Discovery of a large accumulation of natural hydrogen in Bourakebougou (Mali)

Alain Prinzhofer[1], **Cheick Sidy Tahara CISSE**[2] **and Aliou Boubacar Diallo**[3]

[1] Alain Prinzhofer – Corresponding author

GEO4U, Scientific Director

alain.prinzhofer@geo4u.com.br

Rua Tavares Bastos 123

Catete

22221-030 Rio de Janeiro – Brazil

[2] Cheick Sidy Tahara CISSE

PETROMA

c.cisse@petroma-ca.com

[3] Aliou Boubacar Diallo

PETROMA, President

abdor@petroma-ca.com

Abstract

Recent exploratory wells in Mali (Bourabougou field) targeting natural hydrogen were a success and provide a new understanding of a first test well exploited by PETROMA (Bougou-1), and a comprehension of continental hydrogen functioning systems. Based on extensive gas data of a pioneer well and preliminary geochemical data obtained from a dozen exploratory wells in the vicinity, it is possible to confirm the presence of an extensive hydrogen field featuring at least five stacked reservoir intervals containing significant hydrogen that cover an estimated area well superior to 8 kilometers in diameter. Results underline the potential economic interest of future natural hydrogen exploitation in continental onshore areas. A “hydrogen system” is presented with a kitchen of generation in the cratonic basement. The relatively pure hydrogen reservoirs are associated with traces of methane, nitrogen and helium. The geological stratigraphic accumulation of hydrogen is linked to the presence of multi overlaid doleritic sills and aquifers that seem to play a role to disable upward gas migration and leakage. The occurrence of a mixture of gas and water acting with an artesian activity confirms the presence of over-pressured fluids. This results in a geyser-type eruptive diphasic surface fluid in many of the wells. The “gas lift” system and the presence of traces of highly unstable carbon monoxide is linked to a recent hydrogen gas charge to reservoirs from underground aquifers, erupting with associated water. The Mali wells underscore the non-fossil source of hydrogen gas and presents features of a sustainable energy. The current estimate of its exploitation price is much cheaper than manufactured hydrogen, either from fossil fuels or from electrolysis.

Keywords: Natural Hydrogen, Mali, geology, geochemistry, sustainable resource exploration.

Introduction

Natural hydrogen seeping out as a gas from hydrothermal systems in mid-oceanic ridges has been detected in the 1970's (Whelan and Craig, 1979; Charlou et al., 2002; Marcaillou et al., 2011). Hydrogen sourcing out has also been observed few years later in ophiolites (Neal and Stanger, 1983; Abrajano et al., 1988; 1990) and in continents (Goebel et al., 1983; 1984; Angino et al., 1984; 1990; Coveney et al., 1987). However, it is still mainly considered as a geological curiosity for the majority of researchers and natural hydrogen has only recently been taken seriously as a potential clean source of energy for humankind (Petersen, 1990). One advantage lies in combustion, as the end product is water, rendering hydrogen technically a clear and sustainable source of energy. Manufactured hydrogen is abundantly used in chemistry (Prinzhofer and Deville, 2015) and its role as an energy vector drives the energy industrial sectors to massively invest in the use of hydrogen for electricity storage and production. Recent developments of flux energies (eolian, photovoltaic) induces the use of hydrogen as a buffer of electricity (through electrolysis and fuel cells) because of the non-continuous production of electricity through these processes all the while associated to a clear difficulty to store electricity directly and in large quantity.

The discovery of various natural hydrogen seeps combined with surface indices in continental areas, i.e. near industrial centers have underlined a feasible industrial exploitation (Ikorsky et al., 1999; Sherwood-Lollar et al., 2007; Newell et al., 2007; Larin et al., 2015; Zgonnik et al., 2015; Brière and Jerzykiewicz, 2016; Guélard et al., 2017).

Recent published studies have discussed hydrogen associated with ophiolites (Oman: Sano et al., 1993; Deville et al., 2010; 2011. New Caledonia: Deville and Prinzhofer, 2016. Turkey: Hosgörmez et al., 2007; 2008. Philippines: Vacquand et al., 2018). Other documented studies present hydrogen data from very widely distributed continental areas: In Russia (Larin et al. 2015), in the United States/North Carolina (Zgonnik et al. 2015) and in Brazil (Moretti et al. 2018).

This paper presents updated geochemical considerations based on a hydrogen site in Mali, Africa. The area is located near the village of Bourakebougou about 50 km north of Bamako where an old water well (drilled in 1987) was quickly plugged and temporarily abandoned because of an unexpected gas explosion. In 2011, the oil and gas company PETROMA uncemented the well, in the objective of acquiring exploration rights for the block 25 production (Figure 1). A pilot hydrogen production was made for the first explored Bougou-1 well, which lasted about 5 years. Additional drilling of two stratigraphic wells close to 100 km North of Bourakebougou by PETROMA was an incentive to initiate a broader exploration campaign with a series of 18 shallow wells in the surrounding of the pioneer Bougou-1 well. Main geological and geochemical information obtained from a dozen of the total eighteen 2017-2018 wells will be discussed in this paper and put in a broader perspective. Detailed geochemical data of cores and rock samples and gas samples collected during these drilling will follow in an upcoming technical paper.

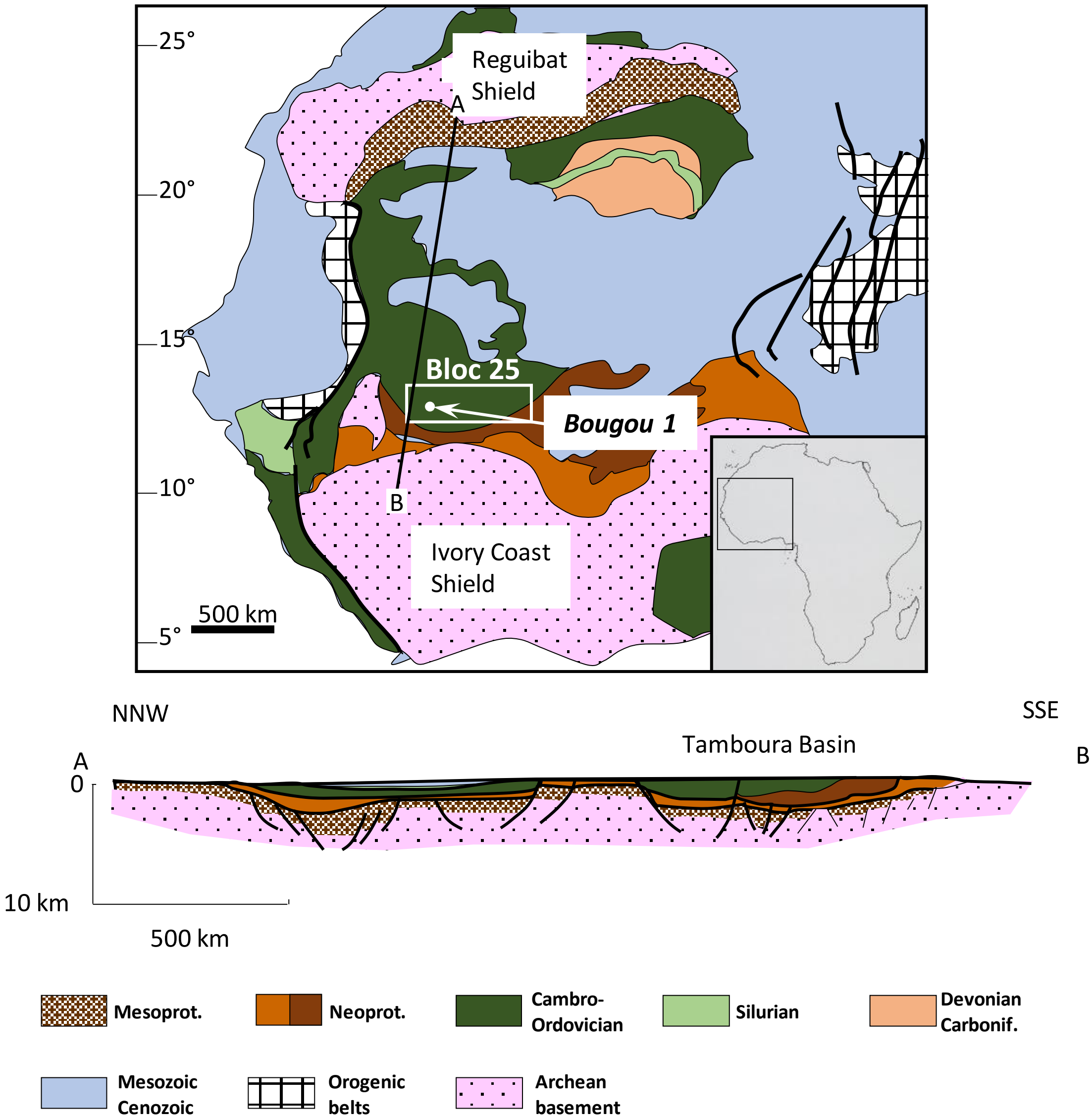

Figure 1: Geological map of the Taoudeni Basin and north-south cross-section showing the structural style of the basin passing close to the wells of Bourakebougou (Mali). Figure from Villeneuve (2005) and Albert-Villanueva et al. (2016). SGI, Supergroup I: a, Char Goup, b., Atar Group Carbonates, c, Atar Group siliciclastics, d, Assabet el Hassiane Group, e, glacial deposits of Bakoye Group; SG2, Supergroup 2; SG3, Supergroup 3; SG4, supergroup 4.

Different objectives are proposed with natural hydrogen R&D. The first one is an understanding of the mechanisms involved in a hydrogen system (generation process, T-P conditions of generation, flux of generation versus time, migration, accumulation, natural leakage and oxidation of H_2). A second objective is to provide practical guidelines for hydrogen exploration, based on sound geology, geophysics and geochemistry. This paper focusses on shallow hydrogen gas accumulations, with less emphasis on deep generation kitchen pods.

Rock and fluid geochemistry issued from results of the latest exploratory wells in Mali carry paramount scientific interest. However, as a reminder, it is not the first time that substantial hydrogen has been accounted for, and documented from Mali (N. Africa, Brière and Jerzykiewicz, 2016) and Kansas (USA, Goebel et al., 1983). Nonetheless, in both cases, wells were initially drilled for oil and gas or water and the presence of hydrogen was fortuitous. The fact that a Malian company has specifically targeted a hydrogen discovery with an extensive exploration campaign is a world's first.

Geological setting

The initial Bourakebougou water well ("Bougou-1") was drilled in Proterozoic sedimentary formations, interlayered with dolerite sills of Triassic age. These formations are part of the Taoudeni Basin, large sedimentary system present mainly in Algeria, Mauritania and Mali. The Paleozoic and Mesozoic upper part of the basin (mainly in Algeria) is famous for its hydrocarbon potential (Craig et al., 2008). On the other hand, the lower Proterozoic section is much poorer in organic matter content (less than 1 percent) and no significant hydrocarbon discovery has ever been made so far in this area. The studied area is located in the Tamboura sub-basin, consisting in a graben filled with Neo-Proterozoic and lower Paleozoic sediments (Figure 1).

A preliminary geochemical soil monitoring was performed in various areas of the block 25 in Mali prior to the exploration of upcoming drilled wells. Results of soil enrichment in non-hydrocarbons showed a surprising hydrogen concentration profile in 1-meter depth samplings. Maps displayed hydrogen spiking around the structure in a full ring. This likely is resulting from regular upward hydrogen seeping. In the center of the circular structure hydrogen gas exultations have also been recorded. Hydrogen seeping out of circular depressions (figure 2), as is actually observed in various continental zones, is perhaps a first indicator for hydrogen exploration (Larin et al., 2015; Zgonnik et al., 2015). This may be significant as a first elementary guideline for enriched soils containing H_2 and should be pursued and validated at grand scale in different areas of Mali, or other parts of the world for that matter.

The presence of substantial hydrogen gas in all the wells located in the vicinity of the Bourakebougou structure implies the existence of a large natural hydrogen system. As a reminder, hydrogen gas is a low molecular weight compound and, as such, has a high mobility allowing hydrogen to migrate large vertical distances from a potentially deep kitchen pod of generation to a shallow accumulation/reservoir.

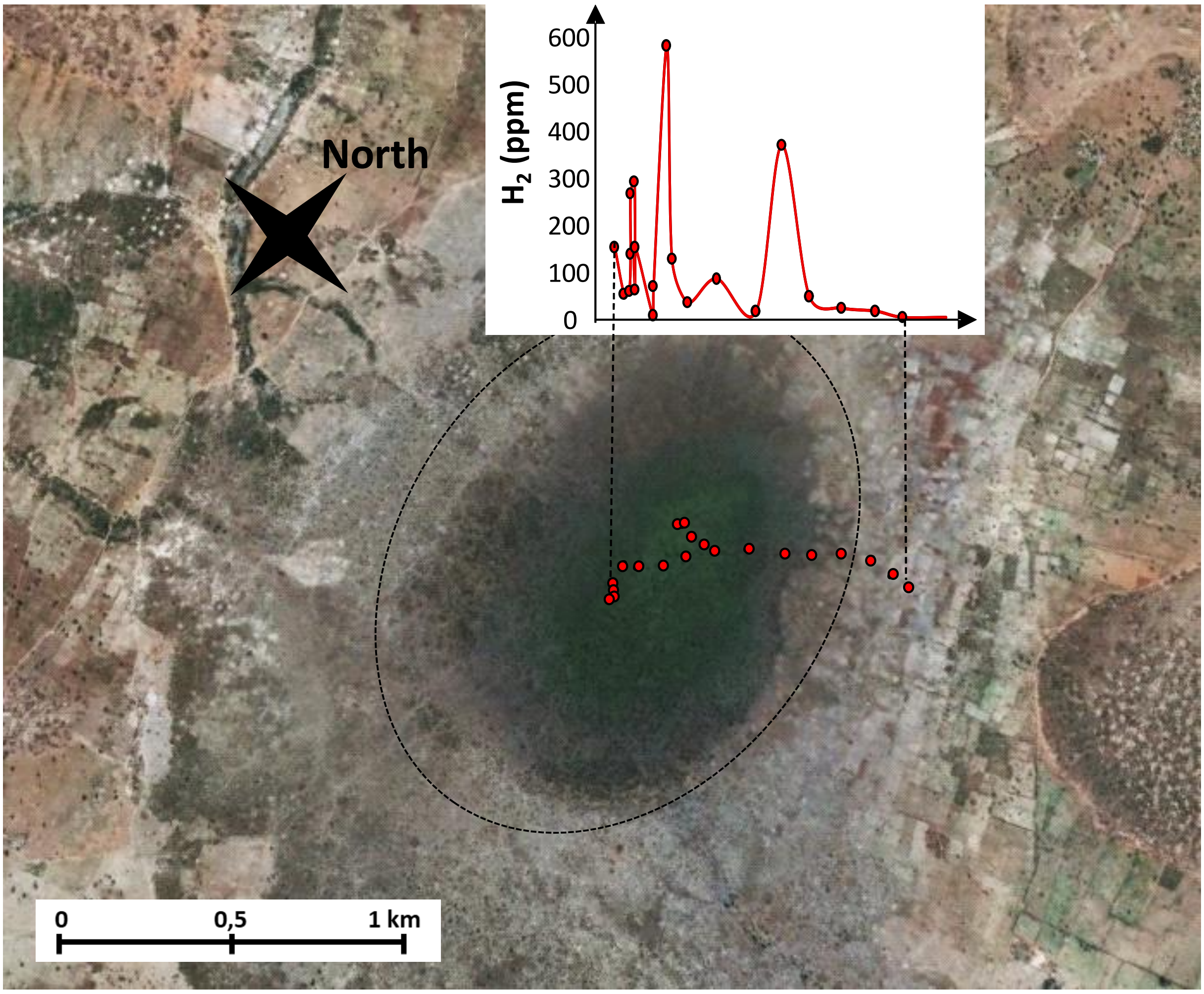

Figure 2: Surface geochemistry of a circular structure located East of the block 25 of PETROMA and close to the village of Gassola. A profile of the hydrogen concentrations (in ppm) is also presented. The coordinates of the center of the structure are a latitude of 13.194605° and a longitude of -6.242527°.

The Bourakebougou Pioneer well (1987)

The Bourakebougou water well, Bougou-1, was cemented after a gas explosion occurred during drilling operations. The incident occurred when a measured drilled depth of 112 meters was reached. Bougou-1 well was unplugged in 2011 in order to use it as a pilot well for a local hydrogen production. A production of a gas predominantly composed at 98% of hydrogen, 1% of nitrogen and 1% of methane was reported at that time. Hydrogen was then produced as an energy resource to supply local electricity through an engine with internal combustion to the nearby village. The project proved to be a success for the nearby town and has lasted for years now.

Rock geochemistry

Geochemical rock analyses were performed on 29 cuttings from two stratigraphic wells (F1 and F2 wells, depths of 2067m and 2339m respectively) 100 km North of Bourakebougou (in the area of 13.84°

of latitude and -8.12 of longitude), following the Bougou-1 well, in order to study the petroleum potential, the carbon content and various indices important for the determination of petroleum potential of the Malian part of the Taoudeni basin. Figure 3 presents pyrolysis data (Rock Eval-6) obtained from the neo-Proterozoic sediments sampled at depths from 100 to 2000m. Carbon content measured in cuttings presented low Total Organic Carbon content (TOC) which seems to refute the presence of potential hydrocarbon source-rocks in this part of the basin (average of 0.28%, with minimum and maximum values from 0.02 to 0.94% (Figure 3). Moreover, plotted in a modified Van Krevelen diagram with Hydrogen Index (HI) versus oxygen Index (OI) (Figure 3a), the hydrogen indices are very low whereas the oxygen indexes are extremely high, indicative of a severe oxidation of organic matter traces. Geochemical data also underline an absence of any petroleum potential due to low Hydrogen Index between 1.9 and 150 mg HC/g Rock (average of 29 mg HC/g Rock). Figures 3c and 3d show that the two pyrolysis derived parameters HI and OI have decreasing values with the % TOC. It can be inferred that those rock samples which are less depleted in organic matter have in fact lowest petroleum potential. This leads to the conclusion that there is an absence of hydrocarbon prone source rocks and therefore little hydrocarbon potential in this area of the Taoudeni Basin.

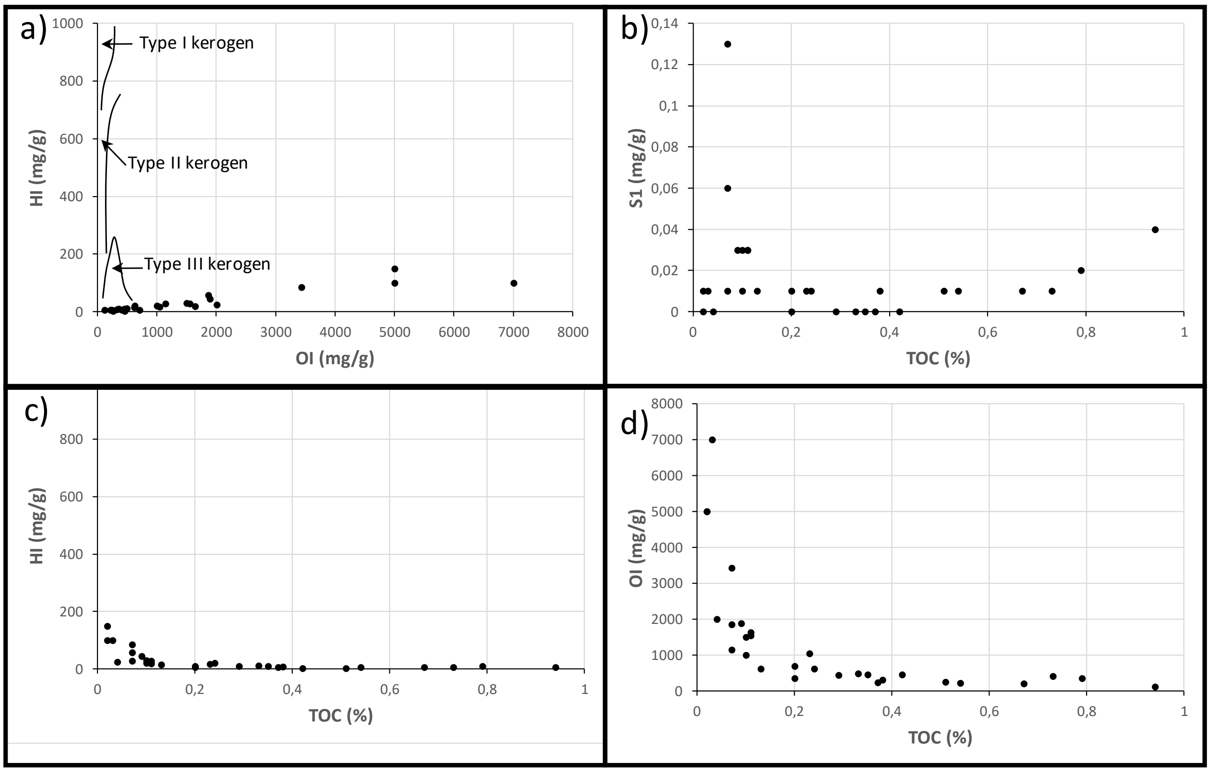

Figure 3: RockEval data of some rocks with organic matter of the neo-Proterozoic Tamboura graben. a) Hydrogen Index (HI) versus Oxygen Index (OI). b) Free hydrocarbons (S1 peak) versus Total Organic Carbon (TOC). c) Hydrogen Index (HI) versus Total Organic Carbon (TOC). d) Oxygen Index (OI) versus Total Organic Carbon (TOC).

Chemical gas composition

It was mentioned that Bougou-1 pioneer well contained predominantly hydrogen with traces of nitrogen and methane. Bougou-1 gas composition presents different chemical features as compared to other case studies, where the gases associated to hydrogen are present in widely different proportions. Figure 4 presents different chemical compositions of natural hydrogen gas occurrence from different geological settings. Plotted data are from gas samples originating either from sampled drilled wells (Kansas and Bougou-1) or gases collected in surface macro-seeps (Oman, Turkey, New Caledonia, Philippines). In the Bougou-1 well shown in red on the ternary plot, the gas content appears the richest in hydrogen proportion, whereas other onshore gases from different areas always have presented higher proportions of methane and nitrogen.

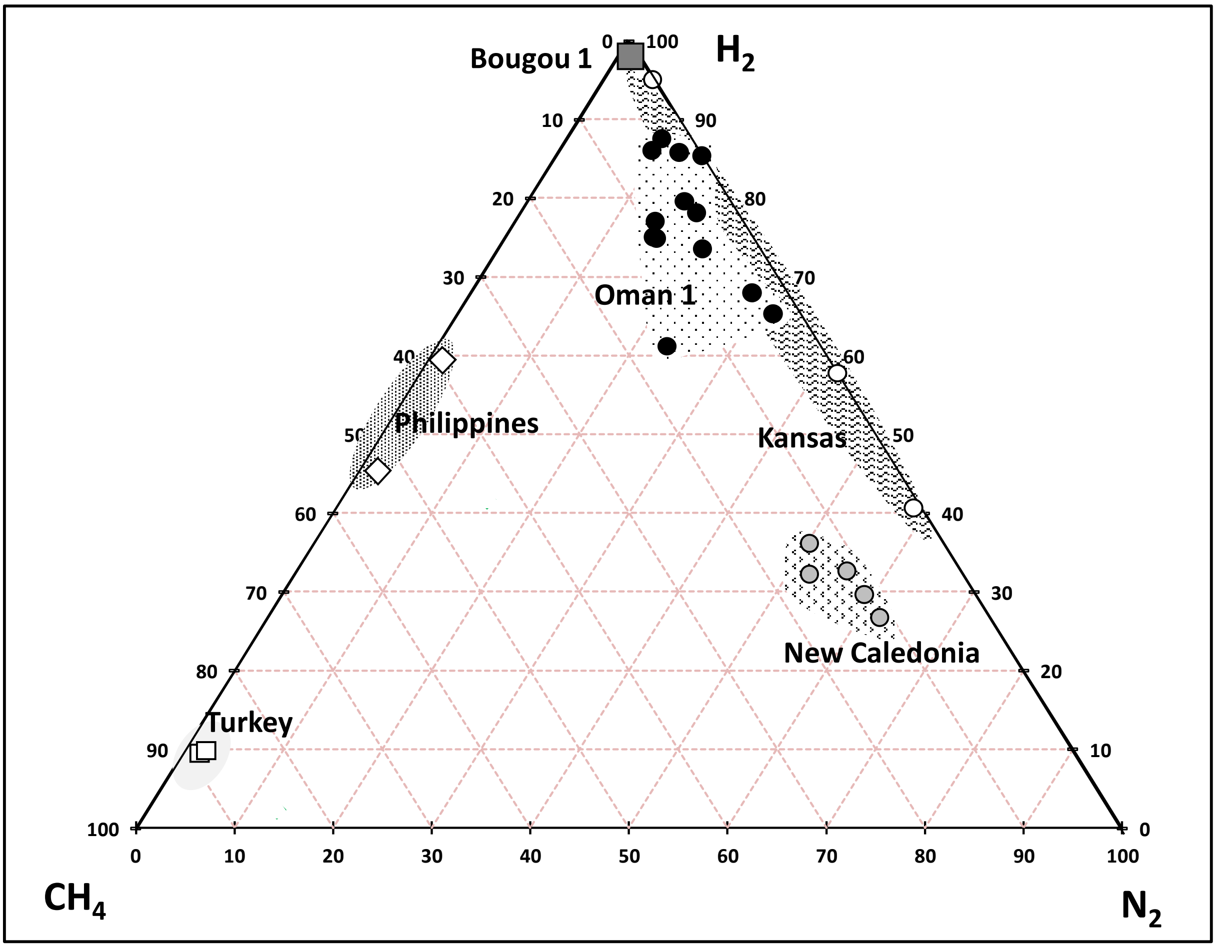

Figure 4: Ternary diagram with the relative proportions of hydrogen, methane and nitrogen, for various gas samples containing natural hydrogen. Oman and Philippines: macro gas seeps, from Vacquand et al., 2018. New Caledonia, macro gas seeps, from Deville and Prinzhofer, 2016. Turkey, macro gas seeps, from Hosgörmez et al., 2007. Kansas, gas well, production test from Guélard et al., 2017.

The Bougou-1 gas sample is associated with traces of hydrocarbon gases (methane, ethane, propane, iso- and normal-butane, neo-, iso- and normal-pentane), helium and carbon dioxide. The chemical composition is presented in Table 1, as well as the carbon and hydrogen isotopic ratios of different measured species.

Compound	Concentration % (TCD)	Concentration ppm (FID)	$\delta^{13}C$	δD
He	4,90E-02			
H_2	9,74E+01			-702
CO_2	4,00E-02			
N_2	1,20E+00			
O_2	0,00E+00			
C1		1,30E+04	-40,4	-249
C2		2,16E+02	-32,1	-165
C3		2,72E+01	-31,0	
iC4		3,83E+00	-26,1	
C4		5,00E+00	-38,1	
neoC5		5,20E-01	-32,6	
iC5		1,18E+00	-20,5	
C5		4,10E-01	-49,7	

Table 1: chemical composition (hydrocarbon and non-hydrocarbon compounds) and isotopic analyses (carbon and hydrogen stable isotopes) of Bougou-1 gas, Bourakebougou Village (Mali). The carbon isotopic ratios are presented in $\delta^{13}C$ unit, variation in per mil compared to the PDB (Peedee Belemnite) international standard, and hydrogen isotopic ratios in δD unit, variation in per mil compared to the SMOW (Standard Mean Oceanic Water) international standard

Based on published data from Sherwood-Lollar *et al. (*2008), the proportions of C2-C5 linear hydrocarbons clearly show an abiotic origin for these hydrocarbons (Figure 5). Abiotic hydrocarbon gas compounds are generated through a hydrogenation of mineral carbon and have a different genetic origin than the more usual thermogenic gases (thermal cracking of organic matter) or biological gas (biological activity of methanogens producing mainly methane). Bougou-1 gas is therefore assumed of abiotic origin from this interpretation. Moreover, this is consistent with the Tambura basin sedimentary rocks which have been characterized as organic matter-lean rocks and would limit the probability of any potential for thermogenic hydrocarbon generation. One plausible explanation on the origin of methane in this well is a hydrogenation mechanism where carbon dioxide CO_2 is hydrogenated into CH_4. The reduction of CO_2 may occur either from a bacterial activity or a catalytically driven chemical reaction. On the other end, the generation of heavier hydrocarbons is likely to proceed through a Fisher-Tropsch process type chemical reaction (degenerated polymerization), at relatively high temperature and without any biological associated process. Considering that the kitchen of generation of the various gas compounds of the well may be in the continental basement, the pressure/temperature conditions may be compatible with a Fisher-Tropsch process. Taking in consideration the actual setting and results, it can be tentatively assumed that the Bougou-1 hydrocarbon gas compounds have mainly an abiotic origin.

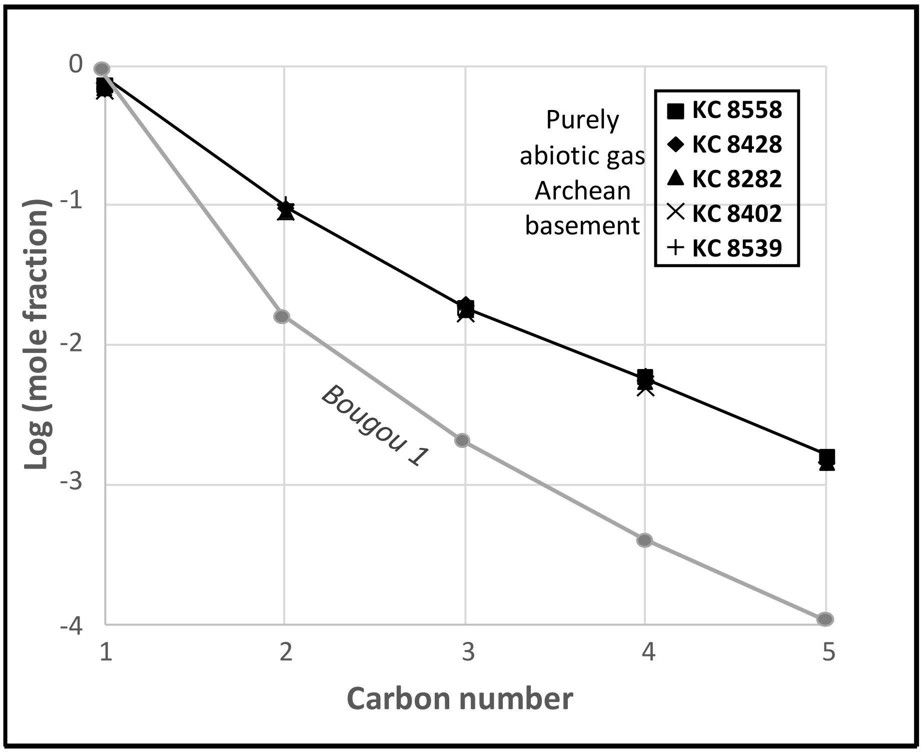

Figure 5: relative proportions of normal-paraffin hydrocarbon gas compounds, with carbon numbers from 1 (methane) to 5 (normal-pentane), taken from Sherwood-Lollar et al., 2008. Comparison of the pattern of the Bougou-1 well with Archean gases analyses by Sherwood-Lollar et al. (2008) and interpreted as generated through an abiotic process.

Stable carbon isotopes

The geochemical stable carbon isotopes measured by GC-C-IRMS (Gas Chromatography Combustion Isotopic Ratios Mass Spectrometer) and represented as $\delta^{13}C$ ratios for each linear hydrocarbon present unusual trends which are hardly compatible with purely thermogenic, biological or abiotic sourced (Figure 6). The very light isotopic signatures, highlighted with $\delta^{13}C$ of normal-butane and normal-pentane for example, in this case, can be explained by an abiotic polymerization process. However, the heavier isotopic signatures of iso-alkanes isomers (iso-butane, neo- and iso-pentane) can be better explained if they are assumed to have a thermogenic origin. This has been shown to occur and it is known that a polymerization process favors mainly the paraffinic, linear hydrocarbons (Szatmari, 1989). In view of the present data, it can be tentatively concluded that there is a mixed mechanism between an abiotic process and trace of thermal cracking of organic matter. As the total hydrocarbon proportion of the gas is around 1%, each of these processes remains however quite marginal.

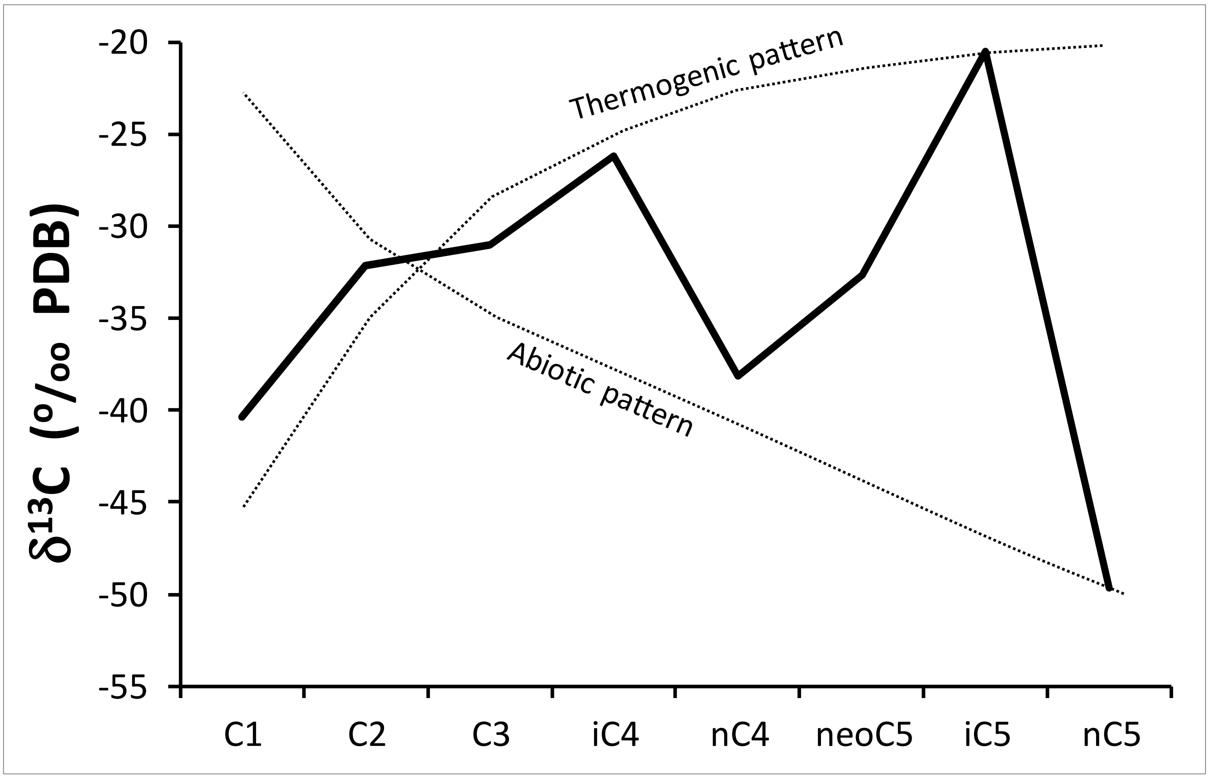

Figure 6: Carbon isotopic ratios pattern for the gas of Bougou-1 expressed in per mil versus PDB. The complex pattern is interpreted as a mixture between an abiotic gas containing without any isoprenoid molecule, and a thermogenic dry gas, containing all the compounds. The grey dashed lines represent standard values of $\delta^{13}C$ for a purely and a purely abiotic gas. The black line represents the Bougou-1 composition, fitted with a mixture of the two thermogenic and abiotic endmembers, as the chemical proportions are very different for each endmember.

Noble gas isotopes

Noble gas isotope studies are well adapted to trace physical processes affecting crustal or mantle fluids, as well as quantifying the origins of the fluids from superficial, crustal or mantellic origin (Prinzhofer, 2013). Their chemically inert property renders them conservative when exchanging between different geological reservoirs, whereas some radiogenic isotopes (^{4}He, ^{40}Ar, …) may be used for chronological and source-characterizing purposes.

Noble gas concentrations (He, Ne, Ar, Kr and Xe) and respective isotopic ratios were analyzed and are reported in Table 2. Data show no air contamination in the analyses (Figure 7a) of ^{20}Ne, ^{36}Ar and ^{84}Kr, while there is a signature due to the Air Saturated Water reservoir (ASW, i.e. noble gases solubilized in aquifers through the recharge zones). The fractionation that can be accounted for, independent of the ASW signature cannot be due to a mixture, because no other endmember is known to have such signature on Earth. Therefore, it is suggested to represent a fractionation process due to migration. The enrichment of light isotopes (^{20}Ne versus ^{36}Ar and ^{36}Ar versus ^{84}Kr) may explain the observed signatures, as they may be relatively enriched during a migration process (Prinzhofer et al., 2000). Helium and argon have a large radiogenic component, indicating a deep source from metasediments or from the basement (Figure 7b). As the isotopic ratios of mantle helium ($1.12\ 10^{-5}$) and mantle argon ($3\ 10^{4}$) are very different from the measured ones from the Bougou-1 gas, it may be concluded that no trace of any mantle contribution has been evidenced.

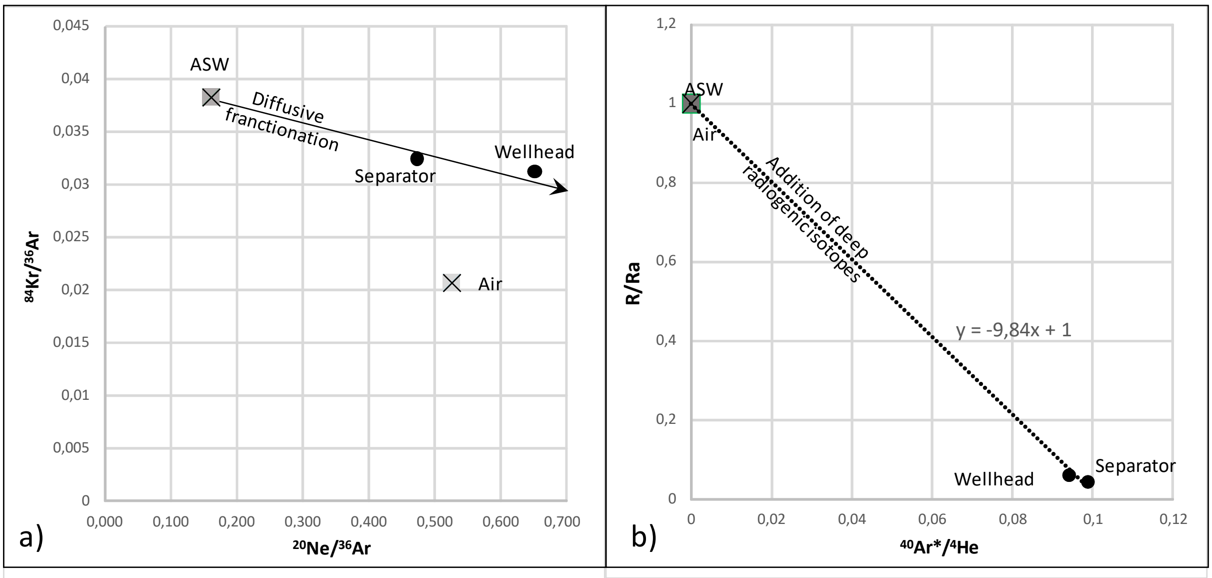

Figure 7: ratios between different noble gas isotopes. a) Fossil isotopic ratios $^{84}Kr/^{36}Ar$ versus $^{20}Ne/^{36}Ar$. b) radiogenic isotopes R/Ra (equivalent to $^{3}He/^{4}He$ normalized with the atmospheric ratio of 1.6 10^{-6}) versus the radiogenic proportion of ^{40}Ar ($^{40}Ar^{*}$) over the radiogenic ^{4}He.

Concentrations	Separator	Wellhead
^{4}He (ppm)	547	552
^{20}Ne (ppm)	0,244	0,381
^{36}Ar (ppm)	0,516	0,586
^{84}Kr (ppb)	16,7	18,3
^{129}Xe (ppb)	0,91	1,39
Isotopic ratios		
$^{40}Ar/^{36}Ar$	400	384
$^{3}He/^{4}He$	6,1E-08	8,2E-08

Table 2: Helium concentrations and fossil noble gas isotope concentrations (^{20}Ne, ^{36}Ar, ^{84}Kr and ^{129}Xe in ppm) and isotopic ratios of argon ($^{40}Ar/^{36}Ar$) and helium ($^{3}He/^{4}He$)

Absolute concentrations of fossil noble gases may be further used to calculate an estimation of the Gas/Water ratio at physical equilibrium (Prinzhofer, 2013). It is considered that the fossil isotopes (^{20}Ne, ^{36}Ar, ^{84}Kr and ^{129}Xe) present concentrations in aquifers controlled by the atmospheric concentrations (which did not change in the last billion years) and the solubility of these compounds in water at the recharge zones of the aquifers. When a vapor phase (here hydrogen gas) enters in contact with aquifer water, these fossil isotopes equilibrate between the water and the vapor phase, with concentrations depending on the solubilities and the relative proportions of vapor and water, allowing to calculate a gas/water ratio. The estimated Gas/Water ratio calculated for Bougou-1 gas, is approximately $1m^3/1m^3$. Such a value indicates that Bougou-1 gas has been equilibrated with the same volume of water (at STP conditions).

2018 exploratory wells

The wells are located within a radius of 8 km and the total depths for the different wells ranges from 105 meters to 1807.4 meters. The total length of core drillings reaches 5.4 km. A map of the well positions is presented Figure 8.

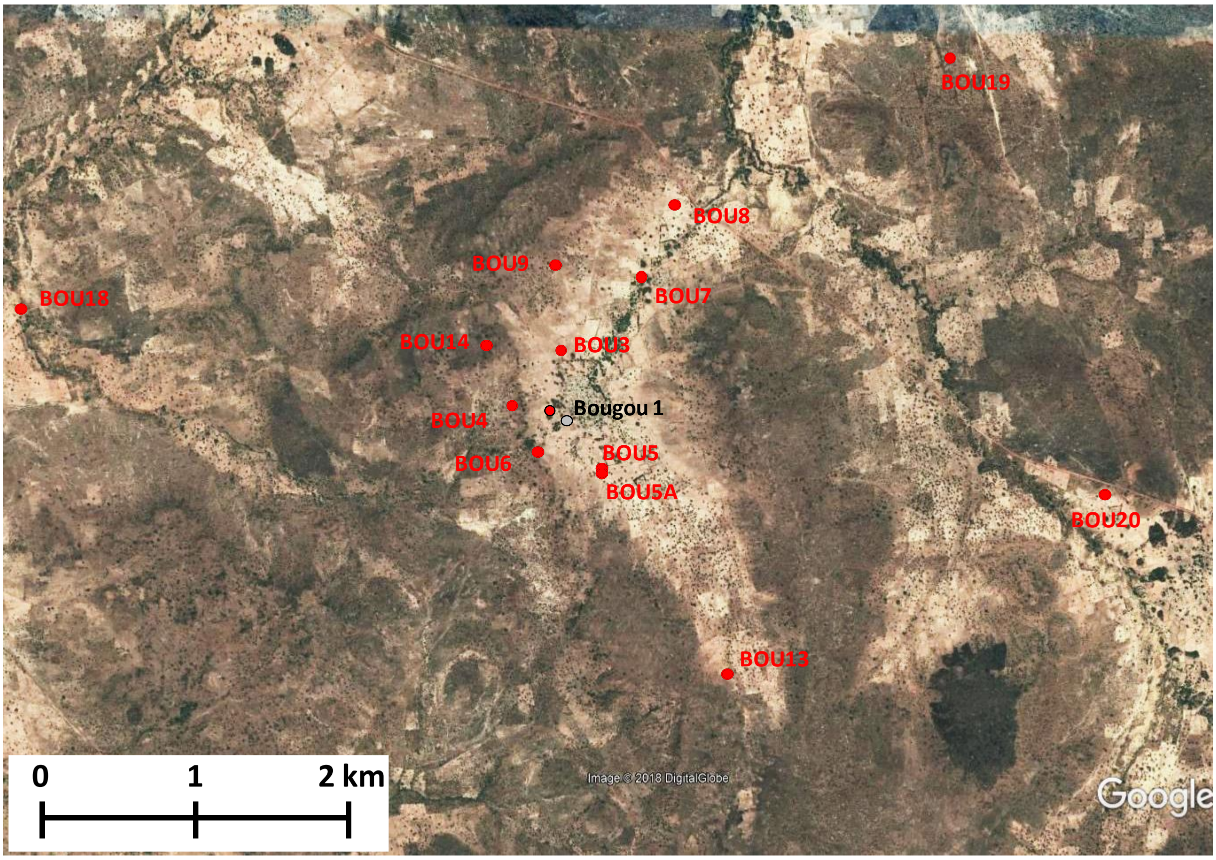

Figure 8: GoogleEarth satellite image of the Bourakebougou area (Mali). The well numbers and positions are shown with circles.

The recently drilled wells in Mali seem to confirm the hydrogen influx in this area. These wells bring a large dataset of rock and fluid samples that undoubtedly will help constrain and characterize the hydrogen system. At this time however, many high-resolution analyses are underway and only scarce geochemical results are available.

The Neo-Proterozoic sediments are characterized by sandstones, marls, silts, pelites and limestones formations. Lithofacies show that carbonates rocks are constituted of calcite, dolomite and siderite. Their texture may appear at times as marble as well as karstified carbonates. Sandstones bodies present variable porosities and are described as closed porosity to coarse grained and highly porous. Grain dissolution and other diagenetic process are evidenced, because of the presence of karst and geods. Horizons of coarse breccias have also been noted by the well geologist. Basement has been reached in only one well (Well Bougou-6). The basement rocks are characterized as plutonic rocks composed of granite, granodiorite, diorite, syenite and aplite.

The mineralogy is also described as composed of iron containing minerals, present at different oxidation state, like magnetite, hematite, pyrite, chalcopyrite.

Based on field description made during the actual drilling phase, wells show numerous sills and intrusions of dolerite. The texture of magmatic rocks is aphanitic close to the sill walls, giving clues that these magmatic rocks have intruded themselves in relatively “cold” formations, inducing chilled margins of the intrusions. The magmatism of this area is dated around 200 million years (Sebai et al., 1991) and emitted in a very narrow time interval.

Continuous gas detection and recording of fluids was made while drilling in exploratory wells. The resulting reported geochemical gas compositions show a predominance of hydrogen gas (H_2), with variable proportions of methane in all the wells. The H_2/CH_4 ratios range between values of 10 to 500 (for the Bougou-1 gas, the ratio is of 98). Traces of H_2S and CO (both above 1000 ppm concentrations) were identified in few wells.

The origin of the H_2S gas compound has been suggested to be related to the interaction between sulfur and other compounds (H_2, H_2O) which could be generated through a shallow biologic activity. This situation is somewhat expected in anoxic sediments. The other health hazardous gas encountered in some wells is carbon monoxide, very often at concentrations above 1000 ppm. This gas is never observed in natural sedimentary sequences, but occasionally detected with extensive drilling bit metamorphism. Carbon monoxide is a reactive gas, whose geological residence time is very short. Concentrations above 1000 ppm cannot be interpreted solely on artificial bit metamorphism during drilling and a more plausible explanation is linked to some active geochemical processes undergoing in subsurface fluids.

When discussing hydrocarbon geochemical signatures, it was mentioned that some of the hydrocarbon compounds were likely associated with abiotic processes and CO_2 reduction following the Sabatier’s chemical reaction and/or Fisher-Tropsch polymerization. In these reactions, carbon monoxide is as a matter of fact found to be an essential intermediate compound during these processes. Therefore, its presence in relatively high concentration during drilling may indicate a steady-state concentration associated with its generation and destruction during the chain of chemical reactions involved with hydrocarbon generation. The presence of carbon monoxide thus can reinforce the notion of recent and sustainable geological generation of natural hydrogen in this area.

Permeability fluid barriers in Mali wells

A schematic cross-section joining several wells is presented Figure 9. It appears that 5 different reservoirs may be defined, separated by dolerite sills.

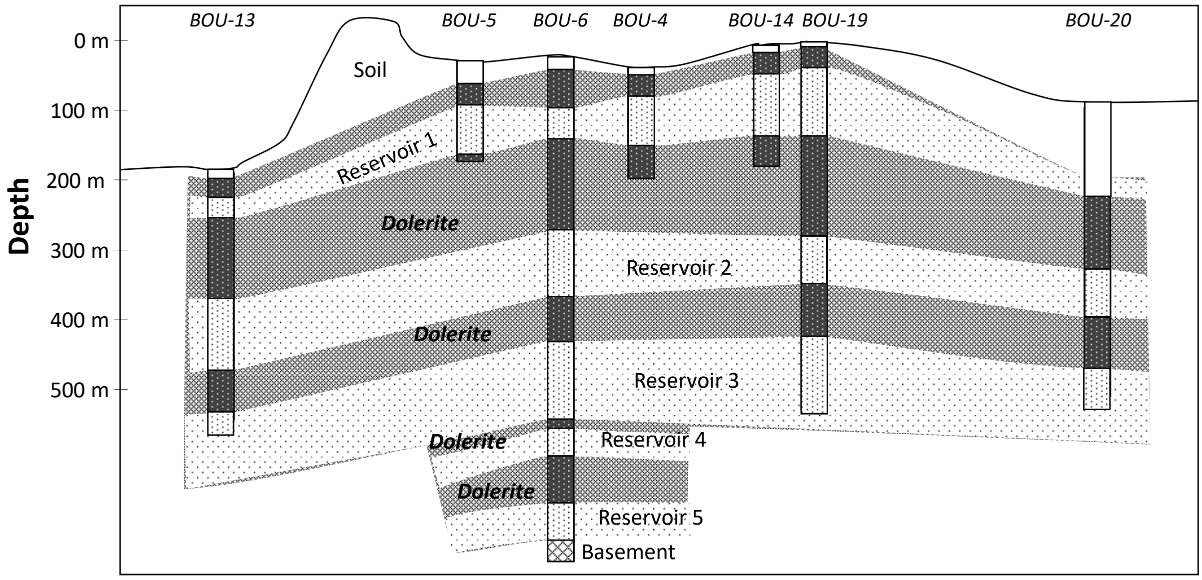

Figure 9: schematic cross-section of the Bourakebougou gas field, passing through several wells described in this work

Water was noted to gush out of some of the wells as observed with two artesian wells, propping up to the surface with gas bubbles. This observation is important in trying to understand the buildup and release of hydrogen at the surface when hydrogen mobilizes through shallow sediments. A possible interpretation is that water is surging upwards because of pressure buildup with associated dissolved gas at the surface, with a seemingly geyser dynamic.

A similar sedimentological model seems to be repeating itself in nearby wells which have at least five defined stacked hydrogen-rich reservoirs. The most superficial accumulation is found at a shallow depth near 100 meters which stratigraphically corresponds to the unique shallow Bougou-1 reservoir. The effective permeability fluid barrier is considered to be superficial dolerites, outcropping in the whole area near Bourakebougou. The fact that this 100-meter-deep accumulation is observed in all newly drilled wells shows with little doubt that the regional extension is quite large (~ 8 km estimated) and may well underline that the hydrogen system at play in this part of Mali is generating a substantial volume of gas.

If the presence of different dolerite levels has been identified on the geochemical logging reports of all these new wells, it is interesting to note that new additional details have emerged for example from the deeper intervals of the Bougou-6 well (Fig. 10). Indeed, in this well, the seals may apparently be other than solely dolerite sills. The presence of breccias noted by the field geologist in fact could play a role and behaving as impermeable seals, even though they are highly porous.

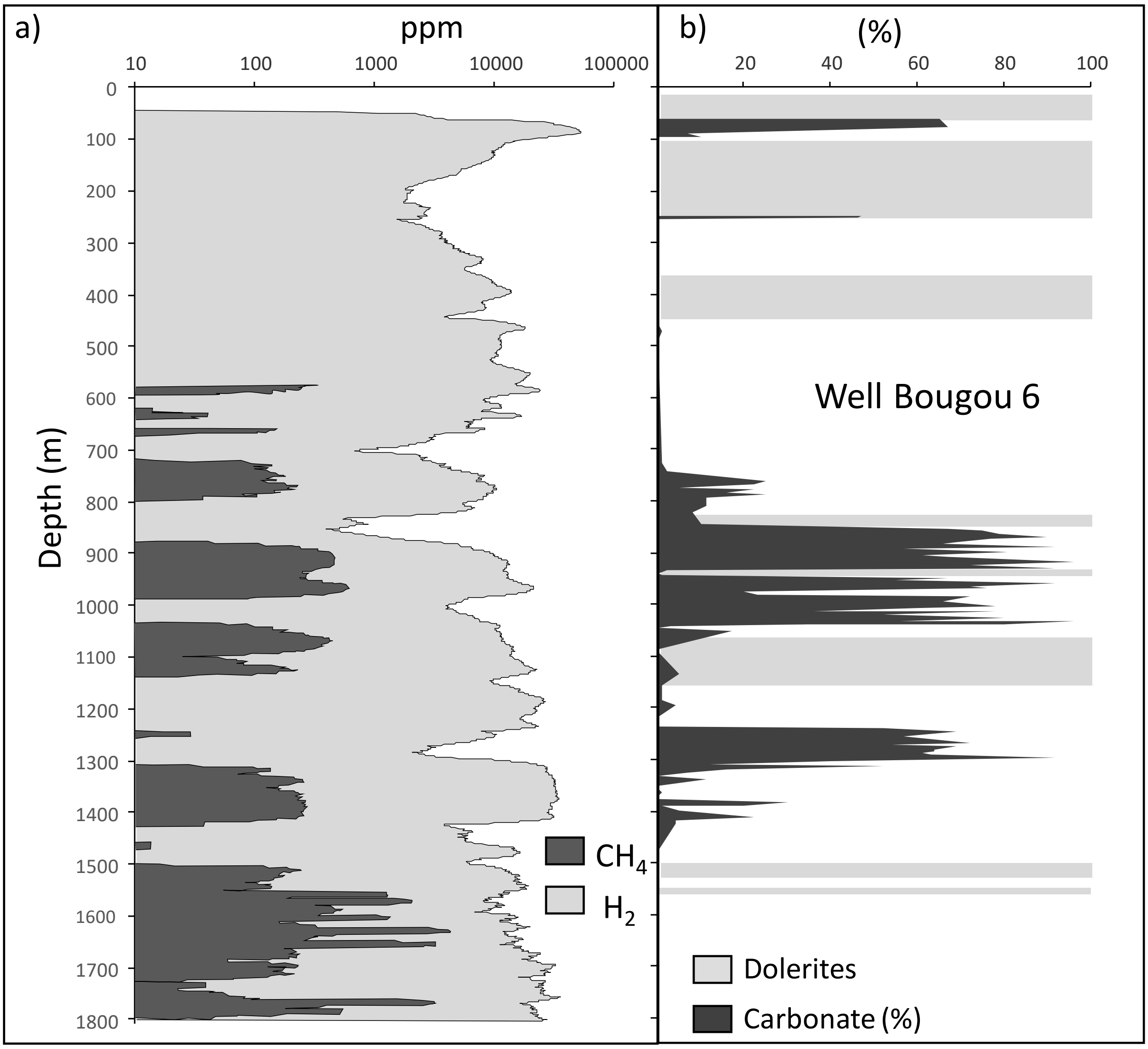

Figure 10: Simplified gas-log (a) and mineralogical-log (b) of the deepest well drilled in this study (Bougou-6). The concentrations of methane (dark grey in figure 10a) and hydrogen (light grey in figure 10a) are represented versus depth, as well as the dolerite sills (light grey in figure 10b) and the proportion of carbonates (dark grey in figure 10b).

This is technically possible if one considers the very low solubility of hydrogen in water (twice smaller than methane, and 50 times smaller than CO_2). In that case, it can be suggested that water itself behaves as an impermeable media as it is present in breccias and other possible porous rocks. The fact that we observe the "gas lift" process during sediment penetration indicates that water acts physically in the hydrogen migration and entrapment process, as it is located above the hydrogen phase.

It should be reminded that water, taking the role of a fluid barrier at shallow depths, is in opposition to the conventional scheme of petroleum systems: as water is denser, it is mostly always positioned below oil and gas traps. The exceptions being shallow aquifers above cap rocks. One explanation to understand the physical mechanism associated with the pseudo geyser (composed of mostly water and bubbling gas) is that a gas recharge is in place below shallow water aquifers. The latter do not have time to equilibrate through buoyancy above the water table because of a slow migration through the sedimentary rocks. When the well penetrates sediments, a gas phase is liberated and carries up water by depressurization.

Ultimately, this indicates that hydrogen gas has charged sediments very recently in the structures, without any equilibrium time to move through the water at respective densities. The relative recent charge of hydrogen to these depths reiterates the notion of some sort of sustainable source of energy and not a fossil one.

Discussion

Main reservoir rocks in this area of Mali, where hydrogen has been observed to occur, are characterized as carbonates despite indices of hydrogen shows also present in sandstones and other detritic rocks.

At the reservoir scale, the accumulations of hydrogen and methane present shifted maxima which oscillate in intensity with depth (Figure 11). The “caprocks” seem to be of different mineral nature for methane and hydrogen. In this example, both gases do not appear to be trapped simultaneously at equivalent depths. Moreover, marble layers do not seem to retain hydrogen while methane appears to be accumulated below thick carbonate sedimentary bodies.

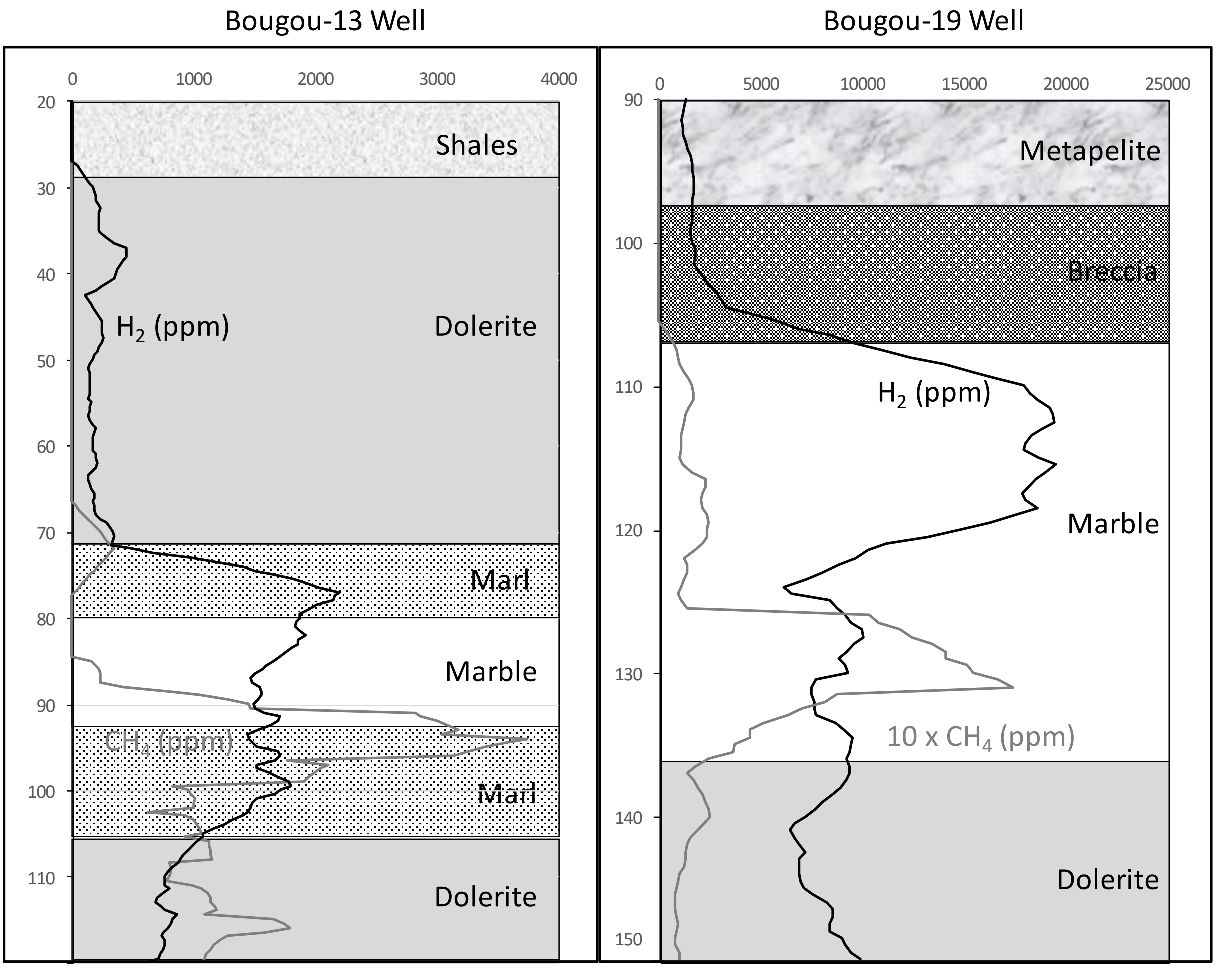

Figure 11: Details of the gas logging of the wells Bougou-13 and Bougou-19. The gas concentrations of hydrogen (black line) and methane (grey line) are represented versus depth (meters). A simplified mineralogical log is also presented.

Concerning the apparent differential sealing efficiency for methane and hydrogen, it is not well defined at this time and clearly deserves more investigation, in particular by studying and modeling gas-water-rock interactions. Chemical models which take into account physical parameters controlling gas migration (water solubility, mineral adsorption, advection and diffusion parameters, etc.) would be necessary.

Conclusions

Recently drilled wells in Mali show significant hydrogen discoveries in the vicinity of Bourakebougou, at a distance of 50 km north of Bamako, and present unique geochemical and geological features of an active hydrogen system. This opens new perspectives of a future industrial exploitation of hydrogen.

The hydrogen natural system is a recent science. As a comparison, oil and gas exploration began in the middle of the 19th century with an immediate success, and little knowledge about the petroleum system, generation, source rocks and migration of hydrocarbons. Much later, in the 1930's, advances in analytical chemistry allowed to understand and link the organic origin of petroleum. The full understanding of the functioning of a petroleum system (generation, migration, accumulation, alteration and leakage) came only in the 1960's.

Hydrogen accumulation in sediments might well be a technical challenge to understand its mechanism and may follow a similar fate before the "Hydrogen System" be fully understood. However, as for oil production, we may consider already that natural hydrogen accumulations have been clearly demonstrated in Mali, opening a pathway to an industrial exploitation. The cost associated with the exploitation of 1kg of natural hydrogen may be estimated to be 2 to 10 times smaller than the cost of manufactured hydrogen, rendering this new source of energy quite attractive for the future of our energy consumption.

Scientific and practical features of a natural hydrogen system as seen in Mali have been outlined and can be summarized:

- From a scientific point of view, natural hydrogen in Mali is associated with neo-Proterozoic sediments. This geological time is characterized by cold temperatures on Earth and a reduction of the oxygen proportion in the atmosphere, inducing reducing conditions in the sedimentary rocks.
- It appears that natural hydrogen accumulations are not limited to the vicinity of Bourakebougou, but present additional sites extending regionally up to a minimum of 8 km. Surface geochemistry indicates that the occurrence of hydrogen seeps extends up to 150 km.
- Apart from the relatively shallow gas accumulation of Bougou-1 well, known from the first drilled well in 1987 at around 100 meters depth, four additional sedimentary layers enriched in hydrogen have been encountered in deeper horizons (down to 1800 m) from a dozen newly drilled wells in this area.

- Hydrogen generation is suggested to occur deeper than present reservoir depths and most probably issued from the basement, as demonstrated with the occurrence of large amounts of radiogenic helium and argon, associated with deep nitrogen.
- The associated hydrocarbon gas compounds are generated through a reduction of CO_2 with H_2. This reduction is likely to be a chemical reaction which takes place at relatively high temperature, although a biological generation cannot be excluded.
- The present Mali hydrogen accumulations can be explained because of the presence of numerous sills of dolerites that act as fluid barriers. Water levels however also seem to play a role as permeability barriers, easily understood as H_2 is practically insoluble in water at shallow depths.
- Some of the recent wells present an "artesian" water flow mechanism, enriched in hydrogen gas. This "geyser" dynamic may be due to a "gas lift" not so well understood process, and/or to overpressures in the fluids of the subsurface. This would be in favor of a recent gas charge, making the natural hydrogen kitchen a sustainable source of energy, in opposition with hydrocarbon accumulations associated with residence times of million years, far from our human time of consumption.
- Sustainable renewed hydrogen accumulations are emphasized with the presence of carbon monoxide, a highly reactive gas compound which cannot be fossil in the subsurface.

Acknowledgements

We thank Isabelle Moretti and Joao Batista Françolin for reviewing the first draft of the manuscript. Thanks also to Caroline Magnier for fruitful discussions and proof reading.

References

Abrajano T. A., Sturchio N. C., Bohlke J. K., Lyon G. L., Poreda R. and Stevens C. (1988) Methane-hydrogen gas seeps, Zambales Ophiolite, Philippines: deep or shallow origin? Chem. Geol. 71(1–3), 211–222. https://doi.org/10.1016/0009-2541(88)90116-7.

Abrajano T. A., Sturchio N. C., Kennedy B. M., Lyon G. L., Muehlenbachs K. and Bohlke J. K. (1990) Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Philippines. Appl. Geochem. 5(5–6), 625–630. https://doi.org/10.1016/0883-2927(90)90060-I.

Albert-Villanueva E., Permanyer A., Tritlla J., Levresse G. and Salas R. (2016): Solid hydrocarbons in Proterozoic dolomites, Taoudeni Basin, Mauritania. Journal of Petroleum Geology, vol. 39 (1), p. 5-28

Angino, E. E., Coveney, R. M. J., Goebel, E. D., Zeller, E. J., & Dreschhoff, G. A. M. (1984). Hydrogen and nitrogen - origin, distribution, and abundance, a followup. Oil & Gas Journal, 82(49), 142–146.

Angino, E. E., Zeller, E. J., Dreschhoff, G. A. M., Goebel, E. D., & Coveney, R. M. J. (1990). Spatial distribution of hydrogen in soil gas in central Kansas, USA. In, Durrance, E.M.; Galimov, E.M.; Hinkle, M.E.; Reimer, G.M.; Sugisaki, R.; and Augustithis, S.S., Geochemistry of gaseous elements and compounds. Theophrastus Publishers, Athens, Greece, 485–493.

Brière D. and Jerzykiewicz T. (2016): On generating a geological model for hydrogen gas in the southern Taoudeni Megabasin (Bourakébougou area, Mali). International Conference and Exhibition AAPG, Barcelona, Spain, 3-6 April 2016, pp. 342.

Coveney R. M. J., Goebel E. D., Zeller E. J., Dreschhoff G. A. M. and Angino E. E. (1987) Serpentinization and origin of hydrogen gas in Kansas. AAPG Bull. 71, 39–48.

Charlou J. L., Donval J. P., Fouquet Y., Jean-Baptiste P. and Holm N. (2002) Geochemistry of high H_2 and CH4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36° 14'N, MAR). Chem. Geol. 191, 345–359.

Craig J.L., Rizzi C. et al. (2008) : Structural styles and prospectivity in the Precambrian and Paleozoic hydrocarbon systems of North Africa. In: Salem M.J., Oun K.M. and Essed A.S. ed., The Geology of East Lybia, Gutenberg Press, Malta, 4, p. 51-122.

Deville E., Prinzhofer A., Pillot D., Vacquand C. and Sissman O. (2010) Peridote-water interaction generating migration pathways of N_2-H_2-CH_4-rich fluids in subduction context: common processes in the ophiolites of Oman, New-Caledonia, Philippines and Turkey. Am. Geophys. Union Trans., T13A–2184D.

Deville E., Prinzhofer A., Pillot D. and Vacquand C. (2011) Natural flows of H_2 and associated diagenetic processes of atmospheric CO_2 capture and sequestration: a study in the ophiolites of Oman. In Proceedings of the Offshore Mediterranean Conference, OMC 2011 (Paper# ISBN 9788894043686, 9pages).

Deville E. and Prinzhofer A. (2016) The origin of N_2-H_2-CH_4-rich natural gas seepages in ophiolitic context: a major and noble gases study of fluid seepages in New Caledonia. Chem. Geol. 440, 139–147.

Goebel, E. D., Coveney, R. M. J., Angino, E. E., & Zeller, E. J. (1983). Naturally occurring hydrogen gas from a borehole on the western flank of the Nemaha anticline in Kansas. American Association of Petroleum Geologists, Bulletin, 67(8), 1324.

Goebel, E. D., Coveney, R. M. J., Angino, E. E., Zeller, E. J., & Dreschhoff, G. A. M. (1984). Geology, composition, isotopes of naturally occurring H_2/N_2 rich gas from wells near Junction City, Kansas. Oil & Gas Journal, 82(19), 215–222.

Guélard J., Beaumont V., Guyot F., Pillot D., Jezequel D., Ader M., Newell K. D. and Deville E. (2017) Natural H_2 in Kansas: deep or shallow origin? Geochem. Geophys. Geosyst. G3 18. https://doi.org/10.1002/2016GC006544.

Hosgörmez H. (2007) Origin of the natural gas seep of Cirali (Chimera), Turkey: site of the first Olympic fire. J. Asian Earth Sci. 30(1), 131–141.

Hosgörmez H., Etiope G. and Yalc¸in M. N. (2008) New evidence for a mixed inorganic and organic origin of the Olympic Chimaera fire (Turkey): a large onshore seepage of abiogenic gas. Geofluids 8(4), 263–273. https://doi.org/10.1111/j.1468-8123.2008.00226.x.

Ikorsky S. V., Gigashvili G. M., Lanyov V. S., Narkotiev V. D. and Petersilye I. A. (1999) The investigation of gases during the Kola superdeep borehole drilling (to 11.6 km). Geol. Jb. D107, 145–152.

Larin N., Zgonnik V., Rodina S., Deville E´ ., Prinzhofer A. and Larin V. N. (2015) Natural molecular hydrogen seepages associated with surficial, rounded depression on the European craton in Russia. Nat. Resour. Res. 24(3), 363–383. https://doi.org/10.1007/s11053-014-9257-5.

Marcaillou C., Mun˜oz M., Vidal O., Parra T. and Harfouche M. (2011) Mineralogical evidence for H_2 degassing during serpentinization at 300 °C/300 bar. Earth Planet. Sci. Lett. 303(3–4), 281–290. https://doi.org/10.1016/j.epsl.2011.01.006.

Moretti I., D'Agostino A., Werly J., Ghost C., Defrenne D. and Gorintin L. (2018). Pour la Science, secial issue in partnership with Engie, march 2018, p. 24-25

Neal C. and Stanger G. (1983) Hydrogen generation from mantle source rocks in Oman. Earth Planet. Sci. Lett. 66, 315–320. https://doi.org/10.1016/0012-821X(83)90144-9.

Newell, D. K., Doveton, J. H., Merriam, D. F., Sherwood Lollar, B., Waggoner, W. M., & Magnuson, M. L. (2007). H_2-rich and hydrocarbon gas recovered in a deep Precambrian well in northeastern Kansas. Natural Resources Research, 16(3), 277–292.

Petersen H.C. (1990): Does natural hydrogen exist? International Journal of Hydrogen Energy, Vol. 15, page 55

Prinzhofer A., Guzman-Vega M. A., Battani A & Escudero M. (2000): Gas geochemistry of the Macuspana Basin, Mexico : thermogenic accumulations in sediments impregnated by bacterial gas. Marine and Petroleum Geology, vol. 17, p. 1029-1040.

Prinzhofer A. (2013): Noble gas in oil and gas accumulations. In “Noble Gases as Geochemical Tracers”, Chapter 9, pp. 224-247. Pete Burnard Ed., Springer Verlag.

Prinzhofer A. and Deville E. (2015): Hydrogène naturel. La prochaine révolution énergétique ? Edition Belin (13th of May 2015), 187p.

Sano Y., Urabe A., Wakita H. and Wushiki H. (1993) Origin of hydrogen-nitrogen gas seeps, Oman. Appl. Geochem. 8(1), 1–8. https://doi.org/10.1016/0883-2927(93)90053-J.

Sebai A., Feraud G., Bertrand H. and Hanes J. (1991): $^{40}Ar/^{39}Ar$ dating and geochemistry of tholeiitic magmatism related to the early opening of the Central Atlantic rift. Earth and Planet. Sci. Lett., vol. 104, Issues 2–4, Pages 455-472

Sherwood-Lollar B., Voglesonger K., Lin L.-H., Lacrampe- Couloume G., Telling J., Abrajano T. A., Onstott T. C. and Pratt L. M. (2007) Hydrogeologic controls on episodic H_2 release from Precambrian fractured rocks–energy for deep subsurface life on Earth and Mars. Astrobiology 7, 971–986.

Sherwood Lollar B, Lacrampe-Couloume G., Voglesonger K., Onstott T.C., Pratt L.M. and Slater G.F. (2008): Isotopic signatures of CH4 and higher hydrocarbon gases from Precambrian sheld sites: a model for abiogenic polymerization of hydrocarbons. Geochim. Cosmochim. Acta 72, pp. 4778-4795.

Szatmari P. (1989) Petroleum formation by Fischer-Tropsch synthesis in plate tectonics. Am. Assoc. Pet. Geol. Bull. 73, 989–998.

Vacquand C., Deville E., Beaumont V., Guyot F., Sissmann O., Pillot D., Arcilla C. and Prinzhofer A. (2018): Reduced gas seepages in ophiolitic complexes: Evidences for multiple origins of the H_2-CH_4-N_2 gas mixture. Geochim. Cosmochim. Acto, 2223, p. 437-461.

Villeneuve M., 2005. Paleozoic basins in West Africa and the Mauritanide thrust belt. Journ. African Earth Sci., 43, 166-195.

Welhan J. A. and Craig H. (1979) Methane and hydrogen in East Pacific Rise hydrothermal fluids. Geophys. Res. Lett. 6, 829–831.

Zgonnik V., Beaumont V., Deville E., Larin N., Pillot D. and Farrell K. (2015) Evidences for natural hydrogen seepages associated with rounded subsident structures: the Carolina bays (Northern Carolina, USA). Prog. Earth Planet. Sci. 2, 31. https://doi.org/10.1186/s40645-015-0062-5.