J. Mater. Environ. Sci. 6 (8) (2015) 2076-2082 *Bengamra et al.*
ISSN : 2028-2508
CODEN: JMESCN

Mineralogy of atmospheric dust deposits in the Naima-El Aioun basin (Eastern Morocco)

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Received 12 Dec 2014, Revised 26 June 2015, Accepted 26 June 2015
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Abstract
The Naima-El Aioun basin is a rural zone with a semi-arid climate, characterized by reduced organic matter soil and fragile vegetable cover. Soils are removed easily by winds which confer to this zone a dusty atmosphere. This situation becomes more drastic by the particle emissions from cement factory and her raw materials careers (limestone and clay). To study the dust deposits in this zone, 41 passive sensors were distributed randomly around the cement factory located in the Naima-El Aioun basin. They collect the dust deposits by gravitation's effect. To identify the dust mineralogy, X-rays diffraction (XRD) Analysis is used. It allows the distinction and the identification of the industrial dust origin (cement factory) and the natural one. Furthermore, XRD shows that the chimney dust emissions and the one collected by passive sensors installed inside the factory, does not contain the cement. However, the dust contains essentially the calcite ($CaCO_3$) that is the principal mineralogical component of the industrial particle emissions. Otherwise the natural dusts (soil particles) are rather characterized by quartz (SiO_2) as a principal mineralogical component. Thus, the calcite/quartz ratio can be used as a good tracer of the atmospheric particles, originated from the cement factory.

Keywords: Cement factory, dust deposits, mineralogy, XRD, tracer.

1. Introduction
Atmospheric dust is an important source of air pollution, particularly in dry climates. Mineral dust contains high concentrations of many metals known to have toxic effects not only on plants and animals but also on Humans.
A cement industry offers an excellent opportunity for studying the dust emissions during the process of cement manufacture, considerable quantities of dust are emitted from handling, spillage and leakages. Dust is produced from quarrying of the major raw material limestone to packing final cement product [1].
The cement dust emissions are dispersed by the wind over important areas. So they can affect the various components of the environment as air [2,3], water [4], soil [5,6] and vegetation [7-9]. The human health is particularly sensitive to this type of pollution. Recent pathological studies have shown the effect of dust inhalation on the workers respiratory system in cement factories [10-12]. This effect has in impact also on population living near the production unities [2,13,14]. Because of their contact with cement dust, some harmful effects have been proved on the skin and the eyes [1,15,16].
The aim of this work is to determine the mineralogy of dust deposits in the Naima-El Aioun area and look for the tracer of cement particulate emissions.

2. The manufacture cement process in Oujda cement factory
The Portland cements process at Oujda cement factory consists of mixing the raw materials of limestone (80%) and clay (20%) for producing the pre-homogenized component. However, other minerals (sand SiO_2, bauxite Al_2O_3 and iron Fe_2O_3) can be added to these materials to reach the ideal geochemistry composition. The pre-homogenized mixture is then introduced into the calcinations kilns to be heated at 1450 °C. During this stage, CO_2 is rejected and the Ca, Si, Al and Fe elements are recombined to give the various components of Portland cement. These components, in their major part, are tricalcic silicates ($Ca_3Si_2O_5$ or C_3S), dicalcium silicates (Ca_2SiO_4 or C_2S), tricalcium aluminates ($Ca_3Al_2O_6$ or C_3A) and tetracalcic aluminoferrites ($Ca_4Al_2Fe_2O_{10}$ or

C_4AF) [17-20]. In a normal Portland cement, the relative proportion of these minerals is: C_3S = 50 to 75%, C_2S = 10 to 20%, C_3A=5 with 10% whereas C_4AF= 10% [19].

Limestone is the main component in cement process. In Oujda city, cement plants are located near limestone quarries (200 meters). The carbonated dust from extraction and crushing are added to the dust emitted from chimneys. The clay is used in small quantities compared to limestone. The manufacturing process of cement using the dry method adopted by Oujda cement factory is very polluting. Each stage of the manufacturing process of cement generates particulate emissions.

3. Geographical and geological framework of study area

The study area is located in the Oujda-Taourirt corridor (Eastern Morocco), which is bordered respectively in the North and the South by the Beni Snassen belt and the Oujda Mountains (Fig. 1). This sector extends over a surface from approximately 900 km²; it includes the cement factory. It is subdivided in seven rural communities (Ain Lahjar, Rislane, Sidi Bou Houria, Labsara, Naïma (Sidi Moussa Lamhaya), Mestferki and Ain Sfa).

From the geological point of view, the Western Beni Snassen belt and the Oujda Mountains consist of a Paleozoic basement (schist and granite) surmounted by the Triassic volcano-sedimentary complex [21,22] which is covered by the Jurassic carbonated formations. The corridor Naima-El Aioun is a plain corresponding to a large subsiding basin in which have accumulated the sediment of tertiary and quaternary age [23].

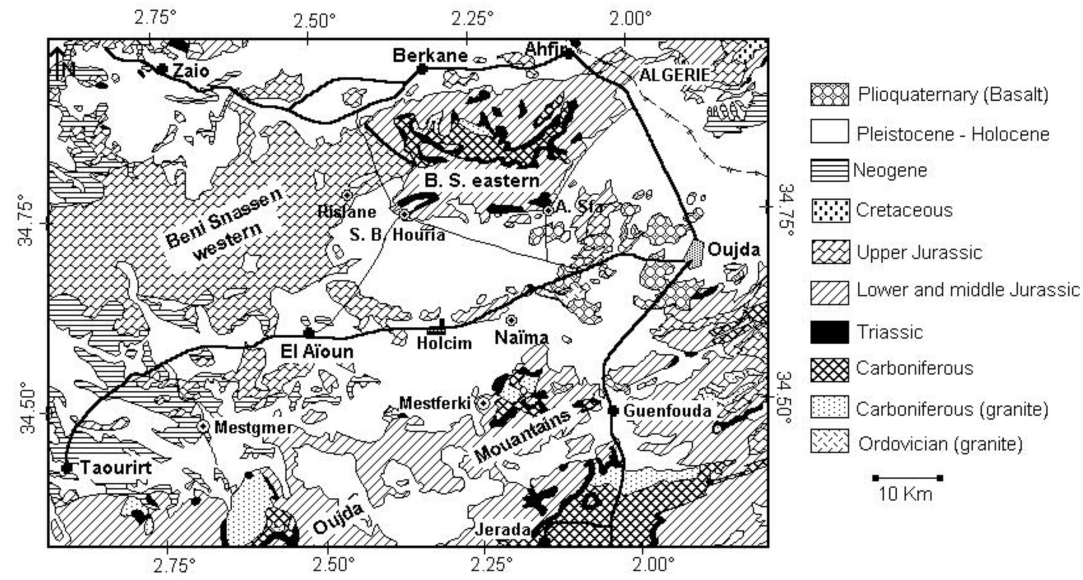

Figure 1: Geological map of the Study area.

4. Material and methods

To study the spatial distribution of the dust deposit in the Naima-El Aioun basin, 41 passive captors were installed towards the eight directions of the wind rose and on a radius which varies from 15 to 20 km (Fig. 2). The sampling stations were chosen to be at the proximity of residents which control permanently these captors.

The nomenclature, adopted to index the sensors, is based on the abbreviation of the corresponding commune name (Ain Lahjar (AL), Rislane (RN), Sidi Bou Houria (BH), Labsara (BS), Sidi Moussa Lamhaya (SM), Mestferki (MK) and Ain Sfa (AS).

The sensor corresponds to a simple instrument with a funnel of 31,5 cm diameter (Fig. 3). This funnel is made by galvanized zinc and connected using a tube to a bottle of a volume of 10 litters volume in order to avoid the overflow at the important falls of rain. To prevent the objects of big size to penetrate inside the funnel, 15 cm height of fence is added. This instrument is supported by high structure of 1,35 meters made by galvanized iron.

The dust deposits collected monthly (30 ± 2 days) are often mixed with rainwater, which requires a careful separation at laboratory of the solid fraction using a filter of 0.45 µm porosity. The retained particles are dried in desiccators for 48 hours and then weighed. The dust deposits collected during march 2001 were analyzed by DRX (total sample) at the laboratory of mineralogy of the Valencia University (Spain). The equipment used is an x-rays diffractometer (Siemens D5000), equipped with a copper anticathode with a tension applied of 40 kV and an intensity of 30mA.

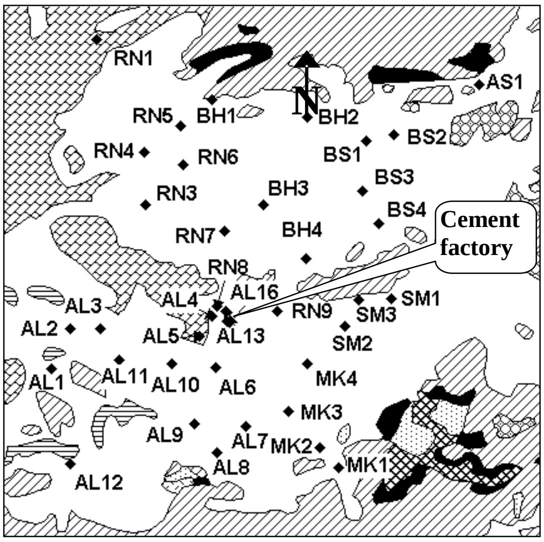

Figure 2: Passive captors position**.**

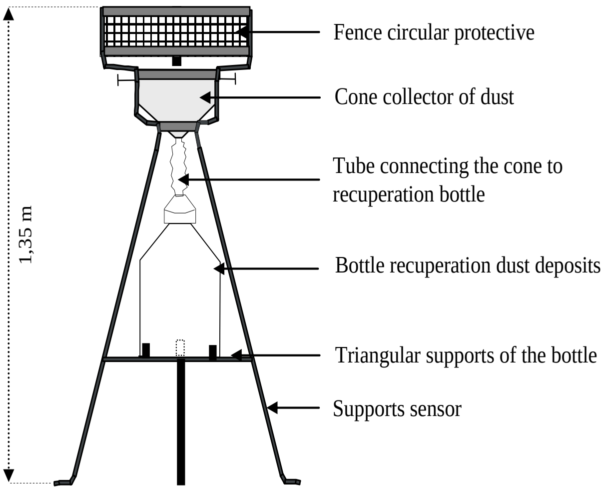

Figure 3: Particulate sensor constitution.

5. Results and discussions.

5.1. Cement mineralogy and dust emissions of chimney

The materials used for manufacture Portland cement in oujda factory are limestone (80%) and clay (20%). This mixture gives what we call prehomogenized mixture. This last is characterized by a strong content of calcite (>80%) comparatively to quartz. But it contains small amounts of dolomite (Fig. 4).

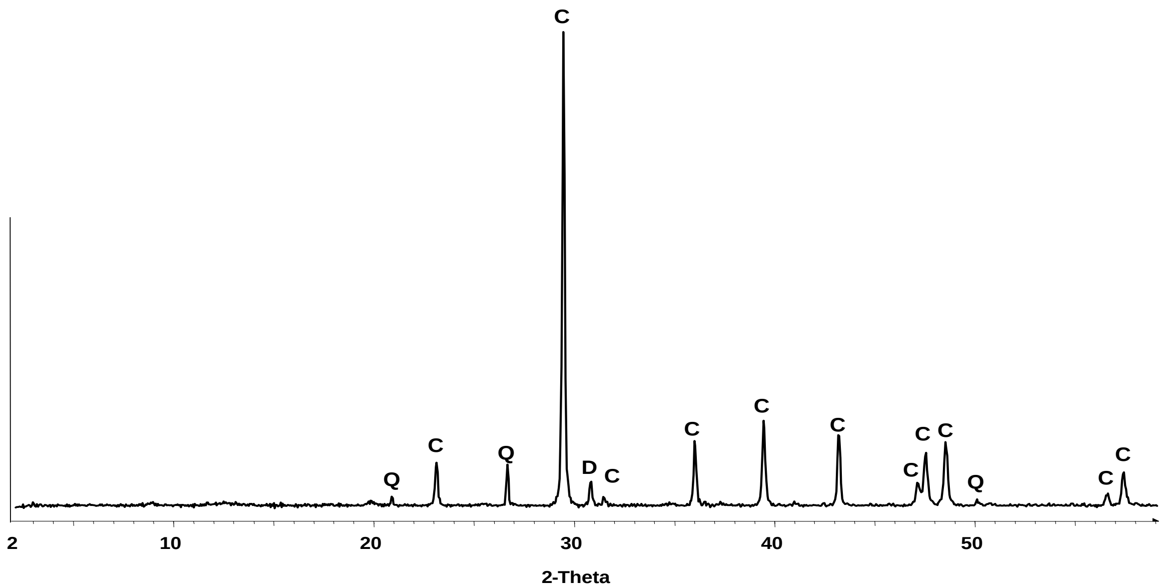

Figure 4: XRD Pattern of prehomogenized mixture.
C = calcite, D = dolomite, Q = quartz.

The diffractogram of the chimney dust emissions is similar to this one obtained with the pre-homogenized mixture. It present no peaks within the interval 2θ between 29 and 35°, this means the absence of any cement in the dust (Fig. 5).

The spectrogram of the cement shows peaks within interval 2θ from 29 to 35°. These peaks correspond to tricalcic silicates ($Ca_3Si_2O_5$ or C_3S), dicalcium silicates (Ca_2SiO_4 or C_2S), tricalcium aluminates ($Ca_3Al_2O_6$ or C_3A) and of the tetracalcic aluminoferrites ($Ca_4Al_2Fe_2O_{10}$ or C_4AF). They represent the typical mineral clinker and cement phases.

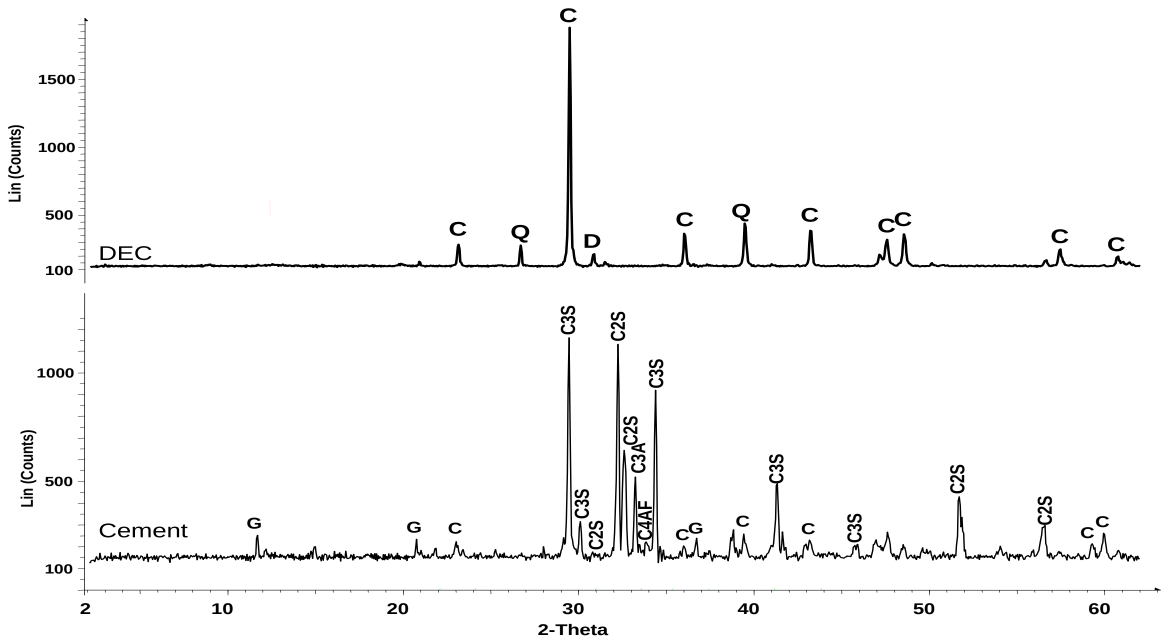

Figure 5: XRD Pattern of the dust emitted from chimney (DEC), and of the Portland cement.
C = calcite, G = gypsum, Q = quartz, C_2S = dicalcium silicate, C_3S = tricalcium aluminate,
C_4AF = tetracalcium aluminoferrite, C_3A = tricalcium aluminate.

5.2. Mineralogy of dust deposits around the cement plant

The objective of this analysis is to compare the chimney dust mineralogy to the one collected in the immediate vicinity of the cement factory (AL13, AL15, AL16 and RN8) (Fig. 6).

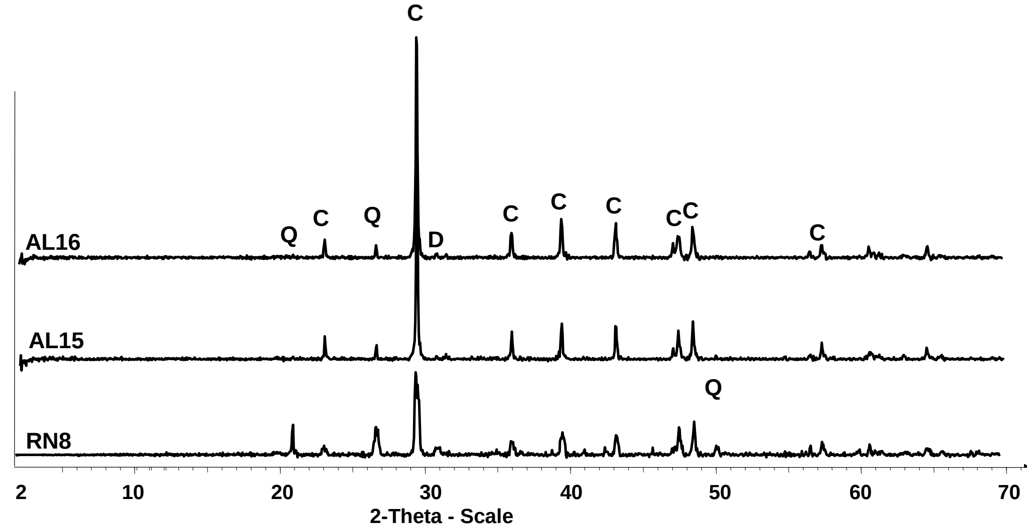

Figure 6: XRD Pattern of the dusts deposited within the cement factory and it's near neighbourhoods.
I = illite, K = kaolin, Q = quartz, C = calcite, D = dolomite, F = feldspatz.

The spectrograms of the dust deposits (Fig. 6) show the same characteristics with the dust emitted by the chimney. They don't contain peaks like in the clinker and cement (C_3A, C_2S, C_3A and C_4AF) spectrograms; their principal peak corresponds to calcite.

5.3. Soil mineralogy of Naima-El Aioun basin

The spectrogram of soils presents a predominance of quartz than calcite (Fig. 7). However, the calcite content vary from 15 to 30%. They would result from the carbonate encrusting phenomenon due to the washing Jurassic formations bording Oujda-Taourirt corridor. In the Naima-El Aioun basin, the scarcity of plant cover is due to the poorness of organic matter in the soils (2 to 3.6%) [23]. This phenomenon makes the soils vulnerable to wind erosion and therefore generates an important quantity of dust.

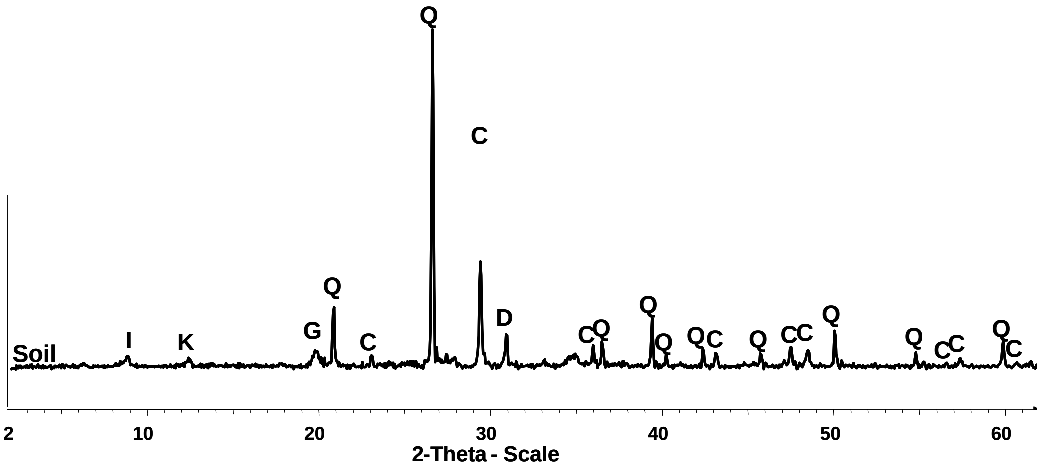

Figure 6: Pattern XRD of Naima-El Aioun soil.

I = illite, K= kaolin, Q = quartz, C = calcite, D = dolomite, F = feldspatz, G = gypsum.

5.4. Mineralogy of the dust deposited inside the sensors

In the following, only the standard diffractograms will be presented to show the various mineral phases. These diffractograms show that the principal minerals are quartz, calcite, feldspar and dolomite. This mineralogical composition is associated with a clay phases formed by kaolin and illite. These clay minerals present peaks with low intensities, masked by the four minerals cited above. The same mineral composition is founded also in the other sampling stations, they constitute the basic mineral phase of the sedimentary dust of the Naima-El Aioun corridor. On the sensors installed near the factory chimney (AL15, AL16 and RN8), we notes the predominance of calcite (Fig. 8).

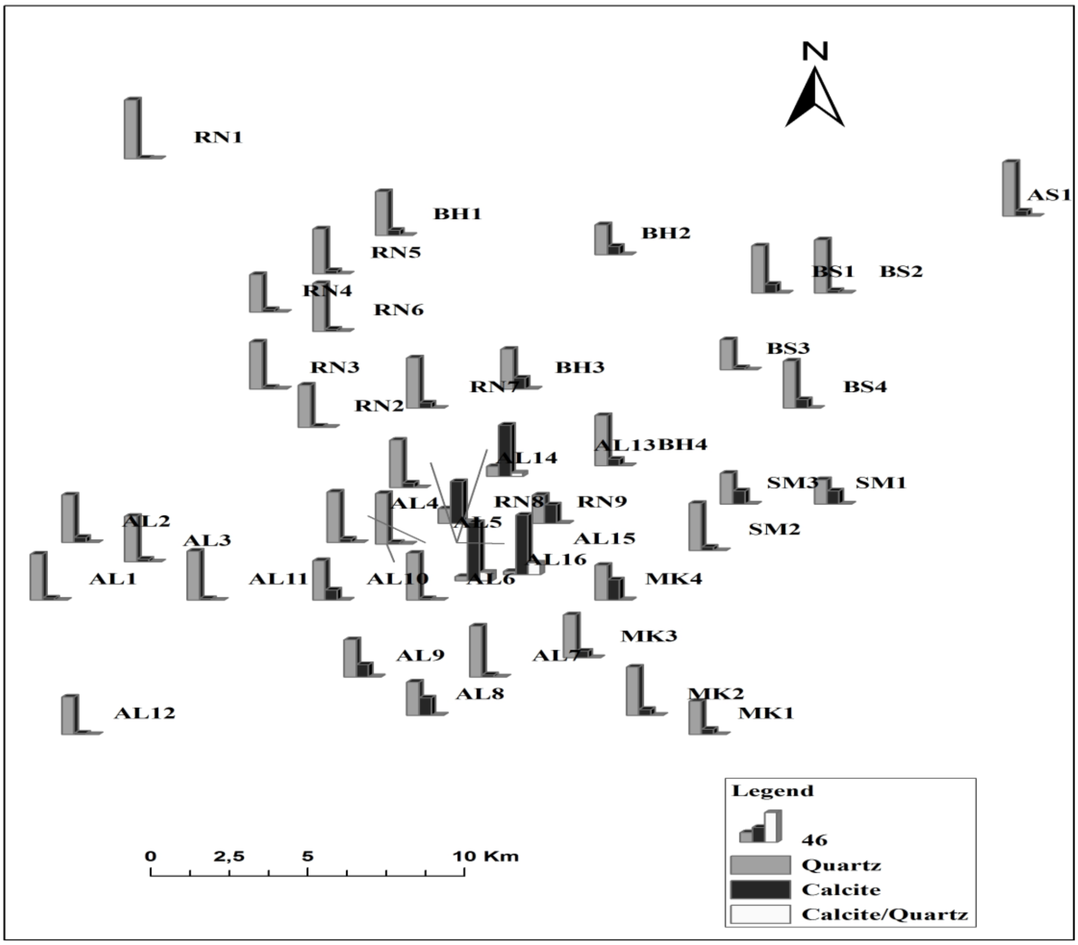

Figure 8: Spatial distribution of calcite, quartz and ratio calcite/quartz.

This calcite abundance is originated mainly from the cement factory activities, in particular the chimney dust emissions. However, the re-mobilization of the soils also contributes to these quantities of calcite. The dusts of the sensors MK4, SM1, RN9, BH4 and BS4, located at the east part of the factory, display relatively high calcite contents. This could be explained by the transport of the factory dust emissions by the west winds.

The industrial dusts analyzed are essentially composed by calcite (92 % on average) and some traces of quartz (4%), feldspar (1%), dolomite (2%) and clay minerals (1%). On the other hand, natural dust is rich on quartz (69%). The other phases present the following mean contents: calcite (10%), feldspar (9%), dolomite (8%) and clay minerals (4%).

Querol et al., [24] confirm that chemical and mineralogical composition of natural particles varies according to the soil characteristics of the region, but these are usually constituted by calcite ($CaCO_3$), quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), clay minerals (mainly caolinite, $Al_2Si_2O_5(OH)_4$, and illite, $K(Al,Mg)_3SiAl_{10}(OH)$), feldspars ($KAlSi_3O_8$ and $(Na,Ca)(AlSi)_4O_8$) and lower proportions of gypsum ($CaSO_42H_2O$) and iron oxide (Fe_2O_3), amongst others. It must be pointed out that soil re-suspension may originate at a local scale or may be transported from distant arid regions

As demonstrated by Rodríguez *et al*. [25] most of these peak concentrations of crustal particulates are recorded during Sahara dust outbreaks over the Iberian Peninsula. Sahara / Sahel dust transported over the EU is made up of clay minerals and quartz with minor proportions of Ca and Mg carbonates, sulphate, nitrate and carbonaceous particles [26-28].

The dolomite would be originated from the Jurassic carbonate of Beni Snassen and Oujda Mountains. The two other mineral phases correspond to plagioclases and K-feldspars; they would be originated respectively from Quaternary and Triassic basalts of Beni Snassen and Oujda Mountains. The clay minerals would result essentially from the wind erosion of Triassic clays, the quaternary soils and the Palaeozoic schist.

Conclusion

The mineralogical study of the dust deposit in the Naima-El Aioun basin and in particular around the cement factory of Oujda shows their consistence on the silica dust remobilized by wind deflation and on carbonated dust of double origin: (Cement factory and local soils).

The mineralogical composition of emitted dust by the cement factory is identical to that of pre-homogenized mixture (clay + limestone), it is mainly (> 80%) formed by calcite ($CaCO_3$).

The dusts emitted by the chimney cement factory, like those deposited on the sensors placed at the vicinity of the factory are cement free, but they are characterized by high quantities of calcite.

The dusts deposited in the rural communes bordering the cement factory are also deprived of cement dusts and are characterized by a high content of quartz. This is a result of natural dusts dues to re-mobilization of the soil which is itself due to the aridity of this area. Ultimately, the mineralogical analysis by x-rays diffraction highlighted that the calcite/quartz ratio, can be used as a tracer of atmospheric particulate pollution resulting from the cement factory.

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