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## Reduced gas seepages in ophiolitic complexes: Evidences for multiple origins of the H<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub> gas mixtures

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### ► To cite this version:

Christèle Vacquand, Eric Deville, Valérie Beaumont, François Guyot, Olivier Sissmann, et al.. Reduced gas seepages in ophiolitic complexes: Evidences for multiple origins of the H<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub> gas mixtures. *Geochimica et Cosmochimica Acta*, 2018, 223, pp.437 - 461. 10.1016/j.gca.2017.12.018 . hal-01845998

**HAL Id: hal-01845998**

**<https://ifp.hal.science/hal-01845998>**

Submitted on 20 Jul 2018

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1 **Reduced gas seepages in ophiolitic complexes:**  
2 **Evidences for multiple origins of the H<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub> gas mixtures**

3

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13

14 **Key-words:** ophiolite, serpentinization, hydrogen, abiotic methane, deep nitrogen

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25 **Highlights**

26 ⇨ Gas generation during serpentinization

27 ⇨ Deep origin of nitrogen seepages in obducted ophiolitic complexes

28 ⇨ Multiple sources of gas and gas mixing in ophiolitic complexes

29 ⇨ Multiple sources of carbon during abiotic methane generation

30

31 **ABSTRACT**

32

33 This paper proposes a comparative study of reduced gas seepages occurring in ultrabasic to  
34 basic rocks outcropping in ophiolitic complexes based on the study of seepages from Oman,  
35 the Philippines, Turkey and New Caledonia. This study is based on analyses of the gas  
36 chemical composition, noble gases contents, stable isotopes of carbon, hydrogen and nitrogen.  
37 These seepages are mostly made of mixtures of three main components which are H<sub>2</sub>, CH<sub>4</sub>  
38 and N<sub>2</sub> in various proportions. The relative contents of the three main gas components show 4  
39 distinct types of gas mixtures (H<sub>2</sub>-rich, N<sub>2</sub>-rich, N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> and H<sub>2</sub>-CH<sub>4</sub>). These types are  
40 interpreted as reflecting different zones of gas generation within or below the ophiolitic  
41 complexes. In the H<sub>2</sub>-rich type associated noble gases display signatures close to the value of  
42 air. In addition to the atmospheric component, mantle and crustal contributions are present in  
43 the N<sub>2</sub>-rich, N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> and H<sub>2</sub>-CH<sub>4</sub> types. H<sub>2</sub>-bearing gases are either associated with ultra-  
44 basic (pH 10-12) spring waters or they seep directly in fracture systems from the ophiolitic  
45 rocks. In ophiolitic contexts, ultrabasic rocks provide an adequate environment with available  
46 Fe<sup>2+</sup> and alkaline conditions that favor H<sub>2</sub> production. CH<sub>4</sub> is produced either directly by  
47 reaction of dissolved CO<sub>2</sub> with basic-ultrabasic rocks during the serpentinization process or in  
48 a second step by H<sub>2</sub>-CO<sub>2</sub> interaction. H<sub>2</sub> is present in the gas when no more carbon is  
49 available in the system to generate CH<sub>4</sub>. The N<sub>2</sub>-rich type is notably associated with relatively  
50 high contents of crustal <sup>4</sup>He and in this gas type N<sub>2</sub> is interpreted as issued mainly from  
51 sediments located below the ophiolitic units.

52

53

54 **Introduction**

55

56 Serpentinization generates natural emission of H<sub>2</sub> on Earth. The process is inherent to  
57 exposure of reduced mantle rocks to hydration conditions in a wide range of thermal  
58 conditions, at least up to the critical temperature of water (374°C). This occurs commonly at  
59 mid-oceanic ridges where hydrothermal fluid circulation at high temperature provides  
60 conditions for ferromagnesian mineral alteration. Indeed, at mid-oceanic ridges H<sub>2</sub>-rich fluids  
61 are associated with N<sub>2</sub> and CH<sub>4</sub> contents and on black smokers with CO<sub>2</sub> (Welhan and Craig,  
62 1979; Kelley and Früh-Green, 1999; Charlou et al., 2002; Kelley et al., 2001, 2005; Gallant  
63 and Von Damm, 2006; Kumagai et al., 2008; and others). Natural H<sub>2</sub> seepages are also  
64 reported onshore, in former oceanic rocks present in ophiolite complexes. Notably, H<sub>2</sub>  
65 seepages associated with these ultrabasic rocks have been reported in the Sultanate of Oman  
66 (Neal and Stanger, 1983; Sano et al., 1993; Vacquand, 2011; Boulart et al., 2013; Miller et al.,  
67 2016), the Philippines (Abrajano et al. 1988, 1990) and Turkey (De Boer et al., 2007;  
68 Hosgörmez et al., 2008; Etiope et al., 2011). These gas seepages are often associated with  
69 ultra-basic springs (pH 10-12) that are present in many basic-ultrabasic rock exposures. Such  
70 ultra-basic waters have been interpreted as evidences of active serpentinization (Barnes et al.,  
71 1967, 1978; Neal and Stanger, 1983; Abrajano et al., 1988, 1990; Sano et al., 1993; Bruni et  
72 al., 2002; Cipolli et al., 2004; Deville et al., 2011; Szponar et al., 2013; Etiope et al., 2013;  
73 Chavagnac et al., 2013; Cardace et al., 2015; Meyer-Dombard et al., 2015; Woycheese et al.,  
74 2015; Deville and Prinzhofer, 2016). In these cases, H<sub>2</sub>-rich gas is either dissolved or present  
75 as free gas bubbling in the ultra-basic water. In other cases, H<sub>2</sub>-rich gas seepages occur in  
76 rock fractures and can locally burn spontaneously. This is notably the case of the famous  
77 Chimaera near Antalya, place of the first Olympic flame, which are known to be burning  
78 since antiquity (De Boer et al., 2007; Hosgörmez et al., 2007, 2008) and the site of “Los  
79 Fuegos Eternos” in the Philippines known since the Spanish colonization (Abrajano et al.,  
80 1988, 1990). H<sub>2</sub>-bearing gases discovered in ophiolitic rocks onshore show lower contents in  
81 helium than those discovered in terrestrial context in non-ophiolitic rocks (Coveney et al.,  
82 1987; Ikorsky et al., 1999; Sherwood-Lollar et al., 2007; Larin et al., 2015; Zgonnik et al.,  
83 2015; Guélard et al., 2017).

84 H<sub>2</sub> is generally considered as produced by water reduction that occurs simultaneously to the  
85 hydration of ultrabasic or basic rocks, *i.e.*, according to serpentinization reactions. In the case  
86 of ophiolitic settings, it is generally supposed to happen at low temperature (Moody, 1976;

87 Neal and Stanger, 1983; Abrajano et al., 1988; Etiope et al., 2011). The process driving this  
88 reduction is the change of valence of transition metals, notably ferrous iron Fe<sup>II</sup> into ferric  
89 iron Fe<sup>III</sup>, iron being the most abundant transition metal in ultrabasic and basic rocks. Fe<sup>II</sup> is a  
90 major component in ultrabasic rocks in the ophiolitic units within minerals such as olivine and  
91 pyroxene. It contributes to the formation of Fe<sup>III</sup>-bearing minerals, such as magnetite. These  
92 mineral assemblages are observed in the field, where peridotites are largely serpentized,  
93 mostly along fracture systems. The question of H<sub>2</sub> provenance in oceanic hydrothermal  
94 context has been largely approached by petrographic studies and experimental simulations  
95 (Allen and Seyfried, 2003; Yoshizaki et al., 2009; Klein et al., 2009; Marcaillou et al. 2011;  
96 Neubeck et al. 2011; Shibuya et al., 2015) and numerical modelling (McCollom and Bach,  
97 2009; Klein et al., 2009; Marcaillou et al., 2011). Fe<sup>II</sup> is initially provided by different  
98 minerals (such olivine and pyroxene) in the first stages of hydration, but also by serpentine or  
99 ferrous iron hydroxide, which are produced by the alteration processes, thus allowing the H<sub>2</sub>  
100 production to go on after olivine and pyroxene have all been transformed (Marcaillou et al.,  
101 2011). These studies have shown that depending on thermodynamic conditions, temperature,  
102 water chemistry (notably carbonate content, sulphate content and alkalinity), water/rock  
103 ratios, different mineral assemblages and sequences are obtained as by-products together with  
104 different rates and amounts of H<sub>2</sub>. According to the numerical model proposed by McCollom  
105 and Bach (2009), the highest rates of H<sub>2</sub> production are obtained at high temperature (about  
106 315°C) while serpentine and magnetite are the main mineral assemblage of the by-products.  
107 Onshore H<sub>2</sub>-bearing gas seepages yield not only H<sub>2</sub> but also methane and nitrogen, resulting  
108 in a three-component gas mixture with proportions varying in a very large range. The origin  
109 and the processes of generation of CH<sub>4</sub> and N<sub>2</sub> associated to H<sub>2</sub> are still a matter of discussion  
110 in terrestrial ophiolitic units. In the present paper, the geochemical properties of reduced gas  
111 seepages from four ophiolite massifs: 1) the Semail ophiolite in the Sultanate of Oman, 2) the  
112 Zambales ophiolite in the Philippines, 3) the Antalya ophiolite in southern Turkey and 4) the  
113 New Caledonia ophiolite are compared in the light of local geological features to better  
114 understand the conditions for di-hydrogen, methane and di-nitrogen production in the  
115 geological context of these ophiolite complexes (Fig. 1, 2, 3).

116

## 117 **Geological settings**

118

119 The ophiolitic units in which this study was conducted correspond to wide ophiolitic massifs  
120 (Fig. 1) containing rocks which have not been subjected to high pressure-low temperature

121 (HP-LT) conditions. Peridotites rocks are little serpentized in wide areas (much less than  
122 ophiolites involved in HP-LT conditions). These ophiolites units have been obducted on  
123 sediments (Fig. 2) belonging to different paleogeographic domains, either oceanic or  
124 continental, which contain, in all cases, clastics and carbonates. The fractures in the peridotite  
125 host serpentine and carbonate veins, mainly Mg-bearing carbonates (magnesite,  
126 hydromagnesite and dolomite). In the ophiolite-hosted fractured aquifers, groundwater  
127 circulations is controlled by fracture hydraulic conductivity. Ultra-basic surface seepages  
128 have been found in these ophiolitic massifs and they generally discharge close to the contact  
129 between the mantle rocks and overlying former oceanic crust rocks (Moho), and along the  
130 basal thrust plane of the ophiolite sequence. This is probably related to favorable drainage  
131 conditions in the fractured rocks at the base of the ophiolitic units and to drainage control by  
132 the more massive gabbroic units compared to the more fractured peridotites below. They  
133 release high pH fluids (commonly higher than 10) which are rich in  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{H}_2$  and  $\text{CH}_4$ .  
134 More specifically, the Oman ophiolite has been extensively studied, as it is the best large  
135 exposed massif of this type in the world (see Hopson *et al.*, 1981; Ceuleneer, 1991; Nicolas *et*  
136 *al.*, 1996, 2000; Python and Ceuleneer, 2003; Arai *et al.*, 2006 and many others). This  
137 ophiolite corresponds to parts of the oceanic lithosphere of the Arabian Sea which have been  
138 obducted on the Arabian plate during late Cretaceous times.  $\text{H}_2$ -rich gas seepages associated  
139 with  $\text{Ca}^{2+}$ - $\text{OH}^-$ -rich groundwater in the Semail ophiolite of Oman were first studied by Neal  
140 and Stanger (1983). They proposed that  $\text{H}_2$  is the by-product of a low temperature (20-50°C)  
141 serpentinization that depends on  $\text{Fe}^{\text{II}}$  hydroxide availability and oxidation by meteoric water  
142 that occurs in 2 stages: 1) oxidation by atmospheric  $\text{O}_2$  dissolved in meteoric water; 2)  
143 oxidation by water. Sano *et al.* (1993) provided a new insight by analyzing noble gases. Their  
144 results confirmed that  $\text{H}_2$ -rich gas samples are inherited from interaction of meteoric water  
145 with  $\text{Fe}^{\text{II}}$  although they propose a high temperature for the reaction (300°C).  
146 In the Philippines, gases were sampled in the Zambales massif, which is located in the north-  
147 western part of the Luzon Island (Nicolas and Violette, 1982; Hawkins and Evans, 1983;  
148 Abrajano *et al.*, 1988; Yumul *et al.*, 1998; Encarnacion *et al.*, 1999). The gas seepages occur  
149 either as bubbling in alkaline springs or seeping out from fractured rocks, locally  
150 spontaneously burning as, for instance, in Los Fuegos Eternos and Nagsasa. Gas seepages in  
151 the Zambales massif were first studied by Abrajano *et al.* (1988; 1990). In their paper, they  
152 concluded that both mantle origin and serpentinization are consistent with their analytical  
153 results and they proposed a temperature of 110-125°C for serpentinization.

154 The ophiolite of the Antalya region, in southern Turkey, has been extensively studied (Juteau  
155 et al., 1977; Robertson and Woodcock, 1980; Glover and Robertson, 1998a, b). Also, the  
156 associated sedimentary sequences have been investigated (Bozcu and Yagmurlu, 2001), while  
157 oil seepages have also been observed less than 20 km away from the Chimaera site  
158 (Hosgörmez *et al.*, 2008). The site of the Chimaera gas seepage has the most spectacular gas  
159 outlet since the flames are more intense than those in Zambales, Philippines, and are also  
160 more colorful because of a greater content in methane, relatively to the H<sub>2</sub>. H<sub>2</sub> seepages  
161 associated with the site of the first Olympic fire was first reported by Hosgörmez et al. (2008).  
162 From their chemical and isotopic study, they concluded that gas seepages originate from both  
163 thermogenic maturation of organic matter and serpentinization. In a later publication, Etiope  
164 et al. (2011) confirmed previous conclusions and proposed a temperature lower than 100°C  
165 for serpentinization.

166 The ophiolite of New Caledonia is among the largest onshore massifs of ultrabasic rocks  
167 preserved on Earth. The peridotites nappe was emplaced during Eocene times over (1) a  
168 basement of arc-derived formations of Pre-Cretaceous age which are overlain by basalts and  
169 formations of the Central Range that include sandstones, siltstones, graywackes, claystones  
170 with coal of Cretaceous age and Tertiary carbonate turbidites and volcanoclastic deposits, and  
171 (2) a tectonic unit of oceanic basalts of Upper Cretaceous to Eocene age, with back-arc or  
172 fore-arc affinities which underlies the peridotites nappe (Paris, 1981). H<sub>2</sub>-bearing gas  
173 seepages associated to alkaline to hyper-alkaline waters were found in the southern part of the  
174 Massif du Sud (bay of Prony) within the peridotite nappe (Deville et al., 2010; Monnin et al.,  
175 2014; Deville and Prinzhofer, 2016), while N<sub>2</sub>-rich seepages were found below the ophiolitic  
176 units in the area of La Crouen (Deville and Prinzhofer, 2016).

177

## 178 **Materials and methods**

179

180 Gases were sampled in stainless steel tubes with helium-proof valves for chemical  
181 composition and noble gas analyses and in glass tubes for stable isotopic composition  
182 analyses. Gas sampling devices were evacuated (10<sup>-3</sup> Pa vacuum) before sampling. When  
183 possible, stainless steel tubes were swept twice by the sampled gas. When gas was collected  
184 in water springs, streams or in the sea (Oman, some places in the Philippines and New-  
185 Caledonia), pH, Eh and temperature were measured directly in the field (Table 1).

186 The chemical compositions of gases were determined by gas chromatography (GC) with a  
187 Varian GC3800. Measurement uncertainties are below 0.01% mol for hydrocarbons (FID) and

188 for other gases (TCD). The measurements of the isotopic ratios  $^{13}\text{C}/^{12}\text{C}$  ( $\text{CH}_4$  and  $\text{CO}_2$ ) and  
189 D/H in ( $\text{CH}_4$  and  $\text{H}_2$ ) were performed on a MAT 253 (Thermo Fischer) mass spectrometer  
190 coupled with a gas chromatograph (GCC-IR-MS). The results are reported in  $\delta$  units relative  
191 to Pee Dee Belemnite (PDB) for carbon and Standard Mean Ocean Water (SMOW) for  
192 hydrogen, respective analytical uncertainties being of 0.5‰ and 5‰. Nitrogen isotopic  
193 compositions were measured relative to air with a MAT 253 mass spectrometer.  $\text{N}_2$  has been  
194 purified in a vacuum line.  $\text{CH}_4$  and  $\text{H}_2$  were oxidized in a Cu-oxide oven to  $\text{CO}_2$  and water  
195 vapor, respectively. These produced gases were cryogenically trapped for separation from  $\text{N}_2$ .  
196 Analytical uncertainty for the measurement of  $\delta^{15}\text{N}$  is lower than 0.1‰.  
197 The noble gases elementary compositions were determined by quadrupole mass spectrometry  
198 (Table 2). The QUADRAR line allows determining the contents of  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$  and Kr.  
199 The mass spectrometer is a Prisma quadripole QMA/QME200 (Pfeiffer Vacuum) with an  
200 open ion source. The analyzer allows measurements of compounds with a mass over charge  
201 ratio from 0 to 100. Global relative uncertainties for quantification of noble gases with this  
202 method are within the following range: He:  $\pm 15\%$ ; Ne:  $\pm 20\%$ ; Ar:  $\pm 10\%$ ; Kr:  $\pm 12\%$ .  
203 Helium isotopic ratios and contents were determined with a high-resolution magnetic sector  
204 mass spectrometer Micromass GV 5400 equipped with a modified Nier type electron impact  
205 source (Bright). The global relative uncertainty ( $1\sigma$ ) on the quantification of  $^4\text{He}$  is  $\pm 4\%$ . The  
206 uncertainty on the quantification of the  $^3\text{He}/^4\text{He}$  ratio is  $\pm 2\%$ .

207

## 208 **Results**

209

210 The sites studied in Oman are scattered over Northern Oman and comprise 14 spots of gas  
211 bubbling in water (Fig. 1A). Most of the gas samples were taken in ultra-basic springs of the  
212 Semail ophiolite and three samples were taken in non-alkaline thermal springs (Rustaq,  
213 Nakhal and Al Ali) seeping from formations structurally located below the ophiolite nappe  
214 (Table 1). In the Philippines, 3 spots were sampled in the Zambales ophiolite. One site  
215 (Mangatarem) corresponds to an ultra-basic thermal spring with abundant bubbling gas,  
216 whereas the two others correspond to gas directly seeping from fractures of the peridotites  
217 (Table 1). One site corresponds to the Los Fuegos Eternos burning gas close to the Coto  
218 Chromite mine (Abrajano et al., 1988, 1990), the other one is located above the Nagsasa bay  
219 (Abrajano et al., 2006; Fig. 1B). The gas vents sampled in Turkey were seeping out of the  
220 fracture system of the ophiolite unit in the area of Chimaera, south of Antalya (Fig. 1C). In



221 New Caledonia, all gas samples were bubbling in water (some in alkaline springs of the area  
222 of the bay of Prony, others in the non-alkaline thermal springs of the area of La Crouen;  
223 Deville and Prinzhofer, 2016; Fig. 1D).

224

#### 225 *Chemical and isotopic composition of the gas*

226

227 The gas chemical compositions are listed in Table 1. Gas mixtures contain H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> as  
228 major components. Figure 4 displays H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> molecular contents of all samples in a  
229 triangular diagram. Four distinct types of gas mixtures can be identified according to their  
230 respective contents in H<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>. Three of these types are associated with water seeps:  
231 H<sub>2</sub>-rich type; N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type and N<sub>2</sub>-rich type. The water properties associated to these gas  
232 seepages are listed in Table 1 and illustrated on a Pourbaix diagram on figure 5. The last type  
233 (H<sub>2</sub>-CH<sub>4</sub>) corresponds to gas seepages in fractures without associated water flow.

234 Carbon and hydrogen isotopic composition ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) of H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and nitrogen  
235 isotopic composition ( $\delta^{15}\text{N}$ ) of N<sub>2</sub> are reported in Table 2.  $\delta\text{D}$  of H<sub>2</sub> values are very negative  
236 and comprised in a narrow range from -756 to -699‰, except for the sample from Nagsasa  
237 (Philippines) with  $\delta\text{D}$  of H<sub>2</sub> = -664‰ (Fig. 6, 7). The highest values of  $\delta\text{D}$  of CH<sub>4</sub> correspond  
238 to the highest contents of methane (Fig. 8A). Relative carbon and hydrogen isotopic  
239 compositions of methane are presented in Figure 8B. High values of  $\delta^{13}\text{C}$  of CH<sub>4</sub> were  
240 obtained, up to +7.9‰, while  $\delta\text{D}$  of CH<sub>4</sub> are ranging from -428 to -130‰.

241 Hydrogen isotopic fractionation between H<sub>2</sub> and CH<sub>4</sub> depends on seepage types. The highest  
242 isotopic fractionations between species are observed on dry seepages where  $\delta\text{D}$  values of  
243 methane are the highest recorded in this study (Table 2). The nitrogen isotopic compositions  
244 were also measured for 4 samples.  $\delta^{15}\text{N}$  values range from -0.3 to +0.5‰ (Table 2).

245 Noble gases contents and their isotopic ratios, when measured, are given in Table 2. The  
246 samples of the H<sub>2</sub>-rich type are very close to the air end-member with a slight crustal  
247 contribution. Those of the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type show higher N<sub>2</sub> and CH<sub>4</sub> contents and present  
248 either a crustal (Oman), or mantle (Kaoris, New Caledonia) or crust plus mantle contribution  
249 (Oman). The samples of the H<sub>2</sub>-CH<sub>4</sub> type present both crustal and mantle contributions, with a  
250 very marked mantle contribution for the Nagsasa sample (Zambales, Philippines). N<sub>2</sub>-rich  
251 samples are made of a mixing between air and crust end-members.

252

#### 253 *Gas types*

254

255 According to the gas compositions, four types can be defined (Fig. 4):

256 1) *The H<sub>2</sub>-rich type* shows dominant H<sub>2</sub> contents (61.0 to 87.3% mol) associated with some N<sub>2</sub>  
257 (less than 35% mol) and some CH<sub>4</sub> (less than 20 mol%; Fig. 4 and 8A). This type is  
258 encountered in Oman (Neal and Stanger, 1983; Sano et al., 1993; Deville et al., 2010, 2011;  
259 Vacquand, 2011; Boulard et al., 2013; Miller et al., 2016) and this type of gas exclusively  
260 seeps as bubbles from ultra-basic springs (pH between 11 and 12; Fig. 5) associated to  
261 negative to very negative Eh (from -45 to -780 mV; Fig. 5; table 1). In addition to the high  
262 OH<sup>-</sup> ion concentration responsible for the high pH, the waters are calcium-rich (Neal and  
263 Stanger, 1985). Consequently, in the alkaline springs, spectacular precipitations of calcium  
264 carbonate (calcite and aragonite) are observed due to the reaction of Ca<sup>2+</sup> and OH<sup>-</sup> ions with  
265 the CO<sub>2</sub> of the atmosphere (see supplementary material). These waters show high electrical  
266 conductivities in accordance with their relatively high salinity, essentially related to the  
267 presence of Cl<sup>-</sup> and Na<sup>+</sup> ions (Cl<sup>-</sup> between 120 and 380 mg/l; Na<sup>+</sup> between 150 and 420 mg/l;  
268 Neal and Stanger, 1985; Kelemen et al., 2011). The temperatures of these sources are almost  
269 ambient to slightly warm (between 22.5 and 35 °C). The δ<sup>13</sup>C values of methane are very high  
270 (among the highest values known on Earth, between -13 and +8‰; Table 2; Fig. 8B). The gas  
271 composition shows N<sub>2</sub> vs fossil noble gas <sup>36</sup>Ar ratios (Table 2; Fig. 9) comprised between the  
272 air and water in equilibrium with air (classically mentioned as ASW for Air Saturated Water).

273  
274 2) *The N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type* is characterized, by higher N<sub>2</sub> values (from 45 to 65 mol%) compared  
275 to the previous gas type. Therefore N<sub>2</sub> becomes the main gas. H<sub>2</sub> contents range from 25 to 36  
276 mol%. CH<sub>4</sub> concentrations are similar to those of the H<sub>2</sub>-rich type (below 20 mol%; Fig. 4).  
277 This second gas type is mainly found in New Caledonia (Deville and Prinzhofer, 2016) but  
278 also in some springs of Oman and of the Philippines. This type of gas mixture seeps also in  
279 ultra-basic springs. These springs are generally warmer than those of the H<sub>2</sub>-rich type, up to  
280 40.1°C in New Caledonia and pH values are slightly lower, ranging from 10.5 to 11.3. They  
281 are, as well, associated with precipitations of calcium carbonate (see supplementary material).  
282 The N<sub>2</sub>/<sup>36</sup>Ar ratios of this gas type are different from the previous type and higher than those  
283 recorded for ASW and air (Table 2; Fig. 9). These ratios are also correlated with H<sub>2</sub>/<sup>36</sup>Ar and  
284 <sup>4</sup>He/<sup>36</sup>Ar ratios (Deville and Prinzhofer, 2016). δ<sup>13</sup>C of methane recorded for this gas type  
285 ranges between -38.5 and -32.4‰ (Deville and Prinzhofer, 2016).

286

287 3) *In the N<sub>2</sub>-rich type*, the dominant gas compound is N<sub>2</sub> (over 91 mol%). Gas mixture is H<sub>2</sub>-  
288 free with low CH<sub>4</sub> contents (up to 2.7 mol% in New Caledonia), plus substantial amounts of  
289 helium (values above 0.1 mol%). This type of springs was found in Oman (Sano et al., 1993;  
290 Vacquand, 2011) and New Caledonia (Deville and Prinzhofer, 2016) where they occur in the  
291 same structural position, *i.e.*, at the base of ophiolitic nappes (either in the sole of the nappes  
292 or in the sediments immediately below the nappes).  $\delta^{13}\text{C}$  values of CH<sub>4</sub> in this type are  
293 between -39.2 and -12.1‰. These gases come out in the form of bubbling springs with less  
294 alkaline water than previously recorded (pH from 7.5 to 10) and variable Eh (from -230 to  
295 +146 mV). The N<sub>2</sub>/<sup>36</sup>Ar ratios are very high (Table 2; Fig. 9). R/Ra ratios of the gases are  
296 consistently low (between 0.06 and 0.08, except for the sample collected in Al Ali where it  
297 was not possible to avoid air contamination because of access difficulties when sampling the  
298 gas and high temperature of the spring, above 66°C; Tables 1 and 2; Fig. 10). The dissolved  
299 species in the associated waters are very different from those of the waters containing H<sub>2</sub>  
300 gases. They show lower concentrations of Na<sup>+</sup> and K<sup>+</sup> ions and contain HCO<sub>3</sub><sup>-</sup> ions, which is  
301 not the case of the ultra-basic springs with H<sub>2</sub> seepages (Neal and Stanger, 1985). In all cases  
302 these springs are warm to hot (from 37.9 to above 66°C; Table 1).

303  
304 4) *The H<sub>2</sub>-CH<sub>4</sub> type* shows mostly H<sub>2</sub> and CH<sub>4</sub> in variable proportions. This type of gas vent is  
305 characterized by focused and relatively high gas flows (> 1 l/s), coming directly out of the  
306 rock fractures in the absence of water. This gas type was found in the Philippines and in  
307 Turkey where it was mentioned respectively by Abrajano et al. (1988; 2006) and Hosgörmez  
308 et al. (2008). It has not been found in New Caledonia but Neal and Stanger (1983) mentioned  
309 locally focused high gas flows seeping out directly from fractures of ultrabasic rocks in Oman  
310 (> 10 l/s). The CH<sub>4</sub>/H<sub>2</sub> ratio is commonly higher compared to the types associated to alkaline  
311 springs, except for the case of Nagsasa in the Philippines. The gas is able locally to  
312 spontaneously ignite as it is the case in Turkey (Chimaera) and the Philippines (Los Fuegos  
313 Eternos and Nagsasa) forming visible flames when the CH<sub>4</sub>/H<sub>2</sub> ratio is high. Nitrogen is  
314 nearly absent of these dry gas seepages (less than 2 mol%; Fig. 4) whereas since the gas is  
315 seeping out from fractures of rocks located above the water table, we would have expected  
316 that the gas would be much more easily naturally contaminated by air than in the previous  
317 cases which are bubbling in water. Indeed, these H<sub>2</sub>-CH<sub>4</sub> gases do not display predominantly  
318 atmospheric features and <sup>20</sup>Ne and <sup>84</sup>Kr concentrations are quite low compared to other types  
319 of gas mixtures (Table 2).  $\delta^{13}\text{C}$  values of CH<sub>4</sub> are high and fairly constant (between -12 and -

320 5‰; Fig. 8), as well as  $\delta D$  of  $CH_4$  which range from -175 to -130‰. The  $\delta D$  values of  $CH_4$   
321 are higher when compared to the  $H_2$ -rich and  $N_2$ - $H_2$ - $CH_4$  gas types (Table 1), while the  $\delta D$   
322 values of  $H_2$  vary between -756 and -664‰, generally in the same order of magnitude as those  
323 recorded in the  $H_2$ -rich and  $N_2$ - $H_2$ - $CH_4$  gas types (Table 1; Fig. 6). The differences of  $\delta D$   
324 values of  $CH_4$  suggest different processes for  $CH_4$  genesis and probably different sources for  
325 hydrogen and carbon (see discussion below).

326

## 327 **Discussion**

328

### 329 *Main characteristics of the different gas types*

330

331 Comparing the different gas types, several characteristic features can be noticed. Gases  
332 bubbling in springs always contain  $N_2$  that is not related to air contamination (see below),  
333 while gas seepages in fractures without associated water flows are  $N_2$ -poor. The gas bubbling  
334 in springs show  $CH_4$  contents that never exceed 20 mol%. The specificity of the  $H_2$ - $CH_4$  gas  
335 type seeping in fractures without associated water flow is that their  $CH_4$  contents locally reach  
336 high levels and that  $\delta D$  of  $CH_4$  is significantly higher compared to the  $\delta D$  of  $CH_4$  in the other  
337 gas types (Fig. 8). The water temperature tends to increase in the different types of springs  
338 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  
339 springs is associated to ultra-basic conditions only when  $H_2$  is present, whereas water is less  
340 or not basic in the springs of the  $N_2$ -rich gas type. We propose that the chemical  
341 characteristics that define gas types reflect differences in origin and transport pathways of gas  
342 mixtures.

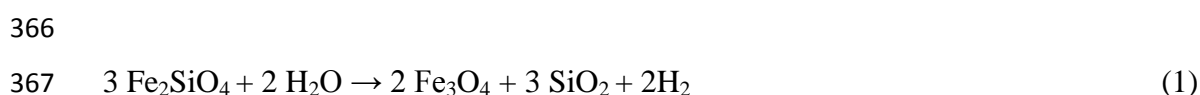
343

### 344 *Hydrogen origin*

345

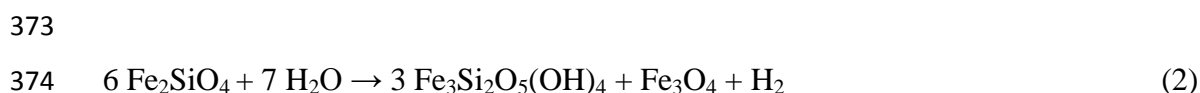
346 As mentioned in introduction,  $H_2$  sources of gas seepages in ophiolitic contexts are classically  
347 credited to modern hydration processes at low temperature during the weathering of ultrabasic  
348 and basic rocks (mostly peridotite and gabbro). At depth, within ophiolitic rocks, biological  
349 production of  $H_2$  by fermentation processes is probably a sluggish process due to the paucity  
350 of potential organic substrates. High-temperature serpentinization (above 300°C) is a well-  
351 known process but at temperatures below 300°C serpentinization can occur as well (Moody  
352 1976). Indeed, experimental studies simulating land-based peridotite systems have shown that

353 H<sub>2</sub> can be generated during serpentinization at temperatures below 100°C (Mayhew et al.,  
 354 2013; Okland et al., 2014; Neubeck et al., 2011). On hydrogen-bearing gas seepages  
 355 associated with high pH waters in ophiolitic context (Neal and Stanger 1983; Sano *et al.*  
 356 1993; Cipolli *et al.* 2004; Hosgörmez *et al.* 2008; Abrajano *et al.*, 2006; Vacquand, 2011), H<sub>2</sub>  
 357 would result from the interaction between ultrabasic rocks and water flows at depth in the  
 358 fracture system, in anoxic conditions, by reduction of water and oxidation of metals (Fe<sup>II</sup>,  
 359 Mn<sup>II</sup>, Ni<sup>II</sup>...), Fe<sup>II</sup> being by far the most abundant electron donor in ultrabasic-basic rocks.  
 360 During the serpentinization process, Fe<sup>II</sup>-rich minerals, such as olivine [(Mg<sup>II</sup>,Fe<sup>II</sup>)<sub>2</sub>SiO<sub>4</sub>] are  
 361 oxidized and form Fe<sup>III</sup>-bearing minerals, such as magnetite [Fe<sub>2</sub><sup>III</sup>Fe<sup>II</sup>O<sub>4</sub>] or Fe<sup>III</sup>-bearing  
 362 serpentine (Evans et al., 2008), with coeval reduction of water generating H<sub>2</sub>. Olivine is a  
 363 magnesium-iron nesosilicate forming a solid solution series between a Mg-endmember and a  
 364 Fe- endmember. During olivine dissolution, the olivine Fe-endmember (fayalite, Fe<sub>2</sub>SiO<sub>4</sub>)  
 365 tends to react as,



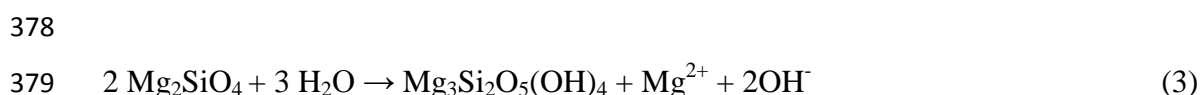
366  
 367 *Fayalite + water → Magnetite + silica + dihydrogen*

368  
 369  
 370 At temperature below 150°C, dissolution of the olivine Fe-endmember is even  
 371 thermodynamically more favorable when Fe-chrysotile is formed (Oze and Sharma, 2005)  
 372 according to the following reaction,



369  
 374 *Fayalite + water → Fe-Chrysotile + Magnetite + dihydrogen*

375  
 376  
 377 The Mg-endmember of olivine (Forsterite, Mg<sub>2</sub>SiO<sub>4</sub>) reacts as,

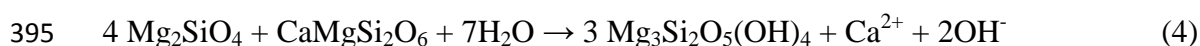


378  
 379 *Forsterite + water → Chrysotile + magnesium ions + hydroxyl ions*

380  
 381  
 382 In presence of dissolved inorganic carbon (DIC) in subsurface, Mg<sup>2+</sup> ions are consumed to  
 383 produce magnesium-bearing carbonates (which are widespread in fractures systems of all the  
 384 ophiolitic massifs studied here; see below), and (if available) remaining Mg<sup>2+</sup> ions are prone  
 385 to react with OH<sup>-</sup> to form brucite, Mg(OH)<sub>2</sub> (which is commonly found in the ultra-basic  
 386 springs studied here, notably in Oman; Neal and Stanger, 1984) leaving finally OH<sup>-</sup> available

387 in solution. In the case of New Caledonia, where alkaline seepages interact with sea water,  
 388 this results in massive production of brucite due to the reaction between  $\text{OH}^-$  and  $\text{Mg}^{2+}$  present  
 389 in sea water as it is the case of the seepages studied in New-Caledonia (Launay and Fontes,  
 390 1985). More generally, as proposed by different authors, the coupled hydration of Mg-olivine  
 391 and Ca-bearing pyroxene of peridotite rocks makes the water enriched in  $\text{Ca}^{2+}$  and  $\text{OH}^-$   
 392 (Barnes et al., 1967; Neal and Stanger, 1984; Bruni et al., 2002; Kelemen et al., 2011; Miller  
 393 et al., 2016),

394



396 *Forsterite + Clinopyroxene + water*  $\rightarrow$  *Serpentine + calcium ions + hydroxyl ions*

397

398 As such, the interaction between peridotite and water during serpentinization is a potential  
 399 source of  $\text{H}_2$  caused by ferrous iron oxidation and water reduction associated with a rise of pH  
 400 due to  $\text{OH}^-$  production and associated with the presence of  $\text{Ca}^{2+}$  in the ultra-basic water. The  
 401 richer in iron is the olivine, the more  $\text{H}_2$  and the less  $\text{OH}^-$  are produced.

402 It has been experimentally demonstrated that highly fractured/altered peridotite is more prone  
 403 to generate  $\text{H}_2$  than a massive unaltered peridotite suggesting a role of the reacting surfaces  
 404 and possibly that  $\text{Fe}^{\text{II}}$ -bearing secondary formed minerals, such as  $\text{Fe}^{\text{II}}$ -bearing brucite and  
 405 serpentine, and the presence of N-species may also contribute to form  $\text{H}_2$  (experiments at  
 406  $25^\circ\text{C}$ ; Okland et al., 2014, see also Klein et al., 2015).

407 The conditions of generation of  $\text{H}_2$  can be estimated notably using hydrogen isotopic data. In  
 408 the studied ophiolitic massifs, whatever are the characteristics of the  $\text{H}_2$ -bearing gas types,  $\delta\text{D}$   
 409 values of  $\text{H}_2$  are all very low in the analyzed gas samples (between -756 and -664‰).  
 410 Abrajano (1988) mentioned,  $\delta\text{D}$  values of  $\text{H}_2$  at -581 and -599‰ in the Los Fuegos Eternos  
 411 of the Philippines. The lowest values are among the lowest recorded on Earth and they are  
 412 significantly lower compared to  $\delta\text{D}$  of  $\text{H}_2$  of hydrothermal sites on mid-oceanic ridges for  
 413 which the values are more dispersed and generally higher (between -700 and -300‰; Fig. 6).  
 414  $\delta\text{D}$  values of  $\text{H}_2$  observed in oceanic settings decrease with temperature and appear as a  
 415 thermometer for  $\text{H}_2$  production at isotopic equilibrium with seawater (Proskurowski et al.,  
 416 2006). Low  $\delta\text{D}$  values of  $\text{H}_2$  in ophiolitic massifs are classically considered as revealing  
 417 relatively low temperatures of the generation of  $\text{H}_2$  (Neal & Stanger 1983). Indeed, using  
 418 either (1) the Horibe and Craig (1995)  $\text{H}_2\text{O}$ - $\text{H}_2$  and  $\text{CH}_4$ - $\text{H}_2$  geothermometers which consider  
 419 isotope fractionations between liquid  $\text{H}_2\text{O}$  or  $\text{CH}_4$  and  $\text{H}_2$ , or (2) Bottinga's 1969 water vapor-  
 420 hydrogen method, this strongly suggests that the generation of  $\text{H}_2$  occurred at lower

421 temperature conditions than at most of the hydrothermal vents of mid-oceanic ridges. H<sub>2</sub>O–H<sub>2</sub>  
422 is seen as the preferred geothermometer but it implies that chemical equilibrium between H<sub>2</sub>  
423 and H<sub>2</sub>O has been reached (see discussion below). It is possible that chemical and isotopic  
424 equilibrium have been achieved between H<sub>2</sub> and CH<sub>4</sub> (see the following paragraph). Whatever  
425 the geothermometer used, either the Horibe and Craig (1995; Fig. 7) H<sub>2</sub>O–H<sub>2</sub> and CH<sub>4</sub>–H<sub>2</sub>  
426 geothermometers, or the Bottinga (1969) geothermometer, we obtained relatively narrow  
427 windows of temperature conditions in the ranges 17 to 42°C for H<sub>2</sub> of the H<sub>2</sub>-rich type and  
428 24–50°C for H<sub>2</sub> of the N<sub>2</sub>–H<sub>2</sub>–CH<sub>4</sub> gas type, whereas the temperature conditions seem much  
429 more heterogeneous and reach much higher temperatures in the H<sub>2</sub>–CH<sub>4</sub> gas type, notably for  
430 the samples of the Philippines (up to 136°C, taking into account the  $\delta D_{H_2}$  values from  
431 Abrajano et al., 1988).

432 To decipher the conditions of generation of H<sub>2</sub>, it is possible to compare H<sub>2</sub> contents with  
433 those of other compounds such as noble gases tracers (Ballentine et al., 2002a and b; Zhou et  
434 al., 2005; Burnard et al., 2013; Prinzhofer, 2013; Prinzhofer and Deville, 2013). Notably, the  
435 H<sub>2</sub>-rich gas type displays N<sub>2</sub>/<sup>36</sup>Ar ratios between ASW and air (Table 2; Fig. 9). These  
436 features are consistent with a genesis process involving surface water charged with dissolved  
437 atmospheric components (ASW) as the main fluid reacting with the rock for H<sub>2</sub> production. In  
438 this case, H<sub>2</sub>O inherited from meteoric water, initially in equilibrium with atmospheric  
439 components, is probably consumed at depth in the fracture system of the ophiolites by  
440 water/mineral interactions. Following this interpretation, as a consequence of water  
441 consumption and H<sub>2</sub> production, initial gas/water equilibrium with atmosphere is disrupted  
442 and atmospheric nitrogen and noble gases are mixed with neo-formed gases (H<sub>2</sub> and CH<sub>4</sub>) and  
443 migrate upwards with no further addition of another gas component. The preservation of  
444 atmospheric relative proportions of fossil noble gases (<sup>20</sup>Ne, <sup>36</sup>Ar, <sup>84</sup>Kr) suggests that these  
445 groundwaters reacted at a relatively shallow depth. For deeper depths of gas/water phases  
446 interaction, the difference of noble gas solubility from the surface conditions' ones (as P and  
447 T are much higher) would fractionate the relative proportions of these compounds. The <sup>4</sup>He  
448 contents (< 20 ppm), are in good agreement with Neal and Stanger's (1985) interpretation  
449 which asserts that Ca<sup>2+</sup>-OH<sup>-</sup> water originates from meteoric water recharging at high  
450 elevations. The presence of <sup>4</sup>He in subsurface gas is classically interpreted as the result of a  
451 lengthy residence time at depth allowing <sup>4</sup>He to accumulate significantly due to natural  
452 radioactive decay of <sup>235</sup>U, <sup>238</sup>U and <sup>232</sup>Th present in crustal rocks (Ballentine and Burnard, 2002).  
453 Paukert et al. (2012) considered, from their modelling of CO<sub>2</sub> consumption, that such  
454 meteoric waters reached its high pH values after 6500 years. This geological short time frame

455 is consistent with the low  $^4\text{He}$  contents of these gases, which are roughly displaying  
456 atmospheric signatures.

457 Considering the  $\text{N}_2\text{-H}_2\text{-CH}_4$  and  $\text{H}_2\text{-CH}_4$  gas types, the interpretation that  $\text{H}_2$  generation is  
458 simply a result of interaction between meteoric water and ophiolitic rocks is not sustainable  
459 anymore because, notably,  $\text{N}_2/^{36}\text{Ar}$  ratios are not comprised between ASW and air and noble  
460 gas contents are different from Air or ASW. This is consistent with a  $\text{H}_2$  generation process  
461 which occurred deeper than in the  $\text{H}_2$ -rich gas type, in higher temperature conditions as  
462 already suggested by  $\delta\text{D}$  values of  $\text{H}_2$ .

463

#### 464 *Methane origin*

465

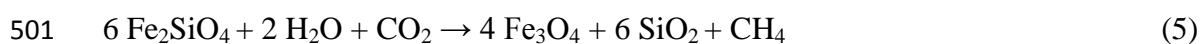
466 Methane generation associated with fluid-rock interaction in ophiolitic contexts remains  
467 unclear. In terrestrial ultrabasic-basic contexts at moderate temperatures (below  $150^\circ\text{C}$ ),  
468 methane is interpreted to result from carbon hydrogenation involving mainly sources of  
469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

475 In the case of hydrogenation processes of carbon, considering potential hydrogen sources  
476 ( $\text{H}_2\text{O}$  or  $\text{H}_2$ ), hydrogen in  $\text{CH}_4$  can be considered as primary (*i.e.*, issued from  $\text{H}_2\text{O}$  reacting  
477 with carbon and preceding  $\text{H}_2$  production; Abrajano et al., 1988; Oze and Sharma, 2005; Suda  
478 et al. 2014; Okland et al., 2014), or secondary (*i.e.*, issued from an  $\text{H}_2$  intermediate by  
479 reactions between carbon and  $\text{H}_2$ ; Berndt et al., 1996; Foustoukos and Seyfried, 2004; Horita  
480 and Berndt, 1999; McCollom and Seewald, 2001; McCollom, 2016; Neubeck et al., 2011).  
481 The experiments of Okland et al. (2014) suggest indeed a possible primary production of  $\text{CH}_4$   
482 during hydration of ultrabasic rocks without an  $\text{H}_2$  intermediate, notably with moderately  
483 altered peridotites. In both cases, hydrogen is issued from  $\text{H}_2\text{O}$ , either primarily or  
484 secondarily. Suda et al. (2014), based on a study of hydrogen isotopic data of  $\text{CH}_4$ ,  $\text{H}_2$  and  
485  $\text{H}_2\text{O}$  (Fig. 7), defined different domains corresponding to different processes allowing to  
486 distinguish  $\text{CH}_4$  generation by hydrogenation from water (primary) or from  $\text{H}_2$  (secondary).  
487 Primary  $\text{CH}_4$  production is regarded as a direct interaction between  $\text{Fe}^{\text{II}}$ -rich minerals and



488 dissolved CO<sub>2</sub>. CH<sub>4</sub> production tied to ferrous mineral reactions with CO<sub>2</sub> has not yet been  
 489 fully explored (Neubeck et al., 2016) but there is some indication from experimental reactions  
 490 of olivine that passivating layers of silica may coat reactive surfaces and slow related CH<sub>4</sub>  
 491 generation (Garcia et al., 2010). However, early production of CH<sub>4</sub> (before H<sub>2</sub> production) has  
 492 been documented by experimentation on natural peridotite rocks, at low temperature (25°C),  
 493 especially on fractured and altered peridotite, and these experiments showed a coeval  
 494 production of H<sub>2</sub> and CH<sub>4</sub> (Okland et al., 2014), in the same proportions as those measured in  
 495 this study for the H<sub>2</sub>-rich gas type. The presence of CO<sub>2</sub> is a favorable factor for olivine  
 496 dissolution (Oze and Sharma, 2005), which releases aqueous Fe<sup>II</sup>. Primary production of CH<sub>4</sub>  
 497 from H<sub>2</sub>O and CO<sub>2</sub> (DIC in water) is achieved in a similar way as the H<sub>2</sub> production through  
 498 the oxidation of iron (see above). The reaction of the Fe-endmember of olivine in presence of  
 499 dissolved CO<sub>2</sub> can be summarized by the following reaction,

500

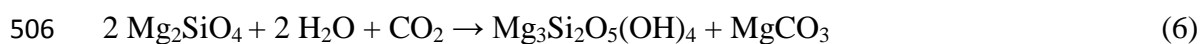


502 *Fayalite + water + carbon dioxide → Magnetite + silica + methane*

503

504 while a coeval reaction occurs considering the Mg-endmember,

505

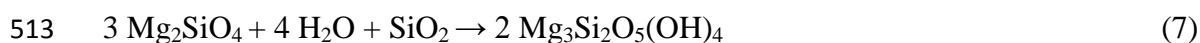


507 *Forsterite + water + carbon dioxide → Serpentine + magnesite*

508

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

512



514 *Forsterite + water + silica → Serpentine*

515

516 Also, Fe<sup>II</sup>-bearing brucite-type minerals (for example amakinite) and Fe<sup>II</sup>-bearing serpentines  
 517 are also good candidates to react with dissolved CO<sub>2</sub>, as suggested by experiments (Okland et  
 518 al., 2014).

519 Applying the reasoning of Suda et al. (2014) mentioned above to our samples, would suggest  
 520 that gases from the H<sub>2</sub>-CH<sub>4</sub> type (dry seepages in fractures) contain methane which is  
 521 considered as primary while, in water-related seepages, the analytical results are more

522 compatible with a secondary CH<sub>4</sub> generated from an H<sub>2</sub> intermediate (gas samples collected in  
523 ultra-basic springs showing δD values of CH<sub>4</sub> between -400 et -200‰; Fig. 7).

524 As suggested by Suda et al. (2014) and according to the reactions shown above, a  
525 simultaneous production of methane and magnesite can occur. Mg-bearing carbonates  
526 (magnesite and dolomite) are indeed abundant in fractures in the peridotites of Oman and they  
527 are supposed to have been formed at temperatures in the range 30 to 60°C (Kelemen et al.,  
528 2011). Methane and magnesite, have both high and similar δ<sup>13</sup>C values (δ<sup>13</sup>C<sub>CH<sub>4</sub></sub> between -13  
529 and +8‰, δ<sup>13</sup>C<sub>magnesite</sub> between +2 and +8‰; see supplementary material). This is compatible  
530 with a non-atmospheric carbon origin of CH<sub>4</sub> that could derive from mantellic or metamorphic  
531 CO<sub>2</sub> or from carbonate destabilization. These values are different from the carbonates  
532 signatures found at the surface in the ultra-basic springs where carbon is interpreted as issued  
533 from atmospheric CO<sub>2</sub> which after fractionation during carbonate precipitation give δ<sup>13</sup>C  
534 values between -28 and -5‰ (Kelemen et al., 2011; see also supplementary material).

535 Considering secondary production of methane, via an H<sub>2</sub> intermediate, several pathways of  
536 CH<sub>4</sub> generation involving different sources of carbon can be considered, either (1) organic  
537 carbon (or reduced carbon including elementary C) found in sediments below the ophiolites  
538 notably, or else (2) carbon issued from deep sources from the mantle or from the crust (for  
539 example Dissolved Inorganic Carbon issued mantle gas or from carbonates within the  
540 sediments). Indeed, H<sub>2</sub> produced by serpentinization is susceptible to be subsequently  
541 consumed in a CH<sub>4</sub> producing reaction, involving a source of carbon which can be C<sup>o</sup>, CO or  
542 CO<sub>2</sub>, according to the general reaction (Deville and Prinzhofer, 2016),

543



545

546 In the case  $x = 0$ , the source of carbon can correspond to reduced carbon in sediments  
547 (graphite or overmature organic matter). In the case  $x = 1$ , the source of carbon corresponds to  
548 CO. CO has indeed, been mentioned as traces in the gas of the ophiolites of Oman (Sano et  
549 al., 1993). It might correspond to an intermediate compound preceding methane generation. In  
550 the case  $x = 2$ , this corresponds to the classical Sabatier reaction. Considering generation of  
551 high δ<sup>13</sup>C methane associated with ultrabasic contexts, it is frequently considered that it  
552 corresponds to Fisher-Tropsch Type (FTT) reaction, meaning the abiotic path of the Sabatier  
553 reaction (Szatmari, 1989; Horita and Berndt, 1999; Sherwood-Lollar et al., 1988, 1993a&b,  
554 2006, 2007; Kelley et al., 2001; Charlou et al., 2002; Foustoukos and Seyfried, 2004;

555 McCollom and Seewald, 2006; Taran et al., 2007; Proskurowski et al., 2008; and others, see  
556 references in Etiope and Sherwood-Lollar, 2013). In the Sabatier reaction, CO<sub>2</sub> is reduced to  
557 CH<sub>4</sub> through the oxidation of H<sub>2</sub> (so the reaction is controlled by H<sub>2</sub> activity).  
558 The kinetics of FTT reactions are slow at the temperatures considered here (below 150°C) but  
559 Fisher-Tropsch reactions are well-known to be favored by catalytic processes. Heterogeneous  
560 catalysis, promoted by minerals present in the ophiolitic rocks, such as chromite, magnetite,  
561 sulfides or awaruite can possibly trigger these reactions (Mayhew, 2013; Etiope and Ionescu,  
562 2015 and references therein). For instance, close to Los Fuegos Eternos (in the Philippines),  
563 chromite (well-developed in the Coto mines) may promote the catalytic production of CH<sub>4</sub>.  
564 Also, the area of Chimaera in Turkey shows chromite mines (in which an explosion caused  
565 the death of tens of underground workers). The area of Prony (New Caledonia) shows also  
566 chromite outcrops as well as at many places in the ophiolite of Oman.  
567 Catalytic processes might also be associated with biological activity, which is well-known to  
568 reduce the activation energy necessary for chemical reactions. The Sabatier chemical reaction  
569 is actually equivalent to one of the classical routes to generate microbial methane (by CO<sub>2</sub>  
570 reduction) via hydrogenotroph-methanogen microorganisms. In the case of sedimentary  
571 environment with widely available sources of light C provided by organic compounds, it  
572 produces methane with  $\delta^{13}\text{C}$  generally lower than -50‰, far below the values obtained in the  
573 gas seepages of the ultra-basic springs (between -12.8 and +7.9‰; Fig. 8), even if locally in  
574 ultra-basic springs  $\delta^{13}\text{C}$  of methane are lower than -50‰ (Morrill et al., 2013). However, in  
575 some conditions (notably in the case of hyperthermophilic archaea),  $\delta^{13}\text{C}$  values of methane  
576 can be high (Takai et al., 2004, 2008). The presence of hydrogenotrophic microorganisms has  
577 been mentioned in oceanic hydrothermal fields (Bradley and Summons, 2010) and in ultra-  
578 basic springs of ophiolitic units (Brazelton et al., 2013), and the occurrence of methanogens in  
579 ultrabasic contexts (Takai et al., 2004; Brazelton et al., 2006) raise the question, notably in  
580 Oman, of the microbial production of methane with elevated  $\delta^{13}\text{C}$  in ultra-basic groundwaters  
581 (Miller et al., 2016). This interpretation is still challenged (see discussion between Etiope,  
582 2017 and Miller et al., 2017) but, if it is confirmed, this would suppose that biological activity  
583 might contribute to elevated  $\delta^{13}\text{C}$  methane from inorganic sources of carbon under extreme  
584 carbon limitation. However, methanogens collected in ultra-basic springs at the surface are  
585 not necessary representative of the conditions of generation of methane at depth because there  
586 is no carbon available in the ultra-basic water flowing from depth (Neal and Stanger, 1985,  
587 see also below). Methane generation via methanogen microorganisms observed at the surface

588 might be a surficial process resulting from a reaction between hydrogen issued from depth  
589 and a source of carbon provided by atmospheric CO<sub>2</sub>. If the source of deep carbon is  
590 important, as in sedimentary environments with fossil organic matter, the use of isotopically  
591 light carbon in the widely available organic matter is favored by microbial activity. However,  
592 this is not possible in the case of strong restriction of the available carbon as in ophiolitic  
593 rocks, especially when the initial sources of carbon are heavy (like carbonates or mantle).  
594 Biological processes generating CH<sub>4</sub> from H<sub>2</sub> and CO<sub>2</sub> with progressively increasing  $\delta^{13}\text{C}_{\text{CH}_4}$   
595 have been documented in large scale geological gas storages of town gas (Buzek et al., 1994).  
596 In addition, the presence of methanotrophs in the ultra-basic springs also contribute to  
597 increase the  $\delta^{13}\text{C}$  values of the residual methane (Miller et al., 2016).

598 In the present study, the different values observed for  $\delta^{13}\text{C}$  of CH<sub>4</sub> probably reflect different  
599 sources of carbon or different CH<sub>4</sub> generation processes. The present study shows that (a) H<sub>2</sub>-  
600 rich gases from Oman display  $\delta^{13}\text{C}$  of CH<sub>4</sub> between -12.8 and +7.9‰, while (b) in the  
601 Philippines  $\delta^{13}\text{C}$  of CH<sub>4</sub> are ranging between -13.5 and -5.6‰ which is compatible with the  
602 results obtained by Abrajano et al. (1988), (c) in Turkey gases from H<sub>2</sub>-CH<sub>4</sub> type display a  
603  $\delta^{13}\text{C}$  of CH<sub>4</sub> values between -7.9 and -11.9‰ (Horgormez et al., 2008 and this study),  
604 whereas (d) for New-Caledonia some gases from N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type values are between -38.5  
605 and -32.4‰ (Deville and Prinzhofer, 2016). Consequently, two different types of signatures  
606 were observed corresponding initial probably (despite of fractionation processes) to two  
607 different carbon sources. The first one (high  $\delta^{13}\text{C}$  between -13 and +8‰) would correspond  
608 most probably to an inorganic carbon source, while the second one (lower  $\delta^{13}\text{C}$  between -39  
609 and -32‰) corresponds probably to an organic source. The high  $\delta^{13}\text{C}$  of CH<sub>4</sub> from Oman, the  
610 Philippines and Turkey might correspond to a carbon source, probably CO<sub>2</sub>, found as DIC in  
611 the reacting waters. Two different origins may be proposed for this inorganic carbon. It may  
612 correspond to mantle degassing, as it might be the case in the Philippines in link with the  
613 vicinity of the active volcanism of the Pinatubo system related to an active subduction zone,  
614 as suggested by noble gas analyses especially for one gas sample with high R/Ra values (Fig.  
615 10), or it may come from the dissolution of carbonate rocks (for instance the carbonate  
616 sediments present under the ophiolites), as it might be the case in Oman (Nicolas et al., 2000)  
617 and Turkey (Juteau et al., 1977). Note that the H<sub>2</sub>-bearing gas samples studied here (as well as  
618 those analyzed in previous studies) show only locally tiny traces of CO<sub>2</sub> for which  $\delta^{13}\text{C}_{\text{CO}_2}$   
619 measurements have to be considered with caution (not reported in table 2). The measurements  
620 in the N<sub>2</sub>-rich gas type of Oman (seeping out from below the ophiolites), in which CO<sub>2</sub>

621 contents are more important (data from Sano et al., 1993, and this study, Table 1 and 2), gave  
622 values between -19.4‰ and -9.6‰ which are consistent with an origin from sedimentary  
623 rocks below the ophiolites (metamorphism and/or carbonate destabilization).

624 Methane with  $\delta^{13}\text{C}$  values comprised between -39 and -32‰, in New Caledonia, could simply  
625 be issued from an organic source (Deville and Prinzhofer, 2016). In agreement with the  
626 absence or low contents of  $\text{C}_{2+}$  in the gas mixtures (below 0.01%), methane may originate  
627 from a reaction between  $\text{H}_2$  and a mature/overmature organic matter or graphite present in the  
628 sediments below the ophiolites.

629 Also note that, in addition to the absence or very low contents of  $\text{CO}_2$  in  $\text{H}_2$ -bearing gas  
630 samples, neither  $\text{HCO}_3^-$  nor  $\text{CO}_3^{2-}$  have been found in the ultra-basic springs, notably in the  
631 case of Oman (Neal and Stanger, 1985) suggesting that almost the entire stock of available  
632 DIC was converted into  $\text{CH}_4$  under extreme carbon limitation. Also, no form of organic matter  
633 or graphite are known within the peridotites of the areas studied. This limitation probably  
634 allows  $\text{H}_2$  to be present in the gas, otherwise all the generated  $\text{H}_2$  would have been consumed  
635 to generate  $\text{CH}_4$ , as it was suggested by Milesi et al. (2016) in the Solimes Basin in Brazil.

636 In both,  $\text{H}_2$ -rich and  $\text{N}_2$ - $\text{H}_2$ - $\text{CH}_4$  gas types,  $\text{CH}_4$  contents being lower than 20 mol%, this  
637 suggests a very limited carbon source compared with the  $\text{H}_2$ - $\text{CH}_4$  gas type (Fig. 4 and 8).  
638 Indeed, if we consider carbonic acid in rain water as the initial main source of carbon, its  
639 contribution is regarded as limited and rapidly buffered, whereas if the carbon source  
640 corresponds to carbonate rocks or deep  $\text{CO}_2$  fluxes, the amount of carbon available is more  
641 abundant at depth but the connection with the ophiolites depends on the hydrodynamics and  
642 the available carbonate dissolved in circulating water.  $\text{H}_2$ - $\text{CH}_4$  gas type might correspond to  
643 such a system connected to deep sources of carbon.

644 Considering oceanic hydrothermal vents, values of  $\delta\text{D}$  of  $\text{CH}_4$  probably record the isotopic  
645 fractionation associated to a primary process involving a carbon compound with water, to  
646 produce methane. If open system conditions apply,  $\delta\text{D}$  of  $\text{CH}_4$  depends on isotopic  
647 equilibrium at the given temperature. For dry seepages in fractures, data are in agreement with  
648 these conditions. For seepages in water, a different process would provide scattered and very  
649 low  $\delta\text{D}$  values of  $\text{CH}_4$  (Fig. 6), either because the system is closed and isotopic equilibrium is  
650 not reached or because a different secondary process (eventually biology) is influencing the  
651 isotopic composition of hydrogen in methane. As such, the very low values of  $\delta\text{D}$  of methane  
652 in spring water raise the question of a possible microbial role in methane generation.

653 For the H<sub>2</sub>-CH<sub>4</sub> and N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas types a remarkable correlation exists between H<sub>2</sub> and CH<sub>4</sub>  
654 when normalized to <sup>36</sup>Ar (Fig. 11A) wherever is the site studied in Oman, in the Philippines  
655 and New Caledonia. A similar correlation exists between H<sub>2</sub> and CH<sub>4</sub> when normalized to  
656 <sup>84</sup>Kr, (Fig. 11B). For the CH<sub>4</sub>-H<sub>2</sub> and N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas types, this suggests that, independently  
657 of the considered ophiolite and geological context, generations of H<sub>2</sub> and CH<sub>4</sub> are coupled and  
658 both related to a deep process which is independent of interactions with ASW shallow  
659 aquifers. Conversely, these correlations do not exist for the H<sub>2</sub>-rich gas type which is in  
660 agreement with the interpretations proposed above that this type of gas underwent more  
661 influences with ASW aquifers. Also, this correlation is not observed in the samples of Turkey  
662 possibly due to a mixing with thermogenic methane. Indeed, according to other studies, some  
663 samples, notably in Turkey (H<sub>2</sub>-CH<sub>4</sub> type), might comprise a thermogenic component. It has  
664 been considered that high methane content cannot be attributed univocally to dissolved  
665 carbonates reduction by H<sub>2</sub>, for example in Chimaera (Turkey), up to 40 mol% of the CH<sub>4</sub> has  
666 been estimated to be thermogenic gas originating from a source rocks with highly mature  
667 kerogen in a Mesozoic limestone nearby (Hosgörmez et al., 2008; Etiope et al., 2011). This is  
668 in good agreement with occurrences of C<sub>2</sub>+ (C<sub>2</sub>-C<sub>6</sub> alkanes) in the gas analyzed in Turkey  
669 (Hosgörmez et al., 2008; Etiope et al., 2011, and this study, see table 2). However, whatever  
670 the geographic location of samples is, dry seepages display higher CH<sub>4</sub> relative contents  
671 together with higher δD of CH<sub>4</sub> when compared to gas seepages in water. This suggests that it  
672 can be linked to a different process as mentioned above (primary methane production) and  
673 probably higher temperature during production of methane. Gas mixtures belonging to the H<sub>2</sub>-  
674 CH<sub>4</sub> type correspond probably to highly reactive zones of water reduction at higher  
675 temperature with less carbon restriction.

676

677 *Nitrogen origin*

678

679 In the subsurface, nitrogen gas can have different origins, either atmosphere via the  
680 hydrodynamism of air equilibrated water, or sediments (organic matter, or ammonium-  
681 bearing clay minerals, or nitrogen-bearing salt in evaporites present in sedimentary rocks), or  
682 else the deep crust or mantle degassing (Jenden et al., 1988; Zhu et al., 2000; Ballentine and  
683 Sherwood-Lollar, 2002b). Nitrogen contents within ophiolitic rocks are low but experimental  
684 studies have however shown that adsorbed N-species can be leached out while H<sub>2</sub> and CH<sub>4</sub>  
685 are produced from altered peridotites (Okland et al., 2014).

686 Considering the geochemical results of this study, N<sub>2</sub> present in the gas of the H<sub>2</sub>-rich type  
687 shows N<sub>2</sub>/<sup>36</sup>Ar and N<sub>2</sub>/<sup>84</sup>Kr ratios generally equivalent or slightly higher than those of ASW,  
688 suggesting mainly an atmosphere origin for N<sub>2</sub> via a fractured aquifer (Fig. 12A and B).

689 Samples of the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas type, which show higher N<sub>2</sub> contents than H<sub>2</sub> contents  
690 compared to the H<sub>2</sub>-rich gas type display notably a nitrogen enrichment relative to <sup>36</sup>Ar and  
691 <sup>84</sup>Kr (Fig. 12A and B), suggesting an addition of non-atmospheric nitrogen. This contributes  
692 to dilute the neo-formed H<sub>2</sub> and CH<sub>4</sub> (Deville and Prinzhofer, 2016). Samples of the N<sub>2</sub>-rich  
693 gas type show a <sup>4</sup>He enrichment correlated with the N<sub>2</sub> enrichment when compared to  
694 atmosphere (Fig. 13). This suggests that non-atmospheric N<sub>2</sub> might be of crustal origin  
695 associated to radiogenic helium from depth. The R/Ra ratio (<sup>3</sup>He/<sup>4</sup>He ratio of the sample  
696 normalized over the same ratio for the air = 1.384 × 10<sup>-6</sup>) suggests that a crustal component  
697 exists in most of the samples and locally a mantle component is observed in the Philippines  
698 (Fig. 10).

699 The differences between the H<sub>2</sub>-rich type and the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type are possibly linked to the  
700 existence of two different reactive zones for the production of H<sub>2</sub>-rich fluids in peridotitic  
701 ground waters: one (H<sub>2</sub>-rich) being more surficial than the other (N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub>-rich) and that  
702 two different reactive fluids should be considered: (1) a meteoric fluid in the more surficial  
703 environment (H<sub>2</sub>-rich) and (2) a deep N<sub>2</sub>-bearing fluid with crustal signature, probably issued  
704 from sediment metamorphism from below the obducted ophiolitic units.

705 Samples of the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type could also result from the mixing of H<sub>2</sub>-rich gas and N<sub>2</sub>-rich  
706 gas. These N<sub>2</sub>-rich samples contain mostly N<sub>2</sub> and no or little H<sub>2</sub>. Because they were found in  
707 hot water springs, displaying pH between 6.9 and 10 and relatively high <sup>4</sup>He contents which  
708 suggest a different origin, probably deeper according to water temperature (reaching locally  
709 66°C) and in a crustal environments as suggested by the high <sup>4</sup>He contents. This deep N<sub>2</sub> is  
710 probably not directly produced within the peridotite units. The geological context suggests  
711 rather an origin from the underthrust sediments below the ophiolitic units, so in this case N<sub>2</sub>  
712 would be issued more probably from the buried sediments, either from the water of hydrated  
713 clay (clay dewatering) or from the destabilization of ammonium-bearing clays. Reaction of  
714 such deep fluids with peridotite or mixing these fluids with H<sub>2</sub>-rich gas type are susceptible to  
715 generate fluids with the chemical signatures of the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas type where N<sub>2</sub> dilutes H<sub>2</sub>  
716 and is found in excess relative to ASW or air. Throughout the study of the 4 types of gas, it  
717 appears that the presence of nitrogen in the mixture is always linked to the presence of water  
718 at the seepage. This gas is almost absent from the dry seepages (H<sub>2</sub>-CH<sub>4</sub> type).

719  $\delta^{15}\text{N}$  measurements in the nitrogen-dominant gas types ( $\text{N}_2\text{-H}_2\text{-CH}_4$  and  $\text{N}_2\text{-rich}$ ), gave values  
720 of  $-0.3\text{‰}$  in Rustaq (Oman), which is consistent with previous studies (Sano et al, 1993) and -  
721  $0.1\text{‰}$  in Mangatarem (Philippines; table 2), whereas  $\delta^{15}\text{N}$  measurements in the  $\text{H}_2\text{-CH}_4$  gas  
722 type gave values comprised between  $-2.8\text{‰}$  and  $-2.1\text{‰}$  in the Chimaera gas seepages of  
723 Turkey (Hosgörmez et al., 2008) and  $+0.5\text{‰}$  in Nagsasa in the Philippines (Table 2). The  
724  $\delta^{15}\text{N}$  value for atmospheric nitrogen being  $0\text{‰}$  (Sano and Pillinger, 1990; Nishizawa et al.,  
725 2007), it cannot be clearly distinguished from the values measured in the  $\text{N}_2\text{-H}_2\text{-CH}_4$  and  $\text{N}_2\text{-}$   
726 rich samples considering potential sampling bias plus analytical uncertainties of the  
727 measurements. Although these results are compatible with an atmospheric nitrogen  
728 component in the  $\text{N}_2\text{-H}_2\text{-CH}_4$  and  $\text{N}_2\text{-rich}$  gas mixtures, this atmospheric component is not a  
729 contamination as shown by the  $\text{N}_2/^{36}\text{Ar}$  ratios for instance. This  $\text{N}_2$  might thus be issued from  
730 pore water trapped in the sediments (initial ASW) below the ophiolites or from the  
731 metamorphism of clays from the sediments underthrust below the ophiolitic units.  
732 However, such a nitrogen isotopic value is not a clear diagnostic. Although it is compatible  
733 with an atmospheric value, it does not exclude other origins like deeper components from  
734 mantle and/or crust because a multiple origin of nitrogen is indeed supported by the results of  
735 the noble gas analyses.

736 Noble gas contents suggest that there are at least two different sources of  $\text{N}_2$ . The plot of  $\text{R/Ra}$   
737 versus  $^{20}\text{Ne}/^4\text{He}$  (Fig. 10) shows that the  $\text{N}_2$ -bearing gases are ranging on a mixing line  
738 between the crust and the atmospheric end-member. In the  $\text{H}_2$ -rich type, the  $\text{N}_2/^{36}\text{Ar}$  ratio is  
739 close to the air and ASW ratios (Fig. 12A). This implies that  $\text{N}_2$  in this gas originates from the  
740 atmosphere and was carried by an aquifer equilibrated with the atmosphere or that the main  
741 nitrogen component is acquired during the gas migration upwards through the aquifer. The  
742 other samples ( $\text{N}_2\text{-H}_2\text{-CH}_4$  and  $\text{N}_2\text{-rich}$ ) do not align on these atmospheric ratios. They display  
743 a nitrogen enrichment relative to  $^{36}\text{Ar}$  (Fig. 12A) and the contents are much too high to be  
744 only due to extraction from an aquifer related to free gas flows toward the surface.

745 From the plots of figures 12A and B, it can be inferred that  $\text{N}_2\text{-rich}$  type gases in Oman and  
746 New Caledonia consist of a mixture of an atmospheric component and an almost pure  
747 nitrogen end-member. The proportion of the nitrogen component varies in a large range (from  
748 10 to 90% mol).  $^4\text{He}$  is mainly a radiogenic product issued from the continental crust. It  
749 cannot be produced in such amounts by mantle-derived ultrabasic rocks. Thus, the  $\text{N}_2\text{-rich}$   
750 gases can be interpreted as a crustal gas with a  $^4\text{He}$  component. A potential interpretation for  
751 the origin of deep  $\text{N}_2$  could be that it was produced in the sediments and/or metasediments  
752 buried under the ophiolitic units. In this case, the source could be the interstitial water in the



753 sediments and/or the solid matrix of the sediments (organic matter or ammonium in clay  
754 sediments).

755

## 756 **Conclusion**

757

758 Integrating the results of previous studies and original results in different areas of the world,  
759 this multi-tracer approach provided new insights on gas seepages in ophiolitic contexts. Four  
760 types of gas mixtures were defined, three of them being associated with water springs and  
761 characterized by the presence of N<sub>2</sub>, CH<sub>4</sub> in proportions under 20 mol% and the presence of  
762 H<sub>2</sub> within the ultra-basic springs. The fourth type corresponds to focused gas flows seeping  
763 out directly from fractures (without water flow) and characterized by high proportions of CH<sub>4</sub>  
764 and low N<sub>2</sub>. In all cases, H<sub>2</sub> is interpreted as a consequence of oxidation of Fe<sup>II</sup>-rich minerals  
765 present in the ophiolitic rocks (even though a contribution by microorganisms by dark  
766 fermentation processes cannot be ruled out). Taking into account the pH conditions associated  
767 with the H<sub>2</sub> generation, Fe<sup>III</sup>-bearing mineral were formed at the vicinity of the sites of  
768 oxidation of Fe<sup>II</sup>-bearing mineral without an important mobility of Fe<sup>2+</sup>. A relatively shallow  
769 H<sub>2</sub> production is substantiated in the H<sub>2</sub>-rich gas type by its association with quasi-  
770 atmospheric noble gases. It is consistent with the D/H isotopic data of H<sub>2</sub> that may correspond  
771 to a fluid rock reaction occurring at low temperature (probably below 50°C), whereas higher  
772 temperatures are suspected for the H<sub>2</sub> production in the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas type and notably in the  
773 H<sub>2</sub>-CH<sub>4</sub> gas type (probably above 100°C locally). The preservation of H<sub>2</sub> in the gas is directly  
774 related to extreme limitation of carbon in the geological setting. It is probably related to the  
775 carbon capture associated with massive precipitation of carbonates due to high-pH  
776 conditions. Concerning CH<sub>4</sub>, multiple origins are supported by the carbon isotopic data. The  
777 carbon and hydrogen sources are various. Both, a primary CH<sub>4</sub> (from H<sub>2</sub>O reacting with DIC)  
778 and a secondary CH<sub>4</sub> (from an H<sub>2</sub> intermediate reacting with a C source) are suspected for the  
779 H<sub>2</sub>-CH<sub>4</sub> gas type and for N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> and H<sub>2</sub>-rich gas types, respectively. In the gas mixtures,  
780 N<sub>2</sub> appears to have two distinct origins: an atmospheric component and a deep crustal  
781 component, as it was highlighted by the noble gas analyses. The different processes described  
782 involve different types of fluids, which are: a shallow meteoric fluid, a crustal fluid carrying  
783 metamorphic N<sub>2</sub>, a deep mantle originating fluid carrying primordial CO<sub>2</sub>. Depending on the  
784 location with respect to the geodynamical context (Fig. 14), these different fluids interact and  
785 mix in different proportions, yielding the types of gas mixture observed at the surface  
786 seepages. The shallower kitchen is interpreted as the H<sub>2</sub>-rich gas type from meteoric water

787 interacting with the ophiolite. The deepest kitchen is interpreted as the H<sub>2</sub>-CH<sub>4</sub> gas type from  
788 a deep fluid (carrying CO<sub>2</sub> from the mantle, or from dissolved carbonates or organic carbon)  
789 interacting with the ophiolite. H<sub>2</sub>-CH<sub>4</sub> gas flows are generally more localized (focused) and  
790 these flows are generally higher than the other H<sub>2</sub>-bearing gas flows. This is probably due to  
791 the fact that they are generated at greater depth and at higher temperature conditions. This  
792 probably induces the individualization of a gas phase preventing H<sub>2</sub> to react during the rise  
793 toward the surface, notably by preventing any biological consumption of H<sub>2</sub> which required  
794 an aqueous media. The N<sub>2</sub>-bearing fluids are probably generated mostly from the sediments  
795 located below the ophiolitic units and migrate upwards forming the N<sub>2</sub>-rich gas type when  
796 reaching the surface or the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type if mixing occurs between the N<sub>2</sub>-rich and the H<sub>2</sub>-  
797 rich types (Fig. 14).

798

### 799 **Acknowledgements**

800

801 The authors would like to thank Georges Ceuleneer for his precious help and knowledge on  
802 the field in Oman, Mr Al Attaly for his enthusiasm towards our research and the information  
803 and help provided in Oman, Americus Perez and Zaymon Calucin for their help on the field in  
804 the Philippines, Christophe Chevillon and François Leborgne from the « Province Sud de  
805 Nouvelle-Calédonie, service de la mer et de la protection du lagon » who helped us very  
806 efficiently in New-Caledonia, Long Li for the nitrogen isotopes measurements performed at  
807 the IPGP. This work was achieved on IFPEN funds.

808

809

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811

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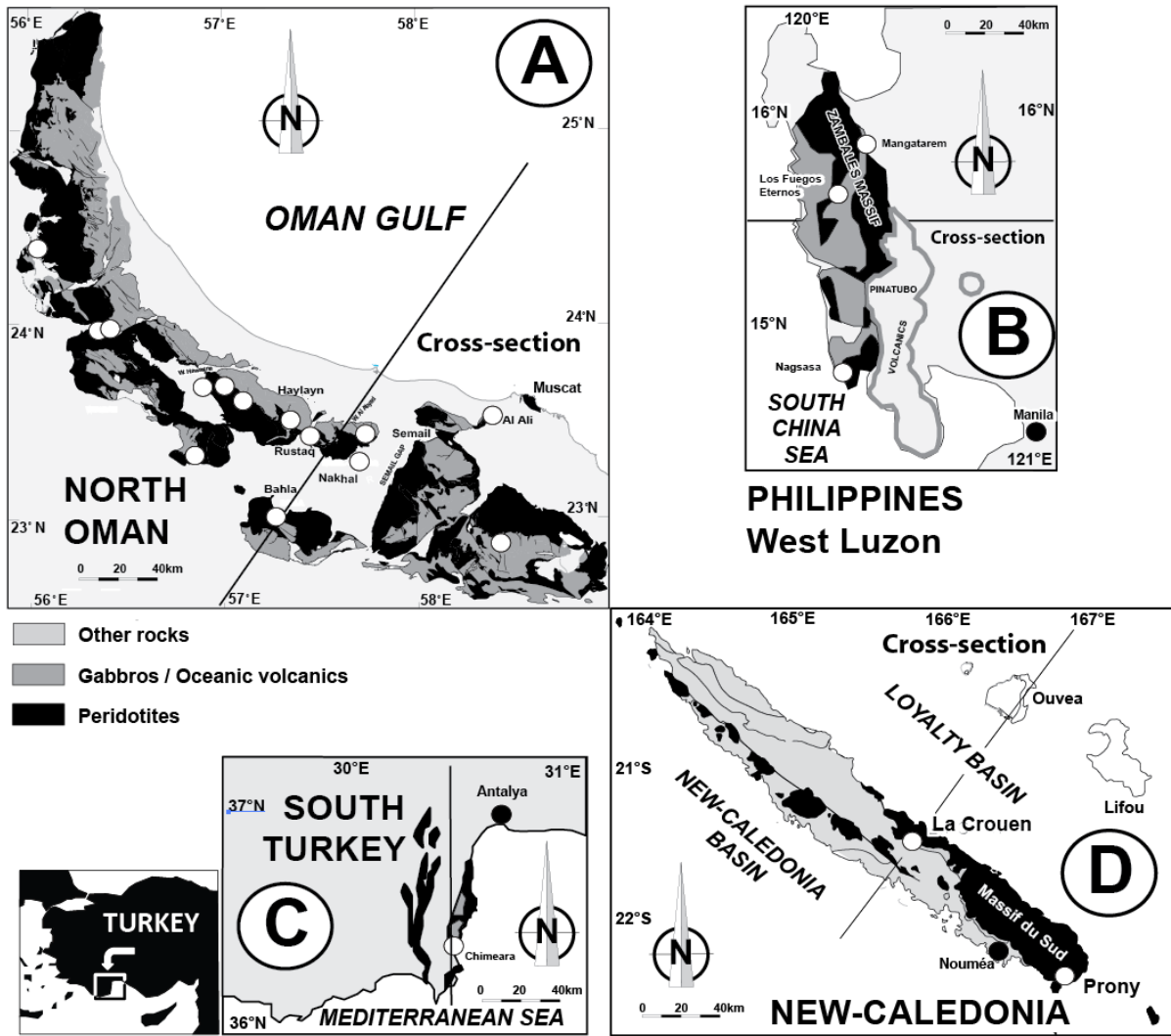
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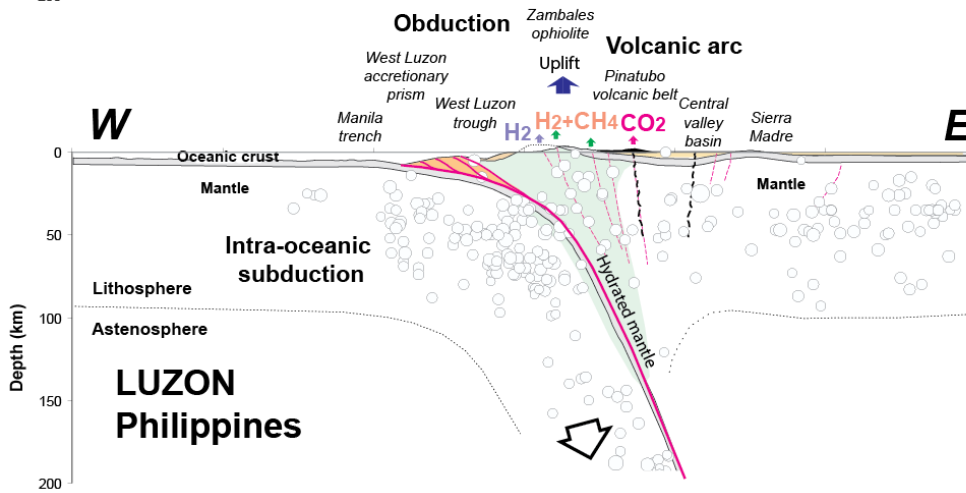
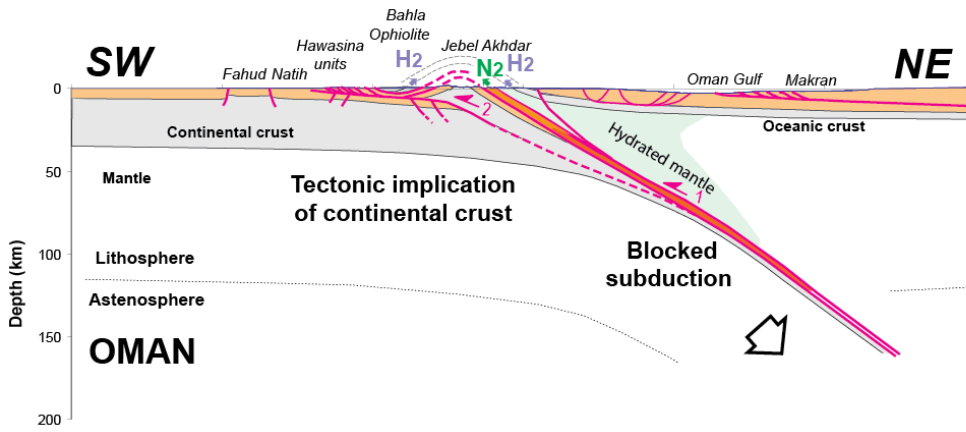
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1189 **Figure 1** – Structural sketch-maps of the different sites studied in this work in Oman (A), the  
 1190 Philippines (B), Turkey (C) and New-Caledonia (D) (same scale), with the location of the  
 1191 sampling sites and the location of the cross-sections shown in figure 2. The gas seepages are  
 1192 associated with ophiolitic ultrabasic rocks. Gas was sampled from different types of seepages:  
 1193 gas seeping in water which originates from ultrabasic or hot springs and gas seeping from  
 1194 fractures without water flow.

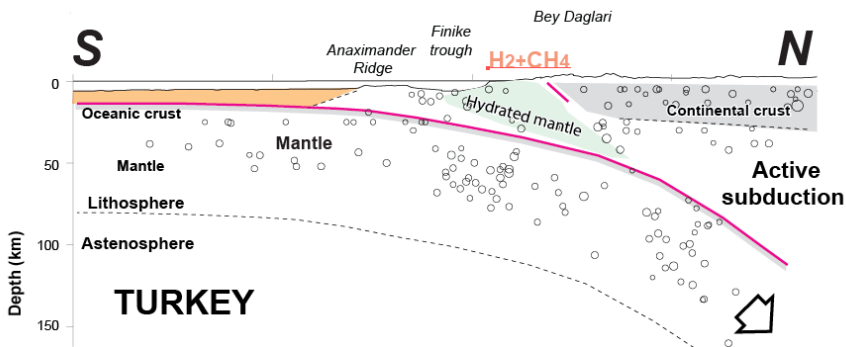
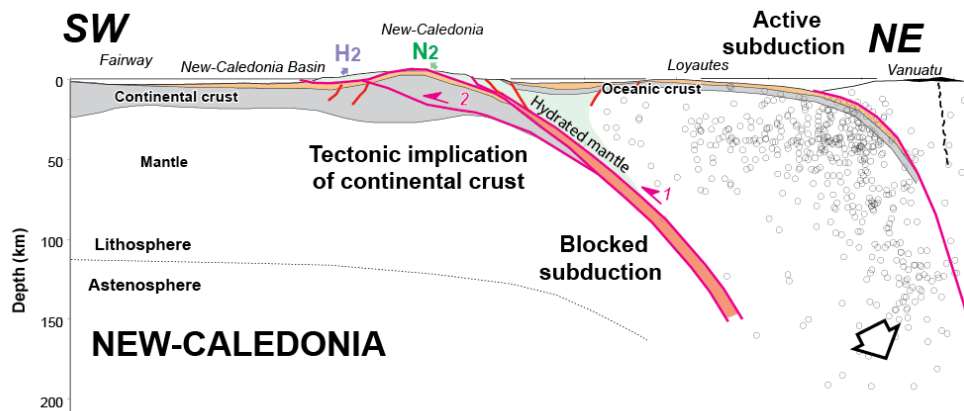
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1200 **Figure 2** - Geological cross-sections of the different sites studied in this work (same scale;  
1201 earthquake epicenters from USGS data base). A 2D cross-section for the area of Chimaera in  
1202 Turkey is not shown because of too complex 3D geometry in a transform fault system.

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**A**

**B**

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**C**

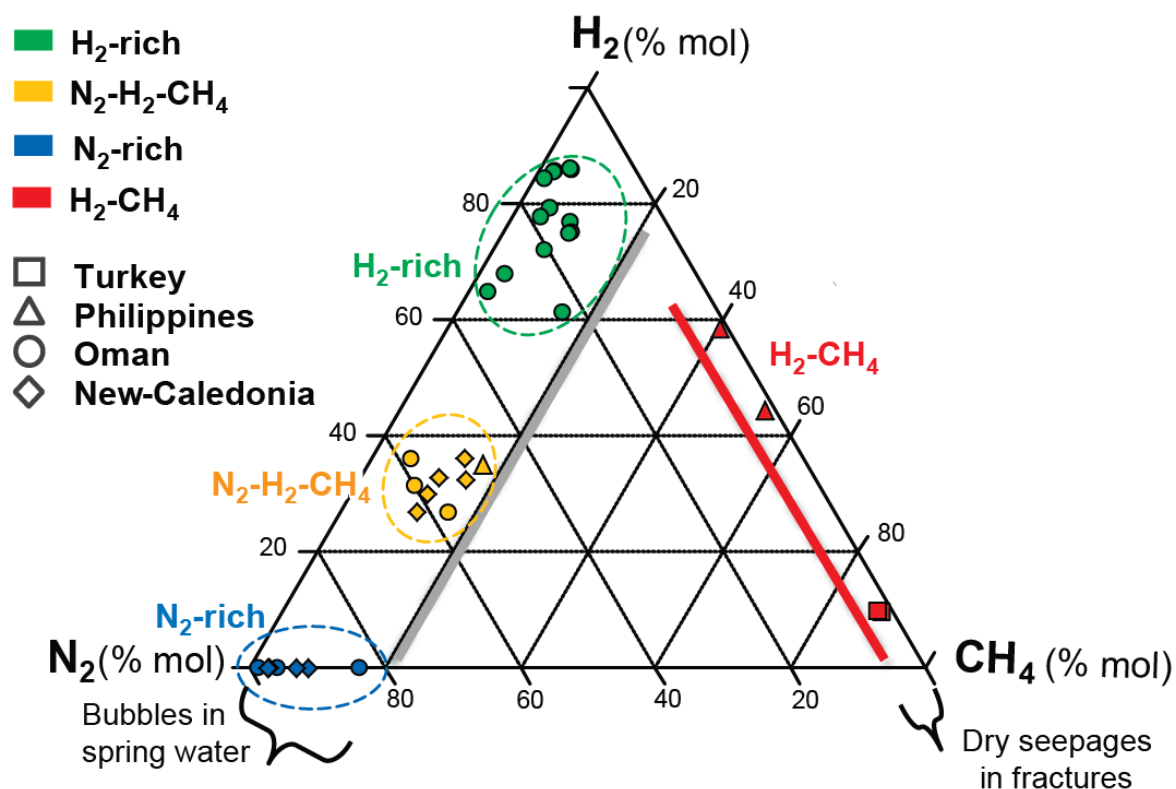


**D**

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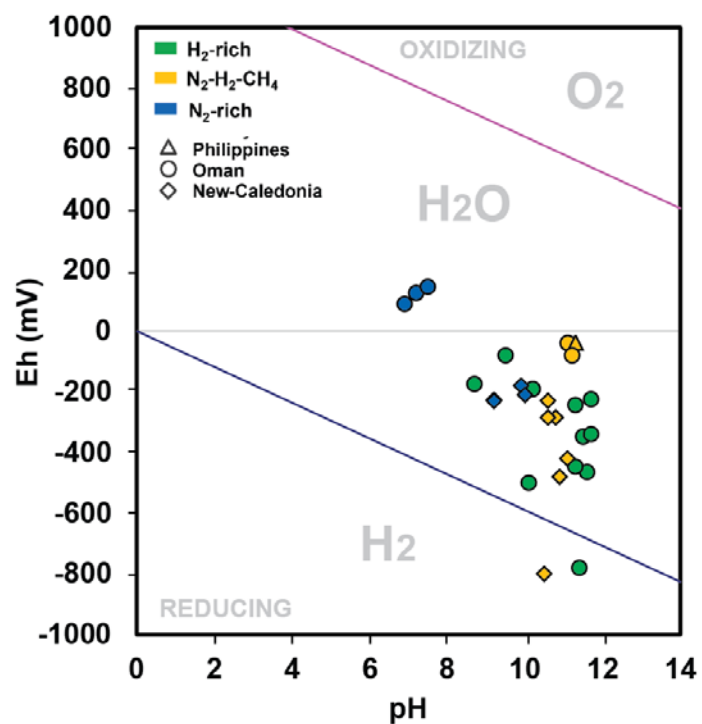
1211 **Figure 3** – Examples of gas seepages. **A:** Bubbling  $H_2$ -rich gas flow in ultra-basic water  
1212 (Oman). **B:** Bubbling  $N_2$ - $H_2$ - $CH_4$  gas flow (foreshore of the Baie du Carénage, New  
1213 Caledonia). **C:** Bubbling  $N_2$ -rich gas flow (Rustaq, Oman). **D:** Burning  $H_2$  - $CH_4$  gas flow  
1214 (Chimaera, Turkey).

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1217 **Figure 4** - The major components of the gas mixtures sampled in Turkey, Oman, New  
 1218 Caledonia and the Philippines : H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in a triangular diagram (% mol). Four  
 1219 different types of gas mixtures can be defined according to the relative contents of H<sub>2</sub>, N<sub>2</sub> and  
 1220 CH<sub>4</sub>. Distinct chemical features correspond to distinct seepages styles : N<sub>2</sub>-containing gas  
 1221 mixtures are associated with water and seep in water streams, whereas N<sub>2</sub>-free mixtures  
 1222 correspond to dry seepages which seep out of fractures of massive rocks and locally ignite  
 1223 spontaneously. The different types of water-associated seepages correspond also to specific  
 1224 water physical properties, notably pH and temperature (see Fig. 5).

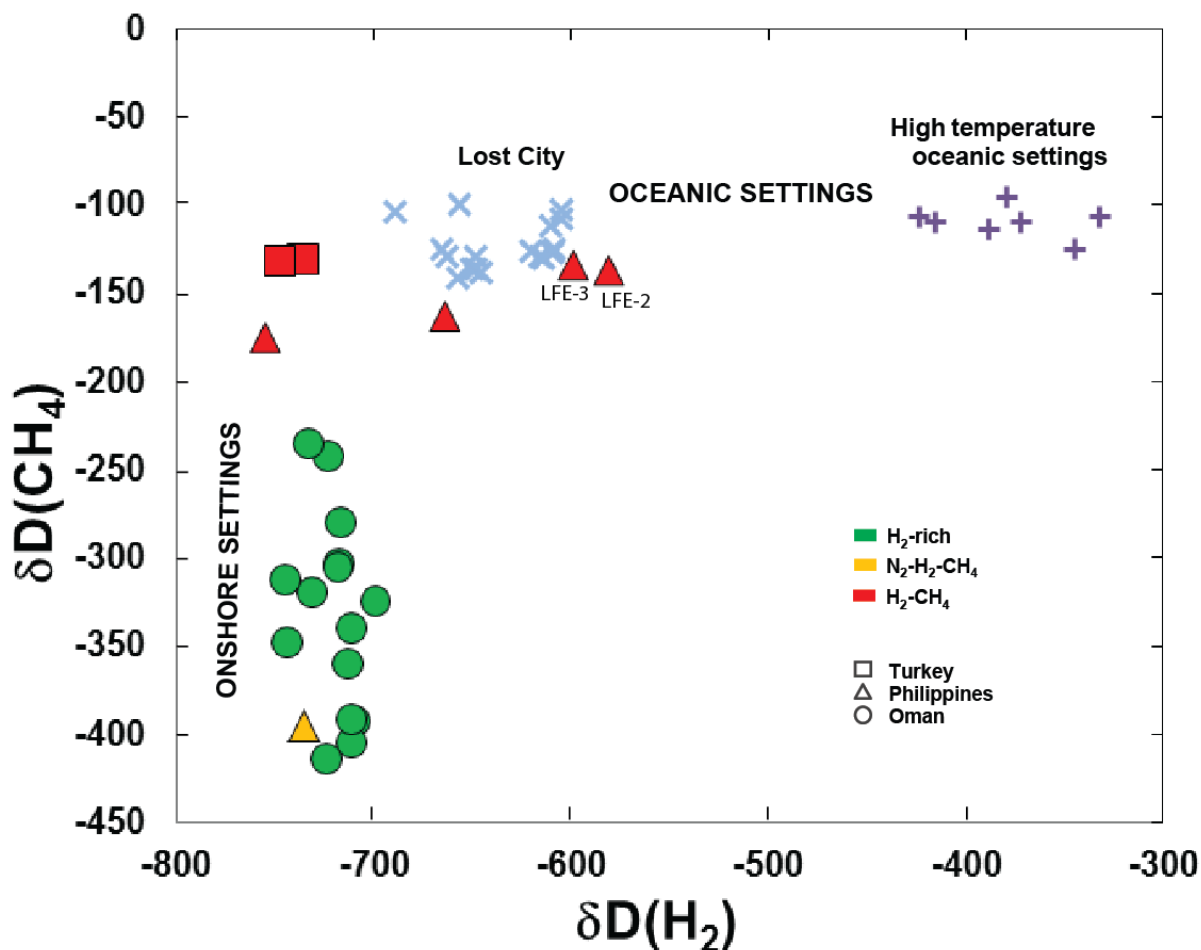


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1226 **Figure 5** - Pourbaix diagram pH-Eh of the water where the gas samples were collected in  
1227 springs. Oblique lines (blue and pink) separate the stability fields of H<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub>.

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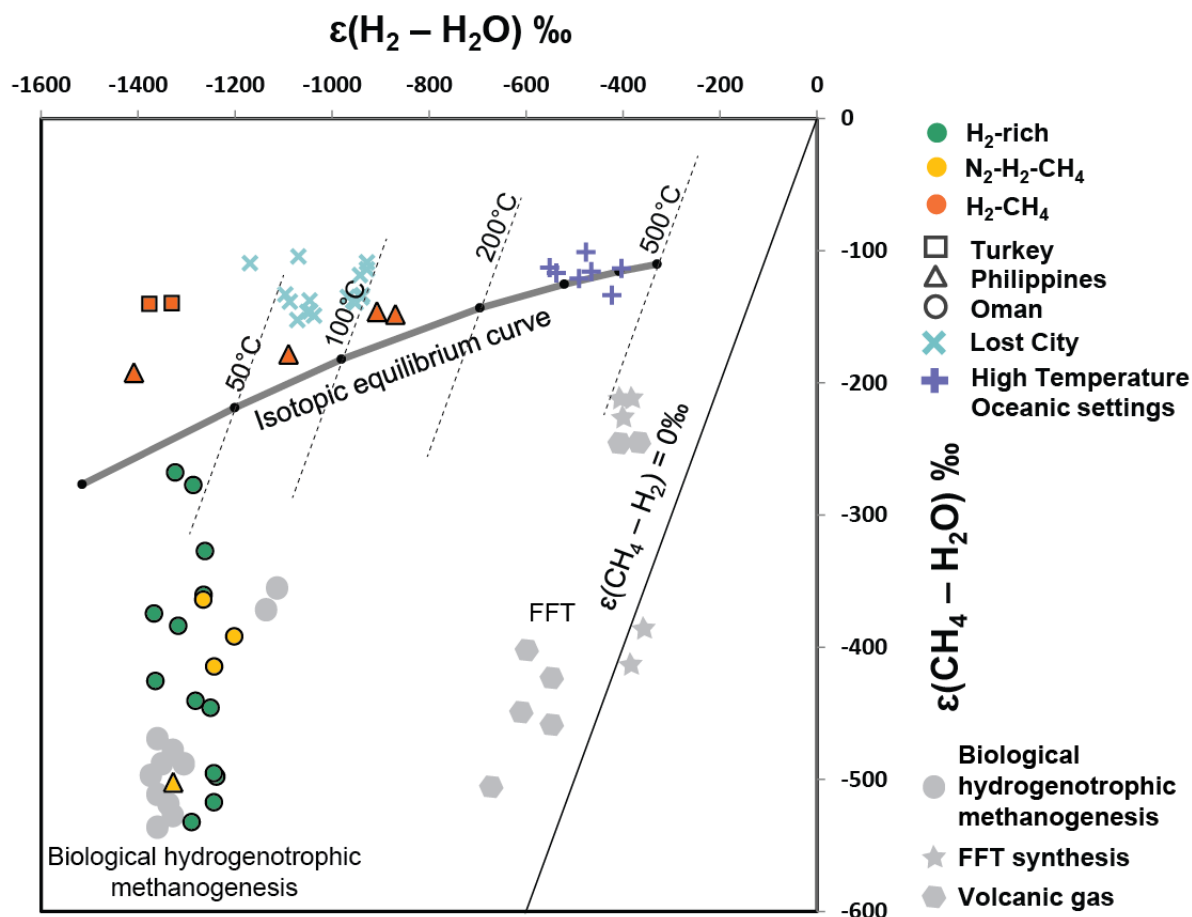


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1231 **Figure 6** - Comparison of hydrogen isotopic compositions of  $CH_4$  and  $H_2$  for onshore  
 1232 settings (data from this work and two points, LFE-2 and LFE-3, from Abrajano et al.,  
 1233 1988) and oceanic settings (Proskurowski et al., 2006). While a narrow range of  $CH_4$   
 1234 isotopic composition is observed for oceanic settings these values are lower for  
 1235 onshore settings and cover a large range. The values for the gas seeping out of  
 1236 fractures without associated ultra-basic water ( $H_2$ - $CH_4$  gas type) are close to those of  
 1237 oceanic setting at Lost City and might indicate a similar generation process. In  
 1238 contrast to the  $CH_4$  isotopic compositions, the  $H_2$  isotopic compositions display a large  
 1239 range in oceanic settings (dependent on temperature) and a narrow range in terrestrial  
 1240 settings for gas seeping from ultra-basic springs.

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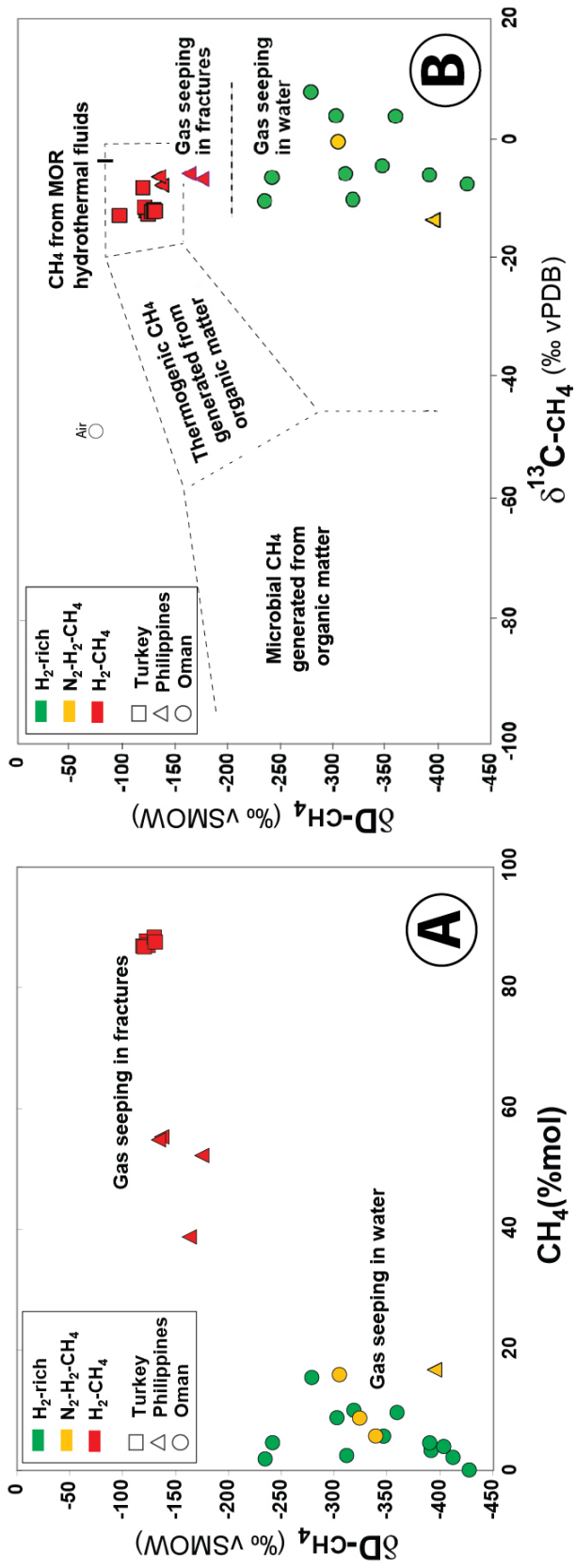


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1244 **Figure 7** -  $\text{CH}_4$ - $\text{H}_2$ - $\text{H}_2\text{O}$  hydrogen isotope systematics. Data for biological hydrogenotrophic  
 1245 methanogenesis are from Balabane et al. (1987), Valentine et al. (2004) and Okumura et al.  
 1246 (2016). FFT synthesis refer to experiments investigating abiogenic methane production in the  
 1247 gas phase (Taran et al., 2010) and aqueous phase (Fu et al., 2007; McCollom et al., 2010).  
 1248 There data were presented in a similar diagram in Suda et al. (2014). This figure shows  $\epsilon(\text{H}_2$ -  
 1249  $\text{H}_2\text{O}_{\text{aq}})$  versus  $\epsilon(\text{CH}_4$ - $\text{H}_2\text{O}_{\text{aq}})$  for the samples from Oman, the Philippines and Turkey,  
 1250 compared to values from oceanic settings. The value  $\epsilon$  is calculated according to the  
 1251 following equations :  $\epsilon = 1000 \ln \alpha$  with  $\alpha(\text{H}_2\text{O}_{\text{aq}}-\text{H}_2) = 1.0473 + 201036/T^2 + 2.060 \times 10^9/T^4 +$   
 1252  $0.180 \times 10^{15}/T^6$  and  $\alpha(\text{H}_2\text{O}_{\text{aq}}-\text{CH}_4) = 1.0997 + 8456/T^2 + 0.9611 \times 10^9/T^4 - 27.82 \times 10^{12}/T^6$ .  
 1253 The thin line indicates the  $\text{CH}_4$ - $\text{H}_2$  equilibrium fractionation at a given temperature.  
 1254 According to this interpretation,  $\text{CH}_4$  from fractures (dry seepages) would be produced  
 1255 directly from  $\text{H}_2\text{O}$  and DIC whereas, in the  $\text{H}_2$ -rich and  $\text{N}_2$ - $\text{H}_2$ - $\text{CH}_4$  gas mixtures seeping in  
 1256 alkaline springs, an  $\text{H}_2$  intermediate (possibly biologically mediated secondary process) would  
 1257 produce  $\text{CH}_4$ .  $\delta\text{D}$  of spring water is considered to be close to zero ‰ from the study made in  
 1258 Oman by Neal and Stanger (1985; values between -11.2 and +10.7‰).

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Fig 8

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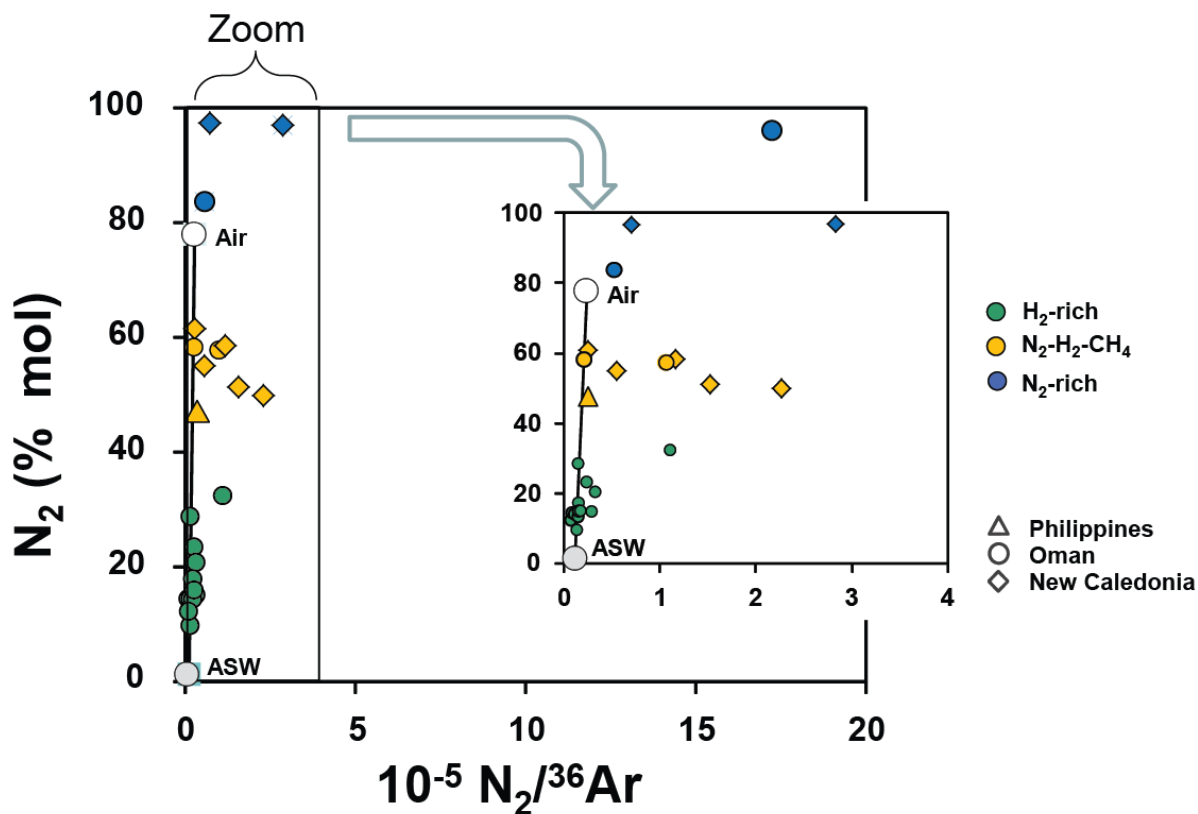
1264 **Figure 8 – A.** Diagram showing  $\delta D(\text{‰})$  values of  $\text{CH}_4$  vs  $\text{CH}_4$  contents. This shows that the  
1265  $\text{H}_2$  - $\text{CH}_4$  gas type shows higher  $\text{CH}_4$  contents and  $\delta D$  values of  $\text{CH}_4$  than the other gas types.

1266 **B.** Diagram showing carbon versus hydrogen isotopic composition of  $\text{CH}_4$  including data  
1267 from Abrajano et al. (1988) and Hosgörmez et al. (2008), domains are simplified after Scholl  
1268 (1983), Whiticar (1999), Etiope and Sherwood-Lollar (2013). The classic microbial domain  
1269 presented here refers to gas generated from an organic substrate. This domain might be wider  
1270 in the case of microbial gas generated from inorganic carbon. The carbon isotopic  
1271 compositions of  $\text{CH}_4$  are among the highest values recorded on Earth. The range of the carbon  
1272 isotopic values of  $\text{CH}_4$  is relatively narrow and allows no distinction between the different  
1273 types of gas mixtures whereas the hydrogen isotopic values of  $\text{CH}_4$  are scattered between -  
1274 430‰ and -100‰ and show distinct ranges comparing dry seepages in fractures and seepages  
1275 in ultra-basic water. This corresponds probably to different  $\text{CH}_4$  generation processes. Note  
1276 that none of the groups plot in the classical domains of conventional microbial gas or  
1277 conventional thermogenic gases. Domain for  $\text{CH}_4$  of Mid-Oceanic Ridges hydrothermal fluids  
1278 is from Proskurowski et al. (2006) and Kawagucci et al. (2016).

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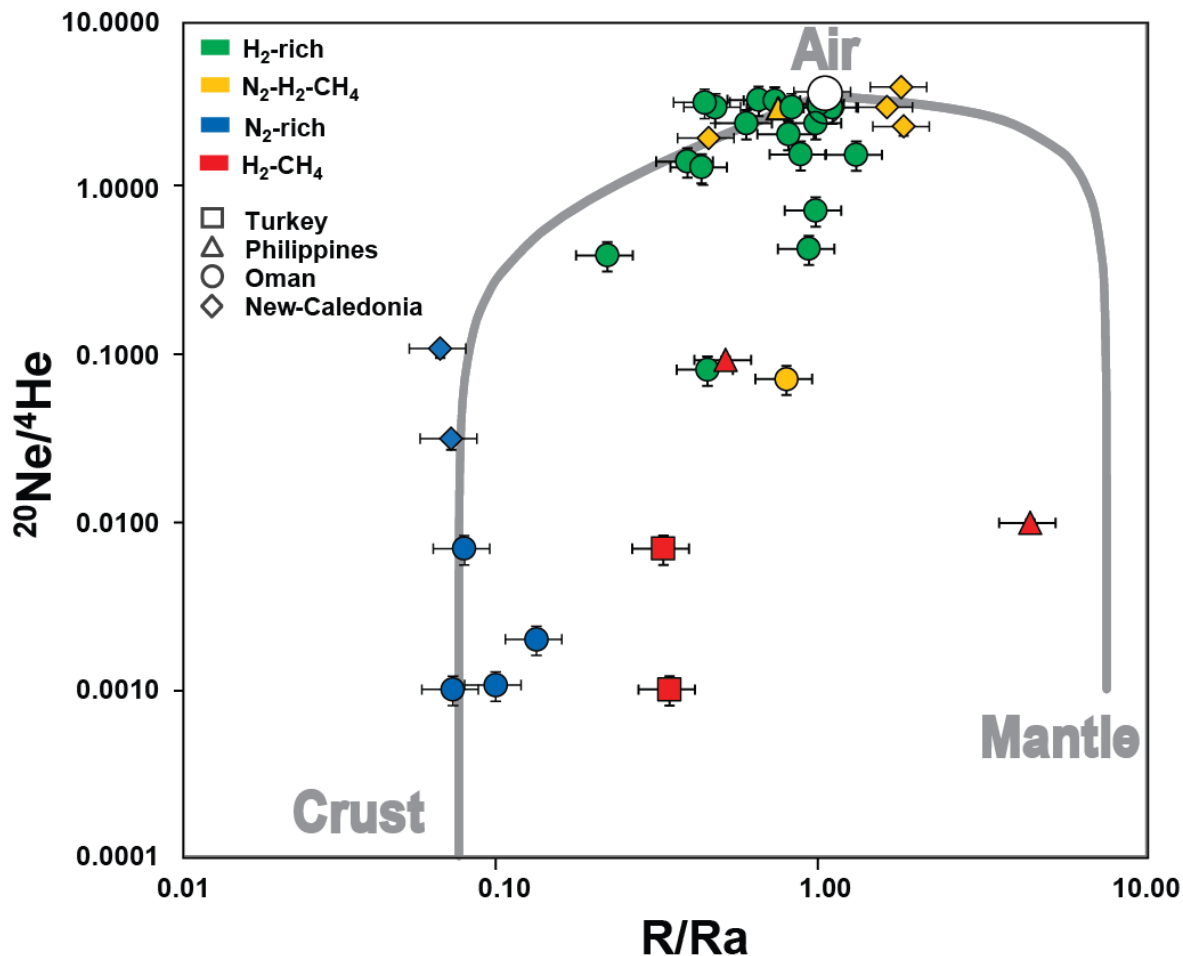


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1282 **Figure 9** -  $N_2$  content vs  $N_2/^{36}Ar$  diagram, depicting nitrogen excess in samples relative to  
 1283 atmospheric  $^{36}Ar$ . The values from the  $H_2$ -rich type gather along a mixing line between air  
 1284 and air equilibrated water, implying that probably only inherited atmospheric  $N_2$  can be found  
 1285 in the gas mixture, whereas the other types show a  $N_2$  excess, suggesting that non-  
 1286 atmospheric  $N_2$  is present in the gas mixture.

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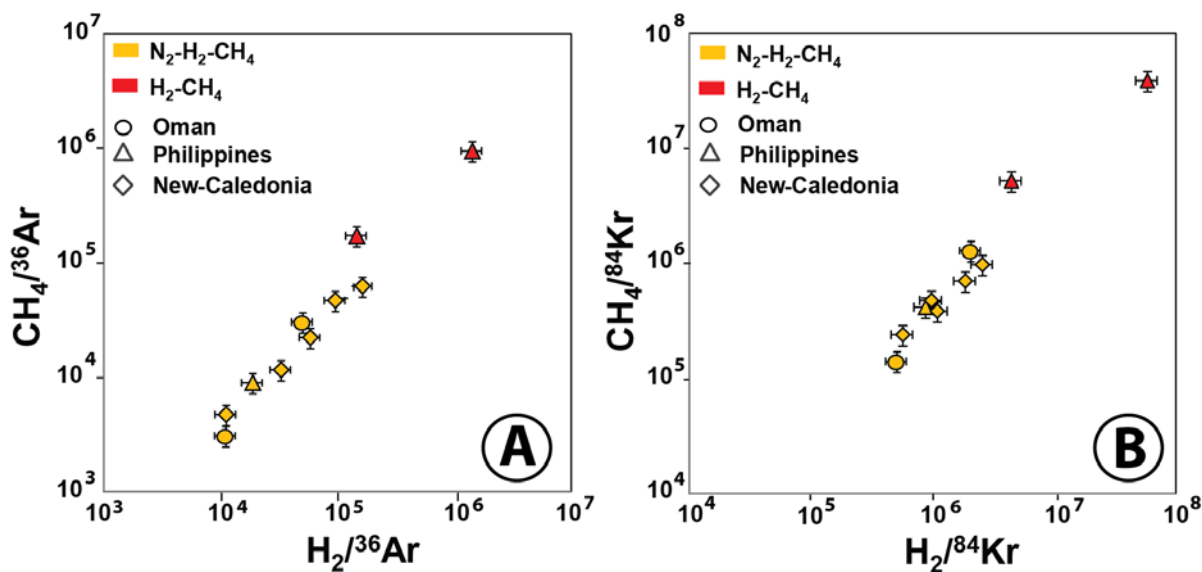
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1290 **Figure 10** - Mixing diagram  $^{20}\text{Ne}/^4\text{He}$  vs  $R/R_a$  ( $^3\text{He}/^4\text{He}$  ratio of the sample normalized over  
 1291 the same ratio for the air =  $1.384 \times 10^{-6}$ ). The noble gas data show that except the  $\text{H}_2$ -rich type  
 1292 which plots around the atmospheric end-member and indicates a single shallow aquifer  
 1293 signature, the other gas mixtures have signatures that result from the interaction of several  
 1294 fluids originating either from the mantle or from the crust. The  $\text{N}_2$ -rich type is interpreted as  
 1295 resulting from the mixing of atmospheric and crustal end-members whereas a mantle  
 1296 contribution is recorded for samples of the  $\text{N}_2$ - $\text{H}_2$ - $\text{CH}_4$  and  $\text{H}_2$ - $\text{CH}_4$  types.

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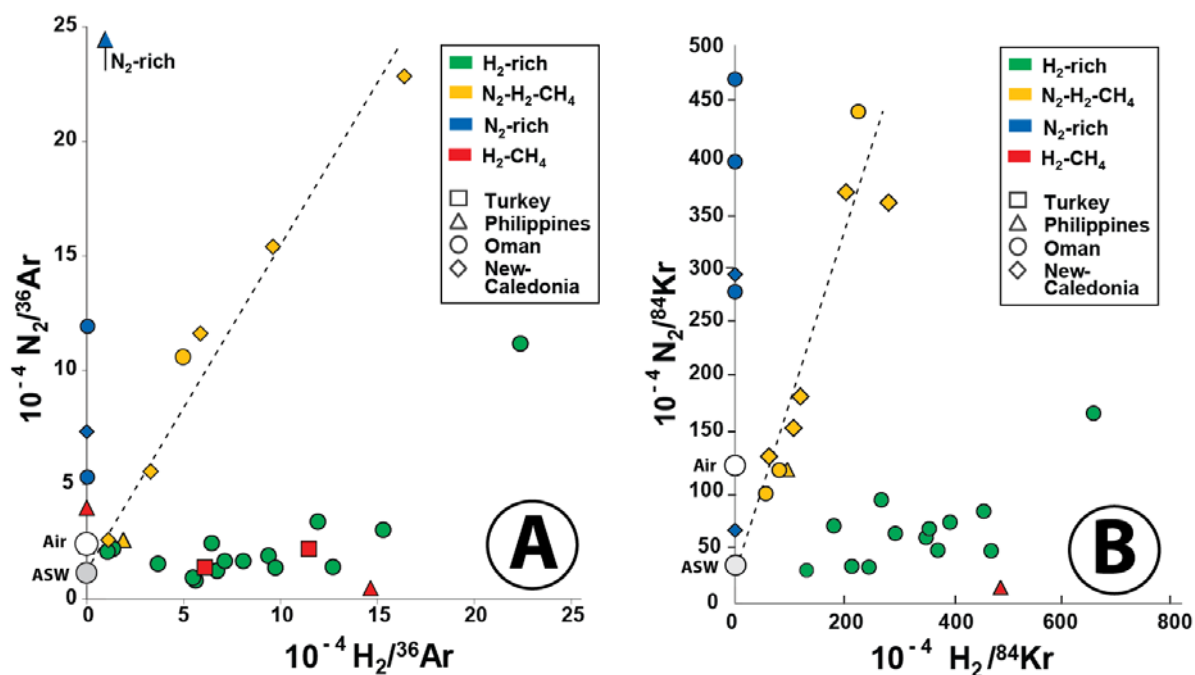
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1299 **Figure 11** – Mixing diagrams comparing H<sub>2</sub> and CH<sub>4</sub> contents normalized over <sup>36</sup>Ar and <sup>84</sup>Kr  
 1300 contents. **A.** This diagram shows a correlated enrichment in CH<sub>4</sub> vs H<sub>2</sub> when normalized over  
 1301 <sup>36</sup>Ar (linear correlation with R<sup>2</sup>= 0.9894). **B.** This diagram shows also a correlated enrichment  
 1302 in CH<sub>4</sub> vs H<sub>2</sub> when normalized over <sup>84</sup>Kr (linear correlation with R<sup>2</sup>= 0.9953).

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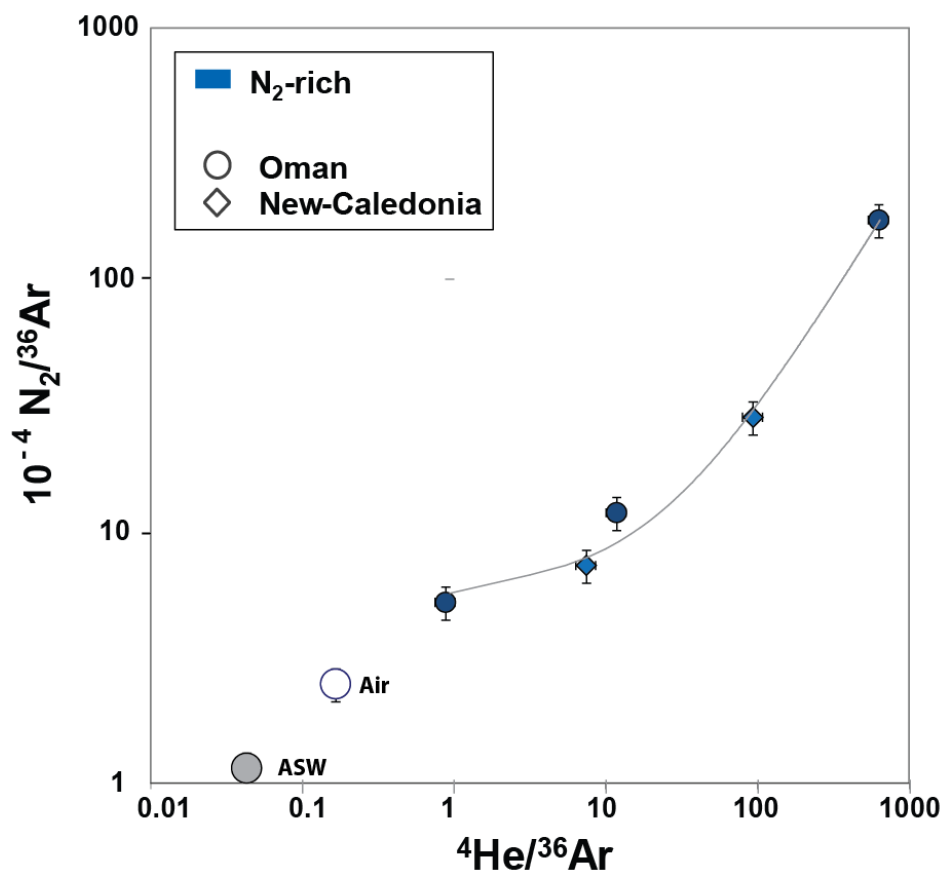


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1307 **Figure 12** – Mixing diagrams comparing H<sub>2</sub> and N<sub>2</sub> contents normalized over <sup>36</sup>Ar and <sup>84</sup>Kr  
 1308 contents. **A.** The H<sub>2</sub>/<sup>36</sup>Ar vs N<sub>2</sub>/<sup>36</sup>Ar diagram shows different enrichment trends in H<sub>2</sub> vs N<sub>2</sub>  
 1309 between the H<sub>2</sub>-rich gas type and the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas type. Note the good linear correlation  
 1310 between H<sub>2</sub>/<sup>36</sup>Ar and N<sub>2</sub>/<sup>36</sup>Ar for the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas type (linear correlation R<sup>2</sup>= 0.9785). **B.**  
 1311 The H<sub>2</sub>/<sup>84</sup>Kr vs N<sub>2</sub>/<sup>84</sup>Kr diagram, as the previous diagram, shows different enrichment trends  
 1312 in H<sub>2</sub> vs N<sub>2</sub> between the H<sub>2</sub>-rich gas type and the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas type. Note the good linear  
 1313 correlation between H<sub>2</sub>/<sup>84</sup>Kr and N<sub>2</sub>/<sup>84</sup>Kr for the N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> gas type (linear correlation with  
 1314 R<sup>2</sup>= 0.9739).

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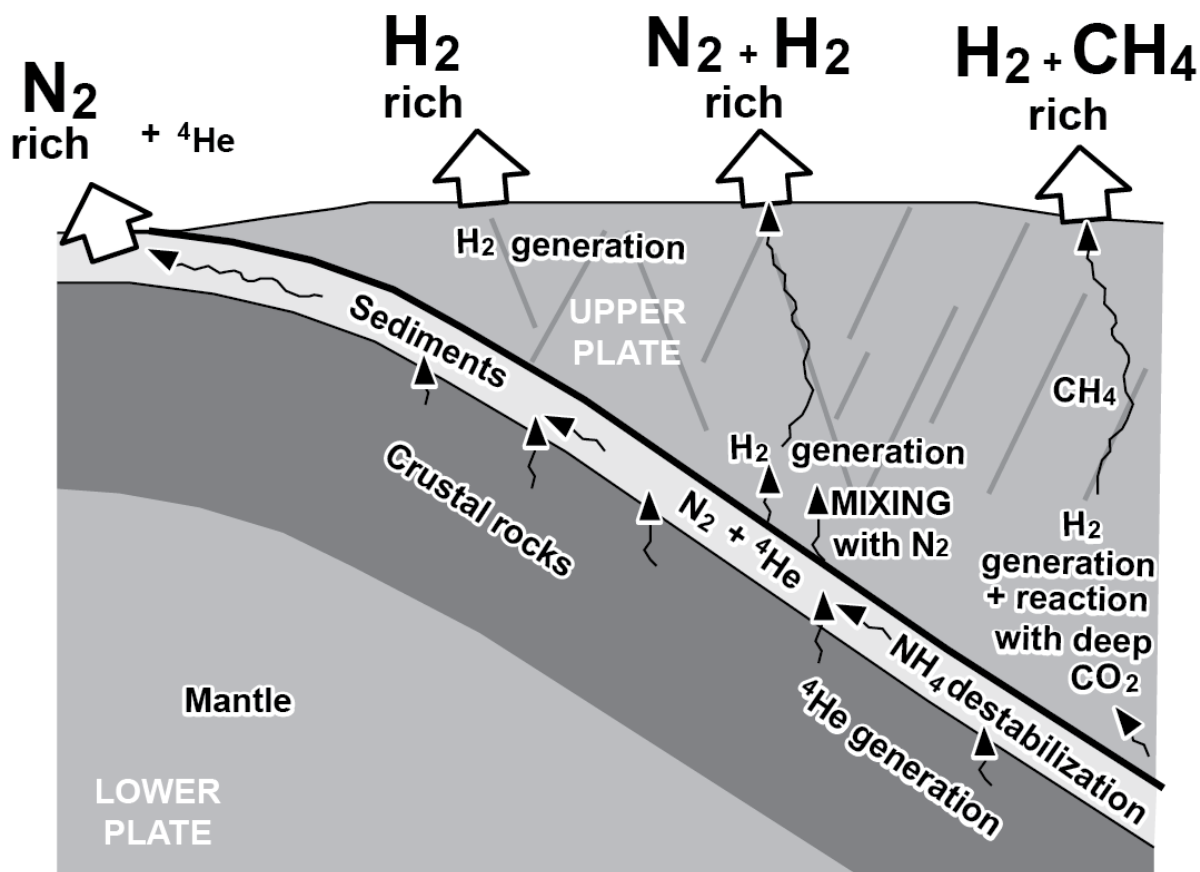
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1319 **Figure 13** -  $^4\text{He}/^{36}\text{Ar}$  vs  $\text{N}_2/^{36}\text{Ar}$  mixing diagram for the gas samples of the  $\text{N}_2$ -rich gas type.

1320 This diagram shows a correlated enrichment in  $^4\text{He}$  vs  $\text{N}_2$  when normalized over  $^{36}\text{Ar}$  (linear  
 1321 correlation with  $R^2 = 0.9993$ )

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1325 **Figure 14** - Synthetic conceptual cross-section of an ophiolitic system with the different gas  
 1326 generation zones and different types of seepages.

1327 In this interpretative sketch, H<sub>2</sub> is generated within the ophiolite at different depths by  
 1328 reduction of water, leading to different types of seepages depending on the other fluids  
 1329 interacting with H<sub>2</sub>. When H<sub>2</sub> is generated in a shallow aquifer, it migrates upwards and seeps  
 1330 out of the rock as a H<sub>2</sub>-rich gas seep. H<sub>2</sub> generated in a deeper generation zone interacts with  
 1331 deep fluids which can be (1) a N<sub>2</sub>-rich fluid issued from the sediments and the mantle below,  
 1332 leading to a N<sub>2</sub> and H<sub>2</sub>-rich gas, or (2) a fluid rich in CO<sub>2</sub>, allowing the production of CH<sub>4</sub> and  
 1333 the formation of a gas mixture that seeps at the surface as a H<sub>2</sub>-CH<sub>4</sub> gas seepages. N<sub>2</sub>-rich  
 1334 seepages occur when the deep N<sub>2</sub>-bearing fluid does not interact strongly with H<sub>2</sub>-rich fluids  
 1335 on its migration pathway.

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1337

Sites	Coordinates (decimal degrees)		Water T, pH, Eh			gas composition						
			(°C)			Mol (%)						
			T	pH	Eh	He	H <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2+</sub>	
<b>H<sub>2</sub>-rich type</b>												
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	
<b>N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type</b>												
Oman	Abyad 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	
<b>N<sub>2</sub>-rich type</b>												
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
<b>H<sub>2</sub>-CH<sub>4</sub> type</b>												
Philippines	Nagsasa	14.837	120.1282	-	-	-	<0.01	58.5	1.2	38.7	<0.01	<0.01
	Los Fuegos Eternos	15.5718	120.1513	-	-	-	<0.01	44.5	1.5	52.2	<0.01	<0.01
Turkey	XI2	36.4318	30.4557	-	-	-	<0.01	9.4	1.8	88.4	<0.01	0.3
	XI3	36.4352	30.4532	-	-	-	<0.01	9.7	2.2	87.6	<0.01	0.3
<b>Reference compositions</b>												
air								5E-05	78.08	2E-04	0.04	
ASW								9E-07	1.23	6E-06	0.03	

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1340 **Table 1.** Temperature, pH and Eh of the studied springs. Major gas analyses (mol%).

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Sources/Wells		Per mil vs PDB		Per mil vs SMOW		Per mil vs atm	noble gases composition				
		$\delta^{13}\text{C}$		$\delta\text{D}$		$\delta^{15}\text{N}$	(ppm)				
		$\text{CO}_2$	$\text{CH}_4$	$\text{H}_2$	$\text{CH}_4$	$\text{N}_2$	$^4\text{He}$	$^{20}\text{Ne}$	$^{36}\text{Ar}$	$^{84}\text{Kr}$	R/Ra
<b>H<sub>2</sub>-rich type</b>											
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
<b>N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub> type</b>											
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
<b>N<sub>2</sub>-rich type</b>											
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
	Nakhla	-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
	Aiguille de Prony	-	-12.1	-	-	-	-	-	-	-	-
	Aiguille de Prony	-	-16.4	-	-	-	-	-	-	-	-
<b>H<sub>2</sub>-CH<sub>4</sub> type</b>											
Philippines	Nagsasa	-	-5.6	-664	-163	0.5	4.68	0.047	0.41	0.01	4.35
	Los Fuegos	-	-6.5	-756	-175	-	4.38	0.419	3.04	0.10	0.49
	Eternos	-	-6.5	-756	-175	-	4.38	0.419	3.04	0.10	0.49
Turkey	Turkey XI2	-	-11.8	-736	-130	-	151.2	1.098	0.82	0.01	0.31
	Turkey XI3	-	-11.8	-748	-131	-	140.5	0.080	1.59	0.02	0.33
<b>reference compositions</b>											
air		-8.6 to -7.6	-47.7 to -41.2	+100 to +200	-70 to -90	0	5.24	16.453	31.57	0.65	1
ASW							0.05	0.172	1.07	0.04	1

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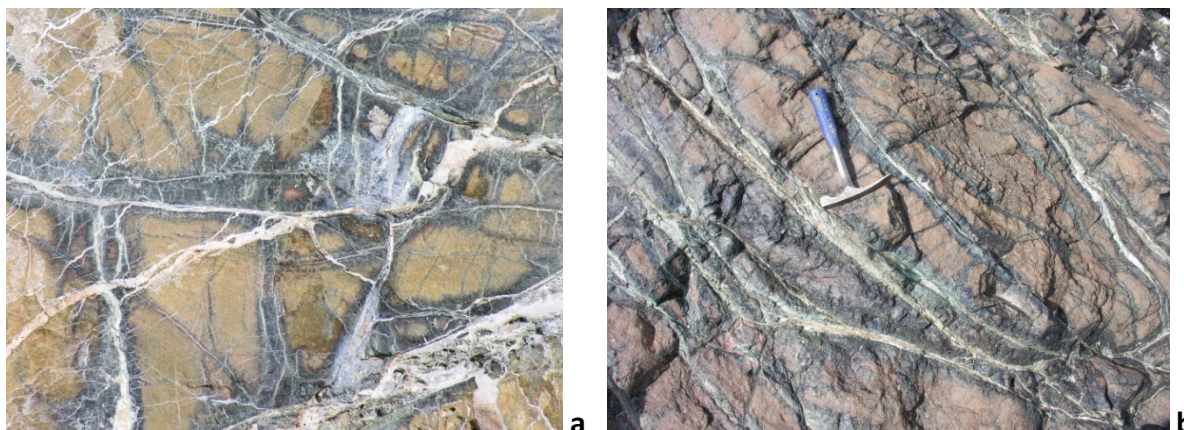
1345 **Table 2.**  $\delta^{13}\text{C}$  (PDB) values of  $\text{CO}_2$  and  $\text{CH}_4$  (‰).  $\delta\text{D}$  (SMOW) values of  $\text{H}_2$  and  $\text{CH}_4$  (‰).  
1346 Noble gas analyses  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  (ppmv), and R/Ra (helium isotopic ratios normalized  
1347 to the air isotopic  $\text{Ra} = ^3\text{He}/^4\text{He} = 1.4 \cdot 10^{-6}$ ).  $\text{C}_2+$  contents in all the gas samples are very low,  
1348 below the threshold of analytical precision ( $< 0.01\%$ ). Global relative uncertainties (at  $1\sigma$ ) for  
1349 quantification of noble gases with the method used is estimated in the range He:  $\pm 10\%$ ; Ne:  
1350  $\pm 20\%$ ; Ar:  $\pm 5\%$ ; Kr:  $\pm 10\%$ . The global relative uncertainty ( $1\sigma$ ) for the R/Ra ratio is in the  
1351 range  $\pm 2\%$ .

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**SUPPLEMENTARY MATERIAL.**

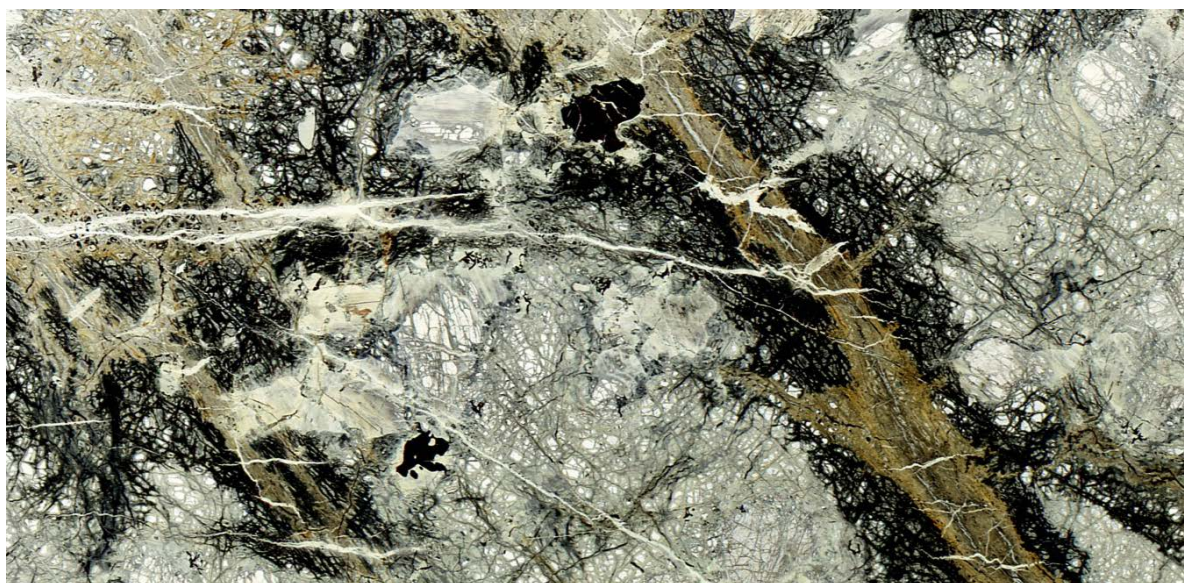
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1356 **Figure S1 a and b-** Photos illustrating alteration processes in the peridotites of Oman. Brow  
1357 zones correspond to poorly serpentinized peridotites, black zones correspond to serpentinized  
1358 parts along the fractures which are filled by Mg-Ca carbonate cements.

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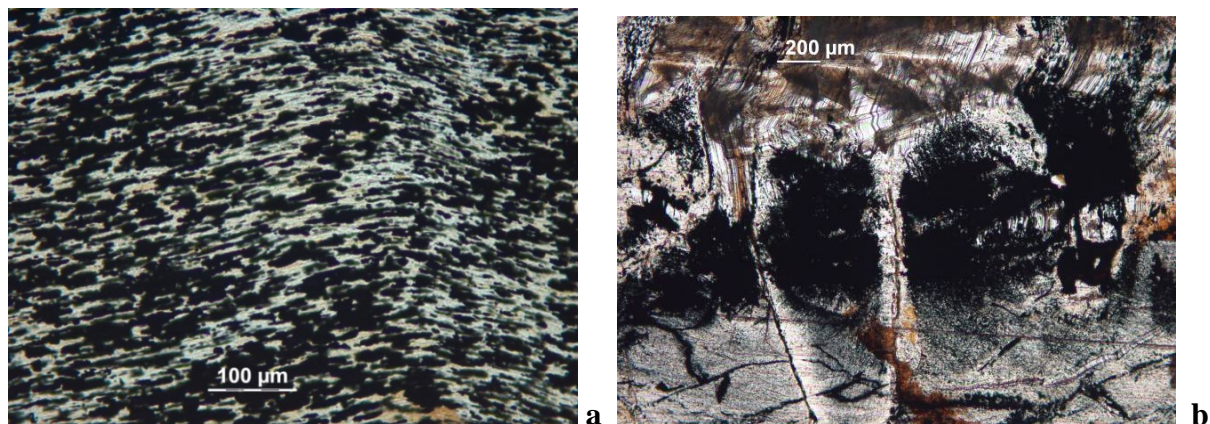
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**2 cm**

1363 **Figure S2 -** Photo of a thin section illustrating alteration processes in the peridotites of Oman.  
1364 grey zones correspond to poorly serpentinized peridotites, black zones correspond to  
1365 serpentinized parts along the fractures which are filled by Mg-Ca carbonate cements which  
1366 appear in brown.

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1373 **Figure S4** - An example of a blue pool in Oman (Sayah). Note the blue color related to the  
1374 formation of carbonates in water. A precipitate of aragonite and brucite is observed at the  
1375 bottom of the basin.





1376

1377 **Figure S5** - Another example of a blue pool in Oman. The water in these basins shows pH  
1378 values generally between 11 and 12. A film of calcite develops on the water surface and a  
1379 precipitate of aragonite and brucite is deposited at the bottom of the basin.

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1382 **Figure S6** - Calcite film appearing on the surface of ultra-basic water (Oman).

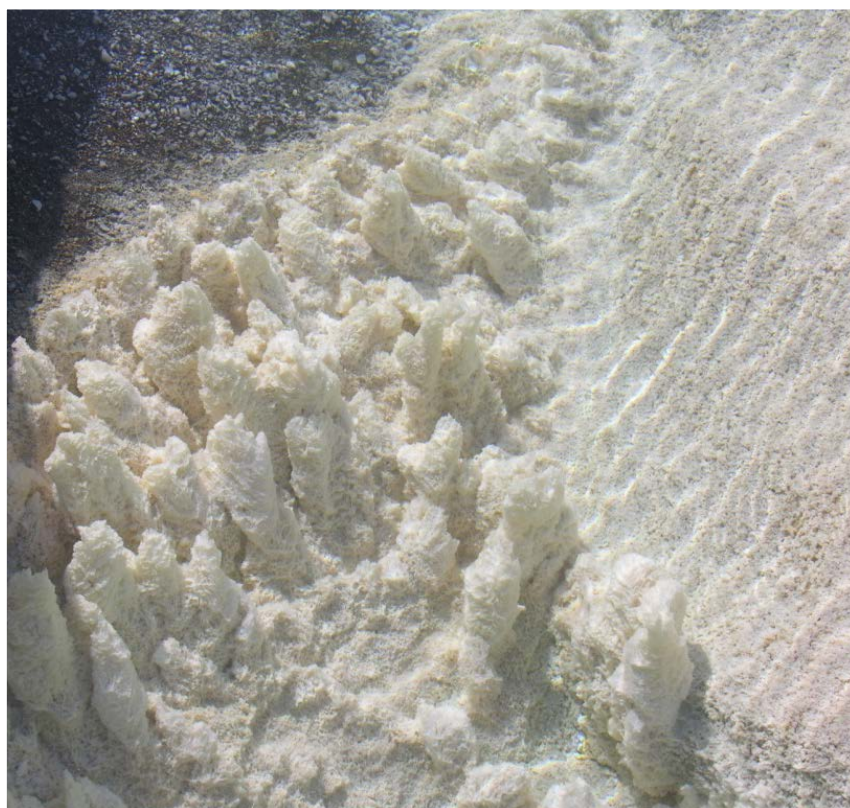


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1385 **Figure S7** - Aragonite precipitation in ultra-basic water (Oman).



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1387 **Figure S8** - Aragonite chimneys forming in ultra-basic water (Oman).

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1391 **Figure S9** - Needles of primary Brucite in the foreshore of the Baie des Kaoris (New  
1392 Caledonia).

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Sample	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Type of rock	RXD
WAA3	11.53	2.19	Carbonated peridotite	magnesite
O26A	33.19	8.15	Carbonate cement in fracture	magnesite
O2	31.18	-8.28	Carbonate cement in fracture	dolomite
WAA1	29.58	-6.65	Carbonate cement in fracture	dolomite
O1	30.2	-6.53	Carbonate cement in fracture	dolomite
O35B	28.99	-12.47	Surface carbonate crust	aragonite, calcite
O16A	23.57	-9.14	Surface carbonate crust	calcite
O31	29.21	-8.91	Surface carbonate crust	aragonite
O18	28.96	-8.16	Surface carbonate crust	dolomite, calcite
O11	18.11	-4.15	Surface carbonate crust	calcite
O10	23.87	-1.48	Surface carbonate crust	calcite
O23B	29.29	-10.51	Surface carbonate crust	aragonite, dolomite

1395

1396 **Table S1** -  $\delta^{13}\text{C}$  PBD (‰) and  $\delta^{18}\text{O}$  SMOW (‰) of carbonate rocks (carbonated peridotite,  
 1397 carbonate cement in fracture, surface carbonate crust) associated with the ophiolites of Oman.

1398