269
GEOME 2
Manuscript received: April 19, 2014
Accepted: June 18, 2014

Geologica Macedonica, Vol. **28**, No. 1, pp. 27–32 (2014)
In print: ISSN 0352 – 1206
On line: ISSN 1857 –8586
UDC: 725.9:552.46]:543.42(497.731)

Original scientific paper

PRELIMINARY INVESTIGATIONS OF DETERIORATION ON MONUMENT TO FALLEN SOLDIERS IN THE SECOND WORLD WAR IN ŠTIP, REPUBLIC OF MACEDONIA

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A b s t r a c t: This paper gives an explanation of the origin and formation on the minerals which are formed as a consequence on deterioration. Several small marble samples were collected for research by Scanning electron microscopy (SEM), coupled with an energy dispersive X-ray spectrometer (EDS). SEM is especially useful because it gives elemental, mineralogical and morphological data at the same time. Loss of face characters and presence of black crusts are evident. The results show that the black crusts consisting of gypsum, calcite and elements such as Si, Al, Fe, Pb, Ti, Zn and Mn, were being formed from interaction between the marble surface and atmospheric pollutants. Dissolution of calcite from the surface by rain water, CO_2 and SO_2 enables the Fe compounds to become enriched and oxidized on the surface. Clay minerals are occur in the finishing layers covering the surface on the monument and they originated from atmospheric dust naturally deposited.

Key words: мarble; deterioration; black crust; soil dust; environmental conditions

INTRODUCTION

In honor of the lives lost in 1974 the Assembly of the Municipality of Štip erected memorial to fallen soldiers in the Second World War. The monument is located on the eastern side of the fortress Isar. The memorial monument is an unique structure made of marble stone. After 40 years of exposure to environmental conditions it is showing signs of deterioration.

Deterioration is a consequence of alteration of rocks at Earth's surface through physical and chemical reactions with the atmosphere and the hydrosphere. Physical weathering is the mechanical fragmentation of rocks from stress acting on them. Physical weathering breaks the rock mass into small particles. It is strictly a physical process involving no change in chemical composition. The most important types of physical weathering are ice wedging and sheeting, or unloading.

Chemical weathering involves chemical reactions with minerals that progressively decompose the solid rock. Chemical weathering alters the rock by chemical reactions between elements in the atmosphere and those in the rocks. Most geologists believe that chemical weathering is most important in terms of total amount of rock breakdown. In most places, however, the two processes work together, each facilitating the other, so that the final product results from a combination of the two processes. The major types of chemical weathering are dissolution, acid hydrolysis, and oxidation.

All carbonate materials are sensitive to acidic environments. The impact of acid deposition on the weathering of carbonate stone has long been recognized (Reddy, 1987; Lipfert, 1989; Webb et al., 1992; Camuffo, 1992). All carbonate materials are sensitive to acidic environments.

Natural rain is weakly acidic, because of the presence of gaseous acid compounds in the environment. In normal conditions, marble degradation goes on slowly, it may take centuries. Nevertheless, the acids contained in the acid rain are capable to transform $CaCO_3$, by chemical reactions, into soluble salts which are washed away, giving rise to the formation of holes on the surface of the artifacts, due to loss of material.

Human activities bring about emission of stronger acids in the atmosphere, that react with marble artifacts giving rise to faster degradation phenomena. Of course, the rate of degradation depends on the concentration of such acid pollutants in the air. It is known that the marble is especially sensitive to acid weathering conditions (Attewell and Taylor, 1990).

Acid rains are one of the main degradation agents for marble artefacts. In acid rain, the primary contributions of hydrogen ions, in addition to natural sources of acidity, are sulfurous, sulfuric, and nitric acids, which lower the pH of rain and accelerate the weathering processes (Sharma et al., 2007; Vlasov and , Frank-Kamenetskaya, 2006; Frank-Kamenetskaya et al.. 2009). Acid rain contains carbonic, nitric and sulfuric acid, that are produced by oxidation and dissolution in water of gaseous oxides (CO_2, NO_2 and SO_2), present in the air as chemical pollutants.

RESULTS AND DISCUSSION

The research was carried out on the memorial monument to fallen soldiers in the Second World War. The monument is located on the eastern side of the fortress Isar in Štip. Location and view of the memorial monument are showed in Fig. 1.

Fig. 1. Location and view of the memorial monument to fallen soldiers in the Second World War, Štip

Fig. 2. Dendritic black and thin black encrustation

Loss of face characters and presence of black crusts are evident. The encrustation examined is formed on exposed marble as products of the interaction between the stone surface and atmospheric pollutants (dendritic black and thin black encrustation, Fig 2). Black crust is mixture of crystals of calcium carbonate and calcium sulfate. Such salts, which are formed on marble surface due to acid rains, are first washed away and later, because of water evaporation, are precipitated again, often incorporating black carbon particles.

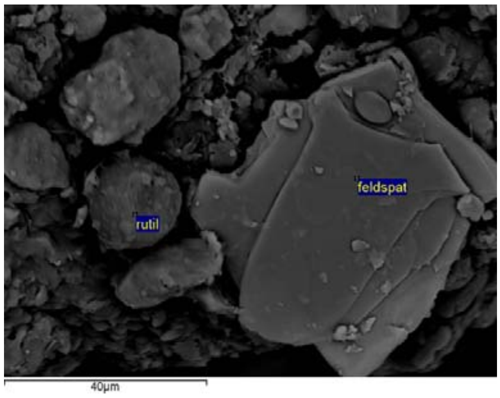

Fig. 3. SEM image of rutile and feldspar

Figure 3 shows SEM images of rutile and feldspar, while Fig. 4 shows SEM images of Fe oxide. The chemistry of rutile, feldspar and Fe oxide is given on Tables 1 and 2, respectively. The iron oxides play a role as colouring patina, together with organic matter from the bioactivity.

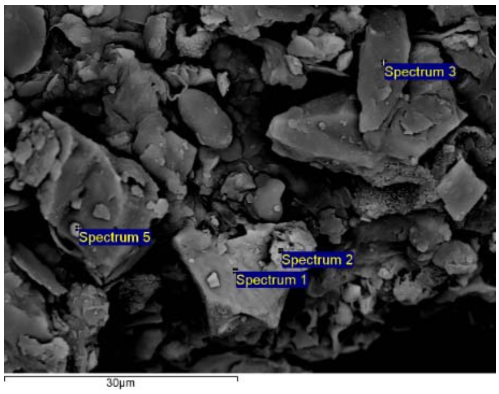

Fig. 4. SEM image of Fe oxide

Table 1

Chemical analyses of rutile (1) *and feldspar* 2

Sample / Element	1	2
	Weight (%)	
Al	3.27	16.21
Si	3.99	24.58
K	0.44	9.07
Ca	0.50	–
Ti	49.23	0.46
Fe	1.52	3.95
O	41.06	45.72
Totals	100.00	100.00

Table 2

Chemistry of Fe oxide

Element	Weight (%)
Mg	0.81
Al	0.91
Si	0.91
Ti	6.03
Mn	0.60
Fe	65.42
O	25.32
Totals	100.00

EDX spectrums of rutile, feldspar and Fe oxide are given in Figs. 5, 6 and 7 respectively.

Dissolution of calcite from the surface by rain water, CO_2 and SO_2 enables the Fe compounds to become enriched and oxidized on the surface. SEM images of calcite and dolomite are given on Figs. 8 and 9.

On Table 3 are given chemical analyses of calcite, dolomite and organic particles.

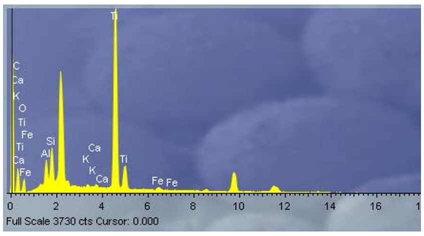

Fig. 5. EDX spectrum of rutile

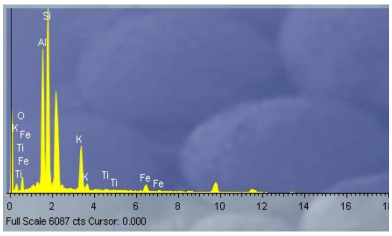

Fig. 6. EDX spectrum of feldspar

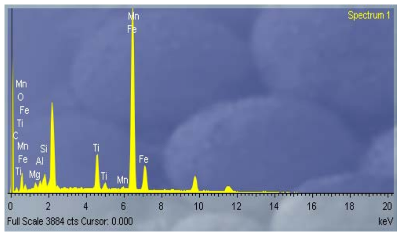

Fig. 7. EDX spectrum of Fe oxide

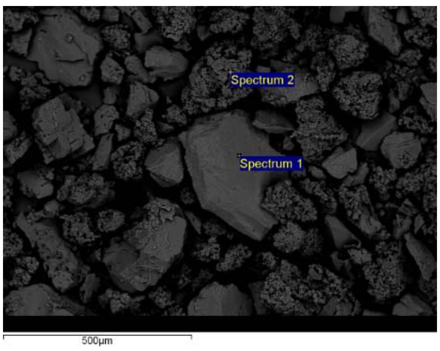

Fig. 8. SEM image of calcite

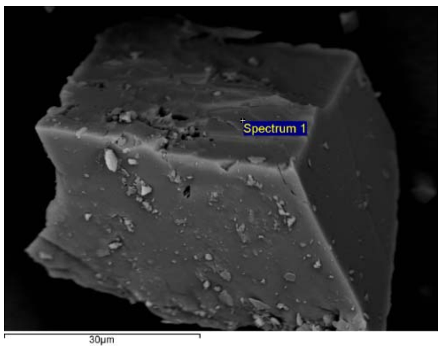

Fig. 9. SEM image of dolomite

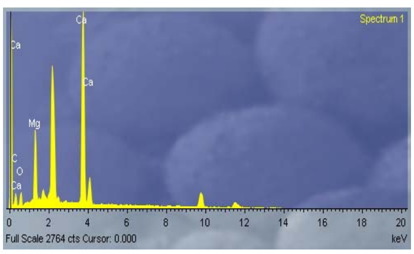

Fig. 10. EDX spectrum of calcite

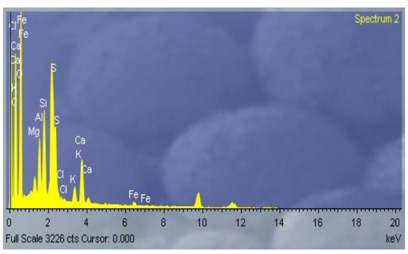

Fig. 11. EDX spectrum of organic particle

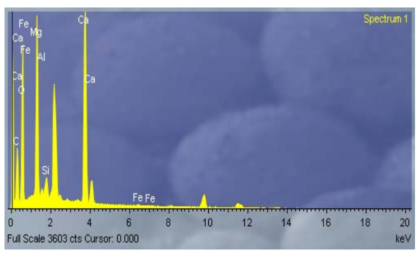

Fig. 12..EDX spectrum of dolomite

Table 3

Chemistry of calcite (1), dolomite (2) and organic particles enriched in S, Cl and Ca (3)

Sample 8	1	Sample 4	2	Sample 8	3
Element	Weight %	Element	Weight %	Element	Weight %
Mg	15.29	Mg	24.29	Mg	3.04
Ca	53.35	Al	1.50	Al	9.61
O	31.36	Si	2.09	Si	13.83
Totals	100.00	Ca	36.48	S	7.78
		Fe	1.06	Cl	1.02
		O	34.57	K	3.94
		Totals	100.00	Ca	12.74
				Fe	3.27
				O	44.78
				Totals	100.00

Sulphation has been recognized to be one of the main causes responsible for the carbonatic rocks deterioration processes in urban environments (Camuffo et al., 1983; Garcia-Vallès et al., 1998; Maravelaki-Kalaitzaki, 2005; Gross et al., 2006; Siegesmund et al., 2007; Kramar and Mirtič, 2008).

There are two ways of gypsum formation:

In the first way, calcium sulfite is formed with reaction of calcite and sulfur dioxide, then it reacts with oxygen and water. The formation of gypsum can be schematized as

$$CaCO_3 + SO_2 + H_2O \rightarrow CaSO_3 \cdot 1/2H_2O$$

$$CaSO_3 \cdot 1/2H_2O + O_2 + H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

Another definite formation is the adsorption of sulfur dioxide in rain water, liquid atmospheric aerosols, or moist film supported on a stone surface where it is oxidized to form a sulfuric acid solution that dissolves the calcium carbonate by gypsum formation (Bernal and Bello, 2003):

$$SO_2 + O_2 + H_2O \rightarrow H_2SO_4$$

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

Gypsum is formed on the calcareous stones when sulphur dioxide or its oxidizing product reaches the stone surface by two mechanisms. The first of these is "dry" deposition where the pollutant in gaseous form interacts with the surface by winds and turbulence, and the second is wet deposition, where the pollutant, as an oxidized or derived species dissolved in atmospheric moisture, is presented to the stone surface during precipitation as acid rain (Garland, 1978).

Figure 13 shows sulphation in our samples. EDX spectrum of gypsum is given in Fig. 14. Table 4 shows the chemistry of gypsum.

Various microorganisms such as bacteria, microfungi, algae and lichens are present (Fig.15). Their activity accelerates the dissolution of the carbonate rocks by the aggressive digestive products, accumulation of the moisture and by favoring the accumulation of aggressive salts and air pollutants in the external layer of the stone.

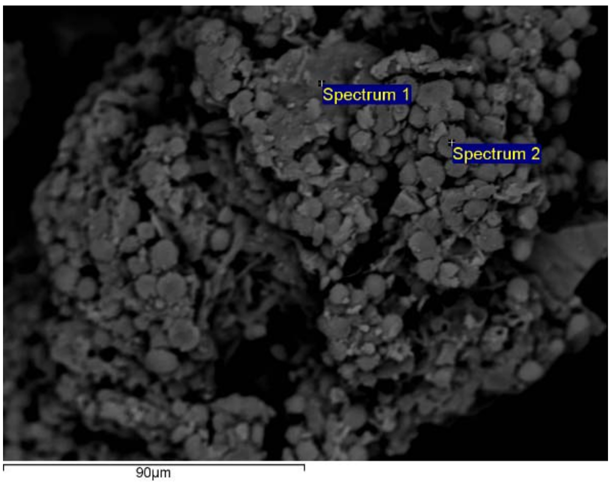

Fig. 13. SEM images of gypsum

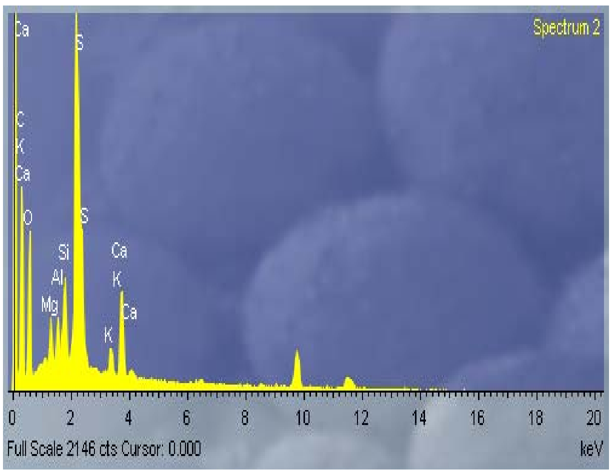

Fig. 14. EDX spectrum of gypsum

Table 4

Chemistry of gypsum

Element	Weight (%)
Mg	6.95
Al	6.11
Si	9.58
S	8.07
K	5.94
Ca	20.82
O	42.53
Totals	100.00

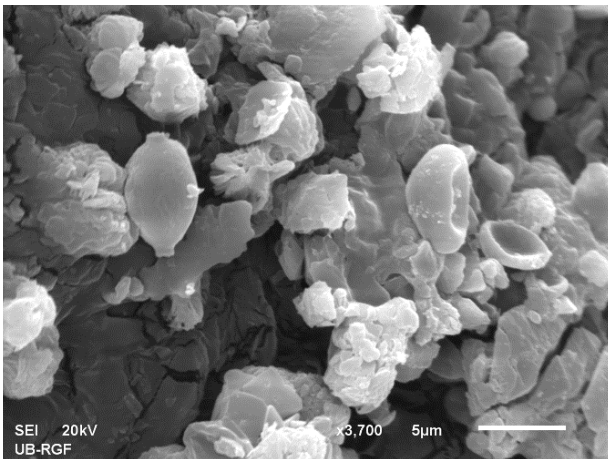

Fig. 15. SEM image of microorganisms

CONCLUSION

After summarizing the data collected in this research, we can confirm that loss of face characters and presence of black crusts are evident. The black crust is usually present on the outer surface of marble in those parts of monument sheltered from intense rain action and has various thickness and extention. The results show that the black crusts consisting of gypsum, calcite and elements such as Si, Al, Fe, Pb, Ti, Zn and Mn were being formed from interaction between the marble surface and atmospheric pollutants. Dissolution of calcite from the surface by rain water, CO_2 and SO_2 enables the Fe compounds to become enriched and oxidized on the surface. Clay minerals are occur in the finishing layers covering the surface on the monument and they originated from atmospheric dust naturally deposited. The degree of marble sulphation depends on the local conditions, mineral composition, porosity and fissuring, and structure/texture peculiarities.

The metasomatic crystallization of gypsum, occurring on the marble surface in the urban environment, is contemporaneous with the activity of many micro-organisms. The presence of numerous micro-organisms in the crust supports the hypothesis that the selective diffusion of some chemical elements into the black crust might be connected with micro-organisms acting as biogenic carriers.

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Р е з и м е

ПРЕЛИМИНАРНИ ИСПИТУВАЊА НА ВЛОШУВАЊЕТО НА СОСТОЈБАТА НА СПОМЕНИКОТ НА ПАДНАТИТЕ БОРЦИ ВО ВТОРАТА СВЕТСКА ВОЈНА ВО ШТИП, РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: мермер; црна кора-прекривка; влошување; гипс

Во овој труд се презентирани резултатите добиени со испитување на состојбата на мермерниот споменик на паднатите борци од Втората светска војна, лоциран на тврдината Исар во Штип, Република Македонија. Овие испитувања се направени со методот на СЕМ/ЕДС (скaнинг-електронска микроскопија / енергетски дисперзивна спектроскопија). Од добиените резултати може да се заклучи дека постојат одредени оштетувања на споеменикот, кои се последица на надворешните влијанија. Тие се манифестираат како црна кора-прекривка изградена од кристали на калциумкарбонат и калциумсулфат, како и елементите Si, Al, Fe, Pb, Ti, Zn и Mn, кои потекнуваат од интеракцијата помеѓу површината на мермерот и атмосферските загадувачи. Минералите на глина се појавуваат во горните слоеви на прекривката и се по потекло од атмосферската прашина која е природно депонирана.

Кристализацијата на гипс врз мермерните споменици во урбани средини зависи од минералниот состав, структурата, текстурата и порозноста на карпата, од локалните услови и активноста на многу микроорганизми. Присуството на бројни микроорганизми во кората ја поддржува хипотезата дека селективната дифузија на некои хемиски елементи во црната прекривка (или кора) може да биде поврзана со микроорганизмите кои дејствуваат како биогени пренесувачи.