Single particle characterisation and sources of tropospheric aerosols in the Negev desert (Israel)

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Abstract.
Individual aerosol particles collected in the Negev desert in Israel during a summer and winter campaign in 1996-1997 were analysed by scanning electron microscopy and transmission electron microscopy with energy-dispersive X-ray analysis. Hierarchical cluster analysis was performed to interpret the data on the basis of particle diameter and composition. Eleven particle classes (groups) provided clues on sources and/or particle formation. The summer samples were enriched in sulphates and mineral dusts; the winter samples contained more sea salts, aged sea salts and industrial particles. Mineral dust and sea-salt particles became more abundant with increasing particle size, while sulphates and other sulphur-containing particles increased with decreasing particle size. The fine size fraction below 1 μm diameter was enriched in secondary particles and showed evidence of atmospheric processing. The secondary sulphate particles were mainly attributed to long-range transport. A regional conversion from calcite to sulphate occurred during summer. Industrial particles originating from local pollution appeared during winter.

1. INTRODUCTION

The impact of atmospheric aerosols on visibility and climate depends on the chemical composition and the size of the particles and a detailed knowledge of the aerosol composition is also needed for source identification and apportionment. The Aerosol Radiation and Chemistry Experiment (ARACHNE), which is ongoing since 1995 in the Israeli Negev Desert, is a comprehensive study of chemical, physical and optical characteristics of the aerosols, of their interactions, source areas and of their direct radiative forcing on the climate of the eastern Mediterranean. ARACHNE comprises long-term studies [1-3] and intensive field campaigns, including one in the summer of 1996 [4,5] and one in late winter/spring 1997 [6]. The previous work in ARACHNE dealt with measurements of bulk aerosol properties and supporting trace gases. As the atmospheric aerosol is a complex mixture of individual particles which interact with the surrounding air in various ways, it is not sufficient to obtain size-resolved chemical composition data at the macroscopic (bulk) level. The chemical aerosol composition and other aerosol characteristics have to be determined at the individual particle level in order to improve our understanding of both the direct and indirect aerosol forcing on climate [7]. Electron microprobe and analytical scanning electron microscopy (SEM) are commonly used for characterising large series of individual particles [8]. Transmission electron microscopy coupled with a microanalysis system (TEM-EDS) is well suited for determining the nature of ultra-fine particles, since it can provide chemical (elemental composition), structural (phase composition), and morphological data on the submicron scale. It has been shown to be quite useful for characterising marine aerosols [9,10].

In order to complement the previous bulk analytical aerosol studies of ARACHNE, we performed morphological and chemical characterisations by SEM and TEM on selected aerosol samples to gain insights in the composition of individual particles as a function of size and in the relation between the particle characteristics and the sources (and source regions) of the aerosol particles.

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2. EXPERIMENTAL

2.1 Sample collection

Aerosol samples were collected in the Negev desert at Sde Boker, Israel, (30°51'N, 34°47'E, 470 m above sea level) (Figure 1), during summer 1996 (20 June to 10 July) and winter 1997 (18 February to 15 March).

![Figure 1. Sampling site – Sde Boker, Negev desert (Israel)](image)

Collections for SEM analysis were performed during daytime with a "Gent" stacked filter unit (SFU) sampler [11]. This device is equipped with a Gent PM10 inlet and separates the atmospheric particles into two size fractions by sequential filtration through two 47-mm-diameter Nuclepore polycarbonate filters with pore sizes of 8.0 µm (Apiezon-coated) and 0.4 µm filter (non-coated). The particles collected on the 8.0 µm filter range between 2 and 10 µm aerodynamic diameter (AD) and will be referred to as the coarse size fraction, while those on the 0.4 µm filter are smaller than 2 µm AD (fine size fraction). The samples for analysis by TEM were collected on a Cu grid covered with holey carbon film. The TEM grids were placed in a PIXE International cascade impactor; they collected the 2-8 µm AD size fraction, and the sampling time was 20 min. In discussing the bulk aerosol data from the two campaigns, Formenti et al. [5] and Ichoku et al. [6] focused on five days for the summer (22, 23, 29 June, 4 and 7 July 1996) and winter (21, 26, 27 February, 1 and 6 March 1997) periods. These days were selected because they were representative for the different types of atmospheric influences and conditions during the two campaigns. Samples from the same dates were selected for SEM microanalysis. Table 1 gives the details for collection of the samples together with the dust and pollution levels reported by Formenti et al. [5] and Ichoku et al. [6].

2.2 Single-particles analysis

Qualitative and semi-quantitative analysis of individual particles in the SFU filter samples was performed with a scanning electron microscope (SEM) (JEOL JSM-6300) equipped with an energy-dispersive X-ray detector (EDX) (Princeton Gamma-Tech, NJ). Working conditions were set at an accelerating voltage of 20 kV, a beam current of 1 nA, and the detector 60 mm from the sample. The take-off angle for the EDX detector was fixed at 30°. The magnifications were x2000 and x1000 for the fine and the coarse filter samples, respectively. With these working conditions, the minimum particle diameter to be observed is 0.7 µm for the coarse and 0.35 µm for the fine filter samples. Analyses were performed in the automated mode with the "Integrated Microanalyser for Imaging and X-ray" (IMIX) program (Princeton Gamma-Tech). A particle is recognised when its backscattered electron intensity is larger than a preset threshold and its diameter larger than the minimum size. The X-ray spectrum acquisition time was fixed at 20 s. Only elements with \( Z \geq 11 \) could be detected due to the presence of a Be entrance window for the Si (Li) detector.
A preset number of 1,000 particles were analysed for each sample, thus a total of 20,000 particles was investigated for both campaigns. For each particle recognised, the composition and size were measured. The transmission electron microscopy (TEM) analyses were done with a CM20-Philips (The Netherlands) instrument and they were performed at 200 kV accelerating voltage. The X-ray spectrum was acquired with energy-dispersive spectrometry (EDS) which allowed the detection of elements with Z ≥ 11. The counting time for each particle analysis was fixed at 60 s. Quantitative X-ray analysis for the S-rich particles was impossible because the sulphur compounds were lost during the spectrum acquisition. However, the qualitative compositional information in combination with structural measurements commonly provided a reliable particle identification. The crystal structure was identified through the measurement of several selected area electron diffraction (SAED) patterns for the particle on a double tilt specimen stage and from comparing these patterns with crystallographic library data [12].

Table 1. Collection details for the samples analysed by scanning electron microscopy and selected atmospheric data for the sampling days

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>Sampling time (local hour)</th>
<th>1PM&lt;sub&gt;f&lt;/sub&gt; µg/m&lt;sup&gt;3&lt;/sup&gt;</th>
<th>1Sr &lt;sup&gt;1&lt;/sup&gt;S µg/m&lt;sup&gt;3&lt;/sup&gt;</th>
<th>2SO&lt;sub&gt;2&lt;/sub&gt; ppbv</th>
<th>3CN cm&lt;sup&gt;3&lt;/sup&gt;</th>
<th>4Na&lt;sub&gt;12&lt;/sub&gt; cm&lt;sup&gt;3&lt;/sup&gt;</th>
<th>5BC&lt;sub&gt;4&lt;/sub&gt; µg/m&lt;sup&gt;3&lt;/sup&gt;</th>
<th>6N&lt;sub&gt;2&lt;/sub&gt; only %</th>
<th>7TMD&lt;sub&gt;f&lt;/sub&gt; %</th>
<th>8Ind&lt;sub&gt;f&lt;/sub&gt; %</th>
<th>9Dust Level</th>
<th>10Pollution level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer campaign</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>22.06.1996</td>
<td>10:29-19:32</td>
<td>18.7</td>
<td>2.64</td>
<td>2</td>
<td>12,500</td>
<td>1570</td>
<td>0.77</td>
<td>7</td>
<td>23</td>
<td>7</td>
<td>high</td>
<td>medium</td>
</tr>
<tr>
<td>23.06.1996</td>
<td>12:29-19:51</td>
<td>24.2</td>
<td>2.50</td>
<td>3.5</td>
<td>10,500</td>
<td>1500</td>
<td>1.71</td>
<td>&lt;1</td>
<td>4</td>
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<td>high</td>
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<tr>
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<td>2.07</td>
<td>0.5</td>
<td>2500</td>
<td>750</td>
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<td>21</td>
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<td>&lt;1</td>
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<td>low</td>
</tr>
<tr>
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<td>09:41-19:38</td>
<td>34.5</td>
<td>5.58</td>
<td>2.5</td>
<td>7500</td>
<td>1400</td>
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<td>24</td>
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<td>2500</td>
<td>800</td>
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<td>5</td>
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<tr>
<td>Winter campaign</td>
<td></td>
<td></td>
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<tr>
<td>21.02.1997</td>
<td>08:24-18:10</td>
<td>28.3</td>
<td>1.19</td>
<td>&lt;0.1</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.56</td>
<td>&lt;1</td>
<td>5</td>
<td>&lt;1</td>
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<td>low</td>
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<tr>
<td>26.02.1997</td>
<td>09:00-18:18</td>
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<td>4670</td>
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<td>1.79</td>
<td>0.1</td>
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<td>N.A.</td>
<td>0.79</td>
<td>21</td>
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<td>25</td>
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<td>low</td>
</tr>
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<td>01.03.1997</td>
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<td>&lt;1</td>
<td>11</td>
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<td>0.4</td>
<td>3696</td>
<td>N.A.</td>
<td>1.23</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>20</td>
<td>medium</td>
<td>low</td>
</tr>
</tbody>
</table>

PM: fine particle mass; Sr: fine Sr concentration from bulk analysis; CN: condensation nuclei number concentration; Na<sub>12</sub>: accumulation mode particle number; BC: fine black carbon concentration; N<sub>2</sub> only: fine N<sub>2</sub> only particles; TMD<sub>f</sub>: fine transformed mineral dust particles; Ind<sub>f</sub>: industrial particles; N.A. not available.

<sup>1</sup>Maenhaut et al. (unpublished results); <sup>2</sup>taken from ref. [5] for the summer campaign and from ref. [6] for the winter campaign.

2.3 Hierarchical Cluster Analyses

The results of the SEM-EDX single particle analysis were pre-processed with the PRODPP program developed at the University of Antwerp. The X-ray intensities were normalised to the sum of the intensities of Kα and Lα peaks detected for the particle. The relative intensities for the major elements detected were used as a proxy for the particle composition. Only elements with intensity above 1% of the total intensity were considered.

Data reduction and interpretation, in particular classification of particles with similar chemical composition into "particle classes", was performed by hierarchical cluster analysis (HCA) based on Euclidean distances and with Ward's error sum as similarity measure. The HCA was done using the Integrated Data Analysis System (IDAS) software package described by Bondarenko et al. [13]. The clustering was performed using an autoscaling procedure in order to assign an equal "weight" to each element defined as a variable. After such autoscaling the variables have non-zero mean and unit variance.

The chemical composition of each cluster (or class) is expressed as percentages of the elemental X-ray intensities and the abundance of each cluster is given as particle number percentage. More detailed information on this method can be found elsewhere [14].
This statistical procedure was applied to the SEM-EDX data of each individual coarse and fine filter. To assess the particle composition as a function of particle size, the EDX data of the coarse and fine filters were combined and sorted out into eight particle size classes (0.35-0.5 μm, 0.5-0.75 μm, 0.75-1 μm, 1-1.5 μm, 1.5-2 μm, 2-4 μm, 4-6 μm and larger than 6 μm). All sizes are based on the average projected diameters as measured with the SEM. Then HCA was performed on each particle size class for the summer and the winter campaigns.

2.4 Number size distribution

The particle number size distributions were calculated for each sampling day as \( dN/d\log D_p \), where \( N \) is the number of particles in one size class (thereby including the data from both the coarse and fine filters) and \( D_p \) is the corresponding size range diameter (in μm) as deduced from the SEM-EDS measurements. Because of the difference in magnification used, the scanned area for the fine filter is four times smaller than for the coarse filter. Hence, the number of fine filter particles in one defined size class was corrected with a weighing factor of 4 and thus, the total number of particles was calculated using the formula: \( N = (N_c + 4N_f) / 5 \) where \( N_c \) is the number of coarse particles in one size class and \( N_f \) is the number of fine particles in the same size class. Besides size distributions for each sampling day, average size distributions for the summer and winter campaigns were also calculated.

The number size distribution \( (dN/d\log D_p) \) for the sulphate droplets collected on the TEM grids was estimated from the particle morphologies on the carbon collection film. Because of degradation effects in the microscope it was impossible to derive the exact particle size by the method suggested by Ayers [15]. Loss of water induced by the TEM high vacuum decreased the apparent particle diameter, while the particle impaction during the collection and post-sampling crystallisation provided spreading for (partly) liquid particles and thus increased the apparent particle size. Fortunately, most of the time, residua of particles still retained the morphology created on impact. Based on methods described by Zhang et al. [16] an empirical relationship between the diameter \( (d_c) \) and height \( (h) \) of the spherical caps of particles on carbon films was used: \( h = 0.2889 d_c \)

where \( d_c \) is read directly from the electron microscope pictures; \( d_c \) was inferior to 0.5 μm for all samples. Then, the volume and the geometric diameter of the particles in the air were estimated. Finally, \( dN_{count}/d\log D_p \) was calculated with \( N_{count} \) being the number of counted particles from the electron microscope pictures.

The number size distributions obtained from the TEM data were approximate because of the low number of counted particles (250); furthermore, particles < 50 nm were underestimated because of the collection with the cascade impactor.

3. RESULTS AND DISCUSSION

3.1 Particle types and associated sources

On the basis of HCA, the SEM-EDX data for all filters were classified in 11 different clusters (particle classes), with each cluster having a distinct elemental composition. Between 5 and 10 of these clusters were present in the individual samples. Each particle class is assigned to a particular component in terms of its mineralogy and/or its possible origin. The 11 particle types (clusters) are described here:

1/ The aluminosilicate particle type is characterised by high relative X-ray intensities for Si and Al (Si + Al > 70% of the total intensity) and with minor relative intensities of Fe, K and/or Ca. The main source of these particles is the erosion andolian dispersion of rocks and soils. Kaolinite, illite, montmorillonite and feldspars are the most abundant aluminosilicate minerals found in Israel, especially during dust storm periods [17,18].

2/ CaCO\(_3\) particles are characterised by a relative intensity of Ca higher than 70%. Carbon could not be detected with the measurement system but we assumed that these particles correspond to calcium carbonates. In this group of terrestrial calcium carbonates, limestone (calcite) is probably the major
contributing compound. It was earlier supposed to originate from calcareous soils in Israel and adjacent countries [17,19].

3/ CaSO₄ particles are identified by an approximately equal abundance of Ca and S, varying between 40 and 50%. Two main origins were proposed for these particles in the Israel aerosol: gypsum from desert evaporation pans or sabchas [18,20], on one hand, and CaSO₄ formation from a complete reaction between CaCO₃ and atmospheric SO₂ or H₂SO₄ [21,22], on the other hand. Gypsum and anhydrite, emitted by the chemical industry producing super-phosphate located in the north of the country, were mentioned as a minor source of CaSO₄ in Haifa Bay and Tel Aviv [23], but they are not expected to contribute much to the CaSO₄ at the Sde Boker site.

4/ Other mineral dust particles contain crustal rock erosion products and mineral soil dust: (i) Si-rich particles with Si as the major element (relative X-ray intensity of Si > 80%) which presumably consist of SiO₂ (e.g., quartz); (ii) Fe-rich particles (Fe in the range of 50 to 80%) which either contain some sulphur (S < 15%) or not; the Fe-rich particles without S are considered to be oxides (hematite, magnetite) or oxyhydroxide (goethite) and the ones with S are assumed to be sulphur iron minerals (pyrite); the latter occur frequently in arid regions; (iii) Ti-rich particles which presumably consist of rutile (TiO₂) or ilmenite (FeTiO₃); finally, (iv) mixed mineral dust agglomerates, e.g., calcite-quartz, Ca-Mg-Si-containing particles resulting from aggregation of quartz and dolomite, and Si-Al-Ca-(Fe and/or K)-containing particles consisting of calcite and/or iron oxides associated with aluminosilicates. As expected, the other mineral dust particles were mostly detected in the coarse size fraction.

5/ Sea-salt particles are characterised by a high intensity of Cl (> 50%) together with Na, Mg and/or K. These chloride components are crystallised in the atmosphere from seawater droplets [24].

6/ Aged sea-salt particles are defined as particles containing Na, Mg, K and a variable contribution of S (from 10 to 80%) with Cl present (< 50%) or without Cl. These particles originate from the reaction of sea salt with atmospheric SO₂ and/or H₂SO₄ giving rise to a Cl depletion, S enrichment, and sulphate formation. Generally, they are found in the fine size fraction, but there is evidence that the reaction also occurs for the coarsest particles [25].

7/ Transformed mineral dust contains Ca (> 30%) and/or Mg (< 30%) with a variable fraction of S (ranging from 10 and 50%) and probably results from the incomplete transformation of carbonates (calcite and dolomite) with atmospheric sulphur components. Sometimes, Si (< 20%) is found in the coarsest fraction, indicating an aggregation of Ca-S and quartz particles.

8/ S-only particles show no association with other detectable elements above Z = 10. They are assigned to secondary sulphates formed from gaseous SO₂ occurring along the atmospheric transport pathway. Their composition ranges from sulphuric acid to ammonium sulphates and they are ubiquitous in the finest size fraction of the aerosol [10,26]. The source of these fine particulate sulphur secondary aerosols in Israel is mainly anthropogenic [19]. The dominant source regions for the Sde Boker site seem to be in Central and Eastern Europe. By applying trajectory statistics calculations for the long term Sde Boker data set from the 3-year period 1995-97, Ptasinski et al. [3] found that the major source region of the fine sulphur appears to be Ukraine, followed by the west coast of the Black Sea, and Greece. Recent studies indicated that marine biogenic sulphate, derived from the oxidation of dimethylsulphide (DMS), accounts for 6 to 22% of the total concentration of non-sea-salt sulphate in the Mediterranean region during the summer period [27,28].

9/ Industrial particles can be subdivided in two distinct groups:

(i) Lead and/or zinc (5 - 50%) containing particles sometimes associated with K and S. They show very low X-ray intensities compared to the other particle groups, which suggests the presence of a high abundance of low Z elements (Z < 11), implying an organic, carbonaceous or nitrate matrix. An association of metals together with K, S and low Z elements indicates a urban, industrial and/or waste incineration source [23,29]. The trajectory statistics calculations of Ptasinski et al. [3] indicated that fine black carbon and fine lead at Sde Boker originate mainly from local and regional sources (in Israel, Saudi Arabia and other countries in the region) while the main source of fine zinc is in Russia.

(ii) A second group contains S (10-45%) and low Z elements (Z < 11). The compounds associated with this group can be mixed salts of sulphate and nitrate and/or mixing of sulphate and carbonaceous particles
as has been commonly observed [9]. Sometimes K is also present in these particles. Possible sources are industrial emissions, power plants, residual fuel burning and biomass burning [30,31].

10/ *P-rich* particles contain P in the range between 14 and 28%. Associated elements are calcium and silicon and sometimes sulphur. Two sources within Israel could be responsible for phosphorus in the Negev aerosols: phosphate mining activities at Dimona to the North of Sde Boker and fertiliser industries in the Haifa Bay area, which produce H₂SO₄, H₃PO₄, superphosphate and triple superphosphates [23]. However, the latter source type is not expected to contribute much to the aerosol at Sde Boker.

11/ A remaining particle group of indistinct composition was also defined. It contains particles that can not be classified in one of the previous particle classes. The main contributors in this group are mixed particles originating from particle aggregation (e.g., dust (Ca) and/or marine (Cl, Na) aerosols associated with sulphur). The analysis of a number of individual particles showed conclusively that this particle type does not result from artefacts in data treatment by HCA. The presence of these particles may result from an aggregation of particles either in the atmosphere or during sampling.

3.2 Micro-characterisation and sources of summer campaign particles

The results of the HCA classification and composition of the coarse and fine size fractions for each summer SFU sample are shown in Figure 2.

![Figure 2. Percentages of 11 particle types in the coarse and fine SFU size fractions on 5 summer days](image-url)
It appears that the two major natural aerosol particle types that prevail in Israel are sea salt and mineral dust. This is due to the location of the country between the Mediterranean Sea and the desert. Three-dimensional backward trajectories calculated for five days with arrival at Sde Boker at low altitude (960 hPa) indicated that for the summer days the air masses all came from Southern Europe (mainly from Greece and southern Italy) across the Mediterranean and followed the Israeli coast before reaching the sampling site (Figure 3).

![Map of air mass back trajectories](image)

**Figure 3.** Five-day air mass back trajectories, calculated for arrival at the Sde Boker site at 960 hPa and 12:00 UT, for 4 of the 5 summer sampling dates.

### 3.2.1 Terrestrial influence and mineral particle characterisation

Mineral dusts (aluminosilicates, CaCO₃ and others mineral dust classes) are the major particle types in the coarse size fraction (>50% of the number of particles) while they are also prominent in the fine fraction (>30%). Local dust events (so-called dust devils) occurred almost daily in the summer afternoon and contribute to the results. According to the high content of fine and coarse mineral dust particles, the 22, 23 June, 4 and 7 July samples are highly influenced by terrestrial sources.

The TEM-EDS analyses of the summer samples showed that the mineral particles are composed of Si, Al, K, Mg and Fe and to a lesser extent Ca. The Ca-containing particles were identified as calcite. They were found as individual particles or in clay-calcite aggregates. The Si, Al (or Mg) - rich particles showed morphologic features of clay mineral particles. Three clay particle types were observed: the first one, and most abundant, were particles that contain Si and Al (sometimes K) and had a characteristic euhedral plate shape. The hexagonal electronic diffraction pattern indicated that they are clay platelets of well-crystallised kaolinite (Al₄Si₄O₁₀(OH)₈) or illite, when K is present (KₓAl₂Si₄₋ₓAlₓO₁₀(OH)₂) [32] (Figure 4). The second type of clay minerals occurred in thick well-defined platelike form and contained Si, Mg and O; they had a hexagonal diffraction pattern characteristic of talc particles (Mg₃Si₄O₁₀(OH)₂) [32]. Sometimes, Fe appeared in the EDS spectra without variation in the Si/Mg ratio and without changing the SAED pattern. Thus, surface coating of talc with amorphous iron compounds such as ferrhydrite or goethite is likely. Finally, clay particles containing Si, Al and Fe with a ratio Al/Fe = 1 were also identified. The diffraction patterns indicated that they were polyphasic particle aggregates composed of...
folded particles of smectite coated with fine-grained hematite. Hematite-induced reddening of the clays is
due to summer dehydration of free iron oxyhydroxide that is commonly found in Mediterranean soil [33].
For the fine size fraction on 7 July (a day with no particular pollution event), 12% of the particles are
CaSO₄ and 13% transformed mineral dust. The fine CaSO₄ on this day is probably from local soil origin and
the transformed mineral dust particles (both coarse and fine) are most likely the result of the
aggregation of mineral together with gypsum, a process recently described by Falkovich et al. [18]. The
average particle size of ca. 2 µm for the transformed mineral dust particles the fine size fraction confirms
the aggregate formation.

Figure 4. TEM images of particles from terrestrial origin consisting of kaolinite (a) and hematite (b)

3.2.2 Pollution particle chemistry and sources

Polluted days were identified on the basis of the high concentrations of SO₂, fine particle bulk sulphur and
fine particle mass [5]. According to these criteria, 22 and 23 June and 4 July can be identified as polluted
days with the highest pollution event occurring for the last date (Table 1). The major pollution particle
types provided by HCA for the samples from these days are the fine S-rich particles (both S-only and
transformed mineral dust) and the industrial particles. For the fine fraction sample of 4 July, 24% of the
particles are S-only compounds, 38% transformed mineral dust and 3% industrial particles, while for the
fine fraction of 22 June, there are 23% transformed mineral dust, 7% S-only and 7% industrial particles.
In contrast, only 4% transformed mineral dust and 12% industrial aerosols are found in the 23 June fine
fraction sample. The S-only particles consist of non-sea-salt sulphate compounds, such as sulphuric acid,
ammonium sulphate or ammonium bisulphate, which are predominantly formed by gas-to-particle
conversion of anthropogenic SO₂. Most of the particles identified by TEM in the polluted day samples
were pollutant particles (primary aerosols such as industrial particles or secondary sulphate particles).
The secondary sulphate particles could be distinguished by the high S level in the EDS spectrum and by a
typical spherical or rod shape morphology. They were sensitive to the electron beam; a halo around the
particles indicated the initial particle size (Figure 5). This phenomenon is recognised as a manifestation of
particle dehydration [34]. In order to identify the material, SAED patterns were obtained from the residue
shown in Figure 5. The interplanar distances of the ED pattern and related zone axis coincide with the
pure crystalline ammonium sulphates (NH₄)₂SO₄, and more acidic sulphate (NH₄HSO₄ and H₂SO₄). The
number of (NH₄)₂SO₄ particles was larger than that of NH₄HSO₄ and H₂SO₄ particles.
Formenti et al. [5] found that fine particle bulk sulphur (Sₖ) correlated with the fine particle mass (PMₔ),
but not with the SO₂ level. In the present work we observed a correlation between the fine S-only particle
abundance, PMₔ and Sₖ for the 4 July and the 22 June samples (Table 1). In spite of comparable
atmospheric data for 22 and 23 June, no S-only particles were identified in the 23 June sample.
The detailed analysis showed that the industrial particle class for the fine size fraction on 23 June contained on average 40% S, which was always associated with other elements (Pb, K and Ca) and low Z elements. Particles aggregates containing sulphates, soot and lead, presumably formed by atmospheric mixing, were identified by TEM for 23 June (Figure 6).

The particle aggregation explains why the HCA tends to classify S-containing particles in the industrial particle group and not in the S-only class. Formenti et al. [5] concluded from the condensation nuclei (CN) and accumulation mode particle (N_{0.12}) number concentrations, which are a measure of fresh and aged pollution, respectively, that the fine anthropogenic sulphate originated mainly from long-range transport on 4 July (CN = 7500 cm^{-3}, N_{0.12} = 1400 cm^{-3}) (Table 1). The S-only particles, measured on such polluted day, are most likely mainly ammonium sulphate particles that were formed along the transport pathway from SO_{2} that was emitted by distant sources. The meteorological conditions in the eastern Mediterranean during summer are consistent with a long lifetime of secondary sulphate particles which was estimated as being up to 6 days in the absence of precipitation [35]. Luria et al. [19] suggested that most of the sulphate in the region results from long-range transport. In addition, Matvev et al. [36] estimated that the long-range transported sulphur flux into Israel accounts for between 50% and 90% of the particulate sulphate. The 5-day back trajectory for 4 July (Figure 3) shows that the air masses arriving at 960 hPa had passed over the Athens
area before reaching the Israeli coast and could thus have transported long-lived secondary pollution aerosols. On the other hand, the air mass also resided for 24 hours over the industrial coast before reaching Sde Boker. The last section of the transport pathway is most likely at the origin of the high SO₂ and CN number concentrations observed at the Sde Boker site. On the TEM grid of 4 July we observed a high abundance of ammonium sulphate particles and a small number of H₂SO₄ particles. This is consistent with the fact that the lifetime of (NH₄)₂SO₄ (6 days) is longer than that of H₂SO₄ (a few days) [35]; it confirms that the sulphate on polluted days is advected by long-range transport.

A fresh local pollution origin was assigned by Formenti et al. [5] to the 22 June (CN = 12,500 cm⁻³ and N₀₁₂ = 1570 cm⁻³) and the 23 June (CN = 10,500 cm⁻³, N₀₁₂ = 1500 cm⁻³) sampling days. The fine fraction samples from these dates exhibited the highest concentrations of industrial particles (Figure 2). The industrial particle class cluster contained S (34% relative intensity), low Z elements (22%), Zn (20%), K (8%), Fe (8%), and Pb (8%) for the 22 June sample, and S (41%), low Z elements (35%), Ca (9%), Si (6%), K (6%), and Pb (3%) for the 23 June sample. For these two sampling days, aggregates of sulphates (mostly (NH₄)₂SO₄) and particles of industrial origin (soot and/or metal containing particles) were systematically found with the TEM (Figures 6 and 7), indicating that particle aggregation processes prevailed during the fresh local pollution. In addition, the high number of mixed sulphate and soot particles found by TEM in the samples suggests that the droplets of ammonium sulphates and acidic sulphates were formed initially through heterogeneous nucleation on carbon particle surfaces (Figure 7). Finally, we observed a significant number (20%) of Zn-containing particles in the fine fraction sample of 22 June. In the TEM analysis Zn-rich particles are identified by a granular aspect and a diameter of 0.5 - 1 μm. Their EDS spectra show both an intense peak of Zn and a small one of S, which is in agreement with the SEM-EDS results for the industrial particle subclass that contains Zn and S. The proportion of S found by TEM-EDS analysis is low compared to that obtained with SEM-EDS which is explained by the destruction of sulphate under the TEM electron beam. The Zn-containing particles are likely metallic aggregates that originated from industrial emissions and contained a surface sulphate layer. According to Ptasinski et al. [3] the main Zn source region is located in Russia. The air mass back trajectory with arrival at 900 hPa (not shown) showed for the 22 June a pathway through Eastern Europe via the eastern part of Turkey. Thus, some of the metallic particles may well be brought to the Sde Boker site by long-range transport.

Figure 7. TEM images of internally (a) and externally (b) mixed (NH₄)₂SO₄ and soot particles

3.2.3 Carbonate to sulphate conversion

High numbers of fine transformed mineral dust particles together with a depleted fine carbonate fraction were observed in the 22 June and 4 and 7 July samples. This was particularly evident for the 4 July
sample in which no fine CaCO₃ particles were observed. The fine transformed mineral dust particles group in the samples from the summer and winter campaigns exhibited a Ca intensity varying from 48 to 62% and a S intensity from 17 and 21%. The low S contents could reflect an incomplete reaction between fine carbonate particles and atmospheric SO₂ and/or H₂SO₄. We also detected sulphur enriched calcium particles on the TEM grids. The typical morphology is shown in Figure 8 (particles without special shape and particles with rod shape).

![Figure 8. TEM image (a) and EDS spectrum (b) of Ca-S rich particle](image)

The EDS analyses indicated that Ca and S were always present in variable proportions. The SAED patterns matched those for the insoluble anhydrite form of calcium sulphate (CaSO₄) or bassanite (CaSO₄, 0.5H₂O). The particles were often not well crystallised. There is a possibility that the calcium sulphates were originally hydrated but lost water and crystallinity in the microscope. Moreover, some small Ca-bearing particles (~ 50 nm) were also found that were coated with sulphate droplets. In this case, the Ca-S particles became only visible after complete destruction of the sulphate particles. Their SAED pattern matched with a tetragonal soluble anhydrite form. Simulation experiments in a controlled atmosphere indicated that the formation of calcium sulphate particles from CaCO₃ and SO₂ is complete within 16 hours in 90% relative humidity [37]. In low humidity desert conditions a slower formation rate and consequently both complete and incomplete reactions (depending on the particle size) can be expected.

Some of the Ca-S rich particles within the transformed mineral dust cluster could in principle be aggregates of gypsum and calcite. However, the mean diameters of the CaCO₃ and CaSO₄ particles in the fine size fraction were 1.6 μm and 0.7 μm, respectively, and the transformed mineral dust particles had a diameter of maximum 1.2 μm, while particles with a diameter of around 2 μm would be formed in the case of mechanical aggregation of CaCO₃ and CaSO₄ particles. Also, we did not observe mechanical aggregates of CaCO₃ and CaSO₄ by TEM. Hence, we suggest that the fine Ca-S particles originated from calcite to sulphate conversion in the atmosphere, i.e., from reactions between calcite and H₂SO₄ with a fine calcite solubilisation/recrystallisation chemical process, rather than that they were formed by aggregation of calcite and natural gypsum and/or anhydrite mineral particles.

Because CaCO₃ is a dominating mineral in the Negev desert dust, the fine limestone to fine Ca-S rich particle conversion is probably a regional or local process rather than a long-range process involving transported particles. The formation of the CaSO₄ particles probably occurs in less than two days (as was seen in simulation experiments) and could thus occur regionally and/or locally.
3.2.4 Marine influence and sulphate particle origin

The 29 June SFU sample had high proportions of sea salt (35% in the coarse size fraction) and aged sea salt (12% in the fine fraction) indicating an important marine source contribution (Figure 2). This is in agreement with the high concentrations of Cl (2900 ng/m³) and Na (1670 ng/m³) obtained by bulk analysis for the coarse SFU filter sample from 29 June (Maenhaut et al., unpublished). The TEM analyses for the sample from the same day clearly showed Na-Cl and Na-S particles as major marine particle components. As expected, halite (NaCl) was identified. The Na-S particles had a rod shape, the SAED pattern matched the monoclinic form of sodium sulphate (Na₂SO₄ (III)). The Na₂SO₄ was likely formed by the reaction of NaCl with atmospheric H₂SO₄ under marine atmospheric conditions. The non-common monoclinic form of Na₂SO₄ most likely arises from a transformation induced by the high vacuum in the microscope. Actually, the particles changed to the monoclinic form for the most stable phase (thenardite form (V)) under atmospheric conditions, when exposed to moist air. Supplementary Na/Ca/S particles had a rod shape and were around 200 nm long.

Sulphates of Na and Ca are able to form a variety of structures. We found that the common form of evaporite mineral was a slightly distorted orthorhombic form of Na₂SO₄ (thenardite). The compound was less sensitive to the electron beam than pure Na₂SO₄ compounds, suggesting a stabilisation of the sulphate by cation substitution. Although a variable Na/Ca peak intensity ratio was observed, the crystal structure was not significantly changed. All Na/Ca/S compounds are described in the literature as mixed-cation sulphates and typically originate from marine sources [9].

The 29 June was considered by Formenti et al. [5] as an unpolluted day (Table 1). Since the concentrations of SO₂, CN, N₁₀,ₐ, PM₁ and BC were all low (Table 1), one can conclude that there was also very little local pollution on this particular day. However, the HCA (Figure 2) showed a high fine S-only particle number (20%) which is in agreement with the significant concentration of fine S obtained by bulk analysis (2.07 μg/m³) (Table 1). Most likely, the fine S-only particles were secondary sulphate particles that were predominantly advected by long-range transport. However, because of the important marine impact on 29 June, one cannot exclude that there was a minor contribution to the S-only particles from natural secondary sulphates, derived from marine biogenic dimethylsulphide (DMS) [24,26]. Ganor et al. [26] estimated that the biogenic sulphate accounts for between 6 and 22% of the total concentration of non-sea-salt sulphate in the Mediterranean region during the summer period. The 29 June may have been a day with a marine biogenic sulphate contribution.

Finally, in the SFU sample from 29 June we found a significant number of fine CaSO₄ particles (15%) with a mean diameter of 0.7 μm. As there were a large number of fine S-only particles in the same SFU sample, it is logical to conclude that the fine CaSO₄ particles resulted from the complete conversion of fine calcium carbonate mineral dust into calcium sulphate. However, CaSO₄ particles in marine influenced samples may also result from the reaction of SO₂ or H₂SO₄ with coccolith (CaCO₃) as described for remote Pacific marine aerosols [38,39]. By TEM analysis of the 29 June sample we found significant amounts of fine CaSO₄ and mixed (Ca, Na)SO₄ particles, but there were no CaCO₃ crystals in sea-salt aggregates.

3.2.5 Particle number size distributions for the summer samples

The particle number size distributions, as derived from the summer SFU samples, are shown in Figure 9a. For the 29 June and 4 July samples, containing the highest S-only particle abundance, the number size distribution peaks in the range of 0.3-0.6 μm. This result is consistent with the diameter of sulphate particles in Israel as obtained by Ganor et al. [23]. The size distribution of the industrial particles peaked between 0.5 and 0.8 μm, thus at a somewhat larger value than that of the S-only particles. The peak for the 7 July sample around 0.9 μm can be attributed to fine CaSO₄ particles. The size distributions for the 22 June, 23 June, 4 July and 7 July samples exhibit a bimodal feature with a maximum
around 0.4 \( \mu \text{m} \) which is due to sulphate and a broad shoulder ranging from 0.8 \( \mu \text{m} \) to 2 \( \mu \text{m} \) which can be attributed to mineral dust and/or sea-salt particles.

![Summer particles (Coarse + fine)](image)

(a)

![Particle number size distributions](image)

(b)

**Figure 9.** Particle number size distributions for the SFU samples from the summer campaign (a) and for fine sulphates in the TEM sample from 4 July (b)

A tentative number size distribution for ammonium sulphates in the TEM sample of 4 July is shown in Figure 9b. The particle size derived from the TEM analysis is the geometric diameter estimated from the images on the collecting grids. Figure 9b indicates that the sulphate particles were mainly present in the size range between 0.09 and 0.4 \( \mu \text{m} \). These particle sizes are larger than the sizes of 0.01-0.13 \( \mu \text{m} \) that are expected for newly formed particles [40]. The figure presents the main characteristics of the number size distribution of ammonium sulphate particles that were advected by long-range transport to the Sde Boker site.
3.3. Micro-characterisation and sources of winter campaign particles

3.3.1 Terrestrial influence and mineral particle characterisation

The chemical compositions for the fine and coarse size fractions of the SFU samples from the winter campaign are presented in Figure 10. According to the HCA, the 21 February, 26 February and 6 March samples are mainly influenced by continental sources.

Figure 10. Percentages of 11 particle types in the coarse and fine SFU size fractions on 5 winter days.
The abundance of mineral dust ranges between 73 and 90% in the fine and between 73 and 93% in the coarse size fraction. The large abundance of "other mineral dust" in the coarse size fraction of the 21 February sample is due to mineral particle aggregation resulting from a high dust event (Table 1). Dust storms occur frequently during the winter and they are responsible for high atmospheric concentrations of mineral dust, including aluminosilicates, limestone and gypsum particles [18]. The 5-day air mass back trajectories for 960 hPa arrival level at Sde Boker (Figure 11) indicated that on the two most dusty days (21 February and 6 March) the air came from eastern and south-eastern Europe over the Mediterranean, Egypt and across the Sinai desert.

![Figure 11. Five-day air mass back trajectories, calculated for arrival at the Sde Boker site at 960 hPa and 12:00 UT, for the 5 winter sampling dates]

3.3.2 Marine origin and particle chemistry

The large percentages of sea-salt particles in the coarse size fraction (32%) and associated aged sea-salt particles (42% in the coarse and 16% in the fine fraction) for the 27 February sample reflect the impact of the marine source. The 960 hPa air mass trajectory for the 27 February sample came from Ukraine, passed over the Black Sea and crossed the Mediterranean Sea before reaching the Negev. The long time spent over the sea explains the particle composition is dominated by marine particles.

With a lesser abundance, sea-salt-like particles (sea salt and aged sea salt) were also detected in the 26 February and 6 March samples at 31% and 9%, respectively, of the total number of particles in the coarse size fraction. On 26 February (which was a dusty day) the air came from Europe over Turkey and the Mediterranean, but in contrast to the two most dusty days, there was only a short travel path over the desert before arrival at the Sde Boker site. As a consequence, the influence of the Mediterranean was more important and marine aerosols were prominently present.
Particles of marine origin were also seen in the TEM-EDS analyses. They contained Na and Cl with or without square projection morphology and had a SAED pattern suggesting NaCl compounds. Most of the particles were beam sensitive aggregates composed of Na, Na/S, and Ca/Na/S/Cl round or rod shaped particles agglomerated on a NaCl crystal surface (Figure 12).

Na-containing particles were identified as NaNO₃ and were beam sensitive round shaped particles. Halos around the particles were observed, indicating dehydration. Other constituents of the particle aggregates were mixed-cation sulphates.

Coarse square shaped Na/Ca/S/Cl particles with a size of 2 μm were also observed. EDS from the centre to the exterior of these particles showed a depletion of Cl while the S peak intensity increased, indicating a S enrichment in the particle surface.

![Figure 12. TEM image of particles from marine origin consisting of NaCl, NaNO₃, Na₂SO₄ and mixed cation sulphates](image)

Actually, these particles were surrounded with needle shaped ones containing Na/Ca/S or Na/S as major elements. The SAED pattern obtained from the centre of the particles with a square projection showed a NaCl structure with minor elements such as Mg. In contrast, the SAED patterns from the edge of the square particles and from the needle particles exhibited the same but slightly distorted orthorhombic Na₂SO₄ structure.

Conversion of sodium chloride into sodium sulphate is often observed for marine aerosols [9]. Because all marine particles are very beam sensitive, it is hard to obtain SAED patterns that are sufficiently intense for providing good structural information. For the same reason it is not possible to use high resolution TEM that could give information about the structural transitions during the particle formation. However, all our TEM results about particulate composition, morphology, and association of particles agree with the TEM data that have been obtained for marine particles from the North Atlantic and Pacific [9,26,34], indicating that similar chemical particle transformation processes occur in the various marine atmospheres. Finally, similarly as for the summer sample that was highly impacted by marine particles, we found a significant abundance of fine CaSO₄ particles in the marine influenced winter samples. They likely result from CaCO₃ to calcium sulphate conversion. The fact that CaSO₄ particles were found by TEM in the sea-salt aggregates confirms this hypothesis.

### 3.3.3 Pollution particle chemistry and sources

1 March is described by Ichoku et al. [6] as one of the most polluted days of the winter campaign, with a high concentration of SO₂ (9.6 ppbv) and CN (22,189 cm⁻³) (Table 1) indicating that the pollution was from local/regional origin. SEM-EDX indicated there there were high concentrations of Ca, P and S, but no S-only particles (Figure 10). The bulk analysis of the fine SFU filter sample from this date gave high fine PM (23.7 μg/m³), high fine S (2.69 μg/m³) and high fine P (590 ng/m³) levels (Maenhaut et al.,
unpublished). The HCA showed that there were two main groups of P compounds in the fine size fraction: a Ca (65%) / P (28%) containing cluster which accounted for 41% of the total number of particles and a Ca (58%) / P (23%) / S (16%) group at 34%. The coarse size fraction was composed of Ca (66%) / P (25%) compounds (39% of the total number of particles), CaCO₃ (18%), other mineral dusts (19%) and transformed mineral dusts (16%). Using nuclear microprobe analysis, Maenhaut et al. [41] identified complex particle aggregates of calcium phosphate and CaCO₃ and/or CaSO₄ in the Sde Boker aerosol. Our results are fully consistent with these previous observations. Ca-P-rich particles were also identified by TEM, but their SAED patterns did not match any crystal structure and were typical for amorphous material. Unfortunately, the Ca-P phases could thus not be identified. The P-rich components originate mainly from the phosphate mining activities in Dimona to the north of the sampling site. The 960 hPa back trajectory for 1 March (Figure 11) indicates that the air mass made a small detour to the north of Sde Boker on this particular day.

Pollutant particles, as represented by industrial and/or S-only particles were identified in the 26 February, 27 February and 6 March fine fraction samples at abundances of 11%, 46% and 20%, respectively. With only 11% of pollutant particles, the 26 February sample was only moderately influenced by pollution, but the other two samples were rather strongly influenced by fine pollution derived particles. Despite the low concentrations of SO₂ and CN (Table 1) on 26 and 27 February and 6 March, which indicate unpolluted days [6], S-only and industrial particles were observed on these dates (S-only particles only on 27 February). The industrial particles contained S, low Z elements, and metals (mainly Pb) and are presumably aggregates of secondary sulphates, carbonaceous particles, and metal-rich particles. The S-only particles of 27 February are most likely secondary sulphates that were advected by long-range transport. The 950 hPa air mass back trajectory (Figure 11) for 27 February shows that the air came from Ukraine, which was identified by Ptasinski et al. [3] as a major source region of fine sulphur. Long-range transport from eastern Europe was also recognised as a main source of secondary sulphate by Luria et al. [19].

![Winter particles (fine + coarse)](image)

Figure 13. Particle number size distributions for the SFU samples from the winter campaign
3.3.4 Particle number size distributions for the winter samples

The particle number size distributions for the 21 February, 26 February, and 6 March samples (Figure 13) are comparable. They are unimodal with a maximum around 1 μm. This is in agreement with the high mineral dust contribution. The industrial particle contribution for the 26 February sample is too small to show up in the figure. For the 6 March sample, the industrial particles have a mean diameter of 1 μm, and they contribute to the single broad mode. The size distribution of the 27 February sample is highly influenced by marine aerosols; it shows some resemblance with the particle number size distributions in summer. The distribution has a bimodal character, with a high particle number around 0.4 μm and a shoulder around 0.9 μm. The high amount of fine particles is attributed to fine sulphates and the shoulder to sea-salt particles. The bimodal size distribution of 1 March results from the phosphate compounds with mean size around 1 μm and from the mixed industrial particles and S-rich phosphates with sizes between 0.5 and 0.7 μm. Finally, the mean number size distribution of the 5 winter samples is bimodal, with a distinct peak around 1 μm which reflects the significant contribution of mineral dust particles during wintertime.

3.4 Seasonal differences in particle types, variability of the chemical composition as a function of particle size and number size distribution of compounds

![Graph showing particle numbers by type and season](image)

Figure 14. Average percentages of 11 particle types in the summer and winter SFU sample sets

The HCA data of the fine and coarse SFU filter samples were combined as explained in sections 2.3 and 2.4 and average contributions from each of the 11 particle types (classes) were calculated for the separate summer and winter SFU sample sets (Figure 14). For the terrestrial particle types limestone (CaCO3) and CaSO4, about the same relative abundances are found for the summer and winter sample sets. The aluminosilicate particles are more important in the summer sample set, while the other mineral dust particles are more abundant in the winter sample set. The other mineral dust particles are mainly present as agglomerates and their formation is favoured during the dust storms that occur during wintertime. S-only and transformed mineral dust particles are clearly more important in summer than in winter, while the opposite is true for the industrial, P-rich, sea-salt and aged sea-salt particles. The concentration of fine S, as derived from the bulk analysis, was clearly higher in summer than in winter. The atmospheric and
meteorological conditions during summer favour the formation and long-range transport of secondary fine sulphate particles; hence, S-only and transformed mineral dust particles dominate during summer. The elevated abundance of industrial particles during winter may be due to a larger contribution of particles from local and regional sources. The high abundance of P-rich particles in the winter sample set is entirely due to the high contribution from the sample of 1 March.

The HCA data of the fine and coarse SFU filter samples were also used to examine the relative contribution of the 11 particle types as a function of particle diameter, as measured by SEM. The average results for the summer and winter sample sets are shown in Figure 15. For both seasons a similar dependence of chemical composition as a function of size is observed. The results are in agreement with data obtained by bulk analysis [1,4–6]. The CaCO₃ particle number decreases with decreasing size, whereas the abundance CaSO₄ and transformed mineral dust particles increases with decreasing size. The opposite behaviour for CaCO₃ and CaSO₄ seems to be a reflection of the limestone-to-sulphate conversion in the atmosphere.

Figure 15. Average contribution, as a function of particle diameter, of 11 particle types for the summer and winter SFU sample sets.
For both the summer and winter sample sets, there is no significant variability in the abundance of aluminosilicates and aged sea-salt particles for sizes below 3 μm. For larger sizes, the abundance of aluminosilicates and of CaCO₃ decreases, while that of "other mineral dust" increases, reflecting the aggregation of particles. Similarly, the decrease in sea-salt particle number abundance (and the slight increase in aged sea-salt abundance) with decreasing particle size seems to be a reflection of a reaction between fine sea salt and acidic sulphates in the atmosphere.

Figure 16. Average number size distributions for 11 particle types in the summer and winter SFU sample sets

Average number size distributions for each of the 11 particle types in the summer and winter campaigns were obtained by combining the average particle number size distributions (Figures 9a and 13) and the particle compositional data as a function of size (Figure 15), and are shown in Figure 16. Mineral particles are found more abundantly in particles larger than 1 μm, while industrial and S-only particles are more prominent at sizes below 1 μm. The bimodal feature of the "other mineral dusts" shows the heterogeneity
of this particle class which includes individual mineral particles (e.g., quartz) of around 1 μm and mineral aggregates with a large size. The fact that CaSO₄ is mainly present in the size range below 1 μm suggests that it originates mainly from calcite-to-sulphate conversion. The sea-salt component shows a bimodal distribution for both campaigns. Aged sea salt and transformed mineral dusts also display a bimodal distribution, but with a more pronounced fine size fraction. Our results can be compared with the size distributions obtained by bulk analysis of cascade impactor samples from the same campaigns. For the summer campaign, Maenhaut et al. [4] obtained unimodal coarse mode size distributions for the mineral dust elements (Al, Si, Ca, Ti, Fe), whereas S was predominantly associated with submicrometer-sized particles, in accordance with our distribution for the S-only particles. Ichoku et al. [6] obtained bimodal size distributions for Na and S during the winter campaign, which is in agreement with our size distributions for sea salt and S-containing material.

4. CONCLUSIONS

SEM-EDX combined with HCA allowed us to characterise the chemical composition and the size of aerosol particles at Sde Boker in the Negev desert (Israel) for representative days of summer and winter sampling campaigns. The results were related to air mass back trajectories, to data from bulk analyses, and to SO₂ concentration and condensation nuclei number data reported in previous studies [5,6]. As expected, natural mineral dust particles, including aluminosilicates, calcites, and sometimes gypsum (and/or anhydrite) were the dominant aerosol particle types, especially in the supermicrometer size fraction. Other natural particle types were sea salt and to a lesser extent natural S-rich components. The chemical composition of the anthropogenic particles during pollution events was dependent upon the type of pollution event (local/regional versus pollution from long-range transport). The secondary sulphate particles resulted mainly from long-range transport, while the metal-rich particles originated from both local/regional sources and from long-range transport. The "transformed mineral dust" particles consisted mainly of Ca-S rich particles which were formed by the incomplete transformation of CaCO₃ by atmospheric SO₂/H₂SO₄ into calcium sulphate particles. Pure CaSO₄ particles were also identified and were in part gypsum and/or anhydrite, which are commonly found in desert regions, and in part calcium sulphate particles, which resulted from a complete conversion of calcite into sulphate. The particle types, which were found in the individual samples, could in general well be related with the transport pathways and source regions, as identified by the air mass back trajectories.

The atmospheric aerosol at Sde Boker is a mixture of particles from marine and continental natural and anthropogenic sources. During most days, continental natural and marine particles dominated the coarse mode for both the summer and winter sample sets, whereas anthropogenic S-rich and metallic particles were dominant in the fine size fraction. The size distribution of the particle types suggested that fine sea salt and calcium carbonate reacted with acidic S compounds (SO₂, H₂SO₄, S-only particles) in the polluted atmosphere.

SEM-EDX of individual particles forms a invaluable complement to the bulk analysis of aerosols. It provides information on the composition, state of mixing, and chemical transformation of aerosols at the individual particle level. However, the technique cannot adequately analyse particles that are smaller than about 0.3 μm. With TEM one can analyse those smaller particles and, in addition, TEM can provide the phase composition of the particles. We used TEM for detailed studies on mineral dust particles, sulphates, Ca-S rich transformed mineral dust and sea-salt aerosols. For a high pollution day of summer, ammonium sulphates and more acidic compounds such as NH₄HSO₄ were identified. It was found that the reaction of fine carbonate aerosols with SO₂ and/or S-rich particles gives rise to the formation of fine calcium sulphates such as bassanite or anhydrite. The formation of the fine calcium sulphates probably occurs in less than two days and locally. Under clean marine conditions in winter we still detected S-rich particles. Some of these were transformed sea-salt particles, as has also been observed in other studies. The marine particles at Sde Boker exhibited similar characteristics as marine particles from the North Atlantic and Pacific, indicating that similar chemical particle transformation processes occur in the various marine atmospheres.
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