

RESEARCH ARTICLE

Natural H₂ in Kansas: Deep or shallow origin?

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Key Points:

- Reappraisal of a persistent regional H₂ production in intracontinental settings, Kansas, USA
- H₂ occurrences in intracratonic context: a crustal origin and a surficial origin
- Geochemical properties of reduced gas combination in intracontinental settings

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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 free gas phase with more than 80 mole % of H₂, followed by 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) deep crustal H₂: water reduction associated to iron oxidation in the Precambrian basement; (2) reactions occurring in the tubing, primarily attributed to high contents of reduced iron and/or dissolved organic carbon (DOC = 4.1 mg L⁻¹) in the water. The low δD values averaging -760‰ are attributed to a low temperature process, possibly a re-equilibration with water. 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 midocean ridges [Welhan and Craig, 1979; Charlou et al., 2002; Proskurowski et al., 2008; Keir, 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 and Stevenson, 1988; Holm, 1992; Martin et al., 2008].

Studies of surface and subsurface fluid flows in fracture systems in Precambrian continental crust also provide evidences for natural H₂ production in the continental lithosphere [Lin et al., 2005a; Sherwood Lollar et al., 2007, 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 surface globally [Goodwin, 1996]. This environment has a distinctly lower geothermal gradient than midoceanic 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 [Neal and Stanger, 1983; Etiope et al., 2011; Deville and Prinzhofer, 2016]. Sherwood Lollar et al. [2014] claimed that the production rates of H₂ could reach 0.36–2.27 × 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 nonfossil-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, 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.

Indeed, *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.

Since 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 trips (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 Pennsylvanian aquifer at the base of the sedimentary section. Fluids from this last well were sampled by Donald C. Clark in 2008 and 2011. Our team conducted four sampling trips: in March 2012, November 2013, May and August 2014. 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 (Figures 1a and 1b), 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-Centroid Rift System (MRS) (Figure 1b), 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 (Figure 1a). This uplift is mainly a product of early

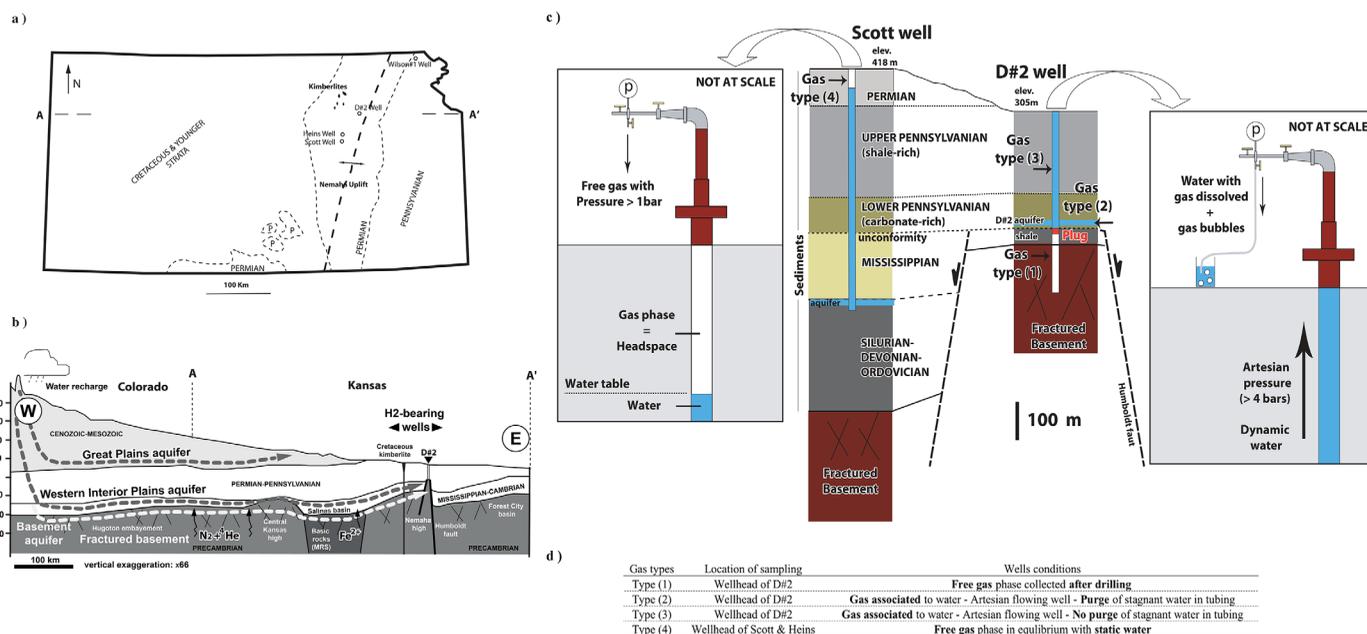


Figure 1. (a) and (b) Geological and structural schematic map of Kansas, and localization of Heins#1, Scott#1 and Sue Duroche#2 (D#2) wells (modified from *Bickford et al.* [1979] and *Coveney et al.* [1987]). (c) and (d) Schematic representation and informative table of the well conditions during sampling at Sue Duroche#2 (D#2) wellhead (water with gas dissolved) and at Scott#1 and Heins#1 wellhead (static gas phase).

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 Missourian-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 (Figures 1a and 1b). These kimberlites are lower Cretaceous in age and are the only non-Precambrian intrusive rocks known in the area. They can be strongly serpentinized and contain abundant lizardite and magnetite, which induces localized strong positive magnetic anomalies that aids in their detection [Brookins, 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 (Figure 1b). 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 Pennsylvanian, and then about 90 m of the underlying Precambrian basement (Figure 1b). The well gives access to a Pennsylvanian 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 (Figure 1c). 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 (Figures 1b and 1c). 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 well bore is filled with 605 m of water, capped with 65 m of headspace [Coveney *et al.*, 1987] (Figure 1c). 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, 1984; Angino *et al.*, 1984, 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 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 $+1.8\text{‰}$) [Coveney et al., 1987; Vacquand, 2011] and were thus nondiagnostic.

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 km²) 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, possibly underlying subsurface faults. 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]. Traces of 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 $\delta^{13}\text{C} -57\text{‰}$, $\delta D 362\text{‰}$) suggested a biogenic production. The R/Ra ratio ($^3\text{He}/^4\text{He}_{\text{sample}}/^3\text{He}/^4\text{He}_{\text{atmosphere}}$) of 0.035 indicated 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 areas 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 serpentinization 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, 2001], (2) radiogenic effect on organic matter or water [Lin et al., 2005a, 2005b], (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 and Matsuo, 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. All fluids (gas and water) were sampled at

the wellheads. The well conditions were different according to the wells and the field trips and are described hereafter. Gas types (1–4, see Figures 1c and 1d) are defined according to these well conditions at the time of sampling.

3.1.1. Gas Sampling

Heins#1 and Scott#1 wells give access to a free gas phase (referred to as gas type (4) as shown in Figures 1c and 1d) 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 well conditions apply to these different field trips: the Sue Duroche#2 well was producing before sampling in March 2012 and August 2014, while it was opened for production, exclusively for sampling purpose in November 2013 and May 2014. This affected the nature and origin of the fluids. Indeed, in the first case, the stagnant waters from the well tubing were drained off before sampling: gas referred to as type (2) was obtained. In the second case, these stagnant waters were sampled, and provided gas referred to as type (3). These well conditions and associated gas types are schematized in Figures 1c and 1d.

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 was opened and was producing at least a day before sampling. In these conditions, the stagnant waters in the well tubing have been drained off before sampling (gas type (2)).

For the three subsequent field trips (November 2013, May 2014, and August 2014), 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.

3.1.2. Water Sampling and on Site Analyses

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, contents, and speciation of iron (limits the loss of dissolved Fe(II) through oxidative precipitation) were measured by spectrophotometry on site according to methods developed by Podda and Michard [1994] and Viollier et al. [2000], respectively. Other samples were devoted to DOC (dissolved organic carbon) analysis at IPGP (Paris, France).

Table 1. Physico-Chemical Parameters of Sue Duroche#2 Water Measured at Wellhead^a

	16 Mar 2012	16 May 2014	17 May 2014	17 May 2014	18 May 2014	29 Aug 2014	29 Aug 2014	30 Aug 2014	1 Sep 2014	2 Sep 2014
Date			a.m.	p.m.	a.m.	11:00 a.m.	02:00 p.m.	1:00 PM	09:00 a.m.	11:00 p.m.
pH	7.4	8.62	7.78	7.63	7.6	6.9	7	7.4	7.4	7.1
T (°C)	21	11.8	19.4	16.6	16.6	24.3	22.7	24	19.2	22.6
Sal (g/L)	55	-	-	-	-	55.8	55.8	54.9	55.8	56.3
Cond (mS/cm)	80	68	68	67.2	58	79.8	79.8	78.7	79.8	80.4
ORP (mV)	-388					-172.8	-262.3	-266	-213	-186
Location	Aquifer	Tubing	Tub + Aq	Tub + Aq	Aquifer	Aquifer	Aquifer	Aquifer	Aquifer	Aquifer

^apH, temperature (T (°C)), salinity (Sal (g/L)), conductivity of the water at 25°C (C25 (mS/cm)), and oxidation-reduction potential (ORP (mV)).

3.2. Analytical Methods

Gas composition—gas chromatograph (GC) 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 specific external standards. These standards are "Air Liquide TM" "Saphir" quality gas mixtures, including H₂, He, N₂, CO₂, O₂, CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, and *i*-C₄H₁₀, available in the laboratory at different concentration, to encompass the specific sample compositions. Each analysis was bracketed with blanks (i.e., runs without a sample). The analyses are given with a precision of ±5%.

Gas chromatograph-combustion-isotopic ratio mass spectrometry (GC-C-IRMS) 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 internal reference gas (CO₂) was calibrated with the international gas reference standards RM8562, RM8563, and RM8564 with respective $\delta^{13}\text{C}_{\text{VPDB}}$ equal to $-3.76 \pm 0.03\text{‰}$; $-41.56 \pm 0.04\text{‰}$; $-10.45 \pm 0.03\text{‰}$ [Verkouteren and Klinedinst, 2004] (the δ notation stands for $\delta^{13}\text{C}_{\text{VPDB}} = 1000 \times (R_{\text{sample}} - R_{\text{VPDB}})/R_{\text{VPDB}}$). Repeatability and accuracy of the analysis of our internal reference allow us to obtain a relative uncertainty on the $\delta^{13}\text{C}$ value of $\pm 0.4\text{‰}$.

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 elution times for δD analysis. The instrument is calibrated by measuring an internal reference gas (H₂), calibrated itself after the international reference standard NBS30, which $\delta\text{D}_{\text{VSMOW}}$ is equal to $-65.7 \pm 0.3\text{‰}$ [Gonfiantini et al., 1995] (the δ notation stands for $\delta\text{D}_{\text{VSMOW}} = 1000 \times (R_{\text{sample}} - R_{\text{VSMOW}})/R_{\text{VSMOW}}$). Repeatability and accuracy of the analysis of our internal reference allow us to obtain a relative uncertainty on the δD value of $\pm 4\text{‰}$ for CH₄ and $\pm 6\text{‰}$ H₂ ($\pm 1\sigma$). Data are corrected from interferences of H₃⁺ ions.

Vacuum line-IRMS analyses- $\delta^{15}\text{N}$ composition: Isotopes of N₂ were analyzed at IGP (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 purification starts with a cryogenic separation at liquid nitrogen temperature. The noncondensable gases at this temperature, including N₂, H₂, O₂, CH₄, and He, are then inserted in a high vacuum line maintained down to 10⁻⁵ mbar. H₂, CH₄ are oxidized through a CuO reactor maintained at 950°C for 30 min and then cooled to 450°C. Resulting CO₂ and H₂O are cryogenically trapped at liquid-nitrogen boiling temperature. Excess oxygen is then resorbed and the NO_x potentially generated, during the previous oxidation phase are reduced into N₂ in a Cu reactor maintained at 600°C. The resulting gases (N₂ and He) are then quantified and collected using a mercury Toeppler pump, in vials for measurements by GC-IRMS. This 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 $\delta^{15}\text{N}_{\text{Air}} = 0\text{‰}$ (the δ notation stands for $\delta^{15}\text{N}_{\text{Air}} = 1000 \times (R_{\text{sample}} - R_{\text{Air}})/R_{\text{Air}}$). Repeatability and accuracy of the analysis of our internal reference allowed us to obtain a relative uncertainty on the $\delta^{15}\text{N}$ value of $\pm 0.5\text{‰}$, 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 ultrahigh vacuum preparation line. Only samples in stainless steel tubes were analyzed in order to guarantee a negligible air noble gas contamination after sampling. The ultrahigh 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 analyzed 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 an 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 ⁴⁰Ar/³⁶Ar ratio are controlled weekly by an air standard analysis. The ⁴⁰Ar/³⁶Ar 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 nonlinearity of the mass discrimination factor. The ⁴⁰Ar/³⁶Ar is calculated based on the air reference of 295.5 ± 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 ²⁰Ne/²²Ne and ²⁰Ne/²¹Ne ratios. Interference of CO₂ on mass 44 with ²²Ne is always negligible. A procedural blank for the entire line is measured every week and does not exceed 1 ± 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: ± 10%; Ne: ± 20%; Ar: ± 5%; Kr: ± 8%, and for the quantification of the ratio ⁴⁰Ar/³⁶Ar: ± 1%.

³He/⁴He 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 μA 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 ³He/⁴He 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 ³He/⁴He ratio is achieved by repeated analyses of an air standard with a known composition of ⁴He 5.24 ppm and ³He/⁴He 1.39 10^{−6} [Ozima and Podosek, 2002]. The uncertainty (2σ) on the quantification of ⁴He is of ±8%. For the ³He/⁴He ratio it is of ±4%.

Table 2. Fe Contents and Speciations (Fell and Fell) of the Water of Sue Duroche#2 Well (August 2014)^a

Date	Ech	[Fell] (μM)	[Felll] (μM)	Fe tot. (μM)	Location
31 Aug 2014	Aug 2014-D3	1150	270	1420	Aquifer
31 Aug 2014	Aug 2014-D3	1160	340	1500	Aquifer

^aThe analyses were made on the field by spectrophotometric measurements according to *Viollier et al.* [2000] method.

4. Results

4.1. Water Characteristics

Water from the Sue Duroche#2 well is weakly reduced (average $E_h = -248$ meV) and neutral to 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 characteristics of the Sue Duroche#2 well water is its high Fe concentration of 1.1 mM (Table 2). 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 ~4.1 mg L⁻¹ (Table 3) which is considered as an intermediate DOC value [*Wassenaar et al.*, 1990; *Aravena and Wassenaar*, 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 4. It includes analytical data provided by Donald Clark (CFA Oil, the operator of the well) performed on: (1) a free gas phase collected immediately after drilling in 2008 (gas type (1), see Figures 1c and 1d); (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 (gas type (4)) are compiled in Table 5. The compositions recorded are similar to Sue Duroche#2: N₂, H₂, and CH₄, are major components, and He is a minor component, although the gas type are different (Figures 1c and 1d). Note that the compositions are not normalized and not corrected from possible atmospheric contamination in both Tables 4 and 5 except for data acquired in 2008 [from *Vacquand*, 2011]. One sample is characterized by atmospheric proportions of O₂ (sample D#2-1-nov2013, 20.3 mole % O₂), which is likely due to atmospheric contamination during sampling. The CO₂ proportion is generally lower than 1 mole %. The evolution over time of N₂, H₂, CH₄, and He proportions of Sue Duroche#2 well together with Scott#1 and Heins#1 wells are shown in Figures 2a–2c.

4.2.1. Sue Duroche#2 Well

High amplitude variations in H₂, CH₄, He, and N₂ 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 4). These variations are attributed to different well conditions during the fluids sampling as mentioned in the sampling section and illustrated in Figures 1c and 1d.

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)). In November 2013, gas of type (3), exclusively, was collected

Table 3. Dissolved Organic Carbon (DOC) Contents in the Water of Sue Duroche#2 Well^a

Date	DOC (mg/L)	Location
May 2014-D2	2.0	Tub + Aq
May 2014-D2	2.0	Tub + Aq
May 2014-D2	2.9	Tub + Aq
May 2014-D2	4.2	Tub + Aq
Aug 2014-D2	5.4	Aquifer
Aug 2014-D2	5.4	Aquifer
Aug 2014-D5	6.0	Aquifer
Aug 2014-D5	4.8	Aquifer

^aThe analyses were made at IGP by Shimadzu TOC V CSH measurements.

at the Sue Duroche#2 well: the well was produced during less than 24 h, the minimum duration of production needed to purge the stagnant waters, according to the recorded flows. In May 2014, the samples were collected over several days: both gases of types (2) and (3) were collected. In March 2012 and August 2014, the well was allowed to flow before the sampling trips, stagnant water were drained off: gas type (2), exclusively, was collected. The compositions of the gases sampled in March 2012 and August 2014 are considered as representative of the aquifer whereas in November 2013 and at the beginning of

Table 4. Sue Duroche#2 Well: Gas Compositional (mole %) and Isotopic (‰) Analyses

Sample	Sampling Date	Sampling Hours	Gas Type	Mole (%)							Isotopes (‰)			
				He	H ₂	O ₂ /Ar	N ₂	CO ₂	C1	Σ C2-C5	δ D H ₂ ^a	δ D CH ₄ ^b	δ ¹³ C CH ₄ ^c	δ ¹⁵ N N ₂ ^d
				*	91.8	0.2	4.7	3.2	0.1	0.00				
				0.5	7.7	2.8	84.7	1.6	2.0	n.d.	n.a.	n.a.	-64.3	n.a.
D#2-1	16 Mar 2012	-	(2)	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	17 Mar 2012	-	(2)	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	17 Mar 2012	-	(2)	1.7	19.7	0.9	74.3	0.1	3.3	0.06	-754	-345	-59.1	n.a.
D#2-1	12 Nov 2013	10:25 a.m.	Air	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	12 Nov 2013	10:30 a.m.	(3)	1.4	1.4	3.6	54.7	0.0	38.9	0.02	-770	-403	-21.9	n.a.
D#2-3	12 Nov 2013	11:00 a.m.	(3)	1.7	1.2	0.7	51.6	0.0	44.9	0.02	-757	-402	-21.5	n.a.
D#2-4	12 Nov 2013	05:00 p.m.	(3)	1.7	0.3	0.4	54.8	0.0	42.8	0.02	-770	-402	-21.0	n.a.
D#2-5	13 Nov 2013	09:45 a.m.	(3)	2.3	1.1	0.4	56.6	0.0	39.5	0.02	-758	-399	-21.4	n.a.
D#2 Vacu7	13 Nov 2013	10:00 a.m.	(3)	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	16 May 2014	06:00 p.m.	(3)	1.4	8.7	0.4	56.7	0.0	32.7	0.02	-759	-403	-20.1	2.5
D#2-2	17 May 2014	02:30 p.m.	(2)+(3)	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	17 May 2014	02:30 p.m.	(2)+(3)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-799	-370	-43.0	n.a.
D#2-3	18 May 2014	11:30 a.m.	(2)	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	18 May 2014	11:30 a.m.	(2)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-792	-313	-51.5	n.a.
D#2-4	18 May 2014	01:00 p.m.	(2)	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	18 May 2014	01:45 p.m.	(2)	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	29 Aug 2014	00:20 p.m.	(2)	2.6	1.0	0.4	88.1	0.0	7.9	0.01	-717	-344	-51.5	n.a.
D#2-2	29 Aug 2014	03:20 p.m.	(2)	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	29 Aug 2014	04:45 p.m.	(2)	2.6	1.6	0.3	87.1	0.0	8.4	0.01	-726	-345	n.a.	n.a.
D#2-4	30 Aug 2014	02:00 p.m.	(2)	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	30 Aug 2014	05:40 p.m.	(2)	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	31 Aug 2014	11:45 a.m.	(2)	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	31 Aug 2014	02:30 p.m.	(2)	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	2 Sep 2014	11:45 a.m.	(2)	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	29 Aug 2014	00:20 p.m.	(2)	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	29 Aug 2014	03:20 p.m.	(2)	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	29 Aug 2014	04:35 p.m.	(2)	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	30 Aug 2014	02:00 p.m.	(2)	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	31 Aug 2014	02:25 p.m.	(2)	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	2 Sep 2014	11:45 a.m.	(2)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	2.3

Note: (*) He was not distinguished from H₂. (n.a.) not analyzed. (b.d.l.) Below detection limits. (1) Personal communication of Donald Clark. Analyzed on free 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‰. The gas samples containing "vacu" were sampled in vacutainers, the others were sampled in steel tube cylinder.

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. H₂, CH₄, He, and N₂ proportions are stable only from the third day of production (D3) (Figure 2a). The large differences in gas compositions observed at the day-scale thus illustrate the difference between the water from the well tubing and the water from the aquifer (Figure 2a).

Overall, the general trend for the gases is a drastic decrease in H₂ percentage: from 91.7 mole % in 2008 in the free gas phase, to 0.1 mole % bubbling out from the Pennsylvanian aquifer at atmospheric pressure in August 2014. In addition to H₂ present before the plugging, small recharges of H₂ 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 CH₄ is below 5 mole % until November 2013 when it increases to 44.9 mole % in the wellhead (D#2-3 November 2013). In the subsequent sampling trips though, the CH₄ proportion measured for the gas from the aquifer was less than 9 mole %. 3 mole % is the final trend observed in the aquifer in August 2014. As for H₂, the highest levels of CH₄, 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 N₂ concentration increases with time. Its proportion ranges from 51.6 mole % in November 2013 (D#2-3 November 2013) in a sample that also records substantial CH₄ to 93.3 mole % in August 2014 (D#2-7 August 2014). The concentration is fairly constant in the gas from the aquifer, with a maximum value of 3.1 mole % (D#2-2 May 2014). 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/N₂ ratios were similar in

Table 5. Scott#1 and Heins#1 Wells: Gas Compositional (mole %) and Isotopic (‰) Analyses

Well	Sampling Date	Source	Gas Type	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	12 Aug 1982	Goebel et al. [1984]	(4)	-	39.0	2	65.0	-	-	-	-	0.5	-	-	-	-	-
Scott ¹	26 Aug 1982	Goebel et al. [1984]	(4)	-	25.0	11.4	71.0	<0.01	-	-	-	0.04	-	-	-	-	-
Scott	26 Aug 1982	Goebel et al. [1984]	(4)	-	41.0	1.8	58.0	<0.01	-	-	-	0.06	-	-	-	-	-
Scott ²	20 Sep 1982	Goebel et al. [1984]	(4)	tr	42.6	20.4	32.2	0.3	-	tr	2.07	-	-	-	-	-	-
Scott ²	20 Sep 1982	Goebel et al. [1984]	(4)	-	56.0	-	41.0	0.9	-	tr	0.92	-	-	-	-	-	-
Scott	27 June 1983	Goebel et al. [1984]	(4)	-	33.6	1	64.8	-	-	-	-	-	-796	-	-	-	-
Scott	27 Jun 1983	Goebel et al. [1984]	(4)	<0,1	39.4	0.5	60.1	-	-	-	-	-	-	-	-	-	-
Scott	14 Sep 1983	Goebel et al. [1984]	(4)	-	-	-	-	-	-	-	-	-	-740	-	-	-0.2	-
Scott ³	12 Jun 1984	Coveney et al. [1987]	(4)	0.002	1.4	0.01	96.0	0.002	-	1.1	-	0.002	-	-	-	-	-
Scott ³	7 Jul 1984	Coveney et al. [1987]	(4)	-	-	-	-	-	-	-	-	-	-836	-	-	-0.2	-
Scott ⁴	20 Jul 1984	Coveney et al. [1987]	(4)	-	5.0	-	-	-	-	-	-	-	-	-	-	-	-
Scott ³	14 Jun 1985	Coveney et al. [1987]	(4)	<0,02	4.5	1	92.8	0.5	-	1.1	-	0.01	-818	-	-	-	-
Scott ⁶	8 June 2008	Vacquand [2011]	(4)	0.08	18.3	cor.	75.4	0.02	5.7	n.a.	n.a.	6.241	-775	-423	-31.5	n.a.	n.a.
well water ⁷	2 Feb 1983												-103	-	-	-	-13.2
Heins ¹	7 Sep 1983	Goebel et al. [1984]	(4)	0.9	24.2	8.6	75.9	<0.1	0.9	-	-	-	-	-	-	-	-
Heins ¹	7 Sep 1983	Goebel et al. [1984]	(4)	0.81	36.7	3.9	67	<0.1	0.8	-	-	-	-	-	-	-	-
Heins	22 Sep 1983	Goebel et al. [1984]	(4)	-	-	-	-	-	-	-	-	-	-826	-	-	-0.45	-
Heins ³	12 Jun 1984	Coveney et al. [1987]	(4)	-	29.5	1.4	63.6	0.03	-	-	<0.006	-	-	-	-	-	-
Heins ³	7 Jul 1984	Coveney et al. [1987]	(4)	-	-	-	-	-	-	-	-	-	-810	-	-	-0.7	-
Heins ⁴	20 Jul 1984	Coveney et al. [1987]	(4)	-	56-80	-	-	-	-	-	-	-	-	-	-	-	-
Heins ⁵	14 Jun 1985	Coveney et al. [1987]	(4)	0.06	35.1	4.5	59.5	0.3	0.1	0.7	-	-	-776	-	-	-	-
Heins ⁵	8 Jun 2008	Vacquand [2011]	(4)	0.20	24.0	cor.	28.8	0.13	46.2	n.a.	n.a.	46.85	-776	-438	-25.0	n.a.	n.a.
Heins(1)	12 Mar 2012	This study	(4)	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)	12 Mar 2012	This study	(4)	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)	14 Aug 2014	This study	(4)	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.

Note: 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) Semiquantitative assays by quadrupole mass spectrometer on site by U.S. Geological Survey (Denver). (5) Courtesy of Ivan Barnes (1985, personal communication, U.S. Geological Survey), 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.

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 CH₄, H₂, or both.

4.2.2. Scott#1 Well

H₂ relative concentrations in the gas phase of the Scott#1 well were first measured in 1982 [Goebel et al., 1984] (Table 5). Values ranged from 25 to 56 mole %. Particularly striking are the high concentrations of O₂ coexisting with H₂ (in a ratio of 1/2), as well as O₂/N₂ ratios much higher than those of the atmosphere (Scott 26 August 1982 and 20 September 1982). H₂ proportion varies from 1.4 mole % (12 June 1984) to 56 mole % (20 September 1982). While the H₂ proportion was substantial in the Scott#1 gas from August 1982 to June 1983 (25–56 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 He contents 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 IPFEN 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 contents 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).

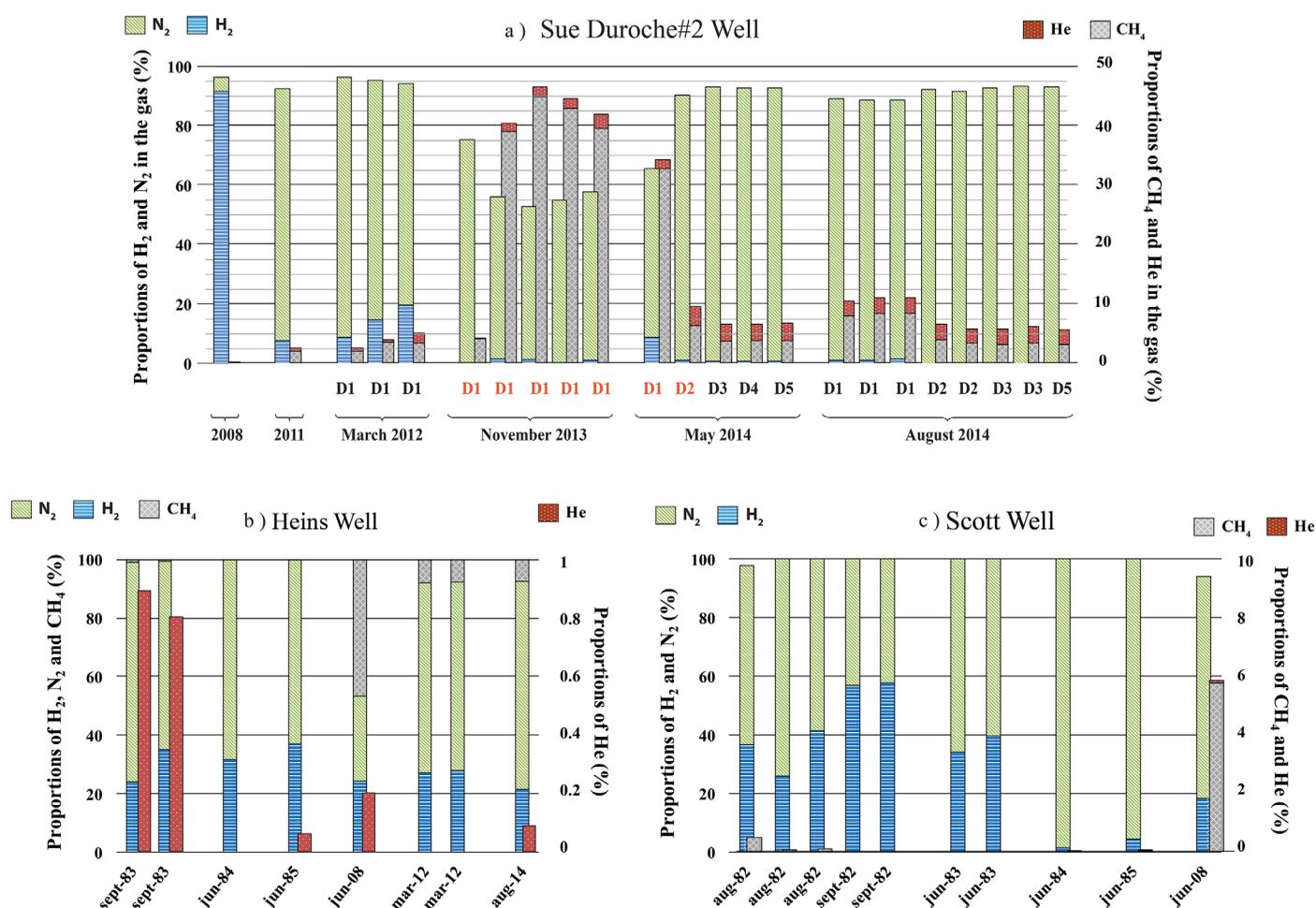


Figure 2. Compositional variations (mole %) of major gas components. For (a) Sue Duroche#2, (b) Scott#1, and (c) Heins#1 wells according to sampling date. For Sue Duroche#2, sampling dates are in red when the well has not been produced before sampling (fluids from tubing, gas type 3), in black when the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

4.3. C, H, N Isotope Compositions

Carbon, hydrogen, and nitrogen isotopic compositions in CH_4 , H_2 , and N_2 are shown in Table 4 for the Sue Duroche#2 well, and in Table 5 for Scott#1 and Heins#1 wells. $\delta^{13}\text{C}$ values of CH_4 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), Figure 1c) and (b) -50.7‰ to -64.3‰ , which corresponds to gas in the Pennsylvanian aquifer (gas type (2), Figure 1c). The series of samples taken in May 2014 illustrate this effect with a $\delta^{13}\text{C}$ of -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 CH_4 concentration. The most negative $\delta^{13}\text{C}$ values of CH_4 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 CH_4 in the Pennsylvanian aquifer at the Sue Duroche#2 well is -53.6‰ (gas type (2)). This value, which is highly enriched in ^{12}C , is classically considered as characteristic of microbial methane (see discussion later). The average value for $\delta^{13}\text{C}$ of CH_4 from gas type (3) of the Sue Duroche#2 well is -21.2‰ . The δ_{DCH_4} values in the Sue Duroche#2 well range from -402.7‰ (D#2-2 November 2013) to -290.7‰ (D#2-6 August 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 CH_4 in Scott#1 and Heins#1 wells are similar to those of gas type (3) of the Sue Duroche#2 well, with respective averages of -423‰ and -439‰ for δD and from -31.5‰ to -25.3‰ for $\delta^{13}\text{C}$.

Table 6. Sue Duroche#2 Well Noble Gas Composition and Isotopic Ratios

Sample	Sampling Date	Sampling Hours	Gas Type	Noble Gas (ppm)								σ					
				⁴ He	²⁰ Ne	³⁶ Ar	⁸⁴ Kr	⁴⁰ Ar/ ³⁶ Ar	³ He/ ⁴ He	⁴ He/ ⁴⁰ Ar*	⁴ He	²⁰ Ne	³⁶ Ar	⁸⁴ Kr	⁴⁰ Ar/ ³⁶ Ar	³ He/ ⁴ He	⁴ He/ ⁴⁰ Ar*
Atm	-	-	-	5.24	16.45	31.57	0.65	295.5	1.39E-06								
ASW	-	-	-	0.05	0.17	1.07	0.04	0.24	2.01								
D#2	2008	-	(1)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
D#2	2011	-	(2)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
D#2-1	16 Mar 2012	-	(2)	10,978	3.45	8.53	0.19	419.2	2.1E-07	10.40	1238.8	0.4	0.3	1.1E-02	1.29	2.6E-08	0.09
D#2-2	17 Mar 2012	-	(2)	8199	2.43	8.20	0.20	413.4	2.0E-07	8.48	924.8	0.3	0.3	1.2E-02	1.69	9.4E-08	0.09
D#2-Vacu 3	17 Mar 2012	-	(2)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
D#2-1	12 Nov 2013	10:25 a.m.	Air	1050	16.01	28.83	0.62	306.8	1.4E-07	3.24	76.0	2.4	0.9	2.2E-02	3.62	1.5E-08	0.77
D#2-2	12 Nov 2013	10:30 a.m.	(3)	12,786	4.78	10.24	0.25	376.9	1.5E-07	15.33	921.7	0.7	0.3	9.3E-03	4.42	2.6E-08	0.11
D#2-3	12 Nov 2013	11:00 a.m.	(3)	16,495	3.07	6.25	0.16	453.9	1.4E-07	16.65	1189.1	0.5	0.2	6.3E-03	5.60	1.8E-08	0.06
D#2-4	12 Nov 2013	05:00 p.m.	(3)	15,676	2.16	6.63	0.18	459.3	1.4E-07	14.43	1131.0	0.3	0.2	7.5E-03	5.66	1.5E-08	0.06
D#2-5	13 Nov 2013	09:45 a.m.	(3)	20,458	2.23	6.66	0.17	457.6	1.5E-07	18.94	1484.3	0.3	0.1	5.7E-03	2.02	1.5E-08	0.03
D#2 Vacu7	13 Nov 2013	10:00 a.m.	(3)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
D#2-1	16 May 2014	06:00 p.m.	(3)	14,413	3.19	6.57	0.17	417.8	1.3E-07	17.95	668.3	0.2	0.1	4.5E-03	6.59	1.8E-08	0.03
D#2-2	17 May 2014	02:30 p.m.	(2)+(3)	31,076	4.93	9.72	0.22	436.5	1.5E-07	22.68	1440.3	0.3	0.1	5.5E-03	6.64	1.3E-08	0.03
D#2-Vacu1	17 May 2014	02:30 p.m.	(2)+(3)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
D#2-3	18 May 2014	11:30 a.m.	(2)	28,089	4.30	9.45	0.22	442.4	1.4E-07	20.24	1301.5	0.4	0.1	5.4E-03	6.76	1.3E-08	0.03
D#2-Vacu2	18 May 2014	11:30 a.m.	(2)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
D#2-4	18 May 2014	01:00 p.m.	(2)	31,159	4.91	10.36	0.24	441.4	1.3E-07	20.61	1443.5	0.3	0.1	6.0E-03	6.67	1.3E-08	0.03
D#2-5	18 May 2014	01:45 p.m.	(2)	31,870	4.59	10.32	0.25	440.7	1.3E-07	21.26	1477.4	0.4	0.1	6.6E-03	6.85	1.7E-08	0.03
D#2-1	29 Aug 2014	00:20 p.m.	(2)	28,343	6.01	10.68	0.26	429.0	1.3E-07	19.88	675.0	0.5	0.2	5.2E-03	1.47	1.5E-08	0.04
D#2-2	29 Aug 2014	03:20 p.m.	(2)	25,523	5.33	9.65	0.24	428.0	1.5E-07	19.96	626.8	0.5	0.2	4.9E-03	1.46	1.8E-08	0.04
D#2-3	29 Aug 2014	04:45 p.m.	(2)	25,145	4.76	9.85	0.24	431.7	1.4E-07	18.74	605.2	0.4	0.2	5.1E-03	1.58	4.4E-08	0.04
D#2-4	30 Aug 2014	02:00 p.m.	(2)	25,859	5.56	10.90	0.32	415.3	1.5E-07	19.79	617.4	0.5	0.2	6.3E-03	1.34	2.4E-08	0.04
D#2-5	30 Aug 2014	05:40 p.m.	(2)	21,817	6.65	11.88	0.30	397.5	1.4E-07	18.01	520.8	0.6	0.2	6.3E-03	1.18	1.5E-08	0.05
D#2-6	31 Aug 2014	11:45 a.m.	(2)	28,860	6.19	11.51	0.27	418.4	1.7E-07	20.40	687.8	0.6	0.2	5.3E-03	1.30	2.5E-08	0.04
D#2-7	31 Aug 2014	02:30 p.m.	(2)	27,467	5.21	9.95	0.25	432.5	1.4E-07	20.15	655.2	0.5	0.2	5.0E-03	1.40	1.4E-08	0.04
D#2-8	2 Sep 2014	11:45 a.m.	(2)	26,757	5.61	11.24	0.28	421.1	1.4E-07	18.94	638.5	0.5	0.2	5.6E-03	1.26	1.6E-08	0.04

Note: (-) not available. (n.a.) not analyzed.

The δD of H_2 is relatively constant in the Sue Duroche#2 well, ranging from -717‰ (D#2-1 August 2014) to -799‰ (D#2-vacu1) with an average value of -760‰ . For the Scott#1 and Heins#1 wells, the average values are -793‰ and -781‰ , respectively. The δD values of H_2 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 5).

Measurements of nitrogen isotopes in N_2 emphasize that N_2 from Heins#1 is not isotopically different from the atmosphere (Heins August 2014, $\delta^{15}N_{Vs\text{ Atm}} = -0.2\text{‰}$), as previously discussed by Goebel *et al.* [1984] and Coveney *et al.* [1987]. However, N_2 from the Sue Duroche#2 well records positive $\delta^{15}N_{Vs\text{ Atm}}$ values ranging from $+2.1\text{‰}$ (D#1-vacu1 August 2014) to $+3.0\text{‰}$ (D#1-2 August 2014). With respect to the precision of these measurements ($\pm 0.5\text{‰}$), the values are significantly different from atmosphere. Most of the nitrogen isotope measurements were performed on gases sampled in vacutainers. They were submitted to variable air contamination up to 31%, if we assume that all oxygen in samples is atmospheric, which maximal effect would be lowered the $\delta^{15}N$ of -1.1‰ . We consider the measured values as minimal values. These values do not show any significant change over time, with an average of $+2.5\text{‰}$.

4.4. Noble Gases

Compositions of noble gases from the Sue Duroche#2 well are shown in Table 6; for Scott#1 and Heins#1 wells, result from this work and Vacquand [2011] are shown in Table 7. Figures 3a and 3b shows the air-normalized noble gas abundances for 4He , ^{20}Ne , ^{36}Ar , and ^{84}Kr as well as the isotopic ratios for $^{40}Ar/^{36}Ar$, $^3He/^4He$, and $^4He/^{40}Ar^*$. 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 ($Ne > Ar > Kr$), 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.

Table 7. Scott#1 and Heins#1 Wells: Noble Gas Compositions and Isotopic Ratios

Well	Sampling Date	Source	Gas Type	Noble Gas (ppm)							σ						
				⁴ He	²⁰ Ne	³⁶ Ar	⁸⁴ Kr	⁴⁰ Ar/ ³⁶ Ar ^a	³ He/ ⁴ He ^b	⁴ He/ ⁴⁰ Ar*	⁴ He	²⁰ Ne	³⁶ Ar	⁸⁴ Kr	⁴⁰ Ar/ ³⁶ Ar	³ He/ ⁴ He	⁴ He/ ⁴⁰ Ar*
Atm	-	-	-	5.24	16.45	31.57	0.65	295.5	1.39E-06	-	-	-	-	-	-	-	
ASW	-	-	-	0.05	0.17	1.07	0.04	0.24	1.39E-06	-	-	-	-	-	-	-	
Scott ^a	Jun 8	Vacquand [2011]	(4)	11	13.88	17.24	0.33	-	-	-	-	-	-	-	-	-	
Heins ^a	Jun 8	Vacquand [2011]	(4)	374	10.73	18.19	0.33	-	-	-	-	-	-	-	-	-	
Heins(1)	Mar 12	This study	(4)	540	12.86	26.89	0.53	-	2.21E-07	-	60.9	1.39	0.98	0.03	5.31E-08	-	
Heins(2)	Mar 12	This study	(4)	598	14.12	27.95	0.56	-	2.25E-07	-	67.5	1.52	1.03	0.03	2.76E-08	-	
Heins(3)	Aug 14	This study	(4)	476.58	17.87	26.05	0.55	297.24	1.52E-07	10.5	11.40	1.61	0.43	0.01	0.88	1.87E-08	0.05

^aData listed from Vacquand [2011].
Note: (-) Not available.

The Sue Duroche#2 sample which contains 20.3% O₂ presents a noble gas pattern similar to the air (Figure 3b). This observation confirms the singular air contamination for this sample.

The Sue Duroche#2 noble gases have weakly depleted ADNG (³⁶Ar from 6.3 to 11.9 ppm) with variable ⁴He contents (8199–31,870 ppm). The ⁴⁰Ar/³⁶Ar mean ratio of 431 is superior to the air value of 295.5 [Nier, 1950]. The ³He/⁴He mean ratio is 1.5 × 10⁻⁷ with values ranging from 1.3 × 10⁻⁷ to 2.1 × 10⁻⁷. The ⁴He/⁴⁰Ar* ratios range from 8.5 to 22.7 with a mean value of 18.0 ± 3.6. These values are higher than the mean crustal ⁴He/⁴⁰Ar* ratio determined at 4.92 by Ballentine et al. [1991].

The Heins#1 well presents ADNG compositions close to the air values (³⁶Ar from 18.2 to 27.95 ppm) (Figure 3a). The ⁴⁰Ar/³⁶Ar 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 (374–598 ppm) giving a mean isotopic composition of He of 2.0 × 10⁻⁷, different from the air value (1.39 × 10⁻⁶) [Ozima and Podosek, 2002]. The ⁴He/⁴⁰Ar* ratio of 10.5 measured in August 2014 is higher than the mean crustal ⁴He/⁴⁰Ar* ratio determined at 4.92 by Ballentine et al. [1991].

The Scott#1 well noble gas shows ADNG slightly depleted compared to the air (³⁶Ar = 17.2 ppm) (Table 7). 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

Four types of gases, sampled at wellheads, are considered in this study (Figures 1c and 1d and Tables 8 and 9): (1) free gas observed, right after drilling, at the Sue Duroche#2 well, before the well was plugged back from the basement; (2) gas exsolved from the water that originates from the Pennsylvanian aquifer at the sedimentary section of the Sue Duroche#2 well, collected after the stagnant water was drained off; (3) gas exsolved from the water that was stagnant in the tubing of the Sue Duroche#2 well (which shows punctual H₂ 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 re-equilibration of the air saturated water (ASW) component in the water due to the degassing of H₂, N₂, CH₄, 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 (~4.3 × 10⁻³) and is expected to be much lower in the aquifer condition due to higher artesian pressure. Considering very low gas/water ratios, it is expected that the noble gas composition in the gas phase in equilibrium with an ASW phase will be characterized by an air-like composition [Ballentine et al., 1991; Prinzhofer, 2013]. We can verify this solubility effect by comparing ²⁰Ne/³⁶Ar ratios with the calculated effect of degassing ASW at surface conditions following Henry's law as described by Ballentine et al. [1991]. This confirms that the ADNG recovered from Sue Duroche#2 aquifer water is derived from water degassing rather than by air contamination. At 1 bar and 20°C, ASW contains 4.8 × 10⁻⁵ mol/m⁻³ of ³⁶Ar as predicted by the solubility of argon in freshwater [Crovetto et al., 1982] and based on argon atmospheric content (9340 ppm). Considering that all ³⁶Ar in the gas phase results from exsolution of the water phase, the normalizing of major gas

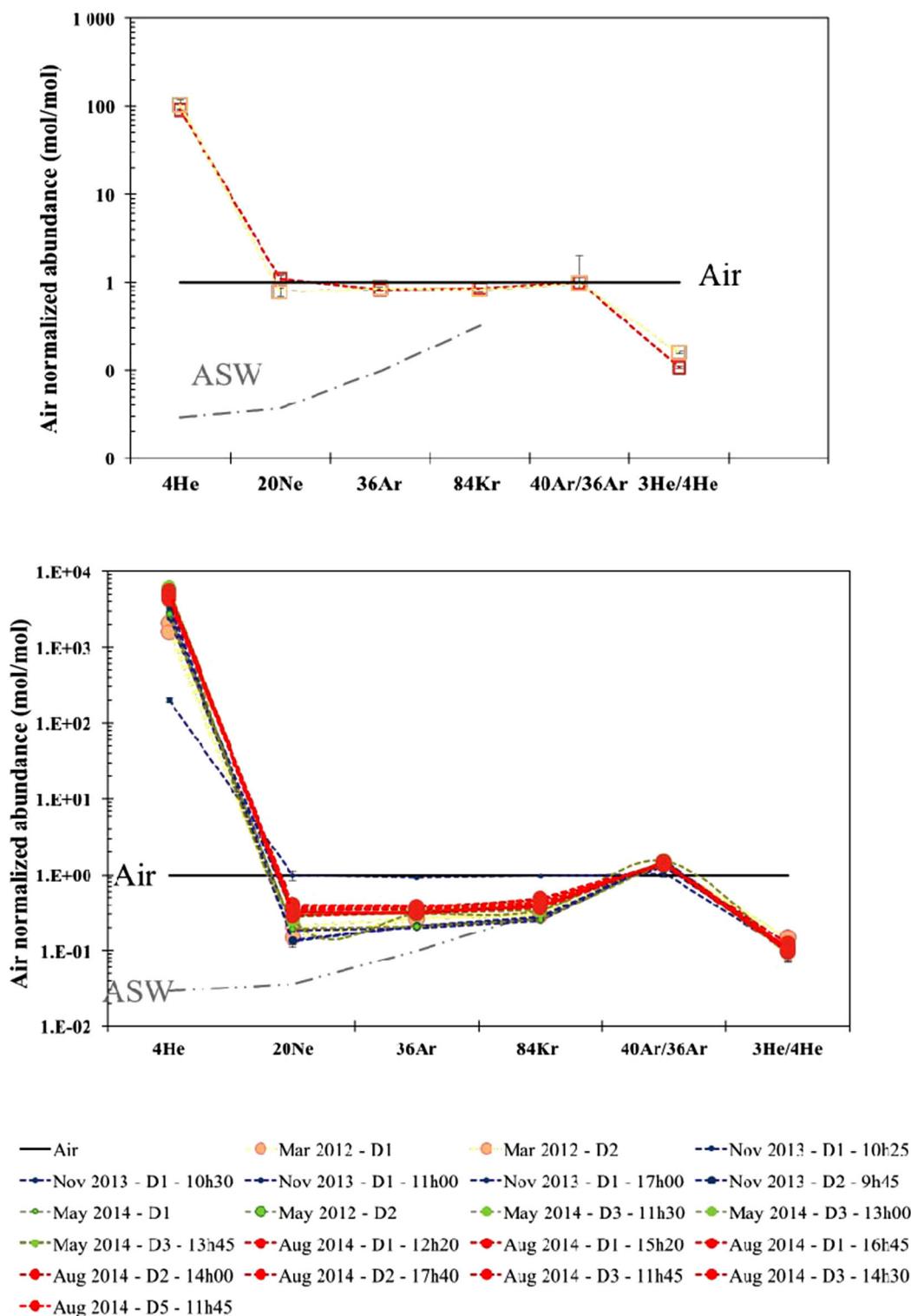


Figure 3. Relative abundance of air-normalized isotope composition of noble gas (^4He , ^{20}Ne , ^{36}Ar , ^{84}Kr , $^{40}\text{Ar}/^{36}\text{Ar}$, and $^3\text{He}/^4\text{He}$) for (a) Heins#1 well (b) Sue Duroche#2 well. Sample values are normalized to the air abundances. Normalization value used 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 and Podosek, 2002].

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 (Figures 4 and 5).

Table 8. Average Chemical and Isotopic Composition of Each Gas Type^a

Gas Types	H ₂ (%)		CH ₄ (%)		N ₂ (%)		He (%)		dD H ₂ (‰)		dD CH ₄ (‰)		d ¹³ C CH ₄ (‰)		d ¹⁵ N N ₂ (‰)									
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max						
Type (1) ^b	91.8		0.1		4.7		*		n.a.		n.a.		n.a.		n.a.									
Type (2)	0.1	3.8	19.7	2.0	4.2	8.4	74.3	88.6	93.3	0.5	2.2	2.9	-792	-747	-757	-376	-320	-291	-59.1	-53.6	-50.7	2.1	2.5	3.0
Type (3)	0.3	2.5	8.7	32.7	39.8	44.9	51.6	58.2	75.0	0.1	1.4	2.3	-770	-763	-717	-403	-402	-399	-21.9	-21.2	-20.1	2.4	2.5	2.5
Type (4)	1.4	29.3	56.0	0.1	9.5	46.2	28.8	63.7	96.0	0.06	0.3	0.9	-836	-786	-740	-477	-436	-419	-31.5	-26.6	-20.8	-0.7	-0.4	-0.2

^aThe minimum and maximum values are specified and encompass the mean value.

^bValue of the single measurement available.

Note: n.a. nonanalyzed. *could not separate from H₂ because of the too high H₂ concentration.

5.2. Origin of Gas

5.2.1. Helium

The Sue Duroche#2 ³He/⁴He 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] (Figure 4a). This isotopic ratio of helium can result from several contributions. The large excess of He (⁴He/²⁰Ne > 2676) compared to the atmospheric or ASW composition (⁴He/²⁰Ne < 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 are enriched in ³He, with ³He/⁴He ranging from 8.42×10^{-6} to 1.40×10^{-5} [O’Nions and Oxburgh, 1983]. The last episode known of mantellic fluid contribution (kimberlites) in the geological history of Kansas is Cretaceous in age [Coveney *et al.*, 1987]. 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 CO₂ fields with a magmatic origin are known, such as the Sheep Mountain and Bravo Dome [Gilfillan *et al.*, 2008]. The low abundances in CO₂, and the extremely low CO₂/³He ratios of our samples (CO₂/³He < 2×10^5) argue against a mantle contribution (MORB CO₂/³He ratio ranging 1–10 × 10⁹) [Marty and Jambon, 1987] for the abundant ³He. However, these low CO₂ abundances could also be the result of CO₂ precipitation. In these conditions, we cannot rule out a mantle contribution only based on this ratio.

We can calculate the maximal proportion of mantle He in the Sue Duroche#2 gas if we consider two fixed end-members: (1) radiogenic ³He/⁴He = 1.3×10^{-8} [Gerling *et al.*, 1971], (2) mantle ³He/⁴He = 8.42×10^{-6} [O’Nions and Oxburgh, 1983]. Using this following relationship:

$$X (\%) = (R_{\text{Sample}} - R_{\text{Radiogenic}}) / (R_{\text{Mantle}} - R_{\text{Radiogenic}}) \times 100$$

The contribution of mantle helium in Sue Duroche#2 gas with such hypotheses is of 1.5%.

Another possibility explaining such ³He/⁴He 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

Table 9. Average the Water Properties Corresponding to Each Gas Type^a

Gas Types	pH		T (°C)		Sal (g/L)		C25 (mS/cm)		ORP (mV)						
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max					
Type (1)	-		-		-		-		-						
Type (2)	6.9	7.3	7.6	16.6	21.4	24.3	54.9	55.4	56.3	58	77	80	-388	-283	-173
Type (3)	8.6^b				11.8^b		n.a.				68^b		n.a.		
Type (4)	-		-		-		-		-		-		-		

^aThe minimal and maximal values are specified and encompass the mean value.

^bValue of the single measurement available.

Note: (-) These gases are not associated to water that can be sampled at wellhead.

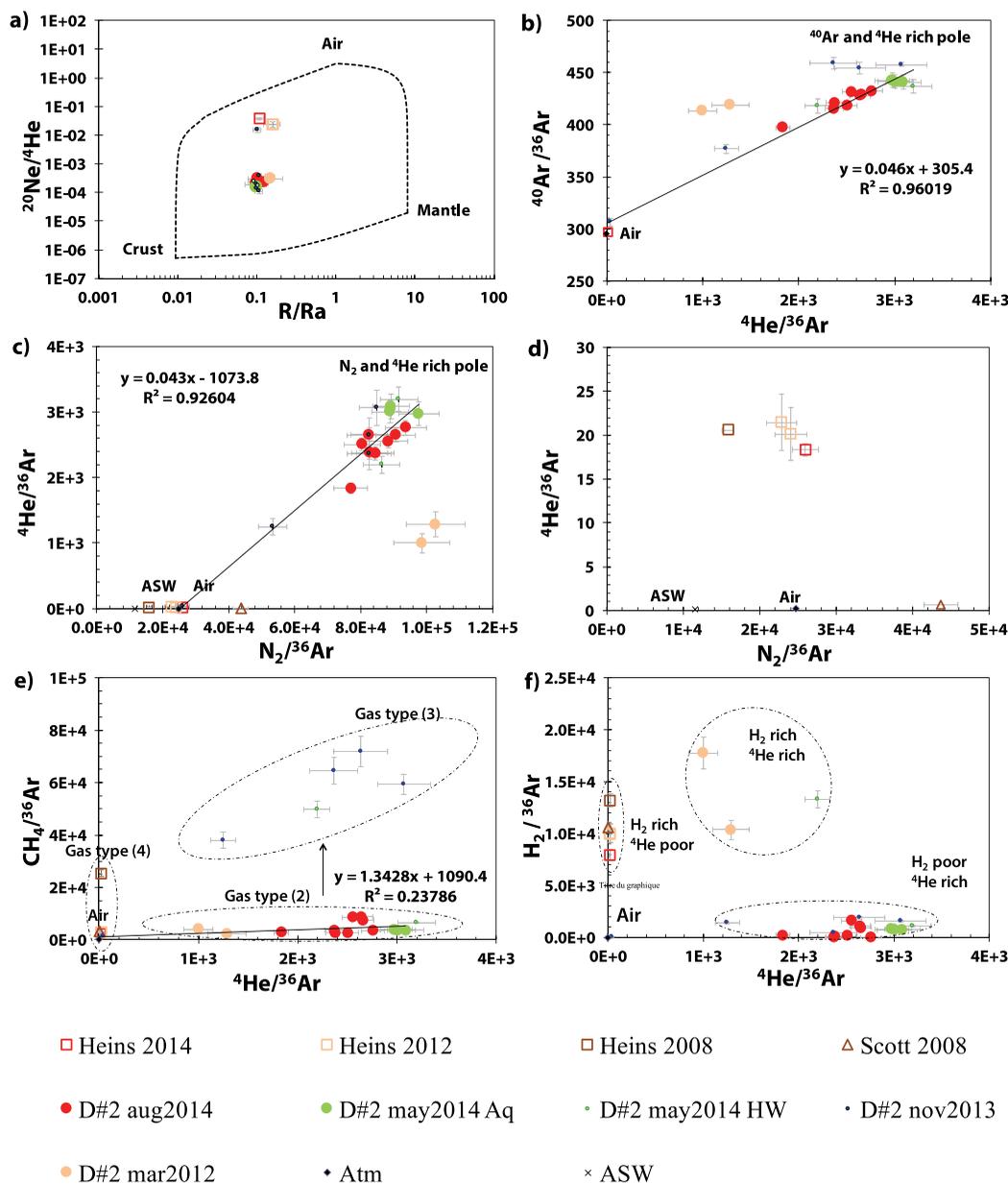


Figure 4. $^{20}\text{Ne}/^4\text{He}$ versus R/R_a ($^3\text{He}/^4\text{He}$ air normalized) and three end-member mixing lines: radiogenic, mantle, and Air. Mantle R/R_a calculated from *R* mentioned by *O’Nions and Oxburgh* [1983], crust R/R_a from *Gerling et al.* [1971], and air R/R_a from *Ozima and Podosek* [2002]. (a)–(f) Variations of $[\text{He}]$, $[\text{Ar}]$, $[\text{CH}_4]$, $[\text{N}_2]$, 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.

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. Calculating the ratio of the ^3He over the ^4He radiogenic production rate [*Castro et al.*, 2000] using 100 ppm Li content results in a $^3\text{He}/^4\text{He}$ ratio of 2.2×10^{-7} . Given the available data it is impossible to discriminate between a mantle and a radiogenic origin for the ^3He excess compared to the mean $^3\text{He}/^4\text{He}$ production ratio of the crust of 1.3×10^{-8} [*Gerling et al.*, 1971]. First scenario would imply 1.5% mantle contribution in gas and

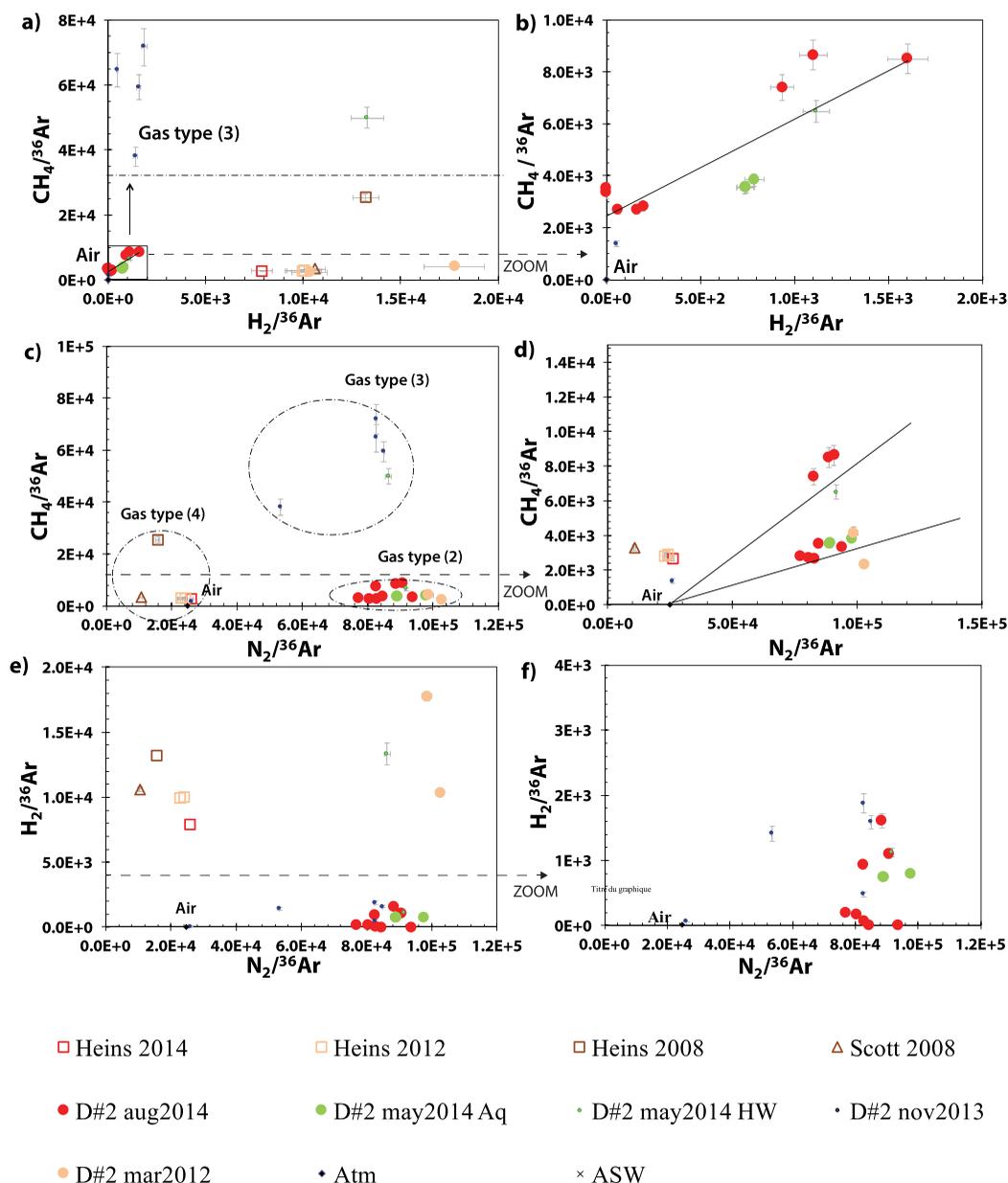


Figure 5. (a)–(f) Variations of [CH₄], [N₂], [H₂], normalized to an atmospheric noble gas content [³⁶Ar]. Sue Duroche#2 well: circles (large one for gas type 2, small one for gas type 3); Heins#1 well: squares and Scott#1 well: triangles.

second scenario would imply a concentration at least of 100 ppm in Li in rocks. In both cases, the large majority of He is of radiogenic origin.

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 (Figure 4a).

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 ⁴⁰Ar (Table 6). ⁴He and ⁴⁰Ar proportions (Figure 4b) 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. The ⁴He/⁴⁰Ar* ratios of the Sue Duroche#2 gas and the Heins#1 gas are largely higher than the crustal ratio measured by Ballentine *et al.* [1991]. Classically these values are interpreted in the literature as a higher diffusion of He compare to Ar at

low temperature [Stuart *et al.*, 1995; Ballentine and Burnard, 2002; Kendrick and Burnard, 2013]. The radiogenic fluids present in Sue Duroche#2 gas and Heins#1 gas are produced at low temperature compared to metamorphic environment.

5.2.2. Nitrogen

High N₂ proportions are found in the different types of gas (Figures 2a, 2b, 2c, and 2d and Table 8). In the aquifer at the Sue Duroche#2 well—gas type (2)—N₂ is correlated with ⁴He and ⁴⁰Ar (Figures 4b and 4c): all Sue Duroche#2 samples distribute on a mixing line between an N₂ and ⁴He-rich end-member and an atmospheric end-member. N₂ and He are probably associated with the same source. The minimal $\delta^{15}\text{N}$ values, as defined in the result section, ranges from +2.1‰ to 3‰, which is consistent with a crustal origin of N₂ (release of ammonium from metasedimentary rocks) in the aquifer [Bebout and Fogel, 1992; Boyd and Philippot, 1998; Mingram and Bräuer, 2001]. This positive isotopic signature of N₂ is probably not simply due to a fractionation of N₂ 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. N₂ with a minimal average $\delta^{15}\text{N}$ of +2.5‰ may result from the mixing between atmospheric N₂ (issued from ASW = 0‰, not considering here the atmospheric contamination discussed in the result section) and another source such as metamorphic N₂ [Mingram and Bräuer, 2001; Svensen *et al.*, 2008]. The N₂ isotopic composition of Kansas basement rocks [Guelard, 2016], 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 and 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 N₂ with almost identical isotopic signatures for both elements (³He/⁴He and $\delta^{15}\text{N}$) as for the Sue Duroche#2 gas. The link between N₂ and He is not visible in the Scott#1 and Heins#1 gas samples (Figure 4d). Even if Heins#1 shows higher ⁴He/³⁶Ar ratios, no N₂ enrichment compared to atmosphere is observed. Due to the atmospheric signature of noble gases versus N₂, the Scott#1 and Heins#1 N₂ budget is probably largely due to air dilution (Figure 4a), suggesting mixing and attendant contamination with air in free gas at the wellhead. Gas of type (4) is characterized by atmospheric noble gas contents. It is likely that atmospheric signature overrides the original one inherited from the water in contact with the free gas (Figures 1c, 1d, and 3).

5.2.3. Dihydrogen

H₂ and ⁴He proportions normalized to ³⁶Ar (Figure 4f) 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 (Figures 5e and 5f), indicating that N₂ and H₂ do not originate from a common source. δD values for H₂ are low and homogenous despite the differences in H₂ proportions and the gas type (Figure 6a). 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 (Figure 6d). These low isotopic values do not reflect the necessary process involved in the production of H₂. Such light values can be the result of re-equilibration with water at well temperature, as suggested by Coveney *et al.* [1987]. 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 types (1) and (2)—and a surficial one, H₂ being produced in the tubing of the well—types (3) and (4).

5.2.3.1. Deep H₂

Gas type (1) which was initially seeping out from the Sue Duroche#2 well before plugging at the top of the basement was very rich in H₂ (91.8%). Note that, recently, the PETROMA private company mentioned the discovery of a similar small shallow gas field in Mali, about 50 km north of Bamako (also in a cratonic context), in which the gas is made of up to 98% of H₂ with some methane and helium [Briere and Jerzykiewicz, 2016].

Gases of types (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 (Figure 4f). However, the low H₂ contents of gas type (2) can result from a depletion/consumption of this very reactive gas in the Pennsylvanian aquifer. In counterpart, this depletion induces higher relative contents of the nonreactive 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. Among the hypotheses proposed in the literature, radiolysis of water and reduction of water coupled to Fe(II) oxidation are those favored by Lin *et al.* [2005a, 2005b] and Sherwood Lollar *et al.* [2014] to explain H₂ production in crystalline Precambrian rocks. The presence in the basement of

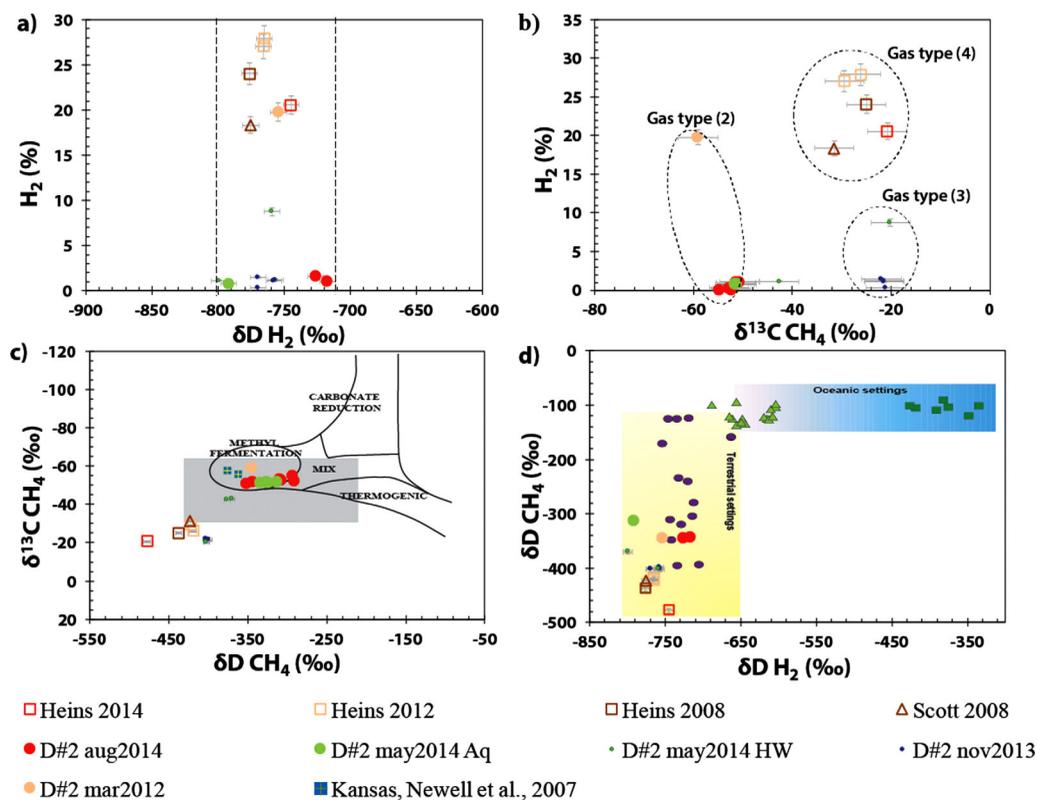
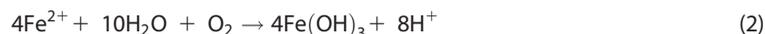
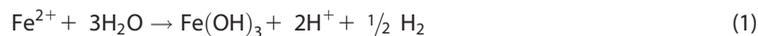


Figure 6. (a) (top, left) $\delta D H_2$ versus $[H_2]$. (b) (top, right) $\delta D CH_4$ versus $[H_2]$. (c) (bottom, left) $\delta^{13}C CH_4$ versus $\delta D CH_4$. (d) (bottom, right) $\delta D H_2$ versus $\delta D CH_4$. (a)–(d) Sue Duroche#2 well: circles (large one for gas type 2, small one 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 (Italy), Philippines, Turkey, and Oman [Etioppe et al., 2011; Vacquand, 2011].

Fe-bearing rocks (Gabbros referred to as basic rocks (MRS) in Figure 1b) together with the magnetic anomaly observed in the area rather suggest that Fe(II) oxidation produces H_2 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 toward the east, over and through Fe-rich rocks in the MRS (Figure 1b) [Jorgensen et al., 1993; Musgrove and Banner, 1993; Macfarlane, 2000]. According to $^3He/^4He$ ratio, enriched in 3He when compared to the classic crustal value (Figure 4a), one can argue that a mantle input can contribute significantly to Kansas H_2 -bearing gases accumulations (R/R_a between 9.2×10^{-2} and 1.5×10^{-1}). In this prospect, a mantle origin for H_2 cannot be definitely excluded, although other processes can produce 3He in the crust such as 6Li induced fission, as described beyond. Biogenesis of H_2 and CH_4 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 H_2

Surficial H_2 can be attributed to processes reported in the literature such as (1) biological fermentation of organic matter, that could be assisted with Fe^{2+} [Ma et al., 2016] or (2) the corrosion of steel tubing ($Fe(0)$) at low temperature by salted water with low sulphate contents [Angino et al., 1984; Goebel et al., 1984]. Herein, (3) we propose a third mechanism for H_2 formation: water splitting at low temperature catalyzed by dissolved compounds, for instance, organic carbon and Fe(II). The redox conditions (Oxidation-Reduction Potential (ORP) Tables 1 and 9) 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 H_2 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 H_2 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 O_2 in the considered environment. Reaction (2) takes place in the presence of O_2 and does not lead to H_2 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 catalyze reaction (1) once all O_2 is consumed [Weber *et al.*, 2006; Georgi *et al.*, 2007; Niu *et al.*, 2011]. H^+ produced by these reactions can be consumed notably by the corrosion of the steel tubing and this could explain the pH measured in the water flowing out from the tubing (Tables 1 and 9).

5.2.4. Methane

About 0.1% of CH_4 is present in gas type (1) which originates from Precambrian basement. Isotopic compositions for CH_4 in this gas type are not available to help in discussing its origin. However, one can assume that in basement conditions, it could be produced through either biogenic pathway: acetoclastic fermentation or CO_2 reduction; or abiogenic pathways: Fischer-Tropsch Type (FTT) reactions. The very low CH_4 concentration compared to H_2 ($\text{H}_2/\text{CH}_4 = 918$), the low abundance of organic matter in crystalline basement rocks precludes acetoclastic fermentation while the absence of higher hydrocarbons (ethane or propane) in the gas phase tends to preclude FTT reactions. It leads us to favor a recombination of H_2 with CO_2 according to the biogenic processes.

The gas type (2) show CH_4 contents from 2% to 8.4%. The $\delta^{13}\text{C}$ and δD values of the CH_4 in these gases suggest a biologic origin through acetoclastic fermentation (Figure 6c) which is consistent with the presence of lignite and the DOC contents in the water.

The gas type (3) display a relative concentration enrichment in CH_4 when compared to the gas type (2) (Figures 4e, 5c, and 5d). This suggests that CH_4 can be produced in the tubing. The $\delta^{13}\text{C}$ and δD values of the CH_4 of these gases with respective mean value of -21.2‰ and -402‰ are similar to those of gas type (4), suggesting a similar process of origination (Figures 5c and 6c). According to Whiticar [1999] such values are attributed to artificial processes (such as those occurring during drilling) or metamorphism. Such a possibility is excluded in our case. More recently, *Etiopie and Ionescu* [2014] suggest that these kinds of CH_4 isotopic compositions can be issued from abiotic CH_4 formation catalyzed by ruthenium at low temperature. Herein, C and H isotopic compositions of CH_4 for gas types (3) and (4) are strongly enriched in ^{12}C and depleted in ^2H (Figure 6c) and the gas samples show the highest H_2 proportions compare to gas type (2). To explain these isotopic characteristics, we propose that the CH_4 is produced by biological H_2 autotrophy with an inorganic source of carbon (Dissolved Inorganic Carbon) in a closed system (CO_2 reduction). Such an interpretation is supported by the absence of hydrocarbon gases of higher molecular weight than methane.

These atypical isotopic values of CH_4 are similar to gas samples from Precambrian basement reported by *Sherwood Lollar et al.* [2006]. *Sherwood Lollar et al.* [2006] indeed suggest that the association of high concentrations of H_2 with ^{13}C -enriched and ^2H -depleted CH_4 may indicate that CH_4 is produced by biological H_2 autotrophy in the deep subsurface, as it is proposed herein. Although their existence is not yet unequivocal, a growing body of evidences supports the existence of litho-autotrophic H_2 microbial systems (Slimes) in the subsurface [*Chapelle et al.*, 2002; *Nealson et al.*, 2005]. We thus suppose that a specific catalyst or microorganisms (methanogens) may play a role in CH_4 production in water close to the tubing of Kansas wells.

5.2.5. CO_2

The CO_2 proportion observed in this gas (Table 4) is generally lower than 1 mole %. This CO_2 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 to 424 m depth. Just after drilling, this well flowed free gas enriched in H_2 (91.8%)—gas type (1). This H_2 cannot be assigned to corrosion of tubing because the well was not cased yet, nor to drilling processes because H_2 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) (Figure 2a). The radiogenic signature of the gas in the sedimentary aquifer strongly suggests a connection for fluids between the Pennsylvanian 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 (Figure 2a). Gas from the Sue Duroche#2 well does not show any consistent correlation between H₂ and crustal signatures (e.g., ⁴He or N₂) (Figures 4f, 5e, and 5f). 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 unlike H₂. Assuming that in the aquifer all the H₂ and N₂ are coming from a constant flux from the basement, and comparing the H₂/N₂ ratios between gas type (1) and gas type (2), we can deduce that more than 99% of H₂ coming from the basement has been consumed in the aquifer. 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 H₂. In this intracratonic context and contrary to ophiolitic context, the Sue Duroche#2 water presents a crustal-type pH (6.9–7.7) which allows Fe(II) to be dissolved and then mobilized within the water of sedimentary aquifer (Figure 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 (Figure 7).

An alternative hypothesis, radically different could explain the high H₂ proportions just after the drilling, the drop of H₂ and the appearance of CH₄ after setting of the deep plug. This hypothesis suggest that H₂ is exclusively issued from the Pennsylvanian sedimentary aquifer. Indeed, a correlation between CH₄ and H₂ is observed in the gas issued from this aquifer at (gas type (2)) in that the higher the H₂ proportion, the greater the enrichment in CH₄ (Figures 5a and 5b). This observation, together with the isotopic composition of methane, could be consistent with a simultaneous biological production of H₂ and CH₄. In an equilibrated ecosystem, acetoclastic bacteria are known to live with H₂-producing microorganisms [Nealson *et al.*, 2005], but

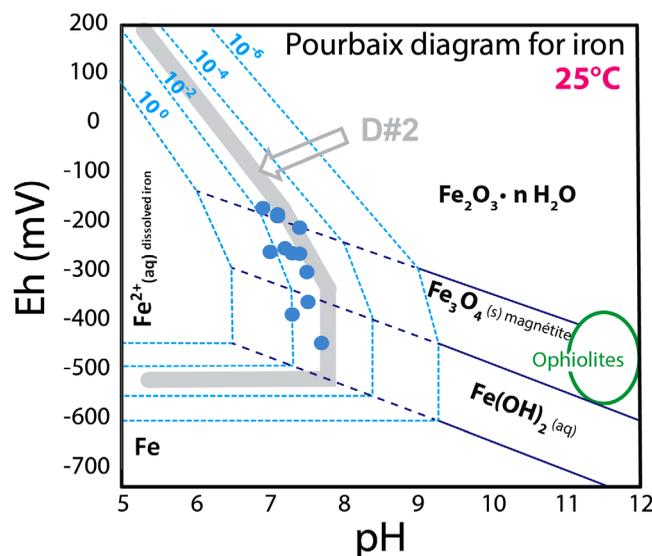


Figure 7. Eh-pH Pourbaix diagram at atmospheric pressure and 25°C. Blue line represent domain limit of Fe²⁺ for different [Fe²⁺]. Grey line represent Fe²⁺ domain limit for Sue Duroche#2 [Fe²⁺].

produced H₂ is not in any abundance because it is directly consumed. The Pennsylvanian sedimentary aquifer at the Sue Duroche#2 well is a karstic reservoir underlying younger strata containing lignite. One possibility is the creation of a new ecosystem, with flash biodegradation right after the drilling. Available organic substratum is consumed by microorganisms colonizing the environment like in landfills. Indeed, in landfills, H₂ producers are known to develop before CH₄ producers, inducing H₂ proportions observable on day-scale times [Tchobanoglous *et al.*, 1993]. In these conditions, the gas type (1) would be issued from flash biodegradation in this aquifer. This gas would progressively evolve to gas type (2) with the development of methanogens in the ecosystem.

However, this hypothesis is unlikely in regard of the free gas phase (gas type (1)) pressure observed right after drilling and the low recharges lately observed for CH₄ through time. It leads us to reject this hypothesis of H₂ originating initially (gas type (1)) exclusively from biogenic processes in sedimentary levels.

5.3.2. Recharge Events

We noticed in tubing gas from the Sue Duroche#2 well that H₂ recharge events are observable between each sampling field trip—gas type (3)—despite the decrease of H₂ proportion in the aquifer—gas type (2) (Figure 2a). This observation could be the result of either (1) a reaction taking place in the tubing of the well that generates H₂ and/or (2) an accumulation in the wellhead of H₂ still present in the aquifer (H₂ 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 H₂ in the wellhead. This is not the case. We therefore suggest that the H₂ found in the tubing—gas type (3)—is not a H₂ coming from aquifer like it is in gas types (1) and (2). We further note that in type (3) gas, H₂ 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 (Figures 4a and 4f). The hydrologic settings of Scott#1, Heins#1, and Sue Duroche#2 wells are very different (Figures 1c and 1d). 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#2 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 (Figures 1c and 1d). 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 free 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 meters 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 the gases in the aquifer 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 produced from the combination of an evolution of Eh-pH conditions in the tubing, which could favor H₂ production (Figure 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” of 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 results 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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