THE MUD VOLCANOES FROM BERCA: A SIGNIFICANT GEOLOGICAL PATRIMONY SITE OF THE BUZĂU LAND GEOPARK (ROMANIA)

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Abstract. The mud volcanoes from the Berca region of the Buzău County are the most representative sites of mud volcanoes in Romania, and one of the most significant geological sites of the Buzău Land Geopark. These mud volcanoes occur on an anticline situated in the inner extremity of the Foreland zone of the Eastern Carpathians. The ocurrence of this phenomenon is linked, as in other world regions, to the highly developed diapirisim of the area; mud migrates at the surface throughout faulted flanks of the anticline, from Middle Miocene deposits at a depth of around 3,000 m. Two sites of the Berca area, namely Pâclele Mari and Pâclele Mici, have been studied in detail, by field observation and GPS surveys. This paper presents data on the geology of the region, the geochemistry of the ejected fluids (most synthesizing previous data), as well as the morphology of the mud volcanoes, which show various sizes and shapes evidenced by our investigation on over 100 such structures.

Keywords: mud volcanoes, geology, morphology, geochemistry, central Romania

1. INTRODUCTION

The term mud volcano refers to formations created by geo-exuded slurries (usually, including water) and gases. Around 80% or even more of the gas released from these structures, including the Romanian ones, is methane, with much less carbon dioxide, nitrogen, and other gases (Baciu *et al.*, 2007; Etiope *et al.*, 2002; Filipescu & Humă, 1979). Ejected materials are often the slurry of fine solids suspended in liquids that may include water, which is frequently acidic or salty, and hydrocarbon fluids.

Mud volcanoes have been identified on land and in shallow water, but it has been estimated that a significant number of such structures exists on continental slopes and abyssal plains. Mud volcanoes are known to occur on all continents; however, in Europe, only few such structures are present, *i.e.* in the Taman Peninsula, Kerci Peninsula, in the northern front of the Apennines, and in Sicily, but, also, nearby Rome, recently emerged in 2013 (Higgins *et al.*, 1974; Milkov, 2000; Etiope *et al.*, 2004b, among many others); in Romania, mud volcanoes appear mostly in the extra-Carpathian area, but such phenomena were described also from the intra-Carpathian area, *i.e.*, the Transylvanian region (Grigoraş, 1961; Paraschiv, 1970; Baciu *et al.*, 2007).

The most famous mud volcanoes in Romania are placed in the southern part of the Eastern Carpathian belt, in the Buzău County. The phenomenon can be noticed on several separate locations near the Berca commune, from which two areas, named Pâclele Mici and Pâclele Mari are nature reserves; they are placed in the southern part of the Buzău Land Geopark. Both nature reserves have been protected areas of national interest, since the year 2000, belonging to the Category IV (following the IUCN classification). These nature reserves, both geological and botanical, are named **Vulcanii Noroioşi de la Pâclele Mari** (*The Mud Volcanoes from Pâclele Mari*) and **Vulcanii Noroioşi de la Pâclele Mici** (*The Mud Volcanoes from Pâclele Mici*), but these areas were declared protected since 1924, the object of protection being the landscape displayed by the relief, as well as the halophyte plant species.

The mud volcanoes from the Berca region of the Buzău County have been known for a long time by local people; in the region, the name of the hills surrounding the mud volcanoes is 'The Dragon Hills', due to the gas emanation of the area. The first reference in the geological literature was made by the French geologist Coquand (1867), followed by the contribution of the Romanian geologist Cobălcescu (1883); the first to analyze the

gas from the ejected mud in the Berca region was Costăchescu (1906). Afterwards, starting with the beginning of the 20th century, detailed investigations were made by Teisseyre (1910, 1911 and 1924), Krejci-Graf (1935a and 1935b), followed by Ciocârdel (1949); the last-mentioned author linked the occurrence of mud volcanoes from the region to the hydrocarbon accumulation in geological structures, *i.e.*, the anticline Berca-Arbănaşi. Considerations on the stratigraphy of the region were published by Macarovici (1961), while the palaeontological content of the drillings from the region was analyzed by Voicu (1975).

In the second half of the last century, several detailed geomorphologic investigations of the Berca region were made by Romanian geographers, who identified a depression in the sector where the mud volcanoes occur (Badea & Bălteanu, 1971; Sencu, 1985); Sencu (1985) offered also a morphological classification of the volcano cones from Berca. A first synthesis of the Romanian mud volcano occurrences, including that from the Berca region of the Buzău County, is due to Peahă (1965). Recent additional considerations on the mud volcanoes from Berca, made by analyzing satellite images, were published (Abdellaoui *et al.*, 2005).

Significant contributions regarding the composition of the gases released by the mud volcanoes in the Berca region were brought by Etiope *et al.* (2004); Baciu *et al.* (2007, 2010), and Frunzeti *et al.* (2012). The interrelation between the occurrence of the mud volcanoes in the Berca region, the intensity of the mud and gas emanations and the seismicity of the region, linked to the strongly active Vrancea zone of the Romanian Carpathian bend, was detailed by Baciu & Etiope (2005). The mineralogy and the chemistry of the mud ejected through the volcano cones from the Pâclele Mari and Pâclele Mici geological sites of the Berca region were published by Shnyukov *et al.* (2009) and Madeja & Mrowczyk (2010).

The importance of the mud volcanoes "*Vulcanii noroioşi*" from the Buzău County, as a geological reserve, was pointed out already in the middle of the last century by Moşneagă (1958). From a geo-touristic point of view, the works published by Dicu (2005), Madeja & Mrowczyk (2010) and Bardintzeff (2011) are to be noted.

This paper provides new data on the occurrence of the mud volcanoes from Berca, including the morphology and sizes of the cones, as well as the geochemistry of the emanations. A detailed study of this phenomenon, including an up-to-date geological interpretation of the unique sites Pâclele Mari and Pâclele Mici from Berca, situated in the Buzău Land Geopark, are also presented herein, together with a comparison with other mud volcano sites.

2. GEOLOGICAL SETTING

Vulcanii Noroioşi de la Pâclele Mari (*The Mud Volcanoes from Pâclele Mari*) (Fig. 1) is a (geological and botanical)

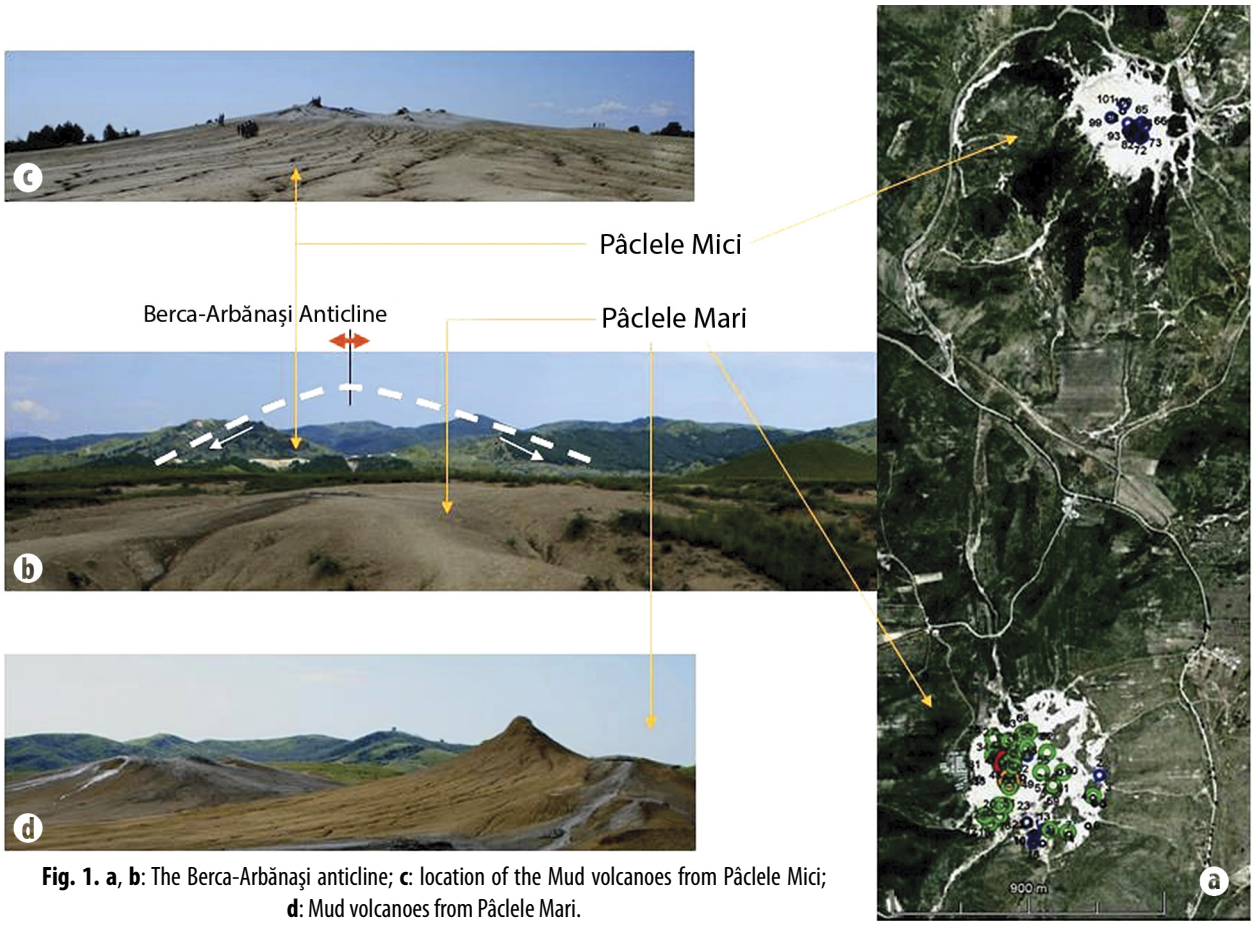


Fig. 1. a, **b**: The Berca-Arbănaşi anticline; **c**: location of the Mud volcanoes from Pâclele Mici; **d**: Mud volcanoes from Pâclele Mari.

nature reserve, placed on the administrative territory of the Scorțoasa commune of the Buzău County. The site (Latitude N: 45°20'22" and Longitude E: 26°42'28") is situated at an altitude of 322 m, on a surface of 22 ha. The name is connected to the large size of three volcanoes, over 1.5 m, situated in the center of the plateau.

Vulcanii Noroioşi de la Pâclele Mici (*The Mud Volcanoes from Pâclele Mici*) (Fig. 1) is a (geological and botanical) nature reserve, placed on the administrative territory of the Berca commune of the Buzău County. The site (Latitude N: 45°21'31" and Longitude E: 26°42'42") is situated at 341 m altitude, on a surface of 16.5 ha. The crater size varies between 10 and 100 cm.

The Berca region, included in the southern extremity of the Buzău Land Geopark (Fig. 2), where the Mud Volcanoes are situated, belongs, geologically, to the outermost geological structure of the Inner Foredeep of the Carpathian region. This region is known as one of the most significant in Romania regarding the hydrocarbon resources, which are trapped in the Oligocene, Miocene (Burdigalian, Maeotian and Sarmatian) and Pliocene (Pontian, Dacian and Romanian) sediments (Paraschiv, 1975). The exploitation of hydrocarbons in the region started already at the end of the 19th century and continues nowadays. The geological exploration indicates that the eastern flank of the Berca-Arbănaşi anticline contains oil and gas reserves on the whole length, while the western flank encloses hydrocarbons only around the localities Pâclele and Beciu (Grigoraş, 1961; Paraschiv (1975). Around the latter locality, another site with mud volcanoes developed during the last decades; the cones are not spectacular like those from Pâclele Mari and Pâclele Mici from Berca, but, around the structures, a mixture of salty mud and oil may be seen.

In the Inner Foredeep, outer part, between the Slănic and Buzău valleys, the Berca-Beciu-Arbanaşi anticline is disposed on a length of 30 km. This anticline, striking NS is affected by longitudinal and transverse faults. The recognized stratigraphic succession of this anticline is composed of Pliocene, *i.e.*, Upper Pontian, Dacian and Romanian sediments, as well as Upper Miocene, such as Lower Pontian deposits, the latter occurring in a small area in the axial part of the anticline. In this area, the two fields (Pâclele Mari and Pâclele Mici) of mud volcanoes (Fig. 2) are located.

On the whole area where active and older structures of inactive mud volcanoes occur, rock fragments of clays, sandstones, gypsum and limestones are spread. Commonly, coquinas, mainly Sarmatian in age, containing brackish water bivalves and gastropods could be found.Among the rock fragments, there are also huge blocks of sandstone or limestones, with a volume >1 m^3 and a weight up to 2 tones; their presence is indicative for an intense tectonic in the Berca area in the geological past, when, probably, the activity of the mud volcanoes was much more intense than nowadays.

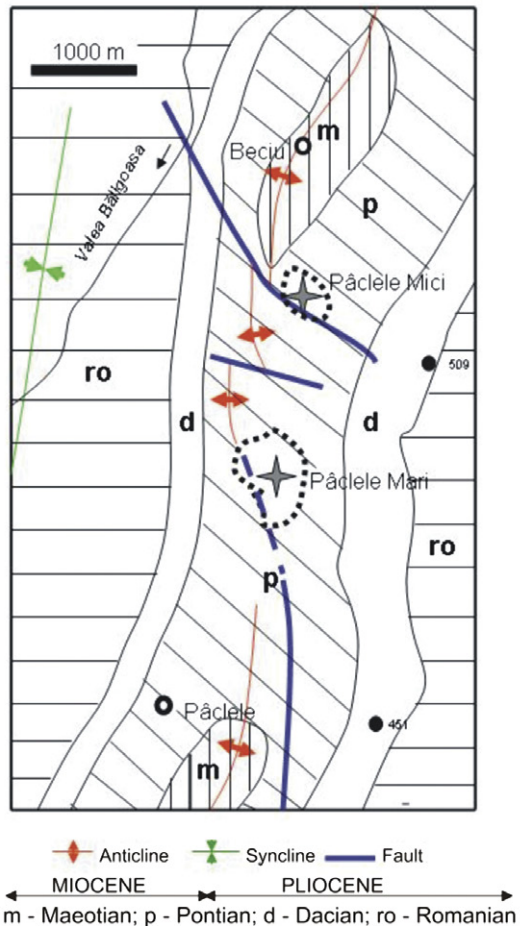


Fig. 2. Geological map of the Berca region, showing the location of Pâclele Mari (*The Mud Volcanoes from Pâclele Mari*)) and Pâclele Mici (*The Mud volcanoes from Pâclele Mici*), redrawn and modified after Ciocârdel (1949).

The mud flows are rich in crude oil and "sample" Sarmatian and Badenian rock fragments (fossiliferous limestones, sandstones, clays and salt) during their ascent. The mud volcanoes occurrence is linked to the natural gas (methane) seeps along the faults. In their ascent, the gasses drive upward water from the water table, as well as mud resulting from the soaked marls which overflow through small craters. Thus, small (3-4 m tall) fans are formed. At Pâclele Mari, the mud layer is about 20 m thick and it lies on a 1000 x 600 m area (Peahă, 1965; Sencu, 1985).

Detailed lithological and micropaleontological investigations were undertaken on the cores that proceed from the various drillings in the area; among them, 2341 Berca, placed at around 1 km NE from the Nature Reserve Pâclele Mici, was the deepest, reaching a depth of 3330 m and crossing a succession of sediments belonging (from young to old) to the Romanian, Pontian, Maeotian and Sarmatian (Voicu, 1975). The age of the deposits correlated with the tectonic pattern of the area allow Sencu (1985) to assume that the depth of the mud formation in the Berca area is around 3,000 m.

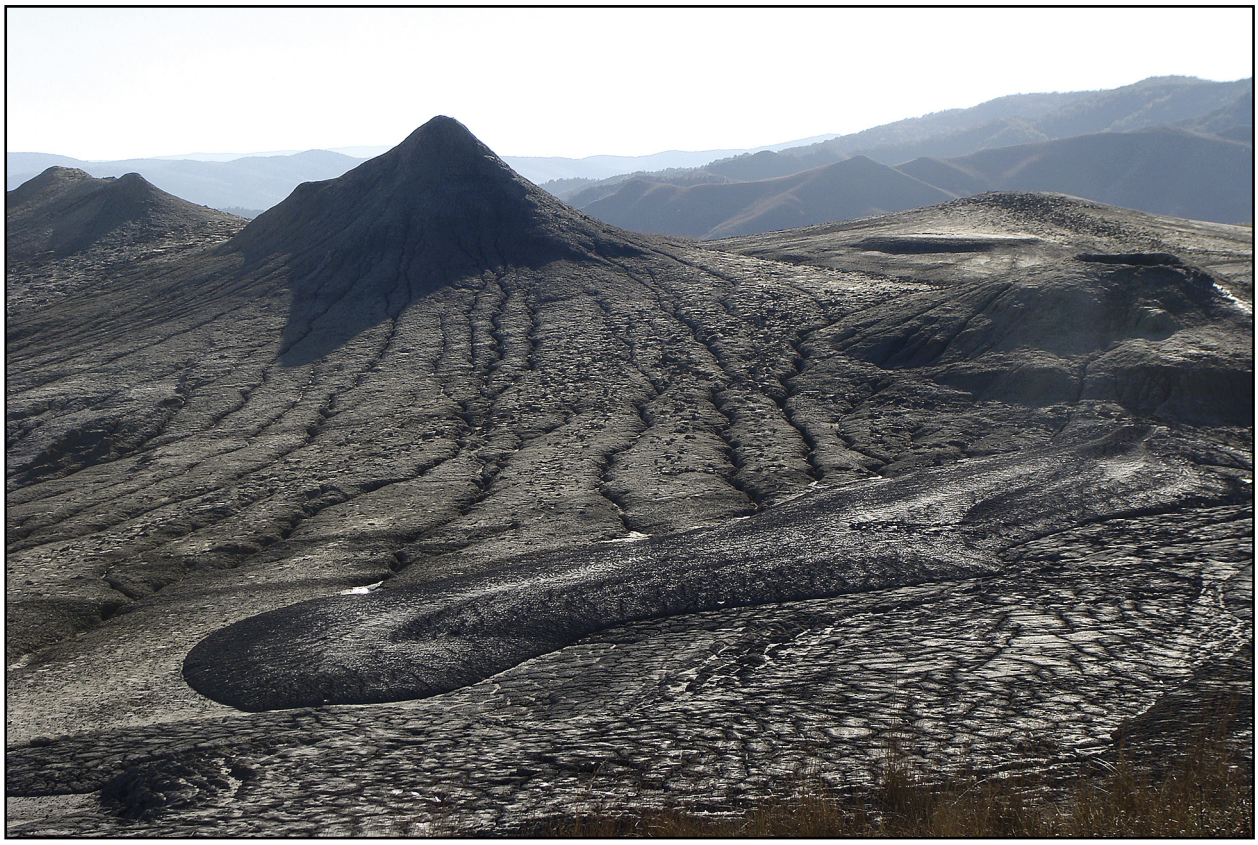


Fig. 3. The Mud Volcanoes Pâclele Mari (Photo: Andrei Briceag).

The existence of numerous faults along with the very high structural position of the hydrocarbon-saturated Middle and Late Miocene deposits deposits triggered, in some places, the partial deterioration of the field sealing conditions. The longitudinal and transverse fault system created pathways to the hydrocarbons (especially, gas), allowing the migration towards the surface and producing the occurrence of the Mud Volcanoes in the area.

3. GEOCHEMISTRY

Former studies on the chemistry of the gases ejected in the area of Mud volcanoes from Pâclele Mici and Mud volcanoes Pâclele Mici, but also at various depths of the Drilling 2341 (Filipescu & Humă, 1979) indicate that the methane content is high, that is, over 95 % (Table 1). Small amounts of CO_2 (1.1-2.7%), N_2 (0.03-0.14%), H_2 (0.022-0.71%) and Ar (0.001-0.002%) are also present.

Table 1. Composition of gases identified in hydrocarbons (drilling 2341 Berca) and at the gas emission from the mud volcanoes from Berca Pâclele Mici and Pâclele Mari (after Filipescu & Humă, 1979).

Depth/site	Methane	Ethane	Propane	Butane	Pentane	Hexane	Heptanes	Metilciclopentane	Metilciclohexane	Argon	Nitrogen	CO_2	HC
Drilling No. 2341 Berca	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**9**	**11**	**12**	**13**	**14**	**15**
2618-2601 m	97.9	1.5	0.30	0.072	0.012	0.0050	0.0009	0.0012	0.036	0.002	0.033	0	1.97
2877-2871 m	95.0	2.7	0.66	0.14	0.021	0.001	0.0009	0.0024	0.022	0.004	0.140	1.1	3.7
3331-3002 m	95.4	0.8	0.14	0.045	0.001	0.0001	0.0008	0.00008	0.71	0.001	0.120	2.7	1.1
Pâclele Mici	98.1	0.08	0.03	0.001	0.001	0.001	0	0	0	0.05	0.16	1.5	0.11
Pâclele Mari	95.7	0.82	0.3	0.056	0.009	0.0014	0	0	0	0.07	0.60	2.3	1.23

An interesting comparison between the CH_4 fluxes noticed in the microseepage and vent outputs of several mud volcano areas from Romania and Azerbaijan (Table 2) was published by Baciu *et al.* (2007). The emission in the region of the mud volcanoes from Berca (in the southern part of the Buzău Land Geopark) show significantly higher values than in other mud volcano areas from Romania and from other countries, *i.e.*, Azerbaijan, where the phenomenon of mud volcanoes is also common (Table 2).

To note that concerning the gas discharge of the mud volcanoes from the Berca region the time between the occurrence of the gas in the cone and its wasting in the atmosphere is around 3-5 seconds. Afterwards, in the ejected mud, remain degasified alveoli (Fig. 4).

The water chemistry of the mud volcanoes in both protected areas, Pâclele Mari and Pâclele Mici (Sencu, 1985), show that the water emerging from the cones have a very high content of NaCl (44,266-64,885 mg/l), medium values of bicarbonates (2,206-3,074 mg/l) and extremely low content of sulphates (19.72-74.12 mg/l) – Table 3.

4. MORPHOLOGY OF THE MUD VOLCANOES FROM BERCA

4.1. General morphology

In general, the mud volcanoes show a high variety of cone shapes and sizes. Commonly, the onshore mud volcanoes are located, all over the world, in zones devoid of vegetation (= *„tassik"*, after Higgins & Saunders, 1974), floored by blocky clays and saline waters. One of the first mud volcano classification was made by Shih (1967), based on the study of mud volcanoes from Taiwan. Taking into account the geomorphologic shape, the author established five types: the mud cone, the mud shield, the mud maar, the pool mud and the mud hole. Additionally, other classification of the mud volcanoes were published, based on various criteria, such as seismic features (Yusifov and Rabinowitz, 2004), morphology and evolution (Gál, 2009) and morphogenesis and geochemistry (Aliyev *et al.*, 2002 and 2009).

The volcano shape and size is determined by the viscosity of ejected fluids (mud, water and detritus), as well as the

Table 2. Comparison between CH_4 fluxes in the microinfiltrations identified in Romania and Azerbaijan (after Baciu *et al.*, 2007). MV = mud volcano; DS = dried infiltration.

Country/Localization	Sample source	Surface	Microseepage output	Vent output	Total output	Specific Flux t/km²/year
		km²	tons/year			
Pâclele Mici (Romania, outer Eastern Carpathian region)	MV	0.62	128	255	383	618
Pâclele Mari (Romania, outer Eastern Carpathian region)	MV	1.62	430	300	730	451
Fierbători (Romania, outer Eastern Carpathian region)	MV	0.025	20	17	37	1480
Andreaşu (Romania, outer Eastern Carpathian region)	DS	0.0004	26	24	50	125000
Sărmăşel (Romania, Transylvania)	DS	0.007	16	5	21	3000
Homorod (Romania, Transylvania)	MV	0.005	0.5	0.5	1	200
Bazna (Romania)	DS	0.002	0.4	-	0.4	200
Lokbatan (Azerbaijan)	MV	2.98	139	-	342	115
Kechaldag (Azerbaijan)	MV	0.77	90	4	94	122
Dashgil (Azerbaijan)	MV	1.4	220	623	843	600
Yanardag (Azerbaijan)	DS	0.01	233	-	68	6800
Bakhar (Azerbaijan)	MV	0.7	36.5	8.4	45	64

Table 3. Composition of the water from the Pâclele Mari Mud Volcanoes (PMA) and the Pâclele Mici Mud volcanoes (PMI) (after Sencu, 1985).

Location	Cations					Anions			Fixed Residuum mg/l	Total Mineralization mg/l
	Ca	Mg	Na	K	NH_4	Cl	SO_4	HCO_3		
PMA	1370	326	25503	262	33	42600	53	732	74100	70881
PMI	134	151	20426	222	24	31200	37,4	1940	56000	54226

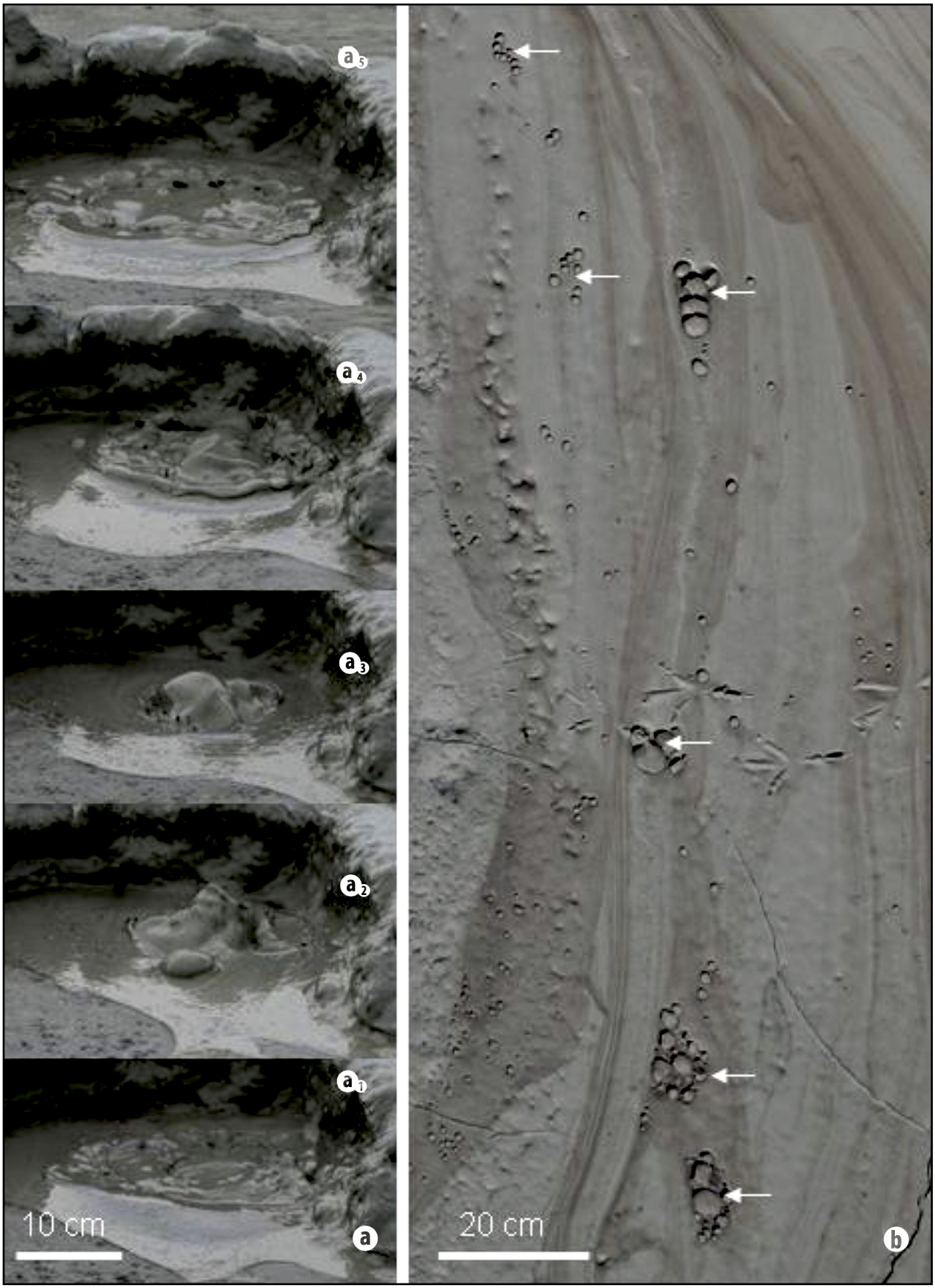


Fig. 4. a: Phases of gas bubble occurrence (a_1 up to a_5) in a vent at Pâclele Mari; **b**: degasified alveoli in the ejected mud at Pâclele Mici (Photo: Ştefan Szobotka, July 2010).

quantity and gas pressure. In the Berca region, these features have led to the occurrence of various shapes: positive ones, such as the pointed cones, flat and spherical shields, and negative ones, *i.e.* holes with water, mud and gas emissions (Peahă, 1965). Basically, the shape of the mud volcano is determined by the nature of ejected fluids (Baciu *et al.*, 2010; Gál, 2010). The convex shapes (cones) are formed when the ejected mud has a high viscosity, while the concave shapes (holes with mud) are related to low mud/water ratio.

Herein, we use a morphological classification of the mud volcanoes, considering as characteristic the following features: (i) the mud cone, which may be pointed or with lateral ejections; (ii) the mud pool, with punctiform ejections, multiple ejections and diffuse ejections; (iii) the mud lobe, whose aspect is linked to the field characteristic and the quantity of mud delivered, leading to the occurrence of single lobe, double lobes or multiple lobes (Fig. 5). In fact, the mud lobe represents the first episode of the mud ejection process and substantially contributes to the edifice of the mud volcanoes, by adding material to the cone flanks.

4.2. Geomorphology of the Berca mud volcanoes

Our studies, started 5 years ago, point out the presence of a high number of surface vents, cones, pools and holes in the Berca region, *i.e.,* 101; 64 of them are situated at Pâclele Mari and 37 at Pâclele Mici. The dimension and size of the identified mud volcanoes (Tables 4 and 5), GPS positioned (Fig. 6), have been investigated in detail.

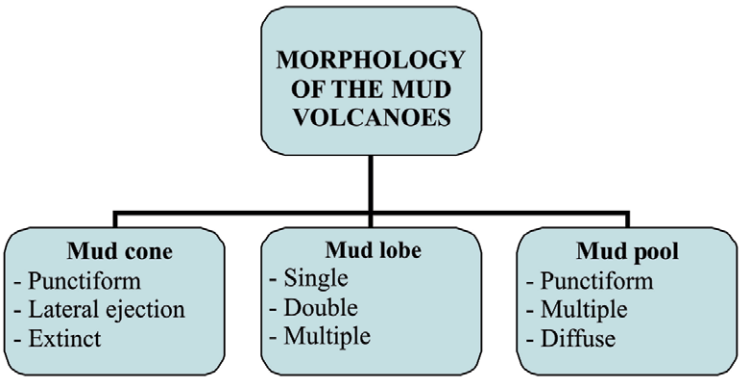


Fig. 5. Morphological features of the Pâclele Mari and Pâclele Mici mud volcanoes.

Table 4. Dimensions and GPS position of mud volcanoes from Pâclele Mari.

PUNCTIFORM EJECTIONS

No.	Cone no. from Fig. 6	Cone base diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
1	**1**	5.35	45°20'18.4"	26°42'39.5"
2	**2**	57.70	45°20'21.5"	26°42'39.0"
3	**6**	26.80	45°20'16.1"	26°42'37.3"
4	**7**	6.10	45°20'15.2"	26°42'34.4"
5	**11**	25.00	45°20'15.3"	26°42'29.1"
6	**12**	8.00	45°20'15.1"	26°42'29.6"
7	**15**	93.75	45°20'16.4"	26°42'28.0"
8	**20**	28.75	45°20'17.4"	26°42'22.4"
9	**21**	150.00	45°20'16.8"	26°42'23.8"
10	**22**	110.00	45°20'17.1"	26°42'23.9"
11	**37**	172.50	45°20'22.9"	26°42'24.1"
12	**39**	40.00	45°20'22.4"	26°42'24.5"
13	**40**	13.10	45°20'23.5"	26°42'25.1"
14	**44**	55.70	45°20'23.3"	26°42'25.7"
15	**49**	115.50	45°20'21.4"	26°42'25.3"

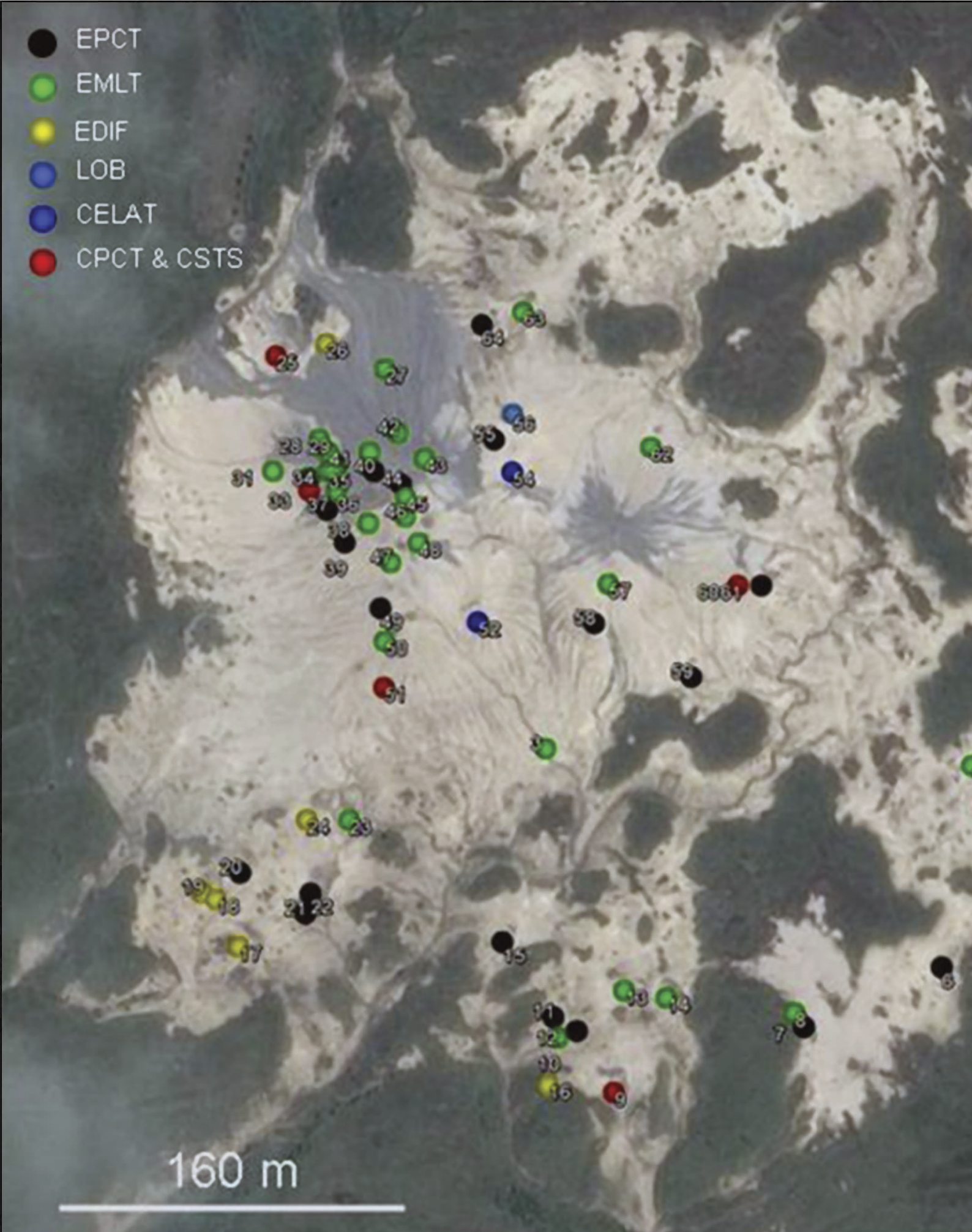
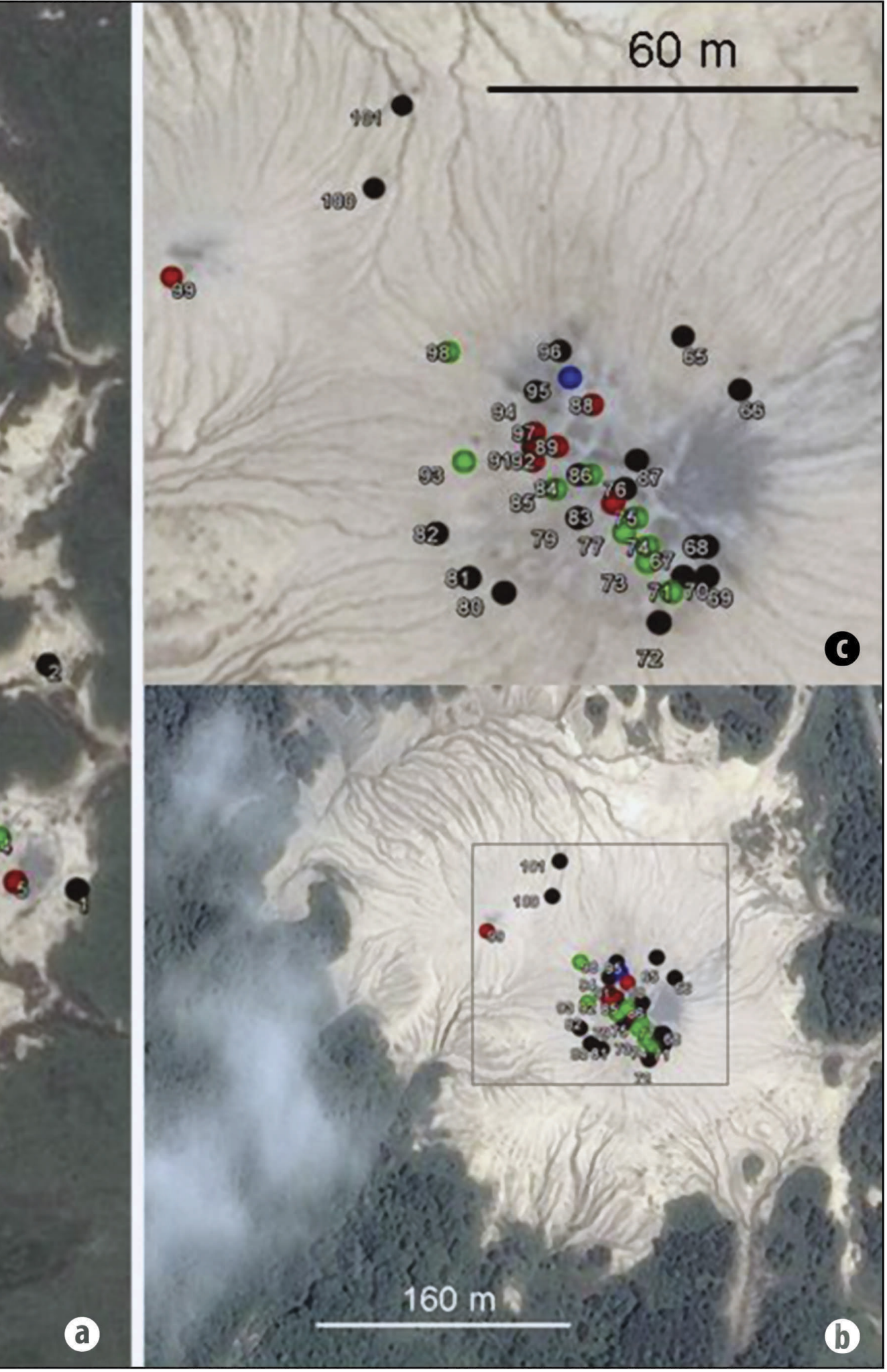


Fig. 6 – Mud cones and ejections at (**a**) Pâclele Mari and (**b**) Pâclele Mici id
Legend: **EPCT** – punctiform ejections; **EMLT** – multiple ejections; **EDIF** – diffuse ejections; **LOB** – bilateral ejectio



lentified in July 2010 (position on www.google.earth).
ons; **CELAT** – cone with lateral ejection; **CPCT** & **CSTS –** punctiform cone and inactive cone.

Tabel 4 (continued)

No.	Cone no. from Fig. 6	Cone base diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
16	**55**	150.00	45º20'24.0"	26º42'27.7"
17	**58**	11.00	45º20'21.2"	26º42'29.9"
18	**59**	123.50	45º20'20.4"	26º42'32.0"
19	**61**	121.40	45º20'21.8"	26º42'33.5"
20	**64**	288.75	45º20'25.8"	26º42'27.4"

MULTIPLE EJECTIONS

No.	Pool no. from Fig. 6	Pool diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
1	**4**	29.00	45º20'19.1"	26º42'38.0"
2	**8**	166.65	45º20'15.4"	26º42'34.2"
3	**10**	62.00	45º20'15.0"	26º42'29.2"
4	**13**	51.80	45º20'15.7"	26º42'30.6"
5	**14**	258.75	45º20'15.6"	26º42'31.5"
6	**23**	243.75	45º20'18.2"	26º42'24.7"
7	**27**	382.00	45º20'25.1"	26º42'25.3"
8	**28**	232.50	45º20'24.0"	26º42'23.9"
9	**29**	270.00	45º20'23.8"	26º42'24.1"
10	**30**	233.00	45º20'23.6"	26º42'24.3"
11	**31**	350.00	45º20'23.5"	26º42'22.9"
12	**32**	200.00	45º20'23.4"	26º42'23.7"
13	**34**	175.00	45º20'23.5"	26º42'24.2"
14	**35**	192.20	45º20'23.5"	26º42'24.1"
15	**36**	463.50	45º20'23.2"	26º42'24.3"
16	**38**	1110.00	45º20'22.7"	26º42'25.0"
17	**41**	375.00	45º20'23.8"	26º42'25.0"
18	**42**	256.00	45º20'24.1"	26º42'25.6"
19	**43**	360.00	45º20'23.7"	26º42'26.2"
20	**45**	185.00	45º20'23.1"	26º42'25.8"
21	**46**	207.15	45º20'22.8"	26º42'25.8"
22	**47**	189.40	45º20'22.1"	26º42'25.5"
23	**48**	230.80	45º20'22.4"	26º42'26.1"
24	**50**	507.70	45º20'20.9"	26º42'25.4"
25	**57**	166.60	45º20'21.8"	26º42'30.2"
26	**62**	118.20	45º20'23.9"	26º42'31.1"
27	**63**	388.60	45º20'26.0"	26º42'28.3"
28	**64**	288.75	45º20'25.8"	26º42'27.4"

Tabel 4 (continued)

DIFFUSE EJECTIONS

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
1	**16**	85.25	45°20'14.3"	26°42'29.0"
2	**17**	174.00	45°20'16.3"	26°42'22.4"
3	**18**	150.00	45°20'17.0"	26°42'21.9"
4	**19**	465.00	45°20'17.1"	26°42'21.6"
5	**24**	360.00	45°20'18.2"	26°42'23.8"
6	**26**	20.30	45°20'25.5"	26°42'24.0"

BILATERAL LOBES

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
1	**56**	885.50	45°20'24.4"	26°42'28.1"

PUNCTIFORM CONES

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
1	**5**	23.00	45°20'18.5"	26°42'38.3"
2	**9**	9.15	45°20'14.2"	26°42'30.4"
3	**25**	117.75	45°20'25.3"	26°42'22.9"
4	**33**	130.40	45°20'23.2"	26°42'23.7"
5	**51**	171.45	45°20'20.2"	26°42'25.4"
6	**60**	48.50	45°20'21.8"	26°42'33.0"

CONE WITH LATERAL EJECTIONS

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
1	**52**	39.25	45°20'21.2"	26°42'27.4"
2	**54**	55.00	45°20'23.5"	26°42'28.1"

Table 5. Dimensions and GPS position of mud volcanoes from Pâclele Mici.

PUNCTIFORM EJECTIONS

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
1	**65**	58.70	45°21'30.6"	26°42'45.1"
2	**66**	70.80	45°21'30.2"	26°42'45.6"
3	**67**	45.65	45°21'29.1"	26°42'45.2"
4	**68**	56.25	45°21'29.1"	26°42'45.3"
5	**69**	32.90	45°21'28.9"	26°42'45.3"
6	**70**	6.50	45°21'28.9"	26°42'45.1"
7	**72**	2.65	45°21'28.6"	26°42'44.9"
8	**76**	40.40	45°21'29.5"	26°42'44.6"

Tabel 5 (continued)

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitude N	Longitude E
9	**79**	15.50	45°21'29.3"	26°42'44.2"
10	**80**	43.30	45°21'28.8"	26°42'43.6"
11	**81**	7.75	45°21'28.9"	26°42'43.3"
12	**82**	3.20	45°21'29.2"	26°42'43.0"
13	**84**	79.40	45°21'29.6"	26°42'44.2"
14	**87**	23.00	45°21'29.7"	26°42'44.7"
15	**94**	32.50	45°21'30.2"	26°42'43.8"
16	**96**	21.20	45°21'30.5"	26°42'44.0"
17	**100**	44.40	45°21'31.8"	26°42'42.2"
18	**101**	61.10	45°21'32.5"	26°42'42.4"

MULTIPLE EJECTIONS

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitudinal N	Longitudinal E
1	**71**	36.60	45°21'28.8"	26°42'45.0"
2	**73**	67.50	45°21'29.0"	26°42'44.8"
3	**74**	135.90	45°21'29.1"	26°42'44.8"
4	**75**	32.30	45°21'29.3"	26°42'44.7"
5	**77**	26.60	45°21'29.2"	26°42'44.6"
6	**85**	49.00	45°21'29.5"	26°42'44.0"
7	**86**	91.60	45°21'29.6"	26°42'44.3"
8	**93**	97.50	45°21'29.7"	26°42'43.2"
9	**98**	64.30	45°21'30.5"	26°42'43.0"

PUNCTIFORM CONE

No.	Cone no. from Fig. 6	Vent diamter (cm)	GPS Coordinates	
			Latitudinal N	Longitudinal E
1	**83**	21.40	45°21'29.4"	26°42'44.5"
2	**88**	30.00	45°21'30.1"	26°42'44.3"
3	**89**	23.60	45°21'29.8"	26°42'44.0"
4	**90**	40.60	45°21'29.8"	26°42'43.8"
5	**92**	24.00	45°21'29.7"	26°42'43.8"
6	**97**	65.00	45°21'29.9"	26°42'43.8"
7	**99**	79.70	45°21'31.1"	26°42'40.4"

CONE WITH LATERAL EJECTION

No.	Cone no. from Fig. 6	Vent diameter (cm)	GPS Coordinates	
			Latitudinal N	Longitudinal E
1	**91**	53.60	45°21'29.8"	26°42'43.8"
2	**95**	29.50	45°21'30.3"	26°42'44.1"

In July 2010, in Pâclele Mari and Pâclele Mici areas, 38 mud volcanoes with punctiform ejections were observed, 37 with multiple ejections, 6 with diffuse ejections, 1 bilateral lobe, 12 punctiform cones, 2 cones with lateral ejection, and 4 cones that were inactive (Table 6; Fig. 7).

5. MUD VOLCANO EJECTIONS FROM BERCA

5.1. Punctiform mud ejections

This type of ejection is the most commonly encountered in the Berca area, with 20 occurrences at Pâclele Mari and 18 at Pâclele Mici (Table 6 and Fig. 8). These ejections appear, either as a single mud flow on the soil (Fig. 8a), or, frequently, as small elliptical depressions (Figs 8b, c, f and g), with concentric pellicles of oil (Fig. 8c); rarely, the depressions are circular, being placed, either in an apex of a small cone (Fig. 8d), or, directly, on the soil (Fig. 8e). Seldom, small depression groups may occur (Fig. 8h).

5.2. Multiple mud ejections

Multiple mud ejections are the second frequent ejections in the Berca area; in all, 37 such occurrences have been recorded, 28 at Pâclele Mari and 9 at Pâclele Mici (Table 6). This type of ejection contains several punctiform ejections, which are located in a mud pool, usually, circular (Figs 9a, c and d), but also several small such pools may be noticed (Fig. 9b) which are situated very close to each other (Fig. 9e). In some places, oil pellicles are present, as well as various hydrocarbon oxidation products, floating in the mud (Figs 9b, c and d).

5.3. Diffuse ejections of salty water and mud

This type of ejection sporadically occurs, being encountered only in the SW part of the Pâclele Mari mud volcano perimeter. They do not show any structure (Figs 10a and b); the ejections of mud and salty water occur directly throughout the weak limonitized rocks, making a very short cone, up to a few cm (Fig. 10c).

5.4. Mud lobes

The mud lobes in the studied areas exhibit very spectacular sizes and shapes. The newly formed lobes may be partially superposed on older dried ones, where mud cracks are visible (Figs 11a, b and c). In the Berca region, depending on the geomorphology, the occurrence of several mud layers could lead to the formation of a plateau displaying composite cones, similarly with the structures recorded in the stratovolcanoe appearence.

5.5. Punctiform cones

This kind of structure is characterized by the presence of a well developed cone, with the centre in the apex of the vent. Sometimes, the cone is intact (Fig. 12b); it may be also partly cracked (Fig. 12a), or flanked by lateral bunged channels (Fig. $12a_1$); in other places, the cone contains two adjacent apical vents (Fig. 12c). With some cones, the central crater is broken and the mud is flowing throughout a semicircular channel, bordered by marked shields (Fig. 12d). In such structures, the cone diameter exceeds 1 m at Pâclele Mari , while at Pâclele Mici the diameter is up to 80 cm (Fig. 15c).

Table 6. Number and morphological types of mud cones from Pâclele Mari and Pâclele Mici. PCT = punctiform ejections; EMLT = multiple ejections; EDIF = diffuse ejections; LOB = bilateral ejections; CPCT = punctiform cone; CELAT = cone with lateral ejection; CSTS = inactive cone.

	Type of ejection				Mud cone			Total
	EPCT	EMLT	EDIF	LOB	CPCT	CELAT	CSTS	
Pâclele Mari	20	28	6	1	6	1	2	**64**
Pâclele Mici	18	9	-	-	7	1	2	**37**
Total	**38**	**37**	**6**	**1**	**13**	**2**	**4**	**101**

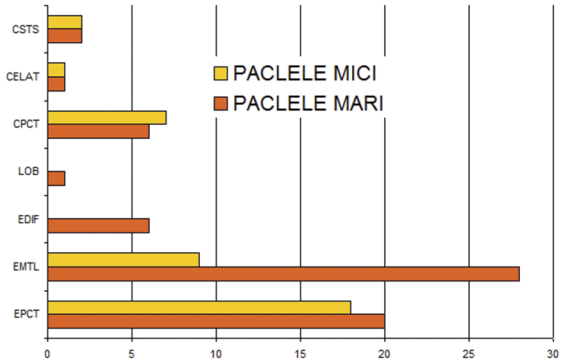


Fig. 7. Number of ejection types of the mud cones occurring in Pâclele Mari and Pâclele Mici (the abbreviations correspond to those from Table 6).

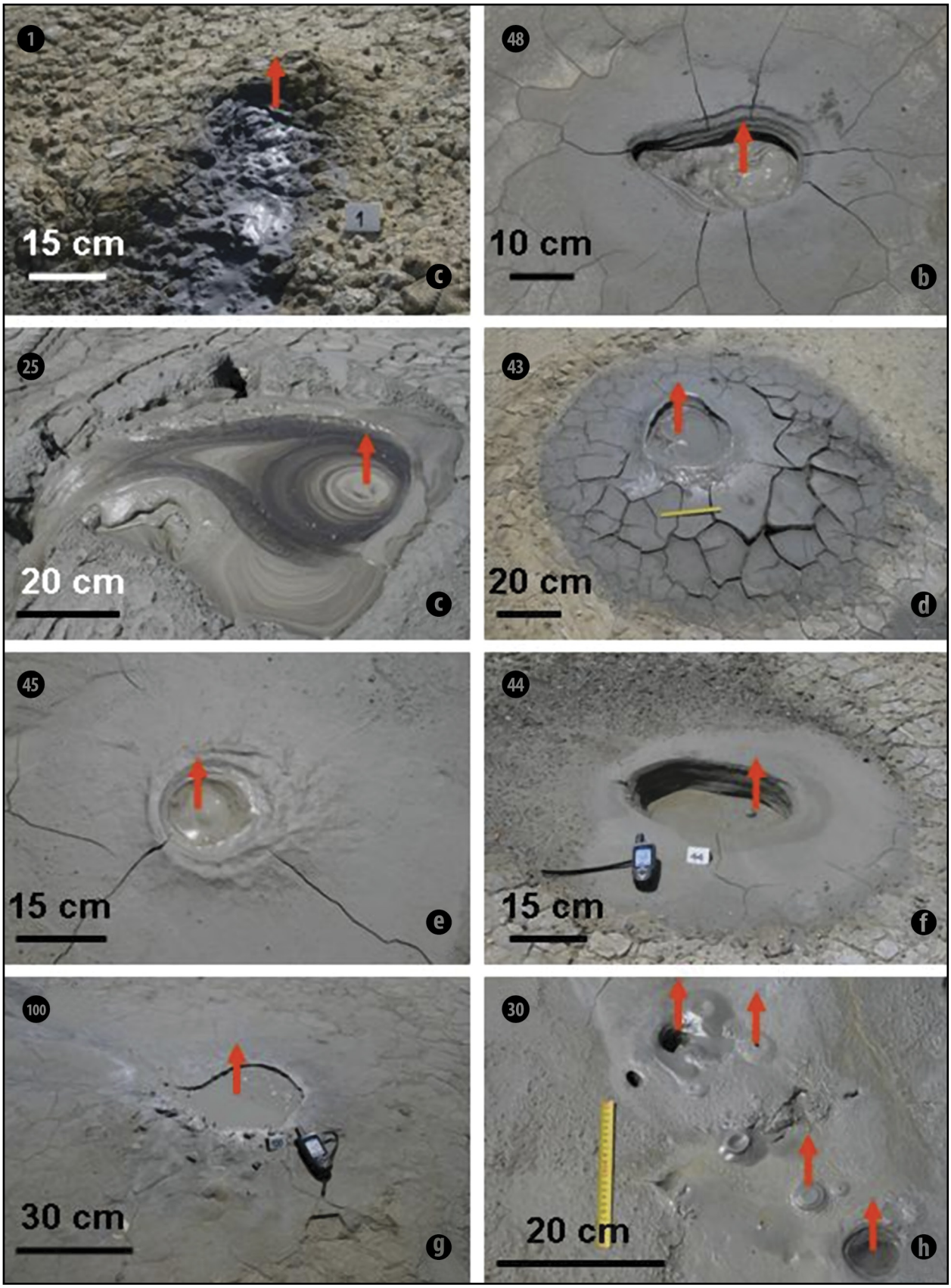


Fig. 8. Punctiform mud ejection no. 1, 25, 30 and 43-45 from Pâclele Mari and no. 100 from Pâclele Mici; No. of each structure corresponds to those from Fig. 6 (Photo: Titus Brustur).

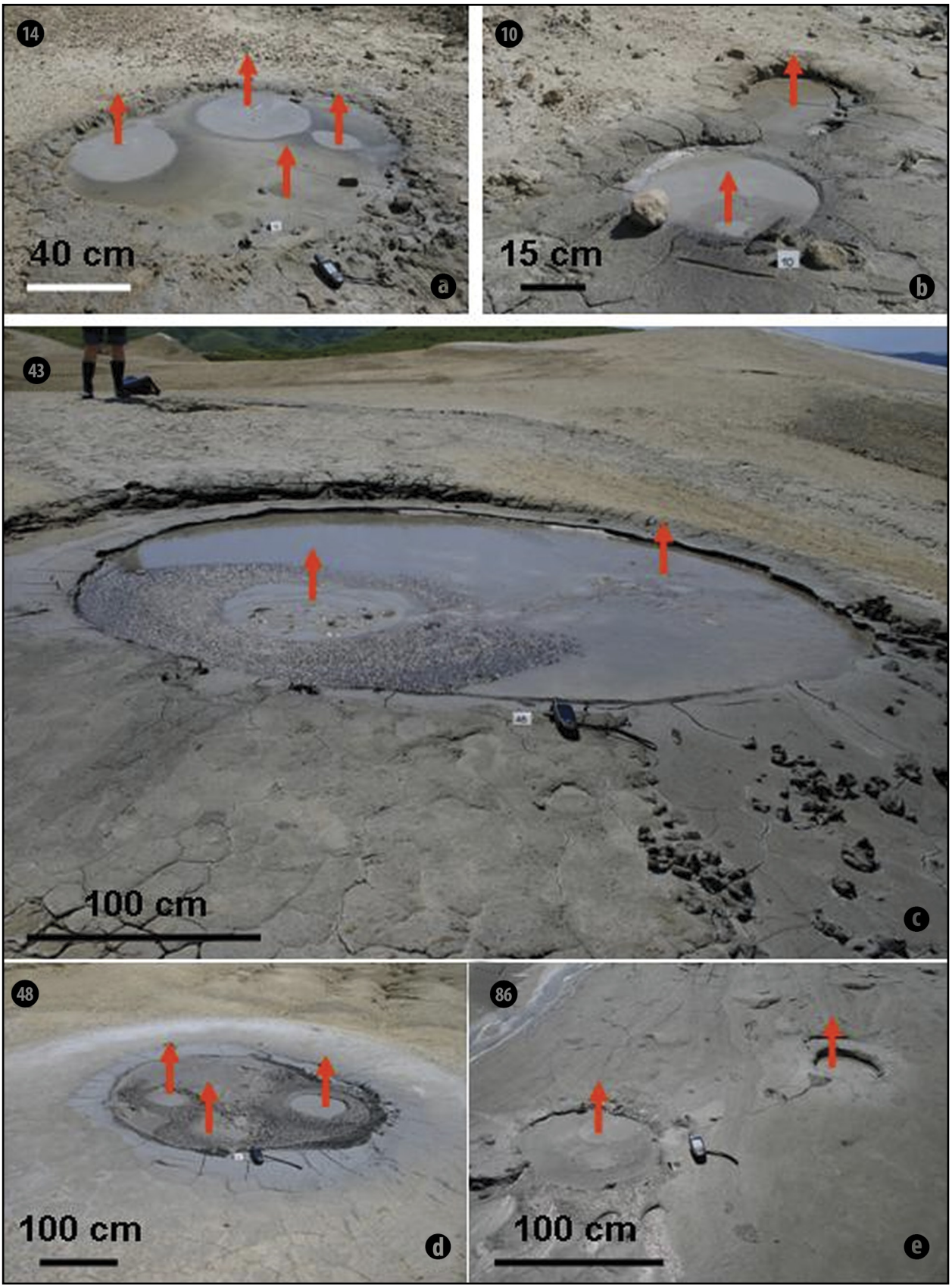


Fig. 9. Multiple mud ejections no. 10, 14, 43 and 48 from Pâclele Mari and no. 86 from Pâclele Mici; No. of each structure corresponds to those in Fig. 6 (Photo: Titus Brustur).

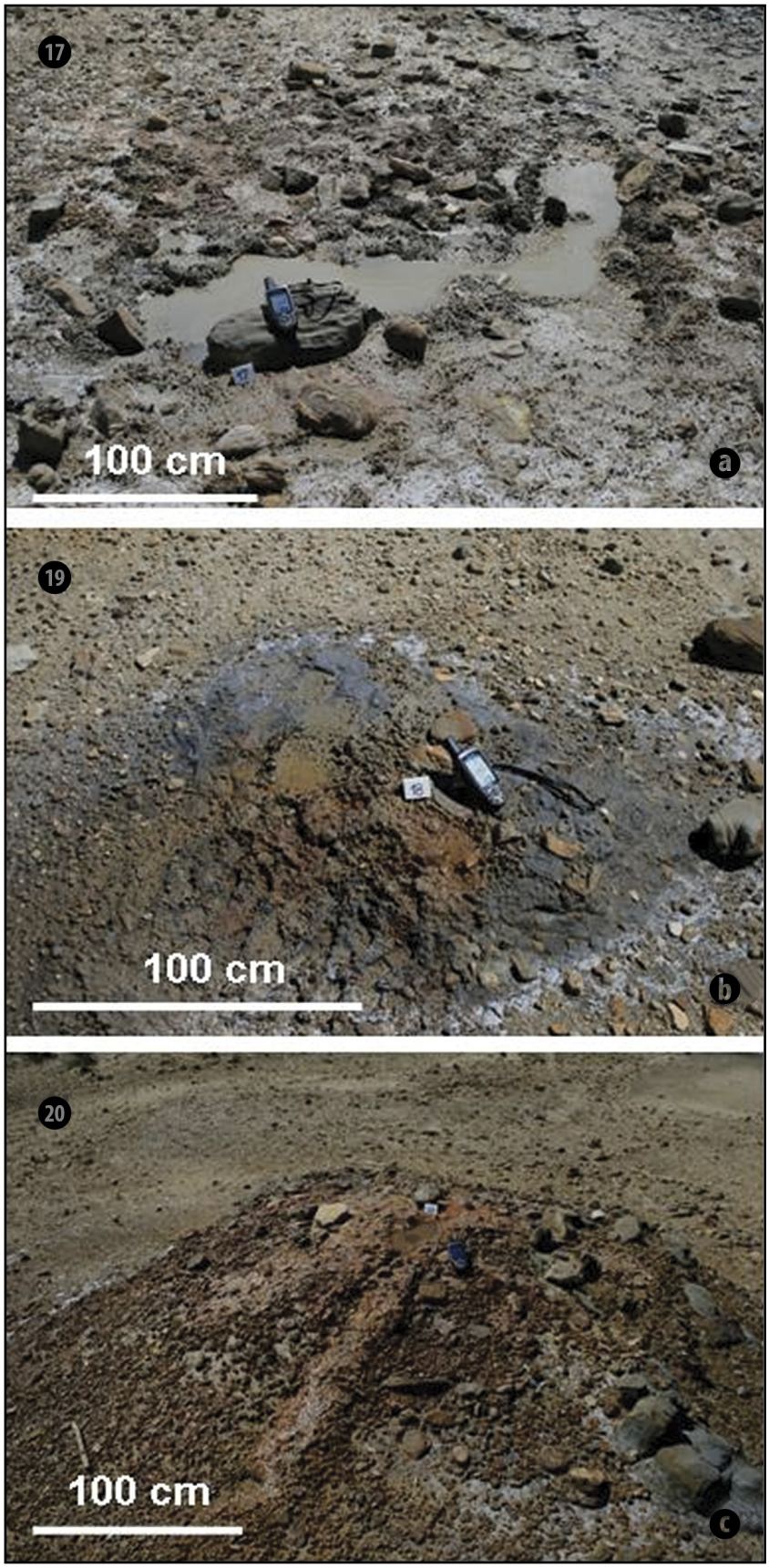


Fig. 10. Diffuse ejection with salty water and mud no. 17, 19 and 20 from Pâclele Mari; No. of each structure corresponds to those in Fig. 6 (Photo: Titus Brustur).

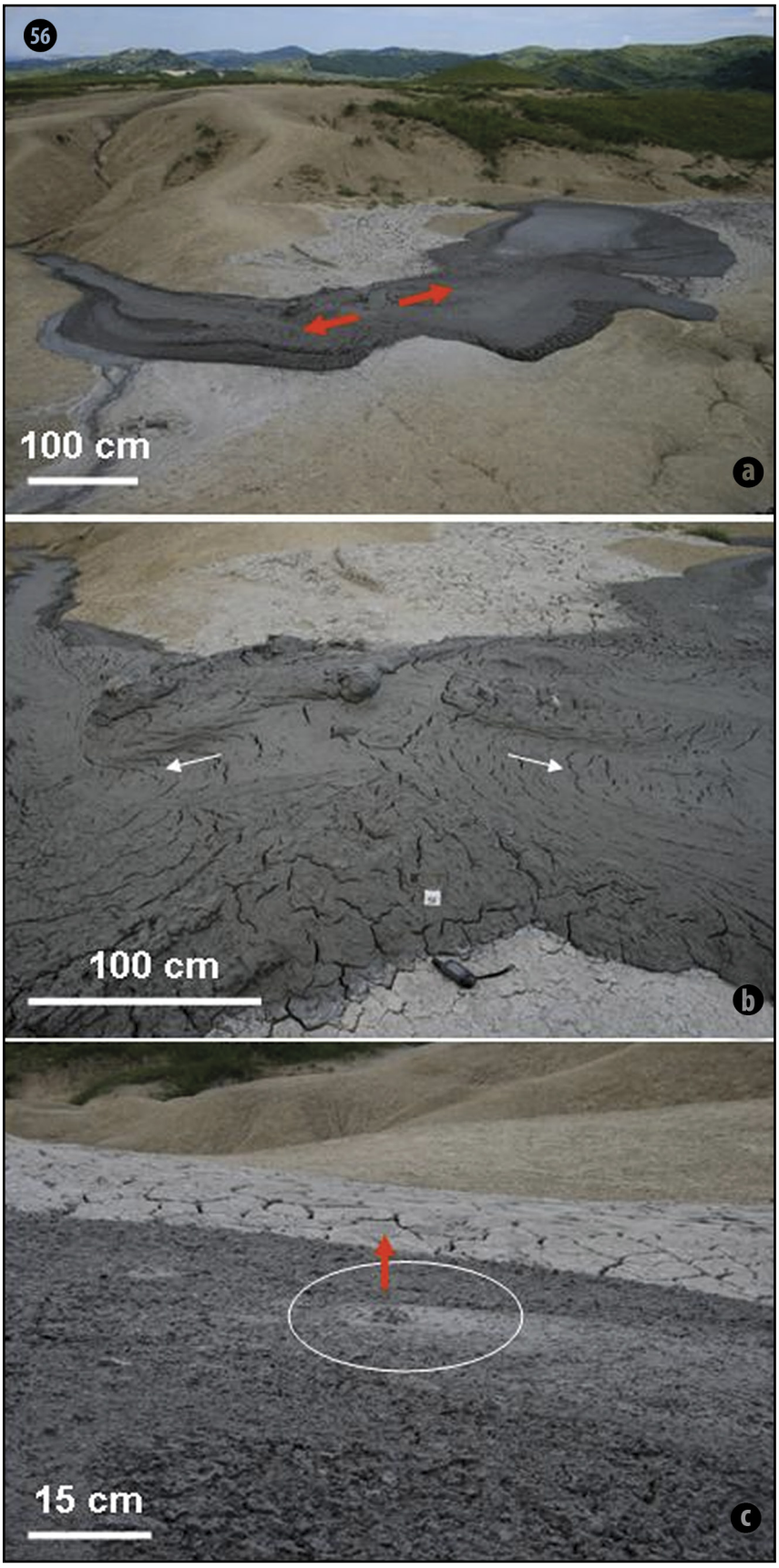


Fig. 11. Bilateral mud lobe no. 56; (**a**, **b**) Pâclele Mari and related punctiform ejection; (**c**) Partially superposed on an older dried lobe with mud cracks; No. of each structure corresponds to those from Fig. 6 (Photo: Titus Brustur).

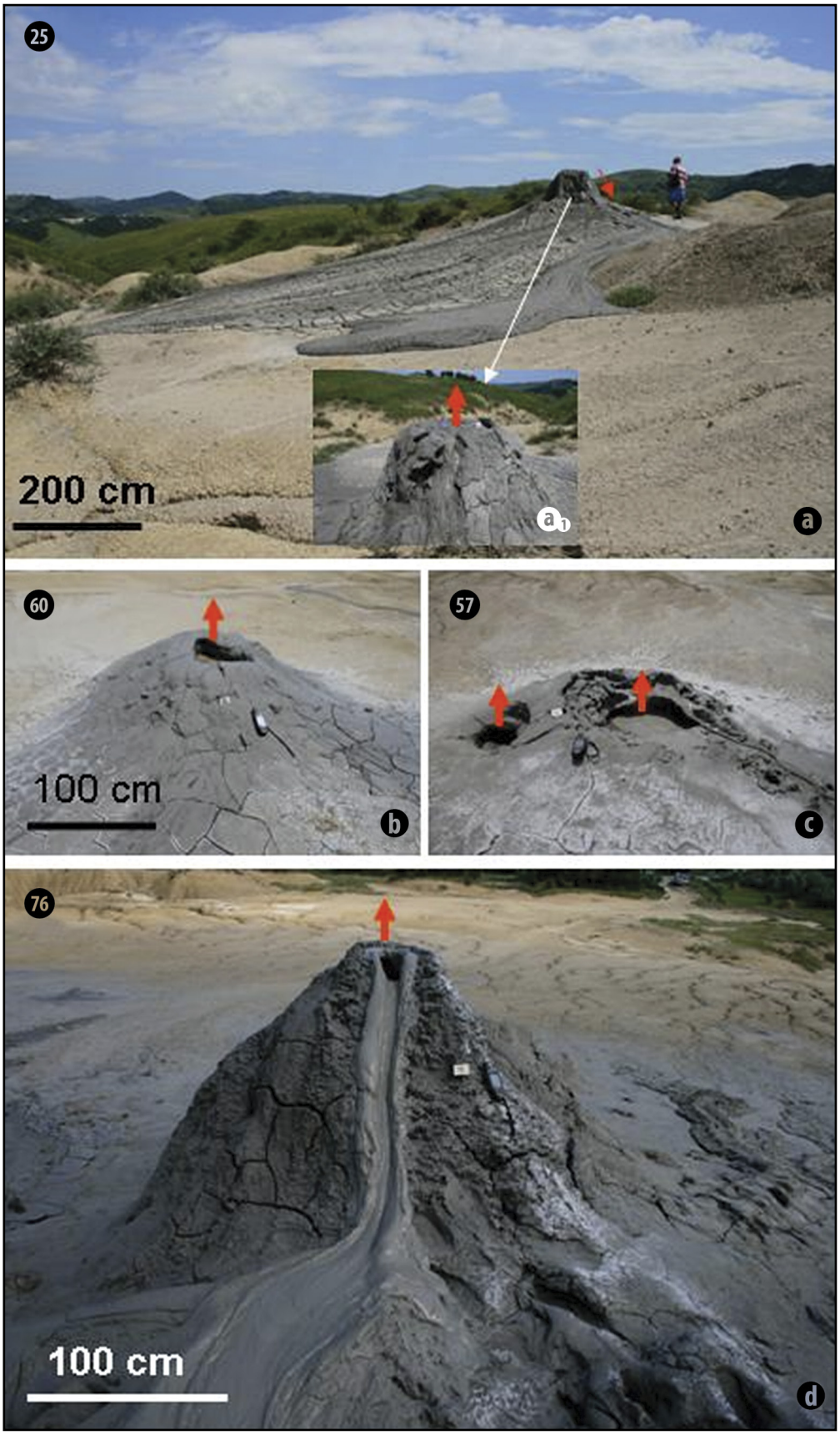


Fig. 12. Punctiform cones with one vent no. 25, 60 and 76 and with an adventiv vent (no. 57) at Pâclele Mari (**a**, **b**, **c**) and Pâclele Mici (**d**); No. of each structure corresponds to those from Fig. 6 (Photo: Titus Brustur).

5.6. Cone with lateral ejection

Some cones, with a central circular vent (Fig. 13a) relatively deep (Fig. 13a$_1$), have fissures on the flanks, as well as 1-5 cm in diameter circular holes that eject the mud. Occasionally, the summit of the cone is completely blocked, while the mud is moved out of a lateral circular orifice that continues with a short semicircular channel (Fig. 13b).

5.7. Inactive cones

Few inactive cones have been noticed at Pâclele Mari and at Pâclele Mici; the ejection channel is filled in with mixed mud and rock fragments (Fig. 14a$_1$). At Pâclele Mari, such structures are up to 6 m tall (Fig. 14a). Inactive vents along the flanks of the mud volcano and gully exposures mudflow deposits provide evidence of past gas emisssions, with numerous mud cracks (Fig. 14b).

In general, a dominance of relatively small punctiform ejections could be seen in both mud volcano sites. By contrast, the dimensions of multiple ejections is higher, between 100 and 300 cm, in Pâclele Mari mud volcanoes, while in Pâclele Mici mud volcanoes, most ejections are up to 100 cm. Similarly, the diffuse ejections are bigger on the Pâclele Mari site, while on the Pâclele Mici site, most of them are up to 50 cm (Fig. 15).

6. DISCUSSION AND CONCLUDING REMARKS

Subaerial mud volcanoes are known in up to 30 regions in the world, mostly, situated near convergent plate boundaries or suture zones (Higgins & Saunders, 1974; Hedberg, 1974; 1980; Dimitrov, 2002). Largely, in various inland settings, including deltaic ones, the mud volcanism phenomenon is linked to the diapirism, as well as to the presence of the hydrocarbons, *i.e.* methane generation (Higgins & Saunders, 1974; Kopp, 1985; Aslan *et al.*, 2001).

Almost a quarter of the onshore mud volcanoes is related to the Alpine-Carpathian-Himalayan belt, where they are known to occur in Italy (S part - Sicily, central - around Rome and N part), Romania (Eastern Carpathians and Transylvania), around the Black Sea (Ukraine and Russia), in Azerbaijan and Pakistan (Abbate *et al.*, 1970; Ahmed, 1969; Basov & Ivanov, 1996; Dimitrov, 2002; Feyzullayev, 2012, among many others).

The herein described mud volcanoes from Berca are located in the Inner Foredeep of the Eastern Carpathians, in an area where oil and gas exploitation exists since the last century and frequently salt diapirs occur. Moreover, the Berca region of the Buzău Land Geopark is situated close to one of the most active seismic zones in Europe, the Vrancea region. Hence, all these features largely favored the occurrence of the mud volcanoes in the region. Besides, the underlying strata of the Berca area are Middle Miocene up to Pliocene sediments, mainly clays. Hence, as assumed by Hedberg (1974), the methane generation and clay-mineral diagenesis highly contributed to the setting of overpressure conditions and mud volcanism. At Berca, the mud volcanoes appear in the core of an anticline; mud, halite and hydrocarbons migrated along the faulted flanks of this structure, being ejected at the surface.

Even much smaller in size, the Pâclele Mari and Pâclele Mici mud volcanoes of Berca (Eastern Carpathians, Romania) show morphological similarities to those from Azerbaijan. In both regions, several relatively volcanic cones are distributed on highlands that are constituted by ejected products, while the mud release is not continuous, its ejection being characterized by very active intervals, alternating with stagnant ones (Ahmed, 1969; Baciu *et al.*, 2007).

Methane emissions (CH_4) of the mud volcanoes from the Pâclele Mari and Pâclele Mici sites were estimated at 730 tones/year and 383 tones/year, respectively (Etiope *et al.*, 2004a). Notably, in the Berca area, beside the well-known Pâclele Mari and Pâclele Mici mud volcanoes, there are two other active zones in the neighborhood, namely, Beciu and Fierbători; for all these 4 mud volcano sites, a total gas emission was calculated at around 1,350 tones/year, a value similar to that reported for the same number of giant mud volcanoes from Azerbaijan (Frunzeti *et al.*, 2012). Hence, the quantity of methane release in the Berca region is very high, compared to that measured in other regions, *i.e.* Taiwan, where the total methane exhaling yearly from major vents is around 29 tones (Yang *et al.*, 2004), a value similar to the one in Sicily (Etiope *et al.*, 2002).

The composition of the exhalations recorded in all the sites of mud volcanoes from Berca is comparable; the gas contains over 95% CH_4 and a very small quantity of CO_2, up to 3 %. Taking into account these data, only one gas reservoir is suggested to account for the gas composition of the mud volcanoes. This composition corresponds also to that recorded in the drillings located in the Berca region, from cores taken at around 3,000 m depth. Usually, the mud volcanoes expel several products, such as gas, mud, water, rock fragments and oil, but the source is located at various depths. In general, the source of mud does not exceed 3-4 km (Feyzullayev, 2012). In agreement with these findings and own data, we assume that the mud provenance in the Berca area is located at the depth of around 3,000 m, where Middle Miocene deposits are located.

Another feature encountered in the Pâclele Mari and Pâclele Mici sites is the presence, in the mud, of the boron chemical element, a characteristic that is present also in the mud volcanoes around the N Black Sea, *i.e.*, the Kerch and Taman regions (Shnyukov *et al.*, 2009).

The mud volcanoes located in the Foreland of the Eastern Carpathians in the Buzău County is not the single occurrence in Romania. In the Transylvanian Basin, mud volcanoes were described as far back as the last century (Ciupagea *et al.*, 1970), in 69 locations (Spulber, 2010). Investigating the mud volcanoes from the eastern and central parts of Transylvania, Gál (2010) suggested a classification based on morphology,

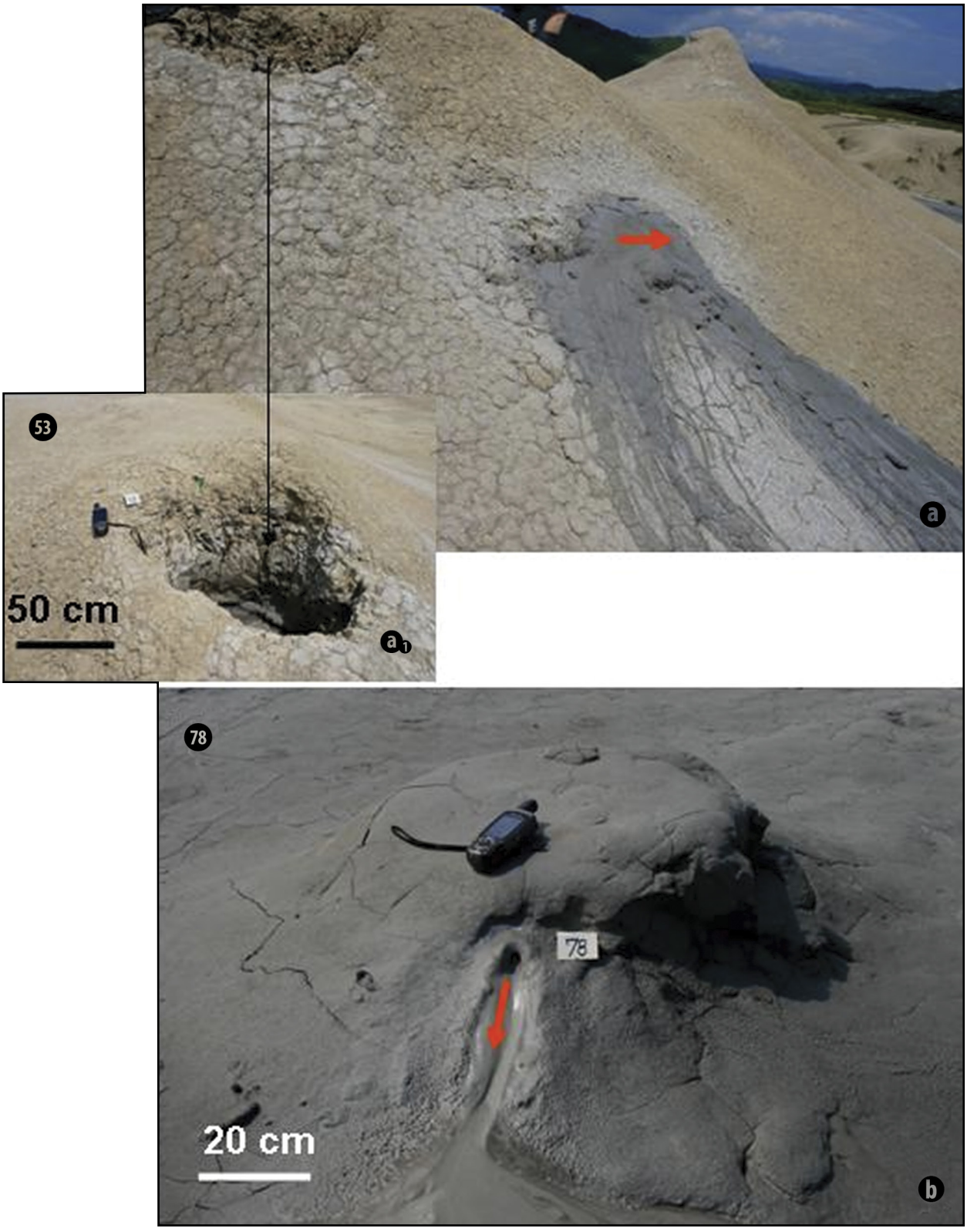


Fig. 13. Cone showing a lateral ejection (no. 57) of Pâclele Mari (**a**) and no. 78 of Pâclele Mici (**b**); No. of each structure corresponds to those in Fig. 6 (Photo: Titus Brustur).

Fig. 14. Inactive vent no. 54 of Pâclele Mari (**a**) and no. 91 (b) of Pâclele Mici; No. of each structure corresponds to those in Fig. 6 (Photo: Titus Brustur).

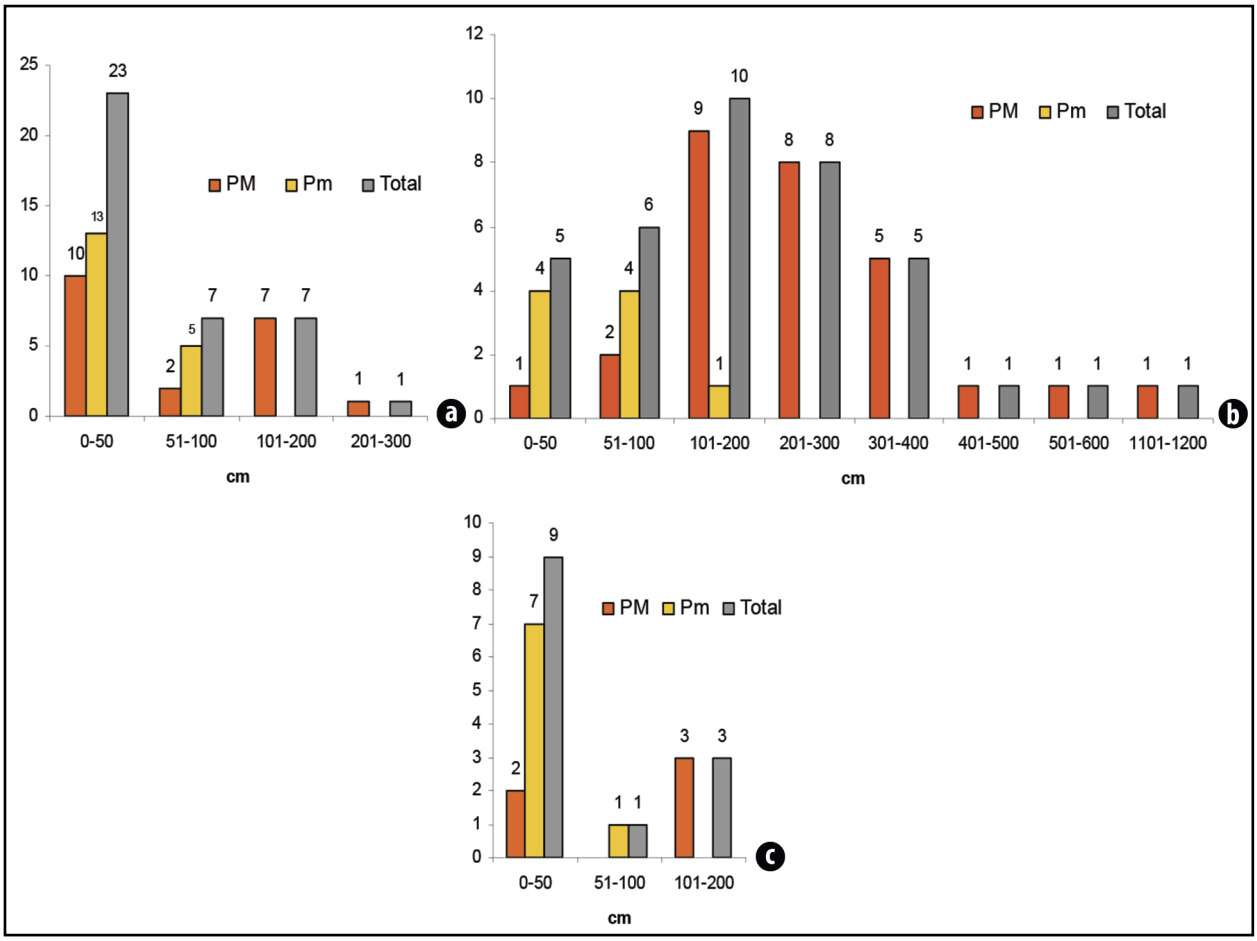


Fig. 15. Number and dimensions of various ejection types from Pâclele Mari and Pâclele Mici: (a) punctiform; (b) multiple; (c) diffuse.

as follows: mud pool, mud cone, mud dome and mud caldera. The author firstly studied the inner structure of the mud feeder channel and recognised three types: (1) narrow feeder channel <15 cm, represented by a fissure; (2) feeder channel that widens into mud intrusions; (3) feeder channel that widens in the shape of a funnel. Probably, the multiple ejections described by us in the extra-Carpathian area, on the Pâclele Mari and Pâclele Mici sites, are due to the presence of a feeder channel of types 2 and 3, as described by Gál (2010) from the inner Carpathian regions.

Recently, new occurrences of mud volcanoes were reported from the Republic of Moldavia, being located in the eastern part of the Prut River basin (Ursu *et al.*, 2004-2005). As for other mud occurrences from N Romania, *i.e.*, at Vulturi, N of the Iaşi locality, the ejection of the alkaline artesian waters from the region may be linked to this phenomenon. The presence of the mud volcanoes was first reported as far back as the 19th century in N Romania, close to the Iaşi locality, in the Repedea Hill (Cobălcescu, 1862); the author, assumed, in the first geological paper published in Romanian, that the occurrence of mud vents is due to 'subsurface hydrostatic changes'. During the last century, many mud vents were discovered in N part of the Moldavian Platform from Romanian territory, linked to the occurrence of salty springs (Enculescu, 1911) or gas released in the atmosphere (Macarovici, 1945).

Highland surfaces contain active and inactive cone-shaped vents, which are commonly up to 2 m tall. Salty waters occur together with the mud, as well as numerous pellicles of oil. Due to the salty soil, scarce or anomalous vegetation occur nearby the active vents, but also around the inactive ones. Halophyte plants, such as *Nitraria schoberi* and *Obione verucifera*, grow on the margin of the fields. Rarely, the species *Schoenoplectus lacustris* (Fam. *Cyperaceae*) occurs. This species is a halophile plant, good indicator of areas where active mud volcanoes occur (Gál, 2010). To note that, during the summer of 2014, the authors of this paper identified a new area where newly formed mud volcanoes occur, at the exit from the Bădila village (latitude N 45°14'56"N; longitude: E 26°29'30"), at around 20 km west from Berca, nearby the Buzău Valley. In the area, there is already a protected area of national interest corresponding to the IUCN category III (Nature Reserve, Geological and Botanical), namely Sarea lui Buzău (The Buzău Salt), where salt springs and salt efflorescence appear. The newly discovered site of mud volcanoes is situated towards NW at around 2 km in respect with the protected area Sarea lui Buzău.the

mud cones have a small size, up to 20-30 cm, being much smaller than those of the Berca mud volcanoes. Around these newly emerged structures, some halophilic plants, such as *Schoenoplectus lacustris*, are present, as well as rock fragments, mostly Miocene; some of ythe identified rock fragments are coquinas typical for the Middle Miocene (*i.e.*, regional stage Sarmatian).

Recently, Bonini (2012) indicated that the presence of the mud volcanoes could be a good indicator of tectonic stress. Following this observation, the monitoring of the mud volcano activity from the Berca region could bring important contributions on the geological structure, and seismic activity of the region, known to be one of the highest in Europe, related to the Vrancea zone.

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