Silicates Fragmentation a Source of Atmosphere Dispersed Nano-particulate Matter

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Air pollution represents one of the most important issues concerning the urban environment. Street dust samples collected in Cluj-Napoca, Romania contain silicates particles. XRD analysis evidenced mainly quartz, kaolinite, and muscovite (e.g. clay), which belong to silicates. SEM-EDX analysis confirms the XRD results, establishing connections between particles shape and their composition. The identified quartz nano particles have 90 nm diameter and are surrounded by small clay nano particles which have the diameter between 40 and 60 nm. The Si-O bonding is very strong, while the Si-O-Al bonds are weaker allowing a pronounced cleavage in the clay particle. Thus, quartz particles are tougher due to Si-O bonds in the hexagonal lattice, meanwhile clay features layers of SiO_4 tetrahedrons stacked into a fold by Si-O-Al bonds which are less strong than Si-O bonds. These arrangements of silicate particles explain how the dynamics in the urban environment causes an intensive dust fragmentation, which is developed on the weaker crystallographic planes. The fact is sustained by the crystallographic calculation performed on the XRD patterns, where the cleavage planes are observed (e.g. (002) planes). Furthermore, silicate nano-particles were clearly evidenced by AFM and TEM images on the street dust samples made by adsorption from the dust aqueous dispersion. The floating particles collected form the atmosphere contain the same particles observed in the street dust mainly the quartz and clay nano particles.

Key words: silicates, fragmentation, nanoparticles, atmosphere pollution

Silicates are minerals based on Si and O in various compositions according to their source. Silicates represent the essence of *lithos* the generic stone which is found everywhere on earth. They are present in the urban environment in natural soils (sand particles, clay soils, etc.) or as a component of built environment (e.g. sand contained in concrete and plasters). All silicates found in urban environment are subjected to multiple interactions with the environment resulting particulate matters which migrate into the streets forming the well known street dust [1, 2]. Several sources are known: natural ones (such as: green areas decay, soil degradation) [3,4] and anthropogenic ones (such as: decaying of built environment [5], car traffic and combustion emissions [6 - 8], and the rust of unprotected metallic structure [4, 9]).

Once formed up, the street dust is exposed to a dynamic environment, where several forces act at the particle level. The relative particle movement is caused mainly by air currents and car traffic. In these conditions particles are subjected to collision and abrasion, which conduct to mechanical failure consisting in broken particles. All of them are affected by atmospheric dispersion [10, 11]. The questions are: how fine will be the particles after an intensive fragmentation and how they will be dispersed into the atmosphere. We aim to observe how affected are silicates in this manner.

Experimental part

Sampling and methods

The samples were collected from 1 October to 31 December 2015. The sampling site is situated in an urban area, with average automotive traffic and significant industrial facilities, around Dambovitei Street, Cluj-Napoca City, Romania (Global Position Coordinates according Google Earth are: 46°46'55.7"N; 23°37'49.5"E). The traffic intensity is often situated around 10 cars per minute. Cluj-Napoca is the third city in Romania as urban and industrial development. An European Automatic Air Monitoring Station is situated in Dambovitei Street (it is under authority of Environment Protection Agency).

Street dust sampling: Weekly street dust samples were collected once a week from at least 10 different points, in the proximity of air monitoring station, using a portable vacuum cleaner. The vacuum cleaner bag was emptied in the laboratory and the collected sample was roughly sieved to eliminate bigger particles and further preserved in polyethylene vials (HDPE). Four weekly samples are collected per month. The final monthly average representative street dust sample (SD) was obtained by mixing together 50 g from each weekly sample for 24 h in a mechanical homogenizer.

SD sample was used as powder for XRD and SEM analysis. XRD sample was prepared by SD powder deposition on a sample holder with neutral wax. SD powder was spreaded on a double adhesive carbon tab for SEM investigation. The adhesive surface of carbon tab assures a good particle immobilization, so the vacuum of SEM sample chamber is preserved.

An aqueous dispersion of SD was prepared by mixing 10 g of SD powder into 100 mL deionized ultra pure water. After an intense agitation, 3 mL of dispersion were extracted into an eppendorf vial for TEM investigation. The sample for AFM was prepared by vertical adsorbtion on glass slide from the agitated SD dispersion.

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The European Automatic Air Monitoring Station in Dambovitei Street supervises and registers permanently the air quality parameters such as PM 10 (particles with aerodynamic diameter < 10μm) and PM 2.5 (particles with aerodynamic diameter < 2.5 μm). PM 10 and PM 2.5 level is daily measured automatically and the data are registered in Cluj-Napoca environmental database. This station has a high level of automatization and is currently in use for urban environment monitoring by the Environment Protection Agency of Cluj-Napoca (agency under Romanian Government auspices) It was implemented under European Union environmental policy for urban environment in respect with EC/50/2008 regulation [12].

The average representative floating particle sample (FP) is collected by the station via wet deposition in a glass sampling recipient with distilled water for entire sampling period 1 October to 31 December 2015. A particulate aqueous dispersion is formed. Further, the monthly amount of FP is determined from this dispersion by gravimetric method according to the standard procedures.

The FP dispersion was intensively agitated and 3 mL were extracted into an eppendorf vial for TEM investigation. The rest of dispersion was dried by water evaporation at a temperature below the water boiling point to avoid the alteration of physical and chemical state of particles. Glass slides were deposited on the bottom of evaporation recipient; a consistent particle layer was formed on the glasses after complete drying. Glass slides were used for SEM, AFM, and XRD analysis.

XRD investigations were performed on a DRON 3 diffractometer equipped with computerized module, using $Cu_{K\alpha}$ monochromatic radiation. The mineral identification was performed using MATCH 1.0 Powder Diffraction Data Base powered by Crystal Impact Company. All XRD spectra were registered in 2 theta range from 25 to 100 degrees. Considering the high level of mineralization of investigated samples, the diffractometer calibration was performed on Quartz monocristal sample, the calibration data were verified with Match 1.0 data, a very good concordance was observed for 2 theta angle positions and for peaks intensity range.

AFM investigation was performed on a JEOL JSPM 4210 Scanning Probe Microscope. The tapping mode was used for all AFM images, obtained with a silicon nitride conical shape cantilever NSC 11 type manufactured by Micromasch Company. Tapping mode is a component of AC mode of work in AFM. The scanning calibration is performed in the JSPM 4210 microscope with an automated procedure called *auto tune*. It establishes the optimum parameters for scanning such oscillating frequency around of 300 KHz, and the scan rate in a range from 1 to 2 Hz. The images were processed at high resolution in the standard manner using the JEOL Win SPM 2.0 processing soft.

SEM analysis was performed on a JEOL, JSM 5600 LV Scanning Electron Microscope in SEI mode (Secondary Electron Image) using a Everhart – Thornley Detector (ETD) and with EDX (Energy Dispersive Spectrum) elemental analysis. The EDX measurement needs a proper calibration. It was effectuated with elemental standards within the standard maintenance procedures of JSM 5600 LV Scanning Electron Microscope.

TEM investigation was performed on a JEOL, JEM 1010 Transmission Electron Microscope. All samples for TEM microscopy were aqueous dispersions of involved particulate (SD and FP) samples.

Results and discussions

Dambovitei Street is situated at the conjunction area between industrial facilities and residential neighborhood for workers in the eastern side of Cluj-Napoca City, Romania. It is characterized by an average car traffic (e.g. 10 – 15 cars per min), but is confronted with large number of parking positions (due to the large number of blocks with flats). Dambovitei street dust (SD) is a complex particulate matter originated in adjacent soil decaying and industrial emissions mixed together by the complex movement mediated by car traffic and air currents.

The mineral composition of SD sample was revealed by XRD analysis, recording a pattern in a wide range of diffraction angles from 25 to 100 degrees 2 theta. The resulted peaks are very well developed having a sharp shape (fig. 1).

The dominant mineral is quartz, followed by clay minerals (muscovite and kaolinite) and calcite. These minerals originate mainly in natural dust sources like adjacent soil decay, they are typical for Cluj – Napoca soil formed in sedimentary period of Badenian during retreating Thethys sea from Transylvanian Basin [13, 14]. There also were found significant amounts of iron hydroxide crystallized as goethite and lepidocrocite. These minerals occur via anthropogenic dust sources from unprotected metallic structure rust and cars body corrosion [4].

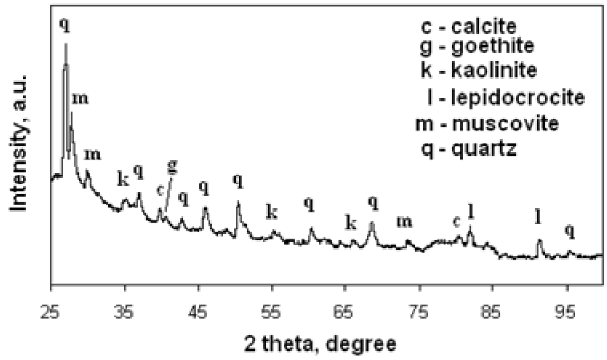

Fig. 1. XRD pattern resulted for SD sample

We notice that the dominant mineral in SD sample belongs to the silicate class: quartz (tectosilicates family) - an silicon oxide SiO_2 with hexagonal crystallization; muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$ and kaolinite $Al_2Si_2O_5(OH)_4$ (phylosilicates family). The crystallization mode influences the particles shape and properties. We used SEM microscopy to distinguish isolate quartz and clay particles from SD sample (fig. 2).

Quartz particles have a rounded shape (i.e. equiaxed particle – almost the same diameter in all directions) with blunted edges in agreement with hexagonal symmetry. The particle surface is slightly irregular due to the consecutive abrasion caused by continuous street dust movements, figure 2a. Prove that observed particle is quartz is given by EDX analysis (table 1). We observe that the particle contains almost O and Si in stoichiometric proportion of SiO_2. There are also found some traces elements such as K, Al, Ca and Na, which result form

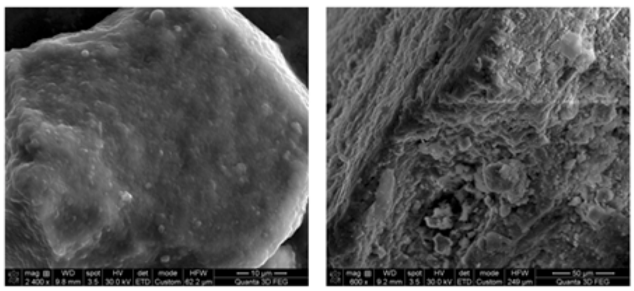
a b

Fig. 2. SD sample collected from Dambovitei Street: a)quartz particle and b) clay particles conglomerate

Element	C	O	Na	Mg	Al	Si	P	Nb	K	Ca	Ti	Fe
Quartz, wt%	-	35.92	0.25	-	0.66	61.06	0.80	-	1.18	0.14	-	-
Clay, wt. %	3.17	34.72	3.98	0.91	11.50	33.60	0.97	0.88	1.87	3.01	0.22	5.17

Table 1
EDX RESULTS FOR QUARTZ PARTICLE AND CLAY CONGLOMERATE IN FIGURE 2

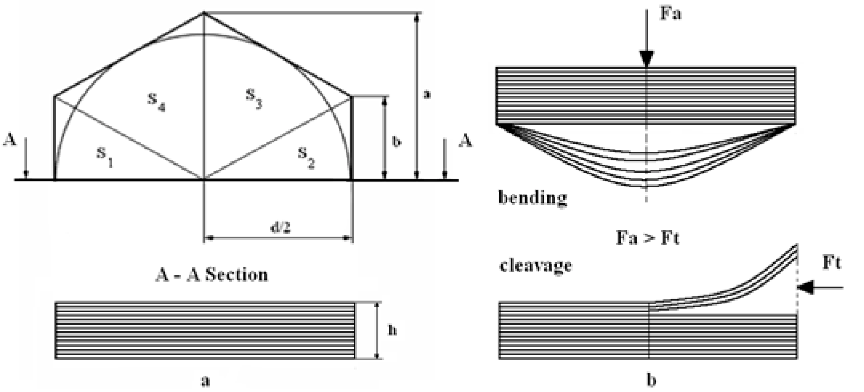

Fig. 3. Clay particle model: a) geometrical shape and b) external forces acting on the clay particle

smaller clay particles adsorbed on the observed quartz particle. This is typical morphology for quartz particles found in SD samples, proving intensive abrasion among particles.

Applying axial forces onto quartz particles, greater than particle mechanical resistance, will conduct to a suddenly crack. To break a quartz particle needs a loading around 2000 MPa [15]. Fresh broken quartz particles feature small sharp shards with sharp edges (many of them becoming quartz slivers) due to the lack of cleavage plans in its hexagonal crystal lattice. The surface of fresh broken quartz particles is also irregular. The fragmentation mechanism in quartz particle allows to form new particles having smaller diameter than in initial state.

After abrasion effect, these small sharp particles become blunted, having a general shape similar to the initial particle but with diameter considerably reduced. For example an 800 nm diameter quartz particle is observed in TEM image, Figure 4a, positioned in center – right of microstructure. This is the explanation why we found quartz particles in a wide range of dimensions but with similar shapes.

Clay particles form more complexes structures as observed in figure 2b. This is due to their lamellar structure of crystal lattice. Many of clay lamellas in figure 2b have oblique position like the ones situated in the upper left side of SEM image. The center of SEM image is occupied by well individualized clay lamellas having almost horizontal position in a wide range of dimensions from only 1 to 30 μm. EDX analysis for clay mixture evidence the major composition formed by Al; Si; O and K (table 1). These elements are basic for muscovite and kaolinite. The presence of small amounts of elements like Na, Mg, Fe and Ca is explained by several natural imperfections which occur in the mixed soils: local varieties occurred in the muscovite lamellas where some K atoms are replaced by Na; traces of ferro - magnesian black mica (e.g. biotite) occurred among muscovite particles (amount below XRD sensitivity); and finally trace occurrence of ferroxidic matter derived from rusted structure which may contain Ti, Nb, P besides Fe.

Clays crystal structure is based upon SiO_2 tetrahedrons sheets connected together by intercalated Al atoms in kaolinite and K atoms in muscovite (in some particular cases Na, Mg and Fe are involved). The SiO_2 tetrahedrons sheets exhibit a very strong bonding assuring a high mechanical strength meanwhile the Al and K bonding between these sheets is weaker being susceptible for cleavage. Overall, the clay morphology features a pseudo-hexagonal shape of the SiO_2 tetrahedrons sheet (fig. 3a). The planar dimensions are given by the hexagon side *a* and the planar diameter *d* measurable on the micro-photographs [16]. The height of clay particles *h* is given by the number of sheets contained.

If an axial force is applied on the surface of a clay particle, it will be bent as presented in figure 3b. The high mechanical strength of SiO_2 tetrahedrons sheets resists to the axial force tendency to break the particle. A tangential force applied perpendicularly to the sheets border will cause particle cleavage. This fact will reduce the particle height maintaining almost the same planar dimension. After several cleaving cycles the particle will be so thin that the axial force will be strong enough to crack the SiO_2 tetra-hedrons sheets causing complete fragmenting of the initial particle (fig. 4b). In this manner clay particles could achieve very small dimensions. We suppose that nano level could be achieved by abrasion induced by SD movement in urban environmental conditions.

The fragmentation mechanism described for quartz and clay particles is proved by microscopic investigation of SD sample dispersion in deionized water. TEM images are

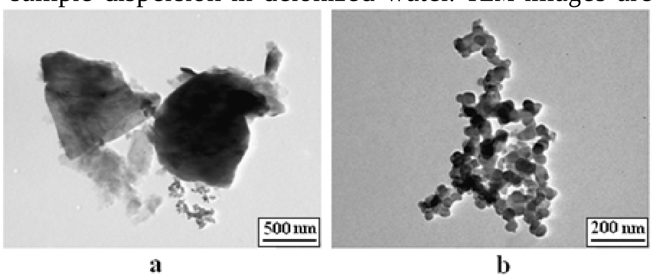

Fig. 4. TEM images proving SD particles fragmentation until nanostructural level: a) Clay and quartz submicron particle and b) clay nanoparticles

presented in figure 4. PM 1 is a critical step among PM emissions representing particulate matter with maximum diameter of 1μm [10 – 12]. Several PM 1 particles were observed in SD aqueous dispersion (fig. 4a); in the left side of TEM image is a quarter of a pseudo-hexagonal clay particle having a planar dimension of 700 nm. This particle thickness is very low (around 100 nm), since it appears semi-transparent in the TEM beam. In the right side of TEM image(fig. 4a), a quartz PM 1 particle is observed. It appears opaque in TEM beam proving its spherical shape. The diameter is situated around 800 nm.

Beneath these two PM 1 particles appear more fragmented ones with diameters ranging from 40 nm to 200 nm. It is a wide domain of submicron dimensions. It is very interesting that well individualized nanoparticles were identified in SD sample. Such particles are observed better at high magnification in figure 4b. A well nano-structured film is formed: quartz nano-particles have around 90 nm and feature a dark aspect due to their spherical shape. Clay particles are smaller around 40 nm and exhibit a light aspect due to their low thickness, and surround quartz particles. The SD nano-particles deposition film is better observed in AFM microscopy. This is a powerful tool for investigation of complex nanostructures [17 – 19].

The completely dry SD thin film adsorbed on glass surface was investigated by AFM in tapping mode assuring an optimal particles scanning. One of the most representative obtained images is presented in Figure 5. The surface topography (fig. 5a) reveals well adsorbed particles forming a complex film of nanoparticles. Two layers are observed: the first one is formed by the bigger nanoparticles (quartz) which have 28 nm height, and the second one has lower height around 13 nm being formed by clay nanoparticles. Clay nanoparticles surround quartz ones as observed also by TEM microscopy in figure 4b. Phase image (fig. 5b), evidences a good assembly of the adsorption film into a compact manner and proves that the scanning regime was optimal, assuring a good investigation, without faults and artifacts.

The SD thin film structure is better observed in 3D image,(fig. 5c), where the quartz particles presenting rounded shape (having around 90 nm diameter) appear in

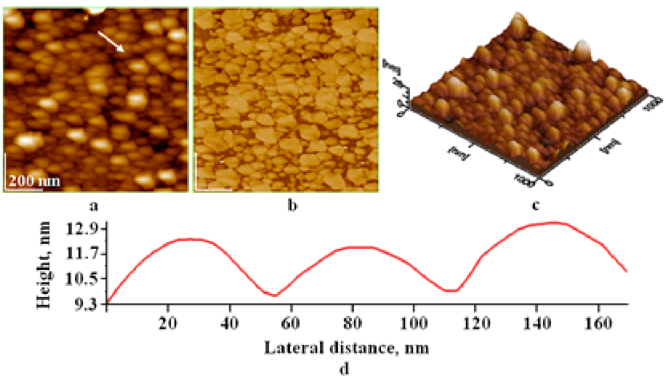

Fig. 5. AFM images for SD sample collected from Dambovitei Street, particle layer of adsorbtion on glas: a) topographic image, b) phase image, c) 3D image of figure (a), and d) profile on the white arrow in topographic image (a). Scanned area 1 µm x 1 µm

and form a lower layer. Their diameter is situated around 40 nm as observed in profile detail, Figure 5d. Facts revealed by AFM are in strong concordance with TEM observations.

The physicochemical investigations reveal the intensive fragmentation of silicates particles inside of SD samples, the nanostructural level being achieved. Now, the question is if these small mineral fractions are able to be dispersed into the atmosphere. Some research is focused on particulate matter ability to form atmospheric dispersion by correlating their diameter and density [20, 21]. It is a logical approach of the problem which assures us that smaller fractions found in SD sample are able to be dispersed into the atmosphere. Hence, we aim to bring solid evidence to prove the ability of dust nanostructural fraction to be lifted into the air. It is a relatively simple quest if professional air quality monitoring systems are used. The collection of particulate matter from atmosphere samples (FP) was done with the automatic air monitoring station owned by the Environment Protection Agency of Cluj-Napoca.

The mineral composition of FP was determined by XRD analysis, the pattern presented in figure 6. It features well

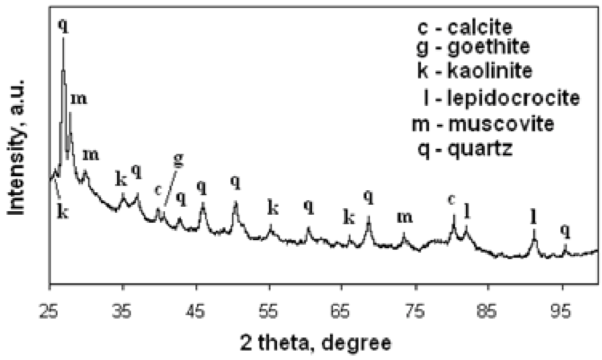

Fig. 6. XRD pattern resulted for FP sample

developed diffraction peaks proving the high crystallinity of the FP sample. The resulted composition is similar with the one resulted for SD. The dominant minerals in FP are Quartz, muscovite and kaolinite (all of them belong to silicate family) followed by calcite, lepidocrocite, and goethite. It is strong evidence that particles from SD are lifted into atmosphere by air currents and automotive traffic.

FP morphology was observed by SEM microscopy (fig. 7a). It is a complex mixture of micro and nano-particles having different shapes: rounded like quartz particles, lamellar like clay particles. Most of quartz particles are included in PM 10 category and clay particles are preponderant included in PM 2.5 category. There are also found particles having 1µm diameter and below which are included in the PM 1 class. Many of them are submicron fraction of silicates, even nano-fractions could be present there.

EDX investigation of FP gives us another important evidence of its origin from street dust (table 2). The resulted elemental composition of FP is similar with the one observed for quartz and clay particles from SD. It is

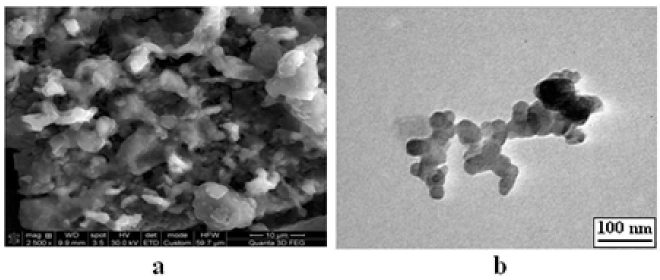

Fig. 7. FP sample collected from Dambovitei Street: a) SEM imaging b) TEM imaging

dominated by O and Si, the basic elements for silicates, and other specific for clays (such as: K, Na, and Mg). Presence of 13.26 wt. % Ca is explained by the amount of calcite identified in XRD spectrum. The presence of Fe in EDX spectrum of FP is in good concordance with lepidocrocite and goethite found in XRD spectrum.

Nano fractions of silicates are so small that could not be observed in SEM microphotography, TEM microscopy was employed to reveal them. TEM image is presented in figure 7b. A quartz particle (featuring a darken aspect) having 90 nm diameter is observed in the upper right side of the image. It is surrounded by clay particles (having a translucent aspect) with diameter ranging between 40 and 60 nm. It is a similar situation with TEM investigation of SD sample. In fact it is a prove that the fragmented silicates at nano-structural level from SD were well dispersed into the atmosphere, being after all an important component in FP.

The FP nanostructure is better observed in AFM investigation (fig. 8). The topographic image reveals an uniform and compact adsorption film (fig. 8a), with well

Element	C	O	Na	Mg	Al	Si	Mo	K	Ca	Fe
FP, wt%	1.83	40.68	2.90	1.84	3.42	30.34	2.34	2.66	13.26	0.72

Table 2
EDX RESULTS FOR FP SAMPLE IN FIGURE 7a

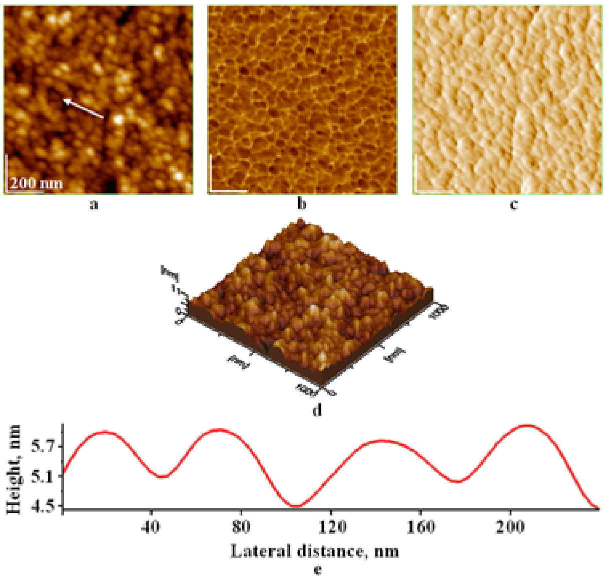

Fig. 8. AFM images for FP sample collected from Dambovitei Street, particle layer of adsorbtion on glas: a) topographic image, b) phase image, c) amplitude image, d) 3D image of figure (a), and e) profile on the white arrow in topographic image (a). Scanned area 1 µm x 1 µm.

2015	PM 2.5, µg/m^3			PM 10, µg/m^3		
Month	average	minimum	maximum	average	minimum	maximum
October	12.09	2.36	34.81	23.84	7.25	55.30
November	21.30	4.17	46.60	31.12	10.34	49.86
December	23.36	3.45	45.87	29.99	3.81	49.50

Table 3
PARTICULATE MATTER EMISION IN ATMOSPHERE MEAUREMENTS

individualized particles. In this case, we have a single layer of particles with a maximum height of 11 nm, a similar value with clay particles layer observed at SD sample. It is a logical approach to believe that the particle layer observed for FP sample is formed mostly form clay particles. In fact we found only two particles having around 90 nm with quartz shape, the other having clay shape. The uniformity and compactness of particle layer as well as each particle well individualized are evidenced with great accuracy by phase and amplitude images (figs. 8a, c). These images show that the scanning was performed in optimum condition and no defects occurs.

3D representation of the topographic image (fig.8d), allows to observe how well were adsorbed clay particles on the solid substrate. There also can be observed two quartz particles having appearance of small white spots. Profile detail (fig. 8e), allow us to calculate the average diameter of clay particles which results around 40 nm, in good concordance with TEM investigation.

Since, PM 1 is still not classified as a standard reference for air parameter monitoring all these nano and submicron fractions are assimilated into PM 2.5 class which is currently monitored and included in monthly environmental reports. PM 10 and PM 2.5 are permanently monitored in Cluj-Napoca with the automatic stations from Environment Protection Agency of Cluj County. The emissions values for the reference period are presented in table 3.

PM 10 variation shows values below of the maximum accepted daily level of 50 µg/m^3 according to European Environment Protection Agency (EEPA) [10]. The average value of PM 10 in October is significant low (23.84µg/m^3), while for November and December it increases to around 30 µg/m^3 (table 3). Such increasing were reported in literature for cold seasons [22, 23]. This increasing is certainly related to the interaction of SD with antiskid material spread on the road to prevent cars sideslip. The quartz particles in antiskid material have around 5 mm diameter and present a compact structure with rounded shape. These act as milling bodies in contact with street dust during car circulation [16]. The weather was partially humid during 2015 late autumn, but in many days the roadside was dry, allowing dust particles to be lifted into the atmosphere. The 30 October 2015, when a slightly limit overtaking was registered (55.30 µg/m^3), was a Friday, a typical day with increased car traffic, combined with favorable atmospheric conditions, so the particulate matter was dispersed more intensively than in other days. Overall, PM 10 emission in Cluj-Napoca during October – December 2015 does not present environment problems.

PM 2.5 daily maximum accepted level is about of 25 µg/m^3 according to EEPA [12]. The average values for the reference period are situated below this limit. We observe an increasing tendency from October to December 2015 from 12.09 to 23.36 µg/m^3. It is an expected variation considering the observed fragmentation of clay particles under the action of external forces. The presence of milling bodies from antiskid material seems to increase the amount of finest particles. As observed many of they are submicron or even nano particles. The PM 2.5 variation is strongly related to the car traffic (more influenced than PM 10 emissions), an emission pattern being observed. In weekends when the traffic is relatively low, were registered values of 3-5 µg/m^3. In the other days such as Tuesday, Wednesday, Friday the emissions are increased 12 – 24µg/m^3.

In each month there was a day when the limit was exceeded, maximum registered values being presented in table 3. The situation proves that an intensive fragmentation of small particles is involved. Although the average monthly values of PM 2.5 are in good range, the punctual increases over the limit may induce some concern about citizens' safety. Such unwanted situations could be avoided by a better understanding of the fragmentation processes in SD particles. It is relatively easy to implement a better street dust management, beginning with limitation of dust sources, continued with a better dust removal from the street area and finally, usage of a good antiskid material.

Conclusions

Street dust samples collected from Dambovitei Street in Cluj-Napoca, Romania contain silicates particles. XRD analysis evidenced mainly quartz, kaolinite, and muscovite (e.g. clay), which belong to silicates. SEM-EDX analysis confirms the XRD results, establishing connections between particle shape and their composition. The identified quartz nano particles have 90 nm diameter and are surrounded by small clay nano particles which have the diameter between 40 and 60 nm. The lack of slipping planes in quartz leads to sharp edged particles, which become rounded due to the mechanical abrasion in SD movements. Clay's fragmentation is favored by consecutive cleavage of silica sheets at low thickness under tangential forces, and after that axial bending will conduct to the particle cracking. The fragmentation was so intense that small fractions were identified. Furthermore, silicate nano-particles were clearly evidenced by AFM and TEM images on the street dust samples made by adsorption from the dust aqueous dispersion.

The floating particles collected from the atmosphere contain the same particles observed in the street dust, mainly the quartz and clay nano particles. The same nano-particles were observed in FP: quartz particles having 90 nm diameter and clay particles having around 40 nm diameter. The increasing of PM 2.5 and PM 10 in the cold seasons is strongly related to the efficacy of silicates fragmentation favored by presence of antiskid material which acts like milling bodies. The intensive fragmentation at low particle size correlated with intense traffic registered in some days (one day per month) leads to values of PM 2.5 which exceed the limit. It could be an environmental concern because the appearance of a potential health risk. This potential risk could be diminished by a better street dust management.

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