

1 **Appendix A: Modeling of S_n chemistry**

2 There is a concern that S₂ photolysis can be an additional source of S(³P), and the
 3 estimation of isotope enrichment factor for photolysis needs to take account of S₂. In
 4 order to test this, we have run some photochemical models. We note here that the S_n
 5 chemistry is quite complex and the rate constants are poorly constrained. Here, we
 6 used the rate constants from the main text and those tabulated by Ueno et al. (2009) to
 7 gain a first order understanding of the importance of the reactions. The reactions
 8 considered are:

9

| Reactions | Rate Constants (for 26 mbar OCS) |
|---|---|
| R1a) OCS + $h\nu \rightarrow$ CO + S(¹ D) | $0.74 \times 10^{-3} \text{ s}^{-1}$ |
| R1a) OCS + $h\nu \rightarrow$ CO + S(³ P) | $0.26 \times 10^{-3} \text{ s}^{-1}$ |
| R2a) OCS + S(¹ D) \rightarrow CO + S ₂ | $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ |
| R2b) OCS + S(³ P) \rightarrow CO + S ₂ | $2.7 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ |
| R3) S(¹ D) + OCS \rightarrow S(³ P) + OCS | $15 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ |
| R7a) S ₂ + $h\nu \rightarrow$ 2S | $2 \times 10^{-2} \text{ s}^{-1}$ |
| R7b) S ₃ + $h\nu \rightarrow$ S + S ₂ | $2 \times 10^{-2} \text{ s}^{-1}$ |
| R7c) S ₄ + $h\nu \rightarrow$ 2 S ₂ | $2 \times 10^{-2} \text{ s}^{-1}$ |
| R8a) S ₂ + S ₂ + M \rightarrow S ₄ + M | $2.8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ |
| R8b) S ₂ + S + M \rightarrow S ₃ + M | $1.0 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$ |
| R8c) S + S ₃ + M \rightarrow S ₄ + M | $2.8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ |
| R8d) S ₄ + S ₄ + M \rightarrow S ₈ + M | $2.8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ |
| R9) S + S ₃ \rightarrow 2 S ₂ | $1.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ |
| R10) S _n \rightarrow wall loss | 0.01, 0.1, 1 s ⁻¹ |

10

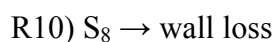
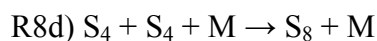
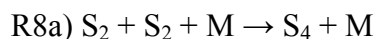
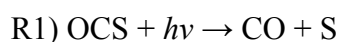
11 Wall loss rate constant (k_{10}) is varied at 0.01, 0.1, and 1 s⁻¹. Following Matt
 12 Johnson's suggestion, the rate is derived assuming the diffusivity (D) of 0.01, 0.1, and
 13 1 cm²/s, and by a conventional formula of $5.8 D/r^2$, where r is the radius of the cell
 14 (2.4 cm) (e.g., Calvert and Pitts, 1966; Fowles et al., 1967). Higher diffusivity (\approx 3.7
 15 cm²/s) is expected for low-pressure OCS experiments (without N₂). This wall loss

1 kinetics has little effect for the overall reaction scheme since the main loss of S₂ is
2 through S₂+ S₂ → S₄ (R_{8a}). The S₂ photolysis rate is the rate from de Almeida and
3 Singh (1986) multiplied by 5 to account for higher photon flux from Xe lamp at ≈ 280
4 nm compared to the solar flux. This photolysis rate is a factor of 20 higher than what
5 was used by Ueno et al. (2009).

6 Recombination reaction involving atomic S (e.g., R8b, R8c) is insignificant
7 because of the low S number density due to fast OCS+S reaction (R2). Important
8 reactions are found to be:

9

Reactions



10

11 The steady state number density for S₂ is (2.5±0.1)×10¹³ (cm⁻³), which is
12 largely due to the balance between the source (≈2k₁[OCS]) and the sink (≈k_{8a}[S₂]² M+
13 k_{7a}[S₂]) reactions. Here, k_{8a}[S₂]² M >> k_{7a}[S₂] under experimental conditions, and thus,
14 [S₂] ≈ (2k₁/k_{8a})^{1/2}, when M is OCS. S₂ number density would be even lower for
15 experiments with added N₂ because R8a is a third body reaction.

16 Using this number density, the S production from S₂ photolysis is found to be
17 less than 0.1 % compared to that of S derived from OCS photolysis. For 26 mbar OCS
18 experiment, for example,

19 S production from OCS photolysis: 2k₁[OCS] = 2×10⁻³ s⁻¹×6.6×10¹⁷ cm⁻³ = 1.3×10¹⁵
20 cm⁻³ s⁻¹

21 S production from S₂ photolysis: k_{7a}[S₂] = 2×10⁻² s⁻¹×2.5×10¹³ cm⁻³ = 5×10¹¹ cm⁻³ s⁻¹

22 Unless S₂ photolysis produces very large (>100 ‰?) isotope effect, its isotope
23 fractionation will not be observed in our experiments (<0.1 ‰ effect). Such large

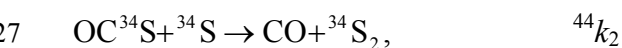
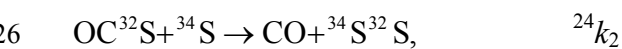
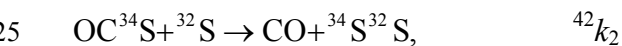
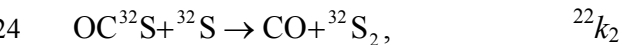
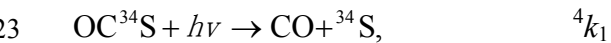
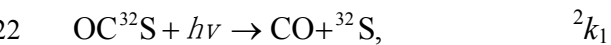
1 isotope effect is not impossible but is unlikely except for isotope self-shielding or
2 potentially ozone-like symmetry-dependent isotope effects. There is a slight chance
3 that the symmetry-dependent isotope effect could happen but our experiment was not
4 designed to test it.

5 More importantly, the S₂ absorption band at around 280 nm (Herman and
6 Herman, 1963) was not detected using our CCD spectrometer (grating is blazed at 250
7 nm), suggesting that isotope self-shielding of S₂ is also unlikely to be significant
8 under our experimental conditions. This also puts an upper range of S₂ number
9 density; if the peak absorption cross section for S₂ is between 10⁻¹⁷ and 10⁻¹⁶ cm⁻³ at
10 280 nm, and if we conservatively estimate that detection limit for our spectrometer is
11 1 % absorption, S₂ density would not be any higher than 10¹³ or 10¹² cm⁻³, which is
12 consistent with model calculation. This level is much lower than the column density
13 where isotope self-shielding is expected ($\sigma m l \approx 1$, i.e., $m = [S_2] \approx 10^{15}$ cm⁻³). Once S₂
14 is combined to form S₃ and S₄, these species exhibit little vibrational structures in
15 absorption cross-sections (Billmers and Smith, 1991), and thus self-shielding is not
16 expected for S₃ or S₄.

17

18 **Appendix B: Derivation of Eq. (3)**

19 Here, we consider OCS photolysis and following sulfur abstraction reaction in a
20 system with two sulfur isotopes (³²S and ³⁴S). Reactions and their rate constants to be
21 considered are:



28

1

2 Rate equations for atomic sulfur are,

$$3 \quad \frac{d[{}^{32}\text{S}]}{dt} = {}^2k_1[\text{OC}^{32}\text{S}] - {}^{22}k_2[\text{OC}^{32}\text{S}][{}^{32}\text{S}] - {}^{42}k_2[\text{OC}^{34}\text{S}][{}^{32}\text{S}] \quad (1)$$

$$4 \quad \frac{d[{}^{34}\text{S}]}{dt} = {}^4k_1[\text{OC}^{34}\text{S}] - {}^{24}k_2[\text{OC}^{32}\text{S}][{}^{34}\text{S}] - {}^{44}k_2[\text{OC}^{34}\text{S}][{}^{34}\text{S}] \quad (2)$$

5 Assuming the steady state for these atomic sulfur,

$$6 \quad [{}^{32}\text{S}] = \frac{{}^2k_1[\text{OC}^{32}\text{S}]}{{}^{22}k_2[\text{OC}^{32}\text{S}] + {}^{42}k_2[\text{OC}^{34}\text{S}]} \quad (3)$$

$$7 \quad [{}^{34}\text{S}] = \frac{{}^4k_1[\text{OC}^{34}\text{S}]}{{}^{24}k_2[\text{OC}^{32}\text{S}] + {}^{44}k_2[\text{OC}^{34}\text{S}]} \quad (4)$$

8 Rate equations for S_2 are:

$$9 \quad \frac{d[{}^{32}\text{S}_2]}{dt} = {}^{22}k_2[\text{OC}^{32}\text{S}][{}^{32}\text{S}] \quad (5)$$

$$10 \quad \frac{d[{}^{34}\text{S}^{32}\text{S}]}{dt} = {}^{24}k_2[\text{OC}^{32}\text{S}][{}^{34}\text{S}] + {}^{42}k_2[\text{OC}^{34}\text{S}][{}^{32}\text{S}] \quad (6)$$

11 From (5) and (6),

$$12 \quad \frac{d[{}^{34}\text{S}^{32}\text{S}]}{d[{}^{32}\text{S}_2]} = \frac{{}^{24}k_2[{}^{34}\text{S}]}{{}^{22}k_2[{}^{32}\text{S}]} + \frac{{}^{42}k_2[\text{OC}^{34}\text{S}]}{{}^{22}k_2[\text{OC}^{32}\text{S}]} \quad (7)$$

13 From (3), (4), and (7),

$$14 \quad \frac{d[{}^{34}\text{S}^{32}\text{S}]}{d[{}^{32}\text{S}_2]} = \frac{{}^{24}k_2}{{}^{22}k_2} \cdot \frac{{}^4k_1[\text{OC}^{34}\text{S}]}{{}^2k_1[\text{OC}^{32}\text{S}]} \cdot \frac{{}^{22}k_2[\text{OC}^{32}\text{S}] + {}^{42}k_2[\text{OC}^{34}\text{S}]}{{}^{24}k_2[\text{OC}^{32}\text{S}] + {}^{44}k_2[\text{OC}^{34}\text{S}]} + \frac{{}^{42}k_2[\text{OC}^{34}\text{S}]}{{}^{22}k_2[\text{OC}^{32}\text{S}]} \quad (8)$$

$$15 \quad = \frac{[\text{OC}^{34}\text{S}]}{[\text{OC}^{32}\text{S}]} \left(\frac{{}^4k_1}{{}^2k_1} \gamma + \frac{{}^{42}k_2}{{}^{22}k_2} \right) \quad (9)$$

16 where,

$$17 \quad \gamma = \frac{1 + \frac{{}^{42}k_2[\text{OC}^{34}\text{S}]}{{}^{22}k_2[\text{OC}^{32}\text{S}]}}{1 + \frac{{}^{44}k_2[\text{OC}^{34}\text{S}]}{{}^{24}k_2[\text{OC}^{32}\text{S}]}} \quad (10)$$

18 Here, we define, the isotope fractionation factors for the photolysis and sulfur

1 abstraction reaction as:

$$2 \quad \alpha_1 = \frac{{}^4k_1}{{}^2k_1} \quad (11)$$

$$3 \quad \alpha_2 = \frac{{}^{42}k_2}{{}^{22}k_2} \quad (12)$$

4 According to the rule of geometric mean (Bigeleisen, 1955),

$$5 \quad \alpha_2 = \frac{{}^{42}k_2}{{}^{22}k_2} \approx \frac{{}^{44}k_2}{{}^{24}k_2} \quad (13)$$

6 This is valid unless “clumped” isotope effect is considered. Thus, the factor γ is very
7 close to unity.

8 The isotope fractionation factor for the overall reaction is:

$$9 \quad \alpha = \frac{1}{2} \cdot \frac{d[{}^{34}\text{S}^{32}\text{S}]/d[{}^{32}\text{S}_2]}{[\text{OC}^{34}\text{S}]/[\text{OC}^{32}\text{S}]} \quad (14)$$

10 The factor 1/2 is a symmetry factor for S_2 . According to equations (9–14),

$$11 \quad \alpha = \frac{1}{2}(\alpha_1 + \alpha_2) \quad (15)$$

12 Because $\varepsilon = \alpha - 1$, the isotope fractionation is:

$$13 \quad \varepsilon = \frac{1}{2}(\varepsilon_1 + \varepsilon_2) \quad (16)$$

14

15 Reference

16 de Almeida, A. A. and Singh, P. D.: Photodissociation lifetime of ${}^{32}\text{S}_2$ molecule in
17 comets, *Earth, Moon, Planets*, 36, 117-125, 1986.

18 Bigeleisen, J.: Statistical mechanics of isotope systems with small quantum
19 corrections. I. General considerations and the rule of the geometric mean, *J.*
20 *Chem. Phys.*, 23, 2264, doi:10.1063/1.1740735, 1955.

21 Billmers, R. I. and Smith A. L.: Ultraviolet-visible absorption spectra of equilibrium
22 sulfur vapor: Molar absorptivity spectra of S_3 and S_4 , *J. Phys. Chem.*, 95,
23 4242-4245, 1991.

24 Calvert, J. G. and Pitts, J. N.: *Photochemistry*, John Wiley & Sons, New York, 1966.

25 Fowles, P., deSorgo, M., Yarwood, A. J.: The reactions of sulfur atoms. IX, *The*

1 flash photolysis of carbonyl sulfide and the reactions of S(¹D) atoms with
2 hydrogen and methane, J. Am. Chem. Soc., 89, 1352-1362,
3 doi:10.1021/ja00982a13, 1967.

4 Herman, L., and Herman, R.: Perturbations in the S₂ spectrum, Nature, No.4863,
5 677-677, 1963.

6 Ueno, Y., Johnson, M. S., Danielache, S. O., Eskebjerg, C., Pandey, A., and Yoshida,
7 N.: Geological sulfur isotopes indicate elevated OCS in the Archean atmosphere,
8 solving faint young sun paradox, P. Natl. Acad. Sci. USA, 106, 14784-14789,
9 2009.