Supplementary information to: Investigating the effect of enhanced oil recovery on the noble gas signature of casing gases and produced waters from selected California oil fields

Geological history

1.1. Fruitvale geological and production history

The Fruitvale Oil Field is located on the southern edge of the Bakersfield arch (a faulted southwest dipping homocline) and has been in production since 1928 (Preston, 1931). The stratigraphy of interest in order of increasing depth are the Kern River Formation (Pleistocene), Etchegoin Formation (Pliocene), Chanac Formation (Pliocene-Miocene) and the Santa Margarita Formation (Miocene) (Hluza, 1965; CALGEM, 2020a; Supplementary Figure 1a). Oil is mostly produced from the Chanac Formation, which consists of the Mason Parker, Martin and Kernco reservoirs, and are non-marine discontinuous fan deposits (Hluza, 1965; DOGGR, 1998). There is also limited production from marine deposits of the basal Etchegoin Formation and Santa Margarita Sandstone. The oil is thought to have originated from the Monterey Formation to the west of the field (Lillis and Magoon, 2007). A detailed geological history can be found in Hluza (1965).

The reservoir has a relatively low salinity of 0.095 Molarity (M) in comparison to other oil fields due to significant recharge over geological timescales from the Kern River and other streams draining the Sierra Nevada (McMahon et al., 2018). Average reservoir temperature is thought to be 51.3^{o}C (CALGEM, 2020b). Oil density (relative to water; given in American Petroleum Institute (API) gravity units) is 18.5^{o} in the Chanac and Etchegoin and 16.7^{o} in the Santa Margarita reservoir. Porosity within the reservoirs is ~ 25% (Stephens, et al., 2019). Permeability within the Chanac Formation is between 2-3 millidarcy (mD); however, permeability is significantly higher in the Santa Margarita Formation where it averages 975 mD (EPA, 2019). There is no evidence of gas cap formation (DOGGR 1998; CALGEM, 2020a). Average field parameters can be found in Supplementary Table 1.

Injection of fluids for both water disposal and enhanced oil recovery (EOR) began in the 1960s, with a combination of water flooding (since 1962), cyclic steam injection (since 1964), and water disposal. Over 87 million m^3 of water was injected between 1977 and 2018 (CALGEM, 2020b). The majority of the injected water is produced water from the oil wells; however, there is a small proportion of wastewater from refineries (Wright et al., 2019). Injection has not caused any significant change in reservoir salinity (Stephens et al., 2019). A combination of the long production-injection history at the Fruitvale Oil Field has resulted in temporal variations in the overall hydrocarbon and produced water production volumes (McMahon et al., 2018). For sample wells that have seen injection, injected volumes are between 3.01 x10^6 and 9.71 x10^6 m^3.

1.2. Lost Hills geological and production history

Oil production at Lost Hills began in 1910. The oil field is located on an asymmetrical northwest doubly plunging anticline that formed from a fault bend fold initiated by a step in the Lost Hills thrust fault (Medeweff, 1989). The stratigraphy of the anticline with increasing depth is: alluvium; Tulare Formation (Pleistocene, fluvial sands and clays); upper Etchegoin Formation (Pliocene, marine diatomaceous sands and clays); lower Etchegoin Formation (Pliocene, low permeability marine diatomaceous sands and clays) and; Monterey Formation (Miocene Belridge Diatomite, brown shales of the Reef Ridge Shale and the Cahn zone (Land, 1984)) (Supplementary Figure 1b). A detailed geological history for the field can be found in Land (1984). The source rock is believed to be within the Miocene Monterey Formation, (Philippi, 1965; Kruge and Williams, 1982; Kruge, 1986). Most of the hydrocarbons found within the formation are solvent extractable, which suggest that the hydrocarbons have migrated from a different source or they were formed at relatively low thermal maturity (Claypool et al., 1979). The Belridge Diatomite (304-914 m deep) is the main reservoir unit; however, there is additional production in both deeper and shallower units, such as the deeper Cahn zone. During production, no separate gas phase has been encountered in either reservoir (CALGEM, 2020a,b).

The permeability and porosity in the Belridge Diatomite are variable due to changes in clay, sand, and silt content across the formation and the transition of the silica in the diatoms and microplankton from Opal-A to Opal CT, due to dissolution and reprecipitation (Mizutani, 1977; Pisciotto and Garrison, 1981; Soutar et al., 1981). However, in general they have high porosity (up to 65%) and low permeability (~0.1 mD; Barry et al., 2018), which results in some difficulties during extraction and a high density of wells required. Variability in porosity and other reservoir properties, along with reservoir evolution with production and EOR have resulted in a reservoir temperature range between 44-69 ^{o}C and salinities from 0.54 M to 0.6 M (Supplementary Table; 1; CALGEM, 2020a). Oil density is homogenous across the wells sampled at 23.1 ^{o}, with the exception of LH-O5, which is 21.5 ^{o}.

In the Lost Hills Oil Field, the Belridge Diatomite has undergone a mixture of water flooding, CO_2 flooding, and hydraulic fracturing since 1962 and the Tulare Formation has been steam flooded since 1964 (Land, 1984). The breakthrough time for this these fluids to the producing wells has been shown to be less than a month (Zhou et al, 2002). Production within diatomite is also commonly stimulated by hydraulic fracturing (Jordan and Heberger, 2014). Water disposal at Lost Hills has also increased from 160,000 m^3/yr in 1973 to 4.8 million m^3 in 2009 (Gillespie et al., 2019). This disposal was initially into both the Tulare and Etchegoin Formation; however, from 1990, disposal was solely into the Etchegoin Formation. With the exception of LH-09, all wells have been subjected to some EOR fluid injection within 500 m of the well; the amount of injected fluid to these wells varies between 5.1×10^4

- $4.7x10^{7}$ m^3. Injected volumes in the field have only been digitized since 1977; however, it is estimated that injection prior to this only accounts for 2% of the total injection in the field.

1.3. Belridge geological and production history

Oil was discovered near North Belridge, California, between 1911 (South Belridge Oil Field) and 1912 (North Belridge Oil Field). The fields were developed on an elongated anticline. Oil and gas producing wells penetrate into the Tulare Formation (Pleistocene), Belridge Diatomite of the Miocene Monterey Formation, and the Temblor (Oligocene) Formation (Supplementary Figure 1c). A more detailed geological history can be found in (Taylor and Soule, 1993; Miller et al., 1990; Fredrich et al., 2000; Hill et al., 1995, Allan and Lalicata, 2011). Hydrocarbons in the Temblor Formation are thought to be from Eocene source rocks, whereas oil in the Monterey and Tulare Formations are thought to have sources from the Monterey Formation to the east of the field (Allan and Lalicata, 2011).

Similarly to within the Lost Hills Oil Field, changes in clay, sand, and silt content across the formation and the transition from Opal-A to Opal CT of silica in the diatoms and microplankton, have caused variable porosity and permeability within the Belridge Diatomite Formation (Mizutani, 1977; Pisciotto and Garrison, 1981; Soutar et al., 1981). Average effective porosity in the Belridge Diatomite reservoir is 36.7- 55.4% and permeability between 0.1-1 mD (Allan and Lalicata, 2012). Within the Tulare Formation porosity ranges from 30-40% and permeability from 35- 4000 mD (EPA, 2016). Porosity in the Temblor Formation is between 10 and 40% and permeability varies from 7-10,000 mD (Downey and Clinkenbeard, 2005). Oil density within the sampled diatomite reservoir range from 22.2^{o} to 32^{o} (Table 1), while the shallower formations are expected to have heavier oil (11-15^{o}; Smith, 2012). Measured reservoir fluid salinity were 0.54 -0.65 M and temperatures were 44.8-99.4 ^{o}C with the average temperature of 60.8 ^{o}C (Supplementary Table 1; Gannon et al., 2018). Production data are not consistent with a gas cap present in the Diatomite reservoirs (DOGGR, 1998, CALGEM, 2020).

South Belridge Oil Field has been subjected to steam and water flooding and hydraulic fracturing (DOGGR, 1998). The field has seen the largest total volume of water and steam injection of the sampled fields (~1400 million m^3 from 1960-2017; CalGEM, 2020a). Water disposal is almost entirely into the Tulare Formation. 98.2% of injection in the North Belridge Oil Field is for EOR (McMahon et al., 2018). The sampled wells in North Belridge Oil Field have injected volumes of between 2.24 $x10^{7}$ to 3.64 $x10^{7}$ m^3 water within 500 m (CalGEM, 2020a).

1.4. Orcutt geological and production history

Oil was first discovered in the Orcutt Oil Field in 1901, and the production in the field began shortly after (Isaacs, 1992). It was originally named the ‘Santa Maria Oil Field’ and changed its name to ‘Orcutt

Oil Field’ due to the discovery of a much larger field nearby. The Santa Maria basin is defined by west-northwest trending open fold and some narrow closely spaced fold, with sub parallel Cenozoic age faults (Namson and Davis, 1990). The Orcutt Oil Field lies on one of these anticlines, known as the Orcutt Anticline, which is a broad flat crested asymmetrical anticline and is likely a fault bend fold from the Pruisana –Solom Thrust (Namson and Davis, 1990). Additional second order folds, which initiated 6-3 Ma, are present because of continued shortening (Woodring and Bramlette, 1950; Isaacs, 1992; Namson and Davis, 1990). Notably, there are numerous west-northwest trending high angle faults cut the anticline, the most important being the Orcutt fault, which is a reactivated normal fault that created an ideal trap for the oil. The stratigraphy of interest in ascending order consists of: 1) early-mid Miocene Point Sal Formation (marine facies consisting of siltstone mudstone and thin sandstones); 2) Miocene Monterey Formation (shale, cherts and diatoms); 3) late Miocene- early Pliocene Sisquoc Formation (diatom rich and includes Tinsquaic sandstone and the basin facies); 4) mid-late Pliocene Foxen Formation (mud and silt stones); 5) late Pliocene-Pleistocene Paso Robles Formation (sand gravel and clays) 6) recent Pleistocene deposits (Orcutt sands, terraces and alluvium)(Supplementary Figure 1d; Woodring and Bramlette, 1950; Isaacs, 1992). The Monterey Formation consists of 3 members, i) lower phosphatic shale and porcelaneous shale, ii) mid chert and cherty shales, iii) upper-procelaneous shale and diatomaceous strata. Oil is thought to have been generated in Monterey Formation within the syncline between the Orcutt and Lompoc Oil Fields, where they diagenetic grade and thermal maturity potential is greatest (Pisciotto, 1981; Isaacs and Tomson, 1990). Within the Orcutt Oil Field, most of the production is from the fractured rocks within the Monterey Formation (75%), with limited production from other fractured rocks (2%). The remaining production is from the Point Sal Formation and Sisquoc Formation, which act as conventional reservoirs (Crawford, 1971; DOGGR, 1991, 1992).

Reservoir temperatures vary from 49-71 ^{o}C across the reservoir, due to changes in reservoir properties (e.g., porosity) and differential production and EOR. Oil density is also variable between 14- 27.5 ^{o} across the reservoir; however, the samples were largely homogenous at 21.4 ^{o} with only O-02 at 22.9 ^{o} (Table 1). Well logs from the Orcutt Oil Field give average temperatures for the Monterey Formation at 60 ^{o}C, Point Sal Formation at 74 ^{o}C and Sisquoc Formation at 42 ^{o}C. Salinities in the formation waters are 0.72 M, 0.48 M and 0.18 M for the Monterey, Point Sal and Sisquoc, respectively (CALGEM, 2020a, Seitz 2021). Porosity in the different formations vary from 15-70% and permeability is thought to be ~5-10 mD (Beyer et al., 1985; Carpenter, 2016) There is no evidence for gas nor a secondary gas cap within the field (CALGEM, 2020b).

Cyclic steam injection into the diatomite in the Monterey Formation at Orcutt Oil Field began in 2005 and now about 96 wells in the field are using this technique (Elias et al., 2010; Pacific Coast Oil Trust, 2020). During this process, steam is injected into the reservoir and left to soak for a few days before the well is produced by flowing the hot oil and water to the surface, and repeated. Additionally, since 2009, the Sisquoc Formation has been water flooded in order to maintain reservoir pressure. O-02 and O-06 have not been affected by injection, the remaining wells have with between 2.0×10^6 – 9.8×10^7 m^3 injected within 500 m of the wells. Hydraulic fracturing was allegedly trialled in the oil field in 1991 (Kamori and Hauksson, 1992).

References

Allan M. E. and Lalicata J. J. (2012) The Belridge Giant Oil Field - 100 Years of History and a Look to a Bright Future. *Search and Discovery Article #20124*.

Barry P. H., Kulongoski J. T., Tyne R. L., Landon M. K., Gillespie J. M., Stephens M. J., Hillegonds D. J., Byrne D. J. and Ballentine C. J. (2018) Tracing enhanced oil recovery signatures in casing gases from the Lost Hills oil field using noble gases. *Earth and Planetary Science Letters* **496**, 57–67.

Beyer, L.A., Robbins, S.L., Clutsom, F.G., (1985) Basic data and preliminary density and porosity profiles for twelve borehole gravity surveys made in the Lost Angeles, San Joaquin, Sana Maria and Ventura Bains, California. USGS Report 85-42.

Bowersox, J.R., 1990. Geology of the Belridge Diatomite, northern South Belridge field, Kern County, California, in: Structure, stratigraphy, and hydrocarbon occurrences of the San Joaquin Basin, California, Pacific Sections, SEPM and AAPG, Book 64 and Guidebook 65, pp 215–223.

Carpenter, C. (2016) Case Study: Steam-Injection Step Rates Tests Run in the Orcutt Oil Field. *Journal Petroleum Technology.* **68** (06) 78-79.

Claypool G. E., Baysinger J. P., Lubeck C. M. and Love A. H. (1979) Organic geochemistry Geologic Studies of the Point Conception Deep Stratigraphic Test Well OCS-CAL 78–164 No. 1, Outer Continental Shelf, Southern California, United States H.E Cook (Ed.), USGS Open File Rept. 79-1218 (1979), 109-124

Crawford, F. D., 1971, Petroleum potential of Santa Maria province, California, in Cram, I. H., ed., Future petroleum provinces of the United States—Their geology and potential: Tulsa, American Association of Petroleum Geologists, 316–328.

CALGEM (2020a) *Online Production and Injection Data*., California Department of Conservation, CALGEM publication. Available at: ftp://ftp.consrv.ca.gov/pub/oil/Online_Data/Production_Injection_Data.

CALGEM (2020b) *Online Well data*. Available at: https://secure.conservation.ca.gov/WellSearch.

DOGGR (1991) *76th Annual Report of the State Oil and Gas Supervisor*., California Department of Conservation, DOGGR publication.

DOGGR (1992). *California oil and gas fields volume 2- Southern, Central Coastal, and Offshore*. California Department of Conservation, DOGGR publication.

DOGGR (1998) *California oil and gas fields volume 1-Central California*., California Department of Conservation, DOGGR publication.

Downey, C. and Clinkenbeard, J.C. (2005) An Overview of geological carbon sequestration potential in California. CGS Special report. West Coast Regional Carbon Sequestration Partnership. California Geological Survey Sacramento. Available at: https://www.osti.gov/servlets/purl/903323

Elias R., Wilson M. L., Vassilellis G. D. and Bust V. K. (2010) Successful Thermal Recovery of Heavy Oil from an Ultratight Reservoir Renews Development of the 100-Year-Old Orcutt Oil Field. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers. Available at: https://www.onepetro.org/conference-paper/SPE-135520-MS [Accessed June 3, 2019].

EPA. (2016) Aquifer exemption record of decision. South Belridge Oil Field-Tulare Formation Available at: https://www.epa.gov/sites/production/files/2017-02/documents/fruitvale_rod.pdf

EPA. (2019) Aquifer exemption record of decision. Santa Margarita Formation of the Fruitvale Oil Field. Available at: https://www.epa.gov/sites/production/files/2020-03/documents/epa_rod_south_belridge_ae-2020-03-13.pdf

Fredrich, J.T., Arguello, J.G. 2000. Geomechanical modelling of reservoir compaction, surface subsidence, and casing damage at the Belridge Diatomite field. *SPE Reservoir Evaluation & Engineering* **3** (04), 348–359.

Gannon, R.S., Saraceno, J.F., Kulongoski, J.T., Teunis, J.A., Barry, P.H., Tyne, R.L., Kraus, T.E.C., Hansen, A.M., and Qi, S.L., 2018, Produced water chemistry data for the Lost Hills, Fruitvale, and North and South Belridge study areas, Southern San Joaquin Valley, California: USGS data release, https://doi.org/10.5066/F7X929H9

Gillespie J. M., Davis T. A., Stephens M. J., Ball L. B. and Landon M. K. (2019) Groundwater salinity and the effects of produced water disposal in the Lost Hills–Belridge oil fields, Kern County, California. *Environmental Geosciences* **26**, 73–96.

Hill, D.W., Sande, J.J., Doe, P.H. (1995) Oil gravity distribution in the diatomite at South Belridge Field, Kern County, CA: Implications for oil sourcing and migration. *AAPG Bulletin* **79**(4)

Hluza, A.G. (1965). Summary of operations, California oil fields. California Department of Conservation, Division of Oil and Gas **51**.

Isaacs, C.M. (1992), Petroleum geology of the Santa Maria Basin Assessment Province, California for the 1987 National Assessment of undiscovered oil and gas resources: USGS Open-File Report 89-450-C.

Isaacs C. M. and Tomson J. H. (1990) *Reconnaissance study of petroleum source-rock characteristics of core samples from the Sisquoc and Monterey Formations in a north-south subsurface transect across the onshore Santa Maria basin and in surface sections along the Santa Barbara-Ventura coast, Southern California*., USGS Open-File Report 89-108.

Jordan P. D. and Heberger M. G. (2014) Historic and Current Application of Well Stimulation Technology in California. In *Advanced Well Stimulation Technologies in California (BLM)* Available at: https://ccst.us/wp-content/uploads/160708-blm-3.pdf [Accessed July 14, 2020].

Kamori, H. and Hauksson, E. (1992) A slow earthquake in the Santa Maria Basin, California. *Bulletin of the Seismological Society of America* **82**(5), 2087-2096.

Kruge M. A. (1986) Biomarker geochemistry of the Miocene Monterey Formation, West San Joaquin Basin, California: Implications for petroleum generation. *Organic Geochemistry* **10**, 517–530.

Kruge M. A. and Williams L. A. (1982) Silica diagenesis in the Monterey Formation (miocene) in the Lost Hills oil field, San joaquin Valley, California. *AAPG Bulletin*, 37–42.

Land, P.E. (1984) Lost Hills oil field. California Dept. Conservation, Division of Oil and Gas TR32. https://www.conservation.ca.gov/calgem/pubs_stats/Pages/technical_reports.aspx (accessed March 30, 2021).

Lillis P. G. and Magoon L. B. (2007) *Petroleum systems of the San Joaquin Basin Province, California -- geochemical characteristics of oil types: Chapter 9 in Petroleum systems and geologic assessment of oil and gas in the San Joaquin Basin Province, California*., Reston, VA. Available at: http://pubs.er.usgs.gov/publication/pp17139.

McMahon P. B., Kulongoski J. T., Vengosh A., Cozzarelli I. M., Landon M. K., Kharaka Y. K., Gillespie J. M. and Davis T. A. (2018) Regional patterns in the geochemistry of oil-field water, southern San Joaquin Valley, California, USA. *Applied Geochemistry* **98**, 127–140.

Medeweff D. A. (1989) Growth Fault-Bend Folding at Southeast Lost Hills, San Joaquin Valley, California. *AAPG* **73**.

Miller, D.D., McPherson, J.G., Covington, T.E. (1990) Fluviodeltaic reservoirs, South Belridge Field, San Joaquin Valley, California. Casebooks in Earth Science: Sandstone Petroleum reservoirs. Eds: Barwis, McPherson, Studlick. Springer. New York.

Mizutani S. (1977) Progressive ordering of cristobalitic silica in the early stage of diagenesis. *Contributions to Mineralology Petrology* **61**, 129–140.

Namson, J., and Davis, T.L., 1990, Late Cenozoic fold and thrust belt of the southern Coast Ranges and Santa Maria Basin, California*: AAPG Bulletin* 74, 467-492.

Pacific Coast Oil Trust (2020) Pacific Coast Oil Trust - Trust Overview - Properties Overview. *Properties overview*. Available at: http://royt.q4web.com/trust-overview/properties-overview/default.aspx [Accessed October 7, 2020].

Philippi G. T. (1965) On the depth, time and mechanism of petroleum generation. *Geochimica et Cosmochimica Acta* **29**, 1021–1049.

Pisciotto K. A. (1981) Diagenetic trends in the siliceous facies of the Monterey Shale in the Santa Maria region, California. *Sedimentology* **28**, 547–571.

Pisciotto, K. A., and Garrison, R. E., 1981, Lithofacies and Depositional Environments of the Monterey Formation, California, *in* Garrison, R. E., and Douglas, R. G., eds., The Monterey Formation and related siliceous rocks of California: Los Angeles, Pacific Section, *Society of Economic Paleontologists and Mineralogists*, 97–122.

Preston H. M. (1931) *Summary of Operations, California Oil Fields*, DOGGR, California Department of Natural Resources.

Scheirer, A.H., Magoon, L.B., 2007. Age, distribution, and stratigraphic relationship of rock units in the San Joaquin Basin Province, California. USGS Professional Paper 1713.

Schwartz, D.E., 1988. Characterizing the lithology, petrophysical properties, and depositional setting of the Belridge diatomite, South Belridge field, Kern County, California, in: Studies of the Geology of the San Joaquin Basin, Pacific Section, *Society of Economic Paleontologists and Mineralogists* 60, 281–301.

Seitz, N.O., Kulongoski, J.T., Marcusa, J.A. Marcusa, and Qi, S.L., 2021, Produced water chemistry data collected from the Orcutt oil field, 2018, Santa Barbara County, California: USGS data release, https://doi.org/10.5066/P936ZEZW.

Soutar, A., Johnson, S. R., and Baumgartner, T. R., 1981, In search of modern analogs to the Monterey Formation, *in* Garrison, R. E., and Douglas, R.G., eds., The Monterey Formation and related siliceous rocks of California: Los Angeles, Pacific Section*, Society of Economic Paleontologists and Mineralogists*, 123–147.

Smith, T. (2012) The Many Lives of Belridge. GEOExPro, 9 (2), https://www.geoexpro.com/articles/2012/09/the-many-lives-of-belridge [accessed January 15, 2021].

Stephens M. J., Shimabukuro D. H., Gillespie J. M. and Chang W. (2019) Groundwater salinity mapping using geophysical log analysis within the Fruitvale and Rosedale Ranch oil fields, Kern County, California, USA. *Hydrogeology Journal* **27**, 731–746.

Taylor T. R. and Soule C. H. (1993) Reservoir Characterization and Diagenesis of the Oligocene 64-Zone Sandstone, North Belridge Field, Kern County, California. *AAPG Bulletin* **77**, 1549–1566.

Woodring W. P. and Bramlette M. N. (1950) *Geology and Palaeontology of the Santa Maria district, California*, USGS Professional Paper 222.

Wright M. T., McMahon P. B., Landon M. K. and Kulongoski J. T. (2019) Groundwater quality of a public supply aquifer in proximity to oil development, Fruitvale oil field, Bakersfield, California. *Applied Geochemistry* **106**, 82–95.