Marine and Petroleum Geology xxx (2017) 1–14

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo

Research paper

Hydrocarbon seeps in Romania: Gas origin and release to the atmosphere

Calin Baciu [a], Artur Ionescu [a, b, *], Giuseppe Etiope [c, a]

[a] Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania
[b] MTA-ELTE Volcanology Research Group, Budapest, Hungary
[c] Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, Italy

ARTICLE INFO

Article history:
Received 6 October 2016
Received in revised form
11 June 2017
Accepted 12 June 2017
Available online xxx

Keywords:
Hydrocarbon seeps
Mud volcanoes
Gas geochemistry
Methane
Romania

ABSTRACT

Romania is one of the countries with the largest number of surface hydrocarbon seeps in the world. Seeps may be an important tool for petroleum exploration as they can provide useful information regarding source rock maturity, reservoir quality, and secondary gas alterations. Seeps also represent an important source of methane, ethane, and propane to the atmosphere. To date, the genetic characterization of natural gas in Romania has only been based on molecular composition, without isotopic information. Here, we present an overview of investigations performed over the past 15 years for the main Romanian hydrocarbon seeps, and report the molecular and isotopic compositions of gas, and the fluxes of methane, ethane and propane to the atmosphere. We assessed gas origin and secondary alterations in 17 seeps from several Romanian petroleum systems, and potential source rock types and maturity have been evaluated. As previously inferred, gas within the Transylvanian Basin is largely microbial, but also displays indications of a minor thermogenic component that is likely related to a deep petroleum system. Carpathian Flysch and Foredeep petroleum systems contain thermogenic gas, with clear evidence of biodegradation in some cases. Thermogenic gas generation modelling and maturity plots suggest that most Romanian gases originate from mature type II and III kerogen (%R_o: 2–3). For cases of high flux seeps, gas has the same hydrocarbon molecular composition as the reservoir, while in weaker seeps and some mud volcanoes gas is altered by molecular fractionation (a loss of C_2 and C_3 during gas migration). Gas seep geochemistry, in general, reflects the different geological and maturity conditions of basins where seeps are located. A vertical sequence of petroleum systems has been suggested in some basins by seeps displaying different maturity and secondary alterations. Measurements of methane flux to the atmosphere from 94 seeps display a wide range of emissions (kilograms to hundreds of tons per year), with a total, conservative estimated methane emission of approximately 3000 t y^{-1}. Microseepage may also release a similar quantity of methane. Consequently, seepage is a substantial contributor to natural emissions of methane on a national level.

1. Introduction

Although its available petroleum reserves are relatively small on a global scale, Romania is still one of the most important European oil and gas producers (BP, 2016). Romania is also among the countries with the longest tradition of petroleum production in the world. With more than 150 years of oil extraction and more than 100 years of gas extraction, approximately five billion barrels of oil and 40 trillion cubic feet of gas have been cumulatively produced in Romania. Over this period of time, a large amount of geological and reservoir data have been acquired. A first synthesis for the geochemistry of natural gas in Romania was published by Filipescu and Huma (1979) who presented a geochemical database for main hydrocarbon fields based on gas-chromatographic analyses together with short geological descriptions of hydrocarbon-bearing structures. No isotopic data were reported, and this type of data has been missing from Romanian literature for three successive decades.

The first isotopic data related to Romanian hydrocarbons were published in 2008 for the methane seep of Gheraiesti-Bacau, located in eastern Romania (Baciu et al., 2008). A few additional

* Corresponding author. Faculty of Environmental Science and Engineering, Babes-Bolyai University Cluj-Napoca, Romania.
E-mail address: artur.ionescu@ubbcluj.ro (A. Ionescu).

http://dx.doi.org/10.1016/j.marpetgeo.2017.06.015
0264-8172/

papers containing isotopic data followed (Etiope et al., 2009a, 2009b; Frunzeti et al., 2012), although, to date, a comprehensive dataset for petroleum systems in Romania is still missing from the scientific literature. Due to intense tectonics caused by Carpathian orogenesis and post-orogenic basin uplift (e.g., the Transylvanian Basin), numerous hydrocarbon seepage systems (as defined by Abrams, 2005) developed, making Romania one of the countries in the world with the largest number of surface hydrocarbon seeps (470 seeps have been catalogued; Etiope, 2015; Ionescu et al., 2017). Surface manifestations include gas seeps (sometimes forming "everlasting fires"), mud volcanoes, oil seeps, and methane-rich water springs. A distribution of documented seeps is provided in Fig. 1.

Seeps, generally linked to subsurface pressurized reservoirs, are an important tool for petroleum exploration and may provide useful information related to source rock maturity, the quality of a reservoir, and secondary alterations (Link, 1952; Etiope et al., 2009a, 2009b). Seeps are also important natural sources of greenhouse gas (methane) and photochemical pollutants (ethane and propane) to the atmosphere (e.g., Etiope and Milkov, 2004; Etiope, 2009; Etiope and Ciccioli, 2009). On a global scale, seepage in sedimentary basins and gases released from geothermal manifestations represent the second natural source of methane to the atmosphere after wetlands (Etiope, 2012, 2015). Geological gas sources in Romania should also be assessed on a national level because they appear to be a major contributor of natural methane emissions in Europe.

In the context of the depletion of reservoirs, significant interest has been given to the intensification of exploration for both conventional and unconventional oil and gas resources. Modern geochemical investigations, including isotopic data, are recognized as valuable tools for more efficient petroleum exploration and for a better understanding of the genesis and evolution of hydrocarbon accumulations. Based on an investigation of a wide set of surface manifestations, this research provides insight into the geochemistry of some of Romania's petroleum systems. In this work, and for the first time, we present all of the molecular and isotopic data available for 17 major Romanian seeps (Fig. 1). The data have been gradually obtained by our research team since 2000 and have only been partially published. In the following, we compare the molecular composition of seeping gas with that of reservoirs located within the same petroleum system, for the main productive basins in Romania, and shed new light on gas origins, secondary alterations, and potential source rock types and maturity. The data include measured methane fluxes from 17 seeps where we performed geochemical analyses, and fluxes from 77 additional seeps (Supplementary Material, Table S1). Using these data, we developed a wide flux dataset from which emission factors could be derived for estimating total seepage output for the country. Based on the molecular composition of seeping gas, total emissions were also determined for the photochemical pollutants ethane and propane.

2. Geological setting and description of the seepage sites

2.1. General geological setting

The Romanian territory overlaps a large portion of the

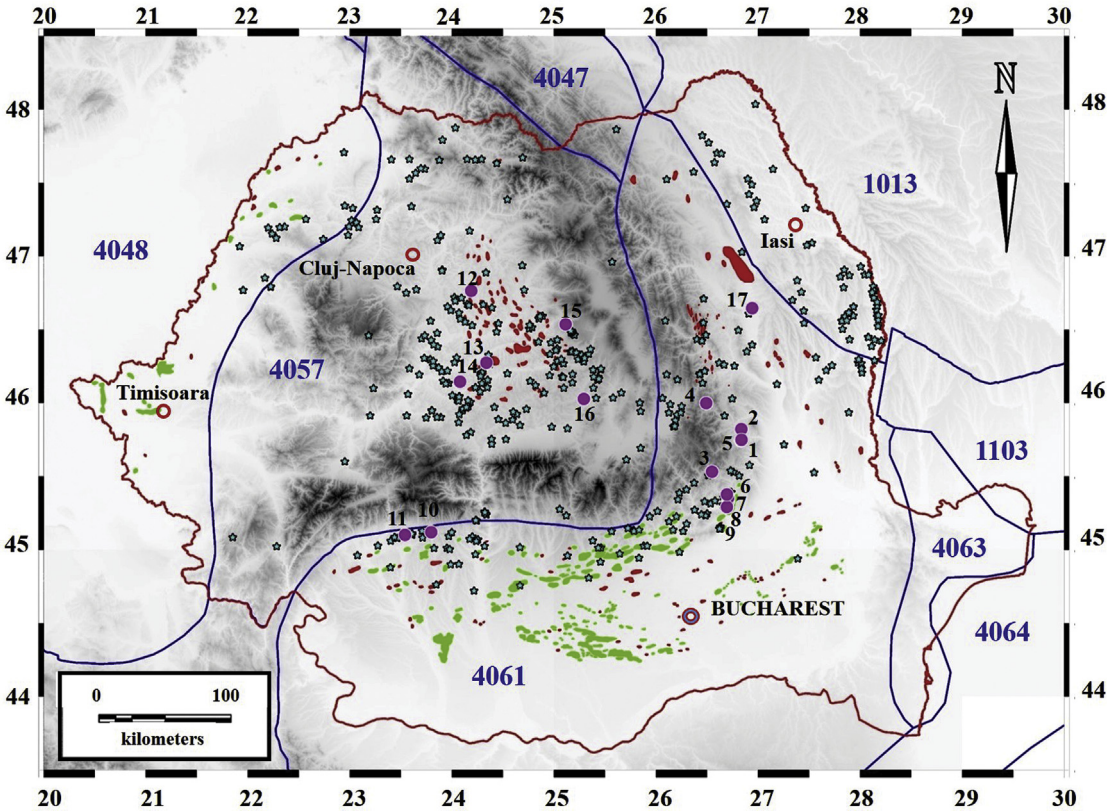

Fig. 1. Map showing the distribution of the documented seeps in Romania (blue stars). Oil fields in green, gas fields in red. Geological provinces (Pawlewicz et al., 2002): 1013 – Ukrainian Shield; 1103 – Dobrogea Foreland; 4047 – North Carpathian Basin; 4048 – Pannonian Basin; 4057 – Transylvania; 4061 – Carpathian-Balkanian Basin; 4063 – Dobrogea Orogen; 4064 – Western Black Sea Basin. Seeps investigated in detail in this work (violet circles): 1 – Andreiasu; 2 – Raiuti; 3 – Lopatari; 4– Lepsa; 5 – Andreiasu MV; 6 – Beciu; 7 – Paclele Mari; 8 – Paclele Mici; 9 –Fierbatori; 10 – Alimpesti; 11 – Sacelu; 12 – Sarmasel; 13 – Deleni; 14 – Tauni; 15 – Praid; 16 – Homorod; 17 – Bacau. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Please cite this article in press as: Baciu, C., et al., Hydrocarbon seeps in Romania: Gas origin and release to the atmosphere, Marine and Petroleum Geology (2017), http://dx.doi.org/10.1016/j.marpetgeo.2017.06.015