Isotopic studies of the sulfur component of the stratospheric aerosol layer[1, 2]

By A. W. CASTLEMAN, JR, H. R. MUNKELWITZ and B. MANOWITZ, *Brookhaven National Laboratory, Upton, New York 11973, USA*

(Manuscript received July 31, 1973)

ABSTRACT

A major fraction of the large-size population of the Junge aerosol layer is comprised of sulfates thought to be of terrestrial origin. In order to obtain direct evidence concerning the importance of various contributing sulfur sources, as well as the significance of *in situ* gas-to-particle reactions, we undertook an extensive study of the sulfur concentration and isotopic ratio of particles, collected from 1962 to 1971 in the lower stratosphere over a wide range of latitudes. The data show that the major perturbations to the low-level persistent aerosol layer result from a few explosive volcanic eruptions. The extent of the initial tephra contribution to the layer gradually subsides, but particles are continuously replenished by aerosols formed from the gaseous portion of the eruptions. Trends in δS^{34} enrichment following an event are consistent with a simple one-dimensional model accounting for both transport and chemical reaction. During periods of comparative volcanic quiescence, the isotopic ratios of stratospheric sulfates in both Hemispheres exhibit a similar value, suggesting continual input from a common equatorial source.

Introduction

Although optical effects had long suggested the existence of occasional dust clouds in the upper atmosphere, it wasn't until the direct sampling studies of Junge et al. (1961) that a persistent and globally distributed stratospheric aerosol layer was verified. Subsequent to this work, the nature of the layer has been the subject of intense investigations and its general physical and chemical properties are now reasonably well documented. Junge et al. (1961a, 1961b) established that sulfur was the predominant elemental constituent of the large size fraction of these aerosols and, from an observation of a minimum in the particulate concentration at the tropopause, concluded that the particles were probably generated *in situ* by the photo-oxidation of trace sulfur containing gases.

The general distribution of this aerosol layer was further documented by Friend (1966), Bigg et al. (1970), and later by Lazrus et al. (1971), each of whom reconfirmed the predominance of sulfate anions. There is conflicting evidence about the relative importance of ammonium compared to hydrogen as the cation, but it appears that observational evidence of the former may have at least partly arisen from tropospheric contamination of the samples before their analyses (1973).

Because of both size range and location, stratospheric aerosols lead to scattering of the earth's incident radiation and could have a direct influence on its albedo. Since there is evidence (Koide & Goldberg, 1971), that the tropospheric sulfur burden has increased during the latter half of this century, primarily due to rising industrial emissions, particular concern exists regarding the relative importance of the various possible sources of sulfur compounds contributing to the layer. This raises the possibility that man's activities could have a long-term influence on the global climate, and it is clearly imperative that the significance of the various sources be properly identified.

[1] Based on a paper delivered by A. W. Castleman, Jr at the International Symposium on Atmospheric Trace Gases, Mainz, Germany, April 2–6, 1973.

[2] This work was performed under the auspices of the U.S. Atomic Energy Commission and was supported by the Environmental Protection Agency under an interagency agreement.

Although some investigators consider explosive volcanic eruptions to be the only source with sufficient energy to penetrate the tropopause to any great extent, attempts (Hogg, 1963; Volz, 1965; Volz & Goody, 1962) to correlate both the physical properties and the concentration of these aerosols with volcanic activity have met with only limited success. Nevertheless, the major perturbation to the total stratospheric dust layer which resulted from the catastrophic eruption of Mt. Agung (8½° S, 115½° E) in March 1963 is well documented. Subsequent to the eruption of 18 March 1963, a marked change was noted in the nature and concentration of aerosols collected in the stratosphere of both the Northern and Southern Hemispheres. Mossop (1964) reported as much as a ten times increase in number concentration of aerosols collected in the Southern Hemisphere following the eruption, and obtained evidence of insoluble particles within the droplet-like phase which comprised the major portion of the aerosol. Friend (1966) found a three times increase in particle number concentrations for stratospheric samples collected during the same time period at midlatitudes in the Northern Hemisphere.

Concurrently, other investigators making atmospheric optical measurements in both the Northern (Meinel & Meinel, 1963) and Southern Hemispheres (Hogg, 1963) reported enhanced scattering. Volz (1965) summarized a number of such optical measurements and, in addition, reported independent measurements of twilight intensity at a fixed angle of elevation prior to (Volz & Goody, 1962) and following the Agung eruption. His data have the advantage of utilizing the same observational method both before and after the eruption and show that atmospheric turbidity increased by up to a factor of 20 during the latter part of 1963.

A direct quantitative comparison of data obtained by various direct and optical sampling methods is difficult to make, and the extent to which volcanoes have contributed to the Junge layer has, until recently (Castleman et al., 1973), remained unresolved. Prior to the recent work, Cronin (1971) reviewed the subject and suggested that disagreement is also due to a failure among investigators to recognize the varied character and location of volcanic eruptions. He discussed the significance of two major belts of volcanic activity located in the arctic and equatorial latitudes, and noted that eruptions in the arctic latitudes where the tropopause is lower need be of considerably less magnitude than those in equatorial regions to be of comparable importance. However, since there is a general poleward stratospheric circulation, this suggestion would have to be modified if the particles arise primarily from relatively slow gas-to-particle reactions. In fact, Rosen et al. (1972) recently investigated the effect on the stratosphere of the eruption of Alaid (51° N, 155½° E) and found that the 20 km aerosol layer was unperturbed by this event.

In order to obtain direct evidence for the primary sources of the sulfur component of stratospheric aerosols, we undertook a study of sulfur concentrations and the S^{32}/S^{34} isotopic ratios of selected stratospheric aerosol samples. A comparison of the relative values and observed trends with the dates and locations of major volcanic eruptions (Cronin, 1971; Lamb, 1970; Friend, private communication), has provided important new evidence concerning the origin and production mechanisms of the aerosol layer. Isotopic ratios are sensitive to both the source of the sulfur compounds and, because of the mass dependence of reaction rates, subsequent chemical and physical conversions during transport. Thus, the technique provides unique and definitive data on which to base a model of stratospheric aerosol formation. This paper details our findings.

Experimental

The Health and Safety Laboratories of the AEC (HASL) and the Department of Defense (DOD), have routinely collected stratospheric particulate samples at various altitudes and geographic locations for over a decade. During this period there have been a number of violently explosive volcanic eruptions (Cronin, 1971; Lamb, 1970; Friend, private communication) which are thought to have penetrated the tropopause.

The archives of HASL and DOD contain samples whose analyses provide an invaluable record of the stratospheric sulfate burden. In order to implement the present study, appropriate stratospheric aerosol samples were selected from the existing libraries with due regard to considerations of time, geographic location,

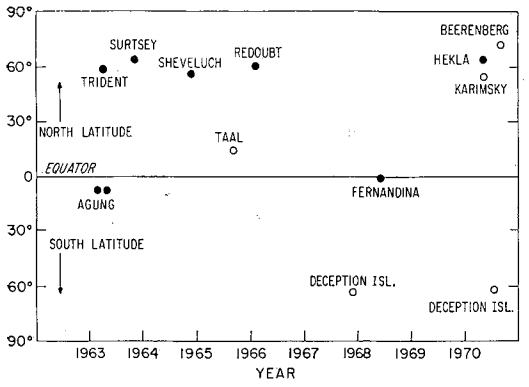

Fig. 1. Location of some important explosive volcanic eruptions of the past decade.

and collection altitude with respect to the height of the tropopause. The samples were subjected to mass spectrometric analyses in our laboratory for isotopic enrichment; subsequently, concentration measurements were also made. Samples were selected both for periods of active volcanic eruptions and at times when the volcanic contributions to the stratospheric aerosol layer would be expected to be at a minimum.

The collection media for these samples was Institute of Paper Chemistry (IPC) 1478 filter paper, impregnated with dibutoxyethylphalate. This paper was specially designed as a sampling medium and has good small particle retention properties for the conditions under which it was used. The physical properties of these filters have been well characterized by other investigators (The Institute of Paper Chemistry, 1960; Stern et al., 1960) and will not be discussed here.

The two most abundant stable isotopes of sulfur, S^{32} and S^{34}, were utilized in making the present study. For purposes of comparison, it is convenient to express relative changes in isotope ratio in terms of a del value, defined by the well known relationship

$$\delta S^{34} = \left(\frac{S^{32}/S^{34}\ (\text{standard})}{S^{32}/S^{34}\ (\text{sample})} - 1 \right) 1\,000$$

Del is expressed in units of parts per mil and, in the case of sulfur, is customarily referred to the standard ratio for meteoritic sulfur, namely 22.210. Clearly, a sample with a higher abundance of the S^{34} isotope will have a positive del relative to the standard, while one with a lower abundance of the S^{34} isotope will exhibit a negative del value.

The location and approximate date of some important eruptions which took place during the past decade are shown in Fig. 1. Those eruptions which are either known or believed to have penetrated the tropopause are indicated as closed points, while those about which there is some doubt are shown as open points. Efforts were made to bracket each eruption with a number of high volume samples. In practice this proved difficult and in many cases impossible since many samples had either been used by the collecting agency, or had insufficient quantity for a meaningful isotopic analysis. Wherever possible, in order to minimize sample inhomogenities, whole filters were used for our analyses. In no instance was less than ½ a filter

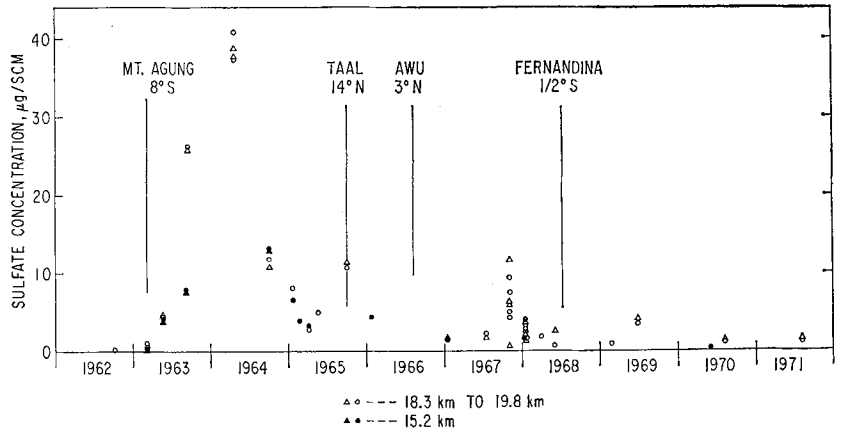

Fig. 2. Sulfate concentration, Southern Hemisphere, 0° S to 43° S.

Table 1. *Southern Hemisphere isotope ratios and concentrations*

Mo.	Day	Year	Latitude (Degrees)	Longitude (Degrees)	Altitude (km)	Determined from blank		Determined from average	
						Concentration (μg/scm)	δS^{34}	Concentration (μg/scm)	δS^{34}
Oct.	9	1962	40½ S	145½ E	18.3	—	—	0.07	N.D.
Mar.	11	1963	40½ S	146 E	15.2	0.05[a]	+11.6[a]	0.21	+ 7.5
Mar.	12	1963	42½ S	147 E	19.8	0.7[a]	+ 6.0[a]	1.03	+ 5.2
May	21	1963	41½ S	146½ E	18.3	4.4[a]	+16.4[a]	4.6	+15.8
May	21	1963	41 S	146½ E	15.2	3.9[a]	+ 4.6[a]	4.1	+ 4.6
Sep.	10	1963	41½ S	146½ E	15.2	7.7	+11.8	7.9	+11.6
Sep.	11	1963	41 S	146 E	18.3	25.7	+ 7.8	26.1	+ 7.7
Apr.	26	1964	17 S	145 E	19.8	38.7	0	40.8	+ 0.1
Apr.	26	1964	17 S	145 E	19.8	35.4	− 1.5	37.3	− 1.2
Oct.	6	1964	42 S	146½ E	18.3	10.8	−17.3	11.8	−15.5
Oct.	6	1964	41½ S	146 E	15.2	12.8	− 2.5	13.2	− 2.4
Jan.	26	1965	40 S	145½ E	15.2	—	—	6.6	− 6.4
Jan.	26	1965	40 S	146 E	18.3	—	—	7.0	−20.4
Feb.	23	1965	40 S	146½ E	15.2	—	—	3.9	− 6.0
Apr.	6	1965	42½ S	147 E	19.2	—	—	2.7	−19.8
Apr.	7	1965	40½ S	147 E	15.2	—	—	3.2	− 8.7
May	18	1965	42½ S	147 E	18.3	—	—	5.0	−24.4
Oct.	5	1965	42½ S	147½ E	18.3	11.3	N.D.	10.6	− 3.9
Jan.	25	1966	42½ S	147½ E	15.2	—	—	4.4	+ 2.1
Jan.	10	1967	37 S	68 W	15.2	1.6	− 3.1	1.2	− 3.6
July	17	1967	37½ S	68 W	18.3	1.8	N.D.	2.1	N.D.
Nov.	6	1967	47 S	68 W	19.2	11.6	+ 3.3	9.4	+ 3.1
Nov.	6	1967	35 S	68 W	19.2	6.4	+ 2.9	5.0	+ 2.6
Nov.	6	1967	47 S	68 W	18.3	0.6	N.D.	4.2	+ 2.5
Nov.	8	1967	18 S	74 W	18.3	5.9	+ 0.9	7.5	+ 1.5
Jan.	8	1968	37 S	69 W	15.2	—	—	1.5	+ 4.6
Jan.	18	1968	18 S	74 W	18.3	1.2	0	1.6	+ 4.8
Jan.	19	1968	31 S	68½ W	18.3	2.6	+ 1.5	3.4	+ 4.1
Jan.	18	1968	18 S	74 W	19.2	0.7	N.D.	1.2	+ 2.0
Jan.	19	1968	38 S	68 W	19.2	2.0	+ 0.7	2.8	+ 6.4
Jan.	19	1968	47 S	68 W	19.2	3.6	− 1.4	3.8	+ 0.3
Apr.	2	1968	18 S	74 W	18.3	—	—	1.8	− 9.4
June	5	1968	1 S	81 W	19.2	2.5	0	0.7	N.D.
Feb.	20	1969	27 S	71 W	18.3	—	—	0.8	− 1.3
July	28	1969	42½ S	68 W	19.2	4.2	− 0.7	3.6	− 1.9
Aug.	30	1970	36½ S	74 W	18.3	1.5	+ 0.2	1.1	− 0.8
June	3	1970	34 S	65 W	15.2	0.1	N.D.	0	N.D.
Aug.	15	1971	29 S	76 W	18.3	1.4	+ 2.4	1.3	+ 2.5

[a] Determined from an average of selected papers.

used and in the majority of these cases opposing quadrants were analyzed. These precautions are believed to have minimized errors likely to arise due to non-uniform sample collection on the airfoils.

The detailed analytical procedure used in our investigation has been given elsewhere (Tucker, 1969). Briefly it consists of the following steps: sulfate is leached from the filter, precipitated, and quantitatively measured. The precipitate is then converted to AgS, which is subsequently combusted to SO_2. The isotopic composition of the sample SO_2, and "standard" SO_2 obtained from meteoritic sulfur, are compared using a Nuclide Associates dual-beam mass spectrometer.

The IPC foils used in this study were not specifically intended to sample stratospheric sulfates, and blank filters were found to contain trace sulfur contamination. Thus, it was necessary to correct the measured isotope ratios and concentrations for this background. The re-

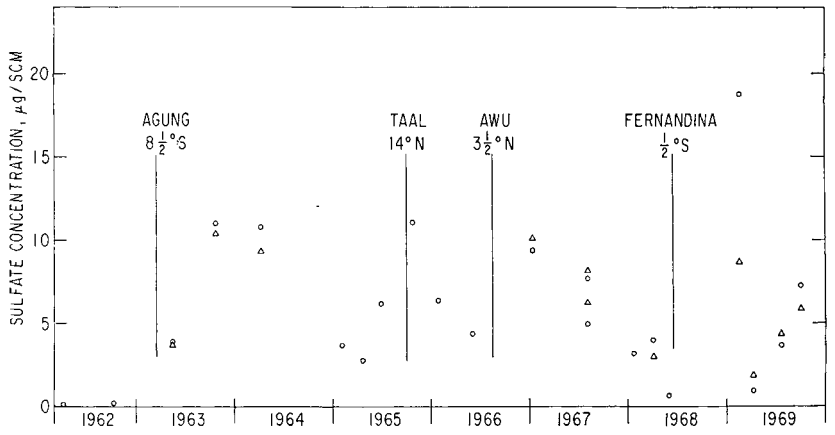

Fig. 3. Sulfate concentration, Northern Hemisphere, 0° N to 34° N latitude, 18.3 km to 19.8 km altitude.

quisite correction was made in two different ways: If available, a primary blank filter was obtained and processed at the same time as the sample. In many cases, however, the age of the filters precluded obtaining blank material, and it was necessary under these circumstances to make corrections using only average values for the blank. Wherever possible each sample was corrected by both methods. The blank isotope ratio and concentration values proved to be reasonably consistent, and good agreement was usually obtained for those samples subjected to the two methods of correction. In order to minimize local inhomogenities in stratospheric composition, long duration, high volume samples were deliberately selected for analysis; this selection method served the dual function of minimizing background correction errors.

Results

A plot of the sulfate concentration for stratospheric aerosols collected in the Southern Hemisphere from 1962 through 1971 is given in Fig. 2. (Numerical data are given in Table 1.) Concentrations are corrected for background and expressed as micrograms of sulfate per standard cubic meter of filtered air (μg/scm). The concentration values were computed using air volumes supplied by the collection agencies. Samples corrected for background using a primary blank are plotted with triangular points, while data evaluated using an average blank are designated by a circle.

A clear correlation between sulfur concentration and volcanic activity can be seen from the data. The perturbation to the total stratospheric dust burden by the paroxysmal eruption of Mt. Agung has been well documented, and as can be seen from our data, there was a large change in the sulfate concentration as well. The data show that the Southern Hemisphere sulfate concentration increased two orders of magnitude within a year after the eruptions. A small perturbation is also visible following Taal (14° N, 121° E) with lesser contributions from Awu (3½° N, 125½° E) and Fernandina (½° S, 92° W).

A similar effect can be seen in Fig. 3 regarding the increase in sulfate concentration of aerosols collected in the stratosphere of the Northern Hemisphere from 1962 to 1969. Appropriate data are given in Table 2. It appears that the eruptions of Taal, Awu, and Fernandina made a more significant contribution to the stratospheric sulfur inventory of the Northern than the Southern Hemisphere. Unfortunately, due to the sample requirements of the respective collection agencies, there is a paucity of appropriate samples available for this time period in the Southern equatorial latitudes.

The del values obtained from an analysis of the aerosols collected in the Southern Hemisphere are plotted in Fig. 4 and tabulated in Table 1. The data show an abrupt decline in δS^{34} concentration subsequent to the eruption of Agung, and a somewhat lesser decline in magnitude after the eruption of Fernandina.

As discussed in the next section, data on the

Table 2. *Northern Hemisphere isotope ratios and concentrations*

Mo.	Day	Year	Latitude (Degrees)	Longitude (Degrees)	Altitude (km)	Determined from blank: Concentration (μg/scm)	Determined from blank: δS^{34}	Determined from average: Concentration (μg/scm)	Determined from average: δS^{34}
Apr.	2	1962	7 N	80 W	18.3	—	—	0.11	+1.0
Oct.	9	1962	7 N	78½ W	18.3	—	—	0.2	+3.0
May	16	1963	7 N	78½ W	18.3	3.7[a]	+5.7[a]	3.9	+5.6
Oct.	22	1963	8½ N	79 W	18.3	10.4	+6.2	11.0	+6.0
Apr.	7	1964	8½ N	79 W	18.3	9.3	+8.5	10.8	+7.9
Jan.	13	1965	8 N	79 W	18.3	—	—	4.1	−1.2
Apr.	19	1965	8 N	79 W	18.3	—	—	2.8	−2.2
June	28	1965	8 N	80 W	19.2	—	—	5.8	−5.9
Oct.	20	1965	8 N	80 W	18.9	—	—	11.1	−2.4
Jan.	26	1966	8 N	80 W	18.9	—	—	6.4	−2.7
May	31	1966	7½ N	78 W	18.3	—	—	4.4	+1.1
Jan.	10	1967	7½ N	80 W	19.2	10.1	+0.6	9.4	+0.3
Aug.	1	1967	7½ N	80 W	18.3	8.2	+1.8	7.7	+1.6
Aug.	2	1967	18 N	85½ W	19.2	6.3	−1.0	5.1	−2.8
Jan.	21	1968	7 N	79 W	18.3	—	—	3.2	+5.0
Apr.	2	1968	7 N	80 W	19.2	3.0	+0.9	4.1	+1.6
June	6	1968	11 N	80 W	18.3	—	—	0.7	N.D.
Oct.	1	1968	20 N	85 W	18.3	5.9	+4.5	7.3	+4.4
Feb.	17	1969	10 N	80 W	19.8	8.7	−3.4	18.8	+2.4
Apr.	9	1969	34 N	103 W	18.3	1.9	−2.8	1.0	−2.9
July	21	1969	7½ N	80 W	19.5	4.4	+1.7	3.7	+0.8

[a] Determined from an average of selected papers.

sulfur isotopic ratio for these samples provides additional evidence for the major source of sulfur compounds contributing to the Junge layer, as well as important chemical and transport processes operative after injection.

The data plotted in Figs. 2 and 4 largely represent samples collected at altitudes ranging from 18.3 to 19.8 km; some data points at 42° S were obtained from those collected at 15.2 km. However, in all cases the samples were taken above the respective tropopause of the local region. Data representing lower (15.2 km) and upper (18.3 to 19.8 km) altitudes are differentiated using darkened and open points, respectively. At a given time, the samples taken at different altitudes show nearly the same sulfate concentration values, but there is a definite bias in del values, lower ones existing preferentially at the upper altitudes.

The del values for aerosols collected in the stratosphere of the Northern Hemisphere are given in Fig. 5 and Table 2; these data also display a rise followed by a significant decrease in del value following an important volcanic eruption. The cyclic trend in del value from 1966 to 1969 is not as regular as that seen directly after Agung, undoubtedly because of the short-time interval between the eruptions of Taal and Awu. Nevertheless, the same general trends are seen in both Hemispheres.

Other samples, collected in the arctic stratosphere from 58° N to 72° N and covering the time period 1962 to 1967, exhibit the same increase in sulfate concentration and decline in S^{34} enrichment, as a function of volcanic activity. The results of the analyses of these samples are shown in Fig. 6*a*, 6*b*, and tabulated in Table 3. The three predominant eruptions are Surtsey (63° N, 20½° W), Sheveluch (56½° N, 162° E) and Mt. Redoubt (60½° N, 153° W).

Discussion and comparison with other work

Junge (1963) sampled the sulfate aerosol layer from 40° S to 70° N latitude in 1959 and reported absolute concentrations of sulfur between 1 and 4×10^{-15} g/cm³ at 20 km altitude

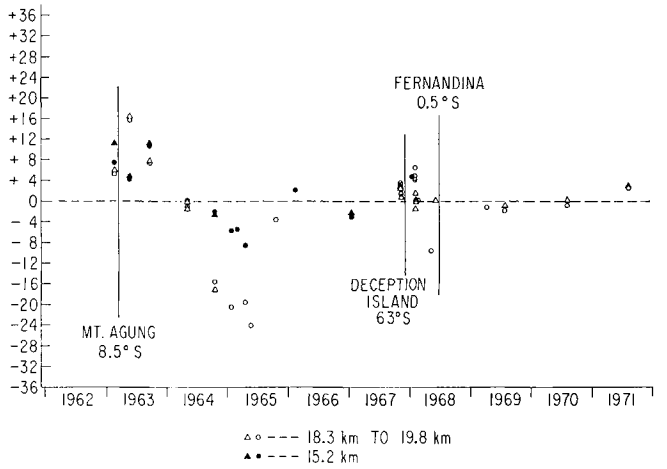

Fig. 4. Sulfur isotopic ratio, del ^{34}S, Southern Hemisphere, 0° S to 43° S.

prior to Agung. This corresponds to a sulfate concentration of 0.04 to 0.15 μg/scm of air. The results of our analyses of four pre-Agung stratospheric samples are 0.05, 0.07, 0.11 and 0.20 μg/scm. Although perhaps fortuitous, the data are seen to be in good agreement with Junge's concentration measurements. It should be noted, however, that a total of twelve pre-Agung foils were analyzed and eight of these yielded a result less than or equal to background. At the pressures and velocities of the present study, the IPC foils have a collection efficiency of greater than 80 % for Aitken nuclei. Therefore, these data tend to discount speculation that Junge's values were unrealistically low due to the supposed inefficiency of impactors for collecting Aitken particles.

Volz's (1969) twilight color ratio measurements indicate that stratospheric aerosol concentrations over the last two decades were at a minimum prior to the eruption of Agung. The concentration trends observed in our work are generally in good agreement with the optical trends, and also support this belief.

As seen in Fig. 3, subsequent to the Agung eruption, the sulfur concentration of the Northern Hemisphere increased, reached its peak in late 1963, and generally declined until the September 1965 eruption of Taal. Grams & Fiocco (1967), using optical radar based at Lexington,

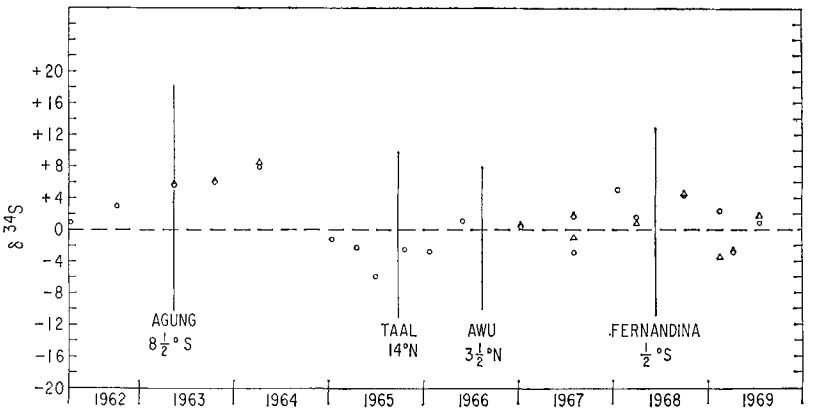

Fig. 5. Sulfur isotopic ratio, $\delta^{34}S$, Northern Hemisphere, 0° N to 34° N latitude, 18.3 km to 19.8 km altitude.

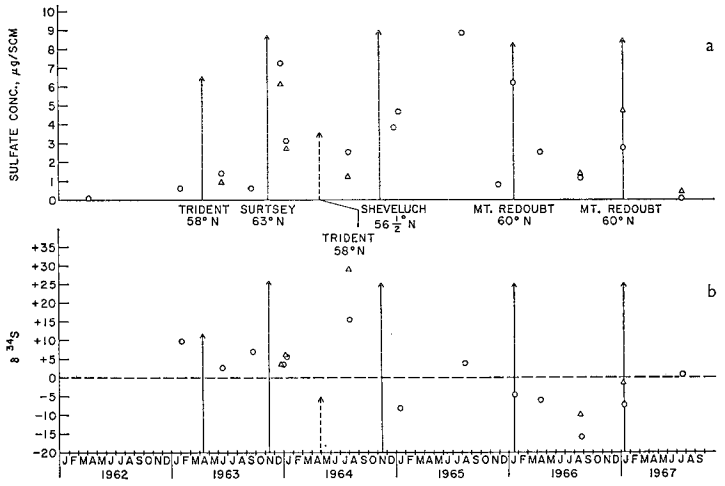

Fig. 6. Northern Hemisphere, 58° N to 73° N, 16.7 to 19.2 km altitude.

Massachusetts, observed the same generally decreasing trend in total stratospheric dust burden through the early summer of 1965.

On February 5, 1965 Shedlovsky & Paisley (1966) collected stratospheric aerosols on a polystyrene filter at 39° N latitude and an altitude range between 19 and 21 km. They reported a sulfur concentration of 3.75×10^{-12} g/cc at S.T.P., corresponding to a sulfate concentration of 11.3 μg/scm. This value probably represents an upper limit because their measurement was subject to some uncertainty due to possible chloride ion interference with the sulfur analysis. Values ranging from 2.8 to 5.8 μg/scm were obtained in this study at 8° N latitude at about the same time.

Table 3. *Arctic region isotope ratios and concentrations*

Mo.	Day	Year	Latitude (Degrees)	Longitude (Degrees)	Altitude (km)	Determined from blank		Determined from average	
						Concentration (μg/scm)	δS^{34}	Concentration (μg/scm)	δS^{34}
Apr.	10	1962	71½ N	143 W	18.3	—	—	0.05	N.D.
Feb.	5	1963	70 N	144 W	15.2	—	—	0.6	+10.0
June	18	1963	70 N	143½ W	15.2	0.9	N.D.	1.4	+ 3.3
Sep.	24	1963	70 N	144 W	18.3	—	—	0.6	+ 7.3
Dec.	30	1963	70 N	144 W	18.3	6.1	+ 3.8	7.2	+ 3.7
Jan.	14	1964	70 N	144 W	15.2	2.6	+ 6.2	3.1	+ 5.7
Aug.	10	1964	70 N	144 W	18.3	1.2	+29	2.5	+15.7
Dec.	28	1964	73 N	143½ W	18.3	—	—	3.8	N.D.
Jan.	12	1965	72½ N	143½ W	15.2	—	—	4.6	−5.7
Aug.	9	1965	72 N	143 W	18.9	—	—	8.8	+3.8
Dec.	1	1965	70 N	144 W	15.2	—	—	0.8	−24[a]
Jan.	25	1966	73 N	143½ W	18.9	—	—	6.2	− 4.5
Apr.	19	1966	68 N	145 W	15.2	—	—	2.5	− 5.9
Aug.	23	1966	68 N	145 W	15.2	1.6	− 9.7	1.1	−16.4
Jan.	9	1967	69 N	144½ W	18.3	4.7	− 1.5	2.7	− 7.0
July	25	1967	72½ N	143½ W	15.2	0.4	+ 0.7	0.06	−31[a]

[a] Not plotted.

The sulfate concentration of the Southern Hemisphere reached its maximum value early in 1964 and subsequently declined. As expected, a comparison of the relative concentrations of the respective Hemispheres shows that the largest effects of the Agung eruption occurred in the Southern Hemisphere. This is in agreement with measurements of atmospheric optical properties (Grams & Fiocco, 1967; Dyer of Hicks, 1968) in the respective Hemispheres.

The explosive eruption of the Taal volcano on September 28, 1965 caused the stratospheric sulfur inventory to again abruptly increase; this is seen from the data plotted in Fig. 3. On August 12, 1966 the explosive eruption of Awu injected still more sulfur into the stratosphere. Other investigators have generally overlooked the importance of this latter event which had a total eruptive duration of less than one day. However, the observed height of the eruption cloud was more than 10 km and, in fact, the ash blanketed a ship in the Celebes Sea (at 2°40′ N, 122°28′ E) to a depth of one-half inch (Cronin, private communication).

Rosen (1968) has compared the particle concentrations measured over Panama (10° N latitude) in September of 1966 with those over Minneapolis (45° N) in April 1965, and Churchill (60° N) in June 1966, and noted a decrease in dust concentration with latitude. He attributed the observed profiles to an equatorial dust source. As readily discerned from Figs. 3 and 6*a*, occassional volcanic eruptions (with ensuing poleward airflow) were probably responsible for the concentration gradient. He reports a total aerosol concentration of about 10^{-12} g/cm^3 (presumably at ambient conditions) over Panama, which corresponds to a total mass of about 14 μg/scm. This value for total dust concentration is in good agreement with the values obtained in this study for the total sulfate concentration, and therefore his conclusion that sulfur comprised only about 0.3% of the total mass is subject to question.

After the considerable increases caused by Taal and Awu, the stratospheric sulfate concentrations of both the Northern and Southern Hemisphere again declined. This trend was reversed by the explosive eruption of Fernandina in June of 1968. The major explosion of June 11 dissipated an estimated 10^{21} ergs of energy and was detected by infrasonic apparatus over a wide area (Simkin & Howard, 1970). It was in all probability the largest explosive volcanic event since Agung, and the eruption undoubtedly vented large quantities of gas to the stratosphere. The resultant perturbations to both concentration and isotopic ratios, as found by the present study, are clearly attributable to this event.

The sulfate concentration data amassed in this study clearly show that major perturbations to the stratospheric aerosol layer have resulted from a few infrequent volcanic eruptions of large magnitude. In addition to the concentration data, a consideration of the corresponding trends in the del values of the aerosols provides additional information on the source and subsequent transport of material entering the stratosphere. Since these ratios are sensitive to chemical and physical conversions following injection, they are useful in assessing the relative quantity of sulfate injected directly, compared to that resulting from *in situ* oxidation processes.

In order to interpret the significance of the isotopic ratios plotted in Figs. 4, 5, and 6*b*, due consideration must be given to the quantity, chemical state, and initial isotopic composition of the injected material, as well as that of preexisting material already in residence. The del values of sulfur compounds resulting from biogenic and inorganic processes vary over a wide range, and it is erroneous to conclude that specific values can be used as a "fingerprint" to establish the significance of a given source. Samples of volcanic sulfur compounds range from -20 to $+20$, the actual specific values depending on location and oxidation state of the emanating products. Nevertheless, given processes generally lead to similar trends in isotopic enrichment.

We made a very limited isotopic ratio study of particles and tephra collected from several volcanoes, and found all values to be positive (see Table 4). Although there is no *a priori* reason to suppose that this will be the fact in all cases, the results of stratospheric samplings directly after all major eruptions show a tendency toward positive values.

Immediately after an eruption, the majority of the material collected in particle sampling consists of finely divided tephra. The magnitude of the positive del values of the stratospheric aerosols collected shortly after the eruptions vary somewhat as expected; undoubtedly they represent a weighted average of the values of

Table 4. *Sulfur isotopic ratios for volcanic tephra*

Source	Description	δS^{34} ‰
Hekla	Sulfate collected from fume of Hekla volcano	+1.8
Hekla	Ash collected 9 km north of vent	+1.8
Blanco Fracture Zone, Oregon	Undersea volcanic lava	+0.9
Mt. Mayon	Lava—blown into atmosphere from 1968 eruption	+6.3
Mt. Arenal	Fine ash from nuee ardente—Aug. 1, 1968	+2.6
Kilauea	Basaltic pumice—1961 eruption	+1.0

the injected tephra together with those of the background stratospheric aerosol and the limited quantity of particles formed by the conversion of gases to particles in the rising plume. It should be noted that an extensive study (Lazrus et al., to be published) of the del value of stratospheric aerosols collected in times of volcanic quiescence showed the values average 2.6 ± 0.3‰ over wide ranges of latitudes in both the Northern and Southern Hemispheres.

It is expected that the particulate matter initially injected into the stratosphere by the eruption cloud would gradually diminish via settling processes; the rate of elimination from the stratosphere is determined by particulate size and injection altitude, as well as overall stratospheric-tropospheric global exchange processes. Several-tenth micron particles in the lower stratosphere generally have average residence times of 1 to 1½ years. Therefore, it is reasonable to expect that aerosols sampled at progressively later times subsequent to an eruption would contain an ever decreasing amount of tephra and an increasing amount of aerosol formed in the stratosphere from the gaseous portion of the eruption cloud.

In the present study, aerosols sampled at progressively later times exhibited an ever increasing degree of depletion of the S^{34} isotope (decreasing δS^{34}) with respect to the "standard". For short intervals following major eruptions, the additional sulfate contributed by all other processes is comparatively negligible and the observed continual change in sulfur isotopic composition for stratospheric aerosols is clearly the result of fractionation processes. In situations with negligible further input and undergoing reactions such as gas-to-particle conversion, as the reaction proceeds to completion, the sulfate product would be expected to exhibit an unidirectionally changing isotopic composition. The direction that this change would take, however, is difficult to assess.

Trudge & Thode (1950) have calculated equilibrium constants from partition function ratios for sulfur exchange reactions. These calculations indicate that the S^{34} isotope tends to concentrate in the sulfate. Non-equilibrium situations involving complex molecules are particularly difficult to assess from first principles. However, for the case of SO_2 conversion to sulfate particles in power plant plumes where tracing the direct course of the reaction has been effected, a decrease in the del value of the unreacted gas has been observed (Tucker, 1969). This trend is also borne out by the present study. On the basis of the foregoing findings, as the injected volcanic gases diffuse upward in the stratosphere they would be expected to continually convert to particles from gas whose del value is progressively decreasing. Assuming that relaxation times for the operative chemical processes are not much faster than those for the transport processes, the gas (which eventually becomes converted to particulate matter) with progressively lower del values should preferentially concentrate at the higher altitudes.

Considerations of chemical reaction and transport

Further interpretation requires an assessment of the rates of transport and chemical reaction for SO_2 after injection into the stratosphere. An accurate calculation of this sulfate distribution as a function of time and altitude requires the solution of a set of simultaneous equations; these include the three dimensional equation of motion, coupled with an equation for conservation of mass including appropriate expressions for the important chemical reactions. Based on present incomplete knowledge of stratospheric motions as well as the concentrations of potentially important reaction species, and even the rates of many of the possible chemical reactions of some import, such sophistication is impossible, and indeed, unwarranted.

A simple one-dimensional model, while naive, is instructive in gaining further insight into the origin of the Junge layer in terms of the present findings.

Several authors (Scott et al., 1969; Mohnen; Friend et al., 1973) have postulated chemical reaction schemes to explain the formation of the layer by *in situ* reactions. The hypotheses may generally be classified in four groups: (1) photoexcitation of the SO_2 molecule, followed by subsequent oxidation steps, (2) surface reactions on preexisting particles, (3) reaction with existing free radicals, or (4) direct reaction between NH_3 and SO_2.

The low quantum yield for the direct photolysis of SO_2 found in recent experiments (Friend et al., 1973) suggests that (1) is not the predominant mechanism, especially since there are several possible free radical reactions which are almost certainly faster. Although the rates of various postulated mechanisms falling under the fourth classification have not been completely assessed, recent work (Friend et al., 1973; Castleman) tends to discount this as a serious contender compared to (3). Likewise, it can be shown that (2) is also likely to be negligible compared to (3) for the particle concentrations of $\leqslant 1$ cm^{-3} existing in the lower stratosphere.

At one time, the three body oxidation of SO_2 by O atoms was believed to be rapid, and it was thought that SO_2 would have a relatively short life-time in the stratosphere. Recently, Davis (1973) remeasured the appropriate reaction rate coefficients and showed that, with N_2 as the third body, the reaction rate was much lower than previously thought. His work also showed the reaction to have a positive activation energy. Based on the redetermined rates, and assuming $[O] \sim 10^5$ atoms cm^{-3}, the relaxation time for SO_2 oxidation by this mechanism would be more than 10^9 seconds.

Davis (1973) has also determined a value for the oxidation of SO_2 by HO_2, giving an approximate rate constant of 9×10^{-16} cm^3 molecule^{-1} sec^{-1} for a two-body reaction leading to the formation of SO_3. During the course of laboratory studies (Castleman), we observed that OH radicals also lead to SO_2 oxidation. However, the value of the rate constant has not been definitely established as yet, and the importance of this mechanism cannot be assessed at this time. Using calculated values for the HO_2 concentration of $\sim 10^8$ molecules cm^{-3}, (two orders of magnitude higher than the predicted concentration for OH), we estimate a relaxation time for SO_2 of $\sim 10^7$ seconds.

The trends in the del value data given in the prior section clearly suggest an *in situ* oxidation process rather than merely the redistribution of aerosols. The latter process, by itself, would show no isotopic dependence with time or altitude. An *in situ* oxidation mechanism is further substantiated by the concentration data which usually displays a peak value at times longer than 10^7 seconds after an eruption. This is far in excess of times required for circumferential global mixing; the latter should be an order of magnitude faster. Therefore, these delay times are also indicative of a gas-to-particle conversion mechanism with a time constant in the neighborhood of 10^7 seconds. The reason that the delay times are not the same after each eruption is not clear, but may be attributable to the composition of the individual volcanic effluents which could, in turn, influence reaction times.

It is instructive to estimate the average vertical distance which SO_2 might be expected to diffuse during the period of time required for its conversion to SO_3, and subsequent nucleation to particles. One dimensional diffusion models contain, in a series expression, an exponential of the dimensionless term Dt/l^2. Here, t is time, D the eddy diffusion coefficient, and l a measure of the diffusion distance. Taking $Dt/l^2 \sim \frac{1}{2}$, the mean distance traversed during a given time may be computed. Using an appropriate value (Junge et al., 1961*a*) for D, and the relaxation time for SO_2 oxidation given above, it is estimated that on the average, the SO_2 molecule will diffuse vertically several kilometers from the point of injection. This is consistent with the altitude dependence of the isotopic ratio findings of the present study.

It should be noted that the altitude dependence of the del values is governed not only by the simultaneous transport and reaction of the SO_2 isotopes, but also by the settling of the particles of varying isotopic composition subsequent to their formation. The average time of the particle spent at a particular altitude sampled, even with due allowances for sampling height variations between missions, is comparatively very short. Therefore, it can be expected that particles collected at progressively later times following an eruption represent those

formed at higher altitudes which have eventually settled into the sampling region. Settling velocities for particles of the mean size found in the stratosphere are about 10^{-2} cm/sec, and the particles formed at 18–19 km should not influence the del value of those in the 15–16 km region until about 3×10^7 seconds after their formation. This is reasonably consistent with the displacement in cyclic trends for the data given in Fig. 4. The cyclic trend in these del values exhibits an upturn toward the end of 1965. This is possibly a manifestation of the influence of tephra from the Taal eruption.

Invariably, the del value of particles sampled at any specific attitude after an eruption is observed to decrease with time. This trend is consistent with the relationship

$$\delta_p = \delta_g + 1000\beta[nx - 1]$$

where β is the fractional difference in the rate constants of the heavier and lighter isotopes, x is the fraction of the SO_2 converted for each time interval, and δ_p is the del value of the particles formed from gas injected into the stratosphere with original value δ_g. This relationship is readily derived for an irreversible first-order reaction and is valid for the pulse injection of gases followed by incremental conversion and subsequent particle removal. Here, n represents the nth incremental conversion step. At progressively later times, the influence of the volcanically injected material becomes negligible, and the del value again rises to an average established by other contributing sources.

Conclusions

The data given in this paper clearly show that volcanic emissions represent the major source perturbing the sulfate concentration of the stratosphere. The remaining question concerns the origin of the sulfate which contributes to the persistence of the Junge layer in times of relative volcanic quiescence. Newell et al. (1969) has shown that tropical upwelling is a major mechanism of tropospheric air-mass transport into the stratosphere at levels above 100 mb (16½ km). Tropical regions are rich in biogenic sulfur and it is reasonable to assume that tropical upwellings would also be a major contributor to the persistant "background" stratospheric aerosol. Our data lend considerable support to this contention.

The data show that the concentration of the stratospheric aerosol layer always returns to low values of several tenths of a microgram per standard cubic meter after several years with no major volcanic input. The surprisingly consistent isotopic del value of $2.6 \pm 0.3‰$ found in *both* Hemispheres away from the equatorial zone clearly suggests a common source of background stratospheric sulfate and indicates transport via upwellings from an equatorial zone.

Man's activities contribute (Kellogg et al., 1973; Friend, 1973) ~40% of the tropospheric sulfur burden in the Northern Hemisphere, but only about 5% in the Southern Hemisphere. It is to be expected, then, that the sulfur isotopic composition of SO_2 above haze layers and effusing upward toward the tropopause would be considerably different in the two Hemispheres. Sulfate in the Junge layer would be expected to display this difference if continued input by eddy diffusion over the entire globe was a significant contributor. This conclusion that input by tropical upwelling predominates over eddy diffusion could be confirmed by comparing background del values for SO_2 gas in the vicinity of the tropopause in each Hemisphere, and awaits further research.

Acknowledgements

This research was performed under the auspices of the U.S. Atomic Energy Commission and was supported by the Environmental Protection Agency under an interagency agreement.

We thank Mr. P. Krey (HASL-AEC), Dr. W. Melson (Smithsonian Institution), and individuals in the DOD for assistance in obtaining samples; Professors C. Junge (MPI-Mainz), R. Newell (MIT), and J. Friend (NYU) for helpful discussions during the course of the work; and Dr. L. Newman and Mr. J. Forrest for performing the concentration and del value analyses.

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ИЗОТОПНЫЕ ИССЛЕДОВАНИЯ КОМПОНЕНТ, СОДЕРЖАЩИХ СЕРЫ, В СЛОЕ СТРАТОСФЕРНОГО АЭРОЗОЛЯ

Основной частью крупной фракции аэрозольного слоя Юнге являются сульфаты, повидимому, земного происхождения. Чтобы получить прямое подтверждение важности различных источников серы, также как и значимости локальных реакций газов с частицами, мы предприняли широкое исследование концентраций серы и изотопных отношений частиц, собранных в нижней стратосфере в течение 1962–71 гг. в широком интервале широт. Данные указывают, что основные возмущения постоянного слоя аэрозоля низкого уровня происходят благодаря немногим взрывным вулканическим извержениям. Размеры первоначального вклада твердого аэрозоля в этот слой постепенно уменьшаются, но частицы постоянно замещаются аэрозолями, формируемыми из газовых вкладов извержений. Тренды в обогащении $\delta\ S^{34}$, следующие за событием, согласуются с простой одномерной моделью, описывающей как перенос, так и химическую реакцию. В течение периодов относительного затишья вулканов, изотопные отношения стратосферных сульфатов в обоих полушариях имеют аналогичные значения, что предполагает постоянный приток из общего экваториального источника.