SULFUR ISOTOPE RATIO TECHNIQUE*

A. W. Castleman, Jr., and H. R. Munkelwitz
Brookhaven National Laboratory
Upton, New York 11973

October 1974

* 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.

† Submitted for publication in CIAP Series, Monograph 1.

Introduction

A major fraction of the large-size population of the stratospheric aerosol layer is comprised of sulfates, ^(1,2,3) thought to be of terrestrial origin. The general distribution of this aerosol layer has been documented by Junge, ⁽⁴⁾ and Rosen, ⁽⁵⁾ Bigg et al., ⁽⁶⁾ among others, each of whom reconfirmed the predominance of sulfate anions. Presently, there is conflicting evidence about the relative importance of ammonium compared to hydrogen as the cation. ⁽⁷⁾ Based on both theoretical considerations and observations of a minimum in the particulate concentration at the tropopause, Junge et al. ⁽¹⁾ concluded that the particles were probably generated in situ by the photooxidation of sulfur containing gases. Until recently, however, there was no direct evidence for this hypothesis.

Sulfur compounds of terrestrial origin such as SO_2 , and possibly H_2S , may enter the stratosphere by three major processes. These include vertical transport via tropical upwellings and major storms, eddy diffusional processes, and injection by explosive volcanic eruptions. As will be seen in what follows, the last of these processes presents a significant impulsive loading to the stratosphere on numerous, but irregular intervals. For instance, the major perturbation to the total stratospheric dust layer which resulted from the catastrophic eruption of Mt. Agung ($8\frac{1}{2}^\circ\text{S}$, $115\frac{1}{2}^\circ\text{E}$) 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 ⁽⁸⁾ 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 ⁽²⁾ 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⁽⁹⁾ and Southern Hemispheres⁽¹⁰⁾ reported enhanced scattering. Volz⁽¹¹⁾ summarized a number of such optical measurements and, in addition, reported independent measurements of twilight intensity at a fixed angle of elevation prior to and following⁽¹²⁾ the Agung eruption. These 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 stratospheric aerosol layer, and especially the sulfur burden, had remained largely unresolved for a number of years.

Recently, however, the techniques of isotopic ratio tracing have been employed in order to elucidate the mechanisms responsible for the formation of the layer as well as establish the significance of volcanic compared to the other possible sources. The results of these studies have been quite revealing. Isotopic ratios are sensitive to both the source of sulfur compounds and also, because of the mass dependence of reaction rates, subsequent chemical and physical conversions during transport. In the case of the element sulfur, the studies utilized the two most abundant stable isotopes of sulfur, S³² and S³⁴, in order to facilitate a comparison; the relative changes in isotope ratio are commonly defined by the relationship:

$$\delta S^{34} = \left(\frac{S^{32}/S^{34}(\text{standard})}{S^{32}/S^{34}(\text{sample})} - 1 \right) 10^3$$

Δ 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 δ relative to the standard while one with a lower abundance of the S^{34} isotope will exhibit a negative δ value.

It is instructive to note that δ values of sulfur compounds resulting from natural and biogenic processes vary over a wide range and it is erroneous to conclude that specific values can be used as a "finger print" to establish the significance of a particular source. This variable nature is the result of fractionation due to differences in chemical behavior of sulfur isotopes during exposure to reactive environments and can take place in unidirectional reactions, as well as those which approach equilibrium. Nevertheless, given processes generally lead to specific trends in isotopic enrichment and if trends rather than absolute values are assessed, the technique provides unique and definitive data on which to base a model of stratospheric aerosol formation.

Castleman et al. (13, 14) have applied this technique to a study of the Junge layer, and have reported results of the sulfur concentration and isotopic ratio of numerous selected stratospheric samples. Relevant δ values obtained from an analysis of aerosol samples collected in the Southern Hemisphere for the time period 1962 to 1971 are plotted in Fig. 1. The data clearly show an abrupt decline in S^{34} enrichment subsequent to the 1963 eruption of Agung volcanoes and a somewhat lesser decline in magnitude after the eruption of Fernandina. Additional data (13) from samples collected in the Northern Hemisphere during the same time period show a similar effect. A corresponding plot of the sulfate concentration for The Southern Hemisphere stratospheric aerosols is given in Fig. 2.

The data plotted in Figs. 1 and 2 represent samples collected largely 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 δ values, lower ones existing preferentially at the upper altitudes.

Immediately after an eruption, the majority of the material collected in particle sampling undoubtedly consists of finely divided tephra. As noted previously, the δ values of volcanic sulfur can exhibit a considerable range of values, the exact nature of which depend on the location of the particular source and the oxidation state of the emanating material. The magnitude of the positive δ values of the stratospheric aerosols collected shortly after the eruptions vary somewhat as expected; undoubtedly they represent a weighted average of the values of 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 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 particular size and injection altitude, as well as overall stratospheric-tropospheric global exchange processes. It should be noted that several-tenth micron particles present in the lower stratosphere generally have average residence times of 1 to $1\frac{1}{2}$ 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; it is expected that the latter could be formed in the stratosphere from the gaseous portion of the eruption cloud.

In the work of Castleman et al.^(13,14) (1973 a, b) aerosols sampled at progressively later times were found to exhibit 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 was comparatively negligible and the observed continual change in sulfur isotopic composition for stratospheric aerosols was 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. 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) with progressively lower δ values should preferentially concentrate at the higher altitudes; this is consistent with the observed isotopic trends.

Several authors^(15,16,17) have postulated chemical reaction schemes to explain the formation of particulate by in situ reactions. The hypotheses may be generally classified into four groups: A) photoexcitation of the SO_2 molecule, followed by subsequent oxidation reactions, B) surface reactions on pre-existing particles, C) reaction with existing free radicals, or D) direct reaction between NH_3 and SO_2 .

The low quantum yield⁽¹⁷⁾ for the direct photolysis of SO_2 found in recent experiments suggests that (A) is not the primary mechanism. This is further suggested by the fact that 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^(17,18) tends to discount these as serious contenders compared to (C).

Surface reactions (B) cannot be totally discounted, but they are unlikely⁽¹⁹⁾ to be of dominate importance in the formation of these sulfates. At the low particle concentrations known to exist in the undisturbed stratosphere, it is not unreasonable to assume that the heterogeneous mechanisms are comparatively less important than the homogeneous chemical reactions.

Following conversion to SO_3 , subsequent reactions with water vapor would eventually lead to the formation of sulfuric acid particles via the heteromolecular nucleation process. Later, these particles may partially react with NH_3 , diffusing into the stratosphere, and this may explain the occasional observation of $(\text{NH}_4)_2\text{SO}_4$ in the stratospheric aerosol. In the case of volcanic injection, NH_3 , SO_2 , and perhaps H_2S , may be injected together, possibly leading to a larger percentage of ammonium sulfate. Present knowledge is insufficient to estimate the relaxation times for these conversion reactions and, for lack of evidence to the contrary, a direct correspondence between the SO_2 -reaction relaxation time and the time for particulate formation can be assumed. In any event, the times are long enough so that substantial quantities of SO_2 gas may be expected to reach the altitudes of the Junge layer by eddy diffusion before being completely converted to particles.

In agreement with the suggestions of Junge et al.,⁽¹⁾ the trends in the del value data clearly support 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. The likelihood of an in situ oxidation mechanism is also indicated by the concentration data which were found to display a peak value at times longer than 10^7 seconds. The reason that the delay times are not the same after each eruption is not clear, but may be attributable to differences in the composition of the individual volcanic effluents which could, in turn, influence reaction times.

All of the isotopic δ values of particles sampled at a selected altitude after an eruption decrease with time. These trends can be rationalized in terms of 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 a given time interval, and δ_p is the δ value of the particles formed from gas injected into the stratosphere with original value δ_g . This relationship was derived for the case of 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 n^{th} incremental conversion step. At progressively later times, the influence of the volcanically injected material becomes negligible and, the δ again rises to an average value established by other contributing sources.

This raises a question regarding the major source which sustains the layer during periods of relative volcanic quiescence. Newell et al. ⁽²⁰⁾ have shown that tropical upwelling is a major mechanism of tropospheric air-mass transport into the stratosphere at levels above 100 mb (16-1/2 km). Tropical regions are rich in biogenic sulfur and it is reasonable to assume that these upwellings would also be a major contributor to the persistent "background" stratospheric aerosol.

The stratospheric aerosol concentration data in Fig. 1 shows that the layer always returns to low values of several tenths of a microgram of sulfate per standard cubic meter after several years with no major volcanic input. Concurrently, the isotopic ratio of the sulfate tends to a small positive value. A similar trend is evident in data taken in the Northern Hemisphere. ⁽¹³⁾ A surprisingly consistent average isotopic δ value of $2.6 \pm 0.3\%$ is found for both Hemispheres. These

results clearly suggest a common source of background stratospheric sulfate, probably transported via upwellings from an equatorial zone.

Man's activities contribute $\approx 40\%$ of the tropospheric sulfur burden in the Northern Hemisphere^(21, 22) 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. The δ values of the sulfate in the Junge layer in the two hemispheres should display this difference if continued input by eddy diffusion over the entire globe was a significant contributor; no difference in δ value has been found. These results do not entirely rule out contributions via large tropical storms convecting materials into the stratosphere. However, measurements of the δ value of sulfate present in cloud water collected at low levels showed positive values in excess of +13. Although not totally conclusive, in the absence of more extensive data, these results strongly suggest that aerosols carried upward in large storm clouds make only a minor contribution to the persistent globally distributed layer.

The conclusion that input by tropical upwelling predominates over eddy diffusion could be confirmed by comparing δ values for SO_2 gas sampled in the vicinity of the tropopause in each Hemisphere; this awaits further research.

Figure Captions

Fig. 1 Sulfur Isotopic ratio, $\Delta \delta^{34}\text{S}$, Southern Hemisphere, 0° to 43° S.

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

Fig. 1

Fig. 2

References

1. Junge, C. E., Chagnon, C. W., and Manson, J. E., J. Meteorol. 18, 81, (1961).
2. Friend, J. P., Tellus 18(2), 465, (1966).
3. Lazrus, A. L., Gandrud, B. and Cadle, R. D., J. Geophys. Res. 76, 8083, (1971).
4. Junge, C. E., and Manson, J. E., J. Geophys. Res. 66, 2163.
5. Rosen, J., J. Geophys. Res. 73, 479, (1968).
6. Bigg, E. K., Ono, A., and Thompson, W. J., Tellus 22, 550, (1970).
7. Junge, C. E., Remarks during discussion at International Symposium on Atmospheric Trace Gases, Mainz, Germany, April 2-6, (1973).
8. Mossop, S. C., Nature 203, 824, (1964).
9. Meinel, M. P., and Meinel, A. B., Science 142, 582, (1963).
10. Hogg, A. R., Aust. J. Science 26, 119, (1963).
11. Volz, F. E., Tellus 17, 513, (1965).
12. Volz, F. E., and Goody, R. M., J. Atmos. Sci. 19, 385, (1962).
13. Castleman, A. W., Jr., Munkelwitz, H. R., Manowitz, B., Tellus 26(1,2) 222, (1974).
14. Castleman, A. W., Jr., Munkelwitz, H. R., Manowitz, B., Nature 244, 345, (1973).
15. Scott, W. D., Lamb, D., and Duffy, D., J. Atmos. Sci. 26, 727, (1969).
16. Mohnen, V. A., Publication No. 165, Atmos. Sci. Res. Cent., SUNY, Albany, N. Y. 12222.
17. Friend, J. P., Leifer, R., and Trichon, M., J. Atmos. Sci. 30, 465, (1973).

18. Castleman, A. W., Jr., to be published.
19. Castleman, A. W., Jr., "Nucleation Processes and Aerosol Chemistry,"
Space Science Review, submitted.
20. Newell, R. E., Vincent, D. G., and Kidson, J. W., Tellus 21, (1969).
21. Kellogg, W. W., et. al., Science 175, 587, (1973).
22. Friend, J. P., The Global Sulfur Cycle. In, Chem. Lower Atmos.
(Ed., S. I. Rasool) (Plenum Press).