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HYDROGEOCHEMISTRY OF MINERAL WATERS FROM THE EASTERN CARPATHIANS – TRANSYLVANIAN BASIN BOUNDARY

- Extended abstract of the PhD Thesis -

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The **"DOCTORAL STUDIES FOR EUROPEAN PERFORMANCES IN RESEARCH INOVATION (CUANTUMDOC)"** project POSDRU/107/1.5/S/79407, is a strategic project which has as general objective „*The implementation of the managerial, research and educational strategies for the improvement of the initial training of the future researchers through doctoral studies program, according to the Bologna process, by the development of the research specific proficiency, but also of some other common outcomes: research management, linguistic and communication skills, scientific documentation, elaboration, publication and scientific communication, modern ITC equipment utilisation, entrepreneurship transfer of the research results. The human capital development for research and inovation will contribute to long-term doctoral training at European Union level with interdisciplinary concern. The PhD students financial support will provide their participation to national doctoral programs, as well as the research internship in European Union universities and research institutes. The project main objective is the training of a young researcher adapted to the new economic and technological environment having theoretical, practical, economic and managerial knowledge, which will be able to promote the sustainable development and the environmental protection principles.* "

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Key-words:
Springs, stable isotope, geochemistry, noble gases, Eastern Carpathians, Transylvanian Basin

Contents

1. Introduction

The Eastern Carpathians besides its splendid landscapes hosts valuable natural resources, among which ‘water’ may be considered one of the most important. Due to several processes from the geological past that gave birth to the Carpathian chain and its surrounding, the infiltrated water passes through a large variety of rocks, becomes enriched in dissolved constituents and associated gases. This is the history in a nutshell of the mineral waters from the Eastern Carpathians, used for bottling and for their therapeutical value since historical times.

The presence of mineral waters used to have a strong impact on the social, economic and cultural life of Transylvania.

On a worldwide scale, the consumption of bottled mineral water, as a preferable alternative to tap water, has constantly expanded, especially during the last two decades (Birke et al., 2010; Fügedi et al., 2010; Dinelli et al., 2012). The scientific community has also shown increased interest in particular aspects related to the genesis, occurrence, geochemical characteristics, and quality of the mineral water (Cartwright et al., 2002; Gros, 2003; Schofield and Jankowski, 2004; Afsin et al., 2006; Cruz et al., 2006; Bodis et al., 2010; Ma et al., 2010; Mondal et al., 2010; Dowgiallo, 2012; Dupalova et al., 2012).

Most of the mineral water brands found in the market are bottled in the Eastern Carpathians and many renowned spas, ruined in the present, are hosted there. Although the existence of large water resources has recently boosted the development of the mineral water bottling industry in the area, the knowledge on the origin and circulation of the water resources is still very poor.

The study area represents the boundary between the Neogene to Quaternary volcanic chain on the Eastern Carpathians and the sedimentary units of the Transylvanian Basin. The geological complexity (volcanoes, hydrocarbons, evaporites, sedimentary sequences etc.) may be perceptible in the geochemical characteristics of the mineral waters.

Standing on the shoulders of giants, like Johann Crantz, Lucas Wagner, István Kibédi Mátyus, János Bányai, Artemiu Pricăjan and many others who put the basis of hydrogeochemistry in our country, with all the respect for their contributions, we aim to build on their previous discoveries.

With no claim to be exhaustive, this thesis, entitled **Hydrogeochemistry of mineral waters from the Eastern Carpathians – Transylvanian Basin boundary**, accounts for a better insight on the presently ongoing hydrogeochemical processes that are involved in the existence of mineral waters.

Using new analytical tools we provide data on 104 mineral water springs of different chemical types following the Carpathian chain from the north to south. In the area of Rodna-Bârgăului-Călimani Mountains a number of 28, in the area of Gurghiu-Harghita Mountains, 35 sparkling mineral waters, together with 41 highly mineralized saline waters from the Transylvanian Basin were investigated in the period of time 2011-2013.

We provide new data on the chemical composition of the mineral waters in terms of major ions and trace elements, the source of dissolved ions and stable isotopic composition ($\delta^{18}O$, δD), to reveal their origin and dynamics. For a more complex view the geochemistry and isotopic composition of associated common and noble gases (CO_2, CH_4, He) was studied. With this thesis we try to raise attention to the vulnerability and protection of our mineral water resources.

It cannot be left out of consideration my personal motivation and attachment to the study area and to this field of research. As a child I have very often encountered mineral water springs in the form of ‘bubbling pools and springs’. Since then I have been curious and eager to know more about the forces and processes governing their existence.

2. Geotectonic setting of the study area

The mountain range of the Eastern Carpathians cover an area of 33 500 km^2 limited in the north by the border with Ucraine and the Prahova Valley in the south. Our research area covers the western summit of the Carpathian mountain range from Rodnei and Bârgăului Mountains in the north, towards the Călimani-Gurghiu-Harghita volcanic chain and Perșani Mountains in the south, at the Transylvanian Basin boundary, a 200 km long transect between the Someșul Mare and the Olt River.

The geographical altitudes range between 2000-2100 m a.s.l (Rodnei and Călimani Mts.) to 1300-1900 m a.s.l. (Bârgăului, Gurghiu and Harghita Mts.) and 700-800 m a.s.l. (Perșani Mts. at Racoș Defile). The geographical altitudes in the eastern Transylvanian Basin varies between 290-700 m a.s.l. (Pop, 2006)

The climate conditions represent the transition from basinal averages to mountain-type climate. The average annual temperature records are approximately 7°C at the bottom of the mountains and drops to 0 at the top levels. The amount of rainfalls is growing from 800 mm/year from basinal areas to 1400 mm/year on the mountain tops with differences depending on the mountainside orientation. The western summits are usually more exposed to precipitation due to the wet air masses coming from the west. The hydrographic networks show radial distribution due to the height of the mountain space. Water from the small creekst is collected by main rivers, such as Someșul Mare, Bistrița, Mureș, Târnava Mare, Târnava Mică, Homorodul Mare, Homorodul Mic and Olt rivers (Pop, 2006).

The Alpine tectonic activity in the Carpathian-Pannonian region had initiated during the Cretaceous with the closure of the Tethys Ocean. The intensification of the compressional forces during the Neogene lead to the south-west oriented subduction of a small oceanic basin beneath the continental microplates Tisa-Dacia. As a result of their collision with the Eurasian plate in the Sarmatian, and the assimilation of crustal material, magma generation and magmatic activity had started (Rădulescu and Dumitrescu, 1982, Seghedi et al, 1995). The igneous formations (magmatic bodies and volcanoes) are part of the magmatic arc that appeared at the eastern edge of the Tisa-Dacia continental terrain, on the Carpathian accretionary prism (Rădulescu and Săndulescu, 1973, Rădulescu and Dumitrescu, 1982, Săndulescu, 1984, Royden, 1993, Szakács and Seghedi 1995b, Mason et al., 1998, Pécskay et al., 2006).

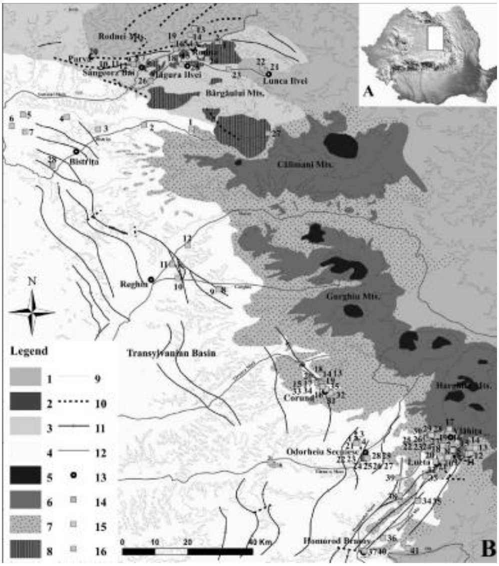

Fig.1. A. Sketch of Romania with the study area marked with white rectangle. **B.**The geologic map of the study area, #1 The Eastern Carpathians, #2 Salt outcrops, #3 Paleogene sedimentary deposits of the Bârgăului Mts., #4 Miocene sedimentary deposits of the Transylvanian Basin, #5,6,7 the Neogene to Quaternary volcanic chain Călimani-Gurghiu-Harghita Mts.: #5 Proximal facies of the volcanic chain (volcanic craters), #6 Intermediate facies of the volcanic chain (lava flows, massive volcanics), #7 Distal facies of the volcanic chain (piroclastic deposits), #8 Magmatic intrusions of the Bârgăului Mts., #9 Topographic contours, #10 Faults and fractures, #11 Folds, #12 Rivers, #13 Localities, #14,15,15 The investigated mineral waters:#14 NaCl-type highly mineralized waters, #15 CO_2-rich mineral waters from the Rodna-Bârgău-Călimani area, #16 CO_2-rich mineral waters from Gurghiu-Harghita area.

(modified after Bleahu et al., 1968; Ianovici et al., 1968; Joja et al., 1968; Marinescu et al., 1967; Mureșan et al., 1968; Peltz et al., 1983; Popescu et al., 1968; Ticleanu et al., 1980).

Within this volcanic chain three major segments can be distinguished from north to south: Oaș-Gutâi Mountains, Țibleș-Rodna-Bârgău – also known as the „subvolcanic area” – and the Călimani-Gurghiu-Harghita volcanic range. The first and the third showed intensive volcanic activity; the second has differences especially in the evolution of magmas and their surface manifestations, consisting of magmatic intrusions (Băncilă, 1958, Rădulescu and Dumitrescu, 1982).

3. Geochemical features of mineral waters and associated gases form the Eastern Carpathians

When speaking about mineral water or defining the notion of “mineral water”, three aspects must be taken into consideration: geological, medical and social aspects or trends regarding water consumption. These aspects, together with the actual definition of the „mineral water” changed during history from the past until the present.

The first definitions of the notion of “mineral water” appeared from Hintz and Grünhut, in 1907 in the German book of baths, Deutscher Bäderbuch, defining the ”mineral water” as water containing dissolved solids above 1000 mg/l, special chemical elements, higher temperature and/or dissolved gases. Based on these assumptions the definitions adopted by the Transylvanian authors (Hankó 1896; Bányai, 1934a, b; Straub, 1950; Pricăjani, 1972) focus more on the origin and geological aspect of the groundwater, together with the chemical limitation of the 1000 g/l.

Nowadays the European Parliament and Comission within the Directive 2009/54/EC defines the notion of mineral water as a: *„microbiologically wholesome water originating in an underground water table or deposit and emerging from a spring tapped at one or more natural bore exits. Natural mineral water can be clearly distinguished from ordinary drinking water: a). by its nature, which is characterized by its mineral content, trace elements or other constituents and, where appropriate, by certain effects; b). by its original purity. The characteristics referred to in point 1, which may give natural water properties favorable to health, shall have been assessed from the following point of view: geological and hydrological, physical, chemical and physico-chemical, microbiological, if necessary, pharmacological and clinical.*”

Three types of mineral waters were defined according to the total dissolved constituents: low mineral content with mineral salt content as a fix residue, not greater than 500 mg; very low mineral content, not greater than 50 mg/l and rich in mineral salts, value greater than 1500 mg/l.

As a result of the increasing water consumption in Europe, the EU adopted within the Water Framework Directive (2006/60/EC) a series of regulations and standards for the groundwater protection against pollution and degradation (2006/118/EC), the exploitation and marketing of natural mineral water (80/777/EC), the quality of drinking water (80/778/EC) and bathing water (76/160/EC).

These directives were implemented in the legislation of each state member; for Romania the Order No. 87 of the National Agency for Mineral Resources from May, 2008, article 403 from the Monitorul Oficial, summarizes the legislation on exploitation and utilization of mineral waters as mineral resources.

The present state of knowledge on the mineral water springs and gases from the Eastern Carpathians (definition of “mineral water”)

In Romania, depending on its location, special terminology is applied when speaking of sparkling mineral waters. The expressions „borcut” is used is the northern part of the country, while „borvíz” in the central parts, both meaning the same thing: CO_2 rich mineral water, similar to the expression „cevice” used in Ucraine.

The mineral water resources of the Eastern Carpathians are renowned since historic times when the first spas, like Sărățel, Unieș (Chintăuan, 1998), Borsec, Vâlcele, Odorheiu Secuiesc (Téglás, 1897; Pricăjan and Airinei, 1979) and the salty fountains of the Transylvanian Basin (Fischer, 1887) were constructed at several places by the Romans.

The first studies on the location and therapeutic value of the mineral waters from the study area date back to the 18th Century. The balneology and use of mineral waters in the 18th Century was characterized by the existence of some small important local spas for aristocrats: Anieș (Băile Dombhat), Rodna, Sângeorz Băi, Borsec, Vâlcele, Băile Tușnad, Sovata, Băile Selters, Lueta, Băile Chirui and different small bubbling pools, where local people met for treatment, healing or for entertainment. Often these local spas were compared to German spas, based on the similarity of the water's chemical composition or to advertise local values (Orbán, 1871; Boleman, 1887; Hankó, 1896).

Some of the mineral waters were used for drinking cures and also bottling industry began to flourish at Corund, Băile Seiche, Odorheiu Secuiesc, Băile Homorod (Chintăuan, 1998; Zepeczaner, 2009)

From the late 19th Century and the beginning of the 20th Century the study of mineral waters focused more on hidrogeology and an attempt to synthesize and define the mineral water types, based on chemistry and geology was carried out.

In the 20th Century important contributions to the classification of mineral waters and detailed prospecting studies on mineral water resources are given by several authors. Finally few data on the stable isotopic composition complete the present day state of knowledge on the origin of mineral waters and gases from the Eastern Carpathians.

Chemical types of mineral waters in the Eastern Carpathians

The origin of mineral waters was highly debated among scientist. The juvenile origin of mineral waters was based on the assumption that mineral waters are fluids degassing from the hot arising magma and are new in the hydrological cycle. The more popular meteoric origin considers mineral waters as groundwaters that during their underground path, as a result of water-rock interaction occurring at a certain depth and temperature have attained high mineralization and dissolved gases.

The mineral waters from Romania have a high hidrochemical variety determined by the geological structure of the country. In the Carpathian region there are three major units influencing the chemical composition of mineral waters: the Carpathian thrust-and-fold belt, the Transylvanian Basin and the Neogene to Quaternary volcanic arc.

Several authors tried to group the mineral waters based on hydrochemical features. Bányai (1934a) defines 5 mineral water types: CO_2-rich mineral waters in the proximity of the volcanic chain, NaCl, high salinity waters, in the Transylvanian Basin, H_2S-rich mineral waters in the Carpathian flisch area, mixed type of waters and geothermal springs.

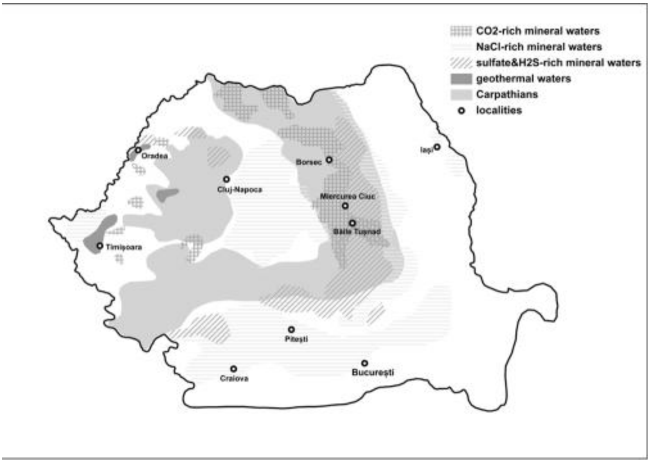

Fig.2. Sketch figure of the main mineral water types of Romania with special focus on the Eastern Carpathians: CO_2-rich mineral waters (blue grid), NaCl-rich mineral waters (green lines), sulfate and H_2S-rich mineral waters (orange lines), mixed waters (overlapping of different types, ex. in the SE Carpathians), geothermal waters (red areas). (modified after Pricăjan, 1972)

Isotopes in the study of mineral waters from the Eastern Capathians

The use of isotopes in the research of groundwaters is a relatively innovative method. This method is a suitable tool for several applications; ex. determining the origin of the groundwater, to reveal geochemical processes like evaporation, water-rock interaction, residence time, mixing etc., that groundwater goes through during its path. The stable isotopes, as conservative tracers are complementary to chemical information and provide insights into several processes that are difficult to trace by chemical means.

Natural gases associated to mineral waters

The term “natural gas” denotes substances that on 1bar pressure and 20ºC are in a gaseous state. In the geospheres the abundances of gases differ according to their type. The Universe is consideret to be made up mostly by H_2 (89.2%) and He (10.7%). The other elements, O_2, C, N_2 and Ne etc. are far in a lower amount.

Common gases

In Romania, the Transylvanian Basin hosts hydrocarbon deposits, almost pure dry CH_4, in Badenian and Sarmatian deposits. They are highly influenced by the tectonic alignments and fractures and and also by the CO_2 emissions, especially in the eastern part of the basin (Cristuru Secuiesc, Odorheiu Secuiesc, Praid hydrocarbon structures), where the Neogene-Quaternary volcanic chain is found.

4. Materials and methods

The water samples were collected along a 200 km transect at the boundary between the Eastern Carpathians and the Transylvanian Basin marked by the contemporary presence of volcanic and sedimentary formations, including evaporites. From North to South, following the volcanic chain samples were collected from several locations: Valea Vinului, Șanț, Rodna, Anieș, Parva, Sângeorz Băi, Lunca Ilvei, Măgura Ilvei, Ilva Mare, Colibița, Mureșenii Bârgăului, Josenii Bârgăului, Mintiu, Tăure, Blăjenii de Jos, Dumitra, Viișoara, Jabelnița, Aluniș, Idelciu de Jos, Corund, Odorheiu Secuiesc, Băile Homorod, Vlăhița, Băile Chirui, Lueta, Merești, Mărtiniș, Sânpaul, Homorod Brașov, Racoș.

Materials and the methods are described in the following starting with the sketch figure that summarized the steps of measurements.

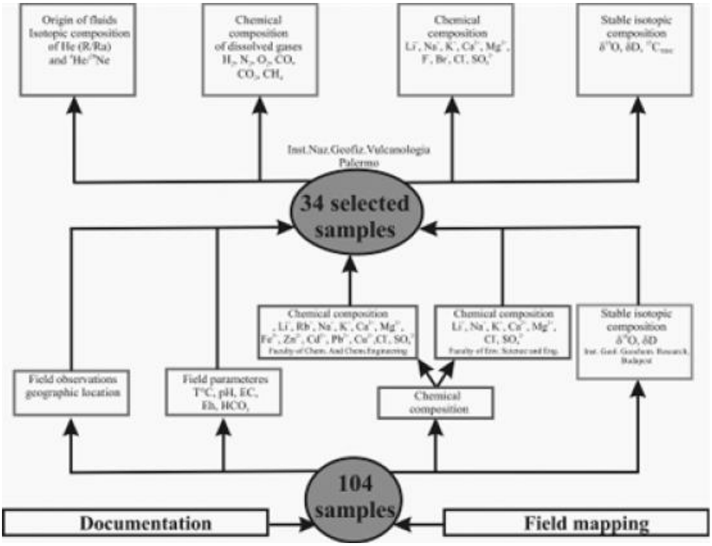

Fig.4. Summarizing sketch figure of the methodologies applied within the research.

Determination of chemical composition of sampled were performed simultaneously in **Cluj-Napoca**, in the laboratories of **Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering** and **Faculty of Environmental Science and Engineering**. Stable isotopic composition of water was determined in **Budapest, in the Institute for Geological and Geochemical Research of the Hungarian Academy of Sciences,** tritium measurements were performed in the **Institute for Nuclear Research of the Hungarian Academy of Sciences, Debrecen.**

Chemical composition of dissolved gases, stable isotopic composition of gases and chemical composition of water from 34 selected samples was performed in **Palermo, in the Instituto Nazionale di Geofisica e Vulcanologia (INGV)** during a 4-month-scholarship.

Sampling and sample handling

Waters of 104 springs and spas were collected; the sampling and sample handling, as well as the quantification of different components were made according to the EPA (or international standards) prescriptions (Clesceri and Greenberg, 1989; Ordinul 161/16.02.2006)

For determination of chemical composition water samples were filtered with 0.45 millipore filters, collected in 500 ml PET bottles, conserved on spot with 1 ml of suprapur conc. HNO_3 acid and kept at 4ºC. Samples for anion determinations with ion chromatography were filtered and kept at 4ºC.

Samples for stable isotopic composition ($\delta^{18}O$ and δD) of water were collected in 50 ml PET bottles with special caps avoiding any fractionation caused by evaporation and kept at 4ºC.

Samples for dissolved gases and stable isotopes of helium and $^{13}C_{TDIC}$ were taken in 240 ml glass bottles, sealed in the field by silicon/rubber septa using special pliers. All of the sampled were collected taking care to avoid air contamination.

5. Geochemistry of fluids in the investigated area

A total of 104 mineral water springs, wells and spas were considered for the measurement of physical and chemical parameters, major elements and stable isotopic composition (Table 1, 2, 3, 4, 5, 6, see Appendix). For detailed analysis on chemical composition of dissolved gases 34 selected samples were chosen; analysis on isotopic composition of noble gases was performed on a number of 24 selected samples (Table 7, 8, see Appendix). On highly saline samples (Corund and Homorod Brașov) that have shown isotopic shifts in both $\delta^{18}O$ and δD we have investigated also tritium, for determination of active recharge of springs (Table 9, Section 5.3).

For a discussion on the hydrogeochemistry of the waters, the investigated area is divided into three parts. The first two sections (5.1 and 5.2) deal with the hydrogeochemistry of sparkling mineral waters from Rodna-Bârgău and Călimani Mountains and Gurghiu-Harghita Mountains respectively. In the third section (5.3) the hydrogeochemistry of highly mineralized waters is described in detail. Discharge of the springs vary between very low (0.01 l/s) to very high, up to few tens of l/s.

Hydrogeochemistry of CO_2-rich mineral waters from Rodna-Bârgău and Călimani Mountains

The northern part of the study area covers a ~60 km transect following three major walleys, the Someșul Mare, Ilva and Bistrița where the sedimentary and metamorphic units of Bârgăului and Rodnei Mountains occur that are pierced by magmatic intrusions and in the south the sedimentary units are bordered by the largest volcanic structure of the Neogene to Quaternary volcanic chain, Călimani Mountains. The marginal sedimetary units of the Transylvanian Basin are characterized by evaporitic sequences (Fig.5, Table 1, 2, see Appendix)

Results of the field measurements and location of samples (UTM WGS84 coordinates) of 28 water samples from Someșul Mare, Ilva and Bistrița Valleys are listed on Table 1. The analytical results of both chemical (major ions: Cl, SO4, HCO_3, F, Br, Na, K, Mg, Ca, Rb, Li and trace elements: Fe, Zn, Cd, Cu and Pb) and isotopic composition ($\delta^{18}O$ and δD) are listed in Table 2.

Water chemistry

The physico-chemical parameters measured on the field show wide spatial variability: temperatures in the range of 3 – 12.4°C, pH between 5.04 and 7.86, redox potential between -106.6 and 92.8. In terms of Total Dissolved Solids (TDS) all the mineral waters are highly mineralized ranging between 290 and 10463 mg/l (Table 1, 2, see Appendix). The highest values, above 3000 mg/l have been measured in both Someș and Ilva Valleys, in 15 samples out of 28, at Anieș (#5), Sângeorz Băi (#6, 7, 8, 9, 10, 11 and 12), Lunca Ilvei (#21, 22) and in Poiana Ilvei (#26).

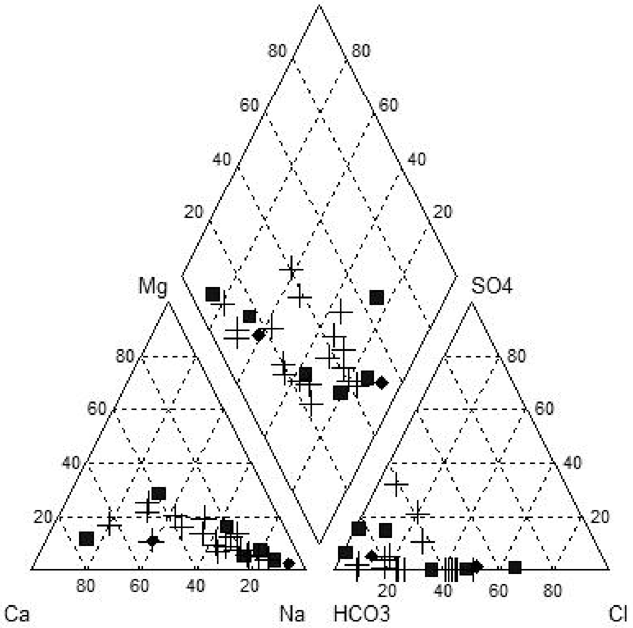

Fig. 6. Chemical composition (major ions) of the mineral waters from the northern area – Piper plot. Symbols as following: crosses, samples from Someșul Mare area, blue squares, samples from Ilva area and black diamonds, samples from Bistrița.

The wide range of TDS accounts for a variety of geochemical features of the sampled waters. Na^+ and Cl^-, are the main dissolved ions, displaying concentrations between 0.08 and 62.39 meq/l and 0.70 – 141.1 meq/l, respectively. The other cations, Ca^{2+} (1.12 – 24.65 meq/l), K^+ (0 – 4.41 meq/l), Mg^{2+} (0.49 –10.83 meq/l), and Li^+ (0 – 1.87 meq/l) are electrically balanced by SO_4^{2-} (0 – 2.78) meq/l and HCO_3^- (measured in the field, ranging between 2.5 – 81 meq/l. Due to the large concentration ranges the chemical composition is evaluated in terms of major ions contents by the Piper and Langelier-Ludwig diagram (Figs.6, 7). Three major groups can be identified according to the plots, Ca–Mg–HCO_3, Na–K–HCO_3 and Na–Cl, in full agreement with the types identified by Chintăuan, 1998. The three identified water types are Ca-Mg-HCO3, Na-K-HCO3 and Na-Cl type of waters.

Stable isotopic composition and origin of mineral waters

On the δD-δ^{18}O diagram (Fig. 10 and 11) samples are shown with respect to the local and global rainwater isotope composition (Local Meteoric Water Line – LMWL; Costinel et al., 2009; Global Meteoric Water Line – GMWL; Craig, 1961). The isotopic composition of the sampled waters shows δ^{18}O values ranging between –10.61 and –7.70‰ vs. V-SMOW, with δD between –75.28 and –59.80‰ vs. V-SMOW, thus most of the springs lie between the LMWL and GMWL. Since no data on the LMWL is available from the Eastern Carpathians the LMWL is derived from rainwaters from Râmnicu Vâlcea area, with elevation, topography and climate similar to the investigated area (Costinel et al., 2009).

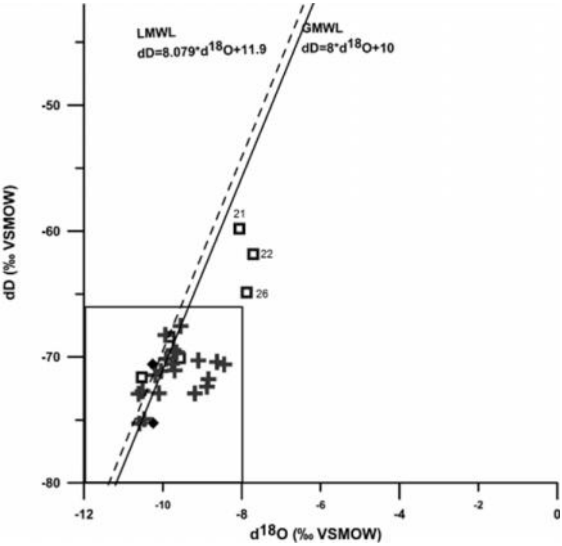

Fig.10. δD vs. δ^{18}O isotopic composition of the 28 samples. δD vs. δ^{18}O on LMWL with the equation $\delta D=8.079*\delta^{18}O+11.9$, from Râmnicu Vâlcea area (Costinel et al., 2009) and GMWL with equation $\delta D=8*\delta^{18}O+10$ (Craig, 1961).Symbols as following: red crosses, samples from

Someșul Mare area, blue squares, samples from Ilva area and black diamonds, samples from Bistrița.

Isotopic shift towards heavier oxygen isotope composition can be noticed in the case of springs from Lunca Ilvei (# 21 and 22), Poiana Ilvei (# 26) and Sângeorz Băi (# 6, 7, 9, 10, 11 and 12) in the absence of significant shifts in deuterium. Most of the samples plot between the GMWL and LMWL showing a meteoric origin. Our results are consistent with the previous analyses on the mineral water springs from Rodna-Bârgăului area which point to the presence of deep circulating fluids having a modified isotopic composition (Papp, 2000).

5.2. Hydrogeochemistry of Gurghiu-Harghita Mountains

The southern part of the study area covers a 40 km transect at the boundary between the Gurghiu and Harghita Mountains and the Transylvanian Basin marked by the contemporary presence of volcanic and sedimentary formations including evaporites. The large compositional variability recorded in the collected waters (Table 3, 4, see Appendix) denotes the occurrence of several Water-Rock Interaction (WRI) processes between the infiltrating waters and the host rocks. The occurrence of aquifers mixings, water infiltration at deep levels through faults and gas (CO_2) dissolution along the hydrogeological path are considered as the most probable processes responsible for the water's final geochemical features.

The results of the field measurements together with the location (UTM WGS84 coordinates) of the 35 water samples from Odorheiu Secuiesc, Lueta, Băile Chirui, Homorod, Vlăhiţa and Corund areas are listed on Table 3. The analytical results of both chemical (major ions: Cl, SO4, HCO3, F, Br, Na, K, Mg, Ca, Rb, Li and trace elements: Fe, Zn, Cd, Cu and Pb) and isotopic composition ($\delta^{18}O$ and δD) are listed in Table 4.

Water chemistry

The physico-chemical parameters measured on the field show wide spatial variability: temperatures in the range of 9.5 – 25.0°C, pH between 5.48 and 7.45, redox potential between -29.0 and 85.4. In terms of Total Dissolved Solids (TDS) all the mineral waters are highly mineralized ranging between 295 and 48188 mg/l (Table 3, 4, see Appendix), with most of the values in the interval of 2000 – 4000 mg/l. The highest values have been measured in Lueta (#5, 7, 9 and 10) in Vlăhiţa (#21) and springs from Odorheiu Secuiesc (#3 and 4).

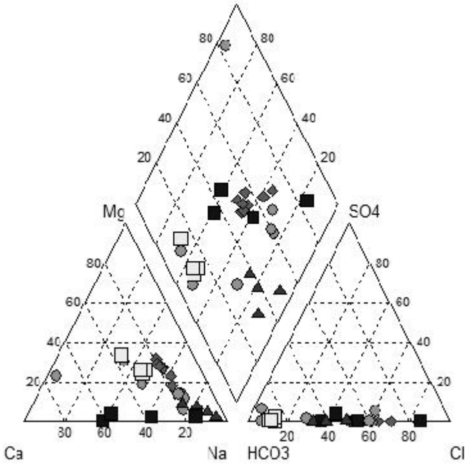

Fig. 15. Chemical composition (major ions) of the mineral waters from the southern area – Piper plot. Symbols as following: blue squares, samples from Odorheiu Secuiesc, red triangles, samples from Lueta, yellow squares, samples from Băile Chirui, orange circles, samples from Vlăhița, green diamonds, samples from Băile Homorod, black crosses, samples from Corund.

The wide TDS range accounts for a variety of geochemical features of the sampled waters. Na^+ and Cl^-, are the main dissolved ions, displaying concentrations between 1.10 and 723.56 meq/l and 0.08 – 678.18 meq/l, respectively. The other cations, Ca^{2+} (1.04 – 30.14 meq/l), K^+ (0.04 – 5.60 meq/l), Mg^{2+} (0.09 –26.38 meq/l), and Li^+ (0 – 0.64 meq/l) are electrically balanced by SO_4^{2-} (0 – 4.28) meq/l and HCO_3^- (measured in the field, ranging between 3.5 – 109 meq/l. Due to the large concentration ranges the chemical composition is evaluated in terms of major ions contents by the Piper and Langelier-Ludwig diagram (Figs.15, 16). The plot highlights that the collected water samples can be grouped in three major water types Ca–Mg–HCO_3, Na–K–HCO_3 and Na–Cl similar to the northern group.

Stable isotopic composition and origin of mineral waters

The δD-$\delta^{18}O$ diagram (Fig. 19, 20) shows the distribution of the samples with respect to the local rainwater isotope composition (Local Meteoric Water Line – LMWL; Costinel et al., 2009) and the Global Meteoric Water Line - GMWL (Craig, 1961). The isotopic composition of the sampled waters shows $\delta^{18}O$ values ranging between –11.58 and –1.35‰ vs. SMOW, with δD between –80.7 and –44.3‰, thus most of the springs lie between the LMWL and GMWL. Isotopic shift towards heavier oxygen isotope composition can be noticed in the case of springs from Lueta (# 5, 6, 7, 8, and 9), Odorheiu Secuiesc (# 1, 4) and Vlăhiţa (# 20, 21) in the absence of significant shifts in deuterium. Extreme shifts both in oxygen and deuterium compared to the other samples are observed only in the case of spring #10 from Lueta, with isotopic composition of $\delta^{18}O$= –1.35‰ and δD= –44.3‰ (Table 4, Fig. 19, 20).

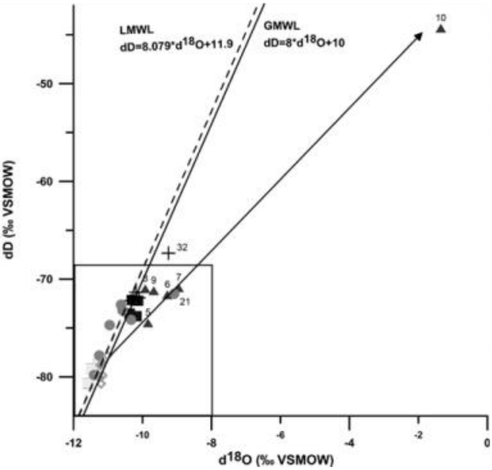

Fig.19. δD vs. $\delta^{18}O$ isotopic composition of the 35 samples. δD vs. $\delta^{18}O$ on LMWL with the equation $\delta D=8.079*\delta^{18}O+11.9$, from Râmnicu Vâlcea area (Costinel et al., 2009) and GMWL with equation $\delta D=8*\delta^{18}O+10$ (Craig, 1961). Symbols as following: blue squares, samples from Odorheiu Secuiesc, red triangles, samples from Lueta, yellow squares, samples from Băile Chirui, orange circles, samples from Vlăhița, green diamonds, samples from Băile Homorod, black crosses, samples from Corund.

5.3. Hydrogeochemistry of highly mineralized waters from the Transylvanian Basin

Following the direction of the volcanic chain from north to south, in a 200 km transect, 41 highly mineralized waters, springs, fountains and wells were mapped, together with the investigation of their chemical and isotopic composition (Fig. 23, Tables 5 and 6, Appendix).

The investigated locations included salty fountains in the northern part of the area (Bistrița Bârgăului, Josenii Bârgăului, Mintiu, Tăure, Dumitra, Blăjenii de Jos, Livezile), salty fountains and springs in the Mureș and Gurghiu Valley (Orșova, Jabelnița, Idelciu de Jos and Aluniș), highly mineralized and CO_2-rich springs from Corund and springs and fountains and wells of the south-eastern part of the basin (Odorheiu Secuiesc, Cristuru

Secuiesc, Lueta, Merești, Crăciunel, Mercheașa, Păuleni, Mărtiniș, Homorod Brașov and Racoșul de Jos).

Water chemistry

The physico-chemical parameters of highly mineralized waters, measured on the field, show similar spatial variability than the CO_2-rich waters: temperatures in the range of 3 – 22.2°C, pH between 5.68 and 8.49, redox potential between -94.5 and 71.7. In terms of Total Dissolved Solids (TDS) all the mineral waters are highly mineralized ranging between 1244 and 383 048 mg/l (Table 5, 6, see Appendix), with most of the samples showing extreme values above 300 000 mg/l. The samples from Corund (#131 15, 16 17, 18, 19), Odorheiu Secuiesc (#21) and Homorod Brașov (#37, 40) contain also dissolved CO_2 up to ~3000 mg/l.

In all the samples Na^+ and Cl^-, are the main dissolved ions, displaying concentrations between 18.80 and 7892.89 meq/l and 16.70 – 5915.43 meq/l, respectively. The other cations, Ca^{2+} (3.10 – 189.34 meq/l), K^+ (0.17 – 94.22 meq/l), Mg^{2+} (0.23 –142.62 meq/l), and Li^+ (0 – 12.30 meq/l) are electrically balanced by SO_4^{2-} (0.04 – 88.04) meq/l and HCO_3^- (measured in the field, ranging between 2 – 123.6 meq/l. Due to the large concentration ranges the chemical composition is evaluated in terms of major ions contents by the Langelier-Ludwig diagram (Figs.23). The plot highlights that all the collected water samples are of Na–Cl type.

Isotopic composition

The stable isotopic composition of the saline waters investigated is listed on Table 6 (see Appendix). Values scatter between -82.46 and -12.13 for δD and -11.52 and +8.67 for $\delta^{18}O$, with most of the samples lying on the meteoric water line and some samples (#13, 14, 15, 16, 17, 18 and 19 from Corund, #21 from Odorheiu Secuiesc, #39 from Mărtiniș and # 37 and 40 from Homorod Brașov) showing an isotopic enrichment for both isotopes.

Tritium was determined for saline samples from Corund (#14, 15, 16, 18) and Homorod Brașov (#40), ranging between 0 for sample # 16 and 1.106 for #18 (Table 9).

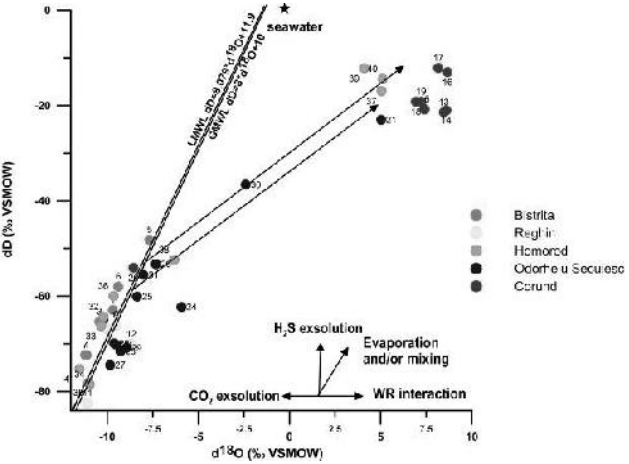

Fig.25. Stable isotopic composition of the investigated saline waters. Sample distribution according to location. Symbols as following: orange dots, samples from Bistrița, yellow dots, samples from Reghin, green dots, samples from Homorod, blue dots, samples from Odorheiu Secuiesc, red dots, samples from Corund.

5.4. Geochemistry of dissolved gases

Due to the geological variety of the area (recent volcanism of the Eastern Carpathians, thick sedimentary deposits, salt diapirs and hydrocarbon deposits of the Transylvanian Basin) a wide range of volatiles can be produced which interact with the infiltrating water. The wide ranges of physical and chemical parameters recorded for the mineral waters, implies as much variability in the dissolved gas phase (Tables 7 and 8) due to either the endogenic production of volatiles and the gas-water interactions which always affect the pristine composition of the gas assemblage depending on the water/gas mass balance and the time-length of the interactions.

The recorded chemical and isotopic features are hereafter discussed in terms of gas sources related to different tectonic environments and interaction processes acting on the circulating fluids that are responsible for the final composition of the dissolved gas phase.

Chemical composition of dissolved gases

Several mineral waters are associated with gas phases showing strong bubbling gases. Table 7 lists the samples using the ID names from 1 to 34 grouped as North and South according to their geographical location with respect to the volcanic range. The field data (physic-chemical parameters: temperature, pH, electrical conductivity and salinity) with the chemical composition of the mineral waters are shown for each sample in Tables 1, 2, 3, 4, 5 and 6, see Appendix. The chemical composition of the dissolved gases is reported in Table 7, while the isotopic composition of helium and carbon is listed in Table 8.

Starting from the gas-chromatographic analyses, the composition of the dissolved gas phase was calculated taking into account the solubility coefficients (Bunsen coefficients “β”) of each gas specie, the volume of the gas extracted (in cm^3) and the volume of the extracted water sample (in cm^3) as described by Italiano et al. (2009, 2013).

The gas-chromatographic analyses (see Table 7) show that CO_2, ranging from 9 to 1987 cm^3/L_{H2O} is by far the most abundant component of the dissolved gas phase. The other components, with contents lower by one order of magnitude, display N_2 ranging from 2.4 to 15.8 cm^3/L_{H2O}, O_2 between 0.01-7.6 cm^3/L_{H2O}, CH_4 from $1.6x10^{-4}$ to 7.3 cm^3/L_{H2O} and He ranging between $3x10^{-5}$ and $2.3x10^{-2}$ cm^3/L_{H2O}.

Isotopic composition of helium and carbon

Table 8 lists the results of helium isotopic analyses normalized to the atmosphere and expressed as R/Ra values (where R= $^3He/^4He$ sample;

Ra =atmospheric $^3He/^4He$ ratio = 1.4×10^{-6}). The $^4He/^{20}Ne$ ratio ranges between 0.3 and 126.2 that, if compared to 0.267 assumed to be the representative $^4He/^{20}Ne$ for an Air Saturated Water (Holocher et al., 2002), it spans from almost atmospheric (sample #15) to >400 times with respect to the ASW (Sample 33, Table 8). Based on the measured $^4He/^{20}Ne$ ratios, and assuming all ^{20}Ne of atmospheric provenance, the atmospheric He contribution was estimated and subtracted from the measured value. The correction is based on known $^4He/^{20}Ne$ values for ASW, assuming a recharge temperature of 10 ºC The $^3He/^4He$ values corrected for air contamination (R/Ra $_c$) range between 0.18 and 0.96 overlapping the range normally associated to crustal volatiles and giving clues of contribution from magmatic volatiles.

Although our data deal with the dissolved gases, they are in good agreement with former results from free gases (e.g. Althaus et al., 2000; Vaselli et al., 2002; Etiope et al., 2004, Baciu et al., 2007; Table 8).

Due to the method we adopted for carbon isotopes determination, the CO_2 amounts extracted from acidified water represent the total content of dissolved carbon (TDC). The measured carbon isotopic composition of the total dissolved carbon species spans on a $\delta^{13}C_{TDC}$ range of more than 27 δ units between -17.02 and +10.12‰ PDB (Table 8). The recorded data are associated to samples with high dissolved CO_2 contents and sites where travertine deposits are recognized. Contrastingly, samples from the southern sector display low $\delta^{13}C_{TDC}$ values (from -0.82 to -17.02‰ vs PDB) associated to high dissolved CH_4 contents in CO_2-dominated gas-phase (Table 7).

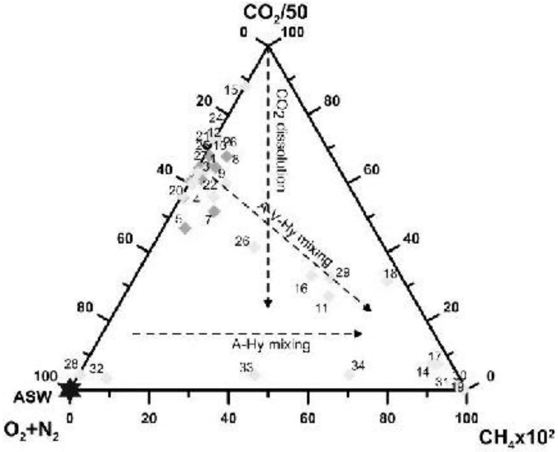

Fig.37. The triangular diagram shows the relative contents of atmospheric-type components (N_2 and O_2) besides CO_2 and CH_4 coming from crustal and magmatic sources. The samples distribution highlights the occurrence of GWI processes that significantly change the composition of the pristine gas phase: CO_2 dissolution and mixings. Mixings occur between atmospheric (A) and hydrocarbons (Hy) and atmospheric, hydrocarbon and volcanic (V) gas species.

Most of the samples plot along a N_2-CO_2 and a N_2-CH_4 mixing lines showing that the dissolved gas phase is always a mixture of the above mentioned components. The samples falling along the CO_2-N_2 mixing line show an almost constant ASW-CO_2 ratio of 95 which is about 3000 times the atmosphere with an increasing CH_4 component (samples from the Eastern Carpathians. #5 Anieș, #7 Sângeorz Băi, #11, 16 Corund, #18 Odorheiu Secuiesc, #20, 23 Băile Homorod #26 Băile Chirui and #29 Vlăhita). While it is reasonable to assume that CH_4 comes from hydrocarbon reservoirs as for the Transylvanian Basin boundary (low CO_2/N_2 ratio on Fig. 3; samples #28 from Vlăhita, #30 from Merești, 32 from Crăciunel, #33 from Homorod Brașov, #34 from Racoș), we cannot assert that CO_2 is only of volcanic origin. The mixing line N_2-CH_4 shows that only a few samples display negligible CO_2 contents resulting of a binary mixing between ASW and and hydrocarbons-rich source.

Figure 37 also highlights the occurrence Gas Water Interactions (GWI) leading to CO_2 dissolution. In fact, although CO_2 is always dominant in the dissolved gases (Table 7), the less soluble species (He, N_2, CH_4) denote concentrations well above the equilibrium with the ASW which testifies that besides mixings phenomena between shallow (atmospheric-type) and deep (volcanic and crustal-type) volatiles, the occurrence of GWI processes at variable extents account for the final composition of the dissolved gas phase.

6. Conclusions

Following the Carpathian range from Rodnei Mountains in the north to Harghita Mountains in the south, on the boundary with the Transylvanian Basin, we have investigated a total of 104 mineral water springs, wells and fountains, displaying different chemical and isotopic composition. In the area of Rodna-Bârgăului-Călimani Mountains a number of 28, in the area of Gurghiu-Harghita Mountains, 35 sparkling mineral waters, together with 41 highly mineralized saline waters from the Transylvanian Basin were analyzed in the period of time 2011-2013 in terms of major ions, trace elements, stable isotopic composition, dissolved gases and tritium analyses for selected samples.

For a discussion on the hydrogeochemistry of the waters we have divided the study area into three parts. In the first two sections we deal with the hydrogeochemistry of sparkling mineral waters from Rodna-Bârgău-Călimani Mountains and Gurghiu-Harghita Mountains respectively. In the third section the hydrogeochemistry of highly mineralized waters is discussed in detail. The geochemistry of dissolved gases is approached separately to highlight processes affecting origin and migration of deep fluids.

The 60-km-transect of the northern part of the study area covers three major valleys; the Someșul Mare, Ilva and Bistrița, where the sedimentary and metamorphic units of Bârgăului and Rodnei Mountains occur that are pierced by magmatic intrusions and volcanic edifices. The mineralized CO_2-rich waters are grouped based on their major ion content into three major chemical types, Ca–Mg–HCO_3, Na–K–HCO_3 and Na–Cl. The origin of these waters is meteoric with several processes involved in their chemical and isotopic composition eg. water-rock, gas-water interaction and mixing with deep fluids.

The 40-km-transect from south is located at the boundary between the Gurghiu and Harghita Mountains and the Transylvanian Basin, marked by the contemporary presence of volcanic and sedimentary formations including evaporites. The large compositional variability recorded in the collected waters denotes the occurrence of several water-rock interaction processes between the infiltrating waters and the host rocks. The occurrence of aquifers mixings, water infiltration at deep levels through faults and gas (CO_2) dissolution along the hydrogeological path are considered as the most probable processes responsible for the water's final geochemical features. Considering the widespread presence of evaporitic formations, the waters are highly affected by the halite dissolution displaying in the increase of TDS values. Mixings of different proportions during waters ascent towards the surface explains the venting of waters marked by various geochemical features.

The isotopic compositions together with the geothermometric estimations indicate that in the northern as well as in the southern parts of the study area, the waters are not in equilibrium with the host rocks and they are dominated by several contemporary active processes, such as rock dissolution, mixing with cold groundwater, and ion exchange.

In comparison with the CO_2-rich waters, the highly saline waters from the Transylvanian Basin display totally different geochemical characteristics indicating a more complex history.

The investigated locations included salty fountains in the northern part of the area (Bistrița Bârgăului, Josenii Bârgăului, Mintiu, Tăure, Dumitra, Blăjenii de Jos, Livezile), salty fountains and springs in the Mureș and Gurghiu Valley (Orșova, Jabelnița, Idelciu de Jos and Aluniș), highly mineralized and CO_2-rich springs from Corund and springs and fountains and wells of the south-eastern part of the basin (Odorheiu Secuiesc, Cristuru Secuiesc, Lueta, Merești, Crăciunel, Mercheașa, Păuleni, Mărtiniș, Homorod Brașov and Racoșul de Jos).

All the investigated waters are of Na–Cl type, in particular cases associated with bubbling gases. As suggested by the major ion composition and their geographical location with respect to the halite diapiric alignment we assume dissolution of halite as the main controlling factor for salinity which is further affected by freshwater mixing and/or dilution, regardless of the water's initial provenance. Most of the investigated samples display isotopic composition similar to meteoric water; in few exceptions extreme shifts are identified in both isotopes, reaching positive values for oxygen. Contrastingly to meteoric waters, shifted saline samples do not show any seasonal variation consistent with the lack of an active recharge revealed by tritium analyses. We assume the presence of two components in the investigated groundwaters, with different origin and isotopic composition, interacting with the halite deposits. One is a meteoric component represented by highly saline waters located on the meteoric water line and one non-meteoric component, upwelling at several parts of the study area, mostly at the southern part, at Corund, Odorheiu Secuiesc, Mărtiniș and Homorod Brașov. The saline waters investigated show a common end-member from the point of view of the isotopic composition with different waters all around the world, investigated in different geochemical environments.

Based on the wide range of interpretations on brines our samples from the Transylvanian Basin could be extremely evolved seawater but the presence of dehydration water is not excluded. Minor contribution to the isotopic shift may be also give by dissolved gases (CH_4 and H_2S) and organic matter.

The wide ranges of physical and chemical parameters recorded for the mineral waters, implies as much variability in the dissolved gas phase due to the endogenic production of volatiles and the gas-water interactions which always affect the pristine composition of the gas assemblage depending on the water/gas mass balance and the time-length of the interactions. Due to the geological variety of the area (volcanic to sedimentary units) a wide range of volatiles can be produced which interact with the infiltrating water.

The investigated samples displayed gas phases containing dominantly CO_2, together with other gases, N_2, O_2, CH_4 and He. The values recorded for those waters coming from evaporites and hydrocarbon reservoirs of the Transylvanian Basin and located close to the relatively recent volcanic products of the Călimani-Gurghiu-Harghita and Perșani Mountains; fully overlap the whole range including both magmatic and crustal-originated volatiles.

Although CO_2 is always dominant in the dissolved gases, the less soluble species (He, N_2, CH_4) denote concentrations well above the equilibrium with the Air Saturated Water which testifies that besides mixings phenomena between shallow (atmospheric-type) and deep (volcanic and crustal-type) volatiles, the occurrence of GWI processes at variable extents account for the final composition of the dissolved gas phase.

The occurrence of mixing process between different water bodies (carrying dissolved gases of different origin) or inside the same water-body between He from different sources (e.g. because of helium migration through faults) are considered as responsible for the recorded values. The high helium content and the $^3He/^4He$ ratio measured in the hydrocarbon gases of Homorod are clear indications of mixing processes between a deep volcanic component with shallower crustal volatiles (hydrocarbon reservoirs) due to the presence of faults.

The data we have provided on the chemical and isotopic composition of waters and gases from the Eastern Carpathians and Transylvanian Basin revealed the involvement of complex interactions and active processes. Further investigations in the future on Sr isotopic composition of brines, chemical and isotopic composition on free gases, seasonal investigations covering a longer period of time, geochemical modeling should give a more accurate view on the ongoing processes.

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