16 pages

Final Report NASA Contract NAG2-28

VOLCANIC IMPACT ON STRATOSPHERIC AEROSOL CHEMISTRY

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Final Report Covering the Period March 1980 to December 1983

A. Project Summary

This project was initiated as a supplemental program to analyze filter samples collected by the National Center for Atmospheric Research (NCAR) group using the multiple-filter sampler on the U-2. Al Lazrus and Bruce Gandrud of NCAR designed and built the sampler which was capable of exposing a number of 110-mm filters in sequence to ram air flow. Two types of filters, IPC cellulose and polystyrene, were used throughout this study, both of which had high blank levels for the trace elements determined. The levels of most trace elements in the stratosphere are so low under normal circumstances that none can be seen. During periods of volcanic injection into the stratosphere the levels of many elements are significantly higher and measurements of the ash content can easily be made. Following the eruption of Mt. St. Helens, samples collected in the stratosphere contained significant levels of ash that appeared to be unfractionated during the eruption, as it had a composition similar to that of the volcanic rocks and ash found around the mountain.

During 1982, a "mystery cloud" appeared in the stratosphere and samples of this revealed that it was also of volcanic origin. Although the volcano which produced this cloud was never identified, it was probably one of the Indonesian volcanoes, which were erupting during this time period. Following the El Chichonal eruption in 1983, several U-2 flights were made to sample the stratospheric cloud. On one of these flights a polystyrene filter was exposed, which showed the presence of large quantities of sulfur, but no other elements in excess of the filter blanks.

To improve the collection of particles for chemical analysis, a new sampling system was developed for use on the U-2. This sampler consisted of an electrostatic collection of particles between 1- and 0.01-μm diameter directly onto electron microscopic grids, followed by a thermal precipitation for the

smaller particles. The system was built and tested in the laboratory, but due to the time scale for construction and the end of this project, the sampler was never flown on the U-2.

B. Description of the Sampling System and Filters Used

The sampling system that was used for this study was designed and built at NCAR by Bruce Gandrud and Al Lazrus (1). This system used ram flow to bring air into the wing tank of the U-2 aircraft, where 110-mm filters can be placed in the air stream to collect the particles. The primary use of the system was to measure sulfate and other water-soluble ions found in stratospheric particulates. Our portion of the project involved the analysis of the samples by instrumental neutron activation analysis (INAA) to investigate trace element concentrations.

The two types of filters used had relatively high blank values for trace elements. The cellulose IPC filters, which are normally used for stratospheric sampling, are relatively free of water soluble ions, but contain very high levels of trace elements. The polystyrene filter had lower blanks, but had much lower flow rates and were, therefore, unacceptable. Table 1 gives a comparison of the flow rates of the two filter types in the U-2 along with those for two much cleaner filter types used on the ground at the South Pole for the collection of atmospheric particles for chemical analysis. From this table it is obvious that the IPC filters have almost a factor of ten higher flow rate than the other filters used. The blank values for the four types of filters discussed are shown in Table 2. From these data, it is easy to see that for most elements shown, the blank values for the IPC filters are much higher than those for any of the other filters. The low flow rates of the polystyrene make them useless, as their blank levels are not low enough to compensate for the low flow rate.

In Table 3, results are shown for calculations of the time required to collect a sample equal in concentration to a blank filter using the flow rates (Table 1), blank values (Table 2) and assuming a concentration of each element in the air sample equal to that found at the South Pole (2). This calculation can be used as a gauge of the chances of measuring elemental concentrations at a relatively clean location. The South Pole is the cleanest location on the earth's surface, and probably represents a maximum level for the stratosphere when no volcanic injections have occurred. For the IPC filters the only elements that have a chance of being observed in the clean, unperturbed stratosphere are Br, As and Se. The polystyrene filters are even worse, with only Br and Sb being equal to blank values with a sampling time of approximately one day. The Nuclepore filters likewise are not very good, and the Fluoropore filters appear as the best possibility to obtain data on low stratospheric concentrations of trace elements. These filters must be pumped as they creat a large pressure drop across them when used. We proposed to contruct a sampler to use these filters, but due to size constraints and cost, a pumped system of sufficient capacity could not be designed and we chose to develop a sampling system for single particle measurements which allow one to drastically reduce the blank values. During the term of this project a total of approximately 80 filters and blanks were analyzed for nearly 35 elements and sulfur wasn't the only element routinely observed over blank levels. During periods of volcanic activity many other elements were also observed on the filters as indicated in the reprints enclosed.

Because of the high blank levels in filters available to us as piggy back experimenters, we could obtain useful information only on samples collected by the U-2 during volcanic events in the stratosphere. Another area of work that was successful was the measurement of radioactivity on the filters. Gamma-ray

measurements of ^{7}Be and fission products from Chinese nuclear weapon tests were done on all samples collected by the U-2.

C. Studies of Mt. St. Helens Stratospheric Plume (1980)

Samples of ash and particles were collected by the NASA U-2 aircraft on May 19, 1980 following the eruption of Mt. St. Helens. These samples were analyzed by INAA for 35 elements. The results published in Science (3) showed that the chemical composition of particles in the stratospheric plume was very similar to that of ash that fell out near the volcano and the rocks that make up the volcano. Apparently very little chemical fractionation occurred during the eruption, as the primary ash cloud in the stratosphere was produced by a phreatic explosion. Later sampling of the plume during more quiescent phases showed that the chemistry of the plume reflected the enrichment of many elements as volatile halide compounds. This enrichment process was not important in the earlier explosion that reached the stratosphere as evidenced by the stratospheric data (see Sect. J), but was very significant for low level tropospheric injection.

D. Studies of the Mystery Cloud (1982)

During the Spring of 1982, a cloud was observed in the stratosphere by Lidar measurements at Mauna Loa in Hawaii and at Langley, Virginia. The U-2 aircraft was used to sample the cloud on May 7, 1982, and the filters obtained were analyzed by neutron activation analysis. Four filter samples were found to have elemental concentrations in excess of the filter blanks. Although the concentrations observed were not very high, they did show evidence of a component with a composition similar to crustal dust and a number of other elements which were enriched relative to crustal dust. In Fig. 1, the logarithm of the enrichment factor (EF) for one of the samples is shown. The EF is defined as:

$$EF = \frac{(X/Al)_{sample}}{(X/Al)_{crust}}$$

where X refers to the concentration of an element which is normalized to the Al concentration and then to crustal dust, in this case Taylor's crustal abundance data (4). The elements Se, Br, Cu, Cr, W, Zn and As are always found enriched in volcanic plumes, so their appearance here would be indicative of a volcanic source for the cloud. The high levels of I, Hf and Nd are suspicious and are believed to be contamination or are related to rather unique chemistry of the volcanic system and source area.

E. Stratospheric Radioactivity

During the initial phase of this work, measurements of radioactivity were conducted on the U-2 filter samples. In general, the only radioisotope observed was ^{7}Be, due to the detection technique used, γ-ray spectroscopy. The spectrum of each sample was taken on a Ge(Li) γ-ray detector for several hours prior to analysis by INAA. On all of the stratospheric samples, ^{7}Be could be easily measured and on a set of samples collected in November and December of 1980, large concentrations of fission products were also observed.

An example of the normal ^{7}Be and sulfate data are shown in Figs. 2 and 3. Figure 2a shows the sulfate concentration versus altitude for the Poker Flat flight series in July of 1979. The sulfate concentrations appear to peak at an altitude between 15 and 16 km. Figure 2b shows the ^{7}Be data for the same four flights. The concentration of the peaks at an altitude of about 20 km. The ratio of sulfur to ^{7}Be versus altitude is plotted in Fig. 3 and, as can be seen, the ratio is highest for the low altitude samples, which will be admixing down into the troposphere.

The fission product data are contained in the reprint enclosed (Sect. J). Briefly, we observed large quantitites of the fission products ^{95}Nb, ^{95}Zr,

^{141}Ce, ^{144}Ce, ^{103}Ru, ^{106}Ru, ^{131}I and ^{137}Cs during the flight series in July of 1981. By comparing the ratios of these isotopes it was possible to calculate the detonation data of the weapon as October 16 ±4 days, which corresponds well with the known date.

F. References

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G. Talks (speaker underlined)

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2. W. H. Zoller, T. Vossler and N. K. Aras, "Trace Element Analysis of the St. Helens Plumes", Mt. St. Helens Volcano Workshop, NASA Ames Laboratory, Moffett Field, CA, July, 1980.

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5. W. H. Zoller, "The Chemistry of Atmospheric Aerosols and the Effects of Volcanism", Instituut voor Nucleaire Wetenschappen Ruksuniversiteit, Ghent, Belgium, Oct., 1980.

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8. W. H. Zoller, "Chemists and Volcanoes: Mt. St. Helens - A Case Study", Keynote Address, Education Awards Luncheon, 15th ACS Middle Atlantic Regional Meeting, Washington, D.C., January 1981.

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H. Publications

1. T. Vossler, D. L. Anderson, N. K. Aras, J. M. Phelan and W. H. Zoller, Trace Element Composition of the Mt. St. Helens Plume: Stratospheric Samples from the May 18th Eruption, Science 208, 827-830 (1981).

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3. W. H. Zoller, D. L. Anderson, M. P. Failey, J. L. Moyers and B. W. Mosher, *Nuclear Activation Analysis Methods and the Evaluation of Volcanic* Deposits and Emissions, in Proc. of the 4th Int. Conf. on Nuclear Methods in Environmental and Energy Research, Univ. of Mo., Columbia, Apr. 1980, J. R. Vogt, ed., CONF 800433, pp. 96-105.

Table 1

Flow Rates for Filters (11 cm diam)

Filter Type	Flow Rate		Conditions
	L/m	L/cm^2-hr	
IPC	1,400	880	ram air (U-2)
Polystyrene	150	95	ram air (U-2)
Nuclepore (0.4 (μm)	100	610	pumped (MLO - South Pole)
Fluoropore (1 μm)	300	190	pumped (MLO - South Pole)

Table 2

Comparative Filter Blanks (ng/cm^2)

Element	IPC	Polystyrene	Nuclepore	Fluoropore
Na	208	20	1.4	3.1
Al	120	34	2.8	7.8
Mn	4.5	1.0	0.047-0.084	0.050-0.260
Fe	220	42	3.8-4.2	4.2-14
Co	0.17	0.031	0.0093-0.0095	0.030-0.050

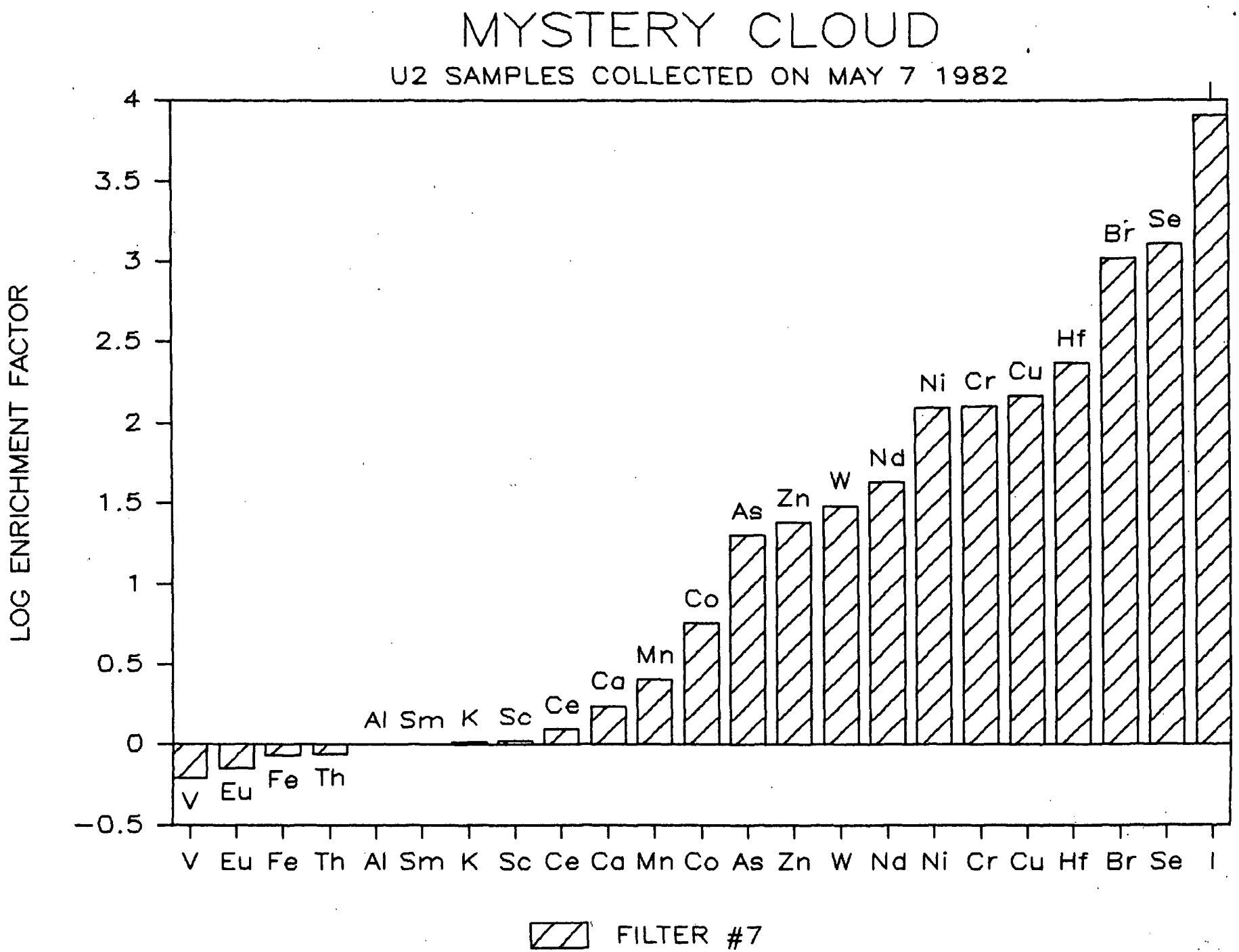
Element	IPC	Polystyrene	Nuclepore	Fluoropore
Cl	460	98	40	6.6
Br	1.2	6	1.0	0.08
As (pg)	30	80	14-73	2.5-260
Se (pg)	<40	70	5.3-23	1.2-5.3
In (pg)	<	2.1	<0.2	<0.2
Sb (pg)	164	1,400	5.6-25	18-21

Table 3

Sampling Time Required to Equal Blank Concentrations[a]

Element	IPC	Polystyrene	Nuclepore	Fluoropore
Na	72	64	67	4.9
Al	170	440	540	50
Mn	380	790	560	20
Fe	400	710	970	36
Co	390	660	3,000	320
Cl	200	400	240	13
Br	0.52	24	6.1	0.16
As	4.8	120	31	1.8
Se	7.3	120	14	1.0
In	<20	420	<60	<20
Sb	220	18	100	110

[a]Assumes an atmospheric concentration equal to that found at the South Pole (2).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U2 SAMPLES COLLECTED ON MAY 7 1982
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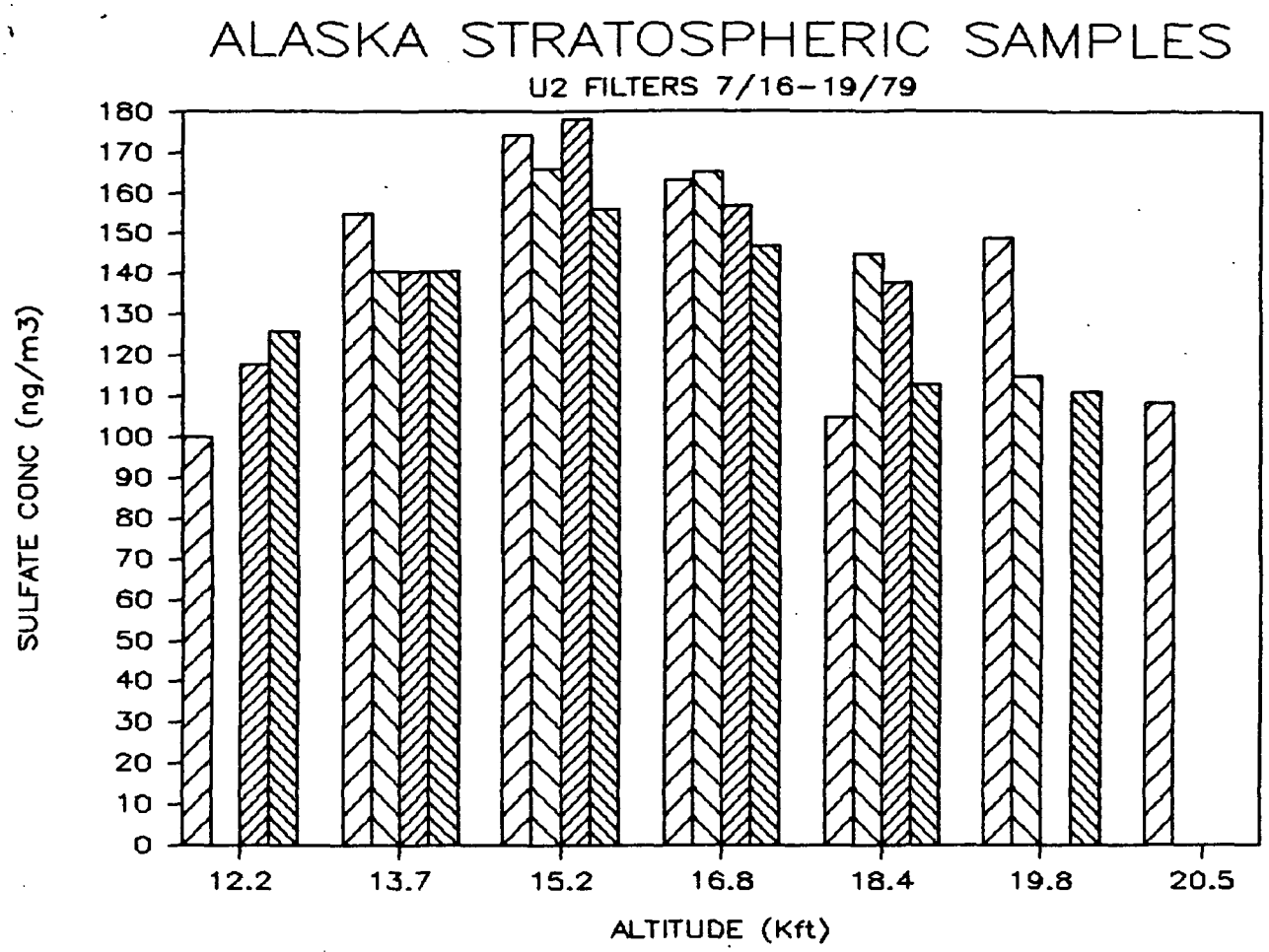
3.5
3
2.5
2
1.5
1
0.5
0
−0.5
V Eu Fe Th Al Sm K Sc Ce Ca Mn Co As Zn W Nd Ni Cr Cu Hf Br Se I
FILTER #7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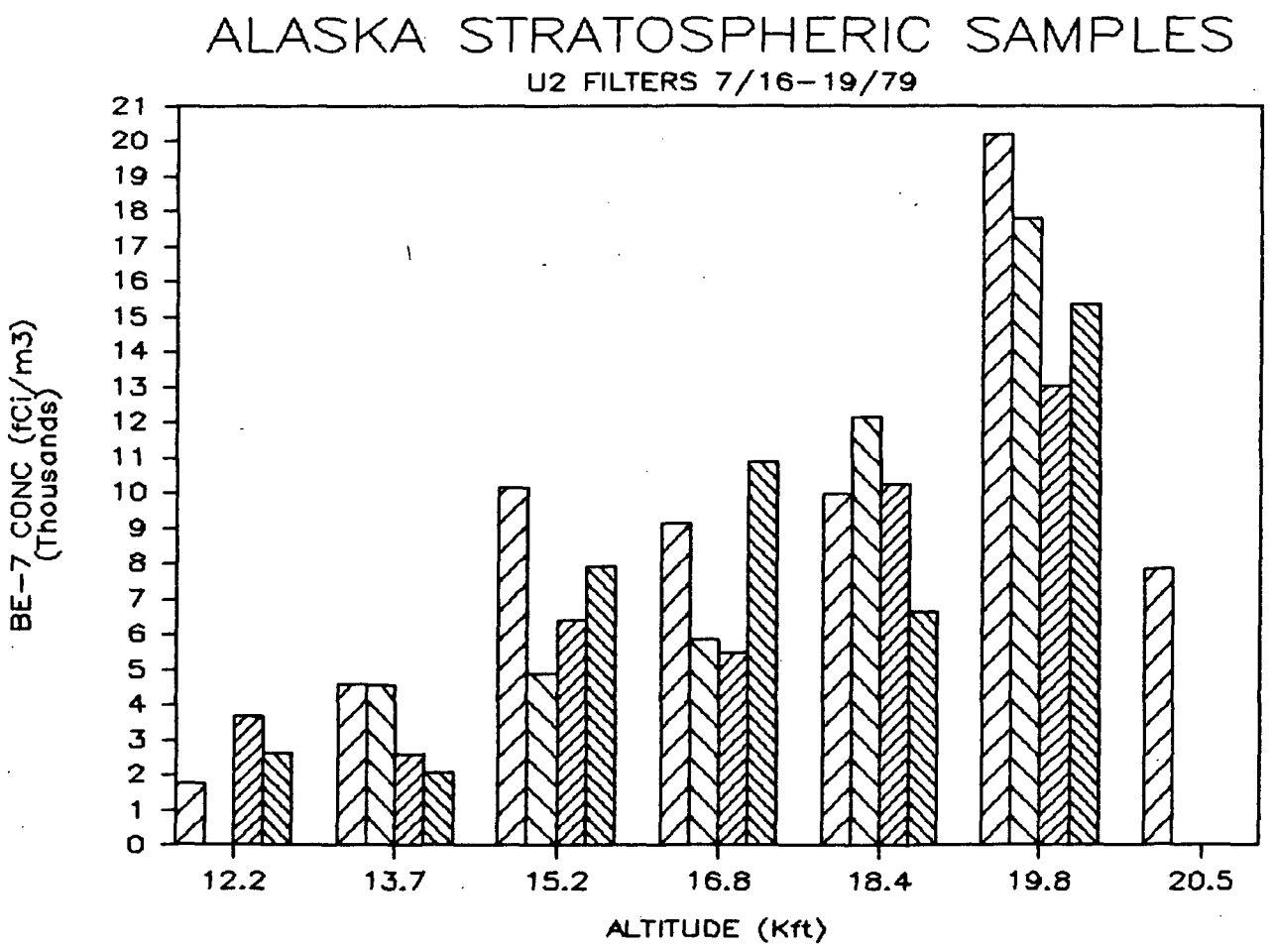
ALTITUDE (Kft)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(Thousands)
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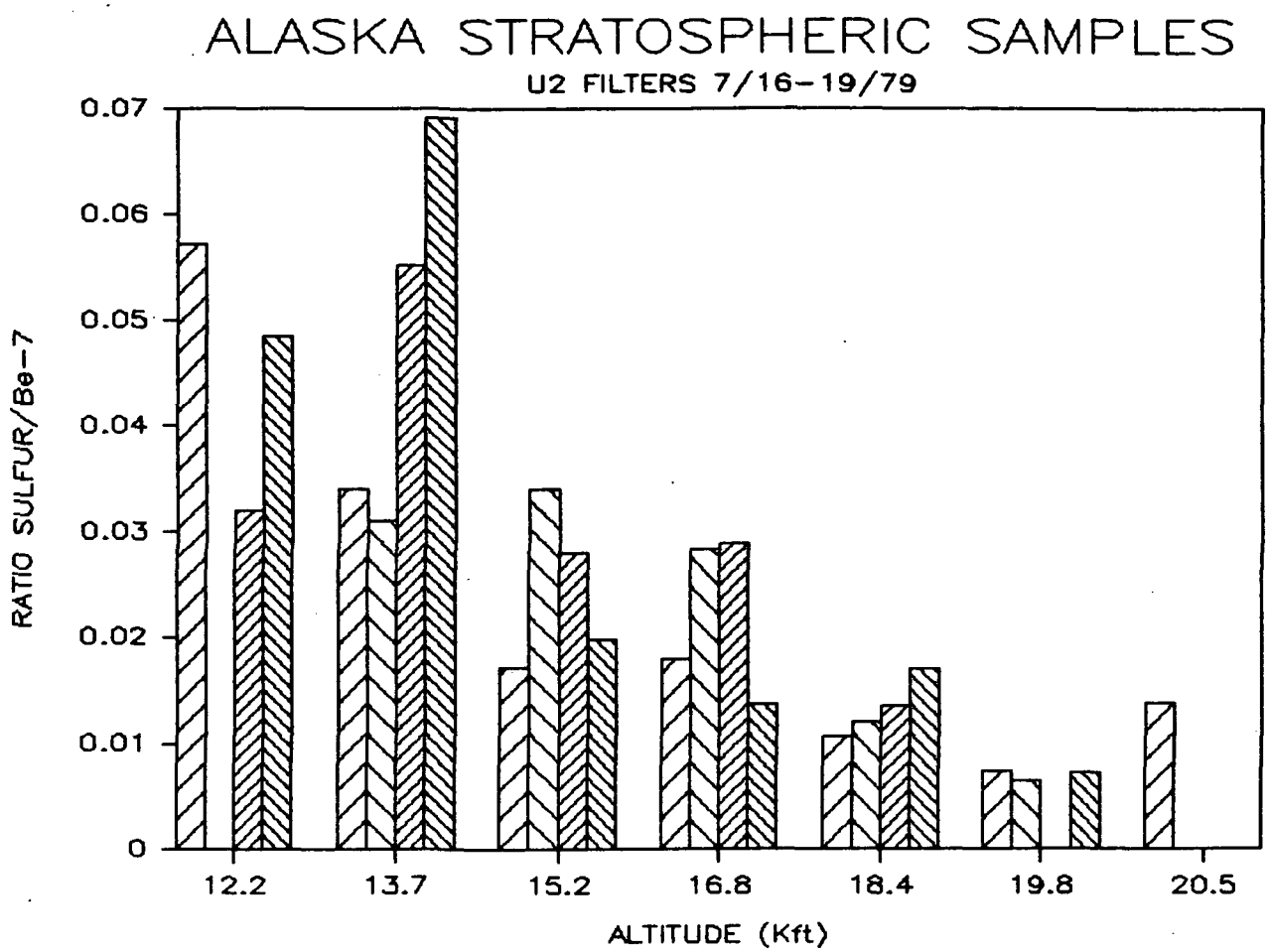
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