



1

2

*Geochemistry Geophysics, Geosystems*

3

Supporting Information for

4

**A novel method for the extraction, purification and characterization of noble gases in  
5 produced waters**

5

6

R.L. Tyne<sup>1\*</sup>, P.H. Barry<sup>2</sup>, D.J. Hillegonds<sup>1</sup>, A.G. Hunt<sup>3</sup>, J.T. Kulongoski<sup>4</sup>, M.J. Stephens<sup>5</sup>,  
7 D.J. Byrne<sup>6</sup>, C.J. Ballentine<sup>1</sup>

8

9

<sup>1</sup> Department of Earth Sciences, University of Oxford, Oxford, UK

10

<sup>2</sup> Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic  
11 Institution, Woods Hole, MA, USA.

11

12

<sup>3</sup> USGS, Denver Federal Center, Denver, CO, USA

13

<sup>4</sup> USGS, California Water Science Center, San Diego, CA, USA

14

<sup>5</sup> USGS, California Water Science Center, Sacramento, CA, USA

15

<sup>6</sup> CRPG-CNRS, Université de Lorraine, Nancy, France

16

\*Correspondance email: rebecca.tyne@earth.ox.ac.uk

17

18

**Contents of this file**

19

20

Text S1 to S3

21

Figures S1 to S2

22

Tables S1 to S3

23

24

**Introduction**

25

This supporting information provides more details about the extraction system and procedure

26

used in the analysis of noble gases from produced waters. It includes information about the

27

standards and blanks run through the system and corrections required. There is also a more

28

detailed description of the Fruitvale oil field where the samples analyzed were taken from. Figure

29

S1 and S2 provide additional information about the oil wells and the study area respectively. Table

30

S1 is a list of all the equation parameters from this paper, S2 includes information relating the

31

wells sampled and S3 is the calculated concentrations and ratios in different phases from the

32

measured values in samples in Cu tubes (Gannon et al., 2018).

33

34 **Text S1. Analytical Methods for produced water analysis**

35 S.1.1. Gas Purification System

36 After noble gases are extracted from the fluid/multiphase sample and transferred into the sample  
37 transfer vessel (section 2), it is attached to the existing gas purification system, which consists of  
38 volumes C-I (Figure 1). Volume C represents the sample inlet volume; gas inlet is either from the  
39 transfer vessel or from an air-standard tank. Volume D is a known volume ( $69.7 \pm 0.6 \text{ cm}^3$ ), fitted  
40 with a 1000 Torr capacitance manometer, at laboratory temperature (set at 17 °C and recorded  
41 every 15 minutes) enabling the gas pressure to be determined and allowing for the clean-up to  
42 be monitored. Volume E is an expansion volume. Volume F is the initial clean up volume,  
43 consisting of a finger of titanium (Ti) sponge held at 950 °C. The second clean-up volume is volume  
44 G, where the system is interfaced with both a SAES GP-50 getter at 250 °C and SAES NP-10 getter  
45 at room temperature. It is also interfaced, via a pipette, to a Hidden Analytical HAL-200  
46 quadrupole mass spectrometer (QMS); the QMS is held at vacuum by a dedicated ion pump.  
47 Volume H is another expansion volume and Volume J represents the inlet volume onto the  
48 automated prep-system.

49 Initially, the gas purification system is pumped to a vacuum (with E2, E3, 1, 2 and 11 closed) of at  
50 least  $4 \times 10^{-6}$  mbar on the high vacuum side of the turbomolecular pump. Once vacuum is reached,  
51 all remaining valves are closed and the background pressure on the capacitance manometer is  
52 recorded. The sample is expanded into volume C and D by opening valves E2, 3, 5 and 6, and the  
53 initial pressure recorded. Valves 7 and 8 are opened to establish water vapor flow and sample gas  
54 transfer back through the capillary and into the hot titanium. After 30 minutes the 'transferred'  
55 gas pressure is recorded and E2 is closed. The sample is exposed to titanium sponge held at 950  
56 °C for 10 minutes to chemically remove any hydrocarbons, water vapor and reactive gases (Stout  
57 & Gibbons, 1955). The titanium sponge is then cooled to room temperature for 10 minutes,  
58 allowing the removal of hydrogen (Stout & Gibbons, 1955). Valves 9, 11, 12 and 13 are then  
59 opened, exposing the sample to the SAES getters for further gas clean-up for 10 minutes. The hot  
60 getter is designed to remove  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$ , and the cold to remove  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  
61  $\text{N}_2$  and  $\text{O}_2$  (SAES Getters, 1986). The gas pressure is monitored to ensure the sample has  
62 successfully been purified and the pressure returns to background. A small aliquot of gas is  
63 transferred into the QMS by closing valve 13 and opening valve 14. The aliquot is analyzed in the  
64 QMS to estimate purified noble gas concentrations prior to inlet to the automated preparatory

65 line and the data is used to make volumetric splits appropriate for inlet into the noble gas mass  
66 spectrometers.

67

### 68 S.1.2. Automated Preparatory system

69 The automated preparatory system is controlled by the Thermo Qtegra software version  
70 1.6.1221.34. It consists of two volumes, J and K (Figure 1). Volume J interfaces the stainless-steel  
71 cryogenic trap and the charcoal cryogenic trap, as well as containing an ion gauge to measure  
72 pressure. Volume K consists of two SAES NP-10 getters, one of which is set to operate (heated),  
73 the volume is also interfaced with both the mass spectrometers, a turbo pump, standards tanks  
74 (for both Ar and internal air standard) and a separate extraction system beyond P12. At the start  
75 of a sample analysis, the system is held at vacuum with all valves closed.

76 The gas is expanded into Volume J and the Ar, Kr, Xe are frozen down onto a nude stainless-steel  
77 cryogenic trap held at 15 K for 10 minutes; the He and Ne are then expanded into volume K and  
78 frozen onto the 10 K charcoal trap (by opening P1 and P2). After 10 minutes, valve 17 on the gas  
79 purification system is closed and the 10 K charcoal trap is heated to 34 K to release the He. The  
80 He is expanded into volume L (opening P4) then inlet into the Helix SFT (opening P6 for 30 s for  
81 equilibration). Any remaining He is removed and the temperature of the 10 K trap was then raised  
82 further to 90 K to release the Ne. This is inlet to the ARGUS VI. Once the Ne analysis is complete,  
83 the volumes are pumped and the 24 K stainless steel trap is heated to 200 K and an aliquot of Ar  
84 is inlet to the ARGUS VI. The trap temperature is dropped to 50 K and valves P1-P4 closed, to  
85 isolate residual Kr and Xe fractions before the remaining Ar is removed out of volume K. The Kr  
86 and Xe fractions are then separated from any Ar remaining on the steel cryogenic trap, by three  
87 sequential heating and cooling cycles, where volume K is pumped by the turbo pump and the  
88 stainless-steel trap heated to 70 K, (i.e., pump, warm to 70 K, cool to 52 K, pump). After the third  
89 cycle, Kr and Xe fractions are simultaneously let into the Argus VI for analysis.

### 90 S.1.3. Analytical protocol

91 The samples are analyzed for noble gas concentrations and isotopes using the Helix SFT and Argus  
92 IV mass spectrometers, which are interfaced by an automated preparatory system. The Helix SFT  
93 is used for helium ( $^3\text{He}$ ,  $^4\text{He}$ ) analysis, while the Argus VI is used to measure neon ( $^{20}\text{Ne}$ ,  $^{21}\text{Ne}$ ,  
94  $^{22}\text{Ne}$ ), argon ( $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ,  $^{39}\text{Ar}$ ,  $^{40}\text{Ar}$ ), krypton ( $^{78}\text{Kr}$ ,  $^{80}\text{Kr}$ ,  $^{82}\text{Kr}$ ,  $^{83}\text{Kr}$ ,  $^{84}\text{Kr}$ ,  $^{86}\text{Kr}$ ) and xenon ( $^{124}\text{Xe}$ ,  $^{126}\text{Xe}$ ,  
95  $^{129}\text{Xe}$ ,  $^{130}\text{Xe}$ ,  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$ ,  $^{136}\text{Xe}$ ). Immediately after the gas is inlet into the mass spectrometer,  
96 they are scanned and peak centered for all the desired isotopes using a combination of a multi-  
97 collection and a peak jumping protocols. Helium data is collected with 100 collection cycles, and

98 the remaining elements using 30 collection cycles. All isotopes are collected using a 4.19 s  
99 integration time. Signals are calculated by using either exponential or linear regression lines back  
100 to time zero (time of inlet) depending on the fit of data to get the smallest statistical errors.

## 101 **Text S2: Standards, Blanks and Corrections**

102 It is critical to characterize the standards, blanks and required corrections when making noble gas  
103 measurements in order to ensure data reliability. We describe the methods and results for  
104 analyzing standards, and the data corrections identified.

### 105 S.2.1. Internal air standards

106 Internal air standards are run prior to processing unknown samples, and daily following both  
107 sample and ASW analysis. An air tank (pressure: 1010 mBar, temperature: 14 °C and humidity:  
108 71%), on the automated preparatory system (Figure 1), releases a known aliquot (between valves  
109 P8 and P9) of standard gas. This aliquot is gettered on two SAES NP-10 getters (one of which is set  
110 to operate) on the automated preparatory system and is then prepared and measured the same  
111 way as a sample (with the exception of He, which is not initially frozen down) on the automated  
112 preparatory system (see section S.1.2, S.1.3.). The internal air standards are used to monitor and  
113 correct for changes in the machine performance, and account for any changes in machine  
114 sensitivity between analyses. Over a period of a week, the internal air standards variations are  
115 stable at 0.33 % for  $^4\text{He}$ , 0.64 %  $^{20}\text{Ne}$ , 0.66 %  $^{40}\text{Ar}$ , 1.2 %  $^{84}\text{Kr}$  and 0.92 % for  $^{132}\text{Xe}$ .

116

### 117 S.2.2. Blank contribution and corrections

118 Due to the unknown and variable composition of produced waters, it is important to have low  
119 blank levels to ensure there is no significant contribution from residual or background gases.  
120 Three different blanks (preparatory system blank, procedural blanks and full system blank) are  
121 run during analysis to ensure the system was running with low blank contributions.

122 Preparatory system blanks are run daily on the automated preparatory system in the same way  
123 as the internal air standard, with the only difference being no air was released from the tank.

124 Preparatory system blanks made up less than 0.05 % of the ASW signals. Procedural blanks involve  
125 following the protocols for both the gas purification system and automated preparatory system.

126 These are run at the beginning of a run in the laboratory and subsequently, once a week during  
127 sample analyses. They are used to ensure the systems (e.g. it is noted that the SAES NP-10 and  
128 GP-50 getters are a particular source of background gas that can affect blank levels) are  
129 sufficiently clean between samples. A maximum blank contribution to samples of less than 3% is

130 required for the key indicator isotopes ( $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ar}$ ,  $^{82}\text{Kr}$ ,  $^{84}\text{Kr}$ ,  $^{86}\text{Kr}$ ,  $^{130}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{136}\text{Xe}$ ). A  
131 3% limit was chosen to be beneath the level of uncertainty associated with the ASWs. If the blanks  
132 have a higher signal than desired, the analysis is halted and the systems is baked and pumped on,  
133 in order to lower the backgrounds. Additional blanks are run until a desired level is reached. Full  
134 system blanks follow sample inlet and processing protocols, and also include the extraction  
135 system and an empty copper tube (only clamped at one side) attached to the system and pumped  
136 to vacuum. These experiments yield very similar results to the procedural blanks and therefore  
137 only procedural blanks are analyzed regularly, as the slightly amended method of extraction could  
138 result in errors not seen within the samples.

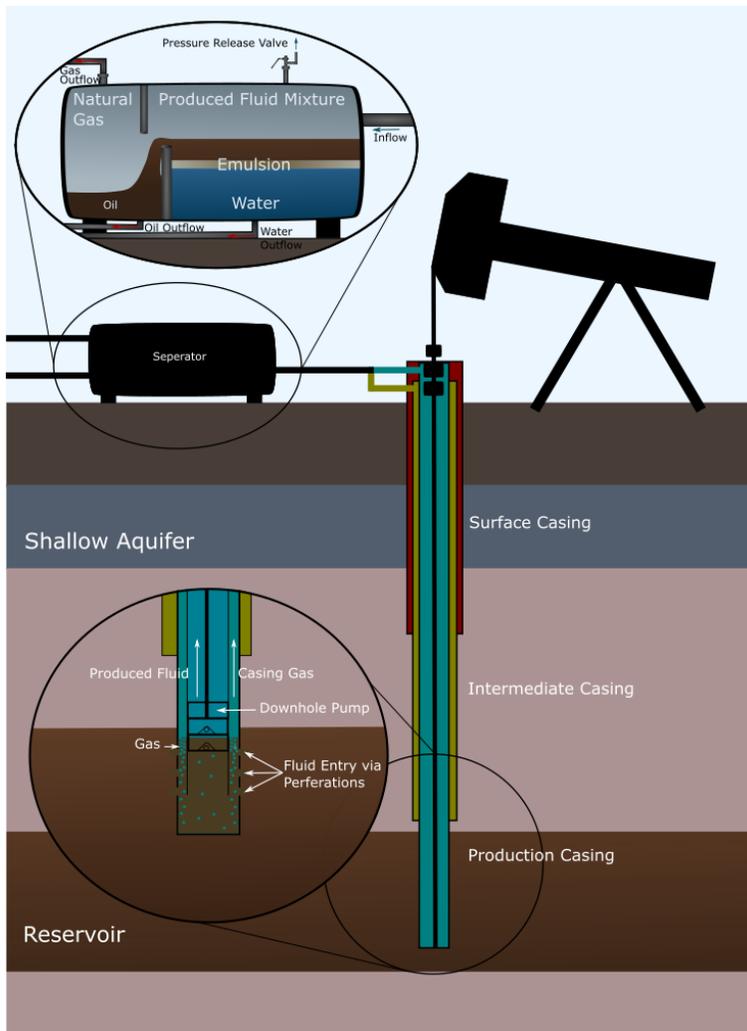
### 139 S.2.3. $^{40}\text{Ar}^{++}$ and $^{44}\text{CO}_2^{++}$ Corrections

140 Due to isobaric interferences within the mass spectrometer, both  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  signals must be  
141 corrected for contributions from  $^{40}\text{Ar}^{++}$  and  $^{44}\text{CO}_2^{++}$  respectively. The proportion of doubly charged  
142  $^{40}\text{Ar}$  was determined by inletting clean Ar gas and monitoring both  $^{40}\text{Ar}^+$  and  $^{40}\text{Ar}^{++}$  peaks (e.g.  
143 Ballentine et al., 1991). The size of the doubly-charged peak was calculated to be consistently  
144 11.3% of the  $^{40}\text{Ar}^+$ . Argon background at mass 40 was then monitored during Ne isotope  
145 measurement to allow correction for the doubly-charged Ar contribution. The  $^{44}\text{CO}_2^{++}$  is negligible  
146 compared to  $^{22}\text{Ne}$  (<1%) and thus, no  $^{44}\text{CO}_2^{++}$  correction was applied.

### 147 **Text S3. Geological and Production history Fruitvale**

148 Fruitvale oil field is located on the Bakersfield arch, a westerly dipping faulted homocline the  
149 central part of which exhibits pronounced flattening (Hluza, 1965). The important formations for  
150 oil production and produced water disposal, in order of increasing depth are the Kern River  
151 Formation (Pleistocene), Etchegoin Formation (Pliocene), Chanac Formation (Pliocene-Miocene)  
152 and the Santa Margarita Sandstone Formation (Miocene) (Figure S2.; Hluza, 1965, DOGGR, 2018).  
153 The Etchegoin and Santa Margarita Formations were both deposited under marine environments  
154 whilst the Chanac Formation was deposited in a fluvial environment and consist of siliciclastic  
155 deposits (Preston, 1931, Hluza, 1965). The oil is thought to have originated from the Monterey  
156 Formation to the west (Lillis & Magoon, 2007). Since 1929, oil has been mainly produced from  
157 the westerly dipping Chanac Formation between 960- 1350 m (DOGGR, 1998). This formation is  
158 made up of the Mason Parker, Martin and Kernco reservoirs (Hluza, 1965). These represent non-  
159 marine discontinuous sequences of fan deposits and the oil reservoirs are bound to the east by  
160 the Fairhaven normal fault (Hluza, 1965). There is also limited production from the basal Miocene  
161 Etchegoin Formation from the discontinuous Fairhaven sands, which formed in an estuarine

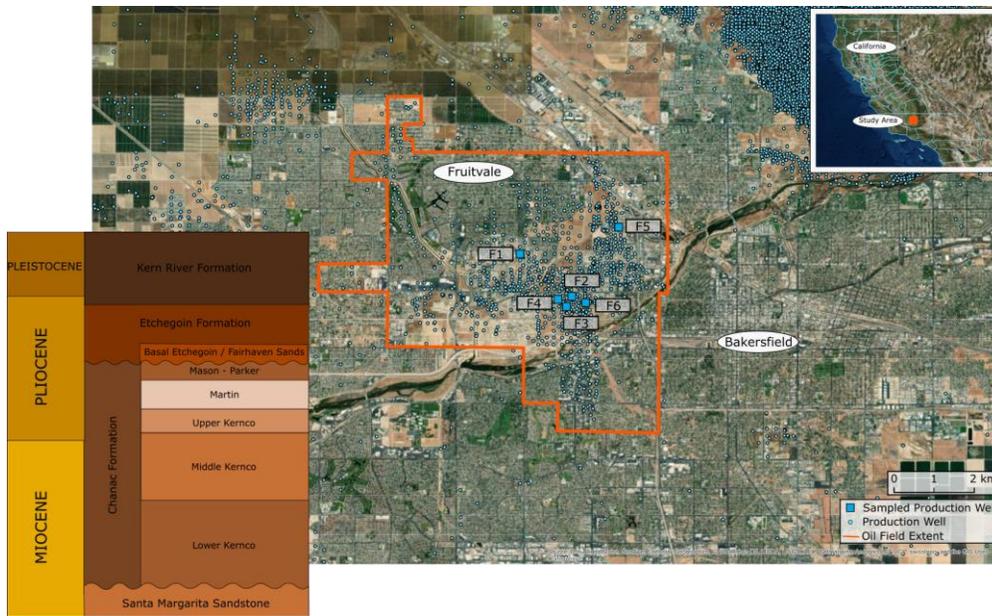
162 depositional system. Samples for this study were taken from the central and eastern zones of the  
163 field, from wells producing in the Etchegoin, Chanac and Santa Margarita Formations.  
164 Enhanced oil recovery in Fruitvale began in the 1960's. The field has undergone both water  
165 flooding (since 1962) and cyclic steam injection (since 1964) (DOGGR, 1998). Between 1977 and  
166 2018 over  $87 \times 10^6 \text{ m}^3$  of water has been injected for water and steam flooding of the reservoirs  
167 as well as produced water disposal (DOGGR, 2018).  
168



169

170 **Figure S1.**

171 Schematic conceptual diagram of an oil well set-up based on the wells sampled at the Fruitvale  
172 oil field, California, U.S.A. The system is purely an oil-water system. Oil enters the well and  
173 decompresses due to the pumping allowing for gas formation. This gas travels up in the casing  
174 and the produced fluids are pulled up the center of the well. As the produced fluids rise,  
175 decreasing pressure results in more exsolution of gas. The gas, oil and water are then piped to a  
176 separator and separated.



177

178 **Figure S2.**

179 Map showing the location of where the produced water samples (large blue squares) were  
 180 collected in the Fruitvale oil field (outlined in orange). The small blue circles represent all the  
 181 production wells in Fruitvale and the surrounding oil fields. Well location and oil field boundary  
 182 data are from the California Division of Oil, Gas, and Geothermal Resources (DOGGR, 2017). Inset  
 183 shows a stratigraphic column for the field modified from DOGGR (1992) and Scheirer and Magoon  
 184 (2007).

185

186

187

188

189

190

191

192

193

194

195

196

197

198

199

200

201

202

203

204

205

206

Parameter Description	Symbol	Units
Volume water	$V_w$	$\text{cm}^3$
Volume oil	$V_o$	$\text{cm}^3$
Volume gas	$V_g$	$\text{cm}^3$
Volume total	$V_t$	$\text{cm}^3$
Volume average ASW	$V_{\text{asw av}}$	$\text{cm}^3$
Henry's Coefficient for gas and water systems	$K_i^{\text{gw}}$	$\text{atm kgmol}^{-1}$
Henry's Coefficient for gas and oil systems	$K_i^{\text{go}}$	$\text{atm kgmol}^{-1}$
Partial pressure of i in the atmosphere	$P_i$	Gpa
Temperature of equilibration	T	K
Elevation of equilibration	h	m
Salinity	s	M
Concentration expected of i in ASW	$C_i^{\text{ex asw}}$	$\text{cm}^3\text{cm}^{-3}$
Concentration of i in ASW	$C_i^{\text{asw}}$	$\text{cm}^3\text{cm}^{-3}$
Signal sample	$S_i$	fA
Signal average ASW	$S_i^{\text{asw av}}$	fA
Amount of i in water	$n_i^w$	mol
Amount of i in oil	$n_i^o$	mol
Amount of i in gas	$n_i^g$	mol
Total amount of i	$n_i^t$	mol
Concentration of i in water	$C_i^w$	$\text{molcm}^{-3}$
Concentration of i in oil	$C_i^o$	$\text{molcm}^{-3}$
Concentration of i in gas	$C_i^g$	$\text{molcm}^{-3}$

207 **Table S1.**  
 208 Parameters used for concentration calculations and models.

209

Sample ID	Site ID	COGG ID	API	Site type	Sample Date
F1	352336119043201	4_FRUT_PW01	02906886	Oil Well	7/26/2016
F2	352256119034201	4_FRUT_PW02	02958737	Oil Well	7/26/2016
F3	352246119034801	4_FRUT_PW03	02908164	Oil Well	7/26/2016
F4	352253119035701	4_FRUT_PW04	02908174	Oil Well	7/26/2016
F5	352401119025901	4_FRUT_PW05	02906854	Oil Well	7/26/2016
F6	352250119033001	4_FRUT_PW06	02908153	Oil Well	7/26/2016

210 **Table S2.**  
 211 Information on sample sites. Additional data from these wells can be found in Gannon et al.  
 212 (2018).

213

214 **Table S3.**  
 215 Calculated concentration of noble gas isotopes ( $\text{molcm}^{-3}$ ), isotope ratios and  $^{20}\text{Ne}/^{36}\text{Ar}$  values in  
 216 each phase, at the wellhead. Samples are from the Fruitvale oil field (under production  
 217 conditions). If a given phase was not present within the sample taken, the concentrations in that  
 218 phase were calculated assuming that equilibrium had been reached. Errors are given as one  
 219 standard deviation. Recharge conditions were 15°C, 0M, 0m elevation. The original measured  
 220 concentrations in  $\text{cm}^3\text{g}^{-1}$  (fluid) at standard temperature and pressure were reported in Gannon  
 221 et al. (2018).