Tracing enhanced oil recovery signatures in casing gases from the Lost Hills oil field using noble gases

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Abstract

Enhanced oil recovery (EOR) and hydraulic fracturing practices are commonly used methods to improve hydrocarbon extraction efficiency; however, the environmental effects of such practices remain poorly understood. EOR is particularly prevalent in oil fields throughout California where water resources are in high demand and the disposal of large volumes of produced water may affect groundwater quality. Consequently, it is essential to better understand the fate of injected (EOR) fluids in California, and other subsurface petroleum systems, as well as any potential effect on nearby aquifer systems. Noble gases can be used as tracers to understand hydrocarbon generation, migration, and storage conditions, as well as the relative proportions of oil and water present in the subsurface. In addition, a noble gas signature diagnostic of injected (EOR) fluids can be readily identified. We report noble gas isotope and concentration data in casing gases from oil production wells in the Lost Hills oil field, northwest of Bakersfield, California, and injectate gas data from the Fruitvale oil field, located within the city of Bakersfield. Casing and injectate gas data are used to: 1) establish pristine hydrocarbon noble-gas signatures and the processes controlling noble gas distributions, 2) characterize the noble gas signature of injectate fluids, 3) trace injectate fluids in the subsurface, and 4) construct a model to estimate EOR efficiency. Noble gas results range from pristine to significantly modified by EOR, and can be best explained using a solubility exchange model between oil and connate/formation fluids, followed by gas exsolution upon production. This model is sensitive to oil-water interaction during hydrocarbon expulsion, migration, and storage at reservoir conditions, as well as any subsequent modification by EOR.

1. Introduction

Noble gases are excellent tracers of a variety of subsurface fluid flow processes due to their inert nature and distinct isotopic signatures. Noble gas isotopes and relative concentrations can be used to provide limits on the volumes of differently sourced fluids that have contributed to any particular system (Ballentine et al., 1991; 1996; 2002). Terrestrial reservoirs (i.e., atmospheric, crustal and mantle) have diagnostic noble gas isotopic compositions, and fluids derived from each reservoir can be differentiated. Noble gases from fluids in sedimentary basins have been used to successfully quantify physical exchange mechanisms between water, oil and gas phases in conventional and unconventional hydrocarbon systems (Ballentine et al., 2002; Hunt et al., 2012; Prinzhofer, 2013; Darrah et al., 2014; 2015; Wen et al., 2015; 2016; Barry et al., 2016; 2017; Byrne et al., 2018).

Noble gases are also useful tracers of fugitive natural gases detected in groundwater (Darrah et al., 2014; 2015; Wen et al., 2015; Harkness et al., 2017) and for understanding the effects of CO_2 injection and EOR (LaForce et al., 2014; Gyore et al., 2015; Sathaye et al., 2016). To date, the use of noble gas signatures as tracers of reservoir processes in oil dominated systems is not well-developed, and requires precise characterization of noble gas signatures of oil reservoir fluids. However, subsurface hydrocarbon systems are intrinsically complex, marked by multiphase interactions (e.g., Barry et al., 2017) and affected by a range of natural geologic and anthropogenic processes. As a result, determining proportions of gas, oil, and formation water is difficult using geophysical (e.g., seismic, wireline logs, continuous core) and traditional geochemical techniques (Batzle and Wang, 1992; Schoell, 1980). For example, geochemical variability within a hydrocarbon system is controlled by the timing and origin of hydrocarbon charge, secondary fluid migration, and the relative distribution of regional trapping structures. Further complicating these signatures is the superimposed effect of EOR techniques, including steam or CO_2 flooding, and unconventional techniques such as hydraulic fracturing (e.g., Darrah et al., 2014).

In this study, a novel geochemical approach is used to differentiate between source and secondary (EOR) geochemical features in an actively producing hydrocarbon system. This distinction is critical, as it provides the necessary baseline values for fingerprinting any fugitive hydrocarbons that might be identified in nearby aquifer systems, which are valuable natural resources as a source of water supply for drinking water and agricultural irrigation (Mount et al., 2014). A primary goal of the California State Water Resource Control Board’s (SWRCB) Oil and Gas Regional Groundwater Monitoring Program (RMP) is to determine if any fluid exchange has occurred between regions affected by oil and gas activities and the surrounding groundwater (Taylor et al., 2014). The RMP will investigate approximately 100 onshore oil fields, thus providing information to resource management agencies about relative risks to groundwater. This study utilizes noble gas concentrations and isotope ratios in order to understand the extent of exchange between oil and formation waters. Our models describe how noble gas concentrations and elemental ratios evolve as 1) natural formation waters (i.e., air saturated water [ASW]) interact and exchange with oil in a pristine system, and 2) what the secondary effects of human-induced EOR are on the noble gases within a subsurface petroleum system.

2. Lost Hills Production History

Oil was discovered in the Lost Hills area in 1910, which is located in the southwestern portion of San Joaquin Valley, approximately 220 km northeast of Los Angeles and 70 km northwest of Bakersfield (Long et al., 2015), California, USA. The Lost Hills field currently produces oil, with no separate hydrocarbon gas phase (or 'gas-cap') being encountered. Details about geologic and depositional history are provided in the Supplementary Material.

Oil and gas operators commonly inject water and steam into subsurface petroleum-bearing rocks (e.g., Tulare Formation, Etchegoin Formation) throughout the San Joaquin Valley in order to promote secondary recovery of hydrocarbons and to maintain adequate fluid pressures in petroleum reservoirs. Injected fluids commonly consist of briny produced, surface or well water. The Tulare Formation was extensively steamflooded, beginning in 1964. The Diatomite, within the Monterey Formation, was waterflooded, hydraulically fractured, and subjected to CO_2 injection, with the earliest hydraulic fracturing occurring in 1962 (Land, 1984). All wells where injection has occurred (since 1977) in the Lost Hills field are shown in Figure 1a. Tracers injected into the Belridge Diatomite of the Monterey Formation have been shown to breakthrough to the oil producing wells in less than one month, which may indicate a naturally fractured reservoir (Zhou et al., 2002). The total number of injection wells (within a 100 and 500 meter radius of the sample well) has been tabulated in Table 1 along with aggregate injection volumes. Supplementary Figures S3-S7 show the injection history of Lost Hills (since 1977) and the proximity to wells sampled in this study. Digitized records of injection volumes per well prior to 1977 were not available, but for the entire Lost Hills field, injection occurring during 1952-1976 accounted for about 2% of total historic injections.

Formation water at Lost Hills has salinity between 0.54-0.60 M NaCl and an average reservoir temperature of 57°C. All oil gravities (expressed as API) are homogeneous at approximately 23.1, apart from sample ‘LH-05’, which has an API of 21.5. All temperature, salinity and API data are taken from (n=7) well-logs in the Lost Hills area. Heavier oil occurs in the (overlying) Tulare Formation (12-18 API).

3. Methods

3.1 Sample Collection

In October 2016 (n=10) gas samples were collected: seven oil wells (and a duplicate) in the Lost Hills field were sampled, and two injection sites in the Fruitvale field. We assume that all injection fluids are air-dominated, as they are all stored in surface tanks, which are not sealed effectively enough to prevent interaction with the atmosphere.

Samples were collected from well casing and injectate gases as part of the SWRCB’s RMP. Casing gases are pressurized gases that exsolve from produced fluids within the wellhead, whereas injectate gases are those that are re-injected as part of the EOR process. All Lost Hills samples are derived from oil systems and the gas samples collected were producing ‘casing gases’. Notably, Lost Hills casing gas samples were collected from both wells that have been recently subjected to EOR, and wells that have been producing oil without enhanced recovery methods. In contrast, Fruitvale samples were collected from the gas phase of co-mingled injectate fluids held in storage tanks, directly from different oil wells. The goal of collecting injectate gas samples was to determine the noble gas signature of fluids and gases associated with EOR. Samples from each site are geochemically distinct from one another, and represent co-mingling of injectate fluids with air additions, likely from leaking surface storage tanks.

Gases from each location were collected in copper tubes for noble gases using standard techniques (Burnard, 2013). Necessary precautions were taken during sampling to ensure sample integrity. For example, noble gas samples were collected in 3/8" diameter, refrigeration-grade copper tubes, which were connected using hose clamps and reinforced polytetrafluoroethylene tubing to a 2-stage pressure regulator attached directly to the wellhead. The regulator was used to step down the pressure from the wellstream to 1-2 bars. The copper tubes were then flushed with the produced gas to avoid air contamination and the gas outlet was submerged in a bucket of water to prevent any backflow of air into the system. After ten minutes of flushing the Cu-tubes were sealed with stainless steel clamps (Weiss, 1968).

3.2 Noble Gas Results

Noble gas analyses were performed at the University of Oxford using standard techniques (details in Supplementary Material). Lost Hills helium (^{4}He) concentrations range from 0.1 to 7.5 × 10^{-6} cm^{3}STP/cm^3, where STP is defined as Standard Temperature and Pressure. Samples are strongly radiogenic and have helium isotope (^{3}He/^{4}He) values ranging between 0.018 ± 0.001 and 0.060 ± 0.003 R_A (Table 2), reported relative to the air value $R_A = 1.38 \times 10^{-6}$ (air = 1R_A; Clarke et al., 1976). Fruitvale helium (^{4}He) concentrations range from 2.9 to 3.2 × 10^{-6} cm^{3}STP/cm^3. A single helium isotope (^{3}He/^{4}He) value of 0.125 ± 0.006 R_A was determined for the 'FR-03' sample. All noble gas data are reported in Table 2 along with 1σ uncertainties.

Lost Hills neon (^{20}Ne) concentrations range from 1.85 to 24.0 × 10^{-9} cm^{3}STP/cm^3. Measured ^{20}Ne/^{22}Ne ratios vary between 9.38 ± 0.005 and 10.17 ± 0.005; deviations from the atmospheric ^{20}Ne/^{22}Ne value of 9.8 are likely due to a combination of nucleogenic ^{22}Ne production and mass fractionation effects. Measured ^{21}Ne/^{22}Ne values vary between 0.0283 ± 0.0001 and 0.0305 ± 0.0002. Similarly, ^{21}Ne/^{22}Ne isotopic ratios in excess of the air value (0.0290) can be attributed to mass fractionation and nucleogenic crustal ^{21}Ne addition. Fruitvale neon (^{20}Ne) concentrations are higher and range from 79.7 to 606 × 10^{-9} cm^{3}STP/cm^3. Measured ^{20}Ne/^{22}Ne and ^{21}Ne/^{22}Ne ratios are nearly identical to air.

Lost Hills argon (^{36}Ar) concentrations range from 0.02 to 0.09 × 10^{-6} cm^{3}STP/cm^3 and reveal significant deviations from the atmospheric ^{40}Ar/^{36}Ar value of 298.56 (Lee et al., 2006), with measured ^{40}Ar/^{36}Ar values varying between 299 ± 1.50 and 334 ± 1.67. Fruitvale argon (^{36}Ar) concentrations range from 0.19 to 1.22 × 10^{-6} cm^{3}STP/cm^3 and show smaller deviations from air, with measured ^{40}Ar/^{36}Ar values varying between 295 ± 1.5 and 311 ± 1.6. Both areas show a resolvable radiogenic ^{40}Ar contribution within the petroleum system. Argon isotopes (^{40}Ar/^{36}Ar) inversely correlate with ^{20}Ne concentrations, suggesting that the source of the ^{20}Ne is also a source of air-like argon isotopes, particularly in the Fruitvale samples. Measured ^{38}Ar/^{36}Ar values are predominantly air-like (0.1885; Lee et al., 2006; Burnard, 2013) and vary between 0.189 ± 0.003 and 0.197 ±0.003.

Lost Hills krypton (^{84}Kr) concentrations range from 1.42 to 6.27 × 10^{-9} cm^{3}STP/cm^3 and from 4.59 to 26.5 × 10^{-9} cm^{3}STP/cm^3 in Fruitvale samples. Lost Hills samples overlap and extend above air values (0.303; Aregbe et al., 1996) with respect to ^{86}Kr/^{84}Kr, ranging between 0.29 ± 0.001 and 0.39 ± 0.002, whereas Fruitvale samples range from 0.31 ± 0.001 to 0.49 ± 0.001, plotting above the air-value, most likely due to mass fractionation processes.

Lost Hills xenon (^{132}Xe) concentrations range from 0.73 to 2.12 × 10^{-9} cm^{3}STP/cm^3 (Table 2). Lost Hills ^{132}Xe/^{130}Xe values range between 6.56 ± 0.03 and 6.58 ± 0.03, and are distinctly lower than air values (^{132}Xe/^{130}Xe$_{air}$ = 6.60705; Pepin, 2000). Fruitvale xenon (^{132}Xe) concentrations range from 1.73 to 2.02 × 10^{-9} cm^{3}STP/cm^3. Fruitvale ^{132}Xe/^{130}Xe values bracket air ratios, ranging between 6.57 ± 0.03 and 6.67 ± 0.03.

4. Discussion

4.1 Sample integrity and classification

Before interpreting and discussing the variability in gas samples collected from the Lost Hills and Fruitvale oil fields, it is first necessary to classify sample types. Only injectate gas samples (n=2) were collected from Fruitvale, and these are broadly similar to air-like noble gases (i.e., ^{20}Ne/^{36}Ar). These gases represent headspace gases in closed surface storage tanks, however there is a strong atmospheric signal, likely due to air leaks in the tanks. Casing gases (n=7) were collected from Lost Hills; these gases are exsolved from produced fluids (i.e., oil and water) as it is pumped to the surface, and noble gas isotope ratios are distinct from air. Lost Hills samples are sourced from either the Belridge Diatomite member or the deeper Cahn member of the Monterey Formation (consisting of the Brown and Antelope shales; stratigraphic cross section – Figure S2).

Cahn gas samples (LH-10 and LH-09) have lower non-radiogenic noble gas concentrations (e.g., ^{20}Ne, ^{36}Ar) and relative ratios (e.g., ^{20}Ne/^{36}Ar), which plot in the range expected for solubility partitioning between gas and oil (Figure 3a and 3b), and are thus considered ‘pristine’ or unaffected by air-like injection. In contrast, Diatomite samples have higher non-radiogenic noble gas concentrations, relative elemental ratios (above the water solubility range), and exhibit air-influenced noble gas isotope ratios (Table 2), all of which are attributed to the injection of air-saturated fluids related to recent EOR activities, which are much more prevalent in the vicinity of Diatomite samples. In Table 1, we show the number of injection wells (since 1977) within an area with a 100m, and a 500m radius from each sampled well. This table also provides the median injection depth, and the total volume of injectate from the injection wells identified. The Diatomite sample (LH-04) has the most pristine noble gas signature amongst all Diatomite samples, and is in fact the oldest well in production (since 1990; DOGGR, 1998). Well ‘LH-04’ is also located approximately 1km to the north of the densest injection area (Figure 1a) and has had no injection since 1977 from wells within an area with a 100m radius, suggesting that injection fluids do not traverse such distances.

Two samples were collected from the Cahn member: 'LH-10' (collected in duplicate; Table 2), which has been in production since 2001 and 'LH-09', which has been in production since 1981 (DOGGR, 1998). Notably, these wells also do not have any injection wells located within a 100m radius (Table 1; Figure S6). The duplicate analyses (LH-10) are highly reproducible (within 1%), which provides a high level of confidence in the integrity of the sampling, transport and storage procedure (Table 2; supplemental info S3.1). The relatively unmodified Cahn samples are best explained by a closed system equilibrium exchange model (4.3.1), which is used to determine the extent of hydrocarbon interactions with fluids in the reservoir and/or during migration from source to reservoir. In contrast, Diatomite wells have a higher density of injection wells within a 100m radius (Figure S4) and a higher cumulative injection volume (Table 1) in that radius. As a result, Diatomite samples are considerably 'less pristine', marked by excess air-derived noble gases. We surmise that these excess noble gas signals are the result of surface fluid injection; however, they can be corrected and volumetric ratios of water to oil can be calculated. In section 4.3.3, we quantify the extent of EOR using a radiogenic ^{4}He model. Determining initial noble gas values for pristine and EOR affected regions of each formation is imperative for interpreting the extent of fluid exchange between oil fields and nearby aquifers.

All gases are strongly radiogenic with respect to helium isotopes; however, Fruitvale injectate samples have higher ^{3}He/^{4}He ratios, closer to the ratio of air (Figure 2), which is consistent with a larger air contribution. EOR samples generally have higher concentrations of air-derived noble gases than pristine samples and more air-like elemental ratios (e.g., ^{20}Ne/^{36}Ar; Figure 3), both of which are consistent with air-entrainment during re-injection. Lost Hills gases show a range from pristine crustal signatures – indicative of closed-system exchange with formation fluids – to slightly aircontaminated and/or diluted signatures in the EOR region. In 4.5 we present a radiogenic model that explains the disparate ^{4}He contents in Lost Hills samples by evoking dilution associated with recent EOR activity.

4.2.1 Original non-radiogenic noble gas inventory

In order to quantify the extent of interaction between an oil phase and formation waters in the subsurface (i.e., determine subsurface water-oil ratios), we must first constrain the original noble gas inventory of ASW in deep meteoric water. As with previous solubility models (e.g., Ballentine et al., 1991; Ballentine et al., 1996; Zhou et al., 2005; Barry et al., 2016; Barry et al., 2017; Tolstikhin et al., 2017), we assume that air-derived noble gases (^{20}Ne, ^{36}Ar, ^{84}Kr and ^{132}Xe) are originally input into the subsurface, dissolved in groundwater (i.e., ASW), during aquifer recharge. It is assumed that once groundwater recharge has occurred, the atmospheric noble gas characteristics of these fluids are conservative, as they are isolated from further additions of light (^{20}Ne,^{36}Ar) air-derived noble gases, which do not have significant subsurface sources. In contrast, addition of radiogenic and/or mantle-derived noble gases to deep meteoric waters will result in a distinct isotope signal. Initial noble gas solubility in water is a function of recharge conditions (temperature, salinity and recharge elevation), but generally increases with mass (Ne<Ar<Kr<Xe). Therefore, the initial ASW noble gas inventory in formation water can be approximated using solubility coefficients (K_{GW}) at a given temperature and salinity (Crovetto et al., 1982; Smith and Kennedy, 1983). In Lost Hills we assume 15°C recharge of freshwater at sea-level elevation; notably if different recharge conditions are used to calculate the initial noble gas inventory, this will have only a minor effect on noble gas reconstructions (see section 4.2.2).

4.2.2 Reconstructing noble gas concentrations in oil

During petroleum production, oil is pumped from the reservoir to the surface, resulting in decompression and eventual gas exsolution. The gas-oil-ratio (GOR) is typically measured at the wellhead by combining the volume of gas produced with the volume of oil produced. The volumes are typically reported by the oil industry as Standard Cubic Feet per Barrel of Oil (SCF/BBL). We convert these to SI units (m^3 of gas/m^3 of oil), using eq. 1:

$$\mathrm{GOR_{metric}} = \frac{(\mathrm{GOR_{imperial}})(0.028316)}{0.1589873} \tag{1}$$

The GORs vary as a function of time and production history and some Lost Hills wells do not currently produce gas, and thus we use a time-integrated average GOR value from the Diatomite member to reconstruct the concentration of noble gases in the oil phase.

The concentration of a given noble gas, originally in the oil (in units of mol/Kg oil) phase at Reservoir Temperature and Pressure (RTP) (i.e., prior to production and exsolution), is estimated using the following equation:

$$[\mathrm{C_i^{oil}}] = \frac{[\mathrm{C_i^{gas}}](\mathrm{GOR_{metric}})}{(\mathrm{SG})(22.4)} \tag{2}$$

Where $[\mathrm{C_i^{gas}}]$ is the gas concentration of noble gas *i* in the gas phase, in units of cm^3STP/cm^3 (Table 2). This calculation assumes one mole of gas occupies 22.4 L at STP. The specific gravity (SG) of oil is in units of g/cm^3 and is a function of oil gravity: typically expressed in American Petroleum Institute (API) gravity units (i.e., inverse of density). The specific gravity of a given oil can be calculated using eq. 3 (Petrosky and Farshad, 1993):

$$\mathrm{SG} = \frac{141.5}{\mathrm{API}+131.5} \tag{3}$$

In Table 2 the measured gas concentrations for all air-derived noble gas species$[\mathrm{C^g_{i(meas)}}]$ (units are cm^3STP/cm^3) are provided. In Table 3 measured API, SG, metric GOR, and calculated concentrations in oil $[\mathrm{C_i^{oil}}]$ (units are mol/Kg oil) are given along with solubility coefficients ($\mathrm{K_{WO}^{M}}$), calculated using Kharaka and Specht, 1988 at RTP (Lost Hills = 57°C and 0.57 M NaCl). Importantly, the calculation in equation 2 assumes equilibrium between the produced fluids and gases; if equilibrium is not reached then estimates of initial concentration in oil will be skewed. We also assume that gas concentrations are representative of a time-integrated average or production conditions.

Importantly, we use an average integrated GOR (=107.6) from Diatomite wells in order to model the Lost Hills data. We compiled production data at each well sampled in Lost Hills, and took an average value of all Diatomite sourced samples. Notably, there are differences in GOR between Diatomite and Cahn sourced wells, however due to the fact that all wells have a common API, we assume a common GOR in order to do reconstructions (Eq. 2). Determining an accurate GOR is critical for converting measured gas concentrations into concentrations in the reservoir. It is evident from the variation of the wellhead GOR values (measured during sample collection) that they are not always representative of virgin GOR conditions. Furthermore, historical well-log data demonstrate that GORs vary significantly over sustained periods of production. For example, measured GORs vary by nearly 4 orders of magnitude in the Lost Hills field, whereas measured noble gas concentrations vary by just 1 order of magnitude within the same fields (Figure 4). The fact that we observe relatively little variability in noble gas concentrations, suggests that using an average integrated GOR value is most appropriate.

4.3.1 Assessing pristine samples with an equilibrium model

As oil is produced and migrates from source to reservoir, noble gases are partitioned from deep formation connate/formation waters into the oil phase ($\mathrm{K_{WO}}$) in a predictable manner, based on empirically-derived solubility coefficients (Kharaka and Specht, 1988). Predicted concentrations are fixed by several parameters, including: 1) the initial noble gas inventory in ASW ($[C_i^{asw}]$), 2) temperature and salinity conditions where phase exchange occurs (reservoir conditions) in the hydrocarbon system, and 3) density of oil (API). Recharge conditions (i.e., freshwater at 15°C) are assumed for the first set of parameters. Temperature, salinity and API are constrained for each sample by measured values at the wellhead during sample collection. For Lost Hills we use 57°C and 0.57 M NaCl, which represents an average between Diatomite and Cahn samples. Oil density was used on a well-by-well basis, however most Lost Hills wells are homogeneous (Table 3).

Using an estimate of the initial noble gas content of undegassed oil ($[C_i^{oil}]$) in the reservoir (calculated in Eq. 2; Table 3), we constructed a solubility model (after Ballentine, 1996; Barry et al., 2016), which predicts the relative volume of water that is required to have exchanged with an oil phase (assuming equilibrium conditions), in order to produce the observed noble gas concentrations in casing gases. Eq. 4 is modified from Barry et al., 2016:

$$\frac{V_o}{V_w} = \frac{[C_i^{asw}]}{[C_i^{oil}]} - \left[\frac{(K_{WO}^{M})}{(SG)(K_{GW}^{M})}\right] \tag{4}$$

We note that (K_{GW}^{M}) is the reservoir temperature and salinity specific Henry's constant (Crovetto et al., 1982; Smith and Kennedy, 1983), K_{WO}^{M} is the reservoir temperature and salinity specific Henry's constant at a given specific gravity (Kharaka and Specht, 1988). Thus, we use Eq. 4 in order to calculate $\frac{V_o}{V_w}$ at reservoir conditions.

4.3.2 Model sensitivity: implications for exchange and migration

We note that calculated $\frac{V_o}{V_w}$ values are highly dependent on input assumptions (i.e., recharge and reservoir temperature and salinity conditions as well as measured API gravity). In the Lost Hills (Cahn and Diatomite) system, reservoir temperatures range between 44-69 °C, whereas salinity in the reservoirs spans a relatively narrow range of

0.54-0.60 M NaCl, both based on down-borehole data. Using an average reservoir temperature of 57°C and salinity of 0.57 M NaCl we calculate $\frac{V_o}{V_w}$ at reservoir conditions using Eq. 4, and values are given in Table 1.

Cahn $\frac{V_o}{V_w}$ values range between 0.17-0.36, which is in good agreement with the range in $\frac{V_o}{V_w}$ (0.33-0.37) calculated indirectly by integrating the oil to water volume ratio in all Cahn wells, using historical well-log data (Table 1). The agreement between these two independent estimates suggests that this geochemical approach is well calibrated. Importantly, this method enables down borehole volumetric estimates to be made in the absence of well-log data.

The model was also run for Diatomite samples and calculated a significantly lower range in $\frac{V_o}{V_w}$ (0.01-0.11), which also overlaps with integrated well-log data estimates (0.05-0.19) from the Diatomite samples. Notably, none of these values are corrected for the effect of EOR, however details of the correction are provided in 4.3.3 and the corrected values are tabulated in Table 1. The integrated Diatomite estimates ($\frac{V_o}{V_w}$ from 0.05-0.19) are significantly lower than the Cahn estimates, suggesting greater water-oil interaction and partitioning. We suggest that the difference in $\frac{V_o}{V_w}$ is directly related to migration distance, and thus the $\frac{V_o}{V_w}$ can be used as a semi-quantitative ‘secondary-migration odometer’. Importantly, the range for the Diatomite samples encompasses the solubility model-derived $\frac{V_o}{V_w}$ of 0.05-0.11, for ^{20}Ne and ^{36}Ar estimates respectively. Again, the agreement between the two independent estimates lends credence to the geochemical approach. Outputs from sample ‘LH-08’ clearly suggest that this particular sample has been isolated and subjected to much less water than the other Diatomite samples. This is likely the result of geologic compartmentalization, whereby portions of the reservoir have been segregated and experience a different amount of contact with extraneous fluids. In this instance, the sample would be subjected to significantly less water contact, and thus would retain a much higher $\frac{V_o}{V_w}$.

In contrast, a longer migration pathway would result in more interaction with formation water, and thus a lower $\frac{V_o}{V_w}$. In view of the possible range in $\frac{V_o}{V_w}$ that could explain the Lost Hills dataset; we have conducted a data inversion in order to determine the best-fit $\frac{V_o}{V_w}$ value for Cahn and Diatomite samples respectively. Using a data inversion technique we fit variables in the conceptual model (Eq. 4) to measured data by minimizing the square of the residuals between model-derived (i.e., predicted) $\frac{V_o}{V_w}$ and measured $\frac{V_o}{V_w}$ values (Figure 5). Specific gravity, initial noble gas concentrations in ASW and partition coefficients are fixed (see Table 3), based on assumed recharge conditions. Neglecting helium – which is dominated by radiogenic contributions, and heavy noble gases which are disproportionately modified by excess heavy noble gases (section 4.4) – two observables remain: ^{20}Ne and ^{36}Ar concentrations in oil, which allows us to solve using data inversion for $\frac{V_o}{V_w}$ (e.g., Ballentine and Hall 1999). The best-fit $\frac{V_o}{V_w}$ can thus be inverted for both ^{20}Ne and ^{36}Ar concentrations in oil separately, providing a range in possible $\frac{V_o}{V_w}$ values.

In Figure 5 we show measured noble gas concentration in oils vs. model predicted values, at a predicted $\frac{V_o}{V_w}$ value of 0.322, based on a best fit for Ne and Ar using the inverse technique described above. At RTP conditions there is very good agreement for both Cahn samples, whereas the Diatomite samples have measured/modeled values >1, and show a marked enrichment in Ne and Ar, likely due to EOR (see section 4.3.3 for discussion). The disparity is the direct result of EOR, the effects of which are discussed in detail in section 4.3.3. Sample 'LH-08' is a clear outlier, plotting anomalously below all other samples, suggesting that this sample has evolved differently than the other samples – perhaps due to geological isolation. Heavy noble gas enrichment (only Kr is shown) relative to the light noble gases remains pervasive in all samples; notably this is a phenomenon that has been observed previously and is discussed in section 4.4. Agreement between predicted and measured $\frac{V_o}{V_w}$ demonstrate that the solubility model presented here (Eq. 4) is highly effective at identifying oil-water interaction in the subsurface. The findings also have important implications for the mass balance of the system, i.e., the observation that Cahn samples have higher $\frac{V_o}{V_w}$ (Table 1) implies less water contact, and thus a relatively short migration pathway, as is observed in Diatomite samples. This observation is consistent with the low permeability and high porosity nature of the Lost Hills hydrocarbon system, as such systems would be expected to limit the amount of fluid migration.

The model presented here is a zero-dimensional solubility exchange and mixing model that explains noble gas variations in Lost Hills casing gases. We use measured gas concentrations to determine $\frac{V_o}{V_w}$ and surmise that differences between Cahn and Diatomite samples are the result of different migration pathways and EOR contributions. Previously, Sathaye et al., 2016 used a reactive transport model to demonstrate noble gas fractionation during subsurface gas migration, showing a characteristic pattern of initial co-enrichment of noble gases from both water and gas phases in banks at the gas front, followed by a depletion of the dissolved noble gas. This is an important observation, however, this enrichment would not be preserved if the leading edge passes through the system and, for example, is produced at the surface. We suggest that the Lost Hills system is unlikely to preserve the leading edge of the injected water as these are large volumes injected over time relative to the reservoir volume and the respective phases should approach the solubility controlled equilibrium conditions that we model. If equilibrium conditions were not reached, the Sathaye et al., 2016 model would provide an alternative explanation for the observed enrichments in EOR modified samples. Differentiating between these two processes is difficult to test using the available data set, but should be carefully considered. However, we argue that despite the source of the noble gas enrichment (air-entrainment during injection or noble gas banking) we can effectively correct back to solubility conditions and calculate relative differences in $\frac{V_o}{V_w}$.

4.3.3 Assessing EOR using air derived noble gases

Fruitvale data provide direct evidence that injectate fluids are geochemically similar to air-like signatures (Figures 3), as they have orders of magnitude higher air-derived noble gas concentrations (i.e., ^{20}Ne, ^{36}Ar) and air-like isotope ratios (Table 2). As a result, we can differentiate between pristine hydrocarbon signatures – that can be explained by an equilibrium exchange model and samples that have been recently subjected to other methods of EOR, and thus have higher measured noble gas concentrations than predictions would indicate (Figure 5). The equilibrium model (Eq. 4) assumes that an oil phase was in direct contact with a water phase, and that equilibrium was reached at reservoir conditions. The '1st bubble' value (Figures 6a, 6b) represents the point at which there is an infinitesimally small volume of oil partitioning or 'stripping' noble gases from a significantly larger water volume, during initial charging of the reservoir, and importantly, no excess air entrainment from EOR is present. As the amount of oil relative to water increases, the system evolves along the line from infinitely small $\frac{V_o}{V_w}$ towards infinitely large $\frac{V_o}{V_w}$. As the $\frac{V_o}{V_w}$ increases, the noble gas concentration in oil decreases due to dilution. In Figure 6a, we show the predicted evolution of the oil phase at different $\frac{V_o}{V_w}$, combined with three different predicted EOR trajectories. The predicted EOR trajectories represent modeled two-component exchange between formation water and an oil phase (i.e., no gas-cap), followed by air-like addition assumed to be associated with recent EOR activities. Clearly, Diatomite samples have a more pronounced EOR signature (Figure 6), characterized by a range in ^{20}Ne/^{36}Ar well above the range predicted by simple solubility exchange. The convergence of the predicted EOR trajectory (colored lines) and the $\frac{V_o}{V_w}$ line (black) represents the initial pristine conditions which evolve along the EOR trajectories after the addition of different amounts of air. Notably, the $\frac{V_o}{V_w}$ evolves over the lifetime of the hydrocarbon system, whereas the effect of EOR is only superimposed upon those pristine gas signatures. As a result, the point at which the two predictive trends converge, the pristine $\frac{V_o}{V_w}$ can be estimated. This is referred to as the EOR corrected $\frac{V_o}{V_w}$ value and oil to water ratios following correction for the EOR component are tabulated in Table 1 (denoted with an asterisk). In Figures 6a,b there are distinct, mixing trajectories for deeper Cahn samples and another for Diatomite samples. There is also a single outlying Diatomite sample 'LH-08' that falls on a completely different trend, perhaps due to geologic isolation.

It is important to note that other factors could also affect the predicted EOR trajectories on Figures 6a,b. The solubility model assumes simple two-component exchange between deep meteoric formation water and an oil phase, followed by air addition associated with recent EOR activities. In Lost Hills, there is no evidence for a gas phase at depth, which would cause fractionation in the opposite direction (i.e., towards lower $^{20}Ne/^{36}Ar$ values) as mixing with EOR fluids (Figures 6a,b). Instead, the modeling results indicate that gases only exsolved during production. This observation is also entirely consistent with geological constraints in that there is no ancillary evidence for gas-cap formation.

Diatomite $\frac{V_o}{V_w}$ model values range from 0.01 to 0.11, whereas Cahn $\frac{V_o}{V_w}$ model values range from 0.17 to 0.36. The disparity between estimates suggests that Diatomite samples have been exposed to significantly more water than the Cahn samples. Water could be introduced in several different ways. For example the disparity could be the result of: 1) the depth of the samples, whereby samples in the Diatomite may have a similar hydrocarbon source but have likely seen more water during migration, resulting in lower $\frac{V_o}{V_w}$; 2) the relative permeabilities of the reservoirs, for example, oil in tight shales are not exposed to as much water as those in more porous Diatomite units above; 3) the relative porosities of the reservoirs, for example, Diatomite samples higher porosity than the Cahn samples, so there would be more water within each bulk volume of Diatomite than of Cahn; 4) injection and human induced water pumping. Importantly, none of these explanations are mutually exclusive and the resulting signatures are likely the result of a combination of all factors. Importantly, when we correct $\frac{V_o}{V_w}$ for EOR addition (Table 1) there is still a disparity, albeit less pronounced. This suggests that there is a natural difference between reservoirs, but the disparity is further exaggerated by addition of human induced water. Nonetheless, volumetric estimates appear robust, as they are supported by independently determined volumetric estimates from well production logs.

4.4 Heavy noble gas enrichments

Heavy noble gases (Kr and Xe) are preferentially adsorbed onto organic sediments, which, when liberated into the fluid system, provide an additional heavy noble gas isotopic signature (Torgersen and Kennedy, 1999; Zhou et al., 2005). Importantly, a pristine (or enriched) ASW signature is distinct from air-like compositions that have been identified in EOR injectate. There are clear heavy noble excesses in all Lost Hills samples relative to predictions from the solubility exchange model (Figures 3a,b), with the most pronounced enrichment occurring in the Cahn. As a result, solubility models – that utilize heavy noble gas concentrations – are unable to accurately predict volumetric oil-water ratios, and thus are not given in Table 1. Such heavy noble gas enrichments have previously been observed and discussed in detail (Torgersen and Kennedy, 1999; Zhou et al., 2005; Barry et al., 2016). In organic laden lithologies – such as shales and cherts – Kr and Xe preferentially absorb onto minerals relative to He, Ne and Ar (e.g., Podosek et al., 1981). Interestingly, the ratio of excess Kr/Xe is consistent (~3.1) throughout the entire Lost Hills system (i.e., in both Cahn and Diatomite wells – apart from well ‘LH-08’), varying by only 13%, even as total concentration of Xe varies by nearly 30%. In contrast, Ne varies by 95% due to the strong control of solubility partitioning. We surmise that as heavy noble gas enriched lithologies are buried to pressures and temperatures where hydrocarbons are generated, they release heavy noble gases and enrich the deep meteoric formation waters (Hiyagon and Kennedy, 1992; Torgersen and Kennedy, 1999; Zhou et al., 2005). As oils form, this enriched noble gas signature partitions into the hydrocarbon phase. Alternatively, oil interaction with sediments may directly partition heavy noble gases into the oil phase, prior to interaction with the deep meteoric formation waters. These processes could operate sequentially or simultaneously and thus potentially complicate interpretation of measured hydrocarbon signatures. As is evident in Figure 5 and Table 3, heavy noble (Kr, Xe) gases are ubiquitously enriched in gases derived from oils and thus yield lower $\frac{V_o}{V_w}$ than Ne and Ar derived estimates, however heavy noble gas $\frac{V_o}{V_w}$ values are not considered robust and therefore are not given in Table 1.

4.5 Assessing EOR efficiency using radiogenic helium

Radiogenic noble gas isotopes (e.g., ^{4}He, ^{40}Ar) are continuously produced in the Earth's crust and can yield temporal information about fluids. The concentration of radiogenic nuclides can be predicted by estimating flux rates in open fluid systems (Torgersen and Clarke, 1985; Torgersen and Ivey, 1985; Castro et al., 1998a; 1998b; Kulongoski et al., 2005; Zhou and Ballentine 2006; Torgersen 2010). In a closed hydrocarbon system, the well-constrained production rate of radiogenic helium can be combined with measured ^{4}He concentrations to estimate isolation ages (Tolstikhin et al., 1996; 2017; Solomon et al., 1996; Cook et al., 1996; Ballentine et al., 2002; Holland et al., 2013; Barry et al., 2017). In such systems, parent radionuclide concentrations in source rocks are critical, as is the efficiency of radiogenic discharge from the rock into the fluid phase (Tolstikhin et al., 2010; 2017; Hunt et al., 2012; Lowenstern et al., 2014; Darrah et al. 2014; Barry et al., 2015).

These radiogenic nuclides are then transferred into the surrounding formation waters. The amount of ingrowth and subsequent exchange is a function of U and Th abundance in the source mineral, reservoir temperature, salinity, rock thickness, and porosity. When radiogenic laden waters come into contact with oil, the noble gases are partitioned exactly the same way as atmospheric-derived noble gases in groundwater (e.g., ^{20}Ne and ^{36}Ar), according to known relative partitioning behavior (i.e., Ki/Kj).

Helium isotope results suggest that the Lost Hills oils are predominantly radiogenic, with He-isotope values ranging from 0.018-0.060 R_A (Figure 2). Assuming binary mixing between crustal (0.007 R_A; Zhou and Ballentine, 2006) and sub-continental lithospheric mantle (SCLM) endmembers (6.1 R_A; Day et al., 2015), we calculate a crustal contribution between 99.1 to 99.8%. We choose SCLM as the mantle endmember as this is a continental setting, with no evidence of direct mantle contributions. If arc or canonical upper mantle values are assumed the calculation would not be significantly affected. This indicates that SCLM contributions to the system are typically less than 1%, consistent with observed mantle contributions near the San Andreas Fault (Kennedy et al., 1997), yet insignificant for modeling purposes. In Lost Hills, the two samples (i.e., 'LH-10'and 'LH-09') that tap the deeper Cahn member are the most radiogenic, with the lowest ^{3}He/^{4}He and the highest ^{4}He concentrations of all samples (>5.3 x 10^{-6} cm^{3}STP/ cm^3). In contrast, shallower samples from the Diatomite sequence have slightly less radiogenic signals, marked by broadly similar ^{3}He/^{4}He values and lower ^{4}He concentrations (< 2.9 x 10-6 cm^{3}STP/ cm^3). This disparity could be the result of the more U and Th rich nature of the deeper shales vs. the above-lying Diatomite sequences, which is supported by gamma log data. Alternatively, this could be due to the fact that older shales had more time to accumulate helium than the younger Diatomite. Despite the source of the [^{4}He] disparity, the observation that both Cahn samples – as well as a single Diatomite sample (LH-04) – have high ^{4}He concentrations, helps establish the background radiogenic signal, prior to EOR. The lower [^{4}He] in the remaining Diatomite samples (including outlying sample LH-08), therefore suggests dilution has occurred, which is attributed to EOR-induced oil expulsion, which has effectively liberated noble gas barren oil, thus decreasing radiogenic ^{4}He concentrations in oil by an order of magnitude or more. This observation provides strong ancillary support for the hypothesis that variations in the air-derived noble gases are the direct result of EOR, and not simply a source difference between the deeper and shallower units. Due to moderately high helium concentrations in the EOR fluids themselves (~3×10^{-6} cm^3STP/cm^3), they cannot be easily evoked as the diluting agent and instead it must be the liberation of oil that in fact dilutes [^4He] of oils in place.

The noble gas partitioning model presented in 4.3.1 indicates that Diatomite sample 'LH-04' has remained in production without EOR (Table 1) since the 1990s and thus has experienced the least secondary modification. As a result, we adopt a starting radiogenic ^4He starting composition of 2.9×10^{-6} cm^3STP/cm^3 (i.e., the measured 'LH-04' value). By assuming simple dilution of ^4He-laden oil by mixing with ^4He-barren oil – liberated by injection – "EOR efficiency" can be estimated. EOR efficiency is thus defined as the amount of oil liberated by EOR, required to effectively dilute the noble gas signature of the oil in place. Using this approach, we estimate that EOR is between 48 and 97% effective in the Diatomite (Table 1). Not surprisingly, EOR efficiency is broadly inversely correlated with air-derived ^{36}Ar concentrations in gases, however the lack of a strong correlation suggests that each well has experienced a slightly different evolution due to local rock conditions (i.e., porosity, permeability), which also exert a control overall EOR efficiency. For example, sample 'LH-08', considered to be geologically compartmentalized, has the highest $\frac{V_o}{V_w}$ as well as the highest EOR efficiency (97%) of all wells measured. If baseline noble gas values can be established for each well, then a quantitative measure of EOR efficiency can be assessed at any well that is sampled in the future.

5. Summary

In this study we present noble gas isotope and concentration data from casing gases derived from the Lost Hills oil field in the San Joaquin basin, California, as well as injectate data from the Fruitvale oil field. These data help establish both noble gas baseline values and EOR efficiencies. We show that within the Lost Hills petroleum system, the Cahn member remains largely pristine whereas the Diatomite member is

EOR modified with respect to noble gases. Only with knowledge of both source and secondary (EOR) features can a proper mass balance of the crustal system (i.e., both hydrocarbon and hydrogeological systems) be established, which will be critical for identifying and tracing the origin of any potential fugitive gases identified in nearby aquifers. For example, based on these results, we would predict lower air-derived noble gases and higher radiogenic ^{4}He concentrations in any fugitive fluids derived from the Cahn reservoir and higher air-derived noble gases and lower radiogenic ^{4}He concentrations if fluids derived from Diatomite. This study represents a successful calibration of noble gas technique for determining the effect of EOR on casing gas samples.

In summary, we have:

1) Established pristine hydrocarbon noble gas signatures in the Lost Hills (Cahn and Diatomite) casing gas samples and identified the processes controlling observed signatures; Cahn member samples retain the most pristine signatures that can be explained by a 2-phase solubility model.

2) Characterized injectate signatures in Fruitvale injectate gases; these values inform our models as to typical injectate signatures, which are air-like in nature with respect to noble gas elemental ratios.

3) Demonstrated the effect of injectate signature and effect in EOR wells; Diatomite samples which are disproportionately modified by EOR are marked by more air-like noble gas signatures, and radiogenic isotopes that appear heavily diluted by EOR.

4) Used a model to estimate EOR efficiency; Diatomite gas data reveal variability in EOR efficiency (48-97%) within this reservoir.

Figure Captions

Fig. 1a) Map showing the location of where casing gases were collected in the Lost Hills Oil Field. Diatomite casing gases are shown as red triangles apart from sample LH-08, which is shown as an orange triangle (as it plots distinctly in several subsequent figures). Cahn casing gases are shown as green circles. The location of injection (EOR) wells are also shown as (small) yellow circles. This labeling scheme is used in all subsequent figures. ^{20}Ne/^{36}Ar values are shown in parentheses next to each well name; the highest ^{20}Ne/^{36}Ar values were measured in the densest regions of injection, whereas the lowest ^{20}Ne/^{36}Ar values have limited injection in their vicinity.

Fig. 1b) Map of Injectate gases collected (large green squares) in the Fruitvale Oil Field and their proximity to all other injection wells in the region (small yellow circles). ^{20}Ne/^{36}Ar values are shown in parentheses next to each well name. Notably, the two injectate samples that we collected had high (air-like) ^{20}Ne/^{36}Ar values.

Fig. 2a) Helium isotopes (^{3}He/^{4}He) vs. helium concentrations (10^{-6} cm^{3}/STPcm^{3}) in casing gases. Helium isotopes are normalized to air (where air = $1R_A$). All He-isotope values are strongly radiogenic, however Cahn samples (green circles) have systematically higher He concentrations vs. Diatomite samples (red and orange triangles). Diatomite samples were subjected to substantially more EOR and are considered to have been diluted by liberation of ^{4}He-free oil during EOR. 1σ uncertainties are estimated to be less than 5% and this error is represented by the size of the symbols.

Fig. 2b) Helium isotopes (^{3}He/^{4}He) vs. ^{4}He/^{20}Ne in casing gases. Cahn samples (green circles) have systematically higher ^{4}He/^{20}Ne values vs. Diatomite samples (red and orange triangles). Diatomite samples were subjected to substantially more EOR and are considered to have been diluted by liberation of ^{4}He-free oil during EOR, thus lowering the $^{4}He/^{20}Ne$. 1σ uncertainties are estimated to be less than 5% and this error is represented by the size of the symbols.

Fig. 3a) Non-radiogenic ($^{20}Ne/^{36}Ar$) vs. ^{36}Ar (10^{-6} $cm^3/STPcm^3$) concentrations in casing gases and injectate gases. Cahn samples (green circles) retain the lowest (most pristine) $^{20}Ne/^{36}Ar$ values. Diatomite samples (red and orange triangles) show higher (more air-like) $^{20}Ne/^{36}Ar$ values. Injectate samples (green squares) are even more air-like with respect to their $^{20}Ne/^{36}Ar$ values. The air value is show as a blue diamond. 1σ uncertainties are represented by the size of the symbols.

Fig. 3b) Spider diagram showing the average elemental ratios of air-derived noble gases for Cahn, Diatomite, Injectate, ASW and Air. Notably, Cahn samples plot furthest from Air and closest to '1st-bubble' solubility values. Diatomite samples plot intermediate between Air and '1st-bubble' solubility values. Critically, the Injectate (EOR) samples plot nearly identically to Air, showing the strong air-like signature associated with EOR.

Fig. 4) Non-radiogenic ^{20}Ne (10^{-9} $cm^3/STPcm^3$) concentrations in casing gases vs. integrated gas-to-oil ratio (GOR), calculated from historic well-log data. 1σ uncertainties are represented by the size of the symbols.

Fig. 5) Measured concentrations of non-radiogenic noble gases (^{20}Ne, ^{36}Ar, ^{84}Kr) in oil vs. predicted (i.e., calculated using Eq. 2) values in oil at reservoir temperature and salinity. Notably, Cahn samples are in good agreement with each other and cluster near unity for Ne and Ar, suggesting a coherent $\frac{V_o}{V_w}$ can be calculated. In contrast, Diatomite samples (apart from LH-08) have much higher measured vs. predicted noble gas concentrations in oil, which we attribute to addition of EOR. 1σ uncertainties are represented by the size of the symbols.

Fig. 6a) Non-radiogenic (^{20}Ne/^{36}Ar) vs. ^{20}Ne concentrations in oil (mol/kg oil) in casing gases. The black line represents the predicted solubility behavior as an oil system evolves from right to left. At the starting point, $\frac{V_o}{V_w}$ = infinitely small (1st bubble) and as the oil interacts with more water (during migration) the predicted value moves towards the left, where $\frac{V_o}{V_w}$ = infinitely large. Colored lines are mixing trajectories with air-like gases, which are closely linked to EOR Injectate gases. At the intersection of the solubility prediction and mixing with air, the air-corrected $\frac{V_o}{V_w}$ is given. 1σ uncertainties are represented by the size of the symbols.

Fig. 6b) Non-radiogenic (^{20}Ne/^{36}Ar) vs. ^{36}Ar concentrations in oil (mol/kg oil) in casing gases. The black line represents the predicted solubility behavior as an oil system evolves from right to left. At the starting point, $\frac{V_o}{V_w}$ = infinitely small (1st bubble) and as the oil interacts with more water (during migration) the predicted value moves towards the left, where $\frac{V_o}{V_w}$ = infinitely large. Colored lines are mixing trajectories with air-like gases, which are closely linked to EOR Injectate gases. At the intersection of the solubility prediction and mixing with air, the air-corrected $\frac{V_o}{V_w}$ is given. 1σ uncertainties are represented by the size of the symbols.

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