The use of noble gas isotopes in detecting methane contamination of groundwater in shale gas development area: an overview of technology and methods

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Abstract

Groundwater contamination by stray gas (mainly methane) in areas of shale gas development has captured the public's, political and scientific attention. However, sources and potential mechanisms of groundwater contamination are still debated. Noble gases can provide useful information on fluid migration for discerning scale, conditions, and physical mechanisms. In this study, details about analytical technology and theoretical approach of noble gases in tracing groundwater contaminations are presented. In addition, applications of noble gases isotopes for determining contamination sources and potential pathways are explored and reviewed. Recent developments are discussed and highlighted focusing on new utilities of noble gas isotope parameters in evaluating groundwater contamination. Some usages of indicators ($^4$He/$^{20}$Ne, CH$_4$/Ar, $^4$He/CH$_4$, etc.) are discussed through specific research articles. And it is a new trend to make comprehensive use of multiple geochemical parameters to determine the occurrence, source, and process of methane pollution in groundwater.

Keywords: Groundwater contamination, isotope tracing, stray gas, noble gas, shale gas development area
1 Introduction

Shale gas has become an increasingly important source of natural gas in the United States and many other countries, due to the development of hydraulic fracturing and horizontal drilling technology. Nevertheless, both horizontal drilling and hydraulic fracturing operations require a significant amount of freshwater, which results in water consumption and also drinking water contamination. Evidence has been found in many countries that the development of shale gas resources by hydraulic fracturing possibly leads to fugitive gas contamination of the overlying aquifers. Thus, despite the economic benefits of shale gas extraction, public concerns about environmental issues are growing.

Shale gas development may contaminate ground and surface waters by a number of mechanisms (Fig. 1) and thereby impact either public or private drinking water. The stray gas, which refers to natural gas present in shallow aquifers of undetermined origin, may come from shallow or deep thermogenic gas accumulations of natural or anthropogenic origin (caused by shale gas develop activities), from shallow microbial sources or a combination of both. On one hand, horizontal drilling and hydraulic fracturing technology require injection of fracturing fluid, which contains up to 1084 chemicals into the shale during the extraction process. If the fracturing fluid penetrates underground or overflows during rainy seasons, it can easily pollute local shallow and underground waters. On the other hand, shale gas may leak out of gas wells into shallow aquifers and dissolve. This migration may be caused by natural fracture systems and failing or improperly installed casings in the natural gas wells. Although groundwater contamination caused by drilling and hydraulic fracturing are ubiquitous, its sources need to be determined and the impact of these potential pathways (e.g., horizontal drilling, hydraulic fracturing, and wellbore) on...
water quality remains controversial.  

![Diagram](image)

Fig. 1: Seven possible scenarios that may account for the presence of elevated hydrocarbon gas levels in shallow aquifers. Reprinted from Ref. 34, Copyright (2014), with permission from the NAS.

Many researchers have studied groundwater contamination by using molecular and stable-carbon-isotope compositions of hydrocarbons. These tracers are traditionally used to identify the sources of hydrocarbon dissolved in groundwater and distinguish biogenic or thermogenic sources (Fig. 2). However, new methods were needed to distinguish natural processes from fugitive gas contamination. Noble gases can provide fluid migration information to complement hydrocarbon geochemistry, because they are chemically inert and have distinct isotopic composition in atmosphere, crust, and mantle. In addition, noble gases can exactly quantify hydrocarbon migration because each inert tracers (He, Ne, Ar, Kr, and Xe) has a unique solubility and diffusion constants when fractionated during fluid migration. So, many researchers have begun to exploit noble gases to investigate sources and potential
pathways of groundwater contamination.31,34-36,60-65

Fig. 2: Hydrocarbon gas isotope fingerprinting approaches for identifying sources of natural gas. MH: Hydrogenotrophic methanogenesis, MF: acetate fermentation, ME: methanogenesis in evaporitic environments. Reprinted from Ref. 52, Copyright (2019), with permission from the ACS.

2 Empirical and theoretical approach

Three unique geochemical characteristics of stable noble gases enhance their utility as geochemical tracers of crustal fluids:56 First, unlike the hydrocarbon composition, stable noble gases (He, Ne, Ar, Kr, Xe) are a set of non-reactive geochemical tracers. The inert nature of noble gases enables its original composition is independent of microbial activity, chemical reactions (e.g., sulfate reduction), or changes in oxygen fugacity.54,55,67 Second, the concentration of noble gases in subsurface fluids (e.g., freshwater, natural gas) are extremely low, thus, strongly fractionated noble gas ratios can be transferred between the gas or water phase, consequently, they can reflect extraordinary tiny changes in groundwater.57 Third, noble gases in geological fluids are primarily derived from three sources: atmosphere, crust, and mantle, all of which show
distinct isotopic and elemental signatures.\textsuperscript{54,68} The distinction in abundance and isotope ratios of noble gases can not only discern the sources (Table 1)\textsuperscript{69} of groundwater contamination but also identify the specific migration (Fig. 3).\textsuperscript{34,53,62}

Fig. 3: Schematic diagram illustrating noble gas components in various reservoir and their immigration.

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Table 1 Average concentrations and isotopic ratios of the principal reservoirs of noble gas compounds.\(^{69}\)

|                          | \(^4\)He | \(^{20}\)Ne | \(^{36}\)Ar | \(^{84}\)Kr | \(^{132}\)Xe | R/Ra | \(^{20}\)Ne/\(^{22}\)Ne | \(^{21}\)Ne/\(^{22}\)Ne | \(^{40}\)Ar/\(^{36}\)Ar |
|--------------------------|----------|------------|------------|-----------|------------|------|-------------------|-------------------|-------------------|
| Atmosphere (ppm)         | 5.24     | 16.5       | 31.4       | 0.65      | 0.023      | 1    | 9.8               | 0.029             | 295.5             |
| ASW\(^a\) (20°C, fresh water) \(\mu\)mol/m\(^3\) | 2.04     | 7.67       | 47.8       | 1.83      | 0.039      | 1    | 9.8               | 0.029             | 295.5             |
| MORB\(^b\) Mantle       | 36,600   | 1.04       | 1          | 0.029     | 0.004      | 8    | 12.5-13.8         | 0.06-0.063        | 40,000            |
| Continental Crust        | -        | -          | -          | -         | -          | -    | 0.02              | 0.08-0.10         | 0.4-0.52          |

\(a\). ASW: Atmospheric Saturated Water.

\(b\). MORB: Mid-Ocean Ridge Basalt.

In addition, noble gases have different solubility and diffusion constants in different fluid phases (e.g., oil, natural gas, and groundwater, Table 2),\(^{44,57-60}\) the relative fractionation of noble gases during these fluids migration could provide more information for indicating their potential migration pathways (Fig. 4).\(^{57}\) The mechanism of gas transport to shallow aquifers is the key to distinguish between natural and anthropogenic sources of hydrocarbons in groundwater. In crustal fluids, noble gases fractionate only by well-constrained physical mechanisms (e.g., diffusion, phase partitioning).\(^{54}\) The specific diffusion and solubility constants of each noble gas can quantify hydrocarbon migration, and when paired with hydrocarbon composition and inorganic water chemistry, noble gases can help differentiate between natural geological migration of hydrocarbon gases and anthropogenic contamination.\(^{34,44}\)
Fig. 4: Evolution of $^{84}$Kr/$^{20}$Ne and $^{36}$Ar/$^{20}$Ne ratios for oil, water and gas phases at thermodynamic equilibrium, for temperatures varying from 0 to 230°C, and gas/water and oil/water. Reprinted from Ref. 69, Copyright (2013), with permission from the Springer Nature.

Table 2 Parameter used in single-stage and two-stage fractionation models.

| Temperature (℃) | Salinity (M) | Henry's Constants for Water Phase (atm) |
|----------------|-------------|--------------------------------------|
|                |             | He  | Ne  | Ar  | Kr  | Xe  |
| 18             | 0           | 141451 | 118016 | 35161 | 18919 | 10624 |
| 90             | 0           | 118960 | 122481 | 64440 | 42970 | 30453 |
| 150            | 0           | 73115  | 85056  | 52966 | 40265 | 29684 |

| Temperature (℃) | Salinity (M) | Henry's Constants for Oil Phase (atm) |
|----------------|-------------|--------------------------------------|
|                |             | He  | Ne  | Ar  | Kr  | Xe  |
| 90             | 0           | 26286 | 23374 | 6078  | 2557  | 1150  |
| 150            | 0           | 15766 | 15022 | 6162  | 3103  | 2359  |
The atmospheric noble gas isotopes (e.g., $^{20}$Ne, $^{36}$Ar, $^{84}$Kr, $^{130}$Xe), which derived from solubility equilibrium with the atmosphere during groundwater recharge, are essential potential tracers for fugitive gas contamination because they have a consistent source globally and are sensitive tracers to water-gas interactions.$^{34,44,70,71}$ The phenomenon of “stripping” will occur when crustal gases migrate through groundwater, which means the atmospheric noble gases that originally dissolved in groundwater, will partition into the bubble phase and migrate quickly.$^{44,71,72}$ Meanwhile, these atmospheric gases would redistribute according to their respective solubility.$^{56}$ If subsurface fluids migrated by two-phase advection (i.e., brine + free gas) both helium and neon would be gathered in the migrated gas phase, yet, in the free gas, the concentration of light noble gas isotopes decrease with the gas/water ratio increases. However, in single-phase fluids, noble gases would not experience any quantifiable fractionation, but would also resulting in an increase in the $^4$He/$^8$CH$_4$, because of radiogenic $^4$He which came from surrounding rocks.$^{35}$ So, when the similar gas fractionation processes in gas-rich samples >1 km from drilling are spot, we could confirm hydrocarbon gases are able to migrate significant distances from target shale formations to shallow aquifers following hydraulic stimulation. Otherwise, it appears that hydrocarbon gases have not interacted with the water-saturated crust fluid, so, the most likely pathway that they migrated thousands of feet into shallow aquifers is either (a) along the well annulus, (b) through faulty or corroded casing, or (c) along legacy or abandoned wells (Fig. 1).$^{44}$

In previous studies, the isotopic composition (e.g., $^{20}$Ne/$^{22}$Ne, $^{21}$Ne/$^{22}$Ne, or $^{40}$Ar/$^{36}$Ar) and relative abundance of ASW (i.e., $^{20}$Ne/$^{36}$Ar) and crustal (i.e., $^4$He, $^4$He/$^8$CH$_4$, $^4$He/$^{20}$Ne, or $^4$He/$^{36}$Ar) gas components are often used to identify the source, mixtures, history of migration, and interactions that occur between fluids (e.g., gas and
water) in the Earth’s crust (Fig. 3 and 4). Methane, ethane, and radiogenic $^4\text{He}$ (produced by the decay of U and Th) dominate thermogenic natural gases, while $^{20}\text{Ne}$ and $^{36}\text{Ar}$ are sourced predominantly from the atmosphere, so, the $\text{CH}_4/^{36}\text{Ar}$ and $^4\text{He}/^{20}\text{Ne}$ ratios allow a direct comparison of the proportion of thermogenic natural gases and ASW components.

On the whole, these facts make noble gases ideal natural tracers for studying the sources, potential transport mechanisms, and potential pathways on groundwater contamination. And recent studies make good use of noble gases in studying groundwater quality problems in natural gas development areas.

3 Noble gas isotope instrumentation

Molecular composition can be measured by a gas chromatograph, and a quadrupole mass spectrometer (QMS) or a magnetic deflection mass spectrometer. Although gas chromatograph and QMS have several advantages over magnetic deflection mass spectrometer, it cannot analyze the low concentration isotopes in noble gases (e.g. $^3\text{He}$: $\sim10^{-13}$ cm$^3$ STP/g in groundwater, Kr isotopes: $\sim10^{-8}$ cm$^3$ STP/g, Xe isotopes: $\sim10^{-8}$ cm$^3$ STP/g) due to its low mass resolution, low sensitivity and low precision of isotope measurements. Magnetic deflection mass spectrometers were first introduced for noble gases analysis in the 1960s. Nowadays, specific noble gas isotope-ratio mass spectrometer (NG-IRMS) has been used to measure the abundance and isotopic composition of noble gases. A typical noble gas analysis system mainly contains three parts: pumping system, purification system and analytical system (Fig. 5).
NG-IRMS is a static vacuum analysis equipment which can measure extremely trace amount samples (e.g. $^3$He: $10^{-14}$ ppm), and in order to achieve this function the whole system needs to be maintained ultra-high vacuum (UHV) using Ion Pump, Turbo Pump, Diffusion Vacuum Pump, and Dry Scroll Vacuum Pumps, etc. The purification line should be stainless steel tubes and use all-metal valves, thus the whole purification system can be heated to 300 °C. The purification devices, Cold Finger (within liquid nitrogen or mixture of dry ice and alcohol), Getter (e.g., SAES® GP50 and NP10) and Titanium Sponge Furnace, should also be installed on the purification line to remove interfering gases (water vapor, C$_1$ - C$_4$, O$_2$, N$_2$, and CO$_2$, etc.). Finally, the vacuum in the mass spectrometer section is extremely high ($10^{-8}$ to $10^{-10}$ Pa), and the purification line section can acquire a vacuum of $10^{-7}$ to $10^{-8}$ Pa. The Cryogenic Trap (Fig. 6) can separate noble gas components (He, Ne, Ar, Kr, and Xe) by lowering the temperature, as the different components will condense on the condensation plate when the temperature...
lower than their respective saturated vapor pressure. Activated charcoal on the cold head of Cryogenic Trap is for better separate He and Ne.

![Schematic diagram of Cryogenic Trap and its cold head.](image)

**Fig. 6:** The schematic diagram of Cryogenic Trap and its cold head.

### 4 Sample preparation and analysis procedures

#### 4.1 Groundwater samples collection

Noble gases are highly volatile, it is important to avoid gas exchange between the water sample and the atmosphere during sampling, transport, and storage. So, appropriate containers and collection methods should be selected to get groundwater samples. There are three types of sampling vessels for water sample: Giggenbach-type container, traditional copper tube and lead-glass containers. Giggenbach-type glass container have a potential risk of helium leak. Copper tube is not
suitable for water samples containing acidic volatiles (HCl, HF, H$_2$S, and/or SO$_2$) that may react severely with copper. Lead-glass container can conquer the disadvantages of Giggenbach-type glass container and copper tube, but it cannot retain redox conditions of sulfur species.\textsuperscript{77} In recent researches, both copper tube and lead-glass containers were used to hold samples, because there were no acidic volatiles in groundwater, and no need to retain the redox conditions.\textsuperscript{34-36,59,61-63,65,66,70,73}

Groundwater may contain subsurface-produced gases (e.g. CO$_2$, CH$_4$, He) whose abundance and isotopic composition are different from those in atmosphere.\textsuperscript{81} So, it is essential to avoid contamination from atmospheric compositions when we collected groundwater samples. To avoid any air bubbles being generated or captured during sampling, the copper tube/lead-glass container should be flushed through groundwater for approximately 10 min. After groundwater sample was collected into the container, both ends of the container should be sealed underwater using pinch-off clamps,\textsuperscript{83} and groundwater must be transferred into the containers as soon as possible so that it does not have any significant gas loss or gain.
4.2 Gas Extraction and Purify

Dissolved gases must be extracted from groundwater for analyzing abundance and isotopic composition of noble gases. The ultra-high vacuum (UHV) degassing method is used for degassing dissolved gases in water. In this method, the copper tube container (Filled with >200ml groundwater samples) is directly connected to a stainless extraction vessel (with a specific volume), which will be pumped to UHV by Rotary and Turbo Pumps. When the extraction vessel pressure reduces to about $10^{-5}$ Pa, it should be separated from the vacuum pumps by closing the relevant valves. Then, one of the pitch-off clamps that close to the extraction vessel could be opened, and the sealed part
of the copper tube is reopened by a special pair of pliers. Subsequently, the water is transferred from the copper tube into the extraction vessel, and groundwater began to degas in the vessel due to the large volume and lower pressure. To enhance the degassing efficiency an ultrasonic oscillator can be used to produce turbulence in the molecular boundary layer of the water and to enlarge the active surface area of gas exchange. If a lead-glass container is used to collect groundwater samples, this extraction equipment also can be employed, and the main extraction processes are the same.

The extraction vessel is connected to the purification line. After degassing, the released gases are introduced into the purification line by opening relevant valves. Aliquots of the samples were expanded into a volume calibrated container at room temperature. Then a Cold Figure at dry ice + alcohol temperature was used to remove the water vapor. After that, samples are expanded to a Ti Sponge Furnace preheated to 900 °C and then cooled to room temperature over 15 minutes to remove interfering gases (C$_1$ - C$_4$, H$_2$O, O$_2$, N$_2$, and CO$_2$, etc.). Subsequently, samples are equilibrated with a Zr-Al getter at room temperature, to remove H$_2$. Finally, the purified samples (only He, Ne, Ar, Kr, and Xe) were pumped into a Cryogenic Trap at ~10K. Then, the samples were ready to be released and inlet into NG-IRMS for determination.

### 4.3 Noble gas measurement procedures

After the extraction and purification stages, the Cryogenic Trap was heated to 49K to release He and then inlet into the NG-IRMS for analysis, then evacuate the mass spectrometer and the storage volume. Subsequently, the temperature of Cryogenic Trap went up to 84K to release Ne and then expanded into NG-IRMS. When measure Ne, a charcoal trap (at 77.3K) mounted on the NG-IRMS is used to remove any residual $^{40}$Ar.
in order to reduce interference on the $^{20}$Ne measurements. Then, Ar, Kr, and Xe are released one by one from the Cryogenic Trap at 210K, 245K, and 290K and inlet into NG-IRMS for determination respectively. The releasing temperature of each noble gas (He, Ne, Ar, Kr, or Xe) is not the same in different studies due to the equipment condition.$^{31,59,62-66,89-91}$ He, $^{20}$Ne, $^{40}$Ar and $^{36}$Ar are generally measured on a Faraday cup. Other noble gas isotopes are usually determined on the electron multiplier in ion counting mode.$^{73,91}$

A calibrated amount of air standard and a procedural blank need to be performed before, during and after the sample analysis exactly in the same manner as the sample measurement.$^{92}$ Mass spectrometer sensitivity and mass discrimination should be calibrated by comparison to the air standards and blank data.$^{89,92}$ During noble gas isotopes analysis, appropriate mass peaks are monitored to correct the interferences caused by the doubly charged ions of $^{40}$Ar$^{2+}$ and $^{44}$CO$_2^{2++}$. $^{59,73,89,92}$ The measurement errors were ±1% and 1-5% for He and the other noble gases, respectively.

5 Applications of noble gases in groundwater contamination

Oil-water-gas partitioning processes are well recorded in the fractionation of noble gas elemental abundance. Pinti$^{93}$ and Ballentine$^{55}$ found interactions between groundwater and the hydrocarbons have been on a greater scale than often envisaged in models of hydrocarbon formation and migration and established the atmosphere-derived and radiogenic noble gases tracer system and the mode of oil-water interactions. Zhou$^{59}$ first used noble gases to construct a physical model that describes the interaction between the groundwater system and the produced gas by Rayleigh fractionation model of groundwater degassing. Darrah$^{34,35}$ provided a new application of noble gas to investigate the fugitive gas contamination of groundwater. In recent years, many researchers around the world used these theories to discuss the hotspot issues that
impacts of shale gas development on groundwater quality. The specific application cases are as follow:

5.1 Tracing sources of methane

Thermogenic natural gas is rich in Methane and Radiogenic $^4$He, while $^{20}$Ne and $^{36}$Ar are mainly from the atmosphere and enter natural gas reservoirs through the interaction with formation water. $^{4}$He/$^{20}$Ne and $\text{CH}_4$/36Ar ratios allow a direct comparison of the proportion of thermogenic and ASW components, due to the similar respective solubility constants of $^4$He and $^{20}$Ne ($\beta_{^4\text{He}}/\beta_{^20\text{Ne}}=1.2$ at 10ºC, STP) as well as $\text{CH}_4$ and $^{36}$Ar ($\beta_{\text{CH}_4}/\beta_{^36\text{Ar}}=1$ at 10ºC, STP). $^{34,35,44,60}$

The presence of methane in groundwater would lead to exsolution of noble gases. And this exsolution will be more severe for the light noble gases (e.g., $^{20}$Ne) than the heavier ones ($^{84}$Kr and $^{132}$Xe) as the lighter noble gases will go preferentially into the gas phase. $^{95,96}$ Normally, $^{20}$Ne excess in groundwater was expected to result from incorporation of excess air. $^{97}$ But heavy noble gases were less affected by the excess air component than light noble gases. $^{36}$ Wen et al. $^{36}$ collected four groundwater samples with elevated methane concentrations showed visible fractionation for $^{84}$Kr and $^{132}$Xe which caused by a continuous source of natural gas actively migrating into these water wells. However, through comparing the noble gas data of stray gas, Barnett Shale gas and Strawn Group gas they proposed that the source of stray gas in groundwater was likely the Strawn Group, not Barnett Shale. And this hypothesis was further reinforced by the fact that $F(^{132}\text{Xe}/^{36}\text{Ar})$ in water samples is not correlated with distance to the nearest natural gas well. What’s more, there is no correlation between $\text{CH}_4$/36Ar ratios and Cl concentrations in water, which indicate no anthropogenic deep brine migration.

Crustal noble gases (radiogenic noble gases) $^4$He*, $^{21}$Ne*, and $^{40}$Ar* can be also used to identify the source of methane present in the groundwater. $^{31}$ Eymold et al. $^{62}$
evaluated groundwater of Karoo Basin with a comprehensive suite of tracers including noble gas abundance and isotopic composition, and provide the first comprehensive baseline report of the groundwater characteristics for this region. In his research, the $^{4}\text{He}^*$, $^{21}\text{Ne}^*$, and $^{40}\text{Ar}^*$ correlate to each other and to various hydrocarbon tracers, which suggests a clear presence of thermogenic methane in shallow aquifers of Karoo Basin. Meanwhile, a marked excess in $^{20}\text{Ne}$ and highly elevated ratios of $^{20}\text{Ne}/^{36}\text{Ar}$ without any observable increases in $^{36}\text{Ar}$ also suggested the mixing of an exogenous thermogenic natural gas.

### 5.2 Transport mechanisms

$^{4}\text{He}/\text{CH}_4$ and $^{20}\text{Ne}/^{36}\text{Ar}$ records important clues about the transport mechanisms by which the hydrocarbon-rich brine reached the surface, because when shallow groundwater mixing with migrated gas could have elevated $^{4}\text{He}/\text{CH}_4$ and $^{20}\text{Ne}/^{36}\text{Ar}$ ratios.\textsuperscript{62,65}

Darrah et al.\textsuperscript{34} established numerical models to investigate and constrain the subsurface conditions and mechanisms of gas transport to shallow aquifers (Fig. 8). The first model mechanism (gray dash line) supposed gas and groundwater migrated as a single-phase fluid (no gas-phase, $V_{\text{gas}}/V_{\text{liquid}} = 0$). In this model, ASW derived noble gas (e.g., $^{20}\text{Ne}$ and $^{36}\text{Ar}$) would not experience any fractionation,\textsuperscript{57} but the groundwater would accumulate radiogenic $^{4}\text{He}$ from the surrounding rocks causing the increase in the $^{4}\text{He}/\text{CH}_4$. In the second and third model (solubility fractionation during the advection of a fluid with a gas phase and a 2-phase fluid), gases would partition according to their respective solubility (Fig. 4, Table 2). The solubility fractionation of noble gases associates with the $V_{\text{gas}}/V_{\text{liquid}}$, geothermal gradient, and Bunsen solubility constants.\textsuperscript{98,99} In Fig. 8, the red dashed lines indicate the temperature-dependent fractionation of $^{20}\text{Ne}/^{36}\text{Ar}$ and $^{4}\text{He}/\text{CH}_4$, the green line (fourth model) shows the
aqueous diffusion of gases and solutes within a static single-phase methane-rich brine. According to the third migration model, Darrah et al.\textsuperscript{35} proposed that Marcellus natural gases migrated from stratigraphic fractures into shallow Upper Devonian aquifers and equilibrate with groundwater. From the elevated $^{4}\text{He}/\text{CH}_4$, $^{20}\text{Ne}/^{36}\text{Ar}$, and $\delta^{13}\text{C}$, they also inferred three sequential stages of fluid migration and post-genetic alteration in northern Appalachian Basin (NAB).\textsuperscript{35}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8}
\caption{$^{4}\text{He}/\text{CH}_4$ versus $^{20}\text{Ne}/^{36}\text{Ar}$ in dissolved gas in shallow groundwater samples. The four migration models from a single source of the Marcellus gas: (1) simple 1-phase advection (gray line); (2 and 3) solubility fractionation during the advection of a fluid with a gas phase (i.e., a free-phase gas (2) and a 2-phase fluid (3)), sorted by temperature (red dashed lines); and (4) primary diffusion (green line).}
\end{figure}

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\section*{5.3 Transport pathways}

The concentrations of dissolved ASW (e.g., $^{20}\text{Ne}$ and $^{36}\text{Ar}$) can explain the
interactions that occurred between hydrocarbon gas and water.  

Significant excesses of $^{20}$Ne and correspondingly elevated ratios of $^{20}$Ne/$^{36}$Ar in NAB groundwater confirmed that fault systems may cause the transport of exogenous hydrocarbon-rich brines from Devonian source rocks into overlying Upper Devonian aquifer over geologic time and consequently contaminated the shallow groundwater in NAB. However, the groundwater samples from Piceance Basin, Colorado, did not show evidence of $^{20}$Ne/$^{36}$Ar and $^4$He/CH$_4$ enrichment, the presented hydrocarbons in shallow aquifers were attributed to substantial free-gas migration or diffusion. Methane concentrations, isotopic compositions, and noble gases showed the thermogenic methane was not due to natural mixing of gas-rich formation water with shallow groundwater or natural migration of a free-gas phase, but leaked from abandoned natural well.

The CH$_4$/$^{36}$Ar ratio can also provide information about the depth of groundwater equilibration, due to methane saturation (bubble point) increases with depth while the abundance of $^{36}$Ar is decided by ASW contributions at recharge. Darrah et al. supposed seven scenarios (Fig. 1) that could account for the elevated hydrocarbon levels in shallow aquifers overlying the Marcellus and Barnett Shales. Scenario 1 and 2 show the natural sources of hydrocarbons in groundwater. In scenario 3, the elevated hydrocarbon came from the exsolution of hydrocarbon gas already present in shallow aquifers driven by drilling activities. According to this migration mode, the released hydrocarbon must undergo a phase-separated process that would release hydrocarbon gases from brine without altering the CH$_4$/$^{36}$Ar or $^4$He/$^{20}$Ne in either the migrated gas or the residual fluid because of the similar partition coefficients between the respective gases. But scenarios 4 (well annulus), 5 (faulty casing), and 7 (legacy/abandoned wells) would transmit deep thermogenic gases to groundwater with minimal fractionation of
hydrocarbon gas, so result in high CH\textsubscript{4}/\textsuperscript{36}Ar and \textsuperscript{4}He/\textsuperscript{20}Ne ratios. Darrah’s data had higher CH\textsubscript{4}/\textsuperscript{36}Ar and \textsuperscript{4}He/\textsuperscript{20}Ne ratios in migrated gas and residual fluid, So, they concluded that the fugitive gases in shallow aquifers overlying Marcellus and Barnett Shales were leaked through annulus cement, production casings, and underground well failure rather than scenario 3 and 6.

**5.4 Combined with other geochemical data**

Bernard diagrams (C\textsubscript{1}/C\textsubscript{2+} versus \(\delta^{13}C_1\)) and Schoell diagrams (\(\delta D_1\) versus \(\delta^{13}C_1\)) often used to identify the origin of methane (Microbial, thermogenic, and/or abiotic) (Fig. 2).\textsuperscript{52} However, due to the role of secondary processes, such as migration and microbial oxidation of hydrocarbons can further alter initial gas isotope values and C\textsubscript{1}/C\textsubscript{2} ratio, the content and isotopes of methane usually insufficient step toward distinguishing sources of many natural gases (include shale gas). Eymold et al.\textsuperscript{62} investigated methane-rich spring and groundwater samples in Karoo Basin by analyzing water parameters, dissolved ion chemistry, water isotopes, major gas geochemistry, hydrocarbon gas geochemistry, compound-specific stable isotopes of hydrocarbons, noble gas elemental and isotope geochemistry. They found a series of correlations between these tracers: Helium and Neon concentrations correlate positively with methane, ethane, Cl, and Br; \textsuperscript{3}He/\textsuperscript{4}He ratio decreased with both increasing concentrations of \textsuperscript{4}He and increasing ratios of He/Ne, and it also displays significant negative correlations to \(\delta^{13}C_1\), \(\delta^{13}C_2\), and C\textsubscript{1}/C\textsubscript{2+}; The \textsuperscript{21}Ne/\textsuperscript{22}Ne correlates significantly to the proportion of \textsuperscript{4}He, salinity, the concentrations of methane and other hydrocarbon gases and hydrocarbon stable isotopes of hydrogen; The \textsuperscript{40}Ar/\textsuperscript{36}Ar also correlates strongly to salinity. Through the relation of these different geochemical data, they evaluated the characteristics of methane occurrence, source, and processes that naturally occurring hydrocarbon contamination in shallow aquifers.
6 Conclusions and perspectives

Shale gas production has dramatically increased after hydraulic fracturing and horizontal drilling were applied to shale gas development. However, coming along with energy boom, the potential for drinking-water contamination in shallow aquifers has aroused significant concerns among publics, politics and scientific, simultaneously. To evaluate the source and potential pathways of the contamination in groundwater have extremely important role in improving the drink-water quality in the areas that shale gas development. Noble gas compositions preserved in shallow groundwater do not only have chemically inert, but also have distinct isotopic and elemental signatures in the mantle, crust, hydrosphere, and atmosphere, as well as unique solubility and diffusion constants during fluid migration. All these characteristics enhance their utility as geochemical tracers of crustal fluids. So, noble gases provide an advantageous supplement for studying the occurrences, sources, and processes that methane contamination in shallow aquifers. As discussed in this study, noble gas tracers (e.g., \( ^4\text{He}/^{20}\text{Ne}, \text{CH}_4/^{36}\text{Ar}, ^{20}\text{Ne}/^{36}\text{Ar}, ^4\text{He}/\text{CH}_4, ^{84}\text{Kr}/^{36}\text{Ar}, \) and \( ^{132}\text{Xe}/^{36}\text{Ar} \)) provide increasingly important clues for determining groundwater contaminations.

From recent studies, we can easily find that noble gas tracers have been widely used in the researches of the occurrence of methane or stray gas in groundwater.\(^{44,52,61,62,100}\) Meanwhile, we should focus on variables with less variance in natural samples (e.g., ethane, compound-specific isotopes, noble gases) as opposed to the unilateral application of highly variable methane levels alone.\(^{101}\) What’s more, the multiple geochemical tracers system, that combined of noble gas elemental (He, Ne, Ar) and isotope geochemistry (\( ^1\text{He}/^4\text{He}, ^{20}\text{Ne}/^{22}\text{Ne}, ^{21}\text{Ne}/^{22}\text{Ne}, ^{20}\text{Ne}/^{36}\text{Ar}, ^{40}\text{Ar}/^{36}\text{Ar} \)), with major gas geochemistry (e.g., N\(_2\)), hydrocarbon gas geochemistry (C\(_1\)-C\(_5\)), compound-specific stable isotopes of hydrocarbons (\( \delta^{13}\text{C}_1, \delta^{13}\text{C}_2 \)), water isotopes
(δD_{H_2O}, \delta^{18}O_{H_2O}), water parameters (pH, Eh, electrical conductivity, temperature), dissolved ion chemistry (e.g., Na, Ca, Cl, Br), and tritium (\textsuperscript{3}H), could provide more powerful tools for studying the sources and migration pathways of methane contamination in shallow aquifers.\textsuperscript{44,52,62,63,101,102} Future work should focus on how to sufficiently combine noble gas data with the conventional geochemical tracers, water parameters and dissolved ion chemistry data. We should establish more and new tracer system model by correct data analysis and statistical approach to evaluate the groundwater contamination issue in natural gas development areas.\textsuperscript{101}

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