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

3
4 Christèle Vacquand^a, Eric Deville^a, Valérie Beaumont^a, François Guyot^b, Olivier
5 Sissmann^a, Daniel Pillot^a, Carlo Arcilla^c, Alain Prinzhofer^{a, d}

6
7 ^a IFP Energies nouvelles, 1 & 4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex,
8 France

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

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

12 ^d Present address: GEO4U, Praia de Botafogo 501, 22250-040 Rio de Janeiro, Brazil

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

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18 Corresponding author: Eric Deville

19 *E-mail address:* eric.deville@ifpen.fr

20 *Telephone number:* +33 1 47 52 69 54

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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 H₂, CH₄
38 and N₂ in various proportions. The relative contents of the three main gas components show 4
39 distinct types of gas mixtures (H₂-rich, N₂-rich, N₂-H₂-CH₄ and H₂-CH₄). These types are
40 interpreted as reflecting different zones of gas generation within or below the ophiolitic
41 complexes. In the H₂-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 N₂-rich, N₂-H₂-CH₄ and H₂-CH₄ types. H₂-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 Fe²⁺ and alkaline conditions that favor H₂ production. CH₄ is produced either directly by
47 reaction of dissolved CO₂ with basic-ultrabasic rocks during the serpentinization process or in
48 a second step by H₂-CO₂ interaction. H₂ is present in the gas when no more carbon is
49 available in the system to generate CH₄. The N₂-rich type is notably associated with relatively
50 high contents of crustal ⁴He and in this gas type N₂ is interpreted as issued mainly from
51 sediments located below the ophiolitic units.

52

53

54 **Introduction**

55

56 Serpentinization generates natural emission of H₂ 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 H₂-rich fluids
61 are associated with N₂ and CH₄ contents and on black smokers with CO₂ (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 H₂ seepages are also
64 reported onshore, in former oceanic rocks present in ophiolite complexes. Notably, H₂
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, H₂-rich gas is either dissolved or present
75 as free gas bubbling in the ultra-basic water. In other cases, H₂-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). H₂-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 H₂ 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^{II} into ferric
89 iron Fe^{III}, iron being the most abundant transition metal in ultrabasic and basic rocks. Fe^{II} 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^{III}-bearing minerals, such as magnetite. These
92 mineral assemblages are observed in the field, where peridotites are largely serpentinized,
93 mostly along fracture systems. The question of H₂ 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^{II} 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 H₂
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 H₂. According to the numerical model proposed by McCollom
105 and Bach (2009), the highest rates of H₂ 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 H₂-bearing gas seepages yield not only H₂ 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 CH₄ and N₂ associated to H₂ 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 Ca^{2+} , OH^- , H_2 and 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. H_2 -rich gas seepages associated
139 with Ca^{2+} - OH^- -rich groundwater in the Semail ophiolite of Oman were first studied by Neal
140 and Stanger (1983). They proposed that H_2 is the by-product of a low temperature (20-50°C)
141 serpentinization that depends on Fe^{II} hydroxide availability and oxidation by meteoric water
142 that occurs in 2 stages: 1) oxidation by atmospheric 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 H_2 -rich gas samples are inherited from interaction of meteoric water
145 with Fe^{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 H₂. H₂ 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). H₂-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 N₂-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 (10⁻³ 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 $^{13}\text{C}/^{12}\text{C}$ (CH_4 and CO_2) and
189 D/H in (CH_4 and 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 δ 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. N_2 has been
194 purified in a vacuum line. CH_4 and H_2 were oxidized in a Cu-oxide oven to CO_2 and water
195 vapor, respectively. These produced gases were cryogenically trapped for separation from 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 ^4He , ^{20}Ne , ^{36}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 (1σ) on the quantification of ^4He 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 H₂, N₂ and CH₄ as
228 major components. Figure 4 displays H₂, N₂ and CH₄ 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 H₂, CH₄ and N₂. Three of these types are associated with water seeps:
231 H₂-rich type; N₂-H₂-CH₄ type and N₂-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 (H₂-CH₄) corresponds to gas seepages in fractures without associated water flow.

234 Carbon and hydrogen isotopic composition ($\delta^{13}\text{C}$ and δD) of H₂, CH₄, CO₂ and nitrogen
235 isotopic composition ($\delta^{15}\text{N}$) of N₂ are reported in Table 2. δD of H₂ values are very negative
236 and comprised in a narrow range from -756 to -699‰, except for the sample from Nagsasa
237 (Philippines) with δD of H₂ = -664‰ (Fig. 6, 7). The highest values of δD of CH₄ 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 CH₄ were
240 obtained, up to +7.9‰, while δD of CH₄ are ranging from -428 to -130‰.

241 Hydrogen isotopic fractionation between H₂ and CH₄ depends on seepage types. The highest
242 isotopic fractionations between species are observed on dry seepages where δD 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 H₂-rich type are very close to the air end-member with a slight crustal
247 contribution. Those of the N₂-H₂-CH₄ type show higher N₂ and CH₄ contents and present
248 either a crustal (Oman), or mantle (Kaoris, New Caledonia) or crust plus mantle contribution
249 (Oman). The samples of the H₂-CH₄ type present both crustal and mantle contributions, with a
250 very marked mantle contribution for the Nagsasa sample (Zambales, Philippines). N₂-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 H₂-rich type* shows dominant H₂ contents (61.0 to 87.3% mol) associated with some N₂
257 (less than 35% mol) and some CH₄ (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⁻ 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 Ca²⁺ and OH⁻ ions with
265 the CO₂ 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⁻ and Na⁺ ions (Cl⁻ between 120 and 380 mg/l; Na⁺ 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 δ¹³C 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 N₂ vs fossil noble gas ³⁶Ar 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 N₂-H₂-CH₄ type* is characterized, by higher N₂ values (from 45 to 65 mol%) compared
275 to the previous gas type. Therefore N₂ becomes the main gas. H₂ contents range from 25 to 36
276 mol%. CH₄ concentrations are similar to those of the H₂-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 H₂-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 N₂/³⁶Ar 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 H₂/³⁶Ar and
284 ⁴He/³⁶Ar ratios (Deville and Prinzhofer, 2016). δ¹³C of methane recorded for this gas type
285 ranges between -38.5 and -32.4‰ (Deville and Prinzhofer, 2016).

286

287 3) *In the N₂-rich type*, the dominant gas compound is N₂ (over 91 mol%). Gas mixture is H₂-
288 free with low CH₄ 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 CH₄ 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 N₂/³⁶Ar 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 H₂
300 gases. They show lower concentrations of Na⁺ and K⁺ ions and contain HCO₃⁻ ions, which is
301 not the case of the ultra-basic springs with H₂ 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 H₂-CH₄ type* shows mostly H₂ and CH₄ 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 CH₄/H₂ 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 CH₄/H₂ 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 H₂-CH₄ gases do not display predominantly
318 atmospheric features and ²⁰Ne and ⁸⁴Kr concentrations are quite low compared to other types
319 of gas mixtures (Table 2). $\delta^{13}\text{C}$ values of CH₄ are high and fairly constant (between -12 and -

320 5‰; Fig. 8), as well as δD of CH_4 which range from -175 to -130‰. The δD 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 δD
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 δD
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 prings 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 δD of CH_4 is significantly higher compared to the δD 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.

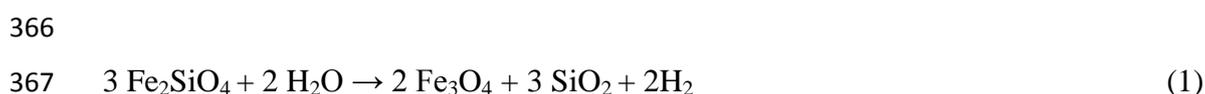
343

344 *Hydrogen origin*

345

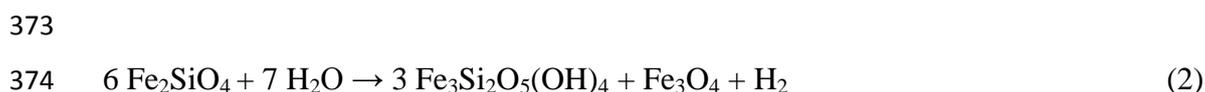
346 As mentioned in introduction, H_2 sources of gas seepages in ophiolitic contexts are classically
347 credited to modern hydration processes at low temperature during the weathering of ultrabasic
348 and basic rocks (mostly peridotite and gabbro). At depth, within ophiolitic rocks, biological
349 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 H₂ 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), H₂
 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^{II},
 359 Mn^{II}, Ni^{II}...), Fe^{II} being by far the most abundant electron donor in ultrabasic-basic rocks.
 360 During the serpentinization process, Fe^{II}-rich minerals, such as olivine [(Mg^{II},Fe^{II})₂SiO₄] are
 361 oxidized and form Fe^{III}-bearing minerals, such as magnetite [Fe₂^{III}Fe^{II}O₄] or Fe^{III}-bearing
 362 serpentine (Evans et al., 2008), with coeval reduction of water generating H₂. 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, Fe₂SiO₄)
 365 tends to react as,



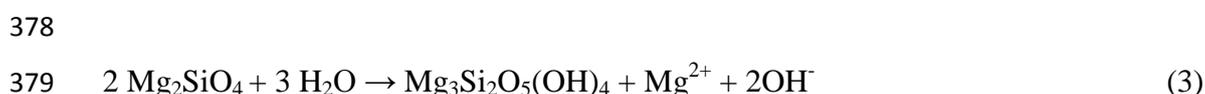
366
 367 *Fayalite + water → Magnetite + silica + dihydrogen*

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
 370
 371
 372
 373
 374
 375 *Fayalite + water → Fe-Chrysotile + Magnetite + dihydrogen*

376
 377 The Mg-endmember of olivine (Forsterite, Mg₂SiO₄) reacts as,



376
 377
 378
 379
 380 *Forsterite + water → Chrysotile + magnesium ions + hydroxyl ions*

381
 382 In presence of dissolved inorganic carbon (DIC) in subsurface, Mg²⁺ 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 Mg²⁺ ions are prone
 385 to react with OH⁻ to form brucite, Mg(OH)₂ (which is commonly found in the ultra-basic
 386 springs studied here, notably in Oman; Neal and Stanger, 1984) leaving finally OH⁻ 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 OH^- and 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 Ca^{2+} and 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 H_2 caused by ferrous iron oxidation and water reduction associated with a rise of pH
 400 due to OH^- production and associated with the presence of Ca^{2+} in the ultra-basic water. The
 401 richer in iron is the olivine, the more H_2 and the less OH^- are produced.

402 It has been experimentally demonstrated that highly fractured/altered peridotite is more prone
 403 to generate H_2 than a massive unaltered peridotite suggesting a role of the reacting surfaces
 404 and possibly that Fe^{II} -bearing secondary formed minerals, such as Fe^{II} -bearing brucite and
 405 serpentine, and the presence of N-species may also contribute to form H_2 (experiments at
 406 25°C; Okland et al., 2014, see also Klein et al., 2015).

407 The conditions of generation of H_2 can be estimated notably using hydrogen isotopic data. In
 408 the studied ophiolitic massifs, whatever are the characteristics of the H_2 -bearing gas types, δD
 409 values of H_2 are all very low in the analyzed gas samples (between -756 and -664‰).
 410 Abrajano (1988) mentioned, δD values of 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 δD of 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 δD values of H_2 observed in oceanic settings decrease with temperature and appear as a
 415 thermometer for H_2 production at isotopic equilibrium with seawater (Proskurowski et al.,
 416 2006). Low δD values of H_2 in ophiolitic massifs are classically considered as revealing
 417 relatively low temperatures of the generation of H_2 (Neal & Stanger 1983). Indeed, using
 418 either (1) the Horibe and Craig (1995) H_2O - H_2 and CH_4 - H_2 geothermometers which consider
 419 isotope fractionations between liquid H_2O or CH_4 and H_2 , or (2) Bottinga's 1969 water vapor-
 420 hydrogen method, this strongly suggests that the generation of H_2 occurred at lower

421 temperature conditions than at most of the hydrothermal vents of mid-oceanic ridges. H₂O–H₂
422 is seen as the preferred geothermometer but it implies that chemical equilibrium between H₂
423 and H₂O has been reached (see discussion below). It is possible that chemical and isotopic
424 equilibrium have been achieved between H₂ and CH₄ (see the following paragraph). Whatever
425 the geothermometer used, either the Horibe and Craig (1995; Fig. 7) H₂O–H₂ and CH₄–H₂
426 geothermometers, or the Bottinga (1969) geothermometer, we obtained relatively narrow
427 windows of temperature conditions in the ranges 17 to 42°C for H₂ of the H₂-rich type and
428 24–50°C for H₂ of the N₂–H₂–CH₄ gas type, whereas the temperature conditions seem much
429 more heterogeneous and reach much higher temperatures in the H₂–CH₄ gas type, notably for
430 the samples of the Philippines (up to 136°C, taking into account the δD_{H_2} values from
431 Abrajano et al., 1988).

432 To decipher the conditions of generation of H₂, it is possible to compare H₂ 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 H₂-rich gas type displays N₂/³⁶Ar 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 H₂ production. In
438 this case, H₂O 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 H₂ production, initial gas/water equilibrium with atmosphere is disrupted
442 and atmospheric nitrogen and noble gases are mixed with neo-formed gases (H₂ and CH₄) and
443 migrate upwards with no further addition of another gas component. The preservation of
444 atmospheric relative proportions of fossil noble gases (²⁰Ne, ³⁶Ar, ⁸⁴Kr) 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 ⁴He
448 contents (< 20 ppm), are in good agreement with Neal and Stanger's (1985) interpretation
449 which asserts that Ca²⁺-OH⁻ water originates from meteoric water recharging at high
450 elevations. The presence of ⁴He in subsurface gas is classically interpreted as the result of a
451 lengthy residence time at depth allowing ⁴He to accumulate significantly due to natural
452 radioactive decay of ²³⁵U, ²³⁸U and ²³²Th present in crustal rocks (Ballentine and Burnard, 2002).
453 Paukert et al. (2012) considered, from their modelling of CO₂ 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 ^4He 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 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 H_2 generation process
461 which occurred deeper than in the H_2 -rich gas type, in higher temperature conditions as
462 already suggested by δD values of H_2 .

463

464 *Methane origin*

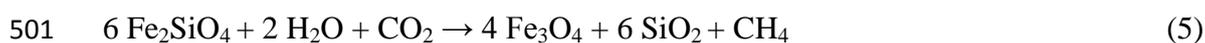
465

466 Methane generation associated with fluid-rock interaction in ophiolitic contexts remains
467 unclear. In terrestrial ultrabasic-basic contexts at moderate temperatures (below 150°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 (H_2O or H_2), hydrogen in CH_4 can be considered as primary (*i.e.*, issued from H_2O reacting
477 with carbon and preceding 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 H_2 intermediate by
479 reactions between carbon and 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 CH_4
482 during hydration of ultrabasic rocks without an H_2 intermediate, notably with moderately
483 altered peridotites. In both cases, hydrogen is issued from H_2O , either primarily or
484 secondarily. Suda et al. (2014), based on a study of hydrogen isotopic data of CH_4 , H_2 and
485 H_2O (Fig. 7), defined different domains corresponding to different processes allowing to
486 distinguish CH_4 generation by hydrogenation from water (primary) or from H_2 (secondary).
487 Primary CH_4 production is regarded as a direct interaction between Fe^{II} -rich minerals and

488 dissolved CO₂. CH₄ production tied to ferrous mineral reactions with CO₂ 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 CH₄
 491 generation (Garcia et al., 2010). However, early production of CH₄ (before H₂ 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 H₂ and CH₄ (Okland et al., 2014), in the same proportions as those measured in
 495 this study for the H₂-rich gas type. The presence of CO₂ is a favorable factor for olivine
 496 dissolution (Oze and Sharma, 2005), which releases aqueous Fe^{II}. Primary production of CH₄
 497 from H₂O and CO₂ (DIC in water) is achieved in a similar way as the H₂ production through
 498 the oxidation of iron (see above). The reaction of the Fe-endmember of olivine in presence of
 499 dissolved CO₂ 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^{II}-bearing brucite-type minerals (for example amakinite) and Fe^{II}-bearing serpentines
 517 are also good candidates to react with dissolved CO₂, 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 H₂-CH₄ 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 CH₄ generated from an H₂ intermediate (gas samples collected in
523 ultra-basic springs showing δD values of CH₄ 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 δ¹³C values (δ¹³C_{CH₄} between -13
529 and +8‰, δ¹³C_{magnesite} between +2 and +8‰; see supplementary material). This is compatible
530 with a non-atmospheric carbon origin of CH₄ that could derive from mantellic or metamorphic
531 CO₂ 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 CO₂ which after fractionation during carbonate precipitation give δ¹³C
534 values between -28 and -5‰ (Kelemen et al., 2011; see also supplementary material).

535 Considering secondary production of methane, via an H₂ intermediate, several pathways of
536 CH₄ 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, H₂ produced by serpentinization is susceptible to be subsequently
541 consumed in a CH₄ producing reaction, involving a source of carbon which can be C^o, CO or
542 CO₂, 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 δ¹³C 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, CO₂ is reduced to
557 CH₄ through the oxidation of H₂ (so the reaction is controlled by H₂ 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 CH₄.
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 CO₂
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 a reaction between hydrogen issued from depth
589 and a source of carbon provided by atmospheric CO₂. 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 CH₄ from H₂ and CO₂ 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 CH₄ probably reflect different
599 sources of carbon or different CH₄ generation processes. The present study shows that (a) H₂-
600 rich gases from Oman display $\delta^{13}\text{C}$ of CH₄ between -12.8 and +7.9‰, while (b) in the
601 Philippines $\delta^{13}\text{C}$ of CH₄ 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 H₂-CH₄ type display a
603 $\delta^{13}\text{C}$ of CH₄ values between -7.9 and -11.9‰ (Horgormez et al., 2008 and this study),
604 whereas (d) for New-Caledonia some gases from N₂-H₂-CH₄ 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 CH₄ from Oman, the
610 Philippines and Turkey might correspond to a carbon source, probably CO₂, 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 H₂-bearing gas samples studied here (as well as
618 those analyzed in previous studies) show only locally tiny traces of CO₂ 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 N₂-rich gas type of Oman (seeping out from below the ophiolites), in which CO₂

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 C_{2+} in the gas mixtures (below 0.01%), methane may originate
627 from a reaction between 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 CO_2 in H_2 -bearing gas
630 samples, neither HCO_3^- nor 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 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 H_2 to be present in the gas, otherwise all the generated H_2 would have been consumed
635 to generate CH_4 , as it was suggested by Milesi et al. (2016) in the Solimes Basin in Brazil.

636 In both, H_2 -rich and N_2 - H_2 - CH_4 gas types, CH_4 contents being lower than 20 mol%, this
637 suggests a very limited carbon source compared with the H_2 - 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 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. H_2 - CH_4 gas type might correspond to
643 such a system connected to deep sources of carbon.

644 Considering oceanic hydrothermal vents, values of δD of 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, δD of 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 δD values of 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 δD of methane
652 in spring water raise the question of a possible microbial role in methane generation.

653 For the H₂-CH₄ and N₂-H₂-CH₄ gas types a remarkable correlation exists between H₂ and CH₄
654 when normalized to ³⁶Ar (Fig. 11A) wherever is the site studied in Oman, in the Philippines
655 and New Caledonia. A similar correlation exists between H₂ and CH₄ when normalized to
656 ⁸⁴Kr, (Fig. 11B). For the CH₄-H₂ and N₂-H₂-CH₄ gas types, this suggests that, independently
657 of the considered ophiolite and geological context, generations of H₂ and CH₄ 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 H₂-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 (H₂-CH₄ 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 H₂, for example in Chimaera (Turkey), up to 40 mol% of the CH₄ 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 C₂+ (C₂-C₆ 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 CH₄ relative contents
671 together with higher δD of CH₄ 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 H₂-
674 CH₄ 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 H₂ and CH₄
685 are produced from altered peridotites (Okland et al., 2014).

686 Considering the geochemical results of this study, N₂ present in the gas of the H₂-rich type
687 shows N₂/³⁶Ar and N₂/⁸⁴Kr ratios generally equivalent or slightly higher than those of ASW,
688 suggesting mainly an atmosphere origin for N₂ via a fractured aquifer (Fig. 12A and B).

689 Samples of the N₂-H₂-CH₄ gas type, which show higher N₂ contents than H₂ contents
690 compared to the H₂-rich gas type display notably a nitrogen enrichment relative to ³⁶Ar and
691 ⁸⁴Kr (Fig. 12A and B), suggesting an addition of non-atmospheric nitrogen. This contributes
692 to dilute the neo-formed H₂ and CH₄ (Deville and Prinzhofer, 2016). Samples of the N₂-rich
693 gas type show a ⁴He enrichment correlated with the N₂ enrichment when compared to
694 atmosphere (Fig. 13). This suggests that non-atmospheric N₂ might be of crustal origin
695 associated to radiogenic helium from depth. The R/Ra ratio (³He/⁴He ratio of the sample
696 normalized over the same ratio for the air = 1.384 × 10⁻⁶) 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 H₂-rich type and the N₂-H₂-CH₄ type are possibly linked to the
700 existence of two different reactive zones for the production of H₂-rich fluids in peridotitic
701 ground waters: one (H₂-rich) being more surficial than the other (N₂-H₂-CH₄-rich) and that
702 two different reactive fluids should be considered: (1) a meteoric fluid in the more surficial
703 environment (H₂-rich) and (2) a deep N₂-bearing fluid with crustal signature, probably issued
704 from sediment metamorphism from below the obducted ophiolitic units.

705 Samples of the N₂-H₂-CH₄ type could also result from the mixing of H₂-rich gas and N₂-rich
706 gas. These N₂-rich samples contain mostly N₂ and no or little H₂. Because they were found in
707 hot water springs, displaying pH between 6.9 and 10 and relatively high ⁴He 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 ⁴He contents. This deep N₂ 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 N₂
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 H₂-rich gas type are susceptible to
715 generate fluids with the chemical signatures of the N₂-H₂-CH₄ gas type where N₂ dilutes H₂
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 (H₂-CH₄ 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‰ in Rustaq (Oman), which is consistent with previous studies (Sano et al, 1993) and -
721 0.1‰ 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‰ and -2.1‰ 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‰ (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 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 N_2 . The plot of R/Ra
737 versus $^{20}\text{Ne}/^4\text{He}$ (Fig. 10) shows that the N_2 -bearing gases are ranging on a mixing line
738 between the crust and the atmospheric end-member. In the 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 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}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). ^4He 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 ^4He component. A potential interpretation for
751 the origin of deep 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 N₂, CH₄ in proportions under 20 mol% and the presence of
762 H₂ 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 CH₄
764 and low N₂. In all cases, H₂ is interpreted as a consequence of oxidation of Fe^{II}-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 H₂ generation, Fe^{III}-bearing mineral were formed at the vicinity of the sites of
768 oxidation of Fe^{II}-bearing mineral without an important mobility of Fe²⁺. A relatively shallow
769 H₂ production is substantiated in the H₂-rich gas type by its association with quasi-
770 atmospheric noble gases. It is consistent with the D/H isotopic data of H₂ 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 H₂ production in the N₂-H₂-CH₄ gas type and notably in the
773 H₂-CH₄ gas type (probably above 100°C locally). The preservation of H₂ 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 CH₄, multiple origins are supported by the carbon isotopic data. The
777 carbon and hydrogen sources are various. Both, a primary CH₄ (from H₂O reacting with DIC)
778 and a secondary CH₄ (from an H₂ intermediate reacting with a C source) are suspected for the
779 H₂-CH₄ gas type and for N₂-H₂-CH₄ and H₂-rich gas types, respectively. In the gas mixtures,
780 N₂ 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 N₂, a deep mantle originating fluid carrying primordial CO₂. 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 H₂-rich gas type from meteoric water

787 interacting with the ophiolite. The deepest kitchen is interpreted as the H₂-CH₄ gas type from
788 a deep fluid (carrying CO₂ from the mantle, or from dissolved carbonates or organic carbon)
789 interacting with the ophiolite. H₂-CH₄ gas flows are generally more localized (focused) and
790 these flows are generally higher than the other H₂-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 H₂ to react during the rise
793 toward the surface, notably by preventing any biological consumption of H₂ which required
794 an aqueous media. The N₂-bearing fluids are probably generated mostly from the sediments
795 located below the ophiolitic units and migrate upwards forming the N₂-rich gas type when
796 reaching the surface or the N₂-H₂-CH₄ type if mixing occurs between the N₂-rich and the H₂-
797 rich types (Fig. 14).

798

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800

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810 **References**

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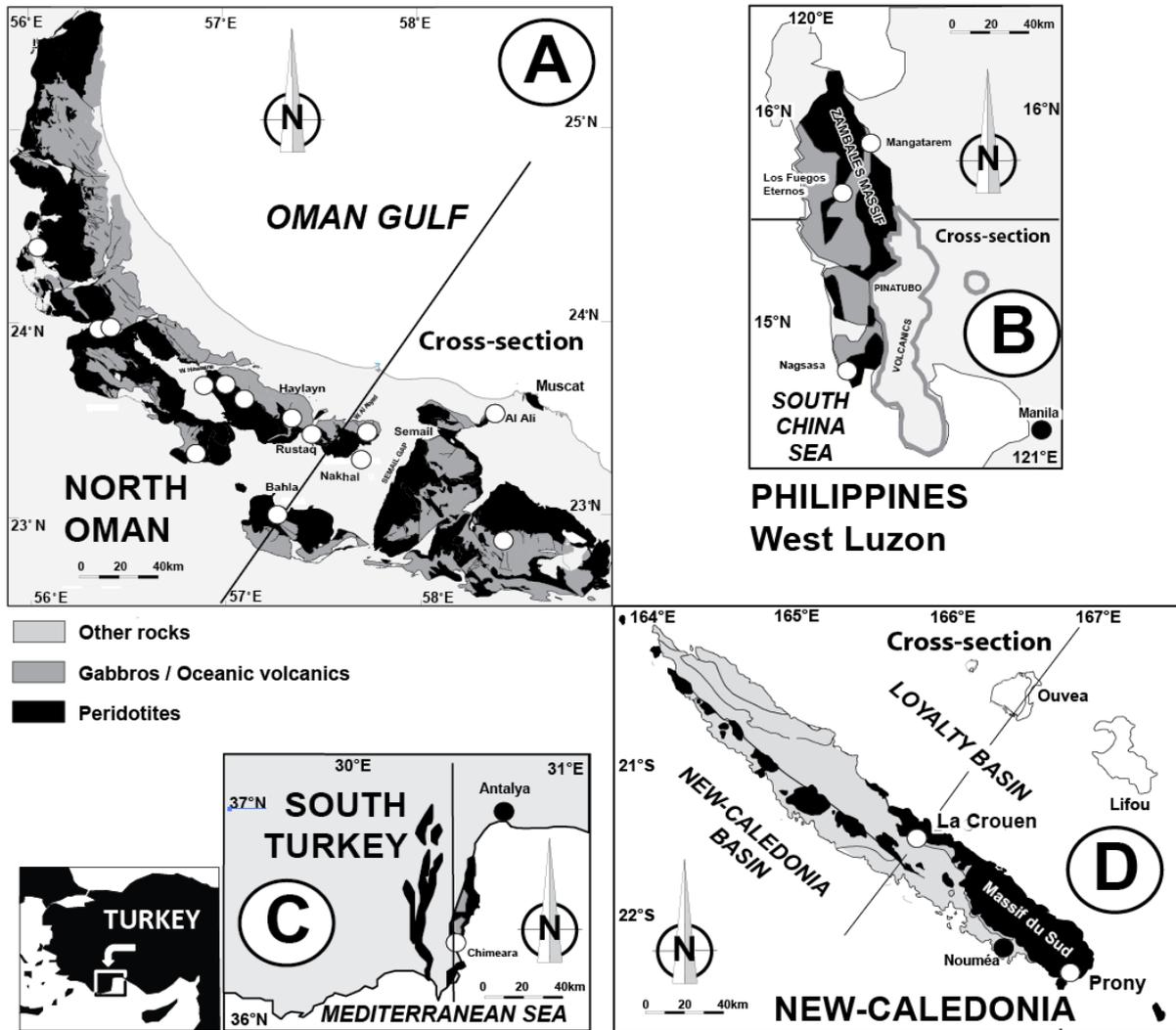
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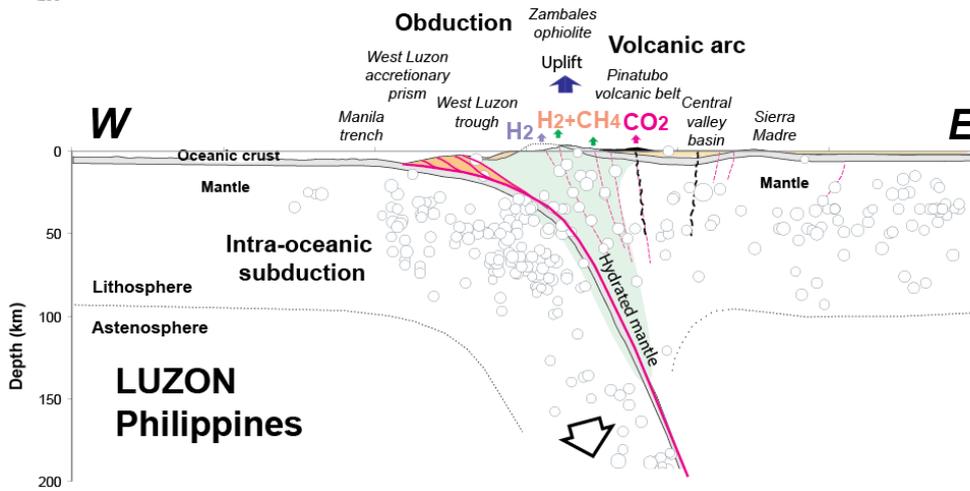
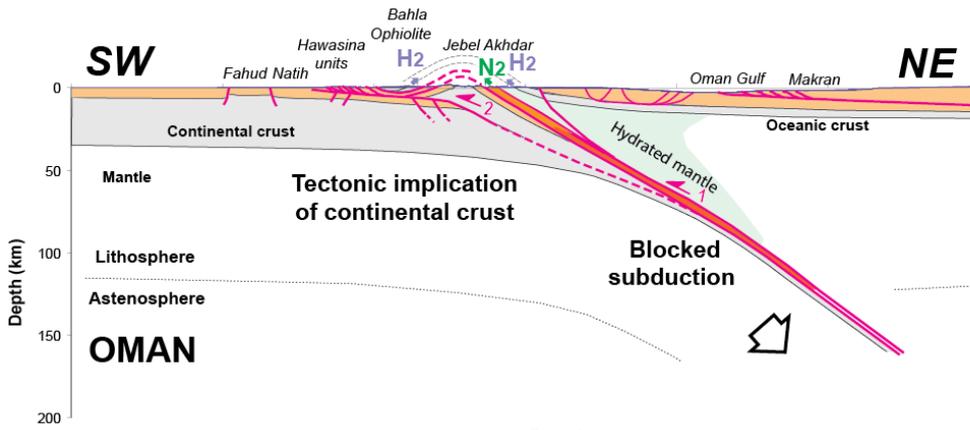
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1189 **Figure 1** – Structural sketch-maps of the different sites studied in this work in Oman (A), the
 1190 Philippines (B), Turkey (C) and New-Caledonia (D) (same scale), with the location of the
 1191 sampling sites and the location of the cross-sections 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.

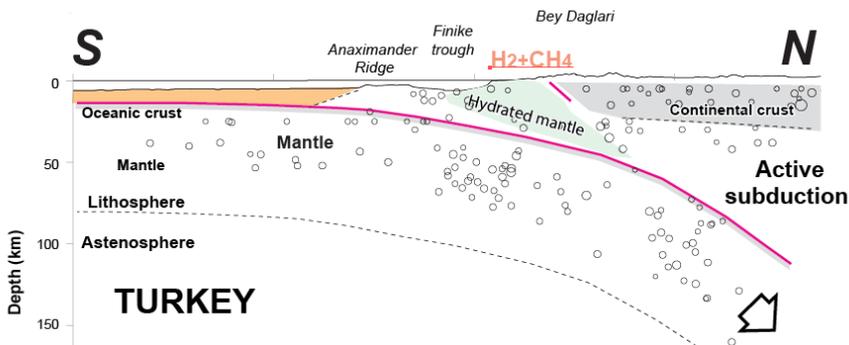
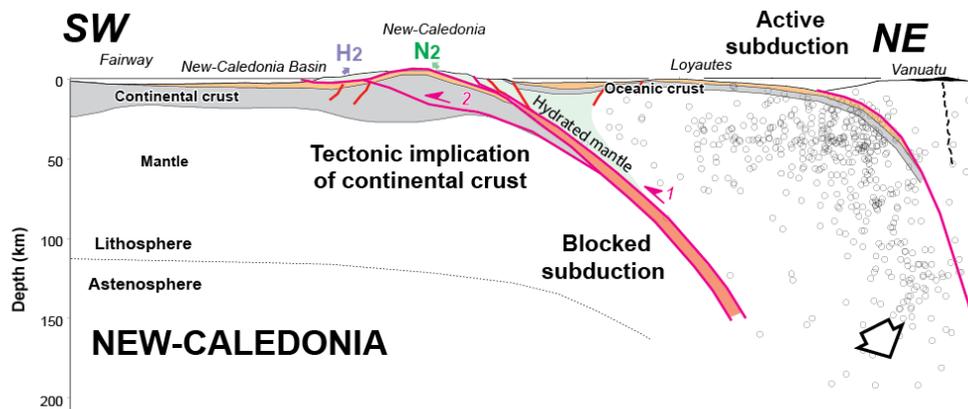
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1200 **Figure 2** - Geological cross-sections of the different sites studied in this work (same scale;
1201 earthquake epicenters from USGS data base). A 2D cross-section for the area of Chimaera in
1202 Turkey is not shown because of too complex 3D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

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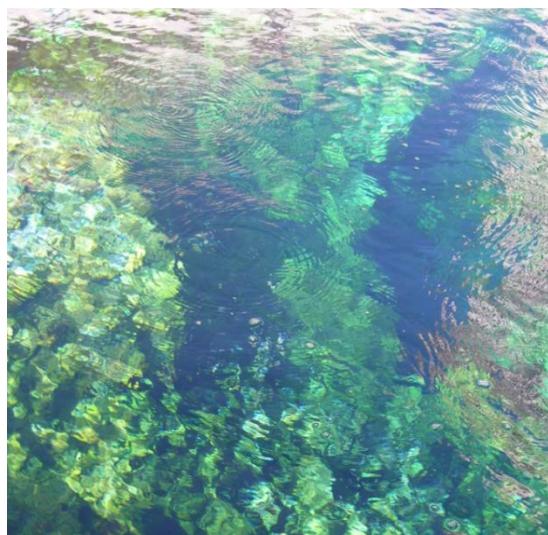
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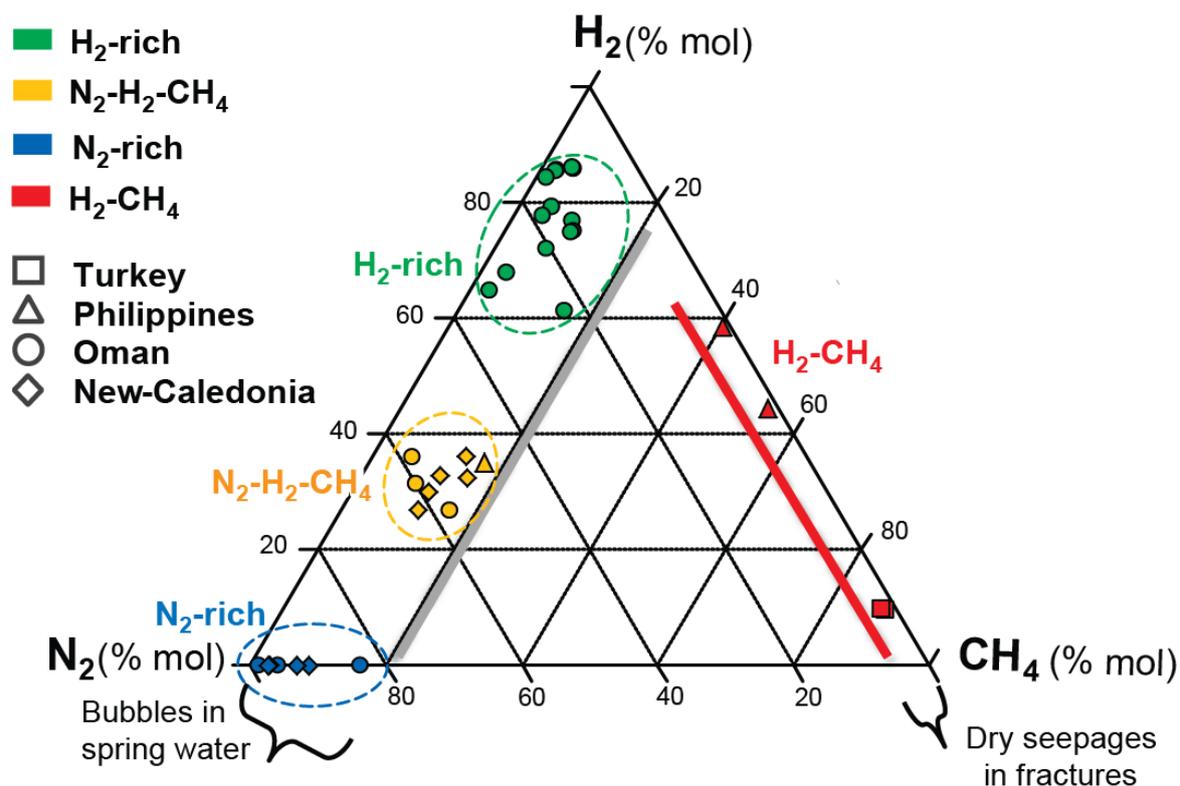


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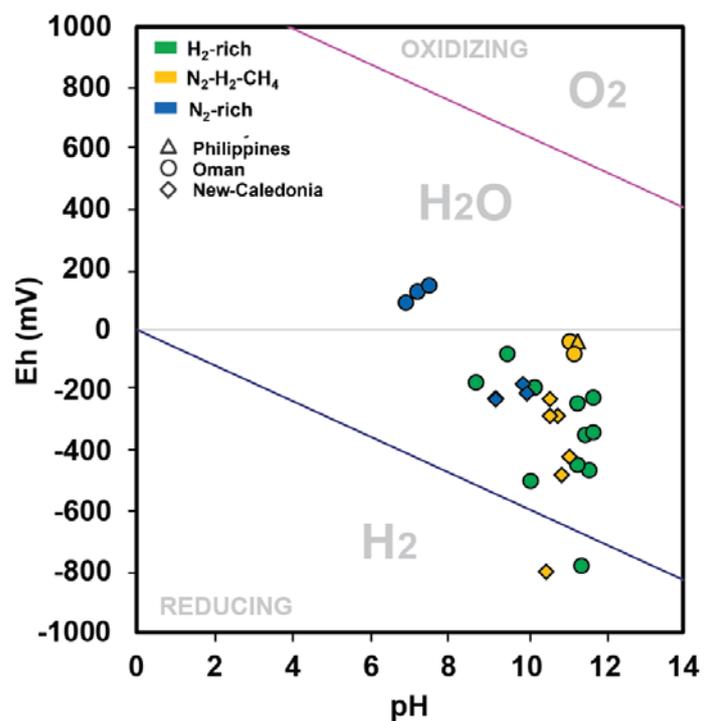
1211 **Figure 3** – Examples of gas seepages. **A:** Bubbling H_2 -rich gas flow in ultra-basic water
1212 (Oman). **B:** Bubbling N_2 - H_2 - CH_4 gas flow (foreshore of the Baie du Carénage, New
1213 Caledonia). **C:** Bubbling N_2 -rich gas flow (Rustaq, Oman). **D:** Burning H_2 - CH_4 gas flow
1214 (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 : H₂, N₂ and CH₄ in a triangular diagram (% mol). Four
 1219 different types of gas mixtures can be defined according to the relative contents of H₂, N₂ and
 1220 CH₄. Distinct chemical features correspond to distinct seepages styles : N₂-containing gas
 1221 mixtures are associated with water and seep in water streams, whereas N₂-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).

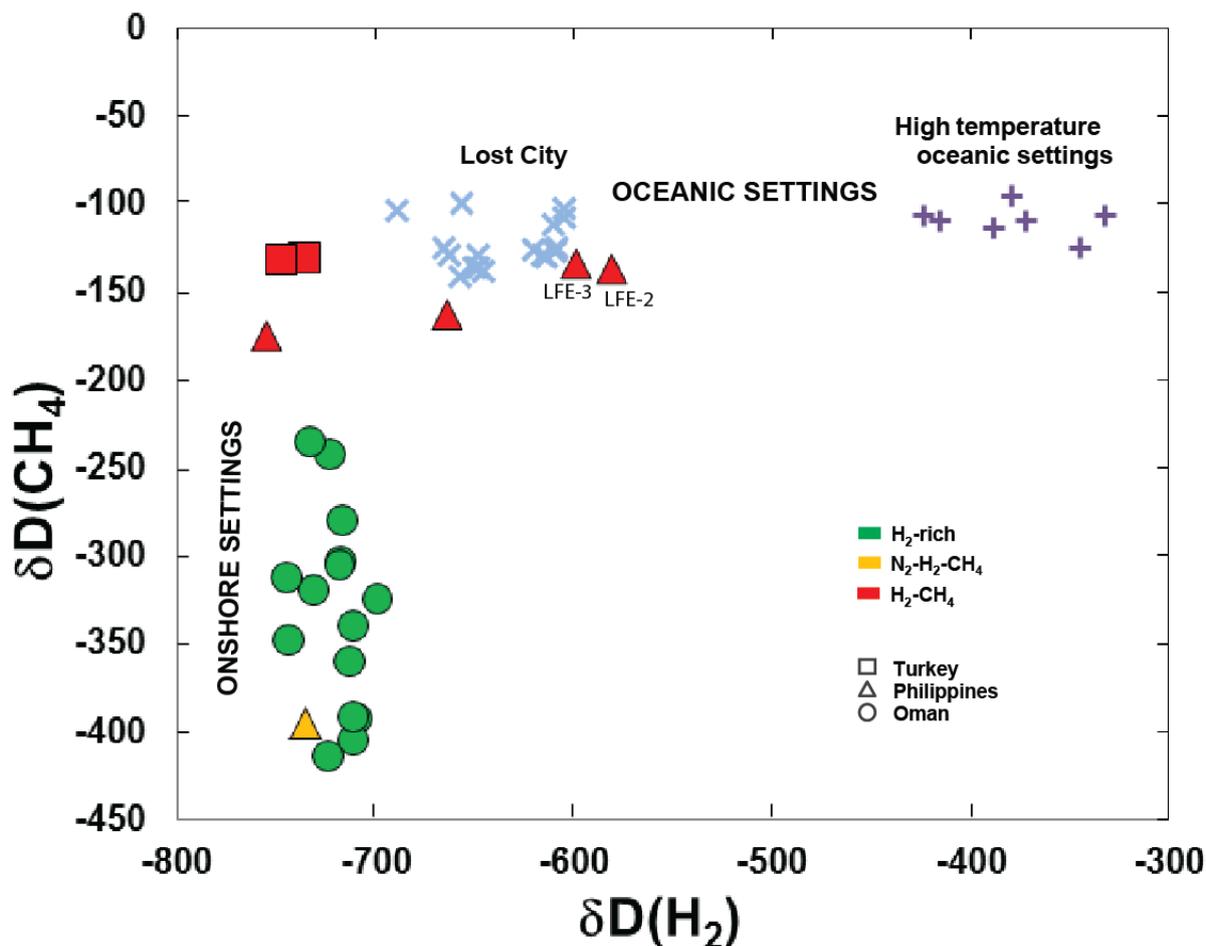


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1226 **Figure 5** - Pourbaix diagram pH-Eh of the water where the gas samples were collected in
 1227 springs. Oblique lines (blue and pink) separate the stability fields of H₂, H₂O and O₂.

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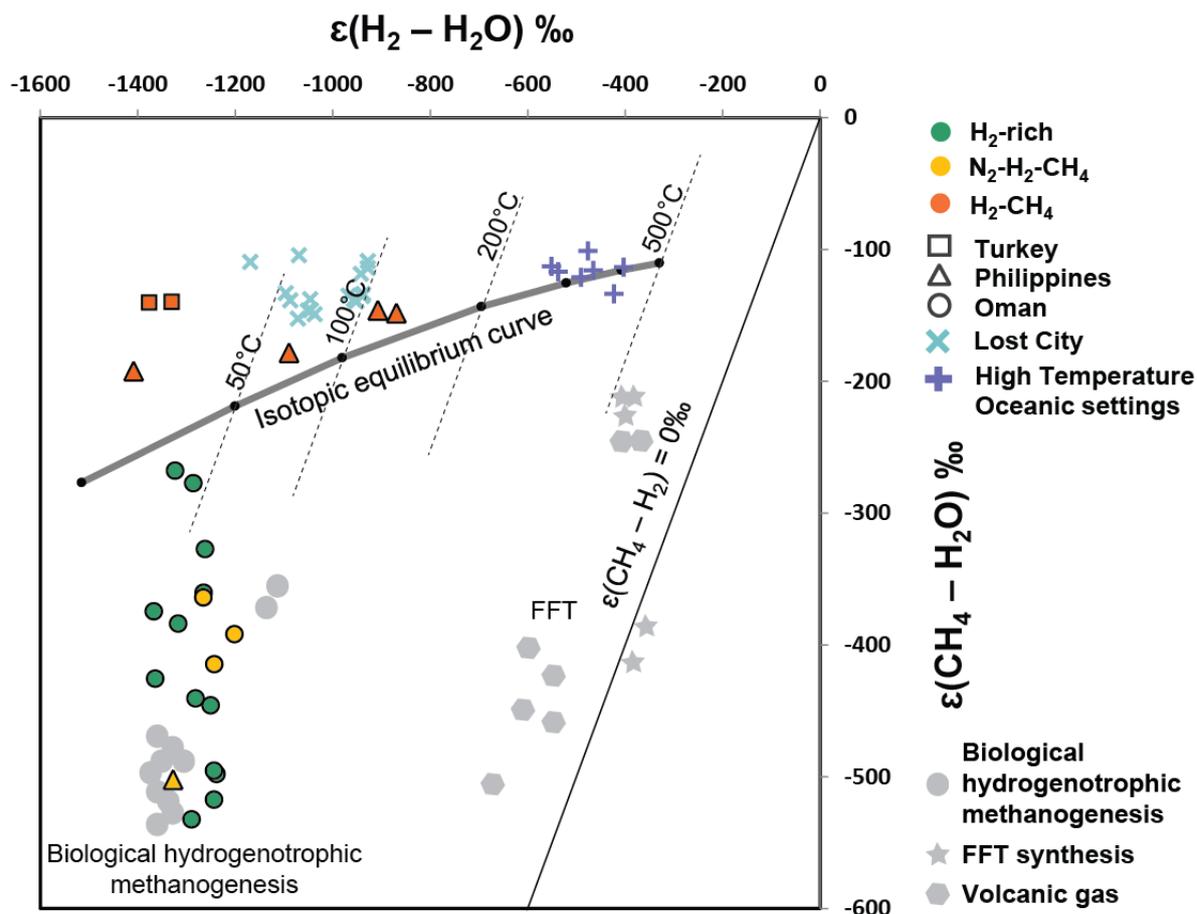


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1231 **Figure 6** - Comparison of hydrogen isotopic compositions of CH_4 and H_2 for onshore
 1232 settings (data from this work and two points, LFE-2 and LFE-3, from Abrajano et al.,
 1233 1988) and oceanic settings (Proskurowski et al., 2006). While 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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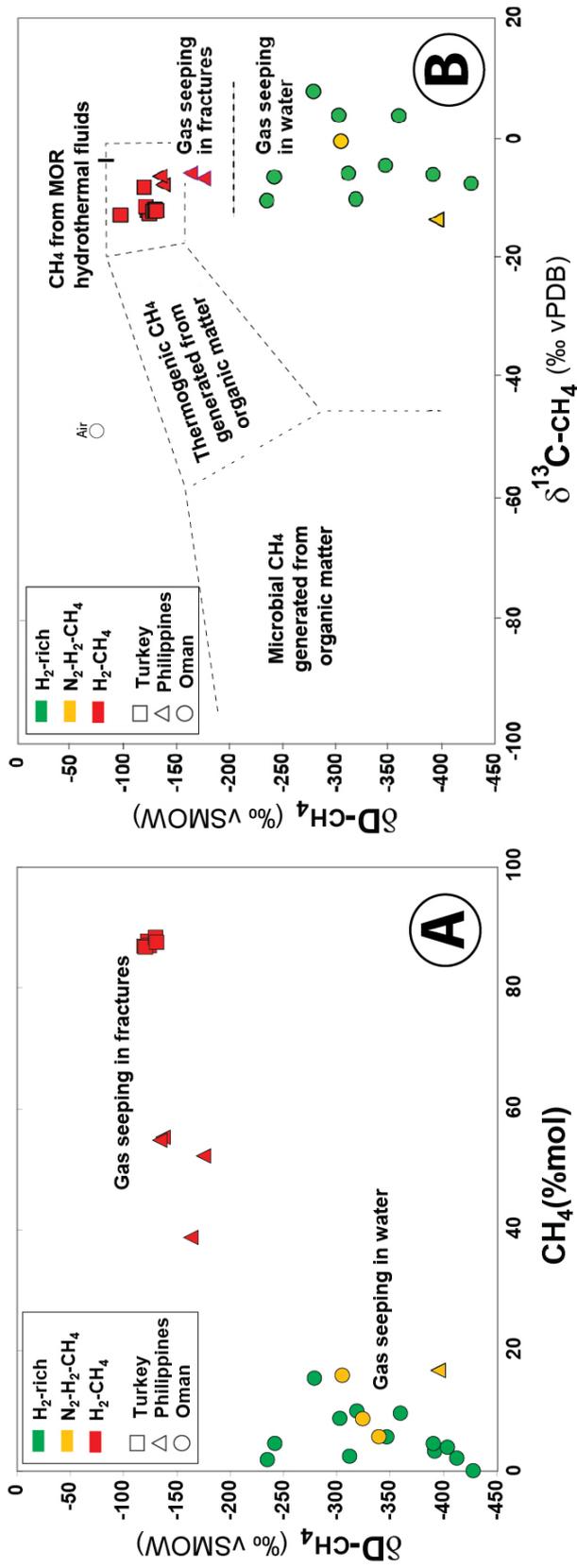


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1244 **Figure 7** - CH_4 - H_2 - H_2O hydrogen isotope systematics. Data for biological hydrogenotrophic
 1245 methanogenesis are from Balabane et al. (1987), Valentine et al. (2004) and Okumura et al.
 1246 (2016). FFT synthesis refer to experiments 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 ϵ 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 CH_4 - H_2 equilibrium fractionation at a given temperature.
 1254 According to this interpretation, CH_4 from fractures (dry seepages) would be produced
 1255 directly from H_2O and DIC whereas, in the H_2 -rich and N_2 - H_2 - CH_4 gas mixtures seeping in
 1256 alkaline springs, an H_2 intermediate (possibly biologically mediated secondary process) would
 1257 produce CH_4 . δD 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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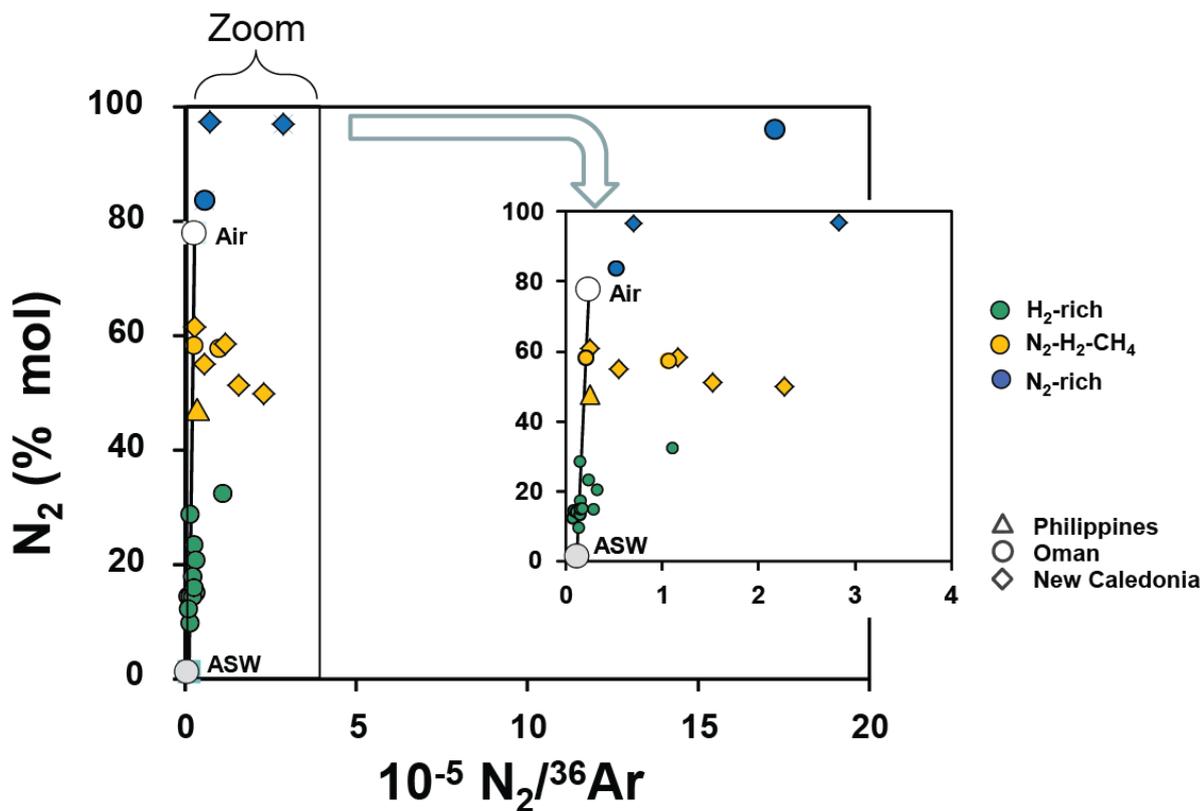
Fig 8

1263

1264 **Figure 8 – A.** Diagram showing $\delta D(\text{‰})$ values of CH_4 vs CH_4 contents. This shows that the
1265 H_2 - CH_4 gas type shows higher CH_4 contents and δD values of CH_4 than the other gas types.
1266 **B.** Diagram showing carbon versus hydrogen isotopic composition of 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 CH_4 are among the highest values recorded on Earth. The range of the carbon
1272 isotopic values of CH_4 is relatively narrow and allows no distinction between the different
1273 types of gas mixtures whereas the hydrogen isotopic values of 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 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 CH_4 of Mid-Oceanic Ridges hydrothermal fluids
1278 is from Proskurowski et al. (2006) and Kawagucci et al. (2016).

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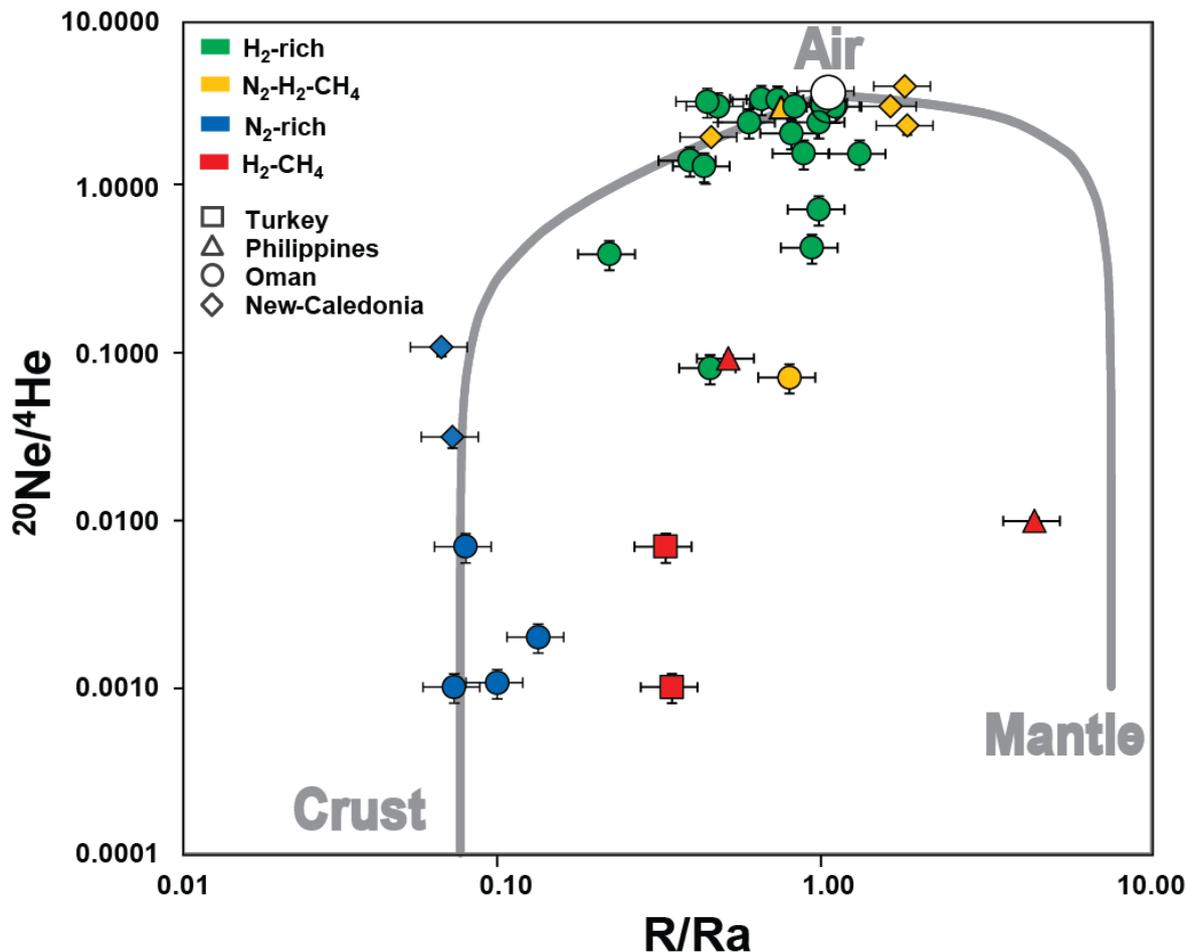


1281

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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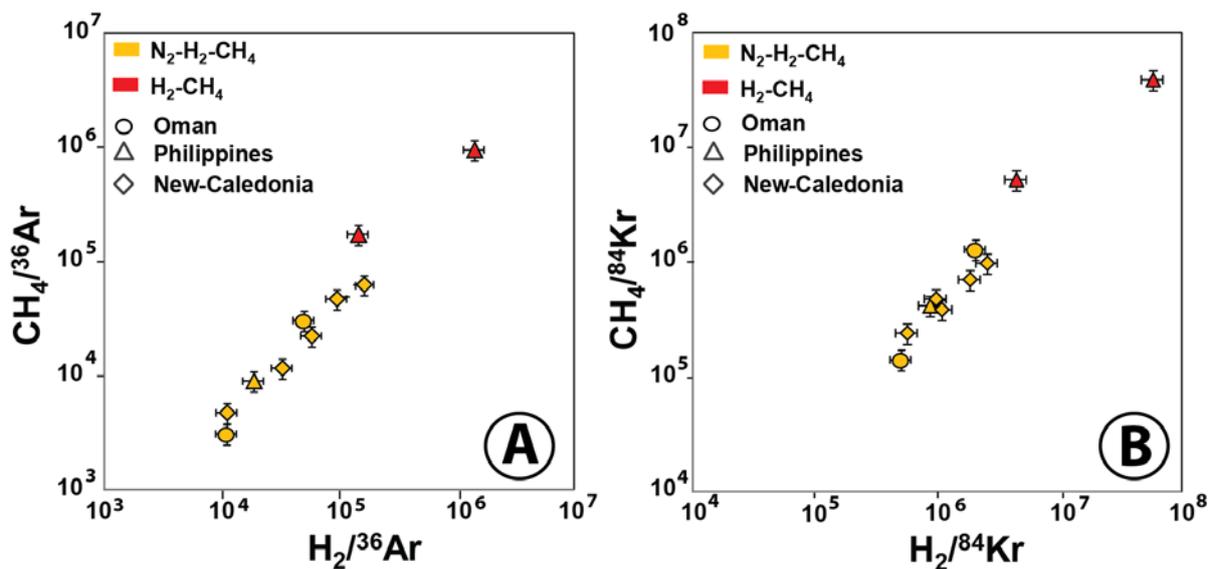
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1289

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 = 1.384×10^{-6}). The noble gas data show that except the 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 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 N_2 - H_2 - CH_4 and H_2 - CH_4 types.

1297



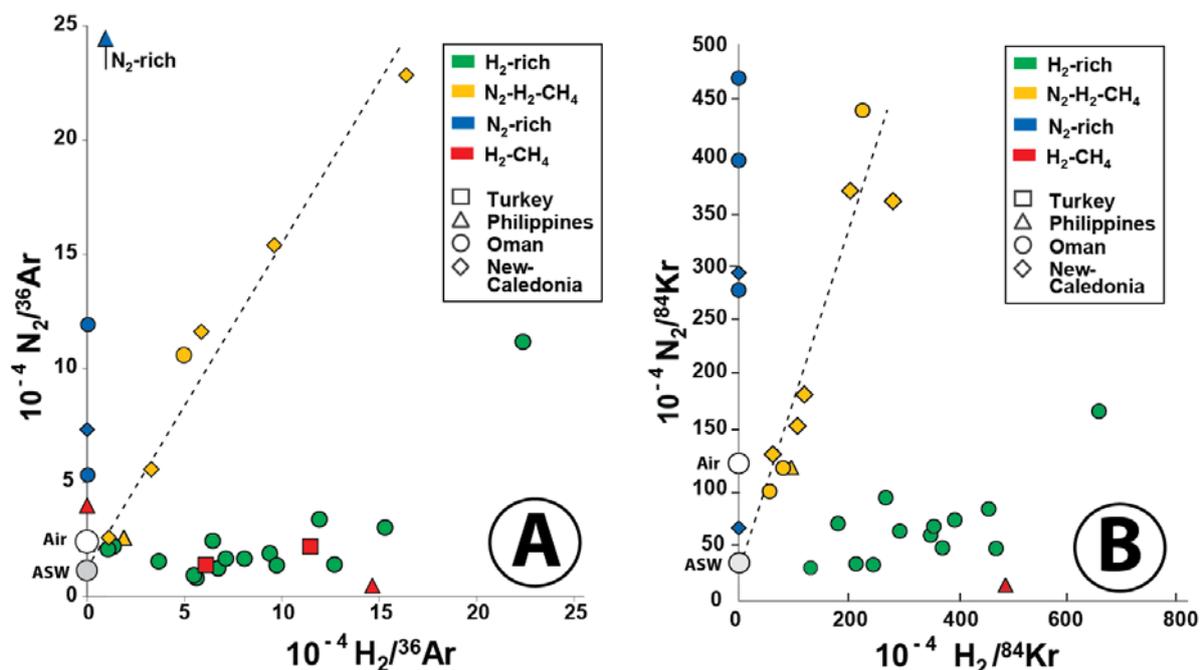
1298

1299 **Figure 11** – Mixing diagrams comparing H₂ and CH₄ contents normalized over ³⁶Ar and ⁸⁴Kr
 1300 contents. **A.** This diagram shows a correlated enrichment in CH₄ vs H₂ when normalized over
 1301 ³⁶Ar (linear correlation with R²= 0.9894). **B.** This diagram shows also a correlated enrichment
 1302 in CH₄ vs H₂ when normalized over ⁸⁴Kr (linear correlation with R²= 0.9953).

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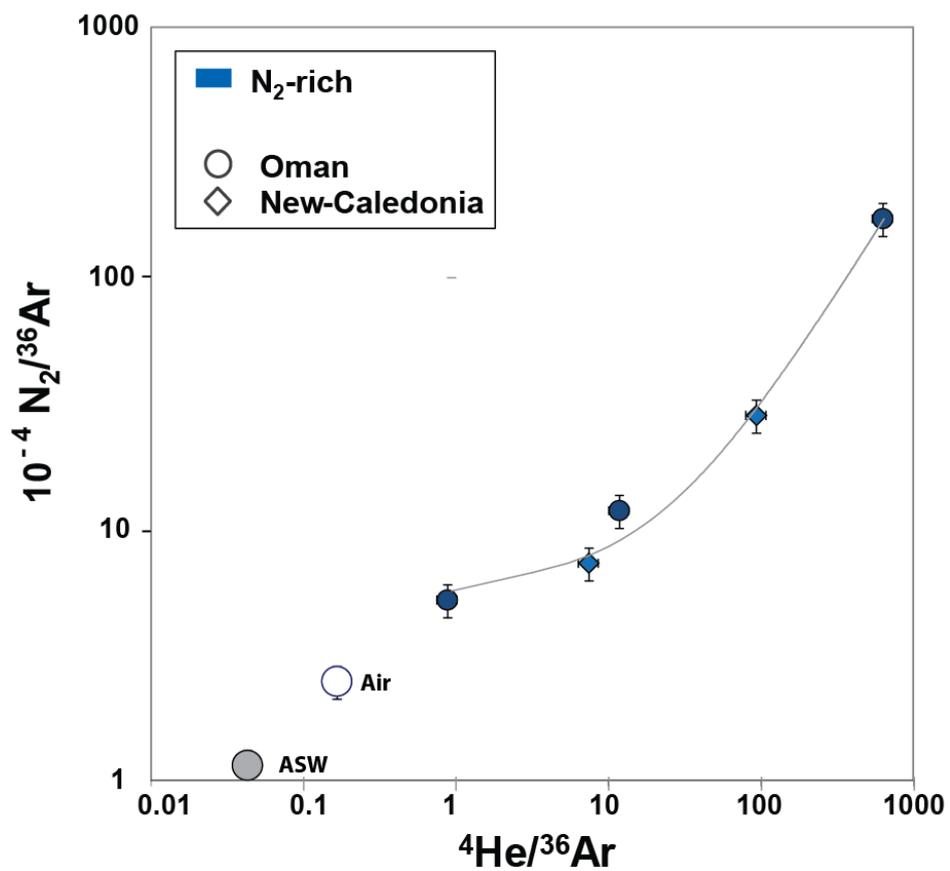


1306

1307 **Figure 12** – Mixing diagrams comparing H₂ and N₂ contents normalized over ³⁶Ar and ⁸⁴Kr
 1308 contents. **A.** The H₂/³⁶Ar vs N₂/³⁶Ar diagram shows different enrichment trends in H₂ vs N₂
 1309 between the H₂-rich gas type and the N₂-H₂-CH₄ gas type. Note the good linear correlation
 1310 between H₂/³⁶Ar and N₂/³⁶Ar for the N₂-H₂-CH₄ gas type (linear correlation R²= 0.9785). **B.**
 1311 The H₂/⁸⁴Kr vs N₂/⁸⁴Kr diagram, as the previous diagram, shows different enrichment trends
 1312 in H₂ vs N₂ between the H₂-rich gas type and the N₂-H₂-CH₄ gas type. Note the good linear
 1313 correlation between H₂/⁸⁴Kr and N₂/⁸⁴Kr for the N₂-H₂-CH₄ gas type (linear correlation with
 1314 R²= 0.9739).

1315

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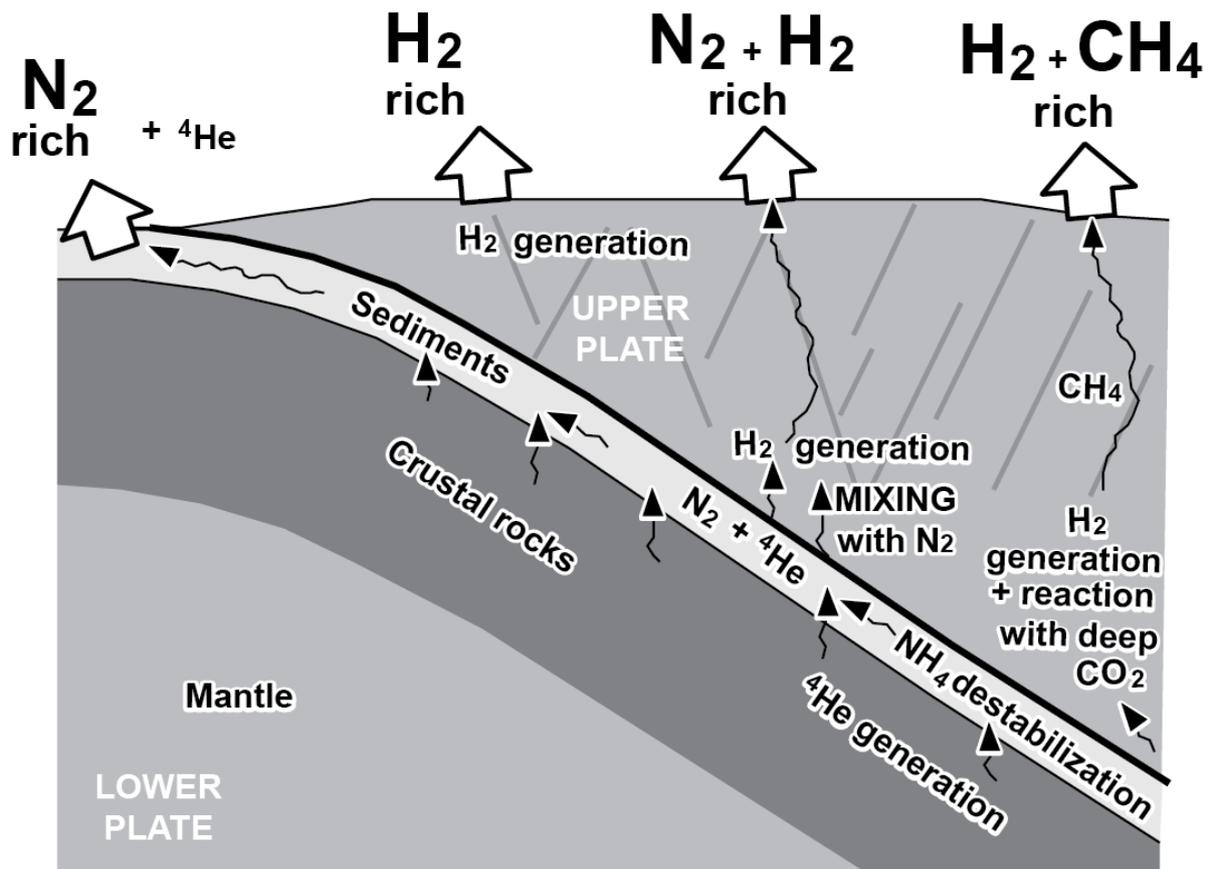
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1318

1319 **Figure 13** - $^4\text{He}/^{36}\text{Ar}$ vs $\text{N}_2/^{36}\text{Ar}$ mixing diagram for the gas samples of the N_2 -rich gas type.

1320 This diagram shows a correlated enrichment in ^4He vs N_2 when normalized over ^{36}Ar (linear
1321 correlation with $R^2 = 0.9993$)

1322



1323

1324

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, H₂ 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 H₂. When H₂ is generated in a shallow aquifer, it migrates upwards and seeps
 1330 out of the rock as a H₂-rich gas seep. H₂ generated in a deeper generation zone interacts with
 1331 deep fluids which can be (1) a N₂-rich fluid issued from the sediments and the mantle below,
 1332 leading to a N₂ and H₂-rich gas, or (2) a fluid rich in CO₂, allowing the production of CH₄ and
 1333 the formation of a gas mixture that seeps at the surface as a H₂-CH₄ gas seepages. N₂-rich
 1334 seepages occur when the deep N₂-bearing fluid does not interact strongly with H₂-rich fluids
 1335 on its migration pathway.

1336

1337

Sites	Coordinates (decimal degrees)		Water T, pH, Eh			gas composition						
			(°C)			Mol (%)						
			T	pH	Eh	He	H ₂	N ₂	CH ₄	CO ₂	C ₂₊	
H₂-rich type												
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
N₂-H₂-CH₄ type												
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
N₂-rich type												
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
H₂-CH₄ type												
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
Reference compositions												
	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%).

1341

Sources/Wells		Per mil vs PDB		Per mil vs SMOW		Per mil vs atm	noble gases composition				
		$\delta^{13}\text{C}$		δD		$\delta^{15}\text{N}$	(ppm)				
		CO_2	CH_4	H_2	CH_4	N_2	^4He	^{20}Ne	^{36}Ar	^{84}Kr	R/Ra
H₂-rich type											
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
N₂-H₂-CH₄ type											
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
N₂-rich type											
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	-	-	-	-	-	-	-	-
H₂-CH₄ type											
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	-	-11.8	-736	-130	-	151.2	1.098	0.82	0.01	0.31
Turkey	Turkey XI2	-	-11.8	-748	-131	-	140.5	0.080	1.59	0.02	0.33
	Turkey XI3	-	-11.8	-748	-131	-	140.5	0.080	1.59	0.02	0.33
reference compositions											
	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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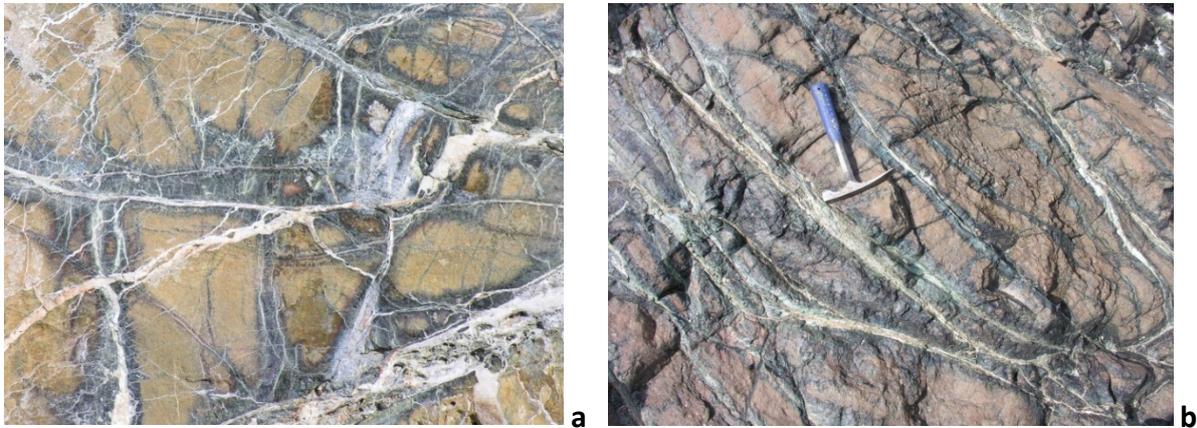
1345 **Table 2.** $\delta^{13}\text{C}$ (PDB) values of CO_2 and CH_4 (‰). δD (SMOW) values of H_2 and CH_4 (‰).
1346 Noble gas analyses ^4He , ^{20}Ne , ^{36}Ar , ^{84}Kr (ppmv), and R/Ra (helium isotopic ratios normalized
1347 to the air isotopic $\text{Ra} = ^3\text{He}/^4\text{He} = 1.4 \cdot 10^{-6}$). C_2+ contents in all the gas samples are very low,
1348 below the threshold of analytical precision ($< 0.01\%$). Global relative uncertainties (at 1σ) 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 (1σ) for the R/Ra ratio is in the
1351 range $\pm 2\%$.

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SUPPLEMENTARY MATERIAL.

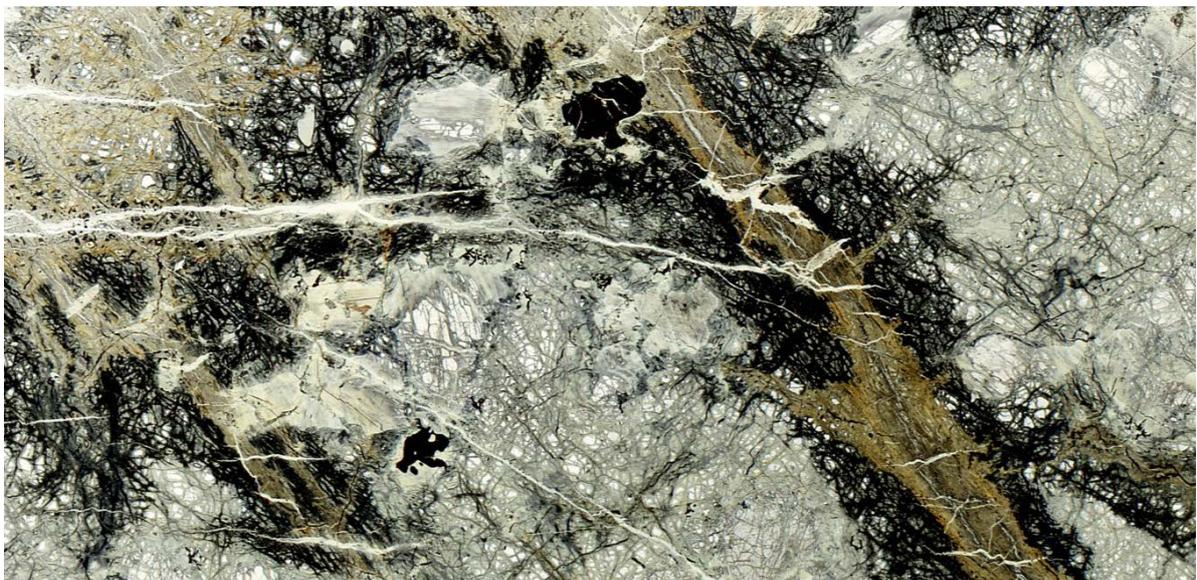
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1355

1356 **Figure S1 a and b-** Photos illustrating alteration processes in the peridotites of Oman. Brown
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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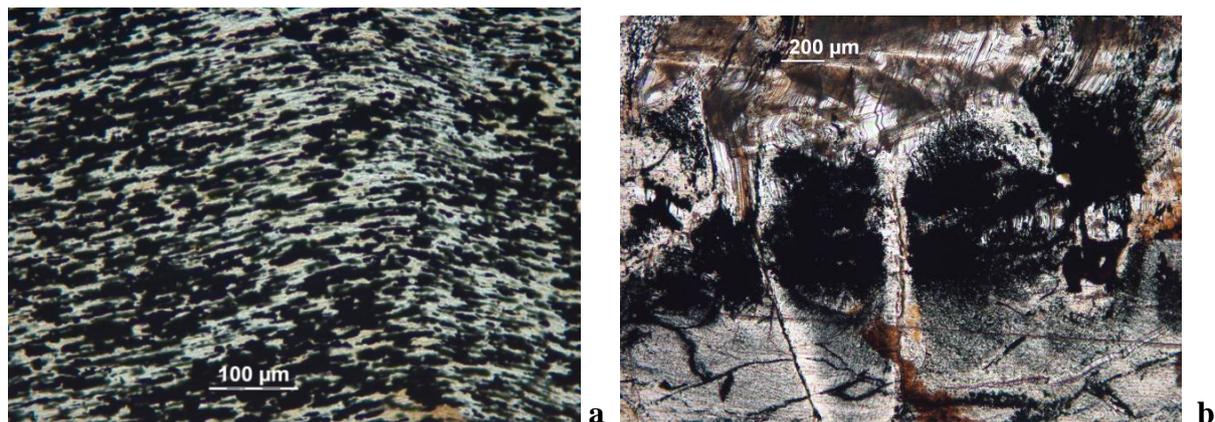
1362

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.

1367

1368



1369

1370 **Figure S3 a and b** - Photos of thin sections showing magnetite aggregates.



1371

1372

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.

1380



1381

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

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1384

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).

1393

1394

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