

AN OUTLOOK ON THE INTERPRETATION OF THE HYDROCHEMICAL DATA OF THE GEOTHERMAL SYSTEM ORADEA-FELIX, ROMANIA

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ABSTRACT

This study outlines once more the importance of hydrochemistry in the general context of geothermal research. The monitorization of each well all over its life is useful, supplying data that **can** shows the variations, the changes of downhole conditions. Once more being **one** of the geo-scientific discipline, hydrochemistry **can** contribute **as** a part **to** the development of the conceptual model.

The users of geothermal energy can gain many benefits from this energy, on the condition to have aid to **use** correctly and carefully reliable data.

We have done the monitorization of the geothermal system Oradea-Felix that contains two different types **of** water. This is the first assessment with **an** interpretation of data obtained in 15 years of monitorization, such a long time interval indicating some changes of geothermal water chemistry.

Introduction

The research on hydrochemical situation of geothermal system it must be consider a very important activity from economic point of view. One economic aspect which must be take into consideration is the fact that this resource it is not renewable, and wrong actions, wrong interventions, or a wrong exploitation can lead to its premature depletion.

In this region from the multitude of data on the chemical composition of geothermal waters, we can distinguish from the beginning different types of aquifers in different reservoirs.

The hydrochemical indicators for establishing the main chemical features **of** the aquifer were: pH, conductivity, TDS (total dissolved solids), organic substances, hardness, Silica, phenolic compounds, boric acid; anionic components: chloride, nitrite, nitrate, bicarbonate.. carbonate, sulfate. phosphate;

cationic components: ammonium, sodium, potassium, calcium, magnesium, iron.

The aquifer embedded in the *Triassic reservoir* has the total mineralization around 1g/L and the water is calcium-magnesium-sulfate-bicarbonate type. The aquifer embedded in the *Cretaceous reservoir* has the total mineralization around 0.5-0.9g/L, the water character being calcium-magnesium-bicarbonate-sulfate type.

These varieties of characteristics of geothermal water need a detailed study related not only to the physical-chemical characteristics but also to their interrelations and even the water-rocks interaction's.

Provided that we **can** find some significant distinction or similitude among different geothermal sources (wells), it must be interpreted **as** a unitary system, dynamic and equilibrated, each with the own specific conditions.

Hydrochemistry of Triassic aquifer

This aquifer is located in a Triassic limestone-dolomite reservoir, with favorable conditions for water accumulation, **at** 2000-3000m depth (average 2500m). The geothermal waters of this reservoir reach a temperature of 67 -105° C **All** wells are producing artesian. The main flow of circulation is from the East to **West**, following a preferential path along the fractures in basement. The fractured deep structure and the carstic structure of the zone binds the reservoirs (Triassic **and** Cretaceous aquifers) leading to a geothermal system. It is a convergent flow towards Felix Spa This is also providing hydrochemical **data**.

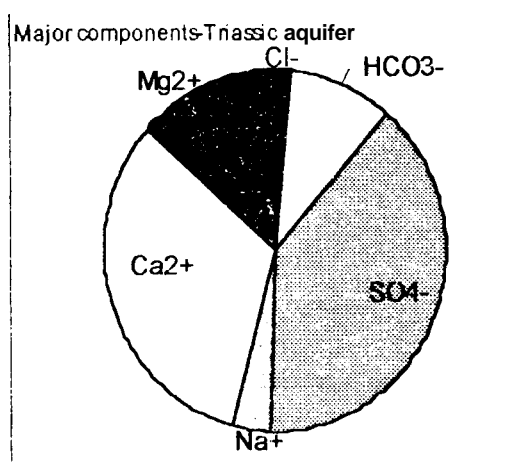
In fact there are more, but the Triassic geothermal aquifer was constantly investigated in 6 wells. The time interval taken into consideration by this paper is 1971-1990

By processing the elementary data from chemical analyses, we obtained the following results (average values).

Table 1: The percentage composition of the equivalent of the main elements in Triassic geothermal aquifer

Well no.	Cl mcq %	HCO ₃ mcq %	SO ₄ mcq %	Na mcq %	Ca ²⁺ mcq %	Mg ²⁺ mcq %
4004	3,95	24,28	71,76	8,29	61,7	27,23
4005	3,14	16,42	80,44	5,83	66,9	24,92
4006	3,18	18,67	78,15	6,96	65,4	25,51
4081	1,42	13,22	85,34	4,54	63,0	30,21
4767	4,54	27,77	67,69	11,8	62,9	21,23
4797	2,36	16,77	80,86	4,62	64,5	29,45

Figure 1 was obtained by plotting grand average values of major components.



The water type results as main feature. Particularizing each well by the ionic composition a detailed individualization can be notice as following:

- 4004: its water belongs to the class of strong sulfate –weak bicarbonate –strong calcium –moderate magnesium;
- 4005: its water belongs to the class of strong sulfate –strong calcium –weak magnesium;
- 4006: its water belongs to the class of strong sulfate –weak bicarbonate –strong calcium- moderate magnesium;
- 4081: its water belongs to the class of very strong sulfate –strong calcium –moderate magnesium;
- 4767: its water belongs to the class of strong sulfate –weak bicarbonate –strong calcium –moderate magnesium;
- 4797: its water belongs to the class of strong sulfate –weak bicarbonate –strong calcium – weak magnesium.

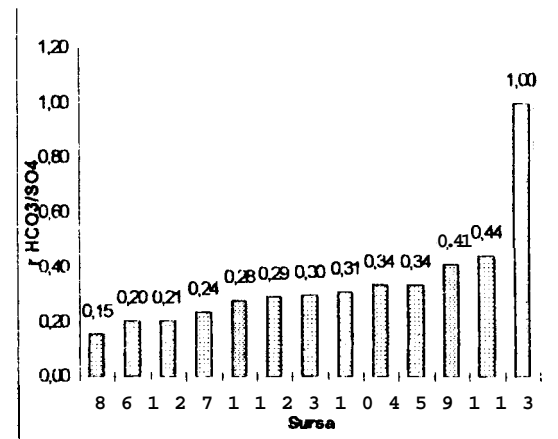
Legend 1:

- 1 Oradca 1709
- 2 Oradca 1715
- 3 Oradca 1716
- 4 Oradca 1717
- 5 Oradca 4004
- 6 Oradca 4005
- 7 Oradca 4006
- 8 Oradca 4081
- 9 Oradca 4767
- 10 Oradca 4795
- 11 Oradca 4796
- 12 Oradca 4797
- 13 Livada 507

According to diagrams and tables data, we notice a repeated chemistry till now. This proves a relative high stability of the chemistry of the aquifer in discussion.

From the survey of the characteristic ratio HCO₃/SO₄ it can be remarked that the values are smaller than the unit. The source 13-livada507 does not belong to this aquifer.

Figure 2 The characteristic ratio HCO₃/SO₄ some sources of Triassic aquifer



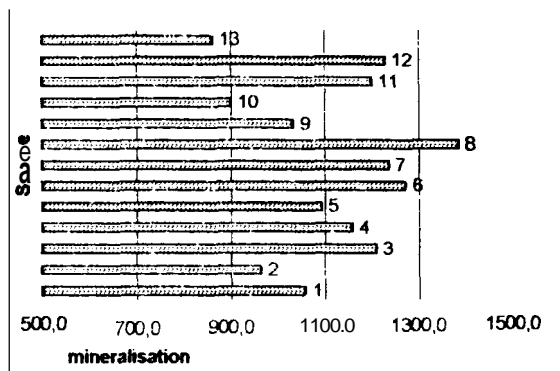
Distinguishing between the hydrochemistry of these wells, we remark that the water from 4801 located in the South of Oradea has the highest content of sulfate (around 18,5%meq/L.), followed by 4005; 4006, 4797; 4004; and finally 4767(11 %meq/L.)

The decrease of sulfate ion at well 4081 compared to well 4767 occurs with an increase of bicarbonate content.

A correlation can be done (see table 1). Figure 3, shows clearly a typical interdependence of ionic concentration, couch as mg/L function by total mineralization. The sulfate ion concentration increases at the same time with the increase of total mineralization, while the bicarbonate ion concentration decreases equally (the Same proportion). The increase of total mineralization, of sulfate ion concentration and the decrease of

bicarbonate ion concentration converge toward well 4081.

Figure 3 the mineralization of the source that belong to Triassic aquifer (see Legend 1)



A perspective of geothermal waters by comparison with Cherebotaev's segments leads to the next conclusion. On their path of flow, the water which dissolved limestone and dolomite till saturation, in a congruent system, contacts a geologic material containing gypsum or anhydrite; a material which is more soluble than limestone or dolomite (in close system) and which under the common ion effect, has began to deposit carbonate simultaneous with the increasing the sulfate ions concentration, till it is reach an equilibrium. Maybe due to this equilibrium, in spite of the hardness of geothermal waters, in this area there was not recorded deposition of scale or incrustation phenomena during completion. Commenting on the microelement composition of this aquifer their abundance surprises. These data were obtained by Spectroscopy of Emission.

The microelements composition of Triassic

Well No.	V (mg/L)	Co (mg/L)	Ni (mg/L)	Mn (mg/L)
4004	2.1×10^{-3}	-	4.5×10^{-3}	5.2×10^{-3}
4005	3.5×10^{-3}	-	1.8×10^{-3}	6.9×10^{-3}
4006	5.4×10^{-3}	-	1.1×10^{-3}	3.3×10^{-3}
	4.8×10^{-3}	-	-	1.3×10^{-3}
	4.2×10^{-3}	8.9×10^{-4}	3.8×10^{-3}	2.6×10^{-3}
	8.8×10^{-3}	-	8.5×10^{-3}	4.6×10^{-3}

data. It is not a perfect identity; each well in its own conditions reflects a dynamic equilibrium integrating

the specific characteristics of the entire hydrothermal structure.

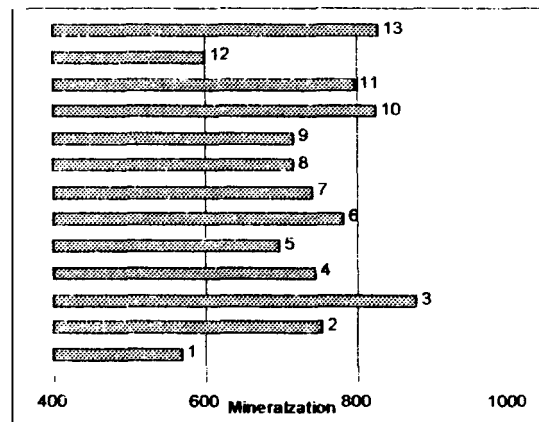
Hydrochemistry of Cretaceous

This geothermal area was the subject of various researches, or applied works. The first data were recorded in 1833 (A. Baue). Many teams worked along years in this area, enriching the scientific and technical knowledge regarding it.

The description of hydrogeologie must be correlated to the extremely favourable structural conditions of reservoir (A. Tenu, 1975). This aquifer lies down in a carstic structure as well as a very well developed fissured structure. The depth is extremely fracture, very tectonized. These conditions ensure the ascension path of thermal water from depth. The upper layer constitute from limestone is an ideal preservation of the energetic potential and in the same time an ideal storage area.

The perimeter is located at 10km Southwest from the town of Oradea, in the zone of Felix Spa. This reservoir is from a physical point of view, the continuation of the regional Mesozoic hydrostructure of Pădurea Craiului, as its terminal part. The average depth of accumulation is at 1800-2000m. The geothermal waters of this reservoir reach a temperature of 45-80°C.

Figure 4. The mineralization of the source that belong to Cretaceous aquifer (see legend 2)



The Cretaceous geothermal aquifer was constantly investigated in 9 wells, in fact there are more, and there also are 4 natural springs. The time interval taken in consideration paper is 1971-1990. The hydrochemical indicators for establishing the main chemical features of the aquifer were the same with those investigate in the Triassic aquifer.

The thermal water hydrochemistry the whole is calcium-magnesium-bicarbonate-sulfate type, very low mineralized. It is like the Triassic aquifer but the dominant ion is reversed, sulfate instead of bicarbonate. The prevalent feature is given here by bicarbonic ion.

By processing the elementary data from chemical analyses, we obtained the following results.

Table 3: The percentage composition of the equivalent of main the elements in Cretaceous geothermal aquifer

Well no. /Source	Cl ⁻ meq %	HCO ₃ ⁻ meq %	SO ₄ ⁻ meq %	Na ⁺ meq %	Ca ²⁺ meq %	Mg ²⁺ meq %
1Mai Izbuc	4,03	61,99	33,97	9,17	65,22	24,64
Felix 4003	4,07	63,4	32,4	9,2	69,1	20,6
Felix 4011	4,06	55,01	40,94	9,01	66,10	23,96
Felix 4012	3,43	80,19	16,34	6,74	59,27	32,84
Felix Balint	4,60	57,26	38,14	10,1	58,57	30,19
Felix4087	4,67	71,86	23,49	8,85	68,55	21,27
FelixVila-4	4,20	65,02	30,71	9,19	64,47	25,38
Cordau402	4,24	71,59	24,17	8,9	69,19	20,97
Rontau F2	4,34	57,97	37,69	8,93	63,79	26,22
Frederich	4,85	65,50	29,63	10,5	63,40	25,47
OchiuMare	4,73	74,88	20,37	5,74	65,19	27,61
OchPompei	4,76	69,21	26,01	9,00	63,17	27,14
OchTiganul	3,18	56,92	39,45	13,3	65,12	21,35

Figure 5 is obtained by plotting grand average value of major components

Major components-Cretaceous aquifer

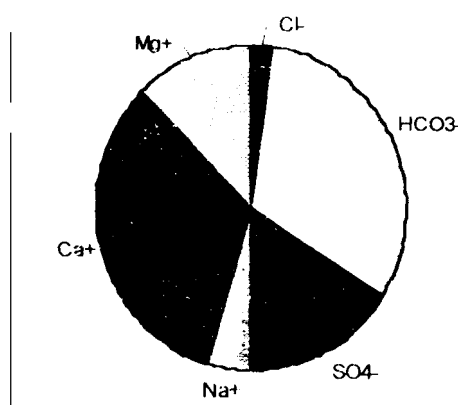


Figure 5

Particularizing each source the by its ionic composition, a detailed individualization can be notice as following:

- Izbuc: its water belongs to the class of strong bicarbonate-weak sulfate --strong calcium - weak magnesium;

- 4003: its water belongs to the class of strong bicarbonate-weak sulfate --strong calcium weak magnesium; .
- 4011: its water belongs to the class of strong bicarbonate- moderate sulfate - strong calcium -weak magnesium;
- 4012: its water belongs to the class of very strong bicarbonate --moderate sulfate --strong calcium - weak magnesium;
- Ralint: its water belongs to the class of strong bicarbonate - moderate sulfate - strong calcium --weak magnesium;
- 4087: its water belongs to the class of strong bicarbonate- weak sulfate --strong calcium - weak magnesium;
- Vila 4: its water belongs to the class of moderate bicarbonate --moderate sulfate - strong calcium --weak magnesium;
- 402: its water belongs to the class of strong bicarbonate - weak sulfate --strong calcium - weak magnesium;
- F-2: its water belongs to the class of strong bicarbonate -moderate sulfate strong calcium --weak magnesium;
- Frederic- it is a thermal spring the water its belong to the class of strong bicarbonate - moderate sulfate - strong calcium --weak magnesium;
- The next sources (OchiuMare, OchPompei, and OchTiganu) are natural emergencies; in fact there are lakes. Their compositions are not relevant for the downhole aquifer being mixed with meteoric water. The prelevation directly from spring being not possible

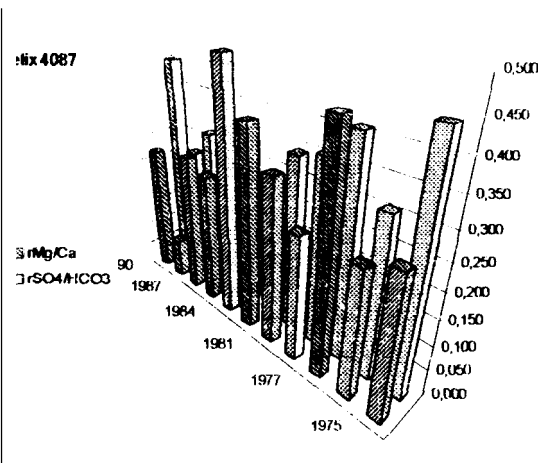


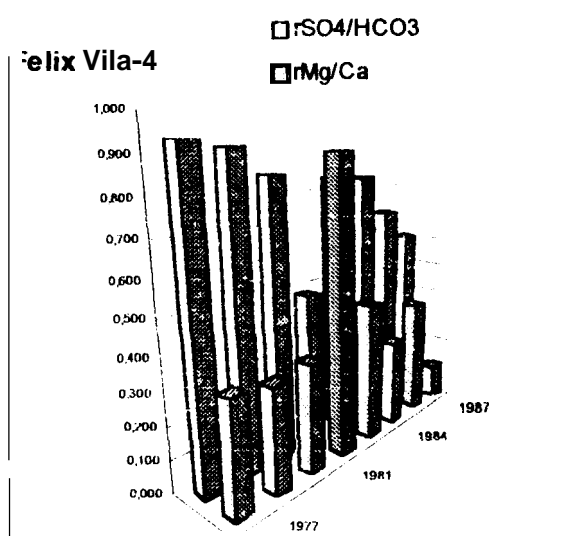
Figure 6. The evolution rSO₄/HCO₃ and rMg/Ca of Felix Vila-4

According to diagrams and tables data, there was not a repeated chemistry along the time. This indicates some changes of the chemistry of the aquifer in

discussion. **Figure 6 --7** shows the chronological evolution of characteristic rapport of two sources that belong to this aquifer.

Figure 7. The evolution rSO_4/HCO_3 and rMg/Ca of Balint

The cationic general characteristic belongs to strong calcium, weak magnesium class. By observing the



anionic distribution, it can be remarked a certain difference among the sources. Distinguishing between these sources, we can notice the higher concentration of bicarbonate at 4012(80,19%), located in the North of Felix Spa; well 4011 has the highest content of sulphate (around 40,94%meq/L.), followed by Balint,

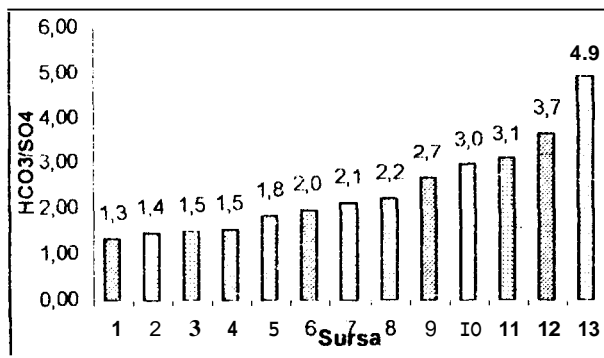


Figure 8 the diagram of HCO_3/SO_4 (average value) of different sources of Cretaceous aquifer

- Legend 2:**
- 1 Felix 4011
 - 2 Ochiul Tiganului
 - 3 Felix Balint
 - 4 Rontau F2
 - 5 1 Mai Izbuc
 - 6 Felix 4003
 - 7 Felix Vila-4
 - 8 1 Mai Frederich
 - 9 Ochiul Pompei
 - 10 Cordau 402

Legend 2:

- 11 Felix 4087
- 12 Ochiul Mare
- 13 Felix 4012

Examining the hydrochemistry variation of characteristic rapport an interesting change can be F2, Izbuc, 4003, Vila 4, Frederich, 402, 4087; and finally 4012(16.34%meq/L.).

The decrease of bicarbonate ion at well 4012 compared to well 4011 is occurs with an increase of sulfate content.

It can be remarked by surveying characteristic ratio HCO_3/SO_4 that the values are greater than the unit, noticed in 1975 at Balint. (see Table 4).

Table 4: The variation of characteristic rapport of Balint geothermal source

Year	rSO_4/HCO_3	rMg/Ca
1887	1,600	0,270
1926	1,900	0,250
1951	1,000	0,270
1960	1,050	0,460
1966	1,170	0,250
1969	0,980	0,290
1975	0,411	0,270
1976	0,431	0,577
1977	0,877	0,365
1981	0,834	0,398
1983	0,646	0,298
1984	0,514	0,150
1986	0,856	1,554
1987	0,500	0,470
1990	0,670	0,330

As regarding the relation between HCO_3 and the mineralization on the Cretaceous reservoir, a systematic increase of HCO_3 can be remarked, but the curve breaks on the Triassic reservoir (see Figure 4). An exception to this are the wells 4087, 402 and 4003, where there probably is a maximum mixture. On the contrary, in the Triassic reservoir HCO_3 decreases at the same rate with the mineralization, as a result of the common ion effect.

Following the frequency of the presence of certain ions in traces along the time, we inferred that the waters of the Cretaceous reservoir could sporadically contain NO_2^- and PO_4^- . This sporadic appearance of NO_2^- and PO_4^- is very interesting and we consider it to be a contamination resulted from the spreading of agricultural fertilizers. The issue may have two aspects

First, there may be a possible pollution of the reservoir with NO_2^- and PO_4^- ions, although in their

sporadic appearances these ions are much below the limit of danger.

Second, such an investigation is very **important** for us; following the chemistry of geothermal waters in the area in question during the period of artificial fertilization, we could find the area where they mix and the contribution of infiltration waters to its general chemistry. In this case the ions NO_2^- and PO_4^- could act as tracers.

The composition in microelements, determined by emissions spectrums on TDS, and by gamma-spectroscopy by means of neutronic activation, indicates a resemblance with the waters of the Triassic reservoir. The frequency of elements such as Vanadium, Cobalt, Nickel and Manganese (see table 5) is the same as in the Triassic reservoir (see Table 2). Approximately the same frequency was also found in the case of isotope analyses.

Table 5: The concentration in microelements of the waters belonging to wells from Felix - 1 Mai area.

Well No.	V (mg/L)	Co (mg/L)	Ni (mg/L)	Mn (mg/L)
Izbuc	2.1×10^{-3}	-	2.2×10^{-3}	2.5×10^{-3}
4003	2.9×10^{-3}	4.3×10^{-3}	1.9×10^{-2}	1.4×10^{-2}
4011	1.3×10^{-3}	-	1.5×10^{-3}	4.1×10^{-3}
4012	1.1×10^{-4}	-	-	-
Bah t	9.9×10^{-4}	5.2×10^{-4}	-	5.6×10^{-3}
4087	5×10^{-4}	-	-	3.0×10^{-3}
Vila-4	8.0×10^{-4}	8.9×10^{-4}	-	6.0×10^{-3}
402	5.0×10^{-4}	-	-	3.3×10^{-3}

Table 6: The frequency of appearance of certain isotopes in the geothermal waters and rocks of the Cretaceous reservoir (qualitative)

Isotope	4003	Lime stone*
^{40}Sc	+	+
^{47}Sc	+	+
^{51}Cr	+	+
^{56}Mn	+	+
^{58}Mn	-	-

* Limestone from Zece Hotare

sotope	4003	Lime stone*
^{59}Fe	+	+
^{58}Co	-	+
^{63}Zn	-	-
^{71}Zn	-	-
^{82}Br	+	-
^{84}Sr	-	-
^{85}Sr	+	+
^{87}Sr	-	-
^{100}Ag	+	+
^{124}Sb	-	-
^{128}I	-	-
^{132}Cs	-	+
^{134}Cs	+	-
^{131}Ba	+	-
^{137}Ba	-	+
^{140}La	+	-
^{142}La	-	-
^{148}Pm	-	+
^{152}Eu	+	-
^{156}Eu	-	+
^{181}Hf	+	+
^{188}Hf	-	-
^{190}Ir	+	+
^{191}Pt	-	-
^{199}Pt	-	-
^{196}Au	-	-
^{198}Au	-	-
^{206}Bi	+	+
^{238}Np	-	-

The microelements that are present in geothermal water were identified on TDS by Gamma-spectroscopy Technique and Neutronic Activation Techniques and are indicating a resemblance between the Triassic aquifer and Cretaceous aquifer

Conclusions

We consider that this study of the distribution of microelement isotopes in geothermal waters is very important and it should be enlarged on.

As a matter of fact, this investigation was aimed not only to improve the study on the chemistry of the geothermal waters, but also to have in view the ratio of Strontium isotopes as a possible tracer for the path of underground waters in the area. Still, the small number of determinations didn't allow us an approach from this point of view. We succeeded to establish the methodology of research and also to elaborate the first data regarding the isotopic composition of some geothermal waters and rocks from cores extracted from well 4768 as well as for rocks collected from Padurea Craiului Mountains. Chemical and isotopic

analyses might be done both in waters and in rocks in order to get a clear idea on the forming mechanism of the chemistry of geothermal waters.

The Triassic, and Cretaceous aquifers, although separated, are hydrochemically related, constituting a unitary hydrothermal system.

The modifications of their chemistry support the geophysical research in this direction.

We consider this study as an incipient phase, unfortunately the lack of financial and technical means stopped the research and many aspects are not explored yet.

We would also like to draw the attention on the differences in the hydrochemistry, which we consider a signal for those using these waters, as these waters could be profitably exploited for a long time provided a careful analysis is done in due time

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