oceanic tholeiites, which are presumably derived from the asthenosphere. We conjecture that mantle plumes must arise in the mantle below the asthenosphere. The source materials for the Hawaiian volcanic rocks have higher $^{3}He/^{4}He$ and lower $^{40}Ar/^{36}Ar$ ratios than those of the oceanic tholeiites. If we assume that the primordial components of rare gases are depleted in the source region of the oceanic tholeiites, we can explain the isotopic differences between the two sources. Such a model is compatible with the concept of a "depleted mantle" for the source region of the oceanic tholeiites (*13*). In this case, the source region from which a mantle plume arises still retains a relatively primordial character, including high $^{3}He/^{4}He$ and low $^{40}Ar/^{36}Ar$ ratios.

Our results also provide evidence of mixing between the mantle plume and the source materials of the oceanic tholeiites (materials of the asthenosphere or lithosphere, or both) as observed in the Hawaiian volcanic rocks. The strontium, lead, and neodymium isotopic ratios in the Hawaiian volcanic rocks may also be interpreted in this way.

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References and Notes

1. E. D. Jackson and T. L. Wright, *J. Petrol.*, **11**, 405 (1970); T. L. Wright, *U.S. Geol. Surv. Prof. Pap. 735* (1971).
2. E. D. Jackson, *Proc. 23rd Int. Geol. Congr.* **1**, 135 (1968); H. Kuno and K. Aoki, *Phys. Earth Planet. Inter.* **3**, 273 (1970).
3. A. M. Stueber and M. Ikuramuddin, *Geochim. Cosmochim. Acta* **38**, 207 (1974).
4. W. B. Clarke, M. A. Beg, H. Craig, *Earth Planet. Sci. Lett.* **6**, 213 (1969); B. A. Mamyrin, I. N. Tolstikhin, G. S. Anufriyev, I. L. Kamenskiy, *Dokl. Akad. Nauk SSSR* **184**, 1197 (1969); E. W. Hennecke and O. K. Manuel, *Nature (London)* **257**, 778 (1975).
5. I. Kaneoka and N. Takaoka, *Earth Planet. Sci. Lett.* **39**, 382 (1978).
6. N. Takaoka, *Mass Spectrosc. (Tokyo)* **24**, 73 (1976).
7. J. E. Lupton and H. Craig, *Earth Planet. Sci. Lett.* **26**, 133 (1975); J. Dymond and L. Hogan, *ibid.* **38**, 117 (1978).
8. H. Craig and J. E. Lupton, *ibid.* **31**, 369 (1976).
9. B. A. Mamyrin, I. N. Tolstikhin, G. S. Anufriyev, I. L. Kamenskiy, *Geokhimiya* **11**, 1396 (1972).
10. H. Craig, J. E. Lupton, J. A. Welhan, R. Poreda, *Geophys. Res. Lett.* **5**, 897 (1978).
11. J. E. Lupton, R. F. Weiss, H. Craig, *Nature (London)* **266**, 244 (1977).
12. W. J. Morgan, *Bull. Am. Assoc. Pet. Geol.* **56**, 203 (1972); J. T. Wilson, *Can. J. Phys.* **41**, 863 (1963).
13. R. W. Kay and N. J. Hubbard, *Earth Planet. Sci. Lett.* **38**, 95 (1978).
14. G. B. Dalrymple and J. G. Moore, *Science* **161**, 1132 (1968).
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Stratospheric Sulfuric Acid Layer: Evidence for an Anthropogenic Component

Abstract. *Recent measurements of small aerosol particles in the stratosphere over Laramie, Wyoming, indicate low-concentration background conditions. A comparison of measurements made some 20 years ago with the present background concentration reveals the possibility of an increase of 9 percent per year. Since the aerosol particles are predominantly sulfuric acid droplets which form in the stratosphere from tropospheric sulfur-containing gases, such an increase may be related to man-made sulfur emissions.*

A layer of small aerosol particles has been known to be present in the stratosphere for some time. Although volcanic eruptions appear to increase the concentration of these particles, the question of whether such a layer would still be present in the absence of such volcanic activity has never been answered, to our knowledge. In this report we present measurements which address this question.

The stratospheric aerosol concentration has been measured by balloon-borne particle counters at Laramie, Wyoming (41°N), since 1971. Measurements at varying latitudes revealed the global time behavior of the aerosol layer during a low-concentration period in 1972 and 1973 (*1*-*4*). The enhancement of the stratospheric aerosol layer, due to the volcanic eruption of Fuego Volcano, Guatemala (14°N), in late 1974, was also studied in detail by means of particle counter measurements at Laramie (*5*). Continuation of the measurements during 1977 through 1979 has revealed another volcanically quiescent period, this time of greater duration than that in early 1974. These latter measurements now appear to have established the current background stratospheric aerosol concentration. The determination of such a background concentration is important because, being related to tropospheric sulfur-containing gases, it may be a measure of anthropogenic effects on the stratosphere and, because of the frequency and slow decay of large volcanic eruptions, this background concentration is probably reached, on the average, only every 10 or 20 years.

The layer of aerosol particles, which girdles the globe at a height of about 20 km, is responsible for the predawn and postsunset purple atmospheric glow and has become known as the stratospheric aerosol layer, sulfate layer, or Junge layer after its discoverer. Using particle impact samplers on balloons and aircraft during the period 1957 through 1960, Junge's group determined that for particles of radii 0.1 to 1.0 μm a relative concentration maximum exists in the altitude range from 18 to 23 km. Sample analysis revealed sulfur as the predominant element, and Junge and his coworkers postulated that a tropospheric sulfur-containing gas (such as SO_2 or H_2S), injected into the stratosphere, underwent a gas-to-particle conversion process (*6*).

Junge's pioneering measurements terminated shortly thereafter. Other researchers verified the existence of the layer, studied its composition, and delineated its structure (*7*). The substantial eruption in 1963 of Agung Volcano on Bali (8°S), considerably altered stratospheric conditions, increasing the stratospheric particulate loading by at least an order of magnitude in the Northern Hemisphere and probably more in the Southern Hemisphere (*7*). The observation of higher stratospheric aerosol concentrations for several years after 1963 cast suspicion and doubt on the considerably more conservative values Junge had measured before 1963. However, it now appears that during certain nonvolcanic periods the stratospheric aerosol concentration does decrease to very low but finite values and that Junge's measurements were probably correct.

The instrument that we used detects aerosol particles in situ during balloon ascent with a vertical resolution of about 250 m to an altitude of about 28 km. Through analysis of light scattered by individual particles as they are drawn through the instrument, the concentrations of particles in two size ranges, $r \geq 0.15$ μm and $r \geq 0.25$ μm, are determined. A detailed description of the instrument has been given in (*1*).

The time history of the maximum in the stratospheric particle mixing ratio (number of particles per milligram of air) from monthly balloon soundings through 1979 at Laramie is given in Fig. 1. The altitudes at which these maxima occurred were generally in the range of 18 to 23 km. The enhancement due to the Fuego eruption in late 1974 is apparent in Fig. 1, as is the accompanying change in size distribution; that is, the volcanic aerosol is characterized by a ratio of the mixing ratios for $r \geq 0.15$ μm to $r \geq 0.25$ μm of about 3, whereas for nonvolcanic

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periods this ratio is about 5.5. It appears that aerosol that could be identified with Fuego was probably absent by mid-1977, and we are apparently now observing the natural stratospheric aerosol background with peak mixing ratios of 6 particles per milligram for $r \geq 0.15$ μm and 1.1 particles per milligram for $r \geq 0.25$ μm (concentrations of 0.5 cm^{-3} and 0.1 cm^{-3} at 20 km, respectively). As shown in (*8*), the concept of a background aerosol concentration is supported by the fact that, when subtracted from the observed mixing ratio during the period of excess aerosol due to Fuego, the mixing ratio shows an exponential decay. This is the pattern one would expect the time variation to display for simple diffusion and sedimentation which holds throughout most of the volcanic aerosol decay phase, as indicated by the variation in size distribution.

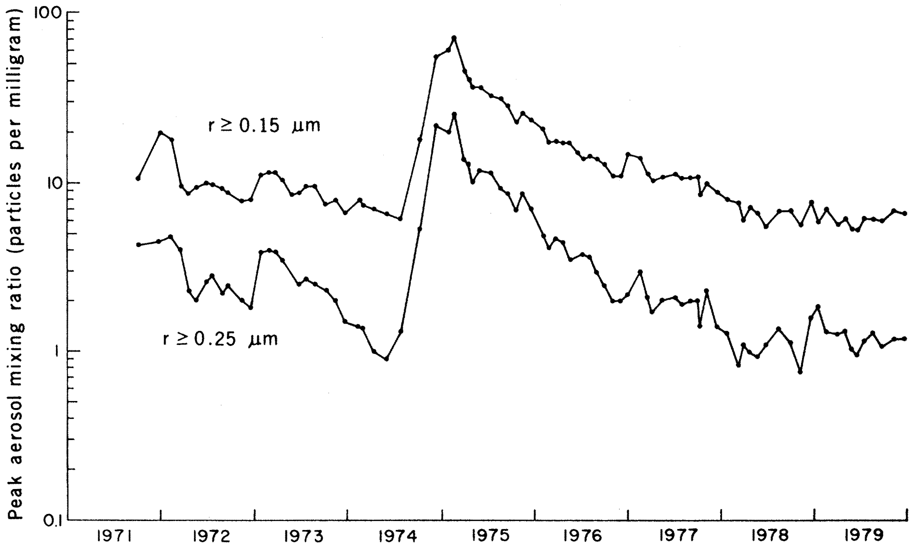

Fig. 1. Maximum in the stratospheric aerosol mixing ratio versus time from 87 balloon soundings at Laramie, Wyoming.

Most current models of stratospheric aerosol formation are based on the known H_2SO_4 composition of the aerosol and assume that H_2SO_4 vapor is formed in the stratosphere from tropospheric sulfur-containing gases and that the vapor condenses on preexisting condensation nuclei to form the aerosol (*9*). In the case of violent volcanic eruptions, sulfur reaches the stratosphere directly, probably in the form of SO_2, and after oxidation and hydration forms H_2SO_4 (*9*). We argue that the background aerosol is probably not due to direct volcanic injections because it has remained constant for nearly 2 years; the lifetime of these particles in the stratosphere is about 8 to 10 months (*8*). The possibility of small volcanic eruptions to the stratosphere occurring at the proper frequency and magnitude to sustain this background concentration now appears slim. Even the substantial eruption of La Soufriere, St. Vincent Island (14°N), in April 1979 (*10*) has not had any apparent effect on the 20-km stratospheric aerosol layer at northern mid-latitudes.

It is reasonable to postulate that the background aerosol is due to gaseous sulfur sources other than eruptive volcanic sources, that is, ones having a constant or at least very slowly varying time dependence. If one could show that this background does not vary with time, the possibility of anthropogenic contributions could be eliminated. On the other hand, if one could discern a slow time variation, future background concentrations could be predicted.

Among time-invariant tropospheric sources, we can identify sulfur-containing gases such as dimethyl sulfide [$(CH_3)_2S$] and CS_2 from the oceans (*11*), H_2S from marshy areas, and SO_2 from the average of all quiescent volcanic fumaroles and minor eruptions (*7*). Carbonyl sulfide (OCS) also may be a member of the latter component, although the volcanic source of OCS in minor eruption plumes was observed to be trivial in comparison to other sulfur compounds (*12*). Slowly varying sources would include most anthropogenic releases of sulfurous gases, primarily SO_2, OCS, and CS_2, the latter two from industrial sources such as coal combustion, coal gasification, refinery sulfur recovery plants, NO_x catalytic converters used in power plants and automobiles, oil shale-processing plants, and, in the case of CS_2, various commercial applications. It is estimated that 10^8 kg of CS_2 were released to the atmosphere by industrial processes in the United States in 1973 (*13*).

Although violent volcanic eruptions are quite capable of directly injecting SO_2 into the stratosphere, the eddy diffusion process which must be invoked to place quiescent tropospheric SO_2 emissions into the stratosphere is too slow to permit a gas as reactive and water-soluble as SO_2 to survive in appreciable concentrations (*14*). Consequently, sulfur must be transported into the stratosphere in the form of a gas other than SO_2 during volcanically quiescent periods.

Crutzen (*14*) suggested the possible stratospheric importance, during nonvolcanic periods, of OCS and CS_2, arguing that SO_2, H_2S, and $(CH_3)_2S$ react very strongly with the hydroxyl radical (OH) and that these compounds have estimated lifetimes in the troposphere of only a few days; the reaction of OCS with OH has a lifetime of about 500 days (*15*). According to Crutzen's mechanism of stratospheric aerosol formation, OCS diffuses into the stratosphere where it is photodissociated and eventually forms SO_2, thus avoiding the natural tropospheric SO_2 filter; CS_2 could also contribute to this mechanism, as both SO_2 and OCS are photolysis products of CS_2 (*16*).

Tropospheric concentrations of OCS, as determined by gas chromatographic analysis of air samples, seem uniformly in the 500-pptv (parts per trillion by volume) range globally (*17*). Stratospheric measurements of OCS (*18*), also determined by gas chromatographic analysis of collected samples, indicated values of about 15 pptv at 31 km whereas at 15 to 20 km values consistent with ground-level measurements (200 to 500 pptv) were observed. Spectroscopic measurements of stratospheric OCS (*19*) are in essential agreement with these data and confirm that the photodissociation process occurs predominantly between 20 and 30 km, just above the peak in the aerosol distribution.

Models of stratospheric aerosol formation suggest that OCS contributes a large fraction of the aerosol sulfur during nonvolcanic periods (*20*). In terms of budgetary considerations, 500 pptv of OCS at 15 km corresponds to a flux into the stratosphere of about 10^7 molecule cm^{-2} sec^{-1} (*14*), a value similar to that required to sustain the seasonal variations of the stratospheric aerosol during periods of volcanic inactivity (*1*).

Since OCS and CS_2 appear to be tropospheric sulfur sources of greater importance than SO_2 for the quiescent stratosphere and since their source may be largely anthropogenic, it appears worthwhile to investigate the possibility that the background aerosol is being formed predominantly by anthropogenic sulfur sources. One would expect the changes from such a source to be rather slow. From our data alone, a time variation in the background cannot yet be determined. The present 2-year background period is not long enough to permit a slope to be determined; and the previous low period in 1974, just prior to the eruption of Fuego (see Fig. 1), cannot be conclusively designated as a background period, as the mixing ratio did not level off. In order to investigate the possibility of a long-term variation, we must look to earlier periods when the stratosphere may have been in a background condition. This leads us to a consideration of the original measurements of Junge in 1959 to 1960. That this may have been a background period is suggested not only by the low concentrations measured by Junge but also by the fact that in 1977 normal incidence solar radiation at Mauna Loa Observatory in Hawaii very nearly returned to values measured in the period from 1958 to 1962 (*21*). These conditions had not been observed during the intervening period.

It was necessary to thoroughly review Junge's measurements to ascertain that they are indeed comparable to our data. We have determined that data obtained with custom-built, altitude-independent impactors in 1959 and 1960 best represent background conditions for $r \gtrsim 0.15$ μm aerosol (*8*). The data obtained with these impactors, measured on balloon flights between November 1959 and October 1960 at middle northern latitudes (*22*), are shown in Fig. 2 along with 19 background $r \geq 0.15$ μm profiles that we measured between March 1978 and January 1980. Except for one sounding, the 1960 profiles appear quite uniform with a peak concentration of about 0.1 ± 0.03 cm^{-3} at 20 km (a mixing ratio of about 1.1 ± 0.3 mg^{-1}). Figure 2 suggests that the 20-km aerosol concentration has apparently increased by a factor of about 5 during the approximately 20-year period.

The average upper tropospheric (10 to 12 km) aerosol concentrations have also apparently increased (and possibly by more than an order of magnitude) during the 20-year period (Fig. 2). It is difficult to reconcile this conclusion with the short tropospheric lifetimes involved. Even at the South Pole where local perturbations should be as small as one might find anywhere, we have found the tropospheric minima for $r \geq 0.15$ μm to be $\gtrsim 0.1$ cm^{-3} (*4*). Another possible explanation for this apparent discrepancy is that the size calibration of the custom-built impactor was seriously in error; however, an analysis of the calculated efficiency, based on the use of currently known aerosol parameters, did not reveal any sizable errors (*8*). Calibrations with aerosols of known size indicated that the impactors were functioning properly (*6*). For these reasons, the 1960 measurements are quite probably representative of $r \geq 0.15$-μm particle concentrations in the stratosphere for that period, but the lowest (12 km) points, obtained below the tropopause, remain questionable.

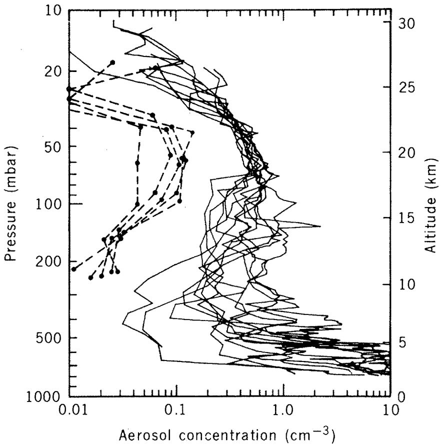

Fig. 2. Comparison of Junge's aerosol concentration profiles (broken lines) of 1959 to 1960 and 19 $r \geq 0.15$ μm profiles measured between March 1978 and January 1980.

If we assume that Junge's observation of 1.1 ± 0.3 mg^{-1} for $r \gtrsim 0.15$ μm represents a background condition for 1 January 1960 and that 19 years later it had increased to 6 ± 0.5 mg^{-1}, the time constant, if the increase proceeded exponentially, is 11.5 ± 2 years or an increase of 9 ± 2 percent per year.

In the measurements of atmospheric transmission at Mauna Loa, there was a possibility of a long-term decrease of about 0.2 percent from 1958 to 1976 (*21*). The albedo due to the stratospheric aerosol layer has been calculated to be about 0.1 to 0.15 percent for present aerosol concentrations and would have been about one-fifth as much in 1960 or negligible (*3, 8*). This would at least appear to be consistent with the atmospheric transmission trend.

There is some evidence that the background stratospheric aerosol concentration may have been increasing during the past 20 years at a rate of about 9 percent per year. This corresponds to a doubling time of about $7\frac{1}{2}$ years so that, if continued, an order of magnitude increase over present values could be expected in 25 years. Such an increase would be similar to that caused by the eruption of Fuego in 1974 and would cause a considerably enhanced twilight. Further sulfur emissions could result in permanent stratospheric temperature increases and surface temperature reduction, as apparently occurred in a transient but nonnegligible fashion after the eruption of Agung in 1963 (*23*).

A future increase in sulfur emission to the atmosphere does not seem unreasonable in view of the expected continued increase in coal utilization, catalytic conversion, and oil shale-processing with the resulting emission of OCS and CS$_2$ and the consequent stratospheric impact. Thus, if we are indeed presently observing the stratospheric aerosol background concentration and if even only a small part of this is anthropogenic, then the problem merits scrutiny. Careful monitoring of OCS, CS$_2$, and background stratospheric aerosol concentrations appears essential.

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References and Notes

1. D. J. Hofmann, J. M. Rosen, T. J. Pepin, R. G. Pinnick, *J. Atmos. Sci.* **32**, 1446 (1975).
2. J. M. Rosen, D. J. Hofmann, J. Laby, *ibid.*, p. 1457.
3. R. G. Pinnick, J. M. Rosen, D. J. Hofmann, *ibid.* **33**, 304 (1976).
4. D. J. Hofmann, J. M. Rosen, J. M. Kiernan, J. Laby, *ibid.*, p. 1782.
5. D. J. Hofmann and J. M. Rosen, *J. Geophys. Res.* **82**, 1435 (1977).
6. C. E. Junge, C. W. Chagnon, J. E. Manson, *J. Meteorol.* **18**, 81 (1961).
7. J. M. Rosen, *Space Sci. Rev.* **9**, 58 (1969); R. D. Cadle and G. W. Grams, *Rev. Geophys. Space Phys.* **13**, 475 (1975).
8. D. J. Hofmann and J. M. Rosen, *Univ. Wyoming, Atmos. Phys. Rep. AP-56* (1979).
9. J. M. Rosen, D. J. Hofmann, S. P. Singh, *J. Atmos. Sci.* **35**, 1403 (1978); R. P. Turco, P. Hamill, O. B. Toon, R. C. Whitten, C. S. Kiang, *ibid.* **36**, 699 (1979).
10. M. P. McCormick, P. Hamill, W. P. Chu, *Eos* **60**, 833 (1979).
11. J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, *Nature (London)* **237**, 452 (1972); J. E. Lovelock, *ibid.* **248**, 625 (1974).
12. R. D. Cadle, *J. Geophys. Res.* **84**, 6961 (1979).
13. T. O. Peyton, R. V. Steele, W. R. Mabey, *Carbon Disulfide, Carbonyl Sulfide: Literature Review and Environmental Assessment* (Publication PB-257947, National Technical Information Service, Springfield, Va., 1976).
14. P. J. Crutzen, *Geophys. Res. Lett.* **3**, 73 (1976).
15. M. J. Kurylo, *Chem. Phys. Lett.* **58**, 238 (1978).
16. W. P. Wood and J. Heicklen, *J. Phys. Chem.* **75**, 854 (1971); N. D. Sze and M. K. W. Ko, *Nature (London)* **278**, 731 (1979); *ibid.* **280**, 308 (1979).
17. F. J. Sandalls and S. A. Penkett, *Atmos. Environ.* **11**, 197 (1977); P. J. Maroulis, A. L. Torres, A. R. Bandy, *Geophys. Res. Lett.* **4**, 510 (1977).
18. E. C. Y. Inn, J. F. Vedder, B. J. Tyson, D. O'Hara, *Geophys. Res. Lett.* **6**, 191 (1979).
19. W. G. Mankin, M. T. Coffey, D. W. T. Griffith, S. R. Drayson, *ibid.*, p. 853.
20. O. B. Toon, R. P. Turco, P. Hamill, C. S. Kiang, R. C. Whitten, *J. Atmos. Sci.* **36**, 718 (1979).
21. B. G. Mendonca, K. J. Hanson, J. J. DeLuisi, *Science* **202**, 513 (1978).
22. C. W. Chagnon and C. E. Junge, *J. Meteorol.* **18**, 746 (1961).
23. J. E. Hansen, W.-C. Wang, A. A. Lacis, *Science* **199**, 1065 (1978).
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