

Characterizing the Noble Gas Isotopic Composition of the Barnett Shale and Strawn Group and Constraining the Source of Stray Gas in the Trinity Aquifer, North-Central Texas

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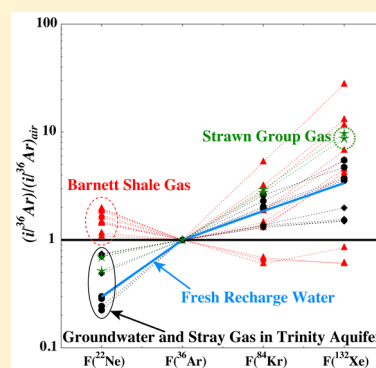
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Supporting Information

ABSTRACT: This study presents the complete set of stable noble gases for Barnett Shale and Strawn Group production gas together with stray flowing gas in the Trinity Aquifer, Texas. It places new constraints on the source of this stray gas and further shows that Barnett and Strawn gas have distinct crustal and atmospheric noble gas signatures, allowing clear identification of these two sources. Like stray gas, Strawn gas is significantly more enriched in crustal $^4\text{He}^*$, $^{21}\text{Ne}^*$, and $^{40}\text{Ar}^*$ than Barnett gas. The similarity of Strawn and stray gas crustal noble gas signatures suggests that the Strawn is the source of stray gas in the Trinity Aquifer. Atmospheric $^{22}\text{Ne}/^{36}\text{Ar}$ ratios of stray gas mimic also that of Strawn, further reinforcing the notion that the source of stray gas in this aquifer is the Strawn. While noble gas signatures of Strawn and stray gas are consistent with a single-stage water degassing model, a two-stage oil modified groundwater exsolution fractionation model is required to explain the light atmospheric noble gas signature of Barnett Shale production gas. These distinct Strawn and Barnett noble gas signatures are likely the reflection of distinct evolution histories with Strawn gas being possibly older than that of Barnett Shale.



INTRODUCTION

Despite low or moderately rising natural gas prices, projected production of natural gas from unconventional shale gas and tight oil plays are forecasted to increase from 13.6 Tcf (trillion cubic feet) in 2015 to 29.0 Tcf in 2040 due to abundant domestic resources and technology improvements (e.g., hydraulic fracturing (HF) and horizontal drilling).¹ As a result, their share of total U.S. dry natural gas production will grow from 50% in 2015 to 69% in 2040.¹ Such a dramatic expansion of unconventional natural gas production has ignited public concern that production activities such as HF may allow migration of natural gas from targeted formations such as the Marcellus or Barnett Shales (depth of 1800 m to >2000 m) into shallow aquifers (<500 m), thereby threatening drinking water supplies.

The presence of stray gas in shallow groundwaters has been reported both within the Marcellus and Barnett Shale footprints.^{2–7} Stray gas in groundwaters may originate from shallow or deep thermogenic gas accumulations^{2,4,6–9} of natural or anthropogenic origin, from shallow microbial sources^{10–12} or from a combination of both.^{10,13–15} Here, “stray gas” refers to natural gas present in shallow aquifers of an undetermined origin. In particular, within the Barnett Shale footprint in the Fort Worth Basin, a few groups have investigated the presence

of elevated levels of methane in the shallow Trinity Aquifer with respect to its source and migration mechanisms.^{6,7,16,59}

While these studies agree that the shallow Strawn Group is likely the source of the stray gas in the Trinity Aquifer, they diverge with respect to an anthropogenic versus natural origin. Earlier studies using a combination of carbon isotopes and light noble gases⁶ concluded that the presence of stray gas in the Trinity Aquifer may have an anthropogenic origin due to faulty production wells.⁶ In contrast, a more recent study of Trinity groundwaters using the entire set of stable noble gases supports a natural origin for this stray gas and argues that some of the drinking water wells reached noncommercially exploited natural gas accumulations in the Strawn Group.⁷

Kornacki and McCaffrey¹⁶ tentatively concluded that stray gas in the Trinity Aquifer in Parker County is of thermogenic origin migrating from the Strawn Group as opposed to the Barnett Shale. Their conclusions were based on nitrogen and carbon dioxide contents of groundwater and hydrocarbon samples. However, microbial activity and oxidation can alter the

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original geochemical signature and thus, obscure the original sources and/or mechanisms of fluid migration.^{3,17} In contrast, stable noble gases (He, Ne, Ar, Kr, and Xe) are chemically inert and are thus transported without being affected by chemical reactions.^{18,19} Noble gases in subsurface fluids (e.g., freshwater and natural gas) are derived from the atmosphere, crust, and mantle, all of which show distinct isotopic and elemental signatures.^{18–22} This makes noble gases ideal natural tracers for studying the origin and evolution of crustal fluids in sedimentary basins.^{14,23–31} In most subsurface fluids in sedimentary systems, noble gases are dominated by an atmospheric origin (Air Saturated Water or ASW) and/or a crustal component deriving primarily from radioactive decay of U, Th, and ⁴⁰K.¹⁸ Here, the crustal component is identified with the “*” notation.

In this study, analyses of the complete set of stable noble gases are presented (He, Ne, Ar, Kr, and Xe) for Barnett Shale and Strawn Group production gas together with stray gas, i.e., a gas phase present in the Trinity Aquifer in Parker and Hood counties, Texas. Both atmospheric and crustal noble gas volume fractions and isotopic ratios are provided. This new production gas and stray gas data set, together with recently published groundwater noble gas data from the Trinity Aquifer,⁷ places new constraints on the source of stray gas in the shallow Trinity Aquifer and further shows that Barnett Shale and Strawn Group production gas have distinct crustal and atmospheric noble gas signatures allowing clear identification of these two sources. This new comprehensive noble gas data set reinforces the notion that the source of stray gas in the Trinity Aquifer is indeed the Strawn Group as opposed to the Barnett Shale. Of greater significance, however, this study demonstrates that noble gases alone can be used with confidence to discriminate between different natural gas sources in hydrocarbon reservoirs to identify the sources of gas phases (flowing natural gas) present in shallow groundwaters. This is accomplished through the introduction of two novel approaches: (1) measurement and analysis of the entire set of stable noble gases in shale gas, and (2) simultaneous analysis of both, natural shale gas from different sources as well as natural gas phases present in groundwater, allowing for direct comparison of these different signatures and therefore, fingerprinting of this flowing gas. This new noble gas technique, which, in addition to incorporating the entire set of noble gases combines analysis of both crustal and atmospheric components, should present a significant advancement to assist in studies of groundwater contamination by stray gas by making possible not only identification of the flowing gas source (stray gas) but also aiding at determining whether or not the presence of stray gas in groundwater is natural or anthropogenic (e.g., Wen et al.⁷).

MATERIALS AND METHODS

Barnett Shale, Strawn Group, and Trinity Aquifer. The Fort Worth Basin, where the Barnett Shale and Strawn Group are located, is a north–south elongated trough covering roughly 38 100 km² in north-central Texas in the southern United States (Figure S1 of the Supporting Information, SI).^{32,33} It is floored by a Precambrian basement. The Barnett Shale of Late Mississippian age (~331–323 Ma) is the primary petroleum source rock in the Fort Worth Basin and found at a depth of ~1800 m in the study area (Figure S2).^{32–36} The thickness of the Barnett shale varies from >330 m in the core area to between 60 and 120 m in the counties at the periphery including in Parker and Hood counties.⁵⁹ The Barnett Shale

cropps out south of Hood County next to the Llano Uplift where Precambrian rocks are exposed. The Barnett Shale gets thicker and deeper toward the northeast of its domain close to the intensively drilled core area. Overlying the Barnett Shale are, from oldest to youngest, the ~150–200 m thick Marble Falls (mostly carbonates) and ~600–700 m thick mostly siliciclastic Bend/Atoka Formations, of Late Mississippian and Lower Pennsylvanian age (~323–299 Ma).^{37,38} In Parker and Hood counties, the Strawn Group is >750 m thick and dips toward the northwest. The Strawn Group is a fluvio-deltaic system comprised of sandstone units and shales with some limestones.³⁸ Unlike the Barnett Shale, the Strawn group is not a source rock.³³ The Lower Strawn (Pennsylvanian Kickapoo Creek Formation) is shale rich and contains sand bodies sometimes charged with hydrocarbons.³⁸ Its top subcrops in the Parker-Hood cluster area where it is unconformably overlain by Cretaceous rocks of the Trinity Group. The Cretaceous sequence locally contains basal sand-dominated strata (Twin Mountain Formation) overlain by carbonate-dominated strata forming bluffs (Glen Rose Formation).⁴² All Cretaceous formations dip toward the east and have been eroded in western Parker County. The Strawn Group and the overlying Cretaceous formations also include minor coal seams.^{16,39,40} Montgomery et al.³⁴ and Pollastro et al.³³ suggested that significant migration of hydrocarbons, both oil and gas, occurred from the Barnett Shale into the Strawn Group over time, thereby charging commercially produced reservoirs. In addition, the presence of many randomly distributed noncommercially exploited natural gas accumulations in the Strawn Group are known to exist.³⁷ The timing of migration, however, is poorly constrained. Large sections of the basin have also undergone conventional production for decades, including the study area where most of the produced gas originated from the Strawn Group.

The Cretaceous Trinity Group hosting the Trinity Aquifer is the main source of drinking water in Parker and Hood counties.^{16,41} In the study area, the Cretaceous sedimentary cover is very thin (<200m³⁸). Basal sands of the Trinity Group overlie the Strawn Group in an angular unconformity (Figure S2).^{16,42} Predevelopment hydraulic heads in the Trinity Aquifer indicate that the general direction of flow in the study area is along dip from the outcrop to the east.⁴²

There are no mapped faults at the surface in Parker and Hood counties but several exist at depth, impacting at least some of the Paleozoic section. In addition to the Ouachita thrust belt on the eastern edge of the Barnett, a major fault, “the Mineral Wells fault”, trending SW–NE is present in southern Denton and northern Parker counties (Figure S1).^{33,43} This fault, which was active throughout the Paleozoic, appears to be rooted in the Precambrian basement.^{33,34} Several minor normal faults parallel to it are present in the Fort Worth Basin, including in southern Parker county.³³

Sampling and Analytical Methods. Eleven wells were sampled (Figure 1, Table S1) in Parker and Hood Counties, in North-Central Texas for collection of 15 natural gas samples for analysis of volume fractions and isotopic ratios of He, Ne, Ar, Kr, and Xe (Tables S2 and S3). These include four stray flowing gas samples (gas phase in the subsurface) from two wells drilled as water wells but with flowing gas and abandoned due to gas lock of the water pumps, ten gas samples from eight Barnett Shale production wells and one gas sample from a Strawn Group production well (Tables S2 and S3). Samples for noble gas analyses were collected in copper tubes.^{14,44} Gas

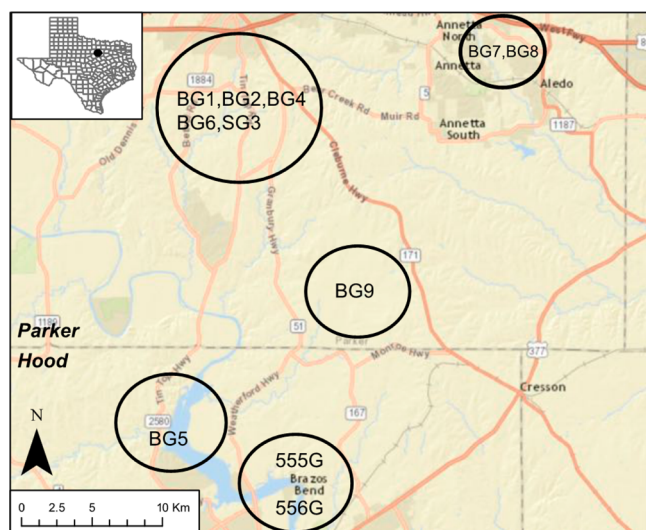


Figure 1. Approximate location of all collected stray gases from water wells and production gases from Barnett and Strawn gas wells.

samples collected at water well 555G and 556G as well as production wells BG5 and BG9 carry the A and B notation for first and second sample collected, respectively. An inflatable bladder was used as packer to isolate a short section of the wellbore above the water level. The natural-gas pressure buildup purged the air from the restricted section and allowed easy sampling at the surface. The air column in water well 556G was purged for approximately 30 min prior to collecting sample 556GA and for an additional 30 min prior to collecting sample 556GB. Because purging time is longer prior to collecting sample 556GB than sample 556GA, less air contamination is expected in 556GB compared to 556GA. For all other wells, atmospheric contamination during sampling was minimized by allowing the natural gas to flush through the system for approximately 10 min. Three copper tubes (555GB, BG2, SG3) were clamped and divided into 2 segments. Each segment of gas sample was measured individually for noble gas volume fractions and isotopic ratios. All replicated analyses from the same copper tube are listed with the suffix -1 or -2 (Tables S2 and S3).

Noble gas measurements were carried out in the Noble Gas Laboratory at the University of Michigan. He and Ne were analyzed in a Thermo Scientific Helix SFT mass spectrometer while Ar, Kr, and Xe were sequentially inlet into an ARGUS VI mass spectrometer using a computer-controlled double-head cryo-separator. Extraction, purification, and analysis procedures are described in detail in SI Text S1.

Stray gas and produced gas were collected using Isotech Isobag and Isotube technologies, respectively, for measurement of abundances of methane (CH_4). Produced gas was analyzed by Isotech. Stray gas analyses for individual hydrocarbon and nonhydrocarbon gas components were carried out at the University of Texas at Austin using a two-channel Agilent 7890 Series Gas Chromatograph (GC). Detector responses have been calibrated using certified gas standards from Airgas, Inc. at a precision of ± 1 mol % for each compound. No methane content is available for well 555G due to air contamination.

RESULTS AND DISCUSSION

Noble Gas Signatures versus Methane Content. Sample ID, sampling date, well depth, and methane abundance

are provided in Table S1. Total dissolved ^4He , ^{22}Ne , ^{36}Ar , ^{84}Kr , and ^{132}Xe volume fractions and isotopic ratios are listed in Tables S2 and S3, respectively. $^3\text{He}/^4\text{He}$ ratios (R) are normalized to the atmospheric ratio R_a , where $R_a = (1.384 \pm 0.013) \times 10^{-6}$.⁴⁵

Water wells 555G and 556G are 94 and 91 m deep, respectively. These two water wells penetrate the Strawn Group according to drilling logs and are shallower than sampled Strawn gas well SG3 (544 m) which, in turn, is significantly shallower than all sampled Barnett gas wells with depths ranging from 1591 to 1985 m (Table S1).

Water wells 555G and 556G have been venting natural gas since they were completed.³⁷ The presence of flowing gas has been verified throughout the entire water column of well 555 during inspection with a camera.³⁷ A gas flow of 2.5 and 3.3 L/min at these two wells, respectively, was measured at the time of collection, November 2014. CH_4 (C_1) is largely dominant over all other components at well 556G with 73.6% by volume (Table S1). CH_4 is also the dominant component of Barnett and Strawn natural gas samples with values ranging from 75.1% to 82.1%. The highest CH_4 volume fraction is found in Strawn gas well SG3 (Table S1). Barnett and Strawn gas molecular ratios $C_1/(C_{2+})$ are up to 6 and their $\delta^{13}\text{C}_{\text{CH}_4}$ values are larger than -50‰ , strongly suggesting that natural gases in both the Barnett and Strawn formations are of thermogenic origin.⁵⁹

Measured ^4He volume fractions in wells 555 and 556 vary from 2.33×10^{-3} to 4.37×10^{-3} . (Figure 2A; Table S2). Total ^4He volume fraction in the Strawn gas sample is 1.84×10^{-3} , a value slightly lower than that in stray gas samples from water wells but significantly higher than that of collected Barnett gases in this study which range from 1.86×10^{-4} to 6.71×10^{-4} (Figure 2A; Table S2) (see also Darrah et al.⁶). From Figure 2A, no obvious correlation is observed between total ^4He and methane content for either Barnett or Strawn gases. Crustal ^4He volume fractions ($^4\text{He}^*$) for all gas samples (SI Text S2; Table S2) vary between 1.82×10^{-4} and 4.31×10^{-3} and account for most of the measured He (97.6% to 100%). Similar to total He, crustal He volume fractions do not display an obvious correlation with methane content in these samples (Figure 2B). For all samples, R/R_a ratios vary between 0.0205 ± 0.0005 and 0.0426 ± 0.0004 (Figure 2C; Table S3), and correspond to typical crustal production values of 0.02–0.05.²⁷

All $^{21}\text{Ne}/^{22}\text{Ne}$ ratios are above the atmospheric value of 0.029¹⁸ and reflect the addition of crustally produced $^{21}\text{Ne}^*$ with values varying between 0.0295 ± 0.0001 and 0.0582 ± 0.0020 (Figure 2D; Table S3). Crustal $^{21}\text{Ne}^*$ volume fractions for all gas samples are highly variable and range from 1.00×10^{-11} to 2.44×10^{-10} , representing contributions varying between 2.2% and 50.2% of total ^{21}Ne (Table S2; SI Text S2). The highest crustally produced $^{21}\text{Ne}^*$ contribution by far is found in Strawn natural gas as opposed to the Barnett Shale, where the lowest $^{21}\text{Ne}^*$ contributions are found. No crustally produced $^{21}\text{Ne}^*$ was estimated for samples BG5A, BG5B and BG7 due to the observation of mass-dependent fractionation in these samples (SI Text S3). Unlike ^4He , atmospheric ^{21}Ne contributions for all samples are much higher and vary between 49.8% and 97.8% of total ^{21}Ne . Here too, no obvious correlation is observed between $^{21}\text{Ne}/^{22}\text{Ne}$ ratios and methane content for Barnett and Strawn gases (Figure 2D). Measured $^{20}\text{Ne}/^{22}\text{Ne}$ for stray gas sample 556GA is greater than the atmospheric value of 9.80¹⁸ suggesting the presence of a limited amount of mantle Ne.^{20,46} Samples 555GA, 555GB (average of

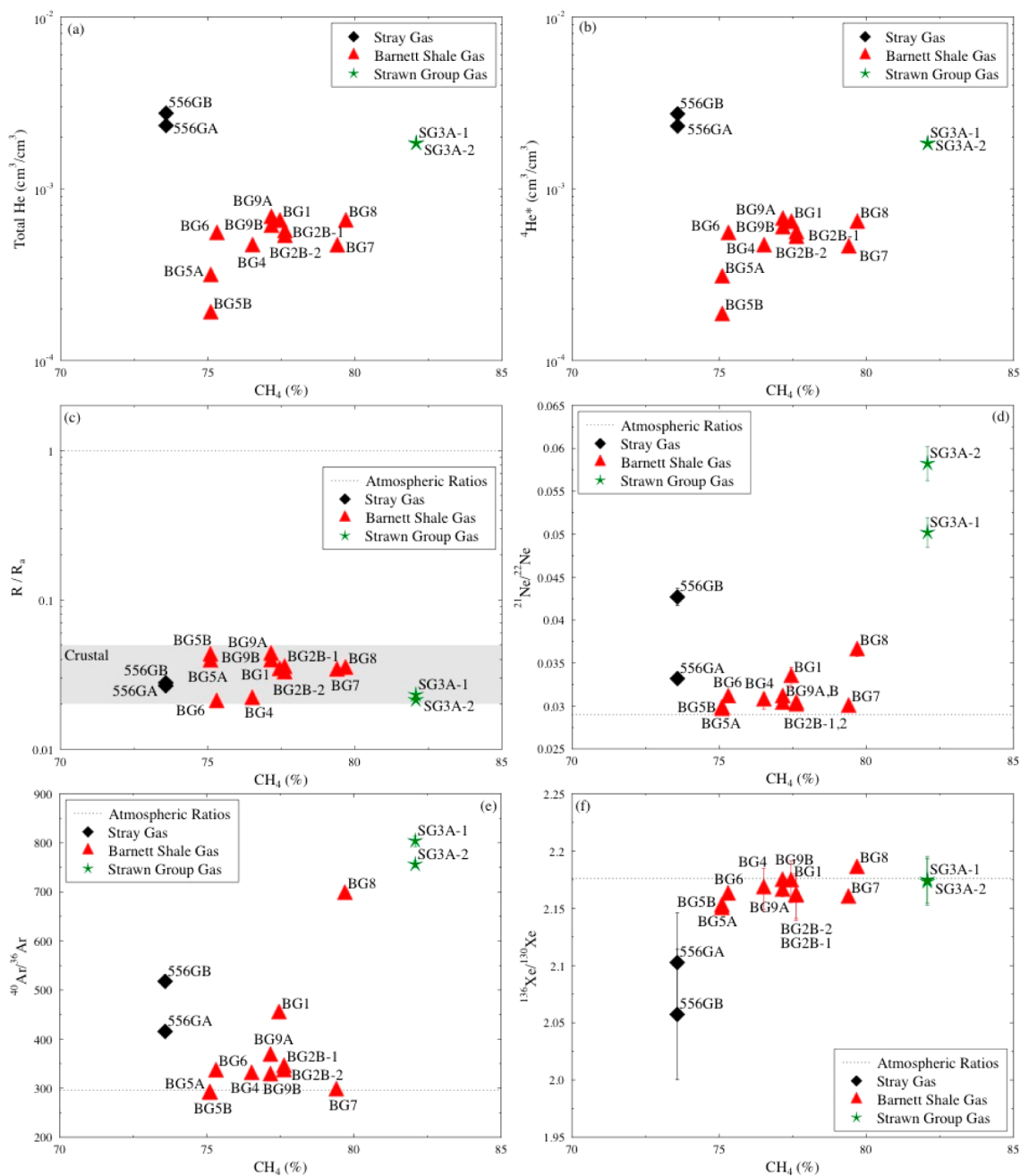


Figure 2. (a) total ^4He volume fractions, (b) $^4\text{He}^*$ volume fractions, (c) R/R_a ratios, (d) $^{21}\text{Ne}/^{22}\text{Ne}$ ratios, (e) $^{40}\text{Ar}/^{36}\text{Ar}$ ratios, and (f) $^{136}\text{Xe}/^{130}\text{Xe}$ ratios as a function of methane volume fractions for all gas samples. Corresponding atmospheric and crustal noble gas values are indicated by dashed lines and shadow area, respectively.

555GB-1 and 555GB-2), and 556GB display $^{20}\text{Ne}/^{22}\text{Ne}$ ratios indistinguishable from the atmospheric value within a 2-sigma error. Both Strawn gas measurements display $^{20}\text{Ne}/^{22}\text{Ne}$ ratios below 9.80, and suggest the incorporation of crustal $^{22}\text{Ne}^*$. The presence of crustal $^{22}\text{Ne}^*$ is not surprising as Strawn natural gas displays the highest $^{21}\text{Ne}^*$ and both crustally produced $^{21}\text{Ne}^*$ and $^{22}\text{Ne}^*$ share one common parent isotope, ^{25}Mg . Typical $^{20}\text{Ne}/^{22}\text{Ne}$ crustal production ratio is $\sim 0.3^{47}$ (SI Text S4). In contrast, all Barnett Shale production gas samples, without exception, display significantly higher $^{20}\text{Ne}/^{22}\text{Ne}$ ratios (Table S3), all above the atmospheric value, ranging from 10.003 ± 0.016 to 10.335 ± 0.012 . With the exception of samples BG5A, BG5B, and BG7, which might display high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios partly due to mass-dependent fractionation (e.g., molecular

diffusion; SI Text S3), high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios in all other Barnett samples are likely due to the presence of a mantle component.

Except for samples BG5A, BG5B, and BG7, all other samples display $^{40}\text{Ar}/^{36}\text{Ar}$ ratios above the atmospheric value of 295.5 (Figure 2E; Table S3), reflecting the addition of crustal $^{40}\text{Ar}^*$, with $^{40}\text{Ar}/^{36}\text{Ar}$ values varying between 325.12 ± 0.12 and 803.66 ± 11.03 . As previously observed for $^{21}\text{Ne}/^{22}\text{Ne}$, Strawn natural gas displays the highest $^{40}\text{Ar}/^{36}\text{Ar}$ values, indicating the presence of greater amounts of crustally produced $^{40}\text{Ar}^*$ compared to Barnett Shale and stray gas (Figure 2E; Table S2). This contrasts to the lower $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in Barnett Shale production gas (287.50 ± 0.04 to 695.06 ± 2.04) and is further discussed below. Crustal $^{40}\text{Ar}^*$ volume fractions (cf., SI Text

S2) are significant and vary widely with respect to total ^{40}Ar (9.1% to 63.2%), ranging from 2.68×10^{-6} to 1.03×10^{-4} for all samples (Table S2).

Kr isotopic ratios (e.g., $^{86}\text{Kr}/^{84}\text{Kr}$, Table S3) are all indistinguishable from atmospheric values. Similar to Kr isotopic ratios, except for samples BG5A, BG5B, BG6, and BG7, all other samples display $^{136}\text{Xe}/^{130}\text{Xe}$ values indistinguishable from that of the atmosphere (2.176¹⁸), pointing to the absence of a crustally and/or mantle produced Xe component (Figure 2F; Table S3). Low $^{136}\text{Xe}/^{130}\text{Xe}$ values in samples BG5A, BG5B, BG6, and BG7 might be due to mass-dependent fractionation (SI Text S3).

Overall, noble gas measurements show that Strawn production gas is significantly more enriched in crustal $^4\text{He}^*$, $^{21}\text{Ne}^*$, and $^{40}\text{Ar}^*$ than Barnett Shale production gas and thus, point to rather distinct noble gas signature between these two sources. These distinct noble gas signatures reflect either higher concentrations of parent elements in the Strawn Group or more likely, they reflect the presence of older natural gas in the Strawn Group than that currently in place in the Barnett Shale. Natural gas in the Strawn Group may have been generated at an earlier time in the Barnett Shale and subsequently migrated to the Strawn Group before the Barnett Shale reached maximum burial and thermal maturity at which time natural gas currently present in the Barnett Shale was generated. This is also consistent with findings by previous studies.^{33,34,48,58,60,61}

Barnett Shale versus Strawn Group and Stray Natural Gas—Crustal and Atmospheric Noble Gas Signatures.

As shown above, crustal noble gas signatures of Barnett Shale and Strawn Group natural gas are significantly different (e.g., $^4\text{He}^*$, $^{21}\text{Ne}^*$, $^{40}\text{Ar}^*$; Figure 2) and allow discrimination between production natural gas from these two formations. Here, to identify the source of stray gas in these water wells and to further distinguish between Barnett and Strawn natural gas, we examine the evolution of $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ isotopic ratios with the inverse of their atmospheric dominant isotopes ^{22}Ne and ^{36}Ar , respectively.

Figure 3A shows a plot of $^{40}\text{Ar}/^{36}\text{Ar}$ ratios versus $1/^{36}\text{Ar}$ values for all our natural gas samples together with Barnett and Strawn production gas samples reported by Darrah et al.⁶ The air value is also shown (blue square). Lower $^{40}\text{Ar}/^{36}\text{Ar}$ and $1/^{36}\text{Ar}$ values point to a greater atmospheric contribution while higher values reflect the addition of crustally produced $^{40}\text{Ar}^*$ accompanied by corresponding decreasing amounts of an atmospheric contribution⁴⁹. Here, a linear correlation passing through the air value points to mixing between two end-members, one represented by air, the other represented by a crustal component enriched in $^{40}\text{Ar}^*$.^{14,49} The volume fraction of $^{40}\text{Ar}^*$ is defined by the slope of the observed linear regression line. From Figure 3A, it is apparent that Barnett Shale and Strawn Group natural gas display two distinct trends. Indeed, $^{40}\text{Ar}^*$ volume fractions for Strawn natural gas are significantly higher than those of the Barnett Shale and vary between 4.94×10^{-5} and 1.54×10^{-4} (regression lines a and b). In contrast, significantly lower $^{40}\text{Ar}^*$ volume fractions are observed in the Barnett Shale with values varying between 3.30×10^{-6} and 1.14×10^{-5} (regression lines c and d). Such variations could suggest a distinct geochemical composition for these two formations and, in particular, different concentrations of ^{40}K , the $^{40}\text{Ar}^*$ parent element. Alternatively, and maybe more likely, it points to the presence of an older Strawn natural gas compared to Barnett Shale gas, a finding which is also

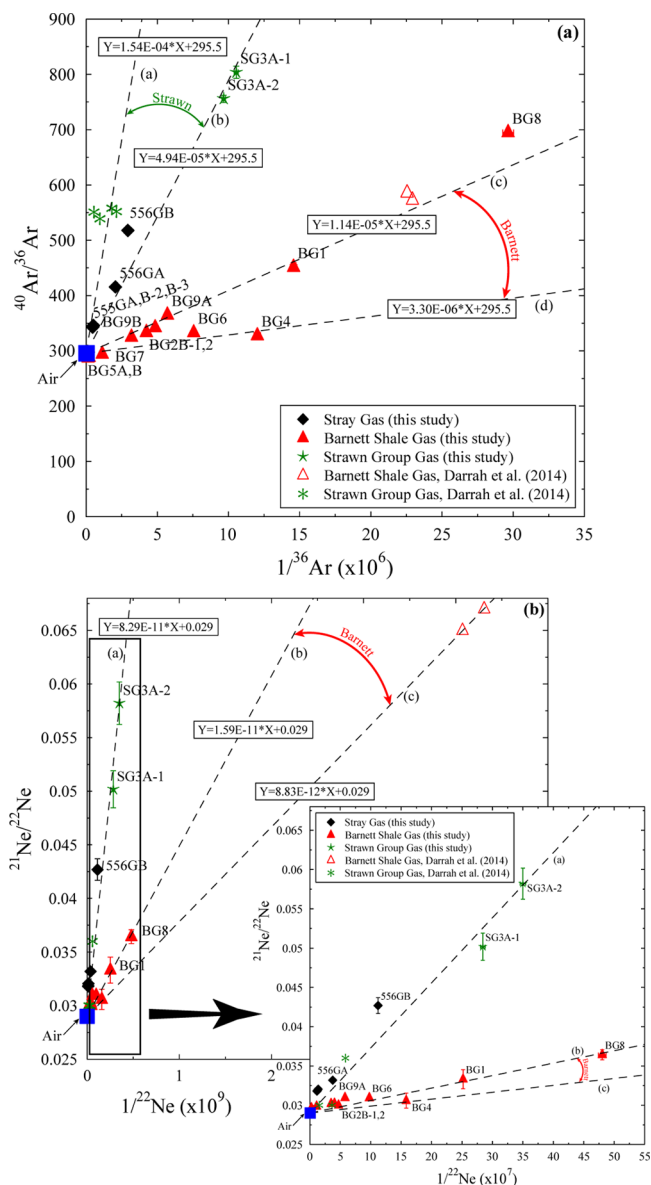


Figure 3. (a) $^{40}\text{Ar}/^{36}\text{Ar}$ versus $1/^{36}\text{Ar}$ and (b) $^{21}\text{Ne}/^{22}\text{Ne}$ versus $1/^{22}\text{Ne}$ for all gas samples in this study as well as Barnett Shale and Strawn Group gas samples from Darrah et al.⁶ Linear regression lines are also shown for certain groups of gas samples (see text). Air values are shown for comparison.

consistent with previous findings based on evidence given by oil and gas geochemistry of the Fort Worth Basin^{60,61} suggesting that gas reservoirs were filled before Barnett Shale gas reached its current maturity. Of relevance is the fact that all stray gas samples fall on or between the regression lines defined by the $^{40}\text{Ar}^*$ volume fraction signature of the Strawn Group. This observation strongly supports the origin of the stray gas in the Trinity Aquifer as being the Strawn Group. In contrast, the observed mismatch between our stray gas samples and the $^{40}\text{Ar}^*$ signature of Barnett Shale natural gas argues against this formation as the source of the stray gas. These results support previous findings by Darrah et al.⁶ and Kornacki and McCaffrey¹⁶ who also tentatively concluded that the Strawn Group was the likely source of stray gas in the Trinity Aquifer.

A similar conclusion to that of $^{40}\text{Ar}^*$ volume fractions can be drawn by analyzing the crustally produced $^{21}\text{Ne}^*$. This is clearly

seen in Figure 3B where $^{21}\text{Ne}/^{22}\text{Ne}$ ratios are plotted as a function of $1/^{22}\text{Ne}$ values for all our natural gas samples and those reported by Darrah et al.⁶ for Barnett and Strawn production gas. Here too, the crustally produced $^{21}\text{Ne}^*$ volume fractions in the Strawn natural gas have a value of 8.29×10^{-11} , which is significantly higher than that of Barnett Shale natural gas. From Figure 3B it can be clearly seen that stray gas samples fall on or very close to the mixing line defined by mixing between air and crustally produced Strawn natural gas. Barnett natural gas samples have a clearly distinct crustally produced ^{21}Ne signature with $^{21}\text{Ne}^*$ volume fraction contributions significantly lower than the Strawn and varying between 8.83×10^{-12} to 1.59×10^{-11} . The combined set of crustal $^{21}\text{Ne}^*$ and $^{40}\text{Ar}^*$ signatures of Strawn natural gas reinforces the notion that stray gas in the Trinity Aquifer does indeed originate in the Strawn Group. Another aspect of this analysis that strengthens our conclusions is the fact that both $^{21}\text{Ne}^*$ and $^{40}\text{Ar}^*$ volume fractions from this study and that of Darrah et al.⁶ for both the Strawn Group and Barnett Shale gas are rather consistent.

Analysis of the atmospheric component of noble gases further strengthens our findings by showing somewhat distinct noble gas signatures for both Barnett Shale and Strawn Group production gas and by pointing to a Strawn-like signature for stray gas in the Trinity Aquifer. This is particularly apparent when analyzing the noble gas signature of the lighter noble gases ^{22}Ne and ^{36}Ar . Indeed, unlike Kr and Xe, these are not subject to an additional atmospheric contribution from organic matter.^{50–54} In the discussion that follows, ^{22}Ne , ^{36}Ar , ^{84}Kr , and ^{132}Xe contents of all gases in this study are assumed to originate from recharge water in equilibrium with the atmosphere (ASW) at 18 °C at an elevation of 274 m, i.e., conditions corresponding to modern mean annual air temperature (MAAT) and average elevation of all sampled wells in this study. It should be noted that temperature differences of ± 5 °C will have a negligible impact on our findings. Data from Darrah et al.⁶ are not discussed below due to the lack of heavy noble gas data in their study.

Figure 4 and Table S4 show $F(^{22}\text{Ne})$, $F(^{84}\text{Kr})$, and $F(^{132}\text{Xe})$ ratios for all gas samples, i.e., shale gas and water well flowing gas (this study) in addition to Trinity Aquifer groundwater samples with high methane content (samples 355, 358, 369, 555) reported by Wen et al.⁷ $F(^{22}\text{Ne})$, $F(^{84}\text{Kr})$, and $F(^{132}\text{Xe})$ represent measured $^{22}\text{Ne}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$, and $^{132}\text{Xe}/^{36}\text{Ar}$ ratios normalized to corresponding air values (thick black line, Figure 4). ASW values for a temperature of 18 °C are also shown (light blue line, Figure 4; see also Table S4). $F(^{22}\text{Ne})$, $F(^{84}\text{Kr})$, and $F(^{132}\text{Xe})$ values for all stray gas samples are located between ASW and air values (Figure 4). Because the solubility of light noble gases (e.g., ^{22}Ne) in water is lower than that of heavy noble gases (e.g., ^{132}Xe), light noble gases in the Trinity Aquifer groundwater will go preferentially into the gas phase when groundwater is undergoing gas stripping. This results in elevated $F(^{22}\text{Ne})$ but lower $F(^{84}\text{Kr})$ and $F(^{132}\text{Xe})$ values in the gas phase compared to the initial ASW values. As expected, Trinity Aquifer groundwater samples with high methane content and thus more likely with the presence of a free gas phase (black circles) display relative depletion in the light ^{22}Ne isotope and relative enrichment of heavy ones compared to ASW (Figure 4). Thus, a simple single-stage groundwater degassing model in a closed or open system at 18 °C can adequately explain both, observed atmospheric noble gas ratios in stray gases as well as in Trinity Aquifer groundwater samples

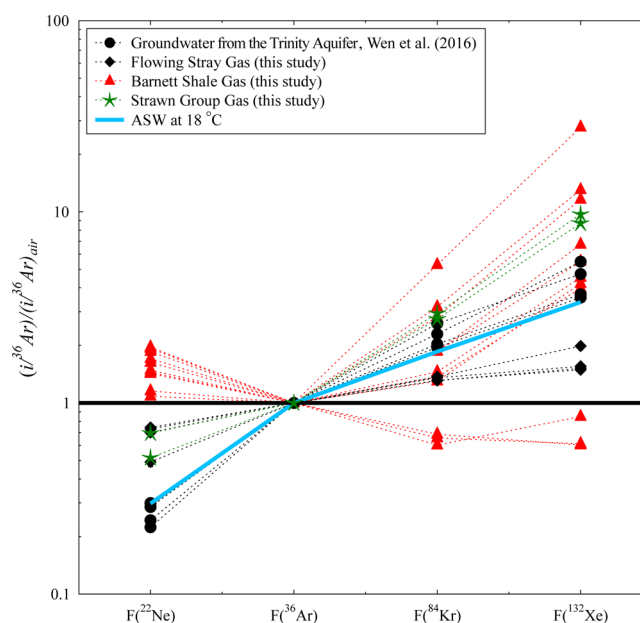


Figure 4. $F(^{22}\text{Ne})$, $F(^{84}\text{Kr})$, and $F(^{132}\text{Xe})$ are plotted for gas samples. $F(^{22}\text{Ne})$, $F(^{84}\text{Kr})$, and $F(^{132}\text{Xe})$ are measured $^{22}\text{Ne}/^{36}\text{Ar}$, $^{84}\text{Kr}/^{36}\text{Ar}$, and $^{132}\text{Xe}/^{36}\text{Ar}$ ratios normalized to corresponding air values. F values of ASW at the temperature of 18 °C (light blue line) and air (black line) are shown. F values for groundwater samples from the Trinity Aquifer with high methane content in the study area⁷ are also shown.

(Figure 4; cf., SI Text S5), an observation that is consistent with previous findings.⁷ Of relevance is the fact that $F(^{22}\text{Ne})$ values of stray gas mimic those of Strawn natural gas, an observation which can also be explained by the single-stage groundwater degassing model. This observation further supports the source of stray gas in the Trinity Aquifer as being the Strawn Group. Unlike Strawn production gas, however, all Barnett production gas displays distinctly high $F(^{22}\text{Ne})$ values (Figure 4), all above that of air and suggests that a simple single-stage water degassing model for the Barnett Shale gas is not consistent with the light noble gas signature. However, a two-stage oil modified groundwater exsolution (OMGE) fractionation model⁵⁵ can explain the light atmospheric noble gas signature observed in Barnett Shale production gas (Figure 5; SI Text S5). This can be clearly seen in Figure 5 where $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{132}\text{Xe}/^{36}\text{Ar}$ values are plotted as a function of $^{22}\text{Ne}/^{36}\text{Ar}$ for all gas samples. Air and ASW at 18 °C values are also shown for comparison, with $^{22}\text{Ne}/^{36}\text{Ar}$ values of 0.053 and 0.016, respectively. Calculated closed- and open-system fractionation curves for an escaped gas phase that is in equilibrium with ASW at 18 °C are also indicated (curved and dashed black lines, respectively). From Figure 5, it is apparent that although Strawn and stray gas display $^{22}\text{Ne}/^{36}\text{Ar}$ values that are consistent with predicted values following the groundwater degassing model, $^{22}\text{Ne}/^{36}\text{Ar}$ values in Barnett production gas are higher than the maximum predicted $^{22}\text{Ne}/^{36}\text{Ar}$ value of 0.053 in the gas phase assuming a simple groundwater degassing model. However, it is apparent that all measured Barnett gas $^{22}\text{Ne}/^{36}\text{Ar}$ ratios fall within the range predicted by the OMGE model for varying enrichment levels of ^{84}Kr and ^{132}Xe . Both Strawn and Barnett production gas display enrichment of the heavy atmospheric noble gases to varying degrees. This could be explained by sedimentary ^{84}Kr and ^{132}Xe excess noble gases of atmospheric origin adsorbed by organic matter (Figure S4),^{50–54} possibly sourced from the organic rich material in the Barnett Shale. It should be noted

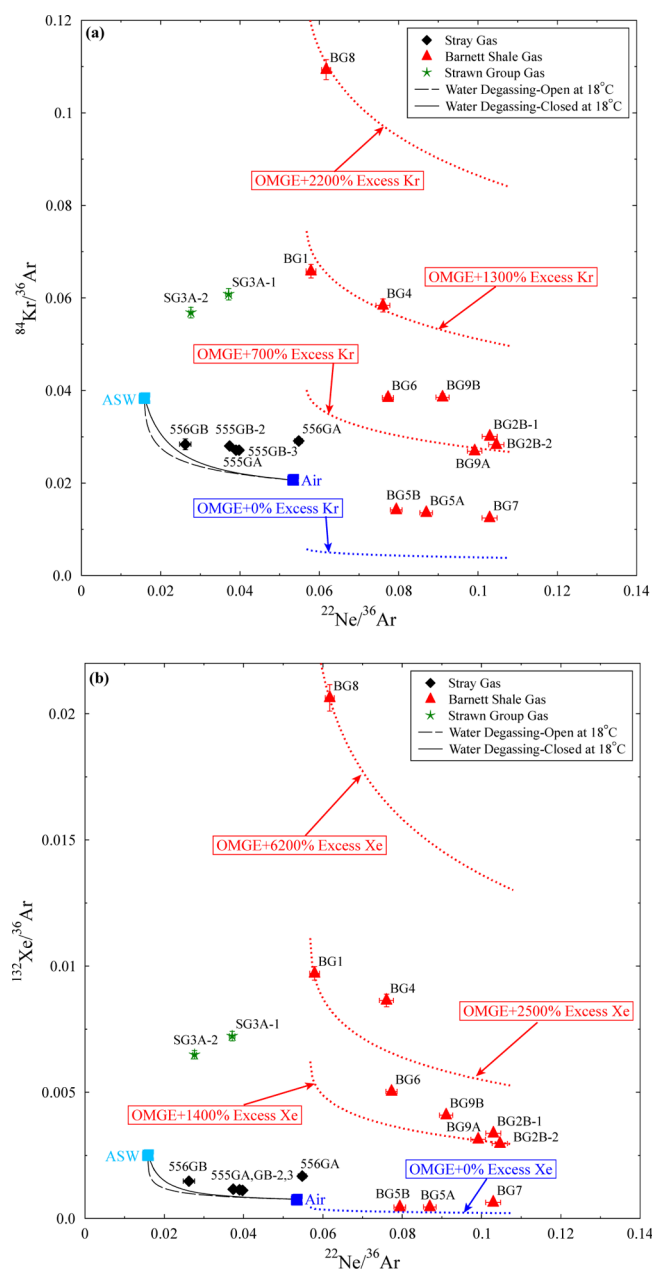


Figure 5. (a) $^{84}\text{Kr}/^{36}\text{Ar}$ versus $^{22}\text{Ne}/^{36}\text{Ar}$ and (b) $^{132}\text{Xe}/^{36}\text{Ar}$ versus $^{22}\text{Ne}/^{36}\text{Ar}$ are shown for our gas samples. Predicted values in the gas phase following a single-stage groundwater degassing model for closed-system (black curve) and open-system (black dashed curve) are shown in (a) and (b). Calculated values in the gas phase following the oil-modified groundwater exsolution (OMGE) model with varying amount of sedimentary noble gas are also shown (blue and red dotted curves; see also SI Text S5).

that the OMGE model is also in agreement with current knowledge of the Barnett Shale as the primary source rock for both oil and gas in the Fort Worth Basin.^{34,38,48,56,57} These results support distinct evolution histories for Strawn and Barnett Shale production gas.

Overall, the novel approach used here which involves the use of the entire set of noble gases, a combined analysis of both the atmospheric and crustal components as well as analysis of both, shale gas from different formations and flowing stray gas shows that noble gases alone can be used to distinguish between different sources of shale gas, either due to their distinct

evolution histories, different parent elements' amount and/or distinct ages. More specifically, this study discriminates natural gas from the Barnett Shale and Strawn Group based solely on their noble gas signatures and shows that this noble gas signature can be used to identify the source of methane present in the shallow Trinity Aquifer in Central Texas. It further shows that the source of methane in the Trinity Aquifer is likely the Strawn Group, further reinforcing previous findings by Darrah et al.,⁶ Kornacki and McCaffrey,¹⁶ and Wen et al.⁷ When such an approach is used together with noble gas analysis of groundwater samples where the presence of stray gas is detected, it can also help decipher whether such occurrences have a natural or anthropogenic origin. Thus, the noble gas approach employed in this study should make a positive contribution in addressing and resolving problems of groundwater contamination by stray gas.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b06447.

Supporting Texts S1–S5, Figures S1–S4, Tables S1–S5, and additional references (PDF)

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Notes

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