Preliminary data for the Kushla rectorite mud, Eastern Rhodopes, Bulgaria

Първоначални данни за ректоритовата глина от с. Кушла, Източни Родопи

Mariana Yossifova[1], Stoyan Georgiev[1], Stefan Marinov[2], Maya Stefanova[2], Sevdalina Valcheva[3]
Мариана Йосифова[1], Стоян Георгиев[1], Стефан Маринов[2], Мая Стефанова[2], Севдалина Вълчева[3]

[1] Geological Institute, BAS, Acad. G. Bonchev str., bl. 24, 1113 Sofia, Bulgaria; E-mail: mariana@geology.bas.bg
[2] Institute of Organic Chemistry with Centre of Phitochemistry, BAS, 1113 Sofia, Bulgaria; E-mail: stif@orgchm.bas.bg
[3] Sofia University “St. Kliment Ohridski”, 15 Tzar Osvoboditel Blvd., 1504 Sofia, Bulgaria; E-mail: sevdan@abv.bg

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Since the early days, clays have been used for therapeutic purposes. Nowadays, they are used as active ingredients or as excipient in formulations for a variety of purposes. Despite their wide use, little information is available in literature on their content of trace elements and radionuclides (Silva et al., 2011). Such is the case with the so called “mumiyo” outcropping near to Kushla village (Eastern Rhodopes), which local people have mined and used for generations. They get it orally or as an external medicine. Recently, some Bulgarian mass media popularized it. In this work we present for the first time its mineral and chemical composition in order to constrain better its medical features and possible application.

Eastern Rhodopes were the scene of wide spread volcanic activity during the Paleogene. The Lower Oligocene Kushla caldera is located to the south of the town of Zlatograd (at the border area of Bulgaria and Greece) and represents one of the most prominent volcanic explosive activities in the region (Georgiev et al., 2010). The studied mud-bearing zones represent lens-like bodies (with dimensions up to 10 m in lateral and vertical directions) that are hosted in the moderately to densely welded rhyolitic ignimbrites connected with the main paroxysmal caldera-forming eruption.

A composite sample (1 kg) is taken from one of the occurrences near to the village of Kushla. Mineralogical investigations on 5 samples were performed by powder X-ray diffraction (XRD) using a diffractometer with Ni-filtred CuKα radiations at Institute of Mineralogy and Crystallography – BAS. Sixteen pieces were studied by binocular microscope and scanning electron microscopy (SEM) performed on JOEL Superbrobe 733 equipped with EDS at Geological Institute – BAS. The elemental concentrations were determined using X-ray fluorescence (XRF) at ETH Zurich and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at Geological Institute – BAS. The C_{total} were determined by high temperature burning at 1371 °C and infrared detection at Eurotest Control JSC. The S_{total}, ash yield and moisture were analysed by standard methods at Institute of Organic Chemistry with Centre of Phytochemistry – BAS.

The studied mud is a black-colored earthy dull bonded, plastic when it is wet matter (Fig. 1). It characterizes with 89.68 wt% ash yield, 4.71% moisture and 2.3% total carbon.

The major mineral constituent identified in the mud is rectorite (Fig. 2). The other phases that were established have a subordinate presence. Quartz, illite, montmorillonite, K-feldspar and calcite were identified by XRD and Mn-oxide/hydroxide or carbonate with impurities of Fe, Fe-oxide/hydroxide or carbonate and glass spheres were identified by electron microprobe analyses. The quartz, Mn-bearing phase,

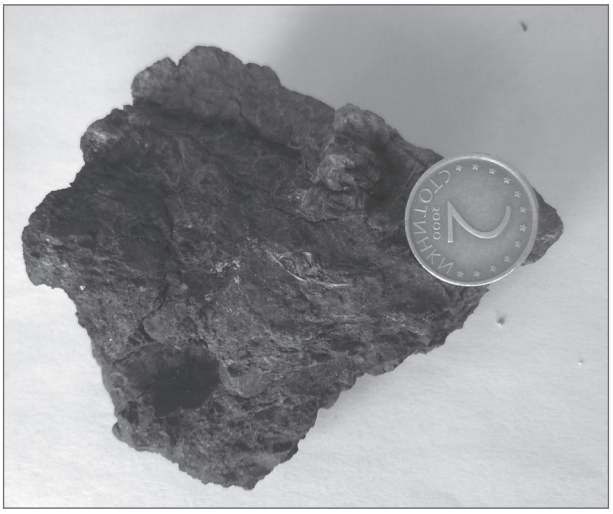

Fig 1. Photograph image of the Kushla mud

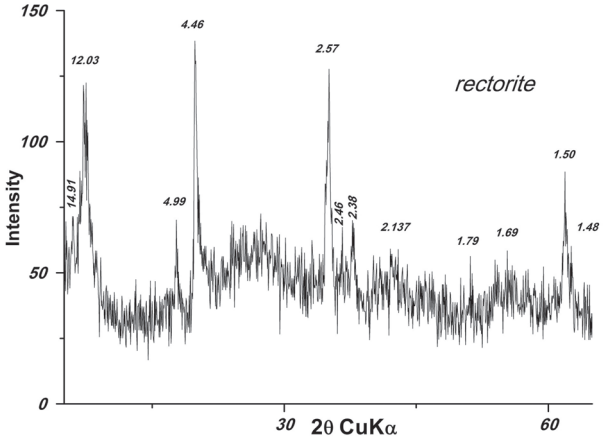

Fig 2. X-ray powder diffraction pattern of the Kushla mud

Fe-bearing phase and spheres were observed as lenses or individual grains. In Bulgaria, rectorite has been found for the first time in acid volcanic rocks from the Eastern Rhodopes Mountain (Stefanov, Yanev, 1979) and later (Stefanov, Bahneva, 1989) from hydrothermally argillized rhyolites exposed to the west of the town of Smolyan, Central Rhodopes.

Table1. Elemental content in the Kushla mud

Major elements, wt %		Trace elements, ppm			
SiO_2	47.07	Be	6.96	Ce	127.4
TiO_2	0.87	Sc	16.9	Pr	11.26
Al_2O_3	27.31	V	139.6	Nd	38.97
Fe_2O_3	4.10	Cr	28.1	Sm	7.18
MnO	0.16	Co	12.1	Eu	1.62
MgO	1.30	Ni	11.8	Gd	6.83
CaO	1.95	Cu	18.4	Tb	1.02
Na_2O	1.63	Zn	85.2	Dy	6.26
K_2O	6.21	Ga	25.7	Ho	1.24
P_2O_5	0.74	As	1.4	Er	3.56
LOI*	10.18	Rb	363.9	Tm	0.54
Total	101.50	Sr	74.7	Yb	3.75
C_{total}	2.30	Y	41.56	Lu	0.53
S_{total}	0.12	Zr	280.9	Hf	6.75
		Nb	17.03	Ta	1.14
		Mo	47.8	W	4.94
		Cs	53.9	Pb	22.1
		Ba	280.9	Th	25.2
		La	64.8	U	23.1

*LOI – loss on ignition at 1050 °C

The mineral and organic compositions of the Kushla mud differs it from the classical mumiyo or shilajit, that is not a rock but a complex mixture of organic humic substances, plant and microbial metabolites occurring in the rock rhizospheres (Ghosal, 1993) and has a total mass loss in air amounts to 67.6% (Wilson et al., 2011).

The sample studied was analysed for 50 chemical elements (Table 1). The major elements (>1% by weight) are Si, Al, K, Fe, C and Ca, and the minor elements are Mg, Ti, P, S, Na and Mn (0.1–1%). All elemental concentrations were compared with the published data for world clays by Grigoriev (2009). Most of the elements have a coefficient of concentration (CC) <2 while some of them show higher concentrations, especially Mo (CC 30), U (5.4), Cs (4.2), P (4.1), Rb (2.7), and Be (2.3).

The Kushla mud (known from the local people as "mumiyo") is represented by dominant amount of rectorite. Considering the presence of carbonate minerals, the presence of low content <2.3% of organic carbon can be supposed. Because of the increased amounts (in ppm) of Mo (47.8), U (23.1), Cs (53.9), P (3200), Rb (363.9) and Be (7.0), its oral treatment should be reconsidered and additional analyses are still in progress.

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