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## VOLCANIC ACTIVITY IN THE KOŽUF MOUNTAIN AREA AND IMPLICATIONS FOR THE DISTRIBUTION OF RARE EARTH ELEMENTS IN DIATOMITE AND TRIDYMITE

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**A b s t r a c t:** This paper presents the results of an investigation into the distribution of rare earth elements (REEs) in diatomite and tridymite from the Kožuf Mountain volcanic area. The REEs comprise fifteen chemical elements from lanthanum to lutetium (atomic numbers 57–71), characterized by similar chemical properties. In order to study their distribution, samples of the Vitačevo diatomite and Alsar tridymite sediments were taken and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The chondritic normalization curves show enrichment in light rare earth elements (LREEs), a negative europium (Eu) anomaly in all samples, and a progressive depletion of heavy rare earth elements (HREEs). Two hypotheses are discussed: the nature of the parent rocks of the sediments (volcanic rocks of the Kožuf Mountain) and the physico-chemical conditions of sedimentation, particularly complexation and oxidation-reduction phenomena. There is a strong correlation between the distribution of REEs in volcanic rocks and the distribution of REEs in sedimentary diatomite and the acidic volcanics (tridymite).

**Key words:** diatomite; tridymite; rare earth elements; Kožuf Mountain

### 1. INTRODUCTION

Diatoms are a type of single-celled algae found in lakes, streams and oceans. They are abundant today and were common in many ancient environments. Diatom skeletons are a delicate lattice of silica (SiO<sub>2</sub>) and each species has a distinctive skeleton. Diatom “blooms” can occur several times a year and large blooms can produce billions of individual diatoms. The diatoms then die and their skeletons settle to the bottom of the water body (Wallace et al., 2006).

The freshwater diatomites found in the Kožuf Mountain area formed over periods of thousands to millions of years. The Pliocene climate in the region was mild and wet but gradually became drier in the late Pliocene (Dumurdžanov et al., 2004). Rain fell in the mountains and streams and then carried the water down into the lowlands, some of which had natural dams and thus contained lakes. The streams also carried important nutrients, such as phosphorus, from the hills into the lakes. The Tikveš Plio-

cene lake formed on the periphery of the large Kožuf Mountain volcanic activity zone. The eruption of lava flows typically dammed the streams feeding into the lake. This happened in the central part of the volcanic area, where extensive pyroclastic materials flowed into the lake (Figure 1; Boev, B. 1988; Wallace et al., 2006).

In the geological past, diatom accumulations in some lakes occurred over thousands of years, producing a thick layer that eventually formed diatomite. Diatomite is a soft, very fine-grained sedimentary rock with a chalk-like appearance. These silica-rich rocks are very finely porous and low in density; they will float on water until they become saturated (Reka et al., 2018).

In the Kožuf Mountain volcanic area, diatomite is found in the Vitačevo sedimentary lake sequences, forming a horizon in there deposited volcanic materials (Figure 2).

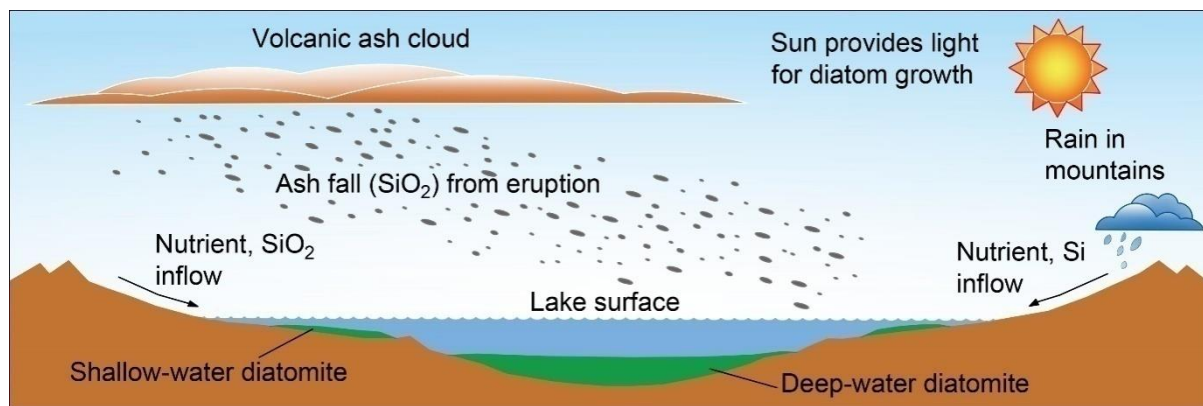


Fig. 1. This diagram shows the settling of a diatomite deposit in a lake (Wallace et al., 2006)

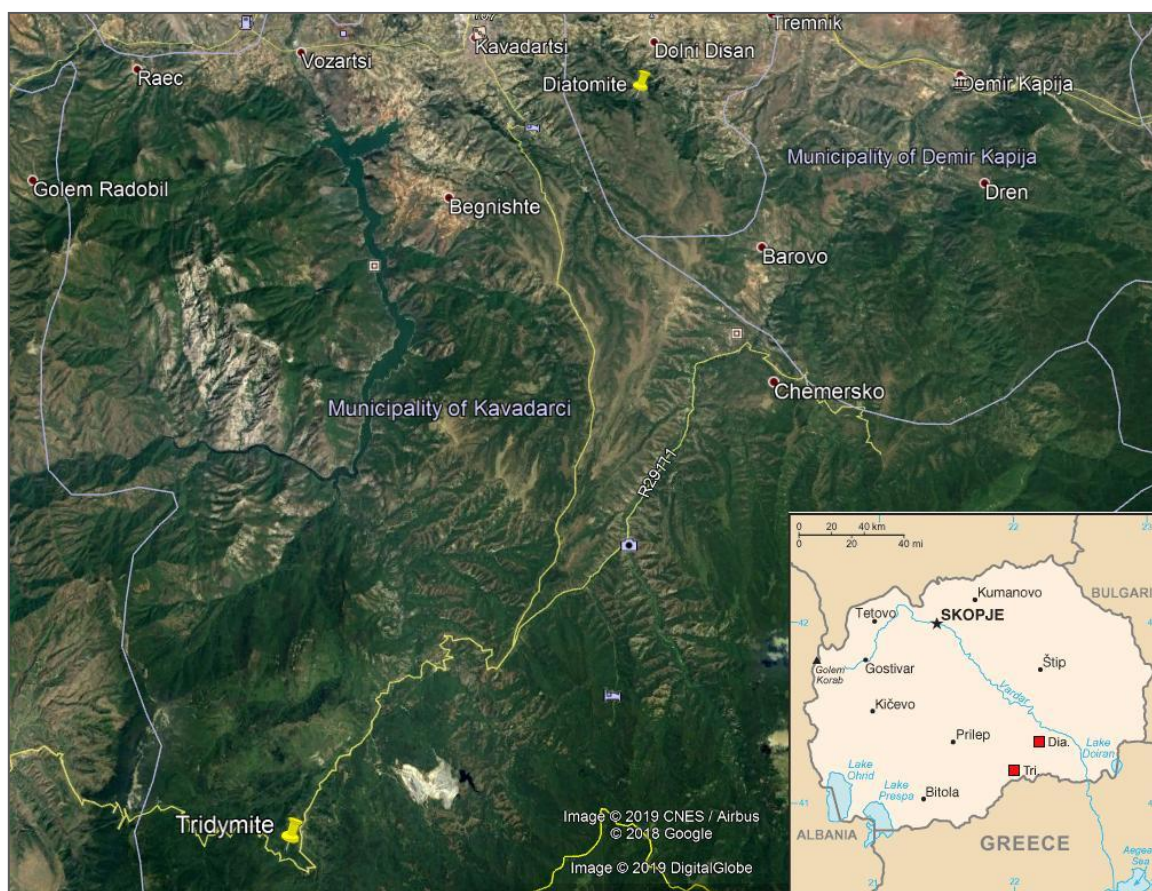


Fig. 2. Position of diatomite and tridymite in the Kozuf volcanic area (Google Maps, 2019; [www.drivingdirectionsandmaps.com/macedonia-google-map/](http://www.drivingdirectionsandmaps.com/macedonia-google-map/))

The thickness of the diatomite horizon is between 50 and 100 cm. Micropalaeontological investigations of the diatom flora have revealed a rich and diverse association of benthic and planktonic diatoms (Stojanova et al., 2010). With regard to quantity, benthic forms were found to be more common and particularly dominated by *Epithemia hyndmanii* W. Smith. The presence of plankton repre-

sentatives of the type *Cyclotella meneghiniana* Kutzing is rarer.

The rare earth elements (REEs, from La through to Lu) are a coherent geochemical group characterized by a single oxidation state: REE (III), except for cerium (Ce) and europium (Eu). During the last few decades, REEs have become important geochemical tracers used to understand and describe



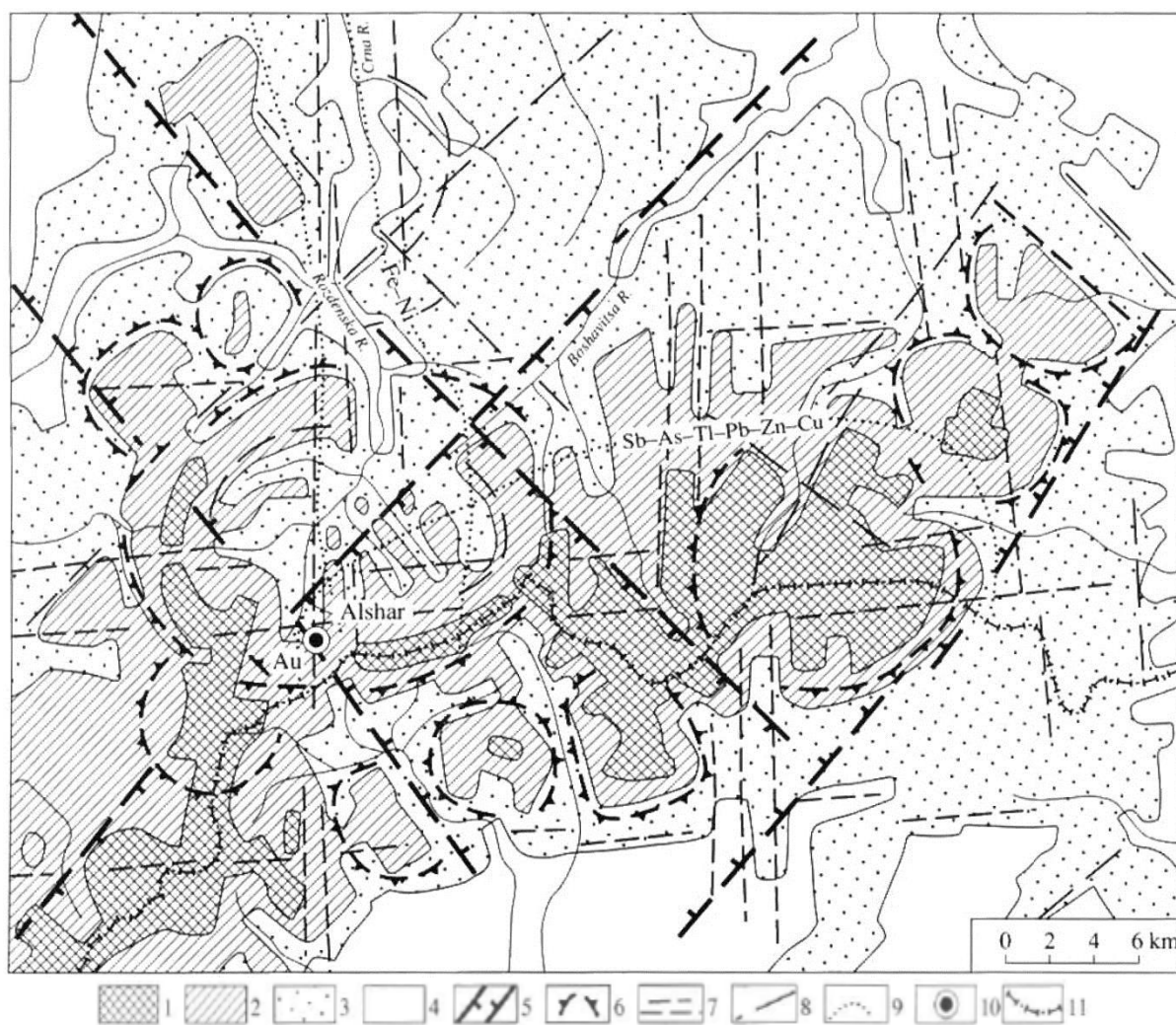
the chemical evolution of the earth's continental crust (Goldstein & Jacobsen, 1988; McLennan, 1989; Gaillardet, 1995; Dupre et al., 1996). Moreover, REEs have been used as analogues for actinide elements in studies related to radioactive waste disposal, in order to demonstrate their general immobility in weathering environments (Wood, 1990).

Despite this, many studies have indicated that REEs may be significantly mobilized during weathering processes and may behave non-conservatively (Braun et al., 1990; Sholkovitz et al., 1994). However, little is known about REE distribution and fractionation during weathering and river transport.

### GENERAL CHARACTERISTICS OF THE VOLCANIC ACTIVITY OF KOŽUF MOUNTAIN

The volcanic rocks that formed during the Pliocene along the transverse tectonic structures of the Vardar strike are revealed in the Kožuf and Kozjak mountains, on the southern margins of the Tikveš-Mariovo Tertiary basin. Volcanic activity is evidenced by the occurrence of large masses of pyroclastic materials and numerous volcanic heaps,

formed by frozen supply channels (Boev, 2013). Generally, the volcanic domes are distributed in an east to northeast extension zone (Figure 3), most commonly on tectonic structures that intersect older structures with a northwest orientation (the Vardar strike).



**Fig. 3.** Morphostructural scheme of the Kožuf volcanic area (Volkov et al., 2006)

- (1–4) Hypsometric levels (m): (1) 1500–2000 m; (2) 1000–1500 m; (3) 500–1000 m; (4) < 500 m; (5) Zones of diagonal dislocations; (6) Boundaries of the ring structures; (7) Deep orthogonal faults; (8) other faults; (9) Geochemical halos; (10) Alšar deposit; (11) Macedonian-Greek border

The transverse tectonic structures are of non-tectonic age, having been formed in the Pliocene, and lie parallel to the northern margin of the Aegean valley between Thessaloniki and Kavala.

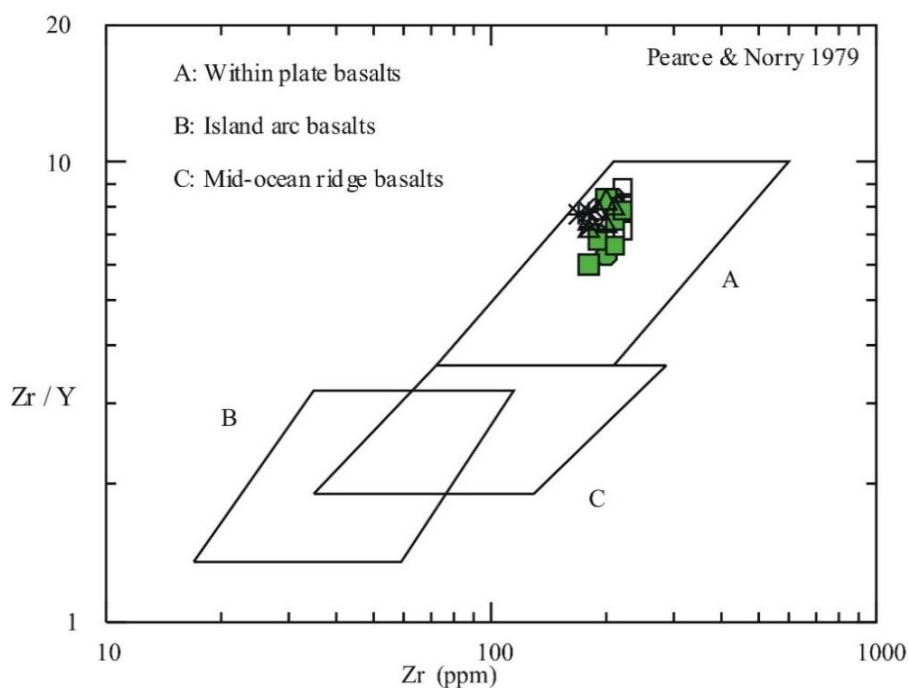
Volcanic activity in the Kožuf and Kozjak mountains is represented by various types of volcanic rock, volcanoclasts (volcanic breccias and tuffs) and conglomerates. Volcanoclasts occur as sedimentary layers in the southern parts of the Tikveš–Mariovo Tertiary basin, where they comprise the topmost parts of the sediments. In some places, the volcanoclasts are 200 to 300 m thick. The volcanic rocks present are alkali basalt (in small bodies), quartzlatites (delenites), andesite-latites (trachyandesites), transitional latite-quartzlatite, and quartzlatite-latite (delenite-latite), in addition to latite, trachyte, trachyrhyolites and rhyolites (Boev, 1988; Boev, 2013).

Conclusions given in Boev (1988) relate to the origin of the magmas that formed the volcanic rocks

of the Kožuf district. Magma sources are considered to have been located at the margin between the continental crust and the mantle. Isotopic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio data are presented that support this assumption.

Further investigations carried out by Boev et al. (1990) confirmed the earlier assumptions about the origin of the magma that provided the material for the formation of the volcanic rocks. Values determined for the isotopic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio were found to be within 0.708568 of those obtained by Boev (1988) for the volcanic rocks of Kožuf Mountain.

Figure 4 shows the relationship between the volcanic rocks of Kožuf Mountain and the individual geotectonic areas in which magmatic processes took place. The diagram indicates that data obtained for the volcanic rocks of Kožuf Mountain plot in the field of continental, slab-like basalts or the so-called “within-plate basalts”.



**Fig. 4.** Relationship between the volcanic rocks of Kožuf Mountain and individual tectonic zones (based on Pearce & Norry, 1979, from Boev, 1988)

This confirmation can be applied to explain the processes that contributed to the formation of the volcanic rocks in the Kožuf Mountain area.

It should be mentioned that Continental Flaw Basalt (CFB) is related to the evolution of continen-

tal rift areas. Explanations for the genesis of the magmas that provided the material for the volcanic rock formation during the consolidation processes should be studied with respect to the development of the structures present in the continental areas (Boev et al., 2016).



The chemistry of the magmas related to continental rift zones is conditioned by the heterogeneity of mineral and chemical compositions of the sources in the envelope, the degree of partial melting and depth of its occurrence, and the amount of magma that is extruded onto the surface. There are, currently, only poor geophysical data in relation to the presence of magmatic sources in the upper parts of the petrographic provinces. Such data will be important to understand the fractionation crystallization along with the evolution of the chemistry of the magmas.

The major problem in the study of continental magmatism is the estimation of the role of the envelope in the genesis of primary magmas. There are some geophysical data that indicate the existence of a diapir in the envelope, which moved upwards along the axis of the rift structure. Thinning of the lithosphere in a wider area could have caused a significant enlargement of the melt zone that underlies the axis of the rift structure but is still within the envelope. Thus, the greatest influence of the envelope on the processes of partial melting was exerted in the rift zones with the greatest thinning of the crust and the greatest uplifting of the envelope.

The genesis of the volcanic rocks around Kožuf Mountain can be best explained within the evolution of the Vardar zone as a rift zone, with rifting recurring several times during its evolution.

Based on the available data relating to the magmatic activity that took place in the Vardar zone from the Oligocene to the Pleistocene, it can be assumed that this geotectonic unit was shaped by the

processes that took place in a continental rift zone (Boev and Jelenković, 2012).

The primary magmas that were formed by these processes were extruded to the surface along individual structures (which formed as a result of the evolution of the area), changing their composition by contamination and assimilation in the process. In addition, normalized values of the distribution of REEs (Figure 5) can be applied to explain the genesis of the volcanic rocks.

Figure 5 shows that there is no pronounced anomaly of Eu and no predominance of fractionation processes of primary magma materials. The change in chemical composition of the extrusive magma that yielded the series of volcanic rocks observed can be explained by the assimilation processes that the magma performed as it passed through different lithologic environments; the magma would have assimilated the existing rocks but altered its own composition as well. According to their mode of occurrence and spatial distribution, the volcanic rocks of Kožuf Mountain are riftogenic, that is, formed by magmatic activation in the marginal area between the earth's crust and the upper envelope. This can be inferred from the isotopic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, which amount from 0.7088 to 0.7090 (Boev, 1988).

The consolidation time and the occurrence of volcanic rocks in the area were calculated as being between 6.0 and 1.8 m.y. using the K/Ar method (Boev, 1988), and this is consistent with their stratigraphic age.

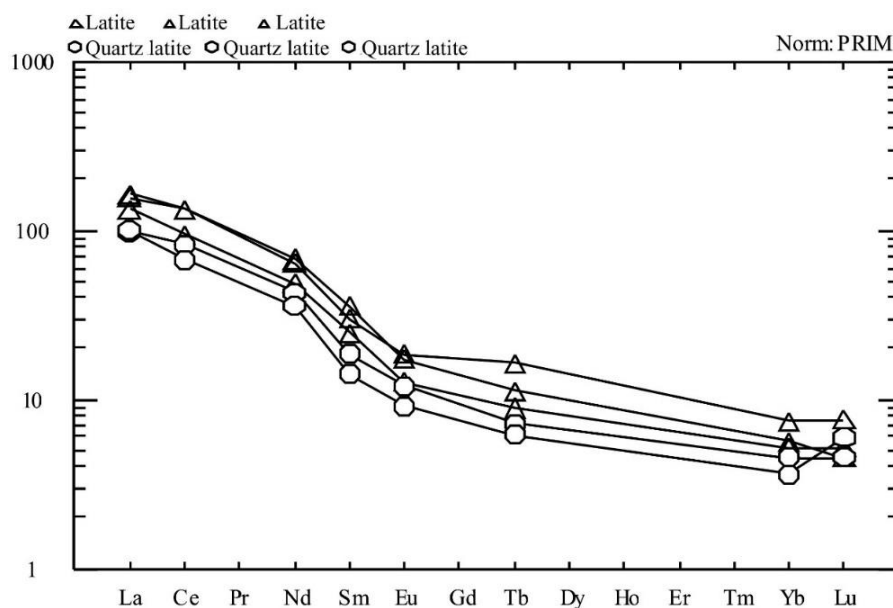


Fig. 5. The REE contents of the Kožuf Mountain volcanic rocks (Boev, 1988)

## MATERIALS AND METHODS

Ten samples were collected for mineralogical and geochemical investigation: five samples from the diatomite occurrence in the Ovčka Reka river and five samples from the tridymite layers in the locality of Majdan.

The mineralogical content of the collected samples was determined using a Siemens D 500 X-ray diffractometer equipped with an automated computer and a Cu-monochromatic X-ray tube at 40 KV and 30 mA. A Rietveld-like analysis of the X-ray spectra was performed, fitting each Bragg reflection profile with two Voigt functions for the  $K\alpha_1$  and  $K\alpha_2$  lines with the same width. The intensities of these doublets were calculated from structure factors using kinematic scattering theory and the appropriate intensity factors (Gusev and Rempel, 2004). Quantitative analysis of the mineral phases present was performed using the DIFRAC-11 software package and program support by Evaluation (EVAL) and Identification Diffraction Reflex (IDR).

REEs were analyzed at the Actlabs' facility, in Ontario, Canada. Since it is well known that REEs are among the most difficult elements to analyze properly, it was essential that the samples were ground so that 95% of the material passed through 200  $\mu\text{m}$  mesh sieve, to ensure the complete fusion of resistate minerals. The analysis required a lithium metaborate/tetraborate fusion with subsequent analysis by ICP-OES and inductively coupled plasma mass spectrometry (ICP-MS). Although the lithium metaborate-tetraborate fusion dissolution procedure has long been recognized as the best technique for ensuring that geological samples go into solution,

historically it has not been proven to be highly compatible with ICP-MS sample-introduction systems. However, research and development conducted by Actlabs into sample introduction into the ICP-MS has solved this shortfall. A robotic fusion process ensures very reproducible results, which was not possible with a manual fusion process, and highly accurate results can now be obtained in a cost-effective and rapid manner. The advantage of this procedure over XRF for major oxide analysis is that it is more matrix-independent and any rock type (including sulphide-bearing samples) can be analyzed without special calibration or pre-treatment. A mass balance was required as an additional quality control technique and elemental totals of the oxides should be between 98 and 101%. Geochemical analysis was performed by the ICP-MS technique using an Agilent 7500 (Babington type atomiser) instrument. The power of the plasma was set at 1500 W with a pump speed of 0.1 rps, an integration time of 0.3 s, and a total acquisition time of 8.0 s (Agilent Technologies, 2005).

Determination of the phase content by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) was also performed.

Eventual Eu anomalies were calculated as:

$$\text{Eu}^* = \frac{\text{Eu}_N}{\sqrt{\text{Sm}_M \cdot \text{Gd}_N}},$$

while the Ce anomaly was calculated as:

$$\text{Ce}^* = \frac{3 \cdot \text{Ce}_N}{2 \cdot \text{La}_N + \text{Nd}_N}.$$

## RESULTS AND DISCUSSION

The field investigations carried out in the Kožuf Mountain area unambiguously proved the presence of layers of volcanic glass in the vicinity of the volcanic Alšar caldera (Figure 4). These layers are about 2 m thick and the volcanic glass is white and has a porous texture. Also, field studies have proved the existence of layers of diatomite occurring within the volcanoclastic sedimentary rocks (tuffs and volcanic conglomerates) (Figure 6).

The layers of diatomite have thicknesses between 0.5 and 1.0 m and also have a porous texture and white colour. Tests made using the XRD method on volcanic glass samples show that this is a high temperature modification of the  $\text{SiO}_2$  com-

pound tridymite (Figure 7), with a small amount of cristobalite and muscovite.

The chemical composition is close to the stoichiometric composition of quartz. XRD studies of the diatomite samples (Figure 8) show them to be sediment with a larger amount of quartz in its composition.

SEM and EDS examinations of volcanic glass samples (Figure 9) show that it has an exceptionally porous structure with pronounced elements remaining from pre-crystallization.

As it may be seen from the results above the composition of the tridymite slightly deviates from

the ideal composition of 46.74% Si and 53.26% O in favour of oxygen.

Studies performed using the SEM-EDS method (Figure 10) show that it is an organic sediment

(there is a huge presence of fossil algae-diatoms) whose chemical composition is very close to that of quartz.



Fig. 6. Tridymite layer of Kožuf Mountain

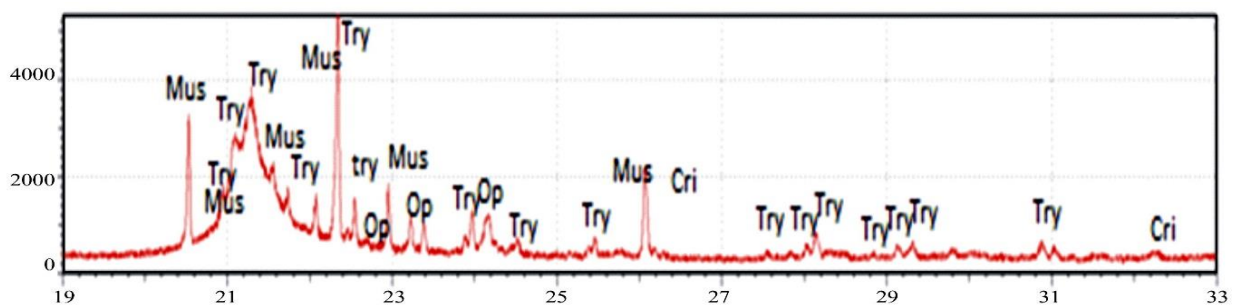


Fig. 7. XRD of tridymite from Kožuf Mountain



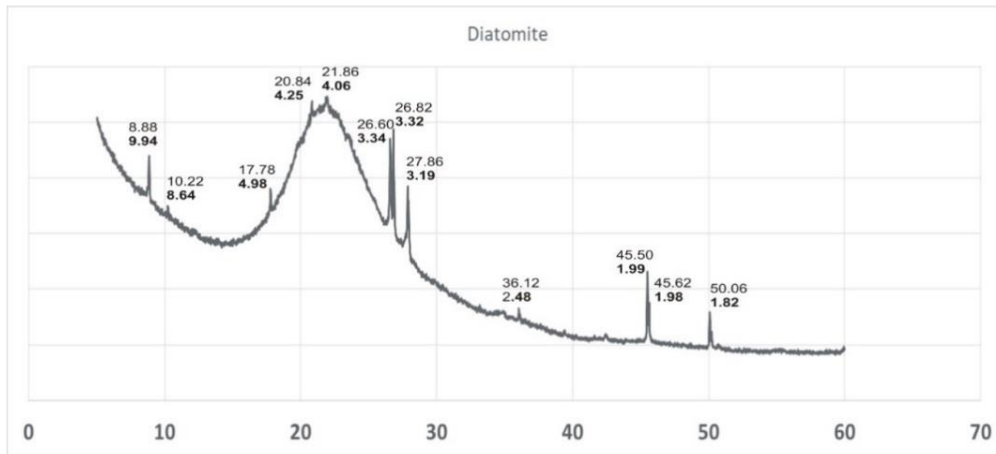
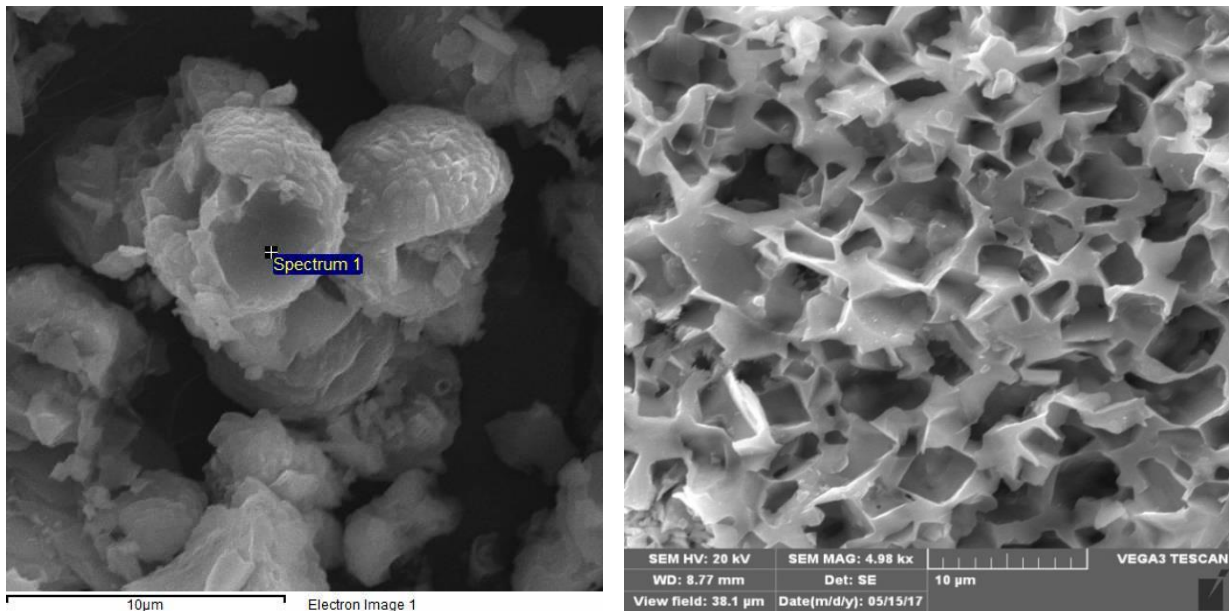


Fig. 8. XRD of diatomite from Kožuf Mountain



Element	Weight %	Atomic %
O K	49.71	63.44
Si K	50.29	36.56
Totals	100.00	100.00

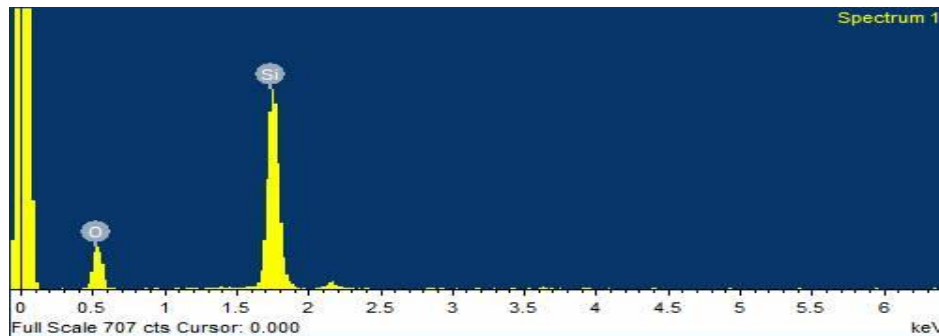
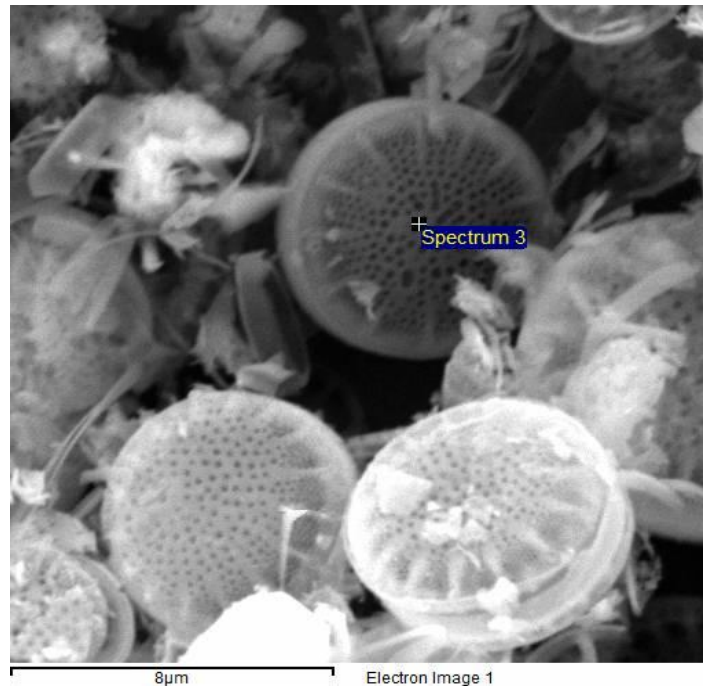
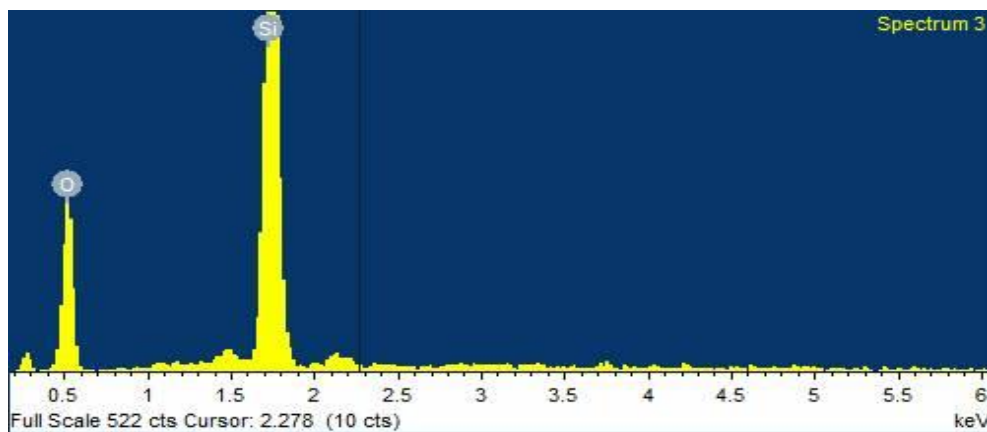


Fig. 9. SEM-EDS of tridymite from Kožuf Mountain



Element	Weight %	Atomic %
O K	54.70	67.95
Si K	45.30	32.05
Totals	100.00	100.00



**Fig.10.** SEM-EDS of diatomite from Kožuf Mountain

Among the remains of fossil algae-diatoms, the presence of volcanic dust (Figure 11) with a composition very close to that of volcanic rocks has been found.

The results obtained by the study of the geochemical composition of volcanic glass (tridymite) through the application of the ICP-MS-FUS method are shown in Table 1. The results obtained indicate that these two sediments have very similar geochemical compositions, which leads to the conclusion

that volcanic activity also had an important role in the formation of diatomites.

As it can be seen from above  $\text{SiO}_2$  showed average values of 90.17%, which compared with an average values of Cerro San Cristobal deposits in Mexico (Fronzel, 1962) and Mule Springs in Oregon, USA (Deer et al., 1963), with 95.1% and 99.03%  $\text{SiO}_2$  respectively, showed slight decrease. All other oxides  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$  manifested concentrations quite similar to



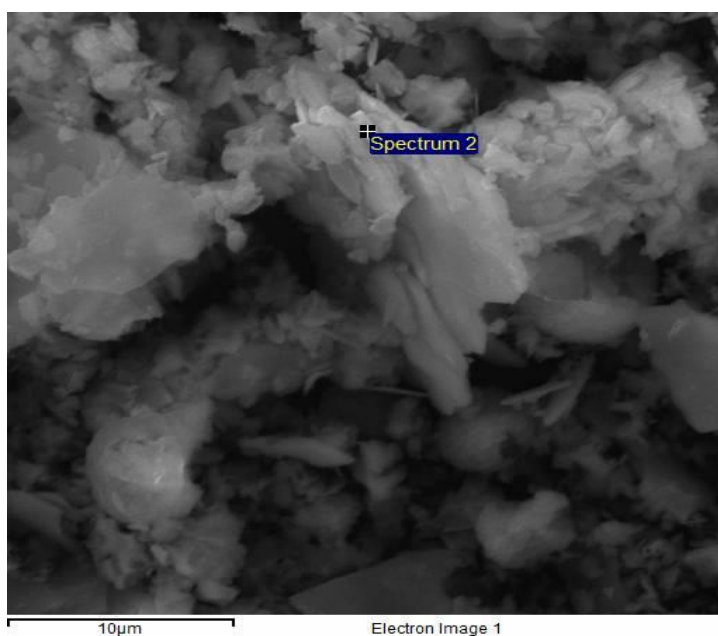
those of Cerro San Cristobal and Mule Springs (Frondele, 1962; Deer et al., 1963).

The results obtained by the study of the geochemical composition of the diatomite through the application of the ICP-MS-FUS method are shown in Table 2.

As it can be seen from above  $\text{SiO}_2$  showed average values of 89.8%, which compared with and average values of several World's deposits (Danil de Namor et al., 2012) of 75.3%,  $\text{SiO}_2$  is a signifi-

cant increase while the most similar in this regard are diatomite deposits near Guandong and Shenzhou in China. Due to the fact that  $\text{SiO}_2$  was significantly increased all other oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$  etc.) manifested concentrations of several magnitudes lower compared to some other deposits (Danil de Namor et al., 2012).

Table 3 below shows the correlation coefficients that have been obtained based on the determined geochemical composition.



Element	Weight %	Atomic %
O K	58.32	71.50
Mg K	1.83	1.48
Al K	11.46	8.33
Si K	22.63	15.81
K K	5.75	2.88
Totals	100.00	100.00

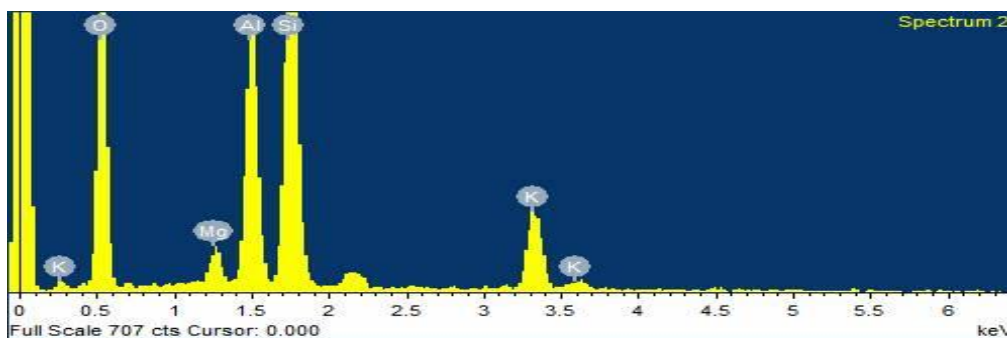


Fig.11. SEM-EDS of volcanic ash from Kožuf Mountain

Table 1

*Chemical and geochemical composition of tridymite from Alšar caldera (ICP-FUS-MS)*

Analyte symbol	Unit symbol	M1	M2	M3	M4	M5
SiO <sub>2</sub>	%	87.84	91.46	90.16	90.66	90.75
Al <sub>2</sub> O <sub>3</sub>	%	2.77	1.36	2.17	1.18	1.48
Fe <sub>2</sub> O <sub>3</sub> (T)	%	0.45	0.31	0.31	0.28	0.29
MnO	%	0.005	0.004	0.003	0.003	0.004
MgO	%	0.2	0.19	0.27	0.18	0.2
CaO	%	0.16	0.14	0.12	0.13	0.11
Na <sub>2</sub> O	%	0.78	0.12	0.14	0.1	0.13
K <sub>2</sub> O	%	0.72	0.41	0.71	0.35	0.44
TiO <sub>2</sub>	%	0.046	0.048	0.095	0.041	0.046
P <sub>2</sub> O <sub>5</sub>	%	< 0.01	< 0.01	0.01	< 0.01	< 0.01
LOI	%	5.82	6.4	6.15	6.36	6.05
<b>Total</b>	<b>%</b>	<b>98.79</b>	<b>100.4</b>	<b>100.1</b>	<b>99.28</b>	<b>99.51</b>
Sc	ppm	< 1	< 1	< 1	< 1	< 1
Be	ppm	29	31	33	27	26
V	ppm	9	10	16	12	13
Cr	ppm	< 20	< 20	20	< 20	< 20
Co	ppm	< 1	< 1	< 1	< 1	< 1
Ni	ppm	< 20	< 20	< 20	< 20	< 20
Cu	ppm	< 10	< 10	< 10	< 10	< 10
Zn	ppm	< 30	< 30	< 30	< 30	< 30
Ga	ppm	3	2	3	1	2
Ge	ppm	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
As	ppm	9	7	7	7	12
Rb	ppm	18	13	24	12	15
Sr	ppm	6	4	4	4	4
Y	ppm	0.8	< 0.5	0.6	< 0.5	< 0.5
Zr	ppm	16	15	24	15	16
Nb	ppm	1	1.1	2.1	1	1.1
Mo	ppm	< 2	< 2	< 2	< 2	< 2
Ag	ppm	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
In	ppm	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sn	ppm	< 1	< 1	< 1	< 1	< 1
Sb	ppm	2.7	2.9	3.2	2.8	3
Cs	ppm	1	1	1.3	1.1	1.4
Ba	ppm	23	22	34	23	30
La	ppm	0.36	0.17	0.17	0.14	0.15
Ce	ppm	1.17	0.91	1	0.87	0.91
Pr	ppm	0.09	0.04	0.05	0.04	0.04

Analyte symbol	Unit symbol	M1	M2	M3	M4	M5
Nd	ppm	0.35	0.2	0.3	0.31	0.23
Sm	ppm	0.09	0.04	0.07	0.06	0.04
Eu	ppm	0.021	0.009	0.008	0.006	0.006
Gd	ppm	0.12	0.06	0.07	0.05	0.05
Tb	ppm	0.02	< 0.01	0.01	< 0.01	< 0.01
Dy	ppm	0.1	0.04	0.07	0.05	0.06
Ho	ppm	0.02	0.01	0.02	0.01	0.01
Er	ppm	0.07	0.04	0.06	0.05	0.05
Tm	ppm	0.013	0.007	0.012	0.01	0.009
Yb	ppm	0.11	0.06	0.09	0.08	0.07
Lu	ppm	0.018	0.009	0.017	0.014	0.012
Hf	ppm	0.4	0.3	0.6	0.4	0.4
Ta	ppm	0.07	0.05	0.12	0.08	0.05
W	ppm	0.7	0.8	1.9	1.7	3.7
Tl	ppm	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Pb	ppm	< 5	< 5	< 5	< 5	< 5
Bi	ppm	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Th	ppm	0.14	0.08	0.17	0.1	0.06
U	ppm	1.11	1.11	1.4	1.06	1.08

Table 2

*Geochemical analyses of diatomite from Kožuf Mountain (ICP-MS-FUS method)*

Analyte	Unit	Detection limit	Analysis method	D1	D2	D3	D4	D5
SiO <sub>2</sub>	%	0.01	FUS-ICP	89.68	89.72	89.15	90.21	90.47
Al <sub>2</sub> O <sub>3</sub>	%	0.01	FUS-ICP	0.61	0.63	0.64	0.62	0.62
Fe <sub>2</sub> O <sub>3</sub> (T)	%	0.01	FUS-ICP	0.22	0.25	0.23	0.28	0.24
MnO	%	0.001	FUS-ICP	0.005	0.007	0.005	0.004	0.005
MgO	%	0.01	FUS-ICP	0.07	0.07	0.07	0.07	0.07
CaO	%	0.01	FUS-ICP	0.22	0.23	0.2	0.21	0.2
Na <sub>2</sub> O	%	0.01	FUS-ICP	0.09	0.1	0.1	0.09	0.1
K <sub>2</sub> O	%	0.01	FUS-ICP	0.11	0.11	0.11	0.11	0.12
TiO <sub>2</sub>	%	0.001	FUS-ICP	0.03	0.031	0.031	0.031	0.03
P <sub>2</sub> O <sub>5</sub>	%	0.01	FUS-ICP	0.03	0.04	0.03	0.03	0.03
LOI	%		FUS-ICP	9.16	9.21	9.1	9.01	8.89
<b>Total</b>	<b>%</b>	<b>0.01</b>	<b>FUS-ICP</b>	<b>100.2</b>	<b>100.4</b>	<b>99.67</b>	<b>100.7</b>	<b>100.8</b>
Sc	ppm	1	FUS-ICP	< 1	< 1	< 1	< 1	< 1
Be	ppm	1	FUS-ICP	1	1	1	1	1
V	ppm	5	FUS-ICP	26	24	22	25	25
Cr	ppm	20	FUS-MS	< 20	< 20	< 20	< 20	< 20
Co	ppm	1	FUS-MS	< 1	< 1	< 1	< 1	< 1

Analyte	Unit	Detection limit	Analysis method	D1	D2	D3	D4	D5
Ni	ppm	20	FUS-MS	< 20	< 20	< 20	< 20	< 20
Cu	ppm	10	FUS-MS	< 10	< 10	< 10	< 10	< 10
Zn	ppm	30	FUS-MS	< 30	< 30	< 30	< 30	< 30
Ga	ppm	1	FUS-MS	< 1	< 1	< 1	< 1	< 1
Ge	ppm	0.5	FUS-MS	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
As	ppm	5	FUS-MS	< 5	< 5	< 5	< 5	< 5
Rb	ppm	1	FUS-MS	6	6	7	7	7
Sr	ppm	2	FUS-ICP	17	17	16	17	16
Y	ppm	0.5	FUS-MS	3.9	4.1	4	3.6	3.7
Zr	ppm	1	FUS-ICP	24	27	26	24	25
Nb	ppm	0.2	FUS-MS	4.8	5	4.8	4.6	4.5
Mo	ppm	2	FUS-MS	< 2	< 2	< 2	3	< 2
Ag	ppm	0.5	FUS-MS	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
In	ppm	0.1	FUS-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sn	ppm	1	FUS-MS	< 1	< 1	< 1	< 1	< 1
Sb	ppm	0.2	FUS-MS	4.1	3.9	3.3	3.6	3.6
Cs	ppm	0.1	FUS-MS	2.5	2.7	2.8	2.8	2.6
Ba	ppm	2	FUS-ICP	50	51	49	49	48
La	ppm	0.05	FUS-MS	3.38	3.53	3.33	3.18	3.31
Ce	ppm	0.05	FUS-MS	3.7	3.86	3.67	3.37	3.58
Pr	ppm	0.01	FUS-MS	0.61	0.62	0.62	0.56	0.59
Nd	ppm	0.05	FUS-MS	2.43	2.74	2.42	2.34	2.32
Sm	ppm	0.01	FUS-MS	0.48	0.47	0.46	0.37	0.39
Eu	ppm	0.005	FUS-MS	0.074	0.065	0.087	0.071	0.07
Gd	ppm	0.01	FUS-MS	0.36	0.43	0.4	0.4	0.36
Tb	ppm	0.01	FUS-MS	0.06	0.07	0.07	0.06	0.06
Dy	ppm	0.01	FUS-MS	0.44	0.4	0.44	0.36	0.36
Ho	ppm	0.01	FUS-MS	0.09	0.09	0.1	0.08	0.08
Er	ppm	0.01	FUS-MS	0.3	0.31	0.31	0.27	0.28
Tm	ppm	0.005	FUS-MS	0.049	0.046	0.047	0.046	0.043
Yb	ppm	0.01	FUS-MS	0.34	0.29	0.32	0.31	0.28
Lu	ppm	0.002	FUS-MS	0.058	0.049	0.053	0.052	0.044
Hf	ppm	0.1	FUS-MS	0.2	0.3	0.2	0.1	0.2
Ta	ppm	0.01	FUS-MS	0.02	0.05	0.03	0.01	0.01
W	ppm	0.5	FUS-MS	< 0.5	0.6	< 0.5	< 0.5	< 0.5
Tl	ppm	0.05	FUS-MS	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Pb	ppm	5	FUS-MS	6	< 5	< 5	< 5	< 5
Bi	ppm	0.1	FUS-MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Th	ppm	0.05	FUS-MS	0.67	0.68	0.69	0.65	0.63
U	ppm	0.01	FUS-MS	2.39	2.23	2.07	2.29	2.42

Table 3

*Correlation coefficients for REE in diatomite and tridymite  
(significant interelemental correlations pointed by red color)*

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1													
Ce	0.999	1												
Pr	0.999	0.999	1											
Nd	0.998	0.997	0.996	1										
Sm	0.990	0.994	0.993	0.991	1									
Eu	0.979	0.979	0.985	0.970	0.976	1								
Gd	0.991	0.991	0.991	0.992	0.980	0.977	1							
Tb	0.992	0.993	0.993	0.992	0.987	0.984	0.996	1						
Dy	0.989	0.992	0.993	0.986	0.996	0.988	0.981	0.988	1					
Ho	0.989	0.992	0.993	0.988	0.994	0.989	0.986	0.992	0.996	1				
Er	0.997	0.999	0.999	0.997	0.996	0.983	0.990	0.994	0.996	0.996	1			
Tm	0.994	0.994	0.995	0.992	0.991	0.983	0.987	0.986	0.994	0.992	0.996	1		
Yb	0.986	0.985	0.989	0.982	0.987	0.986	0.979	0.979	0.994	0.989	0.989	0.997	1	
Lu	0.978	0.978	0.981	0.976	0.984	0.977	0.972	0.971	0.991	0.985	0.983	0.994	0.998	1

As it can be seen all the REE elemental pairs showed high positive correlations: La–Pr (0.999), Ce–Pr (0.999), Pr–Er (0.999), Nd–Er (0.997), Sm–Er (0.996), Eu–Ho (0.989), Gd–Tb (0.996), Tb–Er (0.994), Dy–Ho (0.996), Ho–Er (0.996), Er–Dy (0.996), Tm–Yb (0.997) and Yb–Lu (0.998). Some of the most representative correlations are shown in Figure 12.

Table 4 shows the content of the REEs in the diatomite sediment and tridymite sediment, while Table 5 presents the normalized values of the REE.

The REE content, relative enrichment of light rare earth elements (LREE) content, and high content of large ion lithophile (LIL) elements indicate that the primary melt consisted of crystallized garnet (conformable with a residual plagioclase melt). The pressure in such systems amounts to some 15 kb (equivalent to depths of 45 to 50 km).

From geophysical data obtained from the continental crust beneath Kožuf, it can be inferred that the crust is approximately 40 km thick.

Based on the aforementioned data a conclusion can be drawn that magma sources were located in the marginal region between the upper envelope and the lower crust, taking into consideration erosional processes over a period of several million years (Boev and Jelenković, 2012).

Trace elements, especially REEs, are widely used to model the petrogenesis and evolution of igneous, sedimentary and metamorphic rocks (Haskin, 1984; Fleet, 1984); REEs are generally regarded as being insensitive to hydrothermal alteration. However, the body of literature supporting REE mobility during hydrothermal processes has been rapidly increasing over the last two decades (Nesbitt, 1979; Alderton et al., 1980; Humphris, 1984; Marsh, 1991; Bau, 1991; Williams-Jones and Wood, 1992; Gouveia et al., 1993; Mongelli, 1993; Prudencio et al., 1993; Van der Weijden and Van der Weijden, 1995).

Recently, the potential of REEs to provide information about ore-forming processes (through REE mobility or immobility) has been widely recognized, and detailed REE investigations have been performed on many metallic deposits (Taylor and Fryer, 1980; Campbell et al., 1984; Giere, 1986; Lottermoser, 1992; Parr, 1992; Wood and Williams-Jones, 1994; Bierlein, 1995; Bierlein et al., 1999). The distribution and mobility of trace elements in the altered host rock and its ores may be able to indicate the constraints regarding the physico-chemical characteristics of the ore-bearing fluids and may also contribute to our understanding of the ore-forming processes (Lottermoser, 1992).



REE contents in diatomite (D1–D5) and tridymite (T1–T5) were normalized to the chondrite standard value of REEs as quoted from the data of Boynton (1984). The abundance, characteristic parameters and distribution pattern of REEs in the five

samples analyzed from the area of Kožuf Mountain are distinctive (Table 5 and Figure 13).

The distribution trends are shown as log-normalized REE abundances versus the atomic numbers of the REEs (Figure 13).

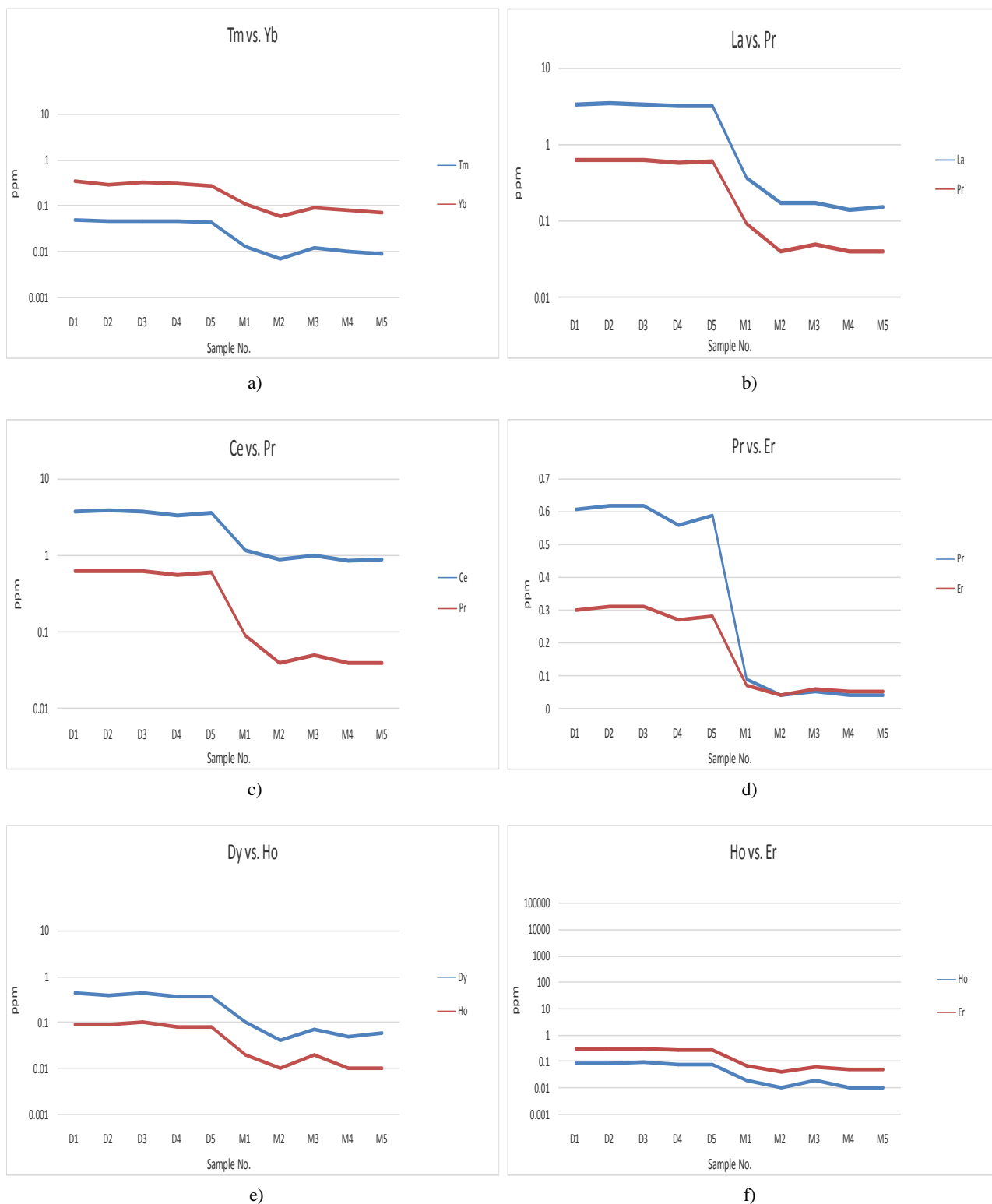


Fig. 12. The most representative elemental correlation pairs, diatomite sediment/tridymite sediment

Table 4

*REEs in diatomite and tridymite in the area around Kožuf Mountain (by FUS-MS; in ppm).*

Sample	D1	D2	D3	D4	D5	M1	M2	M3	M4	M5
La	3.38	3.53	3.33	3.18	3.31	0.36	0.17	0.17	0.14	0.15
Ce	3.7	3.86	3.67	3.37	3.58	1.17	0.91	1	0.87	0.91
Pr	0.61	0.62	0.62	0.56	0.59	0.09	0.04	0.05	0.04	0.04
Nd	2.43	2.74	2.42	2.34	2.32	0.35	0.2	0.3	0.31	0.23
Sm	0.48	0.47	0.46	0.37	0.39	0.09	0.04	0.07	0.06	0.04
Eu	0.074	0.065	0.087	0.071	0.07	0.021	0.009	0.008	0.006	0.006
Gd	0.36	0.43	0.4	0.4	0.36	0.12	0.06	0.07	0.05	0.05
Tb	0.06	0.07	0.07	0.06	0.06	0.02	0.01	0.01	0.01	0.01
Dy	0.44	0.4	0.44	0.36	0.36	0.1	0.04	0.07	0.05	0.06
Ho	0.09	0.09	0.1	0.08	0.08	0.02	0.01	0.02	0.01	0.01
Er	0.3	0.31	0.31	0.27	0.28	0.07	0.04	0.06	0.05	0.05
Tm	0.049	0.046	0.047	0.046	0.043	0.013	0.007	0.012	0.01	0.009
Yb	0.34	0.29	0.32	0.31	0.28	0.11	0.06	0.09	0.08	0.07
Lu	0.058	0.049	0.053	0.052	0.044	0.018	0.009	0.017	0.014	0.012
Hf	0.2	0.3	0.2	0.1	0.2	0.4	0.3	0.6	0.4	0.4
Ta	0.02	0.05	0.03	0.01	0.01	0.07	0.05	0.12	0.08	0.05
W	0.5	0.6	0.5	0.5	0.5	0.7	0.8	1.9	1.7	3.7
Tl	0.05	0.05	0.05	0.05	0.04	0.05	0.05	0.05	0.05	0.05
Pb	6	5	5	5	5	5	5	5	5	5
Bi	0.1	0.1	0.1	0.1	0.1	0.1	0.09	0.1	0.1	0.1
Th	0.67	0.68	0.69	0.65	0.63	0.14	0.08	0.17	0.1	0.06
U	2.39	2.23	2.07	2.29	2.42	1.11	1.11	1.4	1.06	1.08

Table 5

*The REE results from the area of Kožuf Mountain were normalized using the average C1 chondrite abundances of Boynton (1984)*

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
D1	10.90	4.58	5.00	4.05	2.46	1.01	1.39	1.27	1.37	1.25	1.43	1.51	1.63	1.8
D2	11.39	4.78	5.08	4.57	2.41	0.88	1.66	1.48	1.24	1.25	1.48	1.42	1.39	1.52
D3	10.74	4.54	5.08	4.03	2.36	1.18	1.54	1.48	1.37	1.39	1.48	1.45	1.53	1.65
D4	10.26	4.17	4.59	3.90	1.90	0.97	1.54	1.27	1.12	1.11	1.29	1.42	1.48	1.61
D5	10.68	4.43	4.84	3.87	2.00	0.95	1.39	1.27	1.12	1.11	1.33	1.33	1.34	1.37
M1	1.16	1.45	0.74	0.58	0.46	0.29	0.46	0.42	0.31	0.28	0.33	0.4	0.53	0.56
M2	0.55	1.13	0.33	0.33	0.21	0.12	0.23	0.21	0.12	0.14	0.19	0.22	0.29	0.28
M3	0.55	1.24	0.41	0.50	0.36	0.11	0.27	0.21	0.22	0.28	0.29	0.37	0.43	0.53
M4	0.45	1.08	0.33	0.52	0.31	0.08	0.19	0.21	0.16	0.14	0.24	0.31	0.38	0.43
M5	0.48	1.13	0.33	0.38	0.21	0.08	0.19	0.21	0.19	0.14	0.24	0.28	0.33	0.37

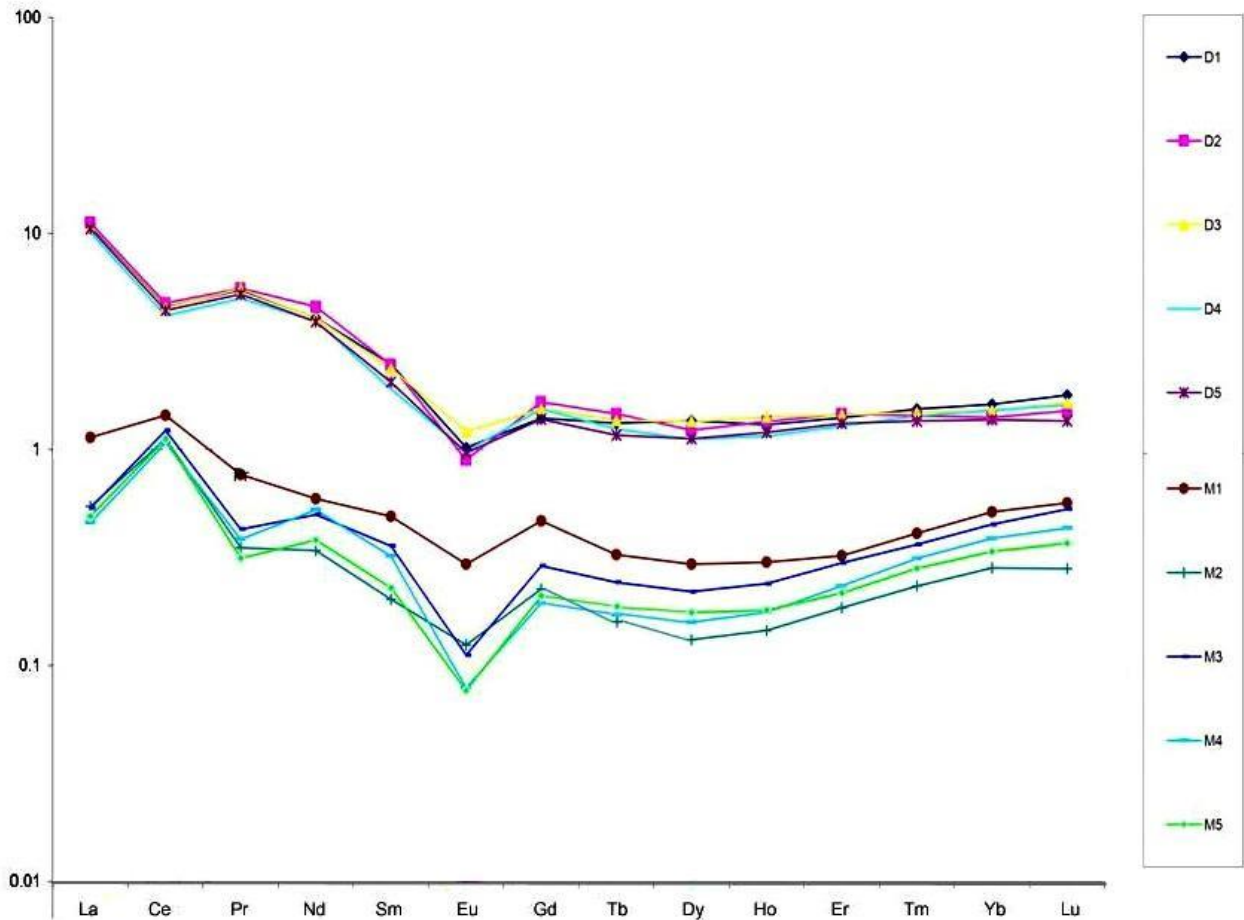


Fig. 13. REE normalized plots of diatomite and tridymite from the area of Kožuf Mountain

Higher REE contents were found for diatomite in comparison to tridymite, which sometimes were even ten times higher. Namely, the  $\Sigma\text{REE}$  in diatomite is higher ( $\Sigma\text{REE}_{\text{diatomite}} = \sim 36.63\text{--}40.55$  ppm) than that in tridymite ( $\Sigma\text{REE}_{\text{tridymite}} = \sim 4.14\text{--}7.97$  ppm) while the ratio of the sum of LREEs to the sum of heavy rare earth elements (HREEs) for both was  $\Sigma\text{LREE}/\Sigma\text{HREE} = \sim 1.219\text{--}2.609$  and  $\text{La}_N/\text{Yb}_N = \sim 1.184\text{--}8.194$ . The distribution patterns belong to the “LREE enriched” type. Specifically, the fractionation is obvious for the LREE ( $\text{La}_N/\text{Sm}_N = \sim 1.452\text{--}5.400$ ) but not obvious for the HREE ( $\text{Gd}_N/\text{Yb}_N = \sim 0.5000\text{--}1.194$ ). Further calculations showed a negative Eu anomaly for both diatomite and tridymite, while Ce showed negative anomalies for diatomite and positive ones for tridymite (Table 6).

As can be seen, Eu showed a negative anomaly for both diatomite and tridymite ( $\text{Eu}^* = \sim 0.3296\text{--}0.6190$ , with an average of 0.5430), while Ce showed a transition from a positive anomaly for tridymite to a negative one for diatomite ( $\text{Ce}_{\text{tridymite}}^* = \sim 1.500\text{--}2.5299$  and  $\text{Ce}_{\text{diatomite}}^* = \sim 0.5123\text{--}0.5339$ ).

Table 6

Calculated Eu and Ce anomalies for the area of Kožuf Mountain

Sample	Eu anomaly	Ce anomaly
D1	0.5462	0.5315
D2	0.4400	0.5243
D3	0.6190	0.5339
D4	0.5671	0.5123
D5	0.5698	0.5268
M1	0.6304	1.5000
M2	0.5460	2.3706
M3	0.3528	2.3250
M4	0.3296	2.2817
M5	0.4005	2.5299

This indicates that the weak, negative Ce anomalies and negative Eu anomalies (Table 6) suggest a reducing, ore-forming environment (Bau, 1991), probably after an initial oxidizing stage. The negative Eu anomaly in tridymite probably reflects the fact that Eu may be leached out of footwall rocks

in the hottest part of the hydrothermal system (Gale et al., 1997). Negative Ce anomaly in diatomite (a depletion in Ce relative to La and Nd) end slight upward enrichment in heavy REE's relative to light REE's shows patterns representative for sea water (DeBaar et al., 1985).

## CONCLUSION

The tridymite with approximately 85% SiO<sub>2</sub>, diatomite with about 90% SiO<sub>2</sub> and volcanic ash with about 30% SiO<sub>2</sub> are dominant in the composition of the studied diatomite-bearing tuffs at Kožuf Mountain. The studied trace elements in the tridymite and diatomite showed low concentration of the elements characteristic of the Kožuf volcanic region such are Sb-As-V and others, as well as Zr, Ba, Be, Sr characteristic for volcanic Pliocene tuffs.

As it was seen from the REE data, relative enrichment of LREE and high content of LIL elements indicated primary melt mainly composed of crystallized garnet and pressures of those systems probably were approximately 15 kb (~ depths of 45 to 50 km).

The rare earth elements exhibit a mild anomaly of the europium, which has a negative tendency in both the diatomite and tridymite ( $Eu^* = \sim 0.3296-0.6190$ ), probably pointing out that Eu may be leached out of footwall rocks in the hottest part of the particular hydrothermal system (Gale et al., 1997). Opposite, Ce showed a transition from a positive anomaly for tridymite to a negative one for diatomite ( $Ce_{\text{tridymite}}^* = \sim 1.500-2.5299$  and  $Ce_{\text{diatomite}}^* = \sim 0.5123-0.5339$ ), which suggests a reducing, ore-forming environment (Bau, 1991), probably after an initial oxidizing stage. All REEs in tridymite and diatomite are strongly correlated among themselves, with all correlation coefficients equal or higher than 0.97.

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## Резиме

**ВУЛКАНСКАТА АКТИВНОСТ НА ПЛАНИНАТА КОЖУФ И ИМПЛИКАЦИИТЕ ЗА ДИСТРИБУЦИЈАТА НА ЕЛЕМЕНТИТЕ НА РЕТКИ ЗЕМЈИ ВО ДИЈАТОМИТИТЕ И ТРИДИМИТИТЕ****Иван Боев<sup>1</sup>, Горан Тасев<sup>1</sup>, Далибор Серафимовски<sup>1</sup>, Блажо Боев<sup>1</sup>**<sup>1</sup>*Факултетот за природни и технички науки, Универзитетот „Гоце Делчев“ во Штип,  
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blazo.boev@ugd.edu.mk***Клучни зборови:** дијатомити; тридимити; елементи на ретки земји; планина Кожуф

Во овој труд се претставени резултатите од истражувањата на дистрибуцијата на елементите на ретки земји (REE) во дијатомитите и тридимитите од вулканската област на планината Кожуф. Ретките земји содржат петнаесет хемиски елементи, од лантан до лутециум (атомските броеви 57–71), кои се карактеризираат со слични хемиски својства. Заради проучување на нивната дистрибуција беа земени примероци од дијатомитите на Витачево и тридимитските седименти во Алшар, кои беа подложени на анализа со примена на масена спектрометрија со индуктивно спрегната плазма (ICP-MS). Кривите на хондритски нормализираните вредности покажуваат збогатување на REE со

лесни елементи (LREE), негативна аномалија на еуро-пиумот (Eu) во сите примероци, како и прогресивно осиромашување со тешки елементи (HREE). Разгледани се две хипотези: природата на матичните карпи на седиментите (вулкански карпи од планината Кожуф) и физичко-хемиските услови на седиментацијата, особено феномените на комплексирање и оксидо-редукција. Постои силна корелација помеѓу дистрибуцијата на елементите на ретките земји (REE) во вулканските карпи и дистрибуцијата на елементите на ретките земји во седиментните дијатомити и киселите вулканити (тридимити).