

# Sulfur dioxide oxidation and isotope fractionation as a function of pH

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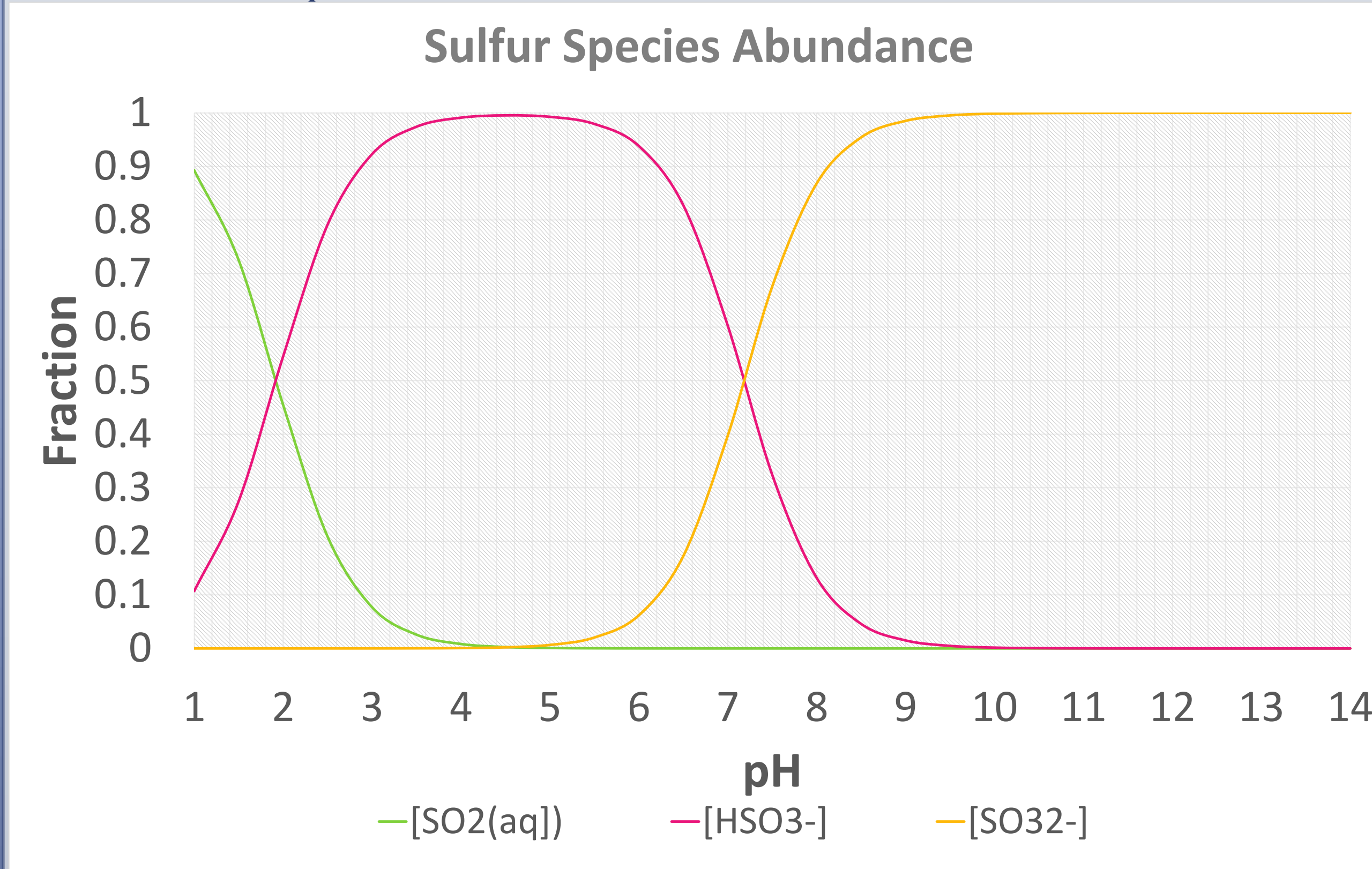
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## Background

Acid rain is a serious environmental issue which is induced by the oxidation of atmospheric sulfur dioxide, nitric oxide, and nitrogen oxide. These gases are mostly released by the combustion of fossil fuels (Larssen et al., 2006). Entire ecosystems can be disturbed by increased acidity in the soil and water bodies, and it can negatively affect species in aquatic environments. Acid rain also has tremendous impacts on human society because of the economic impacts of acid rain, in addition to environmental issues associated with acid rain. Acid rain can cause the deterioration of buildings that are made of sand stone, limestone, and marble and there are economic costs that are associated with the restoration of these buildings (Singh and Agrawal, 2008). The increased acidity can interfere with aquatic species reproductive habits and increase 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 a lack of information regarding the mechanism behind the isotope fractionation (Harris et al., 2012). Sulfur isotope ratios can be used to pinpoint locations or sources that produce large amounts of atmospheric sulfur dioxide.

## Hypothesis

The following experiments attempted to determine if the fractionation that occurs during the oxidation reaction between the sulfite species and oxygen is dependent on the pH of the solution that the sulfite is in. By studying the mechanisms behind the oxidation reaction, the isotopic signatures produced by these mechanisms can be used to trace different pathways of S(IV) oxidation and fractionation associated with these pathways and find solutions to the environmental problems due to acid rain.



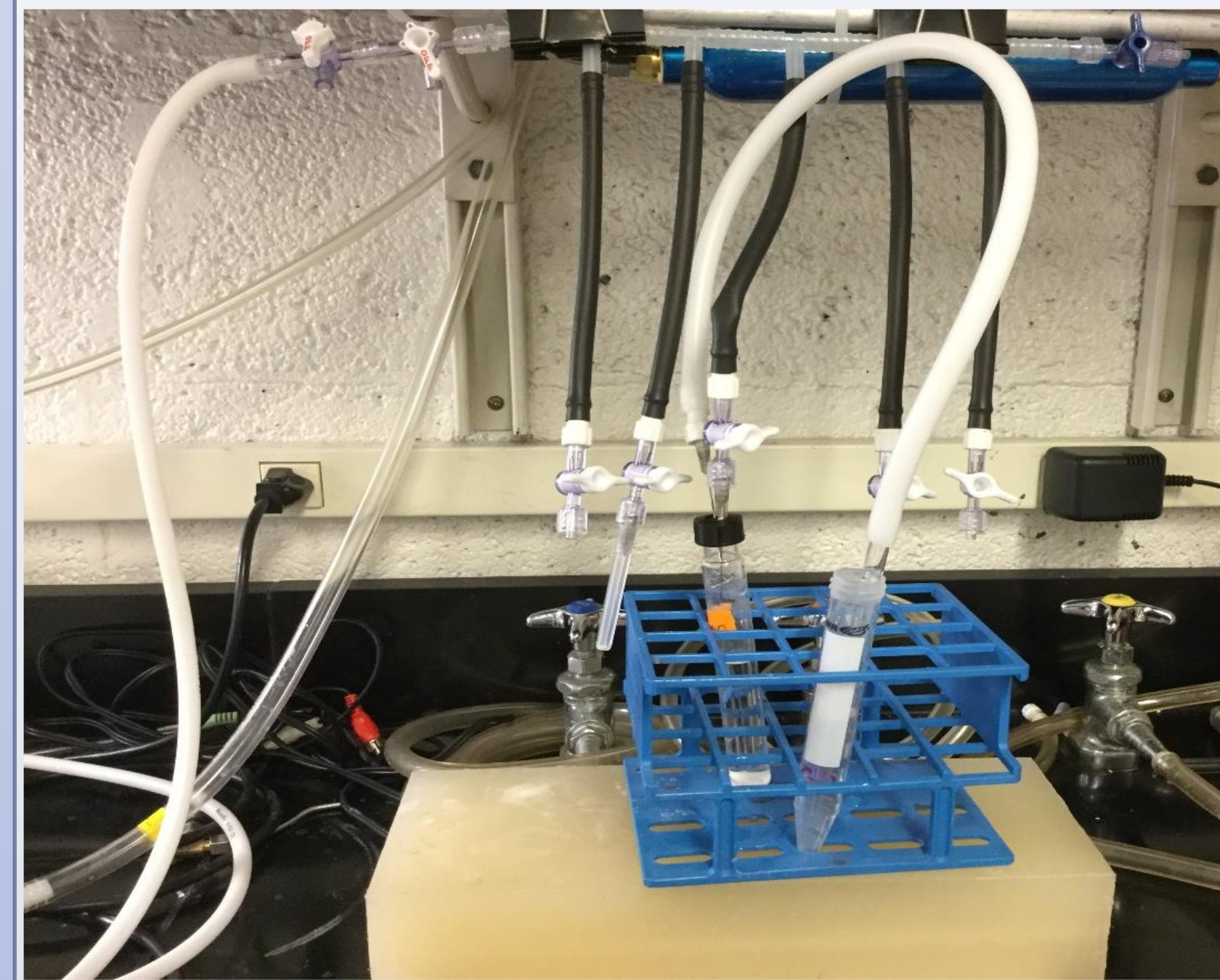
**Figure 1:** Bjerrum plot of different sulfur species at different pH levels.

## Methods

The oxidation process was contained in sealed tubes for several days and a degassing apparatus was used to recover the residual  $\text{HSO}_3^-/\text{SO}_3^{2-}$  by adding concentrated HCl to the solution. This acid converted the residual sulfur species to gaseous  $\text{SO}_2$ , and this gas was pumped away from the oxidized sulfate and then trapped in a concentrated  $\text{H}_2\text{O}_2$  and NaOH solution. The NaOH in solution would shift the pH of the solution so that the  $\text{SO}_2$  would convert to a different sulfur dioxide species which would be oxidized by the  $\text{H}_2\text{O}_2$ . After trapping in the  $\text{H}_2\text{O}_2$  solution,  $\text{BaCl}_2$  was added to the tubes and trapping solution to precipitate the sulfate as barite.

The sulfur isotopes of the barite were analyzed using an ISOPRIME isotope ratio mass spectrometer in the Stable Isotope Laboratory at the University of Maryland, College Park. The uncertainties associated with measurements were estimated based off the external precisions of IAEA-S1 and NBS-127 measurements.

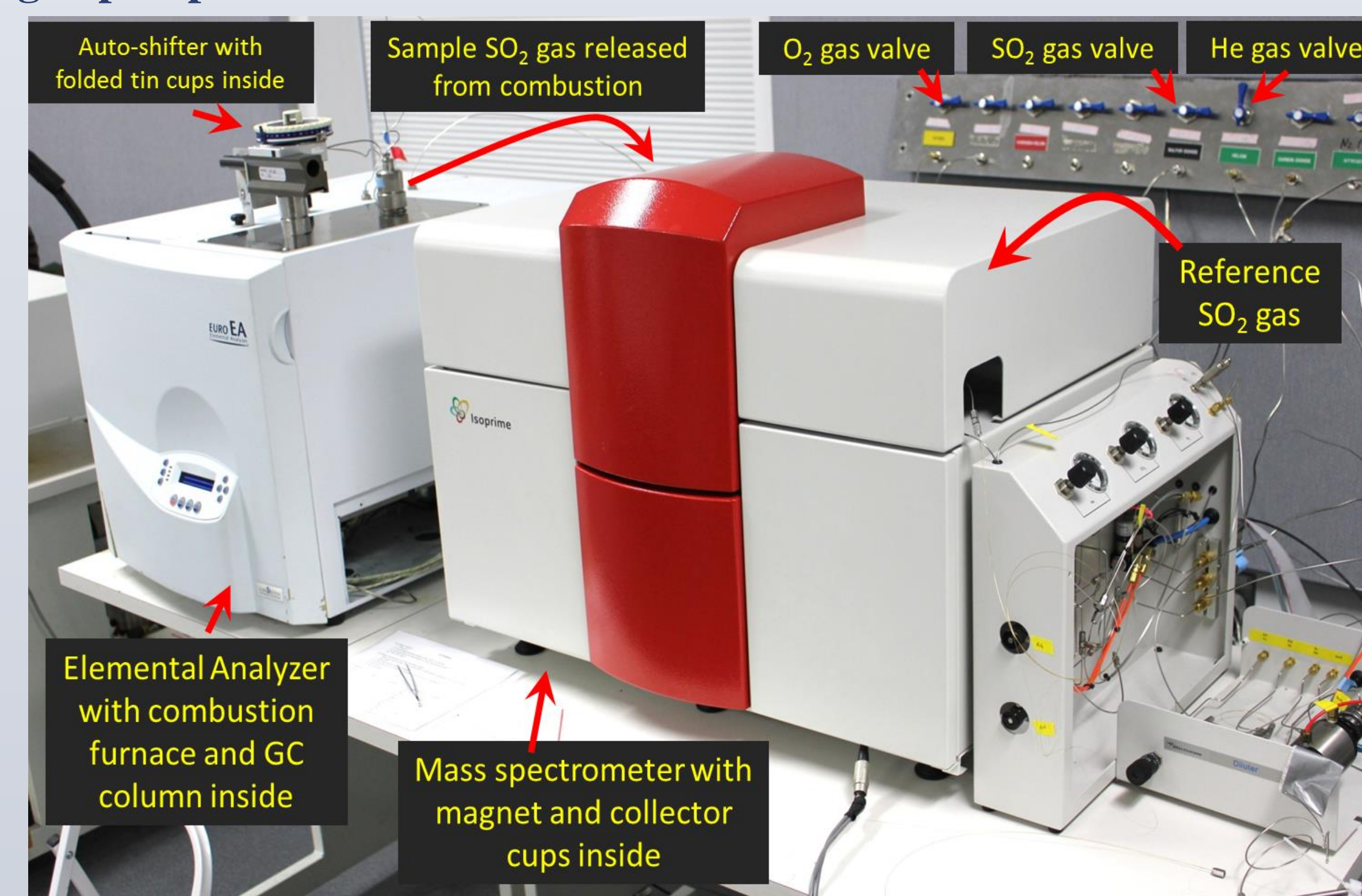
## Methods cont.



**Figure 2:** Initial degassing apparatus with house nitrogen pump and reaction tubes



**Figure 3:** Condensed distillation apparatus



**Figure 4:** IsoPrime Mass Spectrometer

## Results

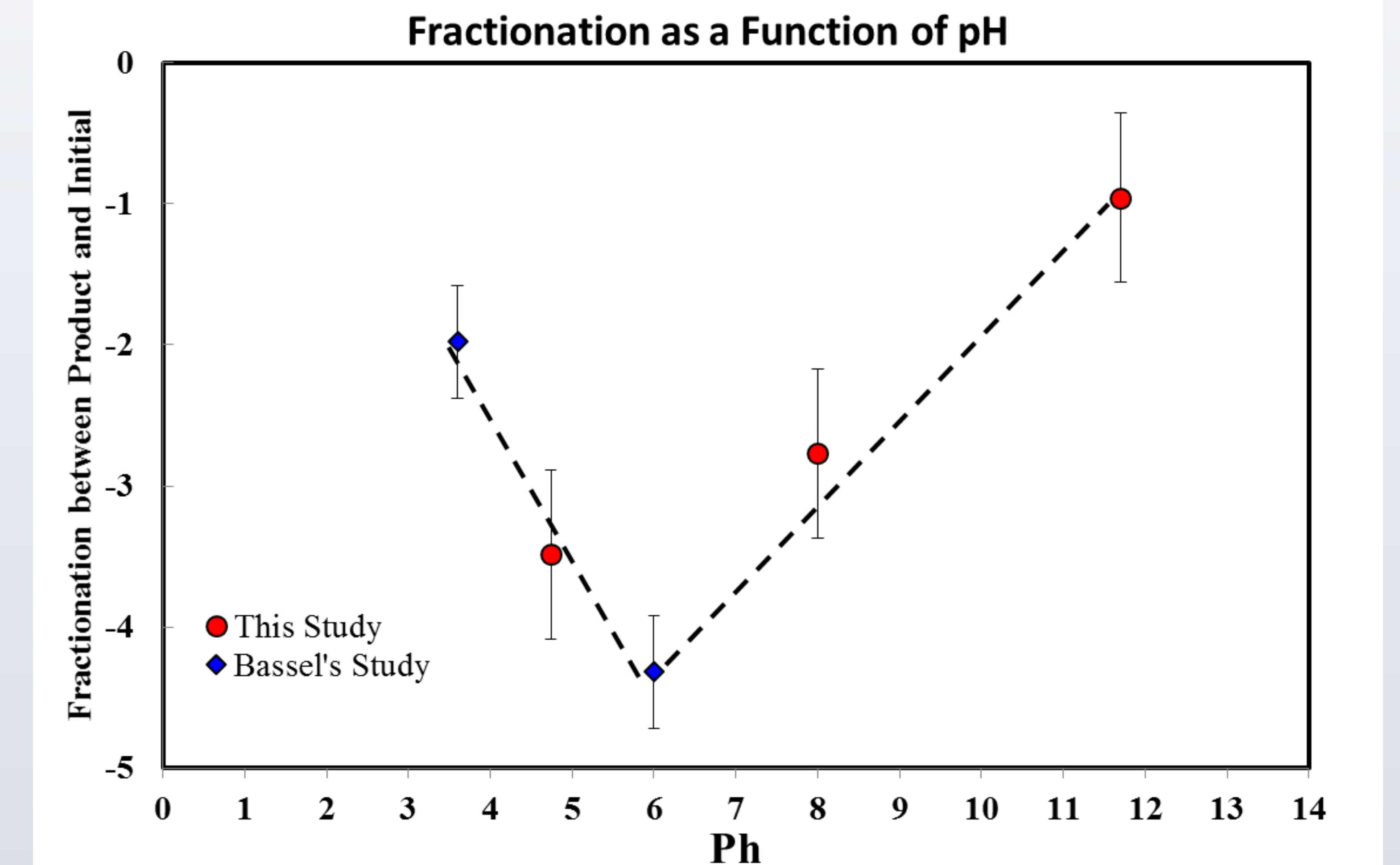
Sample ID	# of Analysis	True Values	Measured Values	2 St Dev	2 St Error
NBS-127	16	21.10	21.10	0.10	0.02
IAEA-S1 (NZ-S1)	16	-0.30	-0.30	0.11	0.03

**Table 1:** Values for recent measurements for NBS-127 and IAEA-S1

Ph	Product(‰)	Residue(‰)	Fractionation (Δ=product-initial)
11.7	-7.84 ± 0.22	-5.53 ± 0.22	-1.89 ± 0.24
11.7	-6.08 ± 0.22	-5.41 ± 0.22	-0.03 ± 0.24
8.0	-8.51 ± 0.22	-6.30 ± 0.22	-2.60 ± 0.25
8.0	-8.84 ± 0.22	-5.50 ± 0.22	-2.94 ± 0.24
4.74	-9.50 ± 0.18	-5.24 ± 0.18	-3.71 ± 0.23
4.74	-9.60 ± 0.18	-5.49 ± 0.18	-3.96 ± 0.23
4.74	-9.16 ± 0.18	-5.34 ± 0.18	-3.62 ± 0.24
4.74	-9.02 ± 0.18	-5.37 ± 0.18	-3.19 ± 0.24
4.74	-8.68 ± 0.18	-5.00 ± 0.18	-2.94 ± 0.25

**Table 2:** Sulfur Isotopes for Product and Residue

## Results cont.



**Effect of pH on Sulfite Oxidation Fractionation Factors**

## Discussion

Based on the collected data from this study, and another simultaneous study, there seems to be a correlation between the pH of the bisulfite solution and the fractionation factors of the oxidation reaction. The fractionation factors had a negative trend between pH 3.6 and 6; a change in the slope of the graph after pH=6, and an upwards trend between pH=6 and pH=11.7. These data supports the hypothesis that changing pH yields changes in isotope fractionation. This also indicates that there is a fractionation associated with oxidation and at least one oxidation reaction occurs. Mass balance issues were constantly improved and recovery techniques were modified throughout the course of the experiment. The nitrogen bubbling rate was adjusted and a condensed distillation apparatus was used to maximize residual sulfur dioxide recovery. A recent experiment revealed that there is a fractionation associated with trapping and converting the sulfur dioxide to sulfite. Further work could be done to completely understand this process.

## Acknowledgements

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## References

- Harris, E., Sinha, B., Hoppe, P., Foley, S., Borrmann, S., Fractionation of sulfur isotopes during heterogeneous oxidation of  $\text{SO}_2$  on sea salt aerosol: A new tool to investigate non-sea salt sulfate production in the marine boundary layer. *Atmos. Chem. Phys.* 12, 4619 (2012). Doi:10.5194/acp-12-4619-2012
- Larssen, T., et al. Acid Rain in China. *Environmental Science and Technology*. 2006. 418-425. Oana, S. and Ishikawa, H. 1966. Sulfur isotopic fractionation between sulfur and sulfuric acid in the hydrothermal solution of sulfur dioxide. *Geochem. J.* 1, 45-50.
- Singh, A., and Agrawal, M. Acid rain and its ecological consequences. *Journal of Environmental Biology*. 2008, 15-24.