УНИВЕРЗИТЕТ „ГОЦЕ ДЕЛЧЕВ" - ШТИП
ФАКУЛТЕТ ЗА ПРИРОДНИ И ТЕХНИЧКИ НАУКИ

UNIVERSITY GOCE DELCEV - STIP
FACULTY OF NATURAL AND TECHNICAL SCIENCES

UDC: 622:55:574:658

ISSN:1857-6966
DOI: 10.46763/NRT

Природни ресурси и технологии
Natural resources and technology

Број 1
No 1

Година 15
Volume XV

Јуни 2021
June 2021

УНИВЕРЗИТЕТ „ГОЦЕ ДЕЛЧЕВ” – ШТИП
ФАКУЛТЕТ ЗА ПРИРОДНИ И ТЕХНИЧКИ НАУКИ

Природни ресурси и технологии
Natural resources and technologies

Јуни 2021
June 2021

ГОДИНА 15
БРОЈ 1

VOLUME XV
NO 1

UNIVERSITY “GOCE DELCEV” – STIP
FACULTY OF NATURAL AND TECHNICAL SCIENCES
DOI: https://www.doi.org/10.46763/NRT21151

ПРИРОДНИ РЕСУРСИ И ТЕХНОЛОГИИ
NATURAL RESOURCES AND TECHNOLOGIES
За издавачот
Проф. д-р Зоран Десподов

Редакција и администрација | **Address of the editorial office**
Универзитет „Гоце Делчев" - Штип | Goce Delcev University - Stip
Факултет за природни и технички науки | Faculty of Natural and Technical Sciences
ул. „Гоце Делчев" 89, Штип | Goce Delcev 89, Stip
Република Северна Македонија | Republic of North Macedonia
URL: | https://js.ugd.edu.mk/index.php/NRT/index

Содржина / Contents

UDC: 622.36'17:504.12]:904(497.713)
DOI: https://www.doi.org/10.46763/NRT211510065j

IMPACT OF GYPSUM FROM THE ZGROPOLCI LANDFILL (CHEMICAL INDUSTRY – HIV- VELES) ON THE SCULPTURES AT THE ARCHAEOLOGICAL SITE STOBI, NORTH MACEDONIA

Mitko Jancev[1], Ivan Boev[1]

[1]Faculty of Natural and Technical Sciences, "Goce Delcev" University in Stip, Blvd. Krste Misirkov 10-A, P.O, Box 210, 2000 Stip, North Macedonia
mitko.31315@ugd.edu.mk, ivan.boev@ugd.edu.mk

Abstract. The paper presents the results of the examinations of PM-10 particles from ambient air at the archeological site Stobi, in the period of June 2020. The results obtained by applying the SEM-EDS method indicate the presence of the mineral gypsum/anhydrite in morphological forms that are very similar to the gypsum present in the landfill for waste phosphorous gypsum in the vicinity of the village Zgropolci (HIV-Veles).

Key words: gypsum, archeological, ambient air

ВЛИЈАНИЕ НА ГИПСОТ ОД ДЕПОНИЈАТА ЗГРОПОЛЦИ (ХЕМИСКА ИНДУСТРИЈА-ХИВ-ВЕЛЕС) ВРЗ СКУЛПТУРИТЕ ОД АРХЕОЛОШКИОТ ЛОКАЛИТЕТ СТОБИ, СЕВЕРНА МАКЕДОНИЈА

Митко Јанчев[1], Иван Боев[1]

[1]Факултет за природни и технички науки, Универзитет „Гоце Делчев", Штип
mitko.31315@ugd.edu.mk, ivan.boev@ugd.edu.mk

Апстракт. Во трудот се прикажани резултатите од испитувањата на ПМ-10 честичките од амбиенталниот воздух на археолошкиот локалитет Стоби, во периодот на месец јуни 2020 година. Добиените резултати со примена на методата СЕМ-ЕДС укажуваат присуство на минералот гипс/анхидрит во морфолошки облици кои се многу слични со гипсот кој е присутен во депонијата за отпаден фосфорен гипс во околината на селото Згрополци (Хив Велес).

Клучни зборови: гипс, археолошки, амбиенатален воздух.

1. Introduction

The sculptures made of marble and limestone have a special place in the archeological site Stobi; from this aspect their protection has special importance. The archeological site Stobi is located in the Republic of North Macedonia (Fig. 1) near Gradsko, next to the highway Skopje-Thessaloniki. The archeological site dates back to Roman times and is very rich in important cultural and historical monuments represented by sculptures, religious artifacts, mosaics, pillars, etc. (Boev et al, 2008). Many of these sculptures at the Stobi site show signs of intense surface degradation of the marble as a result of anthropogenic factors such as air humidity, temperature changes, air pollution with PM-10 particles, saline solutions, aggression of microbiological communities etc. (Bulakh, 2005; Vlasov and Frank-Kamenetskaya, 2006). Monitoring of the Stobi site involved setting up an ambient air monitoring station and collecting ambient air samples (Frank-Kamenetskaya et al., 2003, 2005; Lepeshkina et al., 2005). The results show the presence of gypsum in the samples taken from ambient air and this in turn imposes the need for the protection of marble statues in Stobi. It should be mentioned that, as a consequence of the interaction of PM-10 particles from ambient air with sculptures made of marble or limestone, a patina appears (surface erosion and forming of thick black crusts, the presence of biological films, stone detachment, microkarst, alveolar weathering and others) (Camuffo et al., 1983; Garcia-Vallès et al., 1998; Feely et al., 2000; Maravelaki-Kalaitzaki, 2005; Gross et al., 2006; Siegesmund et al., 2007; Kramar and Mirtič, 2008).

This paper presents the examinations of the PM-10 particles composition from ambient air at the locality Stobi with special reference to the presence of gypsum / anhydrite mineral forms.

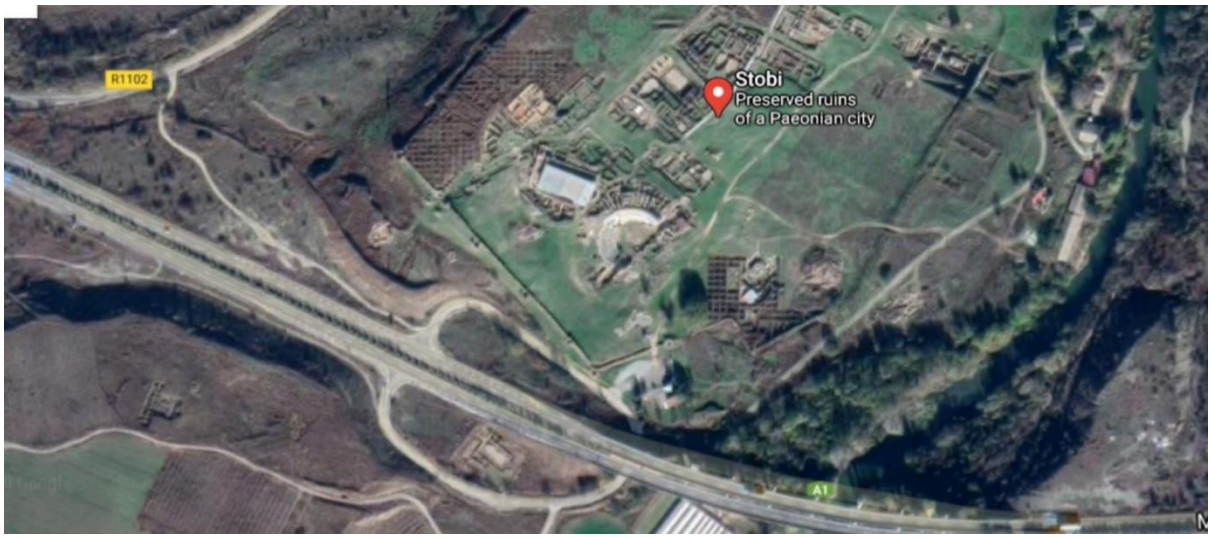

Fig. 1. Location of the archeological site Stobi (North Macedonia)

2. Methodology

Monitoring at sites is performed in full compliance with the requirements of MKS EN 12341: 2014 Ambient air - Standard method of gravimetric measurement for determination of PM-10 or PM 2.5 mass fraction from suspended solid particles, and the results are compared with the Regulation on boundary values for levels and types of pollutants in ambient air and alert thresholds, deadlines for reaching threshold values, tolerance margins for threshold value, target values and long-term goals (Official Gazette of RM No. 50/05 and No.183/2017) (Fig. 2).

Fig. 2. Ambient air station installed on the archeological site Stobi

Determination of the PM-10 particles mineral composition was made using the method of electronic microanalysis (SEM).

Scanning electron microscopy SEM analyses and electron micro-photographs were conducted using a VEGA3LMU scanning electron microscopy (SEM). The study utilized semi-quantitative analysis using internal standards. The standards used are as follows: O: SiO_2; Na: albite; Mg: MgO; Al: Al_2O_3; Si: SiO_2; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr.

The samples were covered with gold before analysis in order to provide conductivity of the sample.

3. Results and comments

The station for determining the presence of PM-10 particles in ambient air at the locality Stobi was set up in June 2020 and a number of filters were collected for their further processing using the SEM method. The presence of PM-10 particles in the ambient air at the locality Stobi in the research period ranges from 15 to 20 micrograms per cubic meter (mmg/m^3) (Fig. 3). Regarding the quantitative representation of PM-10 particles, it can be concluded that they are within permissible values of 50 mg/mg and that their impact on the cultural monuments at the Stobi locality should not be expected. However, when we enter the examinations of mineral forms present on the filters that have a concentration of PM-10 particles, which is in the allowed threshold values, we get a different picture of the possible impact of PM-10 particles on the sculptures made of marble or limestone at the Stobi locality.

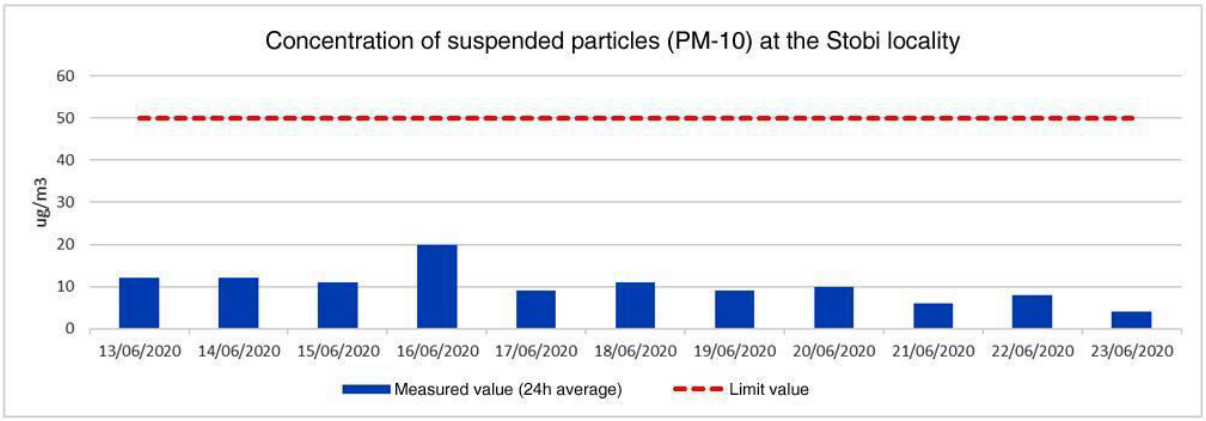

Fig. 3. Concentration of suspended particles (PM-10) at the Stobi site

Examinations of PM-10 particles using the SEM-EDS method show the presence of gypsum / anhydrite in the composition of the particles. Elemental particle analysis shows the presence of CaO in the interval of 40.21 to 41.19% and the SO_3 content in the range of 57.23 to 58.81%. (Table 1.). Morphological forms of gypsum / anhydride (Figs. 4, 5, 6, 7, 8, 9) indicate the fact that these particles are not all the result of their formation as aerosols in the interaction of acid rains, but that there are also particles brought from a nearby phosphorus gypsum landfill located near the village of Zgropolci at a distance about 5 km from the archeological locality Stobi.

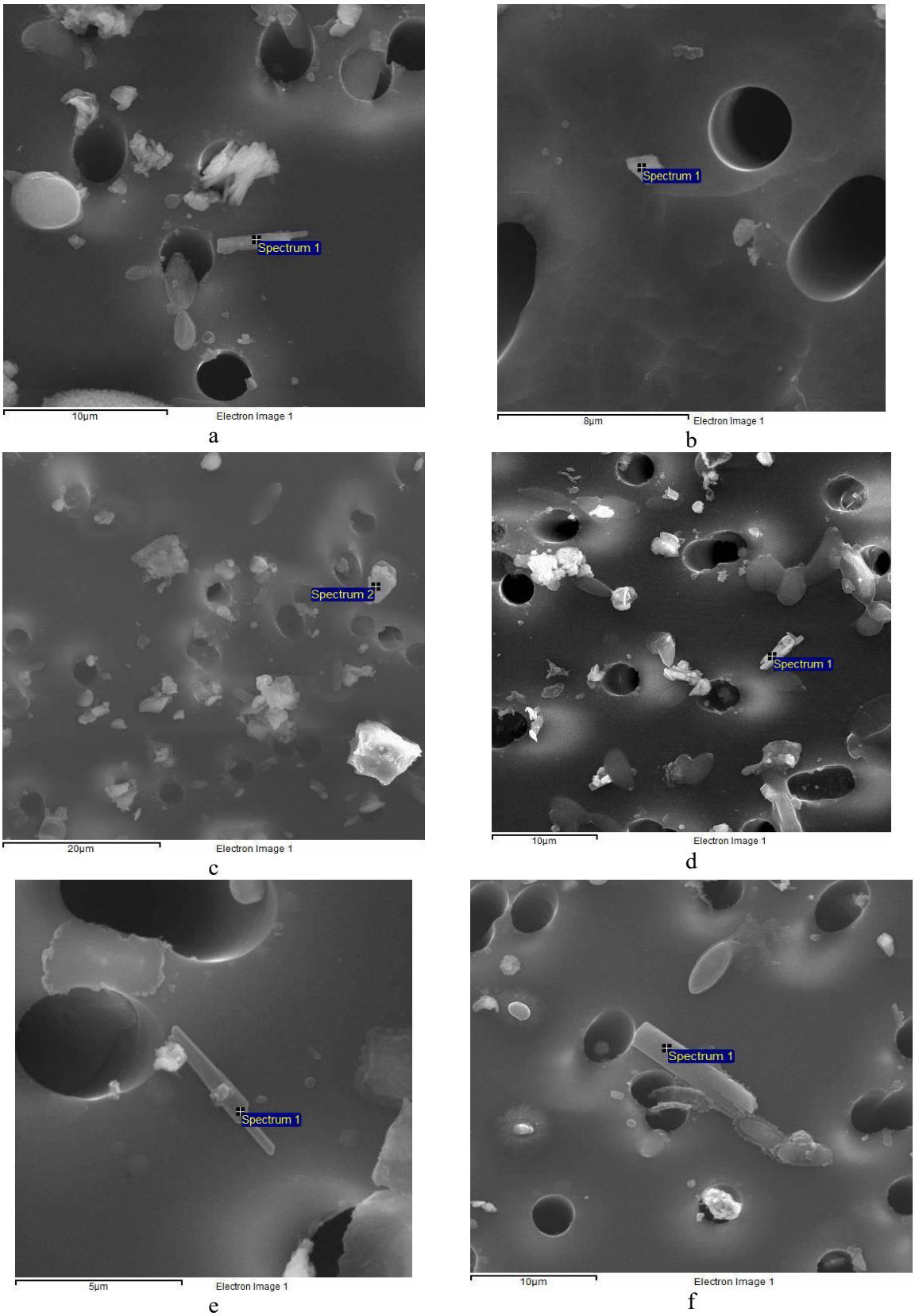

Fig.4. SEM-EDS results of gypsum/anhydrite from PM-10 of Stobi area

Table 1. Chemical composition of gypsum/anhydrite from ambient air on the Stoby locality

Elements		CaO	SO_3
Sample			
a	1	40.21	58.81
	2	40.33	58.21
b	1	40.11	39.89
	2	59.00	59.85
c	1	39.72	60.01
	2	38.92	61.02
d	1	41.19	57.23
	2	40.05	58.91
e	1	40.77	39.56
	2	58.99	60.01
f	1	39.32	59.79
	2	38.54	60.02

4. Conclusion

Acid precipitation affects the stone, primarily in two ways: dissolution and modification. When sulfuric, and nitric acids in polluted air react with the calcite in marble and limestone, the calcite dissolves. Rough surfaces, removed material, and loss of carved details can be seen in the exposed parts of buildings and monuments. The stone material can be completely removed on the surface or only on the parts that are in greater reaction.

Gypsum is soluble in water; although it can form anywhere on stone surfaces exposed to gas, sulfur dioxide (SO_2) is usually washed away. It remains only on the protected areas that are not directly washed away by rain. Gypsum is white, but the crystals form nets that trap dirt particles and pollutants, so the crust looks black. Over time, the black crust cracks and breaks, revealing the decaying stone beneath.

The occurrence of gypsum / anhydrite in PM-10 particles at the archeological site Stobi is a clear direction in terms of protecting sculptures made of marble and limestone at this site and, on the other hand, it indicates the fact of solving the problems related to the landfill for phosphorus gypsum in the vicinity of the village Zgropolci (HIV-Veles).

References

Blažo Boev, Tena Šijakova-Ivanova, Lidija Robeva-Čukovska, Ivan Boev (2008) Mineral researches of the examples of the archeological locality “Stobi” using the method of the X-ray diffraction, Geologica Macedonica, Vol. 22, pp. 27–41

Bulakh, A.G. (ed). 2005, *Examination of a stone in monuments of architecture: bases, methods, examples*. Nauka, Saint Petersburg, 198 p. (in Russian).

Camuffo, D., del Monte, M. & Sabbioni, C. 1983, Origin and growth mechanisms of the sulfated crusts on urban limestone. *Water, Air, and Soil Pollution*, 19: 351-359.

Engineering. In *Proceedings of the International geotechnical conference dedicated to Tercentenary of Saint Petersburg* (Ilichev, V.A., Ulitsky, V.M., Eds.), Saint Petersburg – Moscow: ASV Publisher, vol. 1, p. 191-197.

Frank-Kamenetskaya, O.V., Vlasov, D.Yu., Bulakh, A.G. & Marugin, V.M. 2003, Evalution of historical monuments state on the base of Qualimetrical Expertise Reconstruction of Historical Cities and Geotechnical Frank-Kamenetskaya et al. Studia UBB, Geologia, 2009, **54** (2), 17 – 22 22

Frank-Kamenetskaya, O.V., Vlasov, D.Yu., Marugin, V.M. & Lepeshkina, N.F. 2005, Methodology of rock monuments state monitoring in the urban environment. *Geology and evolutionary geography*. Saint Petersburg, p. 12-16 (in Russian).

Feely, J., Williams, S. & Fowles, P. 2000, An initial study into the particulates emitted during the laser ablation
of sulphation crusts. *Journal of Cultural Heritage*, 1: 65-70.

Garcia-Vallès, M., Vendrell-Saz, M., Molera, J. & Blazquez, F. 1998, Interaction of rock and atmosphere: patinas on Mediterranean monuments. *Environmental Geology*, 36 (1-2): 137-149.

Gross, C.M., Brimblecombe, P., Bonazza, A., Sabbioni, C. & Samagni, J. 2006, Sulfate and carbon compounds in black crusts from the Cathedral of Milan and Tower of London. In *Heritage, Weathering and Conservation* (Fort, M., Alvarez de Buergo, M., Gomez-Heras, M. & Vazquez-Calvo, C., Eds.), Taylor & Francis Group, London, p. 441-446.

Kramar, S., Mirtič, B. 2008, Characterization of black crusts of Robba´s fountain statues, Ljubljana (Slovenia). *RMZ – Materials and Geoenvironment*, 55 (4): 490–504.

Lepeshkina, N.F., Frank-Kamenetskaya, O.V., Vlasov,D.Yu. & Marugin, V.M. 2005, Complex of analytics and statistics methods by monuments monitoring in urban environment. In *Proceedings of the International Conference Solar Renewable Energy News – Research and Applications*, p. 127-129, Firenze.

Maravelaki-Kalaitzaki, P. 2005, Black crusts and patinas on Pentelic marble from the Parthenon and Erechtheum (Acropolis, Athens): characterization and origin. *Analytica Chimica Acta*, 32: 187-198.

Siegesmund, S., Torok, A., Hupers, A., Muller, C. & Klemm, W. 2007, Mineralogical, geochemical and microfabric evidences of gypsum crusts: a case study from Budapest. *Environmental Geology*, 52: 385-397.

Vlasov, D.Yu., Frank-Kametskaya, O.V. 2006, Natural rock decaying in the urban environment. *Transactions of Saint Petersburg Naturalist Society*, 96: 156-170 (in Russian).