Sulfur isotope ratios and the origins of the aerosols and cloud droplets in California stratus

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ABSTRACT

Marine aerosols often have sulfur-to-chloride ratios greater than that found in seawater. Sulfur isotope ratios ($^{34}S/^{32}S$) were measured in aerosol and cloud droplet samples collected in the San Francisco Bay Area in an attempt to understand the processes that produce the observed sulfur-to-chloride ratios. Seawater sulfur usually has very high sulfur isotope ratios; fossil fuel sulfur tends to have smaller isotope ratios and sulfur of bacteriogenic origin still smaller. Samples collected in unpolluted marine air over the hills south of San Francisco had sulfur isotope ratios that were significantly lower than the values for samples collected in nearby areas that were subject to urban pollution. The highest sulfur isotope ratios were found in the offshore seawater. The results suggest bacteriogenic origins of the marine air sulfur aerosol material. The low isotope ratios in the marine air cannot be explained as a mixture of seawater sulfur and pollutant sulfur, because both tend to have higher isotope ratios.

Introduction

From past studies where sulfur compounds and chlorides were measured in the aerosols and droplets associated with California coastal stratus (Ludwig & Robinson, 1970, 1971), it has been evident that more sulfur compound material is present in the aerosols and droplets than can be accounted for by sea spray origin unless the two materials were not released in amounts proportional to their seawater concentrations. The surplus of sulfur was found in spite of the fact that samples were taken in air that was clearly of marine origin. Other studies have also found excess sulfur in marine aerosols. For example, Holzworth (1959) also found sulfate-to-chloride ratios greater than seawater values in California coastal aerosols. Lodge et al. (1960) found excess sulfur at weather station "November", about midway between the Hawaiian Islands and the California coast, and Lazrus et al. (1970) found a surplus in Puerto Rican oceanic clouds.

The observed sulfur-to-chloride ratios can be interpreted as an excess of sulfur compound materials, a deficit of chloride, or some combination of the two, but there is considerable reason to believe that sulfur compounds of non-sea-salt origin are important in determining the observed sulfur-to-chloride ratios. The worldwide sulfur cycle (Robinson & Robbins, 1970; Kellogg et al., 1972) suggests that sources of oceanic sulfur other than sea spray are required to balance the complete cycle. The mechanism that is usually proposed entails the release of hydrogen sulfide, followed by oxidation steps leading to sulfate aerosol. Lovelock et al. (1972) have suggested a different mechanism where dimethyl sulfide plays the same role as hydrogen sulfide in the more conventional explanations. Regardless of the exact materials and the processes affecting them, the evidence accumulated in the development of a worldwide sulfur cycle strongly suggests that sulfur is added to the marine aerosol from sources other than sea spray.

A deficit of chloride in the aerosols would indicate the selective loss of the chlorides, probably as a gas, and probably as hydrogen chloride or chlorine. Gaseous chlorine compounds are present in the atmosphere, but according to Valach (1967), most do not originate from sea salt. Duce (1969), has argued that sea salt may be a major contributor to the atmospheric gaseous chlorine compounds. He points out that conversion of only 10 percent of the sea

salt chlorine would produce about 70 times the estimated volcanic emissions that Valach suggested as a major source of atmospheric chlorine compounds. Although there may be chloride losses from sea salt, the evidence remains that sulfur from non-sea-salt sources substantially contributes to the observed sulfur-to-chloride ratios. The question of the origins of the non-sea-salt sulfur naturally arises; this is the question addressed in this paper.

It has been suggested that sulfur sources might be identified by the ratio of the stable isotopes ^{34}S and ^{32}S (Dequasie & Grey, 1970; Manowitz et al., 1970; Grey & Jensen, 1972). Seawater ratios of $^{34}S/^{32}S$ are greater than those associated with most petroleum and natural gases. The fossil fuel sources, in turn, generally have greater $^{34}S/^{32}S$ ratios than the sulfur compounds generated by anaerobic bacteria, such as those that might be found on the ocean bottom or tidelands (Jensen, 1962). The possibilities for ambiguity are clear, but if the principal sources of sulfur in marine air are either sea spray or biogenic, then it should be possible to differentiate between the two on the basis of sulfur isotope ratios.

Sampling and Analytical Methods

A cyclone separator was used to remove particles larger than about 3 μm radius from the sampled air stream. This system can collect the large samples required for isotope ratio analyses. In the cyclone separator, air enters a cylindrical collector tangentially and leaves the device through a tube at its center. As the air whirls through the cylinder, the larger droplets are forced to the walls and are deposited there by centrifugal forces.

The design of the instrument used for this program is based on the proportions given by Perry (1963). The separator is made of aluminium, and it is 10 inches (25.4 cm) in diameter and about 35 inches (114 cm) tall. With these dimensions, its collection efficiency for 3 μm radius droplets is about 50 percent when the flow rate is 5.7 m^3 min^{-1} (200 ft^3 min^{-1}).

A filter was placed in the outlet line from the cyclone separator. Of the air leaving the cyclone, about 1.7 m^3 min^{-1} passed through the 8- to 10-inch, prewashed glass fiber filter. According to the manufacturer (Gelman Instrument Company, Ann Arbor, Michigan), these filters have collection efficiencies greater than 98 percent for particles as small as 0.05 μm. Even with the large sampling rates that were used, it was necessary to sample for total periods of several hours, usually spread over different days, to obtain samples large enough for isotope ratio analysis. The larger cyclone samples were sometimes extracted more frequently than the filter samples.

Since fog is not uniformly dense, there were periods when little fog was passing through the cyclone. During such times, some of the previously collected fog water might have evaporated, leaving nucleus material deposited on the walls. A refluxing procedure was used to extract this material. The inlet to the instrument was plugged, and the top of the cyclone, through which the outgoing air passes, was replaced with a conical, ice-cooled refluxing head. Condensation inside the cone runs down the inside walls of the instrument. The water for this refluxing was contained in a collector flask at the bottom of the instrument. If sufficient fog water collected in the flask, it was boiled and used for refluxing. Usually, it was necessary to add about 100 to 200 ml of specially distilled, deionized water. The refluxing generally continue for an hour or two. A refluxing procedure was also used to extract the filter samples.

The isotope ratio analyses were performed at the University of Utah, where a modification of the standard procedure for concentrating sulfur samples for isotope ratio analysis (Dequasie & Grey, 1970) was developed and tested in order to accomodate the small fog samples.

Although the total amounts of sulfur were small, concentrations were high enough in the sample extracts to make the usual ion exchange concentration process unnecessary. Experiments were conducted to determine if reducing the sulfates directly from solution, with the accompanying dilution of the reducing acids by the aqueous solution, would result in non-quantitative yields. The experiments showed that quantitative results were possible, when the samples were reduced directly from solution. Seawater samples were analyzed by precipitation of barium sulfate, followed by reduction.

The rest of the processing of all samples (aerosol, droplet or seawater) is quite similar to that described by Dequasie & Grey (1970).

Table 1. *Sulfur isotope ratios*

Collection dates	Site: Sample type	$\delta\,^{34}S$ (per mille)
13, 18, 19 August 1970	Skyline: stratus droplets	−10.1
27 August 1970	Skyline: stratus droplets	− 7.0
27 August and 2, 3, 19 September 1970	Skyline: stratus particles	− 5.1
19 September 1970	Skyline: stratus droplets	− 4.0
12 August 1970	Skyline: aerosol	− 3.7
2, 3 September 1970	Skyline: stratus droplets	− 3.3
4, 7, 9 June 1971	Skyline: stratus particles	− 3.0
13, 18, 19 August 1970	Skyline: stratus particles	− 2.9
14 August 1970	Skyline: aerosol	− 1.3
18 July 1973	Grizzly Peak: stratus particles	− 1.3
30 November and 1, 27 December 1972	Brannan Island: fog particles	0.3
6 April 1973	Grizzly Peak: stratus droplets	0.3
18 July 1973	Grizzly Peak: stratus droplets	0.4
6 April 1973	Grizzly Peak: stratus particles	0.6
21 August 1970	Seashore: aerosol	3.1
18, 19, 20 January 1971	SRI: fog droplets	3.5
11, 13, 25 May and 2, 3 June 1971	Skyline: stratus droplets	4.4
11, 25, 26 June 1971	Skyline: stratus droplets	4.5
11, 13, 25 May and 2, 3 June 1971	Skyline: stratus particles	5.5
22 October 1971	SRI: aerosol	5.8
12 June 1973	Grizzly Peak: stratus particles	5.8
21 October 1971	SRI: aerosol	6.7
11, 25, 26 June 1971	Skyline: stratus particles	8.3
30 November and 1, 27 December 1972	Brannan Island: fog droplets	8.5
12 June 1973	Grizzly Peak: stratus droplets	9.2
23 October 1971	SRI: aerosol	9.3
18, 19, 20 January 1971	SRI: fog particles	9.4
10 October 1970	37.25° N, 123.05° W: Surface seawater	9.7
19 September 1973	Grizzly Peak: stratus particles	10.0 ± 3
27 April and 2, 22, 31 May 1973	Grizzly Peak: stratus droplets	10.0
13 September 1973	Grizzly Peak: stratus droplets	11.9
24 February 1971	36.8° N, 121.88° W: 300-m seawater	12.5
10 October 1970	37.40° N, 122.55° W: Surface seawater	13.3
10 October 1970	37.32° N, 123.00° W: Surface seawater	13.7
24 February 1971	36.80° N, 121.88° W: Surface seawater	17.0

The reduced sample in the form of hydrogen sulfide is bubbled through a cadmium acetate solution. The resulting cadmium sulfide is converted to silver sulfide by the addition of ammonium hydroxide and the silver nitrate. The precipitated silver sulfide is removed by filtration, dried, and converted to sulfur dioxide by roasting with an excess of copper oxide in a 1 000°C Mullite combustion tube under vacuum. The copper oxide provides an oxygen source of consistent isotope ratio for the standards and samples.

The sulfur dioxide produced by the preprocessing was introduced into the C.E.C. 21-401 dual-collector mass spectrometer through a new inlet system specially designed to accommodate small samples. The entire assembly was kept small to minimize the volume of connecting tubes and the length of runs. A small appendage was used near the capillary inlet to permit the entire sample to be cryopumped into the small volume between valves so that adequate pressure could be obtained with very small samples.

The isotope ratio analyses are expressed in terms of the deviation of the $^{34}S/^{32}S$ ratio of the samples from that of the standard:

$$\delta^{34}S = 1\,000\left[\frac{(^{34}S/^{32}S)_x - (^{34}S/^{32}S)_{st}}{(^{34}S/^{32}S)_{st}}\right] \text{ per mille}$$

where the subscripts x and st refer to sample and standard, respectively. The standard used for these analyses was meteoric troilite, with an $^{34}S/^{32}S$ ratio of 0.0450045. The estimated accuracy of the analyses is ± 0.3 per mille (Grey, 1970).

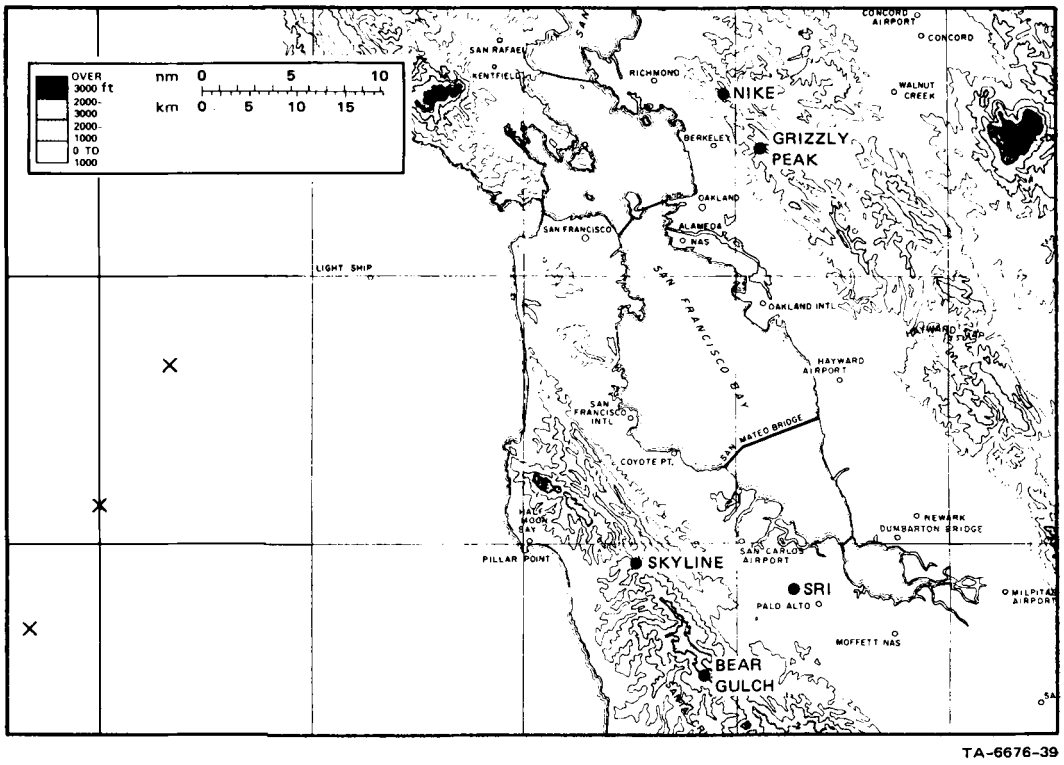
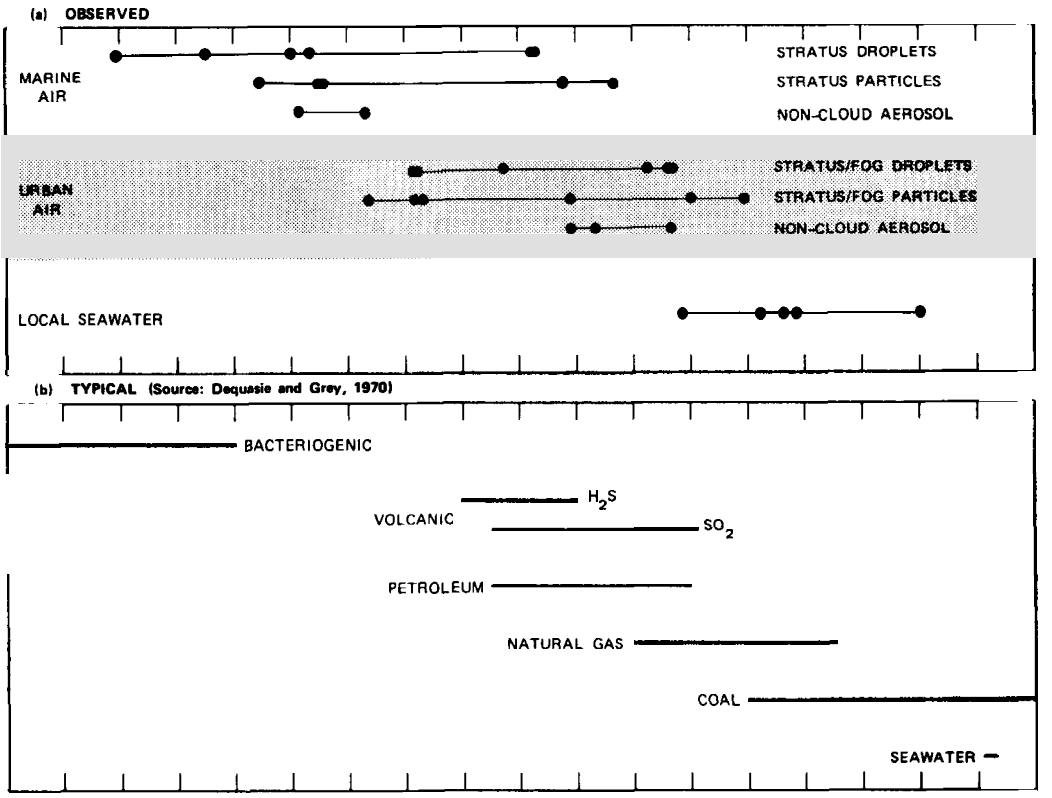


Fig. 1. Location of sampling sites.

Results

Table 1 shows the sulfur isotope ratios for samples collected during 1970 through 1973. The list is ordered from the smallest to the largest values of $\delta^{34}S$. The number of significant figures shown for the isotope ratios is an indication of sample size and analysis reliability. Marine stratus droplet samples and marine stratus particle samples were collected at the location labeled Skyline in Fig. 1. Sampling at this site was done during periods of westerly winds. There are virtually no sources of pollution to the west, between the site and the ocean. The samples referred to as aerosol in Table 1 were collected directly on filters, without the cyclone, during fog-free periods with westerly winds. One of the filter samples, listed as 'Seashore: aerosol,' was collected about 70 km south of San Francisco in the surf spray zone, about 100 m from shore.

Urban fog droplets, fog particles, and aerosol samples were collected at Stanford Research Institute (SRI) in the suburban western littoral of San Francisco Bay. The area has some light industrial activities and considerable vehicular traffic. Other urban influenced samples were collected in the hills east of Berkeley (Grizzly Peak) and at a state park in the San Joaquin River delta (Brannan Island, not shown in Fig. 1). The 1970 seawater samples were collected by the U.S. Coast Guard at three locations, from 70 km southwest to about 40 km southwest of the Golden Gate Bridge (marked by *X*'s in Fig. 2). The 1971 seawater samples were provided by William Broenkow of the California State University Marine Laboratories at Moss Landing, California. They were collected from the surface waters and also from a depth of 300 m, about 7 km offshore in Monterey Bay (not shown in Fig. 1). The offshore seawater samples were collected because it was felt that this area might well have isotope ratios of the sulfur compounds that are appreciably different from the values that are usually found elsewhere. Differences are to be



expected because of upwelling, biological activity, contamination from shipping, and the discharge of waters through the Golden Gate.

Discussion

Fig. 2 shows the same data presented in Table 1, but from the figure it is more readily seen that there is a pronounced tendency for the urban sulfur to be heavier than the marine air sulfur; the seawater sulfur, even with its probable contamination, is heaviest of all. The lower part of the figure shows the typical range of isotope ratios for various sources of sulfur, based on data from Dequasie & Grey (1970). From these data, it is not possible to infer any differences between the origins of droplet nuclei and those of the less active particles that do not grow to droplet size.

The sulfur compounds collected from marine aerosols are generally lighter than those collected from urban aerosols; the urban sulfur compounds, in turn, are lighter than those found in seawater. The probability is less than 1 percent (Wilcoxon's sum of ranks test; Langley, 1970) that the marine and urban samples, or the urban aerosol and the seawater samples, are drawn from the same population. The likelihood that the seawater and the marine aerosol samples were drawn from the same population is less than 0.2 percent. Thus, the sulfur isotope ratio data provide strong evidence that most of the sulfur compounds found in these marine aerosols do not arise from sea salt sulfur.

The differences cannot be explained on the basis of mixing between seawater aerosols and urban aerosols to produce the low values found in the marine aerosol. The values of the sulfur

isotope ratios found in seawater and those in the local urban aerosol are both greater than those in the marine air particulates; there is no way that a mixture could have values less than either of its components. It is quite probable that the marine aerosol does contain some sea salt material and some material of urban origin. Thus, it can be inferred that those sulfur compounds that do not come from urban or sea salt sources may have even lower isotope ratios than indicated by the data in the table.

The results presented provide direct evidence that the sources of large amounts of sulfur materials in the atmospheric aerosol are neither urban nor oceanic. Similar conclusions have already been indirectly drawn from the worldwide sulfur cycle (Robinson & Robbins, 1970; Kellogg et al., 1972). As indicated by Fig. 2, the fact that these sulfur compounds are isotopically light argues for an anaerobic bacterial origin (Dequasie & Grey, 1970; Grey & Jensen, 1972), but until more is known about the sulfur isotope ratios in biogenic dimethyl sulfide, the results cannot be used to judge the importance of this compound in the atmospheric sulfur cycle.

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ОТНОШЕНИЯ ИЗОТОПОВ СЕРЫ И ПРОИСХОЖДЕНИЕ АЭРОЗОЛЕЙ И ОБЛАЧНЫХ КАПЕЛЬ В СЛОИСТЫХ ОБЛАКАХ В КАЛИФОРНИИ

Морские аэрозоли часто имеют отношения серы к хлоридам бóльшие, чем в морской воде. Отношения изотопов серы ($^{34}S/^{32}S$) измерялось в пробах аэрозоля и облачных капель, собранных в области залива Сан Франциско, с целью понять процессы, приводящие к наблюдаемым отношениям серы к хлоридам. Сера в морской воде обычно имеет очень высокие отношения изотопов серы; сера из ископаемых топлив имеет тенденцию иметь меньшие отношения изотопов, а сера бактериогенного происхождения — еще меньшие отношения. Пробы, собранные в незагрязненном морском воздухе над холмами к югу от Сан Франциско, имели отношения изотопов, которые были значительно ниже, чем для изотопов, собранных в близлежащих областях, подвергаемых городским загрязнениям. Самые высокие отношения изотопов серы были найдены в прибрежной морской воде. Эти результаты указывают на бактериогенное происхождение вещества аэрозолей с серой в морском воздухе. Низкие изотопные отношения в морском воздухе не могут быть объяснены как результат смеси серы морской воды и серы загрязнений, поскольку оба этих источника обладают тенденцией иметь более высокие изотопные отношения.