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

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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. Manmade 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.

Introduction – 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, 2023a). In a 'net zero emissions by 2050' scenario, annual demand is expected to be around 150 million tonnes by 2030 (IEA, 2023a). 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 \$1-2 kg⁻¹, giving a global market in the range of \$82-164 billion (KPMG, undated).

Between 1996-2003, annual global helium production fluctuated between 100 and 140 million cubic metres (17,800-24,920 tonnes), rising to between 155 and 184 million cubic metres (26,700-32,800 tonnes) 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 of production (>90%). Today US production accounts for almost half of the global production with Qatar near 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 (Figure 1). MRI scanners (22%) and controlled atmospheres (22%) for semiconductor 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 \$1.76 billion (Figure 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 tonnes 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 tonnes of lithium carbonate were produced in 2022, whilst the projection for 2023 is 964,000 tonnes 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 \$8.2 billion with anticipated growth to about \$19 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 H₂ in the lithosphere have doubled based on estimated contributions from water-rock reaction such as serpentinization, and H₂ production via radiolysis (Sherwood Loller *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 depressurised 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(SiO₃)₂), petalite (a framework silicate, LiAlSi₄O₁₀) and micas in solid solution (e.g. zinnwaldite, K(Fe,Li)₂Al(Al,Si)₄O₁₀(F,OH)₂; and lepidolite K(Li,Al)₃(Al,Si,Rb)₄O₁₀(F,OH)₂). However, lithium has also long been known to be hosted in deep geothermal systems (e.g. Berthold and Baker, 1976; McKibben & 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; Sanjuan *et al.* 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 minimises impact to the natural environment (atmosphere, biosphere, hydrosphere and geosphere) and be sustainable for long human timescales (100s to 1000s 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 sustainable credentials than is the case today.

The IEA (2023b) calculated that the average carbon footprint for each tonne of hydrogen produced was around 7 tonnes 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 versus 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 renewable sourced electricity. At a minimum, this would still mean that the hydrogen production industry would have a 100 million tonne annual CO₂ 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, in review). At > 300 million tonnes per annum of greenhouse gas emissions, the global helium industry has a carbon footprint larger than all but twenty 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; Figure 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 (Bustos-Gallardo *et al.* 2021).

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 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 sulphuric acid mist, generation of NO_x and SO₂, and high water and power usage (Gao *et al.* 2023). For example, for mining of lithium from spodumene, some 15 tonnes of CO₂ are produced for every tonne 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 realised (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 absorption 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 WWI that the strategic value of helium as a safe lift gas for military dirigibles was recognised. 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 angewandte Chemie in der Luftfahrt" (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 Jr, 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 ^4He . The lighter ^3He isotope is cosmogenic, inherited by the Earth at formation and has an abundance of about 1/10,000 that of ^4He . Here we are interested in ^4He . 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 concentrations 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 is dissolved and re-precipitated in faults and fractures, controlled by the redox conditions of the environment (Coward 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 (Cheng *et al.* 2021; Stute *et al.* 1992, Castro *et al.* 1998 and Tyne *et al.* 2022) whilst advection is dominant in regions of recent tectonic activity (Danabalan *et al.* 2022, Halford *et al.* 2022; Lowenstern *et al.* 2014, Caracausi *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; Karolytė *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 ($\delta^{15}\text{N}$) composition of the N_2 end member associated with the economic ^4He in the Kansas–Texas Hugoton–Panhandle gas field has a narrow range (-3.00 to $+2.45\text{‰}$). These values are comparable with those observed in both crustal, low-temperature metamorphism and the release of ammonia from clays (-5.00 to $+4.00\text{‰}$) (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 versus 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 co-efficient 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 geological time. For example, Cheng *et al.* (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 5h 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 x more concentrate 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. Although because of hydrogen's lower density than methane and that cryogenics are required to liquify it, storage of large quantities of hydrogen are difficult. Unfortunately, the conventional means of hydrogen manufacture from coal and from methane both have carbon dioxide as an unwanted waste product. Emission of CO₂ 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 to the use of blue hydrogen in which production is from methane with the resultant CO₂ 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 finding 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.

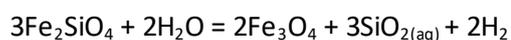
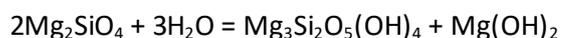
Natural, molecular hydrogen exists as a free gas in a myriad geological and biological settings (Sherwood Lollar *et al.* 2014; Zgonnik, 2020) but the only acknowledged hydrogen producing field is the accidentally discovered Bourakebougou Field in Mali (Prinzhofer *et al.* 2018). Bourakebougou produces hydrogen for local use. It has a purity of 98 % H₂ 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, hydrogen gases have been discovered at two locations in the Amadeus Basin Australia (Leila *et al.* 2022), whilst in the USA similar mixed composition gas has been found in Kansas (Newell *et al.* 2007; Guélard *et al.* 2017) and hydrogen has also been reported from well drilled recently in Nebraska (Ball and Czado, 2022). Low but significant concentration 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.

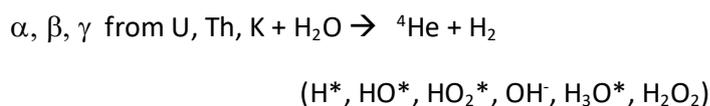
Oxidation of iron from Fe²⁺ to Fe³⁺ occurs during serpentinization (Equation 1) and alteration of ophiolite and greenstone belt lithologies liberating hydrogen via the paired reactions of olivine end members fayalite and forsterite with water. Reaction of fayalite with water in the temperature range 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 on-going as fractures and surface areas are propagated (Sherwood Lollar *et al.*; 2007; 2014; Sleep and Zoback, 2007).

Equation 1 Serpentinization: peridotite + water yields OH⁻ and H₂:



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.

Equation 2 Ionising radiation dissociates water



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 occur 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 hydrogenise 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 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. Karolytè *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 over-mature 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 crystallisation 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 lifecycle of the igneous systems is also important, from source enrichment and tectonic context (Koopmans *et al.* 2024; Simons *et al.* 2017; Ballouard *et al.* 2023), magmatic cooling and crystallisation (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. Puzolu *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 which 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 versus 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 use 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 decarbonising 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 which 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 compositions of hydrogen bearing gases varies widely (Figure 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 Karolytė *et al.* (2022), Ward *et al.* (2004) and Sherwood Lollar *et al.* (2006) have shown, the methane may be a product of microbes metabolising 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 which 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 resides 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 from solid rock or from Andean salars.

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

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Figure Captions

Figure 1 Global helium production by nation (compiled from data accessible in USGS 2024)

Figure 2 Global helium production and annual average helium price (compiled from data accessible in USGS 2024).

Figure 3 San Pedro de Atacama salar showing extent of areas developed for brine evaporation. Main image from Google Earth, inset shows location of satellite image.

Figure 4 Lithium content of geothermal brines and co-produced brines from petroleum fields compared with that in salars (From Gluyas and Fowler, 2024). Data sources, 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).

Figure 5 Hydrogen, nitrogen, methane ternary plot for gases from Mali (Prinzhofer *et al.* 2018), Kansas, USA (Guélard *et al.* 2016), South Australia (Martin, 2024), Oman (Sano *et al.* 1993), Philippines (Abrajano *et al.* 1988), Copper Cliff, Ontario (Li *et al.* 2021), Türkiye (D'Alessandro *et al.* 2018), Finland (Sherwood Lollar *et al.* 1993), Kidd Creek, Ontario (Li *et al.* 2021), New Caledonia (Deville and Prinzhofer 2016), Witwatersrand, South Africa (Karolytè *et al.* 2022), Mponeng, South Africa (Sherwood Lollar *et al.* 2006), Wilson well, Kansas (Newell *et al.* 2007), Australia (Leila *et al.* 2022), Tanzania (Helium One Global, 2024) and UK (average from gas fields in Gluyas and Hichens 2003). 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.

Table Captions

Table 1 Concentrations of hydrogen, helium and lithium in Earth systems (for comparison 10% = 100,000 ppm, 10,000,000 ppb and 10,000,000,000 ppt)

Table 2. Helium closure temperatures for helium-retentive minerals (from Danabalan et al 2022)

Table 3 Main methods of hydrogen manufacture and natural hydrogen

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	Geosphere	Hydrosphere	Atmosphere
	Units alongside elements	Units alongside elements	ppm
Hydrogen	0.15 wt% in water, hydrocarbons & as H ₂	10.7 wt%	0.5-1.0 as H ₂ , variable as H ₂ O
Helium	8 ppb	7.2 ppt	5.2
Lithium	20 ppm	0.18 ppm	nil

Table 1

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

Table 2

Colour	Source of energy	Source of hydrogen	Production process	CO ₂ emissions (kgCO ₂ /kgH ₂)	Cost \$/kg H ₂
Green	Renewable	Fresh water	Hydrolysis	0.3 ^a	4.5-12 ^d
Grey	Electricity non-renewable	Methane	Methane reformation	9.8-13.7 ^{a&c}	0.98-2.93 ^d
Blue	Renewable	Methane	Methane reformation + CCS	0.8-8.8 ^{b&c}	1.8-4.7 ^d
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

^aMoberg & Bartlett, 2022; ^bIncer-Valverde et al 2023; ^cDe La Cruz 2024; ^dSchelling 2023; ^ePoljak, 2021; ^fBrandt, 2023; ^gbased on the average finding cost of methane in the USA Aublinger (2014) and adjusted for energy density.

Table 3

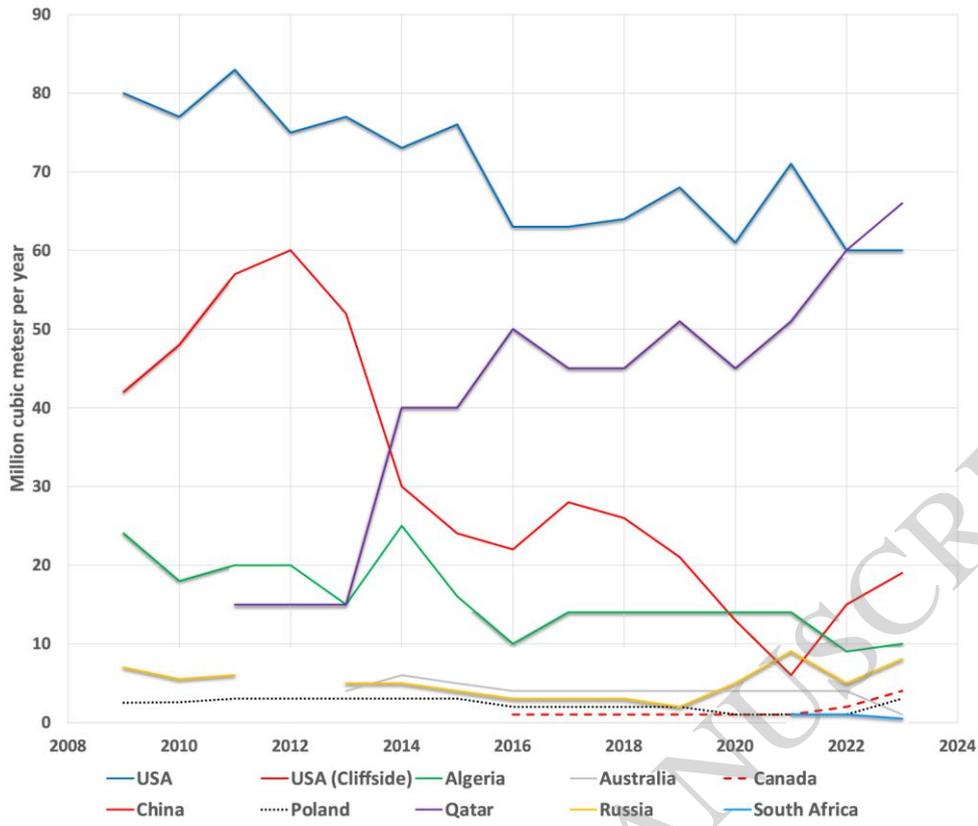


Figure 1

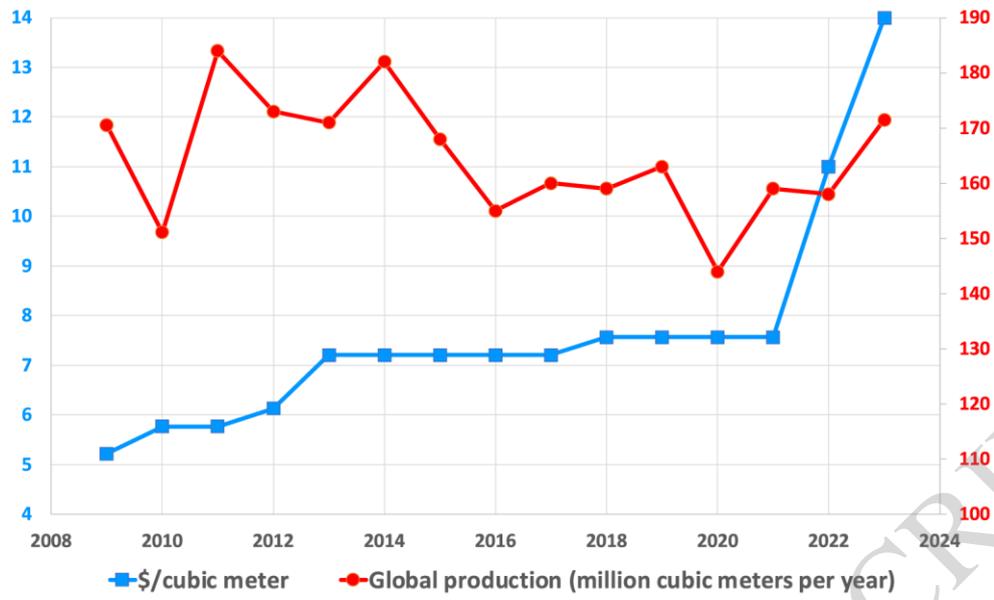


Figure 2

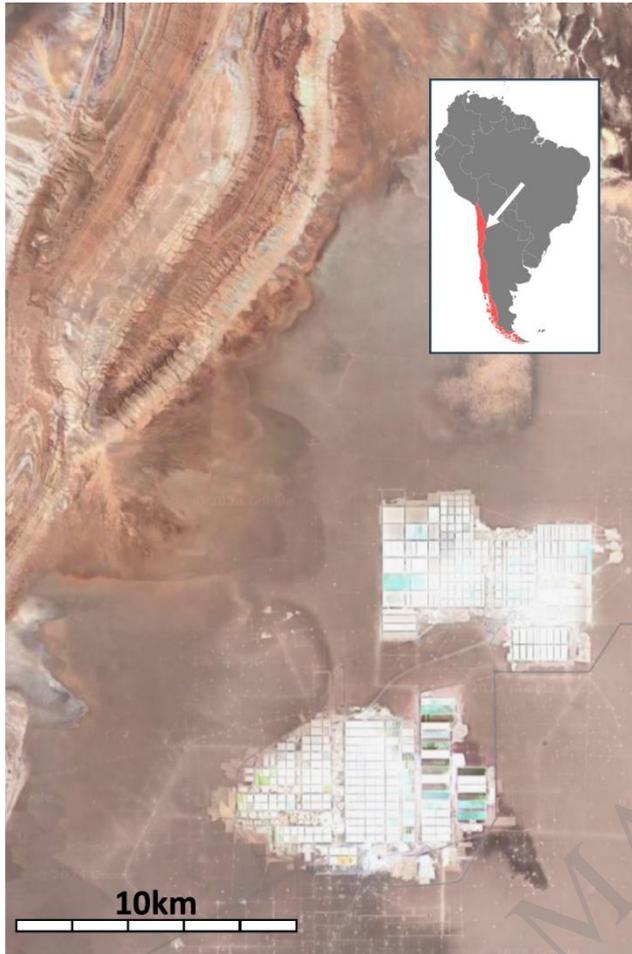


Figure 3

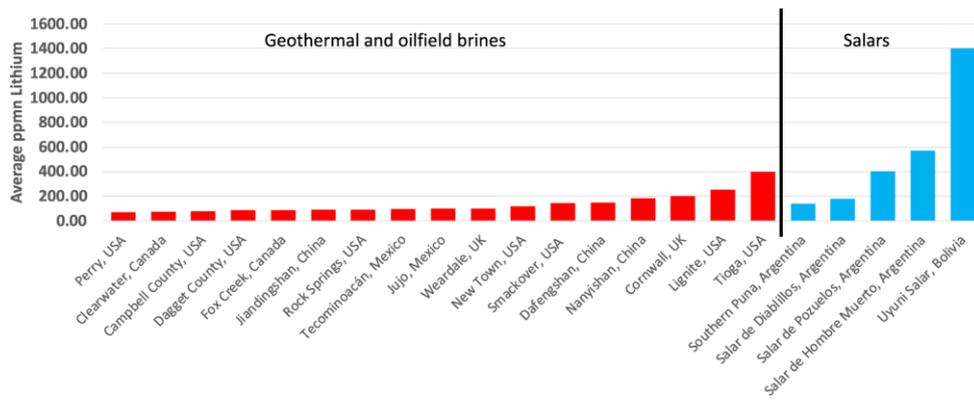


Figure 4

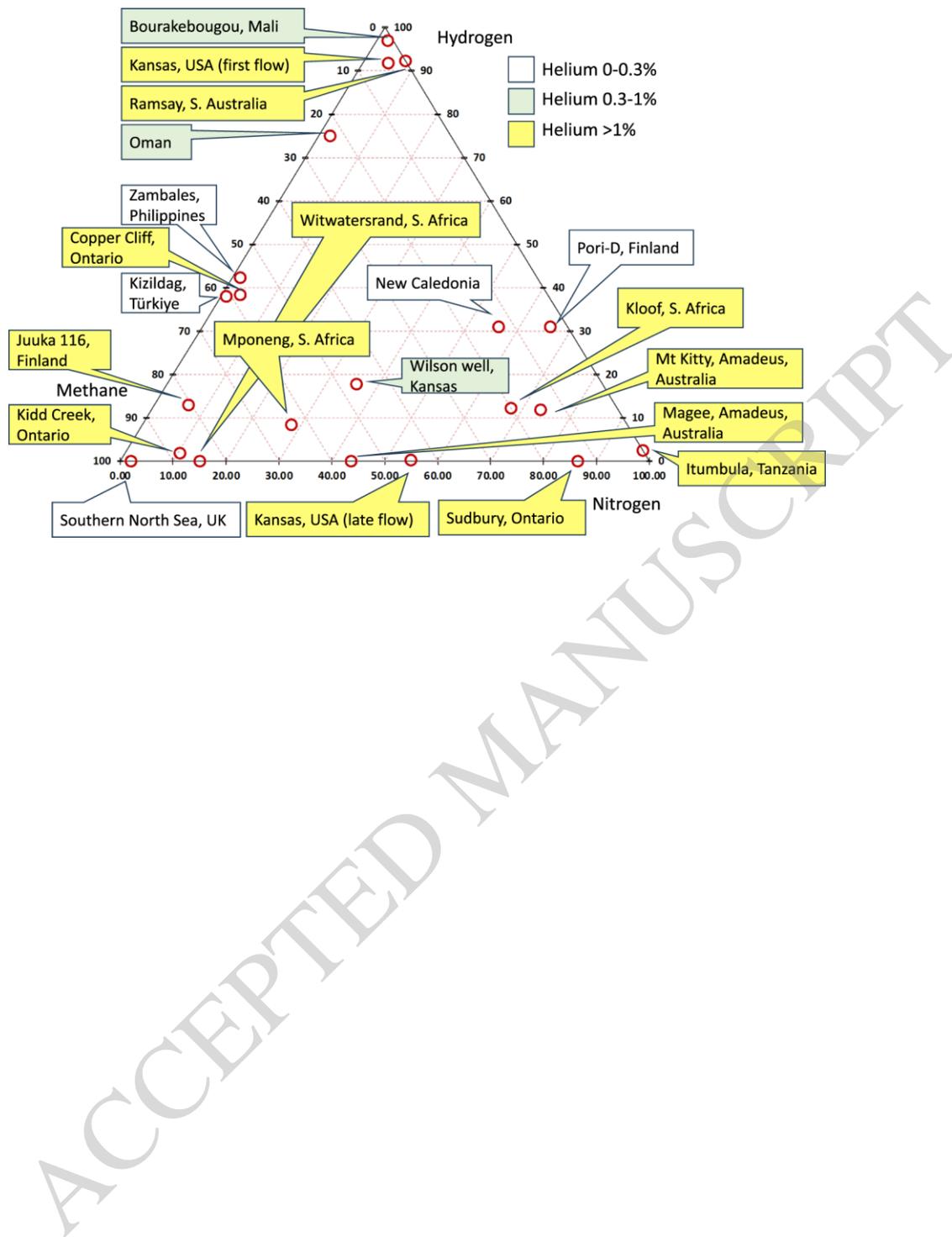


Figure 5