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ул. „Гоце Делчев“ 89, Штип	Goce Delcev 89, Stip
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ХЛОРАРГИРИТ И АКАНТИТ ВО ПМ-10 ЧЕСТИЧКИТЕ ВО ОБЛАСТА ТИКВЕШ

Иван Боев[1], Блажо Боев[1]

[1]Факултет за природни технички науки, Универзитет „Гоце Делчев", Штип
e-mail: ivan.boev@ugd.edu.mk

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Апстракт

Истражувањата кои се направени со примена на електронската микроскопија (СЕМ-ЕДС-техниката ги потврдуваат резултатите кои се направени со рентгенската дифракција на честичките ПМ-10 од областа Тиквеш. Со овие истражувања недвосмислено е докажано присуството на антропогени минерални фази, како и присисуство на минерални фази кои имаат литогено потекло. Антропогените минерални фази се претставени со: хлорит, магнетит, амфибол, хлораргирит, акантит, како и метални форми на железо и никел. Литогенотго потекло на минералите е докажано со присуството на: кварц, калцит, плагиоклас и глиновити минерали.

Клучни зборови: *ПМ-10 честички, хблораргирит, акантит, СЕМ-ЕДС техники*

CHLORARGYRITE AND ACANTHITE IN PM-10 PARTICLES IN TIKVES AREA

Ivan Boev[1] and Blazo Boev[1]

[1]Faculty of Natural and Technical Sciences, "Goce Delcev" University, 2000 Stip
e-mail: ivan.boev@ugd.edu.mk

Abstract

The investigations performed by applying electron microscopy (SEM-EDS technique) unequivocally confirmed the results made by using XRF, the X-ray diffraction and the results from the determination of chemical composition of particles PM-10 with the application of the ICP-AES and ICP-MS. From the results performed with all of the applied techniques it can be concluded that the presence of specified mineral phases that have typically anthropogenic origin are registered as well as the mineral phases that have lithogenic origin or the origin of the present geological structure. Therefore, it can be concluded that the urban dust with a sizes below 10 μm (PM-10) in the Tikveš area originated from lithogenic and anthropogenic processes. It can be concluded that the phase composition of the particles PM10 from Tikveš area consisting of mineral phases which have anthropogenic origin confirmed by the high content of Fe, Ni, Cu, Zn, Ag, Cr (present in higher content in the ore processed in the ferronickel smelter), and by the presence of the minerals like: chlorite, amphibole, pyroxene, magnetite, chromites, Ag-minerals (chlorargyrite), metallic forms of Mn-Cr, Cu-Zn (also present in the ore processed in the smelter plant). The lithogeneic origin of the part of PM10 is confirmed by the presence of minerals quartz, calcite or plagioclase clay minerals.

Key words: *PM-10 particles, hlorargirite, acantite, SEM-EDS-tecnique*

1. Introduction

To describe the origin and characteristics of particles very different terms are used. There is a tendency to accidentally usage the terminology, which has different meanings in popular and scientific context. Here are some of them (Harrison, 1999):

- Suspended particulate matter (SPM) and total suspended particles (TSP). Both terms indicate the total number of particles in the air; often measured by sampling a larger volume without selection the amount of the sampled air.
- Particulate matters (PM). Sometimes this form is used as a short term, but more often as PM10 or PM2.5. PM10 is the mass concentration of particulate matters (PM) due to particles that pass through the selected air flow, and have 50% efficiency of particles with an aerodynamic diameter of 10 μm. PM2.5 concentration is appropriate particle with a diameter of 2.5 μm.
- Fine particles. In general, these are particles with a diameter lower than a few μm. Sometimes is used as synonymous with PM2.5.

- Ultra-fine or nanoparticles. The particles with a diameter less than 0.2 μm (usually size expressed in nanometers - nm).
- Aerosols. Any solid or liquid particles suspended in the air.
- Larger dust. Huge portions of material that is usually formed during the mechanical process like grinding or crushing. The size range may sometimes be defined.
- Dust. Particles smaller than previous ones, usually bigger than 1 μm.
- Smoke. Particles formed during incomplete combustion processes, as a mixture of carbon and condensed volatiles. Usually their size is less than 1 μm.
- Black smoke. Suspended particles which are determined by using reflective method of coloring. The range of size is not specified, but recent measurements showed no particles larger than 10 μm aerodynamic diameter, and 50% particle size diameter of about 4 μm, so measurements can correspond to the respirable fraction.
- ACGIH and ISO conventions. Human breathing system over evolution was adapted to perform filtration of larger particles at an early stage, and the percentage of particles introduced to lung largely depends on the particle size. American Conference of Government Industrial Hygienists (ACGIH) and the International Standardization Organization (ISO) have defined the fractions of particles based on the ability of the human breathing system.

2. Materials and Methods

2.1 Sampling

Attic dust samples were collected from 27 old rural houses from 13 settlements in the Tikveš Valley in 2008. The houses were of similar age (constructed after 1982, the year the ferro-nickel smelter plant was build). In every settlement, attic dust was collected from 2 or 3 houses on different sites. The collection of attic dust samples was performed according to the adopted protocol (Šajn, 2003, 2005; Balabanova et al., 2010, 2011; Bačeva et al., 2011; Stafilov et al., 2012). Attic dust was collected with a plastic brush in polyethylene bags. The surface layer from the attic timber was discarded away and the finest dust was collected. The fraction of attic dust smaller in size than 0.125 mm was prepared by sieving.

The dust samples (particulate matters, PM10) were collected by the standard procedures by setting up two mobile stations, one in the area of the village of Vozarci (near the iron ferronickel smelter plant) and the other in the urban part of the town of Kavadarci. Ten samples have been collected in the area of the village of Vazarci, and 13 from the urban part of Kavadarci.

The sampling device consists of three integral, conductive plastic cassettes sampling head, where the design does not allow a significant spilling around the filter. The sampling head consists of a cylindrical protective casing and filter holder with an auxiliary filter. The protective layer of the filter holder is made of stainless material. The filter should be tight so that no significant leakage around the filter at various pressures up to approximately 50 kPa. The length of the shell should be from 0.5 to 2.5 times of the diameter of the filter. If the wind speed measurement shows higher velocity than 5 m/s, the longer length of casing diameter of 2.5 should be used. Flow control should also be achieved by using flow controller. The sampling pump should be capable of maintaining a pressure through the filter at least 50 kPa, flow between 8 l/min and 30 l/min, depending on the diameter of the filter used.

In order to obtain better analytical sensitivity, the flow rate of 8 m/l is required if a filter with a diameter of 25 mm is used. The flow is equivalent to the main side of the filter with a speed of approximately 35 cm/s, resulting the pressure of approximately 50 kPa. Sampling pump should be able to maintain the overall flow with a ±10% throughout the sampling period.

To start a measurement, the sampling head should be placed at a height of approximately 1.5 meters from the ground. If the sampling head used previously is mounted, a 5 μm celulous auxiliary filter should be put as a base for the sampling head, to set up a filter previously treated with a gold vapors. Then, the filters are tighten in the sampling head so that the filter lies on the auxiliary filter.

The membrane filter should be coated with the thin golden layer before sampling. Gold will protect the filter in the process of plasma ashing and will improve the contrast between the fibers of SEM image. This gold layer should be applied on the side for dust collection, i.e. the smooth and brighter side with a layer of approximately 30 nm thickness. Within 2 minutes from the start of sampling, the flow should be adjusted to 2 l/min per square centimeter (this value should not vary more than ±10% during the sampling). This corresponds to a volume of 1000 liters per square centimeters of effective filter area in a sampling period of approximately 8 hours.

2.2 Mineralogical characterization

The mineralogical content of the collected dust samples was determined using an X-Ray Siemens D 500 equipped with an automated computer and a Cu-monochromatic lamp working at 40 KV and 30 mA. Quantitative analysis of the mineral phases present was performed using the DIFRAC-11 software package and program support by EVAL and IDR.

The values given for the quantitative composition of the analyzed samples represent an average of 3 replicates. For QA and QC of the measurements referent materials and standards from various mineralogical compositions were used: BDS 17385/96 (standard for ore and ore concentrates for X-Ray diffraction quantitative phase analysis), ST SEV 3534-82 (SpS-quartz sand), ST SEV 2981-81 (KN-2, limestone), ST SEV 2980-81 (MpA-copper ore), USZ 47-2008 (granite “MGT-1”). In several cases standard addition method was applied by using some of the aforementioned RM and satisfactory values for the recoveries were obtained.

3. Results and discusion

Determination of phase content by Scanning Electron Microscopy (SEM) - Energy Dispersive Spectroscopy (EDS) and X-Ray diffraction

It was found by EDS analyses that the filters contained several aluminosilicate phases, including quartz, illite, plagioclase, and possibly amphibole/pyroxene and chlorite. Silica (SiO_2) particles are characterized by high content of Si and O. The pure silica particles have natural and anthropogenic origins (Li et al., 2010b). These particles have tubular structure. It is the most abundant chemical constituent of Earth’s crust and a major component of sandstone and granite. Thus, the most abundant source for this particle type is soil related.

Alumosilicate particles are composed primarily of feldspar (Si, Al, Ca or Si, Al, Na) and clay (Si, Al or Si, Al, Fe). Their origin is mainly crustal, but they can also come from erosion of buildings constructions and from road dust. Other elements are present in minor content in the alumosilicate particles. These particles mainly present an angular shape, ranging from polyhedral to sharp one. Illite and plagioclass were identified (Fig.1).

Particles with a high content of Ca (mass fraction <50%) fall into the calcium rich particles. Carbonate minerals include calcite ($CaCO_3$) with the traces of other dust related elements which are the common constituent of soil and often observed in the individual aerosol particle analysis (Lu et al., 2006). These particles are irregular fragments with distinct rough surfaces on all faces originated from building construction and demolition and commonly found in Earth’s crust. The morphology of this small particle suggests its mineral origin. Calcium carbonate was observed on and around clay minerals.

The particles of manganochromite and stainless steel were also observed. Metals, metal oxides, and metal oxyhydroxides were also found with clay minerals. Minor nickel was found associated with metal oxides and stainless steel. Also, metals, metal oxides, and metal oxyhydroxides were found with clay minerals. Hydrated phases, observed to be volatile under the electron beam, presumably produced water vapor or carbon dioxide as an effect of heating. Minor nickel was found associated with metal oxides.

Several alumosilicates with varying elemental compositions could not be conclusively identified. Gypsum was also observed. Metals, metal oxides, and metal oxyhydroxides were found with clay minerals. Hydrous phases, observed to be volatile under the electron beam, presumably produced water vapour or carbon dioxide as an effect of heating.

Silver and associated minerals were observed in some sample. Chlorargyrite (Fig. 2), with minor acanthite (Fig.3). Palache, et al (1951), Berry, et al (1962) Silver mineral, can be of crustal origin, but may also come from human activities such as industrial processes.

4. Conclusion

In the dusts from this region metal oxides and sulfides; magnesium silicate with iron oxide ; magnesium silicate with zinc, iron oxide ; and aluminosilicate coated by iron, chromium, titanium and nickel oxides and/or sulfide have been also identified. This group of particles mainly corresponds to Fe oxides with irregular morphology which are assumed to be soil related. Minor nickel was found associated with metal oxides . Metals, metalloxides, and metal oxyhydroxides were found with clay minerals. Because these minerals are present in the ore processed in the ferronickel smelter plant which is situated in this area, we can conclude that the content of these particles in the analyzed samples come from human activities in the metallurgical plant.

Silver chloride is not toxic at low concentrations and is used in medical and disinfecting applications. However, if swallowed or inhaled in high concentrations, it may cause irritation of mucous membranes, greyish discoloration of the internal tissues (argyria) and kidney damage. Skin or eye contact with silver chloride can cause greyish discoloration of the skin and tissues.

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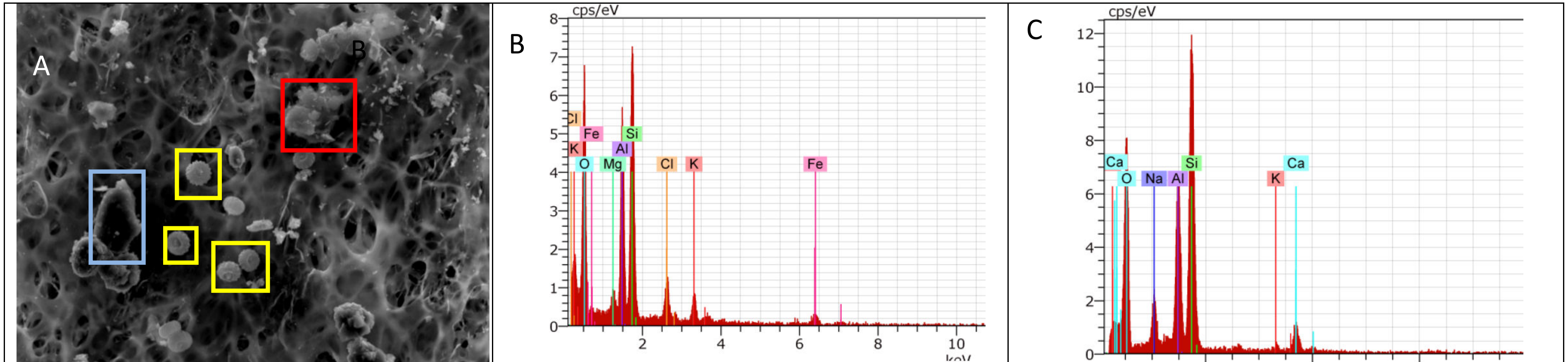

B) Acquisition 80

El	AN	Line	unn. C [mass %]	norm. C [mass %]	Atom. C [At.%]
O	8	K-series	46.26	52.32	67.71
Mg	12	K-series	1.83	2.07	1.77
Al	13	K-series	11.17	12.64	9.70
Si	14	K-series	17.38	19.65	14.49
Cl	17	K-series	3.52	3.98	2.32
K	19	K-series	3.06	3.47	1.84
Fe	26	K-series	5.19	5.87	2.18
		Total::	88.4 %		

C) Acquisition 81

El	AN	Line	unn. C [mass %]	norm. C [mass %]	Atom. C [At.%]
O	8	K-series	46.51	46.09	59.95
Na	11	K-series	5.99	5.93	5.37
Al	13	K-series	14.26	14.14	10.90
Si	14	K-series	28.20	27.94	20.70
K	19	K-series	0.90	0.89	0.47
Ca	20	K-series	5.05	5.00	2.60
		Total::	100.9 %		

Figure 1. BSE photos of sample sowing illite (red), plagioclass (blue), pollen spores (yellow). B) EDS spectrum of illite, C) EDS spectrum of plagioclass

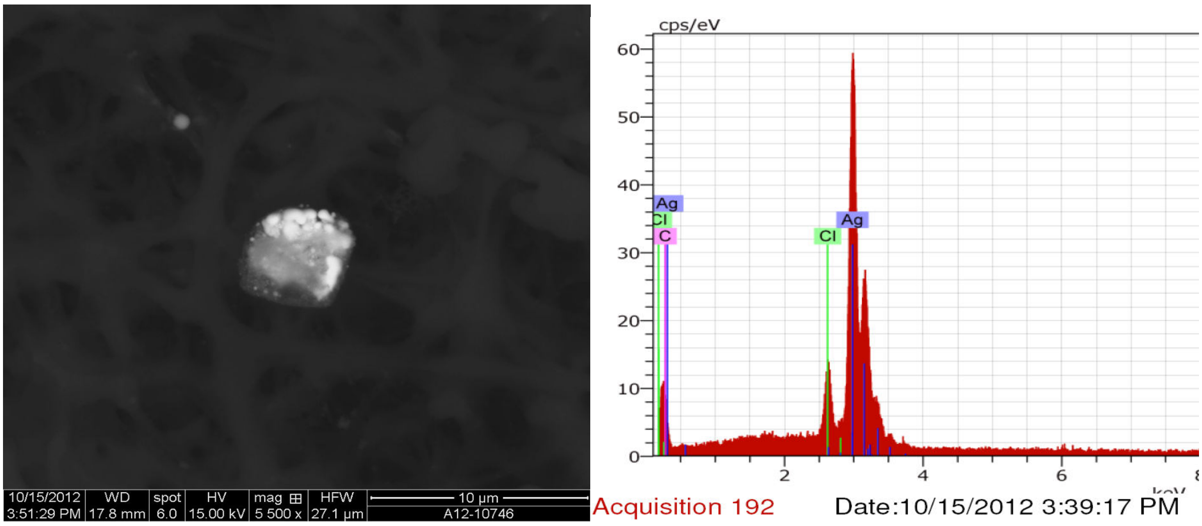

Figure 2. BSE images of Chlorargyrite

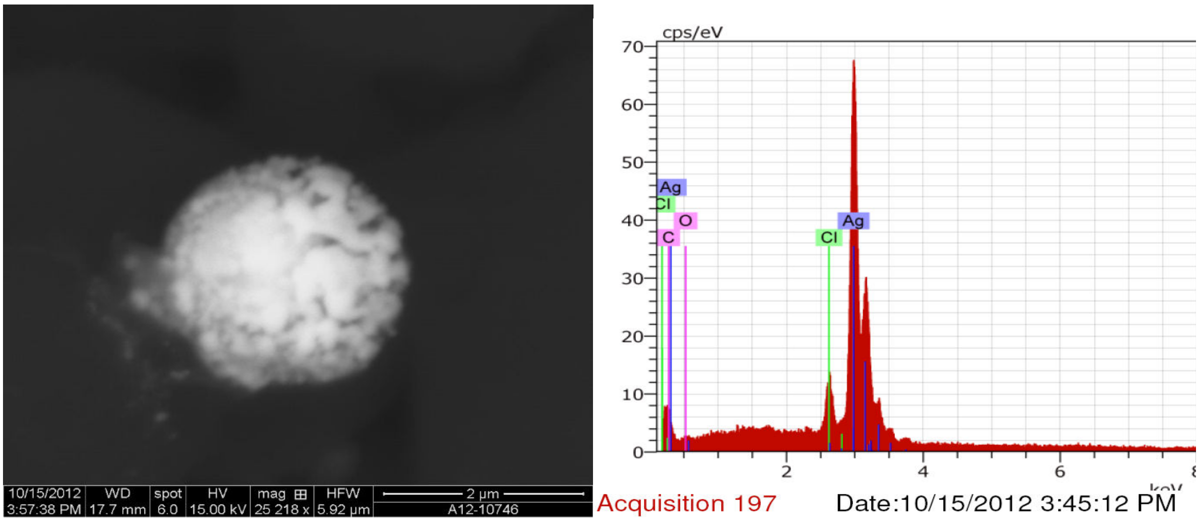

Figure3. BSE image of chlorargirite

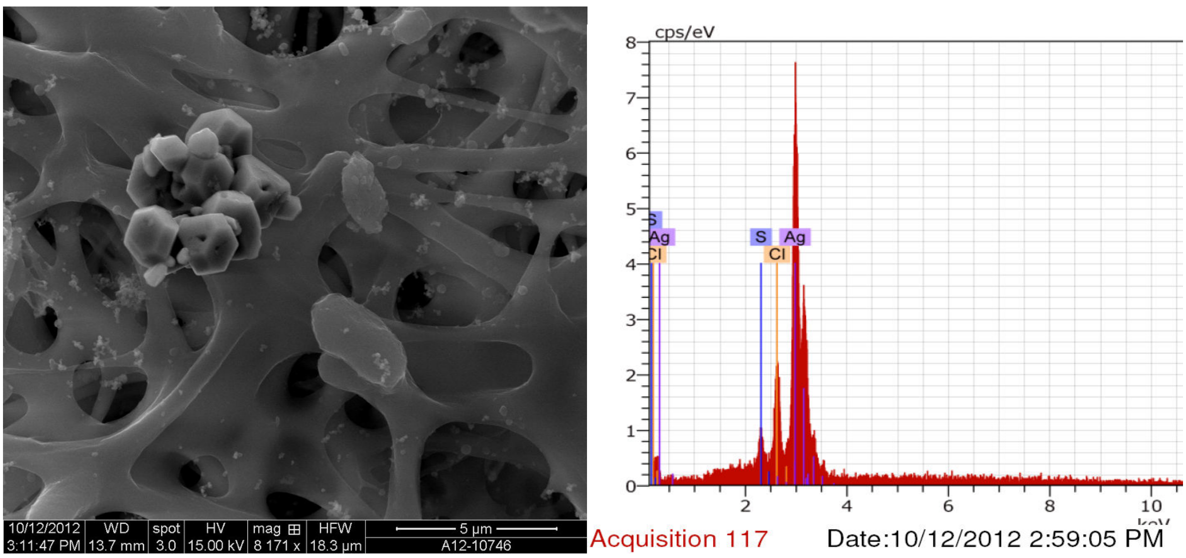

Figure 4. BSE image of acanthite and chlorargirite