.26	200 (10 × 20)	420	100	1.5
S25-O_3	0.63	160 (8 × 20)	390	100	1.8
S30-O_3	0.063	60 (3 × 20)	100	100	3.0
S31-O_3	0.063	60 (3 × 20)	90	100	2.5
S33-O_3	0.063	60 (3 × 20)	110	100	3.6
S34-O_3	0.063	60 (3 × 20)	100	100	2.5
S35-O_3	0.063	60 (3 × 20)	110	100	3.0
S36-O_3	0.063	60 (3 × 20)	140	100	3.3
S37-O_3	0.063	60 (3 × 20)	120	100	2.8
S38-O_3	0.063	60 (3 × 20)	120	100	2.6
S40-O_3	0.063	60 (3 × 20)	110	100	2.3
S41-O_3	0.063	60 (3 × 20)	120	100	2.6
S42-O_3	0.063	60 (3 × 20)	120	100	3.0
Sulf-C					
S16-O_3	0.063	60 (3 × 20)	150	100	4.1
S19-O_3	0.063	60 (3 × 20)	200	100	5.7
S26-O_3	0.063	60 (3 × 20)	180	100	5.0
S28-O_3	0.063	60 (3 × 20)	160	100	4.6
S29-O_3	0.063	60 (3 × 20)	160	100	5.0
S32-O_3	0.063	60 (3 × 20)	150	100	4.2
S43-O_3	0.063	60 (3 × 20)	130	100	4.7
S44-O_3	0.063	60 (3 × 20)	180	100	4.7
S45-O_3	0.063	60 (3 × 20)	180	100	4.5
S46-O_3	0.063	60 (3 × 20)	200	100	5.0
S47-O_3	0.063	60 (3 × 20)	260	100	6.7
S48-O_3	0.063	60 (3 × 20)	265	100	7.3
S49-O_3	0.063	60 (3 × 20)	265	100	7.3
S50-O_3	0.063	60 (3 × 20)	260	100	6.5

S51-O_3	0.063	60 (3 × 20)	255	100	6.7
S52-O_3	0.063	60 (3 × 20)	265	100	7.2
S53-O_3	0.063	60 (3 × 20)	270	100	6.7
S54-O_3	0.063	60 (3 × 20)	235	100	6.2
S55-O_3	0.063	60 (3 × 20)	255	100	5.9
S56-O_3	0.063	60 (3 × 20)	250	100	5.7
S57-O_3	0.063	60 (3 × 20)	200	100	5.4
S58-O_3	0.063	60 (3 × 20)	200	100	5.3
S59-O_3	0.126	100 (5 × 20)	360	100	5.2
S60-O_3	0.063	60 (3 × 20)	180	100	4.0
S61-O_3	0.063	60 (3 × 20)	190	100	4.3
S62-O_3	0.063	60 (3 × 20)	205	100	4.8
Silica gel					
S18-O_3	0.063	60 (3 × 20)	110	20	0.4
S10-O_3	0.063	100 (5 × 20)	240	30	0.6
S11-O_3	0.0063	20 (1 × 20)	40	20	1.0
N-O_3					
Number	**Mass of $NaNO_2$(g)[a]**	**Total trapping time (minute)**	**Total reaction time (minute)**	**Yield**	**Raw $\Delta^{17}O$ (‰) (n=4, 1σ)**
N1-O_3	0.0069	40 (2 × 20)	80	100	14.3 ± 0.1
N2-O_3	0.0138	80 (4 × 20)	150	100	14.2 ± 0.1

a. Measured in silver capsules.

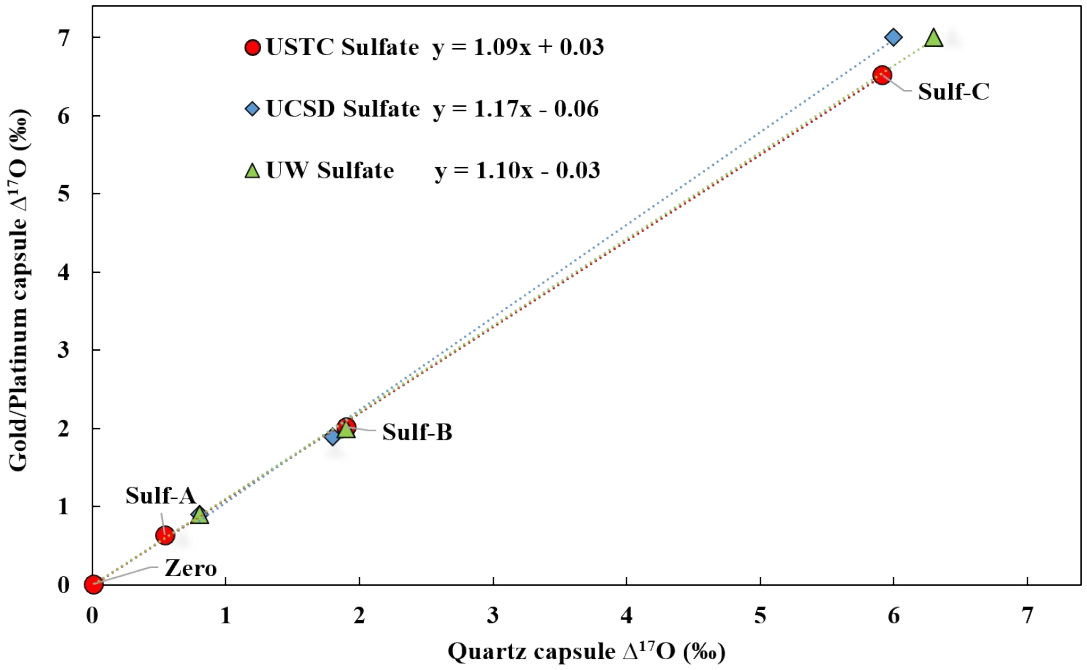

Figure S1. Mean $\Delta^{17}O$ values of Sulf-A, Sulf-B and Sulf-C measured in platinum capsules versus in quartz capsules. Results of similar phenomena (i.e., oxygen isotope exchange with quartz) from UW[2] and UCSD[3] were also plotted for comparison.

References

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