Noble gas fractionation during subsurface gas migration

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Abstract

Environmental monitoring of shale gas production and geological carbon dioxide (CO₂) storage requires identification of subsurface gas sources. Noble gases provide a powerful tool to distinguish different sources if the modifications of the gas composition during transport can be accounted for. Despite the recognition of compositional changes due to gas migration in the subsurface, the interpretation of geochemical data relies largely on zero-dimensional mixing and fractionation models. Here we present two-phase flow column experiments that demonstrate these changes. Water containing a dissolved noble gas is displaced by gas comprised of CO₂ and argon. We observe a characteristic pattern of initial co-enrichment of noble gases from both phases in banks at the gas front, followed by a depletion of the dissolved noble gas. The enrichment of the co-injected noble gas is due to the dissolution of the more soluble major gas component, while the enrichment of the dissolved noble gas is due to stripping from the groundwater. These processes amount to chromatographic separations that occur during two-phase flow and can be predicted by the theory of gas injection. This theory provides a mechanistic

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basis for noble gas fractionation during gas migration and improves our ability to identify subsurface gas sources after post-genetic modification. Finally, we show that compositional changes due to two-phase flow can qualitatively explain the spatial compositional trends observed within the Bravo Dome natural CO₂ reservoir and some regional compositional trends observed in drinking water wells overlying the Marcellus and Barnett shale regions. In both cases, only the migration of a gas with constant source composition is required, rather than multi-stage mixing and fractionation models previously proposed.

1. Introduction

Noble gases are used as tracers in a variety of subsurface fluid flow processes due to their non-reactivity, low natural concentrations, and distinct isotopic signatures [1]. Noble gas isotopes have been used to trace the fluid sources and migration pathways of hydrocarbons in sedimentary basins [2, 37, 16], to quantify trapping processes in natural CO₂ reservoirs [11, 12, 41] and to identify fugitive natural gas in shallow groundwater [18, 8, 7].

Shale gas now provides the largest share of US natural gas production [23, 15] and the potential contamination of shallow groundwater by fugitive gases is a major public concern [36, 44, 18, 3]. The identification of fugitive gases in drinking water aquifers is challenging because most aquifers overlying shale gas resources already contain dissolved thermogenic methane due to regional groundwater flow [47, 8, 31]. A promising method to distinguish fugitive gases from natural gas migration is the use of noble gases to constrain both the migration distance and source [8]. Further development of this

16 method requires a mechanistic understanding of the compositional changes
17 that occur during gas migration.

18 A second emerging energy technology is the mitigation of CO₂ emissions
19 by carbon capture and storage in deep saline aquifers [35, 42]. This technol-
20 ogy builds on decades of industry experience with gas flooding for enhanced
21 oil recovery [34, 20]. Several pilot projects show that CO₂ injection and
22 monitoring are feasible [30]. Nonetheless, the long-term security of geologi-
23 cal CO₂ storage and the possibility of leakage are major concerns that have
24 to be addressed [10, 43]. Natural CO₂ reservoirs provide important analogs
25 for the fate of CO₂ in the subsurface and demonstrate that very large accu-
26 mulations of CO₂ can be stored over millennial timescales [41]. The inter-
27 pretation of natural analogues is largely based on noble gases [11, 12] and
28 therefore requires an understanding of their behavior during CO₂ migration
29 in the subsurface. Similarly, noble gases may provide important information
30 about the pore space accessed and the dissolution that has occurred during
31 the initial stages of a CO₂ storage project [13].

32 Despite the recognized importance of two-phase flow [39, 16, 8, 7], noble
33 gases are commonly interpreted using zero-dimensional mixing and fraction-
34 ation models [11, 12, 8]. Currently the relationship between these models
35 and the underlying physical processes that control the evolution of gas com-
36 position is not clear. The aim of this manuscript is therefore to provide an
37 understanding of the behavior of noble gases in two-phase flow.

38 To this end, Section 2 presents well-characterized two-phase displacement
39 experiments that demonstrate the compositional changes due to partitioning
40 of noble gases between the phases. In Section 3 these observations are first

discussed using mass-balance arguments, before we outline the application of gas injection theory to noble gas fractionations in Section 4. This theory predicts the observed compositional trends and provides a framework for understanding post-genetic changes in gas composition. Finally, the experimental observations and theoretical predictions are compared with published observations in natural CO₂ reservoirs and groundwater overlying shale gas resources in Section 5.

2. Two-phase gas fractionation experiments

Previous observations from shale gas production and geological CO₂ storage show that gas migration leads to the enrichment of both noble gases initially dissolved in the brine and those that are introduced with the gas phase [11, 12, 8, 7]. To investigate the mechanism that leads to the simultaneous enrichment of both co-injected and dissolved atmospheric noble gases, we performed four-component two-phase column displacement experiments.

Gas with a CO₂/argon ratio of 50 was injected with a constant volume flow rate. The gas displaced the water from the top of the column towards the bottom to obtain a gravity stabilized displacement. The effluent liquid and gas were collected in helium-filled glass vials and subsequently analyzed in a gas chromatograph. For a detailed description of the experimental method see supplementary materials Section 2. Two experiments with different initial dissolved gases were conducted. Experiment 1 was performed in a 122 cm long and 1 cm inner diameter glass column packed with glass beads of 150-212 micron diameter. The column was initially filled with water saturated with 2 Atm of neon. Experiment 2 was performed in a steel column of length 100 cm

65 and 1 cm inner diameter, filled with quartz sand with a mean grain diameter
66 of 100 microns. The column was initially filled with water saturated with
67 CH_4 at 2 Atm. We chose CH_4 as the dissolved gas in the second experiment,
68 because its higher solubility leads to a larger chromatographic separation.

69 Figs. 1 and 2 show the results of the four-component gas displacement
70 experiments. To account for the finite sampling intervals, gas composition
71 is presented in units of volume flow rate as a function of pore volumes in-
72 jected. Gas breakthrough occurs before one pore volume has been displaced,
73 indicating the presence of pore water behind the gas front (Fig. 2A). Typical
74 residual water saturations in the column at the end of the experiment were
75 40%.

76 Two distinct noble gas banks are seen in the first experiment. Fig. 1A
77 shows the effluent flow rate of neon, which was initially present as a dissolved
78 component in the water. The first gas eluting from the column is highly
79 enriched in neon that has been stripped from the residual water remaining
80 behind the gas front. Shortly thereafter, the injected gas arrives and is
81 enriched in argon, due to the dissolution of the highly soluble CO_2 (Fig. 1B
82 and 1C). Finally, the retarded CO_2 front breaks through and the CO_2 /Argon
83 ratio reverts to the injected ratio of 50.

84 In the second experiment, water with dissolved CH_4 was displaced with
85 the same CO_2 /argon mixture (Fig. 2). The initial mass of dissolved gas, in
86 experiment 2 is greater due to the higher solubility of CH_4 relative to neon.
87 The stripping of this dissolved gas leads to the formation of a larger and
88 more distinct bank (Fig. 2B) that coincides with a decrease in the volume
89 flow rate of water (Fig. 2A). The argon bank is clearly separated from the

CH₄ bank and precedes the CO₂ front, similar to experiment 1. After the CO₂ breakthrough, the gas effluent composition matches the injected gas and CH₄ has been completely stripped from the water remaining in the column. Note, the small CH₄ concentrations ahead of the gas front are due to exsolution of dissolved CH₄ into the sampling head space, giving an indication of the initial dissolved concentration. This illustrates the reduction of CH₄ concentration in the residual water behind the gas front, relative to the initial dissolved concentration.

Our experiments show two types of behavior that are compatible with the overarching trends that emerge from previous work on noble gas fractionations associated with shale gas production and geological CO₂ storage: First, co-injected noble gas isotopes that are less soluble than the main gas component become increasingly enriched as migration proceeds. This is due to the preferential dissolution of the more soluble major gas components, an effect that is pronounced in CO₂-rich gases. Second, atmospheric noble gases are stripped from air-saturated groundwater and enriched above atmospheric values as migration proceeds. This combination of processes enriches the front of the migrating gas in both co-injected and atmospheric noble gases, but depletes atmospheric noble gases behind the gas front.

3. Mass-balance interpretation of experimental results

The quantitative interpretation of these experiments requires a coupling of the dynamics of two-phase flow with the partitioning of the components between the differentially moving phases. Before addressing this coupling in Section 4 we will first show that the basic features can be understood by

Figure 1: Experimental elution curves from a two phase displacement of neon-saturated water by CO_2 -argon mixture. Gas volume flow rates at the column outlet are shown as function of pore volumes injected: **A)** Neon, **B)** Argon, and **C)** CO_2 . Subplots A and B show the arrival of two highly enriched noble gas banks ahead of the main CO_2 front.

Figure 2: Experimental elution curves from a two-phase displacement of CH_4 -saturated water by CO_2 -argon mixture. Volume flow rates at the column outlet are shown as function of pore volumes injected: **A)** Water, **B)** Argon and CH_4 , and **C)** CO_2 . Subplot B shows the arrival of two highly enriched gas banks ahead of the main CO_2 front.

114 considering the mass balance in a plug-flow.

115 We consider a piston like displacement with a constant residual satura-
 116 tion, s_{wr} . The length of the column is ℓ and its pore volume is V_p . Gas of
 117 uniform composition is injected at the constant pressure, p_g , and constant
 118 volumetric rate, Q . Assuming an ideal gas, the molar injection rate into
 119 the column is given by $p_g Q / (RT)$, where R is the gas constant and T is the
 120 temperature of the injected gas. Due to the low viscosity of the gas most
 121 of the pressure drop occurs in the water ahead of the gas front and we will
 122 assume that the gas pressure is constant at the injected value throughout the
 123 column.

124 In both experiments gas breakthrough, t_b , is observed before one pore-
 125 volume has been injected, $t_b < V_p / Q$ (Figs. 1 and 2). This is a result of the
 126 residual water saturation, s_{wr} , which reduces the pore space accessible to the
 127 gas to $V_g = V_p(1 - s_{wr})$. In the absence of dissolution, mass balance requires
 128 that gas breakthrough occurs at $t_b^* = V_g / Q$ after $n_b = p_g V_g / (RT)$ moles have
 129 been injected (Fig. 3A). Typical residual saturations in our experiments are
 130 0.4, suggesting that an immiscible gas should break though after 0.6 pore
 131 volumes.

However, the observed gas breakthrough in the experiment occurs at pore
 volumes between 0.70 and 0.75. This delayed arrival of the gas is due to
 dissolution of the injected CO_2 , (Fig. 3B). The fraction of the gas that
 remains in the gas phase is given by

$$\mathcal{F}_i = \frac{1 - s_{wr}}{1 + (RT H_i - 1) s_{wr}}, \quad (1)$$

132 where H_i is the Henry's law solubility constant for species i . If n_b moles of
 133 a pure gas are injected, its position is given by $x_i = \mathcal{F}_i \ell$. The breakthrough

will occur after $t_b = t_b^*/\mathcal{F}_i$ pore-volumes have been injected. In the case of pure CO₂, breakthrough is predicted to occur after 0.93 pore-volumes have been injected.

If argon is co-injected, it will advance further than the more soluble CO₂, according to Equation 1. In a piston-like displacement with constant gas saturation behind the front, the argon must accumulate in a bank just ahead of the CO₂ to maintain constant gas pressure (Fig. 3C). The width of this argon bank is $\Delta x_{\text{Ar}} = p_{\text{Ar}}/p_g(\mathcal{F}_{\text{Ar}} - \mathcal{F}_{\text{CO}_2})\ell$, where p_{Ar} is the partial pressure of argon in the injected gas and p_g is its total pressure. The front of the injected gas after injection of n_b moles is located at $x_{\text{inj}} = x_{\text{CO}_2} + \Delta x_{\text{Ar}}$. The breakthrough is expected at $t_b = t_b^*\ell/x_{\text{inj}}$. For the case of injection of CO₂ and Ar at a ratio of 4:1 the breakthrough occurs at approximately 0.84 pore volumes injected.

Finally, if the initial water contains a dissolved noble gas such as neon, it will be stripped from the residual water and accumulate in a bank of pure neon at the front of the migrating gas (Fig. 3D). The width of this neon bank is given by

$$\Delta x_{\text{Ne}} = \frac{x_{\text{inj}}s_{wr}H_{\text{Ne}}p_{\text{Ne}}}{(1 - s_{wr})p_g/(RT) + s_{wr}H_{\text{Ne}}(p_g - p_{\text{Ne}})}, \quad (2)$$

where p_{Ne} is the partial pressure of neon that the water has been equilibrated with. The position of the gas front after the injection of n_b moles is therefore $x_g = x_{\text{inj}} + \Delta x_{\text{Ne}}$ and the breakthrough occurs after $t_b = t_b^*\ell/x_g$ moles have been injected. This leads to breakthrough of the gas after the injection of 0.83 pore volumes.

The discussion above used a injected gas that contained more argon than the experiments to make the argon bank visible in Fig. 3. With the ex-

154 perimental values we expect neon, argon and CO₂ breakthrough after 0.93,
 155 0.92, and 0.91 pore volumes injected. The CO₂ breakthrough is 0.16 pore
 156 volumes later than that observed experimentally in Fig. 1. Some of this
 157 discrepancy may be due to the simplifying assumption of a plug flow. How-
 158 ever, we show in Section 4.6 that the gas saturation changes very little after
 159 breakthrough. Therefore, the late breakthrough suggests too much CO₂ dis-
 160 solves in the mass-balance calculation. Given that equation 1 is independent
 161 of the gas pressure and the Henry’s law solubility constant for CO₂ is well
 162 known, it is likely that the CO₂ has not accessed the entire residual water at
 163 breakthrough. This suggests that aqueous CO₂ diffusion is not fast enough
 164 to transport CO₂ from the gas-water interface into the entire residual water
 165 volume during the two hours required for CO₂ breakthrough. Using equation
 166 1 and a CO₂ breakthrough of 0.75, we estimate that the effective residual
 167 saturation to be $s_{wr}^* = 0.25$.

168 **4. Theory of gas injection**

169 The analysis of the gas fronts presented in Section 3 assumes a plug flow
 170 with constant saturation and is based on additional implicit assumptions
 171 such as the ordering of the fronts and the formation of pure noble gas banks.
 172 These are motivated by experimental observations but difficult to justify oth-
 173 erwise. Analytic solutions to the governing conservations laws for two-phase
 174 flow with partitioning of components provide these answers. Such a *theory of*
 175 *gas injection* has been developed in petroleum engineering and successfully
 176 predicts compositional changes in laboratory experiments with fluid-fluid dis-
 177 placements [48, 46, 9, 24]. Insights derived from this theory have been applied

Figure 3: Plug-flow mass balance models with increasing number of components. All figures show injection of a gas from left to right into a water-filled porous medium. Displacement is assumed to be a plug flow with residual water saturation, $s_{wr} = 0.4$. **A)** Injection of an immiscible gas into pure water. **B)** Injection of pure CO₂ into pure water. Dissolution reduces the length of the gas plume to $x_{CO_2}/\ell = 0.63$. **C)** Injection of a 80% CO₂ and 20% argon into pure water. Accumulation of low-solubility argon increases the length of the gas plume to $x_{inj}/\ell = 0.72$. **D)** Injection of 80% CO₂ and 20% argon into neon-saturated water. Neon degassed from the residual water forms a bank at the front of the gas plume, increasing the plume length to $x_g/\ell = 0.73$. The lengths of all gas plumes are scaled to the column length ℓ . The Henry's law coefficients at 25°C are $H_{Ar} = 1.4 \cdot 10^{-3}$, $H_{Ne} = 4.5 \cdot 10^{-4}$, and $H_{CO_2} = 0.034 \text{ mol}/(\text{L} \cdot \text{atm})$.

178 to design gas-injection operations in the oil and gas industry [20]. However,
 179 it is currently not recognized that the theory of gas injection also provides a
 180 framework to understand the noble gas fractionations observed above. Due
 181 to the non-linearity of two-phase flow and the coupling of multiple partial
 182 differential equations, the full theory is rather complex [25, 32]. Here, we can
 183 only outline the development and illustrate it by constructing the particular
 184 analytical solution for the experiments discussed above. In Section 4.1 we
 185 review the basic characteristics of immiscible two-phase displacements that
 186 form the foundation for the theory of gas injection. Sections 4.2 to 4.4 re-
 187 view the basic framework of the theory of gas injection, before we develop
 188 the analytic solution relevant to our experiments in Section 4.5.

189 *4.1. Saturation profiles in two-phase displacements*

190 Fig. 2A shows a typical water effluent history for a two-phase displace-
 191 ment experiment. Before the injected gas has reached the end of the column,
 192 only water is eluted. The injected gas breaks through before one pore-volume
 193 has been injected, indicating that significant amounts of water remain in the
 194 column. The flux of water drops significantly during breakthrough and after-
 195 wards the flux declines slowly towards zero. Below we show that these basic
 196 features of the effluent history are captured by Buckley-Leverett theory for
 197 incompressible and immiscible two-phase flow in a porous medium [5, 25, 32].

During two-phase flow, gas and water only occupy a fraction of the pore-
 space, called their saturation $0 \leq s_w, s_g \leq 1$, where $s_w + s_g = 1$. The relative
 permeability of each phase, k_{rp} , is proportional to its saturation [50, 27]
 (Fig. 4A). For the primary drainage, i.e., the injection of a gas into a porous

Figure 4: Solution for immiscible gas injection into water. **A)** Relative permeabilities to gas and water, k_{rg}, k_{rw} . **B)** Fractional flow of gas phase, f_g , with $M = 10$ and $s_{wr}=0.2$. The shock saturation for initial gas saturation of zero is shown by the tangent point to the fractional flow curve. **C)** Derivative of the fractional flow function with respect to gas saturation df_g/ds_g . **D)** Gas saturation profile as a function of speed, assuming $q/\phi = 1$. **E)** Gas saturation profiles at various times. The profile at a given time is obtained by multiplying the propagation speed by t . **F)** Outlet gas (s_g) and water (s_w) saturation as a function of pore volumes injected (PVI). PVI is proportional to time for an injection with constant flow rate. Therefore, at the end of the column, $x=1$, PVI is equal to the inverse of speed.

medium fully saturated with water, the relative permeabilities are given by

$$k_{rg} = k_{rg}^* \left(\frac{s_g - s_{gc}}{1 - s_{wr} - s_{gc}} \right)^{n_g} \quad \text{and} \quad k_{rw} = \left(\frac{1 - s_g - s_{wr}}{1 - s_{wr} - s_{gc}} \right)^{n_w}, \quad (3)$$

where k_{rg}^* is the end-point relative permeability of the gas, and n_g and n_w are the relative permeability exponents of the gas and water phases, respectively. In the column flow experiments considered here the residual water saturation is typically 0.4. The critical gas saturation s_{gc} is the minimum gas saturation required for the gas phase to flow.

Consider the flow of two immiscible and incompressible phases in a homogeneous porous column in the absence of gravity. The mass balance of the gas is given by

$$\phi \frac{\partial s_g}{\partial t} + \frac{\partial f_g q}{\partial x} = 0 \quad \text{or} \quad \frac{\partial s_g}{\partial t} + \frac{q}{\phi} \frac{df_g}{ds_g} \frac{\partial s_g}{\partial x} = 0, \quad (4)$$

where q is the volumetric flux, f_g is the fractional flow of the gas, and ϕ is the porosity [28]. The fractional flow of gas is controlled by the relative permeabilities and viscosities of the two fluids, $f_g = k_{rg}/(k_{rg} + Mk_{rw})$, where $M = \mu_g/\mu_w$ is the viscosity ratio. The fractional flow curve shown in Fig. 4B illustrates that the fraction of fluid transport in the gas phase is not linearly proportional to the gas saturation. At very low gas saturations, the low relative permeability prevents efficient transport in the gas, so that $f_g < s_g$. As the gas saturation increases, transport in the gas becomes dominant, $f_g \gg s_g$. This is due to the low viscosity of the gas relative to water, $M \ll 1$.

Equation 4 is an advection equation for s_g . The speed at which each gas saturation propagates is given by $\lambda(s_g) = \frac{q}{\phi} \frac{df_g}{ds_g}$, where q/ϕ is the interstitial fluid velocity in the saturated porous medium ahead of the gas front. Equation 4 is non-linear because λ depends s_g as shown in Fig. 4C. The location

216 of each saturation along the column at any particular time, t , is given by
 217 $x = \lambda(s_g)t$. This leads to the multi-valued saturation profile shown in Fig.
 218 4D, because λ is a non-monotonic function of s_g . To avoid this, a shock
 219 front must exist and can be found by the tangent construction shown in Fig.
 220 4B [5, 25, 29]. This shock propagates at a speed equal to the slope of the
 221 tangent line. For injection into a fully saturated column the shock speed is
 222 given by $\Lambda(\hat{s}_g) = f_g(\hat{s}_g)/\hat{s}_g$, where $\hat{s}_g$ is the shock saturation. The shock sat-
 223 uration is determined by the tangency condition, i.e., the requirement that
 224 the propagation speed is equal to the shock speed, $\lambda(\hat{s}_g) = \Lambda(\hat{s}_g)$. This con-
 225 struction gives rise to a gas saturation effluent profile where an initial rapid
 226 change in saturation is followed by a gradual increase (Fig. 4D and E). The
 227 arrival of the shock in gas saturation leads to an initial rapid drop in the
 228 flux of water eluted that is followed by a gradual decline. This matches the
 229 patterns of eluted water observed in our experiments (Fig. 2A). These basic
 230 features are retained even if the gas is compressible and in the presence of
 231 weak gravitational forces.

232 The basic concepts outlined in this section can also be applied to a two-
 233 phase displacement with partitioning of components. In this case, multiple
 234 coupled advection equations must be solved. For the conditions relevant to
 235 our experiments, this leads to the formation of multiple shock fronts which
 236 bound the two noble gas banks that are observed. The main difficulty in
 237 the multi-component case is the identification of the correct solution path in
 238 composition space as outlined below.

239 *4.2. Governing equations for multi-component two-phase flow*

In the multi-component gas-liquid system the bulk composition of the pore fluids is given by

$$\mathbf{C} = \phi(1 - s_g)\mathbf{c}_l + \phi s_g\mathbf{c}_g, \quad (5)$$

240 where ϕ is the porosity, s_g is the gas saturation and the compositions within
 241 the liquid and gas phases are given by $\mathbf{c}_l$ and $\mathbf{c}_g$, respectively. In this nota-
 242 tion, bold symbols indicate a vector of compositions. Individual components
 243 within this vector will be indicated by an additional subscript, so that $c_{l,\text{Ar}}$,
 244 $c_{g,\text{Ar}}$ and C_{Ar} are the concentrations of argon in the liquid, gas and mixture,
 245 respectively. At local chemical equilibrium, the partitioning of the compo-
 246 nents between the phases is governed by a set of partition coefficients, such
 247 that $c_{l,i} = H_i c_{g,i}$, where H_i is Henry's law coefficient of component i . If $\mathbf{C}$ and
 248 the H_i values are known, the gas saturation, s_g , and the phase compositions,
 249 $\mathbf{c}_l$ and $\mathbf{c}_g$, can be determined [49].

In the limit of negligible hydrodynamic dispersion and capillary diffusion, local chemical equilibrium, incompressible phases, and a homogeneous porous medium, the change in $\mathbf{C}$ due to two-phase flow with partitioning between the phases is governed by a system of coupled non-linear hyperbolic partial differential equations

$$\frac{\partial \mathbf{C}}{\partial t} + \frac{\partial \mathbf{F}(\mathbf{C})}{\partial x} = 0, \quad (6a)$$

250 where $\mathbf{F}(\mathbf{C})$ is a flux vector that only depends on $\mathbf{C}$, so that the system is
 251 quasi-linear [29]. This system of conservation equations is the extension of
 252 Equation 4 to the multi-component case. The entries of $\mathbf{F}$ are the fluxes of

the individual chemical components and $\mathbf{F}$ is not to be confused with the flux vector in a multi-dimensional flow problem that indicates the direction of flow. Figs. 5A and 5B show that these fluxes are piece-wise defined [32]: linear in the single-phase region and non-convex in the two-phase region. In the two-phase region the fluxes of the components are closely related to the fractional flow function discussed in Section 4.1.

While the theory is developed for an arbitrary number of components [32], a four-component system is sufficient for the discussion of the experimental data presented above and the field data discussed below. This allows the graphical presentation of the analysis in the three-dimensional tetrahedron representing composition space, shown in Fig. 5C.

In all experiments discussed in Section 2, the injected gas comprises a major component, G , and a co-injected noble gas, g . The initial liquid comprises the major component, L , i.e., water, and a dissolved gas, l . The initial condition representing the injection of a two-component gas into a liquid containing a dissolved gas can be written as

$$\mathbf{C} = \begin{cases} \mathbf{C}_{\text{inj}} = (C_G, C_g, 0, 0), & x < 0, \\ \mathbf{C}_{\text{ini}} = (0, 0, C_L, C_l) & x > 0. \end{cases} \quad (6b)$$

Given this particular initial condition, the analytic solution is restricted to two of the triangular surfaces of the tetrahedron. The analysis can be presented in a two-dimensional diamond, as shown in Fig. 5C. For the theoretical example considered below, the Henry's law coefficients are ordered as follows: $H_g < H_l < H_G \ll H_L$, so that the minor gases are less soluble than the main gas component.

Figure 5: **A)** Flux function for the main liquid component L along the injection tie line is shown in red. The injection tie line connects C_1 and C_3 in subfigure C. The tangent constructions for waves $\mathcal{W}_1$ and $\mathcal{W}_2$ are shown by black lines and the corresponding tangent points are C_2 and C_3 . **B)** Flux functions for the g - L crossover and l - L initial tie lines are shown in green and blue. The chords representing waves $\mathcal{W}_3$ and $\mathcal{W}_4$ are shown in black. **C)** The 3D figure in the upper left shows the four-component tetrahedron representing composition space. The large 2D diamond shows the g - G - L and g - L - l faces of the tetrahedron. The red and blue shaded regions represent the single-phase gas and liquid regions, respectively. The tie lines connecting the equilibrium liquid and gas compositions in the white two-phase region are shown as dashed black lines and form a set of composition paths. The other set of composition paths is shown as full black lines. The solution path for initial condition (6b) and solution structure (9) is shown as a green line.

270 *4.3. Solution structure*

The solution of a genuinely non-linear system of three strictly hyperbolic equations comprises three waves or fronts that separate regions of constant composition [29]. However, the eigenvalues of the Jacobian matrix, $\nabla_c \mathbf{F}$, are not ordered and therefore system (6a) is not strictly hyperbolic. This introduces an additional transitional wave and associated intermediate state [17]. The general solution of the four-component two-phase flow problem has the following structure

$$\mathbf{C}_{\text{inj}} \xrightarrow{\mathcal{W}_1} \mathbf{C}_2 \xrightarrow{\mathcal{W}_2} \mathbf{C}_3 \xrightarrow{\mathcal{W}_3} \mathbf{C}_4 \xrightarrow{\mathcal{W}_4} \mathbf{C}_{\text{ini}} \quad (7)$$

271 and comprises four waves, $\mathcal{W}_p$, that separate three regions of constant com-
 272 position given by the intermediate states, $\mathbf{C}_2$, $\mathbf{C}_3$, $\mathbf{C}_4$. From a geochemical
 273 and observational perspective, the composition of the intermediate states is of
 274 greatest interest. Due to the non-linear couplings in (6a), the compositions of
 275 these intermediate states are not bounded by the initial and injected compo-
 276 sitions. This allows noble gas fractionations that evolve towards compositions
 277 that are not simple mixtures between the initial and injected compositions.

278 *4.4. Solution construction in composition space*

Similar to incompressible two-phase flow discussed in Section 4.1, the solution of (6) is self-similar and the concentration profiles simply stretch over time in the direction of displacement [32]. This allows the reduction to a non-linear eigenvalue problem

$$(\nabla_c \mathbf{F} - \lambda_p \mathbf{I}) \mathbf{r}_p = 0, \quad p \in [1, 2, 3]. \quad (8)$$

279 The eigenvectors, $\mathbf{r}_p = d\mathbf{C}/d\eta$, determine directions in composition space
 280 that allow all components to travel with the same speed, given by λ_p [38].
 281 These eigenvalues are analogous to the propagation speed of the saturation
 282 front, λ , in Section 4.1. Here η is a arc-length variable in composition space.
 283 The solution is constructed in composition space where the eigenvectors of
 284 (8) define the grid of composition paths shown in Fig. 5C. Starting with $\mathbf{C}_{\text{inj}}$,
 285 the solution follows paths with increasing speeds towards $\mathbf{C}_{\text{ini}}$. The interme-
 286 diate states, $\mathbf{C}_2$, $\mathbf{C}_3$ and $\mathbf{C}_4$, are located at the points where the solution
 287 switches paths. If λ_p increases along the path, the associated wave is a con-
 288 tinuous rarefaction, $\mathcal{R}_p$, that spreads with time. In contrast, a decrease of
 289 λ_p along the path leads to the formation of a discontinuous self-sharpening
 290 shock, $\mathcal{S}_p$, that propagates with the a speed given by the jump condition
 291 $\Lambda_p = [\mathbf{F}]_p/[\mathbf{C}]_p$, where the brackets indicate the jump in the quantity across
 292 the shock. Finally, the non-convex two-phase flux function, shown in Fig. 5A,
 293 allows the formation of composite waves $\mathcal{R}\mathcal{S}_p$, $\mathcal{S}\mathcal{R}_p$, or $\mathcal{S}\mathcal{R}\mathcal{S}_p$. The Buckley-
 294 Leverett solution for immiscible two-phase flow discussed in Section 4.1 is
 295 such a composite wave, namely a rarefaction-shock, $\mathcal{R}\mathcal{S}$. Once the compo-
 296 sition path of the solution is known, the concentration profiles are obtained
 297 from the variation of λ_p along the path and the jump condition for the shocks.
 298 For details of the solution construction, see SI Appendix Section 1 and the
 299 following references [19, 32].

300 4.5. *Solution for noble gas fractionation during gas migration*

The initial condition (6b) corresponds to the migration of a gas phase
 containing a noble gas though groundwater containing a different dissolved
 (noble) gas. Fig. 5C shows the composition path of the solution and Fig. 6A

the gas saturation profile. The wave structure of this solution is given by

$$\mathbf{C}_{\text{inj}} \xrightarrow{\mathcal{SR}_1} \mathbf{C}_2 \xrightarrow{\mathcal{S}_2} \mathbf{C}_3 \xrightarrow{\mathcal{S}_3} \mathbf{C}_4 \xrightarrow{\mathcal{S}_4} \mathbf{C}_{\text{ini}}. \quad (9)$$

301 The gas saturation shows a typical Buckley-Leverett profile with gradual
 302 increase in gas saturation along $\mathcal{SR}_1$, as discussed in Section 4.1. The slow
 303 increase in gas saturation is due to the low viscosity of the gas relative to
 304 the displaced liquid. However, ahead of the main saturation shock, $\mathcal{S}_2$, is
 305 a region of lower saturation. The concentration profile in Fig. 6B shows
 306 that the main gas component, G , is absent because it has dissolved into
 307 the residual water behind the main shock. The low-saturation region is
 308 divided into two compositionally distinct segments by $\mathcal{S}_3$. In the section
 309 directly ahead of the main shock, the composition is given by $\mathbf{C}_3$ and is
 310 highly enriched in the injected noble gas, g , after the dissolution of G . The
 311 front of the low-saturation region is highly enriched in the atmospheric noble
 312 gas, l , and its composition is given by $\mathbf{C}_4$. This noble gas has been stripped
 313 from the groundwater inside the gas plume and is concentrated at the front of
 314 the migrating gas to values much larger than the initial air saturated values
 315 (Fig. 6C).

316 4.6. Comparison with Neon-Argon- CO_2 Experiment

317 The previous section presents a four-component gas displacement with
 318 idealized coefficients to illustrate the main features of the solution. In par-
 319 ticular, the solubilities had to be exaggerated to make the single-phase re-
 320 gions visible in Fig. 5. The solution is also shown as concentration profiles
 321 as a function of velocity, similar to Fig. 4D. In contrast, the experimental
 322 observations show effluent concentration as a function of volume injected.

Figure 6: Self-similar saturation and composition profiles for initial condition (6b) and solution structure (9) are given as function of propagation speed. **A)** Gas saturation along the direction of displacement. The speeds of the discontinuous waves are given by the chords in Fig. 5A and 5B. The speed along the continuous portion between $\triangle$ and $\square$ is given by dF_L/dC_L in Fig. 1A. Gas **B)** and liquid **C)** phase concentration of components along the direction of displacement. The three regions of constant composition correspond to the three intermediate states. Two banks highly enriched in l and g form at the front of the displacement. No gas is present in the white area corresponding to the initial liquid, ahead of $\mathcal{W}_4$. Note that g is present in the liquid phase to the left of $\mathcal{W}_2$, but its concentration is too low to be visible. In contrast, the dissolved gas l is only present in the liquid to the right of $\mathcal{W}_3$.

323 To facilitate comparison between theory and experiments, Fig. 7 shows
324 theoretical elution curves using the appropriate solubilities of neon, argon,
325 and CO_2 for the experiment shown in Fig. 1. Similar to the experimental
326 results, this solution shows a small bank of neon at first gas arrival, followed
327 by a larger bank of argon, and finally the arrival of the injected CO_2 -argon gas
328 mixture. Matching the arrival times of the different fronts requires a nearly
329 constant and high gas saturation within the gas plume. In the two-phase flow
330 model, this is achieved by reducing the mobility of the gas at low saturations.
331 The combination of a nearly constant gas saturation within the plume and
332 noble gas banks of pure composition makes the simple mass balance model
333 of Section 3 a useful approximation. Similar to the mass balance model, the
334 gas injection solution approximation to the experiment arrives later than the
335 experimental gas arrival, due to incomplete CO_2 dissolution into the residual
336 water during the timescales of the experiment.

337 The theoretical solution neglects the effects of dispersion and therefore
338 predicts sharp fronts that separate pure noble gas banks. In the experiments,
339 both hydrodynamic dispersion and the discrete sampling intervals contribute
340 to smearing of the compositional fronts. The theoretical model predicts banks
341 of similar concentration and differing width, while the experiment shows
342 overlapping banks of similar width and differing concentration. This indicates
343 that the length-scale of smearing is comparable to the width of the noble gas
344 banks. The maximum concentration of argon and neon within the banks
345 does not reach their theoretical value due to this smearing effect. The ratio
346 of the maximum observed concentrations in the banks is comparable to the
347 ratio of the noble gas bank widths in the theory.

Figure 7: Analytical gas injection solution approximating Experiment 1. **A)** Relative permeability curves for liquid and gas phases. The liquid phase relative permeability (blue) has an exponent $n_w=1.05$ and residual water saturation of 0.4. Gas phase relative permeability (red) has an exponent $n_g=3$ with a critical gas saturation of 0.2 and end point relative permeability (k_{rg}^*) of 0.2. **B)** Fractional flow of the gas phase as a function of gas saturation. The gas:liquid viscosity ratio is 60. **C)** Theoretical effluent curve using realistic solubilities of neon, argon, and CO₂ at standard pressure and temperature. The shaded areas show the composition of the effluent gas, while the blue curve represents the saturation of the liquid phase at the column outlet. Similar to the mass balance model, this creates a narrow neon bank, followed by a bank of pure argon, before the system reverts to the injected CO₂-argon mixture. After the end of the pure argon bank, the liquid phase saturation s_L slowly decreases towards the residual saturation of 0.4.

348 5. Field observations of Noble Gas fractionation in two-phase flow

349 Here we introduce three field data sets from previous publications. These
350 studies illustrate the results of noble gas fractionation during two-phase flow
351 of natural gas through groundwater. The first data set contains samples of
352 gas composition from a continuous gas emplacement process at Bravo Dome,
353 NM . The second and third data sets contain dissolved gas measurements
354 from shallow groundwater in the Marcellus and Barnett shales. The observed
355 distributions in these groundwater areas are likely the result of multiple gas
356 migration events. As such, the Bravo Dome case is conceptually closer to the
357 experimental results of Section 2.

358 5.1. *Bravo Dome natural CO₂ reservoir*

359 Bravo Dome is a large natural CO₂ reservoir that contains approximately
360 1.3 Gt of almost pure magmatic CO₂ trapped beneath a regional evaporite
361 seal [4, 41]. In map view the flow was approximately radial away from the
362 pressure maximum in the west (Fig. 8A). After entering the reservoir, the
363 gas flowed nearly horizontally beneath the cap rock for approximately 60 km
364 (Fig. 8C).

365 Noble gases in Bravo Dome have been studied extensively and provide
366 constraints on the dynamics of the reservoir [11, 12]. The concentrations of
367 atmospheric ²⁰Ne are lower than expected from degassing and require that
368 CO₂ entered the reservoir as a free gas phase that stripped ³⁶Ar, ²⁰Ne and
369 other dissolved gases from the reservoir brine. The extreme fractionation of
370 ²⁰Ne/³⁶Ar is interpreted as evidence for re-dissolution of noble gases stripped
371 from the brine. The noble gas dynamics are therefore interpreted as a two-

stage process of initial stripping and later re-dissolution [11].

Recent mass balance estimates show that significant dissolution must have occurred during CO₂ emplacement [40, 41]. The effective residual water saturation in the field is similar to that of the laboratory experiments, approximately 40%, and should cause fractionation of noble gases during the emplacement. Bravo Dome provides an opportunity to test the theoretical predictions against field data, because of the simple filling history, the long migration distance, and the large effective residual brine saturation.

In the context of the theory introduced above, the main gas component, G , corresponds to CO₂, the noble gas isotope introduced with the gas, g , is ³He and the dissolved noble gas isotope, l , is ²⁰Ne. Figs. 8B and 8D show concentration profiles of previously published ³He and ²⁰Ne data in the Bravo Dome gas as a function of approximate migration distance [11]. Close to the source, ³He is constant at the injected value. At the front of the migrating gas the dissolution of CO₂ has increased the concentration of ³He. Close to the source of the gas, ²⁰Ne concentrations are significantly reduced relative to the atmospheric levels ahead of the gas. The ²⁰Ne stripped from the groundwater in the interior of the migrating gas plume has accumulated at the front. Here, its concentration is significantly higher than the initial atmospheric value in the brine leading to re-dissolution.

These field data are consistent with the experimental observations (Figs. 1B and 2B), and in and theoretical predictions of noble gas enrichments (Fig. 6B). The model of combined multi-phase flow and partitioning shows that stripping and re-dissolution can occur simultaneously in different parts of the migrating gas.

Monitoring of the produced gas during the Cranfield CO₂ enhanced oil recovery (CO₂-EOR) project in Mississippi showed similar enrichments of ⁴He, ³He and ²⁰Ne at the in the initial gas after breakthrough. This illustrates that the formation of noble gas banks also occurs on engineering timescales and may therefore provide an important monitoring tool for gas injection projects [13].

5.2. Dissolved gases in groundwater above the Marcellus and Barnett shales

In regions where shallow groundwater contains dissolved thermogenic methane, dissolved noble gases have been invoked as a tool to differentiate natural methane migration from fugitive gases associated with shale gas development [8]. In this case, the thermogenic source gas characteristics are identical, but the natural methane migration is thought to occur over much longer distances. Therefore, an understanding of compositional changes during migration is necessary to discriminate these two processes. In this case, gas composition has to be inferred from the dissolved gases measured in the groundwater. Due to near instantaneous equilibration, the dissolved gas concentrations mirror the gas phase compositions.

During gas migration from the reservoir to the shallow groundwater, more soluble gas components such as CH₄ dissolve into the water so that less soluble components, such as ⁴He, become enriched in the gas. Simultaneously, atmospheric noble gases initially dissolved in the groundwater, such as ²⁰Ne, are stripped from the water and accumulate at the front of the gas plume. This process is analogous to the theoretical displacement considered above, where CH₄ acts as G , ²⁰Ne acts as l , and ⁴He as g .

While theory predicts chromatographic separation between ⁴He and ²⁰Ne

Figure 8: **A)** Bottom hole pressure at the onset of commercial CO_2 extraction from the Bravo Dome reservoir interpolated from 373 wells [41]. The high pressure zone and noble gas isotopes suggest that the CO_2 source is in the west. The markers indicate locations of wells that were sampled for noble gases [6]. **B)** ^3He and ^{20}Ne concentrations from the Bravo Dome natural CO_2 field as a function of distance from entry point shown in subfigure A. Both isotopes are enriched in banks at the gas front. Concentrations are normalized by maximum values in the field.

422 banks (Fig. 6B and 6C), our two-phase flow experiments show that hydro-
423 dynamic dispersion will cause the noble gas banks to overlap (Fig. 1). This
424 leads to a simultaneous enrichment of both ^4He and ^{20}Ne at the gas front
425 (Fig. 9A). This co-enrichment process leads to noble gas concentrations which
426 cannot be explained using simple mixing models between air-saturated water
427 and thermogenic natural gas.

428 Marcellus groundwater samples show similar co-enrichment of ^4He , ^{20}Ne
429 and CH_4 (Fig. 9B). This suggests that the groundwater contacted methane
430 that had migrated a substantial distance, indicating natural migration [8].
431 In contrast, some samples from the Barnett shale lack this co-enrichment
432 suggesting a shorter migration pathway with less noble gas exchange. The
433 samples with the highest CH_4 concentrations are depleted in ^{20}Ne and en-
434 riched in ^4He relative to air-saturated groundwater.

435 Previous work has interpreted depletion of dissolved atmospheric noble
436 gases as a signal of fugitive gas contamination [8]. The counter-intuitive
437 observation that natural gas migration can either enrich or deplete dissolved
438 atmospheric noble gases is explained by the experiments and theory presented
439 here. Gas migration simultaneously enriches ^{20}Ne (l) at the front of the gas
440 plume and depletes it in the interior (Fig. 6B and 1B). The groundwater
441 samples in the Barnett shale (Fig. 9C) with depleted ^{20}Ne represent the
442 stripped interior of the gas plume.

443 In the case of fugitive gases associated with faulty well construction, the
444 migration distance is reduced and the accumulation of dissolved atmospheric
445 noble gases during migration to the shallow groundwater is limited. Upon
446 arrival in the shallow groundwater, the unaltered methane is still depleted

Figure 9: **A)** Gas phase compositions for experimental two-phase displacement of neon-saturated water by a CO_2 -argon mixture shown Fig 1. Similar to the Marcellus field data, dispersion causes the two noble gas banks to overlap, leaving the front of the plume simultaneously enriched in argon (g) and neon (l). **B)** Marcellus and **C)** Barnett groundwater noble gas concentrations [8], normalized to concentration in air-saturated water. The solid black line connects estimated dissolved gases in water at equilibrium with Marcellus reservoir gas [16], the theoretical noble gas bank, and air-saturated water. The noble gas bank represents the saturation limit of dissolved ^4He and ^{20}Ne in shallow groundwater. Note that the source noble gas composition for the Barnett shale is unknown, and is assumed to be identical to the Marcellus gas.

447 in atmospheric noble gases relative to air saturated groundwater, thereby
448 stripping the dissolved noble gases from the shallow groundwater.

449 **6. Conclusion**

450 We combine experiments and theory to explain noble gas fractionation
451 observed in the field. These separations are a result of two-phase flow in the
452 subsurface. Understanding these changes is required to fingerprint subsurface
453 gas sources. This understanding is essential for environmental monitoring of
454 shale gas production and geological CO₂ storage, as well as hydrocarbon
455 exploration.

456 Two-phase flow experiments and gas injection theory show that dissolved
457 gases are stripped from groundwater within the migrating gas and enriched in
458 a bank at the front. Similarly, insoluble components co-injected with the mi-
459 grating gas are also enriched at the front, due to the preferential dissolution
460 of the more soluble main gas component. This leads to a characteristic pat-
461 tern of co-enrichment of insoluble gas components at the front of migrating
462 gas, followed by depletion of initially dissolved gases from the groundwater.

463 This pattern has been observed in concentrations of atmospheric and co-
464 injected noble gases in natural CO₂ reservoirs [12, 6], CO₂-EOR projects
465 [13], conventional gas fields [16], and in shallow groundwater overlying shale
466 gas resources [8]. These compositional changes provide a powerful tool to
467 monitor fugitive gases during shale gas development and to estimate dissolu-
468 tion trapping during geological CO₂ storage. Gas injection theory provides
469 a framework for noble gas fractionation during subsurface gas migration and
470 hence the interpretation of noble gas observations in the field.

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