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Key Points:

- Hyperalkaline spring waters are anoxic. An elevated high O2 content in free gases results from air contamination.
- The relationship between H_2 and CH_4 contents of free gases is consistent with the conversion of fully oxidized carbon (CO_2).
- The H_2-CH_4 relation is consistent with a Sabatier reaction in the gas or a methane production by hydrogenotrophic methanogens in the water.

Abstract

Serpentinization is a natural process that transforms ferromagnesian minerals such as olivine into serpentine and that produces waters at very high pH and gases enriched in methane (CH_4) and hydrogen (H_2). We report the composition of gases venting at two springs (Bain des Japonais and Rivière des Kaoris) of the serpentinizing environment of the Prony Bay (New Caledonia) collected eight times between 2011 and 2014, along with in situ measurements (temperature, pH, oxydo-reduction potential, dissolved oxygen content) of on-land alkaline springs of the Southern New Caledonia ophiolite. Venting gases are mainly composed of H_2, CH_4 and N_2 and their composition has slightly varied during the 4-year field survey. An elevated oxygen (O_2) content in a high-pH water sample is due to air uptake during surface flow. O_2-corrected gas compositions along with those published for gas data obtained at similar serpentinizing environments (Italy, Turkey, Philippines, Oman) show that the H_2 and CH_4 concentrations display a linear correlation with a slope close to the value corresponding to the CH_4 production from carbon dioxide rather from a less oxidized carbon such as carbon monoxide. Although these data are consistent with the stoichiometry of the Sabatier reaction, as such in the gas phase, it is also possible that microbial hydrogenotrophic methanogenesis takes place in the aqueous phase followed by degassing. A diagram is proposed that outlines the partitioning of H_2 and CH_4 between the gaseous and aqueous phases and the need to consider a two-phase flow in the hydrology of these hyperalkaline environments.

Plain Language Summary

Serpentinization is a natural process that transforms ferromagnesian minerals such as olivine into serpentine. This process is accompanied by the formation of high-pH water, hydrogen and methane. This forms a unique ecological niche for microorganisms adapted to extreme pH and/or involved in the hydrogen and/or methane cycles. There is an ongoing debate on the mechanisms at play and on the contribution of abiotic versus biogenic reactions. An analysis of the composition of free gases collected in hyperalkaline springs of New Caledonia combined with literature values for similar sites worldwide shows that the formation of methane follows the stoichiometry of a Sabatier-type reaction involving fully oxidized carbon (CO_2) and not carbon monoxide (CO) as required by a Fischer-Tropsch-Type process. Although it could be concluded that methane production occurs in the gas phase, and as such would be abiotic, it does not rule out the possibility that the relationship between gaseous hydrogen and methane is due to methane production and hydrogen consumption by microorganisms in the aqueous phase followed by degassing.

1 Introduction

Natural environments with waters at pH above 11 have received considerable attention in the last decades due to the wide range of scientific questions that they relate to : abiotic formation of hydrocarbons (e.g. [*Etiope and Sherwood Lollar*, 2013; *Price et al.*, 2017; *Sissmann et al.*, 2019], origin of life and deep subsurface biosphere (e.g., [*Menez et al.*, 2012; *Schrenk et al.*, 2013], alteration of the oceanic crust (e.g. [*Debret et al.*, 2019; *Fryer et al.*, 2020; *Ligi et al.*, 2013], natural formation of hydrogen as an energy source (e.g. [*Truche et al.*, 2020], geological storage of CO_2 [*Kelemen and Matter*, 2008; *Kelemen et al.*, 2011], the analogy with planetary surfaces like Mars or Europe [*Holm et al.*, 2015; *Szponar et al.*, 2012], energy and matter fluxes between geochemical reservoirs [*Plank and Manning*, 2019].

Sites of discharge of such very high pH waters are found on land in Oman [*Chavagnac et al.*, 2013b; *Miller et al.*, 2016; *Paukert et al.*, 2012; *Stanger*, 1985], in Northern Italy; [*Boschetti and Toscani*, 2008; *Chavagnac et al.*, 2013b; *Cipolli et al.*, 2004], in Cyprus [*Neal and Shand*, 2002], in the Philippines [*Cardace et al.*, 2015], in California [*Boschetti et al.*, 2017; *Morrill et al.*, 2013], in Ontario [*Sader et al.*, 2007], in Newfoundland [*Szponar et al.*, 2012], in Portugal [*Marques et al.*, 2008], in Greece [*D'Alessandro et al.*, 2018a], in Turkey [*Meyer-Dombard et al.*, 2015; *Yuce et al.*, 2014], in Jordan [*Khoury et al.*, 1992], in New Caledonia [*Monnin et al.*, 2014] and in Spain [*Giampouras et al.*, 2019]. Such hyperalkaline waters are also found underwater in the ocean, at the Lost City Hydrothermal Field on the Atlantis massif off the Mid-Atlantic ridge [*Kelley et al.*, 2001; *Kelley et al.*, 2005] and in the mud volcanoes of the Marianna forearc [*Fryer et al.*, 1989; *Fryer et al.*, 2018; *Mottl et al.*, 2004]. The Maqarin site in Jordan is a peculiar case where the natural combustion of bituminous marls and the alteration of the rocks created by a phenomenon that has been called pyrometamorphism lead to the formation of extremely alkaline water, with pH value up to 12.5 [*Alexander et al.*, 1992; *Khoury et al.*, 1992]. Apart from the Maqarin site, these hyperalkaline waters originate from the serpentinization of ultramafic rocks that can be found on land in ophiolites (e.g. Oman, Liguria, etc.), in an ultramafic complex created by continental collision such as Cabeço de Vide in Portugal [*Marques et al.*, 2008; *Marques et al.*, 2018], at the seafloor where plate tectonics has

exposed ultramafic rocks to alteration, such as at the Lost City site (Northern Atlantic), or at the decollement zone of the subducting plate in the case of the Marianna forearc mud volcanoes [*Mottl et al.*, 2004]. The discharge of these waters is focused and occurs at springs where they lead to the formation of carbonate concretions, in the form of tuffs in Oman [*Chavagnac et al.*, 2013a] or submarine pinnacles at Lost City [*Kelley et al.*, 2005] and in the Prony Bay in New Caledonia [*Launay and Fontes*, 1985; *Monnin et al.*, 2014; *Pelletier et al.*, 2006].

While the discharge zones (springs) are easily recognized in the field, the recharge of these hydrological systems is poorly or not at all characterized. The geographic extension of a given hydrothermal system, the characterization of the inflowing water, its residence time and the role of the composition of the geological formation (its lithology, its physical and thermal structure) are general questions on any hydrological system. They are rarely documented for hyperalkaline hydrothermal systems [*Christofi et al.*, 2020; *Dewandel et al.*, 2005; *Lods et al.*, 2020; *Marques et al.*, 2018]. A classification of high-pH springs based on the location of the output (marine or continental) and on the origin of the circulating fluid based on the salinity of the spring waters has been proposed [*Monnin et al.*, 2014]. Thus, a first category is defined by the fresh high-pH spring waters found in continental environments like in Oman, Liguria, Portugal, Philippines, Greece, and Turkey. The second main category contains hyperalkaline waters with salinities similar to that of seawater discharging at springs located in the marine environment, the Lost City site being the archetype of this category [*Kelley et al.*, 2001; *Kelley et al.*, 2005; *Seyfried Jr et al.*, 2015]. This is also the case of the Marianna mud volcanoes, where the high-pH waters have seawater-like salinities, but a very complex geological history linked to their origin in the dehydration of the subducting Pacific plate in the Marianna subduction zone [*Hulme et al.*, 2010; *Mottl et al.*, 2004]. In nearly every case, the inflowing water (recharge) of these hyperalkaline hydrothermal systems is continental (meteoric, runoff) water (low salinity) for systems fully located on continents and seawater for fully marine environments.

Two hyperalkaline hydrothermal systems do not fit in this classification. The Aqua de Ney spring is located inland about 200 km from the Northern California Coast. Its water (pH $\approx$ 12) has a salinity similar to that of seawater and is a case of a high-pH saline water discharging in a continental environment [*Blank et al.*, 2017; *Feth et al.*, 1961]. It has been proposed that it originates from the

123 dehydration of the Pacific plate subducting below the American continent [*Boschetti et al.*, 2017]. The
124 other system that does not fit in the classification is in Prony Bay (southern lagoon of New Caledonia)
125 where alkaline springs located in the lagoon discharge fresh waters into the marine environment
126 [*Monnin et al.*, 2014].

127 Globally, these hyperalkaline waters contain elevated concentrations of methane and hydrogen
128 [*Etiope and Whiticar*, 2019]. Gas venting is commonly observed but not at every location, while
129 dissolved gases have been analyzed in numerous hyperalkaline springs (see the review of [*Etiope and*
130 *Whiticar*, 2019]. Gas bubbles have been sampled in Oman [*Boulart et al.*, 2013; *Vacquand et al.*,
131 2018], in the Voltri ophiolite in Liguria (Northern Italy) [*Boschetti et al.*, 2013; *Boulart et al.*, 2013;
132 *Etiope and Whiticar*, 2019], at several locations in the Philippines [*Abrajano et al.*, 1988; *Vacquand et*
133 *al.*, 2018] and in Turkey [*D'Alessandro et al.*, 2018b; *Vacquand et al.*, 2018] and in New Caledonia
134 [*Vacquand et al.*, 2018]. The gases are mainly composed of dihydrogen (H_2), dinitrogen (N_2) and
135 methane (CH_4), with trace amounts of higher alkanes, carbon dioxide and monoxide and helium.
136 Oxygen is not always measured or reported. It can be found in noticeable concentrations, for example
137 up to 15% for one of the samples of the Kisecik spring in the Kizildag ophiolite in Turkey
138 [*D'Alessandro et al.*, 2018b] or the Zambales springs in the Philippines [*Abrajano et al.*, 1988]).

139 The Prony Bay hydrothermal field (PBHF), that has been studied during the HYDROPRONY
140 cruise in 2011 [*Pelletier et al.*, 2011], comprises several underwater springs in the Prony Bay, with the
141 Aiguille de Prony being the most prominent, and two costal main sites at the northernmost part of the
142 Prony Bay, the Bain des Japonais, a spring that is uncovered at low tide and the Bain des Kaoris that is
143 located above the water level [*Monnin et al.*, 2014]. A number of other springs and seepages of high
144 pH waters are known inland from the coast (Grande Terre) many 10s of kilometers north from Prony
145 Bay ([*Maurizot et al.*, 2020]; Fig. 1). We here present in situ measurements of pH, oxidation-reduction
146 potential (ORP), dissolved oxygen and temperature of these on-land spring waters, along with the
147 compositions of free gases collected at the Bain des Japonais and at the Kaoris springs during a survey
148 carried out between 2011 and 2014.

149 The oxic/anoxic characteristic of the high pH waters has been determined from in situ
150 measurements of the oxygen content directly at the springs, but also from the gas chromatography

analysis of the free gases. We address the question of air contamination of the samples and propose a way to correct it. These new data are then compared to sites of alkaline springs in other countries where gas venting is observed. This allows to address the question of the stoichiometry of methane production and hydrogen consumption and therefore the nature of the carbon pool in low temperature serpentinizing environments.

2 Location and geological setting of the springs

2.1 The springs of the Prony Bay

The Prony Bay springs have been previously described ([*Monnin et al.*, 2014] and references therein). The Kaoris spring is located above the sea level at the northeastern end of the Bay along the Kaoris River. The Bain des Japonais, which is submerged at high tide, is located on the Baie du Carénage, at the northwestern end of the larger Prony bay [*Monnin et al.*, 2014]. These two sites, 2.2 km apart, are easily accessed using a shallow-draft boat. They have been visited several times between 2011 and 2014 (Table S2).

2.2 On-land springs

The spring north of the Yaté Lake (called Nord Yaté) has been visited only once on August 8, 2013, while the other on-land springs were sampled during the 2014 fall (Nov. 17 to Dec. 15) (Fig. 1).

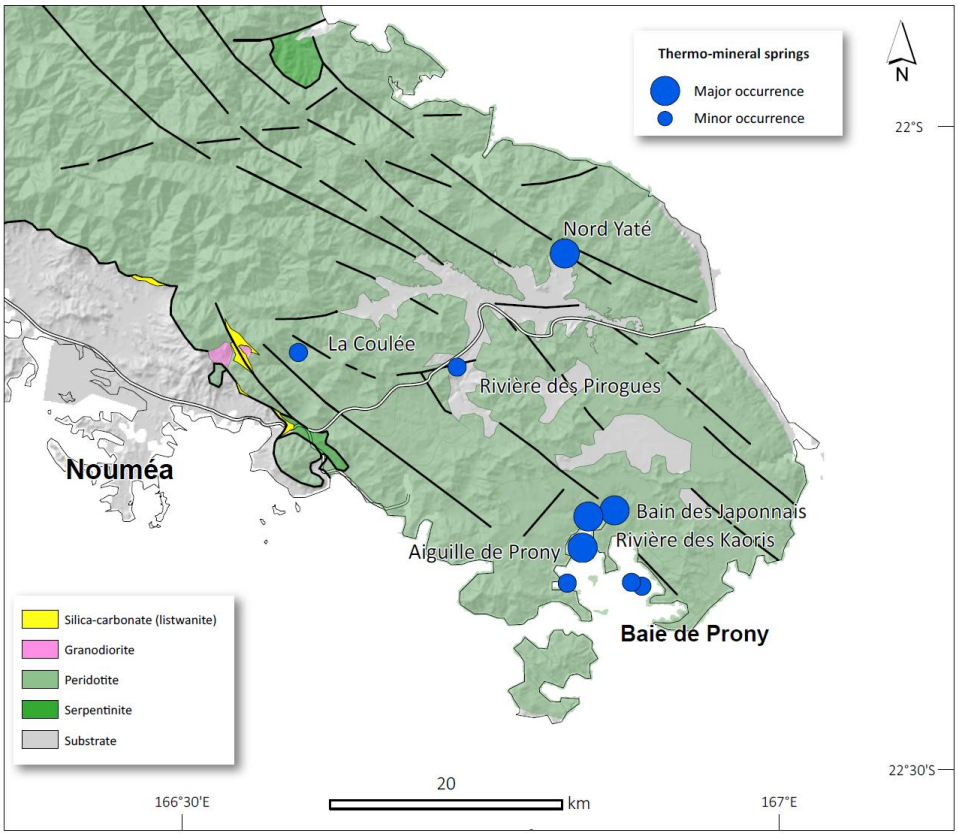


Figure 1 – Location of the high pH springs in southern New Caledonia (after [Maurizot et al., 2020]).

The spring "La Coulée" is located in the outskirts of Nouméa in the valley of the river "La Coulée" and is easily accessed. The main water outlet is about two meters above the river bed in a shallow (about 10-cm deep) pool (Fig. 2). The pools below are fed by water overflowing from the upper pool. Very intermittent gas bubbling has been observed in the upper pool, but no sample could be taken because of the very slow discharge (a bubble every 10 mn or so).

The spring "Rivière des Pirogues" is a little bit further away and can be accessed by dirt roads. The high pH water outlet is a seepage located within the bed of a tributary of the Pirogues River in fractured rocks above a large (about 30 m wide) water pool formed at the junction with the Pirogues river. Bubbling in this pool has been observed about two meters from the rocky bank, but again no sample could be taken. This spring does not build carbonate pools like the spring "La Coulée" (Fig. S1).

189 The spring of the Montagne des Sources (also named Rivière du Rocher) is located in a reserve.
190 The access is totally restricted because this is where the city of Nouméa is getting its water supply
191 from (Fig. S1). A strenuous 5-hour hike in the river bed is required to get to the spring. The spring is a
192 30-m long spectacular suite of large pools located right above the river bed and below a forest (Figure
193 S1). These pools are about 1.5 m in diameter and about 1.5 m deep for the deepest one. Water flows at
194 a high rate through an outlet situated in the middle of the wall of the structure. The pools contain
195 varying amounts of branches and leaves from the trees above. Sampling and observations have been
196 difficult and less extensive than anticipated because of the very bad weather and heavy rain on the day
197 of our visit (Dec. 3, 2014).

198 The spring on the Northern side of the Yaté Lake cannot be reached by land. Water samples
199 were collected during a visit to the spring by helicopter on August 8, 2013, therefore with limited time
200 on the site. Similarly to the Coulée spring, it is located right above the river bed (Fig. S1). The high-
201 pH water builds up small terraces that are common characteristics of these peculiar springs, as can be
202 observed for example at La Coulée spring (Fig. 2), in Oman and Liguria [*Chavagnac et al.*, 2013a;
203 *Chavagnac et al.*, 2013b] or in California at the Cedars spring [*Suzuki et al.*, 2013].

204 Although they have been included in previous studies of New Caledonia alkaline springs [*Cox*
205 *et al.*, 1982; *Deville and Prinzhofer*, 2016; *Vacquand et al.*, 2018], the springs of the Canala area are
206 somewhat different than those further South. The geological substratum is different and the pH (≈ 9)
207 of its waters is lower than that at the other studied sites [*Cox et al.*, 1982; *Maurizot et al.*, 2020;
208 *Quéméneur et al.*, 2021].

209

210 3 Sampling procedures, in situ measurements and analytical methods
211

212 3.1 Free gas sampling procedure and in situ measurements: pH, oxidation-reduction 213 potential, temperature and dissolved oxygen
214

215 Gas samples were collected in 10-ml glass vials by the water displacement technique. It consists
216 in filling the vial with spring water and immersing it upside down in the spring above the gas bubbles.
217 The captured bubbles displace the water from the vial which is then closed with a rubber stopper when

there is no water left (then sealed with an aluminum cap). It was noticed that an air bubble can be trapped in the rubber stopper, leading to air contamination. Even if great care is taken, air uptake during sampling is not totally unavoidable. For example, several gas compositions reported by [*Neal and Stanger*, 1983] and [*Sano et al.*, 1993] for Oman show that almost pure air has been sampled.

The samples were kept at 4°C in the laboratories in Nouméa (IRD) and in Marseille (MIO). They were kept at room temperature (i.e. plane cargo bays and lockers) while travelling between New Caledonia and metropolitan France (i.e. for about 30 hours).

Temperature, pH, oxidation-reduction potential (ORP) and the dissolved oxygen content were measured directly in the springs with the appropriate probes using a using a WTW Multi 3420® Multimeter that allows recording the measurements over a time period with a fixed step (Fig. S2). Temperature and pH were measured during all the campaigns using a SenTix 940® pH electrode in which a thermocouple allows temperature to be measured. ORP (Oxidation-Reduction Potential in reference to the Ag/AgCl standard) and dissolved oxygen were measured only in 2014 after the acquisition of the appropriate probes (SensoLyt ORP 900-P® for the redox potential and FDO 925® for dissolved oxygen).

3.2 Gas analyses

The gas analyses (dissolved and gaseous) were carried out in three different laboratories: MIO (Mediterranean Institute of Oceanography) in Marseille (France), at the Laboratoire des Cycles Géochimiques et ressources (LCG) IFREMER Brest (France) and at the NASA Ames Research Center (Moffett Field, California).

At MIO (Marseille) the gas composition was determined using a Shimadzu GC 8A gas chromatograph equipped with a thermal conductivity detector (GC/TCD) and a concentric column CTR1 (Alltech, USA). Argon was used as carrier gas at a flow rate of 60 mL/min; temperature of the injector and the detector was fixed at 150°C. All analyses were run in duplicate.

At in the NASA Ames Research Center, The concentrations of free gases were analyzed by a Shimadzu GC 8A gas chromatograph equipped with a thermal conductivity detector (GC/TCD) and

two columns (Alltech, USA). Operating conditions for H_2, O_2, CH_4, and CO_2 analyses are as follows: the carrier gas is nitrogen at a pressure of 100 kPa; temperature of the column is fixed at 150°C and that of the injector and the detector is fixed at 200°C. N_2 was determined by difference based on previous estimates [*Monnin et al.*, 2014].

At IFREMER Brest, two analytical devices have been used: a gas chromatograph μGC R3000 from SRA equipped with three analytical modules to determine hydrogen, oxygen, nitrogen, methane to hexane and carbon dioxide concentrations, and a Agilent 7890A gas chromatograph equipped with a 32 m, 0.32mm Porapak Q column and a triple detection system (TCD-FID-mass detector) to analyze hydrocarbons at low concentrations. The TCD and FID are used for quantitative analysis while the mass spectrometer is used for the purpose of verification of the compounds or identification of unknown compounds against the NIST05 library. The injection and calibration were performed as described by [*Donval et al.*, 2020].

The data and the laboratories where the analyses have been made are reported in Table S2.

4 Results

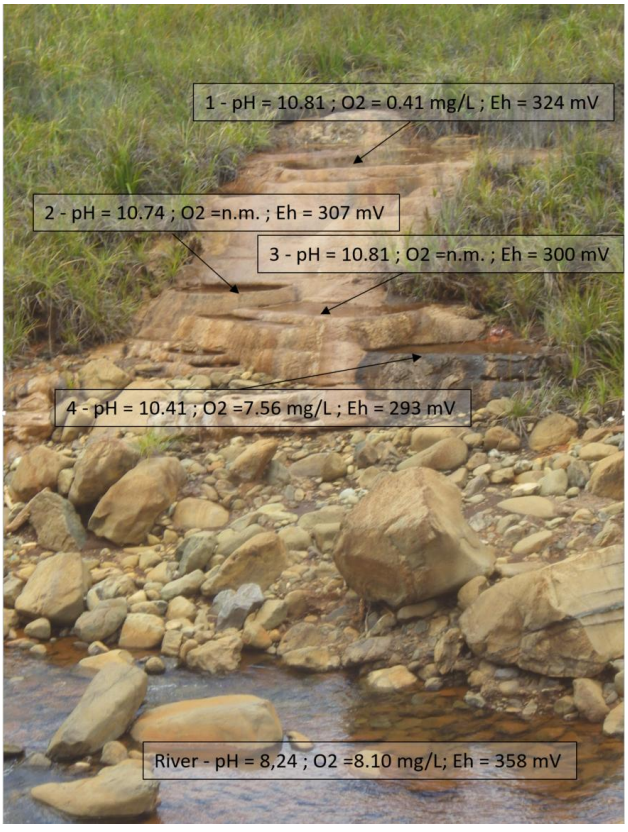
4.1 In situ measurements: temperature, pH, ORP and dissolved oxygen

4.1.1 Temperature and pH

The in-situ parameters (Table S1) were recorded during 30 mn at the springs of La Coulée and Pirogues. Dissolved oxygen and ORP required an equilibration time of a few minutes (Fig. S2). The water temperatures at all the on-land springs are between 26 and 32°C, similar to that for the Kaoris (32°C) but a little bit lower than those for the Bain des Japonais (38°). At La Coulée, the water temperature measured in the upper pool is 27°, lower than the air temperature which was 30° or even higher on the days of sampling.

pH is constant at Pirogues at a value of 10.88 but varies over 0.2 pH units at La Coulée between 10.81 and 11.05 (Table S1). There is a correlation between temperature and pH at La Coulée in the upper pool (Fig. S2). The temperature variation can be due to a convection effect of the thin water

274 layer. Indeed, the discharging water temperature is between about 27°C while the air temperature on
275 the days of measurements were over 30°C.
276
277 4.1.2 The dissolved oxygen content
278
279 At La Coulée, the water discharges in the upper pool from where it flows down to the other
280 pools. The oxygen content of the water in the upper pool is 0.4 mg/L, 7.56 mg/L in the lower pool and
281 8.24 mg/L in the river (Fig. 2). The Eh values are the same in all the pools. The water discharging at
282 the upper pool becomes oxygenated by air uptake when it flows downhill. This air and thus the CO_2
283 uptake lead to a small decrease in pH of 0.4 unit. Thus, for a given spring, variable values of *in situ*
284 parameters can be obtained when measured away for the outlet.
285



286
287 *Figure 2 – The high-pH spring of La Coulée. The water discharges in the upper pool (1) and flows*
288 *down toward the river through the upper (2) and lower (3) intermediate pools. It gets oxygenated on*

289 *the way, as indicated by the elevated O_2 content in the lower pool (4), at a value close to that of the*
290 *river. n.m.: not measured.*

291 The Pirogues and Coulée springs have similar oxygen content between 0.2 and 0.4 mg/L, which
292 classifies them as anoxic [*Berner*, 1981]. At the Montagne des Sources, the oxygen content of the very
293 large and deep pool is 3.0 mg/L while the water flowing at a fast rate from the outlet in the middle of
294 the formation (Fig. S1) is quite oxygenated (with a O_2(aq) content of 6.9 mg/L; Table S1).
295

296 4.1.3 The oxidation-reduction potential
297

298 The ORP values are measured in situ in reference to the Ag/AgCl standard. They have been
299 corrected for the potential difference between the Ag/AgCl and the hydrogen electrodes and thus
300 termed Eh (Fig. S2). There are marked differences in the Eh values between the springs, between the
301 days of measurement for the same spring and sometimes even within the time of recording (30 mn).

302 Eh at the spring Rivière des Pirogues has markedly varied between Dec. 2 and 12, 2014 (Fig
303 S1). There is also a small Eh maximum at Pirogues for the data of Dec. 2. Very sporadic bubbling (a
304 few events per hour) have been observed at La Coulée and also at the Pirogues site. For this latter
305 spring bubbles were observed not in the seepage of the spring where the water flows on the rocks
306 without being retained in a pool, but on the side of the very large pool (about 20 m wide) built by the
307 river about 10 meters downstream from the spring (Fig. S1). It has been shown in many instances that
308 gas bubbles forming in these high pH springs contain elevated concentrations of hydrogen (along with
309 methane and nitrogen). This has been documented for the Prony bay [*Deville and Prinzhofer*, 2016;
310 *Monnin et al.*, 2014]. We have observed at the Bain des Japonais in the Prony bay that gas bubbling
311 disrupts the ORP measurement when a gas bubble hits the probe. This may explain the Eh maximum
312 and the increase from -300 to -200 mv in Dec.2 at Pirogues (Fig. S1). This H_2-enriched gas venting
313 may also be the cause of the dispersion of the Eh values.
314

315 4.1.4 Comparison with other high-pH springs worldwide
316

317 *4.1.4.1 The dissolved oxygen content*
318

319 Unfortunately, the dissolved oxygen concentration is not reported for every spring or seepage
320 area documented in the literature. The dissolved oxygen concentration of the New Caledonia springs
321 and of other high-pH springs worldwide are displayed versus pH in Fig. 3. These measurements were
322 made using different methods: with an oxygen probe (this work; [*Cardace et al.*, 2015; *Etiope et al.*,
323 2016; *Rempfert et al.*, 2017; *Suzuki et al.*, 2013], on site spectrophotometric measurements based on
324 the indigo carmine reagent [*Canovas et al.*, 2017] and gas chromatography analysis of the dissolved
325 gases using the headspace method [*Etiope et al.*, 2016]. In order to give the order of magnitude of
326 oxygen saturation, we used the dissolved oxygen content of pure water at equilibrium with the
327 atmosphere (i.e. for an oxygen partial pressure of 0.2 bar) at 25°C (8.3 mg/L) (Fig. 3). An accurate
328 calculation would require taking into account the temperature and the composition of the aqueous
329 phase (the Setchenov correction to Henry's constant). For example, oxygen solubility in pure water at
330 40°C is 6.41 mg/L. The three values reported for river waters close to the alkaline springs in New
331 Caledonia and a non-alkaline spring in Ronda (Spain; [*Etiope et al.*, 2016]) are close to values of
332 oxygen saturation in pure water (Fig. 3). The present data for New Caledonia, but also the data for
333 Oman [*Canovas et al.*, 2017], for the Manleluag springs in the Philippines [*Cardace et al.*, 2015] and
334 for the Ronda springs in Spain [*Etiope et al.*, 2016] show that at almost constant pH, the oxygen
335 content of the water samples collected in the high-pH springs can vary from zero to values close to
336 saturation. The waters at The Cedars springs in California [*Suzuki et al.*, 2013] and of the Argolida and
337 Othrys spring in Greece [*D'Alessandro et al.*, 2018a; *Etiope et al.*, 2013] are either totally anoxic or
338 have a very low oxygen content. Water samples collected in boreholes in Oman [*Rempfert et al.*,
339 2017] or at the CROMO site (Coast Range Ophiolite Microbial Observatory) in Northern California
340 [*Crespo-Medina et al.*, 2014] are also oxygen free. The example of La Coulée spring show that
341 elevated dissolved oxygen concentrations measured away from the outlet result from atmospheric
342 oxygen dissolution due to air uptake. On the other hand, this air contamination provides carbon
343 dioxide to the water that contributes to the formation of the carbonate concretions building the pools
344 [*Chavagnac et al.*, 2013a; *Leleu et al.*, 2016]. Similarly, [*Meyer-Dombard et al.*, 2015] have shown

how the carbon content of the waters in the stream created by the discharge of a high pH fluid at Chimarea springs (Turkey) increases with the distance from the source because of air uptake.

These data show that the high-pH waters discharging at the springs are oxygen-free, when they are collected directly at the outlet. This is in agreement with the fact that oxygen is the first oxidant consumed in the subsurface either through biological consumption or via the oxidation of ferric iron [*Leong and Shock*, 2020; *Neal and Stanger*, 1983]. It is then concluded that the hydrologic system discharging these high-pH waters is oxygen-free and that the venting gases should not contain any oxygen. Therefore, the compositions of the gases venting at the seeps must then be corrected for this air contamination.

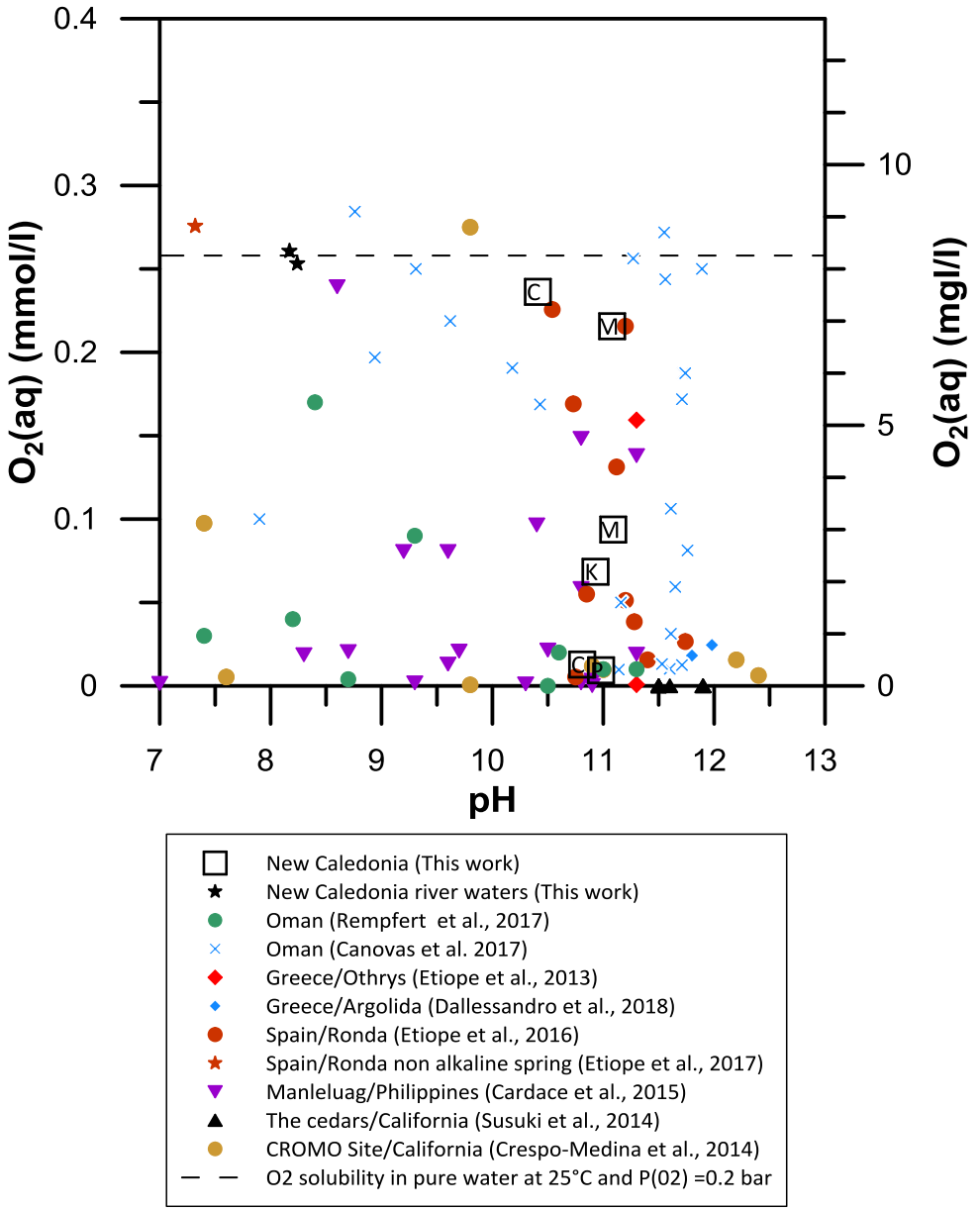


Figure 3 – The dissolved oxygen concentration of the New Caledonia hyperalkaline springs and of other springs worldwide. The dashed line is the value of oxygen saturation in pure water at 25°C. The symbols for New Caledonia are: C = La Coulée, P = Pirogues, M = Montagne des Sources, K = Kaoris.

4.1.4.2 The oxidation-reduction potential

The data set is very scattered with no clear relationship between Eh and pH (Fig. 4). The redox conditions for the reduction of water are met for the Bain des Japonais and the Pirogues spring in New Caledonia (this work) and the Cedars springs in California. The ORP value for the Tahtakopru spring

366 of the Kilzidag ophiolite in Turkey [*Yuce et al.*, 2014] and for a spring called Carénage in New
367 Caledonia, which corresponds to the Bain des Japonais [*Deville and Prinzhofer*, 2016] are below the
368 water reduction limit, -800 mV for a pH of 10.52 and -870 mV for a pH of 10.59, respectively. There
369 is an ambiguity in the Eh values reported in the literature as the reference potential (Ag/AgCl or H_2) is
370 not always mentioned (e.g. [*Paukert et al.*, 2012]). Some of the values reported in Fig. 4 may be the
371 values given by the ORP probe (i.e. in reference to the Ag/AgCl standard) and thus may be too high
372 by about 200 mV (Fig. S2). Such a correction would bring the redox potential of the Carenage and
373 Tahtakopru springs close to the water reduction limit, i.e. corresponding to reaction (1):

$$\boldsymbol{H_2O(l) + e^- = H_2(g) + OH^-(aq)} \quad \textbf{(1)}$$

374 These data show that these high-pH waters display the most reducing conditions at the surface
375 of the Earth. No correlation with the oxygen content of the waters was observed.

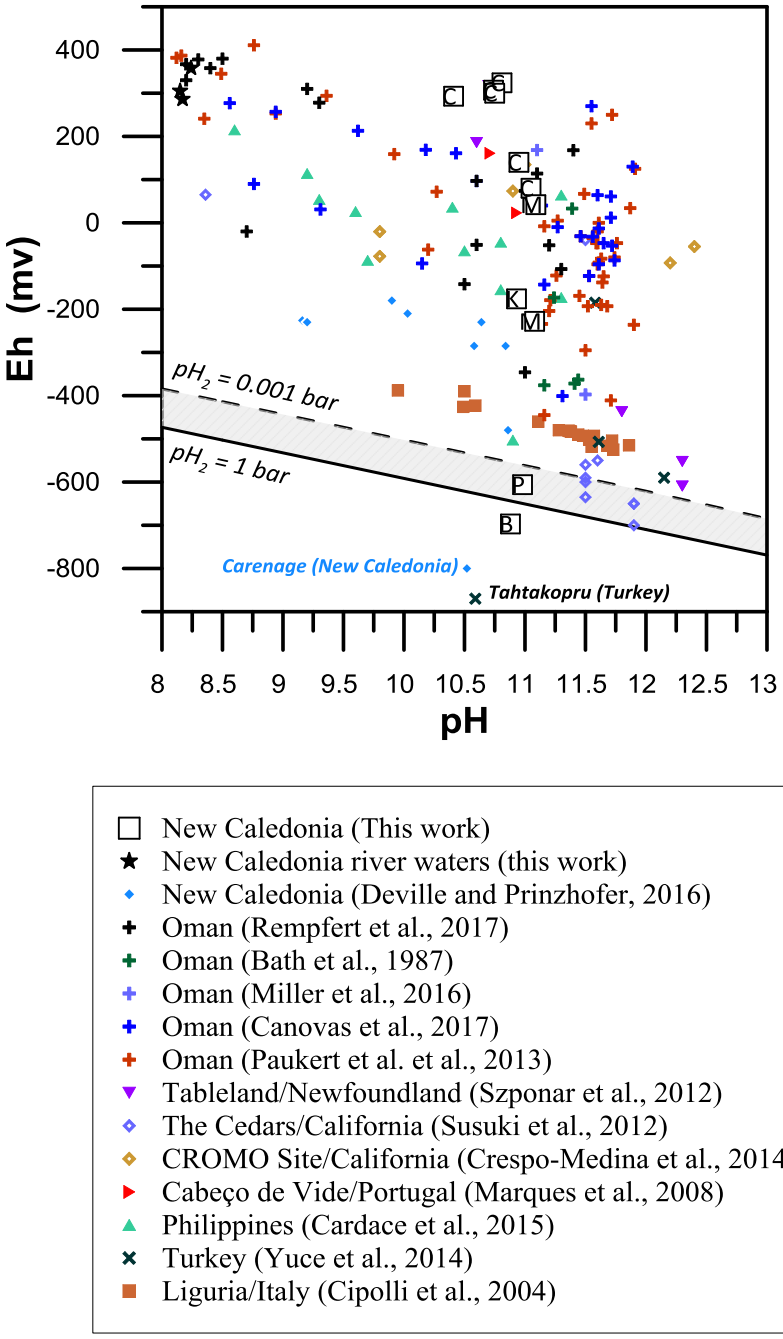


Figure 4 – The oxidation-reduction potential Eh versus pH. The dashed lines correspond to the water reduction reaction (eq. 2) at 25°C for the two mentioned hydrogen partial pressures. The symbols for New Caledonia are: B= Bain des Japonais, C = La Coulée, P = Pirogues, M = Montagne des Sources, K = Kaoris. The Carenage spring is the name given to the Bain des Japonais by [Deville and Prinzhofer, 2016]. The Tahtakopru spring is one of the springs of the Kilzilgag ophiolite (Turkey; [Yuce et al., 2014]).

4.2 The composition of the gases venting at the Bain des Japonais and Kaoris springs

The gas samples were collected between October, 2011 and November, 2014 at eight different dates in two springs of the Prony Bay (Table S2). At a given date, the concentration values are scattered, between 5 and 40% for H_2 and between 5 and 25% for CH_4 (Fig. 5). H_2 values are similar for the two springs, but CH_4 is lower at the Kaoris than at the Bain des Japonais. Some of the samples contain elevated concentrations of oxygen that we have attributed to air contamination (Table S2). Assuming that the nitrogen content of air is four times larger than its oxygen content and that air and the sampled gases are perfect gases, a corrected nitrogen content (in percentage) in each gas sample can be calculated using:

$$P_{N_2}(corr.) = P_{N_2}(raw) - 4\,P_{O_2}(raw) \quad (2)$$

In eq. 2, "raw" designates the results of the chemical analysis (ionic chromatography). The hydrogen and methane concentrations are then recalculated using this corrected nitrogen concentration.

Data reveal a slightly increasing trend for H_2 and slightly decreasing for CH_4 during the four-year survey (Fig. 5). The scatter of the data is also due to the number of samples collected at a single date (Fig. 6).

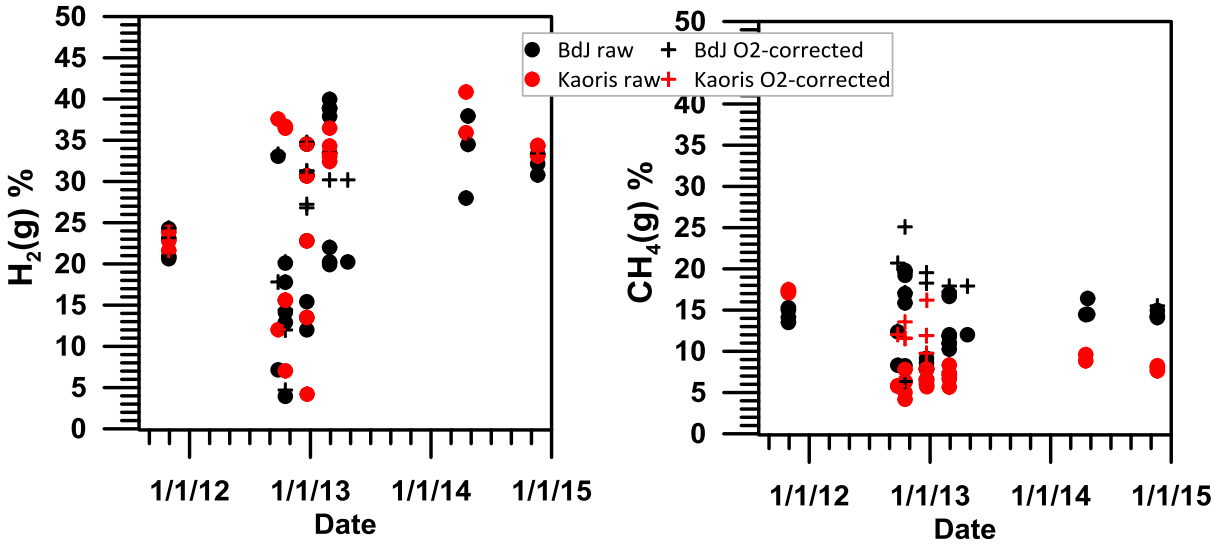


Figure 5 – Uncorrected (filled dots) and O_2-corrected (crosses) hydrogen and methane contents of the gases venting at the Bain des Japonais (black symbols) and at the Kaoris spring (red symbols).

When the number of samples collected at a given date allows it (e.g. Oct. 17, 2012; Table S2), the data show a correlation between the methane and hydrogen contents (Fig. 6). This correlation also appears on the entire data set, with different trends for the Kaoris and for the Bain des Japonais. Data depicted in Figs. 5 and 6 also show that the hydrogen content of the gases can fluctuate during the time of sampling on a given day, for example between 20 and 35% on Oct. 17, 2012. Because gas flow is steady at these two springs, it takes less than half an hour to collect 5 samples. It also shows that the conversion of hydrogen to methane (see below) is also very rapid, otherwise the methane concentration would not be correlated to that of hydrogen. In future studies, it will be necessary to note, not only the date of sampling, but also the hour.

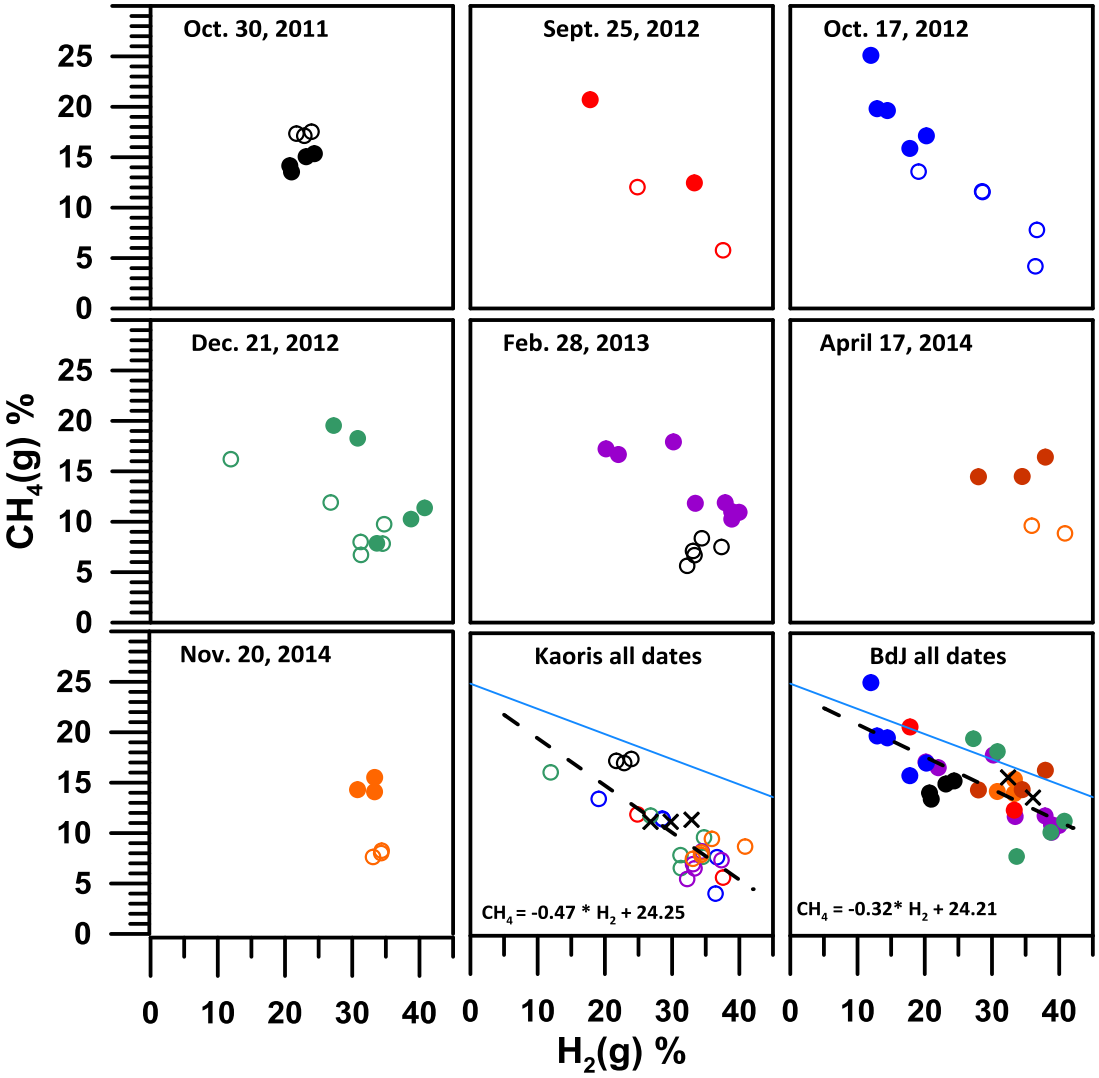


Figure 6 – The $CH_4(g)$ concentration of the Bain des Japonais and the Kaoris springs versus that of $H_2(g)$ for each date and for the whole data set. Open dots: Kaoris; filled dots: Bain des Japonais (BdJ); crosses: Vacquand et al. 2018. The dashed lines are fits to the data and the formulas are the expressions of the linear regressions. The plain lines represent the variation of the methane and hydrogen concentrations due to the reaction of fully oxidized carbon (such as CO_2) with hydrogen to produce methane, thus with a slope of -0.25 (see text and Fig. 7).

4.3 A comparison of the gas composition of New Caledonia alkaline springs with similar sites worldwide

Gas venting is commonly observed in hyperalkaline springs, but not in all of them. Whereas it is revealed by bubbles in spring waters, it can be detected as "dry" seeps in serpentinized peridotites [*Zgonnik et al.*, 2019]. The compositions of free gases venting in Oman, Italy (Liguria and Elba Island), Turkey and the Philippines have been corrected for O_2 contamination and recalculated for the N_2-H_2-CH_4 system, as done for New Caledonia (Fig. 7; see plots for each location in Fig. S3). It has already been shown that gases can be classified into a few types, such as H_2-rich, CH_4-rich or N_2-rich [*Boulart et al.*, 2013; *D'Alessandro et al.*, 2018b; *Deville and Prinzhofer*, 2016; *Vacquand et al.*, 2018].

The present data point to three categories (Fig. 7):

1) Gases with little or no hydrogen (CH_4-N_2 gases). The methane content of these CH_4-N_2 gases varies within a large range, between 0 and 100%. They are found in the Voltri ophiolite in Liguria (Northern Italy; [*Boschetti et al.*, 2013; *Boulart et al.*, 2013; *Etiope and Whiticar*, 2019], in the Gulderen and Gokdere springs of the Kilzidag ophiolite in Turkey [*D'Alessandro et al.*, 2018b], in the submarine seeps offshore the Elba Island (Italy; [*Sciarra et al.*, 2019], in the sample collected at the submarine Aiguille de Prony in the Prony Bay in New Caledonia [*Vacquand et al.*, 2018] and in the Chimarea seeps (Turkey) where venting gases are almost pure methane with less than 10% of either N_2 or H_2 [*Etiope et al.*, 2011; *Vacquand et al.*, 2018]. [*Vacquand et al.*, 2018] report the very peculiar composition of a gas sample of the Aiguille de Prony (New Caledonia) collected in the vial containing

444 a degassing water, and as such not a free gas sample *per se*. It contains no hydrogen and only a very
445 small quantity (5%) of methane and as such is almost pure nitrogen. Several samples collected in
446 Oman by [*Neal and Stanger*, 1983] are merely air, but the gas sample pure nitrogen at the Huwayl
447 Qufays spring is pure nitrogen.

448 2) Gases with little or no nitrogen (CH_4-H_2 gases). They vent in the dry seeps of Los Fuegos
449 Eternos and Nagsasa Bay in the Philippines [*Abrajano et al.*, 1988; *Vacquand et al.*, 2018], of the
450 Kurtbagi area in the Kilzidag ophiolite (Turkey; [*D'Alessandro et al.*, 2018b; *Yuce et al.*, 2014] and
451 also of the Chimarea seeps (Turkey; [*Etiope et al.*, 2011; *Vacquand et al.*, 2018]).

452 3) The compositions of gases collected in New Caledonia (this work; [*Vacquand et al.*, 2018]),
453 in Oman [*Boulart et al.*, 2013; *Neal and Stanger*, 1983; *Sano et al.*, 1993; *Vacquand et al.*, 2018], at
454 the Mangatarem site in the Zambales ophiolite (Philippines; [*Vacquand et al.*, 2018]), and at the
455 Tahtakopru springs of the the Kilzidag ophiolite (Turkey; [*D'Alessandro et al.*, 2018b] can be grouped
456 into the N_2-H_2-CH_4 type. They build a trend from almost pure hydrogen, as found in Oman, to N_2-CH_4
457 gases containing no hydrogen and no more than 20% of methane, as found in Liguria at Acquasanta
458 [*Etiope and Whiticar*, 2019], Branaga [*Boschetti et al.*, 2013] and GOR35 (one of the springs of Lago
459 Lavagnina; [*Boulart et al.*, 2013]) and at Gulderen spring of the Kilzidag ophiolite [*D'Alessandro et*
460 *al.*, 2018b]. Free gases for which hydrogen is dominant (>60%) have been collected in Oman by
461 [*Sano et al.*, 1993] in 1982-1983 and by [*Neal and Stanger*, 1983] at dates that are not mentioned, but
462 likely at the same period as Sano et al., and by [*Vacquand et al.*, 2018] between 2008 and 2012. While
463 these data are in fair agreement at high hydrogen content, in spite of the scatter, they differ at
464 hydrogen concentrations below 60%. [*Boulart et al.*, 2013] report Omani gas compositions with
465 hydrogen concentrations lower that those reported by [*Vacquand et al.*, 2018], although the samples
466 have been collected mostly at the same locations. The three points with the lowest H_2 contents
467 (20<H2<40%) are nevertheless in agreement. Also, the data for New Caledonia reported by these two
468 research groups [*Boulart et al.*, 2013; *Vacquand et al.*, 2018] are in full agreement, so that it is
469 unlikely that these differences for Oman are due to different sampling or analytical methods.
470

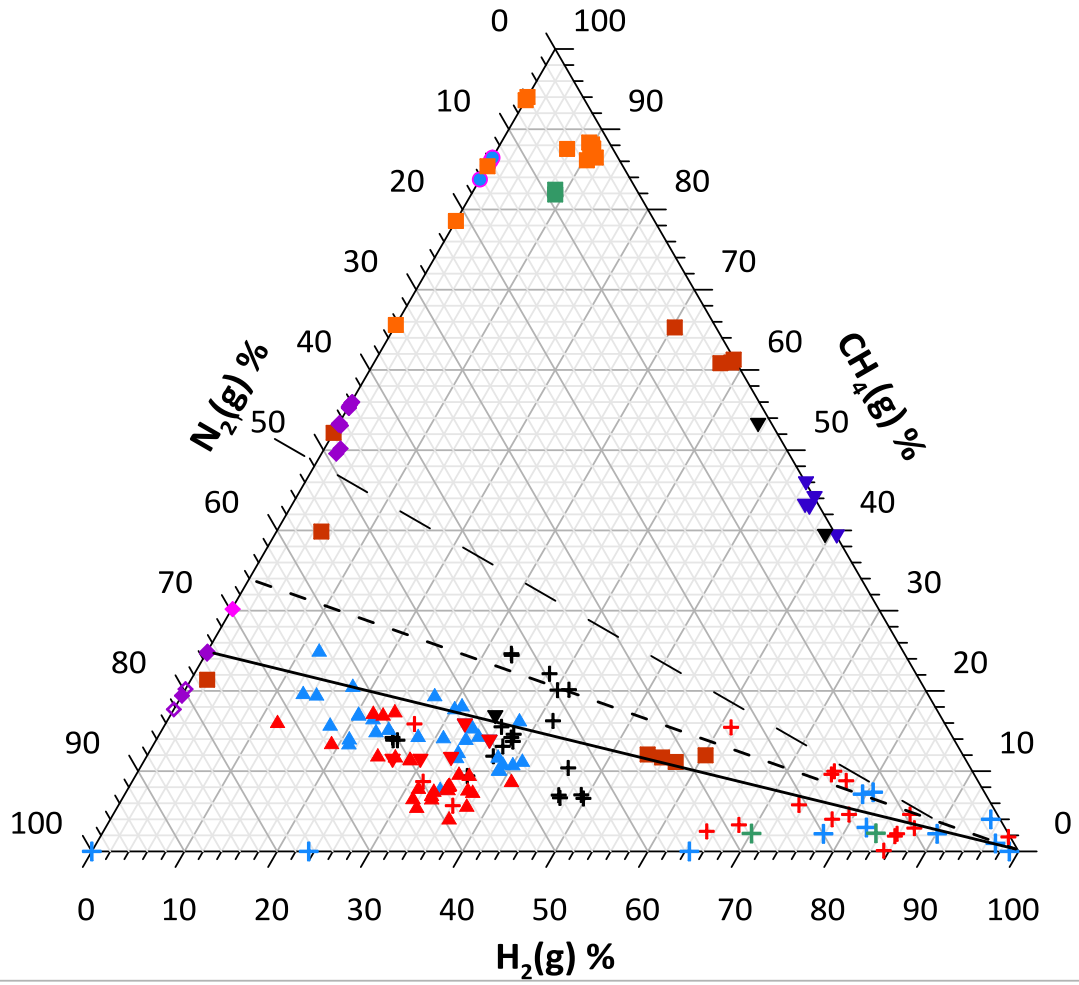


Figure 7 – A triangular plot of the O_2-corrected free gas compositions in serpentinizing environments. The black plain line is the line with a slope of -0.25 corresponding to the Sabatier reaction involving CO_2. The short dash line has a slope of -0.33 corresponding to a Fisher-Tropsch-type reaction involving carbon monoxide (see text). The long dash line represents the reaction of elemental carbon with hydrogen (slope -0.5).

5 Discussion

The present analysis of the free gas composition is based on the observation that the endmember high-pH waters discharging at the springs are totally devoid of oxygen, meaning that oxygen is consumed in the subsurface and that gases venting at the surface should also be oxygen-free. Small amounts of oxygen would not drastically change the correction (eq. 2). Oxygen is very rapidly consumed when oxic waters flow into geological formations (see the examples of oxygen dynamics in karstic environments; [*Monnin et al.*, 2019; *Young et al.*, 2018]). This lends support to the conclusion that the hydrothermal systems responsible for the discharge of high-pH waters at the surface are anoxic.

The composition of gas samples collected the same day at a given spring in New Caledonia is variable (Fig. 6). Such a very rapid (hourly) variation of the hydrogen concentration of gases emitted at the surface has been documented in the so-called "fairy circles" in Brazil [*Myagkiy et al.*, 2020]. The hydrogen concentration is roughly increasing (and the methane roughly decreasing) with time, for the period of the survey (3 years). The four data sets for the Oman gas samples have been sampled at dates that span from the early eighties ([*Neal and Stanger*, 1983; *Sano et al.*, 1993] to the beginning of the years 2010 [*Boulart et al.*, 2013; *Vacquand et al.*, 2018]. All these data point to a time variation of the free gas compositions, that for now cannot be related to seasonal or climatic change but certainly reveal the dynamics of the hydrothermal system. Only long-term monitoring, with measurements at high frequency can provide further insight into this variation.

Serpentinization is the aqueous alteration of metallic minerals such as olivine to produce serpentine. It can be represented by:

$$\mathbf{3}\left(\boldsymbol{Mg},\ \boldsymbol{Fe^{II}}\right)_{\mathbf{2}}\boldsymbol{SiO_4}(\boldsymbol{s}) + \mathbf{4}\boldsymbol{H_2O}(\boldsymbol{l}) \rightleftharpoons \mathbf{Mg_3Si_2}\boldsymbol{O_5}(\mathbf{OH})_4(\boldsymbol{s}) + \boldsymbol{Fe_3O_4}(\boldsymbol{s}) + \boldsymbol{H_2}(\boldsymbol{aq}) \qquad (3)$$

This reaction produces hydrogen, which at first is dissolved (which is indicated by $H_2(aq)$ in Eq. 3). When the hydrogen concentration reaches the saturation value, a gas phase is produced (degassing, bubbling):

$$\boldsymbol{H_2}(\boldsymbol{aq}) \rightleftharpoons \boldsymbol{H_2}(\boldsymbol{g}) \qquad (4)$$

Hydrogen can react with carbon-containing substances to produce methane. There are several ways to write this hydrogen consumption. All of them represent a well-defined mechanism. They also place strong constrains on the nature (for example carbon oxidation state) and the physical state (aqueous or gaseous) of the reactants. For example, hydrogen consumption to give methane through hydrogenotrophic methanogenesis (thus driven by methanogens), and therefore necessarily in the aqueous phase, can be represented by:

$$\boldsymbol{CO_2(aq) + 4H_2(aq) \rightleftharpoons CH_4(aq) + 2H_2O(l)} \quad (5)$$

In eq. 5, carbon is totally oxidized, for example as in carbonic acid. Again the methane concentration in the aqueous phase can reach the saturation value and methane will degas:

$$\boldsymbol{CH_4(aq) \rightleftharpoons CH_4(g)} \quad (6)$$

A methane production in the gas phase could be written in a similar way, which corresponds to the Sabatier reaction:

$$\boldsymbol{CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(l)} \quad (7)$$

Strictly speaking, the Sabatier reaction is a catalyzed process at elevated temperatures (400-500°C) converting carbon dioxide into methane (methanation). Both Eqs. 6 and 7 have the same stoichiometry: four moles of hydrogen are consumed to produce one mole of methane. In a plot of the methane versus the hydrogen content this would be represented by a line with a slope of -0.25.

The Fisher-Tropsch reaction is the conversion of carbon monoxide into alkanes:

$$\boldsymbol{nCO(g) + 2(2n+1)H_2(g) \rightleftharpoons C_nH_{2(n+1)}(g) + nH_2O(l)} \quad (7)$$

One of the criteria distinguishing the Sabatier reaction from the Fisher-Tropsch process is that the first one leads to an almost pure methane (methanation) while the second one leads to a more complex mixture of higher alkanes. Methane production following a Fisher-Tropsch scheme can be written as:

$$\boldsymbol{CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(l)} \quad (9)$$

In a plot of the methane versus the hydrogen content of the gas, eq. 9 would be represented by a line with a slope of -0.33.

524 Elemental carbon has been considered as a possible source of carbon in methane production in
525 serpentinizing environments (e.g. [*Vacquand et al.*, 2018]):

$$\boldsymbol{C(s) + 2H_2(g) \rightleftharpoons CH_4(g)} \quad (10)$$

526 Reaction 10 consumes two moles of hydrogen to produce one mole of methane, thus leading to a line
527 with a slope -0.5 in a methane versus hydrogen plot.

528 Serpentinization can be described as a process starting with the production of hydrogen (eq. 3)
529 followed by hydrogen consumption, either in the gas phase (eq. 7) or in an aqueous solution (eq. 5) to
530 produce methane. The data reported in Fig 7 are more consistent with the stoichiometry of the
531 reactions involving fully oxidized carbon (eq. 5 and 7) than with those involving less oxidized carbon
532 (eq. 8) or reduced carbon (eq. 9). As such, in a strict sense, it should be termed Sabatier-type reaction
533 instead of Fischer-Tropsch type (FFT). This distinction is more significant than what it seems as it
534 directly relates to the ongoing debate on the nature of the carbon source in low temperature
535 serpentinization. Increasingly complex reaction schemes and carbon substrates are now contemplated
536 and discussed (e.g. [*Menez*, 2020; *Reeves and Fiebig*, 2020]).

537 Yet this correlation between the hydrogen and methane contents of the H_2-CH_4-N_2 gases does
538 not distinguish a process taking place in the gas phase from a reaction in an aqueous solution followed
539 by degassing. It also implies that nitrogen is produced simultaneously with hydrogen consumption and
540 methane formation. If this was not the case, for example if nitrogen was coming from deeper sources
541 such as sediments, crustal or mantle rocks below the ophiolites [*Vacquand et al.*, 2018], it would be
542 found in all samples so that H_2-rich gases would be diluted by this deeply-sourced nitrogen and their
543 composition would move away from the pure H_2 apex and from the CH_4-H_2 gas type (Fig. 7). It can be
544 proposed that the chemical changes brought by serpentinization provide the necessary conditions for
545 the production of gaseous nitrogen from dissolved nitrate, i.e. denitrification. Such a process which is
546 mediated by bacteria at surface conditions, has not been studied so far in hyperalkaline environments.

547 The data for the Kaoris spring (and to a lesser extend for the Bain des Japonais) (this work)
548 show a CH_4 content lower than the stoichiometry of the Sabatier reaction (Fig. 7; Fig S3). This can be

attributed to a consumption of methane, but it is difficult to consider such a consumption in the gas phase (apart from burning). Methanotrophs and methanogens have already been identified in several alkaline springs such as Prony Bay (in both Kaoris and Bain des Japonais springs) [*Frouin et al.*, 2018; *Mei et al.*, 2016; *Postec et al.*, 2015; *Quemeneur et al.*, 2014], the Voltri ophiolite (Liguria, Italy) [*Brazelton et al.*, 2017; *Quéméneur et al.*, 2015], the Santa Elena ophiolite (Costa Rica) [*Crespo-Medina et al.*, 2017], the Oman ophiolite ([*Kraus et al.*, 2020; *Rempfert et al.*, 2017]; Kraus et al., 2020) and the Cedars springs (California) [*Suzuki et al.*, 2013]. Methane consumption or production by microorganisms take place in the aqueous phase. Again transfer of gases from the gas phase to the aqueous phase (and conversely) plays a role in the methane and hydrogen budget of the system. It would be erroneous to conclude that a Sabatier-type reaction in the gas phase necessarily implies an overall abiotic formation of methane.

The origin of methane (abiotic, biogenic, thermogenic, magmatic) can be inferred from a variety of criteria, each of them with its advantages and pitfalls (e.g. [*Etiope and Whiticar*, 2019; *Reeves and Fiebig*, 2020]. Gases venting in fractures (dry) seeps and in springs were suggested to belong to the abiotic methane domain in a δ^2H versus $\delta^{13}C$ diagram [*Vacquand et al.*, 2018]. Data for Oman, Philippines, Liguria, Turkey and Elba Island indeed plot within the of abiotic field empirically defined from isotopic data for methane venting in serpentinizing environments [*Milkov and Etiope*, 2018] (Fig. 8). This field has likely been delimited in part using the same data as reported in Fig. 8. Unfortunately the study of Milkov and Etiope does not provide a simple way of tracking down the data used to delimit the abiotic methane domain. This field can be subdivided into the dry seeps and the springs [*Vacquand et al.*, 2018]. Note that the Gokdere spring of the Kildizag ophiolite (Turkey) lies in the "dry seeps" domain.

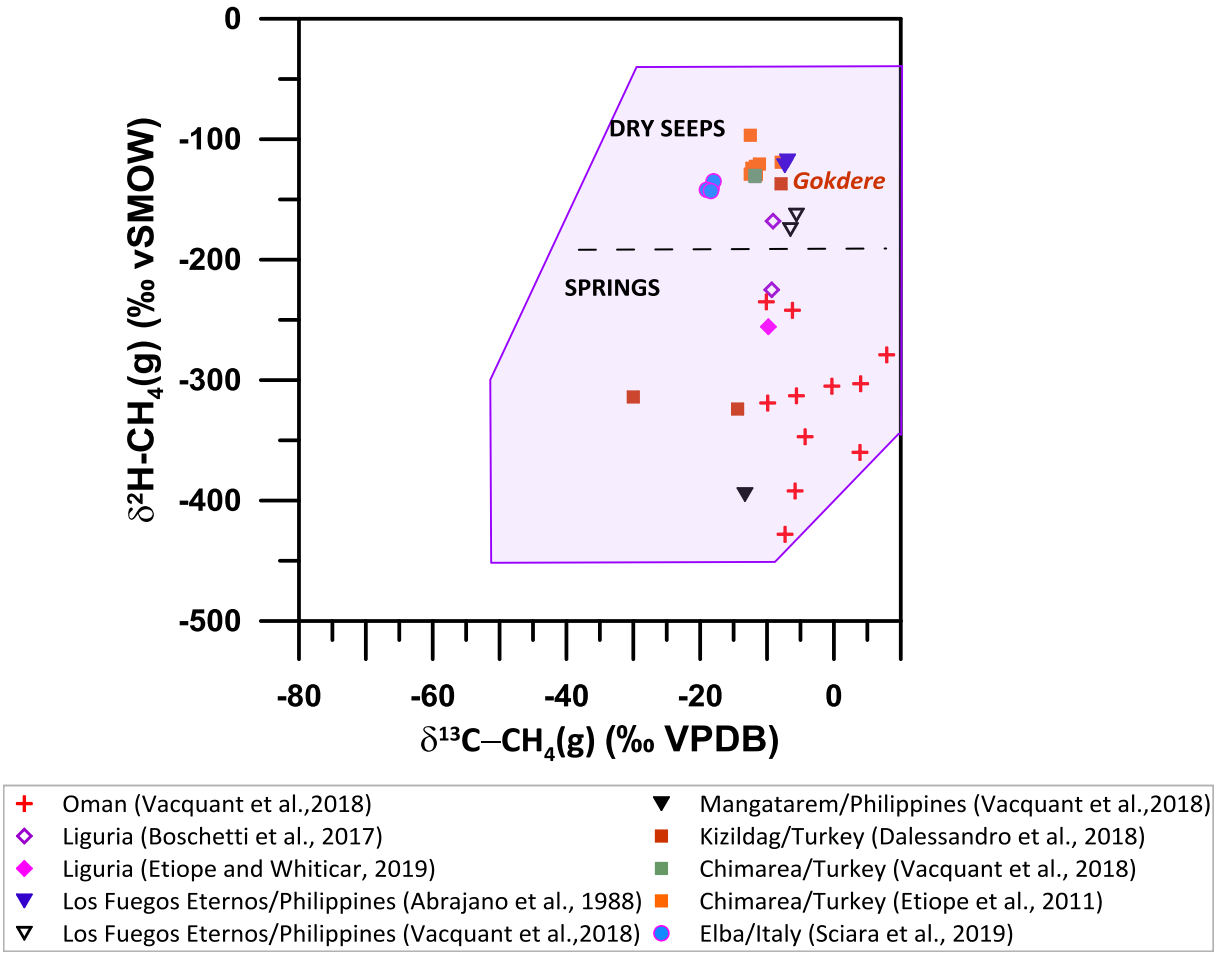


Figure 8 – The δ^2The hydrogen-methane relationship can also be seen as a picture of different stages of the evolution of the hyperalkaline hydrothermal systems in different regions, as a result of the local hydrological conditions, differences in lithology thus leading to different residence times of the waters and the gases in the subsurface. It can be speculated that the H_2-rich gases in Oman would then be the first step, after which methane starts forming in increasingly large amounts up to the point where all the hydrogen is consumed to reach the end point of the CH_4-N_2 gases.

It is also very likely that the flow path and the rate of flow of gases and waters are different. Etiope and Whiticar (2019) have shown that the carbon in the methane is older than 50 000 years as it is ^{14}C free whereas the age of the waters in hyperalkaline springs determined from ^{14}C in aqueous carbonate is only a few thousand years. As such this infers in an apparent decoupling of the sources of the waters and gases sampled at the surface. Serpentinization is an aqueous alteration process, so that hydrogen is first produced in an aqueous (liquid) environment. A gas phase will form only when the

hydrogen concentration exceeds saturation. The formation of methane may take place in this gas phase, as proposed by Etiope and Whiticar (2019). Methane can then dissolve into the water and be used as a substrate by methanotrophs.

Figure 9 presents a diagram that summarizes the observations and conclusions of this work. It highlights the relationship between the gas and aqueous phases, but cannot explain the reason why gases in dry seeps do not contain nitrogen. The δ^2H and $\delta^{13}C$ isotope data (Fig. 8) point to isotopic δ^2H-CH_4(g) signatures different for dry seeps than those for springs. This may indicate different mechanisms at play in the generation of methane. Serpentinization is the first step of the water-rock interactions during which hydrogen is generated by the reduction of water and the oxidation of metals. Because it is an aqueous process, hydrogen is forming within the aqueous phase, and a gas phase will form only when its concentration exceeds saturation. Methane can then be generated within this gas phase by a Sabatier reaction. Methane will dissolve into the aqueous solution where it can support the development of methanotrophs. The methane budget in the gas will be due to its production by the Sabatier process and its consumption by its dissolution in the water. In the aqueous phase, the methane budget will result from its uptake from the gas phase, its consumption by methanotrophs, but also its formation by potential methanogens.

Clumped isotope data for CH_4 and an analysis of the dissolved gas data will be reported in separate publications.

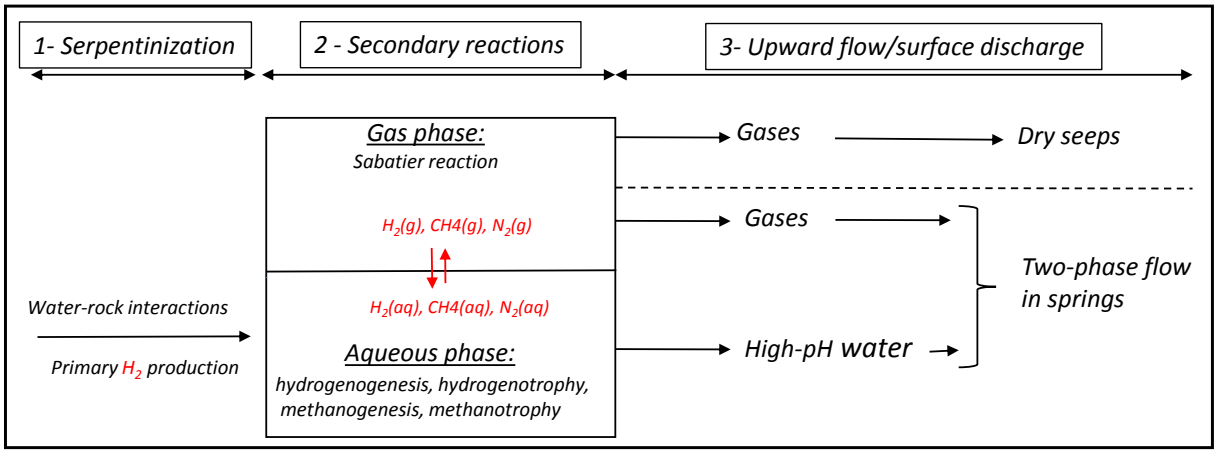


Figure 9 – A diagram summarizing the hydrogen, methane, and nitrogen budgets in the serpentinizing environment. The first step is hydrogen production by the serpentinization reaction. The hydrogen concentration increases in the water up to the point where saturation is exceeded, and a gas phase forms. In Step 2, methane is produced by a secondary process with the stoichiometry of the Sabatier reaction. Nitrogen is also produced during this step (see text). The gases are reactive in both the gas and the aqueous phases and their concentrations are linked by a solubility relationship. In the last step (3) gases and water flow toward the surface to discharge at dry seeps and springs.

6 Conclusions

- The dissolved oxygen concentrations measured *in situ* in the New Caledonia on-land springs along with literature data on alkaline springs worldwide show that high-pH waters discharging at the springs are anoxic. Therefore gases venting at the spring should also not contain any oxygen. It is then necessary to correct gas compositions for atmospheric oxygen contamination.
- The compositions of gases collected at the Kaoris and Bain des Japonais springs in New Caledonia over a four-year period (2011–2014) show daily variations and some trends during the duration of the survey. Free gases collected in Oman by four different research groups over a period of about 20 years also display varying compositions. It can be cautiously concluded that there is a time variation of composition of free gases venting in these serpentinizing environments, at the hour scale as well as at the seasonal or yearly scale.
- The hydrogen and methane contents of free gases collected in New Caledonia along with those of Oman, the Mangatarem (Philippines) spring and the Tahtakopru (Turkey) springs define a trend of H_2-CH_4-N_2 gases going from almost pure hydrogen to N_2-CH_4 gases (with CH_4 around 25%). The slope of this trend is consistent with the stoichiometry of methane production from an oxidized carbon source such as carbon dioxide or carbonic acid. It also implies that nitrogen is produced simultaneously with methane.
- The stoichiometry of the hydrogen-methane reaction is consistent with a Sabatier reaction in the gas phase or a methane production by hydrogenotrophic methanogens in the aqueous

633 phase. The two mechanisms can take place at the same time and can be coupled through the
634 transfer of gases from the water to the gas phase and conversely. This last point can be
635 constrained by the study of the concentration of dissolved gases to investigate the conditions
636 at which the water degasses.
637

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The supplementary information for this paper is availablel at the CNRS HAL archive (https://hal.archives-ouvertes.fr/).

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