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Bulk Level to Individual Particle Level Chemical Composition of Atmospheric Dust Aerosols (PM_5) over a Semi-Arid Urban Zone of Western India (Rajasthan)

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ABSTRACT

Mineral dust particles in the lower atmosphere may significantly influence radiative and optical budgets, along with the net chemical balance, through their interactions with ambient chemicals. Their ability to absorb/scatter incoming radiation strongly depends on their chemical composition (i.e., distribution of major crustal elements), but as yet there is no adequate regional database with regard to this for the Indian region. To create a regional database of background mineral dust from a semi-arid zone of western India, we measured the chemical composition of ambient particles (with aerodynamic diameter ≤ 5 μm; PM_5), collected from seven locations of Jaipur city (in the vicinity of Thar Desert; Rajasthan) at varying altitudes, during late-winter of 2012. The chemical compositions of the sampled particles at both bulk and individual levels were measured using X-ray fluorescence (XRF) and Scanning Electron Microscope equipped with Energy Dispersive X-ray (SEM-EDX) techniques, respectively. Significant differences in chemical compositions were observed among the seven sites, yet the bulk chemical compositions of the particles were broadly consistent with those of individual particles. Average elemental ratios of Mg/Al, Si/Al, K/Al, Ca/Al, Mn/Al, Fe/Al were found to be 0.44 ± 0.22, 1.96 ± 0.90, 0.65 ± 0.22, 1.52 ± 0.40, 0.84 and 1.54 ± 1.67, respectively. We also estimated the complex refractive index (RIs at 550 nm wavelength) for the studied sites, yielding an average n and k (the real and imaginary parts of RI, respectively) of (1.56 ± 0.03) + (6.5 ± 4.6) × $10^{-3}i$, with the aerosols collected from Kukas Hill area (27.02°N, 75.85°E) having the highest iron (Fe) mass fraction (~43%). Non-crustal elements e.g., Cu, S, C, Ag and Pb were found only in aerosols over the main city Birla Temple (Jaipur) at ground level (26.89°N, 75.81°E).

Keywords: PM_5; Mineral dust aerosols; Rajasthan; Chemical composition; Refractive index.

INTRODUCTION

About 50% of the global production of tropospheric aerosols consists of mineral aerosol particles, originating mainly from the deserts and their borders (Andrea *et al.*, 1986). Quantitatively ~1000–3000 Tg of mineral dust particles are injected into the troposphere annually (Andreae, 1995). Introduced mineral dust particles into the lower atmosphere are capable of traveling long distances before their eventual dry/wet deposition (Husar *et al.*, 2001; Fairlie *et al.*, 2007). Mineral dust particles originating from the desert regions can potentially influence heterogeneous atmospheric chemistry and thus regional as well as global climate (Ravishankara, 1997; Buseck and Posfai, 1999; Tegen *et al.*, 2003; Xu *et al.*, 2004; Bauer *et al.*, 2007). Besides, they can scatter/absorb incoming solar radiation influencing net radiative/optical forcing of the region (Sokolik and Toon, 1996, 1999; Sokolik *et al.*, 2001; Mishra *et al.*, 2008a, b, 2012). There are considerable uncertainties in the regional radiative/optical forcings, mainly due to strong variability of the atmospheric dust burden and the lack of chemical composition data (Kandler *et al.*, 2007). Many modeling studies also point to the uncertainties accountable to the lack of physico-chemical properties of mineral dust, as a limiting factor in estimating their climatic impact (e.g., Myhre and Stordal, 2001). Studies dealing with these aspects suggest that the climate forcing and heterogeneous atmospheric chemistry of individual mineral dust particles strongly depend on their mineral components (e.g., calcite, dolomite, and hematite) (Krueger *et al.*, 2004; Kelly and Wexler, 2005). As far as the Indian region is concerned, it has been shown that the chemical composition of mineral dust especially hematite fraction can significantly influence optical properties (such as single scattering albedo, asymmetry factor) by Mishra and Tripathi

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(2008a). Subsequently, Mishra *et al.* (2008b) also assessed the effect of mineral dust particle composition and shape on radiative forcing of dust aerosols. Recently Mishra *et al.* (2012) further studied effects of particle shape, hematite content and semi-external mixing with carbonaceous species.

The Thar Desert of Rajasthan is considered as the biggest regional dust source in India, from where large amount of dust originates and subsequently dispersed to the heavily populated Indo-Gangetic plains (IGP) in spring inter-monsoon season, and finally reaches all the way up to the India Ocean (through adjacent seas Arabian Sea and Bay of Bengal). With rapid development and urbanization of the state, mineral dust can get mixed with local pollution and that can significantly alter their optical properties (Mishra *et al.*, 2012). State capital of Rajasthan, Jaipur (26.89°N, 75.81°E), also popularly known as *Pink city* is surrounded by several old forts situated on the medium scale barren mountains such as Amber, Jaigarh, Nahargarh of varying altitude ranging from 500–1000 m from ground level. Besides these Kukas hills (~500–800 m from ground) are situated on outer Jaipur along the Delhi-Jaipur Highway (NH-8). Additionally, The Rajasthan state is known for its rich mineral resources especially marble and granite rocks. Makarana (~110 km west of Jaipur) is known as active limestone mining area, famous for its Makarana marbles.

Hence aerosol particles over this semi-arid urban location of Jaipur city could be influenced by regional topography/ geology and emissions due to ongoing anthropogenic activities (such as rock mining, vehicular pollution, road/ building constructions etc.). The chosen sampling time (late-February) of this expedition is expected to provide local scale variability in aerosol composition for which regional detailed chemical and physical database of ambient aerosols is highly sparse. To create such database at bulk as well as individual particle level, we collected atmospheric aerosols (particle of aerodynamic diameter < 5 μm (PM_5) and few bulk particles as well (total suspended particulate; TSPs)) from six selected locations of Jaipur situated at different altitudes and one aerosol sample from the Makarana mining area. We collected ambient aerosol samples from the five heighted places around the Jaipur city to capture regionally representative dataset. Two locales (i) Birla Temple Jaipur and (ii) Makarana mining area, are chosen where one can expect aerosols to be influenced by local scale activities such as urban vehicular pollution and rock mining and cutting activities, respectively. Purpose of covering these locales was to capture regional heterogeneity in the measured data. PM_5 size ambient particles were chosen for sampling because studies by Negi *et al.* (1996, 2002) that have shown size of mineral dust particles in general vary (from aerodynamic diameter ~5 to ~50 μm) and particles with size 1–5 μm (PM_5) were found to be embedded on the surface of the large particles. Also due to their high residence time, interact more with the incoming radiation compared to large particles (Mishra and Tripathi, 2008). Although the presence of larger particles near the source cannot be ignored, their contribution to the total global annual averaged dust load is negligible (Miller *et al.*, 2006). The modeling study by Miller *et al.* (2006) suggests that the total global annual averaged dust load in the atmosphere is mainly due to dust particles of aerodynamic radii < 10 μm with those of radii 1–2 μm making the largest contribution to it. In addition, PM_5 size particles of mineral dust are more likely to undergo long range transportation via prevailing winds.

Bulk chemical compositions of collected mineral dust particles were assessed using X-ray Fluorescence (XRF) technique, whereas selected individual particles from each site were imaged and analyzed for their chemical composition using Scanning electron microscope coupled with Energy dispersive X-ray (SEM-EDX) facility of National Physical Laboratory (NPL-New Delhi).

To the best of our knowledge, this is a first report from a semi-arid urban zone of western India comprising ambient aerosol particle composition both at bulk as well as individual level. Obtained database of background mineral dust aerosols originating from the semi-arid zone (in the vicinity of the Thar Desert) thus may prove to be highly helpful in ascertaining regional optical and radiative properties of ambient aerosols.

STUDY AREA AND METHODOLOGY

As mentioned before, ambient aerosol particles of size fraction PM_5 were collected from six sites of Jaipur of varying altitude plus one site representing active mining area i.e., Makarana (~120 km west of Jaipur). Details of all the collection sites and environmental conditions during sampling are summarized in Table 1. Fig. 1 shows the sampling locations, picture of installed apparatus used for particle sampling and key atmospheric backgrounds photographed from sampling locations. All the aerosol samples were collected on φ37 mm Teflon and pre-combusted quartz filters as collection substrates installed on low-volume air samplers APM-801 (*Envirotech*®). The air flow rates were generally kept at 1–1.5 L/min (LPM) (Table 1). A few total suspended particulate matter (TSPM) samples mainly from Kukas area were collected on φ25 mm filters. Mineral dust particles are generally of relatively coarser size aerosols, PM_5 size fraction of these aerosols should ideally belong to size fraction that is capable of reaching relatively higher altitude and getting dispersed in the atmosphere via long range transport. For particle imaging and analyzing morphological parameters small square plates of tin (of size 1 × 1 mm^2; thickness ~0.1 mm) were placed on Teflon filters. Before collection exposure sides of tin plates were marked and after collection these plates were carefully stored in small micro-biological specimen tubes and labeled for SEM-EDX analyses in NPL. Details on dust morphological characterization and morphological parameters have been discussed in a companion paper (Mishra *et al.*, submitted manuscript). Collection-substrates (Teflon filters) were weighed before and after sampling using a *METLER*® balance to calculate mass concentrations of particles. Bulk chemical composition of PM_5 particles collected over all the sites were analyzed non-destructively using XRF technique. Measurements were carried out using Rigaku ZSX Primus wavelength Dispersive XRF spectrometer. The XRF-spectrometer has an Rh-target,

Table 1. Details of sampling locations, collection parameters and environmental conditions during the field campaign of Jaipur city.

Site Name	Date of collection	Latitude	Longitude	Approx. height of sampling (MAGL)	Total time (min)	Flow rate (LPM)	$[PM_5]$ µg/m^3	Weather	Wind direction
Lower Jaigarh Fort	19-02-2012	26.984	75.851	600	240	1.2	34.7	Sunny	N-NW
Jaigarh Fort	20-02-2012	26.982	75.844	1000	360	1.0	250.0	Partly sunny	W-SW
Nahargarh Fort	21-02-2012	26.94	75.816	800	360	1.5	185.2	Bright Sunny followed mild dust storm	W
Kukas Near NH-8	22-02-2012	27.036	75.892	10	360	1.5	55.6	Clear sky	E
Kukas Hill	22-02-2012	27.027	75.919	800	150	1.5	44.4	Sunny	E
Makarana Mining area	23-02-2012	27.042	74.714	50	240	1.5	500.0	Mostly sunny	W
Birla Temple Jaipur	25-02-2012	26.893	75.816	10	240	1.5	222.2	Sunny	N

end-window, 4 kW, sealed X-ray tube as the excitation source and scintillation counter (SC) for heavy elements and flow proportional counter (F-PC) for light elements as the detectors. Chemical composition of some of the selected individual particles collected on tin substrate were studied using a SEM (ZEISS EVO MA-10) equipped with an EDX spectrometer (Oxford Link ISIS 300). SEM is capable of resolving 3 nm size particle at 30 KV accelerating voltage. Energy dispersive spectrometer attached to the SEM can identify the elements having atomic numbers of the elements from beryllium (Be) to uranium (U) with a spectral resolution of 133 eV.

WIND TRAJECTORIES

From the known overall climatology of the Jaipur area, it is clear that during the month of February typical wind speeds vary from 0 to 4 m/s (calm to gentle breeze), rarely exceeding 8 m/s (moderate breeze) at ground level. Hence, this is probably an ideal time to capture the physical and chemical characteristics of background mineral dust of local origin. Winds are blowing most often from the west, occasionally from the east and south west. For shorter time intervals, winds are also found to be blowing from the southeast and north (source: http://weatherspark.com/averages/33936/2/Jaipur-Rajasthan-India). In order to inspect a more realistic view for our sampling period i.e., 19–25 February, 2012, seven days backward trajectory analyses were carried out to identify the transport pattern of the air masses arriving at 500 m above ground level using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) [source: http://ready.arl.noaa.gov/hysplit-bin/trajasrc.pl]. Fig 2 illustrates the typical air mass flows on different days of sampling period i.e., 19–25 February, 2012. As all the samples sites are not spatially very far from each other (Table 1), we have chosen single latitude and longitude position (26.94°N, 75.82°E) to compute backward trajectories, with the assumption that air masses over this location is representing a common scenario for all the studied sites. Fig. 2 shows winds directions prevalent during the sampling period i.e., 19–25 February. On 19-February, winds were found to be originating from north-northwest, while next day winds were also from southwest. On 21 February, winds were found to be blowing from western side, next day exactly opposite scenario was observed i.e., winds seem to be originating from east, northeast side. On 23 and 25 February, winds were mainly blowing from north-northwest (Fig. 2). Thus, backward wind trajectories computed using HYSPLIT model corroborates the fact during the month of February; winds over the Jaipur city are not coming from any specific direction and local erosion can dominate atmospheric mineral dust particles in this dry period. This was the reason why late February was chosen for conducting this experiment.

RESULTS AND DISCUSSION

Results are presented in the following sub-sections. Elemental compositions of sampled PM_5 particles at bulk

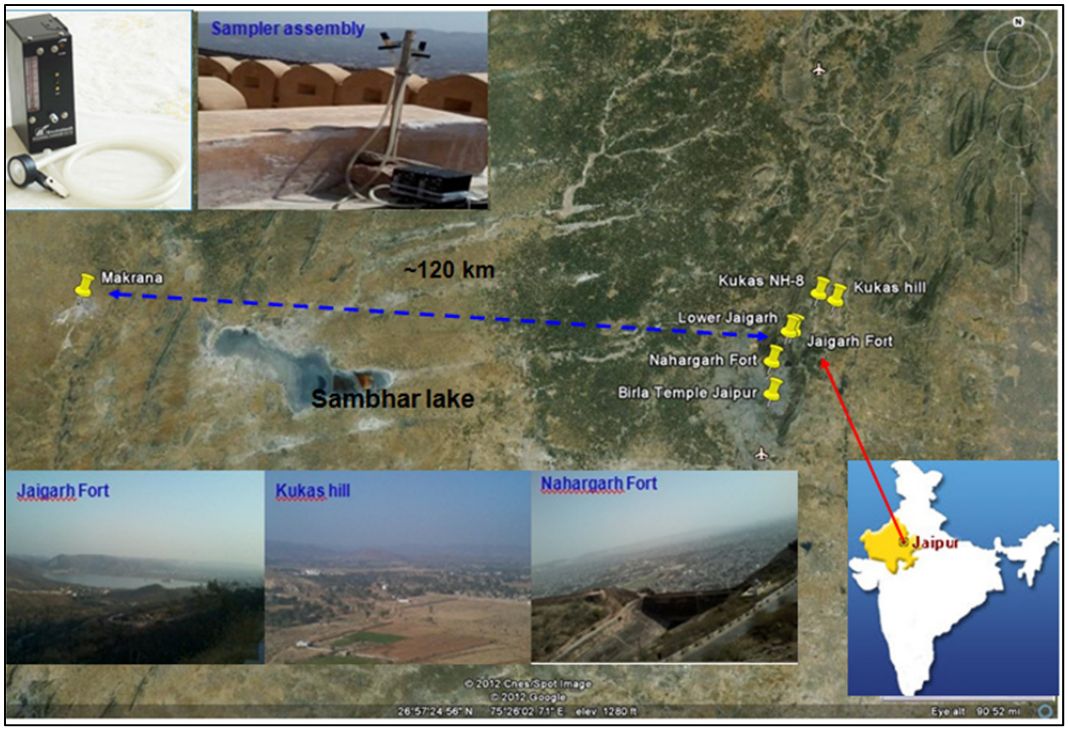

Fig. 1. Site locations of collected atmospheric dust samples from hill regions of Jaipur city Rajasthan (India). Inserted panels show typical sites, micro-volume sampler and sampler assembly. The base map of site location is adapted from Google earth.

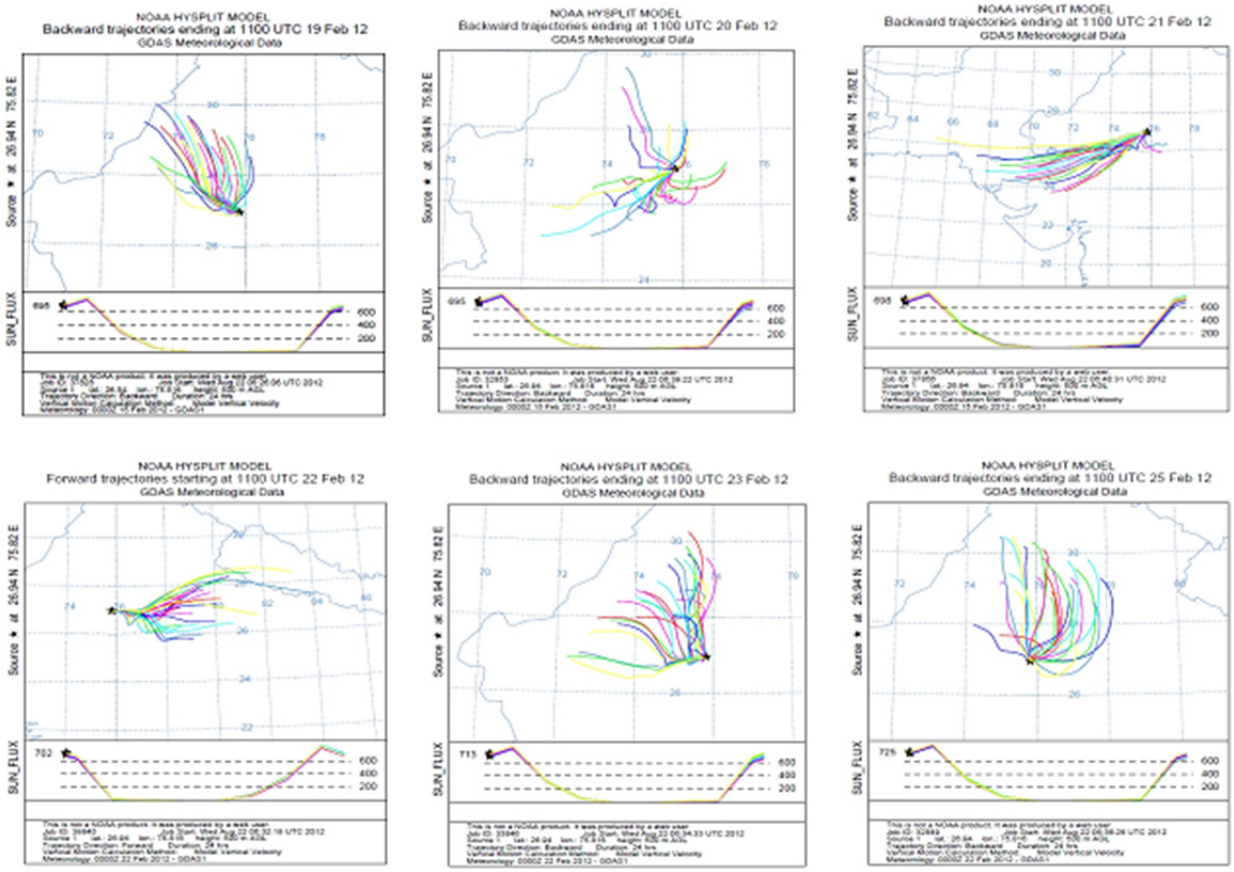

Fig. 2. Seven day back trajectory analyses (using NOAA HYbrid Single -Particle Lagrangian Integrated Trajectory (HYSPLIT) Model accessed via website (http://ready.arl.noaa.gov/hysplit-bin/trajasrc.pl) for the sampling dates (Table 1) in order to ascertain the long-range transport of air masses.

level (determined using XRF spectrometer) are discussed first, followed by selected individual particle chemical compositions (determined by SEM-EDX) along with particle images. Salient features of elemental composition of ambient particles over Jaipur are discussed in the context of published literature, thereafter.

Elemental Composition of PM_5 Particles at Bulk Level

Mass concentrations of ambient PM_5 size particles over Jaipur show large variations. Minimum PM_5 mass concentration (34.7 μg/m^3) was found over lower Jaigarh, near Amber fort (Table 1), whereas maximum PM_5 mass concentration (499.8 μg/m^3) was found near Makarana mining area of Rajasthan) (Fig. 3(a)). Major elements found in PM_5 particles are Si, Al, Cr, Fe, Mg, K, Ca, Mn and S, variability in their respective mass concentrations is shown in Fig. 3(b). In general, common major crustal elements found in atmospheric particles over all the sites are Si, Al, Fe, however, maximum variability was shown by Fe (Fig. 3(b)). Elemental mass fractions showed considerable variability for key crustal elements e.g., Ca and Fe and K (Table 2); average Element/Al ratios found in this study were compared with those of average upper continental crust (Ruidnick and Gao, 2003) and Saharan mineral dust (Formenti *et al.*, 2003). Table 2 reveals mineral dust particles sampled in this study showing significantly higher values of Ca/Al, Fe/Al and K/Al ratios. Using measured elemental data, we estimated respective elemental oxides (Table 3). Using elemental oxide data, we also estimated the portion of total mass accounted by elemental oxides of major crustal elements viz. Si, Al., Ca, Mg, K and Fe. Total mass accountable by crustal elements viz. Si, Al, Ca, Mg, K and Fe for lower Jaigarh, Nahargarh fort, Kukas highway NH-8, Jaigarh fort and Birla temple area are ~81%, 45%, 40%, 30% and 16% respectively. Maximal mass fraction accountable by crustal elemental oxides appears to be from aerosols over Kukas hill area (~99%) due to higher Fe content. Using elemental oxide data it is possible to estimate spectral variation of refractive indices (RIs), which are vital data input for estimation of optical properties. Except for the Makarana area, Fe was found to be abundant at all the studied sites with highest mass fractions of Fe found in aerosol particles over Kukas hill area (Table 2). We also note that higher Cr concentrations found in ambient PM_5 particles over almost all the sampled sites (Table 2; Fig. 3(b)).

In addition, we also determined enrichment factors of elements using Si as a reference crustal element and using mean elemental ratio with respect to Si in upper continental crust (Rudnick and Gao, 2003). Maximum enrichment factors were obtained for Fe especially over Kukas hill and Kukas NH-8 highway. Following Fe, Ca and K were also found to be enriched in PM_5 particles over Jaigarh, Nahargarh, Birla Temple and Makarana mining area (Fig. 3(d)).

Average elemental ratios of Mg/Al, Si/Al, K/Al, Ca/Al, Mn/Al, Fe/Al of PM_5 aerosols (at bulk level) were found to be 0.44 ± 0.22, 1.96 ± 0.90, 0.65 ± 0.22, 1.52 ± 0.40, 0.84 and 1.54 ± 1.67 respectively. Average Si/Al ratio in ambient PM_5 particles over Jaipur are thus well within the overall variability of Si/Al ratios of Saharan dust (typical value

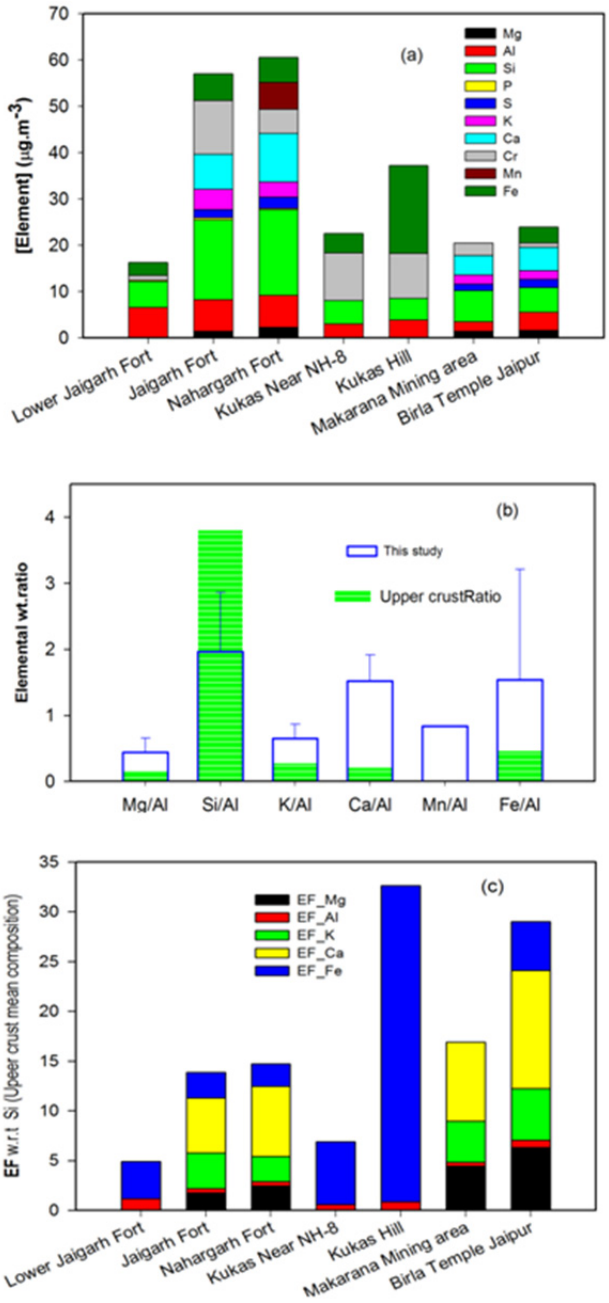

Fig. 3. (a) Variability in measured elemental concentrations in PM_5 particles for all sites, as determined by XRF analyses. (b) Observed elemental ratios with respect to Al in comparison to respective elemental ratios found in upper continental crust. (c) Observed enrichment factors of element with respect to Si.

~2.3; Formenti *et al.*, 2001). The average elemental mass ratios in the work of Kandler *et al.* (2007) who sampled Saharan dust from Spain are 2.14 (Si/Al), 0.20 (K/Al), 0.28 (Ca/Al), and 0.58 (Fe/Al). Noteworthy is the fact that ambient dust over Jaipur shows higher average K/Al, Ca/Al and Fe/Al ratios. Higher Ca/Al ratios are consistent with findings of Tindale and Pease (1999), who reported Ca rich dust over the Arabian Sea, most likely originated from the Thar Desert region. Average Ca/Al ratio in bulk

Table 2. Variability observed in elemental mass fractions and characteristic average Element/Al ratios in the context of average upper continental crust and Saharan mineral dust.

Site Name	Mg %	Al%	Si%	P%	S%	K%	Ca%	Cr%	Mn%	Fe%
Lower Jaigarh Fort	-	18.80	16.27	0.63	-	-	-	3.16	-	7.94
Jaigarh Fort	0.62	2.65	6.91	0.18	0.70	1.74	3.04	4.65	-	2.32
Nahargarh Fort	1.24	3.72	10.00	0.15	1.27	1.78	5.64	2.84	3.12	2.93
Kukas Near NH-8	-	5.39	9.17	-	-	-	-	18.48	-	7.53
Kukas Hill	-	8.75	10.37	-	-	-	-	21.81	-	42.82
Makarana Mining area	0.30	0.40	1.33	-	0.29	0.39	0.84	0.55	-	-
Birla Temple Jaipur	0.76	1.72	2.40	-	0.79	0.87	2.27	0.42	-	1.53
Average ratios	Mg/Al		Si/Al	P/Al	S/Al	K/Al	Ca/Al	Cr/Al	Mn/Al	Fe/Al
This study	0.44 ± 0.22	1.00	1.96 ± 0.90	0.05 ± 0.02	0.45 ± 0.20	0.65 ± 0.22	1.52 ± 0.40	1.46 ± 1.20	0.84	1.54 ± 1.67
Mean upper crust	0.18	1	3.82	0.01	-	0.29	0.31	-	0.01	0.48
Saharan dust sampled from Spain			2.14			0.2	0.28			0.58
Saharan dust	-	-	2.03, 2.21, 2.32	0.012 ± 0.002	-	0.18, 0.21, 0.24	0.20, 0.36, 0.60	-	-	0.54, 0.52, 0.54

Table 3. Estimated elemental oxides in weight percentages over all the sites.

Site Name	MgO%	Al_2O_3%	SiO_2%	P_2O_5%	SO_4%	K_2O%	CaO%	Cr_2O_3%	MnO_2%	Fe_2O_3%
Lower Jaigarh Fort		35.52	34.81	1.45				4.62		11.35
Jaigarh Fort	1.04	5.01	14.79	0.41	2.09	2.09	4.25	6.79		3.32
Nahargarh Fort	2.06	7.03	21.39	0.35	3.80	2.14	7.90	4.14	4.93	4.18
Kukas Near NH-8		10.18	19.62					27.00		10.76
Kukas Hill		16.53	22.19					31.87		61.21
Makarana Mining area	0.50	0.76	2.84		0.88	0.47	1.18	0.80		
Birla Temple Jaipur	1.26	3.24	5.12		2.36	1.04	3.18	0.61		2.19

aerosols (TSPM) collected from Ahmedabad (known to receive mineral dust from the Thar Desert during late winter February–March) varied from 0.75 to 1.25 with a mean value of 1.04 ± 0.13 (Rastogi and Sarin, 2009). Similarly higher Ca/Al, K/Al and Fe/Al ratios have been reported in aerosols over Bay of Bengal during late inter-monsoon season, when calcareous mineral dust originating from the Thar Desert is expected to be the major contributor of crustal elements (Srinivas and Sarin, 2012). Thus observed elemental ratios especially Ca/Al, K/Al and Fe/Al measured in this study could be used as representative elemental ratios of the background mineral dust of this semi-arid zone (in the vicinity of the Thar Desert). Though individual particle chemical compositions are presented in the next section, it is important to mention here that individual particle chemical compositions measured by SEM-EDX were found to be in good agreement with bulk level chemical compositions.

Significant enrichment of Fe in ambient particles over Kukas hill and surrounding region (Kukas NH-8 highway) is important as Fe is a key element (in the form of mineral hematite; Fe_2O_3) for incoming solar (visible) energy absorption and thus heating the atmosphere (Lafon *et al.*, 2006). Besides Fe, Cr is also high in ambient PM_5 particles over almost all the sites studied and specifically over Kukas hill region. Cr/Al ratio show significant variability with an average value of 1.46 ± 1.2 (Table 2). Though the Kukas hill area is along the sides of Delhi-Jaipur National highway (NH-8), an area with a busy vehicular traffic, however absence of non-crustal elements (e.g., Cu, Ni, Pb, S, potential indicator of local vehicular emission) disfavors the possibility of enhanced Fe and Cr due to vehicular emission. Since the Kukas industrial area is also known for various other activities such as assembling heavy vehicles (trucks and buses) which involve welding that may be a plausible source of extra Fe in local aerosols. To pin point which type of anthropogenic activity is responsible for high Fe inventory to ambient aerosol particles, certainly a more number of samples and data are required to gain further insights of ambient particle chemistry over Kukas area. Nonetheless, the observed Fe rich ambient particles certainly appear to be capable of influencing regional optical/radiation budgets significantly.

Elemental Composition of Individual Particles

Over all 235 particles were analyzed for estimation of morphological parameters in this study (Mishra *et al.*, submitted manuscript). From which, a total of 25 individual particles were analyzed by EDX for chemical composition; from that a total 15 typical individual particles along with their chemical composition are shown in Figs. 4–7 (~2–4 particles per sample). It is true that number of particles analyzed by EDX should be as high as possible in order to get better statistical comparison with XRF measured bulk chemical composition. However it also noteworthy here, that individual particles were manually selected for imaging and spot EDX analysis and hence it is a labor intensive and time consuming work.

Hence, selected individual mineral dust particles from all the seven sites were imaged and their elemental compositions were determined using spot-EDX. From this data, a few representative particle images along with elemental composition are presented in Figs. 4–7. Highly non-spherical particles were found with predominance of 'Layered" (Ca, Si rich), "Angular" structures (Si rich) and "Flattened" particles over all the sites (Mishra *et al.*, submitted manuscript). Most of the particles appear to be aggregates of different mineralogical composition as corroborated by their SEM images (Figs. 4–7). The elemental data of individual particles (Figs. 4–7) indicate that particles contain mainly Si, Al, Ca, Mg, K, and Fe as crustal elements besides C and O oxides (Table 4). For almost all the individual particles the sum of all measured elements including C, N, O (Table 4) add up to ~100, indicating that estimated elemental distribution nearly reflects the particle's total chemical composition. Particles from Kukas hill and surrounding area (Kukas highway NH-8) are Fe rich but poor in Ca, while particles from Makarana and Birla Temple are Ca rich and Fe poor. From the Table 4 and Fig. 5, it can be seen that most of the individual particles also show significant Fe enrichments, corroborating bulk level measurements (section 4.1) of higher Fe contents of aerosols over Kukas hill and surrounding regions.

Few particles also showed presence of S. Na was found only in minor amount in aerosols over Jaigarh-Nahargarh, Kukas NH-8 highway, Makarana (Figs. 4–6); except a crystal structured particle found over main city Birla Temple (Jaipur) showed Na in higher amount (~29%) (Fig. 7). Ca, Mg, Si, Al and Fe were found to be abundant in the majority of particles. Na, K, S, Na, Cl were also present in a few particles. Among crustal elements, Ti intriguingly was found only in two individual particles. Non-crustal elements e.g., Cu, Ag and Pb (plausible indicators of anthropogenic pollution) were found to be abundant only in a very few individual particles (two particles over Birla Temple and one from Kukas NH-8 night sample). Presence of S in particles collected from Makarana, Birla temple Jaigarh and Nahargarh which showed Ca as a significant crustal component indicate that Gypsum ($CaSO_4.2H_2O$) may be probable mineral phase of Ca. On the other hand, absence of S in particles which show Fe as abundant component, disfavor presence of Fe sulfides or sulfates. Hence, Fe may be present in form of its oxides such hematite, magnetite. Fig. 5 shows a few Fe-rich particles from Kukas area. In a previous study Negi *et al.* (1996) studied TSPM and its elemental composition from Mount Abu, Rajasthan (high altitude region in the vicinity of Thar Desert) and reported particles with higher Fe contents. Chemical composition data of individual particles from the Makarana mining area show significant Ca contents (Fig. 6) as can be expected being an active lime stone mining area, higher amounts of C and N oxides indicate significant mixing of carbonaceous material probably originating from drilling activities. Non-crustal elements which are known to be of anthropogenic origin were found only in aerosol over Birla Temple e.g., significant mass fractions of Cu, Pb, Ag along with S indicating their presence as sulfides (Fig. 7). Aerosol particles collected from Birla Temple area also showed higher

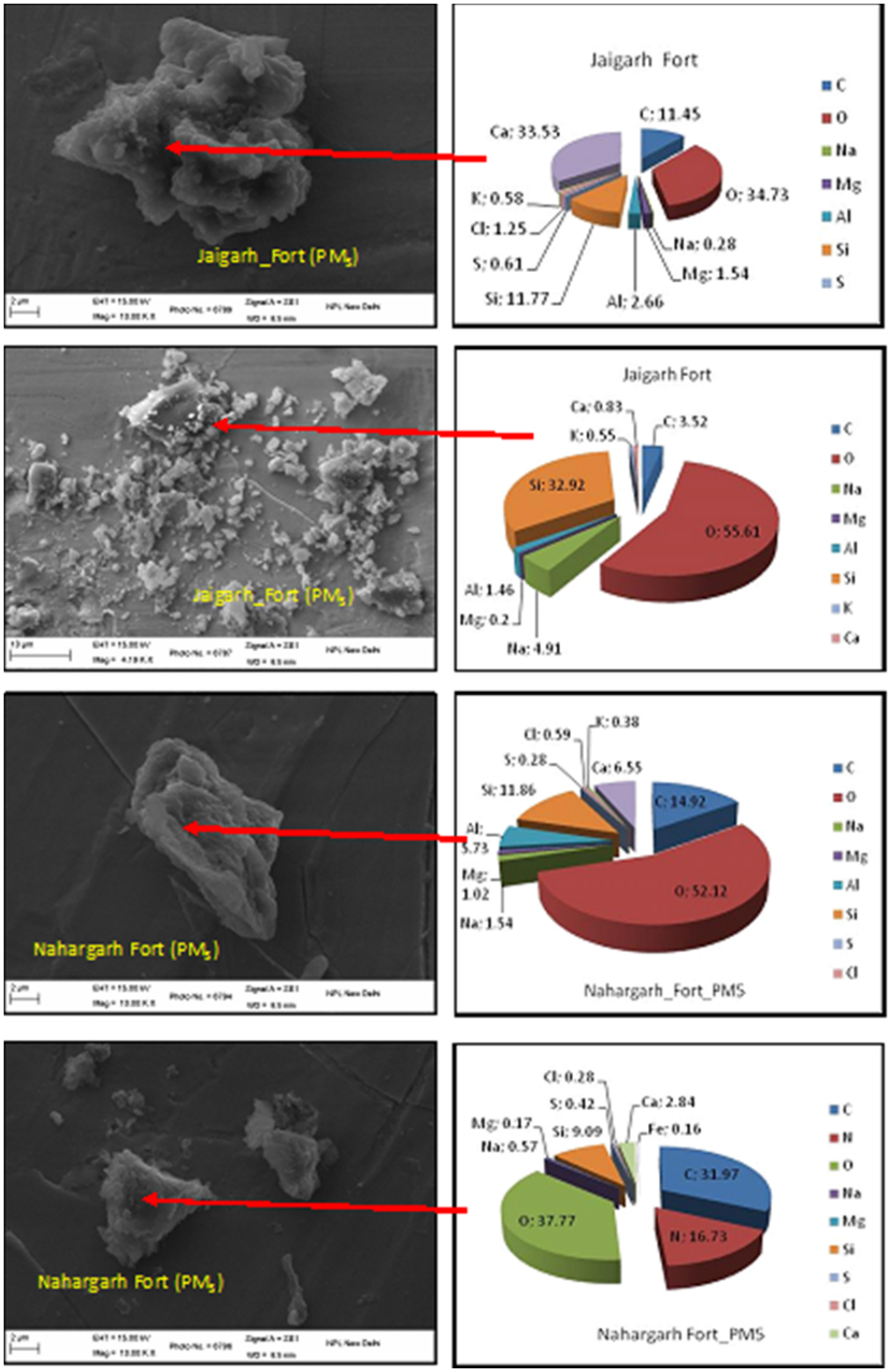

Fig. 4. SEM images and chemical compositions of individual mineral dust particles over Jaigarh and Nahargarh forts (Jaipur, Rajasthan). See text for likely minerals inferred from chemical composition.

C mass fractions possibly owing to local scale urban activities such vehicular traffic.

Major clastic minerals reported in the eastern Thar Desert region are quartz, plagioclase, K-feldspar, amphibole, mica and chlorite (Peterson, 1968). Non-clastic mineral assemblage however is variable and comprises of both evaporite minerals and carbonates (Roy *et al.*, 2008). Using measured elemental composition of individual particles, we assessed probable mineral phase abundant in aerosols over different sites following Kandler *et al.* (2007, 2009) (Table 4). The probable mineral phases of the background mineral dust sampled in this study, thus, are consistent with previous studies of

Table 4. Elemental distribution of studied individual aerosol particles and inferred (most likely) minerals for the measured chemical composition.

Site	C	N	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe	Cu	Ag	Pb	Probable Mineral phase
Jaigarh	3.52		55.61	4.91	0.2	1.46	32.92			0.55	0.83						Quartz, Plagioclase
Jaigarh	11.45		34.73	0.28	1.54	2.66	11.77	0.61	1.25	0.58	33.53						Gypsum, carbonates
Nahargarh	14.92		52.12	1.54	1.02	5.73	11.86	0.28	0.59	0.38	6.55						Gypsum, carbonates
Nahargarh	31.97	16.73	37.77	0.57	0.17		9.09	0.42	0.28		2.84		0.16				Carbon rich partcile
Kukas_hill_TSPM	0.82		48.86		1.32	6.77	30.37			1.38	0.48	0.21	9.79				Hematite, Magentite
Kukas_hill_TSPM	64.24		28.7	1.56	0.44	0.2	2.04		0.46	0.53	1.67		0.17				
Kukas Hill_PM5	5.07	1.43	32.98		1.14	11.34	18.34			4.91	0.5		24.3				Hematite, Magentite
Kukas NH8_Night_TSPM	6.56	1.59	46.3	3.48	0.37	10	26.3			1.05	1.8		2.54				Hematite, Magentite
Kukas NH8_Night_TSPM	81.1		12.47			0.8					4.4		0.57	0.65			Carbon rich particle
Kukas NH8_Night_PM5	1.04		49.7		0.72	18.27	22.75			0.68	0.53	1.44	4.87				Hematite, Magentite
Makarana	27.68	8.54	43.42	1.5	2.16	0.6	5.76	2.82	0.61		5.59						Carbon rich partcile
Makarana	37.17	32.21	14.2								16.43						Carbon rich partcile
Birla Temple JP	37.41		33.81		1.69	2.31	2.28		1.11		18.96		2.43				Carbon rich partcile
Birla Temple JP	8.88		1.76					25.9	0.74					61.16	1.53		Cu rich particle
Birla Temple JP	9.84	1.7	4.06	29.2					52.8							0.3	Salt rich evaporite

Peterson, (1968) and Negi *et al.* (1996) as both the studies indicated presence of quartz (Si rich), hematite (Fe rich) and carbonates Ca rich minerals.

Relationship between Particle Aspect Ratio and Chemical Composition

Though detailed morphologies of the studied particles have been presented in Mishra *et al.* (submitted manuscript), we attempt here to examine any relationship between measured aspect ratios (ARs; from Mishra *et al.*, submitted manuscript) and measured chemical composition. Si and Al are the only two such elements which were found to be abundant in all the samples, and Si/Al ratio varied in a range 1.96 ± 0.9 (Table 2). Si/Al ratios of six different sites appear to be positive correlated with the measured mean Aspect ratios (ARs) of particles (r^2 = 0.82; n = 6; Fig. 8(a)). Though total numbers of data point are relative small for a statistically sound relationship, yet we have attempted to understand plausible causes for such a relationship. The Si/Al ratios are mainly controlled by the relative proportion of quartz and clay and, thus, depend upon proportions of coarse and fine mode particles. Lafon *et al.* (2006) have found different Si/Al ratios for different impactor stages representing fine and coarse modes. Higher Si/Al ratios of particles therefore are indicative of higher proportion of coarse mode faction containing more quartz (Si rich) in ambient aerosol particles, while lower Si/Al ratios are indicative of higher fine mode fraction (clay fraction enriched in Al). A positive correlation between Si/Al ratio and ARs of particles is probably indicating that particles having higher coarse mode fraction are also more of non-spherical in nature, compared to particles with the lower Si/Al ratio, while the relatively higher fine size fraction are closer to spherical shapes. This observation thus indicates that how abundances of crustal elements could be related to physical properties of the particles.

Spatial Variability of Refractive Index of Mineral Dust Particles over Jaipur

The dust aerosols are composite mixtures of different minerals. Chemical composition of dust aerosols is thus an important factor for estimating optical parameters such as their complex refractive indices. Using elemental oxide data (Table 2), considering all Fe to be present as hematite of density 5.3 gm/cc and density of mineral dust to be 2.65 gm/cc (Lee *et al.*, 2009), we computed volume fractions of hematite in dust aerosols over six sites. Except Kukas hill area which showed very high Fe contents, average volume fraction of hematite is estimated as 3.18 ± 1.94, which agrees well with the estimated hematite content (< 4% Fe_2O_3) over Thar Desert (Mishra and Tripathy, 2008a). Using these volume fractions of hematite we then computed real and imaginary parts of refractive index (at 550 nm) over six sites of the Jaipur city (Fig. 8(b)). Refractive index (real and imaginary) of mineral dust has been calculated using Bruggman's effective medium mixing rule (Bohren and Huffman, 1998) at 550 nm following the approach adopted and discussed earlier by Mishra and Tripathi (2008a). The estimated hematite percentage is the major input in governing

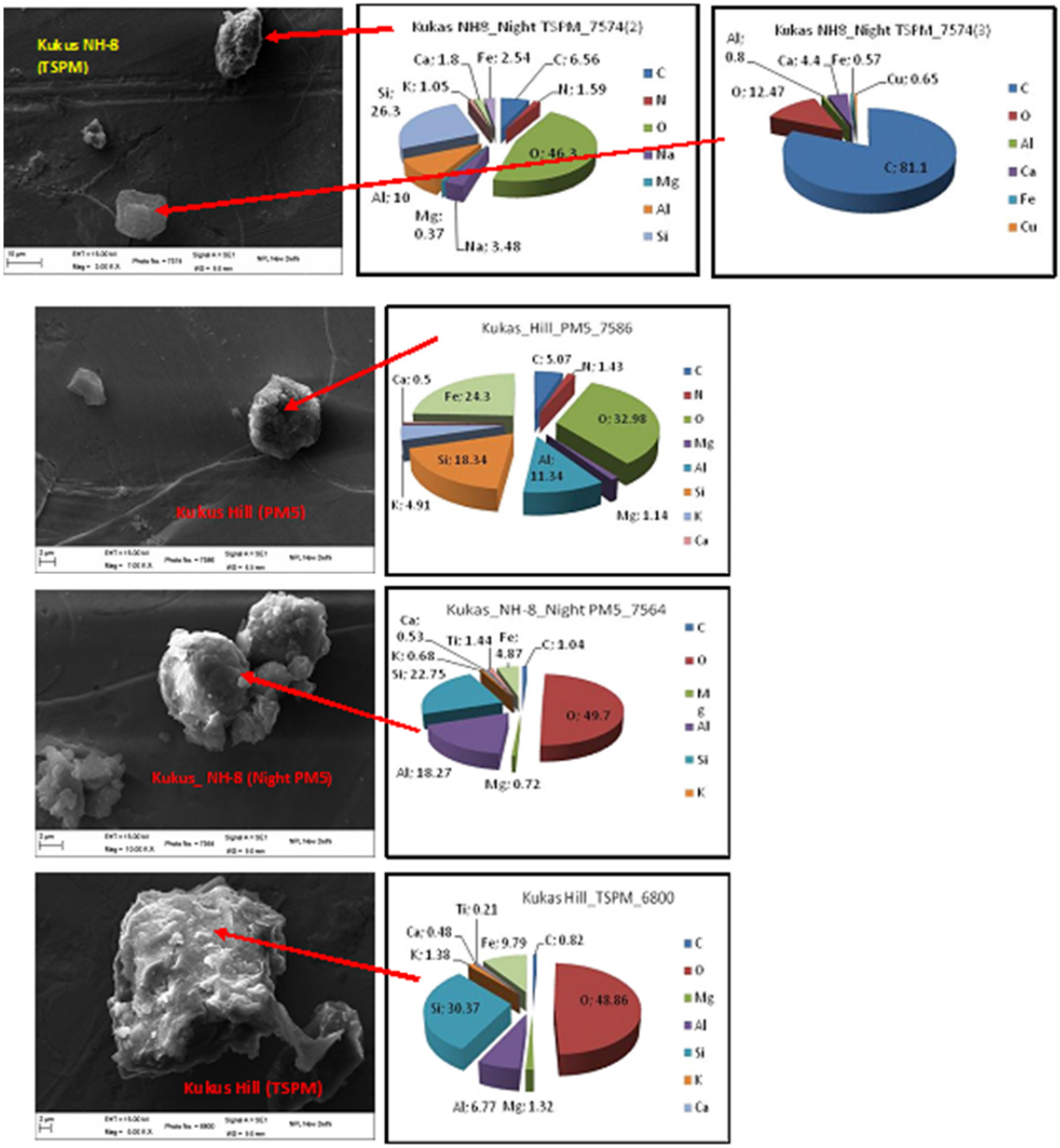

Fig. 5. SEM images and chemical compositions of individual mineral dust particles over Kukas hill and Kukas highway (Delhi-Jaipur).

the refractive indices. The details for the calculation of indices have been discussed in the companion paper by Mishra *et al.* (submitted manuscript), where the sensitivity of mineral dust optics with respect to its morphology and mineralogy has been discussed. Except for Kukas hill area, estimates of real and imaginary parts of refractive index, i.e., average n and k for all the other sites vary in a relatively narrow range $(1.56 \pm 0.03) + (6.5 \pm 4.6) \times 10^{-3}i$. For the Saharan area with the mean value RI_{550nm} is reported to be as $1.58 + 1.1 \times 10^{-3}i$, whereas the global mean RI_{550nm} for global mineral dust (based on FAO/UNESCO Digital Soil Map of the World) is reported to be $(1.59 \pm 0.02) + (1.2 \pm 0.5) \times 10^{-3}i$ (Smith and Grainger, 2009). Real parts n of RI estimated for Indian region agrees well with global/Saharan mineral dust data while imaginary parts k shows higher values. Claquin *et al.* (1998) reported that the imaginary part of refractive index k is significantly influenced by natural chemical composition/variability of particles which can lead to significant variations (as high as ~40%) in aerosol forcing calculations, underscoring the importance of region-specific data for validity of such estimations. As far as Kukas hill region is concerned, it appears that more samples and representative data are required to ascertain physico-chemical properties of aerosols over this region.

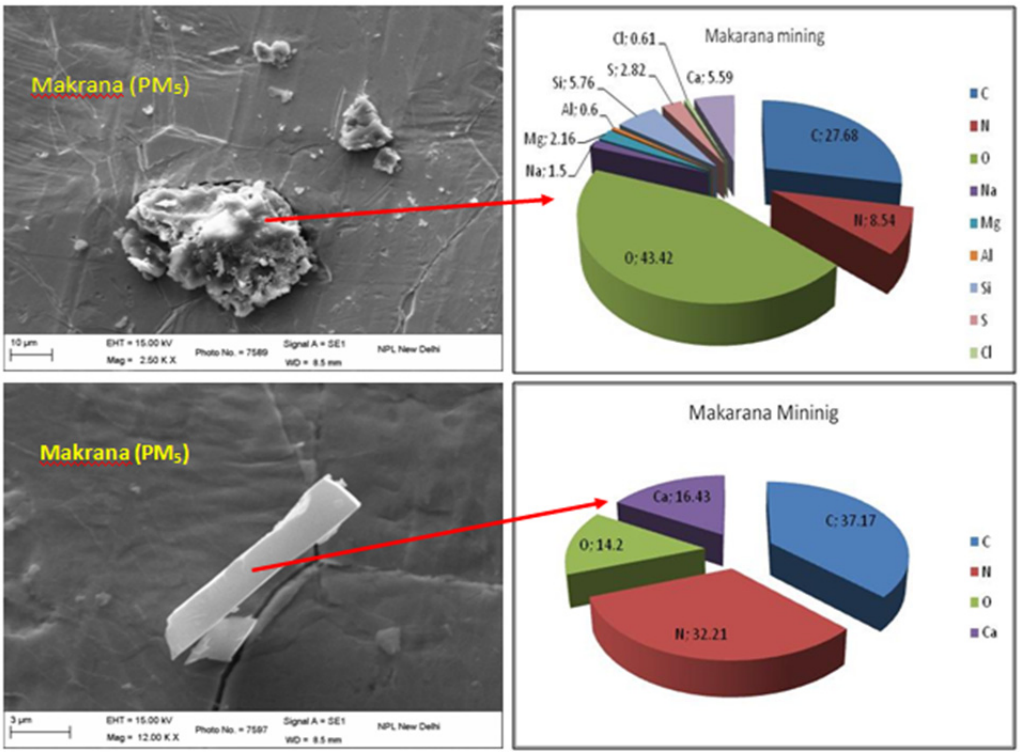

Fig. 6. SEM images and chemical compositions of individual mineral dust particles from Makarana mining area (Rajasthan, India).

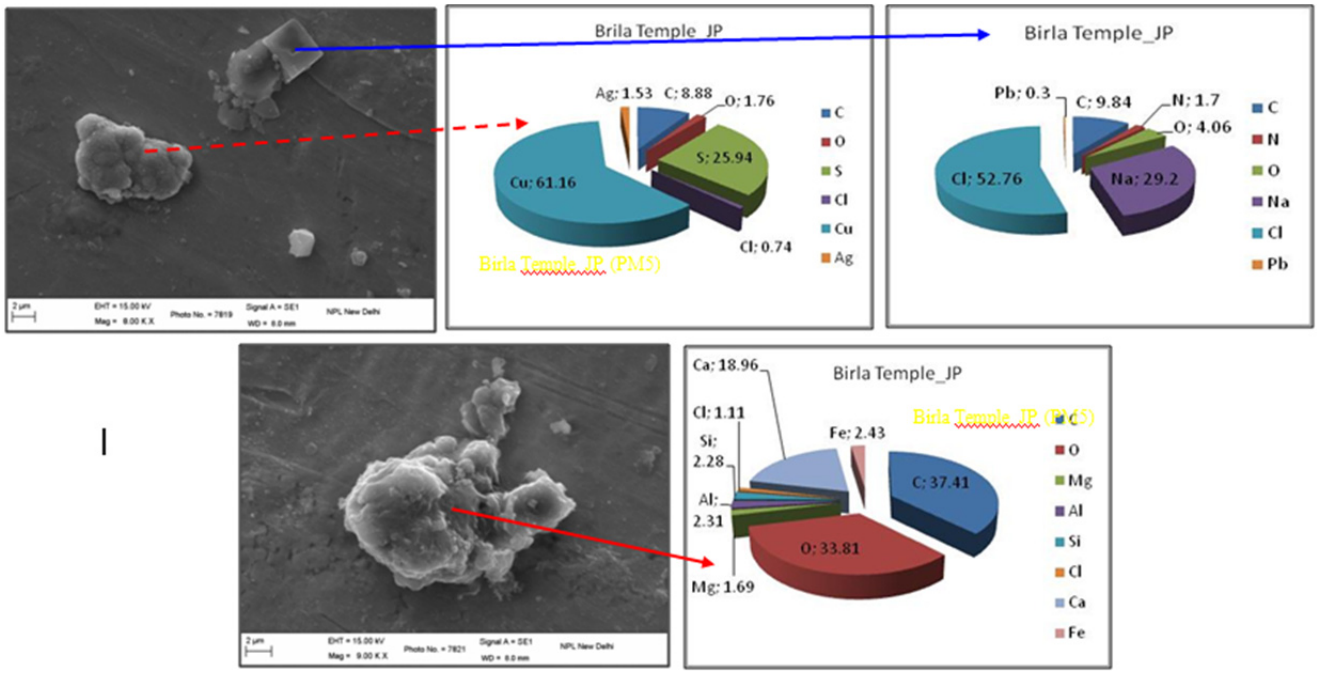

Fig. 7. SEM images and chemical compositions of individual mineral dust particles over the main city (Birla Temple; Jaipur).

SUMMARY

Most of the ambient particles were found to be highly non-spherical in shape (Mishra *et al.*, 2014, submitted manuscript) and composed of crustal elements e.g., Si, Al, K, Mg, Ca and Fe. Ambient particles over Kukas Hill area showed highest iron (Fe) mass fraction (~43%). Chromium (Cr) was also found to be abundant in the sampled mineral dust particles over almost all the sites. It is noteworthy, because Cr enriched dust particles over Indian plains are generally thought to be of Arabic (Oman) origin. Non-crustal elements were found only over the main city (Birla Temple, Jaipur)

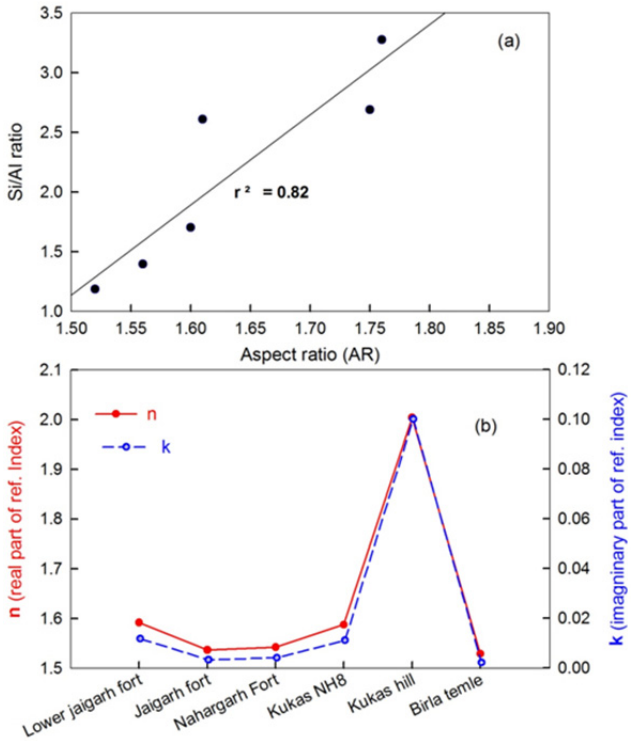

Fig. 8. (a) Inter-relationship between aspect ratio of particles with Si/Al ratio. (b) Complex refractive indices (n and k) of particles sampled over six different site of Jaipur.

at ground level. In addition, based on individual particle chemical composition quite a few carbon rich particles were also observed. An overall consistency was observed between bulk level and individual level chemical composition.

Both bulk level and individual particle level chemical composition of particles reveal predominance of crustal elements (Si, Al, Ca, Fe, K, and Mg, K) in ambient aerosols over Jaipur city. Highly non-spherical particles were found to be present with significantly varying chemical composition, yet individual particle chemical compositions measured by EDX were found to be in good agreement with bulk level chemical compositions measured by XRF. Maximum mass concentration of particles was found over Makarana as can be anticipated being active mining area. Higher carbonaceous and nitrogenous portion might be due to emissions of fuel used in on-site rock cutting machines. Particles from all the sites at elevated heights (Table 1), in general, were found to be devoid of non-crustal elements except city downtown Birla Temple area (at ground level), indicating dominant background mineral dust characteristics overall in the ambient atmosphere. Among all sites, particles over Kukas hill and surrounding regions appear to be maximum Fe and Cr enriched. In absence of any other specific non-crustal elemental abundance, to find out exact causes of the observed enrichment is difficult to ascertain, nonetheless, irrespective of the natural or anthropogenic influence high Fe content in aerosols over this area may have important bearing on regional optical properties of aerosols as Fe in the form of hematite (Fe_2O_3) is considered as a potential absorber of incident radiation in visible range (Lafon *et al.*, 2006; Mishra and Tripathy, 2008b).

This is a first step of the our ongoing detailed physico-chemical characterization of atmospheric particles for generating region-specific database of ambient aerosols from the vicinity of the Thar Desert region, that could greatly help better estimation of optical constants of mineral dust (governing optical/radiative properties) and characterizing long range transport of dust aerosols all the way up to northern Indian Ocean through Indo-Gangetic plains.

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