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Determining fluid migration and isolation times in multiphase crustal domains using noble gases

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ABSTRACT

Geochemical characteristics in subsurface fluid systems provide a wealth of information about fluid sources, migration, and storage conditions. Determining the extent of fluid interaction (aquifer-hydrocarbon connectivity) is important for oil and gas production and waste storage applications, but is not tractable using traditional seismic methods. Furthermore, the residence time of fluids is critical in such systems and can vary from tens of thousands to billions of years. Our understanding of the transport length scales in multiphase systems, while equally important, is more limited. Noble gas data from the Rotliegend natural gas field, northern Germany, are used here to determine the length scale and isolation age of the combined water-gas system. We show that geologically bound volume estimates (i.e., gas to water volume ratios) match closed-system noble gas model predictions, suggesting that the Rotliegend system has remained isolated as a closed system since hydrocarbon formation. Radiogenic helium data show that fluid isolation occurred 63–129 m.y. after rock and/or groundwater deposition (ca. 300 Ma), which is consistent with known hydrocarbon generation from 250 to 140 Ma, thus corroborating long-term geologic isolation. It is critical that we have the ability to distinguish between fluid systems that, despite phase separation, have remained closed to fluid loss from those that have lost oil or gas phases. These findings are the first to demonstrate that such systems remain isolated and fully gas retentive on time scales >100 m.y. over >10 km length scales, and have broad implications for saline aquifer CO_2 disposal site viability and hydrocarbon resource prediction, which both require an understanding of the length and time scales of crustal fluid transport pathways.

INTRODUCTION

Noble gases have been extensively used in both paleogroundwater (Aeschbach-Hertig and Solomon, 2013; Kipfer et al., 2002) and hydrocarbon system studies to constrain recharge and hydrocarbon generation and accumulation conditions (Ballentine et al., 2002; Holland and Gilfillan, 2013; Prinzhofer, 2013; Byrne et al., 2017). The dissolution of noble gases into groundwater is controlled by partial pressure, water temperature, and salinity at recharge. For example, atmosphere-derived noble gas concentrations in groundwaters are used to determine paleo–recharge temperatures in young (<50 k.y.) groundwaters to within ±0.3 °C (e.g., Ballentine and Hall, 1999; Kipfer et al., 2002). Using these well-defined controls on noble gas concentrations in groundwater, it is possible to calculate the extent and character (i.e., fractionation) of noble gas distribution between any gas or oil phase that interacts with water, using estimates of subsurface system pressure, temperature, and salinity. These data further preserve details about the hydrocarbon/water volume ratio and whether the system is open to gas loss (Ballentine et al., 1996; Zhou et al., 2005; Barry et al., 2016). Radiogenic noble gases, which are isotopically distinct from the air-derived noble gases dissolved in water, accumulate in groundwater systems and can be used to investigate mean fluid residence (e.g., Torgersen, 2010; Aggarwal et al., 2014). This technique has previously been applied to a number of systems, including fracture fluids in deep crustal basement rocks with mean residence times of >1 b.y. (e.g., Holland et al., 2013).

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ROTLIEGEND HYDROCARBON SYSTEM

The Rotliegend hydrocarbon system (northern Germany) consists of two subfields, West Rotliegend and East Rotliegend (Fig. 1, top), that are geochemically distinct (Fig. 2). The gases are stored in the tight sandstones of the Permian Rotliegend formation that were deposited in a sabkha setting (Glennie, 1970, 1972). Thermal subsidence of the basin in the late Permian resulted in the widespread transgression of Zechstein seas, which in turn led to the deposition of extensive evaporites throughout the basin. The Zechstein salts are a regional seal for underlying gas accumulations, including those studied here.

The Rotliegend fields are closed on three sides by normal faults, and are dip closed to the north-northwest (Ehrl and Schueler, 2000) (Fig. 1, bottom). The graben structures that delineate these fields are ~10 km long and 3 km wide; the main Dethlingen Sand within the reservoir interval has a crest at ~4600 m depth and occupies 28 km^2 (Ehrl and Schueler, 2000). Rotliegend gases are sourced from Westphalian coal and carbonaceous shales that are dominated by gas-prone type III kerogen (Cornford, 1998; Gautier, 2003). We developed a one-dimensional finite rifting model to provide quantitative constraints on the thermal history of the Westphalian source interval that can be used to estimate the timing of hydrocarbon generation. The basin model was built in the Petromod software package (https://www.software.slb.com; see the GSA Data Repository[1]) applying standard concepts and approaches described in Hantschel and Kauerauf (2009). Subsurface geology (obtained from well logs and seismic data) is broken down into the individual formations that make up the sedimentary package, included in the model with their associated thicknesses, lithologies, and ages. A heat flow history was developed that includes a peak heat flow event at 300 Ma as a result of volcanic intrusions in the region, followed by decay to the present-day heat flow of 49 mW/m^2. The model applies standard thermal conductivities, compaction states, and radiogenic heat production from U-, Th-, and K-bearing minerals. From the derived thermal history, gas generation was simulated using the hydrocarbon

[1]GSA Data Repository item 2017255, supplementary information about the closed system model, radiogenic production, and thermal modeling, is available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.

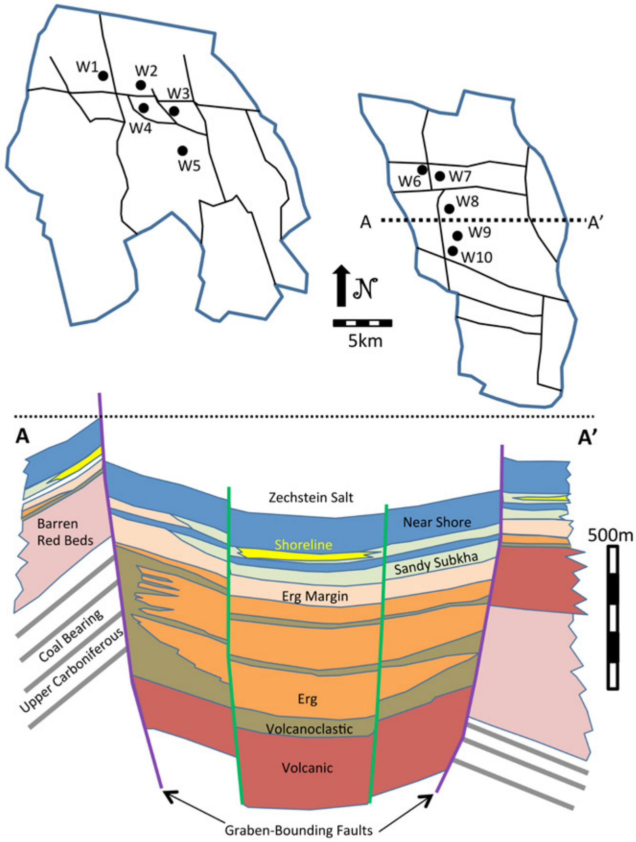

Figure 1. Top: Map of fields and sample locations. Bottom: Cross section through the East Rotliegend (northern Germany) graben structure from A-A′, showing the main stratigraphic sequences.

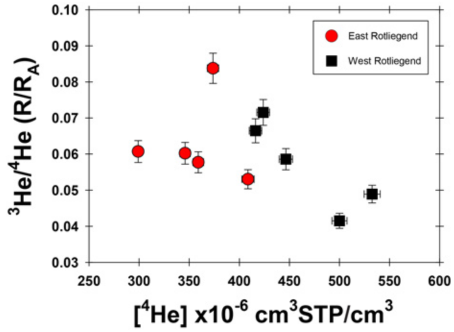

Figure 2. He isotopes ($^3He/^4He$) versus ^4He concentrations. STP—standard temperature and pressure conditions; R_A = air $^3He/^4He$.

generation kinetic model of Vandenbroucke et al. (1999). This modeling suggests that the Westphalian source rocks were locally buried to a depth where temperatures reached 195 °C ca. 150 Ma, and reached a maximum of ~230 °C between 50 and 10 Ma. Modeling of gas generation suggests that it was generated in two distinct pulses: one ca. 250–140 Ma that was interrupted by a period of uplift and erosion, and a second pulse following further burial, from ca. 80 Ma to present day (Fig. DR2 in the Data Repository). Hydrocarbon migration into the fields occurred along the flanks of the graben. The reservoir temperature was cooler (50–150 °C) during the first charge, and warmer (110–180 °C) for the second charge.

The Rotliegend graben is considered a classic closed system because gas is thought to have migrated and been trapped in the tight sandstones, with the Zechstein salt acting as an excellent seal to loss. The fact that this petroleum system is closed to loss was the primary motivation for targeting it for noble gas characterization. Estimates of in-place static gas/water volume ratios provide a critical reference for comparing noble gas model estimates of gas-water interaction. In Rotliegend, such geologic volumetric gas/water ratios were calculated by integrating information from multiple well logs (providing constraints on interval thicknesses, porosity, water saturation, and free water level) and depth maps for the main producing interval, the Wustrow reservoir (see the Data Repository). Using this approach a minimum geologic gas/water estimate of 0.11 is calculated for the entire graben and a maximum of 0.60 is calculated for only the Wustrow formation (Fig. 1).

NOBLE GAS PARTITIONING MODEL

By focusing on air-derived noble gases in crustal systems, diagnostic signatures can be exploited to determine mechanisms by which crustal fluids (i.e., oil and gas) form, migrate, and interact with one another (e.g., Bosch and Mazor, 1988; Ballentine et al., 1991, 1996; Zhou et al., 2005; Torgersen and Kennedy, 1999; Gilfillan et al., 2009; Jung et al., 2013; Barry et el., 2016). When hydrocarbons interact with air-saturated formation water, noble gases are systematically partitioned between phases. In a gas-water system, noble gases initially dissolved in the air-saturated water partially exsolve into the gas phase according to empirically derived partition coefficients (Henry's constants). This process is referred to as gas stripping of noble gases. With knowledge of the initial noble gas composition of the air-saturated water (determined by groundwater recharge conditions) and measured noble gas concentrations in the hydrocarbon phase, it is possible to calculate the extent of hydrocarbon-water interaction and therefore predict a volumetric gas/water (G/W) ratio (e.g., Barry et al., 2016).

Important input parameters for these models include groundwater recharge conditions and reservoir conditions, which are well constrained by discovery well pressure (650 bar), temperature (170 °C), and salinity (2 M NaCl). Groundwater recharge conditions control the initial inventory of noble gases in the system and are assumed to be modern 10 °C seawater. We assume that hydrocarbons are initially devoid of any atmospherically derived noble gases, and only acquire them during interaction with air-saturated water (Bosch and Mazor, 1988). Using these input parameters (i.e., known reservoir and recharge conditions) we find that ^{20}Ne and ^{36}Ar concentrations are best explained by a closed-system G/W model and small (0.025%–0.030% for East Rotliegend; 0.016%–0.020% for West Rotliegend) secondary air contributions (Fig. 3). Extremely low noble gas concentrations in crustal systems make these samples exceptionally sensitive to air additions. Due to the near constant amount required for each field contribution of the secondary air component in Rotliegend, we surmise that it is either intrinsic to the respective reservoirs (i.e., a drilling remnant) or introduced during sampling. Regardless of the source of the air component, the ^{20}Ne and ^{36}Ar concentrations in the Rotliegend gases can be explained by a narrow range of gas-water exchange (Fig. 3), resulting in convergence of noble gas–derived G/W estimates (0.22 ± 0.08) with the geologic G/W estimates (0.11–0.60). Noble gas G/W estimates overlap with the lower geologic G/W estimates, suggesting that hydrocarbon gases must have exchanged with water from the entire Rotliegend graben and not just in the current reservoir units (Wustrow and Dethlingen). Alternatively, gas could have encountered additional water during migration to the graben (thus decreasing the G/W estimate), and then only interacted with the more limited volume of water present in the Wustrow or Dethlingen.

RADIOGENIC AGE MODEL

An independent radiogenic groundwater age model provides supporting evidence that the Rotliegend methane field is, in fact, a closed system. Radiogenic noble gas nuclides (e.g., ^4He)

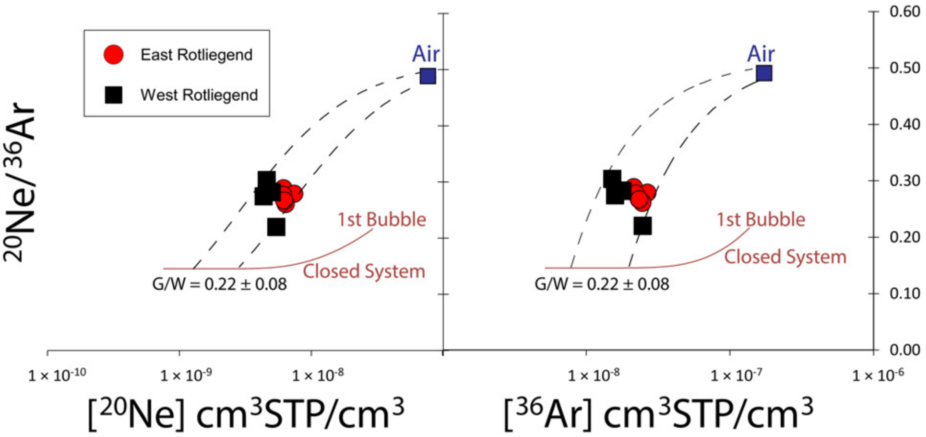

Figure 3. $^{20}Ne/^{36}Ar$ versus ^{20}Ne and ^{40}Ar concentrations are shown for East Rotliegend and West Rotliegend, Germany, relative to predicted closed-system modeling results (brown solid line) and the effect of secondary air addition (black dotted lines). East Rotliegend samples require 0.016%–0.020% air addition, whereas West Rotliegend samples require 0.025%–0.030% air addition. The extent of gas exchange, expressed as the gas/water ratio (G/W), encompasses a narrow range between 0.14 and 0.30 in the Rotliegend system. STP—standard temperature and pressure conditions.

are produced in crustal rocks by the radiogenic decay of parent nuclides (e.g., $^{238, 235}U$, ^{232}Th), and are subsequently transferred into the surrounding groundwater. Ingrowth is a function of parent nuclide abundance in the source mineral, efficiency of transfer, and reservoir conditions (e.g., temperature, thickness, and porosity). The concentration of ^4He within hydrocarbon reservoirs is controlled by the extent of hydrocarbon interaction with groundwater and the open or closed nature of the exchange. The consequence of long-term isolation in hydrocarbon related systems is readily apparent in radiogenic noble gas enrichments and can be used to extract temporal information about the system (e.g., Zhou and Ballentine, 2006). Helium (^4He) concentrations range from 299.1 to 408.6 × 10^{-6} cm^3 STP/cm^3 (STP—standard temperature and pressure conditions) in the East Rotliegend gas field and from 416.2 to 532.6 × 10^{-6} cm^3 STP/cm^3 in the West Rotliegend gas field (Fig. 2; Table 1). Helium isotope ratios show that Rotliegend gases are strongly radiogenic; East Rotliegend $^3He/^4He$ values range between 0.053 and 0.084 R_A, reported relative to the air value R_A = 1.4 × 10^{-6} (air = 1R_A; Clarke et al., 1976), whereas West Rotliegend samples vary from 0.042 to 0.072 R_A (Fig. 2).

The average measured concentration of radiogenic ^4He from East Rotliegend (357 × 10^{-6} cm^3 STP/cm^3) and West Rotliegend (464 × 10^{-6} cm^3 STP/cm^3) are used to estimate the initial concentration of ^4He in the groundwater (prior to gas stripping) as 2.18 × 10^{-2} cm^3 STP/cm^3 H_2O and 3.75 × 10^{-2} cm^3 STP/cm^3 H_2O for each field, respectively (see the Data Repository). This initial concentration represents the amount that is required to have originally been in the water that was subsequently stripped of its noble gases, to form the respective gas reservoirs in Rotliegend. This calculation assumes that ^4He is partitioned to the same extent as the atmospherically derived noble gases (e.g., ^{36}Ar). The estimated concentration in the initial water can then be combined with a predicted in situ accumulation rate within the water-saturated graben lithology. We calculate a ^4He accumulation rate of 2.6 × 10^{-10} cm^3 STP ^4He/cm^3 H_2O yr^{-1}, by combining the calculated crustal ^4He flux of 1.2 × 10^{-7} cm^3 STP ^4He/cm^2 yr^{-1} (see the Data Repository; Zhou and Ballentine, 2006) from the entire graben (thickness = 658 m), with a porosity of 9.5%, into a reservoir with an average thickness of 37.5 m. Identical graben and reservoir thickness values were used to calculate geologic G/W estimates. When this ^4He accumulation rate is combined with the initial concentration estimate of radiogenic ^4He in the formation water, it yields an average age for the aquifer water between 63 ± 20 and 73 ± 23 Ma for the East Rotliegend field and between 104 ± 33 and 129 ± 41 Ma for the West Rotliegend field. Errors on age estimates are a function of uncertainties on model assumptions (see the Data Repository). If the radiogenic inventory was acquired prior to hydrocarbon generation, then this estimate is consistent with rock and/or groundwater deposition ca. 300 Ma, followed by hydrocarbon generation from 250 to 140 Ma. It is important that this estimate does not require any input of deeper ^4He into this system and provides independent evidence for a closed system. The observation that $^4He/^{40}Ar^*$ ($^{40}Ar^*$ = air-corrected radiogenic Ar) values span a limited range (6.7–10.6) is consistent with more radiogenic and slightly older ages in the West Rotliegend field (mean $^4He/^{40}Ar^*$ = 9.8) compared with the East Rotliegend field (mean $^4He/^{40}Ar^*$ = 6.9), followed by uniform partitioning after radiogenic noble gases are acquired.

TABLE 1. NOBLE GAS COMPOSITIONAL AND GAS ISOTOPE SYSTEMATICS OF ROTLIEGEND (GERMANY) GASES

Sample	^4He × 10^{-6} cm^3 STP/cm^3	^{20}Ne × 10^{-9} cm^3 STP/cm^3	^{40}Ar × 10^{-6} cm^3 STP/cm^3	^{84}Kr × 10^{-12} cm^3 STP/cm^3	^{132}Xe × 10^{-12} cm^3 STP/cm^3	$^3He/^4He$ (R/R_A)	$^4He/^{40}Ar^*$	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	$^{40}Ar/^{36}Ar$	$^{86}Kr/^{84}Kr$	$^{132}Xe/^{130}Xe$
East Rotliegend												
W8	359.1 ± 5.4	6.18 ± 0.09	48.9 ± 0.7	402.4 ± 13	24.9 ± 0.4	0.058 ± 0.001	8.4 ± 0.2	9.26 ± 0.009	0.047 ± 0.0001	2281 ± 9.1	0.306 ± 0.001	6.587 ± 0.02
W7	408.6 ± 6.2	7.43 ± 0.11	61.3 ± 0.9	449.5 ± 6.7	72.4 ± 1.1	0.053 ± 0.001	7.7 ± 0.1	9.50 ± 0.010	0.049 ± 0.0001	2299 ± 9.2	0.305 ± 0.001	6.685 ± 0.02
W6	299.1 ± 4.4	6.13 ± 0.09	47.5 ± 0.7	343.1 ± 5.1	32.3 ± 0.5	0.061 ± 0.002	7.3 ± 0.2	9.68 ± 0.010	0.050 ± 0.0002	2143 ± 8.6	0.304 ± 0.001	6.688 ± 0.02
W10	373.8 ± 5.6	6.42 ± 0.10	52.0 ± 0.8	410.5 ± 6.2	35.8 ± 0.5	0.084 ± 0.002	8.4 ± 0.2	9.56 ± 0.010	0.049 ± 0.0001	2108 ± 8.4	0.304 ± 0.001	6.645 ± 0.02
W9	345.9 ± 5.2	6.23 ± 0.09	49.0 ± 0.7	540.5 ± 8.1	41.6 ± 0.6	0.060 ± 0.002	8.2 ± 0.2	9.70 ± 0.010	0.050 ± 0.0002	2097 ± 8.4	0.304 ± 0.001	6.650 ± 0.02
West Rotliegend												
W5	423.9 ± 6.4	4.37 ± 0.07	40.5 ± 0.6	321.4 ± 4.8	31.7 ± 0.5	0.072 ± 0.002	11.9 ± 0.2	9.54 ± 0.010	0.061 ± 0.0002	2542 ± 10	0.304 ± 0.001	6.637 ± 0.02
W3	416.2 ± 6.3	4.61 ± 0.07	39.4 ± 0.6	334.3 ± 5.0	34.4 ± 0.5	0.066 ± 0.002	11.9 ± 0.2	9.40 ± 0.009	0.059 ± 0.0002	2593 ± 10	0.306 ± 0.001	6.627 ± 0.02
W4	532.6 ± 8.0	5.44 ± 0.08	58.1 ± 0.9	391.1 ± 5.9	38.1 ± 0.6	0.049 ± 0.001	10.5 ± 0.2	9.58 ± 0.010	0.058 ± 0.0002	2348 ± 9.4	0.305 ± 0.001	6.649 ± 0.02
W2	446.5 ± 6.7	5.03 ± 0.08	48.1 ± 0.7	453.1 ± 6.8	43.7 ± 0.7	0.059 ± 0.001	10.5 ± 0.2	9.47 ± 0.009	0.061 ± 0.0002	2692 ± 11	0.303 ± 0.001	6.649 ± 0.02
W1	500.0 ± 7.5	4.85 ± 0.07	53.5 ± 0.8	398.7 ± 8.0	25.1 ± 0.4	0.042 ± 0.001	10.3 ± 0.2	9.59 ± 0.010	0.063 ± 0.0002	3114 ± 12	0.304 ± 0.001	6.640 ± 0.02

Note: STP—standard temperature and pressure conditions.

CONCLUSIONS

Noble gas compositions have been used to estimate G/W ratios in the Rotliegend gas field, Germany. Volumetric G/W ratios reveal information about connected water volumes and geologic compartmentalization, which are critical factors when considering the nature of aquifer support for hydrocarbon production and can also substantially influence the economic viability of an accumulation. Using traditional seismic methods, it is currently very difficult to determine whether a water leg has regional aquifer support, or is simply part of a local fluid system. Regional aquifer connectivity may provide pressure support for oils being produced from a reservoir, or may represent a risk to long-term production for gas-only systems. In contrast, only local aquifer support may result in pressure decline during production for oil, or decrease the risk of water breakthrough in gas-producing wells. Any approach that can discriminate between local and regional water connectivity through assessment of the connected water volume is therefore very desirable. In this study, we report convergence between static geologic G/W estimates (0.11–0.60) and light noble gas solubility model estimates (0.14–0.30), which, when coupled with radiogenic constraints, suggest that ancient fluid environments in the shallow crust were isolated 129 ± 41 m.y. to 63 ± 20 m.y. after rock and/or aquifer deposition (ca. 300 Ma) and have since remained isolated. When this result is considered in the context of known closed-system behavior of noble gases in paleo–crustal fluids and the recent findings of isolated fluids in basement rock older than 1 Ga (Lippmann-Pipke et al., 2011; Holland et al., 2013), it strongly suggests that pockets of crustal fluids can remain isolated on any known geologic time scale over significant length scales (greater than tens of kilometers). These finding have broad implications for CO_2 sequestration (Bachu, 2000; Kovscek, 2002; Haszeldine, 2009; Ehlig-Economides and Economides, 2010) and long-term nuclear waste disposal, both of which depend on the long-term isolation of multiphase fluids in crustal domains for their success.

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REFERENCES CITED

Aeschbach-Hertig, W., and Solomon, D.K., 2013, Noble gas thermometry in groundwater hydrology, *in* Burnard, P., ed., The noble gases as geochemical tracers: Berlin, Springer, p. 81–122, doi:10.1007/978-3-642-28836-4_5.

Aggarwal, P.K., et al., 2014, Continental degassing of ^{4}He by surficial discharge of deep groundwater: Nature Geoscience, v. 8, p. 35–39, doi:10.1038/ngeo2302.

Bachu, S., 2000, Sequestration of CO_2 in geological media: Criteria and approach for site selection in response to climate change: Energy Conversion and Management, v. 41, p. 953–970, doi:10.1016/S0196-8904(99)00149-1.

Ballentine, C.J., and Hall, C.M., 1999, Determining paleotemperature and other variables by using an error-weighted, nonlinear inversion of noble gas concentrations in water: Geochimica et Cosmochimica Acta, v. 63, p. 2315–2336, doi:10.1016/S0016-7037(99)00131-3.

Ballentine, C.J., O'Nions, R.K., Oxburgh, E.R., Horvath, F., and Deak, J., 1991, Rare gas constraints on hydrocarbon accumulation, crustal degassing and groundwater flow in the Pannonian Basin: Earth and Planetary Science Letters, v. 105, p. 229–246, doi:10.1016/0012-821X(91)90133-3.

Ballentine, C.J., O'Nions, R.K., and Coleman, M.L., 1996, A magnus opus: Helium, neon, and argon isotopes in a North Sea oilfield: Geochimica et Cosmochimica Acta, v. 60, p. 831–849, doi:10.1016/0016-7037(95)00439-4.

Ballentine, C.J., Burgess, R., and Marty, B., 2002, Tracing fluid origin, transport and interaction in the crust: Reviews in Mineralogy and Geochemistry, v. 47, p. 539–614, doi:10.2138/rmg.2002.47.13.

Barry, P.H., Lawson, M., Meurer, W.P., Warr, O., Mabry, J.C., Byrne, D.J., and Ballentine, C.J., 2016, Noble gases solubility models of hydrocarbon charge mechanisms in the Sleipner Vest methane field: Geochimica et Cosmochimica Acta, v. 194, p. 291–309, doi:10.1016/j.gca.2016.08.021.

Bosch, A., and Mazor, E., 1988, Natural gas association with water and oil as depicted by atmospheric noble gases: Case studies from the southeastern Mediterranean coastal plain: Earth and Planetary Science Letters, v. 87, p. 338–346, doi:10.1016/0012-821X(88)90021-0.

Byrne, D.J., Barry, P.H., Lawson, M., and Ballentine, C.J., 2017, A review of noble gases in conventional and unconventional systems, *in* Lawson, M., et al., eds., From source to seep: Geochemical applications in hydrocarbon systems: Geological Society of London Special Publication, (in press).

Clarke, W.B., Jenkins, W.J., and Top, Z., 1976, Determination of tritium by mass spectrometric measurement of ^{3}He: International Journal of Applied Radiation and Isotopes, v. 27, p. 515–522, doi:10.1016/0020-708X(76)90082-X.

Cornford, C., 1998, Source rocks and hydrocarbons of the North Sea, *in* Glennie, K.W., ed., Petroleum geology of the North Sea—Basic concepts and recent advances: London, Blackwell Scientific Publishers, p. 376–462, doi:10.1002/9781444313413.ch11.

Ehlig-Economides, C., and Economides, M.J., 2010, Sequestering carbon dioxide in a closed underground volume: Journal of Petroleum Science Engineering, v. 70, p. 123–130, doi:10.1016/j.petrol.2009.11.002.

Ehrl, E., and Schueler, S.K., 2000, Simulation of a tight gas reservoir with horizontal multifractured wells: Society of Petroleum Engineers European Petroleum Conference Paper SPE 21218-MS, doi:10.2118/65108-MS.

Gautier, D.L., 2003, Carboniferous-Rotliegend total petroleum system description and assessment results summary: U.S. Geological Survey Bulletin 2211, 29 p., http://pubs.usgs.gov/bul/b2211.

Gilfillan, S.M., et al., 2009, Solubility trapping in formation water as dominant CO_2 sink in natural gas fields: Nature, v. 458, p. 614–618, doi:10.1038/nature07852.

Glennie, K.W., 1970, Desert sedimentary environments: Developments in Sedimentology 14: Amsterdam, Elsevier, 222 p.

Glennie, K.W., 1972, Permian Rotliegendes of northwest Europe interpreted in light of modern desert sedimentation studies: American Association of Petroleum Geologists Bulletin, v. 56, p. 1048–1071.

Hantschel, T., and Kauerauf, A.I., 2009, Fundamentals of basin and petroleum systems modeling: Dordrecht, Springer Science & Business Media, 404 p.

Haszeldine, R.S., 2009, Carbon capture and storage: How green can black be?: Science, v. 325, p. 1647–1652, doi:10.1126/science.1172246.

Holland, G., and Gilfillan, S., 2013, Application of noble gases to the viability of CO_2 storage, *in* Burnard, P., ed., The noble gases as geochemical tracers: Berlin, Springer, p. 177–223, doi:10.1007/978-3-642-28836-4_8.

Holland, G., Lollar, B.S., Li, L., Lacrampe-Couloume, G., Slater, G.F., and Ballentine, C.J., 2013, Deep fracture fluids isolated in the crust since the Precambrian era: Nature, v. 497, p. 357–360, doi:10.1038/nature12127.

Jung, M., Wieser, M., von Oehsen, A., and Aeschbach-Hertig, W., 2013, Properties of the closed-system equilibration model for dissolved noble gases in groundwater: Chemical Geology, v. 339, p. 291–300, doi:10.1016/j.chemgeo.2012.08.006.

Kipfer, R., Aeschbach-Hertig, W., Peeters, F., and Stute, M., 2002, Noble gases in lakes and ground waters: Reviews in Mineralogy and Geochemistry, v. 47, p. 615–700, doi:10.2138/rmg.2002.47.14.

Kovscek, A.R., 2002, Screening criteria for CO_2 storage in oil reservoirs: Petroleum Science and Technology, v. 20, p. 841–866, doi:10.1081/LFT-120003717.

Lippmann-Pipke, J., Lollar, B.S., Niedermann, S., Stroncik, N.A., Naumann, R., van Heerden, E., and Onstott, T.C., 2011, Neon identifies two billion year old fluid component in Kaapvaal Craton: Chemical Geology, v. 283, p. 287–296, doi:10.1016/j.chemgeo.2011.01.028.

Prinzhofer, A., 2013, Noble gases in oil and gas accumulations, *in* Burnard, P., ed., The noble gases as geochemical tracers: Berlin, Springer, p. 225–247, doi:10.1007/978-3-642-28836-4_9.

Torgersen, T., 2010, Continental degassing flux of ^{4}He and its variability: Geochemistry, Geophysics, Geosystems, v. 11, Q06002, doi:10.1029/2009GC002930.

Torgersen, T., and Kennedy, B.M., 1999, Air-Xe enrichments in Elk Hills oil field gases: Role of water in migration and storage: Earth and Planetary Science Letters, v. 167, p. 239–253, doi:10.1016/S0012-821X(99)00021-7.

Vandenbroucke, M., Behar, F., and Rudkiewicz, J.L., 1999, Kinetic modelling of petroleum formation and cracking: Implications from the high pressure/high temperature Elgin Field (UK, North Sea): Organic Geochemistry, v. 30, p. 1105–1125, doi:10.1016/S0146-6380(99)00089-3.

Zhou, Z., and Ballentine, C.J., 2006, ^{4}He dating of groundwater associated with hydrocarbon reservoirs: Chemical Geology, v. 226, p. 309–327, doi:10.1016/j.chemgeo.2005.09.030.

Zhou, Z., Ballentine, C.J., Kipfer, R., Schoell, M., and Thibodeaux, S., 2005, Noble gas tracing of groundwater/coalbed methane interaction in the San Juan Basin, USA: Geochimica et Cosmochimica Acta, v. 69, p. 5413–5428, doi:10.1016/j.gca.2005.06.027.

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