

ARSENIC, HEAVY METALS AND RARE EARTH ELEMENTS IN TRAVERTINE LIMESTONE QUARRY IN THE MARIOVO AREA, NORTH MACEDONIA

Ivan Boev, Tena Šijakova Ivanova, Sonja Lepitkova

Faculty of Natural and Technical Sciences, "Goce Delcev" University, Stip, North Macedonia
ivan.boev@ugd.edu.mk

Abstract: Travertines in the Mariovo area are an extremely important raw material for obtaining architectural and decorative stone used in construction. In this region, there are six locations where travertine is exploited and this paper presents the results obtained from the mineralogical and geochemical tests of samples taken from the Mariovo travertines. The tests performed show that these are relatively young sedimentary rocks that are basically made of calcite, and in which the concentration of arsenic and heavy metals is extremely low. This finding supports the further use of these rocks as architectural and decorative stone.

Key words: arsenic; rare earth elements; travertine; Mariovo

INTRODUCTION

Arsenic (As) is a toxic and cancerogenic element, depending on its oxidation state. Elevated concentrations of arsenic and heavy metals in nature can be found as a consequence of natural geological processes, such as the occurrence of arsenic and heavy metals in groundwater associated with the presence of geothermal systems or water-rock interactions, under specific geochemical conditions (Angelone et al., 2009). Also, certain industrial activities, such as coal mining and the exploitation of sulfide minerals can lead to the occurrence of elevated concentrations of arsenic and heavy metals (Craig, 1986; Stoepler, 1992; Amini et al., 2008).

This paper focuses on the first assessment of the content of arsenic, heavy metals and rare earth elements in the multi-colored travertines in the Mariovo area, which in most cases are exploited as architectural decorative stone.

Geographical position and geological composition of the Pelagonian zone

The Mariovo area, geographically speaking, is spread across three municipalities on the territory of the Republic of North Macedonia, namely: the municipality of Bitola, the municipality of Prilep, and the municipality of Kavadarci. This area covers

about 1000 km² and is mainly geologically located in the so-called Pelagonian zone (Figure 1). In the following text, we will briefly present this exceptionally important geological zone within the Balkan Peninsula. Within the Mariovo area, there are several localities where travertine is exploited as an architectural decorative stone.

The Pelagonian massif is the largest unit of the belt. It is located between the Vardar zone and the Dinaric (west of Vardar) ophiolite belt on the territories of North Macedonia and Greece (Lerin "terrane") (Most, 2003). The high-grade metamorphic rocks (amphibolite-facies with eclogitic relicts) can be divided into two parts: a lower complex made up of biotite and two-mica gneisses, amphibolites, gneisses and epidote-hornblende, leucocratic gneisses, orthogneisses and, an upper complex made up of gneisses, micas, amphibolites, calcareous schists and massive marbles (Sivec marbles) (Dumurdžanov, 1985).

The Pelagonian metamorphic complex is a crystalline core with a continental type of crust, which, like the Serbian-Macedonian massif, is built up mostly of the oldest Precambrian formations. This geotectonic unit is separated from the neighboring units by deep regional faults. It is bounded to the north by the Kyustendil-Skopje-Debar fault, to

the east by the Serbian-Macedonian massif, and to the west by the Western Macedonian zone. To the south it continues into Greece where it dips into the Aegean basin (Figure 1). (Boev I. et al., 2021).

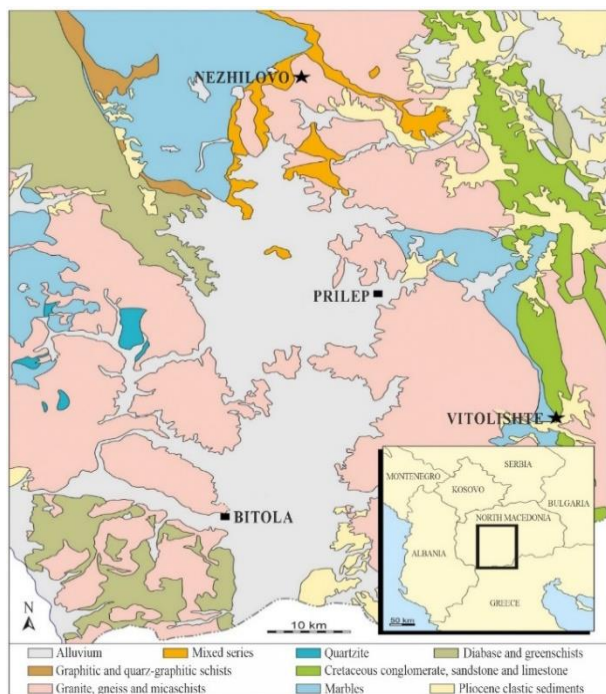


Fig. 1. Pelagonian metamorphic complex (Boev I., 2021)

From a stratigraphic-lithological point of view, the Pelagonian metamorphic complex (often known as the Pelagonian horst anticlinorium) consists of complexly dislocated Precambrian metamorphic crystalline rocks (gneisses, gneiss-granites, mica schists, cipolins and marbles), as well as regionally metamorphic complexes including large masses of palinogenic granites and smaller masses of andesites (Palinkaš et al., 2012). Several characteristic rock series are present in the Pelagonian metamorphic complex. The northern part of the massif consists of four series. Two of them (the gneisses and mica schists series) belong to the lower metamorphic complex, while the other two (the mixed series and the marble series) are part of the upper metamorphic complex (Bermanec et al., 2001; Radusinović et al., 1971; Žorž et al., 1988/89, 1999; Barić, 1964). Within the Pelagonian massif is located the largest neotectonic depression in the Republic of Macedonia with a length of 65 km and an average width of 15 km. This neotectonic depression is filled with Miocene, Pliocene and Quaternary sediments (Dumurdžanov et al., 2004).

Age determinations with the Rb-Sr method in the northern parts of the massif in North Macedonia

and recent U-Pb determinations in Greece (Florina "terrane") indicate a (polymetamorphic) Neoproterozoic age for these complexes (up to 700 Ma in the metagranites), with a very important metamorphic and magmatic event from the Late Carboniferous of c. 300 Ma (Himmerkus et al., 2007).

Local geology

The sedimentary rocks of the Pliocene sedimentary basin of Mariovo can basically be divided into two parts, namely: Upper Pliocene (represented by limestones, travertines-quartzlatite breccias and volcanic-sedimentary rocks) and Lower Pliocene (represented by gravels, sands, clays and occurrence of coal layers).

Lower Pliocene sediments represent the basal part of the Pliocene sedimentation which begins with transgressive material of gravel and sand. It is widely distributed around the village of Vitolište where through detailed geological explorations for coal their average thickness of about 50 m has been determined. Over them lies a younger series of gravels, sands and clays, which are poorly stratified and sorted. They have also been determined in several places northwest of Vitolište in the form of cloths.

Over the previously mentioned complex lie Upper Pliocene sediments which are represented by volcano-sedimentary formations, quartzlatite agglomerates and tuffs, quartzlatite breccias, and limestones. Of the previously listed, the most significant are the limestones (travertines) which actually represent the final phase of the Pliocene sedimentation. They occur on an area of about 20 km² between the villages of Bešište, Polčište, and Manastir (Temovski et al., 2024).

MATERIALS AND METHODS

Six samples of travertine were collected from the localities where travertine occurs in the Mariovo area, namely: Vrpsko, Trojaci, Dekova Dabica, Manastir, Sirma Galica, Melnica (Figure 2). In all localities where travertine occurs, it is characterized by a crystalline structure, a porous texture, and the travertines are yellowish to brownish in color, in very rare cases there is also the appearance of gray-white series.

The collected materials were processed using X-ray diffraction methods, SEM-EDS methods, as well as ICP-OES and ICP-MS methods.

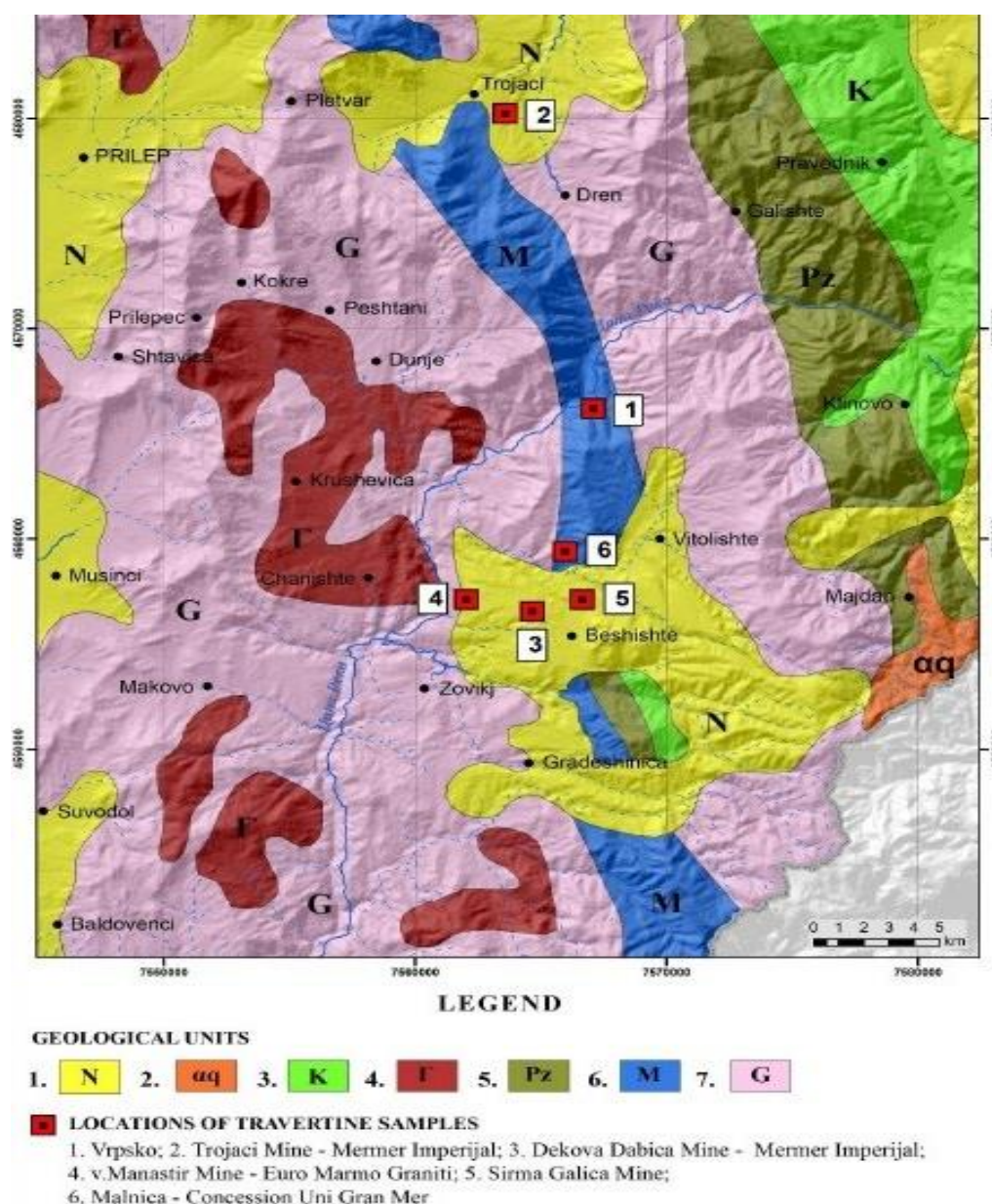


Fig. 2. Geological map of Mariovo and site of the samples of travertine

Lithogeochemistry and whole rock analysis and XRD diffraction

The most aggressive fusion technique employs a lithium metaborate/tetraborate fusion. Fusion is performed by a robot at Actlabs-Canada, which provides a fast fusion of the highest quality in the industry. The resulting molten bead is rapidly digested in a weak nitric acid solution. The fusion ensures that the entire sample is dissolved. It is only with this attack that major oxides including SiO₂, refractory minerals (i.e., zircon, sphene, monazite, chromite, gahnite, etc.), REE and other high field strength elements are put into solution. High sulphide-bearing rocks may require different treatment but can

still be adequately analyzed. Analysis is by ICP-OES and ICP-MS.

The quality of the data is exceptional and can be used for the most exacting applications.

X-ray diffraction patterns were recorded on an Ultima IV diffractometer (Rigaku, Tokyo, Japan). The X-ray beam was Ni-filtered. CuK α ($\lambda = 0.154178$ nm) radiation was used generated by setting the tube voltage at 40 kV and the tube current to 40 mA. The scan rate of 5.5°/min in a 2 θ range from 3.5 to 60 was adjusted.

SEM analyses were performed with a scanning electron microscope TESCAN SEM VEGA3 LMU with an Oxford EDS detector, within the AMBIKON laboratory at the University of Applied Sciences – Štip.

SEM-EDS RESULTS AND DISCUSSION

Mineralogy

The term travertine is most often used in a broader sense, including all lacustrine limestones formed under certain climatic control and under the influence of water sources. A great variety of travertine deposits has been described, depending on many variables, such as the physical and biological processes present during their formation (Valero-

Garcés et al, 2001). Travertines, mainly composed of calcite or aragonite, have low to moderate porosity, and are generally defined as chemical sediments (precipitates) around water sources, along rivers or lakes (Pentecost, 2005).

The samples of travertine taken from the Mariovo area were subjected to mineralogical examinations using the methods of XRD and SEM-EDS. The obtained results are shown in the figures 3, 4, 5.

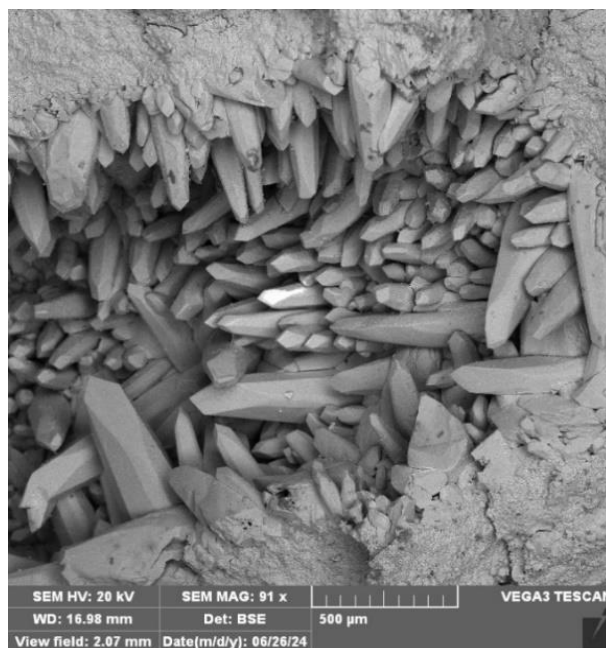
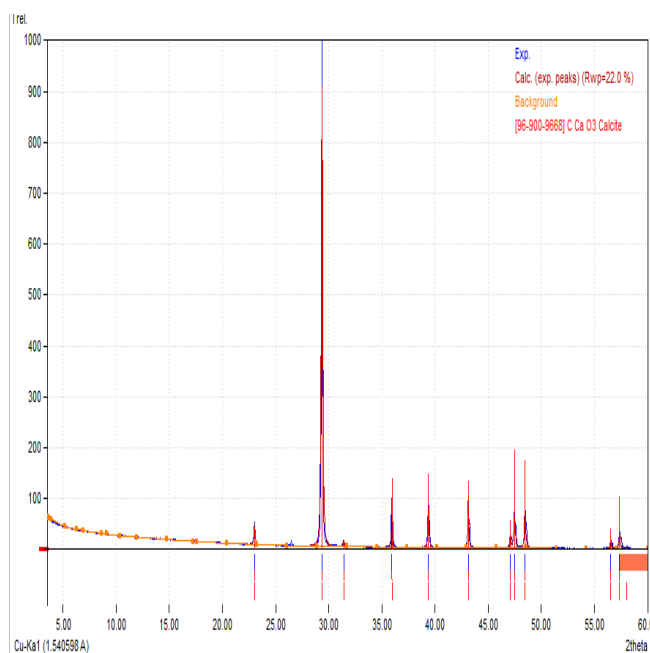


Fig. 3. XRD and SEM of travertine of Vrpsko

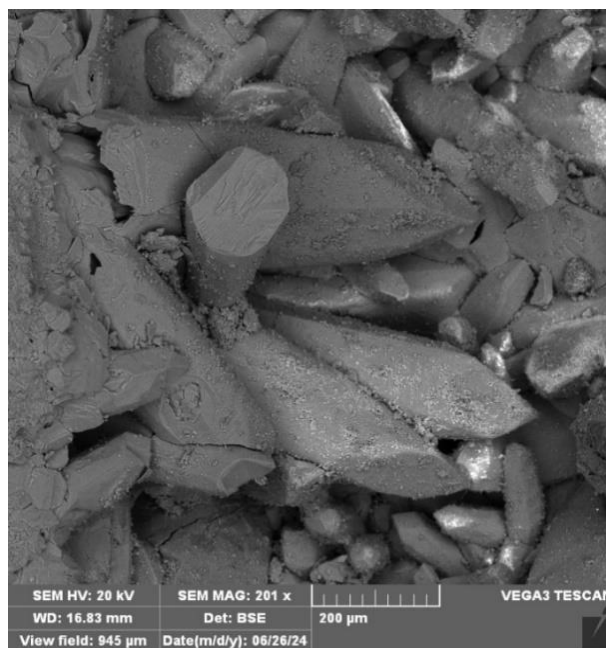
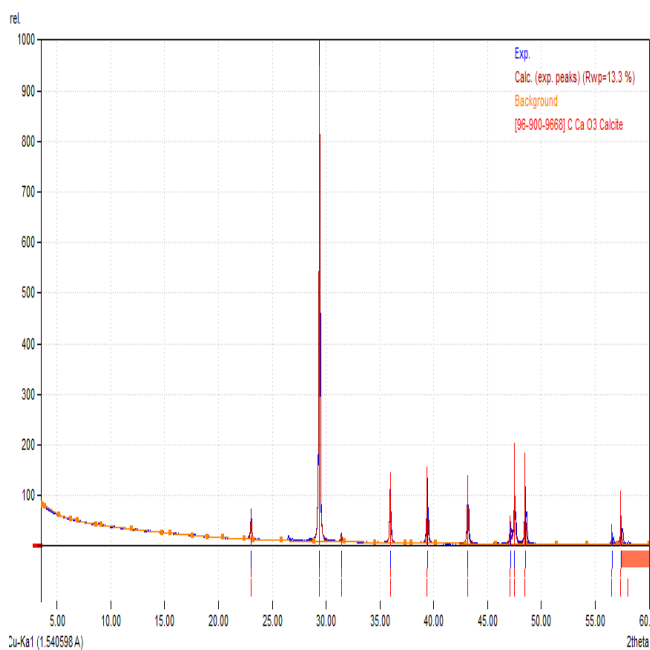


Fig. 4. XRD and SEM of travertine of Trojaci

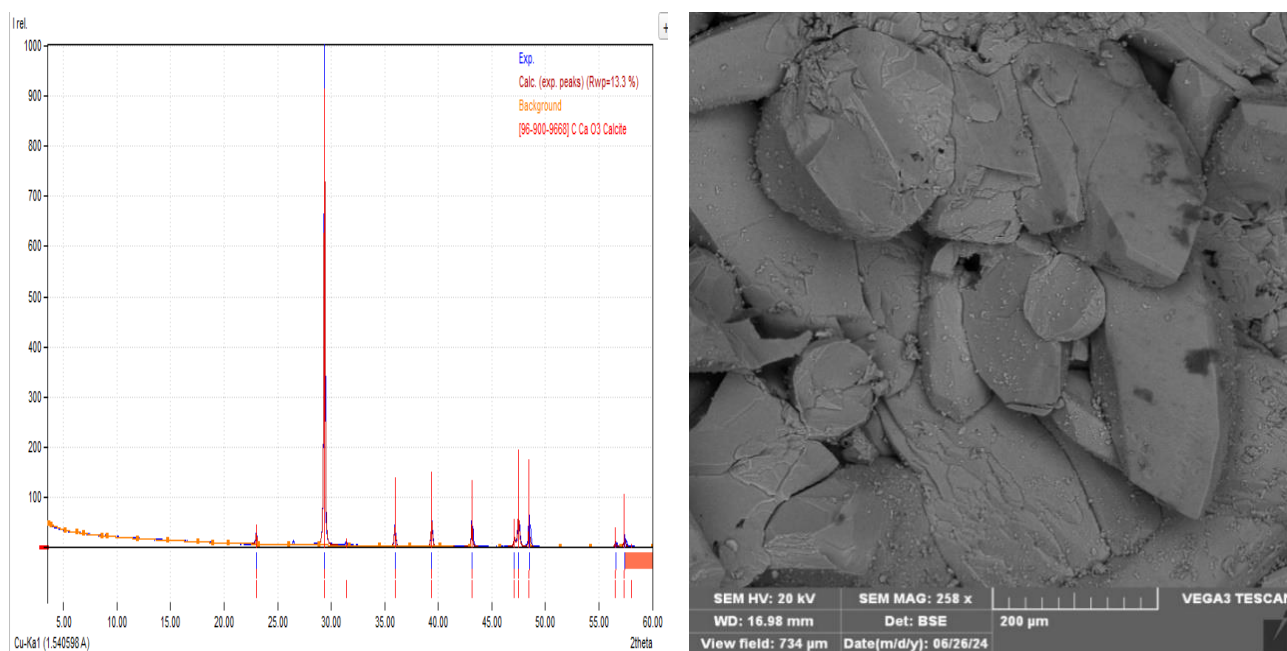


Fig.5. XRD and SEM of travertine of Manastir

From the results shown, it can be concluded that these are relatively pure travertines that are made up only of the mineral calcite.

Geochemistry

In Table 1, the chemical and geochemical characteristics of the travertines from the Mariovo area are shown.

From the presented geochemical analyses of the travertines from the Mariovo area, it can be concluded that these are carbonate rocks which, in terms of the presence of other elements, besides

CaO, have a very low presence of other elements (SiO_2 , Al_2O_3 , Fe_2O_3 , MnO). These travertines are exceptionally young occurrences and therefore they are very little contaminated with other elements.

The arsenic content in these travertines is relatively low and ranges from 5 to 30 ppm, which is a relatively low concentration compared to some other similar rocks (Kampouroglou et al., 2013).

The presence of elements from the group of Ni, Fe, Cr, Cu, Co is small, i.e., there is a low concentration of these elements and on this basis these rocks cannot be classified as contaminated rocks (Kampouroglou et al., 2013).

Table 1

Chemical and geochemical characteristic of the Mariovo travertine (ICP-MS)

	Vrpsko	Trojaci	Dekova Dabica	Manastir	Sirma Galica	Melnica
%						
SiO_2	0.14	1.42	0.12	0.48	1.92	7.92
Al_2O_3	0.05	0.65	0.03	0.14	0.75	2.81
Fe_2O_3	0.04	0.16	0.02	0.29	0.26	0.98
MnO	0.045	0.005	0.01	0.037	0.06	0.02
MgO	0.16	0.45	0.34	0.29	0.52	0.61
CaO	56.42	54.91	55.38	56	54.33	48.87
Na_2O	0.01	0.04	0.03	0.03	0.06	0.23
K_2O	0.01	0.11	0.01	0.02	0.1	0.57
TiO_2	0.002	0.015	0.001	0.003	0.026	0.1112

	Vrpsko	Trojaci	Dekova Dabica	Manastir	Sirma Galica	Melnica
P ₂ O ₅	0.03	0.07	0.01	0.02	0.04	0.08
LOI	42.86	42.38	43.24	42.97	42.1	38.12
Total	99.77	100.2	99.21	100.3	100.2	100.3
ppm						
Sc	1	1	1	1	1	2
Be	1	1	1	1	2	2
V	5	5	5	9	6	20
Cr	20	20	20	20	20	20
Co	1	1	1	1	1	1
Ni	20	20	20	20	20	20
Cu	10	10	10	10	20	20
Zn	30	30	30	30	30	30
Ga	1	1	1	1	1	4
Ge	0.5	0.5	0.5	0.5	0.5	0.5
As	5	5	5	30	5	7
Rb	1	6	1	1	8	29
Sr	72	50	156	144	137	199
Y	0.5	1.7	0.5	0.6	3	4.3
Zr	3	7	3	13	19	45
Nb	0.2	0.4	0.2	0.2	0.7	3.2
Mo	2	2	2	2	2	2
Ag	0.5	0.5	0.5	0.5	0.5	0.5
In	0.1	0.1	0.1	0.1	0.1	0.1
Sn	1	1	1	1	1	1
Sb	0.2	0.2	0.2	0.2	0.2	0.2
Cs	0.1	2.1	0.1	0.3	3	10.9
Ba	12	25	34	37	56	239
La	0.15	1.49	0.05	0.63	5.31	12.6
Ce	0.26	2.47	0.05	1.05	8.91	21.6
Pr	0.03	0.35	0.01	0.1	0.97	2.25
Nd	0.17	1.49	0.05	0.49	3.61	8.69
Sm	0.02	0.28	0.01	0.05	0.62	1.41
Eu	0.009	0.054	0.005	0.008	0.11	0.292
Gd	0.03	0.27	0.01	0.06	0.51	0.97
Tb	0.01	0.04	0.01	0.01	0.07	0.14
Dy	0.04	0.24	0.01	0.06	0.4	0.75
Ho	0.01	0.05	0.01	0.01	0.08	0.15
Er	0.02	0.15	0.01	0.04	0.24	0.41
Tm	0.005	0.025	0.005	0.005	0.038	0.06
Yb	0.02	0.14	0.01	0.03	0.27	0.41
Lu	0.002	0.018	0.002	0.003	0.045	0.052

	Vrpsko	Trojaci	Dekova Dabica	Manastir	Sirma Galica	Melnica
Hf	0.1	0.1	0.1	0.1	0.3	0.9
Ta	0.01	0.01	0.01	0.01	0.02	0.15
W	0.5	0.5	1	0.5	1.5	0.5
Tl	0.05	0.05	0.05	0.05	0.07	0.31
Pb	5	5	5	5	5	12
Bi	0.1	0.1	0.1	0.1	0.1	0.1
Th	0.05	0.54	0.05	0.26	2.19	6.86
U	0.07	1.07	0.06	0.4	0.41	1.27

Rare earth element abundance patterns in all 6 samples, normalized to the North American Shale Composite (NASC), (Gromet et al., 1984), are shown in Figure 6. The lines indicate a trend of normalized REE concentrations. As it can be seen from the Figure 6, there is slight enrichment of the Light Rare Earth Elements (LREE) on the left side compared to the Heavy Rare Earth Elements (HREE) on the right side of the plot. The degree of LREE enrichment was quantified by (La/Yb) NASC values (Elias et al., 2019), which ranged between 0.48 and 2.98 with an average value of 1.53. Also, a negative Eu anomaly (a dip in the plot at the position of Europium, indicating its lower concentration relative to the other REEs) is distinct

of Eu/Eu* range from 0.15 to 0.50. In all 6 samples was determined that they have total REE values lower than NASC. Namely, Σ REE concentrations in these 6 samples ranged from 0.242 to 49.784 in comparison with Σ REENASC of 167.26. Correlation analysis indicated that Σ REE concentrations generally increased with an increase of (La/Yb) NASC. These results reflected REE were nonuniformly accumulated by sediments during their transport (Liu et al., 2021). Thus, LREE enrichments could result from the chemical weathering of silicates in crustal materials, which led to higher levels of LREE in sediments (Oliveira et al., 2003; Lin et al., 2013).

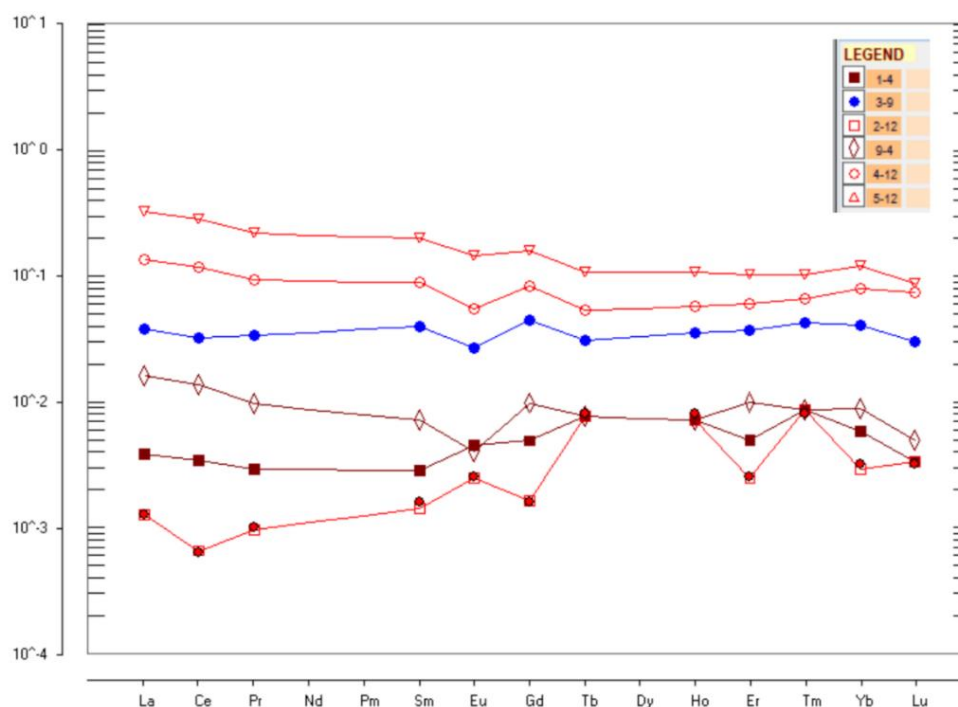


Fig. 6. NASC-normalized REE patterns for samples 1–6 (Haskin and Frey, 1966)

CONCLUSION

From the conducted research on the travertines present in the Mariovo area, it can be concluded that these are relatively young sediments, that are not contaminated with As and heavy metals at all, and from that aspect it can be said that these are rocks

that are exceptionally clean and suitable for use as architectural decorative stone. The presence of elements from the group of rare earths indicates a strong connection of these elements with their presence in the volcanism of Kožuf Mountain.

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Резиме

АРСЕН, ТЕШКИ МЕТАЛИ И ЕЛЕМЕНТИ НА РЕТКИ ЗЕМЈИ ВО КАМЕНОЛОМИТЕ ЗА ТРАВЕРТИН ВО МАРИОВО, СЕВЕРНА МАКЕДОНИЈА

Иван Боев, Тена Шијакова-Иванова, Соња Лепиткова

Факултет за природни и технички науки, Универзитет „Гоце Делчев“,
бул. Крсте Мисирков 10А, ШТИП, Северна Македонија
ivan.boev@ugd.edu.mk

Клучни зборови: арсен; елементи на ретки земји; травертин; Мариово

Травертините во Мариово се исклучително важна сировина за добивање архитектонски и украсен камен кој се користи во градежништвото. Во овој регион има шест локации каде се експлоатира травертинот и во овој труд се претставени резултатите добиени од минералошките и гео-хемиските испитувања на примероците земени од мариов-

ските травертини. Извршените тестови покажуваат дека се работи за релативно млади седиментни карпи кои во основа се состојат од калцит, а во кои концентрацијата на арсен и тешки метали е исклучително мала. Овој наод ја поддржува понатамошната употреба на овие карпи како архитектонски и украсен камен.

