On the meteoritic component of stratospheric aerosols

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ABSTRACT

The chemical analysis of aerosols collected at 19–21 km altitude on a polystyrene filter is reported. S and/or Cl, Fe, Na and Cr were detected. The mixing ratio of sulfur containing particulates at this altitude is $\leqslant 2.9 \times 10^{-9}$ g S/g dry air. The Fe/Na ratio is 1.2 ± 1.2 similar to that of crustal rocks. The chondritic meteorite component of the collected Fe and Na is < 10 %, and the annual influx of submicron chondritic material to the earth is estimated to be $< 9 \times 10^4$ metric tons.

Introduction

The chemical composition of stratospheric aerosols has been shown by JUNGE *et al.* (1961) and JUNGE & MANSON (1961) to consist primarily of sulfate, presumably a mixture of ammonium and sodium sulfates. In addition, aluminum, silicon, chlorine, calcium and iron were reported as being detected.

There are several different possible source materials which can contribute to stratospheric aerosols. These include atmospheric H_2S and SO_2 which are photochemically oxidized to sulfate, erosion products of continental surfaces, oceanic salts, volcanic debris and extraterrestrial material accreted by the earth. These sources are all significantly different as regards their chemical composition. Thus, it may be possible to determine the relative importance of such sources to stratospheric aerosols from a more thorough knowledge of the aerosol chemical composition. The purpose of this paper is to report some air concentrations of a number of elements in the low stratosphere and to relate these data to the extraterrestrial component.

Experimental

Aerosols were collected in the lower stratosphere by filtration utilizing a high altitude sampling U.S. Air Force airplane. The flight occurred February 5, 1965, over the continental United States at 39° N latitude over an altitude range of 19–21 km; the flight length was 3800 km. Because the amount of material collected was expected to be small, the inorganic contamination level of the filter must be extremely low. To minimize this contamination it was decided to use a "pure" organic filter composed of polystyrene fibers.

1. *Preparation of filters*

A technique to produce polystyrene fibers for filters has been described by THUMAN (1959). A similar technique for generating and collecting polystyrene fibers was constructed. Briefly, the process is: polystyrene is prepared by redistilling styrene monomer and polymerizing it by heating at 110°C. A 4–6 % solution of polystyrene in redistilled methylene chloride is prepared and placed in a polyethylene container fitted with a needle valve, nozzle and surrounding jet. Purified, filtered N_2 is used to force the polystyrene solution out of the nozzle. Upon evaporation of the solvent, fibers of polystyrene remain which are collected on a dacron scrim. The generation of these fibers is done inside a 60 cm diameter tube with a blower at one end. Air, which is drawn through Delbag polystyrene filters, carries the polystyrene fibers to the scrim. A mat is built up until the pressure drop across it is ~ 25 mm H_2O at a flow rate of ~ 75 cm/sec. The weight of the mat is ~ 4 g/10^3 cm^2. The fibers are fairly uniform in size, ranging from 0.05–0.5 μm in diameter, Fig. 1. A schematic diagram of the filter making apparatus is shown in Fig. 2. The mat with its backing is placed in the aircraft filter holder which is then

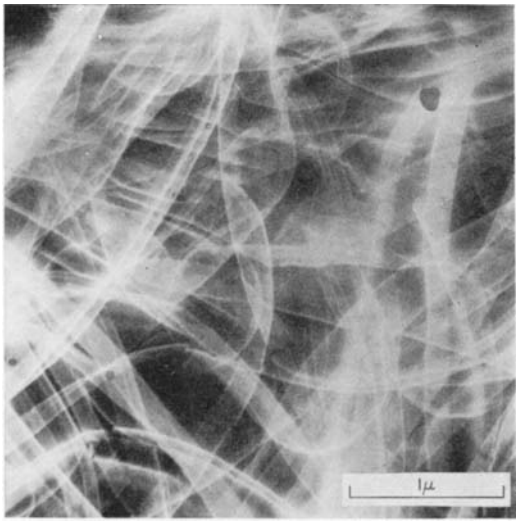

FIG. 1. Electron micrograph of polystyrene fibers generated from a 4 % solution.

sealed in polyethylene and delivered to the aircraft. A series of blank control filters was prepared in the same manner from the same polystyrene solution, placed in filter holders and installed on the aircraft.

2. *Analysis*

After the flight, an aliquot of the filter was taken, ~300 cm², corresponding to approximately one fourth of the total filter area. Analysis for a number of elements was performed by the technique of neutron activation. The filter aliquot was irradiated for 4 hours at a thermal neutron flux of 1×10^{13} n/cm² sec. A Co–Al wire monitored the total number of neutrons during the irradiation. The sample was received in the laboratory approximately 12 hours after the end of the irradiation.

The sample was placed in a flask with carriers for Na, S, Cr, Mn, Fe, Co, Cu, Sr, and Au and decomposed by vacuum destructive distillation. After treatment with HNO_3, $HClO_4$ and then HCl the sample was placed on a cation column. $AuCl_4^-$ and $SO_4^=$ pass through the column. Au was purified by extraction into ethyl acetate followed by reduction to the metal with hydroquinone. The 418 Kev γ of Au^{198} was counted and followed for decay. $BaSO_4$ was precipitated from the aqueous phase after the ethyl acetate extraction and β counted with an end window proportional counter. An absorption curve was measured to ensure that S^{35} was the activity.

The cations were eluted from the column and CuS precipitated. The Cu was purified by a $Fe(OH)_3$ scavenge, reduction to Cu^+ and precipitation of CuSCN. The positron anihilation radiation, 0.51 Mev, was measured and the 12.9 h decay of Cu^{64} followed. $Fe(OH)_3$ was precipitated with NH_4OH along with $Cr(OH)_3$ and $Mn(OH)_2$. These hydroxides were dissolved in HNO_3 and MnO_2 precipitated with $NaBrO_3$. The MnO_2 was dissolved and reprecipitated and the 0.84 Mev γ of 2.58 h Mn^{56} measured and its decay followed. $Fe(OH)_3$ was precipitated from the first bromate filtrate, and Fe purified by extraction into isopropyl ether followed by reprecipitation of the hydroxide and ignition to Fe_2O_3. The 1.10 and 1.29 Mev γ's of Fe^{59} were counted. $BaCrO_4$ was precipitated from the first bromate filtrate, perchromic acid was extracted into ethyl ether and back extracted into NH_4OH. The 0.32 Mev γ of Cr^{51} was counted. CoS was precipitated from the NH_4OH filtrate and Co purified by anion exchange, $Fe(OH)_3$ scavenging, and electroreduction to the metal. The 1.17 and 1.33 Mev γ's of Co^{60} were counted. $SrCO_3$ was precipitated from the CoS filtrate, purified and collected as $SrCO_3$. After weighing, it was dissolved in HCl and Y^{90} allowed to grow into equilibrium. The Y^{90} was milked, β counted and the 64 h decay was followed. Sodium zinc uranyl acetate was precipitated from the $SrCO_3$ filtrate and converted to NaCl. The 1.37 and 2.76 MeV γ's of 15 h Na^{24} were measured and the decay followed.

The Co–Al monitor wire was weighed and the Co^{60} determined by γ counting after several weeks. In all irradiations the Co^{60} disintegration rate corresponded to within 10 % of a flux of 1×10^{13} n/cm² sec.

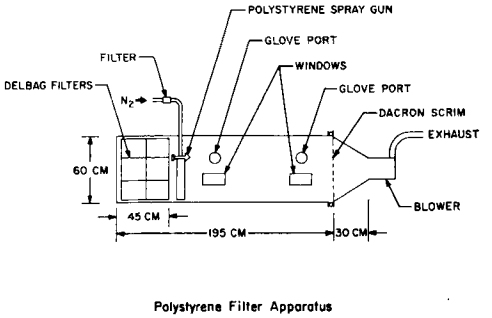

FIG. 2. Schematic of polystyrene filter preparation.

TABLE 1. *Analysis of filter blanks.*

Filter	Na ppm	S[a] ppm	Cr ppm	Mn ppm	Fe ppm	Co ppb	Cu ppm	Au ppb
1	1.66		0.20		1.99	7.3	1.35	5.99
A	0.47		1.20		4.70	36.5	0.82	4.44
B	0.38		0.84		4.06	30.0	1.22	2.44
5A	0.53		0.25		1.31	11.1	0.53	2.49
5B	0.65		0.61		2.47	12.4	0.40	4.65
9A	2.28	491	0.80	0.112	2.91	30.1	0.61	9.93
9B	3.23	648	1.07	0.192	5.19	28.3	0.52	9.43
9C	1.58	466	1.58	0.298	6.25	47.8	0.72	
9D	1.99	504	0.56	0.181	5.37	31.0	0.51	8.77
4A	4.69	143	1.33	0.396	10.30	33.6	3.41	
4B	0.19	382	0.38	0.105	2.59		0.65	6.84
4C	2.39	566	2.72	0.376	8.52	36.9	3.25	
4D	1.57		3.11	0.400	9.80		1.68	
Average	1.66 ± 1.25	457 ± 149	1.13 ± 0.86	0.258 ± 0.117	5.04 ± 2.85	27.7 ± 11.9	1.21 ± 0.98	6.11 ± 2.68
Delbag	3.07	11,600	0.19	0.135	3.9	7.4	7.1	5.79
IPC	67.4 ± 9.5		0.03	0.03 ± 0.05	11.2 ± 0.6	$27. \pm 8$	1.67 ± 0.07	4.5

[a] Maximum S due to Cl interference.

Results

Using the Co^{60} monitor data the activities of each of the measured nuclides, except Sr^{90}–Y^{90}, were converted to mass of element present using tabulated neutron cross section data. Although some of these cross sections are not known too accurately, they are all known to better than a factor of two. Any errors in the mass of a particular element will be common to all the measurements, so the relative amounts will be correct.

A total of 13 blanks from four control filters previously described were analyzed in the same manner. These filters went through the identical handling steps as the exposed filter, including fabrication, installation and recovery from the same aircraft and neutron activation analysis. In addition, results obtained for Delbag Microsorban polystyrene filter and IPC cellulose filter material used in the Star Dust project are given in Table 1. The values for the 13 blanks unfortunately are not as uniform as one would like with resulting standard deviations ranging from 33–81 %. Comparing the contamination levels of the two polystyrene filters it is seen that the one prepared by us has less contamination for S and/or Cl, Na and Cu, approximately equal contamination for Mn, Fe and Au, and greater contamination for Cr and Co. The IPC filter contains more Na and Fe, equal levels of Co, Cu and Au, and less contamination for Cr and Mn.

The flown filter was analyzed in three aliquots. Each sample was weighed, activated, and treated as the blanks. From the average value of the 13 blanks the estimated contamination in the aliquot was determined and the net mass of each element determined. In each aliquot the Sr^{90} content was measured and the volume of air sampled computed using 11 dpm Sr^{90}/m^3 air STP as the Sr^{90} content of the low northern stratosphere in February 1965 (FEELY, 1965). The uncertainty in the volume measurement is approximately 25 %. The last column in Table 2 gives the air concentrations as determined, or upper values when appropriate. The error in each number is based solely upon the standard deviation of the 13 blanks. Counting, weighing errors, etc. are small compared to the blank scatter and are not included. An arithmetic mean has been calculated for the element concentrations, otherwise the upper limit is the average of the individual errors, i.e., Mn, Cu and Au.

Although the errors are large, a number of conclusions can be drawn. The detectable elements appear to be S and/or Cl, Fe, Na and Cr in decreasing order of air concentration. Un-

TABLE 2. *Summary of flown filter results.*

Element	Sample[a]	Total μg	Blank Correction μg	Mass Concentration 10^{-14} g/cm³ air STP
Na	2A	8.16	3.76 ± 2.83	2.29 ± 1.45
	2B	7.97	2.89 ± 2.18	4.45 ± 1.91
	2C	4.53	3.32 ± 2.50	0.81 ± 1.66
				2.52 ± 1.54
S	2B	1607	796 ± 260	712 ± 228
	2C	972	914 ± 300	38 ± 198
				375 ± 347
Cr	2A	2.45	2.56 ± 1.95	-0.06 ± 1.02
	2B	2.70	1.97 ± 1.50	0.64 ± 1.31
	2C	2.82	1.26 ± 1.72	0.35 ± 1.13
				0.31 ± 0.28
Mn	2B	0.42	0.45 ± 0.30	-0.03 ± 0.26
	2C	0.45	0.52 ± 0.24	-0.05 ± 0.16
				$\leqslant 0.21$
Fe	2A	10.6	11.4 ± 6.4	-0.41 ± 3.32
	2B	14.9	8.8 ± 5.0	5.33 ± 4.38
	2C	16.5	10.1 ± 5.7	4.24 ± 3.78
				3.05 ± 2.49
Co	2A	.093	$.063 \pm .027$	$.016 \pm .014$
	2B	.041	$.048 \pm .021$	$-.006 \pm .018$
	2C	.045	$.056 \pm .024$	$-.007 \pm .016$
				$.001 \pm .010$
Cu	2A	2.58	2.74 ± 2.22	$-.08 \pm 1.16$
	2B	1.74	2.11 ± 1.71	$-.32 \pm 1.48$
	2C	1.58	2.42 ± 1.96	$-.56 \pm 1.31$
				$\leqslant 1.32$
Au	2A	.0295	$.0138 \pm .0061$	$.0081 \pm .0032$
	2B	.0051	$.0107 \pm .0047$	$-.0056 \pm .0042$
	2C	.0042	$.0122 \pm .0054$	$-.0080 \pm .0035$
				$\leqslant .0036$

[a] The volumes of air sampled by $2A = 1.92 \times 10^8$ cm³ STP; $2B = 1.14 \times 10^8$ cm³ STP; $2C = 1.51 \times 18^8$ cm³ STP.

fortunately, the S and Cl concentrations cannot be resolved because of interfering reactions. Sulfur was analyzed by measuring the S^{35} induced activity in the sample produced by the $S^{34}(n,\gamma)S^{35}$ reaction. However, any chlorine present will also produce S^{35} via the $Cl^{35}(n,p)S^{35}$ reaction. The cross sections for these reactions are comparable but the isotopic abundance of Cl^{35} is 75 % while that of S^{34} is only 4 %. Thus, any chlorine present will significantly interfere with the sulfur analysis. The filter material is produced from a chlorinated solvent which probably is the cause of the high sulfur blank. The maximum particulate sulfur concentration of 3.75×10^{-12} g S/cc air STP corresponds to a mixing ratio $\leqslant 2.9 \times 10^{-9}$ g S/g dry air. The upper limit for the particulate sulfur mass concentration per unit volume of air at ~ 20 km altitude, where $\varrho = 8.89 \times 10^{-5}$ g/cc, is 2.6×10^{-18} g S/cc. This is approximately 60 times larger than the estimated value of JUNGE *et al.* (1961), which covered particles in the 0.23–1.48 micron radius range. More recently, Friend *et al.* (DEFENCE ATOMIC SUPPORT AGENCY, 1964) have collected aerosols at 60,000 feet covering a size range of 0.14–0.74 μm radius. The mean volume concentration of the aerosol was determined to be 1.7×10^{-14} cm³/cc. Analysis indicated the particles consisted primarily of ammonium sulfate and/or ammonium peroxy disulfate. Assuming a density of 2 for this aerosol and a 25 % sulfur content, the sulfur mass concentration is 8.5×10^{-15} g S/cc, corresponding to a particulate S mixing ratio of 7.3×10^{-11} g S/g air. MARTELL (1965) has reestimated the total aerosol mixing ratio in the lower stratosphere using the data of JUNGE *et al.* (1961). Taking into account both Aitken nuclei and a generally accepted large particle distribution which decreases more steeply with radius than indicated by JUNGE *et al.* (1961) the total aerosol mixing ratio at 20 km is estimated to be 6.7×10^{-11} g/g dry air. This corresponds to a S mixing ratio of $\sim 2 \times 10^{-11}$ g S/g air assuming the aerosol is primarily ammonium sulfate and/or sulfuric acid. Because of the large uncertainty in the sulfur measurements reported in this paper it is premature to consider any discrepancy with the other measurements and calculations.

This work began in an attempt to measure the meteoritic component of stratospheric aerosols. Because of the very low signal to noise ratio not much can be said but a few calculations bearing on the subject can be performed.

It is reasonable to assume that the chemical composition of extraterrestrial material accreted by the earth, i.e., micrometeorites, meteors, cosmic dust, is chondritic. The Fe/Na ratio in chondrites is 36, whereas the ratios for average crustal rocks and oceanic salts are 1.8 and 10^{-8} respectively. The measured ratio in the collected sample is 1.2 ± 1.2. Although the error is large the indications are that chondritic type material contributions are small if indeed present. The ratio is most easily explained by a mixture of 2/3 crustal rock and 1/3 oceanic salt. A 2σ

confidence level gives a maximum Fe/Na ratio of 3.6. If we consider a model of crustal rocks plus chondritic material or oceanic salts plus chondritic material then the meteoritic component in either case is $<10\,\%$ of the total Fe + Na. NEWKIRK & EDDY (1964) have estimated the relative concentration of meteoric debris in aerosols at 20 km and conclude that over the size range 0.1–2.0 μm it represents a negligible fraction, $<10\,\%$. Above 25 km, however, it apparently represents a major part of the dust for $r > 0.3$ μm.

Finally an upper limit to the submicron influx rate of extraterrestrial material to the earth can be calculated. Assuming that all of the Fe in the filter sample is from chondritic material, i.e., 25 %, the meteoritic mass concentration is 1.2×10^{-13} g/cc air STP. If we assume the stratosphere is uniformly mixed then the total inventory of meteoritic material in this reservoir is $\leqslant 9.3 \times 10^{10}$ g, taking the mass of air in the stratosphere as 10^{21} grams. The residence time of stratospheric radioactive fallout is the order of 1 year, which means that in steady state the influx rate to the stratosphere is equal to the stratospheric inventory. Hence, an upper limit to the submicron chondritic material influx rate is $<9 \times 10^4$ metric tons per year. It should be emphasized that this calculation is valid only for particles with a 1 year stratospheric residence time. Calculations of fall velocities (JUNGE *et al.* 1961) of spherical particles of density 2 as a function of size and altitude limit such particles to <1 μm radius. Estimates of extraterrestrial particle accretion by the earth cover a wide range from 8 to 3.6×10^6 metric tons per year; see SCHMIDT (1963) for a summary of the data. The highest estimates reported were obtained from satellite measurements whereas most of the other values were obtained from analysis of particles collected in polar snows and ocean sediments. All of these measurements included particles with radii > 1 μm. The contribution of such particles to the total influx mass depends upon the size distribution function. NEWKIRK & EDDY (1964) approximate the distribution as $r^{-3.5}$ for $0.1\ \mu\text{m} < r < 3\ \mu\text{m}$ so that particles of a few μm in size will still contribute to the total mass. For $r > 3$ μm the distribution varies much more steeply with r and only a small fraction of the total mass is contained in such particles.

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МЕТЕОРИТНЫЙ КОМПОНЕНТ СТРАТОСФЕРНЫХ АЭРОЗОЛЕЙ

Докладываются результаты химического анализа аэрозолей, собранных на высоте 19–21 км с помощью полистиреннового фильтра. Обнаружены S и (или) Cl, Fe, Na, Cr, Co. Концентрация частичек на этой высоте меньше или равна $5 \cdot 10^{-9}$ г S на г сухого воздуха. Отношение Fe/Na равно $1{,}5 \pm 1$ т. е. аналогично этому отношению для горных пород. Доля вещества каменных метеоритов в собранных аэрозолях меньше 10%, и годовой приток этой материи оценивается в $1{,}5 \cdot 10^6$ м.