AN EXPERIMENTAL INVESTIGATION OF MULTIPLE SULFUR ISOTOPE FRACTIONATIONS DURING HETEROGENEOUS REACTIONS BETWEEN SO$_2$ AND ACTIVATED CARBON

A Thesis in
Geosciences
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

December 2011
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This thesis is written as a manuscript to be submitted for publication in *Geochimica et Cosmochimica Acta*: “Multiple sulfur isotope fractionations during chemisorption and reduction of SO$_2$ by activated carbon at 200 °-250 °C” by Hiroshi Hamasaki, Yumiko Watanabe, and Hiroshi Ohmoto. Therefore, this manuscript follows the guidelines for manuscripts for *Geochimica et Cosmochimica Acta*.

**Abstract**

Recent theoretical and experimental investigations on multiple sulfur isotope fractionations (Lasaga et al., 2008; Watanabe et al., 2009) have suggested the possible importance of reactions between solid organic compounds and oxidized sulfur species in the creation of anomalous isotope fractionation of sulfur (AIF-S) in nature. In order to understand the details of chemical and isotopic fractionation processes involving chemisorption and redox reactions, we have conducted laboratory experiments to analyze reactions between SO$_2$(g) and powdered activated carbon (AC; BET surface area = ~460 m$^2$/g) at 200° and 250 °C in a specially constructed closed system. During each of the three series of experiments, which lasted for up to 480 hours, we monitored the changes with time in $p$SO$_2$(g) due to adsorption/desorption of SO$_2$(g) on/from the AC, and periodically sampled aliquots of SO$_2$(g) for S isotope analyses. The SO$_2$-reacted AC was analyzed for its chemical composition using an X-ray photoelectron spectrometer (XPS), an elemental analyzer (EA). Different forms of S-bearing compounds were sequentially extracted by H$_2$O, HCl, Cr-solution, and Kiba solution as Ag$_2$S, and analyzed for $^{32}$S, $^{33}$S, and $^{34}$S abundance ratios.

Results of the experiments and analyses indicate that three kinds of S-bearing species were continuously incorporated in the AC during reaction with SO$_2$(g) at 200-250 °C: (A) weakly adsorbed SO$_2$ (i.e., SO$_2$(w. ads)) which was in chemical (and probably isotopic) equilibrium with SO$_2$(g); (B) strongly adsorbed SO$_2$ (i.e., SO$_2$(w. ads)), which was degassed at 300-400 °C from the AC at the end of each series of adsorption/desorption
experiments; and (C) non-degassable S compounds (i.e., S_{(NDG)}). After reacting with a total of 10.97 mmoles of SO_{2(g)}, the AC obtained 1.26±1.20 mmoles of SO_{2(s. ads)} and 1.12±0.05 mmoles of S_{(NDG)}. Approximately 60% of the S_{(NDG)} occurred as oxidized-S compounds (i.e., S-O-C compounds) that were extracted by water and recovered as BaSO_{3} (and/or BaSO_{4}), ~20% as reduced-S compounds (i.e., S-C compounds) that were extracted by Cr-reducing solution, and the remaining ~20% as unidentified (but probably reduced S-bearing) residual S-compounds that were extracted by Kiba solution. The sequence of reactions among these S-bearing clusters was estimated to be: SO_{2(g)} = SO_{2(w. ads)} \Rightarrow SO_{2(s. ads)} \Rightarrow (S-O-C)_{AC} \Rightarrow (S-C)_{AC}, representing the trends of increasing S/O and S/C ratios of the AC caused by continuous oxidation of C to CO_{2}. The bonding energy for the SO_{2(w. ads)} was estimated to be ~30 kJ/mol.

Large kinetic isotope fractionations of sulfur isotopes occurred during the adsorption/reduction processes. Compared to the δ^{34}S of co-existing SO_{2(g)}, the δ^{34}S values of the oxidized S-bearing species increased to 4±1‰ for SO_{2(w. ads)}, +2.4±0.4 to +7.3±0.4‰ for SO_{2(s. ads)} and +11.6±0.7‰ for S-O-C species, but the reduced-S-C species (i.e., Cr-reducible S, and the residual S) are enriched in the lighter isotopes with the δ^{34}S values of -8.3±0.7‰. The δ^{33}S - δ^{34}S relationships of the S species incorporated in the AC follow the normal (i.e., mass-dependent) isotopic fractionation, but their Δ^{33}S values are slightly positive (Δ^{33}S = 0 to +0.14‰). The preferential enrichments of heavier isotopes in the adsorbed S-O bearing species, and the preferential enrichments of lighter isotopes in the reduced S species during the reduction of oxidized-S species, agree with the theoretical predictions.

Based on comparisons of our results with those of other experimental studies on
TSR and the S isotopic characteristics of H$_2$S (and other S-bearing compounds) in petroleum, natural gas, and some ore-forming solutions, we suggest the following: (1) The natural TSR probably occurred by solid C-bearing compounds (e.g., dead bodies of (micro)organisms and kerogen), rather than by gaseous, aqueous, or liquid C-bearing compounds. (2) The small isotopic fractionations between H$_2$S and their source SO$_4^{2-}$ (i.e., $\Delta^{34}$S = $\delta^{34}$S$_{H2S}$ – $\delta^{34}$S$_{SO4}$ = -10 to 0‰) in petroleum and natural gas that has previously been interpreted as a result of nearly-complete thermochemical reduction of SO$_4^{2-}$ in closed systems is instead caused by TSR involving solid C-bearing compounds.

The results of our study also suggest that the large AIF-S signatures ($\Delta^{33}$S = -1.37 to +1.84‰) observed for SO$_4^{2-}$ in some air pollutants (Ding et al., 2006) were probably created by chemisorption isotope effects between coal and the SO$_2$ generated by the burning of pyrite-rich coal. Because the adsorption energy for the surface S-O compounds varies depending on the physical and chemical properties of solid C-bearing compounds, as well as the S-O speciation, some kerogen in Archean sediments, at a particular maturation stage, may have had small adsorption energy to produce AIF-S signatures during TSR.
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### Abbreviation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>AIF-S</td>
<td>Anomalous Isotope Fractionation of Sulfur isotopes</td>
</tr>
<tr>
<td>BBOT</td>
<td>2,5-(Bis(5-tert-butyl-2-benzo-oxazol-2-y1)) thiophene</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>BSR</td>
<td>Bacterial Sulfate Reduction</td>
</tr>
<tr>
<td>CRS</td>
<td>Cr Reducible Sulfur</td>
</tr>
<tr>
<td>DIW</td>
<td>De-Ionized Water</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental Analyzer</td>
</tr>
<tr>
<td>Ga</td>
<td>Giga years ago</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>IC</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>IRMS</td>
<td>Isotope Ratio Mass Spectrometer</td>
</tr>
<tr>
<td>MCL</td>
<td>Material Characterization Lab of the Pennsylvania State University</td>
</tr>
<tr>
<td>MDF-S</td>
<td>Mass Dependently Fractionated Sulfur isotopes</td>
</tr>
<tr>
<td>MDL</td>
<td>Mass Dependent Line</td>
</tr>
<tr>
<td>MIF-S</td>
<td>Mass Independently Fractionated Sulfur isotopes</td>
</tr>
<tr>
<td>PAL</td>
<td>Present Atmospheric Level</td>
</tr>
<tr>
<td>PSUWS</td>
<td>PSU (Pennsylvania State University) Working Standard of SF$_6$</td>
</tr>
<tr>
<td>TFL</td>
<td>Terrestrial Fractionation Line</td>
</tr>
<tr>
<td>TSR</td>
<td>Thermochemical Sulfate Reduction</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>V-CDT</td>
<td>Vienna Canyon Diablo Troilite</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectrometer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
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</table>
Acknowledgements

I am fully grateful for the patient guidance and dedicative supports of Dr. Hiroshi Ohmoto and Dr. Yumiko Watanabe during this study. I have learned much about scientific integrity and have experienced much joy in the scholarly pursuit of knowledge. You have been my role models. I would like to thank Dr. Michel Arthur and Dr. James Kubicki for giving useful comments and suggestions on my data analysis, and for providing inputs on our manuscript. I would like to express appreciation to Dr. Tony Lasaga for his advise on experimental design. I appreciate reviews and comments by Mr. Ian Johnson, Mr. Jamie Brainard, Mr. Andrew Chorney, and Mr. Tom Rushton. Thanks to Dr. Tsubasa Otake and Dr. Kosei Yamaguchi for helping me throughout my graduate work as veterans of Ohmoto’s laboratory. I also would like to thank Mr. Dennis Walizer for helping me many times in operating the mass spectrometer for analysis of multiple sulfur isotopes, Mr. Vince Bojan for the discussions on identification of S-bearing compounds with XPS data, and Mr. Doug Smith for the glass blowing lectures and modification of a Pyrex reaction system. I have learned the importance of technicians, and how they provide the backbone for scientific research.

This research was supported by grants from the NASA Astrobiology institute (NNA09DA76A) through Dr. Hiroshi Ohmoto and the National Science Foundation (EAR 10-24550) through Dr. Yumiko Watanabe. I also acknowledge financial support from The Ministry of Education, Culture, Sports, Science and Technology of Japan.

To my friends and family:
I would appreciate the friendships of Mr. Ra’meses Ramirez and Ms. Koya Ohmoto. You have always encouraged me, and made me laugh through the hard times. Thanks to Mr. Ian Johnson for giving me an opportunity to work as his field assistant in Pilbara. Those three months are unforgettable moments in my life. I am grateful to my father and mother, Mr. Motoharu Hamasaki and Ms. Youko Hamasaki for their unconditional love. This thesis is dedicated to all of you in appreciation for your continued support and encouragement.
1. Introduction

The presence of sulfide and sulfate minerals with anomalous isotope fractionations of sulfur (AIF-S) in sedimentary rocks older than ~2.4 Ga in age, but the virtual absence of AIF-S in younger rocks, have been considered by many recent geoscientists as the definitive evidence for a dramatic change from an anoxic to oxic atmosphere ca. 2.4 Ga (e.g., Kasting et al., 2001; Pavlov and Kasting, 2002; Holland, 2006). This is because, until recently, the only known process to create AIF-S was UV photolysis of SO$_2$ in an O$_2$-poor atmosphere. However, a theoretical study by Lasaga et al. (2008) and an experimental study by Watanabe et al. (2009) have shown that chemical reactions between solid organic compounds and gaseous (or aqueous) sulfur-bearing species may cause AIF-S under certain conditions. This study is intended to investigate the details of chemical and sulfur isotopic fractionation processes during reactions between a simple solid carbon compound (activated carbon) and SO$_2$ gas at 200 ° and 250 °C

1.1. Background

Sulfur has four isotopes $^{32}$S, $^{33}$S, $^{34}$S and $^{36}$S, with the average abundances of 95.04%, 0.75%, 4.20%, and 0.015% respectively (Coplen et al., 2002). Since the theoretical works by Bigeleisen and Mayer (1947), researchers have recognized that most natural samples show the following sulfur isotopic relationships:

\[
\delta^{33}S_i (\text{‰}) = 0.515 \times \delta^{34}S_i (1)
\]

and

\[
\delta^{36}S_i (\text{‰}) = 1.89 \times \delta^{34}S_i (2)
\]

where subscript $i$ refers to a sulfur-bearing compound, and $\delta^{33}S_i$, $\delta^{34}S_i$, and $\delta^{36}S_i$ are defined as permil deviations of the $^{33}S/^{32}S$, $^{34}S/^{32}S$, and $^{36}S/^{32}S$ ratios of compound $i$ from that of the international standard (V-CDT: Vienna Canyon Diablo Troilite), such as

\[
\delta^{33}S_i (\text{‰}) = \frac{(^{33}S/^{32}S)_i}{(^{33}S/^{32}S)_{\text{V-CDT}}} - 1 \times 1000 (3)
\]

The $^{32}S/^{34}S$ ratio of V-CDT is determined as 22.649 (Ding et al., 2001).

Relationships (1) and (2) occur because the magnitude of isotopic fractionation during most (bio)chemical reactions depends primarily on differences in isotope mass. For this reason, (1) and (2) are often called as equations for the “mass-dependent fractionation (MDF)”, “terrestrial fractionation (TF)”, or the “normal fractionation (NF)” of sulfur isotopes.
Deviations of isotopic compositions of $i$ from the MDF relationships are typically expressed by:

$$
\Delta^{33}S_i = \delta^{33}S_i - 0.515 \times \delta^{34}S_i 
$$  \hspace{1cm} (4)

$$
\Delta^{36}S_i = \delta^{36}S_i - 1.89 \times \delta^{34}S_i 
$$  \hspace{1cm} (5)

$$
33\theta' = \frac{\delta^{33}S_i}{\delta^{34}S_i} 
$$  \hspace{1cm} (6)

and

$$
36\theta' = \frac{\delta^{36}S_i}{\delta^{34}S_i} 
$$  \hspace{1cm} (7)

When $\Delta^{33}S_i$ and/or $\Delta^{36}S_i$ values fall outside the ranges of $0 \pm 0.2\%$ and $0 \pm 0.4\%$ respectively, and $33\theta'$ and/or $36\theta'$ values fall outside the ranges of $0.51 \pm 0.01$ and $1.9 \pm 0.1$ respectively, the sample is considered to contain mass independently fractionated sulfur isotopes (MIF-S) (Farquhar and Wing, 2003) or anomalously-fractionated sulfur isotopes (AIF-S) (Lasaga et al., 2008).

Hoering (1988) reported that some Archean-aged barites displayed distinct AIF-S signatures: $\Delta^{33}S = -0.46\%$ and $\Delta^{36}S = +2.15\%$. However, it was a report by Farquhar et al. (2000a) that generated great interests among geoscientists studying multiple sulfur isotope geochemistry. Farquhar et al. discovered that sulfide and sulfate minerals from some sedimentary rocks of Archean age possessed AIF-S signatures, mostly positive $\Delta^{33}S$ values (-0.8 to +2.0\%) for sulfides and mostly negative $\Delta^{33}S$ values (-1.3 to +1.9\%) for sulfates. Farquhar et al. (2001) reported that SO$_2$ photolysis in an O$_2$-free atmosphere by a UV laser with a 193 nm wavelength produced S$^0$ and SO$_4^{2-}$ with large positive $\Delta^{33}S$ values (+59.9 to +69.3\%) and negative $\Delta^{33}S$ values (-23.3 to -12.8 \%), respectively.

Subsequent researchers recognized that many (but not all) sedimentary rocks >2.45 Ga in age possessed AIF-S signatures (e.g., Mojzsis et al., 2003; Ono et al., 2003; Papineau et al., 2006; Philippot et al., 2007; Goldman et al., 2008; Ono et al. 2009a,b; Shen et al., 2009). Through photochemical modeling, Pavlov and Kasting (2002) suggested that the S$^0$ produced by photo-dissociation of SO$_2$ would not be preserved if the atmospheric $pO_2$ was higher than ~1 ppm. Based on these studies, many geoscientists have accepted the theory that the AIF-S signatures in sedimentary samples were created by UV photolysis of volcanic SO$_2$ in an oxygen poor atmosphere, and that the AIF-S record is the smoking gun for the “Great Oxidation Event (G.O.E.)” at 2.45 Ga. However, many serious problems exist with this theory:

2
(1) The discrepancy between the AIF-S signatures produced by photochemical reactions and those of sedimentary rocks (Fig. 1): UV photolysis of SO\(_2\) with 193 nm created elemental sulfur with large positive \(\Delta^{33}\)S (+59.9 to +69.3‰) and large negative \(\delta^{34}\)S (-85.0 to -39.1‰) values (Farquhar et al., 2001). In contrast, natural pyrites with AIF-S signatures typically possess positive \(\Delta^{33}\)S (0 to +11‰) and positive \(\delta^{34}\)S (0 to +30‰) values (e.g., Farquhar et al., 2000a; Hu et al., 2003; Mojzsis et al., 2003; Ono et al., 2003; Bekker et al., 2004; Papineau et al., 2005; Whitehouse et al., 2005; Cates and Mojzsis, 2006; Johnston et al., 2006; Ono et al., 2006; Bao et al., 2007; Farquhar et al., 2007; Hou et al., 2007; Kamber and Whitehouse, 2007; Kaufman et al., 2007; Ono et al., 2007; Papineau et al., 2007; Philippot et al., 2007; Domagal-Goldman et al., 2008; Johnston et al., 2008; Partridge et al., 2008; Ueno et al., 2008; Guo et al., 2009; Ono et al., 2009a,b; Shen et al., 2009; Thomazo et al., 2009). There is no obvious mechanism to significantly increase the \(\delta^{34}\)S values from the photochemically produced S\(^0\) values (-85.0 to -39.1‰) to those of natural FeS\(_2\) (0 to +30‰). Naraoka and Poulson (2008) and Lyons (2008) have recognized that the absorption spectra of SO\(_2\) isotopologues are extremely complex in a wavelength region ~180 to ~230 nm, which causes the AIF-S signature of the products of UV photolysis to be extremely sensitive to the wavelength of a UV source. When a broad-band UV lamp, which produces the UV spectra similar to the natural sun light, was used in the SO\(_2\) photolysis, the S\(^0\) had positive \(\Delta^{33}\)S (+15±5‰) and positive \(\delta^{34}\)S (+180±10‰) values with \(\delta^{33}\)S/\(\delta^{34}\)S values of 0.54-0.6 (Matsterson et al., 2011); these \(\delta^{34}\)S-\(\Delta^{33}\)S trends are not consist with the majority of the Archean data (Fig. 1).

(2) The existence of AIF-S signatures in post-2.45 Ga samples: AIF-S signatures were found in post-2.45 Ga materials. Young (2009; personal communication 2010) found AIF-S signatures (-0.55 to +1.25‰) in 1.9 Ga black shales near the Outokumpu massive sulfide deposits in Finland. AIF-S signatures have also been found in present-day sulfate aerosols which were probably produced by burning of pyritic coal: \(\Delta^{33}\)S values of -1.37 to +1.84‰ for Beijing aerosols (Ding et al., 2006) and 0 to 0.47‰ for California-Los Angeles aerosols (Romero and Thiemens, 2003). Sulfate associated with some volcanic ashes in ice cores are found to show AIF-S signatures: \(\Delta^{33}\)S = -0.50 to +0.67‰ (Savarino et al., 2003) and -1.03 to +1.41‰ (Baroni et al., 2007).
(3) The existence of general correlations between AIF-S signatures and lithology of sedimentary rocks: Pyrite crystals in many Archean-age shales have been found to show no AIF-S signatures (Farquhar et al., 2000; Whitehouse et al., 2005; Ohmoto et al., 2006; Ono et al., 2006; Farquhar et al., 2007); this is difficult to explain if the S came from the atmosphere. Pyrites with no AIF-S are generally hosted in C\textsubscript{org}-poor shales (Watanabe et al., 1997; Ohmoto et al., 2006). Most pyrite crystals with AIF-S signatures occur in organic C-rich black shales (C\textsubscript{org} = 1-15 wt%) that have been hydrothermally altered (Ohmoto et al., 2006; Kaufman et al., 2007; Watanabe et al., 2008). The existence of positive correlations between contents of pyrite and C\textsubscript{org} suggests that pyrite was generated by H\textsubscript{2}S derived from reduction of sulfate by organic matter, either through bacterial sulfate reduction (BSR), or thermochemical sulfate reduction (TSR).

(4) SO\textsubscript{2}-poor Archean volcanic gas: If the Archean continental mass was much smaller than today, most of the mantle degassing would have occurred through submarine hydrothermal systems where the dominant S-bearing specie was H\textsubscript{2}S, rather than SO\textsubscript{2} (Kump and Barley, 2007). Also H\textsubscript{2}S would have been more abundant than SO\textsubscript{2} in subaerial volcanic gas, if the Archean mantle beneath the continental crust was not as oxidized as today (Ohmoto, 2009). Because UV photolysis of H\textsubscript{2}S does not produce AIF-S (Farquhar et al., 2000b) volcanic outputs during the Archean likely did not acquire AIFs signatures in the atmosphere.

Recognition of the above problems in the SO\textsubscript{2}-UV-photolysis model led Watanabe et al. (2009) to hypothesize that AIF-S signatures in sedimentary rocks were generated during reactions involving organic matter and SO\textsubscript{4}\textsuperscript{2-} under hydrothermal conditions. To test this hypothesis Watanabe et al. (2009; in prep.) conducted a series of experiments of TSR at 150-200 °C using powdered amino acids, solid sulfate, and water. The experiments produced reduced compounds (H\textsubscript{2}S and Cr-reducible S compounds) with distinct AIF-S signatures, ranging in δ\textsuperscript{34}S values from -16.2 to +5.1‰ relative to the initial sulfate S, and Δ\textsuperscript{33}S values from +0.1 to +2.3‰ (Fig. 2). They have recognized that the AIF-S generation occurred in TSR experiments using simple amino acids (glycine and alanine), but not with complex amino acids (e.g., arginine) or with kerogen extracted from sediments (Watanabe et al., in prep.). Based on these experimental data and the correlations between AIF-S and the lithology of host rocks, Watanabe et al. (2009)
suggested that the creation of AIF-S was favored prior to ~2.4 Ga when simple, reactive organic matter accumulated in large rift-related basins under large-scale submarine hydrothermal conditions. Therefore, according to their model, the AIF-S record of sedimentary rocks may be linked to the thermal and biological evolution of early Earth, not to the atmospheric evolution.

Concurrently with the experimental investigations by Watanabe et al. (2009; in prep), Lasaga et al. (2008) carried out a theoretical study on multiple sulfur isotope fractionations during heterogeneous reactions (i.e., chemisorption) between solid surfaces and gaseous (or aqueous) sulfur-bearing species. The results of their computations, which were based on quantum chemistry and ab-initio models, predicted that AIF-S signatures could be generated if the chemisorption energy was less than about ~30 kJ/mol and a discontinuity occurs in the number of bound energy levels for the adsorbed species (e.g., C_{surface}-SO\textsubscript{2} species on a graphite surface) of different sulfur isotopes (Fig. 3). The magnitude of AIF-S during a heterogeneous reaction increases with increasing temperature. Balan et al. (2009) computed the wavefunction probabilities of the bound and unbound species in a finite-size box where the boundary wall was set at 30 Å from a solid surface and found that significant overlaps between the two wavefunction probabilities existed, and thereby concluded that chemisorption processes would not produce AIF. However, in a laboratory or natural system, the boundary wall typically occurs more than 1 µm (>10\textsuperscript{4} Å) away from a solid surface. Lasaga et al. (in prep) have shown that in such systems, the unbound states (i.e., free molecules, such as SO\textsubscript{2}) are distributed equally throughout such a system and the overlap of bound and unbound wavefunctions is zero. Thus, they conclude that the suggestion by Lasaga et al. (2008) of the importance of chemisorption for the creation of AIF-S is valid.

1.2. Objectives

Considering the theory of chemisorption isotope effects, we hypothesized that the TSR in the Watanabe et al. experiments proceeded through the following three steps: (1) adsorption of aqueous SO\textsubscript{4}\textsuperscript{2-} on the surfaces of C-bearing solid compounds; (2) reduction of the adsorbed SO\textsubscript{4}\textsuperscript{2-} by C (and H and N) atoms to form reduced S-bearing clusters in the solid phase; (3) reactions between the reduced S-bearing clusters and H\textsubscript{2}O to form H\textsubscript{2}S_{(aq.}
g) and (4) desorption of H$_2$S(aq, g). The theory by Lasaga et al. (2008) predicted that: (a) the AIF-S signatures may be generated during the first step; (b) the adsorbed SO$_4^{2-}$ species may have positive $\delta^{34}$S and $\Delta^{33}$S values with respect to the initial SO$_4^{2-}$; (c) the second step may cause mass-dependent isotopic fractionation; and (d) the third step may cause AIF-S with negative $\delta^{34}$S and negative $\Delta^{33}$S values for the desorbed H$_2$S. This study was conceived to test the above hypothesis by investigating the details of chemical and isotopic fractionations during reactions between a simple solid C-bearing compound (activated carbon) and a simple sulfur-bearing gaseous compound (SO$_2$) at elevated temperatures in a dry system. The results from this study were also expected to help us understand the conditions and isotopic characteristics of H$_2$S (and other S-bearing compounds) in petroleum, natural gas, and some ore-forming fluids.

2. Experimental Procedures

Many researchers have conducted laboratory experiments on the adsorption of SO$_2$(g) by activated carbon and other carbon-bearing compounds, mostly because of the needs to develop efficient methods to scavenge SO$_2$ from various gas mixtures, such as those generated by combustion of pyrite-bearing coal and petroleum. Most of these experiments were carried out at low temperatures (T <100 °C) using activated charcoal (Shiels, 1929; Davini, 1989; Boudou et al., 2003; Zhang et al., 2007), but some using activated palm wasters ( Lua and Guo, 2001). Experiments at a 100-170 °C range have been carried out using activated carbon (Davini, 1991) or using lignite (Lee et al., 1994).

High temperature (T = 600-900 °C) reactions between activated carbon and other carbon-bearing compounds have also been investigated by many researchers to understand both the adsorption characteristics of SO$_2$ and the redox reactions between SO$_2$ and carbon, such as the amount of composition of gaseous species (e.g., SCO, S$_2$, CO, CO$_2$, etc) and solid species (C-S-O compounds) (Zawadzki, 1987). However, no investigation has been made on S isotope effects during reactions between SO$_2$(g) and C-bearing compounds.

The results of previous investigations indicate that the SO$_2$ adsorption on carbon-bearing compounds is influenced by the physical and chemical characteristics of the solid phase (e.g., grain size, specific surface area, chemical composition, crystal structure), the
partial pressure of SO₂, humidity, and most importantly the temperature of reaction. Generally, SO₂ adsorption decreases with increasing temperature. Many previous studies were conducted in systems open to SO₂(g) where gas with certain pSO₂ values was passed over AC at certain flow rates. Such experimental methods simulate typical SO₂-rich environments in industry (e.g., coal combustion). However, closed-system experiments are more suitable to determine the chemical and isotopic fractionations between SO₂ and activated carbon.

2.1 Starting Material

The activated charcoal (AC) used in this study was irregular in shape and size, typically 3-5 mm-sized elongated fragments. They were crushed and sieved to powders with grains of 0.25-1.0 mm in diameter. The BET surface area of the powder before reaction was 457.7 m²/g. Chemical analysis of the AC by an elemental analyzer (EA) indicates the C content of ~83 wt%; the remaining ~17 wt% is composed mostly of O (~15 wt%), H (0.7 wt%), and N (0.7 wt%). 1.999 gm of AC was heated at 300 °C for 3 days and desorbed 0.25 gm of H₂O from the AC, corresponding to ~13% of the 1.999 gm. Therefore, these O, H, and N atoms probably represent the O₂, CO₂, H₂O, and N₂ gases that were adsorbed on the AC while exposed to the atmosphere.

2.2. Experimental System

We have conducted three series of experiments at 200-250 °C using the AC and SO₂(g) in a specially designed closed system, constructed with Pyrex-glass (Fig. 4). The primary reason for choosing a closed system, rather than an open system, was that we intended to investigate the details of chemical and isotopic reactions (e.g., reaction types and rates; isotopic fractionation factors) during both adsorption and desorption processes. The experimental system, connected to a vacuum pump, is comprised of 7 sections (V₁ – V₇) that can be isolated or connected by high-vacuum type Teflon stopcocks. The volume of each section was determined by measuring the change in pressure of N₂ (and He as an inert gas) gas as each section is sequentially connected to a calibrated expansion volume (V₇ = 1136.8 mL). V₁ (26.3 mL) and V₂ (29.0 mL) are cryogenic traps to transfer SO₂ from a SO₂ tank to the experimental system and to purify the SO₂ gas. V₃ is a U-tube
reaction cell with a volume of 27.3 mL without AC and 15.0 mL with AC. \( V_4 \) (13.4 mL) is a transition section to cold trap \( V_5 \) (40.4 mL) with an attached pressure manometer (M). \( V_6 \) (136.8 mL) is a transition section to gas sampling ports. The reaction cell (\( V_3 \)) was wrapped with a heating tape and connected to a temperature controller. Thermocouple thermometers monitored the temperatures at both the bottom and top parts of the reaction cell during the experiments.

2.3. Experimental Procedures

Based on the results of several preliminary experiments to understand the adsorption characteristics of the AC, we have determined the optimum amounts for the adsorption experiments were about 1.884 gm of AC (= 1.56 gm C = 130 mmol of C) and 2.5 mmol of SO\(_2\) when the gas was expanded through \( V_3 \), \( V_4 \) and \( V_5 \); this volume (\( V_3 + V_4 + V_5 = 68.8 \) mL) represents a subsystem of the entire system (\( V = 260.9 \) or 1397.7 mL), but referred to as the “system” in subsequent discussions because SO\(_2\) was present only in this subsystem during the adsorption by activated carbon. The SO\(_2\) amount of ~2.5 mmol in the “system” will allow us to sample several aliquots of SO\(_2\)(system) during the adsorption/desorption experiments, and to recover enough amount of S-bearing compounds from the AC at the end of experiments for chemical and isotopic analyses.

**Series I Experiment (200 °C):** 1.884 mg of AC was placed in the reaction cell (\( V_3 \)), and silica wool was placed on both ends of the AC to prevent a loss of AC during evacuation. The reaction cell was wrapped with a heating tape, and evacuated for 120 hours at 300 °C to completely degas the adsorbed gas (O\(_2\), CO\(_2\), H\(_2\)O, N\(_2\)) from the AC. When the air pressure dropped and stabilized at <1 torr, temperature of the reaction cell was lowered to 200 °C.

SO\(_2\) gas was introduced into sections \( V_4+V_5 (= 53.8 \) mL), and the \( p\)SO\(_2\) was adjusted to 839.5 torr by pumping out some SO\(_2\), which yielded 2.43 mmole of \( n\)SO\(_2\). This SO\(_2\) was expanded through the “system” (= \( V_3+V_4+V_5 = 68.8 \) mL) to react with the heated AC. A simple expansion of the SO\(_2\) from 53.8 mL to 68.8 mL should have yielded a \( p\)SO\(_2\)(system) value of 656.5 torr at the beginning of reaction with the AC (i.e., \( t = 0 \) hour). The \( p\)SO\(_2\)(system) decreased very rapidly to 431.8 torr after 1 min, to 389.9 torr after 2
hours, and leveled at ~380 torr after 3 hours (Table 2 and Fig. 6a), indicating very rapid adsorption of \( \text{SO}_2\) on the AC, and attainment of equilibrium between \( \text{SO}_2\) and the \( \text{SO}_2\) incorporated in the AC (i.e., \( \Sigma S(\text{AC}) \)) in ~3 hours.

At the beginning of the adsorption experiments, the gas in the system was pure \( \text{SO}_2\); thus \( P_{\text{system}} = P_{\text{SO}_2(\text{system})} \). However, as the reaction continues between \( \text{SO}_2\) and AC, other gases (e.g., \( \text{CO}_2\), \( \text{SCO}\)) may be generated to cause \( P_{\text{SO}_2(\text{system})} < P_{\text{system}} \). The first aliquot of \( \text{SO}_2\) was sampled at \( t = 24 \) hrs when \( P_{\text{system}} = 378.7 \) torr. The amount of \( \text{SO}_2\) in the “system” (= \( V_3 + V_4 + V_5 \)) at this time (i.e., \( n_{\text{SO}_2(\text{system})} \)) can be calculated as: 

\[
(2.43 \text{ mmol}) \times \frac{378.7 \text{ torr}}{656.6 \text{ torr}} = 1.40 \text{ mmol},
\]

if the gas was pure \( \text{SO}_2\). This indicates that 1.03 mmol (= 2.43 - 1.40) of S was incorporated in AC as \( \Sigma S(\text{AC}) \). The \( n_{\text{SO}_2} \) in section \( V_5 \) (40.4 mL) was isolated from \( V_3 \) and \( V_4 \) (i.e., 58.7% of the \( n_{\text{SO}_2(\text{system})} \)) and transferred to a sampling tube that contained 20 ml of 20% \( \text{H}_2\text{O}_2\) solution and cooled with liquid nitrogen. Therefore, 0.82 mmol (= 1.40 mmol x 58.7%) of \( n_{\text{SO}_2} \) was withdrawn from the system, if the withdrawn gas was pure \( \text{SO}_2\). After the sampling, \( V_5 \) was re-connected to \( V_3 + V_4 \). This caused immediate decreases in \( P_{\text{system}} \) and \( n_{\text{SO}_2(\text{system})} \) to 156.3 torr and 0.58 mmol, respectively. \( P_{\text{system}} \) gradually increased and stabilized at 228.2 torr at \( t = 26.3 \) hours, i.e., an increase of 71.9 torr, indicating that the \( \text{SO}_2\) adsorbed on the AC was partially desorbed and attained new equilibrium between \( \text{SO}_2\) and \( \text{SO}_2(\text{adsorbed}) \) in 2.3 hours. The second sampling of \( \text{SO}_2(\text{system}) \) was carried out when the \( P_{\text{system}} \) stabilized at 228.2 torr. The third through eighth samplings were carried out in a similar manner. At the end of the eighth sampling (\( t = 39.1 \) hr), the \( P_{\text{system}} \) and \( n_{\text{SO}_2(\text{system})} \) decreased to 10.7 torr and 0.04 mmol, respectively.

After the collections of \( \text{SO}_2\) at 200 °C, we raised the temperature of the reaction cell to 300 °C and kept it there for one hour, which caused an increase of \( P_{\text{system}} \) to 65.8 torr and \( n_{\text{SO}_2(\text{system})} \) to 0.20 mmol (if pure \( \text{SO}_2\)) due to the desorption of strongly attached adsorbed \( \text{SO}_2\). All the gas in the “system” (= \( V_3 + V_4 + V_5 \)) was sampled as the “strongly-adsorbed \( \text{SO}_2\)” and designated as \( \text{SO}_2(\text{s. ads}) \), whereas the \( \text{SO}_2\) that was easily desorbed from the AC at the experimental temperature was termed the “weakly-adsorbed \( \text{SO}_2\)” and designated as \( \text{SO}_2(\text{w. ads}) \).

**Series II Experiment (250 °C):** The AC from Series I experiment was kept in the reaction cell, and reacted with 2.50 mmol of new \( \text{SO}_2\) at 250 °C. Sampling of 6 aliquots
of SO$_2$(system) was carried out over 87 hours in a manner similar to Series I experiment. After the sixth sampling, the strongly adsorbed SO$_2$(s. ads) was degassed at 400 °C and recovered.

**Series III Experiment (200 °C):** The “system” volume was expanded from 68.8 mL to 1342.4 mL with an addition of an expansion volume (V$_7$), and 6.04 mmol of new SO$_2$(g) was reacted at 200 °C with the old AC from Series I and II experiments. Sampling of 21 aliquots of SO$_2$(system) and the SO$_2$ degassed at 300 °C (i.e., SO$_2$(s. ads)) were carried out over a period of 480 hours.

3. Analytical Methods

3.1. Recovery of SO$_2$(g) as BaSO$_4$

Sampling of SO$_2$ from the experimental system was carried out by freezing it in a Pyrex-glass tube which contained 20 ml of 20% H$_2$O$_2$ solution and cooled with liquid nitrogen. When the tube was warmed to room temperature, the SO$_2$ and H$_2$O$_2$ reacted to form H$_2$SO$_4$. The H$_2$SO$_4$ was converted to BaSO$_4$ by an addition of 20 ml of 25% BaCl$_2$ solution. The solution and BaSO$_4$ were transferred to a centrifuge tube; BaSO$_4$ precipitates were separated from solution by centrifuge, then rinsed with deionized water, dried in an oven at 60 °C for 12 hours, and weighed with a microbalance to determine the amount of SO$_2$ recovered.

We have conducted several tests to evaluate the efficiency of this SO$_2$-recovery method by using pure SO$_2$(g) of varying amounts. The results (Fig. 5) indicate that the recovered amounts of BaSO$_4$ were always less than the expected values at 100% recovery, but there is an excellent correlation between the expected amounts (Y) and the recovered amounts (X):

\[ Y = 1.02X + 0.02 \text{ (mmol)} \] (8)

Equation (8) suggests that on average 0.02 mmol (= 4.67 mg) of BaSO$_4$ powders were lost during the recovery processes, most likely due to adhesion on walls of the sampling- and centrifuge tubes. Therefore, we have used this equation, together with the recovered BaSO$_4$ amounts, to calculate the amounts of recovered SO$_2$(g).
3.2. X-ray Photoelectron Spectroscopy of Activated Carbon

We used an X-ray photoelectron spectrometer (XPS) (Kratos AXIS Ultra Photoelectron Spectrometer) of the Material Characterization Laboratory of The Pennsylvania State University to identify the speciation and amounts of sulfur compounds formed on the surfaces of AC by reactions with SO$_2$. The XPS analysis allows identification of surface speciation (top 1-10nm). Quantitative data can also be obtained from peak area analyses. AC before and after the adsorption experiments were pulverized and analyzed with XPS. Analyses of the data were carried out using CasaXPS program (Casa Software Ltd.).

3.3. Sequential Sulfur Extraction from Activated Carbon

We employed a four-step sequential extraction of S-bearing species from the SO$_2$-reacted AC using H$_2$O, HCl, Cr-solution (Canfield et al., 1986), and Kiba solution (Kiba et al., 1957). Water-soluble S species were recovered as BaSO$_4$ (and/or BaSO$_3$), whereas the other S-species were recovered as Ag$_2$S. Their amounts were determined by a microbalance. A detailed procedure is described in Fig A2 of Appendix.

3.4. Chemical Analyses of Activated Carbon by Elemental Analyzer

C, H, N, and S contents of the AC before and after the adsorption experiments were determined with an elemental analyzer (EA) (CE Instruments, NC2500) at Ohmoto Laboratories. The O contents (wt%) of the AC were calculated as 100 – (C+H+N+S)wt% (Table 5). We have also analyzed the C/H/N/S ratios of the AC after each step of the sequential sulfur extraction to determine the amounts of S leached by different solutions.

3.5. Sulfur Isotope Analyses

BaSO$_4$ samples from the sampled SO$_2$(g) and those from water-soluble S species in SO$_2$-reacted AC were converted to ZnS using Thode solution (Thode, 1961). The ZnS was further converted to Ag$_2$S by reacting with AgNO$_3$ solution. Ag$_2$S samples were converted to SF$_6$ by reacting with F$_2$ gas at 275 °C for 12 hours in nickel reaction tubes. The generated SF$_6$ gas was purified through a series of cryogenic traps and a gas chromatography (Ono et al., 2006), and introduced to a VG Prism mass spectrometer at
Ohmoto Laboratory for isotope analyses. The abundance ratios of $^{32}$S, $^{33}$S, and $^{34}$S in the SF$_6$ gas from a sample were determined from the abundance ratios of m/z = 127 ($^{32}$SF$_5^+$), 128 ($^{33}$SF$_5^+$), and 129 ($^{34}$SF$_5^+$) of the sample and those of the Penn State Working Standard (PSUWS).

4. Results and Interpretations of the Chemical Data

4.1. Speciation and Amounts of S incorporated in the Activated Carbon during Reactions with SO$_2$ (g)

From the changes with time in the P$_{\text{system}}$ values during adsorption/desorption experiments (Tables 2-4; Figs. 6a, 7a, and 8a), we can distinguish three kinds of sulfur-bearing compounds that were incorporated in the AC: (1) the SO$_2$ that was weakly adsorbed on AC and quickly responded to changes in the P$_{\text{system}}$ at 200-250 °C (i.e., SO$_2$(w. ads)); (2) the SO$_2$ released from the AC at temperatures 100-150 °C higher than the experimental temperatures, suggesting that this SO$_2$ was strongly adsorbed on the AC surface (i.e., $n$SO$_2$(s. ads)); and (3) the non-degassable S-species that remained in the AC even after degassing at 300-400 °C (i.e., $n$S_{(NDG)}). Therefore, the total amount (number of mol) of S incorporated in the AC (i.e., $n$S$_{(AC)}$) at time (t) during the experiments is:

$$nS_{(AC)} = nS_{(init)} - n\Sigma SO_2_{(sampled)} - nSO_2_{(system)}$$  \hspace{1cm} (9)

and

$$nS_{(AC)} = nSO_2_{(w. ads)} + nSO_2_{(s. ads)} + nS_{(NDG)}$$  \hspace{1cm} (10)

where $nS_{(init)}$, $n\Sigma SO_2_{(sampled)}$, and $nSO_2_{(system)}$ are, respectively, the initial amount of S in the system, the total amount of SO$_2(g)$ withdrawn from the system through time t, and the amount of remaining SO$_2(g)$ at time t.

Because of the possibility that the gas in the experimental system was increasingly contaminated by S-O-C-bearing gases (e.g., CO$_2$, COS) due to redox reactions between SO$_2$ and activated carbon, we have computed the values of $nSO_2_{(sampled)}$, $n\Sigma SO_2_{(sampled)}$, and $nS_{(AC)}$ after each sampling in two ways: one is by assuming that the sampled gas is pure SO$_2$, and the other is by using the recovered amounts of BaSO$_4$ and equation (8) (Tables 2-4).

In Series I experiment (T = 200±10 °C, V$_{\text{system}}$ = 68.8 mL, and $nS_{(init)}$ = 2.43 mmol), at t = 24 hrs when the first aliquot of SO$_2_{(system)}$ was withdrawn, the $nSO_2_{(system)}$ decreased to 1.44±0.05 mmol, while the amount of S incorporated in the AC (i.e., $nS_{(AC)}$) increased.
from 0 to 0.99±0.04 mmol (Table 2). Due to the successive withdrawals of 8 aliquots of SO$_2$(system), the values of $n$SO$_2$(system), $n$SO$_2$(sampled), and $n$ΣS(AC) decreased to 0.04±0.01 mmol, 0.06±0.01 mmol, and 0.07±0.04 mmol, respectively. The amount of $n$SO$_2$ degassed at 300 °C (i.e., $n$SO$_2$(s. ads)) was 0.22±0.02 mmol, and the $n$ΣS(AC) further decreased to -0.13±0.04 mmol (Table 2).

In Series II experiments ($T = 250±3$ °C, $V_{\text{system}} = 68.8$ mL, and $n$S$_{\text{init}} = 2.50$ mmol), the maximum $n$ΣS(AC) value was 0.74±0.01 mmol at $t = 72$ hrs when the first aliquot of SO$_2$(system) was withdrawn. This value decreased to 0.19±0.05 mmol after the withdrawal of 6 aliquots of SO$_2$(system) at 250 °C and to 0.04±0.09 mmol after degassing at 400 °C. The $n$SO$_2$(s. ads) value of 0.20±0.03 mmol at the end of Series II experiment was essentially the same as that of Series I.

In Series III experiment ($T = 200±5$ °C, $V_{\text{system}} = 1358.7$ mL, and $n$S$_{\text{init}} = 6.42$ mmol), the $n$ΣS(AC) value continued to increase from 0 to 0.85±0.57 mmol through sampling of the first three samples ($t = 60$ hours), indicating that the equilibrium between SO$_2$(system) and ΣS(AC) was established only after ~60 hours. After ~60 hours, the $n$ΣS(AC) value continued to decrease to 0.11±0.09 mmol after sampling of 21 aliquots of SO$_2$(system) through $t = 474$ hrs and to 1.12±0.05 mmol after degassing at 300 °C. The $n$SO$_2$(s. ads) value of 1.26±1.20 mmol at the end of Series III experiment was essentially the same as those of Series I and II.

We have taken the second method to calculate the $n$S$_{\text{(NDG)}}$ value from the measured S/C ratio of the SO$_2$-reacted AC (i.e., 0.0086±0.0004 atomic ratio; Table 5). The calculated $n$S$_{\text{(NDG)}}$ value is 1.12±0.05 mmol, if the amount of C in the AC remained the same as the initial value (130 mmol), or 0.90±0.04 mmol if ~20% of the initial amount of C was degassed as CO$_2$ due to the reaction with SO$_2$, which may be reasonable (see Section 4.2). The third method we employed was to extract the total S$_{\text{(NGS)}}$ from the AC as H$_2$S using Kiba (Sn$^{II}$-chloride) solution (Kiba et al., 1955), precipitate the H$_2$S as Ag$_2$S, weigh the dried Ag$_2$S, and determine the S content of the Ag$_2$S by EA. The results of two analyses yielded the S contents of 1.27±0.02 wt% in AC (Table 5, corresponding to 0.75±0.01 mmol of $n$S$_{\text{(NDG)}}$, if the amount of C remained at 130 mmol. However, because the recovery of S from C-rich compounds by Kiba solution is typically ~75%, the actual $n$S$_{\text{(NDG)}}$ would be higher than ~1.0 mmoles. Therefore, by comparing the
$nS_{\text{NDG}}$ values estimated from the three methods, we may conclude that the true $nS_{\text{NDG}}$ was $1.12 \pm 0.05$ mmol.

X-ray photoelectron spectroscopic (XPS) analyses of the AC before and after the SO$_2$-adsorption experiments indicate that the AC before the experiments was free of S-bearing compounds, but the non-degassable S in the AC (i.e., $S_{\text{NDG}}$) is comprised of at least two types of S-bearing species (Fig. 9). Comparing the XPS spectra of the AC with those of various S-bearing compounds (Fig. 9), we may suggest that: the specie(s) with a strong peak at 174-167 eV are oxidized S-bearing species (i.e., S-O-C species), such as sulfate, sulfite, SO$_2$, and sulfone; and those with strong peak(s) at 167-163 eV are reduced S-bearing species (i.e., S-C species), such as $S^0$, thiophene, mercaptan, and cystein. The abundance ratio of the S-O-C species to the S-C species, based on the peak-area ratios, is 77 to 23.

The leachate of SO$_2$-reacted AC by H$_2$O at room temperature (or at 100 °C) produced precipitates of BaSO$_3$ (and/or BaSO$_4$) when BaCl$_2$ was added, suggesting that water-soluble S species were sulfite ($SO_3^{2-}$)- and/or sulfate ($SO_4^{2-}$)-like species. The HCl treatment of the AC did not generate H$_2$S, indicating the $S_{\text{NDG}}$ did not contain simple S$_2$-bearing species; this interpretation is also supported by the XPS spectra (Fig. 9). However, the treatment of the AC with Cr-reductive solution generated H$_2$S and precipitated ZnS by reaction with Zn-acetate solution, indicating that the $S_{\text{NDG}}$ contained polysulfide-like reduced sulfur species, such as $S^0$ and –C-S-S-S-C- species. We have estimated the amounts of S-bearing species during successive leaching both by measuring the amounts of the precipitates (Table 6) and by measuring the S/C ratios of the AC after each step of sequential extraction (Table 5). The results indicate that the $1.17 \pm 0.12$ mol of the $S_{\text{NDG}}$ is composed of $0.63 \pm 0.11$ mol (~60%) of sulfite- (or sulfate)-like species (i.e., S-O-C species), $0.25 \pm 0.08$ mmol (~20%) of polysulfide-like S-C species (i.e., S-C species), and $0.25 \pm 0.03$ mmol (~20%) of the residual S species (Table 6). The residual sulfur species may include some S-O-C and S-C compounds, as its treatment with Kiba solution generated some H$_2$S (Table 5). Overall, the abundance ratios of the oxidized S-O-C species and the reduced S-C species estimated from the sequential sulfur extraction are similar to those obtained by the XPS analyses (i.e., ~75/25) (Table 6 and Fig. 9).
4.2. Sequence and Rates of Chemical Reactions

The changes in the amounts of SO$_2$(w. ads), SO$_2$(s. ads), S$_{(\text{NDG})}$ through time during the Series I-III experiments (Tables 2-4; Figs. 6a-8a), and the chemical analyses of the AC suggest the following series of reactions were occurring during the reaction between SO$_2$(system) and the AC at 200 ° and 250 °C:

1. $\text{SO}_2(\text{system}) = \text{SO}_2(\text{w. ads})$ (R.1)
2. $\text{SO}_2(\text{w. ads}) \Rightarrow \text{SO}_2(\text{s. ads})$ (R.2)
3. $\text{SO}_2(\text{s. ads}) \Rightarrow \text{S}_{(\text{NDG})}$ (R.3)

R.1 and R.2 are chemisorption reactions, whereas R.3 is a redox reaction between SO$_2$ and C atoms, which can be written as the one producing the S-O-C species, and the other producing the S-C species:

$$a\text{SO}_2(\text{s. ads}) + b\text{C} \Rightarrow S_a\text{O}_{2a-2c}\text{C}_{b-c} + c\text{CO}_2$$ (R.3A)

and

$$S_a\text{O}_{2a-2c}\text{C}_{b-c} + (a-c)\text{C} \Rightarrow S_a\text{C}_{b-c} + (a-c)\text{CO}_2$$ (R.3B)

where $S_a\text{O}_{2a-2c}\text{C}_{b-c}$ and $S_a\text{C}_{b-c}$, respectively, represent S-O-C and S-C species in the AC, and $a$, $b$, and $c$ are stoichiometric coefficients that may vary with time (Fig. 10). R.3A and R.3B suggest that the formations of S-O-C and S-C compounds are continuous reactions in which the S/O and S/C ratios of the S$_{(\text{NDG})}$ continues to increase with time (Fig. 11).

The rapid response of the P$_{\text{system}}$ to the changes in $n\text{SO}_2(\text{system})$ due to the SO$_2$ sampling (Figs. 6a-8a) indicates that equilibrium is easily attained in R.1. If equilibrium was also easily attained in R.2, $n\text{SO}_2(\text{s. ads})$ would have become ~0 when $n\text{SO}_2(\text{system})$ decreased to ~0. However, the releases of significant amounts of SO$_2(\text{s. ads})$ at temperature 100-150 °C higher than the reaction temperature after $n\text{SO}_2(\text{system})$ decreased to ~0, indicate that R.2 was not easily reversible, and that the forward reaction of R.2 determined the amount of SO$_2(\text{s. ads})$. Similarly, R.3 was most likely unidirectional.

The equilibrium constant for R.1 may be written as:

$$K_1 = \frac{a\text{SO}_2(\text{w. ads})}{a\text{SO}_2(\text{system})} = \frac{[n\text{SO}_2(\text{w. ads})/SA_{(\text{AC})}]}{p\text{SO}_2(\text{system})}$$ (11)

where $SA_{(\text{AC})}$ refers to the surface area of the activated carbon:

$$SA_{(\text{AC})} = 1.884 \text{ gm} \times 457.7 \text{ m}^2/\text{gm} = 862.3 \text{ m}^2$$

Figure 12a shows the relationships between the $p\text{SO}_2(\text{g})$ and $n\Sigma S_{(\text{AC})}$ values for the Series I, II, and III experiments, where $n\Sigma S_{(\text{AC})} = n\text{SO}_2(\text{w. ads}) + n\text{SO}_2(\text{s. ads}) + n\Sigma S_{(\text{NDG})}$ (see eq. 10).
During the early stages of experiments (i.e., at high \( p_{SO_2} \) conditions), \( n_{SO_2(s, ads)} \gg n_{SO_2(w, ads)} \) (Tables 2-4). Therefore, \( n_{\Sigma S(AC)} \approx n_{SO_2(w, ads)} \). The Series I and III experiments were both carried out at 200 °C with the same \( SA_{(AC)} \), but with different \( p_{SO_2(initial)} \), \( n_{SO_2(initial)} \), and \( V_{system} \) values: \( p_{SO_2(I)} = 656.5 \text{ torr} \) vs \( p_{SO_2(III)} = 82.7 \text{ torr} \) at \( t = 0 \); \( n_{SO_2(I)} = 2.43 \text{ mmol} \) vs \( n_{SO_2(III)} = 6.04 \text{ mmol} \) at \( t = 0 \); \( V(I) = 68.8 \text{ mL} \) vs \( V(III) = 1358.7 \text{ mL} \). If equation (11) was applicable to our experiments, we should see the \( n_{\Sigma S(AC)} \) values in Series III experiments to be \( \sim \frac{1}{8} \) of Series I.

During the Series I – III set of reactions, the surface area of the AC increased from 457.7 to 514.3 m\(^2\)/g. However, since the change in \( SA_{(AC)} \) is small, we may write an apparent equilibrium constant for R.1 as:

\[
K_{1}' = \frac{n_{SO_2(w, ads)}}{n_{SO_2(system)}}
\]  

(12)

Fig. 12b shows the \( n_{SO_2(system)} \) vs \( n_{\Sigma S(AC)} \) values for the Series I, II and III experiments. During the early stages of the Series I experiment, both \( n_{SO_2(s, ads)} \) and \( n_{S(NDG)} \) were most likely \( \sim 0 \). Therefore, when the first sampling was carried out, \( n_{\Sigma S(AC)} \approx n_{SO_2(w, ads)} \approx 1.01 \text{ mmol} \) and \( n_{SO_2(system)} = 1.44\pm0.04 \text{ mmol} \) (Table 2). That is, for Series I, we obtain:

\[
K_{1(200 \text{°C})}' = \frac{1.01}{(1.44\pm0.04)} = 0.68\pm0.06
\]  

(13)

and

\[
n_{SO_2(w, ads)} = (0.68\pm0.06) \times n_{SO_2(system)}
\]  

(13’)

The difference between equation (13’) and that for the best-fit line for Series I data points (\( n_{\Sigma S(AC)} = 0.687 \times n_{SO_2(system)} + 0.055 \text{ mmol} \)) arose, because the \( n_{SO_2(w, ads)} \) values continued to deviate from the \( n_{\Sigma S(AC)} \) values due to the continuous increases in \( n_{SO_2(s, ads)} + n_{S(NDG)} \) values (see eq. 10), which reached to 0.06 mmol at the end of the Series I experiment. Note this \( n_{\Sigma S(AC)} \) compares well with the value of 0.08\pm0.05 mmol estimated from the \( n_{SO_2(g, initial)} \) and \( n_{\Sigma SO_2(sample)} \) values (Table 2).

In Series II, the first set of \( n_{SO_2(system)} \) and \( n_{\Sigma S(AC)} \) values were 1.76\pm0.01 mmol and 0.74\pm0.01 mmol, respectively (Table 3). Therefore, for Series II

\[
K_{1(250 \text{°C})}' = \frac{0.74\pm0.01}{1.76\pm0.01} = 0.42\pm0.01
\]  

(14)

and

\[
n_{SO_2(w, ads)} = (0.42\pm0.01) \times n_{SO_2(system)}
\]  

(14’)

The difference between Equation (14’) and that for the best-fit line for Series II data points (\( n_{\Sigma S(AC)} = 0.333 \times n_{SO_2(system)} + 0.191 \text{ mmol} \)) occurred by the same reasons as in Series I.
There is a considerable scatter of data from Series III experiment, especially those obtained during the early stage of experiment when the \( n_{SO_2(\text{system})} \) was greater than ~3 mmol (Fig. 12). The scatter of the data may mean that the equilibrium between \( SO_2(\text{w. ads}) \) and \( SO_2 \) had not yet been attained when the \( SO_2 \) samplings were carried out, especially when the \( n_{SO_2(\text{system})} \) was >~4 mmol. In the region \( n_{SO_2(\text{g})} <~2 \) mmol, the \( n_{\Sigma S(AC)} \) values are essentially constant at ~0.3 mmol, indicating that the \( (n_{SO_2(\text{s. ads})} + n_{S(NDG)}) \) exceeded the \( n_{SO_2(\text{w. ads})} \) because of the increased importance of R.2 and R.3 with time.

Equation (13) and (14) indicate that the adsorption of weakly-bounded \( SO_2 \) on the AC surface at 200 °C was about twice as high as that at 250 °C when \( n_{SO_2(\text{system})} \) values were the same. The decrease in the adsorption capacity with an increasing temperature has been well known in the literature (e.g., Cheng and Harriott, 1986). The free energy of reaction for R.1 at standard state (\( \Delta G^0_R \)) can be calculated from the \( K_1 \) values at 200 ° and 250 °C and the following relationship:

\[
\Delta G_R = \Delta G^0_R + RT \ln K_1' = 0
\]  

where \( R \) is gas constant (8.314 J/mol/K). That is

\[
\ln K_1' = - (\Delta G^0_R / R) / T
\]

The plot of \( \ln K_1' \) vs 1/T (Fig. 13) yields the \( - (\Delta G^0_R / R) \) value of 3595±1150, corresponding to the \( \Delta G^0_R \) value of -29.8±9.7 kJ/mol. This value may be compared with the values of -10.7 to -36.3 kJ/mol reported by previous researchers for the adsorption of \( SO_2 \) on activated carbon (Lua and Guo, 2001; Karatepe et al., 2008).

The forward rates of reactions 2 and 3 (i.e., \( R_2^f \) and \( R_3^f \), respectively) can be written as:

\[
R_2^f \cdot t = n_{SO_2(\text{s. ads})}
\]  

\[
R_2^f = k_2^f \cdot n_{SO_2(\text{w. ads})}
\]  

\[
R_3^f \cdot t = n_{S(NDG)}
\]  

and

\[
R_3^f = k_3^f \cdot n_{SO_2(\text{s. ads})}
\]

where \( k_2^f \) and \( k_3^f \) are the forward rate constants, and \( t \) is time in hour. Since the values of \( t, n_{SO_2(\text{s. ads})}, \) and \( n_{S(NDG)} \) are known, we can easily calculate the \( R_2^f, R_3^f, \) and \( k_3^f \) values (Table 7). For the calculation of \( k_2^f \), we have assumed the average \( n_{SO_2(\text{w. ads})} \) during each series of experiment was one half that of the \( n_{SO_2(\text{w. ads})} \) at the first \( SO_2 \) sampling. Results of calculations (Table 7) indicate that the \( k_2^f \) values of Series I and II are 0.0100±0.0010
and 0.0046±0.0015, respectively, whereas the $k^f$ values kept increasing from 0.0029±0.0059, and then to 0.0213±0.0204 through Series II and III. These data suggest that the surface of the AC became saturated (i.e., steady-state) with SO$_2$(s. ads) by the end of the Series II experiment, and the conversion of SO$_2$(s. ads) to S$_{(\text{NDG})}$ through R.3 is temperature dependent. R.3 continued through Series I-III to continuously increase the $n$S$_{(\text{NDG})}$ and $n$ΣS$_{(\text{AC})}$ meaning the redox reactions R.3A and R.3B continued to become more important with time.

We interpret that Reaction 3A and 3B are continuous reactions, and that the redox reactions between SO$_2$(g) and C atoms in the AC occur primarily in the surface layers of the AC. Since these reactions involve breaking of the C-C bonds (i.e., depolymerization), we would expect that the surface area of the AC to have continuously increased during the reaction with SO$_2$ (Fig. 11). Indeed, the specific surface area had increased from 457.7 to 514.3 m$^2$/g. The oxidized C atoms (i.e., CO$_2$) escaped the AC, but the reduced S atoms remained in the AC because there were no H atoms in the system. If the system had contained abundant H atoms, either as H$_2$O, H$_2$(g), and/or C-H compounds, some of the reduced S atoms would have been converted to H$_2$S$_{(\text{ads})}$ and to H$_2$S$_{(\text{g})}$ or H$_2$S$_{(\text{aq})}$.

5. Results and Interpretations of the Sulfur Isotope Data

5.1. $\delta^{34}$S and $\Delta^{33}$S values of the initial SO$_2$(g) and the uncertainties

Twenty-five replicate analyses (including the entire processes of conversion of Ag$_2$S to SF$_6$ and isotopic analyses) of an international Ag$_2$S standard IAEA-S1 ($\delta^{34}$S$_{\text{IAEA-S1-VCDT}} = -0.30\%$, $\Delta^{33}$S$_{\text{IAEA-S1-VCDT}} = +0.10\%$; Ding et al., 2001) were performed over the 8 month period of this study to assess the accuracy and reproducibility of sulfur isotope measurements. These analyses have yielded the $\delta^{34}$S values of the IAEA-S1 with respect to the PSUWS (i.e., the Penn State working standard, cryogenically purified 99.99% pure SF$_6$ gas from Spectra Gases Inc.) of -6.95±0.07 (1σ)$\%$, ranging from -7.06 to -6.79$\%$ and $\Delta^{33}$S value of 0.078±0.031 (1σ)$\%$, ranging from 0.025 to 0.137$\%$.

Nine replicate analyses of the initial SO$_2$(g), ranging in amounts from 0.06 to 1.08 mmol, have yielded the $\delta^{34}$S$_{\text{PSUWS}}$ values of +2.88±0.16 (1σ)$\%$, ranging from 2.69 to 3.13$\%$, and the $\Delta^{33}$S of +0.038±0.027 (1σ)$\%$, ranging from -0.012 to 0.078$\%$ (Table. 8). Reproducibility of the $\delta^{34}$S and $\Delta^{33}$S values for the starting SO$_2$(g) was worse than those
for IAEA-S1 standard, because the isotopic analyses of SO$_2$(g) involved many more analytical steps than those of Ag$_2$S: conversion of SO$_2$(g) to H$_2$SO$_4$, to BaSO$_4$, to Ag$_2$S, and to SF$_6$. Incomplete conversions or collections of samples at any stage could have caused the variations in the S isotopic values. Since the sulfur isotope analysis of a SO$_2$ gas sample from the experimental system was typically carried out only once, we have assigned the uncertainties of ±0.20‰ to $\delta^{34}$S and ±0.03‰ to $\Delta^{33}$S of the measured values against the PSUWS, and the ±0.40‰ to $\delta^{34}$S and ±0.06‰ to $\Delta^{33}$S when comparing the values between different samples, such as between an experimental product and the starting SO$_2$(g).

5.2. $\delta^{34}$S and $\Delta^{33}$S values of the experimental products

Table 8 and Figures 14-16 present the isotopic data of sampled SO$_2$(g) and SO$_2$(s, ads) from Series I-III, respectively. The S$^{34}$S values are presented in both against the PSU working standard (PSUWS) and the initial SO$_2$(g) values. Figures 14-16 show some obvious and important isotopic relationships among different S-bearing compounds in the experimental samples: (1) The $\delta^{34}$S values of SO$_2$(g) generally decreased with time during the adsorption/desorption experiments: by ~0.5‰, ~0.8‰, and ~0.6‰ in Series I, -II, and –III, respectively. This indicates that the heavier S atoms were preferentially incorporated in the AC. (2) $\delta^{34}$S values of the strongly adsorbed SO$_2$(s, ads), which was released at 100-150 °C higher than the experimental temperature, are significantly higher than the initial SO$_2$(g) by ~2.4‰ in Series I, ~3.5‰ by Series II, and ~7.3‰ by Series III. (3) At the end of Series I-III experiments, non-degassable sulfur-bearing species in the AC possessed $\delta^{34}$S values highly fractionated from the initial SO$_2$(g): ~+3.8‰ for the S$_{\text{NDG}}$; ~+11.6‰ for the water-soluble S-bearing species (i.e., S-O-C species); ~−8.3‰ for the Cr-reducible S (i.e., polysulfide-like C-S species); and ~−5.0‰ for the residual sulfur-bearing compounds (Table 6; Fig. 17).

Accuracy of the isotope analyses may be evaluated from the following isotope mass-balance equations:

$$\delta^{34}S_{\text{NDG}} = \delta^{34}S_{\text{S-O-C}} F_{\text{S-O-C}} + \delta^{34}S_{\text{C-S}} F_{\text{C-S}} + \delta^{34}S_{\text{res.S}} F_{\text{res.S}}$$

(21)

where $\delta^{34}S_{\text{S-O-C}} = +11.6\pm0.7‰$, $\delta^{34}S_{\text{C-S}} = -8.3\pm0.7‰$, and $\delta^{34}S_{\text{res.S}} = -5.0\pm0.4‰$ (Table 6; Fig. 17). $F_i$ is the mole fraction of specie $i$ in the $nS_{\text{NDG}}$: $F_{\text{S-O-C}} = 0.56\pm0.10$, $F_{\text{C-S}} =
0.23±0.08, and $F_{(\text{res.S})} = 0.23±0.06$. Then, the $\delta^{34}S_{(\text{NDG})}$ value can be calculated as $+3.5±2.5\%$ which agrees with the measured $\delta^{34}S_{(\text{NDG})}$ value of $+3.8±0.4\%$.

The $\delta^{34}S$ value for the $\Sigma SO_2(\text{sampled})$ through Series I-III experiment can be estimated from the following mass-balance calculations:

$$
\delta^{34}S_{SO_2(\text{initial})} = 0 \\
= \delta^{34}S_{\Sigma SO_2(\text{sampled})} F_{\Sigma SO_2(\text{sampled})} + \delta^{34}S_{SO_2(\text{s. ads}} F_{(\text{s. ads})} + \delta^{34}S_{S(\text{NDG})} F_{(S(\text{NDG})})
$$ (22)

where $\delta^{34}S_{SO_2(\text{initial})} = 0\%$, $\delta^{34}S_{SO_2(\text{s. ads}} = +7.3\%$, $\delta^{34}S_{S(\text{NDG})} = +3.8±0.4\%$. $F_i$ is the mole fraction of specie $i$ with respect to the sum of $(n\Sigma SO_2(\text{sampled}) + nSO_2(\text{s. ads}) + nS(\text{NDG})$:

$F_{\Sigma SO_2(\text{sampled})} = 0.79±0.09$, $F_{(\text{s. ads})} = 0.13±0.09$, and $F_{(S(\text{NDG})}) = 0.09±0.01$. Therefore, the calculated $\delta^{34}S_{\Sigma SO_2(\text{sampled})}$ value become $-1.9±1.2\%$. For comparison, the individual $\delta^{34}S_{SO_2(\text{g})}$ values, mostly fall between $-0.5±0.4\%$ and $0±0.4\%$. Therefore, we may conclude that the $\delta^{34}S_{\Sigma SO_2(\text{sampled})}$ value is $-0.3±0.7\%$.

In our experimental procedures, we could not directly determine the $\delta^{34}S$ and $\Delta^{33}S$ values of the weakly bound $SO_2(\text{w. ads})$, or the isotopic fractionations accompanying the adsorption and desorption of $SO_2(\text{w. ads})$. However, if we apply a general rule that heavier isotopes are preferentially enriched in compounds with stronger bonding energy, we may predict the following relationships: $\delta^{34}S_{SO_2(\text{system})} (~0\%) < \delta^{34}S_{SO_2(\text{w. ads})} < \delta^{34}S_{SO_2(\text{s. ads})} (+7.3±.4\%) < \delta^{34}S_{SOC} (+11.6±.7\%)$. Considering also that the bonding energy for the $SO_2(\text{w. ads})$, $29.8±9.7$ kJ/mole, is weak enough to cause AIF-S effects (Lasaga et al., 2008), we may suggest that the $\delta^{34}S_{SO_2(\text{w. ads})}$ value was closer to the $\delta^{34}S_{SO_2(\text{s. ads})}$ than to the $\delta^{34}S_{SO_2(\text{system})}$; therefore, the $\delta^{34}S_{SO_2(\text{w. ads})}$ at the end of Series I-III was probably $+4±1\%$. The $\Delta^{33}S_{SO_2(\text{w. ads})}$ value may be similar to the $\Delta^{33}S_{SO_2(\text{s. ads})}$, i.e., between 0 and $+0.15\%$.

The observed $\delta^{34}S$ relationships among the oxidized-S-bearing species, i.e., $\delta^{34}S_{SO_2(\text{system})} (~0\%) < \delta^{34}S_{SO_2(\text{w. ads})} < \delta^{34}S_{SO_2(\text{s. ads})} (+7.3±0.4\%) < \delta^{34}S_{SOC}$ ($+11.6±0.7\%)$, may suggest a continuous increase in the isotopic fractionation factors with continuous increases in the S/C and S/O ratios of the sulfur-bearing species incorporated in the AC. However, an alternative explanation, based on the surface reaction model (Lasaga, 1992), is as follows: Surface characteristics of the AC were so variable that the bonding energy for the weakly-adsorbed $SO_2(\text{w. ads})$ was also quite variable, causing large variations in the $\delta^{34}S_{SO_2(\text{w. ads})}$ and $\Delta^{33}S$ values. The $SO_2(\text{w. ads})$
adsorbed at surface sites with the highest bonding energy (e.g., sites of crystal defects) would show the highest increase in $\delta^{34}\text{S}_{\text{SO}_2(\text{ads})}$ value (e.g., $>+12\%$ from the $\text{SO}_2(\text{system})$), but the smallest increase in $\Delta^{33}\text{S}_{\text{SO}_2(\text{ads})}$. Since the $\text{SO}_2(\text{ads})$ adsorbed on crystal defects would enter in reactions 3A at a faster rate than the $\text{SO}_2(\text{ads})$ adsorbed on defect-free surface, the S-O-C species would have higher $\delta^{34}\text{S}$ values than the $\text{SO}_2(\text{s. ads})$ and $\text{SO}_2(\text{s. ads})$. This interpretation will imply that the variable isotopic fractionation (e.g., 4-12‰) occurred mostly during the first step (i.e., weak adsorption).

Our interpretation for the sequence of chemical reactions in the AC (Fig. 11) implies that the Cr-reducible S (i.e., “polysulfide-like” C-S species; $\delta^{34}\text{S} = -8.3 \pm 0.7\%$) formed by the reduction of S-O-S species ($\delta^{34}\text{S} = +11.6 \pm 0.7\%$) by the C atoms in the AC. It would imply that the kinetic isotope effect accompanying this reduction process is about -20‰. This kinetic isotope effect is similar to the kinetic isotope effects of -4.4 to 11.0 ‰ for residual sulfate and -12.5‰ to -6.0‰ for produced H$_2$S by the thermochemical sulfate reduction by aqueous glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) at $T = 200$ to $340$ °C (Kiyosu, 1980). Note, however, that the isotopic fractionation factors of about -20‰ in our experiments was between reduced S in solid phase and oxidized S in solid, whereas those by Kiyosu (1980) were between aqueous sulfide and aqueous sulfate. The significance of this difference will be discussed in the following section.

$\Delta^{33}\text{S}$ values of the $\text{SO}_2(\text{g})$ continuously decreased from +0.04 to $\sim$-0.10 ‰. $\Delta^{33}\text{S}$ values of the $\text{SO}_2(\text{ads})$ are essentially identical to the $\Delta^{33}\text{S}$ value of the last $\text{SO}_2(\text{g})$ samples of Series I-III (i.e., $\sim$-0.06 to 0.05‰). In contrast, all types of S-bearing species that constitute the non-degassable S possess small, but distinctly positive, $\Delta^{33}\text{S}$ values (+0.03 to +0.14‰). These $\Delta^{33}\text{S}$ values agree with the prediction by Lasaga et al. (2008) that $\Delta^{33}\text{S}$ of adsorbed species would have positive values, but their magnitudes will be less than $\pm$0.2‰ if the bonding energy for the adsorbed species exceeded $\sim$30 kJ/mol under specific physical and chemical conditions. The similar $\Delta^{33}\text{S}$ values between the S-C and S-O-C species in our experiments suggest that the S-O-C reduction occurred through mass-dependent processes.
6. Discussion: Chemical and Isotopic Fractionations of Sulfur during Reactions between Sulfate and Solid Organic Compounds

In this section, we will compare the results of our study with those obtained by previous investigators. We will also discuss the significance and implications of our study in understanding (a) the processes of multiple sulfur isotope fractionations in Watanabe et al.’s (2009) amino acid – sulfate reactions and (b) the origins of sulfide sulfur in petroleum, natural gas, and low temperature ore-forming fluids.

6.1. Comparisons of experimental data on SO$_2$-AC reactions

SO$_2$-AC reactions at $<$200 °C have been studied by many investigators (e.g., Shiels, 1929; Davini, 1989; Davini, 1991; Rubel and Stencel, 1997; Lua and Guo, 2001; Boudou et al., 2003; Zhang et al., 2007; Karatepe et al., 2008) to understand the adsorption characteristics of SO$_2$ on AC. Reactions at $>$600 °C have been investigated primarily to understand the redox reactions between SO$_2$ and AC. Important findings from the previous studies and also from this study include the following: (1) the saturated adsorption values of SO$_2$ on AC are typically in the range of ~1 to ~0.1 mmol SO$_2$ per gram of AC in the temperature range of 25-200 °C (Davini, 1989; Davini, 1991; Rubel and Stencel, 1997; Lua and Guo, 2001; Boudou et al., 2003; Zhang et al., 2007; Karatepe et al., 2008); (2) SO$_2$ adsorption on AC decreases with increasing temperature (Rubel and Stencel, 1997; Lua and Guo, 2001; Karatepe et al., 2008); (3) SO$_2$ adsorption on AC is significantly influenced by physical and chemical characteristics of system and activated carbons (e.g., surface area, purity of the activated carbon, open/close system, and chemical surface conditions) (Karatepe et al., 2008); (4) SO$_2$-AC reactions at 600-900 °C generate various gases (CO, CO$_2$, COS, CS$_2$, and S$_2$) and C-O-S compounds in AC (Blackwood and McCarthy, 1973; Humeres et al., 2002). Although we did not determine the chemical compositions of the generated gas, we have demonstrated from chemical and isotopic analyses of the SO$_2$-reacted AC that the redox reactions occurred between SO$_2$ and AC even at 200 °C.
6.2. Processes of Multiple Sulfur Isotope Fractionations during Sulfate – Amino Acid Reactions

Based on investigations of multiple sulfur isotope fractionations during reactions between sulfates and amino acid powders at 150-200 °C, Watanabe et al. (2009) and Watanabe et al. (in prep) found that the Cr-reducible S species (i.e., “polysulfide-like” S-C compounds) formed in the amino acid crystals and the liberated H$_2$S$_{(g)}$ possessed positive $\Delta^{33}$S values (up to +2.3‰), as predicted by Lasaga et al. (2008). However, their $\delta^{34}$S values widely varied from -17 to +16‰ relative to the initial SO$_4^{2-}$ (Fig. 2), whereas the theory of chemisorption isotope fractionation predicts the $\delta^{34}$S of the adsorbed species to be greater than that of aqueous (or gaseous) S-bearing species (Lasaga et al., 2008). This apparent discrepancy between the experimental and theoretical values can now be explained in the light of experimental data from this study.

Analogous to the reactions between gaseous SO$_2$ and activated carbon powders, reactions between aqueous SO$_4^{2-}$ and amino acid powders probably occurred through the following steps: (1) formation on the surfaces of amino acid crystals of weakly-adsorbed SO$_4^{2-}_{(w.\,ads)}$ that had variable, but positive, $\delta^{34}$S values (possibly from ~+3 to ~+15‰ relative to the initial SO$_4^{2-}$) and variable, but positive, $\Delta^{33}$S values (possibly from ~0.5 to ~+3‰); (2) successive transformations of the SO$_4^{2-}_{(w.\,ads)}$ to SO$_4^{2-}_{(s.\,ads)}$ and to S-O-C species with trends of increasing $\delta^{34}$S and decreasing $\Delta^{33}$S values; (3) continuous reduction of the S-O-C species by the C (and possibly H and N) atoms in amino acid to form “polysulfide-like” S-C species that have the $\delta^{34}$S$_{(SC-SOC)}$ ($=\delta^{34}$S$_{SC}$ - $\delta^{34}$S$_{SOC}$) values of ~-20‰, which results in the $\delta^{34}$S$_{(SC)}$ values ranging from ~-17 to +16‰ in the $\Delta^{33}$S$_{SC}$ similar to the $\Delta^{33}$S$_{(SOC)}$ values (i.e., mass-dependent reduction); and (4) reaction between the “polysulfide-like” S-C species and H$_2$O to form H$_2$S$_{(aq,g)}$ that has an isotopic composition similar to the S-C species.

6.3. Origins of Sulfide Sulfur in Petroleum, Natural Gas and Ore-forming Fluids

Thermochemical sulfate reduction (TSR) by carbon-bearing compounds have been investigated by numerous researchers. This is mostly because the H$_2$S and other S-bearing compounds in petroleum and natural gas and those in some ore-forming fluids appear, based on their sulfur isotopic characteristics and other geochemical data, to have
been generated by TSR at ~100°-200 °C (see summary in Ohmoto and Goldhaber, 1997). Some of the important questions concerning TSR have been: (1) What carbon compounds have been most responsible for TSR in nature? (2) What conditions (T, P, catalysis, etc) are required for the TSR? (3) What are the mechanisms and kinetics of the TSR? (4) What control the kinetic isotopic fractionation of sulfur? Results of our investigation on SO$_2$(g)-AC reactions shed light on these questions.

Previous researchers have evaluated various C-bearing compounds for their possible role in TSR in nature, including gaseous species (methane, propane), aqueous species (dextrose, fructose, ethanol, methanol, formaldehyde, acetic acid), and petroleum. However, laboratory experiments of TSR using these compounds failed to reduce sulfate at temperatures below ~250 °C (see Kaiser, 1988 and Ohmoto and Goldhaber, 1997 for summaries). In contrast, Watanabe et al. (2009) have demonstrated that sulfate is easily reduced to Cr-reducible S species in the solid phase (i.e., formation of S-C compounds) and to H$_2$S by simple amino acid powders (glycine, alanine) + H$_2$O at temperatures as low as 150 °C. Our experiment did not produce H$_2$S, because the system was free of H atoms (i.e., no H$_2$O and no C-H compounds), but did produce the Cr-reducible S (i.e., S-C compounds) in the AC at 200 °C. If H$_2$O had been present, reactions with the C-S compounds would have produced H$_2$S and hydrogen polysulfides. Therefore, we may conclude that TSR through heterogeneous reactions (i.e., solid-aqueous, solid-gas) occur much easier than in homogeneous reactions (i.e., gas-gas, gas-aqueous, aqueous-aqueous reactions), suggesting the important role of surface reactions (i.e., chemisorption) in promoting TSR, as suggested from the kinetic theory (e.g., Lasaga, 1992; Lasaga et al., 2008). Therefore, we may suggest that the solid C-bearing compounds (i.e., dead bodies of (micro)organisms and kerogen) geochemically play a more important role in natural TSR compared to gaseous, aqueous, or liquid compounds.

The small isotopic fractionations between H$_2$S and their source SO$_4^{2-}$ (i.e., $\delta^{34}$S = $\delta^{34}$S$_{H_2S} - \delta^{34}$S$_{SO_4^=}$ = -10 to 0‰) in petroleum and natural gas have previously been interpreted as a result of nearly-complete thermochemical reduction of SO$_4^{2-}$ in closed systems (e.g., Ohmoto and Goldhaber, 1997). However, the results of this study suggest that the small fractionations may be the results of TSR involving solid C-bearing
compounds, because the $\text{H}_2\text{S}$ was generated from reduction of the S-O-C clusters in kerogen that had higher $\delta^{34}\text{S}$ values than the source $\text{SO}_4^{2-}$ (e.g., gypsum/anhydrite).

6.4. AIF-S in natural samples

The results of this and Watanabe et al. (2009)’s investigations also suggest that reactions between C-bearing solid compounds and oxidized sulfur-bearing species do not always produce AIF-S. As theorized by Lasaga et al. (2008), the magnitude of $\Delta^{33}\text{S}$ (and $\Delta^{36}\text{S}$) depend on various parameters that influence the formation of adsorbed species, including (but not restricted to) the physical and chemical characteristics of organic compounds, types of S-bearing compounds, and temperatures. For example, Watanabe et al. (2009) found no AIF-S (i.e., $\Delta^{33}\text{S} < \pm 0.2\%\) from reactions between simple amino acids (alanine or glycine) and $\text{S}^0$ or sulfite, and between complex amino acids (arginine, tryptophan, and histidine) and sulfate. But they did find AIF-S from reactions between alanine (or glycine) and sulfate, and stronger AIF-S signatures when mixtures of alanine and glycine were used (Watanabe et al., in prep.). In this study, we found no AIF-S from reactions between $\text{SO}_2$ and AC, and also between coal (anthracite) and $\text{SO}_2$ at 200-250 °C (unpublished data). However, the finding of AIF-S signatures (-1.37 to +1.84‰) for the air pollutants in the Beijing-area air (Ding et al., 2006) suggests that higher temperature reactions between coal and the $\text{SO}_2$ generated from the combustion of pyrite-rich coals may have generated the AIF-S.

It is well known that many organic C-rich shales of Archean age possess AIF-S signatures (e.g., Ohmoto et al., 2006; Kaufman et al., 2007; Ono et al., 2009b), that not all organic C-rich shales of Archean age possess AIF-S signatures (Ohmoto et al., 2006), and that, except for ~1.9 Ga pyrite samples from the Outokump area (Young, 2009; personal communication 2010), AIF-S signatures have not been found in post ~2.4 Ga sedimentary rocks, regardless of their organic C contents. Ohmoto et al. (2006) and Watanabe et al. (2009) have suggested that the AIF-S signatures were generated by TSR involving sulfate-rich seawater and reactive organic matter during the early stage of diagenesis of sediments that accumulated under the influence of large-scale and long-lived submarine hydrothermal environments. These authors did not imply that the amino acid generated from the decay of biomolecules during diagenesis/hydrothermal stages
were directly involved in the generation of AIF-S in the pre-2.4 Ga sedimentary rocks. An important task for future research on multiple sulfur isotope geochemistry is to identify the specific types of organic matter (e.g., remnants of specific organisms) that generated large AIF-S signatures in Archean-age sediments.

7. Summary and Conclusions

We have conducted three series of experiments in a specially constructed closed system to investigate the chemical and isotopic fractionations of sulfur during reactions between SO$_2$(g) and activated carbon (AC) powders at 200-250 °C. The following is a summary of important observations and interpretations of the experimental results:

1. During reactions with SO$_2$(g), the AC incorporated three kinds of S: (i) weakly adsorbed SO$_2$(w. ads) which quickly established chemical equilibrium (and probably isotopic equilibrium) with SO$_2$(g); (ii) strongly adsorbed SO$_2$(s. ads), which became saturated by the end of Series I experiment; and (iii) non-degassable S species, which continued to increase its amount through Series I-III experiments.

2. The non-degassable S in the AC includes at least three different types of S clusters in the AC: (a) water-soluble, “sulfite- or sulfate-like” S-O-C clusters (i.e., S$_{SOC}$); (b) Cr-solution reducible, “polysulfide-like” S-C clusters (i.e., S$_{SC}$); and (c) unidentified residual S-species (i.e., S$_{resid}$).

3. Sequence of reactions for the formation of the different types of S-bearing species in the AC was: SO$_2$(g) $\Rightarrow$ SO$_2$(w. ads) $\Rightarrow$ SO$_2$(s. ads) $\Rightarrow$ S$_{SOC}$ $\Rightarrow$ S$_{SC}$

4. The differences in $\delta^{34}$S values between the final products and the initial ($\approx$ final) SO$_2$(g) were: +4±1‰ for SO$_2$(w. ads); +7.3±0.4‰ for SO$_2$(s. ads); +11.6±0.7‰ for S$_{SOC}$; -8.3±0.7‰ for S$_{SC}$; and -5.0±0.4‰ for S$_{res}$. 

5. All reaction products in the AC possess small, but positive $\Delta^{33}$S values (0 to 0.14‰).

6. $\Delta^{34}$S$_{\text{reduced S}}$ – oxidized S ($=\delta^{34}$S$_{\text{red.S}}$ – $\delta^{34}$S$_{\text{oxid.S}}$) values in the AC were around -20‰, which are similar to the $\Delta^{34}$S$_{H_2S}$-SO$_4$ values obtained by previous researchers for TSR using aqueous organic C compounds.
Comparing the data from this investigation, those by Watanabe et al. (2009; in prep.), and sulfur isotopic characteristics of petroleum, natural gas, ore-forming fluids, and sedimentary rocks, we suggest the following:

(A) \( \text{H}_2\text{S} \) and other reduced S-species in petroleum, natural gas, and some ore-forming fluids formed from TSR at 100-200 °C by utilizing solid C-bearing compounds (e.g., kerogen), rather than gaseous, aqueous, or liquid compounds.

(B) \( \Delta^{34}\text{S}_{\text{H}_2\text{S}-\text{SO}_4} \) values for TSR involving solid C-bearing compounds are -10 to 0‰, compared to the values -25 to -15‰ for those for TSR by aqueous C-bearing species.

(C) Most (if not all) AIF-S signatures in natural samples were caused by chemisorption reactions with or without redox reactions. Future research should be directed to: (i) identify the specific kerogen type that produced AIF-S signatures in organic C-rich sediments; (ii) investigate the chemisorption isotope effects involving non-C-bearing solid phases (e.g., goethite, hematite, clays) in order to understand AIF-S signatures in organic C-poor sedimentary rocks.
References


Appendix A. X-ray Diffraction for the Purity Check of the Recovered BaSO₄

Prior to the series of adsorption experiments, the purity of BaSO₄, prepared through the same procedure of section 3.1, was evaluated with an X-ray diffractometer (XRD) operated by Ms. Nichole Wandering, a technician of the Material Characterization Lab (MCL) of The Pennsylvania State University. The XRD spectra overlapped a peak pattern of BaSO₄ (Fig. A1), and no other peaks were identified.
Appendix B. Sequential Sulfur Extraction Procedure from the Activated Carbon for Chemical and Isotopic Analyses

To separately extract different types of sulfur-bearing compounds from the SO$_2$-reacted AC for isotopic analyses, we applied a four-step sequential extraction procedure (Fig. A2) using a glass extraction system. The procedure allows us to extract separately water-soluble S species (e.g., sulfite, SO$_3^{2-}$, and sulfate, SO$_4^{2-}$), HCl-soluble S species (e.g., monosulfides S$_2^-$), Cr-reducible S species (e.g., elemental S, S$_0$, and polysulfides, S$_x^{2-}$) (Canfield et al., 1986), and non-Cr-reducible S species (e.g., SOC compounds).

Water-soluble S was extracted at two different temperature conditions. First, water-soluble S was extracted at 25 °C from 300 mg of powdered SO$_2$-adsorbed AC by a reaction with a 100 mL of N$_2$-purged deionized water (DIW) for 2 hours in a 250 mL flask under N$_2$ flow. Sequentially, residual AC was centrifuged and rinsing with DIW three times. The solid residue was reacted with a 100 mL of N$_2$-purged DIW again at 100 °C for 2 hours, and then centrifuged to collect the solid residue. Each the solute, after collecting 10 mL for ion chromatograph (IC) analysis, was oxidized by addition of 10 mL of 20% H$_2$O$_2$ solution to convert all sulfur in the solutes to sulfate. The sulfate was precipitated as barium sulfate (BaSO$_4$) by reacting with 20 mL of 25% barium chloride (BaCl$_2$) solution. After centrifugation and decantation with DIW for three times, BaSO$_4$ was dried in a low temperature oven overnight, and was weighed. BaSO$_4$ was reduced to H$_2$S with a Thode reagent (Thode et al., 1961) for isotope analyses.

HCl-soluble S was also extracted from the residual AC after the water-soluble S extraction at two different temperature conditions. First, HCl-soluble S was extracted at 25 °C from the residual AC by a reaction with 100 mL of N$_2$-purged 6N-hydrochloric acid solution for 2 hours in a 250 mL flask under N$_2$ flow. After decantation and rinsing with DIW three times, the solute was analyzed with an IC for determining S content. Sequentially, HCl-soluble S extraction at 180 °C was conducted with the same manner after the decantation and centrifugation of the residual AC. The remaining AC after the HCl-soluble S extractions was placed in a 250 mL flask for the extraction of Cr-reducible S.

Cr-reducible S was extracted following the procedure developed by Canfield et al. (1986). The remaining AC from the earlier procedure was reacted with a 30 mL of chromium (II) reductive solution for ~2 hours at 180 °C in a 250 mL flask under a N$_2$ flow. The chromium (II) reductive solution was prepared from 15 mL of 12N-hydrochloric acid, 345 mL of DIW, 182 g of chromium (III) chloride hexahydrate, and 105 gm of amalgamated zinc. This solution only reduces native S and polysulfides to H$_2$S. The remaining AC was centrifuged and decanted with DIW three times, and dried for 6 hours before undergoing the extraction of all the remaining S species by the Kiba reagent (Kiba et al., 1957).

The remaining S species, non-Cr-reducible S, was extracted following the procedure developed by Kiba et al. (1955). The Kiba reagent can extract sulfur from diverse sulfur-bearing materials (Kiba et al., 1955), and is also used for the total sulfur extraction. The reagent was prepared as follows: in a 1000 mL pyrex flask, 300 mL of orthophosphoric acid was dehydrated at 280 °C for an hour under vacuum. After cooling the phosphoric acid down to 150 °C, 40 gm of tin (II) chloride dehydrate were added, and the mixture was heated up to 280 °C for an hour under a N$_2$ flow. The dried remaining
AC was reacted with the Kiba reagent at 280 °C for ~2 hours under N₂ flow, and elevated H₂S was collected with a trap of 100mL zinc acetate solution as ZnS.

Sulfur content of dried AC samples after each S extraction step was measured using the elemental analyzer (EA) (CE instrument Inc. NC2500) in Ohmoto’s laboratory. The H₂S released from each step was carried by a N₂ flow to a 2% acetic acid trap, and then trapped in 100 mL of the zinc acetate solution as zinc sulfide (ZnS). The zinc acetate solution was prepared from 40 g of zinc acetate and 30 mL of glacial acetic acid, and diluted to 1000 mL by DIW. ZnS is converted to silver sulfide (Ag₂S) by mixing with a 20 mL of 0.01 M silver nitrate solution (AgNO₃). Precipitated Ag₂S is gently boiled for >5 minutes, and washed with DIW and few drops of 1% ammonium hydroxide solution (NH₄OH) before centrifugation and decantation of the precipitate. After drying for approximately 6 hours, Ag₂S is weighed and wrapped in aluminum foil for S isotope analysis.
Appendix C. Sulfur isotope analyses

For measurements of sulfur isotope ratios using a conventional gas-source isotope-ratio-mass-spectrometer (IRMS), S-bearing compounds are converted to either sulfur dioxide or sulfur hexafluoride (SF$_6$). The SF$_6$ method is better suited for precise determination of sulfur isotope ratios, because fluorine has only one isotope.

The sulfur isotope analytical system in Ohmoto’s laboratory is comprised of five major units: a Ni tube fluorination system where Ag$_2$S is converted to SF$_6$, a laser fluorination system, a gas chromatography (GC) (Fig. A6), a cryogenic system to purify the SF$_6$, and an IRMS (VG Prism) (Fig. A7).

The tube fluorination system has six Ni reaction tubes. To convert Ag$_2$S to SF$_6$, 1 to 5 mg of Ag$_2$S was wrapped in a 1.5 cm$^2$ piece of aluminum foil, loaded into a tube, and fluorinated at 275 °C in a F$_2$ atmosphere in which the pressure was adjusted at an F$_2$ amount corresponding to ~3 times of required amount. It takes approximately 12 hours for conversion of Ag$_2$S to SF$_6$. Residual F$_2$ and non-condensable gases were went through a KBr trap and then pumped away while the generated SF$_6$ was condensed in a liquid nitrogen trap. The SF$_6$ and other gases (e.g., H$_2$O, CO$_2$, CFO compounds) were defrosted from this trap at room temperature. To separate out the non-SF$_6$ gases, cryogenic traps and a GC were used prior to the introduction of SF$_6$ gas into the IRMS. GC purification of SF$_6$ was carried out using a 1/8”-diameter, 12’-long molecular sieve 5Å and a 1/8”-diameter, 12’-long HaysepQ column and with a 99.999% helium carrier flow (Fig. A7). The SF$_6$ peak was identified (monitered) by a thermal conductivity detector, and the SF$_6$ was isolated by freezing at liquid nitrogen temperature (-196 °C) in a collection loop.

Then, the SF$_6$ was thawed and introduced into the IRMS for determining the abundance ratios of m/z = 127 ($^{32}$SF$_5^+$), 128 ($^{33}$SF$_5^+$), and 129 ($^{34}$SF$_5^+$) where m/z represent a mass-to-charge ratio.

All isotope data were reported in ‰ as $\delta^{34}$S and $\Delta^{33}$S relative to the PSU working standard (PSUWS: Ultra high pure SF$_6$). The $\delta^{33}$S and $\delta^{34}$S values of the PSUWS reference gas relative to the international standard IAEA S-1, for which $\delta^{33}$S and $\delta^{34}$S is −0.05 and -0.3‰ respectively in definition, are 3.52 and 7.00‰, respectively. To evaluate reproducibility and uncertainty of S isotope measurements, IAEA-S1 and initial SO$_2$ samples (taken from SO$_2$ tank used for the series of the adsorption experiments) had been repeatedly measured.
Table 1. Amounts and isotopic values of BaSO₄ obtained from pure SO₂(g) at various pressures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$p$SO₂(g) (torr)</th>
<th>Recovered BaSO₄ (mmol)</th>
<th>Expected BaSO₄ (mmol)</th>
<th>δ$^{34}$S psu ‰</th>
<th>Δ$^{33}$S psu ‰</th>
<th>Note</th>
</tr>
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<td>IS-28.9</td>
<td>28.9</td>
<td>0.057</td>
<td>0.063</td>
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<td>IS-50.8</td>
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Table 2. Changes with time in SO$_2$ amount during Series I experiment (initial $\Sigma S = 2.43$ mmol, $AC = 130$ mmol, $V_{\text{system}} = 68.8$ mL, $V_{\text{aliquot}} = 40.4$ mL, $A_{\text{surface}} = 457.7$ m$^2$/g, $T = 200$ °C).

| Sample No. | Temp (°C) | Elapsed time (hrs) | System pressure (torr) | $p_{\text{(system)}}$ | System SO$_2$ (mmol) | $nS_{\text{O}_2(\text{system})}$ | System SO$_2$ recovered (mmol) | $nS_{\text{O}_2(\text{sampled})}$ | Sampled SO$_2$ (mmol) | $\Sigma$ Sampled SO$_2$ (mmol) | $\Sigma S$ incorporated in AC (mmol) | $nS_{\text{AC}}$ | $\Sigma S_{\text{incorp.}}$ (mmol) | $nS_{\text{O}_2(\text{desorb})}$ | Desorbed SO$_2$ (mmol) | Desorption rate R (mmol/hr) |
|------------|-----------|---------------------|------------------------|----------------------|----------------------|-------------------------------|-----------------------------|----------------------|--------------------------|-----------------------------|----------------|-----------------------------|------------------------|---------------------|---------------------|
| I-24.0     | 200±3     | 24.0                | 378.7                  | 1.40                 | 1.49                 | 0.84                          | 0.82                        | 0.87                 | 0.82                     | 0.87                        | 1.03            | 0.94                        |                        | -0.83               | -49.91              |
|            | 200±3     | 24.1                | 156.3                  | 0.58                 | 0.61                 | 0.50                          | 0.50                        | 0.53                 | 1.32                     | 1.40                        | 0.76            | 0.66                        | 0.27                    | 0.29                | 0.12 0.13 |
| I-26.3     | 195±5     | 26.2                | 228.2                  | 0.84                 | 0.90                 | 0.84                          | 0.84                        | 0.53                 | 1.32                     | 1.40                        | 0.76            | 0.66                        | 0.27                    | 0.29                | 0.12 0.09 |
| I-28.5     | 196±5     | 28.5                | 151.0                  | 0.56                 | 0.56                 | 0.56                          | 0.56                        | 0.53                 | 1.65                     | 1.73                        | 0.55            | 0.47                        | 0.21                    | 0.18                | 0.10 0.09 |
| I-30.0     | 198±4     | 30.0                | 104.9                  | 0.39                 | 0.39                 | 0.21                          | 0.23                        | 0.23                 | 1.88                     | 1.96                        | 0.39            | 0.31                        | 0.16                    | 0.16                | 0.11 0.11 |
| I-31.5     | 196±5     | 31.5                | 70.2                   | 0.26                 | -                    | 0.15                          | 0.15                        | 2.03                 | 2.11                     | 0.29                        | 0.22            | 0.22                        | 0.22                    | 0.29                | 0.22    |
|            | 196±5     | 31.6                | 29.0                   | 0.11                 | -                    | 0.11                          | 0.11                        | 0.11                 | 0.11                     | 0.11                        | 0.21            | 0.12                        | 0.09                    | 0.09                | 0.04    |
(Table 2, continued)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temp (ºC)</th>
<th>Elapsed time (hrs)</th>
<th>Press system (torr)</th>
<th>System SO₂ (nSO₂ system) (mmol)</th>
<th>SO₂ recovered (mmol)</th>
<th>Sampled SO₂ (nSO₂ sampled) (mmol)</th>
<th>Σ sampled SO₂ (nΣSO₂ sampled) (mmol)</th>
<th>ΣS incorp. in AC (nΣSAC) (mmol)</th>
<th>Desorbed SO₂ (nSO₂ desorb) (mmol)</th>
<th>Desorption rate R (mmol/hr)</th>
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</table>

Foot notes:
Values in regular fonts: measured values. Values in italic fonts: calculated (estimated) values.

ΣS incorporated in AC: \( nΣS_{AC} = nSO₂_{system at t=0} - nSO₂_{system at t} - nΣSO₂_{sampled} \).

S recovery yield: determined by the amount of SO₂ recovered as BaSO₄.

a Calculated assuming \( p_{system} \) is solely derived from SO₂(g).

b Calculated using the equation of \( Y = 1.02X + 0.02 \) mmol, in which \( X \) is the recovered amount of BaSO₄ (mmol) and \( Y \) is the estimated amounts of SO₂(g) sampled (see Fig. 5).

c Due to a BaSO₄ sample lost, use "0.15" from (i) in \( nSO₂_{sampled} \) of I-31.5.
Table 3. Changes with time in SO$_2$ amount during Series II experiment (initial $\Sigma S = 2.50$ mmol, $AC = 130$ mmol, $V_{system} = 68.8$ mL, $V_{aliquot} = 40.4$ mL, $A_{surface} = 457.7$ m$^2$/g, $T = 250$ °C).

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<th>Temp (°C)</th>
<th>Elapsed time (hrs)</th>
<th>System pressure (torr)</th>
<th>System SO$_2$ $n$SO$_2$ (system)</th>
<th>System BaSO$_4$ $n$SO$_2$ (system)</th>
<th>BaSO$_4$ recovered (mmol)</th>
<th>Sampled SO$_2$ $n$SO$_2$ (sampled)</th>
<th>Sampled SO$_2$ $n$SO$_2$ (sampled)</th>
<th>$\Sigma$SO$_2$ in AC $n$SO$<em>2$ ($\Sigma$S$</em>{AC}$)</th>
<th>$\Sigma$S incorp. in AC $n$SO$<em>2$ ($\Sigma$S$</em>{AC}$)</th>
<th>Desorbed SO$_2$ $n$SO$_2$ (desorb)</th>
<th>Desorption rate R (mmol/hr)</th>
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<td>0.73</td>
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</table>
(Table 3, continued)

<table>
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<th>Sample No.</th>
<th>Temp (ºC)</th>
<th>Elapsed time (hrs)</th>
<th>System pressure (torr)</th>
<th>System SO₂ (n\text{SO}_2\text{(system)})</th>
<th>BaSO₄ recovered (n\text{SO}_2\text{(sampled)})</th>
<th>Sampled SO₂ (n\text{SO}_2\text{(sampled)})</th>
<th>ΣSampled SO₂ (n\Sigma\text{SO}_2\text{(sampled)})</th>
<th>Σincorp. in AC (n\Sigma\text{AC})</th>
<th>Desorbed SO₂ (n\text{SO}_2\text{(desorb)})</th>
<th>Desorption rate (R) (mmol/hr)</th>
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</tr>
</tbody>
</table>

Footnotes:

Values in regular fonts: measured values. Values in italic fonts: calculated (estimated) values.

\(\Sigma S\) incorporated in AC: \(n\Sigma S_{\text{AC}} = n\text{SO}_2\text{(system at } t = 0) - n\text{SO}_2\text{(system at } t) - n\Sigma\text{SO}_2\text{(sampled)}\).

S recovery yield: determined by the amount of SO₂ recovered as BaSO₄.

\(a\) Calculated assuming \(p\text{system}\) is solely derived from \(\text{SO}_2\text{(g)}\).

\(b\) Calculated using the equation of \(Y = 1.02X + 0.02\text{ mmol}\), in which \(X\) is the recovered amount of BaSO₄ (mmol) and \(Y\) is the estimated amounts of \(\text{SO}_2\text{(g)}\) sampled (see Fig. 5).
Table 4. Changes with time in SO$_2$ amount during Series III experiment (initial $\Sigma$S = 6.04 mmol, AC = 130 mmol, V$_{\text{system}}$ = 1358.7 mL, V$_{\text{aliquot}}$ = 181.4 mL, A$_{\text{surface}}$ = 457.7 m$^2$/g, T = 200 °C).

<table>
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<th>Sample No.</th>
<th>Temp (°C)</th>
<th>Elapsed time (hrs)</th>
<th>System pressure $p_{\text{system}}$ (torr)</th>
<th>System SO$_2$ nSO$_2$(system) (i)$^a$ (ii)$^b$</th>
<th>BaSO$_4$ recovered (mmol) (i)$^a$ (ii)$^b$</th>
<th>Sampled SO$_2$ nSO$_2$(sampled) (mmol) (i)$^a$ (ii)$^b$</th>
<th>$\Sigma$sampled SO$_2$ n\Sigma SO$_2$(sampled) (mmol) (i)$^a$ (ii)$^b$</th>
<th>$\Sigma$S incorp. in AC n\Sigma S$_{AC}$ (mmol) (i)$^a$ (ii)$^b$</th>
<th>Desorbed SO$_2$ nSO$_2$(desorb) (mmol) (i)$^a$ (ii)$^b$</th>
<th>Desorption rate R (mmol/hr) (i)$^a$ (ii)$^b$</th>
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</thead>
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(Table 4, continued)

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<th>Sample No.</th>
<th>Temp (°C)</th>
<th>Elapsed time (hrs)</th>
<th>System pressure (torr)</th>
<th>System SO$_2$ ($n$SO$_2$(system))</th>
<th>BaSO$_4$ recovered (mmol)</th>
<th>Sampled SO$_2$ ($n$SO$_2$(sampled)) (i)$^a$</th>
<th>Sampled SO$_2$ ($n$SO$_2$(sampled)) (ii)$^b$</th>
<th>Σsampled SO$_2$ ($nΣSO_2$(sampled)) (i)$^a$</th>
<th>Σsampled SO$_2$ ($nΣSO_2$(sampled)) (ii)$^b$</th>
<th>ΣS incorp. in AC ($nΣS_{AC}$) (mmol)</th>
<th>Desorbed SO$_2$ ($nSO_2$(desorb)) (i)$^a$</th>
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### Table 4, continued

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temp (°C)</th>
<th>Elapsed time (hrs)</th>
<th>System pressure (torr)</th>
<th>System SO$<em>2$ recovered $p</em>{(\text{system})}$ (i)$^a$ (ii)$^b$ (mmol)</th>
<th>System SO$_2$ (system at t = 0) (i)$^a$ (ii)$^b$ (mmol)</th>
<th>BaSO$_4$ recovered (mmol)</th>
<th>Sampled SO$<em>2$ (sampled) $n</em>{\text{SO}_2}$ (i)$^a$ (ii)$^b$ (mmol)</th>
<th>Sampled SO$<em>2$ (sampled) $n</em>{\Sigma \text{SO}_2}$ (i)$^a$ (ii)$^b$ (mmol)</th>
<th>$\Sigma$S incorp. in AC $n_{\Sigma S_{\text{AC}}}$ (i)$^a$ (ii)$^b$ (mmol)</th>
<th>Desorbed SO$<em>2$ (desorb) $n</em>{\text{SO}_2}$ (i)$^a$ (ii)$^b$ (mmol)</th>
<th>Desorption rate (mmol/hr)</th>
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<tr>
<td>III-378.0</td>
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<td>0.57</td>
<td>0.70</td>
<td>0.07</td>
<td>0.08</td>
<td>0.09</td>
<td>5.50</td>
<td>5.15</td>
<td>0.05</td>
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<td>III-402.0</td>
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<td>0.04</td>
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<td>0.09</td>
<td>5.57</td>
<td>5.24</td>
<td>0.04</td>
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<td>III-450.0</td>
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<td>III-450.0</td>
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<td>6.1</td>
<td>0.45</td>
<td>0.39</td>
<td>0.06</td>
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<td>474.0</td>
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<td>0.05</td>
<td>0.05</td>
<td>0.07</td>
<td>5.68</td>
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<td>III-474.0</td>
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<td>474.1</td>
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<td>III-480.0</td>
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<td>III-480.0</td>
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<tr>
<td>Total</td>
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<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Footnotes:
- Values in regular fonts: measured values. Values in italic fonts: calculated (estimated) values.
- $\Sigma$S incorporated in AC: $n_{\Sigma S_{\text{AC}}} = n_{\text{SO}_2(\text{system at t = 0})} - n_{\text{SO}_2(\text{system at t})} - n_{\Sigma \text{SO}_2(\text{sampled})}$.
- Recovery yield: determined by the amount of SO$_2$ recovered as BaSO$_4$.
- $^a$ Calculated assuming $p_{(\text{system})}$ is solely derived from SO$_2(g)$.
- $^b$ Calculated using the equation of Y = 1.02X + 0.02 mmol, in which X is the recovered amount of BaSO$_4$ (mmol) and Y is the estimated amounts of SO$_2(g)$ sampled (see Fig. 5).
- $^c$ Due to a BaSO$_4$ sample lost, use "0.12" from (i) in nSO$_2(\text{sampled})$ of III-330.
Table 5. C/H/N/S analyses by an elemental analyzer (EA) and the wet chemical methods of the activated carbon before and after Series I-III experiments, and through sequential S extractions.

<table>
<thead>
<tr>
<th>ID</th>
<th>Description</th>
<th>Nos. of analysis</th>
<th>Solid chemical analyses by EA</th>
<th>Wet chemical analysis</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C (wt%)</td>
<td>H (wt%)</td>
</tr>
<tr>
<td>A</td>
<td>AC before experiment</td>
<td>2</td>
<td>83.28±.36</td>
<td>0.66±.08</td>
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<tr>
<td>B</td>
<td>AC after I-III experiments</td>
<td>4</td>
<td>83.52±4.12</td>
<td>0.96±.26</td>
</tr>
<tr>
<td>C</td>
<td>Leachate of B by H₂O &amp; HCl solutions</td>
<td>2</td>
<td>0.76±.02</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>Residual AC of C &amp; E</td>
<td>4</td>
<td>85.42±3.35</td>
<td>0.71±.12</td>
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<tr>
<td>E</td>
<td>Reduced S in B &amp; D by Cr solution</td>
<td>4</td>
<td>85.42±3.35</td>
<td>0.71±.12</td>
</tr>
<tr>
<td>F</td>
<td>Residual AC of E</td>
<td>6</td>
<td>84.84±2.02</td>
<td>1.06±.05</td>
</tr>
<tr>
<td>G</td>
<td>Reduced S in F by Kiba solution</td>
<td>2</td>
<td>1.27±.02</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>Reduced S in B by Kiba solution</td>
<td>2</td>
<td>-</td>
<td>-</td>
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</table>

Foot notes:
- O contents calculated as: O(wt%) = 100 - (C+H+N+S)(wt%)
- H₂O soluble S and HCl soluble S may correspond to sulfate and/or sulfite S.
- Cr-soluble S corresponds to polysulfides (including native S).
- Reduced S corresponds non-Cr-reducible S (e.g., organic-S).
- Kiba-solution S corresponds all S species, including sulfate, sulfite, polysulfide, organic-S, and C-S compounds.
Table 6. Summary of the chemical and isotopic data from the SO$_2$-activated carbon reactions.

<table>
<thead>
<tr>
<th>Series</th>
<th>Temperature (°C)</th>
<th>Reaction time (hrs)</th>
<th>Initial $\Sigma S$ (mmol)</th>
<th>$\Sigma S_{(sampl)}$ (mmol)</th>
<th>$\Sigma S_{(w. ads)}$ a (mmol)</th>
<th>$\Sigma S_{(s. ads)}$ b (mmol)</th>
<th>$\Sigma S_{(NDG)}$ (mmol)</th>
<th>$S_{(S-O-C)}$ (mmol)</th>
<th>$S_{(S-C)}$ (mmol)</th>
<th>$S_{(resid.)}$ (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>200</td>
<td>40</td>
<td>2.43</td>
<td>2.32±.04</td>
<td>0.49±.02</td>
<td>0.19±.01</td>
<td>-0.13±.04</td>
<td>0.49±.02</td>
<td>0.00±.00</td>
<td>0.00±.00</td>
</tr>
<tr>
<td>II</td>
<td>250</td>
<td>88</td>
<td>2.50</td>
<td>2.35±.05</td>
<td>0.37±.01</td>
<td>0.14±.04</td>
<td>0.04±.09</td>
<td>0.37±.01</td>
<td>0.00±.00</td>
<td>0.00±.00</td>
</tr>
<tr>
<td>III</td>
<td>200</td>
<td>480</td>
<td>6.04</td>
<td>5.52±.16</td>
<td>0.18±.07</td>
<td>1.03±1.44</td>
<td>1.12±.05</td>
<td>0.18±.07</td>
<td>0.00±.00</td>
<td>0.00±.00</td>
</tr>
<tr>
<td>Total</td>
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<td></td>
<td>608</td>
<td><strong>10.97</strong></td>
<td><strong>10.19±.25</strong></td>
<td><strong>1.12±.05</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| $\delta^{34}$S ‰ relative to initial SO$_2$ | 0.0 | -0.5 to -0.8 | 2.4 to 7.3 | 3.8±.4 | 11.6±0.7 | -8.3±.7 | -5.0±.4 |
| $\Delta^{33}$S ‰ relative to initial SO$_2$ | 0.0 | -0.14 to 0.03 | -0.09 to 0.01 | 0.01±0.04 | 0.12±0.02 | 0.07±0.02 | 0.05±0.06 |

Footnotes:
- Abbreviations: $\Sigma S_{(sampl)}$: strongly adsorbed SO$_2$; $\Sigma S_{(NDG)}$: total non-degassable S in AC; $S_{(S-O-C)}$: water soluble oxidized S in AC; $S_{(S-C)}$: reduced sulfur compounds dissolved by Cr-reductive solution; $S_{(resid.)}$: residual S compounds.
- Uncertainty in the $\Sigma S_{(sampl)}$, initial $\Sigma S$, and $\Sigma S_{(w. ads)}$ values are ±0.03 mmol.
- Uncertainties in the $\delta^{34}$S and $\Delta^{33}$S values are ±0.4‰ and ±0.06‰ respectively.
- $\Sigma S_{(w. ads)}$: estimated average amount of SO$_2$ during the series of experiment = 1/2 of the SO$_2$ at the fist sampling.
- Desorbed at higher temperature.
Table 7. Calculated equilibrium constant (K), rates (R), and rate constants (k) for the reactions between SO$_2$(g) and activated carbon.

<table>
<thead>
<tr>
<th>Series</th>
<th>Temp (°C)</th>
<th>Reaction time (hrs)</th>
<th>$K_1^f = n_{SO_2(ads)}/n_{SO_2(g)}$</th>
<th>$R_2^f = n_{SO_2(ads)}/RT$ (mmol/hr)</th>
<th>$k_2^f = R_2^f/n_{SO_2(ads)}$ (hr$^{-1}$)</th>
<th>$R_3^f = \sum_{S_{(NDG)}}/RT$ (mmol/hr)</th>
<th>$k_3^f = R_3^f/\sum_{SO_2(ads)}$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>200</td>
<td>40</td>
<td>0.68±0.06</td>
<td>0.0049±0.0003</td>
<td>0.0100±0.0010</td>
<td>-</td>
<td>-</td>
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<tr>
<td>II</td>
<td>250</td>
<td>88</td>
<td>0.42±0.01</td>
<td>0.0017±0.0005</td>
<td>0.0046±0.0015</td>
<td>0.0005±0.0010</td>
<td>0.0029±0.0059</td>
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<tr>
<td>III</td>
<td>200</td>
<td>480</td>
<td>0.42±0.01</td>
<td>0.0021±0.0030</td>
<td>0.0191±0.0273</td>
<td>0.0024±0.0001</td>
<td>0.0213±0.0204</td>
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</tbody>
</table>
Table 8. Sulfur isotopic compositions of the SO\textsubscript{2(g)} and reaction products (All values are relative to the PSU standard.).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. of experiment (°C)</th>
<th>Nos. of analysis</th>
<th>$\delta^{33}\text{S}_{\text{psu}}$ (%)</th>
<th>$\delta^{34}\text{S}_{\text{psu}}$ (%)</th>
<th>$\Delta^{33}\text{S}_{\text{psu}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial SO\textsubscript{2(g)}</td>
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<td>18</td>
<td>1.52±0.07</td>
<td>2.88±0.16</td>
<td>0.038±0.027</td>
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<td>I-24.0</td>
<td>200±3</td>
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<td>1.67</td>
<td>3.25</td>
<td>0.000</td>
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<td>I-26.3</td>
<td>195±5</td>
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<td>1.41</td>
<td>2.65</td>
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<tr>
<td>I-28.5</td>
<td>196±5</td>
<td>1</td>
<td>1.53</td>
<td>2.95</td>
<td>0.015</td>
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<tr>
<td>I-34.0</td>
<td>195±5</td>
<td>1</td>
<td>1.35</td>
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<td>195±5</td>
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<td>I-39.0</td>
<td>192±6</td>
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<td>1.18</td>
<td>2.40</td>
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<tr>
<td>I-40.0: desorbed SO\textsubscript{2}</td>
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<td>1</td>
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<td>II-72.0</td>
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<td>-0.008</td>
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<td>II-78.0</td>
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<td>1.46</td>
<td>2.78</td>
<td>0.027</td>
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<td>II-84.0</td>
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<td>1.32</td>
<td>2.65</td>
<td>-0.045</td>
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<tr>
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<tr>
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<td>2.79</td>
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<td>300</td>
<td>1</td>
<td>5.32</td>
<td>10.21</td>
<td>0.046</td>
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C: H\textsubscript{2}O&HCl-soluble S in B | 2 | 7.64±0.36 | 14.52±0.66 | 0.158±0.020 |
E: Cr-reducible S in B and D | 9 | -2.71±0.34 | -5.46±0.65 | 0.106±0.024 |
G: Non-Cr-reducible S in F | 3 | -1.02 | -2.16 | 0.093 |
H: Total S in AC after Series I-III | 8 | 3.47±0.12 | 6.64±0.20 | 0.054±0.035 |
Fig. 1. Comparisons of the multiple S isotope data on: (i) pre-2.4 Ga sedimentary rocks (Modified after Otake and Watanabe, 2011 in press); (ii) S\(^0\) and SO\(_4^{2-}\) from UV photolysis of SO\(_2\) by 193 nm UV laser (Farquhar et al., 2001); and (iii) S\(^0\) and SO\(_4^{2-}\) from UV photolysis of SO\(_2\) by a broadband UV lamp (Masterson et al., 2011).
Fig. 2. AIF-S isotope data from amino-acid (powder) – sulfate reactions at 150-200 °C. Data are from Watanabe et al. (2009) and Watanabe et al. (in prep.).
Fig. 3. A Morse potential curve of S-O bound energy levels for $^{32}$S, $^{33}$S, $^{34}$S, and $^{36}$S atoms, and energy levels for the four sulfur atoms at $n=0$ and $n=5$ in a SO$_2$ surface adsorbed layer (modified after Lasaga et al. (2008). Note that $^{32}$S is missing from the upper most energy level.
**Fig. 4.** A schematic figure of the experimental system.
Fig. 5. Comparison between the recovered amounts of BaSO$_4$ and these expected from 100% collection of pure SO$_2$ samples.
Fig. 6. (a). The change with time in the system pressure, $P_{\text{system}}$, due to adsorption on, and desorption from, the activated carbon (AC) during Series I experiment at 200 °C. Note the value of $P_{\text{system}}$ after sampling aliquots of SO$_2$($g$) are computed from mass balance. The $P_{\text{system}}$ increase for the last point was due to degassing from the AC at 300 °C. (b). Calculated values for the amounts of SO$_2$($\text{sampled}$) ($\Diamond$), $\sum$SO$_2$($\text{sampled}$) sampled from the system ($\blacktriangle$), SO$_2$($s$, ads) that was released at 300 °C ($\bullet$), and the $\sum S$ incorporated in the AC ($\square$) in Series I.
Fig. 7. (a). The change with time in the system pressure, $P_{\text{system}}$, due to adsorption on, and desorption from, the activated carbon (AC) during Series II experiment at 250 °C. Note the value of $P_{\text{system}}$ after sampling aliquots of SO$_2$(g) are computed from mass balance. The $P_{\text{system}}$ increase for the last point was due to degassing from the AC at 400 °C. (b). Calculated values for the amounts of SO$_2$(system) (●), $\sum$SO$_2$(sampled) sampled from the system (▲), SO$_2$(s, ads) that was released at 400 °C (●), and the $\sum S$ incorporated in the AC (□) in Series II.
Fig. 8. (a). The change with time in the system pressure, $P_{\text{system}}$, due to adsorption on, and desorption from, the activated carbon (AC) during Series III experiment at 200 °C. Note the value of $P_{\text{system}}$ after sampling aliquots of SO$_2$(g) are computed from mass balance. The $P_{\text{system}}$ increase for the last point was due to degassing from the AC at 300 °C. (b). Calculated values for the amounts of SO$_2$(sampled) (●), $\sum$SO$_2$(sampled) sampled from the system (▲), SO$_2$(s. ads) that was released at 300 °C (★), and the $\sum$S incorporated in the AC (□) in Series III.
Fig. 9. (a) XPS spectra of the activated carbon before and after Series I-III experiments, compared with (b) the main peak positions of various compounds of oxidized S-C compounds (designated as S-X-O compounds) and reduced S-C compounds: the ranges (bars) are from a handbook of X-ray Photoelectron Spectroscopy by Perkin-Elmer Corporation, and the stars are from previous literatures (H₂SO₄ 169.4 eV (Wren et al., 1979), NaHSO₃ 165.8 eV (Yu et al., 1990), S 163.7 eV (Kelemen et al., 1990), SO₂ 167.4 and 168.1 eV (Wagner and Taylor, 1982; Lindberg et al., 1970), CS₂ 163.6 and 163.7 eV (Wagner and Taylor, 1982; Lindberg et al., 1970)).
Fig. 10. The amounts of: $\sum \text{SO}_2(\text{initial})$, $\sum \text{SO}_2(\text{g})$ sampled, $\text{SO}_2(\text{s, ads})$, which was released from the AC at 300-400 °C, and non-degassable S ($S_{\text{NDG}}$) after Series I, II, and III experiments. The non-degassable S is comprised of water-soluble S (~56%) which corresponds to the S-O-C compounds, Cr-reducible S (~20%) which corresponds to the C-S compounds, and the residual S (~24%) which is unidentified.
Fig. 11. Schematic diagrams of SO$_2$(ads), S-O-C, and S-C clusters in activated carbon during reactions with SO$_2$(g).
Cross plots of the total amounts of S incorporated in the AC \( (n\sum S_{(AC)}) \) vs (a) the \( p_{(system)} \), and vs. (b) the \( nSO_2_{(system)} \), where \( n\sum S_{(AC)} = nSO_2_{(w, \, ads)} + nSO_2_{(s, \, ads)} + nS_{(NDG)} = nSO_2_{(system, \, init)} - n\sum SO_2_{(sampled)} - nSO_2_{(system \, at \, t)} \). Solid lines represent the best-fit lines for the experimental points. The equations are for the best-fit lines.

**Fig. 12.** Cross plots of the total amounts of S incorporated in the AC \( (n\sum S_{(AC)}) \) vs (a) the \( p_{(system)} \), and vs. (b) the \( nSO_2_{(system)} \), where \( n\sum S_{(AC)} = nSO_2_{(w, \, ads)} + nSO_2_{(s, \, ads)} + nS_{(NDG)} = nSO_2_{(system, \, init)} - n\sum SO_2_{(sampled)} - nSO_2_{(system \, at \, t)} \). Solid lines represent the best-fit lines for the experimental points. The equations are for the best-fit lines.
Fig. 13. Cross plots of $\ln K_1^{'\prime}$ vs $1/T$, where $K_1^{'\prime} = nSO_2(\text{ads})/nSO_2(\text{system})$. 
Fig. 14. Sulfur isotopic compositions of sampled SO$_2$(g) and SO$_2$(s. ads) from Series I. (a): $\delta^{34}$S, (b): $\Delta^{33}$S.
Fig. 15. Sulfur isotopic compositions of sampled SO$_2$(g) and SO$_2$(s. ads) from Series II. (a): $\delta^{34}$S, (b): $\Delta^{33}$S.
Fig. 16. Sulfur isotopic compositions of sampled SO$_2$(g) and SO$_2$(s. ads) from Series III. (a): $\delta^{34}$S, (b): $\Delta^{33}$S.
Fig. 17. Summary diagram of $\delta^{34}S$ and $\Delta^{33}S$ values of $SO_2(g)$, $SO_2(s, ads)$, and SCO, SC, and residual S of the sequential S extraction from SO$_2$-adsorbed AC. Ranges of the $\delta^{34}S$ and $\Delta^{33}S$ error bar is ±0.16‰ and ±0.027 ‰ respectively.
Appendices for AN EXPERIMENTAL INVESTIGATION OF MULTIPLE SULFUR ISOTOPE FRACTIONATIONS DURING HETEROGENEOUS REACTIONS BETWEEN SO$_2$ AND ACTIVATED CARBON

Fig. A1. XRD peak intensities and patterns of three BaSO$_4$ from initial SO$_2$(g) oxidation.

Fig. A2. A schematic diagram of a sequential sulfur extraction.

Fig. A3. An photo of the SO$_2$ gas adsorption system.

Fig. A4. A photo of a Pyrex reaction cell without a heating tape.

Fig. A5. A photo of a Pyrex sampling tube.

Fig. A6. A schematic illustration of the PSU sulfur isotope purification system with a dual fluorination system (tube and laser) for high precision multiple sulfur isotope analysis.

Fig. A7. The layout of a GC unit of the PSU sulfur isotope purification system.
Fig. A1.  (A) XRD peak intensity and pattern of three BaSO$_4$ from SO$_2$(g) oxidation with H$_2$O$_2$(aq) (blue, red, and black peaks); (B) Peak pattern of barite (BaSO$_4$) (blue spikes), and (C) barium sulfate (Ba(SO$_3$)$_{0.3}$(SO$_4$)$_{0.7}$) (purple spikes).
Fig. A2. Schematic diagram of a sequential sulfur extraction. Final product is Ag$_2$S for sulfur isotope analysis. DIW means deionized water.
Fig. A3-A5. (A3) image of the SO$_2$ gas adsorption system; (A4) a Pyrex reaction cell without a heating tape, and (A5) a Pyrex sampling tube.
(A6) Schematic illustration of the PSU sulfur isotope purification system with a dual fluorination system (tube and laser) for high precision multiple sulfur isotope analysis. P is a manometer. Red dot circled is a GC unit, and detail configuration is shown in (A7) layout of a GC unit of the PSU sulfur isotope purification system modified after Ono et al. (2006).

Fig. A6-A7. (A6) Schematic illustration of the PSU sulfur isotope purification system with a dual fluorination system (tube and laser) for high precision multiple sulfur isotope analysis. P is a manometer. Red dot circled is a GC unit, and detail configuration is shown in (A7) layout of a GC unit of the PSU sulfur isotope purification system modified after Ono et al. (2006).