Chimaera, A large Abiotic Gas Seep in Turkey*

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Abstract

Abiotic gaseous hydrocarbons are generated by chemical reactions, without organic matter being involved, under a wide range of temperatures (Etiope and Sherwood Lollar, 2013); trace amounts occur in volcanic and geothermal systems but, in addition to some submarine hydrothermal-serpentinization systems at Mid-Ocean Ridges (e.g., Proskurowski et al. 2008), large amounts of methane were recently discovered in an increasing number of sites on land, in seeps or springs from ultramafic rocks characterized by low temperature serpentinization driven by meteoric waters (e.g., Etiope et al., 2011; 2013a; 2013b; Boulart et al., 2013). An outstanding occurrence of dominantly abiotic methane in these systems is that of the Chimaera seep, in Turkey, which is probably the biggest onshore abiotic gas seep on Earth (Hoşgörmez et al., 2008; Etiope et al., 2011). Chimaera (from the mythological fire-breathing creature told by Homer in *The Iliad*) is an archeological site near Çirali, in the Antalya Gulf, famous for the natural flames issuing from the ground along the flank of a mountain in the Olympos National Park (Figure 1a-b). The ground is formed by serpentinized peridotite rocks, belonging to the Tekirova ophiolite, crossed by a large fault, a tectonic contact between peridotites and limestones. The gas, composed of about 87% methane and 10% hydrogen, escapes from this fault producing at least 20 large flames, up to a half meter in height. Methane is dominantly abiotic ($\delta^{13}C$: -12 ‰ VPDB; $\delta^{2}H$: -129 ‰ VSMOW), and it escapes from both focused (visible) vents in rock fractures and pervasively as an invisible seepage throughout the area; at least ~200 tonnes of CH_4 are released every year into the atmosphere. In a survey conducted in 2012, we found a second seepage site on the top of the mountain, about 300 m from Chimaera, with two actively burning gas vents and numerous burned trees over an area of at least 2000 m^2 (Figure 1c). The trees were likely killed by episodic burning of

gas from the ground. The total emission of methane into the atmosphere could be approximately several hundred tonnes per year. Radiocarbon (^{14}C) analyses of CH_4 (performed at Isotech Labs, Illinois) have demonstrated that gas is fossil (percent of modern carbon ~ 0), i.e., older than 50,000 years. This is the first radiocarbon analysis ever done on methane issuing from serpentinized rocks. The fossil character of the gas suggests that, at least in the Chimaera case, abiotic synthesis is not a modern or contemporary process. Gas could have originated throughout long times after ophiolite emplacement (Alpine orogenesis obduction). Land-based serpentinization may have first produced hydrogen, which successively migrated into suitable rocks in the presence of CO_2 (probably derived from meteoric water or from the adjacent limestones) and metal catalysts, which are necessary to support Fischer-Tropsch type (FTT) reactions, generally invoked as a main mechanism of abiotic gas production. In analogy with thermogenic gas seeps, the enormous continuous flux of gas implies that abiotic methane must come from a pressurized accumulation or reservoir at depth. It would be hard to imagine that methane production by FTT or any other abiotic mechanism (but also H_2 production by serpentinization) would be so rapid as to sustain and balance the continuous output of hundreds of tonnes per year. It is more likely that Chimaera seepage system is analogous to typical thermogenic seeps which are fed by pressurized reservoir; gas moves by pressure-driven advection and is channelled along a permeable fault. Considering that the "eternal flames" are active since at least 2 millennia (they were documented by Pliny the Elder in *Naturalis Historia, <79 AD*), simple calculations suggest that the total amount of methane emitted so far would be of the order of 400 million cubic meters. The initial amount of methane stored in the reservoir (the ultimate reserve) could have been in the order of thousands of million cubic meters, similar to a conventional biotic gas field. No studies have been made to assess the present-day reserve in this area.

The Chimaera case would suggest that reservoirs of abiotic gas are possible. At least for its surface manifestation and huge gas flux, Chimaera is however an extraordinary case; so far, big abiotic gas seeps have not been documented in other countries. All other seeps in land-based serpentinization sites (e.g., Los Fuegos Eternos in the Philippines, Poison Bay seep in New Zealand), and the various methane-bearing hyperalkaline spring,s such as those in Oman, Italy, Greece, Portugal, Canada (see a recent review by Etiope and Schoell, 2014) release much lower amounts of gas. Still the methane output is often considerable and could require the need of a gas accumulation. Radiocarbon analyses of CH_4 are necessary in this respect.

It is known that fractured igneous rocks can act as hydrocarbon reservoirs in atypical and deep petroleum systems (Farooqui et al., 2009; Schutter, 2003). Serpentinization reactions, for example, generate large increases in volume and thus induce high local strains and stresses with episodic cracking and increases in rock permeability. As a consequence, serpentinized rocks form competent reservoirs for many oilfields, such as in Texas and Cuba (Smith et al., 2005), and inputs of material from igneous rocks into petroleum pools are possible (e.g., Szatmari et al., 2011). Therefore, some abiotic gases, formed by the FTT reactions, may give minor contributions to the hydrocarbon pool where located in or adjacent to igneous rocks. Occurrences of minor amounts of abiotic gas in commercial fields in China (e.g., in the Songliao Basin; Ni et al., 2009) and in the United States (Jenden et al., 1993) have been suggested, based upon ^{13}C-enrichments in methane, mantle signatures in the helium isotopic composition, and the carbon isotopic inverse trend in alkane gases. As recently as the early 1990s, commercial accumulations of abiotic CH_4 have not been identified by the petroleum industry, and far less than 1% CH_4 in most oil and gas fields is abiotic (Jenden et al., 1993). However, abiotic methane may have a carbon isotopic composition that overlaps with biotic gas (Etiope and Schoell, 2014). Thus, the origin of gas in atypical petroleum systems characterized by igneous rocks should be re-examined by using modern geochemical interpretative techniques.

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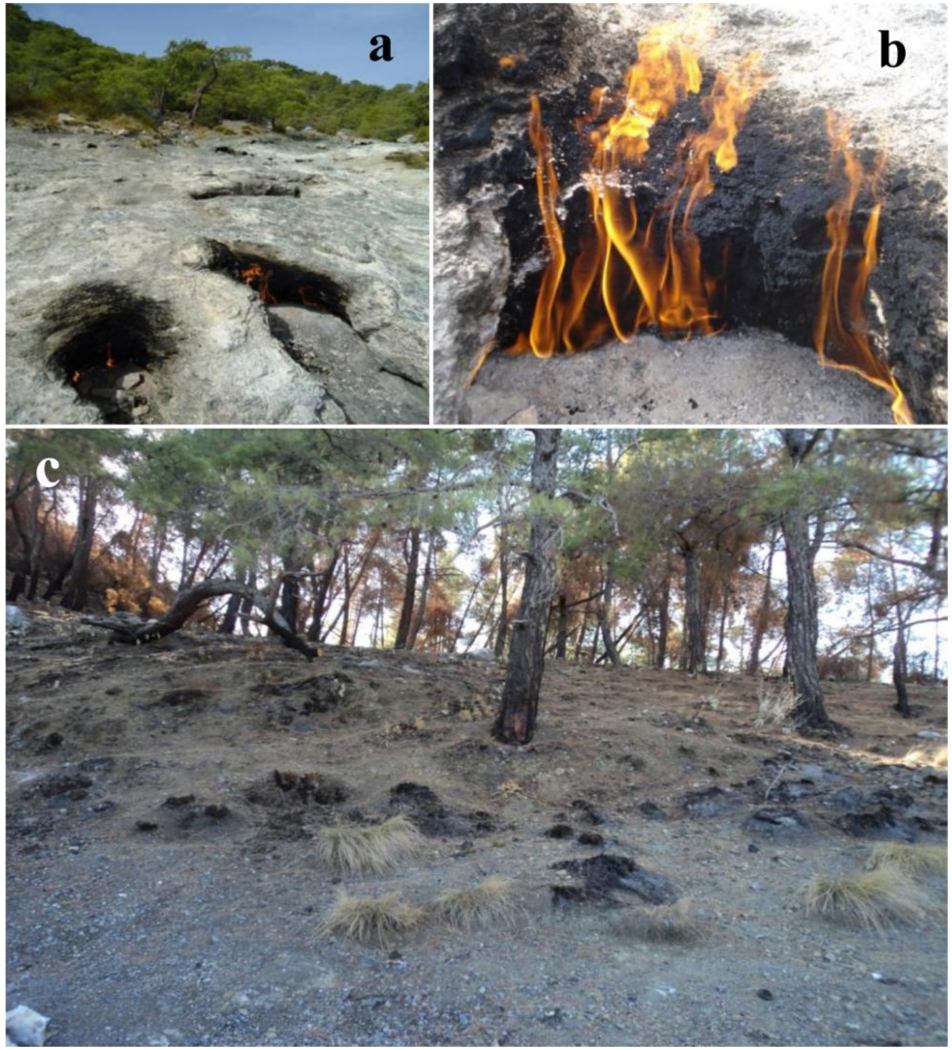

Figure 1. a-b: Images of the Chimaera seep with burning gas issuing from fractures in a peridotite outcrop of Tekirova ophiolite. c: A second seepage site, about 300 m from the main Chimaera seep, with burned soil and trees.