PRELIMINARY STUDY OF MUD VOLCANOES IN BANAT (SOUTHWEST ROMANIA)

Stela URUIOC[(1)], **Smaranda MÂŞU**[(2)], **Adrian SINITEAN**[(1)], **Mariana ALBULESCU**[(3)], **Horia POPOVICI**[(3)]

[(1)]*Department of Biology, West University of Timişoara, Faculty of Chemistry-Biology and Geography, Pestalozzi street, no. 16, Timişoara, uruioc.stela@yahoo.com, adisinitean@yahoo.com*

[(2)]*INCD-ECOIND Timişoara, andatee@yahoo.com*

[(3)]*Department of Chemistry, West University of Timişoara, Faculty of Chemistry-Biology and Geography, Pestalozzi street, no. 16, Timişoara, malbulescu@yahoo.com, popovici.horia@cbg.uvt.ro*

Abstract. The mud volcanoes area from Banat covers a surface of 900 m^2. The main mud volcano, known as Forocici volcano (FG), is of gryphon type (11/9 m), characterized by a bubbling pool (*salse*). Moreover, there are six secondary craters of smaller size and tens of vents in the area that show the emission points of gas and less mud. Gas eruptions from FG contain CO_2, CH_4, CO and H_2S. The CO_2 emissions were determined only qualitatively, estimating that these could surpass 15%. Concentration of CH_4 is about 12-13%. Concentration in H_2S and CO is between 0.4-0.8 ppm. Water from FG has a concentration of 0.020-0.050 ppm for Cr and 0.014-0.050 ppm for Ni. Fe reaches the highest concentrations (0.060-2.400 ppm). The water of FG is a mixture between deep water, phreatic and meteoric water. The soil around the volcanoes has in its first 5 cm a normal concentration for Cr, Pb and Zn. *The vegetation*, gathered from inside the gryphon, accumulates higher quantities of heavy metals than the same species that develop under normal field conditions. All these data represent an important contribution for the understanding of the output of mud volcanoes and their activity upon the environment.

Key words: gryphon, salse, gas emissions, gas eruptions, water chemistry, heavy metals

1. INTRODUCTION

The study of mud volcanoes (MVs) area and the necessity of protecting and preserving them within the sustainable development concept has become, since long ago, the preoccupation of scientists. MVs are not only a source of direct information through the fluid material carried by water, gases, and mineral suspensions brought from the deep zones of the terrestrial crust, but also represent a touristic interest area. Mud volcanoes are formed by tectonic processes, overpressure buildup in compressional settings, or by maturation and degassing of rapidly buried organic-rich sediments (Higgins and Saunders, 1974; Fowler *et al.*, 2000; Kopf and Behrmann, 2000; Milkov, 2000; Kopf, 2002).

MVs activity manifested as mud, water and gas eruptions determines specific landscapes at the surface of terrestrial crust known as gryphons (mud volcanoes with cone height lower than 3 m and the outer slope with small inclination, that permits mud exterior seepage), mud cones (cone height smaller than 10 m, through which mud and rock fragments are expelled), salses (mud volcanoes with craters filled up with water forming a lake, through which gas emissions break in), springs (cones smaller than 0.5 m, through which water gets out under pressure and dominates over gases)(Hovland *et al.* 1997; Guliyev and Feyzulayev, 1997; Aliyev *et al.* 2002). Released gases can be a mixture of hydrocarbons (dominantly CH_4) or CO_2. In both cases, gases can be followed by small quantities of N_2, H_2S, NH_3 and noble gases. The significance of mud volcanoes as natural sources of atmospheric methane (CH_4) is already recognized (Etiope *et al.*, 2002, 2004). The mud and fluids have a deep origin, but are sometimes stored in intermediate-depth mud chambers (Planke *et al.*, 2003).

In eastern Romania, studies on mud volcanoes from Berca and Andreiaşu (Buzău county) documented CH_4, CO_2, N_2 emissions with crustal origin (Etiope *et al.*, 2004). In southwest Romania, previous studies on mud volcano from Banat were done by Bizerea (1965) and Uruioc *et al.* (2007).

The current paper proposes a preliminary study about the mud volcano area, bringing new data about the composition of mud, water and gas emissions. First data on the heavy metal content in water, soil and vegetation are presented.

Geotectonic setting and description of mud volcanoes

The Banat plain, of which the studied area is part of, is composed of Neogene-Quaternary sedimentary rocks with thicknesses over 5000 m (Oros, 1991). The basement of the sedimentary rocks is composed of pre-Mesozoic metamorphic rocks and Mesozoic ophiolites. This is pierced by Pliocene basalts (Lucareţ) of subcrustal origin (Hertz *et al.*, 1973, in Visarion and Săndulescu, 1979). Besides, the basement is intruded by plutonic banatitic rocks (Bocşa, Surduc, Govăjdia, Ivanda, Timişoara, Utvin, Bazoş, Biled, Calacea) (Visarion and Sandulescu, 1979). Their spatial position is reflected by the existence of some deep faults and epicenters of normal earthquakes placed on the same direction (Oros, 1991) (Fig. 1).

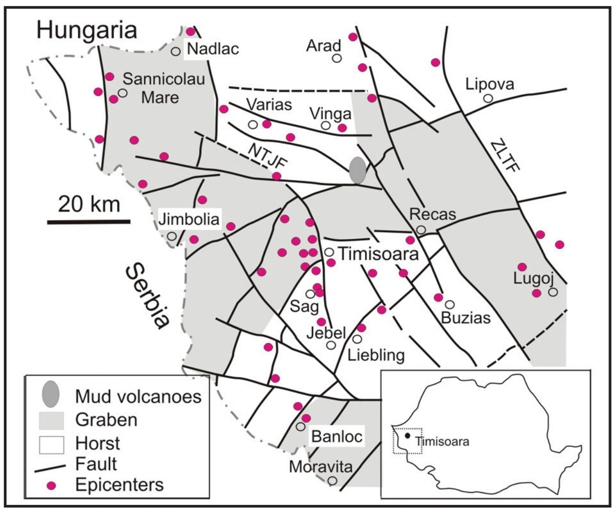

Fig. 1 Seismotectonic map of the Banat Plain (redrawn after Oros, 1991), showing the location of major faults, earthquakes epicenters and mud volcanoes. Inset map shows location of the area in Romania. Abbreviations: NTJF-Nădlac-Timişoara-Jebel Fault; ZLLF – Zărand-Lipova-Lugoj Fault

The deep and active character of the faults that separate tectonic blocks is confirmed by thermal and mineral water occurences (Biled, Călacea, Timişoara, Buziaş, Pişchia, Lipova, Ivanda) and by mofettes (Buziaş), releasing helium, radon, argon and other gases with crustal origin (Oros, 1991).

The origin of gases from Fibiş valley is probably the same. Borugă and Airinei (1981) remarked the presence of CO_2 in Banat in different permeable layers. In their ascending way, CO_2 emissions found under pressure encounter the aquifer water that carry them along, on fissures or fault planes (Bizerea, 1965). Water moistens marl and shale layers and forms a sodden and gaseous mud, that reaches the surface through more openings. In the Fibiş valley from the Vinga plain of Banat there is a mud volcano of gryphon type with an elliptic shape crater (9/11 m diameter, 1.5-1.8 m deep) named Forocici (FG) (Fig. 2 and 3). Because the crater gryphon is filled up with water - dominated pools with gas seeps, we also adopted the salse term of Hovland *et al.* (1997). The activity of the seething cauldron Forocici consists of gas eruptions, water and turbulent gas bubbling. It is often characterized by rude gurgling noises to the delight of visitors. The turbulent bubbling of the gas causes mud to be carried up for deposition around the edges of the gryphon. In dry periods, when water disappears completely in the FG interior, activity continues through secondary, decimetric craters with spherical mud calottes.

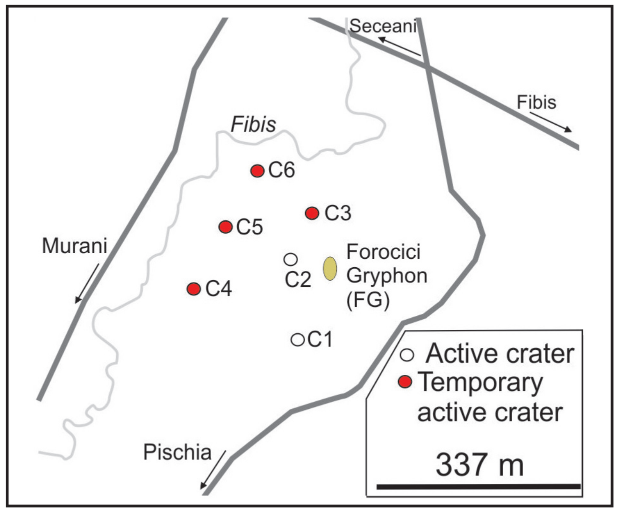

Fig. 2 The distribution of mud volcanoes in Fibiş Valley

Fig. 3 Forocici gryphon (FG) of salse type characterized by bubbling pool with gas seeps

There are also 6 secondary craters (with diameters between 4/4 m and 1/1 m) out of which two are temporarily active, showing have tens of vents (of centimetric and milimetric dimensions) with gas and water eruptions (Fig. 2). The crater C1 is of salse type (gas-bubbling water pool) (Fig. 2 and 4). All are placed along the valley, on the NNE-SSV direction, over a surface of approximately 900 m^2.

Fig. 4 Crater C1 of salse type (gas-bubbling water pool)

Mud volcano shape is generally concave developing at soil level (Crater C1, C2, C3, C4, C5, C6) with the exception of FG which has a gryphon type cone. Mud volcano activity can be best observed during the periods rich in rainfalls. Then, the gas under pressure along with the ground and meteoric water gets to the surface through cracks, generating new craters in the proximity of the existent ones. Mud volcano fields are covered with specific vegetation characteristic for river meadows.

2. MATERIALS AND METODS

Soil, water and vegetation samples were collected from the mud volcanoes area. Field work was performed at Forocici gryphon (FG), at crater C1 and at Apa Acră spa (AAS) from which water samples were collected. Water, soil and plant samples were collected on six separate occasions during the course of this study: November 2005 and 2006, March and May 2007, May 2008 and September 2009. The heavy metal content of samples have been determined at INCD-ECOIND Timişoara laboratory using Varian Atomic Absorption Spectrophotometer. The gases (CH_4, CO and H_2S) from FG were collected by immersing a glass funnel in the pool and then measured by Crowcon Detection instruments LTD Custodian, a portable gas detector. CO_2 presence was determined only qualitatively from visual observations. Heavy metal contents of FG water, of soil and vegetation were assessed for the first time within the framework of these studies.

3. RESULTS AND DISCUSSIONS

The study of the gas emissions in the field, as well as laboratory analyses of the water, soil and plant samples, yielded the results given below.

Gas emanations from FG are represented by CO_2, CH_4, CO and H_2S. The CO_2 emissions were determined only qualitatively estimating that these could surpass 15%. This gas is responsible for mud volcanoes eruptive activity. Its origin can be crustal (Bizerea, 1965; Oros, 1991). The CO_2 flux may, however, be highly variable with time, due to climatic variations and to tectonic activity in the area (Etiope *et al.*, 2004). Emissions of CO_2 and CH_4 show that these mud volcanoes represent an unavoidable source of greenhouse gases for the atmosphere (Etiope *et al.*, 2004). Concentration of CH_4 is about 12-13%. Previous studies did not mention the presence of CH_4 in this area. It can derive from organic material dissolution in anaerobic conditions, or from another source of hydrocarbons. Concentration in H_2S and CO is 0.4-0.8 ppm. Gas emissions from vents were not measured.

Water from FG, collected from the rocks sweeped by water and gases, has a concentration of 0.020-0.050 ppm for Cr and 0.014-0.050 ppm for Ni (Table 1).

Table 1. Time variation of heavy metals concentration from water of gryphon „Forocici" (FG) (all values in ppm)

Time	November 2005	November 2006	March 2007	May 2007	May 2008	September 2009
Temp (°C)	19.2	19.5	19.0	23.5	24.0	25.0
pH	6.85	7.10	7.00	7.10	7.00	7.00
Cd	bdl*	bdl*	bdl*	bdl*	bdl*	bdl*
Cr	0.027	0.040	0.020	0.050	0.030	0.028
Cu	bdl*	bdl*	bdl*	bdl*	bdl*	bdl*
Fe	2.400	2.900	1.940	0.060	1.085	1.990
Ni	0.036	0.022	0.014	0.050	0.030	0.020
Pb	bdl*	bdl*	bdl*	bdl*	bdl*	bdl*
Zn	bdl*	bdl*	bdl*	0,740	bdl*	bdl*

bdl* - below detection limit

Fe records the highest concentrations (0.060-2.400 ppm). The Fe presence as hematite was also observed at the ground surface in springs, by the emanations of CO_2 and in outcrops (Uruioc, 2002). The Fe origin can be biogenic as a product of ferrobacteria (Bizerea, 1965), or paleoclimatic, the Fe resulting from paleo-alteration of some silts deposited during the Pleistocene (Florea, 1964; Rogobete and Ţărău, 1997). Red siltic clay, rich in Fe, washed by mud and fluids, can derive from other warmer or cooler bioclimatic areas (Ianoş *et al.*, 1997). The high concentration of Fe remains a problem still to be solved in the future studies.

Concentrations in heavy metals are controlled by the mineralized liquids brought from deep areas of the terrestrial crust. The water from FG is a mixture between deep water, phreatic and meteoric water (Planke *et al.*, 2003).

Data presented in Table 1 show a variation in time of metal content. This can be explained by different content of the fluid flow and by annual or seasonal variations of water level in the gryphon.

Water from C1 does not contain Cr ions and shows a lower content of Fe than water from FG, while water from AAS (1500 m south of FG) does not contain Cr, having Cu ions instead (Table 2).

Table 2. Metal concentration of water seeps from FG, C1 and AAS (all values in ppm)

Site	Forocici Gryphon (FG)	Crater (C1)	Apa Acră Spa (AAS)
pH	7.10	7.00	7.20
Cd	bdl*	bdl*	bdl*
Cr	0.040	bdl*	bdl*
Cu	bdl*	bdl*	0,662
Fe	2.900	1.900	1.900
Ni	0.022	0.025	0.020
Pb	bdl*	bdl*	bdl*
Zn	bdl*	bdl*	bdl*

bdl* - below detection limit

Modifications regarding composition are due to penetration of deep layers by ascensional water under gas pressure. Water composition and concentration in chemical elements are controlled by lithologic background, by diagenetic processes and by water mixture (Planke *et al.*, 2003).

Soil presents in its first 5 cm a normal content for Cr, Pb and Zn according to the MAPM 756 /1997 decree (Table 3). Cu (20.90 ppm) and Ni (22.00 ppm) are exceptions, their content exceeding the normal limits. It is possible that higher concentrations could be found in the subjacent horizons, still not tested, where these heavy metals would be eluviated depthward by meteoric water.

Table 3. Heavy metal content of soil formed at the limit between the crater and FG cone (all values in ppm)

Site	Forocici Gryphon (FG)	Normal limits, ord. MAPM 756/1997
pH	7.10	
Cd	bdl*	1
Cr	5.30	30
Cu	20.90	20
Fe	7.500	-
Ni	22	20
Pb	7	20
Zn	49.12	100

bdl* - below detection limit

Plants that grow on the formed soil at the limit between the crater and FG cone contain Cr, Cu, Pb, Zn, Mn and Fe (Table 4). The analysis of flowers grouped in ament, belonging to *Salix cinerea* (P0), showed that the ament does not accumulate Ni, but show high concentrations of Fe-Mn (235-255 ppm), Zn (127 ppm) and less Cu (6 ppm). *Salix sp.* can uptake over 200 l of water daily (Gatlift, 1994). Every year, *Salix* also drops aments that are incorporated in soil through bioaccumulation processes that could lead to an important concentration of heavy metals in soil. It is possible that they be recovered in deep horizons.

Table 4. Heavy metal content of plants (all values in ppm)

Plants	*Salix cinerea*	*Polygonum aviculare*		
Sample	P0	P1	P2	P3
Cd	bdl*	bdl*	bdl*	bdl*
Cr	bdl*	bdl*	bdl*	bdl*
Cu	5.96	11.64	6.79	4.10
Fe	234.9	639.2	961.3	365.8
Ni	bdl*	bdl*	bdl*	bdl*
Mn	255.2	116.5	111.7	64.0
Zn	127.6	45.8	127.6	21.7

bdl* - below detection limit

Another studied plant belongs to *Polygonum* genus. This plant was sampled from the superior terrace of the gryphon (P1, P2 sample), where it develops very well when water level from crater comes down at least 0,5 cm. P1 and P2 samples were compared with sample P3, gathered from approximately 500 m from the main crater. This area is not under the influence of mud volcano activity.

It was shown that *Polygonum* species, gathered from inside the gryphon, accumulates higher quantities of heavy metals than the same species that develops under normal field conditions.

All these data represent a significant contribution for a better knowledge of mud volcanoes and the impact of their activity upon the environment. Thus, they will be used as documentation in order to propose the investigated area for protection. Mud volcanoes are themselves unique monuments and need to be protected.

4. CONCLUSIONS

In the Fibiş valley there are six mud volcanoes with temporary activity, concave in shape and lacking cones (C1, C2, C3, C4, C5, C6), as well as a gryphon type volcano (FG) with permanent activity and tens of vents of centimetric and milimetric dimensions.

Gas emissions from FG are represented by CO_2, CH_4, CO and H_2S. We assumed that the water from FG is a mixture between the one coming from depth of the terrestrial crust, water from the phreatic level and the meteoric one. Water composition and concentration in chemical elements is controlled by the lithologic background, diagenetic processes and water mixing.

The content in metals, sometimes very different from one sample to another, suggests a large variation in activity of the gryphon. Metal contents in soils is within normal limits for the Banat area.

The vegetation, collected from inside the gryphon, accumulates higher quantities of heavy metals than the same species that develop under normal field conditions. The data obtained will enter a data base related to the impact of mud volcano activity upon local biodiversity.

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