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COMPARATIVE ANALYSIS OF HUNGARIAN MAAR-TYPE OIL SHALES (ALGINITES) ON THE BASIS OF SULFUR CONTENT

L. PÁPAY

Department of Mineralogy, Geochemistry and Petrography,
University of Szeged
P.O. Box: 651 H-6701 Szeged, Hungary

Basaltic volcanism has built tuff rings (maars) around the craters of Western Hungary and the Balaton Highlands within the Carpathian Basin during the Pliocene. Oil shales (alginites) have been found in four maar basaltic tuff craters so far. Some years ago the distribution of sulfur in alginites from two craters at Pula and Gérce villages was determined. This paper presents additional data on the sulfur content and forms of further alginite deposits from adjacent craters at Egyházaskesző village in order to find an explanation for the reasons of the differences in the total sulfur content and forms among the samples from the twin maars with the help of modern research methods. Furthermore, the alginites from the four craters are compared on the basis of their sulfur content.

Despite the same sedimentation conditions and petrological composition, the total sulfur content (average $S_t^a = 2.3\%$) of the samples taken from the crater at Egyházaskesző differs not only from that of the neighbouring crater at Várkesző (average $S_t^a = 0.7\%$) but also from the data of the samples from the tuff rings at Pula (average $S_t^a = 0.4\text{--}0.5\%$) and Gérce (average $S_t^a = 0.5\%$). The reason for the moderately high total sulfur content of the alginite-bearing samples from the crater at Egyházaskesző is not precisely known. According to a former theory, the higher-salinity water from Lake Pannon might have infiltrated through the pores and fissures of the tuff ring to this crater lake, resulting in an increase in the total sulfur content. Results of recent investigations did not corroborate the presence of continuous Lake Pannon coverage in these areas. Most likely, large amount of sulfur compounds got into the crater lake at Egyházaskesző as a part of a post-volcanic activity disrupting the majority of planktonic life. Therefore the oil shales of Egyházaskesző contain the largest amounts of total sulfur among the Hungarian maar-type alginites. Furthermore, these alginite deposits are of the smallest thickness.

Introduction

In the western part of Hungary about a hundred individual alkali basalt centres have been recognized [1–4]. They are mostly isometric bodies 0.1 to 10 km in diameter and 5 to 150 m thick, covering an area of 0.02 to 60.0 km². Location of the basalt and basaltic tuff bodies in W Hungary is presented in Fig. 1.

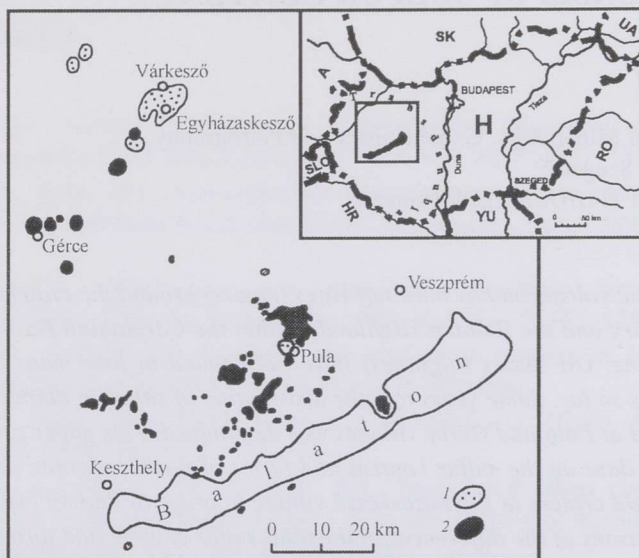


Fig. 1. Basalt and basaltic tuff regions in Transdanubia, W Hungary ([4] with some modifications): 1 – subsurface rocks; 2 - surface rocks

The erupting basic magma gave rise to both stratovolcanoes and formation of special tuff rings – maars. The basalt tuff constituting the rim of the craters was attacked by weathering and erosion. Because of the heavy weathering of the volcanic glass in the rock, the water of the crater lake became extremely enriched with macro- and micronutrients. The wealth of mineral and organic nutrients led to marked growth of some living organisms, particularly the planktonic green algae, especially one species, the *Botryococcus braunii* [5]. The organic material in the maar-type deposits has been identified as a kind of oil shale derived mainly from algal remains [6], and the deposits have been termed alginites.

Organic-rich sediments have been found in four maar-type basaltic tuff craters so far [7, 8]. The K/Ar radiometric age data support the opinion that these craters are of the same age: at Pula 4.25 ± 0.17 , at Gércse 4.55 ± 0.31 , at Várkesző 4.25 ± 0.32 [9] and at Egyházaskesző 4.15 ± 0.34 million years [10].

According to the diatomological investigation [11], the sediment of the crater lakes at Pula and Gércse was deposited in shallow, stagnant water. The

water of the crater lakes may have had a maximum salinity of 3 ‰ and a pH of about 7.6.

The characteristics of the Hungarian alginite and alginite-bearing bentonite make them suitable for application first of all in the agriculture i.e. for reducing the rate of acidification of soils, the leaching of fertilizers, and the amounts of nitrates and phosphorus infiltrated into the soil [12–14]. As a natural substance, alginite is not harmful to the environment.

For oil shales and shale-like rocks from different regions of the world, the total sulfur content within the range of 0.2 to 8.3 % has been reported [15]. In the low- and high-sulfur oil shales the pyritic sulfur fraction is in the range of 0.3 to 4.0 %. The organic sulfur varies between <0.1–5.1 %, whereas the sulfate sulfur quantity is low – maximum 0.3 % [16–18].

The purpose of the present research was to determine the distribution of sulfur among different bound forms present in alginite samples taken from the boreholes Vkt-1 (Várkeszű) and Ekt-34 (Egyházaskeszű), and to compare these data with others concerning previously examined Hungarian maar-type alginites [19].

Samples and Analytical Methods

Altogether twelve alginite-bearing samples examined have been taken from two boreholes: Vkt-1 – from depths between 34 to 41 m, and Ekt-34 – from depths of 47 to 71 m. The air-dried samples were ground to grain size $d \approx 200 \mu\text{m}$ in a ball agate mill.

The total sulfur and sulfate sulfur were converted into BaSO_4 and weighed gravimetrically. CO_2 content of the samples was determined by gas-volumetric method. These analytical methods are presented in the previously published study [19].

The pyritic sulfur content was determined with a new method developed by Mr. M. Emszt (personal communications). The process is the following: some drops of alcohol and distilled water were added to 0.5–1.0 g of the fine-powered samples to wet. Then the samples were treated with 15–20 ml 1 : 1 HCl to remove carbonates. After 5–10 min boiling the mixture was cooled down, the residue was filtered and later washed six to eight times with hot distilled water. The sulfate content of the acid solution was determined from the filtrate. The residue was oxidized with 20 ml HCl + 20 ml H_2O_2 . After the fizzing ceased the whole material in the laboratory glass was held on a boiling water-bath for 1 h. Finally, the pyritic sulfur was converted into BaSO_4 with 10 % BaCl_2 and weighed gravimetrically.

The data received with this new method were compared to those of a previously employed method based on reduction in the presence of Cr(II)-ions. According to *t*-test, there was no significant difference between the two methods when used for analysing twenty samples of alginites and brown coal with a total sulfur content <3 %.

Table 1. Distribution of Sulfur Varieties in Alginite from the Boreholes Ekt-34 and Vkt-1, Including Data for Moisture, Ash, Carbonate and Organic Carbon Content, %

Interval, m	W^d	A^d	C^{carb}	C_{org}^*	S_p^d	$S_{SO_4}^d$	S_{org}^d (diff.)	S_p^{diff}	$S_{SO_4}^{diff}$	S_{org}^{diff} (diff.)
Borehole Ekt-34										
34.2-34.5	9.0	73.2	<0.05	2.70	1.4	0.2	0.3	7.8	1.1	1.7
35.5-36.0	7.3	78.2	0.3	5.69	1.6	0.2	0.6	11.0	1.4	4.1
37.0-37.5	6.4	81.7	1.3	2.17	2.2	0.2	1.4	18.5	1.7	11.8
38.5-39.0	6.1	71.0	<0.1	10.54	3.5	0.4	1.4	15.2	1.7	6.1
39.5-40.0	4.7	64.7	2.6	11.20	2.4	0.2	0.6	7.8	0.6	2.0
40.0-40.5	3.4	69.0	3.9	9.30	2.1	0.3	0.3	7.6	1.1	1.1
40.5-40.8	4.5	75.9	1.2	9.12	2.6	0.2	0.7	13.2	1.0	3.5
Borehole Vkt-1										
47.0-48.0	5.4	74.6	1.1	5.98	0.7	0.2	0.4	3.5	1.0	2.0
53.0-54.0	5.9	71.6	0.6	8.51	0.2	0.09	0.08	0.9	0.1	0.4
59.0-60.0	5.5	66.1	1.1	11.46	0.2	0.07	0.03	0.7	0.25	0.1
62.7-63.5	4.60	69.0	0.9	13.86	0.5	0.3	0.05	1.9	0.6	0.2
70.0-71.0	4.9	61.9	0.1	17.80	2.0	0.4	0.2	6.0	1.2	0.6

Notes: W^d – analytical moisture, wt%; A^d – ash (air-dried sample), wt%; C^{carb} – inorganic or carbonate bond forms carbon content wt%; C_{org} – total organic carbon content (TOC), wt%.

S_p^d , $S_{SO_4}^d$, S_{org}^d , S_{org}^{diff} – total, pyritic (+ sulfide), sulfate, organic (by difference) sulfur content in air-dried sample.

S_p^{diff} , $S_{SO_4}^{diff}$, S_{org}^{diff} – total, pyritic (+ sulfide), sulfate, organic (by difference) sulfur content in dry, ash-free basis.

* Data from [20].

Results and Discussion

The results of experiments are summarized in Table 1.

The sulfur in oil shale, as in coal, exists in inorganic and organic forms. In fossil fuels the bulk of the inorganic sulfur occurs mostly as iron disulfides (pyrite or marcasite), other sulfide minerals may be present in minor quantities. A higher quantity of iron sulfates is generally an indication of sample weathering. Similar to coal, organosulfur compounds as aliphatic or aromatic thiophenes, mercaptans, sulfides, disulfides and their numerous derivatives are present in organic matter of oil shales.

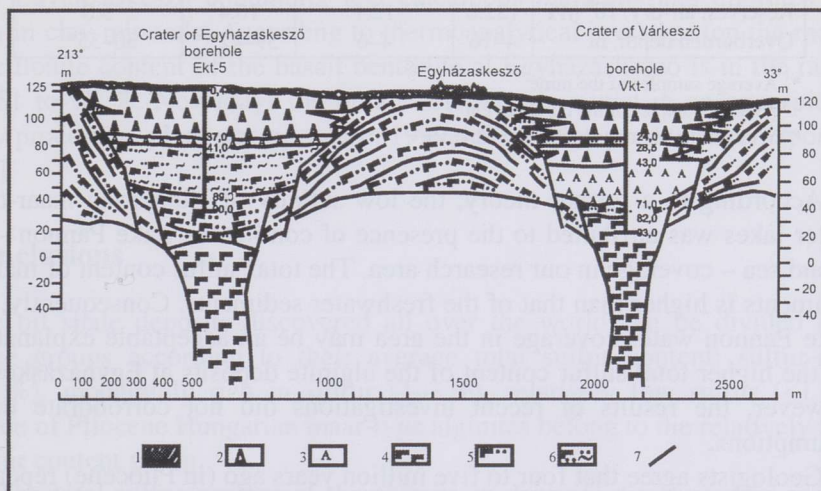


Fig. 2. Geological profile across maar tuff craters, Egyházaskesző, Hungary ([21] with some modifications after Solti): 1 – soil; 2 – bentonite; 3 – alginite (oil shale); 4 – basalt; 5 – basalt tuff; 6 – basalt tuffite; 7 – fault

There is a significant difference in the total sulfur content among the samples from the adjacent craters. Although there is no essential petrological difference between the two craters, the total sulfur content of alginites from the borehole Ekt-34 is higher than that of the Vkt-1 ones. As pointed out by Solti [10], the tuff crater of Egyházaskesző is genetically identical with the Várkesző ring, some couple of hundred metres away, and their mineral deposits are qualitatively similar (Fig. 2). In both craters the alginite deposits are covered with about 35–40 m basalt bentonite sequences. At the same time the maximum thickness of the alginite deposits is 30 m at Várkesző and 4–6 m (~4 m alginitic bentonite and 2.5 m alginite layer) in the Egyházaskesző crater. In addition, the previously discovered alginite deposits attain a maximum thickness of 45 m at Pula and 70 m at Gércse. Further important data are presented in Table 2.

Table 2. Major Average Chemical Values and Geological Data of the Hungarian Alginite Deposits (data pooled from [14, 22] and this study)

Indices	Locality			
	Gérce	Pula	Várkesző	Egyházaskesző
C_{org} , %	3.4	21.1* ¹ –27.4* ²	11.5	7.3
C_{carb}^d , %	2.3	2.6* ¹ –2.8* ²	0.8	1.3
S_i^a , %	0.5	0.4* ² –0.5* ¹	0.7	2.3
Area of deposit, km ²	2.1	0.445	0.3	0.63
Reserves, air-dry, 10 ⁶ MT	122.6	12.1	10.4	5.0
Overburden depth, m	4–16	4–6	39–42* ³	30–35* ³

*¹ Average samples of the mine.

*² Average samples of the borehole Put-7.

*³ With basalt bentonite body in overburden.

According to a former theory, the low salinity of Hungarian maar-type crater lakes was attributed to the presence of continuous Lake Pannon – an inland sea – coverage in our research area. The total sulfur content of marine sediments is higher than that of the freshwater sediments. Consequently, the Lake Pannon water coverage in the area may be an acceptable explanation for the higher total sulfur content of the alginite deposits at Egyházaskesző. However, the results of recent investigations did not corroborate these assumptions.

Geologists agree that four to five million years ago (in Pliocene) repeated eruptions of final alkali basalt volcanism characterized the entire Carpathian Basin. Faunal and paleogeographic evidence indicate that in the early Late Miocene Lake Pannon was finally disconnected from its neighbouring basins and gradually evolved into a large brackish to freshwater lake [23–26]. The salinity of Lake Pannon might have been around 14–16 ‰ during the Late Miocene [27]. Geologists are of different opinion, whether Lake Pannon surrounded the above-mentioned tuff rings following the close-up of the Pliocene volcanism [28–31] or fluvial sedimentation dominated these areas. According to a former theory, the higher salinity water from Lake Pannon might have infiltrated through the pores and fissures of the tuff ring to the crater lake at Egyházaskesző. This is the reason for the relatively high total sulfur content of the matter in this maar crater.

According to seismic, magnetostratigraphic and paleobiogeographic research, Lake Pannon was restricted to the area of the present-day Serbia, Vojvodina and Slavonia, some hundred kilometres S-SE of our research area. Thus, fluvial-marsh sedimentation dominated the areas surrounding the craters [32–34]. In my opinion, most likely a relatively large amount of sulfur compounds got into the crater lake at Egyházaskesző owing to the post-volcanic activity disrupting the majority of planktonic life. Thanks to this

the oil shales of Egyházaskesző contain the largest amounts of total sulfur and these alginite deposits are the thinnest among Hungarian maar-type alginites. The sequence of distribution of sulfur among four discovered Hungarian maar-type oil shales is generally as follows:

pyritic sulfur \geq organic sulfur $>$ sulfate sulfur.

On the basis of comparison of the average values derived from the qualitative analysis of the alginite-bearing samples from the four maar-type tuff crater, it can be established that there is a difference in the carbonate carbon content between previously discovered maar alginite deposits at Pula and Gérce, and the twin craters at Egyházaskesző. The samples from Várkesző and Egyházaskesző containing less calcareous materials and alginites are rich in clay minerals. According to thermoanalytical investigation the montmorillonite content of the basalt bentonite at Egyházaskesző is in the range of 51 to 95 %. Nowadays the basalt bentonite is mined in an open-pit. A new processing plant was opened in 1999, 85 % of the products are exported [35].

Conclusions

The oil shale deposits discovered all over the world can be divided into three groups according to their average total sulfur content: sulfur-rich (≥ 3 %), moderately rich in sulfur (1–3 %), relatively low sulfur (≤ 1 %). Three of Pliocene Hungarian maar-type alginites belong to the relatively low sulfur content group.

The total sulfur content of the alginite in deposits discovered in one of the maar craters at Egyházakesző village is higher than that of the other Hungarian alginites known up to date. The reason for the moderately rich total sulfur content of the alginite-bearing samples taken from the crater at Egyházaskesző is not precisely known. Most likely, a relatively large amount of sulfur compounds got into the crater lake at Egyházaskesző owing to the post-volcanic activity disrupting the majority of planktonic life. Therefore the oil shales of Egyházaskesző contain the largest amounts of sulfur, and these alginite deposits are the thinnest ones of Hungarian maar-type alginites.

The sequence of distribution of sulfur among the four discovered Hungarian maar-type oil shales is generally as follows:

pyritic sulfur \geq organic sulfur $>$ sulfate sulfur.

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