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Barry et al. Supplementary Material

CLOSED-SYSTEM MODEL

Noble gases derived from ASW reveal information about the hydrocarbon form, migration history, reservoir connectivity, and the open and closed system nature of a crustal system (e.g., Bosch and Mazar, 1988; Ballentine et al., 1991; 1996; Zhou et al., 2005; Pinti and Marty, 1995; Torgersen and Kennedy, 1999; Gilfillan et al., 2008; 2009; Hunt et al., 2012; Jung et al., 2013; Darrah et al., 2014; 2015; Barry et al., 2016). The closed-system model developed by Barry et al., (2016) assumes that the hydrocarbon gases interact with ASW, migrate away and remain isolated in the reservoir. We assume that a volume of gas (G) equilibrates with a static water volume (W), initially containing ASW concentrations of noble gas. Once the gas reaches the trap there is negligible additional exchange at the gas-water contact and there is no loss of gas from the trap. Subsequent volumes of gas passing through and equilibrating with the same water then reach the same reservoir, where they mix with previous volumes of gas. Notably, a perfect seal is unlikely to exist in reality; however, for the purpose of our hypothetical closed-system model, we consider the extent of loss to be negligible.

Partitioning is a function of reservoir temperature (T_R) in Kelvin, water density (ρ_w) – typically assumed to be unity, and Henry's constant (K_i^M), given in units of molality. One mole of an ideal gas at STP occupies 22400 cm³.

Therefore we can simplify partitioning into one term, called 'H', defined as:

$$H = \frac{22400 T_R \rho_w}{1000 \times 273.15 K_i^M} \quad (1)$$

The term 'F' describes the extent of partitioning between an assumed volume of gas 'G' and water packet 'W' at a given K_i^M . If G is infinitesimally small relative to W, F approaches 1 (i.e., a very small bubble of G strips a very small amount of gas from W). The F value can be calculated using the equation:

$$F = \frac{H}{H + \frac{G}{W}} \quad (2)$$

Gas concentrations are measured at standard temperature and pressure (STP), and thus we use the term Z as a compression factor that enables conversion from Standard Temperature and Pressure (STP) to Reservoir Temperature and Pressure (RTP; see main text for assumptions), where $STP = 273.15$ at 1 bar and P_R = discovery reservoir pressure (bar).

$$Z = \frac{[273.15 P_R]}{T_R} \quad (3)$$

The fraction (F) of gas stripping per degassing step (for a given species ‘i’) is governed by Eq. 4. The measured gas concentration $[C_{i(meas)}^g]$ at any degassing step ‘d’ (instantaneous signature) is taken to represent an admixture of all previous steps (accumulated signature), using the following the equation:

$$[C_{i(meas)}^g] = \frac{([n_i^{asw}] - [n_i^{asw}] F^d) 22400}{Z G d} \quad (4)$$

Where $[n_i^{asw}]$ represent the number of moles originally in the ASW. If all constants are removed and combined, we can call this term ‘U’:

$$U = \frac{[C_{i(meas)}^g] Z G}{22400 [n_i^{asw}]} \quad (5)$$

We can then rewrite Eq. 4 as:

$$U d = 1 - F^d \quad (6)$$

Importantly, this equation now simultaneously has the term ‘d’ in the exponential and product form, which can be easily solved for using a Lambert transcendental function (ω):

$$d = \frac{1}{U} - \frac{1}{\ln(F)} \omega \left(F^{\frac{1}{U}} \ln \frac{F}{U} \right) \quad (7)$$

The volumetric $\frac{V_g}{V_w}$ can be calculated by combining the d value calculated in Eq. 7 with the assumed G and W volume values:

$$\frac{\text{gas}}{\text{water}} = \frac{dG}{W} \quad (8)$$

The gas to water ratio, indicated by the noble gases, in this closed-system model is the total volume of gas present in the reservoir relative to the total volume of water the gas equilibrated with during its ascent.

RADIOGENIC PRODUCTION

Radiogenic ^4He is produced in the crust by α decay of the ^{235}U , ^{238}U and ^{232}Th . In a simple (in situ) scenario, the ^4He concentration is directly proportional to the concentrations of these radioelements in the crust, and time. After production, several mechanisms result in the release of ^4He from minerals (e.g., recoil, diffusive loss, fracturing and mineral breakdown, metamorphism and/or alteration; Torgersen, 1980; Ballentine and Burnard, 2002; Farley, 2002; Zhou et al., 2006). However, the Rotliegend system cannot be explained by in situ production in the reservoir alone, and instead requires He contributions from the entire graben, which is entirely consistent with volumetric considerations.

There are numerous examples of groundwater systems that have concentrations of noble gases orders of magnitude higher than can possibly be explained by local (i.e., in reservoir) production, release and accumulation (e.g., Torgersen and Clarke, 1985; Takahata and Sano, 2000; Kipfer et al., 2002; Barry et al., 2015). Importantly, such calculations assume that no ^4He is accumulated in detrital minerals in the matrix prior to sedimentation. In deeper and older fluid systems, the contribution of inherited ^4He trapped in the aquifer rocks only represents a minor component compared with other sources (Torgersen, 1980), and thus this is a safe assumption.

We calculate a ^4He flux of $1.2 \times 10^{-7} \text{ cm}^3 \text{ STP } ^4\text{He}/\text{cm}^2 \text{ yr}^{-1}$ from the 658m thick Rotliegend graben, which has an average continental crust like composition ($[\text{U}] = 2.8\text{ppm}$ and $[\text{Th}] = 10.7\text{ppm}$). The accumulation rate of radiogenic ^4He ($\text{cm}^3\text{STP } ^4\text{He}/\text{cm}^2\text{H}_2\text{O yr}^{-1}$) in the 37.5m reservoir can then be calculated using equation 9:

$$\text{He accumulation rate} = (A_{\text{He}} \text{ flux} / \varphi * h) \quad (9)$$

Where:

φ = rock porosity (assumed to be 9.5%)

h = graben thickness (658 m)

With knowledge of the ^4He concentration in the gas phase, the gas/water volume ratio and estimates of the temperature and salinity conditions under which partitioning occurred; the initial ^4He concentrations in the groundwater can be calculated. Due to the fact that the major portion of the radiogenic noble gases cannot be sourced in situ (within the reservoir), it is reasonable to assume that radiogenic noble gases are partitioned between the groundwater and gas phase in the same way as air-derived noble gases. The initial (pre-partitioning) $^4\text{He}/^{36}\text{Ar}$ can be calculated for the groundwater using the following equation:

$$\left(\frac{^4\text{He}}{^{36}\text{Ar}}\right)_{\text{initial}} = \left(\frac{^4\text{He}}{^{36}\text{Ar}}\right)_{\text{gas}} \left(\frac{\left(\frac{V_{\text{gas}}}{V_{\text{water}}}\right) + \left(\frac{K_{\text{He(gas)}}}{K_{\text{He(water)}}}\right)}{\left(\frac{V_{\text{gas}}}{V_{\text{water}}}\right) + \left(\frac{K_{\text{Ar(gas)}}}{K_{\text{Ar(water)}}}\right)} \right) \quad (10)$$

Where:

$(^4\text{He}/^{36}\text{Ar})_{\text{initial}}$ = initial $^4\text{He}/^{36}\text{Ar}$ in groundwater

$(^4\text{He}/^{36}\text{Ar})_{\text{gas}}$ = $^4\text{He}/^{36}\text{Ar}$ in the gas phase

$V_{\text{gas}}, V_{\text{water}}$ = volumes of gas and groundwater in contact

$K_{\text{He(gas)}}, K_{\text{He(water)}}$ = solubilities of He in gas and groundwater

$K_{\text{Ar(gas)}}, K_{\text{Ar(water)}}$ = solubilities of Ar in gas and water

Due to the fact that ^{36}Ar is entirely derived from air-dissolved into the groundwater, the concentration of ^{36}Ar in seawater in equilibrium with air (at 10°C) is known ($1.05 \times 10^{-6} \text{ cm}^3 \text{ STP } ^{36}\text{Ar}/\text{cm}^3 \text{ H}_2\text{O}$). The initial crustal radiogenic ^4He in groundwater can then be calculated by multiplying the initial $^4\text{He}/^{36}\text{Ar}$ by the known $[^{36}\text{Ar}]$ content. The resultant $[^4\text{He}]$ content can then be used to calculate the residence time of the fluids according to equation 11:

$$\text{Age (yr)} = \text{initial}[^4\text{He}] \text{ in groundwater} / \text{He accumulation rate} \quad (11)$$

Notably, isolation ages range between 63 ± 20 and 73 ± 23 Ma and 104 ± 33 – 129 ± 41 Ma for the East and West Rotliegend, respectively. These ages represent the time between source rock deposition and hydrocarbon charge. Average $^4\text{He}/^{36}\text{Ar}$ values are adopted for the each field in order to calculate the initial helium concentration in groundwater. The standard deviation of all values from each field is used to calculate the expected range for each field. Uncertainties are a function of estimated uncertainties of all assumed values; we conservatively estimate 10% uncertainty in U-Th contents, 22% uncertainty on rock density, 20% uncertainty on porosity estimates, 3% uncertainties in the known composition of air (used for normalization) and 1% error in thicknesses of the units. We calculate the combined error using a standard error propagation formulae (Ku, 1966).

THERMAL MODELING OF SOURCE AND RESERVOIR INTERVALS AND HYDROCARBON GENERATION TIMING

Paleothermometry techniques, coupled with basin modeling, provide a means of constraining the thermal history of different elements of the Rotliegend petroleum system. Both the reservoir (Wustrow and Dethlingen sands of the Rotliegend formation) and the source intervals (Carboniferous Westphalian coal measures) are currently at their maximum burial depths. While the present day temperature of the reservoir interval can be constrained directly from bottom hole temperature measurements in the original exploration and later producing wells, the temperature of the source rock has to be estimated based on the observed geothermal gradient and the likely lithologies that separate the reservoir and the source intervals. To calculate the time that hydrocarbons were generated in the source rock and migrated to the reservoir interval, one needs to constrain the thermal history of the source rock in addition to the present day thermal structure of the subsurface. As such, a 1-D basin model was developed using the Schlumberger Petromod[®] petroleum systems modeling software to simulate the burial history at a well Z3 in the West Rotliegend field. This was built using the lithologies and interval thicknesses that were observed during drilling down to the Rotliegend interval (contained within Isopach 267_292 in Fig. DR1), with regional isopachs used to constrain the thicknesses and lithologies of the intervals that underlie the reservoir interval.

This burial history was used as a basis for developing a thermal history for the Westphalian coal interval (isopach 311_315 in the Fig DR1.). In addition to the subsurface geology, development

of the thermal history required (1) an estimate of basal heat flow through time, (2) sediment compaction state, lithologically-dependent thermal conductivities, radiogenic heat production, and (3) water depth and sediment-water interface temperatures through time. The heat flow history was developed using downhole vitrinite reflectance profiles, and incorporates a heating event with a peak of approximately 70 mW/m^2 at 300 Ma associated with Autunian volcanic intrusions that decays to a present-day heat flow of 49 mW/m^2 . Compaction, thermal conductivities and radiogenic heat production were calculated directly from the penetrated and inferred lithologies. The sediment-water interface temperature history is an automated calculation within the Petromod[®] software. In general, the burial history and resulting thermal history follows that of the Northern Germany model in Cornford (1998), though the extent of Late Cretaceous inversion is less significant at the locations modeled here.

Hydrocarbon generation is simulated using the kinetic model of Vandenbrouke et al (1999) which was developed from coal samples from the North Sea. The Westphalian coal source interval is estimated to be 80 meters in thickness within the approximately 1700 m package of shale and sandstone. For the purpose of the hydrocarbon generation timing modeling, the interval has been divided into 5 layers, with the coal source interval located in the top Westphalian interval. By doing this, we are able to determine the latest possible timing of hydrocarbon charge given that this would progress through hydrocarbon generation at a later time than the deepest layer within this package. Hydrocarbon yield as a function of time was calculated for the source interval, and converted to a percent of total hydrocarbon yield as a function of time (Fig. DR2). The most significant period of gas generation was between 250 and 140 Ma, when 85% of all hydrocarbons were generated. A later period of gas generation is possible after 80 Ma, though this likely represents a volumetrically small proportion of the hydrocarbons that charged the Rotliegend reservoirs. Our model is consistent with previous predictions of Gautier (2003) which also suggest there may have been two episodes of gas generation and migration in this region of the basin.

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SUPPLEMENTARY FIGURES

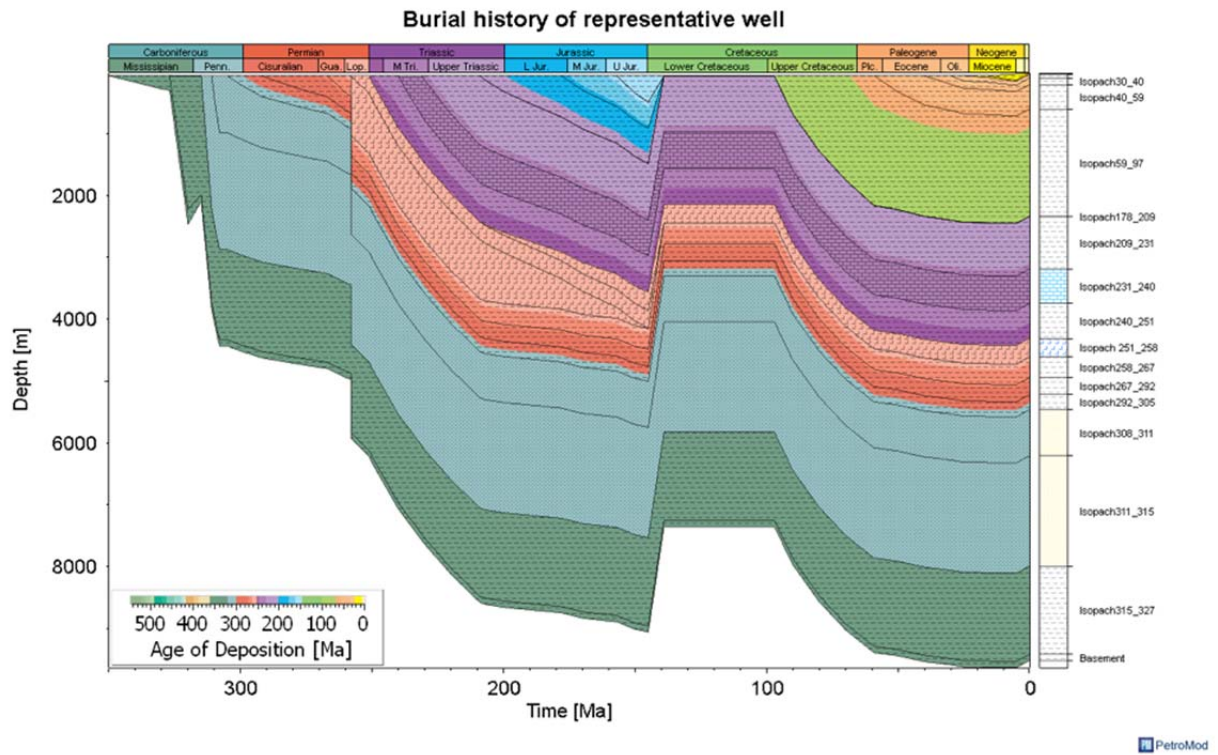


Figure DR1. Burial history at a representative location of the West Rotliegend field. The Rotliegend reservoir interval is represented in this model by isopach 267- 292, while the Westphalian coal source interval is located in the upper part of isopach 311 – 315.

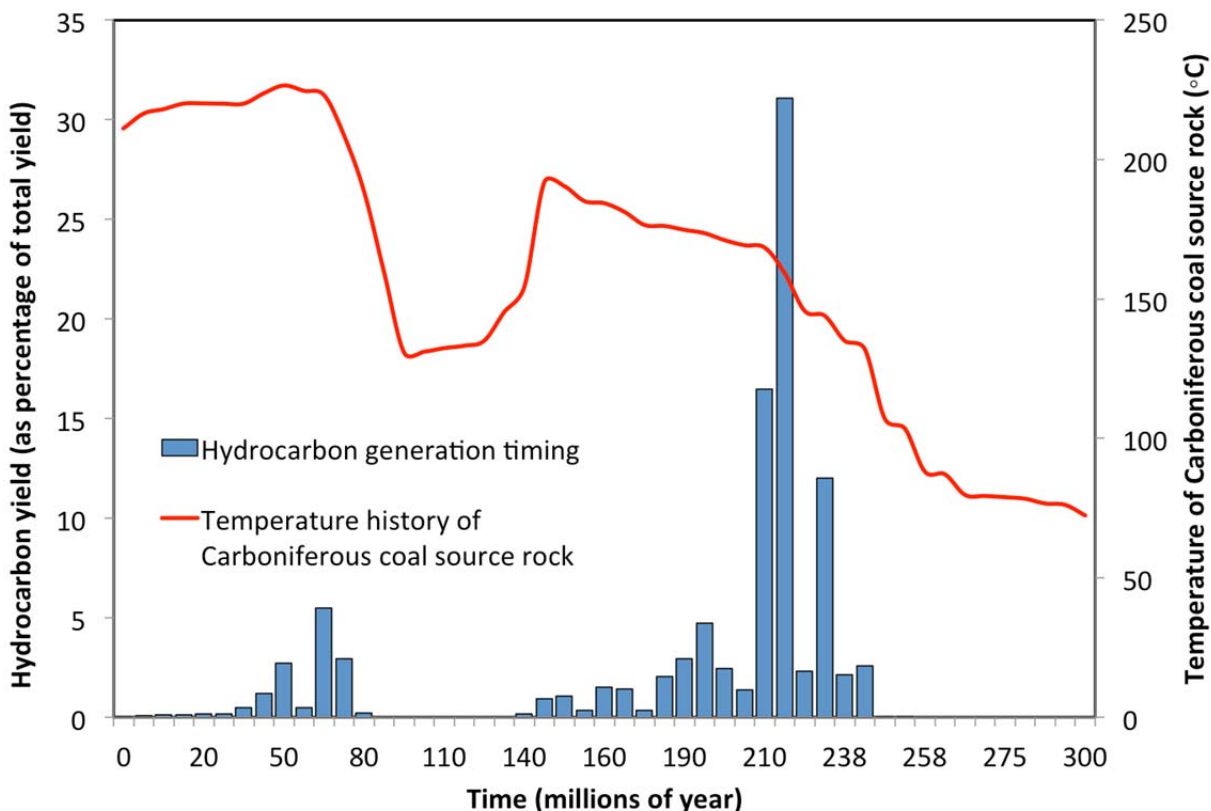


Figure DR2. Thermal history of the source interval alongside volume percent hydrocarbon yield as a function of time calculated using the kinetic model of Vandembrouke (1999). Two periods of gas generation are predicted to coincide with increasing temperatures of the source interval from 250 – 140 Ma and 80 Ma to present. The first episode represents approximately 85% of total generated hydrocarbons.

Table SM1. Compositional and stable isotope systematics of Rotliegend gases.

Compositions						Stable Isotopes			
Sample	CH ₄ (±2%)	C ₂ H ₆ (±2%)	C ₃ (±2%)	CO ₂ (±2%)	N ₂ (±2%)	δ ¹³ C (CH ₄) (±0.1‰)	δ ¹³ C (C ₂ H ₆) (±0.1‰)	δ ¹³ C (CO ₂) (±0.1‰)	δD (CH ₄) (±1.0‰)
East Rotliegend									
W8	84.60	1.52	0.05	0.56	13.23	-26.6	-22.7	-7.8	-130
W7	81.81	1.49	0.05	0.84	15.77	-26.2	-23.5	-6.4	-127
W6	84.86	1.44	0.05	0.80	12.81	-25.9	-23.4	-7.3	-127
W10	84.54	1.51	0.06	0.71	13.13	-26.7	-23.1	-8.4	-129
W9	84.59	1.56	0.06	0.72	13.03	-26.5	-23.2	-8.0	-128
West Rotliegend									
W5	90.05	1.36	0.07	0.11	8.35	-27.1	-23.0	-7.8	-128
W3	90.14	1.37	0.07	0.16	8.21	-27.0	-21.6	-8.4	-129
W4	87.92	1.28	0.06	0.12	10.57	-26.6	-23.1	-8.8	-130
W2	88.02	1.32	0.06	0.17	10.38	-26.3	-22.9	-7.3	-129
W1	87.38	1.22	0.06	0.17	11.10	-26.1	-22.6	-7.0	-130