[PS]Compositional Changes to Gas Migrating through Water-Saturated Rock*

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Abstract

Due to the low solubility of hydrocarbon gases and inert gases in water, natural gas composition is commonly assumed to be unaltered by migration. This may not be the case. Although gases are sparingly soluble in water, the water–gas ratio is high during migration. Therefore, mass of dissolved gases along a migration pathway may approach those of the migrating gas, especially where the migration pathway is long or where diffusion of dissolved gases increases the effective water-gas ratio. Concentrations in gas-phase and dissolved gas were simulated for gas migrating through a stationary water-saturated medium. Where no gas was dissolved in water, gas concentrations changed as predicted by Rayleigh fractionation. Gas ratios at the leading edge of the gas can show moderate compositional fractionation, but the main result is loss of gas-phase volume as the gases dissolve in water. Where gases are dissolved in water, gas ratios in the leading edge of the gas quickly approach equilibrium with the dissolved gas ratios. Consequently, a compositional front develops that separates gas compositions altered by water interaction near its leading edge from unaltered gas compositions near the location where gas enters the system. This front moves farther behind the leading edge with time and farther away from the gas entry point as the total volume of migrating gas in the system increases. The compositional front velocity is controlled by the concentrations of dissolved gas in the water and the intrinsic water-gas ratio. If migration distances are long, a significant volume of gas with composition similar to that dissolved in water may develop behind the leading edge. The altered gas enters traps first, but it is mixed with later, unaltered gas such that its original altered composition may not be evident from the bulk gas in the trap. These models demonstrate that migrating gas or small gas accumulations may develop different compositions due to water interaction during migration, that the volume of altered gas may be significant, and that compositional differences developed during migration are diluted as gas charges large accumulations. Water interaction may explain a number of compositional phenomena: (1) minor gas

compositional variations in gas fields, (2) utility of mud gas isotopes and compositional changes for identifying gas accumulations, and (3) deviations of seep gas compositions from gas compositions in leaking gas pipelines.

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Concentrations in gas-phase and dissolved gas were simulated for gas migrating through a stationary water-saturated medium. Where no gas was dissolved in water prior to gas migration, gaseous components in the migrating gas changed as predicted by Rayleigh fractionation. Component ratios at the leading edge of the gas can show moderate compositional fractionation, but the main result is loss of gas-phase volume as the gases dissolve.

Where gases are dissolved in water, component concentrations in the leading edge of the gas quickly approach equilibrium with the dissolved gas components. Consequently, a compositional front develops within the migrating gas. The front separates gas compositions altered by water interaction (near the leading edge) from unaltered gas (near the gas input point). This front moves farther behind the leading edge with time and farther away from the gas entry point as the total volume of migrating gas in the system increases. The compositional front velocity is controlled by the concentrations of dissolved gas in the water and the intrinsic water-gas ratio. If migration distances are long, a significant volume of gas with composition similar to that dissolved in water may develop behind the leading edge. The altered gas enters traps first, but it is mixed with later, unaltered gas such that its original altered composition may not be evident from the bulk gas in the trap.

These models demonstrate that migrating gas and gas accumulations may develop different compositions due to water interaction during migration, that the volume of altered gas may be significant, and that compositional differences developed during migration are diluted as gas charges large accumulations. Water interaction may explain a number of compositional phenomena: (1) minor gas compositional variations in gas fields, (2) utility of mud gas isotopes and compositional changes for identifying gas accumulations, and (3) deviations of seep gas compositions from gas compositions in leaking gas pipelines.

Terminology

The term "gas" is commonly used to refer both to a phase and to a component within the gas phase. To avoid confusion, the term "gas" will be restricted to describing the phase. Methane, ethane, nitrogen, etc. will be referred to collectively and generally as "species" or "components" that may be dissolved in water or form a gas.

Figure 1. Comparison of modeled and experimentally determined apparent Henry's constants for methane and nitrogen. (A) Freshwater Henry's constants for methane. (B) Saltwater Henry's constants for methane. (C) Nitrogen Henry's constants for methane. Please contact author for citations to data shown on these figures.

Introduction

It is commonly assumed that composition and isotopic ratios of migrated natural gases are mainly indicative of the gas generation and gas mixing (e.g., Whiticar 1994). Alteration by migration through a water-saturated rock is assumed minor. When past studies have evaluated gas interaction with water, the emphasis is on diffusive fractionation (e.g., Prinzhofer et al. 2000), because diffusion is assumed to have a greater potential for altering gas compositions. These are reasonable assumptions, because inert (N_2, Ar, He) and hydrocarbon (methane, ethane, propane, butanes) gaseous components are sparingly soluble in water and brines under most subsurface conditions. Low solubility implies that small masses of these components are present or can be stored in water. If solubility is sufficiently low, the bulk gas composition will not be significantly altered by water interaction. This hypothesis has been validated in general by the compositional similarity between natural gases in economic reservoirs and natural gases generated by pyrolysis in the laboratory.

However, there are settings where water-gas ratio is sufficiently high to offset the low storage potential of the aqueous phase. One such setting is gas migrating through water-saturated rock. Water saturation during gas stratal migration is high, resulting in high water-gas volumetric ratios. Concentrations of components in a migrating gas could in theory be altered significantly by dissolution-exsolution effects. Water-gas ratio is even higher if diffusion of components into or from adjacent beds is considered. High water-gas ratios during migration therefore cause an apparent paradox. If migrating gases have the potential for alteration by water interaction during migration, why do reservoired gases show such minor effects of water interaction?

The purpose of this poster is to show by numerical and analytical modeling that water interaction during migration can significantly alter migrating gas composition. Model results demonstrate how this alteration occurs, where in the migrating gas components are lost and added, and why compositional changes caused by water interaction during migration rarely affect the composition of gases in economically large gas accumulations.

Gas component solubility data and models are first reviewed to provide a basis for understanding gas-water interaction. Two types of alteration are then reviewed: (1) fractionation caused by differential solubility and (2) compositional alteration caused by mixing between the migrating gas and gas dissolved in the pore water. Numerical modeling shows how the balance of these two effects alter compositions of gas interacting with water. Based on concepts developed from these models, analytical models are then used to understand the development of compositional variations within migrating gases. Mass-balance models are used to demonstrate why the compositional changes developed during migration do not greatly affect gas compositions in economic-sized gas reservoirs. Overall results are then used to develop guidelines on where gases are likely to be altered by migration and where they are likely to remain unaltered.

Gas Solubilities in Water

Solubility data are readily available for common hydrocarbon (methane, ethane, propane, n-butane) and inert (nitrogen, argon, helium) gaseous components in pure water at subsurface pressures and temperatures. Data are also available for solubility of many of these gaseous components in brines.

For modeling purposes, solubility of a component is controlled by environmental variables: pressure, temperature, and water salinity. Solubilities of hydrocarbon and inert components are normally modeled by equations of state at the pressures and temperatures of petroleum reservoirs; however, the iterative nature of these models is not suitable for insertion into simple models of water interaction with gases during migration. For this study, component solubilities were modeled by empirical extended Henry's law relationships. Henry's law describes solubility at infinitesimal concentrations, where the Henry's constant, H_o, is a function of temperature only. For a sparingly soluble gas species i:

$$ x_i = \lim_{f_i \to 0} \frac{f_i}{H_{o,i}} $$

Where x_i is the mole fraction in water, f_i is fugacity, and $H_{o,i}$ is Henry's constant.

THE LARGER THE HENRY'S CONSTANT, THE LOWER THE SOLUBILITY

The components methane, ethane, propane, i-butane, n-butane, nitrogen, argon, and helium will be considered here. For low temperature and pressure settings (<50° C, <10 MPa), Henry's constants determined from the data in Wilhelm et al. (1977) were used. At higher pressures and temperatures, solubility departs somewhat from a linear relation to fugacity. Henry's law for sparingly soluble components can be approximated for modeling purposes by using an effective Henry's constant H_e, where H_e is a function of temperature, pressure, and salinity. Data for argon and i-butane solubility at high pressures and temperatures is limited, so solubility models at high pressure and temperature were not developed for argon and i-butane. Fugacity is approximated by the partial pressure (the mole fraction of a gas species multiplied by the total pressure). The resulting empirical Henry's law is:

$$ x_i = \frac{p_{z,i}}{H_{e,i}} $$

Where x_i is the mole fraction in water, $p_{z,i}$ is partial pressure, and $H_{e,i}$ is the effective Henry's constant.

The following relations between the effective Henry's constant will be used for modeling for higher pressure and temperature models. The effective Henry's constants are in units of bars, T in degrees K, and salinity in weight fraction NaCl equivalent. Fit of models to methane and nitrogen data are shown by Figure 1 at left.

$$ H_{methane} = 10^{\wedge}[-3.1172E{-}10\ T^4 + 5.9266E{-}07\ T^3 - 4.3331E{-}04\ T^2 + 0.1403\ T - 11.953 + 3.181E13\ (P/T^3)^3 - 1.702E09\ (P/T^3)^2 + 4.476E04\ (P/T^3) + 1.96{*}S] $$

$$ H_{ethane} = 10^{\wedge}[-7.6277E{-}10{*}T^4 + 1.3916E{-}6{*}T^3 - 9.6294E{-}4{*}T^2 + 0.29567{*}T - 28.927 + 76695\ (P/T^2)^2 + 380.58\ {*}(P/T^2) + 1.96{*}S] $$

$$ H_{propane} = EXP(552.64799 + 0.078453{*}T - 21334.4/T - 85.89736{*}LN(T))/100 $$

$$ H_{n-butane} = (-5.1328E{-}02{*}T^3 + 4.6363E{+}01{*}T^2 - 1.2346E{+}04{*}T + 9.6967E{+}05){*}(1{+}15{*}S) $$

$$ H_{nitrogen} = 10^{\wedge}[log(-2.0327E{-}5T^4 + 0.051419\ T^3 - 45.862\ T^2 + 16883\ T - 2071200) - 3341.1\ (P/T^2)^2 + 56.957\ {*}(P/T^2) + 1.96{*}S] $$

$$ H_{helium} = (1{+}4.7S)(9.4691E{-}03{*}T^3 - 1.5150E{+}01{*}T^2 + 6.6090E{+}03{*}T - 7.3046E{+}05) $$

Relative Gas and Water-Dissolution Storage

Gas will always dissolve in water; in fact, a gas phase cannot coexist with water as a stable phase unless the fugacity in water equals the fugacity in the gaseous phase. If a gas phase is present, components of that gas are stored in water. Dissolution kinetics are rapid, especially in porous media where the gas has a high surface area in contact with water. Migrating gas rapidly equilibrates with the water through which the gas migrates.

The relative storage of a gaseous species in the gas and water phases can be described by the ratio of the volume of gas needed to store a mole of gas to the volume of water needed to store a mole of the same gas species, where both volumes are measured at the subsurface pressure and temperature of interest. Whole volume of gas is the gas constant multiplied by the absolute temperature and the compressibility factor Z and divided by pressure. The compressibility factor is estimated using the reduced temperature and pressure following standard models (e.g., Reid et al., 1977). The volume of water containing a mole of dissolved gas at the same subsurface conditions can be calculated from Henry's law and the molar volume of water.

The volume of gas is divided by the sum of the volumes of gas and water to give the gas saturation at which there is equal storage in the water and gas phases for the component of interest. Gas saturation at equal storage can be compared directly to the gas saturations measured in reservoirs and modeled during migration. Where saturation at equal storage is similar to measured or calculated gas saturation in rocks, water interaction is likely to be significant.

The range of gas saturations with equal volumetric and dissolution storage of hydrocarbon and non-hydrocarbon (inert) natural gases can be demonstrated by saturations of pure methane and pure nitrogen gases, respectively (Figure 2). The solubility of methane and nitrogen were modeled as a function of depth in a basin with normal pore pressure gradient and an average thermal gradient of 30°C/km and surface temperature of 20°C. With the exception of the acid gases CO_2 and H_2S, other gaseous species rarely occur as a near pure phase, so their solubility will be considered relative to other species in gas mixtures.

Results: Nitrogen dissolution storage equals gas volumetric storage between about 0.007 and 0.017 (0.7 to 1.7%) gas saturation in a water-saturated rock (Figure 2). Methane water storage equals gas storage between about 0.01 and 0.036 (1% – 3.6%) gas saturation. The least gas is stored in water where the gas saturation is lowest. This occurs at higher pore-water salinity and intermediate depths (Figure 2). Stating results in another way, pore systems with gas saturation less than values estimated in Figure 2 will have more methane and nitrogen dissolved than migrate in its pore water than in its gas phase. Gas saturations at equal storage fall within the range of gas saturations modeled for gas migration. Water interaction with migrating gas is therefore expected where gas saturation is low.
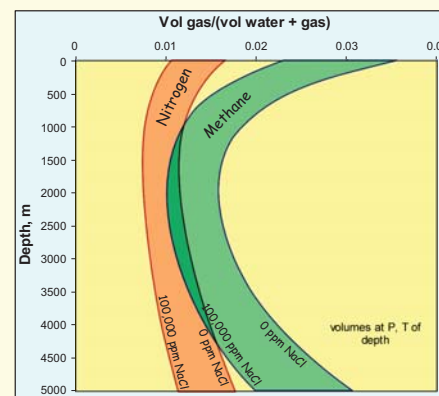

Figure 2. Nitrogen and methane solubility at subsurface conditions expressed as the gas saturation where gas and water have equal storage per unit volume at subsurface conditions. Higher saturation indicates greater dissolution storage in water. Assumed conditions are normal pressure gradient (1.0 g/cc pore-pressure gradient), 30°C/km thermal gradient, and 20°C surface temperature. Pore water salinity is varied from 100,000 ppm NaCl (left sides of color trends) to fresh water (0 ppm NaCl; right sides of color trends).

Models for Gas Interaction with Water

Processes Changing Gas Compositions

Water-gas interaction can cause three types of changes: fractionation changes caused by differential solubility of components in water, mixing changes caused by mixing of components dissolved in water with components in the gas phase, and diffusion-fractionation changes that result from different diffusivity of dissolved components in water. Diffusion-related fractionation will not be discussed here.

Fractionation by differential solubility. Gaseous components more soluble in water will selectively accumulate in the water phase. Selective dissolution will increase the ratio of less soluble components to the more soluble components in the gas phase as the gas interacts with water. The fractionation factor is controlled by the Henry's constants of the components of interest.

Although the fractionation concept is quite straightforward, it is difficult to model analytically for the generalized interaction between a multicomponent gas migrating through water with initial dissolved gas concentrations. Boundary conditions for Rayleigh fractionation are not met except in some specialized cases at the leading edge of the migrating gas.

The component concentration in water also depends on its mole fraction in the gas phase. The component mole fraction in the gas phase changes both by changes to the component and by changes to other components in the gas as each interacts with water. A differential equation can be written to describe changes over small volumes of water interaction if one assumes that the other molar concentrations are constant. This assumption is not valid where all component concentrations are altered by gas-water interaction.

There is essentially no equilibrium carbon isotopic fractionation between gaseous methane and dissolved methane (Fuex 1980). It is generally assumed that isotopic fractionation between gas and water for the other light hydrocarbon gases is also negligible. Kinetic (diffusive) fractionation is probable but is not considered here.

Mixing of dissolved and gaseous species. The concentrations of components in the gas and water mix as they equilibrate. Components in both phases mix, even where components are undersaturated in water. Isotopic mixing and bulk compositions mix as gas equilibrates with the water. Isotopic mixing effects will alter component isotopic composition in the gas even where that component dissolves into the pore water.

Component and isotopic mixing can be calculated by mass balance where solubility fractionation is known. Because solubility fractionation cannot be precisely estimated (see left), analytical mixing model results may also deviate from numerical results.

Approaches to Modelling

Analytical models cannot be used to describe the generalized problem of gas-water interaction, so numerical models are used. A fixed volume of initial gas is mixed with water in a stepwise manner as described in the following section. The model tracks gas compositional and isotopic changes with cumulative water/gas ratio.

This type of model does not mimic gas migration. The gas-water ratio during gas migration is fixed by the saturation whereas water/gas ratio in this type of model increases with interaction. However, the model does demonstrate that gas-water interaction during migration forms compositional fronts within the migrating gas. This "front" concept can be used to model changes in component and isotopic composition in other models.

Three types of models are used in this study:

1. A stepwise model describing changes of composition and volume of a pulse of gas as it interacts incrementally with larger cumulative volumes of water. This model is described in the next section.
2. An analytical model is used to describe the position of a compositional front within gas migrating through a water-saturated medium at a fixed saturation. This model best describes the controls on compositional variations within migrating gas.
3. A bulk mass-balance model will be used to determine the overall effect of water interaction on gas accumulations of various sizes where the gas has migrated along pathways of various volumes.

Stepwise Gas-Water Interaction Model

This model describes changes in gas composition as the gas moves through stationary water and interacts with the water in a stepwise manner. Water volume is approximately conserved due to the low concentrations of gaseous components dissolved in water. Gas volume is not conserved; it changes as components exsolve into the gas or dissolve into the water. At each step, a volume of water interacts with the altered volume and composition of gas. The water-gas ratio increases with each water volume added. Because gas volume changes with interaction, water/gas ratio is indexed to the initial volume of gas.

Concentrations of dissolved and gaseous species change only by mixing and compositional fractionation by differential solubility. Total pressure and temperature are held constant and ideal gas behavior is assumed; therefore, gas molar volumes and Henry's constants do not change during modeling.

Interaction is stepwise. Dimensions of the model are j (position on the migration path) and t (time step). Each position (and time step) corresponds to a fixed volume of water because water does not move. At each time step, a fixed volume of gas is injected into the system at the injection point (j=0). Earlier injected gas moves one water volume farther from the injection point (j,t to j+1,t+1) and interacts with the water at the new position (Figure 3). The leading edge of the gas phase is at position j+t until all of the initial pulse of gas dissolves into water. Where the first volume of gas is dissolved, the second gas volume becomes the leading edge, so the gas phase initiates at j-1+t, etc.

The model follows moles in each phase rather than molar concentrations. The total moles of species i (M_i^t) at j,t are the sum of the gas moles (M_i^g) from j-1,t-1 and the dissolved moles (M_i^d) from j,t-1. The moles in the gas phase M_i^g at j,t are then calculated from M_i^t and the gas volume (L_g) from j,t-1.

Gas volume at the leading edge of a migrating mass of gas may change sufficiently between time steps such that iteration is necessary. The value of M_i^g is first calculated using L_g at j-1,t-1. The M_i^g are summed, and the corrected gas volume from this sum is used to iterate to the corrected gas volume.

Water equilibrates in the stationary water between time steps are quite small at positions behind the leading edge of the gas. Iteration of the gas volume is not necessary for sufficiently small volumes of water interacting with the gas at each time step. Due to the model design, interactions at exceptionally high water/gas ratios are relatively large water/gas ratios at each step. This causes some numerical dispersion at high water/gas ratios.

Boundary conditions:
1. Mole fractions of all species i in the gas at the injection point (j=0) are constant at all times ($f_{i,0,t} = C_i$).
2. Mole fractions of all species i in the water phase (x_i) are the same at all positions j at t=0 ($x_{i,j,0} = C_i$) and interacts with the water at the new position (j,t to j+1,t+1) and interacts with the water. Therefore, $x_{i,j,t} = x_{i,j,0} = C_i$ at all positions where gas is not present.
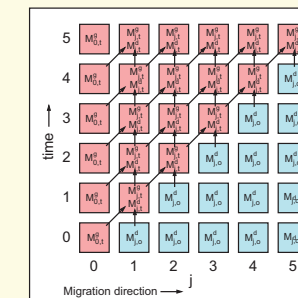

Figure 3. Schematic gas-water interaction model. Initial water concentrations are $M_{0,7}^w$ in all cells. At each time, a fixed volume of gas (red) with concentrations $M_{0,7}^g$ is injected from the left side, and all earlier gas volumes shift to the right one water volume. The gas front moves right one water volume to follow j+t. Total moles of species i is the sum of the gas moles of i from the previous time and water volume plus the dissolved moles of i from the previous time and the same water volume. The gas moles after equilibration is then calculated from the total moles and the modified gas volume.

Modeled Conditions

General

These models can be applied to any compositions of dissolved or free gases at any diagenetic temperature and pressure for which the Henry's constants can be estimated. To simplify the presentation, results for two gas compositions and two migration conditions will be presented. Results for these models show the type of behavior that applies to most gas compositions and migration conditions.

Migration Conditions

Migration conditions affect the Henry's constants and the gas volumetrics due to changes in pressure, temperature, and salinity. Two generalized conditions were modeled: Deep and shallow. Deep migration simulates natural subsurface gas migration at approximately 2 km depth under hydrostatic pore pressure, moderate thermal gradient, and pore water with sea-water salinity (Table, below right). Henry's constants for the deep migration models were calculated using equations presented earlier. Shallow migration simulates conditions during artificial gas leakage, such as leakage from a shallow-buried pipeline (Table, below right). Shallow migration approximates gas migration at about 20 m burial under average surface temperature through fresh water. Henry's constants in the shallow migration models were taken from Wilhelm et al. (1977).

Gas Compositions

Gas-phase composition at the injection point is that of "gas 1" in the table (below right) for shallow and deep migration conditions. Initial dissolved component concentrations are described by the molar compositions of "gas 2" in equilibrium with the water at P, T of interest by the concentration factor, the ratio of the sum of fugacities to the total pressure. Concentration factor of 1 implies that the water is saturated with gas 2. Concentration factor of 0.5 indicates that water has half the dissolved components needed to fully saturate the water with gas 2. Concentration factor of zero indicates no dissolved gaseous components in water prior to migration. As gas and water interact, both composition and saturation change. Deep subsurface conditions are modeled with no argon or isobutane in the system because the Henry's constants for these gaseous species are not known at deep migration conditions.

Migration Conditions											
	Temp. °C	Press. bar	Salinity, wt frac.	Methane	Ethane	Propane	n-Butane	i-Butane	Nitrogen	Argon	Helium
							Henry's Constants, kilobar				
Shallow	20	3	0	36.87	26.47	32.11	38.59	59.88	80.69	37.15	145.2
Deep	80	197	0.03	108.43	488.19	88.09	190.23	—	166.02	—	149.6

Gas Compositions (mole percent)										
	Methane	Ethane	Propane	n-Butane	i-Butane	Nitrogen	Helium	Argon	$\delta^{13}C$, methane (per mil)
Shallow									
Gas 1	85	7	3		1.1	1.1	2.799	0.0009	0.0001	-35.4
Gas 2	90	1.1	0.55	0.38	0.38	7.5897	0.0001	0.0002	-76
Deep									
Gas 1	85	7	2.2			2.799	0.001	—	-35.4
Gas 2	90	1.1	0.55	0.76		7.5897	0.0003	—	-76

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Stepwise Model Results

Interaction is tracked using ratio of water to original gas volume (horizontal axes on figures). Two types of results are shown: (1) compositional changes at the leading edge of the gas as it interacts with successively greater water volumes and (2) gas compositional changes along the migration path at some time after interaction starts. Water/gas ratio increase from left to right. Results are reported in ratios to either methane or nitrogen, to remove effects of varying composition and volume of the bulk gas.

Results are presented for three water saturations: unsaturated water (no dissolved gases), saturated water (water completely saturated with gas 2), and water 50% saturated with gas 2. Leading edge results for both shallow and deep conditions are shown; but variations along the migration path are shown only for shallow conditions because general results for deep conditions are similar.

Unsaturated Water

Leading Edge

Figure 4 shows volume and component ratios at the leading edge of a gas body migrating through water initially containing no dissolved gas (zero saturation) as a function of water/gas ratio. A liter of gas dissolves after interacting with about 28 liters of water at shallow conditions and about 85 liters of water at deep conditions. Component ratios change with interaction, but for most components, these changes are significant only where gas volume is about 20% or less of its initial volume. Gas enrichment is controlled by solubility fractionation; the components least soluble in water enriches in the gas phase as other gases dissolve. Mixing is not possible due to the absence of dissolved gases in the initial water.

Behind Leading Edge

Figures 5 - 7 show compositional and gas volume changes with distance behind the leading edge at different normalized times under shallow conditions. Both distance and time are normalized to water/gas ratio of the first pulse of gas. Ethane/methane (Figure 5) and nitrogen/methane (Figure 6) are used to illustrate how a component that is enriched in the water phase (ethane) and enriched in the gas phase (nitrogen) change with distance behind the leading edge of the gas and the relationship of these changes to changes in total gas volume.

Compositional ratio and gas volume changes are near the leading edge at early time; far behind the leading edge, compositional ratios are those of injected gas. Water rapidly equilibrates with the input gas so gas volumes behind the front are close to injection gas. Component ratios in gas change by selective dissolution. The position where ratios change from the input ratio lag farther behind the leading edge with time. The different ethane/methane and nitrogen/methane fractionation causes distinctly non-linear ethane/methane vs. nitrogen/methane cross plot trends (Figure 7). Trends become more hyperbolic with increasing time.
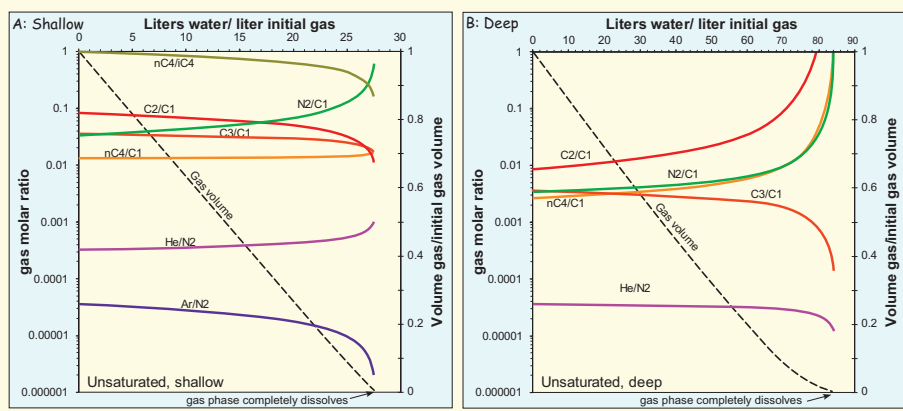

Figure 4. Component ratios and volume in the first pulse of a gas as a function of water interaction where water originally contained no dissolved gas components. A. Migration under shallow conditions. B. Migration under deep conditions.
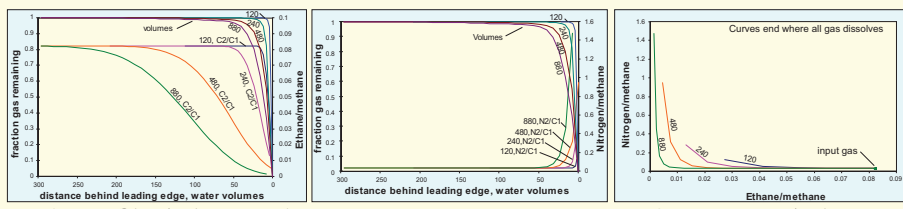

Figure 5. Ethane/methane ratio and gas volume as a function of normalized distance behind leading edge and normalized time. Unsaturated water at shallow conditions. Numbers on curves are normalized time.

Figure 6. Nitrogen/methane ratio and gas volume as a function of normalized distance behind leading edge and normalized time. Unsaturated water at shallow conditions. Numbers on curves are normalized time.

Figure 7. Nitrogen/methane ratio has a pattern similar to a non-linear mixing pattern due to consistent ratio of fractionation factors. Unsaturated water at shallow conditions. Numbers on curves are normalized time.

Saturated Water

Leading Edge

Water is saturated with gas 2, not gas 1. Components exchange to bring water into equilibrium with gas 1. This changes the gas volume. The volume of the first gas pulse decreases by 7% at constant shallow conditions (Figure 8A) and increases by 17 % at deep conditions (Figure 8B). Composition changes are dominated by mixing because gas volume changes (and thus dissolution fractionation) are small. Gas compositions at the leading edge rapidly explore the composition of gas in equilibrium with the dissolved gas. Once the gas has equilibrated to the water, no further compositional changes are possible. Some components such as He have such low concentrations in water that larger water volumes are needed to reach equilibrium.

Behind Leading Edge

Gas volume changes behind the leading edge are also small (Figures 9 and 10). Component ratios change systematically from those of the injected gas far from the leading edge to those of gas equilibrated with water near the leading edge. Compositional changes occur as compositional "fronts" of varying width. Fronts are narrower where compositional changes are in the same direction as fractionation. Fronts widen and lag farther behind the leading edge with time. The widening of the front with time is at least partially a numerical dispersion effect due to large volume of water added at each time step. Cross-plots of methane carbon isotopic ratio against nitrogen/methane and ethane/methane ratio show predominantly non-linear mixing patterns where mixing is less linear at later times (Figure 11). Near the nitrogen-rich (dissolved gas) end member, fractionation affects nitrogen/methane ratio (ellipse, Fig. 11).
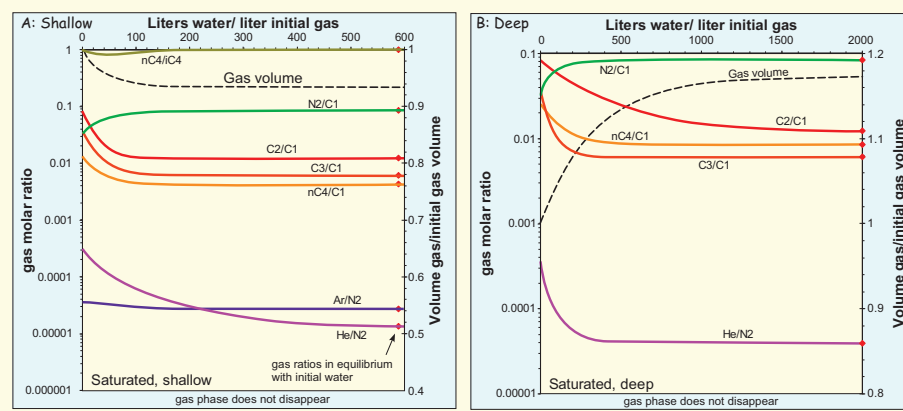

Figure 8. Concentration ratios and gas volume as a function of water interaction for gas and water saturated with a slightly drier gas. (A, left): shallow conditions. (B, right): deep conditions.
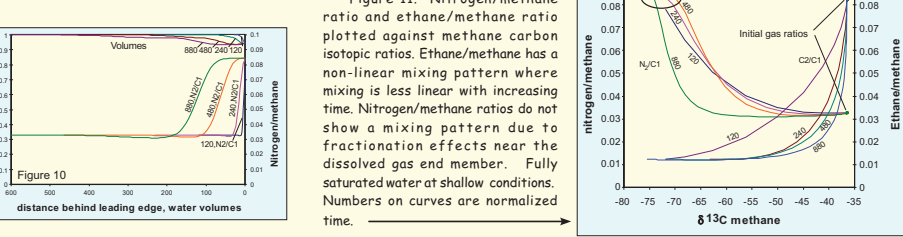

Figure 9. Ethane/methane ratio and gas volume as a function of normalized distance behind leading edge and normalized time. Fully saturated water at shallow conditions. Numbers on curves are normalized time.

Figure 10. N2/methane ratio and gas volume as a function of normalized distance behind leading edge and normalized time. Fully saturated water at shallow conditions. Numbers on curves are normalized time.

Figure 11. Nitrogen/methane ratio and ethane/methane ratio plotted against normalized distance behind leading edge and normalized time. Fully saturated water at shallow conditions. Numbers on curves are normalized time.

50% Saturated Water

Leading Edge

Where water contains dissolved gases at 50% saturation, gas at the leading edge dissolves completely after about twice the volume of the unsaturated water. Component ratio changes at the leading edge of the gas are more complex due to interaction of compositional fractionation and mixing. The ethane/methane ratio in deep settings (Figure 12B) and the nitrogen/methane ratio in shallow settings (Figure 12A) do not approach those of the dissolved water at the leading edge until immediately prior to gas-phase disappearance due to their strong compositional fractionation.

Behind Leading Edge

Compositional changes are quite complex near the leading edge (Figures 13, 14). As with other models, a compositional front develops behind the leading edge separating altered gas from the leading edge from gases with unaltered compositional ratios. In shallow settings, gas ethane/methane has a gas 2 ratio at the leading edge. The ratio decreases slightly where high water/gas supply sufficient methane to alter the gas phase, then rises to the injected (gas 1) ratio farther behind the leading edge (Figure 13). Nitrogen/methane abruptly increases from Gas 2 values behind the leading edge. Because high concentrations of nitrogen in water results from the interaction of mixing at the leading edge, fractionation farther behind the leading edge and finally equilibration of components in water to injection (gas 1) values yet farther behind the leading edge. As with other models, both component ratio fronts move farther behind the leading edge with time and water interaction.

Cross-plots of compositional ratios against methane carbon isotopes (Figure 15) show predominantly non-linear mixing patterns far from the gas 2 end member. Near the gas 2 end-member, nitrogen/methane significantly exceeds the mixing trend due to fractionation. Ethane/methane is slightly less than the expected mixing trend, also due to dissolution fractionation.
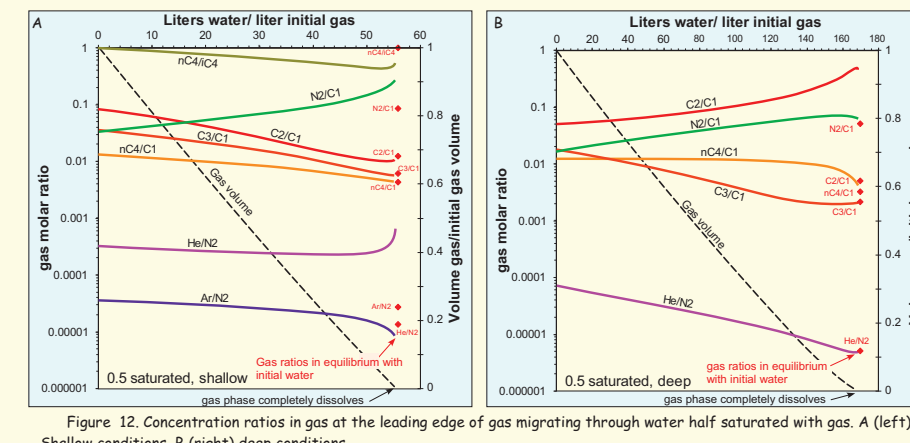

Figure 12. Concentration ratios as gas at the leading edge of gas migrating through water half saturated with gas. A (left). Shallow conditions. B (right) deep conditions.
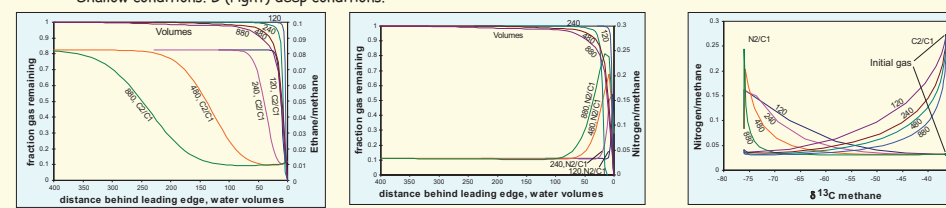

Figure 13. Ethane/methane ratio and gas volume as a function of normalized distance behind leading edge and normalized time. Half-saturated water at shallow conditions. Numbers on curves are normalized time.

Figure 14. Nitrogen/methane ratio and gas volume as a function of normalized distance behind leading edge and normalized time. Half-saturated water at shallow conditions. Numbers on curves are normalized time.

Figure 15. Nitrogen/methane ratio and ethane/methane ratio plotted against methane carbon isotopic ratio. Neither ratio shows a mixing pattern due to fractionation effects near the dissolved gas end member. Farther from the end member, patterns are quite similar to non-linear mixing. Half-saturated water at shallow conditions. Numbers on curves are normalized time.

Generalized Patterns and Summary

Isotopic Variations

Methane carbon isotopic ratio is altered only by mixing. Where no dissolved methane is in pore water, methane isotopic composition does not change (Figure 16). At low saturation of dissolved methane in water (<10%), methane carbon isotopes in the gas are altered only where composition of methane in the gas phase adjacent to the water. The gas phase dissolves before the methane can acquire the isotopic ratio of the dissolved methane; therefore, the volume of the isotopically altered gas is quite small. As the saturation of dissolved methane in water increases, mixing becomes more significant, and isotopic ratios alter more at lower water/gas ratios. At high saturation of dissolved methane in water (>80%), methane in the leading edge of the migrating gas acquires an isotopic composition essentially identical to that of the methane initially dissolved in water. Results are similar for shallow conditions, with minor differences caused by the different masses of methane in the gas and water phases. Results are also similar for later pulses of gas, with the exception that the onset of mixing behavior is offset to higher water/gas ratios.

Compositional Ratios

Gas compositional ratios at the leading edge of a migrating gas body are altered by both fractionation and mixing (Figure 17). Fractionation dominates where concentrations of dissolved gas are low. Gas volume decreases by dissolution into water and fractionation follows a Rayleigh pattern. The direction of compositional fractionation is controlled by relative solubility of the two gases. Figure 17 shows ethane/methane ratio at the leading edge under deep conditions. Ethane is less soluble than methane and accumulates at the leading edge. The gas phase dissolves before the methane can acquire the isotopic ratio of the dissolved methane. The magnitude of the fractionation is proportional to the inverse of the ratios of their Henry's coefficients. A less soluble gas becomes concentrated at the leading edge of the gas body, whereas a more soluble gas is depleted.

As concentration of dissolved components in water increase, mixing effects become apparent. Mixing dominates over fractionation where concentrations of gases dissolved in water are high and where volumes of remaining gas become low near its leading edge. In Figure 17, ethane/methane in gas equilibrated to initial water is lower than that of the injected gas. The ethane/methane decreases with water interaction where mixing dominates. Where water has low dissolved gas concentrations, the gas phase will dissolve before mixing significantly influences the gas compositional ratio (Figure 17, curves 0 - 0.7). Compositional changes are caused mainly by fractionation as the gas dissolves into water. At high dissolved gas concentrations (curves 0.7 - 1), mixing masks most fractionation effects, and gas near the leading edge acquires the composition and isotopic ratios of the gas dissolved in the water. At intermediate dissolved gas concentrations (0.5 - 0.7), fractionation effects develop first, followed by a reversal caused by mixing.

Fractionation effects can be enhanced behind the leading edge. High ratios in gas elevate the ratios dissolved in water. The altered water releases some of the stored, less soluble gas into the next gas pulse. This causes the next gas pulse to have an even higher compositional front. A relatively abrupt compositional front separates the fractionated gas near the leading edge from the unaltered gas comprising the majority of the gas body. Mixing effects cause the compositional front to shift farther behind the leading edge with total migration distance and total amount of water interaction.
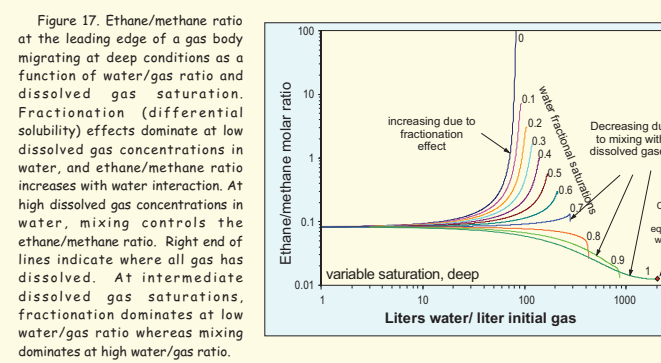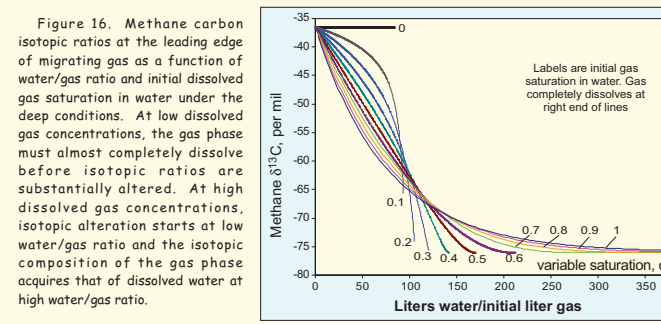

Figure 16. Methane carbon isotopic ratio of gas as a function of migrating gas as a function of water/gas ratio and initial dissolved gas saturation in water under the deep conditions. At low dissolved gas concentrations, the gas phase must almost completely dissolve before isotopic ratios are substantially altered. At high dissolved gas concentrations, isotopic alteration starts at low water/gas ratio and the isotopic composition of the gas phase acquires that of dissolved water at high water/gas ratio.

Figure 17. Ethane/methane ratio at the leading edge of a gas body migrating at deep conditions as a function of water/gas ratio and dissolved gas saturation. Fractionation (differential solubility) effects dominate at low dissolved gas concentrations in water, and ethane/methane ratio increases with water interaction. At high dissolved gas concentrations in water, mixing controls the ethane/methane ratio. Right end of lines indicate where all gas that dissolved at intermediate dissolved gas saturations, fractionation dominates at low water/gas ratio whereas mixing dominates at high water/gas ratio.

Introduction to Migration Model

Weaknesses of Stepwise Model

Up to this point, time and distance of interaction has been tracked using normalized water/gas ratios by exposing a small gas volume to successive water volumes. Although the stepwise model provides insights into the mixing and fractionation processes controlling compositional variation during water-gas interaction, the stepwise model does not simulate gas migration in water-saturated rock for the following reasons:
• Gas migrates through water-saturated rock with some gas saturation. If the carrier bed is uniform, gas saturation is uniform along the migration pathway. The gas saturation is the gas/water ratio divided by one plus the gas/water ratio. Thus, gas/water ratio (and water/gas ratio) is a fixed boundary condition for gas migration in a porous carrier bed. The water/gas ratio changes during stepwise models: in fact, the water/gas ratio is used to track the compositional evolution of the model. Boundary conditions for gas-water interaction in migration models are therefore different from those of stepwise models.
• The water/gas ratios used to track interaction in the stepwise model are difficult to convert to physical distances and time by themselves. By choosing sufficiently small initial gas volumes, the physical distance (and time) corresponding to the water/gas ratio can be arbitrarily short. The rather broad, diffuse compositional fronts modeled in the stepwise models shrink to step functions of the physical migration distance when small gas volume steps are used
• From pure bookkeeping considerations, the value of the water/gas ratio in the stepwise model is ambiguous for all gas pulses after the first compositional front. In later pulses, the water/gas ratio seen by the gas differs from that seen by the water. The water-gas ratio of later gas pulses therefore cannot be defined clearly and the index for interaction, the water/gas ratio, cannot be transferred to physical space.
• Finally, the stepwise model introduces a numerical dispersion that broadens the width of the compositional front. The water volumes added at each model step are finite, not infinitesimal. The larger water volumes that are used to model effects of large cumulative water/gas ratios exceed the step size needed to minimize numerical dispersion. Numerical dispersion causes compositional fronts to widen with water interaction.

Compositional Fronts

One of the major results of the stepwise model is demonstration that alteration of migrating gas by water interaction creates compositional fronts. The stepwise model further demonstrates that compositional fronts for different component ratios occur at different positions behind the leading edge.

Compositional fronts are narrow physical zones separating gases with different compositions. Gas between the leading edge of the migrating gas and the front is altered by water interaction. Gas between the front and the gas input position is unaltered. Two types of compositional fronts develop. Where initial dissolved gas concentrations are low, compositional fronts are caused by dissolution fractionation. Where initial dissolved gas concentrations are high, compositional fronts are caused by mixing of dissolved and input gas. Fractionation compositional fronts are of minor importance because fractionation is significant only where the gas volume is greatly reduced. A small total gas volume means that compositionally fractionated gas will be relatively rare and volumetrically insignificant.

The stepwise model was not designed to determine the physical width of these compositional fronts. Concentrations in a migrating gas phase near a compositional front are controlled by diffusion in the gas phase and heterogeneity of the pore structure. These effects are not simulated by the stepwise model; therefore, physical width of the compositional front in a real system cannot be estimated by the stepwise model. The normalized nature of the stepwise model can be scaled to whatever physical dimension is desired. If gas and water volumes in liters or cubic meters, the width of the concentration front is on the scale of meters. Where gas and water volumes are measured in ml or μl, the width of the concentration front in the stepwise model is a few mm. The potentially abrupt nature of the compositional front is entirely consistent with our expectation for a system with relatively low storage capacity in water. Because of the potential role of physical dispersion, compositional fronts can be arbitrarily narrow.

With this insight and the recognized limitations of the stepwise model, an alternate model was constructed to evaluate compositional changes in migrating gas. The model assumes that compositional fronts develop which are similar to those simulated by the stepwise model. The compositional front for each component separates gas with the initial gas composition from gas with composition in equilibrium with that component dissolved in water near the leading edge.

The position of compositional fronts can be calculated from mass balance. All of a gaseous component dissolved in water is swept into the leading part of the migrating gas mass ahead of its compositional front. Behind the front, the concentration of the component in gas is that of the input gas. The volume of dissolved gas along a pathway can be used to calculate the position of the compositional front relative to the leading edge of the gas.
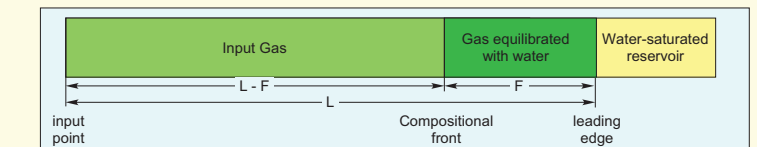

Figure 18. Schematic distribution of a gas component used to determine the position of the compositional front as a function of total length of the gas-saturated migration path.

Analytical Model for Compositional Front Position

The positions of compositional fronts for each component are determined by mass balance. The mass of component i dissolved in pore water along the entire path prior to gas interaction is equal to the amount of the component stored as gas and dissolved gas between the front and the leading edge. The distance of the front behind the leading edge (F) is proportional to the total length of the migration pathway (L, Figure 18). Models will have results for zero dispersion (abrupt concentration fronts). The center of a broad front will lie at the same position as that of a zero-dispersion front.

The position of a compositional front behind the leading edge for component i is described as the ratio (F/L), where (F/L) = 0 at the leading edge and (F/L) = 1 at the inlet (position where gas enters the carrier bed). Uniform porosity, saturation, and dissolved component concentrations are assumed. Mass balance gives:

$$\frac{F}{L_i} = \frac{f_i^u}{f_i^e} = \frac{S}{(1 - s_g) + \frac{s_g H_i V_m}{RT}}$$

where S is the saturation of total gaseous components in water prior to interaction with gas. s_g is the fractional gas-phase saturation along the migration pathway after interaction. H_i is the Henry's constant for the component of interest, R is the gas constant, T is absolute temperature, and V_m is the molar volume of water. The term f_i^e is the mole fraction of a component in an infinitesimal gas fraction prior to interaction with water. The term f_i^u is the mole fraction of the same component in the gas phase between the front and the leading edge. The ratio f_i^u/f_i^e is close to 1 in almost all circumstances and is exactly 1 where S=1 and s_g=0.

Different components in the same gas system will have different F/L. Differences between positions of different compositional fronts result in different f_i^u which affect F/L at positions farther from the leading edge. This effect is small and ignored here. (i.e., f_i^u/f_i^e is assumed to equal 1 for all settings).

Compositional Changes to Gas Migrating through Water-Saturated Rock

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Position of Compositional Fronts and Gas Compositional Ratios in Migrating Gas

General Patterns

The F/L is mostly controlled by the Henry's constants, gas saturation, and saturation of the dissolved gases in water prior to gas-water interaction. Low solubility gases (large Henry's constants) have lower F/L than high solubility gases. The only effect of component concentrations on F/L is their effect on f_i^∞/f_i^T. Compositional effects on f_i^∞/f_i^T are typically small, so compositional effects on F/L will be small in most settings. Concentration effects will be greatest where s_g is high and S is low. Model results shown on this poster all have assumed f_i^∞/f_i^T equal to 1 at all concentrations.

Henry's constants changes with environmental conditions. Figure 19 illustrates variations in F/L due to Henry's constant changes with depth for fixed gas saturation ($s_g = 0.03$) and saturation of dissolved gases in water (S=1).

Where water is completely saturated with gas and the Henry's constants are fixed, F/L is a function of the gas saturation (s_g). At $s_g=0$, F/L is 1 for all components (all gas in the migration pathway is dissolved gas). F/L decreases for all components as gas saturation increases. With $s_g = 3\%$ at shallow conditions, the majority of components in the migrating gas are derived from the water (F/L > 0.5; Figure 20). The exceptions are sparingly soluble components such as He. All F/L is quite small at reservoir gas saturations ($s_g > 0.6$).

F/L is linearly proportional to the saturation of dissolved components in water prior to water-gas interaction (S; not figured). Multiply F/L in Figure 20 by the value of S to estimate F/L for shallow conditions where pore water is not completely saturated. All compositional ratio fronts shift away from the leading edge (F/L increases) as S increases and s_g decreases.
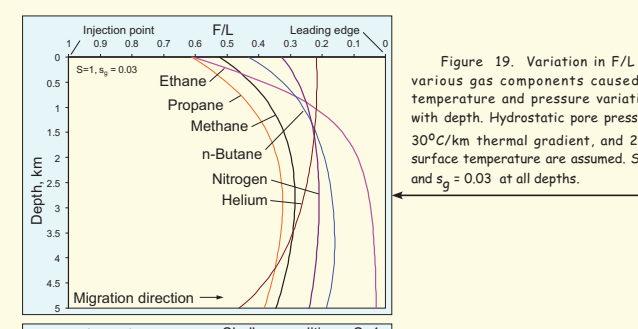
Ratio Variations Along the Migration Path

Ratios involve two components; therefore, ratios will change at two F/L positions, the F/L of the denominator component front and the F/L of the numerator component front. Where the two components have similar Henry's constants, the ratio will appear to have a single compositional front. Each isotopic ratio of interest has a single front located at the F/L for the gas component containing the isotope of interest.

Distribution of gas ratios under various assumptions are shown in Figure 21. At shallow depth, 3% s_g and S=1, the compositional ratio fronts of most species are far from the leading edge of the migrating gas body (Figure 21B). Decreasing s_g to 1% pushes all ratio fronts even farther from the leading edge (Figure 21A). Increasing s_g to 30% moves all ratio fronts closer to the leading edge (Figure 21C). Changing the conditions from shallow to deep changes the relative positions of different ratio fronts in response to changing Henry's constants (Figure 21D).

Figure 21. Variation of position with compositional ratio fronts and methane $\delta^{13}C$ under different conditions (A). 1% gas saturation ($s_g = 0.001$) and water initially fully saturated with gas (S=1) at shallow conditions. (B) 3% gas saturation ($s_g = 0.03$) and water initially fully saturated with gas (S=1) at shallow conditions. (C) 30% gas saturation ($s_g = 0.3$) and water initially fully saturated with gas (S=1) at shallow conditions. (D) 3% ($s_g = 0.03$) gas saturation and water fully saturated with gas at deep conditions. See panel 1 for description of depth conditions.

Figure 19. Variation in F/L for different gas components caused by temperature and pressure variations with depth. 30°C/km thermal gradient, and 20°C surface temperature are assumed. S = 1 and $s_g = 0.03$ at all depths.
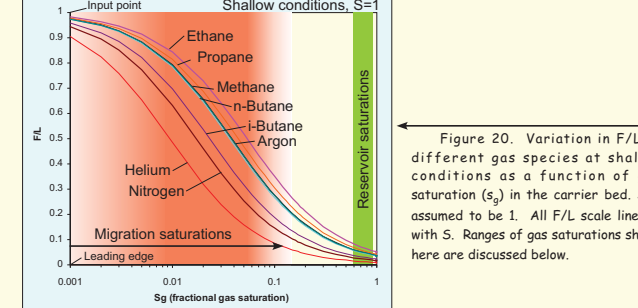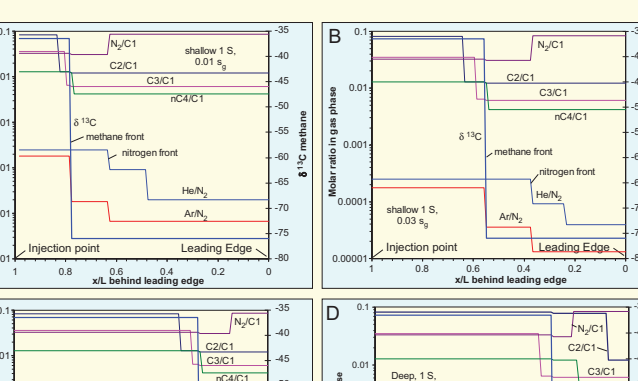

Figure 20. Variation in F/L of different gas species at shallow conditions as a function of gas saturation (s_g) in the carrier bed. S is assumed to be 1. All F/L scale linearly with S. Ranges of gas saturations shown here are discussed below.

Gas Saturation During Migration and Entrapment

Gas Saturations in Economic Reservoirs

Gas saturations are commonly measured in both conventional and unconventional accumulations. Typical gas saturations in clay-free conventional reservoirs close to irreducible water are 0.8 and 0.9. Gas saturations in tight gas sandstones are typically somewhat lower, between about 0.5 and 0.8 (Shanley et al. 2004; Byrnes et al. 2009). Lower gas saturations typically are not productive in tight reservoirs (Shanley et al. 2004).

Gas Saturations during Migration

Simulations and experimental data indicate that secondary migration is quite low and close to the critical gas saturation during natural gas migration. The critical gas saturation is the minimum gas saturation needed for measurable gas-phase permeability. It corresponds roughly to the average saturation of a sample at the point when the first continuous non-wetting pathway extends through the sample (Byrnes et al. 2009).

A large data set of Cretaceous sandstones have a mode of critical gas saturation close to 3%, and a range from less than 1% to about 35% (Figure 22; Byrnes et al. 2009). This is similar to previous literature studies (summarized in Byrnes et al. 2009). High permeability rocks have a greater fraction of samples with low critical saturation than low permeability rocks (Figure 23; Byrnes et al. 2009). Based on these results, gas saturation during migration probably averages somewhere between 1 and 3% in carrier beds with reasonably high permeability.
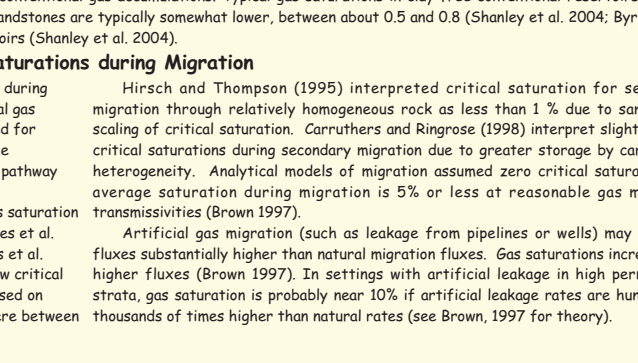
Hirsch and Thompson (1995) interpreted critical saturation for secondary migration through relatively homogeneous rock as less than 1% due to sample-size scaling of critical saturation. Carruthers and Ringrose (1998) interpret slightly higher critical saturations during secondary migration due to greater storage by carrier bed heterogeneity. Analytical models of migration assumed zero critical saturation, yet average saturation during migration is 5% or less at reasonable gas migration transmissivities (Brown 1997).

Artificial gas migration (such as leakage from pipelines or wells) may have gas fluxes substantially higher than natural migration fluxes. Gas saturations increase with higher fluxes (Brown 1997). In settings with artificial leakage in high permeability strata, gas saturation is probably near 10% if artificial leakage rates are hundreds to thousands of times higher than natural rates (see Brown, 1997 for theory).

Figure 22. Frequency of critical gas saturations measured on 150 Mesaverde Sandstone samples. Data from Byrnes et al. (2009).

Figure 23. Critical gas saturations of Mesaverde Sandstone samples plotted against gas permeability measured at 4000 psi confining stress. Data from Byrnes et al. (2009).

Implications for Water Interaction with Migrating Gas

Water Interaction During Migration

Natural gas migration occurs at such low gas saturations that water/gas ratios are high, and water interaction with gas is likely. Modeling results show that the gas altered by water interaction accumulates behind the leading edge, and most of the migrating gas is unaltered by water interaction farther from the leading edge of the gas body (Figure 24).

At water/gas ratios consistent with gas saturation during natural migration, the altered gas comprises a significant fraction of the total length of the migration pathway where water along the pathway is close to saturated for gas (Figures 19-21). As gas is added to the system at the input point, the migrating path lengthens so the system retains its high water/gas ratio (Figure 24). The fraction of the migration pathway with altered gas is fixed by the migration conditions, so the length containing altered gas lengthens as the migration path lengthens.

Models do not include dispersion or diffusion. Dispersion will broaden compositional fronts giving mixed gases instead of two unmixed gases along the migration path. Diffusion of dissolved components in water towards or away from the migration path will alter gas independent from the leading edge of the migrating gas. These effects are sensitive to the rate of gas migration and have not been modeled in this study.
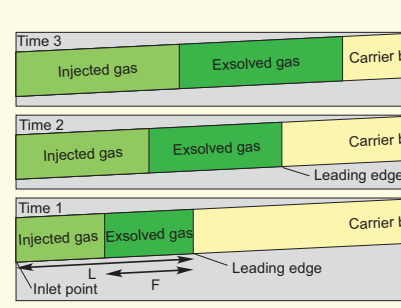
Effects of Termination of Migration Pathways

Migration pathways cannot extend forever. Some crop out to form seeps. Others charge gas accumulations. Termination of migration pathways alters the simple compositional patterns modeled here.

If the migration pathway crops out (i.e. a gas seep), the migration pathway cannot lengthen as more gas charges the carrier bed. Gas is lost at the seep and the effective water/gas ratio decreases. The altered gas (gas with exsolved components) is closest to the leading edge, so altered gas is selectively lost (Figure 25). The fraction of unaltered gas in the migration pathway increases as the compositional fronts approach the seep. Ultimately, the compositional fronts reach the seep and seeping gas is unaltered inlet gas (Figure 25).

A similar phenomenon occurs where migrating gas charges a trap (Figure 26). The migration length is fixed, so any additional gas charge flushes the altered gas from the migration pathway into the trap. The trap reservoir has a higher gas saturation than the migration pathway, so effects of water interaction with gas in the reservoir are negligible. Overall average water/gas ratio decreases as the trap is charged. Alteration by water interaction during migration could be preserved in the trap if gas does not mix completely at the trap fills. Otherwise, the altered gas may be diluted to the point where it is no longer recognized.
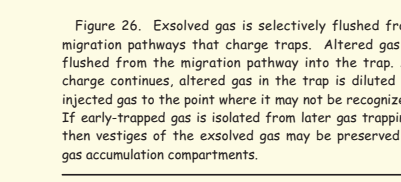

Figure 24. Distribution of exsolved gas in a carrier bed during migration. The exsolved gas forms a fixed fraction of the total gas pathway length, so the physical length of the exsolved gas increases as the pathway lengthens.

Figure 25. Where the carrier bed intersects the surface to form a gas seep, the exsolved gas is the first to be flushed from the pathway. Seepage of natural seeps is likely to be old enough that all exsolved gas is flushed from the pathway. However, gas samples from artificial seeps collected soon after seep initiation may be altered by water interaction.

Figure 26. Exsolved gas is selectively flushed from migration pathways that charge traps. Altered gas is flushed from the migration pathway into the trap. As charge continues, altered gas in the trap is diluted by injected gas to the point where it may not be recognized. If early-trapped gas is isolated from later gas trapping, then vestiges of the exsolved gas may be preserved in gas accumulation compartments.

Exsolved Components in Reservoired Gas

Reservoirs have water/gas ratios less than 1 due to high gas saturation. If the reservoir is considered by itself, water interaction effects are negligible. However, gas migrates through water-saturated carrier beds with water/gas ratios significantly greater than 1 prior to charging the trap. Water interaction effects developed during migration might be preserved in gas accumulations.

Settings where reservoired gas may show effects of water interaction are evaluated by mass balance. The mass of dissolved gas in the migration path and the reservoir is calculated and compared to the total migrated gas. The gas saturation during migration and the degree of saturation of the pore water are rarely known, so values are selected to maximize the dissolved gas component. Water interaction effects are maximized where water is fully saturated with gas (S=1) and gas saturation along the migration pathway is low ($s_g \to 0$).

Methane alteration is used as an example. Figure 27 plots fractions of methane in an accumulation exsolved from water as a function of migration distance and accumulation size. The continuous thread model (Schowalter 1979) was assumed for gas migration. A small cross sectional area of gas migration (500 m by 1 m) was assumed following conclusions of Brown (1997).

The fraction of methane derived from dissolved storage increases as the accumulation size decreases and the migration distance increases. Smaller economic accumulations (<10 BCF) will contain less than 10% exsolved methane except where migration distance is long. Large accumulations (>100 BCF) will have less than about 1% exsolved methane for all modeled migration distances. Similar results are calculated for other hydrocarbon gases. Inorganic gases such as helium and nitrogen had such low concentrations in thermogenic gases that water interaction effects may be evident for these gases even in large accumulations.

To conclude, the hydrocarbon gas geochemical signature in most economic accumulations is that of the gas source, not hydrocarbons exsolved from water during migration. This is caused by the low overall water/gas ratio in systems with large economic gas accumulations. It is for this reason that hydrocarbon gas geochemistry has proven so successful for identifying type and thermal maturity of the gas source, even where gas has migrated through a significant volume of water-saturated carrier bed. Small gas accumulations may have sufficiently large water/gas ratios that reservoired hydrocarbon gases might retain their alteration during migration.
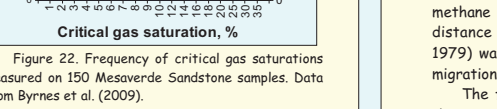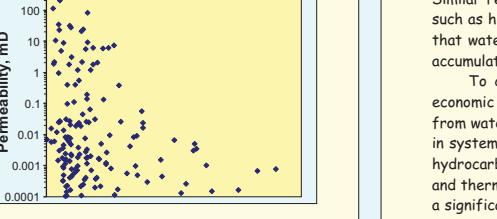

Figure 27. Maximum fraction of dissolved methane in gas accumulations as a function of volume of migration pathway accumulation as migration distance. Model assumes infinitesimal gas saturation during migration, 20% porosity, and a migration pathway 1 m thick by 500m wide. Migration occurs at 2 km in a normal pressured basin through sea-water salinity water. Water is assumed to be completely saturated with methane prior to migration.

Implications for Gas Geochemical Interpretation

Natural Gas Interpretation

The context and setting of a gas sample should be considered during the interpretation process so that the potential for water interaction effects can be identified. Even where a potential for water interaction is identified, demonstration or proof that the gas is altered by water interaction is difficult or impossible unless samples of gas exsolved from water are available. Such samples are quite rare in deep sedimentary basins. At best, mud-gas compositions guide our understanding of dissolved hydrocarbon gas compositions, but these are difficult to convert to absolute concentrations in the pore water.

Reservoirs. The vast majority of gas samples evaluated for exploration and production come from economic-sized accumulations. The water/gas ratio is quite low in most large gas accumulations due to the small pore volume of the migration pathway compared to the gas volume in the reservoir. Hydrocarbon gases in large, economic accumulations are not likely to be altered by water interaction during migration or in the reservoirs. Hydrocarbon gases will reflect source and thermal maturity, according to well established criteria. Dilution of altered gas by unaltered gas occurs in the trap. If a reservoir compartment in a large trap is isolated early in charging, gases in this compartment might show evidence for water interaction. Small gas accumulations formed by long-distance migration are more likely to show effects of water interaction due to their higher water/gas ratio. Some economic gas accumulations may form by exsolution during regional exhumation (Cramer et al. 2002; Brown 1997a). Gas in such accumulations may be predominantly dissolved gas despite their large size.

Migrating Gas. If the migrating gas pathway is sampled close to its leading edge, the gas samples may have compositions characteristic of the dissolved gas rather than the gas source (Figure 24). Gas samples from near the inlet point to the migration pathway will have characteristics of the gas source unaltered by water interaction. In supercharged petroleum systems, many migrating gas pathways will be connected to traps or seeps. The altered gas is likely to be lost, and sampled shows will be hydrocarbon gas charged to the system that is relatively unaltered by water interaction.

Natural gas seeps will almost certainly show characteristics of the gas source rather than gas altered by water interaction. Unless the seep starts fortuitously just before sampling, the leading edge with dissolved gas will have leaked from the migration pathway (Figure 25). Seep samples may also be altered by microbial processes which are not considered here.

Artificial Leakage Interpretation

Unlike natural migration, water migration resulting from pipeline or well leakage might be sampled soon after initiation of leakage, and it is more likely that effects of water alteration will be detected by early seep sampling. Shallow depth also allows measurement of dissolved gas concentrations in the migration pathway from water samples collected in shallow wells.

If pore water lacks significant dissolved gas, compositional fractionations might be seen in early seep samples which may be difficult to relate to compositions of samples collected later from the same or other seeps and monitor wells. Where dissolved gases are near saturation, early gas samples may have composition in equilibrium with dissolved gas rather than leaking gas. This may lead to an interpretation that the seeping gas is indigenous and natural rather than caused by leakage. Although the gas itself is native and natural, its accumulation at the leading edge of the artificial migration pathway is the result of leakage. With time, the true nature of the gas will become apparent. Both fractionation and mixing effects are likely to disappear at a monitoring station as compositional fronts pass that position.

Artificial leakage may be characterized by leakage rates much higher than natural migration rates. This may raise the gas saturation, so positions of compositional fronts may be close to the leading edge of the leaking gas. The compositional fronts may pass through monitoring stations soon after initiation of seepage. Minor pathways of leaked gas may have lower migration rates, lower gas saturations, and therefore longer times before the gas compositional front reaches the monitoring station. This may lead to confusing mapped distributions of leaked gas compositions. Overall, water interaction may cause compositional variations with time and position more complex than might be expected by simple leakage and migration patterns without water interaction. Seep and aquifer areas affected by artificial leakage sites may have to be sampled over an extended time to truly identify areas affected by the leaked gas.

Conclusions

Water interaction changes gas compositions by fractionation and mixing. Fractionation results for different solubility in water. Fractionation is most likely during migration through pore water without dissolved gaseous components. It is not likely to alter the composition of a significant volume of gas, because fractionation is associated with the small remaining volume of gas after most has been dissolved in water. All fractionation effects will be localized to a very narrow zone at the leading edge of the migrating gas mass. Mixing alters migrating gas composition where gaseous components are dissolved in pore water. Mixing can alter a significant volume of gas where water/gas ratios are high and dissolved gaseous components nearly saturate the water.

Gases altered by water interaction along the migration path accumulate at the leading edge of a migrating gas body. The leading edge of a migrating gas acquires the compositional ratios of the exsolved gas. Compositional fronts separate gases exsolved from water in the leading part of the migrating gas from the unaltered gases injected into the carrier bed. Positions of these compositional fronts are controlled by the saturation of dissolved gas in water before interaction, the saturation of the migrating gas in the rock, and the Henry's constants for the gas species of interest. Where saturation of dissolved gas is high and saturation of the migrating gas is low, water-gas interaction alters a significant fraction of the gas in the migration pathway.

The compositional effects of gas interaction with water are most likely to be detected in samples from natural or artificial gas migration pathways through water-saturated rock. Effects of water interaction are not likely to be evident in large, economic gas accumulations due to low water/gas ratios of the combined migration path-reservoir system. However, the setting from which a gas is sampled should always be considered when evaluating compositional data to evaluate the potential for water alteration. In artificial seeps, water interaction can make the detection and mapping of leakage effects more ambiguous.
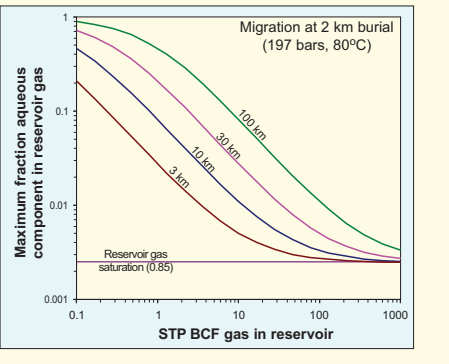
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