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**Quantifying the Role of Groundwater in the Biogenic Stimulation of Methane Production  
Using Noble Gas Tracers**

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**Introduction:** Noble gases have proven to be a versatile tool in the investigation of natural gas and hydrocarbon systems. They are chemically inert and occur in small enough quantities for noble gas production from natural radioactivity to significantly alter their isotopic signature, providing fluid source and age information. Similarly, small quantities of magmatic fluid addition or noble gases derived from the atmosphere, dissolved in groundwater, are readily resolved due to their respective unique isotopic signature (Sherwood Lollar and Ballentine 2009; Ballentine et al 2002). Indeed, the processes that control the amount of noble gases dissolved in water at recharge are understood well enough to invert observed groundwater noble gas concentrations to derive the temperature of water recharge and past climate information to better than  $\pm 0.5^{\circ}\text{C}$  (Ballentine and Hall 1999). If the groundwater contacts either oil or a gas phases, the noble gases are partitioned between the phases in proportion to their solubility. The concentration and relative proportions of the ‘groundwater’ derived noble gases in the sample oil or gas phase then have the potential to provide a quantitative measure of the volume of water contacted by that phase and whether in an open or closed system (Zartman et al., 1961).

While the principles of noble gas tracing of groundwater/hydrocarbon interaction are long established, it is only more recently that developments in analytical techniques and solubility databases have enabled these properties to be fully exploited. For example, the  $\text{CH}_4/^{36}\text{Ar}$  ratio of a natural gas can be used to identify whether  $\text{CH}_4$  gas fields have been transported from source to trap in solution or as a free gas phase (Ballentine et al., 1991);  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  together enabled the volume of groundwater required for diagenetic closure of oil migration pathways in the North Sea oil fields to be determined (Ballentine et al., 1996); He and Ne isotopes identify the critical role of the regional groundwater system in providing the transport medium for commercial helium concentrations in the Hugoton Panhandle giant gas field and, combined with nitrogen isotopes, identifies two distinct crustal nitrogen sources in the same system (Ballentine and Sherwood Lollar 2002); and  $^3\text{He}/\text{CO}_2$  ratios combined with carbon isotopes identifies and quantifies the role of gas dissolution in groundwater vs precipitation as sinks for a trapped subsurface  $\text{CO}_2$  phase (Gilfillan et al., 2009).

**Groundwater and Biogenic Methane Production:** Groundwater plays an important role in methane gas formation, migration, accumulation, storage and reservoir processes. It can bring microbes to isolated or sterilized subsurface environment to produce biogenic methane. On the

basin scale it can control the secondary migration of natural gases. Groundwater can remove the more soluble gases from the reservoir by gas dissolution. The chemistry of groundwater is also responsible for the pore creation or destruction of a gas reservoir. While the potential for groundwater to control these systems has been identified, few tools exist to quantify these processes and assess their importance or viability. In particular, role of groundwater in stimulating biogenic methane gas production is not well understood and remains an open question.

We present two case studies that demonstrate how noble gases can be used to develop physical models that describe gas-groundwater interaction, quantify the amount and age of groundwater associated with gas production and estimate the magnitude of in-situ microbial methane production. Two study sites are the coalbed methane gas field in San Juan Basin, New Mexico, USA (Zhou et al., 2005, Zhou et al 2006). This work provides the foundation for the second case study, identifying the role of groundwater in stimulating microbial shale gas methane production in the Upper Devonian New Albany Shale in the Illinois Basin, USA (Schlegel et al., submitted). Findings from both these studies have implications for targeting undeveloped microbial gas accumulations, improving natural gas reservoir estimates, the potential of in-situ methanogen stimulation, and understanding biologic cycling of carbon in subsurface reservoirs.

**The San Juan Basin:** In the San Juan Basin study, 28 gas samples from producing wells in the artesian overpressured high production region of the basin were taken together with 8 gas samples from the underpressured low production zone as a control. Stable isotope and major species determination clearly characterize the high production region as dominantly biogenic in origin, and the underpressured low production region as having a significant admixture of thermogenic coal gas.  $^3\text{He}/^4\text{He}$  ratios increase from  $0.0836R_a$  at the basin margin to  $0.318R_a$  (where  $R_a$  is the atmospheric value of  $1.4 \times 10^{-6}$ ), indicating a clear but small mantle He signature in all gases. Elemental ratios of water-derived  $^{20}\text{Ne}/^{36}\text{Ar}$  and crustal  $^4\text{He}/^{40}\text{Ar}^*$  are different from the gas/water equilibrium solubility values and can be explained by a simple Rayleigh fractionation model where gas bubbles passing through water distill the noble gases into the gas phase. Low  $^{20}\text{Ne}$  concentrations compared to the model-predicted values can be accounted for by dilution of the groundwater-associated gas by desorbed coalbed methane. This Rayleigh fractionation and dilution model together with the gas production history allows us to quantify the amount of water involved in gas production at each well. The quantified water volumes in both underpressured and overpressured zones range from  $1.7 \times 10^3 \text{ m}^3$  to  $4.2 \times 10^5 \text{ m}^3$ , with no clear distinction between over- and underpressured production zones.

These results conclusively show that the volume of groundwater seen by coal does not play a role in determining the volume of methane produced by secondary biodegradation of these coalbeds. There is no requirement of continuous groundwater flow for renewing the microbes or nutrient components. Another potential implication may be related to well spacing. More production wells can be placed without affecting the presently producing wells. The observed strong mass related isotopic fractionation of  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios can be explained by a noble gas concentration gradient in the groundwater during gas production, which caused partial diffusive re-equilibration of the noble gas isotopes. Excess  $^{136}\text{Xe}$  and  $^{84}\text{Kr}$  in our samples can only be accounted for by  $^{136}\text{Xe}$  and  $^{84}\text{Kr}$  associated with the desorbed coalbed methane. Xe and

Kr isotopes are volumetrically trapped in the coal matrix and released as the coal is biodegraded to form methane.

Crustal radiogenic  $^4\text{He}$  accumulation in groundwater is an established dating tool. Based on physical models describing hydrocarbon/groundwater interaction developed by the noble gases in the hydrocarbon phase, initial crustal radiogenic  $^4\text{He}$  concentrations in the groundwater can be calculated. Considering both in situ  $^4\text{He}$  production and  $^4\text{He}$  from external crustal flux, this allows the  $^4\text{He}$  groundwater ages to be derived. In the San Juan Basin study, the solubility controlled Rayleigh fractionation model of noble gases is used to determine an initial  $^4\text{He}$  concentration in the groundwater associated with methane producing wells. The  $^4\text{He}$  groundwater ages in the San Juan Basin coalbed methane gas field range between  $1.65 \times 10^4$  and  $4.84 \times 10^5$  years. In the underpressured area of the San Juan Basin the groundwater ages increase as a function of the distance from basin margin recharge, but in the overpressured area, there is no clear trend. The dates derived for the groundwater in the underpressured area are consistent with  $^{14}\text{C}$  dates and hydrological modeling dates. This study illustrates the strengths and weaknesses of this technique. The principle uncertainties involved in the  $^4\text{He}$  dating of the groundwater associated with hydrocarbon reservoirs are the parameters used in the calculation of the  $^4\text{He}$  accumulation rate in the groundwater. They are aquifer thickness, porosity and radioelement concentrations and in particular an accurate quantification of the external  $^4\text{He}$  flux into the groundwater. However, there are many environments where no other dating tool exists, relative dates from systems interacting with the environment are valid. In these cases the hydrocarbon phase groundwater ages obtained give the only estimates available.

**In the Illinois Basin**, 34 formation water and gas samples were analyzed for stable isotopes, Chloride, tritium,  $^{14}\text{C}$  and noble gases.  $^{20}\text{Ne}/^{36}\text{Ar}$  ratios (0.08 to 0.33) are similar to the range found in air-equilibrated water (0.14-0.18).  $^{84}\text{Kr}/^{36}\text{Ar}$  and  $^{132}\text{Xe}/^{36}\text{Ar}$  ratios (0.035-0.056 and  $13.8\text{-}35.0 \times 10^{-4}$ , respectively) are also similar to the range found in air saturated water. In these samples we assume that there has been minimal fractionation of the inert gases, with near complete transfer of the noble gas in the water to the gas phase. The  $^4\text{He}$  ages for groundwater in the New Albany Shale were determined in the same way as the determination of ages in the San Juan Basin. When considering an external flux of  $^4\text{He}$  from the upper and lower crust, the average groundwater age range between 0.082 and 1.2 Ma (average 0.59 Ma) for representative crustal values. Within the Illinois Basin, there is a clear spatial coherence between the different sample populations, the microbial gases which are closer to recharge zones have a younger  $^4\text{He}$  groundwater age than the deeper thermogenic methane which has an older  $^4\text{He}$  associated groundwater age. These results are consistent with chloride and  $\delta^{18}\text{O}$  data from the New Albany Shale, which show elevated values towards the basin center in the thermogenic methane area indicating limited flushing by fresh water, as compared to the microbial methane area nearer to the basin margins. All locations in the study area have been influenced by Pleistocene recharge; however, deep saline brines have not been completely flushed, suggesting that the basin fluids are fairly stagnant. Using  $^4\text{He}$  ages, the magnitude of in-situ microbial methane production is estimated to range from 10-1000 TCF/Ma, which is  $\sim 10^4$  to  $10^6$  times slower than average laboratory methane production rates from coals, implying that laboratory experiments may be fundamentally different than in-situ conditions.

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