DUVALO

A GEOLOGICAL PHENOMENON NEAR OHRID

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Abstract

The phenomenon Duvalo in the vicinity of Ohrid has always been subject of interest among scientist and the general public. All geological manifestations occurring at this locality are a constant challenge for anyone attempting to research or explain them. So far, some researchers consider this structure is representing a solfatara while others consider it a mofette or fumarole. There are even articles in newspapers stating it represents the only “active volcano” on the Balkan Peninsula.

With the aim to clarify some important facts for the location and eliminate the multitude of arbitrary and unprofessional interpretations and information, within the frame of this article are presented results of analysis of all the available geological and geomorphological existing documentation for the phenomenon. Based on such detailed analysis with taking into consideration the character of its activity, the composition and the measured temperature of the gasses, geomorphological features etc., the occurrence is classified as a “dry mofette”. The presence of the H₂S gas in mofettes appearing on non-magmatic regions is very unusual and requires further research. Therefore, at the end of the paper are presented the minimum required investigations which will help define the origin of gasses at the Duvalo occurrence.

Key words: Duvalo, Kosel, Ohrid, Republic of Macedonia, solfatara, mofette, fumarole, dry mofette.

THE OBJECT AND PURPOSE OF THE STUDY

The locality of Duvalo near the village of Kosel in the vicinity of Ohrid has become the subject of more detailed and expert research. Duvalo is a geological phenomenon which has been given different characterisation (solfatara, mofette, fumarole) by different authors. The subject of our study is to define its real nature. All geological manifestations occurring at this locality are a

constant challenge for anyone attempting to research or explain them.

The purpose of this paper is to present more complete and clearer findings about the locality, which will eliminate the multitude of arbitrary and unprofessional interpretations and information regarding this phenomenon.

CHARACTERISTICS OF THE DUVALO LOCALITY

Geographical disposition

The Duvalo locality is located in the southeastern part of the Republic of Macedonia, in the Ohrid Region, near the village of Kosel, 7km north of the city of Ohrid. The absolute geographical disposition of the central part of the Duvalo locality is 41° 09' 39" longitude and 20° 50' 33" latitude.

The Duvalo topographical locality is located at the contact point of Galichica Mountain and the Ohrid Valley, at about 770 m altitude. It borders the valley of Koselska River to the north, Galichica Mountain branches (the Motrula elevation, 1012 m above sea level) rise to the east, the Valley of Skrebatska

River is located north and the Ohrid Valley is located west of the Duvalo locality.
 In respect to road access, the Duvalo locality is near the road Podmolje-Ohrid-Bitola-Prilep-Gradsko (at approximately 50 m.).
 Traffic communications that pass through Ohrid further stretch in the direction of Kichevo-Gostivar-

Skopje, then Struga-Kjafa San-Albania, Struga-Debar-Mavrovo-Gostivar with a leg from Debar to Albania and Ohrid-St.Naum-Podgradec in Albania. Administratively, the Duvalo locality is located in the area of the village Kosel and falls under the Municipality of Ohrid.

Figure 1. Geographical disposition of the Duvalo locality, Kosel village, Ohrid region [7]

Figure 2. Topographic disposition of the Duvalo locality, Kosel village, Ohrid region [1, 22, 15]

Figure 3. Geographic and topographic disposition of the Duvalo locality, Kosel village, Ohrid region
 (Source: Google Earth. July 15, 2017, August 25, 2018)

Geomorphological features

The Duvalo locality is immediately surrounded by Galichica Mountain and the branches of Plakenska Mountain (Mazatar as well as many other elevations) stretching westward to the Botun Gorge on one side and the Ohrid-Struga Valley, more precisely - the Ohrid Valley on the other. The contact point between these two macrostructures is a point of tectonic movements and manifestations. In the case of the Duvalo locality they come in the form of mofettes/solfataras.

Various erosive and accumulative fluvial and denudation processes are a constant occurrence in the locality. Some of them have been caused by natural processes. Due to the tilting, friability and swelling of the ground, its surface is partially

covered with intense erosion zones (coasts, furrows, ridges), zones with a relatively sharper inclination (caused by mining since the time of sulphur exploitation at the locality) and zones with erosive and accumulative activities stretching along the dry valleys in the locality. The rest of the locality is shaped by anthropogenic influences meaning that digging (due to sulphur exploitation from the 16th to 19th century) has caused more intense erosion processes, while disposal of tailings has caused the formation of anthropogenic accumulative forms (bumps, landfills and dumps). Unfortunately, these processes still go on today along with activities of refuse disposal at the locality (Fig. 4).

Figure 4. Geomorphological classification of the ground at the Duvalo locality

1. CO₂ and H₂S duvalos and exhalations zone, 2. Evaporative exhalations zone, 3. Erosion zone,
 4. Erosion and accumulation zone, 5. Anthropogenic accumulation of tailings and refuse zone
- (Photo B.Markoski, 2018)

Contemporary geomorphological processes

Contemporary geomorphological processes are mainly related to the constant neotectonic movements and various types of erosive and accumulative processes.

Neotectonic movements are a frequent occurrence in the wider Ohrid region. However, they are so slow that they usually go unnoticed by the population,

although exceptions arise at times of more intense seismic activity. Seismic activity in the area around Duvalo near Kosel is particularly high. Measurements show that most of the earthquakes' epicenters are in the immediate vicinity of the locality, mainly a few kilometers to the east and to the north of the village of Kosel.

Figure 5. Erosive fluvial and denudation forms in altered rocks in the Duvalo locality

Erosion processes and forms in the area around the Duvalo locality are particularly common. The reasons for it are: a relatively sharp land inclination, terrain exposition, relatively larger amounts of rain, a loose sedimentary foundation of the land etc., leading to the formation of a large number of valleys, smaller and larger river valleys, hilly elevations, mountain slopes, landslides, various denudation forms and other.

Particularly distinguished in the immediate vicinity of Duvalo are the elevations Benoglas 912 m and Jasika 1079 m to the north, and Motrula 1012 m and Koljo 1042 m to the east. Spread between these two mountain branches is the valley of Koselska river along with multiple smaller river valleys, dry ravines and a dry riverbed.

The base of the Motrula elevation (1012 m) is where the Duvalo locality is located. Due to increased amounts of CO₂ (carbon dioxide) and H₂S (sulphur dioxide) however, the ground lacks a plant cover, which has resulted in its susceptibility to a certain degree of erosion (Fig. 5).

Accumulative processes and forms affecting the immediate area of the Duvalo locality are a common feature of the plains of the Ohrid Valley. As Duvalo is located between the valleys of Koselska and Skrebatska rivers, it is spared from a more intense accumulation of torrent materials. Above it there is an insignificant part of a wooded catchment area, therefore the amount of erosion materials that actually arrive at Duvalo is quite small. The locality is subject to erosion during rainfall, but due to the relatively mild inclination of its land no larger amounts of accumulation material are collected (Fig. 4).

Geological features

The geological features of the Duvalo locality presented here are commonly significant characteristics of the entire wider region, naturally encompassing the immediate area around Duvalo.

Historical data on Duvalo

Historic documents and data confirm the existence of a sulphur exploitation activity in the Duvalo locality near the village of Kosel, Ohrid area since the period from the 16th to the 19th century [18].

The earliest scientific research at the Duvalo locality with recorded data dates from 1925 when S.Trojanovikj described the Duvalo locality [19] and phenomenon, including information regarding: -temperature and composition of gasses emitted from the phenomenon; its activity depending on weather conditions; -character of nearby sources of “medicinal waters”; -composition of cones near the locality; -remnants of past sulphur exploitation etc. More detailed scientific research was conducted in 1956 and 1957 by the Office for Geological

Research – Ohrid, with the purpose of ascertaining sulphur reserves in the area [20]. During one of the researches conducted by the Institute of Physiology at the Faculty of Medicine in Skopje, it was established that the amount of gasses being emitted from Duvalo amounts to 0,2 l/sec, and their chemical composition is as follows: CO₂ - 98.062%, H₂S – 0.838% and inert gasses - 1.1% [12]. In 1977 there was another research conducted on the phenomenon. Emitted gasses were discovered with the following content: CO₂ - 94,8-95,0; H₂S - 0,8; (first test) and CO₂ - 90-92; H₂S - 0,8; (second test). In the period between 1964 and 1972 systematic geological research was conducted and among other documents a 1:100000 scale basic geological map with map key was developed, sheets Ohrid K34-102 and Pogradec K34-114 [21, 22]. April 10th to 17th. 1981, the Geological Survey in Ljubljana, under the guidance and authorship of Danilo Ravnik, conducted geothermal research of the thermal areas near Debarska banja and the Duvalo locality near Kosel, Ohrid region [4]. The Duvalo locality and phenomenon was also mentioned and analysed by Hoffmann N. Et al. in 2010, where it was characterized as a hydrothermal field connected to a fault structure, emitting H₂S and CO₂ gasses from fumaroles, mofettes, solfataras, but without more specific data. In 2017 Milutinovikj et al. commented, among other things, on the issue of why the phenomenon was named solfatara or a volcano (authors’ comments regarding their viewpoints are given hereafter).

The research also included a review of the entire literature and research identified so far. It could therefore be agreed that the analysis of the Duvalo locality is complete.

Multiple journalist articles and information exist regarding the genesis of the Duvalo locality, which are often being (intentionally or unintentionally) misrepresented by reporters, sometimes due to a lack of understanding of this phenomenon. This is the reason why information on Duvalo often takes the form of factographic data. However, in order to avoid any arbitrary statements, the following text offers more detailed scientific and expert analyses related to natural (geomorphological, geological and other features) as well as some anthropogenic characteristics of the Duvalo locality.

Geological features of the wider area and the Duvalo locality

The wider region enclosing the Duvalo phenomenon belongs to a geotectonic unit known as Western-Macedonian Zone, and the terrains are made up of Paleozoic, Triassic, Jurassic, Neogene and Quaternary formations.

According to cartographic and textual data (a geological map for sheet Ohrid 34-102 of the basic geological map: 1:100000 and a respective map key), the geological structure of the wider area around the Duvalo locality (Fig. 6) consists of: **Paleozoic (Devon)** represented by (Sqse) quartz-sericite schists (phyllitic schists); (Sq) metasandstones; (M) marbleized limestones; ($\delta\gamma$) granodiorites; ($\xi\delta$) sienodiorites; (ξ) syenites; (π) granosyenitic porphyry; **Mesozoic (Triassic and Jurassic)** represented by (T_2^1) clastic-carbonate facies with outbursts of rhyolites and diabases; (χT_2^1) rhyolites; ($\beta\beta T_2^1$) diabases; ($T_2^{1,2}$) carbonate-chert facies; ($T_2^{1,2}$) dolomitites; ($T_2^{1,2}$) platy

limestones with cherts; ($T_2^{1,2}$) massive limestones; (σSeJ) peridotites and serpentinites; (υJ) gabbro; ($\beta\beta\text{J}$) diabases; (γ) leucocratic granites; **Cenozoic (Tertiary and Quaternary with Pleistocene and Holocene)** represented by j (lake and pond sediments); ts (terra rossa); pr (proluvium); d (slope breccias); al (alluvium) [21, 22]. The nature of this paper is such that details on these geological environments are not shown, but they were used as the basis for a series of geographical, geological, geomorphological, tectonic and other research in order to reach some conclusions about the Duvalo locality, among other things.

Figure 2. Figure 6) Geological composition of the wider area around the Duvalo locality:

(Sqse) Quartz-sericite shales (phyllitic shales); (Sq) Metasandstones;

(M) Marbleized sandstone; ($\delta\gamma$) Granodiorites; ($\xi\delta$) Sienodiorites; (ξ) Syenites;

(π) Granosyenitic porphyry; (T_2^1) Clastic-carbonate facies with outbursts of rhyolites and diabases; (χT_2^1) Rhyolites; ($\beta\beta T_2^1$) Diabases; ($T_2^{1,2}$) Carbonate-chert facia; ($T_2^{1,2}$) Dolomitites; ($T_2^{1,2}$) Platy limestones with cherts; ($T_2^{1,2}$) Massive limestones; (σSeJ) Peridotites and serpentinites; (υJ) Gabbro; ($\beta\beta\text{J}$) Diabases; (γ) Leucocratic granites; j (lake and pond sediments); ts (terra rossa); pr (proluvium); d (slope breccias); al (alluvium) [21]

During the Alpine orogenesis the entire terrain underwent intense dynamometamorphic changes, manifested by cataclasis and cleavage of rocks. Cataclasis is most visible in intrusive rocks, and after cleavage of the filitoids a secondary sericite is formed, as a result of dynamometamorphism.

*Tectonic features of the wider area
and of the Duvalo phenomenon zone*

The wider area of the Duvalo phenomenon belongs to the tectonic unit Western-Macedonian zone. The tectonic development of the land is related to the Hercynian as well as the Alpine orogeny (Fig. 6). Paleozoic sediments were regionally metamorphosed and folded in synclinal and anticlinal structures by Hercynian orogeny, while Alpine orogeny conditioned strong dynamometamorphism accompanied by intense folding of the ground and modification of Hercynian structures.

In later phases of Alpine orogeny, meaning late Lower or early Mid-Pliocene, the ground underwent quite intense radial tectonic movement that formed multiple tectonic grabens (the most significant one being the Ohrid graben).

More significant tectonic structures in the wider area of the Duvalo phenomenon are the Openichka brachysyncline (7), Lekocherejska brachysyncline (11) and the Galichica horst-syncline (12).

The Openichka brachysyncline is made up of phyllitic shales and metasands and is oriented in a northwest-southeast direction.

The Lakocherejska brachysyncline is made up of phyllitic shales and is oriented in a north-south direction.

Triassic sediments have folded during the Alpine orogenesis, and their most distinguished structure is the 35 km long Galichica horst-syncline (12) forming the mountain massif Galichica, Istochka and Petrinska Mountains.

Neotectonics

Radial tectonics were quite intense at the beginning of Mid-Pliocene, bringing about the formation of the most significant structure in the Duvalo phenomenon – the Kosel fault (26) and its accompanying faults stretching in an east-west direction (it is precisely in the village of Kosel that this fault intersects other faults covered in Quaternary sediments and it is here that CO₂ and H₂S gasses are released). The Kosel fault passes by the village of Kosel, and on its way going southwards it passes by the villages Velgoshti, Ramno and Velestovo.

Regionally, the Kosel Fault is located on the east edge of the Ohrid graben towards the mountain massif Galichica, Istochka and Petrinska Mountain.

Actually, this part of the region is host to a few steep parallel normal faults stretching in a north-south direction (a fault system known as Peshtani-Petrina faults). Going in the direction of south to north, the faults in this system stretch along the peripheral area of the lake from St.Naum to the village of Peshtani, and continue through the villages of Velestovo-Velgoshti-Kosel-Vapila-Botun-Pesochani and Stogovo Mountain up to the Kosovrasti baths near Debar. All of these faults stretching in a north-south direction are intersected by smaller faults stretching in the direction of northwest-southeast, while in the southern part of the area they stretch in an east-southeast to east direction (Fig. 6).

Two of the more notable faults that appear to the south of the Kosel fault are known as the Velestovo fault and the Konsko fault. As mentioned before, the cascade faults that stretch in the north-south direction are deeper and marked by several other features:

- The faults have formed and restricted the Ohrid graben on the east side, continuing northwards and going through Stogovo Mountain and in a north-south direction;
- Upper Pliocene saw more intense tectonic activity, which led to the formation of the mountain massif Galichica, Istochka and Petrinska mountains as well as the deepening of the lake's eastern part causing the lake's water to withdraw to the east of the wider area of the Struga Valley and Debartsa;
- Exhalations (informally: duvalos) of underground gasses occur in certain segments. Such duvalos appear along the line of the Velestovo-Velgoshti-Kosel-Vopila villages, but also in the areas of Botun and Pesochani, near the Kosovrasti baths and the Debar baths. Underground gasses are emitted on the surface resulting in intense desintegration and whitening (alteration) of surrounding rocks.

Also worth mentioning is the Jablanitsa fault occurring along the western edge of the Ohrid depression, as well as the Drim and Sateska faults on the north side of the depression. [21, 22].

All of the fault structures mentioned above have registered contemporary seismic activity along them. This activity is the result of vertical movement, but horizontal movement has also been registered along with movement from the right in submeridial direction [16].

*Geological interpretation
of the Duvalo phenomenon*

The mineral-petrographic and stratigraphic features of the Duvalo locality and its surrounding area have so far received a certain amount of attention.

However, as previously stated, geological research was conducted in 1925, 1947 and 1956-1957 as well as after, but without paying attention neither specifically to the genesis of the phenomenon nor to the origin of gasses emitted from it or any other similar occurrence in the area.

From the literature available to us we can conclude that in the past this phenomenon was defined as a mofette, solfatara, fumarole etc. In view of better defining this natural geological phenomenon, we

will present the definitions of these occurrences which are frequently found in literature.

Fumarole (It. *Fumarola*) – from the Latin *fumare* (smoke, fume) is a crack or an opening located in a crater on the sides or the base of a volcano, and is a source of hot gasses. One distinction of fumaroles is the emission of water vapor and gasses such as CO_2 , SO_2 , HCl , H_2S . Many geologists are of the opinion that *fumaroles* are found near active volcanoes and in dormant volcano areas.

Figure 7. The appearance of the “old duvalo” of CO_2 and H_2S gasses in the Duvalo locality near Kosel
(photo B. Markoski, 2018)

Figure 8. The appearance of a new duvalo of CO_2 and H_2S gasses 20 meters south of the old duvalo in the Duvalo locality near Kosel
(photo B. Markoski, 2018)

Figure 9. Emanations of phyllite alterations under the influence of CO_2 and H_2S gasses and sulphuric acid in the Duvalo locality, near the village of Kosel
(photo B. Markoski, 2018)

Figure 10. Whitening and alteration of rocks (a reaction of exhalations of H_2S and H_2O due to rainfall) by H_2SO_3 – sulphuric acid in the Duvalo locality Near the village of Kosel
(photo B. Markoski, 2018)

Solfatara - comes from the Italian *solfo* – sulphur and is used as a synonym for fumaroles that emit predominantly sulfuric gasses.

Mofette (Fr. *Mofette*) – represents a crack or opening in a volcanic area emitting CO_2 gasses, water vapor and other gasses: nitrogen, hydrogen, methane. Gas temperatures do not exceed 100°C , but they cause animals in mofette areas to suffocate which is why these places are called “valleys of death”.

With the purpose of coming to more justified conclusions about the type of occurrence that the

Duvalo phenomenon is, we have gathered all available data regarding the geological and geochemical features of this phenomenon and similar occurrences in the area. Taken into consideration in the process was the research and the opinions of Trojanovikj S. 1925 [19]; Izmailov N. 1948 [10, 11]; The Office for Geological Research – Ohrid 1956/57 [12]; The Geological Office 1970; Sherif A 2001 [18]; Hoffmann N. 2010 [6]; Milutinovikj et al. 2017 [16] and others. Taking into consideration world literature definitions and looking into all previous

interpretations, it is our opinion that the Duvalo phenomenon probably belongs to the category of phenomena known as **dry mofettes**. Such a rare occurrence on a land without recent magma activity is an exceptional natural phenomenon worldwide. The presence of the H₂S gas in mofettes appearing on non-magmatic ground is an unusual occurrence, which is yet another reason to dedicate scientific attention to the locality and the wider area. The authors of this research verify and further explain the views of previous researchers through a series of photoillustrations (Fig. 7, 8, 9 and 10).

Seismogenic features and manifestations in the wider area

The seismic activity in the wider area of the Duvalo phenomenon was more specifically treated in various periods in time, most often by domestic researchers. According to Arsovski and Hadjievski, the Western-

Macedonian zone encompassing the Duvalo phenomenon has a predominantly meridian direction of extension. It is subject to strong earthquakes $M > 6$, $I > IX$ which repeat relatively frequently [2, 17, 14].

According to Chernich D. and Drogeshka K., a large number of earthquakes have occurred in the Ohrid-Struga seismotectonic zone (Table 1), however an earthquake sequence that started on 18.6.2017 in the Peshtani-Ohrid-Struga epicentral area and the most intense one during that sequence happened on 3.7.2017 at 13 o'clock and 18 minutes $M=4.9$ and $I=VII$ degrees according to EMS-98. The epicenter of the earthquake was 10 km east of the city of Ohrid in the immediate vicinity of the village of Skrebatno (5km distance from the village of Kosel).

An overview of separate data on multiple earthquakes in the Ohrid region and more specifically in the area of the Duvalo locality shows that, in general, the magnitude of earthquakes here does not exceed 5 degrees.

Table 1. Strongest earthquakes in the epicentral area
 Peshtani-Ohrid-Struga before and after 1901 [9]

Year	Month	Day	Hour	Min	Sec	φ	λ	H(km)	ML	Io
Strongest earthquakes before 1901										
527	00	00	00	00	0	41.10	20.79	0	6.1	IX
1893	05	02	07	00	0	41.10	20.80	0	5	VII
1893	05	02	15	15	0	41.09	20.80	0	5.6	VIII
Strongest earthquakes after 1901										
1905	04	04	10	24	41.8	41.16	20.82	25	5.3	VII
1964	12	09	19	06	16.3	41.06	20.81	15	5	VII
1962	07	17	19	44	46.7	41.17	20.74	18	4.6	VI
1964	12	09	18	28	34.4	41.00	20.79	10	4.6	VII
1911	03	05	00	55	0	41.00	20.69	15	4.4	VI-VII
1954	04	19	05	37	0	41.14	20.77	18	4.4	VI
1932	03	24	01	35	0	41.02	20.74	14	4.2	VI
1906	11	29	08	40	0	41.00	20.80	15	4.1	VI
1965	02	12	04	52	58.3	40.99	20.83	15	4	VI
Earthquakes in 2017										
2017	07	03	11	18	18.5	41.17	20.91	1.7	5.0	VII-VIII
2017	07	02	09	39	07.4	41.17	20.94	1.0	4.0	VI
2017	07	03	18	30	11.1	41.16	20.87	8.4	4.0	VI

Source: Chernich D., Drogeshka K., (2017), Seismological observatory at the Faculty of Mathematics and Natural Sciences, "Ss. Cyril and Methodius" University, Skopje.

Recent manifestations in the Duvalo phenomenon locality

The Duvalo locality is characterized by various recent manifestations and occurrences that arise from natural and anthropogenic influences. Due to the nature of the Duvalo locality, there is constant manifestation of gas exhalations from inside the ground. They evaporatively show up on almost the entire surface of the locality, and exhalatively – in craters that emit CO₂ and H₂S

gasses (Fig. 11). According to scientific surveys and experience of the local population, gas manifestations during dry periods are moderate, while the sulphur smell (colloquially - "a bad egg smell") is stronger and vice versa in wet periods (during periods of rainfall gas manifestations are explosive) (Fig. 12), but the sulphur smell is milder.

Figure 11. The duvalos “craters” zone with CO₂ and H₂S gas exhalations in the Duvalo locality near the village of Kosel, Ohrid region.
The Old duvalo and new duvalos in the locality after the earthquakes in 2017
(Photo B.Markoski 2018)

Regarding the activity of this phenomenon, all researchers mentioned above generally agree with the initial conclusion of Trojanovikj from 1925 – that during dry periods there is a stronger smell and a whistling sound in Duvalo, while during periods of rainfall bubbling is the predominant sound. Also supporting this is the fact that in 2014 an increased activity of Duvalo was noted, meaning denser smoke, and it was also established that during that time there was no seismic activity, so this increased activity was interpreted as a natural process taking place after abundant rainfall (Fig. 12).

The so-called explosiveness of gasses in the Duvalo locality is the result of water entering the cracks from which these gasses are being emitted that prevents the normal emission of gasses. This causes for gas pressure in the ground to rise and when it becomes sufficiently high it ejects the water mixed with gasses in the shape of small water capillaries of “smoke” (as it is known among the local population). All of this is accompanied by a bubbling sound and emission of a larger amount of mixed gas and water (Fig. 12).

Figure 12. Increased activity of the Duvalo mofette near the village of Kosel after abundant rainfall [20]

Since the Duvalo locality is located on a fault line and the immediate area is also covered with transverse faults, this is an area of increased seismic activity which most certainly casts its reflection on the Duvalo locality as well. Namely, in the past there was one distinguished “crater” hole on the locality, but after the sequence of about 1 000

earthquakes occurring during a 2-3 month period (June, July and August 2017), 10 new holes appeared ranging from 20 to 80 cm in diameter. This change is logical since the seismic activity could have caused a disturbance in the evaporational directions of the gas exhalations.

Figure 13. Insert 1 of the CO₂ and H₂S gasses “crater” exhalations zone in the Duvalo locality near the village of Kosel, Ohrid region
(New duvalo holes in the locality after the earthquakes in 2017)
(Photo B.Markoski 2018)

Figure14. Insert 2 of the CO₂ and H₂S gasses “crater” exhalations zone in the Duvalo locality near the village of Kosel, Ohrid region (New duvalo holes in the locality after the earthquakes in 2017)
(Photo B.Markoski 2018)

Figure 15. Insert 3 of the CO₂ and H₂S gas “crater” exhalations zone in the Duvalo locality near the village of Kosel, Ohrid region (New duvalo holes in the locality after the earthquakes in 2017)
(Photo B.Markoski 2018)

Figure 16. Insert 4 of the CO₂ and H₂S gasses “crater” exhalations zone in the Duvalo locality near the village of Kosel, Ohrid region (New duvalo holes in the locality after the earthquakes in 2017)
(Photo B.Markoski 2018)

During a field visit on 09/19/2018 in conditions of sunny weather with disperse clouds, 21°C temperature, wind speed of 9 km/h north direction, air humidity of 64% and 1023 mbar air pressure at the location, a relatively strong smell of H₂S could be felt [8]. A few clearly visible gass emitting holes have been registered on site (with a low to insignificant pressure at the time of the visit) (Fig. 13, 14, 15, 16), as well as a larger number of manifestations of thin sulphur scum deposits and a

certain degree of rock modification (phyllites) on the surface of the ground (Fig. 17, 18, 19, 20).

A comparison between the current state and previous data mostly regarding one particularly outstanding gas emitting “crater”, shows that activity on this site ranges from very high to very low, meaning that the phenomenon is of a geologically dynamic character. A certain manifestation (inactive at the moment the survey was conducted) was noticed in the vicinity of Vapila village as well.

Needs and directions of future geological research at the Duvalo locality

As can be concluded from previous available literature, the locality encompassing the Duvalo phenomenon has always been found interesting by geologists working in the area. However, all of the research has usually been pointed in a different direction or has only mentioned the phenomenon in passing, so we get the impression that, scientifically, some dilemmas and issues still remain open.

Figure 17. Insert 1, land swelling due to evaporational manifestations of CO₂ and H₂S gasses.

A- a footprint on a swollen patch,

B-evaporational swollen patch

(Photo B.Markoski 2018)

Figure 19. Insert 3, manifestations of sulphur scum deposits on the surface of rock masses under the influence of sulphuric acid in the Duvalo locality (Photo B.Markoski 2018)

Worldwide, there are numerous studies on determining the origin of gasses with predominant CO₂ content that come out on Earth's surface through mofettes, where areas with recent or older magma activity, tectonic zones and sedimentation basins are being treated separately. Research is done from a variety of aspects, but it is generally important to determine the origin of CO₂ (whether it has come from a magma source, the Earth's mantle, the deep or shallow Earth core, decarbonation processes of carbonates making up the Earth core, regional metamorphism of carbonate

One of the dilemmas identified regarding the Duvalo phenomenon concerns the origin of gasses. Available literature has been examined with the purpose of solving this issue and that in the framework of other research as well as by using similar examples that have been found relevant in the explanation of the Duvalo phenomenon case (or they serve as guidelines for future purpose-built geological research).

Figure 18. Insert 2, evaporational manifestation of CO₂ and H₂S gasses in water-filled zones and rock and mineral dissolution in the Duvalo locality near the village of Kosel, Ohrid region

(Photo B.Markoski 2018)

Figure 20. Insert 4, manifestations of sulphur scum deposits on the surface of rock masses under the influence of sulphuric acid in the Duvalo locality (Photo B.Markoski 2018)

rocks, contact metamorphism of carbonates, whether the source is organic etc.)

An interesting example is presented by Giustini et al. 2013, where through all-encompassing research of the chemistry and the isotope relationship of He, C ($\delta^{13}\text{C}$) and H (δD) in emanations along faults in the San Vittorino valley it was determined that 75% of the CO₂ originated from termometamorphic reactions of limestones, between 6 and 22% - from sediment deposits rich in organic matter, and from 0 to 6% from the mantle [5]. In a number of tested samples taken from the most significant fault area,

the content of CO₂ originating from Earth's mantle was 24-42%. Similar research and tests were conducted in other places throughout the world as well.

Table 2. Activity at the Duvalo phenomenon location on 09/19/2018

Ordinal number	Coordinates		Dimensions (length/width/depth)	Character of the phenomenon
	X	Y		
1	7486763	4558408	40x20x10cm	With a visible hole
2	7486761	4558418	50x50x30cm	With a visible hole
3	7486779	4558422	10x10cm	Surface manifestation of sulphur
4	7486776	4558427	10x10cm	Surface manifestation of sulphur
5	7486773	4558429	10x10cm	Surface manifestation of sulphur
6	7486774	4558423	50x50x30cm	With a visible hole
7	7486787	4558435	10x10cm	Surface manifestation of sulphur
8	7486782	4558439	10x10cm	Surface manifestation of sulphur
9	7486762	4558442	30x20cm (4 holes)	With a visible hole
10	7486747	4558501	10x5cm	Surface manifestation of sulphur
11 Vapila	7486541	4559217	Sulphur scum on phyllite surfaces at the base of the Benoglas (peak) elevation	Surface manifestation of sulphur

Source: Author measurements and notes

The data mentioned, in the context of the Duvalo phenomenon (and regarding gas origin) could be in mutual correlation considering they explain the tectonic character of the phenomenon on one hand and thermometamorphic reactions of carbonates under earth's surface and aquifers in the area, on the other. For a further scientific verification of this statement, we should follow Whycherley (1999) who states that stable isotopes of ($\delta^{13}\text{C}_{\text{CO}_2}$) are not sufficient to determine the origin of CO₂ which is why results should always be compared to isotope analyses of noble (inert) gasses (He, Ar, Ne) [23]. However, the origin of the gasses emitted in the area of the Duvalo phenomenon has so far been related to thermometamorphic reactions of carbonates and groundwater in the fault at the locality [9].

Based on the preliminary research of some of the abovementioned similar phenomena throughout the world, some conclusions can be drawn and questions can arise that are applicable to the Duvalo phenomenon as well:

- By its nature, it can be presumed that the Duvalo phenomenon falls under the category of so-called dry mofettes.
- According to data from drill-hole no.1, and no.2 (to some extent), gathered in 1956-1957, a deep fault structure is clearly present (drill-hole no.1 – presence of limestone blocks in a sand foundation, starting from an 11,0 m depth and reaching a depth of 43,0 m) on the locality itself, which completely matches the general tectonic composition of the area. Also evident is the presence of gas emanating phenomena along faults to the south and to the north of Duvalo, as well as of transversing fault

structures, landing additional support to the presumption that these are gas emanations that appear along deep fault structures [12].

- Does emanation have any connection to Devonian migmatites appearing in the area between Petrino and Openitsa?
- Is there a connection between the Duvalo locality and Jurassic diabbases appearing near the village of Skrebatno (representing the nearest magmatic phenomenon to Duvalo – at approximately 5km air distance from Kosel)?
- Are exhalations a consequence of regional metamorphism to which deeply positioned Devonian marblized limestones are subjected, where along the faults gasses emanate to the surface of the Earth?
- Do gasses come from the mantle of Earth's core and reach its surface through active fault structures or is it a question of mixed origin gasses?
- What led to the eruption of gasses during the 1956/1957 drilling works (the drilling technology is unknown, therefore it is unclear whether the eruption was caused by the fluid that was used or by drilling through gas "pockets", or other reasons).
- The origin of H₂S is a huge enigma.

The questions above can only be answered through future scientific research in the area of the Duvalo locality, as well as in the wider region where other, weaker gas exhalations occur. For that purpose, attention must be paid to experiences of past research conducted in regions where mofette fields appear, as well as research regarding magmatic and

non-magmatic fields present in Europe: Italy, Hungary, France, Czech Republic, Romania, as

well as in the USA, Australia and other countries in the world.

SUMMARY

The Duvalo locality is located in the Southwestern part of the Republic of Macedonia, in the Ohrid region, near the village of Kosel at about 7km to the north of the city of Ohrid. The absolute geographical position of the central zone of the Duvalo locality is at 41° 09' 39'' latitude and 20° 50' 33'' longitude. Topographically, the Duvalo locality is located at the contact point of Galichica Mountain and the Ohrid Valley, at approximately 770 m altitude between the valley of Koselska river and the valley of Skrebatska river.

The Duvalo locality is immediately surrounded by Galichica Mountain and the branches of Plakenska Mountain and the Ohrid-Struga graben (also known as the Ohrid valley). Tectonic movements and manifestations occur at the contact point of these two macrostructures. In the case of the Duvalo locality they manifest in the shape of mofettes/solfataras.

According to cartographic data, the geological structure of the wider area around the Duvalo locality (Fig. 6) consists of: (Sqse) quartz-sericite schists (phyllitic schists); (Sq) metasediments; (M) marbleized limestones; ($\delta\gamma$) granodiorites; ($\xi\delta$) sienodiorites; (ξ) syenites; (π) granosyenitic porphyry; (T_1^2) clastic-carbonate facies with outbursts of rhyolites and diabases; (χT_1^2) rhyolites; ($\beta\beta T_1^2$) diabases; ($T_1^{1,2}$) carbonate-chert facies; ($T_2^{1,2}$) dolomites; ($T_2^{1,2}$) platy limestones with cherts; ($T_2^{1,2}$) massive limestones; (σSeJ) peridotites and serpentinites; (υJ) gabbros; ($\beta\beta J$) diabases; (γ) leucocratic granites; j (lake and pond sediments); ts (terra rossa); pr (proluvium); d (slope breccias); al (aluvium) [21, 22]. These data are a further basis for a series of geographical, geological, geomorphological, tectonic and related research used to draw conclusions regarding the Duvalo locality as well.

According to Milutinovikj, whitening and deterioration (alterations) of the surface that occur

in surrounding Paleozoic schists and other rocks, are a result of weak exhalations of H_2S , that combined with rainwater create sulphuric acid that erodes and alters rocks.

Regarding the phenomenon's activity, researchers mainly agree with the initial conclusion Trojanovikj made in 1925 – that during dry periods Duvalo has a stronger smell and a whistling sound is heard, while during rainy periods bubbling is the dominant sound [19]. Supporting this is also the fact that in 2014 Duvalo experienced an increased activity with an emission of dense smoke, which led to the increased activity being interpreted as a natural process following abundant rainfall (cluttering water cracks, increased gas compression underground resulting in explosiveness) (Fig. 12). According to world literature definitions, available data and interpretations by most researchers, our conclusion is that the Duvalo phenomenon is located on a fault line; it is the result of tectonic processes, and according to the CO_2 content of 98%, the phenomenon probably belongs to the dry mofettes category.

The origin of CO_2 – carbon dioxide is at the moment being explained as the result of the pressure and presence of water in carbonate rocks. After being released, the carbon dioxide uses fault lines and cracks to break out on the ground's surface.

Regarding the origin of H_2S – sulphur hydrogen, conditions for formation of sulphates (water, pressure, temperatures, rock masses containing sulphur, chemical connections between elements and minerals etc.) are probably less favourable, so the amount of H_2S is smaller, about 0,8%. Scientific findings show that part of the schists here contain sulphur [9], so in such conditions of scarceness of these sulphur containing rocks and minerals in deep fault zones and weaker conditions for impregnation results in a smaller amount of H_2S exhaled on the surface of the ground.

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REFERENCES

- [1] АКН – Агенција за недвижности, Топографски карти, листови Охрид, размер 1:200000, 1:100000, 1:50000 и 1:25000, Скопје.,
- [2] Arsovski, M. and Hadzievski D. (1970) Correlation between neotectonics and the seismicity of Macedonia, Tectonophysics, 9 129-142, (Tuka ima za zemjotresi vo ohrid za period 1900-1970).
- [3] Цвијик Ј. (1906). Основе за географију и геологију Македоније и Старе Србије. Посебно издање Срп. Краљ. Акад. књ. I и II, Београд.

- [4] Geoloski zavod Ljubljana, (1981) Geoelektricnih ispitivanja termalnih podruchja kod Debarske Banje i kod Ohrida (Kosel), 1981 (изработил Ravnik Danilo).
- [5] Giustini F, Blessing M, Brilli M, Lombardi S, Voltattorni N, Widory D. (2013). Determining the origin of carbon dioxide and methane in the gaseous emissions of the San Vittorino plain (Central Italy) by means of stable isotopes and noble gas analysis. Applied Geochemistry, Vol. 34. 2013, pp. 90-101.
<https://doi.org/10.1016/j.apgeochem.2013.02.015>.
- [6] Hoffmann, N., Reicherter, K., Fernandez-Steege T. and Grutzner C. (2010) Evolution of ancient Lake Ohrid: a tectonic perspective. Biogeosciences, 7, 3377–3386, doi:10.5194/bg-7-3377-2010
- [7] <https://commons.wikimedia.org/w/index.php?curid=7800377>
- [8] <https://www.timeanddate.com/weather/republic-of-macedonia/ohrid/historic>
- [9] Ивановски Т. (1956). Геолошки извештај за сулфурните појави на селата Косел, Песочани, Вапила и Велгоште. Стручен фонд на геолошки завод Скопје.
- [10] Измајлов Н. (1948). Скица на каолинови појави кај село Велгошти, Геолошки Завод на НРМ, Скопје.
- [11] Измајлов Н. (1956). Железноруден басен во Западна Македонија. Трудови на Геолошки Завод на НРМ, Св.7, Скопје.
- [12] Илоски Г., Ивановски Г., Орачески С. (1957). Извештај за сулфурните појави кај с.Косел-Охридско, Биро за геолошки истражувања – Охрид.
- [13] Kosmat F. (1924). Geologie der zentralen balkanhalbinsel,. Berlin.
- [14] Medvedev, S., W.Sponheuer and V. Kärnik, 1965. Seismic Intensity Scale Version MSK64 by, UNESCO/NS/SEISM/28, Paris, 7 May 1965, 7 pp.
- [15] Маркоски Б., (2003) Картографија, Геомап-Скопје, (Универзитетски учебник)
- [16] Милутиновиќ З., Шалиќ Р., Думурџанов Н., Дрогрешка К., Черних Анастасовска Д., Пекевски Л., Чејковска В., Најдовска Ј. (2017). Сеизмичка опасност со осврт на сеизмичката активност во Охридското епицентрално подрачје во периодот јуни-јули 2017. Стручен текст во списание Порта 3.
- [17] Михајловиќ Ј. (1951). Земјотресни области во Македонија. Трудови на Геолошки Завод на НРМ, Св.2, Скопје.
- [18] Шериф А. (2001) Рударството во Македонија во време на османлиското владеење, ИНИ, Логос-А, Скопје.
https://books.google.mk/books?output=html_text&id=3-VEs1_7NjMC&dq=duvalo%2C+Kosel%2C&jtp=89
- [19] Тројановиќ С. (1925). Сулфатара у Коселу. Геол. анал. Балкан. Пол. Београд. Књ.VIII.
- [20] [tps://www.mia.mk/Mobile/mk/Home/RenderSingleNews/254?newsID=132813424](https://www.mia.mk/Mobile/mk/Home/RenderSingleNews/254?newsID=132813424)
- [21] ВГИ, (1977) ОГК – Основна геолошка карта на Република Македонија, лист Охрид K34-102 (размер 1:100000)
- [22] ВГИ, (1975-1980) Топографски карти, листови Охрид, размер 1:200000, 1:100000, 1:50000 и 1:25000, Белград,
- [23] Wycherley, H., Fleet, A. and Shaw, H., (1999). Some observations on the origins of large volumes of carbon dioxide accumulations in sedimentary basins. Marine and Petroleum Geology, 16, 489- 494