

Sulfur isotope effects for the $\text{SO}_{2(\text{g})}$ - $\text{SO}_{2(\text{aq})}$ system

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Abstract Sulfur isotope fractionation ($^{34}\text{S}/^{32}\text{S}$) factors were determined for the $\text{SO}_{2(\text{g})}$ - $\text{SO}_{2(\text{aq})}$ system. The influence of temperature on the investigated sulfur isotopes separation between phases was studied as well.

Key words isotopic fractionation of SO_2 • mass spectrometer • sulfur isotope effect

Introduction

Sulfur is an important element of organic matter. Due to its high chemical reactivity, it takes part in biological and geological processes in which isotope effects occur.

Two methods are used to determine the equilibrium constants for isotope exchange reactions: theoretical calculations [1, 4, 5] and experiment. Using the well-known methods of statistical mechanics, partition function ratios for many isotopic sulfur compounds have been calculated. These partition function ratios are then used to determine equilibrium constants for many possible exchange reactions involving the isotopes of sulfur. The results indicated that considerable fractionation of the sulfur isotopes can be expected in laboratory and naturally occurring processes.

The purpose of the present paper is the experimental determination of sulfur isotope fractionation between gaseous SO_2 and SO_2 dissolved in water. An isotopic exchange reaction between any pair of compounds may be written as follows:



where AX_n and BX_m denote two different compounds with element X (X – light isotope and X' – heavy isotope). The isotope fractionation factor between two substances, AX_n and BX_m is defined as:

$$(2) \quad \alpha = \frac{R_{\text{AX}_n}}{R_{\text{BX}_m}}$$

where R for sulfur isotopes is defined as:

$$(3) \quad R_{\text{AX}_n} = \left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{AX}_n}, \quad R_{\text{BX}_m} = \left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{BX}_m}$$

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As absolute isotope ratios are difficult to obtain, ratios are generally measured against a standard and presented as deviations δ (enrichment of ^{34}S in relation to ^{32}S in per mil):

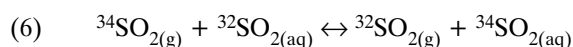
$$(4) \quad \delta^{34}\text{S}[\text{‰}] = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \cdot 1000$$

Meteoritic sulfur (troilite (FeS) from the Canyon Diablo meteorite, Arizona, USA) is used as international standard because of its rather constant $\delta^{34}\text{S}$ compared with terrestrial samples. Enrichment of ^{34}S between solution (L) and gas (G) phase is given by [2]:

$$(5) \quad \Delta^{34}\text{S}_{\text{L-G}}[\text{‰}] = \left[\frac{\delta_{\text{L}} + 1000}{\delta_{\text{G}} + 1000} - 1 \right] \cdot 1000 = \alpha - 1$$

Experimental procedure

Reaction vessels of 340 cm^3 volumes were filled with 30 cm^3 of water and then with SO_2 from a cylinder until the pressure of the gas above water reached one atmosphere. The sulfur fractionation factor was determined for the reaction:



The equilibration was conducted in the close system for about 20 h at constant temperature. The experiment was carried out between 18 to 70°C , the reaction vessel was thermostated with an accuracy of $\pm 0.5^\circ\text{C}$. The mixture in the reaction vessel was mixed during the equilibration. After isotopic exchange, the gas phase and the solution were separated and oxidized by 3% H_2O_2 . Sulfates from each phase were precipitated as BaSO_4 by using BaCl_2 .

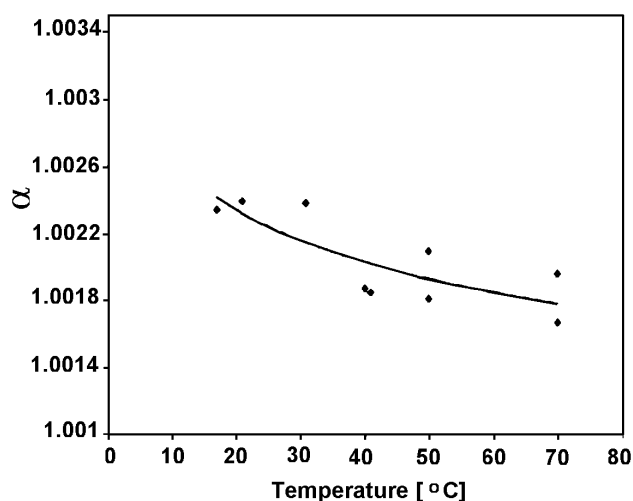


Fig. 1. $^{34}\text{S}/^{32}\text{S}$ isotope fractionation factor (α) between SO_2 gas and SO_2 dissolved in water ($p = 1 \text{ atm}$).

The BaSO_4 precipitates were washed with distilled water, dried and subsequently transformed in to SO_2 in a vacuum line for sulfur isotopic analysis by mass spectrometry (the precision of α determinations was 0.24‰). The mixture of BaSO_4 and NaPO_3 in Cu boats was heated to $650\text{--}700^\circ\text{C}$ and the pure SO_2 produced was collected in a "cold finger". The reaction was complete within 7–10 min. The oxygen isotopic composition of the SO_2 was totally controlled by ^{18}O content in NaPO_3 , when the weight ratio of the reagent to sample exceeded 6:1 [3].

Results and discussion

The experimental results presented in Fig. 1 show that the isotopically heavier molecule is enriched in the solution compared with the gas phase (normal isotope effect).

When the liquid phase was mixed, the solubility of SO_2 was higher compared with the non-mixed system and the isotope separation factor was found to be lower (1.00256 at 18°C vs. 1.003 ± 0.00024). With increasing temperature both the solubility of SO_2 and the fractionation factor α decrease. The enrichment of the heavier isotopic species ($^{34}\text{SO}_2$) in the aqueous phase may be mainly due to its lower hindered translational frequency as compared with that of $^{32}\text{SO}_2$. However, a quantitative interpretation of the isotope fractionation and its temperature dependence would require information on the shifts of the internal vibrational frequencies of SO_2 molecule when it is transferred from gaseous into the aqueous phase.

Conclusion

The sulfur isotope fractionation factors ($^{34}\text{S}/^{32}\text{S}$) were determined experimentally for the system $\text{SO}_{2(\text{g})}$ - $\text{SO}_{2(\text{aq})}$. With increasing temperature both the solubility of sulfur dioxide and the fractionation factor decrease, at 18°C $\alpha = 1.00256$, and at 70°C $\alpha = 1.00174 \pm 0.00024$.

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