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AEROSOL–SOIL FRACTIONATION FOR NAMIB DESERT SAMPLES

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Abstract—Four soil samples, collected in the central Namib Desert, were fractionated by dry sieving and aerosol generation into 16 size fractions in the range 0.15–300 μm diameter. The mass-size function of each soil and the dust (mineral aerosol) generated from the soil were studied. Due to the preferential lifting of smaller soil particles by the air stream, the soil underwent strong physical fractionation resulting in the bulk of the dust being found in the range of 1.3–10.3 μm, whereas the bulk of the soil was found in the range 63–300 μm. The concentrations of 11 elements in eight soil size fractions (from <45 to >300 μm) obtained by dry sieving were measured by X-ray fluorescence analysis while the concentration for these elements in eight size ranges (from <0.15 to >10.3 μm) obtained by aerosol generation were determined by particle-induced X-ray emission. The concentrations of the elements Al, Si, K, Rb and Sr were found to vary by less than a factor of two throughout the particle size range studied. However, the concentration of the elements Ca, Ti, Mn, Fe, Y and Zr increased when the particle size decreased below 150 μm to reach a maximum around 63–45 μm and then to decrease. The concentrations of the elements in the generated aerosol particles were found to be more similar to those in the bulk soil than any particular size fraction. For the aerosol size fraction, elemental enrichment factors were calculated with respect to the composition of average crustal rock, average soil, the bulk Namib soil and the small size fraction of the Namib soil. For several elements, the enrichment factors varied quite significantly, depending on the choice of the reference material. The elemental ratios in the mineral aerosol were also compared to those in the atmospheric aerosol from the Namib Desert. It was confirmed that there is a marine contribution for S, Cl and Sr in the Namib natural aerosol. The composition of the mineral aerosol generated in this study should be useful in source apportionment studies for the Namib Desert and surrounding regions.

Key word index: Aerosols, desert, Namib, fractionation, X-ray analysis.

INTRODUCTION

Deflation of soils at the Earth's surface constitutes an important source of wind-blown dust. The annual production of dust is estimated to be of the order of 250×10^6 tons on a global basis (Prospero *et al.*, 1983), although widely differing estimates have been suggested. The main source areas of the wind-blown dust are the arid and seasonally arid regions of the world (Prospero, 1981). The dust produced in the arid regions is fed in the wind systems and transported over large distances. Such dust has been found in places as remote as Antarctica (Maenhaut *et al.*, 1979; Tuncel *et al.*, 1989).

The annual production of airborne dust from the Sahara and its pathways are fairly well understood. However, the production of dust from deserts in the Southern Hemisphere (Namib and Kalahari Deserts) is less well studied. The data available shows that, along the Atlantic coast, there is a dramatic fall in the amount of mineral dust present in the air across the Equator in the southeast trade winds as the influence of the North African desert falls off. Thus, the desert regions of southern Africa are not a massive source of mineral aerosol for the ocean (Chester *et al.*, 1984). Mineral dust from these areas is oriented in a northwest direction due to the southeasterly trade winds (Schütz, 1980).

Because of the rapid fallout of large size particles, the composition of the airborne dust might not reflect that of the soil from which it was generated. This necessitates the study of the chemical composition of dust as related to that of the soil.

The enrichment of elements in an aerosol sample can be inferred from size distributions and enrichment

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factors. The composition of average crustal rock or average soil is generally used for enrichment factor calculations. According to Rahn (1976), none of these is a satisfactory reference material because crustal rock is not easily weathered and soil may differ in its composition from the aerosol. Thus, there is a need to search for a suitable reference material.

Comparison of natural background aerosol in a remote continental area, where pollution sources are minimal, with aerosols artificially generated from the main source contributing to the aerosol in that area, might give an insight into the soil–aerosol fractionation effects.

In this study the mass-size function and the size distribution of the chemical composition of four Namib soils, as well as the aerosols generated from these soils, were studied. Several reference materials for the calculation of the enrichment factors were compared. Also, the aerosols generated from these soils were compared to the natural aerosol of the Namib Desert (Annegarn *et al.*, 1983) and to the composition of the aerosol in several remote areas (Lawson and Winchester, 1979). The suitability of the crustal elements in mineral aerosol for source apportionment studies is discussed.

EXPERIMENTAL

The soils in the vicinity of Gobabeb

The soil samples were collected near the Namib Research Institute at Gobabeb, situated in the middle of the Namib Desert, in central Namibia, on the Kuiseb river bed, at 23° 45′S 15° 03′E. This site is 100 km away from the nearest town, Walvis Bay (population 25,000). Vehicle movements in the direct vicinity of the station were limited to 2–4 per day.

The soil of the Namib Desert in the vicinity of Gobabeb has been fully described by Schulze (1969), Goudie (1972), Scholz (1972) and Tyson and Seely (1980). South of Gobabeb extends a vast sea of sand dunes. According to Besler and Marker (1979), these sand dunes originate from the weathering of the underlining sandstone. The sand of the dunes has a brownish colour, lighter near the coast, and a reddish brown colour predominating towards the interior. The main minerals constituting the light-coloured dune sand are feldspar and quartz with secondary mineral constituents of monazite, staurolite and chlorite. The dark dune sand has garnet, monazite, opaque ore minerals and feldspar as main constituents, and chlorite, zircon, epidote, staurolite, tourmaline and ilmenite as minor constituents.

The plains between the dune ridges are covered with a reddish grey dense limestone crust containing large pebbles in its upper portion and covered with quartz gravels. The reddish grey crust contain 41.5% $CaCO_3$.

On the plains north of the Kuiseb River, two principal soil types can be distinguished. These are the syrosems or raw mineral soils and a soil with limestone or gypsum crusts.

Along both banks of the Kuiseb River, flood-loams with a dirty brown colour occur. These flood-loams contain gypsum and are also rich in NaCl. The composition of the flood-loams reflects the influence of the different areas inundated by different floods.

Because of the gypsum and the calcite crusts, surface Namib soil is known to contain a high calcium content. Analysis by XRF of about 200 surface soil samples from the Namib showed an average calcium content of 2%, which is almost twice as high as the world's average (Evens, 1978).

Soil sample collection

Four soil samples were collected. Sample 1 is from one of the numerous sand dunes (20 km south of Gobabeb), which covers the base plain south of the Kuiseb River, towards South Africa. Sample 2 is from the base between the dunes in that area. Sample 3 is from the Kuiseb river bed, which is dry except for one average precipitation event per year: the sample can be considered as an average for the region. Sample 4 is from the plain north of Gobabeb, which stretches out to Angola.

All samples were collected with a plastic scoop and stored in plastic bags.

Soil sample preparation and analysis

Each of the four Namib soil samples was fractionated by dry sieving to give size fractions of diameter >300, 300–250, 250–200, 200–150, 150–100, 100–63, 63–45 and <45 μm, i.e each sample set consisted of the bulk soil and these eight fractions (subsamples). From each subsample as well as from the bulk soil, an aliquot of about 0.03 g was mixed with 10 ml of bidistilled water and ground for 2 min with a McCrone Micronizing mill using corundum grinding elements. Three millilitres of the resulting slurry was pipetted on a Mylar film glued to a Teflon ring, which fitted the sample holder, and dried in an oven at 60 °C for about 8 h. Thus, intermediately thick samples were obtained. This method of sample preparation was introduced by Van Grieken *et al.* (1979). Three targets were prepared from each soil fraction. These targets were analysed by means of energy-dispersive X-ray fluorescence spectrometry (EDXRF). The EDXRF spectrometer used was a Tracor X-ray TX 5000 unit (Tracor X-ray Mountain View, CA, U.S.A.), which is a microcomputer-based energy-dispersive spectrometer with a rhodium X-ray tube. Two experimental set-ups were used to acquire the spectra for the light and heavy elements. For the light elements (Mg–Cl), an accelerating voltage of 15 kV and a 0.1 mA tube current with a cellulose filter were used, while for the heavy elements (K–Zr), a 35 kV accelerating voltage, a 0.35 mA tube current and a thin rhodium filter were used.

Spectrum evaluation and quantification were performed by means of the AXIL-QXAS software package (He, 1991).

Aerosol generation and analysis

A 1 kg aliquot from each soil was placed in a plexi-glass chamber, the design of which is shown in Fig. 1. The plexi-glass chamber was placed in a laminar flow clean air hood. A stream of filtered air was blown over the soil sample, at a velocity of about 10 $m\,s^{-1}$, by a fan fixed at the rear of the chamber. The chamber was divided into three, incompletely separated compartments by two layers of plexi-glass. The soil was placed in the lower compartment. The layers above this compartment provide some sort of a cut-off: very large particles will settle before they reach the upper compartment. At the top of the chamber, the dust (mineral aerosol) generated by the air is collected by sucking the air through an impactor using a vacuum pump. The impactor was a PIXE International (Tallahassee, FL, U.S.A), Model I-1 inertial cascade impactor. This impactor, when operated at 1 $\ell\,min^{-1}$, fractionates the aerosol into size fractions of >16, 16–8, 8–4, 4–2, 2–1, 1–0.5 and 0.5–0.25 μm equivalent aerodynamic diameter (EAD) for stages 7–1, respectively. The collection surface was KIMFOL polycarbonate film of 1.5 μm thickness. It was coated with vaseline for stages 7–2 and with paraffin for stage 1. In addition a back-up filter collected particles of less than 0.25 μm. Fourteen impactor samples were collected from these soils. The collection time ranged from 30 s to 2 min depending on the type of the soil. Dust is easily generated from soils rich in small particles.

The aerosol samples were analysed by means of particle-induced X-ray emission (PIXE). The samples were irradiated by a 2.4 MeV proton beam, supplied by the compact isochronous cyclotron of the University of Ghent. Full details about the PIXE experimental set-up, analytical procedure, calibration and uncertainties are given elsewhere (Maenhaut *et al.*, 1981; Maenhaut and Raemdonck, 1984). A modified version of the AXIL program (Maenhaut and Vandenhaute, 1986) was used to evaluate the spectra. For the aerosol samples, the particle mass actually collected on each stage was not determined. Therefore, the PIXE analysis of these samples provided absolute elemental amounts (in ng per stage), not concentrations. From the EDXRF results of the dry sieved soil size fractions, it was observed that the concentration of the elements Al and K did not show large variations with particle size. We assumed that this trend will continue throughout the aerosol particle size range collected with the cascade impactor. Therefore, the particle mass for each stage of the cascade impactor samples was calculated on the basis of the Al and K masses determined by PIXE and the average EDXRF concentrations of the oxides of these elements in the soil (average of the eight dry sieved fractions and the bulk samples). Subsequently, all absolute elemental PIXE data were converted into concentration values.

RESULTS AND DISCUSSION

Accuracy

The accuracy of the overall procedure was estimated by the analysis of reference soil samples available from the International Atomic Energy Agency (soil 5 and soil 7). From each soil sample three targets were prepared as above and analysed by EDXRF. The results obtained in this work and the certified values are compared in Table 1. The analytical result, in most cases, agrees fairly well with the certified value.

Mass-size function of the soil and aerosols (physical fractionation)

For the aerosol samples, the aerodynamic equivalent diameter was converted to the geometric diameter through (Hesketh, 1977):

$$d_p = d_a \sqrt{\frac{C_a}{C_p \rho_p}}, \qquad (1)$$

where d_p is the geometric diameter, d_a is the aerodynamic equivalent diameter, C_p and C_a are the Cunningham correction factors for particles of diameters d_p and d_a, respectively, and ρ is particle density.

The Cunningham correction factor can be calculated using the equation:

$$C = 1 + \frac{(6.21 \times 10^{-4})T}{d}, \qquad (2)$$

where T is the temperature in K, and d is the particle diameter in μm.

The above equation can be used to obtain C_a from d_a (i.e. by replacing d in the equation by the aerodynamic equivalent diameter). As for soil particles, a ρ_p value of 2.4 was adopted. This value is the average between quartz and clay minerals densities (Avallone and Baumeister, 1986). Hence, in the right-hand side of Equation (1) we are left with one unknown, i.e. C_p. As a first approximation, $C_p = C_a$ was assumed and a first estimate of d_p was calculated from Equation (1). This value of d_p was used in Equation (2) to produce a new C_p. The new value of C_p was then used in Equation (1) to produce a new value of d_p, and so on. The number of iterations depends on the accuracy required. This

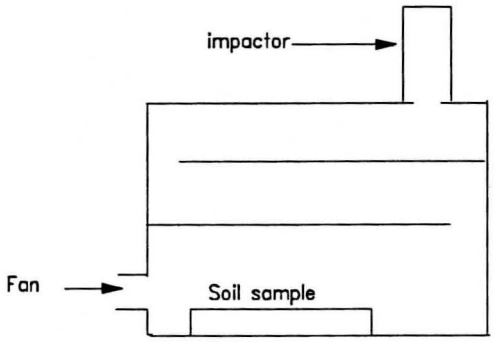

Fig. 1. Schematic diagram of the plexi-glass chamber used for mineral aerosol generation.

Table 1. Comparison of the EDXRF results obtained in this work with the certified values for reference soil samples

	IAEA soil 5		IAEA soil 7	
Element	Certified ± SD	Measured ± SD	Certified (confidence interval) (significance level 0.05)	Measured ± SD
Al (%)	8.19 ± 0.28	8.37 ± 0.3	4.7 (4.4–5.1)	3.1 ± 0.2
Si (%)	(33)	24 ± 2	18 (16.9–20.1)	19 ± 3
K (%)	1.86 ± 0.15	2.1 ± 0.2	1.21 (1.13–1.27)	1.4 ± 0.1
Ca (%)	(2.2)	2.9 ± 0.3	16.3 (15.7–17.4)	18.8 ± 1.2
Ti (%)	(0.47)	0.75 ± 0.03	0.3 (0.26–0.37)	0.47 ± 0.04
Mn (ppm)	852 ± 37	1110 ± 80	631 (604–650)	774 ± 60
Fe (%)	4.45 ± 0.19	5.4 ± 0.3	2.57 (2.52–2.63)	3.3 ± 0.3
Rb (ppm)	138 ± 7.4	117 ± 12	51 (47–56)	50 ± 3
Sr (ppm)	(330)	319 ± 21	108 (103–114)	124 ± 14
Y (ppm)	(21)	22 ± 3	21 (15–27)	30 ± 7
Zr (ppm)	(221)	221 ± 24	185 (180–201)	180 ± 6

resulted in the conversion of the <0.25, 0.25–0.5, 0.5–1, 1–2, 2–4, 4–8, 8–16 and >16 μm EAD mentioned above to the <0.15, 0.15–0.30, 0.3–0.6, 0.6–1.3, 1.3–2.6, 2.6–5.1, 5.1–10.3 and >10.3 μm geometric diameters, respectively. All further references to aerosol diameter are to the geometric diameters.

The mass-size functions for the four soil samples and the dust generated from these soils are shown in Figs 2a and 2b.

Soil 1 has most of its mass in the particle size range 200–300 μm. Dry sieving of this soil did not produce a weighable mass with $d<63$ μm. The aerosol generated from this soil has most of its mass between 1.3 and 10.3 μm. Soil 2, which is a fine sand, has most of its mass between 63 and 200 μm. The fraction of this soil with $d<45$ μm is about 8% and the aerosol generated from the soil has much of its mass in the range >10.3 μm. The aerosol from soil 3, which is also fine sand with most of its mass between 100 and 250 μm, shows essentially the same mass-size function as the aerosol from soil 2. Soil 4 is formed largely from fine sand with most of its mass at 63–150 μm and the aerosol from this soil has most of its mass between 2.6 and 10.3 μm. These results reveal the strong physical fractionation at the soil–air interface during the production of mineral aerosol resulting in the bulk of aerosol appearing where only a small fraction of the soil mass exists. Since soils undergo such strong mass fractionation, the size fraction between 1.3 and 10.3 μm, which forms the bulk of the mineral aerosol, might differ in the chemical composition from the bulk soil.

Size distribution of the elemental concentrations of the soil and aerosols (chemical fractionation)

Because of the uncertainties on the data for stage 1 and the back-up filter of the cascade impactor, these will not be included in the discussion.

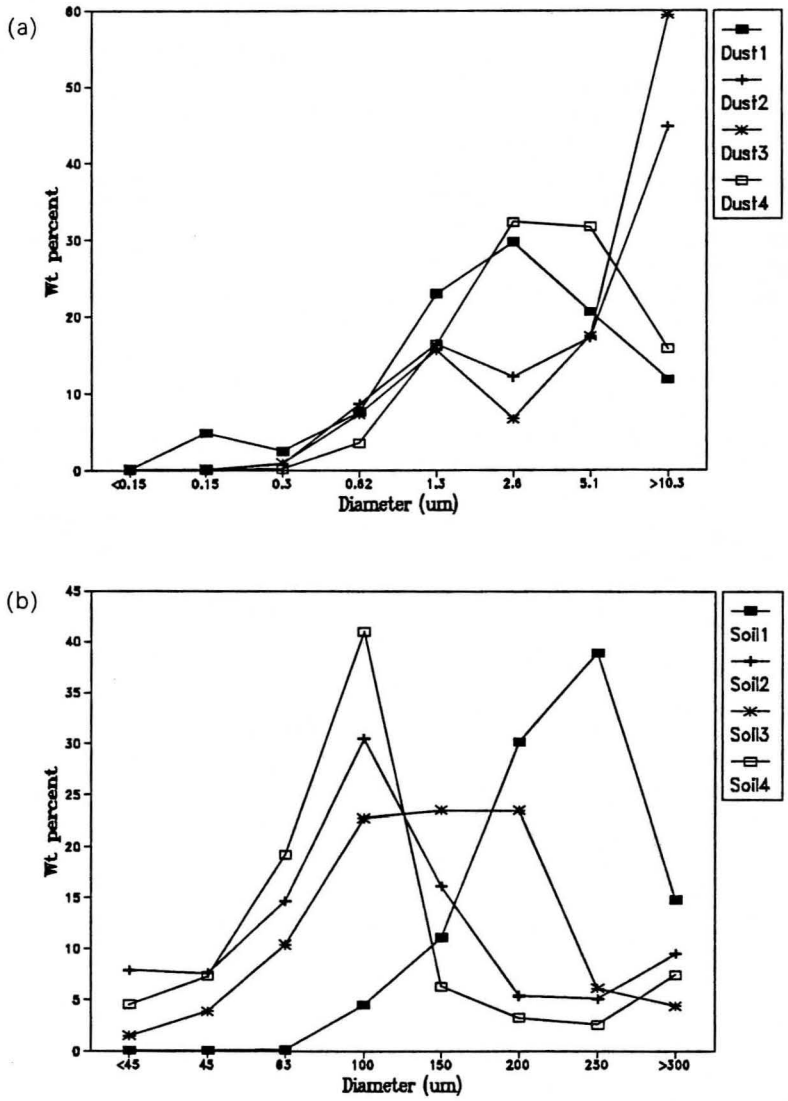

Fig. 2. Mass-size functions for the soil samples as derived from (a) dry sieving and (b) for the aerosol dust generated from the soil.

Examination of the size distribution of the elemental concentrations over the entire range of particle size revealed no major discontinuities of concentration pattern with particle size at the juncture between the two modes of soil fractionation, i.e. dry sieving and aerosol generation. Generally, the elemental concentrations showed little variability with particle size at the large particle sizes ($d > 200$ μm) and for the small particle sizes ($d < 10.3$ μm).

For each element, the pattern of concentration variation vs particle size was fairly similar for the four soils. In the following, the average concentrations, shown in Fig. 3, will be discussed. For the dry sieved soil samples (from < 45 to > 300 μm), each concentration is the average of 12 measurements (three targets from each size fraction of the four soils) and for the aerosol size fractions, each concentration is the average of 14 measurements, i.e. 14 impactor samples. The elements can be classified into two different groups according to the similarity of their size distributions. These groups are:

The elements Al, Si, K, Rb *and* Sr (*Fig.* 3*a*). The concentration of these elements appear to be constant, within a factor of about two, over the entire particle size range. Sample-to-sample variations in the size distribution were not significant.

The elements Ca, Ti, Mn, Fe, Y *and* Zr (*Fig.* 3*b*). The size distributions of these elements in the four samples were rather similar. Figure 3b shows the average concentrations for these elements. The concentration of calcium in the soils starts to increase when the particle size decreases below 150 μm, and reaches a maximum in the aerosols around the particle size range 2.6–5.1 μm and decreases thereafter. The concentration of the elements Ti, Mn, Fe, Y and Zr also increases for particle sizes below 150 μm, but reaches a maximum at about 45 μm and then decreases. In the aerosol size range below 10.3 μm, the concentration remains constant within a factor of two.

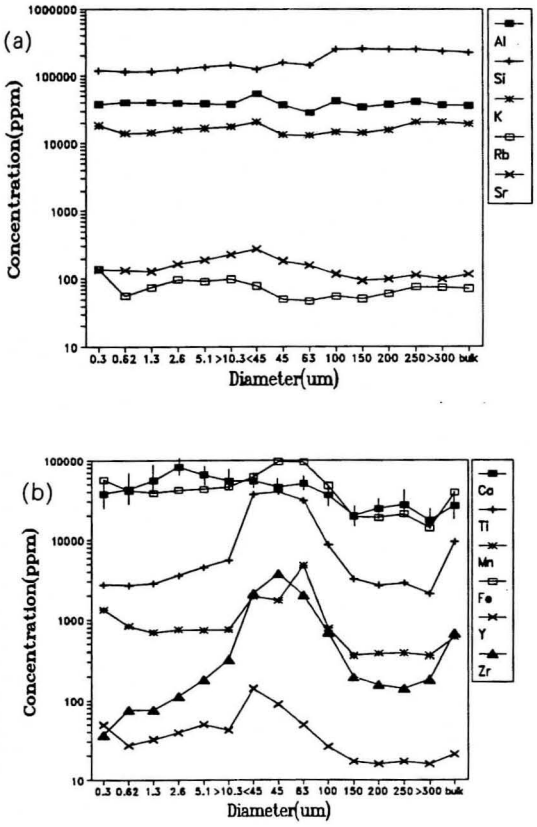

Fig. 3. Average elemental size distributions for Namib soil and its mineral aerosol: (a) Al, Si, K, Rb and Sr; (b) Ca, Ti, Mn, Fe, Y and Zr. The error bars for calcium denote ±1 standard deviation; they were smaller for other elements.

Similar studies of chemical fractionation of the soil have only been reported by Miller *et al.* (1972) and Schütz and Rahn (1982). Overall, our results are in agreement with these former studies. Miller *et al.* (1972) observed a positive fractionation between bulk soil and dust generated from this soil for the elements Al, Ca, Fe, Mn and Ti and a negative fractionation for Si. Schütz and Rahn (1982) reported a positive fractionation in the particle size range < 16 μm relative to the large particle sizes for all the elements they studied, except for silicon. These authors did not discuss the drop in elemental concentration for particle size < 45 μm although it was evident from their plots of elemental concentrations and enrichment factors. Also, Stuart *et al.* (1988) found aerosol generated from street dust to be depleted in silicon relative to aerosol generated from soil.

The increase in elemental concentrations at the small particle sizes is attributed by Schütz and Rahn (1982) to result from the fact that there is a great variety of mineral species, including feldspars, mica and clay mineral species, at the small particle sizes, whereas for the large particle sizes, a smaller number of mineral species such as quartz and calcite dominate. The drop in the elemental concentration for particle size range < 63 μm is more difficult to explain. However, in sediments the concentrations also peak at a certain particle size range, i.e. at 20–100 μm diameter (Füchtbauer and Müller, 1970). The constancy of the concentration in the aerosol particle range (0.3–10.3 μm) can be explained by similar mineralogical content at these particle sizes, i.e. similar clay mineral content.

The similarities in size distributions in the two element groups might reflect mineralogical associations. Tentative diffraction studies showed that the soils contain feldspar (possibly alkali feldspar such as plagioclase which explains the association of Al, Si, K and Rb) and mica which also consists of K, Al and Si with possible minor substitution by Mn, Fe, Ti and Cr (e.g. muscovite $KAl_2(AlSi_3O_{10})(OH)_2$).

The zirconium in the soils may be attributed to the presence of zirconite ($CaZrTi_2O_7$). The fact that the titanium size distribution shows very good similarity to that of zirconium suggest that there is some

association between these elements. Zirconite was not detected by the diffraction method but it commonly occurs in association with calcite (Roberts *et al.*, 1974). However, the major fraction of the titanium can be attributed to ilmenite ($FeTiO_3$), which forms a minor constituent of the dark coloured dunes (Scholz, 1972). Calcite was detected in the soils and accounts for the high concentration of calcium observed. Gypsum, which may have a marine source (Andreae *et al.*, 1986), was detected in aerosols from the Namib (Annegarn *et al.*, 1983).

Enrichment factor calculations

Enrichment factor calculation is used extensively in aerosol studies. To calculate the enrichment of the elements in an aerosol sample relative to their proportion in the mineral aerosol (dust), the composition of the mineral aerosol is required. Since the exact composition of the mineral aerosol is not available, certain surrogates are used. These include average bulk crustal rock, average bulk soil and remote continental aerosol composition. Since soil is easily weathered and covers about 93% of the Earth's continental surface, it is obvious that soil rather than rock is the true precursor of mineral aerosol and should be used instead of rock to approximate the composition of mineral aerosol in enrichment factor calculations. However, perhaps because the data on crustal rock are more detailed, most workers have used the data for the rock composition for the enrichment factor calculation. In using soil as reference material there are also the questions of whether to use local or average soil and bulk or a certain fraction of the soil. In the previous section we have seen that the chemical composition of soil is size dependent; in what follows we will consider the question of enrichment factor calculation and compare the use of crustal rock (Mason, 1966), average soil (Vinogradov, 1959), Namib bulk soil, the smallest fraction of the Namib soil and the average composition of the mineral aerosol generated from the Namib soil (14 impactor samples; six stages for each impactor).

Enrichment factors were calculated using aluminium as reference element. As previously indicated, the concentration of this element varies by less than a factor of two throughout the particle size range considered. Thus, the enrichment factors bear close similarity to the size distributions shown in Figs 3a and 3b. The average enrichment factors (average of 12 measurements for each of the eight dry sieved size fractions; average of 14 measurements for each of the six aerosol size fractions) using the above-mentioned materials as reference are shown in Figs 4a–4e for Si, K, Ca, Ti, Fe and Zr, respectively.

Figure 4a shows the Si/Al ratio and the enrichment factors for Si. The highest enrichment factor is obtained using the smallest fraction of Namib soil, the aerosol or average crustal rock as reference material, because the Si/Al ratio is somewhat higher in average soil and bulk Namib soil than in the aerosol dust and in average crustal rock. This is in accordance with the decrease in the Si/Al ratio with decreasing particle size. Figure 4a also shows the size distribution of the Si/Al ratio. The Si/Al ratio decreases from a value of 6 at the large particle sizes to a value of 3 at the aerosol particle sizes. A similar decrease in Si/Al ratio is also reported by Miller *et al.* (1972), who found the Si/Al ratio to decrease from 3.4 in soil to 2.2 in the dust generated from the soil. Also, Rahn (1976) indicated that the Si/Al ratio in atmospheric aerosols is on average 2.2, which is lower than the value of 3.4 in crustal rock (Mason, 1966) and the value of 4.63 in average soil (Vinogradov, 1959). The high ratio observed here for the soil dust aerosol falls well within the range of 2.9–5.7 of Si/Al ratios reported for the aeolian dust from different arid regions in the world (Pye, 1987).

The low Si/Al ratio at the aerosol particle sizes as compared to the large particle sizes is suggested by Rahn (1976) to result from the higher clay content at these particle sizes as compared to the large particle sizes. The Si/Al ratio in clay minerals ranges between 1.04, for kaolinite and muscovite, and 2.07, for montmorillonite (Mason, 1966). To explain that clay minerals (with diameter of <2 μm) lower the Si/Al ratio for the entire aerosol particle size range (diameter 0.3–>10.3 μm), Rahn (1976) suggested that they are present in the form of aggregates and/or coating on quartz particles. This assumption is supported by Gillette *et al.* (1972), who observed several layers of coating by clay particles on large particle size quartz. The enrichment factors for the elements K, Rb and Sr did not show large variations with particle size. Figure 4b shows the enrichment factors for Potassium calculated relative to the reference materials mentioned above. The lowest enrichment factor is obtained when bulk Namib soil is used as a reference material. The small size fraction of Namib soil and the aerosol generated from this soil gave similar enrichment values. Figure 4b also indicates that the Namib soil is enriched in potassium relative to the average soil and to the crustal rock. The average soil gave the highest enrichment factor.

Figure 4c shows the enrichment factors for calcium calculated relative to the reference materials mentioned above. Because the Namib soil is enriched in calcium, a high enrichment factor is obtained relative to crustal rock and average soil, while the enrichment factor calculated from the local soil and mineral dust is close to unity.

Figure 4d shows the enrichment factors for titanium. Titanium appears to be depleted in the aerosol particle size range when bulk Namib soil and the small fraction of this soil are used as reference materials. This indicates a higher Ti/Al ratio for the bulk and the small fraction of Namib soil as compared to the average crustal rock and average soil. This can be explained by the presence of titanium-containing minerals such as ilmenite and zirconite in the Namib soil. With the other reference materials, the enrichment

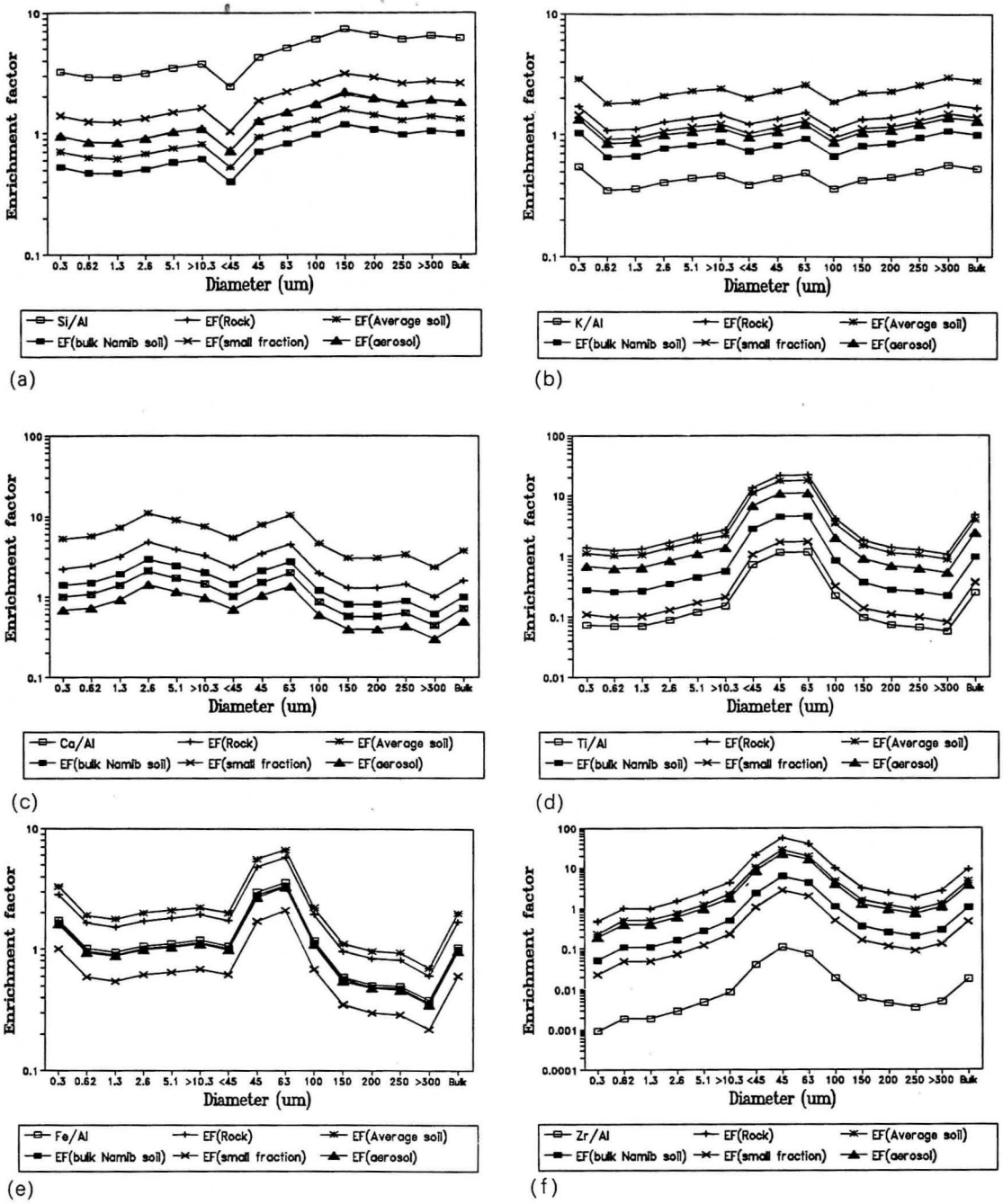

Fig. 4. Average enrichment factors for several elements in Namib soil and its mineral aerosol, using average crustal rock (Mason, 1966), average soil (Vinogradov, 1959), bulk Namib soil, the smallest size fraction of Namib soil and the mineral aerosol generated from Namib soil as reference material: (a) Si, (b) K, (c) Ca, (d) Ti, (e) Fe, (f) Zr.

factor of titanium is around unity for the aerosol size fractions, but much larger for the soil particle sizes 45–100 μm apparently due to the enrichment of titanium-containing minerals in this size range. The enrichment factors found for the particles of 100–300 μm are essentially the same as those found for the aerosol fraction.

Figure 4e shows the enrichment factors for iron. The plots show some similarity with those for titanium. However, the enrichment factors for iron at the aerosol particle sizes are about twice as large as at the large particle sizes (150–300 μm) and very similar to that for the bulk soil. The enrichment factors for zirconium (Fig. 4f) show essentially the same size distribution as those for titanium.

With regard to the long-range transport of mineral aerosol, model calculations by Schütz (1980), indicate that the bulk of aerosol mass found at distances

> 1000 km will be formed from particles of radii < 10 μm. Hence, its composition will be similar to that of the bulk soil but different from any other fraction of the soil. Because of the constancy of the elemental concentrations in particles with radii < 10 μm, further transport should not alter the mineral aerosol composition. This was experimentally confirmed by Rahn *et al.* (1979) for the transport of Saharan dust over a 2400-km cruise track in the North Atlantic.

As a summary for the aerosol particle sizes, Table 2 presents the average enrichment factors relative to aluminium for the full size range 0.3–10.3 μm relative to the reference materials mentioned above. The data show that the enrichment factor calculated using either the bulk or the small particle fraction of Namib soil are almost always lower than the enrichment factors calculated using the other reference materials. This is specially true for the elements Ca, Ti, Y (for the small particle size) and Zr. Only Sr, Rb and, to some extent K, show similar enrichment factors.

Comparison with aerosol collected in the Namib and other remote continental aerosols

It is of interest to relate the results from this work to the studies on the composition of the continental atmospheric background aerosols, as carried out by Annegarn *et al.* (1983) for the Namib Desert, and by Lawson and Winchester (1979) for several remote sites in South America. The latter authors proposed that the average elemental ratios for the crustal elements in their aerosol samples are a better choice for enrichment factor calculations than the ratios in either average crustal rock or soil, and they denoted their average aerosol composition by standard crustal aerosol (SCA). Our results are also compared with the results obtained by Ganor *et al.* (1991) on the composition of aerosols in Israel following dust storms and with the data from Kushelevsky *et al.* (1983) on aerosols from Israel with high total suspended particulate (TSP) values.

In Table 3 the ratios of the elements to iron in the artificially generated aerosol for the particle size range 0.3–2.6 μm are compared to the corresponding ratios in the studies mentioned above. Compared to the artificially generated aerosol from the Namib soils, the natural atmospheric aerosol in the Namib Desert shows ratios to Fe that are high for the elements S, Cl and Sr, but similar for the elements K, Ca, Ti and Mn. In contrast to the metallic elements discussed above, sulphur showed quite variable concentrations in the aerosols generated from the four soils. For soils 1 and 3, similar S/Fe ratios were observed, but they were higher by a factor of 10 than in the aerosols generated from soils 2 and 4. The large difference in the S/Fe ratios for the two groups of soils can be explained by the geology of the area. The Namib Desert is known to contain a gypsum crust which resulted from the transformation of the calcareous sediment underlying this crust. According to Martin (1963), the sulphur necessary for this transformation is generated as follows: the Benguela Current carries water rich in nutrients which allow the growth of very rich plankton and fauna; during the summertime, the destruction of this plankton and fish fauna by the hot subtropical high salinity water brought by the north or west wind produces large quantities of H_2S that, after oxidation, are capable of transforming $CaCO_3$ to gypsum. It is possible that the soil samples with high sulphur content (nos 1 and 3) originated from the gypsum crust. Calcium was also found to be somewhat more elevated in these two samples than in soil samples 2 and 4. Also, gypsum crusts are softer and more easily decomposed than limestone crusts (Scholz, 1972). The S/Fe ratio in the atmospheric aerosol from the Namib is more than twice the average S/Fe ratio in the soil dust aerosols. This suggests that more than half of the sulphur in the atmospheric aerosol originates from a non-mineral source. According to Annegarn *et al.* (1983), this excess sulphur is brought in from the ocean. That there is a substantial marine influence on

Table 2. Enrichment factors for the aerosol generated from Namib soil as calculated relative to average crustal rock (Mason, 1966), average soil (Vinogradov, 1959), bulk Namib soil and the smallest fraction of Namib soil ($d < 45\mu m$)

Element	Rock	Average soil	Local soil	Smallest fraction of local soil
Si	1.0±0.1	0.7±0.1	0.6±0.1	1.5±0.2
K	1.3±0.1	2.2±0.2	0.8±0.1	1.1±0.1
Ca	3.3±0.7	7.6±1.7	2.0±0.5	1.5±0.3
Ti	2.0±0.3	1.6±0.2	0.4±0.1	0.23±0.02
Mn	1.6±0.2	1.6±0.2	1.2±0.1	0.5±0.1
Fe	1.7±0.4	2.0±0.5	1.0±0.2	0.6±0.1
Rb	2.1±0.3	1.7±0.2	1.2±0.2	1.7±0.2
Sr	1.0±0.3	1.2±0.3	1.6±0.4	1.0±0.3
Y	2.7±0.9	1.6±0.5	2.0±0.6	0.4±0.1
Zr	2.6±0.9	1.7±0.5	0.13±0.05	0.9±0.3

Table 3. Elemental ratios to iron in the aerosol generated from Namib soil ($d = 0.3$–$2.6\ \mu m$), in atmospheric aerosols collected in the Namib Desert (Annegarn *et al.*, 1983), in the Standard Crustal Aerosol (Lawson and Winchester, 1979) and in aerosol from Israel (Ganor *et al.*, 1990; Kushelevsky *et al.*, 1983)

Ratio	Dust from Namib soil	Namib atmospheric aerosol	Standard Crustal Aerosol	Aerosol* following dust storms	Aerosol† with high TSP values
Al/Fe	1.1±0.2	—	2.0±1.4	1.42	—
Si/Fe	3.1±0.7	—	4.5±1.5	6.1	7.4
S/Fe	0.22±0.3	0.7±0.4	—	0.08	1.27
Cl/Fe	0.15±0.2	2.6±1.5	—	0.07	0.09
K/Fe	0.39±0.1	0.4±0.1	0.2±2.0	0.29	0.48
Ca/Fe	1.7±0.4	1.6±0.4	0.4±1.9	4.4	7.1
Ti/Fe	0.08±0.01	0.09±0.01	0.1±1.2	0.13	0.09
Mn/Fe	0.020±0.003	0.018±0.001	—	0.018	0.014
Sr/Fe	0.004±0.003	0.013±0.002	—	0.013	—

*Ratio of the means.
†Ratio calculated from enrichment factors.

the atmospheric aerosol composition is confirmed by the high Cl/Fe ratio in the atmospheric aerosol as compared to that in the mineral aerosol.

The Ca/Fe ratio is slightly lower in the mineral aerosol than in the atmospheric aerosol from the Namib. This suggests that the calcium in the atmosphere is mainly from mineral origin and that the oceanic contribution for this element is only marginal. However, it should be indicated that the areas covered by the gypsum and calcite crusts are small compared to the vast sea of sand dunes. These crusts may have been over-represented in our soil samples as compared to the actual situation in the field, and, consequently, the oceanic contribution to the atmospheric Ca and S levels may be significantly larger than that inferred on the basis of our data.

The Ti/Fe and Mn/Fe ratios for the atmospheric aerosol and the artificially generated aerosol are very similar to each other, thus indicating that the atmospheric Ti and Mn levels are fully attributable to soil dust dispersion.

Strontium is enhanced by a factor of four in the atmospheric aerosol as compared to the mineral aerosol. This suggests an oceanic contribution for this element in the atmospheric aerosol.

From a comparison of the composition of the SCA with that of the artificially generated Namib soil aerosol, it appears that there are very significant differences. Al, Si, Ti are depleted in the mineral aerosol with respect to the SCA, whereas K and Ca are enhanced. Clearly, the enhancement for calcium results from the fact that the Namib soil is rich in calcium.

The most noticeable discrepancies between the artificially generated aerosol from Namib and the aerosols from Israel (Ganor *et al.*, 1991; Kushelevsky *et al.*, 1983) are the high Si/Fe and Ca/Fe in the latter.

The use of elemental ratios for source apportionment studies

In source apportionment studies of aerosols, it is necessary to know the composition of the particles emitted by each source (the so-called source profiles). In order to be able to differentiate between mineral aerosol from different sources (different types of soil) such mineral aerosol should have different composition. Unfortunately, this is not the case for the four types of soil examined here (i.e. mineral aerosol derived from each of the four soils are all similar) so that it would appear that for mineral aerosol, elemental concentrations cannot be used as tracers in source apportionment studies. This view is also held by Schütz and Rahn (1982) and Schütz *et al.* (1990). However, the fact that there are differences in the major crustal elemental ratios in SCA and aerosol generated from Namib soil indicates that differences in the composition between aerosols from different regions do exist. It may be possible to use these differences in the elemental ratios for source apportionment studies to differentiate between aerosol from different regions. Elemental ratios to selenium have been used to differentiate between pollutant aerosols from the interior of the U.S.A. and those from the Northeast (Rahn and Lowenthal, 1985).

Another possibility for the source apportionment studies for mineral aerosol is provided by mineralogical analysis. Schütz and Sebert (1987) suggested the use of calcite and palygorskite as tracers for aerosol originating from the northern Sahara. Also, Chester *et al.* (1984) were able to differentiate between aerosols originating from the Sahara Desert and those originating from southern Europe on the basis of their clay mineral content.

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