The Use of Noble Gases to Constrain Subsurface Fluid Dynamics in the Hydrocarbon Systems

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Geochemical techniques have been widely applied to study the generation and migration of hydrocarbons in sedimentary basins over the last several decades. Diagnostic biomarkers and stable carbon and hydrogen isotopes (such as δ^{13}C and D) are generally used to identify the sources and thermal maturity of hydrocarbons and to reveal the accumulation process and mechanism of oil and gas reservoirs. However, some questions, such as secondary migration processes and pathways of oil and gas, and the relationship between groundwater flow and hydrocarbon transport, remain unclear and challenging. The low abundance and chemical inertness properties allow noble gases to serve as robust tools for tracing subsurface fluid flow. Additionally, they can be used for identifying and quantifying the role of the concomitant groundwater related to the generation and migration of hydrocarbons. This paper reviews the previous modeling work on using noble gases to study the fluid flow, flow paths, and gas/oil-water interactions in hydrocarbon systems. Noble gases from various sources can be readily identified due to their distinct isotopic and elemental signatures. Atmosphere-derived noble gases can be used to evaluate the amount of involved aquifer water associated with the hydrocarbon system and determine the groundwater migration paths and flow rates. Radiogenic noble gases accumulate over time, providing information about the subsurface fluid residence time. Questions concerning the specific trapping sites and mechanisms that affect heavy noble gas adsorption into organic sediments are still unresolved. Investigating the hydrocarbon generation, migration, and subsurface crustal fluid interactions in the hydrocarbon reservoirs can improve our understanding of noble gases as useful tracers in the subsurface environment and provide valuable geological evidence for the exploration and production of petroleum sources.

Keywords: hydrocarbon migration, noble gases, groundwater, fluid interaction, subsurface

INTRODUCTION

Oil and gas have served as useful energy sources for the rising demand for energy worldwide (Burruss and Laughrey, 2010; Darrah et al., 2014; Wen et al., 2015). In recent years, the exploration targets progressively extend to the deep reservoirs (>4,500 m), the deep-sea reservoirs (>300 m), and the unconventional oil and gas reservoirs. The unconventional reservoirs include shale oil and gas reservoirs, tight oil and gas reservoirs, and coalbed methane reservoirs (Jia, 2020; Jin et al., 2021). Meanwhile, the academic community has widely recognized the application of geochemical techniques to study the generation and migration of hydrocarbons in sedimentary basins over the last several decades. For example, the analysis of biomarkers and stable carbon and hydrogen isotopes (such as $\delta^{13}C$ and D) provides information about the types of source rock and thermal maturity, allowing further investigations on burial and thermal histories of sedimentary basins (Schoell, 1984; Zhu et al., 2007; Dai et al., 2012; Cheng et al., 2015; Volk and George, 2019). Besides, combining TOC and porosity data with burial and thermal history, the geological and geochemical models for two sets of shales were established to estimate free gas contents in organic-rich shales in the Weiyuan area of Sichuan Basin, China (Zhou et al., 2014). However, the multiple sources, complicated migration, accumulation processes, pathways, and loss of prior accumulated oil and gases complicated our understanding of oil and gas reservoirs. For example, it is difficult to determine the thermal maturities, oil types, and sources of the light oils/condensates because they barely contain high molecular weight compounds and the available geochemical information generally are limited (Peng and Jia, 2021). Therefore, efficient and robust methods and technologies are urgently required in the confront of hydrocarbon exploration and development (Larter et al., 1996; Fetter et al., 2019).

Noble gases have proven to be powerful tools to understand many geological processes better (e.g., liquid-gas interactions or gas migration) in the subsurface hydrocarbon systems due to their properties of low abundance and chemical inertness (Ozima and Podosek, 2002; Porcelli et al., 2002; Hunt et al., 2012). Noble gases consist of helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe). Noble gas production from natural radioactivity significantly modifies their isotopic signatures and provides fluid source and age information (Sano and Wakita, 1985; Smith, 1985; Kennedy et al., 1990). Similarly, small amounts of mantle-derived noble gases or atmosphere-derived noble gases in equilibrium with groundwater are readily distinguished due to their unique isotopic signatures. In addition, noble gases are unaffected by inorganic or organic chemical reactions. They are only sensitive to physical processes, such as multi-phase interaction (mixing, diffusion, and phase partitioning). These properties permit noble gases as ideal tracers for investigating the origin and evolution of subsurface fluids in oil and gas systems (Pinti and Marty, 1995; Hilton, 1996; Prinzhofer and Battani, 2003; Hunt et al., 2012; Roulleau et al., 2016; Karolytè et al., 2021; Liu et al., 2021).

This paper reviews the previous modeling work on the use of noble gases to study the fluid flow, flow paths, and gas/oil-water interactions in hydrocarbon systems. The investigation of hydrocarbon generation, migration, and subsurface crustal fluid interactions in the hydrocarbon reservoirs by using noble
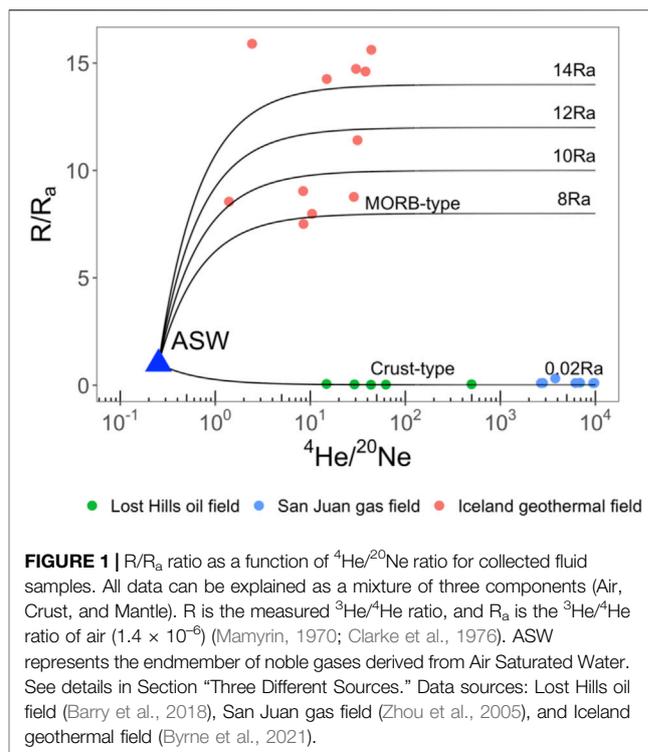

FIGURE 1 | R/R_a ratio as a function of $^4He/^{20}Ne$ ratio for collected fluid samples. All data can be explained as a mixture of three components (Air, Crust, and Mantle). R is the measured $^3He/^4He$ ratio, and R_a is the $^3He/^4He$ ratio of air (1.4×10^{-6}) (Mamyrin, 1970; Clarke et al., 1976). ASW represents the endmember of noble gases derived from Air Saturated Water. See details in Section "Three Different Sources." Data sources: Lost Hills oil field (Barry et al., 2018), San Juan gas field (Zhou et al., 2005), and Iceland geothermal field (Byrne et al., 2021).

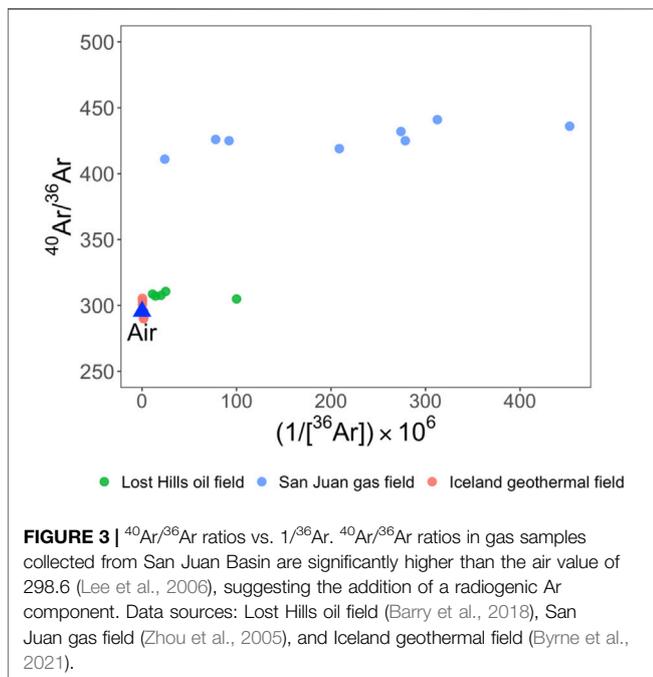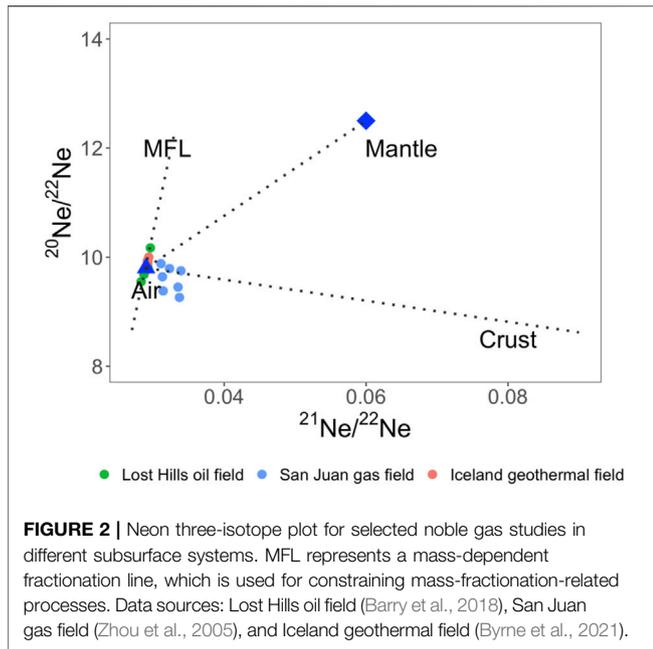gases as tracers in subsurface environments contributes to the exploration and production of petroleum reservoirs.

DESCRIPTION OF NOBLE GASES

Properties of Each Noble Gas Element

• He

Helium has two stable isotopes: ^3He and ^4He. ^3He is the primordial helium isotope originating during planetary formation and is primarily associated with tectonic and volcanic activities during geological evolution (O'Nions and Oxburgh, 1988). In contrast, ^4He is produced from the radioactive decay of U and Th in the convective mantle and crust. Atmospheric ^3He and ^4He can escape to space. ^4He can be replenished from the crust.

Due to several orders of magnitude differences in $^3He/^4He$ ratios in the crust and mantle, $^3He/^4He$ ratios are used to distinguish various crustal and mantle sources. Samples from mid-ocean ridge basalts (MORB) have uniform $^3He/^4He$ ratios of ~$8R_a$ (where R_a is the air $^3He/^4He$ ratio of 1.4×10^{-6}) (Graham, 2002), whereas the $^3He/^4He$ ratio in the crust is ~$0.02R_a$ (Graham, 2002). In addition, some ocean island basalts (OIB) samples from Hawaii and Iceland are characterized by significantly high abundance in ^3He with the $^3He/^4He$ ratios as high as $30R_a$ (Graham, 2002), suggesting the presence of mantle plumes or thermal upwelling from the deep Earth. Measured $^4He/^{20}Ne$ ratios in samples relative to the air ratio (0.032) serve as a sensitive tracer of the degree of atmospheric contamination (Sano et al., 1985; Kipfer et al., 2002; Barry et al., 2013; Wen

FIGURE 2 | Neon three-isotope plot for selected noble gas studies in different subsurface systems. MFL represents a mass-dependent fractionation line, which is used for constraining mass-fractionation-related processes. Data sources: Lost Hills oil field (Barry et al., 2018), San Juan gas field (Zhou et al., 2005), and Iceland geothermal field (Byrne et al., 2021).

FIGURE 3 | $^{40}Ar/^{36}Ar$ ratios vs. $1/^{36}Ar$. $^{40}Ar/^{36}Ar$ ratios in gas samples collected from San Juan Basin are significantly higher than the air value of 298.6 (Lee et al., 2006), suggesting the addition of a radiogenic Ar component. Data sources: Lost Hills oil field (Barry et al., 2018), San Juan gas field (Zhou et al., 2005), and Iceland geothermal field (Byrne et al., 2021).

et al., 2018). If the measured $^4He/^{20}Ne$ ratios are significantly higher than the air ratio, we can assume that the air contamination in samples is negligible (**Figure 1**).

•Ne

Neon has three stable isotopes: ^{20}Ne, ^{21}Ne, and ^{22}Ne. ^{20}Ne is produced by carbon-burning during stellar nucleosynthesis and was trapped by the Earth during accretion (Clayton, 2007), resulting in large amounts of ^{20}Ne in the air. By contrast, the

FIGURE 4 | A schematic conceptual model showing three distinct sources of noble gas isotopes modified in hydrocarbon systems, redrawn from Ballentine et al. (2002).
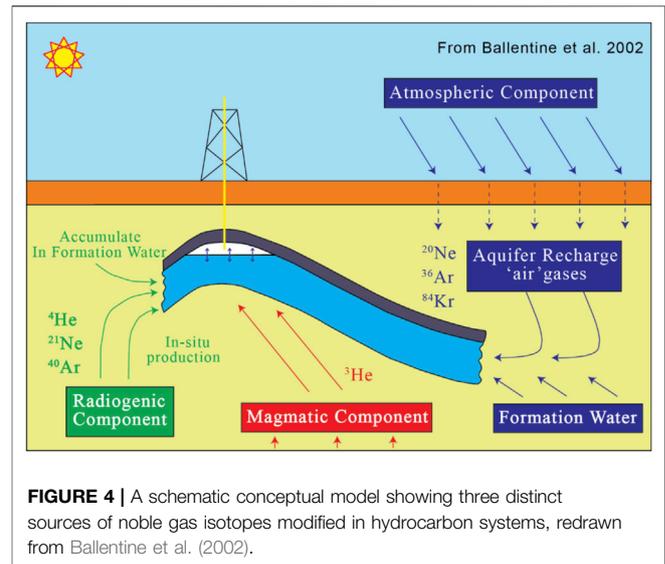
occurrence of ^{20}Ne in the crust and mantle is negligible. ^{21}Ne and ^{22}Ne are both nucleogenic, but ^{22}Ne has a relatively low abundance compared to ^{21}Ne. Similar to He, atmospheric, mantle and crustal Ne component endmembers have been readily defined ($^{20}Ne/^{22}Ne_{air}$ = 9.80, $^{21}Ne/^{22}Ne_{air}$ = 0.029, $^{20}Ne/^{22}Ne_{mntl}$ = 12.5, $^{21}Ne/^{22}Ne_{mntl}$ = 0.06, $^{20}Ne/^{22}Ne_{crust}$ = 0.30, $^{21}Ne/^{22}Ne_{crust}$ = 0.52) (Ballentine, 1997; Ballentine and Burnard, 2002). Therefore, it is possible to resolve the contribution of the atmospheric, mantle, and crustal Ne components (**Figure 2**).
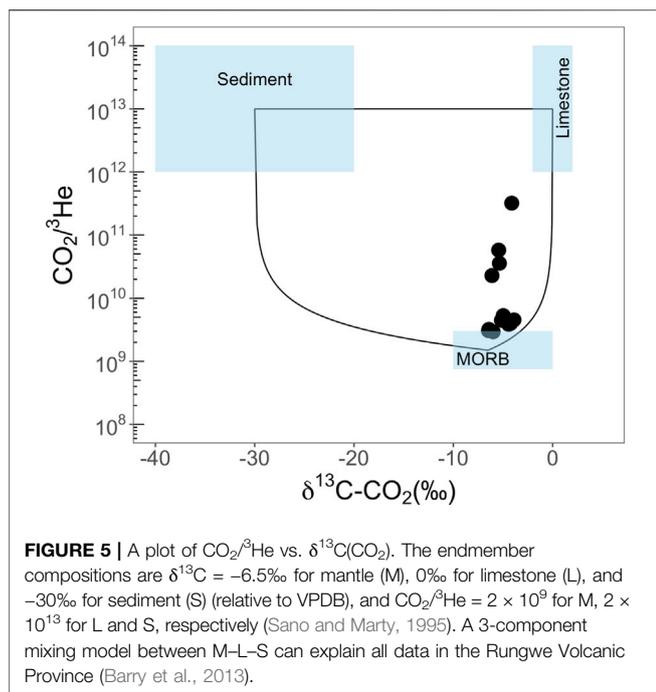
•Ar

Argon has three stable isotopes: ^{40}Ar, ^{38}Ar, and ^{36}Ar. ^{40}Ar is produced by the radioactive decay of ^{40}K in the crust, while ^{38}Ar production is dominated by the α-decay of ^{35}Cl and ^{37}Cl in the crust. ^{36}Ar production in the crust is relatively small compared to that in the air. The $^{40}Ar/^{36}Ar$ in the air is 298.6 (Lee et al., 2006). The non-atmosphere-derived excess ^{40}Ar ($^{40}Ar*$) can be calculated based on the atmosphere-derived $^{40}Ar/^{36}Ar$ ratio of 298.6 (Ballentine and Burnard, 2002) (**Figure 3**).

•Kr and Xe

Krypton and xenon have six and nine stable isotopes, respectively: ^{78}Kr, ^{80}Kr, ^{82}Kr, ^{83}Kr, ^{84}Kr, ^{86}Kr, ^{124}Xe, ^{126}Xe, ^{128}Xe, ^{129}Xe, ^{130}Xe, ^{131}Xe, ^{132}Xe, ^{134}Xe, and ^{136}Xe. Among them, ^{84}Kr and ^{132}Xe are the most abundant isotopes in each group, accounting for 57.00% and 26.89% of total Kr and Xe abundances in the air, respectively.

Three Different Sources

Noble gases in crustal fluids are derived from three sources: the atmosphere, crust, and mantle (**Figure 4**). The distinct isotopic and elemental signatures enable noble gases from various sources to be readily identified (Ozima and Podosek, 2002; Porcelli et al., 2002; Prinzhofer, 2013).

FIGURE 5 | A plot of $CO_2/^3He$ vs. $\delta^{13}C(CO_2)$. The endmember compositions are $\delta^{13}C$ = −6.5‰ for mantle (M), 0‰ for limestone (L), and −30‰ for sediment (S) (relative to VPDB), and $CO_2/^3He$ = 2 × 10^9 for M, 2 × 10^{13} for L and S, respectively (Sano and Marty, 1995). A 3-component mixing model between M–L–S can explain all data in the Rungwe Volcanic Province (Barry et al., 2013).

Three main terrestrial reservoirs for noble gases are discussed as follows.

Air Saturated Water

Atmosphere-derived noble gases (e.g., ^{20}Ne, ^{36}Ar, and ^{84}Kr) are introduced into the subsurface reservoirs by recharge water, which was previously in solubility equilibrium with the atmosphere (Air Saturated Water, ASW). Notably, these isotopes have no significant radiogenic production in the subsurface.

ASW noble gases are fractionated due to the noble gas solubility differences in the water. When the temperature is below 350 K, noble gas solubility in water generally increases with the mass, except that He and Ne have similar solubilities (Crovetto et al., 1982). The concentration of noble gases in the groundwater is associated with several factors, including partial pressure of the noble gases in the atmosphere, the temperature at which equilibration occurs, groundwater salinity, and recharge elevation (Kipfer et al., 2002). Given these quantities, ASW noble gas values can be readily calculated using Henry's law. However, it should be noted that the values predicted by Henry's law equilibration are commonly lower than empirical measurement data. This phenomenon is referred as gas surplus "excess air," which most probably results from re-equilibration of entrapped air with water (Heaton and Vogel, 1981; Kipfer et al., 2002).

Among ASW noble gases, neon is most affected by "excess air" compared to heavier noble gases. Atmospheric noble gas isotopic ratios in water are not significantly affected by the equilibrium partitioning. They are the same as those isotopic ratios in the air because the isotopes of a given noble gas have the same properties with regards to solubility.

The ASW noble gas elemental and isotope compositions in crustal fluids are critical for understanding the interactions among various crustal subsurface fluids (groundwater, geothermal fluid, oil, and gas). For example, the depletion of atmospheric noble gases caused by subsurface boiling and steam separation processes during fluid ascent has been found in many tectonically active areas, such as Los Humeros Geothermal Field (LHGF), Mexico (Pinti et al., 2017), and Atlantis II Deep, Red Sea (Winckler et al., 2000). This indicates the occurrence of a thermal event, and it is possible to reconstruct the thermal histories in those active regions (Ma et al., 2009).

In a hydrocarbon system, groundwater and hydrocarbons were concomitantly existed and synchronously evolved (Cheng et al., 2017, 2019, 2022). Since the hydrocarbon phase is initially free of atmospheric noble gases, the measured atmospheric noble gases in oil and gas reservoirs are a result of interactions between groundwater and the hydrocarbon system (Bosch and Mazor, 1988; Hiyagon and Kennedy, 1992; Pinti and Marty, 1995; Zhou et al., 2005; Byrne et al., 2018a). Consequently, the measured atmospheric noble gases can be used to evaluate the amount of involved aquifer water associated with the hydrocarbon system (Zhou et al., 2005; Barry et al., 2016), as well as to determine the groundwater migration paths and flow rates (Heilweil et al., 2012).

Furthermore, atmospheric noble gas ratios (e.g., $^{20}Ne/^{36}Ar$) can also be used to identify the extent of air contamination (Barry et al., 2016). If atmospheric noble gas ratios in samples are close to those in the air, noble gas compositions are significantly affected by air contributions. Air contamination can occur during sampling, delivery, or storage procedures. Samples contaminated by air cannot be used to discuss the initial system situation (Ballentine et al., 2002; Barry et al., 2016).

Crust

The crust contains approximately 40% of the Earth's radioactive elements (Vinogradov, 1988; Rudnick and Fountain, 1995). It serves as an important reservoir where radiogenic noble gases can be generated in addition to the atmosphere. The three most important radiogenic isotopes in the crust are $^4He^*$, $^{21}Ne^*$, and $^{40}Ar^*$, where the crustal noble gases are denoted with a "*" notation. $^4He^*$, $^{21}Ne^*$, and $^{40}Ar^*$ have different origins. $^4He^*$ is produced by spontaneous α-decay of ^{235}U, ^{238}U, and ^{232}Th. $^{40}Ar^*$ is generated due to the electronic capture of ^{40}K (Ballentine and Burnard, 2002; Ozima and Podosek, 2002). $^{21}Ne^*$ is mainly produced by reactions between α particles (derived from U-Th decay) and O, Mg, and F nuclei in crustal rocks (Wetherill, 1954).

Crustal noble gases are initially produced within the minerals/rocks and then subsequently introduced into various subsurface crustal fluid systems. The crustal radiogenic noble gas concentrations and elemental ratios in fluids are dependent on several factors, including the contents of U, Th, and K in the source and/or host rocks, production rates and release properties of different noble gases, and degree of mixing and interaction among various crustal fluids (Zartman et al., 1961; Torgersen et al., 1989; Ballentine and O'nions, 1994; Ballentine et al., 1994; Pinti and Marty, 1995; Castro et al., 1998).

For instance, some researchers have found that $^4He^*$ is easier released than $^{40}Ar^*$ at low temperatures (Mamyrin and Tolstikhin, 1984; Elliot et al., 1993; Ballentine and Burnard,

2002), resulting in the higher $^4He^*/^{40}Ar^*$ ratios in low-temperature bacterial gases compared to those in high-temperature thermogenic gases. Therefore, the ratios of crustal radiogenic isotopes (e.g., $^4He^*/^{21}Ne^*$, $^4He^*/^{40}Ar^*$, and $^{21}Ne^*/^{40}Ar^*$) are robust tools to trace the release temperatures (Torgersen and Clarke, 1985; Torgersen et al., 1989; Baxter et al., 2002).

Furthermore, radiogenic noble gas isotopes in hydrocarbon systems can be used to quantify the concentrations of $^4He^*$ in the active water phase, allowing the estimation of the subsurface fluid residence time (Zhou et al., 2005; Zhou and Ballentine, 2006; Schlegel et al., 2011; Barry et al., 2017).

In addition, the studies on the ^4He/heat flux ratio in the crust reservoirs have been used to reconstruct the past thermal events and tectonic activities that occurred in regions during geological timescales (Stute et al., 1992; Castro and Goblet, 2005; Castro et al., 2007).

Mantle

The Earth's mantle is another important reservoir for noble gas generation, accumulation, and transportation. The primordial mantle-derived noble gases were originally trapped during the early accretion of the Earth (Ozima and Podosek, 2002) and are characterized by distinct isotopic signatures. As described previously, helium is an ideal tracer of mantle contribution due to its low abundance in the air [5.24×10^{-6} cm^{3}STP (^4He)/cm^3] and distinct crustal and mantle $^3He/^4He$ ratios. However, mantle-derived helium in samples with low $^3He/^4He$ values ($0.1R_a > {}^3He/^4He > 0.02R_a$) cannot be quantified when local Li concentrations are high (small amounts of ^3He can be produced associated with neutron interactions with Li) or there are cosmogenic He contributions. In these cases, high $^{20}Ne/^{22}Ne$ ratios, $^{21}Ne/^{22}Ne$ ratios, and $^{40}Ar/^{36}Ar$ ratios should also be considered to discriminate mantle contributions.

Mantle volatiles (e.g., ^3He and CO_2) can be used to investigate the geological evolution of subsurface fluid systems as they migrate through deep-seated faults and fractures and can be subsequently trapped in the shallow crust for substantial geological periods (Sherwood Lollar et al., 1997; Gilfillan et al., 2008; Zhou et al., 2012). For example, Sherwood Lollar et al. (1997) proposed that magmatic fluids have $CO_2/^3He$ ratios ranging between 10^9 and 10^{10}. $CO_2/^3He$ ratios higher than this range would suggest negligible mantle contributions in those reservoirs. On the other hand, values below this range may be attributed to the partial loss of mantle CO_2 and dilution possibly by CH_4/N_2. Three potential endmembers (mantle (M), limestone (L), and sediment (S)) contributing to the CO_2 inventory proposed by Sano and Marty (1995) can distinguish the origin of CO_2 from different components (Barry et al., 2013; Karolytė et al., 2019) (**Figure 5**).

METHODOLOGY

Sample Collection

Because the abundances of noble gases are extremely low in the natural environment, any contact with air will significantly affect the measurement results. Therefore, careful sampling work is fundamental for subsequent successful analyses. To avoid air contamination, helium leak-tight and 50 cm long refrigeration grade 10 mm outer diameter internally polished copper tubes have been widely used for sample collection in noble gas communities (Kennedy et al., 1990; Ballentine et al., 1991; Zhou et al., 2005; Gilfillan et al., 2008). Stainless steel clamps are used to hold the copper tube during sampling. During the sampling procedure, well gases were allowed to flush through copper tubes for 10 min prior to sampling (Zhang et al., 2019; Li et al., 2020).

Sample Analysis

Noble gas abundances and isotopic ratios are generally determined using a noble gas mass spectrometer. In the laboratory, the sample copper tubes were mounted on an all-metal UHV (Ultra High Vacuum) system designed specifically to extract, purify, and separate noble gases. Most reactive gases (hydrocarbons, H_2S, CO_2, and CO, etc.) in the samples are decomposed and removed from the system using a combination of a titanium sponge and getters with no effect on the noble gases. After the removal of reactive gases, the mixture of noble gases (He, Ne, Ar, Kr, and Xe) was separated using a series of cryogenic traps prior to the inlet into the noble gas mass spec for analysis (Karolytė et al., 2019; Li et al., 2020, 2021; Byrne et al., 2021). A known amount of air standard and a procedural blank are analyzed following the same procedures as for the sample measurement prior to each sample run. The noble gas elemental abundances for each sample are calculated by normalizing to those of air standards after blank correction.

THE APPLICATION OF NOBLE GASES IN HYDROCARBON SYSTEMS

Hydrocarbon systems are complex multiphase subsurface environments, consisting of a unit of active source-rock, all related hydrocarbon accumulations, and the geological features and processes that are necessary for the hydrocarbon accumulations to exist (Byrne et al., 2018b). Noble gas geochemical analyses provide a useful technique for constraining physical behavior occurring within hydrocarbon systems. This can be used to better characterize the subsurface fluid dynamics, such as processes during hydrocarbon generation, migration, and accumulation, oil/gas-water interactions, and residence time of fluids.

Determining the Genetic Fingerprint of Natural Gas Using Noble Gas Geochemistry

Four parameters, including C_2^+ concentration, carbon and hydrogen isotope variations in methane ($\delta^{13}C(CH_4)$, δD (CH_4)), and carbon isotope variation in ethane $\delta^{13}C(C_2H_6)$, are generally used for assessing the characteristics of natural gases from different sources (Schoell, 1983, 1988). Natural gases in a gas reservoir can be classified as biogenic gas with a $\delta^{13}C(C_1)$ less than $-60‰$ and thermogenic gas with a $\delta^{13}C(C_1)$ greater than
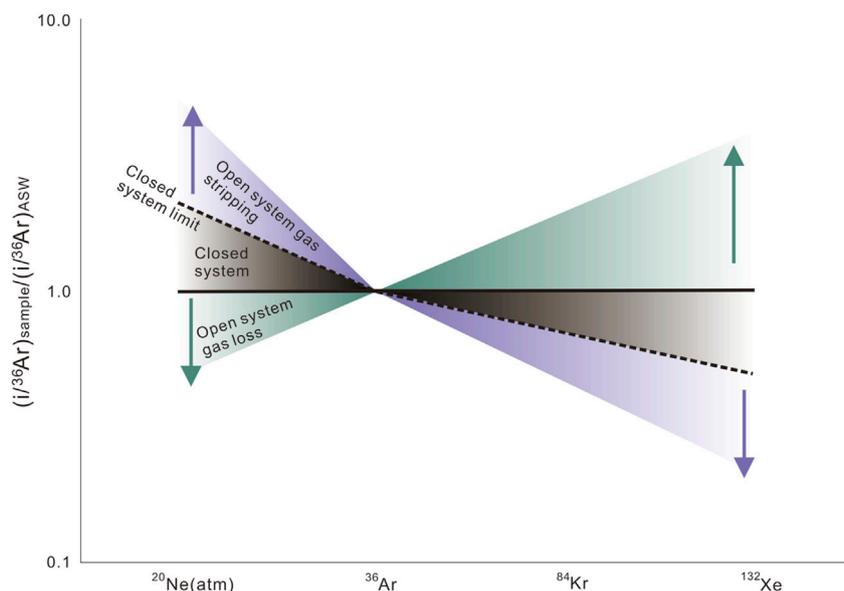
FIGURE 6 | $(i/^{36}Ar)_{sample}$ vs. $(i/^{36}Ar)_{ASW}$ plot for ^{20}Ne (atm), ^{84}Kr, and ^{132}Xe showing the expected noble gas ratios under different theoretical conditions (modified from Bosch and Mazor, (1988); Karolytė, (2019)).

−50‰ (Schoell, 1983, 1988). As thermal evolution proceeds, natural gases become more enriched in $\delta^{13}C$ and a low amount of heavier hydrocarbons (C_2^+) (Schoell, 1983; Jenden et al., 1993; Hunt et al., 2012). When the organic matter reaches the high to over-mature stage, the natural gas is characterized by almost entirely methane (C_1) with heavier hydrocarbons (C_2^+) less than 1% (Schoell, 1980, 1983; Tissot and Welte, 1984). However, traditional stable isotopes (C, H) can be affected by biological activities, chemical alterations, or redox reactions that may occur in the subsurface sometimes, which would complicate the investigation of subsurface hydrocarbon systems (Turner, 1982; Byrne et al., 2021). Noble gas isotopes serve as an additional constraint to complement existing techniques thanks to their chemical inertness. They are adequate to distinguish between different gas sources and identify possible physical processes over geological time (Hunt et al., 2012).

For example, Prinzhofer (2013) had shown that the two gas "families" had been differentiated by analyzing carbon isotope and noble gas isotope data. The $^4He/^{40}Ar^*$ ratios are higher for biological gases because ^4He is expelled more easily than ^{40}Ar from the parent mineral lattice at low temperatures. As for ASW-derived noble gases, the higher ^{136}Xe concentration in biological gases (lower $1/^{136}Xe$) suggests that biological gas underwent more interaction with the nearby aquifer water than thermogenic gas.

Noble Gases as Sensitive Tracers for Identifying Physical Processes Within Hydrocarbon Systems
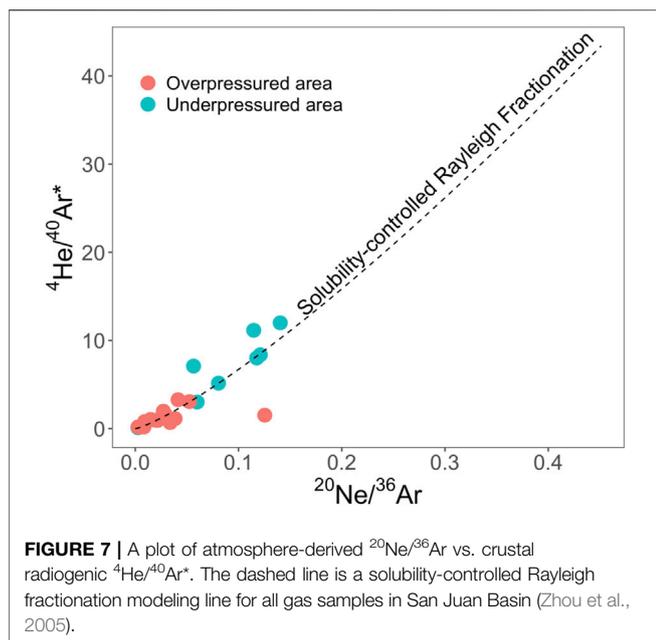
Noble gases are sensitive to physical mechanisms within a hydrocarbon system during geological timescales. Groundwater has been considered important for hydrocarbon generation,

migration, and accumulation. For example, groundwater can bring microbes into a previously sterile subsurface environment to generate biogenic hydrocarbons. In addition, groundwater can dissolve the hydrocarbons and carry them to trapping structures (Zhou et al., 2005; Schlegel et al., 2011).

To determine the extent of hydrocarbon and groundwater interactions, three possible processes that may take place during hydrocarbon-groundwater exchange have been summarized (Barry et al., 2016): (i) total degassing model, which assumes all noble gases have been lost from the water phase; (ii) equilibrium model, which means groundwater and hydrocarbon phase reached equilibrium at reservoir P, T, and salinity; and (iii) open and closed system gas-stripping models. There is no gas loss in the closed system model, while noble gases are accumulated in the reservoir due to groundwater gas stripping processes.

When the temperature is lower than 350 K, the noble gas solubility in water is positively correlated with the increase of noble gas masses (Crovetto et al., 1982). Variations in the noble gas elemental and isotopic ratios can explain the history of multi-component interactions (i.e., water–gas–oil) within a given hydrocarbon system (Byrne et al., 2018b).

Barry et al. (2016) showed that in a closed gas-stripping system, $(^{20}Ne/^{36}Ar)_{Sample}/(^{20}Ne/^{36}Ar)_{ASW}$ values in the gas phase would start from above the ASW line and then keep going down towards the line until reaching the line $(^{20}Ne/^{36}Ar)_{Sample} = (^{20}Ne/^{36}Ar)_{ASW}$. In contrast, heavier noble gases (Kr, Xe) would start from below the ASW line and then keep going up towards the line until reaching the line $(i/^{36}Ar)_{Sample} = (i/^{36}Ar)_{ASW}$. However, in an open gas-stripping system, noble gas partitioning processes would continue after noble gas ratios in the gas phase are equal to their ASW values. As a result, gases are characterized by relatively lower $^{20}Ne/^{36}Ar$ ratios and higher

FIGURE 7 | A plot of atmosphere-derived $^{20}Ne/^{36}Ar$ vs. crustal radiogenic $^4He/^{40}Ar^*$. The dashed line is a solubility-controlled Rayleigh fractionation modeling line for all gas samples in San Juan Basin (Zhou et al., 2005).

$^{84}Kr/^{36}Ar$ and $^{132}Xe/^{36}Ar$ concerning their ASW ratios (**Figure 6**).

To determine possible processes responsible for the water-oil/gas partition, an open system Rayleigh fractionation model below is most frequently used to interpret the noble gas data in many hydrocarbon systems. Rayleigh fractionation can be formulated by

$$([A]/[B])_{water} = ([A]/[B])_o \times P^{(\alpha-1)} \qquad (1)$$

where $([A]/[B])_{water}$ is the noble gas elemental ratio in the water phase, $([A]/[B])_o$ is the initial A/B ratio in the liquid (water) phase, P is the fraction of B remaining in the water phase, and α is the fractionation coefficient.

Two physical processes may occur in the hydrocarbon systems and can describe the partitioning of the noble gases between water and oil/gas phases in the subsurface. One is solubility-controlled fractionation; the other is diffusion-controlled fractionation.

The solubility-controlled fractionation coefficient is given for a gas/liquid system. α is defined as:

$$\alpha = \frac{\frac{\gamma_A}{\Phi_A}K_A^d}{\frac{\gamma_B}{\Phi_B}K_B^d} \qquad (2)$$

Dimensionless Henry's constants K^d were derived from empiric equations (Crovetto et al., 1982). Fugacity coefficients Φ and liquid activity coefficients γ were calculated following. Smith & Kennedy, (1983) and Ballentine et al. (2002).

The difference in diffusion properties in noble gases can cause preferential partitioning of noble gases from groundwater into the gas phase, as documented by Zhou et al. (2005). The mass-dependent noble gas fractionation process can generate the observed kinetic isotopic fractionation.

Assuming a gas i with mass M_i diffuses through a gas g with an average molecular mass M_g, the reduced mass M_i^* is then

expressed as follows (Marty, 1984; Jähne et al., 1987; Ballentine et al., 2002)

$$M_i^* = \frac{M_i \times M_g}{M_i + M_g} \qquad (3)$$

where M_i and M_g denote the mass of isotopes i and g, the average mass of the medium of the boundary layer where diffusion occurs. The value of M_g approaches infinity because of the large hydrogen bonds in the water phase (Zhou et al., 2005). Therefore, the reduced mass M_i^* can be equal to M_i (Jähne et al., 1987; Lippmann et al., 2003). As the diffusion coefficients are proportional to the inverse of the square root of their reduced mass, the diffusion-controlled fractionation coefficient α is defined by:

$$\alpha_{A/B} = \sqrt{\frac{M_B}{M_A}} \qquad (4)$$

where A and B denote noble gas isotopes, and M_A and M_B represent their respective masses.

For example, the isotopic fractionation of $^{20}Ne/^{22}Ne$ and $^{38}Ar/^{36}Ar$ ratios in the San Juan Basin suggested diffusion behavior caused by noble gas concentration gradients created during gas production (Zhou et al., 2005). An open system Rayleigh fractionation degassing model can interpret the relationship between water-derived $^{20}Ne/^{36}Ar$ and crustal $^4He/^{40}Ar^*$ (**Figure 7**). However, the measured ^{20}Ne concentrations are significantly lower than the values predicted by a Rayleigh fractionation-degassing model, suggesting gas that interacted with groundwater has possibly been diluted by desorbed coalbed methane. Combined with the local gas production histories, the amount of water associated with gas production can be derived at each well (Ballentine et al., 1991; Zhou et al., 2005).

Quantitative Estimates of Gas-Water Ratio

As discussed previously, groundwater plays a significant role in establishing the noble gas systematics of hydrocarbon systems. Knowledge of the connected water volumes and the extent of water-gas exchange can help better understand subsurface fluid transport pathways and the subsequent involvement of water with reservoir processes (Robinson and Gluyas, 1992; Aplin et al., 1993; Ballentine et al., 1996). Additionally, groundwater behavior also has significant implications for hydrocarbon resource prediction.

When hydrocarbons interact with air-saturated formation water in the subsurface environment, noble gases are easily migrated into the hydrocarbon reservoirs due to the relatively low solubilities in the water phase. It is assumed that hydrocarbons are initially devoid of any atmospherically derived noble gases, which can be introduced into the hydrocarbon reservoir during gas-water exchange processes (Bosch and Mazor, 1988). Therefore, ASW noble gases can serve as useful tracers for assessing the extent of hydrocarbon–water interaction (e.g., volumetric gas/water (G/W) ratio). This helps to better understand hydrocarbon production, accumulation, migration pathways, and reservoir

conditions (Bosch and Mazor, 1988; Ballentine et al., 1991; Barry et al., 2016, 2017).

With knowledge of the initial noble gas composition of the air-saturated water (determined by groundwater recharge conditions) and measured noble gas concentrations in the hydrocarbon phase, it is possible to constrain the processes (i.e., open vs. closed system) and quantify the extent of hydrocarbon-water interaction, and thus predict a volumetric gas/water (G/W) ratio. Barry et al. (2017) had suggested the relatively lower V_g/V_w from noble gas estimates than static geological forecasts occurs because the "geological" assessment of gas–water volumetric ratios only consider gas and water volumes in the local reservoir without the consideration of any water or gas present in deeper structures, migration pathways or source rock. Therefore, gas water ratio calculations using noble gases can provide more effective tools for constraining all formation water encountered in the hydrocarbon system, not only the reservoir interval.

Fluid Residence Time Determination

Knowledge of groundwater ages is vital for subsurface resources (such as hydrocarbon and groundwater) investigation and exploration. The accumulation of crustal radiogenic components (e.g., ^{4}He, ^{21}Ne, ^{40}Ar) in the groundwater can provide useful information for groundwater-dating studies (Zhou and Ballentine, 2006; Schlegel et al., 2011; Wen et al., 2015; Byrne et al., 2018b). For example, ^{4}He dating results in the Illinois Basin showed that older groundwater ages were associated with thermogenic methane. In comparison, younger ages were associated with microbially generated methane, suggesting that noble gas dating tools can constrain the onset and extent of microbial methane generation (Schlegel et al., 2011).

Fluid residence time can be estimated based on resolved radiogenic noble gases (e.g., ^{4}He, ^{21}Ne, ^{40}Ar) that accumulate in subsurface fluids due to radioactive decay of uranium, thorium, and potassium over geologic timescales (Torgersen and Clarke, 1985; Castro et al., 1998; Ballentine and Burnard, 2002; Barry et al., 2017). Due to the low solubilities in the groundwater, noble gases will preferentially partition into the gas phase during water-gas interactions. Water-gas interactions also result in the migration of accumulated crustal noble gases and other dissolved atmospheric noble gases (e.g., ^{36}Ar) from the water to the gas phase (Ballentine et al., 1991; Zhou and Ballentine, 2006). Therefore, crustal and atmosphere-derived noble gases allow us to estimate the initial crustal noble gas concentrations in the water phase prior to the phase separation and, thus, to acquire residence times for the associated water phase (Zhou et al., 2005; Zhou and Ballentine, 2006; Schlegel et al., 2011).

Radiogenic residence time in the fluid is calculated for two scenarios: (1) It is assumed that only *in-situ* radiogenic noble gases (^{4}He, ^{21}Ne*, ^{40}Ar*) have accumulated in the reservoir, called a "closed" system. (2) In addition to *in-situ* production, an external crustal noble gas flux (upper crust + lower crust) has been introduced into the study area on a geological timescale. In this "open system," it is assumed that the external crustal source is uniform across the sedimentary basin. Therefore, the amount of

crustal radiogenic components in the groundwater system can be expressed as:

"Closed" system

$$[C_i]_{H2O} = [C_i]_{in\,situ\,production} \tag{5}$$

"Open" system

$$[C_i]_{H2O} = [C_i]_{in\,situ\,production} + [C_i]_{external\,flux} \tag{6}$$

where $[C_i]_{H2O}$, $[C_i]_{in\,situ\,production}$, and $[C_i]_{external\,flux}$ are the concentrations of the isotope i accumulated in the water, produced *in situ* and external flux (cm^{3}STPg^{-1} H$_2$O), respectively.

The *in-situ* production of isotope i can be expressed as:

$$[C_i]_{in\,situ\,production} = \frac{\rho \wedge P_i(1-\varphi)}{\varphi}t \tag{7}$$

where $\rho_{aquifer}$ is the density of aquifer (g/cm^3), Λ is release efficiency from mineral to water, which is assumed to be 1 (Torgersen, 1980; Torgersen and Clarke, 1985), φ is rock porosity, t is groundwater residence time (years), and P_i is the crustal production rate of isotope i in the reservoir rock (cm^{3}STPg^{-1} yr^{-1}).

As the radiogenic ^{4}He, ^{21}Ne*, and ^{40}Ar* are produced by radioactive decay of uranium, thorium, and potassium over geologic timescales (Ballentine and Burnard, 2002), the production rate P_i can be calculated using the following equations (Craig and Lupton, 1976; Torgersen, 1980; Ballentine and Burnard, 2002)

$$P_4 = 0.2355 \times 10^{-12} \times [U] \times \{1 + 0.123 \times ([Th]/[U] - 4)\} \tag{8}$$

$$P_{21} = \{(1.48 \times [U] + 0.186 \times [Th]) \times [O] + (0.105 \times [U] + 0.0179 \times [Th]) \times [Mg]\} \times 10^{-22} \tag{9}$$

$$P_{4/40} = \{(3.115 \times 10^6 + 1.272 \times 10^5) \times [U] + 7.710 \times 10^5 \times [Th]\}/(102.2 \times [K]) \tag{10}$$

where P_4, P_{21}, and P_{40} denote the production rates of ^{4}He, ^{21}Ne*, and ^{40}Ar* in the rock, respectively. [U], [Th], and [K] are the U, Th, and K concentrations in the rock in ppm, respectively. [O] and [Mg] are O and Mg contents in the rock.

$[C_i]_{external\,flux}$ can be calculated by

$$[C_i]_{external\,flux} = \frac{F_i}{\varphi h}t \tag{11}$$

$$F_i = P_i \times \rho \times H \tag{12}$$

where F_i represents the average external crustal radiogenic isotope flux (^{4}He, ^{21}Ne*, ^{40}Ar*), ρ_{crust} denotes the density of the crust, H denotes the thickness of crust (cm), and h denotes the thickness of aquifer (cm).

It has been shown that in most sedimentary basins, such as the Michigan Basin and San Juan Basin, the addition of external crust flux into the reservoir is present and must be considered in the calculation of groundwater ages (Zhou and Ballentine, 2006; Schlegel et al., 2011; Wen et al., 2015; Byrne et al., 2018a). Several orders of magnitude differences in these two sets of

radiogenic ages strongly suggest that *in-situ* production is negligible compared to external flux additions. The significantly younger residence time than reservoir formation age indicates no significant preservation of formation water.

Heavy Noble Gas Enrichment

Oil and gas fields in contact with ancient basinal brine often show excesses of $^{84}Kr/^{36}Ar$ and $^{130}Xe/^{36}Ar$ relative to those values found in ASW. $^{130}Xe/^{36}Ar$ enrichment factors up to ~200 relative to those ASW values have been observed in various systems, such as the Elk Hills oil field, California and Delaware Basins, and SE New Mexico (Torgersen and Kennedy, 1999; Kennedy et al., 2002; Holland et al., 2013).

Two possible mechanisms may be responsible for these observed heavy noble gas enrichments. The first is gas-oil interaction, and the second is the release of heavy noble gases initially trapped on source rocks. Bosch and Mazor (1988), Kharaka and Specht (1988), and Barry et al. (2016) have shown that the interactions between oil and gas can result in the relative abundance pattern of heavy noble gases enrichment. Heavy noble gas elemental fractionation patterns are much more extreme than light noble gas elemental fractionation patterns during the interaction with oil. However, it is still elusive to constrain the influence of oil on heavy noble gases. The second reason for heavy noble gas enrichments can be potentially attributed to the addition of sedimentary components from the source rock during geological evolution. Similar Kr-Xe enrichments have been observed in gas reservoirs in the North Sea (M. C. van Soest et al., 2000), natural gas samples from the Sleipner Vest gas field (Barry et al., 2016), and coalbed gases from the San Juan Basin (Zhou et al., 2005). They suggested that atmosphere-derived heavy noble gases (Kr and Xe) can be initially adsorbed and trapped in organic-rich sedimentary lithologies (e.g., shales and cherts), then escape into the fluid system and mixed with the hydrocarbon phases, providing an additional source of these noble gases. These "additional" components have an isotopic composition indistinguishable from the air but lead to a relative gas abundance pattern highly enriched in the heavy noble gases (Kr and Xe) (Torgersen and Kennedy, 1999; Kennedy et al., 2002). Questions concerning the specific trapping sites and mechanisms that affect heavy noble gas adsorption are still unresolved (Torgersen and Kennedy, 1999).

CONCLUSION

The application of noble gases in understanding hydrocarbon reservoirs has been increasing in recent years alongside improved measurement techniques, allowing the measurement of more noble gas isotopes with better accuracy and precision. However, difficulties in interpreting noble gas results still hinder the adoption of noble gas analysis as a routine geochemical analytical tool in hydrocarbon systems. For example, the noble gas-derived gas/water ratios are lower than static geological estimates. This is because the entire history of

hydrocarbon-water interaction within the system has been considered during calculation rather than only considering the accumulation itself. Besides, the mechanisms that can absorb heavy noble gases into organic-rich sediment are yet to be resolved. Their explanation would benefit the investigation of adsorption versus free gas stored in porosity. Despite some limitations, noble gas isotope characterization has the obvious advantage that complications arising from chemical reactions can be confidently neglected and the assumption of ideal gas behavior is likely to be much closer to reality than for other gas species (Byrne et al., 2021). Noble gas isotopic composition and abundance can be used to place constraints on fluid sources, their mass balance, phase interactions, and the mechanisms of transport required to bring the fluid to the site of sampling. We therefore suggest that the use of noble gases may provide a robust tool for future research into subsurface hydrocarbon systems.

This paper summarizes noble gases studies on constraining origin, migration, and accumulation processes of crustal fluids in the hydrocarbon systems, providing further insights into underground fluid dynamics. The combination of noble gases and stable carbon isotope approaches can effectively differentiate distinct genetic groups of natural gases. Noble gas elemental and isotopic compositions can be used to construct physical models to describe the interaction between natural gas, oil, and groundwater, improving our understanding of the role of groundwater in different systems. These models can also be applied to estimate groundwater radiogenic noble gas concentrations that can be used to date hydrocarbon-associated water as well as the volume of water associated with hydrocarbon generation. An improved understanding of the applicability of noble gases as effective tracers in subsurface environments will aid scientific and regulatory evaluation of natural systems (e.g., hydrocarbon and groundwater) and subsurface exploration and development.

AUTHOR CONTRIBUTIONS

YL, HFH, and CC conceived the study. HYH performed data interpretation. HFH provided funding and supervision. YL wrote the manuscript with assistance and editing from all co-authors.

FUNDING

ACKNOWLEDGMENTS

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