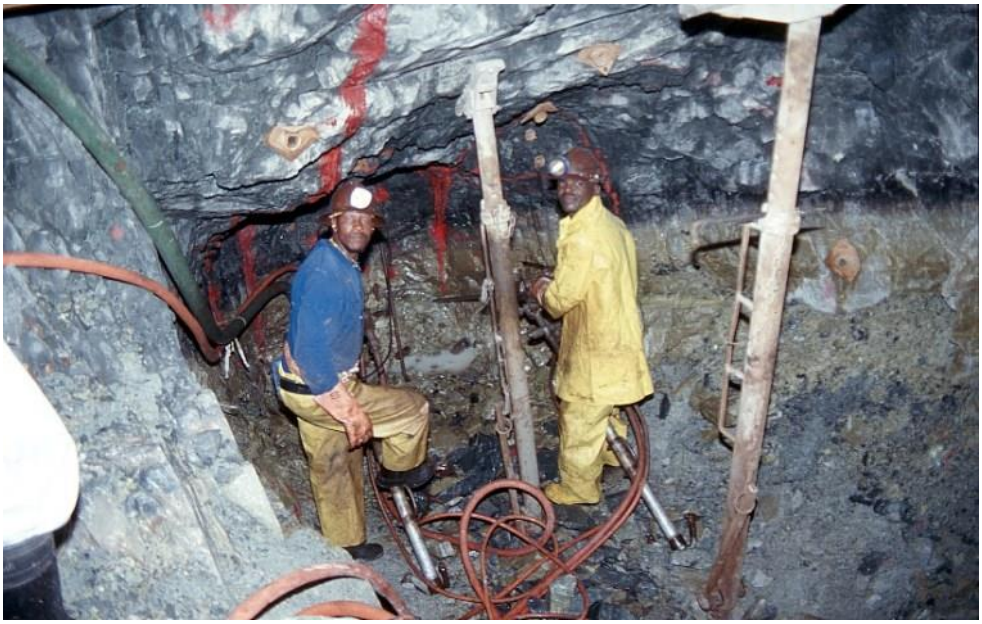
# Physical resources 2022-5

## *Ancient deep groundwater*

PUBLISHED ON *July 15, 2022*

Worldwide, billions of people depend on groundwater for their water needs from wells, deep boreholes and natural springs. Even surface water in rivers and lakes is directly connected to that moving sluggishly below the surface. In fact the surface water level marks where the water table coincides with the land surface. From season to season the water table rises and falls and so too do river and lake levels, depending on fluctuations in rainfall, snow melt, evaporation and extraction. Where it is present, vegetation plays a role in the hydrological cycle, through transpiration from roots through stems and leaves, from which it is exhaled by minute pores or stomata; effectively plants are able to pump water through their tissues to a height of up to a hundred metres. Groundwater, like that at the surface, moves under gravity roughly parallel to the slope of the land surface from the place where precipitation infiltrates soil and rock. But the deeper it is the slower the flow and the less it is in direct contact with surface processes to be replenished by infiltration. Wells and boreholes rarely penetrate deeper than a few hundred metres, so that the vast bulk of groundwater is never used. Indeed most deep groundwater would not be drinkable or suitable for irrigation since over millennia or longer it dissolves material from the rock that contains it to become saline. In some deep sedimentary aquifers it may actually be composed of seawater trapped at the time of sedimentation.



Damp conditions in the Mponeng gold mine near Johannesburg, South Africa, the world's deepest at 3.8 km below the surface with planned expansion to 4.3 km (Credit: AngloGold Ashanti)

The pore spaces in sandstones and fractures in limestones, the most common aquifers, are not the only conduits for groundwater. Crystalline igneous and metamorphic rocks are generally full of minute fractures resulting from their tectonic history. The deepest mines in crystalline basement, such as the gold mines of the Johannesburg area in South Africa, penetrate almost 4 km below the

surface, yet are by no means dry and have to be pumped to stave off flooding. The water is a brine containing sodium and calcium chloride with high concentrations of dissolved, reduced gases such as hydrogen, methane and ethane ($C_2H_6$). Studies of the proportions of oxygen isotopes in the water reveal that the water in the fractures is very different from that in modern rainwater: this fluid is completely isolated from the modern hydrological cycle and is very old indeed. Just how old has now been determined (Warr, O. *et al*. 2022. $^{86}$Kr excess and other noble gases identify a billion-year-old radiogenically-enriched groundwater system. *Nature Communications* v. **13**, Article number 3768; DOI: 10.1038/s41467-022-31412-2).

Brine extracted from a borehole in the floor of the Moab Khotsong gold/uranium mine also contains the noble gases helium, neon, argon, krypton and xenon. Noble gases are present in today's atmosphere, so conceivably they may have originally entered the brine in rain water that seeped along fractures. However, when their isotopes are measured their proportions are very different from those in air. There are excesses of $^{4}$He, $^{21}$Ne, $^{22}$Ne, $^{40}$Ar, $^{86}$Kr and several isotopes of Xe. These isotopes are emitted during the radioactive decay of uranium, thorium and $^{40}$K, the main heat producing isotopes in the crust and mantle. Oliver Warr of the University of Toronto Canada and geochemists from Oxford University UK, Princeton University and the New Mexico Institute of Mining and Technology US, and the Sorbonne France show that originally atmospheric noble gases have been enriched in these radiogenic isotopes. Their present isotopic proportions therefore give clues to the time when air dissolved in groundwater was trapped in the host rock more than a billion years ago. A complicating factor is that the host rocks themselves are dated at about three times that age. They suggest that the fractures systems were initiated by the Vredfort asteroid impact at 2.0 Ga to form aquifers, but they became isolated from hydrological circulation around 1.2 Ga and now now contain the world's oldest groundwater.

One of the implications of the study is that such trapped water may be present at depth in the crust of Mars, despite its current aridity. Another is that, because the fluid contains hydrogen, sulfate ions and hydrocarbon gases, it can potentially support organisms that use them to power their metabolism and reproduce. In 2008 microbes were found living in similar ancient groundwater 2.4 km below the surface in the Kidd Creek Mine, Canada, at a level of around 5 thousand cells per millilitre (50 times less than in surface water). They are powered by reduction of sulfate ions to sulfide. In 2008 another peculiar discovery in the deep biosphere emerged from the Mponeng gold mine near Johannesburg, South African (the world's deepest) in the form of a living sulfate reducing bacterium *Desulforudis audaxviator*. DNA analysis of the ancient water revealed that it was the sole inhabitant, a biological mystery confirmed by later deep-biosphere studies in Death Valley, USA, and Siberia.

**See also:** Researchers uncover life's power generators in the Earth's oldest groundwaters, *EurekaAlert*, 5 July 2022; Mantle link with biosphere, July 2009

# *Naturally occurring hydrogen: an abundant green fuel?*

PUBLISHED ON *March 1, 2023*

Burning hydrogen produces only water vapour, so it is not surprising that it has been touted as the ultimate 'green' energy source, and increasingly attracts the view that the 'Hydrogen Economy' may replace that based on fossil fuels. It is currently produced from natural gas by 'steam reforming' of methane that transforms water vapour and $CH_4$ to hydrogen and carbon monoxide. That clearly doesn't make use of the hydrogen 'green' as the CO becomes carbon dioxide because it reacts with atmospheric oxygen; it is termed 'grey hydrogen'. But should it prove possible to capture CO and store it permanently underground in some way then that can be touted as 'blue hydrogen' thereby covering up the carbon footprint of all the rigmarole in getting the waste CO into a safe reservoir. However, if carbon-free electricity from renewables is used to electrolyse water into H and O the hydrogen aficionados can safely call it 'green hydrogen'. It seem there is a bewildering colour coding for hydrogen that depends on the various options for its production: 'yellow' if produced using solar energy; 'red' if made chemically from biowaste; 'black' by coking coal using steam; 'pink' is electrolysis using nuclear power; and even 'turquoise' hydrogen if methane is somehow turned into hydrogen and solid carbon using renewables – a yet-to-be-developed technology! Very jolly but confusing: almost suspiciously so!

But not to be forgotten is the 'white' variety, applied to hydrogen that is emitted by natural processes within the Earth. Eric Hand, the European news editor for the major journal *Science* has written an excellent Feature article about 'white' hydrogen in a recent issue (Hand, E. 2023. Hidden hydrogen. *Science*, v. **379**, article adh1460; DOI: 10.1126/science.adh1460). Hand's feature is quirky, but well-worth a read. It is based on the proceedings of a Geological Society of America mini-conference about non-petroleum, geological energy resources held in October 2022. He opens with a bizarre anecdote related by a farmer who lives in rural Mali. The only drilling that ever went on in his village was for water, and many holes were dry. But one attempt resulted in 'wind coming out of the hole'. When a driller looked in the hole, the 'wind' burst into flame – he had a cigarette in his mouth. The fire burned for months. Some 20 years later the story reached a Malian company executive who began prospecting the area's petroleum potential, believing the drilling had hit natural gas. Analysis of the gas revealed that it was 98% hydrogen – now the village has electricity generated by 'white' hydrogen.

Mantle rock in the Oman ophiolite, showing cores of fresh peridotite, surrounded by brownish serpentinite and white magnesium carbonate veins (credit: Juerg Matter, Oman Drilling Project, Southampton University, UK)

So how is hydrogen produced by geological processes? Some springs in the mountains of Oman also release copious amounts of the gas. The springs emerge from ultramafic rocks of the vast ophiolite that was emplaced onto the Arabian continental crust towards the end of the Cretaceous. The lower part of this obducted mass of oceanic lithosphere is mantle rock dominated by iron- and magnesium-rich silicates, mainly olivine [$(Mg,Fe)_2SiO_4$ – a solid solution of magnesium and iron end members]. When saturated with groundwater in which $CO_2$ is dissolved olivine breaks down slowly but relentlessly. The hydration reaction is exothermic and generates heat, so is self-sustaining. Olivine's magnesium end member is hydrated to form the soft ornamental mineral serpentine ($Mg_3Si_2O_5(OH)_4$) and magnesium carbonate. Under reducing conditions the iron end member reacts with water to produce an iron oxide, silica and hydrogen:

$$3Fe_2SiO_4 + 2H_2O \rightarrow 2\ Fe_3O_4 + 3SiO_2 + 3H_2$$

Gases emanating from mid-ocean ridges contain high amounts of hydrogen produced in this way, for example from Icelandic geothermal wells. But Mali is part of an ancient craton, so similar reactions involving iron-rich ultramafic rocks deep in the continental crust are probably sourcing hydrogen in this way too. Hydrogen production on the scale of that discovered in Mali seems to be widespread, with discoveries in Australia, the US, Brazil and the Spanish Pyrenees that have pilot-scale production plants. The US Geological Survey has estimated that around 1 trillion tonnes of 'white' hydrogen may be available for extraction and use

Hydrogen, like other natural gases, may be trapped below the surface in the same ways as in commercial petroleum fields. But petroleum-gas wells emit little if any hydrogen mixed in with methane. That absence is probably because petroleum fields occur in deep sedimentary basins well above any crystalline basement. The geophysical exploration that discovers and defines the traps in petroleum fields has never been deployed over areas of crystalline continental crust because as far as the oil companies are concerned they are barren. That may be about to change. There is another exploration approach: known hydrogen seepage seems to deter vegetation so that the sites are in areas of bare ground, which have been called 'fairy circles'. These could be detected easily using remote sensing techniques.

Artificially increasing serpentine formation by pumping water into the mantle part of ophiolites, such as that in Oman, and other near-surface ultramafic rocks is also a means of carbon sequestration, which should produce hydrogen as a by-product (see: Global warming: Can mantle rocks reduce the greenhouse effect?, July 2021). A 'two-for-the-price-of-one' opportunity?

# *The Moon may have water resources in its soil*

PUBLISHED ON *March 29, 2023*

Apart from signs of water ice in permanently shadowed areas of some polar craters, the Moon's surface has generally been considered to be very dry. Rocks returned by the various Apollo missions contain minute traces of water by comparison with similar rocks on Earth. They consist only of anhydrous minerals such as feldspars, pyroxenes and olivines. But much of the lunar surface is coated by regolith: a jumble of rock fragments and dust ejected from a vast number of impact craters over billions of years. It is estimated to be between 3 and 12 m deep. Much of the finer grained regolith is made up of silicate-glass spherules created by the most powerful impacts.

The scientific and economic (i.e. mining) impetus for the establishment of long term human habitation on the lunar surface hangs on the possibility of extracting water from the Moon itself. It is needed for human consumption and as a source through electrolysis of both oxygen and hydrogen for breathing and also for rocket fuel. The stupendous cost, in both monetary and energy terms, of shifting mass from Earth to the Moon clearly demands self-sufficiency in water for a lunar base occupied for more than a few weeks.

The lunar regolith at Tranquillity Base bearing an astronaut's bootprint (Credit: Buzz Aldrin, NASA Apollo 11, Photo ID AS11-40-5877)

Remote sensing that focussed on the ability of water molecules and hydroxyl ($OH^-$) ions to absorb solar radiation with a wavelength of 2.8 to 3.0 micrometres was deployed by the Indian lunar orbiter Chandrayaan-1 that collected data for several months in 2008-9. The results suggested that $OH^-$ and $H_2O$ were detectable over a large proportion of the lunar surface at concentrations estimated at between 10 parts per million (ppm) up to about 0.1%. Where did these hydroxyl ions and water molecules come from and what had locked them up? There are several possibilities for their origin: volcanic activity that tapped the Moon's mantle (magma could not have formed had some water not been present at great depths); impacts of icy bodies such as comets; even the solar wind that carries protons, i.e. hydrogen atoms stripped of their electrons. Conceivably, protons could react with oxygen in silicate material at the surface to produce both $OH^-$ and $H_2O$ to be locked within solid particles. To assess the possibilities a group of researchers at Chinese and British institutions have examined in detail the 1.7 kg of lunar-surface materials collected and returned to Earth by the 2020 Chinese Chang'e 5 lunar sample return mission (He, H. and 27 others 2023. A solar wind-derived water reservoir on the Moon hosted by impact glass beads. *Nature Geoscience*, online article; DOI: 10.1038/s41561-023-01159-6)

He *et al*. focussed on glass spherules formed by impact melting of lunar basalts, whose bulk composition they retain. The glass 'beads' contain up to 0.2 % water, mainly concentrated in their outermost parts. This alone suggests that the water and hydroxyl ions were formed by spherules being bathed in the solar wind rather than being of volcanic or cometary origin and trapped in the glass. An abnormally low proportion of deuterium ($^2H$) relative to the more abundant $^1H$ isotope of hydrogen in the spherules is consistent with that hypothesis. Indeed, the high temperatures involved in impact melting would be expected to have driven out any 'indigenous' water in the source rocks.

The water and $OH^-$ ions seem to have built up over time, diffusing into the glass from their surfaces rather than gradually escaping from within.

An awful lot of regolith coats the lunar surface, as many of the images taken by the Apollo astronauts amply show. So how much water might be available from the lunar regolith? The Chinese-British team reckon between $3.0 \times 10^8$ to $3.0 \times 10^{11}$ metric tons. But how much can feasibly be extracted at a lunar base camp? The data suggest that a cubic metre (~2 t) of regolith could yield enough to fill 4 shot glasses (~0.13 litres). Using a solar furnace and a condenser – the one in full sunlight the other in the shade – is not, as they say, 'rocket science'. But for a minimum 3 litres per day intake of fluids per person, a team of 4 astronauts would need to shift and process roughly 100 $m^3$ of regolith every day. Over a year, this would produce a substantial pit. But that assumes all the regolith contains some water, yet the data are derived from the surface alone …**See also:**Glass beads on moon's surface may hold billions of tonnes of water, scientists say. *The Guardian*, 27 March 2023.

# *A major breakthrough in carbon capture and storage?*

PUBLISHED ON *November 20, 2024*

Carbon capture and storage is in the news most weeks and is increasingly on the agenda for some governments. But plans to implement the CCS approach to reducing and stopping global warming increasingly draws scorn from scientists and environmental campaigners. There is a simple reason for their suspicion. State engagement, in the UK and other rich countries, involves major petroleum companies that developed the oil and gas fields responsible for unsustainably massive injection of $CO_2$ into the atmosphere. Because they have 'trousered' stupendous profits they are a tempting source for the financial costs of pumping $CO_2$ into porous sedimentary rocks that once contained hydrocarbon reserves. Not only that, they have conducted such sequestration over decades to drive out whatever petroleum fluids remaining in previously tapped sedimentary strata. For that second reason, many oil companies are eager and willing to comply with governmental plans, thereby seeming to be environmentally 'friendly'. It also tallies with their ambitions to continue making profits from fossil-fuel extraction. But isn't that simply a means of replacing the sequestered greenhouse gas with more of it generated by burning the recovered oil and natural gas; i.e. 'kicking the can down the road'? Being a gas – technically a 'free phase' – buried $CO_2$ also risks leaking back to the atmosphere through fractures in the reservoir rock. Indeed, some potential sites for its sequestration have been deliberately made more gas-permeable by 'fracking' as a means of increasing the yield of petroleum-rich rock. Finally, a litre of injected gas can drive out pretty much the same volume of oil. So this approach to CCS may yield a greater potential for greenhouse warming than would the sequestered carbon dioxide itself.

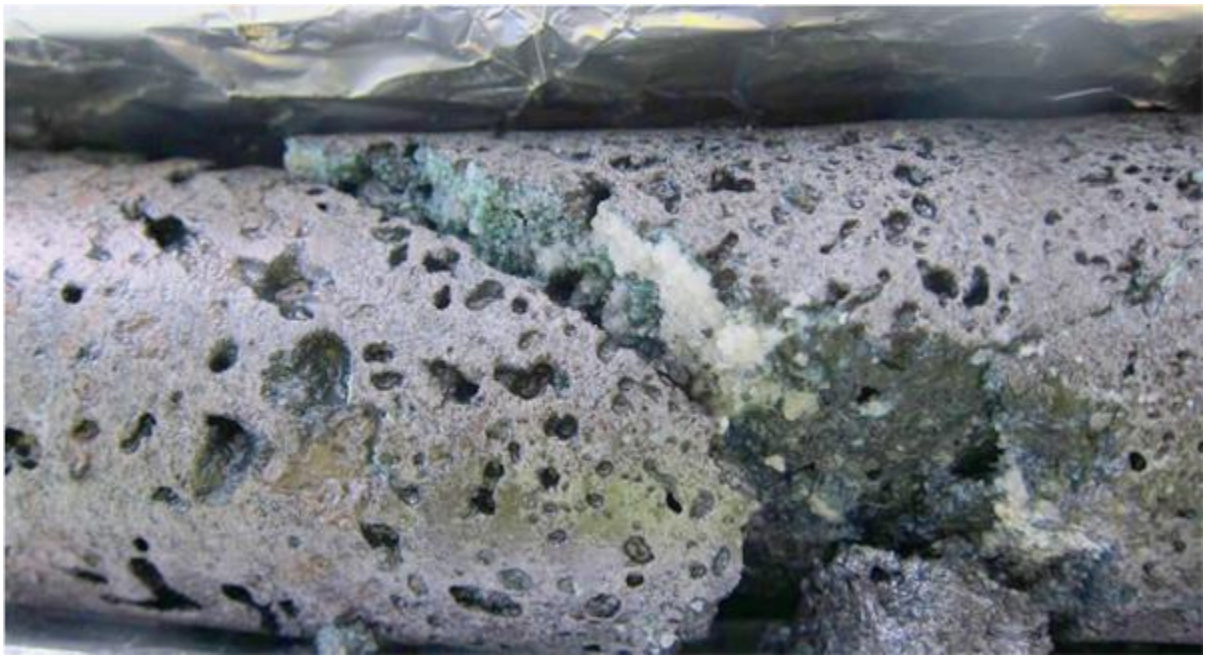


Image of calcite (white) and chlorite (cyan) formed in porous basalt due to $CO_2$-charged water-rock interaction at the CarbFix site in Iceland. (Credit: Sandra Ósk Snæbjörnsdóttir)

Another, less widely publicised approach is to geochemically bind $CO_2$ into solid carbonates, such as calcite ($CaCO_3$), dolomite ($CaMgCO_3$), or magnesite ($MgCO_3$). Once formed such crystalline solids are unlikely to break down to their component parts at the surface, under water or buried. One way of doing this is by the chemical weathering of rocks that contain calcium- and magnesium-rich minerals, such as feldspar ($CaAl_2Si_2O_8$), olivine ($[Fe,Mg]_2SiO_4$) and pyroxene ($[Fe,Mg]CaSi_2O_6$) . Mafic and ultramafic rocks, such as basalt and peridotite are commonly composed of such minerals. One approach involves pumping the gas into a Icelandic borehole that passes through basalt and letting natural reactions do the trick. They give off heat and proceed quickly, very like those involved in the setting of concrete. In two experimental field trials 95% of injected $CO_2$ was absorbed within 18 months. Believe it or not, ants can do the trick with crushed basalt and so too can plant roots. There have been recent experiments aimed at finding accelerants for such subsurface weathering (Wang, J. *et al*. 2024. $CO_2$ capture, geological storage, and mineralization using biobased biodegradable chelating agents and seawater. *Science Advances*, v. **10**, article eadq0515; DOI: 10.1126/sciadv.adq0515). In some respects the approach is akin to fracking. The aim is to connect isolated natural pores to allow fluids to permeate rock more easily, and to release metal ions to combine with injected $CO_2$.

Chelating agents are biomolecules that are able to dissolve metal ions; some are used to remove toxic metals, such as lead, mercury and cadmium, from the bodies of people suffering from their effects. Naturally occurring ones extract metal ions from minerals and rocks and are agents of chemical weathering; probably used by the aforesaid ants and root systems. Wang and colleagues, based at Tohoku University in Japan, chose a chelating agent GLDA (tetrasodium glutamate diacetate – $C_9H_9NNa_4O_8$) derived from plants, which is non-toxic, cheap and biodegradable. They injected $CO_2$ and seawater containing dissolved GDLA into basaltic rock samples. The GDLA increases the rock's porosity and permeability by breaking down its minerals so that Ca and Mg ions entered solution and were thereby able to combine with the gas to form carbonate minerals. Within five days porosity was increased by 16% and the rocks permeability increased by 26 times. Using electron

microscopy the authors were able to show fine particles of carbonate growing in the connected pores. In fact these carbonate aggregates become coated with silica released by the induced mineral-weathering reactions. Calculations based on the previously mentioned field experiment in Iceland suggest that up to 20 billion tonnes of $CO_2$ could be stored in 1.3 $km^3$ of basalt treated in this way: about 1/25000 of the active rift system in Iceland (3.3 x $10^4$ $km^2$ covered by 1 km of basalt lava). In 2023 fossil fuel use emitted an estimated 36.6 bllion tons of $CO_2$ into the atmosphere.

So, why do such means of efficiently reducing the greenhouse effect not receive wide publicity by governments or the Intergovernmental Panel on Climate Change? Answers on a yellow PostIt™ please . . .

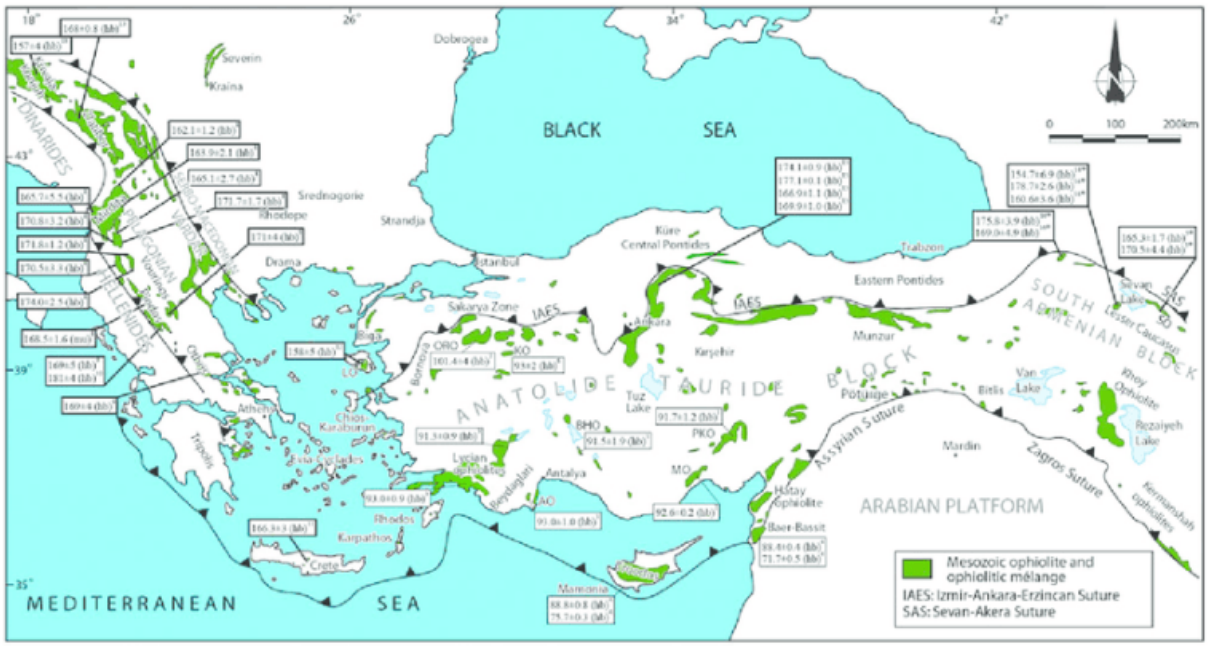
# *Global natural hydrogen resources: a CO2 free future??*

PUBLISHED ON *December 19, 2024*

The idea of a 'Hydrogen Economy' has been around for at least six decades, its main attraction being that when hydrogen is burned it combines with oxygen to form $H_2O$. It might seem to be the ultimate 'green' energy source, but it is currently being touted by governments and petroleum companies in what is widely regarded as 'green washing'. The technology favoured by that axis uses steam reforming of the methane that dominates natural petroleum gas, through the reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

It's actually not much different from producing coke gas from coal, which began in the 19th century and is now largely abadoned. Because carbon monoxide (CO) reacts with atmospheric oxygen to form $CO_2$ this process is by no means 'green' and is properly referred to as '**grey**' hydrogen. Only if the CO is stored permanently underground could steam reforming not add to greenhouse warming. That puts the approach in the same category as 'carbon capture and storage', with all the possible difficulties inherent in that technology, which has yet to be demonstrated on a large scale. Such hydrogen is classified as a '**blue**'. Colour coding hydrogen is described nicely by the British National Grid. They give another six varieties. **Green** and **yellow** hydrogen are produced by electrolysing water using wind or solar power respectively. The **pink** variety uses nuclear power in the same fashion. **Black** or **brown** hydrogen is that produced by coking coal or stewing-up brown coal (lignite) which amazingly are contemplated in Australia and Germany. There is even a **turquoise** variety can be produced if methane is somehow turned into hydrogen and solid carbon using renewables. There is another category (**white**) which is hydrogen produced by a variety of natural, geochemical processes.




Distribution of ophiolites around the Eastern Mediterranean and Black Seas. Many orogenic belts are endowed to a similar extent. (Credit: Gültekin Topuz, Istanbul Technical University)

Earth-logs discussed white hydrogen in March 2023 when news emerged of gas that was 98% hydrogen leaking from a water borehole in Mali. The local people harnessed this surprising resource to generate electricity for their village. It also emerges in springs from ultramafic rocks, having formed through weathering of the mineral olivine:

$$3Fe_2SiO_4 + 2H_2O \rightarrow 2\ Fe_3O_4 + 3SiO_2 + 3H_2$$

Much the same reaction occurs beneath the ocean floor where hydrothermal fluids alter basalts and in geothermal springs that emerge from onshore basalt lavas. Such 'white' hydrogen emissions are widespread. So an unknown, but possibly huge amount of hydrogen is leaking into the atmosphere continuously. Because of its tiny nucleus – just a single proton – atmospheric hydrogen quickly escapes to outer space: what a waste! Equally as interesting is that inducing the breakdown of ultramafic rock to yield hydrogen, by pumping water and carbon dioxide into them, may also be a means of leak-free carbon sequestration. This produces the complex mineral serpentine and magnesium carbonate. The reaction gives off heat and so is self sustaining until pumping is stopped.

It has been estimated that by 2050 the annual global demand for hydrogen will reach 530 million t. Just how big is the potential resource to meet such a demand? Natural weathering and hydrothermal processes have always functioned. Some of the hydrogen produced by them may have built-up in reservoirs like the one in Mali, some is escaping. Neither the magnitude of annual natural generation of hydrogen nor the amount trapped in porous sedimentary rocks are known in any detail. A recent survey of how much may be trapped gives a range from $10^3$ to $10^{10}$ million metric tons (Ellis, G.S. & Gelman, S.E. 2024. Model predictions of global geologic hydrogen resources. *Science Advances*, v. **10**, article eado0955; DOI: 10.1126/sciadv.ado0955), most probably 5.6 trillion t. If only a tenth of that is recoverable, replacing fossil-fuel energy with that from white hydrogen to achieve net-zero $CO_2$ emissions would be sustainable for about 400 years. That magnitude of trapped hydrogen reserves well exceeds all proven reserves of natural gas.

This estimate assumes using only hydrogen that has been naturally produced and stored beneath the Earth's surface. Basalts and ultramafic rocks exposed at the land surface as ophiolites – ancient oceanic crust thrust onto continental crust – are abundant on every continent. Inducing hydrogen-producing chemical reactions in them by pumping water and $CO_2$ into them is little different from the technology being used in fracking. This potential resource is effectively limitless. Combined with renewable energy technology, a hydrogen economy has no conceivable need for fossil fuels, except as organic-chemistry feedstock. Such a scenario for stabilising climate is almost certainly feasible. It could use the capital, technology and skills currently deployed by the petroleum industry that is currently driving society and the Earth in the opposite direction. It is capable of drilling 10 km below the continental surface or the ocean floor, and even into the Earth's mantle that is made of . . . ultramafic rock.