Journal of Groundwater Science and Engineering Vol.9 No.3: 245—255

Journal homepage: http://gwse.iheg.org.cn

# Source identification of methane in groundwater in shale gas development areas: A critical review of the state of the art, prospects, and future challenges

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**Abstract:** Shale gas exploration and development carry the risk of causing groundwater contamination and enhancing the greenhouse effect through methane leakage. Identifying the source of abnormal methane in groundwater of shale gas development areas is becoming a research hotspot in the fields of groundwater and climate change. This paper reviews the traditional methodology in identifying sources of methane and its deficiency in groundwater application. Then potential and advantages of using noble gases were discussed on how to overcome these limitations of the traditional method. Finally, based on noble gas, the current application status and future challenges of methane source identification in groundwater were analyzed. It can be summarized as: (1) due to chemical and/or microbial processes in the aquifer system, the traditional methodology for methane source identification, which utilizes molecular and isotopic compositions of hydrocarbon gas, has multiple interpretationsand large uncertainties; (2) the non-reactive nature and well-characterized isotopic compositions of noble gases in the atmosphere, hydrosphere, and crust, make noble gases ideal indicators of the sources of methane in groundwater. Moreover, the mechanism of formation and release of crustal noble gas prevent shale gas signatures from being interfered with by natural gas; (3) the key scientific tasks surrounding the use of noble gases for methane source identification include quantitatively separating the components of atmosphere-derived, mantle-derived, and crust-derived noble gases from the bulk noble gases in groundwater. It quantifies the solubility fractionation of noble gases induced by water-gas interaction during methane migration to the aquifer. The application of noble gases can bring a new perspective to tracing the source of methane in groundwater and is of great significance to the protection of groundwater quality in shale gas development areas and mitigation of climate change.

**Keywords:** Noble gas; Isotope; Source identification of methane; Shale gas; Groundwater

Received: 10 Dec 2020/ Accepted: 16 Mar 2021

## Introduction

Shale gas refers to unconventional natural gas that is trapped within organic-rich shale formations as free gas in cracks and matrix pore spaces, and as absorption gas (Zhang et al. 2018a; Cui et al. 2020). China has the largest shale gas exploitation potential in the world, and its recoverable shale gas resources are about 31.5 trillion $m^3$, accounting for 15% of the world's recoverable resources; this means that shale gas is expected to play a crucial role in the remodeling of China's energy structure (Tollefson, 2013; Le, 2018).

The main component of shale gas is methane. It is considered 'clean' energy, but it has a greater greenhouse effect than $CO_2$ (Jackson et al. 2020). The comprehensive thermal potential of methane is 21 times that of $CO_2$ (Sun, 2017). Since 2004, methane leakage from large-scale shale gas fields has become a significant contributor to the acceleration of global warming (Saunois et al.

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DOI: 10.19637/j.cnki.2305-7068.2021.03.007

Zheng ZX, Liu LX, Cui XS. 2021. Source identification of methane in groundwater in shale gas development areas: A critical review of the state of the art, prospects, and future challenges. Journal of Groundwater Science and Engineering, 9(3): 245-255.

2016; Gvakharia et al. 2017; Alvarez et al. 2018; Howarth, 2019; Nisbet et al. 2019).

Shallow groundwater is an essential transporter of methane, with the solubility of methane in pure water at a temperature of 17°C and pressure of 1 atm being 3.5 mg/100 mL (Osborn et al. 2011). Being able to effectively identify if the dissolved methane in groundwater originated from shale gas can lead to rapid recognition of shale gas leakages and the prevention and control measures. In addition, the USA Environmental Protection Agency (2016) issued the final evaluation report titled "Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States", which concluded that hydraulic fracturing is a potential factor in the abnormal increase of methane in groundwater in shale gas exploitation areas.

Groundwater is an important water resource in China, while methane is a flammable and explosive gas. Groundwater with high concentrations of methane poses a risk to drinking and industrial water (Sun and Xie, 2010). Therefore, the rapid expansion of shale gas development has triggered an intense public debate over possible groundwater contamination by methane and greenhouse effects through methane leakage.

It is worth noting that methane in aquifers is not only sourced from shale gas. Notably, in China's main shale gas development areas, such as Sichuan, Chongqing, and other southern regions, biogas production and application in rural areas over the last 40 years have made microbial methanogenesis another important source of dissolved methane in groundwater (Wei et al. 2010). Identifying the source of methane in the groundwater of shale gas development areas is of great significance for maintaining groundwater quality and mitigating climate change. It can help to determine whether shale gas contaminates groundwater and leaks to the atmosphere. Consequently, it is becoming a new hotspot in the fields of groundwater and climate change research (Osborn and Mclntosh, 2010; Osborn et al. 2011; Vengosh et al. 2014; Bordeleau et al. 2015; Bai et al. 2017; Mclntosh et al. 2019; Rivard et al. 2019; Sun et al. 2019; Cao et al. 2020a; Pietersen et al. 2021).

This paper systematically analyzes and summarizes the limitations of identifying sources of methane in groundwater through genetic fingerprinting of hydrocarbon gases, and looks forward to complementing the traditional identification methods and overcoming the existing problems by using the geochemical advantages of noble gases.

## 1 Traditional methodology in identifying sources of methane and its deficiency in groundwater application

### 1.1 Indicators of the source of methane based on molecular and isotopic characteristics of hydrocarbon gas and by-product gas

Deep thermogenic gas (shale gas) from kerogen pyrolysis, and shallow biogenic gas from the reductive metabolism of anaerobic microorganisms are two main sources of methane in groundwater in shale gas development areas (Osborn and Mclntosh, 2010; Osborn et al. 2011; Mclntosh et al. 2019). Effectively distinguishing between these two sources of methane can assist in the identification of abnormal methane in groundwater. Based on mechanisms of hydrocarbon generation for different genetic biogenic gases, a large number of studies have investigated the formation and evolution of molecular and stable isotope compositions of hydrocarbon and by-product gases. A series of traceable indicators and characteristic values have been obtained for the identification of methane generation.

The mechanisms of hydrocarbon generation make the molecular composition of hydrocarbons in thermogenic gas different from those in biogenic gas. Whiticar (1999) researched the generation of thermogenic and biogenic gas, and reported that thermogenic gas contains significant amounts of higher chain alkanes (e.g. ethane, propane, and butane). The ratio of the concentration of methane to higher chain alkanes (abbreviated as $CH_4/C_2H_6+$) is usually less than 100, while biogenic gas is mainly composed of methane and carbon dioxide, contains few high chain alkanes, and $CH_4/C_2H_6+$ is generally more than 1 000 (Fig. 1a). However, with the increasing degree of thermal evolution of source rocks, the relative content of high chain alkanes in thermogenic gas decreases gradually, forming a dry gas reservoir dominated by methane (Zhang, 2006). Most of China's commercial shale gas fields headed by the Fuling block in Chongqing are dry gas reservoirs (Zhang et al. 2018b). Thus, using molecular compositions of hydrocarbon gases to identify the source of methane in groundwater in China is of limited effectiveness.

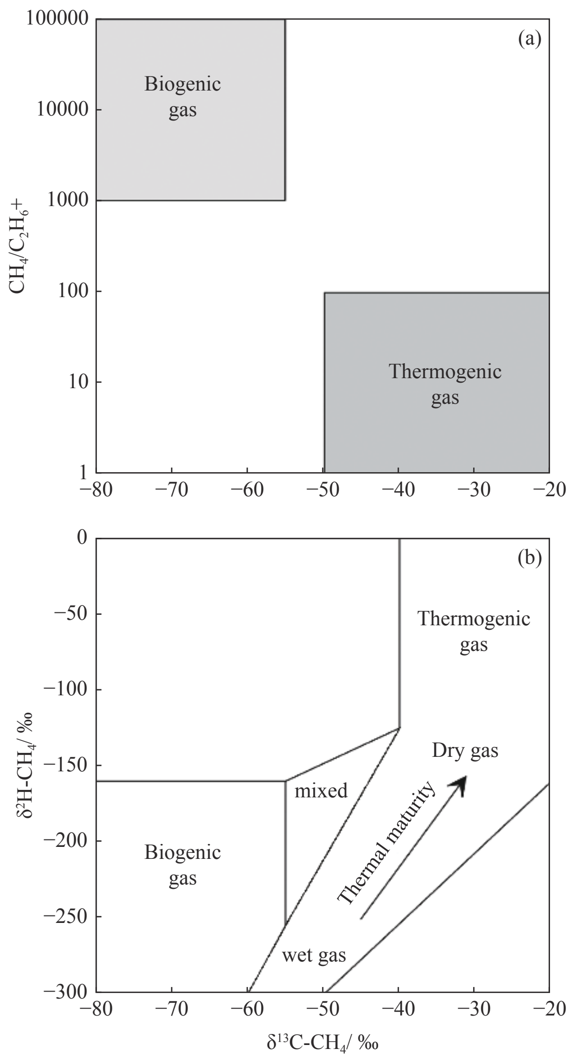

**Fig. 1** (a) Typical values of $CH_4/C_2H_6$+ versus $\delta^{13}$C-$CH_4$ in thermogenic and biogenic gas; (b) Typical values of $\delta^{13}$C-$CH_4$ versus $\delta^2$H-$CH_4$ in thermogenic and biogenic gas

With the development of isotope technology, scholars in oil and gas exploration have found that hydrocarbon isotopes change regularly with increasing maturity, migration fractionation, and microbial action during hydrocarbon generation (Qu, 2015). These findings provide not only a new theoretical basis for hydrocarbon migration tracing but also a new inspiration for gas source identification. Schoell (1980) reported that thermogenic gas is characterized by high $\delta^{13}$C-$CH_4$ (−25‰ to −50‰) and high $\delta^2$H-$CH_4$ (−240‰ to −120‰), while biogenic gas is characterized by low $\delta^{13}$C-$CH_4$ (−55‰ to −75‰) and low $\delta^2$H-$CH_4$ (−340‰ to −160‰) (Fig. 1b). According to the kinetic fractionation model of carbon isotopes in shale gas, Chung et al. (1988) stated that carbon isotopes ($\delta^{13}$C-$CH_4$ to $\delta^{13}$C-$C_5H_{12}$) have a good linear relationship with the reciprocal of carbon number. Dai (2011) determined the relationship between carbon isotopes of ethane and the maturity of source rocks, and demonstrated that the $\delta^{13}$C-$C_2H_6$ of oil gas (type I and II kerogen pyrolysis gas, the same kind as shale gas) is essentially less than −28‰. Martini et al. (1998) studied the fractionation effect of carbon isotopes in the process of methanogenesis by $CO_2$ reduction, and found that methanogens preferentially reduced the $^{12}$C, resulting in the enrichment of $^{13}$C in the gas phase; thus, $\delta^{13}$C-$CO_2$ in biogenic gas was usually greater than −20‰.

The above-mentioned traditional methodology was used in identifying the source of abnormal methane in the groundwater of shale gas development areas. Across the northeastern Appalachian Basin, the largest shale gas field in the USA, the majority of shallow groundwater had detectable methane with thermogenic stable-isotope fingerprints (e.g. $\delta^{13}$C-$CH_4$ and $\delta^2$H-$CH_4$). In northeastern Pennsylvania, a subset of shallow drinking water wells consistently showed elevated methane, ethane, and propane concentrations (i.e. relatively low hydrocarbon ratios ($CH_4/C_2H_6$+). A subset of shallow groundwater with evidence for stray gas contamination displays isotopic reversals ($\Delta^{13}C = \delta^{13}CH_4 - \delta^{13}C_2H_6 > 0$). These findings imply that the high methane in shallow aquifers from these shale gas fields is predominantly thermogenic in origin. Huang et al. (2017) determined that trace methane in the aquifer of the Fuling shale gas field in Chongqing originated from microbial acetic acid fermentation according to the characteristic values of $\delta^{13}$C-$CH_4$, $\delta^{13}$C-$CO_2$, and $\alpha^{13}C_{CH4\text{-}CO2}$ in groundwater.

## 1.2 Deficiency of traditional indicators in groundwater application

The series of carbon and hydrogen isotope characteristics provide an accurate methodology for the genetic identification of gas-phase methane. However, chemical reactions, microbial activities, and even physical processes can alter the molecular and isotopic compositions of hydrocarbons and their by-product gases, thus obscuring the original geochemical signature of genetic gases dissolved in groundwater (Fig. 2).

Oxidation of methane by methanotrophic bacteria in the aquifer reduces the value of $CH_4/C_2H_6$+, but enriches $^{13}$C in the remaining methane, resulting in biogenic gas showing the characteristics of thermogenic gas. Sulfate-reducing microorganisms preferentially oxidize high chain alkanes

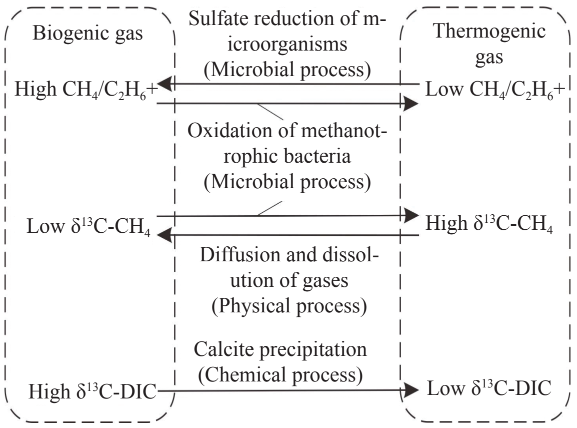

**Fig. 2** Impact of microbial, chemical, and physical processes on the traditional indicators of methane source, i.e. molecular and isotopic compositions of hydrocarbon and by-product gases

to provide electrons for metabolism, which increases the value of $CH_4/C_2H_6+$ and enriches $^{13}C$ in the remaining high chain alkanes and methane (Kessler et al. 2006), resulting in thermogenic gas that has the characteristics of a mixture containing both biogenic and thermogenic methane.

The common process of $CaCO_3$ precipitation in groundwater can also cause carbon isotope fractionation. When the precipitation rate of $CaCO_3$ is less than 40 mmol/min, $HCO_3^-$ is enriched in $^{12}C$ (Turner, 1982), thus masking the microbial signature of the by-product ($CO_2$) of biogenic methane. In addition, some physical processes can also cause large fractionation of carbon isotopes (Xia and Tang, 2012). Under specific geological and/or hydrogeological conditions, isotopically light methane ($^{12}C^1H_4$) has a higher diffusion coefficient and lower solubility than isotopically heavy methane ($^{13}C^1H_4$ and $^{13}C^1H_3{}^2H$). Therefore, during methane migration, the methane in the gas phase that would dissolve in groundwater is enriched in $^{12}C$, and $\Delta\delta^{13}C$-$CH_{4[\text{liquid phase-gas phase}]}$ can reach up to 5‰ (Pape et al. 2010).

The effects of chemical reactions, microbial activities, and/or physical processes that directly or indirectly influence the indicators of methane source can lead to multiple interpretations when using traditional methodologies identifying sources of methane in groundwater. The representative indicators of biogenic gas in traditional methods: (1) $CH_4/C_2H_6+ > 1\ 000$, can be interpreted as thermogenic gas affected by sulfate reduction of microorganisms in groundwater; (2) $\delta^{13}C$-$CH_4$ (−55 ‰ to −75 ‰), can be explained as thermogenic gas affected by diffusion and multiple dissolutions during methane migration before/after entering groundwater. Moreover, the ideal indicators of thermogenic gas in traditional methods: (1) $CH_4/C_2H_6+ < 100$, can be demonstrated as biogenic gas affected by oxidation of methanotrophic bacteria in groundwater; (2) $\delta^{13}C$-$CH_4$ (−25 ‰ to −50 ‰), can be illustrated as thermogenic gas affected by oxidation of methanotrophic bacteria in groundwater; (3) $\delta^{13}C$-$CO_2 <$ −20 ‰, can be interpreted as biogenic gas affected by calcite precipitation in groundwater. Therefore, a new method of methane source identification suitable for complex hydrogeochemical processes needs to be established. The new index system needs to meet the following criteria: (1) non-reactive nature: Unaffected by microbial activities and chemical reactions; (2) clarity: Well-characterized molecular and isotopic compositions in natural gases with different origins; (3) anti-interference: Still able to be distinguished and traced effectively after mixing of gases with different origins.

## 2 Potential and advantages of using noble gases to identify the source of methane in groundwater

Noble gases have been widely used to study the origin of geological fluids and for initial temperature tracing of fluids in the fields of oil-gas geology and metallogenic theory since their discovery due to their inert chemical behavior and distinct distribution in different layers of Earth (Ballentine et al. 1994; Aeschbach-Hertig et al. 2000; Battani et al. 2000; Ballentine et al. 2002a; Wei and Chen, 2016; Cao et al. 2020b; Ju et al. 2020; Byrne et al. 2021; Horstmann et al. 2021). Similarly, the geochemical advantage of noble gases can bring new potential to identify the source of methane in groundwater, which is expected to provide a solution to the current drawbacks of traditional methane source identification.

### 2.1 Non-reactive nature of noble gases

Noble gases are non-reactive, nonmetallic elements in group 18 of the periodic table, and include helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). Noble gases are the least reactive of all known elements. The outer energy levels of noble gases are full because each of them has eight valence electrons. The only exception is helium, which has just two electrons. However, helium also has a full outer energy level, because its only energy level (energy level 1) can hold a maximum of two electrons. A full outer energy level is the most stable arrangement of electrons. As a result, noble gases, which have octet structure, cannot become more stable by reacting with other elements and gaining or losing valence electrons. Therefore, noble gases are rarely involved in chemical reactions and rarely form compounds with other elements.

Based on noble gases, the distinguishing indicator of the methane source is not affected by the post-genetic effects such as microbial activities and chemical reactions in groundwater. It can retain the fingerprint of noble gases carried by natural gas from different origins for a long time in groundwater. Therefore, indicators of noble gas can avoid the main defects of traditional methodology in source identification of methane when applied to groundwater.

## 2.2 Well-characterized molecular and isotopic compositions of noble gas in natural gases with different origins

The distinct isotopic compositions and ratios of noble gases in the atmosphere, crust, and mantle make the differentiation of methane in groundwater based on noble gas possible (Fig. 3).

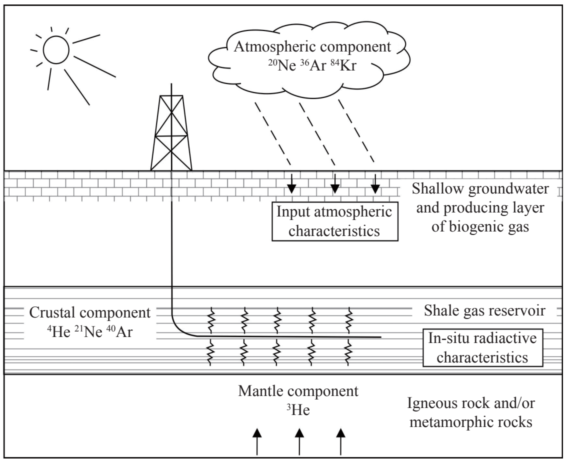

**Fig. 3** Schematic diagram of a shale gas reservoir and the methane producing layer, showing characteristic isotopic compositions in shale gas and biogenic gas. Well-characterized isotopic compositions of noble gases in the atmosphere, crust, and mantle are also plotted

The atmosphere is the main source of noble gases in groundwater, with the meteoric source of air-saturation water (ASW) being recharged to the subsurface through rainfall (Solomon et al. 1996). The unique advantage of applying noble gas geochemistry to groundwater studies is that ASW is constant globally for both characteristic isotopic compositions and its ratios (Van Der Hoven et al. 2005). The solubility of noble gases in groundwater is a function of temperature, atmospheric pressure (elevation dependent), and salinity (Aeschbach-Hertig et al. 1999). According to Henry' s law, when the noble gas reaches the dissolution equilibrium state, the solubility increases with the atomic mass of the noble gas: He < Ne < Ar < Kr < Xe (Weiss, 1971a; Weiss, 1971b).

The biogenic gas is mainly produced in the vadose zone and shallow aquifers with a typical ASW noble gas composition characterized by near solubility levels: $^{4}$He = 4.0×10$^{-8}$ to 4.5×10$^{-8}$ cm$^{3}$ STP/g; Ne = 17.5×10$^{-8}$ to 22.0×10$^{-8}$ cm$^{3}$ STP/g; Ar = 2.8×10$^{-4}$ to 4.9×10$^{-4}$ cm$^{3}$ STP/g; and $^{84}$Kr = 3.5×10$^{-4}$ to 6.9×10$^{-4}$ cm$^{3}$ STP/g (Fig. 4) (Weiss, 1971a; Weiss, 1971b; Ballentine et al. 2002a). In addition, the isotopic ratios of noble gases in biogenic gas dissolved groundwater are similar to those in atmosphere: $^{3}$He/$^{4}$He = 1.36×10$^{-6}$ or 0.983$R_a$ (Where $R_a$ is the ratio of a sample relative to the atmosphere; $^{3}$He/$^{4}$He of atmosphere = 1.384×10$^{-6}$); $^{20}$Ne/$^{22}$Ne= 9.8; $^{21}$Ne/$^{22}$Ne = 0.028 9; $^{38}$Ar/$^{36}$Ar = 0.188; $^{40}$Ar/$^{36}$Ar = 295.5; $^{20}$Ne/$^{36}$Ar = 0.13 to 0.18), and $^{84}$Kr/$^{36}$Ar = 0.035 to 0.040) (Ozima, 2002).

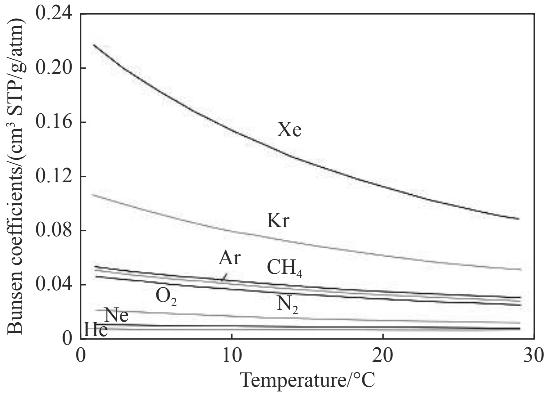

**Fig. 4** Solubility (Bunsen coefficients) of noble gases, methane, nitrogen, and oxygen in pure water with temperature

The main noble gases in the crust that are produced from the radioactive decay of U, Th, and K in minerals are $^{4}$He (from the α-decay of $^{235,\,238}$U and $^{232}$Th), $^{21}$Ne (from $^{4}$He + $^{18}$O → $^{21}$Ne + n) and $^{40}$Ar (from the electron capture decay of $^{40}$K) (Wetherill, 1954; Wei et al. 2015). Shale gas, which is generated in the deep crust, contains crustal noble gas components. Thus, shale gas has similar isotopic characteristics to crustal noble gas, which can be distinguished from those in ASW. Typical isotopic ratios of crustal noble gases are: $^3He/^4He$ = 0.01$R_a$ to 0.02$R_a$; $^{20}Ne/^{22}Ne$ = 9.6 to 10.0; $^{21}Ne/^{22}Ne$ = 0.029 to 0.060; $^{40}Ar/^{36}Ar$ = 295.5 to 1 100.0; and $^4He/^{21}Ne = 2.2\times10^7$ (Ballentine et al. 2002a). In addition, because the content of $^4He$, $^{21}Ne$, and $^{40}Ar$ in crustal noble gas is two to three orders of magnitude higher than that of ASW (Hunt et al. 2012), the indicators of methane source based on noble gases can still easily identify groundwater pollution by shale gas when a small amount of shale gas has mixed with a large amount of biogenic gas.

Therefore, well-characterized molecular and isotopic compositions of noble gas in natural gases with different origins are expected to be ideal indicators of sources of methane in groundwater.

### 2.3 Anti-interference of shale gas indicators based on crustal noble gas to conventional natural gas

Many shale gas fields in northern China (e.g. Qaidam Basin, Ordos Basin, Tarim Basin, etc.) overlap with conventional oil and shale gas fields, thus conventional natural gas carrying crustal noble gas is also a potential source of methane pollution for groundwater. Since conventional natural gas also contains crustal noble gas, the signature of groundwater methane pollution by shale gas based on noble gas can be interfered.

The formation and release of radiogenic noble gases in the crust are based on mineral composition and stratigraphic environment. Noble gases produced by radioactive decay in minerals need to pass through the binding of mineral grains to be incorporated into the geological fluid. The diffusion coefficient of noble gases, which is the key parameter in releasing noble gases from mineral grains to geological fluids, is a function of lithology and formation temperature. For example, the noble gas retentivity of quartz is higher than that of feldspar, dolomite, and clay minerals, and the diffusion coefficient increases with the formation temperature or thermal maturity (Ballentine et al. 1994; Ballentine and Burnard, 2002b). Helium which has a high diffusion coefficient compared with large atomic weight noble gases (e.g. neon and argon) because of its small atomic radius, can diffuse through quartz on geologic time scales as short as decades, especially in the high temperatures of hydrocarbon formations, and thus equilibrate with geological fluids (e.g. shale gas, conventional natural gas, and formation water) in the crust. Therefore, the content of $^4He$ in geological fluids is positively correlated with the formation age and the uranium content in the formation (Darrah et al. 2014). By contrast, $^{21}Ne$ is only released from quartz into geological fluids at higher temperatures (about 80℃) (Hunt, 2000), and $^{40}Ar$ is only released from calcite, K-feldspar, and clay minerals into geological fluids at even higher temperatures (about 220℃) (Ballentine et al. 1994).

The concentration of radioactive elements ($^{235}U$, $^{238}U$, $^{232}Th$, and $^{40}K$) in shale, the decay rate of radioactive elements (noble gas production rate), and the diffusion coefficients of $^4He$, $^{21}Ne$, and $^{40}Ar$ (which are dependent on mineral phase and formation temperature) can impart unique molecular and isotopic characteristics of noble gases onto geological fluids. This makes radiogenic noble gases a high-precision indicator of shale gas and improves the anti-interference of noble gas signatures of methane sources compared to conventional natural gas. Hunt et al. (2012) studied the formation and released mechanisms of radiogenic noble gases in typical marine black shales in the northern Appalachian Basin, and stated that the noble gases in shale gas have different isotopic characteristics from the adjacent Ordovician limestone formation. Abanda and Hannigan (2006) reported that black shales are typically enriched in uranium as a result of uranium adsorption onto organic-rich particles during sediment deposition. Wang et al. (2020) reported that the shale of the Silurian Longmaxi Formation has high contents of uranium and thorium and generated a large amount of helium while forming large quantities of hydrocarbon gases. These studies suggest that shale gas is enriched in radiogenic $^4He$ and $^{21}Ne$ compared to conventional natural gas that mainly occurs in limestone and sandstone. Therefore, shale gas and conventional natural gas have distinguishable ratios of these radiogenic gases.

## 3 Application and future challenges of using noble gas in groundwater methane source identification

### 3.1 Indicators of the source of methane in groundwater based on noble gas

The research of source differentiation of methane in groundwater based on noble gas is still in its infancy. The limited and related case studies mainly focused on the Marcellus formation in Appalachian Basin that is the largest and the most favorable shale gas reservoir in the USA (Hunt et al. 2012; Darrah et al. 2014; Darrah et al. 2015a; Darrah et al. 2015b; Wen et al. 2016; Wen et al. 2017)

The atmospheric noble gases ($^{20}Ne$, $^{36}Ar$) are essential potential tracers for fugitive shale gas contamination because they have a consistent source globally and are sensitive tracers to water-gas interactions (Ballentine et al. 2002a; Gilfillan et al. 2009; Darrah et al. 2015a). When large volumes of shale gas carrying crustal noble gases migrate through water, the normal levels of atmospheric gases decrease by "stripping" as they partition into the bubble phase and migrate buoyantly (Gilfillan et al. 2009; Darrah et al. 2013). In shallow groundwater, natural "stripping" has been observed only in volcanic and geothermal systems and above rice paddies (Gilfillan et al. 2009; Darrah et al. 2013). Hence, the decreased content of atmospheric noble gases ($^{20}Ne$, $^{36}Ar$) and increased content of crustal noble gas ($^{4}He$, $^{21}Ne$), $CH_4$ in groundwater rather than those in ASW could indicate the introductions of large volumes of shale gas in gas-phase (Darrah et al. 2015a).

Due to biogenic methane from landfills can also induce "stripping" (Dowling et al. 2002), the content ratio of noble gas may be a more sensitive indicator of methane source in groundwater. Shale gas is rich in radiogenic $^{4}He$, while $^{20}Ne$ and $^{36}Ar$ are mainly from the atmosphere. In addition, similar respective solubility constants of $^{4}He$ and $^{20}Ne$ (Bunsen coefficient ratio for $^{4}He$ vs. $^{20}Ne$ ($\beta_{He}/\beta_{Ne}$) is 1.2 at 10°C STP), as well as $CH_4$ and $^{36}Ar$ (Bunsen coefficient ratio for $CH_4$ vs. $^{36}Ar$ ($\beta_{CH4}/\beta_{Ar}$) is about 1.0 at 10°C STP) which lead to the $^{4}He/^{20}Ne$ and $CH_4/^{36}Ar$ can be used for direct comparison of thermogenic and biogenic gas after "stripping" (Byrne et al. 2017; Cao et al. 2020b). Darrah et al. (2014) suggested that fugitive shale gas contamination occurred in Marcellus shale gas fields at distances of less than one kilometerfrom unconventional drill sites, according to the elevated values of $^{4}He/^{20}Ne$ and $CH_4/^{36}Ar$ in groundwater rather than those in ASW.

In low gas to water conditions, whether it is shale gas or biogenic gas that pollutes groundwater (i.e. as $V_{gas}/V_{groundwater}$ approaches 0), trace gases with different solubilities would little fractionate as they partition from gas-phase to groundwater (Gilfillan et al. 2009; Darrah et al. 2015b). In this scenario, Darrah et al. (2015b) stated that the $^{4}He/CH_4$ in groundwater introduced by natural biogenic gas will be much lower than that in shale gas, and the $^{20}Ne/^{36}Ar$ in groundwater will remain consistent with ASW, while the $^{4}He/CH_4$ in groundwater polluted by shale gas will be much higher than that in shale gas, and the $^{20}Ne/^{36}Ar$ in groundwater will be higher than that in ASW.

The mechanism of formation and release of crustal noble gas can impart the unique signature of trace gases onto geological fluids. Thus, shale gas and conventional natural gas could have distinguishable ratios of these radiogenic gases. Darrah et al. (2014) reported that the values of $^{4}He/^{40}Ar$ and $^{4}He/^{20}Ne$ in Barnett shale gas are significantly higher than those in conventional natural gas that is produced from Strawn formation and concluded that the origin of methane in groundwater of Barnett shale gas field is Strawn-produced gas. Hunt et al. (2012) stated that the values of $^{4}He/^{40}Ar$ and $^{21}Ne/^{40}Ar$ in Marcellus shale are considerably higher than those in adjacent Ordovician source rocks that is near crustal production levels. Wen et al. (2016) placed constraints on the source of methane found in groundwater within the Barnett shale footprint in Texas by using dissolved noble gases, with particular emphasis on $^{84}Kr$ and $^{132}Xe$. They stated that lack of correlation of $^{84}Kr/^{36}Ar$ and $^{132}Xe/^{36}Ar$ fractionation levels along with $^{4}He/^{20}Ne$ with distance to the nearest gas production wells does not support the notion that methane present in these groundwaters migrated not from Barnett shale formation but from conventional natural gas produced from Strawn formation.

## 3.2 Challenge and key research tasks in future

As mentioned above, many studies have been carried out to identify the source of methane in groundwater through the comprehensive analyzes of noble gases and their isotopes. However, few studies focused on the baseline levels of radiogenic and thermogenic noble gases in groundwater before shale gas development. Affected by tritium decay, magmatic activity, and the mixing of geological fluids from non-shale gas reservoirs, young groundwater hosted in shallow aquifers of the active structure area contains crustal and mantle noble gases in natural conditions, thus masking the fingerprint of noble gases in the shale gas. Therefore, quantitative analysis of the noble gases in groundwater to determine baseline levels from the atmosphere, crust, and mantle would be one of the key tasks in establishing the theory and methodology of identifying sources of methane in groundwater of shale gas development areas. Moreover, water-gas interactions occurring during methane migration can cause molecular fractionation as a result of the solubility differences of noble gases through a free gas-phase advection or a dual-phase advection. This may increase or reduce the characteristic indicator of noble gases for methane source identification, thus affecting the sensitivity of using noble gases to identify sources of methane in groundwater. Therefore, quantifying solubility fractionation of noble gases would be another key task in establishing the theory and methodology of identifying sources of methane in groundwater.

## 4 Conclusions

(1) The traditional method of using molecular and isotopic compositions of hydrocarbon and by-product gases to identify sources of methane in groundwater is affected by chemical reactions and microbial activities occurring in aquifer systems, which can obscure the original geochemical signature of genetic gas dissolved in groundwater.

(2) The non-reactive nature and well-characterized isotopic compositions of noble gases in the atmosphere, hydrosphere, and crust make noble gases ideal indicators of distinguishing thermogenic gas and biogenic gas. Moreover, the mechanism of formation and release of crustal noble gas can impart a unique signature of trace gases onto shale gas, which can be distinguished from conventional natural gas.

(3) The contents ($^{20}$Ne, $^{36}$Ar, $^{4}$He) and ratios ($^{4}$He/$^{20}$Ne, $CH_4$/$^{36}$Ar, $^{4}$He/$CH_4$, $^{20}$Ne/$^{36}$Ar, $^{4}$He/$^{40}$Ar, $^{21}$Ne/$^{40}$Ar) of noble gas components have been used for source differentiation of methane in groundwater. However, the research of source differentiation of methane in groundwater based on noble gas is still in its infancy. The key research tasks surrounding the use of noble gases for methane source identification include quantitatively separating the components of atmosphere-derived, mantle-derived and crust-derived noble gases from the bulk noble gases in groundwater, and quantifying the solubility fractionation of noble gases induced by water-gas interactions during methane migration to the aquifer.

## Acknowledgements

This study was supported by the Basic Research Fund Project of Chinese Academy of Geological Science (SK202110), National Natural Science Foundation of China (Grant No. 41302192), Natural Science Foundation of Hebei Province of China (Grant No. D2018504011), National Natural Science Foundation of China (Grant No. 41502336), Basic Research Fund Project of Chinese Academy of Geological Science (SK202005) and China Geological Survey (Grant No. DD20190555).

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