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# AN UNUSUAL CASE OF LOW CONCENTRATION MINERAL BRINES IN THE GEOTHERMAL WATERS FROM BEIUȘ BASIN (NORTHWESTERN ROMANIA)

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## Abstract

*The aim of the BrineRIS project is to explore brines in RIS countries potential for critical metal extraction In the frame of this project the concentration of mineral brines in three geothermal wells located in the Beiuș Basin (northwestern Romania) was determined by analyzing the water from the wells. Until recently no reliable trace element data were available from Beiuș basin. Following the new analyses, the geothermal water extracted by TRANSGEX SA company from wells F-3001H, F-3003H, and F-3005H revealed exceptionally low concentrations of associated chemical compounds. The Li-concentration is only ~ 22 – 32 µg/l. Zn, I, Rb and As present in similar concentrations, while other trace elements (e.g. Co, V, Ti) are below detection limit. The Sr (~ 540 – 680 µg/l), Ba (~ 170 – 200 µg/l) and B (~ 70 – 100 µg/l) concentrations are slightly elevated, but still low. Therefore, the water in this "geothermal reservoir" can be classified as relatively potable, but it is not appropriate for critical metal extraction. In this paper, some documented concentrations from previous years have been compared to recent concentrations. In addition, the relationship between geology and water chemistry is emphasized in order to determine the reason for the absence of solutes that were expected to be found in this water.*

**Keywords:** *geothermal brines, mineral concentrations, Beiuș Basin, Romania*

## 1. Introduction

Europe's extractive industry is more recently focusing on 'green mining', looking at various alternatives for recovering useful minerals. This is thanks to new European anti-pollution regulations, which also focuses on finding solutions that make mining less polluting than in the past. One of the feasible solutions to this challenge has become the exploitation of metals from geothermal brine. The brines can bring various chemical elements directly from the earth to the surface, which are useful for maintaining production in various European industries, and particularly for technological development. Of course, most of the studies are focusing on lithium recovery, which is a strategic material today, but also on other rare elements such as Sr, Sc, Ta, V.

Generally, the chemistry of the various brines is the product of water – rock interaction processes, thus in geological environments where brines is related with trace metal rich formations, high concentration of these metals in the brines are expected. For example, if Li is the target element, brines associated with Li-rich rock types, like rare-metal granites, granitic pegmatites and greisens have the highest potential (Gautneb et al., 2021; Gourcerol et al., 2019).

Sanjuan et al. (2016) identified only six geothermal areas is Europe with lithium concentrations higher, than 150 mg/l (125 to 480 mg/l), in Germany, Italy, France and the United Kingdom. Most of these reservoirs (except the UK one) has high temperature (> 120°C) and high salinity (TDS > 56 g/l), with high Na and Cl concentrations.

Based on their results they distinguish three types of Li-rich geothermal systems: (1) Ultra-high temperature (>350 °C), (2) low to medium temperature (120-250 °C), (3) very low temperature (<100°C) geothermal systems. A low temperature geothermal system with high Li-potential occurs only in South Crofty mine well, Cornwall, UK only (Edmunds et al., 1985). From the geothermal areas mentioned above the Upper Rhine graben is the most promising one, where the main source of the Li is the Li-mica dissolution from the Triassic Buntsandstein, a micaceous continental sandstone, although alteration of granite probably elevates the Li-content as well.

Many other brines containing Li are described in the literature, with lower concentrations. However, as the technology is getting developed, more and more brines will be economically extractable. Geothermal wells in general have a potential to have elevated content of Li, mainly if they are rich in Na and Cl. According to Sanjeev (2023), 364 geothermal heat plants and 140 geothermal plants are operating in Europe, while further 300 power and heat plant are under development. All these plants are potential Li-sources. Some examples are the Vicano–Cimino Volcanic District and Sabatini Volcanic District (Central Italy), where brines originated from the mixing of two different type of water. (Cinti et al., 2014; 2017). Oil field brines often contain significant concentrations (up to 20 mg/l) of Li, as in the case of the Eastern oil and gas region, Ukraine (Reva et al., 2021), as well as in the Paris basin, France (up to 3 mg/l) (Fontes and Matray, 1993) and the North German Basin (Lüders et al., 2006). High Li-concentrations could also be detected in brines connected to anhydrite-bearing salt deposits, e.g. the Gorleben and Morsleben salt structures, northern Germany (Mertineit and Schramm, 2019). Li-rich geothermal systems occur in the Larderello geothermal system, Italy, where the high concentration is the result of interaction between magmatic and contact metamorphic fluids (Cathelineau et al., 1994). It is also possible that surface and groundwaters connected to hard-rock Li-deposits have slightly elevated Li-concentrations, as in the case of the Cinovec deposit (Toupal et al., 2022), Southeastern Ireland spodumene deposit (Kavanagh et al., 2017) and the Gonçalo spodumene mine in Portugal (Rodrigues et al., 2019). Maximum Li-concentration at these sites occasionally can reach 70-100 µg/l, although the average is significantly lower (around 20 µg/l). High Li-content was measured in Hungarian groundwaters as a result of granite alteration (Jancsek et al., 2023).

Based on our previous knowledge, Beius area are characterized with the occurrence of thermal karst water. The composition of this type of water is mainly the result of the dissolution of calcite, dolomite, and gypsum. Environmental conditions (rainfall, temperature, soil carbon dioxide) are also important, as they determine the rate of dissolution (White, 2015). Karst waters usually contain low amount of trace elements, although the organic matter and some accessory minerals can serve as sources of these. Some elements may be enriched in special cases: Ba often presents due to the dissolution of barite, U and Mo are connected to minor sulphide mineralisations in dolomites, Sr and Li to evaporitic layers, V to organic matter (Kilchmann et al., 2004). Marton (2013) thought, that relatively high trace elements contents in karst waters might occur due to plate tectonic movements, and these elements originate from high depths through fracture systems.

Nowadays several projects aim to explore brines with high metal (especially Li) recovery potential, including BrineRIS project. One of the main objectives of this project is to identify new potential sources in the RIS countries rich in trace metals. To achieve this aim, the overview of already existing brine geochemistry data and the collection and analyses of new brine samples are also important. Thus, in order to determine the potential in brines that can be exploited, an attempt has also been made in Romania, specifically in the Beiuș Basin (Bihor County). However, karstic waters rich in trace metal are relatively rare, but as these waters are believed to be related with the overlying magmatic intrusions, thus they are promising targets from the point of view of the project. The importance of the results of the new water chemical analyses are further highlighted by the fact, that it is the first time, when reliable trace element data are reported in the literature for these brines.

Since the 1960s, a number of deep boreholes for the exploration and exploitation of geothermal waters in northwestern Romania have been drilled. Some of them are now administrated by *TRANSGEX S.A.* and are continuously or intermittently operated or used as injection wells. Four of these wells are situated in the Beiuș Basin: F-3001H, F-3003H, F-3005H, and F-3004I. The F-3001H well will have been in continuous operation for 20 years in 2024. F-3003H and F-3005H have been operational since 2010 and 2022, respectively. Since 2011, the wells have extracted an average of 16 l/s from the reservoir, which has increased to more than 43 l/s in 2023.

## 2. Geological setting

Situated between the Pădurea Craiului Mountains to the north, the Codru-Moma Mountains to the south (Mutihac, 1990), and the Bihor Mountains to the east and southeast, the Beiuș Basin is an intramontane (Figure 1), post-tectonic basin dominated by a hilly, stepped plain relief (Badea et al., 1976). The depressional appearance of this basin is rather the result of the erosion of the Crișul Negru River and its tributaries, which flow from the central part of the Western Romanian Carpathians towards their north-western edge, implicitly from the margins of the slopes outlining the basin.

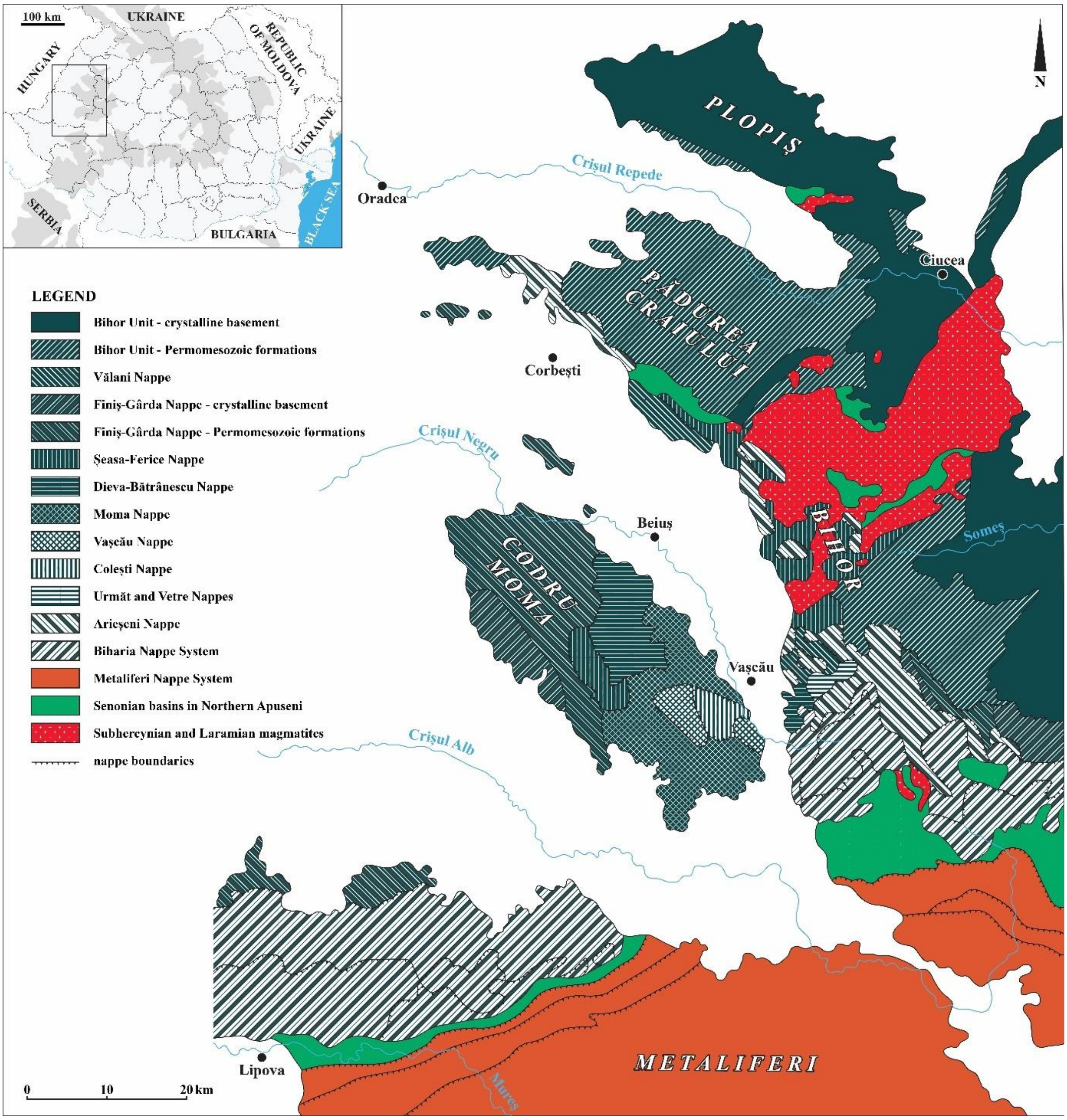

***Figure 1.*** *Simplified tectonic sketch of the western part of Apuseni Mountains (modified after Bleahu et al., 1994) and its location within Romania, showcasing the Beiuș Basin alongside Crișul Negru River*

The sedimentary evolution of the Beiuș Basin began during the Badenian period (Paucă, 1936; Ianovici et al., 1976), and persisted throughout the Sarmatian *s.s.* and Pannonian *s.s.* The Badenian is characterized by a lower torrential-detritic complex, which is succeeded by a higher organic complex consisting of algal and coralline limestone (Paucă, 1936; Dinu et al., 1991). The Sarmatian is characterized by a transgressive event, which is documented only by the presence of Volhynian. This event is observed through the presence of a diatomic complex at the base, as described by Orășanu (2015). The subsequent sedimentary sequence consists of detritic and calcareous littoral sediments, followed by neritic sediments containing clay marl and fine-grained sand alternating with pelitic beds, as reported by Dinu et al. (1991). The Pannonian exhibits significant development over the basin, including a range of clastic sediments such as clay, marl, silt, sand, and gravel (Dinu et al., 1991). The process of the subsidence that is now observable inside the Beiuș Basin occurred throughout the Quaternary. This latter stage completes the sedimentary succession with deluvial and alluvial deposits located mostly along the Crișul Negru River.

The basement of the basin comprises a diverse assemblage of Mesozoic, Paleozoic, and Proterozoic rocks that are associated with the Alpine tectonic units (Dinu et al., 1991). The tectonic history of the area is a complex and prolonged process, characterized by many phases that ultimately resulted in the formation of a series of overlapping and closely situated subsided tectonic nappes. Hence, it can be said with certainty that the current location is inside the Codru Belt System, as stated by Bleahu et al. (1994).

Based on the internal drilling data from *TRANSGEX SA*, it can be concluded that in the region of the boreholes is situated in an area characterized by sunken blocks. This area is highly probable to be associated with the Finiș-Gârda Nappe, or potentially a compartment of the Dieva-Bătrânescu Nappe. Furthermore, these nappes are positioned directly over the Bihor Autochthonous Unit, as depicted in Figure 1. The drill logs show Permo-Werfenian quartzite sandstone, grey and black dolomite in the Lower Triassic, red argillite series in the Upper Triassic, and a combination of micritic limestone and black argillite in the Jurassic. The ”geothermal reservoir” is comprised of Triassic dolomite, which may be found at varying depths in F-3001H (1850-2480 m), F-3003H (1580-2280 m), and F-3005H (1891-2726 m) as seen in Figure 2. Additional information on the geology and tectonics of the basin may be found in the works of Dinu et al. (1991) and Orășeanu (2015).

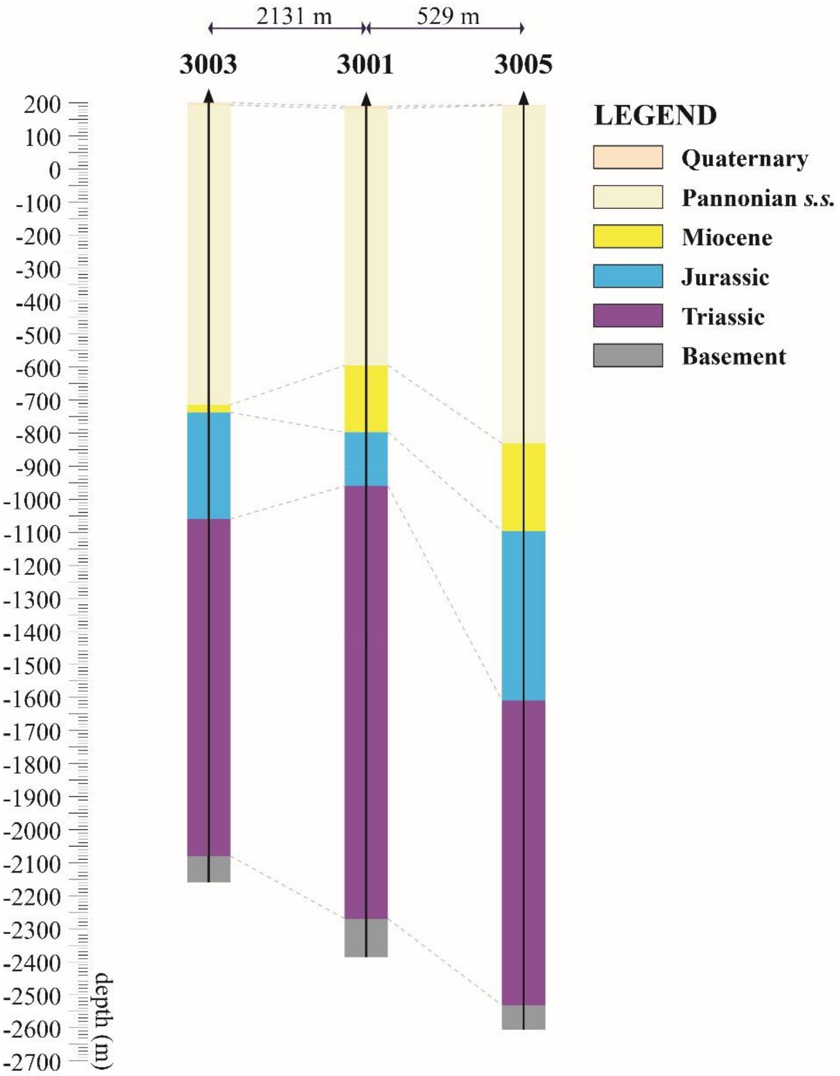

***Figure 2.*** *Well data showcasing the depth of the crosscut chronostratigraphic units*

## 3. Sampling and analyses

Two sample sets were taken from each of the wells F-3001H, F-3003H, F-3005H (Figure 3). A set of samples was composed of three subsamples with volumes of 0.5 dl for one and 1 for two. The samples were taken and stored in plastic bottles. For the measurements of rare earth elements, the samples were kept in a 0.5 dl bottle, after filtration and acidification (to ensure the preservation of the water). The two 1 l samples were taken without filtration. One of them was measured for general water chemistry, the other for $NH_4$ and COI. This second one was also preserved with acidification. During the sampling, some field measurements were also carried out as summarized in Table 1.

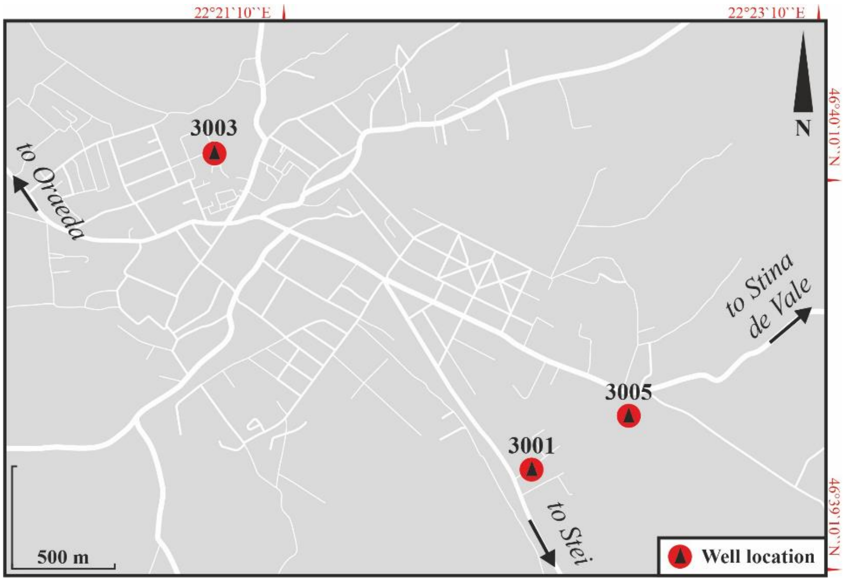

***Figure 3.*** *Simplified map of Beiuș Municipality showing the location of F-3001H, F-3003H and F-3005H wells.*

The chemical analyses of the samples were carried out by two independent laboratories. *Laboratory of Mecsekérc Ltd.* made the trace element measurements according to MSZ-EN-ISO standards, with the application of inductively coupled plasma mass spectrometry. They also measured some physical parameters, such as *pH* and conductivity. At the *Institute of Water Resources and Environmental Management* at the *University of Miskolc (hereinafter shortened IWREM-UM)*, macro and trace elements were measured with an Agilent 4210 type MP-AE spectrophotometer, while the sulphate, nitrite, ammonium, and phosphate were determined using a HACH DR3900 spectrometer. Carbonate and hydrogen carbonate were analyzed according to MSZ 448/11-86, and the chloride ion according to the MSZ 448/15-82 standard. Usually, the detection limits of *Mecsekérc Ltd.* are lower. The two laboratories provide similar results, with unsignificant differences, however, in case of Ca, *Mecsekérc Ltd.* measured twice as high concentration as *IWREM-UM* (45-52 mg/l compared to 20-22 mg/l).

***Table 1.*** *Physical – chemical parameters of brines measured in the field*

| | **unit** | **F-3001H** | **F-3003H** | **F-3005H** |
|---|---|---|---|---|
| ***pH*** | - | 8 | 8.25 | 7.81 |
| **conductivity** | µS/cm | 516 | 465 | 508 |
| **dissolved $O_2$** | $O_2$mg/l | 5.84 | 6.18 | 4.58 |
| **Eh** | mV | 171.8 | 59.4 | 100.7 |
| **T** | °C | 33.8 | 39.1 | 29.6 |
| **$O_2$ saturation** | % | 81.7 | 95.1 | 60.8 |

## 4. Results

### 4.1. Parameters of the Beiuș brines

The chemical data obtained by the two different laboratories are summarized in Table 2 and Table 3. The water of all three wells has nearly neutral *pH*, relatively low total dissolved solid (TDS) content, 45-52 mg/l and 20-22 mg/l Ca content (according to *Mecsekérc Ltd.* and *IWREM-UM* respectively), 19-25 and 14-16 mg/l Mg, 39-60 and 25-35 mg/l sulphate, 238-268 and 244-268 mg/l $HCO_3$, 4,5-6 and 4,4-5 mg/l K, 10-18 and 4,4-12 mg/l Na. These concentrations indicate Mg-bicarbonate type water on the piper plot (Figure 4, note that data on the piper plot are represented in meq/l, rather than mg/l). Older data from 2009, 2010 and 2011 also show the same chemical character, as well as data from 1999 reported by Orăşeanu (2015). This water type is typical for Ca-Mg rich karst waters worldwide (e.g., Chao et al., 2017; Jebreen et al., 2018; Kovács and Szőcs, 2016; Lucon et al., 2018), as well as for karst springs in the Romanian Apuseni Mts. and Southern Carpathians (Hoaghia et al., 2021; Török et al., 2023). The chemical similarity for karst waters is not surprising as the main reservoir rock of the Beiuș wells is dolomite. Trace element concentrations are usually low. For most of the elements the maximum is around 10 µg/l (e.g. 20-30 µg/l Li, 3-4 µg/l Sc, 10-60 µg/l Zn), thus they are often below detection limit (e.g. Be, rare earth elements, Co, Cu, Pb, Zn, Mo, Ti, V, Zr). Trace elements occurring in relatively higher concentrations are B (60-100 µg/l), Ba (170-210 µg/l) and Sr (~0.5-0.8 mg/l, with slightly higher values indicated by the *IWREM-UM* laboratory). Although these trace element concentrations are relatively low, they are higher than average trace element concentrations in Romanian karstic waters, where Ba, Mn and Li concentrations are usually less than 50, 3 and 5 µg/l (however maximum values can reach 760, 128 and 68 µg/l, respectively). Higher values were measured in the Apuseni Mts. than in the Southern Carpathians (Török et al., 2023). Although too few data are available to make reliable correlation analyses, it seems that Ba correlates well with Ca, $HCO_3^-$, Fe and Mn; and Sr with $SO_4^{2-}$, Cl, Na, K, Li, Cs, Rb, Sc.

Low metal concentrations do not make it economically viable to extract them from these brines. According to Sanjuan et al. (2022), mainly hot brines (>120°C) with high TDS (>56 g/l), high Na and Cl concentrations (>18 and >25 g/l, respectively) are capable to contain significant concentration of Li. Li-rich brines have usually Na-chloride type character on the piper plot, also proved by Hungarian groundwater data collected in the frame of the BrineRis project (Németh et al., 2023). Although originally as high Li contents as >150 mg/l was recommended as the limit of economic extractability (Sanjuan et al., 2022), nowadays the more and more advanced techniques make it possible to recover Li even from brines with as small concentration as 10-20 mg/l (Annunzi et al., 2023), although even this value is much higher than those of the Beiuș water.

Beiuș area was examined also in the frame of the CHPM2023 project taking into consideration its combined heat, power, and metal extraction potential. Dominguez et al. (2018) report two brine composition from the area. One of these previous samples were characterized with 12 mg/l Sr, 129 µg/l Li, 40 µg/l Mn, 32 µg/l Ba (the other sample has lower values). This Mn concentration is comparable to the result of the new analysis, the Ba is slightly lower, while Sr and Li are higher. However, Li concentration is low, Perșa et al. (2019) considered metal concentrations – especially the Sr concentration – as promising from the point of view of metal extraction. Unfortunately, in this report there is no information about the exact place of origin of the analyzed samples.

Of course, the phenomenon, that thermal waters are poor in trace elements is not unique. It is usually the consequence of the lack of formations rich in trace elements, or the low capability of waters to dissolve these elements. In Hungary relatively hot waters (~ 80 °C) with low Li-concentrations were reported with $HCO_3$ character and paleometeoric origin (Fekete et al., 2009; Varsányi and Ó. Kovács, 2009). In the Mura basin, Slovenia, Na-$HCO_3$ type medium temperature thermal waters with low trace elements concentration, except the slightly elevated (100 – 200 µg/l) B, Ba and Sr occurs in the vicinity of trace element rich waters. Here the authors explain the difference with the present of dissolved $CO_2$, which makes the dissolution and complexation of trace metals more effective (Kralj, 2004).

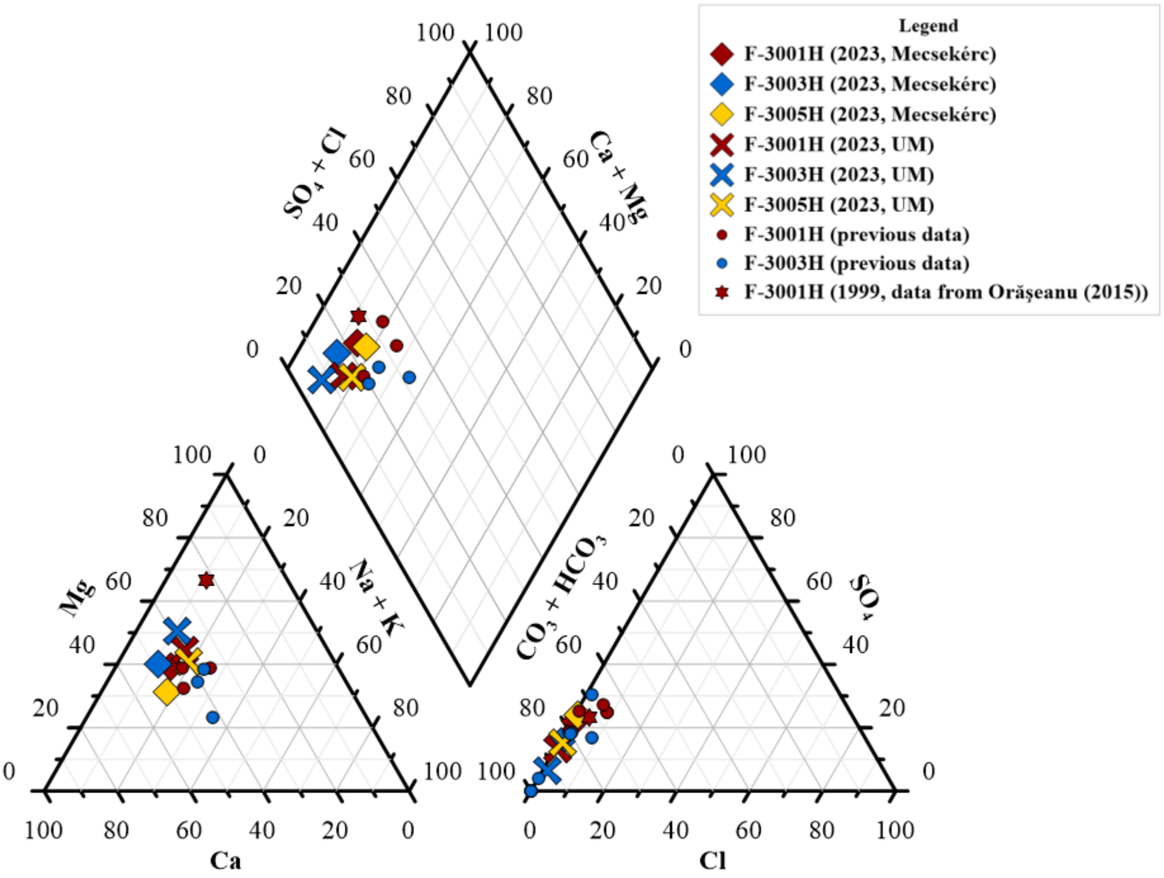

***Figure 4.*** *Piper plot representing the chemical composition of the Beiuş brine samples, based on the new analysis of Mecsekérc Ltd. and IWREM-UM, on some previous internal data from TRANSGEX SA (for the years 2009, 2010 and 2011), and on data published by Orăşeanu (2015) from 1999.*

***Table 2.*** *Physical – chemical parameters of the brines measured by the laboratory of Mecsekérc Ltd. Some of the results are below detection limit (marked with "<"). The laboratory is not accredited to measure parameters marked with **

| | **unit** | **F-3001H** | **F-3003H** | **F-3005H** | | **unit** | **F-3001H** | **F-3003H** | **F-3005H** |
|---|---|---|---|---|---|---|---|---|---|
| ***pH*** | - | 6.8 | 7.1 | 7.4 | **As** | µg/dm$^3$ | 7.41 | 6.48 | 6.5 |
| **conductivity (25°C)** | µS/cm | 468 | 459 | 479 | **Be** | | <0.2 | <0.2 | <0.2 |
| **TDS** | | 315 | 315 | 330 | **Bi** | | <0.1 | <0.1 | <0.1 |

| | **unit** | **F-3001H** | **F-3003H** | **F-3005H** | | **unit** | **F-3001H** | **F-3003H** | **F-3005H** |
|---|---|---|---|---|---|---|---|---|---|
| **KOI PS** | mg/ dm$^3$ | 1.22 | 1.37 | 1.31 | **Cd** | | 0.14 | 0.11 | 0.1 |
| **Ca** | | 45.2 | 49.2 | 52 | **Ce*** | | <0.1 | <0.1 | <0.1 |
| **Mg** | | 23.7 | 24.7 | 19.4 | **Cs** | | 1.89 | 1.4 | 1.97 |
| **alkalinity** | mmol/ dm$^3$ | 3.9 | 4.4 | 3.9 | **Dy*** | | <0.1 | <0.1 | <0.1 |
| **$HCO_3$** | mg/ dm$^3$ | 238 | 268 | 238 | **Er*** | | <0.1 | <0.1 | <0.1 |
| **$CO_3$** | | <3 | <3 | <3 | **Eu*** | | <0.1 | <0.1 | <0.1 |
| **total hardness** | CaO mg/ dm$^3$ | 119 | 126 | 118 | **Gd*** | | <0.1 | <0.1 | <0.1 |
| **$CO_3$ hardness** | | 109 | 123 | 109 | **Hg** | | <0.1 | <0.1 | <0.1 |
| **$SO_4^{2-}$** | mg/ dm$^3$ | 54 | 39 | 60 | **Ho*** | | <0.1 | <0.1 | <0.1 |
| **$NO_3^-$** | | <0.1 | <0.1 | <0.1 | **La** | | <0.05 | <0.05 | <0.05 |
| **$NO_2^-$** | | <0.1 | <0.1 | <0.1 | **Lu*** | | <0.1 | <0.1 | <0.1 |
| **$NH_4^+$** | | <0.03 | 0.04 | <0.03 | **Nd*** | | <0.1 | <0.1 | <0.1 |
| **$Cl^-$** | | 2 | 1 | 2 | **Pb** | | 0.1 | <0.1 | <0.1 |
| **$F^-$** | | 0.82 | 0.58 | 0.72 | **Pd** | | <0.05 | <0.05 | <0.05 |
| **$PO_4^{2-}$** | | 0.03 | <0.03 | <0.03 | **Pr*** | | <0.1 | <0.1 | <0.1 |
| **Ag** | µg/ dm$^3$ | <2 | <2 | <2 | **Pt** | | <0.05 | <0.05 | <0.05 |
| **Al** | mg/ dm$^3$ | 0.023 | 0.013 | <0.01 | **Rb** | | 12.7 | 9.88 | 12.7 |
| **B** | µg/ dm$^3$ | 104 | 66.2 | 83.7 | **Rh** | | <0.06 | <0.06 | <0.06 |
| **Ba** | | 172 | 211 | 201 | **Sb** | | <0.15 | <0.15 | <0.15 |
| **Co** | | <5 | <5 | <5 | **Sc*** | | 3.92 | 3.22 | 3.88 |
| **Cr** | | <5 | <5 | <5 | **Se** | | 0.13 | 1.39 | <0.1 |
| **Cu** | | <5 | <5 | <5 | **Sm*** | | <0.1 | <0.1 | <0.1 |
| **Fe** | mg/ dm$^3$ | 0.091 | 0.333 | 0.045 | **Sn** | | 1.13 | 0.7 | <0.3 |
| **K** | mg/ dm$^3$ | 5.85 | 4.5 | 5.94 | **Tb*** | | <0.1 | <0.1 | <0.1 |
| **Li** | µg/ dm$^3$ | 28.2 | 21.9 | 31.6 | **Te** | | <0.1 | <0.1 | <0.1 |
| **Mn** | | 0.009 | 0.015 | 0.035 | **Th** | | <0.2 | <0.2 | <0.2 |
| **Mo** | | <5 | <5 | <5 | **Tl** | | 0.37 | <0.05 | <0.05 |
| **Na** | mg/ dm$^3$ | 13.5 | 10.5 | 17.9 | **Tm*** | | <0.1 | <0.1 | <0.1 |
| **Ni** | µg/ dm$^3$ | 6.2 | <5 | <5 | **U** | | 0.06 | 52.7 | 0.15 |
| **P** | | <500 | <5 | <5 | **W** | | <0.5 | <0.5 | 0.64 |
| **Si** | mg/ dm$^3$ | 19.8 | 15.4 | 20.4 | **Y** | | <0.2 | <0.2 | <0.2 |
| **Sr** | µg/ dm$^3$ | 619 | 537 | 678 | **Yb*** | | <0.1 | <0.1 | <0.1 |
| **Ti** | | <5 | <5 | <5 | **Zr** | | <0.7 | <0.7 | <0.7 |
| **V** | | <10 | <10 | <10 | **I*** | | 14.9 | 16.9 | 12.4 |
| **Zn** | | 48.6 | 61.9 | 14.4 | | | | | |

***Table 3.*** *Chemical parameters of brines measured by the laboratory from IWREM-UM. All the concentrations are given in mg/l. Some of the results are below detection limit (marked with "<")*

| | **F-3001H** | **F-3003H** | **F-3005H** | | **F-3001H** | **F-3003H** | **F-3005H** |
|---|---|---|---|---|---|---|---|
| **Ag** | 0.6 | 0.6 | 0.3 | **Mn** | <0.1 | 2 | 0.1 |
| **Al** | 4.8 | 4.4 | 4.9 | **Mo** | <0.1 | <0.1 | <0.1 |
| **B** | <0.1 | <0.1 | <0.1 | **Na** | 9.7 | 4.4 | 12.4 |
| **Ba** | 0.2 | 0.2 | 0.3 | **Ni** | <0.1 | <0.1 | <0.1 |
| **Be** | <0.1 | <0.1 | <0.1 | **Sc** | <0.1 | <0.1 | <0.1 |
| **Ca** | 21.9 | 20.5 | 22.2 | **Si** | 16 | 12.6 | 16.3 |
| **Cd** | <0.1 | <0.1 | <0.1 | **Sr** | 0.7 | 0.6 | 0.8 |
| **Co** | <0.1 | <0.1 | <0.1 | **Ti** | <0.1 | <0.1 | <0.1 |
| **Cr** | <0.1 | <0.1 | <0.1 | **V** | <0.1 | <0.1 | <0.1 |
| **Cu** | <0.1 | 0.1 | 0.1 | **Y** | <0.1 | <0.1 | <0.1 |
| **Dy** | <0.1 | <0.1 | <0.1 | **Yb** | <0.1 | <0.1 | <0.1 |
| **Er** | <0.1 | <0.1 | <0.1 | **Zn** | 0.6 | 3.1 | 0.2 |
| **Eu** | <0.1 | <0.1 | <0.1 | **Zr** | <0.1 | <0.1 | <0.1 |
| **Fe** | <0.1 | 0.2 | <0.1 | **$NH_4^+$** | 0.12 | 0.14 | 0.15 |
| **Ho** | <0.1 | <0.1 | <0.1 | **$HCO_3$** | 250.1 | 268.4 | 244 |
| **K** | 4.8 | 4.4 | 4.9 | **$Cl^-$** | 1.5 | 2 | 2 |
| **La** | <0.1 | <0.1 | <0.1 | **$SO_4^{2-}$** | 30 | 15 | 35 |
| **Li** | <0.1 | <0.1 | <0.1 | **$NO_3^-$** | 6.6 | 4.8 | 6.2 |
| **Lu** | <0.1 | <0.1 | <0.1 | **$NO_2^-$** | 0.01 | 0.007 | 0.01 |
| **Mg** | 15 | 16.5 | 13.8 | **$PO_4^{3-}$** | 0.2 | 0.1 | 0.3 |

## 4.2. Changes of concentrations over time

In case of F-3001H and F-3003H wells some older physical and chemical data (without trace elements) are also available in the database of TRANSGEX SA Company, from years 2008, 2009, 2010, 2011, 2013 and 2018 (Na and K concentrations are available only from 2009, 2010 and 2011), furthermore from 1999 for the F-3001H well (Orăşeanu, 2015). Data from Orăşeanu (2015) show extraordinarily high Mg and low Ca concentrations compared to the newer ones, but probably the values are erroneously exchanged in this publication.

Major ion concentrations are represented as a function of time on Figure 5. As there is no information about the intervening years, lines on the graph do not represent real data. As the sampling during the years was not systematic and the conditions of sampling and analyses are not known, the data are not considered to be real time series.

Based on the figure it is obvious, that the two wells are characterized with different chemical trends, however, there are common features, such as relatively higher measured $SO_4^{2-}$ values in 2009 or $Cl^-$ maximums in 2011 and 2018. The differences in the compositions highlight the fact that the two wells cannot be completely characterized by the same lithology since they are situated relatively far from each other (Figure 3). Based on the lithological information the two wells are separated from each other at least by a normal fault, with NE-SW direction. In case of well F-3001H Cl- correlates with $SO_4^{2-}$, $K^+$ with $Mg^{2+}$, furthermore $Na^+$ with Ca+. In case of well F-3003H Ca+ correlates with Cl-, SO42- with Na+ and Ca+.

Generally, the most significant concentration changes are connected to $SO_4^{2-}$, (values between 42 – 70 mg/l in F-3001H and 8 –88 mg/l in F-3003H, respectively) and $Ca^{2+}$ (between 26.8 – 62 mg/l and 28 – 56 mg/l). In case of F-3001H, deviations of $Na^+$ (values between 11.1 – 33.6 mg/l), and $Mg^{2+}$ (20 – 48.1 mg/l are significant, furthermore F-3003H is characterized with an extraordinary high Fe value in 2013 (3.2 mg/l, compared to the usual 0.2 mg/l). Changes can occur due to the effect of mixing with meteoric or magmatic fluid, but sampling parameters (season, depth), the rate of outflow, or the method of analyses can also have an effect on the results although unfortunately, there is no information about these parameters. The results of the new analysis (year 2023) are near to the average.

Although trace element data are not known from the previous years, Pearson correlation relationships between the chemical compounds of the three different wells suggest that their concentration changes are partly connected to the major ion concentrations. Generally, with regard to the main elements, it makes no sense to talk about a systematic change in the composition of brine over time. Of course, this does not exclude the possibility that the concentration of certain trace elements will decrease over time, as the reservoir rock depleted. However, it is more likely that these brines had never really high trace metal contents, as there are no significant (and constant) changes in their major ion composition since the previous 15 – 20 years, that in the case of the thermal waters of the western Hungarian basin, where new aquifer layers have increasing influence on chemistry as the production continues (Szalkai & Kovács, 2016). Furthermore, the newly drilled F-3005H well also yield brine with similarly poor trace element concentration.

Although concentration values of Li (129 μg/l), Sr (12040 μg/l), and Fe (2.3 mg/l measured by Dominguez et al. (2018) in a brine sample from Beius basin are significantly higher than any of the new samples indicate, it does not prove that the trace metal concentration of the brines are depleted with time, as other elements were detected in lower (e.g. Ba (32 μg/l), Zn (1.5 μg/l)), or similar (e.g. Mn, Rb, As) concentration, compared to the new data. On the other hand, it is probable that the trace element as well as the major ion concentrations are not constant over time.

## 4.3 Relationship between brine chemistry and lithology

The composition of the brines is usually the result of water-rock interaction processes. Persa et al. (2019) collected samples from the same extraction wells described in this study, from neighboring springs and mine waters, and examined them after evaporation by scanning electron microscopy, FTIR and X-ray powder diffraction. They detected the presence of aragonite, brucite, dolomite, clay minerals, and amorphous hydrated silica, as well as bassanite, hydroboracite, nitrocalcite, epsomite and halite. The results suggested that Mg-bearing minerals precipitate more likely from these geothermal brines originated from the dolomite dominant reservoir, when compared to other spring and mine waters. Slightly elevated Sr-concentration is also developed due to the abundant carbonate minerals of the well reservoir, as proposed also by Török et al. (2023) in the case of the Romanian karst springs. Although probably there should be some mineralization beneath the Beiuș Basin (Perșa et al., 2019), low trace element concentrations indicate that there is no interaction with the examined wells, and the supply of the wells cannot come from the formations rich in trace metals.

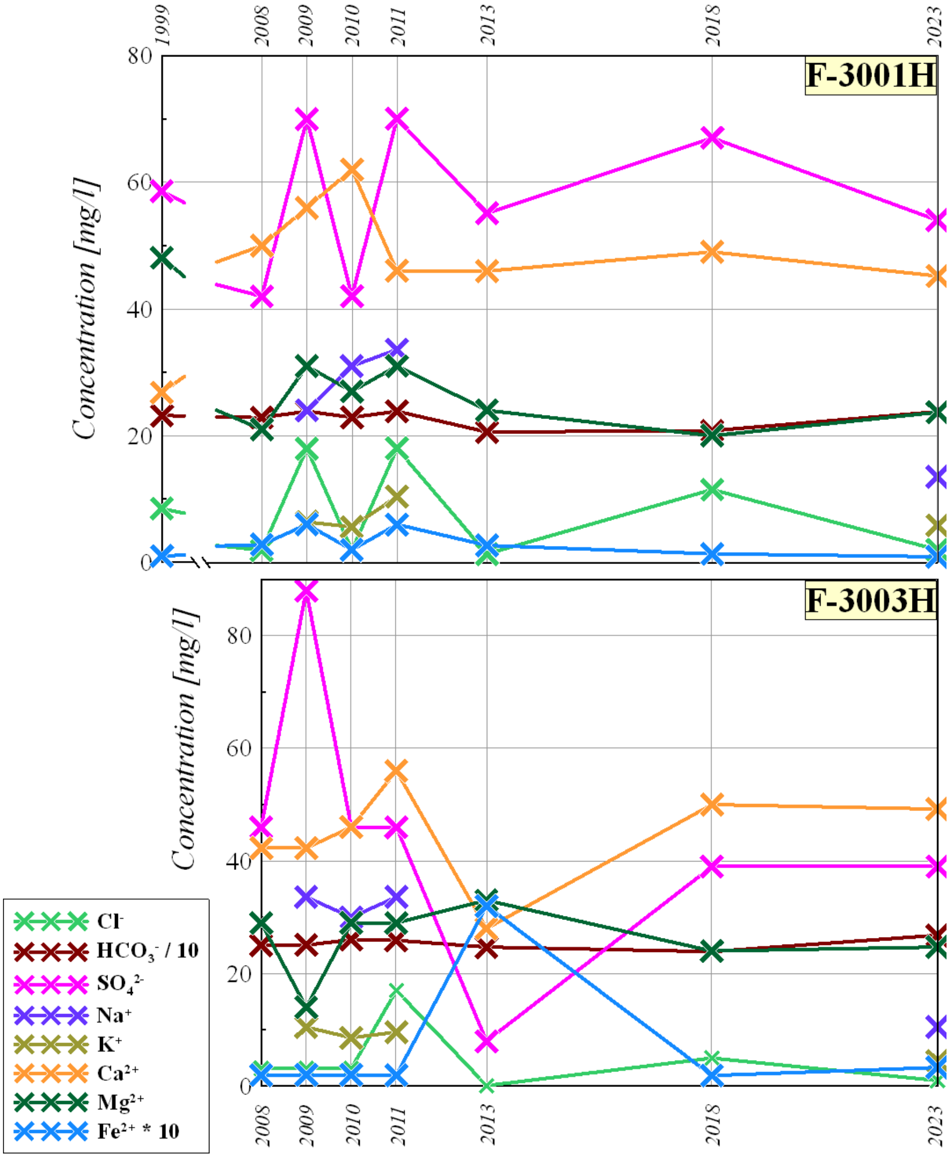

***Figure 5.*** *Major ion concentrations are as a function of time in wells F-3001H (above) and F-3003H (belove). For the representation of year 2023, the data provided by Mecsekérc Ltd. are used. The lines do not represent real trends. The concentration of* $HCO_3^-$ *is divided by 10, while the concentration of Fe is multiplied by 10, to make them representable in the same scale than the other chemical compounds.*

## 5. Summary

Water samples were collected from three wells, from Beiuș basin, to check their potential for metal extraction. The waters proved to be Mg-bicarbonate type, which refers to their relationship with the reservoir carbonates. All samples are depleted in trace elements, except Sr content which is slightly elevated. According to measurements from previous years major ion concentrations are not constant with time; however, the changes are not systematic. Trace element data are lacking from the previous databases, making it impossible to draw conclusions about the change of trace elements over time. Although the presented results indicate that the brines are not related to any mineralized basement (or at least their physical-chemical parameters do not enable to dissolve the trace metals), it cannot be excluded that at the time of the starting of operation the wells yielded water with higher trace element concentrations, and later become depleted. A counter argument for this assumption that the recently drilled well F-3005H also yields trace element depleted water and all the samples show different major ion chemistry and lower temperature than metal rich brines usually have.

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