Sulfur dioxide oxidation and isotope fractionation as a function of pH

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Abstract

Acid rain is produced by oxidation of compounds such as sulfur dioxide, and causes damage to human structures and to the natural environment. Sulfur dioxide is released via fossil fuel combustion and when sulfur dioxide dissolves in water, it oxidizes to produce sulfate and sulfuric acid. Sulfur isotopes can be used to identify a source of pollution but when sulfur dioxide is oxidized, the isotopes fractionate and this introduces complexity to the source identification process. Sulfur dioxide, bisulfite, and sulfite will be oxidized by air during oxidation experiments that will vary the pH. Ultimately, changing pH will yield changes in isotopic redistribution in sulfur species and the pH of the solution of bisulfite is related to the fractionation of the sulfate produced in the oxidation reaction. The experiments conducted were set at certain pH levels through the use of buffer solutions to ensure the pH of the solution remains constant throughout the duration of the experiment. After oxidation, the remaining sulfite species in solution will be converted to gaseous sulfur dioxide by acidification using HCl. The sulfur dioxide will be pumped into another solution containing hydrogen peroxide and sodium hydroxide to oxidize the sulfur dioxide and trap in solution. After trapping, barium chloride will be added to precipitate barite which will be separated from the solution, weighed and prepared for mass spectrometer analysis and the sulfur isotope ratios in the barite will be analyzed. These ratios have provided some insight into the isotope fractionation process by revealing a correlation between pH and the fractionation factor. The analysis of the samples yielded results in the form of $\delta^{34}S$ for sample and each standard. The fractionation factor, α_{34} on average was -2.71 ± 0.25 at pH equal to 4.0 and at pH=4.74, the fractionation factor average was -3.31 ± 0.25. At pH=8.0, the average fractionation factor was -0.99 ± 0.25 and at pH=11.7, the average fractionation factor was -2.88 ± 0.25. The fractionation factor is a ratio of the reaction rates for ^{32}S and ^{34}S and for batches one and two are expected because the reaction rate for the lighter isotope requires less energy and should be faster. A third experiment was conducted at higher levels of pH and also demonstrated a correlation between pH and isotope fractionation but there were issues with mass balance and isotope balance. A fourth experiment revealed that the disparity with isotope balance is related to isotope fractionation as a result of incomplete sulfur dioxide trapping.

1 Introduction

Acid rain is a serious environmental issue which is induced by the oxidation of atmospheric sulfur dioxide, nitric oxide, and nitrogen dioxide which are mostly released by the combustion of fossil fuels (Larssen et al., 2006). Coal is a significant contributor to atmospheric sulfate especially in North China (Han et al., 2016). In addition, acid rain has an economic impact as The Chinese State Environmental Protection Administration has set the costs of acid rain at $13 billion (Larssen et al., 2006). Increased levels of fossil fuel consumption lead to increased amounts of sulfur dioxide being released into the atmosphere. Acid rain can cause the deterioration of buildings that are made of sand stone, limestone, and marble (Singh and Agrawal, 2008). The sulfur in acid rain reacts with calcium carbonate, a common constituent of these materials, to form calcium sulfate which washes away whenever it rains (Singh and Agrawal, 2008). Although sand stone is not made of calcium carbonate, the cement can be calcium carbonate which will react with sulfur dioxide to produce calcium sulfate (Singh and Agrawal, 2008). Acid rain does not only affect buildings, but entire ecosystems can be disturbed by increased acidity in the soil or negatively affecting species that live in aquatic environments by interfering with their reproductive habits and by increasing their cortisol levels, which represents an increase in stress (Singh and Agrawal, 2008).

Sulfur isotopes can be used to trace the source of atmospheric sulfur dioxide but the interpretation of the sulfur isotope ratios is difficult because there is not much information about the isotopic fractionation (Harris et al., 2012). Sulfur isotope ratios can be used to pinpoint locations or sources that produce large amounts of atmospheric sulfur dioxide. However, when sulfur dioxide is oxidized to produce sulfate, the isotopes fractionate and this fractionation is not fully understood. Further analysis of isotope fractionation as a function of pH will determine if the isotopic composition of sulfate produced by the oxidation of sulfur dioxide and the isotopic composition of starting sulfur depends on pH. Previous experiments such as Harris et al. (2012) did not used pH as one of the parameters but concluded that sulfur isotope fractionation may be dependent on pH.

1.1 Sulfur dioxide chemistry

(1) $SO_2 + H_2O \rightleftarrows HSO_3^- + H^+$

(2) $4HSO_3^- + 3O_2 \rightleftarrows 4SO_4^{2-} + 2H_2O$

(3) $SO_{2(g)} \rightleftarrows SO_{2(aq)}$

(4) $SO_{2(aq)} + H_2O \rightleftarrows H_2SO_3$

(5) $H_2SO_3 \rightleftarrows HSO_3^- + H^+$

(6) $HSO_3^- \rightleftarrows SO_3^- + H^+$

(From Harris et al., 2012)

Atmospheric sulfur is the main source of acid rain and originates from anthropogenic and natural sources (Zhang et al., 2010). Gaseous sulfur dioxide is released to the atmosphere via the burning of coal. Gaseous sulfur dioxide dissolves in to water to produce aqueous sulfur dioxide (3). As pH is increased, aqueous sulfur dioxide produces bisulfite and hydrogen ions and at higher pH levels, the bisulfite can disassociate to produce sulfite and additional hydrogen ions (5 & 6). The production of sulfate by the oxidation of sulfur dioxide is the main cause of acidity in acid rain, although sulfur dioxide in solution still contributes a minor amount to acidity. In addition, the bisulfite in solution oxidizes with oxygen in water or air and produces sulfate (2). During this oxidation process, the sulfur isotopes fractionate and the manner in which they fractionate is not fully understood.

2 Methods

The preliminary experiment involves using numerous test tubes and several stock solutions. The preliminary experiment to demonstrate feasibility involves making three stock solutions, 0.1 M acetic acid, 0.1 M sodium acetate, and 0.5 M sodium bisulfite.

To prepare the test tubes for a preliminary test, four 17 ml tubes were sealed and degassed with nitrogen gas for about 30 minutes. Additional deionized water was degassed to create the buffer solution in the test tube. The water bath was set to 25 degrees Celsius. The tubes were all labeled one through four and tubes one and two will undergo oxidation at pH=4 and tubes three and four will undergo oxidation at pH=4.74. 1.69 ml of 0.1 M acetic acid solution and 0.31ml of 0.1 sodium acetate were added to tubes one and two to set the pH=4. For tubes three and four 1.0 ml of 0.1 M acetic acid and 1.0 ml of 0.1 M sodium acetate were added to set the pH=4.74. All test tubes were adjusted to 10ml by adding 10ml of water and then degassed for 20 minutes. After 20 minutes, 2.0 ml of sodium bisulfite was added to each test tube and then the solution was degassed for an additional 10 minutes. Four ml of air was added to tubes one and three, and eight ml of air be added to tubes two and four. All the test tubes were placed in the water bath to react for approximately 70 hours. Tubes three and four were in the water bath for approximately 70 hours before being removed. A 1M barium chloride dihydrate solution was prepared and a degassed 0.1M sodium acetate solution was prepared for future trials. A 5 M HCl solution was prepared to be injected into tubes three and four to shift the most abundant (S(IV) species to gaseous sulfur dioxide. Tubes three and four were connected to a nitrogen gas source and to two other test tubes, three 'a' and four 'a', that contained hydrogen peroxide and barium chloride. After the hydrochloric acid solution was injected to tubes three and four, the nitrogen gas source was turned on to purge the sulfur dioxide into tubes three 'a' and four 'a'. Nitrogen gas was flushed through tubes three and four for approximately two hours before being removed from the pumping apparatus and returned to the water bath. After an additional 40 hours in the water bath, tubes three, three 'a', four, and four 'a' were removed to collect the barite. Barium chloride was added to tubes three and four to precipitate barite. A house vacuum was used to draw solution through a filter to collect barite. The barite from each tube was placed in individual microcentrifuge tubes that were placed in a Multi-Blok Heater to dry the samples. Tubes one and two were removed from the water bath after approximately 118 hours. The same barite precipitation process for tubes three and four were repeated for tubes one and two. After tubes one, one 'a', two, and two 'a' have been in the water bath for the second time, they will be separated from solution and will undergo the process for tubes three, three 'a', four, and four 'a'. After all the barite from the tubes has been collected they will be weighed for mass yield and for analysis. 10 ml of 0.5 M sodium bisulfite and several milliliters of hydrogen peroxide were added into another tube and placed in the water bath to convert the bisulfite to sulfate. Hydrogen peroxide will be used to oxidize bisulfite to produce bisulfate and sulfate in solution (7). This sulfate will then be extracted by precipitating as barite and eventually analyzed. Tubes one, one 'a', two, and two 'a' were placed back into the water bath after the precipitation process to completely precipitate barite.

Image 1: Experiment set up. Black tube flushes nitrogen into left tube (tubes one-four in experiment) and sulfur dioxide gas is purged into tube on right (tubes one 'a'-four 'a') which is oxidized and precipitated as barite.

(7) $HSO_3^- + H_2O_2 \rightleftarrows HSO_4^- + H_2O$

(From Harris et al., 2012)

After sample collection, the barite samples were weighed and recorded to determine the mass yield for each test tube and determine if enough barite was available for analysis. In order to analyze the samples, standards were weighed and recorded. NBS127, a barium sulfate standard and NZS1, a silver sulfide standard were weighed and prepared for analysis in an isotope ratio mass spectrometer. Approximately 200 μg of standard or sample and a small amount of vanadium pentoxide were added to a small aluminum capsule. These capsules were analyzed in the Gas source Mass Spectrometry lab using an isotope ratio mass spectrometer (Appendix VI).

A second experiment has been started to clarify results from the first experiment. The second experiment used the same stock solutions from the previous experiment. 1.0 ml of 0.5 M sodium acetate and 1.0 of 0.5 M ml acetic acid were added to five different test tubes. 8 ml of milli q was added to each test tube. Nitrogen gas was not used to purge the tubes of oxygen and instead 2 ml of 0.5 M sodium bisulfite were added to each tube to initiate the oxidation reaction. The tubes were labelled one through five and oxidized for one week. After the samples reacted for a week, they were prepared for nitrogen pumping. The same nitrogen pumping method was used as the previous experiment. 1.0 ml of NaOH was added to each tube to ensure that any gaseous sulfur dioxide would be trapped as an aqueous sulfur species. Additionally, 10 ml of hydrogen peroxide was to each tube to completely oxidize the sulfite to sulfate. After pumping was complete after two hours, 1.0 ml of BaCl solution was added to precipitate any sulfate in solution. After precipitating barite, the tubes were filtered and dried using the same Multi-Blok heater. The samples were then weighed to determine the yield of each sample and then prepared for analysis.

A third experiment was initiated to focus on resolving any issues in the first and second experiments. This set of experiments are set at higher pH levels such as pH=8 and pH=11.7. Each tube for pH=8 was filled with 1.0 ml Na_2HPO_4 and 1.0 ml NaH_2PO_4 and then adjusted to 10 ml by adding 8 ml of milli q. For pH=11.7, 2.0 ml Na_2HPO_4 was added to each tube and adjusted to 10 ml by adding 8 ml of milli q. Tubes 1 and 2 are set to pH=11.7 and tubes 3 and 4 are set to pH=8. After each tube was filled with the appropriate buffer solution 2.0 ml of 0.5 M $NaHSO_3^-$ was added to each tube to initiate the oxidation reaction. After one week of reacting, the tubes were prepared for nitrogen pumping by adding 10 ml of hydrogen peroxide and 1.0 ml of NaOH to another set of tubes, labeled 1A through 4A. In order to initiate pumping, 2 ml of HCl and 1 ml of milli q were added to tubes 1-4. The same nitrogen pumping technique used in previous experiments was used for this experiment. After nitrogen pumping 1.0 ml of BaCl solution was added to each tube to precipitate barite. After the barium chloride was added the barite was separated from the supernatant liquid by using a centrifuge. The centrifuge allowed the supernatant liquid to be poured off and the remaining barite was placed in the oven to dry out the samples and prepare them for analysis. The barite was weighed and then prepared for analysis on the mass spectrometer.

Table 1	**Set 1**	**Set 2**	**Set 3**
A	SO_3^{2-}	SO_3^2	SO_3^2
B			
C	HSO_3^-	HSO_3^-	HSO_3^-
D			

Following the third experiment, another set of tests were initiated that would be completed after the recovery technique was corrected because of inefficiency. The first experiment was initiated on March 23, 2017, and the second experiment was initiated on March 27, 2017. A sodium sulfite solution was made by adding 1.26 g of sodium sulfite to 100 ml of deoxygenated water and a sodium hydroxide solution was made by adding 0.83 g of sodium

Table 2	**Set 1**	**Set 2**	**Set 3**
A, pH=8	SO_3^{2-}	SO_3^2	SO_3^2
B, pH=11.7			
C, pH=8	HSO_3^-	HSO_3^-	HSO_3^-
D, pH=11.7			

hydroxide to 100 ml of deoxygenated water. A bisulfite solution was also made by adding 0.4 g of sodium hydroxide and 1.26 g of sodium sulfite to 100 ml of deoxygenated water. For this experiment 12 tubes were filled entirely with milli q. They were divided into sets of four for a total of three sets. The four tubes in each set were labeled A through D. For the first set of tubes, set 1, 2 ml of milli q was removed and then 1 ml of solution was added. For set 2, 3 ml of milli q was removed and 1 ml of solution was added. For set 3, 3 ml of milli q was removed and 2 ml of solution was added. For tubes A and B, the sulfite solution was added and the bisulfite solution was added to tubes C and D.

Another group of tubes were set up for another experiment that would use buffer solutions instead of only milli q. The new set would use two different pH levels of pH=8 and pH=11.7 and the same design for the sets where a certain amount of head space is created and the same amounts of solution are injected. After additional work on refining the recovery method, then these experiments would be completed.

More tests were completed to determine the efficiency of the nitrogen pumping and trapping. Six tubes were labeled NaOH + peroxide and six other tubes were labeled HCl + SO_2. However, only four tubes were used for each set. The NaOH + peroxide tubes were labeled 1 to 4 and the HCl + SO_2 tubes were labeled A to D. For the first set of four tubes, approximately 10 ml of hydrogen peroxide and 2.5 ml of sodium hydroxide were added. 2 ml of HCl was added to the tubes labeled HCl + SO_2. The same nitrogen pumping technique was used for these tubes, but instead of short needles introducing the gaseous sulfur dioxide into the NaOH + peroxide tubes, longer needles were used that reached the bottom of the basic hydrogen peroxide solution. In addition, a specific amount of sulfite solution was added to each HCl + SO_2 tube. Because there were only four functioning nitrogen nozzles, only four tubes were used but 4 ml of bisulfite solution was added to tube A, 3 ml to tube B, 2 ml to tube C, and 1 ml to tube D. After nitrogen was pumped for two hours, 1.0 ml of barium chloride solution was added to tubes 1-4. This experiment was a test run for the method which resulted in precipitation of barite. The experiment was replicated so that the new samples would be ready for filtering and weighing. Instead of scraping the barite off the filter paper and weighing the barite, the filter papers were weighed before using them to filter the barite from solution. The samples were placed in dry in a cupboard that would prevent dust or other particles from altering the weight. The weight for the filter paper was recorded prior to weighing and then the barite and filter paper were weighed and the weight was recorded.

When the trapping method was refined, the experiments from March 23rd, and March 27th were prepared for analysis. Both of these experiments oxidized for several weeks prior to injecting 0.5 ml of 1.0 M barium chloride into the tubes to precipitate the oxidized sulfate. However, the solubility of barium sulfite was underestimated and the barium chloride precipitated barium sulfite and barite. 0.1 ml of 5 M hydrochloric acid was added to each tube to dissolve the barium sulfite. The solutions were mixed to ensure that all the barium sulfite was dissolved and then transferred to boiling flasks that were connected to a condensed distillation apparatus in the fume hood. Before the boiling flasks were connected to the apparatus, the trap solution was connected so that any possible leak would be captured in the trap solution which consisted of hydrogen peroxide and sodium hydroxide. Only six samples could be pumped with nitrogen at a time, so four groups of tubes were processed at one time. The technique for this experiment was identical to previous experiments. Nitrogen would be pumped through the system to purge it of oxygen, then 2.0 ml of 5 M hydrochloric acid was added to convert the residual sulfite to gaseous sulfur dioxide. The nitrogen would transfer the sulfur dioxide into the trap solution where it would be captured as sulfite and oxidized to produce the residual sulfate. After pumping nitrogen for two hours, an additional 1.0 ml of HCl was added to each boiling flask and left for another 30 minutes. The boiling flasks and trap solutions were removed from the fume hood and transferred to 50 ml centrifuge tubes by pouring and rinsing with milli q. The trap solution tubes were labelled with the date the experiment started, which tube it was, and SO_2 so they corresponded with the respective boiling flask. For tube 3/23 1A, the corresponding trap solution tube was labelled 3/23 1A SO_2. When the tubes were correctly labelled, 1.0 ml of 1.0 M barium chloride was added and barite was precipitated. Because the solutions were acidic due to the added HCl, barium sulfite precipitation was not considered to be an issue. After barium chloride was added, the solutions were mixed and the other groups of tubes were prepared for the condensed distillation apparatus. After the barium chloride was thoroughly mixed in the tubes, they were placed in a centrifuge which would determine the relative amount of barite for each tube. Tubes with a lack of barite were not filtered and tubes that had enough barite were filtered using a vacuum pump and pre-weighed filter papers. 38 samples were filtered, including control groups which contained approximately 10 ml of hydrogen peroxide and 1.0 ml of bisulfite or sulfite solution. After filtering all of the samples, they were placed in small plastic trays and into a cupboard to dry before preparing them for analysis. The filter papers were weighed and the difference between the filter paper and the filter paper and sample were recorded to calculate percent yield. The barite was scrapped off each filter paper and placed in small sealable tubes. Then the samples were prepared for analysis in the Gas source Mass Spectrometry lab like previous experiments.

3 Discussion

For the first experiment bisulfite will be the dominant species in the buffer solution and the experiment will quantify the isotope fractionation between aqueous sulfate and bisulfite at various pH levels. The results from the isotope ratio mass spectrometer from experiment one for batches one and two are consistent with expected results. The fractionation factor is less than one which is expected because the reaction rate, R_1, for ^{32}S requires less energy (8). However, the fractionation factor for batches three and four is greater than one which indicates that R_2 is greater than R_1 (10). Because R_1 requires less kinetic energy, it should be greater than R_2, but this is not what these data suggests. Another experiment has started that will provide new information on the fractionation factors. The results from batch one and two can be interpreted as kinetic isotope fractionation because the reaction rate of bisulfite with ^{32}S was generally faster than the reaction rate of bisulfite with ^{34}S. Batches three and four demonstrate reverse isotope fractionation which indicates that the product sulfate was enriched with ^{34}S. There are some disparities with mass balance for each experiment which may be due to inefficient nitrogen pumping or improper weighing techniques which have been resolved in recent experiments.

(8) $R_1 = R^{32}SO_3^- + O_2 \rightleftarrows {}^{32}SO_4^{2-}$

(9) $R_2 = R^{34}SO_3^- + O_2 \rightleftarrows {}^{34}SO_4^{2-}$

(10) $\alpha = R_2/R_1 \neq 1$

SampleID	δ^{34}S (2σ)	PH(initial)	Injected Air (ml)	Reaction Time (hours)	Fraction of Oxidation Conversion	Fractionation Factor (‰)	Mass Balance
#1 (Barite) #1a (Residual Bisulfite)	-8.55 ± 0.22 -5.18 ± 0.22	4.00	20.00	140	0.10	**-2.65 ± 0.23**	-5.72 ± 0.20
#2 (Barite) #2a (Residual Bisulfite)	-8.57 ± 0.22 -5.64 ± 0.22	4.00	24.00	140	0.16	**-2.76 ± 0.24**	-6.20 ± 0.19
#3 (Barite) #3a (Residual Bisulfite)	-4.9 ± 0.22 -5.95 ± 0.22	4.74	4.00	70	0.19	**1.29 ± 0.25**	-5.77 ± 0.18
#4 (Barite) #4a (Residual Bisulfite)	-5.26 ± 0.22 -5.75 ± 0.22	4.74	8.00	70	0.18	**0.88 ± 0.24**	-5.75 ± 0.19
# 0 (Bisulfite, Stock solution)	**-6.05 ± 0.22**	N/A	N/A	N/A			

Experiment 1 results

SampleID	δ^{34}S (2σ)	PH(initial)	Injected Air (ml)	Reaction Time (hours)	Fraction of Oxidation Conversion	Fractionation Factor (‰)	Mass Balance
#1 (Barite) #1a (Residual Bisulfite)	-9.50 ± 0.18 -5.24 ± 0.18	4.74	10.00	140	0.11	**-3.57 ± 0.23**	-5.70 ± 0.16
#2 (Barite) #2a (Residual Bisulfite)	-9.60 ± 0.18 -5.49 ± 0.18	4.74	15.00	140	0.10	**-3.67 ± 0.23**	-5.92 ± 0.16
#3 (Barite) #3a (Residual Bisulfite)	-9.16 ± 0.18 -5.34 ± 0.18	4.74	20.00	140	0.16	**-3.31 ± 0.24**	-5.94 ± 0.15
#4 (Barite) #4a (Residual Bisulfite)	-9.02 ± 0.18 -5.37 ± 0.18	4.74	10.00	140	0.16	**-3.15 ± 0.24**	-5.96 ± 0.15
#5 (Barite) #5a (Residual Bisulfite)	-8.68 ± 0.18 -5.00 ± 0.18	4.74	15.00	140	0.20	**-2.86 ± 0.25**	-5.74 ± 0.15
# 0 (Bisulfite, Stock solution)	**-6.15 ± 0.18**	N/A	N/A	N/A			

Experiment 2 results

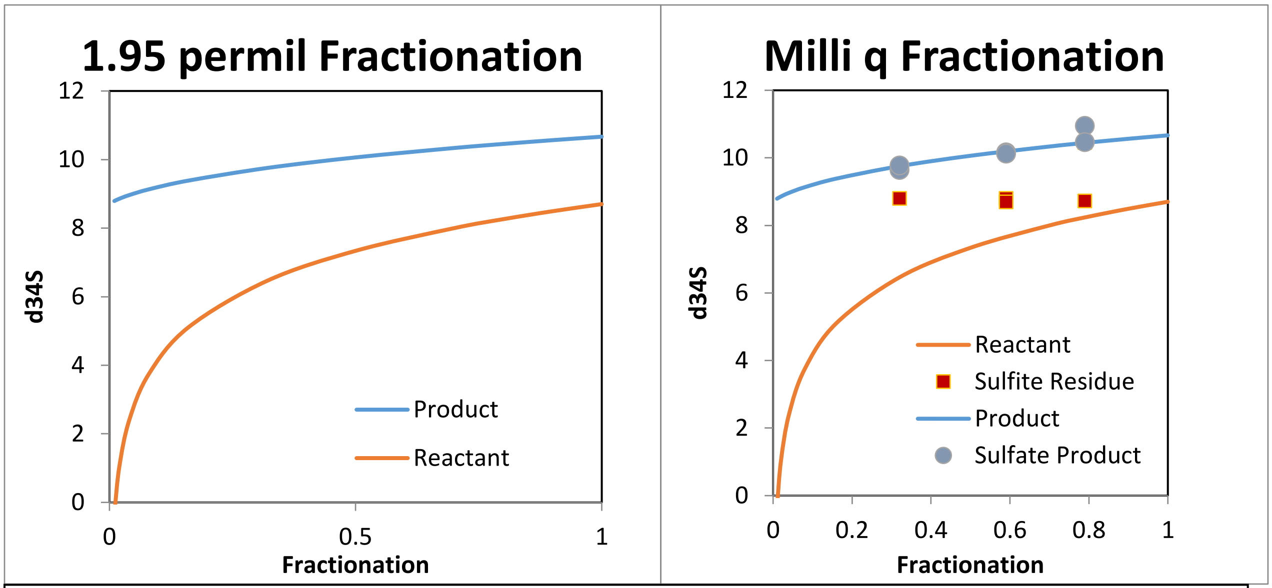
SampleID	δ^{34}S (2σ)	PH(initial)	Injected Air (ml)	Reaction Time (hours)	Fraction of Oxidation Conversion	Fractionation Factor (‰)	Mass Balance
#1 (Barite) #1a (Residual Bisulfite)	-7.84 ± 0.22 -5.53 ± 0.22	11.7	5.00	140	0.15	**-1.95 ± 0.24**	-5.88 ± 0.16
#2 (Barite) #2a (Residual Bisulfite)	-6.08 ± 0.22 -5.41 ± 0.22	11.7	5.00	140	0.15	**-0.03 ± 0.24**	-5.53 ± 0.15
#3 (Barite) #3a (Residual Bisulfite)	-8.51 ± 0.22 -6.30 ± 0.22	8.0	5.00	140	0.18	**-2.74 ± 0.25**	-6.59 ± 0.16
#4 (Barite) #4a (Residual Bisulfite)	-8.84 ± 0.22 -5.50 ± 0.22	8.0	5.00	140	0.13	**-3.01 ± 0.24**	-5.50 ± 0.18
# 0 (Bisulfite, Stock solution)	**-6.05 ± 0.22**	N/A	N/A	N/A			

Experiment 3 results

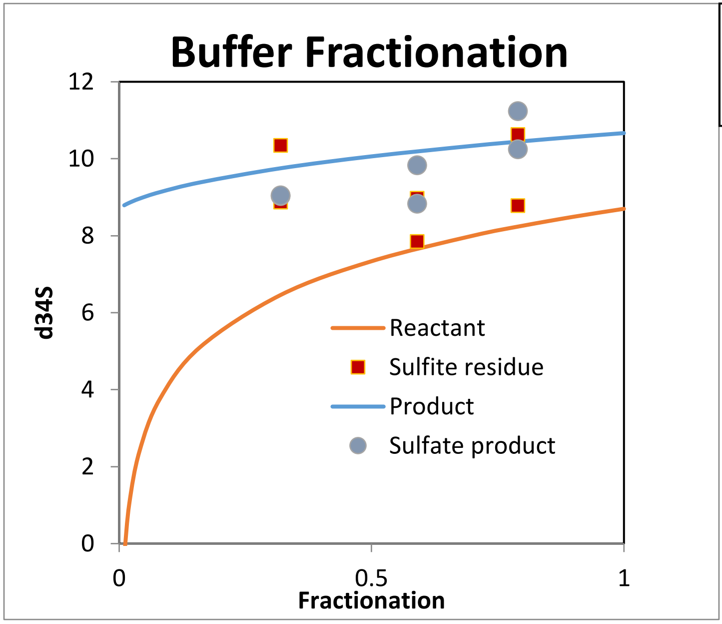
At higher pH tests, there will be some sulfite ions in the buffer solution and these ions will exchange isotopes with bisulfite which results in a product with enriched ^{34}S (Eldridge et al., 2016). The first experiment showed that the degassing recovery yield should be improved, or a better method should be used to convert the residual bisulfite to sulfate instead of using hydrogen peroxide.

The second and third experiment yielded reasonable and interpretable results but there are still minor mass balance issues. After the third experiment the efficiency of the recovery technique was scrutinized and eventually was tested by examining the mass yield from nitrogen pumping. The results indicated that the recovery technique was not efficient as previously anticipated. The recovery technique for all experiments has been inefficient at best because of lack of conversion to sulfate via hydrogen peroxide and the misuse of filter paper. After initiating the third experiment by introducing oxygen to the sulfite solution, minor experiments that were not intended to yield results from the mass spectrometer were conducted to determine the actual efficiency in the nitrogen pumping. Initially the barite was separated from solution by filtering with a vacuum pump but then the barite was scraped off the filter paper and then weighed. This results in some barite potentially remaining on the filter paper and resulting in a lower yield estimate. However, the experiment that is currently undergoing will use a technique that involves weighing the filter paper prior to filtering the barite so the measurement of the mass yield will be as accurate as possible. Currently, the most efficient technique for nitrogen pumping involves using an apparatus in the fume hood that is a completely closed system. The methods are the same but nitrogen will be constantly pumping through the system. There are two hydrogen peroxide and sodium hydroxide solutions that will capture any sulfur dioxide that is pumped from the initial reaction so that there is a smaller risk of losing any sulfur dioxide. These data suggests that there is a pH dependent fractionation because of the varying fractionation factors between each experiment. The fractionation factor at lower pH levels is more negative than those at higher pH levels.

There have been complications resulting from the fourth set of experiments. The results revealed that there is still uncertainty with the efficiency of trapping the residual sulfite from solution. Previous experiments revealed that there were issues with the residual sulfite trapping process and the following experiments revealed another issue because incomplete trapping of sulfur dioxide results in isotopic fractionation. This unexpected fractionation complicates interpretations. A Rayleigh distillation curve was calculated to project a unidirectional reaction with a set fractionation. When compared to the model fractionation, the 3/23 experiments with sulfite, these data is not correlated. This demonstrates that there is an issue with the experiment design which was unrecognized until the most recent experiments because variable amounts of oxygen were used

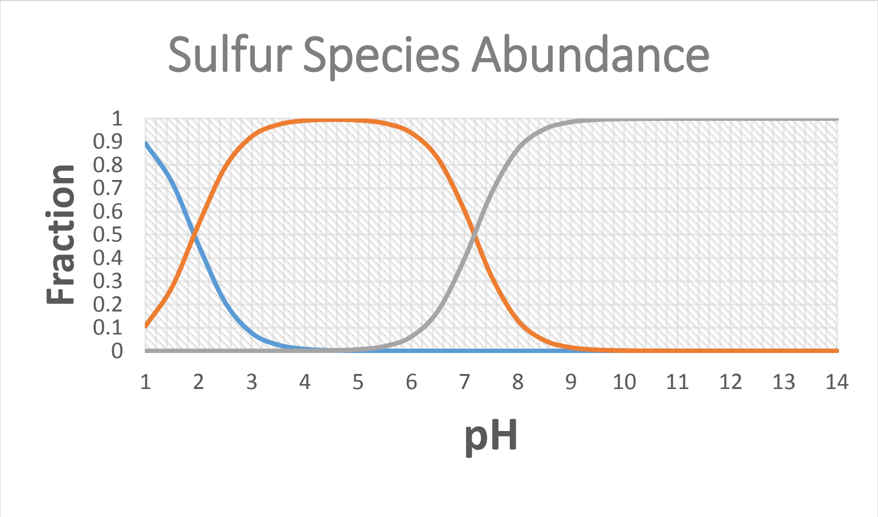


Graph 1 and 2: Rayleigh distillation curves for a model curve with 1.95 permil fractionation and milli q with sulfite residue and sulfate product.



Graph 3: Buffer fractionation suggests that the buffer may affect the chemistry and ultimately the fractionation.

in the 3/23 experiments. There is a fractionation associated with the trapping and conversion of sulfur dioxide degassed from the sulfite solutions which might warrant an independent study because of its complexity.



Graph 4: Bjerrum plot of sulfur species abundance as a function of pH.

Additionally, for the 3/23 and 3/27 experiments, when bisulfite was injected as the sulfur source, these tubes did not yield product for pure water experiments and did not yield consistent results when the solution contained a buffer. Milli q filled each tube for the 3/23 experiment and because bisulfite and sulfite are present in approximately equal amounts at pH=7.0, this could result in a lack of sulfite oxidizing to sulfate (Graph 4). For the buffer experiments at pH=8.0, there is still bisulfite present in solution which may also interfere with the amount of sulfite converted to sulfate. When the pH is set at 11.7, the sulfur source is still introduced as bisulfite which may remain in solution and also may interfere with the oxidation process.

Mass balance for the 3/23 and 3/27 experiments has improved although there are still samples where mass balance has not been closed (Appendix IX). Using the condensed distillation apparatus has helped with the recovery technique, and weighing the filter paper before using it has allowed for increased accuracy of yield estimates. The disparity in mass balance yields could be a result of inconsistent methods in the lab, but all samples were gathered using the same precision and methods. Isotope balance was misconstrued by unpredicted chemical reactions involving the sulfur dioxide process. As mentioned previously, there is a fractionation associated with trapping and converting the sulfur dioxide to sulfite. The majority of tubes in the recent experiment experienced an enrichment in δ^{34}S compared to the starting reactants. Because the sulfate is expected to be enriched in δ^{34}S because of kinetic fractionation, the fact that the sulfur dioxide is enriched in the product indicates that the capturing technique still is problematic. However, the results for solutions with just milli q demonstrate the reproducibility of the experiment. The buffer solution complicated matters because the fractionation for sulfite in buffer solutions were scattered and did not yield reasonable results.

The uncertainty is based off the standard deviation of the standards and is reported as 0.11. There was a data correction applied to all of the data points. It involved correcting the raw data by adjusting the points to the true δ^{34}S value which is 21.1 for NBS-127 and -0.30 for NZS1. A line connects these two points when plotted on a true δ^{34}S graph and the equation for this line will be used to correct the data because of the drift from the true δ^{34}S values.

3.1 Testing the hypothesis

The goal of the experiment was to determine if the isotope fractionation during the oxidation process was dependent on pH. Several experiments demonstrated that there is a correlation between fractionation and pH. As the experiment designed was refined after repeated iterations, it became clear that mass balance and isotope balance were the mass issues with the experiment. Although there are improvements in closing mass balance, unpredicted complications interfered with closing mass balance, and the variability because of buffer solutions and the trapping method resulted in unreasonable and data that are difficult to interpret. The first experiment analysis yielded reasonable results for batches one and two but the results for three and four were not as expected. The ratios indicated that the reaction rate for ^{34}S was faster than the reaction rate for ^{32}S when the reaction rate for ^{32}S should be faster because it requires less energy. However, because there is an exchange between bisulfite and sulfite ions at high pH levels, this exchange may account for enrichment in heavier sulfur isotopes. The second experiment concluded that the results from the first experiment were incorrect but also showed that there were still issues with mass balance because of the sulfur dioxide recovery technique. A third experiment involved using a different residual sulfite recovery technique. It involved pumping nitrogen into the system at a slower rate than before and calibrating the nitrogen flow rate before connected it to the tubes. Previously, the nitrogen was pumped in before it was calibrated and may have caused some sulfur dioxide to escape the system because it was forcibly pushed out of the closed tubes. However, the results from the third experiment exposed additional issues with mass balance because the yields were still less than ideal. The recovery method was investigated and refined to include a condensed distillation apparatus. This apparatus increased the mass yields but there are still samples where the amount of barite is less than expected. The weighing process was also modified because prior to the fourth set of experiments, there were small amounts of barite left on the filter papers. This is because the barite was filtered using a vacuum filter, but the barite was scraped off of the paper before it was completely dry and scraping the barite will not ensure that all the barite is collected. For the fourth experiment, the filter papers were weighed before using them to filter the barite from the supernatant liquid. The fourth experiment also demonstrated that there is a degree of complexity to the experiment that was not previously anticipated. After several different approaches to resolving the trapping of sulfur dioxide, the fourth experiment showed that there are still issues with sulfur dioxide trapping. The Rayleigh distillation curves revealed that the residual sulfite does not follow the model Rayleigh distillation curve. This indicates that there is a fractionation during the trapping and conversion process for sulfur dioxide. The sulfur dioxide trapping issue must be resolved before testing the hypothesis because there are many complications involving pumping and trapping the sulfur dioxide.

3.2 Conclusion

Improving the sulfur dioxide recovery technique is the first step to accurately testing the hypothesis. Additional studies should consider the independent fractionation process involved with the trapping of sulfur dioxide. The separation of residual sulfite from the precipitate sulfate has proven to a complicated mechanism because of the possibility of precipitating barium sulfite if the solution is not acidic. These experiments have demonstrated that there is a pH correlation with isotope fractionation but there are still issues involving mass balance and isotope balance, but these issues can be addressed. Studies should also consider the complexity behind the fractionation factor during sulfur dioxide trapping, which was acknowledged during the fourth experiment. Additionally, buffer solutions may not be the ideal method to control pH because of the issue with the Rayleigh distillation curve. The buffer solution data does not suggest that there is an easy way to interpret the fractionation.

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Appendix I

The acetic acid stock solution was prepared by adding 0.574 ml of acetic acid to 25 ml milli q water. The final volume was adjusted to 100 ml.

Appendix II

The sodium acetate 0.1 M stock solution was prepared by adding 0.41 g of sodium acetate to 25 ml of water.

Appendix III

The sodium bisulfite solution was prepared by adding 6.50 g to 125 ml of degassed milli q. The water was degassed by inserting an airstone and pumping nitrogen gas into the solution for approximately one hour.

Appendix IV

5.0 M HCl solution was prepared by adding 49.27 ml of concentrated HCl to 70.73 ml of water.

Appendix V

1.0 M BaCl solution was prepared by adding 29.31 g of BaCl to 120 ml of water.

Appendix VI

Table of samples for isotope ratio mass spectrometer analysis (numbers in μg)

NBS-127 227	NBS-127 206	NBS-127 165	NBS-127 184	S1 244	S1 209	1 200	1A 163
2 210	2A 192	3 178	3A 179	4 209	4A 206	0 193	NBS-127 285
NBS-127 190	S1 194	S1 230					

Appendix VII

Sample Number	Name	Acquisition date	RT (Sec)	Height (nA)	Type	Weight (mg)
SampleNo/s	DataFileName/s	AcquisitionDate/s	RetTimeSecs	MajorHeightnA	SampleType/s	SampleWeight/s
6	11162016_NBS127_R1.raw	16/11/16 12:09	135.2	5.28	Elem	0.23
7	11162016_NBS127_R2.raw	16/11/16 12:15	137.5	5.77	Elem	0.21
8	11162016_NBS127_R3.raw	16/11/16 12:21	136.2	5.15	Elem	0.17
9	11162016_NBS127_R4.raw	16/11/16 12:26	136.2	5.97	Elem	0.18
10	11162016_NZS1_R1.raw	16/11/16 12:32	135.4	7.48	Elem	0.24
11	11162016_NZS1_R2.raw	16/11/16 12:38	136.0	5.18	Elem	0.21
12	11162016_Wong1.raw	16/11/16 12:44	135.8	5.76		0.20
13	11162016_Wong1A.raw	16/11/16 12:49	136.4	4.89		0.16
14	11162016_Wong2.raw	16/11/16 12:55	136.3	5.87		0.21
15	11162016_Wong2A.raw	16/11/16 13:01	136.2	5.47		0.19
16	11162016_Wong3.raw	16/11/16 13:07	136.6	4.96		0.18
17	11162016_Wong3A.raw	16/11/16 13:13	135.9	5.64		0.18
18	11162016_Wong4.raw	16/11/16 13:18	136.5	4.42		0.21
19	11162016_Wong4A.raw	16/11/16 13:24	136.6	5.92		0.21
20	11162016_Wong0.raw	16/11/16 13:30	135.8	5.90		0.19
21	11162016_NBS127_R5.raw	16/11/16 13:36	135.5	9.10	Elem	0.29
22	11162016_NBS127_R6.raw	16/11/16 13:41	135.7	6.30	Elem	0.19
23	11162016_NZS1_R3.raw	16/11/16 13:47	135.9	6.08	Elem	0.19
24	11162016_NZS1_R4.raw	16/11/16 13:53	135.6	6.68	Elem	0.23

Sample Number	Name	S34			Elemental Composition
SampleNo/s	DataFileName/s	DisplayDelta1	DisplayDelta2	SMOWConverted	
6	11162016_NBS127_R1.raw	12.38	0.00	30.86	13.47
7	11162016_NBS127_R2.raw	12.18	0.00	30.86	13.48
8	11162016_NBS127_R3.raw	12.14	0.00	30.86	13.78
9	11162016_NBS127_R4.raw	12.10	0.00	30.86	14.53
10	11162016_NZS1_R1.raw	-8.81	0.00	30.86	13.37
11	11162016_NZS1_R2.raw	-8.61	0.00	30.86	10.75
12	11162016_Wong1.raw	-16.78	0.00	30.86	12.68
13	11162016_Wong1A.raw	-13.49	0.00	30.86	13.41
14	11162016_Wong2.raw	-16.81	0.00	30.86	12.92
15	11162016_Wong2A.raw	-13.95	0.00	30.86	12.85
16	11162016_Wong3.raw	-13.24	0.00	30.86	12.72
17	11162016_Wong3A.raw	-14.28	0.00	30.86	13.67
18	11162016_Wong4.raw	-13.60	0.00	30.86	10.09
19	11162016_Wong4A.raw	-14.09	0.00	30.86	13.23
20	11162016_Wong0.raw	-14.40	0.00	30.86	13.52
21	11162016_NBS127_R5.raw	12.26	0.00	30.86	13.98
22	11162016_NBS127_R6.raw	12.26	0.00	30.86	14.25
23	11162016_NZS1_R3.raw	-8.77	0.00	30.86	13.42
24	11162016_NZS1_R4.raw	-8.76	0.00	30.86	13.22

Appendix VIII

Sample	sample weight (g)	(mg)	sulfur (millimole)	d34S
control SO32- A	0.016527	16.527	0.071	8.84 ± 0.24
control SO32- B	0.016481	16.481	0.071	8.70 ± 0.24
control HSO3- A	0.037317	37.317	0.160	9.07 ± 0.24
control HSO3- B	0.033358	33.358	0.143	9.03 ± 0.24
3/23 1A	0.0049030	4.90	0.021	10.16 ± 0.24
3/23 1A SO_2	0.0096070	9.61	0.041	8.70 ± 0.24
3/23 1B	0.0044290	4.43	0.019	10.13 ± 0.24
3/23 1B SO_2	0.0087060	8.71	0.037	8.69 ± 0.24
3/23 2A	0.0030000	3.00	0.013	9.64 ± 0.24
3/23 2A SO_2	0.0051660	5.17	0.022	9.72 ± 0.24
3/23 2B	0.0037860	3.79	0.016	9.77 ± 0.24
3/23 2B SO_2	0.0106370	10.64	0.046	8.80 ± 0.24
3/23 3A	0.0055740	5.57	0.024	10.95 ± 0.24
3A SO2	0.0128620	12.86	0.055	10.45 ± 0.24
3/23 3B	0.0062520	6.25	0.027	10.47 ± 0.24
3/23 3B SO_2	0.0235230	23.52	0.101	8.73 ± 0.24
3/23 3C	0.0073770	7.38	0.032	6.16 ± 0.24
3/23 3C SO_2	0.0085040	8.50	0.036	9.33 ± 0.24
3/23 3D	0.0059460	5.95	0.025	5.99 ± 0.24
3/23 3D SO_2	0.0066280	6.63	0.028	12.00 ± 0.24
3/27 1A	0.0044570	4.46	0.019	8.83 ± 0.24
3/27 1A SO_2	0.0066920	6.69	0.029	8.79 ± 0.24
3/27 1B	0.0058720	5.87	0.025	9.83 ± 0.24
3/27 1B SO_2	0.0068020	6.80	0.029	7.85 ± 0.24
3/27 1C	0.0052310	5.23	0.022	8.48 ± 0.24
3/27 1C SO_2	0.0017650	1.77	0.008	7.48 ± 0.24
3/27 2A	0.0094430	9.44	0.040	9.03 ± 0.24
3/27 2A SO_2	0.0080440	8.04	0.034	10.34 ± 0.24
3/27 2B	0.0092130	9.21	0.039	9.05 ± 0.24
3/27 2B SO_2	0.0049400	4.94	0.021	8.87 ± 0.24
3/27 3A	0.0062940	6.29	0.027	10.25 ± 0.24
3/27 3A SO_2	0.0104580	10.46	0.045	10.62 ± 0.24
3/27 3B	0.0060460	6.05	0.026	11.24 ± 0.24
3/27 3B SO_2	0.0220060	22.01	0.094	8.78 ± 0.24
3/27 3C	0.0059480	5.95	0.025	8.98 ± 0.24

Appendix IX

Sample	sample weight (g)	(mg)	sulfur (millimole)	Total Sulfur Recovered	Initial sulfur	Recovery yield
control SO32- A	0.016527	16.527	0.071			
control SO32- B	0.016481	16.481	0.071			
control HSO3- A	0.037317	37.317	0.160			
control HSO3- B	0.033358	33.358	0.143			
3/23 1A	0.004903	4.903	0.021			
3/23 1A SO_2	0.009607	9.607	0.041	0.062	0.071	87.92%
3/23 1B	0.004429	4.429	0.019			
3/23 1B SO_2	0.008706	8.706	0.037	0.056	0.071	79.59%
3/23 2A	0.003000	3.000	0.013			
3/23 2A SO_2	0.005166	5.166	0.022	0.035	0.071	49.48%
3/23 2B	0.003786	3.786	0.016			
3/23 2B SO_2	0.010637	10.637	0.046	0.062	0.071	87.39%
3/23 3A	0.005574	5.574	0.024			
3/23 3A SO2	0.012862	12.862	0.055	0.079	0.141	55.85%
3/23 3B	0.006252	6.252	0.027			
3/23 3B SO_2	0.023523	23.523	0.101	0.128	0.141	90.21%
3/27 1A	0.004457	4.457	0.019			
3/27 1A SO_2	0.006692	6.692	0.029	0.048	0.071	67.55%
3/27 1B	0.005872	5.872	0.025			
3/27 1B SO_2	0.006802	6.802	0.029	0.054	0.071	76.79%
3/27 2A	0.009443	9.443	0.040			
3/27 2A SO_2	0.008044	8.044	0.034	0.075	0.071	105.96%
3/27 2B	0.009213	9.213	0.039			
3/27 2B SO_2	0.004940	4.940	0.021	0.061	0.071	85.75%
3/27 3A	0.006294	6.294	0.027			
3/27 3A SO_2	0.010458	10.458	0.045	0.072	0.141	50.75%
3/27 3B	0.006046	6.046	0.026			
3/27 3B SO_2	0.022006	22.006	0.094	0.120	0.141	84.99%

Honor Code:
“I pledge on my honor that I have not given or received any unauthorized assistance or plagiarized on this assignment.”

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