Sources of atmospheric sulfur compounds

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Abstract—Sulfate samples from rain and snow water, collected in Japan and in U.S.A. have been studied isotopically in an attempt to determine the sources of atmospheric sulfur. $\delta^{34}\text{S}$ values of the samples are 5 to 18 ‰ lighter than that of sea water sulfate. Based on these isotopic data, it is suggested that the most important sources of atmospheric sulfate are hydrogen sulfide derived from bacterial reduction of sulfate and SO_2 from industrial activities. Sea spray sulfate is a minor contributor.

In industrial sites, the sulfur in precipitation indicates depletion in ^{34}S , viz. +3.2 to +7.3 ‰ in contrast to $\delta^{34}\text{S}$ values in non-industrial sites, that vary from +12.3 to +19.0 ‰. It is suggested that the lighter isotopic composition of atmospheric sulfur may be explained by the contribution of light sulfur from sulfur bearing fuels through industrial burning.

INTRODUCTION

Sulfur is always found as a trace component in the atmosphere where it occurs in particles as SO_4^{2-} and in gases as SO_2 and H_2S . It is also an important constituent of condensation nuclei. The presence of SO_2 in polluted or industrial atmospheres is well known, whereas its quantitative data for non-polluted areas are inadequate. Researches on the origins of atmospheric sulfur have been reported by ERIKSSON (1960, 1963), ÖSTLUND (1959), JUNGE and WERBY (1958), JUNGE (1960), and JENSEN and NAKAI (1961).

The study of sulfate to chloride ratios in air and rain water samples collected in Japan by SUGAWARA *et al.* (1949) indicates that rain water near sea coasts has higher sulfate to chloride ratios than does sea water, and lower ratios than does air. From these results, they concluded that sea spray sulfate produces two different types of salt particles in the atmosphere; viz. one is of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and the other of NaCl and MgCl_2 , and the hygroscopic salt particles of the latter type form nuclei in oceanic and coastal rains and are returned rapidly to the sea, whereas the non-hygroscopic sulfate particles form comparatively stable aerosol to survive in the atmosphere and to be brought inland. On the other hand, JUNGE and WERBY (1958) indicated from studies of the ratios of sulfate to chloride in rain water from U.S.A. that over oceans sulfate of non-marine origin is a small fraction

of the total sulfate present because sea water is logically the most important source, but over land sulfate of marine origin apparently decreases to negligible amount.

JUNGE and WERBY (1958) suggested the existence of sulfate sources other than sea water. JUNGE (1960) suggested that industrial SO_2 is sufficient to account for the total amount of atmospheric sulfate over large continents.

Hydrogen sulfide is produced through bacterial reduction of sulfate and decomposition of organic materials by bacteria that are ubiquitous in ground and near shore sediments, and is oxidized to sulfate in the atmosphere. In this paper, following sources of the sulfate in the atmosphere are considered: 1) Industrial sulfur, 2) Bacteriogenic sulfur, 3) Sea spray sulfate, and 4) Volcanic sulfur. In order to determine the validity of those four suggested sources of atmospheric sulfur, we have attempted to apply sulfur isotopic studies to the problem of the sources of sulfate in precipitation.

THE ISOTOPIC DISTRIBUTION OF ATMOSPHERIC SULFUR

Initially, SO_4^{2-} samples of rain waters collected in Japan were selected because they should contain both industrial sulfur and oceanic SO_4^{2-} (Fig. 1). The analyses of such samples might provide a small scale example of how this type of study could be applied to a continent. In addition to the analyses of Japanese samples, rain water SO_4^{2-} and snow SO_4^{2-} samples in North America were analyzed isotopically.

The isotopic results of SO_4^{2-} in rain water obtained are listed in Tables 1 and

Fig. 1. The location map of rain and snow samples examined.

2, and are plotted in Fig. 2 in comparison with similar measurements of sea water SO_4^{2-} .*

Table 1. Isotopic composition of sulfate in rain water and sea water from Japan supplied by E. KAMATA

Sample location	Sample	Sulfate content (mg S/l)	Isotopic composition $\delta^{34}\text{S}$ (‰)
Tokyo (A)*	Rain	3.0	+7.3
Tokyo (B)*	Rain	2.9	+7.3
Tokyo (C)*	Rain	—	+5.0
Nagoya (B)*	Rain	0.77	+5.9
Nagoya (C)*	Rain	—	+3.2
Wakayama**	Rain	1.2	+7.3
Nara**	Rain	0.43	+6.3
Kurume (A)	Rain	1.0	+15.6
Kurume (B)	Rain	0.70	+12.8
Kurume (C)	Rain	—	+15.6
Tottori (A)	Snow	0.90	+13.2
Tottori (B)	Rain	0.77	+15.1
Matsumoto	Rain	—	+12.3
East China Sea	Sea water	—	+20.7
Wakayama	Sea water	—	+20.7

* Industrial sites.

** Near industrial sites.

Table 2. Isotopic composition of sulfur in snow, rain and sea waters sampled in U.S.A.

Sample location	Sample	Sulfate content (mg S/l)	Isotopic composition $\delta^{34}\text{S}$ (‰)
New Haven, Conn.	Snow	1.2	+5.9
		1.2	+6.2
Pittsfield, Mass.	Rain	0.23	+19.0
		0.26	+18.9
Branford Bay No. 1, Conn.	Sea water (4.5 m depth)	666	+20.3
Branford Bay No. 2, Conn.	Sea water (5.5 m depth)	640	+20.5
Long Island Sound, Conn.	Sea water (7.0 m depth)	725	+20.5
Gulf of Mexico	Sea water (surface)	881	+20.6
Gulf of Mexico	Sea water (3,500 m depth)	785	+20.4

* The mass analyses of samples are compared with troilite from Cañon Diablo meteorite as a standard with a $^{34}\text{S}/^{32}\text{S}$ ratio of 0.0450045 as follows:

$$\delta^{34}\text{S} (\text{‰}) = \left[\frac{^{34}\text{S}/^{32}\text{S} (\text{sample})}{^{34}\text{S}/^{32}\text{S} (\text{std.})} - 1 \right] \times 1,000$$

Fig. 2. Sulfur isotopes of sulfate in precipitation and sea water, and of sulfur in industrial coal.

Based on the sulfur isotopic compositional data of Japanese samples, two types of rain water are apparent, one includes $\delta^{34}\text{S}$ values ranging from +3.2 to +7.3‰, the other between +12.3 and +15.6‰. The former includes samples from or near industrial sites and the latter samples collected in non-industrial sites. Apparently ^{34}S is depleted in the samples from industrial sites. The sulfur isotopic composition of sea water SO_4^{2-} , however, is remarkably constant at +20.7‰, which is more enriched in ^{34}S than either type of rain waters. The data of SO_4^{2-} for the rain and snow samples in North America not only correlate with the industrial type and non-industrial type of isotopic analyses in Japanese samples, but those of sea water samples also further demonstrate the constancy in $\delta^{34}\text{S}$ values of sea water sulfate.

DISCUSSION OF RESULTS

Natural sources of atmospheric sulfur

All of the $\delta^{34}\text{S}$ results indicate that rain and snow SO_4^{2-} is depleted in ^{34}S in comparison with the $\delta^{34}\text{S}$ value of sea water SO_4^{2-} . Even if some of the rain water SO_4^{2-} is originally marine, the results require additional sources of SO_4^{2-} that are

depleted in ^{34}S . Various sources have already been suggested. Some SO_4^{2-} is formed in the atmosphere presumably by the oxidation of SO_2 and H_2S . This is based upon JUNGE's (1960) analyses which show that the total amount of SO_2 and H_2S in the atmosphere is always about 1 to 2 orders of magnitude higher than the excess SO_4^{2-} (SO_4^{2-} of non-maritime origin) in aerosols. JUNGE's measurements indicate that the variations in the $\text{SO}_2/\text{H}_2\text{S}$ ratio with time are due to changes in SO_2 concentration, whereas the H_2S concentration is rather onstant. Furthermore, H_2S and SO_2 concentrations determined by JACOBS *et al.* (1958) indicate that, even in New York City, where air is polluted primarily by industrial activities, the H_2S content of air is low and rather constant through the year.

It does seem apparent, therefore, that the H_2S is of natural bacterial origin, and SO_2 is derived from human activities or produced by oxidation of H_2S . The SO_2 can be oxidized to SO_3 by photochemical oxidation and catalitic oxidation, and SO_3 is readily transferred to H_2SO_4 that dissolves in rain water.

Even though coastal samples may still contain SO_4^{2-} derived from sea spray, enrichment of ^{32}S in them does suggest that H_2S formed by bacterial reduction of sulfate in tidal flats and coastal belts may be an important source of sulfur in the atmosphere (NAKAI and JENSEN, 1964). Data on the isotopic compositions of sulfide produced presumably by the biochemical reduction of sulfate in bottom sediments, are listed in Table 3 for both marine and fresh water samples. Such sulfides exhibit $\delta^{34}\text{S}$ values lighter than the co-existing sulfate; the $\delta^{34}\text{S}$ values of sulfides range approximately from -10 to -20 ‰ for marine samples and from -3.5 to $+1.6$ ‰

Table 3. Sulfur isotopes of sulfate in sea and lake waters, and of sulfide in sediments

Sample location	Depth (m)	SO_4^{2-} in water* content (mg S/l)	$\delta^{34}\text{S}$ (‰)	Acid soluble sulfide in sediments $\delta^{34}\text{S}$ (‰)
Sea				
Long Island Sound, Conn., U.S.A.	7.0	725	+20.5	-12.2
Branford Bay, Conn., U.S.A.	4.5	666	+20.3	-21.8
	3.5	640	+20.5	-20.8
Lake				
Linsley Pond, Conn., U.S.A.	13.0	—	+9.5	+1.6
Queechy Lake, Conn., U.S.A.	12.0	4.6	+5.8	+0.4
Mt. Tom Pond, Conn., U.S.A.	13.5	5.1	+6.1	-3.0

* Sampled from deep water layers.

for fresh water samples, and the isotopic fractionation factors between sulfate and co-existing sulfide $\left(\frac{{}^{34}\text{S}/{}^{32}\text{S}(\text{SO}_4^{2-})}{{}^{34}\text{S}/{}^{32}\text{S}(\text{H}_2\text{S})} \right)$ are 1.033 to 1.043 and 1.005 to 1.011, respectively.

Based on laboratory fermentation experiments using pure culture cells, THODE *et al.* (1951) and JONES and STARKEY (1957) have obtained the isotopic fractionation factors between sulfate and produced sulfide varying from 1.003 to 1.018. NAKAI and JENSEN (1960) have obtained values varying from 1.005 to 1.017, using raw culture techniques. Recently, however, NAKAI and JENSEN (1964) revealed that the bacterial reduction of SO_4^{2-} to H_2S , in unidirectional reactions with a limited SO_4^{2-} supply in a closed system, brings forth fractionation factors that can be calculated by the following equation:

$$r = \frac{R_{\text{SO}_4^{2-}}}{R_{\text{S}^{2-}}} = \frac{1 - F}{F^{1 - (K_2/K_1)} - F}$$

F = fraction of the initial SO_4^{2-} remaining; F is 1 at the start of the reaction and approaches 0 as reaction progresses.

$R_{\text{S}^{2-}}$ and $R_{\text{SO}_4^{2-}}$ = ${}^{34}\text{S}/{}^{32}\text{S}$ ratio of produced S^{2-} and residual SO_4^{2-} at F , respectively.

K_1 and K_2 = the rate constants in the reduction for light and heavy isotopes, respectively.

We found that the K_1/K_2 ratio in the above equation averages 1.020, indicating that ${}^{32}\text{S}$ is reduced to H_2S two percent faster than ${}^{34}\text{S}$. F values should be less than unity. Consequently, the next relation can be introduced, *i.e.*,

$$F^{1 - (K_2/K_1)} - F < 1 - F.$$

Therefore, for $R_{\text{S}^{2-}}$ and $R_{\text{SO}_4^{2-}}$:

$$r = \frac{R_{\text{SO}_4^{2-}}}{R_{\text{S}^{2-}}} > 1.$$

This indicates that the isotopic composition of H_2S produced is always enriched in ${}^{32}\text{S}$ in comparison with the original SO_4^{2-} .

In the case of an unlimited supply of SO_4^{2-} in an open system the following relation is derived by using the K_1/K_2 value of 1.020.

$$r = \frac{R_{\text{SO}_4^{2-}}}{R_{\text{S}^{2-}}} = 1.020.$$

So, if H_2S is produced in an open system and released to atmosphere, its isotopic composition should be 20 ‰ lighter than that of original SO_4^{2-} .

The most important source of SO_4^{2-} , from which H_2S is produced by bacterial reduction, is presumably pore water of near shore sediments, but the amount of H_2S being produced from swamps, sewage disposal areas and sluggish streams is still

Table 4. Sulfur isotopes of volcanic gases
(determined by OANA and SAKAI)

Fumarole	Temp. (°C)	(1/m ³)	H ₂ S $\delta^{34}\text{S}(\text{‰})$	(1/m ³)	SO ₂ $\delta^{34}\text{S}(\text{‰})$	Total S* $\delta^{34}\text{S}(\text{‰})$
Showashinzan						
A-1	722	0.008	—	0.14	+4.4	+4.4
A-6	695	0.009	—	0.10	+5.5	+5.5
B-1b	260	0.10	+5.5	0.003	+13.9	+5.7
B-5	446	0.11	+4.4	0.004	+9.3	+4.6
B-6	347	0.12	+4.3	0.004	+9.2	+4.5
C-2	605	0.079	+5.1	0.047	+7.1	+6.0
C-3	187	0.17	+1.7	0.002	+10.0	+1.8
Nasu						
M-1	489	3.2	-0.7	3.4	+4.4	+1.9
M-2	195	5.9	-0.9	0.36	+6.1	-0.5
M-2b	352	3.5	-1.2	0.88	+10.1	+1.1

* Weighted mean of SO₂ and H₂S.

unknown. Furthermore, lakes can also be a source of H₂S. ERIKSSON (1963) has stressed that an appreciable amount of sulfur is supplied as H₂S from oceans into the atmosphere. ÖSTLUND and ALEXANDER (1963), however, reported that a layer of only a few feet of oxygenated sea water may prevent the escape of H₂S generated in the underlying mud.

Even though volcanism is a minor source for rain water SO₄²⁻ as estimated by KOYAMA *et al.* (1965), volcanic gases do add sulfur compounds to the atmosphere. Sulfur compounds in volcanic gases are predominantly SO₂ and H₂S, and the ratios of them vary with fumarolic temperatures. SAKAI and NAGASAWA (1958) have studied quantitatively and isotopically the sulfur compounds in volcanic gases. Recently, OANA and SAKAI studied the sulfur compounds from Volcano Showashinzan and Nasu in detail. Some of their results are presented in Table 4. The SO₂/H₂S ratios and the fractionation factors between SO₂ and H₂S differ with varying fumarolic temperatures. The isotopic compositions of total sulfur, weighted mean $\delta^{34}\text{S}$ of SO₂ and H₂S, however, are comparatively constant for all fumaroles, *viz.* from -0.5 to +6.9 ‰. The $\delta^{34}\text{S}$ values of volcanic gases, therefore, are enriched in ³²S in comparison with sea water sulfate.

All of the natural sources of rain water SO₄²⁻ examined above have $\delta^{34}\text{S}$ values lighter than sea water sulfate.

Anthropogenic sources of atmospheric sulfur

According to JUNGE and WERBY (1958), the amount of sulfur emitted into the air by human activities was 1.2×10^8 tons for the whole earth in 1956. This presents only one-third of the total amount of excess SO₄²⁻ brought down by precipitation.

Table 5. Isotopic composition of sulfur in industrial coals in Japan

Coal Mine	Total sulfur content* (%)	Isotopic composition $\delta^{34}\text{S}$ (‰)
Kyushu No. 1	1.54	+23.5
Kyushu No. 1'	1.44	+23.9
Kyushu No. 2	3.05	+11.9
Kyushu No. 2'	3.14	+11.9
Kyushu No. 3	1.49	+22.1
Hokkaido No. 1	0.33	+18.3
Hokkaido No. 2	0.35	+15.1

* Determined by Parr Bomb method.

Koyama *et al.* (1965) estimated that in Japan the amounts of SO_4^{2-} from sources except sea spray, fuel and volcanoes are 6.5×10^6 tons, and correspond to 75 % of the total fallout of SO_4^{2-} , 8.7×10^6 tons, and sulfur emitted by fuel is only 1.8×10^6 tons as SO_4^{2-} in 1959. Our isotopic results, however, indicate that rain water SO_4^{2-} collected from industrial sites are significantly more enriched in ^{34}S than are samples from non-industrial sites. Therefore, it is inferred that these samples from industrial sites contain SO_4^{2-} derived predominantly from atmospheric oxidation of isotopically light SO_2 emitted by industrial activities.

If the $\delta^{34}\text{S}$ composition of industrial fuels could be determined, the amount of industrial sulfur in the precipitation samples would possibly be estimated. For this purpose, five coal samples were obtained from two of the most productive Japanese

Fig. 3. Apparatus for coal burning experiment.

Table 6. Results of burning experiments of coal in the laboratory

Sample No. of coal		Kyushu No. 1	Kyushu No. 2	Kyushu No. 3
Sulfur in coal used				
Total S				
Content	(%)	1.54	3.05	1.49
$\delta^{34}\text{S}$	(‰)	+23.5	+11.9	+22.1
Soluble $\text{SO}_4^{=}$				
Content	(%)	0.001	0.031	0.001
$\delta^{34}\text{S}$	(‰)	—	—	—
Sulfur resulted by burning experiment				
Ash	(%)	16.7	18.1	6.7
Evolved SO_2				
% of S to original coal		0.57	1.87	0.90
$\delta^{34}\text{S}$	(‰)	+16.9	+6.6	+18.2
Soluble $\text{SO}_4^{=}$ in ash				
% of S to original coal		0.38	0.48	0.39
$\delta^{34}\text{S}$	(‰)	+24.8	+12.8	+25.1
Sulfur uncollected*				
% of S to original coal		0.59	0.70	0.20
$\delta^{34}\text{S}$	(‰)	+29.0	+25.3	+34.4

* Calculated values.

coal mines. The isotopic composition of the total sulfur in the samples are presented in Table 5 and Fig. 2. Unfortunately, the relatively broad spread in their isotopic compositions, from +11.9 to +23.5 ‰ in $\delta^{34}\text{S}$ values, presents a difficulty in explaining the enrichment of ^{32}S in atmospheric $\text{SO}_4^{=}$ samples collected near industrial sites, all of which have $\delta^{34}\text{S}$ compositions lighter than +7.3 ‰.

Isotopic fractionation, however, might be expected in the process of coal burning. In order to test such, laboratory burning experiments were performed on Kyushu coal samples Nos. 1, 2 and 3. The apparatus used is shown in Fig. 3. Coal samples of 2 to 3 g were placed in a combustion tube. A constant stream of air, which was purified by bubbling through 1N NaOH solution, was passed through the system with the coal samples heated. The resulting SO_2 was oxidized to $\text{SO}_4^{=}$ by iodine solution, precipitated as BaSO_4 , converted to silver sulfide, burned to SO_2 , and analyzed isotopically. The sulfate remained in the ash was leached with distilled water, precipitated as BaSO_4 , and analyzed isotopically. These experimental results are shown in Table 6 and Fig. 4.

The analytical and isotopic results indicate that the water soluble $\text{SO}_4^{=}$ in the ash is produced during the burning process of coal, because the amount of soluble $\text{SO}_4^{=}$ remaining in ash is always 1 to 2 orders of magnitude higher than in the original coal. Quantitative and isotopic analyses indicate that 37 to 61 % of the original sulfur contained in the coal samples produced SO_2 gas and 16 to 26 %

Fig. 4. Sulfur isotopic fractionation in coal-burning experiments.

remained in the ash as sulfate, and that the SO₂ gas produced was always enriched in ³²S, while the soluble sulfate in the ash was enriched in ³⁴S in reference to the total sulfur of the original coal samples. The sulfur in the amount of 10 to 40 % of original sulfur could not be collected during the burning experiment, and is supposed to have been converted to SO₃ and fixed in the experimental system. The δ³⁴S values expected for this sulfur can be calculated to be +25 to +35 ‰ as shown in Table 6. It is evident that the lighter isotope goes predominantly to SO₂. The difference in δ³⁴S between the SO₂ produced and the total sulfur contained in the coal samples is still not large enough to explain the comparatively light isotopic composition of atmospheric sulfur from industrial sites.

It is expected, however, that during the process of coal burning and transportation of fume to the atmosphere through the exhaust path of stacks longer than that of the laboratory burning apparatus, the SO₂ reacts with oxygen in air to produce more SO₃ than in the burning experiment. The isotopic fractionation factors between SO₂ and SO₃ ($[^{34}\text{SO}_3/^{32}\text{SO}_3]/[^{34}\text{SO}_2/^{32}\text{SO}_2]$) increase with lowering temperature as shown in Table 7.

KOYAMA *et al.* (1965) estimated the coal and oil consumption in 1959 to be 5.5×10^7 and 2.3×10^7 tons respectively in Japan, and then from the following data calculated the δ³⁴S values of total fuels to be +9.4 ‰; average sulfur contents =

Table 7. Equilibrium constants for exchange reaction between SO_3 and SO_2 (SAKAI, 1957)

Temperature ($^{\circ}\text{C}$)	25	50	100	500	1,000
$\left(\frac{{}^{34}\text{SO}_3}{{}^{32}\text{SO}_3}\right) / \left(\frac{{}^{34}\text{SO}_2}{{}^{32}\text{SO}_2}\right)$	1.020	1.016	1.015	1.003	1.003

0.35 and 1.76 %, $\delta^{34}\text{S}$ values = +19.6 and +4.6 ‰ for coal and oil, respectively. If the $\delta^{34}\text{S}$ value of +9.4 ‰ is accepted as that of the total fuel, and sulfur isotopic fractionation in the burning process of oil is assumed to be similar to that of coal, the difference in $\delta^{34}\text{S}$ between the SO_2 produced in the burning experiments and the original sulfur can enough explain the light isotopic composition of atmospheric sulfur from industrial sites.

Further investigations are necessary to be able to explain fully the sources of atmospheric sulfur. But we suggest that an application of sulfur isotope chemistry to studies on the origin of atmospheric sulfur is a prime method by which further knowledge may be obtained.

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