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Research paper

A thermogenic hydrocarbon seep in shallow Adriatic Sea (Italy): Gas origin, sediment contamination and benthic foraminifera

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ABSTRACT

Gaseous and liquid hydrocarbons are seeping from sandy sea bottom ~10 m deep, about 2.4 km NNE of Civitanova Marche harbour, in central Adriatic Sea (Italy). We investigated the origin of the gas, the presence of a wide range of aromatic and aliphatic hydrocarbons and trace metals in shallow sediments, as well as the stable carbon and oxygen isotope composition of benthic foraminifera. In absence of detailed seismic images and subsurface geochemical data, we tried to estimate the source rock type and maturity based only on seep gas geochemistry. Molecular and isotopic composition of gas bubbles showed that the CH_4-rich gas is thermogenic ($\delta^{13}C_{CH_4} \sim -55‰$; $\delta^{2}H_{CH_4} \sim -280‰$; $C_1/(C_2+C_3) < 100$) with isotopic features that are compatible with low maturity source rocks belonging to the Emma-Scaglia (carbonate source rocks) Petroleum System (Upper Trias to Paleocene). Gas could then be stored in a biodegraded hydrocarbon pool, as suggested by ^{13}C enrichment in propane ($\delta^{13}C_3$: −24‰) and CO_2 ($\delta^{13}C_{CO_2}$: +12‰). Fluid seepage might be due to a local fracture zone corresponding to the intersection of NNW–SSE thrust faults with a NE–SW regional transversal deformation belt. Compared to other shallow marine seeps in Europe, the amount of methane released into the atmosphere is negligible (10^2–10^3 kg of CH_4 per year); but the seep also releases ethane and propane (10^3–10^4 L per year), which are photochemical pollutants and are not emitted by microbial gas seeps. Compared to a reference site one nautical mile far from the seep, the seabed sediments show higher concentrations of various classes of chemicals, such as benzene, toluene and ethylbenzene, semivolatile and non volatile aliphatic hydrocarbons (C_{10}–C_{40}), and phenols (2-methylphenol and 2,4-dichlorophenol). These compounds likely derive from the oil seepage. The sediments at the seepage site and those at the reference site have similar concentrations of trace metals (arsenic, barium, cadmium, chromium, copper, iron, manganese, nickel, lead, vanadium, zinc, mercury), typical of uncontaminated and shallow coastal areas. Finally, we provided the first data on foraminifera associated to thermogenic hydrocarbons. No endemic foraminifera species or authigenic carbonates occur in the sediments. Carbon isotopic composition of *Quinqueloculina padana* where oil slick prevails is less variable than in the gas bubbling site. However, thermogenic methane and oil do not apparently decrease the $\delta^{13}C$ value of foraminifera carbonate shell.

1. Introduction

Natural hydrocarbon seeps are widespread in Italy along the several petroleum systems from the Po Plain to Sicily, where active Neogene tectonics produced cross-stratal migration pathways which are very permeable to gas migration from reservoirs to the surface (Martinis, 1969; Etiope et al., 2007; Martinelli et al., 2012).

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In Italy at least 82 active seeps have been documented on land and, based on historical literature, other 256 manifestations have been catalogued as inactive or uncertain, waiting for verification in the field (Burrato et al., 2013). Offshore Italy, however, only a small number of active submarine seeps have been documented, mainly based on geophysical remote sensing, in the Adriatic Sea (Conti et al., 2002; Panieri, 2006; Geletti et al., 2008; Donda et al., 2013), in the Sicily channel (Holland et al., 2003) and in the Ionian Sea (Praeg et al., 2009). While the gas origin, thermogenic or microbial, of the onshore Italian seeps has been widely studied (e.g., Etiope et al., 2002, 2007; Tassi et al., 2012), the molecular and isotopic composition of submarine seeps related to hydrocarbon basins has not been analysed so far. Isotopic analyses of the seeping gas offer an extraordinary opportunity to assess hydrocarbons reservoir nature and quality (e.g., biodegradation) and source rock type and maturity without drilling (e.g., Etiope et al., 2009a, 2009b; 2013), thus providing fundamental insights into petroleum fluid dynamics in a basin. Terrestrial and shallow water seeps release methane to the atmosphere, where it serves as potent greenhouse-gas. On a global scale gas seepage is the second natural source of methane after wetlands (e.g., Etiope and Klusman, 2010; Etiope, 2012). Thermogenic gas seeps also release ethane and propane (Etiope and Ciccioli, 2009), which are photochemical pollutants and ozone precursors. Their amount in the gas depends on the thermal maturity of the source rock. In addition, submarine seeps can be a natural source of pollutants for the marine environment, as they may release chemicals such as volatile hydrocarbons (C_6–C_{10}) and polycyclic aromatic hydrocarbons (PAHs), which represent the more typical contaminants analysed in anthropogenically polluted and potentially toxic marine sediments (Neff, 2002). Finally, submarine seeps may host benthic foraminifera which are indicators of methane seepage both in modern marine environment and in the fossil record (Sen Gupta et al., 1997; Rathburn et al., 2000; Panieri, 2006; Martin et al., 2007; Panieri et al., 2012 and references therein).

Here we present the first geochemical study of a submarine hydrocarbon seep in Italy, including the three topics mentioned above: gas geochemistry, chemicals in sediments and benthic foraminifera. The investigated seep, named Fontespina, is located in the central Adriatic coast, 2 km from Fontespina village, near Civitanova Marche (Figs. 1 and 2). Gas bubble plumes and oil slicks on the sea surface have been observed in this area for decades by fishermen and local port authorities, but the origin of the gas has never been studied. The Adriatic basin has both biogenic (microbial) and deep thermogenic petroleum systems (Mattavelli et al., 1991), and modern (non-fossil) microbial methane can generally form in shallow coastal areas (e.g., Garcia-Gil, 2002; Judd, 2004; Panieri, 2006). Our first objective was to identify these possible sources. More generally, determining composition, origin and depth of provenance of Fontespina gas helps to characterize its impact on the atmosphere (i.e., whether it emits only methane or other hydrocarbons) and to assess the Total Petroleum System (TPS), i.e. the whole hydrocarbon-fluid system including the essential elements and processes needed for oil and gas accumulations, migration and seepage (Magoon and Schmoker, 2000). Unfortunately there are no subsurface geochemical or detailed seismic data that may help in deciphering the origin of the seep and its role in the TPS. We wanted to verify, however, whether the interpretation offered by the seeping gas is compatible with the already known characters of the underlying petroleum system, i.e. potential source rock type and maturity, and the presence of gas and oil in reservoirs. We analysed the molecular composition of gas bubbles, the stable carbon isotopic ratio of C_1–C_3 alkanes (methane, ethane, propane) and CO_2, the stable hydrogen isotopic ratio of CH_4, and the isotopic ratio ($^3He/^4He$) of helium, as tracer of crustal vs. mantle components. Carbon isotopic composition of CH_4 was also analysed in sediments and water. C_1–C_3 isotopic data have been used to estimate source rocks type and maturity. Then, we estimated in terms of orders of magnitude, the amounts of methane, ethane and propane released to the atmosphere from the main bubbling plumes. Seep sediments collected in close proximity of

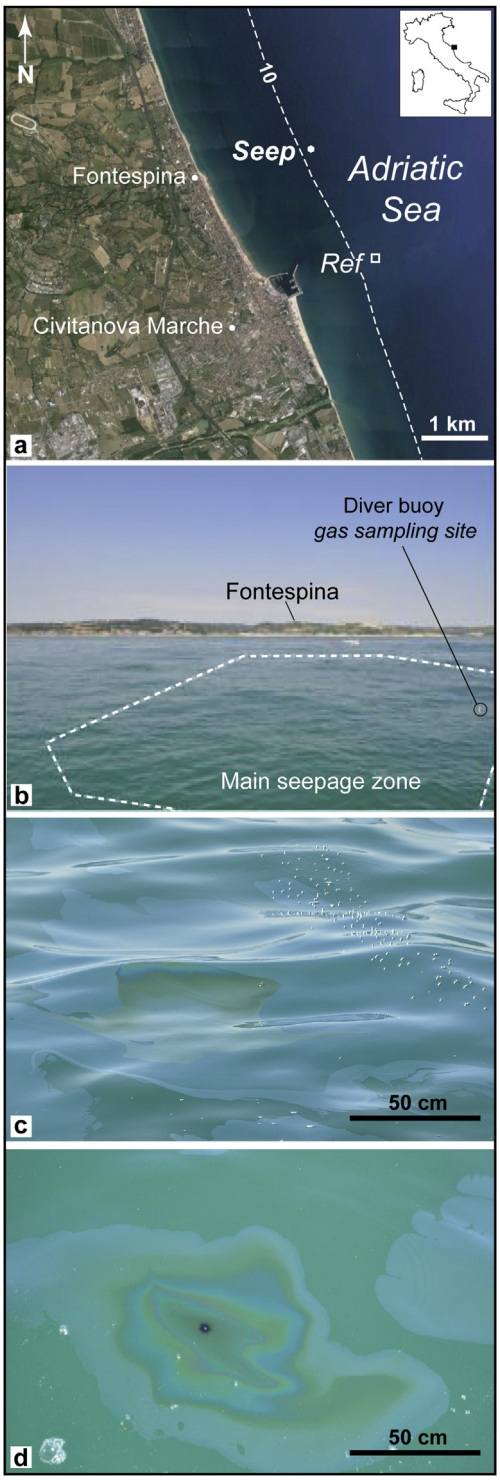

Figure 1. Location of the seep and reference (Ref) sampling site (a; from Google Earth; bathymetry obtained from http://topex.ucsd.edu/WWW_html/srtm30_plus.html) and images of the seepage area (b), with gas bubble plumes (c) and oil slicks (d) on the sea surface.