

Reduced gas seepages in ophiolitic complexes: Evidences for multiple origins of the H₂-CH₄-N₂ gas mixtures

Christèle Vacquand^a, Eric Deville^{a,*}, Valérie Beaumont^a, François Guyot^b,
Olivier Sissmann^a, Daniel Pillot^a, Carlo Arcilla^c, Alain Prinzhofer^{a,1}

^a IFP Energies nouvelles, 1 & 4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France

^b IMPMC, Sorbonne Universités, MNHN, UPMC, CNRS, 61 rue Buffon, 75005 Paris, France

^c National Institute of Geological Sciences, University of the Philippines, Diliman, Quezon City, Philippines

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Abstract

This paper proposes a comparative study of reduced gas seepages occurring in ultrabasic to basic rocks outcropping in ophiolitic complexes based on the study of seepages from Oman, the Philippines, Turkey and New Caledonia. This study is based on analyses of the gas chemical composition, noble gases contents, stable isotopes of carbon, hydrogen and nitrogen. These seepages are mostly made of mixtures of three main components which are H₂, CH₄ and N₂ in various proportions. The relative contents of the three main gas components show 4 distinct types of gas mixtures (H₂-rich, N₂-rich, N₂-H₂-CH₄ and H₂-CH₄). These types are interpreted as reflecting different zones of gas generation within or below the ophiolitic complexes. In the H₂-rich type, associated noble gases display signatures close to the value of air. In addition to the atmospheric component, mantle and crustal contributions are present in the N₂-rich, N₂-H₂-CH₄ and H₂-CH₄ types. H₂-bearing gases are either associated with ultra-basic (pH 10–12) spring waters or they seep directly in fracture systems from the ophiolitic rocks. In ophiolitic contexts, ultrabasic rocks provide an adequate environment with available Fe²⁺ and alkaline conditions that favor H₂ production. CH₄ is produced either directly by reaction of dissolved CO₂ with basic-ultrabasic rocks during the serpentinization process or in a second step by H₂-CO₂ interaction. H₂ is present in the gas when no more carbon is available in the system to generate CH₄. The N₂-rich type is notably associated with relatively high contents of crustal ⁴He and in this gas type N₂ is interpreted as issued mainly from sediments located below the ophiolitic units.

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1. INTRODUCTION

Serpentinization generates natural emission of H₂ on Earth. The process is inherent to exposure of reduced mantle rocks to hydration conditions in a wide range of thermal conditions, at least up to the critical temperature of water

(374 °C). This occurs commonly at mid-oceanic ridges where hydrothermal fluid circulation at high temperature provides conditions for ferromagnesian mineral alteration. Indeed, at mid-oceanic ridges H₂-rich fluids are associated with N₂ and CH₄ contents and on black smokers with CO₂ (Welhan and Craig, 1979; Kelley and Früh-Green, 1999; Charlou et al., 2002; Kelley et al., 2001, 2005; Gallant and Von Damm, 2006; Kumagai et al., 2008; and others). Natural H₂ seepages are also reported onshore, in former oceanic rocks present in ophiolite complexes. Notably, H₂ seepages associated with these ultrabasic rocks have

* Corresponding author.

E-mail address: eric.deville@ifpen.fr (E. Deville).

¹ Present address: GEO4U, Praia de Botafogo 501, 22250-040 Rio de Janeiro, Brazil.

been reported in the Sultanate of Oman (Neal and Stanger, 1983; Sano et al., 1993; Vacquand, 2011; Boulart et al., 2013; Miller et al., 2016), the Philippines (Abrajano et al., 1988, 1990) and Turkey (De Boer et al., 2007; Hosgörmmez et al., 2008; Etiope et al., 2011). These gas seepages are often associated with ultra-basic springs (pH 10–12) that are present in many basic-ultrabasic rock exposures. Such ultra-basic waters have been interpreted as evidences of active serpentinization (Barnes et al., 1967, 1978; Neal and Stanger, 1983; Abrajano et al., 1988, 1990; Sano et al., 1993; Bruni et al., 2002; Cipolli et al., 2004; Deville et al., 2011; Szponar et al., 2013; Etiope et al., 2013; Chavagnac et al., 2013; Cardace et al., 2015; Meyer-Dombard et al., 2015; Woycheese et al., 2015; Deville and Prinzhofer, 2016). In these cases, H₂-rich gas is either dissolved or present as free gas bubbling in the ultra-basic water. In other cases, H₂-rich gas seepages occur in rock fractures and can locally burn spontaneously. This is notably the case of the famous Chimaera near Antalya, place of the first Olympic flame, which are known to be burning since antiquity (De Boer et al., 2007; Hosgörmmez, 2007; Hosgörmmez et al., 2008) and the site of “Los Fuegos Eternos” in the Philippines known since the Spanish colonization (Abrajano et al., 1988, 1990). H₂-bearing gases discovered in ophiolitic rocks onshore show lower contents in helium than those discovered in terrestrial context in non-ophiolitic rocks (Coveney et al., 1987; Ikorsky et al., 1999; Sherwood-Lollar et al., 2007; Larin et al., 2015; Zgonnik et al., 2015; Guélard et al., 2017).

H₂ is generally considered as produced by water reduction that occurs simultaneously to the hydration of ultrabasic or basic rocks, *i.e.*, according to serpentinization reactions. In the case of ophiolitic settings, it is generally supposed to happen at low temperature (Moody, 1976; Neal and Stanger, 1983; Abrajano et al., 1988; Etiope et al., 2011). The process driving this reduction is the change of valence of transition metals, notably ferrous iron Fe^{II} into ferric iron Fe^{III}, iron being the most abundant transition metal in ultrabasic and basic rocks. Fe^{II} is a major component in ultrabasic rocks in the ophiolitic units within minerals such as olivine and pyroxene. It contributes to the formation of Fe^{III}-bearing minerals, such as magnetite. These mineral assemblages are observed in the field, where peridotites are largely serpentinized, mostly along fracture systems. The question of H₂ provenance in oceanic hydrothermal context has been largely approached by petrographic studies and experimental simulations (Allen and Seyfried, 2004; Yoshizaki et al., 2009; Klein et al., 2009; Marcaillou et al., 2011; Neubeck et al., 2011; Shibuya et al., 2015) and numerical modelling (McCollom and Bach, 2009; Klein et al., 2009; Marcaillou et al., 2011). Fe^{II} is initially provided by different minerals (such olivine and pyroxene) in the first stages of hydration, but also by serpentine or ferrous iron hydroxide, which are produced by the alteration processes, thus allowing the H₂ production to go on after olivine and pyroxene have all been transformed (Marcaillou et al., 2011). These studies have shown that depending on thermodynamic conditions, temperature, water chemistry (notably carbonate content, sulphate content and alkalinity), water/rock ratios, different mineral

assemblages and sequences are obtained as by-products together with different rates and amounts of H₂. According to the numerical model proposed by McCollom and Bach (2009), the highest rates of H₂ production are obtained at high temperature (about 315 °C) while serpentine and magnetite are the main mineral assemblage of the by-products. Onshore H₂-bearing gas seepages yield not only H₂ but also methane and nitrogen, resulting in a three-component gas mixture with proportions varying in a very large range. The origin and the processes of generation of CH₄ and N₂ associated to H₂ are still a matter of discussion in terrestrial ophiolitic units. In the present paper, the geochemical properties of reduced gas seepages from four ophiolite massifs: (1) the Semail ophiolite in the Sultanate of Oman, (2) the Zambales ophiolite in the Philippines, (3) the Antalya ophiolite in southern Turkey and (4) the New Caledonia ophiolite are compared in the light of local geological features to better understand the conditions for di-hydrogen, methane and di-nitrogen production in the geological context of these ophiolite complexes (Figs. 1–3).

2. GEOLOGICAL SETTINGS

The ophiolitic units in which this study was conducted correspond to wide ophiolitic massifs (Fig. 1) containing rocks which have not been subjected to high pressure-low temperature (HP-LT) conditions. Peridotites rocks are little serpentinized in wide areas (much less than ophiolites involved in HP-LT conditions). These ophiolites units have been obducted on sediments (Fig. 2) belonging to different paleogeographic domains, either oceanic or continental, which contain, in all cases, clastics and carbonates. The fractures in the peridotite host serpentine and carbonate veins, mainly Mg-bearing carbonates (magnesite, hydromagnesite and dolomite). In the ophiolite-hosted fractured aquifers, groundwater circulations is controlled by fracture hydraulic conductivity. Ultra-basic surface seepages have been found in these ophiolitic massifs and they generally discharge close to the contact between the mantle rocks and overlying former oceanic crust rocks (Moho), and along the basal thrust plane of the ophiolite sequence. This is probably related to favorable drainage conditions in the fractured rocks at the base of the ophiolitic units and to drainage control by the more massive gabbroic units compared to the more fractured peridotites below. They release high pH fluids (commonly higher than 10) which are rich in Ca²⁺, OH⁻, H₂ and CH₄.

More specifically, the Oman ophiolite has been extensively studied, as it is the best large exposed massif of this type in the world (see Hopson et al., 1981; Ceuleneer, 1991; Nicolas et al., 1996, 2000; Python and Ceuleneer, 2003; Arai et al., 2006 and many others). This ophiolite corresponds to parts of the oceanic lithosphere of the Arabian Sea which have been obducted on the Arabian plate during late Cretaceous times. H₂-rich gas seepages associated with Ca²⁺-OH⁻-rich groundwater in the Semail ophiolite of Oman were first studied by Neal and Stanger (1983). They proposed that H₂ is the by-product of a low temperature (20–50 °C) serpentinization that depends on Fe^{II} hydroxide availability and oxidation by meteoric water that occurs in

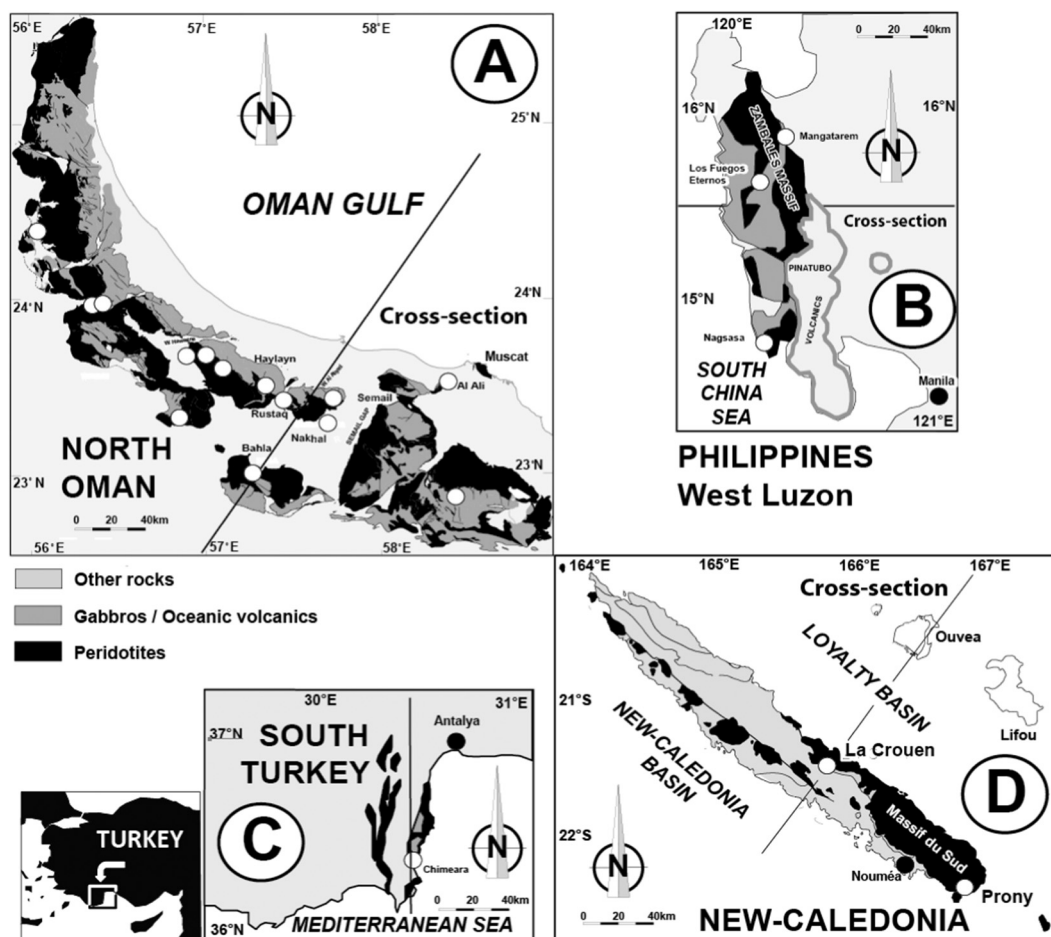


Fig. 1. Structural sketch-maps of the different sites studied in this work in Oman (A), the Philippines (B), Turkey (C) and New-Caledonia (D) (same scale), with the location of the sampling sites and the location of the cross-sections shown in Fig. 2. The gas seepages are associated with ophiolitic ultrabasic rocks. Gas was sampled from different types of seepages: gas seeping in water which originates from ultrabasic or hot springs and gas seeping from fractures without water flow.

2 stages: (1) oxidation by atmospheric O_2 dissolved in meteoric water; (2) oxidation by water. Sano et al. (1993) provided a new insight by analyzing noble gases. Their results confirmed that H_2 -rich gas samples are inherited from interaction of meteoric water with Fe^{II} although they propose a high temperature for the reaction (300 °C).

In the Philippines, gases were sampled in the Zambales massif, which is located in the north-western part of the Luzon Island (Nicolas and Violette, 1982; Hawkins and Evans, 1983; Abrajano et al., 1988; Yumul et al., 1998; Encarnacion et al., 1999). The gas seepages occur either as bubbling in alkaline springs or seeping out from fractured rocks, locally spontaneously burning as, for instance, in Los Fuegos Eternos and Nagasasa. Gas seepages in the Zambales massif were first studied by Abrajano et al. (1988, 1990). In their paper, they concluded that both mantle origin and serpentinization are consistent with their analytical results and they proposed a temperature of 110–125 °C for serpentinization.

The ophiolite of the Antalya region, in southern Turkey, has been extensively studied (Juteau et al., 1977; Robertson and Woodcock, 1980; Glover and Robertson, 1998a,b).

Also, the associated sedimentary sequences have been investigated (Bozcu and Yagmurlu, 2001), while oil seepages have also been observed less than 20 km away from the Chimaera site (Hosgörmez et al., 2008). The site of the Chimaera gas seepage has the most spectacular gas outlet since the flames are more intense than those in Zambales, Philippines, and are also more colorful because of a greater content in methane, relatively to the H_2 . H_2 seepages associated with the site of the first Olympic fire was first reported by Hosgörmez et al. (2008). From their chemical and isotopic study, they concluded that gas seepages originate from both thermogenic maturation of organic matter and serpentinization. In a later publication, Etiope et al. (2011) confirmed previous conclusions and proposed a temperature lower than 100 °C for serpentinization.

The ophiolite of New Caledonia is among the largest onshore massifs of ultrabasic rocks preserved on Earth. The peridotites nappe was emplaced during Eocene times over (1) a basement of arc-derived formations of Pre-Cretaceous age which are overlain by basalts and formations of the Central Range that include sandstones, siltstones, graywackes, claystones with coal of Cretaceous

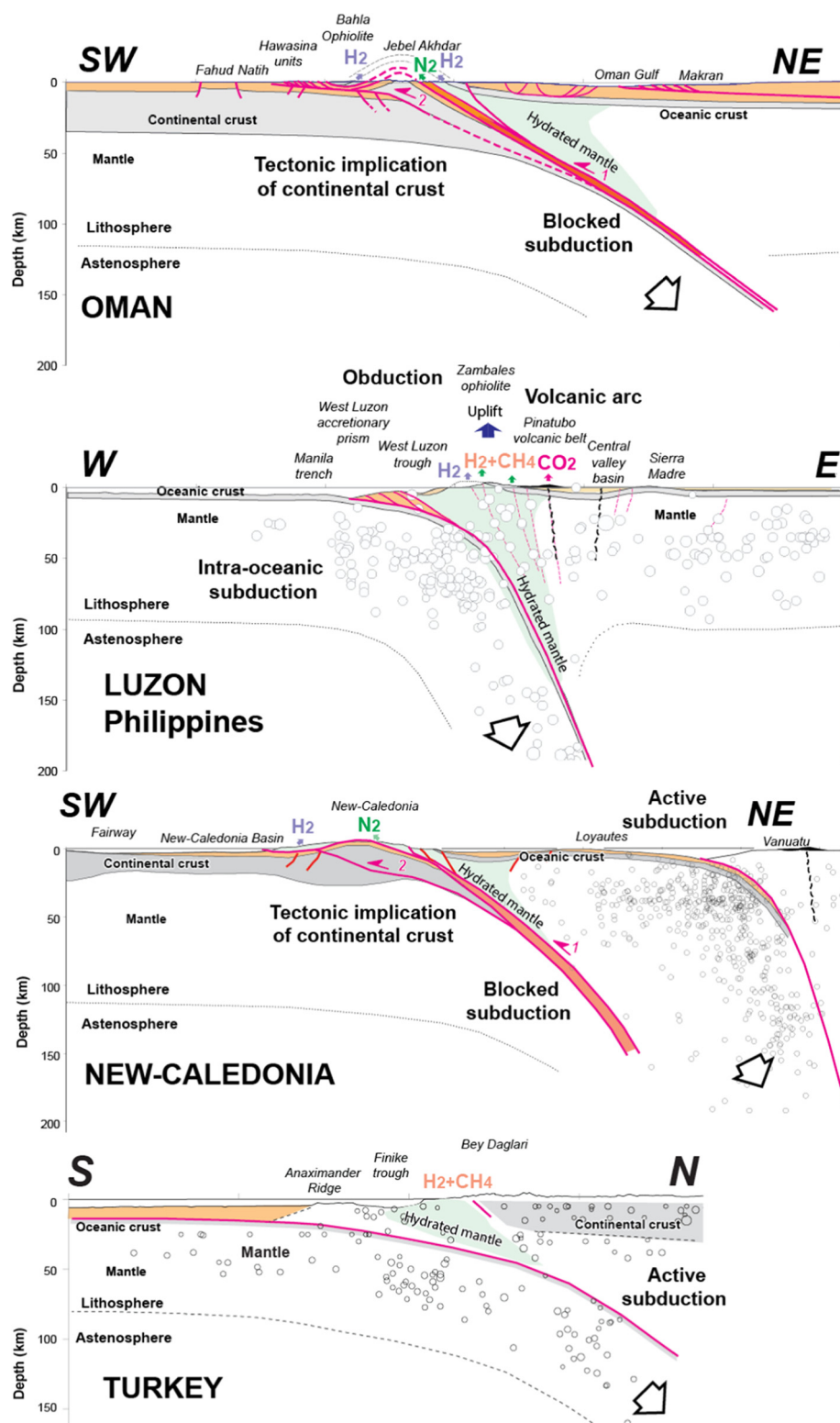


Fig. 2. Geological cross-sections of the different sites studied in this work (same scale; earthquake epicenters from USGS data base).

age and Tertiary carbonate turbidites and volcanoclastic deposits, and (2) a tectonic unit of oceanic basalts of Upper Cretaceous to Eocene age, with back-arc or fore-arc

affinities which underlies the peridotites nappe (Paris, 1981). H₂-bearing gas seepages associated to alkaline to hyper-alkaline waters were found in the southern part of

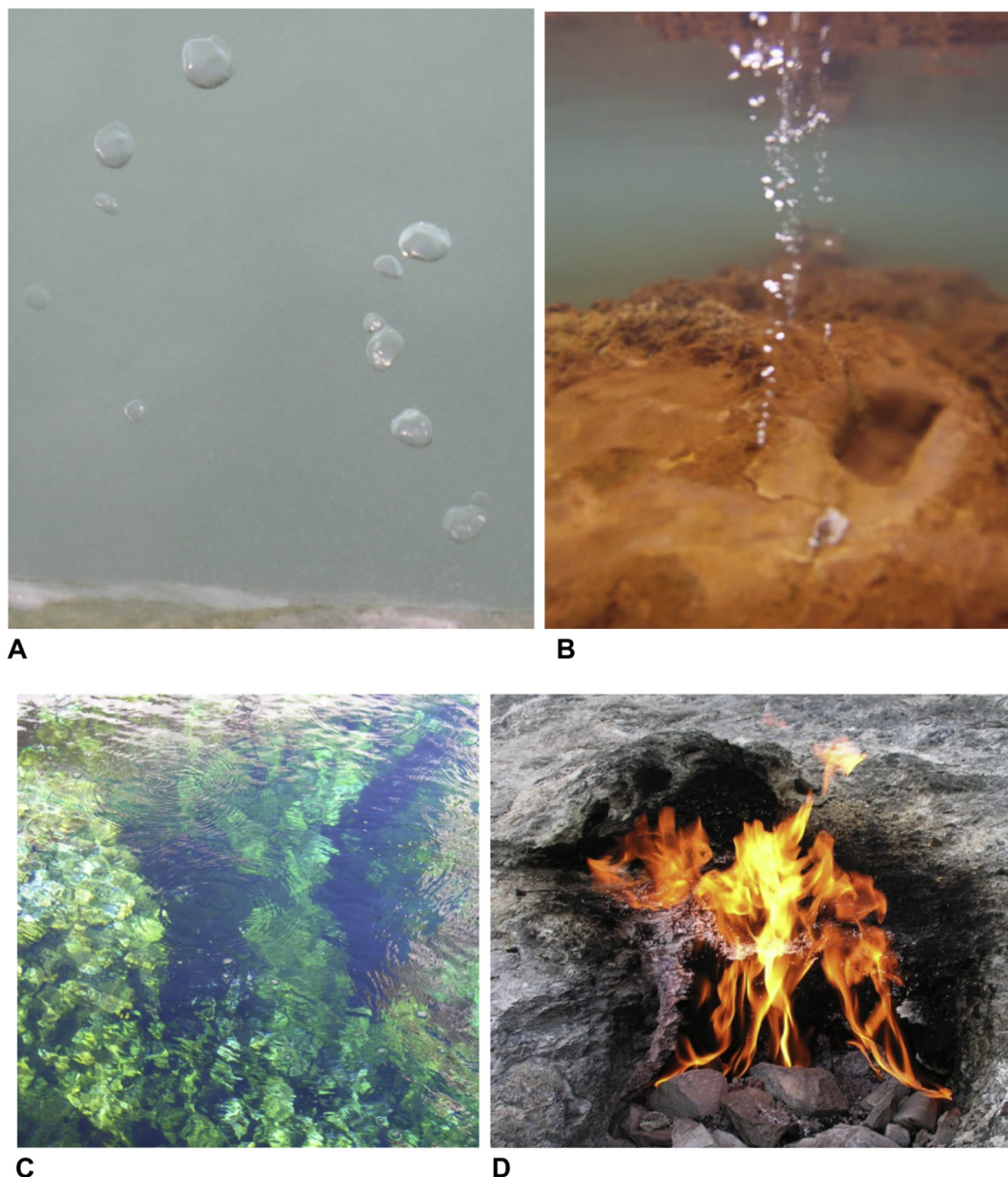


Fig. 3. Examples of gas seepages. (A) Bubbling H_2 -rich gas flow in ultra-basic water (Oman). (B) Bubbling N_2 - H_2 - CH_4 gas flow (foreshore of the Baie du Carénage, New Caledonia). (C) Bubbling N_2 -rich gas flow (Rustaq, Oman). (D) Burning H_2 - CH_4 gas flow (Chimaera, Turkey).

the Massif du Sud (bay of Prony) within the peridotite nappe (Deville et al., 2010; Monnin et al., 2014; Deville and Prinzhofer, 2016), while N_2 -rich seepages were found below the ophiolitic units in the area of La Crouen (Deville and Prinzhofer, 2016).

3. MATERIALS AND METHODS

Gases were sampled in stainless steel tubes with helium-proof valves for chemical composition and noble gas analyses and in glass tubes for stable isotopic composition analyses. Gas sampling devices were evacuated (10^{-3} Pa vacuum) before sampling. When possible, stainless steel tubes were swept twice by the sampled gas. When gas was

collected in water springs, streams or in the sea (Oman, some places in the Philippines and New-Caledonia), pH, Eh and temperature were measured directly in the field (Table 1).

The chemical compositions of gases were determined by gas chromatography (GC) with a Varian GC3800. Measurement uncertainties are below 0.01% mol for hydrocarbons (FID) and for other gases (TCD). The measurements of the isotopic ratios $^{13}\text{C}/^{12}\text{C}$ (CH_4 and CO_2) and D/H in (CH_4 and H_2) were performed on a MAT 253 (Thermo Fischer) mass spectrometer coupled with a gas chromatograph (GCC-IR-MS). The results are reported in δ units relative to Pee Dee Belemnite (PDB) for carbon and Standard Mean Ocean Water (SMOW)

Table 1
Temperature, pH and Eh of the studied springs. Major gas analyses (mol%).

	Sites	Coordinates (decimal degrees)		Water T, pH, Eh (°C)			Gas composition Mol (%)					
		Latitude	Longitude	T	pH	Eh (mV)	He	H ₂	N ₂	CH ₄	CO ₂	C ₂₊
<i>H₂-rich type</i>												
Oman	Magniyat	23.4061	56.8633	32	11.7	−225	<0.01	87.3	9.8	2.9	<0.01	<0.01
	Hawasina	23.6833	56.9396	25.6	11.3	−244	<0.01	85.9	9.4	4.6	<0.01	<0.01
	Bahla 2008	22.9922	57.2932	35	11.6	−465	<0.01	85.7	12.4	1.9	<0.01	<0.01
	Bahla 2010	22.9922	57.2932	34.9	11.4	−780	–	–	–	–	–	–
	Bahla 2012	22.9922	57.2932	34.9	11.3	−447	<0.01	85.7	12.0	2.2	<0.01	0.02
	Kufeis	23.9588	56.4400	22.5	9.5	−80	<0.01	85.4	14.5	0.1	<0.01	<0.01
	Haylayn 2010	23.6199	57.1132	28.2	11.5	−348	<0.01	77.0	14.2	8.8	<0.01	<0.01
	Haylayn 2012-2a	23.6275	57.1152	–	–	–	<0.01	75.0	15.4	9.6	<0.01	<0.01
	Haylayn 2012-2b	23.6275	57.1152	–	–	–	–	–	–	–	–	–
	Haylayn 2012-6	23.618	57.1064	–	–	–	<0.01	77.8	18.1	4.0	0.05	0.05
	Haylayn 2012-8	23.6181	57.1078	–	–	–	<0.01	79.4	16.0	4.6	<0.01	0.01
	Barrage (Jizzi)	24.3282	56.1307	24.7	10.2	−191	<0.01	75.2	14.9	10.0	<0.01	<0.01
	Halhal	23.7172	57.034	27.7	8.7	−175	<0.01	73.4	20.8	5.8	<0.01	<0.01
	Alkar	23.9693	56.4219	31.5	11.7	−340	<0.01	68.1	28.5	3.3	<0.01	<0.01
	Huqain	23.5352	57.3333	31.2	10.1	−500	<0.01	65.1	32.4	2.5	<0.01	<0.01
Lauriers Roses	22.8956	58.3946	29.5	11.2	−45	<0.01	61.0	23.2	15.4	<0.01	<0.01	
<i>N₂-H₂-CH₄ type</i>												
Oman	Abyiad 2010	23.4285	57.6683	32.9	11.1	−420	<0.01	26.9	57.3	15.9	<0.01	<0.01
	Abyad 2012-29	23.4239	57.6722	23.8	11.1	−39	<0.01	36.1	58.2	5.7	<0.01	0.01
	Abyad 2012-30	23.4242	57.6721	37.4	11.2	−82	<0.01	31.4	59.9	8.7	<0.01	0.01
Philippines	Mangatarem	15.7033	120.2825	34.3	11.3	−38	<0.01	35.1	48.0	16.7	<0.01	<0.01
New Caledonia	Baie du Carénage1	−22.3047	166.8408	–	10.8	−285	<0.01	36.1	50.3	13.7	<0.01	<0.01
	Baie du Carénage2	−22.3047	166.8408	40.1	10.5	−800	<0.01	32.4	51.9	15.7	<0.01	<0.01
	Source des Kaoris 1	−22.2992	166.8617	31.6	10.9	−480	<0.01	26.8	61.9	11.3	<0.01	<0.01
	Source des Kaoris 2	−22.2992	166.8617	30.4	10.6	−230	<0.01	32.9	55.3	11.5	<0.01	<0.01
	Source des Kaoris 3	−22.2992	166.8617	30.5	10.6	−285	<0.01	29.8	58.9	11.3	<0.01	<0.01
<i>N₂-rich type</i>												
Oman	Al Ali	23.4701	58.3239	66.3	6.9	89	<0.01	<0.01	97.9	0.2	1.8	0.1
	Rustaq	23.3935	57.4113	45.3	7.2	125	0.2	<0.01	99.2	<0.01	0.7	<0.01
	Nakhal	23.3754	57.8284	37.9	7.5	146	0.1	<0.01	98.9	<0.01	1.0	<0.01
New Caledonia	La Crouen	−21.535	165.8889	41.5	9.2	−226	0.1	<0.01	97.2	2.7	<0.01	<0.01
	La Crouen	−21.535	165.8889	41.5	9.2	−230	0.1	<0.01	97.3	2.7	<0.01	<0.01
	Roc Aiguille	−22.3167	166.8333	23.5	9.9	−180	<0.01	0.1	93.1	5.1	1.7	<0.01
	Roc Aiguille	−22.3167	166.8333	23.5	10.0	−210	<0.01	<0.01	91.4	8.5	0.1	<0.01

Table 2

$\delta^{13}\text{C}$ (PDB) values of CO_2 and CH_4 (‰). δD (SMOW) values of H_2 and CH_4 (‰). Noble gas analyses ^4He , ^{20}Ne , ^{36}Ar , ^{84}Kr (ppmv), and R/Ra (helium isotopic ratios normalized to the air isotopic $\text{Ra} = ^3\text{He}/^4\text{He} = 1.4 \cdot 10^{-6}$). C_2+ contents in all the gas samples are very low, below the threshold of analytical precision ($<0.01\%$). Global relative uncertainties (at 1σ) for quantification of noble gases with the method used is estimated in the range He: $\pm 10\%$; Ne: $\pm 20\%$; Ar: $\pm 5\%$; Kr: $\pm 10\%$. The global relative uncertainty (1σ) for the R/Ra ratio is in the range $\pm 2\%$.

Sources/wells		Per mil vs PDB		Per mil vs SMOW		Per mil vs atm	Noble gases composition				R/Ra
		$\delta^{13}\text{C}$		δD		$\delta^{15}\text{N}$	(ppm)				
		CO_2	CH_4	H_2	CH_4	N_2	^4He	^{20}Ne	^{36}Ar	^{84}Kr	
<i>H₂-rich type</i>											
Oman	Magniyat	–	–12.8	–	–	–	–	–	–	–	–
	Hawasina	–	–6.2	–724	–242	–	1.87	–	6.76	0.20	0.77
	Bahla 12/2008	–	–10.1	–722	–235	–	2.50	3.687	15.19	0.38	0.37
	Bahla 01/2010	–	–	–734	–234	–	20.80	0.224	7.78	0.24	0.17
	Bahla 2012	–	–	–725	–413	–	1.16	0.864	8.80	0.25	0.93
	Kufeis	–	–7.3	–	–428	–	2.70	3.676	15.36	0.43	0.41
	Haylayn	–	4	–718	–303	–	9.43	3.800	11.41	0.24	0.21
	Haylayn 2a	–	3.9	–714	–360	–	0.96	1.552	9.28	0.23	0.84
	Haylayn 2b	–	–	–	–	–	1.31	2.819	8.33	0.22	0.77
	Haylayn 6	–	–	–712	–404	–	0.99	3.068	10.91	0.29	1.05
	Haylayn 8	–	–	–712	–391	–	0.64	2.079	8.45	0.22	0.95
	Barrage (Jizzi)	–	–9.9	–732	–319	–	15.27	1.260	4.91	0.18	0.43
	Halhal	–	–4.3	–744	–347	–	1.50	5.164	6.05	0.12	0.62
	Alkar	–	–5.8	–710	–392	–	2.85	9.750	18.44	0.41	0.70
	Huqain	–	–5.6	–745	–313	–	0.47	1.172	2.90	0.06	0.57
	Lauriers Roses	–	7.9	–717	–279	–	2.34	1.033	9.51	0.25	0.89
<i>N₂-H₂-CH₄ type</i>											
Oman	Abyiad	–	–0.3	–718	–305	–	7.43	0.543	5.41	0.13	0.76
	Abyaid 29	–	–	–711	–339	–	6.05	9.779	26.48	0.49	1.25
	Abyaid 30	–	–	–699	–324	–	3.47	8.680	28.90	0.61	0.93
Philippines	Mangatarem	–	–13.3	–735	–395	–0.1	2.66	8.204	18.62	0.40	0.71
New Caledonia	Baie du Carénage1	–	–32.4	–	–	–	3.88	14.967	2.20	0.14	1.00
	Baie du Carénage2	–	–	–	–	–	6.40	13.032	3.37	0.33	0.43
	Source des Kaoris1	–	–38.5	–	–	–	3.93	12.251	23.99	0.47	1.56
	Source des Kaoris2	–	–34.9	–	–	–	3.99	16.424	9.97	0.30	1.73
	Source des Kaoris3	–	–	–	–	–	3.99	9.550	5.08	0.16	1.76
<i>N₂-rich type</i>											
Oman	Al Ali	–	–	–	–215	–	14.10	12.559	16.03	0.30	0.42
	Rustaq	–16.5	–	–	–	–0.3	352.90	2.589	0.56	0.01	0.08
	Nakhal	–19.4	–	–	–	–	1382.07	1.760	12.12	0.25	0.07
New Caledonia	La Crouen	–	–39	–	–	–	320.92	10.392	3.42	0.33	0.07
	La Crouen	–	–39.2	–	–	–	99.37	11.047	13.30	1.48	0.06
	Roc Aiguille	–	–12.1	–	–	–	–	–	–	–	–
	Roc Aiguille	–	–16.4	–	–	–	–	–	–	–	–

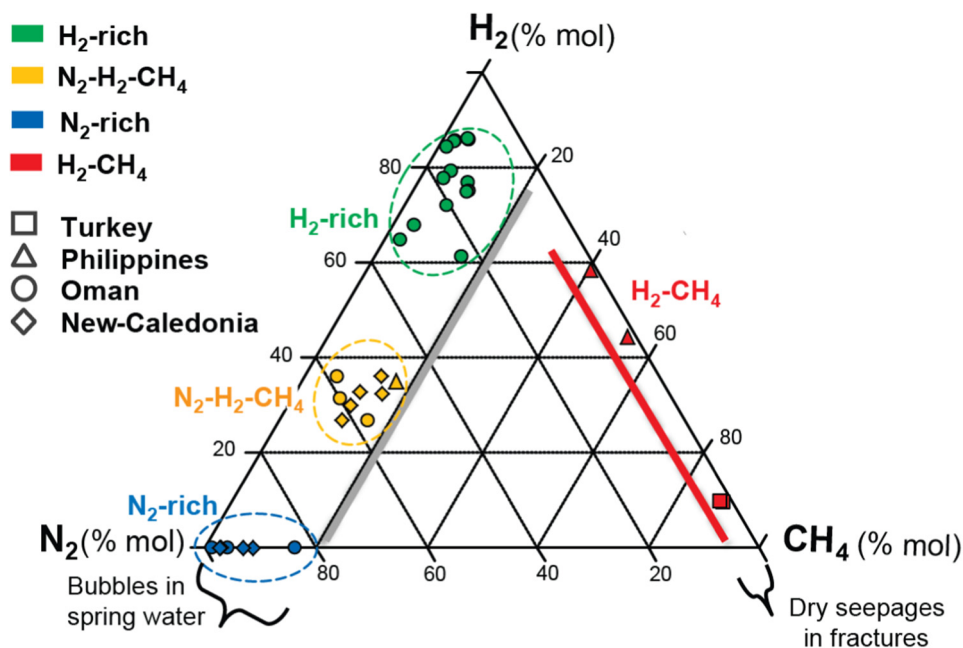


Fig. 4. The major components of the gas mixtures sampled in Turkey, Oman, New Caledonia and the Philippines: H_2 , N_2 and CH_4 in a triangular diagram (% mol). Four different types of gas mixtures can be defined according to the relative contents of H_2 , N_2 and CH_4 . Distinct chemical features correspond to distinct seepages styles: N_2 -containing gas mixtures are associated with water and seep in water streams, whereas N_2 -free mixtures correspond to dry seepages which seep out of fractures of massive rocks and locally ignite spontaneously. The different types of water-associated seepages correspond also to specific water physical properties, notably pH and temperature (see Fig. 5).

150 and 420 mg/l; Neal and Stanger, 1985; Kelemen et al., 2011). The temperatures of these sources are almost ambient to slightly warm (between 22.5 and 35 °C). The $\delta^{13}C$ values of methane are very high (among the highest values known on Earth, between

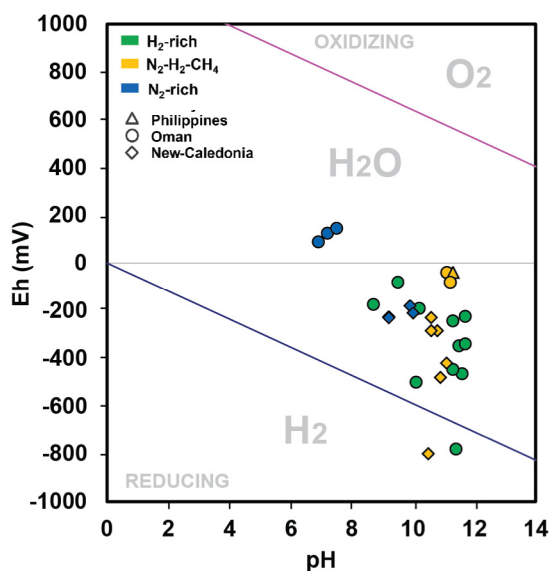


Fig. 5. Pourbaix diagram pH-Eh of the water where the gas samples were collected in springs. Oblique lines (blue and pink) separate the stability fields of H_2 , H_2O and O_2 . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

–13 and +8‰; Table 2; Fig. 8B). The gas composition shows N_2 vs fossil noble gas ^{36}Ar ratios (Table 2; Fig. 9) comprised between the air and water in equilibrium with air (classically mentioned as ASW for Air Saturated Water).

- (2) The N_2 - H_2 - CH_4 type is characterized, by higher N_2 values (from 45 to 65 mol%) compared to the previous gas type. Therefore N_2 becomes the main gas. H_2 contents range from 25 to 36 mol%. CH_4 concentrations are similar to those of the H_2 -rich type (below 20 mol%; Fig. 4). This second gas type is mainly found in New Caledonia (Deville and Prinzhofer, 2016) but also in some springs of Oman and of the Philippines. This type of gas mixture seeps also in ultra-basic springs. These springs are generally warmer than those of the H_2 -rich type, up to 40.1 °C in New Caledonia and pH values are slightly lower, ranging from 10.5 to 11.3. They are, as well, associated with precipitations of calcium carbonate (see supplementary material). The $N_2/^{36}Ar$ ratios of this gas type are different from the previous type and higher than those recorded for ASW and air (Table 2; Fig. 9). These ratios are also correlated with $H_2/^{36}Ar$ and $^4He/^{36}Ar$ ratios (Deville and Prinzhofer, 2016). $\delta^{13}C$ of methane recorded for this gas type ranges between –38.5 and –32.4‰ (Deville and Prinzhofer, 2016).
- (3) In the N_2 -rich type, the dominant gas compound is N_2 (over 91 mol%). Gas mixture is H_2 -free with low CH_4 contents (up to 2.7 mol% in New Caledonia), plus substantial amounts of helium (values above

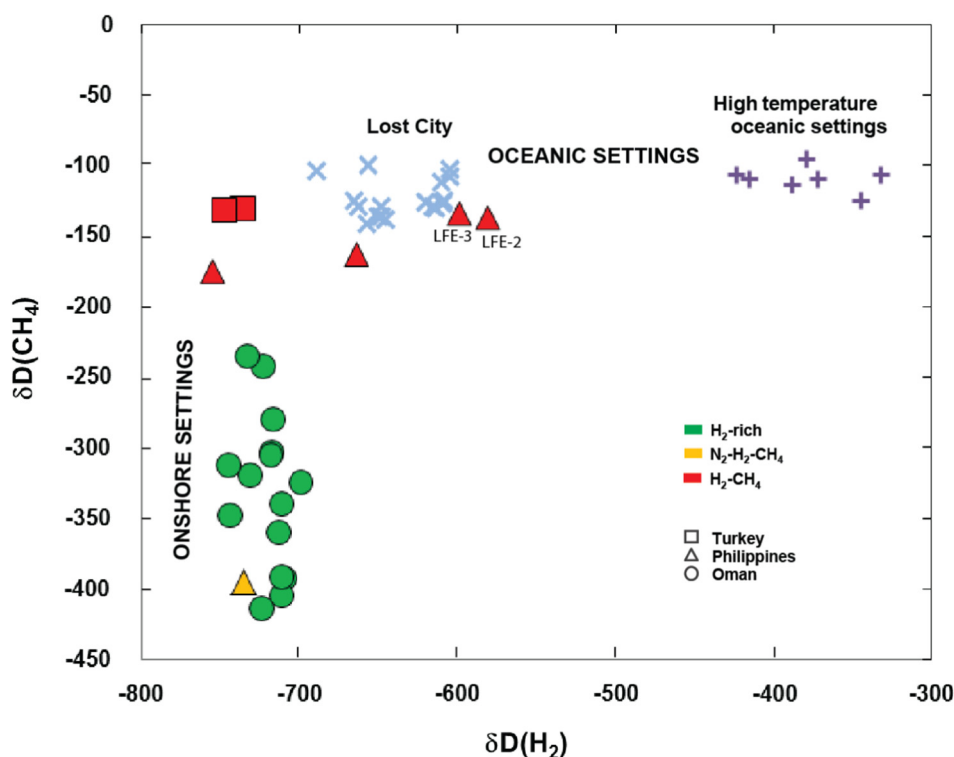


Fig. 6. Comparison of hydrogen isotopic compositions of CH_4 and H_2 for onshore settings (data from this work and two points, LFE-2 and LFE-3, from [Abrajano et al. \(1988\)](#)) and oceanic settings ([Proskurowski et al., 2006](#)). While a narrow range of CH_4 isotopic composition is observed for oceanic settings these values are lower for onshore settings and cover a large range. The values for the gas seeping out of fractures without associated ultra-basic water ($\text{H}_2\text{-CH}_4$ gas type) are close to those of oceanic setting at Lost City and might indicate a similar generation process. In contrast to the CH_4 isotopic compositions, the H_2 isotopic compositions display a large range in oceanic settings (dependent on temperature) and a narrow range in terrestrial settings for gas seeping from ultra-basic springs.

0.1 mol%). This type of springs was found in Oman ([Sano et al., 1993](#); [Vacquand, 2011](#)) and New Caledonia ([Deville and Prinzhofer, 2016](#)) where they occur in the same structural position, *i.e.*, at the base of ophiolitic nappes (either in the sole of the nappes or in the sediments immediately below the nappes). $\delta^{13}\text{C}$ values of CH_4 in this type are between -39.2 and -12.1‰ . These gases come out in the form of bubbling springs with less alkaline water than previously recorded (pH from 7.5 to 10) and variable Eh (from -230 to $+146$ mV). The $\text{N}_2/^{36}\text{Ar}$ ratios are very high ([Table 2](#); [Fig. 9](#)). R/Ra ratios of the gases are consistently low (between 0.06 and 0.08, except for the sample collected in Al Ali where it was not possible to avoid air contamination because of access difficulties when sampling the gas and high temperature of the spring, above 66°C ; [Tables 1 and 2](#); [Fig. 10](#)). The dissolved species in the associated waters are very different from those of the waters containing H_2 gases. They show lower concentrations of Na^+ and K^+ ions and contain HCO_3^- ions, which is not the case of the ultra-basic springs with H_2 seepages ([Neal and Stanger, 1985](#)). In all cases these springs are warm to hot (from 37.9 to above 66°C ; [Table 1](#)).

(4) *The $\text{H}_2\text{-CH}_4$ type* shows mostly H_2 and CH_4 in variable proportions. This type of gas vent is characterized by focused and relatively high gas flows (> 1 l/s), coming directly out of the rock fractures in the absence of water. This gas type was found in the Philippines and in Turkey where it was mentioned respectively by [Abrajano et al. \(1988, 2006\)](#) and [Hosgörmöz et al. \(2008\)](#). It has not been found in New Caledonia but [Neal and Stanger \(1983\)](#) mentioned locally focused high gas flows seeping out directly from fractures of ultrabasic rocks in Oman (>10 l/s). The CH_4/H_2 ratio is commonly higher compared to the types associated to alkaline springs, except for the case of Nagsasa in the Philippines. The gas is able locally to spontaneously ignite as it is the case in Turkey (Chimaera) and the Philippines (Los Fuegos Eternos and Nagsasa) forming visible flames when the CH_4/H_2 ratio is high. Nitrogen is nearly absent of these dry gas seepages (less than 2 mol%; [Fig. 4](#)) whereas since the gas is seeping out from fractures of rocks located above the water table, we would have expected that the gas would be much more easily naturally contaminated by air than in the previous cases which are bubbling in water. Indeed, these $\text{H}_2\text{-CH}_4$ gases do not display predominantly atmospheric features and ^{20}Ne and

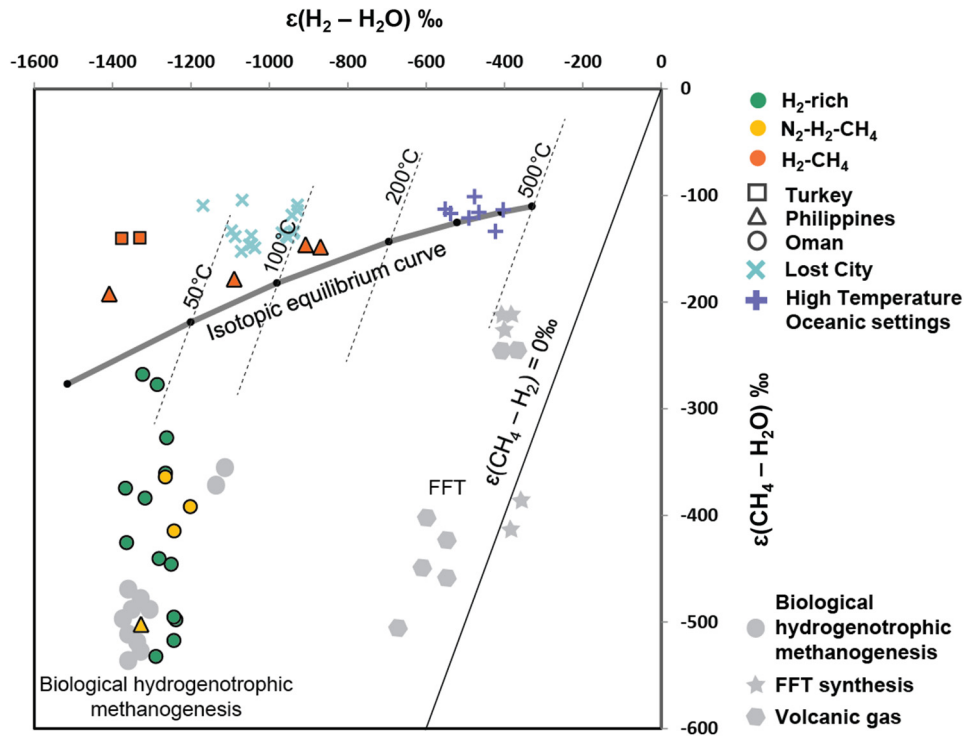


Fig. 7. $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$ hydrogen isotope systematics. Data for biological hydrogenotrophic methanogenesis are from Balabane et al. (1987), Valentine et al. (2004) and Okumura et al. (2016). FTT synthesis refer to experiments investigating abiogenic methane production in the gas phase (Taran et al., 2007) and aqueous phase (Fu et al., 2008; McCollom et al., 2010). There data were presented in a similar diagram in Suda et al. (2014). This figure shows $\varepsilon(\text{H}_2\text{-H}_2\text{O}_{\text{aq}})$ versus $\varepsilon(\text{CH}_4\text{-H}_2\text{O}_{\text{aq}})$ for the samples from Oman, the Philippines and Turkey, compared to values from oceanic settings. The value ε is calculated according to the following equations: $\varepsilon = 1000 \ln \alpha$ with $\alpha(\text{H}_2\text{O}_{\text{aq}}\text{-H}_2) = 1.0473 + 201,036/T^2 + 2.060 \times 10^9/T^4 + 0.180 \times 10^{15}/T^6$ and $\alpha(\text{H}_2\text{O}_{\text{aq}}\text{-CH}_4) = 1.0997 + 8456/T^2 + 0.9611 \times 10^9/T^4 - 27.82 \times 10^{12}/T^6$. The thin line indicates the $\text{CH}_4\text{-H}_2$ equilibrium fractionation at a given temperature. According to this interpretation, CH_4 from fractures (dry seepages) would be produced directly from H_2O and DIC whereas, in the H_2 -rich and $\text{N}_2\text{-H}_2\text{-CH}_4$ gas mixtures seeping in alkaline springs, an H_2 intermediate (possibly biologically mediated secondary process) would produce CH_4 . δD of spring water is considered to be close to zero ‰ from the study made in Oman by Neal and Stanger (1985; values between -11.2 and $+10.7$ ‰).

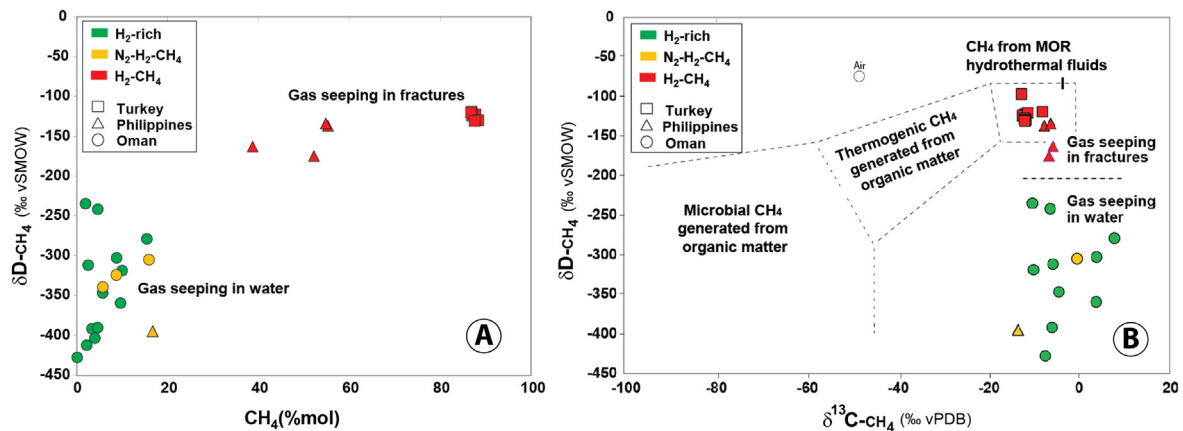


Fig. 8. A. Diagram showing δD (‰) values of CH_4 vs CH_4 contents. This shows that the $\text{H}_2\text{-CH}_4$ gas type shows higher CH_4 contents and δD values of CH_4 than the other gas types. B. Diagram showing carbon versus hydrogen isotopic composition of CH_4 including data from Abrajano et al. (1988) and Hosgörmöz et al. (2008), domains are simplified after Schoell (1988), Whiticar (1999) and Etiope and Sherwood-Lollar (2013). The classic microbial domain presented here refers to gas generated from an organic substrate. This domain might be wider in the case of microbial gas generated from inorganic carbon. The carbon isotopic compositions of CH_4 are among the highest values recorded on Earth. The range of the carbon isotopic values of CH_4 is relatively narrow and allows no distinction between the different types of gas mixtures whereas the hydrogen isotopic values of CH_4 are scattered between -430 ‰ and -100 ‰ and show distinct ranges comparing dry seepages in fractures and seepages in ultra-basic water. This corresponds probably to different CH_4 generation processes. Note that none of the groups plot in the classical domains of conventional microbial gas or conventional thermogenic gases. Domain for CH_4 of Mid-Oceanic Ridges hydrothermal fluids is from Proskurowski et al. (2006) and Kawagucci et al. (2016).

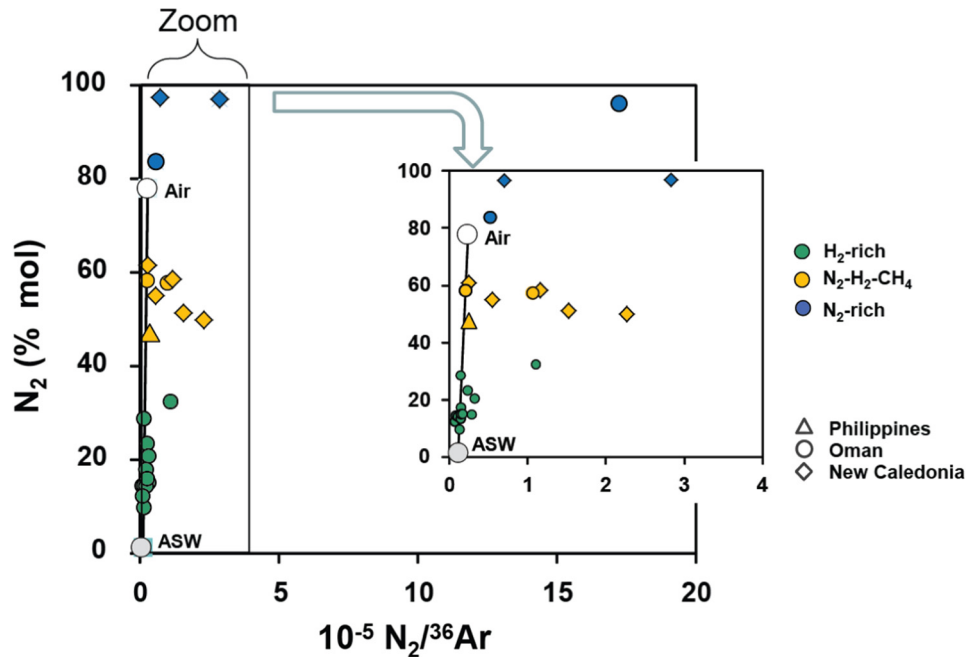


Fig. 9. N_2 content vs $N_2/^{36}Ar$ diagram, depicting nitrogen excess in samples relative to atmospheric ^{36}Ar . The values from the H_2 -rich type gather along a mixing line between air and air equilibrated water, implying that probably only inherited atmospheric N_2 can be found in the gas mixture, whereas the other types show a N_2 excess, suggesting that non-atmospheric N_2 is present in the gas mixture.

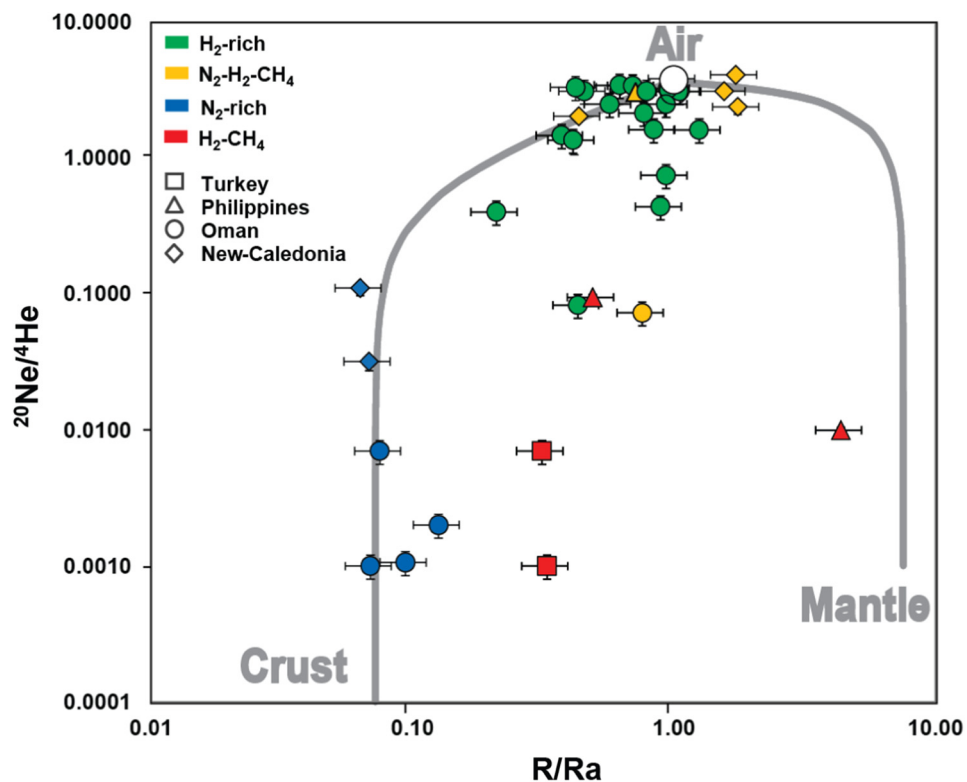


Fig. 10. Mixing diagram $^{20}Ne/^4He$ vs R/Ra ($^3He/^4He$ ratio of the sample normalized over the same ratio for the air = 1.384×10^{-6}). The noble gas data show that except the H_2 -rich type which plots around the atmospheric end-member and indicates a single shallow aquifer signature, the other gas mixtures have signatures that result from the interaction of several fluids originating either from the mantle or from the crust. The N_2 -rich type is interpreted as resulting from the mixing of atmospheric and crustal end-members whereas a mantle contribution is recorded for samples of the $N_2-H_2-CH_4$ and H_2-CH_4 types.

^{84}Kr concentrations are quite low compared to other types of gas mixtures (Table 2). $\delta^{13}\text{C}$ values of CH_4 are high and fairly constant (between -12 and -5‰ ; Fig. 8), as well as δD of CH_4 which range from -175 to -130‰ . The δD values of CH_4 are higher when compared to the H_2 -rich and N_2 - H_2 - CH_4 gas types (Table 1), while the δD values of H_2 vary between -756 and -664‰ , generally in the same order of magnitude as those recorded in the H_2 -rich and N_2 - H_2 - CH_4 gas types (Table 1; Fig. 6). The differences of δD values of CH_4 suggest different processes for CH_4 genesis and probably different sources for hydrogen and carbon (see discussion below).

5. DISCUSSION

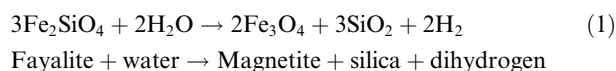
5.1. Main characteristics of the different gas types

Comparing the different gas types, several characteristic features can be noticed. Gases bubbling in prings always contain N_2 that is not related to air contamination (see below), while gas seepages in fractures without associated water flows are N_2 -poor. The gas bubbling in springs shows CH_4 contents that never exceed 20 mol%. The specificity of the H_2 - CH_4 gas type seeping in fractures without associated water flow is that their CH_4 contents locally reach high levels and that δD of CH_4 is significantly higher compared to the δD of CH_4 in the other gas types (Fig. 8). The water temperature tends to increase in the different types of springs from the H_2 -rich, to the N_2 - H_2 - CH_4 and to the N_2 -rich gas types (Table 1). Gas bubbling in springs is associated to ultra-basic conditions only when H_2 is present, whereas water is less or not basic in the springs of the N_2 -rich gas type. We propose that the chemical characteristics that define gas types reflect differences in origin and transport pathways of gas mixtures.

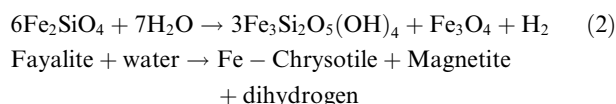
5.2. Hydrogen origin

As mentioned in introduction, H_2 sources of gas seepages in ophiolitic contexts are classically credited to modern hydration processes at low temperature during the weathering of ultrabasic and basic rocks (mostly peridotite and gabbro). At depth, within ophiolitic rocks, biological production of H_2 by fermentation processes is probably a sluggish process due to the paucity of potential organic substrates. High-temperature serpentinization (above 300°C) is a well-known process but at temperatures below 300°C serpentinization can occur as well (Moody, 1976). Indeed, experimental studies simulating land-based peridotite systems have shown that H_2 can be generated during serpentinization at temperatures below 100°C (Mayhew et al., 2013; Okland et al., 2014; Neubeck et al., 2011). On hydrogen-bearing gas seepages associated with high pH waters in ophiolitic context (Neal and Stanger, 1983; Sano et al., 1993; Cipolli et al., 2004; Hosgörmöz et al., 2008; Vacquand, 2011; Abrajano et al., 2006), H_2 would result from the interaction between ultrabasic rocks and water flows at depth in the fracture system, in anoxic con-

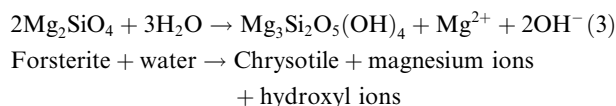
ditions, by reduction of water and oxidation of metals (Fe^{II} , Mn^{II} , Ni^{II} , ...), Fe^{II} being by far the most abundant electron donor in ultrabasic-basic rocks. During the serpentinization process, Fe^{II} -rich minerals, such as olivine $[(\text{Mg}^{\text{II}}, \text{Fe}^{\text{II}})_2\text{SiO}_4]$ are oxidized and form Fe^{III} -bearing minerals, such as magnetite $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}_4]$ or Fe^{III} -bearing serpentine (Evans, 2008), with coeval reduction of water generating H_2 . Olivine is a magnesium-iron nesosilicate forming a solid solution series between a Mg-endmember and a Fe-endmember. During olivine dissolution, the olivine Fe-endmember (fayalite, Fe_2SiO_4) tends to react as,



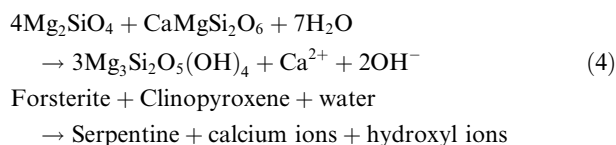
At temperature below 150°C , dissolution of the olivine Fe-endmember is even thermodynamically more favorable when Fe-chrysotile is formed (Oze and Sharma, 2005) according to the following reaction,



The Mg-endmember of olivine (Forsterite, Mg_2SiO_4) reacts as,



In presence of dissolved inorganic carbon (DIC) in subsurface, Mg^{2+} ions are consumed to produce magnesium-bearing carbonates (which are widespread in fractures systems of all the ophiolitic massifs studied here; see below), and (if available) remaining Mg^{2+} ions are prone to react with OH^- to form brucite, $\text{Mg}(\text{OH})_2$ (which is commonly found in the ultra-basic springs studied here, notably in Oman; Neal and Stanger, 1984) leaving finally OH^- available in solution. In the case of New Caledonia, where alkaline seepages interact with sea water, this results in massive production of brucite due to the reaction between OH^- and Mg^{2+} present in sea water as it is the case of the seepages studied in New-Caledonia (Launay and Fontes, 1985). More generally, as proposed by different authors, the coupled hydration of Mg-olivine and Ca-bearing pyroxene of peridotite rocks makes the water enriched in Ca^{2+} and OH^- (Barnes et al., 1967; Neal and Stanger, 1984; Bruni et al., 2002; Kelemen et al., 2011; Miller et al., 2016),



As such, the interaction between peridotite and water during serpentinization is a potential source of H_2 caused by ferrous iron oxidation and water reduction associated with a rise of pH due to OH^- production and associated with the presence of Ca^{2+} in the ultra-basic water. The richer in iron is the olivine, the more H_2 and the less OH^- are produced.

It has been experimentally demonstrated that highly fractured/alterated peridotite is more prone to generate H_2 than a massive unaltered peridotite suggesting a role of the reacting surfaces and possibly that Fe^{II} -bearing secondary formed minerals, such as Fe^{II} -bearing brucite and serpentine, and the presence of N-species may also contribute to form H_2 (experiments at 25 °C; Okland et al., 2014, see also Klein et al., 2015).

The conditions of generation of H_2 can be estimated notably using hydrogen isotopic data. In the studied ophiolitic massifs, whatever are the characteristics of the H_2 -bearing gas types, δD values of H_2 are all very low in the analyzed gas samples (between -756 and -664‰). Abrajano et al. (1988) mentioned, δD values of H_2 at -581 and -599‰ in the Los Fuegos Eternos of the Philippines. The lowest values are among the lowest recorded on Earth and they are significantly lower compared to δD of H_2 of hydrothermal sites on mid-oceanic ridges for which the values are more dispersed and generally higher (between -700 and -300‰ ; Fig. 6). δD values of H_2 observed in oceanic settings decrease with temperature and appear as a thermometer for H_2 production at isotopic equilibrium with seawater (Proskurowski et al., 2006). Low δD values of H_2 in ophiolitic massifs are classically considered as revealing relatively low temperatures of the generation of H_2 (Neal and Stanger, 1983). Indeed, using either (1) the Horibe and Craig (1995) H_2O-H_2 and CH_4-H_2 geothermometers which consider isotope fractionations between liquid H_2O or CH_4 and H_2 , or (2) Bottinga's (1969) water vapor–hydrogen method, this strongly suggests that the generation of H_2 occurred at lower temperature conditions than at most of the hydrothermal vents of mid-oceanic ridges. H_2O-H_2 is seen as the preferred geothermometer but it implies that chemical equilibrium between H_2 and H_2O has been reached (see discussion below). It is possible that chemical and isotopic equilibrium have been achieved between H_2 and CH_4 (see the following paragraph). Whatever the geothermometer used, either the Horibe and Craig (1995; Fig. 7) H_2O-H_2 and CH_4-H_2 geothermometers, or the Bottinga (1969) geothermometer, we obtained relatively narrow windows of temperature conditions in the ranges 17–42 °C for H_2 of the H_2 -rich type and 24–50 °C for H_2 of the $N_2-H_2-CH_4$ gas type, whereas the temperature conditions seem much more heterogeneous and reach much higher temperatures in the H_2-CH_4 gas type, notably for the samples of the Philippines (up to 136 °C, taking into account the δD_{H_2} values from Abrajano et al., 1988).

To decipher the conditions of generation of H_2 , it is possible to compare H_2 contents with those of other compounds such as noble gases tracers (Ballentine and Sherwood Lollar, 2002; Ballentine et al., 2002; Zhou et al., 2005; Burnard et al., 2013; Prinzhofer, 2013; Prinzhofer and Deville, 2013). Notably, the H_2 -rich gas type displays $N_2/^{36}Ar$ ratios between ASW and air (Table 2; Fig. 9). These features are consistent with a genesis process involving surface water charged with dissolved atmospheric components (ASW) as the main fluid reacting with the rock for H_2 production. In this case, H_2O inherited from meteoric water, initially in equilibrium with atmospheric components, is probably consumed at depth in the fracture system

of the ophiolites by water/mineral interactions. Following this interpretation, as a consequence of water consumption and H_2 production, initial gas/water equilibrium with atmosphere is disrupted and atmospheric nitrogen and noble gases are mixed with neo-formed gases (H_2 and CH_4) and migrate upwards with no further addition of another gas component. The preservation of atmospheric relative proportions of fossil noble gases (^{20}Ne , ^{36}Ar , ^{84}Kr) suggests that these groundwaters reacted at a relatively shallow depth. For deeper depths of gas/water phases interaction, the difference of noble gas solubility from the surface conditions' ones (as P and T are much higher) would fractionate the relative proportions of these compounds. The 4He contents (<20 ppm), are in good agreement with Neal and Stanger's (1985) interpretation which asserts that $Ca^{2+}-OH^-$ water originates from meteoric water recharging at high elevations. The presence of 4He in subsurface gas is classically interpreted as the result of a lengthy residence time at depth allowing 4He to accumulate significantly due to natural radioactive decay of ^{235}U , ^{238}U and ^{232}Th present in crustal rocks (Ballentine and Burnard, 2002). Paukert et al. (2012) considered, from their modelling of CO_2 consumption, that such meteoric waters reached its high pH values after 6500 years. This geological short time frame is consistent with the low 4He contents of these gases, which are roughly displaying atmospheric signatures.

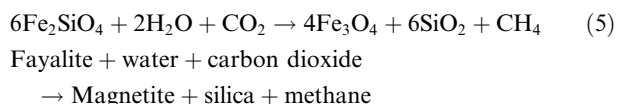
Considering the $N_2-H_2-CH_4$ and H_2-CH_4 gas types, the interpretation that H_2 generation is simply a result of interaction between meteoric water and ophiolitic rocks is not sustainable anymore because, notably, $N_2/^{36}Ar$ ratios are not comprised between ASW and air and noble gas contents are different from Air or ASW. This is consistent with a H_2 generation process which occurred deeper than in the H_2 -rich gas type, in higher temperature conditions as already suggested by δD values of H_2 .

5.3. Methane origin

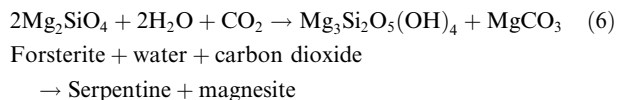
Methane generation associated with fluid-rock interaction in ophiolitic contexts remains unclear. In terrestrial ultrabasic-basic contexts at moderate temperatures (below 150 °C), methane is interpreted to result from carbon hydrogenation involving mainly sources of inorganic carbon. Methane so formed is termed abiogenic (or abiogenic), and is thought to be produced by chemical reactions that do not directly involve organic matter (see discussion in Etiope and Sherwood-Lollar, 2013; with references therein). Eventually, according to the geological conditions, methane produced by fluid-rock interaction can be mixed with biotic methane produced either by microbial processes or by thermogenic degradation of organic matter in sedimentary rocks.

In the case of hydrogenation processes of carbon, considering potential hydrogen sources (H_2O or H_2), hydrogen in CH_4 can be considered as primary (i.e., issued from H_2O reacting with carbon and preceding H_2 production; Abrajano et al., 1988; Oze and Sharma, 2005; Suda et al., 2014; Okland et al., 2014), or secondary (i.e., issued from an H_2 intermediate by reactions between carbon and H_2 ;

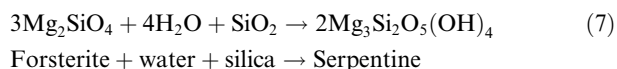
Berndt et al., 1996; Foustoukos and Seyfried, 2004; Horita and Berndt, 1999; McCollom and Seewald, 2001; McCollom, 2016; Neubeck et al., 2011). The experiments of Okland et al. (2014) suggest indeed a possible primary production of CH₄ during hydration of ultrabasic rocks without an H₂ intermediate, notably with moderately altered peridotites. In both cases, hydrogen is issued from H₂O, either primarily or secondarily. Suda et al. (2014), based on a study of hydrogen isotopic data of CH₄, H₂ and H₂O (Fig. 7), defined different domains corresponding to different processes allowing to distinguish CH₄ generation by hydrogenation from water (primary) or from H₂ (secondary). Primary CH₄ production is regarded as a direct interaction between Fe^{II}-rich minerals and dissolved CO₂. CH₄ production tied to ferrous mineral reactions with CO₂ has not yet been fully explored (Neubeck et al., 2016) but there is some indication from experimental reactions of olivine that passivating layers of silica may coat reactive surfaces and slow related CH₄ generation (Garcia et al., 2010). However, early production of CH₄ (before H₂ production) has been documented by experimentation on natural peridotite rocks, at low temperature (25 °C), especially on fractured and altered peridotite, and these experiments showed a coeval production of H₂ and CH₄ (Okland et al., 2014), in the same proportions as those measured in this study for the H₂-rich gas type. The presence of CO₂ is a favorable factor for olivine dissolution (Oze and Sharma, 2005), which releases aqueous Fe^{II}. Primary production of CH₄ from H₂O and CO₂ (DIC in water) is achieved in a similar way as the H₂ production through the oxidation of iron (see above). The reaction of the Fe-endmember of olivine in presence of dissolved CO₂ can be summarized by the following reaction,



while a coeval reaction occurs considering the Mg-endmember,



Over geologic time, in natural environments that include fractured and weathered ultrabasic rocks experiencing diverse aqueous geochemical conditions, passivating silica layers may not be widespread allowing the following reaction,



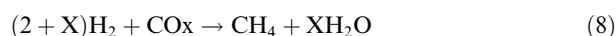
Also, Fe^{II}-bearing brucite-type minerals (for example amakinite) and Fe^{II}-bearing serpentines are good candidates to react with dissolved CO₂, as suggested by experiments (Okland et al., 2014).

Applying the reasoning of Suda et al. (2014) mentioned above to our samples, would suggest that gases from the H₂-CH₄ type (dry seepages in fractures) contain methane which is considered as primary while, in water-related

seepages, the analytical results are more compatible with a secondary CH₄ generated from an H₂ intermediate (gas samples collected in ultra-basic springs showing δD values of CH₄ between −400 et −200‰; Fig. 7).

As suggested by Suda et al. (2014) and according to the reactions shown above, a simultaneous production of methane and magnesite can occur. Mg-bearing carbonates (magnesite and dolomite) are indeed abundant in fractures in the peridotites of Oman and they are supposed to have been formed at temperatures in the range 30 to 60 °C (Kelemen et al., 2011). Methane and magnesite, have both high and similar δ¹³C values (δ¹³C-CH₄ between −13 and +8‰, δ¹³C-magnesite between +2 and +8‰; see [supplementary material](#)). This is compatible with a non-atmospheric carbon origin of CH₄ that could derive from mantellic or metamorphic CO₂ or from carbonate destabilization. These values are different from the carbonates signatures found at the surface in the ultra-basic springs where carbon is interpreted as issued from atmospheric CO₂ which after fractionation during carbonate precipitation give δ¹³C values between −28 and −5‰ (Kelemen et al., 2011; see also [supplementary material](#)).

Considering secondary production of methane, via an H₂ intermediate, several pathways of CH₄ generation involving different sources of carbon can be considered, either (1) organic carbon (or reduced carbon including elementary C) found in sediments below the ophiolites notably, or else (2) carbon issued from deep sources from the mantle or from the crust (for example Dissolved Inorganic Carbon issued from mantle gas or from carbonates within the sediments). Indeed, H₂ produced by serpentinization is susceptible to be subsequently consumed in a CH₄ producing reaction, involving a source of carbon which can be C°, CO or CO₂, according to the general reaction (Deville and Prinzhofer, 2016),



In the case x = 0, the source of carbon can correspond to reduced carbon in sediments (graphite or overmature organic matter). In the case x = 1, the source of carbon corresponds to CO. CO has indeed, been mentioned as traces in the gas of the ophiolites of Oman (Sano et al., 1993). It might correspond to an intermediate compound preceding methane generation. In the case x = 2, this corresponds to the classical Sabatier reaction. Considering generation of high δ¹³C methane associated with ultrabasic contexts, it is frequently considered that it corresponds to Fisher-Tropsch Type (FTT) reaction, meaning the abiotic path of the Sabatier reaction (Szatmari, 1989; Horita and Berndt, 1999; Sherwood-Lollar et al., 1988, 1993a,b, 2006, 2007; Kelley et al., 2001; Charlou et al., 2002; Foustoukos and Seyfried, 2004; McCollom and Seewald, 2001; Taran et al., 2007; Proskurowski et al., 2008; and others, see references in Etiope and Sherwood-Lollar (2013)). In the Sabatier reaction, CO₂ is reduced to CH₄ through the oxidation of H₂ (so the reaction is controlled by H₂ activity).

The kinetics of FTT reactions are slow at the temperatures considered here (below 150 °C) but Fisher-Tropsch reactions are well-known to be favored by catalytic processes. Heterogeneous catalysis, promoted by minerals

present in the ophiolitic rocks, such as chromite, magnetite, sulfides or awaruite can possibly trigger these reactions (Mayhew et al., 2013; Etiope and Ionescu, 2015 and references therein). For instance, close to Los Fuegos Eternos (in the Philippines), chromite (well-developed in the Coto mines) may promote the catalytic production of CH₄. Also, the area of Chimaera in Turkey shows chromite mines (in which an explosion caused the death of tens of underground workers). The area of Prony (New Caledonia) shows also chromite outcrops as well as at many places in the ophiolite of Oman.

Catalytic processes might also be associated with biological activity, which is well-known to reduce the activation energy necessary for chemical reactions. The Sabatier chemical reaction is actually equivalent to one of the classical routes to generate microbial methane (by CO₂ reduction) via hydrogenotroph-methanogen microorganisms. In the case of sedimentary environment with widely available sources of light C provided by organic compounds, it produces methane with $\delta^{13}\text{C}$ generally lower than -50‰ , far below the values obtained in the gas seepages of the ultra-basic springs (between -12.8 and $+7.9\text{‰}$; Fig. 8), even if locally in ultra-basic springs $\delta^{13}\text{C}$ of methane are lower than -50‰ (Morrill et al., 2013). However, in some conditions (notably in the case of hyperthermophilic archaea), $\delta^{13}\text{C}$ values of methane can be high (Takai et al., 2004, 2008). The presence of hydrogenotrophic microorganisms has been mentioned in oceanic hydrothermal fields (Bradley and Summons, 2010) and in ultra-basic springs of ophiolitic units (Brazelton et al., 2013), and the occurrence of methanogens in ultrabasic contexts (Takai et al., 2004; Brazelton et al., 2006) raises the question, notably in Oman, of the microbial production of methane with elevated $\delta^{13}\text{C}$ in ultra-basic groundwaters (Miller et al., 2016). This interpretation is still challenged (see discussion between Etiope, 2017 and Miller et al., 2017) but, if it is confirmed, this would suppose that biological activity might contribute to elevated $\delta^{13}\text{C}$ methane from inorganic sources of carbon under extreme carbon limitation. However, methanogens collected in ultra-basic springs at the surface are not necessary representative of the conditions of generation of methane at depth because there is no carbon available in the ultra-basic water flowing from depth (Neal and Stanger, 1985, see also below). Methane generation via methanogen microorganisms observed at the surface might be a surficial process resulting from a reaction between hydrogen issued from depth and a source of carbon provided by atmospheric CO₂. If the source of deep carbon is important, as in sedimentary environments with fossil organic matter, the use of isotopically light carbon in the widely available organic matter is favored by microbial activity. However, this is not possible in the case of strong restriction of the available carbon as in ophiolitic rocks, especially when the initial sources of carbon are heavy (like carbonates or mantle). Biological processes generating CH₄ from H₂ and CO₂ with progressively increasing $\delta^{13}\text{C}_{\text{CH}_4}$ have been documented in large scale geological gas storages of town gas (Buzek et al., 1994). In addition, the presence of methanotrophs in the ultra-basic springs also contribute to increase the $\delta^{13}\text{C}$ values of the residual methane (Miller et al., 2016).

In the present study, the different values observed for $\delta^{13}\text{C}$ of CH₄ probably reflect different sources of carbon or different CH₄ generation processes. The present study shows that (a) H₂-rich gases from Oman display $\delta^{13}\text{C}$ of CH₄ between -12.8 and $+7.9\text{‰}$, while (b) in the Philippines $\delta^{13}\text{C}$ of CH₄ are ranging between -13.5 and -5.6‰ which is compatible with the results obtained by Abrajano et al. (1988), (c) in Turkey gases from H₂-CH₄ type display a $\delta^{13}\text{C}$ of CH₄ values between -7.9 and -11.9‰ (Hosgörmez et al., 2008 and this study), whereas (d) for New-Caledonia some gases from N₂-H₂-CH₄ type values are between -38.5 and -32.4‰ (Deville and Prinzhofer, 2016). Consequently, two different types of signatures were observed corresponding initial probably (despite of fractionation processes) to two different carbon sources. The first one (high $\delta^{13}\text{C}$ between -13 and $+8\text{‰}$) would correspond most probably to an inorganic carbon source, while the second one (lower $\delta^{13}\text{C}$ between -39 and -32‰) corresponds probably to an organic source. The high $\delta^{13}\text{C}$ of CH₄ from Oman, the Philippines and Turkey might correspond to a carbon source, probably CO₂, found as DIC in the reacting waters. Two different origins may be proposed for this inorganic carbon. It may correspond to mantle degassing, as it might be the case in the Philippines in link with the vicinity of the active volcanism of the Pinatubo system related to an active subduction zone, as suggested by noble gas analyses especially for one gas sample with high R/Ra values (Fig. 10), or it may come from the dissolution of carbonate rocks (for instance the carbonate sediments present under the ophiolites), as it might be the case in Oman (Nicolas et al., 2000) and Turkey (Juteau et al., 1977). Note that the H₂-bearing gas samples studied here (as well as those analyzed in previous studies) show only locally tiny traces of CO₂ for which $\delta^{13}\text{C}_{\text{CO}_2}$ measurements have to be considered with caution (not reported in Table 2). The measurements in the N₂-rich gas type of Oman (seeping out from below the ophiolites), in which CO₂ contents are more important (data from Sano et al., 1993, and this study, Tables 1 and 2), gave values between -19.4‰ and -9.6‰ which are consistent with an origin from sedimentary rocks below the ophiolites (metamorphism and/or carbonate destabilization).

Methane with $\delta^{13}\text{C}$ values comprised between -39 and -32‰ , in New Caledonia, could simply be issued from an organic source (Deville and Prinzhofer, 2016). In agreement with the absence or low contents of C₂₊ in the gas mixtures (below 0.01%), methane may originate from a reaction between H₂ and a mature/overmature organic matter or graphite present in the sediments below the ophiolites.

Also note that, in addition to the absence or very low contents of CO₂ in H₂-bearing gas samples, neither HCO₃⁻ nor CO₃²⁻ have been found in the ultra-basic springs, notably in the case of Oman (Neal and Stanger, 1985) suggesting that almost the entire stock of available DIC was converted into CH₄ under extreme carbon limitation. Also, no form of organic matter or graphite are known within the peridotites of the areas studied. This limitation probably allows H₂ to be present in the gas, otherwise all the generated H₂ would have been consumed to generate CH₄, as it

was suggested by Milesi et al. (2016) in the Solimes Basin in Brazil.

In both, H_2 -rich and N_2 - H_2 - CH_4 gas types, CH_4 contents being lower than 20 mol%, this suggests a very limited carbon source compared with the H_2 - CH_4 gas type (Figs. 4 and 8). Indeed, if we consider carbonic acid in rain water as the initial main source of carbon, its contribution is regarded as limited and rapidly buffered, whereas if the carbon source corresponds to carbonate rocks or deep CO_2 fluxes, the amount of carbon available is more abundant at depth but the connection with the ophiolites depends on the hydrodynamics and the available carbonate dissolved in circulating water. H_2 - CH_4 gas type might correspond to such a system connected to deep sources of carbon.

Considering oceanic hydrothermal vents, values of δD of CH_4 probably record the isotopic fractionation associated to a primary process involving a carbon compound with water, to produce methane. If open system conditions apply, δD of CH_4 depends on isotopic equilibrium at the given temperature. For dry seepages in fractures, data are in agreement with these conditions. For seepages in water, a different process would provide scattered and very low δD values of CH_4 (Fig. 6), either because the system is closed and isotopic equilibrium is not reached or because a different secondary process (eventually biology) is influencing the isotopic composition of hydrogen in methane. As such, the very low values of δD of methane in spring water raise the question of a possible microbial role in methane generation.

For the H_2 - CH_4 and N_2 - H_2 - CH_4 gas types a remarkable correlation exists between H_2 and CH_4 when normalized to ^{36}Ar (Fig. 11A) wherever is the site studied in Oman, in the Philippines and New Caledonia. A similar correlation exists between H_2 and CH_4 when normalized to ^{84}Kr , (Fig. 11B). For the CH_4 - H_2 and N_2 - H_2 - CH_4 gas types, this suggests that, independently of the considered ophiolite and geological context, generations of H_2 and CH_4 are coupled and

both related to a deep process which is independent of interactions with ASW shallow aquifers. Conversely, these correlations do not exist for the H_2 -rich gas type which is in agreement with the interpretations proposed above that this type of gas underwent more influences with ASW aquifers. Also, this correlation is not observed in the samples of Turkey possibly due to a mixing with thermogenic methane. Indeed, according to other studies, some samples, notably in Turkey (H_2 - CH_4 type), might comprise a thermogenic component. It has been considered that high methane content cannot be attributed univocally to dissolved carbonates reduction by H_2 , for example in Chimaera (Turkey), up to 40 mol% of the CH_4 has been estimated to be thermogenic gas originating from a source rocks with highly mature kerogen in a Mesozoic limestone nearby (Hosgörmez et al., 2008; Etiope et al., 2011). This is in good agreement with occurrences of C_2+ (C_2 – C_6 alkanes) in the gas analyzed in Turkey (Hosgörmez et al., 2008; Etiope et al., 2011, and this study, see Table 2). However, whatever the geographic location of samples is, dry seepages display higher CH_4 relative contents together with higher δD of CH_4 when compared to gas seepages in water. This suggests that it can be linked to a different process as mentioned above (primary methane production) and probably higher temperature during production of methane. Gas mixtures belonging to the H_2 - CH_4 type correspond probably to highly reactive zones of water reduction at higher temperature with less carbon restriction.

5.4. Nitrogen origin

In the subsurface, nitrogen gas can have different origins, either atmosphere via the hydrodynamism of air equilibrated water, or sediments (organic matter, or ammonium-bearing clay minerals, or nitrogen-bearing salt in evaporites present in sedimentary rocks), or else the deep crust or mantle degassing (Jenden et al., 1988; Zhu, 2000;

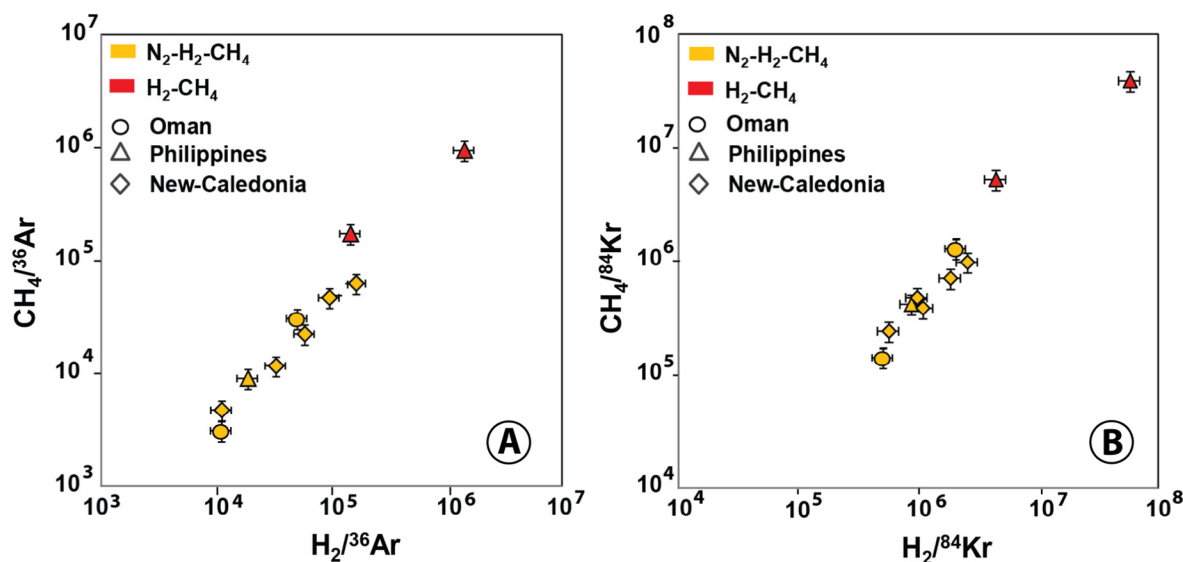


Fig. 11. Mixing diagrams comparing H_2 and CH_4 contents normalized over ^{36}Ar and ^{84}Kr contents. (A) This diagram shows a correlated enrichment in CH_4 vs H_2 when normalized over ^{36}Ar (linear correlation with $R^2 = 0.9894$). (B) This diagram shows also a correlated enrichment in CH_4 vs H_2 when normalized over ^{84}Kr (linear correlation with $R^2 = 0.9953$).

Ballentine and Sherwood Lollar, 2002). Nitrogen contents within ophiolitic rocks are low but experimental studies have however shown that adsorbed N-species can be leached out while H_2 and CH_4 are produced from altered peridotites (Okland et al., 2014).

Considering the geochemical results of this study, N_2 present in the gas of the H_2 -rich type shows $N_2/^{36}Ar$ and $N_2/^{84}Kr$ ratios generally equivalent or slightly higher than those of ASW, suggesting mainly an atmosphere origin for N_2 via a fractured aquifer (Fig. 12A and B).

Samples of the N_2 - H_2 - CH_4 gas type, which show higher N_2 contents than H_2 contents compared to the H_2 -rich gas type display notably a nitrogen enrichment relative to ^{36}Ar and ^{84}Kr (Fig. 12A and B), suggesting an addition of non-atmospheric nitrogen. This contributes to dilute the neo-formed H_2 and CH_4 (Deville and Prinzhofer, 2016). Samples of the N_2 -rich gas type show a 4He enrichment correlated with the N_2 enrichment when compared to atmosphere (Fig. 13). This suggests that non-atmospheric N_2 might be of crustal origin associated to radiogenic helium from depth. The R/Ra ratio ($^3He/^4He$ ratio of the sample normalized over the same ratio for the air = 1.384×10^{-6}) suggests that a crustal component exists in most of the samples and locally a mantle component is observed in the Philippines (Fig. 10).

The differences between the H_2 -rich type and the N_2 - H_2 - CH_4 type are possibly linked to the existence of two different reactive zones for the production of H_2 -rich fluids in peridotitic ground waters: one (H_2 -rich) being more surficial than the other (N_2 - H_2 - CH_4 -rich) and that two different reactive fluids should be considered: (1) a

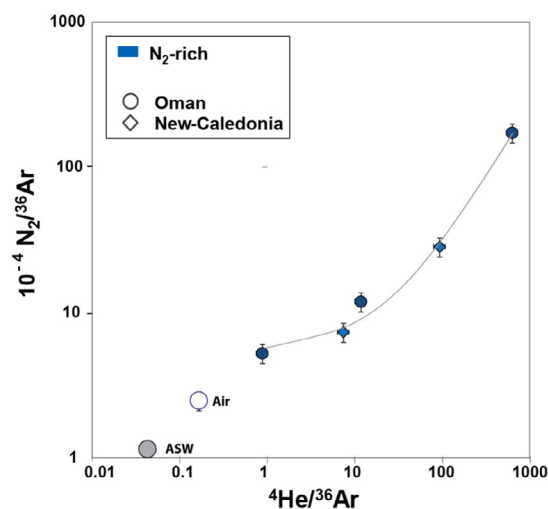


Fig. 13. $^4He/^{36}Ar$ vs $N_2/^{36}Ar$ mixing diagram for the gas samples of the N_2 -rich gas type. This diagram shows a correlated enrichment in 4He vs N_2 when normalized over ^{36}Ar (linear correlation with $R^2 = 0.9993$).

meteoric fluid in the more surficial environment (H_2 -rich) and (2) a deep N_2 -bearing fluid with crustal signature, probably issued from sediment metamorphism from below the obducted ophiolitic units.

Samples of the N_2 - H_2 - CH_4 type could also result from the mixing of H_2 -rich gas and N_2 -rich gas. These N_2 -rich samples contain mostly N_2 and no or little H_2 . Because they were found in hot water springs, displaying pH between 6.9

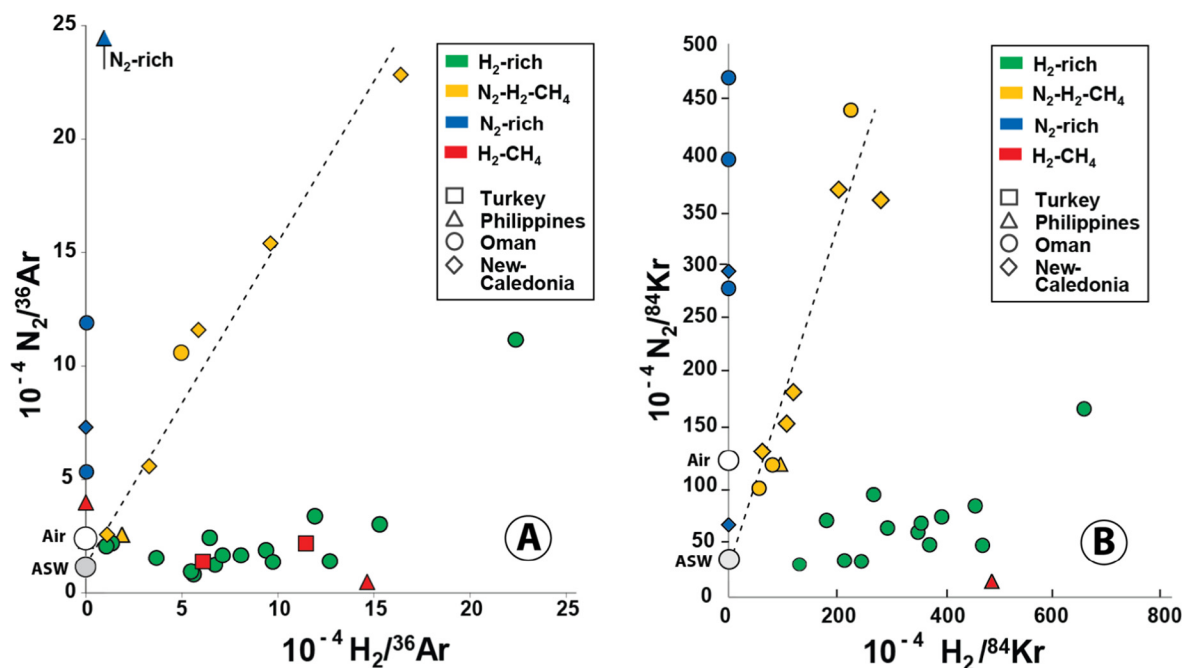


Fig. 12. Mixing diagrams comparing H_2 and N_2 contents normalized over ^{36}Ar and ^{84}Kr contents. (A) The $H_2/^{36}Ar$ vs $N_2/^{36}Ar$ diagram shows different enrichment trends in H_2 vs N_2 between the H_2 -rich gas type and the N_2 - H_2 - CH_4 gas type. Note the good linear correlation between $H_2/^{36}Ar$ and $N_2/^{36}Ar$ for the N_2 - H_2 - CH_4 gas type (linear correlation $R^2 = 0.9785$). (B) The $H_2/^{84}Kr$ vs $N_2/^{84}Kr$ diagram, as the previous diagram, shows different enrichment trends in H_2 vs N_2 between the H_2 -rich gas type and the N_2 - H_2 - CH_4 gas type. Note the good linear correlation between $H_2/^{84}Kr$ and $N_2/^{84}Kr$ for the N_2 - H_2 - CH_4 gas type (linear correlation with $R^2 = 0.9739$).

and 10 and relatively high ^4He contents which suggest a different origin, probably deeper according to water temperature (reaching locally 66°C) and in a crustal environments as suggested by the high ^4He contents. This deep N_2 is probably not directly produced within the peridotite units. The geological context suggests rather an origin from the underthrust sediments below the ophiolitic units, so in this case N_2 would be issued more probably from the buried sediments, either from the water of hydrated clay (clay dewatering) or from the destabilization of ammonium-bearing clays. Reaction of such deep fluids with peridotite or mixing these fluids with H_2 -rich gas type are susceptible to generate fluids with the chemical signatures of the N_2 - H_2 - CH_4 gas type where N_2 dilutes H_2 and is found in excess relative to ASW or air. Throughout the study of the 4 types of gas, it appears that the presence of nitrogen in the mixture is always linked to the presence of water at the seepage. This gas is almost absent from the dry seepages (H_2 - CH_4 type).

$\delta^{15}\text{N}$ measurements in the nitrogen-dominant gas types (N_2 - H_2 - CH_4 and N_2 -rich), gave values of -0.3‰ in Rustaq (Oman), which is consistent with previous studies (Sano et al., 1993) and -0.1‰ in Mangatarem (Philippines; Table 2), whereas $\delta^{15}\text{N}$ measurements in the H_2 - CH_4 gas type gave values comprised between -2.8‰ and -2.1‰ in the Chimaera gas seepages of Turkey (Hosgörmez et al., 2008) and $+0.5\text{‰}$ in Nagsasa in the Philippines (Table 2). The $\delta^{15}\text{N}$ value for atmospheric nitrogen being 0‰ (Sano and Pillinger, 1990; Nishizawa et al., 2007), it cannot be clearly distinguished from the values measured in the N_2 - H_2 - CH_4 and N_2 -rich samples considering potential sampling bias plus analytical uncertainties of the measurements. Although these results are compatible with an atmospheric nitrogen component in the N_2 - H_2 - CH_4 and N_2 -rich gas mixtures, this atmospheric component is not a contamination as shown by the $\text{N}_2/^{36}\text{Ar}$ ratios for instance. This N_2 might thus be issued from pore water trapped in the sediments (initial ASW) below the ophiolites or from the metamorphism of clays from the sediments underthrust below the ophiolitic units. However, such a nitrogen isotopic value is not a clear diagnostic. Although it is compatible with an atmospheric value, it does not exclude other origins like deeper components from mantle and/or crust because a multiple origin of nitrogen is indeed supported by the results of the noble gas analyses.

Noble gas contents suggest that there are at least two different sources of N_2 . The plot of R/Ra versus $^{20}\text{Ne}/^4\text{He}$ (Fig. 10) shows that the N_2 -bearing gases are ranging on a mixing line between the crust and the atmospheric end-member. In the H_2 -rich type, the $\text{N}_2/^{36}\text{Ar}$ ratio is close to the air and ASW ratios (Fig. 12A). This implies that N_2 in this gas originates from the atmosphere and was carried by an aquifer equilibrated with the atmosphere or that the main nitrogen component is acquired during the gas migration upwards through the aquifer. The other samples (N_2 - H_2 - CH_4 and N_2 -rich) do not align on these atmospheric ratios. They display a nitrogen enrichment relative to ^{36}Ar (Fig. 12A) and the contents are much too high to be only due to extraction from an aquifer related to free gas flows toward the surface.

From the plots of Fig. 12A and B, it can be inferred that N_2 -rich type gases in Oman and New Caledonia consist of a mixture of an atmospheric component and an almost pure nitrogen end-member. The proportion of the nitrogen component varies in a large range (from 10 to 90% mol). ^4He is mainly a radiogenic product issued from the continental crust. It cannot be produced in such amounts by mantle-derived ultrabasic rocks. Thus, the N_2 -rich gases can be interpreted as a crustal gas with a ^4He component. A potential interpretation for the origin of deep N_2 could be that it was produced in the sediments and/or metasediments buried under the ophiolitic units. In this case, the source could be the interstitial water in the sediments and/or the solid matrix of the sediments (organic matter or ammonium in clay sediments).

6. CONCLUSION

Integrating the results of previous studies and original results in different areas of the world, this multi-tracer approach provided new insights on gas seepages in ophiolitic contexts. Four types of gas mixtures were defined, three of them being associated with water springs and characterized by the presence of N_2 , CH_4 in proportions under 20 mol% and the presence of H_2 within the ultra-basic springs. The fourth type corresponds to focused gas flows seeping out directly from fractures (without water flow) and characterized by high proportions of CH_4 and low N_2 . In all cases, H_2 is interpreted as a consequence of oxidation of Fe^{II} -rich minerals present in the ophiolitic rocks (even though a contribution by microorganisms by dark fermentation processes cannot be ruled out). Taking into account the pH conditions associated with the H_2 generation, Fe^{III} -bearing mineral were formed at the vicinity of the sites of oxidation of Fe^{II} -bearing mineral without an important mobility of Fe^{2+} . A relatively shallow H_2 production is substantiated in the H_2 -rich gas type by its association with quasi-atmospheric noble gases. It is consistent with the D/H isotopic data of H_2 that may correspond to a fluid rock reaction occurring at low temperature (probably below 50°C), whereas higher temperatures are suspected for the H_2 production in the N_2 - H_2 - CH_4 gas type and notably in the H_2 - CH_4 gas type (probably above 100°C locally). The preservation of H_2 in the gas is directly related to extreme limitation of carbon in the geological setting. It is probably related to the carbon capture associated with massive precipitation of carbonates due to high-pH conditions. Concerning CH_4 , multiple origins are supported by the carbon isotopic data. The carbon and hydrogen sources are various. Both, a primary CH_4 (from H_2O reacting with DIC) and a secondary CH_4 (from an H_2 intermediate reacting with a C source) are suspected for the H_2 - CH_4 gas type and for N_2 - H_2 - CH_4 and H_2 -rich gas types, respectively. In the gas mixtures, N_2 appears to have two distinct origins: an atmospheric component and a deep crustal component, as it was highlighted by the noble gas analyses. The different processes described involve different types of fluids, which are: a shallow meteoric fluid, a crustal fluid carrying metamorphic N_2 , a deep mantle originating fluid carrying primordial CO_2 . Depending on the location with respect to

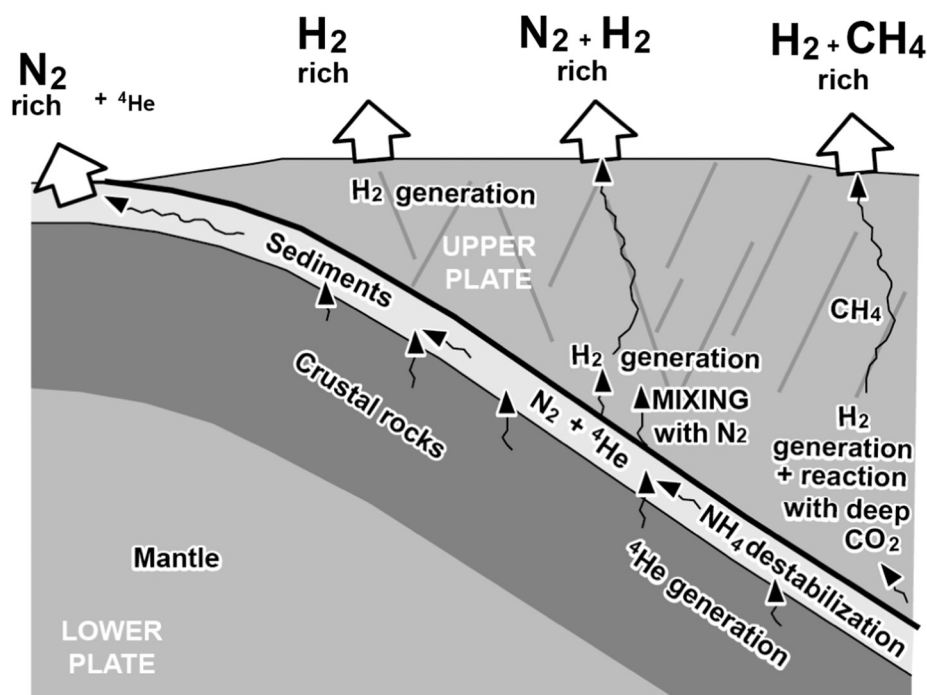


Fig. 14. Synthetic conceptual cross-section of an ophiolitic system with the different gas generation zones and different types of seepages. In this interpretative sketch, H_2 is generated within the ophiolite at different depths by reduction of water, leading to different types of seepages depending on the other fluids interacting with H_2 . When H_2 is generated in a shallow aquifer, it migrates upwards and seeps out of the rock as a H_2 -rich gas seep. H_2 generated in a deeper generation zone interacts with deep fluids which can be (1) a N_2 -rich fluid issued from the sediments and the mantle below, leading to a N_2 and H_2 -rich gas, or (2) a fluid rich in CO_2 , allowing the production of CH_4 and the formation of a gas mixture that seeps at the surface as a H_2 - CH_4 gas seepages. N_2 -rich seepages occur when the deep N_2 -bearing fluid does not interact strongly with H_2 -rich fluids on its migration pathway.

the geodynamical context (Fig. 14), these different fluids interact and mix in different proportions, yielding the types of gas mixture observed at the surface seepages. The shallower kitchen is interpreted as the H_2 -rich gas type from meteoric water interacting with the ophiolite. The deepest kitchen is interpreted as the H_2 - CH_4 gas type from a deep fluid (carrying CO_2 from the mantle, or from dissolved carbonates or organic carbon) interacting with the ophiolite. H_2 - CH_4 gas flows are generally more localized (focused) and these flows are generally higher than the other H_2 -bearing gas flows. This is probably due to the fact that they are generated at greater depth and at higher temperature conditions. This probably induces the individualization of a gas phase preventing H_2 to react during the rise toward the surface, notably by preventing any biological consumption of H_2 which required an aqueous media. The N_2 -bearing fluids are probably generated mostly from the sediments located below the ophiolitic units and migrate upwards forming the N_2 -rich gas type when reaching the surface or the N_2 - H_2 - CH_4 type if mixing occurs between the N_2 -rich and the H_2 -rich types (Fig. 14).

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gca.2017.12.018>.

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