CHAPTER 13

Long-range Impact of Desert Aerosol on Atmospheric Chemistry: Two Examples

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ABSTRACT

Approximately one-half the elements in the atmospheric aerosol occur in near-crustal proportions, and are probably soil-derived. Deserts are likely to be the main contributors of this crustal dust even to remote temperate and polar regions. Multi-elemental analyses of 7 samples of Sahara aerosol collected over the North Atlantic in 1973 revealed that its composition was surprisingly uniform over 2400 km and 8 days, with more than three-quarters of the elements in crustal proportions. Sahara dust accounted for about 80% of the aerosol mass at the surface of the NE-tradewind region of the North Atlantic during this strong outbreak. As an example of the impact of desert dust on aerosol composition even farther from the source, the recent discovery of bands of Asian desert dust in the arctic atmosphere is discussed. During April and May 1976 layers of Asian dust were observed over Alaska. These haze layers completely altered the natural chemistry and physics of the arctic aerosol. As much as one-half million tons of Asian desert dust may enter the Arctic during a 5-day episode. Desert-derived aerosol seems to be chemically different from its parent soil. Only the finest ($r < 1\ \mu m$) soil particles, which are chemically and mineralogically quite different from the bulk soil, are capable of long-range transport through the atmosphere. Crust-air fractionation has already been noted for Si and Al, but may exist for many other elements as well, such as the rare earths, Th, and several heavy metals such as Zn, Sb, As, etc. Analysis of desert soils specifically in the aerosol size range will be important for the future understanding of desert dust in the atmosphere.

13.1 INTRODUCTION

Crustal aerosol, especially that produced from deserts, plays an important role in the physics and chemistry of the atmosphere. Recently this key role has been increasingly recognized, and studies of desert aerosol and its atmospheric effects are rapidly increasing. Nevertheless, surprisingly little is known about many aspects of desert dust.

This paper is concerned with the elemental composition of desert dust in the atmosphere and the extent to which it governs the composition of the aerosol, even

far from deserts. A general introduction will show that a large number of elements in the aerosol throughout the troposphere are essentially exclusively controlled by crustal sources. Then two examples of long-range transport of desert dust into otherwise remote areas will be given, namely Sahara dust over the Atlantic Ocean and Asian dust over Alaska. In each case the impact on the aerosol is striking. The paper will conclude with a discussion of the relations between the composition of desert dust and the aerosol derived from it. The argument will be made that there is no *a priori* reason that the two should be the same. In fact, the physical process of generation of crustal aerosol suggests that it should most likely have a different composition than its parent soil. Data from the world aerosol and from Sahara soils and aerosols in particular will be used to support this hypothesis. The importance of knowing the composition of desert soils as a function of particle size will be stressed.

13.2 GENERAL CHEMICAL IMPORTANCE OF CRUSTAL DUST IN THE ATMOSPHERE

The abundances of many elements in the atmospheric aerosol are controlled by the ubiquitous crustal aerosol. This can be seen most easily by enrichment-factor analysis, that is, by calculating the *enrichment factor* of each element in the aerosol relative to the crust and some reference element. This is usually done for an element by using the following formula:

$$\text{Aerosol Crust Enrichment Factor} = (X/Al)_{aerosol}/(X/Al)_{crust}$$

where X and Al stand for concentrations of element X and the reference element Al. In principle any of several elements (Si, Al, Fe, Ti, Sc, . . .) could be used for the crustal reference element, but Al is the most common choice because it is relatively easily determined and lacks major pollution sources. Fe is the next most common choice. The crustal reference material 'crust' ought of course to be soil, probably desert soil, but is usually taken to be average crust (i.e. rock) because so much better data are available for rock than for soil. All calculations reported here use the average crust of Mason (1966).

The enrichment factors of a large number of aerosols have been calculated and tabulated (Rahn, 1976b). It was found that each element in the world aerosol has a reasonably characteristic range of enrichment factor, with values distributed approximately log-normally. A simple geometric mean over the entire population of aerosol samples considered in this compilation provides a first estimate of the most typical enrichment factor for each element. These geometric mean enrichment factors, from more than 100 aerosols, are shown in Figure 13.1. It can be immediately seen that more than half of the elements have mean enrichments of less than about 7. These elements are therefore present in nearly crustal proportions in the atmosphere. By contrast, the other half of the elements have enrichment

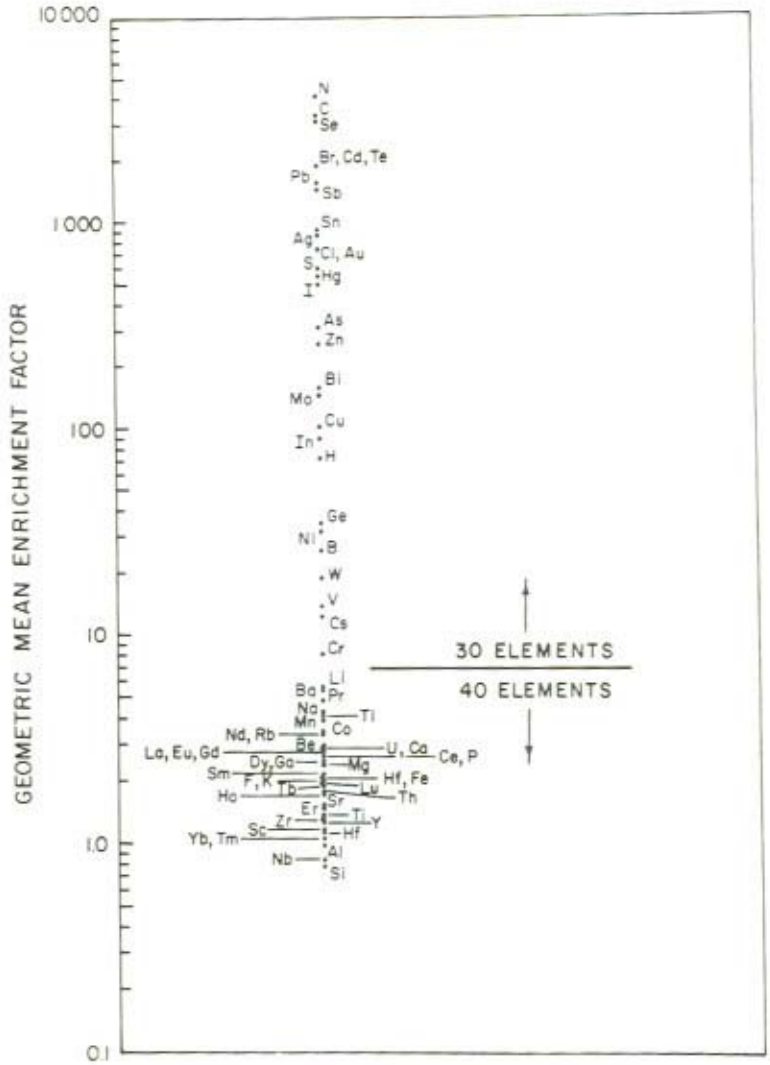

Figure 13.1 Geometric mean enrichment factors

factors between about 10 and 5000, and are therefore not crust-controlled. In general, the sources of these elements in remote atmospheres are not known.

Of the crustal elements in the atmosphere, some have important marine components in marine aerosols, whereas others have no measurable marine components even in the most remote marine regions. These two extremes of behaviour are exemplified by Na and Fe, as shown in the next two figures. Figure 13.2 shows the enrichment-factor diagram for Na (Rahn, 1976b). This type of plot is a scatter

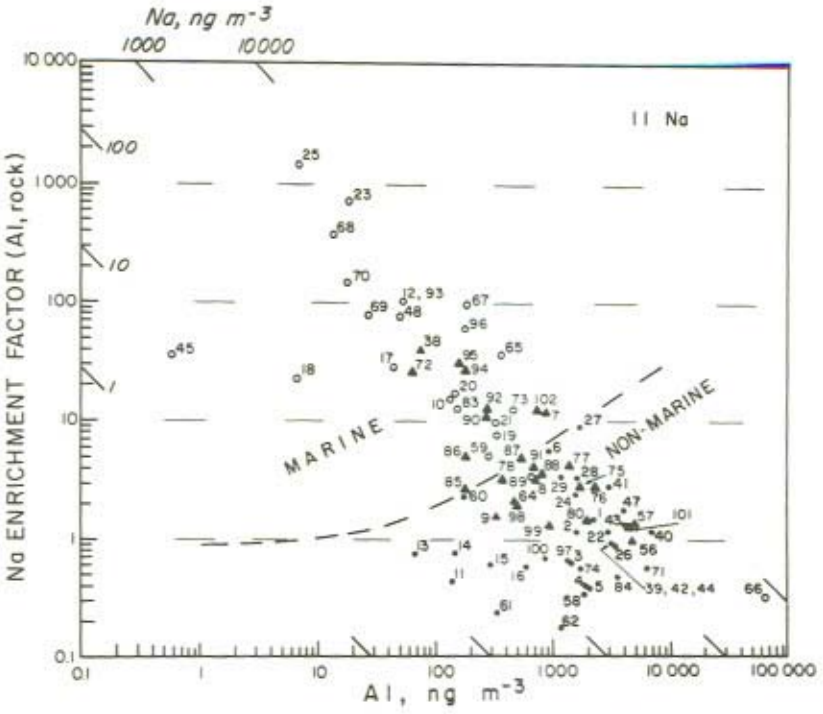

Figure 13.2 Enrichment factor diagram (Na)
Legend: ● = continental regions
▲ = semi-marine points
○ = marine regions

diagram of the aerosol-crust enrichment factor for an element *vs.* the concentration of the reference element Al, both variables being plotted logarithmically. Remote (low Al) points therefore appear on the left and urban (high Al) points appear on the right. The number next to each point is for identification only in Rahn (1976b). Lines of constant concentration of the element in question appear inclined 45° counterclockwise from the vertical. Continental regions are indicated by solid circles, semi-marine points by solid triangles, and marine regions by open circles. For Na a clear-cut marine region can be seen, as evidenced by high enrichments in remote marine and semi-marine areas. Note that in these marine areas the *concentration* rather than the enrichment factor of Na tends toward constancy, being roughly a few tenths to a few micrograms per cubic metre of air.

The opposite behaviour of Fe is shown in Figure 13.3. No matter how remote the area, and no matter whether it is marine, semi-marine, or nonmarine, the enrichment factors of Fe remain for the most part between about 0.7 and 7. Marine and semi-marine points are completely intermingled with nonmarine points. There-

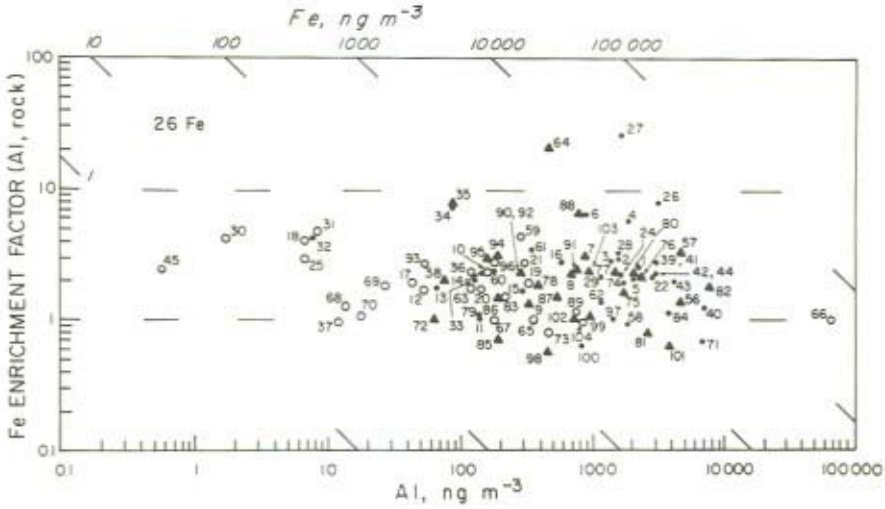

Figure 13.3 Enrichment factor diagram (Fe)
Legend: ● = continental regions
▲ = semi-marine points
○ = marine regions

fore, Fe has no measurable marine component. Even in the most marine areas Fe is crust-controlled.

Table 13.1 summarizes the behaviour of 51 elements in the atmosphere whose concentrations have been measured often enough that enrichment-factor plots can be made. As noted above, approximately half of these elements are crustal or near-crustal in abundance; the other half are enriched. Of the 26 non-enriched and

TABLE 13.1 Classification of Elements by Type of Enrichment-factor Diagram

Non-enriched elements (18)
Li, F, Na*, Mg*, Si, P, K*, Ca*, Sc, Ti, Rb*, Sr* La, Ce, Sm, Eu, Hf, Th
Intermediate elements (8)
V, Cr, Mn, Fe, Co, Ga, Cs*, Ba
Enriched elements (25)
Be, B, C, N, S, Cl*, Ni, Cu, Zn, Ge, As, Se, Br*, Mo, Ag, Cd, In, Sn, Sb, I*, W, Au, Hg, Pb, Bi

*Marine component (10)

intermediate elements, only 7, or about one quarter, show measureable marine components. Thus the study of the composition of desert soils, which make up a large fraction of crustal material injected into the atmosphere, can materially affect our understanding of nearly half the elements in the aerosol.

13.3 SAHARA DUST OVER THE ATLANTIC

During a 1973 cruise of the West German research vessel 'Meteor' across the tropical North Atlantic, a series of 15 high-volume aerosol samples were taken using 8 x 10 inch Delbag Microsorban polystyrene filters and a high-volume vacuum pump (Rahn *et al.*, 1974). Samples were 1 to 2 days in duration, with total volumes of air sampled ranging from 2500 m^3 to 7000 m^3. The cruise track is shown in Figure 13.4, along with the total concentrations of mineral matter collected. As seen in the Figure, at about the midpoint of the cruise the ship encountered a large, strong plume of Sahara dust. The seven samples numbered 9 through 15 from this plume form the basis of this section and will be considered as a unit whose composition is indicative of a single Saharan outbreak.

We felt that this suite of samples was a particularly valuable one, because it was taken on high-efficiency filters which collected all size ranges of the aerosol, as opposed to the popular nylon meshes or sails, which collect particles only larger

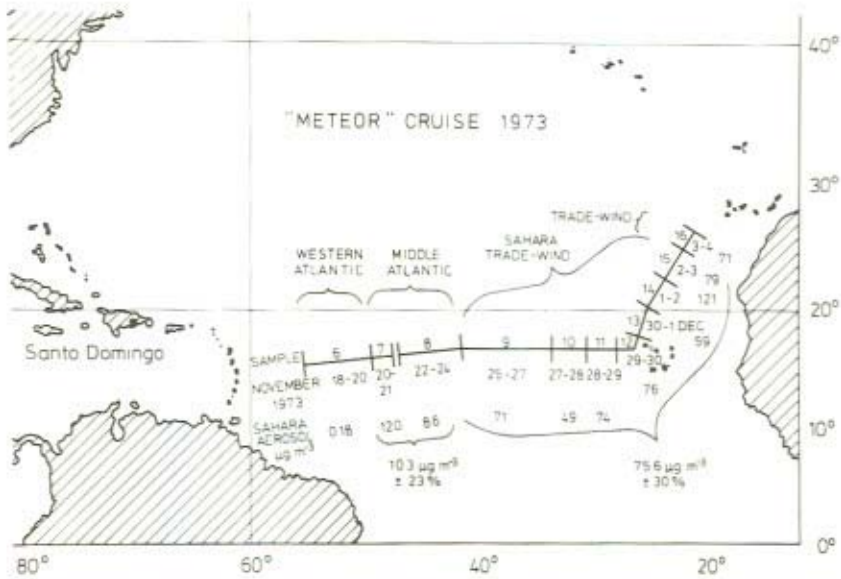

Figure 13.4 'Meteor' 1973 cruise map with dates and total Sahara dust loadings

than 1 μm or so. Furthermore, great pains were taken to avoid ship contamination and to sample as nearly isokinetically as possible. The latter was a particularly important point, because so much of the Sahara aerosol is found in the giant size range ($r > 1$ μm) which is easily missed by nonisokinetic air flow into the sampler. Lastly, the samples were important because they were taken on filters which were chemically very pure, so that they could later be analyzed chemically with a minimum of interference from the filter material itself.

Samples 9 through 15 were collected over a total distance of about 2400 km and an elapsed time of 8 days. The nearest distance to the African shore was about 600 km at the end of sample 15, and the farthest distance from the African shore was about 1300 km, at the beginning of sample 9. The 20 degrees of longitude over which this Sahara plume was sampled represents nearly one-half its total longitudinal displacement on its way from Africa to the Caribbean.

These samples were analyzed by nondestructive neutron activation for as many elements as possible (Rahn *et al.*, 1976). About 40 elements could be determined from 2 irradiations and 4 counts on each sample. In addition to these aerosol samples, 6 Libyan soil and soil-related samples were also analysed, results of which will be discussed in the last section of this paper.

The total concentrations of Sahara aerosol were higher than expected and surprisingly constant. The mean mineral concentration of the 7 samples was 75.6 $\mu g\ m^{-3} \pm 30\%$. Considering the length of the ship's track and the elapsed time during sample collection, a coefficient of variation of only 30% seems very small. The impact of these high concentrations of mineral aerosol on the region can be seen in Figure 13.5, which shows the major components of the Sahara trade-wind aerosol in the strong plume. Of the total aerosol (96.2 $\mu g\ m^{-3}$), sea salt accounts for 15.2 $\mu g\ m^{-3}$, or only 16%. By contrast, Sahara dust accounts for some 79% of the aerosol mass. In other words, the aerosol of this marine region becomes essentially continental when a strong Sahara plume passes over. The remainder of the aerosol (5%) is divided between organic matter and ammonium sulphate.

The composition of the Sahara aerosol seemed to be even more constant than was its total concentration. This is a feature of the aerosol which has not been noted in the few previous reports on its composition, perhaps because less precise analytical techniques than neutron activation were used. On the other hand, perhaps our data represent only a single outbreak, different in composition from others. Whatever its true significance, this constancy is illustrated in Figure 13.6, which is a scatter diagram of the coefficient of variation of the concentration ratio X/Fe for the various elements X *vs.* the analytical uncertainty of the same ratio X/Fe. The diagram clearly shows that the vast majority of elements show variations over the 7 samples which are just about the same as their analytical uncertainties, even down to the 2% level for Sc. In short, we were not able to detect any significant compositional variations within this particular Sahara plume. It is not yet certain whether such homogeneity is a characteristic of all Sahara outbreaks, or whether one outbreak differs measurably from another. What is certain, though, is

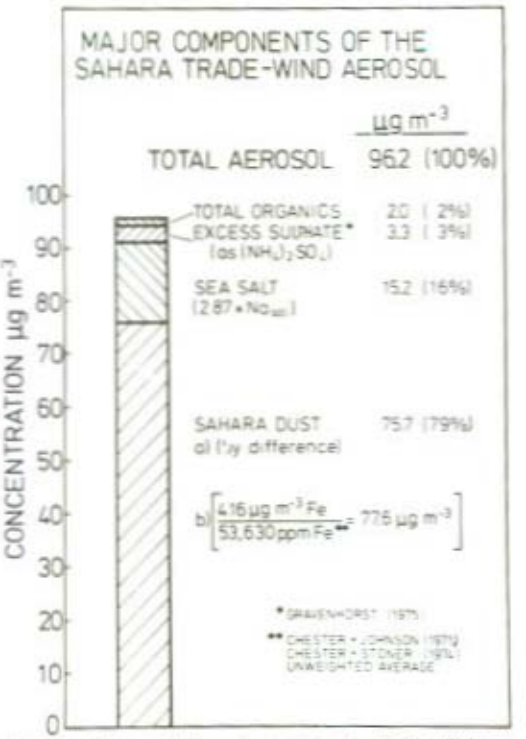

Figure 13.5 Major components of the Sahara trade-wind aerosol

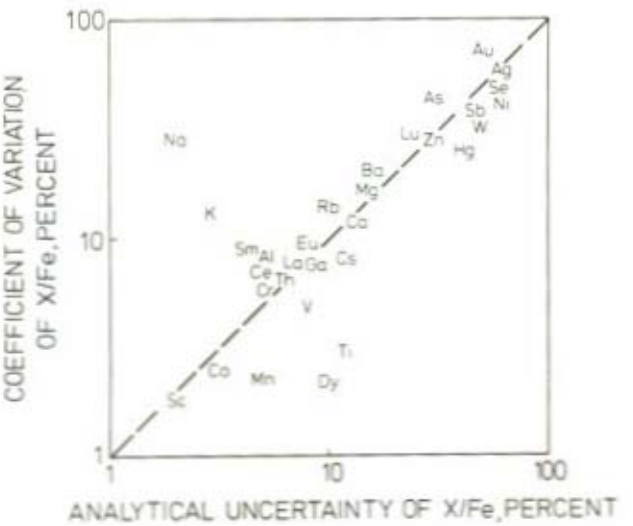

Figure 13.6 Coefficient of variation of X/Fe *vs.* analytical uncertainty of X/Fe

that the scale of this outbreak (2400 km, 8 days) was large, and that this degree of compositional homogeneity is highly unusual within environmental science. The explanation for this intriguing phenomenon must be a constancy of proportions within the Sahara sand and/or extensive mixing of the aerosol before it moves out over the Atlantic. At the moment, however, the relative importance of these two effects is not clear.

This constancy of composition for the Sahara aerosol makes its composition a somewhat more fundamental quantity than it otherwise might be. Figure 13.7 shows this composition, expressed as enrichment factors relative to Fe. The vertical bars are coefficients of variation of enrichment factor over the 7 samples, not the observed scatter directly. There are a number of features of this plot worth pointing out. First, the majority of the elements have enrichment factors of essentially unity, i.e. they are in the proportions of average crustal rock. At least 25 of the elements fit into this category, perhaps more. Only about 5 elements have enrichment factors greater than 7. This situation is to be contrasted with the world aerosol of Figure 13.1 where nearly one-half the elements have enrichment factors of roughly 7 or more. Thus from the enrichment-factor point of view the Sahara aerosol is a relatively simple one, with most elements at or very near crustal proportions. For comparison purposes, Table 13.2 shows the geometric mean ('world') enrichment factors of Figure 13.1 next to the Saharan enrichment factors. In nearly all cases the Saharan enrichments are depressed relative to the global values. The higher the global enrichment factor the more it is depressed in the Sahara aerosol.

There is, however, quite some order to the enrichments of Figure 13.7. The light Group I and II elements Na, K, Ca, and Mg have low enrichment factors, between

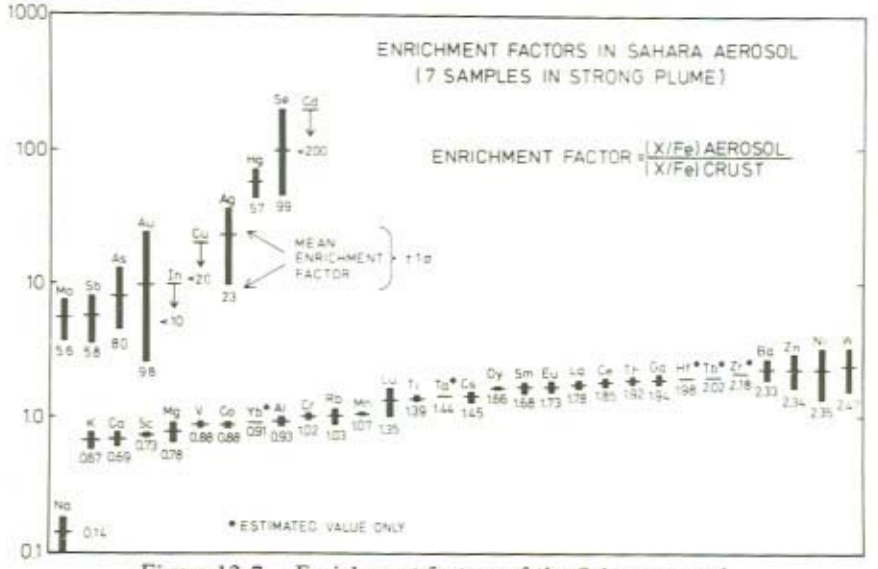

Figure 13.7 Enrichment factors of the Sahara aerosol

TABLE 13.2 Enrichment Factors in the Sahara and World Aerosols

Element	Sahara EF(Fe, rock)	World EF(Al, rock)
Na	0.14	4.4
K	0.67	1.98
Ca	0.69	2.8
Sc	0.73	1.17
Mg	0.78	2.4
V	0.88	14.0
Co	0.88	3.5
Yb	0.91	1.06
Al	0.93	1.00
Fe	1.00	2.1
Cr	1.02	8.1
Rb	1.03	3.4
Mn	1.07	3.9
Lu	1.35	1.95
Ti	1.39	1.39
Ta	1.44	1.14
Cs	1.45	12.4
Dy	1.66	2.5
Sm	1.68	2.1
Eu	1.73	2.7
La	1.78	2.7
Ce	1.85	2.6
Th	1.92	1.78
Ga	1.94	2.5
Hf	1.98	2.0
Tb	2.02	1.92
Zr	2.18	1.36
Ba	2.33	5.5
Zn	2.34	260
Ni	2.35	32
W	2.47	19.1
Mo	5.6	144
Sb	5.8	1430
As	8.0	310
Au	9.8	740
In	<10	90
Cu	<20	102
Ag	23	880
Hg	57	560
Se	99	3100
Cd	<200	1920

0.1 and 0.8. Then comes a group of heavier Group I and II elements plus transition metals with enrichments between 0.8 and 1.4. The rare earths and Th form a group with enrichments between 1.6 and 2.0. A small group of heavy metals is clustered about enrichments of about 2.4. The last group is composed of 7 heavy metals and

semi-metals with enrichments between 5 and 100. Except for Ba, all the elements in these last two groups are highly enriched in the normal aerosol.

The rare earth elements (REE) are a particularly interesting case. With the exception of Lu, they have enrichment factors between 1.6 and 2. These elements are most interesting because their enrichments have just about these same values in the rest of the world aerosol. No major pollution sources are known for the rare earths. Thus they are indisputably of crustal origin in the world aerosol but equally indisputably have enrichments markedly higher than unity. The last section of this paper addresses this point further.

In summary, then, the Sahara aerosol has a composition close to that of the average crust, i.e. low enrichment factors for most all the elements. Elements which are highly enriched in the world aerosol do show modest enrichments in the Sahara aerosol, but it is not yet clear whether this is from the Sahara aerosol itself or from a certain mixing of outside air into the Sahara plume. Certain small enrichments observed in the Sahara plume, for the rare earths in particular, are also observed in the world aerosol and are surely from the dust itself.

13.4 ASIAN DUST OVER ALASKA

The second example of long-range chemical impact of desert dust on the remote aerosol comes from an investigation of the composition and source of arctic haze over Alaska. 'Arctic haze' refers to turbid layers of air which are found often over Alaska and the pack ice to the north during periods of clear weather (Mitchell, 1956). These layers are diffuse, hundreds to thousands of kilometres in horizontal extent, and occur at various levels throughout the arctic troposphere. Their colour is grey-blue in the antisolar direction and reddish-brown in the solar direction, which suggests that they are composed primarily of small aerosol particles. Until recently the only observations of arctic haze were visual. In 1972, 1973, and 1974 however, radiative measurements on these layers near Barrow, Alaska revealed that they had a well-defined extinction, i.e. that they were affecting the radiation balance of the Arctic (Holmgren *et al.*, 1974). The question of the origin of these layers became more significant in 1974 when rough trajectory analysis for a haze episode at Barrow that spring suggested that the air containing the haze may have passed over the highly polluted northeastern United States about 10 days before the episode.

In a joint venture between the University of Rhode Island and the University of Alaska, we have taken filter samples of the haze aerosol itself by flying a light aircraft within a haze layer. Chemical analysis of the aerosol collected, first results of which are reported elsewhere (Rahn *et al.*, 1977), combined with electron microscopy, has revealed that these particles are actually crustal aerosol and that their source is the deserts of eastern Asia. This programme and its results will now be briefly discussed.

During April and May 1976 a series of 15 flights with a specially equipped single-engine Cessna 180 aircraft were made from the Naval Arctic Research

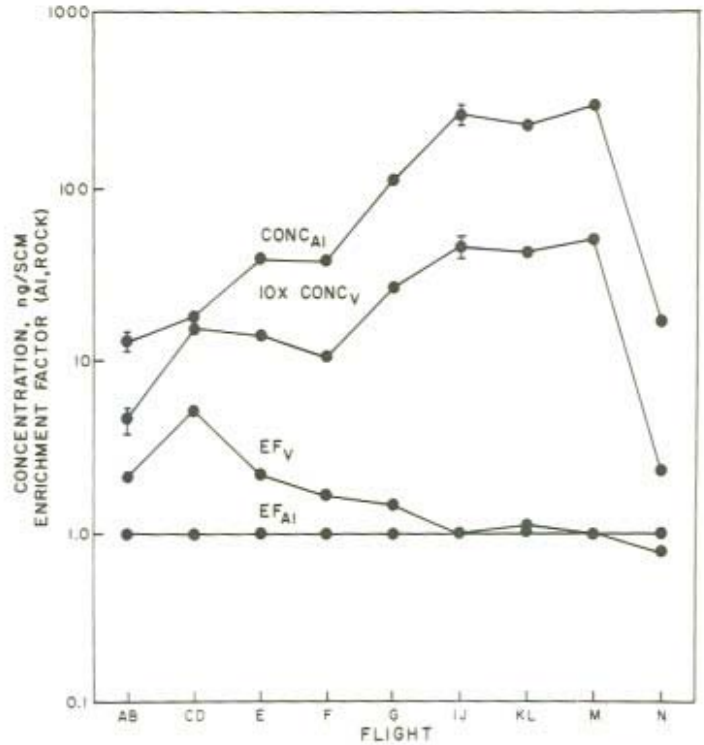

Figure 13.8 Concentration and enrichment factors of V and Al in aerosol over Barrow (Spring 1976)

Laboratory in Barrow, Alaska into the haze layers. High-volume (90 to 360 m^3) samples of aerosol were collected on acid-washed 11-cm Whatman No. 41 cellulose filter paper, low-volume and Nuclepore filter samples were taken for electron microscopy. The high-volume samples were analyzed for 20 to 25 elements by neutron activation, using essentially the same scheme as for the Sahara samples discussed above. Figure 13.8 shows the results for V and Al. This pair of elements provides perhaps the most sensitive and specific test available with neutron activation for deciding whether an aerosol is natural or pollution-derived. The major source of Al into the atmosphere is of course the crust. Vanadium has two major sources, the crust and combustion of residual (#6) oil (Zoller *et al.*, 1973). In remote areas free of significant air pollution the V/Al ratio is very close to that of the bulk crust. In other words, the enrichment factor of V is unity. In urban areas, on the other hand, the V enrichment factor is much higher, varying from 5 to 500 depending on the area and its source of residual oil (Rahn, 1976b). The northeast United States, for example, uses Venezuelan residual oils which are unusually rich in V, so has abnormally high V enrichments. Beside the crust, no other major natural sources of V are known. Thus, V enrichment factors greater than about 1.5

or so signify the presence of air pollution, and V enrichments below 1.5 mean that the aerosol is mostly crustal.

In Figure 13.8 above it can be seen that the early flights were characterized by low concentrations of both V and Al. This was in fact true for all the other elements, i.e. the atmosphere was typically 'clean' arctic air. Enrichment factors for V, however, ranged between 2 and 5, which definitely indicated that the V was pollution-derived. Flights IJ, KL, and M showed much higher concentrations of nearly all elements including V and Al, and corresponded to a visible haze event over Barrow. The elemental concentrations during this period were consistently 10 to 30 times above background levels. But the enrichment factors for V decreased sharply with the onset of the haze, and during the peak of the haze were essentially 1.0. This meant unambiguously that this arctic haze was crustal aerosol rather than pollution aerosol. In particular, it could not possibly have come from the northeast United States or from Europe. Interestingly, the composition of this haze for almost all elements was systematically skewed toward crustal material, as shown in Figure 13.9. Here the enrichment factors of this arctic haze aerosol are compared with

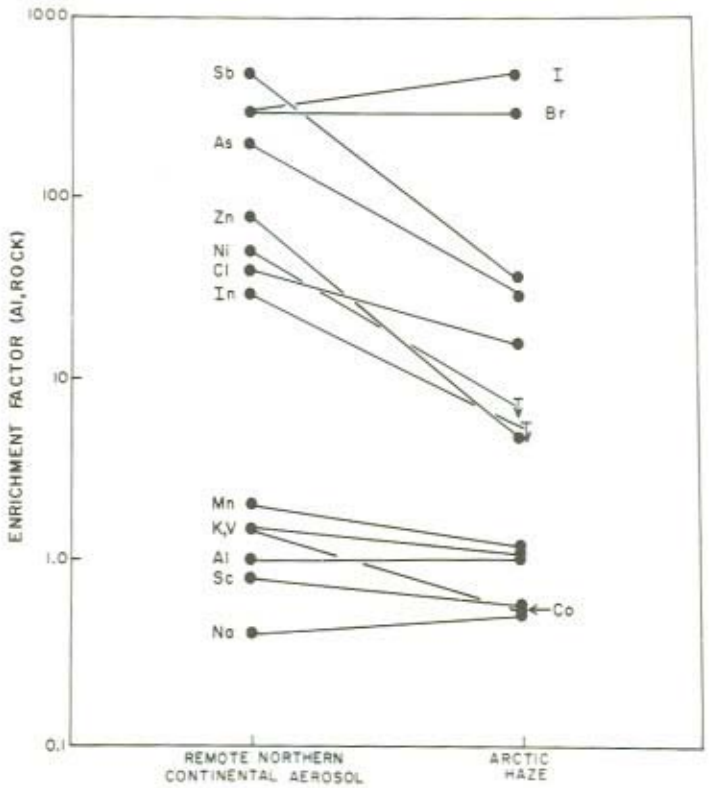

Figure 13.9 Elemental enrichment factors in arctic haze and remote northern continental aerosol

mean enrichment factors of remote northern continental aerosol (Rahn, 1976b). A general lowering of enrichment factors in arctic haze relative to the more typical northern aerosol is clearly seen. The depressant effect is greatest for the elements with the highest enrichments, similar to what was previously observed with the Sahara aerosol.

Electron microscopy of the Nucleopore filters confirmed the chemical conclusion that arctic haze was crustal aerosol. Figures 13.10 and 13.11 are electron micrographs of typical portions of filters CD and IJ, respectively. The magnification of the original 10 × 11 cm negative was 5000X; a convenient reference size for these Figures is the Nucleopore pores which are 0.4 μm in diameter. In sample CD there are many more particles smaller than the pores than larger than the pores. The largest particles are few in number and are less than 1 μm in radius. They appear to be crustal fragments, as evidenced by their angularity. In sample IJ, on the other hand, many more giant particles are seen, with radii up to several μm. Platy layers can easily be seen on several particles; all appear angular and would seem to be crust-derived.

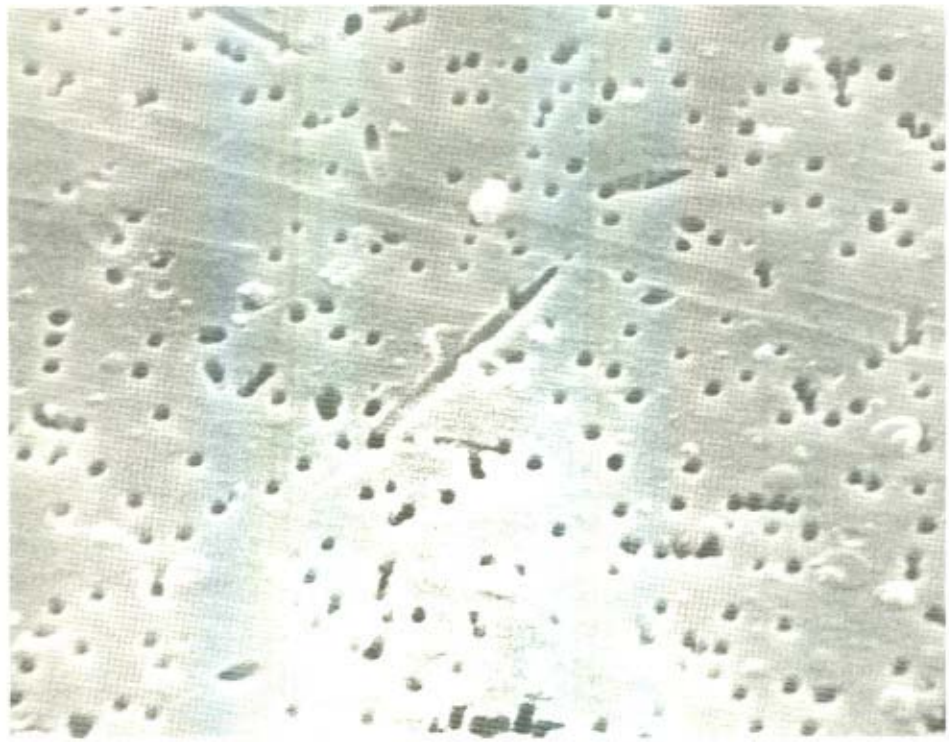

Figure 13.10 Electron photomicrograph of prehaze aerosol over Barrow, Flight CD (Spring 1976). Pore diameter is 0.4 μm

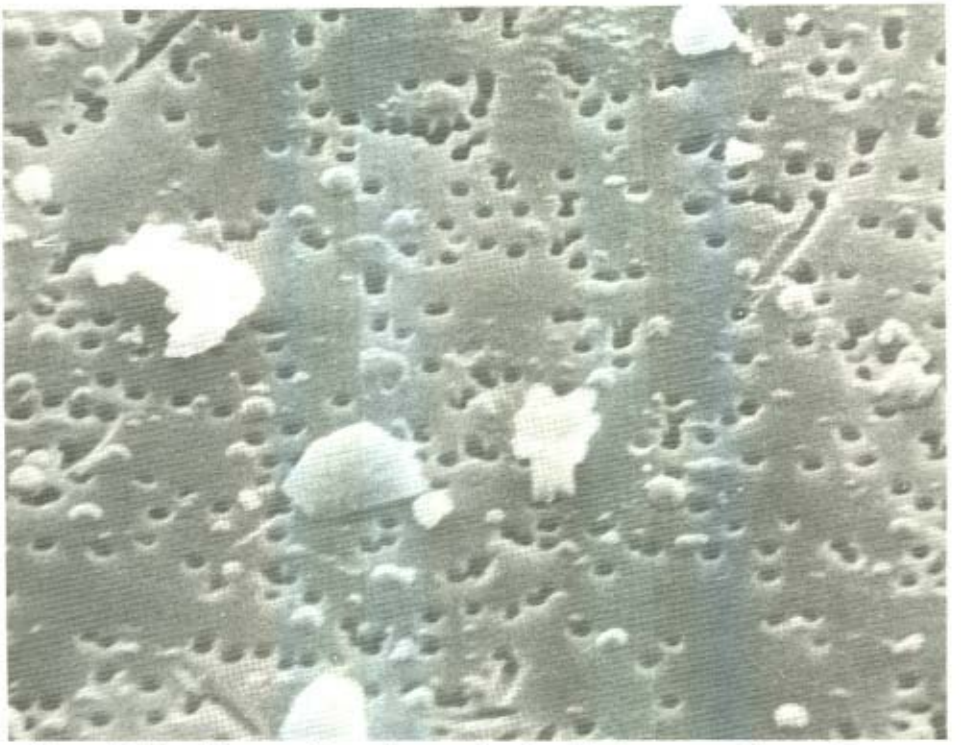

Figure 13.11 Electron photomicrograph of arctic haze aerosol over Barrow, Flight IJ (Spring 1976). Pore diameter is 0.4 μm

What could be the origin of these crustal particles? Alaska was completely snow-covered at the time; even in summer the state is only a very weak source of crustal aerosol. The haze source was clearly far distant. The first clue came from the general synoptic situation for the haze period, shown in Figure 13.12 for the 700-mb level. There was a strong flow of air into Alaska from the south, which had curved from the west and appeared to be traceable back to the Asian mainland, where the great Takla Makan and Gobi deserts are found. Actual 700-mb isobaric trajectories for the sampling period are shown in Figure 13.13; they confirm that episode air had indeed recently passed over these Asian deserts. Furthermore, April 1976 was in general a time of many dust storms in the Asian deserts, and in particular on the days when our trajectories terminated in the deserts there were dust storms. In contrast, however, trajectories for the pre-haze period did not pass over the Asian deserts. Two trajectories, from the 14th and 18th of April, came over the pole to Barrow. They corresponded to sample CD, and E, where the V enrichment factor indicated the presence of air pollution. These two air masses probably originated in Europe and/or the northeast United States, but it is not clear which source was the more important.

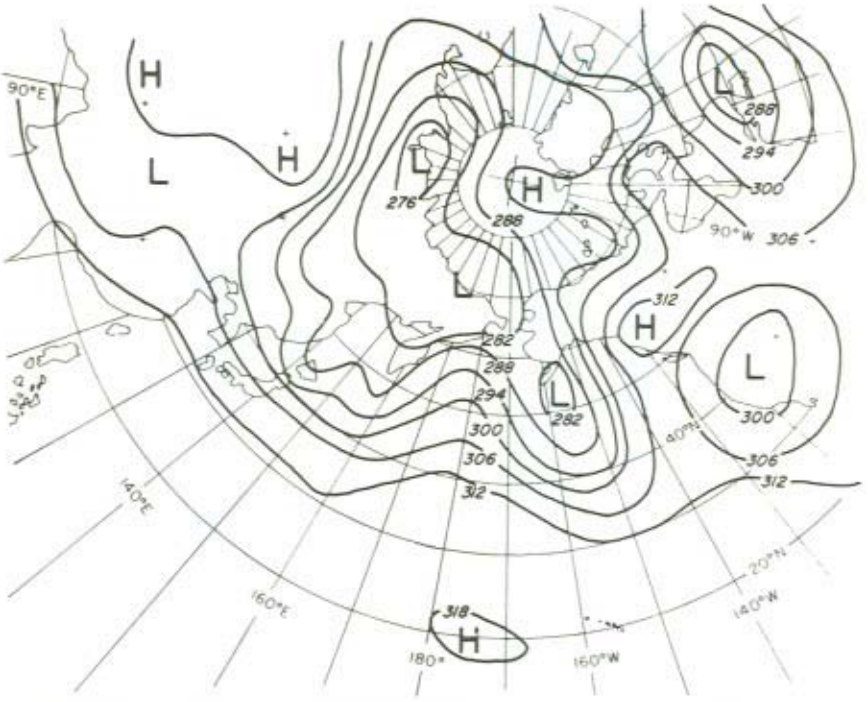

Figure 13.12 Typical 700-mb contour map for arctic haze transport to Alaska. Numbers are heights of 700-mb surface in decametres

It must be emphasized that at the time of this writing it has not yet been definitely proved that the Asian deserts are the true source of arctic haze. No haze bands have been followed from Alaska back to Asia, for example, nor has a band been observed from satellite photography. But our trajectory analysis is supported by several other factors. First, flow patterns conducive to long-range transport from Asia to Alaska do exist and routinely are strong during the spring. Second, the Asian deserts are farther north than the other deserts, lying mostly between 40° and 50° North as opposed to the more normal desert latitude of 20° to 30°. And third, the length of typical trajectories between Asia and Alaska (9000 to 12,000 km) is considerably longer than but not out of line with the well-documented 6000-km path for transport of Sahara dust to Barbados (Carlson and Prospero, 1972).

The mass of Asian desert dust transported into the Arctic seems to be very great. For example, consider some statistics from a 5-day haze episode observed at Fairbanks, Alaska 17–22 February 1976, during which visibilities were reduced from the normal 150 km to less than 30 km, and for which Asian dust seems to be the explanation. Columnar mass loadings derived from radiation measurements had values of about 45 mg m^{-2} (for aerosol density 2.5). Assuming a point source in

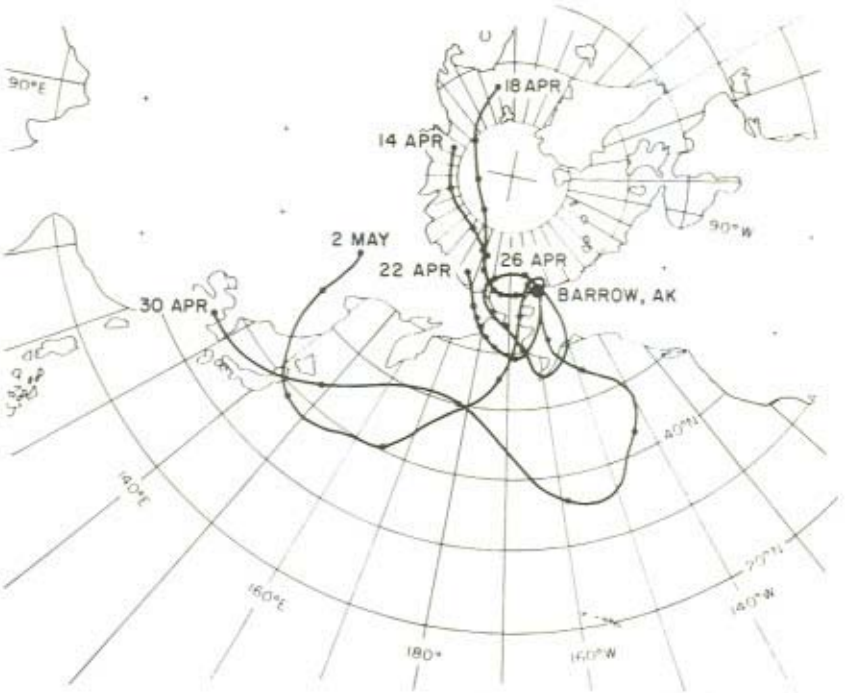

Figure 13.3 700-mb isobaric trajectories of air to Barrow. Numbers refer to date of arrival at Barrow, 1976. Solid circles each 24 hours along trajectory

Asia and a dispersion angle during transport of 5° (typical of volcanic plumes as viewed from satellite photographs), the dust cloud would be about 900 km wide by the time it reached Alaska, or about the width of the state itself. (Indeed during this episode, visibility was poor over the entire north half of the state.) Such a plume travelling at 80 km hr^{-1} would carry 4000 tons of dust into the Arctic per hour, or a half-million tons over the total 5-day episode. This corresponds to skimming off a 0.2 μm layer from a 10° x 10° desert.

Clearly, Asian desert dust must now be considered a major contributor to the overall aerosol burden of the arctic troposphere. It completely alters the aerosol chemistry of that region when it enters, and affects the radiation balance as well. Further study of this phenomenon is essential to reveal what if any climatological impact it has on the Arctic.

13.5 DESERT SOIL VERSUS DESERT AEROSOL

There is mounting evidence that desert soils cannot be directly compared with the aerosol derived from them. Recent parallel research of Gillette (Gillette and Walker, 1975; Gillette, 1976; Patterson *et al.*, 1976, for example) and Schütz and

Jaenicke (Schütz, 1971; Schütz and Jaenicke, 1974) on physical aspects of generation of soil aerosol have elucidated the high degree of physical fractionation that occurs during this process. For our purposes the important ideas can be summarized in a single diagram for the Sahara, Figure 13.14. In this Figure the mass of a typical Libyan soil and its derived aerosol is plotted as a function of particle size. In the soil itself (A) the vast majority of the mass lies between radii 20 and 100 μm. The aerosol approximately 1 μm above this soil (B) has a generally similar pattern, but shows a second mass peak at radius approximately 8 μm. By the time this aerosol has passed far out over the Atlantic (C), the faster-sedimenting particles of the large-size peak have all fallen out, and only the second, smaller-size peak remains. Even it has been shifted to a mean radius of 4 to 5 μm. When part C is compared to part A, it can be seen that virtually the entire mass of the desert aerosol which is capable of long-range transport in the atmosphere ($1\ \mu m < r < 10\ \mu m$) has been

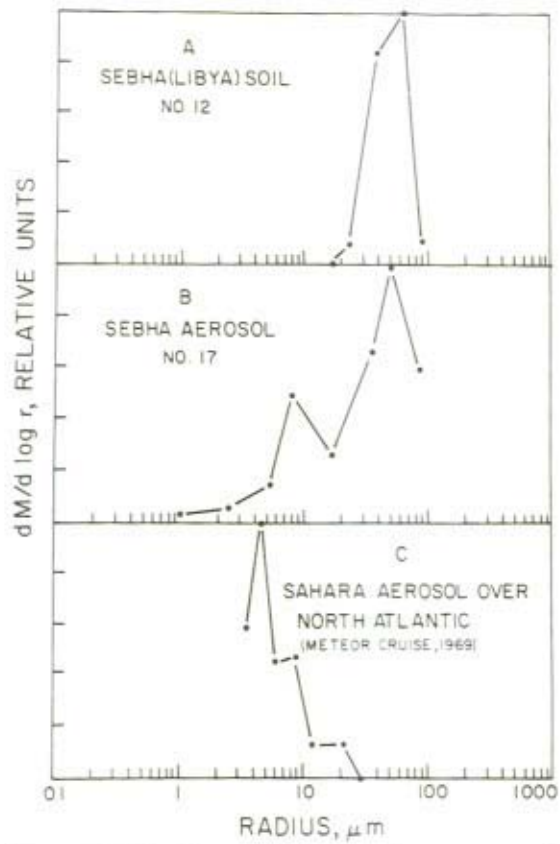

Figure 13.14 Mass distribution for parent soil and derived aerosol, Sahara Desert

derived from only a tiny mass fraction of the soil. It then seems reasonable to expect that the aerosol composition might deviate considerably from the composition of the bulk soil, especially because the lower end of the soil aerosol size range, $r = 1\ \mu m$, is the upper end of the clay-particle size range, and clay particles have a quite different structure and composition from their bulk parent soil.

We have seen above that the travel distance for Asian dust to Alaska is considerably longer than for Sahara dust to Barbados (9000 to 12,000 km *vs.* 6000 km). One might therefore expect mineral dust over Alaska to have a smaller average particle size than Sahara dust over much of the Atlantic, and this appears to be the case. For example, Figure 13.15 is a plot of volume of arctic haze aerosol over Barrow *vs.* radius. The mineral component of this aerosol, i.e. the desert-derived soil fraction, now has its volume (mass) peak at more nearly radius 2 μm. The clay-mineral contribution to this aerosol ought to be very important.

These two examples from the Saharan and Asian desert aerosols serve to demonstrate that one ought to be very careful about extrapolating from composition of desert soils to composition of the derived aerosols. But what about actuality? Is there any evidence that such chemical crust-air fractionation really occurs? There is, and it can be considered for both the general (global) mineral aerosol and for the Saharan case.

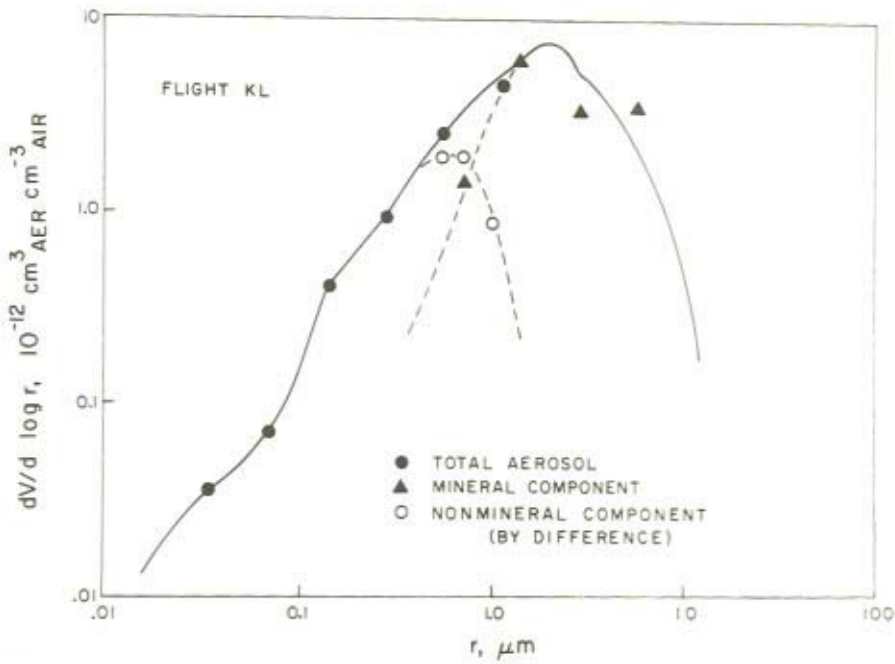

Figure 13.15 Volume distribution for arctic haze aerosol of flight KL (Spring 1976)

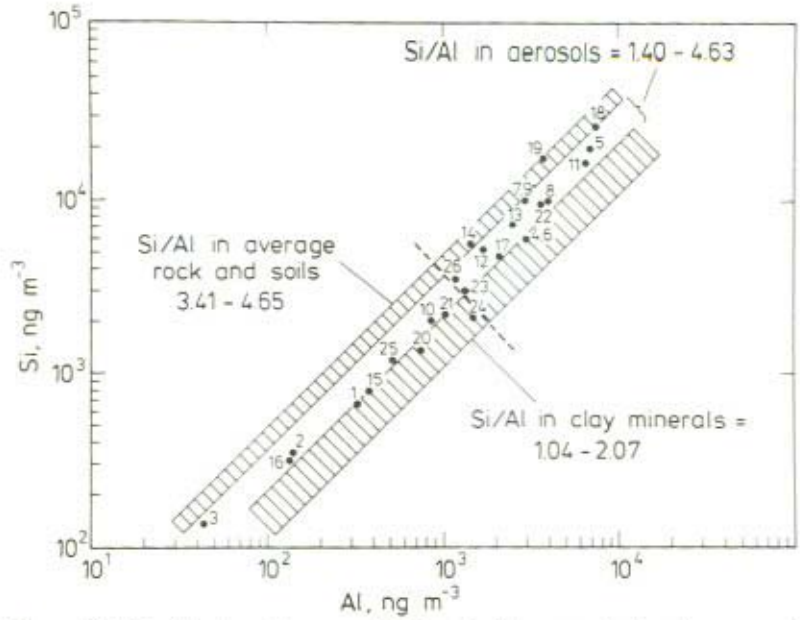

Figure 13.16 Scatter diagram of Si and Al concentration in aerosols (Numbers refer to locations as listed in Rahn, 1976a)

Crust-air fractionation has been demonstrated for Si and Al in the general world aerosol (Rahn, 1976a). This effect is illustrated in Figure 13.16, a scatter diagram of Si and Al concentrations in various aerosols of the world. From this Figure it is immediately evident that the Si/Al ratio of most aerosols, and especially those from remote areas far from dust sources, is distinctly below the average ratio of either bulk crustal rock or bulk soils. The remote-area Si/Al ratio of about 2 is nearly midway between the ratio for average crust and the ratio for clay minerals, suggesting that both of these materials contribute strongly to Si and Al in the aerosol.

Comparison of the composition of Libyan soils with the Sahara aerosol reveals compositional discrepancies of a similar magnitude to the Si–Al case, as well as a more complex soil-aerosol relationship than had been previously imagined. It was found that most elements were more enriched in the soils than they were in the aerosol, that certain elements were more enrichable than others, and that each element had a considerable range of actual enrichments over the suite of soils. Furthermore, all elements determined were more enriched in the small-size range ($r < 16\ \mu m$) than in the larger range ($r > 16\ \mu m$). Because this smaller range closely approximates aerosol sizes, all data considered subsequently in this section refer exclusively to it.

The different enrichments of a given element in the small size fractions of the various soils seem to depend on the percent of the soil mass in the small-size range.

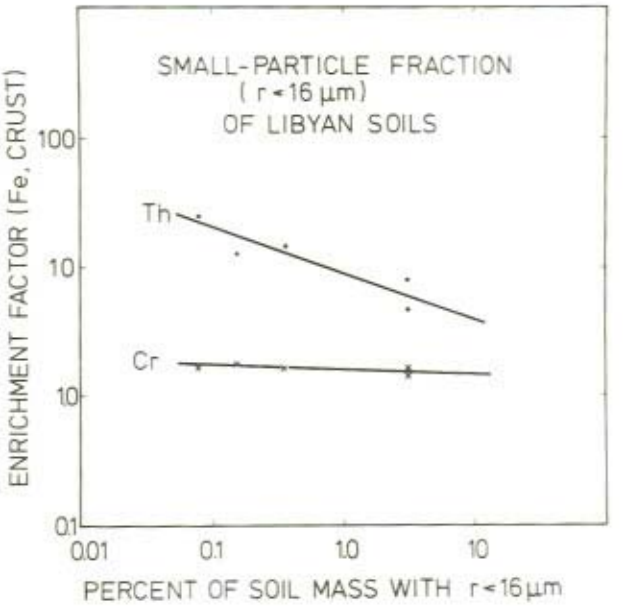

Figure 13.17 Enrichment factors of Th and Cr in $r < 16$ μm fraction of Sahara soils *vs*. percentage of soil mass in this range

When these two variables are plotted against each other, rather neat patterns emerge which bring order to much of the otherwise random scatter of the enrichments. Figure 13.17 shows this for Cr and Th. Cr represents a class of elements that show little variability of enrichment factor from soil to soil, whereas Th shows strongly increasing enrichments with decreasing soil mass in the small-size range. Note that even with Th the scatter about the best-fit line is quite small.

Figure 13.18 shows the same type of plot for more elements in the same soils, but without individual data points. The elements seem to be classifiable into 3 rough groups based on their slope, or 'enrichability': A group with near-zero slope which contains the alkali metals, alkaline earths, and heavy metals such as Zn, Ag, Sb, etc., a second group with intermediate slopes containing most of the transition metals such as Fe, Co, etc., plus other elements such as Mo, Ba, and Ta, and a third group with larger slopes composed of the rare earth elements plus Hf and Th. Note that Eu, which is known in geochemistry for its anomalous behaviour within the REE, has an anomalously low slope in this group.

At this time it is not possible to give a complete interpretation of this plot, except to note that it has demonstrated that soils have changes in composition as a function of particle size that cannot be ignored any longer in atmospheric chemistry. Furthermore, these variations seem to be regular and to depend on the

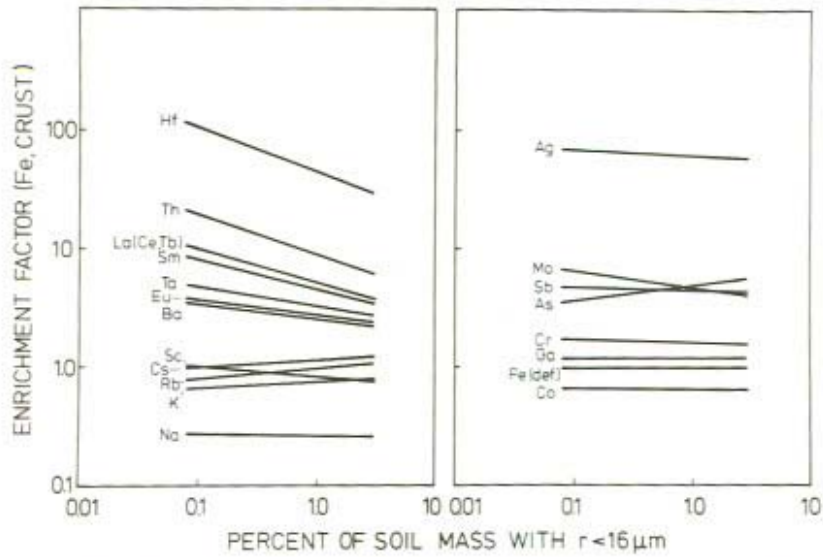

Figure 13.18 Enrichment factors of various elements in $r < 16$ μm fraction of Sahara soils *vs.* percentage of soil mass in this range

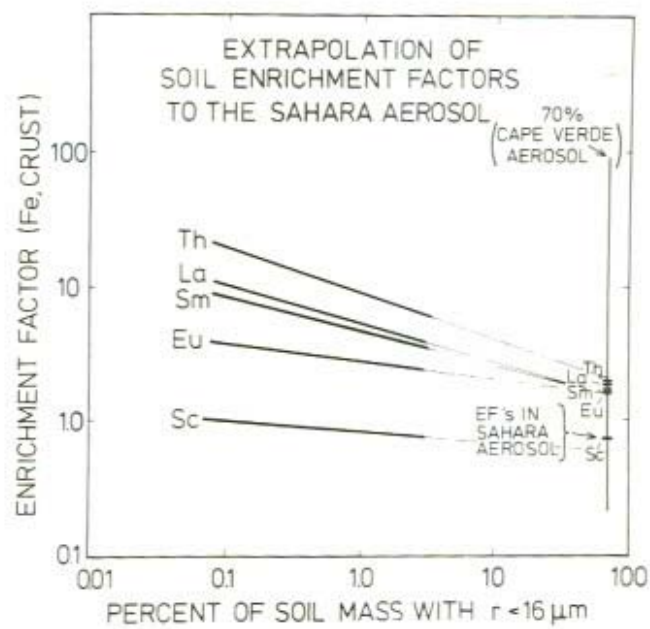

Figure 13.19 Extrapolation of Sahara soil enrichment factors ($r < 16$ μm) to Sahara aerosol

particle size distributions of the soils and the chemistry of the individual elements in some yet-to-be determined way.

In spite of the compositional differences between Sahara soils and Sahara aerosol, it did appear to be possible to extrapolate from the soils to the aerosol and reproduce some features of the aerosol composition by means of the technique shown in Figure 13.19. Here the enrichments of Th, La, Sm, Eu, and Sc are plotted *vs.* the percent of soil mass in the small-size range, as in Figures 13.17 and 13.18 above. This time, however, they are extrapolated to a value of 70% mass less than 16 μm radius, the figure for Sahara aerosol at the Cape Verde Islands. Actual enrichment factors of the elements in the Sahara aerosol are shown by the bars through the 70% line, which are in all cases close to the predicted enrichments.

This extrapolation technique is admittedly indirect and complex. Knowledge of the composition of desert soils as a function of particle size, particularly within the aerosol size range $r < 10$ μm is highly desirable, and would provide a much more direct and simple means of relating aerosol to parent soil. Unfortunately, there is virtually no data available on this topic. High priority should be given to this research in the near future.

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