Evidence of magnetic isotope effects during thermochemical sulfate reduction

Harry Oduro*, Brian Harms*, Herman O. Sintim†, Alan J. Kaufman‡, George Cody§, and James Farquhar**

*Department of Geology and Earth System Science Interdisciplinary Center (ESSIC), University of Maryland, College Park, MD 20742; ‡Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742; †Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015; and ‡Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307

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Thermochemical sulfate reduction experiments with simple amino acid and dilute concentrations of sulfate reveal significant degrees of mass-independent sulfur isotope fractionation. Enrichments of up to 13% for $^{33}$S are attributed to a magnetic isotope effect (MIE) associated with the formation of thiol-disulfide, ion-radical pairs. Observed $^{32}$S depletions in products are explained here by classical (mass-dependent) isotope effects and mixing processes. The experimental data contrasts strongly with multiple sulfur isotope trends in Archean samples, which exhibit significant $^{34}$S anomalies. These results support an origin other than thermochemical sulfate reduction for the mass-independent signals observed for early Earth samples.

Since the report by Farquhar et al., (1) that significant deviations from the terrestrial fractionation line are observed in samples older than approximately 2.32–2.45 Ga (2, 3), considerable effort has been dedicated to identifying the origin and significance of this signal (4–10). The mass-independent signal in these ancient samples is expressed as variations in both $\Delta^{33}$S and $\Delta^{34}$S (1, 4). Given the observations that gas-phase reactions can produce mass-independent signals for both $\Delta^{33}$S and $\Delta^{34}$S, the first studies on this subject attributed this ancient signal to photolytic reactions in the early atmosphere. Subsequent studies also pointed out that the mass-independent reactions may also be produced by variations in the spectrum of light that drives atmospheric photolytic reactions (10–12), and other studies speculated that liquid phase reactions involving weakly bound transition states may account for these variations (7, 13).

In a recent report, Watanabe et al. (7) demonstrated that high temperature reduction of sulfate using alanine and glycine as organic substrates caused moderate mass-independent sulfur isotope fractionations. These authors did not identify the origin of the effect, but suggested that it was either a magnetic isotope effect (MIE) (14) or another type of isotope effect accompanying heterogeneous reactions such as adsorption of S-bearing compounds on surfaces of solids (13). Magnetic isotope effects are expressed in rare cases for isotopes with nuclear magnetic moments, like $^{13}$C, $^{17}$O, $^{29}$Si, $^{199}$Hg, $^{201}$Hg, $^{73}$Ge, $^{23}$U, and $^{33}$S (14, 15, 16). The effect is expressed when the lifetime of a radical pair is sufficient for hyperfine coupling between magnetic nuclei and unpaired electrons to influence interconversions between singlet and triplet states. This coupling in turn changes the proportion of reactive intermediates that can participate in spin-selective reactions. The $^{33}$S nucleus has a spin of 3/2 and a magnetic moment of 0.643 nuclear magnetons and has been implicated in at least one well-characterized example of a $^{33}$S MIE (14, 17–19).

The alternative suggestion relates to a proposal that anomalous isotope effects may be associated with heterogeneous reactions as a result of possible missing vibrational levels involving very weak bound transition states (13). This proposal has been contested by Balan et al. (20), who argue that no effect exists when a more complete treatment of the reaction mechanisms is undertaken.

The flow through reactor experiments yielded two distinct sulfur products as seen in Table S1 (gaseous H$_2$S and chromium-reducible sulfur (CRS)) with anomalous $^{33}$S enrichments (11) from $+0.25$ to $+13.1\%$o, but no significant change in $^{32}$S composition from starting sulfate (Fig. 1A and B). In Carius tube experiments, $^{33}$S enrichments in acid volatile sulfide (AVS) and CRS products were small to undetectable except when S$_2$O or Na$_2$S$_2$O$_5$ was added (see Table S2) to catalyze reduced sulfur production in the reaction products. The mechanistic aspects for the origin of $^{33}$S anomalies via disulfide ion-radical pair reaction routes have been proposed through multiple sulfur isotope measurements and $^{33}$S electron spin resonance (ESR) spectroscopic evidence (24, 25).

Results and Discussion

The flow through reactor experiments yielded two distinct sulfur products as seen in Table S1 (gaseous H$_2$S and chromium-reducible sulfur (CRS)) with anomalous $^{33}$S enrichments (11) from $+0.25$ to $+13.1\%$o, but no significant change in $^{32}$S composition from starting sulfate (Fig. 1A and B). In Carius tube experiments, $^{33}$S enrichments in acid volatile sulfide (AVS) and CRS products were small to undetectable except when S$_2$O or Na$_2$S$_2$O$_5$ was added (see Table S2) to catalyze reduced sulfur production in the reaction products. The flow through reactor experiments yielded two distinct sulfur products as seen in Table S1 (gaseous H$_2$S and chromium-reducible sulfur (CRS)) with anomalous $^{33}$S enrichments (11) from $+0.25$ to $+13.1\%$o, but no significant change in $^{32}$S composition from starting sulfate (Fig. 1A and B). In Carius tube experiments, $^{33}$S enrichments in acid volatile sulfide (AVS) and CRS products were small to undetectable except when S$_2$O or Na$_2$S$_2$O$_5$ was added (see Table S2) to catalyze reduced sulfur production in the reaction products. The mechanistic aspects for the origin of $^{33}$S anomalies via disulfide ion-radical pair reaction routes have been proposed through multiple sulfur isotope measurements and $^{33}$S electron spin resonance (ESR) spectroscopic evidence (24, 25).

1. Prolonged heating of glycine (mp = 262°C) affords three major classes of compounds: (i) small neutral molecules, (ii) carbon and other carbon-based polymers, and (iii) radical intermediates (both heteroatom and carbon-centered radicals) as indicated in Scheme 1 below (27, 28).
2. Sodium sulfate can then be reduced by some of the reducing gases produced in Scheme 1 (e.g., H$_2$, CO, etc.) to give sodium

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**H.O. and J.F. designed research; H.O. and J.F. performed research; H.O. and J.F. contributed new reagents/analytic tools; H.O., B.H., H.O.S., A.J.K., G.C., and J.F. analyzed data; and H.O., B.H., H.O.S., and J.F. wrote the paper.

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1*Here, $\Delta^{33}$S = (1/$^{32}$S)$_{sample}$/(1/$^{32}$S)$_{std}$ and $\Delta^{34}$S = (1/$^{32}$S)$_{sample}$/(1/$^{32}$S)$_{std}$ for different reactions and does not impact the conclusions of this study.

1†Whom correspondence may be addressed. E-mail: hoduro@umd.edu, hoduro@mit.edu, or jfarquha@glue.umd.edu.

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sulfide (1, 2). Trace metal impurities in sodium sulfate can catalyze this reaction. Solid carbon or carbon-based polymers, generated during pyrolysis can also reduce sodium sulfate to sodium sulfide (29, 30) (3):

Na₂SO₄ + 4CO → Na₂S + 4CO₂. [1]
Na₂SO₄ + 4H₂ → Na₂S + 4H₂O, and  [2]
Na₂SO₄ + nC → Na₂S + CO + CO₂.  [3]

3. Sodium sulfide in the presence of trace acid and/or water and heat will generate hydrogen sulfide (H₂S) (4). The acid/water would come from the H₂O, HCN, and COOH generated during glycine pyrolysis (see Scheme 1) or even from the glycine starting material,

Na₂S + 2H-Y → 2NaY + H₂S (Y,CN or OH or H₂NCH₂COO⁻). [4]

4. Hydrogen sulfide can undergo thermolysis (31, 32), which can react with radical intermediates generated during glycine pyrolysis (see Scheme 1) to give thyl radicals as in [5] and [6] (33). Note that these reactions are not spin-selective so no δ¹³S anomaly will result,

HS-H + R’ → HS’ + RH  R, carbon-centered radical  [5]

HS-H + Y’ → HS’ + HY  [6]
Y, heteroatom-centered radical.

5a. The thyl radical (HS’) can recombine with other radicals to give neutral, sulfur-containing molecules. Reactions between free radicals (e.g., 7–9) can be spin-selective (34). The absence of measureable sulfur-33 enrichment in the carbon-bound sulfur (Raney Ni fraction) suggests however that this reaction is not the origin of the isotope effect in these experiments,

HS’ + H’ = [HS’ ‘H]ᵀS → HSH. [7]
HS’ + R’ = [HS’ ‘R]ᵀS → RSH, and [8]
HS’ + ‘Y’ = [HS’ ‘Y]ᵀS → YSH
Y, heteroatom, R, carbon-centered radical. [9]

5b. The products of [7], [8], and [9] can undergo further homolytic cleavage of S-H bonds shown in Scheme 2 to give thyl radical moieties (‘SH, ‘SY, and ‘SR). These thyl radicals have strong reactivity and can also react with other radicals to form polysulfide products via sulfur polymerization (10). Such reactions will not produce sulfur-33 enrichments due to strong spin-orbit coupling (see below),

RS’ + HS’ = [RS’ ‘SH]ᵀS → RS₂H. [10]

6. The thyl radical can also abstract hydrogen from C-H bonds to give carbon-centered radicals. These reactions will not be spin-selective,

HS’ + H-R → H₂S + R’  and  [11]
HS’ + H-R → RSH + R’. [12]

Based on the above sequence of reactions, we propose Scheme 2, which describes the pathway envisioned for production of the observed sulfur-33 enrichments in Cr-reducible sulfur and hydrogen sulfide. We have generalized this sequence of reactions

Scheme 1. Pyrolytic decomposition products of glycine. Solid-state NMR and high resolution ESI-MS (in positive mode) confirm the presence of polymers in the reaction mixture.
by writing it for only R (and not Y and H sulfur bonded radicals). During accidental encounter of free radicals (reactions A and B) in Scheme 2, the statistical distribution of radical pair spin states will be one-fourth singlet and three-fourths triplet states. MIE may occur if this 1:3 proportion is altered by the rapid formation of singlet products upon initial encounter, leaving an excess (>three-fourths) of triplet radical pairs that undergo triplet to singlet conversion. However, these reactions are an unlikely source of MIE because it has been shown that thyl radicals exhibit strong spin-orbit coupling (35, 36) and therefore are expected to experience rapid spin flipping independent of hyperfine coupling.

We instead suggest that the observation of 33S enrichments in the CRS fraction implicates MIE associated with the formation of polysulfide species [reaction C (Scheme 2) and the subsequent network highlighted in the red box]. We suggest this polymerization reaction of sulfur product is mediated by an ion-radical mechanism similar to that proposed by Buchachenko et al. (26). Here RSH acts as an electron donor to RSSH, forming an ion-radical pair intermediate that is initially in a singlet state. Coulombic attraction inhibits dissociation of the radical pair. Here, the radical pair may either (i) reform the original reactants by back electron transfer, (ii) slowly lose H$_2$S$_n$ (where n = 0 or 1) in a non-spin-selective manner, or (iii) undergo singlet to triplet conversion via 33S hyperfine coupling. Back electron transfer from the triplet state is spin forbidden, and therefore the radical pair must lose H$_2$S$_n$ to form an RS$^+\cdot$$_n$/RSS$^-$ radical pair. Subsequent triplet-singlet conversion allows for the radical pair to regenerate singlet species as well as their radical species in a variety of natural systems where organic matter and sulfur radicals are present [e.g., where sulfur radicals control petroleum maturation (37)]. It is possible therefore that sulfur MIE are generated in some settings, and evidence for this effect should be sought.

Experimental Procedure and Methods
Two sets of experiments were undertaken to monitor the products of TSR: (i) flow-reactor experiments and (ii) Carius tube experiments. Reagent grade sodium sulfate (~0.5 mol/L) and powdered glycine were used in both experiments,

$$\text{SO}_4^{2-} + 2\text{H}_2\text{N-CH}_2\text{COOH} + \text{H}_3\text{O}^+ \xrightarrow{(w)\Delta\text{Heal}} \text{H}_2\text{S} + 3\text{CO}_2 + [\text{CH}_2]^+ + 2\text{NH}_3 + 3\text{H}_2\text{O}.$$  

[13]

For the flow reactor experiments, glycine and 1.0 mL sodium sulfate solution were added to a reaction flask, matching the stoichiometry of [13], which was heated continuously at approximately 300°C for 340 h under 15 bubbles/min nitrogen flow. Water lost to evaporation was replenished by injecting 0.5 mL of Milli-Q water through a septum in the reaction flask [three or four times per experiment (Table S1)]. Product hydrogen sulfide carried by the nitrogen flow was isolated by trapping with a Zn-acetate buffer, yielding a white crystalline ZnS precipitate. Solid and liquid residues in the reaction flask were treated by procedures outlined for the Carius tube experiments.

High-purity Pyrex glass Carius tubes (dimension 35.5-cm long, 12-mm outer diameter, ~1.2-mm wall thickness) were loaded with 0.5 mL sodium sulfate solution and glycine to match the
stoichiometry of [13]. Two experiments also included sulfur inter-
mediate species, \( \text{S}_2 \) and \( \text{Na}_2\text{S}_2\text{O}_5 \) (Table S3), to catalyze the pro-
duction of sulfide in reaction products. Sample tubes were placed in a stainless steel jacket before being heated in a muffle furnace at temperatures listed in Table S1. After heating, the Carius tubes were chilled with liquid-nitrogen, crack-opened, and zinc acetate added to fix sulfide.

Solid and liquid fractions were isolated from the Carius tubes and placed into a flask for sequential extraction. The sulfur from reaction products were extracted using sequential reaction with 5 N HCl for AVS; Cr(II) acid distillation in ethanol for S-S\(_n\) (where \( n \geq 1 \) fractions (CRS); Raney Ni desulfurization for carbon bonded sulfur; Thode reducible sulfur for sulfates; and Eschka oxidized sulfur for total organic sulfur (methods described in ref. 38). Recovery was incomplete because some material adhered to the Carius tube wall, but upper estimates of the fraction of Carius Cr-reducible sulfur and Raney Ni redu-
cible sulfur is provided in Table S2. The proportion of Cr-reducible and Raney Ni reducible sulfur relative to Eschka- and Thode-sulfur was determined by the Clime method (39) using a UV-visible double beam (model UVD-3200) scanning spectro-
photometer (Labomed Inc.) before converting sulfur into Ag\(_2\)S for fluorination in Ni bombs, conversion to SF\(_6\) by heated reac-
tion with F\(_2\), and subsequent S-isotopic analysis in a dual inlet ThermoFinnigan-253 mass spectrometer.

A solid-state NMR was acquired for residual solid fractions after the experiments using a Varian/Cheinametics Infinity 300 solid-state NMR spectroscopy. High resolution electrospray ion-
ization (ESI)–MS (resolving power 6,000 fwhm) were also taken for liquid fractions in both a positive ion mode using an AccuTOF (JEOL USA, Inc.) TOF–MS. The spray voltage was set to 2.3 kV, and the capillary and orifice temperatures were maintained at 250 °C and 80 °C, respectively. The instrument was typically operated at the following potentials: orifice 1 = 30 V, orifice 2 = 5 V, ring lens = 10 V. The rf ion guide voltage was generally set to 1,000 V to allow detection of ions greater than \( m/\varepsilon = 100 \). Both solid-state NMR and ESI–MS analyses confirm the presence of neutral molecules, complex carbon-based macromolecules, and polymers that were formed through radical condensation reactions.

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20. Balan E, et al. (2009) Theoretical investigation of the anomalous equilibrium fractiona-
Supporting Information

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SI Text
Analysis of Multiple Sulfur (δ34S, δ33S, and Δ33S) Isotopes. Samples of Ag2S were reacted in Ni bombs with tenfold excess fluorine gas at 230 °C to convert sulfur into sulfur hexafluoride (SF6) gas. The SF6 was cryogenically separated from F2 (at ~196 °C) and then distilled from HF and other trace contaminants at ~115 °C. Final purification of SF6 by GC-thermal conductivity detector was performed on a composite column made up of a one-eighth-inch diameter, 1.83-m long packed column containing type 5A molecular sieves, followed by another one-eighth-inch diameter, 3.66-m long Hayesp–trademark column. Sulfur hexafluoride eluted between 12 and 18 min at He flow rate of 20 mL min−1 and 50 °C column temperature. Sulfur hexafluoride eluting from the column was captured in a spiral glass trap cooled with liquid nitrogen. Sulfur isotope composition of purified SF6 was measured using a ThermoFinnigan MAT 253, dual inlet isotope ratio mass spectrometer with four collectors arranged to measure the intensity of SF6+ ion beams at m/z values of 127, 128, 129, and 131 (32SF6+, 33SF6+, 34SF6+, and 36SF6+). Analytical uncertainties of sulfur isotope measurements, estimated from long-term reproducibility of Ag2S fluorinations are 0.008, 0.02, and 0.20 (1σ) for δ34S, Δ33S, and Δ36S, respectively.

Sulfur isotope ratios are reported using delta (δ) notation (Eq. SI) as a deviation of an isotope,

\[ \delta S = \left( \frac{[S^2/32S]_{\text{samp}}}{[S^2/32S]_{\text{ref}}} \right) - 1. \]  

Equation S1

[ratio in a sample (samp) relative to V-Canyon Diablo triolite standard with an assumed composition of S-1 of \( \delta S = -0.30 \), Δ33S = 0.094, and Δ36S = -0.7, where \( x = 33, 34, \) or 36 reported in units of permil (‰). We do not include the factor of 1,000 included in some other studies.

Equilibrium isotope effects are described by \( (\Delta \delta S / 1.000 + 1) \approx (\delta \delta S / 1.000 + 1)^{0.515} \) and \( (\Delta \delta S / 1.000 + 1) \approx (\delta \delta S / 1.000 + 1)^{1.9} \) and are used to define a reference fractionation array. Deviations from the mass-dependent fractionation array are given using capital delta notation \( \Delta \delta S \), and \( \delta \delta S \), which are defined as:

\[ \Delta \delta S = [(1 + \delta \delta S)^{0.515} - 1] \]  
\[ \delta \delta S = [(1 + \delta \delta S)^{1.9} - 1]. \]  

Note this definition is a different definition than that used in ref. 1. The definition used here is consistent with definitions that normalize to a reference array defined by single-step equilibrium isotope exchange reactions and does not impact the conclusions of this study and only result in small modifications to the calculated \( \Delta \delta S \) and \( \delta \delta S \).

We used only glycine in our experiment to simplify the experiment to one reaction, and because both glycine (Gly, H2N-CHOH) and alanine [Ala, H2N-CH(CH3)-COOH] are classified as simple amino acids with similar \( k_a \) values for the \( \alpha \)-carboxyl (COOH-Gly = 2.4; Ala = 2.3) and \( \alpha \)-amino (NH2− Gly = 9.8; Ala = 9.9) ionizable groups. We expect that hydrolysis and subsequent pyrolysis of both amino acids may yield similar products that will show comparable \( \Delta \delta S \) anomalies at the same experimental conditions, but these effects have not been demonstrated. The isotopic compositions of the flow reactor experiment products have highly variable \( \delta \delta S \) and point to the presence of significant isotope effects operating during the reactions. These experiments are potentially subject to loss of fractionated material that is not trapped by the trapping solutions, but were done as a preliminary effort to reproduce the Watanabe al. (1) results, which they did in a broadly consistent way, but with one experiment yielding a large positive \( \delta \delta S \) with little variation for \( \Delta \delta S \). Variations for \( \Delta \delta S \) are interpreted to reflect conservation of mass-effects related to mixing of pools in the reaction network rather than to be primary anomalous effects. Variations in isotopic composition of sulfur extracts in different experiments are interpreted to result from differences in the carrier flow rate, addition rate for water, and variation in temperature conditions. Because of their design, these experiments did not allow for the capture of possible volatile organic species escape during the reaction and closure of mass balance was not attained. Experiments with Carius tubes (sealed glass tubes) were used as a way to address this issue. These experiments yielded products with smaller, but still significant \( \Delta \delta S \) variability in \( \delta \delta S \) that is associated with significant \( \delta \delta S \) fractionations and is also interpreted to reflect mass conservation effects. Closure of mass balance was not attained in the Carius tube experiments because of the difficulty in recovering all the reaction products from the tube, which adhere to walls of the glass after the reaction.

Table S1. Experiments with continuously flowing nitrogen, very low flow rate normalized to S-isotopic composition

<table>
<thead>
<tr>
<th>Experimental conditions/comments</th>
<th>Sample identification</th>
<th>δ(^{33})S</th>
<th>δ(^{34})S</th>
<th>δ(^{36})S</th>
<th>Δ(^{33})S</th>
<th>Δ(^{36})S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature = 258 ± 10 °C</td>
<td>H(_2)S (product)</td>
<td>-9.71</td>
<td>-19.21</td>
<td>-37.44</td>
<td>0.23</td>
<td>-1.26</td>
</tr>
<tr>
<td>Add 0.5 mL water three times</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction run time = 14 d, 336–340 h</td>
<td>Cr(II) reduction of residue</td>
<td>-5.39</td>
<td>-15.81</td>
<td>-30.84</td>
<td>2.78</td>
<td>-1.02</td>
</tr>
<tr>
<td></td>
<td>Sulfate in residue</td>
<td>-4.17</td>
<td>-8.12</td>
<td>-15.74</td>
<td>0.02</td>
<td>-0.37</td>
</tr>
<tr>
<td>Temperature = 298 ± 10 °C</td>
<td>H(_2)S (product)</td>
<td>-3.94</td>
<td>-9.93</td>
<td>-19.44</td>
<td>1.19</td>
<td>-0.66</td>
</tr>
<tr>
<td>Add 0.5 mL water four times</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction run time = 14 d, 336–340 h</td>
<td>Cr(II) reduction of residue</td>
<td>12.27</td>
<td>-1.52</td>
<td>-3.12</td>
<td>13.05</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>Sulfate in residue</td>
<td>0.44</td>
<td>0.91</td>
<td>1.72</td>
<td>-0.03</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Table S2. Experiments with Carius tube products normalized to starting S-isotopic composition

<table>
<thead>
<tr>
<th>Experimental conditions/comments</th>
<th>Acid volatile sulfur</th>
<th>Cr(II) reduction</th>
<th>Raney Ni reducible sulfur</th>
<th>Thode solution reducible sulfur</th>
<th>Eschka-oxidized sulfur</th>
<th>Total sulfur, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine-sulfate-water</td>
<td></td>
<td>-1.05</td>
<td>-2.09</td>
<td>-4.20</td>
<td>0.03</td>
<td>-0.22</td>
</tr>
<tr>
<td>Temperature = 175–200 °C</td>
<td></td>
<td>-1.27</td>
<td>-2.47</td>
<td>-4.61</td>
<td>0.01</td>
<td>0.08</td>
</tr>
<tr>
<td>Reaction run time = 14 d, 336–340 h</td>
<td>Cr(II) reduction</td>
<td>-3.77</td>
<td>-7.48</td>
<td>-15.19</td>
<td>0.09</td>
<td>-1.03</td>
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<tr>
<td></td>
<td>Raney Ni reducible sulfur</td>
<td>0.15</td>
<td>0.29</td>
<td>0.34</td>
<td>0.00</td>
<td>-0.21</td>
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<tr>
<td></td>
<td>Thode solution reducible sulfur</td>
<td>-7.92</td>
<td>-15.63</td>
<td>-30.79</td>
<td>0.16</td>
<td>-1.30</td>
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<tr>
<td></td>
<td>Eschka-oxidized sulfur</td>
<td>-3.62</td>
<td>-7.15</td>
<td>-14.53</td>
<td>0.07</td>
<td>-0.99</td>
</tr>
<tr>
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<td>Acid volatile sulfur</td>
<td>-4.26</td>
<td>8.31</td>
<td>15.96</td>
<td>-0.01</td>
<td>0.10</td>
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<td>Glycine-sulfate-water</td>
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<td>-7.92</td>
<td>-15.63</td>
<td>-30.79</td>
<td>0.16</td>
<td>-1.30</td>
</tr>
<tr>
<td>Temperature = 250–298 °C</td>
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<td>-0.89</td>
<td>-1.95</td>
<td>-4.02</td>
<td>0.12</td>
<td>-0.31</td>
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<tr>
<td>Reaction run time = 14 d, 336–340 h</td>
<td>Cr(II) reduction</td>
<td>-0.87</td>
<td>-1.71</td>
<td>-3.46</td>
<td>0.01</td>
<td>-0.21</td>
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<td>-14.53</td>
<td>0.07</td>
<td>-0.99</td>
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<tr>
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<td>8.31</td>
<td>15.96</td>
<td>-0.01</td>
<td>0.10</td>
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<tr>
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<td>Eschka-oxidized sulfur</td>
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<td>-2.24</td>
<td>-4.33</td>
<td>0.10</td>
<td>-0.07</td>
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<td>Acid volatile sulfur</td>
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<td>0.17</td>
<td>-1.12</td>
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<tr>
<td></td>
<td>Cr(II) reduction</td>
<td>-2.99</td>
<td>-8.64</td>
<td>-17.14</td>
<td>1.47</td>
<td>-0.79</td>
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<tr>
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<td>Raney Ni reducible sulfur</td>
<td>-2.16</td>
<td>-4.38</td>
<td>-8.88</td>
<td>0.10</td>
<td>-0.57</td>
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<tr>
<td></td>
<td>Thode solution reducible sulfur</td>
<td>3.88</td>
<td>7.54</td>
<td>14.42</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Eschka-oxidized sulfur</td>
<td>-7.80</td>
<td>-15.42</td>
<td>-30.22</td>
<td>0.17</td>
<td>-1.12</td>
</tr>
<tr>
<td></td>
<td>Acid volatile sulfur</td>
<td>-2.99</td>
<td>-8.64</td>
<td>-17.14</td>
<td>1.47</td>
<td>-0.79</td>
</tr>
<tr>
<td>Glycine-sulfate-water</td>
<td></td>
<td>-2.16</td>
<td>-4.38</td>
<td>-8.88</td>
<td>0.10</td>
<td>-0.57</td>
</tr>
<tr>
<td>Temperature = 250–298 °C</td>
<td></td>
<td>-4.30</td>
<td>-8.48</td>
<td>-17.08</td>
<td>0.08</td>
<td>-1.02</td>
</tr>
<tr>
<td>Reaction run time = 14 d, 336–340 h</td>
<td>Cr(II) reduction</td>
<td>3.76</td>
<td>7.32</td>
<td>14.02</td>
<td>-0.01</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Raney Ni reducible sulfur</td>
<td>3.88</td>
<td>7.54</td>
<td>14.42</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Thode solution reducible sulfur</td>
<td>3.76</td>
<td>7.32</td>
<td>14.02</td>
<td>-0.01</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Eschka-oxidized sulfur</td>
<td>-7.80</td>
<td>-15.42</td>
<td>-30.22</td>
<td>0.17</td>
<td>-1.12</td>
</tr>
</tbody>
</table>

Table S3. Starting sulfur species compositions

<table>
<thead>
<tr>
<th>Description</th>
<th>Amount</th>
<th>δ(^{33})S</th>
<th>δ(^{34})S</th>
<th>δ(^{36})S</th>
<th>Δ(^{33})S</th>
<th>Δ(^{36})S</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSO(_4)*</td>
<td>0.5 M (1.6%)</td>
<td>1.51</td>
<td>2.91</td>
<td>5.49</td>
<td>0.01</td>
<td>-0.05</td>
</tr>
<tr>
<td>S(_8)*</td>
<td>2–3 mg</td>
<td>1.48</td>
<td>2.87</td>
<td>5.18</td>
<td>0.00</td>
<td>-0.28</td>
</tr>
<tr>
<td>Na(_2)S(_2)O(_4)*</td>
<td>2–3 mg</td>
<td>-3.67</td>
<td>-7.18</td>
<td>-14.40</td>
<td>0.03</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

*Provided by J.T. Baker, CAS no. 7757-82-6.
†Provided by Alfa Aesar, stock no. 10343.
‡Provided by Sigma Aldrich, batch no. 20425MA.