CHAPTER 5

CHEMICAL AND MINERALOGICAL CHARACTERISTICS OF AIRBORNE DUST

5.1 Introduction

Mineral dust plays an important role in the optical, physical and chemical processes in the atmosphere (Xi and Sokolik, 2012), while dust deposition adds exogenous mineral and organic material to terrestrial surfaces having a significant impact on the Earth's ecosystems and biogeochemical cycles (Jickels *et al*., 2005; Lawrence and Neff, 2009). Dust particles are fine airborne soil and/or weathered or transported rock particles removed from the Earth's surface as a result of wind erosion under certain climatic, meteorological and soil conditions. The Earth's surface is composed of a large number of minerals, which occur in heterogeneous mixtures within rocks and weathering mantles. Analysis of the physical properties and chemical composition of dust aerosols is, therefore, important to determine aerosol sources, mixing processes and transport pathways (Bergametti *et al*., 1989; McConnell *et al*., 2008; Mishra and Tripathi, 2008). It is estimated that 1000 to 3000 Tg of mineral aerosols are emitted annually into the atmosphere over the globe (d'Almeida, 1987; Jones *et al*., 1995), which can be transported over long distances (e.g., Prospero, 1999). The role of dust aerosols in atmospheric processes (i.e. Earth's radiation balance, cloud microphysics, etc) strongly depends on a variety of physico-chemical parameters, size distribution, dust sources, atmospheric lifetime and mixing processes in the atmosphere (Charlson *et al*., 1992; Tegen and Fung, 1994; Andreae, 1996; Frank *et al*., 1996; Sokolik *et al*., 1998; Rosenfeld *et al*., 2008).

Some dust contaminants (soluble and chelatable metallic salts, pesticides, etc) affect human health when they are transported over densely populated areas (Larney *et al*., 1999), retained in residences and other occupied structures (Lioy *et al*., 2002), and they also impact the nutrient loading of waters flowing from adjacent watersheds (Wood and Sanford, 1995) and terminal bodies of water by direct and indirect deposition (Ganor *et al*., 2003; Lawrence and Neff, 2009). PM is a complex mixture of substances suspended in the atmosphere in solid or liquid state with different properties (e.g. variable size distribution or chemical composition amongst others) and origins (anthropogenic and natural). Owing to this mixture of substances, the chemical composition of PM may vary widely as a function of emission sources and the subsequent chemical reactions which take place in the atmosphere (Chow *et al*., 2003; Engelbrecht *et al*., 2009; Mishra *et al*., 2010). Therefore, it is important to determine temporal variations in aerosol concentrations to assess health exposure effects and to improve correlations between source emission rates and ground-based measurements (Christopher *et al*., 2004; Kidwell and Ondov, 2004; Nastos *et al*., 2010). The chemical mass balance is the most commonly used method for assessing PM source contributions (Wilson *et al*., 2002), while statistical methods, such as factor analysis and multi-linear regression (Thurston and Spengler, 1985), have also produced interesting results regarding dust source identification. Elemental and mineralogical analyses have also been used to identify the source regions of dust deposited in Arctic ice caps (Biscaye and Grousset, 1998) and on other depositional surfaces (Shaw, 1980; Lawrence and Neff, 2009).

The Sistan region located in southeastern Iran is a major dust source in southwest Asia (Goudie and Middleton, 2000), often producing intense dust storms that cover Sistan and the southwest of Afghanistan and Pakistan (Alam *et al*., 2011; Rashki *et al*., 2012). Particles from dust storms might also cover farm and grasslands resulting in damage to crops and fill the rivers and water channels with aeolian material. After the extreme drought of 1999, the dust activity over Sistan appears to be increasing in both frequency and severity. Over recent years, ten thousands of people have suffered from respiratory diseases and asthma during months of devastating dust storms in the Sistan basin, especially in the cities of Zabol and Zahak and the surrounding villages (Miri *et al*., 2007). According to the Asthma Mortality Map of Iran, the rate of asthma in Sistan is, in general, higher than in other regions (Selinus *et al*., 2010).

In order to understand the influence of dust on the atmospheric environment, climatic system and health and to establish effective remedial policies and strategies, it is regarded as necessary to investigate the chemical (composition and mineralogy) characteristics of airborne and soil dust over Sistan. To the best of our knowledge there are currently no published studies about the geochemical characteristics and dust mineralogy, and only few about the geology and potential impact of airborne dust on human health in this region, such as the first PM analysis over Zahedan city (Rashki *et al*., 2011), the investigation of the sediment loading during major dust events over the Hamoun basin (Jadidoleslamir *et al*., 2011; Rashki *et al*., 2012) and the effects of droughts and winds on desertification (Ranjbar and Iranmanesh, 2008; Hosseini *et al*., 2010). Moreover, nearby locations, Bagram and Khowst in Afghanistan, were selected for analyzing the mineralogical dust composition, major and trace elements whitin the framework of the Enhanced Particulate Matter Surveillance Program (EPMSP) campaign (Engelbrecht *et al*., 2009). Furthermore, mineralogical and geochemical characteristics of dust were recently examined at Khuzestan province in southwestern Iran (Zarasvandi *et al*., 2011).

In this thesis, an overview of the geological-geochemical characteristics of airborne and soil dust in the Sistan region is given for airborne and soil samples collected during the period August 2009 to August 2010. The chemical constituents during major dust storms over the region are analyzed at two locations, also investigating the relationship between the chemical constituents of the dust storms and those of the inferred (Hamoun) source soils.

5.2 Methods, data and material samples

The amount of sediment loading during major dust storms was measured using passive dust samplers fixed on two monitoring towers (at four and eight meters from ground), with one meter distance between the traps (Fig 3.9), during the period August 2009 to August 2010 (Rashki *et al*., 2012). The towers were installed in two opens locations near Hamoun (31.10°N, 61.51°E and 31.20° N, 61.61°E), and sufficiently far away from any obstacles, so that undisturbed wind flow was entering the samplers (stations A and B in Fig. 3.8). After each measurement, the samplers were evacuated to be ready for measuring the next dust event. The most commonly used passive sampling techniques collect dust using a non-reactive collection pan filled with glass marbles, which serves as the depositional surface (Goossens and Offer, 1994; Reheis and Kihl, 1995). Furthermore, during the summer of 2009, topsoil samples at depths of 0 to 5 cm were collected from different land-use areas in Hamoun and Sistan. These samples were selected and analyzed as they are good indicators of the atmospheric deposition of geochemical elements in the Sistan region.

5.2.1 Chemical and mineralogical analysis

Analyses of the chemical and physical characteristics of dust particles are regarded as essential in studies on the environmental impact of dust storms (Zarasvandi, 2009). Determination of the chemical composition of airborne dust is also necessary for clarifying the likely sources of dust and is important for quantitative climate modeling and understanding the possible effects of dust on health, soils, precipitation, ocean-biogeochemistry and weathering phenomena (Goudie and Middleton, 2006). During the dust-storm days in 2009 and 2010, 132 samples of airborne dust were collected at the two stations in the Sistan region. These samples were analyzed at the University of Pretoria, South Africa, in the Stoneman Laboratory (Geology Department) for major and trace elements, and for minerals by X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) techniques, respectively.

The samples were prepared for XRD analysis using a back loading preparation method. They were analyzed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and receiving slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert High score plus software. The relative phase amounts (weights %) were estimated using the Rietveld method (Autoquan Program). Mineral analysis by XRD is the single most important nondestructive technique for the characterization of minerals such as quartz, feldspars, calcite, dolomite, clay, silt and iron oxides in fine dust. Mineral phase analysis by XRD is one of few techniques that is phase sensitive, rather than chemically sensitive, as is the case with XRF spectrometry. Quantitative mineralogical analyses using XRD technique have been performed by a number of scientists over the globe (e.g., Rietveld, 1969; Sturges *et al.*, 1989; Caquineau *et al.*, 1997; Engelbrecht *et al.*, 2009; Zarasvandi, 2009).

The sample preparation for XRF is made up of two methods, pressed powders and fusions. The former samples were prepared for trace element analyses and the latter for major element analyses. Each milled sample (<75µm) was combined with a polyvinyl alcohol, transferred into an aluminum cup and manually pressed to ten tons. The pressed powders were dried at 100°C for at least 30 minutes and stored in a desiccator before analyses were conducted. For the fusion method, each milled sample (<75µm) was weighed out in a 1/6 sample to flux (Lithium tetraborate) ratio. These samples were then transferred into mouldable Pt/Au crucibles fused at 1050°C in a muffle furnace. Aluminum cooling caps were treated with an iodine-ethanol mixture (releasing agent) and placed on top of the crucibles as they cooled. Some samples needed to be treated with an extra 3g of flux if they continued to crack.

Finally, all geochemical samples were analyzed using the Thermo Fisher ARL 9400 XP+ Sequential XRF. The Quantas software package was used for the major element analyses and the WinXRF software package was used for the trace element analyses. The concentrations of the major elements are reported as oxides in weight percentages, while the trace element concentrations are reported as elements in parts per million (ppm). All the dust samples, airborne and soil, were subjected to microscopic imaging, while Scanning Electron Microscopy (SEM) images were performed for the airborne dust samples at stations A and B.

5.2.2 Enrichment factor analysis

The calculation of Enrichment Factors (EFs) relative to the Earth's upper crust composition can be used to discriminate between the origins of elements from crustal or non-crustal sources (Zhang et al., 2004). EFs of elements in different particle fractions were determined by comparing the concentration of each element against the concentration of a reference (crustal) element to obtain a preliminary idea about possible origin sources, i.e crustal or anthropogenic. Usually silicon (Si), Aluminum (Al) or Iron (Fe) is used as the reference element, but there is no universally accepted rule for its choice. In this study, Si was used as the reference element, as done previously by many investigators (Lee and Hu, 1995; Bilos et al., 2001; Manoli et al., 2002; Choi and Bang, 1999; Han et al., 2005; Wang et al., 2007). Estimates of EF aid in (a) differentiating between element concentrations that originate from human activities and those from natural sources and, in (b) assessing degree of anthropogenic influence (Cong et al., 2007). The appropriateness of choosing Si is attributed to its more significant distribution in coarse particles (83% on average) than other elements, with very low contribution from non-crustal inputs (Wang et al., 2006). The abundance ([E/R] Crust values) of elements in the Earth's crust was taken from Wang et al. (2006). The EFs for crustal material (EF_{crust}) were calculated as follows:

$$EF_{Crust} = [E/R]_{Air} / [E/R]_{Crust} \qquad (5.1)$$

Where E is the elemental concentration, R is a reference element (R = Si in this thesis) of crustal material and $[E/R]_{Air}$ is the concentration ratio of E to R in a collected aerosol sample, and $[E/R]_{Crust}$ is the concentration ratio of E to R in the Earth's crust. Si was used as reference element because it is abundant in the crustal materials, it is usually not of anthropogenic origin and, consequently, values of EF_{Si} are close to one. If EF_{Crust} approaches unity, then crustal soils are most likely the predominant source of element E. In practical terms, if the EF_{Crust} value is above 10, then the element is considered to be of non-crustal origin, possibly anthropogenic (Scheff and Wadden, 1997; Gao *et al*., 2002; Wang *et al*., 2006). EF_{Crust} values in the range of 1 to 5 suggest no significant contribution of anthropogenic sources to the ambient level of these elements. In general, as the EF_{Crust} value increases, the non-crustal source contribution also increases.

5.3 Results and discussion

5.3.1 Mineralogical characteristics of dust

Although the optical and physical properties of dust are well-defined, less knowledge is available about the spatio-temporal variations of the chemical composition of dust. The mineralogical characteristics of dust samples at stations A and B (Fig 5.1a, b) were obtained by means of XRD analysis. The mineralogy percentage composition averaged at all heights for each day is shown in Fig. 5.1a, b for stations A and B, respectively. The chemical formulas of the main mineralogical components are given in Usher *et al*. (2003), as well as the chemical reactions of dust with atmospheric constituents and trace gases during the dust life cycle. The mineralogical composition corresponds to screened samples with diameter <75 μm and can constitute an indication of both regional geology and wind transported dust that is deposited in local soils (Engelbrecht *et al*., 2009). Furthermore, dust mineralogy has been used for the identification of different source regions over the globe (Claquin *et al*., 1999; Krueger *et al*., 2005).

Emphasizing the dust mineralogy at station A, it is seen that the airborne dust is mainly composed of quartz, which is the dominant component (26-40%) for all the days of observations. Calcareous particles, mainly consisting of calcite, is the second dominant mineralogical component over the site with average mass percentage of 22%, while micas (muscovite) contribute 13% and plagioclase (albite), 11%. The remaining components contribute much less to the dust mass, while chlorite (6.3%) is apparent in all dust samples for all days. The others, i.e. dolomite, enstatite, gypsum, halite, etc are present only at some samples with various percentages. It is quite interesting to note that quartz is much more common over Sistan than the feldspars (plagioclase, microcline and orthoclase).

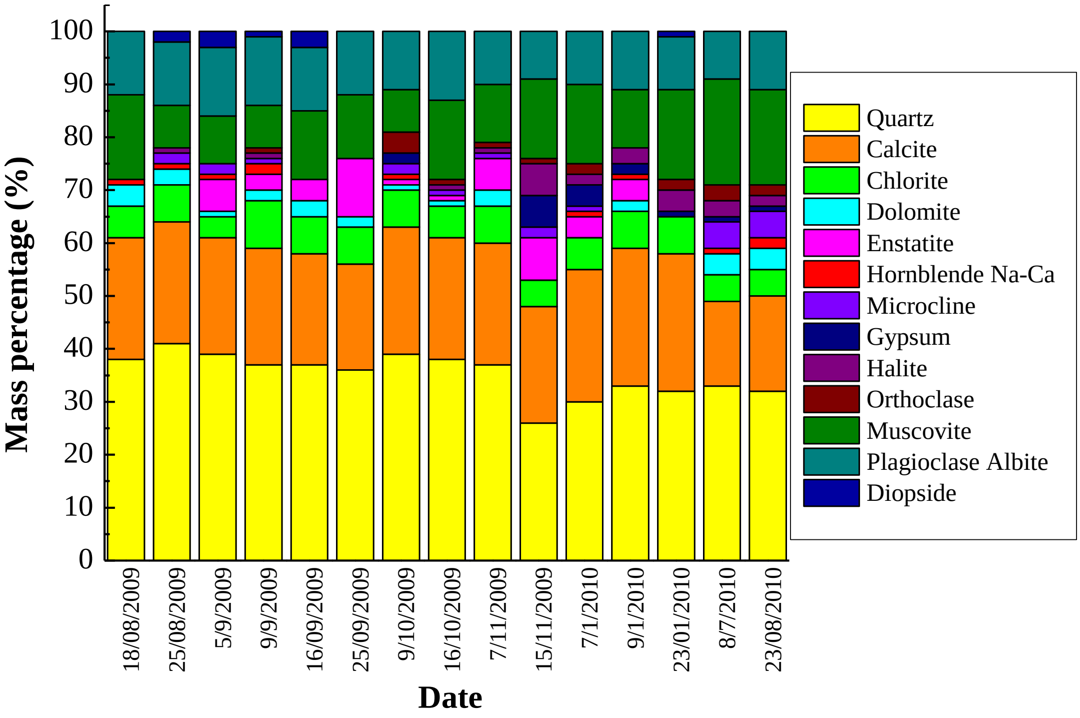

Figure 5.1a: Mineralogical composition as obtained from X-Ray Diffraction (XRD) analysis for airborne dust samples collected on different days at station A (Fig. 3.8).

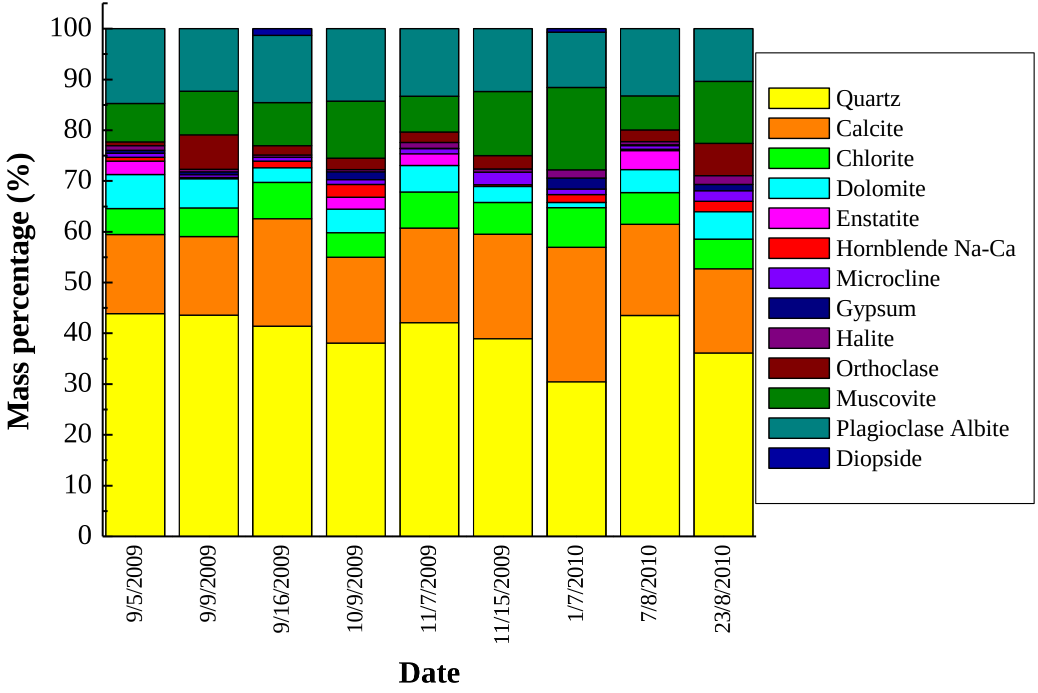

Figure 5.1b: Same as in Figure 3a, but for station B.

The mineralogical analysis for the nine days recorded data at station B (Fig. 5.1b) shows more or less similar results to those obtained for station A and, therefore, any discussion will be given on their comparison (Fig. 5.3). The mineralogical composition has the same descending order as in station A, i.e. quartz (39.8±4.4%), calcite (18.8±3.5%), plagioclase (albite) (12.7±1.4%) and muscovite (10.1±3.2%). On the other hand, dust deposition may influence biogeochemical cycling in terrestrial ecosystems, while dust accumulation in soils can influence texture, element composition and acid neutralizing capacity (Larssen and Carmichael, 2000; Muhs and Benedict, 2006). Furthermore, the chemical and mineralogical composition of soil dust provides useful information about its provenance (Yang *et al.*, 2007), radiative forcing implications (Sokolik and Toon, 1999) and human health effects (Erel *et al.*, 2006). For these reasons, in addition to the airborne dust samples, soil samples were collected at 16 locations around Sistan and Hamoun, at depths ranging from 0 to 5 cm from the soil crust. The results of soil sample mineralogy are summarized in Fig. 5.2.

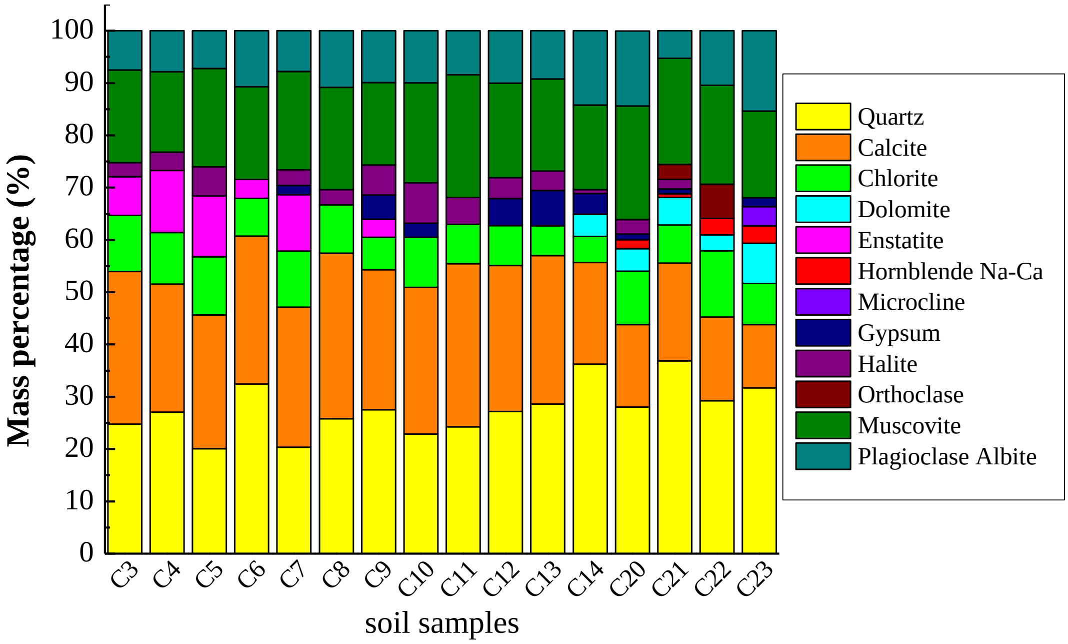

Figure 5.2: Mineralogical composition as obtained from X-Ray Diffraction (XRD) analysis for soil samples collected at various locations in the Hamoun Basin.

From an initial consideration of these results, it is established that the soil samples exhibit similar mineralogy to the airborne dust at both stations, thus suggesting similarity in sources for both airborne and soil dust. On the other hand, some soils in the Sistan region have been primarily formed from dust transported from the Hamoun lakes, presenting large similarities in mineralogy and chemical composition to airborne dust. However, atmospheric chemical reactions involving dust and aerosols of other types can alter the chemical characteristics of dust before its deposition (Dentener *et al.*, 1996). Therefore, the mineralogy of the soil samples may differ significantly in comparison to the results obtained for airborne dust at stations A and B, since some of the soil samples (11 samples) were collected in the Hamoun dried lakes and others (four samples) around stations A and B.

Figure 5.3 summarizes the results from the mineralogical analysis of samples taken at the two stations and from the soil samples, allowing a quantitative comparison between them. The vertical bars correspond to one standard deviation from the mean for both airborne and soil samples. The distance from the source region from whence dust is deposited also influences the particle size distribution, mineralogy and chemical composition of dust. Therefore, generally speaking, at local scales quartz clearly dominates with fractions up to ~50%, while as the distance from the dust source increases, feldspars (plagioclase, microcline) and phyllosilicate minerals (illite and kaolinite) present increased fractions (Arnold et al., 1998; Lawrence and Neff, 2009). However, in our study the dust samples were all obtained within the same area, and therefore are mineralogically similar. Nevertheless, station B, which is located closer to the Hamoun basin, the source of dust exposures, exhibits higher percentages of quartz, while station A (near to Zabol city) exhibits higher concentrations of calcite and muscovite compared to station B. On the other hand, the soil samples exhibit a lower mean percentage for quartz (27.7±4.7) and higher percentages for calcite, chlorite, halite and muscovite compared to the airborne samples.

These mineralogical airborne dust and soil compositions, derived essentially from the Hamoun source region, reflect the composition of the material available from this provenance as well as the relevant grain size characteristics, enabling the wind storms to entrain this material into the lower atmosphere. While most of the minerals (quartz, feldspars of various types, muscovite) can easily be tied to basement-type lithology of generally gneissic-granitic character, others (chlorite, pyroxenes and hornblende) rather suggest mafic parent rocks, as can be inferred from basic mineralogical analysis (e.g., Deer *et al.*, 1966).

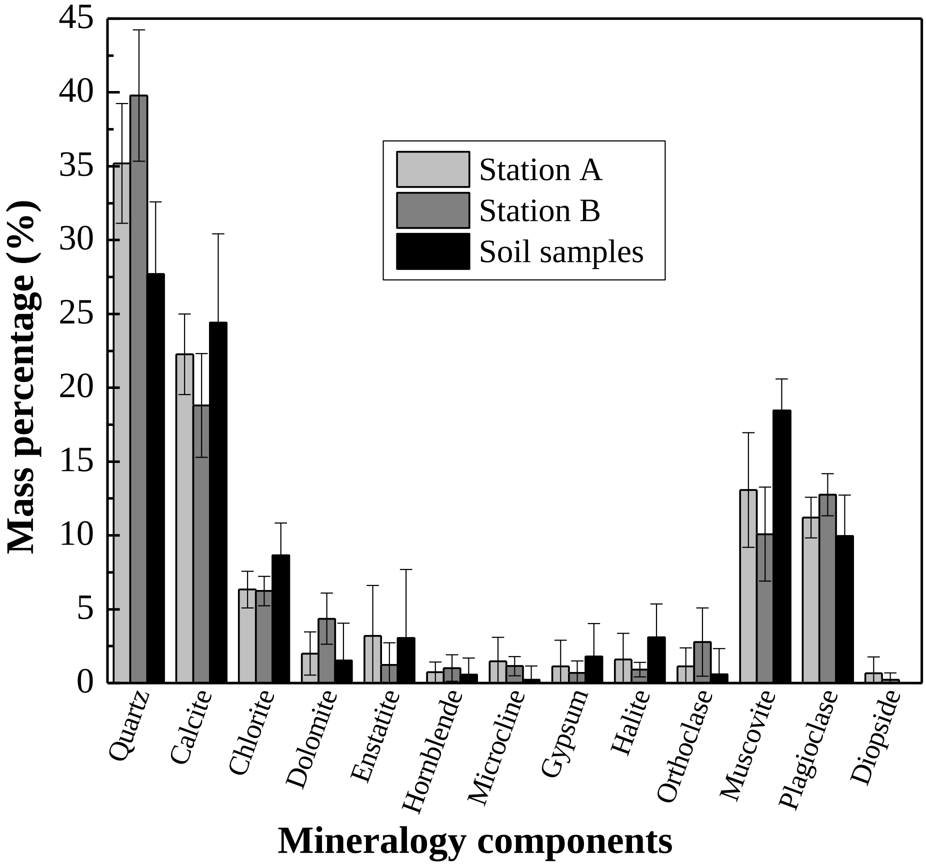

Figure 5.3: Average mineralogy components for airborne dust samples at stations A and B and for soil samples obtained at various locations in the Hamoun Basin. The vertical bars express one standard deviation from the mean.

However, the calcite, dolomite, halite and gypsum suggest evaporite minerals, although both calcite and dolomite can also reflect alteration products of primary acid or mafic rock constituents. The inferred evaporite minerals reflect local derivation of salt from desiccating water bodies in the Hamoun lakes, originally formed from altered transported components via the Hirmand river system. Thus, the semi-quantitative mineral determinations for the airborne dust over the Sistan region support derivation of the particles from well weathered and well eroded (transported) argillaceous alluvium from the extensive Hirmand river system draining Afghanistan and terminating in the Hamoun Basin. The general geology of Afghanistan encompasses extensive terrains of both acidic and mafic rocks, while similar mineralogical composition of dust (i.e. dominance of quartz, but lower percentage of calcite) was found at the Bagram and Khowst sites located in eastern Afghanistan (Engelbrecht et al., 2009). More specifically, they found that these sites are underlain by loess (wind deposited silt), sand, clay and alluvium containing gravel. As shown in Fig. 2.6 and 3.8, as well as in other studies (Engelbrecht et al. 2009; Alam et al., 2011; Rashki et al., 2012 a, b), nearly the whole of Afghanistan is affected by the dust storms originating from Hamoun, since the dust plume usually follows a counter-clockwise direction, carrying wind-blown dust towards eastern Afghanistan. Similarly to our findings, the airborne dust at selected locations in southwestern Iran was found to be composed mainly from quartz and calcite, suggesting detrital sedimentary origin, followed by kaolinite and a minor percentage of gypsum (Zarasvandi, 2009). Furthermore, Engelbrecht et al. (2009) found that airborne dust samples derived from poorly drained rivers and lakes in central and southern Iraq contain substantial calcite (33– 48%), quartz, and feldspar with minor chlorite and clay minerals. Previous studies (Schütz and Sebert, 1987; Reheis and Kihl, 1995) have shown that silicate minerals (quartz, feldspars) and phyllosilicates (illite, kaolinite, smectite/montmorillonite clays, chlorite) dominate eolian dust. Dust samples may also contain substantial amounts of carbonates, oxides, gypsum, halite and soluble salts, but the quantity and percentage of these minerals are quite variable from site to site.

Fig. 5.4 shows the altitude variation of the dust mineralogy for dust samples collected during 9 dust-storm days at 8 heights from station B. The mass percentages correspond to the average values during the dust storms over the region. The results show no clear tendency in the altitude variation of the dust mineralogy, at least within the first eight meters from the ground, suggesting that dust is regionally transported within the lower boundary layer. The surface winds over Sistan control the dust erosion and emission rates (Rashki *et al*., 2012), thus determining the quantity, chemical and mineralogical composition of dust emitted over the region.

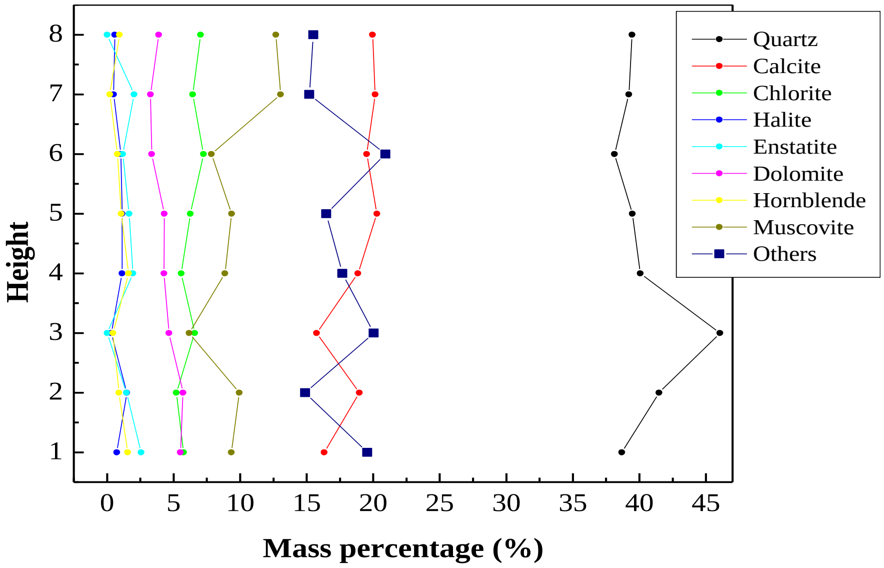

Figure 5.4. Mean altitude variation of dust mineralogy components at station B. *[others: Plagioclase, Orthoclase, Microcline, Gypsum, Bloedite, Diopside, Hornblende Na-Ca]*

5.3.2 Elemental composition of dust

Knowledge of the chemical composition of airborne dust is necessary for clarifying the likely source regions and is important for quantitative climate modeling, in understanding possible effects on human health, precipitation, ocean biogeochemistry and weathering phenomena (Goudie and Middleton, 2006). Chemical analysis of dust provides valuable information about potentially harmful trace elements such as lead, arsenic and heavy metals (Cobalt (Co), Chrome (Cr), Copper (Cu), Nickel (Ni), lead (Pb)). On the other hand, the major-element and ion-chemistry analyses provide estimates of mineral components (Figs. 5.1-5.3), which themselves may be hazardous to human health and ecosystems and which can act as carriers of other toxic substances. The chemical analysis of dust samples at both stations was performed via XRF analysis for the major oxides (Figs. 5.5a, b).

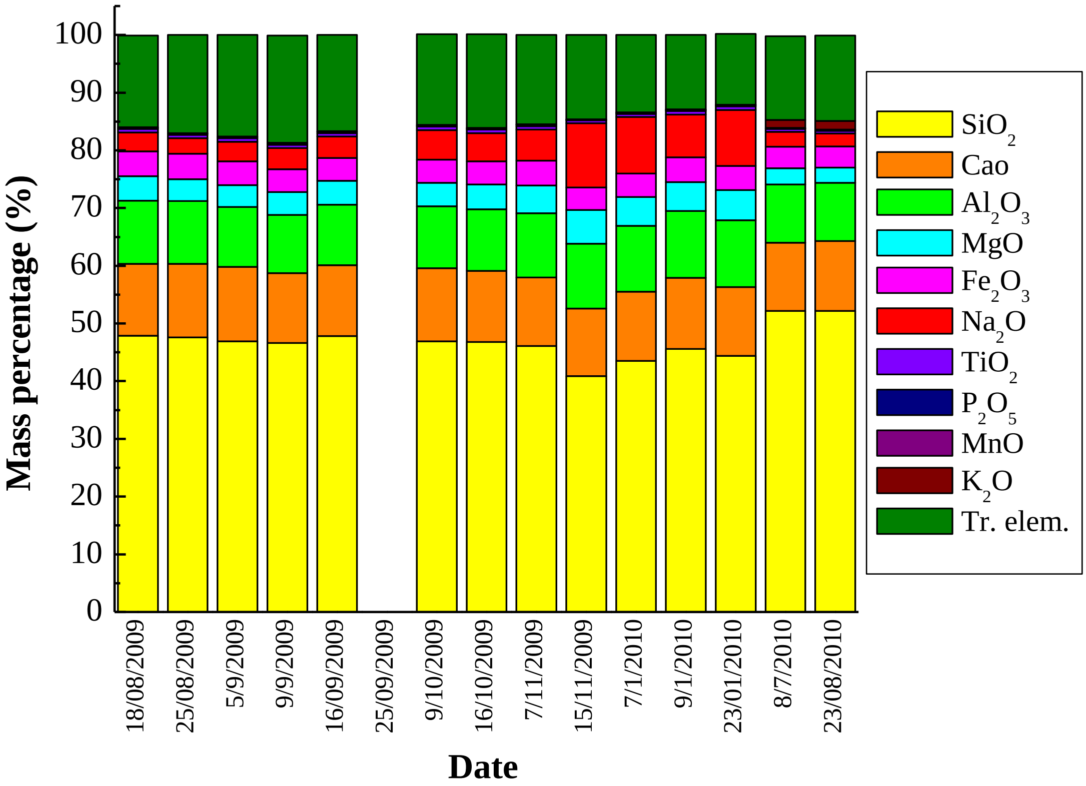

Figure 5.5a: Major elements (oxides) for airborne dust samples obtained on different days at Station A by means of the X-Ray Fluorescence (XRF) analysis.

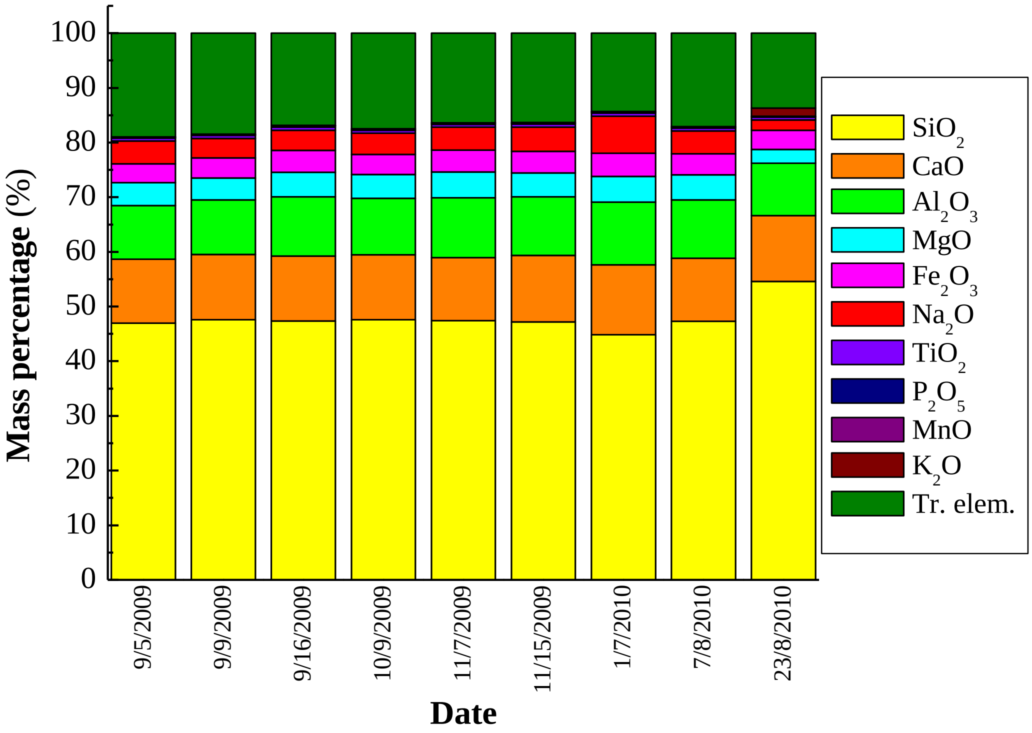

Figure 5.5b: Same as in Figure 5.5a, but at station B.

In general, the analysis reveals that all samples at both stations A and B contain major amounts of Silicon dioxide (SiO_2), mainly in the mineral quartz, variable amounts of Calcium oxide (CaO) in the mineral calcite, plagioclase feldspar and to a limited extent in dolomite, as well as substantial Aluminum oxide (Al_2O_3) concentrations. More specifically, average major elements of airborne dust at both stations indicate a predominant SiO_2 mass component (46.8 – 47.8%) with significant CaO (12-12.2%) and Al_2O_3 (10.4-10.8%) contributions; a few percent of Sodium oxide (Na_2O) (4.2-5.4%), Magnesium Oxide (MgO) (4.3%) and total iron as Iron (III) Oxide (Fe_2O_3) (3.8-4.1%), as well as trace amounts (<1%) of Titanium dioxide (TiO_2), Potassium oxide (K_2O), Phosphorus pentoxide (P_2O_5) and Manganese oxide (MnO), while the remaining major elements (dichromium trioxide (Cr_2O_3), Nickel Oxide (NiO), vanadium pentoxide (V_2O_5), Zirconium oxide (ZrO_2)) were not detected by XRF analysis (Figs. 5.5a, b). When compared to various average shale analyses in the literature (Geosynclinal Average Shale and Platform Average Shale from Wedepohl, 1971; Average Shale from Clarke, 1924; North American Shale Composite from Gromet *et al.*, 1984), the Sistan dust is significantly depleted in SiO_2, Al_2O_3, K_2O and total Fe and significantly enriched in CaO, Na_2O and MgO. The MgO is largely contained in dolomite and, to a lesser extent, in clay minerals such as palygorskite and montmorillonite (Goudie and Middleton, 2001; Engelbrecht et al., 2009). These components can be ascribed to the importance of evaporite minerals such as calcite, dolomite, halite and gypsum (as also suggested by the mineralogical analysis) inferred to have come from the desiccation taking place in the Hamoun dust source region. Furthermore, the elevated values for the trace elements Cl, F and S (Table 5.1) support the latter postulate as it would be expected from an evaporite-rich source for deflation of dust (e.g., Talbot and Allen, 1996). Similar to the present findings, Engelbrecht et al. (2009) determined a high fraction of SiO_2 in silt, less CaO in calcite and slightly more Al_2O_3 in clay minerals at the Khowst site. At both Afghanistan sites (Bagram and Khowst), the SiO_2 was dominant with fractions of about 50 to 55%, followed by Al_2O_3, CaO and MgO.

By comparing the major elements of different dust storms, some interesting relationships are revealed. More specifically, on days (e.g. 15/11/2009, 7/1/2010, 23/1/2010) (Fig. 5.5a) when airborne dust was relatively depleted in SiO_2, enhanced MgO and, particularly Na_2O values were recorded. Conversely, when SiO_2 values were higher (e.g. 8/7/2010, 23/8/2010), both MgO and Na_2O contributions dropped. This suggests that certain intense dust storms were richer in evaporite source material (i.e., elevated MgO and Na_2O) coming from Hamoun dried lake beds, while others had more silica, reflecting weathered rock detritus from the Hirmand river and Afghanistan mountains. An explanation of these variable chemical compositions of dust samples is a real challenge, but it is postulated here that they may reflect local desiccation cycles and, possibly, even micro-climatic changes in the Hamoun-lakes dust source region. Excessive desiccation of the lakes would enhance potential evaporite minerals for deflation in drier periods, while in wetter periods, airborne dust would logically have been derived more from weathered fluvial detritus rich in SiO_2.

Fig. 5.6 summarizes the results of the elemental compositions determined by XRF analysis at both stations. For comparison reasons, the mean elemental composition found for several sites in southwestern Iran (Khuzestan province) (Zarasvandi *et al*., 2009) is also shown. The vertical bars express one standard deviation from the mean. Concerning the major elemental oxides over Sistan, both stations exhibit similar results, well within the standard deviations, suggesting that the transported dust over Sistan is locally or regionally produced with similarity in source region. In contrast, the mean elemental composition of airborne dust over Khuzestan province exhibits remarkable differences from that over Sistan, revealing various source regions and dust mineralogy. More specifically, the SiO_2 percentage is significantly lower and highly variable over Khuzestan, which is also characterized by higher contributions of Na_2O, MgO and K_2O compared to Sistan. The dust storms over southwestern Iran may originate from local sources as well as being transported over medium- and long-ranges from different sources located in Iraq as well as in the Arabian Peninsula. A comparative study of the mineralogy and elemental composition of airborne dust at several locations in Iraq, Kuwait and the Arabian Peninsula (Engelbrecht *et al*., 2009) has shown significantly variable contributions, suggesting differences in overall geology, lithology and mineralogy of these regions. In further contrast, airborne dust over Sistan seems to have its individual characteristics originating from local and well-defined sources.

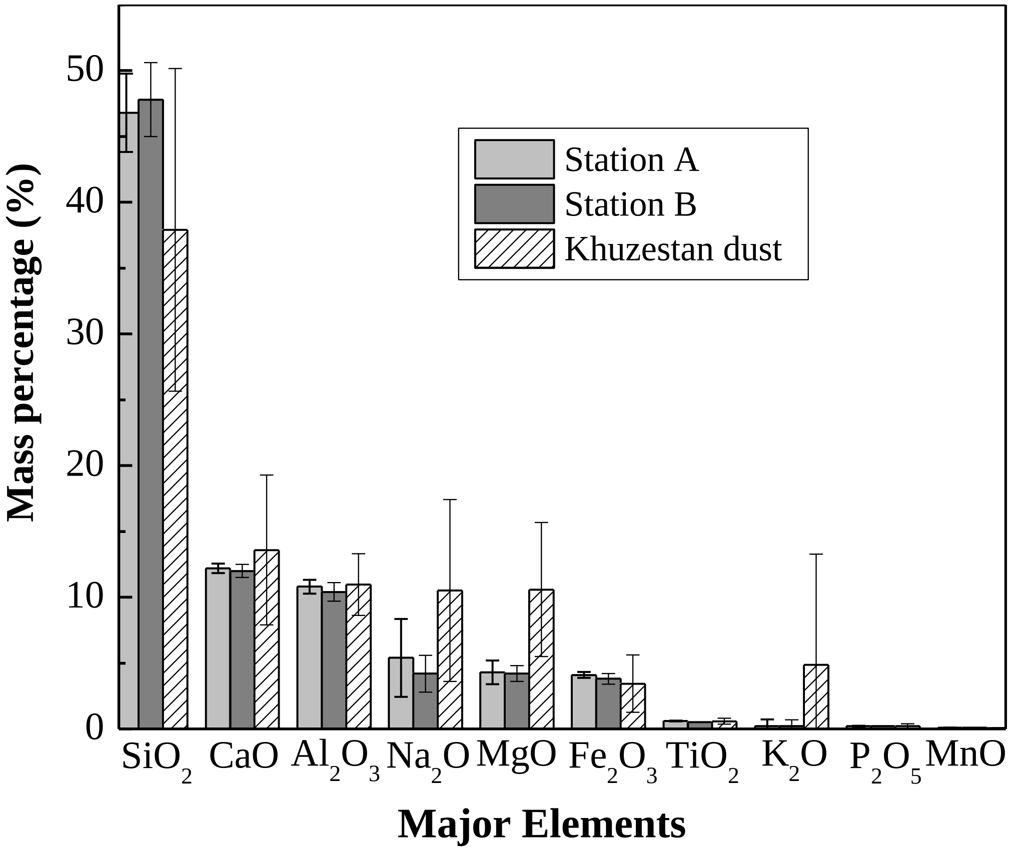

Figure 5.6: Average XRF results for major dust elements at stations A and B. Similar results obtained in Khuzestan Province, southwestern Iran (Zarasvandi *et al.*, 2009) are also shown for comparison reasons.

The Earth's crust is dominated by silicon and aluminum oxides. Numerous studies (Goudie and Middleton, 2001, 2006 and references therein) reviewing the elemental composition of airborne dust over the globe report that mineral dust is composed of ~60% SiO_2 and 10-15% Al_2O_3. The contribution of other oxides, i.e. Fe_2O_3 (~7%), MgO (~2.5%) and CaO (~4%), are, in general, more variable depending on source location. Furthermore, the review study of Usher *et al.* (2003) showed that airborne dust samples collected over the globe have fairly small variations in elemental composition. The CaO concentrations over Sistan are found to be much higher than those (5.5%) summarized in Usher *et al.* (2003).

5.3.3 Trace elements

The average concentrations of trace elements (in ppm) in dust samples collected during major dust storms at stations A and B are summarized in Table 5.1, as obtained from XRF analysis. The results show that the dominant trace elements over Sistan are F and Cl, with the former being dominant in the vast majority of the dust events at station A. However, on two days (8/7/2010 and 23/8/2010) the Cl concentrations were extremely large, thus controlling the average value. There is a lack of observations at station B on 23/8/2010, thus the lower overall Cl concentration. Note that on both these days, the SiO_2 component is large, while MgO and Na_2O are low (Fig. 5.5a). The dominance of chlorine indicates soil salinization in the Hamoun basin and along the Hirmand river and its tributaries. Furthermore, S exhibits higher concentration at station A, while for the other elements the concentrations between the two stations are more or less similar. The concentrations of potentially harmful and toxic elements, like Cesium (Cs), lead(Pb) and Arsenic (As) are, in general, low at both stations; however, Barium (Ba), Chrome (Cr) and Zinc (Zn) present moderate concentrations.

Table 5.1: Average X-ray fluorescence (XRF) values for trace elements of airborne dust at stations A and B

Trace Elements		
Parts per million (ppm)	**Station A**	**Station B**
Cl	28670	15047
F	13938	13456
S	4445	2506
Ba	210	253
Sr	154	125
Zr	83	76
Cr	70	84
V	69	69
Zn	57	51
La	30	32
Rb	24	19
Ni	18	16
Ce	17	16
Cs	14	13
Sc	11	11
Cu	11	11
Pb	10	10

The analysis of the major element ratios provides essential knowledge of the dust chemical composition and source region. The ratios of Si/Al at stations A and B are similar (7.8±0.8 and 8.3±0.9, respectively), due to the presence of silicate and aluminosilicate minerals in most dust samples. The ratios of Mg/Al (0.90±0.16, 0.92±0.12), Ca/Al (3.09±0.19, 3.12±0.19) and Fe/Al (0.51±0.02, 0.49±0.01) at the two stations suggest contributions of clays and Ca-rich (calcite) minerals to the chemical compositions of airborne dusts. In contrast, the Fe/Al ratio is low over Sistan and is nearly half of that found for airborne dust over southwestern Iran and several locations over the globe (Zarasvandi, 2009), but is comparable to that found over central Asia (Kreutz and Sholkovitz, 2000). It should be noted that this ratio remains nearly invariant, ranging from 0.47 to 0.54, for all the collected dust samples at both stations and can be a good surrogate for the dust source region, since any variation in Fe/Al mainly corresponds to variations in clay minerals and not to coating during dust transportation (Goudie and Middleton, 2006). In contrast, the Ca/Al ratio exhibits the highest variations from sample to sample (2.80-3.46), since it is influenced by particle size, with higher values as particle-size increases (Zarasvandi *et al*., 2009). Synoptically, all the ratio values and the low standard deviations suggest similarity in geochemical characteristics over Sistan and a uniform source of airborne dust.

5.3.4 Enrichment factor analysis

The EFs for major and trace elements were calculated via the procedure described in section 3.2 for all the airborne dust samples at both stations (Table 5.2). The results show that the EF values of the main elements Al, Ca and Fe are close to unity, indicating that these elements have not been enriched yet and are composed from natural soil materials. The EF values of elements Sulfur (S), Zn and Arsenic (As) are well below unity suggesting that these elements were not affected by human activities. The overall analysis reveals that the elements found in the dust originate from natural sources and that they are not affected by human activities when they are transported over Sistan. The EF values for the major and trace elements shown in Table 5.2 are more or less similar to those reported by Lawrence and Neff (2009) summarizing the results of several studies over the globe. In contrast, Zarasvandi *et al*. (2009) found that the trace elements Na, Ni, Co, Ba and Cr, are of anthropogenic origin (EF>10) in southwestern Iran. The main reason for this discrepancy is that the above-mentioned trace elements, and particularly the Ba, are associated with anthropogenic and industrial (oil and gas drilling) activities, which are absent in the Sistan region.

Table 5.2: Enrichment Factors (EFs) for the major and trace elements, averaged at stations A and B.

EF(Si)crust					
	A	B		**A**	**B**
Ba	2.08	2.41	**F**	0.53	0.50
La	1.53	1.56	**Zn**	0.51	0.44
Cr	1.53	1.92	**Mo**	0.50	0.49
P	1.38	1.28	**W**	0.43	0.50
V	1.33	1.27	**Ga**	0.43	0.37
Co	1.29	1.20	**Cu**	0.43	0.37
Ti	1.26	1.17	**S**	0.41	0.23
Fe	1.13	1.05	**Zr**	0.41	0.37
Mn	1.07	0.99	**Th**	0.38	0.37
Ce	1.05	0.89	**Ni**	0.37	0.30
Si	1.00	1.00	**K**	0.34	0.28
Sc	0.95	0.93	**Pb**	0.33	0.29
Ca	0.92	0.88	**Sr**	0.24	0.18
Cs	0.88	0.82	**Y**	0.24	0.18
Al	0.78	0.74	**Nb**	0.23	0.20
As	0.63	0.64	**Rb**	0.21	0.16
U	0.61	0.60	**Cl**	0.10	0.05
Mg	0.54	0.52	**Na**	0.07	0.05

5.3.5 Scanning Electron Microscopy (SEM) analysis

Fig. 5.7 summarizes some microscope images as well as the respective Scanning Electron Microscopy (SEM) images for both airborne and soil dust samples collected over the Sistan study area (see Fig. 5.7 caption for details). The microscope images reveal various shapes and colors of airborne and soil dust over the region which were selected for this summary figure. Note the larger dust particles, associated with higher quartz and dolomite and lower calcite mass percentages, having prismatic and crystalline shapes (second row, left in Fig 5.7). On the other hand, the microscope images corresponding to airborne dust taken at stations A and B at heights 4m and 8m, respectively (first and third rows in fig. 5.7) show much smaller dust particle sizes and somewhat of a coating between the particles. Both these samples have a lower quantity of quartz and plagioclase (albite) and higher percentages of calcite, chlorite and muscovite than the previous case (larger particles). The two soil samples collected from the Sistan agricultural lands and in the Hamoun Basin (last row) present remarkable differences in the mineralogy and chemical composition, suggesting that the soil in Hamoun is mainly composed of evaporite minerals with high concentrations of Na_2O. Furthermore, the similar mineralogy and chemical dust composition of the soil sample from Hamoun and the airborne dust sample taken at Zabol during a major dust storm on 9 January 2010 must be emphasized, suggesting not only that the source region of this particular dust outflow was the Hamoun basin but that the alluvial and lacustrine material from Hamoun is deposited widely over the whole Sistan region. In general, higher SiO_2 values in soil crust samples are accompanied by elevated CaO and total Fe values, while there is a strong inverse relationship (r = -0.87) between SiO_2 and Na_2O values. Moreover, SiO_2 is inversely correlated with both MgO (r = -0.96) and Al_2O_3 (r = -0.73), while all the above correlations are statistically significant at 95% confidence level. These results clearly indicate that soil-forming processes downwind of the airborne sampling stations have radically altered the chemistry of the deposited air-transported dust; particularly, sodium and silica components are subject to rapid fluctuations from one sample locality to another. Taking into account that silica will essentially be related to fine air-transported quartz and silt particles while sodium reflects evaporitic material as well as some mica and feldspar minerals, the role of dynamic sorting processes during sedimentation may have played an important role in coating samples. On the other hand, the influence of rain may also be important in altering soil crust compositions (Zarasvandi *et al.*, 2009).

In general, all SEM images show that the dust samples have non-spherical, irregular, crystalline prismatic and rhombic shapes, as do those observed over Khuzestan province, southwestern Iran (Zarasvandi *et al.*, 2009). The dust size is, in the vast majority of the cases, much larger than 10 μm. Previous study analyzing the dust particle size at stations A and B (Rashki *et al.*, 2012) showed that the dust mode size was ~30 μm at station A and ~70 μm at station B, due to closer proximity of the latter to the dust source region (Hamoun basin). However, in some cases the airborne dust is composed of smaller particles with mean diameters of about 1-3 μm. In general, the smaller particles, that are composed mainly from clay minerals, seem to be more spherical, while the larger prismatic and irregular shapes are composed mainly of gypsum and quartz, respectively, as also shown in southwestern Iran (Zarasvandi *et al.*, 2009).

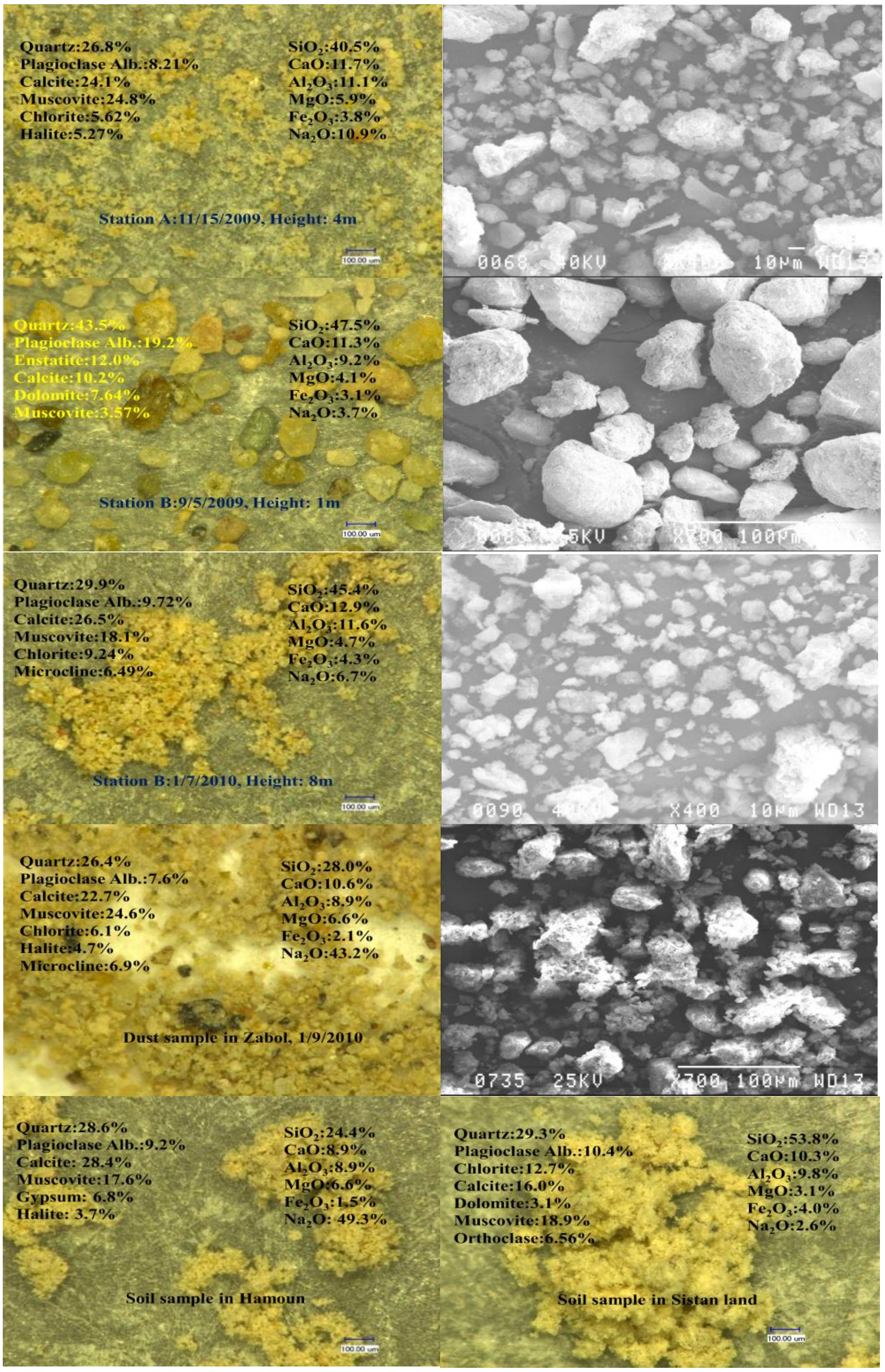

Figure 5.7: Microscope images (left column) and SEM images (right column) for airborne and soil dust samples over Sistan; there are no SEM images for soil samples (last row). The location and the height for the airborne dust samples are given, while the soil samples were collected in Sistan agriculture land and in Hamoun dry-lakes basin. The dust sample in Zabol was collected on the roof of a building during a dust event on 9 January, 2010. For each case, the mineralogy and major elements percentage contribution are given for the main dust components. The scale bar in each image defines the particle size.

5.4 Conclusions

To fully understand mineral dust characteristics and the potential impact on human health, dust mineralogy and geochemical properties were examined in Sistan region, southeastern Iran by collecting airborne and soil samples at two stations and several locations over Sistan and Hamoun basin. The Sistan region is an ideal site to study the nature of dust storms as it receives large amounts of fine alluvial material from the extended Hirmand river system draining much of the Afghanistan highlands, which comprise crystalline basement rocks, Phanerozoic sediments and extensive flood basalts. As a result, large quantities of quartz-rich, feldspar- and mica-bearing silt, as well as mafic material from flood basalt sources and carbonate minerals from dolomites, are transported to the Hamoun wetlands in northern Sistan. Due to droughts at Hamoun and large irrigation projects upstream on the river catchment, extensive desiccation has occurred in the wetlands resulting in large dry lake environments. These have produced large quantities of evaporate minerals to add to the alluvial silts and the combination of these materials provides the provenance for the airborne dust.

Dust aerosol characterization included chemical analysis of major and trace elements by XRF and mineral analysis by XRD. The results showed that quartz, calcite, muscovite, plagioclase and chlorite are the main mineralogy components of dust, in descending order, over Sistan that were present in all the selected airborne dust samples. In contrast, significantly lower percentages for enstatite, halite, dolomite, microcline, gypsum, diopside, orthoclase and hornblende were found, since these elements occurred only in some of the samples at both stations. On the other hand, SiO_2, CaO, Al_2O_3, Na_2O, MgO and Fe_2O_3 were the major elements of dust, while large amounts of F, Cl and S were also found as trace elements. The mineralogy and chemical composition of airborne dust at both stations were nearly the same and quite similar to the soil samples collected at several locations downwind. This suggests that the dust over Sistan is locally emitted, i.e. from the Hamoun Basin, and in few cases can be long-range transported. On the other hand, individual dust storms showed significant differences between either evaporate-dominated aerosols or those characterized by deflation from alluvial silts. These possibly reflect either localized climatic cyclicity or desiccation cycles. However, in some cases the soil samples showed poor comparisons with aerosol compositions, suggesting that dynamic sorting, soil-forming processes and climatic influences, such as rainfall, altered the mineralogy and chemistry in these partially Aeolian deposits. Sistan is also an ideal site for studying dust storms and enrichment factors relative to crustal norms, suggesting that the dust is essentially of crustal rather than anthropogenic origin. SEM analyses of the samples indicated that airborne dust has rounded irregular, prismatic and rhombic shapes and only the finer particles and in few cases can be assumed as spherical.