Appendix A: Analysis of sulfur isotopic composition of stratospheric sulfate aerosol from filter samples from the AIRSTREAM program, 1973-1974

in collaboration with Albi Romero (UCSD), Nicolas Patris (UCSD), and Joel Savarino (UCSD)

A.1. Introduction

The only previous measurements of the sulfur isotopic composition of stratospheric sulfate were made by *Castleman et al.* [1973]. The reported data covers the period immediately preceding the volcanic eruption at Mt. Agung in 1963 and a 10-year period following [*Castleman et al.*, 1973]. The data of *Castleman et al* . [1974] yields δ^{34}S ~ 2.6 +/- 0.3 ‰ for stratospheric sulfate.

Steady-state, quiescent periods in the Junge Layer may be difficult to define. Even minor volcanic eruptions can affect SSA concentrations significantly [*Sedlacek et al.*, 1983]. We have, therefore, attempted to corroborate the early measurements of *Castleman et al*. [1974] with measurements of sulfur isotopic compositions of SSA particles from recognized periods of minimal SSA loading. Furthermore, since the aerosols may reflect the isotopic composition of local sources and transport history, it is necessary to measure the isotopic composition of SSA particles at different latitudes and altitudes.

In this aspect of our work, we measured the sulfur isotopic concentration ratio in the sulfate aerosol collected on composition filter samples which have been stored in the DOE's Environmental Measurements Laboratory (EML). The analyses were performed in collaboration with Mark Thiemens' group at UCSD. Aerosol samples were obtained during the AIRSTREAM project as part of the DOE's HASP (High Altitude Sampling Program), which ran several independent missions from 1957 to 1983 [*EML*, 2002]. Samples were collected at altitudes up to 19 Km.

In addition to determination of the ^{34}S composition, the less abundant ^{33}S and ^{36}S isotopes were also quantified, and will be reported elsewhere [*Romero*, 2002].

For this study, we chose samples collected during the 1973-1974 timeframe, which has been identified as a relatively quiescent period in the domain of the Junge Layer [*Sedlacek et al.*, 1983]. *Sedlacek et al.* [1983] factored into account the effects of minor volcanic eruptions on sulfur aerosol concentrations over an extended period and at various latitudes.

Since this phase of research is ongoing, present results are quite preliminary. Additional samples from the EML archives are also available from early 1979, a period that is also generally acknowledged as representative of a minimum in SSA. However, these samples have not been analyzed at this time.

A.2. Experimental Procedure

Filter samples of stratospheric aerosol which were collected between 1973 and 1974 were obtained from the Environmental Measurements Laboratory in New York, New York (see Appendix 5.1). Samples were prepared and experiments performed at the University of California, San Diego (UCSD). The filter paper used for sample collection was IPC 1478, developed by the Institute of Paper Chemistry in Appleton, WI. The filters are constructed from second-cut cotton linters, are backed for added support with a cotton scrim, and are impregnated with Kronisol (di-butoxyethyl phthalate). The filters obtained were either whole or partial segments of 9” diameter filters. Several of the samples appeared to be slightly discolored. Similar discoloration was found on blanks obtained from the same storage facility. Analyses of the blanks by ion-exchange chromatography showed only minor contamination by sulfur. However, we were unable to quantify the isotopic composition of these sulfur contaminants because of the very low concentrations that were detected (~ 0.1 μmol S).

Since the aerosol loading in the Junge Layer is low, there were also low levels of sulfur present on a given filter. As a consequence, pairs of filters were combined into a single sample. The experimental procedures, which have been developed in the Thiemens laboratory, are described in detail elsewhere [*Bains-Sahota and Thiemens*, 1988; *Bao and Thiemens*, 2000; *Savarino et al.*, 2001].

Individual filters were extracted with 50 mL of millipore water, re-extracted in 2 parts of 35 mL each. The three extractions were combined with the extract from other filters. This extract was then separated on an ion-exchange column. The sulfate is precipitated as $BaSO_4$, and then reduced to H_2S in a mixture of concentrated H_3PO_2 (50% in solution), HI (57% in solution), and HCl (12 N). The liberated H_2S was treated with cadmium acetate to form CdS, then with silver nitrate to form Ag_2S. The Ag_2S is treated with BrF_5 to form SF_6. The SF_6 was then introduced into the mass spectrometer for the analysis of sulfur isotopes (Figure A.1). Conversion of SO_4^{2-} to SF_6 instead of SO_2 allows ^{33}S and ^{36}S as well as ^{34}S to be quantified.

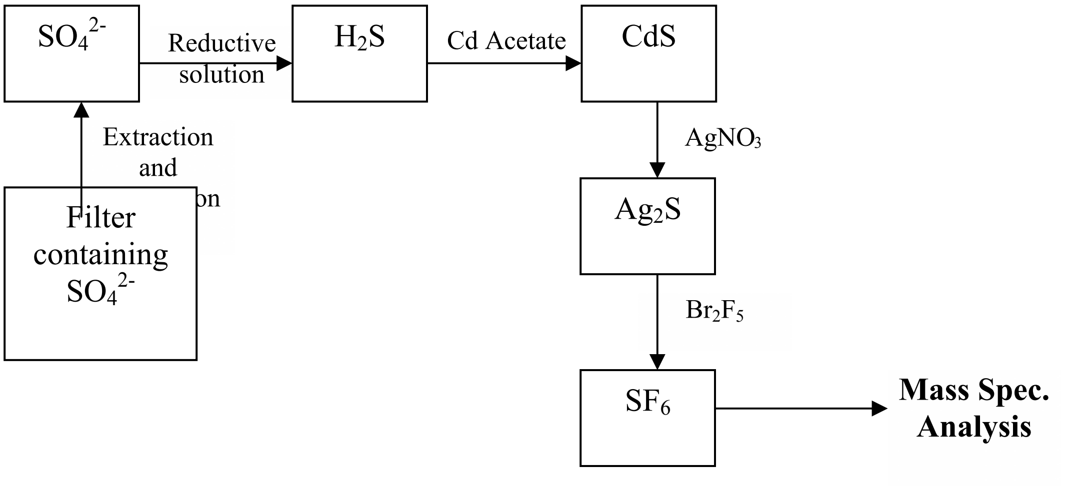

Figure A.1: Schematic for analysis of sulfur isotopes of AIRSTREAM filter samples

Only two samples (4 filters in total) have been analyzed to date. In this preliminary analysis, samples were passed through a silver membrane following purification on the ion-chromatograph to trap the isolated sulfate as Ag_2SO_4, which was then pyrolyzed into SO_2 and O_2. This procedure allows both oxygen and sulfur isotopes to be measured [*Savarino et al.*, 2001]. However, using this scheme, we were unable to recover O_2, and there were significant sulfate losses. We attribute these losses to the presence of trace organic contaminants that we were unable to separate completely from the sulfate. In addition, the organics consumed O_2 upon heating. Under the present experimental conditions, the oxygen (^{18}O and ^{17}O) isotopic composition of the SO_4^{2-} cannot be analyzed. Because the filters are irreplaceable, we have opted to wait until we have developed a better method of purifying the samples of trace organics before proceeding with further experiments.

SF_6 was purified by distillation in a 3-step process, using at each step in a coldfinger bath maintained at -120 ºC in an ethanol/liquid nitrogen slurry. The SF_6 from each of the three steps was allowed to remix, and then re-extracted by the same method. The SF_6 was then purified on a HP 5890A Gas Chromatograph.

The isotopic composition of the SF_6 was measured on a Finnigan MAT 252 Mass Spectrometer that is able to measure $\delta^{36}S$ and $\delta^{33}S$ in addition to $\delta^{34}S$. An SF_6 standard, which was prepared previously and standardized at UCSD, was used

A.3 Results and Discussion

Both pairs of filters that were fully analyzed were collected on June 1973, at northern mid-latitudes, at an altitude of 19.2 km. Sample 7050 was collected at 28-31 °N, 95-100 °W and Samples 7073 and 7075 were collected at 43-40 °N and 112-110 °W. Mass spectrometric measurements show that $\delta^{34}S$ (7050 a+b) = 6.51 ± 0.4 ‰ and $\delta^{34}S$ (7073+7075) = 6.77 ± 0.4 ‰. These measurements are within the experimental uncertainty of one another, and qualitatively similar to the value of $\delta^{34}S$ 2.6 +/- 0.3 ‰ measured for "background" stratospheric sulfate aerosol by *Castleman et al* [*Castleman et al.*, 1973; *Castleman et al.*, 1974].

As noted above, distinct periods of volcanic quiescence are difficult to identify. The last major volcanic eruption before 1973 occurred in 1963 (Mt. Agung,), although minor volcanic eruptions could have increased the aerosol loading significantly. Thus, the loading of the Junge Layer rarely achieved a true steady state. The 11 month period from May 1973 to April 1974 has been identified as being relatively free of volcanic eruptions, including the possible influence of minor volcanic eruptions, by Sedlacek et al.

(1983). Their conclusions were based on the sulfate concentration. However, it is difficult to determine on concentration data alone whether the 1973-1974 minimum was in fact representative of a true steady-state background level of stratospheric sulfate aerosol.

Corroborative evidence such as the isotopic data of *Castleman et al.* [1973, 1974] or the detailed analysis of aerosol distributions [*Thomason et al.*, 1997] is needed. Neither the SAGE (SAGE I: 1979-1981; SAGE II: 1984 +) nor SAM II (Stratospheric Aerosol measurement II 1978 +) instruments were operational during 1973-1974. To our knowledge, there are no corroborative studies covering this period of time.

Another quiescent period has been identified by *Sedlacek et al.* [1983] during the period between October 1978 and October 1979. Aerosol loading and distribution profiles retrieved from the SAGE II instrument [*McCormick*, 1993; *Thomason et al.*, 1997] supports the contention that the boreal spring of 1979 (between March 23 and June 21) appears to be a true minimum.

A.5. Conclusions

Analysis of sulfur composition of sulfate collected on filters during the HASP Airstream project from June 1973 yield a value of $\delta^{34}S \sim 6.6$ ‰, which is in qualitative agreement with the results reported by Castleman et al.(1974). However, uncertainties regarding both the aerosol loading levels and the possibility of sample contamination cannot be ruled out.

Samples collected during the 1979 quiescent period as well as those from later during the 1973-74 period need to be analyzed for $\delta^{34}S$ in order to corroborate the preliminary results presented here.

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Appendix A.A.1: List of samples obtained from the EML archives of the HASP Airstream Project

Year	**Month**	**Filter ID**	**Latitude**	**Longitude**	**Altitude, Km**
Tropics					
1973	6	7003	5-8 S	79-79 W	18.2
1973	6	7005	1-5 N	79-79 W	18.2
1973	6	7037	3S-1N	79-79 W	19.2
1973	6	7039	5-8 N	79-79 W	19.2
1973	9	7278	11-9 N	80-79 W	19.2
1973	9	7372	6-3 S	79-79 W	19.2
1973	9	7396	13-9 N	81-79 W	18.2
1974	1	7883	7-3 S	80-80 W	18.2
1974	1	7916	7-3 S	80-80 W	18.2
1974	1	7938	7-3 S	80-80 W	19.2
Midlatitudes					
1973	5	**6957**	25-29S	73-72W	18.2
1973	6	**6937**	32-29N	102-96W	18.2
1973	6	**6940**	27-25N	93-90W	18.2
1973	6	**6994**	37-33S	65-68W	18.2
1973	6	**7050**	28-31N	95-100W	19.2
1973	6	**7051**		100-106W	19.2
1973	6	**7073**	43-40N	112-110W	19.2
1973	9	**7235**	40-37N	110-108	19.2
1973	9	**7256**	37-33S	65-67W	19.2
1973	9	**7265**	28-31N	39-100W	19.2
1974	1	**7873**	43-40N	113-111W	18.5
Polar					
1973	6	**7109**	72-69 N	143-144 W	18.9
1973	6	**7111**	67-65 N	145-146 W	19.2
1973	6	**7135**	62-65 N	138-147 W	18.5
1973	9	**7304**	72-69 N	145-146 W	19.2
1973	9	**7306**	67-65 N	147-148 W	19.2
1973	9	**7341**	59-62 N	130-138 W	19.2
1973	11	**7517**	67-65 N	145-146 W	18.2
1974	1	**7821**	72-69 N	143-144 W	18.9
1974	1	**7929**	59-62 N	132-139 W	18.9
1974	4	**8134**	72-69 N	143-144 W	18.9