

Insights into deep carbon derived from noble gases

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Science and society are faced with two challenges that are inextricably linked: fossil-fuel energy dependence and rising levels of atmospheric carbon dioxide. Management of remaining hydrocarbon resources, the search for cleaner fuels and increasing interest in subsurface carbon storage all require a better understanding of the deep terrestrial carbon cycle. The coupling of noble gas and carbon chemistry provides an innovative approach to understanding this deep carbon. Whereas carbon geochemistry and isotopic signatures record the history of inorganic and organic reactions that control carbon mobility, the inert noble gases provide unique tracers of fluid origin, transport and age. Together, they have been used to show that groundwater has a key role as both the sink for geologically sequestered carbon dioxide, and in the transport and emplacement of hydrocarbon gas deposits. Furthermore, these tracers have also been used to show that groundwater and subsurface microbiology jointly influence the formation and alteration of fossil-fuel deposits to an extent not previously recognized. The age and distribution of groundwater in fractures in the Earth's crust exert important controls on the Earth's deepest microbial communities.

To understand the deep carbon cycle, we need to develop quantitative estimates of the key physical, chemical and biological controls on carbon mobility. The aim of this Progress Article is to show how the coupling of carbon geochemistry and stable isotopes with noble gas tracers (Box 1) can achieve this for two significant components of the deep carbon cycle: gas–oil–water interactions and subsurface microbiology. Specifically, we discuss the insights that noble gases have provided into the fate of geologically sequestered carbon dioxide, the formation and alteration of hydrocarbon gas deposits, and the timescale and mechanism of carbon cycling in the Earth's deepest microbial communities.

Carbon storage, hydrocarbon reserves and groundwater

Steadily increasing CO₂ emissions are one of society's most pressing concerns, but our addiction to a high-carbon economy cannot be broken overnight. Burial of anthropogenic CO₂ in geological structures may give us some time while we make the transition to low-carbon technologies.

Carbon dioxide is a reactive and soluble gas. Predicting its subsurface behaviour on a decadal timescale can be achieved through careful combination of laboratory and field experiments. However, understanding the fate of injected CO₂ on millennial timescales — which is necessary to ensure reservoir competence and safety — is less straightforward. The key unknown is the CO₂ residence time and mobility once injected. Addressing this issue requires an understanding of how much of the CO₂ reacts with the rock to form immobile carbonate minerals, how much remains in a near pure but buoyant gas phase, and how much dissolves into the groundwater filling the rock pore space, to form a phase less buoyant than water alone. A major breakthrough in addressing these questions has been achieved through the study of naturally occurring CO₂ gas fields^{1,2}.

The elemental and isotopic make-up of noble gases provides insight into the source of CO₂ in continental settings. ³He/⁴He ratios can be used to identify magmatic fluid contributions to subsurface systems in continental settings^{3–5} (Box 1, Fig. 1). Similarly, magmatic CO₂/³He ratios fall in a very tight range compared with many crustal fluids^{6–10}, hence this characteristic 'fingerprint' can be used to identify mantle-derived CO₂ from other CO₂ sources, such

as carbonate minerals in the crust. Measurements of ³He/⁴He and CO₂/³He suggest that a series of natural CO₂ gas deposits related to the Colorado uplift were dominated by magmatic CO₂ input¹. Radiometric ages of the latest surface volcanic activity local to each field indicate that these geological reservoirs have preserved CO₂ for tens of thousands to tens of millions of years¹.

Recently, noble gases have also been used to monitor the fate of geologically sequestered CO₂. CO₂/³He ratios in CO₂-rich gas fields in Colorado, and others in Europe and China (nine in total), show a systematic decrease in CO₂/³He with increasing ²⁰Ne and ⁴He (ref. 2). These low-solubility noble gases are derived from, in the case of ²⁰Ne, equilibration of groundwater with the atmosphere and, in the case of ⁴He, from products of natural radioactive reactions in the crust accumulating in groundwater (Box 1, Fig. 1). The ubiquitous correlation of declining CO₂/³He ratios with increasing ²⁰Ne and ⁴He indicates that the removal of CO₂ is directly related to the volume of groundwater in contact with the gas field.

For each field, changes in CO₂/³He provide a measure of the amount of CO₂ lost; with some fields showing portions of the system where over 90% of the CO₂ has been removed from the gas field (Fig. 2). Most importantly, in the same gas fields, stable carbon isotopes can distinguish between CO₂ lost through simple dissolution into the groundwater and CO₂ lost through precipitation as carbonates (Fig. 2). All gas fields studied show that CO₂ dissolution into groundwater is the main CO₂ sink. Although a small amount of CO₂ precipitation as carbonates (up to 18% in one sample) cannot be ruled out in geological reservoirs dominated by sandstone (Fig. 2a), carbonate-dominated reservoirs (Fig. 2b) show no evidence of precipitation whatsoever. These natural analogues for carbon capture and storage tell us convincingly that dissolution of CO₂ gas into the groundwater provides the only significant CO₂ sink over millennial timescales².

Groundwater–gas interaction in hydrocarbon-rich reservoirs is as important as in CO₂-rich reservoirs. Groundwater flow can transport hydrocarbons to a trapping structure^{11,12}, generate pore space through dissolution or reduce pore space through precipitation, or reduce the quality of hydrocarbon reservoirs by removing some of the more soluble hydrocarbon compounds. There is therefore keen interest in quantifying the extent of this exchange.

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Box 1 | A noble gas overview.

The isotopic and elemental make-up of noble gases from the atmosphere, crust or magmatic gases originating from the Earth's mantle each have a distinct isotopic and elemental 'fingerprint'. The very low concentration of noble gases in most crustal fluids means that small radiogenic noble gas isotope by-products from natural radioactivity (^4He , ^{21}Ne , ^{40}Ar ; Fig. 1) can be readily measured and used to provide fluid-source and residence-time information^{15,23,42,43}. In contrast, ^3He only occurs in significant quantities within the Earth's mantle and is used as an unambiguous tracer of mantle-fluid involvement in deep fluid systems^{3,5,8}. ^3He is most notably linked to volcanic carbon dioxide and has long been used to quantify volatile fluxes at mid-ocean ridges, arcs, subduction zones and related systems^{8,10}, and more recently to identify magmatic carbon dioxide in continental settings^{6,7,9}. In the subsurface, water occupying rock pore-space (groundwater) has often equilibrated with the atmosphere. The atmospheric-derived noble gases (^{20}Ne , ^{36}Ar , ^{84}Kr ; Fig. 1) in groundwaters then preserve a record of the physical conditions (such as surface temperature) when that equilibration last occurred. This property provides an important palaeotemperature record with an accuracy under ideal conditions to $\pm 0.5^\circ\text{C}$ (refs 44–48). Oil or natural gas phases that contact the pore water result in transfer of the noble gases between phases, with distinct fractionation patterns that can then be used to quantify the role of groundwater in these systems^{2,12–15,18,41}.

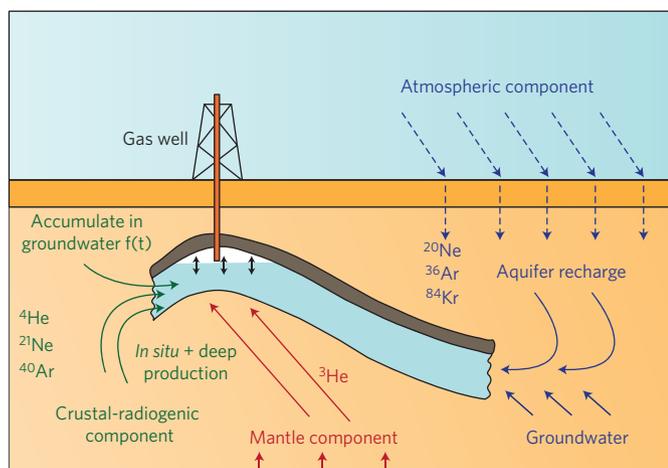


Figure 1 | Schematic showing that noble gases in any subsurface fluid are derived from three sources: the atmosphere, crust and mantle (see Box 1). Each of the noble gas sources has a unique isotopic composition and elemental abundance pattern. Hence noble gas tracers allow quantification of the contribution of differently sourced fluids, independent of subsequent chemical or biological reactions. Changes in noble gas elemental ratios can also be used to calculate their partitioning into various gas and/or liquid phases (oil, water) by degassing or dissolution, respectively. Finally, crustal-radiogenic noble gas accumulation in groundwater occurs as a function of time, $f(t)$, and can provide estimates of residence times (relative ages) based on nucleogenic production reactions that produce noble gases such as ^4He , ^{21}Ne , and ^{40}Ar by decay of U, Th and K (refs 15,23,42,43). Figure after ref. 41.

Noble gas abundance ratios in the hydrocarbon phase — which are controlled by their relative solubilities in the different phases and the groundwater/hydrocarbon volume ratio^{12–15} — can be used to quantify the volume of groundwater in contact with the hydrocarbon gases. This approach permits distinction between gas fields

that have undergone dissolution into, and transport in, groundwater before exsolution into the gas phase, from those that have had little contact with subsurface water^{12,15–18}. The $\text{CH}_4/^{36}\text{Ar}$ ratios can further quantify the temperature and pressure conditions under which the gas exsolved from groundwater¹².

Noble gases can also be used to calculate the volume of water in contact with oil reservoirs. This approach has been used to quantify the role of water in removing pore space in oil reservoir systems^{16,17}, and to gauge changes in oil quality caused by 'water washing' along oil-migration pathways¹⁸.

Before the realization that noble gases could be used to calculate the volume of water in contact with gas and oil reservoirs, the importance of water in controlling these commercially sensitive variables, essential for exploration and reservoir development, could only be guessed at.

Natural gas formation by biodegradation

As society explores the possibility of moving away from coal and oil to cleaner methane and natural gas, the processes controlling natural gas formation by biodegradation are attracting increasing attention. Biodegradation was once thought to be an important process only in shallower aerobic environments, but it has become clear that biodegradation of crude-oil and coal reserves under deeper, anaerobic conditions also generates these increasingly sought-after products^{19,20}. The factors controlling methane and natural gas formation — in particular the nature of the subsurface microbial community and the rates of biodegradation — are undergoing significant re-evaluation. Interactions between groundwater and petroleum/coal are at the centre of the investigations^{19–22}.

Coupling of carbon geochemistry with noble gas tracers provides one of the most promising tools to quantify the extent and timing of subsurface natural gas formation by biodegradation. This approach has been used to pin down the source of methane in one of the largest coal-bed methane reservoirs in the world — in the San Juan basin, New Mexico, USA²² — which accounted for 15.5 billion m^3 of gas in 1992 (ref. 21).

Highly fractured coal-beds in the northern portion of the San Juan basin form a regional aquifer, where commercial volumes of methane are produced from coal biodegradation. Figure 3a shows the covariation of groundwater (atmospheric-derived) noble gases ($^{20}\text{Ne}/^{36}\text{Ar}$) and radiogenic noble gases ($^4\text{He}/^{40}\text{Ar}$) — a correlation also seen in N_2 -rich¹⁵ and CO_2 -rich systems around the world¹². This covariation results from mixing of the differently sourced noble gas components in groundwater before the gases exsolve from solution to create the natural gas phase¹², and is used to create a model that quantifies the relationship between the water, the gases dissolved in the water and biodegraded coal gas (Fig. 3b). Independent verification of this model is provided by the Xe system. The atmospheric-derived $^{136}\text{Xe}/^{36}\text{Ar}$ variation exceeds that predicted by simple groundwater degassing, owing to further release of sedimentary Xe from the coal as it biodegrades¹⁸ (Fig. 3c). The model predicts a relationship between the excess ^{136}Xe ($^{136}\text{Xe}/^{36}\text{Ar}$ ratios) and the relative contribution of groundwater-derived gas to coal-derived gas in the final gas produced (or dilution ratio) — a relationship that is precisely what is observed in the San Juan gas field (Fig. 3d).

Once verified, the model allows the pre-degassing ^4He content of the groundwater to be calculated with confidence. The ^4He age of the groundwater²³ can then be calculated and used to determine the timing of microbial activity. In the case of the San Juan basin, noble gas models place a limit of just tens of thousands of years on the generation of this globally important hydrocarbon reservoir²¹.

Follow the water

An increased recognition of the role of subsurface microbes in the production and alteration of oil and gas deposits has sparked heated debate about the volume and extent of life in the deep subsurface.

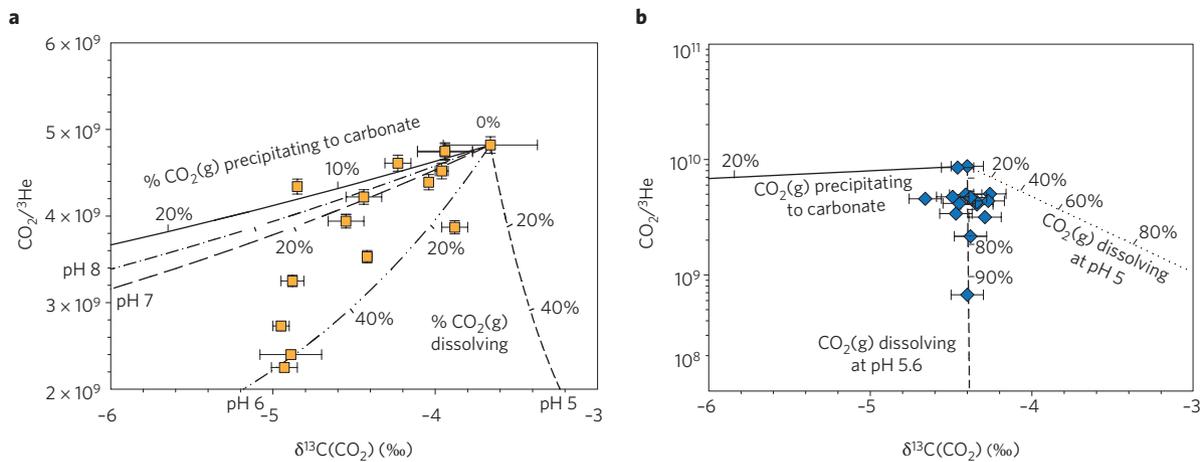


Figure 2 | Combined noble gas and stable isotopes distinguish between and quantify different mechanisms of CO₂ removal from natural CO₂ gas deposits. $\delta^{13}\text{C}(\text{CO}_2)$, the stable carbon isotope value of the residual CO₂ phase, is changed, or ‘fractionated’, by different amounts depending on the loss mechanism. Specifically, CO₂ precipitating as carbonate minerals has a distinct fractionation from CO₂ dissolving to form either aqueous H₂CO₃ or HCO₃⁻. By comparing field data with these well-characterized fractionation models, it was determined that in all gas fields investigated, the major CO₂ sink was dissolution into groundwater at a pH between 5.0 and 5.8 — a pH range at which aqueous H₂CO₃ is the dominant form of dissolved CO₂. **a**, Data from the gas field Bravo Dome, New Mexico, is the most complex system and reflects up to 18% CO₂ loss by carbonate precipitation. **b**, McElmo Dome, Colorado, shows the distinct pattern observed in the majority of the gas fields indicating that the dominant CO₂ sink in natural systems is dissolution into groundwater. Error bars represent analytical uncertainty on the measured data points². Figure after ref. 2.

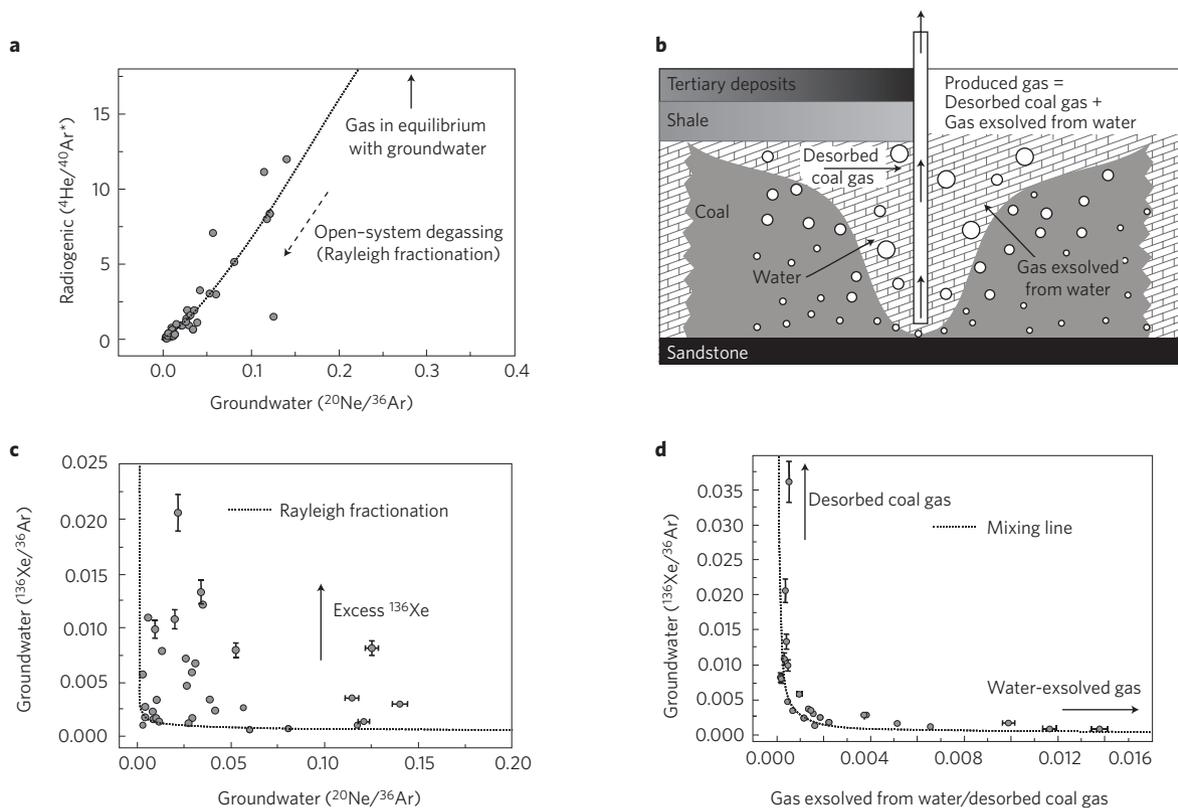


Figure 3 | Principles used to quantify methane generation through microbial biodegradation of coal by integrating noble gas tracers. **a**, Covariation in radiogenic ($^4\text{He}/^{40}\text{Ar}^*$) (where $^{40}\text{Ar}^*$ is corrected for atmospheric ^{40}Ar contribution) and groundwater (atmospheric-derived $^{20}\text{Ne}/^{36}\text{Ar}$) ratios in the San Juan basin coal gases (see text) can be modelled by open-system degassing of groundwater. The model allows the water/gas volume ratio to be calculated and the original groundwater noble gas composition to be reconstructed. **b**, To account for low ^{20}Ne concentrations in the produced gas (not shown), the gases exsolved from groundwater must be diluted by the methane produced by microbial biodegradation and desorption from coal. **c**, Independent evidence of this dilution is provided by atmospheric-derived abundance ratios that show an excess of ^{136}Xe relative to that predicted by the degassing model. **d**, The ^{136}Xe relative to ^{36}Ar fits a simple mixing model between gases exsolving from groundwater, and gas produced by biodegradation and desorption from coal. The excess ^{136}Xe is trapped sedimentary Xe that is released in amounts proportional to the volume of coal that has been biodegraded¹⁸. Error bars represent analytical uncertainty on the measured data points²². Figure after ref. 22.

Biodegraded petroleum is not typically found at depths in the crust that have exceeded temperatures of 80–90 °C, leading some to suggest that this represents the effective limit of heterotrophic subsurface life^{19,24}. However, microorganisms that use chemical substrates produced by water–rock reactions have been found at hydrothermal vents along mid-ocean ridges^{25,26} and off-axis spreading centres²⁷, at continental sites of geothermal activity^{28,29}, and at depths of >2–3 km in fracture waters in Archean rock^{30,31}, indicating that the limits to chemoautotrophic life have yet to be determined.

Key uncertainties include the identity of the carbon sources sustaining the deep biosphere, the rates and mechanisms of carbon cycling far from the photosphere, and hence the scale and significance of this remote and exotic reservoir of the global biogeochemical cycle. Even though carbon geochemistry and stable isotopes, as well as molecular microbiology, have facilitated major advances in identifying the geochemical and microbiological processes involved, coupling these techniques with noble gases once again has a critical role in efforts to constrain the timescales and carbon sources for the deep carbon cycle.

Discovery of chemosynthetic microbial communities at mid-ocean ridges, by the submersible Alvin, launched the exploration of the 'deep hot biosphere'²⁵. In the decades that followed however, awareness increased that chemosynthetic communities are not restricted to high-temperature hydrothermal settings^{26–29}. The terrestrial subsurface also hosts chemoautotrophic ecosystems sustained by the products of water–rock reactions — albeit at lower temperatures and slower rates of reaction^{30–32}. The deep terrestrial biosphere in the tectonically quiescent Precambrian Shields of Canada, Fennoscandia and South Africa^{32,33} is dominated by radiogenic noble gases and crustal-derived carbon sources. The radiogenic noble gases were used to calculate estimates of groundwater residence times³³ (see Box 1). The tracers demonstrate that different generations of fracture waters exist with distinctly different geochemical timescales, microbial communities and biogeochemical carbon cycles³⁴.

Long residence times on the order of 10–25 million years (Myr) were found for the deepest high-salinity fracture waters^{31,33}. Correlations of increasing salinity with highly altered hydrogen and oxygen isotope signatures for the waters, together with increasing concentrations of radiogenic noble gases, suggest that fracture waters were subject to extensive water–rock reactions over geological time, and have been hydrogeologically isolated³⁴. Although these fracture waters contain large concentrations of methane and higher hydrocarbon gases, carbon and hydrogen isotope data indicate these too are the result of local geochemical reactions and are not primarily the products of microbial activity^{31,34}. The ultimate carbon source in these fracture waters has yet to be identified^{31,34,35}. Environmental genomics studies of one such 15–25-Myr fracture-water system revealed a microbial ecosystem of extremely low biodiversity dominated by a SO₄-reducing chemoautotrophic thermophile using hydrogen produced by radiolysis to eke out an existence at maintenance levels 2.8 km below the surface^{31,35}.

In contrast to this spartan ecosystem, shallower fracture waters with residence times derived from noble gases of <1 Myr to a few Myr, and with hydrogen and oxygen isotope values that reflect a palaeometeoric water origin, have a carbon cycle dominated by the imprint of life. Fracture waters in mines to depths of 0.5 km in Sweden^{36,37} and to 1.4 km in South Africa^{38,39} have heterogeneous microbial populations. Geochemical and stable isotope data indicate significant populations of rapidly metabolizing SO₄-reducing and methanogenic bacteria. Carbon isotope values and geochemical signatures indicate that methane is produced by microbial reduction of CO₂ (refs 36 and 40). Rates of microbial methanogenesis — derived from carbon geochemistry, stable isotopes and ⁴He measurements — are fast, at around 100 nM yr⁻¹, compared with those in the high-salinity fracture waters described

above (where rates do not exceed 0.01 nM yr⁻¹)³⁹. The coupling of noble gas tracers with carbon geochemistry again provided the key to recognizing that hydrogeologically isolated fracture networks of geochemically distinct groundwaters exert a major control on the distribution and nature of microbial life and metabolic function in the deep surface.

Coupled constraints on deep carbon

Past decades have seen exciting advances in our understanding of deep carbon. We have rapidly expanded our view of the extent of the planet that is habitable. Future research will focus on defining just how deep life extends beneath Earth's surface, and identifying the underlying controls on microbial metabolic activity and biodiversity. The answers to these questions may provide insight on the evolutionary relationship of deep terrestrial microbial communities to marine sediment-hosted and vent-hosted communities, on the origin of life on Earth, and on the potential for life on other planets and moons. As society struggles with the pressing challenges of hydrocarbon resource management and climate change, future research will need to continue to explore the coupled role of subsurface microbes and groundwater in the production and alteration of oil and gas deposits, in the transport and location of hydrocarbon fuel reservoirs, and the potential to mitigate rising atmospheric carbon dioxide levels by subsurface capture and storage. Coupling of noble gas tracers with carbon geochemistry and stable isotopes can help drive these advances forward. The knowledge generated is essential not only for understanding the evolution of the deep carbon cycle over Earth's history, but also for confronting the anthropogenic perturbations of the carbon cycle that challenge the future.

References

- Gilfillan, S. M. *et al.* The noble gas geochemistry of natural CO₂ gas reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA. *Geochim. Cosmochim. Acta* **72**, 1174–1198 (2008).
- Gilfillan, S. M. *et al.* Solubility trapping in formation water as dominant CO₂ sink in natural gas fields. *Nature* **458**, 614–618 (2009).
- Oxburgh, E. R., O'Nions, R. K. & Hill, R. I. Helium isotopes in sedimentary basins. *Nature* **324**, 632–635 (1986).
- Marty, B., O'Nions, R. K., Oxburgh, E. R., Martel, D. & Lombardi, S. Helium isotopes in alpine regions. *Tectonophysics* **206**, 71–78 (1992).
- Kennedy, B. M. & van Soest, M. C. Flow of mantle fluids through the ductile lower crust: Helium isotope trends. *Science* **318**, 1433–1436 (2007).
- Griesshaber, E., O'Nions, R. K. & Oxburgh, E. R. Helium and carbon isotope systematics in crustal fluids from the Eifel, the Rhine Graben and Black Forest, F. R. G. *Chem. Geol.* **99**, 213–235 (1992).
- Sherwood Lollar, B., Ballentine, C. J. & O'Nions, R. K. The fate of mantle-derived carbon in a continental sedimentary basin: Integration of C/He relationships and stable isotope signatures. *Geochim. Cosmochim. Acta* **61**, 2295–2307 (1997).
- Marty, B. & Tolstikhin, I. N. CO₂ fluxes from mid-ocean ridges, arcs and plumes. *Chem. Geol.* **145**, 233–248 (1998).
- Ballentine, C. J., Schoell, M., Coleman, D. & Cain, B. A. 300-Myr-old magmatic CO₂ in natural gas reservoirs of the west Texas Permian Basin. *Nature* **409**, 327–331 (2001).
- de Leeuw, G. A. M., Hilton, D. R., Fischer, T. P. & Walker, J. A. The He-CO₂ isotope and relative abundance characteristics of geothermal fluids in El Salvador and Honduras: New constraints on volatile mass balance of the Central American Volcanic Arc. *Earth Planet. Sci. Lett.* **258**, 132–146 (2007).
- Toth, J. Cross formational gravity-flow of groundwater: a mechanism of transport and accumulation of petroleum. *AAPG Stud. Geol.* **10**, 121–167 (1980).
- Ballentine, C. J., O'Nions, R. K., Oxburgh, E. R., Horvath, F. & Deak, J. Rare gas constraints on hydrocarbon accumulation, crustal degassing and groundwater flow in the Pannonian Basin. *Earth Planet. Sci. Lett.* **105**, 229–246 (1991).
- Zartman, R. E., Reynolds, J. H. & Wasserburg, G. J. Helium, argon, and carbon in some natural gases. *J. Geophys. Res.* **66**, 277–306 (1961).
- Bosch, A. & Mazar, E. Natural gas association with water and oil as depicted by atmospheric noble gases: case studies from the southeastern Mediterranean Coastal Plain. *Earth Planet. Sci. Lett.* **87**, 338–346 (1988).
- Ballentine, C. J. & Sherwood Lollar, B. Regional groundwater focusing of nitrogen and noble gases into the Hugoton-Panhandle giant gas field, USA. *Geochim. Cosmochim. Acta* **66**, 2483–2497 (2002).
- Pinti, D. L. & Marty, B. Noble gases in crude oils from the Paris basin, France — Implications for the origin of fluids and constraints on oil-water-gas interactions. *Geochim. Cosmochim. Acta* **59**, 3389–3404 (1995).

17. Ballentine, C. J., O'Nions, R. K. & Coleman, M. L. A Magnus opus: Helium, neon, and argon isotopes in a North Sea oilfield. *Geochim. Cosmochim. Acta* **60**, 831–849 (1996).
18. Torgersen, T. & Kennedy, B. M. Air-Xe enrichments in Elk Hills oil field gases: Role of water in migration and storage. *Earth Planet. Sci. Lett.* **167**, 239–253 (1999).
19. Head, I. M., Jones, D. M. & Larter, A. R. Biological activity in the deep subsurface and the origin of heavy oil. *Nature* **426**, 344–352 (2003).
20. Jones, D. M. *et al.* Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature* **451**, 176–181 (2008).
21. Zhou, Z. & Ballentine, C. J. He-4 dating of groundwater associated with hydrocarbon reservoirs. *Chem. Geol.* **226**, 309–327 (2006).
22. Zhou, Z., Ballentine, C. J., Kipfer, R., Schoell, M. & Thibodeaux, S. Noble gas tracing of groundwater/coalbed methane interaction in the San Juan Basin, USA. *Geochim. Cosmochim. Acta* **69**, 5413–5428 (2005).
23. Torgersen, T. & Clarke, W. B. Helium accumulation in groundwater I. An evaluation of sources and the continental flux of crustal ⁴He in the Great Artesian Basin, Australia. *Geochim. Cosmochim. Acta* **49**, 1211–1218 (1985).
24. Wilhelm, A. *et al.* Biodegradation of oil in uplifted basins prevented by deep-burial sterilization. *Nature* **411**, 1034–1037 (2001).
25. Jannasch, H. W. The chemosynthetic support of life and the microbial diversity at deep-sea hydrothermal vents. *Proc. R. Soc. Lond. B* **225**, 277–297 (1985).
26. Shock, E. L. & Schulte, M. D. Organic synthesis during fluid mixing in hydrothermal systems. *J. Geophys. Res.* **103**, 28513–28527 (1998).
27. Kelley, D. S. *et al.* A serpentinite-hosted ecosystem: The lost city hydrothermal field. *Science* **307**, 1428–1434 (2005).
28. Chapelle, F. H. *et al.* A hydrogen-based subsurface microbial community dominated by methanogens. *Nature* **415**, 312–315 (2002).
29. Spear, J. R., Walker, J. L., McCollom, T. M. & Pace, N. R. Hydrogen and bioenergetics in the Yellowstone geothermal ecosystem. *Proc. Natl Acad. Sci. USA* **102**, 2555–2560 (2005).
30. Pedersen, K. Exploration of deep intraterrestrial microbial life: Current perspectives. *FEMS Microbiol. Lett.* **185**, 9–16 (2000).
31. Lin, L.-H. *et al.* Long-term sustainability of a high-energy, low-diversity crustal biome. *Science* **314**, 479–482 (2006).
32. Sherwood Lollar, B. *et al.* Evidence for bacterially generated hydrocarbon gas in Canadian Shield and Fennoscandian Shield rocks. *Geochim. Cosmochim. Acta* **57**, 5073–5085 (1993).
33. Lippmann, J. *et al.* Dating ultra-deep mine waters with noble gases and ³⁶Cl, Witwatersrand Basin, South Africa. *Geochim. Cosmochim. Acta* **67**, 4597–4619 (2003).
34. Sherwood Lollar, B. *et al.* Isotopic signatures of CH₄ and higher hydrocarbon gases from Precambrian Shield sites: A model for abiogenic polymerization of hydrocarbons. *Geochim. Cosmochim. Acta* **72**, 4778–4795 (2008).
35. Chivian, D. *et al.* Environmental genomics reveals a single-species ecosystem deep within Earth. *Science* **322**, 275–278 (2008).
36. Pedersen, K. & Ekendahl, S. Incorporation of CO₂ and introduced organic compounds by bacterial populations in groundwater from the deep crystalline bedrock of the Stripa mine. *J. Gen. Microbiol.* **138**, 369–376 (1992).
37. Pedersen, K. Microbial life in deep granitic rock. *FEMS Microbiol. Rev.* **20**, 399–414 (1997).
38. Lin, L. H. *et al.* Planktonic microbial communities associated with fracture-derived groundwater in a deep gold mine of South Africa. *Geomicrobiol. J.* **23**, 475–497 (2006).
39. Onstott, T. C. *et al.* The origin and age of biogeochemical trends in deep fracture water of the Witwatersrand Basin, South Africa. *Geomicrobiol. J.* **23**, 369–414 (2006).
40. Ward, J. A. *et al.* Microbial hydrocarbon gases in the Witwatersrand Basin, South Africa: Implications for the deep biosphere. *Geochim. Cosmochim. Acta* **68**, 3239–3250 (2004).
41. Ballentine, C. J., Burgess, R. & Marty, B. Tracing fluid origin, transport and interaction in the crust. *Rev. Mineral. Geochem.* **47**, 539–614 (2002).
42. Andrews, J. N. The isotopic composition of radiogenic helium and its use to study groundwater movement in confined aquifers. *Chem. Geol.* **49**, 339–351 (1985).
43. Kipfer, R., Aeschbach-Hertig, W., Peeters, F. & Stute, M. Noble gases in lakes and ground waters. *Rev. Mineral. Geochem.* **47**, 615–700 (2002).
44. Andrews, J. N. & Lee, D. J. Inert gases in groundwater from the Bunter Sandstone of England as indicators of age and paleoclimatic trends. *J. Hydrol.* **41**, 233–252 (1979).
45. Heaton, T. H. E. & Vogel, J. C. 'Excess air' in groundwater. *J. Hydrol.* **50**, 201–216 (1981).
46. Stute, M., Schlosser, P., Clark, J. F. & Broecker, W. S. Paleotemperatures in the southwestern United States derived from noble gases in ground water. *Science* **256**, 1000–1003 (1992).
47. Ballentine, C. J. & Hall, C. M. Determining paleotemperature and other variables by using an error-weighted, nonlinear inversion of noble gas concentrations in water. *Geochim. Cosmochim. Acta* **63**, 2315–2336 (1999).
48. Aeschbach-Hertig, W., Peeters, F., Beyerle, U. & Kipfer, R. Interpretation of dissolved atmospheric noble gases in natural waters. *Wat. Resour. Res.* **35**, 2779–2792 (1999).

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Author contributions

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