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Evaluation of dissolved light hydrocarbons in different geological settings in Romania

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ABSTRACT

The paper presents the first systematic geochemical study on the content of natural gas (methane, heavier alkanes, CO_2), and isotopic composition of methane dissolved in natural springs in Romania, from various tectonic and geological settings. The dissolved methane concentrations in the investigated areas range between 0.08 and 16,359 μg/L. Based on isotopic analyses, the origin of methane in the gas mixture released by the investigated springs has been inferred. The highest concentrations of methane have been measured in the Transylvanian Basin and Carpathian Foredeep. Ethane in relatively high concentrations has been detected in Herculane and Calimanesti-Caciulata areas. Very high concentrations of dissolved CO_2 were determined in the Eastern Carpathians volcanic chain area. Lower amounts of dissolved CO_2 were detected in the Carpathian Foredeep, Southern Carpathians, Transylvanian Basin, and Pannonian Basin. The measured values of $\delta^{13}C$-CH_4 range between −67‰ and +4‰. The methane from the investigated areas is biotic, microbial in the Transylvanian Basin, Pannonian Basin, and Moldavian Platform, and thermogenic in the Carpathian Foredeep. We report for the first time the presence of a presumably abiotic methane component in Romania, from geothermal sources, in the areas of Ciomadul Volcano and Herculane area.

1. Introduction

Romania is one of the richest countries in Europe in terms of surface gas manifestations, including seeps and mofettes. Seeps represent the upward flow of hydrocarbon-rich gases from a subsurface reservoir. The manifestations can be of different types: mud volcanoes, dry seeps (that may generate eternal fires when the flux is very high), and gas-bearing springs. These are often found in hydrocarbon-prone sedimentary basins. Mofettes, on the other hand, are gas emissions consisting mainly of carbon dioxide, often associated with other gases (e.g. H_2S, N_2, He; Etiope et al., 2007). These can be dry emanations of gas, or bubbling pools. Methane and other light hydrocarbons can be found in small amounts also in mofettes and gas manifestations from geothermal areas (Etiope et al., 2007). Hydrocarbon emissions largely occur in Romania in sedimentary basins, but the presence of light hydrocarbons has been mentioned also in volcanic and geothermal areas, where their concentration may reach several percent by volume (Vaselli et al., 2002).

Several studies conducted in North America and Europe have provided data on the methane concentration in groundwater (Table 1). Molofsky et al. (2013), and Schloemer et al. (2016) have sampled a high number of water sources randomly, thus obtaining background concentrations of methane in their study regions. They measured a wide range of values, from the detection limit of the used instruments, to > 40,000 μg/L. The selective sampling performed in the other studies listed in Table 1 allowed the quantification of the dissolved methane in water sources already presumed to contain a certain amount of gas. The methane concentration in the investigated regions varied from < 1 μg/L to tens of mg/L, with lower values in geothermal environments in relation with volcanic systems (e.g. Vulcano and Eastern Carpathians), and higher values in hydrocarbon-prone sedimentary basins. In the eastern Pannonian Basin, Rowland et al. (2011) have measured dissolved methane concentrations exceeding 100,000 μg/L.

Until now, surface manifestations of methane in Romania have been investigated mainly as dry seeps and mud volcanoes in the important hydrocarbon-prone areas, as the Carpathian Foredeep, Transylvanian Basin, and the Moldavian Platform (Baciu et al., 2007, 2008; Etiope et al., 2004; Frunzeti et al., 2012; Pop et al., 2015; Spulber et al., 2010). A first synthesis of the gas geochemical data in Romania, including several gas-bearing springs, has been published by Filipescu and Huma

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Table 1
Concentration of methane in groundwater in different areas from North America and Europe.

Investigated area	No.of samples	CH_4 min (μg/L)	CH_4 max (μg/L)	Sampling	Authors
North-eastern Pennsylvania	1701	0.1	43,000	Random	Molofsky et al., 2013
Lower Saxony	1043	0.02	41,018	Random	Schloemer et al., 2016
North and Central Arkansas	127	0.1	28,494	Selective	Warner et al., 2013
Pennsylvania and New York	69	300	50,400	Selective	Osborn et al., 2011
Alberta	58	1714	15,993	Selective	Cheung et al., 2010
Alberta	186	0.1	42,900	Selective	Humez et al., 2016
UK	139	0.05	16,000	Selective	Darling and Gooddy, 2005, 2006
Vulcano	7	0.6	11.2	Selective	Capasso and Inguaggiato, 1998
Sicily	33	0.2	44,052	Selective	Grassa et al., 2006
Eastern Carpathians	10	0.3	4843	Selective	Kis, 2013
Pannonian Basin	28	50	112,000	Selective	Rowland et al., 2011

(1979). The mentioned work does not contain any isotopic data, making use only of the molecular composition of gases.

The present paper proposes two main objectives. The first is the assessment of methane, and possibly other light hydrocarbon content in springs from different geologic and tectonic settings across Romania. The second objective consists in constraining the origin of methane in relation with the geological environment by using complex geochemical data. The current contribution represents a systematic insight in the geochemistry of dissolved light hydrocarbons in Romania, and includes geochemical data on 172 springs across the country. Out of these localities, the carbon-13 isotopic composition of methane ($\delta^{13}C\text{-}CH_4$) has been measured in > 100 samples.

The results shown here will help in: (1) better assessing the geological and geographical distribution of the different types of methane; (2) evaluating the origin of the dissolved methane in Romania; (3) increasing the knowledge on gas-bearing springs and including them in the national inventory of geogenic greenhouse gases release.

2. Geological setting

The geotectonic setting of Romania is characterized by the convergence of the Tisia-Dacia Domain towards the Eastern-European platform (e.g. Ratschbacher et al., 1993). After the subduction of an oceanic basin between these continental cratons, the orogenic units of the Carpathians have been formed. The Transylvanian Basin is surrounded by the mountain ranges of the Eastern and Southern Carpathians, and Apuseni Mountains (Fig. 1).

In the structure of the Eastern Carpathians, the Median Dacides consist of Precambrian/Palaeozoic metamorphites and Mesozoic (pre-Cenomanian) sediments. The flysch units (Outer Dacides and Moldavides) and Carpathian Foredeep are developing on large areas in the external part of the Eastern Carpathian belt. The thick flysch deposits are involved in complex overthrusted structures. Their evolution is related to the Alpine tectonic activity, started during the Cretaceous with the closure of the Tethys Ocean. The intensification of the compressional stress during the Neogene lead to the southwest oriented subduction of a small oceanic basin beneath the continental microplates Tisia-Dacia, finalized with their collision with the Eurasian plate (Radulescu and Sandulescu, 1973; Royden, 1993). Sedimentation continued with molasse deposits during the Miocene-Pliocene time. At the same time, the South Carpathians Foredeep was filled with sediments, starting with the Eocene. Oil and gas deposits are located in the Paleogene Flysch Zone, and especially in the Carpathian Foredeep, that hosts the most important oil resources of Romania.

As a result of compressional tectonics and assimilation of crustal material, magma generation and magmatic activity started (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 Tisia-Dacia continental terrain, on the Carpathian accretionary prism, on the western side of the Eastern Carpathians (Pecskay et al., 2006; Radulescu and Sandulescu, 1973; Royden, 1993; Szakacs and Seghedi, 1995b).

Within this volcanic chain, three major segments can be distinguished from north to south on the Romanian territory: Oas-Gutai, Tibles-Rodna-Bargau, and Calimani-Gurghiu-Harghita (CGH). Volcanic activity in the Neogene-Quaternary arc started around 21 Ma in the western section of the Carpathians, and moved progressively to the East and South, with ages between 8.3 and 11.9 Ma in Tibles-Rodna-Bargau segment (Pecskay et al., 1996), and around 10 to 0.03 Ma in the CGH segment (Pecskay et al., 2006), the youngest being the twin-cratered Ciomadul volcano (Harangi et al., 2010).

The Tibles-Rodna-Bargau area is characterized by magmatic intrusions that have pierced into different types of rocks, including the crystalline units of the Rodna Mountains and the sedimentary deposits of the Bargau Mountains. The magmatic rocks were described as andesites, dacites and rhyolites.

The Neogene-Quaternary arc Calimani-Gurghiu-Harghita is the southernmost and the longest (160 km) continuous volcanic chain, located between the Carpathian thrust-and-fold belt and the Transylvanian Basin. The andesitic volcanism of the CGH developed as a post-collisional event, when the present structure of the Eastern Carpathians had already been formed. The volcanic range consists of a row of adjacent composite volcanoes and their peripheral volcaniclastic aprons (Szakacs and Seghedi, 1995b).

The chain is formed by linearly distributed, partially overlapping volcanic edifices, monogenetic and medium sized andesitic composite stratovolcanoes, effusive domes and lava flows. The size and complexity of volcanoes decrease from NW to SE along the CGH chain following the migration of activity. Volcanic products are calc-alkaline rocks, mainly andesites, less frequently dacites, and shoshonitic rocks in the southern part of the chain (Seghedi et al., 1995, 2004; Szakacs and Seghedi, 1995b).

The volcaniclastic formation has settled directly on the sedimentary units of the Transylvanian Basin and is composed mainly (60%) of reworked volcanogenic sediments. The thickness of the volcanogenic sediments is 100 to 650 m, having plateau-shape morphology (Szakacs and Seghedi, 1995a, 1995b).

The Southern Carpathians are composed of two major tectonic units, the Getic and Danubian nappes. The base of the Getic nappe consists of high-grade metamorphic rocks, formed as a result of the Variscan reworking. The basement of the Danubian nappes consists of high-grade Precambrian series, intruded by granitic bodies. In the western part of the Southern Carpathians, a noteworthy tectonic element is the Cerna-Jiu Fault (CJF), a NE oriented, right-lateral strike-slip fault, which can be recognized over 300 km, at the loop of the Southern Carpathians, linking the Carpathians and the Balkan mountains. Its displacement was estimated at 30 to 40 km (Berza and Draganescu, 1988). The development of the CJF is related to the right-lateral rotation of the Carpathian nappes around the Moesian plate (Ratschbacher et al., 1993). The Cerna-Jiu disjunctive system cuts the South Carpathians as a narrow belt, best noticeable between the towns