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Deep gases discharged from mud volcanoes of Azerbaijan: New geochemical evidence

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ABSTRACT

This paper presents new geochemical data of hydrocarbon-rich gases released from some mud volcanoes of Azerbaijan. Methane is considerably the most abundant component of all the sampled gases, which show δD-CH_4 and δ^{13}C-CH_4 values likely related to a dominant thermogenic source. These gases are characterized by the presence of more than 20 different cyclic compounds with concentrations up to several μmol/mol. A similar gas composition has recently been found to characterize many mud volcanoes of the Northern Apennines and Sicily (Italy). The data of the Azerbaijan mud volcanoes corroborate the notion that cyclic compounds can be considered reliable tracers for hydrocarbon gas production at considerable depths and temperatures up to 120–150 °C, which correspond to a 6.5–8.3 km depth range assuming an average geothermal gradient of 18 °C/km. This depth interval is consistent with both the depth of potential source rocks imaged seismically beneath some mud volcanoes, and the results of previous estimates that used the $^{13}C/^{12}C$ values of methane and ethane. Such deep-sourced gases and material (fluidized clayey mass and rock fragments) ascend into the core of anticlines and accumulate at shallower reservoirs, where fold-parallel outer-arc faults or fold-orthogonal fractures may penetrate and transfer the fluids to the surface. Finally, the basically equivalent composition of the different hydrocarbon groups (C_2–C_{10} alkanes, aromatics and cyclic) determined in the gases sampled in both Azerbaijan and Italy manifests the lack of evident relationships between the chemistry of light hydrocarbons and the type of source rock.

1. Introduction

Mud volcanoes mostly occur in sedimentary environments in relations to the presence of subsurface pressurized fluids. The gas phase (often represented by methane) is the most important in driving the ascent of subsurface mud–fluid mix and variably sized rock fragments (Jakubov et al., 1971; Brown, 1990; Milkov, 2000; Dimitrov, 2002; Kopf, 2002). Extrusion of this material yields the development of a number of scenic morphological features, of which the conical-shaped mud volcanoes represent the most typical outcome. Mud volcanoes may vary greatly in size, from less than 1 m to the gigantic submarine ('Conical Seamount') serpentine mud volcanoes of the Mariana forearc that may exceed 25 km in diameter and 2 km in height (Fryer and Pearce, 1992; Fryer et al., 1999). These features usually mark zones of active tectonic shortening, where sediments are affected by increasing stresses and temperatures leading to the maturation of organic matter (Higgins and Saunders, 1974; Brown, 1990; Kopf et al., 2001; Kopf, 2002; Deville et al., 2006). Mud volcanoes are particularly frequent along the Alpine–Himalayan collision zone, where they punctuate submerged or exposed accretionary prisms (e.g., Gulf of Cadiz, Somoza et al., 2003; Mediterranean Ridge, Kopf et al., 2001; Makran, Delisle et al., 2002), and the front of fold-and-thrust belts (e.g., Northern Apennines, Bonini, 2007; Carpathians, Baciu et al., 2007; Caucasus, Kopf et al., 2003; Black Sea, Herbin et al., 2008; Caspian Sea area, Jakubov et al., 1971; Yusufzade and Guliyev, 1995).

Mud volcanoes are thus closely associated with petroleum systems, and commonly release hydrocarbon gases dominantly consisting of methane, with significant concentrations of CO_2 and

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C_{2+} organic compounds (e.g. Valyaev et al., 1985; Stamatakis et al., 1987; Lavrushin et al., 1996; Blinova et al., 2003; Schmidt et al., 2005). Investigations on the origin of hydrocarbons discharged from emissions in different natural environments generally rely on the chemical and stable isotopic compositions of C_1–C_3 alkanes (Bernard et al., 1978; Schoell, 1980, 1983, 1988; Chung et al., 1988; Whiticar, 1999). Genetic characterization carried out on isotopic basis on worldwide mud volcanoes has allowed the compilation of a global data-set including more than 140 onshore mud volcanoes. This analysis documents a dominant thermogenic character, the gas phase being thermogenic in the 76% of cases, mixed thermogenic/microbial in the 20%, and only the 4% is entirely microbial (Etiope et al., 2009a,b). The original molecular and isotopic composition of reservoir gas in mud volcanoes may be strongly affected by post-genetic processes, such as molecular fractionation during advective fluid migration and secondary methanogenesis. Therefore, the origin of gases from these natural systems cannot be univocally assessed on the only basis of the above listed geochemical parameters.

A detailed analysis of chemical composition of light hydrocarbons (alkane, cyclic and aromatic compounds) discharged from mud volcanoes and CH_4-rich emissions in Italy has evidenced two distinct groups of thermogenic gases, particularly (i) aromatic-rich gases related to significant hydrothermal fluid contribution, and (ii) cyclic-rich gases expelled from mud volcanoes marking the external compressive front of the Northern Apennines and Sicily (Tassi et al., 2012). We focus on the latter features, which are representative of the most typical worldwide mud volcanoes. Thermodynamic and geological/structural considerations have allowed to propose that the cyclic compounds are likely formed by i) thermal cracking of heavier organic molecules and/or ii) catalytic reforming process consisting of incomplete aromatization of the light alkanes. In particular, these emissions were estimated to originate from organic sources located at depths $\geq$3000 m, in a genetic environment characterized by high pressure and temperatures in the 100–120 °C range, or not exceeding 120–150 °C (Tassi et al., 2012). These conditions may be common to other mud volcanoes, which may be as many as more than 8–900 onshore, 500 on the continental shelves, and even some 5000 mud volcanoes are speculated to occur in deep waters (Guliyev and Feizullayev, 1997; Dimitrov, 2002; Milkov et al., 2003; Etiope and Milkov, 2004).

According to these considerations, we aim to test the temperature–depth conditions of light hydrocarbon gas generation (determined in the Northern Apennines) in other areas of mud volcanism. More specifically, this study aims to find possible relations between the chemistry of the light hydrocarbon fraction and the thermodynamic conditions of the gas source region that may be generally valid in mud volcano systems. We have therefore extended our geochemical investigation to Azerbaijan, which has more onshore mud volcanoes than any other locality on Earth (Jakubov et al., 1971; Guliyev and Feizullayev, 1997). Mud volcanism in Azerbaijan is demonstrably coupled with a number of closely interrelated parameters, specifically (1) subsurface hydrocarbon accumulations (Inan et al., 1997), (2) abnormal fluid overpressures (Feyzullayev and Lerche, 2009), and (3) suitable tectonic structures (Jakubov et al., 1971). The mud volcanoes of Azerbaijan provide ideal conditions because of the accessibility of accurate information regarding parameters that are fundamental to this study, in particular the nature and depth of the main source rock, the regional geothermal gradient, and pore fluid pressure conditions (e.g., Guliyev et al., 2011). We thus use this area as a case study for testing the information that chemistry of the light hydrocarbon gases, in integration with the regional/local geological and tectonic setting, may reveal about the chemical–physical conditions acting at the fluid source region.

2. Terminology and activity of mud volcanoes

'Mud volcano' is a generic term to indicate the various morphologic features associated with the extrusion of subsurface fluids and solid material. Mud volcanoes show impressive morphologic similarities with the magmatic counterpart, and for this reason a number of terms used for mud volcanism are borrowed from magmatic volcanism. Besides 'volcano', other terms shared by both types are 'crater' to indicate the sub-circular collapsed areas topping the variously sized extrusive edifices, 'caldera' to indicate the depressions forming from the withdrawal of subsurface material, and 'vent' to indicate generic openings through which fluids and material are released. The typical conical constructional edifices are termed 'gryphons' and 'mud cones' when tall less than 3 m and 10 m, respectively (see Planke et al., 2003). According to Jakubov et al. (1971) mud cones are up to 40–50 m high, and the term 'mud volcano' should be restricted to the larger edifices, which in Azerbaijan may rise even more than 300–400 m above the surrounding subtle topography and their base may attain widths up to 4–5 km (e.g., Bonini and Mazzarini, 2010). Other manifestations are represented by mud pools (or 'salses') characterized by bubbling gas centers.

Regarding their activity, mud volcanoes normally display a dormant behavior, which most commonly consists in the quiet and continuous expulsion of mud breccia, fluids, and gases at both conical edifices and mud-water pools. Such a dormant activity characterized by gas bubbles rising and popping up the muddy water may be viewed as analog to the 'strombolian' behavior of some igneous volcanoes, where gas bubbles rise through the magma column and burst near the surface in response to pressure decrease. In some cases, the dormant periods are interrupted by sporadic eruptive events that may be characterized by effusive or explosive activity, with large flaming eruptions caused by the self-ignition of the releasing methane (e.g., Mellors et al., 2007).

3. Mud volcanoes of Azerbaijan

Mud volcanoes of Azerbaijan are strongly coupled with the tectonic evolution of the WNW-trending Greater Caucasus fold-and-thrust belt, which has resulted from the still ongoing collision of the Arabian Plate with Eurasia (e.g., Philip et al., 1989; Axen et al., 2001). More than 200 active mud volcanoes have been identified onshore and even more offshore Azerbaijan (Jakubov et al., 1971; Dadashev et al., 1995; Guliyev and Feizullayev, 1997; Dimitrov, 2002; Etiope et al., 2004; Yusifov and Rabinowitz, 2004; Feyzullayev, 2012). The Azerbaijan mud volcanoes distinguish for their remarkable dimensions, as well as for the impressive eruptions they may experience occasionally (Guliyev and Feizullayev, 1997; Aliyev et al., 2001; Mellors et al., 2007).

3.1. Geologic and stratigraphic setting

The Greater Caucasus fold-and-thrust belt is characterized by a dominant south–southwestern structural vergence (e.g., Kopp and Shcherba, 1985). This range exposes a core of Paleozoic basement in its the central part, while its southeastern (Azerbaijan) sector is characterized by S–SSW-verging tight to isoclinal folds, commonly associated with thrusts, deforming Mesozoic and Paleogene–Miocene strata (Rogozhin and Sholpo, 1988; Allen et al., 2003; Alizadeh, 2008; Fig. 1a). The elevation of this range progressively decreases south-eastwards, as this approaches the Absheron Peninsula and the South Caspian Sea. The line of