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Methane and hydrogen in hyperalkaline groundwaters of the serpentinized Dinaride ophiolite belt, Bosnia and Herzegovina

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ABSTRACT

Methane (CH_4) in continental serpentinized peridotites (MSP) has been documented in numerous hyperalkaline (pH > 9) springs and gas seeps worldwide. With a dominantly abiotic origin, MSP is often associated with considerable amounts of hydrogen (H_2), produced by serpentinization. Both gases may fuel microbial activity in igneous rocks and may have played roles in the origin of life. MSP is also a natural CH_4 source for the atmosphere, not included in the global greenhouse-gas budget, yet. Here we document a new and major case of MSP, in the Dinaride ophiolite belt in Bosnia and Herzegovina. CH_4 is dissolved (83–2706 μM) in low temperature (13–30 °C), hyperalkaline (pH 10 to 12.8) waters in six sites, sampled through springs and boreholes. Four sites (Slanac, Vlajići, Kulaši and Lješljani) show CH_4 isotopic signatures typical of abiotic MSP ($\delta^{13}C$: −18.5 to −35.7‰; δ^2H: −221 to −335.4‰); two sites (Vaićeva and Kiseljak) show a dominantly biotic signature ($\delta^{13}C$: −58.8 and −65.1‰; δ^2H: −310.8 and −226.8‰), probably due to mixing with gas from coal-beds adjacent to the ultramafic rocks. H_2 concentration is highly variable (up to 348 μM), ethane, propane and butane reach 0.13 vol.% in total, and helium isotopic composition (R/Ra: 0.12 to 0.48) reflects a dominant crustal signature. The Lješljani site features the highest pH (12.8) and CH_4 emission (~9 ton y^{-1}) in peridotite-hosted hyperalkaline groundwater documented so far. Geological and geochemical data converge towards the hypothesis that, as proposed in similar cases, CH_4 was mainly generated by Sabatier reaction between H_2 (from serpentinization) and CO_2 (from C-bearing rocks, in tectonic contact with the ophiolite, or other CO_2 sources). CH_4-H_2-H_2O disequilibria and Sabatier reaction constraints suggest that CH_4 is not formed in the hyperalkaline water, but in water-free or unsaturated rocks hosting opportune metal catalysts (e.g., chromitites). The amount of methane released to the atmosphere from individual springs is comparable to that of conventional biotic gas seeps/springs in sedimentary basins.

1. Introduction

Abiotic gas in land-based ultramafic rock systems (ophiolites, peridotite massifs and intrusions) has been discovered in an increasing number of countries, in America, Europe, Asia and Oceania, since the 1980s (see reviews in Etiope and Sherwood Lollar, 2013; Etiope and Schoell, 2014; Etiope, 2017a). In the last five years the list of sites with surface manifestations of methane (CH_4) in serpentinized peridotites (hereafter referred as MSP), either in hyperalkaline (pH > 9) springs or gas vents, increased considerably, including today 16 countries (Etiope, 2015, 2017a). CH_4 concentrations may exceed 80 vol.%, and is often associated to variable H_2 amounts that may reach 90 vol.%. MSP has a combination of stable C and H isotope composition that, in most of the cases, is markedly different from that of biotic (microbial and thermogenic) methane and is attributed to an abiotic origin (e.g., Abrajano et al., 1990; Fritz et al., 1992; Etiope and Sherwood Lollar, 2013; D'Alessandro et al., 2016); only a few cases show biotic isotopic signatures (Boschetti et al., 2013a; Wang et al., 2015; Etiope et al., 2016). Fischer-Tropsch Type reactions (FTT), or more

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precisely the Sabatier reaction between carbon dioxide (CO_2) and hydrogen (H_2, from serpentinization), are considered a main pathway for abiotic MSP formation, which typically occurs at low temperatures (<150 °C; Etiope et al., 2016; Young et al., 2017).

The importance of MSP crosses different disciplines, from biology, astrobiology to resource exploration and atmospheric budget of greenhouse gases. In fact, MSP may have played a key role in the origin of life, may fuel microbial life in igneous rocks on Earth (abiotically originated CH_4 is energy source for microbes; e.g., Russell et al., 2010; Schrenk et al., 2013) and other planets (similar methane may be formed on Mars; Etiope et al., 2013a; Oehler and Etiope, 2017), and can be an additional source of gas in petroleum systems hosting ultramafic rocks (Etiope and Schoell, 2014; Etiope et al., 2015). MSP surface seeps and gas-rich springs represent, then, a natural source of CH_4 for the atmosphere. Geological CH_4 seepage is known to be a major natural source of greenhouse gas to the atmosphere (about 50–60 Tg CH_4 y^{-1}), second only to wetlands (Etiope et al., 2008; Etiope, 2012; Saunois et al., 2016; Schwietzke et al., 2016), but bottom-up estimates obtained so far include only the natural gas emissions in sedimentary petroleum basins and geothermal areas. Due to the paucity of flux data, MSP emissions are not estimated on a global scale, yet. Nevertheless, because MSP enters the atmosphere also via diffuse and invisible microseepage throughout peridotite outcrops (Etiope et al., 2011, 2016), and serpentinized peridotites cover at least 3% of the Earth's surface (Guillot and Hattori, 2013), its global emission could be significant.

In this work, we report a new case of MSP occurring in the Dinaride ophiolite belt in Bosnia and Herzegovina. Several hyperalkaline springs, with pH > 10, have been known in this region since when hydrogeochemical and hydrogeological investigations were carried out in the 1970s (Derković, 1973; Barnes et al., 1978; Miošić, 1982). Hyperalkaline waters (pH > 9) are a typical indication of active serpentinization and their chemistry is controlled by the liberation of OH^- and Ca^{2+} during the hydration of olivine and pyroxenes in ultramafic rocks, which is largely driven by meteoric water (e.g., Barnes and O'Neil, 1969; Bruni et al., 2002; Chavagnac et al., 2013). All around the world, these waters (in springs or aquifers) revealed to have systematically considerable amounts of CH_4. We analysed gas dissolved in hyperalkaline groundwater from six sites in the areas of Karanovac, Živinice, Tuzla, Teslić, Prnjavor and Lješljani, hosting springs or boreholes, also used in therapeutic spas. As expected, we found significant amounts of CH_4. In this work we report the molecular composition of the gas (N_2, O_2, CH_4, H_2, CO_2, He, CO, and C_{2+} alkanes from ethane to butane), the stable C and H isotope composition of CH_4, the stable H isotope ratio of H_2, and the helium isotopic ratio. The geochemical data have been interpreted to assess the methane origin and its relationship with hydrogen and other gases, taking into account the geological setting of the aquifers (faults, petrology, geothermal gradients) and the analogy with MSP geochemistry in other sites. The amount of methane released into the atmosphere was estimated based on the water flow rates. Hydrochemistry of the waters is reviewed in Miošić and Samardžić (2015) and new data acquired by us in 2016 will be discussed elsewhere.

2. Geological setting of the peridotite aquifers

2.1. The peridotite massifs

The hyperalkaline springs and boreholes are located at the boundaries of the Balkan peridotite massifs belonging to the Dinaride ophiolite belt, which is part of the Alpine-Himalayan suture zone of the former Neo-Tethys ocean (e.g., Pamić et al., 2002; Hrvatović and Pamić, 2005; Dilek and Furnes, 2011). In particular, the six investigated sites are related to aquifers hosted in the peridotite massifs of Ozren (Vaićeva voda at Karanovac; sample HW1), Krivaja-Konjuh (Slanac at Živinice; HW2; Kiseljak near Tuzla; HW3), Borja (Vlajići at Teslić; HW4-5), Ljubić-Cavka (Banja Kulaši near Prnjavor; HW6) and Kozara (Lješljani; HW7-8) (Fig. 1 and Supplementary Material). The main peridotite massifs, variably associated to cumulate gabbros, diabases and basalts, are those of Krivaja-Konjuh (500 km^2) and Mts. Ozren and Borja (300 and 100 km^2). All massifs are fractured ultramafic bodies, in tectonic contact with sedimentary rocks of the surrounding ophiolite melange, a chaotic complex composed of ultramafics, metasediments, graywackes, chert, amphibolite, clastics, and Middle Triassic to Tithonian limestone. Along the contact, ultramafics are strongly cataclased, mylonitized and serpentinized. All springs and boreholes investigated in this work are located along these contacts (Fig. 1). On the western side, the ophiolite nappes overlay the foredeep flysch and carbonates.

The peridotites are largely represented by lherzolites; primary rocks-forming minerals include olivine, orthopyroxene and clinopyroxene, all of them with high content of MgO, accessory spinel and amphibole. Secondary minerals of the serpentine group (lizardite, clinochrysotile and antigorite), enstatite in bastite and talc, clinopyroxene in uralite and chlorite, and spinel in magnetite, are widely distributed. They are often accompanied by chalcedon, quartz, magnesite and quartz-carbonate rocks (listvenites), especially along the margins of Mt. Ozren massif and in the Teslić area (Pamić and Olujić, 1974). Petrographic and mineralogical details are reported, among others, by Pamić and Desmons (1989) and Pamić et al. (2002). It is opportune to mention also the occurrence of chromitites, because they are considered potential source rocks of abiotic methane due to their high content of powerful metal catalysts, such as ruthenium, which can support the Sabatier reaction at low temperature (Etiope and Ionescu, 2015). Chromitites outcrop mostly in the Krivaja-Konjuh massif (e.g., Duboštica), and in minor amounts in the Ozren and Borja Mts. (Popević, 1971). They occur as layers and lenses in stratified peridotite forming ore zones several hundred meters long and up to 30 m thick. Their subsurface distribution is unknown. Finally, it is worth noting that coal-beds in Pliocene sediments, which can be source of biotic (microbial or thermogenic) methane, overly the ultramafic rocks at Kiseljak, as

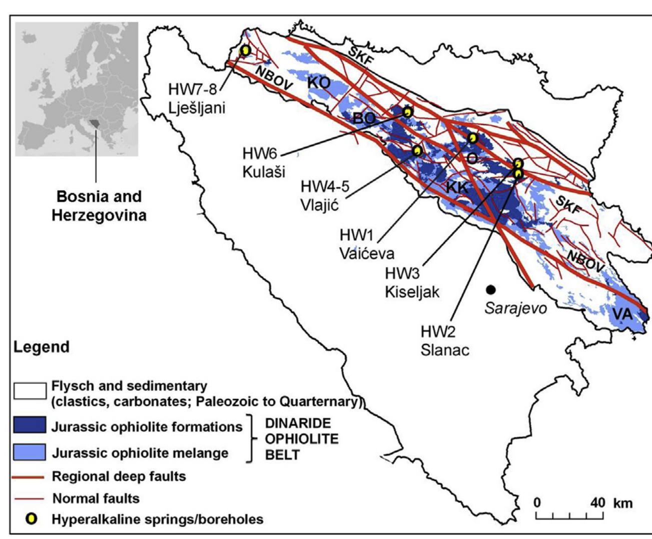

Fig. 1. Geological map of the Dinaride ophiolite belt and location of the investigated sites. Peridotite massifs: KO: Kozara; BO: Borja: O: Ozren; KK: Krivaja-Konjuh; VA: Varda. Regional faults: SKF: Spreca-Kozara Fault; NBOV: Novi Grad-Banjaluka-Olovo-Višegrad Fault. Redrawn and simplified from Hrvatović (2009). Detailed maps of site location are in the Supplementary Material.