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DIFFERENCES IN GAS VENTING FROM ULTRAMAFIC-HOSTED WARM SPRINGS: THE EXAMPLE OF OMAN AND VOLTRI OPHIOLITES

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ABSTRACT

Serpentinisation of mantle rocks, leading to natural venting of hydrogen and methane, has been reported to occur at the global scale, wherever fluids percolate in ultramafic formations. Here we compare gas composition from two on-land, low-temperature, and hyper-alkaline springs hosted on ultramafic rocks in the ophiolite massifs of the Sultanate of Oman and the Ligurian Alps (Voltri Group, Genoa region, Northern Italy). These two settings exhibit similar chemical and mineralogical features but show diverse styles of gas venting. Commonly to all hyper-alkaline springs, gases are characterised by relatively high N_2, very low O_2 and CO_2 concentrations, and a strong enrichment in H_2 and CH_4. The comparison between Oman and Liguria highlights a high variability of the H_2/CH_4 ratios whereby the gas phase of the Oman Ophiolite is enriched in H_2 whereas being CH_4 enriched in the Voltri Ophiolite. These results combined with literature data define three groups that may reflect different stages of serpentinisation producing fluids from hydrogen-dominated to methane-dominated. The origin of these distinct groups might lie in the difference of the mineralogical composition of the rocks within which the fluids circulate, on the degree of alteration of the rocks and finally on the geological/metamorphic history of the ophiolite.

INTRODUCTION

Natural venting of hydrogen (H_2) and associated methane (CH_4) is a common feature of fluid-rock interaction, and in particular of serpentinisation of ultramafic rocks. In the last ten years, this phenomenon has gained significant interest in the scientific and industrial communities, from prebiotic chemistry and astrobiology to energy and mineral resource exploration. Serpentinisation reactions - i.e. the alteration of mantle peridotites by fluids of various origin (e.g., meteoric, seawater) - may naturally produce high amounts of H_2, which leads subsequently to the abiotic formation of CH_4 and possibly higher hydrocarbon (HC) chains via Fischer-Tropsch-Type (FTT) reactions. This FTT process occurs when faults allow fluid penetration within the peridotites and have been identified in different settings: along fracture zones, passive margins, at the wall of rift valleys, at mid-ocean ridges (e.g., Cannat et al., 2010; Charlou et al., 2010), and also in deep igneous and metasedimentary rocks (Sherwood Lollar et al., 2006).

It is now clear that wherever ultramafic rocks are percolated by fluids, alkaline springs are present. In the Deep Sea, a few hydrothermal vents lying on ultramafic rocks are known today, including either high-temperature vent fields (> 350°C) such as Rainbow, Logatchev and Ashadze (Lein et al., 2000; Charlou et al., 2002; Fouquet et al., 2008), or low-temperature ones (~ 100°C) such as Lost City vent field (Kelley et al., 2005; Proskurowski et al., 2008). In recent years, several ones were identified and/or suspected on ultra-slow spreading ridges, e.g., Knipovich, Gakkel and Cayman ridges (Bach et al., 2002; Connelly et al., 2012). On-land, percolation of meteoric water in obducted ophiolite massif produces low-temperature hyper-alkaline springs, which are considered as "analogues" of the Lost City vent field off the Mid-Atlantic Ridge. They are reported in Oman (Neal and Stanger, 1983; Sano et al., 1993; Chavagnac et al., 2013a, 2013b), Philippines (Abrajano et al., 1988), Turkey (Hosgormez, 2007; Etiope et al., 2011), Italy (Cipolli et al., 2004; Chavagnac et al., 2013a; 2013b; Schwarzenbach et al., 2013), California (Blank et al., 2009), Cyprus (Neal and Shand, 2002), Greece (Etiope et al., 2013a), Portugal (Marques et al., 2008; Etiope et al., 2013b), British Columbia (Power et al., 2007), New Zealand (Lyon et al., 1990) and New Caledonia (Launay and Fontes, 1985; Boulart et al., 2012), amongst others. The main differences between submarine vents and on-land warm springs are the nature of the percolating water, i.e. seawater and meteoric fluids, respectively, as well as venting temperature, which is lower than 100ºC in the continental settings. This reveals that the development of hydrogen and methane venting in ultramafic-hosted environment may encompass a broad range of conditions (pressure, temperature, water/rock ratio, etc.) leading to various degrees of advancement in the chemical reactions for the production of natural H_2 and CH_4.

Serpentine results from the interaction of water with Fe-Mg rich minerals, i.e. olivine and pyroxene. During the serpentinisation reactions, Fe^{2+} contained in olivine is oxidised to Fe^{3+} (which may lead to the formation of secondary magnetite) while water reduction produces hydrogen and aqueous hydroxyl responsible for high pH values. Hydrocarbon gases may be generated abiotically via FTT reactions (i.e. Sabatier reaction) through the reduction of carbon dioxide by H_2 to form CH_4 and longer-chain HC (Ingmanson and Dowler, 1977; Shock, 1990; Holm and Charlou, 2001; Konn et al., 2009a; 2009b). Serpentinisation is thus accompanied by the production of methane and light alkanes (Ague, 2000). Note that low-temperature hyper-alkaline waters have lost all their dissolved inorganic carbon (DIC) during the course of serpentinisation reactions (Sader et al., 2007; Chavagnac et al., 2013a).

Large quantities of CH_4 and lesser amounts of light alkanes can be produced by FTT reactions when they are catalysed by magnetite, chromite or awaruite at temperatures around 300°C (Berndt et al., 1996; McCollom and Seewald, 2001; 2007), but also at lower temperatures (de Boer et al., 2007; Hosgormez, 2007, Neubeck et al., 2011; Etiope et al., 2013a). Nevertheless, the sole abiotic origin of HC in ultramafic environments remains questionable in the sense that biologically produced methane can be present at the same locations and it is difficult to distinguish between the two processes (Sherwood Lollar et al., 2006; Konn et al., 2009a; 2009b; Bradley and Summons, 2010; Etiope et al., 2011).

In this contribution, we report new data on the gas chemical composition from two on-land, low-temperature, and hyper-alkaline warm springs hosted on ultramafic rocks of the ophiolite massifs of the Sultanate of Oman and the Ligurian Alps (Voltri Group, Genoa region, Northern Italy). The present dataset complements the ones of Neal and Stanger (1983) and Sano et al. (1993), who first reported the composition of the gases venting in the hyper-alkaline springs of Oman. The composition of gases bubbling in the Ligurian springs is given by Cipolli et al. (2004), Schwarzenbach (2011) and Boschetti et al. (2013). Alteration of these two ophiolites by meteoric waters generates hyper-alkaline springs with a pH > 9 and similar chemical and mineralogical features (Chavagnac et al., 2013a; 2013b) but with great differences in their gas chemical composition.

GEOLOGICAL SETTINGS

Oman Ophiolite

The Semail Nappe in the Northern Mountain of the Sultanate of Oman (Fig. 1) is one of the largest (~ 30.000 km^2) and best exposed (thanks to semi-arid climate) fragment of the oceanic Tethys lithosphere on land (Glennie et al., 1973). Its geological evolution includes magmatic accretion along an oceanic spreading centre in a short time laps from ~ 97 to ~ 95 Ma (Tilton et al., 1981; Tippit et al., 1981; Goodenough et al., 2010; Rioux et al., 2013) immediately followed by intra-oceanic thrusting in a near-ridge environment (Lanphere, 1981; Boudier et al., 1985; Montigny et al., 1988). Its obduction onto the Arabian margin occurred about 70 m.y. ago (Glennie et al., 1973). Petrological and geochemical signatures of igneous rocks of this ophiolite are clearly MORB-related in several districts (Benoit et al., 1996; Ceuleneer et al., 1996; Python and Ceuleneer, 2003; Python et al., 2008). Elsewhere parent melts have a more ambiguous signature that can be attributed to nascent subduction (Pearce et al., 1981) or to incorporation of very-high temperature hydrothermal water in a spreading setting (inducing hydrated melting and modifying liquid lines of descent). A thick pile of neritic carbonates deposited on the top of the ophiolite after subsidence of the Oman margin (Glennie et al., 1973). The present exposure of the ophiolite is related to recent (Mio-Pliocene) uplift of the Oman mountains, likely a prelude to the future collision with Eurasia

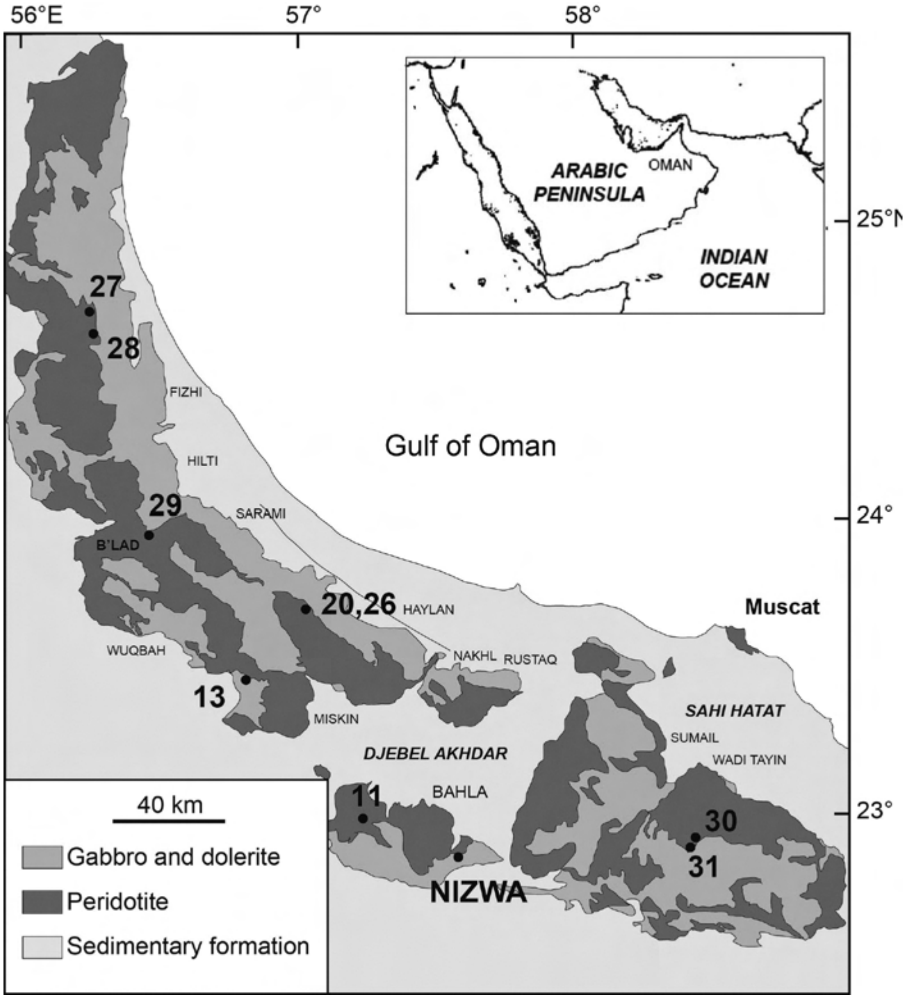

Fig. 1 - Simplified geological map of the Oman ophiolite showing the locations of the investigated springs. For a better comprehension of the surface lithology, the reader may refer to Table 1 where details are given.

(Fournier et al., 2006). Alkaline springs are essentially located in two particular settings: i) at the basal contact between autochthonous sediments and mantle peridotites, and ii) at the contact between the mantle peridotites and the cumulates from the crustal section (the paleo“Moho”). Rare springs are located within the mantle or within the crustal section, away from these major geological discontinuities. When present, these springs and gas vents are located along faults and shear discontinuity zones in the serpentinised ultramafic section, but also in less altered peridotites and gabbroic sections. Release of gases can be directly seen from bubbling within the wadi bed (local Arabic name for small rivers). Gas discharge is also evidenced by pockmarks forming in the precipitates accumulating in the riverbed (Chavagnac et al., 2013a). Neal and Stanger (1983) estimated the gas flows from 10 mL/sec up to 10 L/sec at Nizwa and B’lad (station 29) for the highest flows (Fig. 1).

Although the present climate in Oman is quite dry (117 mm/year average annual rainfall; Kwarteng et al., 2009), the region was characterised rather recently (a period centred on 8.200 years BP) by a much more humid climate with intense rain events related to the end of the last glacial period (Burns et al., 2001). It is likely that a large proportion of the underground aquifers of Oman were refilled during this period, enabling the perennial flow of hyper-alkaline waters (Clark and Fontes, 1990; Dewandel et al., 2005).

Voltri Group, Liguria, Italy

In Liguria, the studied area is located in the Voltri Massif, which is part of the Penninic ophiolites (Internal Ligurides) and forms the transition between the Alps and the Appenine (Fig. 2). It is the largest ophiolite massif in the Alps-Appenine system (Brouwer et al., 2002) composed of three main units: i) a calcschist unit consisting of blueschist to eclogite-facies calcareous metasediments, metavolcanics and slices of serpentinites (Voltri-Rossiglione Unit), ii) a serpentinite unit with highly-altered peridotites including eclogitic metagabbros and metabasalts (Beigua Unit) and, iii) a lherzolite unit (Erro-Tobbio Unit) (Capponi et al., 1994; Brouwer et al., 2002; Bruni et al., 2002; Cipolli et al., 2004; Vignaroli et al., 2010).

The Voltri Group is derived from the Western Tethys ocean that separated European and Adriatic plates in the Middle Jurassic (Bill et al., 2001). It is considered as onland analogue of oceanic lithosphere originated at slow-spreading ridges (Barrett and Spooner, 1977). Indeed, the chemistry of the Beigua metagabbros indicates a tholeitic origin typical of mid-ocean ridges magmatism (Brouwer et al., 2002). The Piedmont-Ligurian Ocean was later (Early Cretaceous) subject to subduction and collision leading to the emplacement of oceanic units onto the European continental crust (Brouwer et al., 2002).

Most of the hyper-alkaline springs found by Cipolli et al. (2004) are located within the Beigua Unit composed of

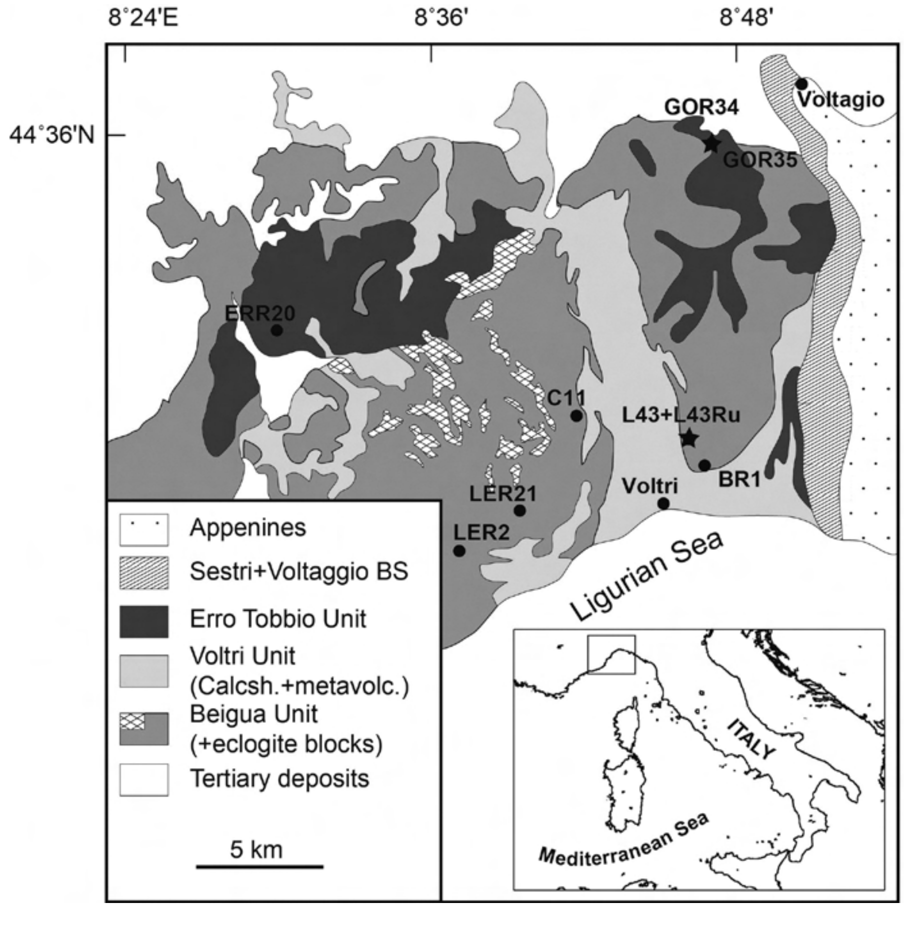

Fig. 2 - Simplified geological map of the Voltri Massif (Liguria, Italy) showing the locations of the investigated springs. Stars indicate the two stations where active gas bubbling was observed.

metagabbros and metabasalts that underwent multistage metamorphic evolution in blueschist to eclogite facies. Only a couple of these springs are hosted on altered lherzolites of the Erro-Tobbio Unit (Fig. 2). These springs emerge along faults and fractures through serpentinites and related rocks.

Springs are usually located in the riverbeds, just above the water level and often harnessed with tubing. Direct gas bubbling was observed only at 3 locations (GOR34, GOR35, L43; Fig. 2) but the discharge was very irregular, sometimes absent for several minutes.

SAMPLING AND ANALYSES

Sampling was performed in June 2010 in Liguria and in January 2011 in Oman. Sampling sites were chosen from a database kindly provided by the Ministry of Water Resources of Oman, while in Liguria, sampling sites were chosen from the database published in Cipolli et al. (2004). Details on locations, hosting lithology/mineralogy, as well as basic chemical composition of the spring waters (pH, temperature, major cations and anions) are summarised in Table 1 and is extensively discussed in Chavagnac et al. (2013b).

21 gas samples from 9 sites were collected in Oman directly from the springs (Fig. 1). In Liguria, a total of 12 samples were collected from the 3 sites where active bubbling was observed (L43, GOR34, GOR35, Fig. 2). All gas samples were collected into crimp-sealed gas glass bottles by water displacement. Dissolved gas samples were also collected at all sites visited in 2010 (7 sites, 15 samples in Liguria) and 2011 (12 sites, 23 samples in Oman) into poisoned ($HgCl_2$), crimp-sealed glass bottles. Dissolved gases were then analysed using the headspace method (Kolb and Ettre, 1997) followed by gas chromatography in the same way as the gas samples, using a SRI 8610C gas chromatograph, fitted with a Flame Ionization Detector/Methanizer (FID-M) for the detection of methane (CH_4), small alkanes (C_1-C_5), CO and CO_2, and a Helium Ionization Detector (HID) for the detection of hydrogen (H_2), oxygen (O_2), and nitrogen (N_2). Methane gas is eluted together with CO and CO_2 on a 3' Molecular Sieve Packed Column, using Hydrogen as the carrier gas, while H_2, O_2, and N_2 are eluted on 6' Silica Gel Packed Column with Helium as the carrier gas.

In both cases, gas compositions are given as non-dried gases, taken into account the water vapour phase.

RESULTS AND DISCUSSION

Water chemistry and gas compositions

The full chemical composition of the hyper-alkaline fluids collected in Oman and Liguria and the composition of the associated mineralogical assemblages formed therein are presented in Chavagnac et al. (2013a; 2013b). For clarity we here summarise the composition, temperature and pH, together with the precipitate mineralogy and geological context (Table 1). Composition of the gas phase and the concentration of dissolved gases in the alkaline waters are given, respectively, in Tables 2 and 3. All the springs investigated in this study discharge hyper-alkaline waters, whose pH values range from 9.5 to 11.7 in Liguria, and from 10.1 to 11.9 in Oman. These waters all belong to the Ca-OH hydro-chemical group characterised by very low magnesium and DIC contents (Table 1) (Chavagnac et al., 2013b). The Ca-OH type - also described as mature waters as they evolved from rainwater to neutral Mg-HCO_3 waters and to high-pH Ca-OH type waters (Bruni et al., 2002) - is typical of waters circulating in a deep and closed ultramafic rocks system affected by present-day, low-temperature serpentinisation (Bruni et al., 2002; Neal and Shand, 2002; Chavagnac et al., 2013b; Etiope et al., 2013a; Schwarzenbach et al., 2013). According to these results, the gases, analysed in this study, are venting from waters coming from a deep aquifer, mainly hosted by serpentinised peridotites and related rocks (Bruni et al., 2002).

Temperatures vary from 21.4 to 23.7°C in Ligurian springs while they range from 20.9 to 29.9°C in Oman. These temperatures are very similar (although slightly higher in Oman springs) while the local climatic conditions are obviously very different between Oman and Northern Italy. Chavagnac et al. (2013b) noted that there was no significant influence of the seasonal variation on the spring water temperature both in Oman and Liguria. As indicated by Neal and Stanger (1984), these temperatures indicate that the water cannot penetrate deeper than the base of the ultramafic formation in Oman, i.e. 5 km.

All the gas samples at both locations are strongly enriched in N_2 and have very low O_2 partial pressures (Tables 2 and 3). This leads to a gas phase N_2/O_2 ratio varying from 130 to 440 in Oman and 417 to 848 in Liguria (atmospheric ratio is ~ 1.9). These values are similar to those found by Etiope et al. (2013a) in the Othrys ophiolite springs (Archani, Greece) as well as other world-wide hyper-alkaline springs (Neal and Stanger, 1983; Abrajano et al., 1988; Cipolli et al., 2004;). Dissolved N_2 and O_2 concentrations vary between 656 to 2135 μM and 5.7 to 23.4 μM, respectively in Oman, and from 600 to 3785 μM and from 3.2 to 31.6 μM, respectively in Liguria. Waters are therefore supersaturated in N_2 (the equilibrium concentration at T = 25°C and Salinity = 0.5 is ~ 400 μM; Hamme and Emerson, 2004) while the dissolved O_2 concentration is below the concentration of a water body at equilibrium with the atmosphere (402 μM at T = 25°C and Salinity = 0.5; Green, 1958). The low $O_{2(aq)}$ content, also observed by Etiope et al. (2013a) in Greece and Boschetti et al. (2013) in Italy, is a characteristic of hyper-alkaline waters and is due to the reducing conditions linked to hydrogen production during serpentinisation process. The actual presence of O_2 in our samples may be due to (air?) contamination during sampling. Similar explanation could be suggested for the high N_2 concentrations; however, contamination alone cannot account the high N_2 content of the gas phase. As reported by Etiope et al. (2013a), variability in dissolved N_2 and O_2 concentrations may rather be related to the meteoric water input into the upwelling spring water, especially in Liguria whereby average annual rainfall is ten times higher than in Oman.

Malatesta et al. (2011) argue that the Voltri Massif exhumed within a serpentinite "channel" whereby plutonic and sedimentary rocks metamorphosed at different pressure and temperature conditions are mixed during their pathway to the surface, wrapped by chlorite-amphibole-talc schists (e.g., Hoogerduijn Strating, 1991). Within these metamorphic rocks, the low-strain serpentinised peridotites contain higher nitrogen concentration (4-6 ppm) than their high-pressure counterparts (1-3 ppm), but still much lower than metasedimentary rocks (100-1700 ppm) (Busigny et al., 2003; Philippot et al., 2007). In the latter, N_2 occurs as ammonium (NH_4) and is substituting potassium in K-bearing minerals (Busigny et al., 2003).

Table 1 - Chemical composition, geological settings and precipitates of the Oman and Liguria hyperalkaline springs.

Sites	Latitude N	Longitude E	T (°C)	pH	SiO_2 (mmol/l)	Mg (mmol/l)	Ca (mmol/l)	K (mmol/l)	Na (mmol/l)	Cl (mmol/l)	Sampling	Geology	Precipitates
Oman													
Site 11	22.9880	57.2890	28.3	11.6	0.05	0.47	0.81	0.27	6.46	5.01	G/DG	Serpentinite	
Site 13	23.4033	56.8577	28.0	11.7	0.00	0.00	1.87	0.16	6.84	4.80	G/DG	peridotite/gabbro, MOHO	Aragonite, Brucite
Site 20	23.6232	57.1092	29.4	11.2	0.04	0.82	0.15	0.18	4.82	3.83	G/DG	Bedded gabbro above peridotite (100 m thick)	Aragonite, Brucite
Site 26	23.6187	57.1080	31.3	11.3	0.02	0.00	0.66	0.22	5.83	3.95	DG	Peridotite (100 m above the Moho)	Aragonite, Brucite
Site 27	24.7008	56.2692	31.2	11.1	0.12	1.40	0.51	0.08	3.02	2.12	G/DG	Wherlite/gabbro, within the crustal section	Aragonite
Site 28	24.5242	56.2845	30.7	10.1	0.08	1.13	0.61	0.09	3.17	3.17	G/DG	Bedded gabbro and ultramafic cumulates, within the crustal section	Aragonite, Mg-calcite, Brucite
Site 29	23.9572	56.4377	23.8	11.6	0.00	0.00	1.03	0.15	6.64	3.83	DG	Serpentinite with gabbro 100 m above	Aragonite (brucite)
Site 30	22.9037	58.4225	27.5	11.7	0.02	b.d.l.	1.96	0.14	6.65	2.81	DG	Peridotite	Aragonite, Brucite
Site 31	22.8907	58.3902	26.4	11.6	0.16	1.83	0.66	0.07	3.49	2.87	G/DG	Peridotite near MOHO	Aragonite (brucite)
Liguria													
ERR20	44.508793	8.499098	23.7	11.1	51.31	0.00	0.33	0.05	0.74	0.50	DG	Serpentinite + metagabbros	Calcite
C11	44.469	8.695346	14.0	11.5	3.62	0.23	0.07	0.04	0.57	0.60	DG	Serpentinite + metagabbros	Calcite
GOR34	44.596363	8.783641	23.7	11.6	10.17	0.01	0.85	0.11	0.85	0.42	G	Serpentinised lherzolites	Calcite+Aragonite
GOR35	44.59655	8.786923	21.4	11.2	45.10	0.12	0.46	0.05	0.32	0.22	G/DG	Serpentinised lherzolites	Calcite
L43	44.458	8.768944	22.6	11.7	33.77	n.a.	0.76	0.13	1.26	0.45	G/DG	Serpentinite + metagabbros	Calcite
L43Ru	44.458	8.768944	20.0	11.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	G	Serpentinite + metagabbros	Calcite
BR1	44.445473	8.778927	17.3	11.5	25.88	n.a.	0.75	0.08	1.05	0.50	DG	Serpentinite + metagabbros	Calcite
LER21	44.424297	8.6582717	17.5	11.3	4.97	n.a.	0.72	0.02	0.43	0.55	DG	Serpentinite + metagabbros	Calcite
LER2	44.40568	8.618569	17.3	9.5	17.84	0.01	0.56	0.10	0.45	0.56	DG	Serpentinite + metagabbros	Calcite

Sampling indicates the type of sample collected (G- gas; DG- dissolved gas).

Table 2 - Chemical compositions of the gases collected in Oman and Liguria hyperalkaline springs.

Sites	**CH_4 (%vol)**	**H_2 (%vol)**	**N_2 (%)**	**O_2 (ppmV)**	**CO (ppmV)**	**CO_2 (ppmV)**	**C_2H_6 (ppmV)**	**C_3H_8 (ppmV)**	**C_4H_{10} (ppmV)**	**C_5H_{12} (ppmV)**
Oman 2011										
Site 11	1.5	10.6	12.4	507.6	n.d.	n.d.	69.6	15.1	4.4	n.d.
Site 11	1.6	10.7	12.7	543.8	n.d.	n.d.	70.3	14.7	5.2	n.d.
Site 11	2.5	11.1	12.7	568.6	n.d.	n.d.	70.7	14.9	5.8	n.d.
Site 13	1.5	10.5	11.2	474.6	n.d.	n.d.	9.9	8.2	n.d.	n.d.
Site 13	1.5	11.3	12.2	570.7	n.d.	n.d.	9.5	7.8	5.7	8.2
Site 20	5.6	11.2	13.3	559.5	n.d.	n.d.	10.1	n.d.	n.d.	n.d.
Site 20	5.5	11.3	12.7	552.3	n.d.	n.d.	11.2	n.d.	n.d.	n.d.
Site 20	6.3	10.9	13.5	563.0	n.d.	n.d.	13.9	n.d.	n.d.	n.d.
Site 20	4.3	11.0	12.8	418.5	n.d.	n.d.	8.2	n.d.	n.d.	n.d.
Site 27	5.2	9.6	25.0	568.5	n.d.	n.d.	84.8	n.d.	n.d.	n.d.
Site 27	5.6	10.0	27.0	788.2	n.d.	n.d.	108.9	n.d.	n.d.	n.d.
Site 27	5.0	9.4	24.0	578.6	n.d.	n.d.	92.3	n.d.	n.d.	n.d.
Site 28B	3.3	10.4	18.0	970.9	n.d.	n.d.	83.5	n.d.	n.d.	n.d.
Site 28B	3.6	10.4	15.5	497.6	n.d.	n.d.	72.7	n.d.	n.d.	n.d.
Site 28C	2.6	9.9	21.7	1639.1	n.d.	n.d.	91.1	n.d.	n.d.	n.d.
Site 28C	3.8	10.7	15.7	616.4	n.d.	n.d.	52.6	n.d.	n.d.	n.d.
Site 28D	4.2	11.0	15.5	480.9	n.d.	n.d.	97.1	n.d.	n.d.	n.d.
Site 28D	4.9	11.5	17.6	610.8	n.d.	n.d.	93.4	n.d.	n.d.	n.d.
Site 28D	4.5	12.1	17.8	673.7	n.d.	n.d.	94.1	n.d.	n.d.	n.d.
Site 31	7.9	10.7	15.7	491.0	n.d.	n.d.	59.7	n.d.	n.d.	n.d.
Site 31	8.0	10.7	15.9	532.1	n.d.	n.d.	61.9	n.d.	n.d.	n.d.
Liguria 2010										
GOR34	35.7	0.2	35.9	447.1	n.d.	n.d.	233.2	n.d.	n.d.	n.d.
GOR34	30.4	0.0	31.5	373.7	n.d.	106.7	212.8	n.d.	n.d.	n.d.
GOR35	10.5	0.0	33.8	459.7	n.d.	107.5	23.5	n.d.	n.d.	n.d.
GOR35	10.7	1.2	33.8	401.5	n.d.	106.7	24.6	n.d.	n.d.	n.d.
L43Ru	34.4	1.0	32.4	559.3	39.2	124.9	359.5	n.d.	n.d.	n.d.
L43Ru	34.4	0.0	32.0	480.3	n.d.	129.7	353.2	n.d.	n.d.	n.d.
L43Ru	33.6	0.0	31.0	386.0	n.d.	123.5	339.7	n.d.	n.d.	n.d.
L43	37.0	0.0	30.7	381.0	n.d.	n.d.	441.3	n.d.	n.d.	n.d.
L43	34.7	0.0	30.7	736.1	n.d.	106.2	390.1	n.d.	n.d.	n.d.
L43	35.6	0.1	31.3	621.4	n.d.	106.5	418.3	n.d.	n.d.	n.d.
L43	36.7	0.1	30.3	373.0	n.d.	n.d.	423.4	n.d.	n.d.	n.d.
L43	35.8	0.0	30.2	356.5	n.d.	n.d.	409.9	n.d.	n.d.	n.d.

n.d.- not detected

Table 3 - Concentration of the dissolved gases in the Oman and Liguria hyperalkaline waters. Concentrations are given in μmol/l.

Sites	Samples	H_2	CH_4	N_2	O_2	CO	CO_2	C_2H_6
Oman 2011								
Site 11	GD1	214.6	36.3	1281.4	13.4	n.d.	n.d.	0.24
Site 11	GD2	215.7	38.4	762.6	7.4	n.d.	n.d.	0.28
Site 13	GD1	333.2	25.4	848.8	7.9	n.d.	n.d.	n.d.
Site 13	GD2	340.8	28.0	725.1	8.7	n.d.	n.d.	n.d.
Site 20	GD2 GV	222.3	96.5	755.2	8.8	n.d.	n.d.	n.d.
Site 20	GD2 PV	341.7	147.6	725.7	7.2	n.d.	n.d.	n.d.
Site 20	GD2 Wadi	26.7	15.1	995.5	12.3	n.d.	n.d.	n.d.
Site 20	GD3 Wadi	65.1	15.5	848.5	10.7	n.d.	n.d.	n.d.
Site 26	GD2	168.6	7.4	846.3	6.7	n.d.	n.d.	n.d.
Site 27	GD1	132.1	84.7	823.6	7.4	n.d.	n.d.	n.d.
Site 27	GD5	184.9	15.4	892.2	11.0	n.d.	n.d.	n.d.
Site 27b	GD1	179.3	71.9	821.6	7.4	n.d.	n.d.	n.d.
Site 27b	GD2	59.4	39.5	2135.2	23.4	n.d.	n.d.	n.d.
Site 28C	GD2	274.2	64.6	1661.4	15.1	n.d.	n.d.	n.d.
Site 28D	GD2	115.7	25.3	872.7	10.4	n.d.	n.d.	n.d.
Site 28G	GD1	377.5	70.2	656.6	5.7	n.d.	n.d.	n.d.
Site 29	GD1	219.5	38.0	827.7	8.2	n.d.	n.d.	n.d.
Site 29	GD2	168.0	31.1	825.8	8.4	n.d.	n.d.	n.d.
Site 30	GD2	338.9	209.2	794.7	8.7	n.d.	n.d.	0.15
Site 30	GD1	227.2	206.0	839.0	9.2	n.d.	n.d.	0.14
Site 31	GD1	48.0	64.4	1382.3	14.9	n.d.	n.d.	n.d.
Site 31	GD1	225.0	68.2	976.2	12.3	n.d.	n.d.	n.d.
Site 31	GD1	98.5	21.1	850.3	10.5	n.d.	n.d.	n.d.
Liguria 2010								
ERR20	2GD	3.8	19.0	711.2	5.2	0.03	0.99	n.d.
ERR20	1GD	4.3	5.8	691.6	4.2	0.02	0.99	n.d.
C11	1GD	1.2	384.5	1066.5	9.7	n.d.	1.23	n.d.
C11	3GD	0.5	349.7	1184.6	11.7	n.d.	1.23	n.d.
C11	2GD	14.6	456.6	806.5	5.0	n.d.	1.18	n.d.
GOR35	1GD	5.8	88.1	1186.7	11.0	n.d.	1.09	n.d.
L43	1GD	2.1	649.4	600.6	3.3	n.d.	1.00	n.d.
BR1	1GD	3.0	279.9	1131.8	10.8	n.d.	1.18	n.d.
BR1	2GD	0.3	278.2	1113.4	10.5	n.d.	1.14	n.d.
BR1	3GD	5.8	285.8	951.4	8.3	n.d.	1.10	n.d.
LER21	1GD	0.0	57.0	1134.8	10.8	n.d.	1.21	n.d.
LER21	2GD	2.5	50.8	1155.6	11.0	n.d.	1,25	n.d.
LER21	3GD	4.1	54.2	1091.4	10.1	n.d.	1.11	n.d.
LER2	1GD	561.6	0.8	3784.9	31.6	n.d.	21.52	n.d.
LER2	3GD	66.7	0.0	2041.2	18.0	n.d.	22.19	n.d.

n.d.- not detected

The higher N_2/O_2 and K/Cl ratios of Liguria samples compared to the Oman ones (as shown in Fig. 3) suggest that serpentinisation-derived waters were in contact with the metasedimentary formation along their pathway, leaching N_2 from the rocks. Note that the nitrogen in the metasedimentary formation was not released during subduction (Philippot et al., 2007).

Another typical feature of low-temperature hyper-alkaline springs is the low concentration in CO_2, both in the gas phase (this work) and in the waters (Chavagnac et al., 2013b). Our measurements (Tables 2 and 3) are therefore coherent with most of the findings in other ophiolites in the world (Neal and Stanger, 1983; Abrajano et al., 1988; Etiope et al., 2011; 2013a). In Oman, CO_2 was detected neither in the gas phase nor in the aqueous phase, while in Liguria, CO_2 is significantly present at concentrations up to 22 μM in the aqueous phase and up to 130 ppm in the vapour phase (actual atmospheric $CO_2 \sim 350$ ppm). The extremely low concentration in CO_2 (below detection limit) in high-pH waters of Oman shows that there is no supply of atmospheric CO_2 to these waters (as suggested by Pfeifer, 1977).

Oman and Voltri hyper-alkaline springs are characterised by a very low DIC content (Chavagnac et al., 2013b, Schwarzenbach et al., 2013; and therefore a very low equilibrium pCO_2) enabling the absorption of atmospheric CO_2 by the waters. This is evidenced by the formation of a thin layer of carbonate precipitates (calcite and/or aragonite) in Oman springs (Table 1, Chavagnac et al., 2013a). At the same time, there may be consumption of CO_2 in waters to form CH_4 and other HC during the FTT reactions (see next paragraph).

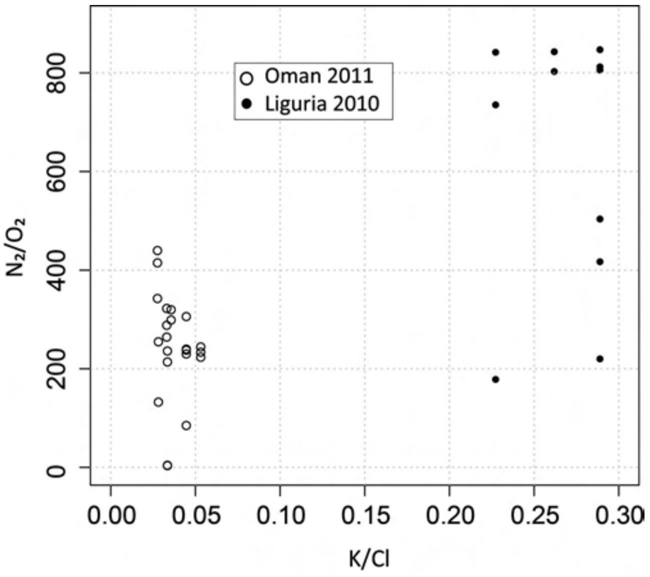

Fig. 3 - The variation of the K/Cl ratio of the alkaline waters versus the N_2/O_2 ratio of the gases for the Liguria and Oman springs.

H_2 and hydrocarbons (C1-C5)

Enrichment of the gas phase in H_2 and CH_4 (Tables 2 and 3) is typical of hyper-alkaline springs. However, a striking difference between Oman and Liguria is in the amount of $H_{2(g)}$ compared to $CH_{4(g)}$. Comparison between Oman and Liguria shows indeed very different styles of H_2 and CH_4 venting while the main geological setting (ultramafic rocks) and the environmental conditions (T, pH) appear similar.

A comparison of H_2/CH_4 ratios for other ultrabasic formations, as depicted in Fig. 4, points to three groups: i) a H_2-dominated group including Oman, Rainbow, Lost City, Logatchev and Socorro Island (Neal and Stanger, 1983; Charlou et al., 2002; Proskurowski et al., 2008; Schmidt et al., 2008; Taran et al., 2010); ii) a CH_4-dominated including the Tekirova Ophiolite (Turkey) (Etiope et al., 2011), the Othrys Ophiolite (Greece) (Etiope et al., 2013a) together with our samples from the Ligurian Alps; iii) a third group, which includes the Zambales ophiolite (Abrajano et al., 1988) and the Bay of Prony (New Caledonia) (Boulart et al., 2012), is intermediate with a ratio close to 1-2. Interestingly, the H_2-dominated group is mostly constituted by vents developing along mid-ocean ridges and characterised by higher temperatures, although Lost City is a low-temperature system compared to Rainbow or Logatchev (Charlou et al., 2002; Proskurowski et al., 2008). Nevertheless, fluid temperatures of the seafloor vents are significantly higher than those of on-land hyperalkaline springs, which are overall below 40ºC. The Oman ophiolite is the sole belonging to the H_2-dominated group. This may be related to a simpler geological history than the other ophiolites, as it was not included in the Alpine collision belt contrary to the CH_4-dominated ophiolites. Indeed, the latter have undergone multi-stage metamorphism during the collision event and their obduction onto the continent.

We propose that the data depicted in Fig. 4 may be related to the influence of geodynamic and geologic context on serpentinisation reactions. The first argument comes from the locations of the hyper-alkaline springs from which gas bubbling is clearly observed. Indeed, in Oman, gas samples were collected from hyper-alkaline springs emerging from the major structural discontinuity at the transition between crustal section and mantle rock (paleo-Moho), and none from hyper-alkaline springs located nearby the basal thrust plane, e.g., the metamorphic structural discontinuity (Chavagnac et al., 2013b). In contrast, gas bubbling in Liguria was observed only at three hyper-alkaline springs emerging from various metamorphosed substratum (highly serpentinised metabasalt/metagabbros and serpentinised lherzolites) wrapped by chlorite-amphibole-talc schists (Hoogerduijn Strating, 1991). These schists may have been used as a conduit by meteoric waters to infiltrate and interact with the substratum, explaining the high N_2 gas content of Liguria hyper-alkaline springs.

Hydrogen

In Oman, H_2 is the second dominant gas after N_2 in the gas phase, ranging from 9.4% (site 27) to 12.1% (site 28) of the total gas volume. The lowest dissolved H_2 concentrations were found in the wadi at site 20 (26.7 to 65 μmol/l) while the highest values were found at site 28 (377 μmol/l). This agrees with the concentrations previously measured (Neal and Stanger, 1983; Sano et al., 1993). Note that H_2 concentrations given by Neal and Stanger (1983) - up to 99% vol - are much higher than ours, probably as a consequence of the different methodologies used for gas measurements and of the fact that Neal and Stanger (1983) values might not have taken into account the water vapour in the total gas volume.

In the Voltri Group, $H_{2(g)}$ concentrations range from 0.011% (L43) to 1.2% (GOR34) of the total gas volume, i.e. 10 to 100 times lower than in Oman. Dissolved H_2 concentrations are relatively low (up to to 5 μmol/l on average) except for two sites (C11 and LER2) where the concentrations are higher (up to 562.6 μmol/l at LER2). A strong variability between samples from the same site can be observed although conditions of sampling were identical from one sample to the other, which may depict a sporadic venting of H_2. This remains to be confirmed by further measurements.

The low H_2 content in the Voltri samples, also reported by Boschetti et al. (2013) for the Voltri Group as well as by Etiope et al. (2013a) in another setting in Greece, seems to be uncommon for hyper-alkaline environments. During the reactions of serpentinisation at moderate temperatures (< 300°C), olivine and pyroxene react with water to form serpentine, brucite, magnetite and various Fe/Ni alloys depending on redox conditions of reactions. Other phases such as talc, amphibole (e.g., tremolite), chlorite and sulfides can complete the parageneses. In fact, as noted by Mevel (2003), this is a succession of simple reactions starting with the silicate dissolution leading to the production of $SiO_{2(aq)}$, which then reacts with Mg^{2+} and OH^- to form the serpentine crystal and the secondary minerals. In the same time, water reacts with metals in silicates, i.e. oxidizing Fe^{2+} contained in olivine into Fe^{3+} which can be incorporated both in serpentine and magnetite (O'Hanley and Dyar, 1993; Evans, 2008; Andreani et al., 2013), and reducing H_2O to $H_{2(g)}$. Hence, the assemblage serpentine-brucite determines the silica activity of the system, which subsequently controls the oxidation of Fe^{2+} to Fe^{3+} and therefore $H_{2(g)}$ production (Evans, 2008; Katayama et al., 2010). Seyfried et al. (2007) also showed in laboratory experiments that a high silica activity could limit the production of H_2. Low H_2 content is then supported by SiO_2 concentrations measured in the Ligurian fluids, which are significantly higher than in Oman

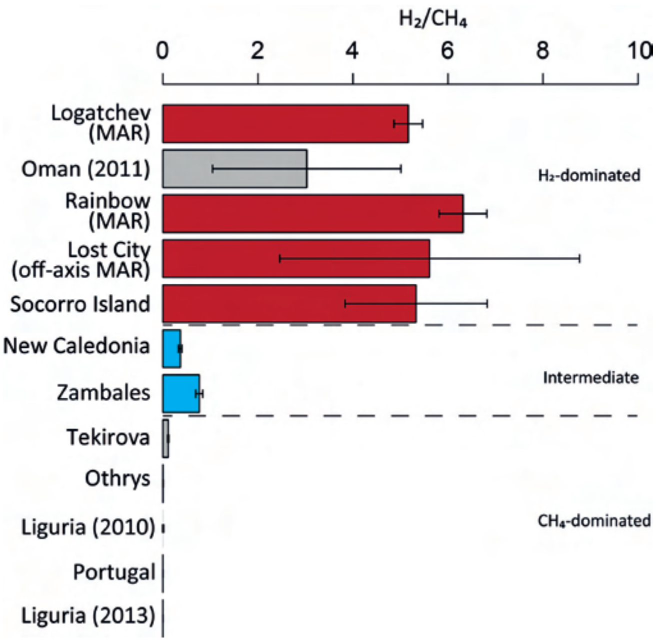

Fig. 4 - Mean H_2/CH_4 ratios for our samples (Oman 2011 and Liguria 2010) compared with various ultramafic environments showing three distinct gas composition groups. Data used here are from Abrajano et al., 1988 (Zambales); Charlou et al., 2002 (Rainbow); Proskurowsky et al., 2008 (Lost City); Taran et al., 2010 (Socorro Island); Etiope et al., 2011 (Tekirova); Boulart et al., 2012 (Bay of Prony); Etiope et al., 2013 (Othrys); Schmidt et al., 2008 (Logatchev); Etiope et al., 2013b (Portugal); Boschetti et al., 2013 (Liguria 2013). Error bars indicate the standard deviation of the gas concentration distribution. Note that Rainbow and Logatchev are considered as high-temperature vent sites (T > 350°C) while Lost City is ~ 90-100°C. The on-land venting sites are considered as low-temperature (T < 40°C). In red, sites developing in a mid-ocean ridge context and in blue in a subduction context.

(Table 1, Chavagnac et al., 2013b). Our data in Oman and Liguria may therefore suggest a first low-silica activity stage producing high amounts of H_2 (Oman) followed by a second stage of higher silica activity derived from the altered mafic rocks, limiting the production of H_2 (Liguria). Episode of a low silica activity fluid metasomatism (rodingitization) is a common feature of ophiolite complexes, taking place primarily during ocean-floor metamorphism and evidenced in terms of lithologies by the occurrence of epidote-rich to diopside-rich rocks in or adjacent to serpentinites (e.g., Schandl et al., 1989). Diopsidites and rodingites were identified both in Oman (Python et al., 2007) and in Liguria (e.g., Dal Piaz et al., 1980). Ferrando et al. (2010) suggest that ophiolite complexes (i.e. the Alpine orogeny), which are subducted then exhumed, may undergo additional episode(s) of serpentinisation and rodingitization during the prograde to retrograde metamorphic path. This would be evidenced by the occurrence of H_2-rich fluid inclusions (and also a Ca metasomatism), but these are rarely preserved and detected in metamorphic environments. However, Peretti et al. (1992) report the occurrence of fluid inclusions in the Malenco peridotites composed of H_2 (0.3-3 mol% of the total gas) within brines (5.1 wt% $CaCl_2$ + 6.4 wt% NaCl) and Ferrando et al. (2010) described fluid inclusions in Bellecombe meta-ophiolites made up 1.0 and 0.4 mol% of H_2 and CH_4, respectively, within brines (6 wt% $CaCl_2$ + 6 wt% NaCl). While both studies illustrate a second episode of Ca-rich and Si-undersaturated reducing fluid percolation, it is unclear whether this event is related to the prograde or late stage metamorphic history of the Alpine orogeny. Nevertheless, these authors clearly identified that H_2-rich serpentinisation-related fluid was produced before the final exhumation of the ophiolite complex.

In addition, temperature and water-rock ratio are two other parameters that have a strong control on Fe speciation during serpentinisation and therefore on H_2 production, as discussed by Klein et al. (2009). In their model calculations, they indicate that at low temperatures (< 150-200°C) and low water-rock ratios (< 0.1 to 5), hydrogen production is related to the formation of Fe^{3+}-serpentine. Andreani et al. (2013) reported similar results on the role of Fe^{3+}-serpentine on H_2 production based on a μ-XANES study of Fe-speciation in serpentine minerals. Besides, they stated that Fe^{3+} goes predominantly into serpentine, rather than into magnetite, for serpentinisation degree up to 75%.

As emphasised in Hellevang et al. (2011), the presence of nitrogen, sulfur and carbon compounds in various redox states may also affect the H_2 generation by limiting the degree of reduction of the aqueous solutions. As for instance, Hellevang et al. (2011) simulated the effect of carbon species on the potential for H_2 generation from an aqueous solution of olivine (Fo90). In natural aquatic systems, the dissolved CO_2 reacts with H_2O to form H_2CO_3, HCO_3^- and CO_3^{2-}. However, due to the serpentinisation reactions, conditions are increasingly reducing, which thermodynamically favour reduction of inorganic carbon to CH_4. Hellevang et al. (2011) summarised the equilibrium as the following:

$$2H_2O + CO_{2(aq)} \longleftrightarrow CH_{4(aq)} + 2O_{2(aq)} \tag{1}$$

According to their experiments, at low carbon content, the aqueous solution is rapidly reduced and allows the formation of significant amounts of H_2. On the opposite, at higher carbon content, more olivine is required to form significant H_2 quantities. In the same experiments, at constant C content, the CO_2 partial pressure decreases as CO_2 is converted to CH_4, allowing O_2 activity to drop, which favours H_2 formation. In our case, the presence of CO_2 both in the gas and aqueous phase from Liguria indicates that the CO_2 is not completely converted to CH_4; hence the aqueous solution may not be significantly reduced to allow H_2 formation at significant levels.

In Oman, the absence of CO_2 in both gas and aqueous phases indicates that all the CO_2 is either converted to CH_4 or consumed by carbonate formation. This is confirmed by the relationship between O_2 and H_2 (Fig. 5; Hellevang et al., 2011), which shows that H_2 generation might be also controlled by the introduction of O_2 in the system.

Methane and hydrocarbons

In Oman, $CH_{4(g)}$, the third most abundant gas, ranges from 1.5% at sites 11 and 13 up to 8% at site 31. In the dissolved phase, concentrations in CH_4 vary from 7.4 μmol/l at site 26 to 209.2 μmol/l at site 30. In Liguria, CH_4 is the second dominant gas after N_2, sometimes the first. The lowest contents were observed at GOR35 (10.5% of the total gas volume) and the highest at L43 (37%). L43 was also characterised by the highest dissolved CH_4 concentration (649.4 μmol/l, the water-atmosphere equilibrium concentration for this station is 2.3 μmol/l), while the lowest was measured at LER2. Intermediate concentrations (~ 300 μmol/l) were found at C11 and BR1.

It is commonly accepted that CH_4 and possibly longer hydrocarbons are forming in hyper-alkaline fluids abiogenically,

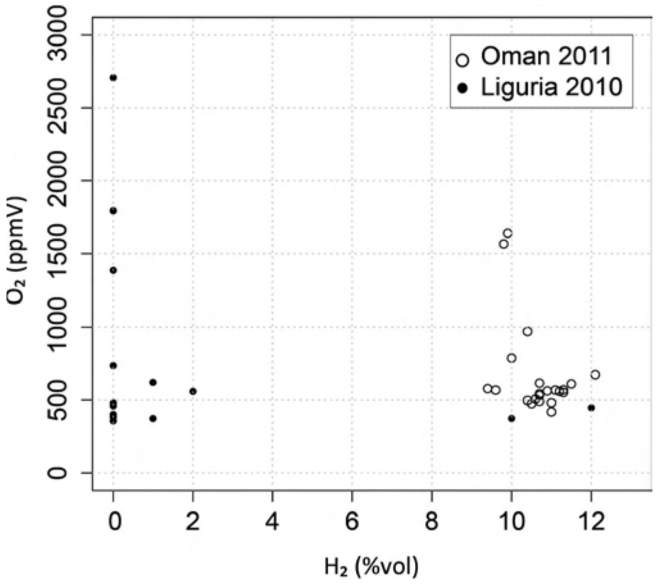

Fig. 5 - The oxygen (O_2) versus hydrogen partial pressure of the Liguria and Oman gases.

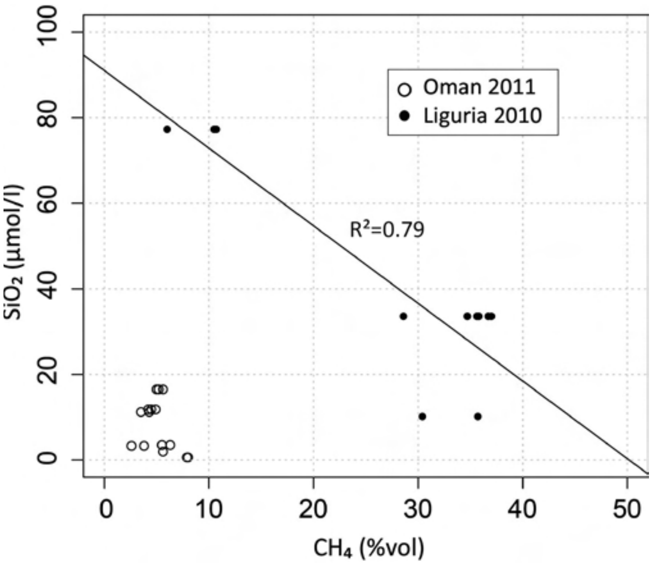

Fig. 6 - The dissolved SiO_2 concentration versus the $CH_{4(g)}$ partial pressure for the Oman and Liguria springs.

through the FTT reactions as the following (Abrajano et al., 1988; Charlou et al., 2002; Hosgormez, 2007; Proskurowski et al., 2008):

$$4H_2 + CO_2 \longleftrightarrow CH_4 + 2H_2O \quad (2)$$

Carbon isotopic composition data previously collected in Oman and Liguria undoubtedly indicate the abiogenic origin of CH_4 ($d^{13}C_1$ ~ -9‰; Neal and Stanger, 1983; Boschetti et al., 2013). However, one cannot exclude another synthesis pathway, which consists in the reduction of formic acid, formaldehyde, methanol and later CH_4 (Seewald et al., 2006).

FTT reactions have been studied for more than a century, to synthesize CH_4 and alkanes from CO at high temperature. However, the efficiency of FTT synthesis from CO_2 (i.e. methanation) is lower under aqueous hydrothermal conditions (Foustoukos and Seyfried, 2004). Provided the presence of catalysts (i.e. magnetite, awaruite and chromite) and at high temperature (> 300°C), FTT reactions from CO_2 can nevertheless produce high amounts of CH_4 and light alkanes (Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001). More recently, Neubeck et al. (2011) studied the generation of H_2 and CH_4, in the 30-70°C range, and demonstrated that the presence of H_2, CO, CO_2 and the necessary catalysts (i.e. magnetite, chromite among others) leads to the generation of CH_4 in a few months, even at low temperature. In fact, in the absence of catalysts, methanation is thermodynamically favoured at temperatures below 100°C although it evolves slowly over time (Etiope et al., 2013a). The relationship between dissolved SiO_2 and CH_4 in Liguria (Fig. 6) shows that the production of CH_4 is controlled by dissolved SiO_2 and therefore by the dissolution of olivine. This is in line with Neubeck et al. (2011) who showed that the dissolved CH_4 concentration is a proxy for olivine dissolution rates.

Besides the role of the catalysts, Oze and Sharma (2005) proposed a possible formation of CH_4 without H_2 mediation during serpentinisation in abundant CO_2 conditions, which is the case in Ligurian springs. However, it is difficult today to establish the role of each parameter, especially since H_2 may be consumed as it is produced, maintaining its concentration at a low level. We may suggest that the high concentration in CH_4 in both the gas and the aqueous phase in Liguria is the result of the FTT reactions, occurring at a later stage of the serpentinisation process while in Oman, the lower amount of magnetite as well as the low content in CH_4 tend to support that the serpentinisation process is at an earlier stage. Nevertheless, we cannot exclude the fact that the availability of carbon in Oman might be a limiting factor for FTT reactions, which is not the case in Liguria (Schwarzenbach et al., 2013).

Traces of light alkanes were found in the gas phase both in Liguria and in Oman. Samples from Liguria showed concentrations of C_2 ranging from 20 ppmV (GOR35) to 441 ppmV (L43), but no HC with longer chains were detected. In Oman, C_2 was present in all samples, from 8.2 ppmV in the wadi (site 20) to 108.9 ppmV at site 27. Higher alkanes (up to C_4) were found only at site 11 with variable concentrations. Only at sites 11 and 30, dissolved C_2 was detected (up to 240 nmol/l) in the spring waters. No dissolved alkanes (C_2 to C_4) were detected in the dissolved phase in the Ligurian samples.

Although finding light alkanes as in our Oman and Ligurian samples is common for ultramafic fluids, their origin remains subject to debate (Proskurowski et al., 2008; Konn et al., 2009a). In the Tekirova ophiolite (Turkey), Hosgormez (2007) and Etiope et al. (2011) showed from the isotopic compositions that the alkanes were not all produced by FTT-reactions, but more probably originated from a strong thermogenic component. However, isotopic studies cannot prove the abiogenic origin of longer-chained HC (> C_5) since a variety of mostly unknown fractionation steps may occur along the synthesis pathways, with a dominance of biogenic source and/or processes hiding their characteristic signature (Konn et al., 2009a).

Although the carbon isotope composition is not yet available for our gas samples, a first estimate of the light alkane distribution can be made with the Schulz-Flory method

(Fig. 7; Flory, 1936). Indeed, the product distribution of hydrocarbons formed during the FTT-reactions generally follows the Schulz-Flory distribution, which is expressed as the following equation:

$$W/n = (1-\alpha)^{n-1}\alpha^{n-1} \quad (3)$$

where W is the molar fraction of HC molecules, n the number of C atoms and α the chain growth probability factor. As a result, the distribution of HC is controlled by the chain growth probability factor, which is typical of abiotic synthesis.

Our data in Oman do not fit this model, confirming that part of the light alkanes are probably generated through degradation of organic matter or thermogenesis in the same way as in Tekirova ophiolite (Etiope et al., 2011). This is especially true for higher hydrocarbons (above C_3). We may suggest that this is also the case of the Voltri ophiolite although longer-chain HC were not detected with our methodology. However, the amount of C_2 seems to be associated with the amount of CH_4, taking into account that the gas venting from the metaperidotites of the Erro-Tobbio coincides with those of the Oman crustal section/peridotite, which are undistinguishable from one another (Fig. 8). Adding the data from Boschetti et al. (2013) to Fig. 8 confirms this trend with an R^2 above 0.85. This tends to indicate that C_2 is derived from abiogenic polymerisation, which has been experimentally demonstrated earlier in Des Marais et al. (1981) by ‘spark-discharge’ gas phase experiments. However, as noted by Proskurowski (2010), uncatalysed polymerisation remains to be proven in aqueous conditions.

CONCLUDING REMARKS

Serpentinisation is a phenomenon that occurs wherever mantle rocks are altered by aqueous fluids. The alteration of the Oman and Liguria ophiolites by meteoric waters indeed generates hyper-alkaline fluids with pH up to 11-12 at temperatures of 20-40°C at the springs. This is accompanied by the production of a gas phase enriched in hydrogen and subsequently methane. Comparison of the gas composition from Oman and Liguria, and more generally from various places over the world, shows significant differences in terms of H_2/CH_4 ratios. Three groups have been identified likely related to different stages in the serpentinisation reactions, from the hydrogen-dominated to the methane-dominated fluids. The distinction between these groups might lie in the difference of rock mineralogical composition in which the fluids circulate, on the degree of rock alteration and finally on the geological history of the ophiolite. To fully understand the present-day serpentinisation reactions leading to the formation of hydrogen, it is necessary to know the depth and the nature (rock composition) of the reaction zone, which remains an undocumented black box to-date.

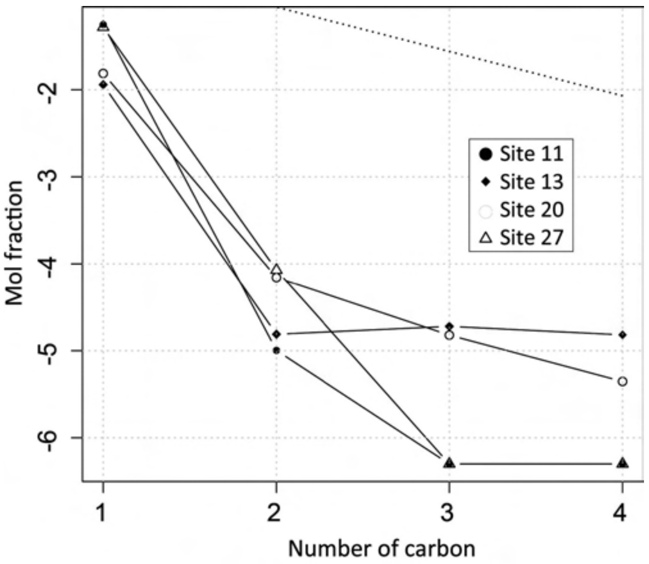

Fig. 7 - Logarithmic distribution of mole fraction as a function of carbon number for Sites 11, 13, 20 and 27 in Oman showing that the Oman hydrocarbon composition does not fit the Schulz-Flory distribution. Dashed line represent a distribution typical of abiotic synthesis (Sherwood Lollar et al., 2008). Mole fraction is calculated as $x_i = n_i/n_{tot}$ with n_i as the amount of i constituent and n_{tot} the total amount of all constituents.

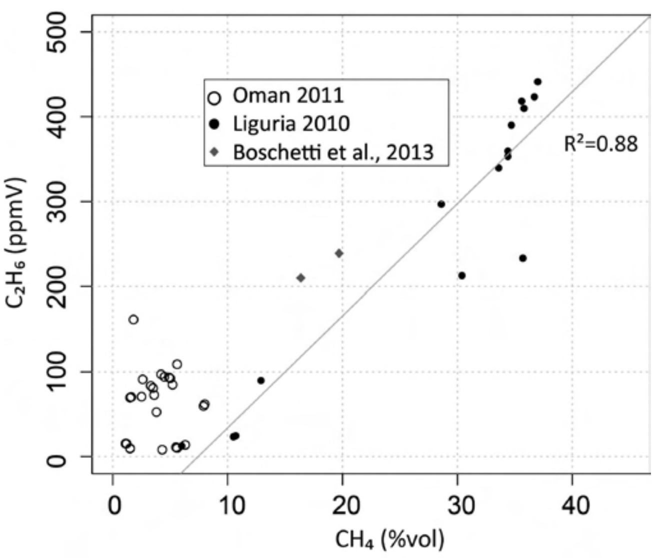

Fig. 8 - The $CH_{4(g)}$ partial pressure versus that of ethane for the Oman and Liguria gases.

The comparison of the Oman and Liguria cases with other hyper-alkaline springs worldwide illustrates even more the diversity of gas venting within ultramafic environments and the complexity of the chemical reactions, which may be controlled by the geodynamic and the geological context. It is clear that ophiolites have evolved differently since their obduction, especially in the context of the Alpine collision belt. The resulting metamorphic history has therefore an impact on the gas composition of the fluids. Hence, is it relevant to describe the current on-land hyper-alkaline springs as analogues of the MAR Lost City hydrothermal system?

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