Articles

Exploring for hydrogen, helium and lithium: is it as easy as 1, 2, 3?

Jon G. Gluyas,[1,2]* Madeleine Humphreys,[2] Rūta Karolytė,[3] Anran Cheng,[3] Barbara Sherwood Lollar[4,5] and Chris Ballentine[6]

[1]Durham Energy Institute, Durham University, Durham DH1 3LE, UK
[2]Department of Earth Sciences, Durham University, Durham DH1 3LE, UK
[3]Snowfox Discovery Ltd, 46 Woodstock Road, Oxford, UK, OX2 6HT
[4]Department of Earth Sciences, University of Toronto, Toronto M5S 3B1, Ontario, Canada
[5]Institute de Physique du Globe, Université Paris Cité, Paris, France
[6]Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, UK
JGG, 0000-0002-9386-7206

*Correspondence: j.g.gluyas@durham.ac.uk

Abstract: Hydrogen, helium and lithium, elements one two and three of the periodic table, are in demand to enable and enhance low-carbon energy technologies. Anthropogenic hydrogen is manufactured from water via methane reforming or from electrolysis. Both are costly and have environmental impacts. Helium is commonly found in low concentrations in association with petroleum gases. Lithium is mined by brine pumping or from igneous rocks, with consequential serious environmental impacts.

Were it possible to economically find hydrogen in its molecular state, then surely such hydrogen would dominate the market. Similarly, helium generated without associated greenhouse gases would also be a market stimulant for a helium industry. What if hydrogen and helium could be co-produced from a single composite discovery? And what if the water leg to such hydrogen and helium deposits were rich in lithium? It, too, would be produced with costs for all elements shared.

Helium is a natural product of crystalline rocks including granite and its generation can liberate hydrogen from interstitial water. These same rocks can be rich sources of lithium and may also deliver geothermal resources. The energy transition may therefore shift what we consider to be important for energy geoscience. The basement may become as important as the basin.

Hydrogen, helium and lithium demand

In 2003, global hydrogen production was around 45 million tonnes (Midilli *et al.* 2005). This figure is, however, only that communicated by merchant sources and represents only about 3% of the total hydrogen market, the remaining 97% is captive internal production and consumption (Midilli *et al.* 2005). Hydrogen has a myriad of uses as a chemical feedstock in the petrochemical industry, food, microelectronics, in the ferrous and non-ferrous metal industries, polymer synthesis and as an energy carrier in low/zero carbon sustainable energy systems. By 2020, demand had approximately doubled to 82 million tonnes (IEA 2021) and with a 3% year-on-year growth over the past few years (IEA 2023*a*). In a 'net zero emissions by 2050' scenario, annual demand is expected to be around 150 million tonnes by 2030 (IEA 2023*a*). The cost of hydrogen depends on the way in which it is manufactured. Today almost all hydrogen is manufactured using methane reformation, so-called grey hydrogen, priced at \$US1–2 kg^{-1}, giving a global market in the range of \$US82–164 billion (KPMG undated).

Between 1996 and 2003, annual global helium production fluctuated between 100 and 140 million cubic metres (17 800–24 920 t), rising to between 155 and 184 million cubic metres (26 700–32 800 t) from around 2010 to today (USGS 2024) (except for a low production return during peak Covid in 2020). Until 1995, the USA had a near monopoly on production (>90%). Today US production accounts for almost half of the global production, with Qatar approaching 40% and most of the rest coming from Algeria (USGS 2024). Australia (now ceased), Canada, Poland, South Africa, China and Russia have minor production, though both Russia and China serve only their bilateral and internal markets (Fig. 1). MRI scanners (22%) and controlled atmospheres (22%) for semi-conductor production and manufacturing processes are the main uses for helium in 2023 (Kramer 2023). The price paid for helium is highly variable as it is a small market and often

supplies are needed to keep critical instrumentation running. Overall, prices have risen by around 400% in the past decade, giving a global market of around \$US1.76 billion (Fig. 2; USGS 2024). Repeated supply crises are limiting growth in the helium market (Kramer 2023) and the future will involve increasing demand and gaps in supply.

In 2002 the global lithium (carbonate) market amounted to 72 000 t with a composite value of US\$390 million (Ebensperger *et al.* 2005). At 19%, demand for use in batteries was just ahead of lubricants (16%) and glazes for ceramics (12%) as the most common uses for lithium (Ebensperger *et al.* 2005). In recent years demand has risen ten-fold and production is failing to meet demand. 737 000 t of lithium carbonate were produced in 2022, whilst the projection for 2023 is 964 000 t and above a million tonnes in 2025 (Chew 2023). Demand from all sectors using lithium has grown with use in batteries (35%) and ceramics and glass (32%) outpacing all others (Inside Exploration 2023). Market value today in 2023 is around \$US8.2 billion with anticipated growth to about \$US19 billion in 2030 (Statista 2023).

Occurrence of hydrogen, helium and lithium on Earth

The concentrations of hydrogen, helium and lithium in the geosphere, hydrosphere and atmosphere are listed in Table 1 (from data in Emsley 2010). Hydrogen is abundant on Earth and unsurprisingly most concentrated in the hydrogeosphere where about 11% by mass is hydrogen, compounded with oxygen as water. It is also present in the atmosphere as water vapour and up to 1 ppm as molecular hydrogen. In the Earth, hydrogen is present in water, hydrocarbons and molecular hydrogen and in total at around 0.15% by mass. Since the figures shown in Table 1 were published, estimates of resources of H$_2$ in the lithosphere have
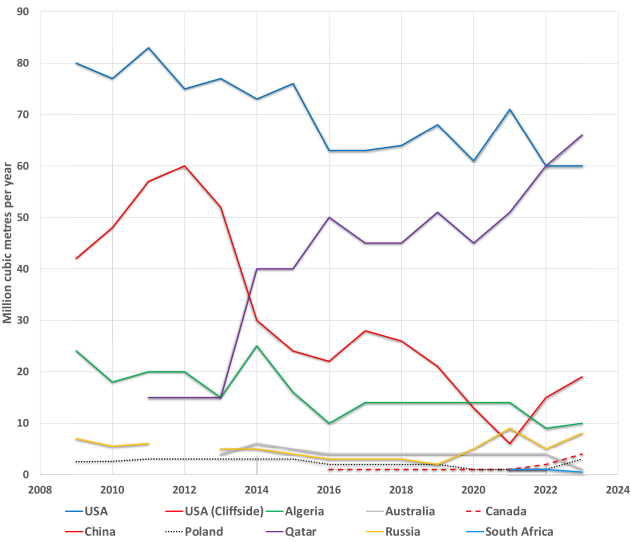
Fig. 1. Global helium production by nation. Source: compiled from data accessible in USGS (2024).

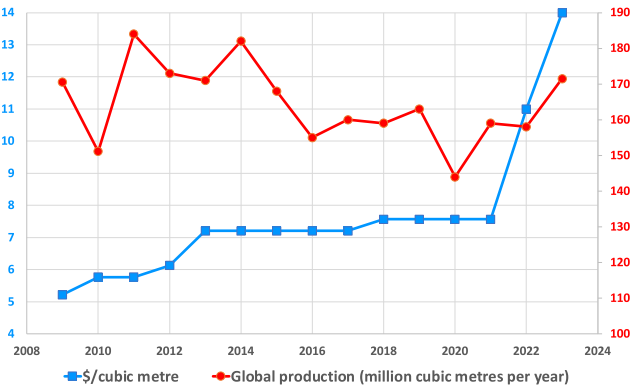**Fig. 2.** Global helium production and annual average helium price. Source: compiled from data accessible in USGS (2024).

doubled based on estimated contributions from water–rock reaction such as serpentinization, and H_2 production via radiolysis (Sherwood Lollar *et al.* 2014).

Helium is the second most abundant element in the universe, the Milky Way galaxy and our own Solar System but not so on Earth. Helium is present as parts per million in the Earth's atmosphere, parts per billion in the geosphere and parts per trillion in oceanic water. The helium in the atmosphere is reasonably uniform in its distribution whereas that in the geosphere is distributed highly heterogeneously. Helium is typically detected in the Earth as a free gas associated with other gases or as an exsolution product when water at depth in the Earth is depressurized during drilling operations. As a commodity within a gas accumulation, it need only be present at

concentrations >0.04% (40 000 ppm) for it to be extracted profitably.

Lithium is sourced from either subsurface connate brines or from igneous rocks. Around 70% of global lithium supply is produced from the subsurface brines in the Andean salars of Chile, Argentina and Bolivia which contain up to 1500 ppm dissolved lithium. Lithium is also extracted by mining. In granites and especially pegmatites, the lithium typically occurs in spodumene (a pyroxene, $LiAl(SiO_3)_2$), petalite (a framework silicate, $LiAlSi_4O_{10}$) and micas in solid solution (e.g. zinnwaldite, $K(Fe,Li)_2Al(Al,Si)_4O_{10}(F,OH)_2$ and lepidolite $K(Li,Al)_3(Al,Si,Rb)_4O_{10}(F,OH)_2$). However, lithium has also long been known to be hosted in deep geothermal systems (e.g. Berthold and Baler 1976; McKibben and Williams 1989) as well as sedimentary formation waters (Collins 1976; Dugamin *et al.* 2021), and in both high-enthalpy and low-enthalpy geothermal fluids, commonly associated geographically with crystalline basement (e.g. Edmunds *et al.* 1985; Sanjuan *et al.* 2016, 2022; Gourcerol *et al.* 2024). Lithium enrichment in these geothermal brines has been attributed to fluid interaction with lithium-enriched host rocks (e.g. Cornwall, Edmunds *et al.* 1985) or to either freshwater or seawater evaporation and groundwater dissolution of evaporites (McKibben *et al.* 1987; Sanjuan *et al.* 2022).

Current extraction techniques and environmental impact

Hydrogen, helium and lithium are all key elements to support the energy transition and supporting humanity's quest for a net zero (carbon emissions) society. Demand for all three elements will continue to grow and yet each must be supplied in a way that minimizes impact on the natural environment (atmosphere, biosphere, hydrosphere and geosphere) and be sustainable for long human timescales (hundreds to thousands of years). Presently, both hydrogen manufacture and helium production are intimately associated with fossil fuel production, use and its consequences. Lithium extraction results in damage to rare and vulnerable environments. Our aim is to show that it should be possible for hydrogen, helium and lithium to be sourced in socially responsible ways, with substantially reduced environmental impact and with much improved sustainability credentials than is the case today.

The IEA (2023b) calculated that the average carbon footprint for each 1 t of hydrogen produced was around 7 t of carbon dioxide equivalent. Using the hydrogen production figures above would suggest that the current carbon footprint of the hydrogen industry is >500 million tonnes per annum and without a change to the production method will be over 1 billion tonnes by 2050. Forward modelling in the same IEA (2023b) paper suggests that the carbon intensity could range between 1 and 11 times mass ratio of carbon dioxide released v. hydrogen produced, depending upon the commitments made by nations and consequential use of technologies associated with production of unabated hydrogen, hydrogen with carbon capture and hydrogen from electrolysis using renewably sourced electricity. At a minimum, this would still mean that the

Table 1. Concentrations of hydrogen, helium and lithium in Earth systems

	Geosphere Units alongside elements	Hydrosphere Units alongside elements	Atmosphere ppm
Hydrogen	0.15 wt% in water, hydrocarbons and as H_2	10.7 wt%	0.5–1.0 as H_2, variable as H_2O
Helium	8 ppb	7.2 ppt	5.2
Lithium	20 ppm	0.18 ppm	zero

For comparison, 10% = 100 000 ppm, 10 000 000 ppb and 10 000 000 000 ppt.

hydrogen production industry would have a 100 million tonne annual CO_2 footprint for the manufacture process alone.

Helium is a noble gas and has no direct carbon footprint because it is found rather than manufactured. However, all production today comes as a minor by-product of natural gas production. In the USA, the lower limit for economic separation of helium from produced natural gas is 0.3%. Both Algeria and Qatar produce helium as a knock-out gas from their natural gas liquification (LNG) process. The main production is from Hassi R'Mel in Algeria at 0.19% helium and Qatar's North Dome at 0.04% helium. Thus, there is an associated carbon footprint for the global helium industry of >300 million tonnes per annum (Gluyas and Fowler 2024). At >300 million tonnes per annum of greenhouse gas emissions, the global helium industry has a carbon footprint larger than all but 20 of the world's nations.

There is no simple way of calculating the full life cycle analysis of lithium extraction for its various uses as this is critically dependent on the source of lithium. For naturally enriched brines extracted from salars, brine is pumped to the surface into shallow ponds for solar-driven evaporation to further concentrate salts in the brines prior to lithium extraction (Stamp et al. 2012). The main environmental impacts are water and soil pollution as well as depletion of water resources in some of the driest environments on the planet (Bustos-Gallardo et al. 2021; Fig. 3). In addition, regulation of the industry is weak (Kaunda 2020) and current use of hydrological resources for extraction of saline brines undermines their future extraction potential (Agusdinata et al. 2018; Bustos-Gallardo et al. 2021).
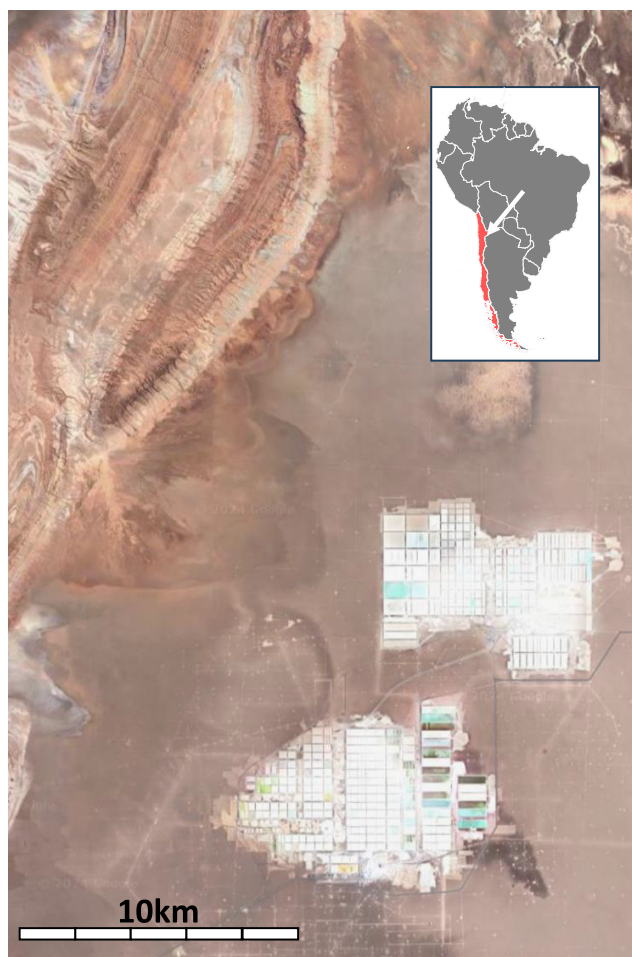

Fig. 3. San Pedro de Atacama salar showing extent of areas developed for brine evaporation. Source: main image from Google Earth (data: Airbus), inset shows location of satellite image.

Mining of hard rock resources is critically dependent on the mineralogy, lithium concentration and igneous expression of lithium-bearing minerals, with each mineral having a distinct extraction route(s). For example, extraction of lithium from zinnwaldite involves high-temperature dehydroxylation of the mica to form spodumene, releasing HF (hydrogen fluoride) which can compromise groundwater chemistry as well as pose challenges to industrial processes through its corrosive potential (Schneider et al. 2017). Spodumene and, to a lesser extent, lepidolite are soluble in acids, but these extraction methods involve significant environmental damage in the form of release of sulfuric acid mist, generation of NOx and SO_2, and high water and power usage (Gao et al. 2023). For example, for mining of lithium from spodumene, some 15 t CO_2 are produced for 1 t of mined lithium (Crawford et al. 2022). Furthermore, any bulk dissolution or decomposition process must also generate significant quantities of waste rock (tailings) containing other major and trace elements such as Fe, Mn, U, Be and F that could negatively impact water quality (e.g. Roy et al. 2022). Conversely, lithium can be extracted directly from other mine tailings where it can be hosted in clays (e.g. from bauxite extraction (Sarker et al. 2022) or from kaolinite works (Siame and Pascoe 2011)).

Finally, production of lithium from low-enthalpy geothermal brines is significantly less efficient in energy terms than that from high-salinity brines, in part because the dilute source (and temperate climate of many European resources) is less suited to evaporative enrichment to concentrate the brines before lithium hydroxide extraction. To that end, direct lithium extraction (DLE) is fast becoming a key process for winning of lithium at low concentrations from connate brines. DLE covers a wide array of technologies, some of which have high fresh-water demand and others high power consumption. Full life-cycle analyses for the different techniques have yet to be fully developed (Vera et al. 2023) and there are associated possibilities for multi-salt extraction of borates, potassium, magnesium, zinc and sodium compounds as secondary products from geothermal and petroleum developments which to date have not been realized (Gluyas et al. 2016; Vera et al. 2023).

A low impact sustainable future

Helium exploration model

Our work began with helium and, as such, the narrative flows most easily if we begin with its story. Helium was first discovered as adsorption lines in the Sun's spectrum, and it was not until 1903 that large quantities were found on Earth. A gas well drilled in Dexter, Kansas, USA blew out but the gas flowing from the well would not burn (McFarland 1903). Analysis showed that whilst most of the gas was nitrogen, a little under 2% was helium. However, it was not until World War I that the strategic value of helium as a safe lift gas for military dirigibles was recognized. A combination of events in 1914 alerted the British Admiralty and these events led to the creation of a helium industry (Gluyas 2019a, b). Early in 1914, German chemist Géza Austerweil published, 'Die angerwandte Chemie in der Luftfart' [Applied chemistry in aviation]. Later that same year a German airship was downed by a British fighter plane equipped with incendiary bullets; no explosion ensued as might have been expected with a hydrogen-filled airship. The implications were profound: Germany had access to helium, Britain did not. Post-war the search was on, with governments of both the USA and Soviet Union putting in place programmes to analyse the composition of gas produced from existing wells (Anderson and Hinson 1951; Boone 1958; Munnerlyn and Miller 1963; Ben'yaminovich 1995). In the USA, helium was identified as a minor component in many such analyses and particularly in the area where Texas, Oklahoma, Kansas and Colorado meet. This area, along

with other serendipitous discoveries in the Mid-West, became the source of nearly all the helium produced globally. Gas with as little as 0.3% helium became the economic threshold for helium extraction.

Apart from drilling close to existing known helium deposits, accidental discovery of helium whilst drilling for natural gas (methane) has been the only way global reserves have been added to the helium inventory, until now. In 2011 we set out to develop and test an exploration strategy for helium based upon that used for petroleum (Danabalan *et al.* 2022). Just like petroleum fluids, it is necessary to understand the source of helium, what causes the source rock to be mature for helium formation, the mechanism whereby helium escapes the source rock (primary migration) and transfers to the reservoir rock (secondary migration, Halford *et al.* 2022), how at some point in that journey the helium exsolves from the connate water (Cheng *et al.* 2023) and accumulates beneath a seal horizon and finally what conditions helium requires to remain in place such that it might be discovered. This is a play fairway analysis.

The source of helium is well established. Most of the helium within the geosphere has been produced by the decay of thorium and uranium. This is so-called radiogenic helium or ^{4}He. The lighter ^{3}He isotope is cosmogenic, inherited by the Earth at formation and has an abundance of about 1/10 000 that of ^{4}He. Here we are interested in ^{4}He. The decay of both thorium and uranium follows first-order thermodynamics, time alone is the controlling factor. The only naturally occurring stable isotope of thorium is ^{232}Th. It has a half-life of 14 billion years with all steps but the first, ^{232}Th to ^{228}Ra, occurring over short periods of nanoseconds to days. The decay series terminates at ^{208}Pb and yields 7 alpha particles (helium nuclei) for each thorium atom. Uranium occurs as one of three natural isotopes, ^{238}U, ^{235}U and ^{234}U. Over 99.2% of uranium is ^{238}U with almost all of the balance being ^{235}U. ^{238}U has a half-life of 4.4683 billion years. The decay series terminates at ^{206}PB by which time 8 alpha particles have been released and, like ^{232}Th, the only slow step in the series is the first, ^{234}Th. The average crustal abundance of thorium is about 40 ppb by weight and that of uranium about 10 ppb by weight (Herring 2012). However, thorium and uranium are substantially more abundant in granitic than basic or ultrabasic rocks. The average granite has around 12 ppm thorium and 4 ppm uranium (Brown and Silver 1955). The maximum concentration observed in igneous rocks is around 50 ppm for both thorium and uranium (Tye *et al.* 2017). In short, a high-quality helium source rock will be ancient (Archean or Proterozoic) and likely granitic. In addition to granitic rocks, most shales rich in organic matter are also enriched in uranium which is fixed in reducing environments. The Cambrian–Ordovician shale of Ranstad, Sweden has 170–250 ppm uranium and elsewhere further enrichment of shales may occur during hydrothermal events (Urban *et al.* 1995). Radioelements can also be concentrated in sediments by secondary fluid migration, when uranium in dissolved and re-precipitated in faults and fractures, controlled by the redox conditions of the environment (Cowart and Burnett 1994).

The helium produced from decay of the radionuclides remains in the crystal lattices of helium-retentive minerals such as apatite, zircon, uraninite or monazite unless above the closure temperature (Table 2). Ranges in closure temperature for individual minerals are due to combinations of differing grain sizes and cooling rates. At higher temperatures the helium will diffuse into the inter and intra-crystalline fluid (primary migration), followed by migration out of the source rock (secondary migration). Diffusion and buoyancy-driven fluid advection act to drive migration of helium into the sedimentary cover from the crust. Diffusion likely controls release of helium in tectonically quiescent regions (Stute *et al.* 1992; Castro *et al.* 1998; Cheng *et al.* 2021; Tyne *et al.* 2022) whilst advection is dominant in regions of recent tectonic activity (Lowenstern *et al.* 2014; Caracausi *et al.* 2022; Danabalan *et al.* 2022; Halford *et al.* 2022).

In nature, helium is always found with nitrogen. The helium to nitrogen ratio lies typically in the 0.02 to 0.2 range (Ballentine and Sherwood Lollar 2002; Sherwood Lollar *et al.* 2006; Kietäväinen *et al.* 2014; Karolyté *et al.* 2022). The reverse is not true, nitrogen can occur alone. We have few data on nitrogen and do not fully understand how and where it pairs with helium. Data on the isotopic (δ^{15}N) composition of the N_2 end member associated with the economic ^{4}He in the Kansas–Texas Hugoton–Panhandle gas field have a narrow range (−3.00 to +2.45‰). These values are comparable with those observed in both crustal, low-temperature metamorphism and the release of ammonia from clays (−5.00 to +4.00‰) (Zhu *et al.* 2000; Ballentine and Sherwood Lollar 2002; Danabalan 2017). Likely, nitrogen and helium share a common process, though their source rocks may differ. Nitrogen, as the major gas, may be a carrier gas phase for the helium or provide the primary mechanism of gas phase formation from solution (Cheng *et al.* 2023).

As a free gas phase, the nitrogen/helium mix will migrate, driven by buoyancy, the same process as for petroleum fluids, until its upward journey is arrested by a low permeability horizon (seal) with underlying porous and permeable horizon (reservoir) with a combined geometry that halts further upward movement of the fluid (trap). The efficacy of a trap in terms of retaining helium and other gases depends upon the rate at which the gases enter the trap v. the rate at which they escape. Capillary entry pressures for helium, carbon dioxide and hydrocarbon gases are similar (Wollenweber *et al.* 2009) but diffusive loss is a function of atomic/molecular mass and helium has a higher diffusion coefficient compared with the other gases. In that regard, salt and other evaporite seals are likely to prove more effective than mudrocks. Nonetheless, traps can retain helium-bearing gases for long periods of

Table 2. Helium closure temperatures for helium-retentive minerals

Mineral	Closure temperature range (°C)	References
Apatite	55–100	Lippolt *et al.* (1994), Wolf *et al.* (1996), Farley (2000), Farley (2002), Shuster *et al.* (2006)
Hematite	90–250	Bähr *et al.* (1994), Farley (2002)
Zircon	180–200	Farley (2002), Reiners (2005), Reich *et al.* (2007), Cherniak *et al.* (2009)
Garnet	590–630	Dunai and Roselieb (1996), Farley (2002)
Monazite	182–299	Boyce *et al.* (2005)
Titanite	150–200	Reiners and Farley (1999), Farley (2002)
Uraninite	*c.* 200	Martel *et al.* (1990), Stuart *et al.* (1994)

From Danabalan *et al.* (2022).

geological time. For example, Cheng et al. (2018, 2023) demonstrated that trapping of helium-bearing free gas in the Williston Basin began 140 million years ago.

An opportunity arose in 2015 to test our hypothesis that nitrogen/helium mixtures could be generated and expelled from ancient granitic source rocks subject to heating so as to effect primary migration of the gas species and to do so in an area not previously known for helium production. The founders of Helium One, a start-up company operating in Tanzania, called us and asked whether the Rukwa area within the East African Rift might be prospective for helium. Helium One had found a couple of old reports containing information on cold gas seeps in ephemeral pools close to Lake Rukwa in Tanzania. East Africa combines ancient granitic crust with a geologically recent heating event in the form of the East African Rift, ideal circumstances for the generation and expulsion of helium. Field work was conducted, the seeps sampled, and gas composition and isotope data analysed. The gases were typically nitrogen and helium with about 10% helium and contained no hydrocarbon or other greenhouse gases (Mtili et al. 2021; Danabalan et al. 2022). Several wells have been drilled in the area in the past few years and each has encountered abundant helium shows. Most recently on 5 February 2024, well Itumbula West-1 flowed gas to surface. The gas is 4.7% helium, 2.2% hydrogen. Nitrogen makes up the balance. At 4.7% the helium content is 18 times greater than the 0.3% economic threshold used in the USA and almost 100× more concentrated than the helium content of gas from North Dome Qatar, which accounts for almost 40% global production.

Hydrogen exploration model

Hydrogen has acquired a coat of many colours in recent years (Table 3). The colours are used to describe the method of hydrogen manufacture. We have assigned a value to each colour for the emissions produced during manufacture. This provides the context for hydrogen exploration. Manufacture is costly in both energy and financial terms. Might finding natural, molecular hydrogen make sense in terms of both cost and reduction of embedded carbon in the manufacture processes?

Hydrogen is a key component of a global energy system transitioned to low carbon. It can substitute for natural gas (methane) in many industrial processes, long-haul transport systems, shipping, aviation (IRENA 2021) and could, subject to availability, be used in households because it has properties similar to methane in terms of transmission and yet on combustion it produces only water vapour and not carbon dioxide. However, because of hydrogen's lower density than methane and the fact that cryogenics are required to liquify it, storage of large quantities of hydrogen is difficult. Unfortunately, the conventional means of hydrogen manufacture from coal and from methane both have carbon dioxide as an unwanted waste product. Emission of CO_2 so produced into the atmosphere is worse than simply burning fossil fuels because the additional energy required for transformation from hydrocarbon to hydrogen is effectively an energy penalty (parasitic load) on the system. Hence the role of hydrogen in the energy transition is the use of blue hydrogen in which production is from methane with the resultant CO_2 captured and stored underground, and green hydrogen as an electrolysis product of fresh water. Blue hydrogen is not emission free and, dependent upon the process used, may have a carbon footprint only a little less than grey hydrogen. Green hydrogen is nominally carbon-free so long as the energy source for the electricity required to liberate hydrogen from water is from a renewable source. For both blue and green hydrogen there is a substantial cost uplift relative to grey and black hydrogen (Table 3) and all types of manufactured hydrogen cost more than methane for an equivalent quantity of energy (calorific value). We have not been able to find a cost for natural hydrogen with which to compare the manufacturing costs for the various types of manufactured hydrogen. We have calculated one based upon an assumption that should a hydrogen exploration and production industry emerge then one would anticipate the finding cost to eventually be comparable with that for methane (Table 3). Unsurprisingly, the calculated 'discovered hydrogen' costs are much lower than 'manufactured hydrogen', as indeed is the carbon footprint of natural hydrogen. It thus makes exploring for hydrogen an attractive quest.

Natural, molecular hydrogen exists as a free gas in a myriad of geological and biological settings (Sherwood Lollar et al. 2014; Zgonnik 2020) but the only acknowledged hydrogen-producing field is the accidentally discovered Bourakebougou Field in Mali (Prinzhofer et al. 2018). Bourakebougou produces hydrogen for local use. It has a purity of 98% H_2 with 1% nitrogen and 1% methane (Maiga et al. 2023). Hydrogen was discovered in South Australia from wells drilled 90 years ago on Kangaroo Island offshore Adelaide (Rezaee 2021). Recent drilling has confirmed the presence of hydrogen in the area with a purity of 73.3% (Collins 2023).

Elsewhere in Australia, mixed nitrogen, helium and hydrogen gases have been discovered at two locations in the Amadeus Basin (Leila et al. 2022), whilst in the USA similar mixed

Table 3. Main methods of hydrogen manufacture and natural hydrogen

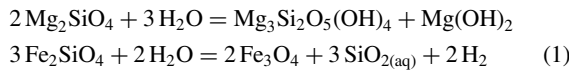| Colour	Source of energy	Source of hydrogen	Production process	CO₂ emissions (kgCO₂/kgH₂)	Cost $US/kg H₂
Green	Renewable	Fresh water	Hydrolysis	0.3[a]	4.5–12[b]
Grey	Electricity non-renewable	Methane	Methane reformation	9.8–13.7[a&c]	0.98–2.93[b]
Blue	Renewable	Methane	Methane reformation + CCS	0.8–8.8[c&d]	1.8–4.7[b]
Brown/black	Electricity non-renewable	Coal	Gasification	20–25[c]	0.45[e]
Natural/gold/white	Not required	Hydrogen	Gas expansion	0.4[f]	0.133[g]

[a]Moberg and Bartlett (2022); [b]Schelling (2023); [c]De La Cruz (2024); [d]Incer-Valverde et al. (2023); [e]Poljak (2021); [f]Brandt (2023); [g]based on the average finding cost of methane in the USA. Aublinger (2014) and adjusted for energy density.
CCS, carbon capture and storage.

composition gas has been found in Kansas (Newell *et al.* 2007; Guélard *et al.* 2017) and hydrogen has also been reported from a well drilled recently in Nebraska (Ball and Czado 2022). Low but significant concentrations of hydrogen have also been recorded in other locations, including in the deep Songliao Basin, NE China at 6000 m in the Songke-2 well at up to 0.7% (Horsfield *et al.* 2022).

Hydrogen is produced in large quantities by two or possibly three geological processes: water–rock interaction, radiolysis of water, and possibly over mature petroleum source rocks and meta anthracite coals.

Oxidation of iron from Fe^{2+} to Fe^{3+} occurs during serpentinization (equation 1) and alteration of ophiolite and greenstone belt lithologies liberating hydrogen via the paired reactions of olivine end members fayalite and forsterite with water. Reaction of fayalite with water in the temperature range 200–320°C produces aqueous silica and hydrogen but is unable to reach equilibrium because forsterite degradation consumes aqueous silica so driving the fayalite reaction to produce ever more dissolved silica and hence hydrogen. The process occurs quickly in geological terms and typically on the time-scale of millions to tens of millions of years (McCollom *et al.* 2016; Leong *et al.* 2023) but can be ongoing as fractures and surface areas are propagated (Sherwood Lollar *et al.* 2007, 2014; Sleep and Zoback 2007).

$$\text{Serpentinization: peridotite } + \text{ water yields OH}^- \text{ and H}_2:$$
$$2\,Mg_2SiO_4 + 3\,H_2O = Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$$
$$3\,Fe_2SiO_4 + 2\,H_2O = 2\,Fe_3O_4 + 3\,SiO_{2(aq)} + 2\,H_2 \tag{1}$$

Hydrogen is also produced indirectly by the decay of potassium, thorium and uranium (equation 2). Alpha, beta and gamma radiation released during decay can dissociate water molecules, with oxygen being sequestered by the rock and hydrogen liberated into solution (Lin *et al.* 2005a, b; Le Caër 2011). This is the same process that generates helium. Alpha particles from the radioactive decay are helium nuclei. Hydrogen produced via radiolysis is mixed with helium and nitrogen as described above and the process is slow, occurring over hundreds of millions to billions of years.

$$\text{Ionizing radiation dissociates water}$$
$$\alpha,\ \beta,\ \gamma \text{ from U, Th, K} + H_2O \rightarrow {}^4He + H_2$$
$$(H*, HO*, HO_2^*, OH^-, H_3O*, H_2O) \tag{2}$$
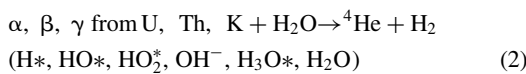
Taken together, the hydrogen produced from the water–rock reaction and radiolysis is about 0.1 to 0.5 million tonnes per annum in the Precambrian continental lithosphere (Sherwood Lollar *et al.* 2014).

Hydrogen is also produced from the very late stages of organic matter maturation, after the generation of liquid and gaseous hydrocarbons but before (at a lower temperature than) graphite formation (Hanson and Hanson 2024). The organic matter maturation processes are essentially complete once burial has raised the organic matter to temperatures of around 200°C. Some methane production continues up to around 330°C and when organic matter is heated to over 500°C (amphibolite-grade metamorphism) it has become graphite; pure carbon. The rate of hydrogen generation from organic matter is likely similar to that for hydrocarbons and occurs typically over a period of a few million to a few tens of millions of years (Gluyas and Swarbrick 2021). However, it is not yet clear how much organic matter might contribute to a global scale total hydrogen budget. Hydrogen generated during late-stage maturation of organic matter might easily mix with and react to hydrogenize earlier-released undersaturated hydrocarbons (Pratt 1934).

Hydrogen liberated from organic matter is likely to be in gas phase and mixed with at least some methane. Primary migration from the source rock would be driven by the pressure differential caused by the generation of the hydrogen and could be up or down. Subsequent, secondary migration would be driven by buoyancy. We speculate that it is also possible that at least some of the hydrogen produced by reaction of ultramafic rock with water may also be as a gas phase. The shattered appearance of some serpentinites has commonly been attributed to volume increase (Malvoisin *et al.* 2017); however, it may reflect release of high-pressure hydrogen, though further work is needed to confirm or reject this hypothesis.

Radiolysis generates hydrogen into solution albeit at very low concentration. Subsequent gas phase formation will be via the same route as for helium (Danabalan *et al.* 2022; Cheng *et al.* 2023).

Secondary migration and entrapment for hydrogen or for hydrogen, nitrogen, helium mixtures are like that for petroleum. For hydrogen though, the story may not be over. Once in the cooler, shallower subsurface, hydrogen may be accessed by microbes as a substrate. Gregory *et al.* (2019), in a review of subsurface, microbial hydrogen cycling, indicated that consumption of aqueous hydrogen could occur at temperatures up to 90°C in the presence of nutrients. The products from bacterial metabolism are methane and water. Karolyté *et al.* (2022) and Lin *et al.* (2006) report on methane plus helium fracture fluids in South Africa, with the methane likely derived from radiolysis-produced hydrogen rather than an organic source rock. Highly saline fluids will limit bacterial activity (Telling *et al.* 2018; Gregory *et al.* 2019) as will high temperatures (>122°C; Armitage 2023) and work is ongoing to determine other conditions favourable to preservation of hydrogen (Sherwood Lollar *et al.* 2006). A free gas phase of hydrogen could also self-protect from microbial consumption because the water content would be reduced to residual saturation.

In exploration terms, natural hydrogen can be found in areas with ancient granitic basement, those in which water/ultramafic rock reaction has occurred, and possibly in the deeper parts of sedimentary basins hitherto dismissed as having source rocks overmature for hydrocarbon generation. To date, most of the discovered natural hydrogen is in basement rocks with low storage capacity (porosity) but potentially high deliverability (permeable fractures). The significant exception is Bourakebougou Field in Mali (Prinzhofer *et al.* 2018), which produces from the cover sequence and possibly the aforementioned Songliao deep basin sedimentary rocks. It is unlikely that Bourakebougou is a geological singularity and the presence of helium in conventional reservoirs is indicative that basement processes can produce gas which migrates into the cover sequence.

By analogy with what we have learned about helium exploration, the chances of finding hydrogen are likely to be improved by selecting areas which not only have suitable source rocks but those with cover sequences containing both seal and reservoir intervals, deposited before the source rocks become depleted. Hydrogen may also be more likely to be found deep within basins in rocks overlying basement (Cheng *et al.* 2023), in hot and/or saline aquifers.

Lithium exploration model

Exploration for hard rock lithium resources requires an excellent understanding of the high-temperature processes that enrich lithium into different minerals during crystallization and distribute those minerals spatially within a granite (*s.l.*) body or into pegmatites. The distributed mineralogy at the grain-scale is also critical for determining the extraction pre-processing paths. The dominant host phase for lithium can vary within an individual igneous body and lithium concentrations can vary spatially down to sub-

crystal scales (Beck *et al.* 2006; Parkinson *et al.* 2007). However, the whole life cycle of the igneous systems is also important, from source enrichment and tectonic context (Simons *et al.* 2017; Ballouard *et al.* 2023; Koopmans *et al.* 2024), magmatic cooling and crystallization (Pichavant 2022), fluid exsolution and hydrothermal alteration/weathering. Low-grade metamorphic overprints, such as chloritization reactions (Jancsek *et al.* 2023) or weathering processes, can affect the lithium abundance and the elements that co-vary with it (e.g. Putzolu *et al.* 2024). For fluoride-rich systems particularly, the mineral host for lithium, as well as for other co-enriched trace elements, can vary significantly during fluid exsolution and transport (e.g. Monnier *et al.* 2022).

It is possible that, as high-grade deposits increasingly become exploited or become less accessible geopolitically, larger but low-grade hard-rock resources in-country may become of more commercial interest. As new discoveries come into focus, we believe that it is morally and environmentally imperative to plan the most efficient (from the perspective of the planet) extraction pathways for multi-element resources so that the maximum benefit, and minimum damage, comes from exploitation.

Our understanding of the processes that govern the dissolution of lithium into brine and the degree to which brines may become enriched in lithium is limited and a topic of active research. For low-enthalpy geothermal brines associated with crystalline intrusions, key processes are the rates and kinetics of interaction of groundwaters with granite at representative natural temperatures and pressures, and the impact on permeability (e.g. Sanchez-Roa *et al.* 2021). These processes interact closely with the mineralogy, mineral stability and key hosts for lithium, and are coupled with hydrological processes (Miao *et al.* 2022). What is clear though is that many subsurface brines, which may be the water leg to petroleum accumulations or the water sources for geothermal systems, are sufficiently lithium rich that it is economic to extract the lithium using direct lithium extraction (DLE).

Two projects in the UK are planning to co-produce lithium and heat from geothermal waters in Cornwall (Cornish Lithium undated) and County Durham (Weardale Lithium undated). Elsewhere at the Salton Sea power station in California, USA, lithium carbonate yield from the same water used to generate about 300 MW of power (capacity) is 60–70 kt (figures calculated from data in Evans 2008). Lithium has also been extracted from co-produced oilfield water at Smackover in Arkansas, USA (Upholt 2024). For these projects, modelling of geothermal flow in fracture pathways and advection–diffusion of lithium in fluids, alongside careful consideration of the placement of extraction and reinjection wells, is crucial to avoid either dilution of lithium or decrease in enthalpy of the fluid.

A comparison between the concentrations of lithium found in salars v. oilfield and geothermal brines is shown in Figure 4. A superficial but possibly quite effective exploration strategy for lithium would be to collate data on the chemical composition of oilfield

and geothermal brines and use the compendium of data so created to select areas for lithium extraction. Such an approach would mimic that used for helium throughout the first century of its extraction and separation from petroleum accumulation gases. Such an approach is likely to be necessary, in the short term, absent of a geological understanding of the process that leads to lithium dissolution from minerals and subsequent concentration.

Discussion

The decarbonizing of energy systems is critical to the energy transition and achieving some sort of sustainability for humankind on planet Earth. The first three elements in the periodic table, hydrogen, helium and lithium, are already playing an important role in lowering the carbon footprint of energy systems and their derivatives in terms of energy-using systems. Hydrogen is, in its molecular state, an energy dense gas which can be stored, transmitted and used in ways that make it a possible substitute for fossil fuels, notwithstanding its lower density than hydrocarbon gas at a similar temperature and pressure and the additional safety measures required during transport and use. However, currently it is a manufactured product and substantial energy is required to produce it from methane or water. Such energy for manufacture must therefore be produced sustainably and with a low carbon footprint. The Earth produces molecular hydrogen in large quantities but, to date, there have been few attempts to find it in sufficient quantities to merit commercial development. That it can be found is demonstrated by the accidental discovery of Bourakebougou in Mali. Significant flows, shows and seeps are known from elsewhere in the world and, as recent drilling results in Nebraska, Tanzania and South Australia have shown, molecular hydrogen can occur in a variety of geological settings (Sherwood Lollar *et al.* 2014). The composition of hydrogen-bearing gases varies widely (Fig. 5), from near pure in the case of Mali to mixtures of hydrogen, helium, nitrogen, carbon dioxide and short-chain hydrocarbons in the Mount Kitty well, Amadeus Basin, Australia (Leila *et al.* 2022).

Near-pure hydrogen, and a lack of helium, is most likely a product of water–rock interaction during serpentinization, greenstone and ophiolite formation. The presence of large quantities of helium and/or nitrogen point towards a radiolysis source. Where hydrogen is found together with methane provides a more challenging interpretation as to the processes involved. Such methane may come from a conventional organic matter source, have an abiotic origin (Sherwood Lollar *et al.* 2002; Xia and Gao 2021) or the co-occurrence with hydrogen may mean they share a common origin from high-maturity organic matter, though this process remains speculative. It is also possible that gas from multiple sources was mixed on route to the trap. Alternatively, as Karolyté *et al.* (2022), Ward *et al.* (2004) and Sherwood Lollar *et al.* (2006) have shown, the methane may be a product of microbes
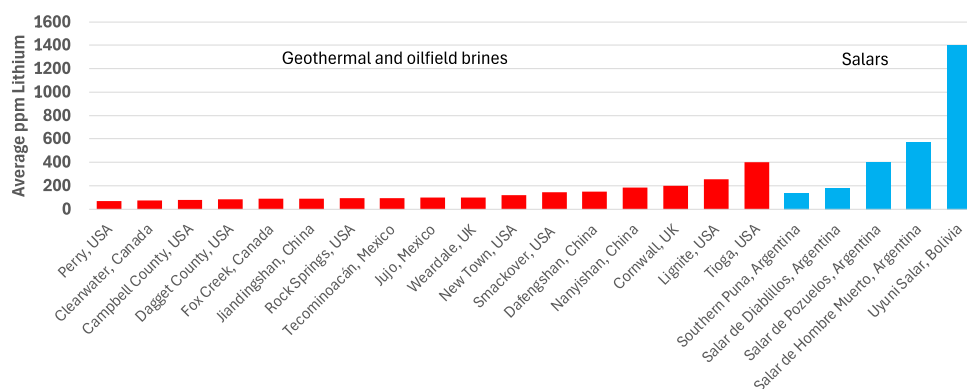

Fig. 4. Lithium content of geothermal brines and co-produced brines from petroleum fields compared with that in salars. Source: from Gluyas and Fowler (2024); data from Collins (1976), Manning *et al.* (2007), Birkle *et al.* (2009), Mernagh *et al.* (2013), Daitch (2018), Wrathall (2020), Lopez Steinmetz *et al.* (2020), Li *et al.* (2021), E3 Lithium (2023).
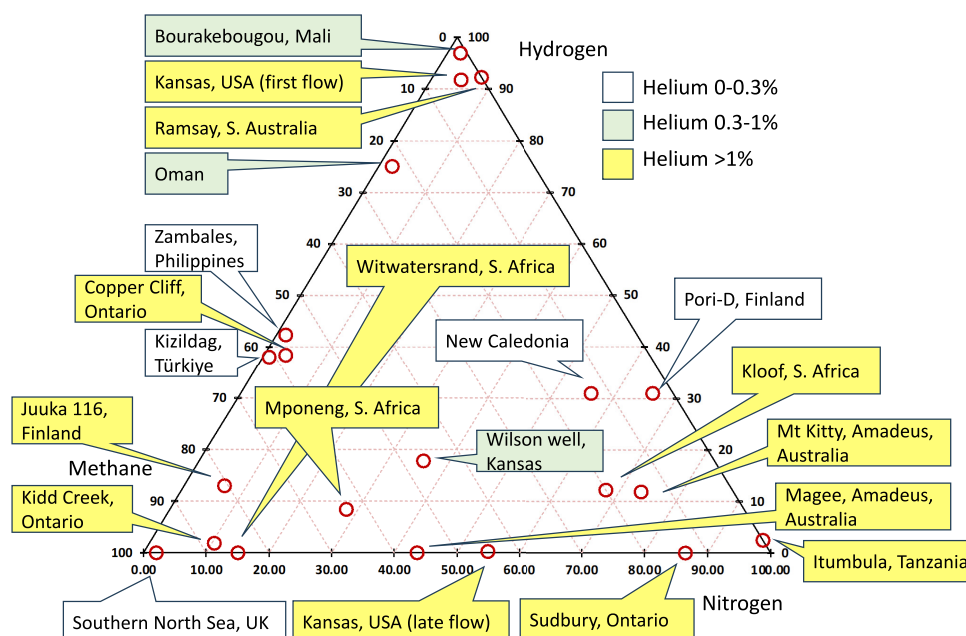
Fig. 5. Hydrogen, nitrogen, methane ternary plot for gases from: Mali; Kansas (USA); South Australia; Oman; Philippines; Copper Cliff and Kidd Creek (Ontario); Türkiye; Finland; New Caledonia; Witwatersrand and Mponeng (South Africa); Wilson well (Kansas); Australia; Tanzania; and UK. For clarity, we have chosen not to plot the methane-dominated, hydrogen-poor samples reported in these papers, reporting only the conventional coal-sourced methane of the Southern North Sea fields. Source: Mali (Prinzhofer *et al.* 2018), Kansas (Guélard *et al.* 2017), South Australia (Martin 2024), Oman (Sano *et al.* 1993), Philippines (Abrajano *et al.* 1988), Copper Cliff (Li *et al.* 2021), Türkiye (D'Alessandro *et al.* 2018), Finland (Sherwood Lollar *et al.* 1993), Kidd Creek (Li *et al.* 2021), New Caledonia (Deville and Prinzhofer 2016), Witwatersrand, South Africa (Karolyté *et al.* 2022), Mponeng (Sherwood Lollar *et al.* 2006), Wilson well (Newell *et al.* 2007), Australia (Leila *et al.* 2022), Tanzania (Helium One Global 2024); UK (average from gas fields in Gluyas and Hichens 2003).

metabolizing what was abiotically produced hydrogen. The detective work required to elucidate the source of hydrogen will require careful capture of the gases and analysis of a wide array of natural tracers such as the noble gases and their isotopic compositions (Byrne *et al.* 2017; Tyne *et al.* 2022; Warr *et al.* 2022).

Helium is sourced from the decay of naturally occurring thorium and uranium occurring in ancient granitic rocks. Traces will occur in virtually all hydrocarbon accumulations because of the widespread occurrence of the thorium and uranium sources. Commercially attractive concentrations of helium in natural gas accumulations are uncommon and result from the mixing of a nitrogen/helium gas phase with the hydrocarbons or partitioning of nitrogen/helium from solution into a pre-existing hydrocarbon gas phase. However, as we have shown, concentrations of helium up to around 100 times greater than that found in hydrocarbon gases do occur in systems where hydrocarbon gases are absent, such as in the recent discovery in Tanzania (Helium One Global 2024). Such greenhouse gas-free helium could provide the helium required by industry for the manufacture of sustainable energy devices as well as medical cryogenics and the other applications for which helium is required.

Our understanding of lithium sourcing is much less well developed, though it is often enriched in pore waters of geothermal systems, themselves commonly associated with helium-yielding granitic rocks.

Conclusions

Demand for hydrogen, helium and lithium will continue to grow as the energy transition progresses. The current approaches to meeting the demand for the three elements are carbon intensive and damage the environment. This need not be so. For helium, we have outlined an exploration strategy that avoids the need to produce it as a minor component of natural gas (methane). That we can find helium in high concentrations absent of greenhouse gases is now proven in one location, Rukwa Tanzania. Others may follow.

While we now know significant quantities of natural hydrogen reside in the Earth's crust, it is too early to know the size of potential reservoirs, the trapping structures, the accessibility of such and the long-term yield of any reservoirs. Resolving these important constraints is the focus of significant investment and exploration globally, for it to become a commodity prized above manufactured hydrogen. However, we now know where it forms in the Earth's crust and can begin to identify areas prospective for its exploration.

Lithium is commonly concentrated in geothermal and petroleum field brines. The co-location with those commodities may enable DLE at lower costs than might otherwise be the case, so enabling lithium to be produced and compete with that currently in the market and coming from either solid rock or Andean salars.

What is very clear is the need to minimize environmental impact, whatever methods humans choose to use for the exploration and exploitation of hydrogen, helium and lithium.

conceptualization (equal), formal analysis (equal), investigation (equal), methodology (equal), validation (equal), writing – original draft (equal), writing – review & editing (equal); **AC**: conceptualization (equal), investigation (equal), methodology (equal), validation (equal), writing – original draft (equal), writing – review & editing (equal); **BSL**: conceptualization (lead), formal analysis (lead), funding acquisition (lead), investigation (lead), methodology (lead), supervision (lead), validation (lead), writing – original draft (lead), writing – review & editing (lead); **CB**: conceptualization (lead), formal analysis (lead), funding acquisition (lead), investigation (lead), methodology (lead), project administration (lead), resources (lead), supervision (lead), validation (lead), writing – original draft (lead), writing – review & editing (lead).

Data availability All data are included in the paper.

References

Abrajano, T.A., Sturchio, N.C., Bohlke, J.K., Lyon, G.L., Poreda, R.J. and Stevens, C.M. 1988. Methane-hydrogen gas seeps, Zambales Ophiolite, Philippines: deep or shallow origin. *Chemical Geology*, **71**, 211–222, https://doi.org/10.1016/0009-2541(88)90116-7

Agusdinata, D.B., Liu, W., Eakin, H. and Romero, H. 2018. Socioenvironmental impacts of lithium mineral extraction: towards a research agenda. *Environmental Research Letters*, **13**, 123001, https://doi.org/10.1088/1748-9326/aae9b1

Anderson, C.C. and Hinson, H.H. 1951. *Helium-bearing natural gases of the United States, Analyses and analytical methods*. United States Department of the Interior, Bureau of Mines report **486**.

Armitage, T. 2023. Reducing microbial risk during underground hydrogen storage. *Hydrogen Storage in Salt Caverns*, 29 March 2023, ERA Research Accelerator, https://www.era.ac.uk/wp-content/uploads/2023/04/07_Armitage_ARUP.pdf [last accessed 7 March 2024].

Aublinger, C. 2014. How much does it cost to produce 1000 cubic feet of gas?, https://seekingalpha.com/article/2707555-how-much-does-it-cost-to-produce-1000-cubic-feet-of-gas [last accessed 15 January 2024].

Bähr, R., Lippolt, H.J. and Wernicke, R.S. 1994. Temperature-induced 4He degassing of specularite and botryoidal hematite: a 4He retentivity study. *Journal of Geophysical Research: Solid Earth*, **99**, 17 695–17 707, https://doi.org/10.1029/94JB01055

Ball, P.J. and Czado, K. 2022. Natural hydrogen: the new frontier. *Geoscientist*, 1 March 2022, https://geoscientist.online/sections/unearthed/natural-hydrogen-the-new-frontier/ [last accessed 8 May 2023].

Ballentine, C.J. and Sherwood Lollar, B. 2002. Regional groundwater focusing of nitrogen and noble gases into the Hugoton–Panhandle giant gas field, USA. *Geochimica et Cosmochimica Acta*, **66**, 2483–2497, https://doi.org/10.1016/S0016-7037(02)00850-5

Ballouard, C., Couzinié, S., Bouilhol, P., Harlaux, M., Mercadier, J. and Montel, J.-M. 2023. A felsic meta-igneous source for Li-F-rich peraluminous granites: insights from the Variscan Velay dome (French Massif Central) and implications for rare-metal magmatism. *Contributions to Mineralogy and Petrology*, **178**, 75, https://doi.org/10.1007/s00410-023-02057-1

Beck, P., Chaussidon, M., Barrat, J.A., Gillet, P. and Bohn, M. 2006. Diffusion induced Li isotopic fractionation during the cooling of magmatic rocks: the case of pyroxene phenocrysts from nakhlite meteorites. *Geochimica et Cosmochimica Acta*, **70**, 4813–4825, https://doi.org/10.1016/j.gca.2006.07.025

Ben'yaminovich, O.A. 1995. Helium in Russia. *Chemical and Petroleum Engineering*, **31**, 60–63.

Berthold, C.E. and Baler, D.H. 1976. Lithium recovery from geothermal fluids, Lithium Resources and Requirements by the Year 2000. *US Geological Survey Professional Paper*, **1005**, 61–74.

Birkle, P., Garcia, B. and Padron, C. 2009. Origin and evolution of formation water at the Jujo–Tecominoacán oil reservoir, Gulf of Mexico.

Part 1: chemical evolution and water–rock interaction. *Applied Geochemistry*, **24**, 543–554, https://doi.org/10.1016/j.apgeochem.2008.12.009

Boone, W.J., Jr 1958. *Helium-bearing natural gases of the United States, Analyses and analytical methods*. Supplement to Bulletin 486, United States Department of the Interior, Bureau of Mines report **576**.

Boyce, J.W., Hodges, K.V., Olszewski, W.J. and Jercinovic, M.J. 2005. He diffusion in monazite: implications for (U–Th)/He thermochronometry. *Geochemistry, Geophysics, Geosystems*, **6**, Q12004, https://doi.org/10.1029/2005GC001058

Brandt, A.R. 2023. Greenhouse gas intensity of natural hydrogen produced from subsurface geologic accumulations. *Joule*, **7**, 1818–1831, https://doi.org/10.1016/j.joule.2023.07.001

Brown, H. and Silver, L.T. 1955. The possibilities of obtaining long-range supplies of thorium, uranium and other substances from igneous rocks. *In*: Page, L.R., Stocking, H.E. and Smith, H.B. (eds) *Contributions to the Geology of Uranium and Thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy*, Geneva, Switzerland, 9–95.

Bustos-Gallardo, B., Bridge, G. and Prieto, M. 2021. Harvesting Lithium: water, brine and the industrial dynamics of production in the Salar de Atacama. *Geoforum; Journal of Physical, Human, and Regional Geosciences*, **119**, 177–189. https://doi.org/10.1016/j.geoforum.2021.01.001

Byrne, D.J., Barry, P.H., Lawson, M. and Ballentine, C.J. 2017. Noble gases in conventional and unconventional petroleum systems. *Geological Society, London, Special Publications*, **468**, 127–149, https://doi.org/10.1144/SP468.5

Caracausi, A., Buttitta, D.. *et al.* 2022. Earthquakes control the impulsive nature of crustal helium degassing to the atmosphere. *Communications Earth & Environment*, **3**, 224, https://doi.org/10.1038/s43247-022-00549-9

Castro, M.C., Goblet, P., Ledoux, E., Violette, S. and de Marsily, G. 1998. Noble gases as natural tracers of water circulation in the Paris Basin: 2. Calibration of a groundwater flow model using noble gas isotope data. *Water Resources Research*, **34**, 2467–2483, https://doi.org/10.1029/98WR01957

Cheng, A., Sherwood Lollar, B., Giunta, T.M., Mundle, S.O.C. and Ballentine, C.J. 2018. Helium distribution in the Williston and the Southwest Ontario basins. *Goldschmidt Abstracts*, **2018**, 403, https://goldschmidtabstracts.info/abstracts/abstractView?id=2018003772 [last accessed 18 February 2024].

Cheng, A., Sherwood Lollar, B. *et al.* 2021. Determining the role of diffusion and basement flux in controlling 4He distribution in sedimentary basin fluids. *Earth and Planetary Science Letters*, **574**, 117175, https://doi.org/10.1016/j.epsl.2021.117175

Cheng, A., Sherwood Lollar, B., Gluyas, J.G. and Ballentine, C.J. 2023. Primary N_2–He gas field formation in intracratonic sedimentary basins. *Nature*, **615**, 94–99, https://doi.org/10.1038/s41586-022-05659-0

Cherniak, D.J., Watson, E.B. and Thomas, J.B. 2009. Diffusion of helium in zircon and apatite. *Chemical Geology*, **268**, 155–166, https://doi.org/10.1016/j.chemgeo.2009.08.011

Chew, C. 2023. World's biggest lithium producers. Reuters, https://www.reuters.com/markets/commodities/worlds-biggest-lithium-producers-2023-04-21/#:~:text=World%20output%20was%20737%2C000%20tonnes,Science%20and%20Resources%20in%20March [last accessed 9 October 2023].

Collins, A. 1976. Lithium abundances in oilfield waters *In*: Vine, J.D. (ed.) *Lithium Resources and Requirements by the Year 2000*. Geological Survey Professional Paper, **1005**, 116–123.

Collins, L. 2023. 'Significant concentrations' of natural hydrogen detected at Australia's first exploration well – raising hopes of world-first commercial exploitation. Hydrogen Insight, https://www.hydrogeninsight.com/production/significant-concentrations-of-natural-hydrogen-detected-at-australias-first-exploration-well-raising-hopes-of-world-first-commercial-exploitation/2-1-1546424 [last accessed 27 February 2024].

Cornish Lithium. Undated. Direct lithium extraction, https://cornishlithium.com/projects/lithium-in-geothermal-waters/direct-lithium-extraction/ [last accessed 7 March 2024].

Cowart, J.B. and Burnett, W.C. 1994. The distribution of uranium and thorium decay-series radionuclides in the environment–a review. *Journal of Environmental Quality*, **23**, 651–662, https://doi.org/10.2134/jeq1994.00472425002300040005x

Crawford, I., Shao-Horn, Y. and Keith, D. 2022. How much CO2 is emitted by manufacturing batteries. MIT Climate Control Portal, https://climate.mit.edu/ask-mit/how-much-co2-emitted-manufacturing-batteries#:~:text=For%20illustration%2C%20the%20Tesla%20Model,kg%20(16%20metric%20tons [last accessed 15 February 2024].

D'Alessandro, W., Yüce, G., Italiano, F., Bellomo, S., Gülbay, A.H., Yasin, D.U. and Gagliano, A.L. 2018. Large compositional differences in the gases released from the Kizildag ophiolite body (Turkey): evidences of prevailingly abiogenic origin. *Marine and Petroleum Geology*, **89**, 174–184, https://doi.org/10.1016/j.marpetgeo.2016.12.017

Daitch, P.J. 2018. *Lithium extraction from oilfield brine*. Master of Science in Energy and Earth Resources and Master of Business Administration thesis, University of Texas at Austin, https://repositories.lib.utexas.edu/bitstream/handle/2152/65645/DAITCH-THESIS-2018.pdf?sequence=1&isAllowed=y [last accessed 2 June 2023].

Danabalan, D. 2017. *Helium: exploration methodology for a strategic resource*. PhD thesis, Durham University, Durham, UK.

Danabalan, D., Gluyas, J.G., Macpherson, C.G., Abraham-James, T.H., Bluett, J.J., Barry, P.H. and Ballentine, C.J. 2022. The principles of helium exploration. *Petroleum Geoscience*, **28**, https://doi.org/10.1144/petgeo2021-029

De La Cruz, F.L. 2024. Over the rainbow: why understanding full value-chain carbon intensity is trumping the colour of hydrogen. Wood Mackenzie, https://www.woodmac.com/horizons/hydrogen-colours-value-chain-carbon-intensity/ [last accessed 18 February 2024].

Deville, E. and Prinzhofer, A. 2016. The origin of N_2-H_2-CH_4-rich natural gas seepages in ophiolitic context: a major and noble gases study of fluid seepages in New Caledonia. *Chemical Geology*, **440**, 139e47, https://doi.org/10.1016/j.chemgeo.2016.06.011

Dugamin, E.J.M., Richard, A., Cathelineau, M., Boiron, M.-C., Despinois, F. and Brisset, A. 2021. Groundwater in sedimentary basins as potential lithium resource: a global prospective study. *Scientific Reports*, **11**, 21091, https://doi.org/10.1038/s41598-021-99912-7

Dunai, T.J. and Roselieb, K. 1996. Sorption and diffusion of helium in garnet: implications for volatile tracing and dating. *Earth and Planetary Science Letters*, **139**, 411–421, https://doi.org/10.1016/0012-821X(96)00029-5

E3 Lithium 2023. The future of Canadian Lithium, https://www.e3lithium.ca/_resources/presentations/corporate-presentation.pdf?v=0.621 [last accessed 2 June 2023].

Ebensperger, A., Maxwell, P. and Moscoso, C. 2005. The lithium industry: its recent evolution and future prospects. *Resources Policy*, **30**, 218–231, https://doi.org/10.1016/j.resourpol.2005.09.001

Edmunds, W.M., Kay, R.L.F. and McCartney, R.A. 1985. Origin of saline groundwaters in the Carnmenellis Granite (Cornwall, England): natural processes and reaction during Hot Dry Rock reservoir circulation. *Chemical Geology*, **49**, 287–301, https://doi.org/10.1016/0009-2541(85)90162-7

Emsley, J. 2010. *Nature's Building Blocks*, 2nd edn. Oxford University Press.

Evans, R.K. 2008. An abundance of lithium, https://web.archive.org/web/20180423214019id_/http://www.evworld.com/library/KEvans_LithiumAbunance_pt2.pdf [last accessed 7 March 2024].

Farley, K.A. 2000. Helium diffusion from apatite: general behavior as illustrated by Durango fluorapatite. *Journal of Geophysical Research: Solid Earth*, **105**, 2903–2914, https://doi.org/10.1029/1999JB900348

Farley, K.A. 2002. (U–Th)/He dating: techniques, calibrations, and applications. *Reviews in Mineralogy and Geochemistry*, **47**, 819–844, https://doi.org/10.2138/rmg.2002.47.18

Gao, T., Fan, N., Chen, W. and Dai, T. 2023. Lithium extraction from hard rock lithium ores (spodumene, lepidolite, zinnwaldite, petalite): technology, resources, environment and cost. *China Geology*, **6**, 137–153, https://doi.org/10.31035/cg2022088

Gluyas, J.G. 2019a. The emergence of the helium industry, the History of Helium Exploration Part 1. *American Association of Petroleum Geologists, Explorer*, January, 16–17, https://explorer.aapg.org/story/articleid/50466/the-emergence-of-the-helium-industry

Gluyas, J.G. 2019b. Helium shortages and emerging helium provinces, the History of Helium Exploration Part 2. *American Association of Petroleum Geologists, Explorer*, February, 18–19, https://explorer.aapg.org/story/articleid/51290/helium-shortages-and-emerging-helium-provinces

Gluyas, J.G. and Fowler, N. 2024. The future of geoenergy – a perspective. *Geoenergy*, **2**, https://doi.org/10.1144/geoenergy2023-058

Gluyas, J.G. and Hichens, H. 2003. *The United Kingdom Oil and Gas Fields Commemorative Millennium Volume*. Geological Society Memoir, **20**, https://doi.org/10.1144/GSL.MEM.2003.020.01.01

Gluyas, J.G. and Swarbrick, R.E. 2021. *Petroleum Geoscience*, 2nd edn. Wiley Blackwell.

Gluyas, J.G., Mathias, S.A. and Goudarzi, S. 2016. North Sea – next life: extending the commercial life of producing North Sea fields. *Geological Society, London, Petroleum Geology Conference Series*, **8**, 561–570, https://doi.org/10.1144/PGC8.30

Gourcerol, B., Sanjuan, B. *et al.* 2024. Atlas of lithium geothermal fluids in Europe. *Geothermics*, **119**, 102956, https://doi.org/10.1016/j.geothermics.2024.102956

Gregory, S.F., Barnett, M.J., Field, L.P. and Milodowski, A.E. 2019. Subsurface microbial hydrogen cycling: natural occurrence and implications for industry. *Microorganisms*, **7**, 53, https://doi.org/10.3390/microorganisms7020053

Guélard, J., Beaumont, V. *et al.* 2017. Natural H_2 in Kansas: deep or shallow origin? *Geochemistry, Geophysics, Geosystems*, **18**, https://doi.org/10.1002/2016GC006544

Halford, D.T., Karolytė, R. *et al*. 2022. High helium reservoirs in the Four Corners area of the Colorado Plateau, USA. *Chemical Geology*, **596**, 120790, https://doi.org/10.1016/j.chemgeo.2022.120790

Hanson, J. and Hanson, H. 2024. Hydrogen's organic genesis. *Unconventional Resources*, **4**, 100057, https://doi.org/10.1016/j.uncres.2023.07.003

Helium One Global 2024. Helium One Global achieves milestone as Itumbula West-1 well yields up to 4.7% helium concentrations, https://www.helium-one.com/helium-one-global-achieves-milestone-as-itumbula-west-1-well-yields-up-to-4-7-helium-concentrations/ [last accessed 18 February 2024].

Herring, J.S. 2012. Uranium and thorium resources. *In*: Meyers, R.A. (ed.) *Encyclopedia of Sustainability Science and Technology*. Springer, New York, NY, https://doi.org/10.1007/978-1-4419-0851-3_21

Horsfield, B., Mahlstedt, N., Weniger, P., Misch, D., Vranjes-Wessely, S., Han, S. and Wang, C. 2022. Molecular hydrogen from organic sources in the deep Songliao Basin, P.R. China. *International Journal of Hydrogen Energy*, **47**, 16750–16774, https://doi.org/10.1016/j.ijhydene.2022.02.208

Incer-Valverde, J., Korayem, A., Tsatsaronis, G. and Morosuk, T. 2023. 'Colors' of hydrogen: definitions and carbon intensity. *Energy Conversion and Management*, **291**, 117294, https://doi.org/10.1016/j.enconman.2023.117294

Inside Exploration 2023. Lithium: applications of an age old element paving the way into the future, https://insidexploration.com/lithium-applications-of-an-age-old-element-paving-the-way-into-the-future/ [last accessed 9 October 2023].

IEA 2021. Global hydrogen review 2021. International Energy Agency, https://iea.blob.core.windows.net/assets/5bd46d7b-906a-4429-abda-e9c507a62341/GlobalHydrogenReview2021.pdf [last accessed 9 October 2023].

IEA 2023a. Global hydrogen review 2023. International Energy Agency, https://iea.blob.core.windows.net/assets/8d434960-a85c-4c02-ad96-77794aaa175d/GlobalHydrogenReview2023.pdf [last accessed 9 October 2023].

IEA 2023b. Towards hydrogen definitions based on their emissions intensity, https://iea.blob.core.windows.net/assets/acc7a642-e42b-4972-8893-2f03bf0bfa03/Towardshydrogendefinitionsbasedontheiremissionsintensity.pdf [last accessed 15 February 2024].

IRENA 2021. *Making the Breakthrough: Green Hydrogen Policies and Technology Costs*. International Renewable Energy Agency, Abu Dhabi.

Jancsek, K., Janovszky, P., Galbács, G. and Tóth, T.M. 2023. Granite alteration as the origin of high lithium content of groundwater in southeast Hungary. *Applied Geochemistry*, **149**, 105570, https://doi.org/10.1016/j.apgeochem.2023.105570

Karolyté, R., Warr, O. *et al*. 2022. The role of porosity in H2/He production ratios in fracture fluids from the Witwatersrand Basin, South Africa. *Chemical Geology*, **595**, 120788, https://doi.org/10.1016/j.chemgeo.2022.120788

Kaunda, R.B. 2020. Potential environmental impacts of lithium mining. *Journal of Energy & Natural Resources Law*, **38**, 237–244, https://doi.org/10.1080/02646811.2020.1754596

Kietäväinen, K., Ahonen, L., Kukkonen, I.T., Niedermann, S. and Wiesberg, T. 2014. Noble gas residence times of saline waters within crystalline bedrock, Outokumpu Deep Drill Hole, Finland. *Geochimica et Cosmochimica Acta*, **145**, 159–174, https://doi.org/10.1016/j.gca.2014.09.012

Koopmans, L., Martins, T. *et al*. 2024. The formation of lithium-rich pegmatites through multi-stage melting. *Geology*, **52**, 7–11, https://doi.org/10.1130/G51633.1

KPMG Undated. The hydrogen trajectory, https://kpmg.com/be/en/home/insights/2021/03/eng-the-hydrogen-trajectory.html [last accessed 9 October 2023].

Kramer, D. 2023. Helium prices surge to record levels as shortage continues. *Physics Today*, September, 18–20.

Le Caër, S. 2011. Water Radiolysis: influence of oxide surfaces on H2 production under ionizing radiation. *Water*, **3**, 235–253, https://doi.org/10.3390/w3010235

Leila, M., Loiseau, K. and Moretti, I. 2022. Controls on generation and accumulation of blended gases (CH4/H2/He) in the Neoproterozoic Amadeus Basin, Australia. *Marine and Petroleum Geology*, **140**, 105643, https://doi.org/10.1016/j.marpetgeo.2022.105643

Leong, J.A., Nielsen, M. *et al*. 2023. H2 and CH4 outgassing rates in the Samail ophiolite, Oman: implications for low-temperature, continental serpentinization rates. *Geochimica et Cosmochimica Acta*, **347**, 1–15, https://doi.org/10.1016/j.gca.2023.02.008

Li, L., Li, K., Giunta, T., Warr, O., Labidi, J. and Sherwood Lollar, B. 2021. N2 in deep subsurface fracture fluids of the Canadian Shield: source and possible recycling processes. *Chemical Geology*, **585**, 120571, https://doi.org/10.1016/j.chemgeo.2021.120571

Lin, L.-H., Slater, G.F., Sherwood Lollar, B., Lacrampe-Couloume, G. and Onstott, T.C. 2005*a*. The yield and isotopic composition of radiolytic H2, a potential energy source for the deep subsurface biosphere. *Geochimica et Cosmochimica Acta*, **69**, 893–903, https://doi.org/10.1016/j.gca.2004.07.032

Lin, L., Hall, J. *et al*. 2005*b*. Radiolitic H2 in continental crust: nuclear power for deep subsurface microbial communities. *Geochemistry, Geophysics, Geosystems*, **6**, https://doi.org/10.1029/2004GC0 00907

Lin, L.H., Wang, P.-L. *et al*. 2006. Long-term sustainability of a high-energy, low-diversity crustal biome. *Science (80)*, **314**, 479–482, https://doi.org/10.1126/science.1127376

Lippolt, H.J., Leitz, M., Wernicke, R.S. and Hagedorn, B. 1994. (Uranium + thorium)/helium dating of apatite: experience with samples from different geochemical environments. *Chemical Geology*, **112**, 179–191, https://doi.org/10.1016/0009-2541(94)90113-9

Lopez Steinmetz, R.L., Salvi, S., Sarchi, C., Santamans, C. and Lopez Steinmetz, L.C. 2020. Lithium and Brine Geochemistry in the Salars of the Southern Puna, Andean Plateau of Argentina. *Economic Geology*, **115**, 1079–1096, https://doi.org/10.5382/econgeo.4754.hal-02989895

Lowenstern, J., Evans, W.. *et al*. 2014. Prodigious degassing of a billion years of accumulated radiogenic helium at Yellowstone. *Nature*, **506**, 355–358, https://doi.org/10.1038/nature12992

Maiga, O., Deville, E., Lavel, J., Prinzhofer, A. and Diallo, A.B. 2023. Characterization of the spontaneously recharging natural hydrogen reservoirs of Bourakebougou, Mali. *Nature Scientific Reports*, **13**, 11876, https://doi.org/10.1038/s41598-023-38977-y

Malvoisin, B., Brantut, N. and Kaczmarek, M.-A. 2017. Control of serpentinization rate by reaction-induced cracking. *Earth and Planetary Science Letters*, **476**, 143–152, https://doi.org/10.1016/j.epsl.2017.07.042

Manning, D.A.C., Younger, P.L., Smith, F.W., Jones, J.M., Dufton, D.J. and Diskin, S. 2007. A deep geothermal exploration well at Eastgate, Weardale, UK: a novel exploration concept for low-enthalpy resources. *Journal of the Geological Society, London*, **164**, 371–382, https://doi.org/10.1144/0016-76492006-015

Martel, D.J., O'Nions, R.K., Hilton, D.R. and Oxburgh, E.R. 1990. The role of element distribution in production and release of radiogenic helium: the Carnmenellis Granite, southwest England. *Chemical Geology*, **88**, 207–221, https://doi.org/10.1016/0009-2541(90)90090-T

Martin, P. 2024. Australia's first well tests for natural H2 begin as Gold Hydrogen seeks insights on its underground discoveries. Hydrogen Insight, https://www.hydrogeninsight.com/production/australias-first-well-tests-for-natural-h2-begin-as-gold-hydrogen-seeks-insights-on-its-underground-discoveries/2-1-1608288 [last accessed 9 March 2024].

McCollom, T.M., Klein, F. *et al*. 2016. Temperature trends for reaction rates, hydrogen generation, and partitioning of iron during experimental serpentinization of olivine. *Geochimica et Cosmochimica Acta*, **181**, 175–200, https://doi.org/10.1016/j.gca.2016.03.002

McFarland, D.F. 1903. Composition of a gas from a well at Dexter, Kansas. *Transactions of the Kansas Academy of Science*, **19**, 60–63, https://doi.org/10.2307/3624173

McKibben, M.A. and Williams, A.E. 1989. Metal speciation and solubility in saline hydrothermal fluids: an empirical approach based on geothermal brine data. *Economic Geology*, **84**, 1996–2007, https://doi.org/10.2113/gsecongeo.84.7.1996

McKibben, M.A., Williams, A.E., Elders, W.A. and Eldridge, C.S. 1987. Saline brines and metallogenesis in a modern sediment-filled rift: the Salton Sea geothermal system, California, USA. *Applied Geochemistry*, **2**, 563–578, https://doi.org/10.1016/0883-2927(87)90009-6

Mernagh, T.P., Bastrakov, E., Clarke, J.D.A. and de Caritat, P. 2013. *A Review of Australian Salt Lakes and Assessment of their Potential for Strategic Resources*. Report number 2013/39, Geoscience Australia.

Miao, W., Zhang, X., Li, Y., Li, W., Yuan, X. and Li, C. 2022. Lithium and strontium isotopic systematics in the Nalenggele River catchment of Qaidam basin, China: quantifying contributions to lithium brines and deciphering lithium behavior in hydrological processes. *Journal of Hydrology*, **614 Part B**, 128630, https://doi.org/10.1016/j.jhydrol.2022.128630

Midilli, A., Ay, M., Dincer, I. and Rosen, M.A. 2005. On hydrogen and hydrogen energy strategies I: current status and needs. *Renewable and Sustainable Energy Reviews*, **9**, 255–271, https://doi.org/10.1016/j.rser.2004.05.003

Moberg, J. and Bartlett, S. 2022. The mirage of blue hydrogen is fading. Green Hydrogen Association, https://gh2.org/blog/mirage-blue-hydrogen-fading#:~:text=Blue%20hydrogen%20requires%20the%20production,every%201%20kilogram%20of%20hydrogen [last accessed 18 February 2024].

Monnier, L., Salvi, S. *et al*. 2022. Mica trace-element signatures: Highlighting superimposed W–Sn mineralizations and fluid sources. *Chemical Geology*, **600**, 120866, https://doi.org/10.1016/j.chemgeo.2022.120866

Mtili, K.M., Byrne, D.J. *et al*. 2021. The origin of high helium concentrations in the gas fields of southwestern Tanzania. *Chemical Geology*, **585**, 120524, https://doi.org/10.1016/j.chemgeo.2021.120542

Munnerlyn, R.D. and Miller, R.D. 1963. *Helium-bearing natural gases of the United States, Analyses*. Second Supplement to Bulletin 486, United States Department of the Interior, Bureau of Mines report 617.

Newell, K.D., Doveton, J.H., Merriam, D.F., Sherwood Lollar, B., Waggoner, W.M. and Magnuson, L.M. 2007. H2-rich and hydrocarbon gas recovered in a deep Precambrian Well in Northeastern Kansas. *Natural Resources Research*, **16**, https://doi.org/10.1007/s11053-007-9052-7

Parkinson, I.J., Hammond, S.J., James, R.H. and Rogers, N.W. 2007. High-temperature lithium isotope fractionation: insights from lithium isotope diffusion in magmatic systems. *Earth and Planetary Science Letters*, **257**, 609–621, https://doi.org/10.1016/j.epsl.2007.03.023

Pichavant, M. 2022. Experimental crystallization of the Beauvoir granite as a model for the evolution of Variscan rare-metal magmas. *Journal of Petrology*, **63**, egac120, https://doi.org/10.1093/petrology/egac120

Poljak, J. 2021. Hydrogen Economics – Which Colour is Cheapest? https://www.linkedin.com/pulse/hydrogen-economics-which-colour-cheapest-john-poljak [last accessed 27 February 2024].

Pratt, E. 1934. Hydrogenation and the Origin of Oil: Part II. Origin and Evolution of Petroleum: Group 3. Variation in Physical Properties.

American Association of Petroleum Geologist Special Publication, **6**, 235–245.

Prinzhofer, A., Tahara Cissé, C.S. and Diallo, A.B. 2018. Discovery of a large accumulation of natural hydrogen in Bourakebougou (Mali). *International Journal of Hydrogen Energy*, **43**, 19315–19326, https://doi.org/10.1016/j.ijhydene.2018.08.193

Putzolu, F., Seltmann, R. *et al.* 2024. Influence of magmatic and magmatic-hydrothermal processes on the lithium endowment of micas in the Cornubian Batholith (SW England). *Mineralium Deposita*, **59**, 1067–1088, https://doi.org/10.1007/s00126-024-01248-5

Reich, M., Ewing, R.C., Ehlers, T.A. and Becker, U. 2007. Low-temperature anisotropic diffusion of helium in zircon: implications for zircon (U–Th)/He thermochronometry. *Geochimica et Cosmochimica Acta*, **71**, 3119–3130, https://doi.org/10.1016/j.gca.2007.03.033

Reiners, P.W. 2005. Zircon (U–Th)/He thermochronometry. *Reviews in Mineralogy and Geochemistry*, **58**, 151–179, https://doi.org/10.2138/rmg.2005.58.6

Reiners, P.W. and Farley, K.A. 1999. Helium diffusion and (U–Th)/He thermochronometry of titanite. *Geochimica et Cosmochimica Acta*, **63**, 3845–3859, https://doi.org/10.1016/S0016-7037(99)00170-2

Rezaee, R. 2021. Assessment of natural hydrogen systems in Western Australia. *International Journal of Hydrogen Energy*, **46**, 33068–33077, https://doi.org/10.1016/j.ijhydene.2021.07.149

Roy, T., Plante, B., Benzaazoua, M., Demers, I., Coudert, L. and Turcotte, S. 2022. Geochemistry of decades-old spodumene mine tailings under a humid continental climate. *Applied Geochemistry*, **146**, 105481, https://doi.org/10.1016/j.apgeochem.2022.105481

Sanchez-Roa, C., Saldi, G.D. *et al.* 2021. The role of fluid chemistry on permeability evolution in granite: applications to natural and anthropogenic systems. *Earth and Planetary Science Letters*, **553**, 116641, https://doi.org/10.1016/j.epsl.2020.116641

Sanjuan, B., Millot, R., Innocent, C., Dezayes, C., Scheiber, J. and Brach, M. 2016. Main geochemical characteristics of geothermal brines collected from the granite basement in the Upper Rhine Graben and constraints on their deep temperature and circulation. *Chemical Geology*, **428**, 27–47, https://doi.org/10.1016/j.chemgeo.2016.02.021

Sanjuan, B., Gourceol, B., Millot, R., Rettenmaier, D., Jeandel, E. and Rombaut, A. 2022. Lithium-rich geothermal brines in Europe: an up-date about geochemical characteristics and implications for potential Li resources. *Geothermics*, **101**, 102385, https://doi.org/10.1016/j.geothermics.2022.102385

Sano, Y., Urabe, A., Wakita, H. and Wushiki, H. 1993. Origin of hydrogen–nitrogen gas seeps, Oman. *Applied Geochemistry*, **8**, 1–8, https://doi.org/10.1016/0883-2927(93)90053-J

Sarker, S.K., Haque, N., Bhuiyan, M., Bruckard, W. and Pramanik, B.K. 2022. Recovery of strategically important critical minerals from mine tailing. *Journal of Environmental Chemical Engineering*, **10**, 107622, https://doi.org/10.1016/j.jece.2022.107622

Schelling, K. 2023. Green Hydrogen to Undercut Gray Sibling by End of Decade. BloombergNEF, https://about.bnef.com/blog/green-hydrogen-to-undercut-gray-sibling-by-end-of-decade/ [last accessed 18 February 2024].

Schneider, A., Schmidt, H. *et al.* 2017. Lithium extraction from the mineral zinnwaldite: Part I: effect of thermal treatment on properties and structure of zinnwaldite. *Minerals Engineering*, **111**, 55–67, https://doi.org/10.1016/j.mineng.2017.05.006

Sherwood Lollar, B., Frape, S.K., Weise, S.M., Fritz, P., Macko, S.A. and Welhan, J.A. 1993. Abiogenic methanogenesis in crystalline rocks. *Geochimica et Cosmochimica Acta*, **57**, 5087–5097, https://doi.org/10.1016/0016-7037(93)90610-9

Sherwood Lollar, B., Westgate, T.D., Ward, J.A., Slater, G.F. and Lacrampe-Couloume, G. 2002. Abiogenic formation of gaseous alkanes in the Earth's crust as a minor source of global hydrocarbon reservoirs. *Nature*, **416**, 522–524, https://doi.org/10.1038/416522a

Sherwood Lollar, B., Lacrampe-Couloume, G. *et al.* 2006. Unravelling abiogenic and biogenic sources of methane in the Earth's deep subsurface. *Chemical Geology*, **226**, 328–339, https://doi.org/10.1016/j.chemgeo.2005.09.027

Sherwood Lollar, B., Voglesonger, K. *et al.* 2007. Hydrogeologic controls on episodic H$_2$ release from Precambrian fractured rocks–energy for deep subsurface life on Earth and Mars. *Astrobiology*, **7**, 971–986, https://doi.org/10.1089/ast.2006.0096

Sherwood Lollar, B., Onstott, T.C., Lacrampe-Couloume, G. and Ballentine, C.J. 2014. The contribution of the Precambrian continental lithosphere to global H$_2$ production. *Nature*, **516**, 379–386, https://doi.org/10.1038/nature14017

Shuster, D.L., Flowers, R.M. and Farley, K.A. 2006. The influence of natural radiation damage on helium diffusion kinetics in apatite. *Earth and Planetary Science Letters*, **249**, 148–161, https://doi.org/10.1016/j.epsl.2006.07.028

Siame, E. and Pascoe, R.D. 2011. Extraction of lithium from micaceous waste from China clay production. *Minerals Engineering*, **24**, 1595–1602, https://doi.org/10.1016/j.mineng.2011.08.013

Simons, B., Andersen, J.C.Ø., Shail, R.K. and Jenner, F.E. 2017. Fractionation of Li, Be, Ga, Nb, Ta, In, Sn, Sb, W and Bi in the peraluminous Early Permian Variscan granites of the Cornubian Batholith: precursor processes to magmatic-hydrothermal mineralisation. *Lithos*, **278–281**, 491–512, https://doi.org/10.1016/j.lithos.2017.02.007

Sleep, N.H. and Zoback, M. 2007. Did earthquakes keep the early crust habitable. *Astrobiology*, **7**, 1023–1032, https://doi.org/10.1089/ast.2006.0091

Stamp, A., Long, D.J. and Wägner, P.A. 2012. Environmental impacts of a transition toward e-mobility: the present and future role of lithium carbonate production. *Journal of Cleaner Production*, **23**, 104–112, https://doi.org/10.1016/j.jclepro.2011.10.026

Statista 2023. Market value of lithium worldwide from 2019 to 2022, with a forecast for 2023 and 2030, https://www.statista.com/statistics/1088734/global-lithium-market-value/#:~:text=By%20the%20end%20of%202023,to%208.2%20billion%20U.S.%20dollars [last accessed 9 October 2023].

Stuart, F., Turner, G. and Taylor, R. 1994. He–Ar isotope systematics of fluid inclusions: resolving mantle and crustal contributions to hydrothermal fluids. *In*: Matsuda, J. (ed.) *Noble Gas Geochemistry and Cosmochemistry*. Terra Scientific, Tokyo, 261–277.

Stute, M., Sonntag, C., Déak, J. and Schlosser, P. 1992. Helium in deep circulating groundwater in the Great Hungarian Plain: flow dynamics and crustal and mantle helium fluxes. *Geochimica et Cosmochimica Acta*, **56**, 2051–2067, https://doi.org/10.1016/0016-7037(92)90329-H

Telling, J., Voglesonger, K., Sutcliffe, C.N., Lacrampe-Couloume, G., Edwards, E. and Sherwood Lollar, B. 2018. Bioenergetic constraints on microbial hydrogen utilization in Precambrian deep crustal fracture fluids. *Geomicrobiology*, **35**, 108–119, https://doi.org/10.1080/01490451.2017.1333176

Tye, A.M., Milodowski, A.E. and Smedley, P.L. 2017. *Distribution of natural radioactivity in the environment*. British Geological Survey Internal Report, **OR/17/001**.

Tyne, R.L., Barry, P.H., Cheng, A., Hillegonds, D.J., Kim, J.-H., McIntosh, J.C. and Ballentine, C.J. 2022. Basin architecture controls on the chemical evolution and 4He distribution of groundwater in the Paradox Basin. *Earth and Planetary Science Letters*, **589**, 117580, https://doi.org/10.1016/j.epsl.2022.117580

Upholt, B. 2024. In Rush for Lithium, Miners Turn to the Oil Fields of Arkansas. *Yale Environment 360*, https://e360.yale.edu/features/arkansas-direct-lithium-extraction#:~:text=A%20well%20in%20the%20Smackover,decade%2C%20though%20not%20in%20Arkansas [last accessed 7 March 2024].

Urban, H., Stribrny, B., Zereini, F. and Ye, Y. 1995. Geochemistry and metallogenesis of Lower Carboniferous black shale-hosted ore deposits, NE Rhenish Massif, FR Germany. *In*: Puettmann (ed.) *Geochemistry of Black Shales in Central Europe*. Ore Geology Reviews, **9**, 427–443.

USGS 2024. Helium statistics and information, National Mineral Information Centre, United States geological Survey, https://www.usgs.gov/centers/national-minerals-information-center/helium-statistics-and-information [last accessed 9 March 2024].

Vera, M.L., Torres, W.R., Galli, C.I., Chagnes, A. and Flexer, V. 2023. Environmental impact of direct lithium extraction from brines. *Nature Reviews Earth & Environment*, **4**, 149–165, https://doi.org/10.1038/s43017-022-00387-5

Ward, J.A., Slater, G.F. *et al.* 2004. Microbial hydrocarbon gases in the Witwatersrand Basin, South Africa: implications for the deep biosphere. *Geochimica et Cosmochimica Acta*, **68**, 3239–3250, https://doi.org/10.1016/j.gca.2004.02.020

Warr, O., Ballentine, C.J., Onstott, T.C., Nisson, D.M., Kieft, T.L., Hillegonds, D.J. and Sherwood Lollar, B. 2022. [86]Kr and other noble gases identify billion-year-old radiogenically-enriched groundwater system. *Nature Communications*, **13**, 3768, https://doi.org/10.1038/s41467-022-31412-2

Weardale Lithium Undated. Lithium carbonate produced County Durham for the first time, https://weardalelithium.co/2023/05/11/lithium-carbonate-produced-from-naturally-occurring-geothermal-brines-in-county-durham-for-the-first-time/ [last accessed on 7 March 2024].

Wolf, R.A., Farley, K.A. and Silver, L.T. 1996. Helium diffusion and low temperature thermochronometry of apatite. *Geochimica et Cosmochimica Acta*, **60**, 4231–4240, https://doi.org/10.1016/S0016-7037(96)00192-5

Wollenweber, J., Alles, S., Kronimus, A., Busch, A., Stanjek, H. and Krooss, B.M. 2009. Caprock and overburden processes in geological CO_2 storage: an experimental study on sealing efficiency and mineral alterations. *Energy Procedia*, **1**, 3469–3476, https://doi.org/10.1016/j.egypro.2009.02.138

Wrathall, J. 2020. Cornish Lithium releases globally significant lithium grades, https://cornishlithium.com/company-announcements/cornish-lithium-releases-globally-significant-lithium-grades/#:~:text=The%20initial%20assay%20results%20show,lithium%20in%20geothermal%20waters%20globally [last accessed 2 June 2023].

Xia, X. and Gao, Y. 2021. Validity of geochemical signatures of abiotic hydrocarbon gases on Earth. *Journal of the Geological Society, London*, **179**, https://doi.org/10.1144/jgs2021-077

Zgonnik, V. 2020. The occurrence and geoscience of natural hydrogen: a comprehensive review. *Earth-Science Reviews*, **203**, 103140, https://doi.org/10.1016/j.earscirev.2020.103140

Zhu, Y., Shi, B. and Fang, C. 2000. The isotopic compositions of molecular nitrogen: implications on their origins in natural gas accumulations. *Chemical Geology*, **164**, 321–330, https://doi.org/10.1016/S0009-2541(99)00151-5