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Natural H₂ in Kansas: deep or shallow origin?

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Key Points:

- A new well provide the opportunity of a reappraisal of a persistent regional H₂ production in intracontinental settings, in Kansas.
- Two different origins are suggested for H₂ production in intra-cratonic context: a crustal origin, a surficial origin.
- Hypotheses of two H₂ are supported by geochemical properties of associated gases, by water associated and completion story of the well.

Abstract

A geochemical study of gas coming from three wells in northeastern Kansas supplements previous studies from the 1980s and points to a persistent regional phenomenon of H₂ production. In 2008, a new well showed, just after drilling, a dry gas phase with more than 80 mole % of H₂, followed by a water production associated with gas. This gas is mainly composed of N₂, He, H₂ and occasionally CH₄, with changing proportions through time. A drastic decrease in H₂ at the well was observed since the aquifer is produced, along with occasional recharges in H₂ evidenced notably in the early phases of gas sampling. We demonstrate that this evolution of gas composition is closely associated to the well completion story. Accordingly, two distinct origins of H₂ are proposed: (1) water reduction associated to iron oxidation in the Precambrian basement (deep crustal H₂); (2) reactions occurring in the tubing, primarily attributed to a high Fe²⁺ content and organic carbon (DOC=4.1 mg.L⁻¹) dissolved in the water. The low δD values averaging -760 ‰ are attributed to low temperature processes, in agreement with both the hypothesis. Furthermore, the suggested origins are supported by the observed gas associations: (a) deep crustal H₂ with radiogenic gases (⁴He and ⁴⁰Ar) and metamorphic N₂ (δ¹⁵N averaging +2.5‰); (b) surficial H₂ with methane produced in the sedimentary aquifer and the tubing by methanogenic organisms.

1. Introduction

The natural production of H₂ has been the subject of several studies over the last decades notably after the discovery of H₂-rich fluids at mid-ocean ridges [Welhan and Craig, 1979; Charlou *et al.*, 2002; Proskurowski *et al.*, 2008; Keir *et al.*, 2010]. In these studies, H₂ was determined to be generated as a result of water interactions with ultrabasic oceanic rocks. These fluids could be a potential trigger for the development of early life [Maher & Stevenson, 1988; Holm, 1992; Martin *et al.*, 2008].

Studies of surface and subsurface fluid flow in fracture systems in Precambrian continental crust also provide evidences for natural H₂ production in the continental lithosphere [Lin *et al.*, 2005; Sherwood Lollar *et al.*, 2007; Sherwood Lollar *et al.*, 2014], with locally focused seepages in circular structures in the sedimentary cover above [Larin *et al.*, 2015; Zgonnik *et al.*, 2015].

Precambrian rocks represent over 70% of the surface area of continental crust globally [Goodwin, 1996]. This environment has a distinctly lower geothermal gradient than mid-oceanic ridges and presents a different mineralogy. Despite these geological differences, H₂ in the Precambrian crust is commonly associated with CH₄ and N₂, just like it is in ophiolitic terranes [Barnes *et al.*, 1978; Neal and Stranger, 1983; Etioppe *et al.*, 2011; Deville & Prinzhofer, 2016]. Sherwood Lollar *et al.* [2014] claimed that the production rates of H₂ could reach 0.36–2.27 X 10¹¹ moles per year in continental areas, which is comparable to estimates from marine systems by Bach *et al.* [2003] and Cannat *et al.* [2010]. It implies a consistent source of energy for the subsurface microbial biosphere community [Nealson *et al.*, 2005]. Furthermore, the understanding of the mechanism of natural H₂ production in this context could be of direct economic interest as well as a source for non-fossil-energy resources.

The origin of continental H₂ is still unclear. Studies in deep mines of the Witwatersrand basin, South Africa, and of the Timmins basin in Ontario, Canada, have suggested a link between dissolved H₂ and the radiolytic dissociation of water [Lin *et al.*, 2005a; Lin *et al.*, 2005b]. Further studies have suggested that in addition to radiolysis, Fe(II) oxidation coupled to H₂O reduction could be responsible for H₂ generation in Precambrian shields. Goebel *et al.* [1984] and Coveney *et al.* [1987] suggested that H₂ formation in Kansas could be caused by serpentinization of basement gabbro or mantle outgassing in to the vicinity of kimberlite pipes.

In the early 1980s, H₂ gas was found in Kansas in wells near the Mid-Centroid Rift System [Goebel *et al.*, 1984; Coveney *et al.*, 1987; Johnsgard, 1988; Angino *et al.*, 1990, Newell *et al.*, 2007]. From 1982 to 1985, two wells (CFA Oil Scott#1 and CFA Oil Heins#1) yielded small amounts of gas containing 29-37 mole % H₂, 65-66 mole % N₂, with only traces of hydrocarbon gases. Sampling campaigns (in 2008, 2012 and 2014) gave additional information about the unusual gas in these wells. Moreover, a new well drilled in 2008 (and plugged in 2015) – the CFA Oil Sue Duroche#2 – allowed the sampling of gas and brine from a Mississippian aquifer at the base of the

sedimentary section. The study of the fluids from this new well, including the molecular and isotopic composition of its major and noble gases, provides new insight on the origin of the H₂ and its associated gases.

2. Geological and geochemical background

2.1. Kansas geology

The studied wells, Heins#1, Scott#1 and Sue Duroche#2, are located in Kansas, USA, in Geary, Morris and Riley counties respectively. They are situated along the Nemaha uplift a few kilometers west of the Humboldt fault ([Fig.1-a & b](#)), which cuts Precambrian basement rocks as well as lower Paleozoic strata. This fault is situated approximately 65 km east of the Kansas segment of Mid-Continent Rift System (MRS) ([Fig.1-b](#)), a 1.1 billion-year-old crustal fracture filled with basalts, gabbros, and arkosic sedimentary rocks extending 2000 km from Lake Superior to Oklahoma, and crossing Kansas NNE-SSW [[Chandler et al., 1989](#); [Ojakangas et al., 2001](#)]. The rocks associated with this rift are exposed in the Lake Superior region, but steep gradients in the magnetic and gravity fields, caused by faulted contacts between the thick sequences of basalt and related mafic intrusives and sedimentary rocks in flanking basins [[Cannon et al., 2001](#)] allow tracing of the feature where it is covered by cratonic Phanerozoic strata. Cores and well cuttings also have recovered gabbro and mafic rocks in contact with sedimentary rocks in Kansas [[Merriam, 1963](#)].

The Nemaha uplift trends NNE-SSW parallel and east of the MRS in eastern Kansas, and into Oklahoma and Nebraska states respectively S and N of Kansas ([Fig.1-a](#)). This uplift is mainly a product of early Pennsylvanian-age deformation. It is structurally asymmetric, with a faulted eastern margin, and a gradually dipping western margin. Mississippian strata and older rocks are tilted and eroded on the flanks of this high and unconformably overlain by Missouriian-age Pennsylvanian strata [[Merriam, 1963](#); [Goebel et al., 1984](#)].

Exposures of kimberlite pipes are found in Riley and Marshall counties, Kansas, about 40 km north of the wells ([Fig.1-a & b](#)). These kimberlites are lower Cretaceous in age and are the only non-Precambrian intrusive rocks known in the area. They can be strongly serpentized and contain abundant lizardite and magnetite, which induces localized strong positive magnetic anomalies that aids in their detection [[Brookins et al., 1970](#); [Goebel et al., 1984](#); [Coveney et al., 1987](#); [Berendsen et al., 2000](#)].

Near the H₂-bearing wells, outcropping Permian beds dip less than 1° westward ([Fig.1-b](#)). Precambrian basement rocks are found below the Paleozoic strata [[Bickford et al., 1979](#)]. Precambrian basement rocks in Kansas are primarily silicic igneous and metamorphic rocks and are not considered as potential targets for oil and gas [[Newell et al., 2007](#)]. Although many wells penetrate a meter or less of the basement in Kansas, only 17 wells have penetrated in excess of 300 m (1000 ft). Most of these were drilled in the 1920s, 1930s and 1940s. Direct information on Kansas Precambrian geology is thus provided by these rare, deep and mostly old wells. The deepest well drilled so far in Kansas penetrated arkoses and basalts in the MRS in 1985 to a depth of 11,296 ft (3443 m). This well did not reveal any hydrocarbons [[Newell et al., 2007](#)]. Data on wells penetrating the Precambrian are sparse in the central part of MRS and on the Nemaha uplift. Whereas the Phanerozoic stratigraphic section is the most complete above the MRS, much of it is not present at the crest of the Nemaha uplift where it is truncated and absent beneath angular unconformities reflecting the structural development of the uplift [[Merriam 1963](#); [Newell et al., 2007](#)].

The Sue Duroche#2 well was drilled in 2008 to a depth of 424 m, penetrating Paleozoic sedimentary strata as old as the Mississippian, and then about 90 m of the underlying Precambrian basement ([Fig.1-b](#)). The well gives access to a Mississippian aquifer located immediately above the basement. Thanks to the natural artesian production of water from this well, we were able to sample gas associated with this water ([Fig.1-c](#)). The Scott#1 well was drilled in 1982 and is located in Geary County a few kilometers southeast of Sue Duroche#2 well. It reaches 677 m and penetrates slightly inclined Paleozoic strata ranging from Mississippian-Devonian to Permian in age ([Fig.1-b & c](#)). The well reaches the upper Devonian-lower Mississippian Chattanooga Shale (commonly called the Kinderhook shale by drillers), but it is plugged at its base and is perforated at the top of a thick sequence of Mississippian limestone. The

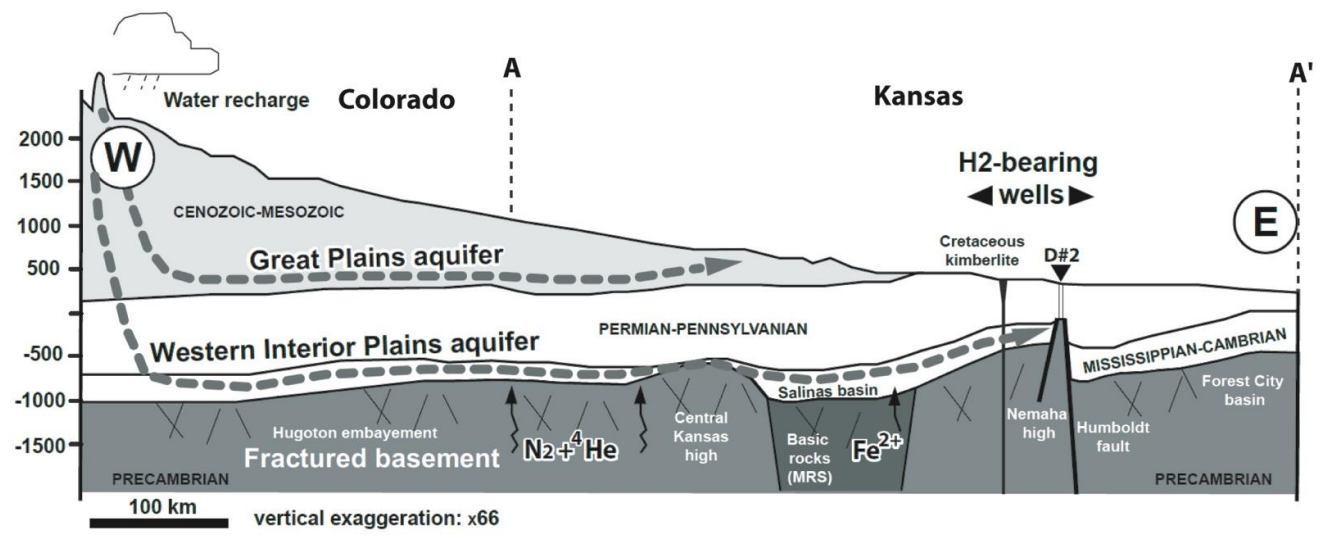
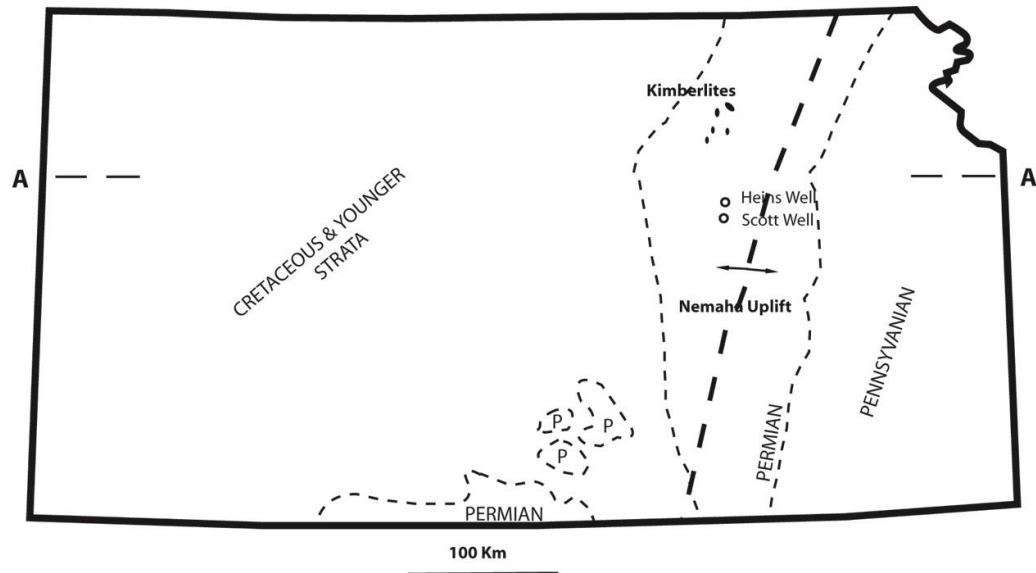


Fig.1.a & b - Geological and structural schematic map of Kansas, and localization of Heins#1, Scott#1 and Sue Duroche#2 (D#2) wells (modified from Bickford et al. 1979, and Coveney et al. 1987).

well bore is filled with 605 m of water, capped with 65 m of headspace [Coveney *et al.*, 1987] (Fig.1-c). The Heins #1 well was drilled in 1981 and is located in Morris County. It reaches a depth of 770 m. The well produces from the same Mississippian strata as the Scott#1 well.

2.2. Initial discovery of natural H₂ in Kansas

In Kansas, several wells drilled since 1980, including the aforementioned Heins#1 and Scott#1 wells, have shown occurrences of gases rich in H₂ and N₂, with subsidiary hydrocarbon gases [Goebel *et al.*, 1983; Goebel *et al.*, 1984; Angino *et al.*, 1984; Angino *et al.*, 1990; Coveney *et al.*, 1987; Newell *et al.*, 2007]. Oxygen mentioned in published analyses of gases from these wells ranges from 0.01 to 20.4%. This O₂ is considered to be atmospheric contamination during sampling. Traces of Ar and He are also present. Due to the poor concentration in CH₄ and CO₂, H₂ is not considered as dominantly microbial [Coveney *et al.*, 1987].

The oxidation of steel pipes and well casings was one of the possible mechanisms by which H₂ could be generated in the Kansas wells [Coveney *et al.*, 1987]. Nevertheless, gases from drilling mud in eight wells were monitored before setting casing, and H₂ gas was detected in seven of these wells [Goebel *et al.*, 1985; Coveney *et al.*, 1987]. Subsequent shows of free gas from these wells contained H₂ [Goebel *et al.*, 1985; Coveney *et al.*, 1987]. The well gases were assumed to be free of H₂S and NH₃ because the gases from the wells are odorless. The gases were recovered from zones open to rocks ranging in age from late Precambrian arkoses to the Pennsylvanian (i.e., Indian Cave Sandstone), Devonian-Mississippian Chattanooga Shale, and Silurian-Devonian Hunton limestone. Gas pressures in the head spaces of the wells were very low, generally only 2-8 psi (<0.55 bar) above atmospheric pressure. The presence of significant H₂ in several uncased wells likely rules out that the free H₂ was caused by rusting of the well casing or tubing.

Between 1982 and 1985, the gases of Scott#1 and Heins#1 showed widely varying H₂/N₂ ratios. In the Scott#1 well, H₂ proportions diminished with sampling between 1984 and 1985. This decrease was interpreted by Coveney *et al.* [1987] to be caused by production tests in early 1984 during which the well was acidized. The drop in H₂ at the Scott#1 well might be of natural origin, but conversely the Heins#1 well, which has not been subjected to such production tests, has maintained a high percentage of H₂ since 1982.

H₂ samples collected from the Heins#1 and Scott#1 wells have shown δD_{SMOW} values of -796‰ and -825‰, which were interpreted by Goebel *et al.* [1984] as reflecting equilibration temperatures between H₂ and water at 30-50 °C. These authors considered that these calculated temperatures might reflect the temperatures of equilibration of H₂ in the wells. Stable isotopes measured on N₂ collected in the Scott#1 and Heins#1 wells were close to atmospheric values (between -0.7 and +1.8‰) [Coveney *et al.*, 1987; Vacquand, 2011] and were thus non-diagnostic.

Surficial measurement of H₂ proportions in soil have also been done by the United States Geological Survey [Johnsgard, 1988; Angino *et al.*, 1990]. This survey started in the summer 1985 in the vicinity of the Scott#1 and Heins#1 wells and ultimately extended over 85 km westward and 80 km northward (an area of ~7000 square kms) by fall of 1987. H₂, He and CH₄ were measured in more than 600 samplings and several localities recorded anomalously high H₂ soil gas values. Some of the highest concentrations of H₂ were associated with intersections of lineaments. Some of the H₂ anomalies also appeared to extend along linear features that are visible on satellite imagery [Johnsgard, 1988; Angino *et al.*, 1990].

A more recent study [Newell *et al.*, 2007] reported gas occurrences in the Precambrian units of the WTW Operating Wilson #1 well in Brown County, in the Forest City Basin, northeastern Kansas. This well corresponds to the deepest penetration into the basement rock in the state to date except for cable-tool well drilled in 1929 and the Texaco Poersch #1 well in 1985 [Newell *et al.*, 2007]. When the well was drilling at 5385 ft (1641.3 m), approximately 1400 ft (427 m) into the Precambrian basement, gas chromatography of the drilling mud suddenly recorded elevated levels of methane, ethane, and propane. Gas obtained after days of swabbing casing perforations solely within the Precambrian, approximated the chemical composition of the gas obtained at the Scott#1 and Heins#1 wells: 17.2% H₂, 1.5% He, 0.6% Ar, 34.6% N₂ and 45.1% CH₄ (corrected from atmosphere contamination and from CO₂ possibly resulting from acidification of the well by injection of hydrochloric and hydrofluoric acid) [Newell *et al.*, 2007]. Little heavier-molecular-weight hydrocarbons were present – only 0.9% C₂ and 0.02% C₃. The isotopic signature of H₂ (average -789 ‰) was comparable to the low δD values at the Heins#1 and Scott#1 wells. The methane isotopic signature (averaging $\delta^{13}C$ -57‰, δD 362‰) suggested a biogenic production. The R/Ra ratio ($^4He/^3He_{sample}/^4He/^3He_{atmosphere}$) of 0.035 indicates a predominantly radiogenic origin of helium from continental crustal rocks [Newell *et al.*, 2007].

These results are not sufficient to draw definitive conclusions on the origin of Kansas H₂. Possible origins are discussed in *Goebel et al.* [1984], *Angino et al.* [1984] and *Coveney et al.* [1987]. These authors concluded that the similarity of the elementary composition of these gases with the ones found in ophiolitic contexts, as well as the presence in the basement of complexes of ultramafic rocks, suggest a generation of H₂ from oxidation of Fe(II) over long time scales. The setting may be analogous to other area where continental serpentinization may be occurring [Abrajano et al., 1988, Charlou and Donval, 1993; Kelley et al., 2001]. The Fe(II) could also be provided by the kimberlites found 40 km north of these two wells which contain serpentinisation textures and abundant magnetite. Other mechanisms are commonly proposed in the literature to explain the origin of free H₂ in intracontinental contexts: (1) bacterial [Boone et al., 1989] or thermogenic decomposition of organic matter [Seewald et al., 2001], (2) radiogenic effect on organic matter or water [Lin et al., 2005], (3) mantle outgassing of primordial fluids which equilibrated isotopically while seeping into the crust [Lawrence and Taviani, 1988; Apps and van de Kamp, 1994], (4) shearing of silicate rocks (microseismicity) in the presence of water and under pressure (e.g., along faults and lineaments) [Kita et al., 1982; Sugisaki et al., 1983; Sato et al., 1986], (5) release and chemical splitting of pore water, ammonium and organic matter during drilling (e.g., drilling effects) [Bjornstad et al., 1994; Bjerg et al., 1997].

3. Sampling and analytical methods

3.1. Sampling

Following the objectives to provide major and noble gases composition for the CFA Oil Heins#1, Scott#1, wells, plus water geochemistry for Sue Duroche#2 well, five field trips were devoted to sampling in June 2008, March 2012, November 2013, May 2014, and August 2014.

Heins#1 and Scott#1 wells give access to a free gas phase at low pressure (atmospheric or above atmospheric pressure) in equilibrium with water located few meters below. Water is therefore not accessible. Free gas was sampled in steel containers previously evacuated and directly connected to the wellheads. In the conditions of gas pressure encountered, it was not possible to flush the steel containers with gas from the well. The containers were filled by expansion of the gas in the pre-evacuated steel containers.

Four different field trips were dedicated to the sampling and analyses of the fluids (gas and water) at the Sue Duroche#2 well. Different sampling approaches were applied. Furthermore, according to the date of the field trip, the well has been produced or not before sampling, which affects the nature and origin of the fluids.

In March 2012, the fluids (gas and water) were sampled in a steel container directly connected to the outlet of the well. The gas separation was achieved in the laboratory on a vacuum line for Gas Chromatography (GC) and Gas Chromatography-Combustion (GC-C) analyses. Additional gas phase samplings were performed in vacutainers®. As the water from the wellhead was allowed to flow in a tray, gas bubbles were captured in vacutainers® previously filled with the fluids from the well and turned upside down in the tray. The well has been produced before sampling. For the three subsequent field trips, gases were separated from water on field. A “degassing bottle” was connected to the outlet of the well with gastight tubing. Before accumulating gas, both bottle and tubing were filled with well water in order to purge out atmospheric gases. Gas accumulates at the top of the bottle connected to a pre-evacuated steel container for gas collection. The steel container was flushed at least three times before collecting the gas.

The physico-chemical properties of the water (see [Table 1](#)) were measured at the outlet of the “degassing bottle”, in a bucket where the water flow was maintained continuously.

Water samples were also collected by syringe through a septum directly connected to a valve on the wellhead, in order to avoid any contact with atmosphere, filtered and/or poisoned when necessary. Alkalinity and iron contents (limits the loss of dissolved Fe(II) through oxidative precipitation) were measured by spectrophotometry on site [Podda & Michard 1994; Viollier et al. 2000]. Other samples were devoted to laboratory analysis at IPGP (Paris, France), notably DOC (dissolved organic carbon).

The well has been produced before sampling in March 2012 and August 2014. It hasn't been produced before sampling in November 2013 and May 2014.

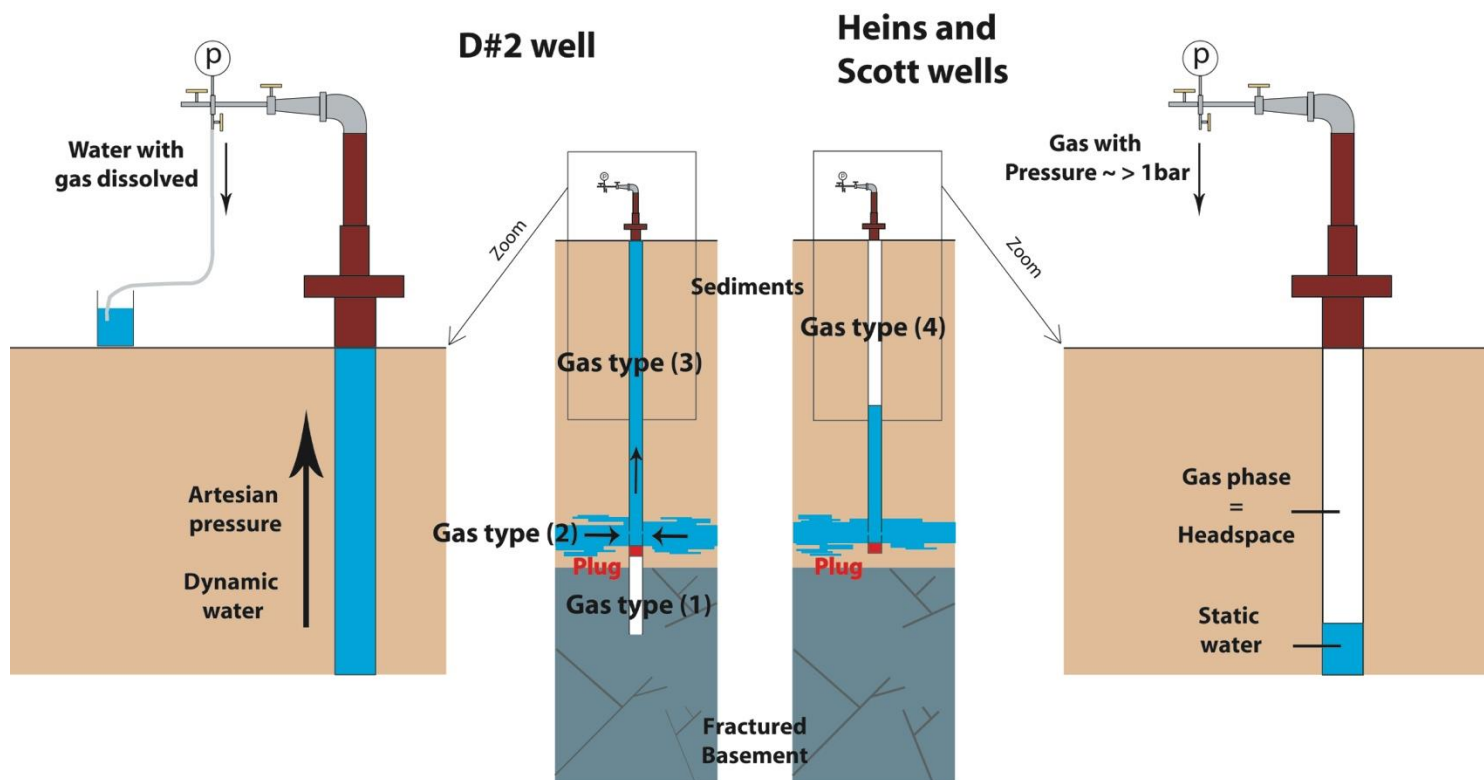


Fig. 1.c – Schematic representation of Sue Duroche#2 (D#2) headwell (water with gas dissolved) and Scott#1 and Heins#1 Headwell (static gas phase)

	03/16/12	05/16/14	05/17/14 a.m.	05/17/14 p.m.	05/18/14 a.m.	08/29/14 11:00 a.m.	08/29/14 02:00 p.m.	08/30/14 01:00 p.m.	09/01/14 09:00 a.m.	09/02/14 11:00 p.m.
pH	7.4	8.6	7.8	7.6	7.6	6.9	7.0	7.4	7.4	7.1
T (°C)	21.0	11.8	19.4	16.6	16.6	24.3	22.7	24.0	19.2	22.6
Sal (g/L)	55.0	-	-	-	-	55.8	55.8	54.9	55.8	56.3
C25 (mS/cm)	80.0	68.0	68.0	67.2	58.0	79.8	79.8	78.7	79.8	80.4
ORP (mV)	-388.0	-	-	-	-	-172.8	-262.3	-266	-213	-186

Table 1 –Physico-chemical parameters of Sue Duroche#2 water (in-situ)

3.2. Analytical methods

Gas composition - GC (Gas Chromatograph) Analyses: analyses for determining the relative molecular composition of the gases were performed by a Varian 3800 high-resolution gas chromatograph (GC) in the laboratory of IFPEN (Rueil-Malmaison, France) from samples obtained in Vacutainers® and/or stainless steel tubes. This GC is equipped with several columns, with two thermal conductivity detectors (TCD) and one flame-ionization detector (FID) operating under He or N₂ as carrier gas. The quantification of H₂ and He is made on TCD with N₂ as the carrier gas, whereas CO₂, N₂, O₂, methane, ethane, propane and butane are analyzed with the other TCD with He as the carrier gas. The FID is used for the quantification of low levels of C1-to-C5 hydrocarbons for better accuracy. Relative concentrations are calculated after calibration of the chromatographic response with external standards of various compounds. Each analysis was bracketed with blanks (i.e., runs without a sample). The analyses are given with a precision of ±5%.

GC-C-IRMS (Gas Chromatograph - Combustion - Isotopic Ratio Mass Spectrometry) analyses: C and H isotopes of CH₄ and H₂ were analyzed in the gas contained in Vacutainer® or stainless steel tubes. The ¹³C/¹²C and D/H isotopic ratios were measured using a MAT253 (Finnigan Mat-Thermo Fischer) triple collection mass spectrometer coupled to a gas chromatograph, operating with He as a carrier gas.

CH₄- C Isotopes: a Porabond Q column, heated at 40°C, permits the release of hydrocarbons at different times. Gases pass through a combustion oven (1000°C), which oxidizes CH₄ into CO₂, which is then transferred to the mass spectrometer. The instrument is calibrated by measuring an internal reference gas (CO₂), itself calibrated with the PDB standard (Pee-Dee Belemnite international reference standard), which has an absolute value of δ¹³C_{PDB} = 0‰ (the δ notation stands for δ¹³C_{PDB} = 1000 × (R_{sample} - R_{PDB}) / R_{PDB}). Repeatability and accuracy of the analysis of our internal reference allows us to obtain a relative uncertainty on the δ¹³C value of ± 0.4‰.

CH₄ and H₂ - H isotopes: after column separation, gases pass through a high temperature reduction/pyrolysis furnace (1420°C). Free H₂ and H₂ from CH₄ pyrolysis are transferred to the mass spectrometer at different times for δD analysis. The instrument is calibrated by measuring an internal reference gas (H₂), calibrated itself with the standard SMOW (Sea Mean Ocean Water, international reference standard), which has an absolute value of δD_{SMOW} = 0‰ (the δ notation stands for δD_{SMOW} = 1000 × (R_{sample} - R_{SMOW}) / R_{SMOW}). Repeatability and accuracy of the analysis of our internal reference allows us to obtain a relative uncertainty on the δD value of ± 4‰ for CH₄ and ± 6‰ H₂ (±1σ). Combination of GC-C and IRMS Delta + XP requires an energy filter to delete ⁴He⁺ formed by gas carrier ionization on m/z=3 collector, which could interfere with D (m/z=2) and H⁺ (m/z=1).

Vacuum line – IRMS analyses – δ¹⁵N composition: isotopes of N₂ were analyzed at IPGP (Paris, France) using the gas captured in Vacutainer® or stainless steel tubes. The N₂ is purified and isolated from other gases thanks to a vacuum line and transferred to an IRMS dual-inlet mass spectrometer Delta + XP (Finnigan Mat-Thermo Fischer) for the isotope analyses. N₂ is quantified manometrically in the vacuum line and compared to GC analysis to avoid non-total extraction, which could lead to isotope fractionation. The instrument is calibrated by measuring an internal reference gas (N₂) that is calibrated with the air standard (international reference standard), which has an absolute value of δ¹⁵N_{Air} = 0‰ (the δ notation stands for δ¹⁵N_{Air} = 1000 × (R_{sample} - R_{Air}) / R_{Air}). Repeatability and accuracy of the analysis of our internal reference allowed us to obtain a relative uncertainty on the δ¹⁵N value of ± 0.5‰, taking in account the N₂ extraction process.

Noble Gases Composition and the ⁴⁰Ar/³⁶Ar ratio: The noble gases elemental abundances and the ⁴⁰Ar/³⁶Ar isotopic ratio were determined by quadrupole mass spectrometry after treatment of the gas sample through an ultra-high vacuum preparation line. Only samples in stainless steel tubes were analyzed in order to guarantee a negligible air noble gas contamination after sampling. The ultra-high vacuum line is evacuated down to 10⁻⁹ mbar by the means of three turbomolecular pumps. The inlet part that connects to the sample tube is evacuated under primary vacuum (<5.1⁻³ mbar) by a roughing pump. An aliquot of the sample is admitted inside a volume of about 10 cm³ where its pressure is adjusted and precisely measured by a thermostated capacitance manometer (MKS Baratron®). A 1.2 cm³ aliquot is then taken out of that volume at a pressure adjusted between 0.1 and 100 mbar (depending on the expected Ar composition). The purification of this aliquot is performed under the action of two titanium foam traps heated at 650 °C during 30 mn. Both traps are cooled down to ambient temperature after purification in order to trap residual H₂. The purification process is monitored thanks to a Pirani gauge. The purified gas is admitted into a portion of the line equipped with an activated charcoal trap and a SAES Getters GP50 ST707 operating at 3 V. The cold trap is maintained at liquid nitrogen temperature (-198°C) in order to trap the heavy gases, Ar and Kr while He and Ne are

analysed by the mass spectrometer. During He and Ne analyses, an activated charcoal cold trap is maintained at liquid nitrogen temperature in the measurement volume for suppressing isobaric interferences of Ar and carbon-bearing compounds on m/z of interest. After pumping out He and Ne, the temperature of the trap is raised to ambient temperature for Ar and Kr to be desorbed and enter the spectrometer for analysis.

The mass spectrometer is a HiQuad quadrupole mass spectrometer (Pfeiffer Vacuum) with an open ion source. The analyzer allows measurements of compounds with a m/z ratio (mass over charge) from 0 to 200 a.m.u (atomic mass unit). The mass spectrometer is equipped with two detectors, a Faraday cup and an electron multiplier (SEM) that can be used alternately. The SEM (SEV 217, Pfeiffer Vacuum) provides a gain of 10,000 compared to the Faraday cup and therefore allows for a high dynamic range of the measurement system.

For each sample, the response of the spectrometer is calibrated by performing systematic analyses of a purified air dose (Calibrated Dose) for which the quantities of He, Ne, Ar and Kr as well as the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio are controlled weekly by an air standard analysis. The $^{40}\text{Ar}/^{36}\text{Ar}$ isotopic ratio is calibrated against the Ar pressure in the mass spectrometer whenever the source is tuned (approximately once a month) in order to correct for the non-linearity of the mass discrimination factor. The $^{40}\text{Ar}/^{36}\text{Ar}$ is calculated based on the air reference of 295 ± 0.5 [Nier, 1950]. All of the analyses are performed with the SEM, comprising 30 successive measurements of the signals associated to m/z ratios 3, 4, 18, 20, 21, 22, 28, 36, 38, 40, 44, 82, 84 and 86. The drift of the signal is corrected to the time of introduction of the gas and the residual background noise measured prior to introduction of the sample is subtracted. The isobaric interferences of 40Ar^{++} and 20Ne^{++} are corrected by a calibration made on the background blank and controlled by the measurements of the $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{20}\text{Ne}/^{21}\text{Ne}$ ratios. Interference of CO_2 on mass 44 with ^{22}Ne is always negligible. A procedural blank for the entire line is measured every week and does not exceed $1 \pm 2\%$ of the signal for each noble gas of a Calibrated Dose (DC) and typical sample analyses. The mean blank is subtracted to the signal of the sample and its standard deviation is integrated to the uncertainty of the sample analysis. The control over the introduction pressure of the sample allows a very low detection limit implying no limitation when analyzing natural samples. Global relative uncertainty (at 2σ) for quantification of noble gases with this method is of: He: $\pm 10\%$; Ne: $\pm 20\%$; Ar: $\pm 5\%$; Kr: $\pm 8\%$, and for the quantification of the ratio $^{40}\text{Ar}/^{36}\text{Ar}$: $\pm 1\%$.

$^3\text{He}/^4\text{He}$ isotopic ratios: Helium isotopic ratios and contents were determined by the means of a high-resolution magnetic sector mass spectrometer Micromass 5400. The gas admitted in the 5400 mass spectrometer is an aliquot of the gas previously purified in the same preparation line as for the quadrupole measurements. He and Ne are both introduced into the mass spectrometer under an optimal partial pressure, allowing very accurate and sensitive quantification. The mass spectrometer is equipped with a modified Nier type electron impact source (Bright). The latter is adjusted in order to obtain an optimal signal for helium, operating at $800 \mu\text{A}$ of trap current and electron energy of near 70 eV. As for the quadrupole, the Micromass 5400 comprises a Faraday cup and an electron multiplier (SEV 217, Pfeiffer Vacuum). These collectors are used alternately for the $^3\text{He}/^4\text{He}$ ratio analysis. The most abundant isotope (^4He) is measured on the Faraday cup whereas ^3He is measured by the electron multiplier. A resolution of 600 is obtained on the electron multiplier and is also necessary and sufficient for a good separation of the HD molecule and ^3He . Thirty successive measurements are performed for each isotope. A statistic regression is made in order to determine the intensity of the signal at the time of gas introduction into the source. The calibration of the $^3\text{He}/^4\text{He}$ ratio is achieved by repeated analyses of an air standard with a known composition of ^4He 5.24 ppm and $^3\text{He}/^4\text{He}$ $1.39 \cdot 10^{-6}$ [Ozima and Podosek, 2002]. The uncertainty (2σ) on the quantification of ^4He is of $\pm 8\%$. For the $^3\text{He}/^4\text{He}$ ratio it is of $\pm 4\%$.

4. Results

4.1. Water characteristics

Water from the Sue Duroche#2 well is weakly reduced ($E_h = -220$ meV) and basic. pH values range from 6.9 to 8.6 (see [table 1](#)). It shows high salinity: 1.5 times that of seawater. The measured temperatures range from 24.3 to 16.6°C. These temperatures are not considered as those of the aquifer but rather as consequence of heating or cooling of the well and sampling devices during the day.

The most striking characteristic of the Sue Duroche#2 well water is its high Fe concentration of 1.1 mM. Such enrichments are rarely observed, although higher Fe contents have been recorded in Mississippi Valley-type brines (~8mM; [Kharaka *et al.*, 1987], which are also rich in Pb, Zn and Mn), . More than 80% of the Fe is in the Fe(II) form, which is coherent with the reduced character of the water and its content in reduced gases. Its DOC

composition is $\sim 4.1 \text{ mg.L}^{-1}$ which is considered as an intermediate DOC value [Wassenar *et al.*, 1990; Aravena *et al.*, 1993]. The alkalinity is equal to 3.1 mM.

4.2. Gas Molecular composition and temporal variations

The compositions of gases from the Sue Duroche#2 well are shown in [table 2](#). It includes analytical data provided by Donald Clark (CFA Oil, the operator of the well) performed on: 1) a free dry gas phase collected immediately after drilling in 2008 (gas type (1), see [Fig.1-c](#)); 2) a gas phase exsolved from well water in 2011 (gas type (2) and (3)). Published and newly acquired gas compositions from the Scott#1 and Heins#1 wells are compiled in [table 3](#). The composition recorded are similar to Sue Duroche#2: N_2 , H_2 and CH_4 , are major components, and He is a minor component, although the gas type are different ([Fig.1-c](#)). Note that the compositions are not normalized and not corrected from possible atmospheric contamination in both [tables \(2 & 3\)](#) except for data acquired in 2008 [from *Vacquand*, 2011]. One sample is characterized by atmospheric proportions of O_2 (sample D#2-1-nov2013, 20.3 mol% O_2), which is likely due to atmospheric contamination during sampling. The CO_2 proportion is generally < 1 mole %. The evolution over time of N_2 , H_2 , CH_4 , and He proportions of Sue Duroche#2 well together with Scott#1 and Heins#1 wells are shown in [Fig.2-a, b & c](#).

4.2.1. Sue Duroche#2 well

High amplitude variations in H_2 , CH_4 , He and N_2 proportions are observed for the gas from Sue Duroche#2 well from one field trip to another. The variations of gas relative proportions are also remarkable at the day scale in 2012, 2013 and 2014 ([table 2](#)). These variations are attributed to different fluids sampling conditions as mentioned in the sampling section and illustrated in [Fig.1c](#).

During the artesian production of water from the Sue Duroche#2 well, the first fluids coming out are those accumulated in the tubing of the well, gas type (3), and it is only after several hours that the well produces fluids coming from the aquifer (gas type (2)). Large differences in gas compositions observed at the day-scale illustrate the difference between the water from the well tubing and the water from the aquifer ([Fig.2-a](#)). In March 2012 and November 2013, all the samples from the Sue Duroche#2 well were collected within a single day, while in May and August 2014 the samplings were collected over several days. In March 2012 and August 2014, the well was allowed to flow for several days before sampling, but the well was not allowed to flow before sampling in November 2013 and May 2014. The gas compositions analyzed from the March 2012 and August 2014 field trips are considered as representative of the aquifer whereas in November 2013 and at the beginning of May 2014, they are representative of the gas contained in stagnant water from the tubing. The evolution of the composition of gases between the tubing and the aquifer is appropriately illustrated by the series of samples collected in May 2014. H_2 , CH_4 , He and N_2 proportions are stable only from the third day of production (D3) ([Fig.2-a](#)).

Overall, the general trend for the gases is a drastic decrease in H_2 percentage: from 91.7 mole % in 2008 in the dry gas phase, to 0.1 mole % bubbling out from the Mississippian aquifer at atmospheric pressure in August 2014. In addition to H_2 present before the plugging, small recharges of H_2 are observed in the first collected samples of May 2014 and August 2014 (D#2-1 May 2014, 8.7 mole % - D#2-3 August 2014, 1.6 mole %).

The relative concentration of CH_4 is below 5 mole % until November 2013 when it increases to 44.9 mole % in the wellhead (D#2-3 Nov 2013). In the subsequent campaigns though, the CH_4 proportion measured for the gas from the aquifer was less than 9 mole %. Three mole % is the final trend observed in the aquifer in August 2014. As for H_2 , the highest levels of CH_4 , considering sampling over several days, are observed within the first collected samples or gas type (3) (D#2-1 May 2014, 32.7 mole % - D#2-3 August 2014, 8.4 mole %).

Overall, the N_2 concentration increases with time. Its proportion ranges from 51.6 mole % in November 2013 (D#2-3 Nov2013) in a sample that also records substantial CH_4 , to 93.3 mole % in August 2014 (D#2-7 Aug2014). He concentration is fairly constant in the gas from the aquifer, with a maximum value of 3.1 mole % (D#2-2 May2014). Its small variations (D#2-1 2012 with 0.6 mole %, D#2-2 2012 with 0.5 mole %) do not necessarily reflect a varying absolute proportion in He. He/ N_2 ratios were similar in November 2013, May 2014 and August 2014, so these variations might be the result of a dilution effect due to other gases, which could be CH_4 , H_2 , or both.

4.2.2. Scott#1 well

H_2 relative concentrations in the gas phase of the Scott#1 well were first measured in 1982 [Goebel *et al.*, 1984] ([table 3](#)). Values ranged from 25 to 56 mole %. Particularly striking are the high concentrations of O_2 coexisting with H_2 (in a ratio of 1/2), as well as N_2/O_2 ratios much higher than those of the atmosphere

Sample	Sampling date	Sampling hours	Mole (%) ^a						Isotopes (‰)				
			He	H ₂	O ₂ and Ar	N ₂	CO ₂	C1	Σ C2-C5	δ D H ₂ ^b	δ D CH ₄ ^c	δ ¹³ C CH ₄ ^d	δ ¹⁵ N N ₂ ^e
D#2 ¹	2008	-	*	91.8	0.2	4.7	3.2	0.1	0.00	n.a.	n.a.	n.a.	n.a.
D#2 ²	2011	-	0.5	7.7	2.8	84.7	1.6	2.0	n.d.	n.a.	-299	-64.3	n.a.
D#2- 1	03/16/2012	-	0.6	8.8	0.2	87.6	0.8	2.0	0.05	b.d.l.	b.d.l.	n.a.	n.a.
D#2- 2	03/17/2012	-	0.5	14.6	0.4	80.8	0.1	3.4	0.20	b.d.l.	b.d.l.	n.a.	n.a.
D#2- Vacu 3	03/17/2012	-	1.7	19.7	0.9	74.3	0.1	3.3	0.06	-754	-345	-59.1	n.a.
D#2- 1	11/12/2013	10:25 a.m.	0.1	0.2	20.3	75.0	0.5	4.0	0.02	n.a.	n.a.	n.a.	n.a.
D#2- 2	11/12/2013	10:30 a.m.	1.4	1.4	3.6	54.7	0.0	38.9	0.02	-770	-403	-21.9	n.a.
D#2- 3	11/12/2013	11:00 a.m.	1.7	1.2	0.7	51.6	0.0	44.9	0.02	-757	-402	-21.5	n.a.
D#2- 4	11/12/2013	05:00 p.m.	1.7	0.3	0.4	54.8	0.0	42.8	0.02	-770	-402	-21.0	n.a.
D#2- 5	11/13/2013	09:45 a.m.	2.3	1.1	0.4	56.6	0.0	39.5	0.02	-758	-399	-21.4	n.a.
D#2 Vacu7	11/13/2013	10:00 a.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.4
D#2- 1	05/16/2014	06:00 p.m.	1.4	8.7	0.4	56.7	0.0	32.7	0.02	-759	-403	-20.1	2.5
D#2- 2	05/17/2014	02:30 p.m.	3.1	1.1	0.5	89.1	0.0	6.3	0.01	b.d.l.	-376	-42.6	n.a.
D#2- Vacu1	05/17/2014	02:30 p.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-799	-370	-43.0	n.a.
D#2- 3	05/18/2014	11:30 a.m.	2.9	0.7	0.5	92.3	0.0	3.6	0.01	b.d.l.	-333	-51.3	2.7
D#2- Vacu2	05/18/2014	11:30 a.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-792	-313	-51.5	n.a.
D#2- 4	05/18/2014	01:00 p.m.	2.9	0.8	0.5	92.1	0.1	3.7	0.01	b.d.l.	-326	-51.6	n.a.
D#2- 5	05/18/2014	01:45 p.m.	2.9	0.8	0.5	92.1	0.1	3.7	0.01	b.d.l.	-324	-51.3	n.a.
D#2- 1	08/29/2014	12:20 a.m.	2.6	1.0	0.4	88.1	0.0	7.9	0.01	-717	-344	-51.5	n.a.
D#2- 2	08/29/2014	03:20 p.m.	2.6	1.1	0.4	87.5	0.1	8.3	0.01	b.d.l.	-352	-50.7	3.0
D#2- 3	08/29/2014	04:45 p.m.	2.6	1.6	0.3	87.1	0.0	8.4	0.01	-726	-345	n.a.	n.a.
D#2- 4	08/30/2014	02:00 p.m.	2.7	0.0	0.5	92.1	1.0	3.8	0.01	b.d.l.	-308	-52.4	n.a.
D#2- 5	08/30/2014	05:40 p.m.	2.4	0.2	2.2	91.5	0.3	3.3	0.01	b.d.l.	-310	-52.9	2.5
D#2- 6	08/31/2014	11:45 a.m.	2.6	0.2	1.3	92.6	0.2	3.1	0.01	b.d.l.	-291	-52.3	n.a.
D#2- 7	08/31/2014	02:30 p.m.	2.7	0.0	0.4	93.3	0.3	3.3	0.01	b.d.l.	-294	-54.8	n.a.
D#2- 8	09/02/2014	11:45 a.m.	2.6	0.1	1.1	93.0	0.2	3.0	0.00	b.d.l.	-296	n.a.	n.a.
D#2- vacu1	08/29/2014	12:20 a.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.1
D#2- vacu6	08/29/2014	03:20 p.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.3
D#2- vacu11	08/29/2014	04:35 p.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.5
D#2- vacu15	08/30/2014	02:00 p.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.5
D#2- vacu27	08/31/2014	02:25 p.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.6
D#2- vacu46	09/02/2014	11:45a.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.3

Table 2 – Sue Duroche#2 well: gas compositional (mol%) and isotopic (‰) analyses. * He was not distinguished from H₂. (n.a) not analyzed. (b.d.l.) Below detection limits. (1) Personal communication of Donald Clark. Analyzed on dry pressured gas by Priority Analytical Laboratory Inc., Wichita, Kansas (USA). (2) Personal communication of Donald Clark. Analyzed on dissolved gas by Isotech Laboratories Inc., Champaign, Illinois (USA). (a) Accuracy ± 5% (b) Accuracy ± 6 ‰ (c) Accuracy ± 4 ‰ (d) Accuracy ± 0.4 ‰ (e) Accuracy ± 0.5 ‰.

Well	Sampling date	Source	Mole (%)									Isotopes (‰)				
			He	H ₂	O ₂	N ₂	CO ₂	C1	Ar	H ₂ O	ΣC1-C5	δ D H ₂ ^a	δ D CH ₄ ^b	δ ¹³ C CH ₄ ^c	δ ¹⁵ N N ₂ ^d	δ ¹⁸ O H ₂ O ^e
Scott ¹	08/12/1982	Goeble et al. 1984	-	39.0	2	65.0	-	-	-	-	0.5	-	-	-	-	-
Scott ¹	08/26/1982	Goeble et al. 1984	-	25.0	11.4	71.0	<0.01	-	-	-	0.04	-	-	-	-	-
Scott	08/26/1982	Goeble et al. 1984	-	41.0	1.8	58.0	<0.01	-	-	-	0.06	-	-	-	-	-
Scott ²	09/20/1982	Goeble et al. 1984	tr	42.6	20.4	32.2	0.3	-	tr	2.07	-	-	-	-	-	-
Scott ²	09/20/1982	Goeble et al. 1984	-	56.0	-	41.0	0.9	-	tr	0.92	-	-	-	-	-	-
Scott	06/27/1983	Goeble et al. 1984	-	33.6	1	64.8	-	-	-	-	-	-796	-	-	-	-
Scott	06/27/1983	Goeble et al. 1984	<0.1	39.4	0.5	60.1	-	-	-	-	-	-	-	-	-	-
Scott	09/14/1983	Goeble et al. 1984	-	-	-	-	-	-	-	-	-	-740	-	-	-0.2	-
Scott ³	06/12/1984	Coveney et al. 1987	0.002	1.4	0.01	96.0	0.002	-	1.1	-	0.002	-	-	-	-	-
Scott ³	07/07/1984	Coveney et al. 1987	-	-	-	-	-	-	-	-	-	-836	-	-	-0.2	-
Scott ⁴	07/20/1984	Coveney et al. 1987	-	5.0	-	-	-	-	-	-	-	-	-	-	-	-
Scott ⁵	06/14/1985	Coveney et al. 1987	<0.02	4.5	1	92.8	0.5	-	1.1	-	0.01	-818	-	-	-	-
Scott ⁶	june-08	Vacquand, 2011	0.08	18.3	cor.	75.4	0.02	5.7	n.a.	n.a.	6.241	-775	-423	-31.5	+0.8	n.a.
well water ⁷	02/02/1983											-103	-	-	-	-13.2
Heins ¹	09/07/1983	Goeble et al. 1984	0.9	24.2	8.6	75.9	<0.1	0.9	-	-	-	-	-	-	-	-
Heins ¹	09/07/1983	Goeble et al. 1984	0.81	36.7	3.9	67	<0.1	0.8	-	-	-	-	-	-	-	-
Heins	09/22/1983	Goeble et al. 1984	-	-	-	-	-	-	-	-	-	-826	-	-	-0.45	-
Heins ³	06/12/1984	Coveney et al. 1987	-	29.5	1.4	63.6	0.03	-	-	<0.006	-	-	-	-	-	-
Heins ³	07/07/1984	Coveney et al. 1987	-	-	-	-	-	-	-	-	-	-810	-	-	-0.7	-
Heins ⁴	07/20/1984	Coveney et al. 1987	-	56-80	-	-	-	-	-	-	-	-	-	-	-	-
Heins ⁵	06/14/1985	Coveney et al. 1987	0.06	35.1	4.5	59.5	0.3	0.1	0.7	-	-	-776	-	-	-	-
Heins ⁶	june-08	Vacquand, 2011	0.20	24.0	cor. ⁶	28.8	0.13	46.2	n.a.	n.a.	46.85	-776	-438	-25.0	n.a.	n.a.
Heins-1	march-12	This study.	0	27.0	0.5*	64.6	0.01	7.8	n.a.	n.a.	7.85	-766	-422	-29.4	n.a.	n.a.
Heins-2	march-12	This study	0	27.9	0.5*	63.7	0.06	7.8	n.a.	n.a.	7.82	-765	-419	-26.2	n.a.	n.a.
Heins-3	08/28/2014	This study	0.09	20.5	4.8*	67.6	0.04	6.9	n.a.	n.a.	6.94	-745	-477	-20.8	-0.2	n.a.

Table 3 – Scott#1 and Heins#1 wells: gas compositional (mol%) and isotopic (‰) analyses. Table revised from Goebel et al. 1984, and Coveney et al. 1987 and new data. (1) Total not normalized to 100; values reported as received from commercial labs. (2) Mass spectrometry at University of Kansas Chemistry Department. (3) Global geochemistry, courtesy of Peter Jenden (GRI Contract 5081-360-0533). (4) Semi-quantitative assays by quadrupole mass spectrometer on site by U.S. Geological Survey (Denver). (5) Courtesy of Ivan Barnes (1985, personal communication), average of three compositional analyses, and for Heins#1 well, two deuterium analyses. (6) Vacquand, 2011, cor. = corrected from air contamination. (7) CFA Oil Company 1 Scott#1 well, Mississippian Kinderhook formation. (*) correspond to O₂ + Ar content. (-) non available. (a) Accuracy ± 10-30 ‰ (b) Accuracy ± 4 ‰ (c) Accuracy ± 0.4 ‰ (d) Accuracy ± 0.5 ‰ (e) Accuracy ± 0.1 ‰. Dotted red outline: acid injection.

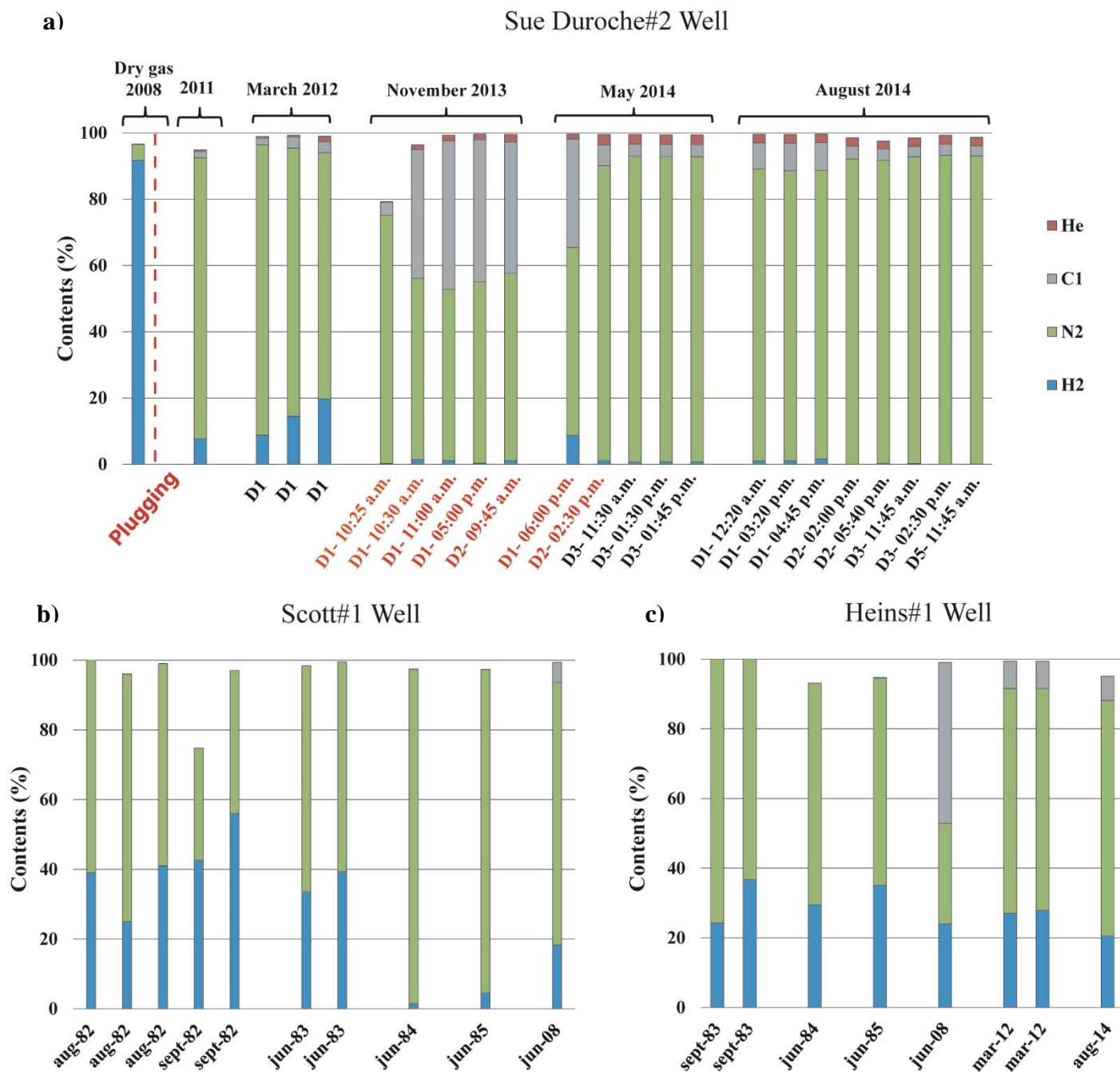


Fig 2– Compositional variations (mol%) of major gas components. For Sue Duroche#2 (a), Scott#1 (b) and Heins#1 (c) wells according to sampling date. For Sue Duroche#2, sampling dates are in red when the well has not been produced before sampling (fluids from tubing, gas type 3), in black when the well has been produced before sampling (fluids from aquifer, gas type 2).

(Scott 26/08/1982 and 20/09/1982). H₂ proportion varies from 1.4 mole % (12/06/1984) to 56 mole % (20/09/1982). While the H₂ proportion was substantial in the Scott#1 gas from August 1982 to June 1983 (25 to 56 mole %), *Goebel et al.* [1984] and *Coveney et al.* [1987] recorded a decrease in H₂ proportion since June 1984 - attributed to the production tests of the well. Sampling in 2008 [*Vacquand*, 2011] showed a renewal of H₂ since June 1985 with proportion rising up to 18.3 mole %. In association with that increase in H₂, CH₄ increased to 5.7 mole % (Scott June 2008), whereas before it was present only as traces. Contrary to the Sue Duroche#2 well, the Scott#1 well does not show ⁴He content significantly different from the atmosphere.

4.2.3. Heins#1 well

H₂ concentrations in the gas phase of this well were measured for the first time in September 1983 by *Goebel et al.* [1984]. From September 1983 to June 1985, *Goebel et al.* [1984] and *Coveney et al.* [1987] showed H₂ proportion ranging from 24 to 80 mole %. We note a slight downward trend in the H₂ proportion since June 1985. In contrast to the Scott#1 well, there has been no drastic decrease in H₂ since June 1984. Twenty-seven years after *Coveney et al.* [1987] last sampled the Heins#1 well, the gas samples from 2008 [*Vacquand*, 2011], and the March 2012 and August 2014 IFPEN field trips still show substantial H₂ (i.e., 20.5 mole % in August 2014). CH₄ appears in the Heins#1 gas well in June 2008 [*Vacquand*, 2011] (46.2 mole %), similarly to the Scott#1 well. He at the Heins#1 well in 2008, 2012 and 2014 are significantly different from the atmosphere, but largely lower than for Sue Duroche#2 well. The highest value measured is 598 ppm (Heins-2 March 2012).

4.3. C, H, N isotope compositions

Carbon, hydrogen and nitrogen isotopic compositions in CH₄, H₂ and N₂ are shown in [table 2](#) for the Sue Duroche#2 well, and in [table 3](#) for Scott#1 and Heins#1 wells. $\delta^{13}\text{C}$ values of CH₄ recorded at the Sue Duroche#2 well display two different ranges of values: a) -20.1 to -21.9 ‰, which correspond to gas accumulated in the tubing (gas type (3), [Fig.1-c](#)), and b) -50.7 to -64.3 ‰, which corresponds to gas in the Mississippian aquifer (gas type (2), [Fig.1-c](#)). The series of samples taken in May 2014 illustrate this effect with a $\delta^{13}\text{C}$ assaying at -20.1 ‰ the first day (D#2-1 May 2014), -42.6 ‰ the second day (D#2-2 May 2014) and -51.6 ‰ the third day (D#2-4 May 2014). The steady decrease in $\delta^{13}\text{C}$ values occurs with a steady decrease in CH₄ concentration. The most negative $\delta^{13}\text{C}$ values of CH₄ at the Sue Duroche#2 well were recorded for the aquifer in March 2012 and August 2014 whereas the highest values were recorded in the tubing in November 2013. The average value for $\delta^{13}\text{C}$ for CH₄ in the Mississippian aquifer at the Sue Duroche#2 well is -52.7 ‰ (gas type (2)). This value, which is highly enriched in ¹²C, is classically considered as characteristic of microbial methane (see discussion later). The average value for $\delta^{13}\text{C}$ of CH₄ from gas type (3) of the Sue Duroche#2 well is -21.2 ‰. The $\delta\text{D}_{\text{CH}_4}$ values in the Sue Duroche#2 well range from -402.7 ‰ (D#2-2 Nov 2013) to -290.7 ‰ (D#2-6 Aug 2014), with values lower than -400 ‰ in gas type (3) and values higher than -350 ‰ in the aquifer (gas type (2)). C and H isotopic signatures of CH₄ in Scott#1 and Heins#1 wells are similar to the those of gas type (3) of the Sue Duroche#2 well, with respective averages of -403 ‰ and -439 ‰ for δD and from -31.5 ‰ to -25.3 ‰ for $\delta^{13}\text{C}$.

The δD of H₂ is relatively constant in the Sue Duroche#2 well, ranging from -717 ‰ (D#2-1 Aug 2014) to -800 ‰ (D#2- vacu1) with an average value of -760 ‰. For the Scott#1 and Heins#1 wells, the average values are respectively -793 ‰ and -781 ‰. The δD values of H₂ in the gas of Heins#1 and Scott#1 wells (measured in 2008 [*Vacquand*, 2011], 2012 and 2014) are similar to those measured by *Coveney et al.* [1987] ([table 3](#)).

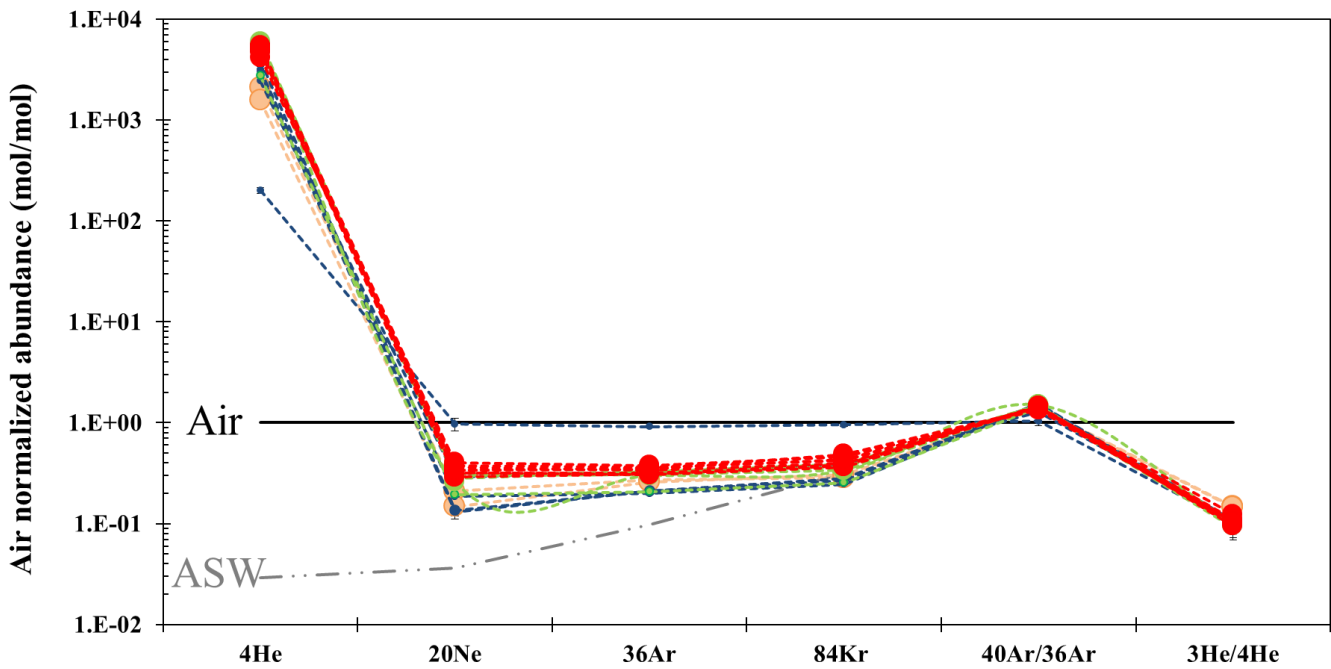
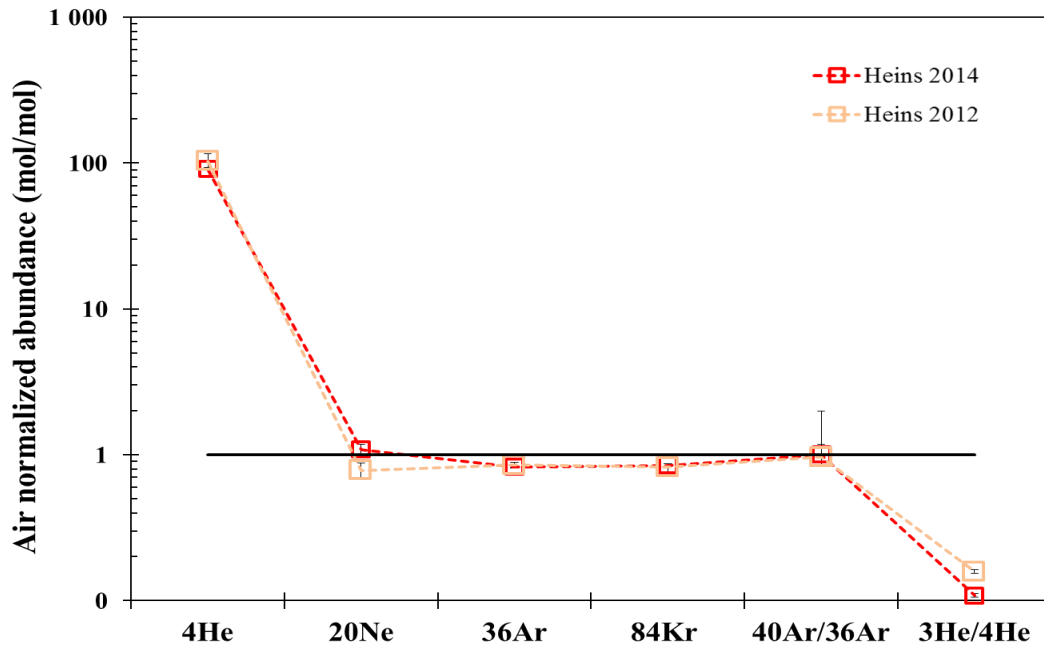
Measurements of nitrogen isotopes in N₂ emphasize that N₂ from Heins#1 is not isotopically different from the atmosphere (Heins Aug 2014, $\delta^{15}\text{N}_{\text{vs Atm}} = -0.2$ ‰), as previously discussed by *Goebel et al.* [1984] and *Coveney et al.* [1987]. However, N₂ from the Sue Duroche#2 well records positive $\delta^{15}\text{N}_{\text{vs Atm}}$ values ranging from +2.1 ‰ (D#1- vacu1 Aug 2014) to +3.0 ‰ (D#1-2 Aug 2014) without any significant change over time, and with an average value of +2.5 ‰. With respect to the precision of these measurements (± 0.5 ‰), the values are significantly different from atmosphere.

Sample	Sampling date	Sampling hours	Noble gas (ppm)						σ					
			4He	20Ne	36Ar	84Kr	40Ar/36Ar	3He/4He	4He	20Ne	36Ar	84Kr	40Ar/36Ar	3He/4He
Atm	-	-	5.24	16.45	31.57	0.65	295.50	1.4E-06						
AEW	-	-	0.05	0.17	1.07	6.23								
D#2- 1	03/16/2012	-	10978	3.45	8.53	0.19	419.2	2.1E-07	1238.8	0.4	0.3	1.1E-02	1.29	2.6E-08
D#2- 2	03/17/2012	-	8199	2.43	8.20	0.20	413.4	2.0E-07	924.8	0.3	0.3	1.2E-02	1.69	9.4E-08
D#2-Vacu 3	03/17/2012	-	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.						
D#2- 1	11/12/2013	10:25 a.m.	1050	16.01	28.83	0.62	306.8	1.4E-07	76.0	2.4	0.9	2.2E-02	3.62	1.5E-08
D#2- 2	11/12/2013	10:30 a.m.	12786	4.78	10.24	0.25	376.9	1.5E-07	921.7	0.7	0.3	9.3E-03	4.42	2.6E-08
D#2- 3	11/12/2013	11:00 a.m.	16495	3.07	6.25	0.16	453.9	1.4E-07	1189.1	0.5	0.2	6.3E-03	5.60	1.8E-08
D#2- 4	11/12/2013	05:00 p.m.	15676	2.16	6.63	0.18	459.3	1.4E-07	1131.0	0.3	0.2	7.5E-03	5.66	1.5E-08
D#2- 5	11/13/2013	09:45 a.m.	20458	2.23	6.66	0.17	457.6	1.5E-07	1484.3	0.3	0.1	5.7E-03	2.02	1.5E-08
D#2 Vacu7	11/13/2013	10:00 a.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.						
D#2- 1	05/16/2014	06:00 p.m.	14413	3.19	6.57	0.17	417.8	1.3E-07	668.3	0.2	0.1	4.5E-03	6.59	1.8E-08
D#2- 2	05/17/2014	02:30 p.m.	31076	4.93	9.72	0.22	436.5	1.5E-07	1440.3	0.3	0.1	5.5E-03	6.64	1.3E-08
D#2- Vacu1	05/17/2014	02:30 p.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.						
D#2- 3	05/18/2014	11:30 a.m.	28089	4.30	9.45	0.22	442.4	1.4E-07	1301.5	0.4	0.1	5.4E-03	6.76	1.3E-08
D#2- Vacu2	05/18/2014	11:30 a.m.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.						
D#2- 4	05/18/2014	01:00 p.m.	31159	4.91	10.36	0.24	441.4	1.3E-07	1443.5	0.3	0.1	6.0E-03	6.67	1.3E-08
D#2- 5	05/18/2014	01:45 p.m.	31870	4.59	10.32	0.25	440.7	1.3E-07	1477.4	0.4	0.1	6.6E-03	6.85	1.7E-08
D#2- 1	08/29/2014	12:20 a.m.	28343	6.01	10.68	0.26	429.0	1.3E-07	675.0	0.5	0.2	5.2E-03	1.47	1.5E-08
D#2- 2	08/29/2014	03:20 p.m.	25523	5.33	9.65	0.24	428.0	1.5E-07	626.8	0.5	0.2	4.9E-03	1.46	1.8E-08
D#2- 3	08/29/2014	04:45 p.m.	25145	4.76	9.85	0.24	431.7	1.4E-07	605.2	0.4	0.2	5.1E-03	1.58	4.4E-08
D#2- 4	08/30/2014	02:00 p.m.	25859	5.56	10.90	0.32	415.3	1.5E-07	617.4	0.5	0.2	6.3E-03	1.34	2.4E-08
D#2- 5	08/30/2014	05:40 p.m.	21817	6.65	11.88	0.30	397.5	1.4E-07	520.8	0.6	0.2	6.3E-03	1.18	1.5E-08
D#2- 6	08/31/2014	11:45 a.m.	28860	6.19	11.51	0.27	418.4	1.7E-07	687.8	0.6	0.2	5.3E-03	1.30	2.5E-08
D#2- 7	08/31/2014	02:30 p.m.	27467	5.21	9.95	0.25	432.5	1.4E-07	655.2	0.5	0.2	5.0E-03	1.40	1.4E-08
D#2- 8	09/02/2014	11:45 a.m.	26757	5.61	11.24	0.28	421.1	1.4E-07	638.5	0.5	0.2	5.6E-03	1.26	1.6E-08

Table 4 –Sue Duroche#2 well noble gas composition and isotopic ratios.
(-) not available. (n.a) not analyzed

Well	Sampling date	Noble gas (ppm)						σ					
		⁴ He	²⁰ Ne	³⁶ Ar	⁸⁴ Kr	⁴⁰ Ar/ ³⁶ Ar	³ He/ ⁴ He	⁴ He	²⁰ Ne	³⁶ Ar	⁸⁴ Kr	⁴⁰ Ar/ ³⁶ Ar	³ He/ ⁴ He
Atm	-	5.24	16.45	31.57	0.65	295.50	0.00						
AEW	-	0.05	0.17	1.07	6.23	0.24	2.01						
Scott ¹	june-08	11	13.88	17.24	0.33	-	-	-	-	-	-	-	-
Heins ¹	june-08	374	10.73	18.19	0.33	-	-	-	-	-	-	-	-
Heins-1	march-12	540	12.86	26.89	0.53	-	2.21E-07	60.9	1.39	0.98	0.03	-	5.31E-08
Heins-2	march-12	598	14.12	27.95	0.56	-	2.25E-07	67.5	1.52	1.03	0.03	-	2.76E-08
Heins-3	08/28/2014	339	14.68	24.90	1.32	297.12	1.63E-07	8.1	1.32	0.41	0.02	0.85	2.40E-08

Table 5 – Scott#1 and Heins#1 wells: noble gas compositions and isotopic ratios.
(1) Data listed from Vacquand, 2011. (-) not available



— Air	—●— Mar 2012 - D1	—●— Mar 2012 - D2
—●— Nov 2013 - D1 - 10:25 a.m.	—●— Nov 2013 - D1 - 10:30 a.m.	—●— Nov 2013 - D1 - 11:00 a.m.
—●— Nov 2013 - D1 - 05:00 p.m.	—●— Nov 2013 - D2 - 9:45 a.m.	—●— May 2014 - D1
—●— May 2012 - D2	—●— May 2014 - D3 - 11:30 a.m.	—●— May 2014 - D3 - 01:00 p.m.
—●— May 2014 - D3 - 01:45 p.m.	—●— Aug 2014 - D1 - 12:20 p.m.	—●— Aug 2014 - D1 - 03:20 p.m.
—●— Aug 2014 - D1 - 04:45 p.m.	—●— Aug 2014 - D2 - 02:00 p.m.	—●— Aug 2014 - D2 - 05:40 p.m.
—●— Aug 2014 - D3 - 11:45 a.m.	—●— Aug 2014 - D3 - 02:30 p.m.	—●— Aug 2014 - D5 - 11:45 a.m.

Fig. 3- Relative abundance of air-normalized isotope composition of noble gas (^4He , ^{20}Ne , ^{36}Ar , ^{84}Kr , $^{40}\text{Ar}/^{36}\text{Ar}$ and $^3\text{He}/^4\text{He}$) for (a) Heins#1 well (b) Sue Duroche#2 well. Sample values are normalized to the air abundances. Normalization value used as a reference is 295.5 for the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio [Nier, 1950]. 1.39×10^{-6} for the $^3\text{He}/^4\text{He}$ ratio [Ozima & Podosek, 2002].

4.4. Noble gases

Compositions of noble gases from the Sue Duroche#2 well are shown in [table 4](#); for Scott#1 and Heins#1 wells, result from this work and *Vacquand* [2011] are shown in [table 5](#). [Fig.3a & b](#) shows the air-normalized noble gas abundances for ^4He , ^{20}Ne , ^{36}Ar and ^{84}Kr as well as the isotopic ratios for $^{40}\text{Ar}/^{36}\text{Ar}$ and $^3\text{He}/^4\text{He}$. The patterns indicate a large ^4He excess compared to atmosphere-derived noble gases (ADNG: ^{20}Ne , ^{36}Ar , and ^{84}Kr). The ADNG abundances are all depleted compared to air values. ADNG Air-normalized patterns for most samples of the three wells show a degree of depletion correlated with the elemental mass of the noble gases ($\text{Ne} > \text{Ar} > \text{Kr}$), which is consistent with a solubility fractionation of air. The atmospheric component found in the water is therefore related to an air saturated water (ASW) component and not the result of air-contamination of the sample.

The Sue Duroche#2 sample which contains 20.3% O_2 presents a noble gas pattern similar to the air ([Fig.3-b](#)). This observation confirms the singular air contamination for this sample.

The Sue Duroche#2 noble gases have weakly depleted ADNG (^{36}Ar from 6.3 to 11.9 ppm) with variable ^4He contents (8199-31870 ppm). The $^{40}\text{Ar}/^{36}\text{Ar}$ mean ratio of 431 is superior to the air value of 295.5 [*Nier*, 1950]. The mean isotopic composition of He is 1.5×10^{-7} with values ranging from 1.3×10^{-7} to 2.1×10^{-7} .

The Heins#1 well presents ADNG compositions close to the air values (^{36}Ar from 18.2 to 27.95 ppm) ([Fig.3-a](#)). The $^{40}\text{Ar}/^{36}\text{Ar}$ mean ratio of 297.2 is close to the air value of 295.5 [*Nier*, 1950]. Despite this atmospheric component, ^4He is found in high proportion (374 to 598 ppm) giving a mean isotopic composition of He of 2.0×10^{-7} , different from the air value [1.4×10^{-6} , *Ozima and Podosek*, 2002].

The Scott#1 well noble gas shows ADNG slightly depleted compared to the air (^{36}Ar = 17.2 ppm) ([table 5](#)). The ^4He contents of 11 ppm is lower than the one of the Sue Duroche#2 and Heins#1 wells but still superior to the atmospheric value (5.2 ppm).

5. Discussion

In the present study, four types of gases can be distinguished ([Fig.1-c](#)): (1) dry gas observed at the Sue Duroche#2 well before the well was plugged back from the basement; (2) gas exsolved from the water in the Mississippian aquifer at the sedimentary section of the Sue Duroche#2 well; (3) gas exsolved from water in the tubing of the Sue Duroche#2 well (which shows punctual H_2 recharges), and (4) free gas collected at Scott#1 and Heins#1 wellheads.

5.1. Atmospheric component in dissolved gas

The ADNG abundances in the gas phase reflect the reequilibration of the air saturated water (ASW) component in the water due to the degassing of H_2 , N_2 , CH_4 , He during the rise of the water in the well. At sampling conditions (1 bar, ambient T), the volume gas/water ratio of Sue Duroche#2 well is low ($\sim 4.3 \times 10^{-3}$) and is expected to be much lower in the aquifer condition due to higher artesian pressure. At 1 bar and 20°C , ASW contains $3.1 \times 10^{-5} \text{ mol/m}^3$ of ^{36}Ar as predicted by the solubility of argon in freshwater [*Crovetto et al.*, 1982] and based on argon atmospheric content (9340 ppm). Considering that all ^{36}Ar in the gas phase results from exsolution of the water phase, the normalizing of major gas contents to ^{36}Ar makes a direct reference to the volume of degassed water. All major gas data are represented as normalized to ^{36}Ar in order to discuss the composition and evolution of the water of the Sue Duroche#2 well ([Fig.4 & 5](#)).

5.2. Origin of gas

5.2.1. Helium

The Sue Duroche#2 $^3\text{He}/^4\text{He}$ ratios, as well as those of Heins#1 wells, are one order of magnitude higher than typical crustal rocks (1.3×10^{-8}) [*Gerling et al.*, 1971] ([Fig.4-a](#)). This isotopic ratio of helium can result from several contributions. The large excess of He ($^4\text{He}/^{20}\text{Ne} > 2676$) compared to the atmospheric, or ASW composition ($^4\text{He}/^{20}\text{Ne} < 3$) rules out the influence of excess air and tritiogenic ^3He , which may only contribute to a negligible extent to the He budget of the Sue Duroche#2 samples [*Solomon, et al.*, 1995; *Castro et al.*, 2000]. Mantle volatile

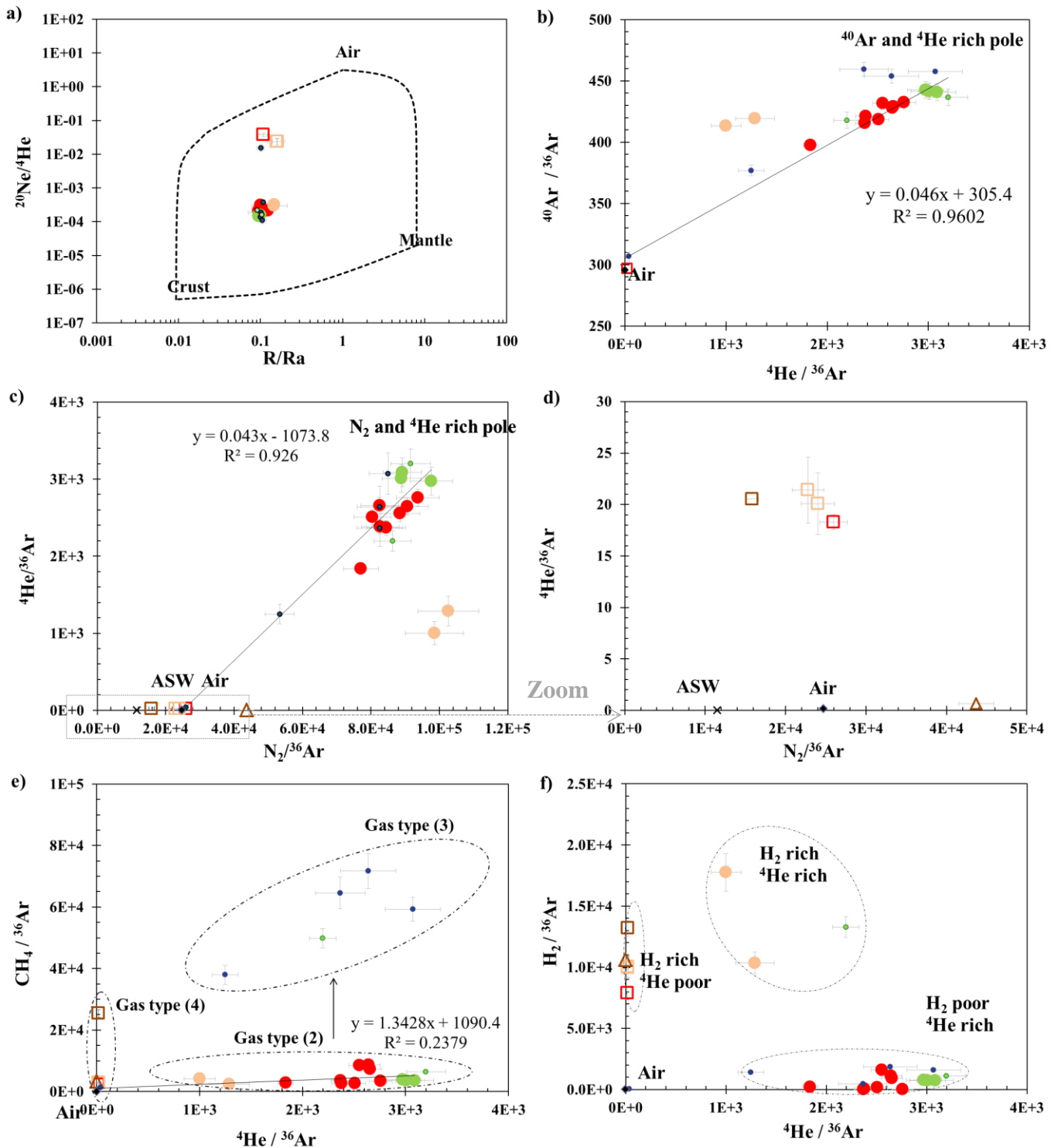


Fig. 4- a – $^{20}\text{Ne}/^4\text{He}$ vs R/Ra ($^3\text{He}/^4\text{He}$ air normalized) and three end member mixing lines: radiogenic, mantle, and Air. Mantelic R/Ra calculated from R mentioned by O’Nions & Oxburg [1983], crust R/Ra from Gerling et al. [1971], and air R/Ra from Ozima & Podosek [2002].

Fig 4- b, c, d, e, f – Variations of [^4He], [^{40}Ar], [CH_4], [N_2], normalized to an atmospheric noble gas content (^{36}Ar). Sue Duroche#2 well: circles (large one for gas type 2, small one for gas type 3); Heins#1 well: squares and Scott#1 well: triangles. ASW = Air Saturated Water.

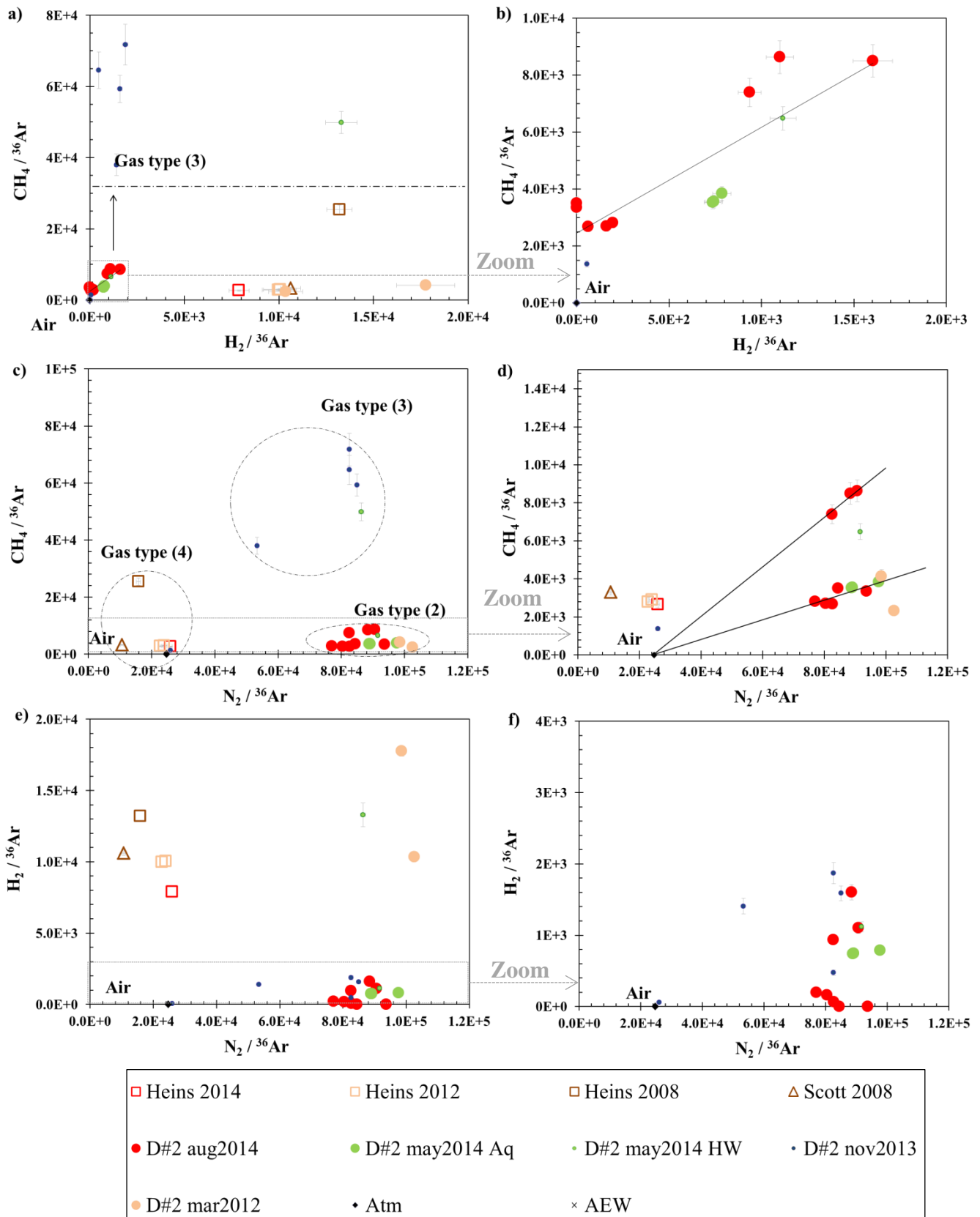


Fig. 5- a, b, c, d, e & f – Variations of $[\text{CH}_4]$, $[\text{N}_2]$, $[\text{H}_2]$, normalized to an atmospheric noble gas content $[\text{Ar}]$. Sue Duroche#2 well: circles (large one for gas type 2, small one for gas type 3); Heins#1 well: squares and Scott#1 well: triangles.

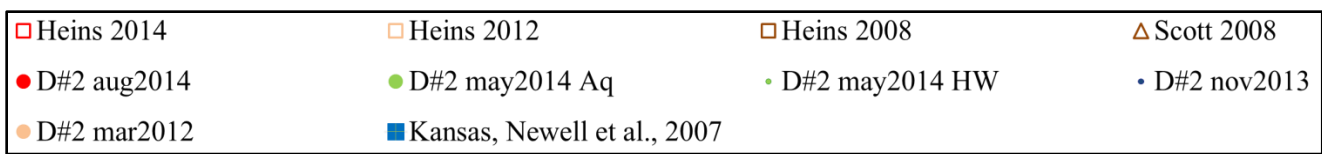
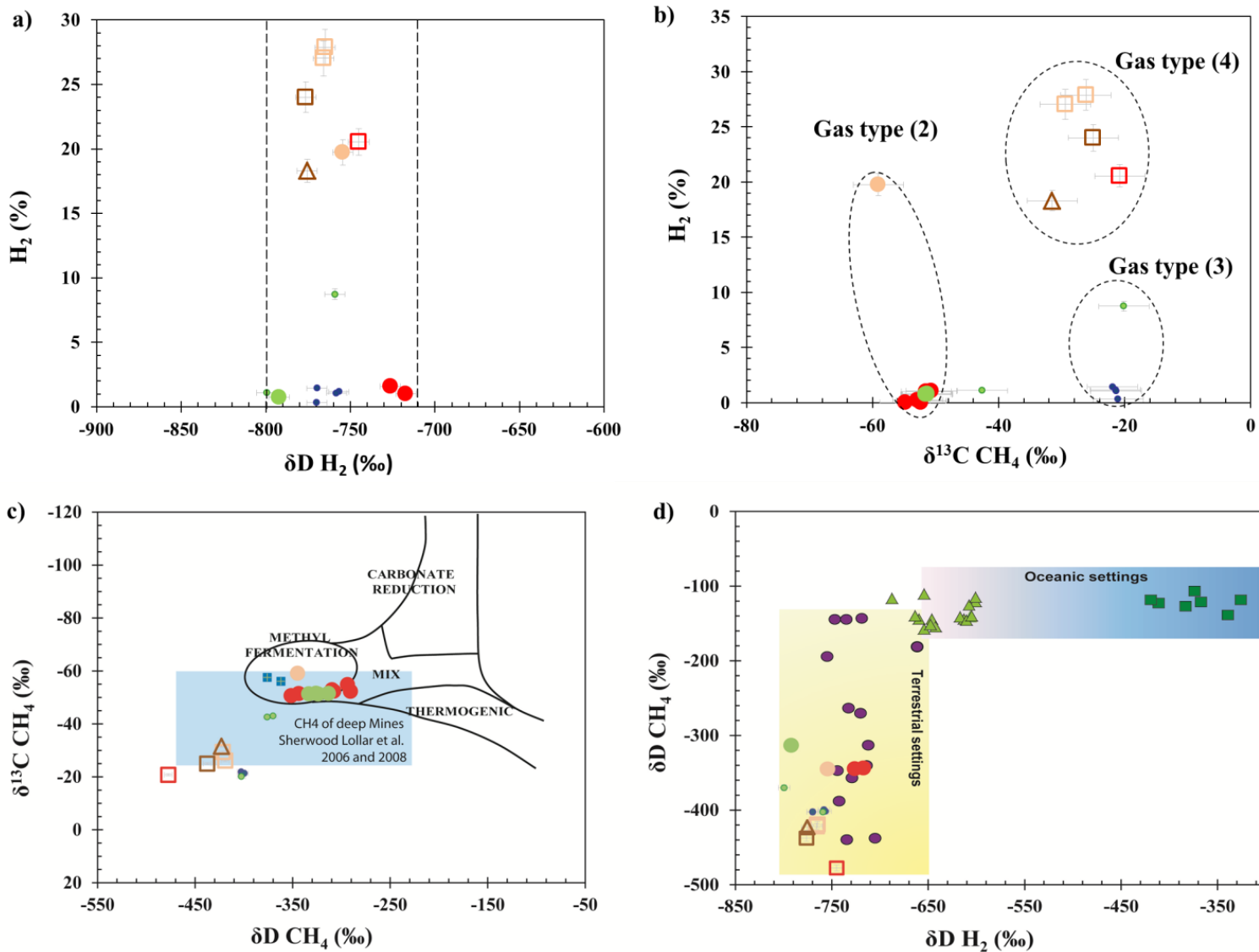


Fig. 6-(a): (top, left) $\delta D H_2$ versus $[H_2]$. (b): (top, right) $\delta D CH_4$ versus $[H_2]$. c: (Bottom, left) $\delta^{13}C CH_4$ versus $\delta D CH_4$. d: (Bottom, right) $\delta D H_2$ versus $\delta D CH_4$.

a, b, c, d: Sue Duroche#2 well: circles (large one for gas type 2, small one for gas type 3); Heins#1 well: squares and Scott#1 well: triangles. c: Little blue squares: the deep well Wilson1# [Newell et al. 2007]. Blue/Grey area: domain of values found in deep Precambrian mines [Sherwood Lollar et al., 2008]. d: Green squares: oceanic settings characterized by high temperature [Proskurowski et al., 2006], Green triangles: oceanic settings characterized by low temperature [Proskurowski et al., 2006]; purple circles: ophiolitic setting in Liguria (Italia), Philippines, Turkey and Oman [Etiope et al., 2011; Vacquand, 2011].

are enriched in ^3He , with $^3\text{He}/^4\text{He}$ ranging from 8.42×10^{-6} to 1.40×10^{-5} [O Nions & Oxburg, 1983]. The last episode known of mantle fluid contribution (kimberlites) in the geological history of Kansas is Cretaceous in age. The mantle volatiles associated with this past magmatic event have probably been degassed to the atmosphere and are likely no longer stored in the upper crust. However, the Humboldt fault located few kilometers East of the wells cuts lower Paleozoic strata as well as Precambrian basement rocks and could be of lithospheric scale. This main structure could potentially be associated with the trapping of mantle helium. The contribution of mantle volatiles to the Central Midwest Regional Aquifer System may also be inherited from the recharge area in the Eastern Rocky Mountains in Colorado and New-Mexico. Volcanic activity as young as Neogene has been reported [Fitton *et al.*, 1991] and numerous CO_2 fields with a magmatic origin are known, such as the Sheep Mountain and Bravo Dome [Gilfillan *et al.*, 2008]. However, the low abundances in CO_2 , and the extremely low $\text{CO}_2/{}^3\text{He}$ ratios of our samples ($\text{CO}_2/{}^3\text{He} < 2 \times 10^5$) argue against a mantle contribution (MORB $\text{CO}_2/{}^3\text{He}$ ratio ranging 1-10 $\times 10^9$, Marty and Jambon, 1987) for the abundant ^3He .

Another possibility explaining such $^3\text{He}/^4\text{He}$ ratios could reside in crustal processes through ^3He production or specific release mechanisms. Martel *et al.* [1990] have shown that preferential release of ^3He from minerals of the Carnmellis Granite is responsible for disequilibrium between circulating fluids and the rock, with a relative enrichment of ^3He in the fluid by a factor of at least 10, the same order of magnitude that is observed between typical crustal and Sue Duroche#2 $^3\text{He}/^4\text{He}$ ratios.

A last potential contribution of ^3He could reside in specific conditions of radiogenic He production. Nucleogenic ^3He is generated by the thermal neutron-induced fission of lithium (${}^6\text{Li}(n,\alpha) {}^3\text{H}(\beta) {}^3\text{He}$) [Martel *et al.*, 1990; Solomon *et al.*, 1992]. The production rate of ^3He by this mechanism, and so the $^3\text{He}/^4\text{He}$ ratio that results from this production, depends upon both the abundance of Li and the neutron fluency. The Sue Duroche#2 water is rich in Li (286 ppm, unpublished data), as a likely consequence of meteoric water interaction with Permian evaporitic deposits known from the Hutchinson Salt Member in the Wellington formation (Meriam, 1963; Gogel, 1981). If we consider a porosity of 0.35 for the aquifer formation (such a value is an average for an aquifer), the Li abundance in water would result in a bulk Li abundance in the rock of ~100 ppm. Calculating the ratio of the ^3He over the ^4He radiogenic production rate [Castro *et al.*, 2000] using a 100 ppm Li content results in a $^3\text{He}/^4\text{He}$ ratio of 2.2×10^{-7} . We therefore favor the explanation of high $^3\text{He}/^4\text{He}$ ratios in the Sue Duroche#2 Mississippian aquifer as originating in nucleogenic production of He in specific Li-rich conditions. We will thus consider all He in Kansas wells as inherited from radiogenic production.

Even if the noble gas compositions could not be measured on gas type (1), those of gas types (2), (3) and (4) plot on a same trend indicating that the gases are sourced by a similar radiogenic component (Fig.4-a).

Gas samples from the aquifer at the Sue Duroche#2 well – gas type (2) – are characterized by high proportions of radiogenic isotopes of the noble gases, e.g. ^4He and ^{40}Ar (table 4). ^4He and ^{40}Ar proportions (Fig.4-b) show that almost all the Sue Duroche#2 samples (except D#2 mar2012) are spread along a mixing line between an atmospheric end-member and a radiogenic end-member.

5.2.2. Nitrogen

High N_2 proportions are found in the different types of gas (Fig. 2-a, b & c). In the aquifer at the Sue Duroche#2 well – gas type (2) –, N_2 is correlated with ^4He and ^{40}Ar (Fig.4-b & c): all Sue Duroche#2 samples distribute on a mixing line between an N_2 and ^4He -rich end-member and an atmospheric end-member. N_2 and He are probably associated with the same source. $\delta^{15}\text{N}$ values are around +2.5 ‰, which is consistent with a crustal origin of N_2 (release of ammonium from metasedimentary rocks) in the aquifer [Bebout *et al.*, 1992; Boyd & Philippot, 1998; Mingram and Bräuer, 2001]. This positive isotopic signature of N_2 is probably not simply due to a fractionation of N_2 isotopes by degassing effect during the sampling because such a fractionation process would favor the lighter isotopes and would thus generate a $\delta^{15}\text{N}$ more negative than the atmosphere. N_2 with $\delta^{15}\text{N} +2.5$ ‰ may result from the mixing between atmospheric N_2 (issued from ASW= 0‰) and another source such as metamorphic N_2 [Mingram and Bräuer, 2001; Svensen *et al.*, 2008]. The N_2 isotopic composition of Kansas basements rocks [Guelard *et al.*, In Prep], with $\delta^{15}\text{N}_{\text{vs Air}}$ ranging between +5 and +10‰, is consistent with this hypothesis. A comparison can be made with the crustal gas present in the Hugoton-Panhandle giant gas field [Ballentine & Sherwood Lollar, 2002] and with the gas issued from KTB-pilot hole fluid production test [Lippmann *et al.*, 2005], which are both rich in He and N_2 with almost identical isotopic signatures for both elements ($^3\text{He}/^4\text{He}$ and $\delta^{15}\text{N}$) as for the Sue Duroche#2 gas. The link between N_2 and He is not visible in the Scott#1 and Heins#1 gas samples (Fig.4-d). Even if Heins#1 shows higher $^4\text{He}/^{36}\text{Ar}$ ratios, no N_2 enrichment compared to atmosphere is observed. Due to the atmospheric signature of noble gases vs N_2 , the Scott#1 and Heins#1 N_2 budget is probably largely due to air dilution (Fig.4-a), suggesting mixing and attendant contamination with air in free gas at the wellhead. As explained previously, gas of type (4) is

characterized by atmospheric contamination, and the atmospheric signature overrides the original one inherited from the water in contact with this free gas (Fig.1-c).

5.2.3. Di-hydrogen

H₂ and ⁴He proportions normalized to ³⁶Ar (Fig.4-f) are not correlated. It seems therefore unlikely that the H₂ is associated with a radiogenic noble gas end-member. A similar conclusion can be drawn from comparing N₂ and H₂ normalized to ³⁶Ar (Fig.5-e & f), indicating that N₂ and H₂ do not originate from a common source. δD values for H₂ are homogenous despite the differences in H₂ proportions and the gas type (Fig.6-a). It is worth noting here that the isotopic composition of hydrogen for the Heins#1 and Scott#1 wells are among the lightest reported in the literature (Fig.6-d). We suggest that strong variations of H₂ content in the Sue Duroche#2 well gas is closely linked to the completion story of the well. This completion story, described below, suggests two different sources for H₂: a deep one, from the crystalline Precambrian basement –gas type (1) and (2)– and a surficial one, H₂ being produced in the tubing of the Sue Duroche#2 well –type (3) and (4).

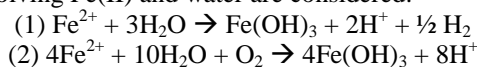
5.2.3.1. Deep H₂

Gases of type (1) and (2) likely originate from fractured Precambrian basement rocks [like those found in Precambrian fractures by *Sherwood Lollar et al.*, 2007]. Such gases are H₂-rich and He-rich. At first sight, this is not in agreement with the H₂ content of type (2) gases (Fig.4-f). However, the low H₂ contents of gas type (2) can result from a depletion/consumption of this very reactive gas in the Mississippian aquifer. In counterpart to this depletion, induces higher relative contents of the non-reactive gases: N₂ and He. Consequently, H₂ in type (2) gas would be a combination of residual H₂ from the basement and newly produced H₂ in the tubing. We consider that the especially low isotopic compositions of H₂ primarily indicate a low temperature for the formation of H₂ whatever are the process and the sources involved.

Among the hypotheses proposed in the literature, radiolysis of water and reduction of water coupled to Fe(II) oxidation are those favoured by *Lin et al.* [2005] and *Sherwood Lollar et al.* [2014] to explain H₂ production in crystalline Precambrian rocks. The presence in the basement of Fe-bearing rocks (Gabbros referred as Basic rocks (MRS) in Fig.1-b) together with the magnetic anomaly observed in the area rather suggest that Fe(II) oxidation produces H₂ in the basement. Regional hydrology is consistent with this hypothesis: water flows over long distances in this region, with a recharge in the Rockies and a circulation towards the east, over and through Fe-rich rocks in the MRS (Fig.1-b) [*Jorgensen et al.*, 1993; *Musgrove & Banner*, 1993; *Macfarlane*, 2000]. According to ³He/⁴He ratio, enriched in ³He when compared to the classic crustal value (Fig.4-a), one can argue that a mantle input can contribute significantly to Kansas H₂-bearing gases accumulations (R/Ra between 9.2 x 10⁻² and 1.5 x 10⁻¹). In this prospect, a mantle origin for H₂ can not be definitely excluded, although other processes can produce ³He in the crust such as ⁶Li induced fission, as described beyond. Biogenesis of H₂ and CH₄ through fermentation cannot be definitely ruled out for the origin of type gas (1), even though organic matter in crystalline basement rocks is not abundant [*Newell et al.*, 2007].

5.2.3.2. Surficial H₂

Surficial H₂ can be attributed to processes reported in literature such as (1) biological fermentation of organic matter, that could be assisted with Fe²⁺ [*Ma et al.*, 2016] or (2) the corrosion of steel tubing (Fe(0)) at low temperature by salted water with low sulfate contents [*Angino et al.*, 1984; *Goebel et al.*, 1984]. Herein, we propose another mechanism for H₂ formation: water splitting at low temperature catalysed by dissolved compounds, for instance, organic carbon and Fe(II). The redox conditions (ORP, Oxidation-Reduction Potential Table 1) observed while sampling the water of the Sue Duroche#2 well present strong variations. This supports the hypothesis that surficial redox reactions are taking place in the tubing. Furthermore, the presence of high Fe(II) contents in water, higher H₂ contents at the first stage of the sampling campaign, together with the observation of Fe(III) precipitation soon after contact of the water with the atmosphere, lead us to infer that Fe(II) is involved in H₂ formation along the tubing. The following reactions involving Fe(II) and water are considered:



These reactions are in competition and depend on the availability of O₂ in the considered environment. Reaction (2) takes place in presence of O₂ and does not lead to H₂ formation. A possible interpretation would be to propose the following sequence: (a) during the first stage of the sampling, water is rapidly in contact with atmosphere, (b) oxygen from air induces formation of Fe(III), (b) the association of Fe(III) with organic matter in the water could

create a dissolved Fe(III)-OM complex available to catalyse reaction (1) once all O₂ is consumed [Weber et al., 2006; Georgi et al., 2007; Niu et al., 2011].

5.2.4. Methane

The crossplot of CH₄ and ⁴He proportions normalized to ³⁶Ar (Fig.4-e), shows a consistent enrichment in CH₄ of the Sue Duroche#2 tubing samples – gas type (3). Comparison of CH₄ and N₂ normalized to ³⁶Ar (Fig.5-c & d) again underlines the CH₄ enrichment in the Sue Duroche#2 tubing samples. CH₄ gas samples of Scott#1 and Heins#1 - gas types (4) - have the same isotopic composition as the gas from the tubing of the Sue Duroche#2 well - gas types (3) - suggesting a similar process of origination (Figs.5-c & 6-c). Their CH₄ has C and H isotopic compositions strongly enriched in ¹³C and depleted in ²H (Fig.6-c). They also show the highest H₂ proportions. To explain these isotopic characteristics, we propose that the CH₄ genetic processes in the tubing water and in the headspace gas is different from the process that accounts for the CH₄ originating in the Mississippian aquifer water at the Sue Duroche#2 well. These atypical isotopic values of CH₄ are similar to gas samples from Precambrian basement reported by *Sherwood Lollar et al.* [2006]. *Sherwood Lollar et al.* [2006] suggest that the association of high concentrations of H₂ with ¹³C-enriched and ²H-depleted CH₄ may indicate that CH₄ is produced by biological H₂ autotrophy in the deep subsurface. Although their existence is not yet unequivocal, a growing body of evidences supports the existence of litho-autotrophic H₂ microbial systems (Slimes) in the subsurface [*Chapelle et al.*, 2002; *Nealson et al.*, 2005]. Abiotic catalyzed processes might also exist, such as the Sabatier reaction, and could explain methane formation from H₂ and CO₂ (4H₂ + CO₂ → CH₄ + 2 H₂O). This Sabatier reaction has not been observed at temperatures of 20-25°C (i.e., the ambient water temperature of the produced water at the Sue Duroche#2 well). We thus suppose that a specific catalyst or microorganisms (methanogens) may play a role in CH₄ production in water close to the tubing of Kansas wells.

5.2.5. CO₂

The CO₂ proportion observed in this gas (table 2), is generally <1 mole %. This CO₂ may have originated from microbial fermentation or respiration activity, but it also could result from water interaction with carbonates.

5.3. Completion reconstitution story of D#2 and evolution of gas composition through time

5.3.1. Crustal fluids and access to crystalline basement

The Sue Duroche#2 well encountered Precambrian granitic basement rocks from 317 m to 424 m depth. Just after drilling, this well flowed dry gas enriched in H₂ (91.8%) – gas type (1). This H₂ cannot be assigned to corrosion of tubing because the well was not cased yet, nor to drilling processes because H₂ resulting from purely artificial drill-bit processes typically yield low proportions of H₂ [*Erzinger et al.*, 2006]. The H₂ produced soon after this well was drilled likely originated within the basement. After the placement of the plug at a depth of 311 m, between the sedimentary aquifer and the underlying basement, H₂ proportion decreased drastically in the gas issued from the aquifer – gas type (2) (Fig.2-a). The radiogenic signature of the gas in the sedimentary aquifer strongly suggests a connection for fluids between the Mississippian aquifer and the Precambrian basement. Crustal gases, such as ⁴He and N₂, are relatively constant over time in the Sue Duroche#2 well, despite the decrease of H₂ with time after the plug-back of the well (Fig.2-a). Gas from the Sue Duroche#2 well does not show any consistent correlation between H₂ and crustal signatures, (e.g., ⁴He or N₂) (Figs.4-f & 5-e & f). We therefore suggest that during drilling, there was mixing between H₂, ⁴He, and N₂ coming from the basement and the sedimentary aquifer. Since the isolation from the basement by a plug, the decrease of H₂ simply via well production would imply a similar decrease of He and N₂, but this was not observed. Instead, the He and N₂ proportions remain stable over time. Since the plugging, we suppose that a weak flux of crustal gas mostly composed by N₂/He/H₂ reached the sedimentary aquifer by diffusion. Due to their low reactivity He and N₂ then accumulated in the aquifer without being consumed like H₂. The lack of correlation between H₂ and other crustal gas coming from basement (e.g. N₂, ⁴He, ⁴⁰Ar) is then likely related to the high reactivity of H₂ compared with N₂ and ⁴He. H₂/⁴He ratios are thus impacted: relative proportions of N₂ and He concomitantly rise as H₂ is consumed. H₂ may have been consumed by microorganisms or may have reduced Fe(III)-bearing minerals in sedimentary rocks. The presence of high proportion in Fe(II) in the Sue Duroche#2 water

could come from reduction of iron oxide-rich rocks in presence of H_2 . In this intracratonic context and contrary to ophiolitic context, the Sue Duroche#2 water presents a crustal-type pH (6.9 to 7.7) which allows Fe(II) to be dissolved and then mobilized within the water of sedimentary aquifer (Fig.7). At higher pH, which is characteristic of ophiolitic settings, Fe(II) oxidation (associated to reduction of water) induces magnetite precipitation and then iron immobility (Fig.7).

Another hypothesis could explain the high H_2 proportions just after the drilling, the drop of H_2 and the appearance of CH_4 after setting of the deep plug. A correlation between CH_4 and H_2 is observed in the aquifer gas from the Sue Duroche#2 well in that the higher the H_2 proportion, the greater the enrichment in CH_4 (Fig.5-a & b). This observation, together with the isotopic composition of methane, could be consistent with a simultaneous biological production of H_2 and CH_4 . In an equilibrated ecosystem, acetoclastic bacteria are known to live with H_2 -producing microorganisms [Nealson *et al.*, 2005], but produced H_2 is not in any abundance because it is directly consumed. The Mississippian sedimentary aquifer at the Sue Duroche#2 well is a karstic reservoir underlying younger Pennsylvanian and Permian strata containing lignite. One possibility is the creation of a new ecosystem after the drilling where available organic substratum is consumed by microorganisms colonizing the environment like in landfills. Indeed, in landfills, H_2 producers are known to develop before CH_4 producers inducing H_2 proportions observable on day-scale times [Tchobanoglous *et al.*, 1993]. However, the observation of methane in measurable quantities in the Sue Duroche#2 well occurred late, in November 2013, more than 4 years after the drilling. This leads us to reject this hypothesis of biogenesis.

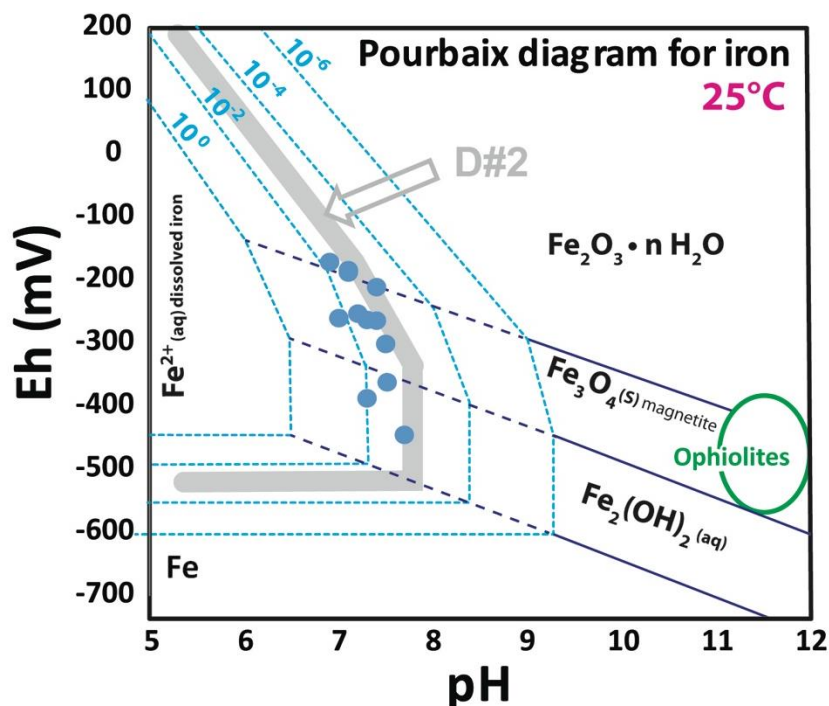


Fig. 7 – Eh-pH Pourbaix diagram at atmospheric pressure and 25°C. Blue line represent domain limit of Fe²⁺ for different [Fe²⁺]. Grey line represent Fe²⁺ domain limit for Sue Duroche#2 [Fe²⁺]

5.3.2. Recharge events

We noticed in tubing gas from the Sue Duroche#2 well that H_2 recharge events are observable between each sampling field trip – gas type (3) – despite the decrease of H_2 proportion in the aquifer – gas type (2) (Fig.2-a). This observation could be the result of either 1) a reaction taking place in the tubing of the well that generates H_2 and/or 2) an accumulation in the wellhead of H_2 still present in the aquifer (H_2 has both a low mass and a low solubility). This latter hypothesis would imply that He (present in the aquifer at the percent level) would also accumulate with H_2 in the wellhead. This is not the case. We therefore suggest that the H_2 found in the tubing - gas type (3) - is not a H_2 coming from aquifer like it is in gas types (1) and (2). We further note that in type (3) gas, H_2 is associated with

high amounts of Fe(II) and dissolved organic matter. These considerations lead us to propose that H₂ and/or CH₄ in gas type (3) form in close connection with the wellhead or tubing

The Scott#1 and Heins#1 wells show the highest H₂ proportions – gas type (4) – but they are associated with the weakest crustal gas signatures (Fig.4-a & f). The hydrologic settings of Scott#1, Heins#1 and Sue Duroche#2 wells are very different (Fig.1-c). Scott#1 and Heins#1 wells have headspace gas in equilibrium with static water. Accumulation of gas in the headspace of the Heins#1 and Scott#1 wells occurs gradually over time. Conversely, the Sue Duroche system is dynamic: this well produces water with dissolved gases thanks to artesian pressure. Water pressure at the Sue Duroche#2 wellhead limits atmospheric contamination whereas the relatively static conditions and low pressure of the headspace gas at the Scott#1 and Heins#1 wells could encourage it to be gradually and readily diluted by atmosphere (Fig.1-c). Moreover, the accumulation of newly formed H₂ related to wellhead or tubing in gas headspace of the wells could explain the highest proportions of H₂ measured in Heins#1 and Scott#1 static headspace gas – gas type (4).

6. Conclusions

This study has shown that wells in Northeastern Kansas have yielded H₂-rich gas for several years. Also, a high proportion of H₂ existed in dry gas soon after the drilling of the Sue Duroche#2 well. This well has been subject to punctual small gas recharges in the following years. Configuration of the wells also has to be taken in account: the Scott#1 and Heins#1 wells are characterized by static water lying at few meter depth below their well heads. This permits gas accumulation in the headspace of these wells, whereas the Sue Duroche#2 well is an artesian well producing water that contains dissolved gases.

The Sue Duroche#2 well initially produced high-H₂ gas when the wellbore was open to fractured Precambrian basement soon after drilling. The gas was thus likely sourced in the basement. The high contribution of crustal gas (e.g., ⁴He, ⁴⁰Ar and N₂ with δ¹⁵N of +2.5‰) in the sedimentary aquifer above the basement in the Sue Duroche#2 well also indicates that these gases originate from the basement. The presence of abundant iron-rich rocks in the basement leads us to propose that H₂ is generated by coupled Fe(II) oxidation and reduction of H₂O. Following the setting of a plug in the Sue Duroche#2 well that isolated the basement from the overlying sedimentary aquifer, a drastic decrease of H₂ was observed that we interpret as due to the isolation of the aquifer from the basement. Then, much of the H₂ present in the sedimentary aquifer was consumed by redox reactions. Gas migration of H₂, He and N₂ from the basement to the sedimentary aquifer probably still occurred after the plugging (as shown by the persistent presence of He and N₂), at the same time that H₂ was consumed in the sedimentary aquifer. Reduction of Fe(III) by H₂ could thus have contributed to elevated Fe(II) concentrations in this aquifer. In parallel, CH₄ and surficial H₂ present in tubing water of the well might be issued from the combination of an evolution of Eh-pH conditions in the tubing, which could favor H₂ production (Fig.5) by means of biological activity (Fe-rich anoxic waters with consistent DOC content). We therefore suggest that recharges of H₂ observed between each field sampling of the Sue Duroche#2 well, are not strongly linked to H₂ coming from the basement. This neo-formed H₂ would rather be issued from reactions of iron(II) oxidation or from organic matter fermentative production of H₂ close to the tubing/water interface. Methane proportion present in this gas might result from autotrophic methanogen H₂-consumers activity.

We suggest that the Scott#1 and Heins#1 wells in their headspaces have both the two “types” H₂ previously discussed: the residual one coming from the basement and the other type that forms in the tubing. Methane found in the tubing of the wells probably result from microorganisms consumption of H₂.

In summary, our results suggest that both deep and shallow origins of H₂ are probable in Kansas. If H₂ presence in the Kansas Precambrian basement is certain, its origin and quantification still deserves new studies from more wells penetrating these formations. However, we observed that when migrating into aquifers of the sedimentary pile, H₂ is mostly consumed even if in some cases, such as in Scott#1 and Heins#1 wells, small parts of this primary H₂ might be preserved by transfer to a free gas phase. A secondary process of H₂ generation has to be involved at Scott#1 and Heins#1, which is likely the same as the one operating in the water of well tubing at the Sue Duroche#2 well. The connections between a source of H₂ in the basement, high Fe(II) concentrations in waters from the sedimentary section, and secondary production of H₂ in water in the tubing need to be further investigated.

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