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Study of rare gases in geothermal waters from Herculane area, Romania (*)(**)

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Summary. — In the south-western part of Romania there is a long and deep fissure following the Cerna river canyon as well as many transversal fissures, especially placed in the region of Herculane Spa. The geothermal water sources (springs and drillings), always accompanied by large amounts of gases, are located where these fissures cross. The presence of granite rocks at the surface is another remarkable characteristic of this area. Nitrogen and methane are the main components of emanated gases, and high helium and radon concentrations were also found. The composition of the gases was determined by using a Dempster mass spectrometer. The radon content from these gases and the rate of radon exhalation from the ground were determined by gamma spectrometry method. The argon isotopes were analyzed by means of a quadrupole mass spectrometer (AMP-4). In the vicinity of transversal fissures, the radon exhalation rates present higher values from all measurements in this area. The ratio $^{4}He/^{20}Ne > 400$ is a very good indicator of the fact that these gases are not contaminated with atmospheric air and therefore the gases come from depth. The $^{4}He/^{40}Ar$ and $^{40}Ar/^{36}Ar$ ratios suggest that the helium in these sources may have a non-negligible part of primordial helium arising from the earth mantle.

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1. – Introduction

Herculane Spa (or the Bath of Hercules) is a well-known resort situated in the Cerna Valley (south-western part of Romania), fig. 1. The Cerna Valley is a deep and long canyon bordered by the Cerna mountains on the right and by the Mehedinti Mountains on the left.

The geothermal waters from the Herculane area, known since the period of the Roman Empire, have their origin in granite and sedimentary rocks (marl and limestone), the latter forming an impermeable roof for this hydrothermal deposit [1]. The waters of

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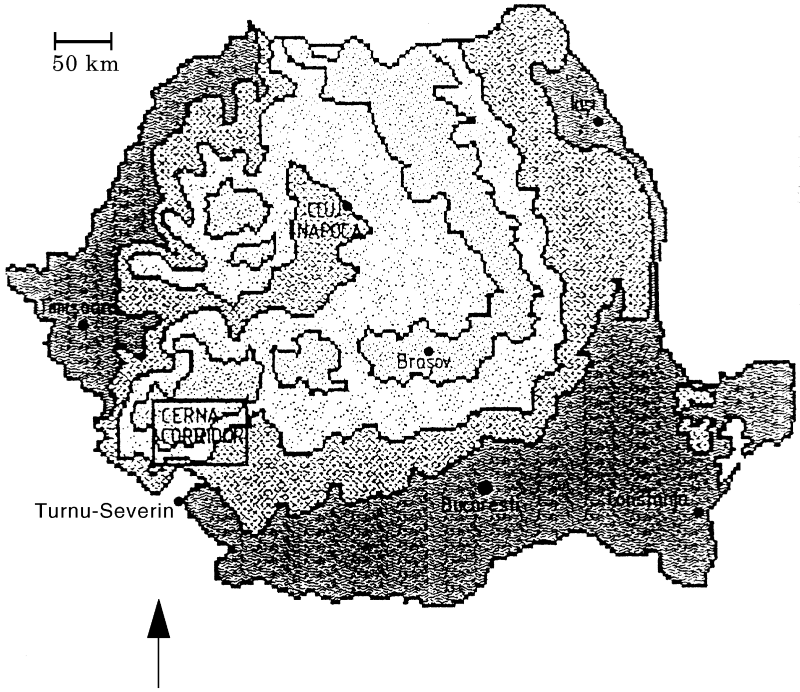

Fig. 1. – Romania map and localisation of the Herculane Spa area.

this deposit are permanently regenerated from three components [2]: a) uphill infiltration water from the Cerna Valley; b) deposit-type waters; c) hot deep waters.

In the area of Herculane Spa, the Cerna corridor presents many transversal fissures (fig. 2). A big and deep fault also follows the Cerna Valley. The geothermal sources

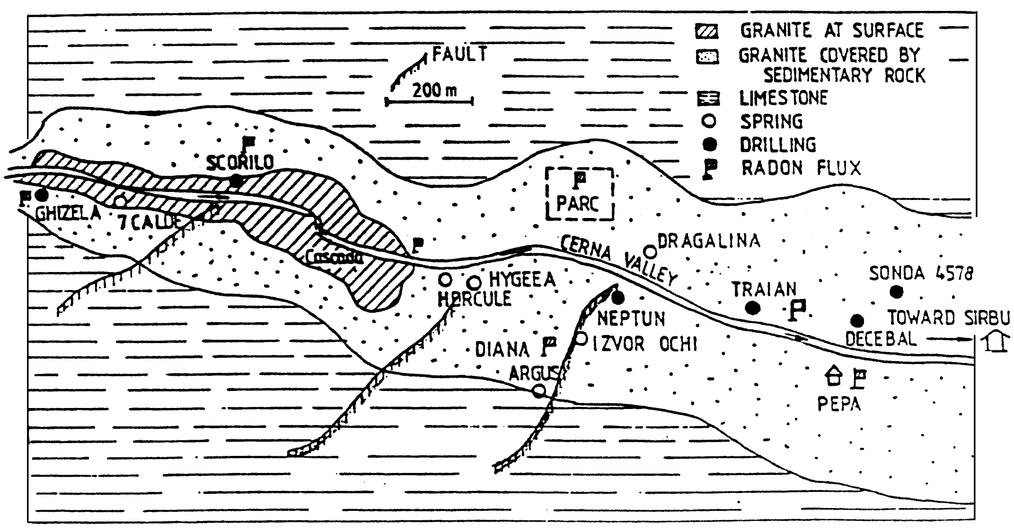

Fig. 2. – Geothermal sources and radon flux measurements sites in the Herculane area.

TABLE I. – *Gas composition of emanated gases from the Herculane Spa area.*

No.	Place	Gas concentration (% volume)							
		CH_4	N_2	C_2H_6	Ar	O_2	SH_2	CO_2	H_2
1	Ghizela (drilling)	—	**82.62**	—	1.47	**14.73**	—	1.18	—
2	Scorilo (drilling)	**2.87**	**95.12**	0.16	1.73	0.12	0.04	0.07	—
3	Sapte Calde Dreapta (spring)	**1.77**	**96.28**	0.04	1.66	0.16	0.01	0.05	—
4	Neptun (drilling)	**60.47**	**35.41**	0.81	0.57	0.02	0.41	0.30	1.72
5	Dragalina (spring)	**67.61**	**28.75**	0.57	0.31	0.05	0.61	0.11	1.85
6	Decebal (drilling)	**70.88**	**25.54**	0.84	0.47	0.04	0.15	0.08	1.98
7	Sonda 5789 (drilling)	**64.77**	**32.13**	0.60	0.36	0.02	0.01	0.02	1.68
8	Traian (drilling)	**64.12**	**31.20**	0.68	0.40	0.06	0.81	0.38	1.76
9	Lime factory (drilling)	**59.51**	**37.06**	0.69	0.60	0.15	0.03	0.66	1.43
10	Coal Mehadia mine	**12.01**	8.05	—	0.17	—	0.14	**79.63**	0.31

are located where these fissures cross. There are 24 sources, including 16 springs and 8 drillings, with a total water flow of 65 000 l/h.

Another remarkable fact is the surface presence of granite rocks 2 km uphill from Herculane Spa. In the zone of the resort, following the Cerna river course, sedimentary rocks progressively cover the granite rocks. The most abundant components of emanated gases from these sources [3] are nitrogen and methane, table I. Systematic studies of the chemical composition have also revealed considerable helium concentrations. There is another distinctive characteristic in the case of the Cerna Valley gases related to their high radon radioactivity level (20–7500 Bq/l, NPT), which is generated by the presence of a granite massif in this area.

Many hypotheses were made regarding the origin of the gases in the Cerna Valley. Because of their great radioactivity, we advanced the idea of a radiogenic origin of helium and argon, but we did not definitely exclude the possibility of an inner origin for He and N_2 and even primordial for He. This fact is supported by the deep tectonic dislocations in this region [4].

2. – Experimental method

Gases emanated from geothermal water sources were collected using two special devices. The samples were gathered from the sources where the gas was always in excess, accompanying the water as gas bubbles. Figure 3a) presents the device for spring sources and fig. 3b) is the device for sampling from drilling sources.

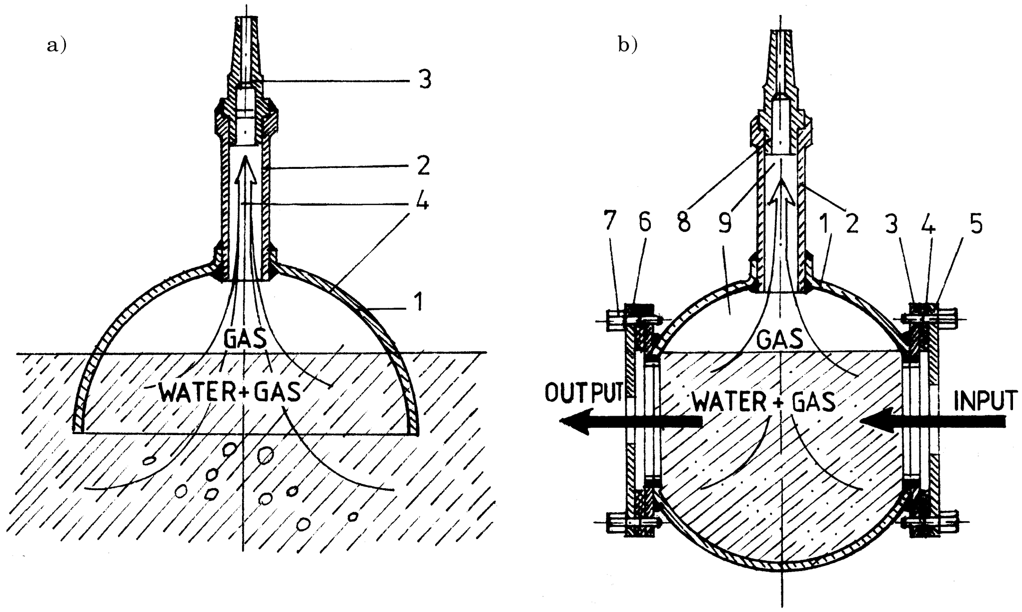

Fig. 3. – a) The device for the sampling of the gases emanated from springs (1: metallic semi-sphere, 2: metallic pipe, 3: joint, 4: gas flow); b) the device for the sampling of the gases emanated from drilling (1: metallic sphere, 2: metallic pipe, 3: metallic fixed flange, 4: gasket, 5, 6: metallic interchangeable flanges, 7: screws for fixing flanges, 8: joint, 9: gas flow).

Helium and also the main components of gases were measured with a Dempster mass spectrometer [5]. The argon isotopic composition was determined by means of an AMP-4–type mass spectrometer.

The small quantity of neon from these samples did not allow the determination of isotopic Ne ratios, because of the contribution of $^{40}Ar^{++}$ to mass peak 20 (^{20}Ne) and the CO_2^{++} contribution to mass peak 22 (^{22}Ne). For Ar the $H_2\,^{34}S$ contribution to mass peak 36 must be taken into account. This contribution was estimated by measuring the height (I) of mass peak 34 ($H_2\,^{32}S$). Also, the presence of propane in the samples, evident in mass peaks 41, 42, 43 and 44 (fig. 4), requires a correction, which takes into account the fragmentation ratio $^{36}I/^{43}I = 0.01$. An important contribution to mass peak 38 (Ar) is brought by propane $(^{38}I/^{43}I)_{\text{propane}} = 0.15$ and also by butane $(^{38}I/^{43}I)_{\text{butane}} =$ 0.02. The radon exhalation rate of the ground was measured by adsorption in activated charcoal (180 g) over the 0.23 m^2 surface and for 12 hours of gathering time [6]. The radon from water and from emanated gases was measured in Marinelli geometry (0.5 L) using a large NaI (Tl) detector connected to a four-channel analyzer.

3. – Results and discussions

Table II presents the results of He, Ar and Rn concentrations in emanated gases for nine of the main sources from the Herculane and Mehadica regions. A high helium

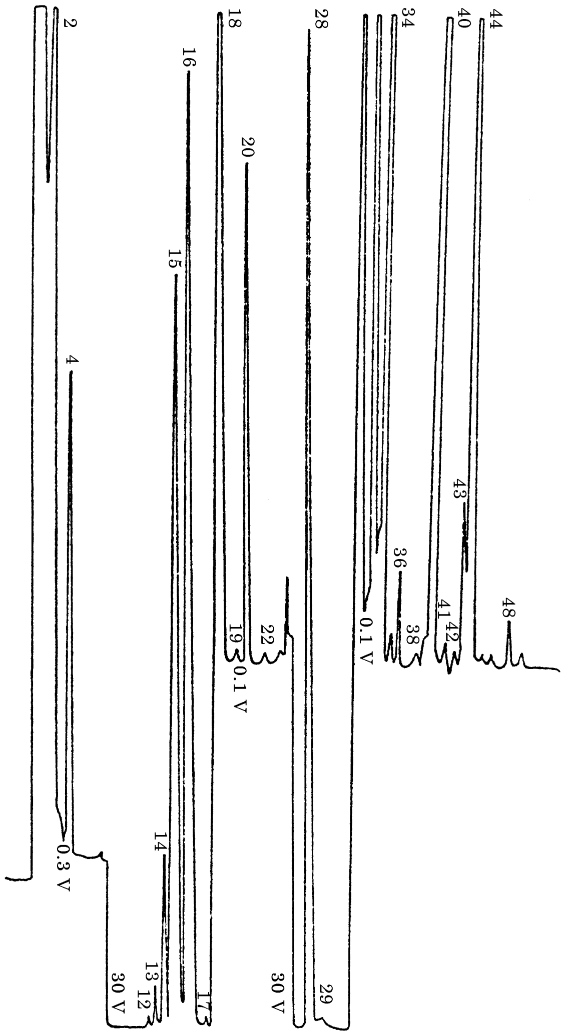

Fig. 4. – A sample of the mass spectra for the gases from the Neptun source obtained with QMS.

content was found, especially in the Mehadica Valley, and a high radon concentration was detected, especially in the case of "Sapte Calde Dreapta" source. The high radon radioactivity of emanated gases may be explained as being due to the presence of granite rocks at the surface, whereas helium can partially originate in the profound rocks (even mantle).

No correlation was observed between the helium content and the radon activity or the radon content. The presence of methane in the case of six sources (see table II) is probably related to the coal deposit of Mehadia, situated about 10 km from the Herculane area, or to the presence of a deep oil source nearby.

To clarify the helium origin in these gases the ratio $^{3}He/^{4}He$ should be measured.

TABLE II. – He, Ar *and* Rn *concentration in emanated gases.*

Source	He (%)	Ar (%)	Rn ($kBq \cdot m^{-3}$)	Main component (%)
Sapte Calde Dreapta	0.43	1.66	**6660**	N_2 : 95.1
Scorilo	0.76	1.73	1110	N_2 : 96.3
Neptun	1.02	0.57	37	CH_4 : 60
Dragalina	0.91	0.31	59	CH_4 : 67
Decebal	0.80	0.47	16	CH_4 : 71
Sonda 4579	0.72	0.36	300	CH_4 : 65
Traian	0.71	0.40	925	CH_4 : 64
Fabrica de var	0.74	0.60	667	CH_4 : 60
Mehadica	**1.85**	1.74	28	N_2 : 96

TABLE III. – *Radon exhalation rate in the Herculane Spa area.*

No.	Source	Radon flux values ($mBq \cdot m^{-2} s^{-1}$)					Observations
		Nov. 1994		March 1995		Mean value	
		Day	Night	Day	Night		
1	Ghizela	7.25	9.25	—	—	8.25	stone soil near swimming pool
2	Spate Calde	12.9	—	—	—	12.9	granite bulky rock
3	Scorilo I	32.6	38	28	26	31.15	pasture soil
4	**Scorilo II**	—	—	60	68	**64**	**fissure presence**
5	Cascada	18.1	24	21.3	26	22.35	starting of sedimentary roks
6	**Argus I**	75.2	—	—	—	**75.2**	**fissure presence**
7	**Argus II**	156	190	193	240	**194.82**	**fissure presence**
8	Pepa	15.9	26.1	17	19.6	19.65	agricultural soil
9	Parc	—	—	21	—	21	agricultural soil
10	Sirbu	13.9	14	20	29	19.23	agricultural soil

The concentration of primary helium in gases can be found by the relation [7]

$$C_p(\text{He}) = [(^3\text{He}/4\,\text{He})_{\text{meas}} - (^3\text{He}/^4\text{He})_{\text{rad}}]/(^3\text{He}/^4\text{He})_p, \tag{1}$$

where $(^3\text{He}/4\text{He})_{\text{rad}} = 3 \cdot 10^{-8}$ and $(^3\text{He}/^4\text{He})_p = 3 \cdot 10^{-5}$.

Table III shows the results of radon exhalation for years 1994 and 1995. The daytime values are generally smaller than nighttime ones and they are closed to the average reference value (20 $mBq/m^2\,s$), except Argus and Scorilo II, in which cases the higher values can be in direct connection with the transversal faults.

Table IV presents the isotopic ratios for three sources from the Cerna Valley and one source from the Mehadica Valley. The high ratios $^4\text{He}/^{20}\text{Ne}$ prove the deep origin of these gases. The atmospheric ratio in the case of $^4\text{He}/^{20}\text{Ne}$ is 0.291. The high ratio $^4\text{He}/^{20}\text{Ne}$ (higher than 400) is valuable information about the primary origin of helium. Such high ratios (150-500) were found in the case of geothermal gases from Japanese sources, whereas the $^3\text{He}/^4\text{He}$ ratios for these Japanese sources were also much higher than the atmospheric ratio [8, 9].

TABLE IV. – *Isotopic ratios for gases from Cerna and Mehadica Valleys.*

Ratio	Neptun	Abator	SCD (*)	Mehadica
$^4He/^{20}Ne$	> 400	> 400	> 400	> 400
$(^4He/N_2)\cdot 10^2$	1.25	1.09	0.45	1.15
$^4He/^{40}Ar$	0.95	1.1	0.33	1.1
$(^{40}Ar/N_2)\cdot 10^2$	1.05	1	1.38	1.04
$^{40}Ar/^{36}Ar$	333	344	301	280
$^{38}Ar/^{36}Ar$	0.2	—	0.18	0.18

(*) Sapte Calde Dreapta.

The $^4He/N_2$ ratios are almost identical for the Neptun, Mehadica and Abator sources ($1.2\cdot 10^{-2}$). In the case of "Sapte Calde Dreapta" this ratio is about between a half and a third of the ratios mentioned above.

A similar behavior is shown by the ratio $^4He/^{40}Ar$, which in the case of "Sapte Calde Dreapta" is 1/3 of the ratio for the other water sources. The contribution of radiogenic argon must be considered for this source.

The $^{38}Ar/^{36}Ar$ ratios exhibit insignificant variations. The ratio $^{40}Ar/^{36}Ar$ varies rather considerably, being 280 in the Mehadica Valley, a smaller value than in the atmosphere. This resembles the situation of the gases in the Japanese volcanic sources, indicating a possible contribution of upper mantle argon with a lower isotopic ratio [10].

The ratio $^{40}Ar/^{36}Ar$ is higher than in the atmosphere for the sources from the Cerna Valley, similar to the gases in the Japanese geothermal sources, indicating the contribution of the radiogenic component. Differing from the Japanese sources, the ratio $^4He/^{40}Ar$ is five or six times higher.

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