

## **Scientific report**

*on the implementation of the project between October – December 2011*

### **GEOGENIC EMISSIONS OF GREENHOUSE GASES FROM GEOTHERMAL AND PETROLEUM SYSTEMS- APPLICATION TO ROMANIA**

#### **PN-II-ID-PCE-2011-3-0537**

The research activities performed between October – December 2011 have been connected mainly to the **Work Package 1** of the project, which regards the definition of the state-of-the-art at national/international level. This package extends on the first 6 months of the project, ending on April 5th 2012. Consequently, the current report refers only to the partial results of the WP1 that have been achieved before December 15th 2012. This WP is an introduction in the research project, a synthesis of the present knowledge in Romania and worldwide; in order to select the potential locations to be investigated and to define the most important objectives of the project. Almost 160 titles were read from the most recent references from the international scientific literature. Also relevant information was gathered from conference materials of the past years, regarding gas geochemistry. Although because of the uncertainty of the meteorological factor, no field campaign was proposed for this period. The good weather condition allowed us to perform a first field campaign, in the western part of the Southern Carpathians, namely the Orsova-Tisovita-Eibental area, in November 2011. In consequence, the **Work Package 2 (WP2) – Field survey in selected areas and laboratory analyses** started earlier than foreseen. Also dissemination activities were performed, by participating at two international conferences. In the field work, but also in the conference presentations, young researchers (PhD students) were involved, which gives to the project a formative character.

#### **WP1 – State-of-the-art at national/international level**

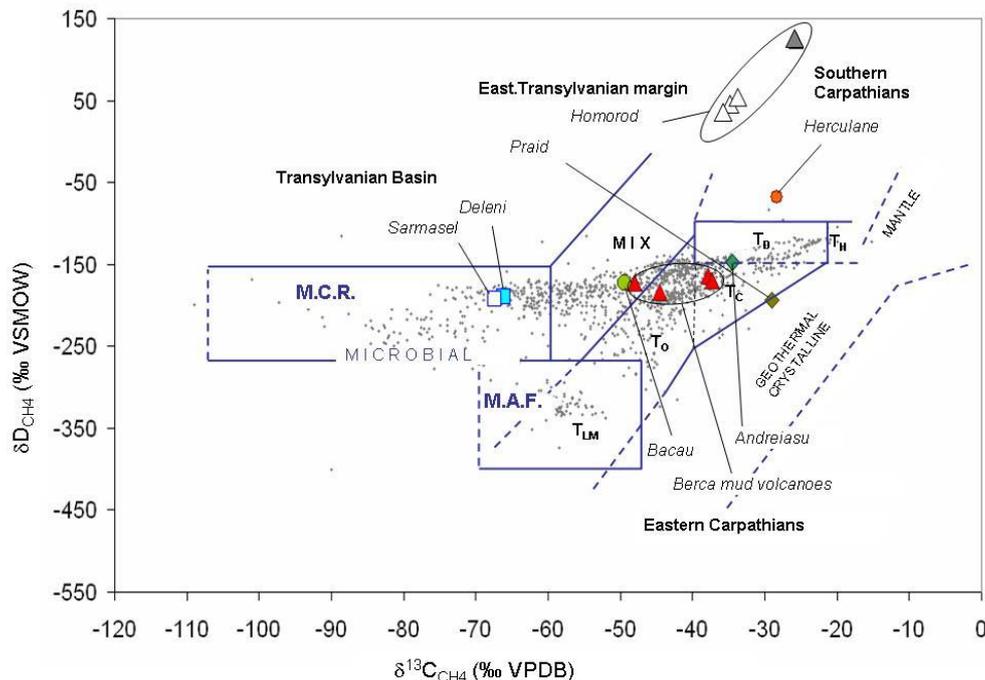
The gas accumulations on the Romanian territory can be attributed to two major categories, based on the geological systems in which they can be found.

1. **Petroliferous systems** (predominantly with methane emissions) –the following regions will be investigated: Transylvanian Basin, some regions from the Carpathian Foredeep, eastern part of the Pannonian Basin (where both methane and carbon dioxide emission are present);
2. **Geothermal/volcanic systems** (predominantly with carbon dioxide emissions) – the regions to be investigated are: Eastern Carpathians, some areas of the Apuseni Mountains and Southern Carpathians (with uncertain geothermal character: Herculane-Mehadica, Calimanesti-Caciulata, areas with hyper-alkaline rocks from the Danube area).

It is little known, that at international level Romania was the first country to extract petroleum at an industrial scale, with the first registered production rate of 1719 barrels in 1857. It must be underlined that this happened one year before the first well of William at Oil Springs, and two years prior to Drake's discovery in Pennsylvania (moment which is considered as the start of the petroleum industry).

In spite of Romania's variety of gas sources, the scientific investigation potential, and the economic importance of gas, very few geochemical studies were published before 2000. It is worth mentioning the book of Filipescu and Huma published in 1979, which is an excellent synthesis on the state-of-the-art of that period for the Romanian territory. The two authors describe in detail and very precisely the chemical characteristics of the gases, connected to the main geological structures. This book and other publications of the time, include only the molecular composition of the, disregarding the isotopic analyses, an important key to determine the origin of gases. A systematic approach for the characterization of the gases was started after the year 2000, in the frame of collaboration between UBB (Calin Baciu) and INGV Roma (Giuseppe Etiope). Studies were performed in different locations in Romania, in Transylvania and the extra-Carpathian areas, which led to the creation of a first database, containing chemical and isotopic data, and fluxes to the atmosphere of the greenhouse gases (GHG).

The isotopic/molecular analyses were performed in prestigious international laboratories, with the help of INGV Roma, without any financial support. This is the reason why the database currently includes a relatively low number of items. The current project offers excellent perspectives for upgrading/updating this database. The research performed by the above mentioned group was published in the scientific literature (Baciu et al. 2005, 2007, 2009; Etiope et al. 2002, 2003, 2004a, 2004b, 2009, 2010, 2011). In these works we quantified the flux of GHG, first of all of methane of geologic origin, between the lithosphere/soil and atmosphere. It is worth mentioning that some of these articles gave new insights on an international scale regarding: the existence of microseepage in the areas of gas manifestations; detailed characterization of the areas with strong gas flux; and helped calculating the total output regarding GHG emissions to the atmosphere.

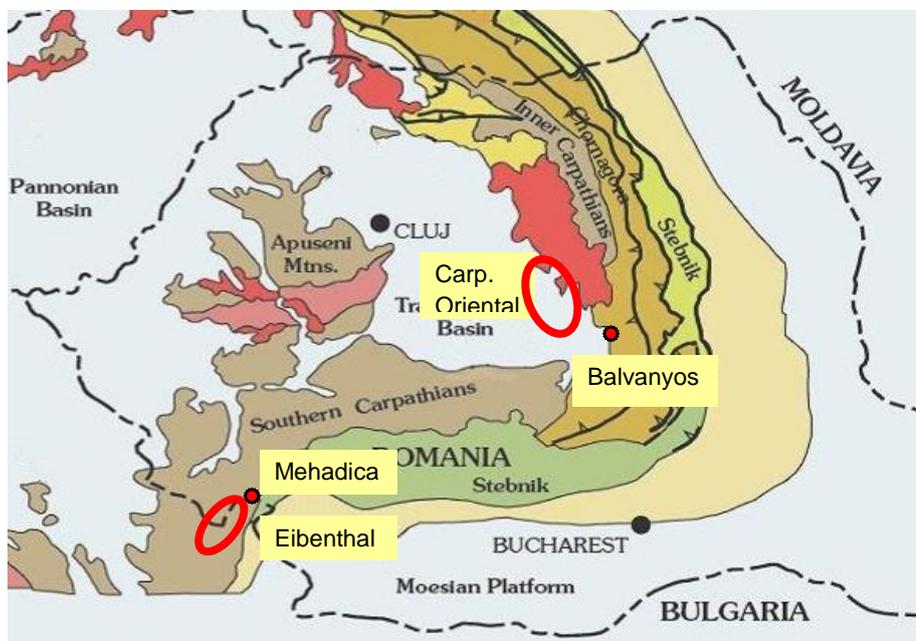


**Fig. 1.** Interpretive diagram regarding the genetic classification of the investigated gases from Romania, based on the isotopic ratio of carbon-13 and deuterium from methane.

The first isotopic data on a natural gas reservoir in Romania were published relatively recently (Baciu et al. 2008). The total amount of data available in the current literature regards only 11 seeps, as a result of the

work of the current project's team. The interpretive technique regarding the usage of deuterium/carbon-13 ratios of methane is shown in figure 1. One can observe the microbial origin of gases from Transylvania, the thermogenic character of mud volcanoes from Buzau area, and a mixt origin (between microbial and thermogenic) of the gases from Bacau region. The Praid gases have a strong geothermal influence, which is explained if we take into account its position close to the Neogene volcanic chain of the Eastern Carpathians. Based on the preliminary isotopic analysis, the gas emissions from Herculane thermal waters have an uncertain position on the diagram. In the framework of this project we propose a more complex determination of the origin of the gas. The most unusual gas composition can be found in Homorod (BV). Small mud volcanoes were found at Homorod, which release nitrogen above 90%, CO<sub>2</sub> approximately 5% and very low concentrations of methane, and above 1% of helium. These are the highest recorded nitrogen and helium contents from any onshore mud volcano. Also the deuterium ratio of methane is the highest ever measured (+124‰) in natural gas. These results were published in Chemical Geology journal (Etiopie et al. 2011). In the present project we will try to extend the research regarding the gases with high nitrogen and helium content, and also with unusual isotopic ratios.

Like the petroleum systems, the geothermal systems are also scarcely studied, regarding their gas geochemistry. A reference paper was published by Vaselli et al. in 2002. This article describes a geochemical transect of the southern part of the Eastern Carpathians. Most of the gases have a high CO<sub>2</sub> content, sometimes with significant amounts of nitrogen. In the present study, the isotopic ratio of carbon from CO<sub>2</sub>, and helium was measured. The results show that CO<sub>2</sub> originates from the thermomethamorphism of the carbonate rocks. Some samples indicate that CO<sub>2</sub> derives from the degradation of organic materials.



**Fig. 2.** Investigated areas between October – December 2011.

**WP2 – Field investigations**

The most representative occurrence of ultrabasic rocks in Romania can be found in the ophiolitic massive of Tisovita-luti, in the SW extremity of the Southern Carpathians. Recently, the gas produced from

ophiolites, has gathered great interest at a worldwide scale. The capacity of the ultrabasic rocks to produce methane, through abiotic processes (Fisher-Tropsch reaction), was studied in several locations (USA, Turkey, etc.). The generation of methane through abiotic processes in the ophiotic rocks is of practical (new source of methane), but also of scientific interest. Studying these sites represents a modality to verify the conditions in which the Fisher-Tropsch reaction, and other linked reaction pathways produce methane on other celestial bodies, like Mars (Etiope et al. 2011). The most stunning location can be found at the Chimaera site in Turkey, where methane is produced abiotically, and creates everlasting fires that are burning for more than 2000 years. These fires are even mentioned in Homers Iliad.

The Tisovita area show favorable premises to have these kind of processes: the presence of serpentized ultramafic rocks; high concentrations of chromium and other metals, which have a catalytic role in the generation of gas, high pH of the subsurface waters (>8). An exploration well is mentioned in the area, which generated a unique mixture of gases: CH<sub>4</sub> = 69.1%, H<sub>2</sub> = 28.7% (Filipescu&Huma, 1979).

A field campaign was undertaken and several samples were collected. In parallel, another location was also visited, the geothermal springs from Mehadica (CS), where gas and water samples were collected.



**Fig. 3.** Investigated sites in Orsova-Eibental-Mehadica area. 1 – Measuring the gas concentration Tisovita; 2 – Spring with gas content in Liubotina Valley; 3 – thermal water near Mehadica.

### **Dissemination activities**

1. **Environment – Landscape – European Identity Conference**, 4-6 November 2011, held at the Faculty of Geography, University of Bucarest ([www.geo.portiledefier.ro](http://www.geo.portiledefier.ro)), with two contributions:
  - a. **B.M. Kis, C. Baci, L. Kekedy-Nagy, B. Czellez, K Karman – Hydrogeochemical studies on some mineral waters from the western part of Harghita County;**
  - b. **N. Frunzeti, C. Baci – Carbon dioxide and methane emission from Balványos Spa, south eastern part of Ciomadu volcano (Romania).**

2. **11<sup>th</sup> International Conference on Gas Geochemistry**, organized by Scripps Institution of Oceanography, San Diego, California, 28 Nov.-4 Dec. 2011. Presented contribution: **C. Baci**, **G. Etiope**, **N. Frunzeti** – *Molecular and isotopic composition of natural gas in Romania*.

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