STUDIA UBB GEOGRAPHIA, LVIII, 2, 2013, pp. 25-38
(RECOMMENDED CITATION)

CONTRIBUTIONS TO THE STUDY OF THE MINERAL WATER SPRINGS OF THE BARAOLT DEPRESSION

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ABSTRACT. - Contributions to the Study of the Mineral Water Springs of Baraolt Depression. At a large scale of integration, Baraolt Depression is part of the mofetta area of the Eastern Carpathian range. After defining the actual limits of the depression, it was possible to identify 44 mineral water springs aligned along the faults that cross the depression. Based on some local natural and human imposed factors (accessibility), 35 were selected for this study. Measurements regarding the temperature, pH and conductivity and chemical analyses for the free CO_2 and the HCO_3 were made in May and August 2011 and January 2012. The collected data helped in trying to identify the aquifer these springs originate from, to make correlations among their physical and chemical characteristics, to emphasize their seasonal fluctuations. The data offer also possibilities to group, to classify these mineral waters. But it seems that a long term seasonal monitoring proceedings of these parameters are necessary to establish rules, if there are any, according to which the activity of these post volcanic phenomena develop.

Keywords: *post volcanic activity, mineral water spring, conductivity meter, total dissolved mineral salt.*

1. INTRODUCTION

The complete ceasing of the volcanic eruptions in the Southern Harghita range, 40 – 35 thousand years ago, did not mean a complete stop of the volcanic activity. Up to now it remained as heat and CO_2 emanation, sedimentation of carbonated rocks and solfatara. Except for the latter, all these can be found in Baraolt Depression and the temperature of the springs, their CO_2 contents and the deposits around some of them speak for themselves.

The research of mineral water springs has a rich bibliography because of scientific curiosity, the spa potential and the possibility of bottling. Without the exigency of completion, references could be made to the researchers of the 20th century: J. Bányai (1934), J. Straub (1950), A. Szabó (1949, 1974), T. Bandrabur (1964, 1973, 1984), J. Harkó (1972), D. Slăvoacă (1956, 1971), A. Pricăjan (1969, 1974, 1985), Şt. Airinei (1970, 1972, 1989), A. Kristo (1978), Z. Kisgyörgy (1977, 1978), E. Péter (1977,

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1984), Z. Makfalvi (1974-1975, 1978, 1980), K. Jakab (1981), Delia Bogdan (1980), E. Szabó and Zsuzsánna S. Szabó (1981), C. Dumitrescu (1984), A. Péter and E. Feru (1998), Cornelia Maieru (1998). In addition, the activities of the Cholnoky Geographic Society of the Faculty of Geography of the Babeş-Bolyai University of Cluj-Napoca can be mentioned. The results of its activity materialized in many scientific articles published between 2007 and 2011 and in a mineral water spring database (www.borviz.org), containing the springs in South Harghita range and Baraolt Depression.

1.1. The limits of the studied area

Baraolt Depression can be identified as a mountain depression being part of the internal curvature sector of the Eastern Carpathians (fig. 1). It borders with Harghita Mountains to the North and North-East, with Baraolt Mountains to the East, South-East and South and with Perşani Mountains to the West. In the South, there is a wide opening towards Braşov Depression on the valley of the Olt River.

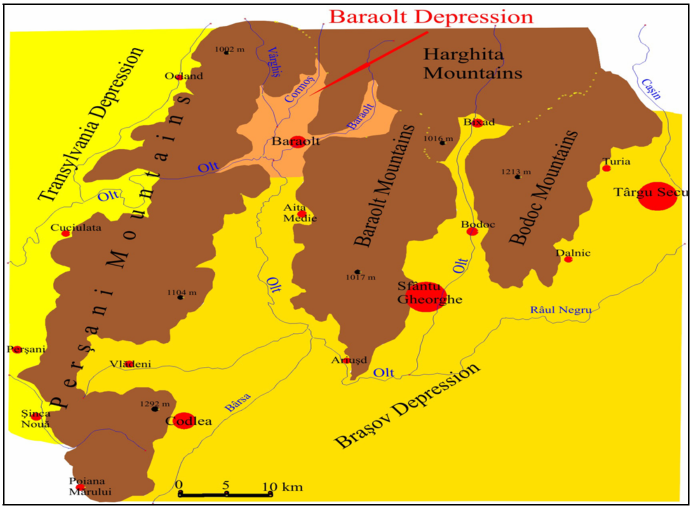

Fig. 1. Geographical position of the Baraolt Depression

In the case of this study, the most relevant limit is the northern one, the border with the Harghita Mountain range, to reveal which mineral water springs may and which may not be included in the area of the depression. Although there were a few springs which are North of these limits, as they were very close, they were also included.

As all the springs occur along the main faults of the region and the main valleys are situated on these, it is necessary to point the northern limits of the depression on these valleys. It crosses the valley of the Volal brook where its floodplain is not narrower than 100 m wide. On the valley of the Cormoş rivulet this border is at the Northern end of Filia village and on the valley of the Baraolt rivulet at its confluence with the Herculian and Pietros creeks.

1.2. Geological elements of the area

The geological structure of the Baraolt Depression is the conjugated result of the chain of geological events that followed each other in this region beginning with the formation of Ceahlău nappe, the drifting of the metamorphic layers of the Eastern Carpathians over the flysch, up to present.

At the end of Pontian period – 5.9 – 5.1 million years before – the activity of the Miercurea Ciuc – Jigodin, Sâncrăeni, Racu, Tirco volcanoes reactivated the North - South Cormoş fault system (G8), its eastern response (g27), the West – East crust fault (G7) and some secondary and local ones, which launched the sinking process of some parts of the Cretaceous peneplain including the actual area of the Baraolt Depression.

The tectonic movements along the crust, regional and local faults and the volcanic eruptions directed each other as direction and intensity, which led to the sedimentation, over the Cretaceous structures, all along the Pliocene and upper Pleistocene, of a molasse stack with a maximum thickness of 450 – 550 m. The paroxysm of the activity of the volcanoes in South Harghita range made possible the formation of three layers of volcanic sediments inserted in the molasse.

In upper Pleistocene the drifting movements along G7 fault strangled the magma basins at the south end of the Harghita range, which completely extinguished the volcanoes 40,000 – 35,000 years before our date.

From the point of view of this study, the most important are the magma basins which provide heat, carbon dioxide, the carbonated rocks of the foundation, those elements of the molasse stack which offer conditions for water storage and provide soluble minerals, and the faults through which the CO_2 and the water can move.

1.3. Short definition of the mineral water

There are two currents regarding this definition: the first one is very strict and refers to the quantity of total dissolved minerals (that must be over 1000 mg/l) and the quantity of free CO_2 (which must be over 250 mg/l), and the other one takes into account the balneal and curative qualities of these waters. The European Union harmonized these two perceptions through 80/777/CEE directive, for satisfying the wishes of the bottling firms. The directive defines four categories of mineral waters according to their total dissolved salt (TDS): very weakly mineralized – with a TDS under 50 mg/l, weakly mineralized – with a TDS between 50 and 500 mg/l, middle mineralized – with a TDS between 500 and 1500 mg/l and rich in dissolved mineral salt – with TDS over 1500.

1.4. The aims of the research

The first aim was to identify those springs which are inside the limits of the Baraolt Depression and to determine some of their physical and chemical characteristics.

According to previous research, it is relevant that these mineral waters originate from the following geological structures: the Cretaceous flysch and all the three volcano-sediment layers. Their occurrence on the surface is done along regional and local faults. So a second aim was to confirm that they indeed originate from the mentioned geological structures, based on some physical and chemical characteristics.

Another aim was to establish correlations between the temperature of the spring and its pH, to emphasize seasonal fluctuations of the measured and analyzed parameters, then, to define some common features to be a basis for classifications and to bring some personal contributions to the research of the mineral waters.

2. METHODS AND INSTRUMENTS

To reveal some of the physical and chemical characteristics of the 44 mineral water springs, identified in Baraolt Depression (fig. 2) and to fulfil the aims of the research, measurements were made regarding the temperature (in Celsius degrees), pH, electric conductivity and chemical analyzes to measure their HCO_3 and free CO_2 content. These activities were performed in May, August 2011 and January 2012.

For temperature and pH determination, we used a digital pH meter with sensor for temperature “pH 3110”, having a “SenTix 81” electrode. Its measurement interval is between 0 and 14 and before starting for field measurements it was calibrated for pH values between 4 and 7.

For electric conductivity determinations we used a digital conductivity meter “Cond 3110”, having a “TetraCon 325” electrode and a measurement interval between 1μS/cm la 2S/cm.

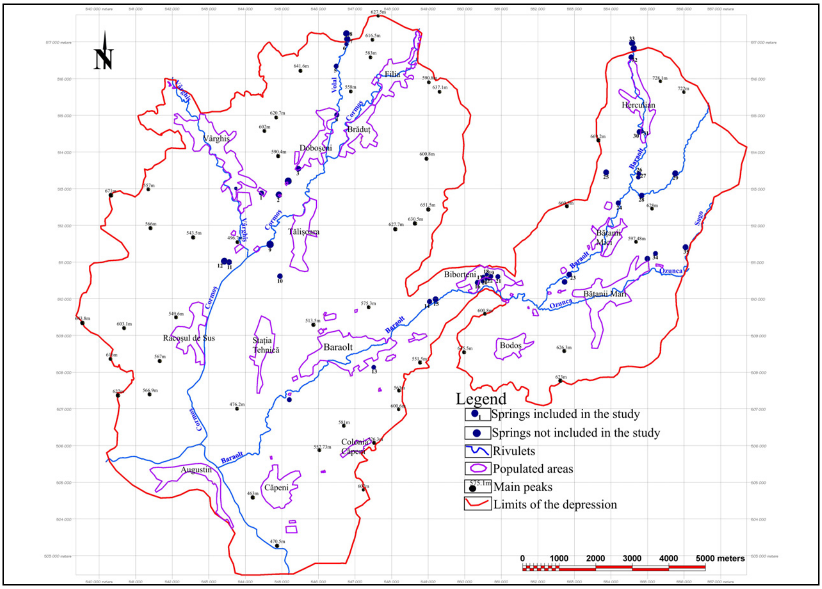

Fig. 2. The position of the mineral water springs in Baraolt Depression

There is a relation between the electric conductivity of the water and the quantity of the total dissolved minerals found in it, according to the formula $TDS = k_e \times EC$, where EC is the electric conductivity and k_e is a coefficient. For the mineral waters a value of 0.65 is generally accepted.

For the determination of free CO_2 and HCO_3 in the chemical analyzes the following principle was used: using a solution of sodium hydroxide, the free carbon dioxide from the water transforms into bicarbonate, the excess of hydroxide is titrated with HCl in the presence of methyl-orange. The chemical reaction is:

$$H_2CO_3 + NaOH \rightarrow NaHCO_3 + H_2O$$

In the case of the free CO_2 determination the calculation is: 4.4 x V x f x 1000, divided to 100, which gives 44 x V x f, where V is ml of HCl with a concentration of 0.1 N used in the titration; f is the factor of the HCl solution of 0.1 N, and 44 is the equivalent in CO_2 corresponding to 1 ml of HCl of 0.1 N. At the determination of the HCO_3 the calculation is the same, just 44 is replaces by 61 – the equivalent in HCO_3 corresponding to 1 ml of HCl of 0.1 N.

Out of the 44 springs, 9 springs were eliminated. In their case, invalid results were expected because of the infiltrations of underground waters or because of the inflow waters from the slopes, or the water of the spring has been stagnating in the drilling for a long time now, or the access for measurements was denied by the land owner.

So 35 springs were left to measure and analyze, which were numbered beginning from Vârghiş towards North to the limits of the depression, then coming back to Tălişoara and Racoşul de Sus, from where they continue towards East and North again, upstream on Baraolt rivulet. The last ones are along Ozunca brook and Sugo brook (tables 1a and 1b).

According to the way these mineral waters reach the surface, they can be divided in natural springs and men influenced ones. Natural springs are considered those whose waters were not surrounded by wooden or concrete tubs. The men influenced ones are those whose waters are brought to the surface by geological, hydrogeological or exploitation drillings. 11 springs may be included in the first category and 24 springs in the second one. Such a division is necessary because the springs coming out through drillings may originate from different aquifers. Considering these facts, after the measurements and analyses, the collected data were separately evaluated. The natural ones are the springs numbered with: 2, 3, 5, 26, 28, 30, 31, 32, 33, 34 and 35 (tables 1a and 1b).

The temperature and pH of all the 35 springs

Table 1a.

Spring number	The name of the springs	T° in C°			pH		
	Date of measurment	May 2011	August 2011	January 2012	May 2011	August 2011	January 2012
1	Vârghiş	17.1	17.1	17.1		6	6.21
2	Doboşeni, Baia Bethlen	11.5	12.1	10.8	6.03	5.9	6.11
3	Doboşeni, Satului	11.7	11.8	10.4	5.96	5.7	6.07
4	Doboşeni, CAP, F1315	14.4	14.3	14.1	6.01	5.83	6.18
5	Doboşeni, Tanya	10.5	11.1	10.2	5.84	5.53	5.94
6	Doboşeni, Valal1 FH1	16.7	16.6	16.2	5.91	5.74	6.07
7	Doboşeni, Valal2 FH2	17	17	16.8	5.98	5.68	5.97

8	Doboşeni, Cab. Valal	16.1	16.1	16.2	5.89	5.69	5.86
9	Tălişoara, Izv. Nebun	21.2	21.3	21.4		6	6.4
10	Tălişoara, Baia	18.9	18.3	19.3		6.11	6.37
11	Racoşul de Sus (farther)	11.6	13.2	11.5		6.04	6.18
12	Racoşul de Sus (closer)	13.7	13.6	13.4		5.65	6.41
13	Baraolt, Herd's road	15.1		14.8		6.41	6.52
14	Biborţeni DJ122(farther)	14.7	15.4	14.9		6.01	6.28
15	Biborţeni DJ122(closer)	16.2	17.1	16.7		6.39	6.61
16	Biborţeni F2SNAM	14.4			6.52		
17	Biborţeni F7ISPIF	16.9	16.9	16.8	6.22	6.12	6.18
18	Biborţeni F8	14.7	14.8	14.7	6.3	6.18	6.28
19	Biborţeni F9	12.9	12.9	13.0	6.18	6.21	6.15
20	Biborţeni F9bis						
21	Biborţeni 1Mai 1951	13.1	13.9	12.4		6.19	6.22
22	Biborţeni, Baia 1	14.6	14.6	14.2	6.32	5.89	5.96
23	Băţanii Mici, Sonda	11.6	12.2	11.5		5.9	6.22
24	Băţanii Mici, Dealul Lorincz	10.7	11.5	10.4		5.7	5.98
25	Băţanii Mici, Dealul Romanilor	12.5	12.8	12		5.03	6.34
26	Băţanii Mici, Rezes1	11	11.6	11.1	6.14	5.85	5.93
27	Băţanii Mici, Rezes2	11.1			6.02		
28	V. Bradul Mare Korises	7.3	13.1	6.2		5.96	6
29	V. Bradul Mare F2SNAM	8.1	10.6	9.8	5.96	5.29	5.9
30	Herculian, Alszegi	10.2	13.2	10.8		5.68	5.57
31	Herculian, Dimeny Agnes	10.3	14.6	9		5.75	5.63
32	Herculian, Agostonhidi	11.7	12.2	10.8		5.25	5.63
33	Herculian, Szenaskerti	13	13.4	12.6		5.38	5.5
34	Băţanii Mari	13.2	14.4	6.2		5.54	5.8
35	Băţanii Mari, Sugo	10.8	15	7.7		5.86	5.83

The TDS, CO_2 and HCO_3 of all the 35 springs

Table 1b.

Sp nb.	The name of the springs	TDS mg/l			CO_2 mg/l			HCO_3 mg/l		
	Date of measurment	May 2011	Aug. 2011	Jan. 2012	May 2011	Aug. 2011	Jan. 2012	May 2011	Aug. 2011	Jan. 2012
1	Vârghiş	1170	1165	1100	1100	1980	1232	1769	1830	1464
2	Doboşeni, Baia Bethlen	865	863	822	1496	1672	1188	1403	1281	1342
3	Doboşeni, Satului	678	687	678	1672	1716	1012	1098	1098	1037
4	Doboşeni, CAP, F1315	820	800	792	1804	1848	1012	1342	1220	1220

5	Doboşeni, Tanya	630	641	629	1848	1848	1144	915	976	976
6	Doboşeni, Valal1 FH1	800	802	731	1496	1672	1232	1220	1220	1220
7	Doboşeni, Valal2 FH2	680	684	669	1496	1892	880	1159	976	1037
8	Doboşeni, Cab. Valal	604	571	559	1452	1848	1056	1037	915	793
9	Tălişoara, Izv. Nebun	1680	1680	1615	1320	1584	484	2745	2562	2562
10	Tălişoara, Baia	1500	1470	1575	1562	1540	616	2318	2318	2196
11	Racoşul de Sus (farther)	1130	1395	1365	1012	2112	1320	1586	2196	2074
12	Racoşul de Sus (closer)	1390	1135	1145	1804	1276	616	2135	1525	1586
13	Baraolt, Herd's road	960	935	873	0	12	88	1037	976	1037
14	Biborţeni DJ122(farther)	800	796	800	528	968	572	2112	1190	1220
15	Biborţeni DJ122(closer)	1790	1765	1750	836	1188	220	1159	2074	2013
16	Biborţeni F2SNAM	860			528			1342		
17	Biborţeni F7ISPIF	1140	1140	1140	1804	1804	1848	1708	1647	1708
18	Biborţeni F8	1000	1000	1010	1672	1716	1716	1342	1403	1403
19	Biborţeni F9	1170	1170	1170	1848	1848	1892	1647	1708	1769
20	Biborţeni F9bis									
21	Biborţeni 1Mai 1951	1075	1080	1000	1320	1716	1232	1342	1769	1342
22	Biborţeni, Baia 1	1325	1340	1310	1672	1452	1364	2074	2013	2074
23	Băţanii Mici, Sonda	947	930	928	1056	1672	528	1403	1464	1464
24	Băţanii Mici, Dealul Lorincz	751	720	713	1760	1848	836	1098	1098	1037
25	Băţanii Mici, Dealul Romanilor	321	281	274	660	427	88	488	427	427
26	Băţanii Mici, Rezes1	730	724	692	1892	1892	880	1098	1037	1098
27	Băţanii Mici, Rezes2									
28	V. Bradul Mare Korises	687	735	715	1716	1584	792	976	1098	976
29	V. Bradul Mare F2SNAM	312	284	278	797	704	440	427	305	244
30	Herculian, Alszegi	443	441	428	2332	2024	1056	671	732	671
31	Herculian, Dimeny Agnes	475	478	465	1992	1408	484	732	854	732
32	Herculian, Agostonhidi	316	325	312	1956	1496	792	549	427	488
33	Herculian, Szenaskerti	213	220	216	1670	1540	748	366	366	305
34	Băţanii Mari	430	438	426	1408	1364	792	549	610	488
35	Băţanii Mari, Sugo	650	689	656	1408	1584	792	854	915	854

At the identification of these springs on the field and on the map it is obvious that they follow certain lines and if they are put on the map of the depression faults, these lines are exactly the faults, so they spring out along them. The 2, 3, and 5 springs are in the western basin and flow out along the Cormoş fault system (G8), and the 26, 28, 30, 31, 32, 33 are in the eastern basin along the eastern response of G8, namely g27. The 34 and 35 springs flow out along the crust fault G7.

Based on these criteria of being part of three groups, we searched for the common physical and chemical properties which characterises each group.

3. RESULTS AND DISSCUSION

The 2, 3, and 5 springs temperature varies just 1°C annually (table 1a). In August the measured temperature was between 11.1 and 12.1°C and in January between 10.2 and 10.8°C.

The values of the pH (table 1a) between 5.53 – 5.9 in summer and 5.94 – 6.1 in winter indicate a moderate acidity with a weak shifting towards alkalinity.

The total quantity of the dissolved mineral salt (TDS) indicates that the waters of these springs (table 1b) belong to the category of medium mineralized ones, the highest value registered was at the spring 2 (Baia Bethen) with 863mg/l, and the lowest one at number 5 (Tanya borvíz) with 629mg/l. A seasonal variation can be noticed: in the warm season the values are higher than in the cold one by 9 to 41mg/l.

If based on the values of the TDS they are medium mineralized, the values of the free CO_2 are a lot over the limit of 250 mg/l (table 1b). For this parameter, a value of 1848 mg/l was determined and there are quite high seasonal fluctuations which reached 704 mg/l.

The analyses made for HCO_3 (table 1b) showed values over 900 mg/l (up to 1403). The most northern spring showed values under 1000 mg/l. It was not possible to reveal seasonal fluctuations as in the case of the other measured or analysed parameters. At some springs the HCO_3 goes down in summer, at others it increases, probable there is no correlation in this case.

In the eastern basin the natural springs are in greater number and at first overview they present noticeable differences from those in the western basin, previously evaluated.

Their temperature (table 1a) varies more between summer and winter, a variation that is not homogenous. There are springs with variations of 6.9°C, but springs with a variation of just 0.5°C.

The acidity of these springs is higher than those of the eastern basin (table 1a), with values of the pH between 5.25 and 5.96 in summer, and between 5.5 and 6.00 in winter. One notices a tendency to alkalinity in winter when the temperature drops.

The quantity of the total dissolved mineral salt (TDS) decreases from South to North (table 1b), from 735mg/l (Körises spring – 28) to 219.5mg/l (Szénáskerti 1 spring – 33). From the southern end of Herculian village there is a passing from medium mineralized waters (TDS between 500 and 1000mg/l) to weakly mineralised ones (TDS under 500mg/l). This fact may indicate a passing from one aquifer to another. A decrease of the values of this parameter can be noticed in the cold season.

In fact the quantity of free carbon dioxide is the one that maintains these waters in the category of mineral waters, as its values reach 2332 mg/l (table 1b). The average of the analyses made during the third field activities is 1458.5 mg/l. This low average is due to the low values determined in the cold season (January 2012). Along the data sets, one notices a serious decrease of the values of this parameter, a two times decrease or even a three times decrease in the case of Dimény Ágnes spring (31). This fact is not true for the other springs of the depression.

The values of the HCO_3 for these six springs from the eastern basin give an average of 732 mg/l (Table1b). Rezes 1 (26) and Körises (28), can be separated, having values around 1000 mg/l. In the case of the others that follow towards North, this parameter decreases to 366 mg/l. Among these springs, Dimény Ágnes (31) can be revealed which is at just 45m East-North-East from Alszegi (30) and there is a difference of over 100 mg/l HCO_3 between them. The seasonal variability of this parameter is like the one at springs in the western basin: the values are increasing during summer and decreasing during winter.

The third group of the natural springs includes those which follow the crust fault G7, and they are numbered with 34 and 35, respectively from Băţanii Mari and the valley of Sugo brook.

The temperature of these two springs presents a wider variation than the other ones, discussed up to this point. In summer it reaches 14 - 15°C and in winter goes down to 6.2 – 7.7°C (table 1a). This fact can suggest that they originate from an aquifer close to the surface or that they stagnate close to the surface time enough to be influenced by the variation of the temperature of the upper geological layers.

The values of the pH (table 1a) are between 5.54 and 5.83, Sugo spring having the lowest variation, just 0.01 at 4.2°C temperature variation.

The total quantity of dissolved mineral salt (TDS) keep these springs in the category of medium-weak mineralized with values around 500 mg/l (table 1b), but the free CO_2 is over 1400mg/l during summer.

The last parameter to be analyzed was that of the HCO_3, which indicates a pretty large difference (around 300 mg/l) between the two springs (table 1b). This fact can suggest that they may originate from different aquifers. Regarding the variations of the data, the same decrease during winter time can be noticed.

In the aggregate, not just the position of the 11 springs suggests their belonging to the three main faults, but also the differences in their measured and analysed physical and chemical properties, which sometimes are significant. Based on these properties, it is possible to reveal approximately the aquifer they belong to or they originate from. So the waters of the natural springs of the western basin have almost constant temperature, are less acid (average pH 5.87) and medium mineralized (TDS does not reach 1000 mg/l). These values suggest that they belong to a deep aquifer, probably in the first volcano-sediment layer, very close to the Cretaceous structure, fact sustained by the highest quantity of HCO_3 (1403 mg/l at Baia Bethlen spring – 12) of all natural springs of the depression. The high quantity of free CO_2 proves once again that they spring out by a major fault, through which this gas, a result of post volcanic activity, may travel.

As it was shown before, the other 24 mineral water springs flow out through geological, hydro geological drillings and special drillings for economic purposes. These latest ones provide mineral waters for bottling. So, all these waters are brought to surface by the willing action of the man and they can be named artificial springs. In table 1a and 1b they were numbered: 1, 4, all from 6 to 25, then 27 and 29.

It is noticeable that these waters spring out through those drillings that were made following the same faults in the depression. So they can provide more data regarding the physical and chemical characteristics of the mineral waters from Baraolt Depression. However, one notices the possibility that waters from different aquifers may spring out through a drilling.

Following the same method of assessment, by grouping these springs according to the faults along which the drillings were made, the group made by the flow outs numbered 4, 6, 7, 8, 9 and 10 can be separated, as they are situated in the western basin, along the G8 fault. After the measurements and the analyses were made, the first finding was that the temperature of each spring is over 11°C, reaching 21.4°C at spring number 9 (table1a). The variation of this parameter between summer and winter is very weak, just from 0.1 to 1.7°C. At the springs numbered with 8, 9, and 10 the temperature increased during winter by 0.1-1°C.

The acidity of these six artificial springs shows an average of 6.02, while the same average value for the natural ones is 5.875. At the first ones we measured values of 6.37 – spring no. 10 (Table 1a), even 6.41 – spring no. 12 (table 1a). Two different facts can be noticed: 1) as in the case of the natural springs the pH of these flow outs shows a shifting towards alkalinity as it is closer to the North limit of the depression; 2) it is not possible to determine a rate between the decline of the water temperature of the springs and the shifting towards alkalinity. For example in the case of the natural spring no. 5 there is a difference of temperature by 0.9°C between summer and winter and a changing of pH from 5.53 to 5.94 (table 1a). But at the artificial spring no.9 (table 1a) there is an increase of temperature from summer to winter by 0.1°C and a shifting in pH from 6 to 6.4.

Regarding the total dissolved mineral salt (TDS), there is a difference between the waters from the drillings from the valley of Volal brook and those situated South of Doboşeni village (table 1b). The measured values at the previous ones do not pass over 820 mg/l, meanwhile at the latest ones this parameter is over 1500 mg/l. It is noticeable the decrease of TDS towards North and its increase at the two which are to South of Doboseni over 1500 mg/l – springs 9 and 10.

The results of the analyses for free carbon dioxide show that the values are as high as in the case of natural springs, generally over 1500 mg/l (Table 1b.). But the decrease in winter time is larger, reaching even 1000 mg/l.

The quantity of HCO_3 is invariable at some flow outs and at others has small fluctuations till 96 mg/l (Table 1b). It is also possible to separate the artificial springs from the North of the western basin: they have lower values and larger fluctuations, up to 132mg/l.

From the amount of the gathered data about this group of springs, it comes out that there is a difference between those which are situated to North of Doboşeni and South of this village. The previous ones are more acid, contain less dissolved mineral salt, less HCO_3, and have a larger variability of the free CO_2 than the latter ones. Those from the South of this village come from or close to the Cretaceous structures, meanwhile the others from the lowest or medium volcano-sediment layer.

Another group of drillings is situated along the G7 fault at Biborţeni village, but they are apart from the others because of the following reasons:

1) the drillings were made with the purpose of bottling the out coming mineral waters;

2) the drillings are no deeper than 50 to 75m;

3) the physical and chemical properties of these waters are greatly influenced by the post volcanic activities of the Tirco volcano and the closeness of the Cretaceous structures (in this area the Cretaceous structures are not even 100 m deep, on the other hand they are on the surface by the horst structure represented here by Cetăţii Peak – 614,1 m, which is not even 200 m away from the drillings).

4) the strangling at Biborţeni is crossed by G7 fault, which offers conditions for the circulation of the post volcanic manifestations of the Tirco and for waters.

Regarding the fact that the waters from these drillings are used for bottling, they are always pumped. The temperature of some of them is invariable, while that of the others fluctuates around the value of 0.5°C (table 1a). From the point of view of the pH, the measurements showed values over 6, reaching 6.52. The values of the TDS show that they are also medium mineralized, most of them have values over 1000 mg/l, but do not pass over 1400 mg/l (table 1b). Based on the previous argumentation, the analyses for the determination of the free CO_2 and HCO_3 confirmed the expected high values. Values between 1320 and 1848 mg/l were determined for the free CO_2 (with an anomaly at spring no. 16 with a value under 1000 mg/l), and between 1342 and 1769 for HCO_3 (table 1b.).

In the eastern basin, along the fault g27 four drillings were made, of which two are very recent – 2009 and 2010 – for mineral waters without, or with low CO_2. They were tested in the period when measurements and analyses were made. The other two are located in the floodplain of the Baraolt rivulet and are numbered with 23 and 24 and the results of the measurements and analyses can be used in comparison (table 1a and 1b).

The seasonal variation of the temperature of these springs is between 0.7 and 1.1°C, the pH is around the value of 6, oscillating between 5.7 and 6.22 (table 1a), the TDS is under 1000 mg/l with a light tendency of dropping in the period when we made the measurements. At the analyses for the free CO_2 the values show an increase in summer even to 1848mg/l and a deep decline in wintertime to 528 mg/l. The values of HCO_3 are also high: 1196 mg/l, 1464 mg/l and their variation is weak: around 60mg/l (table 1b).

A separate category of mineral waters is represented by that group of out flows which appeared after the cessation of the mining activity, through those drillings which went deep, intercepting the Cretaceous structures. These springs were numbered 1, 11, 12, 13 and 14. Among them, spring no.1 was remarked, which flowed out immediately after mining activity stopped, very close to the access well to the underground pit in Vârghiş. The extraction of layers I and III of the lignite helped the waters of an aquifer from the Cretaceous structures to get to the surface. It was enriched with CO_2 through an old fault having NW-SE direction. The temperature of this spring is constant: 17.1°C, pH varies between 6 and 6.21(table 1a), it is medium mineralized: TDS between 1100 and 1170 mg/l, rich in free CO_2 (1100 – 1970mg/l) and in HCO_3 (1461 – 1830 mg/l) (table 1b). The other flow outs of this kind started to spring 2 or 3 years after the activity in the underground pits ceased. In their cases, the possibility of the mixture among different aquifers is a certainty due to the fact that their flow out started after the galleries were flooded and the hydrostatic level came back to normal. Contrary to these facts, measurements and analyses were made to see if they can be included in any of the mineral water groups previously nominated.

Based on the collected data, the two springs located near Racoşul de Sus by the road DC 38 (which connects this village to DJ 131), numbered 11 and 12, are like the springs 9 and 10 (near Tălişoara village) regarding pH (around 6), TDS (close to 1400 mg/l), free CO_2 (with large variations) and high quantity of HCO_3 (between 1500 and 2100 mg/l), but they differ in temperature, which is not over 13.7°C and has seasonal variations about 1.7°C (table 1a and 1b).

The flow out from Baraolt, by the herd road (number 13), is a mineral water having 15°C, pH of 6.52, medium mineralized (TDS between 873 and 960 mg/l), without free CO_2, but with a pretty high quantity of HCO_3 which reaches 1037 mg/l. So it is a mineral water without CO_2, which was helped by a drilling to reach the surface (table 1a and 1b).

The latest drillings, through which the waters came out after the ceasing of the mining activity, are by the road DJ 122 between Baraolt and Biborţeni, numbered 14 and 15. They should be like the flow outs through the drillings of Biborţeni. Their temperature is around 16°C, with oscillations up to 1°C and they have the highest pH among the springs in the depression: 6.61 (table 1a). The TDS is around 700 mg/l at number 14, but at the other one it reaches 1760 mg/l. The quantity of free CO_2 presents large oscillations from 220 to 1188 mg/l and the quantity of HCO_3 is also high, up to 2112 mg/l, but also with large oscillations which may reach 915 – 922 mg/l (table 1b). Based on these data it is almost sure that the waters that reach the surface through these drillings are mixed ones from different aquifers, but are under the influence of those four factors like those in Biborţeni.

4. CONCLUSIONS

The supposition about the origin of the mineral waters from the Baraolt Depression is confirmed by their physical and chemical characteristics. Some of them, mainly those which come to the surface through drillings, come from the Cretaceous structures and others from the volcano-sediment layers.

The mineral waters which come from the Cretaceous structures have temperatures over 15 - 16°C, pH around 6 – 6.2, are rich in minerals, the TDS is over 1000 mg/l, the free carbon dioxide is high, the values are over 1300 – 1500 mg/l, and the quantity of HCO_3 is also high and oscillates around 1800 – 2500 mg/l. All these flow outs are artificial, coming to the surface through drillings, as are the cases at Tălişoara – number 9 and 10 – those at Racoşul de Sus – number 11 and 12 – and that of Vârghiş – number 1. The last three ones sprang after the mining activity stopped.

Those mineral waters that come from the lower volcano-sediment layer have temperatures around 10 – 12°C, with seasonal oscillations around one degree Celsius, the pH is a bit more acid than in the previous ones, with values around 5.53 – 6.1. They are medium mineralized – TDS between 500 and 1000 mg/l and are rich in free CO_2: around 1100 – 1800 mg/l. The quantity of HCO_3 decreases from South (around 1220 mg/l) to North (around 790 mg/l) as the thickness of this layer grows. These are the springs from the western basin along the Cormoş rivulet and Volal brook and in the eastern basin along Baraolt rivulet close to Herculian and along Bradul Mare brook.

A separate group of mineral waters, that detaches itself from the others, is the group in the surroundings of Herculian. Taking into account these data: temperature around 10 - 14°C, with wider oscillations (up to 7°C); more acid pH, going down to 5.25; weak mineralization, as the TDS is under 500 mg/l; low content of carbonate – HCO_3 between 700 and 366 mg/l; very rich in free CO_2 – between 1500 and 2200 mg/l; it can be said that they spring from aquifers situated in the upper volcano-sediment layer, which in this area is 30-40 m thick (A. László, 1999). The closeness of this area to the Cucu volcano makes the CO_2 emanations to be very rich and the presumption that some of these mineral waters could be outflows of the strongly bicarbonated ground water cannot be excluded.

Another separate group of springs can be made from those which are in the area of Biborţeni. Their characteristics are due to the facts listed above and they were so appreciated that are the only ones used for bottling.

The other springs along the G7 fault have the pH, TDS, and HCO_3 totally different, arguments according to which it is possible to say that they come from two separate aquifers. That from Baţanii Mari (34) comes from the upper volcano-sediment layer while the other one (Sugo, 35) from the Cretaceous structures.

During the assessment of the presented physical and chemical properties of the springs, the correlations among these properties were followed. As the temperature and pH were measured, a certain correlation between them was noticeable. But at a closer analysis of the data, this observation proved to be incorrect as the decrease rate of the temperature in winter does not involve a similar rate of pH increase (shifting towards alkaline). Additional arguments to support this are the cases of those springs whose temperature is constant or increases during winter while their pH increases anyway. We tried to establish connections between the decrease of free CO_2 during winter and the decrease of TDS, HCO_3 and the increase of the value of the pH, but the data are confusing. There are cases when the free CO_2 is constant, the TDS insignificantly modifies, the HCO_3 is also constant and the value of pH increases with almost half a unit.

In this train of ideas we can say that a longer data set is needed, at least for seasonal data, to establish correlations among these physical and chemical properties of these springs and probable rhythmicity in the activity of this post volcanic manifestation.

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