

1-1-2017

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Accepted version. "Recombination Reactions as a Possible Mechanism of Mass-Independent Fractionation of Sulfur Isotopes in the Archean Atmosphere of Earth," in *Proceedings of the National Academy of Sciences*, Vol. 114, No. 12 (2017): 3062-3067. DOI. © 2017 National Academy of Sciences. Used with permission.

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# Recombination reactions as a possible mechanism of mass-independent fractionation of sulfur isotopes in the Archean atmosphere of Earth

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## Abstract

A hierarchy of isotopically substituted recombination reactions is formulated for production of sulfur allotropes in the anoxic atmosphere of Archean Earth. The corresponding system of kinetics equations is solved analytically to obtain concise expressions for isotopic enrichments, with focus on mass-independent isotope effects due to symmetry, ignoring smaller mass-dependent effects. Proper inclusion of atom-exchange processes is shown to be important. This model predicts significant and equal depletions driven by reaction stoichiometry for all rare isotopes:  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$ . Interestingly, the ratio of capital  $\Delta$  values obtained within this model for  $^{33}\text{S}$  and  $^{36}\text{S}$  is  $-1.16$ , very close to the mass-independent fractionation line of the Archean rock record. This model may finally

offer a mechanistic explanation for the striking mass-independent fractionation of sulfur isotopes that took place in the Archean atmosphere of Earth.

## Keywords

S-MIF, mass-independent fractionation, Archean atmosphere, sulfur recombination, isotope effect

## Significance

Mass-independent fractionation of sulfur isotopes found in the Archean surface deposits (more than 2.3 billion y old) represents a “smoking gun” of anoxic atmosphere and gives a key element for determining the time of the great oxygenation event. Finding the molecular-level mechanism of these isotope enrichments is essential for understanding the environment on Earth just before, at the time of appearance, and during the evolution of early life. The theory of sulfur recombination processes proposed in this paper offers one possible explanation for the mass-independent fractionation effect, giving geochemists a useful tool for studying the atmospheric chemistry of Archean Earth, based on the rock record available to them today.

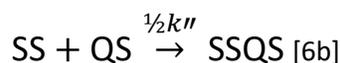
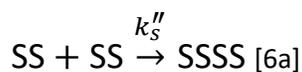
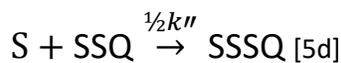
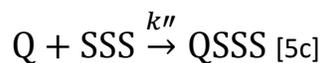
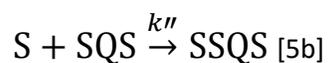
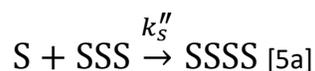
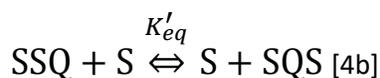
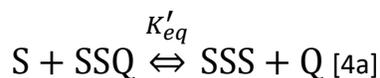
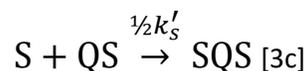
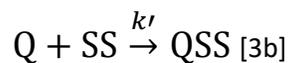
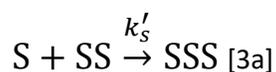
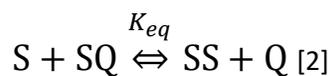
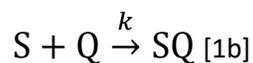
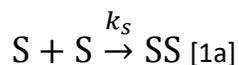
Mass-independent fractionation of sulfur isotopes (S-MIF) in the Archean rock record ([14444–6](#)) serves as strong evidence of an anoxic atmosphere ([74–9](#)), indicating a low-oxygen gas-phase chemistry before 2.3 billion y ago. However, the actual chemical process, or processes, responsible for generation of significant enrichments of sulfur-bearing species in heavy isotopes of sulfur, and leading to mass-independent fractionation, still remains unidentified. Some mass-independent fractionation was observed experimentally in SO<sub>2</sub> photolysis ([104–12](#)) and in nonadiabatic dynamics of SO<sub>2</sub> photodissociation ([13, 14](#)). Another important chemical pathway, specific to a low-oxygen atmosphere ([7, 8, 154–17](#)), is a chain of recombination reactions that start from recombination of photolytically produced sulfur atoms ( $S + S \rightarrow S_2$ ), go through formation of larger sulfur allotropes ( $S + S_2 \rightarrow S_3$ ,  $S_2 + S_2 \rightarrow S_4$ , and  $S + S_3 \rightarrow S_4$ ), and end up at the elemental sulfur ( $S_4 + S_4 \rightarrow S_8$ ) that can be deposited, preserved, and could contribute to S-MIF in the Archean atmosphere. Unfortunately, experimental studies of gas-phase sulfur chemistry and photochemistry are complicated, and their results are often not entirely certain. Moreover, sulfur has four stable isotopes (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S), which leads to a multitude of possible isotopic combinations of reagents and products in the recombination reactions listed above. It is unlikely that all these processes will be characterized experimentally at the required level of detail any time soon. Thus, it is desirable to analyze these reactions theoretically to determine whether a significant enrichment of rare sulfur isotopes is at all possible through these processes, and what steps are the most important.

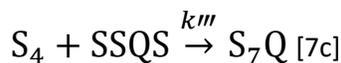
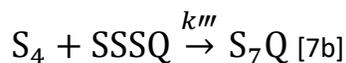
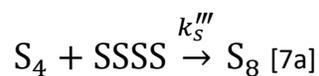
We build upon our experience ([1844–21](#)) with the recombination reaction that forms ozone,  $O + O_2 \rightarrow O_3$ , and is known to produce significant mass-independent fractionation of oxygen isotopes <sup>17</sup>O and <sup>18</sup>O in today’s atmosphere of Earth ([224–24](#)) and in many laboratory experiments ([25, 26](#)). In ozone formation two features essential for the isotope effect are ([25](#)) fast atom-exchange processes that reshuffle isotopes in the mixture (e.g.,  $^{18}O + ^{16}O^{16}O \leftrightarrow ^{18}O^{16}O + ^{16}O$ ) and the experimentally proven symmetry effect that manifests in faster production of asymmetric molecules (e.g.,  $^{18}O^{16}O^{16}O$  vs.  $^{16}O^{18}O^{16}O$ ). In this paper we attempt to export these two major elements from ozone to sulfur, building them into the chain of sulfur recombination reactions at the simplest possible level, with the goal of identifying a possible mechanism of sulfur fractionation.

## Recombination Kinetics

In what follows the symbol S is used for the most abundant sulfur isotope, <sup>32</sup>S, and Q is used for one of the rare isotopes (<sup>33</sup>S, <sup>34</sup>S, or <sup>36</sup>S). It is assumed that those are present in trace amounts, and each can be treated independently from other rare isotopes. All mass-dependent isotope effects on the reaction rates are neglected,

with a focus on the mass-independent symmetry effect and reaction stoichiometry. Namely, the rate coefficients for production of symmetric molecules ( $k_s$ ,  $k'_s$ , and  $k''_s$ , discussed below) are assumed to be the same for different isotopes but are expected to be smaller than the corresponding rate coefficients for asymmetric molecules ( $k$ ,  $k'$ , and  $k''$ ). Equilibrium constants ( $K_{eq}$ ,  $K'_{eq}$ , and  $K''_{eq}$ ) are assumed to be equal to their statistical values, again neglecting mass differences between isotopes and focusing on symmetry and stoichiometry. If the reaction branches onto two, producing two physically different isotopomers of the same isotopologue, we split the rate coefficient accordingly (e.g.,  $\frac{1}{2}k'_s$  and  $\frac{1}{2}k''_s$ , discussed below). The reactions included in this consideration are





Note that here we included only the processes that involve one atom of rare isotope (i.e., no more than one Q per reaction). Although the chain of 20 reactions ([1–7](#)) looks almost incomprehensible we will demonstrate here that with approximations outlined above the chain can be solved analytically, to derive concise expressions for isotopic enrichments:

$$\delta = \frac{f_P}{f_R} - 1, [8]$$

where  $f_R = [Q]/[S]$  is a fraction of isotope Q in the reagents, which is the reservoir of atomic sulfur (thus,  $f_R$  represents the natural abundance), whereas  $f_P$  is the ratio of isotopes in the products. We will go progressively through the reactions ([1–7](#)) to derive expression for  $f_P$  and compute the enrichment  $\delta$  for each stage of the recombination process, namely, for  $S_2$  production, then for  $S_3$ ,  $S_4$ , and finally  $S_8$ .

## Production of $S_2$

The main idea of our treatment is introduced using the simplest processes, reactions [1a](#) and [1b](#), that produce diatomic sulfur molecules from sulfur atoms and could lead to isotope enrichment through production of an SQ molecule. The fraction of isotope Q in the diatomic products, SS (or  $S_2$ ) and SQ, is computed as follows:

$$f_P = \frac{1 \times [SQ]}{2 \times [SS] + 1 \times [SQ]} \approx \frac{1 [SQ]}{2 [SS]} = \frac{1 k[S][Q]}{2 k_s[S][S]} = \frac{k [Q]}{2k_s [S]}.$$

Deriving this expression, first, the approximation was made based on the assumption of a small concentration of isotopically substituted SQ (compared with the concentration of the usual  $S_2$ ), and then the standard second-order kinetics of [1a](#) and [1b](#) was used to introduce rate coefficients. Substitution of this result into [Eq. 8](#) leads to

$$\delta = \frac{k}{2k_s} - 1. [9]$$

It should be taken into account that asymmetric diatomic SQ has twice more rovibrational states, compared with the symmetric SS, where the rotational states with even values of  $j$  are forbidden by symmetry. Due to the number of states, rate coefficients for these processes must obey  $k \approx 2k_s$ . Besides this statistical factor of 2, the larger density of states in SQ should lead to somewhat more efficient energy transfer processes, and even higher recombination rates ([27](#)). Although this effect is conceptually simple, its quantitative characterization requires rigorous quantum-dynamics calculations that are rather costly computationally even for the simplest molecules, such as  $S_2$  and SQ. Here we will only assume that  $k \gtrsim 2k_s$  [slightly larger, by a few percent ([27](#))]. From [Eq. 9](#) it follows that this might lead to some small and positive enrichment  $\delta$ .

However, it should be realized that it is wrong to consider reactions [1a](#) and [1b](#) separately from the reaction ([2](#)) that interconverts  $S_2$  with SQ. Recent electronic structure calculations of potential energy surface for  $S + S_2$  ([28, 29](#)) showed no activation barrier for recombination or atom exchange, which means that the (nearly)

isoergic atom exchange (2) proceeds quickly in both directions, establishing equilibrium between S + SQ and SS + Q. The equilibrium constant is very close to  $K_{eq} = 1/2$ , due to statistical difference in the number of states in symmetric SS (on the product side) and asymmetric SQ (on the reagent side; see reaction 2). Small mass-dependent effects can be neglected. Similar processes are well known to occur during ozone formation, where atom exchange  $^{18}\text{O} + ^{16}\text{O}^{16}\text{O} \leftrightarrow ^{18}\text{O}^{16}\text{O} + ^{16}\text{O}$  is more than three orders of magnitude faster than the recombination reaction itself (25, 26).

Thus, deriving the expression for  $f_P$  one has to introduce the equilibrium constant and use the equilibrium concentration for [SQ] from reaction 2, which leads to

$$f_P = \frac{1}{2} \frac{[\text{SQ}]}{[\text{SS}]} = \frac{1}{2} \frac{1}{[\text{SS}]} \frac{[\text{SS}][\text{Q}]}{K_{eq}[\text{S}]} = \frac{1}{2K_{eq}} \frac{[\text{Q}]}{[\text{S}]},$$

$$\delta_{S_2} = \frac{1}{2K_{eq}} - 1 \approx 0. \quad [10]$$

This result makes sense. Fast atom-exchange processes would quickly reshuffle isotopes between SQ and  $S_2$ , destroying any enrichment generated by small difference  $k \gtrsim 2k_s$ . Thus, no enrichment is possible at the level of  $S_2$  production, at least not due to reactions 1–7. Only if there would be another very fast process (e.g., surface deposition or aerosol formation) that would remove isotopically enriched SQ from the mixture before it loses Q in the atom exchange could the isotope enrichment due to  $k \gtrsim 2k_s$  somehow survive. The practically important conclusion from here is that atom-exchange processes, at least reaction 2 but also reactions 4a and 4b, should be incorporated into the kinetics models of sulfur chemistry (8, 16, 30) to properly describe isotopic enrichments. They have been ignored so far.

## Production of $S_3$

Four reactions (3a–3d) produce triatomic sulfur species from atoms and diatomics. Note that reactions 3a and 3b involve symmetric diatomic reagent, SS. The third atom, S in 3a or Q in 3b, can attach to either side of SS, giving identical products. In contrast, the encounter of S with SQ in reactions 3c and 3d can lead to two distinct products, depending on the reaction site. Thus, rate coefficients for the reactions 3c and 3d are expected to be a factor of 2 smaller than those for reactions 3a and 3b, respectively. The symmetry effect is introduced [by analogy with the famous  $\eta$ -effect in ozone (31)] assuming that rate coefficients for production of asymmetric SSQ in reactions 3b and 3d are somewhat larger than those for production of symmetric species, SSS in 3a and SQS in 3c. Thus, we set  $k' > k'_s$ . Note that this difference is not a factor of 2. In the case of ozone, formed by four reactions analogous to 3a–3d,  $k'$  is larger than  $k'_s$  by 20%, according to laboratory experiments (25). The molecular level origin of this difference is not yet entirely clear and is a subject of intense theoretical research. It is believed that lifetimes of scattering resonances are affected by slight asymmetry of vibrational modes in the asymmetric molecules (20), but other hypotheses have also been proposed (31, 32).

For SSS, SSQ, and SQS among the products the fraction of isotope Q, relative to S, is

$$f_P \approx \frac{1 \times [\text{SSQ}] + 1 \times [\text{SQS}]}{3 \times [\text{SSS}]},$$

where, again, the assumption is made that most of S belongs to the nonsubstituted  $S_3$ . Using second-order kinetics of reactions 3a–3d, and the equilibrium concentration [QS] from reaction 2, this expression transforms as follows:

$$f_P = \frac{[\text{SSQ}] + [\text{SQS}]}{3[\text{SSS}]} = \frac{k'[\text{SS}][\text{Q}] + \frac{1}{2}k'_s[\text{S}][\text{QS}] + \frac{1}{2}k'[\text{S}][\text{QS}]}{3k'_s[\text{S}][\text{SS}]} \\ = \frac{k'[\text{SS}][\text{Q}] + \frac{1}{2}k'_s \frac{[\text{SS}][\text{Q}]}{K_{eq}} + \frac{1}{2}k' \frac{[\text{SS}][\text{Q}]}{K_{eq}}}{3k'_s[\text{S}][\text{SS}]} = \frac{\frac{1}{2}k'_s + (\frac{1}{2} + K_{eq})k'}{3K_{eq}k'_s} \frac{[\text{Q}]}{[\text{S}]}$$

Substituting this result into [Eq. 8](#), and using statistical value of  $K_{eq} = 1/2$ , we obtain

$$\delta = \frac{k'_s + 2k'}{3k'_s} - 1 = \frac{2}{3} \left( \frac{k'}{k'_s} - 1 \right). \quad [11]$$

Because  $k' > k'_s$  this expression gives positive enrichment.

For example, this formula works really well in the case of ozone formation, where  $k' = 1.2k'_s$  leads to  $\delta_{o_3} = 13.3\%$ , in excellent agreement with the laboratory-measured enrichment value of about 13% ([25](#)). It should be stressed that this expression leads to  $\delta = 0$  in the limit of  $k' = k'_s$ , which means that in the case of ozone, where recombination stops at  $\text{O}_3$  and does not go further (no  $\text{O}_4$  or  $\text{O}_8$  are formed at normal conditions), the only possible source of large isotopic enrichment is  $\eta$ -effect,  $k' > k'_s$ .

In the case of sulfur the ratio  $k'/k'_s$  is not known, and it is too early to speculate about its value since the origin of  $\eta$ -effect is not yet entirely clear, even in the case of ozone ([20, 21](#)). If the analogy with ozone is valid, this value would be on the order of 133%.

## Further Importance of Atom Exchange

Also, in the case of sulfur one has to include two atom-exchange processes ([4a](#) and [4b](#)) that reshuffle isotopes between SSQ, SQS, and SSS. Those proceed through formation of an intermediate tetratomic complex (e.g.,  $\text{S} + \text{SSQ} \leftrightarrow \text{SSSQ}^* \leftrightarrow \text{SSS} + \text{Q}$ ) and are also expected to be barrierless, nearly isoergic, and fast processes. This assumption is supported by ab initio calculations ([33, 34](#)) that showed at least two paths for atom exchange: either through rectangular isomer on the triplet surface,  ${}^3\text{B}_{1u} \text{S}_4(\text{D}_{2h})$  that correlates with the ground-state  ${}^3\text{P}$  sulfur atom, or through the “boat” isomer on the singlet surface,  ${}^1\text{A}_1 \text{S}_4(\text{C}_{2v})$  that correlates with photo-excited  ${}^1\text{D}$  sulfur atom.

If we assume that these fast atom-exchange processes dominate over slower atom–diatom recombination reactions, we can introduce the equilibrium concentrations [SSS], [SSQ], and [SQS] and use the corresponding atom-exchange equilibrium constant  $K'_{eq}$  in the expression for  $f_P$ :

$$f_P = \frac{[\text{SSQ}] + [\text{SQS}]}{3[\text{SSS}]} = \frac{1}{3} \frac{[\text{SSQ}]}{[\text{SSS}]} \left( 1 + \frac{[\text{SQS}]}{[\text{SSQ}]} \right) = \frac{1}{3} \left( \frac{1 + K'_{eq}}{K'_{eq}} \right) \frac{[\text{Q}]}{[\text{S}]}$$

Substitution of this result into [Eq. 8](#) gives

$$\delta_{s_3} = \frac{1}{3} \left( \frac{1 + K'_{eq}}{K'_{eq}} \right) - 1 = \frac{1}{3} \left( \frac{1}{K'_{eq}} - 2 \right). \quad [12]$$

We have to set  $K'_{eq} = 1/2$  because the products in [4a](#) and [4b](#) contain symmetric triatomic molecules, with half rotational-vibrational states missing. Substitution of this statistical value into [Eq. 12](#) gives  $\delta_{s_3} = 0$ .

This result makes sense. At a qualitative level, the efficient atom-exchange processes (4a and 4b) will destroy the symmetry-driven enrichment predicted by Eq. 11, because they are likely to have more effect on relative concentrations of [SSS], [SSQ], and [SQS] than the slow atom–diatom recombination reactions (3) that produce these triatomic species. Because the vapor pressure of S<sub>3</sub> is not large (35) some elemental sulfur will be deposited as S<sub>3</sub>, with no enrichment. However, in principle, just as in the case of S<sub>2</sub> discussed above, other fast processes, such as surface deposition or aerosol formation, could compete with atom exchange and still lead to sedimentation of fractionated S<sub>3</sub> (lightly enriched due to η-effect). Computational studies of the atom exchange rates in both S<sub>2</sub> and S<sub>3</sub>, and the kinetics modeling of all these processes together, would be needed to offer more reliable, quantitative treatment.

## Production of S<sub>4</sub>

Five atom–triatomic recombination reactions (5a–5e) and three diatomic–diatomic recombination reactions (6a–6c) can form tetratomic sulfur species. Among the products only the nonsubstituted SSSS (or S<sub>4</sub>) is symmetric, with the corresponding formation rate coefficient  $k_s''$ . Other possible tetratomic species are asymmetric SSSQ and SSQS, with their corresponding recombination rate coefficient  $k''$ . As in the previous sections, we will allow some η-effect and will assume that  $k'' \gtrsim k_s''$ , neglecting all other possible mass-dependent differences of rate coefficients. The actual value of the ratio  $k''/k_s''$  is again unknown, but it is reasonable to expect that it is smaller than  $k'/k_s'$  for triatomic species, because η-effect is a quantum-mechanical effect [not seen in classical trajectory studies of recombination (36)] and, generally, quantum effects are expected to be less important in larger and heavier systems. In this case the fraction of isotope Q relative to S, in the products, is

$$f_P \approx \frac{1 \times [\text{SSSQ}] + 1 \times [\text{SSQS}]}{4 \times [\text{SSSS}]}$$

The atom–triatomic recombination reactions (5a–5e) are likely to be less important for production of S<sub>4</sub> in the ground electronic state <sup>1</sup>A<sub>1</sub>, because they either require an excited <sup>1</sup>D sulfur atom as reagent or they need an additional nonadiabatic pathway for quenching of S<sub>4</sub> from the electronically excited triplet state <sup>3</sup>B<sub>1u</sub> to the ground electronic state (34). Thus, one should focus on diatom–diatom recombination, discussed next.

As outlined in *SI Appendix*, recombination proceeds through formation of a metastable intermediate complex: S<sub>2</sub> + S<sub>2</sub>  $\xrightleftharpoons{K}$  S<sub>4</sub><sup>\*</sup>  $\xrightarrow{k_{stab}}$  S<sub>4</sub> (19, 20, 37). The final step of this process, stabilization of S<sub>4</sub><sup>\*</sup> to stable S<sub>4</sub> (by collision with inert bath gas M, described by second-order rate coefficient  $k_{stab}$ ), is expected to be slow relative to the first step, where equilibrium (described by the equilibrium constant  $K$ ) is quickly established between the reagents S<sub>2</sub> + S<sub>2</sub> and the intermediate species S<sub>4</sub><sup>\*</sup>. The overall recombination rate coefficient  $\kappa$  is given by the product,  $\kappa = K \times k_{stab}$ . The same value of  $k_{stab}$  can be used for all isotopic cases (21); significant differences can come only from the value of equilibrium constant  $K$ , which is the ratio of partition functions for intermediates and reagents. Namely, for the case of major nonsubstituted reaction (6a) we would write  $K = q_{S_4^*}/(q_{S_2} \times q_{S_2})$ , whereas for 6b we have  $K = q_{SSSQ^*}/(q_{S_2} \times q_{QS})$ , and, finally,  $K = q_{SSQS^*}/(q_{S_2} \times q_{QS})$  for 6c. We will neglect small mass-dependent differences and focus on quantum symmetry effect only, which forbids some rovibrational states in symmetric molecules. Rotational symmetry numbers are used for this, equal to 2 for symmetric S<sub>2</sub> and S<sub>4</sub><sup>\*</sup>, and equal to 1 for asymmetric SQ, SSSQ<sup>\*</sup>, and SSQS<sup>\*</sup>, so  $K \sim 1/2 / (1/2 \times 1/2)$ ,  $1/(1 \times 1/2)$ , and  $1/(1 \times 1/2)$  for reactions 6a, 6b, and 6c, respectively. We see that this gives equal values of equilibrium constant  $K$ , and equal recombination rate coefficients  $\kappa$  for the three processes (6a–6c). In the past, equal rate coefficients for the reactions 6a, 6b, and 6c have been used in the kinetics models of the Archean atmosphere (8), and did not give any mass-independent fractionation. One should be aware, however, that such a standard statistical description is strictly valid for stiff molecules only (such as O<sub>3</sub> and S<sub>3</sub>, where the

vibrational motion does not distort molecular shape), when the rotational symmetry number of a rigid rotor is appropriate. However, if the molecule is floppy, then rigorous calculations of rovibrational states on accurate potential energy surface is needed for prediction of the spectrum and meaningful computation of the partition function. Importantly, electronic structure calculations of potential energy surface for  $S_4$  showed that it is floppy ([33](#), [34](#), [38](#), [39](#)). It has a single bond in the middle, consistent with its formation process:



Near the minimum energy point ( $C_{2v}$  symmetry) the molecule has shape of a “boat,” but the bending motion of two terminal S atoms easily reaches the second conformer of equal energy (the flipped-over “boat”), separated from the first conformer by low-energy transition state:



This fast interconversion process was a focus of another recent study ([40](#)) using classical trajectory method. Now, let us imagine that  $S = S$  collides with  $S = Q$  and forms a metastable species. Clearly, two pathways are possible, depending on where the single bond is formed (reagents are in the middle):



It is important to realize that when  $S = S$  collides with  $S = S$  to form metastable species these two possibilities are still there, even though two conformers of  $S_4$  are physically indistinguishable. This tells us that the states of SSSS cover the same configuration space on the potential energy surface as the states of SSSQ and SSQS combined, which effectively doubles the number of states of nonsubstituted  $S_4$ , compared with each isotopically substituted case. Alternatively, one could consider SSSQ and SSQS together as the same species, because they interconvert easily. However, if SSSQ and SSQS are treated separately, as in [6b](#) and [6c](#), then their individual densities of states, partition functions  $q_{SSSQ^*}$  and  $q_{SSQS^*}$ , equilibrium constants  $K$ , and recombination rate coefficients  $\kappa$  should all be reduced by a factor of 2, relative to that of [6a](#).

With this important modification to the rate coefficients we obtain for fractionation of  $S_4$

$$f_P = \frac{2 \times \frac{1}{2} k'' [SS][QS]}{4 k_S'' [SS][SS]} = \frac{k'' [QS]}{4 k_S'' [SS]} = \frac{k''}{4 k_S''} \frac{1}{K_{eq}} \frac{[Q]}{[S]} = \frac{k''}{2 k_S''} \frac{[Q]}{[S]}, \quad [13]$$

$$\delta_{S_4} = \frac{1}{2} \frac{k''}{k_S''} - 1 = \frac{1}{2} \left( \frac{k''}{k_S''} - 1 \right) - \frac{1}{2}.$$

This means that at the level of  $S_4$  production the  $\eta$ -effect, due to  $k'' > k_S''$ , is not the only and in fact not the major source of enrichment. Even if we neglect  $\eta$ -effect by setting  $k'' = k_S''$ , we obtain  $\delta_{S_4} = -500\%$  due to diatom–diatom recombination.

## Production of $S_8$

Three tetratomic–tetratomic reactions ([7a–7c](#)) are possible that have SSSS, SSSQ, and SSQS among the reagents. It can be argued that because  $S_5$  has no chain isomer ([41](#)), and because  $S_5$  is not a part of the overall recombination process ([8](#), [16](#)), the atom exchange in tetratomic species does not happen. It would require formation of a pentatomic chain-like intermediate (e.g.,  $S + SSSQ \leftrightarrow SSSSQ^* \leftrightarrow SSSS + Q$ ), which does not exist. Thus, any atom-exchange processes beyond  $S_3$  can be safely ignored. Also note that because the structure of  $S_8$  is a ring ([41](#)) there is only one asymmetric species among the products,  $S_7Q$ , in addition to nonsubstituted entirely symmetric  $S_8$ . So, the fraction of isotope Q relative to S, in the products, is

$$f_P \approx \frac{1 \times [S_7Q]}{8 \times [S_8]}$$

For molecules this large the quantum  $\eta$ -effect is expected to be small, but for consistency we will still use two different rate coefficients,  $k_s'''$  for production of symmetric and  $k'''$  for production of asymmetric species, as in [7a-7c](#). With these rate coefficients we obtain

$$f_P = \frac{1 [S_7Q]}{8 [S_8]} = \frac{1 k''' [S_4] ([SSSQ] + [SSQS])}{8 k_s''' [S_4] [S_4]} = \frac{1 k''' [SSSQ] + [SSQS]}{8 k_s''' [S_4]}$$

Because there is no atom exchange, this formula cannot be expressed through the abundance in the reservoir,  $[Q]/[S]$ . However, one can write the ratio of isotopes among the reagents of reactions ([7a-7c](#)):

$$f_R \approx \frac{1 \times [SSSQ] + 1 \times [SSQS]}{4 \times [SSSS]} = \frac{1 [SSSQ] + [SSQS]}{4 [S_4]}$$

Substitution of the last two expressions straight into [Eq. 8](#) gives

$$\delta_{S_8} = \frac{1 k'''}{2 k_s'''} - 1 = \frac{1}{2} \left( \frac{k'''}{k_s'''} - 1 \right) - \frac{1}{2}. [14]$$

Here, similar to the case of  $S_4$ , symmetry seems to be not the only and not the main source of the isotope effect. Even in the case of  $k_s''' = k'''$  (i.e., neglecting  $\eta$ -effect) one obtains large negative enrichment of  $\delta_{S_8} = -500\%$ , which is again a depletion in rare isotopes.

## The Overall Enrichments

It should also be taken into account that because production of  $S_8$  is not linked directly to the reservoir of atomic S and Q through atom exchange, but rather starts from tetratomic sulfur molecules that are already expected to be heavily depleted in Q, the last step of recombination hierarchy will magnify the effect. The overall enrichment after  $S_4$  and  $S_8$  production should be computed as

$$\delta = (f_P/f_R)_{S_4} \times (f_P/f_R)_{S_8} - 1$$

leading to the overall depletion of rare isotopes on the order of  $\delta_{S_8} = -750\%$ .

This large integer number should be taken with caution. It represents a theoretical limiting case that involves (i) assigning rate coefficients in reactions [6](#) and [7](#) based on relatively simple statistical arguments, (ii) assuming that all elemental sulfur is deposited only at the end of recombination hierarchy, as  $S_8$ , and (iii) ignoring all other chemistry of atmospheric sulfur. In reality, rate coefficients may be somewhat different from those in [6](#) and [7](#), due to nonstatistical (dynamical) effects. Also, because the vapor pressure of smaller sulfur species is low ([35](#)), some sulfur is likely to be deposited as  $S_2$  and  $S_3$  (not fractionated or lightly enriched), some of it as  $S_4$  (depleted), and the rest as  $S_8$  (heavily depleted), leading to less extreme overall depletion. Finally, the accompanying chemistry ([7](#), [8](#)) and collision-induced dissociation of formed  $S_4$  and  $S_8$  are also expected to reduce the resultant fractionation. At this point very little is known about these processes, and mostly at a qualitative level, so they are not taken into account here. Inclusion of some of these effects into consideration is desirable. Photochemical origin of the enrichment is another viable mechanism that also gives promising results ([42](#)). It should be studied separately and added to the overall picture.

Nevertheless, the isotope effect due to recombination reactions is still expected to be significant and seems to be robust. Note that in the final version of theory we neglected all of the mass-dependent effects (expected to be minor), and even the  $\eta$ -effect effect (important only for triatomic species). The depletion comes, basically, from absence of atom exchange beyond S<sub>3</sub>, and from recombination stoichiometry that is now being declared to represent the major mechanism of the isotope effect. In the future, computational chemistry methods could be used to predict more accurate values of equilibrium constants  $K_{eq}$  and  $K'_{eq}$  for various isotopes and to determine the actual values of rate constant ratios  $k'/k'_s$ ,  $k''/k''_s$ , and  $k'''/k'''_s$ , their temperature and pressure dependencies (37), but this would only lead to minor adjustments compared with the framework presented here.

Based on this analysis it becomes clear that gas-phase recombination reactions of sulfur allotropes would result in deposition of heavily depleted elemental sulfur (longer chains), leaving behind the heavily enriched reservoir of sulfur in the gas phase (small molecules), which, in turn, could enter other atmospheric chemistry, photochemistry, and early biospheric processes, be oxidized to sulfate in aerosols and in the ocean, and finally deposited as enriched sediments. Note that both strongly enriched and strongly depleted samples have been identified in the Archean rock record.

## Mass-Independent Fractionation

Within the framework presented above the values of all enrichments are assumed to be negative, large, and equal to each other:  $^{33}\delta = ^{34}\delta = ^{36}\delta$ . Small deviations from this assumption are possible due to mass dependence of  $K_{eq}$  and  $K'_{eq}$ , due to  $\eta$ -effect, and due to higher natural abundance of the isotope  $^{34}\text{S}$ , but are all expected to be minor and are all ignored here (although they can be added to this theory, as more information about sulfur recombination processes becomes available from computational studies (43) and/or laboratory experiments). Mass-independent fractionations are determined by calculating, for isotopes  $^{33}\text{S}$  and  $^{36}\text{S}$ , the values of

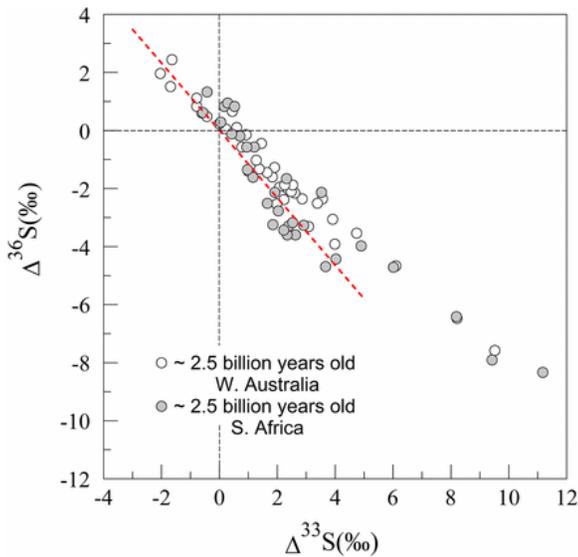
$$^x\Delta = ^{34}\delta - ((1 + ^x\delta)^{x\lambda} - 1)$$

where  $x = 33$  or  $36$ . For the purpose of clarity we do not include in this formula the conversion of  $\delta$  and  $\Delta$  values to the units of per mill (‰), but we can convert final results to this unit. The value of  $^x\lambda$  is defined as

$$^x\lambda = (1/m_{32} - 1/m_x)/(1/m_{32} - 1/m_{34})$$

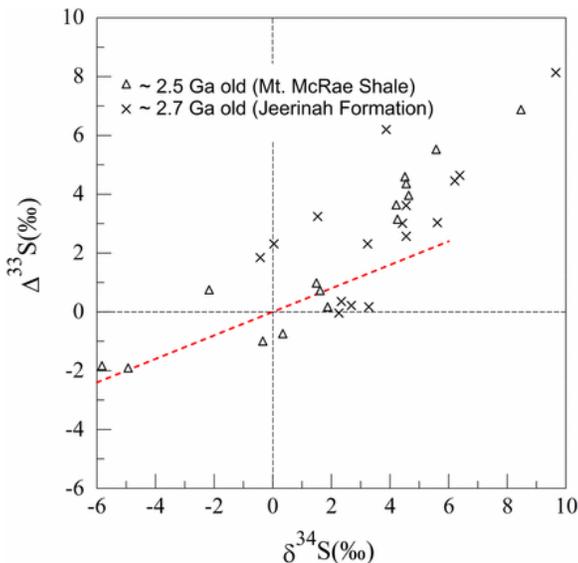
which gives  $^{33}\lambda = 0.515879$  and  $^{36}\lambda = 1.89045$ .

For better qualitative understanding it is useful to make a rough estimate of mass-independent fractionation effect as follows. One can use Taylor series expansion, up to the linear term, to convert the equation for  $\Delta$  into a more transparent one:  $^x\Delta \approx ^{34}\delta - ^x\lambda ^x\delta$ . Next, the mass-independent assumption for enrichments is made,  $^{33}\delta = ^{34}\delta = ^{36}\delta = \delta$ , which gives us simply  $^x\Delta \approx \delta(1 - ^x\lambda)$ . In this way one obtains  $^{33}\Delta \approx \delta/2$  and  $^{36}\Delta \approx -\delta$ . This means that in the elemental sulfur, deposited as a product of gas-phase recombination reactions, one should observe large negative  $^{33}\Delta$  simultaneously with large positive  $^{36}\Delta$ . The residual reservoir of atomic gas-phase sulfur, and the sulfate formed from it, would fall into the opposite quadrant of the  $^{36}\Delta$  vs.  $^{33}\Delta$  plot, where positive  $^{33}\Delta$  comes with negative  $^{36}\Delta$  (Fig. 1). This defines a mass-independent fractionation line on the  $^{36}\Delta$  vs.  $^{33}\Delta$  plot, like that shown in Fig. 1 in red.



**Fig. 1.** Mass-independent fractionation line predicted by this model in comparison with results from the Archean rock record. Data from ref. [4](#) and ref. [6](#); image reproduced from ref. [44](#) with permission from NASA.

The slope of this line should be computed using the exact equation for  $\Delta$ . For  $^{33}\delta = ^{34}\delta = ^{36}\delta = -500\text{‰}$  we obtained  $^{33}\Delta = -199.4\text{‰}$  and  $^{36}\Delta = 230.3\text{‰}$ , which gives the slope of  $-1.16$ , in very good agreement with data obtained from the Archean rock record by Farquhar and coworkers ([1994](#)), who reported the slope of  $-1.0$ , and by Ono et al. ([5, 6](#)) who reported the slope of  $-0.95$ , but also with some photolysis experiments of Farquhar et al. ([10](#)), where the slopes in the range of  $-1.1$  and  $-1.2$  were observed. From [Fig. 1](#) we can see that the actual values of fractionations observed in the rocks are on the order of  $10\text{‰}$ , much smaller than what we predict here for gas-phase recombination reactions, but this also makes sense, because a substantial “dilution” of the magnitude of fractionations is expected during the deposition process, sedimentary chemistry, and preservation of the effect in the rock record that is more than 2.3 billion y old. An essential feature is the ratio between  $^{33}\Delta$  and  $^{36}\Delta$ , which is expected to remain unchanged for stable isotopes, carrying the signature of ancient gas-phase recombination reactions through time. Another frequently used probe of sulfur isotope chemistry in the Archean atmosphere is the ratio between  $^{34}\delta$  and  $^{33}\Delta$ , as shown by the rock record data of Ono et al. ([5](#)) presented in [Fig. 2](#). Our prediction, based on sulfur recombination reactions, defines the line with slope of  $^{33}\Delta/^{34}\delta = +0.4$ , qualitatively consistent with these data too.



**Fig. 2.** Correlation between  $^{34}\delta$  and  $^{33}\Delta$  predicted by this model (the line with a slope of +0.4) compared with two sets of the Archean rock record data from Western Australia (data from ref. 5). Ga, billion years.

## Conclusions

We formulated a hierarchy of isotopically substituted recombination reactions for formation of sulfur allotropes in the anoxic conditions specific to Archean atmosphere of early Earth and demonstrated that it is possible to solve the corresponding system of kinetics equations analytically, to derive concise expressions for isotopic enrichments, focusing on mass-independent effects due to symmetry and under assumption that mass-dependent isotope effects are minor. At the level of  $S_2$  and  $S_3$  no enrichment is possible due to efficient atom exchange. At the level of  $S_4$  a very significant depletion, driven by reaction stoichiometry, is predicted, because the atom exchange processes are not expected to affect molecules larger than triatomic sulfur species. Formation of  $S_8$  magnifies the effect even further, producing heavily depleted elemental sulfur. Because mass-dependent isotope effects are expected to be minor, the enrichments are predicted to be nearly equal for  $^{33}S$ ,  $^{34}S$ , and  $^{36}S$ . Multiple isotopes fractionation (characterized by the ratio of capital  $\Delta$  values for  $^{33}S$  and  $^{36}S$ ) obtained within this framework matches well with the mass-independent fractionation line of the Archean rock record. This relatively simple model may finally offer mechanistic explanation for striking S-MIF in the Archean atmosphere. In the future, the theoretical framework developed here can be applied to other recombination reactions potentially relevant to the MIF of sulfur, such as  $SO + SO \rightarrow S_2O_2$  (42).

## Acknowledgments

I thank James Kasting (Pennsylvania State University) for stimulating discussions. This research was supported by NASA Exobiology Program Grant NNX15AL29G.

## Footnotes

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- Author contributions: D.B. designed research, performed research, analyzed data, and wrote the paper.
- The author declares no conflict of interest.
- This article is a PNAS Direct Submission.
- This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1620977114/-/DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1620977114/-/DCSupplemental).

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