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論文 / 著書情報
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題目(和文)	SO2光化学反応における硫黄同位体非質量依存分別の実験的研究とその太古代大気への適用
Title(English)	Experimental study on sulfur mass-independent fractionation during SO2 photochemistry and its application to Archean atmosphere
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出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第11053号, 授与年月日:2019年3月26日, 学位の種別:課程博士, 審査員:上野 雄一郎,中本 泰史,横山 哲也,綱川 秀夫,奥住 聡
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学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

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（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	地球惑星科学　　コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　理学　）
学生氏名： Student's Name	遠藤　美朗	指導教員（主）： Academic Supervisor(main)	上野　雄一郎
		指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Earth's early atmosphere is essential to understand origin of life, evolution of life, and climate of that time. Before 2.4 Ga, there are believed to be no or very low level of molecular oxygen in the ancient atmosphere. However, there is little consensus about reducing gas species and compositions of the atmosphere at that time. Sulfur mass-independent fractionation (S-MIF) recorded in Archean sedimentary rocks is expected to constrain the chemical and physical states of the ancient atmosphere. Specific photochemical reactions were shown to cause large S-MIF by previous studies (e.g. Farquhar et al., 2001). However, the most basic characteristics of Archean S-MIF, which is $\Delta^{36}S/\Delta^{33}S$ slope, have yet to be reproduced by experiments. In order to clue the ancient atmospheric chemistry, it is essential to understand the mechanism of S-MIF including ^{36}S. I have conducted a series of experiments to examine S-MIF during SO_2 photochemistry.

In Chapter 2, because I noted that fractionation factors in photolysis can be calculated from isotopologue absorption cross sections, I measured photoabsorption cross sections of SO_2 isotopologues ($^{32}SO_2$, $^{33}SO_2$, $^{34}SO_2$, and $^{36}SO_2$) from 190 to 220 nm. This is the first report of $^{36}SO_2$ absorption cross sections. Observed cross sections clearly depended on sample pressures. Owing to careful analysis, I found that this pressure dependence stems from experimental artifact, and the dependence could be corrected. As a result, high accuracy and high precision (less than 1% of error) of cross sections were achieved. Fractionation factors of SO_2 photolysis were estimated to be smaller than a previous study (Danielache et al., 2008). The magnitude of fractionation factors was found to be similar to or below that of Archean S-MIF.

In Chapter 3, I conducted SO_2 photochemical experiments under reducing CO atmosphere and examined sulfur isotope fractionations. In previous studies, because of a limitation of sample amount for quadruple sulfur isotope analysis, isotope fractionations in SO_2 photolysis could not be examined under optically thin SO_2 condition which should be realistic atmospheric condition. I developed a new analytical method of small sample (10 nmol S) for

sulfur isotope analysis, and the experiment under optically thin SO_2 condition was achieved. As a result, the observed S-MIF by photochemical experiments reproduced the characteristic of Archean $\Delta^{36}S/\Delta^{33}S$ slope about −1, for the first time. Moreover, it was found that the S-MIF occurs in self-shielding in SO_2 photolysis and photoexcited SO_2 chemistry. Sulfur mass-independent fractionation in final products reflects mixing of these two mechanisms. In atmosphere, self-shielding should reflect partial pressure of SO_2 and S-MIF in excited SO_2 chemistry should reflect partial pressure of CO or CH_4. Accordingly, to reproduce the Archean $\Delta^{36}S/\Delta^{33}S$ slope, the atmosphere was estimated to contained several kilopascals of CO or CH_4 in the Archean atmosphere.

In Chapter 4, I focused on SO_2 absorption line width dependence of self-shielding. In order to test total pressure dependence of S-MIF, I conducted SO_2 photochemical experiments changing both partial pressures of SO_2 and total pressures. Total pressure dependence of S-MIF in SO_2 photolysis was clearly shown experimentally. Analysis based on the SO_2 absorption line width found that the total pressure dependence comes from pressure broadening of SO_2 absorption lines. At high total pressure such as above 1 bar, the $\Delta^{36}S/\Delta^{33}S$ slope was far from that of the Archean. Based on Chapter 3's model, to reproduce large S-MIF of late Archean, it was found that the Archean atmospheric pressure should be below 1 bar, or the SO_2 was photolyzed in the upper atmosphere.

Finally, In Chapter 5, the possible Archean atmospheric states estimated from quadruple sulfur isotopes were discussed. Based on the results from Chapter 2 to Chapter 4 and using numerical photochemical model, the $\Delta^{33}S$ and $\Delta^{36}S$ values were modeled under various SO_2 column densities, partial pressures of CO, and total pressures. When the results were compared to the geological large S-MIF of late Archean, and to reproduce the S-MIF, it was found to be important that S-MIF in excited SO_2 was conserved in final products. Reducing gas species were discussed using their reaction rate constants with excited SO_2. Consequently, it was found that hydrocarbons including CH_4 cannot explain the late Archean S-MIF and it was concluded that CO is possibly reasonable as reducing gas of excited SO_2.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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