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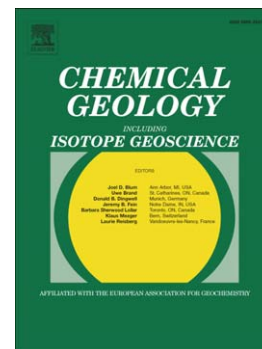
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Abstract

We show the results of a study on the volatiles dissolved in mineral waters discharged over a 200 km-long transect along the Rodna-Bârgău area and Călimani-Gurghiu-Harghita volcanic chain (Eastern Carpathians, Romania). All of the collected mineral water samples carry dissolved gas with carbon dioxide content up to 1.99 cm³STP/gH₂O, and helium content up to 2.3x10⁻⁵ cm³STP/gH₂O. Carbon ($\delta^{13}\text{C}_{\text{TDIC}}$ Total Dissolved Inorganic Carbon, ranging from -15.6 to 5.32‰ vs. VPDB), He systematics (He isotopes in the range of 0.38 - 0.99 Ra, Ra = air-normalized ³He/⁴He ratio) and CO₂/³He ratio spanning over four orders of magnitude from MORB-like values of 2.92x10⁹ to crustal-type values of 3.02x10¹³, coherently indicate the presence of fluids from different crustal sources (e.g. sediments, hydrocarbon reservoirs) besides minor, but detectable contributions of mantle/magmatic-derived fluids (up to 16.45%). Our investigations show that the wide range of chemical and isotopic composition can be explained in

terms of mixings among different gas sources feeding the groundwater and the contemporary occurrence of gas-water interactions like degassing and deposition of carbonates, affecting the circulating waters after their infiltration.

Key-words: Eastern Carpathians, dissolved gases, groundwater, gas-water interactions, helium, $^{13}\text{C}_{\text{TDIC}}$

1. Introduction

The geochemistry of endogenic volatiles in form of free emissions, diffuse soil degassing and dissolved gases in groundwater, together with the quantification of their release into the atmosphere has become important in the past years. Recent studies show the role of dissolved gases in active tectonic settings, volcanic and non-volcanic areas (Sano et al., 1998, 2004; Hilton et al., 2002; Shaw et al., 2003; Chiodini et al. 2004, 2011; Yang et al., 2005; De Leeuw et al., 2007; Italiano et al. 2009, 2014; Ray et al., 2009; Ohba et al., 2010; Pinti et al., 2011; Barry et al., 2013; Sano and Fischer, 2013; Marrero-Diaz et al. 2015; Inguaggiato et al. 2016; Benavente et al. 2016; Birke et al., 2016;). Venting of highly mineralized (TDS>1000 mg/L) sparkling groundwater is a common feature along the Eastern Carpathians making the area an important water resource for Romania. Groundwater during its subsurface migration interact with a wide range of rocks in different geological settings, including volcanic, sedimentary and metamorphic sequences, and a wide range of volatiles coming from the mantle or crustal products.

A large number of springs and wells are spread over the area where the Neogene to Quaternary magmatism produced the shallow intrusions of Rodna-Bârgău Mountains and the 160-km-long volcanic arc of the Călimani-Gurghiu-Harghita Mountains. These mineralized springs also appear in the sedimentary units of the Transylvanian Basin. The last volcanic activity occurred 0.03 My years ago (Harangi et al. 2010), but a series of manifestations remain active, like free CO₂-emissions, bubbling pools and mineral water springs. The groundwater from this area display different chemical composition, salinity and temperature, and contain high amounts of dissolved CO₂ (Kis and Baciú, 2013).

Most of the available studies deal mainly with the geochemical features of waters (Bányai, 1934; Molnar-Amărăscu and Pricăjan, 1961; Pricăjan, 1972; Crăciun et al. 1989; Chintăuan, 1998; Papp, 2000). Only recently, studies have been performed to constrain the origin of free gases, seeps, mofettes (Althaus et al. 2000; Vaselli et al. 2002; Etiope et al. 2004, 2011; Baciú et al. 2007) besides a few data at the youngest segment of the volcanics (Althaus et al. 2000). These studies represent the present-state of knowledge on the geochemistry of volatiles vented in the area. A systematic investigation on the dissolved gases carried by groundwater in the Eastern Carpathians-Transylvanian Basin area has not been conducted yet. As water acts as a gas carrier throughout the hydrological circuit, the composition of dissolved gases in groundwater may

represent an important source of information from deep structures. The gases dissolved in groundwater potentially provide information on subsurface gas-water interactions between the pristine air-equilibrated water (normally infiltrating as Air Saturated Water-ASW) and deep-seated endogenic gases of variable origin (organic, crustal and/or mantle-derived).

This paper accounts for the geochemistry of dissolved gases in the mineral waters vented along the Eastern Carpathians, Rodna-Bârgău area, marked by shallow volcanic intrusions, and the Călimani-Gurghiu-Harghita volcanic chain, at the Transylvanian Basin boundary.

2. Geologic and geodynamic context

The Carpathian Neogene to Quaternary volcanic arc formed along the inner part of the Carpathian orogenic belt, behind the Carpathian accretionary prism. Magmatism was generated by the SW subduction of the Eurasian Plate beneath small continental plates where three, progressively younger, segments were distinguished. The study areas of Rodna-Bârgău and Călimani-Gurghiu-Harghita and Perșani Mountains belong to the Central and the Eastern segment respectively, with intermediate calc-alkaline and basaltic magmatic activity (Rădulescu et al., 1973; Szakács and Seghedi, 1995b; Seghedi et al. 1995). The magmatism developed in the Rodna-Bârgău area between 8.3-11.9 My, in the Călimani-Gurghiu-Harghita segment around 10 My to 30 ky and in the Perșani Mountains between 1.2 My and 600 ky respectively (Pécskay et al., 2006; Harangi et al. 2010). The Rodna-Bârgău area is characterized by intrusive magmatism and lack of volcanic activity (Rădulescu and Dumitrescu, 1982; Ureche, 1999, fig.1). The magmatic products are represented by cone-shaped intrusive bodies composed of andesites, microdiorites, dacites and rhyolites (Băncilă, 1958; Peltz et al. 1971; Rădulescu and Dumitrescu, 1982; Nițoi et al., 2000). The Rodna-Bârgău volcanic intrusions are penetrating Paleogene sedimentary units and metamorphic units of Rodnei Mountains, which consist of crystalline schists, amphibolites and crystalline limestone and dolomites (Mutihac, 1990; Mosonyi, 1998).

The Călimani-Gurghiu-Harghita area is the southernmost and the longest (160 km) continuous volcanic chain, subdivided into four distinct geographical segments: Călimani, Gurghiu, North Harghita, South Harghita made of a row of adjacent composite volcanoes and their peripheral volcanoclastic aprons (Szakács and Seghedi, 1995b, Figure 1). Volcanic products are calc-alkaline rocks, andesites, dacites and in the southern part of the chain shoshonitic rocks

(Rădulescu et al. 1973; Seghedi et al. 1995; Szakács and Seghedi, 1995b; Seghedi et al. 2004). The southernmost part of the study area is characterized by the basaltic volcanic products of the Perșani Mountains (Seghedi and Szakács, 1994; Panaiotu et al., 2004). Around the volcanic cones volcanoclastic aprons have developed, extending over the Neogene sediments of the Transylvanian Basin (Szakács and Seghedi, 1995a, 1995b). The volcanoclastics cover the Paleogene and Neogene sedimentary deposits of the Transylvanian Basin, made up of alternations of marls, silty clays and sandstones, volcanic tuff and salt deposits with a thickness up to 3 km in the eastern side of the Transylvanian Basin (Paucă, 1967; Krézsek and Filipescu 2005; Krézsek and Bally, 2006).

The proximity of the volcanic range is characterized by persistent free gas emanations, dry CO₂ diffuse degassing, bubbling pools and mofettes, and occurrence of sparkling mineral water (Pricăjan, 1972; Vaselli et al. 2002; Jánosi et al. 2005; Kis and Baciú, 2013). Methane emissions are related to natural gas fields of the Transylvanian Basin. Gas reservoirs are located in dome-shaped anticlines at the level of Middle-Upper Miocene detritic sequences, followed by thick salt horizons. Mud volcanoes and dry methane gas seeps are often associated to gas reservoirs. At the Eastern margin of the basin, small mud volcanoes and dry gas seeps were discovered at Odorheiu Secuiesc, Praid, Corund and Homorod (Baciú et al. 2007; Krézsek et al. 2010; Etiope et al. 2011; Ionescu, 2015), locations that were included in our analysis.

The tectonic structure of the area is marked on the north by a NE-SW oriented fault system along the Someș Valley, next to the metamorphic units of Rodnei Mountains. In the southern part the anticlines of the methane reservoirs, and dome-shaped salt diapire structures of the salt, as well as NW-SE overthrust fold system, characterize the tectonic setting (Săndulescu, 1984; Krézsek et al. 2010).

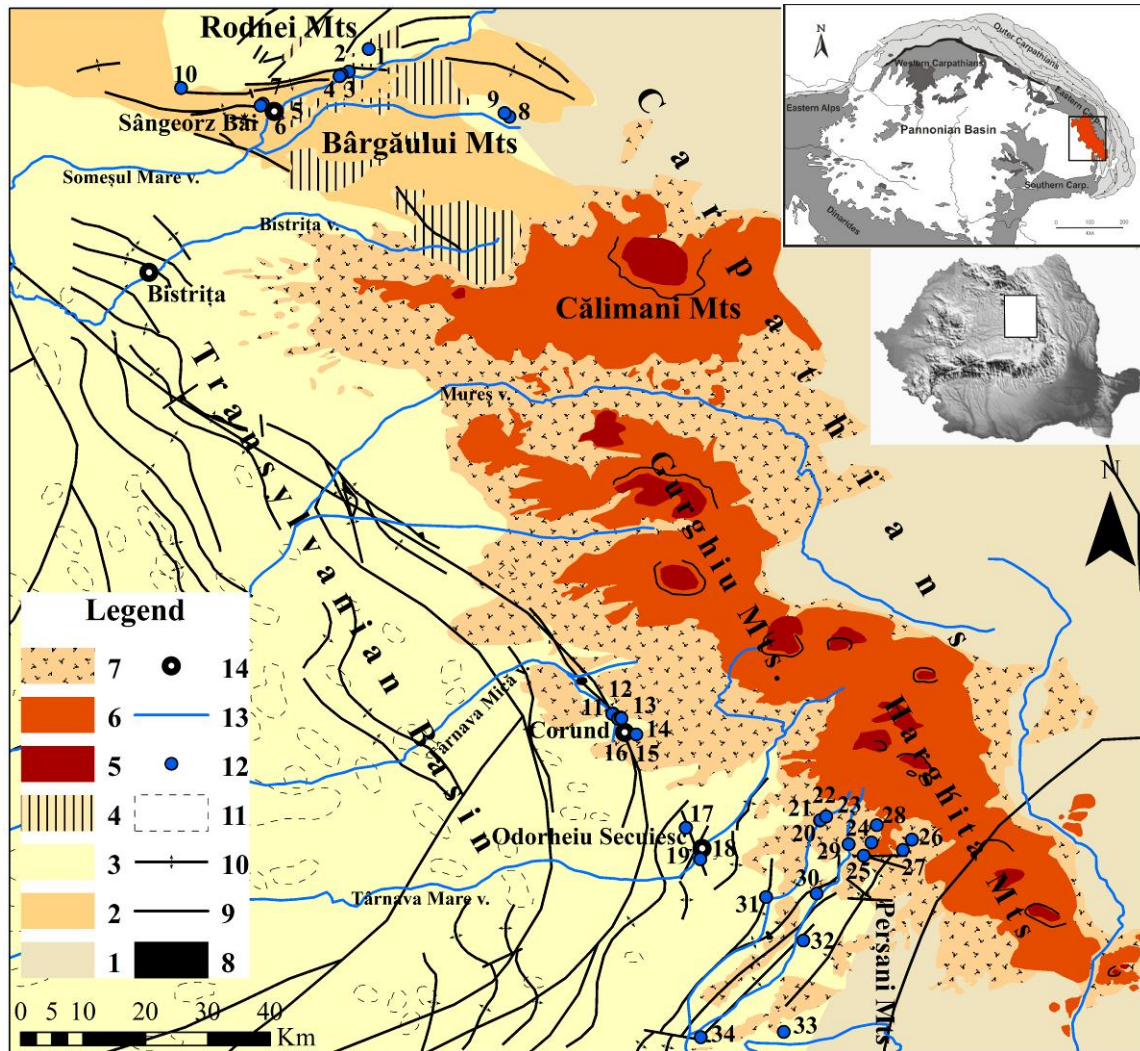


Figure 1 – Geological sketch map of the study area. The numbers of the sampling sites are the same as in the tables. Legend: 1 – Carpathian orogenic belt, 2 – Paleogene sediments of the Transylvanian Basin, 3 – Miocene sediments of the Transylvanian Basin, 4 – Magmatic intrusions, 5 – Volcanic centres, 6 – Proximal volcanic deposits, 7 – Distal volcanic deposits, 8 – Salt deposits, 9 – Faults, 10 – Anticlines, 11 – Hydrocarbon reservoirs, dome structures, 12 – Sampling points, 13 – Rivers, 14 – Localities. (Modified after Răileanu and Rădulescu, 1967; Ianovici et al. 1968; Ticleanu et al. 1980; Peltz et al. 1983)

3. Sampling and analytical methods

Water samples from springs and wells were collected at 34 sites spread over a 200 km-long transect in the boundary area between the Neogene-Quaternary volcanic arc and the sedimentary deposits of the Transylvanian Basin.

The water samples for dissolved gas analyses were stored in 240 cm³ pyrex glass bottles and sealed in the field by silicon/teflon septa using special pliers following the indications and recommendations described in Capasso and Inguaggiato, (1998) and Italiano et al. (2014). All the samples were collected taking care to avoid any air contamination (bottles sealed underwater with no direct contact with air) and kept upside down and with the neck submerged in salty water to avoid helium diffusion through the silicon septum. Chemical and isotopic analyses were performed 2 weeks after sampling, paying attention to minimize the effects on the isotopic composition of helium due to the permeation of atmospheric helium and leakage of dissolved helium through pyrex glass and septum as described in detail in Sano and Fischer, 2013 and Italiano et al., 2014 (Appendix).

Field measurements of temperature, pH, redox-potential (Eh), and electrical conductivity (EC) have been performed by a multi-parameter device (Multi 350i, Weilheim). Contents of dissolved HCO₃ were measured in situ by titration.

The collected samples have been measured at the INGV Palermo geochemical laboratory (Italy), where analyses were carried out following the recommendations and limitations described in Italiano et al. (2014). The dissolved gases were extracted after equilibrium was reached at constant temperature with a host-gas (high-purity argon) injected in the sample bottle (further details found in Italiano et al. 2009, 2013). Chemical analyses were carried out by gas-chromatography (Perkin Elmer Clarus 500, equipped with a double TCD-FID detector) using argon as the carrier gas. Typical uncertainties are within $\pm 5\%$ (1σ).

Out of the 34 samples, 24 were considered for ³He/⁴He ratio determinations. Helium isotope analyses were carried out on gas fractions extracted following the same procedure as for the chemical analyses and purified following methods described in the literature (Sano and Wakita 1988; Italiano et al. 2001). The isotopic analysis of the purified helium fraction was performed by a static vacuum mass spectrometer (GVI5400TFT) that allows the simultaneous detection of ³He and ⁴He ion beams, thereby keeping the ³He/⁴He error of measurement to very low values. This method has been tested for precision and accuracy in Inguaggiato and Rizzo (2004), yielding satisfactory results when water samples are analyzed within 2-3 weeks. Typical uncertainties in the range of low-³He samples are better than $\pm 5\%$ (1σ). Although some He content are lower than in ASW (samples #1, #12, and #15), the measurement can be considered reliable. A fractionation is expected between noble gases with very different diffusivity in waters and the depletion with respect to ASW may indicate that these waters undergone degassing before sampling.

Out of 34 samples, 29 were considered for $\delta^{13}\text{C}_{\text{TDIC}}$ measurements. Samples for carbon isotopes of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{TDIC}}$) were measured at the Hertelendi Laboratory of Environmental Studies, Institute for Nuclear Research, Hungarian Academy of Sciences, Debrecen. In 500 ml of sample water the pH was increased above 11 by adding concentrated solution of NaOH. Afterwards, BaCl_2 solution was added to the water so that the dissolved carbonate was precipitated in BaCO_3 form. Isotopic analyses were carried out with an automated GASBENCH II sample preparation device attached to a Thermo Finnigan Delta Plus XP mass spectrometer. Carbon isotopes of the dissolved inorganic carbon are expressed as $\delta^{13}\text{C}$ values relative to VPDB. The precision of the measurements is better than $\pm 0.1\%$ for $\delta^{13}\text{C}$.

4. Results

Sample IDs, names, geographical coordinates (in WGS84), altitude and source type (spring or well) are listed in Table 1. The molecular composition of the dissolved gases is reported in Table 2, while the isotopic composition of helium and carbon is listed in Table 3.

The collected samples included springs and wells with outlet temperatures between 10.8 and 24.3°C and pH varying between 6.05 and 7.87. The total dissolved solids ranged from 384 mg/L to 275,000 mg/L, while the HCO_3^- content falls between 305-7625 mg/l. Some springs were characterized by travertine deposition due to the high carbonate concentrations.

4.1 – Chemical composition of dissolved gases

The chemical composition of the dissolved gases was calculated taking into account the solubility coefficients (Bunsen coefficients “ β ”) of each gas species, 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 2) show that CO_2 , ranging from 9.06×10^{-3} to $1.99 \text{ cm}^3\text{STP/g}_{\text{H}_2\text{O}}$ is the most abundant component of the dissolved gases. The other components, with contents lower by one order of magnitude, display N_2 ranging from 2.43×10^{-3} to $1.63 \times 10^{-2} \text{ cm}^3\text{STP/g}_{\text{H}_2\text{O}}$, O_2 between 1.19×10^{-5} - $7.61 \times 10^{-3} \text{ cm}^3\text{STP/g}_{\text{H}_2\text{O}}$, CH_4 from 1.64×10^{-7} to $7.26 \times 10^{-3} \text{ cm}^3\text{STP/g}_{\text{H}_2\text{O}}$, H_2 between 1.83×10^{-7} - $9.34 \times 10^{-4} \text{ cm}^3\text{STP/g}_{\text{H}_2\text{O}}$, CO between 7.43×10^{-9} - $5.57 \times 10^{-7} \text{ cm}^3\text{STP/g}_{\text{H}_2\text{O}}$ and He ranging between 3.08×10^{-8} and $2.3 \times 10^{-5} \text{ cm}^3\text{STP/g}_{\text{H}_2\text{O}}$.

4.2 – Isotopic composition of helium and total dissolved inorganic carbon

Table 3 lists the results of helium isotopic analyses normalized to the atmosphere and expressed as R/Ra values (where R = $^3\text{He}/^4\text{He}$ sample; Ra = atmospheric $^3\text{He}/^4\text{He}$ ratio = 1.382×10^{-6} , Sano et al., 2013). The $^4\text{He}/^{20}\text{Ne}$ ratio ranges between 0.3 and 126.2 that, if compared to 0.267 assumed to be the representative $^4\text{He}/^{20}\text{Ne}$ for an Air Saturated Water at 20°C (Holocher et al. 2002), it spans from almost atmospheric (samples #1, 2, 6, 9, 10, 12 and 15) to >400 times with respect to the ASW (Sample #33, Table 3). Based on the measured $^4\text{He}/^{20}\text{Ne}$ 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 $^4\text{He}/^{20}\text{Ne}$ values for ASW, assuming a recharge temperature of 10°C. The $^3\text{He}/^4\text{He}$ values corrected for air contamination (R/Ra_c) range between 0.15 and 0.96 overlapping the range normally associated to crustal volatiles and giving clues of contribution from magmatic volatiles (Mamyrin and Tolstikhin, 1984). In order to check the reliability of the isotopic data measured in dissolved gases, check-points were introduced with some data from bubbling gases from the same sites already reported in literature (see Table 3 marked with italics, Corund (#11, 12, 13, 14, 15, 16 this work; #35 Vaselli et al., 2002), Băile Homorod (#20, this work; #36 Vaselli et al., 2002) and Homorod Brasov (#33 this work; #62-63 Baciú et al., 2007; #72 Etiope et al., 2011) sites. Although our data deal with the dissolved gases, the helium isotopic ratios are in good agreement with former results gained for free gases. Due to the large air He contribution to those samples with He/Ne ratios below 0.5 (#1, 2, 6, 9, 10, 12, 15), they were not considered in the helium discussion.

The measured carbon isotopic composition of the total dissolved carbon species spans over a $\delta^{13}\text{C}_{\text{TDC}}$ range between -15.6 and +5.32‰ VPDB (Table 3).

5. Discussion

Recent papers show the importance of the dissolved gases as indicators of processes occurring in crustal environments, governed by different mechanisms, including chemical and isotopic fractionation, mixings and exchanges between gases moving across different water bodies during its underground circulation, and mixing of fluids of different types (e.g. Chiodini et al. 2004; Ray et al., 2009; Pinti et al., 2011; Barry et al., 2013; Italiano et al. 2014; Marrero-Diaz et al. 2015; Benavente et al. 2016; Birke et al., 2016). Due to the geological variety of the Eastern Carpathians and Transylvanian Basin, wide range of volatiles can be produced which interact with the infiltrating water. The ranges of temperature (from 10.8 to 24.3°C, Tab. 1) and TDS

from 384 to >273,000 mg/L recorded for the mineral waters, implies much variability in the dissolved gas (Tables 2 and 3), due to either the endogenic production of volatiles and the interaction between gas and water which always affect the pristine composition of the gas assemblage, depending on the water/gas mass balance and the time-length of the interactions.

5.1 – Chemistry of dissolved gases

It is well documented that volcanic gases and hydrocarbons (composed mostly by pure methane) are present in form of free gases (seeps and mofettes) in the study area (e.g. Althaus et al. 2000; Vaselli et al. 2002; Etiope et al. 2004; Baciu et al. 2007). The chemical composition of the dissolved gases extracted from the water samples shows the ubiquitous presence of CO₂. Infiltrating air saturated water contain oxygen and nitrogen as the major dissolved gas species with concentrations of 4.8×10^{-3} and 9.6×10^{-3} cm³STP/g_{H2O} at 20°C, respectively. During circulation of water, oxygen content decreases because of bacterial activity and oxidation reactions. Thus the oxygen content and the N₂/O₂ ratios are quite variable in any natural water.

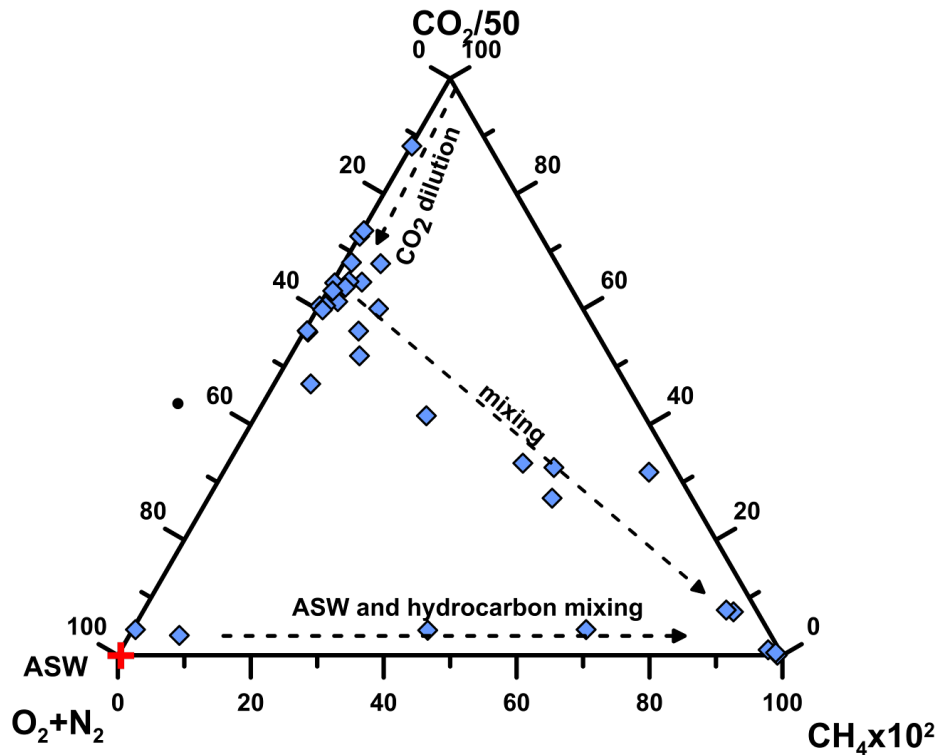


Figure 2 – CH₄ x 10²-CO₂/50-ASW (O₂+N₂) triangular diagram. The diagram shows the relative contents of atmospheric-type components (O₂+N₂), CO₂ and CH₄. The samples distribution highlights mixing of different gas species and the occurrence of gas-water interaction (CO₂ dilution), processes that significantly change the

composition of the pristine gas. Mixings occur between atmospheric and methane and atmospheric, methane and CO₂ gas species. Sample marks: this work, blue filled diamonds.

Figure 2 plots the relative concentrations of the most abundant gas-components, CO₂, CH₄ and O₂+N₂. Most of the samples plot along an ASW diluted-CO₂ and CH₄ mixing line, while some samples plot on a O₂+N₂-CH₄×10² mixing line, showing that the dissolved gas is almost in all cases a mixture of these three main components. The samples falling along the CO₂-O₂+N₂ mixing line show an almost constant CO₂/ASW ratio of 95 which is about 3000 times the atmospheric ratio, with an increasing CH₄ 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). The mixing line O₂+N₂-CH₄ shows that a few samples display low CO₂ contents resulting of a binary mixing between ASW and a methane-rich source. It is reasonable to assume that CH₄ comes from natural gas reservoirs of the Transylvanian Basin boundary (low CO₂/(O₂+N₂) ratio on Fig. 3; samples #28 from Vlăhita, #30 from Merești, 32 from Crăciunel, #33 from Homorod Brașov, #34 from Racoș), also confirmed by literature data (Baciu et al. 2007). Figure 2 also highlights the occurrence of gas-water interaction in the form of CO₂ dilution by atmospheric gases (arrows pointing to ASW). The less soluble species (N₂, CH₄) denote concentrations well above the equilibrium with the ASW which testifies that besides mixing phenomena between a shallow (atmospheric-type) and deep (volcanic and/or crustal-type) source, the occurrence of gas-water interaction processes at variable extents (dilution of the primary deep gas by an atmospheric component carried by the groundwater) account for the final composition of the dissolved gas.

5.2 – Helium isotopes

It is well known that helium comes from three different and well distinguishable sources (mantle, crust and air) marked by different isotopic ratios. Due to its chemical inertness, helium is a useful tracer of different geological environments and its isotopic ratio can be changed mainly because of physical processes such as mixing or degassing (Mamyrin and Tolstikhin, 1984; Ozima and Podosek, 2004). In continental settings, similar to the Eastern Carpathians–Transylvanian Basin boundary, it has been long established that the presence of mantle helium correlates well with tectonic and magmatic activity (Polyak and Tolstikhin 1985; Italiano et al. 2009; Klemperer et al.

2013; Bräuer et al., 2016), thus we evaluate the isotopic signature of the dissolved helium with the aim to constrain its provenance from volcanic or crustal products.

It was proposed that the genesis of the free gases vented over the area of the southern Harghita Mountains are mainly volcanic (Althaus et al. 2000; Vaselli et al. 2002) while the south-eastern Transylvanian Basin is characterized by crustal-type helium associated to methane reservoirs (Etioppe et al. 2004; Baciú et al. 2007). The highest He isotopic ratios of the area have been detected at the proximity of the volcanic arc, at Bálványos, where R/Ra values from 3.04 to 3.19 Ra (Althaus et al. 2000), 4.49, and 4.38 Ra (Vaselli et al. 2002) were measured. The lowest ratios have been detected in bubbling gases from the Transylvanian Basin, at Sărmășel, with values of 0.02 Ra (Baciú et al. 2007).

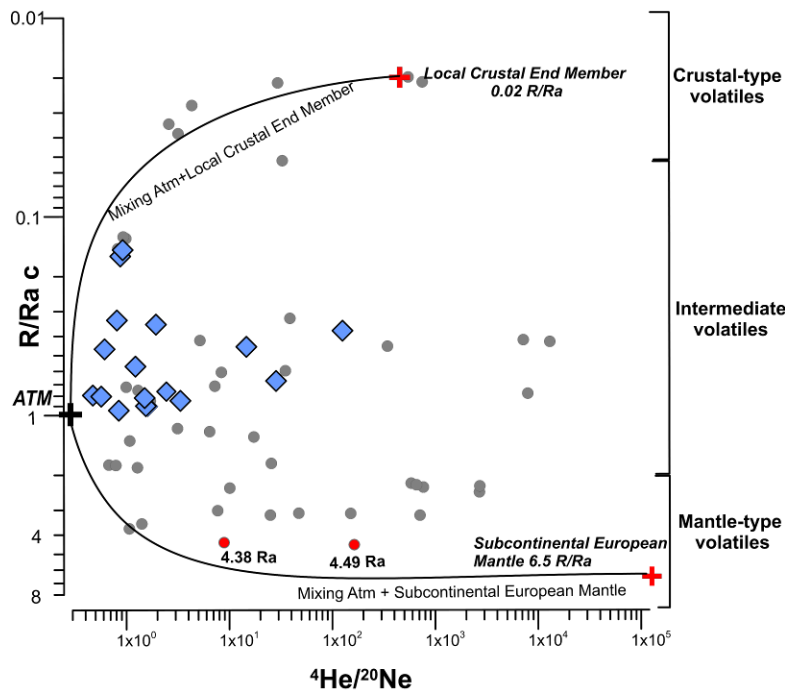


Figure 3 – Helium isotopic ratios (R/Ra values) and $^4\text{He}/^{20}\text{Ne}$ relationships. The theoretical lines represent binary mixing trends of atmospheric helium with mantle-originated and crustal helium. The assumed end members for He-isotopic ratios and $^4\text{He}/^{20}\text{Ne}$ ratios are: ATM (1 Ra, $\text{He}/\text{Ne}=0.267$ at 20°C , Holocher et al., 2002); Subcontinental European Mantle (6.5 Ra and $^4\text{He}/^{20}\text{Ne}$ ratio = 1,000; Dunai and Baur, 1995); Local Crustal End Member represented by the lowest value of 0.02 Ra and $^4\text{He}/^{20}\text{Ne}$ ratio = 10,000. Sample marks: this work blue filled diamonds; literature data for comparison: data after Althaus et al. 2000; Vaselli et al. 2002, Frunzeti, 2013 and Baciú et al. 2007 (grey filled dots), red crosses representing the proposed end members. The marked areas represent the ranges commonly accepted for crustal and volcanic gases, including samples with mantle helium content of 1-15% considered as “intermediate volatiles” (Pik and Marty, 2008).

All the measured isotopic ratios of dissolved helium along the study area are well above the crustal range of 0.02 Ra. The highest ratios in the range of 0.94-0.90 Ra_c, (samples #11, 14, 16 from the Corund area, Fig. 1) and 0.82-0.84 Ra_c (samples #17-18 from the Odorheiu Secuiesc) show ³He contribution of volcanic origin, associated to He/Ne ratios above the ATM taken as 0.267 (Air Saturated Water, at 20°C, Holocher et al., 2002). On the contrary, samples showing very low helium abundance raised the possibility of tritiogenic helium input. In the lack of rainwater tritium compositions for the area we could only estimate the tritium contribution from data on spring waters (Corund, Homorod Braşov, Kis, 2013). At these sites the tritium abundance was very low, between 0.020 and 1.106 TU, meaning that the ³He originating from the decay of these should not be significant, and the contribution of tritiogenic helium is not large.

Assuming that the parent mantle ratio was not significantly different from the 6.5 Ra, represented by the Subcontinental European Mantle (Dunai and Baur 1995), the measured ³He/⁴He ratio might be lowered by input of volatiles produced in the crust. The Subcontinental European Mantle has been taken as mantle-type end member, and the value of 0.02 R/Ra (Baciu et al. 2007) as local crustal end member, to compute the theoretical binary mixing lines of figure 3 (³He/⁴He vs. ⁴He/²⁰Ne ratios; where our samples are plotted together with literature data. The plot shows a very wide range of ³He/⁴He ratios spanning from the range of crustal to volcanic-type volatiles. As expected, most of our samples fall close to the atmospheric ratios. Some samples show a ³He enrichment, and fall in the range between crustal and volcanic volatiles, considered as “intermediate” (Pik and Marty, 2008) and some samples (e.g. #19, 31 and 33) lay on a possible mixing line between the atmosphere and the crustal end member. 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. For instance, the high helium content (>1% by volume) and the ³He/⁴He ratio measured in the hydrocarbon gases of Homorod are clear indications of mixings between a deep volcanic component with shallower crustal volatiles due to the presence of faults, described also by Etiope et al. 2011.

Using the approach based on a ternary mixture (atmospheric, mantle and crust): the measured ³He/⁴He and ⁴He/²⁰Ne ratios (calculation that includes atmospheric components, so for

this reason the uncorrected $^3\text{He}/^4\text{He}$ ratio was used, Sano and Wakita, 1985), and the selected end-members, we estimated the percentage of magmatic helium in our samples. We used the Subcontinental European Mantle as volcanic end-member (6.5 Ra) and 0.267 as representative for $^4\text{He}/^{20}\text{Ne}$ ratio for Air Saturated Water (Holocher et al., 2002) (Figure 4). The figure clearly shows the mixing between the atmospheric and radiogenic helium as well as the presence of magmatic helium in proportions between 2-16.45%. The highest contribution of radiogenic He is recorded in samples from the Transylvanian Basin (marked as T.B. #31 and 33). The “most magmatic” are represented by the samples closer to the recent volcanic products (sample # 14, 16, 17, 18).

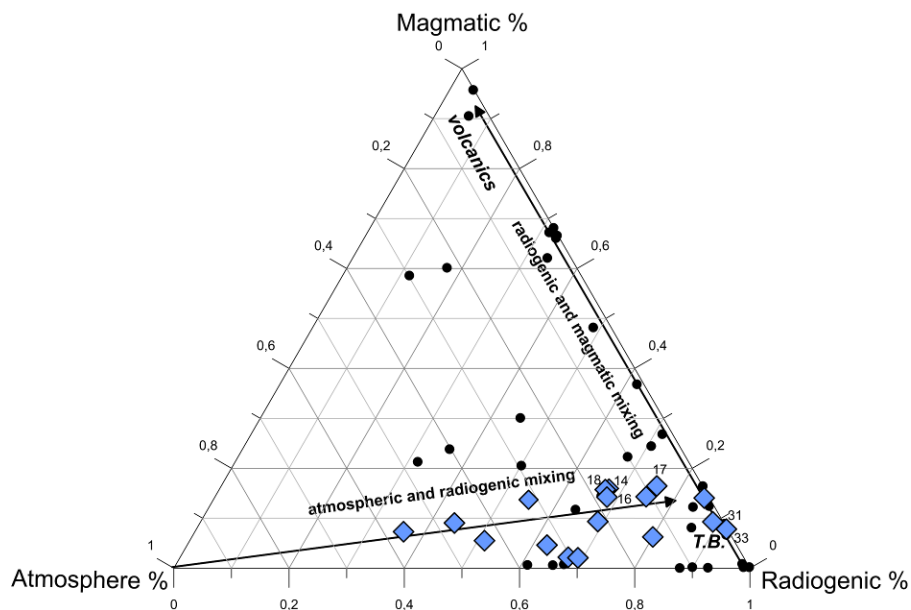


Figure 4 Ternary plot showing the atmospheric, radiogenic and mantle He contribution. The arrows show atmospheric-radiogenic and radiogenic-magmatic mixing. Symbols as in Figure 3, literature data (black dots) are plotted on the figure for reference (data from Vaselli et al., 2002; Althaus et al., 2000; Baciú et al., 2007)

5.3 – Carbon isotopes

Most of the waters display interactions with a CO_2 -dominated gas that partially dissolves in the water as bicarbonate ion. Gaseous CO_2 isotopically equilibrates with HCO_3^- and CO_3^{2-} ions in the solution and the mole fraction of each species will be a function of the pH. The $\delta^{13}\text{C}$ of total dissolved inorganic carbon (TDIC) is known to be a useful geochemical tool for investigating possible rock-water-gas interaction processes when CO_2 is involved as dominant gas species. The

primary natural CO₂-sources, such as mantle-derived, metamorphic and biogenic, have different isotopic signatures which, although partly overlapping because of the isotope fractionation due to the CO₂ reactivity, may provide information on the original signature of the parent gas and the possible fractionation processes responsible for the final carbon isotopic composition. The measured $\delta^{13}\text{C}_{\text{TDIC}}$ cover a range from -15.6 to +5.32 ‰ vs. VPDB showing the existence of multiple C sources besides processes like isotopic fractionation or degassing.

Since the gas-water interaction processes may occur at variable extents during gas uprising, we estimated the theoretical isotopic composition of the gaseous CO₂ that reacted with the groundwater. The $\delta^{13}\text{C}_{\text{CO2aq}}$ and $\delta^{13}\text{C}_{\text{HCO3}}$ can be computed considering the dissolved CO₂ and HCO₃⁻ mole fraction (χ), calculated considering the HCO₃⁻ values and pH, and the isotope enrichment factors (ϵ) for the CO_{2gas}-HCO₃ ($\epsilon\alpha$) and the CO_{2gas}-CO_{2aq} ($\epsilon\beta$) systems, following the equation and methodology given by Deines et al. (1974), Mook et al. (1974), Zhang et al. (1995):

$$\delta^{13}\text{C}_{\text{CO2}} = \delta^{13}\text{C}_{\text{TDIC}} - (\epsilon\alpha * \chi_{\text{HCO3}} + \epsilon\beta * \chi_{\text{CO2}})$$

Further details on the methodology of calculation are given in the Appendix.

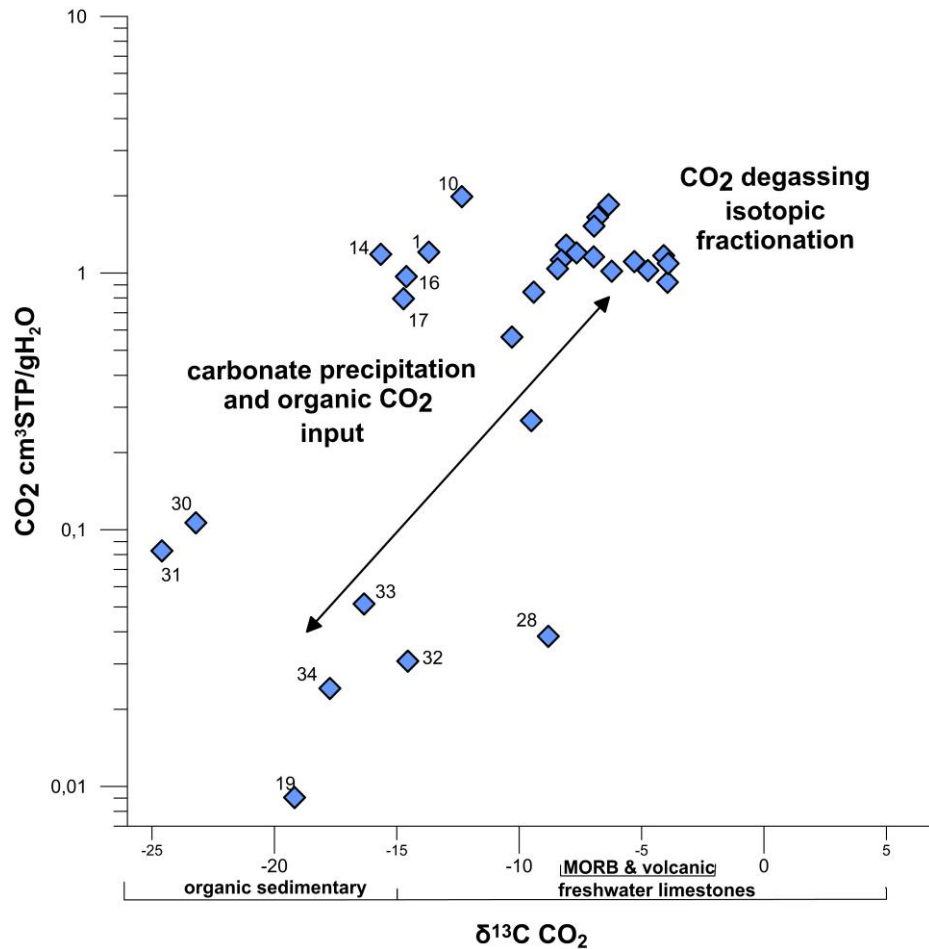


Figure 5 – CO₂ content vs. calculated $\delta^{13}\text{C}_{\text{CO}_2}$. The theoretical isotopic composition of the CO₂ interacting with the groundwater is recalculated following Deines et al., 1974, Mook et al., 1974 and Zhang et al., 1995. The plot depicts a clear direct correlation of CO₂ content and isotopic ratio. The trend contemporary denotes the fractionation with quantitative loss of gaseous CO₂ and its light isotope as well as the occurrence of further fractionation processes. Symbols as in Figure 3.

The recalculated values range between -24.59 to -3.91 ‰ and are plotted on Figure 5. The figure shows a direct correlation between the amount of CO₂ and the estimated isotopic composition. In some samples the high isotopic values (-3.9 to -8 ‰) are in the range proposed for carbon of different sources ($\delta^{13}\text{C}$ of freshwater carbonates ~ -15 to 2 ‰; marine carbonates $\delta^{13}\text{C} \sim -3$ to $+2$ ‰ Hoefs, 2009; magmatic carbon, including MORB and volcanic gases $\delta^{13}\text{C} \sim -7.2$ to -2 ‰, Giggenbach et al., 1991; Sano and Marty, 1995). These samples have dissolved CO₂ content of about $1000 \text{ cm}^3\text{STP/L}$ and are affected by intense gas separation with gas bubbling, visible on

the field. The shifts towards the higher values of carbon isotopic ratios are likely related to carbon fractionation due the preferential loss of $^{12}\text{CO}_2$. This phenomena was also detected for spring waters from the Apennines, with the process of $^{13}\text{CO}_2$ enrichment demonstrated under laboratory conditions (Chiodini et al., 2000, 2011, 2013) and in spring waters from Chile, where the $^{13}\text{CO}_2$ enrichment was attributed to phase separation and related isotopic fractionation between water and gas (Ray et al., 2009).

In contrast, samples shifted towards depleted $^{13}\text{CO}_2$ values (up to -24.6‰) are characterized by the lack of gas bubbling and travertine deposition, or both bubbling and carbonate precipitation occurring at the same time (eg. #1, 10, 14, 16, 17, 19, 30, 31, 32, 33, 34). Freshwater carbonate deposition is associated with the heavy isotope loss and lower isotopic values of the residual gaseous CO_2 (Hoefs, 2009, Ray et al., 2009). Moreover samples # 19, 30, 31, 32, 33 also show relatively high dissolved CH_4 content with respect to the other sites, with isotopic composition of carbon $\delta^{13}\text{C}_{\text{CH}_4}$ ranging between -30 and -17‰ (VPDB) (Ionescu et al., unpublished data), so it is reasonable to assume that organic CO_2 , depleted in ^{13}C , related to hydrocarbons and organic matter (organic carbon $\delta^{13}\text{C} \sim -20$ to -37‰ , Hoefs, 2009; Gamo et al., 2010), as well as carbonate precipitation, responsible for the heavy isotope loss, may account for the final isotopic composition of these samples.

5.4 – $\text{CO}_2/{}^3\text{He}$ ratios

The $\text{CO}_2/{}^3\text{He}$ corrected ratios, including the air-contaminates samples (#1, 2, 6, 9, 10, 12, 15) span over four orders of magnitude (from 2.92×10^9 to 3.02×10^{13}) covering the range proposed for mantle ($2\text{--}7 \times 10^9$ for MORB, Marty and Jambon, 1987) and crustal continental fluids (3×10^{13} , O’Nions and Oxburgh, 1988). Since He isotope ratios can only be modified by the admixture of He with a different isotopic signature, i.e. from a different reservoir, the coexistence of low ${}^3\text{He}/{}^4\text{He}$ ratios (namely high crustal He component) and mantle-like to crustal-like $\text{CO}_2/{}^3\text{He}$ ratios, suggests that the ratio is modified by a mixing of crustal and mantle-derived helium, or, alternatively, the crustal component ratios spans over a wide range due to CO_2 fractionation.

Figure 6 shows that on the basis of the wide range in the $\text{CO}_2/{}^3\text{He}$ c ratio and its relationship with the helium isotopic composition, the origin of CO_2 could be variable. The samples situated in the northern area are falling in the field of crustal volatiles, proven also by the very low proportions

of mantle-derived helium. Considering the geological structure of the northern part of the area, presence of crystalline carbonates and metamorphites, that were crosscut by magmatic intrusions, we might assume that CO₂ comes from the thermal alteration of these carbonates in the deep, due to the heat provided by the magmatics.

The CO₂/³He c ratios calculated for springs and wells located in the southern part of the study area cover a wider range between MORB-like values 2.9x10⁹ (#19) and 3.02x10¹³ (#24). These recorded values overlap the CO₂/³He range including magmatic and crustal values, indicating that there is a contribution of mantle-derived fluids, at proportions discussed in the previous section (up to 16.45% magmatic He, Section 5.2, Fig. 4).

Our samples are clearly affected by secondary processes, like degassing and carbonate precipitation (gas-water interaction at different levels), which modify the original chemical and isotopic compositions. Due to the isotopic fractionation it is hard to make a clear distinction between CO₂ of magmatic and crustal origin, however the isotopic data points to these two major sources. Considering the tectonic setting of the study area, it is possible to have a mixing of the two components. The provenance of CO₂ as suggested by the geologic-tectonic setting and confirmed also by the isotopic composition can be either from magmatic degassing related to the proximity of Neogene volcanic structures, and the presence of crustal-derived fluids related to the alteration of deep-seated carbonates, suggested also by previous authors (Vaselli et al. 2002).

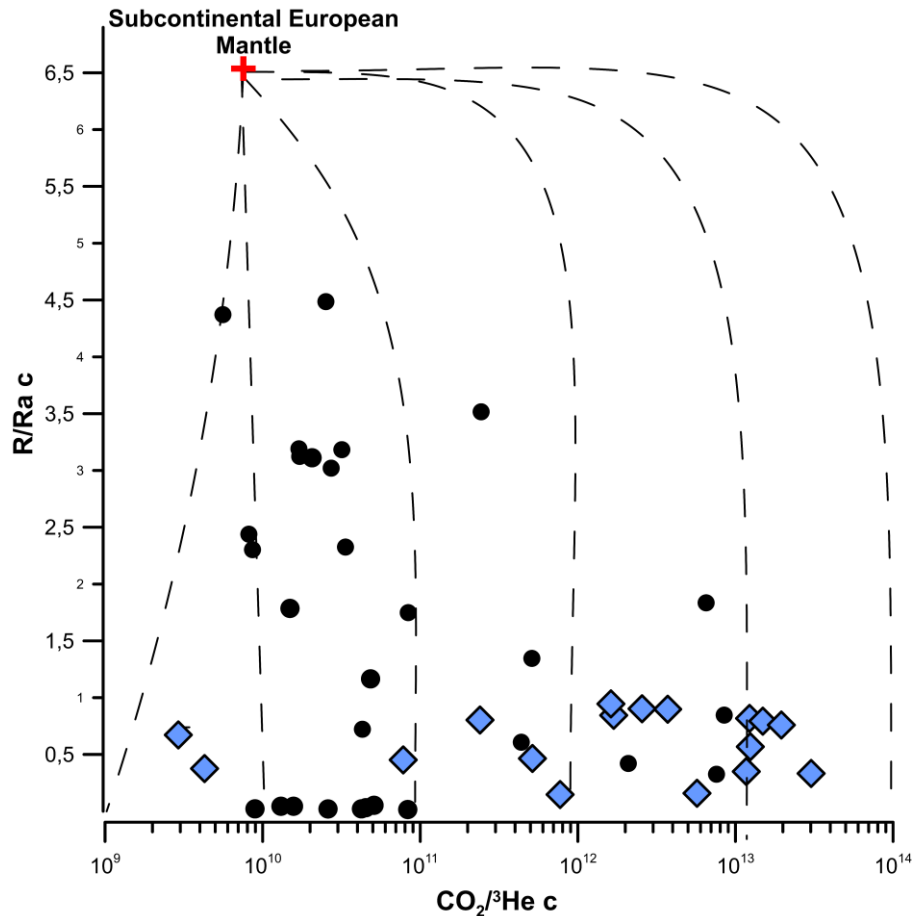


Figure 6 - Correlation diagram between the $\text{CO}_2/{}^3\text{He c}$ ratios and helium isotopic composition ($R/Ra c$). The grey-shaded areas cover the ranges for typical crustal and magmatic volatiles, after Sherwood-Lollar et al., 1997. The volcanic end-member is represented by the Subcontinental European Mantle (Dunai and Baur, 1995) and literature data involved for comparison by Althaus et al., 2000; Vaselli et al., 2002; Baciu et al., 2007. Symbols as in Figure 4.

6. Conclusions

The geochemical investigations on the gases dissolved in mineral waters circulating over the 200 km-long transect across the Transylvanian basin-Eastern Carpathians boundary allowed us to improve the knowledge on the fluids circulating in the area. The 34 mineral waters we collected show remarkable differences, related to the geotectonic setting of the area and, in turn, to different rock types where the circulating groundwater move across. The chemical composition of the dissolved gases shows that they are always a mixture of ASW with CO_2 -dominated volatiles, as well as relevant methane contents. The isotopic composition of helium and carbon allowed to constrain the origin of dissolved volatiles and to show that besides the obvious

atmospheric gas species, both volcanic and crustal gas sources feed the circulating groundwaters. Moreover the final composition (both chemical and isotopic) of the dissolved gases is the consequence of either the mixing of volatiles of different origin and the occurrence in variable extents of secondary processes like degassing and carbonate precipitation.

While mantle-derived helium was already described at the proximity of the volcanoes in free gases, our findings prove that presence of mantle-components, dissolved in the fluids may be present also at ~50 km distance away from the volcanic centres, considered the potential source for mantle volatiles.

The results we obtained clearly show that the geotectonic setting, and secondary processes like degassing, carbonate deposition and isotopic fractionation keep the ultimate control on the composition of the dissolved gases, thus indicating that the interpretation of the geochemical features of the volatiles carried by the circulating waters is a powerful tool to model groundwater circulation and to recover information on the origin and behaviour of the volatiles in the shallow crustal levels.

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APPENDIX

The $\delta^{13}\text{C}_{\text{TDIC}}$ represents the average of the isotopic composition of the dissolved carbon species and can be expressed as the isotopic balance of dissolved carbon species weighted on the respective inorganic carbon contents as equation 1.

$$\delta^{13}\text{C}_{\text{TDIC}} = (\delta^{13}\text{C}_{\text{CO}_2\text{aq}} * \chi_{\text{CO}_2\text{aq}} + \delta^{13}\text{C}_{\text{HCO}_3^-} * \chi_{\text{HCO}_3^-}) / M \quad (1)$$

where χ is the molar fraction and M is the total mass of dissolved carbon.

$\text{CO}_2(\text{aq})$ and HCO_3^- are predominant due to the pH range (6.05-7.87) of the sampled waters, therefore the observed $\delta^{13}\text{C}$ values for dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{TDIC}}$) are a function of the mole fraction of HCO_3^- .

According to Deines et al. (1974), Mook et al. (1974) and Zhang et al. (1995), the $\delta^{13}\text{C}_{\text{CO}_2\text{aq}}$ and $\delta^{13}\text{C}_{\text{HCO}_3^-}$ can be computed considering the isotope enrichment factors (ϵ) for the $\text{CO}_2\text{gas} - \text{HCO}_3^-$ (ϵ_α) and the $\text{CO}_2\text{gas} - \text{CO}_2\text{aq}$ (ϵ_β) systems. The isotopic ratio of the gaseous CO_2 can be recalculated following equation 2

$$\delta^{13}\text{C}_{\text{CO}_2} = \delta^{13}\text{C}_{\text{TDIC}} - [\epsilon_\alpha * \chi_{\text{HCO}_3^-} + \epsilon_\beta * \chi_{\text{CO}_2}] \quad (2)$$

The following table lists the parameters and the results of the calculations:

No.	Sample name	Sample name	pH	ϵ_α	ϵ_β	$\chi_{\text{HCO}_3^-}$	χ_{CO_2}	Total carbon mmoles/l	$\delta^{13}\text{C}_{\text{TDIC}}$ ‰VPDB	calculated $\delta^{13}\text{C}_{\text{CO}_2}$ ‰VPDB
1	Valea Vinului	Izvorul Pipirigi	6.53	9.41	-0.83	0.99	0.01	52	-4.34	-13.69
2	Rodna	Izvorul Doani	6.16	9.40	-0.83	1.01	-0.01	19	2.66	-6.79
3	Anies	Izvorul Hojda	6.31	9.18	-0.83	1.03	-0.03	27	nd	nd
4	Anies	Izvorul Travertin	6.65	9.27	-0.83	1.00	0.00	72	5.29	-3.95
5	Anies	Izvorul Anieş	6.64	9.30	-0.83	1.00	0.00	72	5.17	-4.10
6	Sangeorz Bai	Izvorul 9	6.63	8.95	-0.83	1.00	0.00	81	2.69	-6.22
7	Sangeorz Bai	Izvorul 7	6.58	8.87	-0.83	1.00	0.00	62	4.08	-4.74
8	Lunca Ilvei	Izvorul Ciriloi	6.42	9.48	-0.83	0.99	0.01	32	nd	nd
9	Lunca Ilvei	Izvorul Bolovan	6.51	9.54	-0.83	0.99	0.01	61	nd	nd
10	Parva	Izvorul Carpatia	6.38	9.52	-0.83	0.97	0.03	30	-3.16	-12.34
11	Corund	<i>P12 (Bugyogo)</i>	6.88	9.52	-0.83	1.00	0.00	79	-0.01	-9.51
12	Corund	<i>P9 (Fantana Sarata)</i>	6.28	9.07	-0.83	1.01	-0.01	71	-1.08	-10.30

13	Corund	<i>P7 (Dealul Melcului)</i>	6.58	9.15	-0.83	1.00	0.00	126	2.15	-6.96
14	Corund	<i>P5 (Izvorul Cseredombi)</i>	6.24	9.22	-0.83	1.01	-0.01	9	-6.34	-15.66
15	Corund	<i>P6 (Izvorul Pamu)</i>	6.46	8.75	-0.84	0.99	0.01	16	2.32	-6.35
16	Corund	<i>P1 (Izvorul Dióvapai)</i>	6.08	9.06	-0.83	1.00	0.00	8	-5.51	-14.61
17	Odorheiu Secuiesc	Szejke Izvorul Szejke	6.31	9.07	-0.83	1.03	-0.03	16	-5.4	-14.73
18	Odorheiu Secuiesc	Szejke Well	6.06	8.81	-0.84	1.00	0.00	120	nd	nd
19	Odorheiu Secuiesc	Kápolnásfürdő	7.87	8.99	-0.83	1.00	0.00	9	-10.19	-19.18
20	Homorod	<i>Izvorul Kálmán</i>	6.57	9.28	-0.83	1.00	0.00	18	5.32	-3.92
21	Homorod	Izvorul Fenyős	6.43	9.22	-0.83	0.99	0.01	24	3.8	-5.30
22	Homorod	Izvorul Köpüs	6.27	9.06	-0.83	1.01	-0.01	20	-0.22	-9.41
23	Homorod	Izvorul Lobogó	6.18	9.06	-0.83	1.01	-0.01	21	1.04	-8.08
24	Lueta	Izvorul Délű	6.49	9.29	-0.83	0.99	0.01	37	2.28	-6.94
25	Lueta	Izvorul Nádasszéki	6.25	9.36	-0.83	1.01	-0.01	20	1.81	-7.66
26	Chirui	Lobogó well	6.26	8.82	-0.84	1.01	-0.01	23	nd	nd
27	Chirui	Festő Spring	6.11	9.43	-0.83	1.00	0.00	16	1.19	-8.29
28	Vlăhița	Vlăhița thermal spring	6.79	8.01	-0.84	1.00	0.00	4	-0.82	-8.81
29	Vlăhița	Angol spring	6.07	8.80	-0.84	1.00	0.00	13	0.4	-8.43
30	Merești	Salty fountain	6.09	9.19	-0.83	1.00	0.00	8	-13.98	-23.21
31	Mărtiniș	Salty fountain	6.05	8.96	-0.83	1.00	0.00	5	-15.6	-24.59
32	Crăciunel	Spring	7.38	8.82	-0.84	1.00	0.00	11	-5.74	-14.55
33	Homorod Brașov	<i>Well</i>	7.8	8.93	-0.83	1.00	0.00	75	-7.41	-16.34
34	Racoș	Salty fountain	6.52	8.71	-0.84	0.99	0.01	18	-9.08	-17.73

Table 1

N o.	Site	Sample name	Type	Latitude	Longitude	H m	T° C °C	pH	Eh mv	EC ms/cm	HC O₃ mg/l	TDS mg/l
1	Valea Vinului	Pipirigi spring	b	47°27'18.9"	24°48'51.3"	603	11.9	6.53	15.8	4.95	2562	4558
2	Rodna	Doani spring	b	47°25'21.7"	24°47'07.9"	519	12	6.16	36.8	2.08	1159	1809
3	Anies	Hojda spring	nb	47°25'07.2"	24°46'31.2"	506	13.9	6.31	27.7	2.63	1586	2364
4	Anies	Travertine spring	b	47°24'58.8"	24°46'20.3"	504	13.1	6.65	9.2	6.88	4392	7273
5	Anies	Anies spring	b	47°24'58.2"	24°46'20.8"	492	12.8	6.64	9.8	6.94	4392	7295
6	Sangeorz Bai	9 spring	nb	47°22'35.6"	24°39'42.8"	452	15.9	6.63	10.8	11.1	4941	10104
7	Sangeorz Bai	7 spring	nb	47°22'27.4"	24°39'22.6"	460	16.6	6.58	6.8	6.5	3782	6479
8	Lunca Ilvei	Ciriloii spring	b	47°21'46.44"	25°00'36.3"	779	11.3	6.42	22.2	7.31	1952	5724
9	Lunca Ilvei	Bolovan spring	b	47°21'27.42"	25°01'01.98"	749	10.8	6.51	17.2	11.1	3721	9438
10	Parva	Carpatia spring	b	47°23'57.36"	24°32'38.52"	525	11	6.38	24.1	5.73	1769	4484
11	Corund	Bugyogó spring	b	46°29'55.3"	25°10'00"	535	11	6.88	-3.5	204	4819	184142
12	Corund	Salty Fountain	b	46°29'52.7"	25°09'56.1"	523	14.8	6.28	29.9	206	4392	197155
13	Corund	Csigadombi spring	b	46°29'27.8"	25°10'25.0"	570	14.1	6.58	13.6	207	7625	190267
14	Corund	Cseredombi spring	b	46°29'34.30"	25°10'38.00"	604	13.5	6.24	31.2	2.78	732	2713
15	Corund	Pamu spring	b	46°29'29.4"	25°10'43.5"	621	17.6	6.46	20.2	218	952	206249
16	Corund	Dióvápai spring	nb	46°28'6.00"	25°12'0.00"	616	14.9	6.08	38.6	0.6	3660	622
17	Odorheiu Secuiesc	Szejke spring	nb	46°20'02.07"	25°16'18.06"	524	14.8	6.31	28.5	3.3	976	2652
18	Odorheiu Secuiesc	Szejke Well	nb	46°20'2.4"	25°16'16.74"	533	17.1	6.06	42.4	210	7320	204414
19	Odorheiu Secuiesc	Kápolnásfürdő	nb	46°17'22.08"	25°17'33.66"	503	15.5	7.87	-58.2	13.2	549	7034
20	Homorod	Kálmán spring	b	46°20'40.50"	25°27'53.20"	699	13	6.57	12.9	2.38	1098	1886
21	Homorod	Fenyős spring	b	46°20'42.10"	25°27'54.90"	704	13.5	6.43	22.1	2.84	1464	2423
22	Homorod	Köpüs spring	b	46°21'01.00"	25°28'24.90"	729	14.9	6.27	29.7	2.02	1220	1924

23	Homorod	Lobogó spring	b	46°21'01.30"	25°28'24.00"	71 1	14. 9	6.1 8	35. 6	2.68	1281	2257
24	Lueta	Délú spring	b	46°18'45.42"	25°32'21.42"	74 6	12. 9	6.4 9	17. 7	4.21	2257	4013
25	Lueta	Nádasszéki spring	b	46°17'37.32"	25°31'40.98"	68 7	12. 3	6.2 5	31. 2	4.51	2244	3239
26	Chirui	Lobogó well	b	46°18'10.02"	25°35'12.18"	79 2	17	6.2 6	31. 2	2.13	1403	2029
27	Chirui	Festő Spring	nb	46°19'00.90"	25°35'49.56"	79 8	11. 7	6.1 1	38. 6	1.34	976	1326
28	Vlăhița	Vlăhița thermal spring	b	46°20'15.90"	25°32'49.20"	83 1	24. 3	6.7 9	1.7	0.45	366	385
29	Vlăhița	Angol spring	b	46°18'35.90"	25°30'22.50"	73 3	17. 2	6.0 7	41. 6	2.67	793	2123
30	Merești	Salty fountain	nb	46°14'21.2"	25°27'36.0"	58 0	13. 8	6.0 9	40	243	488	2739 68
31	Mărtiniș	Salty fountain	nb	46°14'03.0"	25°23'13.4"	49 8	15. 8	6.0 5	43. 2	243	305	2750 46
32	Crăciunel	Spring	nb	46°10'17.9"	25°26'27.3"	55 6	17	7.3 8	- 31. 2	8.3	793	5772
33	Homorod Brașov	Well	nb	46°01'57.0"	25°17'34.8"	44 8	16	7.8	- 55. 1	23	4575	1798 8
34	Racoș	Salty fountain	nb	46°02'24.78"	25°24'45.96"	47 2	18	6.5 2	17. 3	243	1098	2743 62

Table 1 – List of the sampled waters including location names, altitude and field data. Coordinates in WGS84, H=elevation, temperature, pH, Eh, , EC, TDS and HCO₃ values. B and NB in the Type column stand for bubbling and non bubbling site respectively.

Table 2.

N o.	Site	Sample name	He	Ne	H ₂	O ₂	N ₂	CO	CH ₄	CO ₂
			cm ³ STP/g _{H2O}							
1	Valea Vinului	Pipirigi spring	3.55x10 ⁻⁸	9.01x10 ⁻⁸	2.53x10 ⁻⁶	2.93x10 ⁻³	7.99x10 ⁻³	4.79x10 ⁻⁸	3.91x10 ⁻⁶	1.21
2	Rodna	Doani spring	5.81x10 ⁻⁸	1.31x10 ⁻⁷	3.10x10 ⁻⁶	2.21x10 ⁻³	1.07x10 ⁻²	1.07x10 ⁻⁷	2.72x10 ⁻⁵	1.65
3	Anieș	Hojda spring	bdl	bdl	5.99x10 ⁻⁷	3.23x10 ⁻³	8.97x10 ⁻³	bdl	3.22x10 ⁻⁷	9.39x10 ⁻¹
4	Anieș	Travertin spring	4.47x10 ⁻⁸	1.83x10 ⁻⁸	bdl	1.77x10 ⁻³	1.25x10 ⁻²	bdl	1.91x10 ⁻⁶	9.22x10 ⁻¹
5	Anieș	Anieș spring	bdl	bdl	3.62x10 ⁻⁶	7.32x10 ⁻³	1.63x10 ⁻²	2.49x10 ⁻⁷	2.74x10 ⁻⁵	1.17
6	Sângeorz Băi	9 spring	1.21x10 ⁻⁷	3.02x10 ⁻⁷	5.55x10 ⁻⁷	2.26x10 ⁻³	7.47x10 ⁻³	5.27x10 ⁻⁷	1.38x10 ⁻⁵	1.02
7	Sângeorz Băi	7 spring	bdl	bdl	bdl	4.69x10 ⁻³	1.02x10 ⁻²	3.55x10 ⁻⁸	4.11x10 ⁻⁵	1.02
8	Lunca Ilvei	Ciriloi spring	bdl	bdl	1.65x10 ⁻⁶	2.98x10 ⁻³	9.13x10 ⁻³	3.02x10 ⁻⁷	8.82x10 ⁻⁶	1.19
9	Lunca Ilvei	Bolovan spring	4.77x10 ⁻⁸	1.53x10 ⁻⁷	bdl	4.88x10 ⁻³	1.29x10 ⁻²	2.52x10 ⁻⁷	1.70x10 ⁻⁶	1.63
10	Parva	Carpatia spring	8.73x10 ⁻⁸	2.55x10 ⁻⁷	bdl	7.61x10 ⁻³	1.59x10 ⁻²	1.07x10 ⁻⁷	1.58x10 ⁻⁵	1.99
11	Corund	Bugyogó spring	1.25x10 ⁻⁷	1.48x10 ⁻⁷	4.58x10 ⁻⁴	6.73x10 ⁻⁵	4.05x10 ⁻³	2.49x10 ⁻⁸	1.01x10 ⁻⁴	2.66x10 ⁻¹
12	Corund	Salty Fountain	3.08x10 ⁻⁸	7.87x10 ⁻⁸	5.14x10 ⁻⁶	1.86x10 ⁻³	4.12x10 ⁻³	4.19x10 ⁻⁷	4.13x10 ⁻⁶	5.64x10 ⁻¹
13	Corund	Csigadombi spring	bdl	bdl	1.30x10 ⁻⁵	2.60x10 ⁻³	6.10x10 ⁻³	4.27x10 ⁻⁷	1.64x10 ⁻⁷	1.16
14	Corund	Cseredombi spring	3.70x10 ⁻⁷	2.29x10 ⁻⁷	bdl	8.13x10 ⁻⁵	1.13x10 ⁻²	2.90x10 ⁻⁸	2.80x10 ⁻³	1.18
15	Corund	Pamu spring	3.44x10 ⁻⁸	1.16x10 ⁻⁷	9.34x10 ⁻⁴	5.50x10 ⁻⁴	4.32x10 ⁻³	5.57x10 ⁻⁷	4.42x10 ⁻⁷	1.85
16	Corund	Dióvápai spring	2.09x10 ⁻⁷	1.35x10 ⁻⁷	3.60x10 ⁻⁶	4.46x10 ⁻⁴	1.26x10 ⁻²	7.01x10 ⁻⁸	2.58x10 ⁻⁴	9.70x10 ⁻¹
17	Odorheiu Secuiesc	Szejke spring	4.02x10 ⁻⁷	1.20x10 ⁻⁷	bdl	1.35x10 ⁻⁴	9.09x10 ⁻³	3.80x10 ⁻⁸	1.78x10 ⁻³	7.95x10 ⁻¹
18	Odorheiu Secuiesc	Szejke Well	8.53x10 ⁻⁸	5.66x10 ⁻⁸	3.82x10 ⁻⁵	2.56x10 ⁻⁴	2.91x10 ⁻³	2.38x10 ⁻⁷	4.80x10 ⁻⁴	1.19
19	Odorheiu Secuiesc	Kápolnásfürdő	3.32x10 ⁻⁶	1.16x10 ⁻⁷	bdl	1.19x10 ⁻⁵	5.49x10 ⁻³	7.45x10 ⁻⁹	7.26x10 ⁻³	9.06x10 ⁻³
20	Băile	Kálmán spring	1.11	9.06	1.61	2.52	1.13	5.24	3.15	1.09

	Homorod		$\times 10^{-7}$	$\times 10^{-8}$	$\times 10^{-5}$	$\times 10^{-3}$	$\times 10^{-2}$	$\times 10^{-8}$	$\times 10^{-5}$	
21	Băile Homorod	Fenyős spring	bdl	bdl	1.55×10^{-6}	2.79×10^{-3}	9.88×10^{-3}	8.07×10^{-8}	2.62×10^{-6}	1.11
22	Băile Homorod	Köpüs spring	bdl	bdl	4.50×10^{-6}	3.60×10^{-3}	9.40×10^{-3}	9.81×10^{-8}	1.05×10^{-6}	8.44×10^{-1}
23	Băile Homorod	Lobogó spring	bdl	bdl	5.01×10^{-6}	3.97×10^{-3}	9.19×10^{-3}	6.11×10^{-8}	3.92×10^{-5}	1.29
24	Lueta	Délői spring	1.09×10^{-7}	1.35×10^{-7}	8.53×10^{-6}	1.86×10^{-3}	9.00×10^{-3}	3.53×10^{-8}	8.71×10^{-7}	1.53
25	Lueta	Nádasszéki spring	bdl	bdl	1.20×10^{-5}	4.50×10^{-3}	$1.07E-02$	8.28×10^{-8}	3.88×10^{-6}	1.20
26	Chirui	Lobogó well	bdl	bdl	1.85×10^{-6}	4.30×10^{-3}	9.99×10^{-3}	8.59×10^{-8}	1.12×10^{-4}	9.04×10^{-1}
27	Chirui	Festő Spring	6.84×10^{-8}	1.45×10^{-7}	5.73×10^{-5}	4.06×10^{-3}	1.07×10^{-2}	5.49×10^{-8}	3.26×10^{-6}	1.13
28	Vlăhița	Vlăhița thermal spring	1.44×10^{-7}	2.52×10^{-7}	5.15×10^{-7}	2.83×10^{-3}	1.37×10^{-2}	2.74×10^{-8}	7.44×10^{-7}	3.85×10^{-2}
29	Vlăhița	Angol spring	1.83×10^{-7}	9.43×10^{-8}	8.32×10^{-6}	8.04×10^{-4}	1.08×10^{-2}	1.27×10^{-7}	3.15×10^{-4}	1.04
30	Merești	Salty fountain	8.49×10^{-8}	9.68×10^{-8}	5.55×10^{-5}	8.02×10^{-4}	3.00×10^{-3}	1.80×10^{-7}	2.20×10^{-3}	1.06×10^{-1}
31	Mărtiniș	Salty fountain	1.69×10^{-6}	1.15×10^{-7}	1.22×10^{-4}	3.63×10^{-4}	2.48×10^{-3}	2.24×10^{-7}	3.62×10^{-3}	8.28×10^{-2}
32	Crăciunel	Spring	1.95×10^{-7}	2.11×10^{-7}	6.44×10^{-7}	2.90×10^{-3}	1.31×10^{-2}	3.04×10^{-8}	1.35×10^{-5}	3.08×10^{-2}
33	Homorod Brașov	Well	2.30×10^{-5}	1.82×10^{-7}	1.83×10^{-7}	5.12×10^{-5}	1.21×10^{-2}	bdl	1.05×10^{-4}	5.14×10^{-2}
34	Racoșul de Jos	Salty fountain	7.24×10^{-8}	1.18×10^{-7}	2.80×10^{-5}	5.37×10^{-4}	2.43×10^{-3}	bdl	7.40×10^{-5}	2.41×10^{-2}
		ASW	4.85×10^{-8}	1.68×10^{-7}		4.80×10^{-3}	9.60×10^{-3}		1.00×10^{-9}	2.40×10^{-4}

Table 2 – Chemical composition of the dissolved gases. Reactive species (H_2 and CO) are not discussed in the text but listed to give comprehensive information on the chemical composition of the dissolved gas species. ASW (air Saturated Water) composition is reported as reference bdl = below detection limits; nd = not determined

Table 3

No.	Site	Sample name	He/Ne	Δ He/Ne	R/Ra	R/Ra c	^3He c	$\delta^{13}\text{C}_{\text{TDC}}$ (‰, VPDB)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰, VPDB)	$\text{CO}_2/^3\text{He}$ c	Reference
1	Valea Vinului	Izvorul Pipirigi	0.39	1.48	0.87	0.59	2.38×10^{-12}	-4.34	-13.69	4.17×10^{13}	a
2	Rodna	Izvorul Doani	0.44	1.66	0.83	0.57	2.77×10^{-12}	2.66	-6.79	3.58×10^{13}	a
3	Anieș	Izvorul Hojda	nd	nd	nd	nd	nd	nd	nd	nd	a
4	Anieș	Izvorul Travertin	2.45	9.18	0.79	0.76	5.04×10^{-12}	5.29	-3.95	1.95×10^{13}	a
5	Anieș	Izvorul Anieș	nd	nd	nd	nd	nd	5.17	-4.10	nd	a
6	Sângeorz Băi	Izvorul 9	0.40	1.50	0.89	0.68	1.10×10^{-11}	2.69	-6.22	8.98×10^{12}	a
7	Sângeorz Băi	Izvorul 7	nd	nd	nd	nd	nd	4.08	-4.74	nd	a
8	Lunca Ilvei	Izvorul Ciriloi	nd	nd	nd	nd	nd	nd	nd	nd	a
9	Lunca Ilvei	Izvorul Bolovan	0.31	1.17	0.95	0.66	2.64×10^{-12}	nd	nd	3.74×10^{13}	a
10	Parva	Izvorul Carpatia	0.34	1.28	0.99	0.94	5.67×10^{-12}	-3.16	-12.34	1.74×10^{13}	a
11	Corund	P12 (Bugyogo)	0.85	3.17	0.96	0.94	6.0710^{-11}	-0.01	-9.51	1.62×10^{12}	a
12	Corund	P9 (Fantana Sarata)	0.39	1.47	0.99	0.96	7.17×10^{-12}	-1.08	-10.30	1.38×10^{13}	a
13	Corund	P7 (Dealul Melcului)	nd	nd	nd	nd	nd	2.15	-6.96	nd	a
14	Corund	P5 (Izvorul Cseredombi)	1.62	6.06	0.92	0.90	3.8710^{-11}	-6.34	-15.66	2.55×10^{12}	a
15	Corund	P6 (Izvorul Pamu)	0.30	1.11	0.85	0.85	-1.44×10^{-12}	2.32	-6.35	-6.91×10^{13}	a
16	Corund	P1 (Izvorul Dióvápai)	1.55	5.80	0.92	0.90	2.6610^{-11}	-5.51	-14.61	3.71×10^{12}	a
17	Odorheiu Secuiesc	Szejke Izvorul Szejke	3.35	12.56	0.86	0.84	5.8510^{-11}	-5.40	-14.73	1.69×10^{12}	a
18	Odorheiu Secuiesc	Szejke Well	1.51	5.64	0.85	0.82	8.11×10^{-12}	nd	nd	1.23×10^{13}	a
19	Odorheiu Secuiesc	Kápolnásfürdő	28.51	106.77	0.68	0.67	1.42×10^{-8}	-10.19	-19.18	2.92×10^9	a
20	Băile Homorod	Izvorul Kálmán	1.23	4.60	0.66	0.57	7.94×10^{-12}	5.32	-3.92	1.24×10^{13}	a
21	Băile Homorod	Izvorul Fenyős	nd	nd	nd	nd	nd	3.80	-5.30	nd	a
22	Băile Homorod	Izvorul Kőpüs	nd	nd	nd	nd	nd	-0.22	-9.41	nd	a
23	Băile Homorod	Izvorul Lobogó	nd	nd	nd	nd	nd	1.04	-8.08	nd	a
24	Lueta	Izvorul Délü	0.81	3.04	0.55	0.33	3.29×10^{-12}	2.28	-6.94	3.02×10^{13}	a

25	Lueta	Izvorul Nádasszéki	nd	nd	nd	nd	nd	1.81	-7.66	nd	a
26	Băile Chirui	Lobogó well	nd	nd	nd	nd	nd	nd	nd	nd	a
27	Băile Chirui	Festő Spring	0.47	1.77	0.91	0.79	6.62×10^{-12}	1.19	-8.29	1.49×10^{13}	a
28	Vlăhița	Vlăhița thermal spring	0.57	2.14	0.90	0.80	2.92×10^{-10}	-0.82	-8.81	2.39×10^{11}	a
29	Vlăhița	Angol spring	1.94	7.27	0.44	0.35	8.44×10^{-12}	0.40	-8.43	1.17×10^{13}	a
30	Merești	Salty fountain	0.88	3.28	0.41	0.16	1.6610^{-11}	-13.98	-23.21	5.70×10^{12}	a
31	Mărtiniș	Salty fountain	14.67	54.95	0.46	0.45	1.1910^{-9}	-15.60	-24.59	7.80×10^{10}	a
32	Crăciunel	Spring	0.93	3.47	0.39	0.15	8.5310^{-11}	-5.74	-14.55	7.71×10^{11}	a
33	<i>Homorod Brașov</i>	<i>Well</i>	<i>126.23</i>	<i>472.79</i>	<i>0.38</i>	<i>0.38</i>	<i>1.89×10^{-8}</i>	<i>-7.41</i>	<i>-16.34</i>	<i>4.28×10^9</i>	<i>a</i>
34	Racoșul de Jos	Salty fountain	0.62	2.31	0.70	0.46	1.72×10^{-10}	-9.08	-17.73	5.15×10^{11}	a
35	<i>Corund</i>	<i>Corund</i>	<i>1.71</i>	<i>6.40</i>	<i>0.87</i>	<i>0.85</i>		<i>-9.18</i>	<i>-9.18</i>	<i>8.24×10^{12}</i>	<i>b</i>
36	<i>Băile Homorod</i>	<i>Homorod Maria</i>	<i>8.39</i>	<i>31.42</i>	<i>0.62</i>	<i>0.61</i>		<i>-2.03</i>	<i>-2.03</i>	<i>4.29×10^{11}</i>	<i>b</i>
37	Doboseni	Doboseni	8.87	33.22	4.27	4.37		-3.25	-3.25	5.73×10^9	b
38	Piriul Capelei	Piriul Capelei	25.60	95.88	1.74	1.75		-3.49	-3.49	8.43×10^{10}	b
39	Harghita Băi	Harghita Băi	1.41	5.28	3.04	3.52		-4.21	-4.21	2.82×10^{11}	b
40	Jigodin Băi	Jigodin Băi	5.20	19.48	0.45	0.42		-3.07	-3.07	1.95×10^{12}	b
41	Sintimbru Băi	Sintimbru Băi	1.08	4.04	1.26	1.35		-2.14	-2.14	5.45×10^{11}	b
42	Tusnad Nadas	Tusnad Nadas	1.28	4.79	1.66	1.83		-4.42	-4.42	7.19×10^{12}	b
43	Lazaresti Nyir	Lazaresti Nyir	7.70	28.84	2.95	3.02		nd	nd	2.79×10^{10}	b
44	Sfinta Ana	Sfinta Ana	25.00	93.63	3.16	3.18		nd	nd	3.20×10^{10}	b
45	Puturosul	Puturosul	10.11	37.87	2.29	2.32		nd	nd	7.46×10^{10}	b
46	Bodoc Perla	Bodoc Perla	0.83	3.11	0.42	0.14		-4.16	-4.16	nd	b
47	Balvanyus	Balvanyus	163.00	610.49	4.48	4.49		nd	nd	2.52×10^{10}	b
48	Slănic	Slănic	39.00	146.07	0.33	0.33		-2.98	-2.98	7.47×10^{12}	b
49	Andrieașu	Andrieașu	29.80	111.61	0.03	0.02		nd	nd	6.11×10^{10}	b
50	Perla Cașinului	Perla Cașinului	0.79	2.96	1.52	1.79		-2.56	-2.56	1.75×10^{10}	b
51	Berca	Berca	32.94	123.37	0.06	0.05		nd	nd	4.44×10^{10}	b
52	Covasna	Covasna	3.14	nd	1.15	1.17		nd	nd	nd	c
53	Balvanyoș Cave	Balvanyoș Cave	47.30	nd	3.10	3.11		nd	nd	nd	c

54	Balvanyoş upper pool	Balvanyoş upper pool	151.00	nd	3.12	3.12		nd	nd	nd	c
55	Balvanyoş lower pool	Balvanyoş lower pool	712.00	nd	3.19	3.19		nd	nd	nd	c
56	Bixad	Bixad	0.68	nd	1.47	1.78		nd	nd	nd	c
57	Bixad	Bixad	1.30	nd	0.80	0.75		nd	nd	nd	c
58	Tuşnad Nagy	Tuşnad Nagy	6.44	nd	1.20	1.21		nd	nd	nd	c
59	Vâlcele	Vâlcele	35.00	nd	0.60	0.60		nd	nd	nd	c
60	Covasna	Covasna	17.30	nd	1.28	1.28		nd	nd	nd	c
61	Balvanyoş	Balvanyoş	1.07	nd	3.04	3.72		nd	nd	nd	c
62	<i>Homorod (polla)</i>	<i>Homorod (polla)</i>	<i>7205.42</i>	<i>nd</i>	<i>0.42</i>	<i>0.42</i>		<i>nd</i>	<i>nd</i>	<i>7.77 x10⁶</i>	<i>d</i>
63	<i>Homorod (pozzo)</i>	<i>Homorod (pozzo)</i>	<i>13035.63</i>	<i>nd</i>	<i>0.43</i>	<i>0.43</i>		<i>nd</i>	<i>nd</i>	<i>6.50 x10⁶</i>	<i>d</i>
64	Bezna	Bezna	551.01	nd	0.02	0.02		nd	nd	2.48 x10 ¹⁰	d
65	Andreiasu	Andreiaşu	4.37	nd	0.09	0.03		nd	nd	1.60 x10 ¹⁰	d
66	Berca 1	Berca 1	2.61	nd	0.13	0.03		nd	nd	4.30 x10 ⁹	d
67	Berca 2	Berca 2	3.20	nd	0.12	0.04		nd	nd	5.87 x10 ⁹	d
68	Berca 3	Berca 3	1.00	nd	0.36	0.13		nd	nd	3.53 x10 ⁹	d
69	Berca 4	Berca 4	0.94	nd	0.38	0.13		nd	nd	8.40 x10 ⁸	d
70	Praid 2	Praid 2	7955.46	nd	0.78	0.78		nd	nd	nd	d
71	Sarmasel	Sarmaşel	755.10	nd	0.02	0.02		nd	nd	8.22 x10 ⁹	d
72	<i>Homorod</i>	<i>Homorod Brasov</i>	<i>nd</i>	<i>nd</i>	<i>0.38</i>	<i>nd</i>		<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>e</i>

Table 3 – Isotopic composition of samples.. $^3\text{He}/^4\text{He}$ ratios are normalized to the atmosphere and listed as R/Ra values ($R=^3\text{He}/^4\text{He}$ isotopic ratio of the sample, R_a = atmospheric $^3\text{He}/^4\text{He}=1.382 \cdot 10^{-6}$) and corrected for the atmospheric helium contamination (R/R_{a_c}) considering the $^4\text{He}/^{20}\text{Ne}$ ratio; $R/R_{a_c} = [R/R_a \cdot (X-1)] / (X-1)$ where X is the ASW-normalized $^4\text{He}/^{20}\text{Ne}$ ratio taken as 0.267 (Holocher et al. 2002). $\Delta\text{He}/\text{Ne} = \text{He}/\text{Ne}_{\text{sample}}/\text{He}/\text{Ne}_{\text{ASW}}$. $\delta^{13}\text{C}_{\text{TDIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ expressed in $\delta\%$ vs. PDB. $\delta^{13}\text{C}_{\text{CO}_2}$ is recalculated following Deines et al., 1974, Mook et al., 1974 and Zhang et al. 1995. Literature data are listed together calculations carried out within this work. Data sources: a = this work; b = Althaus et al. 2000; c = Vaselli et al. 2002; d = Baciu et al. 2007; e = Etiope et al., 2011. ASW (air Saturated Water) data for comparison marked with italics. bdl = below detection limits; nd = not determined

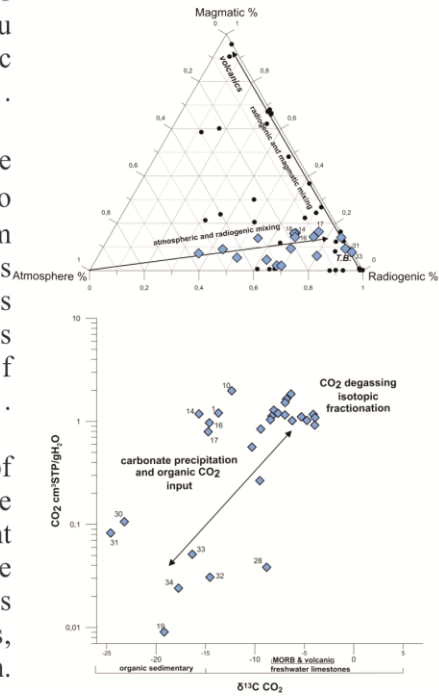
Geochemistry of dissolved gases from the Eastern Carpathians - Transylvanian Basin boundary

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We show the results of a study on the volatiles dissolved in mineral waters discharged over a 200 km-long transect along the Rodna-Bârgău area and Călimani-Gurghiu-Harghita volcanic chain (Eastern Carpathians, Romania).

Carbon isotopes ($\delta^{13}\text{C}_{\text{TDIC}}$), He isotopes in the range of 0.38 - 0.99 Ra) and $\text{CO}_2/{}^3\text{He}$ ratio spanning over four orders of magnitude from MORB-like values to crustal-type values coherently indicate the presence of fluids from different crustal sources besides minor, but detectable contributions of mantle/magmatic-derived fluids.

Our investigations show that the wide range of chemical and isotopic composition can be explained in terms of mixings among different gas sources feeding the groundwater and the contemporary occurrence of gas-water interactions like degassing and deposition of carbonates, affecting the circulating waters after their infiltration.



Graphical abstract

Highlights

- We show the results on the volatiles dissolved in mineral waters discharged in Romania
- $\delta^{13}\text{C}_{\text{TDC}}$ and He indicate the presence of fluids from different crustal sources besides contributions of mantle-derived fluids
- The compositions are the consequence of mixings and occurrence of secondary processes (degassing and carbonate precipitation)
- Our findings prove that presence of mantle-components may be present also at ~50 km distance away from the volcanic centres