

JGR Biogeosciences

RESEARCH ARTICLE

10.1029/2021JG006243

Special Section:

Ophiolites and Oceanic Lithosphere, with a focus on the Samail ophiolite in Oman

Key Points:

- Hyperalkaline spring waters are anoxic. An elevated high O₂ content in free gases results from air contamination
- The relationship between H₂ and CH₄ contents of free gases is consistent with the conversion of fully oxidized carbon (CO₂)
- The H₂-CH₄ relation is consistent with a Sabatier reaction in the gas or methane production by hydrogenotrophic methanogens in the water

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

C. Monnin,
Christophe.monnin@get.omp.eu

Citation:

Monnin, C., Quéméneur, M., Price, R., Jeanpert, J., Maurizot, P., Boulart, C., et al. (2021). The chemistry of hyperalkaline springs in serpentinizing environments: 1. The composition of free gases in New Caledonia compared to other springs worldwide. *Journal of Geophysical Research: Biogeosciences*, 126, e2021JG006243. <https://doi.org/10.1029/2021JG006243>

Received 11 JAN 2021
Accepted 20 AUG 2021

Author Contributions:

Conceptualization: Christophe Monnin

Data curation: Christophe Monnin, Marianne Quéméneur, Roy Price, Julie Jeanpert, Pierre Maurizot, Cédric Boulart, Jean-Pierre Donval, Bernard Pelletier

Formal analysis: Christophe Monnin

The Chemistry of Hyperalkaline Springs in Serpentinizing Environments: 1. The Composition of Free Gases in New Caledonia Compared to Other Springs Worldwide

Christophe Monnin¹ , Marianne Quéméneur² , Roy Price³, Julie Jeanpert⁴ , Pierre Maurizot⁴, Cédric Boulart⁵ , Jean-Pierre Donval⁶ , and Bernard Pelletier⁷

¹Géosciences Environnement Toulouse, (CNRS/UPS/IRD/CNES), Toulouse, France, ²Aix-Marseille University, Université de Toulon, CNRS, IRD, MIO, Marseille, France, ³School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY, USA, ⁴DIMENC (Direction de l'Industrie, des Mines et de l'Energie), Nouméa, Nouvelle-Calédonie, ⁵AD2M UMR 7144 (CNRS, Sorbonne Université), Station Biologique de Roscoff, Roscoff, France, ⁶IFREMER, Unité Géosciences Marines/Laboratoire Cycles Géochimiques, Plouzané, France, ⁷Géoazur (UCA, IRD, CNRS, OCA), Centre IRD de Nouméa, Nouméa, Nouvelle-Calédonie

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 (CH₄) and hydrogen (H₂). 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 H₂, CH₄, and N₂ and their composition has slightly varied during the 4-year field survey. An elevated oxygen (O₂) content in a high-pH water sample is due to air uptake during surface flow. O₂-corrected gas compositions along with those published for gas data obtained at similar serpentinizing environments (Italy, Turkey, Philippines, and Oman) show that the H₂ and CH₄ concentrations display a linear correlation with a slope close to the value corresponding to the CH₄ production from carbon dioxide rather than 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 H₂ and CH₄ 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 (CO₂) 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 & Sherwood Lollar, 2013; Price et al., 2017; Sissmann et al., 2019), origin of life and deep

Funding acquisition: Christophe Monnin, Marianne Quéméneur, Bernard Pelletier

Investigation: Christophe Monnin, Marianne Quéméneur, Roy Price, Julie Jeanpert, Pierre Maurizot, Cédric Boulart, Jean-Pierre Donval, Bernard Pelletier

Project Administration: Christophe Monnin, Marianne Quéméneur, Bernard Pelletier

Writing – original draft: Christophe Monnin

Writing – review & editing: Christophe Monnin, Marianne Quéméneur, Roy Price, Julie Jeanpert, Pierre Maurizot, Cédric Boulart, Jean-Pierre Donval, Bernard Pelletier

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 CO₂ (Kelemen & 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 & Manning, 2019).

Sites of discharge of such very high pH waters are found on land in Oman (Chavagnac, Monnin, et al., 2013; Miller et al., 2016; Paukert et al., 2012; Stanger, 1985), in Northern Italy (Boschetti & Toscani, 2008; Chavagnac, Monnin, et al., 2013; Cipolli et al., 2004), Cyprus (Neal & Shand, 2002), the Philippines (Cardace et al., 2015), California (Boschetti et al., 2017; Morrill et al., 2013), Ontario (Sader et al., 2007), Newfoundland (Szponar et al., 2012), Portugal (Marques et al., 2008), Greece (D'Alessandro, Daskalopoulou, et al., 2018), Turkey (Meyer-Dombard et al., 2015; Yuce et al., 2014), Jordan (Khoury et al., 1992), 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, 2005) and in the mud volcanoes of the Marianna forearc (Fryer et al., 1989, 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, 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, Ceuleneer, et al., 2013) or submarine pinnacles at the Lost City (Kelley et al., 2005) and in the Prony Bay in New Caledonia (Launay & 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, 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 ≈ 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 dehydration of the Pacific plate subducting below the American continent (Boschetti et al., 2017). The other system that does not fit in the classification is in Prony Bay (southern lagoon of New Caledonia) where alkaline springs located in the lagoon discharge fresh waters into the marine environment (Monnin et al., 2014).

Globally, these hyperalkaline waters contain elevated concentrations of methane and hydrogen (Etiope & Whiticar, 2019). Gas venting is commonly observed but not at every location, while dissolved gases have

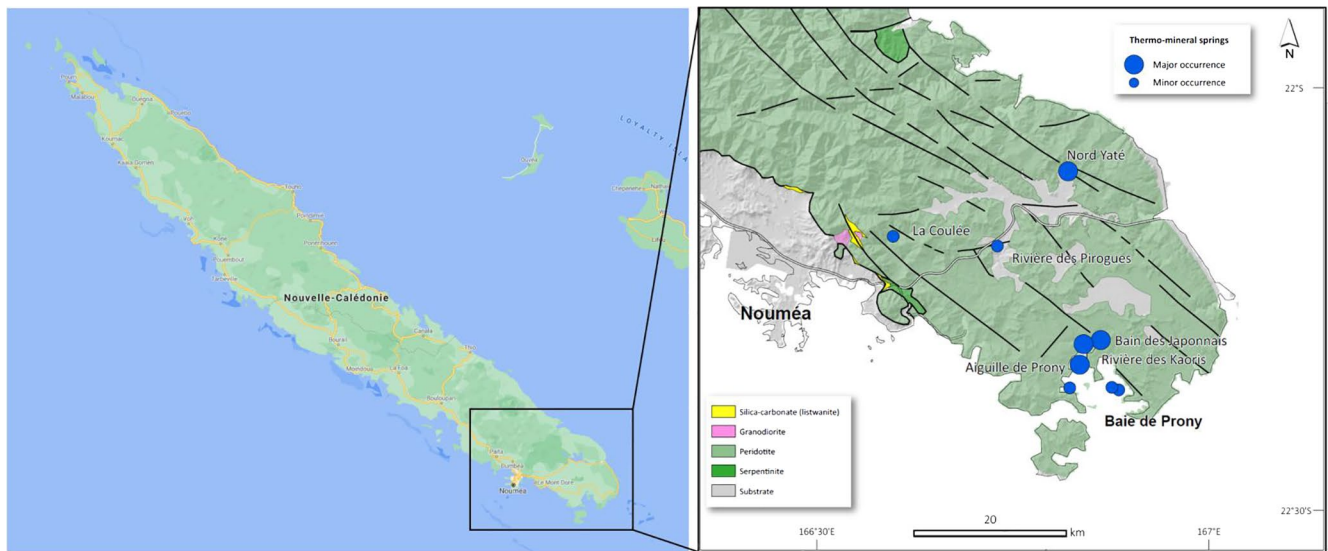


Figure 1. Location of the high pH springs in southern New Caledonia (after Maurizot et al., 2020).

been analyzed in numerous hyperalkaline springs (see the review of Etiope & Whiticar, 2019). Gas bubbles have been sampled in Oman (Boulart et al., 2013; Vacquand et al., 2018), in the Voltri ophiolite in Liguria (Northern Italy) (Boschetti et al., 2013; Boulart et al., 2013; Etiope & Whiticar, 2019), at several locations in the Philippines (Abrajano et al., 1988; Vacquand et al., 2018), and in Turkey (D'Alessandro, Yüce, et al., 2018; Vacquand et al., 2018), and New Caledonia (Vacquand et al., 2018). The gases are mainly composed of dihydrogen (H_2), dinitrogen (N_2), and methane (CH_4), with trace amounts of higher alkanes, carbon dioxide and monoxide, and helium. Oxygen is not always measured or reported. It can be found in noticeable concentrations, for example, up to 15% for one of the samples of the Kisecek spring in the Kizildag ophiolite in Turkey (D'Alessandro, Yüce, et al., 2018) or the Zambales springs in the Philippines (Abrajano et al., 1988).

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

The oxic/anoxic characteristic of the high pH waters has been determined from in situ 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

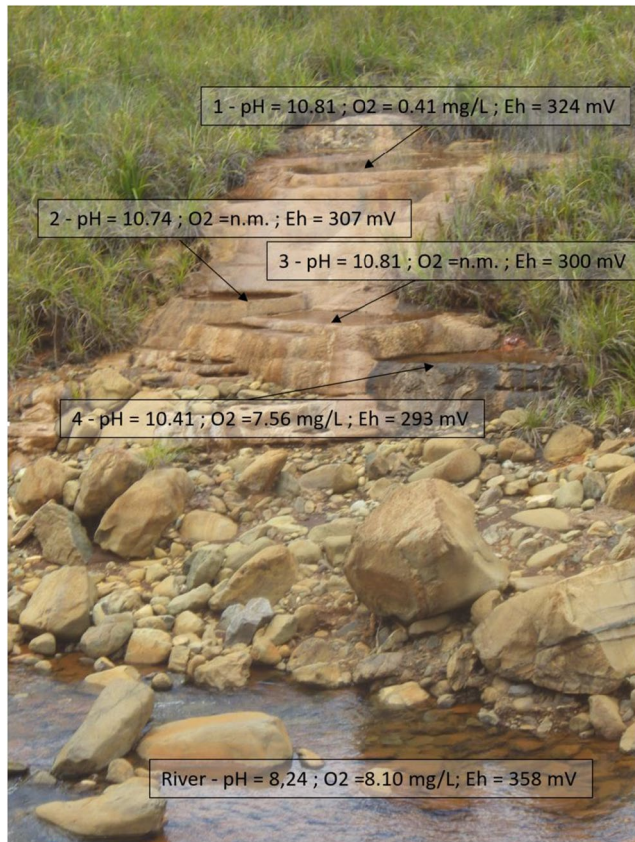


Figure 2. The high-pH spring of La Coulée. The water discharges in the upper pool (1) and flows down toward the river through the upper (2) and lower (3) intermediate pools. It gets oxygenated on the way, as indicated by the elevated O_2 content in the lower pool (4), at a value close to that of the river. n.m.: not measured.

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 (November 17 to December 15) (Figure 1).

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 (Figure 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” (Figure S1).

The spring of the Montagne des Sources (also named Rivière du Rocher) is located in a reserve. The access is totally restricted because this is where the city of Nouméa is getting its water supply from (Figure S1). A 5-h hike in the river bed is required to get to the spring. The spring is a 30-m long suite of large pools located right above the river bed and below a forest (Figure S1). These pools are about 1.5 m in diameter and about 1.5 m deep for the deepest one. Water flows at a high rate through an outlet situated in the middle of the wall of the structure. The pools contain varying amounts of branches and leaves from the trees above.

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

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

3. Sampling Procedures, In Situ Measurements, and Analytical Methods

3.1. Free Gas Sampling Procedure and In Situ Measurements: pH, Oxidation-Reduction Potential, Temperature, and Dissolved Oxygen

Gas samples were collected in 10 ml glass vials by the water displacement technique. It consists in filling the vial with spring water and immersing it upside down in the spring above the gas bubbles. 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 & 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 Marseille (MIO). They were kept at room temperature (i.e., plane cargo bays and lockers) while traveling between New Caledonia and metropolitan France (i.e., for about 30 h).

Temperature, pH, 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 (Figure 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). 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 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). Operating conditions for H₂, O₂, CH₄, and CO₂ 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. N₂ was determined by difference based on previous estimates (Monnin et al., 2014).

At IFREMER Brest, two analytical devices have been used: a gas chromatograph μ GC 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, 0.32 mm 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 min at the springs of La Coulée and Pirogues. Dissolved oxygen and ORP required an equilibration time of a few minutes (Figure 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 (Figure S2). The temperature variation can be due to a convection effect of the thin water layer. Indeed, the

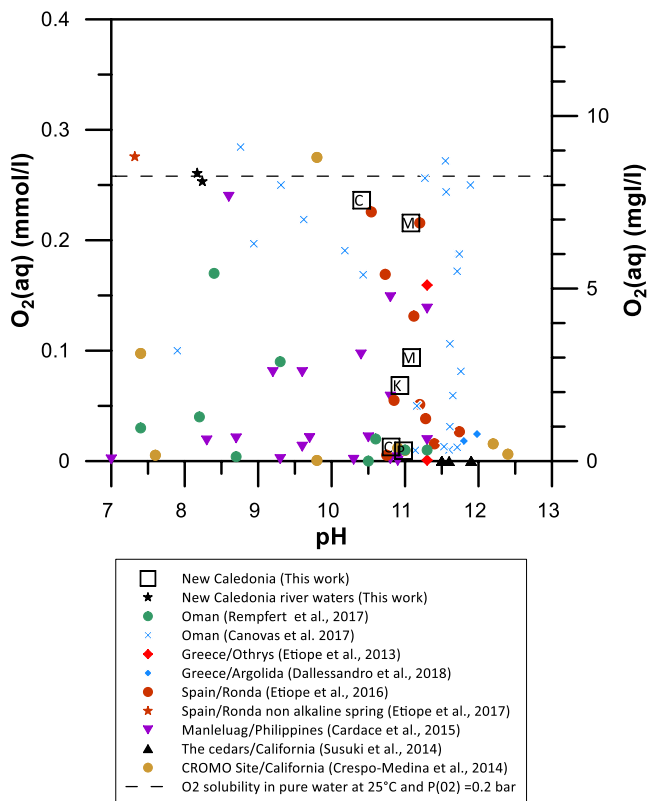


Figure 3. The dissolved oxygen concentration of the New Caledonia hyperalkaline springs and of other springs worldwide. The dashed line is the value of oxygen saturation in pure water at 25°C. The symbols for New Caledonia are: C = La Coulée, P = Pirogues, M = Montagne des Sources, K = Kaoris.

spring where the water flows on the rocks without being retained in a pool, but on the side of the very large pool (about 20 m wide) built by the river about 10 m downstream from the spring (Figure S1). It has been shown in many instances that gas bubbles forming in these high pH springs contain elevated concentrations of hydrogen (along with methane and nitrogen). This has been documented for the Prony bay (Deville & Prinzhofer, 2016; Monnin et al., 2014). We have observed at the Bain des Japonais in the Prony bay that gas bubbling disrupts the ORP measurement when a gas bubble hits the probe. This may explain the Eh maximum and the increase from -300 to -200 mv on December 2 at Pirogues (Figure S1). This H_2 -enriched gas venting may also be the cause of the dispersion of the Eh values.

4.1.4. Comparison With Other High-pH Springs Worldwide

4.1.4.1. The Dissolved Oxygen Content

Unfortunately, the dissolved oxygen concentration is not reported for every spring or seepage area documented in the literature. The dissolved oxygen concentration of the New Caledonia springs and of other high-pH springs worldwide are displayed versus pH in Figure 3. These measurements were made using different methods: with an oxygen probe (this work; Cardace et al., 2015; Etiopie et al., 2016; Rempfert et al., 2017; Suzuki et al., 2013), on site spectrophotometric measurements based on the indigo carmine reagent (Canovas et al., 2017) and gas chromatography analysis of the dissolved gases using the headspace method (Etiopie et al., 2016). In order to give the order of magnitude of oxygen saturation, we used the dissolved oxygen content of pure water at equilibrium with the atmosphere (i.e., for an oxygen partial pressure of 0.2 bar) at 25°C (8.3 mg/L) (Figure 3). An accurate calculation would require taking into account the temperature and the composition of the aqueous phase (the Setchenov correction to Henry's constant). For example, oxygen solubility in pure water at 40°C is 6.41 mg/L. The three values reported for river waters

discharging water temperature is between about 27°C while the air temperature on the days of measurements was over 30°C.

4.1.2. The Dissolved Oxygen Content

At the La Coulée, the water discharges in the upper pool from where it flows down to the other pools. The oxygen content of the water in the upper pool is 0.4, 7.56 mg/L in the lower pool and 8.24 mg/L in the river (Figure 2). The Eh values are the same in all the pools. The water discharging at the upper pool becomes oxygenated by air uptake when it flows downhill. This air and thus the CO_2 uptake lead to a small decrease in pH by 0.4 unit. Thus, for a given spring, variable values of in situ parameters can be obtained when measured away for the outlet.

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

4.1.3. The Oxidation-Reduction Potential

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

Eh at the spring Rivière des Pirogues has markedly varied between December 2 and 12, 2014 (Figure S1). There is also a small Eh maximum at Pirogues for December 2nd data. Very sporadic bubbling (a few events per hour) has been observed at the La Coulée and also at the Pirogues site. For this, latter spring bubbles were observed not in the seepage of the

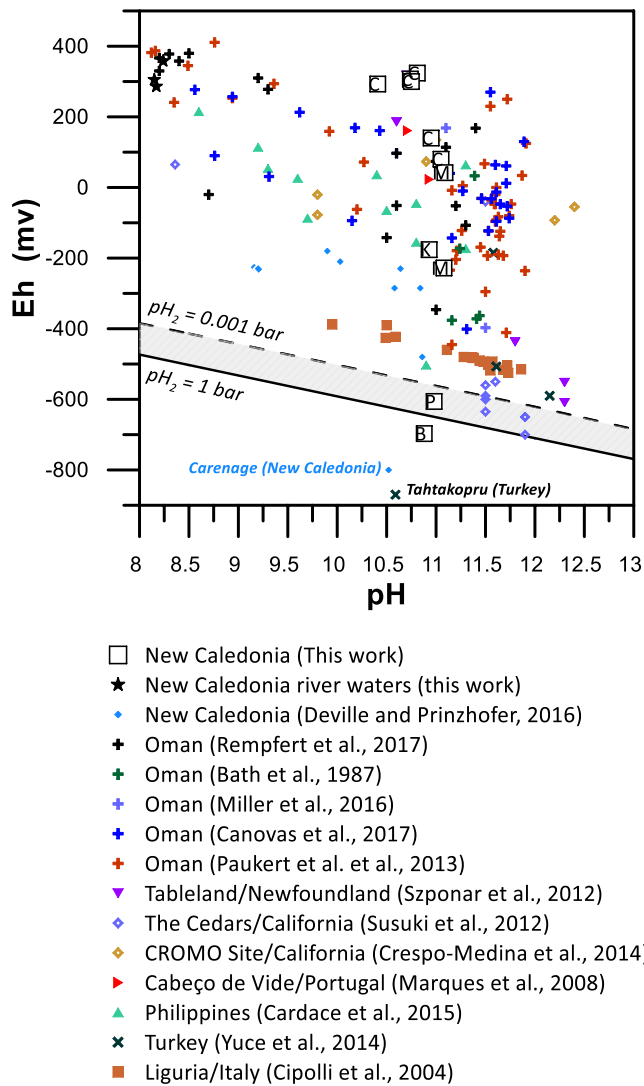


Figure 4. The oxidation-reduction potential Eh versus pH. The dashed lines correspond to the water reduction reaction (Equation 2) at 25°C for the two mentioned hydrogen partial pressures. The symbols for New Caledonia are: B = Bain des Japonais, C = La Coulée, P = Pirogues, M = Montagne des Sources, 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).

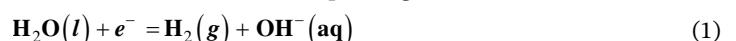
close to the alkaline springs in New Caledonia and a non-alkaline spring in Ronda (Spain; Etiope et al., 2016) are close to values of oxygen saturation in pure water (Figure 3). The present data for New Caledonia, but also the data for Oman (Canovas et al., 2017), for the Manleluag springs in the Philippines (Cardace et al., 2015) and for the Ronda springs in Spain (Etiope et al., 2016) show that at almost constant pH, the oxygen content of the water samples collected in the high-pH springs can vary from zero to values close to saturation. The waters at The Cedars springs in California (Suzuki et al., 2013) and of the Argolida and Othrys spring in Greece (D'Alessandro, Daskalopoulou, et al., 2018; Etiope et al., 2013) are either totally anoxic or have a very low oxygen content. Water samples collected in boreholes in Oman (Rempfert et al., 2017) or at the CROMO site (Coast Range Ophiolite Microbial Observatory) in Northern California (Crespo-Medina et al., 2014) are also oxygen free. The La Coulée spring shows that elevated dissolved oxygen concentrations measured away from the outlet result from atmospheric oxygen dissolution due to air uptake. On the other hand, this air contamination provides carbon dioxide to the water that contributes to the formation of the carbonate concretions building the pools (Chavagnac, Ceuleneer, et al., 2013; 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 ferrous iron (Leong & Shock, 2020; Neal & 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 composition of the gases venting at the seeps must then be corrected for this air contamination.

4.1.4.2. The Oxidation-Reduction Potential

The data set is very scattered with no clear relationship between Eh and pH (Figure 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 of the Kilzilgag ophiolite in Turkey (Yuce et al., 2014) and for a spring called Carénage in New Caledonia, which corresponds to the Bain des Japonais (Deville & Prinzhofer, 2016) are below the water reduction limit, -800 mV for a pH of 10.52 and -870 mV for a pH of 10.59, respectively.

There is an ambiguity in the Eh values reported in the literature as the reference potential (Ag/AgCl or H_2) is not always mentioned (e.g., Paukert et al., 2012). Some of the values reported in Figure 4 may be the values given by the ORP probe (i.e., in reference to the Ag/AgCl standard) and thus may be too high by about 200 mV (Figure S2). Such a correction would bring the redox potential of the Carenage and Tahtakopru springs close to the water reduction limit, that is, corresponding to reaction (1):



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

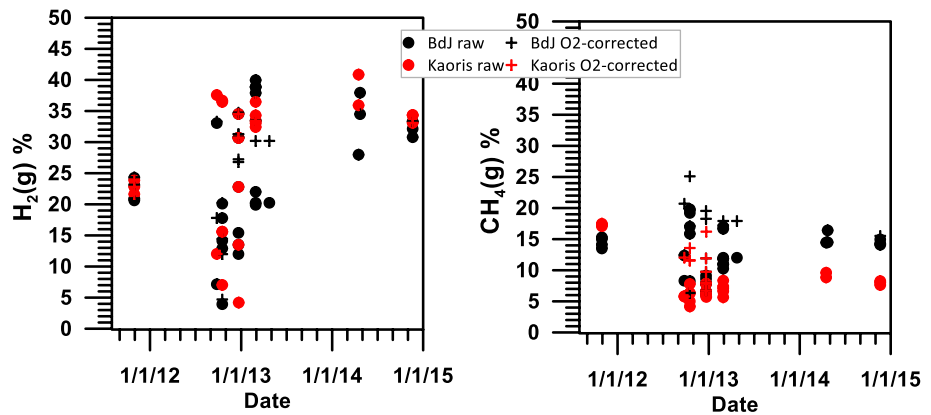


Figure 5. Uncorrected (filled dots) and O₂-corrected (crosses) hydrogen and methane contents of the gases venting at the Bain des Japonais (black symbols) and at the Kaoris spring (red symbols).

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 H₂ and between 5% and 25% for CH₄ (Figure 5). H₂ values are similar for the two springs, but CH₄ 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:

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

In Equation 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 H₂ and slightly decreasing trend for CH₄ during the four-year survey (Figure 5). The scatter of the data is also due to the number of samples collected at a single date (Figure 6).

When the number of samples collected at a given date allows it (e.g., October 17, 2012; Table S2), the data show a correlation between the methane and hydrogen contents (Figure 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 Figures 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 October 17, 2012. Because gas flow is steady at these two springs, it takes less than half an hour to collect five 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.

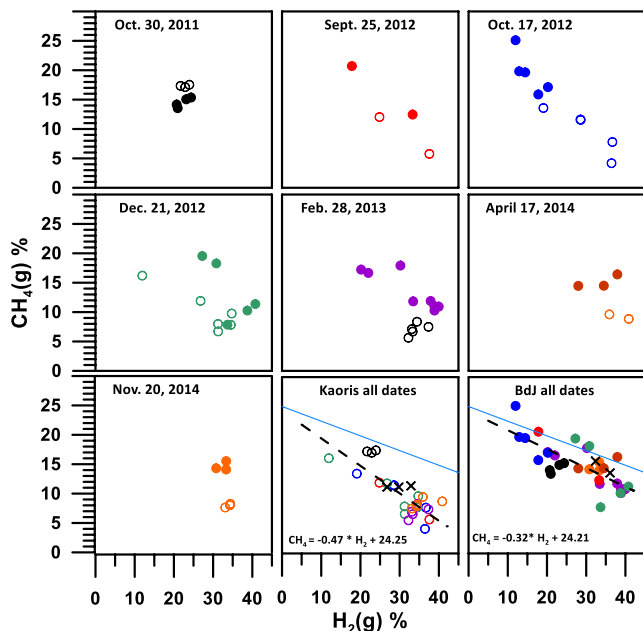


Figure 6. The CH₄(g) concentration of the Bain des Japonais and the Kaoris springs versus that of H₂(g) for each date and for the whole data set. Open dots: Kaoris; filled dots: Bain des Japonais (BdJ); crosses: Vacquand et al. (2018). The dashed lines are fits to the data and the formulas are the expressions 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 CO₂) with hydrogen to produce methane, thus with a slope of −0.25 (see text and Figure 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. However, it is revealed by bubbles in spring water that 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

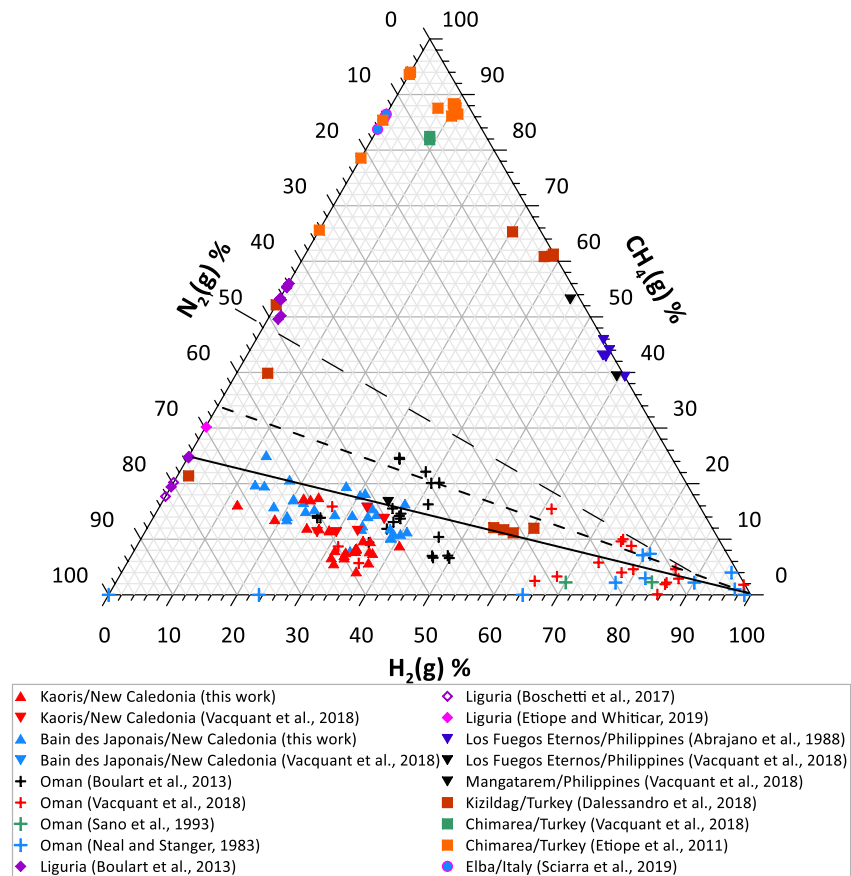


Figure 7. A triangular plot of the O_2 -corrected free gas compositions in serpentinizing environments. The black plain line is the line with a slope of -0.25 corresponding to the Sabatier reaction involving CO_2 . The short dash line has a slope of -0.33 corresponding to a Fisher-Tropsch-type reaction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

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 (Figure 7; see plots for each location in Figure 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, Yüce, et al., 2018; Deville & Prinzhofner, 2016; Vacquand et al., 2018).

The present data point to three categories (Figure 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; Etiopie & Whitar, 2019]), the Gulderen and Gokdere springs of the Kizildag ophiolite in Turkey (D'Alessandro, Yüce, et al., 2018), the submarine seeps offshore the Elba Island (Italy; [Sciarrà et al., 2019]), the sample collected at the submarine Aiguille de Prony in the Prony Bay in New Caledonia (Vacquand et al., 2018), and the Chimarea seeps (Turkey) where venting gases are almost pure methane with less than 10% of either N_2 or H_2 (Etiopie 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 a degassing water, and as such not a free gas sample *per se*. It contains no hydrogen and only a very small quantity (5%) of methane and as such is almost pure nitrogen. Several samples collected in Oman by Neal and Stanger (1983) are merely air, but the gas sample pure nitrogen at the Huwayl Qufays spring is pure nitrogen.
2. Gases with little or no nitrogen (CH_4 - H_2 gases). They vent in the dry seeps of Los Fuegos Eternos and Nagsasa Bay in the Philippines (Abrajano et al., 1988; Vacquand et al., 2018), of the Kurtbagi area in the

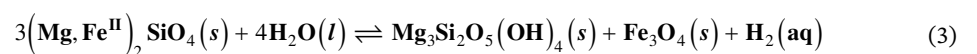
- Kilzidag ophiolite (Turkey; [D'Alessandro, Yüce, et al., 2018; Yuce et al., 2014]) and also of the Chimarea seeps (Turkey; [Etiopie et al., 2011; Vacquand et al., 2018]).
- The compositions of gases collected in New Caledonia (this work; [Vacquand et al., 2018]), in Oman (Boulart et al., 2013; Neal & Stanger, 1983; Sano et al., 1993; Vacquand et al., 2018), at the Mangatarem site in the Zambales ophiolite (Philippines; [Vacquand et al., 2018]), and at the Tahtakopru springs of the Kilzidag ophiolite (Turkey; [D'Alessandro, Yüce, et al., 2018]) can be grouped into the N₂-H₂-CH₄ type. They build a trend from almost pure hydrogen, as found in Oman, to N₂-CH₄ gases containing no hydrogen and no more than 20% of methane, as found in Liguria at Acquasanta (Etiopie & Whitticar, 2019), Branaga (Boschetti et al., 2013) and GOR35 (one of the springs of Lago Lavagnina; [Boulart et al., 2013]) and at the Gulderen spring of the Kilzidag ophiolite (D'Alessandro, Yüce, et al., 2018). Free gases for which hydrogen is dominant (>60%) have been collected in Oman by Sano et al. (1993) in 1982–1983 and by Neal and Stanger (1983) at dates that are not mentioned, but likely at the same period as Sano et al., and by Vacquand et al. (2018) between 2008 and 2012. While these data are in fair agreement at high hydrogen content, in spite of the scatter, they differ at hydrogen concentrations below 60%. (Boulart et al., 2013) report Omani gas compositions with hydrogen concentrations lower than those reported by Vacquand et al. (2018), although the samples have been collected mostly at the same locations. The three points with the lowest H₂ contents (20 < H₂ < 40%) are nevertheless in agreement. Also, the data for New Caledonia reported by these two research groups (Boulart et al., 2013; Vacquand et al., 2018) are in full agreement, so that it is unlikely that these differences for Oman are due to different sampling or analytical methods.

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 (Equation 2). Oxygen is very rapidly consumed when oxidic 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 (Figure 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 & 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:



This reaction produces hydrogen, which at first is dissolved (which is indicated by H₂(aq) in Equation 3). When the hydrogen concentration reaches the saturation value, a gas phase is produced (degassing, bubbling):



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 constraints on the nature (for example carbon oxidation state) and the physical state (aqueous or gaseous) of the

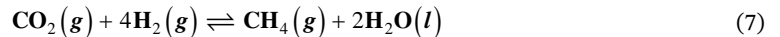
reactants. For example, hydrogen consumption to give methane through hydrogenotrophic methanogenesis (thus driven by methanogens), and therefore necessarily in the aqueous phase, can be represented by:



In Equation 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:

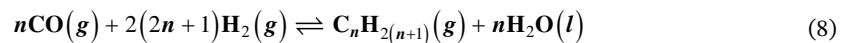


A methane production in the gas phase could be written in a similar way, which corresponds to the Sabatier reaction:

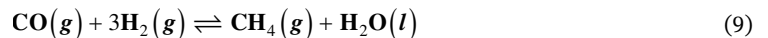


Strictly speaking, the Sabatier reaction is a catalyzed process at elevated temperatures (400°–500°C) converting carbon dioxide into methane (methanation). Both Equations 6 and 7 have the same stoichiometry: four moles of hydrogen are consumed to produce one mole of methane. In a plot of the methane 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:



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:



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

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



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

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

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

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

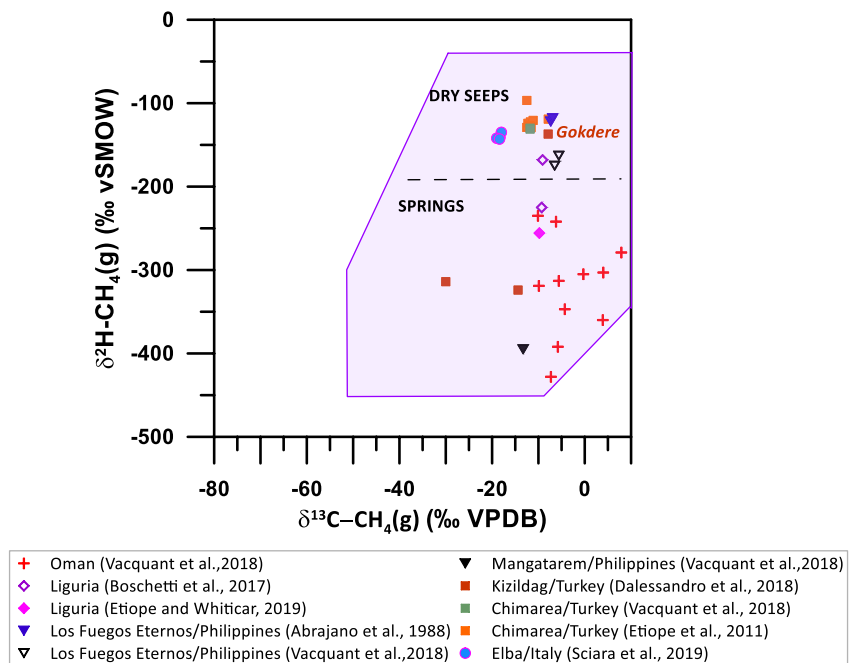


Figure 8. The $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values of methane for the free gases. The purple area is the domain of abiogenic methane delimited by Milkov and Etiope (2018). The horizontal dash line separates the dry seeps from the springs. Gokdere is a spring in the Kizildag ophiolite (Turkey) that lies inside the domain of the dry seeps.

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; Quéménéur 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) and the Cedars springs (California; Suzuki et al., 2013). Methane consumption or production by microorganisms takes 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 abiogenic formation of methane.

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

The 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.

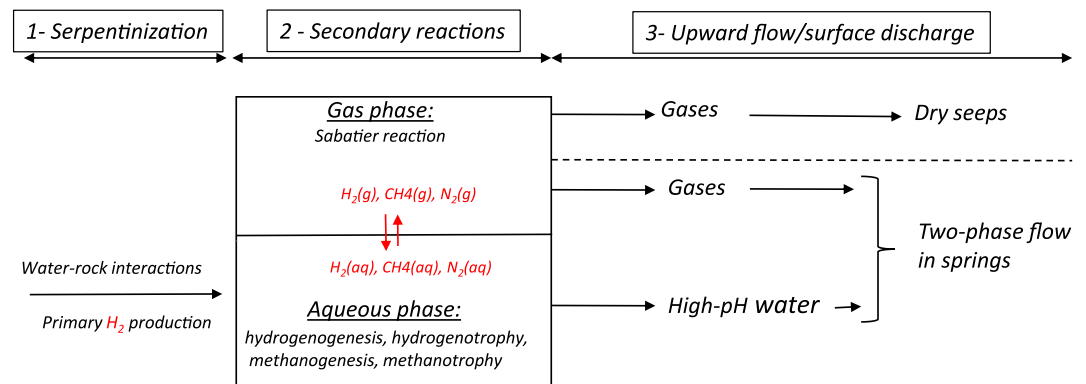


Figure 9. A diagram summarizing the hydrogen, methane, and nitrogen budgets in the serpentinizing environment. The first step is hydrogen production by the serpentinization reaction. The hydrogen concentration increases in the water up to the point where saturation is exceeded, and a gas phase forms. 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.

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 (Figure 8) point to isotopic $\delta^2H-CH_4(g)$ 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 and 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.

6. Conclusions

1. 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.
2. 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.

3. 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.
4. The stoichiometry of the hydrogen-methane reaction is consistent with a Sabatier reaction in the gas phase or methane production by hydrogenotrophic methanogens in the aqueous phase. The two mechanisms can take place at the same time and can be coupled through the transfer of gases from the water to the gas phase and conversely. This last point can be constrained by the study of the concentration of dissolved gases to investigate the conditions at which the water degasses.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The Supporting Information for this study is available at the CNRS HAL archive (<https://hal.archives-ouvertes.fr/hal-03242378>; click on “Voir les fichiers annexes/see related files” on the right side of the screen).

Acknowledgments

The survey of the springs was funded by the Grand Observatoire du Pacifique Sud (GOPS). This work was also supported by the INTERVIE program of Institut des Sciences de la Terre et de l'Univers (INSU/CNRS), the French Institute of Research for Development (IRD) and the MICROPRONY ANR project. The authors thank the environmental service of the Province Sud of New Caledonia for the authorization to sample the springs. The authors thank Michael Kubo and Tori Hoehler of NASA Ames laboratory for their help with the gas analyses. The authors deeply acknowledge the help and support of the sea means service (pilots Miguel Clarke and Samuel Tereua) and the diving service (divers Eric Folcher, Bertrand Bourgeois, and Armelle Renaud) of the IRD center of Nouméa, New Caledonia, for the logistics of the sampling campaigns. The authors also warmly thank Jean Chatelier who organized the logistics and visit to the Montagne des Sources.

References

- Abrajano, T. A., Sturchio, N. C., Bohlke, J. K., Lyon, G. L., Poreda, R. J., & Stevens, C. M. (1988). Methane-hydrogen gas seeps, Zambales Ophiolite, Philippines: Deep or shallow origin? *Chemical Geology*, *71*(1–3), 211–222. [https://doi.org/10.1016/0009-2541\(88\)90116-7](https://doi.org/10.1016/0009-2541(88)90116-7)
- Alexander, W. R., Dayal, R., Eagleson, K., Eikenberg, J., Hamilton, E., Linklater, C. M., et al. (1992). A natural analog of high PH cement pore waters from the Maqarin area of northern Jordan .2. Results of predictive geochemical calculations. *Journal of Geochemical Exploration*, *46*(1), 133–146. [https://doi.org/10.1016/0375-6742\(92\)90104-g](https://doi.org/10.1016/0375-6742(92)90104-g)
- Berner, R. A. (1981). A new geochemical classification of sedimentary environments. *Journal of Sedimentary Research*, *51*(2), 359–365. <https://doi.org/10.1306/212F7C7F-2B24-11D7-8648000102C1865D>
- Blank, J. G., Etiopie, G., Stamenković, V., Rowe, A. R., Kohl, I., Li, S., & Young, E. D. (2017). Methane at the Aqua de Ney Hyperalkaline Spring (N. California USA), a site of active serpentinization. In *Astrobiology science conference 2017*. Houston: Lunar and Planetary Institute.
- Boschetti, T., Etiopie, G., & Toscani, L. (2013). Abiotic methane in the hyperalkaline springs of Genova, Italy. *Procedia Earth and Planetary Science*, *7*, 248–251. <https://doi.org/10.1016/j.proeps.2013.02.004>
- Boschetti, T., & Toscani, L. (2008). Springs and streams of the Taro-Ceno Valleys (Northern Apennine, Italy): Reaction path modeling of waters interacting with serpentinized ultramafic rocks. *Chemical Geology*, *257*(1–2), 76–91. <https://doi.org/10.1016/j.chemgeo.2008.08.017>
- Boschetti, T., Toscani, L., Iacumin, P., & Selmo, E. (2017). Oxygen, Hydrogen, boron and lithium isotope data of a natural spring water with an extreme composition: A fluid from the dehydrating slab? *Aquatic Geochemistry*, *23*, 299–313. <https://doi.org/10.1007/s10498-017-9323-9>
- Boulart, C., Chavagnac, V., Monnin, C., Delacour, A., Ceuleneer, G., & Hoareau, G. (2013). Differences in gas venting from ultramafic-hosted warm springs: The example of Oman and Ligurian Ophiolites. *Ophiolite*, *38*(2), 142–156.
- Brazelton, W. J., Thornton, C. N., Hyer, A., Twing, K. I., Longino, A. A., Lang, S. Q., et al. (2017). Metagenomic identification of active methanogens and methanotrophs in serpentinite springs of the Voltri Massif Italy. *PeerJ*, *5*, 33. <https://doi.org/10.7717/peerj.2945>
- Canovas, P. A., Hoehler, T., & Shock, E. L. (2017). Geochemical bioenergetics during low-temperature serpentinization: An example from the Samail ophiolite, Sultanate of Oman. *Journal of Geophysical Research: Biogeosciences*, *122*(7), 1821–1847. <https://doi.org/10.1002/2017jg003825>
- Cardace, d., Meyer-Dombard, D. A. R., Woycheese, K., & Arcilla, C. A. (2015). Feasible metabolic schema associated with high pH springs in the Philippines. *Frontiers in Microbiology*, *6*. <https://doi.org/10.3389/fmicb.2015.00010>
- Chavagnac, V., Ceuleneer, G., Monnin, C., Lansac, B., Hoareau, G., & Boulart, C. (2013). Mineralogical assemblages forming at hyperalkaline warm springs hosted on ultramafic rocks: A case study of Oman and Ligurian ophiolites. *Geochemistry, Geophysics, Geosystems*, *14*(7), 2474–2495. <https://doi.org/10.1002/ggge.20146>
- Chavagnac, V., Monnin, C., Ceuleneer, G., Boulart, C., & Hoareau, G. (2013). Characterization of hyperalkaline fluids produced by low temperature serpentinization of mantle peridotites in the Oman and Ligurian ophiolites. *Geochemistry, Geophysics, Geosystems*, *14*(7), 2496–2522. <https://doi.org/10.1002/ggge.20147>
- Christofi, C., Bruggeman, A., Kuells, C., & Constantinou, C. (2020). Hydrochemical evolution of groundwater in gabbro of the Troodos Fractured Aquifer. A comprehensive approach. *Applied Geochemistry*, *114*, 104524. <https://doi.org/10.1016/j.apgeochem.2020.104524>
- Cipolli, F., Gambardella, B., Marini, L., Ottonello, G., & Vetuschi Zuccolini, M. (2004). Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO_2 sequestration in serpentinite aquifers. *Applied Geochemistry*, *19*(5), 787–802. <https://doi.org/10.1016/j.apgeochem.2003.10.007>
- Cox, M. E., Launay, J., & Paris, J. P. (1982). Geochemistry of low temperature geothermal systems in New Caledonia. In *Paper presented at Pacific geothermal conference*. Auckland: University of Auckland.

- Crespo-Medina, M., Twing, K. I., Kubo, M. D. Y., Hoehler, T. M., Cardace, D., McCollom, T., & Schrenk, M. O. (2014). Insights into environmental controls on microbial communities in a continental serpentinite aquifer using a microcosm-based approach. *Frontiers in Microbiology*, 5(604). <https://doi.org/10.3389/fmicb.2014.00604>
- Crespo-Medina, M., Twing, K. I., Sanchez-Murillo, R., Brazelton, W. J., McCollom, T. M., & Schrenk, M. O. (2017). Methane dynamics in a tropical serpentinizing environment: The Santa Elena Ophiolite, Costa Rica. *Frontiers in Microbiology*, 8. <https://doi.org/10.3389/fmicb.2017.00916>
- D'Alessandro, W., Daskalopoulou, K., Calabrese, S., & Bellomo, S. (2018). Water chemistry and abiogenic methane content of a hyperalkaline spring related to serpentinization in the Argolida ophiolite (Ermioni, Greece). *Marine and Petroleum Geology*, 89, 185–193. <https://doi.org/10.1016/j.marpetgeo.2017.01.028>
- D'Alessandro, W., Yüce, G., Italiano, F., Bellomo, S., Gülbay, A. H., Yasin, D. U., & Gagliano, A. L. (2018). Large compositional differences in the gases released from the Kizildag ophiolitic body (Turkey): Evidences of prevalingly abiogenic origin. *Marine and Petroleum Geology*, 89, 174–184. <https://doi.org/10.1016/j.marpetgeo.2016.12.017>
- Debret, B., Albers, E., Walter, B., Price, R., Barnes, J. D., Beunon, H., et al. (2019). Shallow forearc mantle dynamics and geochemistry: New insights from IODP Expedition 366. *Lithos*, 326–327, 230–245. <https://doi.org/10.1016/j.lithos.2018.10.038>
- Deville, E., & Prinzhofer, A. (2016). The origin of N₂-H₂-CH₄-rich natural gas seepages in ophiolitic context: A major and noble gases study of fluid seepages in New Caledonia. *Chemical Geology*, 440, 139–147. <https://doi.org/10.1016/j.chemgeo.2016.06.011>
- Dewandel, B., Lachassagne, P., Boudier, F., Al-Hattali, S., Ladouche, B., Pinault, J. L., & Al-Suleimani, Z. (2005). A conceptual hydrogeological model of ophiolite hard-rock aquifers in Oman based on a multiscale and a multidisciplinary approach. *Hydrogeology Journal*, 13(5–6), 708–726. <https://doi.org/10.1007/s10040-005-0449-2>
- Donval, J. P., Guyader, V., & Boissy, E. (2020). A simple method for the preparation and injection of gas mixtures into a gas chromatograph using a two-component device. *Journal of Chromatography A*, 1631, 461579. <https://doi.org/10.1016/j.chroma.2020.461579>
- Etiöpe, G., Schoell, M., & Hosgormez, H. (2011). Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): Understanding gas exhalation from low temperature serpentinization and implications for Mars. *Earth and Planetary Science Letters*, 310(1–2), 96–104. <https://doi.org/10.1016/j.epsl.2011.08.001>
- Etiöpe, G., & Sherwood Lollar, B. (2013). Abiotic methane on Earth. *Reviews of Geophysics*, 51(2), 276–299. <https://doi.org/10.1002/rog.20011>
- Etiöpe, G., Tsikouras, B., Kordella, S., Ifandi, E., Christodoulou, D., & Papatheodorou, G. (2013). Methane flux and origin in the Othrys ophiolite hyperalkaline springs, Greece. *Chemical Geology*, 347, 161–174. <https://doi.org/10.1016/j.chemgeo.2013.04.003>
- Etiöpe, G., Vadillo, I., Whitticar, M. J., Marques, J. M., Carreira, P. M., Tiago, I., et al. (2016). Abiotic methane seepage in the Ronda peridotite massif, southern Spain. *Applied Geochemistry*, 66, 101–113. <https://doi.org/10.1016/j.apgeochem.2015.12.001>
- Etiöpe, G., & Whitticar, M. J. (2019). Abiotic methane in continental ultramafic rock systems: Towards a genetic model. *Applied Geochemistry*, 102, 139–152. <https://doi.org/10.1016/j.apgeochem.2019.01.012>
- Feth, J. H., Rogers, S. M., & Roberson, C. E. (1961). Aqua de Ney, California, a spring of unique chemical character. *Geochimica et Cosmochimica Acta*, 22(2), 75–86. [https://doi.org/10.1016/0016-7037\(61\)90107-7](https://doi.org/10.1016/0016-7037(61)90107-7)
- Frouin, E., Bes, M., Ollivier, B., Quemeneur, M., Postec, A., Debroas, D., et al. (2018). Diversity of rare and abundant prokaryotic phylotypes in the prony hydrothermal field and comparison with other serpentinite-hosted ecosystems. *Frontiers in Microbiology*, 9. <https://doi.org/10.3389/fmicb.2018.00102>
- Fryer, P., Pearce, J. A., & Stokking, L. B. (1989). Ocean Drilling Program Leg 125 preliminary report; Bonin/Mariana region. In *Ocean Drilling Program* (p. 51). College Station, TX: Texas A&M University.
- Fryer, P., Wheat, C. G., Williams, T., Kelley, C., Johnson, K., Ryan, J., et al. (2020). Mariana serpentinite mud volcanism exhumes subducted seamount materials: Implications for the origin of life. *Philosophical Transactions of the Royal Society A: Mathematical, Physical & Engineering Sciences*, 378(2165), 20180425. <https://doi.org/10.1098/rsta.2018.0425>
- Fryer, P., Wheat, C. G., Williams, T., & Scientists, t. E. (2018). Mariana convergent margin and South Chamorro seamount. In *Proceedings of the International Ocean Discovery Program* (Vol. 366). College Station, TX: International Ocean Discovery Program. <https://doi.org/10.14379/iodp.proc.366.2018>
- Giampouras, M., Garrido, C. J., Zwicker, J., Vadillo, I., Smrzka, D., Bach, W., et al. (2019). Geochemistry and mineralogy of serpentinization-driven hyperalkaline springs in the Ronda peridotites. *Lithos*, 350, 22. <https://doi.org/10.1016/j.lithos.2019.105215>
- Holm, N. G., Oze, C., Mousis, O., Waite, J. H., & Guilbert-Lepoutre, A. (2015). Serpentinization and the formation of H₂ and CH₄ on celestial bodies (Planets, Moons, Comets). *Astrobiology*, 15(7), 587–600. <https://doi.org/10.1089/ast.2014.1188>
- Hulme, S. M., Wheat, C. G., Fryer, P., & Mottl, M. J. (2010). Pore water chemistry of the Mariana serpentinite mud volcanoes: A window to the seismogenic zone. *Geochemistry, Geophysics, Geosystems*, 11. <https://doi.org/10.1029/2009gc002674>
- Kelemen, P. B., & Matter, J. (2008). In situ carbonation of peridotite for CO₂ storage. *Proceedings of the National Academy of Sciences of the United States of America*, 105(45), 17295–17300. <https://doi.org/10.1073/pnas.0805794105>
- Kelemen, P. B., Matter, J., Streit, E. E., Rudge, J. F., Curry, W. B., & Blusztajn, J. (2011). Rates and mechanisms of mineral carbonation in peridotite: Natural processes and recipes for enhanced, in situ CO₂ capture and storage. In K. H. Freeman, & R. Jeanloz, (Eds.), *Annual Review of Earth and Planetary Sciences* (Vol. 39, pp. 545–576). <https://doi.org/10.1146/annurev-earth-092010-152509>
- Kelley, D. S., Karson, J. A., Blackman, D. K., Früh-Green, G. L., Butterfield, D. A., Lilley, M. D., et al. (2001). An off-axis hydrothermal vent field near the mid-Atlantic ridge at 30°N. *Nature*, 412(6843), 145–149. <https://doi.org/10.1038/35084000>
- Kelley, D. S., Karson, J. A., Früh-Green, G. L., Yoerger, D. R., Shank, T. M., Butterfield, D. A., et al. (2005). A serpentinite-hosted ecosystem: The lost city hydrothermal field. *Science*, 307(5714), 1428–1434. <https://doi.org/10.1126/science.1102556>
- Khoury, H. N., Salameh, E., Clark, I. D., Fritz, P., Bajjali, W., Milodowski, A. E., et al. (1992). A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan. I: Introduction to the site. *Journal of Geochemical Exploration*, 46(1), 117–132. [https://doi.org/10.1016/0375-6742\(92\)90103-F](https://doi.org/10.1016/0375-6742(92)90103-F)
- Kraus, E. A., Nothhaft, D., Stamps, B. W., Rempfert, K. R., Ellison, E. T., Matter, J. M., et al. (2020). Molecular evidence for an active microbial methane cycle in subsurface serpentinite-hosted groundwaters in the Samail Ophiolite, Oman. *Applied and Environmental Microbiology*, 87. <https://doi.org/10.1128/AEM.02068-20>
- Launay, J., & Fontes, J. C. (1985). Les sources thermales de Prony (Nouvelle Calédonie) et leurs précipités chimiques. exemple de formation de brucite primaire. *Geologie de la France*, 1, 83–100.
- Leleu, T., Chavagnac, V., Delacour, A., Noiriél, C., Ceuleneer, G., Aretz, M., et al. (2016). Travertines associated with hyperalkaline springs: Evaluation as a proxy for paleoenvironmental conditions and sequestration of atmospheric CO₂. *Journal of Sedimentary Research*, 86(11), 1328–1343. <https://doi.org/10.2110/jsr.2016.79>

- Leong, J. A. M., & Shock, E. L. (2020). Thermodynamic constraints on the geochemistry of low-temperature, continental, serpentinization-generated fluids. *American Journal of Science*, 320(3), 185–235. <https://doi.org/10.2475/03.2020.01>
- Ligi, M., Bonatti, E., Cuffaro, M., & Brunelli, D. (2013). Post-Mesozoic rapid increase of seawater Mg/Ca due to enhanced mantle-seawater interaction. *Scientific Reports*, 3. <https://doi.org/10.1038/srep02752>
- Lods, G., Roubinet, D., Matter, J. M., Leprovost, R., Gouze, P., & Oman Drilling Project Science Team. (2020). Groundwater flow characterization of an ophiolitic hard-rock aquifer from cross-borehole multi-level hydraulic experiments. *Journal of Hydrology*, 589, 18. <https://doi.org/10.1016/j.jhydrol.2020.125152>
- Marques, J. M., Carreira, P. M., Carvalho, M. R., Matias, M. J., Goff, F. E., Basto, M. J., et al. (2008). Origins of high pH mineral waters from ultramafic rocks, Central Portugal. *Applied Geochemistry*, 23(12), 3278–3289. <https://doi.org/10.1016/j.apgeochem.2008.06.029>
- Marques, J. M., Etiopie, G., Neves, M. O., Carreira, P. M., Rocha, C., Vance, S. D., et al. (2018). Linking serpentinization, hyperalkaline mineral waters and abiotic methane production in continental peridotites: An integrated hydrogeological-bio-geochemical model from the Cabeço de Vide CH₄-rich aquifer (Portugal). *Applied Geochemistry*, 96, 287–301. <https://doi.org/10.1016/j.apgeochem.2018.07.011>
- Maurizot, P., Sevin, B., Lesimple, S., Collot, J., Jeanpert, J., Robineau, B., et al. (2020). Mineral resources and prospectivity of non-ultramafic rocks of New-Caledonia. In N. Mortimer, (Ed.), *New Caledonia: Geology, geodynamic evolution and mineral Resources* (Vol. 51, pp. 215–245). London: Geological Society London. <https://doi.org/10.1144/M51-2016-9>
- Mei, N., Postec, A., Monnin, C., Pelletier, B., Payri, C. E., Ménez, B., et al. (2016). Metagenomic and PCR-based diversity surveys of [FeFe]-hydrogenases combined with isolation of alkaliphilic hydrogen-producing bacteria from the serpentinite-hosted Prony hydrothermal field, New Caledonia. *Frontiers in Microbiology*, 7(1301). <https://doi.org/10.3389/fmicb.2016.01301>
- Menez, B. (2020). Abiotic hydrogen and methane: Fuels for life. *Elements*, 16(1), 39–46. <https://doi.org/10.2138/gselements.16.1.39>
- Menez, B., Pasini, V., & Brunelli, D. (2012). Life in the hydrated suboceanic mantle. *Nature Geoscience*, 5(2), 133–137. <https://doi.org/10.1038/ngeo1359>
- Meyer-Dombard, D. R., Woycheese, K. M., Yargicoglu, E. N., Cardace, D., Shock, E. L., Gulecal-Pektas, Y., & Temel, M. (2015). High pH microbial ecosystems in a newly discovered, ephemeral, serpentinizing fluid seep at Yanartas (Chimera), Turkey. *Frontiers in Microbiology*, 5. <https://doi.org/10.3389/fmicb.2014.00723>
- Milkov, A. V., & Etiopie, G. (2018). Revised genetic diagrams for natural gases based on a global dataset of >20,000 samples. *Organic Geochemistry*, 125, 109–120. <https://doi.org/10.1016/j.orggeochem.2018.09.002>
- Miller, H. M., Matter, J. M., Kelemen, P., Ellison, E. T., Conrad, M. E., Fierer, N., et al. (2016). Modern water/rock reactions in Oman hyperalkaline peridotite aquifers and implications for microbial habitability. *Geochimica et Cosmochimica Acta*, 179, 217–241. <https://doi.org/10.1016/j.gca.2016.01.033>
- Monnin, C., Chavagnac, V., Boulart, C., Ménez, B., Gérard, M., Gérard, E., et al. (2014). Fluid chemistry of the low temperature hyperalkaline hydrothermal system of Prony Bay (New Caledonia). *Biogeosciences*, 11(20), 5687–5706. <https://doi.org/10.5194/bg-11-5687-2014>
- Monnin, C., Tamborski, J., Bejannin, S., Souhaut, M., Rogues, M., Olivier, P., & van Beek, P. (2019). Freshening of a coastal karst aquifer revealed by the temporal changes in a spring water composition (La Palme, Southern France). *Hydrology*, 6(2), 17. <https://doi.org/10.3390/hydrology6020045>
- Morrill, P. L., Kuenen, J. G., Johnson, O. J., Suzuki, S., Rietze, A., Sessions, A. L., et al. (2013). Geochemistry and geobiology of a present-day serpentinization site in California: The Cedars. *Geochimica et Cosmochimica Acta*, 109, 222–240. <https://doi.org/10.1016/j.gca.2013.01.043>
- Mottl, M. J., Wheat, C. G., Fryer, P., Gharib, J., & Martin, J. B. (2004). Chemistry of springs across the Mariana forearc shows progressive devolatilization of the subducting plate. *Geochimica et Cosmochimica Acta*, 68(23), 4915–4933. <https://doi.org/10.1016/j.gca.2004.05.037>
- Myagkiy, A., Moretti, I., & Brunet, F. (2020). Space and time distribution of subsurface H₂ concentration in so-called “fairy circles”: Insight from a conceptual 2-D transport model. *BSGF-Earth Sciences Bulletin*, 191, 13. <https://doi.org/10.1051/bsgf/2020010>
- Neal, C., & Shand, P. (2002). Spring and surface water quality of the Cyprus ophiolites. *Hydrology and Earth System Sciences*, 6(5), 797–817. <https://doi.org/10.5194/hess-6-797-2002>
- Neal, C., & Stanger, G. (1983). Hydrogen generation from mantle source rocks in Oman. *Earth and Planetary Science Letters*, 66, 315–320. [https://doi.org/10.1016/0012-821x\(83\)90144-9](https://doi.org/10.1016/0012-821x(83)90144-9)
- Paukert, A. N., Matter, J. M., Kelemen, P. B., Shock, E. L., & Havig, J. R. (2012). Reaction path modeling of enhanced in situ CO₂ mineralization for carbon sequestration in the peridotite of the Samail Ophiolite, Sultanate of Oman. *Chemical Geology*, 330–331(0), 86–100. <https://doi.org/10.1016/j.chemgeo.2012.08.013>
- Pelletier, B., Chevillon, C., Menou, J. L., Butscher, J., Folcher, E., Geoffroy, C., et al. (2006). *Plongées, forage et cartographie Baie du Prony et Banc Gail, lagon Sud de Nouvelle-Calédonie, campagne 2005-NC-PL du N.O. ALIS, 13–17 juin 2005 et cartographie baie du Prony N.O. ALIS, 25–26 septembre 2005. Rapports de missions*, 70, 44.
- Pelletier, B., Payri, C., Folcher, E., Butscher, J., Bourgeois, B., Erauso, G., et al. (2011). *Campagne HYDROPRONY du N.O. ALIS, 28 Octobre–13 Novembre 2011* (p. 41). Rapport de mission IRD Nouméa.
- Plank, T., & Manning, C. E. (2019). Subducting carbon. *Nature*, 574(7778), 343–352. <https://doi.org/10.1038/s41586-019-1643-z>
- Postec, A., Quéméneur, M., Bes, M., Mei, N., Benaïssa, F., Payri, C., et al. (2015). Microbial diversity in a submarine carbonate edifice from the serpentinizing hydrothermal system of the Prony Bay (New Caledonia) over 6-year period. *Frontiers in Microbiology*, 6. <https://doi.org/10.3389/fmicb.2015.00857>
- Price, R., Boyd, E. S., Hoehler, T. M., Wehrmann, L. M., Bogason, E., Valtýsson, H. Þ., et al. (2017). Alkaline vents and steep Na⁺ gradients from ridge-flank basalts—Implications for the origin and evolution of life. *Geology*, 45(12), 1135–1138. <https://doi.org/10.1130/G39474.1>
- Quéméneur, M., Bes, M., Postec, A., Mei, N., Hamelin, J., Monnin, C., et al. (2014). Spatial distribution of microbial communities in the shallow submarine alkaline hydrothermal field of the Prony Bay, New Caledonia. *Environmental Microbiology Reports*, 6(6), 665–674. <https://doi.org/10.1111/1758-2229.12184>
- Quéméneur, M., Erauso, G., Bartoli, M., Vandecasteele, C., Wils, L., Gil, L., et al. (2021). Alkalicella caledoniensis gen. nov., sp. nov., a novel alkaliphilic anaerobic bacterium isolated from ‘La Crouen’ alkaline thermal spring, New Caledonia. *International Journal of Systematic and Evolutionary Microbiology*, 71. <https://doi.org/10.1099/ijsem.0.004810>
- Quéméneur, M., Palvadeau, A., Postec, A., Monnin, C., Chavagnac, V., Ollivier, B., & Erauso, G. (2015). Endolithic microbial communities in carbonate precipitates from serpentinite-hosted hyperalkaline springs of the Voltri Massif (Ligurian Alps, Northern Italy). *Environmental Science & Pollution Research*, 22, 1–13624. <https://doi.org/10.1007/s11356-015-4113-7>
- Reeves, E. P., & Fiebig, J. (2020). Abiotic synthesis of methane and organic-compounds in Earth’s lithosphere. *Elements*, 16(1), 25–31. <https://doi.org/10.2138/gselements.16.1.25>

- Rempfert, K. R., Miller, H. M., Bompard, N., Nothaft, D., Matter, J. M., Kelemen, P., et al. (2017). Geological and geochemical controls on subsurface microbial life in the Samail ophiolite, Oman. *Frontiers in Microbiology*, 8(56). <https://doi.org/10.3389/fmicb.2017.00056>
- Sader, J. A., Leybourne, M. I., McClenaghan, B., & Hamilton, M. S. (2007). Low-temperature serpentinization processes and kimberlite groundwater signatures in the Kirkland Lake and Lake Timiskiming kimberlite fields, Ontario, Canada: Implications for diamond exploration. *Geochemistry: Exploration, Environment, Analysis*, 7, 3–21. <https://doi.org/10.1144/1467-7873/06-900>
- Sano, Y., Urabe, A., Wakita, H., & Wushiki, H. (1993). Origin of hydrogen-nitrogen gas seeps, Oman. *Applied Geochemistry*, 8(1), 1–8. [https://doi.org/10.1016/0883-2927\(93\)90053-J](https://doi.org/10.1016/0883-2927(93)90053-J)
- Schrenk, M. O., Brazelton, W. J., & Lang, S. Q. (2013). Serpentinization, carbon, and deep life. In R. M. Hazen, A. P. Jones, & J. A. Baross (Eds.), *Carbon in Earth* (Vol. 75, pp. 575–606). <https://doi.org/10.2138/rmg.2013.75.18>
- Sciarrà, A., Saroni, A., Etiope, G., Coltorti, M., Mazzarini, F., Lott, C., et al. (2019). Shallow submarine seep of abiotic methane from serpentinized peridotite off the Island of Elba, Italy. *Applied Geochemistry*, 100, 1–7. <https://doi.org/10.1016/j.apgeochem.2018.10.025>
- Seyfried, W. E., Jr, Pester, N. J., Tutolo, B. M., & Ding, K. (2015). The Lost City hydrothermal system: Constraints imposed by vent fluid chemistry and reaction path models on subseafloor heat and mass transfer processes. *Geochimica et Cosmochimica Acta*, 163(0), 59–79. <https://doi.org/10.1016/j.gca.2015.04.040>
- Sissmann, O., Price, R., Elvert, M., Heuer, V. B., Prieto, X., Monnin, C., et al. (2019). Abiogenic formation of H₂, light hydrocarbons and other short-chain organic compounds within the serpentinite mud volcanoes of the Marianna Trench. *E3S Web Conference*, 98, 02011. <https://doi.org/10.1051/e3sconf/20199802011>
- Stanger, G. (1985). *The hydrogeology of the Oman mountains*. UK: The Open University.
- Suzuki, S., Ishii, S., Wu, A., Cheung, A., Tenney, A., Wanger, G., et al. (2013). Microbial diversity in The Cedars, an ultrabasic, ultrareducing, and low salinity serpentinizing ecosystem. *Proceedings of the National Academy of Sciences of the United States of America*, 110(38), 15336–15341. <https://doi.org/10.1073/pnas.1302426110>
- Szponar, N., Brazelton, W. J., Schrenk, M. O., Bower, D. M., Steele, A., & Morrill, P. L. (2012). Geochemistry of a continental site of serpentinization, the Tablelands Ophiolite, Gros Morne National Park: A Mars analogue. *Icarus*, 224(2), 286–296. <https://doi.org/10.1016/j.icarus.2012.07.004>
- Truche, L., McCollom, T. M., & Martinez, I. (2020). Hydrogen and Abiotic hydrocarbons: Molecules that change the World. *Elements*, 16(1), 13–18. <https://doi.org/10.2138/gselements.16.1.13>
- Vacquand, C., Deville, E., Beaumont, V., Guyot, F., Sissmann, O., Pillot, D., et al. (2018). Reduced gas seepages in ophiolitic complexes: Evidences for multiple origins of the H₂-CH₄-N₂ gas mixtures. *Geochimica et Cosmochimica Acta*, 223, 437–461. <https://doi.org/10.1016/j.gca.2017.12.018>
- Young, C., Martin, J. B., Branyon, J., Pain, A., Valle-Levinson, A., Marino-Tapia, I., & Vieyra, M. R. (2018). Effects of short-term variations in sea level on dissolved oxygen in a coastal karst aquifer Quintana Roo, Mexico. *Limnology and Oceanography*, 63(1), 352–362. <https://doi.org/10.1002/lno.10635>
- Yuce, G., Italiano, F., D'Alessandro, W., Yalcin, T. H., Yasin, D. U., Gulbay, A. H., et al. (2014). Origin and interactions of fluids circulating over the Amik Basin (Hatay, Turkey) and relationships with the hydrologic, geologic and tectonic settings. *Chemical Geology*, 388, 23–39. <https://doi.org/10.1016/j.chemgeo.2014.09.006>
- Zgonnik, V., Beaumont, V., Larin, N., Pillot, D., & Deville, E. (2019). Diffused flow of molecular hydrogen through the Western Hajar Mountains, Northern Oman. *Arabian Journal of Geosciences*, 12(3), 10. <https://doi.org/10.1007/s12517-019-4242-2>